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On the Theory
of Relaxation Processes*

Contents

I. Introduction

This paper deals with the behavior of a relatively simple system which interacts weakly with a more complicated system acting as a temperature bath. A typical example is a nuclear spin system contained within, and interacting with, a solid or liquid. The conventional theory of transition probabilities[1] is applicable to such a system, but yields only information about the rate of change of the probability amplitude of a state of the system, assuming that the phases of the states of the system are unknown or random.

For a complete quantum mechanical description of a system one must use the density matrix formalism.[2] The conventional theory of transition probabilities assumes that the off-diagonal elements of the density matrix are zero, and gives only the rate of change of the diagonal elements. For a *complete* description of the motion of the system one must also consider the rate of change of the off-diagonal elements of the density matrix, and abandon the assumption (equivalent to the random phase assumption) that these elements are zero.

Spin systems are unusual in that they can readily be prepared in such a way that they must be described by a density matrix with significant off-diagonal elements; for this reason a theory of this type is useful in dealing with such systems. Wangsness and Bloch[3] have developed the theory for single spins and Bloch[4] has extended this theory to fairly general systems. The Wangsness-Bloch theory is mathematically similar to the conventional theory of transition probabilities, but assumes that only the temperature bath, rather than the whole system, is characterized by

Abstract: A general procedure is given for finding the equation of motion of the density matrix of a system in contact with a thermal bath, as for example a nuclear spin system weakly coupled to a crystal lattice. The thermal bath is treated both classically and quantum mechanically, and the theory is similar to, and a generalization of, conventional theories of time proportional transition probabilities. Relaxation of the system by the thermal bath is expressed by a linear matrix operator, and it is stressed that elements of this operator can be regarded as secular or nonsecular perturbations on the equation of motion and can be treated accordingly. When the motion of the system is slow compared to that of the thermal bath, the equation of motion can be expressed in an operator form which is independent of representation. If the system has a time-dependent Hamiltonian which varies slowly compared to the motion of the thermal bath, the same equation of motion is obeyed and the system is relaxed by the bath toward a Boltzmann distribution with respect to its instantaneous Hamiltonian. If the time variation of the Hamiltonian is more rapid, higher order corrections to the equation of motion must be applied. The theory is applied to spin-lattice relaxation of a coupled nuclear spin system in a metal, for arbitrary externally applied fixed magnetic field.

random phases of its quantum states (diagonal density matrix). Fano[5] has shown how to obtain the Wangsness-Bloch theory in an elegant and general form.

The Wangsness-Bloch theory has several limitations. It is expressed in a representation in which the energies of both the system and thermal bath are diagonal. If the thermal bath is a complicated thing, like a liquid, it will be impossible to solve its Hamiltonian, and therefore impossible to evaluate the relaxation constants which come out of the Wangsness-Bloch theory. The effect of the thermal bath can nevertheless be estimated in many cases from the classical mean-square size of its interaction with the system and the rate of the statistical fluctuations of this interaction (correlation time). This point of view was developed by Bloembergen, Purcell, and Pound[6] for the case of nuclear spins in a liquid, relaxed by the fluctuating magnetic fields of other magnetic moments on nearby molecules in the liquid. The same method can be applied to other problems in magnetic resonance.[7, 8, 9] In Section II of this paper we give a general formulation of such a theory and

obtain the density matrix equation of motion of a system relaxed by a randomly fluctuating perturbation. This formalism differs from the previous theories of this type only in that we explicitly consider the off-diagonal elements of the density matrix, whereas previous theories dealt with the rate of change of the diagonal elements (which are identical with the probability amplitudes)[6, 7] or were somewhat less explicit, general and exact in their treatment of the off-diagonal density matrix elements.[8, 9]

Since the Wangsness-Bloch theory is expressed in a representation diagonal with respect to the Hamiltonian of the system being relaxed, it is also necessary to solve this Hamiltonian before applying the theory. In many cases of interest this is impossible, even though it is possible to make a reasonable assumption about the state of the system (i.e. that it is in a canonical distribution with respect to its Hamiltonian or to some other observable). This difficulty cannot in general be avoided, but it turns out that if the motion of the thermal bath is rapid compared to that of the system it relaxes, the equation of motion can be recast in operator form. Such a form is useful because the physical quantities of interest in determining the state of the system are usually traces (diagonal sums) of operators, which can be evaluated in any convenient representation. To get the operator form of the density matrix equation of motion it must be noted that an energy selection rule occurring in the earlier work of Wangsness and Bloch is superfluous (see Sections II, III).

Another limitation of the Wangsness-Bloch theory is that it is applicable only when the Hamiltonian of the system is time-independent, or contains only a small time-dependent part. This limitation can be removed if the Hamiltonian varies sufficiently slowly compared to the thermal bath. If the time-variation of the Hamiltonian is not sufficiently slow, corrections must be applied to the equation of motion. In Section IV we outline a method of obtaining these corrections.

The present theory, like the usual time-proportional transition probability theory and the Wangsness-Bloch theory, is a weak interaction or weak collision theory. If relaxation takes place through strong collisions, each of which changes the state of the system by a large amount, the present theory would not apply, since it would diverge when carried to higher orders of approximation.

While this paper was in preparation, the writer learned that F. Bloch had independently obtained some of the results of Sections III and IV by a somewhat different method.[10] In Appendix A we discuss the similarities and differences between Bloch's work and our own.

II. Random perturbation

We first treat the relaxation of a system by a random semi-classical perturbation. Besides being useful for getting qualitative results when the temperature bath is complicated, this section also provides a relatively simple introduction to some of the ideas in Section III. The present section is a generalization of the paper of Solomon[9] on two-spin systems in liquids.

We consider an ensemble of systems each with Hamiltonian

$$\mathcal{H} = \hbar E + \hbar G(t) \tag{2.1}$$

E is time-independent and has eigenfunctions ψ_α, ψ_β, ψ_γ, etc., with eigenvalues α, β, γ, etc., respectively. In general the wave function of each member of the ensemble can be written

$$\Psi = \Sigma_\alpha c_\alpha \psi_\alpha = \Sigma_\alpha a_\alpha e^{-i\alpha t} \psi_\alpha. \tag{2.2}$$

We define the density matrices

$$\sigma_{\alpha\alpha'} \equiv \langle c_{\alpha'}{}^+ c_\alpha \rangle; \tag{2.3}$$

$$\sigma_{\alpha\alpha'}{}^* \equiv \langle a_{\alpha'}{}^\dagger a_\alpha \rangle = \sigma_{\alpha\alpha'} e^{i(\alpha-\alpha')t}. \tag{2.4}$$

Here $\langle \rangle$ denotes an average over the ensemble, and the dagger denotes complex conjugate. σ is the usual[2] density matrix in the Schroedinger representation, and σ^* is the density matrix in the Heisenberg representation with respect to E (interaction representation). We use σ rather than ρ to emphasize that σ is the density matrix of only part of the system, and does not provide any information about the temperature bath.

$G(t)$ is a Hermitian perturbation which is random in time[11] and is responsible for the relaxation. $G(t)$ is assumed to be different for each member of the ensemble. For the purpose of this paper it will be sufficient to know the correlation matrix of G:

$$P_{\alpha\beta\alpha'\beta'}(\tau) = \langle G_{\alpha\beta}(t)\ G_{\alpha'\beta'}{}^\dagger(t-\tau) \rangle. \tag{2.5}$$

We assume P and $\langle G \rangle$ are independent of time t, which is equivalent to assuming that the external system or bath which gives rise to $G(t)$ is stationary in the statistical sense. For simplicity we assume $\langle G \rangle = 0$; if this is not so, we can redefine E to include $\langle G \rangle$. It is assumed that $P(\infty) = 0$ and $P(\tau) = P(-\tau)$, and the correlation time τ_c is defined by the condition that $P(\tau) \ll P(0)$ if $\tau \gg \tau_c$. Later we will see that τ_c must be small compared to the relaxation time due to the perturbation $G(t)$.

The state of a member of the ensemble at a time t is given by a set of complex numbers $a_\alpha(t)$; at a later time $t+\Delta t$ the $a_\alpha(t+\Delta t)$ can be expanded in the usual time-dependent perturbation theory expansion:

$$a_\alpha(t+\Delta t) = \Sigma_n a_\alpha{}^{(n)}(t+\Delta t), \tag{2.6}$$

where $\quad a_\alpha{}^{(0)}(t+\Delta t) = a_\alpha(t);$

$$a_\alpha{}^{(n+1)}(t+\Delta t) = -i\Sigma_\beta \int_t^{t+\Delta t} a_\beta{}^{(n)}(t') G_{\alpha\beta}(t') e^{i(\alpha-\beta)t'} dt'. \tag{2.7}$$

The density matrix is given to second order by

$$\sigma_{\alpha\alpha'}{}^*(t+\Delta t) = \sigma_{\alpha\alpha'}{}^*(t)$$
$$+ \langle a_{\alpha'}{}^{(1)\dagger}(t+\Delta t)a_\alpha(t) + a_{\alpha'}{}^\dagger(t)a_\alpha{}^{(1)}(t+\Delta t)$$
$$+ a_{\alpha'}{}^{(1)\dagger}(t+\Delta t)a_\alpha{}^{(1)}(t+\Delta t) + a_{\alpha'}{}^\dagger(t)a_\alpha{}^{(2)}(t+\Delta t)$$
$$+ a_{\alpha'}{}^{(2)\dagger}(t+\Delta t)a_\alpha(t) \rangle. \tag{2.8}$$

The integration interval Δt in (2.7) must be much greater than τ_c but much less than the time in which the a_α and σ^* change appreciably. This requirement permits us to make the expansions (2.6) and (2.8) but prevents us from applying the theory to strong-collision phenomena (since τ_c is the length of a single collision and $\Delta t \gg \tau_c$).

The first first-order term in (2.8) is

$$\langle a_{\alpha'}^{(1)\dagger}(t+\Delta t)a_\alpha(t)\rangle =$$

$$i\Sigma_\beta \int_t^{t+\Delta t} \langle a_\beta^\dagger(t)a_\alpha(t)G_{\alpha'\beta}^\dagger(t')\rangle e^{i(\beta-\alpha')t'}dt'. \qquad (2.9)$$

The $a_\alpha(t)$ are not necessarily statistically independent of $G(t)$, but may depend in fact on the value of G for all time less than t. $G(t')$, however, is statistically independent of $G(t)$, and thus of the $a_\alpha(t)$, for $t'-t \gg \tau_c$, by the definition of τ_c.

Thus

$$\langle a_\beta^\dagger(t)a_\alpha(t)G_{\alpha'\beta}^\dagger(t')\rangle \cong \sigma_{\alpha\beta}^* \langle G_{\alpha'\beta}^\dagger(t')\rangle = 0, \qquad (2.10)$$

provided $t'-t \gg \tau_c$. Since the latter condition holds over most of the interval of integration, (2.9) is zero to a good approximation and can be neglected. The other first order term is similarly negligible.

This argument is hardly rigorous or quantitative, since it is possible that these terms are not negligible compared to the second order terms discussed below. Clearly (2.10) is correct to first order in G and (2.9) is independent of Δt (for $\Delta t \gg \tau_c$) and is also non-zero only in second order in G. It is probable, therefore, that we are correct in ignoring these terms. The quantum-mechanical assumption of random phase for the bath, introduced in the next section, is probably related to the assumption used here, that these first order terms can be neglected.

We now consider the second order terms in (2.8). Again using the fact that the $a_\alpha(t)$ are statistically independent of $G(t)$ over most of the range of integration, it is straightforward to show that these terms are linear in σ, and are given by

$$\sigma_{\alpha\alpha'}^{*(2)}(t+\Delta t) = \Delta t\, \Sigma_{\beta\beta'}e^{i(\alpha-\alpha'-\beta+\beta')t}\,\sigma_{\beta\beta'}^*(t)$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (2.11)$$

$$\times [U_{\alpha\alpha'\beta\beta'}+U_{\beta'\beta\alpha'\alpha}-\delta_{\alpha'\beta'}\Sigma_\gamma U_{\gamma\gamma\beta\alpha}-\delta_{\alpha\beta}\Sigma_\gamma U_{\beta'\alpha'\gamma\gamma}],$$

where

$$U_{\alpha\alpha'\beta\beta'} = (\Delta t)^{-1}\int_0^{\Delta t} e^{i(\beta'-\alpha')\tau}P_{\alpha\beta\alpha'\beta'}(\tau)$$

$$\times \{(e^{i(\alpha-\beta-\alpha'+\beta')(\Delta t-\tau)}-1)/i(\alpha-\beta-\alpha'+\beta')\}d\tau. \qquad (2.12)$$

In (2.12) it is assumed that the frequency difference $\alpha-\beta-\alpha'+\beta'$ is not zero; if it is zero the indeterminate expression in the curly brackets is replaced by $\Delta t-\tau$. To get (2.11) we introduced the variable of integration $\tau = t'-t''$ and used the assumptions that $G(t)$ is Hermitian and $P(\tau)$ is an even function of τ. The procedure is similar to that used by Abragam and Pound[7] to evaluate transition prob-

abilities for a similar system; therefore we give only an outline of the calculation in Appendix B below.

We now consider the evaluation of (2.12). We first discuss those $U_{\alpha\alpha'\beta\beta'}$ for which

$$(\alpha-\beta-\alpha'+\beta')\tau_c \ll 1. \qquad (2.13)$$

For such terms we can ignore the τ occurring in the expression inside the curly brackets in (2.12), because the integrand is large only for $\tau < \tau_c$. For the same reason, and because $\Delta t \gg \tau_c$, we can extend the range of integration to infinity. Thus we get

$$U_{\alpha\alpha'\beta\beta'} \cong \{(e^{i(\alpha-\beta-\alpha'+\beta')\Delta t}-1)/i(\alpha-\beta-\alpha'+\beta')\Delta t\}$$

$$\times \int_0^\infty e^{i(\beta'-\alpha')\tau}P_{\alpha\beta\alpha'\beta'}(\tau)d\tau. \qquad (2.14)$$

As before, if $\alpha-\beta-\alpha'+\beta'$ is zero the indeterminate expression in curly brackets in (2.14) is replaced by unity. The most important terms of this type are those of the form $U_{\alpha\alpha\beta\beta}$ and $U_{\alpha\beta\alpha\beta}$.

The terms of (2.12) for which (2.13) does not hold are small compared to those for which (2.13) does hold. For such terms $(\alpha-\beta-\alpha'+\beta')\Delta t \gg 1$ because $\Delta t \gg \tau_c$. Therefore the expression in the brace in (2.11) is of order $1/(\alpha-\beta-\alpha'+\beta')\Delta t$ in magnitude, and these terms are less than $\tau_c/\Delta t$ times those satisfying (2.13). These terms can therefore be neglected.

We now assert that within the same approximation (that is, of order $\tau_c/\Delta t$) our expression for the density matrix at time $t+\Delta t$ agrees with that predicted by the following equation of motion for σ^*:

$$d\sigma_{\alpha\alpha'}^*/dt = \Sigma_{\beta\beta'}e^{i(\alpha-\alpha'-\beta+\beta')t}R_{\alpha\alpha'\beta\beta'}\,\sigma_{\beta\beta'}^*, \qquad (2.15)$$

where

$$R_{\alpha\alpha'\beta\beta'} = J_{\alpha\beta\alpha'\beta'}(\alpha'-\beta')+J_{\alpha\beta\alpha'\beta'}(\alpha-\beta)$$

$$-\delta_{\alpha'\beta'}\Sigma_\gamma J_{\gamma\beta\gamma\alpha}(\gamma-\beta)-\delta_{\alpha\beta}\Sigma_\gamma J_{\gamma\alpha'\gamma\beta'}(\gamma-\beta'), \qquad (2.16)$$

and

$$J_{\alpha\alpha'\beta\beta'}(\omega) = \tfrac{1}{2}\int_{-\infty}^\infty d\tau e^{i\omega\tau}P_{\alpha\alpha'\beta\beta'}(\tau). \qquad (2.17)$$

The solution of (2.15) to first order in R is

$$\sigma_{\alpha\alpha'}^*(t+\Delta t) = \sigma_{\alpha\alpha'}^*(t)$$

$$+\Sigma_{\beta\beta'}\left\{\frac{e^{i(\alpha-\alpha'-\beta+\beta')\Delta t}-1}{i(\alpha-\alpha'-\beta+\beta')}\right\}R_{\alpha\alpha'\beta\beta'}\,\sigma_{\beta\beta'}^*. \qquad (2.18)$$

Again, the expression in the curly brackets is replaced by Δt, if $\alpha-\alpha'-\beta+\beta'$ is zero.

Equation (2.18) agrees with the previously obtained expression for $\sigma^*(t+\Delta t)$, accurate to second order in G, except for those terms in the sum over β and β' for which (2.13) does not hold. By the same argument used previously in connection with such terms, they are less than $\tau_c/\Delta t$ times the other terms in (2.18), and therefore negligible. Thus the solution of (2.15) agrees approximately with the

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correct density matrix, and (2.15) can be regarded as the approximate equation of motion of σ^*. The equation of motion in the Schroedinger representation then follows from (2.15) and (2.4):

$$d\sigma_{\alpha\alpha'}/dt = i(\alpha'-\alpha)\sigma_{\alpha\alpha'} + \Sigma_{\beta\beta'} R_{\alpha\alpha'\beta\beta'} \, \sigma_{\beta\beta'}. \qquad (2.19)$$

The imaginary term in (2.19) describes the unperturbed motion of the system as determined by its Hamiltonian E. The matrix R describes the relaxation of the system by the statistical perturbation $G(t)$. It will be called the *relaxation matrix*. The element $R_{\alpha\alpha\beta\beta}$ is simply the transition probability from state β to state α. It is easy to verify that σ remains Hermitian with unit trace as a result of the equation of motion (2.19).

Since the density matrix of the system must not change by much during the time Δt we must have

$$1/R_{\alpha\alpha'\beta\beta'} \gg \Delta t \gg \tau_c. \qquad (2.20)$$

(2.20) gives the condition of validity of the present theory.

We previously ignored terms of order $\tau_c/\Delta t$. Because of (2.20) we can make this quantity approach $R\tau_c$, which is apparently the lower limit of the error in the equation of motion (2.19).

It is important to remember that those terms of the relaxation matrix $R_{\alpha\alpha'\beta\beta'}$ for which $\alpha-\alpha'-\beta+\beta'$ is not zero are in general ineffective in the relaxation process. This can be seen from the first order solution (2.18) of the density matrix equation of motion. If one regards the relaxation term of (2.19) as a small perturbation on the equation of motion, one is reminded of a similar situation in the perturbation theory of the Schroedinger equation. In that case, a perturbation (or matrix element of a perturbation) does not on the average affect the wave function unless it connects eigenstates of the Hamiltonian having the same energy (more precisely, the eigenstates must have energies differing by not more than the order of magnitude of the perturbation itself). Such a perturbation or matrix element is called *secular*. In the present case, elements of the relaxation matrix for which $\alpha-\alpha' \neq \beta-\beta'$ are equivalent in their general effectiveness to non-secular perturbations or matrix elements in perturbation theory. They connect elements of σ having different unperturbed time dependences, namely $e^{i(\alpha-\alpha')t}$ and $e^{i(\beta-\beta')t}$. Since a relaxation matrix element connecting these terms is time-independent, its effect tends to average out over a period of time $1/|(\alpha-\alpha')-(\beta-\beta')|$. This will be true, however, only if the density matrix is unperturbed by relaxation during this time; i.e. only if

$$R_{\alpha\alpha'\beta\beta'} \ll |\alpha-\alpha'-\beta+\beta'|. \qquad (2.21)$$

Therefore, terms of the relaxation matrix for which (2.19) holds are nonsecular perturbations on the equation of motion of σ, and can be ignored. On the other hand, these terms can be included if it is convenient to do so, because by the same argument their presence will not be felt in the behavior of the system. This fact will be useful later when we treat the case of short correlation time of the thermal bath.

In their earlier work, Wangsness and Bloch[3, 4] con-

sidered only the secular elements of the relaxation matrix, for which $\alpha-\alpha'-\beta'+\beta=0$. Bloch's most recent paper,[10] however, considers both the secular and nonsecular elements of R.

In almost every problem of interest, relaxation takes place through the action of only a relatively few time-dependent perturbations. A nuclear spin in a liquid, for example, can be regarded as relaxed by a fluctuating magnetic field having only three independent (x, y, and z) components.[6] In such a case we can write the interaction $G(t)$ as

$$G_{\alpha\alpha'}(t) = \Sigma_q H^q(t) K_{\alpha\alpha'}{}^q. \qquad (2.22)$$

For a nuclear spin in a liquid, the H^q are the three components of fluctuating magnetic field, and the K^q are the x, y, and z components of the magnetic moment operator. In general, the H^q are real, randomly varying functions of time having correlation functions $\langle H^q(t)H^{q'}(t-\tau)\rangle$ and generalized spectral densities defined by

$$k_{qq'}(\omega) = \tfrac{1}{2} \int_{-\infty}^{\infty} d\tau \, \langle H^q(t)H^{q'}(t-\tau) \rangle \, e^{i\omega\tau}. \qquad (2.23)$$

The K^q must be Hermitian.

The representation of G in (2.22) may appear to be a needless complication, but actually it is frequently a simplification because there are usually fewer $H^q(t)$ than $G_{\alpha\alpha'}(t)$, and frequently the H^q are statistically independent (if $k_{qq'}(\omega)\equiv 0$, H^q and $H^{q'}$ are statistically independent). Sometimes it is more convenient to write the summation (2.22) in such a way that the H^q are complex, rather than real. In order that G be Hermitian, it is then necessary that the terms of the sum (2.22) occur in mutually adjoint pairs. Such a convention is used by Bloembergen[12] in his application of the present theory to the relaxation of a two-spin $\tfrac{1}{2}$ system in a molecule executing hindered rotation.

The relaxation matrix is still given by (2.16), with

$$J_{\alpha\alpha'\beta\beta'}(\omega) = \Sigma_{qq'} K_{\alpha\alpha'}{}^q K_{\beta'\beta}{}^{q'} k_{qq'}(\omega). \qquad (2.24)$$

It is a consequence of (2.19) that σ approaches a state corresponding to equal probability for all states (σ diagonal, with all elements equal).[13] This follows because the transition probabilities $R_{\alpha\alpha\beta\beta}$ between states α and β are equal for transitions in either direction:

$$R_{\alpha\alpha\beta\beta} = R_{\beta\beta\alpha\alpha}. \qquad (2.25)$$

Actually, we know that σ will approach its true thermal equilibrium value

$$\sigma^{(T)} = C \exp(-\hbar E/kT), \qquad (2.26)$$

where C is a normalization constant such that $\Sigma_\alpha \sigma_{\alpha\alpha}{}^{(T)} = 1$, and T is the temperature of the thermal bath giving rise to $G(t)$. This fact was lost in this theory apparently because $G(t)$ was regarded as predetermined independent of the $a_\alpha(t)$.

In Section III we will show, using a different model, that if $\sigma = \sigma^{(T)}$ the density matrix will remain unchanged; i.e. the system is in thermal equilibrium with the bath.[14]

This result is obtained quantum mechanically, but it presumably does not depend on quantum mechanics. The same result should follow from a sufficiently detailed classical calculation, *taking the state of the thermal bath as well as that of the system into account*.

Since the theory of this section leads to the prediction of an approach to equal populations of all states (infinite temperature of the system), the fact of approach to the correct thermal equilibrium state must be introduced here as an ad hoc assumption. The simplest way to do this is to replace σ by $\sigma - \sigma^{(T)}$ in the equation of motion (2.19). In Section III we show that this is correct only in the high temperature limit and that in general one must replace $k_{qq'}(\omega)$ in (2.24) by

$$j_{qq'}(\omega) = k_{qq'}(\omega)e^{-\hbar\omega/2kT}. \tag{2.27}$$

Short Correlation Time

If we have the condition

$$|\alpha - \beta|\tau_c \ll 1, \tag{2.28}$$

satisfied for all non-zero elements of $G_{\alpha\beta}(t)$, then all the spectral densities occurring in (2.19), and defined by (2.17) or (2.23), are equal to their zero frequency values:

$$k_{qq'}(\omega) \cong k_{qq'}(0) = j_{qq'}(0) \quad \text{if} \quad \omega\tau_c \ll 1. \tag{2.29}$$

Equation (2.29) follows from (2.23) because the integrand in (2.23) is small for $\tau > \tau_c$, and $\exp i\omega\tau_c \cong 1$.

Using (2.24) and (2.29) in (2.16) and (2.19), and replacing σ by $\sigma - \sigma^{(T)}$ as mentioned previously and justified in Section III, we have, finally, an operator equation of motion for the density matrix:

$$d\sigma/dt = -i[E,\sigma] - \Sigma_{qq'}[K^q,[K^{q'}, \sigma - \sigma^{(T)}]]k_{qq'}(0). \tag{2.30}$$

The virtue of (2.30) is that it is independent of the representation used. As a result, in many cases it is unnecessary to solve the unperturbed Hamiltonian E because the observable quantities required are diagonal sums of operators which are independent of representation. To get (2.30) we included all the nonsecular terms of the relaxation matrix, but as discussed previously these have no average effect on the behavior of σ.

For many purposes it is useful to use the fact that

$$k_{qq}(0) = j_{qq}(0) \cong \langle (H^q)^2 \rangle \tau_c, \tag{2.31}$$

where τ_c is the correlation time of H^q alone. This point of view has been developed by Pines and Slichter.[8]

Finally we may remark that it is easy to show that if E is time-dependent (and is still identical for every member of the ensemble), the relaxation will be unaffected, and (2.19) and (2.30) will still hold, provided the change in E in time Δt is small compared to E. This can be shown by working in a representation in which $E(t)$, the instantaneous Hamiltonian, is diagonal.

The requirement that E vary only slightly in time Δt means that either the total time varying part of E be small compared to E (as is usually the case in magnetic resonance, in which the rf field is much smaller than the dc magnetic field), or that (since $\Delta t \gg \tau_c$)

$$\tau_c \frac{dE}{dt} \ll E. \tag{2.32}$$

Equation (2.32) relates the magnitudes of the operators E and dE/dt. The magnitude of E does not mean here the total energy (which is arbitrary), but rather the order of magnitude of the difference between diagonal elements of E corresponding to states connected by elements of G and dE/dt. Similarly, the magnitude of dE/dt is the order of magnitude of the difference between such diagonal elements of dE/dt, or the order of magnitude of the off-diagonal elements of dE/dt, whichever is larger.

In Section IV we consider the problem of a time-dependent Hamiltonian from a different point of view.

III. Dynamical interaction with a thermal bath

We now consider the behavior of a *system* with the Hamiltonian E, loosely coupled by a time-independent perturbation G to a temperature *bath* or crystal lattice with Hamiltonian F (henceforth we will use the words *system* and *bath* in this sense only). This treatment is the same as that in Bloch's paper[4] except for the discussions of pseudo-stationary perturbations on the system, non-secular relaxation terms, and the case of short correlation time. The results are similar to those of Section II. For these reasons we will merely outline the calculation and give its results. The reader is referred to Appendix C and to the papers of Wangsness and Bloch[3, 4] for details of the method.

The total Hamiltonian is:

$$\mathcal{K} = \hbar E + \hbar F + \hbar G. \tag{3.1}$$

By definition,

$$[E,F] = 0. \tag{3.2}$$

We assume for the time being that E is time-independent. We work in a representation in which E and F are diagonal; the eigenfunctions of F are denoted by their eigenvalues f and a degeneracy parameter u. The eigenvalues of E are denoted by α, β, and γ, and we can ignore possible degeneracy in these eigenvalues. The state of the system plus thermal bath is now described by the density matrix $\rho_{\alpha f u \alpha' f' u'}$.

In analogy to (2.22), it is convenient to write the perturbation G as a sum of products of two operators involving the system alone or the bath alone:

$$G_{\alpha f u \alpha' f' u'} = \Sigma_q K_{\alpha\alpha'}{}^q H_{fuf'u'}{}^q. \tag{3.3}$$

The properties of the bath are characterized by quantum analogues of the spectral densities[15] $j_{qq'}(\omega)$ introduced in Section II. The calculation outlined below shows that these are given quantum mechanically by

$$j_{qq'}(\omega) = \pi \int_{-\infty}^{\infty} df [\Sigma_{uu'}P(f)$$

$$\times H_{(f-\omega)ufu'}{}^q H_{fu'(f-\omega)u'}{}^{q'}\eta_u(f-\omega)\eta_{u'}(f)]. \tag{3.4}$$

Here $\eta_u(f)$ is the density of states of F, with degeneracy

parameter u, per unit range of the eigenvalue f, and $P(f)$ is given by

$$P(f) = \exp(-\hbar f/kT)/\Sigma_{f'u'}\exp(-\hbar f'/kT) \qquad (3.5)$$

We define the characteristic frequency ω^* of the bath, equivalent[16] to $1/\tau_c$ of Section II, by the requirement that, for all q, q', ω, and ω',

$$j_{qq'}(\omega) \cong j_{qq'}(\omega') \quad \text{if} \quad |\omega - \omega'| < \omega^*. \qquad (3.6)$$

Note that $\hbar\omega^* < kT$, which follows from (3.5) and (3.6) and the fact that $P(f)$ is large only for f within kT of the lowest eigenvalue of F.

We wish to find the equation of motion of the system, described by the reduced matrix ("distribution matrix"[3])

$$\sigma_{\alpha\alpha'} = \Sigma_{fu}\,\rho_{\alpha fu\alpha'fu}. \qquad (3.7)$$

The ensemble-average value of any system-observable represented by the operator O is $\Sigma_{\alpha\alpha'}O_{\alpha\alpha'}\sigma_{\alpha'\alpha}$.

The equation of motion of σ is obtained by solving Schroedinger's equation to second order in G, for a time $t+\Delta t$, assuming that at time t the total density matrix ρ is approximated with sufficient accuracy by a density matrix of the following form:

$$\rho_{\alpha fu\alpha'f'u'} = \sigma_{\alpha\alpha'}(t)P(f)\delta_{ff'}\delta_{uu'}. \qquad (3.8)$$

This density matrix implies that the thermal bath is actually in a state corresponding to thermal equilibrium, and the state of the system is completely described by $\sigma_{\alpha\alpha'}(t)$.

Starting with (3.8) at time t, Schroedinger's equation predicts that ρ assumes a mixed character for time greater than t [that is, it cannot be separated into a product of a system density matrix σ and a thermal bath density matrix, as in (3.8)]. However, the behavior of the reduced matrix σ, defined by (3.7), can be described by a first order differential equation, within a certain order of approximation discussed below. It is then assumed that this equation of motion for σ holds for all time, regardless of the past history of the system, provided the bath remains at thermal equilibrium. In other words, at the end of the interval $t+\Delta t$ it is again assumed that the total density matrix ρ can be adequately approximated by (3.8) [with $\sigma(t)$ replaced by $\sigma(t+\Delta t)$]. This is equivalent to re-randomizing the state of the thermal bath at time $t+\Delta t$ and is a frequently used procedure in the theory of irreversible processes. It leads to seemingly irreversible behavior of the system even though Schroedinger's equation is time-reversible.

This calculation differs from Wangsness and Bloch's only in that Δt (corresponding to their t) is restricted only by the condition $\Delta t \gg \tau_c = \omega^{*-1}$. Wangsness and Bloch make an additional requirement corresponding to $\Delta t \gg |\alpha - \alpha'|^{-1}$, where α and α' are any two states of the system connected by G.

In this way, we get an equation of motion of the following form:

$$d\sigma/dt \equiv [\sigma(t+\Delta t) - \sigma(t)]/\Delta t = i[\sigma, E+M+N] + R\sigma. \qquad (3.9)$$

We now discuss this equation term by term; details of its calculation are outlined in Appendix C.

The operator M is given by

$$M = \Sigma_q K^q\,\Sigma_{fu}H_{fufu}{}^q P(f). \qquad (3.10)$$

M represents the effect of the first order stationary perturbation on the system. In nuclear spin systems it gives rise to chemical shifts. As with any perturbation, off-diagonal elements $M_{\alpha\alpha'}$ can be ignored only if they connect states of different energy: i.e. if

$$M_{\alpha\alpha'} \ll |\alpha - \alpha'|. \qquad (3.11)$$

The operator N represents the effect of the second order stationary perturbation by G and is given by

$$N_{\alpha\alpha'} = \Sigma_{qq'\gamma}K_{\alpha\gamma}{}^q K_{\gamma\alpha'}{}^{q'}$$
$$\times \int_{-\infty}^{\infty} d\omega\, j_{qq'}(-\omega)/\pi(\tfrac{1}{2}\alpha + \tfrac{1}{2}\alpha' - \gamma - \omega) \qquad (3.12)$$

If $|\alpha - \gamma| < \omega^*$ for any two states α and γ connected by G, or if $j_{qq'}(\omega) \neq 0$ only for $|\omega| \gg |\alpha - \gamma|$, N can be approximated by

$$N = -\Sigma_{qq'}K^q K^{q'}\int d\omega j_{qq'}(\omega)/\pi\omega. \qquad (3.13)$$

(3.13) is the form of second order perturbation one gets by regarding the K^q as fixed parameters rather than operators in (3.3), and calculating the average second order perturbation of (3.3) on the lattice or bath. The present analysis shows that, as one might expect, this is justified only if the motion of the system is much less rapid than that of the bath with which it interacts. The appearance of the spectral density in N is interesting and probably significant.

An example of the type of perturbation represented by N is indirect nuclear spin coupling via the electronic spins in a molecule or solid.[17, 18]

The term $R\sigma$ in (3.9) describes the relaxation of the system by the bath

$$(R\sigma)_{\alpha\alpha'} = \Sigma_{\beta\beta'}R_{\alpha\alpha'\beta\beta'}\,\sigma_{\beta\beta'}. \qquad (3.14)$$

In this case the relaxation matrix R is given by

$$R_{\alpha\alpha'\beta\beta'} = \Sigma_{qq'}\{K_{\alpha\beta}{}^q K_{\beta'\alpha'}{}^{q'}[j_{qq'}(\alpha-\beta) + j_{qq'}(\alpha'-\beta')]$$
$$- \delta_{\alpha\beta}\Sigma_\gamma K_{\beta'\gamma}{}^q K_{\gamma\alpha'}{}^{q'}j_{qq'}(\beta'-\gamma)e^{\hbar(\beta'-\gamma)/kT}$$
$$- \delta_{\alpha'\beta'}\Sigma_\gamma K_{\alpha\gamma}{}^q K_{\gamma\beta}{}^{q'}j_{qq'}(\beta-\gamma)e^{\hbar(\beta-\gamma)/kT}\}. \qquad (3.15)$$

Actually, only those terms $R_{\alpha\alpha'\beta\beta'}$ for which $\alpha - \alpha' - \beta + \beta' = 0$ are given by (3.15), and their evaluation is identical to that of time-proportional transition probabilities.[1] Evaluation of those terms for which $\alpha - \alpha' - \beta + \beta' \neq 0$ is somewhat more complicated; integrals must be evaluated which contain logarithmic singularities, but these can be dealt with simply by taking Cauchy principal values. The resulting terms of R are multiplied by a factor like the brace in (2.14). If $|\alpha - \alpha' - \beta + \beta'|\Delta t \gg 1$, these terms are small, but can be regarded as resulting from non-secular perturbations on the equation of motion, as discussed in more detail in Section II. These non-secular terms, as given by (3.15), can be included in the equation of motion if it is convenient to do so.

To evaluate the terms of the relaxation matrix (3.15) it is assumed that the spectral density $j_{qq'}(\omega)$ is a constant over a range of ω equal to $1/\Delta t$. This is necessary because the integrals involved have integrands with kernels of width Δt^{-1}. The error introduced in this way is of the order of $(\omega^*\Delta t)^{-1}$ times R or N. In this case (2.20) is required for the same reason as in Section II, so that the minimum error in (3.15) is of the order of R/ω^*, and (3.9) can be regarded as accurate to within this order of magnitude.

It is easily verified that, as is expected,

$$\Sigma_\beta R_{\alpha\alpha'\beta\beta} \exp[-\hbar\beta/kT] = 0. \tag{3.16}$$

This means that if the system is in a state corresponding to thermal equilibrium, it will remain in that state.[14]

We now examine the range of validity of (3.9). The required condition analogous to (2.20) is

$$M, N, R \ll \omega^* < kT/\hbar. \tag{3.17}$$

In (3.17) the symbols M, N, R refer to the size of the off-diagonal elements of these matrices, and (for M, N) the differences between the diagonal elements of states connected by the matrices M, N, and R. If $R \simeq \omega^*$, the behavior of the system becomes difficult to predict; Kubo and Tomita[19] have treated this situation for the case of a nuclear or electronic spin system.

We also have a requirement that

$$M, N \ll E. \tag{3.18}$$

(3.18) assures us that the Boltzmann factors occurring in (3.15) are approximately correct. If (3.18) is violated, it would be reasonable to replace the Boltzmann factors in (3.15) by those with respect to the Hamiltonian $E+M+N$, but it has not been shown explicitly that this is correct.

There does not seem to be any requirement similar to (3.17) and (3.18) on E versus R, provided all elements of R, except perhaps those obeying (2.21), are included in the equation of motion.

We have assumed so far in this section that E is time-independent. If E varies slowly with time, the remarks at the end of Section II apply here also. Relaxation tends to make the density matrix approach the thermal equilibrium density matrix corresponding to the instantaneous Hamiltonian.

High Temperature and Short Correlation Time

We now suppose that the condition

$$|\alpha-\alpha'| \ll kT/\hbar, \tag{3.19}$$

is satisfied for all α and α' connected by G and dE/dt. We also assume that

$$\sigma - \sigma^{(T)} \ll \sigma^{(T)}. \tag{3.20}$$

(3.20) will almost always be a consequence of (3.19), unless the system is prepared in some unusual way, and $\sigma - \sigma^{(T)}$ will ordinarily be of the order of $\hbar|\alpha-\alpha'|/kT$.

Since $R\sigma^{(T)} = 0$ we can replace $R\sigma$ by $R(\sigma - \sigma^{(T)})$ in (3.9). Having done this, we can replace the $j_{qq'}(\omega)$ by $k_{qq'}(\omega)$, defined in this case by (2.25) and (3.4). By so doing we introduce an error which is second order in $\hbar|\alpha-\alpha'|/kT$,

and thus negligible. This yields an equation equivalent to (2.19) with σ replaced by $\sigma - \sigma^{(T)}$, as mentioned in Section II.

If we make the further assumption of short correlation time,

$$|\alpha-\alpha'| \ll \omega^* < kT/\hbar, \tag{3.21}$$

we can replace the $k_{qq'}(\omega)$ by $k_{qq'}(0)$, and we immediately get the expected result (2.30), with E replaced by $E+M+N$.

If it happens that instead of (3.21) we have $|\alpha-\alpha'| \simeq \omega^*$, $kT/\hbar$ it may be possible to expand the Boltzmann factors and spectral densities in (3.15) in a power series in ω. This will be possible if the $j_{qq'}(\omega)$ are analytic for ω less than or equal to all the frequency differences occurring in (3.15). Each term in the power series can then be written in operator form, so that the equation of motion can again be written in operator form provided the series converges. This method is used in the next section.

IV. Time-Dependent Hamiltonian

The previous sections dealt with the problem of relaxation of a system whose Hamiltonian is stationary or nearly stationary in time. In this section we consider the same problem with a time-dependent Hamiltonian by including explicitly and quantum mechanically in our Hamiltonian the device (oscillator, power supply, and/or experimenter) which gives rise to the time dependence of the Hamiltonian. This procedure is somewhat more satisfying than assuming an a-priori time-dependent Hamiltonian, and it also enables us to get higher order corrections in dE/dt to the equation of motion.

We will use the phrase *external device* to denote the source of the time dependence of the Hamiltonian. The external device is assumed to have a Hamiltonian $\hbar D$ with eigenvalues $\hbar d$. Without loss of generality we ignore possible degeneracy of the eigenvalues of D. The total Hamiltonian E in (3.9) is now replaced by

$$E' = E_0 + \mathcal{E}_1 + D. \tag{4.1}$$

E_0 is the time-independent part of the Hamiltonian of the system. D commutes with E_0 and the K^q, and $\mathcal{E}_1$ is a coupling operator which does not commute with E_0, D, or the K^q. We work in a representation in which D and E_0 are diagonal. For simplicity we assume that

$$(\mathcal{E}_1)_{\alpha d\alpha'd'} = X_{\alpha\alpha'} Y_{dd'}. \tag{4.2}$$

Here α and α' are the eigenvalues of E_0. X is a system-observable and Y is an external device-observable. In general, $\mathcal{E}_1$ will actually be a sum of terms of the form (4.2), and it is easy to extend the theory in that case.

We use the density matrix λ to describe the system plus external device. The system is described by the reduced matrix

$$\sigma_{\alpha\alpha'} = \Sigma_d \lambda_{\alpha d\alpha'd}. \tag{4.3}$$

The external device is described by the reduced matrix

$$\mu_{dd'} = \Sigma_\alpha \lambda_{\alpha d\alpha d'}. \tag{4.4}$$

The external device is so large that it is essentially un-

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affected by its interaction with the system; that is, $E_0 + \mathcal{E}_1$ is a small perturbation on D. Furthermore, the external device and system are regarded as more or less uncorrelated with each other. At any time the state of either can be approximately specified without specifying the state of the other (although the state of the system will in general depend on the past states of the external device). This can be stated in density matrix language by assuming that λ is separable into a system density matrix and an external device density matrix:

$$\lambda_{\alpha d \alpha' d'} \cong \sigma_{\alpha \alpha'} \, \mu_{d d'}. \qquad (4.5)$$

The average expectation value of the external device operator Y is

$$\langle Y \rangle = \Sigma_{d d'} Y_{d d'} \, \mu_{d' d}. \qquad (4.6)$$

It is assumed that the expectation value of Y is the same for every member of the ensemble. This means that

$$\langle Y^2 \rangle \cong \langle Y \rangle^2. \qquad (4.7)$$

(4.7) implies that the external device is in a mixture of eigenstates of the operator Y with eigenvalue approximately $\langle Y \rangle$.

If the interaction $\mathcal{E}_1$ contains several terms of the type (4.2) we must also require that all external device-observables occurring in $\mathcal{E}_1$ be simultaneously measurable. This means that for any two such observables Y_1 and Y_2,

$$\langle Y_1 Y_2 \rangle \cong \langle Y_2 Y_1 \rangle. \qquad (4.8)$$

The restrictions (4.7) and (4.8) are the only ones we place on the state of the external device; in general it can and must be very far from thermal equilibrium.

The density matrix λ obeys the equation of motion (3.9), with E replaced by (4.1) and σ replaced by λ (neglecting the pseudostatic interactions M and N):

$$\partial \lambda / \partial t = -i[E', \lambda] + R\lambda. \qquad (4.9)$$

To get the equation of motion for σ we simply take the diagonal sum over d of (4.9), according to the definition (4.3). The only difficulty is that (4.3) is expressed in a representation in which E_0 and D are diagonal, whereas the relaxation matrix R occurring in (4.9) is expressed by (3.15) in a representation in which $E_0 + \mathcal{E}_1 + D$ is diagonal.

This difficulty can be overcome in the case of short correlation time, expressed by (3.19), where α and α' are here eigenvalues of any two eigenstates of $E_0 + \mathcal{E}_1 + D$ connected by the K^q. We can then expand $j_{qq'}(\omega)$ and $\exp(-\hbar\omega/kT)$ in a Taylor series in ω and retain only the first order terms in ω. The resulting expression for $R\lambda$ can be written in operator form:

$$R\lambda \cong \Sigma_{qq'} j_{qq'}(0) \{ [K^q, [\lambda, K^{q'}]]$$

$$- (\hbar/kT)(\lambda[E', K^q]K^{q'} + K^q[E', K^{q'}]\lambda) \}$$

$$+ \partial j_{qq'}/\partial \omega |_{\omega=0} \{ [[E', K^q], \lambda]K^{q'} + K^q[[E', K^{q'}], \lambda] \}. \qquad (4.10)$$

The equation of motion of λ can now be written in the representation in which E_0 and D are diagonal. Substituting (4.5) for λ on the right, and taking the diagonal sum over d we find that σ obeys the same equation of motion as

λ, equations (4.9) and (4.10), except that E' is replaced by $E_0 + E_1$, with

$$E_1 = X\langle Y \rangle. \qquad (4.11)$$

We assume that the system described by σ is close to its instantaneous equilibrium value $\sigma^{(T)}$ given by (2.26), with $E = E_0 + E_1$. As discussed in Section III under "Short Correlation," the deviation $\sigma - \sigma^{(T)}$ will normally be of the order of $\sigma^{(T)}\hbar(E_0 + E_1)/kT$.

The relaxation term $R\sigma$ can then be simplified further by neglecting all terms except those of zeroth or first order in $\sigma - \sigma^{(T)}$, $|\alpha - \alpha'|/\omega^*$, and $\hbar|\alpha - \alpha'|/kT$. Since $\partial j_{qq'}/\partial \omega$ is of the order of $j_{qq'}/\omega^*$, we can replace σ by $\sigma^{(T)}$ in all but the first term of $R\sigma$. Using the fact that, to first order in $(kT)^{-1}$,

$$kT[\sigma^{(T)}, K^q] \cong \hbar \sigma^{(T)}[K^q, E_0 + E_1] \cong \hbar[K^q, E_0 + E_1]\sigma^{(T)}, \qquad (4.12)$$

we find that the last two terms of $R\sigma$ are of order $\hbar(\alpha - \alpha')/\omega^* kT$ and therefore negligible. The remaining terms of $R\sigma$ combined with the rest of the equation of motion give (2.30), with E replaced by $E_0 + X\langle Y \rangle$.

The external device giving rise to $\langle Y \rangle$ can be quite large and complicated; for example it can be a complete oscillator with battery power supply. As long as the variation of $\langle Y \rangle$ is slow compared to the correlation time of the bath, the above analysis will hold.

If the variation of $\langle Y \rangle$ is too rapid, it may still be possible to calculate its effect by carrying the expansion of $R\lambda$ out to higher order than the first order expression (4.10). As an example, the second order term in $\hbar/kT$ of $R\lambda$ is

$$-\tfrac{1}{2}(\hbar/kT)^2 j_{qq'}(0) \{ \lambda[E, [E, K^q]]K^{q'} + K^q[E, [E, K^{q'}]]\lambda \}. \qquad (4.13)$$

Substituting (4.5) and taking the diagonal sum over d as before, we get for this term

$$-\tfrac{1}{2}(\hbar/kT)^2 j_{qq'}(0) \{ \sigma[E_0 + E_1, [E_0 + E_1, K^q]]K^{q'}$$

$$+ K^q[E_0 + E_1, [E_0 + E_1, K^{q'}]]\sigma$$

$$- i\sigma[\partial(E_0 + E_1)/\partial t, K^q]K^{q'} - iK^{q'}[\partial(E_0 + E_1)/\partial t, K^q]\sigma \}. \qquad (4.14)$$

To get (4.14) we used (4.7) and (if applicable) (4.8), and the fact that $\partial(E_0 + E_1)/\partial t \cong iX \langle [D, Y] \rangle$.

The first two terms of (4.14) are consistent with the assumption that the system relaxes with respect to its instantaneous Hamiltonian, and are in fact the same terms that occur in the power series expansion of $R\sigma$ in (3.9) if E_0 is replaced by the instantaneous Hamiltonian $E_0 + E_1$. The last two terms indicate the error in this assumption. They are negligible compared to the first order terms if

$$\partial(E_0 + E_1)/\partial t \ll (E_0 + E_1)kT/\hbar. \qquad (4.15)$$

Consideration of other second order terms leads to a condition similar to (4.15), with $kT/\hbar$ replaced by ω^*. If these conditions are not obeyed, it is necessary to include in the equation of motion terms of the kind in the last line of (4.14), and perhaps still higher order terms. This may be useful as long as the resulting series of operator terms converges.

This section is not supposed to cover every situation in-

volving a time-dependent Hamiltonian, but only to indicate a general line of attack. Each case must be treated individually. In particular, we have neglected possible relaxation of the system by the external device. If such relaxation occurs it can in some cases be treated classically,[20] or quantum mechanically as in Section III.

V. Applications

The formalism of this paper can be applied to a wide variety of problems, including Brownian motion,[21] modifications of the Bloch equations of motion for spin systems when the radio frequency magnetic field is large compared to the dc magnetic field,[22] and nuclear resonance saturation in solids.[23] Bloembergen has used the random perturbation theory of Section II to treat the relaxation of a pair of identical spin $\frac{1}{2}$ nuclear moments on a molecule exhibiting hindered rotation.[12]

Most of the applications which have not been treated previously[3, 4, 9, 10] are rather complicated, so we restrict this section to a simple example which illustrates the usefulness of the notation and ideas of this paper. This example is the calculation of the relaxation time of a system of coupled nuclear spins in a metal, for arbitrary fixed external magnetic field intensity. As will be seen, the relaxation time changes when the external field becomes comparable to the internal internuclear magnetic fields, and the details of this change will be different depending on whether each nucleus sees approximately the same fluctuating magnetic field (due to the electrons in the metal) as its near neighbors, or whether each nucleus sees a fluctuating magnetic field which is statistically independent of that seen by its near neighbors. The relaxation time is a quantity which can be readily measured[24] at sufficiently low temperatures, and because it depends on the details of the fluctuating fields set up by the electrons in the metal it is a quantity which may provide useful information about the solid state.

We consider only temperatures well below the melting point, so that the positions of the nuclei can be regarded as fixed, and we assume that only one species of nuclear spin is present. The spin Hamiltonian is[25]

$$\hbar E = \mathcal{3C}_0 + \mathcal{3C}_d + \mathcal{3C}_e \tag{5.1}$$

$\mathcal{3C}_0$ is the energy of the spins with respect to the external field:

$$\mathcal{3C}_0 = -g\beta H_0 \sum_j I_{jz} \tag{5.2}$$

where g is the nuclear g-factor, β is the Bohr magneton, H_0 is the applied magnetic field in gauss, assumed to be in the z-direction, and I_{jz} is the z component of the spin angular momentum operator (in units of $\hbar$) of the j'th nucleus.

$\mathcal{3C}_d$ is the classical dipolar interaction:

$$\mathcal{3C}_d = g^2\beta^2 \sum_{k>j} (r_{jk}^{-3} \mathbf{I}_j \cdot \mathbf{I}_k - 3r_{jk}^{-5} \mathbf{r}_{jk} \cdot \mathbf{I}_j \mathbf{r}_{jk} \cdot \mathbf{I}_k), \tag{5.3}$$

where $\mathbf{r}_{jk}$ is the vector connecting the positions of nuclei j and k.

$\mathcal{3C}_e$ is the so-called exchange energy, which in the nuclear spin case usually arises from indirect coupling via the electronic spins (the interaction $\mathcal{3C}_e$ is an example of the operator N in Section III):

$$\mathcal{3C}_e = \sum_{j>k} A_{jk} \mathbf{I}_j \cdot \mathbf{I}_k \tag{5.4}$$

It will be clear to the reader that it is impossible to solve this Hamiltonian, so that the Wangsness-Bloch formalism cannot be applied directly.

For a measurement of the relaxation time, the spin system is perturbed[24] in such a way that it is no longer in the state corresponding to thermal equilibrium. Observations are then made on the spin system as a function of time, in such a way that the spin system is not importantly affected by the method of observation. In general it is impossible to solve the equation of motion (2.30) (which applies in this case because of the rapid motion of the electrons) or even to specify the initial density matrix of the system with precision. Therefore, we must resort to making a simplifying assumption about the state of the system in order to have a meaningful theory (or a meaningful experiment, for that matter). The assumption we make is that the spin system is always in a canonical distribution of states, described by a spin temperature[26] which is different from the lattice temperature: $\sigma \cong \sigma^{(T_s)}$, where T_s is the spin temperature. This is a questionable assumption, but it is probably not grossly incorrect if there is no large rf field applied, and there appears to be no more satisfactory alternative.

At any presently attainable temperature the thermal energy kT is always much larger than the magnetic energy of a nuclear spin, and the same applies to kT_s. Therefore we can write

$$\sigma \cong C[1 - (\mathcal{3C}_0 + \mathcal{3C}_d + \mathcal{3C}_e)/kT_s], \tag{5.5}$$

where C is a normalization constant: $C = (2I+1)^{-N}$.

The ensemble average expectation value of any observable O is given by the diagonal sum (trace) of the product $O\sigma$:

$$\langle\langle O \rangle\rangle \equiv Tr(O\sigma) \equiv \sum_{\alpha\beta} O_{\alpha\beta}\sigma_{\beta\alpha}. \tag{5.6}$$

Using the properties of the spin operators I_j we have

$$\langle\langle \mathcal{3C}_0 \rangle\rangle = -X_0(T_s)H_0^2; \tag{5.7}$$

$$\langle\langle \mathcal{3C}_d \rangle\rangle = [10 \langle (\Delta H)^2 \rangle_{Av}/3H_0^2]\langle\langle \mathcal{3C}_0 \rangle\rangle; \tag{5.8}$$

$$\langle\langle \mathcal{3C}_e \rangle\rangle = \frac{\sum_{j>k} A_{jk}^2 I(I+1)}{Ng^2\beta^2 H_0^2} \langle\langle \mathcal{3C}_0 \rangle\rangle. \tag{5.9}$$

Here $X_0(T_s)$ is the static nuclear susceptibility $\frac{1}{3}Ng^2\beta^2 I(I+1)/kT_s$ corresponding to temperature T_s, N is the total number of nuclear spins, and $\langle (\Delta H)^2 \rangle_{Av}$ is the VanVleck expression for the second moment (in Gauss squared) of the nuclear resonance line which would be observed in a powdered (randomly oriented) sample of the metal:

$$\langle (\Delta H)^2 \rangle_{Av} = \frac{3}{5}g^2\beta^2 I(I+1) \sum_{j>k} r_{jk}^{-6}/N \tag{5.10}$$

The rate of change of the energy of the spin system is given by

$$\frac{d}{dt}\langle\langle \hbar E \rangle\rangle = \hbar Tr\left(E\frac{d\sigma}{dt}\right). \tag{5.11}$$

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If we assume that the density matrix can always be approximated by (5.5), we get from (2.30)

$$\frac{d}{dt}\langle\langle\hbar E\rangle\rangle = -(\langle\langle\hbar E\rangle\rangle - \langle\langle\hbar E\rangle\rangle_0)/T_L, \tag{5.12}$$

where $\langle\langle\hbar E\rangle\rangle_0$ is the thermal equilibrium value of $\langle\langle\hbar E\rangle\rangle$, and

$$\frac{1}{T_L} = -\frac{Tr\,\Sigma_{qq'}[K^{q'},[K^q,E]]k_{qq}(0)E}{TrE^2}. \tag{5.13}$$

T_L is the measured[24] spin-lattice relaxation time of the spin system. To evaluate T_L we must make an assumption about the relaxation mechanism. We wish to restrict ourselves to relaxation by conduction electrons in a metal. The hyperfine interaction between the electronic and nuclear spins is responsible for relaxation in this case, and $\omega^* \simeq kT$, so that the condition for fast correlation time is met. We use the semi-classical formalism of Section II, and consider only two extreme cases.

Case I: Uncorrelated Relaxation

We assume that

$$G = \Sigma_{j,\nu}\,g\beta\,H_{j\nu}(t)I_{j\nu}, \tag{5.14}$$

where $\nu = x,y,z$. In other words, it is assumed that each spin feels a magnetic field $\mathbf{H}_j(t)$ as a result of its interaction with the electrons in the metal. All the $\mathbf{H}_j(t)$ have the same random character and are statistically independent:

$$k_{j\nu j'\nu'}(0) \equiv g^2\beta^2 \int_0^\infty H_{j\nu}(t)H_{j'\nu'}(t-\tau)d\tau$$
$$= \delta_{jj'}\delta_{\nu\nu'}/2T_1. \tag{5.15}$$

It is easily verified that if the spins were non-interacting ($\mathcal{H}_d = 0$), their magnetization would obey the Bloch equations, with $T_1 = T_2$ and T_1 defined by (5.15). Korringa[27] has calculated T_1 quantum mechanically for a real metal.

The factor $\delta_{jj'}$ occurring in (5.15) implies that the field $\mathbf{H}_j$ seen by the nucleus j is uncorrelated with the field $\mathbf{H}_{j'}$ seen by nucleus j', so that all the nuclei are relaxed independently. The factor $\delta_{\nu\nu'}$ implies that each component of the field on a given nucleus is uncorrelated with either of the other two components; i.e. the field $\mathbf{H}_j$ is random in both direction and magnitude.

Physically this corresponds to a metal in which the electron wavelength is short compared to a lattice spacing. In such a case the individual electrons can be regarded as localized in less than a unit cell, and the electronic wave function at one nucleus has little relation to the wave function at a neighbor. The effective hyperfine magnetic field due to the electrons is then also more or less uncorrelated from one nucleus to its near neighbors.

Using (5.14) in (5.13) we get

$$\frac{1}{T_L} = \frac{1}{T_1}\left[\frac{\langle\langle\mathcal{H}_0\rangle\rangle + \delta\langle\langle\mathcal{H}_d\rangle\rangle + \epsilon\langle\langle\mathcal{H}_e\rangle\rangle}{\langle\langle\mathcal{H}_0\rangle\rangle + \langle\langle\mathcal{H}_d\rangle\rangle + \langle\langle\mathcal{H}_e\rangle\rangle}\right], \tag{5.16}$$

with $\delta = \epsilon = 2$.

For large H_0, where $\mathcal{H}_0$ is dominant, $T_L = T_1$ as expected. For small H_0, $T_L \cong \frac{1}{2}T_1$ and relaxation takes place twice as fast. It is not hard to see the reason for this behavior. Individual nuclei are relaxed independently in a time T_1, under the assumption (5.14). If most of the energy $\hbar E$ is in the form of $\mathcal{H}_0$, as it is for large H_0, the energy will approach equilibrium as fast as single spins do, since $\mathcal{H}_0$ is a sum of single spin operators. This rate is $1/T_1$. On the other hand, if H_0 is small, the energy operator is a sum of products of two spin operators, and the expectation value of each of these spin operators will be changed in an average time T_1, so that the average value of the Hamiltonian will change in half this time, or at a rate $2/T_1$. In other words, the energy can change either through a flip of one spin (in time T_1) or of the other spin with which it interacts (in time T_1), and the energy relaxation time should thus be half as large as the individual spin relaxation time.

Case II: Correlated Relaxation

We now consider what would happen if the fluctuating field seen by one nucleus is identical to that at its near neighbors. This would be the case in a metal with an almost empty or full band, in which the wavelengths of the electrons are large compared to a lattice spacing, so that the electrons are unlocalizable and the hyperfine interaction field is more or less the same for near neighbors.

Such spatial correlation can be expressed in terms of the correlation functions of the components of the fluctuating fields $\mathbf{H}_j(t)$:

$$k_{j\nu j'\nu'} = \delta_{\nu\nu'}/2T_1, \tag{5.15a}$$

for all nuclei j and j' which are sufficiently close to contribute appreciably to the spin-spin energy. (5.15a) can hold only if $\mathbf{H}_j(t) = \mathbf{H}_{j'}(t)$.

Substituting in (5.13), we find that T_L is given by (5.16) with $\delta = 3$ and $\epsilon = 0$.

The fact that $\epsilon = 0$ is a reflection of the invariance of the $\mathbf{I}_j\cdot\mathbf{I}_k$ (exchange) interaction under rotation of both spins (j and k) through the same angle. If both spins see identical fluctuating fields they will both be turned through the same angle no matter what the field is. The fact that $\delta = 3$ is similarly a reflection of the strong dependence of the dipolar interaction between two spins on an equal rotation of the two spins through the same angle.

In a real metal[23] the relaxation time will be somewhere between these two cases, usually nearer Case I. The problem is straightforward to work out by the methods of Section III, but is too complicated to include in the present paper, in the absence of any experimental results.

VI. Concluding remarks

The most unsatisfactory features of the theories outlined in this paper are the assumption of re-randomization of the thermal bath [equation (3.8)], and the assumption that the bath and external device are uncorrelated with the system [equations (3.8) and (4.5)]. The first assumption is basic to the theory of irreversible processes, and is discussed in a sophisticated way by Van Hove[28] for quantum mechanical systems, and classically by Brout and Prigogine.[29] We have not attempted to contribute to these dis-

cussions, but have merely tried to treat the more pedestrian problem of finding the most general and convenient density matrix equation of motion which results from these assumptions.

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Appendix A

We will now discuss the independently developed work of Bloch[10] and its relation to the formalism in this paper.

Bloch's paper is primarily concerned with the treatment of relaxation of a system whose Hamiltonian contains an important time dependence, whereas the present paper is aimed more toward the problem of complicated systems with relatively unimportant time variation. Bloch's theory should be applicable to a system with a more rapid time dependence than ours, although his general formalism is necessarily so complicated as to be difficult to apply to any but the simplest physical systems.

Bloch transforms away the system Hamiltonian $\hbar E(t)$ by transforming into a generalized interaction representation. In this representation the interaction G acquires a time dependence which is a function of the time dependence of $E(t)$, and which Bloch assumes can be Fourier analyzed. Presumably this would always be possible if the time dependence of $E(t)$ were reasonable, and it would be relatively easy if $E(t)$ contained only a few sinusoidal components as is usually the case experimentally.

Once the interaction G has been Fourier analyzed, the theory becomes similar to Wangsness and Bloch's earlier work.[3, 4] However, in his current paper[10] Bloch includes a discussion equivalent to our discussion of secular and non-secular relaxation in Section II, generalized to take account of the time dependence of E, and as a result gets the less stringent conditions of validity for the theory which we give in Section III.

Bloch specializes his general theory to treat a slowly varying Hamiltonian, and gets an equation of motion identical in physical content and validity to his earlier work and our Section III. This equation of motion can be applied to systems as complicated as those treated in the present paper, and the only advantages of the treatment we have presented here are that the notation is designed specifically to be applied to complicated systems where possible, and that the connection to the semiclassical theory of Section II is more explicitly made.

Although Bloch's paper does not contain anything like our Section IV, it is likely that his theory could be made to give higher order corrections of the type (4.14). Bloch's formalism is more likely to be useful than our Section IV because he essentially expands the time dependence of the Hamiltonian in a Fourier series, whereas in our Section IV it is expanded in a power series.

Appendix B

We give here some more of the details of the calculation leading to equation (2.11).

The first second-order term of (2.8) is

$$\langle a_{\alpha'}^{(1)\dagger}(t+\Delta t)a_\alpha^{(1)}(t+\Delta t) \rangle =$$

$$\Sigma_{\beta\beta'}\sigma_{\beta\beta'}{}^*(t) \langle \int_t^{t+\Delta t} G_{\alpha'\beta'}{}^\dagger(t')e^{-i(\alpha'-\beta')t'}dt'$$

$$\times \int_t^{t+\Delta t} G_{\alpha\beta}(t'')e^{i(\alpha-\beta)t''}dt'' \rangle. \qquad (B1)$$

To get (B1) we used (2.7), and assumed that the $a_\alpha(t)$ are independent of $G(t')$ (since $t'-t \gg \tau_c$ over most of the range of integration $\Delta t \gg \tau_c$).

Setting $\tau = t'-t''$, and changing to new variables of integration, we get for (B1)

$$\Sigma_{\beta\beta'}\sigma_{\beta\beta'}{}^* \{ \int_0^{\Delta t} d\tau P_{\alpha\beta\alpha'\beta'}(\tau)e^{-i(\alpha-\beta)\tau}$$

$$\times \int_{t+\tau}^{t+\Delta t} dt' e^{i(\alpha-\beta-\alpha'+\beta')t'}$$

$$+ \int_{-\Delta t}^0 d\tau P_{\alpha\beta\alpha'\beta'}(\tau)e^{-i(\alpha-\beta)\tau} \int_t^{t+\Delta t+\tau} dt' e^{i(\alpha-\beta-\alpha'+\beta')t'} \}. (B2)$$

Changing τ to $-\tau$ in the second term, and carrying out the integrations over t', we get the first two terms of (2.11). The last two terms follow similarly from the remaining second order terms of (2.8).

Appendix C

To get the equation of motion (3.9) quantum mechanically, one can either solve the equation of motion[2] of the total density matrix ρ to second order in G, or solve Schroedinger's equation to second order in G and use the definitions of ρ and σ to get the time variation of σ. Wangsness and Bloch[3,4] use the first method; we use the second.

At time t each member of the ensemble is described by a wave function of the form

$$\Psi(t) = \Sigma_{\alpha fu}a_{\alpha fu}(t)e^{-i(\alpha+f)t} \psi_\alpha \varphi_{fu}, \qquad (C1)$$

where φ_{fu} is an eigenfunction of F having eigenvalue f and degeneracy parameter u.

The solution of Schroedinger's equation is given by (C1), with

$$a_{\alpha fu}(t+\Delta t) = \Sigma_n a_{\alpha fu}^{(n)}(t+\Delta t), \qquad (C2)$$

where $\quad a_{\alpha fu}^{(0)}(t+\Delta t) = a_{\alpha fu}(t);$ (C3)

$$a_{\alpha fu}^{(1)}(t+\Delta t) = -\Sigma_{\beta f'u'} G_{\alpha fu\alpha'f'u'}e^{i(\alpha-\beta+f-f')t}$$

$$\times \{ (e^{i(\alpha-\beta+f-f')\Delta t}-1)/(\alpha-\beta+f-f') \} a_{\beta f'u'}(t); \quad (C4) \qquad \mathbf{29}$$

$$a_{\alpha fu}^{(2)} = \Sigma_{\beta f'u'\beta'f''u''} \frac{G_{\alpha fu\beta f'u'}G_{\beta f'u'\beta'f''u''}e^{i(\alpha-\beta'+f-f'')t}}{\beta-\beta'+f'-f''}$$

$$\times \left[\frac{e^{i(\alpha-\beta'+f-f'')\Delta t}-1}{\alpha-\beta'+f-f''} - \frac{e^{i(\alpha-\beta+f-f')\Delta t}-1}{\alpha-\beta+f-f'} \right] a_{\beta'f''u''}(t). \quad (C5)$$

The reduced density matrix $\sigma_{\alpha\alpha'}(t+\Delta t)$ is given by

$$\Sigma_{nn'fu} \langle a_{\alpha'fu}^{(n)}(t+\Delta t)a_{\alpha fu}^{(n')}(t+\Delta t) \rangle e^{i(\alpha'-\alpha)(t+\Delta t)}. \quad (C6)$$

The first term ($n'=n=0$) of (C6) is simply $\sigma_{\alpha\alpha'}(t)$. Subtracting this term, and dividing by Δt, gives the equation of motion (3.9), provided $\sigma(t)$ is assumed given by (3.8). We now discuss in more detail the origin of each term in (3.9).

The commutator $i[\sigma,E]$ comes from the factor $e^{i(\alpha'-\alpha)t}$ in (C6).

The commutator $i[\sigma,M]$ comes from the two first order terms in (C6), i.e. terms with $n'+n=1$. Their evaluation is straightforward, and to get the commutator one can either take the limit $\Delta t \to 0$, or assume a finite Δt, in which case one must go through an argument like that in Section II about non-secular terms of the operator M.

The commutator $i[\sigma,N]$ comes from second order terms of the type given by the product of $a_\alpha^{(0)}$ times that part of $a_{\alpha'}^{(2)}$ which contains the first term in the square bracket in (C5). There are two such terms, and if the non-secular terms are treated as before, these can be written $i[\sigma U - \tilde{U}^\dagger \sigma]$, with the non-Hermitian matrix U given by

$$U_{\alpha\alpha'} \equiv \tilde{U}_{\alpha'\alpha}$$

$$= \Sigma_{qq'\gamma} K_{\alpha\gamma}^q K_{\gamma\alpha'}^{q'} \int_{-\infty}^{\infty} d\omega j_{qq'}(-\omega)/\pi(\alpha-\gamma-\omega). \quad (C7)$$

If we replace $U_{\alpha\alpha'}$ by $N_{\alpha\alpha'}$ we will introduce an error of the order of $(\alpha-\alpha')U(\partial_{jqq'}/\partial\omega)/j_{qq'} \cong (\alpha-\alpha')U/\omega^*$. However, in the time Δt the effect of $U_{\alpha\alpha'}$ on σ is never larger than $U/(\alpha-\alpha')$, if $\alpha \neq \alpha'$, so that the total error introduced in σ is of the order of U/ω^*, which is within the accuracy of the theory in general. Therefore it is permissible to replace U by the Hermitian form N.

The relaxation terms $R\sigma$ come from the remaining second order terms in (C6). As an example, we outline the evaluation of the term in (C6) with $n=n'=1$ which yields the first two terms of the relaxation matrix R.

Changing the sums over f and f' into integrations, and changing variables of integration to f and $\omega = f-f'$, we get for this term

$$\Sigma_{\beta\beta'}\sigma_{\beta\beta'} \Sigma_{qq'} K_{\alpha\beta}^q K_{\beta'\alpha'}^{q'} \int d\omega \, \Delta t \, j_{qq'}(\omega) \, e^{i(\alpha'-\alpha-\beta'-\beta)t}$$

$$\times \left[\frac{(e^{i(\alpha-\beta-\omega)\Delta t}-1)(e^{-i(\alpha'-\beta'-\omega)\Delta t}-1)}{(\alpha-\beta-\omega)\Delta t \, (\alpha'-\beta'-\omega)\Delta t} \right]. \quad (C8)$$

The evaluation of those terms of (C8) for which $\alpha-\beta=\alpha'-\beta'$ is straightforward and is identical to the evaluation of time proportional transition probabilities. In this case it is assumed that $j_{qq'}(\omega)$ can be replaced by the constant $j_{qq'}(\alpha-\beta)$. Since the expression in the square brackets is large only for a range of ω of Δt^{-1} around $\alpha-\beta$, this

introduces an error in R of $R(\partial_{jqq'}/\partial\omega)/\Delta t \, j_{qq'} \cong R/\omega^*\Delta t$ and a corresponding error in σ of the order of R/ω^*. This error is negligible within the accuracy of this theory.

The evaluation of the non-secular terms for which $\alpha-\beta \neq \alpha'-\beta'$ is also accomplished by replacing $j_{qq'}(\omega)$ by a constant. In this case we can replace $j_{qq'}(\omega)$ by either $j_{qq'}(\alpha-\beta)$ or $j_{qq'}(\alpha'-\beta')$, or any convenient intermediate value, by the same argument used above in connection with the replacement of the non-Hermitian matrix U by N. The Cauchy principal value of the integral of the expression in the square bracket in (C8) is easily shown by contour integration to be

$$-2i\pi \frac{e^{i(\alpha-\beta-\alpha'+\beta')\Delta t}-1}{\alpha-\beta-\alpha'+\beta'}. \quad (C9)$$

Taking for $j_{qq'}(\omega)$ in (C8) the symmetric form $\frac{1}{2}j_{qq'}(\alpha-\beta)+\frac{1}{2}j_{qq'}(\alpha'-\beta')$ we get an expression corresponding to that part of the first order (in R) solution of (3.9) contributed by the first two terms of R.

The other two terms of R are obtained similarly from the remaining second order terms of (C6). In the last two terms of R it is possible to change $j_{qq'}(\beta'-\gamma)$ to $j_{qq'}(\alpha'-\gamma)$, or a convenient linear combination thereof, and to change $j_{qq'}(\beta-\gamma)$ similarly, without introducing an error in σ large compared to the existing error in the theory, of order R/ω^*.

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