computed using $C_t^{-1}$ rather than $C_t$ as a measure of strain. Our analysis shows that any other molecular model must give the same or an equivalent result, provided only that terms of order $o(\|G(s)\|)$ may be neglected.

As we have remarked in Sec. 5, the norm $\|G(s)\|$ is small in particular for "slow" motions, and hence the finite linear theory applies in this case. For slow flows in simple fluids, the finite linear theory is actually equivalent to the classical theory of Newtonian fluids, provided that the influence function $h$ satisfies the relation (6.3) with $r>\frac{3}{2}$. This fact and analogous results for fluids of higher order are proved in reference 9.

Rivlin and his co-workers[14] in recent years have developed memory theories involving multiple integrals similar to the second-order theory proposed in Sec. 6. The emphasis in their work has been on the representation theorems following from material objectivity and symmetry. In particular, the representations mentioned here in Secs. 5 and 6 can be derived using their results. An investigation of higher order theories of viscoelasticity based on the existence and complete continuity of Fréchet differentials of order $>2$ would make much more use of such representation theorems.

---

[14] A. J. M. Spencer and R. S. Rivlin, Arch. Ratl. Mech. Anal. 4, 214 (1960).

---

REVIEWS OF MODERN PHYSICS VOLUME 33, NUMBER 2 APRIL, 1961

# Quantum-Mechanical and Semiclassical Forms of the Density Operator Theory of Relaxation*

PAUL S. HUBBARD

*Department of Physics, University of North Carolina, Chapel Hill, North Carolina*

## 1. INTRODUCTION

NUCLEAR magnetic resonance and relaxation involves the interaction of nuclear spins with each other, with externally applied magnetic fields, and with the molecular surroundings of the spins. The Hamiltonian of the system of spins and their molecular surroundings can be written in the form

$$\mathcal{H}=\hbar[E(s,t)+F(q)+G(s,q)], \tag{1}$$

where $\hbar E(s,t)$ is the part of the Hamiltonian that depends only on the spin variables $s$ and the time (for example, the interaction energy of the nuclear magnetic moments with the time-dependent externally applied magnetic fields), $\hbar F(q)$ is the energy of the molecular degrees of freedom $q$, and $\hbar G(s,q)$ is the energy of interaction of the spins and the molecular surroundings. Since the system represented by this Hamiltonian is in general quite complicated, consisting of many nuclei and molecules, it can be appropriately treated by considering an ensemble of such systems and calculating the average behavior by the methods of statistical mechanics.

Bloch[1] has used the density operator formalism of quantum statistical mechanics to derive a differential equation for a reduced density operator $\sigma(s,t)$ in terms of which the ensemble average of the expectation value of any spin operator $Q(s)$ is given by

$$\langle Q\rangle=\mathrm{Tr}[\sigma(s,t)Q(s)]. \tag{2}$$

Redfield[2] has independently derived a similar theory, but it is limited to the case in which $E$ does not depend explicitly on the time. Tomita has developed more specialized density operator theories of magnetic resonance saturation[3] and magnetic double resonance.[4]

Redfield[2] has also derived an equation for $\sigma$ by formulating the problem in another manner, considering an ensemble of systems with Hamiltonians

$$\mathcal{H}=\hbar[E(s)+G(s,t)], \tag{3}$$

where $G(s,t)$ is a random function of the time. The random time dependence of $G$ is usually the result of the random variation with time of coordinates $q$ upon $G$ depends:

$$G(s,t)=G(s,q(t)). \tag{4}$$

Since the time dependence of the $q(t)$ is usually determined by considering the $q$ to be coordinates of a system whose motion is calculated classically, the resulting relaxation theory is called semiclassical. The transition probability method introduced by Bloembergen, Purcell, and Pound[5] (BPP) for the calculation of nuclear magnetic relaxation is in effect a special case of Redfield's semiclassical theory, involving only the diagonal elements of $\sigma$ between eigenstates of $E$, these diagonal elements being proportional to the probable relative populations of the energy levels of $E$ as a

---

* Supported in part by the National Science Foundation.

[1] F. Bloch, Phys. Rev. 105, 1206 (1957).

[2] A. G. Redfield, IBM J. Research Develop. 1, 19 (1957).

[3] K. Tomita, Progr. Theoret. Phys. (Kyoto) 19, 541 (1958).

[4] K. Tomita, Progr. Theoret. Phys. (Kyoto) 20, 743 (1958).

[5] N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. 73, 679 (1948). Hereafter referred to as BPP.

function of time. The BPP method is correct only for cases in which the differential equations for the diagonal matrix elements of $\sigma$ are independent of the off diagonal elements. Redfield's semiclassical theory is restricted to problems in which the spin energy $E$ does not depend explicitly on the time: In addition, it has the disadvantage that Boltzmann factors must be introduced in an *ad hoc* manner in order for the theory to predict the expected Boltzmann form for the density operator of the spin system in thermal equilibrium. Nonetheless, the semiclassical relaxation theory, in which the motion of the molecular surroundings is treated classically, has been very useful in predicting nuclear magnetic relaxation rates in terms of the classical properties of the molecular surroundings, the calculation of the longitudinal relaxation time of water by BPP being a classic example.

In this paper it is shown that both quantum-mechanical and semiclassical forms of a density operator relaxation theory can be derived from a common formulation. The quantum-mechanical form of the theory is similar to that given by Bloch. Both the quantum-mechanical and semiclassical forms of the relaxation theory are applicable when the spin energy $E$ depends explicitly on the time, and both forms of the theory predict without *ad hoc* assumptions the expected thermal equilibrium form of $\sigma$.

As an example, the theory is used to calculate the behavior of a system of $N$ identical spin $\frac{1}{2}$ nuclei in equivalent positions in a liquid when the system is exposed to the usual large constant magnetic field and transverse rotating field, and is relaxed by the dipole-dipole interactions between the nuclear magnetic moments. The rotating field is not considered as a perturbation, so that the results apply in the case of saturation. The results obtained are similar to those of a previous treatment by Tomita[3]; however, it is shown that the validity of the calculation is restricted by the assumption that the dipole-dipole interaction between any two spins is uncorrelated with the dipole-dipole interactions between either of these spins and any other spin.

## 2. GENERAL THEORY

It is shown in quantum statistical mechanics that an ensemble of identical noninteracting systems, each having Hamiltonian $\mathcal{H}$, can be described by a density operator $\rho$ in the sense that the expectation value of any operator $Q$, averaged over the ensemble, is given by

$$\langle Q\rangle=\mathrm{Tr}[\rho(t)Q]. \tag{5}$$

The density operator is a solution of the equation

$$i\hbar(d\rho/dt)=[\mathcal{H},\rho], \tag{6}$$

subject to the condition that for all values of $t$,

$$\mathrm{Tr}[\rho(t)]=1. \tag{7}$$

The density operator describing Maxwell-Boltzmann systems in thermal equilibrium at temperature $T$ is

$$\rho^T=\exp(-\mathcal{H}/kT)/\mathrm{Tr}[\exp(-\mathcal{H}/kT)]. \tag{8}$$

Consider the formulation of the problem of nuclear magnetic resonance and relaxation described in the first paragraph of Sec. 1. The notation here is changed slightly, the Hamiltonian of a representative system now being written

$$\mathcal{H}=\hbar[E^0(s,t)+F(q)+G^0(q,s)], \tag{9}$$

where $\hbar E^0(s,t)$ is the Hamiltonian of the spin part of the system, $\hbar F(q)$ the Hamiltonian of the molecular degrees of freedom or bath, and $\hbar G^0(q,s)$ the Hamiltonian of the interaction between the spin system and its molecular surroundings. The spin energy is now redefined to include the average over an ensemble of baths in thermal equilibrium of the interaction $G^0(q,s)$:

$$E(s,t)\equiv E^0(s,t)+\langle G^0(q,s)\rangle_q, \tag{10}$$

$$G(q,s)\equiv G^0(q,s)-\langle G^0(q,s)\rangle_q, \tag{11}$$

where

$$\langle G^0(q,s)\rangle_q\equiv\mathrm{Tr}[\rho^T(q)G^0(q,s)], \tag{12}$$

$$\rho^T(q)\equiv e^{-\beta F}/\mathrm{Tr}[e^{-\beta F}], \tag{13}$$

and

$$\beta\equiv\hbar/kT. \tag{14}$$

A trace is independent of the representation in which it is evaluated, so any complete set of functions of the bath coordinates can be used in calculating the trace in (12). On using (10) and (11), the Hamiltonian of a system in the ensemble can be written

$$\mathcal{H}=\hbar[E(s,t)+F(q)+G(q,s)]. \tag{15}$$

All interactions of interest can be written in the form

$$G(q,s)=\textstyle\sum_k U^k(q)V^k(s), \tag{16}$$

where $U^k(q)$ and $V^k(s)$ operate, respectively, on variables of the bath and variables of the spin system. $G(q,s)$ can always be written in the form (16) if $G^0(q,s)$ can be so written. $G$ must be Hermitian even though $U^k$ and $V^k$ need not be. This can be accomplished by defining $U^k$ and $V^k$ so that

$$U^{-k}=(U^k)^\dagger,\quad V^{-k}=(V^k)^\dagger, \tag{17}$$

the index $k$ being summed over negative as well as positive integers in (16).

If (15) is substituted in (6), the time dependence of the density operator is determined by

$$id\rho/dt=[E+F+G,\,\rho]. \tag{18}$$

Unitary spin operators $S^{\pm1}(t)$ defined as solutions of

$$dS/dt=iSE,\quad dS^{-1}/dt=-iES^{-1},\quad S^{\pm1}(0)=1, \tag{19}$$

are now introduced. A unitary transformation of an operator $Q$ by the $S^{\pm1}(t)$ produces an operator denoted by $Q'(t)$:

$$Q'(t)\equiv S(t)QS^{-1}(t). \tag{20}$$

A unitary transformation of $Q$ by the bath operators $\exp(\pm iFt)$ results in an operator denoted by $\bar{Q}(t)$. Thus

$$\bar{Q}'(t)=e^{iFt}S(t)QS^{-1}(t)e^{-iFt}. \tag{21}$$

Transformation of Eq. (18) by the operators $S^{\pm 1}(t)\times\exp(\pm iFt)$ gives

$$d\bar{\rho}'/dt=-i[\bar{G}'(t),\bar{\rho}'(t)]. \tag{22}$$

The solution of (22) for $\bar{\rho}'$ at time $t_1=t+\Delta t$ in terms of $\bar{\rho}'$ at time $t$ can be obtained by successive approximations, with the result

$$\bar{\rho}'(t_1)=\bar{\rho}'(t)+\sum_{n=1}^{\infty}\Delta_n\bar{\rho}'(t_1,t)=\sum_{n=0}^{\infty}\Delta_n\bar{\rho}'(t_1,t), \tag{23}$$

where

$$\Delta_0\bar{\rho}'(t_1,t)=\bar{\rho}'(t) \tag{24a}$$

and, for $n\geqslant 1$,

$$\Delta_n\bar{\rho}'(t_1,t)=-i\int_t^{t_1}[\bar{G}'(t'),\,\Delta_{n-1}\bar{\rho}'(t',t)]dt'. \tag{24b}$$

Since the part of the Hamiltonian involving just the bath coordinates is much greater in magnitude than the parts involving the spin variables, $|F|\gg|E+G|$, the state of the bath is affected very little by changes in the spin system. Therefore to good approximation the bath can be considered to be independent of the spin system, and can be assumed to be in thermal equilibrium at all times. Thus, the density operator $\rho(q,s,t)$ describing the bath and spin system is assumed to have the form

$$\rho(q,s,t)=\sigma(s,t)\rho^T(q), \tag{25}$$

where $\rho^T(q)$ is the Boltzmann equilibrium density operator for the bath, given by (13). The reduced density operator $\sigma(s,t)$ describes the spin system in the sense that the average value over the ensemble of a spin operator $Q(s)$ is given by

$$\langle Q(s)\rangle=\mathrm{Tr}[\sigma(s,t)Q(s)], \tag{26}$$

where the trace can be evaluated using any complete set of spin functions or vectors. From (21) and (25),

$$\bar{\rho}'(q,s,t)=\sigma'(s,t)\rho^T(q). \tag{27}$$

If (27) is substituted into (23), and the trace over the bath variables taken, the result can be written

$$\sigma'(t_1)=\sigma'(t)+\sum_{n=1}^{\infty}\Delta_n\sigma'(t_1,t), \tag{28}$$

where

$$\Delta_n\sigma'(t_1,t)=\mathrm{Tr}_q\,\Delta_n\bar{\rho}'(t_1,t), \tag{29}$$

the $\Delta_n\bar{\rho}'(t_1,t)$ for $n\geqslant 1$ being given by (24b), and

$$\Delta_0\bar{\rho}'(t_1,t)=\sigma'(s,t)\rho^T(q). \tag{30}$$

The series in (23) converges rapidly if $\Delta t\equiv t_1-t$ is sufficiently small, and hence so also does the series in (28). The first two terms in the series in (28) are now considered in detail. The higher order terms are assumed to be negligible for values of $\Delta t$ for which the first terms are themselves small compared to $\sigma'(t)$. From (24b), (29), and (30), the first-order term is

$$\begin{aligned}\Delta_1\sigma'(t_1,t)&=-i\int_t^{t_1}\mathrm{Tr}_q[\bar{G}'(t'),\sigma'(t)\rho^T(q)]dt'\\&=-i\int_t^{t_1}[\mathrm{Tr}_q[\rho^T(q)\bar{G}'(t')],\,\sigma'(t)]dt'=0,\end{aligned} \tag{31}$$

since $\sigma'$ does not depend on the bath coordinates $q$, and, for any time $t$,

$$\mathrm{Tr}_q[\rho^T(q)\bar{G}'(t)]=0. \tag{32}$$

The relation (32) follows from the fact that $\exp(\pm iFt)$ commutes that $\rho^T(q)$, and from (11), $\mathrm{Tr}_q(\rho^T(q)G]=0$. It is apparent that the first-order term (31) is identically zero only because $\langle G^0\rangle_q$ has been included in $E$.

The second-order term in (28) is

$$\begin{aligned}\Delta_2\sigma'(t_1,t)=-\int_t^{t_1}dt'\int_t^{t'}dt''\,\mathrm{Tr}_q[\bar{G}'(t'),\\ \times[\bar{G}'(t''),\,\sigma'(t)\rho^T(q)]].\end{aligned} \tag{33}$$

Use is now made of the fact that $G$ can be expressed as a sum of products of a spin operator and a bath operator. On applying the transformations (21) to the expression for $G$, (16), one obtains

$$\bar{G}'(t)=\sum\nolimits_k\bar{U}^k(t)V^{k\prime}(t)=\sum\nolimits_k U^k(t)V^k(t), \tag{34}$$

where in the second form the bar and the prime have been omitted from $U^k(t)$ and $V^k(t)$, respectively, because the time dependence is sufficient to distinguish the transformed operators:

$$U^k(t)=e^{iFt}U^ke^{-iFt}, \tag{35}$$

$$V^k(t)=S(t)V^kS^{-1}(t). \tag{36}$$

The operator $U^k(t)$ is the Heisenberg time-dependent operator for $U^k$ for a system whose Hamiltonian is $\hbar F(q)$, while $V^k(t)$ is the Heisenberg time-dependent operator for $V^k$ for a system whose Hamiltonian is $\hbar E(s,t)$. After substitution of (34) into the second-order term, Eq. (33), the bath operators can be grouped together since they commute with the spin operators. The bath operators can then be rearranged by use of the fact that a trace of a product of operators is unchanged by a cyclic permutation of the operators;

the result is

$$\Delta_2\sigma'(t_1,t)$$

$$=-\int_t^{t_1} dt' \int_t^{t'} dt'' \sum_{kl}\{\mathrm{Tr}_q[\rho^T(q)U^k(t'-t'')U^l]$$

$$\times[V^k(t'),V^l(t'')\sigma'(t)]$$

$$+\mathrm{Tr}_q[\rho^T(q)U^lU^k(t'-t'')][\sigma'(t)V^l(t''),\ V^k(t')]\}. \quad (37)$$

It is assumed that it is possible to expand the time-dependent spin operators $V^k(t)$ in a series or integral of periodic terms. The series case is considered explicitly:

$$V^k(t)=S(t)V^kS^{-1}(t)\equiv\textstyle\sum_r V_r{}^k \exp(i\omega_r{}^kt), \quad (38)$$

where $V_r{}^k$ is a time-independent spin operator and $\omega_r{}^k$ is a number. The relation $V^{-k}=(V^k)^\dagger$ that is frequently satisfied by the operators $V^k$, (17), can be maintained by summing $r$ in (38) over negative as well as positive values, and requiring that

$$(V_r{}^k)^\dagger=V_{-r}{}^{-k}, \quad \omega_{-r}{}^{-k}=-\omega_r{}^k. \quad (39)$$

After substitution of (38) into (37), the variable of integration $t''$ is changed to $\tau=t'-t''$ and the order of integration over $t'$ and $\tau$ then interchanged:

$$\int_t^{t_1} dt' \int_t^{t'} dt'' \rightarrow \int_t^{t_1} dt' \int_0^{t'-t} d\tau$$

$$\rightarrow \int_0^{\Delta t} d\tau \int_{t+\tau}^{t+\Delta t} dt', \quad (40)$$

where as before $t_1=t+\Delta t$. Hence

$$\Delta_2\sigma'(t_1,t)=-\sum_{klrs}\int_0^{\Delta t} d\tau \exp(-i\omega_s{}^l\tau)$$

$$\times\int_{t+\tau}^{t+\Delta t} dt' \exp(i\omega_{rs}{}^{kl}t')$$

$$\times\{A_{kl}(\tau)[V_r{}^k,V_s{}^l\sigma'(t)]$$

$$+A_{lk}(-\tau)[\sigma'(t)V_s{}^l,V_r{}^k]\}, \quad (41)$$

where

$$\omega_{rs}{}^{kl}\equiv\omega_r{}^k+\omega_s{}^l, \quad (42)$$

and the dependence of $\Delta_2\sigma'$ on the bath is contained in the functions $A_{kl}(\tau)$ defined by

$$A_{kl}(\tau)\equiv\mathrm{Tr}_q[\rho^T(q)U^k(\tau)U^l]$$

$$=\mathrm{Tr}_q[\rho^T(q)e^{iF\tau}U^ke^{-iF\tau}U^l]. \quad (43)$$

After the integral over $t'$ in (41) is performed,

$$\Delta_2\sigma'(t_1,t)=-\sum_{klrs}\int_0^{\Delta t} d\tau \exp(-i\omega_s{}^l\tau)\left\{\frac{\exp(i\omega_{rs}{}^{kl}\Delta t)-\exp(i\omega_{rs}{}^{kl}\tau)}{i\omega_{rs}{}^{kl}\Delta t}\right\}\Delta t \exp(i\omega_{rs}{}^{kl}t)$$

$$\times\{A_{kl}(\tau)[V_r{}^k,V_s{}^l\sigma'(t)]+A_{lk}(-\tau)[\sigma'(t)V_s{}^l,V_r{}^k]\}. \quad (44)$$

If $\omega_{rs}{}^{kl}=0$, the value of the first term in braces is its limit as $\omega_{rs}{}^{kl}\rightarrow 0$, $\{1-\tau/\Delta t\}$. Some of the frequencies $\omega_{rs}{}^{kl}$ are zero in all problems: if the relations (39) are satisfied, $\omega_{-rr}{}^{-kk}=0$.

The trace occurring in (43) is now evaluated in a representation in which $F$ is diagonal with eigenvalues $f$. Degenerate states are distinguished by a parameter $d$:

$$A_{kl}(\tau)=\textstyle\sum_{fd}\sum_{f'd'}P(f)e^{if\tau}\langle fd|U^k|f'd'\rangle$$

$$\times e^{-if'\tau}\langle f'd'|U^l|fd\rangle, \quad (45)$$

where

$$P(f)=e^{-\beta f}/\textstyle\sum_{f''d''}e^{-\beta f''}. \quad (46)$$

It is assumed that the energy levels of the bath are so closely spaced that the sums over the eigenvalues in (45) can be replaced by integrals:

$$\sum_{fd}\rightarrow\sum_d\int_{-\infty}^{\infty} df\eta_d(f), \quad (47)$$

where $\eta_d(f)$ is the density of energy levels of $F$ with degeneracy parameter $d$. Hence

$$P(f)=e^{-\beta f}\Big/\sum_{d''}\int_{-\infty}^{\infty} df''\eta_{d''}(f'')e^{-\beta f''}, \quad (48)$$

and

$$A_{kl}(\tau)=\sum_{dd'}\int_{-\infty}^{\infty} df'\int_{-\infty}^{\infty} df\eta_{d'}(f')\eta_d(f)P(f)$$

$$\times\langle fd|U^k|f'd'\rangle\langle f'd'|U^l|fd\rangle e^{-i(f'-f)\tau}. \quad (49)$$

The variable of integration $f'$ in (49) is next changed to $\omega$ by the relation $\omega=f'-f$. The result can be expressed as

$$A_{kl}(\tau)=\int_{-\infty}^{\infty} L_{kl}(\omega)e^{-i\omega\tau}d\omega, \quad (50)$$

where

$$L_{kl}(\omega)=\sum_{dd'}\int_{-\infty}^{\infty} df\eta_{d'}(f+\omega)\eta_d(f)P(f)$$

$$\times\langle fd|U^k|f+\omega,\ d'\rangle\langle f+\omega,\ d'|U^l|fd\rangle. \quad (51)$$

$L_{kl}(\omega)$ is assumed to be a continuous function of $\omega$ that is absolutely integrable over $(-\infty,\ \infty)$. Since $P(f+\omega)=P(f)\exp(-\beta\omega)$, it follows from the definition (51) that

$$L_{lk}(-\omega)=L_{kl}(\omega)\exp(-\beta\omega). \quad (52)$$

From (50) it is apparent that $A_{kl}(\tau)$ is the Fourier transform of $L_{kl}(\omega)$, so that

$$L_{kl}(\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty}A_{kl}(\tau)e^{i\omega\tau}d\tau. \tag{53}$$

Since $L_{kl}(\omega)$ is a continuous function of $\omega$,

$$|L_{kl}(\omega+\Delta\omega)-L_{kl}(\omega)|$$

can be made arbitrarily small by choosing $|\Delta\omega|$ sufficiently small. The rate of change of $L_{kl}(\omega)$ can be rather loosely characterized by a frequency $\omega^*$ such that

$$L_{kl}(\omega+\Delta\omega)\approx L_{kl}(\omega) \quad \text{if} \quad |\Delta\omega|\ll\omega^*. \tag{54}$$

The reciprocal of the characteristic frequency,

$$\tau_c\equiv(\omega^*)^{-1},$$

is called the correlation time of the bath. According to this definition, the characteristic frequency, and hence the correlation time, depend on the temperature. From the relation (52) it follows that $\omega^*$ and $\tau_c$ must satisfy the approximate inequality

$$\tau_c\equiv(\omega^*)^{-1}\gtrsim\beta\equiv\hbar/kT. \tag{55}$$

The correlation time $\tau_c$ can be related to the manner in which the magnitude of $A_{kl}(\tau)$ decreases as $|\tau|$ increases. From (53),

$$L_{kl}(\omega+\Delta\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty}A_{kl}(\tau)e^{i\omega\tau}e^{i\Delta\omega\tau}d\tau,$$

which is apparently approximately equal to $L_{kl}(\omega)$ only if $|\Delta\omega\tau|\ll1$ for all values of $\tau$ for which $A_{kl}(\tau)$ has an appreciable magnitude. Hence $|A_{kl}(\tau)|\approx0$ if $|\Delta\omega\tau|\gtrsim1$, so that, since $|\Delta\omega|\ll\omega^*$,

$$|A_{kl}(\tau)|\approx0 \quad \text{if} \quad |\tau|\gg\tau_c\equiv(\omega^*)^{-1}. \tag{56}$$

Consider now Eq. (44) when

$$\Delta t\gg\tau_c. \tag{57}$$

Since $A_{kl}(\tau)$ and $A_{lk}(-\tau)$ are large only for $|\tau|\lesssim\tau_c$, the integrand is large only for $|\tau|\lesssim\tau_c$. Terms in the sums over $r$, $s$, $k$, and $l$ for which

$$|\omega_{rs}{}^{kl}\Delta t|\lesssim1 \tag{58}$$

have

$$|\omega_{rs}{}^{kl}|\tau_c\ll1, \tag{59}$$

so that in these terms $\exp(i\omega_{rs}{}^{kl}\tau)$ may be replaced by 1. Terms not satisfying (58) are smaller than the terms that do satisfy this relation because of the factor

$$\left\{\frac{\exp(i\omega_{rs}{}^{kl}\Delta t)-\exp(i\omega_{rs}{}^{kl}\tau)}{i\omega_{rs}{}^{kl}\Delta t}\right\}$$

occurring in (44). Hence little error is introduced in $\Delta_2\sigma'(t_1,t)$ by replacing $\exp(i\omega_{rs}{}^{kl}\tau)$ by 1 in all terms. Also, the limit of integration $\Delta t$ can be extended to infinity without appreciably changing the value of the integral, since the integrand in large only for $|\tau|\ll\Delta t$. Thus (44) becomes

$$\begin{aligned}\Delta_2\sigma'(t_1,t)&\\ =-\sum_{klrs}&\left\{\frac{\exp(i\omega_{rs}{}^{kl}\Delta t)-1}{i\omega_{rs}{}^{kl}}\right\}\exp(i\omega_{rs}{}^{kl}t)\\ &\times\int_0^{\infty}d\tau\exp(-i\omega_s{}^l\tau)\{A_{kl}(\tau)[V_r{}^k,V_s{}^l\sigma'(t)]\\ &\qquad+A_{lk}(-\tau)[\sigma'(t)V_s{}^l,V_r{}^k]\}.\end{aligned} \tag{60}$$

The expression (50) for $A_{kl}(\tau)$ is next substituted into (60), the variable of integration $\omega$ in $A_{kl}(\tau)$ is changed to $\omega'=\omega+\omega_s{}^l$ and the integration over $\tau$ performed by use of the relation

$$\int_0^{\infty}e^{-i\omega' t}d\tau=\pi\delta(\omega')-\mathcal{P}\frac{i}{\omega'}, \tag{61}$$

where $\mathcal{P}$ indicates the principal value is to be taken when (16) occurs in an integrand. The result can be expressed as

$$\Delta_2\sigma'(t_1,t)=\int_t^{t+\Delta t}\{R'(\sigma'(t),t')+iR''(\sigma'(t),t')\}dt', \tag{62}$$

where

$$\begin{aligned}R'(\sigma'(t),t')\equiv\pi\textstyle\sum_{klrs}&\exp(i\omega_{rs}{}^{kl}t')\\ &\times\{L_{kl}(-\omega_s{}^l)[V_s{}^l\sigma'(t),V_r{}^k]\\ &\qquad+L_{lk}(\omega_s{}^l)[V_r{}^k,\sigma'(t)V_s{}^l]\}\end{aligned} \tag{63}$$

and

$$\begin{aligned}R''(\sigma'(t),t')\equiv\sum_{klrs}&\exp(i\omega_{rs}{}^{kl}t')\\ &\times\mathcal{P}\int_{-\infty}^{\infty}\{L_{kl}(\omega'-\omega_s{}^l)[V_r{}^k,V_s{}^l\sigma'(t)]\\ &\qquad+L_{lk}(-\omega'+\omega_s{}^l)[\sigma'(t)V_s{}^l,V_r{}^k]\}\frac{d\omega'}{\omega'}.\end{aligned} \tag{64}$$

Expression (64) can be further simplified in the following manner. Interchange of the summation indexes $k$ with $l$ and $r$ with $s$ in the second term in the integrand gives

$$\begin{aligned}R''(\sigma'(t),t')=\sum_{klrs}&\exp(i\omega_{rs}{}^{kl}t')\\ &\times\mathcal{P}\int_{-\infty}^{\infty}\{L_{kl}(\omega-\omega_s{}^l)[V_r{}^k,V_s{}^l\sigma'(t)]\\ &\qquad+L_{kl}(-\omega+\omega_r{}^k)[\sigma'(t)V_r{}^k,V_s{}^l]\}\frac{d\omega}{\omega}.\end{aligned} \tag{65}$$

As before, when $R''$ is integrated with respect to $t'$ over an interval $\Delta t\gg\tau_c$, the terms contributing appreciably to the sum in (65) are those for which $|\omega_{rs}{}^{kl}|\ll\omega^*$. For these terms $\omega_r{}^k$ and $-\omega_s{}^l$ differ from their mean value $\nu_{rs}{}^{kl}\equiv\frac{1}{2}(\omega_r{}^k-\omega_s{}^l)$ by an amount small compared to $\omega^*$. Hence, in view of (54), little error is introduced by replacing $L_{kl}(\omega-\omega_s{}^l)$ with $L_{kl}(\omega+\nu_{rs}{}^{kl})$ and $L_{kl}(-\omega+\omega_r{}^k)$ with $L_{kl}(-\omega+\nu_{rs}{}^{kl})$. If the range of integration is next converted from $(-\infty,\infty)$ to $(0,\infty)$, and the commutators written out explicitly, it is found that half the terms in the integrand cancel, with the result that

$$R''(\sigma'(t),t')=[\sigma'(t),N'(t')],\tag{66}$$

where

$$N'(t')\equiv\sum_{klrs}\exp(i\omega_{rs}{}^{kl}t')V_r{}^kV_s{}^l\times\int_0^\infty[L_{kl}(\nu_{rs}{}^{kl}-\omega)-L_{kl}(\nu_{rs}{}^{kl}+\omega)]\frac{d\omega}{\omega}.\tag{67}$$

If one combines (66), (62), and (31), the expression (28) for $\sigma'(t+\Delta t)$ to second order in the interaction $G$ becomes

$$\sigma'(t+\Delta t)=\sigma'(t)+\int_t^{t+\Delta t}\{R'(\sigma'(t),t')+i[\sigma'(t),N'(t')]\}dt'.\tag{68}$$

The higher order terms in (28) are assumed to be negligible for values of $\Delta t$ for which the fractional change in $\sigma'(t)$ as given by (68) is small. If $|R|$ and $|N|$ denote the magnitudes of the operators multiplying $\sigma'$ in the integrand in (68), we therefore require that $|R|\Delta t$, $|N|\Delta t\ll 1$. Since it has also been assumed in deriving (68) that $\Delta t\gg\tau_c$, Eq. (57), the conditions for which (68) gives $\sigma'(t+\Delta t)$ to good approximation can be summarized as

$$\tau_c\equiv(\omega^*)^{-1}\ll\Delta t\ll|R|^{-1},\quad |N|^{-1}.\tag{69}$$

It is now asserted that the time dependence of $\sigma'$ can be determined with good approximation from the differential equation

$$d\sigma'(t)/dt=i[\sigma'(t),N'(t)]+R'(\sigma'(t),t)\tag{70}$$

if

$$\tau_c\equiv(\omega^*)^{-1}\ll|R|^{-1},\quad |N|^{-1},\tag{71}$$

where $N'(t)$ and $R'(\sigma(t),t)$ are given, respectively, by (67) and (63).

Equation (70) follows formally from (68) if in that equation $\sigma'(t)$ is transposed to the left-hand side, the equation is divided by $\Delta t$, and the limit taken as $\Delta t\to 0$; however, because (68) is valid only if $\Delta t\gg\tau_c$, (69), it is not rigorously permissible to let $\Delta t\to 0$.

The approximate validity of Eq. (70) can be demonstrated in a somewhat more satisfactory manner by showing that step-by-step integration of the equation over appropriate time intervals gives the same result predicted by the previously obtained expression (68). Owing to condition (71), one can choose a $\Delta t$ that satisfies condition (69), so that $\sigma'(t+\Delta t)$ is given accurately in terms of $\sigma'(t)$ by Eq. (68). Furthermore, the relations $|N|\Delta t$, $|R|\Delta t\ll 1$ that follow from (69) are sufficient to ensure that $\sigma'(t+\Delta t)$ as predicted by Eq. (70) is accurately represented by the first-order forward integration of that equation. The result so obtained from (70) is identical with the expression (68). Since $\sigma'$ at a time $t'>t$ can be obtained by successive integrations over intervals $\Delta t$, at each step of which the change in $\sigma'$ is small and agrees with the correct expression (68), it is concluded that the differential equation (70) does indeed accurately predict the time dependence of $\sigma'(t)$.

In order to facilitate the derivation of the semiclassical theory in the next section, we define

$$\begin{aligned}J_{kl}(\omega)&\equiv(\pi/2)[1+e^{-\beta\omega}]L_{kl}(\omega)\\&=\pi\cosh(\beta\omega/2)\exp(-\beta\omega/2)L_{kl}(\omega).\end{aligned}\tag{72}$$

From Eq. (52) it follows that

$$J_{lk}(-\omega)=J_{kl}(\omega),\tag{73}$$

and from (54) and (55)

$$J_{kl}(\omega+\Delta\omega)\approx J_{kl}(\omega)\quad\text{if }|\Delta\omega|\ll\omega^*.\tag{74}$$

Substitution of (72) into (63) and (67) gives, after use of (73),

$$R'(\sigma'(t),t')=\sum_{klrs}\exp(i\omega_{rs}{}^{kl}t')J_{lk}(\omega_s{}^l)\operatorname{sech}\left(\frac{\beta}{2}\omega_s{}^l\right)\left\{\exp\left(-\frac{\beta}{2}\omega_s{}^l\right)[V_s{}^l\sigma'(t),V_r{}^k]+\exp\left(\frac{\beta}{2}\omega_s{}^l\right)[V_r{}^k,\sigma'(t)V_s{}^l]\right\},\tag{75a}$$

$$=\sum_{klrs}\exp(i\omega_{rs}{}^{kl}t')J_{lk}(\omega_s{}^l)\left\{[[V_s{}^l,\sigma'(t)],V_r{}^k]+\tanh\left(\frac{\beta}{2}\omega_s{}^l\right)[V_r{}^k,[V_s{}^l,\sigma(t)]_+]\right\};\tag{75b}$$

$$\begin{aligned}N'(t)=(2/\pi)\sum_{klrs}\exp(i\omega_{rs}{}^{kl}t)V_r{}^kV_s{}^l\int_0^\infty\{&(1+\exp[-\beta(\nu_{rs}{}^{kl}-\omega)])^{-1}J_{kl}(\nu_{rs}{}^{kl}-\omega)\\&-(1+\exp[-\beta(\nu_{rs}{}^{kl}+\omega)])^{-1}J_{kl}(\nu_{rs}{}^{kl}+\omega)\}\frac{d\omega}{\omega}.\end{aligned}\tag{76}$$

A differential equation for $\sigma(t)$ can be obtained from (70) by multiplying on the left-hand side by $S^{-1}(t)$ and on the right-hand side by $S(t)$, and using the relation

$$S^{-1}(d\sigma'/dt)S=i[E,\sigma]+(d\sigma/dt). \tag{77}$$

Equation (70) then gives

$$(d\sigma/dt)+i[E+N,\,\sigma]=R(\sigma), \tag{78}$$

where

$$\begin{aligned}R(\sigma)&\equiv S^{-1}R'(\sigma',t)S\\ &=\textstyle\sum_{kls}\exp(i\omega_s{}^lt)J_{lk}(\omega_s{}^l)\,\operatorname{sech}\left(\frac{\beta}{2}\omega_s{}^l\right)\\ &\quad\times\left\{\exp\left(-\frac{\beta}{2}\omega_s{}^l\right)[S^{-1}V_s{}^lS\sigma,V^k]\right.\\ &\quad\left.+\exp\left(\frac{\beta}{2}\omega_s{}^l\right)[V^k,\sigma S^{-1}V_s{}^lS]\right\}, \qquad (79\text{a})\\ &=\textstyle\sum_{kls}\exp(i\omega_s{}^lt)J_{lk}(\omega_s{}^l)\\ &\quad\times\left\{[[S^{-1}V_s{}^lS,\sigma],V^k]+\tanh\left(\frac{\beta}{2}\omega_s{}^l\right)\right.\\ &\quad\left.\times[V^k,[S^{-1}V_s{}^lS,\sigma]_+]\right\}, \qquad (79\text{b})\end{aligned}$$

use having been made of Eq. (38) to perform the sum over $r$, and

$$N\equiv S^{-1}N'(t)S. \tag{80}$$

The conditions of validity of (78) are given by (71), where now $|R|$ and $|N|$ are, respectively, the magnitudes of (79) and (80).

The quantum-mechanical form of the density operator relaxation theory derived in this section is similar to Bloch's generalized relaxation theory. The significant differences in the present treatment are

(a) the average over the bath coordinates of the interaction $G$ is included in the spin energy $E$, Eq. (10);

(b) the interaction $G$ is written as a sum of products of a spin operator and a bath operator, Eq. (16); and

(c) the correlation time $\tau_c$ is defined in such a manner that it depends on the temperature, Eq. (55).

The change (a) is essential to the derivation of the semiclassical form of the theory in the following section, and the change (b) facilitates that derivation.

### 3. SEMICLASSICAL RELAXATION THEORY

The correlation function $C_{kl}(\tau)$ of $U^k$ and $U^l$ is defined as the average over an ensemble of baths in thermal equilibrium of the symmetrized product of the Heisenberg operators $U^k(t+\tau)$ and $U^l(t)$:

$$\begin{aligned}C_{kl}(\tau)&\equiv\langle\{U^k(t+\tau)U^l(t)\}\rangle_q\\ &=\langle\{U^k(\tau)U^l(0)\}\rangle_q,\end{aligned} \tag{81}$$

where the braces denote the symmetrized product

$$\begin{aligned}\{U^k(t+\tau)U^l(t)\}\equiv\tfrac{1}{2}[&U^k(t+\tau)U^l(t)\\ &+U^l(t)U^k(t+\tau)].\end{aligned} \tag{82}$$

The correlation function can be written in terms of the function $A_{kl}(\tau)$ defined by (43):

$$C_{kl}(\tau)=\tfrac{1}{2}[A_{kl}(\tau)+A_{lk}(-\tau)]. \tag{83}$$

From (83) it follows that

$$C_{kl}(\tau)=C_{lk}(-\tau). \tag{84}$$

If $A_{kl}(\tau)$ is evaluated quantum mechanically as in the previous section, assuming the eigenvalues of the bath Hamiltonian are so closely spaced that they can be considered continuous, $C_{kl}(\tau)$ can be expressed in terms of $L_{kl}(\omega)$ by (50), and hence in terms of $J_{kl}(\omega)$ by use of (72) and (73). The result is

$$C_{kl}(\tau)=\frac{1}{\pi}\int_{-\infty}^{\infty}J_{kl}(\omega)e^{-i\omega\tau}dw. \tag{85}$$

Inversion of Eq. (85) by use of the Fourier integral theorem gives

$$J_{kl}(\omega)=\tfrac{1}{2}\int_{-\infty}^{\infty}C_{kl}(\tau)e^{i\omega\tau}d\tau. \tag{86}$$

With regard to the quantum-mechanical relaxation theory, (86) is simply an alternative expression for $J_{kl}(\omega)$ that is equal to the expression used in the previous section.

Since the properties of the bath enter the relaxation theory only through the functions $J_{kl}(\omega)$, a semiclassical form of the theory, in which the bath is treated classically, can be obtained simply by considering the $C_{kl}(\tau)$ in the expression (86) for $J_{kl}(\omega)$ to be classical correlation functions; that is, $U^k(t+\tau)$ and $U^l(t)$ are considered to be functions of the classical coordinates of the bath rather than quantum-mechanical operators, and the average indicated in (81) is performed classically.

It follows from the fact that $C_{kl}(\tau)$ can be expressed in terms of $A_{kl}(\tau)$, Eq. (83), and from the fact that $A_{kl}(\tau)$ can be considered to be zero for $|\tau|\gg\tau_c$, Eq. (56), that

$$C_{kl}(\tau)\approx 0\quad\text{if } |\tau|\gg\tau_c, \tag{87}$$

where $\tau_c$ is the correlation time previously introduced. The classical correlation function $C_{kl}(\tau)$ goes to zero as $|\tau|$ goes to infinity as a consequence of the fact that $U^k$ and $U^l$ have been defined in such a manner that they individually have zero average value, Eq. (11).

It is important to note that the quantum-mechanical and semiclassical forms of the relaxation theory do not differ in their dependence on the operators of the spin system, but only in the manner in which the quantities $J_{kl}(\omega)$ containing the effects of the bath are evaluated. The usefulness of the semiclassical form of the theory is due to the fact that it is usually very difficult to evaluate the $J_{kl}(\omega)$ quantum mechanically, while a reasonable choice of a classical model of the bath permits the calculation of these functions through the use of Eq. (86).

### 4. SPECIAL CASES

In this section important special cases of the relaxation theory are discussed. The results apply to both the quantum-mechanical and semiclassical forms of the theory.

### A. Spin Hamiltonian Independent of the Time

If the spin Hamiltonian $\hbar E$ does not depend explicitly on the time, the solutions of Eqs. (19) are

$$S^{\pm 1}(t)=e^{\pm iEt}. \qquad (88)$$

Hence

$$V^l(t)\equiv S(t)V^lS^{-1}(t)=e^{iEt}V^le^{-iEt}. \qquad (89)$$

The expression for $V^l(t)$ can be expanded in the form (38),

$$V^l(t)=\textstyle\sum_s V_s{}^l \exp(i\omega_s{}^lt), \qquad (90)$$

if the frequencies $\omega_s{}^l$ are chosen to be the differences between the eigenvalues of $E$, denoted by $E_\alpha$,

$$\omega_s{}^l\equiv E_\alpha-E_{\alpha'}\equiv\omega_{\alpha\alpha'}, \qquad (91)$$

and the operators $V_s{}^l$ are defined by the condition that

$$\langle\alpha|V_s{}^l|\alpha'\rangle\begin{cases}=0 & \text{for a value of } s \text{ for which } \omega_s{}^l\neq E_\alpha-E_{\alpha'},\\ =\langle\alpha|V^l|\alpha'\rangle & \text{for a value of } s \text{ for which } \omega_s{}^l=E_\alpha-E_{\alpha'}.\end{cases} \qquad (92)$$

The correctness of the expansion (90) with the definitions (91) and (92) can be easily demonstrated by showing that a matrix element in any representation of the expression (90) for $V^l(t)$ is the same as the matrix element of expression (89) between the same states. The following relations can also be proved by considering the matrix elements of the expressions and using (91) and (92):

$$V^l=\textstyle\sum_s V_s{}^l, \qquad (93)$$

$$[E,V_s{}^l]=\omega_s{}^lV_s{}^l, \qquad (94)$$

$$S^{-1}V_s{}^lS=V_s{}^l\exp(-i\omega_s{}^lt). \qquad (95)$$

Substitution of (95) into (79) and (80) gives

$$\begin{aligned}R(\sigma)=&\textstyle\sum_{kls} J_{lk}(\omega_s{}^l)\operatorname{sech}\left(\frac{\beta}{2}\omega_s{}^l\right)\\ &\times\left\{\exp\left(-\frac{\beta}{2}\omega_s{}^l\right)[V_s{}^l\sigma,V^k]\right.\\ &\left.+\exp\left(\frac{\beta}{2}\omega_s{}^l\right)[V^k,\sigma V_s{}^l]\right\}, \qquad (96a)\\ =&\textstyle\sum_{kls} J_{lk}(\omega_s{}^l)\left\{[[V_s{}^l,\sigma],V^k]\right.\\ &\left.+\tanh\left(\frac{\beta}{2}\omega_s{}^l\right)[V^k,[V_s{}^l,\sigma]_+]\right\}, \qquad (96b)\end{aligned}$$

$$\begin{aligned}N=&\frac{2}{\pi}\sum_{klrs} V_r{}^kV_s{}^l\int_0^\infty\left\{(1-\exp[-\beta(\nu_{rs}{}^{kl}-\omega)])^{-1}\right.\\ &\times J_{kl}(\nu_{rs}{}^{kl}-\omega)-(1+\exp[-\beta(\nu_{rs}{}^{kl}+\omega)])^{-1}\\ &\left.\times J_{kl}(\nu_{rs}{}^{kl}+\omega)\right\}\frac{d\omega}{\omega}. \qquad (97)\end{aligned}$$

Note that $R(\sigma)$ and $N$ do not depend explicitly on $t$ when $E$ is independent of $t$.

It is now shown that expression (96) for the relaxation term vanishes when $\sigma=\sigma^T$, where

$$\sigma^T\equiv e^{-\beta E}/\mathrm{Tr}[e^{-\beta E}]. \qquad (98)$$

On using (94), one obtains the equation

$$\begin{aligned}(d/d\beta)(e^{-\beta E}V_s{}^le^{\beta E})&=-e^{-\beta E}[E,V_s{}^l]e^{\beta E}\\ &=-\omega_s{}^l(e^{-\beta E}V_s{}^le^{\beta E}).\end{aligned}$$

On integrating, and replacing $\beta$ by $\pm\beta/2$,

$$\begin{aligned}\exp(\mp\beta E/2)V_s{}^l\exp(\pm\beta E/2)&\\ =V_s{}^l\exp(\mp\beta\omega_s{}^l/2).& \qquad (99)\end{aligned}$$

Substitution of (99) into (96a) gives

$$\begin{aligned}R(\sigma)=&\textstyle\sum_{kls}J_{lk}(\omega_s{}^l)\operatorname{sech}(\beta\omega_s{}^l/2)\\ &\times\{[\exp(-\beta E/2)V_s{}^l\exp(\beta E/2)\sigma,V^k]\\ &-[\sigma\exp(\beta E/2)V_s{}^l\exp(-\beta E/2, V^k]\}. \qquad (100)\end{aligned}$$

From expression (100) for $R(\sigma)$, valid when $E$ is independent of $t$, it is apparent that $R(\sigma^T)=0$.

The free relaxation of the magnetization of a system of nuclear spins in a strong constant magnetic field is a case for which the total spin Hamiltonian does not depend explicitly on the time. If $E$ is much greater in magnitude than the interaction $G$ so that $N$ is negligible in comparison to $E$, Eq. (78) reduces to

$$(d\sigma/dt)+i[E,\sigma]=R(\sigma), \qquad (101)$$

where either (96) or (100) can be used for $R(\sigma)$. Since $R(\sigma^T)=0$ in this case, and $\sigma^T$ commutes with $E$, an equilibrium expression for $\sigma$ is the expected Boltzmann form $\sigma^T$.

For the case considered in the previous paragraph it is sometimes convenient to formulate the problem in terms of a spin operator $\chi$ defined as the difference between the reduced density operator and its thermal equilibrium value:

$$\chi(t)\equiv\sigma(t)-\sigma^T. \qquad (102)$$

The operator $\chi$ obeys the differential equation

$$(d\chi/dt)+i[E,\chi]=R(\chi) \qquad (103)$$

subject to the normalization condition $\mathrm{Tr}[\chi]=0$.

### B. High Temperature

The temperature is said to be "high" if, for all the frequencies $\omega_s{}^l$,

$$|\omega_s{}^l|\beta \ll 1, \tag{104}$$

where as before $\beta = \hbar/kT$. Thus, if the temperature is high, $\tanh(\beta\omega_s{}^l/2)$ can be replaced by $(\beta\omega_s{}^l/2)$ with little error, so that expression (79b) gives

$$R(\sigma) = \sum_{kls} \exp(i\omega_s{}^l t) J_{lk}(\omega_s{}^l)\{[[S^{-1}V_s{}^l S, \sigma], V^k] + (\beta\omega_s{}^l/2)[V^k, [S^{-1}V_s{}^l S, \sigma]_+]\}. \tag{105a}$$

In many problems it can be expected that the fractional difference between $\sigma(t)$ and the normalized unit density operator $(1/\mathrm{Tr}[1])$ is less than or of the order of the largest of the values $\beta\omega_s{}^l$ for all times $t$. In such a case, an expression for $R(\sigma)$ correct to first order in $\beta\omega_s{}^l$ can be obtained from (105) by replacing $\sigma$ by $(1/\mathrm{Tr}[1])$ in the term multiplied by $(\beta\omega_s{}^l/2)$, with the result

$$R(\sigma) = \sum_{kls} \exp(i\omega_s{}^l t) J_{lk}(\omega_s{}^l)\{[[S^{-1}V_s{}^l S, \sigma], V^k] + \beta\omega_s{}^l [V^k, S^{-1}V_s{}^l S]/\mathrm{Tr}[1]\}. \tag{105b}$$

For the case in which $E$ is independent of $t$, it was shown in Sec. 4A that $R(\sigma^T) = 0$, so that $R(\sigma) = R(\sigma - \sigma^T)$, where $R$ is given by Eqs. (96) or Eq. (100). If also the temperature is high, so that terms second order in $\beta\omega_s{}^l$ can be omitted with little error, Eq. (96b) gives the much simpler result

$$R(\sigma) = R(\sigma - \sigma^T) = \sum_{kls} J_{lk}(\omega_s{}^l) \times [[V_s{}^l, \sigma - \sigma^T], V^k]. \tag{106}$$

Expression (106) has been obtained by assuming that $\sigma - \sigma^T$ is first order in $\beta\omega_s{}^l$, so that the term

$$\tanh(\beta\omega_s{}^l/2)[V^k, [V_s{}^l, \sigma - \sigma^T]_+]$$

is second order in $\beta\omega_s{}^l$, and can be omitted from Eq. (96b) for $R(\sigma - \sigma^T)$. Equation (106) is correct only to first order in $\beta\omega_s{}^l$.

The expression for $N$ also simplifies if the temperature is high. If $|\omega_s{}^l|\beta \ll 1$, then $|\nu_{rs}{}^{kl}|\beta \ll 1$, so that $\exp[-\beta(\nu_{rs}{}^{kl} \pm \omega)]$ can be replaced by $\exp(\mp\beta\omega)$ in Eq. (76) for $N'$ and Eq. (80) for $N$.

### C. Short Correlation Time

The correlation time is termed "short" if

$$|\omega_s{}^l| \ll \tau_c{}^{-1} \tag{107}$$

for all frequencies $\omega_s{}^l$ occurring in $R(\sigma)$. Consider expression (86) for $J_{kl}(\omega_s{}^l)$. Since $C_{kl}(\tau)$ has appreciable magnitude only for $|\tau| \lesssim \tau_c$, if the correlation time is short it is permissible to replace the factor $\exp(i\omega_s{}^l\tau)$ in the integrand by unity. Hence, for short correlation time,

$$J_{lk}(\omega_s{}^l) \approx \tfrac{1}{2}\int_{-\infty}^{\infty} C_{lk}(\tau)d\tau = J_{lk}(0). \tag{108}$$

Since $\tau_c \gtrsim \beta$, Eq. (55), it follows that if the correlation time is short then also the temperature is high. From (38)

$$\sum_s S^{-1}V_s{}^l S \exp(i\omega_s{}^l t) = V^l,$$

and from (38) and (19)

$$\sum_s \omega_s{}^l S^{-1}V_s{}^l S \exp(i\omega_s{}^l t) = [E, V^l].$$

By use of Eq. (108) and the preceding two relations, one obtains from Eq. (105b) the expression

$$R(\sigma) = \sum_{kl} J_{lk}(0)\{[[V^l, \sigma], V^k] + \beta[V^k, [E, V^l]]/\mathrm{Tr}[1]\}. \tag{109a}$$

For the case in which $E$ is constant, one obtains from (106) by use of (108) and (93) the expression

$$R(\sigma) = R(\sigma - \sigma^T) = \sum_{kl} J_{lk}(0)[[V^l, \sigma - \sigma^T], V^k]. \tag{109b}$$

## 5. RELAXATION BY DIPOLE-DIPOLE INTERACTIONS

As an example, the theory is applied to a situation of considerable importance in nuclear magnetic resonance. We consider a system of $N$ identical nuclei in equivalent positions in the molecules of a liquid, each nuclei having a spin of $\tfrac{1}{2}$ and a gyromagnetic ratio $\gamma$. The system is exposed to the usual strong constant magnetic field and rotating transverse magnetic field:

$$\mathbf{H}(t) = H_0\mathbf{k} + H_1(\cos\omega t\mathbf{i} - \sin\omega t\mathbf{j}). \tag{110}$$

The relaxation mechanism $\hbar G$ consists of the magnetic dipole-dipole interactions between the spins. $G$ can be written in the form

$$G = \sum_{i,j=1}^{N} \sum_{k=-2}^{2} (1 - \delta_{ij}) U_{ij}{}^k V_{ij}{}^k, \tag{111}$$

where

$$U_{ij}{}^k = (3\pi/10)^{\frac{1}{2}}\gamma^2\hbar r_{ij}{}^{-3}(-1)^k Y_2{}^{-k}(\theta_{ij}, \varphi_{ij}). \tag{112}$$

The $Y_2{}^k$ are normalized spherical harmonics defined as

$$Y_2{}^0(\theta, \varphi) \equiv -(5/16\pi)^{\frac{1}{2}}(1 - 3\cos^2\theta), \tag{113a}$$

$$Y_2{}^{\pm 1}(\theta, \varphi) \equiv \mp(15/8\pi)^{\frac{1}{2}} \cos\theta \sin\theta e^{\pm i\varphi}, \tag{113b}$$

$$Y_2{}^{\pm 2}(\theta, \varphi) \equiv (15/32\pi)^{\frac{1}{2}} \sin^2\theta e^{\pm 2i\varphi}, \tag{113c}$$

which satisfy the relations

$$Y_2{}^{k*}(\theta, \varphi) = (-1)^k Y_2{}^{-k}(\theta, \varphi), \tag{114}$$

$$\int_0^{2\pi}\int_0^{\pi} Y_2{}^{k*}(\theta, \varphi) Y_2{}^{k'}(\theta, \varphi) \sin\theta d\theta d\varphi = \delta_{kk'}. \tag{115}$$

$r_{ij}$ is the length of the vector $\mathbf{r}_{ij}$ from the $j$th to the $i$th nucleus, and $\theta_{ij}$ and $\varphi_{ij}$ are the polar angles specifying the direction of $\mathbf{r}_{ij}$. Since $\varphi_{ji} = \varphi_{ij} + \pi$, $\theta_{ji} = \pi - \theta_{ij}$, and $r_{ij} = r_{ji}$,

$$Y_2{}^k(\theta_{ij}, \varphi_{ij}) = Y_2{}^k(\theta_{ji}, \varphi_{ji}), \tag{116a}$$

and

$$U_{ij}{}^k = U_{ji}{}^k. \tag{116b}$$

The spin operators $V_{ij}{}^k$ are defined by

$$V_{ij}{}^0 \equiv -(8/3)^{\frac{1}{2}}[I_i{}^0 I_j{}^0 - \tfrac{1}{4}(I_i{}^1 I_j{}^{-1} + I_i{}^{-1} I_j{}^1)], \tag{117a}$$

$$V_{ij}{}^{\pm 1} \equiv \pm(I_i{}^0 I_j{}^{\pm 1} + I_i{}^{\pm 1} I_j{}^0), \tag{117b}$$

TABLE I. Matrix $d_{kk'}(\theta)$, $c=\cos\theta$, $s=\sin\theta$.

| $k \backslash k'$ | $-2$ | $-1$ | $0$ | $1$ | $2$ |
|---|---|---|---|---|---|
| $-2$ | $\left(\frac{1+c}{2}\right)^2$ | $s\left(\frac{1+c}{2}\right)$ | $\left(\frac{3}{8}\right)^{\frac{1}{2}}s^2$ | $s\left(\frac{1-c}{2}\right)$ | $\left(\frac{1-c}{2}\right)^2$ |
| $-1$ | $-s\left(\frac{1+c}{2}\right)$ | $c^2-\left(\frac{1-c}{2}\right)$ | $\left(\frac{3}{2}\right)^{\frac{1}{2}}sc$ | $-c^2+\left(\frac{1+c}{2}\right)$ | $s\left(\frac{1-c}{2}\right)$ |
| $0$ | $\left(\frac{3}{8}\right)^{\frac{1}{2}}s^2$ | $-\left(\frac{3}{2}\right)^{\frac{1}{2}}sc$ | $\left(\frac{3c^2-1}{2}\right)$ | $\left(\frac{3}{2}\right)^{\frac{1}{2}}sc$ | $\left(\frac{3}{8}\right)^{\frac{1}{2}}s^2$ |
| $1$ | $-s\left(\frac{1-c}{2}\right)$ | $-c^2+\left(\frac{1+c}{2}\right)$ | $-\left(\frac{3}{2}\right)^{\frac{1}{2}}sc$ | $c^2-\left(\frac{1-c}{2}\right)$ | $s\left(\frac{1+c}{2}\right)$ |
| $2$ | $\left(\frac{1-c}{2}\right)^2$ | $-s\left(\frac{1-c}{2}\right)$ | $\left(\frac{3}{8}\right)^{\frac{1}{2}}s^2$ | $-s\left(\frac{1+c}{2}\right)$ | $\left(\frac{1+c}{2}\right)^2$ |

$$V_{ij}^{\pm2}\equiv -I_i^{\pm1}I_j^{\pm1}, \tag{117c}$$

in terms of the spin operators

$$I_i^{\pm1}=I_{ix}\pm iI_{iy},\quad I_i^0=I_{iz}. \tag{118}$$

It is assumed that the average of $G$ over the bath coordinates is zero, which is the case if every direction of the vectors $\mathbf{r}_{ij}$ is equally probable and independent of the length $r_{ij}$, so that the average values of the $Y_2^k(\theta_{ij},\varphi_{ij})$ are zero. This situation usually applies for nuclei in the molecules of a liquid.

Substitution of (112) into (111) gives

$$G=(3\pi/10)^{\frac{1}{2}}\gamma^2\hbar \sum_{i,j=1}^{N}(1-\delta_{ij})r_{ij}^{-3}\sum_{k=-2}^{2}(-1)^k \times Y_2^{-k}(\theta_{ij},\varphi_{ij})V_{ij}^k. \tag{119}$$

The sum over $k$ in expression (119) is in the form of the scalar product of two irreducible spherical tensors of second rank.[6] It is well known that the spherical harmonics $Y_l^m$ constitute a spherical tensor of rank $l$. The quantities $V_{ij}^k$, $k=-2,-1,0,1,2$, are thus also the components of a spherical tensor of rank two, and satisfy the commutation relations

$$[I^\mu,V_{ij}^k]=A_k^\mu V_{ij}^{k+\mu}, \tag{120}$$

where $I^\mu\equiv\sum_i I_i^\mu$, and

$$A_k^0\equiv k, \tag{121a}$$

$$A_k^{\pm1}\equiv[(2\mp k)(3\pm k)]^{\frac{1}{2}}. \tag{121b}$$

The commutation relation (120) can be verified directly by use of the commutation relations for the components of angular momentum operators:

$$\mathbf{I}_i\times\mathbf{I}_i=i\mathbf{I}_i,\quad [\mathbf{I}_i,\mathbf{I}_j]=0 \text{ if } i\neq j, \tag{122a}$$

$$[I_i^\mu,I_j^\nu]=(-1)^{\mu+\nu}(\mu-\nu)I_i^{\mu+\nu}\delta_{ij}. \tag{122b}$$

The quantities $A_k^\mu$ satisfy the following symmetry relations:

$$A_{-k}^{-\mu}=-(-1)^\mu A_k^\mu=A_{-k-\mu}^\mu. \tag{123}$$

The following transformation properties of the quantities $V_{ij}^k$ are needed later:

$$\exp(i\theta I_z)V_{ij}^k\exp(-i\theta I_z)=V_{ij}^k\exp(ik\theta), \tag{124a}$$

$$\exp(i\theta I_y)V_{ij}^k\exp(-i\theta I_y)=\textstyle\sum_{k'}d_{kk'}(\theta)V_{ij}^{k'}, \tag{124b}$$

where $I_z=\sum_i I_{iz}$, etc. The elements of the matrix $d_{kk'}(\theta)$ are listed in Table I, where $\cos\theta$ and $\sin\theta$ are abbreviated, respectively, as $c$ and $s$. Equation (124a) can be obtained by denoting the left-hand side of (124a) by $f(\theta)$, differentiating with respect to $\theta$, and using (120) to obtain the differential equation $f'(\theta)=ikf(\theta)$, the solution of which is Eq. (124a). Equation (124b) can be verified in the following manner. Differentiation of Eq. (124b) with respect to $\theta$ gives

$$\exp(i\theta I_y)[iI_y,V_{ij}^k]\exp(-i\theta I_y)=\textstyle\sum_{k'}d'_{kk'}(\theta)V_{ij}^{k'}.$$

Since $iI_y=\frac{1}{2}(I^1-I^{-1})$, Eqs. (120) and (124b) can be used to obtain

$$\begin{aligned}\textstyle\sum_{k'}d'_{kk'}(\theta)V_{ij}^{k'} &=\tfrac{1}{2}\exp(i\theta I_y)[A_k^1V_{ij}^{k+1}-A_k^{-1}V_{ij}^{k-1}]\exp(-i\theta I_y)\\ &=\textstyle\sum_{k'}\tfrac{1}{2}[A_k^1d_{k+1,k'}(\theta)-A_k^{-1}d_{k-1,k'}(\theta)]V_{ij}^{k'}.\end{aligned}$$

On equating the coefficients of $V_{ij}^{k'}$ on each side of the preceding equation, we obtain the differential equation

$$d'_{kk'}(\theta)=\tfrac{1}{2}A_k^1d_{k+1,k'}(\theta)-\tfrac{1}{2}A_k^{-1}d_{k-1,k'}(\theta).$$

The system of five simultaneous differential equations obtained by putting $k=-2, 1, 0, 1, 2$ in the preceding equation, with the initial condition $d_{kk'}(0)=\delta_{kk'}$, can be readily solved by use of Laplace transforms, giving the values of $d_{kk'}(\theta)$ listed in Table I. It is apparent from inspection of Table I that the matrix elements satisfy the following symmetry relations:

---

[6] M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley & Sons, Inc., New York, 1957).

$$d_{kk'}(\theta)=d_{k'k}(-\theta)=(-1)^{k-k'}d_{k'k}(\theta)=d_{-k',-k}(\theta). \quad (125)$$

Also, since a unitary transformation of $V_{ij}{}^k$ by

$$\exp(i\theta I_y)\exp(-i\theta I_y)=\exp(-i\theta I_y)\exp(i\theta I_y)=1$$

must give $V_{ij}{}^k$:

$$\sum_{k'} d_{kk'}(\theta)d_{k'k''}(-\theta)=\sum_{k'} d_{kk'}(-\theta)d_{k'k''}(\theta)=\delta_{kk''}. \quad (126)$$

The part of the Hamiltonian of the system that involves the spin variables and the time consists of the interaction energy of the nuclear magnetic moments with the applied magnetic field:

$$\hbar E=-\boldsymbol{\mu}\cdot\mathbf{H}(t)=-\gamma\hbar\mathbf{I}\cdot\mathbf{H}(t),$$

where $\mathbf{I}=\sum_i \mathbf{I}_i$. On using expression (110) for $\mathbf{H}(t)$,

$$E=-\omega_0 I^0-(\omega_1/2)(I^1e^{i\omega t}+I^{-1}e^{-i\omega t}), \quad (127)$$

where $\omega_0\equiv\gamma H_0$ and $\omega_1\equiv\gamma H_1$.

The operators representing the components of spin angular momentum in a coordinate system rotating with the applied magnetic field are

$$\tilde{I}^\nu\equiv\exp(i\omega tI^0)I^\nu\exp(-i\omega tI^0)=I^\nu e^{i\nu\omega t}. \quad (128)$$

We wish to calculate the expectation values of these quantities.

The straightforward method of obtaining $\langle\tilde{I}^\nu\rangle=\mathrm{Tr}[\sigma\tilde{I}^\nu]$ is to calculate from (78) the matrix elements of $\sigma$ in a convenient representation, and then use the matrix elements to evaluate the trace if $\sigma\tilde{I}^\nu$. However, it is sometimes possible to avoid explicit calculation of matrix elements by using another procedure. If Eq. (78) is multiplied on the right by $\tilde{I}^\nu$, use made of the relation

$$\frac{d\sigma}{dt}\tilde{I}^\nu=\frac{d}{dt}(\sigma\tilde{I}^\nu)-\sigma\frac{d\tilde{I}^\nu}{dt}=\frac{d}{dt}(\sigma\tilde{I}^\nu)-i\nu\omega\sigma\tilde{I}^\nu,$$

and the trace of the equation taken, one obtains

$$(d/dt)\langle\tilde{I}^\nu\rangle-i\nu\omega\langle\tilde{I}^\nu\rangle+i\,\mathrm{Tr}[E+N,\sigma]\tilde{I}^\nu =\mathrm{Tr}[R(\sigma)\tilde{I}^\nu]. \quad (129)$$

Two of the terms in (129) contain the desired quantities $\langle\tilde{I}^\nu\rangle$. If the other terms in the equation can be reduced to functions of the quantities $\langle\tilde{I}^\mu\rangle$, or to functions of $\langle\tilde{I}^\mu\rangle$, and the expectation values of a few other quantities for which differential equations can be similarly obtained by use of Eq. (78), the equations can in principle be solved for the desired expectation values. It is shown that, for the problem under consideration, Eq. (129) provides three simultaneous differential equations for the quantities $\langle\tilde{I}^\nu\rangle$, $\nu=-1, 0, 1$, if certain conditions to be specified later are satisfied, and hence provides a convenient method of determining $\langle\tilde{I}^\nu\rangle$ for this case.

It is assumed that the applied magnetic field is sufficiently strong such that the term $N$, which is second order in the interaction $G$, is negligible compared to $E$, so that

$$i\,\mathrm{Tr}[E+N,\sigma]\tilde{I}^\nu\approx i\,\mathrm{Tr}[E,\sigma]\tilde{I}^\nu =i\,\mathrm{Tr}\,\sigma[I^\nu,E]e^{i\nu\omega t}, \quad (130)$$

the last equality resulting from cyclic permutation of the elements in the trace and use of Eq. (128). With $E$ given by (127), the commutator $[I^\nu,E]$ is easily evaluated by use of (122b); when the resulting expression for (130) is substituted into (129), one obtains

$$(d/dt)\langle\tilde{I}^\nu\rangle+i\{\nu\Delta_0\langle\tilde{I}^\nu\rangle+(\omega_1/2)(-1)^\nu \times[(\nu-1)\langle\tilde{I}^{\nu+1}\rangle+(\nu+1)\langle\tilde{I}^{\nu-1}\rangle]\} =\mathrm{Tr}[R(\sigma)\tilde{I}^\nu], \quad (131)$$

where $\Delta_0\equiv\omega_0-\omega$.

In order to evaluate the right-hand side of Eq. (131), it is first necessary to identify the operators $V^k$, $U^k$, and $V_r{}^k$ that occur in the general theory. The interaction $G$ for the present problem, given by (111), is the sum of products of a bath operator $U_{ij}{}^k$ and a spin operator $V_{ij}{}^k$, as required by Eq. (16), but now each term is specified by three indexes $i$, $j$, and $k$ rather than by the single index $k$. The general theory derived is hence applicable here with the following changes in notation:

$$\begin{array}{ll} k\rightarrow i,j,k & l\rightarrow i',j',l \\ V^k\rightarrow V_{ij}{}^k & V^l\rightarrow V_{i'j'}{}^l \\ U^k\rightarrow U_{ij}{}^k & U^l\rightarrow U_{i'j'}{}^l \\ \sum_k\rightarrow \sum_{i,j=1}^{N}\sum_{k=-2}^{2} & \sum_l\rightarrow \sum_{i',j'=1}^{N}\sum_{l=-2}^{2}. \end{array} \quad (132)$$

The solutions of Eqs. (19) for $S$ and $S^{-1}$ when $E$ is given by (127) are

$$S=e^{-i(\Delta_0I_z+\omega_1I_x)t}e^{-i\omega I_zt}=e^{-i\theta I_y}e^{-i\omega' I_zt}e^{i\theta I_y}e^{-i\omega I_zt},$$
$$S^{-1}=e^{i\omega I_zt}e^{i(\Delta_0I_z+\omega_1I_x)t}=e^{i\omega I_zt}e^{-i\theta I_y}e^{i\omega' I_zt}e^{i\theta I_y}, \quad (133)$$

where $\omega'=(\Delta_0{}^2+\omega_1{}^2)^{\frac{1}{2}}$ and $\tan\theta=\omega_1/\Delta_0$, so

$$\Delta_0=\omega'\cos\theta, \quad (134a)$$

$$\omega_1=\omega'\sin\theta. \quad (134b)$$

By use of Eq. (133) and Eqs. (124), one obtains

$$SV_{ij}{}^kS^{-1}=\sum_{r=-2}^{2}\{V_{ij}{}^k\}_r\exp(i\omega_r{}^kt), \quad (135)$$

where

$$\{V_{ij}{}^k\}_r\equiv\sum_{k'} d_{kr}(\theta)d_{rk'}(-\theta)V_{ij}{}^{k'}, \quad (136)$$

and

$$\omega_r{}^k\equiv-(k\omega+r\omega'). \quad (137)$$

Equation (135) is in the form of Eq. (38), where now $V_r{}^k$ is replaced by $\{V_{ij}{}^k\}_r$. By again using Eq. (133) and Eqs. (124), and in addition Eq. (126), one obtains

$$S^{-1}\{V_{ij}{}^k\}_rS=\sum_{k'} d_{kr}(\theta)d_{rk'}(-\theta)V_{ij}{}^{k'}e^{i(k'\omega+r\omega')t}. \quad (138)$$

It is assumed that

$$\beta\omega_1,\quad \beta\omega_0,\quad \beta\omega\ll 1, \tag{139}$$

so that the high-temperature condition $|\omega_s{}^l|\beta\ll 1$, Eq. (104), is satisfied. Thus expression (105b), correct to first order in $\beta\omega_s{}^l$, can be used for $R(\sigma)$. By use of Eqs. (137) and (138), and the notational changes (132), one obtains from Eq. (105b)

$$\begin{aligned}R(\sigma)=&\sum_{iji'j'}(1-\delta_{ij})(1-\delta_{i'j'})\sum_{kll's}e^{i(l'-l)\omega t}\\&\times d_{ls}(\theta)d_{sl'}(-\theta)J_{(i'j')(ij)}{}^{lk}(\omega_s{}^l)\\&\times\{[[V_{i'j'}{}^{l'},\sigma],V_{ij}{}^k]\\&\qquad+\beta\omega_s{}^l[V_{ij}{}^k,V_{i'j'}{}^{l'}]/\mathrm{Tr}[1]\},\end{aligned}\tag{140}$$

where, from Eq. (86), with the notational changes (132),

$$J_{(i'j')(ij)}{}^{lk}(\omega)=\tfrac{1}{2}\int_{-\infty}^{\infty}\langle\{U_{i'j'}{}^l(t+\tau)U_{ij}{}^k(t)\}\rangle_q e^{i\omega\tau}d\tau. \tag{141}$$

From (116b) it follows that expression (141) is unchanged by interchange of $i'$ with $j'$ or $i$ with $j$, and from Eq. (73) it follows that

$$J_{(i'j')(ij)}{}^{lk}(\omega)=J_{(ij)(i'j')}{}^{kl}(-\omega). \tag{142}$$

Equation (140) is next multiplied by $\tilde{I}^\nu=I^\nu\exp(i\nu\omega t)$, and the trace taken. Since the trace of a product of operators is unchanged by a cyclic permutation of the operators, the operators can be permuted so that the expression can be written

$$\begin{aligned}&\mathrm{Tr}[R(\sigma)\tilde{I}^\nu]\\&\quad=\textstyle\sum_{iji'j'}(1-\delta_{ij})(1-\delta_{i'j'})\sum_{kll's}e^{i(l'-l+\nu)\omega t}\\&\quad\quad\times d_{ls}(\theta)d_{sl'}(-\theta)J_{(i'j')(ij)}{}^{lk}(\omega_s{}^l)\\&\quad\quad\times\{\mathrm{Tr}\,\sigma[[V_{ij}{}^k,I^\nu],V_{i'j'}{}^{l'}]\\&\quad\quad\quad+\beta\omega_s{}^l\,\mathrm{Tr}[I^\nu,V_{ij}{}^k]V_{i'j'}{}^{l'}/\mathrm{Tr}[1]\}.\end{aligned}\tag{143}$$

By use of Eq. (120) for the commutator of $V_{ij}{}^k$ and $I^\nu$, one obtains from (143) the expression

$$\begin{aligned}&\mathrm{Tr}[R(\sigma)\tilde{I}^\nu]\\&\quad\textstyle\sum_{iji'j'}(1-\delta_{ij})(1-\delta_{i'j'})\sum_{kll's}e^{i(l'-l+\nu)\omega t}\\&\quad\quad\times d_{ls}(\theta)d_{sl'}(-\theta)J_{(i'j')(ij)}{}^{lk}(\omega_s{}^l)A_k{}^\nu\\&\quad\quad\times\{\mathrm{Tr}\,\sigma[V_{i'j'}{}^{l'},V_{ij}{}^{k+\nu}]\\&\quad\quad\quad+\beta\omega_s{}^l\,\mathrm{Tr}[V_{ij}{}^{k+\nu}V_{i'j'}{}^{l'}]/\mathrm{Tr}[1]\}.\end{aligned}\tag{144}$$

Consider the terms in Eq. (144) that involve the trace not containing $\sigma$, and suppose that the trace is evaluated in the uncoupled representation in which $\mathbf{I}_i{}^2$ and $I_i{}^0$ are diagonal for all the individual spins. Since the trace of any component of a spin operator is zero, and since $i\neq j$ and $i'\neq j'$ in the sums in Eq. (144), one can in (144) make the substitution

$$\begin{aligned}\mathrm{Tr}[V_{i'j'}{}^{l'}V_{ij}{}^{k+\nu}]=&\,\delta_{ii'}\delta_{jj'}\,\mathrm{Tr}[V_{ij}{}^{l'}V_{ij}{}^{k+\nu}]\\&+\delta_{ij'}\delta_{ji'}\,\mathrm{Tr}[V_{ji}{}^{l'}V_{ij}{}^{k+\nu}].\end{aligned}\tag{145}$$

Consider next the trace containing $\sigma$ in Eq. (144). The commutator of $V_{ij}{}^{k+\nu}$ with $V_{i'j'}{}^{l'}$ is zero unless at least one of the primed subscripts is equal to one of the unprimed subscripts. Thus

$$\begin{aligned}&[V_{i'j'}{}^{l'},V_{ij}{}^{k+\nu}]\\&\quad=[V_{i'j'}{}^{l'},V_{ij}{}^{k+\nu}][\delta_{ii'}\delta_{jj'}+\delta_{i'j}\,\delta_{ij'}\\&\quad\quad+\delta_{ii'}(1-\delta_{jj'})+\delta_{jj'}(1-\delta_{ii'})\\&\quad\quad+\delta_{i'j}(1-\delta_{ij'})+\delta_{ij'}(1-\delta_{i'j})].\end{aligned}\tag{146}$$

When expressions (145) and (146) are substituted into Eq. (144), use made of the fact that $V_{ij}{}^k$ is unchanged by an interchange of $i$ with $j$, and $J_{(i'j')(ij)}{}^{lk}(\omega)$ is unchanged by an interchange of $i'$ with $j'$ or $i$ with $j$, Eq. (141b), and the sums over the primed indices in the Kronecker deltas performed, the result is

$$\begin{aligned}&\mathrm{Tr}[R(\sigma)\tilde{I}^\nu]\\&\quad=\textstyle\sum_{kll's}e^{i(l'-l+\nu)\omega t}d_{ls}(\theta)d_{sl'}(-\theta)A_k{}^\nu\\&\quad\quad\times\{2\textstyle\sum_{ij}(1-\delta_{ij})J_{(ij)(ij)}{}^{lk}(\omega_s{}^l)\\&\quad\quad\times(\mathrm{Tr}\,\sigma[V_{ij}{}^{l'},V_{ij}{}^{k+\nu}]+\beta\omega_s{}^l\\&\quad\quad\times\mathrm{Tr}[V_{ij}{}^{l'}V_{ij}{}^{k+\nu}]/\mathrm{Tr}[1])+4\textstyle\sum_{ijj'}(1-\delta_{ij})\\&\quad\quad\times(1-\delta_{ij'})(1-\delta_{jj'})J_{(ij')(ij)}{}^{lk}(\omega_s{}^l)\\&\quad\quad\quad\times\mathrm{Tr}\,\sigma[V_{ij'}{}^{l'},V_{ij}{}^{k+\nu}]\}.\end{aligned}\tag{147}$$

It can be shown by evaluation in the uncoupled representation that

$$\mathrm{Tr}[V_{ij}{}^lV_{ij}{}^k]/\mathrm{Tr}[1]=\delta_{k,-l}(-1)^k(\tfrac{2}{3})^2I^2(I+1)^2, \tag{148}$$

where $I$ is the total spin quantum number of each of the identical nuclei. Thus the terms in Eq. (147) that do not contain $\sigma$ reduce to numbers, and do not involve expectation values of the spin components $\tilde{I}^\nu$.

Consider next the terms involving $\sigma$ in Eq. (147). By use of the commutation relations for the components of spin operators, Eq. (122b), the commutator $[V_{ij'}{}^{l'}, V_{ij}{}^{k+\nu}]$ can be reduced to a sum of products of the components of the spin operators of the $i$th, $j$th, and $j'$th nuclei. In the terms in the sums over $i$ and $j$ but not $j'$ in (147), the foregoing commutators occurs with $j'=j$, but $i\neq j$. If the nuclei have spins of $\frac{1}{2}$, so that the following relation is valid,

$$I_i{}^\kappa I_i{}^\mu=\tfrac{1}{2}(\kappa-\mu)(-1)^{\kappa+\mu}I_i{}^{\kappa+\mu}+\tfrac{1}{4}\delta_{\kappa,-\mu}(1+\kappa^2), \tag{149}$$

one can show by actual evaluation that

$$\begin{aligned}[V_{ij}{}^l,V_{ij}{}^k]=\tfrac{1}{2}(-1)^k&\sum_{\mu=-1,0,1}\delta_{k,-l+\mu}(1-\tfrac{1}{2}\mu^2)\\&\times A_{-k}{}^\mu(I_i{}^\mu+I_j{}^\mu),\end{aligned}\tag{150}$$

where the $A_k{}^\mu$ are given by Eqs. (121). Thus the terms involving $\sigma$ in the sums over $i$ and $j$ but not $j'$ in (147) result in an expression linear in the expectation values of the components of the spins. The terms in the sums over $i$, $j$, and $j'$ cannot be so reduced by use of commutation or anticommutation relations because all the terms contain products of three spin operators of three different spins. Furthermore, the sum of these terms is not in general zero. However, for the special case in which the dipole-dipole interaction between spins $i$ and $j$ is uncorrelated with the dipole-dipole interaction between spins $i$ and $j'$, so that

$$J_{(ij')(ij)}{}^{lk}(\omega)=\delta_{jj'}J_{(ij)(ij)}{}^{lk}(\omega), \tag{151}$$

all the terms in the sums over $i$, $j$, and $j'$ in (147) obviously vanish.

On assuming that (151) is satisfied, and using (150) and (148) with $I=\frac{1}{2}$, one obtains from Eq. (147)

$$\begin{aligned}\mathrm{Tr}[R(\sigma)\tilde{I}^{\nu}]=&\textstyle\sum_{kll's}e^{i(l'-l+\nu)\omega t}d_{ls}(\theta)d_{sl'}(-\theta)A_{k}{}^{\nu}\\ &\times\textstyle\sum_{ij}(1-\delta_{ij})J_{(ij)(ij)}{}^{lk}(\omega_s{}^{l})(-1)^{k+\nu}\\ &\times\{\textstyle\sum_{\mu}\delta_{k+\nu,-l'+\mu}(1-\frac{1}{2}\mu^2)A_{-k-\nu}{}^{\mu}\langle I_i{}^{\mu}+I_j{}^{\mu}\rangle\\ &\qquad+\tfrac{1}{2}\beta\omega_s{}^{l}\delta_{k+\nu,-l'}\}.\end{aligned} \tag{152}$$

All of the spins are assumed to be in equivalent positions, which means that the relaxation effect on any one spin of all the other spins is the same for each spin. More specifically,

$$\begin{aligned}&\textstyle\sum_{i}(1-\delta_{ij})J_{(ij)(ij)}{}^{lk}(\omega)\\ &\qquad=\textstyle\sum_{j}(1-\delta_{ij})J_{(ij)(ij)}{}^{lk}(\omega)\equiv J_{lk}(\omega),\end{aligned} \tag{153}$$

where the $J_{lk}(\omega)$ defined by (153) is the same for all values of the index $i$ or $j$ not summed over. On making use of (153), (123), the Kronecker deltas present in (152), and the relation

$$\textstyle\sum_{i}\langle I_i{}^{\mu}\rangle=\sum_{j}\langle I_j{}^{\mu}\rangle=\langle I^{\mu}\rangle=\exp(-i\mu\omega t)\langle\tilde{I}^{\mu}\rangle,$$

one obtains a simplified expression for $\mathrm{Tr}[R(\sigma)\tilde{I}^{\nu}]$ which, when substituted into Eq. (131), gives

$$\begin{aligned}&\frac{d}{dt}\langle\tilde{I}^{\nu}\rangle+i\{\nu\Delta_0\langle\tilde{I}^{\nu}\rangle+(\tfrac{1}{2}\omega_1)(-1)^{\nu}\\ &\qquad\times[(\nu-1)\langle\tilde{I}^{\nu+1}\rangle+(\nu+1)\langle\tilde{I}^{\nu-1}\rangle]\}\\ &=\textstyle\sum_{kll's}e^{-i(k+l)\omega t}J_{lk}(\omega_s{}^{l})d_{ls}(\theta)d_{sl'}(-\theta)A_{k}{}^{\nu}(-1)^{l'}\\ &\qquad\times\{-2\textstyle\sum_{\mu}\delta_{k+\nu,-l'+\mu}(1-\frac{1}{2}\mu^2)A_{-l'}{}^{\mu}\langle\tilde{I}^{\mu}\rangle\\ &\qquad\qquad+\tfrac{1}{2}N\beta\omega_s{}^{l}\delta_{k+\nu,-l'}\}.\end{aligned} \tag{154}$$

If Eq. (154) is written out for $\nu=-1, 0, 1$, one obtains three simultaneous linear inhomogeneous first-order differential equations for the three quantities $\langle\tilde{I}^{\pm1}\rangle$, $\langle\tilde{I}^{0}\rangle$. The equations in general do not have constant coefficients because of the oscillating factors

$$\exp[-i(k+l)\omega t].$$

However, it is fortunate that in most actual applications the oscillating terms are either (a) not present because they are multiplied by zero coefficients, or (b), produce a negligible effect on the time dependence of the quantities $\langle\tilde{I}^{\nu}\rangle$ and can be omitted in the solution of the equations.

The coefficients of the oscillating terms are zero in physical situations in which the average distribution about the position of any one spin of all the other spins is spherically symmetric, as for example when the spins are in liquid molecules whose translational and rotational diffusion is isotropic. In such a case,

$$J_{lk}(\omega)=\delta_{l,-k}J_{l,-l}(\omega), \tag{155}$$

as can be shown from the properties of the spherical harmonics $Y_2{}^{k}$, so that the oscillating terms vanish in (154).

Even when Eq. (155) is not satisfied, it is permissible to omit the oscillating terms from the differential equations (154) if

$$\omega\gg|J_{kl}(\omega)|,\quad|\Delta_0|,\quad\omega_1. \tag{156}$$

If (156) is satisfied, one can choose a $\Delta t$ such that $\omega\gg(\Delta t)^{-1}\gg|J_{kl}(\omega)|$, $|\Delta_0|$, $\omega_1$. A solution of the differential equations by successive approximations for the $\langle\tilde{I}^{\nu}\rangle$ at $t+\Delta t$ in terms of their values at $t$ is given accurately by the first approximation because $|N\beta\omega_s{}^{l}|$ is less than or of the same order of magnitude as the $\langle\tilde{I}^{\nu}\rangle$, and $|J_{kl}(\omega)|\Delta t$, $|\Delta_0|\Delta t$, $\omega_1\Delta t\ll1$. Furthermore, in the time $\Delta t$ in which the relative change in $\langle\tilde{I}^{\nu}\rangle$ is small, the oscillating terms contribute changes that are smaller by a factor of order of magnitude $|\omega\Delta t|^{-1}\ll1$ than the changes produced by the nonoscillating terms for which $k+l=0$. Thus, if (156) is satisfied, the effect of the oscillating terms on the time dependence of the $\langle\tilde{I}^{\nu}\rangle$ is negligible compared to the effect of the nonoscillating terms, so that omission of the oscillating terms in the solution of the differential equations for the $\langle\tilde{I}^{\nu}\rangle$ introduces little error.

If the oscillating terms are omitted for the reasons just discussed, Eqs. (154) can be written in the matrix form

$$\frac{d}{dt}\begin{Bmatrix}\langle\tilde{I}^{-1}\rangle\\ \langle\tilde{I}^{0}\rangle\\ \langle\tilde{I}^{1}\rangle\end{Bmatrix}+\begin{bmatrix}-i\Delta_0+R_{-1,-1} & i\omega_1+R^{-}{}_{10} & R_{-11}\\ i\omega_1/2+R_{0,-1} & R_{00} & -i\omega_1/2+R_{01}\\ R_{1,-1} & -i\omega_1+R_{10} & i\Delta_0+R_{11}\end{bmatrix}\begin{Bmatrix}\langle\tilde{I}^{-1}\rangle\\ \langle\tilde{I}^{0}\rangle\\ \langle\tilde{I}^{1}\rangle\end{Bmatrix}=\begin{Bmatrix}R^{-}{}_{1}{}^{0}\\ R_0{}^{0}\\ R_1{}^{0}\end{Bmatrix}, \tag{157}$$

where the time-independent elements $R_{\nu\mu}$ and $R_{\nu}{}^{0}$ are given, respectively, by

$$\begin{aligned}R_{\nu\mu}\equiv2&\textstyle\sum_{ll's}J_{l,-l}(\omega_s{}^{l})d_{ls}(\theta)d_{sl'}(\theta)(-1)^{l'}\\ &\times(1-\tfrac{1}{2}\mu^2)A_{-l}{}^{\nu}A_{-l'}{}^{\mu}\delta_{l-\nu,l'-\mu},\end{aligned} \tag{158}$$

and

$$\begin{aligned}R_{\nu}{}^{0}\equiv\tfrac{1}{2}N\beta&\textstyle\sum_{ls}J_{l,-l}(\omega_s l)d_{ls}(\theta)d_{s(l-\nu)}(-\theta)\\ &\times A_{-l}{}^{\nu}(-1)^{l-\nu}\omega_s{}^{l}.\end{aligned} \tag{159}$$

It follows from the symmetry properties of the $d_{ls}(\theta)$, Eq. (125), and of the $A_k{}^{\mu}$, Eq. (123), that

$$R_{\nu\mu}=R_{-\nu,-\mu}, \tag{160a}$$

and

$$R_\nu{}^0 = R_{-\nu}{}^0. \tag{160b}$$

The stationary solution of Eqs. (157) can be readily obtained and the results expressed as follows:

$$\begin{aligned}\langle \tilde{I}_x\rangle_{st} &= \tfrac{1}{2}(\langle \tilde{I}^1\rangle_{st} + \langle \tilde{I}^{-1}\rangle_{st})\\ &= (1/D)\{R_0{}^0[R_{10}(R_{-11}-R_{11})+\omega_1\Delta_0]\\ &\qquad + R_1{}^0[R_{00}(R_{11}-R_{-11})+\omega_1{}^2]\},\end{aligned} \tag{161a}$$

$$\begin{aligned}\langle \tilde{I}_y\rangle_{st} &= (1/2i)(\langle \tilde{I}^1\rangle_{st} - \langle \tilde{I}^{-1}\rangle_{st})\\ &= (1/D)\{R_0{}^0[\omega_1(R_{11}+R_{-11})+\Delta_0 R_{10}]\\ &\qquad - R_1{}^0[2\omega_1 R_{01}+\Delta_0 R_{00}]\},\end{aligned} \tag{161b}$$

$$\begin{aligned}\langle I_z\rangle_{st} &= \langle \tilde{I}^0\rangle_{st}\\ &= (1/D)\{R_0{}^0[R_{11}{}^2 - R_{-11}{}^2+\Delta_0{}^2]\\ &\qquad + R_1{}^0[2R_{01}(R_{-11}-R_{11})+\omega_1\Delta_0]\},\end{aligned} \tag{161c}$$

where

$$\begin{aligned}D \equiv{}& R_{00}(R_{11}{}^2 - R_{-11}{}^2+\Delta_0{}^2)+2R_{10}R_{01}(R_{-11}-R_{11})\\ &+\omega_1{}^2(R_{11}+R_{-11})+\Delta_0\omega_1(R_{10}+2R_{01}).\end{aligned} \tag{162}$$

Since $|d_{ls}(\theta)|$, $|V_{ij}{}^k| \lesssim 1$, the condition of validity of the general theory, Eq. (71), applied to Eq. (140) for $R(\sigma)$, is satisfied if condition (139) is satisfied, $\beta\omega$, $\beta\omega_1$, $|\beta\Delta_0| \ll 1$, so that $\exp(\pm\beta\omega_s{}^l/2)\approx 1$, and if

$$|\textstyle\sum_{iji'j'}(1-\delta_{ij})(1-\delta_{i'j'})J_{(i'j')(ij)}{}^{lk}(\omega_s{}^l)| \ll \tau_c{}^{-1}. \tag{163}$$

The quantities $R_{\nu\mu}$ provide a measure of the magnitude of the left-hand side of (163), so that (163) can be replaced by the more easily verified condition

$$|R_{\nu\mu}|^{-1} \gg \tau_c. \tag{164}$$

The expressions for $R_{\nu\mu}$ and $R_\nu{}^0$ are so complicated that further discussion of Eqs. (157) and their stationary solutions (161) is confined to a few interesting special cases.

### A. Free Relaxation

If no rotating field is present, $\omega_1=0$, corresponding to $\theta=0$, so that use can be made of the relation $d_{kk'}(0)=\delta_{kk'}$. If one uses also Eq. (137), $\omega_s{}^l \equiv -l\omega - s\omega'$, Eq. (141a), $J_{l,-l}(\omega_s{}^l)=J_{-l,l}(-\omega_s{}^l)$, and Eqs. (160), the expression for $R_{\nu\mu}$, (158), gives

$$R_{00} = 2\textstyle\sum_l(-1)^l l^2 J_{l,-l}(-l\omega_0) \equiv (1/T_1), \tag{165a}$$

$$R_{11} = R_{-1,-1} = \textstyle\sum_l(-1)^l(6-l^2)J_{l,-l}(-l\omega_0) \equiv (1/T_2), \tag{165b}$$

and

$$R_{\pm 10} = R_{0,\pm 1} = R_{-11} = R_{1,-1} = 0, \tag{165c}$$

and the expression (159) for $R_\nu{}^0$ gives

$$R_{\pm 1}{}^0 = 0 \tag{166a}$$

and

$$R_0{}^0 = \tfrac{1}{2}N\beta\omega_0 \textstyle\sum_l(-1)^l l^2 J_{l,-l}(-l\omega_0) = \langle I_z\rangle^T/T_1, \tag{166b}$$

where

$$\langle I_z\rangle^T \equiv \tfrac{1}{4}N\beta\omega_0 = \tfrac{1}{4}N\gamma\hbar H_0/kT \tag{167}$$

is the equilibrium magnetization at temperature $T$ of a system of $N$ spin $\frac{1}{2}$ nuclei in a magnetic field $H_0$, correct to first order in $\beta\omega_0 = \gamma\hbar H_0/kT$. Use of (165) and (166) reduces Eqs. (157) to

$$(d/dt)\langle \tilde{I}^0\rangle + (1/T_1)\langle \tilde{I}^0\rangle = (1/T_1)\langle I_z\rangle^T, \tag{168a}$$

$$(d/dt)\langle \tilde{I}^{\pm 1}\rangle + (1/T_2 \pm i\Delta_0)\langle \tilde{I}^{\pm 1}\rangle = 0. \tag{168b}$$

The solutions of Eqs. (168) for the components in the laboratory reference frame, $\langle I^\nu\rangle = \langle \tilde{I}^\nu\rangle \exp(-i\nu\omega t)$, are

$$\langle I^0\rangle_t - \langle I_z\rangle^T = c_0 e^{-t/T_1}, \tag{169a}$$

$$\langle I^{\pm 1}\rangle_t = c_{\pm 1} e^{\mp i\omega_0 t} e^{-t/T_2}. \tag{169b}$$

Thus, as might have been expected, in the laboratory reference frame the component of $\langle \mathbf{I}\rangle$ parallel to the constant applied field $H_0$ relaxes exponentially to $\langle I_z\rangle^T$ with time constant $T_1$, and the components of $\langle \mathbf{I}\rangle$ perpendicular to $H_0$ relax to zero with time constant $T_2$ while simultaneously precessing about $H_0$ with the Larmor frequency $\omega_0 = \gamma H_0$.

In order to compare the expressions obtained for the relaxation times $T_1$ and $T_2$ with the results of previous treatments, we define

$$J_l(\omega) \equiv \textstyle\sum_i(1-\delta_{ij})\displaystyle\int_{-\infty}^{\infty}\langle\{F_{ij}{}^{-l}(t+\tau)F_{ij}{}^l(t)\}\rangle e^{-i\omega\tau}d\tau, \tag{170}$$

where

$$\begin{aligned}F_{ij}{}^0 &\equiv r_{ij}{}^{-3}(1-3\cos^2\theta_{ij})\\ &= -r_{ij}{}^{-3}(16\pi/5)^{\frac{1}{2}}Y_2{}^0(\theta_{ij},\varphi_{ij}),\end{aligned} \tag{171a}$$

$$\begin{aligned}F_{ij}{}^{\pm 1} &\equiv r_{ij}{}^{-3}\cos\theta_{ij}\sin\theta_{ij}\exp(\pm i\varphi_{ij})\\ &= \mp r_{ij}{}^{-3}(8\pi/15)^{\frac{1}{2}}Y_2{}^{\pm 1}(\theta_{ij},\varphi_{ij}),\end{aligned} \tag{171b}$$

$$\begin{aligned}F_{ij}{}^{\pm 2} &\equiv r_{ij}{}^{-3}\sin^2\theta_{ij}\exp(\pm 2i\varphi_{ij})\\ &= r_{ij}{}^{-3}(32\pi/15)^{\frac{1}{2}}Y_2{}^{\pm 2}(\theta_{ij},\varphi_{ij}).\end{aligned} \tag{171c}$$

By comparing Eqs. (171) with the definition of $J_{lk}(\omega)$, Eq. (153), which involves Eqs. (141) and (112), it is found that

$$J_{00}(0) = (3/64)(\gamma^2\hbar)^2 J_0(0), \tag{172a}$$

$$J_{1,-1}(-\omega_0) = -(9/32)(\gamma^2\hbar)^2 J_1(\omega_0), \tag{172b}$$

$$J_{2,-2}(-2\omega_0) = (9/128)(\gamma^2\hbar)^2 J_2(2\omega_0). \tag{172c}$$

Hence Eqs. (165) for $T_1$ and $T_2$ can be expressed in terms of either the $J_{l,-l}(-l\omega_0)$ or the $J_l(l\omega_0)$:

$$1/T_1 = 4[-J_{1,-1}(-\omega_0) + 4J_{2,-2}(-2\omega_0)] \tag{173a}$$

$$= (9/8)(\gamma^2\hbar)^2[J_1(\omega_0)+J_2(2\omega_0)], \tag{173b}$$

$$\begin{aligned}(1/T_2) = [&6J_{0,0}(0) - 10J_{1,-1}(-\omega_0)\\ &+4J_{2,-2}(-2\omega_0)]\end{aligned} \tag{174a}$$

$$\begin{aligned}= (9/32)(\gamma^2\hbar)^2[&J_0(0)+10J_1(\omega_0)\\ &+J_2(2\omega_0)].\end{aligned} \tag{174b}$$

Expressions (173b) and (174b) agree in the case of nuclei of spin $\frac{1}{2}$ with the results of Kubo and Tomita,[7] which they obtained by a different method.

The calculation of the longitudinal nuclear relaxation of water by Bloembergen, Purcell, and Pound[5] is a famous example of the usefulness of the semiclassical form of the relaxation theory. The expression for $T_1$ used by BPP was the same as Eq. (173b) except for an incorrect factor of $\frac{1}{2}$ before $J_2(2\omega_0)$. They calculated the correlation functions occurring in $J_1$ and $J_2$ by considering the water molecules to be spheres diffusing classically in a viscous fluid. This simple model resulted in a value of the relaxation time that agreed well with experiment.

It should be remembered that the foregoing expressions were obtained by assuming that the dipole-dipole interaction between any two spins is uncorrelated with the dipole-dipole interaction between either of these spins and any third spin. If this condition, Eq. (151), is not satisfied, the longitudinal free relaxation of the system of spin $\frac{1}{2}$ nuclei is not in general described by a single decaying exponential, but rather by a sum of exponentially decaying terms.[8]

### B. Very Weak Rotating Field near Resonance

If the following condition is satisfied,

$$\omega_1, \quad |\Delta_0| \ll \omega_0, \omega^* \equiv \tau_c^{-1}, \tag{175}$$

so that $\omega' \equiv (\omega_1^2+\Delta_0^2)^{\frac{1}{2}} \ll \omega_0$, $\omega^*$, it is permissible according to Eq. (74) to replace $J_{l,-l}(\omega_s^l)$ by $J_{l,-l}(-l\omega_0)$. The sum over $s$ in Eq. (158) then becomes

$$\textstyle\sum_s d_{ls}(\theta) d_{sl'}(-\theta) = \delta_{ll'},$$

Eq. (126), so that $R_{\nu\mu} = \delta_{\nu\mu} R_{\mu\mu}$, where the nonzero quantities are given by the same expressions obtained for the case of free relaxation, Eqs. (165).

Replacement of $J_{l,-l}(\omega_s^l)$ by $J_{l,-l}(-l\omega_0)$ in (159) leads to the expression

$$\begin{aligned} R_\nu^0 = {} & \tfrac{1}{2} N\beta\omega\delta_{\nu 0} \textstyle\sum_l (-1)^l l^2 J_{l,-l}(-l\omega_0) \\ & -\tfrac{1}{2} N\beta\omega' \textstyle\sum_{ls} J_{l,-l}(-l\omega_0) d_{ls}(\theta) \\ & \times d_{s(l-\nu)}(-\theta) A_{-l}^{\nu} (-1)^{l-\nu} s. \end{aligned} \tag{176}$$

Since from (175) $\omega \approx \omega_0 \gg \omega'$,

$$R_0^0 \approx \langle I_z \rangle^T / T_1, \tag{177a}$$

$$|R_{\pm 1}^0| \ll |R_0^0|. \tag{177b}$$

If one uses (165) and (177), the stationary solutions, Eqs. (161), reduce to the familiar form predicted by the Bloch phenomenological equations,

$$\langle \tilde{I}_x \rangle_{st} = \frac{\omega_1 \Delta_0 T_2^2}{1+(\Delta_0 T_2)^2 + \omega_1^2 T_1 T_2} \langle I_z \rangle^T, \tag{178a}$$

$$\langle \tilde{I}_y \rangle_{st} = \frac{\omega_1 T_2}{1+(\Delta_0 T_2)^2 + \omega_1^2 T_1 T_2} \langle I_z \rangle^T, \tag{178b}$$

$$\langle \tilde{I}_z \rangle_{st} = \frac{1+(\Delta_0 T_2)^2}{1+(\Delta_0 T_2)^2 + \omega_1^2 T_1 T_2} \langle I_z \rangle^T. \tag{178c}$$

The relaxation times $T_1$ and $T_2$ are given, respectively, by (173) and (174); they are independent of the magnitude of the rotating field.

The differential equations (157) assume the form of the Bloch phenomenological equations when conditions (175) are satisfied only if the inequality $|R_{\pm 1}^0| \ll |R_0^0|$, (177b), is interpreted as meaning that it is permissible to replace $R_{\pm 1}^0$ by zero in (157). The fact that the $R_{\pm 1}^0$ are small but not zero means that the transverse components of the expectation value of the spin of the system tend to relax not to zero, but rather to small but finite values that depend on the magnitude of the rotating field and how much its frequency differs from the resonance frequency.

### C. Weak Rotating Field near Resonance

In this section we consider a situation in which the rotating field is strong enough, or the correlation time long enough, that the rate of relaxation of the system is affected by the rotating field. It is assumed that

$$\omega_1, \quad |\Delta_0| \ll \omega_0, \tag{179}$$

so that $\omega' \ll \omega_0$. It is further assumed that, as a consequence of (179),

$$\begin{aligned} J_{l,-l}(\omega \pm \omega') & \approx J_{l,-l}(\omega \pm 2\omega') \\ & \approx J_{l,-l}(\omega) \approx J_{l,-l}(\omega_0), \end{aligned} \tag{180a}$$

$$\begin{aligned} J_{l,-l}(2\omega \pm \omega') & \approx J_{l,-l}(2\omega \pm 2\omega') \\ & \approx J_{l,-l}(2\omega) \approx J_{l,-l}(2\omega_0), \end{aligned} \tag{180b}$$

even though it is not required that $\omega_1$, $|\Delta_0| \ll \omega^*$. Use of relations (180) in (158) leads to the following expressions for $R_{\nu\mu}$:

$$R_{00} = 1/T_1, \tag{181a}$$

$$R_{0,\pm 1} = 0, \tag{181b}$$

$$\begin{aligned} R_{11} & = R_{-1,-1} \\ & = (1/T_2) + (9/2)[(3c^4 - 2c^2 - 1) J_{00}(0) \\ & \quad + 4s^2c^2 J_{00}(-\omega') + s^4 J_{00}(-2\omega')], \end{aligned} \tag{181c}$$

$$\begin{aligned} R_{\pm 1,0} = {} & 3sc[(1-3c^2) J_{00}(0) + 2(2c^2-1) J_{00}(-\omega') \\ & + s^2 J_{00}(-2\omega')], \end{aligned} \tag{181d}$$

$$\begin{aligned} R_{1,-1} = R_{-1,1} = {} & \tfrac{3}{2} s^2 [(3c^2-1) J_{00}(0) - 4c^2 J_{00}(-\omega') \\ & + (1+c^2) J_{00}(-2\omega')], \end{aligned} \tag{181e}$$

where $c = \cos\theta = \Delta_0/\omega'$, $s \equiv \sin\theta = \omega_1/\omega'$, and $T_1$ and $T_2$ are again given by (173) and (174), respectively. Note that if $\omega' \ll \omega^*$, so that $J_{00}(-2\omega') \approx J_{00}(-\omega') \approx J_{00}(0)$, the bracketed expressions in Eqs. (181) vanish, and the expressions reduce to the same form obtained in the previous section where the condition $\omega' \ll \omega^*$ was assumed.

---

[7] R. Kubo and K. Tomita, J. Phys. Soc. Japan **9**, 888 (1954).

[8] P. S. Hubbard, Phys. Rev. **109**, 1153 (1958).

Use of relations (180) in (159) leads to the expression

$$
\begin{aligned}
R_\nu{}^0 = {} & \tfrac{1}{2} N\beta\omega\delta_{\nu 0} \textstyle\sum_l (-1)^l l^2 J_{l,-l}(-l\omega_0) \\
& + \tfrac{1}{2} N\beta\omega' \textstyle\sum_s (-s)\{J_{00}(-s\omega')d_{0s}(\theta) \\
& \times d_{s(-\nu)}(-\theta) A_0{}^\nu (-1)^\nu \\
& + \textstyle\sum_l (1-\delta_{l0}) J_{l,-l}(-l\omega_0) d_{ls}(\theta) \\
& \qquad \times d_{s(l-\nu)}(-\theta) A_{-l}{}^\nu (-1)^{l-\nu}\}. \qquad (182)
\end{aligned}
$$

Since as in the previous section $\omega \approx \omega_0 \gg \omega'$, one obtains again Eqs. (177) for the $R_\nu{}^0$.

As consequence of Eqs. (177) and the form Eqs. (181), the stationary solutions, Eqs. (161), reduce to

$$\langle \tilde{I}_x \rangle_{st} = (1/D)[R_{10}(R_{-11}-R_{11})+\omega_1\Delta_0] R_{00} \langle I_z \rangle^T, \qquad (183\text{a})$$

$$\langle \tilde{I}_y \rangle_{st} = (1/D)[\omega_1(R_{11}+R_{-11})+\Delta_0 R_{10}] R_{00} \langle I_z \rangle^T, \qquad (183\text{b})$$

$$\langle \tilde{I}_z \rangle_{st} = (1/D)[R_{11}{}^2-R_{-11}{}^2+\Delta_0{}^2] R_{00} \langle I_z \rangle^T, \qquad (183\text{c})$$

where

$$
\begin{aligned}
D = {} & R_{00}(R_{11}{}^2 - R_{-11}{}^2 + \Delta_0{}^2) + \omega_1{}^2 (R_{11}+R_{-11}) \\
& + \Delta_0 \omega_1 R_{10}. \qquad (184)
\end{aligned}
$$

Although the conditions (179) and (180) permit the $R_{\nu\mu}$ to be written out explicitly as in Eqs. (181), the expressions are nonetheless still too complicated to be conveniently substituted into Eqs. (183) and (184). The stationary solutions, Eqs. (183), depend on the magnitude and frequency of the rotating field in a considerably more complicated manner than do Eqs. (178), the stationary solutions of the phenomenological equations. Furthermore, Eqs. (183) cannot be transformed to the form of Eqs. (178) by defining two new frequency-independent relaxation times $T_1'$ and $T_2'$, even if these quantities are permitted to depend on the magnitude of the rotating field.

At resonance, $\Delta_0 = 0$, $\omega' = \omega_1$, $\cos\theta = 0$, and $\sin\theta = 1$, so that the expressions (181) for $R_{\nu\mu}$ reduce to

$$
\begin{aligned}
& R_{00} = 1/T_1, \quad R_{0,\pm 1} = R_{\pm 1,0} = 0, \\
& R_{11} = (1/T_2) + (9/2)[J_{00}(-2\omega_1) - J_{00}(0)], \\
& R_{-11} = \tfrac{3}{2}[J_{00}(-2\omega_1) - J_{00}(0)],
\end{aligned}
$$

and hence Eq. (183a) reduces to

$$\langle \tilde{I}_y \rangle_{st,\,\omega=\omega_0} = \frac{\omega_1 T_2'}{1+\omega_1{}^2 T_1 T_2'} \langle I_z \rangle^T,$$

where $T_1$ is given as before by Eq. (173), and $T_2'$, which depends on the magnitude of the rotating field, is defined by

$$1/T_2' = (1/T_2) - 3[J_{00}(0) - J_{00}(-2\omega_1)]$$

in terms of $T_2$, Eq. (174). Thus the absorption mode *at resonance* is of the same form as predicted by the phenomenological equations, Eq. (178b), with the modified $T_2$ given by the preceding equation.

The treatment of relaxation by dipole-dipole interactions presented is similar to the calculation of Tomita,[3] corresponding to his case of "rapidly fluctuating lattice." Tomita assumes that the correlation functions have a decaying exponential time dependence, while the foregoing treatment permits a more general form. The treatment here depends on the assumption that the dipole-dipole interaction between two spins in uncorrelated with the dipole-dipole interaction between either of the spins and any third spin. Tomita appears to make the same assumption from the beginning of his calculation, although he never explicitly states that he is doing so. The validity of the results obtained here and of those given by Tomita is considerably limited by this assumption. A previous calculation of the longitudinal free relaxation of liquid molecules containing three or four equidistant spin $\frac{1}{2}$ nuclei has shown that when cross-correlations between different dipole-dipole interactions is included the relaxation is the sum of two exponentials, but that the coefficient multiplying one of the exponentials is only a few percent of the coefficient multiplying the other exponential.[8] Advantages of the present treatment neglecting cross correlations are that (a) the number of interacting spins in the system is not limited, and intermolecular as well as intramolecular interactions can be included; (b) the transverse as well as the longitudinal component of the expectation value of the nuclear spin is calculated; and (c) the rotating field is included and not treated as a perturbation.

## ACKNOWLEDGMENT

The author thanks Richard L. Hilt for reading the manuscript critically and checking the calculations.