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Generalized Theory of Relaxation

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This paper represents a further generalization, beyond that given recently, of an earlier theory by Wangsness and the author. In common with this theory, it is assumed that the spin system is weakly coupled to its molecular surroundings and that the latter can be considered as a heat reservoir which remains in thermal equilibrium at the absolute temperature T. The condition that the coupling is weak demands that its effects upon the spin system, calculated in first and second approximation and measured in a frequency scale, are small compared to the inverse of the correlation time τ_c as well as of the time $\beta = \hbar/kT$. The principal progress over the earlier work consists in the fact that it imposes no additional conditions upon the energy of the spin system; in particular, it dispenses with the necessity that the dominant part of this energy is independent of the time. A linear differential equation of the first order for the distribution matrix is derived which is valid in this very general case and which contains the earlier results as special cases. The derivation of this Boltzmann equation is carried out in a form which is independent of any particular representation, used for the spin system, and which leads directly to a system of differential equations for the expectation values of spin functions. Beyond the earlier results, it is shown that the coupling with the molecular surroundings leads in second approximation not only to relaxation terms but also to a correction of the spin energy which has the nature of a "self-energy." As a considerably more restricted case, the situation is investigated where the dominant part of the spin energy varies little during a time of order τ_c and β. It is shown that, in this case, relaxation causes the distribution matrix to tend towards the form, corresponding to thermal equilibrium at the instantaneous value of the dominant part of the energy. The case where the frequencies of the spin system as well as their relative rate of variation are small compared to $1/\tau_c$ but arbitrary compared to $1/\beta$, is likewise discussed and shown to lead to a simple form of the Boltzmann equation. The general formalism is finally applied to a spin system with a single spin of value 1/2, exposed to a rotating field. One obtains in this case a phenomenological equation for the expectation value of the spin vector which is far more general than the one derived earlier; instead of requiring merely the knowledge of the longitudinal and the transverse relaxation time, relaxation is here characterized by five time constants which may all be different. The stationary solution is derived and applied to a number of familiar special cases.

1. INTRODUCTION

THE theory of relaxation has received a new impetus through the recent intensive study of nuclear and electronic spin resonances in bulk matter and their wide field of applications. Depending upon the goal, the problems posed have been treated by several different methods, primarily distinguished by the character of simplifying assumptions and by the stage at which they are introduced in order to facilitate the discussion of particular cases.

Foregoing both a complete description and an evaluation of the rather extensive literature, the work of Bloembergen, Purcell, and Pound[1] shall serve as the first example. Important conclusions about their relaxation phenomena are reached here by assuming from the outset that nuclear spin systems are subjected to given fluctuating actions, arising from their molecular surroundings. While it is of great help in interpreting these actions in classical terms, the procedure has the disadvantage that it leads to a thermal equilibrium of the spin system in which all states are equally populated and that it is thus equivalent to the assumption of an infinitely high temperature T. This feature arises not only from the fact that the compensating changes of energy are neglected in the treatment of the molecular surroundings but also from the inconsistency, introduced by regarding its variables as classical functions of the time and retaining an essentially quantum-mechanical description of the spin system. Indeed, the existence of discrete energy levels of the spin system is in contradiction to a consistent classical treatment which demands a continuous variation of the energy and which, in fact, would lead to the proper equilibrium at a finite temperature. On the other hand, opposite transitions between discrete energy levels, induced by a finite spectral frequency ω of the molecular surroundings, must have a relative weight which is given by the Boltzmann factor with the characteristic exponent $\hbar\omega/kT$. The result of equal weights, mentioned above, arises from treating the molecular system in the limit $\hbar \rightarrow 0$ with the same effect upon the Boltzmann factor as going to the limit $T \rightarrow \infty$. The proper finite value of the exponent was shown by Ayant[2] to appear in a natural way through a quantum-mechanical generalization of the concept of a random function.

A different approach has been chosen by Wangsness and the author[3] through formulating the dynamics of relaxation totally within the framework of quantum mechanics. As the principal basic assumption, dissipative features are here introduced by considering the molecular surroundings as a heat reservoir which remains in thermal equilibrium while their exchange of energy with the spin system is fully taken into account. The procedure was first applied in I to the simplest situation where the representative spin system is that of a nucleus, characterized by its spin and magnetic moment and under the superposed action of a strong constant magnetic field $\mathbf{H}_0$ and a weak time-dependent magnetic field $\mathbf{H}_1$. An extension of the same method to

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[1] N. Bloembergen, *Nuclear Magnetic Relaxation* (thesis, Leyden; Schotanus and Jens, Utrecht, 1948); Bloembergen, Purcell, and Pound, Phys. Rev. **73**, 679 (1948).

[2] Y. Ayant, J. phys. radium **16**, 411 (1955).

[3] R. K. Wangsness and F. Bloch, Phys. Rev. **89**, 728 (1956) (referred to as I).

far more general systems was recently presented,[4] assuming that the energy of the spin system contains a dominant time-independent part $\hbar E_0$ and a relatively small time-dependent part $\hbar E_1$ without, however, restricting their form or the nature of the spin system. Under stated conditions, it was thus possible to derive equations which are applicable, irrespective of whether their determining coefficients can be explicitly evaluated or not. Besides permitting the discussion of more general features, they represent a basis for that of particular problems, either in cases where these problems are simple enough to permit a solution in terms of certain constants, to be compared with the experiment, or where the actual situation is so complex that one has to resort to trial solutions, containing plausible features such as, for example, that of a "spin temperature."

Among the more general results of II, it is particularly to be noted that relaxation tends to establish populations of the spin states with Boltzmann factors, determined by the large part $\hbar E_0$ of the spin energy. Another way of formulating this result is to state that the distribution matrix σ assumes in thermal equilibrium the form

$$\sigma_0 = \zeta e^{-\beta E_0}, \tag{1.1}$$

with

$$\beta = \hbar / kT, \tag{1.2}$$

and where

$$\zeta = [\mathrm{Tr}(e^{-\beta E_0})]^{-1} \tag{1.3}$$

represents the inverse diagonal sum of $e^{-\beta E_0}$. While this statement is independent of the representation, it was actually derived[5] in the special representation in which E_0 appears as a diagonal matrix. Under the special circumstances considered in I, where the behavior of the macroscopic polarization is correctly represented by phenomenological equations,[6] Eq. (1.1) leads to a constant equilibrium polarization, determined by the strong and constant magnetic field.

There are, however, cases of interest for which either the constant field is too weak or the applied alternating field too strong for the former to be considered as the dominating part. More generally, there arise situations in which the total energy $\hbar E$ of the spin system depends explicitly upon the time in such a manner that its variation can be appreciable. It is clear that for sufficiently slow variations, irrespective of their magnitude, one can, at any instant, treat the total energy like the previously considered static part $\hbar E_0$ so that the distribution matrix will tend towards the quasi-stationary value

$$\sigma_0 = \zeta e^{-\beta E(t)}, \tag{1.4}$$

with

$$\zeta(t) = [\mathrm{Tr}(e^{-\beta E(t)})]^{-1}, \tag{1.5}$$

which is obtained by replacing E_0 in Eqs. (1.1) and (1.3) by the operator $E(t)$. It has indeed been suggested,[7] in the case of the phenomenological equations, that they should be modified by replacing the constant equilibrium value of the polarization by the instantaneous equilibrium value, corresponding to the total time-dependent magnetic field, in order to obtain a better agreement with experiments at low fields. There arises thus the interesting question whether and to what extent such a procedure can be justified; while there can be no doubt about the result (1.4) being correct in the limit of very slow variations of E, it remains to be seen under which conditions this limit represents a sufficiently good approximation.

The first problem of this type has been treated by Gorter and Kronig[8] for the case of a weak oscillating magnetic field, with resulting expressions for the real and imaginary parts of the susceptibility as functions of the frequency. More recently, Garstens[9] has considered the case of a constant field and an oscillating field at right angles with relaxation provided by collisions of short duration, without assuming the constant field to be necessarily predominant. Similarly it was shown by Wangsness,[10] under the assumption of equal longitudinal and transverse relaxation times, that relaxation by short collisions leads in the case of a rotating field to the same conclusions as the previously mentioned substitution of the instantaneous equilibrium polarization into the phenomenological equations.

The idea that short collisions should result in a tendency to establish equilibrium with respect to the instantaneous field suggests a treatment of the relaxation mechanism in which the assumed shortness of the correlation time $\tau_c = 1/\omega^*$ plays a decisive role. This assumption was already necessary in I and II, and it will be shown here to permit an extension of the earlier method to the case of an arbitrary spin system with an arbitrary time-dependent energy $\hbar E(t)$. Indeed, it is possible, under certain conditions to be discussed below, to derive a differential equation for the distribution matrix which encompasses this quite general case and reduces to the more special Boltzmann equation, derived in II under the assumption of a dominant constant part in the total energy of the spin system. It will further be seen that, more generally than in II, relaxation produces indeed a tendency of the distribution matrix towards the expression σ_0 of Eq. (1.4), provided that the variation of E is inappreciable not only during the correlation time τ_c but also during the time β, defined in Eq. (1.2).[11]

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[4] F. Bloch, Phys. Rev. **102**, 104 (1956) (referred to as II).

[5] Equation (2.35) of II.

[6] F. Boch, Phys. Rev. **70**, 460 (1946).

[7] Codrington, Olds, and Torrey, Phys. Rev. **95**, 607 (1954).

[8] C. J. Gorter and R. Kronig, Physica **3**, 1009 (1936); R. Kronig, Physica **5**, 75 (1938).

[9] M. A. Garstens, Phys. Rev. **93**, 1228 (1954).

[10] R. K. Wangsness, Phys. Rev. **98**, 928 (1955).

[11] Similarly to the remark, made above about the Boltzmann factor, the condition of sufficient shortness of the time β does not appear in the treatment of Garstens and Wangsness who consider the variables of the molecular surroundings as classical functions. Since β vanishes for $\hbar \to 0$, there is no occasion, in this limit, to state the sufficiently small variation of E during this time.

2. BOLTZMANN EQUATION

As in I and II, it shall be assumed that the Hamiltonian of the total system has the form

$$\mathcal{H}=\hbar E+\hbar F+\hbar G, \tag{2.1}$$

where the first and second part stand for the energy of the spin system and the molecular system, respectively, and are operators, acting only upon the variables of the corresponding subsystem. The coupling between the two is represented by the third part, to be considered as a small perturbation. In order to describe given variations of external fields, E will be assumed, in contrast to F and G, to be an explicitly time-dependent operator.

The development of the density matrix ρ in time will be followed in a representation, to be characterized by the double symbol (fu), in which F is diagonal with eigenvalues f and where u denotes any additional quantum numbers, necessary to completely specify a stationary state of the molecular system with a given energy $\hbar f$; the number of such states in the interval df of f is given by $\eta_u(f)df$. While the existence of a dominant constant part E_0 of E made it convenient, in II, to use for the spin system a representation in which E_0 is likewise diagonal, there exists in the case of a general time-dependent operator $E(t)$ no such privileged representation. One is thus led to choosing an arbitrary representation, indicated by the symbol n; this symbol will denote any complete set of quantum numbers which characterize a state of the spin system. The total system will thus be described in a representation, denoted by the triple symbol (nfu).

In order to eliminate the part E from the differential equation

$$d\rho/dt=-i[E+F+G,\rho] \tag{2.2}$$

for the density matrix ρ, a transformation operator $S(t)$ is to be introduced which satisfies the equation

$$dS/dt=iSE(t), \tag{2.3}$$

with its inverse S^{-1}, satisfying

$$dS^{-1}/dt=-iE(t)S^{-1}. \tag{2.4}$$

In consistency with these equations, S and S^{-1} are Hermitian conjugate since E is Hermitian. It should be noted that E and, therefore, also S and S^{-1} are "spin functions," i.e., operators, acting only on the quantum numbers n of the spin system. Introducing, instead of ρ and G, the transformed expressions

$$\rho^*=e^{iFt}S\rho S^{-1}e^{-iFt}, \tag{2.5}$$

$$G_S=SGS^{-1}, \tag{2.6}$$

$$G^*=e^{iFt}G_S e^{-iFt}, \tag{2.7}$$

the elimination from Eq. (2.2) of both E and F is achieved, and it follows with (2.3) and (2.4) that

$$d\rho^*/dt=-i[G^*,\rho^*]. \tag{2.8}$$

Given $\rho^*(t)$ at the time t, the increment during a short time interval τ, keeping linear and quadratic terms in G^*, is obtained from (2.8) by two successive approximations in the form

$$\rho^*(t+\tau)-\rho^*(t)=-i\int_0^\tau[G^*(t+\tau'),\rho^*(t)]d\tau'-\int_0^\tau\left(\int_0^{\tau'}[G^*(t+\tau'),\ [G^*(t+\tau''),\rho^*(t)]]d\tau''\right)d\tau'. \tag{2.9}$$

The analogous relation was used in I[12] and II and applied as explicit matrix relation in a representation where E_0 is diagonal. Similarly, it could be written out and applied as a matrix relation in the (nfu)-representation. In view of the fact, however, that the n representation for the spin system is here quite arbitrary, it is indicated to introduce a notation in which the symbol n does not appear. For this purpose, the general matrix element of an operator O in the (nfu)-representation is to be written in the form

$$(nfu|O|n'f'u')=(n|(fu|O|f'u')|n'), \tag{2.10}$$

with the significance that $(fu|O|f'u')$ will be considered as an operator, specified by the pair of double symbols (fu), $(f'u')$, which acts only upon the variables of the spin system. It follows from this definition that the Hermitian conjugate of this operator is given by

$$(fu|O|f'u')^\dagger=(f'u'|O^\dagger|fu), \tag{2.11}$$

where $O^\dagger$ is the Hermitian conjugate to O and, hence, for two operators O_1 and O_2 that

$$((fu|O_1|f'u')(f'u'|O_2|fu))^\dagger=(fu|O_2^\dagger|f'u')(f'u'|O_1^\dagger|fu), \tag{2.12}$$

to be noted for later purposes. The addition and multiplication rules of any two such operators take the same form which they would have in a pure (fu) representation. With F diagonal in such a representation with eigenvalues f, one has

$$(fu|e^{\pm iFt}|f'u')=e^{\pm ift}\delta_{ff'}\delta_{uu'},$$

and for any spin function Q, such as, for example, S, S^{-1},

$$(fu|Q|f'u')=Q\delta_{ff'}\delta_{uu'}.$$

It is, therefore, from (2.5)

$$(fu|\rho^*|f'u')=e^{i(f-f')t}S(fu|\rho|f'u')S^{-1}. \tag{2.13}$$

The distribution matrix, to be described in the n representation by $(n|\sigma|n')$, has in this notation the invariant definition

$$\sigma=\textstyle\sum_{fu}(fu|\rho|fu). \tag{2.14}$$

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[12] Except for the particular choice $t=0$ and the fact that a small part E_1 was separated from E and included in the first approximation, Eq. (2.9) is equivalent to the Eqs. (2.17), (2.18), and (2.19) of I.

Therefore, from (2.13),

$$\textstyle\sum_{fu}(fu|\rho^*|fu)=\sigma_S, \tag{2.15}$$

with

$$\sigma_S=S\sigma S^{-1}. \tag{2.16}$$

Referring to a statistical average over the molecular system, assumed to be at any instant t in thermal equilibrium at the absolute temperature T, the density matrix at this instant is to be replaced by the expression

$$(fu|\rho(t)|f'u')=\sigma(t)P(f)\delta_{ff'}\delta_{uu'}, \tag{2.17}$$

where

$$P(f)=e^{-\beta f}/(\sum_{f'u'}e^{-\beta f'}), \tag{2.18}$$

and β is given by Eq. (1.2). Equation (2.17) is consistent with the definition (2.14) of σ, and one further obtains with (2.13) and (2.16)

$$(fu|\rho^*(t)|f'u')=\sigma_S(t)P(f)\delta_{ff'}\delta_{u''}. \tag{2.19}$$

In order to carry out the integrations over τ' and τ'' in (2.9), it is necessary, through (2.7), to know the time-dependence of G_S. Although the operator G has no explicit dependence upon t, that of S provides, through the transformation (2.6), a corresponding dependence of G_S. It will be assumed that this transformation results in a series—or integral—of periodic terms of the form

$$G_S(t)=S(t)GS^{-1}(t)=\textstyle\sum_r G^r e^{i\omega_r t}, \tag{2.20}$$

where the operators G^r shall not explicitly depend upon t.[13] Since G must be Hermitian, then in view of the Hermitian conjugate character of S and S^{-1}, G_S must also be Hermitian. Defining

$$\omega_{-r}=-\omega_r, \tag{2.21}$$

one has to demand, therefore, that

$$(G^r)^\dagger=G^{-r}, \tag{2.22}$$

i.e., that G^r and G^{-r} are Hermitian conjugate. In analogy to (2.5) and (2.13), one obtains from (2.7) and (2.20)

$$(fu|G^*(t)|f'u')=\textstyle\sum_r e^{i(f-f'+\omega_r)t}(fu|G^r|f'u'). \tag{2.23}$$

The steps which lead, with the use of Eq. (2.15) and of the expressions (2.19) and (2.23), from the increment (2.9) of ρ^* to that of σ_S and, hence, to a differential equation for this quantity follow in close analogy the procedure, carried out in detail in I and also used in II, to arrive at the Boltzmann equation for the transformed distribution matrix, formerly denoted by σ^*. The frequencies ω_r play here the same role as did formerly the differences of the eigenvalues of E_0 and are, in fact, identical with these differences in the special case where E has the constant value E_0 so that, from (2.3) and (2.4),

$$S^{\pm1}=e^{\pm iE_0t}.$$

If one uses a representation in which E_0 is diagonal, Eq. (2.32) of I and Eq. (2.8) of II are in this case direct consequences of Eqs. (2.13) and (2.23) in this paper. Postponing the discussion of those points which differ from the treatments in I and II, the differential equation for σ_S can be written in the following form:

$$\begin{aligned}\frac{d\sigma_S}{dt}=-i[\Delta_S,\sigma_S]-i\sum_{rs}e^{i\omega_{rs}t}\Bigg(\int_{C_1}&(\sigma_S\{G^rG^s\}^{\omega_r+x}\\ &-e^{-\beta(\omega_r+x)}\{G^r\sigma_SG^s\}^{\omega_r+x})x^{-1}dx\\ -\int_{C_2}&(\{G^rG^s\}^{-\omega_s+x}\sigma_S-e^{-\beta(-\omega_s+x)}\\ &\times\{G^r\sigma_SG^s\}^{-\omega_s+x})x^{-1}dx\Bigg),\end{aligned} \tag{2.24}$$

where the paths of integration C_1 and C_2 follow the real axis from $-\infty$ to $+\infty$ with the exception of the immediate vicinity of the point $x=0$, to be bypassed on the positive imaginary side for C_1 and the negative imaginary side for C_2. The first term on the right side represents the result of the first-order approximation in G with

$$\Delta_S=S\Delta S^{-1}, \tag{2.25}$$

and

$$\Delta=\sum_u\int\eta_u(f)P(f)(fu|G|fu)df. \tag{2.26}$$

This term contributes similarly to E and hence to the unperturbed energy of the spin system as the corresponding term ΔE of Eq. (2.22) in II.

The sum over r and s on the right side of Eq. (2.24) contains the result of the second-order approximation with the following abbreviations:

$$\omega_{rs}=\omega_r+\omega_s, \tag{2.27}$$

$$\begin{aligned}\{G^rG^s\}^\alpha=\sum_{uu'}\int&\eta_u(f)\eta_{u'}(f+\alpha)P(f)\\ &\times(fu|G^r|f+\alpha,u')(f+\alpha,u'|G^s|fu)df,\end{aligned} \tag{2.28}$$

$$\begin{aligned}\{G^rQG^s\}^\alpha=\sum_{uu'}\int&\eta_u(f)\eta_{u'}(f+\alpha)P(f)\\ &\times(fu|G^r|f+\alpha,u')Q(f+\alpha,u'|G^s|fu)df.\end{aligned} \tag{2.29}$$

The last expression contains, for later purposes, an arbitrary spin function Q, but it is used in (2.24) for $Q=\sigma_S$. Equation (2.28) can be considered as a special case of (2.29) with Q chosen as the unit operator. In I

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[13] This assumption implies no more than that of the operator $E(t)$ being likewise expandable in its time dependence as a series or integral of periodic terms and does not, therefore, represent any physical restriction of generality. The case of particular importance for resonance experiments, where E consists of a constant and a periodic term, is particularly suitable for an expansion of the form (2.20) which, however, encompasses far more general situations.

and II, only the imaginary contribution to the integrals of Eq. (2.24) in the immediate vicinity of $x=0$ has been retained, since it is this contribution which has the nature of a damping term and leads thus to relaxation. Although the part corresponding to the integration along the real axis occurs actually also in the earlier treatments,[14] it was there neglected. As will be seen below, it leads, in addition to Δ, to a correction to E of the second order in G. In view of the fact that in I and II the principal part E_0 of E was assumed to be large compared to second-order corrections, this neglect was indeed justified. However, E is here assumed arbitrary and not subjected to such a restriction so that there is no *a priori* reason for neglecting this term, although it can have a noticeable effect only for sufficiently small values of E.

Another difference enters in the conditions of validity of the Boltzmann equation; in I and II they involved the magnitude of E_0,[15] while this quantity can evidently not enter into the more general treatment, presented here. Common to I and II there exist, however, conditions which arise from the required order of magnitude of the time interval τ of Eq. (2.9) and which have to be fulfilled for the validity of the Boltzmann equation (2.24).

Indeed, the direct evaluation of the first-order term, divided by τ, does not lead to the expression given by (2.25) and (2.26) but, instead, to

$$\Delta_S(\tau)=\sum_r e^{i\omega_r t}q_r(\tau)\sum_u \int \eta_u(f)P(f)(fu|G^r|fu)df, \tag{2.30}$$

with

$$q_r(\tau)=(e^{i\omega_r\tau}-1)/(i\omega_r\tau).$$

While it is true, in view of Eq. (2.20) that $\lim_{\tau\to0}\Delta_S(\tau)=\Delta_S$, there are lower limits to be imposed on τ to insure the validity of the second-order terms, so that a milder condition for the smallness of τ has to be established. In fact, denoting the order of magnitude of the first-order term by $|\Delta|$, it is sufficient, for the replacement of $\Delta_S(\tau)$ by Δ_S, to demand that

$$\tau\ll 1/|\Delta|, \tag{2.31}$$

so that for all terms in the summation over r of (2.30) for which

$$\omega_r \lessapprox |\Delta|, \tag{2.32}$$

it is

$$\omega_r\tau\ll 1, \tag{2.33}$$

and one may replace $q_r(\tau)$ by unity. Owing to the presence of the periodic factors $e^{i\omega_r t}$, only these terms cause in fact an appreciable change of σ_S, reached after lapse of a sufficiently long interval of t of order $1/|\Delta|$. On the other hand, terms for which

$$\omega_r\gg|\Delta| \tag{2.34}$$

contribute only changes of σ_S of relative order of magnitude $|\Delta|/\omega_r$ or $|\Delta|/\omega_r^2\tau$ for $\omega_r\tau\approx 1$ or $\omega_r\tau\gg 1$, respectively, so that they are in either case negligible compared to the terms satisfying (2.32). Hence, there occurs, effectively, an automatic suppression of those terms which do not warrant the replacement of $q_r(\tau)$ by unity, and it is permissible to make this replacement throughout in Eq. (2.30), so that $\Delta_S(\tau)=\Delta_S$ under the sole condition (2.31).

Although somewhat more involved, there appear similar conditions for the validity of the second-order terms. If their order of magnitude is denoted by the symbol $|\Gamma|$, one must here demand that

$$\tau\ll 1/|\Gamma| \tag{2.35}$$

in order that all those terms in the summation over r and s of (2.24) are correctly represented for which

$$\omega_{rs}\tau\ll 1. \tag{2.36}$$

Again, the periodic factors $e^{i\omega_{rs}t}$ lead, effectively, to an automatic suppression of all other terms for which the condition (2.36) is not satisfied.

In analogy to I and II, there are further limits to be imposed on τ to justify the form of the second-order terms given in Eq. (2.24) and, in particular, the fact that τ does not appear in these terms. The first condition of this type demands that the limits of integration over x along the real axis are sufficiently extended so that

$$|x|\tau\ll 1, \tag{2.37}$$

where $|x|$ indicates the order of magnitude of either the negative lower limit or of the upper limit of integration. Secondly, if one defines a characteristic frequency ω^* of the molecular surroundings such that, for all values of f which give an appreciable contribution to the integrands in Eqs. (2.28) and (2.29), the functions

$$\eta_{u'}(f+\alpha),\quad (fu|G^r|f+\alpha,u'),\quad (f+\alpha,u'|G^s|fu)$$

do not vary appreciably upon an increment of α, small compared to

$$\omega^*=1/\tau_c, \tag{2.38}$$

then it has to be demanded that

$$\omega^*\tau\gg 1. \tag{2.39}$$

The time τ_c of Eq. (2.38) has the significance of a characteristic correlation time of the molecular system. With $|x|$ to be chosen comparable or even large compared to ω^*, the condition (2.39) includes that expressed by Eq. (2.37). Since $e^{-\beta x}$ varies appreciably only upon an increment of x of order $1/\beta$, the occurrence of the Boltzmann factor $P(f)$ of Eq. (2.18) in the Eqs. (2.28) and (2.29) demands similarly that

$$\tau/\beta\gg 1. \tag{2.40}$$

Summarizing the independent conditions Eqs. (2.31), (2.35), (2.39), and (2.40), one has to demand, therefore,

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[14] It appears, e.g., in Eq. (3.11) of I with $\xi=xt$.

[15] Equation (3.21) in I and (2.33) in II.

that τ must be chosen so as to fulfill the relations

$$(|\Delta|,|\Gamma|)\ll 1/\tau\ll(\omega^*,1/\beta), \qquad (2.41)$$

which is possible, provided that the condition

$$(|\Delta|,|\Gamma|)\ll(\omega^*,1/\beta) \qquad (2.42)$$

is satisfied. It indicates that both of the quantities on the left side be small compared to both of the quantities on the right side without, however, implying a relation of order of magnitude between the members of either pair.[16]

At the same time it should be noted, in view of Eqs. (2.36) and (2.41), that it is permissible to use in Eq. (2.24) the relation

$$\omega_{rs}\ll(\omega^*,1/\beta), \qquad (2.43)$$

since the terms in the summation over r and s for which this relation does not hold are in effect automatically suppressed. The right side of Eq. (2.24) can be greatly simplified by the use of this relation. For this purpose, we write temporarily

$$\begin{aligned}\eta_u(f)\eta_{u'}(f+\alpha)(fu|G^r|f+\alpha,\, u')\\ \times(f+\alpha,\, u'|G^s|fu)=A^\alpha(f+\tfrac{1}{2}\alpha), \qquad (2.44)\end{aligned}$$

where the difference and the average of $f+\alpha$ and f have been introduced as upper index and argument of A, respectively. In the evaluation of the expressions (2.28) and (2.29), there appears thus an integral of the form

$$B^\alpha=\int P(f)A^\alpha(f+\tfrac{1}{2}\alpha)df.$$

If one adds an increment ϵ to α and introduces $f+\frac{1}{2}\epsilon$ as a new variable of integration, noting that from Eq. (2.18)

$$P(f-\tfrac{1}{2}\epsilon)=e^{\frac{1}{2}\beta\epsilon}P(f), \qquad (2.45)$$

one obtains

$$B^{\alpha+\epsilon}=e^{\frac{1}{2}\beta\epsilon}\int P(f)A^{\alpha+\epsilon}(f+\tfrac{1}{2}\alpha)df.$$

In view of the previous assumption concerning the dependence on α of the left side of (2.44), $A^{\alpha+\epsilon}$ differs appreciably from A^α only if ϵ is of the order of the frequency ω^*, introduced in (2.38). If ϵ is small compared to ω^*, it is therefore permissible to write

$$B^{\alpha+\epsilon}=e^{\frac{1}{2}\beta\epsilon}B^\alpha,$$

or, going back to (2.28) and (2.29),

$$\{G^rG^s\}^{\alpha+\epsilon}=e^{\frac{1}{2}\beta\epsilon}\{G^rG^s\}^\alpha$$

and

$$\{G^rQG^s\}^{\alpha+\epsilon}=e^{\frac{1}{2}\beta\epsilon}\{G^rQG^s\}^\alpha \qquad (2.46)$$
$$\text{for } \epsilon\ll\omega^*.$$

Introducing, besides (2.27), the abbreviation

$$\nu_{rs}=\tfrac{1}{2}(\omega_r-\omega_s), \qquad (2.47)$$

it is

$$\omega_r=\nu_{rs}+\tfrac{1}{2}\omega_{rs}, \quad -\omega_s=\nu_{rs}-\tfrac{1}{2}\omega_{rs}.$$

In view of the permissible use of the relation (2.43) and applying (2.46) for $\epsilon=\frac{1}{2}\omega_{rs}$, one may write $\omega_r=-\omega_s=\nu_{rs}$ in the double sum over r and s of Eq. (2.24). Applying this procedure in particular to the contributions arising from the integration along the real axis of x, it is seen that the parts containing $\{G^r\sigma_SG^s\}$ cancel and that in the remaining parts the relation

$$\{G^rG^s\}^{\omega_r+x}=\{G^rG^s\}^{-\omega_s+x}=\{G^rG^s\}^{\nu_{rs}+x}$$

can be used.

The contributions arising from the integration over x in the immediate vicinity of zero, yield the integrand, taken for $x=0$, multiplied with $-i\pi$ and $+i\pi$ for the first and second integral, respectively. The Boltzmann Eq. (2.24) can thus be rewritten in the form

$$\begin{aligned}d\sigma_S/dt+i[\Delta_S+\Gamma_S,\sigma_S]\\ =\pi\sum_{rs}e^{i\omega_{rs}t}(e^{-\beta\omega_r}\{G^r\sigma_SG^s\}^{\omega_r}-\sigma_S\{G^rG^s\}^{\omega_r}\\ +e^{\beta\omega_s}\{G^r\sigma_SG^s\}^{-\omega_s}-\{G^rG^s\}^{-\omega_s}\sigma_S), \qquad (2.48)\end{aligned}$$

with the abbreviation[17]

$$\Gamma_S=\sum_{rs}e^{i\omega_{rs}t}\int_0^\infty(\{G^rG^s\}^{\nu_{rs}+x}-\{G^rG^s\}^{\nu_{rs}-x})x^{-1}dx. \qquad (2.49)$$

The well-defined integral over x in Eq. (2.49) has been obtained by dividing the integration along the real axis into a part from $-\infty$ to 0 and one from 0 to $+\infty$ and

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[16] The conditions (2.23) and (2.25) in II are equivalent to Eqs. (2.33) and (2.36), respectively, of this paper, if one replaces ω_r by $g-g'$, ω_s by $g'''-g''$, and t by τ. In the corresponding notation, it would lead to the suppression of those terms for which, according to Eq. (2.24) and Eq. (2.26) of II, $\omega_r\neq0$ and $\omega_{rs}\neq0$, respectively, assuming that here these terms are of order of magnitude $|E_0|$. This implies, therefore, through Eq. (2.27) of II, that $\tau\gg1/|E_0|$, thus causing the appearance of $|E_0|$ on the right side of the condition (2.33) of II. One obtains from this condition the far less stringent condition of validity of the Boltzmann equation, formulated in the relations (2.42) of this paper, by adding for completeness the quantity $|\Delta|$ on the left side, using the abbreviation (1.2), and, in the absence of any restriction on E, omitting the quantities $|E_1|$ on the left and $|E_0|$ on the right side. While the semiclassical treatment of Garstens and Wangsness demands only the sufficient shortness of the correlation time $\tau_c=1/\omega^*$ (see reference 11), it can be readily seen by a qualitative argument that the shortness of the time β is likewise relevant if quantum features are to be consistently observed. Indeed, the treatment of relaxation processes demands that they can be meaningfully pursued during a time Δt short compared to the relaxation time. The latter being of order of magnitude $1/|\Gamma|$, one therefore has to demand that $\Delta t\ll1/|\Gamma|$. On the other hand, it is necessary for a meaningful definition of the temperature T of the molecular surroundings, that the corresponding indeterminacy ΔE of the energy be small compared to kT. From $\Delta E\ll kT$ and the relation indeterminacy $\Delta E\Delta t\approx\hbar$, one has $kT/|\Gamma|\gg\hbar$ and hence $1/\beta\gg|\Gamma|$ as postulated in Eq. (2.42).

[17] The symbol Γ is here chosen to indicate that the expression (2.49), although neglected in the earlier treatments, is of second order in G, i.e., that it shares this feature with the relaxation coefficients which were introduced in Eqs. (3.16) and (2.17) of I and II, respectively. Under the corresponding particular assumptions, the latter appear actually on the right side of Eq. (2.48). (See reference 18.)

by changing in the former the variable of integration x into $-x$.

In order to show that with σ_S Hermitian the right side of (2.48) is likewise Hermitian, it is to be noted, with the help of Eqs. (2.12) and (2.22), that the Hermitian conjugate of the expressions (2.28) and (2.29) with $Q=\sigma_S$ is given by $\{G^{-s}G^{-r}\}^{\alpha}$ and $\{G^{-s}\sigma_S G^{-r}\}^{\alpha}$, respectively. Noting further with (2.21), (2.27), and (2.47) that

$$\omega_{-s,-r}=-\omega_{rs},\quad \nu_{-s,-r}=\nu_{rs},$$

replacing i by $-i$, r by $-s$, and s by $-r$, it is seen that the operator Γ_S, defined in Eq. (2.49), as well as the sum over r and s in (2.48) are indeed Hermitian. It is also readily shown that the diagonal sum or "trace" of this sum vanishes. For this purpose one needs the relations

$$\begin{aligned}\mathrm{Tr}(\sigma_S\{G^rG^s\}^{\omega_r})&=e^{\beta\omega_r}\,\mathrm{Tr}(\{G^s\sigma_S G^r\}^{-\omega_r})\\ \mathrm{Tr}(\{G^rG^s\}^{-\omega_s}\sigma_S)&=e^{-\beta\omega_s}\,\mathrm{Tr}(\{G^s\sigma_S G^r\}^{\omega_s}),\end{aligned}\tag{2.50}$$

obtained from the fact that the first factor of an operator product in the trace can equally well be written at the end of the product and by replacing in the definition (2.29) the variable of integration f by $f+\alpha$ as well as u by u'. Interchanging in the summation r and s with $\omega_{rs}=\omega_{sr}$ from (2.27), it is then seen that the trace of the right side in Eq. (2.48) vanishes through cancelation of the first term by the fourth and of the third term by the second. Since the trace of the commutator on the left side vanishes identically, one sees therefore that

$$(d/dt)\,\mathrm{Tr}(\sigma_S)=0,$$

thus permitting the normalization

$$\mathrm{Tr}(\sigma_S)=\mathrm{Tr}(\sigma)=1.\tag{2.51}$$

The Eq. (2.48) for σ_S can be used to obtain the Boltzmann equation for the distribution matrix σ. Applying

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

as a consequence of (2.3), (2.4), and (2.16) and multiplying from the left with S^{-1}, from the right side with S, one obtains

$$\begin{aligned}d\sigma/dt+i[E+\Delta+\Gamma,\sigma]&\\ =\pi\sum_{rs}e^{i\omega_{rs}t}(e^{-\beta\omega_r}&\{G_-{}^r\sigma G_-{}^s\}^{\omega_r}-\sigma\{G_-{}^rG_-{}^s\}^{\omega_r}\\ &+e^{\beta\omega_s}\{G_-{}^r\sigma G_-{}^s\}^{-\omega_s}-\{G_-{}^rG_-{}^s\}^{-\omega_s}\sigma),\end{aligned}\tag{2.52}$$

with

$$G_-{}^{r,s}=S^{-1}G^{r,s}S,\tag{2.53}$$

and

$$\begin{aligned}\Gamma=S^{-1}\Gamma_SS=\sum_{rs}e^{i\omega_{rs}t}\int_0^\infty(&\{G_-{}^rG_-{}^s\}^{\nu_{rs}+x}\\ &-\{G_-{}^rG_-{}^s\}^{\nu_{rs}-x})x^{-1}dx.\end{aligned}\tag{2.54}$$

A more convenient form of Eq. (2.52) is obtained by using for the right side the abbreviation $\Gamma(\sigma)$ and by simplifying this expression through the summation over s and r in the first two and the last two terms in the parentheses, respectively. Using Eq. (2.27) and observing that

$$\textstyle\sum_r e^{i\omega_rt}G_-{}^r=S^{-1}(\sum_r e^{i\omega_rt}G^r)S=S^{-1}G_sS=G,\tag{2.55}$$

as a consequence of Eq. (2.20), one obtains thus

$$d\sigma/dt+i[E+\Delta+\Gamma,\sigma]=\Gamma(\sigma),\tag{2.56}$$

with

$$\begin{aligned}\Gamma(\sigma)=\pi\textstyle\sum_r e^{i\omega_rt}(e^{-\beta\omega_r}&\{G_-{}^r\sigma G\}^{\omega_r}-\sigma\{G_-{}^rG\}^{\omega_r}\\ &+e^{\beta\omega_r}\{G\sigma G_-{}^r\}^{-\omega_r}-\{GG_-{}^r\}^{-\omega_r}\sigma),\end{aligned}\tag{2.57}$$

and

$$G_-{}^r=S^{-1}G^rS.\tag{2.58}$$

The principal problem in applying the Boltzmann equation to a particular case, either in the form (2.48) for σ_S or (2.56) for σ, is to find the transformation operator S and its inverse S^{-1}. For given internal energy of the spin system and external actions upon it, i.e., for a given operator $E(t)$, it requires the solution $S(t)$ of Eq. (2.3). Given further the coupling between the spin and molecular system, expressed by the operator G, one obtains then from Eqs. (2.6) and (2.20) the frequencies $\omega_{r,s}$ and the operators $G^{r,s}$ which enter in Eq. (2.48) and from Eq. (2.58) the operators $G_-{}^r$ which enter in Eq. (2.57). The degree of complication in following this procedure as well as in solving thereupon Eq. (2.48) or Eq. (2.56) to obtain $\sigma_S(t)$ or $\sigma(t)$, respectively, will evidently depend upon that of the situation considered. As a relatively simple special case, that of a rotating magnetic field will be treated in Sec. IV.

Once obtained, the knowledge of $\sigma_S(t)$ or $\sigma(t)$ is sufficient to find the expectation value of any spin function Q in its dependence upon time. It is given by

$$\langle Q\rangle(t)=\mathrm{Tr}[Q_S\sigma_S(t)]=\mathrm{Tr}[Q\sigma(t)],\tag{2.59}$$

with

$$Q_S=SQS^{-1}.\tag{2.60}$$

Because of the invariance of the trace, the numerical value of Eq. (2.59) is independent of any particular n representation of the spin system which may be chosen for reasons of convenience.

Similar to Eq. (4.10) of I, it is possible, from the far more general Eq. (2.56), to derive differential equations for expectation values without an explicit knowledge of the distribution matrix σ. Indeed, multiplying Eq. (2.56) by Q and forming the trace, one obtains

$$d\langle Q\rangle/dt+i\langle[Q,E+\Delta+\Gamma]\rangle=\langle\Gamma(Q)\rangle,\tag{2.61}$$

with

$$\begin{aligned}\langle\Gamma(Q)\rangle=\pi\textstyle\sum_r e^{i\omega_rt}(e^{-\beta\omega_r}&\langle\{GQG_-{}^r\}^{\omega_r}\rangle\\ -\langle\{G_-{}^rG\}^{\omega_r}Q\rangle&+e^{\beta\omega_r}\langle\{G_-{}^rQG\}^{-\omega_r}\rangle\\ &-\langle Q\{GG_-{}^r\}^{-\omega_r}\rangle).\end{aligned}\tag{2.62}$$

While it is no simpler, in general, to use this result rather than to solve Eq. (2.56) and then to obtain

$\langle Q\rangle(t)$ from Eq. (2.59), there are special cases, like the one treated in Sec. IV and those discussed in I, where Eqs. (2.61) and (2.62) yield a system of simultaneous differential equations between the expectation values of certain spin functions of particular experimental interest.

3. SLOWLY VARYING EXTERNAL FIELDS

The condition (2.42) for the validity of the Boltzmann equation (2.52) permits its application to the special case $E\approx E_0$ considered in I and II, where E_0, the principal part of E, is independent of the time and satisfies the condition $|E_0|\gg|\Delta|$, $|\Gamma|$. According to Eq. (2.3), the transformation operator S assumes in this case the approximate form

$$S\approx e^{iE_0t}. \tag{3.1}$$

The expansion (2.20) of G_S is obtained by using a representation in which E_0 is diagonal with eigenvalues g. If one writes

$$G=\sum\nolimits_r G^r, \tag{3.2}$$

the operators G^r are then defined by having in this representation nonvanishing matrix elements only between those pairs of eigenvalues (g,g') where the difference

$$g'-g=p \tag{3.3}$$

has a given value p.

It follows, therefore, with

$$\omega_r=-p, \tag{3.4}$$

that

$$[E_0,G^r]=\omega_r G^r, \tag{3.5}$$

and from (3.1), that

$$SG^rS^{-1}=e^{i\omega_rt}G^r. \tag{3.6}$$

This signifies that the frequencies ω_r, appearing in (2.20), have here the significance of differences between the eigenvalues of E_0. It is further to be observed, in view of the condition $|E_0|\gg|\Gamma|$, that only the terms with $\omega_{rs}=0$ will give an appreciable contribution to the right side of Eq. (2.48) and, hence, to that of Eq. (2.52). According to (2.27), the double sum over r and s can thus be replaced by a single sum over the different values of $p=-\omega_r=\omega_s$. Denoting the corresponding operators G^r and G^s by G^p and G^{-p}, respectively, with

$$G_-{}^p=S^{-1}G^pS=e^{ipt}G^p,$$

and

$$G_-{}^{-p}=S^{-1}G^{-p}S=e^{-ipt}G^{-p},$$

as a consequence of Eqs. (2.53) and (3.6), the right side of (2.52) can therefore be written in the form

$$\Gamma(\sigma)=\pi\sum\nolimits_p(2e^{\beta p}\{G^p\sigma G^{-p}\}^{-p} \\ -\sigma\{G^pG^{-p}\}^{-p}-\{G^pG^{-p}\}^{-p}\sigma). \tag{3.7}$$

This notation agrees with that used in Eq. (2.34) of II; except for the neglect of the corrections Δ and Γ, justified in view of their smallness in comparison to E_0, Eq. (2.34) of II is in fact seen, with (3.7), to become identical with Eq. (2.52) of this paper, written out in the representation in which E_0 is diagonal with eigenvalues g.[18]

While the preceding treatment leads to the special cases of I and II and is applicable only if the principal part of E is independent of the time, there exists a similar simplification under the condition that it is sufficiently slowly varying. This condition can be formulated through

$$|dE/dt|/|E|\ll\omega^*,\quad 1/\beta, \tag{3.8}$$

and is evidently always satisfied for sufficiently short values of the correlation time $\tau_c=1/\omega^*$, as well as of the time β, i.e., according to Eq. (1.2) for sufficiently high temperatures. For given values of τ_c and β, the relation (3.8) demands that E consist predominantly of a part $E_0(t)$ which varies relatively little during time intervals of the order of either τ_c or β, but it permits also the existence of an additional small term $E_1(t)$ with a relative rate of change ω, comparable to $|E_0|\approx|E|$, so that $\omega/|E|\approx 1$. With $|dE_1/dt|\approx\omega|E_1|$, the condition (3.8) requires thus

$$|E_1|\ll(\omega^*,1/\beta). \tag{3.9}$$

This situation is of particular interest for resonance experiments, where the resonance condition demands indeed a magnitude of ω comparable to $|E|$. This latter quantity, i.e., the magnitude of the resonance frequencies, is not excluded to be comparable or even large compared to ω^* and $1/\beta$. The same holds thus for the relative rate of change ω of E_1, provided that the magnitude of this rapidly varying term satisfies the condition (3.9) which is also contained in Eq. (2.33) of II.

By virtue of (3.8), the instantaneous eigenvalues of $E(t)$, as well as their differences, to be denoted by $\omega_r(t)$, are slowly varying functions of the time in the sense that they vary appreciably, neither during a time interval of order τ_c nor during one of order β. In analogy to (3.2) and (3.5), one can define a series of operators P^r such that

$$G=\sum\nolimits_r P^r, \tag{3.10}$$

and

$$[E,P^r]=\omega_r P^r. \tag{3.11}$$

These operators are likewise slowly varying and it can

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[18] The symbols defined in Eqs. (2.28) and (2.29) of this paper are in the case $E\approx E_0$ simply related to the relaxation coefficients, defined in II, Eqs. (2.16), (2.17), and (2.45). Referring, for example, to the case where the eigenstates of E_0 are not degenerate, one has, by comparison of this last equation with Eq. (2.29) of this paper, $\pi(g|\{G^pQG^{-p}\}^{-p}|g')=\Gamma_{gg'}{}^p(g+p|Q|g'+p)$ for an arbitrary spin-function Q such as, for example, σ_S and σ; and the matrix element $(g|\Gamma(\sigma)|g')$ of the expression (3.7) in the representation where E_0 is diagonal is seen to be identical with the corresponding symbol on the right side of Eq. (2.34) of II, omitting the quantum numbers v and v'.

be seen that, in analogy to (3.6),

$$SP^rS^{-1}=e^{i\varphi_r}G^r, \tag{3.12}$$

with

$$\varphi_r(t)=\int_0^t \omega_r(t')dt', \tag{3.13}$$

where G^r is another slowly varying operator. While for $t=0$, i.e., $S=1$, one has $G^r=P^r$, it is possible, after a sufficient lapse of time, that G^r differs appreciably from P^r.

Except for the replacement of $\omega_{rs}t$ by $\varphi_r+\varphi_s$, the form of the Boltzmann equation (2.52) can be seen to remain unaltered. Indeed, the procedure of forward integration over the time interval τ, which led to Eq. (2.52) and, hence, to Eq. (2.56) is equally applicable here since the condition $\tau\gg(\tau_c,\beta)$, implied by Eq. (2.41), is compatible with a choice of τ such that all slowly varying functions can, during this interval, be replaced by their instantaneous value at the time t. The expression (2.57) is thus to be replaced by

$$\Gamma(\sigma)=\pi\sum\nolimits_r e^{i\varphi_r}(e^{-\beta\omega_r}\{G_-{}^r\sigma G\}^{\omega_r}-\sigma\{G_-{}^rG\}^{\omega_r} +e^{\beta\omega_r}\{G\sigma G_-{}^r\}^{-\omega_r}-\{GG_-{}^r\}^{-\omega_r}\sigma), \tag{3.14}$$

where the definition of $G_-{}^r$ is still given by Eq. (2.58) and where G^r and ω_r, instead of being independent, are slowly varying functions of the time t.

The expression (3.14) can be considerably simplified. In the first place, it follows from (3.12) that

$$e^{i\varphi_r}G_-{}^r=e^{i\varphi_r}S^{-1}G^rS=P^r,$$

so that

$$\Gamma(\sigma)=\pi\sum\nolimits_r(e^{-\beta\omega_r}\{P^r\sigma G\}^{\omega_r}-\sigma\{P^rG\}^{\omega_r} +e^{\beta\omega_r}\{G\sigma P^r\}^{-\omega_r}-\{GP^r\}^{-\omega_r}\sigma). \tag{3.15}$$

It follows further, from (3.11), that

$$\partial/\partial\beta(e^{-\beta E}P^re^{\beta E})=-e^{-\beta E}[E,P^r]e^{\beta E}=-\omega_re^{-\beta E}P^re^{\beta E},$$

and since

$$(e^{-\beta E}P^re^{\beta E})_{\beta=0}=P^r,$$

one has, through integration from 0 to β,

$$e^{-\beta E}P^re^{\beta E}=e^{-\beta\omega_r}P^r \tag{3.16}$$

and, analogously,

$$e^{\beta E}P^re^{-\beta E}=e^{\beta\omega_r}P^r. \tag{3.17}$$

Inserting these expressions in Eq. (3.15), and including σ in the curly brackets of the second and fourth terms, one obtains

$$\Gamma(\sigma)=\pi\sum\nolimits_r(e^{-\beta E}\{[P^r,e^{\beta E}\sigma]G\}^{\omega_r} +\{G[\sigma e^{\beta E},P^r]\}^{-\omega_r}e^{-\beta E}). \tag{3.18}$$

This form is not only more concise than that given by Eq. (3.14) but it also has the advantage of showing directly the fact, mentioned in Sec. I, that relaxation will establish a tendency of the distribution matrix towards the value σ_0, given by Eq. (1.4), provided that the condition (3.8) is satisfied. Indeed, one has

$$e^{\beta E}\sigma_0=\sigma_0e^{\beta E}=\zeta. \tag{3.19}$$

Being a mere number, i.e., proportional to the unit operator, ζ evidently commutes with P^r so that one has $\Gamma(\sigma_0)=0$, and hence

$$\Gamma(\sigma)=\Gamma(\sigma-\sigma_0). \tag{3.20}$$

The corrections Δ and Γ on the left side of Eq. (2.52) can be incorporated in the total energy of the spin system by substituting E for $E+\Delta+\Gamma$, and it is permissible, in view of the condition (2.42) and of Eq. (2.46), to make the same substitution in (3.18). With E and ω_r referring to this newly defined total energy of the spin system, Eq. (2.56) can thus be written in the form

$$d\sigma/dt+i[E,\sigma]=\Gamma(\sigma), \tag{3.21}$$

or with Eq. (3.20)

$$d\sigma/dt+i[E,\sigma]=\Gamma(\sigma-\sigma_0), \tag{3.22}$$

with $\Gamma(\sigma)$, and hence $\Gamma(\sigma-\sigma_0)$, given by Eq. (3.18). Introducing further the deviation,

$$\chi=\sigma-\sigma_0, \tag{3.23}$$

of the distribution matrix σ from the value σ_0, corresponding to the instantaneous equilibrium, and noting that E commutes with σ_0, one has for χ the inhomogeneous equation,

$$d\chi/dt+i[E,\chi]-\Gamma(\chi)=-d\sigma_0/dt, \tag{3.24}$$

with the condition of normalization

$$\mathrm{Tr}(\chi)=0$$

as a consequence of Eq. (2.51) and the fact that one has, from Eqs. (1.4) and (1.5), $\mathrm{Tr}(\sigma_0)=1$. Equation (3.24) shows that the deviation from the instantaneous equilibrium distribution is proportional to the rate of variation σ_0 and, hence, to that of $E(t)$.

It is to be noted that the condition (3.8) for the validity of Eq. (3.18) permits E and, hence, some of the frequencies ω_r to have magnitudes comparable or even large compared to the inverse correlation time ω^*. Consequently, $\Gamma(\sigma)$ may contain features arising from an appreciable dependence of the curly brackets in Eq. (3.18) upon ω_r.[19] A further simplification is obtained, however, if not only the condition (3.8) but also the condition

$$|E|\ll\omega^*, \tag{3.25}$$

equivalent to $\omega_r\ll\omega^*$, is satisfied. It is then possible to

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[19] In the simplest case, treated in I, this feature underlies the distinction between the longitudinal and the transverse relaxation times T_1 and T_2, respectively. The former arises from the terms in (3.18) where the magnitude of the frequency ω_r is equal to that of the Larmor frequency of precession in the strong field, while the latter corresponds to those where $\omega_r=0$.

apply Eqs. (2.46) for $\alpha=0$, $\epsilon=\pm\omega_r$ and to write

$$\{[P^r,e^{\beta E}\sigma]G\}^{\omega_r}=e^{\beta\omega_r/2}\{[P^r,e^{\beta E}\sigma]G\}^0,$$

and

$$\{G[\sigma e^{\beta E},P^r]\}^{-\omega_r}=e^{-\beta\omega_r/2}\{G[\sigma e^{\beta E},P^r]\}^0,$$

respectively. Using further, in analogy to Eqs. (3.16) and (3.17),

$$e^{-\beta\omega_r/2}P^r=e^{-\beta E/2}P^r e^{\beta E/2},$$

and

$$e^{\beta\omega_r/2}P^r=e^{\beta E/2}P^r e^{-\beta E/2},$$

it is then possible, through Eq. (3.10), to carry out the summations over r in Eq. (3.18), with the result

$$\Gamma(\sigma)=\pi(\{[e^{-\beta E/2}Ge^{\beta E/2}\sigma,G]\}^0 +\{[G,\sigma e^{\beta E/2}Ge^{-\beta E/2}]\}^0). \quad (3.26)$$

It is seen, as in the more general expression (3.18), that $\Gamma(\sigma_0)=0$, so that the Eqs. (3.21), (3.22), and (3.24) retain their validity but permit, in this case, the use of the simpler form Eq. (3.26) for $\Gamma(\sigma)$ and, hence $\Gamma(\sigma-\sigma_0)$, $\Gamma(\chi)$. It is this fact which, in essence, represents the justification of the treatment presented by Wangsness.[20]

In addition to the expression $\Gamma(\sigma)$ for the right side of Eqs. (2.52) and (2.56), given by Eq. (3.18) under the condition (3.8) and by Eq. (3.26) under the additional condition (3.25), there exists a third simple form of $\Gamma(\sigma)$ which may be useful. It is obtained if the condition (3.8) is replaced by the less stringent one

$$|dE/dt|/|E|\ll\omega^*, \quad (3.27)$$

maintaining at the same time the condition (3.25). In contrast to the two previous cases of this section, no condition for the shortness of the time β of Eq. (1.2) has to be satisfied beyond that implied by (2.42). Provided that the condition (3.27) is not violated,[21] this case allows thus the application towards lower temperatures than the case which resulted in Eq. (3.26). With the notations of Sec. II, the conditions (3.27) and (3.25) can be combined into the condition

$$\omega_r\ll\omega^*, \quad (3.28)$$

valid for all frequencies ω_r which enter in their defining equation (2.20). They permit therefore in (2.57) the application of the formulas (2.46) for $\alpha=0$, inserting $\pm\omega_r$ for ϵ, $G_-{}^r$ for G^r, and G for G^s with the result

$$\Gamma(\sigma)=\pi\sum_r e^{i\omega_r t}\{e^{-\beta\omega_r/2}[G_-{}^r\sigma,G] +e^{\beta\omega_r/2}[G,\sigma G_-{}^r]\}^0. \quad (3.29)$$

The summation over r in this expression can be formally carried out by noting from (2.20) that

$$\sum_r e^{i\omega_r t\mp\frac{1}{2}\beta\omega_r}G^r=S(t\pm\tfrac{1}{2}i\beta)GS^{-1}(t\pm\tfrac{1}{2}i\beta),$$

i.e., by replacing in this formula t by $t\pm\frac{1}{2}i\beta$. Therefore, by applying $S^{-1}(t)$ from the left and $S(t)$ from the right on both sides of this equation, one has with (2.58)

$$\sum_r e^{i\omega_r t\mp\frac{1}{2}\beta\omega_r}G_-{}^r=U(\pm\beta,t)GU^{-1}(\pm\beta,t), \quad (3.30)$$

where

$$U(\pm\beta,t)=S^{-1}(t)S(t\pm\tfrac{1}{2}i\beta), \quad (3.31)$$

and

$$U^{-1}(\pm\beta,t)=S^{-1}(t\pm\tfrac{1}{2}i\beta)S(t). \quad (3.32)$$

The operators $U^{\pm1}$ are thus known if the transformation function S and its inverse are known; they can also be determined as solutions of a differential equation, obtained by taking the partial derivative with respect to β on both sides of Eqs. (3.31) and (3.32) and observing Eqs. (2.3) and (2.4). Indeed, omitting the argument t in $U^{\pm1}$, one has thus

$$\partial U(\pm\beta)/\partial\beta=\mp\tfrac{1}{2}U(\pm\beta)E(t\pm\tfrac{1}{2}i\beta), \quad (3.33)$$

and

$$\partial U^{-1}(\pm\beta)/\partial\beta=\pm\tfrac{1}{2}E(t\pm\tfrac{1}{2}i\beta)U^{-1}(\pm\beta), \quad (3.34)$$

respectively, with the "initial" condition for $\beta=0$, obtained from (3.31) and (3.32), that

$$U(0)=U^{-1}(0)=1. \quad (3.35)$$

If one applies Eq. (3.30) to (3.29), the latter then becomes

$$\Gamma(\sigma)=\pi\{[U(\beta)GU^{-1}(\beta)\sigma,G] +[G,\sigma U(-\beta)GU^{-1}(-\beta)]\}^0 \quad (3.36)$$

as a generalization of Eq. (3.26). This latter equation is directly obtained if, in addition to (3.27), one postulates also $|dE/dt|/|E|\ll1/\beta$, thus demanding the fulfillment of the complete condition (3.8) as well as that of Eq. (3.25). Indeed, this additional condition implies that the variation of $E(t)$, treated as an analytical function of t, upon an increase of its argument of order of magnitude $|\beta|$ is negligible, thus allowing the replacement in (3.33) and (3.34) of $E(t\pm\frac{1}{2}i\beta)$ by $E(t)$. The solution, satisfying (3.35), of these differential

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[20] Wangsness'[10] procedure is indeed based upon the validity of the condition (3.25). Contrary to the more general case of Eq. (3.18) (see reference 19), it does not permit the distinction between T_1 and T_2. A further simplification, implied in his treatment, consists in the assumption of a sufficiently high temperature, i.e., of a sufficiently small value of β. Since $\chi=\sigma-\sigma_0$ will, in first approximation, be proportional to β, it is permissible in $\Gamma(\chi)$ on the left side of Eq. (3.24), obtained by replacing σ by χ, to let $\beta=0$. The error thus committed will be only of order β^2. The (single) relaxation time is then independent of E and, hence, of the time. This feature is indeed implied by using the phenomenological equations with constant values of T_1 and T_2 and with $\mathbf{M}_0$ introduced as the instantaneous equilibrium polarization.

[21] It should be noted that the definition of the correlation time τ_c in Eq. (2.38) or of the characteristic frequency ω^* of the molecular surroundings refers to the dependence upon α of the integrands in (2.28) and (2.29). Through their additional dependence upon f, the integrands are weighted with the Boltzmann factor $P(f)$ which favors the lower values of f, the lower the temperature of the molecular surroundings. Owing to the fact that the dependence upon α is related to that upon f, the effective order of magnitude of ω^* will thus depend upon the temperature. With the motion of the molecular surroundings slowed down for lower temperatures, one may in general expect ω^* to decrease with decreasing temperature. This decrease being of entirely different origin from the linear decrease of $1/\beta$ with decreasing temperature, which has nothing to do with the specific nature of the molecular surroundings, the clear distinction between the orders of magnitude of the two frequencies ω^* and $1/\beta$ remains nevertheless in force.

equations has then the simple form

$$U(\pm\beta)=e^{\mp\beta E/2},\quad U^{-1}(\pm\beta)=e^{\pm\beta E/2}, \tag{3.37}$$

with E to be taken at its instantaneous value $E(t)$. The substitution of the operators U and U^{-1}, given by (3.37), into (3.36), yields indeed Eq. (3.26) and thus represents an independent check upon this expression for $\Gamma(\sigma)$ and its conditions of validity.

4. ROTATING MAGNETIC FIELD

To illustrate the very general results obtained in the previous section, Eqs. (2.56) and (2.61) will here be applied to a special case which is not only of experimental interest but lends itself also to a relatively simple explicit treatment. The representative spin system is in this case that of a single spin $I=\frac{1}{2}$, with magnetic moment μ', and, hence, with a gyromagnetic ratio $\gamma=2\mu'/\hbar$, exposed to an external magnetic field with components

$$H_x=(\omega_1/\gamma)\cos\omega t,\quad H_y=-(\omega_1/\gamma)\sin\omega t,\quad H_z=\omega_0/\gamma. \tag{4.1}$$

The quantities ω_0 and ω_1, with the dimensions of a frequency, are constant and represent a measure of the fixed component in the z-direction and of the transverse component, rotating with the circular frequency ω, respectively.

The energy of the spin system, divided by $\hbar$, has here the form

$$E=-\omega_0 I_z-\omega_1(I_x\cos\omega t-I_y\sin\omega t), \tag{4.2}$$

where I_x, I_y, I_z are the components of the spin operator $\mathbf{I}$. By direct substitution, one verifies that the solutions of Eqs. (2.3) and (2.4) for the transformation operator S and its inverse can be written in the form

$$S=e^{-i(\Delta_0 I_z+\omega_1 I_x)t}e^{-i\omega I_z t}, \tag{4.3}$$

and

$$S^{-1}=e^{i\omega I_z t}e^{i(\Delta_0 I_z+\omega_1 I_x)t}, \tag{4.4}$$

respectively, with the abbreviation

$$\Delta_0\equiv\omega_0-\omega. \tag{4.5}$$

Owing to the fact that their exponents do not commute, the product of the two exponentials in (4.3) and (4.4) cannot be combined into a single exponential and their order is essential. An exception arises, of course, for negligible values of ω_1 where Eq. (4.3) is seen to be equivalent to Eq. (3.1). A more convenient form is obtained by introducing the operators,

$$S_\omega=e^{-i\omega I_z t}, \tag{4.6}$$

$$S_{\omega'}=e^{-i\omega' I_z t}, \tag{4.7}$$

$$S_\theta=e^{-i\theta I_y}, \tag{4.8}$$

and their inverse, with

$$\omega'=(\Delta_0^2+\omega_1^2)^{\frac{1}{2}}, \tag{4.9}$$

and $\tan\theta=\omega_1/\Delta_0$, so that

$$\Delta_0=\omega'\cos\theta, \tag{4.10}$$

and

$$\omega_1=\omega'\sin\theta. \tag{4.11}$$

Indeed, the transformations

$$S_\theta I_x S_\theta^{-1}=I_x\cos\theta-I_z\sin\theta, \tag{4.12}$$

$$S_\theta I_y S_\theta^{-1}=I_y, \tag{4.13}$$

$$S_\theta I_z S_\theta^{-1}=I_x\sin\theta+I_z\cos\theta \tag{4.14}$$

represent a rotation of the spin vector $\mathbf{I}$ by the angle θ around the y-axis. In particular, multiplying the last equation on both sides with $\omega' t$, observing Eqs. (4.10) and (4.11), and applying the result to the first and second exponential in Eqs. (4.3) and (4.4) respectively, one obtains

$$S=S_\theta S_{\omega'}S_\theta^{-1}S_\omega, \tag{4.15}$$

and

$$S^{-1}=S_\omega^{-1}S_\theta S_{\omega'}^{-1}S_\theta^{-1}. \tag{4.16}$$

The coupling energy $\hbar G$ of Eq. (2.1) with the molecular system is here due to the interaction of the magnetic moment with a magnetic field $\mathbf{H}'$, arising from the molecular surroundings. If one introduces the vector operator

$$\mathbf{h}=-\gamma\mathbf{H}', \tag{4.17}$$

the components $h_{x,y,z}$ of $\mathbf{h}$ have the dimension of a frequency and are to be represented by matrices which are diagonal in the variables of the spin system. With the notations

$$I^0=I_z,\quad I^{\pm1}=I_x\pm iI_y, \tag{4.18}$$

and

$$h_0=h_z,\quad h_{\pm1}=\tfrac{1}{2}(h_x\mp ih_y), \tag{4.19}$$

one has

$$G=(\mathbf{h}\cdot\mathbf{I})=\textstyle\sum_\mu h_\mu I^\mu, \tag{4.20}$$

and from Eqs. (2.6) and (2.20)

$$G_S=\textstyle\sum_\mu h_\mu S I^\mu S^{-1}=\sum_r G^r e^{i\omega_r t}, \tag{4.21}$$

as the defining equation for the operators G^r and the frequencies ω_r. In order to obtain explicit expressions for these quantities, it is necessary to express the result of the three transformation operators (4.6), (4.7), and (4.8) upon the spin operators I^μ. The former two transformations represent rotations around the z-direction by the angles ωt and $\omega' t$ and hence yield, through Eq. (4.18),

$$S_\omega I^\mu S_\omega^{-1}=e^{-i\mu\omega t}I^\mu, \tag{4.22}$$

and

$$S_{\omega'}I^\lambda S_{\omega'}^{-1}=e^{-i\lambda\omega' t}I^\lambda, \tag{4.23}$$

respectively. Since one deals with a rotation around the y direction by the angle θ, the result of the transformation S_θ and of its inverse $S_\theta^{-1}=S_{-\theta}$ can be expressed in the form

$$S_\theta I^\lambda S_\theta^{-1}=\textstyle\sum_\nu q_\nu^\lambda I^\nu, \tag{4.24}$$

and

$$S_\theta^{-1} I^\mu S_\theta = \textstyle\sum_\lambda p_\lambda{}^\mu I^\lambda. \tag{4.25}$$

The indices λ, μ, ν in Eqs. (4.20) to (4.25) are meant to assume independently the values -1, 0, 1. Upon using Eqs. (4.12) to (4.14) and (4.18), the elements of the matrices p and q in (4.24) and (4.25) are explicitly given by the following equations:

$$\begin{aligned} &p_1{}^1 = p_{-1}{}^{-1} = q_1{}^1 = q_{-1}{}^{-1} = \tfrac{1}{2}(\cos\theta + 1),\\ &p_{-1}{}^1 = p_1{}^{-1} = q_{-1}{}^1 = q_1{}^{-1} = \tfrac{1}{2}(\cos\theta - 1),\\ &p_0{}^0 = q_0{}^0 = \cos\theta,\\ &p_0{}^1 = p_0{}^{-1} = -2p_1{}^0 = -2p_{-1}{}^0 = -q_0{}^1 = -q_0{}^{-1}\\ &\qquad = 2q_1{}^0 = 2q_{-1}{}^0 = \sin\theta. \end{aligned} \tag{4.26}$$

They satisfy the relations:

$$q_\mu{}^\lambda(\theta) = p_\mu{}^\lambda(-\theta), \tag{4.27}$$

$$\textstyle\sum_\lambda p_\lambda{}^\mu q_{\mu'}{}^\lambda = \delta_{\mu\mu'}, \tag{4.28}$$

$$\textstyle\sum_\mu p_\lambda{}^\mu q_\mu{}^{\lambda'} = \delta_{\lambda\lambda'}, \tag{4.29}$$

$$p_{-\lambda}{}^{-\mu} = p_\lambda{}^\mu, \tag{4.30}$$

$$q_{-\lambda}{}^{-\mu} = q_\lambda{}^\mu. \tag{4.31}$$

Through the expressions (4.15) and (4.16) for S and S^{-1} and the successive use of the transformations (4.22) to (4.25), one obtains

$$S I^\mu S^{-1} = \textstyle\sum_{\lambda\nu} p_\lambda{}^\mu q_\nu{}^\lambda e^{-i(\lambda\omega' + \mu\omega)t} I^\nu. \tag{4.32}$$

Inserting this expression in Eq. (4.21) and replacing the index r by the double index (λ,μ) with λ and μ independently assuming the values -1, 0, $+1$, it is

$$G_S = \textstyle\sum_{\lambda\mu} G^{\lambda\mu} e^{i\omega_{\lambda\mu} t}, \tag{4.33}$$

with

$$G^{\lambda\mu} = h_\mu \textstyle\sum_\nu p_\lambda{}^\mu q_\nu{}^\lambda I^\nu, \tag{4.34}$$

and

$$\omega_{\lambda\mu} = -(\lambda\omega' + \mu\omega). \tag{4.35}$$

With the notation (2.58), one obtains from Eq. (4.34), through the inverse transformation with $S_\omega{}^{-1} = S_{-\omega}$ and $S_{\omega'}{}^{-1} = S_{-\omega'}$ as well as the relation (4.29),

$$G_-{}^{\lambda\mu} = S^{-1} G^{\lambda\mu} S = h_\mu \textstyle\sum_\nu p_\lambda{}^\mu q_\nu{}^\lambda e^{-i\omega_{\lambda\nu} t} I^\nu. \tag{4.36}$$

It will now be assumed that the diagonal elements of the matrices $(fu|h_\mu|f'u')$ and, hence, those of G vanish so that from (2.26) $\Delta = 0$. Assuming further a sufficient magnitude of the external magnetic field, so that the second-order correction Γ, given by Eq. (2.54), can be neglected in comparison to E, one can write the Eqs. (2.56) and (2.57) in the form

$$d\sigma/dt + i[E,\sigma] = \Gamma(\sigma), \tag{4.37}$$

with

$$\begin{aligned} \Gamma(\sigma) = \pi \sum_{\lambda\mu} \sum_{\nu\rho} e^{i(\nu-\mu)\omega t} p_\lambda{}^\mu q_\nu{}^\lambda (&e^{-\beta\omega_{\lambda\mu}} \{h_\mu h_\rho\}^{\omega_{\lambda\mu}} I^\nu \sigma I^\rho\\ &- \{h_\mu h_\rho\}^{\omega_{\lambda\mu}} \sigma I^\nu I^\rho + e^{\beta\omega_{\lambda\mu}} \{h_\rho h_\mu\}^{-\omega_{\lambda\mu}} I^\rho \sigma I^\nu\\ &- \{h_\rho h_\mu\}^{-\omega_{\lambda\mu}} I^\rho I^\nu \sigma). \end{aligned} \tag{4.38}$$

With the use of Eq. (4.36), this last expression is obtained from (2.57) through the replacement of the index r by $(\lambda\mu)$, writing $G = \sum_\rho h_\rho I^\rho$, and observing from (4.35) that $\omega_{\lambda\mu} - \omega_{\lambda\nu} = (\nu - \mu)\omega$.

As a further simplification, it will now be assumed that, similar to the treatment of Sec. V in I, the molecular surroundings have the property of isotropy so that, on the average, the cross products of the components of $\mathbf{H}'$ vanish, and their squares have a common value. Applied to Eq. (4.38) and with the notations (4.19), this means that one can write

$$\pi\{h_\mu h_\rho\}^\alpha = e^{\beta\alpha/2} \Phi_\mu(\alpha) \delta_{\rho,-\mu}, \tag{4.39}$$

where, in accordance with the abbreviation (2.28),

$$\begin{aligned} \Phi_\mu(\alpha) = e^{-\beta\alpha/2} \pi \sum_{uu'} \int &\eta_u(f) \eta_{u'}(f+\alpha) P(f)\\ &\times (fu|h_\mu|f+\alpha, u')(f+\alpha, u'|h_{-\mu}|fu) df, \end{aligned} \tag{4.40}$$

and where one has, with Eq. (4.19),

$$\Phi_\mu(\alpha) = \Phi_{-\mu}(\alpha), \tag{4.41}$$

$$2\Phi_1(\alpha) = 2\Phi_{-1}(\alpha) = \Phi_0(\alpha), \tag{4.42}$$

and, as a consequence of Eqs. (4.40) and (4.41),

$$\Phi_\mu(\alpha) = \Phi_\mu(-\alpha). \tag{4.43}$$

With the notations

$$A_{\mu\nu} = \textstyle\sum_\lambda p_\lambda{}^\mu q_\nu{}^\lambda \Phi_\mu(\omega_{\lambda\mu}) \cosh(\beta\omega_{\lambda\mu}/2), \tag{4.44}$$

and

$$C_{\mu\nu} = -\textstyle\sum_\lambda p_\lambda{}^\mu q_\nu{}^\lambda \Phi_\mu(\omega_{\lambda\mu}) \sinh(\beta\omega_{\lambda\mu}/2), \tag{4.45}$$

the expression (4.38) takes then the greatly simplified form

$$\begin{aligned} \Gamma(\sigma) = \sum_{\mu\nu} e^{i(\nu-\mu)\omega t} (&A_{\mu\nu}[[I^\nu,\sigma], I^{-\mu}]\\ &+ C_{\mu\nu}[I^\nu\sigma + \sigma I^\nu, I^{-\mu}]). \end{aligned} \tag{4.46}$$

An alternative way of writing the Eqs. (4.44) and (4.45) is obtained by making use of the relation (4.28). Indeed, these equations can be seen to be equivalent to

$$A_{\mu\nu} = \alpha_\mu{}^+ \delta_{\mu\nu} + \alpha_\mu{}^0 p_0{}^\mu q_\nu{}^0 + \alpha_\mu{}^- (p_1{}^\mu q_\nu{}^1 - p_{-1}{}^\mu q_\nu{}^{-1}), \tag{4.47}$$

and

$$C_{\mu\nu} = \gamma_\mu{}^+ \delta_{\mu\nu} + \gamma_\mu{}^0 p_0{}^\mu q_\nu{}^0 + \gamma_\mu{}^- (p_1{}^\mu q_\nu{}^1 - p_{-1}{}^\mu q_\nu{}^{-1}), \tag{4.48}$$

with the notations

$$\begin{aligned} \alpha_\mu{}^+ &= \tfrac{1}{2}[\Phi_\mu(\mu\omega + \omega') \cosh(\mu\kappa + \kappa') + \Phi_\mu(\mu\omega - \omega')\\ &\qquad \times \cosh(\mu\kappa - \kappa')],\\ \alpha_\mu{}^0 &= \Phi_\mu(\mu\omega) \cosh\mu\kappa - \tfrac{1}{2}[\Phi_\mu(\mu\omega + \omega') \cosh(\mu\kappa + \kappa')\\ &\qquad + \Phi_\mu(\mu\omega - \omega') \cosh(\mu\kappa - \kappa')],\\ \alpha_\mu{}^- &= \tfrac{1}{2}[\Phi_\mu(\mu\omega + \omega') \cosh(\mu\kappa + \kappa')\\ &\qquad - \Phi_\mu(\mu\omega - \omega') \cosh(\mu\kappa - \kappa')], \end{aligned} \tag{4.49}$$

and

$$\begin{aligned}\gamma_\mu{}^+=&\tfrac{1}{2}[\Phi_\mu(\mu\omega+\omega')\sinh(\mu\kappa+\kappa')\\&+\Phi_\mu(\mu\omega-\omega')\sinh(\mu\kappa-\kappa')],\\ \gamma_\mu{}^0=&\Phi_\mu(\mu\omega)\sinh\mu\kappa-\tfrac{1}{2}[\Phi_\mu(\mu\omega+\omega')\sinh(\mu\kappa+\kappa')\\&+\Phi_\mu(\mu\omega-\omega')\sinh(\mu\kappa-\kappa')],\qquad(4.50)\\ \gamma_\mu{}^-=&\tfrac{1}{2}[\Phi_\mu(\mu\omega+\omega')\sinh(\mu\kappa+\kappa')\\&-\Phi_\mu(\mu\omega-\omega')\sinh(\mu\kappa-\kappa')].\end{aligned}$$

The derivation of these expressions is based upon Eq. (4.35), the relation (4.43), and the abbreviations

$$\kappa=\beta\omega/2,\quad \kappa'=\beta\omega'/2.\qquad(4.51)$$

A particular consequence of Eqs. (4.49) and (4.50) is that

$$\alpha_0{}^-=\gamma_0{}^+=\gamma_0{}^0=0.\qquad(4.52)$$

For later use, it is further to be noted that, by changing the sign of the indices λ, μ, ν in (4.44) and (4.45), one has with the Eqs. (4.30), (4.31), and (4.35),

$$A_{\mu\nu}=A_{-\mu,-\nu},\quad C_{\mu\nu}=-C_{-\mu,-\nu}.\qquad(4.53)$$

While it would be perfectly feasible to insert the expression (4.46) in (4.37) and to find appropriate solutions for the distribution matrix σ, it is preferable, in this case, to use Eq. (2.61) directly for expectation values, with Q standing for any one of the components of the spin vector $\mathbf{I}$. Omitting again the corrections Δ and Γ on the left side, inserting the expression (4.2) for E and observing the commutation relations between the components of $\mathbf{I}$, one obtains thus the vector equation

$$d\langle\mathbf{I}\rangle/dt+[\boldsymbol{\omega}\times\langle\mathbf{I}\rangle]=\langle\Gamma(\mathbf{I})\rangle,\qquad(4.54)$$

with

$$\begin{aligned}\langle\Gamma(\mathbf{I})\rangle=\sum_{\mu\nu}e^{i(\nu-\mu)\omega t}(&A_{\mu\nu}\langle[[I^{-\mu},\mathbf{I}],I^\nu]\rangle\\&+C_{\mu\nu}\langle[I^{-\mu},\mathbf{I}]I^\nu+I^\nu[I^{-\mu},\mathbf{I}]\rangle),\qquad(4.55)\end{aligned}$$

and where the components of the vector $\boldsymbol{\omega}$ are given by

$$\omega_x=\omega_1\cos\omega t,\quad \omega_y=-\omega_1\sin\omega t,\quad \omega_z=\omega_0.\qquad(4.56)$$

If one uses the expression (4.46), these equations can also be obtained by multiplying with $\mathbf{I}$ and forming the trace on both sides of Eq. (4.37).

It is the direct consequence of the commutation rules for the components of $\mathbf{I}$, representing any value of the spin, that the double commutator in Eq. (4.55) can be written in the form of a linear expression for these components themselves. On the other hand, it is the particular feature of the case for spin 1/2, that the expression $[I^{-\mu},\mathbf{I}]I^\nu+I^\nu[I^{-\mu},\mathbf{I}]$ either vanishes or becomes a mere number. It is for this reason, similar to the corresponding treatment in I, that Eq. (4.54) reduces for spin 1/2 without further assumptions to a system of linear "phenomenological" equations for the expectation value of the components of $\mathbf{I}$.

By a familiar procedure, to eliminate the explicit time dependence occurring on the left side of Eq. (4.54) through the components ω_x and ω_y of $\boldsymbol{\omega}$ as well as that on the right side through the exponential in Eq. (4.55), it is convenient to transform to a coordinate system which rotates with the magnetic field. This transformation is achieved by

$$(I^\mu)^*=S_\omega{}^{-1}I^\mu S_\omega=e^{i\mu\omega t}I^\mu,\qquad(4.57)$$

where the relation of the starred quantities to the components $I_x{}^*$, $I_y{}^*$, $I_z{}^*$ of the spin vector in the rotating coordinate system is the same as that expressed in Eq. (4.18) for the original quantities, and where these quantities satisfy the same commutation rules. In the case of spin 1/2 one has further, both for the original and the starred components,

$$I_x{}^2=\tfrac{1}{4},\quad I_xI_y+I_yI_x=0,$$

with the corresponding relations obtained by cyclical permutation of x, y, z. By a somewhat lengthy, but straightforward, application of the above-mentioned facts and the use of Eqs. (4.10), (4.11), (4.53), and (4.57), one obtains, from (4.54) and (4.55), for the expectation values of the spin components $I_x{}^*$, $I_y{}^*$, and $I_z{}^*$ in the rotating coordinate system the simultaneous differential equations

$$d\langle I_x{}^*\rangle/dt-\omega'\langle I_y{}^*\rangle\cos\theta+A_x\langle I_x{}^*\rangle+a_x\langle I_z{}^*\rangle=C_x,\qquad(4.58)$$

$$\begin{aligned}d\langle I_y{}^*\rangle/dt+\omega'(\langle I_x{}^*\rangle\cos\theta-\langle I_z{}^*\rangle\sin\theta)&\\+A_y\langle I_y{}^*\rangle=0,&\qquad(4.59)\end{aligned}$$

$$d\langle I_z{}^*\rangle/dt+\omega'\langle I_y{}^*\rangle\sin\theta+A_z\langle I_z{}^*\rangle+a_z\langle I_x{}^*\rangle=C_z,\qquad(4.60)$$

with the constant coefficients

$$\begin{aligned}A_x=&2(A_{11}-A_{1,-1})+A_{00}=2(\alpha_1{}^++\alpha_1{}^-\cos\theta)\\&+\alpha_0{}^++\alpha_0{}^0\cos^2\theta,\qquad(4.61)\\ A_y=&2(A_{11}+A_{1,-1})+A_{00}\\=&2(\alpha_1{}^++\alpha_1{}^0\sin^2\theta+\alpha_1{}^-\cos\theta)\\&+\alpha_0{}^++\alpha_0{}^0\cos^2\theta,\qquad(4.62)\\ A_z=&4A_{11}=4(\alpha_1{}^++\tfrac{1}{2}\alpha_1{}^0\sin^2\theta+\alpha_1{}^-\cos\theta),\qquad(4.63)\\ a_x=&-2A_{01}=-\alpha_0{}^0\sin\theta\cos\theta,\qquad(4.64)\\ a_z=&-2A_{10}=-2(\alpha_1{}^0\sin\theta\cos\theta-\alpha_1{}^-\sin\theta),\qquad(4.65)\\ C_x=&-(C_{10}+C_{01})=-\gamma_1{}^0\sin\theta\cos\theta\\&+\gamma_1{}^-\sin\theta+\tfrac{1}{2}\gamma_0{}^-\sin\theta,\qquad(4.66)\\ C_z=&2C_{11}=2(\gamma_1{}^++\tfrac{1}{2}\gamma_1{}^0\sin^2\theta+\gamma_1{}^-\cos\theta).\qquad(4.67)\end{aligned}$$

The second form of these coefficients is obtained from Eqs. (4.47) and (4.48) with the use of Eqs. (4.26) and the relations (4.52).

The differential equations (4.58), (4.59), and (4.60) represent the generalization of the original phenomenological equations[6] for the case of a rotating magnetic field, referred to the rotating coordinate system. The corresponding equations for the macroscopic polarization are simply obtained by multiplying the expectation values of the spin components with $2n\mu'$ where n

represents the number of spins per unit volume and μ' their common magnetic moment. The stationary solution of the equations above is readily found to be

$$\langle I_x{}^*\rangle=(1/D)[C_x(A_yA_z+\omega'^2\sin^2\theta)-C_z(a_xA_y-\omega'^2\sin\theta\cos\theta)], \quad (4.68)$$

$$\langle I_y{}^*\rangle=(\omega'/D)[-C_x(a_z\sin\theta+A_z\cos\theta)+C_z(A_x\sin\theta+a_x\cos\theta)], \quad (4.69)$$

$$\langle I_z{}^*\rangle=(1/D)[-C_x(A_ya_z-\omega'^2\sin\theta\cos\theta)+C_z(A_xA_y+\omega'^2\cos^2\theta)], \quad (4.70)$$

with

$$D=A_y(A_zA_x-a_za_x)+\omega'^2[A_z\cos^2\theta+(a_x+a_z)\sin\theta\cos\theta+A_x\sin^2\theta]. \quad (4.71)$$

In order to illustrate the great variety of facts contained in these equations, they will be applied to some familiar special cases:

a. Static Field

It is clear that in this case, i.e., for $\omega=0$, the stationary solution must correspond to the equilibrium polarization in a constant magnetic field of magnitude

$$(\omega_0{}^2+\omega_1{}^2)^{\frac{1}{2}}/\gamma=\omega'/\gamma,$$

inclined at the angle θ to the z direction. Indeed, it is seen from (4.49), (4.50), and the relations (4.42), (4.43), that for $\omega=0$ all the coefficients α and γ in Eqs. (4.61) to (4.67) vanish with the exception of

$$\alpha_1{}^0=\Phi_1(0)-\Phi_1(\omega')\cosh\kappa',\quad \alpha_0{}^0=2\alpha_1{}^0,$$
$$\alpha_1{}^+=\Phi_1(\omega')\cosh\kappa',\quad \alpha_0{}^+=2\alpha_1{}^+,$$
$$\gamma_1{}^-=\Phi_1(\omega')\sinh\kappa',\quad \gamma_0{}^-=2\gamma_1{}^-.$$

The coefficients, entering in Eqs. (4.68) to (4.71), are therefore given by

$$A_x=2\alpha_0{}^++\alpha_0{}^0\cos^2\theta,\quad A_y=2\alpha_0{}^++\alpha_0{}^0,$$
$$A_z=2\alpha_0{}^++\alpha_0{}^0\sin^2\theta,\quad a_x=a_z=-\alpha_0{}^0\sin\theta\cos\theta,$$
$$C_x=\gamma_0{}^-\sin\theta,\quad C_z=\gamma_0{}^-\cos\theta,$$

and yield upon insertion

$$\langle I_y\rangle=0,\quad \langle I_x\rangle\cos\theta-\langle I_z\rangle\sin\theta=(A_y/\omega')\langle I_y\rangle=0,$$

and further with $D=2\alpha_0{}^+[(2\alpha_0{}^++\alpha_0{}^0)^2+\omega'^2]$:

$$\langle I_z\rangle\cos\theta+\langle I_x\rangle\sin\theta=\gamma_0{}^-/(2\alpha_0{}^+)=\tfrac{1}{2}\tanh\kappa',$$

i.e., the proper thermal equilibrium value for the component, parallel to the field and the vanishing of the perpendicular components. The asterisk has been omitted in these expressions since, for $\omega=0$, the rotating and the fixed coordinate system are identical.

b. Vanishing Transverse Field

The situation for thermal equilibrium must evidently also be realized if the x and y components of the external field vanish so that one deals with a static field in the z direction. The frequency of rotation has here only a formal significance and the result must be independent of any specific value assigned to ω. According to Eq. (4.1), one has here $\omega_1=0$, and therefore from Eqs. (4.9) and (4.5) $\omega'=\Delta_0=\omega_0-\omega$ and from Eq. (4.11) $\theta=0$. It follows then, from Eqs. (4.61) to (4.67), that

$$A_x=A_y=2(\alpha_1{}^++\alpha_1{}^-)+\alpha_0{}^++\alpha_0{}^0,\quad A_z=4(\alpha_1{}^++\alpha_1{}^-),$$
$$a_x=a_z=0,\quad C_x=0,\quad C_z=2(\gamma_1{}^++\gamma_1{}^-),$$

and from (4.49) and (4.50)

$$\alpha_1{}^++\alpha_1{}^-=\Phi_1(\omega+\omega')\cosh(\kappa+\kappa');$$
$$\gamma_1{}^++\gamma_1{}^-=\Phi_1(\omega+\omega')\sinh(\kappa+\kappa').$$

It is further seen from Eq. (4.51) that $\kappa+\kappa'=\kappa_0=\beta\omega_0/2$ since for $\omega_1=0$ Eqs. (4.5) and (4.9) yield $\omega+\omega'=\omega_0$, so that one obtains from Eqs. (4.68) to (4.71)

$$\langle I_x{}^*\rangle=\langle I_y{}^*\rangle=0,$$

and further, with $D=A_z(A_x{}^2+\omega'^2)$

$$\langle I_z{}^*\rangle=2(\gamma_1{}^++\gamma_1{}^-)/4(\alpha_1{}^++\alpha_1{}^-)=\tfrac{1}{2}\tanh\kappa_0.$$

The vanishing of $\langle I_x{}^*\rangle$ and $\langle I_y{}^*\rangle$ entails also that of $\langle I_x\rangle$ and $\langle I_y\rangle$ and one has $\langle I_z{}^*\rangle=\langle I_z\rangle=\frac{1}{2}\tanh\kappa_0$, representing indeed the proper equilibrium value for a constant external field of magnitude $H_0=\omega_0/\gamma$ in the z direction.

c. Weak Transverse Field near Resonance

While the preceding result is rigorously valid only for $\omega_1=0$, it applies also to a weak transverse field, provided that $\omega_1\ll|\Delta_0|=|\omega_0-\omega|$, i.e., for conditions far removed from resonance. It is invalid, however, if $|\Delta_0|$ is comparable to ω_1, even though the latter quantity may be assumed small, since one has in this case $\theta\neq 0$. The fact that one is dealing with a "weak" transverse field is here implied to mean that $\omega_1\ll\omega\approx\omega_0$ and $\beta\omega_1\ll 1$. With $|\Delta_0|$ comparable to ω_1, ω' is, according to Eq. (4.9), likewise comparable to ω_1, so that the case considered here implies that one has in Eqs. (4.49) and (4.50)

$$\Phi_\mu(\omega+\omega')\approx\Phi_\mu(\omega-\omega')\approx\Phi_\mu(\omega)\approx\Phi_\mu(\omega_0)$$

and, according to Eq. (4.51),

$$\kappa'\ll 1,\quad \kappa\approx\kappa_0=\beta\omega_0/2.$$

Consequently, all the coefficients α and γ in Eqs. (4.61) to (4.67) vanish, with the exception of

$$\begin{aligned}&\alpha_1{}^+=\Phi_1(\omega_0)\cosh\kappa_0,\quad \alpha_0{}^+=\Phi_0(\omega'),\\&\alpha_0{}^0=\Phi_0(0)-\Phi_0(\omega'),\quad \gamma_1{}^+=\Phi_1(\omega_0)\sinh\kappa_0,\end{aligned} \quad (4.72)$$

and one has

$$A_x=A_y=2\alpha_1{}^++\alpha_0{}^++\alpha_0{}^0\cos^2\theta,\quad A_z=4\alpha_1{}^+,$$
$$a_x=-\alpha_0{}^0\sin\theta\cos\theta,\quad a_z=0,\quad C_x=0,\quad C_z=2\gamma_1{}^+.$$

Using, further, (4.10) and (4.11), one obtains then from

Eqs. (4.68) to (4.71):

$$\langle I_x^*\rangle=\Delta_0\omega_1\frac{4\alpha_1^+}{D}\left[1+\frac{\alpha_0^0(2\alpha_1^++\alpha_0^++\alpha_0^0\cos^2\theta)}{\Delta_0^2+\omega_1^2}\right]\tfrac{1}{2}\tanh\kappa_0, \tag{4.73}$$

$$\langle I_y^*\rangle=\omega_1\frac{4\alpha_1^+}{D}[2\alpha_1^++\alpha_0^+]\tfrac{1}{2}\tanh\kappa_0, \tag{4.74}$$

$$\langle I_z^*\rangle=\frac{4\alpha_1^+}{D}[(2\alpha_1^++\alpha_0^++\alpha_0^0\cos^2\theta)^2+\Delta_0^2]\tfrac{1}{2}\tanh\kappa_0, \tag{4.75}$$

with

$$D=4\alpha_1^+(2\alpha_1^++\alpha_0^++\alpha_0^0\cos^2\theta)^2+4\alpha_1^+\Delta_0^2+(2\alpha_1^++\alpha_0^+)\omega_1^2. \tag{4.76}$$

A considerable simplification of this result is obtained if, beyond the conditions stated above, the smallness of ω_1 implies also that $\omega_1\approx\omega'\ll\omega^*$. In fact, this additional condition renders the assumptions made here equivalent to those made in I and II, and in view of the treatment presented in I, the expressions (4.73) to (4.75) must become identical with those obtained from the solution of the phenomenological equations.[6] Indeed, this particular simplicity arises from the fact that it is here permissible to omit in Eqs. (4.72) the distinction between $\Phi_0(\omega')$ and $\Phi_0(0)$ so that $\alpha_0^+=\Phi_0(0)$ and $\alpha_0^0=0$. One obtains then from (4.73) to (4.76) the familiar result

$$\langle I_x^*\rangle=\frac{\omega_1\Delta_0}{1+(\Delta_0T_2)^2+\omega_1^2T_1T_2}\langle I_z\rangle_0,$$

$$\langle I_y^*\rangle=\frac{\omega_1T_2}{1+(\Delta_0T_2)^2+\omega_1^2T_1T_2}\langle I_z\rangle_0,$$

$$\langle I_z^*\rangle=\frac{1+(\Delta_0T_2)^2}{1+(\Delta_0T_2)^2+\omega_1^2T_1T_2}\langle I_z\rangle_0,$$

where $\langle I_z\rangle_0=\frac{1}{2}\tanh\kappa_0$ represents the equilibrium value of $\langle I_z\rangle$ in the absence of a transverse field and where the inverse longitudinal and transverse relaxation times are given by $1/T_1=4\Phi_1(\omega_0)\cosh\kappa_0$ and $1/T_2=1/2T_1+\Phi_0(0)$, respectively.

The fact that relaxation can here be characterized by only two time constants arises from the circumstance that the two frequencies of relevance, occurring as argument in the quantities Φ of Eqs. (4.49) and (4.50), are 0 and ω_0. The general case is actually to be characterized by five time constants, determined by five quantities Φ with the corresponding frequencies 0, ω', $\omega-\omega'$, ω, $\omega+\omega'$ as argument, which may all be different.

The result expressed by Eqs. (4.73) to (4.76) is not quite so general since there occur only three different quantities, $\Phi_1(\omega_0)$, $\Phi_0(\omega')$, and $\Phi_0(0)$, in Eqs. (4.72). Nevertheless, it contains the rigorous formulation of a feature previously pointed out by Bloembergen[1] and Redfield,[22] i.e., that the condition for saturation, obtained from the phenomenological equations, requires a modification for increasing values of the alternating field. This is best seen from the expression for $\langle I_y^*\rangle$, corresponding to absorption, under conditions of exact resonance. Indeed, for $\Delta_0=0$, and hence, for $\cos\theta=0$ and $\omega'=\omega_1$, one obtains, from Eq. (4.74),

$$\langle I_y^*\rangle=\frac{\omega_1T_2'}{1+\omega_1^2T_1T_2'}\tfrac{1}{2}\tanh\kappa_0,$$

with the same significance,

$$1/T_1=4\Phi_1(\omega_0)\cosh\kappa_0,$$

for the inverse longitudinal relaxation time as in the case of the phenomenological equations, but with the modified definition

$$1/T_2'=1/2T_1+\Phi_0(\omega_1)$$

for the inverse of an effective transverse relaxation time. One may be dealing with a dependence of $\Phi_0(\alpha)$ upon α such that even for $\alpha=\omega_1\ll\omega_0$ one has $\Phi_0(\omega_1)\approx\Phi_0(\omega_0)=2\Phi_1(\omega_0)$. Assuming further that $\kappa_0\ll1$, one has then $\Phi_0(\omega_1)=1/2T_1$ and hence $T_2'\approx T_1$, i.e., the value of the effective transverse relaxation time approaches that of the longitudinal relaxation time.

It is to be noted, however, that the effect of the distinction between $\Phi_0(\omega')$ and $\Phi_0(0)$, permitted in Eqs. (4.73) to (4.76), cannot generally be described by the mere introduction of a new transverse relaxation time. Through the occurrence of $\cos\theta$ and the explicit occurrence of Δ_0 in Eqs. (4.73), (4.75), and (4.76), it is seen that the dependence upon Δ_0, i.e., the shape of the resonance line, is at the same time altered from the simple Lorentzian line shape, obtained in the absence of this distinction.

d. Slowly-Rotating Field

The formulas (4.68) to (4.71) contain also the case, considered in greater generality in Sec. III, where, in accordance with the conditions (3.8) and (3.9), either ω or ω_1 are sufficiently small. In agreement with the condition (3.25) it shall also be assumed that $\omega_0\ll\omega^*$, and furthermore, that $\omega_0\ll1/\beta$. The fulfillment of these two additional assumptions underlies the treatment of Wangsness[10] so that his results must be contained in Eqs. (4.68) to (4.71) as a further special case.

The condition for this case is formulated in our notation by

$$\omega,\,\omega'\ll\omega^*,$$

so that the argument of all the quantities Φ in Eqs. (4.49) and (4.50) may be replaced by zero and by the further condition

$$\kappa,\,\kappa'\ll1.$$

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[22] A. G. Redfield, Phys. Rev. 98, 1787 (1955). See particularly Sec. III A.

Neglecting all but the linear terms in κ and κ', the hyperbolic cosines in (4.49) can be replaced by unity and the hyperbolic sines in (4.50) by their argument. The nonvanishing coefficients α and γ are then given by

$$\alpha_1{}^+=\Phi_1(0),\quad \alpha_0{}^+=\Phi_0(0)=2\Phi_1(0),$$
$$\gamma_1{}^+=\kappa\Phi_1(0),\quad \gamma_1{}^-=\kappa'\Phi_1(0),$$
$$\gamma_0{}^-=\kappa'\Phi_0(0)=2\kappa'\Phi_1(0),$$

and it follows from Eqs. (4.61) to (4.67) that

$$A_x=A_y=A_z=4\Phi_1(0),\quad a_x=a_z=0,$$
$$C_x=2\Phi_1(0)\kappa'\sin\theta,\quad C_z=2\Phi_1(0)(\kappa+\kappa'\cos\theta).$$

With Eqs. (4.5), (4.10), (4.11), and (4.50), yielding

$$\kappa+\kappa'\cos\theta=\hbar(\omega+\Delta_0)/2kT=\hbar\omega_0/(2kT),$$

and with $D=4\Phi_1(0)\{[4\Phi_1(0)]^2+\omega'^2\}$ from (4.71), one obtains from Eqs. (4.68) to (4.70)

$$\langle I_x{}^*\rangle=\hbar\omega_1\left[1+\frac{\omega\Delta_0}{[4\Phi_1(0)]^2+\omega'^2}\right]\bigg/(4kT),$$

$$\langle I_y{}^*\rangle=\hbar\omega_1\left[\frac{4\Phi_1(0)\omega}{[4\Phi_1(0)]^2+\omega'^2}\right]\bigg/(4kT),$$

$$\langle I_z{}^*\rangle=\hbar\left[\omega_0-\frac{\omega\omega_1{}^2}{[4\Phi_1(0)]^2+\omega'^2}\right]\bigg/(4kT).$$

Going back to the fixed-coordinate system, one has from Eq. (4.57)

$$\langle I^1\rangle=(\langle I_x{}^*\rangle+i\langle I_y{}^*\rangle)e^{-i\omega t}$$
$$=\hbar\omega_1\left[1+\frac{\omega\Delta_0+4i\Phi_1(0)\omega}{[4\Phi_1(0)]^2+\omega'^2}\right]e^{-i\omega t}/(4kT),$$

and

$$\langle I_z\rangle=\langle I_z{}^*\rangle.$$

The corresponding expressions M_1 and M_z for the macroscopic polarizations are obtained by multiplying $\langle I^1\rangle$ and $\langle I_z\rangle$ with $2n\mu'$. Observing that $2n\mu'\hbar/(4kT)=\chi_0/\gamma$, with $\chi_0=n\mu'^2/(kT)$ being the static susceptibility, and with the notation $M_+=M^1$, $\tau=1/[4\Phi_1(0)]$, $H_1=\omega_1/\gamma$, $\Delta=\Delta_0$, and $\alpha=\omega'$, it is seen that the result thus obtained is indeed identical with that of Wangsness.[23] In particular, it includes the result of Gorter and Kronig,[8] applied to a purely rotating field, i.e., to the case $\omega_0=0$, with the in-phase and out-of-phase component of the susceptibility given by the real and imaginary part of M^1/H_1, respectively.

5. CONCLUSIONS

Being restricted only by the conditions (2.42), the Boltzmann equation (2.56) can be claimed to properly describe a very general class of relaxation phenomena, based essentially upon the assumption that the molecular surroundings can be considered to remain in thermal equilibrium. It is clear that what has been termed here the "spin system" can be considered as any other quantum-mechanical system subjected to any given external actions, and that the "molecular system" is by no means required to consist of molecules but could, for example, be equally represented by electromagnetic radiation in thermal equilibrium.

Applied to nuclear- or electronic-resonance processes, Eq. (2.56) includes all the previously considered situations as special cases and it contains, besides, a great deal of additional information, as is seen in Sec. IV, even for the simple case of a rotating magnetic field. With the further progress of the experimental art and particularly with its extension towards low temperatures, there can be little doubt that many of these additional features will, in due course, become of equal importance to those considered so far.

While this paper was in progress the author was informed about similar work carried out by Redfield[24] who has likewise realized the possibility of extending the earlier treatments to cases where the static part of the spin energy is not dominant. After a general presentation of the semiclassical approach, mentioned in the Introduction of this paper, through time-dependent random perturbations upon the spin system, he follows the procedure of I and II as well as of this paper in formulating a consistent quantum-mechanical treatment, based upon the assumption that the molecular surroundings can be treated as a heat reservoir which remains in thermal equilibrium. As an interesting methodical approach, external actions are introduced by including their producing devices into the total system with a coupling term to the spin system which, originally, does not explicitly depend upon the time. The explicit time dependence of the spin energy, used from the beginning in Eq. (2.1) of this paper, results then from taking the expectation value of the coupling term with regard to the devices under suitable assumptions, chosen to account for their macroscopic character.

Redfield's treatment does not include a development, equivalent to Sec. II of this paper; instead, it is adapted to those cases of Sec. III where in addition to (2.42) the conditions (3.8), (3.28), and, further, the condition $|E|\ll 1/\beta$ are satisfied and it is augmented by indicating a series in ascending powers of parameters which, under strict fulfillment of these conditions, would be negligible. His formulas are likewise presented in a form which is invariant against a particular representation of the spin system and he has also independently observed the occurrence of a second-order correction to the energy of the spin system, arising from its coupling to the molecular surroundings. As an application he treats the relaxation of nuclear spins in a metal for an arbitrary fixed magnetic field intensity. Since the problem is too complex to permit a rigorous solution,

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[23] See reference 10, Eqs. (16) and (17).

[24] A. G. Redfield, IBM Journal 1 (January 1, 1957).

it is assumed that the spin system is at any time in thermal equilibrium with a spin temperature, different from that of the molecular surroundings; a measure for the relaxation time is then obtained from the rate of energy transfer to the molecular surroundings. As mentioned in the Introduction of this paper, the generalization of the method of Wangsness and the author, presented in II, would likewise permit such a treatment of this problem, but it could be applied only for a sufficiently high intensity of the fixed magnetic field. Redfield's results, however, can also be applied to relaxation in an arbitrary small field which is of considerable experimental interest. The author is grateful to Dr. Redfield for having received his manuscript before publication and for an interesting discussion.

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Luminescence of Potassium Iodide*

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When single crystals of potassium iodide are cooled to $-160°C$ and illuminated with light absorbed in the first fundamental band they luminesce with a quantum yield between 0.5 and 1. The excitation and emission spectra of this luminescence are presented. The experiments suggest that pure KI itself luminesces under the above conditions and that the luminescence can be modified by the presence of impurities or defects in the lattice.

I. INTRODUCTION

BECAUSE of their simple structure the alkali halides have played a very important role in the development of solid-state physics and it appears that there is still much to be learned from experiments done on them. For example, consider the result of illuminating a crystal with light absorbed in the first fundamental band. According to one interpretation this results in the excitation of electrons on the negative ions in the lattice. One observes, however, that this also results in a change in the optical properties of the crystal. *F* centers, among other things, appear in the lattice during illumination.[1] It is also found that *F* centers may be ionized by illumination with fundamental band light.[2] This type of observation suggests that the energy of an excited negative ion is not localized at the absorption site but may be transferred through the lattice and produce effects some distance from the point of absorption. Theoretically it is also found that such energy transfer is possible and several mechanisms for the transfer have been proposed.[3] However, it has not as yet been experimentally determined which of these mechanisms is important in the alkali halides.

Another way in which the excited negative ion can get rid of its energy is by the emission of a quantum of light. There is apparently no theoretical reason why this process cannot occur in the alkali halides, but until quite recently no experimental observations of luminescence of these substances during illumination in the fundamental band have been taken seriously. Because of this, it has been generally accepted that such luminescence does not occur. In the past few years, however, several workers have reported a low-temperature luminescence which might be ascribed to pure alkali halides, while others have observed fundamental band luminescence which was apparently connected with the presence of defects in the lattice.[4] The present work was motivated in part by the work mentioned above and also by the realization that a study of the luminescence of single alkali halide crystals excited by illumination in the fundamental band can perhaps help solve the problem of energy transfer mentioned in the first paragraph. It is interesting to determine whether or not the pure, perfect alkali halides will luminesce, but perhaps more important is the use of emission initiated by the excitation of a negative ion in the lattice as a tool in the investigation of energy transfer phenomena. Some experiments to this effect are discussed in the conclusion of this paper.

II. EXPERIMENTAL

In this paper the luminescence of the potassium iodide will be described in terms of its excitation and emission spectra and the quantum yield. Also, the optical absorp-

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