

## The Dynamical Theory of Nuclear Induction\*

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Starting from the microscopic viewpoint, the dynamics of nuclear induction is derived by means of statistical methods. The only essential lack of generality lies in the assumption that the nuclei in the sample are independent of each other, so that the treatment does not account for features arising from spin-spin interaction. By considering the simultaneous action of an arbitrary external field and of the molecular surroundings upon a representative nucleus a system of linear differential equations of the first order is derived for the "distribution matrix." It is analogous to the classical Boltzmann equation for the distribution function and allows, upon integration, to determine the macroscopic average value of any spin function in its dependence upon time. This general result is particularly applied to the time dependence of the macroscopic nuclear polarization, and the conditions are investigated under which it satisfies the phenomenological differential equation originally proposed by one of the authors (F.B.). Besides the fact that this equation does not describe line structures caused by the interaction of neighboring spins its validity is found to be seriously restricted only for nuclei having a spin larger than unity and in cases where, in addition, quadrupole relaxation is essential. It demands in these cases that the molecular surroundings are isotropic, e.g., as in gaseous and liquid samples, and further, that their characteristic frequencies of interaction with the nuclei are large compared to the Larmor frequency so that there exists equality between the longitudinal and the transverse relaxation time.

### 1. INTRODUCTION

IN his original paper on nuclear induction<sup>1</sup> one of the authors has proposed the differential equation,

$$d\mathbf{M}/dt = \gamma\mathbf{M} \times \mathbf{H} - \mathbf{i}M_x/T_2 - \mathbf{j}M_y/T_2 - \mathbf{k}(M_z - M_0)/T_1, \quad (1.1)$$

for the time dependence of the macroscopic nuclear polarization  $\mathbf{M}(t)$  under the influence of an external field  $\mathbf{H}(t)$ . The vectors  $\mathbf{i}$ ,  $\mathbf{j}$ , and  $\mathbf{k}$  are here unit vectors in the  $x$ ,  $y$ , and  $z$  directions, respectively, and

$$\gamma = \mu/I\hbar \quad (1.2)$$

is the gyromagnetic ratio of the nuclei under consideration with magnetic moment  $\mu$  and spin  $I$ . It is further assumed that the external field has the form

$$\mathbf{H}(t) = \mathbf{k}H_0 + \mathbf{H}_1(t), \quad (1.3)$$

where  $H_0$  is strong and constant while  $H_1$  is relatively weak and an arbitrary function of the time  $t$ .  $M_0$  is the equilibrium polarization in the field  $H_0$  and the establishment of thermal equilibrium is in Eq. (1.1) summarized by two constants  $T_1$  and  $T_2$  in the following manner: Starting with an arbitrary magnitude and direction, the  $z$  component of  $\mathbf{M}$  will, in the absence of the field  $\mathbf{H}_1$ , reach the value  $M_0$  with a time constant  $T_1$ , the "longitudinal" relaxation time, and the  $x$  and  $y$  components will vanish with a time constant  $T_2$ , the "transverse" relaxation time.

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<sup>1</sup> F. Bloch, Phys. Rev. **70**, 460 (1946).

While the phenomenological Eq. (1.1) is certainly not rigorously valid under all circumstances, it has nevertheless been found experimentally to represent, in many cases, the proper qualitative or even quantitative description of the observed phenomena; nuclear and molecular data of considerable interest can in these cases be inferred from the shape and magnitude of the observed signals under varying conditions of the external field. It seemed to us worth while, therefore, to develop a theory which starts from the microscopic viewpoint and derives the dynamics of nuclear induction by means of statistical methods. As an application of the considerably more general results, we shall determine the special conditions under which the phenomenological equations can be expected to be valid and where relaxation can be accordingly characterized by the two constants  $T_1$  and  $T_2$ , without reference to particular mechanisms responsible for the greatly varying magnitude of these relaxation times. An excellent investigation of such mechanisms in a variety of important cases has been previously carried out by Bloembergen.<sup>2</sup> His approach is, however, rather different from ours in so far as the molecular surroundings are described by random varying external fields rather than as a quantum-mechanical system interacting with the nucleus, and his treatment of the problem does not include the general dynamical case.

The behavior of the polarization, due to a large number of identical nuclei in a macroscopic sample, is determined by the effect of the external field, of the molecular surroundings, and of neighboring nuclear moments upon the orientation of the magnetic moment of each nucleus. We shall here not attempt a perfectly general theory where all these features are treated

<sup>2</sup> N. Bloembergen, Leiden thesis, 1948 (Schotanus and Gens, Utrecht).

rigorously but shall restrict ourselves to conditions, often experimentally realized, which lead to a relatively simple dynamical description.

Our problem is greatly simplified by assuming that each nucleus under consideration reacts independently of the other nuclei in the sample to the external field and the molecular surroundings and that the latter can be considered as a heat reservoir in thermal equilibrium. In making this assumption, the magnetic moments of neighboring nuclei are taken into account only in so far as they form part of the heat reservoir. We thus restrict the scope of the present paper by excluding those cases in which the magnetic field acting upon a nucleus depends essentially upon the orientation of its neighbors so that they may not be considered as independent. There are many cases where this feature is of importance; it can, for example, lead to a complex line structure in crystals and polyatomic liquids which our simplified approach is inadequate to describe. This approach is, however, perfectly applicable in other cases which are likewise of practical importance; in particular, in gases and dilute liquid solutions the distance between the nuclei under consideration is frequently so large that their interaction can be safely neglected. Furthermore, the action of the molecular surroundings is here often deliberately and greatly increased by adding to the substance paramagnetic atoms or molecules to serve as catalysts for a rapid establishment of thermal equilibrium. To the extent to which the coupling of a nucleus to its surroundings is primarily determined by such catalysts its interaction with the magnetic moments of other nuclei is negligible and our assumption becomes justified.

Treating the molecular surroundings of the nuclei as a general heat reservoir we shall derive, in analogy to the Boltzmann equation for the classical distribution function, a set of first-order linear differential equations for the "distribution matrix"; this matrix determines the average value of the nuclear polarization or of any other quantity which depends upon the orientation of the nuclear spins.

The equations for the distribution matrix will be used to express the time derivative of the average value of an arbitrary spin function in terms of the average value of other spin functions. The resulting set of relations is particularly convenient, in its general form, for finding the conditions under which it reduces to the phenomenological Eq. (1.1) for the components of the nuclear polarization itself. It will be shown that this reduction is automatic for nuclei with spin  $\frac{1}{2}$ ; depending upon the coupling to the molecular surroundings through the nuclear electric and magnetic moments, the reduction for higher values of the spin will be found to take place under certain special conditions which, however, have still a considerable range of practical applicability.

## 2. FORMULATION OF THE PROBLEM

In a completely general theory it would be necessary to consider all the nuclei in interaction with each other and with the molecular system as the total system. Because of the simplifying assumptions, introduced in Sec. 1, it is, however, sufficient to treat only the combined system of one representative nucleus and its molecular surroundings. The macroscopic results for many identical and independent nuclei can then be obtained by statistical averages.

The Hamiltonian of this system will be assumed to have the form

$$\mathcal{H} = \hbar E + \hbar F + \hbar G. \quad (2.1)$$

The first term represents the energy— $(\mathbf{H} \cdot \mathbf{u})$  of the nucleus in the external field  $\mathbf{H}$ . From Eq. (1.2), the magnetic moment  $\mathbf{u}$  is related to the spin vector  $\mathbf{I}$  through the relation  $\mathbf{u} = \hbar\gamma\mathbf{I}$ , and we have therefore

$$E = -\gamma(\mathbf{H} \cdot \mathbf{I}). \quad (2.2)$$

The second and third terms in (2.1) represent the energies of the molecular surroundings and of their interaction with the nucleus, respectively.

We choose a representation in which  $I_z$ , the  $z$  component of the nuclear spin, is diagonal with its eigenvalues given by the magnetic quantum number  $m = -I, -I+1, \dots, +I$ . The energy  $\hbar F$  of the molecular surroundings will likewise be assumed to be diagonal and the eigenvalues of  $F$  will be denoted by a frequency  $f$ ; acting as a heat reservoir, the molecular surroundings must be considered to have very many degrees of freedom so that its energy levels are not only practically continuous but in general also highly degenerate. We shall therefore use another symbol  $s$ , which will specify one of the possibly many states with the same energy  $\hbar f$ .

The dynamical behavior of our system is then described by a set of probability amplitudes  $a_{m,f,s}(t)$  or by the density matrix  $\rho$ , defined in Dirac's notation by

$$(mfs | \rho(t) | m'f's') = a_{m,f,s}(t)a_{m',f',s'}^*(t), \quad (2.3)$$

and satisfying the matrix equation

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

With (2.1), this equation can also be written as

$$d\rho/dt = -i[E + F + G, \rho], \quad (2.4)$$

where the square bracket stands as usual for the commutator. The condition of normalization for the probability amplitudes implies, according to (2.3), that the matrix  $\rho$  must be normalized so as to satisfy

$$\text{Tr}\{\rho(t)\} = \sum_{mfs} (mfs | \rho(t) | mfs) = 1.$$

From a normalized solution  $\rho(t)$  of (2.4) the expectation value of any physical quantity  $Q$ , represented by the matrix  $(mfs | Q | m'f's')$  is obtained in its time dependence

by the relation

$$\langle Q \rangle(t) = \text{Tr}\{Q\rho(t)\}. \quad (2.5)$$

The right side of this equation represents the diagonal sum or "trace" of the matrix product  $Q\rho$ .

With the form (1.3) for the external field we can also write (2.2) in the form

$$E = E_0 + E_1, \quad (2.6)$$

with

$$E_0 = -\omega I_z, \quad (2.7)$$

$$E_1 = -\gamma(\mathbf{H}_1 \cdot \mathbf{I}), \quad (2.8)$$

and where we have used the abbreviation

$$\omega = \gamma H_0 \quad (2.9)$$

for the circular frequency of precession of the nucleus in the strong field  $H_0$ . We shall now consider the nucleus in the field  $H_0$  and the molecular surroundings, uncoupled to each other, as the unperturbed system. With  $E$  of the form (2.6) the terms  $E_0$  and  $F$  in (2.4) will thus be treated as large, while the terms  $E_1$  and  $G$  will represent a small perturbation. In analogy to Dirac's perturbation theory we write therefore

$$\rho = AB\rho^*B^{-1}A^{-1}, \quad (2.10)$$

where  $A = e^{-iE_0t}$  or, with (2.7),

$$A = e^{i\omega I_z t}, \quad (2.11)$$

and

$$B = e^{-iFt}. \quad (2.12)$$

One obtains then from (2.4),

$$d\rho^*/dt = -i[E_1^* + G^*, \rho^*], \quad (2.13)$$

with

$$E_1^* = A^{-1}EA, \quad (2.14)$$

and

$$G^* = B^{-1}A^{-1}GAB. \quad (2.15)$$

The validity of (2.13) is directly verified by substituting (2.10) in (2.4), using (2.6) and the equality

$$B^{-1}A^{-1}E_1AB = A^{-1}E_1A.$$

This equality holds since  $B$ , like  $F$ , is an operator which acts only upon the variables  $f, s$  of the molecular surroundings and therefore commutes with  $E_1, A$ , and  $A^{-1}$ , which act upon  $m$  alone.

Denoting  $\rho$  and  $\rho^*$  at the time  $t=0$  by  $\rho(0)$  and  $\rho^*(0)$ , respectively, we have from (2.10), (2.11), (2.12) that

$$\rho^*(0) = \rho(0). \quad (2.16)$$

From this initial value one obtains by forward integration in two successive approximations the value of  $\rho^*(t)$  at a later time  $t$  in the form

$$\rho^*(t) = \rho(0) + \Delta^{(1)}\rho^* + \Delta^{(2)}\rho^*. \quad (2.17)$$

The first-order increment is

$$\begin{aligned} \Delta^{(1)}\rho^* = & -i \int_0^t [E_1^*(t'), \rho(0)] dt' \\ & -i \int_0^t [G^*(t'), \rho(0)] dt'. \end{aligned} \quad (2.18)$$

In the second-order increment we have to keep the terms which are quadratic in  $G^*$ , but we are allowed to neglect the cross terms of  $E_1^*$  and  $G^*$  as will be further discussed in the next section; it is then found to be

$$\Delta^{(2)}\rho^* = - \int_0^t \left( \int_0^{t'} [G^*(t'), [G^*(t''), \rho(0)]] dt'' \right) dt'. \quad (2.19)$$

For the purposes of this investigation we are interested only in the expectation value of quantities concerning the nuclear spin alone, such as the components of  $\mathbf{I}$ , the angular momentum of the nucleus in units  $\hbar$ . Quantities of this nature will be generally designated as "spin functions"; in our chosen representation they are diagonal in the variables  $f$  and  $s$ , referring to the molecular surroundings and hence of the form

$$(mfs|Q|m'f's') = (m|Q|m')\delta_{ff'}\delta_{ss'}. \quad (2.20)$$

In order to evaluate their expectation values according to (2.5) it is sufficient to know the "distribution matrix"  $\sigma$  defined by

$$(m|\sigma|m') = \sum_{fs} (mfs|\rho|m'fs), \quad (2.21)$$

instead of the general density matrix  $\rho$ . In fact, it follows directly from this definition and from (2.5) that

$$\langle Q \rangle = \text{Tr}\{Q\sigma\} = \sum_{mm'} (m'|Q|m)(m|\sigma|m') \quad (2.22)$$

is the expectation value of a spin function  $Q$  given by the matrix (2.20). In analogy to the transformation (2.10) we can introduce the matrix,

$$(m|\sigma^*|m') = \sum_{fs} (mfs|\rho^*|m'fs), \quad (2.23)$$

which is related to  $\sigma$  by

$$\sigma = A\sigma^*A^{-1}. \quad (2.24)$$

To prove this last relation from (2.10) and from the definitions [(2.21), (2.23)], one merely has to note that  $F$  and, through (2.12), also  $B$ , is diagonal in  $m$  while  $A$  is, according to (2.11) a pure spin function and therefore diagonal in  $f$  and  $s$ . Inserting (2.17) in (2.23), we find that

$$\begin{aligned} (m|\sigma^*(t)|m') = & (m|\sigma^*(0)|m') \\ & + (m|\Delta^{(1)}\sigma^*|m') + (m|\Delta^{(2)}\sigma^*|m'), \end{aligned} \quad (2.25)$$

with

$$(m|\sigma^*(0)|m') = \sum_{fs} (mfs|\rho(0)|m'fs), \quad (2.26)$$

$$(m|\Delta^{(1)}\sigma^*|m') = \sum_{fs} (mfs|\Delta^{(1)}\rho^*|m'fs), \quad (2.27)$$

$$(m|\Delta^{(2)}\sigma^*|m') = \sum_{fs} (mfs|\Delta^{(2)}\rho^*|m'fs). \quad (2.28)$$

In order to evaluate the matrix (2.26) and, by means of the expressions (2.18), (2.19) and the matrices (2.27), (2.28), a knowledge of the density matrix  $\rho$  at the time  $t=0$  is required. Actually it is not this matrix  $\rho(0)$  which is known but rather its statistical average, to be denoted by  $\bar{\rho}(0)$ . It indicates the fact that the surroundings are for  $t=0$  in statistical equilibrium at the absolute

temperature  $T$ . This implies that there exists no phase relation between the probability amplitudes for different states, characterized by  $f$  and  $s$ , and that the probability of finding the surroundings in any one of these states is given by the Boltzmann factor  $P(f)$ , which depends only on the energy  $\hbar f$ . Going back to the definition (2.3) of the density matrix and taking the statistical average of this equation for  $t=0$ , we have, therefore,

$$(mfs|\bar{\rho}(0)|m'f's') = (m|\sigma(0)|m')P(f)\delta_{ff'}\delta_{ss'}. \quad (2.29)$$

The appearance of the arbitrary matrix  $(m|\sigma(0)|m')$  signifies that we maintain complete generality in regard to the initial state of the nucleus. The fact that this matrix represents indeed the distribution matrix at the time  $t=0$  can be verified if one replaces  $\rho(0)$  by  $\bar{\rho}(0)$  in (2.26), noting further that

$$\sum_{f,s} P(f) = 1, \quad (2.30)$$

and that by virtue of (2.11) and (2.24),

$$(m|\sigma^*(0)|m') = (m|\sigma(0)|m'). \quad (2.31)$$

We shall from now on be concerned with statistical averages which are obtained through the replacement of the matrix  $\rho(0)$  by its average  $\bar{\rho}(0)$  of Eq. (2.29). In a strictly consistent notation this replacement should be indicated by placing a bar over the corresponding quantities, such as  $(m|\bar{\sigma}(t)|m')$ ,  $\langle\bar{Q}\rangle$ , etc. To avoid an overburdened notation we shall, however, omit this bar and keep the previous notations with the understanding that in the remaining part of this paper  $\rho(0)$  will be replaced throughout by the matrix (2.29) and that all further relations for the distribution matrices  $\sigma$ ,  $\sigma^*$  and for the expectation values of spin functions refer to their statistical averages.

The expressions (2.27), (2.28) for the statistical average of the increments  $\Delta^{(1)}\sigma^*$  and  $\Delta^{(2)}\sigma^*$  are thus directly obtained by writing Eqs. (2.18), (2.19) in matrix form, replacing  $(mfs|\rho(0)|m'f's')$  by (2.29) and using the equality

$$(mfs|G^*|m'f's') = e^{i(f-m\omega-f'+m'\omega)t}(mfs|G|m'f's'), \quad (2.32)$$

which is valid by virtue of the relations (2.15) and (2.11), (2.12). For the summations over  $f$ , implied by (2.27), (2.28) as well as by the formation of matrix products in (2.18), (2.19) we shall from now on assume that the energy values  $\hbar f$  of the molecular surroundings form practically a continuum. The number of states with a given quantum number  $s$  and with  $f$  between  $f$  and  $f+df$  will be given by

$$dn_s = \eta_s(f)df, \quad (2.33)$$

so that the symbol  $\sum_{f,s}$  is to be replaced throughout by  $\sum_s \int \eta_s(f)df$ . The relation (2.30) has in this notation the form

$$\sum_s \int \eta_s(f)P(f)df = 1, \quad (2.34)$$

and the Boltzmann factor  $P(f)$  in (2.29) is to be written explicitly as

$$P(f) = e^{-\hbar f/kT} / \sum_s \int \eta_s(f')e^{-\hbar f'/kT}df'. \quad (2.35)$$

Following the procedure indicated above and by virtue of (2.31) replacing in (2.29)  $(m|\sigma(0)|m')$  by  $(m|\sigma^*(0)|m')$ , one obtains

$$\begin{aligned} (m|\Delta^{(1)}\sigma^*|m') = & -i \sum_{m''} \int_0^t dt' \{ (m|E_1^*(t')|m'')(m''|\sigma^*(0)|m') \\ & - (m|\sigma^*(0)|m'')(m''|E_1^*(t')|m') \} \\ & -i \sum_s \sum_{m''} \int \eta_s(f)P(f)df \int_0^t dt' \\ & \times \{ e^{-i\omega(m-m'')t'}(mfs|G|m''fs)(m''|\sigma^*(0)|m') \\ & - e^{-i\omega(m''-m')t'}(m|\sigma^*(0)|m'')(m''fs|G|m'fs) \}, \end{aligned} \quad (2.36)$$

and

$$\begin{aligned} (m|\Delta^{(2)}\sigma^*|m') = & - \sum_{s,s'} \sum_{m'',m'''} \int \eta_s(f)P(f)df \int \eta_{s'}(f')df' \int_0^t dt' \int_0^{t'} dt'' \\ & \times \{ e^{i(f-m\omega-f'+m'\omega)t'+i(f'-m''\omega-f+m'''\omega)t''} \\ & \times (mfs|G|m''f's')(m''f's'|G|m'''fs)(m'''|\sigma^*(0)|m') \\ & - e^{i(f'-m\omega-f+m'\omega)t'+i(f'-m'''\omega-f+m''\omega)t''} \\ & \times (m'f's'|G|m''fs)(m''|\sigma^*(0)|m'')(m'''fs|G|m'f's') \\ & - e^{i(f-m'''\omega-f'+m'\omega)t'+i(f'-m\omega-f+m''\omega)t''} \\ & \times (m'f's'|G|m''fs)(m''|\sigma^*(0)|m'')(m'''fs|G|m'f's') \\ & + e^{i(f'-m'''\omega-f+m'\omega)t'+i(f'-m''\omega-f+m'''\omega)t''} \\ & \times (m|\sigma^*(0)|m'')(m''fs|G|m'''f's')(m'''f's'|G|m'fs) \}. \end{aligned} \quad (2.37)$$

To obtain the first term in (2.36) from that in (2.18) it has to be noted that  $E_1$ , defined by (2.8), is a spin function and thus, according to (2.20), to be represented by the matrix

$$(mfs|E_1(t)|m'f's') = (m|E_1(t)|m')\delta_{ff'}\delta_{ss'}. \quad (2.38)$$

$E_1^*(t)$  is therefore by virtue of (2.14) and (2.11) likewise a spin function represented by the matrix

$$(mfs|E_1^*(t)|m'f's') = (m|E_1^*(t)|m')\delta_{ff'}\delta_{ss'}. \quad (2.39)$$

with

$$(m|E_1^*(t)|m') = e^{-i\omega(m-m')t}(m|E_1(t)|m'). \quad (2.40)$$

### 3. THE BOLTZMANN EQUATION FOR THE DISTRIBUTION MATRIX

Equations (2.36), (2.37) for the increments yield, through (2.25), the transformed distribution matrix  $\sigma^*$  at a time  $t$  in terms of its initial value  $\sigma^*(0)$ . The time interval  $t$  must be chosen sufficiently small so that (2.25) represents a good approximation, i.e., that the omitted terms of higher order than the first in  $E_1$  and the second in  $G$  are indeed negligible. To estimate orders of magnitude this condition may be considered equivalent to stating that the lower order terms themselves which have been kept in  $\Delta^{(1)}\sigma^*$  and  $\Delta^{(2)}\sigma^*$  cause these increments to be small compared to the initial value  $\sigma(0)$ . For the linear terms in  $E_1^*$  in Eq. (2.36) it requires

$$\gamma|H_1|t \ll 1, \quad (3.1)$$

where we may define  $|H_1|$  as the "effective" magnitude of the weak variable field  $\mathbf{H}_1$  of Eq. (1.3). Due to the fact that  $E_1^*$  occurs in (2.36) as the integrand in a time integral and because of the relation (2.40) and the definition of  $E_1$  by (2.8), it is seen that the effective magnitude  $|H_1|$  depends greatly upon the frequencies contained in the actual field  $\mathbf{H}_1$ . In the case of greatest practical importance, where  $\mathbf{H}_1$  is transverse and varies with a frequency in the neighborhood of the resonance frequency  $\omega$ , the effective magnitude is of the same order as the actual magnitude of  $\mathbf{H}_1$ ; it is, however, smaller if  $\mathbf{H}_1$  varies with a frequency which differs appreciably from  $\omega$ . Concerning the increments due to the perturbation  $G$  it will be seen later that the linear terms in (2.36) do not have to be considered in this connection and that the quadratic terms in (2.37) become relatively important only after a time  $t$  of the order of the relaxation times  $T_1$  or  $T_2$ , defined in Sec. 1. It is therefore necessary, besides the condition (3.1), to demand both

$$t \ll T_1 \quad \text{and} \quad t \ll T_2. \quad (3.2)$$

We shall now proceed to discuss separately the various terms in (2.36) and (2.37). If we introduce the commutator of the two matrices  $(m|E_1^*|m')$  and  $(m|\sigma^*(0)|m')$ , the first term of (2.36) can be conveniently written in the form

$$-i \int_0^t (m|[E_1^*(t'), \sigma^*(0)]|m')dt'.$$

Upon carrying out the integration over  $t'$  and introducing the matrix

$$(m|K(t)|m') = \hbar \frac{1 - e^{-i\omega(m-m')t}}{i\omega(m-m')} \sum_s \int \eta_s(f) \times P(f)(mfs|G|m'sf)df, \quad (3.3)$$

we find that the second term of (2.36) can be similarly written in the form

$$-(i/\hbar)(m|[K(t), \sigma^*(0)]|m').$$

Besides satisfying the conditions (3.1), (3.2), the time interval  $t$  will from now on be chosen so large that it contains many periods of precession in the constant field  $H_0$ ; i.e., we demand also that

$$\gamma H_0 t = \omega t \gg 1. \quad (3.4)$$

The off-diagonal elements of the matrix (3.3) are small compared to the diagonal elements in the order  $1/\omega t$  and hence negligible in view of (3.4); we can therefore effectively write

$$(m|K(t)|m') = t\Delta E_m \delta_{mm'}, \quad (3.5)$$

where

$$\Delta E_m = \hbar \sum_s \int \eta_s(f) P(f)(mfs|G|mfs)df \quad (3.6)$$

represents the average value of the interaction energy  $\hbar G$ . Equation (3.5) expresses the fact that the first-order effect of the surroundings causes merely a shift of the nuclear Zeeman levels by  $\Delta E_m$ . While such shifts may actually occur, they are not essential for the following discussion and will for simplicity's sake be disregarded by assuming that  $\Delta E_m = 0$ ; this assumption is besides frequently justified by the fact that the perturbations upon the nucleus are of such fluctuating character as to render zero the diagonal matrix elements of  $G$  appearing in (3.6).

We are therefore justified in rewriting (2.36) in the simplified form

$$(m|\Delta^{(1)}\sigma^*|m') = -i \int_0^t (m|[E_1^*(t'), \sigma^*(0)]|m')dt', \quad (3.7)$$

being left solely with the second-order increment (2.37) for the effect of the coupling between the nucleus and its molecular surroundings.

To render the discussion of (2.37) more convenient we shall write this equation in the form

$$(m|\Delta^{(2)}\sigma^*|m') = -\sum_{s,s'} \int \eta_s(f) P(f)df \times \int \eta_{s'}(f') df' (mfs|L|m'f's'), \quad (3.8)$$

where it is seen from carrying out the integrations over  $t'$  and  $t''$  in (2.37) that

$$(mfs|L|m'f's') = \sum_{m'',m'''} \{ (mfs|G|m''f's')(m''f's'|G|m'''fs) \times (m'''|\sigma^*(0)|m') \varphi[f-f'-\omega(m-m''), m'''-m] - (mf's'|G|m''fs)(m''|\sigma^*(0)|m''')(m'''fs|G|m'f's') \times \varphi[f'-f-\omega(m-m''), m''-m+m'-m'''] - (mf's'|G|m''fs)(m''|\sigma^*(0)|m''')(m'''fs|G|m'f's') \times \varphi[f-f'-\omega(m'''-m'), m''-m+m'-m'''] + (m|\sigma^*(0)|m''')(m''fs|G|m'''f's')(m'''f's'|G|m'fs) \times \varphi[f'-f-\omega(m'''-m'), m'-m'''] \}, \quad (3.9)$$

with

$$\varphi[x, n] = \frac{x(e^{in\omega t} - 1) - n\omega(e^{ixt} - 1)}{n\omega x(x - n\omega)} \quad (3.10)$$

The integration over  $f'$  in (3.8) requires integrals of the form

$$\int \chi(x) \varphi[x, n] dx = t \int \chi(\xi/t) \frac{\xi(e^{i\nu} - 1) - \nu(e^{i\xi} - 1)}{\nu\xi(\xi - \nu)} d\xi \quad (3.11)$$

where

$$\xi = xt; \quad \nu = n\omega t. \quad (3.12)$$

For a sufficiently long interval  $t$ , the integration over  $\xi$  may be extended from  $-\infty$  to  $+\infty$  and the function  $\chi$  may be replaced by its value for the argument zero, provided that it is a sufficiently slowly varying function. The expression (3.11) becomes thus effectively

$$t\chi(0) \int_{-\infty}^{+\infty} \frac{\xi(e^{i\nu} - 1) - \nu(e^{i\xi} - 1)}{\nu\xi(\xi - \nu)} d\xi = \pi t\chi(0)(e^{i\nu} - 1)/i\nu. \quad (3.13)$$

It is seen from (3.9) and (3.10) that the quantity  $n$  appearing in the definition (3.12) of  $\nu$  is an algebraic sum of two or four values of the magnetic quantum number and hence an integer. All those terms encountered in the summation over  $m'$  and  $m''$  in (3.9) for which  $n \neq 0$  yield a periodic dependence upon  $t$  and are of relative order of magnitude  $1/\omega t$ , compared to the terms with  $n=0$ , which yield a linear dependence upon  $t$ . The former are therefore negligible compared to the latter if  $t$  is again chosen long enough to satisfy the condition (3.4), so that we can write

$$\int \chi(x) \varphi[x, n] dx = \begin{cases} \pi t\chi(0) & \text{for } n=0, \\ 0 & \text{for } n \neq 0. \end{cases}$$

With Dirac's  $\delta$ -function and the usual  $\delta$ -symbol this result can be expressed in the form

$$\varphi[x, n] = \pi t\delta(x)\delta_{n,0}. \quad (3.14)$$

Using this property of  $\varphi$  in the summation over  $m''$ ,  $m'''$  in (3.9) and in the integration over  $f'$  in (3.8) one obtains

$$(m|\Delta^{(2)}\sigma^*|m') = t \sum_{\tau} \{ 2\Gamma_{m'+\tau, m+\tau}^{-\tau} (m+\tau|\sigma^*(0)|m'+\tau) - (\Gamma_{mm'}^{\tau} + \Gamma_{m'm'}^{\tau}) (m|\sigma^*(0)|m') \}, \quad (3.15)$$

with

$$\Gamma_{mm'}^{\tau} = \pi \sum_{s, s'} \int \eta_s(f) P(f) \times \eta_{s'}(f+\tau\omega) (mfs|G|m+\tau, f+\tau\omega, s') \times (m'+\tau, f+\tau\omega, s'|G|m'fs) df. \quad (3.16)$$

Noting from (2.35) that

$$P(f+\tau\omega) = e^{-\kappa\tau} P(f),$$

with

$$\kappa = \hbar\omega/kT, \quad (3.17)$$

one obtains from (3.16) the relation

$$\Gamma_{m'+\tau, m+\tau}^{-\tau} = e^{-\kappa\tau} \Gamma_{mm'}^{\tau}. \quad (3.18)$$

The result (3.15) can thus be written in the more convenient form,

$$(m|\Delta^{(2)}\sigma^*|m') = t \sum_{\tau} \{ 2e^{-\kappa\tau} \Gamma_{mm'}^{\tau} (m+\tau|\sigma^*(0)|m'+\tau) - (\Gamma_{mm'}^{\tau} + \Gamma_{m'm'}^{\tau}) (m|\sigma^*(0)|m') \}. \quad (3.19)$$

In order that the derivation of the result (3.19) be valid another condition for the length of the time interval  $t$  has to be satisfied. Going back to Eqs. (3.8), (3.9) it is seen that the replacement of the function  $\chi(x)$  by its value for the argument  $x=0$  in (3.13), and hence the appearance of the Dirac  $\delta$ -function in (3.14), requires that products formed by the function  $\eta_{s'}(f')$  and matrix elements of the form  $(mfs|G|m'f's')$  are sufficiently slowly varying functions of the variable  $f'$ . To formulate this condition in a quantitative manner we introduce a "characteristic frequency"  $\omega^*$  of the molecular surroundings, which will indicate the effective scale in which the spread of the frequencies  $f'$  has to be measured. The condition justifying the step from Eq. (3.11) to (3.13) can then be written in the form

$$\omega^*t \gg 1. \quad (3.20)$$

The physical significance of the frequency  $\omega^*$  depends entirely upon the nature of the surroundings, and its order of magnitude may be very different in different cases. In crystals, e.g., it must be expected to be of the order  $k\theta/h$ , where  $\theta$  is the characteristic temperature, used in Debye's theory of the specific heat. In the case of gases,  $\omega^*$  may have the significance of the inverse time during a collision or between collisions, depending upon whether the interaction with the nucleus is directly due to the colliding partner (e.g., if the latter consists of a paramagnetic molecule) or whether it consists of the coupling to the rotation of the molecule, containing the nucleus, whereby transitions between rotational states are of primary importance. A third example is encountered in liquids where  $1/\omega^*$  may be primarily determined by the correlation time and thus dependent upon the viscosity.<sup>2</sup>

The validity of the results (3.7) and (3.19) for the increments of  $\sigma^*$  demands that one can choose a time interval  $t$  which is neither too short nor too long so that all four conditions [(3.1), (3.2), (3.4), (3.20)] are simultaneously satisfied. This evidently requires six conditions which all can be formulated by the relation

$$(\gamma|H_1|, 1/T_1, 1/T_2) \ll (\gamma H_0, \omega^*), \quad (3.21)$$

in the sense that each of the three quantities on the left side must be small compared to each of the two quantities on the right side. It is seen that the relative strength of the constant field  $H_0$  in comparison to the effective magnitude  $|H_1|$  of the variable field, mentioned in Sec. 1, is only a necessary but not a sufficient condition. Neither this condition nor the others implied by (3.21) is of course automatically fulfilled, and they may actually be violated in extreme cases (e.g., in the presence of a very weak constant field). In most practical cases they are, however, well fulfilled so that the conditions (3.21) represent no serious restriction for the applications of our results.

Assuming these conditions to be satisfied, we shall now, as mentioned in the beginning of this section, choose the time interval  $t$  short enough so that the expressions (3.7) and (3.19) represent the corresponding small increments of  $\sigma^*$ . Equation (2.25) can then be written in the differential form

$$d(m|\sigma^*|m')/dt = -i(m|[E_1^*(t), \sigma^*]|m') + \sum_{\tau} \{2e^{-\kappa\tau} \Gamma_{mm'}^{\tau}(m+\tau|\sigma^*|m'+\tau) - (\Gamma_{mm}^{\tau} + \Gamma_{m'm'}^{\tau})(m|\sigma^*|m')\}. \quad (3.22)$$

We shall claim this differential equation to be valid at any time  $t$  despite the fact that Eq. (2.25) refers to a specific initial time  $t=0$ . One might consider this claim to be obviously justified since any one instant can be chosen to be "initial" as well as any other. It must be kept in mind, however, that we have actually distinguished the time  $t=0$  by choosing at this instant the specific form (2.29) for the statistical average of the density matrix. This choice would evidently be strictly satisfied under the hypothetical condition that the interaction between the nucleus and its surroundings is ineffective up to the time  $t=0$  and that the latter had come to thermal equilibrium previous to this instant. However, because of the interaction, this equilibrium would be upset at a later time; and since in reality the interaction remains, of course, always effective, it might seem that our choice is based upon an inconsistency. Nevertheless, it is actually seen to be justified if one considers that the molecular surroundings normally have so very many degrees of freedom that it takes a long time before the interaction with the nucleus affects a sufficient number of them to cause an appreciable deviation from equilibrium conditions. We may safely assume either that this time is too long to matter for our considerations or that the molecular system is in sufficient contact with a "heat reservoir" which re-establishes equilibrium conditions more rapidly than they would be upset by the sole action of the nuclei. Physically this means that the "local heating" in the neighborhood of each nucleus is negligible, i.e., that the heat conduction of the molecular system is sufficiently high so that the heat transferred from the nucleus is carried away before it can effectively react backward upon the latter.

Under these circumstances it is legitimate to obtain the transformed distribution matrix  $\sigma^*$  as a solution of the differential equation (3.22). It remains to derive an equivalent equation for the distribution matrix  $\sigma$  related to  $\sigma^*$  by (2.24). This relation has, in view of (2.11), the matrix form

$$(m|\sigma|m') = e^{i\omega(m-m')t}(m|\sigma^*|m'), \quad (3.23)$$

so that with the further use of (2.7),

$$d(m|\sigma|m')/dt = -i(m|[E_0, \sigma]|m') + e^{i\omega(m-m')t} d(m|\sigma^*|m')/dt. \quad (3.24)$$

Inserting in the last term of (3.24) the expression (3.22), replacing  $\sigma^*$  by  $\sigma$  through (3.23), and using (2.6), one obtains thus

$$d(m|\sigma|m')/dt = -i(m|[E, \sigma]|m') + \sum_{\tau} \{2e^{-\kappa\tau} \Gamma_{mm'}^{\tau}(m+\tau|\sigma|m'+\tau) - (\Gamma_{mm}^{\tau} + \Gamma_{m'm'}^{\tau})(m|\sigma|m')\}. \quad (3.25)$$

In analogy to the classical Boltzmann equation for distribution functions, we shall refer to this system of differential equations as the Boltzmann equation for the distribution matrix  $\sigma$ . It allows the determination of the matrix elements of  $\sigma$  in an external field as a function of time in terms of their values at a given instant and represents the most general result of this investigation. Once this time dependence has been determined, that of the expectation value of any spin function  $Q$  is obtained from (2.22).

Before discussing this problem we shall note some of the properties of (3.25). From the condition of normalization,

$$\sum_{mfs} (mfs|\rho(t)|mfs) = 1,$$

for the density matrix (2.3) given in Sec. 2, one obtains from (2.21) for the distribution matrix  $\sigma$  the normalization,

$$\sum_m (m|\sigma(t)|m) = 1. \quad (3.26)$$

The fact that this condition is compatible with the Boltzmann equation (3.25) can be directly verified by showing that the time derivative of the left side vanishes by virtue of this equation and the relation (3.18).

It can also be verified that the spin states have a stationary Boltzmann distribution in the absence of the alternating field  $H_1$ , where one has from (2.6) and (2.8)  $E=E_0$ . It is expressed by the fact that (3.25) has in this case the time-independent normalized solution,

$$(m|\sigma|m') = e^{\kappa m} \delta_{mm'} \sinh(\kappa/2) / \sinh[\kappa(I + \frac{1}{2})], \quad (3.27)$$

and is essentially based upon the circumstance that  $E_0$  is, according to (2.7), represented by a diagonal matrix so that it commutes with (3.27).

Another case of considerable practical interest is that in which  $kT$  is large compared to the separation  $\hbar\omega$  of the nuclear Zeeman levels in the external field  $H_0$ , so

that according to (3.17)  $\kappa \ll 1$ . Keeping only the linear terms in  $\kappa$ , one has here

$$(m|\sigma|m') = (m|\sigma_0|m') + \kappa(m|\sigma_1|m'), \quad (3.28)$$

with

$$(m|\sigma_0|m') = \delta_{mm'}/(2I+1), \quad (3.29)$$

and where the matrix  $\sigma_1$  is a solution of

$$\begin{aligned} d(m|\sigma_1|m')/dt = & -i(m|[E, \sigma_1]|m') - \sum_{\tau} \{2\Gamma_{mm\tau}(m+\tau|\sigma_1|m'+\tau) \\ & - (\Gamma_{mm\tau} + \Gamma_{m'm\tau})(m|\sigma_1|m')\} \\ & - (2\delta_{mm'}/2I+1) \sum_{\tau} \tau \Gamma_{mm\tau}. \end{aligned} \quad (3.30)$$

4. EXPECTATION VALUES OF SPIN FUNCTIONS

We shall here consider the manner in which expectation values of spin functions vary with the time  $t$ ; in particular, we shall restrict ourselves to the case where the spin function  $Q$  and thereby, according to (2.20), the matrix  $(m|Q|m')$ , does not explicitly depend upon  $t$ . Nevertheless, its expectation value (2.22) will in general be a function of  $t$  through the time dependence of the distribution matrix  $\sigma$ , obtained by integrating the Boltzmann equation (3.25). While this procedure can in principle always be carried out, it may lead to rather involved calculations; an explicit knowledge of the distribution matrix is, however, in many cases not required. Particularly in those cases which lead to the phenomenological equations (1.1) and in which we are especially interested, it is possible to establish directly differential equations for expectation values which are far easier to treat than the general Boltzmann equation (3.25).

We shall therefore form directly

$$d\langle Q \rangle / dt = \sum_{mm'} (m'|Q|m) d(m|\sigma|m') / dt, \quad (4.1)$$

and insert on the right side of the equation the expression for the time derivative of  $\sigma$ , obtained from (3.25). While this insertion leads to no difficulty it does not, in itself, present a simple basis of discussion. A simple form is, however, obtained if we assume that the interaction operator  $G$  of Eq. (2.1) can be expanded in the form

$$G = \sum_{l, \tau} I_l^\tau F_l^{-\tau}, \quad (4.2)$$

where the operators  $I_l^\tau$  will be a pure spin function while the operators  $F_l^\tau$  will act upon the variables of the molecular surroundings alone, and are to be represented by matrices of the form

$$(mfs|F_l^\tau|m'f's') = (fs|F_l^\tau|f's')\delta_{mm'}. \quad (4.3)$$

It will further be assumed that  $I_l^\tau$  is represented by a matrix of the form

$$(m|I_l^\tau|m') = I_{lm}^\tau \delta_{m, m'+\tau}. \quad (4.4)$$

The form (4.2) corresponds to the usual expansion of the energy of interaction between the nucleus and an external electromagnetic field in magnetic dipole, elec-

tric quadrupole, and higher terms. With the indices  $l=1, 2$  for magnetic dipole- and electric quadrupole-interaction, respectively, one has for  $l=1$ ,

$$\begin{aligned} I_1^0 &= I_z, & F_1^0 &= -\gamma H_z', \\ I_1^{\pm 1} &= I_{\pm}, & F_1^{\pm 1} &= -\frac{1}{2}\gamma(H_x' \pm iH_y'), \\ I_1^\tau &= 0, & \text{for } |\tau| > 1; \end{aligned} \quad (4.5)$$

and for  $l=2$ ,

$$\begin{aligned} I_2^0 &= 2I_z^2 - I_x^2 - I_y^2, \\ F_2^0 &= -\{q/4\hbar I(2I-1)\} \partial E_z' / \partial z, \\ I_2^{\pm 1} &= I_z I_{\pm} + I_{\pm} I_z, \\ F_2^{\pm 1} &= -\{q/4\hbar I(2I-1)\} (\partial E_x' / \partial z \pm i \partial E_y' / \partial z), \\ I_2^{\pm 2} &= (I_{\pm})^2, \\ F_2^{\pm 2} &= -\{q/8\hbar I(2I-1)\} (\partial E_x' / \partial x \\ &\quad - \partial E_y' / \partial y \pm 2i \partial E_x' / \partial y), \\ I_2^\tau &= 0, & \text{for } |\tau| > 2, \end{aligned} \quad (4.6)$$

where we have used the abbreviation

$$I_{\pm} = I_x \pm iI_y. \quad (4.7)$$

$\gamma$  stands further for the gyromagnetic ratio (1.2) of the nucleus, and  $q$  for its electric quadrupole moment. The magnetic field components  $H_x', H_y', H_z'$ , as well as the derivatives of the electric field components  $E_x', E_y', E_z'$ , are to be taken at the position of the nucleus and refer to the fields produced by the molecular surroundings; they are therefore to be represented by matrices acting only upon the variables  $f$  and  $s$ . The terms for higher values of  $l$  in (4.2) correspond to higher multipole interactions and their explicit form will not be needed in our further discussion.

Using the form (4.2) of  $G$  and the Eqs. (4.3) and (4.4), one obtains now from (3.16)

$$\Gamma_{mm'\tau} = \sum_{l, \nu} I_{lm}^{-\tau} I_{\nu, m'+\tau} \Phi_{l\nu}^\tau, \quad (4.8)$$

with

$$\begin{aligned} \Phi_{l\nu}^\tau = \pi \sum_{s, s'} \int \eta_s(f) P(f) \eta_{s'}(f+\tau\omega) & (fs|F_l^\tau|f+\tau\omega, s') \\ & \times (f+\tau\omega, s'|F_\nu^{-\tau}|fs) df. \end{aligned} \quad (4.9)$$

By expressing the time derivative of the distribution matrix through the Boltzmann equation (3.25) with the expression (4.8) inserted and using the relation (4.4), one obtains now from (4.1)

$$\begin{aligned} d\langle Q \rangle / dt = -i\langle [Q, E] \rangle + \sum_{\tau, l, \nu} \Phi_{l\nu}^\tau \{2e^{-\kappa\tau} \langle I_\nu^\tau Q I_\nu^{-\tau} \rangle \\ - \langle Q I_\nu^{-\tau} I_\nu^\tau \rangle - \langle I_\nu^{-\tau} I_\nu^\tau Q \rangle\}. \end{aligned} \quad (4.10)$$

Noting the relation

$$\Phi_{l\nu}^{-\tau} = e^{-\kappa\tau} \Phi_{l\nu}^\tau, \quad (4.11)$$

which follows from (4.9) in analogy to (3.18), and the



identity

$$2I_i^{-\tau}QI_{i'}^{\tau} - QI_i^{-\tau}I_{i'}^{\tau} - I_i^{-\tau}I_{i'}^{\tau}Q \\ = I_i^{-\tau}[Q, I_{i'}^{\tau}] + [I_i^{-\tau}, Q]I_{i'}^{\tau},$$

the equation (4.10) can be written in the still simpler form,

$$d\langle Q \rangle / dt = -i\langle [Q, E] \rangle \\ + \sum_{\tau i i'} \Phi_{i i'}^{\tau} \langle I_i^{-\tau} [Q, I_{i'}^{\tau}] + [I_i^{-\tau}, Q] I_{i'}^{\tau} \rangle, \quad (4.12)$$

which is particularly suitable for our further discussions.

We are for our purposes particularly interested in the case where  $Q$  stands for any one of the components of the spin vector  $\mathbf{I}$ . In fact, the expectation value of the magnetic moment  $\mathbf{u}$  of the nucleus is directly given by that of  $\mathbf{I}$  through

$$\langle \mathbf{u} \rangle = \gamma \hbar \langle \mathbf{I} \rangle, \quad (4.13)$$

where  $\gamma$  is the gyromagnetic ratio (1.2). If there are  $n$  nuclei of the considered kind per unit volume whose molecular surroundings have the same properties, one has for the macroscopic polarization vector

$$\mathbf{M} = n \langle \mathbf{u} \rangle = n \gamma \hbar \langle \mathbf{I} \rangle, \quad (4.14)$$

where the expectation values refer to the representative single nucleus, treated in the previous sections. The fact that the macroscopic quantity  $\mathbf{M}$  has to be obtained from a statistical average over expectation values of the microscopic quantities  $\mathbf{u}$  and  $\mathbf{I}$  needs no further consideration here; it has been taken into account in the previous replacement of the actual density matrix by its statistical average through Eq. (2.29). The time dependence of  $\mathbf{M}$  is thus directly given by that of  $\langle \mathbf{I} \rangle$ , and the validity of the phenomenological equation (1.1) demands that the equations obtained from (4.12) with  $Q = I_{x,y,z}$  result in a system of linear differential equations which differs from (1.1) merely by the factor  $n\gamma\hbar$ .

The fact that the first term on the left side of (4.12) has indeed the proper structure, demanded by the corresponding term in (1.1), is immediately seen from the commutation rules

$$[I_x, I_y] = iI_z; \quad [I_y, I_z] = iI_x; \quad [I_z, I_x] = iI_y, \quad (4.15)$$

which yield, with the expression (2.2) for  $E$ ,

$$-i\langle [\mathbf{I}, E] \rangle = \gamma \langle \mathbf{I} \times \mathbf{H} \rangle. \quad (4.16)$$

For the discussion of the second term we neglect the contributions for the values  $l, l' > 2$ . This means that we shall consider only magnetic dipole and electric quadrupole interactions of the nucleus and its surroundings; the higher moments will be neglected both for simplicity's sake and because of their subordinate practical importance. With this understanding, it is also permissible to omit the mixed terms with  $l=1, l'=2$ , or vice versa, for with the magnetic field of Eqs. (4.5) an axial vector and the electric field of Eqs. (4.6) a polar vector, there is no relation between their signs

so that the corresponding quantities  $\Phi_{12}^{\tau}$  and  $\Phi_{21}^{\tau}$ , defined by (4.9), must be indeed expected to vanish.

Using the abbreviation

$$S_i(Q) = \sum_{\tau} \Phi_{i i'}^{\tau} \langle I_i^{-\tau} [Q, I_{i'}^{\tau}] + [I_i^{-\tau}, Q] I_{i'}^{\tau} \rangle, \quad (4.17)$$

we can thus write the result of substituting for  $Q$  the components of  $\mathbf{I}$  in (4.12) in the form

$$d\langle \mathbf{I} \rangle / dt = \gamma \langle \mathbf{I} \times \mathbf{H} \rangle + S_1(\mathbf{I}) + S_2(\mathbf{I}). \quad (4.18)$$

The evaluation of the expressions  $S_1(\mathbf{I})$  and  $S_2(\mathbf{I})$  is straightforward; one has merely to use the expressions of  $I_1^{\tau}$  and  $I_2^{\tau}$ , given in (4.5) and (4.6), to apply the commutation relations (4.15), and to use the fact that  $I_x^2 + I_y^2 + I_z^2 = I(I+1)$ . The procedure is, however, somewhat lengthy, and we shall therefore omit intermediate steps and give the results directly. Combining terms with equal and opposite values of  $\tau$  by means of the relation (4.11) one finds that

$$S_1(I_z) = -2\Phi_{11}^0(1+e^{-\kappa})\langle I_z \rangle \\ + 2\Phi_{11}^1(1-e^{-\kappa})\langle I(I+1) - \langle I_z^2 \rangle \rangle, \quad (4.19)$$

$$S_1(I_{x,y}) = -\Phi_{11}^0\langle I_{x,y} \rangle - \Phi_{11}^1(1+e^{-\kappa})\langle I_{x,y} \rangle \\ - \Phi_{11}^1(1-e^{-\kappa})\langle I_{x,y}I_z + I_zI_{x,y} \rangle, \quad (4.20)$$

$$S_2(I_z) = -2\Phi_{22}^1(1+e^{-\kappa})\langle 8(I_z)^3 - 4I(I+1)I_z + I_z \rangle \\ + 2\Phi_{22}^2(1-e^{-\kappa})\langle 4I(I+1)\langle I_z \rangle^2 - 4\langle I_z \rangle^4 \\ - 5\langle I_z \rangle^2 + I(I+1) \rangle + 4\Phi_{22}^2\langle 1+e^{-2\kappa} \rangle \\ \times \langle 4\langle I_z \rangle^3 - 4I(I+1)I_z + 2I_z \rangle \\ + 4\Phi_{22}^2(1-e^{-2\kappa})\langle I^2(I+1)^2 - 2I(I+1)\langle I_z \rangle^2 \\ + \langle I_z \rangle^4 + 5\langle I_z \rangle^2 - 2I(I+1) \rangle \rangle, \quad (4.21)$$

$$S_2(I_{x,y}) = -9\Phi_{22}^0\langle 2\langle I_{x,y}(I_z)^2 + (I_z)^2I_{x,y} \rangle - I_{x,y} \rangle \\ + \Phi_{22}^1(1+e^{-\kappa})\langle (3-4I(I+1))I_{x,y} \rangle \\ - \Phi_{22}^1(1-e^{-\kappa})\langle 4\langle I_{x,y}(I_z)^3 + (I_z)^3I_{x,y} \rangle \\ + 7\langle I_{x,y}I_z + I_zI_{x,y} \rangle + \Phi_{22}^2(1+e^{-2\kappa}) \\ \times \langle 6\langle I_{x,y}(I_z)^2 + (I_z)^2I_{x,y} \rangle - 4I(I+1)I_{x,y} \rangle \\ + \Phi_{22}^2(1-e^{-2\kappa})\langle 2\langle I_{x,y}(I_z)^3 + (I_z)^3I_{x,y} \rangle \\ + (4-2I(I+1))\langle I_{x,y}I_z + I_zI_{x,y} \rangle \rangle. \quad (4.22)$$

The relation of these expressions to the validity of the phenomenological equations will be discussed in the following section.

## 5. CASES OF VALIDITY OF THE PHENOMENOLOGICAL EQUATION

Equation (4.18) with the general expressions for  $S_1$  and  $S_2$ , given by (4.19) to (4.22), has the same range of validity as the Boltzmann equation simplified by the omission of higher multipole interactions. It has the advantage that it relates the time derivative of the expectation value of  $\mathbf{I}$  directly to the expectation values of other functions of its components. The time dependence of the latter would, however, have to be known in order to integrate (4.18), and it would thus seem that one is led back to the distribution matrix, i.e., to the integration of the general Boltzmann equa-

tion (3.25). Yet there exists a number of important special cases where the expectation values appearing in  $S_1(\mathbf{I})$  and  $S_2(\mathbf{I})$  can be reduced to contain only those of the components of  $\mathbf{I}$  itself. Equation (4.18) represents in this case a set of three simultaneous linear differential equations of the first order between these components, which is not only easier to integrate than (3.25) but actually results, as we shall see, in Eq. (1.1) for the macroscopic polarization. We will now discuss these cases separately.

*Case a,  $I = \frac{1}{2}$ :* This case is particularly simple since a nucleus with spin  $\frac{1}{2}$  has no electric quadrupole moment so that the term  $S_2$  in (4.18) is absent. Noting further that one has here

$$I(I+1) - \langle I_z \rangle^2 = \frac{1}{2}; \quad \langle I_z I_{x,y} + I_{x,y} I_z \rangle = 0,$$

one obtains from (4.19)

$$S_1(I_z) = -\langle I_z \rangle / T_1 + I_0 / T_1, \quad (5.1)$$

$$S_1(I_{x,y}) = -\langle I_{x,y} \rangle / T_2, \quad (5.2)$$

with

$$1/T_1 = 2\Phi_{11}^1(1 + e^{-\kappa}), \quad (5.3)$$

$$1/T_2 = (1/2T_1) + \Phi_{11}^0, \quad (5.4)$$

$$I_0 = (1/2) \tanh(\kappa/2). \quad (5.5)$$

Inserting this result in (4.18) and multiplying this equation according to (4.14) with  $n\gamma\hbar$ , it is seen that one obtains here indeed Eq. (1.1) for the macroscopic polarization with

$$M_0 = n\gamma\hbar I_0 = n\mu \tanh(H_0\mu/kT) \quad (5.6)$$

as the correct equilibrium polarization of nuclei with spin  $\frac{1}{2}$  and magnetic moment  $\mu$  in an external field  $H_0$ . The second equality in (5.6) has been obtained from (5.5), using further (1.2) for  $I = \frac{1}{2}$ , (2.9), and (3.17). We see thus that the general Boltzmann equation (3.25) leads for nuclei with spin  $\frac{1}{2}$  rigorously to the phenomenological equation (1.1).

*Case b,  $\kappa \ll 1$ :* The range of validity of the phenomenological equations is considerably extended by assuming  $\kappa \ll 1$ ; this means, according to Eq. (3.17), that the Zeeman splitting of the nuclear energy levels due to the external field  $H_0$  is small compared to  $kT$ . Actually this is hardly a restriction of the practical applications since  $\kappa$  is of the order of  $10^{-6}$  for fields of about  $10^4 G$  and at normal temperatures; it becomes comparable to unity only at exceedingly low temperatures or in exceedingly strong fields.

The expressions for  $S_1$  and  $S_2$ , given in Eqs. (4.19) to (4.22), are greatly simplified by this assumption which will be made from now on. It has been seen in Sec. 3 that the distribution matrix has in this case the form (3.28) with the dominant part  $\sigma_0$  given by (3.29). Keeping only terms linear in  $\kappa$  it is, in fact, permissible to replace in  $S_1$  and  $S_2$  the terms  $(1 + e^{-\kappa})$  and  $(1 + e^{-2\kappa})$  by 2 since these two expressions appear only in products containing the expectation values of  $I_z$ ,

$I_{x,y}$ ,  $I_z^3$ , and  $(I_{x,y}I_z^2 + I_z^2I_{x,y})$  which are themselves of order  $\kappa$ . To the same order one can replace  $(1 - e^{-\kappa})$  by  $\kappa$  and  $(1 - e^{-2\kappa})$  by  $2\kappa$  and evaluate the expectation values of the spin functions with which these expressions are multiplied by substituting for the distribution matrix its dominant part (3.29). Denoting the approximate expectation values, thus obtained, by the subscript 0, one has

$$\langle I_z^2 \rangle_0 = (1/3)I(I+1);$$

$$\langle I_z^4 \rangle_0 = (1/15)I(I+1)[3I(I+1) - 1],$$

and further

$$\langle I_{x,y}I_z + I_zI_{x,y} \rangle_0 = 0; \quad \langle I_{x,y}(I_z)^3 + (I_z)^3I_{x,y} \rangle_0 = 0.$$

If we omit all terms of higher order in  $\kappa$  than the first, the expressions (4.19) to (4.22) thus simplify

$$S_1(I_z) = -4\Phi_{11}^1\langle I_z \rangle + (4\kappa/3)\Phi_{11}^1I(I+1), \quad (5.7)$$

$$S_1(I_{x,y}) = -(2\Phi_{11}^1 + \Phi_{11}^0)\langle I_{x,y} \rangle, \quad (5.8)$$

$$S_2(I_z) = 32(\Phi_{22}^2 - \Phi_{22}^1)\langle I_z^3 \rangle + 4\{\Phi_{22}^1[4I(I+1) - 1] - \Phi_{22}^2[2I(I+1) - 1]\}\langle I_z \rangle + (4\kappa/15) \times (\Phi_{22}^1 + 4\Phi_{22}^2)[4I(I+1) - 3]I(I+1), \quad (5.9)$$

$$S_2(I_{x,y}) = 6(2\Phi_{22}^2 - 3\Phi_{22}^0)\langle I_{x,y}(I_z)^2 + (I_z)^2I_{x,y} \rangle + \{9\Phi_{22}^0 + \Phi_{22}^1[6 - 8I(I+1)] - 8\Phi_{22}^2I(I+1)\}\langle I_{x,y} \rangle. \quad (5.10)$$

It is seen that the magnetic dipole terms (5.7) and (5.8) have the same form as those given by (5.1) and (5.2), respectively, in the previous case of spin  $\frac{1}{2}$  and thus would, by themselves, lead in the same way to the phenomenological Eq. (1.1) with

$$1/T_1 = 4\Phi_{11}^1, \quad (5.11)$$

$$1/T_2 = (1/2T_1) + \Phi_{11}^0, \quad (5.12)$$

$$I_0 = (\kappa/3)I(I+1), \quad (5.13)$$

and where

$$M_0 = n\gamma\hbar I_0 = (n\mu^2 H_0 / 3kT)(I+1)/I \quad (5.14)$$

represents the correct value of the equilibrium polarization up to terms of order  $\kappa$  and therefore linear in  $H_0$ .

The electric quadrupole terms (5.9) and (5.10) are in general not of the form leading to (1.1) and may invalidate this equation since nuclei with  $I > \frac{1}{2}$  can have a finite quadrupole moment. Their relative importance is, however, frequently found to be small; in the presence of paramagnetic catalysts particularly the magnetic dipole relaxation can easily become dominant unless one is dealing with nuclei of rather large quadrupole moments. Besides, it will be shown below that these terms likewise reduce in certain cases to a form leading to the phenomenological equation so that it remains here valid, even if quadrupole interaction contributes appreciably to the relaxation.

*Case c,  $I = 1$ :* Since nuclei with spin 1 can have no higher moments than those due to a magnetic dipole

and an electric quadrupole, one is here rigorously justified in the earlier omission of all higher interaction terms. One has here further

$$(m|I_z^3|m') = m^3\delta_{mm'} = m\delta_{mm'} = (m|I_z|m'), \quad (5.15)$$

since  $m^3 = m$  for the three possible values  $m=0, \pm 1$ ; and

$$(m|I_{x,y}(I_z)^2 + (I_z)^2 I_{x,y}|m') \\ = (m^2 + m'^2)(m|I_{x,y}|m') = (m|I_{x,y}|m'), \quad (5.16)$$

since  $(m|I_{x,y}|m')$  differs from zero only for  $m=0, m'=\pm 1$  or  $m' = 0, m = \pm 1$ , in all of which cases  $m^2 + m'^2 = 1$ . Using the ensuing relations,

$$\langle I_z^3 \rangle = \langle I_z \rangle, \quad (5.17)$$

and

$$\langle I_{x,y}(I_z)^2 + (I_z)^2 I_{x,y} \rangle = \langle I_{x,y} \rangle, \quad (5.18)$$

one obtains thus from (5.9) with  $I=1$

$$S_2(I_z) = -4(\Phi_{22}^1 + 4\Phi_{22}^2)(\langle I_z \rangle - (2\kappa/3)), \quad (5.19)$$

and from (5.10)

$$S_2(I_{x,y}) = -(9\Phi_{22}^0 + 10\Phi_{22}^1 + 4\Phi_{22}^2)\langle I_{x,y} \rangle. \quad (5.20)$$

Combining these results with (5.7) and (5.8) for  $I=1$ , we see therefore that

$$S_1(I_z) + S_2(I_z) = -(\langle I_z \rangle - I_0)/T_1, \quad (5.21)$$

$$S_1(I_{x,y}) + S_2(I_{x,y}) = -\langle I_{x,y} \rangle/T_2, \quad (5.22)$$

with

$$1/T_1 = 4(\Phi_{11}^1 + \Phi_{22}^1 + 4\Phi_{22}^2), \quad (5.23)$$

$$1/T_2 = \Phi_{11}^0 + 2\Phi_{11}^1 + 9\Phi_{22}^0 + 10\Phi_{22}^1 + 4\Phi_{22}^2, \quad (5.24)$$

and

$$I_0 = 2\kappa/3. \quad (5.25)$$

Inserting (5.21) and (5.22) in (4.18) and multiplying with  $n\gamma\hbar$ , one is thus led again to Eq. (1.1) with the proper value for the equilibrium polarization  $M_0 = n\gamma\hbar I_0$ . In order to obtain for spin 1 from the general Boltzmann equation the phenomenological equation (1.1) one needs thus merely the condition  $\kappa \ll 1$ , which is practically always satisfied.

*Case d*, isotropic molecular surroundings: For spin values larger than unity it is not possible, in general, to reduce the expressions (5.9) and (5.10) to a form which leads to the phenomenological equation. The only cases where this equation can here still be expected to be valid are those in which the coefficients of the expectation values  $\langle I_z^3 \rangle$  and  $\langle I_{x,y}I_z^2 + I_z^2 I_{x,y} \rangle$  vanish, i.e., where one has the relations

$$\Phi_{22}^2 = \Phi_{22}^1 = 3\Phi_{22}^0/2. \quad (5.26)$$

Even in cases where there exist certain relations among the operators  $F_{2\tau}$  ( $\tau=0, \pm 1, \pm 2$ ), defined in (4.6), there is still in general no relation among the corresponding values  $\Phi_{22}^\tau$  because of the different arguments  $f + \tau\omega$  which appear in the integration over  $f$  in (4.9).

The situation is different, however, if the functions containing these arguments are sufficiently slowly

varying so that they do not change appreciably if  $f$  is increased by  $\omega$  or  $2\omega$ . If we use again the "characteristic frequency"  $\omega^*$  of the molecular surroundings, introduced in Sec. 3, this condition can be formulated by

$$\omega^* \gg \omega = \gamma H_0, \quad (5.27)$$

which is evidently compatible with, but more stringent than, the conditions (3.21) for  $\omega^*$ . One has in this case from (4.9)

$$\Phi_{11}^\tau \cong \pi \sum_{s,s'} \int \eta_s(f) P(f) \eta_{s'}(f) (fs|F_{1\tau}|fs') \\ \times (fs'|F_{1-\tau}|fs) df. \quad (5.28)$$

If the molecular surroundings have no preferred directions, there exist relations between the quantities  $F_{1\tau}$  ( $\tau=0, \pm 1$ ) and likewise between the quantities  $F_{2\tau}$  ( $\tau=0, \pm 1, \pm 2$ ), since it is seen from (4.5) and (4.6) that they are proportional to the components of the vector  $\mathbf{H}'$  and to those of the second-rank tensor, formed by the derivatives of  $\mathbf{E}'$ , respectively. As a consequence, there exist here also relations between the corresponding quantities  $\Phi_{11}^\tau$ , given by (5.28).

The manner in which these relations can be obtained will first be illustrated for the quantities  $\Phi_{11}^0$  and  $\Phi_{11}^1$ : Under a rotation of the coordinate system, characterized by three Euler angles, the three quantities  $F_{10}, F_{11}^1$ , and  $F_{1-1}$  given by (4.5) will transform according to the vector transformation of  $H_x', H_y', H_z'$ . The same transformation as that of the quantities  $F_{1\tau}$  is undergone by their matrix elements, appearing in (5.28), and the quantities  $\Phi_{11}^\tau$  will therefore undergo the same transformation as the corresponding products of two vector components. In a notation emphasizing this transformation property, we can write

$$\Phi_{11}^0 \sim \{H_z'^2\}, \quad (5.29)$$

$$\Phi_{11}^1 \sim \frac{1}{4} \{ (H_x' + iH_y')(H_x' - iH_y') \}. \quad (5.30)$$

The result for an isotropic medium can now be obtained from that obtained for a given rotation of the coordinate system by averaging with uniform weight over all three Euler angles. Indicating this process by a bar, we have therefore, in this case,

$$\Phi_{11}^0 \sim \{\overline{H_z'^2}\}, \quad (5.31)$$

$$\Phi_{11}^1 \sim \frac{1}{4} \{\overline{H_x'^2} + \overline{H_y'^2}\}, \quad (5.32)$$

and since

$$\overline{H_x'^2} = \overline{H_y'^2} = \overline{H_z'^2},$$

we have

$$\Phi_{11}^0 = 2\Phi_{11}^1. \quad (5.33)$$

Using this result for the formulas (5.11) and (5.12), obtained for the relaxation times due to pure magnetic dipole interaction, it is seen that one here obtains

$$1/T_1 = 1/T_2 = 2\Phi_{11}^0, \quad (5.34)$$

i.e., the well-known fact that the longitudinal and

transverse relaxation times are equal in an isotropic medium whose characteristic frequency  $\omega^*$  is large compared to the Larmor frequency  $\omega$  of the nuclei.

An analogous procedure leads to the desired relations between the quantities  $\Phi_{22}^\tau$ . In analogy to (5.29) and (5.30) and using the expressions (4.6) for  $F_2^\tau$ , we write

$$\Phi_{22}^0 \sim \{(\partial E_x'/\partial z)^2\}, \quad (5.35)$$

$$\Phi_{22}^1 \sim \{[(\partial E_x'/\partial z) + i(\partial E_y'/\partial z)] \times [(\partial E_x'/\partial z) - i(\partial E_y'/\partial z)]\}, \quad (5.36)$$

$$\Phi_{22}^2 \sim \frac{1}{4} \left\{ \left( \frac{\partial E_x'}{\partial x} - \frac{\partial E_y'}{\partial y} + 2i \frac{\partial E_x'}{\partial y} \right) \times \left( \frac{\partial E_x'}{\partial x} - \frac{\partial E_y'}{\partial y} - 2i \frac{\partial E_x'}{\partial y} \right) \right\}. \quad (5.37)$$

By averaging over the Euler angles of rotation, one has

$$\overline{(\partial E_x'/\partial x)^2} = \overline{(\partial E_y'/\partial y)^2} = \overline{(\partial E_z'/\partial z)^2}.$$

Further, because of the condition  $\text{div } \mathbf{E}' = 0$

$$\overline{\left( \frac{\partial E_x'}{\partial x} \frac{\partial E_y'}{\partial y} \right)} = \overline{\left( \frac{\partial E_y'}{\partial y} \frac{\partial E_z'}{\partial z} \right)} = \overline{\left( \frac{\partial E_z'}{\partial z} \frac{\partial E_x'}{\partial x} \right)} = -\frac{1}{2} \overline{\left( \frac{\partial E_z'}{\partial z} \right)^2}$$

and

$$\overline{(\partial E_x'/\partial z)^2} = \overline{(\partial E_y'/\partial z)^2} = \overline{(\partial E_x'/\partial y)^2} = \frac{3}{4} \overline{(\partial E_z'/\partial z)^2}.$$

The use of these relations in the averages of the right side of the equations (5.35) to (5.37) yields directly the equalities (5.26). With these relations between the quantities  $\Phi_{22}^\tau$  and the relation (5.33) between the quantities  $\Phi_{11}^\tau$ , one obtains now from Eqs. (5.7) to (5.10):

$$S_1(I_z) + S_2(I_z) = -\langle (I_z) - I_0 \rangle / T_1, \quad (5.38)$$

$$S_1(I_{x,y}) + S_2(I_{x,y}) = -\langle I_{x,y} \rangle / T_2, \quad (5.39)$$

with

$$1/T_1 = 1/T_2 = 2\Phi_{11}^0 + 6\Phi_{22}^0 [4I(I+1) - 3], \quad (5.40)$$

and

$$I_0 = \frac{1}{3} \kappa I(I+1). \quad (5.41)$$

Equations (5.38) to (5.41) lead again to the phenomenological equation (1.1). It is interesting to note, however, that the condition of an isotropic molecular medium with high characteristic frequency, which we

have here needed for the validity of the phenomenological equation, leads at the same time to the equality (5.40) of the longitudinal and the transverse relaxation time. While the condition of isotropy is well satisfied in gases and liquids, there exists the possibility, as shown by Bloembergen,<sup>2</sup> that the viscosity of liquids prevents the existence of a sufficiently high characteristic frequency  $\omega^*$  to satisfy the condition (5.27), with the ensuing result that  $T_2$  is appreciably shorter than  $T_1$ . One has therefore to conclude that, with the exception of nuclei of spin 1, the phenomenological equation is in such cases invalid if electrical quadrupole interaction contributes appreciably to relaxation.

## 6. CONCLUSIONS

The dynamics of nuclear induction has been treated here with considerable generality, the only serious restriction lying in the omission of those features for which the spin-spin interaction between neighboring nuclei is essential. Particularly the differential equation (3.25) has, except for this restriction, a practically perfect and general validity. It is true that its derivation required the further conditions (3.21); one must note, on the other hand, that the largest of the three quantities on the left side of this inequality measures the order of magnitude of the line width in the frequency scale so that their required smallness is equivalent to the requirement of relatively narrow resonance lines.

While this condition and thereby the validity of the Boltzmann equation (3.25) is practically always ensured, there are more serious further restrictions to the validity of the very much simpler phenomenological equation (1.1). We shall here briefly summarize them:

1. For  $I = \frac{1}{2}$ : No further restrictions.
2. For  $I = 1$ :  $H_0\mu \ll kT$ .
3. For  $I > 1$  and negligible quadrupole-relaxation:  $H_0\mu \ll kT$ .
4. For  $I > 1$  and appreciable quadrupole-relaxation:  $H_0\mu \ll kT$ ; the molecular surroundings are further required to be isotropic and to have a characteristic frequency large compared to the Larmor frequency of the nuclei. As a consequence of these requirements one has  $T_1 = T_2$ . It is only the last-mentioned restriction which represents a serious limitation to the validity of the phenomenological equation; it demands in practice that the sample consist of a gas or a liquid with low viscosity.

This investigation shows, nevertheless, that there exists a considerable range of validity for the phenomenological equation which accounts for its empirical usefulness. It may finally be hoped that a treatment of similar generality can be developed to include also features of spin-spin interaction and line structure.