TABLE V. N II $2s^2\,2p\,5g$. Observed and calculated levels.

Designation Limit	L	$[K]$	J		Level (cm^{-1}) Obs	$\langle Obs\rangle_{Av}$	Calc
$(^2P_{1\frac{1}{2}})$	H	$[5\frac{1}{2}]$	6	221 364	0.80	0.79	0.79
			5		0.78		
$(^2P_{1\frac{1}{2}})$	H	$[4\frac{1}{2}]$	5	221 323	0.66	0.61	0.59
			4		0.56		
$(^2P_{\frac{1}{2}})$	G	$[4\frac{1}{2}]$	5	221 168	0.37	0.29	0.33
			4		0.18		
$(^2P_{\frac{1}{2}})$	G	$[3\frac{1}{2}]$	4	221 164	0.51	0.51	0.51
			3		0.51		
$(^2P_{1\frac{1}{2}})$	F	$[3\frac{1}{2}]$	4	221 343	0.80	0.72	0.70
			3		0.61		
$(^2P_{1\frac{1}{2}})$	F	$[2\frac{1}{2}]$	3	221 381	...	...	0.08
			2				

$\tilde{E}=221\,289.792\ cm^{-1}$, $\zeta_{2p}=116.237\ cm^{-1}$, $F_2=0.6030\ cm^{-1}$

coupling approximation with the result shown in Table IV.

The observed N II $2s^2\,2p\,5g$ levels, given in Table V, occur in close pairs with a splitting of less than 0.20 cm^{-1}. The arrangement of the pairs is exactly described by the theoretical formulas. The value $\frac{3}{2}\zeta_{2p}=174.36\ cm^{-1}$, derived from this calculation, agrees within experimental errors w tithhe splitting of the ground term $2s^2\,2p\,^2P$ of N III, which is 174.5 cm^{-1} as determined from observations in the extreme ultraviolet.

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Dynamical Theory of Nuclear Induction. II*

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This paper represents the generalization of an earlier theory by Wangsness and the author in which the phenomena of relaxation were treated by considering the interaction of individual nuclear moments with the molecular system and assuming that the latter remains always in thermal equilibrium. Instead of a single nuclear moment, the representative spin system is here allowed to consist of several moments, interacting with each other, and the corresponding general Boltzmann equation for the distribution matrix is developed. A first application is given by investigating the effect of a weak alternating field in the vicinity of resonance conditions. It is seen that the phenomenon of saturation is closely related to the change of populations in states, other than the two between which the resonance transitions occur. This general type of Overhauser effect is shown to be equivalent to that of a dc circuit and it is illustrated by a special example. The general formalism is adapted to the treatment of a nuclear spin system in a strong constant field with particular attention to the structure of resonance spectra in liquids, due to chemical shift and spin coupling. A special case is that where the spin coupling causes a splitting of the lines, large compared to their natural width and their broadening due to the alternating field. An expression for the signal, obtained in this case, is developed and the effect of the spin coupling upon the effective longitudinal and transverse relaxation time is illustrated by the particular example of the two coupled nuclei of spin 1/2 and with independent dipole relaxation. New phenomena appear if the rate of relaxation-transitions is comparable or large compared to the frequency separation of resonance lines, due to spin coupling. The effect of such transitions by some nuclei upon the line width and structure of the resonance of others is investigated, assuming the spin coupling to be small compared to the chemical shift. Similar effects occur to the resonances of a nucleus in a weak alternating field, if other nuclei are at the same time irradiated by an alternating field of different frequency and sufficiently strong so that its effect is comparable or large compared to that of the spin coupling. It is shown that, even for the case of a single kind of nucleus, the presence of the strong field causes a doubling of the resonance with the weak field which can be used to calibrate the strength of the former by a frequency measurement. Another illustration is given in the case of two nuclei and explicit expressions for line width and intensity are given for the example of two nuclei with spin 1/2 and independent dipole relaxation.

1. INTRODUCTION

THE phenomena of nuclear magnetism require the general consideration of a system of nuclear spins, interacting with external fields and with each other. The behavior of the system is further determined by relaxation processes which are due to its interaction with the molecular surroundings. In an earlier paper, referred to below as I, Wangsness and the author[1] have presented a new approach to the problem of relaxation by treating the molecular surroundings as a quantum-mechanical system in thermal equilibrium. Through statistical and perturbation methods they were led to the Boltzmann equation for the distribution matrix which is analogous to the classical distribution function and contains all the information necessary for the description of the spin system.

* Written at CERN, Geneva, during a leave of absence of the author from Stanford University for the academic year 1954–1955.

[1] R. K. Wangsness and F. Bloch, Phys. Rev. **89**, 728 (1953).

An essential restriction in I was made by assuming that each nuclear spin under consideration reacts independently of the other nuclei in the sample to the external fields and to the molecular surroundings. It excluded therefore a rigorous account for those relaxation processes which originate from the interaction of nuclear moments as well as the consideration of systems where the coupling between neighboring nuclear spins causes a structure of the resonance lines. Such structures have been known for a considerable time to occur in crystals[2]; more recently, a considerably finer structure has also been observed in liquids[3] and gases.[4] It is the purpose of this paper to generalize the methods, employed in I, in order to allow the treatment of features which arise from a mutal interaction between nuclear spins. While it was sufficient, in I, to consider a single representative nucleus, it is here necessary to deal with more general spin systems. This leads to an extended theory which contains the earlier results as the simplest special case.

A more complicated case is that in which the representative spin system consists of several nuclei, contained in a molecule and with a coupling of their spins, characteristic for liquids and gases.

In the following papers by Arnold and Anderson, observations under high resolution are presented which reveal a very fine structure of proton resonance spectra in liquids. It was in fact the attempt to establish a quantitative basis for the discussion of the relative intensities and widths of lines, appearing in such spectra, which has led the author to the theory presented here. The case of spin coupling in crystals is likewise contained in the general formalism but it is of considerably greater complexity since it demands in principle that one considers all the nuclei in the crystal together as the spin system. While it is often sufficient to regard merely the interaction of nearest neighbors, there exists also the possibility of spin waves propagating through larger regions. The mechanism of relaxation is thereby greatly complicated and no attempt shall be made here beyond outlining its treatment. Finally it is not necessary to include only nuclei in the spin system. Although the individual carrier of spin and magnetic moment shall be here for brevity called the "nucleus," it is equally possible for the spin system to contain also electrons. As was pointed out by Overhauser,[5] it is in fact of special interest to consider relaxation processes which originate from the coupling between nuclei and electrons. A similar situation arises in cases where the coupling leads to a hyperfine structure with relaxation transitions between the levels of the nucleus-electron system. The bearing of the general theory on this type of "Overhauser effect" will be discussed below.

[2] G. E. Pake, J. Chem. Phys. **16**, 327 (1948).
[3] Gutowski, McCall, and Slichter, Phys. Rev. **84**, 589 (1951); E. L. Hahn and D. E. Maxwell, Phys. Rev. **84**, 1246 (1951).
[4] Smaller, Yasaitis, Avery, and Hutchison, Phys. Rev. **88**, 414 (1952); H. Y. Carr and E. M. Purcell, Phys. Rev. **88**, 415 (1952).
[5] Albert W. Overhauser, Phys. Rev. **92**, 411 (1953).

The formalism will be first developed without specifying the nature of the spin system and it will be used to draw some general conclusions. It is later particularly applied to the case of structures in liquids; special assumptions will be freely introduced in this application with the view to illustrate in a relatively simple manner certain characteristic phenomena rather than to adhere strictly to various actual conditions. Depending upon the latter, one may be faced with problems which require greater computational efforts for their solution. One of the complications may arise from the time-dependence of the applied radio-frequency field; we shall restrict our considerations to a purely monochromatic field and to the superposition of a strong and a weak field with different frequencies. It should be noted, however, that other cases such as transient phenomena and the application of pulsed fields, leading to spin echoes, could equally well be treated from the general equations.

2. THE GENERAL BOLTZMANN EQUATION FOR THE DISTRIBUTION MATRIX

Proceeding in this section in a manner, analogous to that in I, we shall first define the Hamiltonian of the total system in the form

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

where the first part represents the energy of the spin system and depends only upon the spin operators and certain fixed parameters. The second part, representing the energy of the molecular surroundings, is an operator which pertains to all other degrees of freedom of the total system, in particular to those of thermal motion of the molecules. The third part represents a coupling energy between the spin system and the molecular surroundings and it is not subject to any restriction except that it can be treated as a small perturbation.

Let further

$$E=E_0+E_1, \tag{2.2}$$

where $\hbar E_0$ shall be a large, $\hbar E_1$ a relatively small part of the spin energy. This separation is to some extent arbitrary and a matter of convenience. In analogy to the procedure followed in I, it is possible, for example, to include in $\hbar E_1$ merely the contribution to the spin energy, arising from the applied rf field $\mathbf{H}_1(t)$. $\hbar E_0$ contains in this case the spin energy, due to a strong constant field $\mathbf{H}_0$, the coupling energy between different nuclear spins, the quadrupole interaction with fixed electric field gradients, etc., in short all those parts of the spin energy which, irrespective of their relative magnitude, do not explicitly depend upon the time. It may be indicated, on the other hand, to separate certain relatively small parts from $\hbar E_0$ and have them contained in $\hbar E_1$. This type of separation will be later applied to the spin coupling in order to treat cases where the coupling gives rise to effects which are com-

parable or small compared to those caused by the rf field or by relaxation processes.

The quantum-mechanical problem, presented by the Hamiltonian (2.1), will now be solved in a representation in which E_0 and F are both diagonal. The eigenvalues of E_0 will be denoted by g, those of F by f. As in I, it must be noted that the molecular system has very many degrees of freedom so that the values of f must be considered to be practically continuous. Besides, it will be generally highly degenerate so that a stationary state of this system must be characterized by the double system (f,u), where u specifies one of many states with the same energy $\hbar f$. Although it is not essential for many purposes, one may admit that the spin system is likewise degenerate and, in this case, characterize one of its states by the double symbol (g,v), where v specifies states with the same value g. In the absence of degeneracy, a state of the spin system is uniquely determined by g so that the symbol v can be omitted.

The following procedure is closely analogous to that followed in I; it is sufficient, therefore, to present merely a brief outline with special mention, however, of those points which do not enter in the earlier treatment.

The density matrix $\rho(t)$, satisfying the equation

$$d\rho/dt=-i[E_0+F+E_1+G,\rho], \tag{2.3}$$

has in our representation the matrix elements

$$(gvfu|\rho|g'v'f'u').$$

The expectation value $\langle Q\rangle$ of a spin function Q, defined by having matrix elements of the form

$$(gvfu|Q|g'v'f'u')=(gv|Q|g'v')\delta_{ff'}\delta_{uu'} \tag{2.4}$$

requires the knowledge of the distribution matrix

$$(gv|\sigma(t)|g'v')=\sum_{fu}(gvfu|\rho(t)|g'v'fu), \tag{2.5}$$

and is given by

$$\langle Q(t)\rangle=\sum_{gv}\sum_{g'v'}(g'v'|Q|gv)(gv|\sigma(t)|g'v')=\mathrm{Tr}[Q\sigma(t)]. \tag{2.6}$$

ρ will satisfy the normalization condition

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

which, for σ, demands therefore

$$\sum_{gv}(gv|\sigma|gv)=1. \tag{2.7}$$

Defining further the transformed matrices

$$\begin{aligned}&(gvfu|\rho^*(t)|g'v'f'u')\\&\quad=\exp[i(g-g'+f-f')t](gvfu|\rho(t)|g'v'f'u'),\\&(gvfu|G^*|g'v'f'u')\\&\quad=\exp[i(g-g'+f-f')t](gvfu|G|g'v'f'u'),\end{aligned} \tag{2.8}$$

and

$$\begin{aligned}&(gvfu|E_1^*(t)|g'v'f'u')\\&\quad=\exp[i(g-g'+f-f')t](gvfu|E_1(t)|g'v'f'u'),\end{aligned} \tag{2.9}$$

one obtains from (2.3)

$$d\rho^*/dt=-i[E_1^*(t)+G^*,\rho^*]. \tag{2.10}$$

Because of the fact that E_1 is a spin function, Eq. (2.9) can also be written in the form

$$(gv|E_1^*(t)|g'v')=\exp[i(g-g')t](gv|E_1(t)|g'v'), \tag{2.11}$$

with

$$(gvfu|E_1^*(t)|g'v'f'u')=(gv|E_1^*(t)|g'v')\delta_{ff'}\delta_{uu'}.$$

Starting with the initial value $\rho^*(0)=\rho(0)$ for $t=0$, the Eq. (2.10) can be solved by forward integration during a sufficiently short time interval t, keeping only the terms which are linear in E_1^* as well as those, linear and quadratic in G^*. The assumption that the molecular system is in thermal equilibrium at the absolute temperature T is formulated through the replacement of $\rho(0)$ by its statistical average

$$(gvfu|\bar{\rho}(0)|g'v'f'u')=(gv|\sigma(0)|g'v')P(f)\delta_{ff'}\delta_{uu'}, \tag{2.12}$$

with the Boltzmann factor

$$P(f)=\exp(-\hbar f/kT)/\sum_{f'u'}\exp(-\hbar f'/kT), \tag{2.13}$$

and with the understanding that all further equations are meant as statistical averages over the molecular system. It is further assumed that the molecular system shall act as a heat reservoir, i.e., that it shall always remain in thermal equilibrium in spite of its coupling to the spin system and the fact that the latter can be made to deviate from the equilibrium through the action of the applied rf field.[6]

By a generalized but otherwise analogous procedure to that leading to Eq. (3.22) of I, the forward integration of (2.10) leads to the transformed distribution matrix

$$(gv|\sigma^*(t)|g'v')=\sum_{fu}(gvfu|\rho^*(t)|g'v'fu)$$

at the time t. Through (2.5) and (2.8) it can also be written in the form

$$(gv|\sigma^*(t)|g'v')=\exp[i(g-g')t](gv|\sigma(t)|g'v'), \tag{2.14}$$

and is found to depend upon t in a manner which can be expressed by the Boltzmann equation

$$\begin{aligned}&\frac{d}{dt}(gv|\sigma^*|g'v')+i(gv|[E_1^*,\sigma^*]|g'v')\\&\qquad=(gv|\Gamma(\sigma^*)|g'v').\end{aligned} \tag{2.15}$$

[6] V. Fano, Phys. Rev. **96**, 869 (1954).

The abbreviation

$$(gv|\Gamma(\sigma^*)|g'v')$$
$$=\sum_p \sum_{v''v'''} \{2\exp(\hbar p/kT)$$
$$\times\Gamma_{gg'}{}^p(vv'v''v''')(g+p, v''|\sigma^*|g'+p, v''')$$
$$-\Gamma_{gg}{}^p(vv'''v''v')(gv'''|\sigma^*|g'v')$$
$$-\Gamma_{g'g'}{}^p(v'''v'v''v')(gv|\sigma^*|g'v''')\} \quad (2.16)$$

has here been introduced with the symbols

$$\Gamma_{gg'}{}^p(vv'v''v''')$$
$$=\pi\sum_{uu'}\int\eta_u(f)\eta_{u'}(f-p)P(f)$$
$$\times(gvfu|G|g+p, v'', f-p, u')$$
$$\times(g'+p, v''', f-p, u'|G|g'v'fu)df, \quad (2.17)$$

satisfying the relation

$$\Gamma_{gg'}{}^p(vv'v''v''')$$
$$=\exp(-\hbar p/kT)\Gamma_{g'+p,g+p}{}^{-p}(v'''v''v'v). \quad (2.18)$$

In the derivation of these formulas it is assumed that $\eta_u(f)df$ represents the number of states of the molecular system, characterized by u and with an energy between $\hbar f$ and $\hbar(f+df)$.

It is necessary, by the definition of the quantities (2.17), that p assumes either the value zero or such values which, added to the eigenvalues g as well as g' lead to other eigenvalues of E_0. The summation over p on the right side of (2.16) extends therefore for the second and third term in the curly bracket over all energy levels of the system with $\hbar p$ representing the difference between one of these levels and the levels $\hbar g$, $\hbar g'$, respectively, and the same holds for the first term if $g=g'$. For $g\neq g'$, this term demands, however, the more stringent condition that both $g''=g+p$ and $g'''=g'+p$ are eigenvalues of E_0 so that the summation over p is here restricted to those pairs of levels $\hbar g''$ and $\hbar g'''$ which differ from $\hbar g$ and $\hbar g'$ respectively by the common value $\hbar p$. While the first term in the curly bracket of (2.16) is thus always to be retained for $p=0$, it requires in the case $g\neq g'$ exceptional conditions for the eigenvalues of E_0 in order to contribute terms to the summation over p for which $p\neq 0$.

A noteworthy exception of this kind is that, considered in I, which occurs more generally if it is assumed that E_0 contains only the spin energy, due to a constant external field. An eigenvalue of E_0 has in this case the form

$$g=-\sum_r \omega_r m_r, \quad (2.19)$$

where ω_r and m_r represent a set of Larmor frequencies and magnetic quantum numbers, respectively, referring to different nuclei r of the spin system; another set of quantum numbers will lead to the eigenvalue

$$g'=-\sum_r \omega_r m_r'. \quad (2.20)$$

By replacing m_r by $m_r+\tau_r$ in (2.19) and m_r' by $m_r'+\tau_r$ in (2.20), one is led in both cases to another eigenvalue of E_0, provided τ_r is an integer such that not only m_r, m_r' but also $m_r+\tau_r$, $m_r'+\tau_r$ are contained within the limits $-I_r$ and $+I_r$, given by the spin I_r. Unrestricted by the aforementioned conditions, the quantity p in the summation of (2.16) assumes thus in this case all values

$$p=-\sum_r \omega_r\tau_r \quad (2.21)$$

which one obtains from a permissible set of integers τ_r. A state of the spin system can here be characterized by the set of quantum numbers m_r and one can omit the index v if all frequencies ω_r are different and incommensurable so that there is no degeneracy. If one further specializes to the case of a single spin, thus using the symbols m, m', τ instead of g, g', p, one obtains from (2.15) and (2.16) the Eq. (3.22) of I as a special case.

The assumptions, made in the derivation of (2.15) are very similar to those of the special case, treated in I. In the first place, the coupling between spin and molecular system appears only through the quantities Γ of Eq. (2.17) which are quadratic in G while terms, linear in G have been omitted. In analogy to (3.6) in I, the linear terms actually lead to a contribution in the spin energy, divided by $\hbar$, which in our representation has the form

$$(gv|\Delta E|g'v')$$
$$=\delta_{gg'}\sum_u\int\eta_u(f)P(f)(gvfu|G|gv'fu)df. \quad (2.22)$$

Since this term represents a weighted average over the quantities f, u of the molecular system, it can be omitted if the interaction with the spin system consists entirely of fluctuating terms so that G has only matrix elements which are nondiagonal in f. In the general theory, presented here, there exist, however, rather important contributions to the spin energy which enter strictly speaking in the form of (2.22) and have to be retained. The omission of this expression in the derivation of (2.15) demands in this case that the quantity E, introduced in (2.1), is redefined by the inclusion of ΔE.

To exemplify this procedure, we consider the dipole interaction of nuclear moments in a crystal. It depends both on the spin operators and, through the relative positions of the nuclei, on variables of the molecular system, and contributes therefore to the part $\hbar G$ of the total energy (2.1). Unless one includes it from the start in the spin energy $\hbar E$, the static part of the dipole interaction appears thus in the form (2.22) and it removes a high degeneracy, to be further discussed in Sec. 4, through its nondiagonal matrix elements $v\neq v'$. Besides the static part, an expansion of the dipole interaction around the equilibrium position yields further

contributions in ascending powers of the displacements. The linear terms in this expansion give no contribution to (2.22) since their average value vanishes, but they have to be retained in the quantities (2.17) where they appear quadratically, thus contributing to relaxation processes.

Another example, which is of particular interest for the later purposes of this paper, arises in the case of molecules in liquids and gases through the modification of the spin energy by the electrons. Since their spin is not essential in this respect, the electrons are here to be regarded as part of the molecular system and effects of their interaction with the nuclear spins are likewise to be contained in $\hbar G$. As a result, there arises through (2.22) small but important contributions to the spin energy; one of these contributions represents the chemical shift of the effective field, acting upon a nucleus, the other consists of a small rotational invariant interaction between two nuclear spins and both will be further discussed in Sec. 4. In contrast to the case of crystals, the direct dipole interaction is here averaged out as a consequence of the rotation of the molecules, but it enters in relaxation processes through the quantities Γ of (2.17) which are quadratic in G.

In analogy to the condition (3.4) of I, the derivation of (2.22) demands that the forward integration of (2.10) is extended over a time interval t which has to be long enough to satisfy the condition

$$|g-g'|t\gg 1 \tag{2.23}$$

for any two eigenvalues g and g' of E_0, provided that

$$g-g'\neq 0. \tag{2.24}$$

The same condition must be satisfied for the validity of (2.15) in order to justify the appearance of the second and third term in the curly bracket of (2.16). For the justification of the first term in this bracket, it is necessary, on the other hand, that

$$|g-g'-g''+g'''|t\gg 1 \tag{2.25}$$

for any four eigenvalues g, g', g'', g''', provided that

$$g-g'-g''+g'''\neq 0. \tag{2.26}$$

The aforementioned restrictions upon the permissible values of p, to be contained in the summation of (2.16), are in fact closely related to the conditions (2.23) to (2.26). In the special case of I, the relevant quantities (2.24) and (2.26) are all of the same order of magnitude, so that they could be replaced by a single condition. In the more general case, considered here, one may frequently deal with different orders of magnitude; nevertheless, the foregoing conditions upon the duration t shall be symbolized by the single condition

$$|E_0|t\gg 1. \tag{2.27}$$

It has to be kept in mind, however, that $|E_0|$ represents here the various absolute magnitudes of the differences (2.24) and of the double differences (2.26).

It is further necessary, in analogy to (3.20) of I, that

$$\omega^* t\gg 1, \tag{2.28}$$

where ω^* is a characteristic frequency of the molecular system, indicating the effective scale in which the spread of the frequencies f has to be measured.[7] This condition is necessary in order that the matrix elements of G can be considered as sufficiently slowly varying function of f in the integrals over this variable which lead to (2.15). The Boltzmann factor $P(f)$ of Eq. (2.13) enters in the same integrals and its variation must likewise be sufficiently slow. It requires the fulfillment of the additional condition

$$(kT/\hbar)t\gg 1, \tag{2.29}$$

which, actually, was already assumed in I without being explicitly mentioned.

On the other hand, t must be short enough to justify the neglect of terms, higher than those which are linear in E_1 and quadratic in G. This leads to the further conditions

$$|E_1|t\ll 1 \tag{2.30}$$

and

$$|\Gamma|t\ll 1, \tag{2.31}$$

where $|E_1|$ indicates the effective magnitude of E_1, and $|\Gamma|$ that of the quantities, defined in (2.17). One obtains in this manner an equation for the increment of σ^* which is linear in t; in order to replace it by the differential equation (2.15) it is necessary to assume that σ^* contains only frequencies of order of magnitude ν, satisfying

$$\nu t\ll 1. \tag{2.32}$$

Actually this relation, which was likewise implied in I, does not represent an independent condition. It is seen from (2.15) that the order of magnitude of ν is measured by the quantities $|E_1|$ and $|\Gamma|$ themselves so that (2.32) can be considered as a consequence of (2.30) and (2.31).

Analogous to the Eq. (3.21) of I, one can combine the conditions (2.27) to (2.31) in the single condition of validity for (2.15):

$$(|\Gamma|, |E_1|)\ll(|E_0|, \omega^*, kT/\hbar), \tag{2.33}$$

in the sense that each quantity on the left side of this relation must be small to each quantity on the right side. Except for omitting the condition on the variation of $P(f)$, measured by $kT/\hbar$, Eq. (3.21) of I is indeed a special case of the more general condition (2.33). Under the assumptions of I, $|E_0|$ is of the order of the resonance frequency $\omega=\gamma H_0$ and $|\Gamma|$ is of the order of the inverse relaxation times $(1/T_1)$, $(1/T_2)$ which were indeed the quantities used to formulate the condition of validity of the Boltzmann equation.

The differential equation (2.15) for the transformed distribution matrix results, in analogy to (3.25) of I, in

[7] In the customary terminology, the quantity $1/\omega^*$ corresponds to an effective correlation time of the molecular system.

an equation for the distribution matrix defined by (2.5). Using Eqs. (2.2), (2.14), and the identities

$$(gv|E_0|g'v')=g\delta_{gg'}\delta_{vv'}$$

and

$$(gv|[E_0,\sigma]|g'v')=(g-g')(gv|\sigma|g'v'),$$

one obtains

$$\frac{d}{dt}(gv|\sigma|g'v')+i(gv|[E,\sigma]|g'v')=(gv|\Gamma(\sigma)|g'v'), \quad (2.34)$$

where the symbol on the right side is obtained by replacing in (2.16) the matrix elements of σ^* by the corresponding ones of σ.

As in I, it can be seen from (2.15) or (2.34) that these equations are compatible with the condition of normalization (2.7) since they lead through (2.18) to the identities

$$\frac{d}{dt}\sum_{gv}(gv|\sigma^*|gv)=\frac{d}{dt}\sum_{gv}(gv|\sigma|gv)=0.$$

Another obvious and general feature appears in the absence of the term E_1 of E, i.e., by replacing E by E_0 in (2.34) or by letting $E_1^*=0$ in (2.16). Both equations have in this case a stationary solution

$$(gv|\sigma_0|g'v')=(gv|\sigma_0^*|g'v')=\zeta\exp(-\hbar g/kT)\delta_{gg'}\delta_{vv'}, \quad (2.35)$$

where normalization demands

$$\sum_{gv}(gv|\sigma_0|gv)=\sum_{gv}(gv|\sigma_0^*|gv)=1, \quad (2.36)$$

and hence

$$\zeta=1/\sum_{gv}\exp(-\hbar g/kT). \quad (2.37)$$

Equation (2.35) expresses the fact that, in the absence of external actions, the spin system is stationary if it is in thermal equilibrium with the molecular surroundings. The diagonal elements of σ and σ^*, i.e., the probabilities to find the spin system in certain states, follow thus the Boltzmann distribution at the temperature T of the molecular surroundings and their off-diagonal elements vanish because of the absence of phase relations between different states. It is convenient, for later purposes, to introduce instead of σ and σ^* the deviations χ and χ^* from the equilibrium solution by writing

$$\sigma=\sigma_0+\chi, \quad (2.38)$$

$$\sigma^*=\sigma_0^*+\chi^*, \quad (2.39)$$

with

$$\sum_{gv}(gv|\chi|gv)=\sum_{gv}(gv|\chi^*|gv)=0, \quad (2.40)$$

as a consequence of (2.36) and the normalization requirement

$$\sum_{gv}(gv|\sigma|gv)=\sum_{gv}(gv|\sigma^*|gv)=1. \quad (2.41)$$

With the same notation for χ^* and χ as that, used on the right side of (2.15) and (2.34) for σ^* and σ, one obtains from these equations

$$\frac{d}{dt}(gv|\chi|g'v')+i(gv|[E,\chi]|g'v')-(gv|\Gamma(\chi)|g'v')=i\zeta[\exp(-\hbar g/kT)-\exp(-\hbar g'/kT)](gv|E_1|g'v') \quad (2.42)$$

and

$$\frac{d}{dt}(gv|\chi^*|g'v')+i(gv|[E_1^*,\chi^*]|g'v')-(gv|\Gamma(\chi^*)|g'v')=i\zeta[\exp(-\hbar g/kT)-\exp(-\hbar g'/kT)](gv|E_1^*|g'v'). \quad (2.43)$$

An important general conclusion can be drawn from Eq. (2.42): The right side of this equation vanishes in the limit $\hbar(g-g')/kT\to 0$ so that, if $\chi=0$ at any time, it remains always zero. Once in thermal equilibrium, an arbitrary spin system, subjected to arbitrary external fields (contained in E_1), will therefore remain in thermal equilibrium provided that the separation of its energy levels is negligible in comparison to kT. Correspondingly, a deviation from the equilibrium population of the spin states under the influence of external fields can only be expected to occur to the extent to which the finiteness of the temperature is considered.[8]

The special form of the Boltzmann equation, obtained in I, was used to investigate the validity of the phenomenological equations for the macroscopic nuclear polarization. While a rather wide range of validity could be established, it was found that even under the relatively simple earlier assumptions there were cases where the phenomenological equations were not valid. In these cases one can obtain the desired answers by first solving the Boltzmann equation; the resulting form of the distribution matrix leads then through (2.6) to expectation values such as those of the components of the polarization which directly determine the observed nuclear induction signals.

This last procedure will throughout be used in this paper since one cannot expect, under far more general conditions than in I, to arrive at a complete macroscopic

[8] This observation is not in contradiction with the Overhauser effect, where one obtains a nuclear polarization, far in excess to that of the equilibrium distribution. It is essential that the spin system contain here also electronic spins: While energy differences, due to a change of orientation of the nuclear spin in the external constant magnetic field, can be indeed neglected in comparison to kT, this is not the case for the other and far greater energy differences of the spin system which occur in a change of the electronic spin. Indeed it is the ratio of these latter energy differences to kT, which measures the magnitude of the observed effect. A recent theory of J. I. Kaplan [Phys. Rev. **96**, 238 (1954)] is, on the other hand, invalidated by the foregoing observation since it claims a strong nuclear polarization even if one disregards the separation of the electronic levels with respect to kT. For a further discussion of the observations of A. Honig [Phys. Rev. **96**, 234 (1954)] to which the theory of Kaplan refers, compare A. Abragam [Phys. Rev. **98**, 1729 (1955)].

description by means of phenomenological equations. There may be special situations where this is possible without making the same initial assumptions as in I, but they shall here not be investigated. Instead, solutions of the Boltzmann equation will be found for particular external fields and particular spin systems which are of interest; the resulting expressions for the distribution matrix will then be inserted in (2.6) to obtain the expectation values of the relevant spin functions Q which deal with the macroscopic polarization.

It is permissible, for most of the later purposes of this paper, to exclude a degeneracy of the unperturbed spin system. A state of this system is then uniquely characterized by the eigenvalues g of E_0 and the preceding equations of this section are greatly simplified by the omission of the index v. In particular, one obtains in this case from (2.42) and from the expression (2.16), obtained through the replacement of σ^* by χ and the omission of v,

$$\begin{aligned}&\frac{d}{dt}(g|\chi|g')+i(g|[E,\chi]|g')\\&+\sum_p\{(\Gamma_{gg}{}^p+\Gamma_{g'g'}{}^p)(g|\chi|g')\\&-2\exp(\hbar p/kT)\Gamma_{gg'}{}^p(g+p|\chi|g'+p)\}\\&=i\zeta[\exp(-\hbar g/kT)-\exp(-\hbar g'/kT)](g|E_1|g'),\end{aligned}\tag{2.44}$$

with the simplified forms

$$\begin{aligned}\Gamma_{gg'}{}^p=\pi\sum_{u,u'}\int\eta_u(f)\eta_{u'}(f-p)\\\times P(f)(gfu|G|g+p,f-p,u')\\\times(g'+p,f-p,u'|G|g'fu)df\end{aligned}\tag{2.45}$$

and

$$\Gamma_{gg'}{}^p=\exp(-\hbar p/kT)\Gamma_{g'+p,g+p}{}^{-p}\tag{2.46}$$

of Eqs. (2.17) and (2.18), respectively.

The distribution matrix is here further given by

$$(g|\sigma|g')=\zeta\exp(-\hbar g/kT)\delta_{gg'}+(g|\chi|g'),\tag{2.47}$$

as a consequence of (2.35) and (2.38), with the equalities

$$\zeta=1/\sum_g\exp(-\hbar g/kT),\tag{2.48}$$

$$\sum_g(g|\sigma|g)=1,\tag{2.49}$$

and

$$\sum_g(g|\chi|g)=0\tag{2.50}$$

following from (2.37), (2.41), and (2.40), respectively.

It shall finally be noted that

$$(g|\chi|g')=(g'|\chi|g)^*,\tag{2.51}$$

as a consequence of (2.47) and the relation

$$(g|\sigma|g')=(g'|\sigma|g)^*,\tag{2.52}$$

which follows from the fact that the density matrix ρ is by definition Hermitian, so that the same holds in view of (2.5) for the distribution matrix σ.

3. EFFECT OF A WEAK EXTERNAL FIELD WITH A SINGLE FREQUENCY

It shall be assumed in this section that the principal part $\hbar E_0$ of the spin energy includes all terms which do not explicitly depend upon the time. The additional small part $\hbar E_1$ consists then only of the contribution by an external time-dependent field, to be indicated by the notation $E_1=D$. In particular this field shall here be chosen to be monochromatic with a circular frequency ω, so that one has

$$E_1=D=D^+e^{i\omega t}+D^-e^{-i\omega t}.\tag{3.1}$$

The eigenvalues g of E_0 shall not be degenerate and no common difference shall exist between any two of them. It is then implied by the conditions, symbolized in (2.33), that all the finite differences and double differences, given by (2.24) and (2.26) respectively, shall be large compared to the relaxation coefficients Γ of Eq. (2.45) as well as to the effective magnitude $|E_1|$, given by that of the terms D^+ and D^- in (3.1). In fact, the reference to a "weak" field in the title of this section is made in the sense of this relation of orders of magnitude and it can equally well be considered as a condition upon the particular choice of E_0. The treatment of "strong" fields, to be presented later, will be essentially based upon a different separation of the spin energy.

Inserting (3.1) and using the identity

$$(g|E_0|g')=g\delta_{gg'},$$

one obtains from Eq. (2.44)

$$\begin{aligned}&\frac{d}{dt}(g|\chi|g')+i(g-g')(g|\chi|g')+i\{(g|[D^+,\chi]|g')e^{i\omega t}\\&+(g|[D^-,\chi]|g')e^{-i\omega t}\}+\sum_p\{(\Gamma_{gg}{}^p+\Gamma_{g'g'}{}^p)(g|\chi|g')\\&-2\exp(\hbar p/kT)\Gamma_{gg'}{}^p(g+p|x|g'+p)\}\\&=i\zeta[\exp(-\hbar g/kT)-\exp(-\hbar g'/kT)]\\&\times\{(g|D^+|g')e^{i\omega t}+(g|D^-|g')e^{-i\omega t}\}.\end{aligned}\tag{3.2}$$

The fact that E_1 shall be a Hermitian operator requires, according to (3.1), that the matrix elements of D^+ and D^-, appearing in (3.2), satisfy the relation

$$(g|D^+|g')=(g'|D^+|g)^*.\tag{3.3}$$

The general solution of (3.2) contains terms in χ which satisfy the homogeneous equation and decrease exponentially with time constants of the order $1/|\Gamma|$. These transient terms shall be omitted in order to obtain the particular solution of (3.2), pertaining to stationary conditions. The corresponding matrix χ has diagonal elements, independent of the time and nondiagonal elements which alternate with the frequency ω. With

$|\Gamma|$ and $|D^{\pm}|$ small compared to $|g-g'|$ for $g\neq g'$, this solution can be seen to differ appreciably from zero only if ω lies close to one of the different resonance values $|g-g'|$. Selecting a particular resonance frequency $\omega_{ab}=a-b$ by specifying $g=a$, $g'=b$ and $a>b$, the deviation of ω from this resonance frequency is given by

$$\Delta\omega=\omega+b-a \tag{3.4}$$

and is assumed to be small compared to the difference between the specific resonance frequency ω_{ab} and any other resonance frequency $\omega_{gg'}$. All the nondiagonal elements of χ except those between the states a and b are then negligible; in view of (2.51), the latter can be written in the form

$$(b|\chi|a)=ze^{i\omega t},\quad (a|\chi|b)=z^*e^{-i\omega t}, \tag{3.5}$$

with the asterisk, as in (2.51), (2.52), and (3.3), indicating the conjugate complex. Using further for the diagonal elements the abbreviation

$$(g|\chi|g)=\chi_g, \tag{3.6}$$

the stationary solution of (3.2) is then characterized by the complex number z and the set of real numbers χ_g which are all independent of time.

The relations between these constants result from the the various values of g and g' in (3.2), yielding in particular for $g=b$, $g'=a$

$$\begin{aligned}&(\Delta\omega-i\Gamma_{ab})z+(b|D^+|a)(\chi_a-\chi_b)\\&=\zeta[\exp(-\hbar b/kT)-\exp(-\hbar a/kT)](b|D^+|a)\end{aligned} \tag{3.7}$$

with the abbreviation

$$\Gamma_{ab}=\sum_p(\Gamma_{aa}{}^p+\Gamma_{bb}{}^p)-2\Gamma_{ab}{}^0. \tag{3.8}$$

For $g=a$, $g'=b$, there results the conjugate complex equation to (3.7) in view of the relation (3.3), yielding

$$(a|D^-|b)=(b|D^+|a)^*, \tag{3.9}$$

and in view of the equality

$$\Gamma_{ab}=\Gamma_{ba}. \tag{3.10}$$

This equality follows from the definition (3.8), together with the fact $\Gamma_{ab}{}^0=\Gamma_{ba}{}^0$ which can be verified by (2.45) for $p=0$.

One obtains further for $g=g'=a$,

$$\begin{aligned}&\sum_p\Gamma_{aa}{}^p[\exp(\hbar p/kT)\chi_{a+p}-\chi_a]\\&\qquad=-\mathrm{Im}\{(a|D^-|b)z\};\end{aligned} \tag{3.11}$$

for $g=g'=b$,

$$\sum_p\Gamma_{bb}{}^p[\exp(\hbar p/kT)\chi_{b+p}-\chi_b]=\mathrm{Im}\{(a|D^-|b)z\}; \tag{3.12}$$

and finally, for $g=g'\neq a,b$,

$$\sum_p\Gamma_{gg}{}^p[\exp(\hbar p/kT)\chi_{g+p}-\chi_g]=0. \tag{3.13}$$

It shall be noted that the quantities $\Gamma_{gg}{}^p$, obtained from (2.45) with $g=g'$ for all values of g, including a and b, are real and positive in view of the Hermitian character of G. They represent in fact the probability per unit time of a transition of the spin system from g to $g+p$ through its interaction with the molecular surroundings so that the necessary energy $\hbar p$ must be furnished by the latter. The probability per unit time $\Gamma_{g+p,g+p}{}^{-p}$ for the inverse transition differs in view of Eq. (2.46) by the factor $\exp(\hbar p/kT)$ which is indeed the relative probability that the molecular surroundings are ready to absorb rather than to emit the energy $\hbar p$. The contributions $\sum_{p\neq 0}\Gamma_{aa}{}^p$ and $\sum_{p\neq 0}\Gamma_{bb}{}^p$ to the first term of Eq. (3.8) represent therefore the inverse life time of the states a and b, respectively, and are real and positive. The same holds for the remaining term, dealing with relaxation processes without exchange of energy between the spin system and the molecular system, since it can be written in the form

$$\begin{aligned}\Gamma_{aa}{}^0+\Gamma_{bb}{}^0-2\Gamma_{ab}{}^0=\pi\sum_{u,u'}\int\eta_u(f)\eta_{u'}(f)\,|\,(afu|G|afu')\\-(bfu|G|bfu')\,|^2df,\end{aligned}$$

using again the fact that the elements of G in (2.45) are those of a Hermitian matrix. It follows therefore that the expression (3.8) is likewise real and positive.

In the derivation of (3.7), (3.11), and (3.12) there appear actually also terms with time-dependent factors $e^{\pm i\omega t}$, $e^{\pm 2i\omega t}$; in consistency with the assumptions made here, their rapid variation permits, however, the neglect of these terms. Besides, they are rigorously absent if among the matrix elements of $D^{\pm}$, involving the states a and b, only $(b|D^+|a)$ and its conjugate complex $(a|D^-|b)$ are different from zero. This is analogous to the well-known special case of a nucleus in a strong homogeneous field, where one can easily obtain a rigorous solution if one has a rotating rf field and where an oscillating field gives raise to additional rapidly varying terms. These terms cause merely a very slight modification of the solution, obtained by retaining only the component which rotates in the sense of the nuclear precession.[9]

Equations (3.11), (3.12), and (3.13) represent a set of linear inhomogeneous equations for the determination of the constants χ_g in terms of z and z^*. The determinant of these equations vanishes since the corresponding homogeneous equations have evidently a finite solution with χ_g proportional to $\exp(-\hbar g/kT)$. Nevertheless, the inhomogeneous equations have likewise finite solutions since they do not form an independent set. Indeed, the sum of their left sides vanishes identically since it can be verified with the use of (2.46) that

$$\sum_{p,g}\Gamma_{gg}{}^p\exp(\hbar p/kT)\chi_{g+p}=\sum_{p,g}\Gamma_{gg}{}^p\chi_g$$

for any set of values χ_g. The indeterminacy, caused by this identity, is removed by the additional condition

$$\sum_g\chi_g=0, \tag{3.14}$$

[9] F. Bloch and A. Siegert, Phys. Rev. **57**, 522 (1940).

which follows from (2.50) and (3.6). There exists thus a solution of the Eq. (3.11) to (3.14) for the quantities χ_g in the form

$$\chi_g = T_g I, \tag{3.15}$$

where the abbreviation

$$I = \mathrm{Im}\{(a|D^-|b)z\} \tag{3.16}$$

has been introduced and where each of the values T_g is determined by those of the different quantities $\Gamma_{gg}{}^p$ and has the dimension of a time. Let further

$$T_{ab} = T_a - T_b, \tag{3.17}$$

so that

$$\chi_a - \chi_b = T_{ab} I. \tag{3.18}$$

Expressing I through (3.16) in terms of z and z^* and inserting (3.18), the Eq. (3.7) and its conjugate complex represent two simultaneous linear equations for these two conjugate complex quantities. Solving them and inserting the result in (3.5), one obtains

$$\begin{aligned}(b|\chi|a) &= (a|\chi|b)^* \\ &= \zeta[\exp(-\hbar b/kT) - \exp(-\hbar a/kT)] \\ &\quad \times \frac{(b|D^+|a)(\Delta\omega + i\Gamma_{ab})}{(\Delta\omega)^2 + (\Gamma_{ab})^2 + \Gamma_{ab} T_{ab} |D|^2} e^{i\omega t},\end{aligned} \tag{3.19}$$

where (3.9) and the notation

$$|D|^2 = (b|D^+|a)(a|D^-|b) = |(b|D^+|a)|^2 \tag{3.20}$$

have been used.

The matrix element $(b|\chi|a)$ of (3.19) has the same form as the expression $M_x + iM_y$, obtained by solving the phenomenological equations[10] for the transverse components M_x and M_y of the macroscopic polarization under the influence of a rotating rf field with circular frequency ω. The determination of the two expressions leads in fact to the identical problem in the very special case, where the spin system consists of a single representative nucleus with spin 1/2 and where it was shown in I that the Boltzmann equation is equivalent to the phenomenological equation. By comparison with the very much more general result (3.19), it is seen that T_{ab} and $1/\Gamma_{ab}$ are related to the effective longitudinal relaxation time T_1 and to the effective transverse relaxation time T_2, respectively, for the resonance between the two levels a and b of the spin system. They are both real and positive; this was already shown for Γ_{ab} and will be seen below to hold equally for T_{ab}.

Inserting further the value z from (3.5) and (3.19) in (3.16), and using (3.20), one obtains from (3.18)

$$\begin{aligned}\chi_a - \chi_b &= T_{ab} I \\ &= \zeta[\exp(-\hbar b/kT) - \exp(-\hbar a/kT)] \frac{s}{1+s},\end{aligned} \tag{3.21}$$

and from (3.15)

$$\chi_g = \zeta[\exp(-\hbar b/kT) - \exp(-\hbar a/kT)] \frac{T_g}{T_{ab}} \frac{s}{1+s}, \tag{3.22}$$

where the positive quantity

$$s = \frac{\Gamma_{ab} T_{ab} |D|^2}{(\Delta\omega)^2 + (\Gamma_{ab})^2} \tag{3.23}$$

has been introduced.

Instead of the diagonal elements χ_g of χ, introduced in (3.6), one can also use those of the distribution matrix σ. Denoting them correspondingly by σ_g, one has from (2.47)

$$\sigma_g = (g|\sigma|g) = \zeta \exp(-\hbar g/kT) + \chi_g. \tag{3.24}$$

σ_g represents the "population" of the state g, i.e., the probability to find the spin system in that state. (3.21) and (3.22) can then also be written in the form

$$\sigma_a - \sigma_b = \zeta[\exp(-\hbar a/kT) - \exp(-\hbar b/kT)] \frac{1}{1+s}, \tag{3.25}$$

and

$$\begin{aligned}\sigma_g &= \zeta \exp(-\hbar g/kT) - \zeta[\exp(-\hbar a/kT) \\ &\quad - \exp(-\hbar b/kT)] \frac{T_g}{T_{ab}} \frac{s}{1+s}.\end{aligned} \tag{3.26}$$

The normalization condition $\sum_g \sigma_g = 1$ is satisfied in view of (2.48) and the relation

$$\sum_g T_g = 0 \tag{3.27}$$

which follows from (3.14) and (3.15). The phenomenon of "saturation" is exhibited by Eq. (3.25) in the sense that the populations σ_a and σ_b approach equality with increasing values of s; it is for this reason that the quantity (3.23) is properly referred to as the saturation parameter.

The Eq. (3.26) represents the quantitative formulation of the "general Overhauser effect." It states that even for states $g \neq a,b$ which are not directly affected by the alternating field, one is lead in general to a deviation of the population σ_g from the value, corresponding to thermal equilibrium and attained in the absence of the alternating field, i.e., for $s=0$. This deviation is caused by transitions, due to relaxation processes, and reflects the readjustment of the stationary populations, necessitated by the direct effect of the alternating field upon those of the two particular states a and b. The possibility of an enhanced nuclear polarization, pointed out by Overhauser,[5] is directly based upon this mechanism and shall be illustrated below in a particular case.

The problem to solve the Eqs. (3.11), (3.12), (3.13) and hence, with the additional condition (3.14), to obtain the quantities T_g of Eq. (3.15), can be rewritten by introducing, besides the abbreviation (3.16), the notations

$$V_g = \exp(\hbar g/kT)\chi_g, \tag{3.28}$$

[10] F. Bloch, Phys. Rev. **70**, 460 (1946).

and

$$R_{g,g+p}=\exp(\hbar g/kT)/\Gamma_{gg}{}^{p}, \tag{3.29}$$

so that one obtains from (2.46) for $g=g'$ the relation

$$R_{g,g+p}=R_{g+p,g}. \tag{3.30}$$

Equations (3.11), (3.12), and (3.13) take then the form of the Kirchoff laws:

$$\sum_{g'}(V_{g'}-V_a)/R_{ag'}=-I, \tag{3.31}$$

$$\sum_{g'}(V_{g'}-V_b)/R_{bg'}=I, \tag{3.32}$$

$$\sum_{g'}(V_{g'}-V_g)/R_{gg'}=0, \tag{3.33}$$

of a dc circuit with various junctions g, including a and b, in which V_g represents the voltage at the junction g, $R_{gg'}$ the resistance between two junctions g and g' and I the stationary current, entering at the junction a and leaving at the junction b. To complete the analogy with an ordinary dc circuit, it is seen from the definition (3.29) that, just as every quantity $\Gamma_{gg}{}^{p}$, every resistance $R_{gg'}$ is real and positive and from (3.30), that it is equal to $R_{g'g}$. Given the resistances and the current I, the voltages V_g at all the junctions are determined except for a single additive constant.[11] This constant is, however, necessary for the determination of the quantities χ_g through (3.28) and it is actually to be obtained from the condition (3.14) which takes here the following form:

$$\sum_g V_g \exp(-\hbar g/kT)=0. \tag{3.34}$$

The equivalence with the circuit problem will first be used to show that the quantity T_{ab} of Eq. (3.17) is always positive. Indeed, assuming the current I to be positive, none of the voltages V_g for $g\neq a,b$ can be higher than that at the junction a where the current enters nor lower than that at the junction b where it leaves. It follows on the other hand from (3.34) that some of the voltages V_g, including V_a and V_b, must be positive and some others negative so that, necessarily, V_a is positive, and V_b negative. Since, in virtue of (3.28), χ_a and χ_b have the same sign as V_a and V_b respectively, it follows that their difference (3.18), and, hence, T_{ab} is indeed positive. The same conclusion is reached if I is assumed to be negative since the inversion of the sign of the current is accompanied by that of all voltages and hence also by that of χ_a and χ_b.

A particularly simple interpretation of T_{ab} is obtained from the equivalent circuit problem if one makes the assumption $|\hbar g|\ll kT$ which is usually satisfied for a nuclear spin system. One has then, from (3.28), $\chi_g\cong V_g$; and hence, from (3.18), $V_a-V_b\cong T_{ab}I$. This last equation states that the time T_{ab} is in this case to be obtained as the effective resistance, measured between the terminals a and b of the equivalent circuit.

Equations (3.31), (3.32), (3.33) are equally valid if the voltages are related to the quantities σ_g instead of χ_g, i.e., if one replaces (3.28) by

$$V_g=\exp(\hbar g/kT)\sigma_g. \tag{3.28a}$$

Indeed, in view of (3.24), this definition of V_g differs from that of (3.28) merely by the additive constant ζ. One has then

$$\sum_g V_g \exp(-\hbar g/kT)=1, \tag{3.34a}$$

which takes the place of the condition (3.34) and represents, through (3.24), the normalization condition (2.49).

To illustrate how the consideration of the equivalent circuit can be used to discuss the enhancement of the nuclear polarization, we consider a representative spin system which consists of an atom with atomic spin J and nuclear spin I, coupled by hyperfine structure; this represents a slight modification of Overhauser's case[5] where the electronic part of the spin system was represented by the conduction electrons in an alkali. In analogy to this case it will be assumed that one deals with a single valency electron in an s-state and, for simplicity, with a nucleus of spin 1/2. The external magnetic field H_0 shall be strong enough to cause Paschen-Back effect in the sense that its energy of interaction with the electron moment shall be large compared to the hyperfine structure splitting while its interaction with the nuclear moment shall be considered as negligible.

The energy values of the spin system, divided by $\hbar$, have in this case the form

$$g(m_J,m_I)=\omega_0 m_J+W m_I m_J, \tag{3.35}$$

with

$$\omega_0=2H_0\mu_e/\hbar, \tag{3.36}$$

where μ_e is the magnetic moment of the electron and W the hyperfine structure frequency. We shall further choose the notation

$$a=g(\tfrac{1}{2},\tfrac{1}{2});\quad b=g(-\tfrac{1}{2},\tfrac{1}{2});\quad c=g(\tfrac{1}{2},-\tfrac{1}{2});\quad d=g(-\tfrac{1}{2},-\tfrac{1}{2}) \tag{3.37}$$

and choose the frequency of the applied rf field, in accordance with (3.4) to be

$$\omega=\omega_0+W/2+\Delta\omega, \tag{3.38}$$

i.e., in the neighborhood of the resonance frequency for a transition between the states a and b in which the electron changes its spin orientation while the nucleus remains at $m_I=\frac{1}{2}$.

As an essential assumption for the Overhauser effect, it shall further be postulated that relaxation processes, leading to a change of m_I, occur only through the hyperfine structure coupling so that they cause only transitions in which m_I+m_J remains unchanged. Besides, there exist usually much more frequent relaxation

[11] This statement excludes, of course, cases where certain groups of junctions are completely isolated from the remaining circuit. Such junctions can be at an arbitrary common voltage, but this indeterminacy can be avoided by treating an insulation as the limiting case of a very high resistance; the procedure is equivalent to the treatment of a forbidden relaxation transition of the spin system as the limiting case of a very small transition probability.

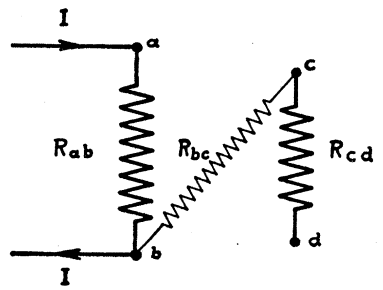

FIG. 1. Equivalent dc circuit for the Overhauser effect.

processes, affecting the electron alone, through transitions in which m_J changes while m_I remains unchanged. This means, with the notation (3.29) and (3.37), that one has relatively small values for R_{ab} and R_{cd}, a finite and relatively large value for R_{bc} and $R_{ad}=R_{ac}=R_{bd}=\infty$.

The equivalent circuit diagram has, therefore, the aspect of Fig. 1. Since no current can pass through the connections bc and cd, one has therefore immediately

$$V_b=V_c=V_d$$

and, hence, from (3.28a),

$$\sigma_b:\sigma_c:\sigma_d=\exp(-\hbar b/kT):\exp(-\hbar c/kT):\exp(-\hbar d/kT). \quad (3.39)$$

This relation, together with (3.34a), i.e., $\sum_g \sigma_g=1$, and (3.25) leads in a simple manner to the values of the populations σ_g and, hence, to the nuclear polarization, defined by

$$\Pi=\sigma_a+\sigma_b-(\sigma_c+\sigma_d)=1-2(\sigma_c+\sigma_d)/(\sigma_a+\sigma_b+\sigma_c+\sigma_d). \quad (3.40)$$

According to (3.26), one has for $s=0$

$$\sigma_a:\sigma_b=\exp(-\hbar a/kT):\exp(-\hbar b/kT)$$

and one obtains in this case with (3.39) from (3.35), (3.37) and (3.40)

$$\Pi_0=\tanh(\hbar\omega_0/2kT)\tanh(\hbar W/4kT), \quad (3.41)$$

i.e., a vanishing polarization in the limit $(\hbar W/kT)\to 0$. The enhancement of the polarization by saturation is most easy to see in this limit by neglecting in the exponents $\hbar W/kT$ but retaining $\hbar\omega_0/kT$ in consistency with the assumption $\omega_0\gg W$, made in (3.35). From (3.39) and (3.25), one obtains then

$$\Pi=\frac{\exp(\hbar\omega_0/kT)-1}{3\exp(\hbar\omega_0/kT)+3}\frac{s}{1+s}, \quad (3.42)$$

i.e., an Overhauser effect in the sense that for $s\gg 1$ the polarization is not governed by the separation of order $\hbar W$ of the nuclear levels but by the much larger separation $\hbar\omega_0$ of the electronic levels.

It should be noted that a deviation from the ideal situation, considered here, i.e., the admission of relaxation processes in which m_I changes without a simultaneous change of m_J, would in the diagram of Fig. 1 correspond to additional finite resistances between ac and bd. The resulting fact, that the voltage at c is thereby brought to a value intermediate between that of a and b, causes the population σ_c to become more nearly equal to σ_a, thus diminishing the effect of saturation upon the nuclear polarization.

4. NUCLEAR SPIN SYSTEM IN A STRONG EXTERNAL FIELD

The general equations of the preceding sections have been developed without specifying the nature of the spin system. By interpreting the term $\hbar E$ in Eq. (2.1) in an appropriate manner, it is in fact not even necessary that this part of the total energy refers to a system of spins. The general Boltzmann equation (2.34) can equally be applied to other systems, provided that its condition of validity (2.33) is satisfied and the results of Sec. 3 allow likewise a more general interpretation of the effect of external perturbations which can be arbitrary as long as they are sufficiently weak and periodic.

Further specifying assumptions are, however, necessary in order to relate the results to particular cases. It shall be assumed, in the following sections, that one deals with a system of nuclear spins which are exposed to a constant external magnetic field H_0 in the z-direction. The part of the spin energy $\hbar E$, due to this field, will be denoted by $\hbar B$ and H_0 shall be sufficiently strong so that B contains the principal contribution to E. The additional part of the spin energy shall be relatively small; it shall consist of the mutual interaction energy $\hbar C$ between the spins and of the contribution which is due to an external time-dependent field $\mathbf{H}_1$, perpendicular to the z-direction, and which shall be denoted by $\hbar D$ in accordance with the notation of Sec. 3.

The spin energy, divided by $\hbar$, has then the form

$$E=B+C+D. \quad (4.1)$$

The various nuclei in the system will be denoted by the index r; nucleus r shall have the spin I_r, the magnetic moment μ_r and the gyromagnetic ratio $\gamma_r=\mu_r/\hbar I_r$. The notations

$$m_r{}^0=I_{zr}, \quad (4.2)$$

and

$$m_r{}^{\pm}=I_{xr}\pm iI_{yr}, \quad (4.3)$$

shall further be used where the operators I_{xr}, I_{yr}, I_{zr} represent the x-, y-, z-component, respectively, of the spin vector $\mathbf{I}_r$. The first part of (4.1) is then given by

$$B=-\sum_r \omega_r m_r{}^0, \quad (4.4)$$

where

$$\omega_r=\gamma_r H_{0r} \quad (4.5)$$

represents the Larmor frequency of the nucleus r, exposed to the constant field H_{0r}.

The distinction between H_{0r} and the external field H_0 arises from the chemical shift, mentioned previously

in the discussion of Eq. (2.22). It causes a slight modification of the effective field, acting upon the nucleus, which is proportional to H_0, so that one has

$$H_{0r}=(1+\epsilon_r)H_0, \tag{4.6}$$

with a numerical constant ϵ_r, characteristic for the electronic environment of nucleus r. This modification is of minor importance in cases where one deals with a system where all nuclei of finite spin are different. The various values of γ_r and, hence, those of ω_r are here normally to be considered as greatly different and incommensurable so that the eigenvalues of B are far from being degenerate. The correction $\epsilon_r H_0$ is, however, important if the spin system contains two or more nuclei of the same kind but placed in different environments in regard to their surrounding electrons. The difference of the chemical shift, measured by the values of ϵ_r, removes here a degeneracy of the eigenvalues of B which would otherwise exist because of the equality of the corresponding values of ω_r. The removal of this degeneracy is complete unless the system contains groups of nuclei which are not only identical but have also the same electronic environment. Such nuclei are called equivalent and their case shall be discussed below.

The form of the second term in (4.1) depends upon the type of spin system, to be considered. In the case of a crystal, the coupling energy $\hbar C$ is primarily due to the direct dipole interaction between the nuclear moments, which was mentioned above in connection with Eq. (2.22). In the same connection it was pointed out that this direct interaction is ineffective for the spin coupling within molecules in a liquid and that there remains here only a much smaller coupling, due to an indirect interaction via the surrounding electrons. It must be invariant against rotation and bilinear in the spin operators of the nuclei and has therefore the form

$$C=\tfrac{1}{2}\sum_{r\neq s} J_{rs}(\mathbf{I}_r\cdot\mathbf{I}_s), \tag{4.7}$$

where the quantities $J_{rs}=J_{sr}$ represent a set of frequencies, independent of the external field and characteristic for the molecule under consideration. Using the notations (4.2) and (4.3), one can also write

$$C=\tfrac{1}{2}\sum_{r\neq s} J_{rs}(m_r{}^0 m_s{}^0+m_r{}^+ m_s{}^-). \tag{4.8}$$

Originating from the field H_1, the last term of (4.1) finally the form

$$D=-\textstyle\sum_r \gamma_r(\mathbf{H}_1\cdot\mathbf{I}_r). \tag{4.9}$$

As in the case of the field H_0, the chemical shift calls, strictly, also for a distinction between the effective field $\mathbf{H}_{1r}$, acting upon the nucleus r and the external field $\mathbf{H}_1$. Being here only of subordinate significance, this distinction shall, however, be omitted to obtain the simpler form (4.9). Introducing the conjugate complex quantities

$$h_r{}^{\pm}=\tfrac{1}{2}\gamma_r(H_{1x}\pm iH_{1y}), \tag{4.10}$$

and using (4.3), as well as the fact that $\mathbf{H}_1$ is perpendicular to the z-direction, one can also write (4.9) in the form

$$D=-\textstyle\sum_r(h_r{}^- m_r{}^+ + h_r{}^+ m_r{}^-). \tag{4.11}$$

The different orders of magnitude, appearing in the contributions to E of Eq. (4.1), require a discussion of its separation into a large part E_0 and a small part E_1. A possible type of separation is obtained by letting

$$E_0=B, \tag{4.12}$$

$$E_1=C+D. \tag{4.13}$$

Besides the other conditions, implied by (2.33), this requires that

$$|B|\gg(|C|,\ |D|,\ |\Gamma|). \tag{4.14}$$

In view of (4.4), the eigenvalues of B are in this case given by

$$g=-\textstyle\sum_r \omega_r m_r, \tag{4.15}$$

where m_r represents the magnetic quantum number of nucleus r so that the left side of (4.14) symbolizes the order of magnitude of the different Larmor frequencies ω_r as well as that of any finite difference $\omega_r-\omega_s$ between two of them. In a strong field H_0, the former are normally of sufficient magnitude to satisfy (4.14) and the same holds for the latter if all the nuclei of the spin system are of different kind. In the presence of identical nuclei which are not equivalent, one deals, however, with considerably smaller frequency differences which are only of the order of the chemical shift and may not be sufficient to justify the condition (4.14) and hence Eqs. (4.12) and (4.13). The procedure to be followed in this case would consist in separating from B the small contribution, due to the chemical shift, and including it in E_1 rather than in E_0. The corresponding change in the eigenvalues (4.15) of B would appear in a redefinition of the Larmor frequencies ω_r by replacing in (4.5) H_{0r} by H_0. One would thus be led to an equality between those values of ω_r which refer to identical nuclei and hence to a degeneracy of the values (4.15), so that the additional quantum number v could not be omitted in the general Boltzmann equation (2.34) or in (2.42). In order to avoid this complication, it shall be assumed below that the chemical shifts are sufficiently large to allow their inclusion in E_0.

An unavoidable degeneracy of the eigenvalues (4.15) appears, however, if the spin system contains groups of nuclei which are equivalent in the sense that they are not only identical but have also the same electronic environment and, therefore, the same Larmor frequency. This situation arises for example in the case of crystals; in fact, one deals here with a very high degeneracy of the eigenvalues (4.15), due to the large number of equivalent nuclei, so that the additional quantum number v of Eq. (2.34) is essential and charac-

terizes actually a very large number of states with the same eigenvalues. As was pointed out in Sec. 2, the static dipole interaction between the nuclei, i.e., the term C in (4.1), may be considered to enter in the form (2.22) into the spin energy. The elements of this matrix which are not diagonal in v will cause a partial removal of the above mentioned high degeneracy but the high order of the corresponding secular problem renders a rigorous treatment prohibitively difficult. Without entering into details, it shall be mentioned here that the problem is closely connected with the existence of spin waves in a crystal and that the removal of the degeneracy by the dipole interaction of the nuclei may be qualitatively accounted for by the introduction of a "spin temperature" which is not necessarily equal to the temperature of the molecular surroundings.

A situation, similar to that of crystals, appears strictly also in the case of liquids and gases which is of particular interest for the further purposes of this paper. To the extent, however, to which the spin interaction between different molecules can be neglected in comparison to that within one molecule, it is here possible to consider the spins in a single molecule, rather than those contained in the whole macroscopic sample, as the representative spin system. This greatly simplifying procedure will be followed for the purposes of this paper; it represents a justified assumption in regard to the spin energy since the interaction between different nuclear moments enters likewise in the form of the average value ΔE of Eq. (2.22) over the molecular surroundings, leaving a noticeable "static" part of the form (4.8) only within the same molecule where the relative distances and angles between the nuclei remain unchanged. The corresponding contribution to ΔE from the interaction between nuclei in different molecules can, however, be omitted since their relative motion is not only random but so rapid that the interaction is almost altogether of the "high-frequency" type, leaving only a negligible contribution to the average value (2.22). A more serious restriction by the simplifying procedure, chosen here, is implied in regard to relaxation mechanisms where the high-frequency terms of the direct dipole interaction are of importance. While it permits the rigorous treatment of intramolecular relaxation, it still demands, as in I, that the fields, acting upon the nuclear spins in a molecule and originating from neighboring molecules, depend upon the variables of the molecular surroundings alone. One can claim no more than qualitative validity for the treatment, presented here, in cases where one deals primarily with intermolecular relaxation, due to the interaction of identical nuclei in different molecules. On the other hand, this situation can in practice be avoided by sufficient dilution with molecules which contain only nuclei with spin zero or with Larmor frequencies sufficiently removed from resonance conditions so that their spins remain in thermal equilibrium with the molecular surroundings and can thus be considered as forming part of the latter.

Even under conditions where it is possible to consider the nuclear spins in a single molecule as the representative spin system, there occur frequently cases of equivalent nuclei. While the ensuing degeneracy of (4.15) demands here rigorously the retention of the index v in Eq. (2.34), this does not cause a serious complication as long as the number N of nuclei in an equivalent group is not too large. Besides, it is known[12] that the total spin I of such a group is a good quantum number with regard to the total spin energy hE. Assuming further that the total spin of an equivalent group does not change in relaxation processes either, the behavior of such a group becomes the same as that of a single nucleus of spin I with the same gyromagnetic ratio as the individual nuclei in this group. The actually existing degeneracy can thus be by-passed by attributing to each equivalent group independently the various possible spin values I with their proper statistical weights. In the case of equivalent nuclei of spin 1/2, I can assume the values $I=\frac{1}{2}N-\nu$, where ν is an integer, satisfying the condition $0\leqq\nu\leqq\frac{1}{2}N$ with the corresponding statistical weight

$$\left[\binom{N}{\nu}-\binom{N}{\nu-1}\right]\Big/\binom{N}{\nu_{\max}}$$

for a given value of ν and, hence, of I.

To simplify the treatment, it shall be assumed below that one deals either with molecules where there exist only equivalent groups of the foregoing type so that the degeneracy is immaterial or where it is absent, due to the fact that there exist no equivalent nuclei. The following discussion will therefore be based upon Eqs. (2.44) to (2.52), obtained in Sec. 2 by the simplifying omission of the index v.

The separation of the spin energy, indicated by Eqs. (4.12) and (4.13) does not impose any conditions upon the relative magnitudes of $|C|$, $|\Gamma|$ and $|D|$. It permits, in particular, the treatment of cases where the effects, due to the field $\mathbf{H}_1$ and those due to relaxation, measured by $|D|$ and $|\Gamma|$, respectively, are comparable or large compared to the coupling effects, measured by $|C|$. Referring to them in this sense as cases of "strong" field or "strong" relaxation, they shall be considered in Secs. 6 and 7. On the other hand, this separation demands in view of (4.14) that the coupling effects are small compared to any internal chemical shifts in a molecule. Although this condition is frequently satisfied, there are also cases where they are comparable.

In order to consider such cases of relatively strong spin coupling, one can introduce another type of separation, given by

$$E_0=B+C, \tag{4.16}$$

[12] E. L. Hahn and D. E. Maxwell, Phys. Rev. 88, 1070 (1952).

and hence

$$E_1=D. \tag{4.17}$$

As a consequence of (2.33) one obtains here instead of (4.14) the conditions

$$(|B|,|C|)\gg(|D|,|\Gamma|), \tag{4.18}$$

which, indeed, do not restrict the relative magnitudes on the left side and permit therefore in particular the treatment of cases with comparable coupling and chemical shift.

This treatment is, on the other hand, restricted by the necessary relative smallness of $|D|$, expressed by (4.18). The same restriction was required in deriving the results of the previous section for a periodic perturbation in the sense that they refer to a "weak" alternating field and these more general results shall be applied below to a nuclear spin system in a strong constant field. It shall be noted that the case

$$|B|\gg|C|\gg(|D|,|\Gamma|) \tag{4.19}$$

can be treated either with the separation given by (4.12), (4.13) or with that, given by (4.16), (4.17) so that the choice between the two is here a matter of convenience.

Before entering into more specific considerations of a nuclear spin system, an expression will be derived which relates the solution of the Boltzmann equation to a quantity $\mathcal{S}$, representing a measure for the directly observed signals of nuclear induction. Except for properties of the receiver circuit, the signals are determined by the components M_x, M_y of the nuclear polarization, perpendicular to the z-direction of the strong field H_0. Denoting the number of representative spin system, i.e., in our case the number of molecules, per unit volume with n, $\mathcal{S}$ will be defined by

$$\mathcal{S}=\frac{d}{dt}(M_x+iM_y)=n\frac{d}{dt}\langle\mu_x+i\mu_y\rangle. \tag{4.20}$$

Since it contains all that has to be known about the nuclear system in order to determine the signals, the complex quantity $\mathcal{S}$ will be used as a measure and will be referred to, for brevity, as the "signal" itself. The angular braces in (4.20) indicate the expectation value and μ_x, μ_y stand to the x- and y-component, respectively, of the total magnetic moment of the spin system. Using the notation (4.3), it is therefore

$$\mu_x+i\mu_y=\sum_r(\mu_{xr}+i\mu_{yr})=\hbar\sum_r\gamma_r m_r^+, \tag{4.21}$$

and hence, with the general definition (2.6) for the expectation value of a spin function

$$\mathcal{S}=\hbar n\frac{d}{dt}\operatorname{Tr}[\sum_r\gamma_r m_r^+\sigma(t)]. \tag{4.22}$$

The distribution matrix σ shall be expressed by the transformed distribution matrix σ^* through (2.14), so that

$$\mathcal{S}=\hbar n\sum_{gv}\sum_{g'v'}\frac{d}{dt}\{(g'v'|\sum_r\gamma_r m_r^+|gv)\times(gv|\sigma^*(t)|g'v')e^{-i(g-g')t}\}. \tag{4.23}$$

In view of the condition (2.33), the rate of change of σ^*, measured by the quantity $\nu\cong|\Gamma|$, $|E_1|$ of Sec. 2 must be small compared to the nonvanishing values $|g-g'|$. It is therefore permissible to retain in the double sum of (4.23) only the terms with $g\neq g'$ and to keep in these terms only the time derivative of the exponential. Using again (2.14) to go back to the distribution matrix σ, one can thus write

$$\mathcal{S}=i\hbar n\sum_{gv}\sum_{g'v'}(g'-g)(g'v'|\sum_r\gamma_r m_r^+|gv)(gv|\sigma|g'v'). \tag{4.24}$$

It should be noted for later purposes that the magnitude of the matrix elements of m_r^+ in (4.24) is restricted in view of the forms (4.12) or (4.16) of E_0. Indeed, substituting these forms in the identity

$$(g'-g)(g'v'|m_r^+|gv)=(g'v'|E_0,m_r^+]|gv),$$

and observing in the commutator $[B,m_r^+]$, with B given by (4.4), that m_r^+ commutes with m_s^0 for $s\neq r$, while $[m_r^0,m_r^+]=m_r^+$ as a consequence of the commutation rules for the components of the spin vector $\mathbf{I}_r$, one obtains

$$(g'-g+\omega_r)(g'v'|m_r^+|gv)=\begin{cases}0 & \text{for } E_0=B\\ (g'v'|[C,m_r^+]|gv) & \text{for } E_0=B+C.\end{cases} \tag{4.25}$$

The matrix elements of m_r^+ vanish therefore in the case $E_0=B$ if $g'-g+\omega_r\neq 0$ and they are negligibly small in the case $E_0=B+C$ if $|g'-g+\omega_r|\gg|C|$.

Using (2.38) and noting that, as a diagonal matrix, σ_0 does not contribute to (4.24), one can also write

$$\mathcal{S}=i\hbar n\sum_{gv}\sum_{g'v'}(g'-g)(g'v'|\sum_r\gamma_r m_r^+|gv)(gv|\chi|g'v'). \tag{4.26}$$

Finally, if there is no degeneracy which requires the retention of v, v', then (4.26) can further be simplified to

$$\mathcal{S}=i\hbar n\sum_{gg'}(g'-g)(g'|\sum_r\gamma_r m_r^+|g)(g|\chi|g'), \tag{4.27}$$

which will later be used in the evaluation of signal magnitudes.

5. NUCLEAR SPIN SYSTEM WITH STRONG SPIN COUPLING

The situation to be considered in this section, refers to the form (4.16) of E_0 and the corresponding condition (4.18) for the various orders of magnitude. The

effect of the coupling term C of (4.1) shall thus be strong, compared to that of the field $\mathbf{H}_1$ and to the effects of relaxation, but its magnitude relative to the chemical shift shall not be subjected to any restrictions.

It is therefore possible to apply the results of Sec. 3, provided that $\mathbf{H}_1$ contains only a single frequency ω. It shall actually be assumed that one deals with a rotating field of magnitude H_1 and with arbitrary phase, neglecting in the usual manner the very small effects[9] which arise in the normal presence of an oscillating field with amplitude $2H_1$. One has then from (4.10)

$$h_r^{\pm}=\tfrac{1}{2}\gamma_r H_1 e^{\mp i(\omega t+\delta)}. \tag{5.1}$$

Inserting in (4.11), one thus obtains D in the form (3.1) with

$$D^{\pm}=-\tfrac{1}{2}H_1 e^{\pm i\delta}\textstyle\sum_r \gamma_r m_r^{\pm}. \tag{5.2}$$

In order to apply the results of Sec. 3 to the signal $\mathcal{S}$ of (4.27), one has to remember that for a frequency ω in the vicinity of the resonance frequency $a-b$, there appear in (4.27) only the matrix elements $(a|\chi|b)$ and $(b|\chi|a)$ of Eq. (3.19) for $g=a$, $g'=b$ and $g=b$, $g'=a$ respectively. The contribution from $g=b$, $g'=a$ can, however, be neglected; it contains in the numerator of (3.19) the factor $(b|D^+|a)$ so that, in the corresponding term of (4.27), there appears the product

$$(a|\textstyle\sum_r \gamma_r m_r^+|b)(b|\sum_r \gamma_r m_r^+|a). \tag{5.3}$$

In view of the restricted magnitudes of the matrix elements previously mentioned as a consequence of (4.25), the second and first factor in this product contain appreciable contributions only from those terms in the summation over r for which ω_r differs by no more than an amount of order $|C|$ from the resonance frequency $a-b$ and its negative $b-a$, respectively. Except in the highly accidental case where some of the values ω_r are within the order $|C|$ equal and opposite to some other values ω_r, the presence of appreciable terms in both factors is therefore excluded so that the product (5.3) and hence the contribution to (4.27) from $g=b$, $g'=a$ can indeed be neglected.

The contribution from $g=a$, $g'=b$ yields, however, from (4.27), using the conjugate complex of (3.19) and Eq. (5.2),

$$\mathcal{S}=\tfrac{1}{2}iH_1\hbar n\zeta[\exp(-\hbar b/kT)-\exp(-\hbar a/kT)](a-b)\times\frac{|(b|\sum_r \gamma_r m_r^+|a)|^2(\Delta\omega-i\Gamma_{ab})}{(\Delta\omega)^2+(\Gamma_{ab})^2+\Gamma_{ab}T_{ab}H_1^2|(b|\sum_r \gamma_r m_r^+|a)|^2/4}\times e^{-i(\omega t+\delta)}. \tag{5.4}$$

An appreciable contribution from the matrix elements in the numerator and denominator of this expression arises here only from those terms in the summation over r for which the corresponding frequencies ω_r are very nearly equal to $a-b$ and therefore also very nearly equal to each other. This near equality of their Larmor frequencies occurs normally only for identical nuclei with equal values γ_r of their gyromagnetic ratios, so that one can write

$$\mathcal{S}=\tfrac{1}{2}iH_1\hbar n\zeta[\exp(-\hbar b/kT)-\exp(-\hbar a/kT)](a-b)\gamma_r^2\times\frac{|(b|\sum_r m_r^+|a)|^2(\Delta\omega-i\Gamma_{ab})}{(\Delta\omega)^2+(\Gamma_{ab})^2+\Gamma_{ab}T_{ab}\gamma_r^2H_1^2|(b|\sum_r m_r^2|a)|^2/4}\times e^{-i(\omega t+\delta)}, \tag{5.5}$$

where the selection of the single value γ_r which appears in this formula can be expressed by the approximate relation

$$\gamma_r H_0\cong a-b. \tag{5.6}$$

The sign of near equality indicates the neglect of the chemical shift of Eq. (4.6) and of terms in $a-b$ of order $|C|$; it does not lead, normally, to an ambiguity in the choice of the single value γ_r, appearing in (5.5), and of the corresponding single kind of nuclei which contribute appreciably to the signal.

The above expression for $\mathcal{S}$ has the same form as that obtained for $\dot{M}_x+i\dot{M}_y$ from the solution of the phenomenological equations[10] with the real and imaginary part of the numerator in (5.5) resulting in the parts of the signal which are in phase or 90 degrees out of phase, respectively, with the rotating field. The equivalent longitudinal and transverse relaxation times are identified by the equations

$$(T_1)_{ab}=T_{ab}|(b|\textstyle\sum_r m_r^+|a)|^2/4 \tag{5.7}$$

and

$$(T_2)_{ab}=1/\Gamma_{ab}, \tag{5.8}$$

respectively.

It was shown in I that the two procedures are equivalent in the case of a single nucleus r with spin 1/2. With only two states a and b, corresponding to $m_r=-\frac{1}{2}$ and $m_r=\frac{1}{2}$, respectively, one has here $(b|m_r^+|a)=1$. A simple check is here obtained by assuming in Eq. (5.3) of I that $\kappa\ll 1$ in which case the quantity Φ_{11}^1 of this equation has the same significance as the inverse of the time T_{ab} in the relation (5.7), yielding thus indeed the same result $T_1=T_{ab}/4$. A complete quantitative check with the phenomenological result is here further obtained by replacing the frequencies a and b in (5.5) by $\frac{1}{2}\gamma H_0$ and $-\frac{1}{2}\gamma H_0$, respectively, with $\gamma=2\mu/\hbar$.

A further simplification of (5.5) arises if H_1 is sufficiently small so that the term, proportional to H_1^2, in the numerator can be neglected, and if $(a,b)\ll kT$. One obtains then

$$\mathcal{S}=\tfrac{1}{2}iH_1 n\zeta\frac{\hbar^2}{kT}(a-b)^2\gamma_r^2\frac{|(b|\sum_r m_r^+|a)|^2(\Delta\omega-i\Gamma_{ab})}{(\Delta\omega)^2+(\Gamma_{ab})^2}\times e^{-i(\omega t+\delta)}. \tag{5.9}$$

The resonance line is here uniquely characterized by the natural width Γ_{ab} and by the intensity, defined

through integration over $\Delta\omega$ in the form

$$\text{Int}=e^{i(\omega t+\delta)}\int \mathfrak{S}d(\Delta\omega)=\frac{\pi}{2}H_1 n\zeta\frac{\hbar^2}{kT}(a-b)^2 \times\gamma_r{}^2|(b|\textstyle\sum_r m_r{}^+|a)|^2. \quad (5.10)$$

The intensity ratios of a group of lines with relatively small differences of their resonance frequency is thus measured by the absolute squares of their corresponding matrix elements $|(b|\sum_r m_r{}^+|a)|^2$.

No special assumption has been made, so far, about the coupling term C of Eq. (4.16), except that it has to be large enough to satisfy the condition (4.18). Its presence affects, however, not only the resonance frequencies $a-b$ of the spin system and the matrix elements $(b|m_r{}^+|a)$ which determine the intensity, but it enters also in the natural line width, affecting it differently for different lines in a spectrum. At the same time the line width will of course depend upon the nature of the coupling between the spin system and the molecular system. In order to investigate in a general manner the dependence of the line width upon both these features, it is convenient to expand the interaction term G of Eq. (2.1) in the form

$$G=\sum_\lambda\sum_{\tau_r} I_\lambda{}^{\tau_r}F_\lambda{}^{-\tau_r}, \quad (5.11)$$

which represents a generalization of the Eq. (4.2) of I. The symbol τ_r stands here actually for a group $(\tau_1, \tau_2\cdots\tau_r\cdots)$ of positive and negative integers, including zero, and $I_\lambda{}^{\tau_r}$ represents, in analogy to (4.4) of I, a spin function with the property

$$(m_r|I_\lambda{}^{\tau_r}|m_r')=I_{\lambda m_r}{}^{\tau_r}\delta_{m_r,m_r'+\tau_r}, \quad (5.12)$$

defined in a representation in which all the operators $m_r{}^0$ of (4.2) are simultaneously diagonal with the magnetic quantum number m_r as eigenvalues. The δ symbol in (5.12) is defined to be unity if $m_r-m_r'=\tau_r$ for all values of r and to be zero otherwise, and the index λ characterizes one spin function $I_\lambda{}^{\tau_r}$ out of the generally several which satisfy the condition (5.12) with individual corresponding numbers $I_{\lambda m_r}{}^{\tau_r}$. The operators $F_\lambda{}^{-\tau_r}$ in (5.11) act upon the variables of the molecular surroundings alone, i.e., they are diagonal either in the quantum numbers m_r or (g,v) of the spin system. The operator pair $F_\lambda{}^{\tau_r}$, $F_\lambda{}^{-\tau_r}$ as well as $I_\lambda{}^{\tau_r}$, $I_\lambda{}^{-\tau_r}$ shall be Hermitian conjugate in order that G represents a Hermitian operator.

While the more general definition (2.17) of the relaxation coefficients could equally well be used and would not add any substantial difficulty, the following developments will be restricted to the simpler form (2.45). One obtains then, in analogy to (4.8), (4.9), and (4.11) of I,

$$\Gamma_{gg'}{}^p=\sum_{\lambda\lambda'}\sum_{\tau_r\tau_{r'}}\Phi_{\lambda\lambda'}{}^{p,\tau_r,\tau_{r'}}(g|I_\lambda{}^{-\tau_r}|g+p)(g'+p|I_{\lambda'}{}^{\tau_{r'}}|g'), \quad (5.13)$$

with

$$\Phi_{\lambda\lambda'}{}^{p,\tau_r,\tau_{r'}}=\pi\sum_{uu'}\int\eta_u(f)\eta_{u'}(f-p)P(f) \times(fu|F_\lambda{}^{\tau_r}|f-p,u')(f-p,u'|F_{\lambda'}{}^{-\tau_{r'}}|fu)df, \quad (5.14)$$

and the relation

$$\Phi_{\lambda'\lambda}{}^{-p,-\tau_{r'},-\tau_r}=\exp(\hbar p/kT)\Phi_{\lambda\lambda'}{}^{p,\tau_r,\tau_{r'}}.{}^{13} \quad (5.15)$$

It will further be noted that the condition

$$\Gamma_{g'g}{}^p=(\Gamma_{gg'}{}^p)^*, \quad (5.16)$$

which follows from (2.45) in view of the Hermitian character of G, is satisfied since the two relations

$$\Phi_{\lambda'\lambda}{}^{p,\tau_r,\tau_{r'}}=(\Phi_{\lambda\lambda'}{}^{p,\tau_r,\tau_{r'}})^* \quad (5.17)$$

and

$$(g''|I_\lambda{}^{\tau_r}|g''')=(g'''|I_\lambda{}^{-\tau_r}|g'')^* \quad (5.18)$$

are valid because of the Hermitian conjugate character of two operators with equal and opposite upper indices τ_r.

The values of the coefficients Φ of Eq. (5.14) depend upon the properties of the spin system only insofar as they contain the transition-frequencies p. The effect of a small spin coupling upon these coefficients will therefore be negligible since it affects only very slightly the eigenvalues g of E_0 and hence their differences p. On the other hand, even a small coupling will have a considerable effect upon the matrix elements of the spin functions if it is comparable to the chemical shift and it will thus appreciably affect the values (5.13) in a manner which does not involve the properties of the molecular surroundings.

In order to demonstrate this general feature in the case of particular relaxation mechanisms, it is convenient to make an assignment of the indices λ and the corresponding operators $I_\lambda{}^{\tau_r}$, $F_\lambda{}^{\tau_r}$ such that (5.11) corresponds to an expansion in powers of the spin vector components of the individual nuclei. Retaining first- and second-order terms in this expansion, one can write

$$G=\sum_{s\tau_s} I_s{}^{\tau_s}F_s{}^{-\tau_s}+\sum_{s\tau_s}\sum_{t\tau_{t'}} I_s{}^{\tau_s}I_t{}^{\tau_{t'}}F_{st}{}^{-\tau_s,-\tau_{t'}}. \quad (5.19)$$

The first term implies that λ refers here to one of the nuclei s and that for $\lambda=s$, one chooses $\tau_r=0$ for $r\neq s$, while τ_s can assume the values 0, 1, -1 with the

[13] The expression (5.14) represents a generalization of the Fourier-transform J, obtained by Y. Ayant [J. phys. radium **16**, 411 (1955)] from the quantum-mechanical analog of a classical correlation function $k(\tau)$. If one assumes in (5.14) $\lambda=\lambda'$, $\tau_r=\tau_r'$, writes $F_\lambda{}^{\tau_r}=\xi$ and assumes no degeneracy of the molecular system by suppressing the indices u, u', one finds indeed

$$\Phi_{\lambda\lambda}{}^{p,\tau_r,\tau_r}=(\hbar\pi/Z)J(-p),$$

where J and Z have the same significance as in Eq. (9) of Ayant. His relation (10) between $J(p)$ and $J(-p)$ is then seen to be equivalent to (5.15) by observing that

$$\Phi_{\lambda\lambda}{}^{p,\tau_r,\tau_r}=\Phi_{\lambda\lambda}{}^{p,-\tau_r,-\tau_r},$$

in view of the Hermitian conjugate character of $F_\lambda{}^{\tau_r}$ and $F_\lambda{}^{-\tau_r}$.

notation

$$I_s^0=m_s^0;\quad I_s^{\pm1}=m_s^{\pm}, \tag{5.20}$$

more closely analogous to that of Eq. (4.5) in I than that introduced in Eqs. (4.2), (4.3) of this paper. Correspondingly, it is

$$F_s^0=-\gamma_s H_{zs}';\quad F_s^{\pm1}=-\tfrac{1}{2}\gamma_s(H_{xs}'\pm iH_{ys}'), \tag{5.21}$$

where the vector $\mathbf{H}_s'$ represents a magnetic field, existing at the location of the nucleus s and originating from the molecular surroundings.

Similarly, the second term in (5.19) implies the assignment of λ to a pair s, t, of nuclei with the same significance of the operators $I_s^{\tau_s}$, $I_t^{\tau_t}$ as in (5.20). For $s\doteq t$, it contains thus the terms, corresponding to quadrupolar relaxation in analogy to Eq. (4.6) of I and with the corresponding relation of the operators $F_{ss}^{-\tau_s,-\tau_{s'}}$ to the gradients of the electric field $\mathbf{E}_s'$ at the position of the nucleus s. In contrast to the first term which expresses the feature of "external" dipole relaxation, the second term of (5.19) contains besides for $s\neq t$ the mechanism of "internal" dipole relaxation, arising from the direct dipole interaction

$$(\boldsymbol{\mu}_s\cdot\boldsymbol{\mu}_t)/r^3-3(\boldsymbol{\mu}_s\cdot\mathbf{r})(\boldsymbol{\mu}_t\cdot\mathbf{r})/r^5, \tag{5.22}$$

between the nuclei s, t with magnetic moments μ_s, μ_t, respectively, and with a relative distance vector $\mathbf{r}$. For molecules in a liquid or a gas the small variation of the magnitude r can be neglected since the principal variation of the vector $\mathbf{r}$ arises from the change of orientation, due to rotation of the molecule. Introducing polar angles φ and ϑ to characterize the orientation of $\mathbf{r}$, one obtains here from the comparison of the term $s\neq t$ in (5.19) with (5.22)

$$\begin{aligned}
&F_{st}^{00}=c_{st}(1-3\cos^2\vartheta);\\
&F_{st}^{1,-1}=F_{st}^{-1,1}=c_{st}(\tfrac{1}{2}-\tfrac{3}{4}\sin^2\vartheta);\\
&F_{st}^{\pm1,0}=F_{st}^{0,\pm1}=-c_{st}\tfrac{3}{2}\sin\vartheta\cos\vartheta e^{\pm i\varphi};\\
&F_{st}^{\pm1,\pm1}=-\tfrac{3}{4}\sin^2\vartheta e^{\pm2i\varphi},
\end{aligned} \tag{5.23}$$

with

$$c_{st}=\hbar\gamma_s\gamma_t/r^3,$$

and where the angles φ and ϑ must be considered as variables of the molecular surroundings.

The insertion of the operators $F_\lambda^{\tau_r}$ in (5.14), corresponding to these various relaxation mechanisms, and the further evaluation of the desired expressions for the line width through (5.13) and (3.8) is straightforward but too lengthy to be carried out in this paper. It will be assumed, instead, that one deals only with the first term in (5.19), i.e., with external dipole relaxation. One obtains then, from (5.13) and (5.14),

$$\Gamma_{gg'}{}^p=\sum_{st}\sum_{\tau_s\tau_t}\Phi_{st}^{p\tau_s\tau_t}(g|I_s^{-\tau_s}|g+p)(g'+p|I_t^{\tau_t}|g'), \tag{5.24}$$

and

$$\Phi_{st}^{p\tau_s\tau_t}=\pi\sum_{uu'}\int\eta_u(f)\eta_{u'}(f-p)P(f)\times(fu|F_s^{\tau_s}|f-p,u')(f-p,u'|F_t^{-\tau_t}|fu)df. \tag{5.25}$$

As a further great simplification, it will be assumed, besides, that the fields $\mathbf{H}_s'$, $\mathbf{H}_t'$, acting upon two different nuclei s and t are uncorrelated so that (5.25) vanishes for $s\neq t$. If one assumes isotropy of the molecular surroundings, which is indeed realized in liquids and gases, only the coefficients

$$\Phi_{ss}^{p\tau_s\tau_s}=\Phi_s^{p\tau_s} \tag{5.26}$$

have to be retained in (5.24) and can be seen, in view of (5.21), to satisfy in this case the relation

$$\Phi_s^{p0}=2\Phi_s^{p1}=2\Phi_s^{p,-1}=\Phi_s^p, \tag{5.27}$$

so that one obtains from (4.24)

$$\begin{aligned}\Gamma_{gg'}{}^p=\textstyle\sum_r\Phi_r^p\{&(g|I_r^0|g+p)(g'+p|I_r^0|g')\\&+\tfrac{1}{2}(g|I_r^{-1}|g+p)(g'+p|I_r^1|g')\\&+\tfrac{1}{2}(g|I_r^1|g+p)(g'+p|I_r^{-1}|g')\}.\end{aligned} \tag{5.28}$$

To illustrate the effect of a spin coupling of the type (4.8) upon the line width and relaxation time, equation (5.28) shall be applied to the simple case of a spin system, consisting of two identical nuclei s and t of spin 1/2 with Larmor frequencies ω_s and ω_t, respectively, which are separated by a relative chemical shift

$$\delta=\omega_s-\omega_t, \tag{5.29}$$

small compared to ω_s and ω_t. Using (4.4) and (4.8), one has here

$$\begin{aligned}E_0=B+C=&-(\omega_s m_s^0+\omega_t m_t^0)\\&+J[m_s^0m_t^0+\tfrac{1}{2}(m_s^+m_t^-+m_s^-m_t^+)],\end{aligned} \tag{5.30}$$

with the four eigenvalues $g=a,\ b,\ c,\ d$, given by

$$\begin{aligned}&a=\bar\omega+\tfrac{1}{4}J,\quad b=\tfrac{1}{2}(\delta^2+J^2)^{\frac{1}{2}}-\tfrac{1}{4}J,\\&c=-\tfrac{1}{2}(\delta^2+J^2)^{\frac{1}{2}}-\tfrac{1}{4}J,\quad d=-\bar\omega+\tfrac{1}{4}J,\end{aligned} \tag{5.31}$$

where

$$\bar\omega=\tfrac{1}{2}(\omega_s+\omega_t). \tag{5.32}$$

From the representation (5.12), the matrix elements of I_r^τ for $\tau=-1,\ 0,\ 1$, and $r=s,\ t$, required in (5.28), are obtained in the form

$$(g''|I_s^\tau|g''')=\sum_{m_sm_t}(g''|m_s+\tau,m_t)(m_sm_t|g''')I_{sm_s}{}^\tau, \tag{5.33}$$

and

$$(g''|I_t^\tau|g''')=\sum_{m_sm_t}(g''|m_s,m_t+\tau)(m_sm_t|g''')I_{tm_t}{}^\tau, \tag{5.34}$$

with

$$I_{r-\frac{1}{2}}{}^1=I_{r\frac{1}{2}}{}^{-1}=1,\ I_{r\frac{1}{2}}{}^1=I_{r-\frac{1}{2}}{}^{-1}=0,\ I_{r\pm\frac{1}{2}}{}^0=\pm\tfrac{1}{2}, \tag{5.35}$$

for $r=s,\ t$.

The transformation functions, entering in (5.33) and (5.34), are in our case given by

$$\begin{aligned}
&(a|m_sm_t)=(m_sm_t|a)=\delta_{m_s-\frac{1}{2}}\delta_{m_t-\frac{1}{2}},\\
&(b|m_sm_t)=(m_sm_t|b)=\alpha^{\frac{1}{2}}\delta_{m_s-\frac{1}{2}}\delta_{m_t\frac{1}{2}}+\beta^{\frac{1}{2}}\delta_{m_s\frac{1}{2}}\delta_{m_t-\frac{1}{2}},\\
&(c|m_sm_t)=(m_sm_t|c)=\beta^{\frac{1}{2}}\delta_{m_s-\frac{1}{2}}\delta_{m_t\frac{1}{2}}-\alpha^{\frac{1}{2}}\delta_{m_s\frac{1}{2}}\delta_{m_t-\frac{1}{2}},\\
&(d|m_sm_t)=(m_sm_t|d)=\delta_{m_s\frac{1}{2}}\delta_{m_t\frac{1}{2}},
\end{aligned}\tag{5.36}$$

with

$$\alpha=1-\beta=\tfrac{1}{2}[1+\delta/(\delta^2+J^2)^{\frac{1}{2}}];\tag{5.37}$$

and one obtains from (5.33) and (5.34), with (5.35) and (5.36),

$$\begin{aligned}
&(b|I_s^1|a)=(a|I_s^{-1}|b)=(d|I_s^1|c)=(c|I_s^{-1}|d)\\
&\quad=(c|I_t^1|a)=(a|I_t^{-1}|c)=(d|I_t^1|b)\\
&\quad=(b|I_t^{-1}|d)=\sqrt{\beta},\\
&-(c|I_s^1|a)=-(a|I_s^{-1}|c)=(d|I_s^1|b)\\
&\quad=(b|I_s^{-1}|d)=(b|I_t^1|a)=(a|I_t^{-1}|b)\\
&\quad=-(d|I_t^1|c)=-(c|I_t^{-1}|d)=\sqrt{\alpha},\\
&-(a|I_s^0|a)=-(a|I_t^0|a)=(d|I_s^0|d)=(d|I_t^0|d)=\tfrac{1}{2},\\
&-(b|I_s^0|b)=(b|I_t^0|b)=(c|I_s^0|c)\\
&\quad=-(c|I_t^0|c)=\tfrac{1}{2}(\alpha-\beta),\\
&-(b|I_s^0|c)=-(c|I_s^0|b)=(b|I_t^0|c)\\
&\quad=(c|I_t^0|b)=(\alpha\beta)^{\frac{1}{2}},
\end{aligned}\tag{5.38}$$

with all other matrix elements of $I_{s,t}^0$, $I_{s,t}^{\pm1}$ equal to zero.

By neglecting the slight variations of the coefficients $\Phi_r{}^p$ of (5.28), due to chemical shift and coupling, i.e., with

$$\Phi_r{}^{a-b}\cong\Phi_r{}^{a-c}\cong\Phi_r{}^{b-d}\cong\Phi_r{}^{c-d}\cong\Phi_r{}^{\bar\omega};\quad\Phi_r{}^{b-c}\cong\Phi_r{}^0,\tag{5.39}$$

the line widths, resulting from the above formulas, can be conveniently expressed in terms of the longitudinal and transverse relaxation times T_{1r} and T_{2r} respectively, which the nuclei $r=s,t$ would exhibit separately, i.e., under the conditions considered in I.

In Eqs. (5.3) and (5.4) of I, the quantities $2\Phi_{11}{}^1$ and $\Phi_{11}{}^0$ can then be replaced by $\Phi_r{}^{-\bar\omega}$ and $\Phi_r{}^0$, respectively, so that

$$\Phi_r{}^{-\bar\omega}=\frac{1}{(1+e^{-\kappa})T_{1r}};\quad\Phi_r{}^{\bar\omega}=e^{-\kappa}\Phi_r{}^{-\bar\omega}=\frac{1}{(1+e^{\kappa})T_{1r}};$$

$$\Phi_r{}^0=\frac{1}{T_{2r}}-\frac{1}{2T_{1r}},\tag{5.40}$$

with

$$\kappa=\hbar\bar\omega/kT.\tag{5.41}$$

From the general expression (3.8) for the line width and with (5.28) and (5.38), one thus obtains the following for the widths of the four lines which have a finite intensity:

$$\begin{aligned}
\Gamma_{ab}&=\beta\left(\frac{1}{T_{2s}}+\frac{1}{1+e^{-\kappa}}\frac{1}{T_{1t}}\right)+\alpha\left(\frac{1}{T_{2t}}+\frac{1}{1+e^{-\kappa}}\frac{1}{T_{1s}}\right),\\
\Gamma_{ac}&=\alpha\left(\frac{1}{T_{2s}}+\frac{1}{1+e^{-\kappa}}\frac{1}{T_{1t}}\right)+\beta\left(\frac{1}{T_{2t}}+\frac{1}{1+e^{-\kappa}}\frac{1}{T_{1s}}\right),\\
\Gamma_{cd}&=\beta\left(\frac{1}{T_{2s}}+\frac{1}{1+e^{\kappa}}\frac{1}{T_{1t}}\right)+\alpha\left(\frac{1}{T_{2t}}+\frac{1}{1+e^{\kappa}}\frac{1}{T_{1s}}\right),\\
\Gamma_{bd}&=\alpha\left(\frac{1}{T_{2s}}+\frac{1}{1+e^{\kappa}}\frac{1}{T_{1t}}\right)+\beta\left(\frac{1}{T_{2t}}+\frac{1}{1+e^{\kappa}}\frac{1}{T_{1s}}\right).
\end{aligned}\tag{5.42}$$

Although they were derived under very special simplifying assumptions, these expressions exhibit some interesting features which can be expected to occur similarly in more general cases: In the first place it should be noted that they contain not only the transverse relaxation times T_{2s}, T_{2t} which would solely determine the line width in the case of separated nuclei, but also the corresponding longitudinal relaxation times T_{1s}, T_{1t}. The significance of these features is best seen in the limit $J/\delta\to0$, where, according to (5.37), one has for $\delta>0$: $\alpha=1$, $\beta=0$. Considering in particular the line a, b, its frequency, according to (5.29), (5.31), and (5.32), is given in this case by $a-b=\omega_t+\frac{1}{2}J$ and corresponds in fact to a transition caused by the applied rf field, in which the nucleus t changes its quantum number m_t by unity while the other nucleus s remains in the state $m_s=-\frac{1}{2}$. Nevertheless, there occur also transitions of the nucleus s, due to the relaxation, which shorten the lifetimes of the initial and final state a and b and hence contribute to the line width Γ_{ab} in the form of the term $[1/(1+e^{-\kappa})](1/T_{1s})$ in addition to the term $1/T_{2t}$ which would alone be present for the separate nucleus t. Similarly, there appears the contribution $[1/(1+e^{\kappa})](1/T_{1s})$ in the width Γ_{cd} of the resonance line corresponding to the transition in which nucleus s remains in the state $m_s=\frac{1}{2}$. For $\bar\omega>0$, this is the lower of the two states of the nucleus s and no relaxation transitions can therefore take place in the limit of very low temperatures, i.e., for $\kappa\to\infty$; this furnishes the reason for which the line width is in this limit given by $1/T_{2t}$ alone.

Another feature of interest lies in the fact that the line widths (5.42) show a strong and different dependence upon the ratio of the coupling constant J to the chemical shift δ, entering through (5.37) in the constants α and $\beta=1-\alpha$. In the usual case $\kappa\ll1$, one obtains

$$\begin{aligned}
\Gamma_{ab}&=\Gamma_{cd}=\beta\left(\frac{1}{T_{2s}}+\frac{1}{2T_{1t}}\right)+\alpha\left(\frac{1}{T_{2t}}+\frac{1}{2T_{1s}}\right),\\
\Gamma_{ac}&=\Gamma_{bd}=\alpha\left(\frac{1}{T_{2s}}+\frac{1}{2T_{1t}}\right)+\beta\left(\frac{1}{T_{2t}}+\frac{1}{2T_{1s}}\right),
\end{aligned}\tag{5.43}$$

and hence two pairs of lines with different widths except in the case $T_{1s}=T_{1t}=T_1$; $T_{2s}=T_{2t}=T_2$, where all four lines have the same width, $1/T_2+1/2T_1$.

To complete the discussion of the case, considered here, the corresponding expressions (5.7) for the effective longitudinal relaxation time of the different resonance lines shall likewise be derived for the case $\kappa\ll 1$. As was pointed out in Sec. 3, T_{ab} is in this case the effective resistance in the equivalent dc circuit, measured between the terminals a and b. Expressing them likewise in terms of the relaxation times of the separate nuclei, the resistances of this circuit are here found to be

$$\begin{aligned} R_{ab}&=R_{cd}=4\left(\frac{\beta}{T_{1s}}+\frac{\alpha}{T_{1t}}\right)^{-1}=R_1,\\ R_{ac}&=R_{bd}=4\left(\frac{\alpha}{T_{1s}}+\frac{\beta}{T_{1t}}\right)^{-1}=R_2,\\ R_{bc}&=\frac{1}{\alpha\beta}\left(\frac{1}{T_{2s}}+\frac{1}{T_{2t}}-\frac{1}{2T_{1s}}-\frac{1}{2T_{1t}}\right)^{-1},\\ R_{ad}&=\infty, \end{aligned} \tag{5.44}$$

and the effective resistance T_{ab} is given by

$$T_{ab}=\left(\frac{1}{R_1}+\frac{1}{R_2+\rho}\right)^{-1}, \tag{5.45}$$

with

$$\rho=\left(\frac{1}{R_3}+\frac{1}{R_1+R_2}\right)^{-1}. \tag{5.46}$$

With the matrix elements

$$\begin{aligned} (b|m_s^+ + m_t^+|a)&=(d|m_s^+ + m_t^+|b)=\sqrt{\beta}+\sqrt{\alpha},\\ (c|m_s^+ + m_t^+|a)&=(d|m_s^+ + m_t^+|c)=\sqrt{\beta}-\sqrt{\alpha}, \end{aligned} \tag{5.47}$$

and derived from (5.38), corresponding to (5.45), with the expressions

$$\begin{aligned} T_{cd}&=T_{ab}=\left(\frac{1}{R_1}+\frac{1}{R_2+\rho}\right)^{-1},\\ T_{ac}&=T_{bd}=\left(\frac{1}{R_2}+\frac{1}{R_1+\rho}\right)^{-1}, \end{aligned} \tag{5.48}$$

one obtains from (5.7) with (5.44), (5.45), and (5.46),

$$\begin{aligned} (T_1)_{ab}&=\frac{T_{1s}T_{1t}}{T_{1s}+T_{1t}}\left[1+\frac{1}{2q}\left(\alpha\frac{T_{1t}}{T_{1s}}+\beta\frac{T_{1s}}{T_{1t}}\right)^2\right](\sqrt{\alpha}+\sqrt{\beta})^2,\\ (T_1)_{ac}&=\frac{T_{1s}T_{1t}}{T_{1s}+T_{1t}}\left[1+\frac{1}{2q}\left(\beta\frac{T_{1t}}{T_{1s}}+\alpha\frac{T_{1s}}{T_{1t}}\right)^2\right](\sqrt{\alpha}-\sqrt{\beta})^2,\\ (T_1)_{cd}&=\frac{T_{1s}T_{1t}}{T_{1s}+T_{1t}}\left[1+\frac{1}{2q}\left(\alpha\frac{T_{1t}}{T_{1s}}+\beta\frac{T_{1s}}{T_{1t}}\right)^2\right](\sqrt{\alpha}-\sqrt{\beta})^2,\\ (T_1)_{bd}&=\frac{T_{1s}T_{1t}}{T_{1s}+T_{1t}}\left[1+\frac{1}{2q}\left(\beta\frac{T_{1t}}{T_{1s}}+\alpha\frac{T_{1s}}{T_{1t}}\right)^2\right](\sqrt{\alpha}+\sqrt{\beta})^2, \end{aligned} \tag{5.49}$$

with

$$q=1+\alpha\beta\left[2\left(\frac{1}{T_{2s}}+\frac{1}{T_{2t}}\right)(T_{1s}+T_{1t})-4\right]. \tag{5.50}$$

As observed in the case of the line widths (5.42), the above expressions show a strong dependence upon the ratio of J and δ, apart from the more obvious one of the "intensity factors" $(\sqrt{\alpha}\pm\sqrt{\beta})^2$. In fact, this dependence, contained in the square brackets, exists here even in the case $T_{1s}=T_{1t}=T_1$, $T_{2s}=T_{2t}=T_2$ through the expression q of (5.50).

Assuming finally either $\alpha=1$, $\beta=0$ or $\alpha=0$, $\beta=1$ and $T_{1s}=T_{1t}=T_{2s}=T_{2t}=T$, one obtains from (5.49) the common value

$$(T_1)_{\text{eff}}=\tfrac{3}{4}T, \tag{5.51}$$

and from the inverse expressions of (5.43) the common value

$$(T_2)_{\text{eff}}=\tfrac{3}{2}T \tag{5.52}$$

for the effective transverse and longitudinal relaxation times respectively. The two values differ thus in this case by a factor two while they would be equal in the corresponding case of separate nuclei.

The particular relations which have been derived here between the effective longitudinal and transverse relaxation times of the different lines in a spectrum are of course based upon the underlying special assumptions concerning the relaxation mechanism, and other relations would be obtained under different assumptions. This fact suggests, on the other hand, that the observation and comparison of the effective values of T_1 and T_2 in the different lines of a spectrum can be used to obtain information about the actual relaxation mechanism.

6. NUCLEAR SPIN SYSTEM WITH WEAK SPIN COUPLING AND STRONG RELAXATION

It was shown in the preceding section that the line widths of a spectrum depend in general upon the relaxation processes, affecting all the nuclei in the spin system. As pointed out in the discussion of the simple example, presented by the Eq. (5.42), one obtains such a dependence even in the limiting case where the coupling constant J is assumed to be small compared to the difference δ of the Larmor frequencies, since the width of lines due to transitions of the spin t are still seen to be broadened by the longitudinal relaxation time of the other spin s. This may seem surprising since one should expect, for vanishing coupling, to find the behavior of independent nuclei, where the resonance width of one nucleus cannot be influenced by transitions due to the relaxation of another nucleus.

One has to keep in mind, however, that the results of Sec. 5 were derived under the assumption of condition (4.18). While it is compatible with the further condition (4.19), i.e., with a spin coupling small compared to the chemical shift, it precludes the treatment

of vanishing coupling in the sense that the effect of this coupling still has to remain large compared to those due to the external rf field and to relaxation. In order to treat cases of arbitrarily small coupling, it is necessary to separate the spin energy according to the scheme of Eqs. (4.12) and (4.13) instead of using the scheme of Eqs. (4.16) and (4.17) which underlies Sec. 5. The corresponding condition (4.14) does not restrict the relative magnitude of the three effects, mentioned previously and is likewise compatible with (4.19). At the same time, it allows the coupling effect also to be small compared to that of the relaxation. In order not to complicate matters too much, it shall here be assumed that one still deals with a sufficiently weak rf field, i.e., one demands

$$|B|\gg|\Gamma|\gg|D|. \tag{6.1}$$

At the same time, the magnitude of the coupling shall be restricted only by

$$|B|\gg|C|\gg|D|, \tag{6.2}$$

without any restriction of the magnitude of $|\Gamma|$ compared to that of $|C|$. It is in this sense that the reference to "strong" relaxation is made in the title of this section; the case of a strong rf field shall be considered in the following section.

In view of Eqs. (4.12) and (4.4), one has here

$$E_0=-\sum_r \omega_r m_r^0. \tag{6.3}$$

Instead of the eigenvalue

$$g=-\sum_r \omega_r m_r, \tag{6.4}$$

one can equally well use the set of magnetic quantum numbers $m_r=(m_1m_2\cdots m_r\cdots)$ to characterize a state of the unperturbed spin system. Introducing further, as in Sec. II, a set of integers τ_r and using Eq. (2.21), the Boltzmann equation (2.34) can then with omission of the index v be written in the form

$$d/dt(m_r|\sigma|m_r')+i(m_r|[E,\sigma]|m_r')=(m_r|\Gamma(\sigma)|m_r'), \tag{6.5}$$

closely analogous to Eq. (3.25) of I, with

$$(m_r|\Gamma(\sigma)|m_r')=\sum_{\tau_r}\{2\exp(-\sum_r \kappa_r\tau_r)\Gamma_{m_rm_r'^{\tau_r}}(m_r+\tau_r|\sigma|m_r'+\tau_r)-(\Gamma_{m_rm_r^{\tau_r}}+\Gamma_{m_r'm_r'^{\tau_r}})(m_r|\sigma|m_r')\} \tag{6.6}$$

and

$$\Gamma_{m_rm_r'^{\tau_r}}=\pi\sum_{uu'}\int\eta_u(f)\eta_{u'}(f+\sum_r\tau_r\omega_r)P(f)\times(m_rfu|G|m_r+\tau_r,\ f+\sum_r\tau_r\omega_r,\ u')\times(m_r'+\tau_r,\ f+\sum_r\tau_r\omega_r,\ u'|G|m_r'fu)df, \tag{6.7}$$

$$\kappa_r=\hbar\omega_r/kT, \tag{6.8}$$

$$\Gamma_{m_r'+\tau_r,m_r+\tau_r}{}^{-\tau_r}=\exp(-\sum_r\kappa_r\tau_r)\Gamma_{m_rm_r'^{\tau_r}}, \tag{6.9}$$

in further analogy to (3.16), (3.17), and (3.18) of I.

To treat the Eq. (6.5), let

$$E=U+V, \tag{6.10}$$

where

$$U=E_0+C \tag{6.11}$$

and contains the part of E which is independent of the time, while

$$V=D \tag{6.12}$$

represents the part due to the external rf field and is hence dependent upon the time. A transformation operator S, and its inverse S^{-1} small further be introduced, such that

$$SUS^{-1}=f(m_r^0), \tag{6.13}$$

so that the matrix, representing this operator, has the form

$$(m_r|SUS^{-1}|m_r')=f(m_r)\delta_{m_rm_r'}, \tag{6.14}$$

i.e., it is diagonal in the m_r-representation with the diagonal elements $f(m_r)$. Indicating further the transformation S by a subscript, i.e., with

$$S\sigma S^{-1}=\sigma_S, \tag{6.15}$$

and

$$SVS^{-1}=V_S, \tag{6.16}$$

one obtains from Eqs. (6.5) and (6.6)

$$\frac{d}{dt}(m_r|\sigma_S|m_r')+i[f(m_r)-f(m_r')](m_r|\sigma_S|m_r')+i(m_r|[V_S,\sigma_S]|m_r')=(m_r|\Gamma_S(\sigma_S)|m_r'), \tag{6.17}$$

with

$$(m_r|\Gamma_S(\sigma_S)|m_r')=\sum_{m_r''m_r'''}(m_r|S|m_r'')\times(m_r''|\Gamma(S^{-1}\sigma_SS)|m_r''')(m_r'''|S^{-1}|m_r'). \tag{6.18}$$

It should further be noted that the expression (4.22) for the signal can also be expressed through the transformed distribution matrix σ_S in the form

$$\mathcal{S}=\hbar n\frac{d}{dt}\operatorname{Tr}[\sum_r\gamma_r(m_r^+)_S\sigma_S(t)], \tag{6.19}$$

with

$$(m_r^+)_S=Sm_r^+S^{-1}. \tag{6.20}$$

To obtain S and f from Eq. (6.13) by a perturbation method, let

$$U=U_0+U_1, \tag{6.21}$$

where in our case, from (6.11) and (6.3),

$$U_0=E_0=-\sum_s\omega_sm_s^0, \tag{6.22}$$

and from (4.8),

$$U_1=C=\tfrac{1}{2}\sum_{s\neq t}J_{st}(m_s^0m_t^0+m_s^+m_t^-). \tag{6.23}$$

Since the principal part U_0 of U is already diagonal in m_r, one can write

$$S=1+S_1+S_2+\cdots;\ S^{-1}=1-S_1+S_1{}^2-S_2+\cdots. \tag{6.24}$$

Inserting (6.21) and (6.24) in (6.13), writing

$$f(m_r^0)=f_0(m_r^0)+f_1(m_r^0)+f_2(m_r^0)+\cdots, \quad (6.25)$$

and comparing terms of equal order, one obtains, up to the second order,

$$U_0=f_0(m_r^0), \quad (6.26)$$

$$[S_1,f_0]+U_1=f_1(m_r^0), \quad (6.27)$$

$$[S_2,f_0]+[S_1,f_1]+S_1(U_1-f_1)=f_2(m_r^0); \quad (6.28)$$

and hence, since $f_0(m_r^0)$, $f_1(m_r^0)$ are represented by matrices which are diagonal in m_r,

$$f_0(m_r)=(m_r|U_0|m_r), \quad (6.29)$$

$$f_1(m_r)=(m_r|U_1|m_r), \quad (6.30)$$

$$f_2(m_r)=(m_r|S_1(U_1-f_1)|m_r). \quad (6.31)$$

With the particular expressions (6.22) and (6.23), one obtains thus

$$f_0(m_r)=-\sum_r \omega_r m_r, \quad (6.32)$$

$$f_1(m_r)=\tfrac{1}{2}\sum_{s\neq t} J_{st}m_s m_t, \quad (6.33)$$

and with the corresponding operator function $f_1(m_r^0)$

$$U_1-f_1=\tfrac{1}{2}\sum_{s\neq t} J_{st}m_s^+ m_t^-. \quad (6.34)$$

Using the commutation rules of m_r^0 with m_r^+ and m_r^-, it is readily verified from (6.27) that

$$S_1=-\tfrac{1}{2}\sum_{s\neq t} J_{st}m_s^+ m_t^-/(\omega_s-\omega_t), \quad (6.35)$$

and one obtains, together with (6.34), from (6.31),

$$\begin{aligned} f_2(m_r)&=-\tfrac{1}{4}\sum_{s\neq t} J_{st}^2(m_r|m_s^+m_t^-m_s^-m_t^+|m_r)/(\omega_s-\omega_t)\\ &=-\tfrac{1}{2}\sum_{s\neq t} J_{st}^2\{[I_t(I_t+1)-m_t^2]m_s\\ &\quad -[I_s(I_s+1)-m_s^2]m_t\}/(\omega_s-\omega_t). \end{aligned} \quad (6.36)$$

The expressions for the functions f_1 and f_2 could also have been obtained by the ordinary perturbation methods, but it is more convenient for a generalization, used in Sec. 7, to derive them in the manner outlined above. While these contributions to f represent only small corrections, relative to f_0, in ascending powers of the ratio of the coupling constants J_{st} to the differences of the Larmor frequencies ω_s and ω_t, their presence yields a structure of the resonance lines which is of importance for the following purposes. Omitting the corresponding small corrections to the intensity and width of the individual lines, it is permissible, on the other hand, to replace S in (6.17), (6.18), and (6.19) by the unit operator, i.e., to suppress the transformation subscript everywhere in these equations. This greatly simplifying procedure is consistent with the condition (6.2) and shall be followed below.

Corresponding to (2.47) and (2.48), one can then write

$$\sigma=\sigma_0+\chi, \quad (6.37)$$

with

$$(m_r|\sigma_0|m_r')=\zeta\exp(\textstyle\sum_r \kappa_r m_r)\delta_{m_r m_r'}, \quad (6.38)$$

and

$$\zeta=1/\sum_{m_r}\exp(\textstyle\sum_r \kappa_r m_r). \quad (6.39)$$

As in Sec. 5, it shall be further assumed that one deals with an rf field of magnitude H_1, rotating with a frequency ω. Using (5.2), one obtains then from (6.12) and with the suppression of the transformation subscript from (6.17):

$$\begin{aligned} &\frac{d}{dt}(m_r|\chi|m_r')+i[f(m_r)-f(m_r')](m_r|\chi|m_r')\\ &\quad+\sum_{\tau_r}\{(\Gamma_{m_r m_r}{}^{\tau_r}+\Gamma_{m_r' m_r'}{}^{\tau_r})(m_r|\chi|m_r')\\ &\quad-2\exp(-\textstyle\sum_r \kappa_r\tau_r)\Gamma_{m_r m_r'}{}^{\tau_r}(m_r+\tau_r|\chi|m_r'+\tau_r)\}\\ &\quad=-\tfrac{1}{2}iH_1\zeta[\exp(\textstyle\sum_r \kappa_r m_r)-\exp(\sum_r \kappa_r m_r')]\\ &\qquad\times\{(m_r|\textstyle\sum_r \gamma_r m_r^+|m_r')e^{i(\omega t+\delta)}\\ &\qquad+(m_r|\textstyle\sum_r \gamma_r m_r^-|m_r')e^{-i(\omega t+\delta)}\}, \end{aligned} \quad (6.40)$$

corresponding to (3.2) except for the omission of the terms which contain both $D^\pm$ and χ and are thus proportional to H_1^2. This omission is consistent with the condition (6.1) for $|D|$.

Because of the principal term f_0 of f, given by Eq. (6.32), $(m_r|\chi|m_r')$ will be essentially different from zero only if ω is in the neighborhood of one specific Larmor frequency ω_t with the quantum number m_t differing from m_t' by ± 1. There exist, however, several resonance frequencies in the immediate vicinity of ω_t with only a slight dependence on the other quantum numbers m_s, due to the relative smallness of f_1 and f_2. In contrast to the treatment, presented in Secs. 3 and 5, it is therefore not permissible to assume that $(m_r|\chi|m_r')$ differs appreciably from zero only for a specific set of values m_t, $m_t'=m_t\pm 1$, m_s, $m_s'=m_s$. Instead, (6.40) represents a set of simultaneous equations for the quantities $(m_s m_t|\chi|m_s, m_t\pm 1)$, characterized by different values of m_s. While all but one of these quantities are vanishingly small for relatively large coupling constants J_{st}, they tend towards a common value as J_{st} becomes comparable or small compared to the transition probabilities per unit time between states of different quantum numbers m_s. Ultimately, there results a resonance where the structure, due to the different states of the nuclei s, and the dependence of the width, due to their relaxation, have disappeared. Since one deals only with relative orders of magnitude, it should be noted that the same behavior occurs for fixed coupling but increasing transition probabilities between the various states m_s. A sufficiently frequent occurrence of these transitions has thus the effect to

eradicate the influence of another nucleus upon the structure and width of the resonance, owing to transitions of the nucleus t.

This general behavior will, for simplicity, be demonstrated for the case that, besides the nucleus t, there exists only one nucleus s in the system. Considering in particular a transition $m_t'=m_t+1$, introducing

$$(m_s m_t|\chi|m_s, m_t+1)=x(m_s m_t)e^{-i(\omega t+\delta)}, \quad (6.41)$$

and assuming κ_s, $\kappa_t \ll 1$, one obtains from (6.40) a system of equations for the constants $x(m_s m_t)$ of the form

$$i[\omega(m_s m_t)-\omega]x(m_s m_t)+\sum_{m_s' m_t'} A(m_s m_t m_s' m_t')x(m_s' m_t') - 2\sum_{\tau_s}\Gamma_{m_s m_s}^{\tau_s}\{x(m_s+\tau_s, m_t) - x(m_s m_t)\}=c(m_t), \quad (6.42)$$

where

$$c(m_t)=\tfrac{1}{2}iH_1\zeta\gamma_t\kappa_t(m_t|m_t^-|m_t+1) \quad (6.43)$$

and

$$\omega(m_s m_t)=f(m_s m_t)-f(m_s, m_t+1). \quad (6.44)$$

The form of Eq. (6.42) is obtained by writing the following for $\tau_t=0$, $m_t=m_t'$:

$$\Gamma_{m_r m_r'}^{\tau_r}=\Gamma_{m_s m_s}^{\tau_s}+\Delta\Gamma_{m_r m_r'}^{\tau_r}, \quad (6.45)$$

where the second term in this equation as well as all the other values of $\Gamma_{m_r m_r'}^{\tau_r}$ are contained in the coefficients $A(m_s m_t m_s' m_t')$. It will further be assumed that these coefficients are relatively small while $\Gamma_{m_s m_s}^{\tau_s}$, and hence the transition probability between m_s and $m_s+\tau_s$, will be allowed to be either small or large compared to the variation of $\omega(m_s m_t)$ with m_s, i.e., compared to the coupling constant J_{st}.

For ω in the vicinity of one of the values $\omega(m_s m_t)$ but separated by an amount, large compared to $\Gamma_{m_s m_s}^{\tau_s}$ from the other values, only the corresponding single quantity $x(m_s m_t)$ will be essentially different from zero. It leads to one of several closely spaced resonamce lines, each characterized by a specific value m_s, with a contribution to the width of the amount $2\sum_{\tau_s}\Gamma_{m_s m_s}^{\tau_s}$, arising from the last term on the left side of (6.42). In the other limiting case of relatively large values of $\Gamma_{m_s m_s}^{\tau_s}$, the principal effect of this term is to produce an approximate independence of the quantities x upon m_s. With the notation

$$x(m_s m_t)=x(m_t)+\xi(m_s m_t), \quad (6.46)$$

the common part $x(m_t)$ is determined by summing (6.42) over m_s, neglecting the small corrections $\xi(m_s m_t)$ and observing that with $\kappa_s \ll 1$ and therefore with $\Gamma_{m_s m_s}^{\tau_s}=\Gamma_{m_s+\tau_s, m_s+\tau_s}^{-\tau_s}$, the contributions of the last term on the left side of (6.42) cancel each other in this summation.

The determining equations for the quantities $x(m_t)$ have thus the form

$$i[\bar{\omega}(m_t)-\omega]x(m_t)+\sum_{m_s' m_t'}\bar{A}(m_t m_s' m_t')x(m_t')=c(m_t), \quad (6.47)$$

where $\bar{\omega}$ and $\bar{A}$ indicate averages over m_s. By substituting (6.46) with the solution $x(m_t)$ of (6.47) into (6.42), it is seen that the corrections $\xi(m_s m_t)$ are indeed small, of the order of the deviations of $\omega(m_s m_t)$ from their average value $\bar{\omega}(m_t)$, divided by the magnitude of the quantities $\Gamma_{m_s m_s}^{\tau_s}$. The common part $x(m_t)$ of (6.46) represents thus the better an approximation, the smaller the value of J_{st} or the larger the values of $\Gamma_{m_s m_s}^{\tau_s}$ so that, in the limit, the resonances are determined by (6.47). It is seen that, for a given value of m_t, there results in this limit a single line with the resonance frequency $\bar{\omega}(m_t)$ and with a width which is not affected by the quantities $\Gamma_{m_s m_s}^{\tau_s}$, i.e., by the relaxation transitions of the nucleus s. Using (6.44) and the expressions (6.32), (6.33), and (6.36) to obtain $f=f_0+f_1+f_2$, one has the following in this approximation:

$$\bar{\omega}=\omega_t-J_{st}^2 I_s(I_s+1)/3(\omega_s-\omega_t). \quad (6.48)$$

In the limit of weak coupling, the resonance frequency is thus independent not only of m_s but also of m_t, with a deviation from the resonance of the separate nucleus t which decreases quadratically with decreasing J_{st}.

An explicit formula, containing both limiting cases of weak and strong relaxation, can easily be obtained if both nuclei s and t have a spin 1/2 with the same relaxation mechanism as that assumed in the derivation of (5.43). According to (6.41), one has here necessarily $m_t=-\frac{1}{2}$. Using the notations

$$x(\pm\tfrac{1}{2}, -\tfrac{1}{2})=x^{\pm}, \quad (6.49)$$

and

$$\omega(\pm\tfrac{1}{2}, -\tfrac{1}{2})=\omega^{\pm}, \quad (6.50)$$

one obtains then from (6.42) the following:

$$\begin{aligned} q^+x^+ + \tfrac{1}{2}(x^+-x^-)&=T_{1s}c,\\ q^-x^- - \tfrac{1}{2}(x^+-x^-)&=T_{1s}c, \end{aligned} \quad (6.51)$$

where

$$q^{\pm}=\left[i(\omega^{\pm}-\omega)+\frac{1}{T_{2t}}\right]T_{1s}, \quad (6.52)$$

and from (6.43)

$$c=c(-\tfrac{1}{2})=\tfrac{1}{2}iH_1\zeta\gamma_t\kappa_t.$$

The signal is here found to be

$$\mathcal{S}=-i\omega\hbar n\gamma_t(x^++x^-), \quad (6.53)$$

where

$$x^++x^-=\frac{2cT_{1s}[\frac{1}{2}(q^++q^-)+1]}{\frac{1}{2}(q^++q^-)+q^+q^-} \quad (6.54)$$

is obtained as a result of the solution of (6.51).

Assuming throughout that $T_{2t} \gg T_{1s}$, the limiting cases of weak or strong relaxation of the nucleus s are

here characterized by the parameter $T_{1s}(\omega^+-\omega^-)$ being considered as large or small compared to unity respectively.

In the limiting case of weak relaxation, one has $|q^-|\gg 1$ for $\omega\cong\omega^+$ and hence, from (6.52) and (6.54),

$$x^+ + x^- = \frac{cT_{1s}}{q^- + \frac{1}{2}} = \frac{c}{i(\omega^+ - \omega) + 1/T_{2t} + 1/2T_{1s}}, \quad (6.55)$$

while one has $|q^+|\gg 1$ for $\omega\cong\omega^-$, and hence,

$$x^+ + x^- = \frac{cT_{1s}}{q^+ + \frac{1}{2}} = \frac{c}{i(\omega^- - \omega) + 1/T_{2t} + 1/2T_{1s}}. \quad (6.56)$$

There result thus two separate resonances at the frequencies ω^+ and ω^- with the common width $(1/T_{2t}) + (1/2T_{1s})$ in agreement with the corresponding expressions $\Gamma_{ab}=\Gamma_{cd}$ of (5.43), obtained for $\alpha=1$, $\beta=0$.

In the limiting case of strong relaxation, one has, on the other hand, both $|q^+|\ll 1$ and $|q^-|\ll 1$ for all values of ω in the interval between ω^+ and ω^- so that one obtains here from (6.54) the following:

$$x^+ + x^- = \frac{2cT_{1s}}{\frac{1}{2}(q^+ + q^-)} = \frac{2c}{i[\frac{1}{2}(\omega^+ + \omega^-) - \omega] + 1/T_{2t}}. \quad (6.57)$$

Strong relaxation results thus in a single resonance at the average frequency $\bar{\omega}=\frac{1}{2}(\omega^+ + \omega^-)$, with a line width which is solely determined by the transverse relaxation time of the nucleus t.

In the two limiting cases of weak and strong relaxation, one can generalize the results for the line width obtained above, to an arbitrary spin I_t of nucleus t and to an arbitrary number of nuclei s, other than t, with arbitrary spins I_s. Maintaining the assumption of an independent dipole relaxation for all nuclei s and t and the condition κ_s, $\kappa_t \ll 1$, one can use the Eqs. (4.8), (5.11), and (5.12) of I to express the relaxation coefficients $\Gamma_{m_r m_r}^{\tau_r}$ through the relaxation times T_1, T_2 of the independent nuclei. In particular, one obtains thus for a nucleus s

$$\Gamma_{m_s m_s}^{\tau_s} = \Gamma_{m_s+\tau_s, m_s+\tau_s}^{-\tau_s} = \frac{1}{4T_{1s}} |(m_s|m_s^-|m_s+\tau_s)|^2, \quad (6.58)$$

which differs from zero only for $\tau_s=1$. Using the corresponding expressions for the nucleus t as well as the relation between $\Gamma_{m_t m_t+1}^0$ and $1/T_{2t}$, and following the analogous procedure which led from (6.40) to (6.42), one finds in the case of weak relaxation the following:

$$\frac{1}{T_2}(m_s m_t) = \frac{1}{T_{2t}} + \frac{1}{T_{1t}}[I_t(I_t+1) - m_t(m_t+1) - 1] + \sum_{s\neq t} \frac{1}{T_{1s}}[I_s(I_s+1) - m_s^2] \quad (6.59)$$

for the line width of a resonance transition from m_t to m_t+1 with fixed values m_s. For a single nucleus $s\neq t$ with $I_s=\frac{1}{2}$ and choosing $I_t=\frac{1}{2}$ so that necessarily $m_t=-\frac{1}{2}$, this expression yields both for $m_s=\frac{1}{2}$ and $m_s=-\frac{1}{2}$ the line width $(1/T_{2t})+(1/2T_{1s})$, in agreement with the result of Eqs. (6.55) and (6.56).

The more general expression (6.59) is of particular interest in molecules, containing several groups of equivalent nuclei, so that not only the quantum numbers m_s, m_t but also the total equivalent spins I_s, I_t can assume different values. In a group s, containing an even number of equivalent nuclei of spin 1/2, it is possible, in particular, to have $I_s=0$ so that there appears in this case no contribution from this group to the last term of (6.59). In the same spectrum, the resonance lines of the nucleus t, characterized by $I_s=0$, can thus be expected to be sharper than those for which $I_s\neq 0$. In view of the very special underlying assumptions about the relaxation processes, formula (6.59) can of course not claim general validity but it contains features which can be subjected to experimental investigation.

As shown in the discussion of (6.42), the contributions to the linewidth, arising from the last term in (6.59), disappear in the limit of strong relaxation of the nuclei s. Similarly, it can be seen that the contribution from the second term vanishes in the limit of strong relaxation of the nucleus t so that the line width of resonance transitions of the nucleus t is reduced to $1/T_{2t}$. This result agrees with that obtained in I under corresponding conditions for a single nucleus; the assumption of "strong" relaxation was here necessarily implied since one dealt with a resonance frequency, independent of the quantum number m_t.

The observation by Arnold, presented in the following paper, of the disappearance of a line structure in alcohol due to proton exchange between different molecules is closely related to the mechanism investigated in this section. Similarly to relaxation, such an exchange has the effect to alter the relative spin orientation of protons within the same molecule and to result in the limit of rapid alterations in a single resonance line at the average frequency of the different resonances, observed in the absence of an exchange. It is the remarkable advantage of the chemical exchange that it affects selectively one proton group in the molecule without changing the spin orientation in other groups and that it depends sensitively upon the chemical composition of the liquid. While relaxation times can also be varied, for example by addition of a paramagnetic catalyst, this would affect the changes of orientation of all protons in the molecule, thus complicating the observed effects. Another difference lies in the fact that the succession of different spin orientations in the case of relaxation depends upon the mechanism involved while it is perfectly random in the case of chemical exchange.

7. NUCLEAR SPIN SYSTEM WITH WEAK COUPLING IN A STRONG ALTERNATING FIELD

Similar effects upon the resonance frequencies and line widths of a nucleus t can be expected to occur, if the transitions of another nucleus s are caused by an alternating field instead of being due to relaxation as discussed in the preceding section. In analogy, these effects should be appreciable, if they are comparable to those of the spin coupling between the nuclei and it is therefore likewise necessary to separate the spin energy according to the scheme of Eqs. (4.12) and (4.13).

It shall be assumed here that the alternating field consists of a superposition of two magnetic fields, rotating with frequencies ω_1, ω_2 and with magnitudes H_1, H_2, respectively. One has thus

$$D=D_1+D_2, \tag{7.1}$$

with

$$D_{1,2}=D_{1,2}{}^{+}e^{i\omega_{1,2}t}+D_{1,2}{}^{-}e^{-i\omega_{1,2}t}, \tag{7.2}$$

and

$$D_{1,2}{}^{\pm}=-\tfrac{1}{2}H_{1,2}e^{\pm i\delta_{1,2}}\textstyle\sum_r \gamma_r m_r{}^{\pm}. \tag{7.3}$$

In order to obtain appreciable transitions of the nucleus s, the frequency ω_1 will be chosen to be close to the Larmor frequency ω_s, and the corresponding magnitude H_1 will be allowed to assume sufficiently large values so that $\gamma_s H_1$ can be comparable or even large compared to C; the reference to a "strong" alternating field in the title of this section refers thus only to the field 1. With the frequency ω_2 close to the Larmor frequency ω_t, it is sufficient, however, to assume H_2 so small that only the linear terms in this magnitude have to be retained for the discussion of the resonances of nucleus t. As another simplifying assumption, it will be assumed that the relaxation effects are small compared to those of the coupling C as well as of the field H_1; one thus deals with weak relaxation in the sense of the preceding section and at the same time with strong saturation of the resonance lines of the nucleus s. While the combination of intermediate relaxation and saturation could equally well be treated, it would add complications which are unnecessary for the purposes of this section.

The various assumptions, made above, in regard to relative orders of magnitude can be formulated in analogy to Eqs. (6.1) and (6.2) by the conditions

$$|B|\gg|C|\gg|\Gamma|\gg|D_2|. \tag{7.4}$$

At the same time, the magnitude of the field H_1 will be restricted by.

$$|B|\gg|D_1|\gg|\Gamma| \tag{7.5}$$

without any restriction of the magnitude of $|D_1|$ compared to that of $|C|$.

While Eqs. (6.3) to (6.10) of the previous section are maintained, the conditions (7.4) and (7.5) require a redefinition of the parts U and V, composing the spin energy E. Thus, Eqs. (6.11) and (6.12) are to be replaced by

$$U=E_0+C+D_1, \tag{7.6}$$

and

$$V=D_2. \tag{7.7}$$

In view of (7.2), neither U nor V are here independent of the time. The time dependence of U can, however, be readily eliminated by a first transformation

$$T=\exp(-i\omega_1 t\textstyle\sum_r m_r{}^0) \tag{7.8}$$

to a frame of reference rotating with the field 1. Indeed, writing

$$\sigma_T=T\sigma T^{-1}, \tag{7.9}$$

Eqs. (6.5), (6.10), (7.6), and (7.7) can be seen to be replaced by

$$\frac{d}{dt}(m_r|\sigma_T|m_r')+i(m_r|[E_T,\sigma_T]|m_r')=(m_r|\Gamma(\sigma_T)|m_r'), \tag{7.10}$$

$$E_T=U_T+V_T, \tag{7.11}$$

$$U_T=E_{0T}+C+D_{1T}, \tag{7.12}$$

$$V_T=D_{2T}, \tag{7.13}$$

respectively, with

$$E_{0T}=-\textstyle\sum_r \Delta_r m_r{}^0, \tag{7.14}$$

$$D_{1T}=D_1{}^{+}+D_1{}^{-}, \tag{7.15}$$

$$D_{2T}=D_2{}^{+}e^{i\Delta t}+D_2{}^{-}e^{-i\Delta t}, \tag{7.16}$$

where the abbreviations

$$\Delta_r=\omega_r-\omega_1, \tag{7.17}$$

$$\Delta=\omega_2-\omega_1 \tag{7.18}$$

have been used. In deriving these equations, use has further been made of the identities

$$Tm_r{}^{\pm}T^{-1}=e^{\mp i\omega_1 t}m_r{}^{\pm};\quad Tm_r{}^0T^{-1}=m_r{}^0. \tag{7.19}$$

Applied to Eq. (4.8), they yield

$$C_T=TCT^{-1}=C. \tag{7.20}$$

This last relation is, in fact, an immediate consequence of the circumstance that the expression (4.7) for C is invariant against rotations.

The expression (7.12) is analogous to (6.11) in the sense that they are both independent of the time. In further analogy to the Eq. (6.13), a transformation operator S will be introduced with the property

$$SU_TS^{-1}=f(m_r{}^0). \tag{7.21}$$

Introducing further, in analogy to (6.15) and (6.16),

$$S\sigma_T S^{-1}=\sigma_{ST}, \tag{7.22}$$

and

$$SV_TS^{-1}=V_{ST}, \tag{7.23}$$

one obtains from (7.10),

$$\frac{d}{dt}(m_r|\sigma_{ST}|m_r')+i[f(m_r)-f(m_r')](m_r|\sigma_{ST}|m_r')$$
$$+i(m_r|[V_{ST},\sigma_{ST}]|m_r')=(m_r|\Gamma_S(\sigma_{ST})|m_r'). \quad (7.24)$$

This equation corresponds to (6.17), with the expression on the right side obtained by substituting in (6.18) σ_S by σ_{ST}. Through the two consecutive transformations T and S, the expression (4.22) for the signal takes here the form

$$\mathcal{S}=\hbar n\frac{d}{dt}\mathrm{Tr}[e^{-i\omega_1 t}\textstyle\sum_r\gamma_r(m_r^+)_S\sigma_{ST}(t)], \quad (7.25)$$

noting (7.19) and with

$$(m_r^+)_S=Sm_r^+S^{-1} \quad (7.26)$$

as in (6.20).

While there exists thus a considerable analogy, after having carried out the transformation T, with the procedure of Sec. 6, there arises the essential difference between E_0 and E_{0T}, given by (6.3) and (7.14), respectively, that all terms in the former expression can be considered as large while the term with $r=s$ in the latter expression must be considered as small, because of the assumed vicinity of ω_1 and ω_s and the corresponding smallness of Δ_s, given by (7.17). Contrary to Eq. (6.24), the transformation operator S has therefore to be chosen in the form

$$S=(1+S_1+S_2+\cdots)S_0;$$
$$S^{-1}=S_0^{-1}(1-S_1+S_1^2-S_2+\cdots), \quad (7.27)$$

where S_1, S_2 can still be considered as small, but where S_0 differs from the unit operator.

S_0 has the defining property of diagonalizing the part of U_T, obtained by omitting all terms which contain the operators $m_t^\pm$ for $t\neq s$. Denoting this part by U_{Ts}, one has from (7.12), (7.14), (7.15), and (4.8)

$$U_{Ts}=-\sum_{t\neq s}\Delta_t m_t^0-(\Delta_s-\sum_{t\neq s}J_{st}m_t^0)m_s^0-\gamma_s H_1 I_{xs}. \quad (7.28)$$

The x direction has here been chosen in the direction of the rotating field H_1, so that the phase factor $e^{\pm i\delta_1}$ in (7.3) disappears and

$$D_1^+ + D_1^- = -H_1\textstyle\sum_r\gamma_r I_{xr}, \quad (7.29)$$

with $I_{xr}=\frac{1}{2}(m_r^+ + m_r^-)$ from (4.3).

Noting further from (4.2) that $m_s^0=I_{zs}$, it is seen that a rotation of the vector $\mathbf{I}_s$ around the y-axis has the desired property to transform U_{Ts} into a function which depends only upon m_r^0. Such a rotation is expressed by choosing the transformation operator

$$S_0=e^{i\theta_s I_{ys}}, \quad (7.30)$$

where

$$\tan\theta_s=\gamma_s H_1/(\Delta_s-\sum_{t\neq s}J_{st}m_t^0), \quad (7.31)$$

and yields

$$S_0U_{Ts}S_0^{-1}=-\sum_{s\neq t}\Delta_t m_t^0-A_s m_s^0, \quad (7.32)$$

with

$$A_s=[(\Delta_s-\sum_{t\neq s}J_{st}m_t^0)^2+\gamma_s^2H_1^2]^{\frac{1}{2}}. \quad (7.33)$$

Both A_s and θ_s are functions of m_t^0 with $t\neq s$. In order to simplify the further discussion, it will now be assumed that the spin system contains, besides the nucleus s, only one other nucleus t so that one obtains from (7.31) and (7.33),

$$\tan\theta_s(m_t^0)=\frac{\gamma_s H_1}{\Delta_s-J_{st}m_t^0} \quad (7.34)$$

and

$$A_s(m_t^0)=[(\Delta_s-J_{st}m_t^0)^2+\gamma_s^2H_1^2]^{\frac{1}{2}}, \quad (7.35)$$

respectively.

Neglecting, as in Sec. 6, the minor corrections, arising from the small contributions $S_1, S_2, \cdots$ in (7.27), the transformation subscript S in Eqs. (7.24) and (7.25) will be considered as referring to the operator S_0 alone by reinterpreting σ_{ST}, V_{ST} and $(m_r^\pm)_S$ in these equations according to

$$\sigma_{ST}=S_0\sigma_T S_0^{-1}, \quad (7.36)$$

and

$$V_{ST}=S_0V_TS_0^{-1}, \quad (7.37)$$

$$(m_r^\pm)_S=S_0m_r^\pm S_0^{-1}, \quad (7.38)$$

instead of (7.22), (7.23), and (7.26), respectively.

With the same understanding, the right side of (7.24) has to be reinterpreted, through (6.18), according to

$$(m_r|\Gamma_S(\sigma_{ST})|m_r')=\sum_{m_r''m_r'''}(m_r|S_0|m_r'')$$
$$\times(m_r''|\Gamma(S_0^{-1}\sigma_{ST}S_0)|m_r''')(m_r'''|S_0^{-1}|m_r'). \quad (7.39)$$

The further problem to determine $f(m_r^0)$ and S_1, $S_2\cdots$ from (7.21) and (7.27) is the same as that discussed in Sec. 6, except that the quantities U, U_0 and U_1 in (6.21) have now the significance

$$U=S_0U_TS_0^{-1}, \quad (7.40)$$

$$U_0=-\Delta_t m_t^0, \quad (7.41)$$

and

$$U_1=-A_sm_s^0-\tfrac{1}{2}[(\gamma_tH_1-J_{st}(m_s^-)_S)(m_t^+)_S$$
$$+(\gamma_tH_1-J_{st}(m_s^+)_S)(m_t^-)_S], \quad (7.42)$$

respectively, with

$$(m_{s,t}^\pm)_S=S_0m_{st}^\pm S_0^{-1}. \quad (7.43)$$

Equations (7.41) and (7.42) replace (6.22) and (6.23) and are obtained by separating the expression (7.40) into a large part U_0 and a small part U_1. U_0 as well as the contribution $-A_sm_s^0$ to U_1 originate, according to (7.32), from the part U_{Ts} of U_T given by (7.28), and the other contributions, due to the field H_1 and the coupling C, originate from the remaining parts of U_T. The expression U_0 must indeed be considered to be large

since $\omega_1 \cong \omega_s$ so that, according to (7.17), $\Delta_t \cong \omega_t - \omega_s$. This quantity is of the order of those symbolized by $|B|$ in the conditions (7.4) and (7.5), and is thus postulated to be large compared to the quantities in U_1 of the order of $|C|$ and $|D|$. As in (7.32), the appearance of m_t^0 in (7.41) without the transformation subscript arises from the fact that θ_s depends only on m_t^0 so that S_0 commutes with m_t^0, leaving it thus unaltered by the corresponding transformation; this transformation affects, however, the operators $m_t^{\pm}$ so that they have to appear in (7.42) with the subscript S.

Considering that the relations (6.26) to (6.31) remain valid with U_0 and U_1 given by (7.41) and (7.42), and that the commutation rules are the same for the transformed and the untransformed spin operators, one obtains in analogy to Eqs. (6.32) to (6.36),

$$f_0(m_s m_t) = -\Delta_t m_t, \tag{7.44}$$

$$f_1(m_s m_t) = -A_s(m_t) m_s = -[(\Delta_s - J_{st} m_t)^2 + \gamma_s^2 H_1^2]^{\frac{1}{2}} m_s, \tag{7.45}$$

$$U_1 - f_1 = -\tfrac{1}{2}[(\gamma_t H_1 - J_{st}(m_s^-)_S)(m_t^+)_S + (\gamma_t H_1 - J_{st}(m_s^+)_S)(m_t^-)_S], \tag{7.46}$$

$$S_1 = (1/2\Delta_t)[(\gamma_t H_1 - J_{st}(m_s^-)_S)(m_t^+)_S - (\gamma_t H_1 - J_{st}(m_s^+)_S)(m_t^-)_S], \tag{7.47}$$

$$\begin{aligned} f_2(m_s m_t) = \frac{1}{4\Delta_t}\{ & (m_s m_t | [\gamma_t H_1 - J_{st}(m_s^+)_S](m_t^-)_S \\ & \times [\gamma_t H_1 - J_{st}(m_s^-)_S](m_t^+)_S | m_s m_t) \\ & - (m_s m_t | [\gamma_t H_1 - J_{st}(m_s^-)_S](m_t^+)_S \\ & \times [\gamma_t H_1 - J_{st}(m_s^+)_S](m_t^-)_S | m_s m_t)\} \\ = \frac{1}{2\Delta_t}\{ & J_{st}^2[I_t(I_t+1) - m_t^2] m_s \cos\theta_s \\ & - [(\gamma_t H_1 - J_{st} \sin\theta_s m_s)^2 \\ & + J_{st}^2(I_s(I_s+1) - m_s^2)(1 - \tfrac{1}{2}\sin^2\theta_s)] m_t\}. \end{aligned} \tag{7.48}$$

In deriving (7.48), use was made of (4.2), (4.3) and of the relations

$$\begin{aligned} (I_{zs})_S &= I_{zs}\cos\theta_s - I_{xs}\sin\theta_s, \\ (I_{xs})_S &= I_{zs}\sin\theta_s + I_{xs}\cos\theta_s, \\ (I_{ys})_S &= I_{ys}, \end{aligned} \tag{7.49}$$

which result from the transformation operator (7.30). It should be noted that according to (7.34), θ_s depends on m_t through

$$\tan\theta_s(m_t) = \frac{\gamma_s H_1}{\Delta_s - J_{st} m_t}. \tag{7.50}$$

As a check it may be observed that for $H_1 = 0$ and hence $\theta_s = 0$, the result for $f = f_0 + f_1 + f_2$ agrees with that obtained in Sec. 6 if one assumes only two nuclei s and t and replaces $\omega_t - \omega_s$ by Δ_t. In the other limiting case of a strong field H_1, satisfying $\gamma_s H_1 \gg |\Delta_s - J_{st} m_t|$, one obtains on the other hand,

$$f_1 = -\gamma_s H_1 m_s, \tag{7.51}$$

and, since in this case $\theta_s = \pi/2$,

$$f_2 = -\frac{1}{2\Delta_t}[(\gamma_t H_1 - J_{st} m_s)^2 + \tfrac{1}{2} J_{st}^2 (I_s(I_s+1) - m_s^2)] m_t. \tag{7.52}$$

The relation of these formulas to the observed effect of a strong field upon the structure of resonances will be discussed below.

In order to obtain the desired signal $\mathfrak{s}$ from (7.25), it is necessary to solve the Eq. (7.24). In analogy to (6.37), one can write

$$\sigma_{ST} = \sigma_1 + \chi_2, \tag{7.53}$$

where σ_1 is independent of the time. The index 1 of this matrix indicates that it depends upon the field H_1 but not upon the field H_2 and that it differs from the matrix σ_0 in (6.37), corresponding to thermal equilibrium, except in the limiting case $H_1 = 0$. The index 2 in χ_2 indicates, on the other hand, an additional dependence upon the field H_2 and, in particular, a proportionality for small values of H_2. Since V_T and hence V_{ST} is, through (7.2) and (7.3), proportional to H_2, it is in this case permissible to neglect terms of the order $V_{ST}\chi_2$.

Substituting (7.53) in (7.24), one sees for $m_r \neq m_r'$ that the off-diagonal elements of σ_1 are of the order of $|\Gamma|/|f(m_r) - f(m_r')|$ or $|\Gamma|/|B|$ and hence are negligible in view of the conditions (7.4) and (7.5) of weak relaxation. It is thus permissible to represent σ_1 by a diagonal matrix of the form

$$(m_r|\sigma_1|m_r') = \sigma_1(m_r)\delta_{m_r m_r'}, \tag{7.54}$$

which has to satisfy the condition

$$(m_r|\Gamma_S(\sigma_1)|m_r) = 0, \tag{7.55}$$

obtained for $m_r = m_r'$. From the terms proportional to H_2, one obtains further, with (7.24) and (7.54):

$$\begin{aligned} \frac{d}{dt}(m_r|\chi_2|m_r') + i[f(m_r) - f(m_r')](m_r|\chi_2|m_r') & \\ - (m_r|\Gamma_S(\chi_2)|m_r') & \\ = i[\sigma_1(m_r) - \sigma_1(m_r')](m_r|V_{ST}|m_r') & \end{aligned} \tag{7.56}$$

for the determination of χ_2.

The condition (7.55) represents a system of homogeneous linear equations for the determination of the quantities $\sigma_1(m_r)$. With the definition of $\Gamma_S(\sigma_1)$, obtained from replacing in (7.39) σ_{ST} by σ_1, one obtains by summing (7.55) over m_r

$$\sum_{m_r}(m_r|\Gamma_S(\sigma_1)|m_r) = \sum_{m_r}(m_r|\Gamma(S_0^{-1}\sigma_1 S_0)|m_r). \tag{7.57}$$

On the other hand, it can be seen from (6.6) that $\sum_{m_r}(m_r|\Gamma(\sigma)|m_r)$ vanishes identically for any matrix σ.

The sum of Eqs. (7.55) is therefore likewise identically zero, i.e., they are not independent. A finite solution is uniquely determined by the condition of normalization

$$\sum_{m_r} \sigma_1(m_r)=1. \tag{7.58}$$

Postulating at the same time

$$\sum_{m_r}(m_r|\chi_2|m_r)=0, \tag{7.59}$$

it is, therefore,

$$\sum_{m_r}(m_r|\sigma_{ST}|m_r)=1, \tag{7.60}$$

which is indeed the condition of normalization for the density matrix in view of the fact that the sum of its diagonal elements does not change under the two successive transformations T and S.

With the normalized solution $\sigma_1(m_r)$ of (7.55), inserted on the right side of (7.56), the problem of finding χ_2 is similar to that, encountered in solving Eq. (3.2). It shall first be noted from (7.13), (7.16), and (7.3) that

$$V_{ST}=-\tfrac{1}{2}H_2[\textstyle\sum_r \gamma_r(m_r{}^+)_S]e^{i(\Delta t+\delta_2)} -\tfrac{1}{2}H_2[\textstyle\sum_r \gamma_r(m_r{}^-)_S]e^{-i(\Delta t+\delta_2)}. \tag{7.61}$$

In analogy to the procedure followed in Sec. III, χ_2 will differ appreciably from zero only if Δ lies in the vicinity of the difference $f(m_r)-f(m_r')$ for two specific sets of values m_r and m_r'. The two matrix elements

$$(m_r|\chi_2|m_r') \quad \text{and} \quad (m_r'|\chi_2|m_r)$$

will in this case have an appreciable value while all other matrix elements of χ_2 are negligible. Writing, in analogy to Eqs. (3.4) and (3.5),

$$\Delta\omega=\Delta+f(m_r')-f(m_r) \tag{7.62}$$

and

$$(m_r'|\chi_2|m_r)=ze^{i\Delta t}, \quad (m_r|\chi_2|m_r')=z^*e^{-i\Delta t}, \tag{7.63}$$

one has then from (7.56) with (7.61),

$$z=\tfrac{1}{2}[\sigma_1(m_r)-\sigma_1(m_r')]H_2e^{i\delta_2} \times(m_r'|\textstyle\sum_r \gamma_r(m_r{}^+)_S|m_r)/(\Delta\omega-i\Gamma_{m_r'm_r}) \tag{7.64}$$

and the conjugate complex equation for z^*.

In order to express the line width $\Gamma_{m_rm_r'}$ in terms of the relaxation coefficients Γ, it is convenient to write

$$(m_r|\Gamma_S(\sigma_{ST})|m_r') = \sum_{m_r''m_r'''}(m_r|\Gamma_S(m_r''m_r''')|m_r')(m_r''|\sigma_{ST}|m_r'''). \tag{7.65}$$

The coefficients $(m_r|\Gamma_S(m_r''m_r''')|m_r')$ on the right side are thus obtained by replacing on the left side σ_{ST} by a matrix where the element $(m_r''m_r''')$ has the value unity while all other matrix elements have the value zero and they are, through (6.6) and (6.18), expressible as linear combinations of the quantities $\Gamma_{m_rm_r'^{\tau_r}}$. One has then

$$\Gamma_{m_r'm_r}=-(m_r'|\Gamma_S(m_r'm_r)|m_r), \tag{7.66}$$

and

$$\Gamma_{m_rm_r'}=\Gamma_{m_r'm_r}{}^*=-(m_r|\Gamma_S(m_rm_r')|m_r'), \tag{7.67}$$

where the right side of (7.67) can indeed be shown to be conjugate complex of the right side of (7.66).

The coefficients, defined through (7.65), can also be used to write the Eq. (7.55) for the quantities $\sigma_1(m_r)$ in the form

$$\sum_{m_r'}(m_r|\Gamma_S(m_r'm_r')|m_r)\sigma_1(m_r')=0. \tag{7.68}$$

The last three equations become comparatively simple if one uses the form (5.11) for the interaction operator G. In analogy to Eqs. (5.13), (5.14), and (5.15), one obtains with the definition (5.12) of the spin operators, from (6.7):

$$\Gamma_{m_rm_r'^{\tau_r}}=\sum_{\lambda\lambda'}\Phi_{\lambda\lambda'^{\tau_r}}(m_r|I_\lambda{}^{-\tau_r}|m_r+\tau_r) \times(m_r'+\tau_r|I_{\lambda'}{}^{\tau_r}|m_r') \tag{7.69}$$

with

$$\Phi_{\lambda\lambda'^{\tau_r}}=\pi\sum_{uu'}\int\eta_u(f)\eta_{u'}(f+\textstyle\sum_r\tau_r\omega_r)P(f) \times(fu|F_\lambda{}^{\tau_r}|f+\textstyle\sum_r\tau_r\omega_r,u') \times(f+\textstyle\sum_r\tau_r\omega_r,u'|F_{\lambda'}{}^{-\tau_r}|fu)df \tag{7.70}$$

and

$$\Phi_{\lambda'\lambda}{}^{-\tau_r}=\exp(-\textstyle\sum_r\kappa_r\tau_r)\Phi_{\lambda\lambda'^{\tau_r}}. \tag{7.71}$$

Using further (6.6) and the definition (6.18) of Γ_S with S, S^{-1} replaced by S_0, $S_0{}^{-1}$, one obtains from (7.65)

$$(m_r|\Gamma_S(m_r''m_r''')|m_r') =\sum_{\tau_r}\sum_{\lambda\lambda'}\phi_{\lambda\lambda'^{\tau_r}}\{2\exp(-\textstyle\sum_r\kappa_r\tau_r)(m_r|(I_\lambda{}^{-\tau_r})_S|m_r'') \times(m_r'''|(I_{\lambda'}{}^{\tau_r})_S|m_r')-(m_r|(I_\lambda{}^{-\tau_r}I_{\lambda'}{}^{\tau_r})_S|m_r'') \times\delta_{m_r'''m_r'}-(m_r'''|(I_\lambda{}^{-\tau_r}I_{\lambda'}{}^{\tau_r})_S|m_r')\delta_{m_rm_r''}\}, \tag{7.72}$$

where the transformation subscript refers to the transformation S_0. Using this expression one obtains from (7.66) and (7.67)

$$\Gamma_{m_rm_r'}=\Gamma_{m_r'm_r}{}^*=\sum_{\tau_r}\sum_{\lambda\lambda'}\Phi_{\lambda\lambda'^{\tau_r}}\{(m_r|(I_\lambda{}^{-\tau_r}I_{\lambda'}{}^{\tau_r})_S|m_r) +(m_r'|(I_\lambda{}^{-\tau_r}I_{\lambda'}{}^{\tau_r})_S|m_r')-2\exp(-\textstyle\sum_r\kappa_r\tau_r) \times(m_r|(I_\lambda{}^{-\tau_r})_S|m_r)(m_r'|(I_{\lambda'}{}^{\tau_r})_S|m_r')\} \tag{7.73}$$

and from (7.68) the equations

$$\sum_{\tau_r}\sum_{\lambda\lambda'}\Phi_{\lambda\lambda'^{\tau_r}}\{(m_r|(I_\lambda{}^{-\tau_r}I_{\lambda'}{}^{\tau_r})_S|m_r)\sigma_1(m_r) -\exp(-\textstyle\sum_r\kappa_r\tau_r)\sum_{m_r'}(m_r|(I_\lambda{}^{-\tau_r})_S|m_r') \times(m_r'|(I_{\lambda'}{}^{\tau_r})_S|m_r)\sigma_1(m_r')\}=0 \tag{7.74}$$

for the determination of the quantities $\sigma_1(m_r)$.

These quantities being known and inserted in (7.64), one obtains from (7.63) the nonvanishing elements of the matrix χ_2. Since the matrix σ_1 is given through (7.54), the matrix σ_{ST} and the signal $\mathcal{S}$ are thus determined by Eqs. (7.53) and (7.25), respectively. Writing the latter in the form

$$\mathcal{S}=\mathcal{S}_1+\mathcal{S}_2, \tag{7.75}$$

and using (7.18) one obtains for the corresponding contributions,

$$\mathcal{S}_1=-i\omega_1\hbar n\sum_{m_r}\sigma_1(m_r)(m_r|\textstyle\sum_r\gamma_r(m_r^+)_S|m_r)e^{-i\omega_1 t}, \tag{7.76}$$

and

$$\mathcal{S}_2=-\frac{i}{2}H_2[\sigma_1(m_r)-\sigma_1(m_r')]\hbar n\Big\{(2\omega_1-\omega_2)\frac{(m_r|\sum_r\gamma_r(m_r^+)_S|m_r')(m_r'|\sum_r\gamma_r(m_r^+)_S|m_r)}{\Delta\omega-i\Gamma_{m_r'm_r}}e^{i[(\omega_2-2\omega_1)t+\delta_2]}$$
$$+\omega_2\frac{|(m_r'|\sum_r\gamma_r(m_r^+)_S|m_r)|^2}{\Delta\omega+i\Gamma_{m_rm_r'}}e^{-i[\omega_2 t+\delta_2]}\Big\}. \tag{7.77}$$

In the absence of the field H_1 one has, according to (7.30) and (7.31), $S_0=1$. The transformation subscript in (7.76) and (7.77) can therefore be omitted and $(m_r^+)_S$ can be replaced by m_r^+ with matrix elements $(m_r'|m_r^+|m_r)$ which differ from zero only for $m_r'=m_r+1$. $\mathcal{S}_1$ as well as the first term in the curly bracket of (7.77) vanish therefore in this case, and there appears only a signal with the frequency ω_2 of the field H_2. For finite values of H_1, there exists however not only the additional part $\mathcal{S}_1$ of the signal with frequency ω_1, but in general also a contribution to $\mathcal{S}_2$ with the combination frequency $2\omega_1-\omega_2$.

The results obtained above will first be illustrated in the very simplest case where the spin system consists only of a single nucleus s with spin 1/2. The absence of another nucleus t is for our purposes equivalent to the assignment $I_t=0$ and hence $m_t=0$. The dependence of θ_s on m_t through (7.50), and according to (7.35), that of A_s through

$$A_s(m_t)=[(\Delta_s-J_{st}m_t)^2+\gamma_s^2H_1^2]^{\frac{1}{2}}, \tag{7.78}$$

disappears therefore in this case so that one has here

$$\tan\theta_s=\gamma_sH_1/\Delta_s, \tag{7.79}$$

and

$$A_s=[\Delta_s^2+\gamma_s^2H_1^2]^{\frac{1}{2}}. \tag{7.80}$$

For the same reason, from (7.44) and (7.48) one obtains $f_0=f_2=0$ and hence $f=f_1$ or, from (7.45) and (7.80),

$$f(m_s)=-A_sm_s=-[\Delta_s^2+\gamma_s^2H_1^2]^{\frac{1}{2}}m_s. \tag{7.81}$$

In applying formula (7.77) to this case it is important to note that, contrary to the case of absence of the field H_1, $(m_s'|(m_s^+)_S|m_s)$ is different from zero also for quantum numbers other than $m_s'=\frac{1}{2}$, $m_s=-\frac{1}{2}$. In fact, one has from (7.49), with $(m_s^+)_S=(I_{xs})_S+i(I_{ys})_S$, the matrix elements

$$(\pm\tfrac{1}{2}|(m_s^+)_S|\pm\tfrac{1}{2})=\pm\tfrac{1}{2}\sin\theta_s, \tag{7.82}$$

and

$$(\pm\tfrac{1}{2}|(m_s^+)_S|\mp\tfrac{1}{2})=\pm\tfrac{1}{2}(1\pm\cos\theta_s), \tag{7.83}$$

which are all different from zero for finite values of H_1 and hence of θ_s. The resonance conditions of the expression (7.77) are obtained by letting $\Delta\omega=0$ so that according to (7.62) and (7.18), the resonance values of ω_2 for given ω_1 are defined by

$$\omega_2=\omega_1+\Delta=\omega_1+f(m_s)-f(m_s'). \tag{7.84}$$

Excluding the case $m_s=m_s'$ which occurs only if $\omega_1=\omega_2$, i.e., if the two fields H_1 and H_2 are indistinguishable, (7.84) leads according to (7.81) to the two possible resonance values:

$$\omega_2^+=\omega_1+[\Delta_s^2+\gamma_s^2H_1^2]^{\frac{1}{2}}, \tag{7.85}$$

for

$$m_s=-m_s'=-\tfrac{1}{2}$$

and

$$\omega_2^-=\omega_1-[\Delta_s^2+\gamma_s^2H_1^2]^{\frac{1}{2}}, \tag{7.86}$$

for

$$m_s=-m_s'=\tfrac{1}{2}.$$

For $\Delta_s=\omega_s-\omega_1>0$, one obtains in the limit $H_1=0$: $\omega_2^+=\omega_s$; $\omega_2^-=2\omega_1-\omega_s$. While the first value expresses the obvious fact that resonance occurs in this case at the frequency ω_s, there exists no physical reason for the resonance to occur at a second frequency. The apparent paradox disappears, however, by considering that one has in this limit $\cos\theta_s=1$ so that for $m_s=-m_s'=\frac{1}{2}$, the matrix element $(m_s'|(m_s^+)_S|m_s)$ vanishes according to (7.83), leaving in the signal, given by (7.77), a finite amplitude for the proper resonance frequency $\omega_2=\omega_s$ alone. The same conclusion is reached for $\Delta_s<0$, with the role of ω_2^+ and ω_2^- inverted and with the fact that one has in this case for $\cos\theta_s=-1$.

For finite values of H_1 there occur, however, finite resonance signals of frequency ω_2 both for $\omega_2=\omega_2^+$ and $\omega_2=\omega_2^-$. By measuring the difference of these two resonance frequencies and noting from (7.85) and (7.86) the relation

$$\omega_2^+-\omega_2^-=2[\Delta_s^2+\gamma_s^2H_1^2]^{\frac{1}{2}}, \tag{7.87}$$

it is thus possible for a known deviation Δ_s of the Larmor frequency ω_s from ω_1 to calibrate the value of γ_sH_1 and hence of H_1 purely in terms of measured

frequencies.[14] According to (7.77) there occurs at each of the two resonances $\omega_2=\omega_2^+$ and $\omega_2=\omega_2^-$ not only a resonance signal of frequency ω_2 but also one of frequency $2\omega_1-\omega_2$ which, in principle, can equally well be used for the calibration of H_1.

In order to calculate the intensity of the signals it is necessary, according to (7.77), to know not only the matrix elements of $(m_s^+)_S$ but also the quantities $\sigma_1(m_r)$. In the case of a single spin $I_s=\frac{1}{2}$, the only possible relaxation mechanism is that of external dipole relaxation, represented by the first term of (5.19). In analogy to (5.26), the coefficients $\Phi_{\lambda\lambda'}{}^{\tau r}$ have here the form

$$\Phi_{ss}{}^{\tau s}=\Phi_s{}^{\tau s}. \tag{7.88}$$

Corresponding to (5.40), they can be expressed through the relaxation times, and one has for $\kappa_s=\hbar\omega_s/kT\ll 1$,

$$\Phi_s{}^{\pm 1}=\frac{1}{2T_{1s}},\quad \Phi_s{}^{0}=\frac{1}{T_{2s}}-\frac{1}{2T_{1s}}. \tag{7.89}$$

Equation (7.74) takes then the form

$$\sum_{\tau s=-1}^{+1}\Phi_s{}^{\tau s}\{(m_s|(I_s{}^{-\tau s}I_s{}^{\tau s})_S|m_s)\sigma_1(m_s) -\exp(-\kappa_s\tau_s)\sum_{m_s'}(m_s|(I_s{}^{-\tau s})_S|m_s') \times(m_s'|(I_s{}^{\tau s})_S|m_s)\sigma_1(m_s')\}=0, \tag{7.90}$$

with $m_s=\pm\frac{1}{2}$ for the determination of the two quantities $\sigma_1(\pm\frac{1}{2})$. Evaluating the matrix elements in this equation according to the transformation equations (7.49) with $I_s{}^0=I_{zs}$, $I_s{}^{\pm 1}=I_{xs}\pm iI_{ys}$, expanding in powers of κ_s with the neglect of quadratic and higher terms, and inserting the values (7.89) in (7.90), one can see that (7.90) has the solution

$$\sigma_1(\pm\tfrac{1}{2})=\tfrac{1}{2}\left\{1\pm\frac{\kappa_s}{2}\frac{T_{2s}\cos\theta_s}{T_{2s}\cos^2\theta_s+T_{1s}\sin^2\theta_s}\right\}, \tag{7.91}$$

which satisfies the condition of normalization

$$\sigma_1(\tfrac{1}{2})+\sigma_1(-\tfrac{1}{2})=1.$$

It shall be noted, as a check, that for $H_1=0$, i.e., $\theta_s=0$, the expressions (7.91) approach the proper equilibrium values $\frac{1}{2}(1\pm\frac{1}{2}\kappa_s)$, obtained from the Boltzmann factors $\exp(\kappa_s m_s)$ for small values of κ_s. For finite values of H_1 there appear, however, deviations from the populations at equilibrium and in the limit of large values of H_1, i.e., for $\theta_s=\pi/2$, one obtains $\sigma_1(\frac{1}{2})=\sigma_1(-\frac{1}{2})=\frac{1}{2}$, i.e., an equalization of the population due to saturation.

Inserting (7.91) in (7.76) and using the expression (7.82) for the diagonal elements of $(m_s^+)_S$, one obtains

$$\mathcal{S}_1=-i\omega_1\hbar n\gamma_s\frac{\kappa_s}{4}\frac{T_{2s}\cos\theta_s\sin\theta_s}{T_{2s}\cos^2\theta_s+T_{1s}\sin^2\theta_s}e^{-i\omega_1 t}, \tag{7.92}$$

or, with (7.79)

$$\mathcal{S}_1=-i\omega_1\hbar n\gamma_s\frac{\kappa_s}{4}\frac{(\Delta_s T_{2s})(\gamma_s H_1 T_{2s})}{(\Delta_s T_{2s})^2+(\gamma_s H_1)^2T_{1s}T_{2s}}e^{-i\omega_1 t},$$

which is indeed the dispersion-signal obtained from the phenomenological equations for $(\gamma H_1)^2T_1T_2\gg 1$ and with the equilibrium polarization

$$M_0=\tfrac{1}{4}\hbar n\gamma_s\kappa_s=(n\mu_s{}^2/kT)H_0.$$

Likewise, using (7.91) and (7.83) to obtain $\mathcal{S}_2$ from (7.77), and defining the intensities in analogy to (5.10) by integrating in the vicinity of each resonance over $\Delta\omega$, one obtains for the signals with frequency ω_2 and $(2\omega_1-\omega_2)$:

$$\mathrm{Int}(\omega_2)=\mp\frac{\pi}{16}H_2\hbar n\kappa_s\gamma_s{}^2\omega_2\frac{T_{2s}\cos\theta_s}{T_{2s}\cos^2\theta_s+T_{1s}\sin^2\theta_s}\times(1\pm\cos\theta_s)^2 \tag{7.93}$$

and

$$\mathrm{Int}(2\omega_1-\omega_2)=\pm\frac{\pi}{16}H_2\hbar n\kappa_s\gamma_s{}^2(2\omega_1-\omega_2)\times\frac{T_{2s}\cos\theta_s}{T_{2s}\cos^2\theta_s+T_{1s}\sin^2\theta_s}\sin^2\theta_s, \tag{7.94}$$

respectively, where the upper sign refers to the choice $m_s'=\frac{1}{2}$, $m_s=-\frac{1}{2}$ and the resonance frequency ω_2^+ of (7.85), the lower sign to $m_s'=-\frac{1}{2}$, $m_s=\frac{1}{2}$ and the resonance frequency ω_2^- of (7.86). It is seen that for $H_1=0$ and $\theta_s=0$, only the intensity (7.93) with the choice of the upper sign remains different from zero and gives in this case the proper behavior of a resonance at $\omega_2=\omega_2^+=\omega_s$ in a weak field H_2. All four intensities are further seen to vanish for $\Delta_s=0$, i.e., for $\theta_s=\pi/2$ so that, according to (7.87) the corresponding value $\omega_2^+-\omega_2^-=2\gamma_s|H_1|$ for the calibration of H_1 can, experimentally, be reached only by extrapolation.

Finally, the line width of the different resonances appears here from (7.73) in the form

$$\Gamma_{m_s m_s'}=\sum_{\tau s=-1}^{+1}\Phi_s{}^{\tau s}\{(m_s|(I_s{}^{-\tau s}I_s{}^{\tau s})_S|m_s) +(m_s'|(I_s{}^{-\tau s}I_s{}^{\tau s})_S|m_s')-2\exp(-\kappa_s\tau_s) \times(m_s|(I_s{}^{-\tau s})_S|m_s)(m_s'|(I_s{}^{\tau s})_S|m_s')\}. \tag{7.95}$$

Inserting the values (7.89) and neglecting $\kappa_s\ll 1$, one obtains thus the common value

$$\Gamma_{\frac{1}{2},-\frac{1}{2}}=\Gamma_{-\frac{1}{2},\frac{1}{2}}=\frac{1}{T_{2s}}-\frac{1}{2}\left(\frac{1}{T_{2s}}-\frac{1}{T_{1s}}\right)\sin^2\theta_s. \tag{7.96}$$

[14] The application of this procedure is shown by W. Anderson [Phys. Rev. **102**, 151 (1956)]. Except for the minor variation to provide frequencies ω_2, other than ω_1, by a dc field modulation which is equivalent to a frequency modulation, this fact has been independently remarked and applied to crystals by A. G. Redfield, Phys. Rev. **98**, 1787 (1955).

Contrary to the case $H_1=0$ with $\theta_s=0$, the line widths depend thus not only upon the transverse but also upon the longitudinal relaxation time of the nucleus s, so that their measurement in its dependence upon H_1 would allow the determination of both of T_{2s} and T_{1s}.

The results obtained above could equally well have been derived from the phenomenological equations since they have been shown in I to be equivalent to the Boltzmann equation in the case of a single spin of value 1/2. However, the treatment presented here has the advantage of a considerable analogy with that of more complicated cases which require necessarily the use of the Boltzmann equation. Such a case is met in going back to a spin system of two coupled spins s and t. With the frequency ω_1 of the field H_1 in the vicinity of the Larmor frequency ω_s, one obtains here appreciable resonance signals, due to the field H_2, not only if ω_2 is likewise in the vicinity of ω_s but also if it is near the Larmor frequency ω_t of the other nucleus t. With $\Delta_t \gg \gamma_s H_1$, corresponding to the condition (7.5), the former resonances have in this case negligible intensities and only the latter ones shall therefore here to be considered. With $\omega_2 \cong \omega_t$, one has from (7.17) and (7.18) $\Delta \cong \Delta_t$ and the resonance condition $\Delta\omega=0$ requires therefore, according to (7.62),

$$f(m_r)-f(m_r')\cong\Delta_t. \tag{7.97}$$

From the principal term f_0 of f, given by (7.44), it is seen that the resonances under consideration occur only if

$$m_t'=m_t+1, \tag{7.98}$$

without, however, any restriction of the quantum numbers m_s, m_s'. Since the matrix of m_s^+ is diagonal in the quantum number m_t, the sum $\sum_r \gamma_r m_r^+$ in Eq. (7.77) can, in view of (7.98), be replaced by the single term $\gamma_t(m_t^+)_S=\gamma_t S_0 m_t^+ S_0^{-1}$. Using the form (7.30) of S_0, one finds

$$(m_r'|\,(m_t^+)_S\,|m_r)=(m_s', m_t+1\,|\,e^{i\theta_s I_{ys}} m_t^+ \times e^{-i\theta_s I_{ys}}|\,m_s, m_t). \tag{7.99}$$

Since θ_s is diagonal in m_t, this can also be written in the form

$$(m_r'|\,(m_t^+)_S\,|m_r)=(m_s'|\,e^{i\theta(m_t)I_{ys}}|\,m_s)\times(m_t+1\,|\,m_t^+|\,m_t), \tag{7.100}$$

where the abbreviation

$$\theta(m_t)=\theta_s(m_t+1)-\theta_s(m_t) \tag{7.101}$$

has been introduced with the dependence of θ_s and hence of θ upon m_t given by (7.50). While

$$(m_t+1\,|\,m_t^+|\,m_t),$$

and hence the matrix element (7.100) is finite, one has $(m_t|\,m_t^+|\,m_t+1)=0$ and hence

$$(m_r|\,(m_t^+)_S\,|m_r')=(m_s|\,e^{-i\theta(m_t)I_{ys}}|\,m_s')\times(m_t|\,m_t^+|\,m_t+1)=0. \tag{7.102}$$

The first term in the curly bracket of (7.77) is therefore absent and the signal S_2, which represents here the resonances of the nucleus t, can thus be written in the form

$$S_2=-\frac{i}{2}H_2[\sigma_1(m_s m_t)-\sigma_1(m_s', m_t+1)]\hbar n\gamma_t^2 \times\frac{|\,(m_s'|\,e^{i\theta(m_t)I_{ys}}|\,m_s)\,|^2\,|\,(m_t+1\,|\,m_t^+|\,m_t)\,|^2}{\Delta\omega+i\Gamma_{m_r m_r'}}\times e^{-i(\omega_2 t+\delta_2)}. \tag{7.103}$$

In the absence of the field H_1, one has $\theta_s=0$ and hence $\theta=0$. The first expression in the numerator of (7.103) has therefore the form $\delta_{m_s m_s'}$, i.e., the resonances of nucleus t are unaccompanied by transitions of the nucleus s. For finite values of H_1, this is however not the case and a resonance of the nucleus t requires for its specification not only the corresponding transition $m_t\rightarrow m_t+1$ of nucleus t, but also the simultaneous transition $m_s\rightarrow m_s'$ of nucleus s, leading thus to a larger number of resonance lines than is observed in the absence of the field H_1.[15] The quantities

$$|\,(m_s'|\,e^{i\theta(m_t)I_{ys}}|\,m_s)\,|^2=W_{m_s m_s'} \tag{7.104}$$

in Eq. (7.103) represent the probabilities that the spin s with component m_s in the z-direction has the component m_s' in a direction obtained from rotating the z-axis by the angle $\theta(m_t)$. They are given by the well-known formula of Majorana.[16] In the special case of $I_s=\frac{1}{2}$, they have the values

$$W_{\frac{1}{2}\frac{1}{2}}=W_{-\frac{1}{2}-\frac{1}{2}}=\cos^2[\theta(m_t)/2],\qquad W_{\frac{1}{2}-\frac{1}{2}}=W_{-\frac{1}{2}\frac{1}{2}}=\sin^2[\theta(m_t)/2]. \tag{7.105}$$

The evaluation of the intensities requires further a knowledge of the values $\sigma_1(m_r)$, to be obtained from the solution of (7.68) or (7.74). This solution will depend upon the type of relaxation mechanism which is assumed and will in general be rather complicated. It will be assumed, for simplicity, that one is dealing again with a spin 1/2 for both nuclei s and t and with the same independent dipole relaxation underlying the discussions in Secs. V and VI. Introducing the further simplification $T_{1s}=T_{2s}$ and with relations, analogous to (7.89), for the nucleus t, assuming likewise $T_{1t}=T_{2t}$, one finds, up to linear terms in κ_s and κ_t:

$$\sigma_1(m_s m_t)=\frac{1}{4}\left[1+\kappa_s m_s\frac{(1+p)\cos\theta^{\pm}+p\cos\theta^{\mp}\cos(\theta^+-\theta^-)}{(1+p)^2-p^2\cos^2(\theta^+-\theta^-)}\pm\tfrac{1}{2}\kappa_t\right], \tag{7.106}$$

[15] This fact has also been pointed out by A. L. Bloom and J. N. Shoolery [Phys. Rev. **97**, 1261 (1955)] who have independently treated the case of irradiation with two frequencies. In the absence of a rigorous theory they were not able, however, to give exact expressions for the intensities in regard to their dependence on changes of population, expressed by the square bracket in (7.103).

[16] See for example F. Bloch and I. I. Rabi, Revs. Modern Phys. **17**, 237 (1945).

with the upper or lower sign for $m_t=\pm\frac{1}{2}$ and where the abbreviations

$$p=T_{1s}/2T_{1t}, \tag{7.107}$$

and

$$\theta^{\pm}=\theta_s(\pm\tfrac{1}{2}) \tag{7.108}$$

have been used. According to (7.50), the last equation is equivalent to

$$\tan\theta^{\pm}=\frac{\gamma_s H_1}{\Delta_s\mp\frac{1}{2}J_{st}}. \tag{7.109}$$

For $H_1=0$, $\theta^+=\theta^-=0$, (7.106) reduces to

$$\sigma_1(m_s m_t)=\tfrac{1}{4}[1+\kappa_s m_s+\kappa_t m_t],$$

which, for κ_s, $\kappa_t\ll 1$, represents indeed the equilibrium population of the state m_s, m_t.

The expression (7.106) can first be used to calculate the signal from the nucleus s given by the part $\mathcal{S}_1$ of Eq. (7.76). Since the matrix, representing $(m_t^+)_S$ has no diagonal elements, one has

$$\mathcal{S}_1=-i\omega_1\hbar n\gamma_s\sum_{m_s m_t}\sigma_1(m_s m_t)(m_s m_t|\,(m_s^+)_S\,|m_s m_t)e^{-i\omega_1 t} \tag{7.110}$$

or, with (7.106) and with the diagonal elements of $(m_s^+)_S$, obtained from (7.49) and (7.108),

$$\mathcal{S}_1=-i\omega_1\hbar n\gamma_s\frac{\kappa_s}{4}\frac{\frac{1}{2}(1+p)(\sin 2\theta^+ +\sin 2\theta^-)+p\sin(\theta^++\theta^-)\cos(\theta^+-\theta^-)}{(1+p)^2-p^2\cos^2(\theta^+-\theta^-)}e^{-i\omega_1 t}. \tag{7.111}$$

Inserting further (7.106) in (7.103) with $m_t=-\frac{1}{2}$ and using the expressions (7.105), where, according to (7.101) and (7.108), $\theta(m_t)=\theta(-\frac{1}{2})=\theta^+-\theta^-$, one obtains the desired expression $\mathcal{S}_2$ for the signal from the nucleus t. While $m_t'=\frac{1}{2}$ and $m_t=-\frac{1}{2}$ for all resonances, m_s and m_s' can independently assume the values $\pm\frac{1}{2}$ so that one is led to four separate resonance lines. Their intensities will accordingly be designated by $\mathrm{Int}(m_s,m_s')$. Under the same assumptions about the relaxation mechanism which led to (7.106), one obtains also the corresponding line widths, to be denoted by $\Gamma(m_s,m_s')$ The result for both is given by the following formulas:

$$\mathrm{Int}(\pm\tfrac{1}{2},\pm\tfrac{1}{2})=\tfrac{1}{4}\pi H_2\hbar n\gamma_t^2\omega_2\left\{\kappa_t\pm\frac{\kappa_s}{2}\frac{\cos\theta^+-\cos\theta^-}{1+p[1+\cos(\theta^+-\theta^-)]}\right\}\cos^2\left(\frac{\theta^+-\theta^-}{2}\right), \tag{7.112}$$

$$\Gamma(\pm\tfrac{1}{2},\pm\tfrac{1}{2})=\frac{1}{T_{2t}}+\frac{1}{2T_{2s}}(1-\cos\theta^+\cos\theta^-)+\frac{1}{4T_{1s}}(1+\cos\theta^+\cos\theta^--2\sin\theta^+\sin\theta^-), \tag{7.113}$$

$$\mathrm{Int}(\pm\tfrac{1}{2},\mp\tfrac{1}{2})=\tfrac{1}{4}\pi H_2\hbar n\gamma_t^2\omega_2\left\{\kappa_t\pm\frac{\kappa_s}{2}\frac{\cos\theta^++\cos\theta^-}{1+p[1-\cos(\theta^+-\theta^-)]}\right\}\sin^2\left(\frac{\theta^+-\theta^-}{2}\right), \tag{7.114}$$

$$\Gamma(\pm\tfrac{1}{2},\mp\tfrac{1}{2})=\frac{1}{T_{2t}}+\frac{1}{2T_{2s}}(1+\cos\theta^+\cos\theta^-)+\frac{1}{4T_{1s}}(1-\cos\theta^+\cos\theta^-+2\sin\theta^+\sin\theta^-). \tag{7.115}$$

While the simplifying assumptions $T_{1s}=T_{2s}$ and $T_{1t}=T_{2t}$ were made in deriving the expressions (7.112) and (7.114) for the intensities, the distinction between T_1 and T_2 for the nuclei s and t has been left in the expressions (7.113) and (7.115) for the line widths. Contrary to the case of vanishing field H_1, they show that for finite values of H_1 and hence of θ^+ and θ^-, the line widths for the resonances of the nucleus t depend not only upon the longitudinal but also upon the transverse relaxation time of the nucleus s.

To complete the results for the resonances of the nucleus t, the corresponding resonance frequencies ω_2 are obtained by letting $\Delta\omega=0$ in (7.62) so that, in analogy to (7.84), they are given by

$$\omega_2=\omega_1+f(m_r)-f(m_r').$$

With m_t and m_t' having the fixed values $-\frac{1}{2}$ and $\frac{1}{2}$ respectively, one obtains from the principal term f_0 of Eq. (7.44) the contribution $\Delta_t=\omega_t-\omega_1$. The other terms f_1 and f_2 depend both on m_s and m_t so that, up to the second order in H_1 and J_{st}, one obtains for the resonance frequencies

$$\omega_2(m_s m_s')=\omega_t+f_1(m_s,-\tfrac{1}{2})-f_1(m_s',\tfrac{1}{2})+f_2(m_s,-\tfrac{1}{2})-f_2(m_s',\tfrac{1}{2}), \tag{7.116}$$

where, in evaluating the second-last and the last term from (7.48), θ_s is to be replaced by θ^- and θ^+, respectively.

While the dependence of the intensities, line widths, and resonance frequencies upon the field H_1 is rather complicated, these expressions become simple in the limiting cases of very small and very large values of H_1. Since in both these cases $\theta^+=\theta^-$, the intensities (7.114) of the resonances for $m_s\neq m_s'$ vanish and there appear only two resonances, corresponding to $m_s=m_s'=\pm\frac{1}{2}$.

According to (7.112), their intensities have in both limiting cases the common value

$$\mathrm{Int}(\pm\tfrac{1}{2},\pm\tfrac{1}{2})=\tfrac{1}{4}\pi H_2\hbar n\kappa_t\gamma_t^2\omega_2. \tag{7.117}$$

For $H_1=0$, $\theta^+=\theta^-=0$, one obtains from (7.113) the common value

$$\Gamma(\pm\tfrac{1}{2},\pm\tfrac{1}{2})=\frac{1}{T_{2t}}+\frac{1}{2T_{1s}}, \tag{7.118}$$

for the line width which checks the corresponding results of Secs. 5 and 6, and the two separate resonance frequencies are here given by

$$\omega_2(\pm\tfrac{1}{2},\pm\tfrac{1}{2})=\omega_t\pm\tfrac{1}{2}J_{st}+\frac{1}{4}\frac{{J_{st}}^2}{\Delta_t}. \tag{7.119}$$

In the limit of strong fields, one has, on the other $\theta^+=\theta^-=\pi/2$ and one obtains hence, besides the value (7.117) for the intensities, the common value

$$\Gamma(\pm\tfrac{1}{2},\pm\tfrac{1}{2})=\frac{1}{T_{2t}}+\frac{1}{2T_{2s}}-\frac{1}{4T_{1s}} \tag{7.120}$$

for the line width and from (7.116), (7.45), and (7.48) the two resonance frequencies

$$\omega_2(\pm\tfrac{1}{2},\pm\tfrac{1}{2})=\omega_t-\frac{1}{2\Delta_t}[\gamma_t{}^2H_1{}^2+\tfrac{1}{2}{J_{st}}^2]\mp\left(\frac{\Delta_s}{\gamma_sH_1}+\frac{\gamma_tH_1}{\Delta_t}\right)J_{st}, \tag{7.121}$$

where higher inverse powers in H_1 than the first have been neglected. It is seen that, except for second order terms, proportional to $1/\Delta_t\cong 1/(\omega_t-\omega_s)$, the separation of the two resonance frequencies disappears, for large values of H_1, proportional to $1/H_1$, and a strong effect of this type has indeed been observed.[17] Besides producing a shift quadratic in H_1, the second order terms have, however, the effect of leaving a separation which is linear in H_1. By minimizing the last term in (7.121), it is seen that the smallest value of the separation is reached for

$$H_1=[\Delta_s\Delta_t/\gamma_s\gamma_t]^{\frac{1}{2}}, \tag{7.122}$$

yielding the minimum separation

$$(\delta\omega_2)_{\min}=2J_{st}[\gamma_t\Delta_s/\gamma_s\Delta_t]^{\frac{1}{2}}. \tag{7.123}$$

Since it is assumed in (7.121) that $\gamma_tH_1\ll\Delta_t$, it is necessary, for the validity of the last two equations, that $(\gamma_t\Delta_s/\gamma_s\Delta_t)^{\frac{1}{2}}\ll 1$. One deals therefore necessarily with a separation $\delta\omega_2\ll J_{st}$, i.e., with a considerable reduction of the separation $\delta\omega_2=J_{st}$, obtained for $H_1=0$.

Because of the fact that strong rf fields of a suitably chosen frequency are able to reduce the separation of certain resonance lines, this method represents a useful tool to identify the nuclei which cause a structure in the resonance of other nuclei. The above discussion shows that further information about the interaction of nuclear moments in molecules may be gained by the observation of the accompanying effects upon line widths and intensities.

VIII. CONCLUSIONS

The Boltzmann equation (2.34) covers a wide range of phenomena, arising from the combined effect of external fields and relaxation. While it serves as a general basis for the treatment of these phenomena, special attention has been given in this paper to features which arise in the nuclear resonance spectra of liquids. Many of these features can be and have been foreseen in a qualitative manner but it seemed worthwhile to demonstrate through specific examples their methodic and quantitative derivation. By similar methods, a considerable extension of the results to many actually existing cases could be achieved; for molecules in a liquid, such an extension calls particularly for the inclusion of internal relaxation. By adapting the theory to the circumstances of specific measurements and by comparison with the experimental results, it should prove of value for obtaining a more quantitative insight into the interplay of spin coupling and relaxation.

[17] See W. A. Anderson, Phys. Rev. **102**, 151 (1956).