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Unitary Theory of Dynamic Polarization of Nuclear Spins in Liquids and Solids

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The dynamic polarization of nuclear spins, or spin pumping as it is often called, is discussed from a unitary point of view by means of a stochastic model. The Hamiltonian of this model describes two spins, I and S, which are influenced by a constant external magnetic field H_0 and a rotating field H_1, which have a dipole, or a contact, interaction, and of which the S spin experiences a randomly fluctuating "local" field $H_L(t)$. The coefficients of the dipole, or the contact interaction, are also random functions of time, all of which serves to replace, as accurately as possible, the influence of the surrounding particles on the two spins. In order to preserve the consequences of the principle of detailed balance, which is essential, the amplitude spectrum of these random functions has to be complex, i.e., nonreal, in a manner depending on the temperature. With several transformations, including a complex stochastic rotation, the interaction representation is obtained, from which equations of motion for the spin polarizations are found by means of an iteration and truncation scheme. In calculating the coefficients of these equations, extensive use is made of the Fokker-Planck equation characterizing the stochastic rotation. The equations are solved with some simplifying assumptions, and an explicit closed-form expression for the polarization of the I spin is derived. This yields the well-known results for the extreme cases of a line-narrowed liquid and of a solid, for the dipole as well as for the contact interaction. In intermediate cases, it yields hybrid effects as a function of all the variables of the problem. Where comparisons are possible, they differ markedly from earlier predictions. This discrepancy is attributed to a defect of other derivations, in which nondiagonal elements of the density matrix are neglected.

I. INTRODUCTION

THE aim of the present work is to study the evolution of a system of interacting spins in an external magnetic field, and especially the phenomenon of the dynamical polarization of nuclear spins in liquids and solids.[1]

In systems containing paramagnetic impurities one can, when the electronic spins are pumped by means of a hyperfrequency magnetic field, observe a nuclear polarization due to processes of different types. One distinguishes the solid effect,[2,3] characteristic of solids with a dipole interaction between the electronic and nuclear spins, the inverted Overhauser effect,[4–6] characteristic of liquids with dipole interaction, and the Overhauser effect,[7–9] characteristic of liquids and solids with contact interaction. There exist, also, intermediate situations, which correspond to "viscous media" and in which the dynamic polarization obtained is of a hybrid nature, representing the transition from a pure solid effect to a pure inverted Overhauser effect.[10] During the present study, we were particularly interested in the phenomenon of the transition from one effect to another, while at the same time trying to account theoretically for the evolution of the polarization with time as a function of the intensity of the hyperfrequency (pumping) field.

In order to characterize the differences between the phenomena of dynamic polarization in liquids and in solids with dipolar coupling, one may consider the energy levels of an electronic spin S and a nuclear spin I, with dipolar interaction. In a liquid this interaction is modulated by the relative movement of the spins, and its average value is thus zero. It therefore cannot mix the Zeeman levels of the system. With a solid, however, since the dipolar interaction is static, it combines the individual states of the Zeeman Hamiltonian, which means that a given hyperfrequency

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field will have a different effect. Indeed, one can induce in a solid the transitions corresponding to the frequencies $\Omega \pm \omega$, Ω and ω being the Larmor frequencies of the S and I spins: in liquids, only the transitions corresponding to an energy exchange $\hbar\Omega$ are permitted. One must take into consideration the electronic spin-lattice relaxation mechanism, which induces spontaneous transitions of the electronic spins between two levels and which yields, via the S-I interaction, the dominant mechanism for nuclear relaxation in solids. The interaction between the electronic spins must also be considered. In the liquid case, it provides the most efficient mechanism of spin-lattice relaxation, but in solids, it gives rise to the spin-spin relaxation which is a source of well-known complications. A satisfactory theory of dynamic nuclear polarization must correctly describe the saturation of the electronic spins as a function of the intensity of the pumping field. We shall now briefly examine the present state of the art from this point of view.

In the case of solids, the first step toward a general theory was made by Motchane.[10] He considered the rate equations for the populations of the Zeeman levels of a nuclear spin I and an electronic spin S, interacting with a (static) dipole force. The equations contain spontaneous transitions (relaxation) satisfying the principle of detailed balance, and also the transitions induced by the pumping field. The latter are, conforming to the ideas first introduced by Bloembergen,[11] proportional to the difference in level population and to $H_1^2 f(\omega)$, where $f(\omega)$ describes the electron resonance line shape which itself depends on the electron spin-relaxation time, and where H_1^2 is the intensity of the pumping field.

This theory has two limitations and contains two doubtful approximations. The limitations, which also apply when only one kind of spin is considered, are the requirement of high fields (in order that the Zeeman levels be well separated) and the condition that the interaction between the S spins is negligible. The approximations, of relevance only because of the interaction with the I spins, lie in the fact that the nondiagonal elements of the density matrix are neglected, viz., those produced directly by the pumping field as well as those produced by the force causing electron spin relaxation in the presence of the high-frequency field.

Abragam and Borghini[12] have taken into account the interaction between the S spins, on the basis of the theory of Redfield,[13] and the theory of Provotorov[14] separately. The validity of this method is restricted to values of H_1 for which these theories apply.[15] A generalized theory[16] valid for all H_1 has not yet been applied to this problem. Moreover, the other limitation and the approximations are still in force.

The case of liquids can be developed in analogy with Ref. 10; the main difference being that the interaction between the S spins gives no problem because it is modulated by the random motion of the liquid. The other difficulties apply, however.

It follows from the above that a unitary theory, covering the transition from liquid to solid, can reasonably be expected only when the interaction between the S spins is negligible, or can adequately be represented by its effect on the S-spin relaxation only. An attempt at such a theory has been made,[17] but with the same limitations and approximations as above. In the present paper we try to take proper account of the nondiagonal elements of the density matrix in order to arrive at a quantitative theory. In principle, our method does not require well-separated Zeeman levels, and thus also applies to very weak external fields.

II. SIMPLIFYING ASSUMPTIONS

From the most general Hamiltonian describing a set of electronic spins S_i and nuclear spins I_i with their interactions with each other, with the lattice, and with external fields, a number of terms will be dropped immediately. They are: the mutual interaction of the I spins and the energy of the I spins in the hf field, this field being at or close to resonance with the S spins. It is assumed that a given I spin interacts with one and only one S spin. A dipole and a contact interaction will be considered separately. This interaction is supposed to dominate the I-spin relaxation, and any direct I-spin-lattice interaction will be neglected.

The object is to calculate the magnetization of the S- and the I-spin system as a function of time. For convenience, we use the initial condition that at $t=0$ the system is in thermal equilibrium at a temperature Θ in the total external field. Although a direct approach, with Green's-function or similar methods, is conceivable, the difficulty of keeping track of all the remaining interactions simultaneously has led us to make two simplifying assumptions about the evolution of the system *ab initio*. First, it is assumed that the lattice serves as a large heat bath, i.e., that it remains in thermal equilibrium at the temperature Θ at all times. Secondly, it is assumed that the orientation of the S spins relative to each other retains its equilibrium distribution at temperature Θ. For liquids this hardly involves an approximation, but for solids this assumption will lead to errors in situations where, under the influence of the hf field, the spin temperature associ-

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ated with the S–S interaction is different from the lattice temperature.

III. STOCHASTIC APPROXIMATION

These assumptions open the way for a decomposition of the system which forms the basis of our treatment. The idea is to reduce the problem to one involving only one representative I-S spin pair and to express the influence of the other S spins and of the lattice in terms of randomly time-dependent "local fields." The general conditions for such a decomposition have been discussed elsewhere.[18] There it was shown that the influence of a heat bath can be described by local fields if it remains in internal thermal equilibrium and if its microscopic relaxation times are short compared with the relaxation times of the system with which it is in contact. When these conditions are met, the properties of the system are obtained with a statistical matrix $\rho_\Theta(t)$ given by

$$\rho_\Theta(t)=\{W(t-i/2k\Theta)W^\dagger(t+i/2k\Theta)\}_{\mathrm{av}}, \qquad (1)$$

where the operator $W(t)$ satisfies the Schrödinger equation

$$i\,dW(t)/dt=[\mathcal{H}(t)+\mathcal{H}_1(t+i/2k\Theta)]W(t). \qquad (2)$$

Here $\mathcal{H}_1(t)$ is the energy of the system due to given, time-dependent, external fields, and $\mathcal{H}(t)$ is the remaining part of the Hamiltonian of the system and owes its time dependence to randomly varying local fields. The average in Eq. (1) has to be taken over a time which is long compared with the correlation time of $\mathcal{H}(t)$, but short compared to the relaxation times of the system. The analytical continuation into the complex plane, implied in Eq. (1), is not unlike that required for equilibrium ensembles. The unusual feature is the appearance of a non-Hermitian term in Eq. (2) when time-dependent fields are present. This can be explained in an elementary way by considering the populations of the levels of the system due to the static part of $\mathcal{H}(t)$. The time-dependent part of $\mathcal{H}(t)$, as well as $\mathcal{H}_1(t)$, considered as a perturbation, causes transitions that change the level populations. But while the former tends to stabilize a canonical distribution, $\exp(-E/k\Theta)$, the latter tends to equalize the populations. Both these trends are easily discerned in Eqs. (1) and (2).

The above-mentioned application to our spin systems oversteps somewhat the limits of validity of this method, even granting the two assumptions. The difficulty is similar to that of applying the theory of Brownian motion to individual molecules: The characteristic time of the local field, describing the effect of neighbors on a given S spin, is essentially equal to the relaxation time of the S spins. This is, at least, the case in solids. In liquids, the random molecular motion eliminates this difficulty. Our theory will be developed as if this characteristic time were short: this could be a source of errors, especially in weak Zeeman fields, when effects of line shape tend to become important. However, we are primarily interested in the polarization of the I spins, and, while this may be influenced by these considerations, the main function of the local fields is to produce the correct relaxation times T_1 and T_2 of the S spins. These two quantities, rather than the statistical properties of the local field, will later on be treated as adjustable parameters.

The statistical matrix for a spin pair, obtained with Eqs. (1) and (2), is not unique, because it depends, through the I-S interaction, on the initial relative location of the atoms carrying the spins I and S. In liquids, where one can average over times long compared with the liquid correlation time, this initial state disappears from (1), but in solids or viscous liquids it does not. We are interested in the average behavior of spin pairs irrespective of their initial configuration. This can be obtained by including, in the symbol $\{\ \}_{\mathrm{av}}$, an ensemble average over all possible initial configurations of the spin pair, to be performed after the short-time averaging. In the following this will always be implied.

IV. EFFECTIVE HAMILTONIAN AND DENSITY MATRIX

With the above specifications the effective Hamiltonian in Eq. (2) takes the following form:

$$\mathcal{H}(t)+\mathcal{H}_1(t+\tfrac{1}{2}i\beta)\equiv\gamma_S H_0 S_z+\gamma_I H_0 I_z+\gamma_S\mathbf{H}_L(t)\cdot\mathbf{S}$$
$$+\gamma_I\gamma_S\mathbf{I}\cdot\mathbf{\Phi}(t)\cdot\mathbf{S}+\gamma_S\mathbf{H}_1(t+\tfrac{1}{2}i\beta)\cdot\mathbf{S}. \qquad (3)$$

$\mathbf{H}_L(t)$ is the local field, $\mathbf{\Phi}(t)$ is the tensor of the I-S interaction, as modulated by the lattice motion. The pumping field H_1 is rotating with frequency Ω in the x-y plane. We have put $\beta=1/k\Theta$.

In the following we are interested only in the high-temperature limit, i.e., in terms to order β. The analytic continuation in Eq. (1) to first order in β is immediately obtained from Eq. (2). With the initial condition mentioned above one finds

$$\rho_\Theta(t)=[\rho_\Theta^0]^{1/2}\{W(t)W^\dagger(t)\}_{\mathrm{av}}[\rho_\Theta^0]^{1/2}+O(\beta^2), \qquad (4)$$

$$\rho_\Theta^0=\exp[-\beta(\gamma_S H_0 S_z+\gamma_I H_0 I_z+\gamma_S\mathbf{H}_1(t)\cdot\mathbf{S})], \qquad (5)$$

$$W(0)=1. \qquad (6)$$

In Eq. (5), the time average of the I-S interaction has been neglected. Owing to the non-Hermitian term $\mathcal{H}_1(t+\frac{1}{2}i\beta)$ in Eq. (2), $W(t)$ is not unitary. The deviation from unitarity is of first order in β, and hence $W(t)W^\dagger(t)=1+O(\beta)$.

The problem is to calculate $\langle\mathbf{S}\rangle_{\Theta,t}$ and $\langle\mathbf{I}\rangle_{\Theta,t}$, where

$$\langle Q\rangle_{\Theta,t}=\mathrm{Tr}\,Q\rho_\Theta(t)/\mathrm{Tr}\,\rho_\Theta(t). \qquad (7)$$

$\langle I_z\rangle_{\Theta,t}$ is of particular interest. These quantities are of first order in β, so the denominator in Eq. (7) can be replaced by its zero-order value:

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[18] J. Korringa, Phys. Rev. **133**, A1228 (1964).

$\mathrm{Tr}\rho_\Theta(t)\rightarrow(2S+1)(2I+1)$. We consider in the following only the case $S=\frac{1}{2}$, $I=\frac{1}{2}$. For that case it suffices to calculate the quantities

$$\langle Q\rangle_t=\tfrac{1}{4}\,\mathrm{Tr}[Q\{W(t)W^\dagger(t)\}_{\mathrm{av}}], \tag{8}$$

where Q is any component of $\mathbf{S}$ or $\mathbf{I}$. To first order in β one has

$$\langle Q\rangle_{\Theta,t}=\langle Q\rangle_t+\tfrac{1}{4}\,\mathrm{Tr}Q\rho_\Theta{}^0, \tag{9}$$

i.e., $\langle Q\rangle_t$ measures the deviation from equilibrium in the instantaneous applied field.

V. INTERACTION REPRESENTATION

We now perform three transformations in order to remove all but the I–S interaction from the Hamiltonian:

$$W(t)=W_1(t)W_2W_3(t)W'(t). \tag{10}$$

(1) $W_1(t)$ is a rotation with frequency Ω in the space of S and with frequency $\omega=\gamma_I H_0$ in the space of I, i.e.,

$$W_1(t)=\exp(-i\Omega S_z t-i\omega I_z t). \tag{11}$$

This gives a new Hamiltonian

$$\mathcal{H}^{(1)}=\Delta\omega S_z+\omega_1 S_x+\tfrac{1}{2}i\beta\Omega\omega_1 S_y+\gamma_S\mathbf{H}_L{}^{(1)}(t)\cdot\mathbf{S}+\gamma_I\gamma_S\mathbf{I}\cdot\mathbf{\Phi}^{(1)}(t)\cdot\mathbf{S}, \tag{12}$$

where

$$\Delta\omega=\gamma_S H_0-\Omega,\qquad \omega_1=\gamma_S H_1, \tag{13}$$

and where $\mathbf{H}_L{}^{(1)}$ and $\mathbf{\Phi}^{(1)}$ are $\mathbf{H}_L$ and $\mathbf{\Phi}$ as seen on the rotating frame. The pumping term has been expanded to first order in β.

(2) W_2 is a rotation to put the new z axis in the space of S in the direction of the effective field:

$$W_2=\exp[-iS_y\arctan(\omega_1/\Delta\omega)], \tag{14}$$

which gives

$$\mathcal{H}^{(2)}=\omega_e S_z+\tfrac{1}{2}i\beta\Omega\omega_1 S_y+\gamma_S\mathbf{H}_L{}^e(t)\cdot\mathbf{S}+\gamma_I\gamma_S\mathbf{I}\cdot\mathbf{\Phi}^e(t)\cdot\mathbf{S}, \tag{15}$$

where

$$\omega_e{}^2=\omega_1{}^2+\Delta\omega^2 \tag{16}$$

and where $\mathbf{H}_L{}^e$ and $\mathbf{\Phi}^e$ are obtained from $\mathbf{H}_L{}^{(1)}$ and $\mathbf{\Phi}^{(1)}$ with this rotation.

(3) $W_3(t)$ is the stochastic and nonunitary transformation which removes all but the interaction term from $\mathcal{H}^{(2)}$. This transformation has been obtained[19] in connection with the derivation of the modified Bloch equations. The following properties of W_3 are of importance for the present problem:

(a) W_3 induces an inhomogeneous transformation of S:

$$W_3{}^\dagger(t)\mathbf{S}W_3(t)=\mathbf{A}(\mathbf{x}(t))\cdot\mathbf{S}-\mathbf{B}(t). \tag{17}$$

(b) $\mathbf{B}(t)$ is a c number and has a limit for "large" t equal to the solution of the modified Bloch equations, minus the thermal equilibrium value of S in the instantaneous field.

(c) $\mathbf{A}(\mathbf{x}(t))$ is a rotation of the frame of reference, given by the complex Euler angles $x_1=\vartheta$, $x_2=\psi$, $x_3=\varphi$.

(d) The time dependence of $\mathbf{x}(t)$ is obtained from a probability $P(\mathbf{x},\bar{\mathbf{x}},t)$ in which $\mathbf{x}$ and its complex conjugate $\bar{\mathbf{x}}$ appear as independent variables, and which satisfies a Fokker-Planck equation, as discussed in Ref. 19. We will assume from now on that the S-spin relaxation is isotropic. This causes an error in solids or viscous liquids in large H_0, but this lack of generality is well compensated by the resulting isotropy of the Fokker-Planck equation, without which the advantage of having the z axis parallel to H_e would be lost. As a result the Fokker-Planck equation takes the form

$$\partial P/\partial t=\mathfrak{F}p,\qquad \mathfrak{F}=\mathfrak{F}_0+\mathfrak{F}_1+\mathfrak{F}_2, \tag{18}$$

with

$$\mathfrak{F}_0=(1/2T)(\mathbf{K}+\bar{\mathbf{K}})^2, \tag{19}$$

$$\mathfrak{F}_1=-\omega_e(K_z+\bar{K}_z), \tag{20}$$

$$\mathfrak{F}_2=-\tfrac{1}{2}\Omega\beta i\omega_1(K_y-\bar{K}_y), \tag{21}$$

where T is the S-spin relaxation time, $\mathbf{K}$ and $\bar{\mathbf{K}}$ are the operators of angular momentum in terms of Euler angles and their complex conjugate, respectively.

The transformed Schrödinger equation takes the form

$$idW'(t)/dt=\mathcal{H}'(t)W'(t), \tag{22}$$

with

$$\mathcal{H}'(t)=\gamma_I\gamma_S\mathbf{I}\cdot\mathbf{\Phi}^e(t)\cdot\mathbf{A}(\mathbf{x}(t))\cdot\mathbf{S}. \tag{23}$$

The term in $\mathbf{B}(t)$, which is of first order in β, has been neglected in Eq. (23), as it gives only contributions of second and higher order.

From this we want to calculate

$$\Delta\mathbf{S}(t)=\tfrac{1}{4}\,\mathrm{Tr}\{W'^\dagger(t)\mathbf{A}(\mathbf{x}(t))\cdot\mathbf{S}W'(t)\}_{\mathrm{av}} \tag{24}$$

and

$$\Delta\mathbf{I}(t)=\tfrac{1}{4}\,\mathrm{Tr}\{W'^\dagger(t)\mathbf{I}W'(t)\}_{\mathrm{av}}. \tag{25}$$

The physical meaning of $\Delta\mathbf{S}(t)$ and $\Delta\mathbf{I}(t)$ follows from Eqs. (9), (17), and (24):

$$\Delta\mathbf{S}(t)=\langle\mathbf{S}\rangle_{\Theta,t}-\langle\mathbf{S}\rangle_B, \tag{26}$$

$$\Delta\mathbf{I}(t)=\langle\mathbf{I}\rangle_{\Theta,t}-\langle\mathbf{I}\rangle_{\Theta,0}. \tag{27}$$

$\langle\mathbf{S}\rangle_B$ approaches, in a time of the order of the S-spin relaxation time, the solution of the modified Bloch equations, and $\langle\mathbf{I}\rangle_{\theta,0}$ is the thermal-equilibrium value in the field H_0. $\Delta\mathbf{I}(t)$ refers to a frame rotating with frequency ω, and $\Delta\mathbf{S}(t)$ refers to a frame rotating with frequency Ω and with the z axis parallel to the effective field. The symbol $\{\ \}_{\mathrm{av}}$ in Eqs. (24) and (25) indicates, as before, a short-time and ensemble average. $\mathbf{\Phi}^e(t)$ and $\mathbf{A}(\mathbf{x}(t))$ will, in the following, be treated as noncorrelated. As the former represents lattice motion, the latter S-spin motion, this is permitted. Products of $\mathbf{\Phi}$ components give rise to lattice cor-

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[19] J. Korringa, J. L. Motchane, P. Papon, and A. Yoshimori, Phys. Rev. **133**, A1230 (1964).

relation functions, while products of **A** components must be averaged using the Eqs. (18)–(21).

VI. EQUATIONS FOR ΔI AND ΔS

We will now derive equations for the quantities of interest by iterating Eqs. (24) and (25) twice with use of Eqs. (22) and (23), neglecting terms of order β^2, and performing a suitable truncation. The first step gives

$$\Delta\mathbf{I}(t)=-\tfrac{1}{4}\,\mathrm{Tr}\int_0^t dt'\int_0^{t'} dt'' \times\{W'^{\dagger}(t'')[\mathcal{H}'(t''),[\mathcal{H}'(t'),\mathbf{I}]]W'(t'')\}_{\mathrm{av}}, \tag{28}$$

$$\Delta\mathbf{S}(t)=-\tfrac{1}{4}\,\mathrm{Tr}\int_0^t dt'\int_0^{t'} dt'' \times\{W'^{\dagger}(t'')[\mathcal{H}'(t''),[\mathcal{H}'(t'),\mathbf{A}(\mathbf{x}(t))\cdot\mathbf{S}]]W'(t'')\}_{\mathrm{av}}. \tag{29}$$

Here one has, instead of the usual commutator,

$$[\mathcal{H}',Q]=\mathcal{H}'^{\dagger}Q-Q\mathcal{H}', \tag{30}$$

which yields the commutator with the Hermitian part of $\mathcal{H}'$, plus the anticommutator with the anti-Hermitian part. These parts are obtained from the splitting:

$$\mathbf{A}=\mathrm{Re}\mathbf{A}+\mathrm{Im}\mathbf{A}, \tag{31}$$

$$\mathrm{Re}\mathbf{A}=\tfrac{1}{2}[\mathbf{A}(\mathbf{x})+\mathbf{A}(\bar{\mathbf{x}})], \tag{32}$$

$$\mathrm{Im}\mathbf{A}=\tfrac{1}{2}[\mathbf{A}(\mathbf{x})-\mathbf{A}(\bar{\mathbf{x}})]. \tag{33}$$

Im**A** is of the order β.

Taking Re**A** in both brackets leads to terms linear and bilinear in **S** and **I**. The latter can be neglected, because they contribute only in the order β^2. Taking Im**A** in the outer bracket, Re**A** for the inner, yields a term proportional to the unit matrix, which contributes to order β. All other terms in Im**A** are of order β^2 or smaller.

The truncation is now performed as follows:

(a) Products of two components of $\mathbf{\Phi}(t)$ are averaged separately as if they were uncorrelated with $W(t)$ and $\mathbf{A}(\mathbf{x}(t))$ and their average is equated to a correlation function, with an assumed correlation time τ, averaged over all possible initial conditions.

(b) In products of the form

$$\{W'^{\dagger}(t'')A_1(\mathbf{x}(t''))A_2(\mathbf{x}(t'))W'(t'')\}_{\mathrm{av}},$$

appearing in Eq. (28) and in which A_i are any components of **A**, with $t''<t'$, $A_2(t')$ is shifted backward in time by means of

$$A_2(\mathbf{x}(t'))\to[\exp(t''-t')\mathfrak{F}]A_2(\mathbf{x}(t'')). \tag{34}$$

A similar approximation was made in Ref. 20; it means, loosely speaking, that the actual statistical time dependence is replaced by the most probable one. Products of three A's, which appear in Eq. (29), are treated similarly:

$$A_2(\mathbf{x}(t'))A_3(\mathbf{x}(t))\to[\exp(t''-t')\mathfrak{F}] \times\{A_2(\mathbf{x}(t''))[\exp(t'-t)\mathfrak{F}]A_3(\mathbf{x}(t''))\}. \tag{35}$$

This procedure is simplified by the fact that the components of **A** are linear combinations of eigenfunctions of the real part of the operator $\mathfrak{F}$, i.e., of $\mathfrak{F}_0+\mathfrak{F}_1$. Introducing rotating components for vectors and tensors, e.g.,

$$\mathbf{I}=(I_0,I_+,I_-), \tag{36}$$

$$I_{\pm}=I_x\pm iI_y,\qquad I_0=I_z, \tag{37}$$

and similarly for **S** and for the tensor **A**, one has

$$(\mathfrak{F}_0+\mathfrak{F}_1)A_{\lambda\mu}=-(T^{-1}+i\lambda\omega_e)A_{\lambda\mu}\qquad(\lambda,\mu=0,+,-). \tag{38}$$

Therefore the exponents in Eqs. (34) and (35) are, in zeroth order of β, simple exponentials, while it is evident that corrections of 1st order in β to (34) and (35) contribute in Eqs. (28) and (29) only terms of higher order.

The result of this time shift is that all functions **A** now occur at the time t''. Terms involving only Re**A** then simplify because of the orthogonality relations of real rotations, and what is left in the right-hand side of Eqs. (28) and (29) are only terms with one factor **A**, and terms with none at all. The former always appear combined with operators **S** to form some component of $\mathbf{A}(\mathbf{x}(t''))\cdot\mathbf{S}$, the latter always are some component of **I**.

Thus, for these terms, the goal of truncation has been achieved, leading as it does to a set of integral equations for Δ**I** and Δ**S**. One further simplification is that the equations for ΔI_x and ΔI_y do not couple with those for ΔI_z and Δ**S**.

The terms in Im**A** in (28) and (29) simplify for a different reason. They do not contain I and S, and their contribution of first order in β therefore does not come from $W'(t)$, but from Im**A**. Consequently one can substitute $W'^{\dagger}(t'')W'(t'')\to 1$ and the problem reduces to evaluation of averages of the form

$$\{\mathrm{Re}A_1(\mathbf{x}(t''))\,\mathrm{Im}A_2(\mathbf{x}(t''))\}_{\mathrm{av}}.$$

This can be done with first-order perturbation theory, treating $\mathfrak{F}_2$ as the perturbation. Details of the calculation are given in the Appendix.

In this manner one obtains from (28) and (29) equations of the following form:

$$\Delta I_z(t)=-\int_0^t dt'\int_0^{t'} dt''[M_{11}(t'-t'')\Delta I_z(t'') +\sum_{\gamma}M_{1\gamma}(t'-t'')\Delta S_{\gamma}(t'')-R_1(t'-t'')], \tag{39}$$

$$\Delta S_{\lambda}(t)=-\int_0^t dt'\int_0^{t'} dt''\exp(T^{-1}+i\lambda\omega_e)(t'-t) \times[M_{\lambda 1}(t'-t'')\Delta I_z(t'') +\sum_{\gamma}M_{\lambda\gamma}(t'-t'')\Delta S_{\gamma}(t'')-R_{\lambda}(t'-t'')]. \tag{40}$$

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[20] J. Korringa and A. Yoshimori, Phys. Rev. **128**, 1060 (1962).

Equations of similar structure hold for ΔI_x and ΔI_y, but they are of no interest here.

The Laplace transform of Eqs. (39) and (40) is

$$[M_{11}(p)+p]\Delta I_z(p)+\sum_{\gamma} M_{1\gamma}(p)\Delta S_\gamma(p)=R_1(p)/p, \tag{41}$$

$$M_{\lambda 1}(p)\Delta I_z(p) + \sum_{\gamma}[M_{\lambda\gamma}(p)+(p+T^{-1}+i\lambda\omega_e)\delta_{\lambda\gamma}]\Delta S_\gamma(p)=R_\lambda(p)/p. \tag{42}$$

The asymptotic values for large t, ΔI_z^∞ and ΔS_γ^∞, are given by

$$\Delta I_z^\infty=\lim_{p\to 0} p\Delta I_z(p), \tag{43}$$

$$\Delta S_\gamma^\infty=\lim_{p\to 0} p\Delta S_\gamma(p). \tag{44}$$

They are therefore to be found from

$$M_{11}(0)\Delta I_z^\infty+\sum_{\gamma} M_{1\gamma}(0)\Delta S_\gamma^\infty=R_1(0), \tag{45}$$

$$M_{\lambda 1}(0)\Delta I_z^\infty + \sum_{\gamma}[M_{\lambda\gamma}(0)+(T^{-1}+i\lambda\omega_e)\delta_{\lambda\gamma}]\Delta S_\gamma^\infty=R_\lambda(0). \tag{46}$$

The polarization time T_I, i.e., the I-spin relaxation time as influenced by the pumping field, is given by

$$T_I=-1/p_{\min}, \tag{47}$$

where $p_{\min}$ is the smallest root of the equation

$$\operatorname{Det}(p)=0, \tag{48}$$

$\operatorname{Det}(p)$ being the determinant of Eqs. (41) and (42).

VII. SIMPLIFYING ASSUMPTIONS AND RESULTS

Up to this point no approximations have been made other than those implied by the stochastic model. In particular, no assumption has been made concerning the magnitude of the S-spin relaxation time T. Also, the constant field H_0 can have any desired value, although it should be remembered that in weak H_0 a rotating pumping field, as we have assumed, is not equivalent with an oscillating one, as used in experiments.

In order to obtain some explicit results we will make two simplifying assumptions, which are satisfied in most cases to which our theory applies, viz.,

$$T\ll T_I \tag{49}$$

and

$$\Omega\gg\omega_e. \tag{50}$$

As T is the S-spin relaxation time in absence of the I–S coupling, Eq. (49) will be invalid in systems such as, e.g., F centers, where the S spin relaxes through its coupling with the I spin. Equation (50) is, by and large, the high-field approximation.

In Eq. (48) for $p_{\min}$, $M(p)$ can now be replaced by $M(0)$, because $M(p)$ is a function of $p+T^{-1}+\tau^{-1}$ only, where τ is the correlation time of relative motion of the two spins. This uses only the weaker inequality $T_I^{-1}\ll T^{-1}+\tau^{-1}$. Next, p can be neglected in the coefficient of $\Delta S_\gamma(p)$ in Eq. (42). Finally, because of the fact that all $M_{ij}(0)$ are of the same order of magnitude, Eq. (48) gives

$$1/T_I=M_{11}(0)+O(M^2(0)T), \tag{51}$$

where the second term is, by virtue of (49), negligible. As also all $R_j(0)$ are of the same order of magnitude, it then follows from (45) and (46) that

$$\Delta I_z^\infty=R_1(0)/M_{11}(0)+O(R(0)T), \tag{52}$$

$$\Delta S_\gamma^\infty=0+O(R(0)T), \tag{53}$$

where again, in view of (49) and (51), the second term is negligible.

The evaluation of the two quantities of interest, ΔI_z^∞ and T_I, therefore requires only the calculation of $M_{11}(0)$ and $R_1(0)$. They have been obtained, in the high-field limit, with the method described above. The other coefficients, $R_\gamma(0)$ and $M_{ij}(0)$, have also been obtained, but will not be given.

We find for M_{11}:

$$M_{11}(0)=(1/20)D\Lambda[14F(\Omega) +6F(\omega)+3(\omega_1/\omega_e)^2G(\omega,\omega_e)], \tag{54}$$

where we have used the abbreviations

$$D=\gamma_I^2\gamma_S^2\langle r^{-6}\rangle, \tag{55}$$

$$\Lambda=T^{-1}+\tau^{-1}, \tag{56}$$

$$F(\omega)=(\Lambda^2+\omega^2)^{-1}, \tag{57}$$

$$G(\omega,\omega_e)=F(\omega+\omega_e)+F(\omega-\omega_e)-2F(\omega). \tag{58}$$

$R_1(0)$ is given by

$$R_1(0)=-(1/20)D\Lambda\tfrac{1}{2}\Omega\beta[\omega_1^2/(\omega_e^2+T^{-2})]\{10F(\Omega) +3(\Delta\omega/\omega_e)[1+(\Lambda T)^{-1}]K(\omega,\omega_e) -3(\omega\Delta\omega/\omega_e^2\Lambda T)G(\omega,\omega_e)\}, \tag{59}$$

with

$$K(\omega,\omega_e)=F(\omega-\omega_e)-F(\omega+\omega_e). \tag{60}$$

From Eqs. (54) and (51) one has for the polarization rate

$$T_I^{-1}=T_I^{-1}(0)+(3/20)D\Lambda(\omega_1^2/\omega_e^2)G(\omega,\omega_e), \tag{61}$$

where

$$T_I^{-1}(0)=\tfrac{1}{10}D\Lambda[7F(\Omega)+3F(\omega)] \tag{62}$$

is the familiar expression for the relaxation rate, caused by the I-S dipole interaction in $H_1=0$.

VIII. INTERPRETATION

Upon substitution of (59) in Eq. (52), ΔI_z^∞ is expressed as the sum of three terms, which can be distinguished by their dependence on T and τ. For a systematic discussion it is of advantage to write the T/τ dependence of the curly bracket of Eq. (59) in terms of the three parameters

$$q_1 = T^2(T+\tau)^{-2}, \qquad q_2 = \tau^2(T+\tau)^{-2}, \qquad q_3 = T\tau(T+\tau)^{-2}. \tag{63}$$

We find

$$\Delta I_z^{\infty} = -\langle S_z\rangle_{\Theta,0}[\omega_1^2/(\omega_e^2+T^{-2})](q_1P_1+q_2P_2+q_3P_3), \tag{64}$$

where

$$P_1 = N^{-1}[10F(\Omega)+3(\Delta\omega/\omega_e)K], \tag{65}$$

$$P_2 = N^{-1}[10F(\Omega)+6(\Delta\omega/\omega_e)K-3(\omega\Delta\omega/\omega_e^2)G], \tag{66}$$

$$P_3 = N^{-1}[20F(\Omega)+9(\Delta\omega/\omega_e)K-3(\omega\Delta\omega/\omega_e^2)G], \tag{67}$$

$$N = 14F(\Omega)+6F(\omega)+3(\omega_1^2/\omega_e^2)G. \tag{68}$$

$\langle S_z\rangle_{\Theta,0}$ is the equilibrium value of S_z in the field H_0, which is approximately equal to $\frac{1}{2}\beta\Omega$, in lieu of which it has been substituted. P_1, P_2, and P_3 are similar in structure: therefore, the first term will dominate when $T \gg \tau$, the second when $T \ll \tau$, while all three contribute when $T \approx \tau$. They are functions of ω_1, $\Delta\omega$, ω, Ω, and Λ. As to the relative value of these frequencies, we have thus far only assumed $\omega_1 \ll \Omega$. We will now illustrate our results for the case that also $\omega \ll \Omega$, which will hold when the S spin is an electronic spin, the I spin a nuclear spin. $\Delta\omega$ will be restricted to the range $|\Delta\omega|/\omega = O(1)$.

In view of the form of K and G, we distinguish between the following extreme cases:

(a) $\Omega \ll \Lambda$, (b) $\omega \ll \Lambda \ll \Omega$, (c) $\Lambda \ll \omega$.

The relative size of T and τ leads to the distinction between

(1) $\tau \ll T$, (2) $T \ll \tau$.

Cases (a1) and *(b1)*, *i.e.*, $\omega \ll \Lambda$ *and* $\tau \ll T$.

One has

$$q_1P_1 = [5(\Lambda^2+\omega_1^2)+6\omega\Delta\omega(\Lambda^2+\Omega^2)(\Lambda^2+\omega_1^2)^{-1}] \times (10\Lambda^2+3\Omega^2)^{-1} \tag{69}$$

and the other terms are negligible, while $\Lambda = 1/\tau$.

(a1). When, in particular, $\Lambda > \kappa\Omega$, $\kappa = O(1)$, one has $\Lambda \gg \omega_1$, while the second term in the square bracket is negligible. This gives

$$\Delta I_z^{\infty} = -\tfrac{1}{2}\langle S_z\rangle_{\Theta,0}\frac{\omega_1^2}{\omega_1^2+\Delta\omega^2+T^{-2}}(1+0.3\tau^2\Omega^2)^{-1}. \tag{70}$$

This is the well-known result for a liquid. The maximum is at $\Delta\omega = 0$; saturation is reached for $\omega_1 T \gg 1$, yielding the value $-\frac{1}{2}\langle S_z\rangle_{\Theta,0}$ if $\Omega\tau \ll 1$.

(b1). When $\omega \ll \Lambda \ll \Omega$, Eq. (69) gives

$$q_1P_1 = \tfrac{5}{3}(\tau\Omega)^{-2}(1+\tau^2\omega_1^2)+2\tau^2\omega\Delta\omega(1+\tau^2\omega_1^2)^{-1}. \tag{71}$$

In this expression, both terms can be of the same order of magnitude, thereby giving a polarization which lacks the symmetry in $\Delta\omega$ of the "liquid" effect, while the system is still a liquid in the sense that $\tau \ll T$, i.e., that the relative motion of the two spins is the primary source of randomness. When, in Eq. (71), $\tau\omega \ll 1$, as will normally be the case, the criterion for the pure liquid effect [i.e., dominance of the first term of Eq. (71)] is

$$\tau^4\omega\Delta\omega\Omega^2 \ll 1. \tag{72}$$

In Ref. 17 the criterion for this was given to be $\tau^3\Omega^2/T \ll 1$, which indicates a failure of the qualitative arguments used there. When the two terms of Eq. (71) are of the same order of magnitude, the polarization is neither even nor odd in $\Delta\omega$. It is easily seen that the magnitude of this hybrid effect is necessarily small. An effect of this type has been observed.[21] The $\Delta\omega$ dependence agreed with Eq. (71), but the observed value was approximately twice as large.

Case (b2) and (c2), i.e., $\Lambda \ll \Omega$ *and* $T \ll \tau$.

One has $F(\Omega) \ll F(\omega)$, and therefore the polarization for $\Delta\omega = 0$ is small. Assuming $|\Delta\omega|/\omega = O(1)$, and neglecting $F(\Omega)$, one has

$$q_2P_2 = \omega\Delta\omega(\omega^2+\omega_e^2+5\Lambda^2) \times [(\omega^2-\omega_e^2)^2+2\Lambda^2(\omega^2+\omega_e^2)+\Lambda^4+\omega_1^2(3\omega^2-\omega_e^2-\Lambda^2)]^{-1} \tag{73}$$

and the other terms are negligible, while $\Lambda = 1/T$. The polarization found from Eq. (73) is an odd function of $\Delta\omega$. The values can be compared with a result obtained in Ref. 10, under identical conditions. It turns out that the result is not the same, but is obtained from Eq. (73) with the replacement

$$(\omega^2+\omega_e^2+5\Lambda^2) \rightarrow (2\Delta\omega^2+2\Lambda^2) \tag{74}$$

in the numerator. We attribute this difference to the fact that in Ref. 10 only the diagonal elements of the density matrix are taken into account. A comparison with Ref. 12 reveals differences of the same origin. Another source of differences lies in the fact that in Ref. 12 the effects of S-S interaction, which we tried to represent by the local field $H_L(t)$, are more appropriately treated by the spin temperature.

(c2) *and* $\omega_1 \ll \omega$. In the particular case that the nuclear levels are resolved ($\Lambda \ll \omega$) and that the pumping field is not too large ($\omega_1 \ll \omega$), Eq. (73) can be simplified. The denominator has a sharp minimum near $\omega_e^2 = \omega^2$, i.e., near $|\Delta\omega| = \omega$, and this yields the well-known "solid effect,"

$$(\Delta I_z^{\infty})_{\Delta\omega=\pm\omega} = \mp\langle S_z\rangle_{\Theta,0}[1+2(\omega_1 T)^{-2}]^{-1}. \tag{75}$$

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[21] J. Leblond, J. L. Motchane, P. Papon, and J. Uebersfeld, Compt. Rend. **265**, 423 (1967).

More precisely, the minima occur at

$$\Delta\omega=\pm\omega[1-\tfrac{1}{4}(\omega_1^2/\omega^2)-\tfrac{1}{2}(\omega^2T^2)^{-1}] \tag{76}$$

and the square width of the peaks is equal to $\frac{1}{2}(\omega_1^2+2T^{-2})$.

The result (75) was also obtained in Ref. 10, as follows immediately from the fact that the two expressions in (74) become identical in the limit $\Lambda^2\ll\omega^2$, $\omega_1^2\ll\omega^2$, and near $\Delta\omega^2=\omega^2$. However, the two expressions still differ, even in this limiting case, for other values of $\Delta\omega$.

(b2). When the above conditions are not satisfied, the polarization still changes sign with $\Delta\omega$, but the maxima are broader and shifted, and the polarization at the peak is substantially smaller.

Cases (a2) and (c1).

These cases are unphysical under the present conditions, and will not be discussed. The intermediate case $\tau\approx T$, for which all three terms of Eq. (64) are important, can either be "solidlike" or "liquidlike," depending on the value of Λ relative to ω and Ω.

Finally, we briefly discuss the polarization time, as given by Eq. (61), in the extreme cases (a1) and (c2). In the "liquid case" (a1), the term proportional to ω_1^2 in the polarization rate is negligible compared with $1/T_I(0)$. In the "solid case" (c2) this term has maxima near $\Delta\omega=\pm\omega$, i.e., near the frequencies for which the dynamic polarization is extreme. More accurately, the maxima occur for

$$\Delta\omega=\pm\omega[1-\tfrac{1}{2}(\omega_1^2/\omega^2)-(\omega^2T^2)^{-1}] \tag{77}$$

and the corresponding rates are

$$T_I^{-1}=T_I^{-1}(0)+\tfrac{3}{20}(D/\Lambda)[\omega_1^2/(\omega^2+\tfrac{3}{4}\Lambda^2)], \tag{78}$$

in general agreement with Ref. 10. An ω_1 dependence of T_I of this type has been observed in a number of cases.[22]

IX. THE CASE OF CONTACT INTERACTION

The method of calculation of the dynamic polarization, illustrated in the foregoing for the case of dipole interaction, can also be used when the two spins have pure contact interaction. In fact, the replacement

$$\mathbf{I}\cdot\mathbf{\Phi}(t)\cdot\mathbf{S}\rightarrow C(t)\mathbf{I}\cdot\mathbf{S},$$

where $C(t)$ is a randomly time-dependent scalar with correlation time τ, greatly simplifies the algebra. A straightforward calculation gives, under the same condition as those used to derive Eq. (64),

$$\Delta I_z^{\infty}=\langle S_z\rangle_{\Theta,0}[\omega_1^2/(\omega_e^2+T^{-2})]$$
$$\times\{1+\tfrac{1}{2}(\Lambda T)^{-1}[(\Lambda^2-\Omega^2)/(\Lambda^2+\Omega^2)]\}. \tag{79}$$

In the "liquid case" (a1), the second term in the square bracket is negligible, while in the "solid case" [(b2) and (c2), i.e., $\Lambda T\approx1$, $\Lambda\ll\Omega$], the second term equals $-\frac{1}{2}$. This confirms earlier theoretical results for these extreme cases,[4] while the general expression (79) shows how the transition, which leads to a factor of 2 between the two limits, takes place.

X. EPILOGUE

In the course of this paper we have made so many simplifying assumptions that it is perhaps in order to review them here.

The principal limitation of our theoretical model lies in the decoupling scheme, which reduces the many-body problem to one involving only one pair of spins, I and S. The assumption that the influence of the surrounding spins and of the lattice can approximately be expressed by a randomly varying local field $H_L(t)$ has been justified on general grounds, but we have gone one step further in requiring that $H_L(t)$ can be treated as if it had a correlation time short compared with the spin-relaxation time. This is essential for describing the influence of $H_L(t)$ in terms of a Fokker-Planck equation. While making this assumption we have assured that it gives the correct relaxation times, and our method also guarantees that the principle of detailed balance is satisfied under normal saturation conditions. Substantial errors can be expected in cases where a spin temperature different from the lattice temperature is produced.

Some further, nonessential assumptions have been made in order to simplify the discussion. We have assumed that the I spin relaxes only through interaction with the S spin, and that the S spin relaxation is isotropic: we have taken the pumping field to be rotating near the Larmor frequency of the S spin, and neglected its influence on the I spin. With these simplifications, the set of linear integral equations (39) and (40) was obtained. The explicit form of these equations was given with some further specializations, viz., that the constant field is large compared with the pumping field, and that the $I-S$ interaction gives only a small contribution to the S-spin relaxation. The solution, Eqs. (64)-(68), of these equations was discussed with the final assumption that $\gamma_I\ll\gamma_S$.

These simplifications nothwithstanding, our final expression for the dynamical polarization still covers most cases of interest. Our results are in full agreement with the well-known results in the two extreme cases, viz., that of a liquid with motional line-narrowing of the S-spin resonance, and that of a solid under normal saturation conditions. This was verified for dipole as well as contact interaction between the two spins. While this gives some confidence in our results for intermediate cases, these differ in important ways from the theoretical predictions published earlier.

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[22] G. E. Schacher, Phys. Rev. **135**, A185 (1964).

"Intermediate" means here not simply the transition from a liquid to a solid, i.e., the case of viscous media, but denotes more intricate inequalities between the various relaxation, correlation, and precession times. We find in particular that the "solid" effect can be obtained in a liquid if the constant field is sufficiently large, in agreement with Ref. 17. Characteristic for the intermediate effect is that the polarization as a function of $\Delta\omega$ is neither even nor odd, but rather unsymmetric in appearance, and small compared with the maximum effect attainable in the extreme cases, in reasonable agreement with experiment.[21]

We attribute the difference between our results and those of other theories to the nondiagonal elements of the density matrix, produced by the pumping field as well as by relaxation. It was, indeed, the main purpose of introducing a soluble model, to take those elements into account.

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APPENDIX

The calculation of R_1 and R_κ of Eqs. (39) and (40) requires the asymptotic evaluation for large t of

$$J_{\lambda\mu}(t)\equiv\sum_{\gamma=0,\pm}\{\mathrm{Re}A_{\lambda\gamma}(t)\ \mathrm{Im}A_{\mu,-\gamma}(t)\}_{\mathrm{av}}, \tag{A1}$$

to the first order in the parameter $\Omega\beta$, appearing in Eq. (21). One has

$$J_{\lambda\mu}(t)=\sum_{\gamma}\iint\mathrm{Re}A_{\lambda\gamma}(\mathbf{x},\bar{\mathbf{x}})\times\mathrm{Im}A_{\mu,-\gamma}(\mathbf{x},\bar{\mathbf{x}})P(\mathbf{x},\bar{\mathbf{x}},t)\,d\mathbf{x}d\bar{\mathbf{x}}, \tag{A2}$$

where P satisfies Eq. (18). With the initial condition

$$P(\mathbf{x},\bar{\mathbf{x}},0)=\delta(\mathbf{x}-\bar{\mathbf{x}})\delta(\mathbf{x}-\mathbf{x}_0), \tag{A3}$$

where $\mathbf{x}_0$ is arbitrary, one has

$$P(\mathbf{x},\bar{\mathbf{x}},t)=\exp(\mathfrak{F}t)\delta(\mathbf{x}-\bar{\mathbf{x}})\delta(\mathbf{x}-\mathbf{x}_0). \tag{A4}$$

Substituting in (A2) and integrating by parts gives

$$J_{\lambda\mu}(t)=[\exp(\mathfrak{F}t)\sum_{\gamma}\mathrm{Re}A_{\lambda\gamma}(\mathbf{x},\bar{\mathbf{x}})\ \mathrm{Im}A_{\mu,-\gamma}(\mathbf{x},\bar{\mathbf{x}})]_{\mathbf{x}=\bar{\mathbf{x}}=\mathbf{x}_0}. \tag{A5}$$

We now decompose the operand of this equation into eigenfunctions of $\mathfrak{F}$. This can be done, to first order in $\Omega\beta$, as follows: According to Eq. (17), the $A_{\lambda\gamma}(\mathbf{x})$ for fixed γ transform as the components of a vector when subjected to the operators of angular momentum, $\mathbf{k}$. This property, and the form of $\mathfrak{F}_0$ and $\mathfrak{F}_1$ in Eq. (19) and (20), gives rise to Eq. (38) which shows that the $A_{\lambda\gamma}$ are eigenfunctions of $\mathfrak{F}_0+\mathfrak{F}_1$. Therefore, sums of products of two factors A, such as appear in Eq. (A5), are decomposed in eigenfunctions of $\mathfrak{F}_0+\mathfrak{F}_1$ by the same equations that decompose products of vector components into their scalar, vector, and tensor parts. This gives functions γ_l^m, $l=0, 1, 2$, $-l\ll m\ll l$. The corresponding eigenvalues of $(\mathfrak{F}_0+\mathfrak{F}_1)$ are E_{lm}. One has

$$\varphi_0^0=\sum_{\alpha}\sum_{\gamma}\mathrm{Re}A_{\alpha\gamma}\ \mathrm{Im}A_{-\alpha,-\gamma}. \tag{A6}$$

$$\begin{aligned}\varphi_1^1&=\sum_{\gamma}(\mathrm{Re}A_{+\gamma}\ \mathrm{Im}A_{0,-\gamma}-\mathrm{Re}A_{0\gamma}\ \mathrm{Im}A_{+,-\gamma}),\\ \varphi_1^0&=\sum_{\gamma}(\mathrm{Re}A_{+\gamma}\ \mathrm{Im}A_{-,-\gamma}-\mathrm{Re}A_{-\gamma}\ \mathrm{Im}A_{+,-\gamma}),\\ \varphi_1^{-1}&=\sum_{\gamma}(\mathrm{Re}A_{0\gamma}\ \mathrm{Im}A_{-,-\gamma}-\mathrm{Re}A_{-\gamma}\ \mathrm{Im}A_{0,-\gamma})\end{aligned} \tag{A7}$$

and corresponding expression for φ_2^m, which will not be needed. $J_{\lambda\mu}$ can be written as

$$J_{\lambda\gamma}=\sum_{lm}a_{\lambda\gamma,lm}\{\varphi_l^m\}_{\mathrm{av}}. \tag{A8}$$

From φ_l^m we obtain the eigenfunctions ψ_l^m of $\mathfrak{F}$ by using of Eq. (21) in first-order perturbation:

$$\psi_l^m=\varphi_l^m+\sum_{l'm'}\frac{(\mathfrak{F}_2)_{l'm',lm}}{E_{l'm'}-E_{lm}}\psi_{l'}^{m'}. \tag{A9}$$

This gives

$$J_{\lambda\mu}(t)=\sum_{l,m}a_{\lambda\mu,lm}\{\psi_l^m\}_{\mathrm{av}}-\sum_{lm}\sum_{l'm'}\frac{a_{\lambda\mu,lm}(\mathfrak{F}_2)_{l'm',lm}}{E_{l'm'}-E_{lm}}\{\psi_{l'}^{m'}\}_{\mathrm{av}}. \tag{A10}$$

As the eigenvalue corresponding to ψ_l^m, which is in zeroth order equal to E_{lm}, contains a term $-\frac{1}{2}l(l+1)/T$, where T is the relaxation time, Eq. (A5) shows that only the terms in ψ_0^0 contribute in Eq. (A10) for large t. Using $E_{00}=0$, this gives

$$J_{\lambda\gamma}(t)\to\left(a_{\lambda\mu,00}+\sum_{-1}^{1}\frac{a_{\lambda\mu,1m}(\mathfrak{F}_2)_{00,1m}}{E_{1m}}\right)[\psi_0^0]_{\mathbf{x}=\bar{\mathbf{x}}=\mathbf{x}_0}. \tag{A11}$$

The terms in $l=2$ are absent because of the selection rule, $\Delta l=\pm1$, for the matrix elements of $\mathfrak{F}_2$. The coefficient $a_{\lambda\mu,00}=0$, as follows from the fact that $J_{\lambda\mu}$, as defined in (A1), contains no zero-order terms in $\Omega\beta$. ψ_0^0 can thus be replaced by φ_0^0, which has the property that $[\varphi_0^0]_{\mathbf{x}=\bar{\mathbf{x}}}=3$. This gives finally

$$J_{\lambda\mu}(t)\to3\sum_{m=-1}^{1}\frac{a_{\lambda\mu,1m}(\mathfrak{F}_2)_{00,1m}}{E_{1m}}. \tag{A12}$$

The coefficients and matrix elements in this equation are easily obtained.