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THEORY OF THE ENVIRONMENT'S INFLUENCE ON THE ANGULAR DISTRIBUTION OF NUCLEAR RADIATION

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ABSTRACT

The effect of electronic relaxation processes on angular correlation and on the angular distribution of radiation from oriented nuclei is investigated. The influence of the environment on the radioactive nuclei is taken into account by reducing the density operator for the total system (nucleus and surroundings mutually interacting) to a density operator for the nucleus alone. Elimination of the unobserved bath variables is performed with the help of Zwanzig's projection operator technique. The Liouville formalism is used throughout. The (initially unspecified) properties of the environment enter the theory via second-order correlation functions, which are defined in terms of equilibrium ensemble averages of certain bath operators, like e.g. the hyperfine field operator.

The matrix elements of the nuclear evolution operator (which is a superoperator in Liouville space) with respect to a complete orthonormal set of multipole operators are just the usual perturbation factors $G_{kk'}^{qq'}$ of PAC theory. The consequent use of the multipole representation yields immediately the final formulae needed in the expression for both the angular distribution of radiation from oriented nuclei and the angular correlation

function. The general theory includes relaxation processes due to magnetic and quadrupole interactions. The important case of pure magnetic interactions is discussed in more detail. Specialization to relaxation caused by randomly fluctuating fields yields a formula which contains both the Abragam-Pound result for time-fluctuating quadrupole interaction, and Micha's extension to randomly time-varying magnetic fields in multidomain ferromagnets. Exact high-temperature solutions are presented for single crystals in a static magnetic field and with magnetic-type relaxation processes (axially symmetric case). For nuclei with spin $I = 1$, the extension to arbitrary temperatures has been considered. The application of the present theory to the problem of multipole relaxation (which arises e.g. in spin-lattice relaxation measurements with NMR/ON technique) is discussed.

I. INTRODUCTION

The influence of static extranuclear perturbations on angular correlation has been exhaustively studied during the last twenty years, and a full account of the important results has been given in standard review articles.[1] Attempts to understand the effects of the fluctuating part of the radioactive nuclei's environment on angular correlation, or on the angular distribution of radiation from oriented nuclei, have almost exclusively been based on the classic paper of Abragam and Pound[2] and, to a much smaller extent, on the Dillenburg-Maris theory of random statistical interactions.[3] In the Abragam-Pound treatment a time-dependent perturbation operator representing the surroundings is added to the static part of the nuclear Hamiltonian. Standard first-order perturbation theory is used to account for the additional interaction.

The Dillenburg-Maris theory gains its conceptual simplicity by postulating the validity of a certain master equation. The transition matrix is left physically unspecified and is only restricted by some invariance properties. The disadvantage of leaving the perturbing interaction mechanism unspecified is that the damping constants appearing in the final angular correlation function play merely the role of fit parameters. For the interpretation of an experiment, this is a rather unsatisfying situation.

The present theory of relaxation effects on angular correlation and on radiation from oriented nuclei is based on a model which has been used by the author[4] to study the influence of electronic relaxation on Mössbauer spectra. The main features of the model are briefly described in Section II. In contradistinction to Coester's density matrix approach to perturbed

angular correlations[5] (PAC), we will not postulate an instantaneously acting, time-dependent, Hamiltonian for the interaction between nuclei and environment, but will instead derive a relaxation operator by reducing the density operator of the entire system (nuclei and surroundings mutually interacting) to a density operator of the nuclei alone. The more general case, in which the entire particular ion, rather than the nuclear spin, is relaxing to its equilibrium state (worked out for Mössbauer relaxation by Afanasev and Kagan[6] and Gabriel et al.[7]), will not be considered in this paper. Spin-lattice relaxation in ionic solids most often requires application of the more general theory. The present approach yields a good description of spin-lattice relaxation in metals, if the interaction Hamiltonian[8] is suitably chosen.

The general equation of motion for the nuclear density operator is a non-Markoffian integro-differential equation, and no explicit, practical useful, solutions (except for over-simplified special examples) are known. Throughout the Sections following Section II, we consider only second-order effects in the interaction between nuclei and environment. A further simplification is achieved by studying only the long-time behavior of the generalized master equation. With respect to the perturbation of a nucleus in the intermediate state (PAC case), the latter approximation implies that the condition $\tau_c \ll \tau_N$ is fulfilled. The correlation time, τ_c, characterizes the behavior of the electronic correlations entering the relaxation operator. (In the definition of Hubbard,[8] τ_c is temperature-dependent because it must satisfy the inequality $\tau_c \gtrsim \hbar/kT$). The second-order approximation is sufficient only if the smallest of the nuclear spin-lattice relaxation times is large compared to τ_c (which is usually true in metals). Of course,

the potential of the generalized master equation is only partly exploited, whenever the assumptions mentioned above are used.

From the equation of motion for the nuclear spin system we get an operator which describes its time evolution. We will show that the matrix elements of the evolution operator with respect to Fano's state multipole representation[9] are exactly the perturbation factors $G_{kk'}^{qq'}(t)$ (we essentially use the notation of FS, whenever possible). We start with the general form of the perturbed directional correlation function for a nuclear double cascade. It is given by the trace expression

$$W(\underline{k}_1, \underline{k}_2; t) = \mathrm{Tr}\{\rho(\underline{k}_2)\, \rho(\underline{k}_1, t)\} . \tag{1}$$

The density matrix $\rho(\underline{k}_1, 0)$ describes the nuclear system immediately after the emission of the first radiation in the direction $\underline{k}_1$ at time $t = 0$. The density matrix $\rho(\underline{k}_2)$ corresponds to the second transition at a later time t. Due to interactions with extranuclear perturbations, $\rho(\underline{k}_1, t)$ is in general different from its value at $t = 0$. We obtain it by acting on the initial density matrix $\rho(\underline{k}_1, 0)$ for the intermediate state with an evolution operator $\hat{\Omega}(t)$ (to be specified in Section II)[10]

$$\rho(\underline{k}_1, t) = \hat{\Omega}(t)\, \rho(\underline{k}_1, 0) . \tag{2}$$

The main problem is to derive, for a given interaction model, an explicit expression for the evolution operator $\hat{\Omega}$ entering

$$W(\underline{k}_1, \underline{k}_2; t) = \mathrm{Tr}\{\rho(\underline{k}_2)\, \hat{\Omega}(t)\, \rho(\underline{k}_1, 0)\} . \tag{3}$$

We notice that a similar expression can be written down for the angular distribution of oriented nuclei, taking into account destruction of the initial orientation state by relaxation effects. In the case (which is of very limited practical importance) where the excited state of a particular nucleus is oriented, we just have to substitute $\rho(\underline{k}_1, 0) \rightarrow \rho_i(0)$ and omit the index 2 in $\rho(\underline{k}_2)$. The angular distribution of the γ-radiation is then given by

$$W(\underline{k}, t) = \mathrm{Tr}\{\rho(\underline{k})\, \hat{\Omega}(t)\, \rho_i(0)\} \; . \tag{4}$$

It is time-dependent, if there is any noticeable interaction of the nucleus, oriented in the excited state at time $t = 0$, with the surroundings.

The more important case is that in which a β-radioactive parent nucleus, with a sufficiently long lifetime, is initially oriented, thus causing an anisotropy in the subsequent transition(s) starting from the excited state of the daughter nucleus. (de Groot *et al.*[11] discuss, for a system without relaxation $(\hat{\Omega} = \hat{1})$, how the angular distribution function (4) has to be modified in this experimental situation.) If the interaction of the parent nucleus with the environment is not negligible, we may again use Eq. (2), replacing $\rho(\underline{k}_1, 0)$ by the density operator ρ_0 for the parent nucleus with spin I_0. The γ-angular distribution is described by

$$W(\underline{k}, t) = \mathrm{Tr}\{\rho(k)\, \rho_\beta(t)\} \; , \tag{5}$$

where $\rho_\beta(t)$ corresponds to the state of the system after the β-decay. In contrast to the PAC case, changes in the γ-anisotropy are caused by reorientation effects in the parent nucleus; thus the time-dependence of

$\rho_\beta(t)$ is merely due to

$$\rho_0(t) = \hat{\Omega}(t)\, \rho_0(0) \; , \tag{6}$$

which replaces (2). Under certain circumstances, the reorientation effects are completely described by introducing time-dependent orientation parameters, $B_k(t)$, in the final expression for the angular distribution (see Section VII).

II. FORMAL DESCRIPTION OF EXTRANUCLEAR INTERACTION

One aim of the present paper is to point out the interrelationship of quantities used in nuclear magnetic relaxation studies and PAC or NMR/ON experiments and to describe in either case the influence of the environment on the nuclear spin system. It is, therefore, natural to base the calculations on physically equivalent models. We apply a procedure which has recently been used to study the influence of electronic relaxation effects on the Mössbauer line shape.[4,7] The method exploits the elegant projection operator technique of Zwanzig,[12] first used by him in problems of nonequilibrium statistical mechanics. The first application to a line shape problem has been given by Fano.[13] All aforementioned theories, as well as most of the nuclear magnetic relaxation theories,[14] are based on a density matrix approach. That the latter is directly applicable to our problem is clear from Eqs. (2) and (6).

We recall some of the main features of the widely used model: The radioactive nuclei (dilutely dissolved in a host lattice, so that their direct interaction can be ignored) are considered to be imbedded in a heat bath responsible for the extranuclear interactions we are interested in. The elimination of the unobserved bath variables is accomplished by means of Zwanzig's formalism, which combines the use of Liouville operators with that of an appropriate projection operator. The Hamiltonian for one particular nucleus is the sum of three terms

$$\mathcal{H} = \mathcal{H}_n + \mathcal{H}_R + \mathcal{H}_{nR} \quad . \tag{7}$$

The Hamiltonian for the nucleus, $\mathcal{H}_n$, includes the interaction with an external magnetic field. (Although we have also investigated the NMR/PAC and NMR/ON situations including relaxation effects, we here restrict ourselves, for the sake of simplicity, to the case where no radiofrequency field is applied.) The second term, $\mathcal{H}_R$, is the Hamiltonian for the reservoir. With respect to the interaction Hamiltonian, $\mathcal{H}_{nR}$, we only assume that it can be written as a scalar product of irreducible tensor operators

$$\mathcal{H}_{Rn} = \sum_k \sum_{q=-k}^{+k} (-1)^q \, T_q^{(k)}(n) \, V_{-q}^{(k)}(R) \tag{8}$$

acting on the nuclear system and the bath, respectively. The density operator for an ensemble of equivalent nuclei in the reservoir, $W(n,R)$, obeys the equation of motion

$$i \frac{\partial W(n,R)}{\partial t} = [\mathcal{H},W] \equiv \hat{\mathcal{H}} \, W(n,R) \qquad (\hbar = 1) \quad . \tag{9}$$

On the right-hand side of (9) we have introduced a special superoperator $\hat{\mathcal{H}}$, the Liouville operator associated with the Hamiltonian, $\mathcal{H}$, and defined by the commutator relation as indicated in (9). The concept of superoperators has been generalized to include, besides the Liouville operator, any superoperator, $\hat{R}$, transforming an ordinary operator, A, of a given Hilbert space into another operator $B = \hat{R}A$ of the same space. In order not to obscure the main physical features of the paper, we have collected the mathematical tools in the appendix. Of special interest for our problem will be the finite-dimensional unitary vector space, $\mathcal{U}$, spanned by the (2I+1) state vectors of the nucleus with spin I, and the associate Liouville space, $\mathcal{L}$,

of dimension $(2I+1)^2$, spanned by the operators A of $\mathcal{U}$. The fact that the operators A, B, ... of $\mathcal{U}$ (transforming a state vector $|\psi\rangle$ into another one, i.e. $|\psi\rangle = A|\psi\rangle$) may be considered elements of the Liouville space, $\mathcal{L}$, is indicated by adopting the notation $|A)$. The action of a superoperator $\hat{R}$ on $|A)$ yields some $|B) = \hat{R}|A)$. The reader is referred to the appendix for details.

The reduction of (9) to an equation of motion for a reduced density operator, $\rho(n)$, of the spin system alone is achieved by Zwanzig's formalism using the special projector[13]

$$P = \rho_T(R)\ \mathrm{Tr}_R \quad , \tag{10}$$

where $\rho_T(R)$ is the equilibrium density operator for the reservoir. The operation (10) performed on $W(n,R)$ yields the reduced density operator, $\rho(n)$, which is independent of the bath variables

$$P\ W(n,R) = \rho_T(R)\ \rho(n) \quad . \tag{11}$$

The irrelevant part $(1-P)\ W(n,R)$ in the decomposition

$$W = PW + (1-P)W \tag{12}$$

is exactly eliminated from (9) by the projector technique. It is very useful to split the Liouville operator $\hat{\mathcal{H}}$ into

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}' + \hat{\mathcal{H}}'' \tag{13}$$

$$\hat{\mathcal{H}}' = \hat{\mathcal{H}}_n + \langle\hat{\mathcal{H}}_{nR}\rangle_R \tag{14}$$

$$\hat{\mathcal{H}}'' = \hat{\mathcal{H}}_R + \{\hat{\mathcal{H}}_{nR} - \langle\hat{\mathcal{H}}_{nR}\rangle_R\} = \hat{\mathcal{H}}_R + \Delta\hat{\mathcal{H}}_{nR} \tag{15}$$

i.e. to combine with $\hat{\mathcal{H}}_n$ the static contribution of the spin-bath interaction, given by the ensemble average

$$\langle\hat{\mathcal{H}}_{Rn}\rangle_R = \mathrm{Tr}_R\{\hat{\mathcal{H}}_{Rn}\ \rho_T(R)\} \quad . \tag{16}$$

The Liouville operators $\hat{\mathcal{H}}'$ and $\hat{\mathcal{H}}''$ obey the relations[4]

$$P\hat{\mathcal{H}}' = \hat{\mathcal{H}}'P, \quad P\hat{\mathcal{H}}''P = 0, \quad P\hat{\mathcal{H}}''(1-P) = P\hat{\mathcal{H}}'' \ , \tag{17}$$

which have been used to simplify the expressions. With the initial condition that at $t = 0$ the combined n-R-system is uncorrelated, i.e. $(1-P)\ W = 0$ for $t = 0$, we derive the following integro-differential equation for $\rho(n)$

$$\frac{\partial\rho(t)}{\partial t} = -\ i\ \hat{\mathcal{H}}'\ \rho(t) - \int_0^t d\tau\ \hat{M}(\tau)\ \rho(t-\tau) \quad . \tag{18}$$

The influence of the heat bath on the nuclei is condensed in the relaxation (super) operator

$$\hat{M}(t) = \mathrm{Tr}_R\{\Delta\hat{\mathcal{H}}_{Rn}\ \exp(-\ it(1-P)\hat{\mathcal{H}})\ \Delta\hat{\mathcal{H}}_{Rn}\ \rho_T(R)\} \quad . \tag{19}$$

We notice that the exact equation of motion is non-local in time. As is well-known from non-equilibrium statistical mechanics the non-Markoffian behavior of (18) arises from the exact elimination of the time-varying irrelevant part of the density operator $W(n,R)$. Equation (18) shows that it is not in general possible to describe the influence of the environment by adding

a time-dependent perturbation to the nuclear Hamiltonian as was assumed e.g. by Coester.[5] For applications to a particular physical problem it is often desirable and also sufficient to study approximate solutions of a problem. We restrict our further calculations to the second-order term in $\hat{\mathcal{H}}_{Rn}$, i.e. we will replace the Liouville operator in the exponential by $\hat{\mathcal{H}}_R$. A rough criterion for this to be valid has been given in the introduction. Using (8) we can factorize (19) into nuclear operator parts modulated by correlation functions depending on the properties of the dissipative lattice system. With

$$v_q^{(k)} = V_q^{(k)} - \langle V_q^{(k)} \rangle_R \tag{20}$$

$$v_q^{(k)}(t) = \exp\{it\hat{\mathcal{H}}_R\}\, v_q^{(k)}(0) = \exp\{it\mathcal{H}_R\}\, v_q^{(k)}(0) \exp\{-it\mathcal{H}_R\} \tag{21}$$

we define correlation functions and their Fourier transforms by

$$C_{kq}^{k'q'}(t) = \frac{1}{2}(-1)^{q+q'} \langle [v_{-q}^{(k)}(t),\, v_{-q'}^{(k')}(0)]_+ \rangle_R$$

$$= \frac{1}{\pi} \int_{-\infty}^{+\infty} d\omega \; J_{kq}^{k'q'}(\omega)\, e^{-i\omega t} \tag{22}$$

$$D_{kq}^{k'q'}(t) = \frac{1}{2}(-1)^{q+q'} \langle [v_{-q}^{(k)}(t),\, v_{-q'}^{(k')}(0)] \rangle_R$$

$$= \frac{1}{\pi} \int_{-\infty}^{+\infty} d\omega \; K_{kq}^{k'q'}(\omega)\, e^{-i\omega t} \quad . \tag{23}$$

Using (A25) and the identity $\langle a(t)\, b(0)\rangle_R = \langle a(0)\, b(-t)\rangle_R$ it can be shown that the following relations hold

$$J_{kq}^{k'q'}(\omega)^* = (-1)^{q+q'}\, J_{k-q}^{k'-q'}(-\omega) = (-1)^{q+q'}\, J_{k'-q'}^{k-q}(\omega) \tag{24}$$

$$K_{kq}^{k'q'}(\omega)^* = (-1)^{q+q'+1}\, K_{k-q}^{k'-q'}(-\omega) = (-1)^{q+q'}\, K_{k'-q'}^{k-q}(\omega) \quad . \tag{25}$$

The quantities defined in (22) and (23) are not independent of each other but related by

$$K_{kq}^{k'q'}(\omega) = \tanh\,(\beta\omega/2)\, J_{kq}^{k'q'}(\omega) \qquad (\beta = 1/kT,\ \hbar = 1\ !) \tag{26}$$

which is analogous to the well-known quantum-mechanical fluctuation-dissipation theorem. We follow the assumption by Wangsness and Bloch[15] that the fluctuations of the magnetic and electric fields (connected with $k = 1$ and $k = 2$ respectively; see Eq. (8)) are uncorrelated and, therefore, restrict ourselves to correlation functions with $k = k'$. In addition, we will be interested mainly in the axially symmetric case which requires $q' = -q$. The correlation functions (24) and (25) are real for $k = k'$ and $q' = -q$.

Introducing (22) and (23) into (19) we find

$$\hat{M}(t) = \sum_{k=1,2} \sum_{q,q'=-k}^{+k} \Big\{ C_{kq}^{kq'}(t)\, \hat{T}_q^{(k)} \exp\,(-it\hat{H}')\, \hat{T}_{q'}^{(k)} \tag{27}$$

$$+ D_{kq}^{kq'}(t)\, \hat{T}_q^{(k)} \exp\,(-it\hat{H}')\, \hat{T}^{+}_{q'}{}^{(k)} \Big\} \quad ,$$

where, according to our notation, $\hat{T}_q^{(k)}$ is the Liouville operator belonging

to the nuclear part of the interaction Hamiltonian (8) and $\hat{T}+_q^{(k)}$ is the super-operator defined by the anticommutator relation

$$\hat{T}+_q^{(k)} X = [T_q^{(k)}, X]_+ \quad , \quad \text{arbitrary } X \quad . \tag{28}$$

The exact formal solution of (18) is easily found by Laplace transformation to be

$$\rho(p) = \hat{\Omega}(p)\, \rho(t=0) \equiv [p\cdot\hat{1} + i\hat{\mathcal{H}}' + \hat{M}(p)]^{-1}\, \rho(t=0) \ , \tag{29}$$

where $\rho(p)$ is the Laplace transform of $\rho(t)$ and

$$\begin{aligned}\hat{M}(p) &= \int_0^\infty dp\, e^{-pt}\, \hat{M}(t) \\ &= \sum_k \sum_{q,q'} \frac{1}{\pi} \int_{-\infty}^{+\infty} d\omega\, \hat{T}_q^{(k)} [p+i\omega+i\hat{\mathcal{H}}']^{-1} \Big\{ J_{kq}^{kq'}(\omega)\, \hat{T}_{q'}^{(k)} \\ &\quad + K_{kq}^{kq'}(\omega)\, \hat{T}+_{q'}^{(k)} \Big\} \quad .\end{aligned} \tag{30}$$

The form of (29) establishes the connection with the Laplace transforms of Eqs. (2) and (6). The evolution operator $\hat{\Omega}(p)$ (or its Laplace inverse $\hat{\Omega}(t)$) is now explicitly defined by (29) in terms of the static nuclear Liouville operator $\hat{\mathcal{H}}'$ and the effective interaction of the nuclei with the lattice $\hat{M}(p)$. The relaxation operator (30) is a function of the spectral density of the correlation functions (22) and (23).

For times $t > \tau_c$, the generalized master equation (18) can be approximated by a Markoffian equation of motion. Since we restrict ourselves to second-order effects in the spin-bath interaction, we may approximate $\rho(t-\tau)$ in the integral of Eq. (18) by the formal solution of the unperturbed Liouville equation, $\rho(t-\tau) = \exp\{-i\hat{\mathcal{H}}'\tau\}\,\rho(t)$. Furthermore, since the correlation functions, and consequently $\hat{M}(t)$, are practically zero for $t > \tau_c$, the upper limit of the remaining integral in Eq. (18) may be pushed to infinity. We will make use of the identity

$$\int_0^\infty \exp(ixt)dt = i\,\frac{1}{x} + \pi\,\delta(x) \tag{31}$$

and decompose

$$\hat{N} \equiv \int_0^\infty M(t)\,\exp(i\hat{\mathcal{H}}'t) = \bar{M} + i\,\bar{\bar{M}}\ . \tag{32}$$

In the representation we will use, both $\bar{M}$ and $\bar{\bar{M}}$ are real, i.e. we separate a second-order energy renormalization $\bar{\bar{M}}$ from the damping term $\bar{M}$. We will give explicit expressions for $\bar{M}$ and $\bar{\bar{M}}$ for the special case of an axially symmetric environment. The approximation leading to the Markoffian equation of motion

$$\frac{\partial\rho(t)}{\partial t} = -\,i\,(\hat{\mathcal{H}}' + \bar{\bar{M}})\,\rho(t) - \bar{M}\,\rho(t) \tag{18a}$$

is valid only for $t > \tau_c$ and this requires $\tau_N \gg \tau_c$ for radioactive nuclei. (For impurities in metals, this condition is fulfilled in many cases.) In the region where τ_c is of the order of magnitude of the mean nuclear lifetime, τ_N, results based on the approximation (32) have only very limited validity. To find a reliable solution in this case we could e.g. first specify the time behavior of the correlation functions in (27) and then look for a solution of the non-Markoffian equation (18). In this paper we will restrict ourselves to the aforementioned approach with the advantage that the noise spectrum of the fluctuating lattice need not be specified at this stage of the theory.

III. CONNECTION BETWEEN THE EVOLUTION OPERATOR AND THE PERTURBATION FACTOR

For definiteness we choose the PAC case to point out the connection between our formalism and that reviewed in the existing comprehensive articles on the subject.[1] We interpret the density operators appearing in (1) as supervectors in the Liouville space and use the definition of scalar product (A9) to rewrite (1) as

$$W(\underline{k}_1, \underline{k}_2; t) = (\rho(\underline{k}_2)|\rho(\underline{k}_1, t)) = (\rho(\underline{k}_2)|\hat{\Omega}(t)|\rho(k_1, 0)) \quad . \tag{33}$$

(In the case of a γ-transition, $\rho(\underline{k}_2)$ is Hermitian.) We now use the expansion of an operator into an orthonormal set of basis operators[16] or basis supervectors in Liouville space. For the problem of extranuclear perturbation of the nuclei in a given state specified by spin I, we choose the normalized spherical tensor operators $U_q^{(k)}$ (their properties are described in (A17) to (A20)) as an appropriate set of basis supervectors. Using (A19) twice, (33) reads

$$W(\underline{k}_1, \underline{k}_2; t) = \sum_{kq,k'q'} (\rho(\underline{k}_2)|U_q^{(k)})(U_q^{(k)}|\hat{\Omega}(t)|U_{q'}^{(k')})(U_{q'}^{(k')}|\rho(\underline{k}_1, 0)). \tag{34}$$

The scalar products are defined by (A9). The evolution operator is labeled by four indices as is characteristic of a superoperator transforming one ordinary operator into another. The k's assume all integral values up to 2I; the multipole orientation q, as it was named by Fano,[9] is specified by all integral values between -k and k. The multipole expansion clearly avoids the cumbersome intermediate steps of the usual calculations performed

within the familiar $\{|Im\rangle\}$ representation. In addition, the transformation properties of the quantities entering (34) become obvious. From comparison of (34) with (FS. 208), both specialized to the unperturbed case $(\hat{\Omega} = \hat{1})$, we immediately find (in terms of spherical harmonics and the coefficients, A_k, defined by (FS. 99))

$$(\rho(\underline{k})|U_q^{(k)}) = A_k\, Y_k^q(\theta,\phi)\, [4\pi/(2k+1)]^{1/2} \tag{35}$$

and thus benefit from the fully worked out theory of unperturbed angular correlations. Returning to the general case we define our perturbation factors by

$$G_{kk'}^{qq'}(t) = (U_q^{(k)}|\hat{\Omega}(t)|U_{q'}^{(k')}) \quad . \tag{36}$$

A simple change of representation (A28) together with the use of (A17) yields

$$G_{kk'}^{qq'}(t) = \sum_{m_a m_b} (U_q^{(k)}|Im_b\, Im_b')(Im_b\, Im_b'|\hat{\Omega}(t)|Im_a\, Im_a')(Im_a\, Im_a'|U_{q'}^{(k')}) \tag{37}$$

$$= \sum_{m_a m_b} (-1)^{2I-m_a-m_b} \sqrt{(2k+1)(2k'+1)} \begin{pmatrix} I & I & k \\ m_b' & -m_b & q \end{pmatrix} \begin{pmatrix} I & I & k' \\ m_a' & -m_a & q' \end{pmatrix}$$

$$\cdot\, (m_b\, m_b'|\hat{\Omega}|m_a\, m_a')$$

The expression on the right-hand side has exactly the general form of the perturbation factor (FS. 209),[31] if the evolution operator $\hat{\Omega}$ can be represented in the special form

$$\hat{\Omega}\, X = \Lambda\, X\, \Lambda^+ \quad (X \text{ an arbitrary operator of } \mathcal{U}) \quad . \tag{38}$$

$\Lambda(t)$ is a unitary operator describing the evolution of the state $|Im\rangle$. The matrix elements of $\hat{\Omega}$ in the $|Im\rangle$- representation are easily calculated from (38) using (A13) and (A14)

$$(m_b\ m_b'|\hat{\Omega}(t)|m_a\ m_a') = \langle m_b|\Lambda(t)|m_a\rangle\langle m_b'|\Lambda(t)|m_a'\rangle^* \quad . \tag{39}$$

From (36) to (39) we learn that the G-operator defined in (FS. 206) is actually a special superoperator in a Liouville space. Consequent use of the concept of Liouville representation leaves no uncertainty about the character of the used quantities and no arbitrariness in labeling them with respect to a given basis.

We recall that we – in contradistinction to usual treatments – will make no use of the standard representation as in (37) and (39), but perform all calculations within the state multipole representation. The general formula for the angular distribution shows us that this is the preferred framework with repsect to the analysis of an experiment. It is also a convenient form for deriving the symmetry relations and general properties of the perturbation matrix $G_{kk'}^{qq'}(t)$.

IV. GENERAL PROPERTIES AND SYMMETRY RELATIONS OF $G_{kk'}^{qq'}$

The reality condition

$$G_{kk'}^{qq'}(t)^* = (-1)^{q+q'}\, G_{kk'}^{-q-q'}(t) \tag{40}$$

implies that the following relations for the real and imaginary parts hold

$$\mathrm{Re}\, G_{kk'}^{qq'}(t) = (-1)^{q+q'}\, \mathrm{Re}\, G_{kk'}^{-q-q'}(t) \tag{41a}$$

$$\mathrm{Im}\, G_{kk'}^{qq'}(t) = (-1)^{q+q'+1}\, \mathrm{Im}\, G_{kk'}^{-q-q'}(t) \quad . \tag{41b}$$

The behavior of $G_{kk'}^{qq'}$ depends, of course, on the properties of $\hat{\Omega}$ and, consequently, on those of $(i\hat{H} + \hat{M})$. If we set Λ equal to the rotation operator D, (38) defines the unitary superoperator $\hat{D}$ associated with the rotation D in the vector space $\mathcal{U}$. In addition to the transformation law of an operator A, which can be rewritten as $A' = DAD^+ \equiv \hat{D}A$, we get for the transformed superoperator after the rotation

$$\hat{R}' = \hat{D}\hat{R}\hat{D}^+ \quad . \tag{42}$$

It follows from the requirement $(A'|\hat{R}'|B') = (A|\hat{R}|B)$ that this is in fact the general transformation law of a superoperator under an arbitrary unitary transformation $\hat{O}$ ($\hat{O}\,\hat{O}^+ = \hat{O}^+\hat{O} = \hat{1}$; unitary with respect to the spur metric (A9) of $\mathcal{L}$). The matrix elements of $\hat{D}$ with respect to the multipole representation $|U_q^{(k)})$ are just the rotation matrices:

$$(U_q^{(k)}|\hat{D}|U_{q'}^{(k')}) = (U_q^{(k)}|D\, U_{q'}^{(k')} D^+) = \sum_{\bar{q}} (U_q^{(k)}|U_{\bar{q}}^{(k')})\, \mathcal{D}_{\bar{q}\,q'}^{(k')}$$

$$= \mathcal{D}_{qq'}^{(k)} \cdot \delta_{kk'} \quad . \tag{43}$$

It is obvious from (43) and (36) that $G_{kk'}^{qq'}$ transforms under rotation (α, β, γ) as

$$(U_q^{(k)}|\hat{\Omega}'|U_{q'}^{(k')}) = \sum_{q_1 q_2} \mathcal{D}_{qq_1}^{(k)}(\alpha, \beta, \gamma)\mathcal{D}_{q'q_2}^{(k')*}(\alpha, \beta, \gamma)$$

$$(U_{q_1}^{(k)}|\hat{\Omega}|U_{q_2}^{(k')}) \quad . \tag{44}$$

In the important case that the physical system is <u>invariant</u> under a certain transformation $\hat{\theta}$, Eq. (42) is modified to $\hat{R}' = \hat{\theta}\,\hat{R}\,\hat{\theta}^+ = \hat{R}$. One of the simplest examples is that of axial symmetry C_∞. The invariance condition for rotation about the symmetry axis applied to (44) leads to the well-known restriction

$$G_{kk'}^{qq'} = \delta_{qq'}\, G_{kk'}^{qq} \qquad (\text{for } C_\infty) \; . \tag{45}$$

It follows from the unitarity of $\hat{\theta}$ and the series expansion of the resolvent (29) that in general

$$\hat{\theta}\,\hat{\Omega}\,\hat{\theta}^+ = [p\cdot\hat{1} + i\,\hat{\theta}\,\hat{\mathcal{H}}'\,\hat{\theta}^+ + \hat{\theta}\,\hat{M}\,\hat{\theta}^+]^{-1} \tag{46}$$

holds. Therefore the symmetry of $G_{kk'}^{qq'}$ is determined by the lowest symmetry of the operators in the denominator.

If the ensemble average over the various orientations of the microcrystals of a polycrystalline source can be expressed as an average over angles (which is almost always tacitly assumed), we find for a polycrystal without a preferential axis, by averaging (44) over all Eulerian angles,

$$\overline{G_{kk'}^{qq'}}^{\alpha,\beta,\gamma} = \delta_{q'q}\,\delta_{k'k}\,G_{kk} = \delta_{q'q}\,\delta_{kk'}(2k+1)^{-1}\sum_{q_1} G_{kk}^{q_1 q_1}, \tag{47}$$

which has been proven for several special cases (see e.g. (FS.231) and (FS. 234)), In polycrystalline sources with a preferential direction (as in the presence of an external magnetic field) the only general restriction is again (45), as in single crystals.

There are other relations for the perturbation factors which follow directly from the multipole expansion of the resolvent (29) – explicitly given in Section V. Using (30) and (36) we conclude that

$$G_{ok}^{oq} = o \qquad (k \neq o) \tag{48}$$

is generally true and not restricted to static extranuclear interactions (compare Alder et al.[17], Section II.2). Equation (48) expresses the trivial fact that the operator $U_o^{(o)}$ commutes with every operator, so that $(U_o^{(o)}|(i\hat{\mathcal{H}}' + \hat{M}) = o$. However, the relation

$$G_{ko}^{qo} = o \qquad (k \neq o) \tag{49}$$

is not generally valid, if relaxation processes must be considered. The reason is apparent from the second term on the right-hand side of (30) which leads to an anticommutator, whereby the previous argument fails. We mention in passing that (49) becomes approximately valid in the high-temperature limit $\beta\omega \ll 1$, because $K_{kq}^{k'q'}(\omega)$ may then be neglected compared to $J_{kq}^{k'q'}(\omega)$.

V. MATRIX ELEMENTS OF THE MULTIPOLE EXPANSION OF THE RESOLVENT

We go back to the Laplace transform of $\hat{\Omega}(t)$ defined in (29). The resolvent, $\hat{\Omega}(p)$, is a function of the static perturbation $\hat{\mathcal{H}}'$ and the damping term $\hat{M}(p)$. The Hamiltonian for static magnetic and quadrupole interactions,

$$\mathcal{H}' = \sum_{K=1,2} \sum_{Q=-K}^{+K} (-1)^Q T_Q^{(K)}(n) F_{-Q}^{(K)} = \mathcal{H}_{magn} + \mathcal{H}_{quad} \tag{50}$$

($F_Q^{(K)}$ stands for the extranuclear static fields <u>including the part induced by the surroundings</u>), can be expressed in terms of the normalized multipole operators $U_Q^{(K)}$. Using the Wigner-Eckart theorem and (A17) we have

$$T_Q^{(K)} = U_Q^{(K)} R_K \quad ; \quad R_K = \langle I \| T^{(K)} \| I \rangle \, (2K+1)^{-1/2} \tag{51}$$

and the matrix elements of the Liouville operator associated with (50) are simply given by

$$(U_q^{(k)} | \hat{\mathcal{H}}' | U_{q'}^{(k')}) = \sum_{K,Q} (-1)^Q R_K F_{-Q}^{(K)} (U_q^{(k)} | [U_Q^{(K)}, U_{q'}^{(k')}])$$

$$= \sum_{K,Q} (-1)^Q R_K F_{-Q}^{(K)} c_{Qq'q}^{Kk'k} \quad . \tag{52}$$

The structure constants, c, are defined in (A24) as the product of a Wigner 3-j and 6-j symbol and a phase factor, which vanishes for $(K+k'+k)$ = even integer. By their definition, the structure constants are different from zero only if $Q+q'=q$ and the triangular conditions for the 6-j symbol are fulfilled.

Because we identified $T^{(1)}$ and $T^{(2)}$ with the tensor operators of the nuclear magnetic moment and quadrupole moment, respectively, the quantity $F^{(1)}$ equals the effective magnetic field (except for the sign, if $\mathcal{H}_{magn} = - \mu \cdot H_{eff}$). FS's definition of the quadrupole Hamiltonian contains an extra factor $4\pi/5$ which is not present in (50). The corresponding quantities are related by

$$T^{(2)} \hat{=} \sqrt{\pi/5} \; (T^{(2)})_{FS} \quad , \quad F_o^{(2)} \hat{=} (V_{zz})_{FS} \quad .$$

In terms of the magnetic moment, μ, and the quadrupole moment, eQ, the R_K of (51) read

$$R_1 = \mu \left[\sqrt{3} \begin{pmatrix} I & 1 & I \\ -I & 0 & I \end{pmatrix} \right]^{-1} \tag{53a}$$

$$R_2 = eQ \left[4 \sqrt{5} \begin{pmatrix} I & 2 & I \\ -I & 0 & I \end{pmatrix} \right]^{-1} \quad . \tag{53b}$$

In the appendix we have collected some useful symmetry relations for the structure constants. Making use of the last equality in (A26) or more directly, of the properties of the scalar product (52), we find

$$(U_q^{(k)} | \hat{\mathcal{H}}' | U_{q'}^{(k')}) = (-1)^{q+q'+1} \, (U_{-q'}^{(k')} | \hat{\mathcal{H}}' | U_{-q}^{(k)}) \quad . \tag{54}$$

Equation (54) implies, in particular, that

$$(U_o^{(k)} | \hat{\mathcal{H}}' | U_o^{(k)}) = 0 \quad . \tag{55}$$

The calculation of the matrix element of $\hat{M}(p)$ is straightforward and yields

$$(U_q^{(k)}|\hat{M}(p)|U_{q'}^{(k')}) = \sum_{K=1,2} \sum_{Q,Q'=K}^{-K} R_K^2 \sum_{k_1 q_1 k_2 q_2} \Bigg\{ c^{Kk_1k}_{Qq_1q}\, c^{Kk'k_2}_{Q'q'q_2} \tag{56}$$

$$\times \frac{1}{\pi} \int_{-\infty}^{+\infty} d\omega\, (U_{q_1}^{(k_1)}|[p+i\omega+i\hat{N}']^{-1}|U_{q_2}^{(k_2)})\; J^{KQ'}_{KQ}(\omega)$$

$$+ c^{Kk_1k}_{Qq_1q}\, d^{Kk'k_2}_{Q'q'q_2}\; \frac{1}{\pi} \int_{-\infty}^{+\infty} d\omega\, (U_{q_1}^{(k_1)}|[p+i\omega+i\hat{N}']^{-1}|U_{q_2}^{(k_2)})\; K^{KQ'}_{KQ}(\omega) \Bigg\}$$

The sums over q_1 and q_2 are redundant. The structure constants, $d^{Kk'k_2}_{Q'q'q_2}$, appear as a consequence of the anticommutator $\hat{T}_{+Q'}^{(K)}|U_{q'}^{(k')}) = R_K|[U_{Q'}^{(K)}, U_{q'}^{(k')}]_+)$ and differ from the likewise labeled c only in the phase. We can express this by giving (A24) the form

$$c^{k_1k_2k_3}_{q_1q_2q_3} = \frac{1}{2}\{(-1)^{k_1+k_2+k_3} - 1\}\; \bar{c}^{k_1k_2k_3}_{q_1q_2q_3} \tag{57}$$

(the definition of $\bar{c}$ being obvious from the comparison of (57) and (A24)). Then

$$d^{k_1k_2k_3}_{q_1q_2q_3} = \frac{1}{2}\{(-1)^{k_1+k_2+k_3} + 1\}\; \bar{c}^{k_1k_2k_3}_{q_1q_2q_3} \quad . \tag{58}$$

In contrast to the c's, the d's vanish for $k_1+k_2+k_3$ = odd integer. The sign changes in the symmetry relations are indicated in (A26) and (A27). (See the remarks following these formulae.)

The phase relations together with the triangular conditions restrict the possible combinations of the multipole orders considerably. For relaxation processes caused by tensor operators of the first rank ("magnetic-type relaxation processes"), $K=k_1=1$, we have the selection rules

$$c^{1k_2k_3}_{Qq_2q_3} = \delta_{k_2k_3}\, c^{1k_2k_2}_{Qq_2q_3} \tag{59a}$$

$$d^{1k_2k_3}_{Qq_2q_3} = \delta_{k_2,k_3\pm 1}\, d^{1k_2k_3}_{Qq_2q_3} \quad . \tag{59b}$$

Analogously, for $K=2$, i.e. if relaxation is due to quadrupole interaction, the upper indices must fulfill at least the conditions

$$c^{2k_2k_3}_{Qq_2q_3} = \delta_{k_2,k_3\pm 1}\, c^{2k_2k_3}_{Qq_2q_3} \tag{59c}$$

$$d^{2k_2k_3}_{Qq_2q_3} = \delta_{k_2,k_3\pm 2}\, d^{2k_2k_3}_{Qq_2q_3} \quad , \tag{59d}$$

for the coefficients c and d to be nonzero. For a system with cylindrical symmetry ($q_1 = q_2$ and $J^{KQ'}_{KQ} = \delta_{Q',-Q}\, J^{KQ}_{KQ}$),[18] it is obvious from (56) that again

$$(U_q^{(k)}|\hat{M}(p)|U_{q'}^{(k')}) = \delta_{qq'}\, (U_q^{(k)}|\hat{M}(p)|U_q^{(k')}) \quad .$$

In the applications, we will be interested mainly in this case. Moreover, for a large number of experiments the magnetic-type relaxation processes are dominant. We specialize (56) to this important case by restricting K to

$K = 1$. By virtue of (59a) and (59b) the sums over k_1 and k_2 can be performed, and we are left with the much simpler expression

$$(U_q^{(k)}|\hat{M}(p)|U_q^{(k')}) = R_1^2 \sum_{Q=-1}^{+1} \left\{ \delta_{kk'}(-1)^Q \left(c^{1kk}_{Qq_1q}\right)^2 \cdot \right. \tag{60}$$

$$\frac{1}{\pi}\int_{-\infty}^{+\infty} d\omega \; (U_{q_1}^{(k)}|[p+i\omega+i\hat{\mathcal{H}}']^{-1}|U_{q_1}^{(k)})J^{1\bar{Q}}_{1Q}(\omega)$$

$$+ \sum_{i=\pm 1} c^{1kk}_{Qq_1q}\, d^{1k'k'+i}_{-Qqq_1} \cdot \frac{1}{\pi}\int_{-\infty}^{+\infty} d\omega \; (U_{q_1}^{(k)}|[p+i\omega+i\hat{\mathcal{H}}']^{-1}|U_{q_1}^{(k'+i)}) \cdot$$

$$\left. K^{1\bar{Q}}_{1Q}(\omega) \right\} .$$

If the quadrupole interaction is negligible compared to the magnetic energy in the $\hat{\mathcal{H}}'$ appearing in the resolvent under the integral, the second term in (60) is nonzero only for $k=k'\pm 1$, because $\hat{\mathcal{H}}_{magn}$ is diagonal. Even if the full $\hat{\mathcal{H}}'$ is not strictly diagonal, it will often be a reasonable approximation to fix the frequencies in the integrand by a diagonal part approximation for the resolvent. To do this we decompose $\hat{\mathcal{H}}' = \hat{\mathcal{H}}_1 + \hat{\mathcal{H}}_2$ where $\hat{\mathcal{H}}_1(\hat{\mathcal{H}}_2)$ has diagonal (non-diagonal) matrix elements only. Then to the lowest approximation

$$(U_q^{(k)}|[x+i\hat{\mathcal{H}}']^{-1}|U_q^{(k)}) \approx [x+(U_q^{(k)}|i\hat{\mathcal{H}}_1|U_q^{(k)}) + (U_q^{(k)}|\hat{\mathcal{H}}_2[x+i\hat{\mathcal{H}}_1]^{-1}\hat{\mathcal{H}}_2|U_q^{(k)}]^{-1}.$$

The above approximation is better the slower the correlation functions $J(\omega)$ and $K(\omega)$ vary within the range of the frequency shift due to exact diagonalization of $\hat{\mathcal{H}}'$ (measured with respect to the frequencies of the diagonal part

approximation). The two parts into which (60) decomposes in the cases mentioned are

$$(U_q^{(k)}|\hat{M}(p)|U_q^{(k)}) = R_l^2 \sum_{Q=-l}^{+l} (-1)^Q \left(c^{lkk}_{Qq_lq} \right)^2 \tag{60a}$$

$$\times \frac{1}{\pi} \int_{-\infty}^{+\infty} \frac{J^{l\bar{Q}}_{lQ}(\omega)\, d\omega}{p+i\omega+i\omega_{kq_l}}$$

$$(U_q^{(k)}|\hat{M}(p)|U_q^{(k\pm l)}) = R_l^2 \sum_{Q=-l}^{+l} c^{lkk}_{Qq_lq}\, d^{lk\pm lk}_{-Qqq_l}$$

$$\times \frac{1}{\pi} \int_{-\infty}^{+\infty} \frac{K^{l\bar{Q}}_{lQ}(\omega)\, d\omega}{p+i\omega+i\omega_{kq_l}}$$

with

$$i\omega_{kq} = (U_q^{(k)}|i\hat{H}_{magn} + \hat{N}_{quad}[p+i\omega+i\hat{H}_{magn}]^{-1}\hat{N}_{quad}|U_q^{(k)}) . \tag{60b}$$

For the pure magnetic case, we have according to (52), (53a), and (A24)

$$\omega_{kq} = R_l\, F_o^{(l)}\, c^{lkk}_{oqq} = R_l\, (-H_{eff})\, q\, (3/[I(2I+1)(I+1)])^{1/2}$$

$$= \frac{(-\mu H_{eff})}{I}\, q = \omega_L q \quad (\text{for all } k;\ \hbar = 1) . \tag{61}$$

For later use we give for this special case the final pairs of matrix elements for $\hat{N} = \bar{M} + i\,\bar{\bar{M}}$ introduced in Eq. (32)

$$(U_q^{(k)}|\bar{M}|U_q^{(k)}) = R_1^2 \sum_{Q=-1}^{+1} (-1)^Q \left(c^{1kk}_{Qq_1q}\right)^2 J^{1\bar{Q}}_{1Q}(\omega_L Q) \tag{62a}$$

$$(U_q^{(k)}|\bar{M}|U_q^{(k\pm1)} = R_1^2 \sum_{Q=-1}^{+1} c^{1kk}_{Qq_1q}\, d^{1k\pm1k}_{-Qqq_1}\, K^{1\bar{Q}}_{1Q}(\omega_L Q) \tag{62b}$$

$$(U_q^{(k)}|\bar{\bar{M}}|U_q^{(k)}) = -R_1^2 \sum_{Q=-1}^{+1} (-1)^Q \left(c^{1kk}_{Qq_1q}\right)^2 I'_Q(\omega_L Q) \tag{62c}$$

$$(U_q^{(k)}|\bar{\bar{M}}|U_q^{(k\pm1)} = -R_1^2 \sum_{Q=-1}^{+1} c^{1kk}_{Qq_1q}\, d^{1k\pm1k}_{-Qqq_1}\, I''_Q(\omega_L Q) \tag{62d}$$

The functions I'_Q and I''_Q are the Hilbert transforms of the correlation functions[4]

$$I'_Q(y) = \frac{1}{\pi} \fint_{-\infty}^{\infty} dx\, \frac{J^{1\bar{Q}}_{1Q}(x)}{x - y} \; ; \; I''_Q(y) = \frac{1}{\pi} \fint_{-\infty}^{+\infty} dx\, \frac{K^{1\bar{Q}}_{1Q}(x)}{x - y} \tag{63}$$

obeying the relations

$$I'_{-Q}(y) = -\, I'_Q(-y) \; ; \; I''_{-Q}(y) = I''_Q(-y) \; . \tag{64}$$

All the correlation functions are real for a system with axial symmetry; therefore the same is true for the matrix elements (62). Using the properties (24), (25), and (64) of the correlation functions and the symmetry relations for the structure constants given in the appendix, we easily prove that for both $k' = k$ and $k' = k\pm1$

$$(U_q^{(k)}|\bar{M}|U_q^{(k')}) = (U_{-q}^{(k)}|\bar{M}|U_{-q}^{(k')}) \tag{65a}$$

$$(U_q^{(k)}|\bar{\bar{M}}|U_q^{(k')}) = -(U_{-q}^{(k)}|\bar{\bar{M}}|U_{-q}^{(k')}) \quad . \tag{65b}$$

We have shown in detail in this section that the various matrix elements necessary for the evaluation of $G_{kk'}^{qq'}$ are expressed in terms of the nuclear multipole moments μ and eQ, the extranuclear static fields, and the correlation functions depending on the properties of the surroundings. The nuclear spin does not appear explicitly but, of course, determines the range of possible k values and the numerical value of the structure constants. The evaluation of the perturbation factors is completely reduced to a simple algebraic task.

VI. CALCULATION OF THE PERTURBATION FACTORS

A. General

We now have the choice either to diagonalize the denominator in the resolvent (29) or to invert a finite-dimensional matrix in the Liouville space. In both cases one has to use a computer for higher spins. We briefly discuss in what follows how the general problem can be adjusted economically to a subproblem defined by the experimental situation. We will study in detail special problems which have exact solutions. In this paper we always use the method of matrix inversion.

In the general case $G^{qq'}_{kk'}(p)$ is given by the inverse of the following $(2I+1) \times (2I+1)$ matrix

$$G^{qq'}_{kk'}(p) = (U_q^{(k)} | [p\cdot\hat{1} + i\hat{N}' + \hat{M}(p)]^{-1} | U_{q'}^{(k')}) \tag{66}$$

with elements defined in Section V. To define what we called subproblem, we consider a γ-γ-correlation experiment. Only the even-even terms of $G^{qq'}_{kk'}$ are of importance in this case. For pure radiation, the maximal k is given by Min $(2I, 2L_1, 2L_2)$; L_1 and L_2 being the multipole orders of the radiations in the cascade. The dimension of the matrix to be inverted is, however, determined by the nuclear spin only. For an ideal experiment it would be sufficient to calculate all possible $G^{qq'}_{kk'}$ (k, k' even integers). The admixtures of the other matrix elements to this relevant submatrix can be taken into account exactly with the help of the so-called partitioning technique. The problem is simplified by the special structure of the matrix $\hat{a} \equiv p\cdot\hat{1} + i\hat{N}' + \hat{M}$, as we will see later. First, we arrange $\hat{a}$ in the following form

$$
(\hat{a}) = \left[\begin{array}{c|cccc|ccc}
k \backslash k' & 0 & 2 & 4 & \cdots & 1 & 3 & 5 \cdots \\
\hline
0 & a_{00} & \cdots & & & a_{01} & a_{03} & \cdots \\
2 & \vdots & a_{22} & & & \cdot & & \\
4 & \vdots & & a_{44} & & \cdot & & \\
\cdot & & & & \cdot & \cdot & & \\
\cdot & & & & \cdot & & & \\
\cdot & & & & \cdot & & & \\
\hline
1 & a_{10} & a_{12} & \cdots & & a_{11} & \cdots & \\
3 & & & & & & a_{33} & \\
5 & \cdot & & & & \cdot & & \cdot \\
\cdot & \cdot & & & & \cdot & & \cdot \\
\cdot & \cdot & & & & \cdot & & \cdot \\
\cdot & \cdot & & & & \cdot & &
\end{array}\right]
= \left[\begin{array}{c|c} A & B \\ \hline C & D \end{array}\right]
\tag{67}
$$

We have suppressed the possible q values in $(U_q^{(k)}|\hat{a}|U_{q'}^{(k')}) = a_{kk'}^{qq'}$ so that every element, $a_{kk'}$, is in fact a matrix itself.[19] Secondly, we partition the total matrix into blocks of two square matrices A and D and the rectangular matrices B and C. The interesting part of the resolvent $\hat{\Omega}$ can be determined from the following theorem for partitioned matrices

$$
(\hat{a})^{-1} = \begin{bmatrix} (A - BD^{-1}C)^{-1} & (BD^{-1}-A)^{-1}BD^{-1} \\ D^{-1}C(BD^{-1}C-A)^{-1} & (D-CA^{-1}B)^{-1} \end{bmatrix} , \tag{68a}
$$

therefore,

$$
(\hat{\Omega})_{kk'} = [(A - BD^{-1}C)^{-1}]_{kk'} \quad (k, k' \text{ even integers}) . \tag{68b}
$$

For $k_{max} > 4$ we are usually interested only in the perturbation factors up to $k = 4$. In a real experiment, higher-order terms, even if theoretically

possible, are not obtained with sufficient accuracy. The described procedure might be used a second time to determine the experimentally relevant $G_{kk'}$ $(k, k' = 0, 2, 4)$.

2. Examples

2.1. Randomly fluctuating fields

Two interesting cases have been discussed in detail. Abragam and Pound[2] have treated the case of a randomly fluctuating quadrupole interaction as it appears e.g. in liquids. Micha[2] extended the method to a multidomain ferromagnetic metal with both an average static magnetic field in each domain and a randomly time-fluctuating component. No external fields are present in either case. The common approach with respect to the time-fluctuating part is to split the ensemble average into an average over directions and magnitudes of the perturbations. If we interpret our bath operators $V_Q^{(K)}$ or $v_Q^{(K)}$ (see Eqs. (8) and (20))as classical fields $F_Q^{(K)}$, as in (50), we must also read the former ensemble average, $\langle \cdots \rangle_R$, as an average over an ensemble of random processes. The main assumptions used by the authors[2] are $\tau_c \ll \tau_N$ and $\bar{\omega}\tau_c \ll 1$ (where $\bar{\omega}$ is either the Larmor frequency in the average static field or ω_{ab}, the splitting of the intermediate state by interactions other than the fluctuating field gradient). In the following we show how the same results can be deduced from our formalism. The first assumption justified the use of the Markoffian approximation, as we mentioned in Section II. The condition $\bar{\omega}\tau_c \ll 1$ allows us to neglect the frequency dependence of the remaining correlation functions, i.e. to write $J_{KQ}^{K\bar{Q}}(\bar{\omega}) \approx J_{KQ}^{K\bar{Q}}(0)$. It follows from (60) that this approximation is equivalent to a cancellation of the static Liouville operator, $\hat{\mathcal{H}}'$, in the integrand.

Because $(U_q^{(k)}|\hat{M}|U_{q'}^{(k')})$ transforms under rotation as $\hat{\Omega}$ (see Eq. (44)) the average of the relaxation matrix over the Euler angles can be expressed in a form analogous to (47), i.e.

$$\overline{(U_q^{(k)}|\hat{M}|U_{q'}^{(k')})}^{\text{angles}} = \delta_{kk'}\,\delta_{qq'}\,(2k+1)^{-1}\sum_{\bar{q}}(U_{\bar{q}}^{(k)}|\hat{M}|U_{\bar{q}}^{(k)}) \equiv \delta_{kk'}\delta_{qq'}\lambda_k. \tag{69}$$

A glance at (56) shows that in the present approximation only the first term contributes, because we have $k_1 = k_2$, $q_1 = q_2$ and the structure constants c and d cannot be different from zero simultaneously. In the first term we can neglect the imaginary part for $\bar{\omega}\tau_c \ll 1$. (It can be shown[4] that for an exponentially decaying correlation function, $C_{KQ}^{K\bar{Q}}(t)$, the Hilbert transform of the associated $J_{KQ}^{K\bar{Q}}(\omega)$ is smaller than $J_{KQ}^{K\bar{Q}}(\omega)$ by a factor $\bar{\omega}\tau_c$.) Substituting the surviving and properly simplified part of (56) into (69), we find

$$\lambda_k = (2k+1)^{-1}\sum_{K=1,2} R_K^2 \sum_{Q=-K}^{+K} (-1)^Q J_{KQ}^{K\bar{Q}}(0) \sum_{k_1 q_1 \bar{q}} \begin{pmatrix} Kk_1k \\ cQq_1\bar{q} \end{pmatrix}^2 \tag{70}$$

$$= 2\sum_{K=1,2} R_K^2 \sum_{Q=-K}^{+K} (-1)^Q J_{KQ}^{K\bar{Q}}(0) \left[\frac{1}{2I+1} - (-1)^{k+K+2I} \begin{Bmatrix} I & K & I \\ I & k & I \end{Bmatrix} \right].$$

The sums over the squared structure constants can be performed using the orthogonality relation for the 3-j symbol and the sum rules (6.2.9) and (6.2.11) of Edmonds' book.[20]

The relaxation constants, (70), are exactly the same as those reported by Abragam and Pound (their Eq. (71)) and Micha (his Eq. (21)).

For $K = 1$ and an exponential correlation function with a single correlation time τ_c we find:

$$\sum_{Q=-1}^{+1} (-1)^Q J_{1Q}^{1\bar{Q}}(0) = \langle (H - \langle H \rangle)^2 \rangle \tau_c = \langle (\Delta H)^2 \rangle \tau_c \quad ,$$

and therefore, using (53a) and the explicit expression for the 6-j symbol and the gyromagnetic ratio instead of μ,

$$\lambda_k = \frac{1}{3} \gamma^2 \langle (\Delta H)^2 \rangle \tau_c \, k(k+1) \quad . \tag{71}$$

The perturbation factor is given by

$$G_{kk}(p) = (2k+1)^{-1} \sum_q [p + i\omega_L q + \lambda_k]^{-1} \tag{72}$$

from which both the time-dependent and the integral attenuation factors are easily derived.

In (70), the sum of $J_{KQ}^{K\bar{Q}}$ over the multipole orientation Q is invariant under rotation. The correlation functions can therefore be described with respect to an arbitrary coordinate system. For an axially symmetric field gradient with an instantaneous symmetry axis along z', we may write

$$\sum_{Q=-2}^{+2} (-1)^Q J_{2Q}^{2\bar{Q}}(0) = \langle V_{z'z'}^{\;2} \rangle \tau_c \quad .$$

The lengthy expression for λ_k (see (FS. 354)) will not be repeated here.

2.2. Static magnetic fields and magnetic relaxation processes. The high-temperature limit

In the last examples the terms depending on the correlation function, $K(\omega)$, dropped out by averaging over the directions. The same mathematical simplification may also be effected in single crystals without the assumption of randomly fluctuating classical fields. We have mentioned at the end of Section IV that, by virtue of (26), the damping part of the relaxation matrix reduces to diagonal form in the multipole representation if $\beta\omega \ll 1$. The frequencies we are concerned with are integral multiples of the Larmor frequency ω_L belonging to the effective field at the nucleus (see Eqs. (62a) and (62b)). The high-temperature limit in nuclear magnetism may in fact include rather low temperatures even if the effective field is high. The study of the analytical solution of the high-temperature approximation is therefore of some interest.

In the following we always assume that the quantization axis is along H_{eff} and that no quadrupole interaction is present. The use of the matrix elements (62) requires $\tau_N \gg \tau_c$, as before. We restrict ourselves to the diagonal terms (62a) and (62c). The solution is then given by

$$G_{kk}^{qq}(p) = (U_q^{(k)} | [p\cdot\hat{1}+i(\hat{\mathcal{H}}_{magn} + \bar{\bar{M}}) + \bar{M}]^{-1} | U_q^{(k)})$$

$$= [p+i\{\omega_L q + (U_q^{(k)}|\bar{\bar{M}}|U_q^{(k)})\} + (U_q^{(k)}|\bar{M}|U_q^{(k)})]^{-1} \qquad (73)$$

which is exact in the present approximation, <u>valid</u> for <u>arbitrary</u> k, and does <u>not</u> explicitly depend on the nuclear spin I. The order of magnitude of the second-order frequency shift cannot be estimated without specifying the

electronic correlation mechanism. It is negligible for $\omega_L \tau_c \ll 1$, but might be appreciable in situations where $\omega_L \tau_c \approx 1$. Using the abbreviations

$$\nu_{kq} = \omega_L q + (U_q^{(k)} | \bar{\bar{M}} | U_q^{(k)}) \; ; \; \lambda_{kq} = (U_q^{(k)} | \bar{M} | U_q^{(k)}) \; , \tag{74}$$

the time-differential perturbation matrix is given by the Laplace inverse of (73),

$$G_{kk}^{qq}(t) = e^{-it\nu_{kq} - \lambda_{kq} t} \quad (t > 0) \; . \tag{75}$$

The time-integral perturbation factors follow immediately from (73) by substitution of $p = 1/\tau_N$ and multiplication by $1/\tau_N$.

The main deviation from the Abragam-Pound solution (70) is that there exist individual damping constants for every multipole orientation q. It follows form (65b) that $\nu_{kq} = -\nu_{k-q}$, i.e. the frequency shift in (74) leads to a symmetrical change in the frequencies at $\pm q$ relative to the center at $q = 0$. The associated damping constants are even functions of q ($\lambda_{kq} = \lambda_{k-q}$). This follows from (65a).

Introducing the explicit expressions

$$c_{oqq}^{1kk} = \alpha q \quad ; \quad \alpha = \sqrt{3} \; [I(I+1)(2I+1)]^{-1/2} \tag{76a}$$

$$c_{\pm 1 q \mp 1 q}^{1\;k\;k} = \mp \alpha \; [(k \pm q)(k \mp q + 1)/2]^{1/2} \tag{76b}$$

into (62a) we find

$$\lambda_{kq} = \gamma^2 \; \{q^2 [J_{10}^{10}(0) + J_{1\bar{1}}^{11}(-\omega_L)] - k(k+1) \; J_{1\bar{1}}^{11}(-\omega_L)\} \tag{77}$$

The appearance of the gyromagnetic ratio shows that the correlation functions are expressed in terms of an effective hyperfine field operator $\underline{H}_{hf}$, i.e. the interaction Hamiltonian has been given the form

$$\mathcal{H}_{Rn} = \sum_{Q=-1}^{+1} (-1)^Q \, T_Q^{(1)}(n) \, V_{-Q}^{(1)} \equiv -\gamma \, \underline{I} \cdot \underline{H}_{hf} \quad . \tag{78}$$

With $\underline{h} = \underline{H}_{eff} - \langle \underline{H}_{eff} \rangle_R$ the correlation functions are then defined by

$$J_{10}^{10}(\omega) = \frac{1}{2} \int_{-\infty}^{+\infty} dt \, \exp\{i\omega t\} \langle \tfrac{1}{2}[h_z(t), \, h_z(0)]_+ \rangle_R \tag{79a}$$

$$J_{1\bar{1}}^{11}(\omega) = -\frac{1}{2} \int_{-\infty}^{+\infty} dt \, \exp\{i\omega t\} \langle \tfrac{1}{2}[h_+(t), \, h_-(0)]_+ \rangle_R = J_{11}^{1\bar{1}}(-\omega) \tag{79b}$$

which shows that to all multipole orders, the damping is determined by secular and non-secular processes. As is well-known from NMR studies, the latter include the effect of transitions induced between the states of different multipole orientations by the transverse components of the hf operator. The secular processes describe the influence of the spread of Larmor frequencies due to the change of the z-component of the hf operator. The damping constants (77) may be expressed in terms of the appropriate longitudinal and transverse spin-lattice relaxation times, T_1 and T_2. Instead of (77), we then have

$$\lambda_{kq} = k(k+1)/2T_1 + q^2(1/T_2 - 1/T_1) \quad . \tag{77a}$$

For rapidly decaying correlations in the electronic system, $\omega_L \tau_c \ll 1$, and isotropic hf interaction, T_1 becomes equal to T_2, and the damping

constants are then independent of the multipole orientation q.

The case $T_1 \neq T_2$ should under favorable conditions be directly observable in a time-differential PAC experiment. Let us look at a typical experimental geometry. We orient the static magnetic field perpendicular to the detector plane and observe the two radiations with collinear counters ($\theta = \pi$). Furthermore, we consider the case $k_{max} = 2$ (realized e.g. in the extensively studied $1^+ \xrightarrow{M1} 2^+ \xrightarrow{E1} 1^-$ cascade of ^{100}Rh). The directional correlation function is then given by

$$W_\perp(\pi;t) = 1 + \frac{1}{4} A_{22} \, [G_{22}^{00}(t) + 3\mathrm{Re}\, G_{22}^{22}(t)]$$

$$= 1 + \frac{1}{4} A_{22} \exp\{-3t/T_1\}[1 + 3 \exp\{-4t(1/T_2 - 1/T_1)\}\cos(\nu_{22}t)],$$

where A_{22} is the correlation factor (FS. 92) of the unperturbed correlation and $\nu_{22} = 2\omega_L + \bar{\bar{M}}_{22}^{22}$. Besides the second-order frequency shift $\bar{\bar{M}}_{22}^{22}$, the relaxation is manifest in the two damping terms. If we eliminate from the experimental data the exponential decay (due to the nuclear lifetime and the relaxation factor $3/T_1$), a damped cosine oscillation should occur according to the second exponential in the equation for $W_\perp(t)$.

2.3. External magnetic field and magnetic relaxation processes, for arbitrary temperatures

We consider a simple example for the general case sketched in Section VI.2.1. Because the results are now no longer independent of the nuclear spin, it must be specified from the outset. We choose the simplest case and take $I = 1$ for the spin of the intermediate state. The dimension of the particular unitary vector space is $N = 2I+1 = 3$. The matrix $(\hat{a})$ introduced in Section VI.1. gets the following explicit form for the present example

$$(\hat{a}) = \begin{bmatrix} p & 0 & 0 \\ 0 & (U^{(2)}|p+i(\hat{\mathcal{H}}_{magn}+\bar{\bar{M}})+\bar{M}|U^{(2)}) & (U^{(2)}|\bar{M}+i\bar{\bar{M}}|U^{(1)}) \\ (U^{(1)}|\bar{M}+i\bar{\bar{M}}|U^{(0)}) & (U^{(1)}|\bar{M}+i\bar{\bar{M}}|U^{(2)}) & (U^{(1)}|p+i(\hat{\mathcal{H}}_{magn}+\bar{\bar{M}})+\bar{M}|U^{(1)}) \end{bmatrix} \tag{80}$$

where the missing indices, q,q', indicate that each element in (80) is itself a square or rectangular matrix. For an axially symmetric system, only terms with $q = q'$ are non-zero. All matrix operations with the supermatrix (80) can then be done as if the elements were simple numbers. We nevertheless use the rigorous matrix notation, because the formulae are then easily generalized to the nonsymmetric case without change in the order of terms. It is a general feature of the resolvent that (besides p in the upper left corner) all elements of the first row vanish. This has been stated in a different way in Eq. (48). The asymmetry of (80) is obvious from the nonvanishing element of the first column and the other "low temperature" nondiagonal matrices in (80).

It follows from (68) that, due to special structure of (80), the first column does not contribute to the inverse of submatrix $(\hat{b})$ labeled by $k = 1,2$. Explicitly, we find

$$G_{00}(p) = \frac{1}{p} \quad ; \quad G^{00}_{i0}(p) = -(\hat{b}^{-1})^{00}_{i1}\,\bar{M}^{00}_{10}\cdot\frac{1}{p} \qquad (i = 1,2)\ , \tag{81}$$

i.e. $G_{00}(t) = 1$, as required, and the even-odd-term is of no interest for γ-γ directional correlations. The remaining $(\hat{b})$ matrix consists of the diagonal square matrices, already known from (73), and the two rectangular matrices belonging to multipole orders $k = 1$ and $k = 2$. Using (74) and (65), we find the following tridiagonal matix (see next page)

$$
(\hat{b}) \equiv \left[\begin{array}{ccccc|ccc}
p-i\nu_{22}+\lambda_{22} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & p-i\nu_{21}+\lambda_{21} & 0 & 0 & 0 & \bar{M}^{11}_{21}-i\bar{\bar{M}}^{00}_{21} & 0 & 0 \\
0 & 0 & p+\lambda_{20} & 0 & 0 & 0 & \bar{M}^{00}_{21} & 0 \\
0 & 0 & 0 & p+i\nu_{21}+\lambda_{21} & 0 & 0 & 0 & \bar{M}^{11}_{21}+i\bar{\bar{M}}^{11}_{21} \\
0 & 0 & 0 & 0 & p+i\nu_{22}+\lambda_{22} & 0 & 0 & 0 \\
\hline
0 & \bar{M}^{11}_{12}-i\bar{\bar{M}}^{11}_{12} & 0 & 0 & 0 & p-i\nu_{11}+\lambda_{11} & 0 & 0 \\
0 & 0 & \bar{M}^{00}_{12} & 0 & 0 & 0 & p+\lambda_{10} & 0 \\
0 & 0 & 0 & \bar{M}^{11}_{12}+i\bar{\bar{M}}^{11}_{12} & 0 & 0 & 0 & p+i\nu_{11}+\lambda_{11}
\end{array}\right] \tag{82}
$$

partitioned in the indicated manner. Equation (82) is a simple example for the application of the partitioning technique, (68), to calculate $(\hat{b}^{-1})_{22} \hat{=} [(A - BD^{-1}C)^{-1}C)^{-1}]_{22}$. The result can be given the form

$$G_{22}^{qq}(p) \hat{=} (\hat{b}^{-1})_{22}^{qq} = [p+i\nu_{2q}+\lambda_{2q} - (\bar{M}_{21}^{qq}+i\bar{\bar{M}}_{21}^{qq})\{p+i\nu_{1q}+\lambda_{1q}\}^{-1}\cdot(\bar{M}_{12}^{qq}+i\bar{\bar{M}}_{12}^{qq})]^{-1} \quad .$$

$$(q = 0, \pm 1, \pm 2;\ I=1) \tag{83}$$

which shows clearly how the low-temperature terms modify the high-temperature solution (73), or (75). For spins $I > 1$, the results are of a similar form.

For specializing (83) to the possible multipole orientations q, we have to keep in mind that $\nu_{ko} = \bar{\bar{M}}_{kk'}^{00} = 0$. This insures that G_{22}^{00} is real as required by the reality condition (40). The perturbation factors with $|q_{max}| = 2$ are exactly those of the high-temperature solution, because $\hat{N}_{21}^{22} = \hat{N}_{12}^{22} = 0$ (see Eq. (82)). Therefore, $G_{22}^{22}(t)$ can be taken from (75). The Laplace inverses of

$$G_{22}^{00}(p) = \frac{p+\lambda_{10}}{(p+\lambda_{20})(p+\lambda_{10}) - \bar{M}_{21}^{00}\,\bar{M}_{12}^{00}} \tag{84a}$$

$$G_{22}^{11}(p) = \frac{p+i\nu_{11}+\lambda_{11}}{(p+i\nu_{21}+\lambda_{21})(p+i\nu_{11}+\lambda_{11}) - (\bar{M}_{21}^{11}+i\bar{\bar{M}}_{21}^{11})(\bar{M}_{12}^{11}+i\bar{\bar{M}}_{12}^{11})} \tag{84b}$$

are easily expressed in terms of the negative roots, $(\alpha_q^{(i)} \pm i\beta_q^{(i)})(i=1,2)$ of the denominators. The time-dependent perturbation factors are superpositions of two exponentials

$$G_{22}^{00}(t) = a_o\, e^{-\alpha_o^{(1)}t} + b_o\, e^{-\alpha_o^{(2)}t} \tag{85a}$$

$$G_{22}^{11}(t) = a_1\, e^{-(\alpha_1^{(1)}+i\beta_1^{(1)})t} + b_1\, e^{-(\alpha_1^{(2)}+i\beta_1^{(2)})t} \quad . \tag{85b}$$

Equation (85a) has the form of the Dillenburg and Maris[3] solution for the particular PAC problem under consideration. A detailed comparison of their statistical theory with our approach will be given elsewhere. In our theory, the effective relaxation constants and modified frequencies (if present) may be expressed explicitly in terms of the electronic correlation functions. The lengthy formulae will not be given here for all components, but only for (85a). The negative roots of the quadratic equation are (I=1)

$$\alpha_o^{(1,2)} = 1/2(\lambda_{10} + \lambda_{20}) \mp 1/2[(\lambda_{10} - \lambda_{20})^2 + 4\bar{M}_{21}^{00}\,\bar{M}_{12}^{00}]^{1/2} \tag{86}$$

$$= -\,2\gamma^2\, J_{11}^{1\bar{1}}(\omega_L)\{2 \pm (\cosh(\beta\omega_L/2))^{-1}\}$$

$$= \frac{1}{T_1}\ \{2 \pm (\cosh(\beta\omega_L/2))^{-1}\} \quad .$$

In deriving Eq. (86), we have used Eqs. (26), (53a), (62), and (77). The temperature dependence of the damping constants is determined partly by the correlation function $J_{11}^{1\bar{1}}(\omega_L)$, and in addition, by a low-temperature correction which follows directly from (26) and is, therefore, independent of the particular interaction model. The cofactors a_o and b_o are also temperature dependent and given by

$$a_o = 1/2(\cosh(\beta\omega_L/2) + 1); \quad b_o = 1/2(1 - \cosh(\beta\omega_L/2)) \quad . \tag{86a}$$

In the high-temperature limit the second term drops out and $G_{22}^{00}(HT) = \exp(-3t/T_1)$ as it should. At extreme low temperatures we get a double root, $\alpha_o^{(1,2)} = 2/T_1$, according to (86) and, therefore, $G_{22}^{00}(LT) = (1-t/T_1)\exp(-2t/T_1)$ (for I=1) .

VII. ANGULAR DISTRIBUTION FROM ORIENTED NUCLEI. RELAXATION EFFECTS

The radiative detection of magnetic resonance[21] in oriented nuclei (NMR/ON) has opened a new experimental method of measuring spin-lattice relaxation for radioactive nuclei at low temperatures. It is, therefore, worthwhile to discuss how the present theory may be applied to this problem. The underlying physical model makes our approach especially appropriate for spin-lattice relaxation in metals, a field investigated intensively by various groups.[21]

The basis of this Section has already been given in the Introduction (see Eqs. (4) to (6)). For practical reasons, we discuss reorientation effects in parent nuclei. Although it is now a well-established experimental fact that the preparation of the initial conditions are of crucial importance in the NMR/ON technique, we will not plunge into the complexities of a theoretical description of the preparation procedure. Let us assume that our parent nucleus can be characterized by a particular axially symmetric density matrix, $\rho_o(t=0)$, at the end of some preparation process. The time evolution of the system of radioactive parent nuclei together with the environment is again fully described by the evolution operator $\hat{\Omega}(t)$.

As in the PAC case, we determine the radiation parameters by comparison with the unperturbed case $\hat{\Omega} = 1$. For a system with cylindrical symmetry, the initial density matrix, $\rho_o(0)$, is fully defined by the $R_o^{(k)}$ components of Fano's statistical tensors (FS. 41b)

$$R_q^{(k)} = \sum_{m_o, m_o'} (-1)^{I_o - m_o} \langle I_o m_o, I_o - m_o' | kq \rangle \langle m_o | \rho_o(0) | m_o' \rangle = (U_q^{(k)} | \rho_o(0)) \ . \tag{87}$$

We mention the following relations for quantities used instead of $R_o^{(k)}$ in the various standard articles[11,22]

$$R_o^{(k)} = G_k(I)^{(\text{de Groot})} = (2I+1)^{-1/2}\, B_k^{(\text{Blin-Stoyle})} \quad . \tag{88}$$

The angular distribution (5), in standard notation, is given by

$$W_{axial}(\underline{k};t) \equiv W(\theta,t) = \sum_{k,k'} U_k\, F_k\, P_k\,(\cos\theta)(U_k^{(0)}|\hat{\Omega}(t)|U_{k'}^{(0)})\, B_{k'}(0)$$

$$= \sum_k U_k\, F_k\, P_k\,(\cos\theta)\, B_k(t) \tag{89}$$

with

$$B_k(t) = \sum_{k'} G_{kk'}^{00}(t)\, B_{k'}(0) \tag{90}$$

according to (36). The $U_k\, F_k$ depend on the decay scheme of the particular nucleus. In the asymmetric case, Eq. (90) has to be generalized to

$$R_q^{(k)}(t) = \sum_{k'q'} G_{kk'}^{qq'}(t)\, R_{q'}^{(k')}(t=0) \quad . \tag{91}$$

In the case that only the directional distribution of the γ-radiation emitted from the daughter nucleus is observed, the sum in (89) contains only even k. Nevertheless, statistical tensors of odd rank contribute to the associated $B_k(t)$ according to (90).

We now show that the problem of reorientation effects in ON studies is intimately related to the theory of multipole relaxation. Schwegler[23] has extensively studied this problem, utilizing methods of irreversible thermodynamics to take into account the dissipative properties of the heat bath. The theory of multipole relaxation has also been sketched in Fano's version of the Wangsness-Bloch theory.[16]

We base the following considerations on the physical model described above. According to the remarks at the end of Section II, the long-time behavior of the system is governed by the differential equation

$$dR_q^{(k)}/dt = d(U_q^{(k)}|\rho_o(t))/dt = \sum_{k'q'} (U_q^{(k)}|-i(\hat{\mathcal{H}}'+\bar{\bar{M}}) - \bar{M}|U_{q'}^{(k')})R_{q'}^{(k')} . \tag{92}$$

The perturbation factors obey the same differential equation, subject to the initial condition $G_{kk'}^{qq'}(t=0)=\delta_{kk'}\delta_{qq'}$. It then follows that

$$G_{kk'}^{qq'}(t) = (U_q^{(k)}|\exp\{-i(\hat{\mathcal{H}}'+\bar{\bar{M}})t-\bar{M}t\}|U_{q'}^{(k')}) , \tag{93}$$

which is, of course, just the inverse Laplace transform of $\hat{\Omega}(p)$, defined in (29) (with $\hat{M}(p)$ replaced by $\hat{N}$). In the case of cylindrical symmetry of the initial density matrix, only the $G_{kk'}^{00}$'s are required in (90). In this case, the imaginary part $\bar{\bar{M}}$ drops out exactly. (It is apparent from (65b) that $\bar{\bar{M}}_{kk'}^{00}=0$ for all k,k'). Except for the case that $\omega_L\tau_c \simeq 1$, the energy renormalization is negligible; therefore we cancel $\bar{\bar{M}}$ in (93), even for asymmetric situations.

Equations (92) and (93) may be rewritten in a form which shows that the assembly of nuclear spins relaxes asymptotically to the temperature of the lattice. This is accomplished by using the fact that the real part of the relaxation operator, M, applied to the equilibrium density matrix for the parent nuclei, $\rho_o^T(\mathcal{H}') = \exp\{-\mathcal{H}'/kT\}/\ \mathrm{Tr}\ \exp\{-\mathcal{H}'/kT\}$ (T = lattice temperature), gives zero

$$\bar{M}\ \rho_o^T(\mathcal{H}') = 0 \quad . \tag{94}$$

Equation (94) implies the following relations between the matrix elements of $\bar{M}$ in the state multipole representation

$$\sum_{k'q'} (U_q^{(k)}|\bar{M}|U_{q'}^{(k')})(U_{q'}^{(k')}|\rho_o^T) = \sum_{k'q'} \bar{M}_{kk'}^{qq'}\ R_{q'}^{(k')}(eq) = 0 \quad . \tag{95}$$

We also conclude that, for the special perturbation matrix (93) (with $\bar{\bar{M}} = 0$),

$$\sum_{k'q'} (U_q^{(k)}|\hat{\Omega}(t)|U_{q'}^{(k')})(U_{q'}^{(k')}|\rho_o^T) = \sum_{k'q'} G_{kk'}^{qq'}(t)\ R_{q'}^{(k')}(eq) = R_q^{(k)}(eq). \tag{96}$$

With

$$\Delta R_q^{(k)}(t) = (U_q^{(k)}|\{\rho_o(t) - \rho_o^T\}) \ , \tag{97}$$

the differential equation (92) now reads

$$d\Delta R_q^{(k)}/dt = \sum_{k'q'} (U_q^{(k)}|-\hat{\mathcal{H}}' - \bar{M}|U_{q'}^{(k')})\ \Delta R_{q'}^{(k')} \tag{98}$$

and has the formal solution

$$\Delta R_q^{(k)}(t) = \sum_{k'q'} (U_q^{(k)}|\exp\{-(i\hat{\mathcal{H}}' + \bar{M})t\}|U_{q'}^{(k')})\Delta R_{q'}^{(k')}(t=0) \ . \qquad (99)$$

For the axially symmetric case, the simpler equation

$$\Delta B_k(t) = B_k(t) - B_k(eq) = \sum_{k'} G_{kk'}^{00}(t)\, \Delta B_{k'}(t=0)$$

$$= \sum_{k'} (U_o^{(k)}|\exp\{-(i\hat{\mathcal{H}}' + \bar{M})t\}|U_o^{(k')})[B_{k'}(t=0) - B_{k'}(eq)] \qquad (100)$$

holds. Substitution of Eq. (100) in (89) yields an expression for the time-dependent angular distribution, generalizing Shirley's Eq. (10), which was used in a discussion of spin-lattice relaxation investigations by NMR/ON techniques.[24]

It is well-known, and apparent from Eqs. (99) and (100), that the angular distribution of radiation emitted from oriented nuclei depends on the preparation of the initial state and on the dynamic properties of the surroundings. A discussion of the latter part has already been given in the preceding Section; the details will not be repeated here. A few remarks might be in order with respect to the case of a static magnetic field and relaxation processes of the magnetic type. It can be shown quite generally, that under these conditions $\hat{\mathcal{H}}_{magn}$ commutes with the axially symmetric relaxation operator, $\hat{M}$. Therefore, the Liouville operator, $\hat{\mathcal{H}}_{magn}$, drops out of Eq.(100), and we are left with

$$\Delta B_k(t) = \sum_{k'} (U_o^{(k)}|\exp\{-\bar{M}t\}|U_o^{(k')})\, \Delta B_{k'}(t=0) \ . \qquad (101)$$

In the high-temperature approximation, where the off-diagonal matrix elements of $\bar{M}$ may be neglected, we already know from Eqs. (74) and (75) that

$$\Delta B_k(t) = \exp\{-\lambda_{ko} t\}\, \Delta B_k(t=0) \quad . \tag{102}$$

For the interaction Hamiltonian (78), the damping constants λ_{ko} follow from (77) and (79b) to be

$$\lambda_{ko} = -k(k+1)\, \gamma^2\, J_{11}^{1\bar{1}}(\omega_L) = k(k+1)/2T_1 \quad . \tag{103}$$

We notice that the relaxation rate is determined by a <u>multiple</u> of the usual longitudinal spin-lattice relaxation time T_1. As mentioned above, this simple result is valid only in the high-temperature limit and in the absence of quadrupole interactions. To cover the entire temperature range, the procedure of Section VI.2.3. has to be used. It is sometimes more convenient to diagonalize the relaxation matrix $\bar{M}$ to determine the relaxation constants. (One of the eigenvalues is always zero [see Eq. (81)]). The solutions are similar to Eq. (86), the solution for I=1. Numerical calculations for higher spins and various initial conditions are in preparation.

VIII. SUMMARY AND DISCUSSION

We have shown that the combined use of the Liouville operator formalism and Fano's expansion of operators into an orthonormal set of multipole operators is also a powerful tool for treating relaxation phenomena in PAC or in experiments with oriented nuclei. An account of the less familiar mathematical means has been added.

The perturbation factors have been given as the multipole representation of a resolvent, which is defined in terms of the Liouville operator for the static extranuclear interactions, and of a relaxation superoperator (defined by the nucleus-bath interaction and the properties of the environment). Several examples have been discussed: (1) Randomly fluctuating fields (Abragam and Pound[2] and Micha[2]). (2) Single crystals in static magnetic fields (external and/or caused by the lattice) with relaxation processes of the magnetic type. The "high-temperature" condition $\omega_L/kT \ll 1$ was assumed to be fulfilled. (3) For nuclei with spin $I=1$, extension of case (2) to arbitrary temperatures. (4) The influence of reorientation effects (relaxation processes) an the angular distribution of radiation from oriented nuclei (general discussion).

The following supplementary remarks are concerned with some approximations made in the general part of the theory and with the quantities entering the final formulae. In the second part of the paper we have used the relaxation operator $\hat{N}$, i.e. we have neglected the memory effects which are contained in the generalized master equation (18). The Markoffian equation of motion (18a) resulting from this approximation is valid only for times long compared to the electronic correlation time, τ_c. Since for radioactive nuclei, the

available time is the nuclear lifetime, τ_N, use of the limiting relaxation operator $\hat{N}$ is justified only when $\tau_c \ll \tau_N$. In a forthcoming note we will discuss the relaxation problem in PAC, including the intermediate case $\tau_c \simeq \tau_N$. The restriction to second-order correlation functions requires, roughly speaking, that $\gamma^2\langle H_{hf}{}^2\rangle_R\, \tau_c{}^2 \ll 1$, which can be seen from Eqs. (74) and (77) to (79). Since the reciprocal nuclear spin-lattice relaxation times are proportional to $\gamma^2\langle H_{hf}{}^2\rangle_R\, \tau_c$, the criterion $\tau_c \ll T_{relax}$ must be valid in addition to and independently of $\tau_c \ll \tau_N$. Conditions like $\omega_L\, \tau_c \ll 1$ have not been used in our theory, except in discussing special situations, as in Section VI.2.1.

The second-order correlation functions $J_{KQ}^{KQ'}(\omega)$ are <u>basic</u> quantities for the particular physical model used here and in related papers. Relaxation effects in NMR, Mössbauer experiments, PAC and NMR/ON may be, and have been, described in terms of essentially the same electronic correlation functions.

In general we must not expect to be able to express the damping constants appearing in the perturbation factors in terms of the two spin-lattice relaxation times used in the Bloch equations for the macroscopic magnetization. Relaxation times measured by conventional NMR characterize the irreversible behavior of only the dipole polarization, although, of course, higher-rank statistical tensors are present for $I > 1/2$. In a directional correlation experiment, for instance, we observe under suitable conditions (at least in principle) damping constants belonging to higher-rank multipolarizations, e.g. by looking at the perturbation factors $G_{22}^{qq}(t)$ and $G_{44}^{qq}(t)$. The same is true for relaxation processes observed using the NMR/ON technique.

The general theory of multipole relaxation (formulated briefly by Fano,[16] in detail by Schwegler,[23] and within our approach in Section VII) yields an increasing number of independent relaxation times for increasing spin valcues. (For a system without any symmetry the maximal number of independent relaxation times is $\{(2I+1)^2 - 1\}$ according to Ref. 16, 23. Even for axial symmetry and $I=1$, we already get 5 independent damping constants.) It seems rather unlikely that all of the possible relaxation times can be determined experimentally, especially for higher spins. Thus, in practice the problem will be to interpret consistently the incomplete smaller set of experimental parameters. Provided that the basic assumptions of the present theory are suitable, the electronic correlation functions $J_{KQ}^{KQ'}(\omega)$ may be used. Only in special cases, like in the ones leading to (77a) or to Eq. (103), the usual spin-lattice relaxation times occur. There, the damping constants are linear combinations of T_1 and T_2 with fixed "geometrical factors", which depend on the multipole order k and the multipole orientation q. That such a simple result is not always valid is clear from the example of Section IV.2.3. (see Eq. (86)).

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IX. APPENDIX

Liouville Representation

We collect here some properties of the quantum mechanical Liouville operator first used by Kubo,[25] then applied to problems of nonequilibrium statistical mechanics by Zwanzig[12] and, subsequently, to line shape problems by various authors.[4,7,13,26] In the present paper we make use of operator techniques described by Fano[16] and applied to the theory of multipole relaxation by Schwegler.[23] For the problem under consideration we are mainly concerned with the special finite-dimensional unitary vector space $\mathcal{U}$ of dimension N (spanned, e.g., by the standard representation $\{I^2, I_z\}$ of a spin system of angular momentum I) and linear operators acting on state vectors of $\mathcal{U}$.

Let us assume for simplicity that the quantum numbers I and m specify the state uniquely. From the complete orthonormal set of vectors $\{|Im\rangle\}$ in $\mathcal{U}$ we define a set of operators $\{|Im\rangle\langle Im'|\}$ which may be considered elements of a unitary space $\mathcal{L}$ (Liouville space) with dimension N^2. Following Sauermann[27] we denote this orthonormal basis in $\mathcal{L}$ by $\{|Im\rangle\langle Im'|\} \equiv \{|ImIm')\}$ or, if no confusion arises, simply by $\{|mm')\}$. Using this "Dirac" notation for the basis operators $|mm')$ in $\mathcal{L}$ and the orthonormality and closure relations

$$(ImIm'|Im_1Im_2) = \delta_{mm_1}\,\delta_{m'm_2} \tag{A1}$$

$$\sum_{mm'} |ImIm')(ImIm'| = \hat{1} \quad \text{(unit operator in } \mathcal{L}) \tag{A1'}$$

we find, in complete analogy to the usual rules of quantum mechanics, for the

decomposition of an operator $A \in \mathcal{U}$, considered as an element of the Liouville space $|A)$,

$$|A) = \sum_{mm'} |ImIm')(ImIm'|A) = \sum_{mm'} |ImIm')\langle Im|A|Im'\rangle \tag{A2}$$

$$(A| = \sum_{mm'} (A|ImIm')(ImIm'| = \sum_{mm'} \langle Im|A|Im'\rangle^* (ImIm'| \quad . \tag{A2'}$$

The advantage of this seemingly complicating notation will soon become evident. To make calculations in the Liouville space it is necessary to introduce superoperators $\hat{R}$, $\hat{S}$, ... (definitions to be given later) denoted by a $\hat{}$, which transform an ordinary operator $A \in \mathcal{U}$ into some $B = \hat{R}A \in \mathcal{U}$. For the expansion of a superoperator $\hat{R}$ we have (suppressing I in all subsequent formulae)

$$\hat{R} = \sum_{mm'} \sum_{m_1 m_2} |mm')(mm'|\hat{R}|m_1 m_2)(m_1 m_2| \tag{A3}$$

The matrix elements of $\hat{R}$ are characterized by four indices. A special example of such a tetradic is the well-known Liouville operator $L \equiv \hat{\mathcal{H}}$ defined, for a given Hamiltonian $\mathcal{H}$, by

$$\hat{\mathcal{H}}A = [\mathcal{H},A] \quad \text{for arbitrary} \quad A \in \mathcal{U} \tag{A4}$$

with matrix elements given by

$$(mm'|\hat{\mathcal{H}}|m_1 m_2) = \langle m|\mathcal{H}|m_1\rangle \ \delta_{m'm_2} - \langle m_2|\mathcal{H}|m'\rangle \ \delta_{mm_1} \tag{A5}$$

The physical significance of this special superoperator $\hat{\mathcal{H}}$ becomes clear if we choose the eigenbasis, say $\{|a\rangle, |b\rangle, \ldots\}$ of $\mathcal{H}$ for our matrix representation. Equation (A5) may then be written as an eigenvalue equation

$$\hat{\mathcal{H}}\|a\rangle\langle b|) \equiv \hat{\mathcal{H}}|ab) = (E_a - E_b)|ab) \ , \tag{A6}$$

i.e., the operator $|ab)$ is an eigenoperator of $\hat{\mathcal{H}}$ belonging to the physically observable beat frequencies $\omega_{ab} \equiv \hbar^{-1}(E_a - E_b)$ as eigenvalues. We obtain a different eigenoperator $|ba)$, corresponding to $\omega_{ba} = -\omega_{ab}$, by Liouville conjugation $|ba) = C_L|ab)$ (with $C_L^{-1} = C_L$), as pointed out by Ben-Reuven.[28]

In addition to (A2) and (A3) we mention the multiplication laws for a superoperator $\hat{R}$ with an ordinary operator A and for two superoperators $\hat{R}$ and $\hat{S}$:

$$(mm'|\hat{R}A) \equiv \langle m|\hat{R}A|m'\rangle = \sum_{m_1 m_2} (mm'|\hat{R}|m_1 m_2)\langle m_1|A|m_2\rangle \tag{A7}$$

$$(mm'|\widetilde{\hat{R}\hat{S}}|\bar{m}\bar{\bar{m}}) = \sum_{m_1 m_2} (mm'|\hat{R}|m_1 m_2)(m_1 m_2|\hat{S}|\bar{m}\bar{\bar{m}}) \tag{A8}$$

So far we have used a very special system of orthonormal basis operators. The generalization to other complete sets of (not necessarily Hermitian) operators is discussed by Fano[16] and is based on the fact that the linear operators $A, B, \ldots$ in a unitary space $\mathcal{U}$ of dimension N span another unitary space $\mathcal{L}$ which can be metrized by defining a scalar product[29]

$$(A|B) = \mathrm{Tr}\,\{A^+B\} \quad \text{(spur metric)} \ . \tag{A9}$$

As mentioned above we use the notation $|A)$, $|B)$, ... to emphasize that these operators are considered to be elements of $\mathcal{L}$. Indeed, the Liouville space $\mathcal{L}$ is a unitary space, since it follows directly from (A9) that for arbitrary vectors $|A)$, $|B)$, $|C)$ and arbitrary complex numbers α,β the properties

$$(A|B)^* = (B|A) \tag{A10}$$

$$(\alpha A+\beta B|C) = \alpha^* (A|C) + \beta^* (B|C) \tag{A11}$$

$$(A|A) \geq 0 \ , \quad \text{if} \quad (A|A) = 0 \quad \text{then} \quad A = 0 \tag{A12}$$

hold. We notice that according to (A9) the special scalar products $(mm'|A)$ and $(A|mm')$ are unambiguously associated to the ordinary matrix elements of the operator A with respect to the basis $\{|m\rangle\}$

$$(mm'|A) = \mathrm{Tr}\ \{(|m\rangle\langle m'|)^+ A\} = \mathrm{Tr}\ \{|m'\rangle\langle m|A\} = \langle m|A|m'\rangle \tag{A13}$$

and

$$(A|mm') = (mm'|A)^* = \langle m'|A^+|m\rangle = \langle m|A|m'\rangle^* \ . \tag{A14}$$

We introduce superoperators $\hat{R}$, $\hat{S}$, ... in $\mathcal{L}$ so that

$$\hat{R}|A) = |\hat{R}A) \quad \text{id defined for all} \quad A \in \mathcal{U}$$

and that

$$\hat{R}|A) = |\hat{R}A) \in \mathcal{L} \qquad \text{or} \quad \hat{R}A \in \mathcal{U} \quad \text{for all} \quad A \in \mathcal{U} \ .$$

They are linear operators if for arbitrary complex numbers

$$\hat{R}\{|\alpha A) + |\beta B)\} = \alpha|\hat{R}A) + \beta|\hat{R}B) \quad .$$

With the help of (A9) we define the adjoint $\hat{R}^+$ of the superoperator $\hat{R}$ by the relation

$$(A|\hat{R}B) = (\hat{R}^+A|B) \quad . \tag{A15}$$

The adjoint of a product of superoperators is, according to

$$(A|\hat{R}\hat{S}B) = (\hat{R}^+A|\hat{S}B) = (\hat{S}^+\hat{R}^+A|B) = ((\hat{R}\hat{S})^+A|B)$$

$$(\hat{R}\hat{S})^+ = \hat{S}^+\hat{R}^+ \quad . \tag{A16}$$

The Liouville operator $\hat{\mathcal{H}}$ is Hermitian if $\mathcal{H}$ is Hermitian. This follows immediately from (A15) which for arbitrary A leads to

$$\hat{\mathcal{H}}^+|A) = |[\mathcal{H}^+,A]) \quad .$$

By (A15) Hermitian $(\hat{R}^+ = \hat{R})$ and unitary superoperators $(\hat{R}^+\hat{R} = \hat{R}\hat{R}^+ = \hat{1})$ are defined.

Expansion in Multipole Operators

The theory of extranuclear perturbations on angular correlations can be formulated within a finite-dimensional unitary vector space; therefore, the mathematical tools discussed above may be applied. The dimension of $\mathcal{U}$ is determined by the spin I of the intermediate nuclear state. It is reasonable to perform all calculations in the same representation in which the final expression for the angular correlation is usually given. In the present paper we therefore use as an appropriate set of basis operators the normalized spherical tensor operators $U_q^{(k)}$ which have the real matrix elements

$$(ImIm'|U_q^{(k)}) \equiv \langle Im|U_q^{(k)}|Im'\rangle = (-1)^{I-m}\sqrt{2k+1}\begin{pmatrix} I & k & I \\ -m & q & m' \end{pmatrix} . \quad \text{(A17)}$$

The index k takes all integral values up to $k = 2I$; q is restricted to $-k \leq q \leq +k$. Including the normalized unit operator $U_0^{(0)} = (2I+1)^{-1/2} \cdot 1$ we have $N^2 = (2I+1)^2$ different operators $U_q^{(k)}$ in $\mathcal{U}$.

To point out the connection with both the first part of this appendix and the notation used by Fano, we interpret the multipole operators as elements of the Liouville space $\mathcal{L}$, denoted by $|U_q^{(k)})$. Then the orthonormality relation reads

$$(U_q^{(k)}|U_{q'}^{(k')}) = \mathrm{Tr}\,\{U_q^{(k)+}\,U_{q'}^{(k')}\} = \delta_{kk'}\;\delta_{qq'} \quad \text{(A18)}$$

and the completeness of the basis $\{|U_q^{(k)})\}$ in $\mathcal{L}$ is expressed by

$$\sum_{kq} |U_q^{(k)})(U_q^{(k)}| = \hat{1} \quad . \tag{A19}$$

The condition (A18) implies that

$$(U_0^{(0)}|U_q^{(k)}) = \mathrm{Tr}\,\{U_q^{(k)}\} = 0 \quad \text{for} \quad k,\, q \neq 0 \quad . \tag{A20}$$

The expansion theorem for an arbitrary operator $A \in \mathcal{U}$ and a superoperator $\hat{R} \in \mathcal{L}$ is simply

$$|A) = \sum_{kq} |U_q^{(k)})(U_q^{(k)}|A) \tag{A21}$$

$$\hat{R} = \sum_{kq} \sum_{k'q'} |U_q^{(k)})(U_q^{(k)})|\hat{R}|U_{q'}^{(k')})(U_{q'}^{(k')}| \quad . \tag{A22}$$

Of special interest are the Liouville operators $\hat{U}_q^{(k)}$ associated to the multipole operators by the definition (A4). The commutator of two multipole superoperators can be reduced to the known result for the commutator of the associate $U_q^{(k)}$'s. This follows from

$$\hat{U}_q^{(k)}\,\hat{U}_{q'}^{(k')}\,A = [U_q^{(k)},[U_{q'}^{(k')}, A]] = [[U_q^{(k)}, U_{q'}^{(k')}], A]$$

$$+ [U_{q'}^{(k')}, [U_q^{(k)}, A]] = \widehat{[U_q^{(k)}, U_{q'}^{(k')}]}\,A$$

$$+ \hat{U}_{q'}^{(k')}\,\hat{U}_q^{(k)}\,A$$

$$\left[\hat{U}_{q_1}^{(k_1)}, \hat{U}_{q_2}^{(k_2)}\right] = \widehat{\left[U_{q_1}^{(k_1)}, U_{q_2}^{(k_2)}\right]} = \sum_{k_3 q_3} c_{q_1 q_2 q_3}^{k_1 k_2 k_3} \hat{U}_{q_3}^{(k_3)} \tag{A23}$$

using the fact that $\left[U_{q_1}^{(k_1)}, U_{q_2}^{(k_2)}\right]$ itself can be expanded into a sum of basis operators. The definition of the expansion coefficients (structure constants) is given by

$$c_{q_1 q_2 q_3}^{k_1 k_2 k_3} = \left(U_{q_3}^{(k_3)} \middle| \hat{U}_{q_1}^{(k_1)} \middle| U_{q_2}^{(k_2)} \right) = \left(U_{q_3}^{(k_3)} \middle| \left[U_{q_1}^{(k_1)}, U_{q_2}^{(k_2)}\right] \right)$$

$$= \mathrm{Tr} \left\{ U_{q_3}^{(k_3)+} \left[U_{q_1}^{(k_1)}, U_{q_2}^{(k_2)}\right] \right\}$$

$$= (-1)^{2I-q_3} \left\{ (-1)^{k_1+k_2+k_3} - 1 \right\} \sqrt{(2k_1+1)(2k_2+1)(2k_3+1)}$$

$$\begin{Bmatrix} k_1 & k_2 & k_3 \\ I & I & I \end{Bmatrix} \begin{pmatrix} k_1 & k_2 & k_3 \\ q_1 & q_2 & -q_3 \end{pmatrix} . \tag{A24}$$

The explicit expression for the structure constants in terms of certain products of 3-j and 6-j symbols has been taken from Judd.[30] In a sketch of the theory of continuous groups Judd also mentions that the tensor operators $U_q^{(k)}$ $(-k \leq q \leq k,\ 1 \leq k \leq 2I)$ can be regarded as infinitesimal operators of the unimodular group in $2I+1$ dimensions, SU_{2I+1}. For this reason we also use the name structure constants for the expansion coefficients. With Racah's definition of the adjoint spherical tensor operator

$$U_q^{(k)+} = (-1)^q \, U_{-q}^{(k)} \tag{A25}$$

and the properties of the trace, several symmetry relations can be established. For example, for fixed position of the first pair of indices,

$$c^{k_1k_2k_3}_{q_1q_2q_3} = \underset{(+)}{-} \, c^{k_1k_2k_3}_{-q_1-q_2-q_3} = (-1)^{q_1} \, c^{k_1k_3k_2}_{-q_1q_3q_2} = \underset{(+)}{-} \, (-1)^{q_1} \, c^{k_1k_3k_2}_{q_1-q_3-q_2} \tag{A26}$$

or, for the permutation of the first two columns and cyclic permutations of columns

$$c^{k_1k_2k_3}_{q_1q_2q_3} = \underset{(+)}{-} \, c^{k_2k_1k_3}_{q_2q_1q_3} = (-1)^{q_1+q_3} \, c^{k_2k_3k_1}_{q_2-q_3-q_1} \quad . \tag{A27}$$

When two signs are given, the upper one has to be taken. The lower signs in parenthesis apply when the c coefficients are replaced by the d coefficients defined in Section V, Eq. (58). The structure constants play a central role not only in the theory of continuous groups but also in practical calculations utilizing the expansion in multipole operators. For some special cases we have given the explicit expressions for the c's. R. Melhorn has written a computer program to calculate (in both decimal and prime factor notation) all structure constants important in the theory of perturbed angular correlation and related problems. The transformation theory of vectors in the Liouville space can be formulated in complete analogy to the ordinary transformation theory of quantum mechanics. Here, we mention only a special case. The change between the state multipole representation $\{|U_q^{(k)})\}$ and the standard representation $\{|ImIm')\}$

follows from (A2) and (A21) by substituting for the arbitrary operator $|A)$ the tensor operator $|U_q^{(k)})$ or the basis operator $|ImIm')$, respectively. This yields

$$|U_q^{(k)}) = \sum_{mm'} |ImIm')(ImIm'|U_q^{(k)}) \tag{A28}$$

$$|ImIm') = \sum_{kq} |U_q^{(k)})(U_q^{(k)}|ImIm') \tag{A29}$$

the elements of the transformation matrix being given by (A17).

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