Stochastic theory of line shape. I. Nonsecular effects in the strong-collision model*

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Starting from a general stochastic-theory result in which the Hamiltonian is taken to jump at random between a number of forms, due, for example, to spin-spin or spin-lattice relaxation, we treat a model for the matrix which describes the relaxation process. In this, it is assumed that the probability of jump of the Hamiltonian from one state to another does not depend on the initial state. This simplifies calculations considerably and the result can be used to study some physical cases. A specialization of this model yields a simple closed-form expression for the line shape which is quite useful in experimental situations.

I. INTRODUCTION

In the stochastic theory of line shape, [1] the radiating system is assumed surrounded by a large heat bath whose effect is to produce explicitly time-dependent interactions at the radiating system. From the point of view of the radiating system, it sees a Hamiltonian which is a random function of time. Thus one constructs an appropriate stochastic-model Hamiltonian which contains all the physical features of the surroundings. The random nature of this Hamiltonian then replaces the interaction terms present in the total Hamiltonian, and in the expression for the line shape the average over the heat bath is replaced by an average over the stochastic variables.

Such a theory of line shape has been given[2] for systems in which the Hamiltonian jumps, as a result of fluctuations like spin-spin or spin-lattice relaxation, between a number of possible forms $V_1, V_2, \cdots, V_n$. The stochastic modulation is assumed to be governed by a stationary Markov process, and the central result is contained in the Laplace transform $U(p)$ of the time-development superoperator which is obtained as

$$U(p)=\left(p1-W-i\sum_j V_j^\times F_j\right)^{-1}, \tag{1}$$

where, in the case of Mössbauer line shape, for example, for the emission of a photon of frequency ω, $p=-i\omega+\frac{1}{2}\Gamma$, with Γ the natural linewidth of the nuclear excited state, W is a stochastic matrix whose off-diagonal element $(a|W|b)$ is equal to the probability per unit time that the Hamiltonian makes a jump from the stochastic state a to the state b, $V_j^\times$ is the Liouville operator corresponding to V_j, the jth form of the Hamiltonian for the radiating system, and F_j is a stochastic matrix defined by

$$(a|F_j|b)=\delta_{ab}\,\delta_{aj}\,. \tag{2}$$

In the stochastic-theory calculation, one eliminates the degrees of freedom for the heat bath by performing an average of $U(p)$ over the stochastic variables

$$\overline{U}(p)=\sum_{ab} p_a(a|U(p)|b)\,, \tag{3}$$

where p_a is the *a priori* probability of the occurrence of the initial stochastic state a. The meaning of the matrix F_j, defined by Eq. (2), becomes clear if we consider the case of no fluctuation at all, viz., $W=0$. In that case, $\overline{U}(p)$ reduces to

$$\overline{U}^0(p)=\sum_a p_a(p1-iV_a^\times)^{-1}\,, \tag{4}$$

the static result, as expected. A knowledge of $\overline{U}(p)$ is required[2] in the case of perturbed angular correlation of γ rays, Mössbauer, magnetic resonance, and other line-shape problems.

In this paper, we make a special assumption on the form of the matrix W which gives the probability of transition of the Hamiltonian from one form to another. We assume that this probability does not depend on the initial state from which the Hamiltonian makes a jump. This means that the new state to which the Hamiltonian jumps is completely uncorrelated to the old state; so we refer to this as a random phase approximation. This, in some cases, [3] is also known as the strong-collision approximation. This assumption enables us to simplify the mathematics considerably and gives us more tractable expressions for the line shape. While our assumption, in some circumstances, may be quite unphysical, it does apply, for example, to some cases of Mössbauer spectra[4] and perturbed angular correlation[5] of γ rays in randomly varying electric field gradients. We shall, in the following paper, illustrate the applicability of the model by treating in detail an electron-paramagnetic-resonance (EPR) experiment[6] on CO_2^- defects in calcite ($CaCO_3$). Even in cases where the result is not strictly applicable, it can still give a qualitative understanding of the changes of line shape with the relaxation rate and serve as an interpolation formula from short to long relaxation times. The regimes of short and long relaxation times are treated by perturbation calculations and the results are discussed physically.

In Sec. V we consider the line-shape problem in a special case of the random-phase-approximation (RPA) model. We assume that the nucleus (in the case of perturbed angular correlations or Mössbauer line shape) finds itself in randomly fluctuating field gradients or magnetic fields where the fields can jump, due to relaxation of surroundings, to all possible directions in space. This assumption of isotropy yields a simple closed-form expression for the line shape.

II. MATHEMATICAL SOLUTION FOR THE RPA MODEL

We consider a process in which the jump of the Hamiltonian from one stochastic state a to another b completely changes the environment. If this be the case, we may assume that the probability of jump from a to b is independent of a and is proportional to p_b, the occupational probability for the state b. So, for the off-diagonal element of the matrix W in Eq. (1), we set

$$W_{ab} = \lambda p_b , \quad a \neq b \tag{5}$$

where λ is a measure of the probability per unit time of a transition from a given stochastic state; λ is the inverse of the average time between two successive jumps.

Now,[2]

$$W_{aa} = -\sum_{b\neq a} W_{ab} ,$$

so that from Eq. (5)

$$W_{aa} = -\lambda + \lambda p_a ,$$

since

$$\sum_b p_b = 1 . \tag{6}$$

Combining Eqs. (5) and (6), we can write W as

$$W = \lambda(\mathcal{T} - 1) , \tag{7}$$

where

$$\mathcal{T}_{ab} = p_b . \tag{8}$$

Evidently, for such a form of W, the principle of detailed balance holds for the transitions

$$p_a W_{ab} = p_b W_{ba} , \tag{9}$$

as is required for a stationary Markov process. This form of the transition matrix was considered previously by Anderson[7] and Kubo[8] in their theories, for which the different forms of the Hamiltonian $V_1, V_2, \ldots V_n$ were taken to commute with each other.

Using the operator identity

$$\frac{1}{A} = \frac{1}{B} + \frac{1}{B}(B - A)\frac{1}{A} , \tag{10}$$

we have, from Eqs. (1) and (7),

$$U(p) = U^0(p+\lambda) + \lambda U^0(p+\lambda)\mathcal{T}U(p) , \tag{11}$$

where

$$U^0(p+\lambda) = \left((p+\lambda)1 - i\sum_j V_j^{\times} F_j\right)^{-1} . \tag{12}$$

From Eqs. (3) and (11) and using the form of the $\mathcal{T}$ matrix given in Eq. (8), we obtain the result

$$\overline{U}(p) = \overline{U}^0(p+\lambda)/[1 - \lambda\overline{U}^0(p+\lambda)] , \tag{13}$$

where

$$\overline{U}^0(p+\lambda) = \sum_{ab} p_a (a|\, U^0(p+\lambda)\,|b)$$

$$= \sum_j p_j [(p+\lambda)1 - iV_j^{\times}]^{-1} , \tag{14}$$

from Eq. (4). $\overline{U}^0(p)$ is the form of $\overline{U}(p)$ in the absence of fluctuations. The result (13) clearly holds also in the high-temperature case when the jump to all stochastic states is equally probable,[4,5] i.e., in Eq. (8), $\mathcal{T}_{ab} = 1/n$. Then Eq. (14) becomes

$$\overline{U}^0(p+\lambda) = \frac{1}{n}\sum_j [(p+\lambda)1 - iV_j^{\times}]^{-1} . \tag{15}$$

III. DISCUSSIONS

In Eq. (13), $\overline{U}(p)$ is expressed entirely in terms of $\overline{U}^0(p+\lambda)$ given by Eq. (14). This simplifies the problem considerably, since we get rid of the stochastic indices in the expression for the line shape. Normally, the solution to the line-shape problem involves the inversion or diagonalization of a matrix given by Eq. (1), which is labeled by both quantum mechanical and stochastic indices. For example, in a Mössbauer experiment, the matrix to be inverted is of dimension $(2I_1+1)(2I_0+1)n$, where I_1 is the spin of the nucleus in the excited state, I_0 the spin in the ground state, and n is the number of different forms of the Hamiltonian.[2] By the above procedure, however, the dimension of the matrix is reduced to $(2I_1+1)(2I_0+1)$, however large n may be.

In the above theory, we replaced the influence of the surroundings on the nucleus by an effective field, so that the nuclear system alone was treated quantum mechanically. However, the expression (13) is also valid in situations where the entire nucleus-electron system has to be treated quantum-mechanically.[9] In that case, the average over the stochastic variables in Eq. (3) has to be replaced by an average over the quantum mechanical states of the electronic system.

IV. PERTURBATION-THEORY CALCULATIONS

We can write

$$V_j^\times = \overline{V}^\times + \Delta_j^\times , \tag{16}$$

where we define $\overline{V}^\times$ by

$$\overline{V}^\times = \sum_j p_j V_j^\times . \tag{17}$$

Thus $\overline{V}^\times$ is the Liouville operator corresponding to the average Hamiltonian $\overline{V}$. It also follows from Eqs. (16) and (17) that

$$\sum_j P_j \Delta_j^\times = 0 . \tag{18}$$

In the following sections, we evaluate Eq. (13) by perturbation theory in different regimes of relative strengths of λ, $\overline{V}^\times$ and $\Delta_j^\times$.

A. Very slow relaxation: $\lambda \ll V_j^\times$

We have, from Eqs. (13) and (15)

$$\overline{U}(p) = \sum_j p_j [(p+\lambda)1 - iV_j^\times]^{-1} \times \left(1 - \lambda \sum_k p_k [(p+\lambda)1 - iV_k^\times]^{-1}\right)^{-1} . \tag{19}$$

To understand the structure of the spectral lines predicted by Eq. (19), we assume that $[V_j, V_k] = 0$. Then we can diagonalize any one of $V_1, V_2, \ldots, V_n$, and the others can be made diagonal simultaneously. In that case, the eigenvalue of the Liouville operator $V_j^\times$ just yields the corresponding frequency[2] ω_j, so that we have

$$\begin{aligned}\overline{U}(p) &= \sum_j p_j \left((p+\lambda) - i\omega_j - \lambda \times \sum_k p_k \frac{(p+\lambda) - i\omega_j}{(p+\lambda) - i\omega_k}\right)^{-1} \\ &= \sum_j p_j \left((p+\lambda) - i\omega_j - \lambda p_j - \lambda \sum_k{}' p_k \frac{(p+\lambda) - i\omega_j}{(p+\lambda) - i\omega_k}\right)^{-1} ,\end{aligned} \tag{20}$$

where the prime means that the term $k = j$ has been omitted from the summation.

Since there is a resonance near $p = i\omega_j + \lambda p_j - \lambda$, we obtain, by the method of successive approximations, from Eq. (20)

$$\overline{U}(p) \approx \sum_j p_j \left(p + \lambda - i\omega_j - \lambda p_j + i\lambda^2 \sum_k{}' \frac{p_j p_k}{\omega_j - \omega_k}\right)^{-1} , \tag{21}$$

since λp_j is very small. In a resonance experiment $(p = i\omega)$, for example, Eq. (21) predicts n sharp lines centered around $\omega_j - \lambda^2 \sum_k' (\omega_j - \omega_k)^{-1} p_j p_k$ and broadened by an amount equal to $\lambda - \lambda p_j$. The result (21) is identical with the one derived by Anderson.[7]

The physical consequences of Eq. (21) are illustrated by a simple example. We consider an NMR experiment in which the nucleus finds itself in a fluctuating environment, so that the effective field jumps between a number of different values $h_1, h_2, \ldots, h_n$. At any given instant, the nucleus will find itself in a field h_1, say, and its magnetic moment will start to precess around this field with the Larmor frequency corresponding to h_1. But now, since the jump rate is very slow, a resonance emission or absorption will occur before the field has any chance to jump to a different value. However, there will always be $n-1$ other groups of nuclei which will find their respective fields to be $h_2, h_3, \ldots, h_n$, so that in this case we expect to observe a series of spectral lines centered around $\omega_1, \omega_2, \ldots, \omega_n$ as predicted by Eq. (21).

B. Intermediate case of relaxation: $\lambda \gg \Delta_j^\times$, $\lambda \sim \overline{V}^\times$

From Eqs. (13), (15), and (16),

$$\overline{U}(p) = \{[\overline{U}^0(p+\lambda)]^{-1} - \lambda\}^{-1} , \tag{22}$$

where

$$\begin{aligned}[\overline{U}^0(p+\lambda)]^{-1} &= \left(\sum_j p_j [(p+\lambda)1 - i\overline{V}^\times - i\Delta_j^\times]^{-1}\right)^{-1} \\ &\approx \left[\left(1 - \sum_j p_j (p+\lambda - i\overline{V}^\times)^{-1} \Delta_j^\times \times (p+\lambda - i\overline{V}^\times)^{-1}\Delta_j^\times\right)(p+\lambda - i\overline{V}^\times)^{-1}\right]^{-1} ,\end{aligned}$$

using Eq. (18) and the fact that $\sum_j p_j = 1$;

$$[\overline{U}^0(p+\lambda)]^{-1} \approx p + \lambda - i\overline{V}^\times + \sum_j p_j \Delta_j^\times (p+\lambda - i\overline{V}^\times)^{-1} \Delta_j^\times .$$

Therefore, from Eq. (22),

$$\overline{U}(p) \approx \left[p - i\overline{V}^\times + \sum_j p_j \Delta_j^\times (p+\lambda - i\overline{V}^\times)^{-1}\Delta_j^\times\right]^{-1} . \tag{23}$$

Since $[\overline{V}, \Delta_j] \neq 0$, in general, the third term inside the parentheses in Eq. (23) will exhibit important nonsecular effects.

C. Very fast relaxation: $\lambda \gg V_j^\times$

We have

$$[\overline{U}^0(p+\lambda)]^{-1} = \left(\sum_j p_j [(p+\lambda)1 - iV_j^\times]^{-1}\right)^{-1}$$

$$\approx (p+\lambda)\left[1+\frac{i\bar{V}^{\times}}{p+\lambda}-\frac{(\bar{V}^{\times})^2}{(p+\lambda)^2}-\sum_j p_j\left(\frac{\Delta_j^{\times}}{p+\lambda}\right)^2\right]^{-1},$$

from Eqs. (16)–(18),

$$[\bar{U}^0(p+\lambda)]^{-1}\approx (p+\lambda)\left[1-\frac{i\bar{V}^{\times}}{p+\lambda}+\sum_j p_j\left(\frac{\Delta_j^{\times}}{p+\lambda}\right)^2\right]. \tag{24}$$

From Eq. (22),

$$\bar{U}(p)\approx\left(p-i\bar{V}^{\times}+\sum_j\frac{p_j(\Delta_j^{\times})^2}{p+\lambda}\right)^{-1}. \tag{25}$$

If $[\bar{V},\ \Delta_j]=0$, the above leads to

$$\bar{U}(p)\approx\left(p-i\bar{\omega}+\sum_j p_j\,\frac{(\Delta\omega_j)^2}{p+\lambda}\right)^{-1}. \tag{26}$$

In this case, the physical picture is the following: The nucleus, at any instant, finds itself, say, in a magnetic field h_1. Its magnetic moment starts to precess around this field, but, since the jump rate is very fast, it can scarcely precess at all before the field jumps to a new value. Thus the magnetic moment of the nucleus cannot follow such a rapid relaxation of the field, and therefore, in effect, it sees an average field $\bar{h}$, so that we get a single line centered around the average Larmor frequency $\bar{\omega}$, as observed from Eq. (26). The term

$$\sum_j p_j\,\frac{(\Delta\omega_j)^2}{p+\lambda}$$

causes broadening which is inversely proportional to λ. Therefore, as the relaxation rate λ gets faster and faster, the line gets narrower and narrower. This is the so-called motional-narrowing effect.[10]

In the case worked out by Anderson,[7] he had $\bar{\omega}=0$, $\Delta\omega_j=(2j-1-n)\,\omega_0$, $p_j=1/n$, $j=1,2,\ldots n$, and $\lambda=n\omega_e/(n-1)$, in his notation. Then in Eq. (26),

$$\bar{U}(p)\approx\left(p+\frac{1}{n}\sum_j\frac{(\Delta\omega_j)^2}{\lambda}\right)^{-1}, \tag{27}$$

since there is a resonance near $p=0$. Therefore the width is given by

$$B=\frac{1}{n}\sum_j\frac{(\Delta\omega_j)^2}{\lambda}=\frac{(n-1)\,\omega_0^2}{n^2\omega_e}\sum_{j=1}^{n}\,[4j^2-4j(n+1)+(n+1)^2]\,,$$

from above,

$$B=\frac{(n-1)^2(n+1)}{3n}\ \frac{\omega_0^2}{\omega_e}\,, \tag{28}$$

the result obtained by Anderson.

It is clear from the above discussion that the results obtained in our theory in the two extreme cases of very slow and very fast relaxation are not qualitatively different from those obtained in the secular theories. However, the intermediate case of relaxation has important nonsecular features which will be examined in detail in the following paper.

V. SPECIALIZATION OF THE RPA MODEL–THE ISOTROPIC CASE

In our central RPA results in Eqs. (13) and (15), n is the number of different forms of the stochastic effective field at the position of the radiating system. We now consider a case where the effective field is constant in magnitude, but can point in any direction in space. Hence, in this limit, we can replace Eq. (15) by

$$\bar{U}^0(p+\lambda)=\frac{1}{4\pi}\int\left(\frac{d\Omega_l}{(p+\lambda)1-iV_l^{\times}}\right), \tag{29}$$

the integration being carried over the solid angle $d\Omega_l$ defined by the direction $\vec{l}$. This model represents some cases of isotropic-magnetic-hyperfine and quadrupole interactions in free atoms undergoing collisions,[11] domain wall motion in ferromagnetic materials due to an applied radio-frequency field,[12] and relaxation effects due to thermal excitations in superparamagnets,[13] among others. We treat this isotropic model to obtain a simple expression for the Mössbauer line shape, valid for all relaxation rates.

The Mössbauer line shape is given by[2]

$$F(p)=\mathrm{Re}(2I_1+1)^{-1}\sum_{\substack{m_0m_1\\ m_0'm_1'}}\langle I_1m_1|A^{\dagger}|I_0m_0\rangle\times\langle I_0m_0'|A|I_1m_1'\rangle(I_0m_0I_1m_1|\bar{U}(p)|I_0m_0'I_1m_1')\,, \tag{30}$$

where $\bar{U}(p)$ is given by Eqs. (1) and (3), with $p=-i\omega+\frac{1}{2}\Gamma$, A is the interaction between the nucleus and the electromagnetic field for the emission of a photon in the direction $\vec{k}$, I_1 is the spin of the excited state of the nucleus, and I_0 that of the ground state. In Eq. (30), it is assumed that the temperature is high enough for the nuclear levels to be equally populated.

We have[14]

$$\langle I_0m_0'|A|I_1m_1'\rangle=2\pi\left(\frac{\hbar c}{Vk}\right)^{1/2}\sum_{L'M'}i^{L'}(2L'+1)^{1/2}D^{(L')}_{M'P}(\phi\theta 0)\times(M_{L'}+iPE_{L'})\,C(I_1L'I_0;m_1'M'm_0')\,, \tag{31}$$

where V is the volume in which the electromagnetic field is normalized, $P=\pm1$, where $P=1$ corresponds to left circular polarization while $P=-1$ corresponds to right circular polarization, the angles θ and ϕ in the rotation $D^{(L)}_{MP}(\phi\theta 0)$ are, respectively, the polar and azimuthal angles of the direction $\vec{k}$ of the propagation of the γ ray, M_L and E_L represent the strengths of the magnetic and electric 2^L poles, respectively, and the C's are the Clebsch-Gordan coefficients. (If time reversal is conserved either M_L or E_L will vanish for a given L.)

Expressing the Clebsch-Gordan coefficients in terms of the $3j$ symbols[15] and substituting Eq. (31) into Eq. (30), we obtain

$$F(p)=\mathrm{Re}\,\frac{4\pi^2\hbar c}{Vk}\sum_{LML'M'P}(-1)^{(L-L')/2}\times D_{MP}^{(L)*}(\phi\theta 0)\,D_{M'P}^{(L')}(\phi\theta 0)(M_L+iPE_L)\times(M_{L'}+iPE_{L'})^*\,\frac{2I_0+1}{2I_1+1}\,G_{LL'}^{MM'}(p)\,, \tag{32}$$

where, in analogy with the case of perturbed angular correlations of γ rays,[16] we define a perturbation factor

$$G_{LL'}^{MM'}(p)=\sum_{m_1m_1'}(-1)^{2I_0+m_0+m_0'}\,[(2L+1)(2L'+1)]^{1/2}\times\begin{pmatrix}I_1 & I_0 & L\\ m_1 & -m_0 & M\end{pmatrix}\begin{pmatrix}I_1 & I_0 & L'\\ m_1' & -m_0' & M'\end{pmatrix}\times(I_0m_0I_1m_1|\,\overline{U}(p)\,|I_0m_0'I_1m_1')\,. \tag{33}$$

The polarization P is not usually observed and is consequently summed over in Eq. (32).

A. Mathematical results

We show, in Appendix A, that the isotropy expressed by Eq. (29) enables one to write down for the superoperator $\overline{U}^0$,

$$\mathfrak{D}\,\overline{U}^0\,\mathfrak{D}^{-1}=\overline{U}^0\,, \tag{34}$$

and, therefore, from Eq. (13),

$$\mathfrak{D}\,\overline{U}\,\mathfrak{D}^{-1}=\overline{U}\,, \tag{35}$$

where $\mathfrak{D}$ is any super rotation operator defined in Appendix A.

By making use of Eq. (35), we prove, in Appendix B, that the perturbation factor in Eq. (33) can be written as

$$G_{LL'}^{MM'}(p)=1/(2L+1)\,G_{LL}^{MM}(p)\,\delta_{LL'}\,\delta_{MM'}\,, \tag{36}$$

where

$$G_{LL}^{MM}(p)=(2L+1)\sum_{\substack{m_0m_1\\ m_0'm_1'}}(-1)^{2I_0+m_0+m_0'}\times\begin{pmatrix}I_1 & I_0 & L\\ m_1 & -m_0 & M\end{pmatrix}\begin{pmatrix}I_1 & I_0 & L\\ m_1' & -m_0' & M\end{pmatrix}\times(I_0m_0I_1m_1|\,\overline{U}(p)\,|I_0m_0'I_1m_1')\,. \tag{37}$$

Writing $\overline{U}(p)$ in Eq. (13) in a power series,

$$\overline{U}(p)=\overline{U}^0(p+\lambda)+\lambda[\overline{U}^0(p+\lambda)]^2+\cdots\,, \tag{38}$$

and substituting in Eq. (37), the first term in the expansion just yields the perturbation factor in absence of fluctuation,

$$G_{LL}^{0\,MM}(p+\lambda)\equiv G_{LL}^0(p+\lambda)=\sum_{n_0n_1}\left[\begin{pmatrix}I_1 & I_0 & L\\ n_1 & -n_0 & M\end{pmatrix}^2\Big/\left[(p+\lambda)+i(V_{n_1}-V_{n_0})\right]\right]\,. \tag{39}$$

This is shown in Appendix C. In Eq. (39), n_0 refers to the ground state of the nucleus, n_1 to the excited state.

We show next, in Appendix D, that the contributions from the rest of the terms in the expansion (38) can all be grouped together in a geometric series, which permits us finally to write down the perturbation factor in a simple closed form,

$$G_{LL}^{MM}(p)\equiv G_{LL}(p)=G_{LL}^0(p+\lambda)/[1-\lambda G_{LL}^0(p+\lambda)]\,, \tag{40}$$

where $G_{LL}^0(p+\lambda)$ is given by Eq. (39) above.

Substituting Eqs. (36) and (40) in Eq. (32) yields, for the Mössbauer line shape,

$$F(p)=\mathrm{Re}\,\frac{8\pi^2\hbar c}{Vk}\,\frac{2I_0+1}{2I_1+1}\times\sum_L\frac{|M_L|^2+|E_L|^2}{2L+1}\left(\frac{G_{LL}^0(p+\lambda)}{1-\lambda G_{LL}^0(p+\lambda)}\right)\,, \tag{41}$$

since $P=\pm1$ for circular polarizations.

The line shape as given by Eq. (41) is valid for all values of the relaxation rate λ and is independent of the angles θ and ϕ, as is expected in the isotropic case. A result identical to Eq. (40) was derived earlier,[11] from a different formalism, for the perturbed angular correlations in the presence of isotropic magnetic hyperfine and quadrupole interactions. There the relaxation was caused by atomic collisions, the effect of which was to make the direction of the effective field at the nucleus random after each collision.

In the following, we evaluate the perturbation factor from Eqs. (39) and (40) in the two cases of fluctuating electric field gradients and magnetic hyperfine fields.

1. *Fluctuating electric field gradients*

As a physical example, we consider the Mössbauer study by Ruby[17] on the ferrous ion in a liquid mixture of phosphoric acid and water ($H_3PO_4+H_2O$). Below the glass transition temperature T_g, a quadrupole doublet is found, but as the temperature is raised above T_g the quadrupole splitting decreases and the spectrum ultimately collapses to a singlet. This is interpreted as being due to the fact that the ferrous ion finds itself in randomly varying electric field gradients.

In Ruby's experiment, the direction of the field gradient can relax to any direction in space with equal probability. Therefore our results (39) and (40) are applicable with

$$V_n = Q[3n^2 - I(I+1)] , \tag{42}$$

where Q is the strength of quadrupole interaction.

Since, in Eq. (39), $I_1 = \frac{3}{2}$, $I_0 = \frac{1}{2}$, we obtain, after using[15] the values of the $3j$ symbols,

$$G^0_{LL}(p+\lambda) = (p+\lambda)/[(p+\lambda)^2 + 9Q^2] , \tag{43}$$

which exhibits two peaks centered around $p = \pm 3Q - \lambda$.

From Eq. (40), the Mössbauer line shape for any value of λ is obtained from

$$G_{LL}(p) = (p+\lambda)/[p(p+\lambda) + 9Q^2] , \tag{44}$$

which, as $\lambda \to \infty$, degenerates into a single line,

$$G_{LL}(p) \to 1/p . \tag{45}$$

Incidentally, Eq. (44) is identical to the result obtained by Tjon and Blume[4] for the Mössbauer line shape of a nucleus which finds itself in an electric field gradient that jumps at random between the x, y, and z axes with equal probability (since $\lambda = 3W$ and $9Q^2 = 3\alpha^2$ in that paper). This is understandable because that result is obtained for a powdered emitter, for which all directions of emission of the γ ray are averaged over. This, together with the additional symmetry of zero quadrupole splitting in the ground state of the Fe^{57} nucleus, leads to an expression identical to our result given by Eq. (44) in the isotropic case. Equation (44) was also used by Ruby to interpret his results for the broadening and collapsing of the two lines for ferrous ions in phosphoric acid.[17] The results are in good qualitative agreement with Eq. (44). From the shape of the spectra in the regime of slow relaxation ($\lambda \approx 0$) [cf., Eq. (43)], Ruby could deduce the strength of the electric field gradient. From a comparison of the observed spectra with Eq. (44), he could also determine the temperature variation of the relaxation rate λ for the direction of the field gradient.

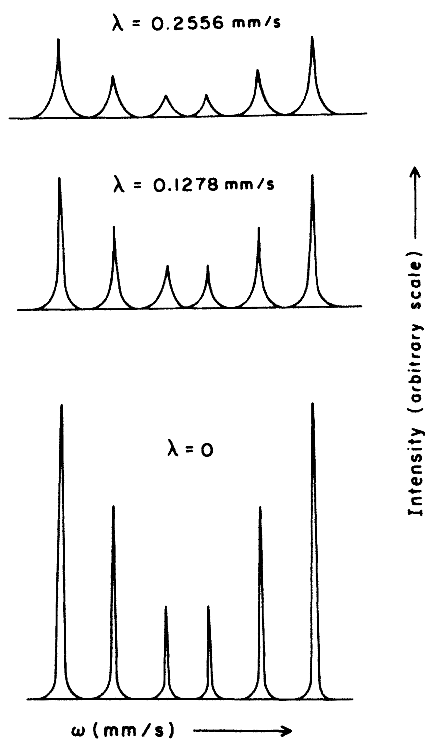

FIG. 1. Mössbauer line shape for an Fe^{57} nucleus in a fluctuating magnetic hyperfine field for different values of the relaxation rate λ in the regime of slow relaxation.

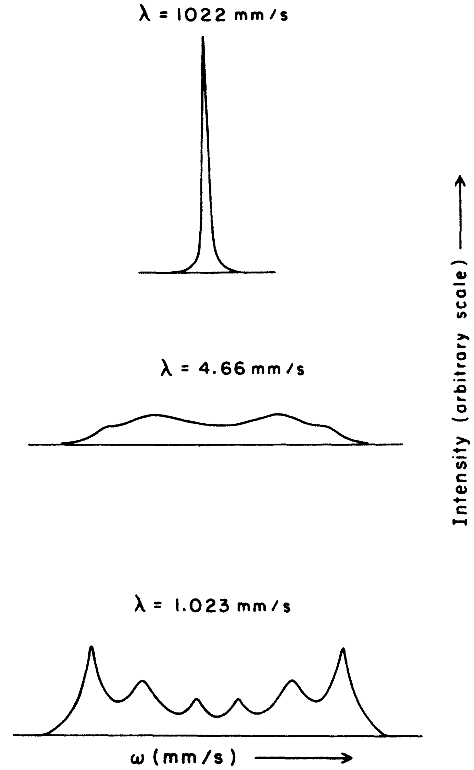

FIG. 2. Mössbauer line shape in the regime of rapid relaxation. In Figs. 1 and 2, we have used (Ref. 20) $\Gamma = 0.00714$ mm/sec, $g_0\mu_N h = -6.11$ mm/sec and $g_1\mu_N h = 3.45$ mm/sec.

2. Fluctuating magnetic hyperfine fields

We consider the case of an Fe^{57} nucleus ($I_1 = \frac{3}{2}$, $I_0 = \frac{1}{2}$, and $L = 1$, for magnetic dipolar transitions) in a magnetic field of constant magnitude h which relaxes among all possible directions in space. The energy difference in Eq. (39) is given by

$$V_{n_1} - V_{n_0} = (g_0 n_0 - g_1 n_1)\mu_N h , \tag{46}$$

where μ_N is the nuclear magneton and g_1 and g_0 are the respective g factors for the excited and ground states of the nucleus.

The results of our calculations for different values of the relaxation rate λ are shown in Figs. 1 and 2. For very slow fluctuations ($\lambda \approx 0$), the full six-line Zeeman pattern is obtained, as expected. On the other hand, when the fluctuation rate is very rapid ($\lambda \approx 1000$ mm/sec), the spectrum degenerates into a single line in the middle. This is because the nuclear moment cannot follow such a rapidly relaxing field, and it therefore experiences a zero hyperfine field. For intermediate values of the relaxation rate λ, the results are qualitatively similar to those found experimentally for Mössbauer lines where relaxation was casued by a rf field[12] or thermal agitation in superparamagnets.[13]

VI. SUMMARY

We have, in this paper, considered the stochastic theory of the line shape of radiation emitted by a system whose Hamiltonian jumps at random between a finite number of possibilities. The nonsecular effects arise from the fact that the different forms of the Hamiltonian do not commute with one another. The transition of the Hamiltonian from one stochastic state to the other has been assumed to be independent of the initial state, and this is what we have called a random phase or a strong collision approximation. This assumption enabled us to give a considerably simplified result for the line shape. The secular and nonsecular effects were illustrated by perturbation-theory calculation. The theory described here is of utility in analyzing perturbed angular correlation, Mössbauer, and magnetic resonance spectra. In the following paper we will discuss the application of our formalism to an EPR experiment on CO_2^- defects in calcite.

In Sec. V we discussed a special case of our RPA model where a complete isotropy was assumed in the nature of interaction of the radiating system with its surroundings. As an example, we obtained the Mössbauer line shape in this case. The result was seen to be useful in analyzing some experimental results.

APPENDIX A

We have, for the matrix elements of $\overline{U}^0(p)$,

$$(I_0 m_0 I_1 m_1 | \overline{U}^0(p) | I_0 m_0' I_1' m_1')$$

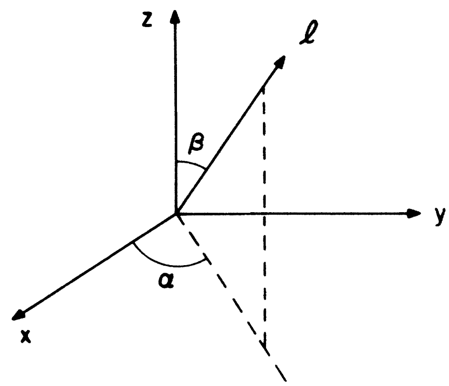

FIG. 3. Orientation of the direction l in terms of the Euler angles α and β. The z axis is taken as the axis of quantization.

$$= \frac{1}{4\pi} \int d\Omega_l \int_0^\infty dt\, e^{-pt} (I_0 m_0 I_1 m_1 | e^{iV_l^\times t} | I_0 m_0' I_1 m_1')$$

$$= \frac{1}{4\pi} \int d\Omega_l \int_0^\infty dt\, e^{-pt} \langle I_0 m_0 | e^{iV_l t} | I_0 m_0' \rangle \times \langle I_1 m_1' | e^{-iV_l t} | I_1 m_1 \rangle , \qquad (A1)$$

using the properties[2] of the Liouville operator.

Now, V_l is of the form $V = -\omega_L I_l$ for magnetic hyperfine interaction, and $V_l = Q(3I_l^2 - I^2)$ for electric quadrupole interaction, where ω_L is a Larmor frequency, Q is the strength of quadrupole interaction, and I_l is the component of the nuclear spin along the direction $\vec{l}$ (see Fig. 3).

Therefore we may write

$$V_l = D^{(I)}(\alpha\beta 0)\, V_z (D^{(I)})^{-1}(\alpha\beta 0) , \qquad (A2)$$

where V_z depends only on I_z, the z component of the nuclear spin and D is a rotation operator. Using Eq. (A2), we have, from Eq. (A1),

$$(I_0 m_0 I_1 m_1 | \overline{U}^0(p) | I_0 m_0' I_1 m_1') = \frac{1}{4\pi} \int d\Omega_l \int_0^\infty dt\, e^{-pt} \sum_{n_0 n_1} \exp[i(V_{n_0} - V_{n_1})t] \times (-1)^{-m_0 - m_0' + 2n_0} D^{*(I_1)}_{n_1 m_1'} D^{*(I_0)}_{-n_0 -m_0'} D^{(I_1)}_{n_1 m_1} D^{(I_0)}_{-n_0 -m_0} , \qquad (A3)$$

where we have used[18]

$$D^{(I)*}_{mn} = (-1)^{m-n} D^{(I)}_{-m-n} . \qquad (A4)$$

We write[15]

$$\frac{1}{4\pi} \int d\Omega_l D^{*(I_1)}_{n_1 m_1'} D^{*(I_0)}_{-n_0 -m_0'} D^{(I_1)}_{n_1 m_1} D^{(I_0)}_{-n_0 -m_0}$$

$$= \frac{1}{4\pi} \int_0^{2\pi} \int_0^{\pi} \sin\beta\, d\alpha\, d\beta \sum_{jmm'} (2j+1) D^{(j)}_{mm'}(\alpha\beta 0) \begin{pmatrix} I_1 & I_0 & j \\ m_1' & -m_0' & m' \end{pmatrix} \begin{pmatrix} I_1 & I_0 & j \\ n_1 & -n_0 & m \end{pmatrix}$$

$$\times \sum_{j' m_1' m_1} (2j'+1) D^{(j')*}_{m_1 m_1'}(\alpha\beta 0) \begin{pmatrix} I_1 & I_0 & j' \\ m_1 & -m_0 & m_1' \end{pmatrix} \begin{pmatrix} I_1 & I_0 & j' \\ n_1 & -n_0 & m_1 \end{pmatrix}$$

$$= \sum_{j m' m} (2j+1) \begin{pmatrix} I_1 & I_0 & j \\ m_1' & -m_0' & m' \end{pmatrix} \begin{pmatrix} I_1 & I_0 & j \\ m_1 & -m_0 & m' \end{pmatrix} \begin{pmatrix} I_1 & I_0 & j \\ n_1 & -n_0 & m \end{pmatrix}^2 , \tag{A5}$$

using the orthogonality of D matrices,

$$\frac{2j'+1}{4\pi} \int_0^{2\pi} \int_0^{\pi} \sin\beta\, d\alpha\, d\beta\, D^{(j)}_{m_1 m_1'}(\alpha\beta 0)\, D^{(j)}_{m m'}(\alpha\beta 0) = \delta_{m_1 m}\, \delta_{m_1' m'} . \tag{A6}$$

Substituting Eq. (A5) into Eq. (A3), we obtain

$$(I_0 m_0 I_1 m_1 | \overline{U}^0(p) | I_0 m_0' I_1 m_1')$$
$$= \sum_{n_0 n_1} \frac{(-1)^{-m_0 - m_0' + 2n_0}}{p - i(V_{n_0} - V_{n_1})} \sum_{jm} (2j+1) \begin{pmatrix} I_1 & I_0 & j \\ m_1' & -m_0' & M' \end{pmatrix} \begin{pmatrix} I_1 & I_0 & j \\ m_1 & -m_0 & M \end{pmatrix} \begin{pmatrix} I_1 & I_0 & j \\ n_1 & -n_0 & m \end{pmatrix}^2 \delta_{MM'} . \tag{A7}$$

Next, we introduce a "super rotation operator $\mathfrak{D}$" and write

$$(I_0 m_0 I_1 m_1 | \mathfrak{D} \overline{U}^0(p) \mathfrak{D}^{-1} | I_0 m_0' I_1 m_1')$$
$$= \sum_{\substack{n_0 n_1 \\ n_0' n_1'}} (I_0 m_0 I_1 m_1 | \mathfrak{D} | I_0 n_0 I_1 n_1)(I_0 n_0 I_1 n_1 | \overline{U}^0(p) | I_0 n_0' I_1 n_1')(I_0 n_0' I_1 n_1' | \mathfrak{D}^{-1} | I_0 m_0' I_1 m_1') ,$$

where we have used the closure relation[21] for the states of Liouville operators,

$$\sum_{n_0 n_1} | n_0 n_1)(n_0 n_1 | = 1 .$$

Now,

$$(I_0 m_0 I_1 m_1 | \mathfrak{D} | I_0 n_0 I_1 n_1) = (I_0 m_0 I_1 m_1 | e^{-i\phi I_u^\times} | I_0 n_0 I_1 n_1) ,$$

for a rotation by an angle ϕ about the direction $\vec{u}$,

$$(I_0 m_0 I_1 m_1 | \mathfrak{D} | I_0 n_0 I_1 n_1)$$
$$= \langle I_0 m_0 | e^{-i\phi I_u} | I_0 n_0 \rangle \langle I_1 n_1 | e^{i\phi I_u} | I_1 m_1 \rangle ,$$

using the properties[2] of Liouville operators,

$$(I_0 m_0 I_1 m_1 | \mathfrak{D} | I_0 n_0 I_1 n_1)$$
$$= \langle I_0 m_0 | D | I_0 n_0 \rangle \langle I_1 n_1 | D^{-1} | I_1 m_1 \rangle , \tag{A8}$$

where D is the ordinary rotation operator.[18] Equation (A8) may be taken as the definition of $\mathfrak{D}$.

Hence

$$(I_0 m_0 I_1 m_1 | \mathfrak{D} \overline{U}^0(p) \mathfrak{D}^{-1} | I_0 m_0' I_1 m_1')$$
$$= \sum_{\substack{n_0 n_1 \\ n_0' n_1'}} D^{(I_0)}_{m_0 n_0} D^{(I_1)*}_{m_1 n_1} D^{(I_0)}_{m_0' n_0'} D^{(I_1)}_{m_1' n_1'} \sum_{n_0'' n_1''} \frac{(-1)^{-n_0 - n_0' + 2n_0''}}{p - i(V_{n_0''} - V_{n_1''})} \sum_{jmm'} (2j+1) \begin{pmatrix} I_1 & I_0 & j \\ n_1' & -n_0' & m' \end{pmatrix} \begin{pmatrix} I_1 & I_0 & j \\ n_1 & -n_0 & m' \end{pmatrix} \begin{pmatrix} I_1 & I_0 & j \\ n_1'' & -n_0'' & m \end{pmatrix}^2 ,$$

where we have used Eq. (A7),

$$= \sum_{n_0'' n_1''} \sum_{jmm'} (2j+1) \frac{(-1)^{-m_0' - m_0 + 2n_0''}}{p - i(V_{n_0''} - V_{n_1''})} \begin{pmatrix} I_1 & I_0 & j \\ n_1'' & -n_0'' & m \end{pmatrix}^2 \begin{pmatrix} I_1 & I_0 & j \\ m_1' & -m_0' & M' \end{pmatrix} \begin{pmatrix} I_1 & I_0 & j \\ m_1 & -m_0 & M \end{pmatrix} D^{*(j)}_{M'm'} D^{(j)}_{Mm'} ,$$

using the contraction relation,[19]

$$\sum_{n_1' n_0'} \begin{pmatrix} I_1 & I_0 & j \\ n_1' & -n_0' & m' \end{pmatrix} D^{(I_1)}_{m_1' n_1'} D^{(I_0)}_{-m_0' -n_0'} = \begin{pmatrix} I_1 & I_0 & j \\ m_1' & -m_0' & M' \end{pmatrix} D^{*(j)}_{M'm'} . \tag{A9}$$

Finally, using[18]

$$\sum_{m'} D^{*(j)}_{M'm'} D^{(j)}_{Mm'} = \delta_{MM'} , \tag{A10}$$

we obtain

$$(I_0 m_0 I_1 m_1 | \mathfrak{D}\bar{U}^0\mathfrak{D}^{-1} | I_0 m_0' I_1 m_1') = \sum_{n_0 n_1} \frac{(-1)^{-m_0-m_0'+2n_0}}{p - i(V_{n_1} - V_{n_0})} \sum_{jm} (2j+1) \begin{pmatrix} I_1 & I_0 & j \\ m_1' & -m_0' & M' \end{pmatrix} \begin{pmatrix} I_1 & I_0 & j \\ m_1 & -m_0 & M \end{pmatrix} \begin{pmatrix} I_1 & I_0 & j \\ n_1 & -n_0 & m \end{pmatrix}^2 \delta_{MM'} . \quad \text{(A11)}$$

Comparing Eqs. (A7) and (A11), we conclude that

$$\bar{U}^0 = \mathfrak{D}\bar{U}^0\mathfrak{D}^{-1} , \quad \text{for any } \mathfrak{D}$$

Therefore Eq. (13) yields

$$\bar{U} = \mathfrak{D}\bar{U}\mathfrak{D}^{-1} . \quad \text{(A12)}$$

The Liouville operator $\bar{U}$, as given by Eqs. (13) and (29), is clearly an isotropic superoperator in the angular-momentum space. Just as an ordinary isotropic angular-momentum operator is invariant under any rotation,[22] so is $\bar{U}$ under the transformation $\mathfrak{D}$, as shown in Eq. (A12). The matrix elements of $\mathfrak{D}$ are given by Eq. (A8) in terms of the matrix elements of an ordinary rotation operator. In that sense, $\mathfrak{D}$ serves as a super-rotation operator in the Liouville space of angular-momentum operators.

APPENDIX B

Using Eq. (A10), we write the perturbation factor in Eq. (33) as

$$G_{LL'}^{MM'}(p) = \sum_{\substack{m_0 m_0' \\ m_1 m_1'}} (-1)^{2I_0+m_0+m_0'} [(2L+1)(2L'+1)]^{1/2} \begin{pmatrix} I_1 & I_0 & L \\ m_1 & -m_0 & M \end{pmatrix} \begin{pmatrix} I_1 & I_0 & L' \\ m_1' & -m_0' & M' \end{pmatrix} \frac{1}{8\pi^2} \iiint d\alpha \sin\beta\, d\beta\, d\gamma$$

$$\times \sum_{\substack{n_0 n_1 \\ n_0' n_1'}} (I_0 m_0 I_1 m_1 | \mathfrak{D}^{-1} | I_0 n_0 I_1 n_1)(I_0 n_0 I_1 n_1 | \bar{U}(p) | I_0 n_0' I_1 n_1')(I_0 n_0' I_1 n_1' | \mathfrak{D} | I_0 m_0' I_1 m_1') ,$$

for an arbitrary super rotation operator $\mathfrak{D}$,

$$= \sum_{\substack{m_0 m_0' \\ m_1 m_1'}} (-1)^{2I_0+m_0+m_0'} [(2L+1)(2L'+1)]^{1/2} \begin{pmatrix} I_1 & I_0 & L \\ m_1 & -m_0 & M \end{pmatrix} \begin{pmatrix} I_1 & I_0 & L' \\ m_1' & -m_0' & M' \end{pmatrix} \frac{1}{8\pi^2} \iiint d\alpha \sin\beta\, d\beta\, d\gamma$$

$$\times \sum_{\substack{n_0 n_1 \\ n_0' n_1'}} D_{n_0 m_0}^{(I_0)*} D_{n_1 m_1}^{(I_1)} D_{n_0' m_0'}^{(I_0)} D_{n_1' m_1'}^{(I_1)*} (I_0 n_0 I_1 n_1 | \bar{U}(p) | I_0 n_0' I_1 n_1') ,$$

using Eq. (A6),

$$= \sum_{\substack{n_0 n_1 \\ n_0' n_1'}} (-1)^{2I_0+n_0+n_0'} [(2L+1)(2L'+1)]^{1/2} \frac{1}{8\pi^2} \iiint d\alpha \sin\beta\, d\beta\, d\gamma \begin{pmatrix} I_1 & I_0 & L' \\ n_1' & -n_0' & N' \end{pmatrix} \begin{pmatrix} I_1 & I_0 & L \\ n_1 & -n_0 & N \end{pmatrix} D_{NM}^{*(L)} D_{N'M'}^{(L')}$$

$$\times (I_0 n_0 I_1 n_1 | \bar{U}(p) | I_0 n_0' I_1 n_1') ,$$

using Eq. (A9).

Finally, we obtain

$$G_{LL'}^{MM'}(p) = \sum_{\substack{n_0 n_1 \\ n_0' n_1'}} (-1)^{2I_0+n_0+n_0'} [(2L+1)(2L'+1)]^{1/2} (I_0 n_0 I_1 n_1 | \bar{U}(p) | I_0 n_0' I_1 n_1')$$

$$\times \begin{pmatrix} I_1 & I_0 & L' \\ n_1' & -n_0' & N' \end{pmatrix} \begin{pmatrix} I_1 & I_0 & L \\ n_1 & -n_0 & N \end{pmatrix} \frac{1}{2L+1} \delta_{LL'} \delta_{NN'} \delta_{MM'} \quad \text{(A13)}$$

where we have used the orthogonality relation[15] for the D functions

$$\frac{2j_1+1}{8\pi^2} \int_0^{2\pi} d\alpha \int_0^{\pi} \sin\beta\, d\beta \int_0^{2\pi} d\gamma\, D_{m_1' m_1}^{(j_1)}(\Omega) D_{m_2' m_2}^{(j_2)}(\Omega) = \delta_{m_1' m_2'} \delta_{m_1 m_2} \delta_{j_1 j_2} . \quad \text{(A14)}$$

Therefore we can write

$$G_{LL'}^{MM'}(p) = \frac{1}{2L+1} G_{LL}^{MM}(p) \delta_{LL'} \delta_{MM'} , \quad \text{(A15)}$$

where $G_{LL}^{MM}(p)$ is given by Eq. (37).

APPENDIX C

From Eqs. (37) and (38)

$$G_{LL}^{0MM}(p+\lambda) = (2L+1)\sum_{\substack{m_0m_1\\m_0'm_1'}}(-1)^{2I_0+m_0+m_0'}\begin{pmatrix} I_1 & I_0 & L\\ m_1 & -m_0 & M\end{pmatrix}\begin{pmatrix} I_1 & I_0 & L\\ m_1' & -m_0' & M\end{pmatrix} \times (I_0 m_0 I_1 m_1|\overline{U}^0(p+\lambda)|I_0 m_0' I_1 m_1') . \quad (A15)$$

Substituting Eq. (A7) into Eq. (A15) and using the relation[15]

$$(2j_3+1)\sum_{m_1m_2}\begin{pmatrix} j_1 & j_2 & j_3\\ m_1 & m_2 & m_3\end{pmatrix}\begin{pmatrix} j_1 & j_2 & j_3'\\ m_1 & m_2 & m_3'\end{pmatrix} = \delta_{j_3j_3'}\delta_{m_3m_3'} , \quad (A16)$$

we obtain Eq. (39) very easily.

APPENDIX D

To prove Eq. (40), we first substitute the series (38) into Eq. (37). Then for any term in the series, we prove the following theorem:

Theorem. If

$$[G_{LL}^{0MM}(p+\lambda)]^r = \sum_{\substack{m_0m_1\\m_0'm_1'}}(-1)^{2I_0+m_0+m_0'}(2L+1)\begin{pmatrix} I_1 & I_0 & L\\ m_1 & -m_0 & M\end{pmatrix}\begin{pmatrix} I_1 & I_0 & L\\ m_1' & -m_0' & M\end{pmatrix} \times (I_0 m_0 I_1 m_1|[\overline{U}^0(p+\lambda)]^r|I_0 m_0' I_1 m_1') , \quad (A17)$$

then it is also true that

$$[G_{LL}^{0MM}(p+\lambda)]^{r+1} = \sum_{\substack{m_0m_1\\m_0'm_1'}}(-1)^{2I_0+m_0+m_0'}(2L+1)\begin{pmatrix} I_1 & I_0 & L\\ m_1 & -m_0 & M\end{pmatrix}\begin{pmatrix} I_1 & I_0 & L\\ m_1' & -m_0' & M\end{pmatrix}(I_0 m_0 I_1 m_1|[\overline{U}^0(p+\lambda)]^{r+1}|I_0 m_0' I_1 m_1') . \quad (A18)$$

Proof. The right-hand side of Eq. (A18) is

$$= \sum_{\substack{m_0m_1\\m_0'm_1'\\m_0''m_1''}}(-1)^{2I_0+m_0+m_0'}(2L+1)\begin{pmatrix} I_1 & I_0 & L\\ m_1 & -m_0 & M\end{pmatrix}\begin{pmatrix} I_1 & I_0 & L\\ m_1' & -m_0' & M\end{pmatrix}(I_0 m_0 I_1 m_1|[\overline{U}^0(p+\lambda)]^r|I_0 m_0'' I_1 m_1'') \times (I_0 m_0'' I_1 m_1''|\overline{U}^0(p+\lambda)|I_0 m_0' I_1 m_1') . \quad (A19)$$

Now, from Eq. (A3), we have

$$\sum_{m_0'm_1'}(-1)^{m_0'}\begin{pmatrix} I_1 & I_0 & L\\ m_1' & -m_0' & M\end{pmatrix}(I_0 m_0'' I_1 m_1''|\overline{U}^0(p+\lambda)|I_0 m_0' I_1 m_1')$$

$$= \sum_{m_0'm_1'}(-1)^{m_0'}\begin{pmatrix} I_1 & I_0 & L\\ m_1' & -m_0' & M\end{pmatrix}\frac{1}{4\pi}\int d\Omega_l\sum_{n_0n_1}\frac{(-1)^{-m_0''-m_0'+2n_0}}{(p+\lambda)+i(V_{n_1}-V_{n_0})}D_{n_1m_1'}^{*(I_1)}D_{-n_0-m_0'}^{*(I_0)}D_{n_1m_1''}^{(I_1)}D_{-n_0-m_0''}^{(I_0)}$$

$$= (-1)^{-m_0''+2n_0}\frac{1}{4\pi}\int d\Omega_l\sum_{n_0n_1}\frac{1}{(p+\lambda)+i(V_{n_1}-V_{n_0})}D_{n_1m_1''}^{(I_1)}D_{-n_0-m_0''}^{(I_0)}\begin{pmatrix} I_1 & I_0 & L\\ n_1 & -n_0 & N\end{pmatrix}D_{NM}^{(L)} ,$$

which is equal to [using the relation (A9)]

$$(-1)^{-m_0''+2n_0}\frac{1}{4\pi}\int d\Omega_l\sum_{n_0n_1}D_{NM}^{(L)}\begin{pmatrix} I_1 & I_0 & L\\ n_1 & -n_0 & N\end{pmatrix}\frac{1}{(p+\lambda)+i(V_{n_1}-V_{n_0})}$$

$$\times \sum_{jmm'} (2j+1) D^{(j)*}_{m'm} \begin{pmatrix} I_1 & I_0 & j \\ m_1'' & -m_0'' & m \end{pmatrix} \begin{pmatrix} I_1 & I_0 & j \\ n_1 & -n_0 & m' \end{pmatrix} ,$$

which equals (expressing the product of two D matrices in terms of $3j$ symbols[15])

$$(-1)^{-m_0''+2n_0} \begin{pmatrix} I_1 & I_0 & L \\ m_1'' & -m_0'' & M \end{pmatrix} G^{0\,MM}_{LL}(p+\lambda) ,$$

where we have used Eqs. (A6) and (39).

Substituting the above result into Eq. (A19) and using Eq. (A17), we get the right-hand side of Eq. (A18), $[G^{0\,MM}_{LL}(p+\lambda)]^r\, G^{0\,MM}_{LL}(p+\lambda)$, which proves the theorem.

Since Eq. (A17) is true for $r=1$ [cf. Eq. (A15)], Eq. (A18) implies that it is true for any r. Therefore we can express Eq. (37) as

$$G^{MM}_{LL}(p) = G^{0\,MM}_{LL}(p+\lambda) + \lambda[G^{0\,MM}_{LL}(p+\lambda)]^2 + \lambda^2[G^{0\,MM}_{LL}(p+\lambda)^3 + \cdots] ,$$

which yields Eq. (40).

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[1]M. Blume, in *Hyperfine Structure and Nuclear Radiations* (North-Holland, Amsterdam, 1968), p. 911.

[2]M. Blume, Phys. Rev. 174, 351 (1968).

[3]R. M. Lynden-Bell, Mol. Phys. 21, 891 (1971); also see J. Roberts and R. M. Lynden-Bell, *ibid.* 21, 689 (1971).

[4]J. A. Tjon and M. Blume, Phys. Rev. 165, 456 (1968).

[5]H. Winkler and E. Gerdau, Z. Phys. 262, 363 (1973); also see E. Gerdau *et al.*, *ibid.* 263, 5 (1973).

[6]R. C. Hughes and Z. G. Soos, J. Chem. Phys. 52, 6302 (1970).

[7]P. W. Anderson, J. Phys. Soc. Jap. 9, 316 (1954).

[8]R. Kubo, J. Phys. Soc. Jap. 9, 935 (1954).

[9]M. J. Clauser and M. Blume, Phys. Rev. B 3, 583 (1971).

[10]A. Abragam, *The Theory of Nuclear Magnetism* (Oxford U.P., London, 1961).

[11]M. Blume, Nucl. Phys. A 167, 81 (1971).

[12]G. J. Perlow, Phys. Rev. 172, 319 (1968).

[13]A. M. Van der Kraan, thesis, Delft Technical Institute, 1972 (unpublished).

[14]M. Blume and O. C. Kistner, Phys. Rev. 171, 421 (1968).

[15]M. Rotenberg *et al.*, *The 3-j and 6-j Symbols* (MIT, Cambridge, Mass., 1959).

[16]Equation (209) in the article by Steffen and Frauenfelder in *Alpha- Beta- and Gamma-Ray Spectroscopy*, edited by K. Siegbahn (North-Holland, Amsterdam, 1968), Vol. 2, p. 997.

[17]S. L. Ruby, in the Proceedings of Mössbauer Conference, Haifa, 1972 (unpublished).

[18]A. Messiah, *Quantum Mechanics* II (North-Holland, Amsterdam, 1965), Chap. XIII.

[19]Equation (228) in Ref. 16.

[20]O. C. Kistner and A. W. Sunyar, Phys. Rev. Lett. 4, 412 (1960).

[21]Appendix of the paper by H. Gabriel, J. Bosse, and K. Rander, Phys. Status Solidi 27, 311 (1968).

[22]S. Dattagupta, thesis (St. John's University, New York, 1974) (unpublished).