PHYSICAL REVIEW B VOLUME 16, NUMBER 1 1 JULY 1977

Stochastic model for classical bath variables and its influence on line-shape expressions

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(Received 7 July 1976)

A stochastic theory of hyperfine spectra is presented in which the coupled nucleus-ion system is treated quantum mechanically, and the interaction between the ionic spin and its surroundings is taken into account via effective fluctuating fields. The theory treats in detail a larger subsystem than the one considered by Clauser and Blume, and it is shown that the Clauser-Blume results can be obtained from the more general result given here, when the rate of fluctuations in the surrounding bath is much faster than the frequencies of the radiating system. A perturbative calculation also enables us to establish a connection between the stochastic- and the many-body-theory results for the line shape. The theory is worked out for Mössbauer line shape but can be applied easily to other related problems in atomic and nuclear spectroscopy. Application of the results derived here to analyze specific experimental situations will be dealt with elsewhere.

I. INTRODUCTION

Among the various stochastic-theory treatments of relaxation effects in Mössbauer line shapes that have appeared in recent years, the most general one so far is due to Clauser and Blume[1] (hereafter referred to as CB). In this theory, the quantum-mechanical nucleus-ion system is treated exactly, while effects of ionic relaxation are introduced via terms in the Hamiltonian which have random properties. The theory is simple, and yet has the same general validity as do most practical applications of *ab initio* treatments.[2]

The CB model assumes the presence of a bath which drives fluctuations into the system, and these fluctuations are assumed to occur on a time scale much faster than the characteristic frequency of the radiating system (see Sec. III B). This physical assumption is incorporated mathematically by assuming that the radiating system (nucleus plus ion) is subject to random pulses of extremely short duration. This assumption is equivalent to the impact approximation used extensively in the theory of pressure broadening of spectral lines in gaseous atoms.[3] The impact approximation assumes that the duration of a collision between atoms in the gas, that is, the duration of the perturbation, is negligibly short compared to the mean time between collisions. In between two collisions, the atoms are supposed to be free. The impact approximation or the CB assumption of short-lived pulses yields a relaxation matrix in the theory which is independent of the frequencies of the resonating system.[4]

While the impact approximation appears to be a reasonable description for binary collisions in a low-density gas, its applicability to fluctuations in solids, where the nucleus-ion system is continually under the influence of perturbations due to the surroundings, is in question. Indeed, recent experimental evidence has demonstrated the inadequacy of the CB model to treat a class of Mössbauer relaxation problems where the relaxation rate of the fluctuations in the bath is comparable to the unperturbed frequencies of the resonating system, and therefore, where the frequency dependence of the relaxation matrix is important.[5] Using techniques of many-body theory, we have earlier presented a calculation in which one obtains a frequency-dependent relaxation matrix, and which gives a satisfactory account of the Mössbauer data in a system where the spin-spin relaxation rate due to dipolar interactions between paramagnetic ions is comparable to the hyperfine frequency.[5]

The theory presented in Ref. 5 and similar theories[6] have the advantage that the elements of the relaxation matrix are specified in terms of some correlation functions which contain detailed information about the variables which are external to the nucleus-ion system. In practice, however, it is very difficult to calculate these correlation functions, and some phenomenological assumptions are usually made regarding their nature.[5] In addition, the method treats the interaction between the radiating system and its surroundings in second-order perturbation theory, and calculations beyond second order, which involve higher-point correlation functions, are indeed quite complex. The stochastic theory of CB, on the other hand, does not require at the outset that perturbations be small. Furthermore, stochastic theories afford us, in some cases, greater physical clarity and insight into the assumptions which make possible a tractable many-body calculation.[7] For this reason, it is very useful to generalize the CB model to situations where the relaxation rate of the fluctuations in the bath is comparable to the unperturbed frequency of the radiating system. We pre-

sent such a calculation in this paper.

As in the CB model, we assume that the ion that contains the Mössbauer nucleus is coupled to its surroundings through effective fluctuating fields whose fluctuations occur as sudden instantaneous pulses. But in contrast to the CB theory, the unperturbed system in our model is taken to be a larger one, comprising the nucleus-ion system plus an effective field coupling of the ionic spin to its surroundings. This is expected to be a more realistic description of fluctuations in solids where, as stated earlier, the ionic spin is continually under the influence of its environment. In the theory presented in Sec. II, we replace the degrees of freedom of the bath external to the nucleus-ion system by certain stochastic variables.[8] With an additional assumption about the transition matrix which governs the stochastic modulation of the Hamiltonian, we show in Sec. III that the average over the stochastic variables can be performed in a closed form. The resulting expression for the line shape [contained in Eq. (19) below] can be easily handled on a computer. Finally, the results of Ref. 5 and of the CB model are also obtained as limiting cases from perturbative calculations in different regions of relaxation times, starting from Eq. (19).

II. THEORY

We adopt a physical picture in which the combined nucleus-ion system is assumed to be subject to fluctuations due to the coupling of the ionic spin with the surroundings. The Hamiltonian is written

$$\mathcal{H}(t)=\mathcal{H}_0+\sum_{j=1}^{n} V_j f_j(t), \tag{1}$$

where $\mathcal{H}_0$ contains all the interactions for the resonating system, e.g., magnetic hyperfine interaction, nuclear and electronic Zeeman interactions, nuclear quadrupolar interaction, ionic crystal-field interaction, etc. The V_j's are quantum-mechanical spin operators for the ion that contains the nucleus, and f_j's are random functions of time which can be chosen to take appropriate values corresponding to the different forms of the Hamiltonian.[8] Thus, for example, we may have

$$\mathcal{H}_0=a\vec{\mathrm{I}}\cdot\vec{\mathrm{S}}, \tag{2}$$

describing a magnetic hyperfine interaction between the nuclear spin $\vec{\mathrm{I}}$ and the ionic spin $\vec{\mathrm{S}}$, and

$$\begin{aligned} &V_1=H_xS_x, \quad V_2=-H_xS_x, \quad V_3=H_yS_y,\\ &V_4=-H_yS_y, \quad V_5=H_zS_z, \quad V_6=-H_zS_z, \end{aligned} \tag{3}$$

$$\begin{aligned} f_1&=\tfrac{1}{48}(1+f)(f^2-4)(f^2-9),\\ f_2&=\tfrac{1}{48}(1-f)(f^2-4)(f^2-9),\\ f_3&=\tfrac{1}{60}(2+f)(1-f^2)(f^2-9),\\ f_4&=\tfrac{1}{60}(2-f)(1-f^2)(f^2-9),\\ f_5&=\tfrac{1}{240}(3+f)(f^2-1)(f^2-4),\\ f_6&=\tfrac{1}{240}(3-f)(f^2-1)(f^2-4), \end{aligned} \tag{4}$$

where the stochastic function $f(t)$ is assumed to take values 1, −1, 2, −2, 3, and −3 at random.[8] Equations (3) and (4) then describe a situation where the ionic spin experiences an effective field that changes its magnitude and direction at random between the $\pm x$, $\pm y$, and $\pm z$ axes. Such fluctuations may arise, for example, due to spin-lattice interactions,[1] coupling of the ionic spin to the conduction electrons,[2] spin-spin coupling between the ion containing the nucleus and its surrounding ions due to dipolar or exchange interactions,[5] etc. Obviously the theory can be generalized easily to situations where more than just six forms of the Hamiltonian can occur.

The model can now be summarized as follows. At random instants of time the coupled nucleus-ion system is subject to pulses which *instantaneously* change the form of the Hamiltonian [see Eq. (9) below]. This will happen, for example, if the effective field at the ionic spin jumps from x axis to y axis, in the above illustrative example. As in the CB model, the pulses are assumed to be randomly distributed with a Poisson distribution, and in between pulses, the system is assumed to be unperturbed. However, unlike the CB model which assumes the unperturbed Hamiltonian to be governed by $\mathcal{H}_0$ only (as is expected to happen in free gaseous atoms in between collisions), the unperturbed Hamiltonian in our model describes a larger system.

The Mossbauer line shape is given by[1]

$$F(p)=\mathrm{re}\int_0^\infty dt\, e^{-pt}\,\mathrm{Tr}\{\rho_{ne}A^\dagger[(\mathcal{U}(t))_{\mathrm{av}}A]\}, \tag{5}$$

where A is a nuclear operator for emission or absorption of radiation, $p=-i\omega+\frac{1}{2}\Gamma$, with Γ the natural linewidth of the resonance, ρ_{ne} is the density matrix for the nucleus-ion system governed by the Hamiltonian $\mathcal{H}_0$, and $\mathcal{U}(t)$ is the so-called time-development superoperator for the system. [The meaning of $(\ )_{\mathrm{av}}$ is discussed below in Eq. (10)]. In our model we have

$$\begin{aligned} \mathcal{U}(t)=e^{i\mathcal{H}^{\times}_{ne}t_1}\mathcal{T}e^{i\mathcal{H}^{\times}_{ne}(t_2-t_1)}\\ \times\mathcal{T}e^{i\mathcal{H}^{\times}_{ne}(t_3-t_2)}\times\cdots\mathcal{T}e^{i\mathcal{H}^{\times}_{ne}(t-t_s)}, \end{aligned} \tag{6}$$

where

$$\mathcal{H}^{\times}_{ne}=\mathcal{H}^{\times}_0+\sum_j V^{\times}_j F_j, \tag{7}$$

is the Liouville operator corresponding to $\mathcal{H}_{ne}$, and F_j is a matrix defined by[8]

$$(a|F_j|b) = \delta_{aj}\delta_{ab}. \tag{8}$$

The stochastic indices a and b correspond to the different values assumed by the random function $f(t)$. [Thus in the example of Eqs. (3) and (4), a and b run from -3 to 3.] The matrix $(a|\mathcal{T}|b)$ or $\mathcal{T}_{ab}$ is the probability that a pulse takes the system (instantaneously) from a stochastic state $|a)$ to $|b)$.

From (6)–(8), the matrix of $\mathfrak{U}(t)$ in the stochastic space can be written

$$(a|\mathfrak{U}(t)|b) = \sum_{cde\cdots} e^{i(\mathcal{H}_0^{\times}+V_a^{\times})t_1}\mathcal{T}_{ac}e^{i(\mathcal{H}_0^{\times}+V_c^{\times})(t_2-t_1)}\mathcal{T}_{cd}e^{i(\mathcal{H}_0^{\times}+V_d^{\times})(t_3-t_2)}\cdots\mathcal{T}_{eb}e^{i(\mathcal{H}_0^{\times}+V_b^{\times})(t-t_s)}. \tag{9}$$

Equation (9) has the following interpretation. At $t=0$, the system "sees" a Hamiltonian $\mathcal{H}_0+V_a$, with the effective field at the ionic spin in the stochastic state $|a)$. The quantum-mechanical state of the system then develops in time until t_1 with the appropriate time-development superoperator $e^{i(\mathcal{H}_0^{\times}+V_a^{\times})t_1}$. At t_1, a pulse hits the system which has a probability $\mathcal{T}_{ac}$ of throwing the system (instantaneously) into a stochastic state $|c)$ governed by the Hamiltonian $\mathcal{H}_0+V_c$. Its quantum-mechanical state then develops in time under $\mathcal{H}_0+V_c$ until t_2 at which time another pulse makes it jump into a stochastic state $|d)$, and so on. Since we have to consider all possible intermediate stochastic states we sum over the stochastic variables c, d, ...

The average we seek in (5) is obtained by summing over the final stochastic states $|b)$, averaging over the initial states $|a)$, and averaging over the type and location (in time) of the pulses, thus

$$(\mathfrak{U}(t))_{\mathrm{av}} = \sum_{s=0}^{\infty} P_s(t)\int_0^t dt_s\int_0^{t_s} dt_{s-1}\cdots\int_0^{t_2} dt_1\, W_s(t_1,\ldots,t_s;t)\sum_{ab} p_a(a|\mathfrak{U}(t_1,t_2,\ldots,t_s;t)|b), \tag{10}$$

where p_a is the *a priori* probability of the occurrence of the initial stochastic state $|a)$, and $P_s(t)$ is the probability that exactly s pulses occur in time t. For random occurrence of the pulses, this is given by the Poisson distribution[1]

$$P_s(t) = [(\nu t)^s/s!]e^{-\nu t}, \tag{11}$$

where ν^{-1} is the mean time between pulses.[9] In this model, ν can be interpreted as the relaxation rate of the fluctuations in the surroundings (see also Sec. III A). Also $W_s(t_1,\ldots,t_s;t)$ is the probability that, given that s pulses occur in time t, these occur at t_1 in dt_1, t_s in dt_s, respectively. Since the points are randomly distributed,

$$W_s = s!/t^s. \tag{12}$$

The average over the stochastic variables a and b in Eq. (10) marks the crucial step which is different from the CB model. In the CB model, the effect of a pulse is taken into account only in an average sense through an effective transition operator τ_{av}. This inherently assumes that fluctuations in the bath system are much faster than the hyperfine frequency (see also Sec. III B) so that the average over the bath variables factors out into products of uncorrelated averages. We make no such assumption in our model and the full average over the degrees of freedom of the bath (i.e., the stochastic variables $a, b, \ldots$) is taken into account in (10).

The subsequent mathematical development is identical to that of CB, and the final result for the Laplace transform [cf., Eq. (5)] of $(\mathfrak{U}(t))_{\mathrm{av}}$ can be written

$$(\mathfrak{U}(p))_{\mathrm{av}} = \sum_{ab} p_a\left(a\left|\left(p - i\mathcal{H}_0^{\times} - i\sum_j V_j^{\times}F_j + \nu(1-\mathcal{T})\right)^{-1}\right|b\right). \tag{13}$$

The solution for the line shape [Eqs. (5) and (13)] therefore involves the inversion (or diagonalization) of a matrix whose dimension is $(2I_e+1)(2I_g+1)(2S+1)^2n$, where I_e is the nuclear spin in its excited state, I_g is the nuclear spin in its ground state, S is the effective spin of the ion, and n is the number of different forms of the Hamiltonian [six, in the example of Eqs. (3) and (4)]. Clearly, the computational labor is increased, since the solution now requires the inversion of a matrix larger than the CB matrix which has a dimensionality $(2I_e+1)(2I_g+1)(2S+1)^2$. However, as we shall show next, by making a special assumption about the matrix $\mathcal{T}$, the stochastic variables can be completely eliminated, however large n may be, thus reducing the problem to the same level of (computational) complexity as the CB solution.

It is appropriate here to make a few remarks regarding the interpretation of (13). The static case ($\nu=0$) yields

$$(\mathfrak{U}^0(p))_{\mathrm{av}} = \sum_j p_j(p - i\mathcal{H}_0^{\times} - iV_j^{\times})^{-1}, \tag{14}$$

using Eq. (8). This corresponds to a situation in which the ion finds itself in a static internal field. The line shape now is a superposition of spectra corresponding to a distribution of internal fields at different parts of the system, each weighted by a factor p_j [cf. Eq. (14)]. However, since $[\mathcal{H}_0, V_j] \neq 0$, in general, the static case does not necessarily lead to a "relaxation-free" case. The "relaxa-

tion-free" case in this model has to be obtained by setting $V_j = 0$ (corresponding to the situation in a *dilute* paramagnet, for example, in which the dipolar spin-spin interaction vanishes) in Eq. (13). In that case, we obtain

$$(\mathfrak{U}(p))_{\rm av}^{\rm free} = \sum_{ab} p_a (a|(p - i\mathfrak{IC}_0^{\times} + \nu - \nu\mathcal{T})^{-1}|b)$$

$$= \frac{1}{p+\nu-i\mathfrak{IC}_0^{\times}} \sum_{s=0}^{\infty} \sum_{ab} p_a (a|\mathcal{T}^s|b) \times \left(\frac{\nu}{p+\nu-i\mathfrak{IC}_0^{\times}}\right)^s .$$

Now, we have

$$\sum_{ab} p_a (a|\mathcal{T}^s|b) = \sum_{abcd\cdots} p_a (a|\mathcal{T}|c)(c|\mathcal{T}|d)\cdots(e|\mathcal{T}|b)$$

$$= \sum_a p_a = 1,$$

using

$$\sum_b (e|\mathcal{T}|b) = 1, \tag{15}$$

since the left-hand side measures the total probability of transition from any stochastic state $|e)$. Therefore

$$(\mathfrak{U}(p))_{\rm av}^{\rm free} = (p - i\mathfrak{IC}_0^{\times})^{-1}, \tag{16}$$

the expected result. This distinction between the static case and the "relaxation-free" case is not present in the CB model.

III. $\mathcal{T}$ MATRIX IN THE RPA

We assume that the probability of transition of the Hamiltonian from one form to another does not depend on the initial stochastic 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, and so we may refer to this as a random-phase approximation[10] (RPA). Admittedly, the RPA is a crude description of the dynamics of the system. However, it is to be noted that the RPA is applied only to the dynamics of the system exterior to the coupled nucleus-ion system, and the latter of course is treated exactly. Since the Mössbauer nucleus is only an indirect "observer" of the dynamics of the surrounding spin system, it is not expected to be too sensitive to the detailed nature of these fluctuations. In terms of many-body perturbation-theory calculations of the line shape, where the theory involves two- and higher-point correlation functions,[5] the RPA affords a suitable decoupling scheme in which the higher-point correlation functions are expressed back in terms of the two-point correlation function. The details of the RPA results are given in Ref. 10. Here we merely quote them.

The RPA assumes

$$\mathcal{T}_{ab} = p_b, \tag{17}$$

which is independent of a, where p_b is the occupational probability for the state $|b)$ [cf. Eq. (10)]. This form of the $\mathcal{T}$ matrix obviously satisfies the detailed balance of transitions at finite temperatures:

$$p_a \mathcal{T}_{ab} = p_b \mathcal{T}_{ba}. \tag{18}$$

Following Ref. 10, the solution for the RPA model can be written

$$(\mathfrak{U}(p))_{\rm av} = \frac{(\mathfrak{U}^0(p+\nu))_{\rm av}}{1 - \nu(\mathfrak{U}^0(p+\nu))_{\rm av}}, \tag{19}$$

where

$$(\mathfrak{U}^0(p+\nu))_{\rm av} = \sum_{j=1}^{n} p_j [(p+\nu) - i\mathfrak{IC}_0^{\times} - iV_j^{\times}]^{-1}. \tag{20}$$

The superoperator $(\mathfrak{U}(p))_{\rm av}$ is thus given entirely in terms of $(\mathfrak{U}^0(p+\nu))_{\rm av}$ which has a dimension of $(2I_e+1)(2I_g+1)(2S+1)^2$. A knowledge of the matrix element of $(\mathfrak{U}^0(p+\nu))_{\rm av}$ then determines the line shape [cf., Eq. (5)].

It should be emphasized that in cases where the RPA assumption is not expected to be valid, one can still go back and use Eq. (13) for the line shape. This of course requires a reasonable model for the $\mathcal{T}$ matrix, depending on the physical situation at hand. The RPA, however, in addition to giving mathematically simpler results, also leads to the existing line-shape-theory results[1,5,6] in a quite straightforward manner. We discuss this below.

Perturbation-theory calculations

1. *Intermediate case of relaxation:* $\nu > V_j^{\times}$, $\nu \sim \mathfrak{IC}_0^{\times}$

This case corresponds to a strongly exchange- or dipolar-coupled system or to a system where the spin-lattice relaxation is very fast. In such a situation, the relaxation rate is larger than the instantaneous strength of the effective field at the ion ($\nu > V_j^{\times}$). However, ν can be comparable to the hyperfine coupling $\mathfrak{IC}_0^{\times}$. Using a result given in Ref. 10, we have in this case,

$$(\mathfrak{U}(p))_{\rm av} \approx \left(p - i\mathfrak{IC}_0^{\times} + \sum_j p_j V_j^{\times} (p+\nu-i\mathfrak{IC}_0^{\times})^{-1} V_j^{\times}\right)^{-1}, \tag{21}$$

$$(\mathfrak{U}(p))_{\rm av} = [p - i\mathfrak{IC}_0^{\times} + R(p)]^{-1}, \tag{22}$$

where

$$R(p)=\sum_j p_j V_j^{\times}(p+\nu-i\mathcal{H}_0^{\times})^{-1}V_j^{\times}. \tag{23}$$

It is to be noted that the relaxation matrix $R(p)$ depends explicitly on the unperturbed Hamiltonian $\mathcal{H}_0$. This frequency dependence has been found to be extremely important in the experimental system studied in Ref. 5. If we now consider the example of Eqs. (3) and (4), and specialize to the case of cubic symmetry, i.e.,

$$H_x=H_y=H_z=H, \tag{24}$$

the R matrix in (23) reduces to a result obtained in Ref. 5. A comparison of the two results enables us to interpret H as the rms field at the ion, and ν as the relaxation rate of the fluctuations in the surroundings of the ion. The results obtained in *ab initio* treatments[6] of the Mössbauer line shape are also essentially contained in Eqs. (22) and (23).

2. *Very fast relaxation:* $\nu > V_j^{\times}$, $\nu > \mathcal{H}_0^{\times}$

In this case, it is assumed that the relaxation rate ν is much larger than both the effective field at the ion as well as the hyperfine interaction. From Ref. 10, we then have

$$(\mathfrak{U}(p))_{\rm av}\approx\left(p-i\mathcal{H}_0^{\times}+\sum_j p_j\frac{(V_j^{\times})^2}{(p+\nu)}\right)^{-1}, \tag{25}$$

up to second order in $V_j^{\times}$.

Following the notation used by CB, we write (25) as

$$(\mathfrak{U}(p))_{\rm av}=(p-i\mathcal{H}_0^{\times}-\mathfrak{W})^{-1}, \tag{26}$$

where the relaxation matrix $\mathfrak{W}$, in this limit, is independent of $\mathcal{H}_0$, and is given by

$$\mathfrak{W}=-\sum_j p_j\frac{(V_j^{\times})^2}{\nu}, \tag{27}$$

since the term p in the denominator in (27) can be neglected in this regime of relaxation.

Thus we find that in this limiting case, the hyperfine interaction has no influence on the relaxation processes, and the relaxation matrix is independent of frequency [cf. Eq. (27)]. This is sometimes referred to as the white-noise case.[5]

To demonstrate the equivalence between the above results and those of the CB model, we specialize to the case of ionic spin $S=\frac{1}{2}$, assume Eq. (24), and also assume $p_j=\frac{1}{6}$ (the infinite-temperature case). Then, we have

$$\mathfrak{W}=-(H^2/3\nu)[(S_x^{\times})^2+(S_y^{\times})^2+(S_z^{\times})^2]. \tag{28}$$

Using the matrix elements of $S=\frac{1}{2}$ Liouville operators,[11] the matrix $\mathfrak{W}$ can be written (the rows and columns are labeled by $\frac{1}{2}\frac{1}{2}$, $-\frac{1}{2}-\frac{1}{2}$, $\frac{1}{2}-\frac{1}{2}$, $-\frac{1}{2}\frac{1}{2}$, respectively)

$$\mathfrak{W}=\frac{H^2}{3\nu}\begin{bmatrix}-1&1&0&0\\1&-1&0&0\\0&0&-2&0\\0&0&0&-2\end{bmatrix}. \tag{29}$$

This is exactly the matrix given by CB in Table II of their paper, if we make the identification

$$H^2/\nu=2\lambda(\sin^2\tfrac{1}{2}h)_{\rm av}, \tag{30}$$

where in the CB notation h is the (dimensionless) measure of the strength of the pulses that "hit" the ionic system and λ^{-1} is the mean time between successive pulses. For a general spin ($S\neq\frac{1}{2}$), the equivalence between (25) and the CB solution can be shown, order by order in perturbation theory, by extending the result in (25) beyond the second order. We do not do this here, however, because the general result, valid for arbitrary strengths of H, is already contained in Eqs. (19) and (20).

A few comments are now in order. Equation (30) gives a microscopic meaning to the CB parameters λ and h (also see Ref. 2). Second, even in this regime of relaxation, H^2/ν, and hence λ, can still be large compared to the hyperfine frequency, and therefore motional narrowing can still be discussed within the framework of the CB model.

In concluding this section, we should remark that even in cases where the RPA model for the $\mathcal{T}$ matrix is not applicable we can still carry out perturbation calculations as above, on the general result in Eq. (13).[12] Of course, the form of the $\mathcal{T}$ matrix in such a case has to be specified (as dictated by the nature of the problem) before any useful result can be given. The $\mathcal{T}$ matrix must also satisfy the requirements that probability is conserved [cf. Eq. (15)], and that detailed balance is preserved for the transitions [cf. Eq. (18)].

IV. CONCLUSION

The stochastic-theory model of Clauser and Blume has been generalized to cover cases where the frequency of the radiating system is comparable to the rate of fluctuations in the surrounding bath. The solution is given in terms of a transition matrix which contains information about the random properties of the Hamiltonian. A special assumption about the transition matrix is shown to simplify the calculations considerably, and the resulting solution is amenable to computer study. Perturbative calculation of the final solution gives us an idea of the region of validity of the Clauser-Blume model. It also enables us to make contact between the stochastic- and the many-body-theory results for the line shape. We feel it is important to establish such a connection between the two ap-

parently different approaches to the theoretical study of line shape.

Although the theory is developed here for Mössbauer spectra, it can readily be adapted to related fields such as perturbed angular correlation of γ rays, electron and nuclear-spin resonance, and other branches of optical spectroscopy. In a future paper, we will discuss the application of our formalism to the subject of perturbed angular correlation of γ rays.

It may be helpful to conclude with the following brief remarks on the historical sequence in which the stochastic theory of line shape has developed, in order to put matters in perspective. Anderson and Kubo,[13] in first applying such ideas, assumed that the characteristic frequencies of the radiating system undergo random modulation due to interaction with the surroundings. This entirely classical theory was later generalized by Blume[8] to include quantum-mechanical properties of the nuclear system although the surrounding electronic system was still treated classically. The need for such a generalization was motivated, in large part, by experimental work which concerned, for example, a nucleus which, because of electronic relaxation, or Jahn-Teller distortions, or jump diffusion of interstitials, and vacancies, finds itself in an electric field gradient that makes transitions between different axes.[14] Later experiments[15] led Clauser and Blume[1] to enlarge the subsystem treated in detail to the coupled quantum-mechanical nucleus-ion system. Subsequent careful study has now established the inadequacy of the Clauser-Blume model,[5] and the necessity of including further degrees of freedom within the subsystem, namely, the interaction of the ionic spin with its environment. The theory presented in this paper carries out this program. Presumably, more refined experimental investigations will raise yet unanswered questions, and it may be necessary to treat the interaction of the ionic spin with its surroundings, not merely in terms of effective fluctuating fields, as done here, but in a much more detailed manner. It is hoped that the scheme developed here provides the ground work for the concomitant refinements the theory will have to undergo.

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