The expressions for $C_{lm}^{\perp}$ and $C_{lm}^{||}$ with $m=0$ are identical with those in Part A, except that we replace x_j, y_j and z_j by X_j, Y_j, and Z_j, respectively. The other coefficients are found from

$$C_{43}^{\perp}=\tfrac{1}{8}\sum_j e_jX_jZ_j(X_j^2-3Y_j^2)[(1/R_j^9)-3(X_j^2+Y_j^2)/R_j^{11}],$$

$$C_{43}^{||}=\tfrac{1}{24}\sum_j e_jX_jZ_j[(1/R_j^9)-(9Z^2/R_j^{11})],$$

$$C_{63}^{\perp}=\tfrac{1}{192}\sum_j e_j(Z_j/R_j^{15})(X_j^3-3X_jY_j^2)(24R_j^4-143Z_j^2R_j^2+143Z_j^4),$$

$$C_{63}^{||}=\tfrac{1}{192}\sum_j e_j(Z_j/R_j^{15})(X_j^3-3X_jY_j^2)(-3R_j^4+66Z_j^2R_j^2-143Z_j^4),$$

$$C_{66}^{\perp}=\tfrac{1}{23040}\sum_j e_j[(6X_j^2/R_j^{13})(X_j^4-10X_j^2Y_j^2+5Y_j^4)$$
$$-(6Y_j^2/R_j^{13})(Y_j^4-10X_j^2Y_j^2+5X_j^4)-(13/R_j^{15})(X_j^2+Y_j^2)(X_j^6-15X_j^4Y_j^2+15X_j^2Y_j^6-Y_j^6)],$$

$$C_{66}^{||}=\tfrac{-1}{23040}\sum_j e_j(13Z_j^2/R_j^{15})(X_j^6-15X_j^4Y_j^2+15X_j^2Y_j^4-Y_j^6).$$

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Mössbauer Spectra in a Fluctuating Environment*

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The Mössbauer line shape in the presence of time-dependent electric field gradients and magnetic fields is considered. Two specific soluble stochastic models are treated: (1) a static electric field gradient with a randomly fluctuating magnetic field which takes on values $+h$ and $-h$, each directed along the axis of the field gradient, and (2) as in (1), but with the fluctuating magnetic field perpendicular to the axis of the field gradient. Example (2) is more complex than (1), since the fluctuating field is in this case capable of inducing transitions between the nuclear levels, while in (1) this is not possible. Specific calculations for the two cases illustrate the differences between them.

I. INTRODUCTION

THE theory of the Mössbauer line shape in the presence of time-dependent perturbations has been considered by a number of authors in recent years.[1–10] These theories have been applied with some success to a variety of problems involving hyperfine fields and electric field gradients in paramagnets and ferromagnets. The time dependence of the hyperfine fields arises from such effects as spin-spin and spin-lattice relaxation, spin waves, and Jahn-Teller distortions. The previous theoretical treatments can be divided into two general categories. The first can be termed perturbation treatments,[1,2,4,8,9] in which one uses the correct Hamiltonian for the entire system, consisting of the Mössbauer emitter, the hyperfine interactions between this nucleus and the electronic spins, and interactions between the electronic spins and one another and between these spins and other degrees of freedom. The line shape is then derived by treating some of these interactions as perturbations. The second category consists of calculations with stochastic models.[3,5,6,7,10] The hyperfine interaction is replaced by a randomly varying external magnetic field or electric field gradient, and the line shape is found in the presence of these fields. The problem here is to construct a Hamiltonian which represents as closely as possible the physical situation, but for which the line shape is soluble exactly. The first approach has the advantage of rigor over the second, but it suffers from the disadvantage that it is applicable only for very slow or very rapid rates of time variation of the hyperfine fields. The stochastic models on the other hand have been solved for all rates of time

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variation. Since most of the interesting effects on the line shape occur for intermediate rates, these models are of considerable interest.

In this paper we consider some of these models in detail. We treat the line shape of a nucleus in a fixed axially symmetric electric field gradient in the presence of a fluctuating magnetic field. This is a model for a nucleus in a paramagnet or a ferromagnet, in the presence of an electric field gradient. The case for which the magnetic field fluctuates along the axis of the field gradient is straightforward and has been treated previously. We consider as well the case where the magnetic field jumps along an axis perpendicular to that of the electric field gradient. Since in this situation the magnetic field may induce transitions between the eigenstates of the field gradient Hamiltonian (this is not possible in the parallel case), there are additional physical effects here which are not present in the parallel case.

In the following section we derive a general expression for the line shape in the presence of time-varying fields. This is applied in Sec. IIIA to the calculation of the line shape for fixed electric field gradient with fluctuating field parallel to the axis of the gradient, and in Sec. IIIB we treat the perpendicular case. Detailed comparison of the two cases is illustrated by calculations appropriate to a model of a paramagnet.

In the following paper we treat another model of physical interest, while in a subsequent paper we will consider the general solution for the line shape in the presence of arbitrarily varying Markoffian perturbations as well as the justification of the stochastic models from first principles.

II. EXPRESSION FOR THE LINE SHAPE

A general expression for the line shape may be derived following the procedures of Lamb,[11] Van Hove,[12] and Singwi and Sjolander.[13] Let $\mathcal{H}^{(+)}$ describe the interaction of the solid with a photon of wave vector $\mathbf{k}$ which is being emitted by the system. Then the probability of the emission of a photon with wave vector $\mathbf{k}$ and frequency ω by the system, which in the process of emitting the photon makes a transition from its initial state $|\lambda\rangle$ to its final state $|\alpha\rangle$, is given by

$$W_{\lambda\alpha}(\mathbf{k})=\frac{|\langle\alpha|\mathcal{H}^{(+)}|\lambda\rangle|^2}{(\omega+E_\alpha-E_\lambda)^2+\frac{1}{4}\Gamma_\lambda^2}. \tag{2.1}$$

The states $|\lambda\rangle$ and $|\alpha\rangle$ represent, in general, eigenstates of the entire solid, including nuclear spin quantum numbers, electronic quantum numbers, etc. It is of course understood that in the initial state $|\lambda\rangle$ the nucleus is in the excited state, while in $|\alpha\rangle$ it is in its ground state. The quantity Γ_λ is the inverse of the natural lifetime of the excited state $|\lambda\rangle$. In most actual cases Γ_λ is independent of the particular sublevel of the excited state. We shall for convenience assume this to be the case. With the aid of the relation

$$[(\omega+E_\alpha-E_\lambda)^2+\tfrac{1}{4}\Gamma^2]^{-1}=(2/\Gamma)\,\mathrm{Re}\int_0^\infty dt\,\exp[i(\omega+E_\alpha-E_\lambda)t-\tfrac{1}{2}\Gamma t] \tag{2.2}$$

one finds

$$W_{\lambda\alpha}(\mathbf{k})=(2/\Gamma)\,\mathrm{Re}\int_0^\infty dt\,\exp(i\omega t-\tfrac{1}{2}\Gamma t)\times\langle\lambda|\mathcal{H}^{(-)}|\alpha\rangle\langle\alpha|U^\dagger(t)\mathcal{H}^{(+)}U(t)|\lambda\rangle, \tag{2.3}$$

where

$$\mathcal{H}^{(-)}=\mathcal{H}^{(+)\dagger}, \tag{2.4}$$

$$U(t)=\exp(-i\mathcal{H}t), \tag{2.5}$$

and $\mathcal{H}$ is the total Hamiltonian for the entire system. The experimentally observed emission probability is simply obtained by averaging Eq. (2.3) over all possible initial states $|\lambda\rangle$ and summing over all final states $|\alpha\rangle$ of the emitter. The result is

$$W(\mathbf{k})=\sum_{\lambda\alpha}p_\lambda W_{\lambda\alpha}(\mathbf{k})=(2/\Gamma)\,\mathrm{Re}\int_0^\infty dt\,\exp(i\omega t-\tfrac{1}{2}\Gamma t)\langle\mathcal{H}^{(-)}\mathcal{H}^{(+)}(t)\rangle, \tag{2.6}$$

where p_λ is the probability that the initial state $|\lambda\rangle$ occurs, $\mathcal{H}^{(+)}(t)=U^\dagger(t)\mathcal{H}^{(+)}U(t)$, and the average is defined by

$$\langle 0\rangle=\sum_\lambda p_\lambda\langle\lambda|0|\lambda\rangle.$$

One way to study the expression (2.6) is to start from the total Hamiltonian of the emitter and use some approximation scheme on Eq. (2.6). However in many cases it is mathematically and conceptually simpler to consider as a model the nucleus in the emitter to be under the influence of explicitly time-dependent forces than to consider the emitter to be an extremely large system. The time-dependent forces on the nucleus are due physically to the interaction of the nucleus with the electronic degree of freedom, lattice vibrations, etc. The expression (2.6) is then simply modified by using instead of Eq. (2.5) the time-ordered operator

$$U(t)=\exp\left[-i\int_0^t\mathcal{H}(t')\,dt'\right], \tag{2.7}$$

where $\mathcal{H}(t')$ is now a time-dependent Hamiltonian for the nucleus. It is also useful to consider the case where the Hamiltonian of the emitter is a *random* function of the time, since this provides a physically reasonable model for a system undergoing fluctuations due to interactions with other degrees of freedom. Such models

[11] W. E. Lamb, Phys. Rev. **55**, 190 (1939).
[12] L. Van Hove, Phys. Rev. **95**, 249 (1954).
[13] K. S. Singwi and A. Sjolander, Phys. Rev. **120**, 1093 (1960).

were used by Anderson and Weiss[14,15] and Kubo[16] in their treatments of the problems of motional and exchange narrowing in magnetic resonance, and these problems are closely related to the ones considered here. If such stochastic Hamiltonians are considered, the observed probability of emission of a photon **k** is the stochastic average of the previously derived expression,

$$W(\mathbf{k})=(2/\Gamma)\ \mathrm{Re}\int_0^\infty dt\exp(i\omega t-\tfrac{1}{2}\Gamma t)\,(\langle\mathcal{H}^{(-)}\mathcal{H}^{(+)}(t)\rangle)_{\mathrm{av}},\tag{2.8}$$

where the $(\ )_{\mathrm{av}}$ denotes the average over the stochastic degrees of freedom in the Hamiltonian. Equation (2.8) provides a general expression for the line shape in the presence of fluctuating fields. Like the expression of Singwi and Sjolander, it gives the Mössbauer line shape as the Fourier transform of a correlation function. The correlation-function expression for the linewidth of a spectral line was derived by Foley[17] and Anderson[18] in their treatments of pressure broadening in optical spectra.

A simple example may illustrate the use of Eq. (2.8). Let us consider a nucleus with an excited state of spin $I_1=\frac{3}{2}$ and a ground state of spin $I_0=\frac{1}{2}$ (e.g., Fe^{57}) in the presence of a static external magnetic field and an electric field gradient along the z axis. We neglect phonon recoil effects and assume that the nucleus is held rigidly fixed. This means that the Debye-Waller factor is unity. (The central calculation in the Mössbauer effect is thus being omitted.) Let the states of the nucleus in the absence of the fields be given by $|I_1m_1\rangle$ and $|I_0m_0\rangle$. The unperturbed Hamiltonian $\mathcal{H}_0$ has the property

$$\mathcal{H}_0\,|I_1m_1\rangle=E_1\,|I_1m_1\rangle,$$

$$\mathcal{H}_0\,|I_0m_0\rangle=E_0\,|I_0m_0\rangle.$$

(For Fe^{57}, $E_1-E_0=14.4$ keV.) The Hamiltonian in the presence of the fields is then given by

$$\mathcal{H}=\mathcal{H}_0+g\mu HI_z+Q(3I_z^2-I^2),\tag{2.9}$$

where

$$g\,|I_1m_1\rangle=g_1\,|I_1m_1\rangle,\ g\,|I_0m_0\rangle=g_0\,|I_0m_0\rangle;\ Q\,|I_0m_0\rangle=0,$$

and g_1 and g_0 are the g factors for the excited and ground states, respectively.

The correlation function then becomes

$$(\langle\mathcal{H}^{(-)}\mathcal{H}^{(+)}(t)\rangle)_{\mathrm{av}}=G(t)=\sum_{m_0m_1,m_0'm_1'}(2I_1+1)^{-1}$$
$$\times(\langle I_1m_1|\mathcal{H}^{(-)}|I_0m_0\rangle\langle I_0m_0|U^\dagger(t)|I_0m_0'\rangle\langle I_0m_0'|\mathcal{H}^{(+)}|I_1m_1'\rangle\langle I_1m_1'|U(t)|I_1m_1\rangle)_{\mathrm{av}},\tag{2.10}$$

where we have assumed that the various initial m_1 sublevels are equally probable, i.e., $p_\lambda=1/(2I_1+1)$. Using Eq. (2.9) we obtain

$$\langle I_0m_0|U^\dagger(t)|I_0m_0'\rangle=\exp[i(E_0+g_0\mu Hm_0)t]\delta_{m_0m_0'},$$

$$\langle I_1m_1'|U(t)|I_1m_1\rangle=\exp[-i(E_1+g_1\mu Hm_1+Q(3m_1^2-15/4))t]\delta_{m_1m_1'}.$$

On substituting this above we find

$$G(t)=(2I_1+1)^{-1}\sum_{m_0m_1}|\langle I_0m_0|\mathcal{H}^{(+)}|I_1m_1\rangle|^2\exp[-i(\omega_0+(g_1m_1-g_0m_0)\mu H+Q(3m_1^2-15/4))t],$$

where $\omega_0=E_1-E_0$ is the frequency of the unsplit line. Performing the integration in Eq. (2.8) we get

$$W(\mathbf{k})=\tfrac{1}{4}\sum_{m_0m_1}\frac{|\langle I_0m_0|\mathcal{H}^{(+)}|I_1m_1\rangle|^2}{(\omega-\omega_0-(g_1m_1-g_0m_0)\mu H-Q(3m_1^2-15/4))^2+\frac{1}{4}\Gamma^2}.\tag{2.11}$$

The matrix elements $\langle I_0m_0|\mathcal{H}^{(+)}|I_1m_1\rangle$ determine the intensity and the polarization of the individual lines, and their dependence on m_1 and m_0 is essentially contained in a Clebsch-Gordan coefficient. As expected, the correlation function expression for the line shape yields a sum of Lorentzians centered at the Zeeman and quadrupole-split points. For Fe^{57}, where the transition matrix elements of $\mathcal{H}^{(+)}$ are of magnetic dipole ($M1$) character, (2.11) gives the familiar 6-line pattern.

III. STOCHASTIC MODELS

A. Fluctuating Magnetic Field Parallel to Electric Field Gradient Axis

In this section we calculate the line shape in the presence of a fluctuating magnetic field which jumps at random between the values $+h$ and $-h$ along the z axis. In addition, we assume the presence of a fixed symmetric electric field gradient along the z axis. The Hamiltonian for the nucleus under these conditions is

$$\mathcal{H}=\mathcal{H}_0+Q(3I_z^2-I^2)+g\mu hI_zf(t).\tag{3.1}$$

[14] P. W. Anderson and P. R. Weiss, Rev. Mod. Phys. **25**, 269 (1963).
[15] P. W. Anderson, J. Phys. Soc. Japan **9**, 316 (1954).
[16] The earlier work of R. Kubo is summarized in his review in the proceedings of the Scottish Universities Summer School: *Fluctuation Relaxation and Resonance in Magnetic Systems*, edited by D. ter Haar (Oliver and Boyd, Edinburgh, 1962), p. 23.
[17] H. M. Foley, Phys. Rev. **69**, 616 (1946).
[18] P. W. Anderson, Phys. Rev. **76**, 471 (1949).

Here $f(t)$ is a random function of time, which takes on the values ± 1. This model Hamiltonian describes in a reasonable approximation the nucleus in the presence of relaxing electronic spins. The third term in Eq. (3.1) with the time-dependent field replaces the actual hyperfine interaction $A\mathbf{I}\cdot\mathbf{S}$ ($\mathbf{S}$ is the electronic spin) together with terms giving the interaction between $\mathbf{S}$ and other degrees of freedom, such as lattice vibrations and other spins in the crystal. The effect of these other interactions is to cause $\mathbf{S}$ to move in a very complicated way, which we represent here as a random fluctuation of a magnetic field. The function f is specified by giving the matrix of probabilities per unit time, W_{ij}, for a transition of $f(t)$ from the value i to the value $j\,(i\neq j)$. (In the case under consideration i, $j=\pm 1$, but more general situations where $f(t)$ takes on a larger number of values can also be treated.) The physical picture of the fluctuations of the electronic spin system are then contained in the quantities W_{ij}. The approach which we use, then, is to give an expression for the line shape in the presence of a randomly fluctuating field in terms of the W_{ij}. We must use some other calculation to obtain the values W_{ij}. For example, if we want the Hamiltonian to represent the nucleus in a paramagnetic ion with spin $\frac{1}{2}$ and $g_\perp=0$, then we should require $W_{+-}=W_{-+}=W$. If the transitions between the paramagnetic levels are due to Raman-type spin lattice relaxation, we expect that W will be proportional to T^7 or T^9. To represent a ferromagnet, we would take $W_{+-}\neq W_{-+}$, since in the presence of spontaneous electronic moments the ion is more likely to be found in (say) the $+\frac{1}{2}$ level. The transition probability would then be due to spin waves.

Let us now return to the calculation of the line shape with the Hamiltonian (3.1). The functions $f(t)$ have been thoroughly studied[15,19–21] and applied to the theory of the line shape in nuclear magnetic resonance. Recently, a number of authors have adapted these results to the case of the Mössbauer effect as well.[3,5,6,7,10] We must now evaluate the correlation function (2.8), for which we may use the expression (2.10), except that

$$\langle I_0m_0 \mid U^\dagger(t) \mid I_0m_0'\rangle = \exp\left[i\left(E_0t+g_0\mu h m_0\int_0^t f(t')\,dt'\right)\right]\delta_{m_0m_0'}$$

and

$$\langle I_1m_1' \mid U(t) \mid I_1m_1\rangle = \exp\left[-i\left(E_1t+Q(3m_1^2-15/4)t+g_1\mu h m_1\int_0^t f(t')\,dt'\right)\right]\delta_{m_1m_1'},$$

so that we obtain

$$G(t)=\tfrac{1}{4}\sum_{m_0m_1} \mid \langle I_0m_0 \mid \mathcal{H}^{(+)} \mid I_1m_1\rangle \mid^2 \exp[-i\omega_0t-iQ(3m_1^2-15/4)t]\left(\exp\left[i(g_0m_0-g_1m_1)\mu h\int_0^t f(t')\,dt'\right]\right)_{\text{av}}. \quad (3.2)$$

The remaining problem is to obtain the stochastic average

$$\left(\exp\left[i\alpha\int_0^t f(t')\,dt'\right]\right)_{\text{av}},$$

where $\alpha=\alpha(m_0m_1)=(g_0m_0-g_1m_1)\mu h$. This problem was solved by Anderson[15] and Sack[20] and details may be found in Abragam's book.[21] The average we need can, according to these authors, then be expressed in terms of the quantities W_{ij}. If $\mathbf{W}$ is the matrix of transition probabilities with diagonal elements determined by $W_{ii}=-\sum_{j(\neq i)}$ and $\mathbf{F}$ is the diagonal matrix whose elements are the permissible values of $f(t)$, then

$$\left(\exp\left[i\alpha\int_0^t f(t')\,dt'\right]\right)_{\text{av}}=\sum_{ij} p_i(j \mid \exp[(i\alpha\mathbf{F}+\mathbf{W})t] \mid i). \quad (3.3)$$

Equation (3.3) can be evaluated in closed form for the case where $f(t)=\pm 1$, since then the matrices $\mathbf{F}$ and $\mathbf{W}$ are 2×2. If $W_{+-}=W_{-+}=W$, we have

$$\left(\exp\left[i\alpha\int_0^t f(t')\,dt'\right]\right)_{\text{av}}=(\cos xWt+x^{-1}\sin xWt)\exp(-Wt), \quad (3.4)$$

where $x=x(m_0m_1)=(\alpha^2/W^2-1)^{1/2}$. A similar, although more complicated, expression can be written down if

[19] H. S. Gutowsky, D. W. McCall, and C. P. Slichter, J. Chem. Phys. **28**, 430 (1954).
[20] R. A. Sack, Mol. Phys. **1**, 163 (1958).
[21] A. Abragam, *The Theory of Nuclear Magnetism* (Oxford University Press, London, 1961), Chap. X.

$W_{+-}\neq W_{-+}$. We do not do this here because it is easier to substitute (3.3) and (3.2) directly into (2.8) to obtain

$$W(\mathbf{k})=(2/\Gamma)\ \mathrm{Re}\sum_{m_0m_1}\tfrac{1}{4}\,|\,\langle I_0m_0\,|\,\mathcal{H}^{(+)}\,|\,I_1m_1\rangle\,|^2\int_0^\infty dt\,\exp[i(\omega-\omega_0-Q(3m_1^2-15/4))t-\tfrac{1}{2}\Gamma t]$$
$$\times\sum_{ij}p_i(j\,|\,\exp[(i\alpha\mathbf{F}+\mathbf{W})t]\,|\,i),\tag{3.5}$$
$$=(2/\Gamma)\ \mathrm{Re}\sum_{m_0m_1}\tfrac{1}{4}\,|\,\langle I_0m_0\,|\,\mathcal{H}^{(+)}\,|\,I_1m_1\rangle\,|^2\sum_{ij}p_i(j\,|\,(p-\mathbf{W}-i\alpha\mathbf{F})^{-1}\,|\,i),$$

where

$$p=-i(\omega-\omega_0-Q(3m_1^2-15/4))+\tfrac{1}{2}\Gamma.$$

This expression may be evaluated numerically for each value of $\omega-\omega_0$ by inverting the matrix $p-\mathbf{W}-i\alpha\mathbf{F}$. It is nevertheless of some interest to examine the analytical expression for the line shape which is obtained by substituting (3.4) and (3.2) into (2.8), since we will then be able to discuss the behavior of the line shape as a function of W. We have

$$W(\mathbf{k})=(2/\Gamma)\ \mathrm{Re}\sum_{m_0m_1}\tfrac{1}{4}\,|\,\langle I_0m_0\,|\,\mathcal{H}^{(+)}\,|\,I_1m_1\rangle\,|^2$$
$$\times\int_0^\infty dt\,\exp[i(\omega-\omega_0-Q(3m_1^2-15/4))t-\tfrac{1}{2}\Gamma t]\{\cos xWt+x^{-1}\sin xWt\}\exp(-Wt).\tag{3.6}$$

The integral in (3.6) may be written as

$$\frac{1}{2}\int_0^\infty dt\,\exp[i(\omega-\omega_0-Q(3m_1^2-15/4))t-\tfrac{1}{2}\Gamma t]\{[1-(i/x)]\exp(ixWt)+[1+(i/x)]\exp(-ixWt)\}\exp(-Wt).\tag{3.7}$$

In the limit of very slow relaxation $[W\ll\alpha(m_0m_1)]$ we have $xW=(\alpha^2-W^2)^{1/2}\approx\alpha$, and $x\gg1$, so that the integral becomes

$$\frac{1}{2}\int_0^\infty dt\,\exp[i(\omega-\omega_0-Q(3m_1^2-15/4)+(g_0m_0-g_1m_1)\mu h)t-(\tfrac{1}{2}\Gamma+W)t]$$
$$+\exp[i(\omega-\omega_0-Q(3m_1^2-15/4)-(g_0m_0-g_1m_1)\mu h)t-(\tfrac{1}{2}\Gamma+W)t].$$

Substituting in (3.6) and performing the integration we obtain

$$W(\mathbf{k})=\tfrac{1}{4}\sum_{m_0m_1}\,|\,\langle I_0m_0\,|\,\mathcal{H}^{(+)}\,|\,I_1m_1\rangle\,|^2\,\{1/[\omega-\omega_0-Q(3m_1^2-15/4)+(g_0m_0-g_1m_1)\mu h]^2+[\tfrac{1}{2}\Gamma+W]^2$$
$$+1/[\omega-\omega_0-Q(3m_1^2-15/4)-(g_0m_0-g_1m_1)\mu h]^2+[\tfrac{1}{2}\Gamma+W]^2\}.\tag{3.8}$$

This is, as expected, just the Zeeman pattern for a nucleus in a magnetic field $+h$ superimposed on one with a magnetic field $-h$. Since the relaxation rate is slow, the line shape is the same as for a static field, except for the slight broadening of the lines by the transition probability W. In the case of very rapid relaxation we expect to see the magnetic effects disappear, leaving only the quadrupole splitting. This is because the fluctuations are so rapid that the nucleus cannot follow them and as a result the nucleus will only feel an average magnetic field, being zero in the cases considered. That this is predicted by (3.6) can be seen by examining (3.7) in the limit $W\gg\alpha$. We have $xW=(\alpha^2-W^2)^{1/2}\approx iW$; $x\approx i$; so that $(\cos xWt+(1/x)\sin xWt)\exp(-Wt)\approx1$, and the line shape has no dependence on the magnetic field. It also follows from (3.6) and (3.7) that the spectra collapse when $x=0$, i.e., when $(g_0m_0-g_1m_1)\mu h=W$. This condition is satisfied for a different value of W for each pair of lines. The inner pair of Zeeman split lines will collapse onto their center of gravity for a smaller value of W than will the outer pair.

In Fig. 1(a) we show a series of spectra which are calculated from (3.5) for fixed values of Q and h and different values of W. As shown previously[3] the fact that the condition $x=0$ occurs for a different value of W for each line leads, in a range of values of W, to asymmetric quadrupole spectra. These spectra will be compared later with the theoretical results for a fluctuating magnetic field *perpendicular* to the quadrupole axis.

B. Fluctuating Magnetic Field Perpendicular to Electric Field Gradient Axis

The problem treated in the preceding section has a number of features which greatly simplified the calculations. First, the Hamiltonian (3.1) is diagonal in I_z, so that the quantum-mechanical aspects of the calculation are simple, and the only problem is the evaluation of the stochastic average. Also, the Hamiltonian at one instant of time will commute with the Hamiltonian at a later instant. This property enables us to dispense with the time-ordering in the definition of $U(t)$ [Eq. (2.7)]. These features mean that the fluctuating magnetic field does not induce transitions between the eigenstates of the quadrupole term in the Hamiltonian. The broadening and narrowing effects are due to the frequency modulation ("adiabatic" effects) by the fluctuating field. In some systems, however, the Hamiltonian (2.1) is not a good approximation to the physical situation, and it is necessary to consider a Hamiltonian which does not have the above properties of (3.1). This is the case, for example, if the fluctuating magnetic field does not jump along the axis of the electric field gradient, but jumps perpendicular to it. This appears to be the case in a series of organic Fe compounds, the penta-coordinate dithiocarbamates,[22] where the axes of quantization of the electronic system and the electric field gradient do not coincide. Let us consider, then, a nucleus governed by the Hamiltonian

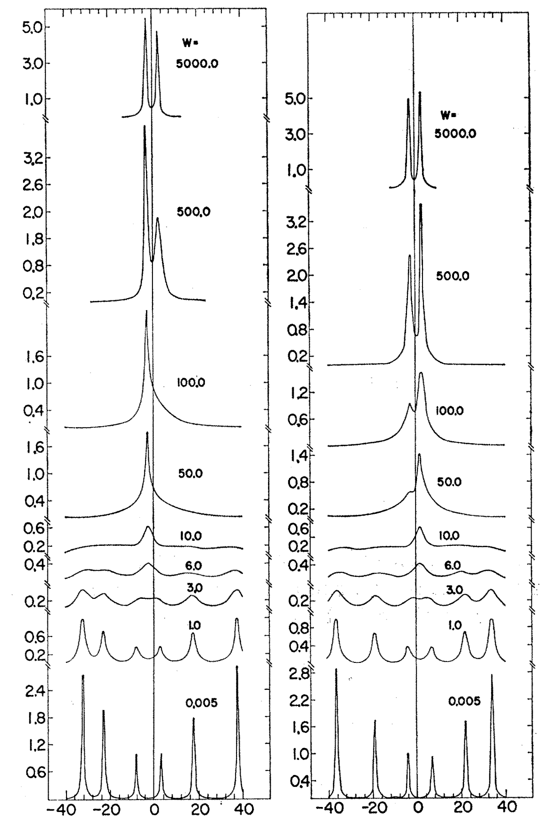
$$\mathcal{H}(t)=\mathcal{H}_0+Q'(3I_x^2-I^2)+g\mu hI_z f(t), \qquad (3.9)$$

where again $f(t)=\pm1$, at random. Equation (3.9) does not have the two properties discussed above; it is not diagonal in I_z, and it does not commute with itself at different times. The fluctuating field in (3.9) is now capable of inducing transitions between the eigenstates of the quadrupolar term, since it does not commute with that term. We expect, then, that the line shape of a system with the Hamiltonian (3.9) will show features which are not exhibited by (3.1); in particular, the "nonadiabatic" effects due to the inducing of transitions by the fluctuating field should occur here. Equation (3.9) can be transformed into a more convenient form by noting that $3I_x^2-I^2=-\frac{1}{2}(3I_z^2-I^2)+\frac{3}{4}(I_+^2+I_-^2)$, where $I_\pm=I_x\pm iI_y$. This is a special case of an asymmetric field gradient, one of whose principal axes is along the direction of the magnetic field. We will therefore treat the somewhat more general Hamiltonian

$$\mathcal{H}(t)=\mathcal{H}_0+Q(3I_z^2-I^2+\tfrac{1}{2}\eta(I_+^2+I_-^2))+g\mu hI_z f(t). \qquad (3.10)$$

When the asymmetry parameter $\eta\to0$ we recover (3.1); while if $Q\to-\frac{1}{2}Q'$, $\eta\to-3$, we obtain (3.9).

In calculating the Mössbauer line shape for systems with the Hamiltonian (3.10) it becomes apparent that the stochastic and quantum-mechanical aspects of the problem do not separate, as is the case for (3.1). The appropriate axes of quantization depend on the rate of fluctuation of $f(t)$. If $f(t)$ fluctuates very rapidly, the nucleus will be unable to follow the magnetic field, so that, if $[f(t)]_{\text{av}}=0$ (i.e., if $W_{+-}=W_{-+}$) the motion of the nucleus will be governed by the quadrupolar Hamiltonian. On the other hand, if the rate of fluctuation of $f(t)$ is very slow, the properties of the system will be determined by the eigenstates of the quadrupolar Hamiltonian together with the Zeeman term. The latter eigenstates differ from the former since, due to the presence of the asymmetry term η, the Zeeman term and the quadrupolar part do not commute with one another.



(a) (b)

FIG. 1. (a) Line shapes for a nucleus with the Hamiltonian $\mathcal{H}(t)=\mathcal{H}_0+Q(3I_z^2-I^2)+g\mu hI_z f(t)$, for different values of the jump rate W of $f(t)$. In units of the natural linewidth Γ we have used $Q=0.8736$ and $h=143.67$. Also $I_1=\frac{3}{2}$, $I_0=\frac{1}{2}$, $g_1=0.102$, and $g_0=-0.806$, as for Fe^{57}. (b) Line shapes for the Hamiltonian $\mathcal{H}(t)=\mathcal{H}_0+Q(3I_x^2-I^2)+g\mu hI_z f(t)$, with the same values of Q and h as in (a).

Our object now is to evaluate the expression (2.8) for the line shape with the Hamiltonian (3.10). We will in this calculation consider explicitly the case where $I_1=\frac{3}{2}$ and $I_0=\frac{1}{2}$, the level scheme for Fe^{57}, since this case is soluble in closed form. We again want to evaluate (2.10), with

$$\langle I_0m_0 \mid U(t) \mid I_0m_0'\rangle = \exp\left(iE_0t+ig_0\mu m_0h\int_0^t f(t')\,dt'\right)\delta_{m_0m_0'}, \qquad (3.11)$$

[22] H. H. Wickman and F. R. Merritt (to be published). We are indebted to Dr. Wickman for drawing our attention to this work, and for sending a prepublication report.

and

$$\langle I_1m_1' \mid U^\dagger(t) \mid I_1m_1\rangle$$

$$=\langle I_1m_1' \mid \exp\left(-iE_1t-i\int_0^t (\mathcal{H}_1(t')+V)dt'\right) \mid I_1m_1\rangle,$$

where

$$\mathcal{H}_1(t)=Q(3I_z^2-I^2)+g\mu hI_zf(t),$$

and

$$V=\tfrac{1}{2}Q\eta(I_+^2+I_-^2).$$

To simplify the problem further we will assume that the emitter is a powdered sample. We must then average $W(\mathbf{k})$ over all directions $\hat{k}$ of emission of the γ ray. Since we already require $m_0=m_0'$, the average over $\hat{k}$,

$$(4\pi)^{-1}\int d\hat{k}\langle I_1m_1 \mid \mathcal{H}^{(-)}(\mathbf{k}) \mid I_0m_0\rangle\langle I_0m_0 \mid \mathcal{H}^{(+)}(\mathbf{k}) \mid I_1m_1'\rangle$$

requires that in addition $m_1'=m_1$ (see, e.g., Rose,[23] p. 74). With this assumption, then

$$W(\mathbf{k})=(2/\Gamma)\ \mathrm{Re}\int_0^\infty dt\ \exp[i(\omega-\omega_0)t-\tfrac{1}{2}\Gamma t]\cdot\tfrac{1}{4}\sum_{m_0m_1} \mid \langle I_0m_0 \mid \mathcal{H}^{(+)} \mid I_1m_1\rangle \mid^2 G_{m_1m_0}(t),$$

with

$$G_{m_1m_0}(t)=\left(\exp\left[ig_0\mu m_0h\int_0^t f(t')dt'\right]\langle I_1m_1 \mid \exp\left[-i\int_0^t (\mathcal{H}_1(t')+V)dt'\right] \mid I_1m_1\rangle\right)_{\mathrm{av}}, \tag{3.12}$$

so that we require only the diagonal matrix element of the time development operator in (3.11). It should perhaps be noted that these nondiagonal elements can also be calculated using the method described below. We consider in detail now the calculation of $G_{m_1m_0}(t)$. Using the identity[24]

$$\exp\left(-i\int_0^t (\mathcal{H}_1(t')+V)dt'\right)=\exp\left(-i\int_0^t \mathcal{H}_1(t')dt'\right)\exp\left(-i\int_0^t \tilde{V}(t')dt'\right)$$

where

$$\tilde{V}(t)=\exp\left(i\int_0^t \mathcal{H}_1(t')dt'\right)V\exp\left(-i\int_0^t \mathcal{H}_1(t')dt'\right),$$

we may write

$$G_{m_1m_0}(t)=\left(\exp\left[i(g_0m_0-g_1m_1)\mu h\int_0^t f(t')dt'-iQ(3m_1^2-15/4)t\right]\langle I_1m_1 \mid \exp\left(-i\int_0^t \tilde{V}(t')dt'\right) \mid I_1m_1\rangle\right)_{\mathrm{av}}. \tag{3.13}$$

Expanding the exponential in the matrix element (3.13) in a time-ordered series gives

$$G_{m_1m_0}(t)=\left(\exp\left[-i(C_1-C_0)\int_0^t f(t')dt'-i\beta t\right]\langle I_1m_1 \mid \sum_{n=0}^\infty(-i)^n\int_0^t dt_1\cdots\int_0^{t_{n-1}}dt_n\tilde{V}(t_1)\tilde{V}(t_2)\cdots\tilde{V}(t_n) \mid I_1m_1\rangle\right)_{\mathrm{av}}, \tag{3.14}$$

where

$$C_1=g_1m_1\mu h,\quad C_0=g_0m_0\mu h,\quad\text{and}\quad \beta=\beta(m_1)=Q(3m_1^2-15/4).$$

Because V has the selection rule $\Delta m=\pm2$, the matrix elements with n odd in (3.14) vanish. Also, since $I_1=\frac{3}{2}$, these selection rules require

$$\langle I_1m_1 \mid \tilde{V}(t_1)\tilde{V}(t_2)\cdots\tilde{V}(t_{2n}) \mid I_1m_1\rangle$$

$$=\langle I_1m_1 \mid \tilde{V}(t_1)\tilde{V}(t_2) \mid I_1m_1\rangle\langle I_1m_1 \mid \tilde{V}(t_3)\tilde{V}(t_4) \mid I_1m_1\rangle\cdots\langle I_1m_1 \mid \tilde{V}(t_{2n-1})\tilde{V}(t_{2n}) \mid I_1m_1\rangle$$

because $\tilde{V}(t_1)\tilde{V}(t_2)$ is diagonal for $I\leq\frac{3}{2}$. Now

$$\langle I_1m_1 \mid \tilde{V}(t_1)\tilde{V}(t_2) \mid I_1m_1\rangle=\langle I_1m_1 \mid \tilde{V}(t_1) \mid I_1m_1\pm2\rangle\langle I_1m_1\pm2 \mid \tilde{V}(t_2) \mid I_1m_1\rangle$$

$$=\langle I_1m_1 \mid \exp\left(i\int_0^{t_1}\mathcal{H}_1(t')dt'\right) \mid I_1m_1\rangle\langle I_1m_1 \mid V \mid I_1m_1\pm2\rangle\langle I_1m_1\pm2 \mid \exp\left(-i\int_0^{t_1}\mathcal{H}_1(t')dt'\right) \mid I_1m_1\pm2\rangle$$

$$\times\langle I_1m_1\pm2 \mid \exp\left(i\int_0^{t_2}\mathcal{H}_1(t')dt'\right) \mid I_1m_1\pm2\rangle\langle I_1m_1\pm2 \mid V \mid I_1m_1\rangle\langle I_1m_1 \mid \exp\left(-i\int_0^{t_2}\mathcal{H}_1(t')dt'\right) \mid I_1m_1\rangle. \tag{3.15}$$

[23] M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley & Sons, Inc., New York, 1957).
[24] See, e.g., U. Fano, Rev. Mod. Phys. 29, 74 (1957).

Only one of the terms $|I_1m_1\pm2\rangle$ actually occurs. For example, if $m_1=\frac{3}{2}$, only $m_1-2=-\frac{1}{2}$ is found. Also, if $\beta=Q(3m_1^2-15/4)$, $-\beta=Q((3m_1\pm2)^2-15/4)$. Setting $C_1'=g_1(m_1\pm2)\mu h$, and noting that $|\langle I_1m_1|V|I_1m_1\pm2\rangle|^2=3Q^2\eta^2$ (independent of m_1), we find

$$\langle I_1m_1|\tilde{V}(t_1)\tilde{V}(t_2)|I_1m_1\rangle=3Q^2\eta^2\exp\left(i\beta t_1+iC_1\int_0^{t_1}f(t')dt'\right)\exp\left(i\beta t_1-iC_1'\int_0^{t_1}f(t')dt'\right)$$
$$\times\exp\left(-i\beta t_2+iC_1'\int_0^{t_2}f(t')dt'\right)\exp\left(-i\beta t_2-iC_1\int_0^{t_2}f(t')dt'\right). \quad (3.16)$$

Substituting this in (3.14) gives

$$G_{m_1m_0}(t)=\left(\exp\left[-i(C_1-C_0)\int_0^t f(t')dt'-i\beta t\right]\right.$$
$$\left.\times\sum_{n=0}^{\infty}(-3Q^2\eta^2)^n\int_0^t dt_1\cdots\int_0^{t_{2n-1}}dt_{2n}\exp\left[i\beta t_1-iC_1\int_0^{t_1}f(t')dt'\right]\cdots\exp\left[-i\beta t_{2n}-iC_1\int_0^{t_{2n}}f(t')dt'\right]\right)_{\mathrm{av}},$$

or on rearranging the terms

$$G_{m_1m_0}(t)=\sum_{n=0}^{\infty}(-3Q^2\eta^2)^n\int_0^t dt_1\cdots\int_0^{t_{2n-1}}dt_{2n}\left(\exp\left[-i\beta(t-t_1)-i(C_1-C_0)\int_{t_1}^t f(t')dt'\right]\right.$$
$$\left.\times\exp\left[i\beta(t_1-t_2)-i(C_1'-C_0)\int_{t_2}^{t_1}f(t')dt'\right]\cdots\exp\left[-i\beta t_{2n}-i(C_1-C_0)\int_0^{t_{2n}}f(t')dt'\right]\right)_{\mathrm{av}}. \quad (3.17)$$

To take the stochastic average of the product, we follow Kubo[16] and introduce the average subject to the condition that $f(t)=i$ for $t=0$ and $f(t)=j$ at t. This restricted average is a matrix and since in our case $i,j=\pm1$, it is a 2×2 matrix. Let $A(t-t_1)$ and $B(t_1-t_2)$ be the 2×2 matrices corresponding to the average of

$$\exp\left(-i\beta(t-t_1)-i(C_1-C_0)\int_{t_1}^t f(t')dt'\right)$$

and of

$$\exp\left(i\beta(t_1-t_2)-i(C_1'-C_0)\int_{t_2}^{t_1}f(t')dt'\right),$$

respectively, subject to the conditions on $f(t)$ given above. Then it is readily shown (see Appendix A) that Eq. (3.17) can be written as

$$G_{m_1m_0}(t)=\sum_{n=0}^{\infty}(-3Q^2\eta^2)^n\int_0^t dt_1\cdots\int_0^{t_{2n-1}}dt_{2n}\sum_{ij}p_i(j|A(t-t_1)B(t_1-t_2)\cdots A(t_{2n})|i), \quad (3.18)$$

where p_i is the probability that $f(0)=i$. Taking the Laplace transform of (3.18) simplifies the series, because each integral is a $2n$-fold convolution, and the Laplace transform of the convolution is equal to the product of the Laplace transforms. Hence

$$\int_0^{\infty}dt\exp(-pt)G_{m_1m_0}(t)$$
$$=\sum_{n=0}^{\infty}(-3Q^2\eta^2)^n\sum_{ij}p_i(j|\tilde{A}(p)[\tilde{B}(p)\tilde{A}(p)]^n|i), \quad (3.19)$$

where $\tilde{A}(p)$ and $\tilde{B}(p)$ are, respectively, the Laplace transforms of $A(t)$ and $B(t)$. The series in (3.19) can now be summed, yielding

$$\int_0^{\infty}dt\exp(-pt)G_{m_1m_0}(t)$$
$$=\sum_{ij}pi(j|\tilde{A}(p)[1+3Q^2\eta^2\tilde{B}(p)\tilde{A}(p)]^{-1}|i). \quad (3.20)$$

To obtain the final expression for (3.20) we must calculate the 2×2 matrices $\tilde{A}(p)$ and $\tilde{B}(p)$, find the inverse of $1+3Q^2\eta^2\tilde{B}(p)\tilde{A}(p)$, and perform the indicated sum over the matrix elements. These matrices may be found in the same way as (3.3) and (3.5), from the procedures of Sack. We have

$$\tilde{A}(p)=[p-\mathbf{W}-i(C_1-C_0)\mathbf{F}+i\beta]^{-1}$$

and

$$\tilde{B}(p)=[p-\mathbf{W}-i(C_1'-C_0)\mathbf{F}-i\beta]^{-1},$$

where $\mathbf{W}$ is again the matrix of transition probabilities, and

$$\mathbf{F}=\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}$$

is the diagonal matrix whose elements are the possible values of $f(t)$. We then find

$$W(\mathbf{k})=(2/\Gamma)\ \mathrm{Re}\tfrac{1}{4}\sum_{m_0m_1}|\langle I_0m_0|\mathcal{H}^{(+)}|I_1m_1\rangle|^2 \times\sum_{ij}p_i(j|\tilde{A}(p)[1+3Q^2\eta^2\tilde{B}(p)\tilde{A}(p)]^{-1}|i),$$

where

$$p=-i(\omega-\omega_0)+\tfrac{1}{2}\Gamma. \qquad (3.21)$$

Obviously this equation can easily be reduced in a straightforward way to an algebraic expression. The result is given in Appendix B. In the limit $\eta\to 0$, Eq. (3.21) reduces to (3.5), as it should. The additional effects discussed above are contained in the matrix B. In Fig. 1(b) we give a series of spectra calculated from (3.21) with values of Q and η chosen so that the parameters Q' of (3.10) and Q of (3.1) are equal, and with h equal to the h used in obtaining Fig. 1(a). Several differences between the two sets of spectra can be observed. In the slow relaxation spectra of the two cases (small W) which are essentially those produced by a static magnetic field the apparent quadrupole shifts differ. The quadrupole shift for the perpendicular case is $-\frac{1}{2}\times$ the shift for the parallel case. This follows from (3.10) with $Q=-\frac{1}{2}Q'$, since for $h\gg Q$, the nondiagonal (asymmetric) terms produce only second-order shifts. There is a small line (corresponding to the $\frac{3}{2}\to-\frac{1}{2}$ transition, which is normally forbidden) which is allowed in the perpendicular case by the admixture, due to the off-diagonal η terms, of the $-\frac{1}{2}$ and $\frac{3}{2}$ sublevels of the excited state. The corresponding $-\frac{3}{2}\to\frac{1}{2}$ transition gives a line that is buried under an allowed transition. As the jump rate W is increased each of the spectra broadens until, for $W\approx 3.0$, the central pair of lines collapses onto its center of gravity. These lines proceed to narrow as the jump rate is increased, and eventually the other magnetic lines collapse onto their centers of gravity. The parallel and perpendicular cases differ considerably in this regime. The high-energy line (consisting of $\pm\frac{3}{2}\to\pm\frac{1}{2}$ transitions) is more broadened in the parallel case, while the low-energy line (consisting of $\pm\frac{1}{2}\to\pm\frac{1}{2}$ and $\pm\frac{1}{2}\to\mp\frac{1}{2}$, with quantization along the x axis) is more broadened in the perpendicular case. This can be understood in the following way. The adiabatic broadening represented by the matrix A is more pronounced for the $\pm\frac{3}{2}\to\pm\frac{1}{2}$ than for the $\pm\frac{1}{2}\to\pm\frac{1}{2}$ transitions, due to the larger effective Zeeman energy. On the other hand the broadening due to the nonadiabatic terms, given by the matrix B, is larger for the $\pm\frac{1}{2}\to\pm\frac{1}{2}$ than for the $\pm\frac{3}{2}\to\pm\frac{1}{2}$ transitions, as can be seen from the expression for B. Due to the presence of the nonadiabatic terms in the perpendicular case the low-energy line is more broadened than the high-energy line. Obviously the nonadiabatic effects dominate over the adiabatic ones in this case. In addition to the above differences in broadening, the peaks in the perpendicular case move successively as the relaxation jump rate is increased to their positions with a splitting of $6Q'$. This movement occurs as the nondiagonal (asymmetry) terms become effective with the averaging out of the magnetic field. A considerable variety of behavior can thus be seen as the jump rate is changed.

Calculations similar to those shown in Fig. 1 can easily be performed for the case, $W_{+-}\neq W_{-+}$, which represents a model for a ferromagnet, by using (3.21). Spectra similar to those found by van der Woude and Dekker[5] should result, with appropriate allowance for nonadiabatic effects. Generalization of these results to fluctuating fields which take on more than two values is also immediate. Equation (3.20) still holds, but the dimension of the matrices $\tilde{A}$ and $\tilde{B}$ is then given by the number of possible values of $f(t)$.

IV. DISCUSSION

In the previous section we have described some stochastic models which can be solved exactly. It was found that there exist marked differences between the cases in which there are nondiagonal matrix elements between different sublevels of the nucleus and in which these elements are not present. In particular the broadening of a definite line in the Mössbauer spectrum due to these nondiagonal elements is quite different from the broadening by the diagonal elements. Furthermore, instead of six lines there will be in general eight lines because $\Delta m=2$ transitions will now also be allowed indirectly.

The calculation given above may present a fair description in general for the Mössbauer line shape in the presence of hyperfine fields. However, it is well to consider briefly a few experimental situations to which it does *not* apply. It is possible to do an experiment using coincidence techniques in which only those photons emitted by the nucleus within a time t after the birth of the excited state are counted.[25] Equation (2.6) is then not applicable, since the derivation of Eq. (2.1) assumes that all photons are counted, regardless of the time at which they are emitted. It is not sufficient to take the integration in Eq. (2.6) from 0 to t instead of from 0 to ∞ in order to adapt that expression to coincidence experiments, unless $\Gamma t\gg 1$. Also, in going from Eq. (2.3) to Eq. (2.6) we have assumed that averaging over the initial states can be accomplished by multiplying by p_λ and summing over λ. This implies that the initial configuration of the system is an equilibrium distribution in that this initial distri-

[25] F. J. Lynch, R. E. Holland, and M. Hammermesh, Phys. Rev. **120**, 153 (1960).

bution of states does not change in time. In other words, we assume that the density matrix of the system commutes with the Hamiltonian. Equation (2.6) is thus not entirely capable of describing the line shape in the presence of phenomena such as "local heating"[26] of the lattice (caused by distortions of the lattice due to the effects of earlier decays of the Mössbauer nucleus). Some of these effects may be treated in the stochastic model by taking the Hamiltonian to be a nonstationary random process, but great care must be exercised in that case. For a discussion of these points see Ref. 27.

The applicability of the models discussed in the present paper to a specific system must be decided by a consideration of the Hamiltonian for that system. A solution for the line shape for more general situations will be given separately.

Finally, it should be noted that the calculations performed here can be taken over to the treatment of perturbed angular correlations of successive γ rays,[28] as well as to the case of nuclear magnetic resonance. The expressions for the matrix elements of $U(t)$, Eqs. (3.3) and (3.11), can then be used in the similar expressions [e.g., Ref. 28, Eq. (9)] to derive the perturbed correlation or the NMR line shapes.

APPENDIX A

In this appendix we show that the restricted average of the second-order term of Eq. (3.17) can be written as

$$X=\int_0^t dt_1\int_0^{t_1} dt_2\left(\exp\left[-i\beta(t-t_1)-i(C_1-C_0)\int_{t_1}^{t} f(t')dt'\right]\exp\left[i\beta(t_2-t_1)-i(C_1'-C_0)\int_{t_2}^{t_1} f(t')dt'\right]\right.$$
$$\left.\times\exp\left[-i\beta t_2-i(C_1-C_0)\int_0^{t_2} f(t')dt'\right]\right)_{\text{av}}^{i,j}$$
$$=\int_0^t dt_1\int_0^{t_1} dt_2 (j\,|\,A(t-t_1)B(t_1-t_2)A(t_2)\,|\,i),\tag{A1}$$

with

$$(j\,|\,A(t)\,|\,i)=\left(\exp\left[-i\beta t-i(C_1-C_0)\int_0^{t_2} f(t')dt'\right]\right)_{\text{av}}^{i,j},\tag{A2}$$

$$(j\,|\,B(t)\,|\,i)=\left(\exp\left[i\beta t-i(C_1'-C_0)\int_0^{t_2} f(t')dt'\right]\right)_{\text{av}}^{i,j}.\tag{A3}$$

Here the superscripts i, j mean that the average over the quantities should be restricted to the conditions that $f(t)=i$ at $t=0$ and $f(t)=j$ at t. In order to show this let us expand the exponentials in (A1) in a series of time-ordered integrals

$$X=\int_0^t dt_1\int_0^{t_1} dt_2 \exp[-i\beta(t-t_1)]\exp[i\beta(t_1-t_2)]\exp(-i\beta t_2)\sum_{mnp}(-i)^{m+n+p}(C_1-C_0)^{m+p}(C_1'-C_0)^n$$
$$\times\int_0^t d\tau_1\cdots\int_0^{\tau_{m-1}} d\tau_m\int_0^{t_1} d\tau_1'\cdots\int_0^{\tau_{n-1}'} d\tau_n'\int_0^{t_2} d\tau_1''\cdots\int_0^{\tau_{p-1}''} d\tau_p'' Y_{ij}(\tau_1\cdots\tau_m;\tau_1'\cdots\tau_n';\tau_1''\cdots\tau_p''),\tag{A4}$$

where

$$Y_{ij}(\tau_1\cdots\tau_m;\tau_1'\cdots\tau_n';\tau_1''\cdots\tau_p'')=(f(\tau_1)\cdots f(\tau_m)f(\tau_1')\cdots f(\tau_n')f(\tau_1'')\cdots f(\tau_p''))_{\text{av}}^{i,j}.\tag{A5}$$

Due to the ordering of the times in (A4), $\tau_1>\tau_2>\cdots>\tau_m>\tau_1'>\cdots>\tau_n'>\tau_1''>\cdots>\tau_p''$, we may write in view of the Markoff character of the stochastic process for (A5)

$$Y_{ij}(\tau_1\cdots\tau_m;\tau_1'\cdots\tau_n';\tau_1''\cdots\tau_p'')=(j\,|\,P(t-\tau_1)FP(\tau_1-\tau_2)\cdots FP(\tau_p'')\,|\,i),\tag{A6}$$

where the matrices $P(t)$ and F are given by

$$P(t)=\exp(Wt),$$
$$F=\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}.$$

With the aid of the property

$$P(\tau_m-\tau_1')=P(\tau_m-t_1)P(t_1-\tau_1'),$$

[26] P. P. Craig, B. Mozer, O. C. Kistner, and R. Segnan, Rev. Mod. Phys. **36**, 361 (1963).
[27] M. Blume, Proceedings of the Asilomar Conference on Hyperfine Structure (to be published).
[28] R. M. Steffen and F. Frauenfelder, in *Perturbed Angular Correlations* (North-Holland Publishing Co., Amsterdam, 1964).

Eq. (A6) reduces to

$$Y_{ij}(\tau_1\cdots\tau_m;\tau_1'\cdots\tau_n';\tau_1''\cdots\tau_p'')=(j\,|\,Y'Y''Y'''\,|\,i),\tag{A7}$$

with

$$\begin{aligned}Y'&=P(t-\tau_1)F\cdots FP(\tau_m-t_1),\\ Y''&=P(t_1-\tau_1')F\cdots FP(\tau_n'-t_2),\\ Y'''&=P(t_2-\tau_1'')F\cdots FP(\tau_p'').\end{aligned}\tag{A8}$$

On substituting (A7) into (A4) we see that the equality (A1) indeed holds. In a similar way it can be shown that the general term in Eq. (3.17) is correct.

APPENDIX B

The expression (3.21) only involves an inversion of a 2×2 matrix and hence can easily be reduced to an algebraic expression. First we note that Eq. (3.21) can be rewritten as

$$W(\mathbf{k})=(2/\Gamma)\ \mathrm{Re}\sum_{m_0m_1}\tfrac{1}{4}\,|\,\langle I_0m_0\,|\,\mathcal{H}^{(+)}\,|\,I_1m_1\rangle\,|^2\sum_{ij}p_i(j\,|\,[\tilde{A}^{-1}(p)+3Q^2\eta^2\tilde{B}(p)]^{-1}\,|\,i).\tag{B1}$$

Then on substituting the explicit expression for $\tilde{A}$ and $\tilde{B}$ into (B1) and performing the matrix inversions we obtain

$$\sum_{ij}p_i(j\,|\,[\tilde{A}^{-1}(p)+3Q^2\eta^2\tilde{B}(p)]^{-1}\,|\,i)=N/D,\tag{B2}$$

where

$$\begin{aligned}N=&\,d(p+i\beta+2W)+3Q^2\eta^2(p-i\beta)\\ D=&\,d[(p+i(\beta-C_1+C_0)+W)(p+i(\beta+C_1-C_0)+W)-W^2]\\ &+3Q^2\eta^2[(p+i(\beta+C_1-C_0)+W)(p-i(\beta-C_1'+C_0)+W)\\ &+(p+i(\beta-C_1+C_0)+W)(p-i(\beta+C_1'-C_0)+W)+2W^2+3Q^2\eta^2],\end{aligned}$$

with

$$d=(p-i\beta)^2+(C_1'-C_0)^2+2W(p-i\beta).$$

We have used here the fact that $p_i=\frac{1}{2}$, and we have taken $W_{+-}=W_{-+}=W$.

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Mössbauer Spectra in a Fluctuating Environment II. Randomly Varying Electric Field Gradients*

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We derive an expression for the Mössbauer line shape in the presence of an electric field gradient which jumps at random between the x, y, and z axes. This Hamiltonian represents an idealized model for the effects on a nucleus of Jahn-Teller distortions, jump diffusion of vacancies, or electronic relaxation. A simplified calculation based on a model in which the field gradient jumps between positive and negative values along the z axis is also given. In certain limiting circumstances the two calculations give similar results: The Mössbauer line shape consists of a single unsplit line for fast jumping, and of a quadrupole doublet for slow transitions. The results of the calculation agree with experiments of Pipkorn and Leider and of Chappert, Frankel, and Blum, as interpreted by Ham.

I. INTRODUCTION

SEVERAL recent Mössbauer-effect experiments on Fe^{2+} in cubic materials have yielded spectra which are interpreted as being produced by a fluctuating electric field gradient at the nucleus.[1–3] Such fluctuations have been attributed to Jahn-Teller effects, jump diffusion of vacancies, or electronic relaxation. Ham[4]

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