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A STOCHASTIC THEORY OF LINE SHAPE

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CONTENTS

I. INTRODUCTION

Some years ago I gave a lecture on the present subject in the first Scottish Summer School.[1] In this article, we shall begin with a brief review of the basic concepts as treated in that lecture, then discuss a few examples of applications, with some generalizations, to physical and chemical problems, and finally comment on some points which are left for future studies.

Shapes or profiles of spectral lines are often very important for obtaining information about the physical system under observation. Thus a spectral profile can tell us the state of a stellar atmosphere, or it can be used as diagnostic for a plasma. The line shape of an NMR spectrum may disclose the internal motion of nuclei in a molecular system. The information thus obtained is admittedly not extremely detailed, but it may be very useful particularly when combined with other information, and often it is the only data available.

As is well known by now, a line shape function $I(\omega)$ is the Fourier transform of the correlation function of a physical variable, for example, a dipole moment of a molecule or an atom, or a magnetic moment of a spin. Thus,

$$I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \langle x^*(0)x(t)\rangle \exp\left[-i\omega t\right] dt / \langle x^* x\rangle \tag{1}$$

where x^* is complex conjugate to x if, as is sometimes convenient, x is conveniently chosen to be complex. Here the motion of the moment x of the system is considered to be a stochastic process induced by the perturbations that arise from the interaction of the system with its environment. Generally the environment consists of a great number of atoms or molecules which move in a complicated fashion; the perturbations it causes can be regarded as stochastic. Thus, the stochastic motion of $x(t)$ is generated by a basic process which represents the interaction. The average denoted by $\langle\ \rangle$ in Eq. (1) means an average over the ensemble of this basic process. The simplest example is given by the equation

$$\dot{x}(t) = i\Omega(t)x(t) \tag{2}$$

where $x(t)$, for instance, is the coordinate of an oscillator, with the frequency $\Omega(t)$ modulated by the random interaction with the environment. Throughout the present paper, the origin of the frequency ω is chosen at the center of the spectral distribution. This means that $\Omega(t)$ in Eq. (2) denotes the random part of the frequency, the constant part being subtracted; namely, we assume that

$$\langle\Omega(t)\rangle = 0$$

Equation (2) is a stochastic equation defining the process $x(t)$ in terms of a given process $\Omega(t)$. If complete knowledge of the derived process $x(t)$ could be obtained, one would be able to reconstruct the original process $\Omega(t)$. The line shape, however, only gives the correlation function of x, and so the information available about the process $\Omega(t)$ is necessarily limited. This means, at the same time, that there exist some general properties of the derived process of the type $x(t)$ of such generality that the details of the basic process are irrelevant. For example, we can generally say that the important elements in Eq. (2) are the amplitude or the variance of $\Omega(t)$ and its coherence. The variance may be characterized by

$$\Delta = \langle\Omega^2\rangle^{1/2} \tag{3}$$

and the coherence by the correlation time τ_c defined by

$$\tau_c = \int_0^\infty \frac{\langle\Omega(0)\Omega(t)\rangle\, dt}{\Delta^2} \tag{4}$$

If the condition

$$\Delta\tau_c \gg 1 \tag{5}$$

is fulfilled, the modulation of the frequency is *slow*, and if

$$\Delta\tau_c \ll 1 \tag{6}$$

then the modulation is *fast*. In the fast modulation case, the spectrum shows the phenomena of *motional narrowing*. The line shape becomes sharp with a Lorentzian form. In the opposite limit of slow modulation, the line shape is a direct reflection of the random distribution of Ω.

The main purpose of this paper is to discuss similar problems which are generalizations of Eq. (2), in order to obtain an understanding of some of the general features of line shapes under various conditions; these conditions are characterized by the relative magnitudes of a few physical parameters relevant for the basic process.

II. RANDOM FREQUENCY MODULATION[2-4]

Here we will summarize some known results for the simplest example of random frequency modulation as defined by Eq. (2). Let us assume that the process $\Omega(t)$ in Eq. (2) is a *projection* of a Markovian process characterized by the evolution operator Γ. This is possible in principle, because the dynamical motion of the environment can be described in terms of a Liouville operator. The set of variables defining the Markovian process is designated by λ. If the variable Ω itself is Markovian, λ consists only of Ω, but in general it has to be supplemented by additional variables to complete the set. Let the function $W(x, \lambda, t)$ be the probability or the probability density for finding the random variables x and λ at the respective values at the time t. Then a systematic method of treating the problem, Eq. (2), is to rewrite it in the form

$$\frac{\partial}{\partial t} W(x, \lambda, t) = -i \frac{\partial}{\partial x} (\Omega x W) + \Gamma W \tag{7}$$

which may be called the *stochastic Liouville equation*.[5] The simplification made in Eq. (7) is that this Liouville or evolution operator is independent of the motion of x; in other words, the reaction of x to the environment is ignored.

If the initial condition,

$$W(x, \lambda, 0) = \delta(x - x')\, \delta(\lambda, \lambda') \tag{8}$$

is imposed, the solution of Eq. (7) is the transition probability from the initial state (x', λ') to the final state (x, λ) in the time interval $(0, t)$. It is convenient to write this probability as

$$(x, \lambda \,|\, W(t) \,|\, x', \lambda')$$

Assuming the process to be stationary, the evolution operator Γ is independent of the time. Furthermore, we assume that the process $\{\lambda\}$ has a

unique equilibrium which is defined by the equation

$$\Gamma P_0(\lambda) = 0 \tag{9}$$

The normalized correlation function of $x(t)$,

$$\phi(t) = \langle x^*(0)x(t)\rangle / \langle x^* x\rangle$$

is now easily seen to be given by

$$\phi(t) = \int dx \sum_{\lambda} \sum_{\lambda'} x(x, \lambda \,|W(t)|\, x', \lambda') \overset{*}{x'} P_0(\lambda')/|x'|^2 \tag{10}$$

which may be written in a more symbolic form as

$$\phi(t) = (0|\, X(t)\,|0) = \sum_{\lambda} \sum_{\lambda'} (\lambda\,|X(t)|\,\lambda') P_0(\lambda') \tag{11}$$

Here we define, in analogy to Dirac's notation the zero (equilibrium) bra and ket vectors,

$$(0\,|\,\lambda') = 1, \qquad (\lambda'\,|\,0) = P_0(\lambda') \tag{12}$$

which satisfy the equations, $(0\,|\,\Gamma = 0, \quad \Gamma\,|\,0) = 0$ and are normalized according to

$$(0\,|\,0) = \sum_{\lambda'} (0\,|\,\lambda')(\lambda'\,|\,0) = \sum_{\lambda'} P_0(\lambda') = 1$$

In Eq. (11), $X(t)$ is a kind of conditional expectation defined by the matrix

$$(\lambda|\, X(t)\,|\lambda') = \int dx \frac{x(x, \lambda \,|W(t)|\, x', \lambda') \overset{*}{x'}}{|x'|^2} \tag{13}$$

The equation for $X(t)$ is obtained from Eq. (7) by multiplying by x and then integrating over x. Thus we find the equation

$$\dot{X}(t) = i\Omega X + \Gamma X \tag{14}$$

with the initial condition,

$$X(0) = \delta(\lambda, \lambda') = \mathbf{1}$$

Note that Eq. (14) is a matrix equation for $(\lambda\,|X(t)|\,\lambda')$. By the Laplace transformation,

$$\int_0^{\infty} \exp\,[-st] X(t)\, dt \equiv X[s] \tag{15}$$

Eq. (14) becomes

$$(s - i\Omega - \Gamma) X[s] = \mathbf{1} \tag{16}$$

This has the obvious solution

$$X[s] = (s - i\Omega - \Gamma)^{-1} \tag{17}$$

The line shape function $I(\omega)$, Eq. (1), is then given by

$$I(\omega) = \frac{1}{\pi} \operatorname{Re} (0| X[i\omega] |0) \tag{18}$$

$$= \lim_{\varepsilon \to 0+} \frac{1}{\pi} \operatorname{Re} (0| X[i\omega + \varepsilon] |0)$$

where the second expression is a more exact definition of the first one.

III. TWO SIMPLE EXAMPLES

First we will discuss two simple examples of the theory summarized in the previous section. They can be applied to a number of problems of physics and chemistry and also are very helpful for obtaining a general understanding of our subject. These simple examples are (*a*) a two-state-jump modulation and (*b*) a Gaussian modulation. [6,7]

In the first example, the frequency Ω is assumed to take only two values,

$$\Omega = \pm\omega_1 \quad \text{or} \quad \Omega = \begin{pmatrix} \omega_1 & 0 \\ 0 & -\omega_1 \end{pmatrix} \tag{19}$$

corresponding to two states, say *a* and *b*, of the environment. Transitions between two states are described in terms of the transition matrix,

$$\Gamma = \frac{\gamma}{2} \begin{bmatrix} -1 & 1 \\ 1 & -1 \end{bmatrix} \tag{20}$$

which has the equilibrium bra and ket vectors,

$$|0) = \begin{pmatrix} 1 \\ 1 \end{pmatrix}, \qquad (0| = (\tfrac{1}{2}, \tfrac{1}{2}) \tag{21}$$

We assume, for simplicity, equal equilibrium population; generalization to unequal equilibrium populations is straightforward.

Thus Eq. (14) takes the form,

$$\dot{X}(t) = \left[i \begin{pmatrix} \omega_1 & 0 \\ 0 & -\omega_1 \end{pmatrix} + \frac{\gamma}{2} \begin{pmatrix} -1 & 1 \\ 1 & -1 \end{pmatrix} \right] X(t) \tag{22}$$

and Eq. (17) becomes

$$X[s] = \begin{pmatrix} s - i\omega_1 + \frac{\gamma}{2} & -\frac{\gamma}{2} \\ -\frac{\gamma}{2} & s + i\omega_1 + \frac{\gamma}{2} \end{pmatrix}^{-1} \tag{23}$$

The line shape function is easily found to be

$$I(\omega) = \frac{1}{\pi} \frac{{\omega_1}^2}{(\omega^2 - {\omega_1}^2)^2 + \omega^2\gamma^2} \tag{24}$$

In the second example of a Gaussian modulation, the frequency Ω takes continuous values and is a Gaussian process. If further it is assumed to be Markovian, the Doob theorem[8] tells us that its correlation function has a simple exponential decay,

$$\langle \Omega(0)\Omega(t) \rangle = \Delta^2 \exp[-\gamma |t|\} \tag{25}$$

It is also described by a Fokker-Planck equation defined by the evolution operator,

$$\Gamma = \gamma \frac{\partial}{\partial \Omega} \left(\Delta^2 \frac{\partial}{\partial \Omega} + \Omega \right) \tag{26}$$

for which the equilibrium bra and ket vectors are

$$|0) \equiv f_0(\Omega) = \frac{1}{(2\pi)^{1/2}\,\Delta} \exp\left[-\Omega^2/2\,\Delta^2\right], \qquad (0| = 1 \tag{27}$$

Thus Eq. (14) takes the form

$$\frac{\partial}{\partial t} X(\Omega, t) = i\Omega X + \gamma \frac{\partial}{\partial \Omega} \left(\Delta^2 \frac{\partial}{\partial \Omega} + \Omega \right) X \tag{28}$$

and Eq. (18) for the line shape function gives

$$I(\omega) = \frac{1}{\pi} \operatorname{Re} \int_{-\infty}^{\infty} d\Omega \, \frac{1}{i(\omega - \Omega) - \Gamma} \, \frac{\exp|-\Omega^2/2\,\Delta^2|}{(2\pi\,\Delta^2)^{1/2}} \tag{29}$$

This equation can be written as

$$I(\omega) = \frac{1}{\pi} \operatorname{Re} \int_{-\infty}^{\infty} d\Omega f(\Omega, \omega) \tag{30}$$

where $f(\Omega, \omega)$ is the solution of the equation

$$\left[(i\omega - \Omega) + \gamma \frac{\partial}{\partial \Omega}\left(\Delta^2 \frac{\partial}{\partial \Omega} + \Omega\right)\right] f(\Omega, \omega) = f_0(\Omega) \tag{31}$$

It is more convenient to rewrite these equations by introducing the transformation,

$$f = \exp\left[-\frac{\Omega^2}{4\Delta^2}\right] g$$

$$\bar{\Gamma} = \exp\left[\frac{\Omega^2}{4\Delta^2}\right] \Gamma \exp\left[-\frac{\Omega^2}{4\Delta^2}\right] = \gamma\left\{\Delta^2 \frac{\partial^2}{\partial \Omega^2} - \frac{\Omega^2}{4\Delta^2} + \frac{1}{2}\right\} \tag{32}$$

Eqs. (30) and (31) then become

$$I(\omega) = \frac{1}{\pi} \operatorname{Re} \int_{-\infty}^{\infty} d\Omega \exp\left[-\frac{\Omega^2}{4\Delta^2}\right] g(\Omega, \omega) \tag{33}$$

$$[i(\omega - \Omega) + \bar{\Gamma}] g(\Omega, \omega) = g_0(\Omega) \tag{34}$$

where the operator $\bar{\Gamma}$ has the harmonic oscillator eigenfunctions as its eigenfunctions with the eigenvalues $n\gamma$ ($n = 0, 1, 2, \ldots$). On the right-hand side of Eq. (34), the function $g_0(\Omega)$ is the zeroth eigenfunction of $\bar{\Gamma}$. When the function $g(\Omega), \omega)$ is expanded in terms of the eigenfunctions of Γ Eq. (34) becomes a set of infinite algebraic equations; this form is useful for numerical computations.

In this Gaussian modulation case, the normalized correlation function of the moment $x(t)$ is given by

$$\begin{aligned} \frac{\langle x^*(0)x(t)\rangle}{\langle x^* x\rangle} &= \exp\left\{-\int_0^t dt_1 \int_0^{t_1} dt_2 \langle \Omega(t_1)\Omega(t_2)\rangle\right\} \\ &= \exp\left\{-\Delta^2 \int_0^t d\tau (t - \tau) e^{-\gamma\tau}\right\} \\ &= \exp\left\{-\frac{\Delta^2}{\gamma^2}(e^{-\gamma t} - 1 + \gamma t)\right\} \end{aligned} \tag{35}$$

The Gaussian assumption yields the first equality. Assumption (25) is used in the second expression on the right-hand side. Thus the line shape function $I(\omega)$ can also be written as

$$I(\omega) = \frac{1}{\pi} \operatorname{Re} \int_0^{\infty} \exp\left\{-\frac{\Delta^2}{\gamma^2}(e^{-\gamma t} - 1 + \gamma t) - i\omega t\right\} dt \tag{36}$$

It should be mentioned that the line shape function $I(\omega)$ can also be

expressed as a continued fraction[9]; namely

$$I(\omega)=\frac{1}{\pi}\cfrac{1}{i\omega+\cfrac{\Delta^2}{i\omega+\gamma+\cfrac{2\Delta^2}{i\omega+2\gamma+\cdots}}} \tag{37}$$

This is most convenient for computer calculation.

Figure 1 shows the line shape for the two-state-jump modulation case.

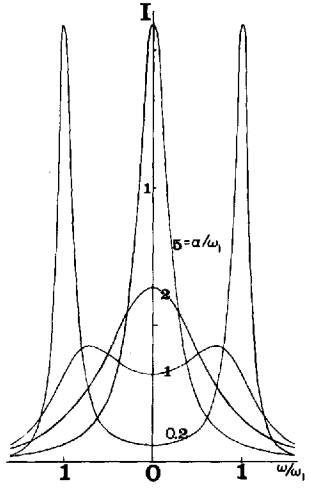

Fig. 1. Line shape for the two-state-jump model. The frequencies are in units of ω_1, $\pm\omega_1$ being the frequencies of the two states. The numbers on curves indicate the modulation rate, $\alpha=\gamma/\omega_1$.

Intensity curves $I(\omega)$ are plotted against the frequency measured in units of ω_1 for various values of the parameter

$$\alpha=\gamma/\omega_1$$

In slow modulation,

$$\alpha\ll 1$$

the shape function is peaked around two resonance frequencies, ω_1 and $-\omega_1$, the width of each line being $\gamma/2$. When the modulation becomes faster, the peaks are broadened, approach each other, then merge into a single peak, and finally, in the fast modulation limit,

$$\alpha\gg 1$$

a sharp Lorentzian line appears at the center.

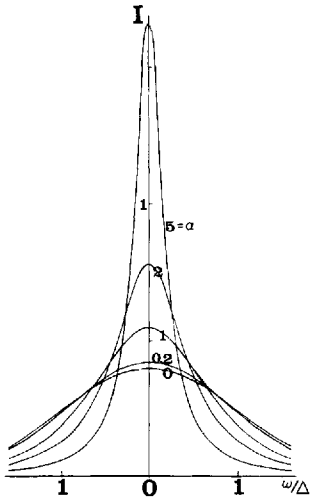

Fig. 2. Line shape for the Gaussian-Markovian modulation, for modulation rates, $\alpha = 5, 2, 1, 0.2, 0$.

Figure 2 is the line shape for a Gaussian modulation. In the slow modulation limit,

$$\alpha = \gamma/\Delta \ll 1$$

the line is Gaussian, reflecting the distribution of Ω itself. In the fast modulation limit,

$$\alpha \gg 1$$

the line becomes Lorentzian with the width equal to $\Delta^2\gamma$. Between the two limits, the line shape shows *motional narrowing* as the modulation rate increases.

IV. COLLAPSE OF AN NMR MULTIPLET

The line shape of an NMR spectrum often shows remarkable changes when physical or chemical conditions are varied. Narrowing of a doublet represented by Eq. (24) is observed in many cases. Here we consider a slightly more complicated example of a proton resonance coupled with another nucleus through an interaction of the type,

$$J\mathbf{I}_p \cdot \mathbf{I} \tag{38}$$

where $\mathbf{I}_p$ is the proton spin and $\mathbf{I}$ is the spin of a coupled nucleus.[10, 11] In the presence of a constant magnetic field, the proton resonance spectrum

consists of a multiplet of $2I+1$ lines corresponding to the $2I+1$ states ($m=-I,\ldots,I$) of the spin I. If there exists a relaxation process, for example, a quadrupole coupling of I to the lattice, transitions will be induced among the states causing random jumps of the effective field $JI_z = Jm$ acting on the proton, and hence jumps of the resonance frequencies

$$\Omega_m = mJ/\hbar,\ m=-I,\ldots,I$$

Under the assumption of quadrupole relaxation, the form of the transition matrix in Eq. (1) is easily determined. The transition rate is characterized by the time constant

$$\alpha = (e^2qQ)^2\tau_c/\hbar^2$$

where e^2qQ is the magnitude of the quadrupole interaction and τ_c is its correlation time. Thus the line shape function $I(\omega)$, Eq. (18), is obtained by first solving the equation[12]

$$i(\omega-\Omega_m)X_m - \sum_{m'}\Gamma_{mm'}X_{m'} = 1 \tag{39}$$

and then by computing the expression,

$$I(\omega) = \frac{1}{\pi}\,\mathrm{Re}\sum_{m=-I}^{I}\frac{X_m(\omega)}{(2I+1)} \tag{40}$$

The modulation of the proton field is *slow* if

$$\alpha = h\gamma/J = (e^2qQ)^2\tau_c/Jh \ll 1$$

and is *fast* if

$$\alpha \gg 1$$

In the first case, the multiplet skeleton is preserved. As the parameter α increases, the multiplet collapse proceeds. In Figures 3 and 4 there are shown examples of computed curves and the corresponding spectra

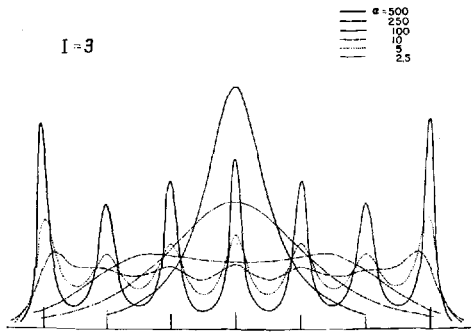

Fig. 3. Collapse of an NMR septet, calculated for increasing values of the parameter α.

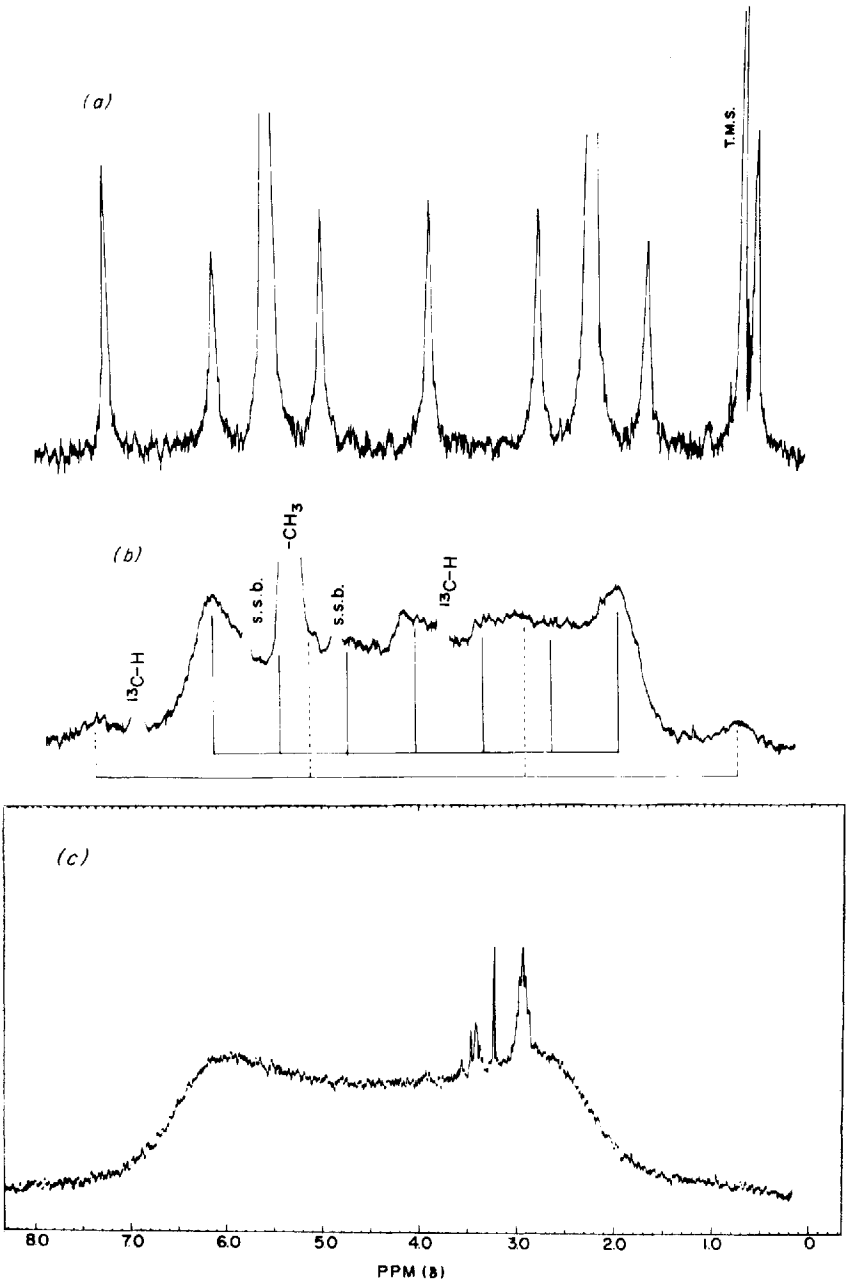

Fig. 4. Observed proton septet spectra, for hydrogen atoms coupled with ^{10}B in (*a*) lithium borohydride, (*b*) trimethylamineborane, and (*c*) *N*-tri(methyl-d_3) borazine.

observed for protons coupled to ^{10}B in various compounds[13]; Figure 4*a* is an observation for lithium borohydride, Figure 4*b* for trimethylamina-borane, and Figure 4*c* for *N*-tri(methyl-d_3) borazine. In the first and second examples, ^{11}B—H quartets are superposed, and in the third case there is a group of impurity peaks. The ^{10}B—H septets in these three observations correspond to the calculated curves with $\alpha = 2.5$, 10, and 100, respectively.

V. LOW FIELD SPIN RESONANCE[9,14]

In a condensed system, the local field on a magnetic spin can be considered as a stochastic process. If a constant magnetic field H_0 is present in the z-direction, the local field $\mathbf{H}(t)$ can be decomposed into the parallel and the perpendicular components. If the constant field is strong enough, this decomposition is meaningful; the parallel component $H_z(t)$ causes adiabatic shifts of the resonance frequency, whereas the perpendicular component $H_\perp(t)$ produces nonadiabatic effects.[6] If only the adiabatic part is considered, the problem is just that treated in Section II, and if the local field $H_z(t)$ is assumed to be a Gaussian process, then the Gaussian model of Section III can be adopted.

When the constant field is weak and the fluctuating field is comparable to or even larger than the constant field, the above decomposition becomes meaningless. There is no way of distinguishing between the adiabatic and nonadiabatic effects. In order to obtain an understanding of this rather complex situation, we have examined a stochastic model,[14] extending the theory in Section II. The stochastic equation of motion of a spin in a random local field is written as

$$\dot{\mathbf{m}}(t) = (\boldsymbol{\Omega}_0 + \boldsymbol{\Omega}(t)) \times \mathbf{m} \tag{41}$$

where $\boldsymbol{\Omega}_0$ represents the constant magnetic field and $\boldsymbol{\Omega}(t)$ the random field, the gyromagnetic ratio being included. The corresponding stochastic Liouville equation takes the form,

$$\frac{\partial}{\partial t} W(\mathbf{m}, \lambda, t) = -(\boldsymbol{\Omega}_0 + \boldsymbol{\Omega}) \times \mathbf{m} \frac{\partial}{\partial \mathbf{m}} W + \Gamma W \tag{42}$$

where, as before, λ is the set of random variables required to complete $\boldsymbol{\Omega}(t)$ to a Markovian process and Γ is its evolution operator, a matrix with respect to the variables λ. The equilibrium distribution $P_0(\lambda)$ is characterized by

$$\begin{aligned} &\Gamma|0) = 0, \qquad (\lambda|0) \equiv P_0(\lambda) \\ &(0|\Gamma = 0, \qquad (0|\lambda) \equiv 1, \qquad (0|0) \equiv \sum_\lambda P_0(\lambda) = 1 \end{aligned} \tag{43}$$

Now the expectation of the moment at the time t is defined by

$$\mathbf{M}(\lambda, t) = \int W(\mathbf{m}, \lambda, t)\mathbf{m}\, d\mathbf{m} \tag{44}$$

this quantity obeys the equation,

$$\frac{\partial \mathbf{M}(\lambda, t)}{\partial t} = \{(\boldsymbol{\Omega}_0 + \boldsymbol{\Omega})x + \Gamma\}\mathbf{M} \tag{45}$$

with the initial condition,

$$\mathbf{M}(\lambda, 0) = \mathbf{m}' P_0(\lambda). \tag{46}$$

More explicitly we write Eq. (45) as

$$\left(\frac{\partial}{\partial t} - \Gamma\right)M_x + (\Omega_z + \omega_0)M_y - \Omega_y M_z = 0$$

$$-(\Omega_z + \omega_0)M_x + \left(\frac{\partial}{\partial t} - \Gamma\right)M_y + \Omega_x M_z = 0$$

$$\Omega_y M_x - \Omega_x M_y + \left(\frac{\partial}{\partial t} - \Gamma\right)M_z = 0, \tag{47}$$

where we have chosen the z axis along the constant magnetic field and denoted the corresponding Zeeman frequency by ω_0. Equation (47), with the initial condition of Eq. (46), can be solved by Laplace transformation. The line shape functions are found by inserting the result into a form Eq. (18) suitably generalized to apply to this case. The longitudinal and the transverse spectral functions are then given by

$$I_{zz}(\omega) = \frac{1}{\pi} \operatorname{Re} \int d\boldsymbol{\Omega} f_{zz}(\boldsymbol{\Omega}, \omega) \tag{48}$$

and

$$I_{xx}(\omega) = \frac{1}{\pi} \operatorname{Re} \int d\boldsymbol{\Omega} f_{xx}(\boldsymbol{\Omega}, \omega) \tag{49}$$

where $f_{zz}(\boldsymbol{\Omega}, \omega)$ and $f_{xx}(\boldsymbol{\Omega}, \omega)$ are determined by the equations,

$$\left\{i\omega - \Gamma + \tfrac{1}{2}(\Omega_x + i\Omega_y)\frac{1}{i\omega - \Gamma + i(\Omega_z + \omega_0)}(\Omega_x - i\Omega_y)\right.$$

$$\left. + \tfrac{1}{2}(\Omega_x - i\Omega_y)\frac{1}{i\omega - \Gamma - i(\Omega_z + \omega_0)}(\Omega_x + i\Omega_y)\right\} f_{zz}(\boldsymbol{\Omega}, \omega) = P_0(\boldsymbol{\Omega}) \tag{50}$$

and

$$\left\{i\omega - \Gamma + \tfrac{1}{2}(\Omega_y + i(\Omega_z + \omega_0))\frac{1}{i\omega - \Gamma + i\Omega_x}(\Omega_y - i(\Omega_z + \omega_0))\right.$$
$$\left. + \tfrac{1}{2}(\Omega_y - i(\Omega_z + \omega_0))\frac{1}{i\omega - \Gamma - i\Omega_x}(\Omega_y + i(\Omega_z + \omega_0))\right\} f_{xx}(\mathbf{\Omega}, \omega)$$
$$= P_0(\mathbf{\Omega}) \quad (51)$$

If we assume a Gaussian-Markovian process for the random field, the evolution operator in Eq. (42) becomes

$$\Gamma = \frac{\partial}{\partial \mathbf{\Omega}}\left(\Delta^2 \frac{\partial}{\partial \mathbf{\Omega}} + \mathbf{\Omega}\right) \quad (52)$$

which is a three-dimensional version of the expression (26); Eqs. (48)–(51) are generalizations of Eqs. (30) and (31). Here we summarize qualitative results of the calculation. Some examples of calculated line shapes are shown in Figures 5–7. Figure 5 shows zero-field resonance curves. The

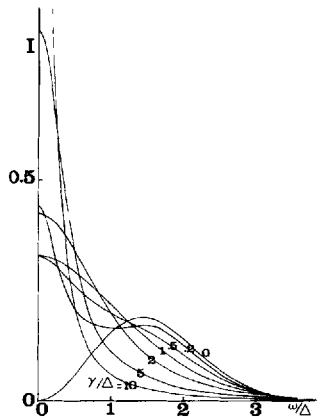

Fig. 5. Zero-field spin resonance spectra for $\gamma/\Delta = 10, 5, 2, 1, 0.5, 0.2, 0$.

curve marked by ∞ is the static modulation limit ($\gamma = 0$) and consists of a delta function at the origin and a broad curve which reflects the distribution of the random field. In the narrowed limit of large γ, the two branches merge into a single peak around the center. For intermediate values of γ, the resonance is broad and may have two peaks or an extended shoulder. Figure 6 shows the longitudinal resonance for the case $\omega_0/\Delta = 3$. General behavior is similar to that of zero-field resonance. The main peak is at the

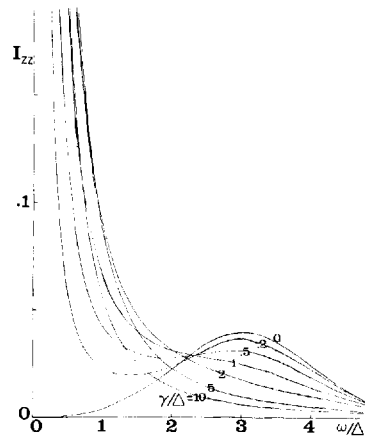

Fig. 6. Longitudinal spin resonance spectra, $I_{zz}(\omega)$, for $\omega_0/\Delta = 3$ and $\gamma/\Delta = 10, 5, 2, 1, 0.5, 0.2, 0$.

origin and the satellite is around $\omega/\Delta \sim 3$. The satellite peak disappears as the modulation becomes faster. The transverse resonance curves are shown in Figure 7 for $\omega_0/\Delta \sim 1$. There, the main peak is around the Zeeman

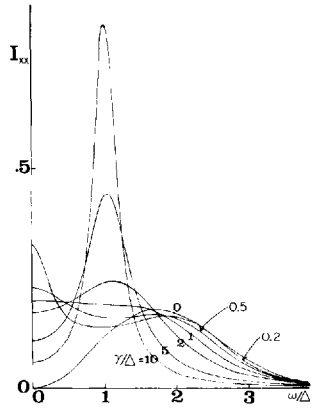

Fig. 7. Transverse spin resonance spectra, $I_{xx}(\omega)$, for $\omega_0/\Delta = 1$ and $\gamma/\Delta = 10, 5, 2, 1, 0.5, 0.2, 0$.

frequency, around $\omega/\Delta \sim 1$ in the figure, while the satellite resonance is found near the center. The main peak grows as the modulation becomes faster, whereas the satellite peak decreases and finally disappears.

VI. SPECTRUM OF EXCITATIONS TO A DOUBLET WITH A RANDOM MODULATION[15]

Consider an atomic system with a singlet ground state a and doublet excited states b, the members of which are denoted by b_1 and b_2. The Hamiltonian for the states (b_1, b_2) is assumed to be

$$H(t) = \begin{bmatrix} \omega_0 & \Omega(t) \\ \Omega(t) & -\omega_0 \end{bmatrix} \tag{53}$$

where the off-diagonal element Ω is supposed to be a random process with a vanishing average, i.e.,

$$\langle \Omega \rangle = 0$$

This random modulation may be caused, for example, by a coupling of the electronic states to the lattice vibrations. The Hamiltonian for the state a is just a constant and may be set, for convenience, to zero.

Now we ask the excitation spectrum from the state a to the excited states. The (un-normalized) shape function is given by

$$I(\omega) = \frac{1}{\pi} \mathrm{Re} \int_0^\infty dt \exp\left[-i\omega t\right] \langle (a|\mu(0)\mu(t)|a) \rangle_{\mathrm{av}} \tag{54}$$

Here μ is the dipole moment with the matrix elements,

$$(a|\mu|b_1) = (b_1|\mu|a) = \mu_1$$

$$(a|\mu|b_2) = (b_2|\mu|a) = \mu_2$$

Now, the Heisenberg equation of motion for $\mu(t)$,

$$\dot{\mu}(t) = \frac{1}{i}(\mu H - H\mu) \tag{55}$$

takes the form,

$$(b'|\dot{\mu}(t)|a) = i \sum_{b''} (b'|H(t)|b'')(b''|\mu(t)|a)$$

We introduce here the transformation matrix $v(t)$ defined by

$$(b'|\mu(t)|a) = \sum_{b''} (b'|v(t)|b'')(b''|\mu|a) \tag{56}$$

Then the matrix $v(t)$ obeys the equation of motion,

$$\dot{v}(t) = iH(t)v(t) \tag{57}$$

with the initial condition

$$v(0) = \mathbf{1}$$

Equation (57) is the stochastic equation of motion for $v(t)$, in which the matrix element $\Omega(t)$ is a random process. This is similar to Eq. (2). This may be written as a stochastic Liouville equation in the form

$$\frac{\partial}{\partial t} W(v, \lambda, t) = -\sum_{jl} \frac{\partial}{\partial v_{jl}} i(H(\Omega)v)_{jl} W + \Gamma W \tag{58}$$

where Γ is the evolution operator for the set of random variables λ that complete Ω to a Markovian process. Corresponding to Eq. (14), we have the equation

$$\dot{V}(t) = iH(\Omega)V + \Gamma V \tag{59}$$

where the matrix $V(t)$ is defined by the equation,

$$V_{jl}(t) = \int \cdots \int (\Pi\, dv_{mn}) v_{jl}(v, \lambda \,|W(t)|\, v', \lambda'), \qquad v' = \mathbf{1} \tag{60}$$

which is a conditional expectation of the matrix $v(t)$. The line shape function (54) is then written as

$$I_c\omega) = \frac{1}{\pi} \operatorname{Re} \int_0^\infty dt \exp\,[-i\omega t]\langle 0| \sum_{jl} \mu_j V_{jl}(t)\mu_1 |0\rangle \tag{61}$$

or as

$$I(\omega) = \frac{1}{\pi} \operatorname{Re} \sum_{jl} \mu_j \langle 0| V_{jl}[i\omega] |0\rangle \mu_l \tag{62}$$

where $V[i\omega]$ is the Laplace transform of $V(t)$; it obeys the equation

$$(s - iH + \Gamma)V[s] = \mathbf{1} \tag{63}$$

Remember that the vector space for the equation is the direct product of two spaces, the space of the electronic states and the space of the random variables λ. It is obvious that the above equation can be applied not only to a doublet but to any multiplet as long as the ground state is a singlet.

Let us now consider the case where the dipole moment couples only one of the excited states, say b_1, to the ground state; namely

$$\mu_1 \neq 0, \quad \text{and} \quad \mu_2 = 0 \tag{64}$$

As another simplification, we assume that the modulation Ω takes only two values $\pm\omega_1$. This is a generalization of the two-state jump model mentioned in Section III. The basic space for Eq. (63) is then 2×2 dimension. It is convenient to write Eq. (63) as

$$\begin{aligned} (s - i\omega_0)\xi - i\Omega\eta + \Gamma\xi &= \xi_0 \\ (s + i\omega_0)\eta - i\Omega\xi + \Gamma\eta &= \eta_0 \end{aligned} \tag{65}$$

where ξ is the component for the state b_1 and η that for the state b_2, each being vectors with two components corresponding to $\Omega = \pm\omega_1$. Solving Eq. (65) for ξ by setting $\xi_0 = 1$, $\eta_0 = 0$, we obtain the element $V_{11}[i\omega]$ in the form

$$V_{11}[i\omega] = \frac{1}{i(\omega+\omega_0) - \Gamma + \Omega \dfrac{1}{i(\omega-\omega_0)-\Gamma}\Omega} \tag{66}$$

where Ω and Γ are operators in the space of the variables λ. For our two-state-jump model they are given by Eqs. (19) and (20). By the assumption (64), the expression (62) is easily found to be

$$I(\omega) = \frac{1}{\pi}\frac{\gamma\omega_1{}^2}{(\omega_0{}^2 + \omega_1{}^2 - \omega^2)^2 + (\omega-\omega_0)^2\gamma^2} \tag{67}$$

In the static limit ($\gamma = 0$), which may usually be called the adiabatic case, the perturbation Ω is constant ($\pm\omega_1$) and the excited states are split into a doublet with the energies

$$\varepsilon = \pm(\omega_0{}^2 + \omega_1{}^2)^{1/2}$$

The excitation spectrum consists of two sharp lines. The lower line at $\omega = -(\omega_0{}^2 + \omega_1{}^2)^{1/2}$ borrows its intensity from the upper line thanks to the mixing caused by the perturbation.

When the modulation becomes faster, i.e., γ increases, the adiabatic approximation becomes worse. In the first stage, each line will broaden; at the same time the lower line loses its intensity. If the modulation is very fast, the random modulation is averaged out, and the spectrum is narrowed to a sharp line at the unshifted position with the full intensity. In this problem, however, there are essentially two parameters, ω_1/ω_0 and γ/ω_0, which determine the condition for narrowing, so that the narrowing process is not simple. If γ is small and the condition

$$4\left(\frac{1}{3}\left(1 + \frac{\omega_1{}^2}{\omega_0{}^2}\right) + \frac{1}{6}\frac{\gamma^2}{\omega_0{}^2}\right)^{3/2} > \frac{\gamma^2}{\omega_0{}^2} \tag{68}$$

is satisfied, two peaks are noticeable. As γ becomes larger and the sign of the above inequality is reversed, the spectrum is singly peaked, but there remains a long shoulder extending to lower frequencies. As γ becomes even larger, this shoulder disappears. Figure 8 gives a few examples of the calculated spectra.

Similar calculations can be made for the continuous modulation case. If the process $\Omega(t)$ is Gaussian and Markovian, the operator Γ takes the

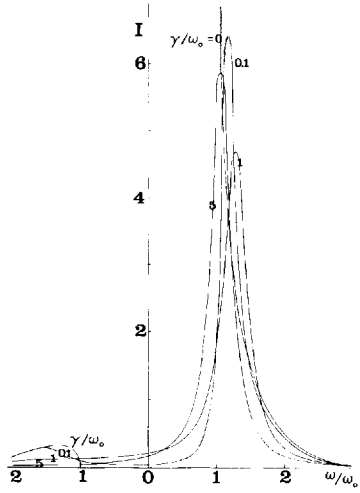

Fig. 8. Excitation spectra to a doublet modulated by a two-state-jump process; for $\omega_1/\omega_0 = 1$ and $\gamma/\omega_0 = 5, 1, 0.1, 0$.

form given by Eq. (26). The line shape function is given by Eq. (62), where we insert, for example, Eq. (66) and the equilibrium state vectors (27). The line shape functions can thus be calculated by using transformations similar to those used in Section III.

Figure 9 shows some examples of the spectrum. In the static limit, the

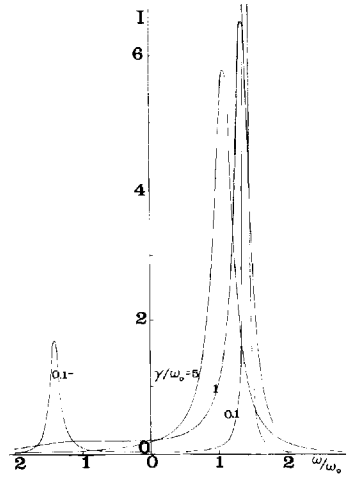

Fig. 9. Excitation spectra to a doublet modulated by a Gaussian-Markovian process; for $\omega_1/\omega_0 = 1$ and $\gamma/\omega_0 = 5, 1, 0.1, 0$.

spectrum consists of two branches; one in the region $\omega > \omega_0$ having an infinite peak at ω_0 and the other in the region $\omega < -\omega_0$. This static spectrum is an image of the Gaussian distribution of Ω. As the modulation becomes faster, this adiabatic picture loses its meaning. The process of narrowing is qualitatively the same as that in the two-state-jump model given by Eq. (67).

VII. RANDOM STARK MODULATION OF A HYDROGEN ATOM[16]

In a gaseous plasma, the electric field fluctuates in space and time as the ions and electrons move in a complicated fashion. If a hydrogen atom is put into such a plasma, it serves as a probe to detect this fluctuating field. The $2s$ and $2p$ states of a hydrogen atom are nearly degenerate, but they are split by the Stark effect in the presence of an electric field. The absorption or emission spectrum due to transitions between the $1s$ and $2p$ levels of a hydrogen atom is thus broadened by the random fluctuation of the electric field. This is a well-known example of pressure broadening,[17,18] but a complication in this problem is that the modulation of the electric field affects not only the spacing of split energy levels but also the direction of the quantization axis. Thus the simple-minded adiabatic approach cannot be used.

From our point of view, this problem is, however, quite the same as that treated in the previous section. We take the excited states to be the four states, $2s$, $2p_x$, $2p_y$, and $2p_z$. The Hamiltonian in this subspace is written as

$$H(t) = \begin{pmatrix} 0 & \Omega_x & \Omega_y & \Omega_z \\ \Omega_x & 0 & 0 & 0 \\ \Omega_y & 0 & 0 & 0 \\ \Omega_z & 0 & 0 & 0 \end{pmatrix} \tag{69}$$

where

$$\boldsymbol{\Omega} = -\mu' \mathbf{E}(t) \tag{70}$$

is the electric field times the factor μ' representing the matrix elements of the dipole moment; namely

$$\mu' = (2s|\,\mu_x\,|2p_x) = (2s|\,\mu_y\,|2p_y) = (2s|\,\mu_z\,|2p_z)$$

If the spectrum is observed for radiation linearly polarized in the x direction, the dipole moment in Eq. (54) is its x component, μ_x, which has a matrix element between $1s$ and $2p_x$ states. Thus, Eq. (61) now reads

$$I(\omega) = \frac{1}{\pi} \operatorname{Re} (0|\, V_{xx}[i\omega]\,|0) \tag{71}$$

where the suffix x means $2p_x$. Instead of Eq. (62), it is more convenient to solve the equation,

$$(i\omega - iH(\mathbf{\Omega}) + \Gamma)\Psi = \Psi_0$$

by using the expansion

$$\Psi = U\,|2s) + X\,|2p_x) + Y\,|2p_y) + Z\,|2p_z)$$

and by imposing the initial condition

$$\Psi_0 = |2p_x)$$

When the components, U, Y, and Z are eliminated, we obtain the solution for X, which is identified with the element $V_{xx}[i\omega]$ in Eq. (71). In this way, the line shape function is found to be

$$I(\omega) = \frac{1}{\pi}\,\mathrm{Re}\,(0|\,\frac{1}{i\omega}\left\{1 - \mathbf{\Omega}\,\frac{1}{i\omega + \Gamma - \mathbf{\Omega}\,\dfrac{1}{i\omega + \Gamma}\,\mathbf{\Omega}}\,\mathbf{\Omega}\right\}|0) \tag{72}$$

where $(0|$ and $|0)$ are, as before, the equilibrium bra and ket states for the operator Γ.

The hardest part of the problem is the determination of the process $\mathbf{E}(t)$ or more precisely the reduction of the complete Markovian process to a tractable process. The simplest approximation to the equilibrium distribution is the Holtzmark distribution which ignores the interaction between ions and electrons.[19] Corrections can be made in successive approximations. Much less is known, however, about the temporal behavior of $\mathbf{E}(t)$. For practical purposes, an extreme limit is commonly assumed.[17] The motion of ions is considered to be slow and the electric field $\mathbf{E}_i$ produced by ions is regarded as *static*. On the other hand, electrons are moving very fast so that the electric field $\mathbf{E}_e$ produced by electrons changes very *fast*. Therefore, this part of the electric field is treated as a perturbation causing transition between the quantum levels of a hydrogen atom split by the static field $\mathbf{E}_i$. Strictly speaking, this is not very accurate, because there are also slow components in the electron field $\mathbf{E}_e(t)$ which cannot be treated in the extreme narrowing approximation.

Here, we shall not go any further into the analysis of this sort. Instead, we show a few examples of line shape functions calculated by Eq. (72) for the Gaussian models, which are characterized by the operator Γ given by Eq. (52). The Gaussian models are not very adequate for the electric field in a plasma, as is seen by the fact that the Holtzmark distribution is far from Gaussian. Still, it may serve to give one an understanding of the

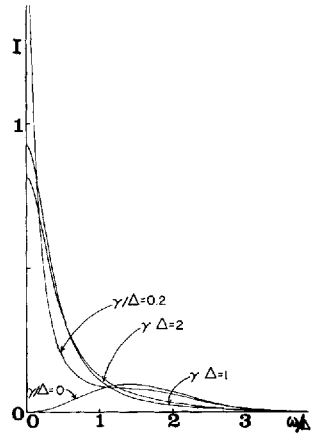

Fig. 10. Random Stark broadening of a hydrogen atom in a Gaussian random field with different modulation speeds ($\gamma/\Delta = 2, 1, 0.2, 0$).

general character of our problem. Figure 10 shows the spectral distribution for a few values of the parameter γ/Δ corresponding to different degrees of narrowing. In the slow modulation case, there exist a sharp peak at the center and two broad side peaks. These side peaks are the image of the distribution of the electric field strength. As the modulation becomes faster, the spectrum merges into a single peak. In Figure 11, two kinds of electric fields are assumed; one is a static field corresponding to the ion field, and the other is a nonstatic field due to the electrons. Both fields are assumed

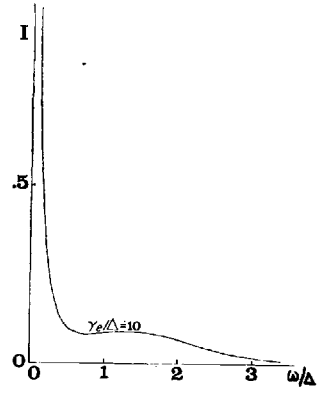

Fig. 11. Random Stark broadening of a hydrogen atom in the superposition of a static Gaussian field E_i and a fluctuating Gaussian field E_e. The modulation rate of E_e is as large as $\gamma_e/\omega = 10$.

to be Gaussian with the same variance. The modulation of electron field is fast, the parameter γ/Δ being chosen as 10. The static field determines the structure, a central peak and two side peaks, which are broadened by electron impacts.

VIII. LINE SHAPE OF MÖSSBAUER SPECTRA

Let us consider, for example, the Mössbauer spectra of ^{57}Fe in a solid. A ^{57}Fe nucleus may feel spin interactions with its neighboring nuclei, or a quadrupole interaction with the electric field gradient produced by the motion of surrounding ions. In the process of gamma-ray emission, these interactions give rise to perturbations of the excited nuclear states as well as to the ground states. The line shape of a Mössbauer multiplet can be treated by the present theory if these interactions are considered as random modulations. The line shape function is now given by

$$I_c\omega) = \frac{1}{\pi} \operatorname{Re} \int_0^\infty dt \exp\left[-i\omega\right] \sum_{a'} \sum_{b'} \langle (a'|\,\mu\,|b')(b'|\,\mu(t)\,|a')\rangle_{\text{av}} \tag{73}$$

where μ is the dipole moment for the gamma-ray transition. We ignore the natural width in this expression because we shall mostly be interested in broadenings larger than the natural widths. But it may be included, if necessary.

The motion of the dipole moment obeys Eq. (56), which is written as

$$(b'|\,\mu(t)\,|a') = i\left\{\sum_{b''} (b'|\,H(t)\,|b'')(b''|\,\mu(t)\,|a') - \sum_{a''} (b'|\,\mu(t)\,|a'')(a''|\,H(t)\,|a')\right\} \tag{74}$$

As in Eq. (57), we introduce the transformation matrix $v(t)$, defined by

$$(b'|\,\mu(t)\,|a') = \sum_{a'} \sum_{b''} (a'b'|\,v(t)\,|a''b'')(b''|\,\mu\,|a'') \tag{75}$$

with the initial condition,

$$v(0) = \mathbf{1}$$

Then we find the equation of motion,

$$(a'b'|\,\dot{v}(t)\,|a''b'') = i\left\{\sum_{b'''} (b'|\,H(t)\,|b''')(a'b'''|\,v(t)\,|a''b'') - \sum_{a'''} (a'''|\,H(t)\,|a')(a'''b'|\,v(t)\,|a''b'')\right\} \tag{76}$$

or

$$\dot{v}(t) = i\bar{H}(t)v(t) \tag{77}$$

where the modified Hamiltonian $\bar{H}(t)$ is defined by the explicit expressions in Eq. (76).

The stochastic equation of motion of $v(t)$, Eq. (77), can be transformed into a stochastic Liouville equation of the type Eq. (7) if a Markovian process can be properly defined to generate the process of $H(t)$. Then we again obtain Eq. (63) for the conditional expectation $V(t)$ defined by Eq. (60). The line shape function is then given by

$$I(\omega) = \frac{1}{\pi} \mathrm{Re} \sum_{a'a''} \sum_{b'b''} (a'| \mu |b')(b''| \mu |a'')(0|(a'b'| V[i\omega] |a''b'')|0) \quad (78)$$

Recently, the stochastic models for the Mössbauer line shape problem have been discussed by several investigators.[20] Such models can be treated in a systematic way as we have described in the above. For example, in a ^{57}Fe nucleus, the spin in the excited state is $I = \frac{3}{2}$ and that in the ground state is $I = \frac{1}{2}$, so that the Hamiltonian is a 6×6 matrix. If a two-state-jump model is adopted, the dimension of the matrix equation, Eq. (63), is $6 \times 2 = 12$. If the stochastic operator is of the type (26), then the equation is a set of six differential equations. These equations can be solved, if necessary, by computers to yield the line shape functions for various values of parameters.

Figure 12 shows two examples of line shape functions for Fe Mössbauer spectra calculated by Tjon and Blume using a similar method.[21] It is assumed that a quadrupole interaction splits the excited state levels and a random hyperfine field is superposed on this. For simplicity the hyperfine field is assumed to take only two values. Figure 12*a* is the case where the hyperfine field is along the direction of the electric field gradient, and Figure 12*b* is the case where it is perpendicular. It is interesting to note that in the intermediate narrowing the spectrum may appear singly peaked, but is again split into two peaks in the extreme narrowing limit.

IX. CONCLUDING REMARKS

In the preceding sections, we have tried to show that our theory has a very wide range of applicability to various physical and chemical problems. The theory is essentially based upon the two equations, (16) and (18). In addition to classical examples such as treated in Sections III–V, it can, with suitable generalizations, be applied to quantum-mechanical systems as discussed in the later sections. In a previous paper of the author,[3] an analysis was made on the equation of the type (16) in order to investigate the structure and some general properties of the inverse operator (17). This analysis showed, in particular, how the narrowing occurs when the

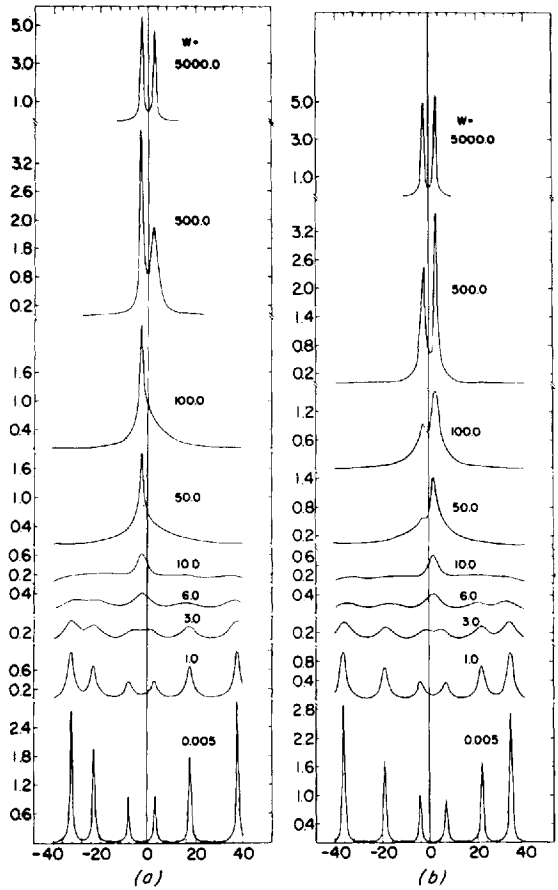

Fig. 12. Mössbauer line shape of ^{57}Fe in a constant eqQ field and a random hyperfine field assumed to be a two-state-jump process for different values of the jump rate W. (*a*) The random hyperfine field along the eqQ axis. (*b*) Perpendicular to the eqQ axis. (Calculations of Tjon and Blume.)

random modulation becomes fast. In the limit of fast modulation, extreme narrowing is realized and the line shape approaches a Lorentzian form. Here we do not repeat this analysis, but only mention that such an analysis can be extended to more general cases where the operators in Eq. (16) are replaced by more complicated ones, as for example, those in Sections V–VIII. It should be kept in mind, however, that, for computational purposes, the basic equation (Eq. (18)), is convenient; it may be that some transformation of the equations is useful, but elaborate manipulation of the equations is not necessarily required.

The strength of the theory has been acquired by making a sacrifice. As already mentioned in Section II, we made the simplification that the evolution operator Γ is independent of x, or the motion of the system under observation; in other words, the reaction of the system to its environment is ignored. This obviously limits the range of applicability of the theory, although it still covers a very large area. A difficulty arising from this simplification is that our theory, in its present form, does not satisfy the requirement that the system approaches equilibrium with its environment in the course of time. For example, consider a spin in a fluctuating local field. It may be assumed to satisfy the equation of motion, Eq. (41). Starting from a given state, the stochastic process of the spin should approach a stationary state which represents thermal equilibrium if the spin is in contact with a large heat bath. This requirement imposes some conditions which must be satisfied by the fluctuating field. In the simple theory of Brownian motion, based on the familiar Langevin equation or its generalization,[22] such conditions appear as the fluctuation–dissipation theorem, which gives a relation between the friction term and the random force. In the spin problem, if the forces on the spin are only the fluctuating local field appearing in the equation of motion, the situation is not so simple as this. It is possible to introduce a friction term into the equation of motion in order to guarantee the approach to equilibrium,[23] but this would not be a final solution of the problem. One side of the problem is related to the generalization of the Brownian motion theory to nonlinear systems, which is discussed in this volume by Professor van Kampen. The problem may be even deeper when we consider quantum-mechanical systems. How can we construct a general theory of Brownian motion of a nonlinear quantum-mechanical system which is in contact with a heat bath and react to external perturbations? To my knowledge this is an unsolved question.

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