Stochastic Theory of Line Shape: Generalization of the Kubo-Anderson Model*

M. BLUME
Physics Department, Brookhaven National Laboratory, Upton, New York 11973

(Received 12 June 1968)

A general solution is presented for the line shape of radiation emitted by a system whose Hamiltonian jumps at random as a function of time between a finite number of possible forms $V_1, V_2, \cdots, V_n$. The solution is valid even if these forms do not commute with one another ($[V_i, V_j] \neq 0$), so that the Hamiltonian need not commute with itself at different times: $[\mathcal{H}(t), \mathcal{H}(t')] \neq 0$. This is a generalization of the Kubo-Anderson model in which it is assumed that the Hamiltonian does commute at different times. The treatment given here thus extends this adiabatic or random-frequency-modulation theory to include the nonadiabatic effects of transitions induced by the fluctuating Hamiltonian. The solution involves the inversion of a matrix and is similar to Sack's solution of the Kubo-Anderson model. The matrix found in the present case is labeled by quantum-mechanical as well as stochastic indices, and it reduces to the form found by Sack when the possible forms of the Hamiltonian commute with one another. Numerical evaluation of line shapes can be accomplished easily with a computer, and in the simplest cases analytical expressions can be found. The applicability of the theory to NMR and Mössbauer line shapes and to perturbed angular correlations is discussed. A specific example of the NMR line shape of a spin-$\frac{1}{2}$ nucleus in a fixed magnetic field and a fluctuating field perpendicular to it is considered in detail as an illustration of the utility of the derived expressions. The solution uses the Liouville-operator notation and this is discussed in an Appendix.

I. INTRODUCTION

THE stochastic theory of motional narrowing as developed by Kubo[1] and Anderson,[2] among others, has been widely applied in the calculation of magnetic resonance and Mössbauer line shapes. According to this theory the frequency of the system (i.e., resonant spin or Mössbauer nucleus) changes at random from one to another of a finite number of possible frequencies, and the line shape may be calculated as a function of the rates of transition between these frequencies. A detailed and elegant derivation of the theory is given by Abragam.[3] An example of the type of system treated is given by the case of a nucleus in a randomly varying magnetic field which jumps between the values $\pm h$ along the z axis. The Hamiltonian for such a system is[4,5]

$$\mathcal{H}(t) = g\mu h I_z f(t), \tag{1}$$

where $f(t)$ is a random function of the time, which takes on the two values ± 1. The Larmor frequency of a nucleus would then jump between the values $\pm g\mu h$ as $f(t)$ jumped between its two possible values. It should be noted that the Hamiltonian (1) has a specific property that is essential to the development of the Kubo-Anderson theory, namely $\mathcal{H}(t)$ commutes with itself at different times: $[\mathcal{H}(t), \mathcal{H}(t')] = 0$. This means that it is possible to diagonalize $\mathcal{H}$ at some instant of time and find that it then remains diagonal at later times. The time variation of $\mathcal{H}(t)$ will then not cause any transitions between the eigenstates of $\mathcal{H}$. The only effect of this variation will be to cause the frequencies of the eigenstates to change with time. For this reason the Kubo-Anderson theory is referred to as the adiabatic, or random-frequency-modulation theory of motional narrowing. It is essentially a classical theory, since the quantum-mechanical problem of the diagonalization of the Hamiltonian is distinct from the problem of the evaluation of the stochastic averages, so that quantum mechanics enters only in the determination of the possible frequencies allowed to the system.

There are circumstances in which this model is inadequate, because of the importance of nonadiabatic effects. For example, if a fixed magnetic field H along the positive x axis is added to Eq. (1),

$$\mathcal{H}(t) = g\mu H I_x + g\mu h I_z f(t), \tag{1'}$$

we find that $[\mathcal{H}(t), \mathcal{H}(t')] \neq 0$. The fluctuating term $g\mu h I_z f(t)$ is now capable of inducing transitions between the eigenstates of I_x. It is also clear that the stochastic and quantum-mechanical aspects of the problem are no longer separate. This is seen by considering the limiting cases of slow and rapid fluctuation. If the values ± 1 of $f(t)$ are equally probable and the rate of transition between them is extremely rapid, the fluctuating term will average to zero, and the x axis will be the appropriate axis of quantization. On the other hand, if the jump rate is very slow, the axes of quantization are the resultants of the fields H along the x axis and $\pm h$ along the z axis, so that the rates of transition [i.e., the stochastic properties of $f(t)$] determine the quantum-mechanical properties of the system.

* Work performed under the auspices of the U.S. Atomic Energy Commission.

[1] R. Kubo, J. Phys. Soc. Japan **9**, 935 (1954); also, see the article in *Fluctuation, Relaxation and Resonance in Magnetic Systems*, edited by D. ter Haar (Oliver and Boyd, Edinburgh, 1962), p. 23.

[2] P. W. Anderson, J. Phys. Soc. Japan **9**, 316 (1954).

[3] A. Abragam, *The Theory of Nuclear Magnetism* (Oxford University Press, London, 1961), Chap. X.

[4] M. Blume, in *Hyperfine Structure and Nuclear Radiations* (North-Holland Publishing Co., Amsterdam, 1968), p. 911. See also, Phys. Rev. Letters **14**, 96 (1965); **18**, 305 (1967).

[5] M. Blume and J. A. Tjon, Phys. Rev. **165**, 446 (1968).

In this paper, a general solution is given for the problem of the line shape of a system whose Hamiltonian makes transitions at random betweeen a series of possible terms $V_1, V_2, \cdots, V_n$ where the operators V_i do not necessarily commute with one another. The solution is, thus, a generalization of the Kubo-Anderson treatment of Markovian modulation to include nonadiabatic as well as adiabatic effects. The form of this solution is very similar to that found by Sack[6] for the Kubo-Anderson model in that it involves the inversion of a finite matrix and is thus suitable for evaluation on a computer or, in the simplest cases, analytically. In the Kubo-Anderson case the matrix to be inverted has elements labeled by the possible values of the stochastic function $f(t)$, while the matrix in the solution to be given here has quantum-mechanical indices as well as stochastic ones. The Sack solution is found as a special case when the quantum-mechanical operators are diagonal.

Two problems involving a Hamiltonian with the noncommutative property mentioned above have been solved in earlier papers by special techniques.[5,7] The first concerned the Mössbauer line shape for a nucleus in a magnetic field that fluctuates along the z axis and a fixed electric field gradient along the x axis, while the second concerned a nucleus in an electric field gradient that jumped at random between the x, y, and z axes. These will be used as illustrations of the general techniques to be presented here. We make use of the stochastic functions $f(t)$ that jump between n different possible values to construct the model Hamiltonian of the system. In the next section, we discuss the general problem and give the solution in Eq. (22). Some examples are considered briefly in Sec. III, and an Appendix treats the properties of the Liouville operator that are used in the solution. Subsequent papers will contain applications of the general solution to specific problems in NMR, Mössbauer line shapes, and perturbed angular correlations of γ rays.

II. SOLUTION OF THE PROBLEM

The mathematical problem that we set is the solution of the line shape of emitted or absorbed radiation by a system whose Hamiltonian is a random function of time, jumping between a finite number n of possible forms. This model is supposed to represent the physical effects of the interaction between the system (e.g., a nuclear spin) and other degrees of freedom (e.g., electronic spins, lattice vibrations, etc.). The random time dependence then replaces the interaction terms in the Hamiltonian, so that in a sense the stochastic variables represent the "heat bath" with which the system interacts.

As examples, we consider the problems treated in Refs. 5 and 7. The Hamiltonian[5]

$$\mathcal{H}(t)=Q(3I_x^2-I^2)+g\mu hI_z f(t), \tag{2}$$

where $f(t)=\pm 1$, describes a nuclear spin in a fixed electric field gradient along the x axis. The randomly varying magnetic field term then represents the effects of relaxation transitions by the ion (presumed to have spin $\frac{1}{2}$) in which the nucleus is embedded. If the ion had spin 1, we would then allow $f(t)$ to take on the values ± 1 and 0. Similarly, the Hamiltonian[7]

$$\begin{aligned}\mathcal{H}(t)=&[1-f^2(t)]Q(3I_z^2-I^2)\\&+\tfrac{1}{2}f(t)[1+f(t)]Q(3I_x^2-I^2)\\&+\tfrac{1}{2}f(t)[1-f(t)]Q(3I_y^2-I^2),\end{aligned} \tag{3}$$

where $f(t)$ jumps between the values ± 1 and 0, describes a nucleus which, because of electronic relaxation, Jahn-Teller distortions, jump diffusion of vacancies, or other physical effects finds itself in an electric field gradient that makes transitions between the x, y, and z axes. The factors $(1-f^2)$, $\frac{1}{2}f(1\pm f)$ have been chosen so that each one is unity for one possible value of $f(t)$ and zero for the others. This example shows how we may construct a general stochastic Hamiltonian that makes transitions between n different forms. We introduce a stochastic function $f(t)$ of the type considered by Kubo and Anderson, which can assume one of n different values: $f(t)=i_1, i_2, \cdots, i_n$. The general form of the type of Hamiltonian we will consider is

$$\mathcal{H}(t)=\sum_j V_j f_j(t), \tag{4}$$

where the V_j are quantum-mechanical operators and the functions $f_j(t)$ are some combination of the basic random function $f(t)$. We might choose $f_j(t)$ so that $f_j(t)=1$ if $f(t)=i_j$, and $f_j(t)=0$ otherwise,[8] but this is not necessary. For the Hamiltonian (3) we would have

$$V_1=Q(3I_z^2-I^2), \qquad f_1(t)=1-f^2(t);$$
$$V_2=Q(3I_x^2-I^2), \qquad f_2(t)=\tfrac{1}{2}f(t)[1+f(t)];$$

and

$$V_3=Q(3I_y^2-I^2), \qquad f_3(t)=\tfrac{1}{2}f(t)[1-f(t)],$$

where $f(t)$ takes on the values ± 1 and 0. For (2), on the other hand,

$$V_1=Q(3I_x^2-I^2), \qquad f_1(t)=1;$$

and

$$V_2=g\mu hI_z, \qquad f_2(t)=f(t).$$

Equation (4) thus provides a very general form for the

[6] R. A. Sack, Mol. Phys. **1**, 163 (1958).
[7] J. A. Tjon and M. Blume, Phys. Rev. **165**, 456 (1968).

[8] This is accomplished by writing

$$f_j(t)=\frac{(f(t)-i_1)\cdots(f(t)-i_{j-1})(f(t)-i_{j+1})\cdots(f(t)-i_n)}{(i_j-i_1)\cdots(i_j-i_{j-1})(i_j-i_{j+1})\cdots(i_j-i_n)}.$$

Hamiltonian of a system whose surroundings fluctuate in time between a finite number of different possibilities. We want, then, to calculate the line shape of photons or other particles emitted or absorbed by a system governed by a Hamiltonian of this form.

The line shape is capable of being expressed as the Fourier or Laplace transform of a correlation function. For example, the Mössbauer line shape is given by Eq. (2.8) of Ref. 5:

$$W(\mathbf{k}) = (2/\Gamma)\ \mathrm{Re} \int_0^\infty dt \times \exp(i\omega t - \tfrac{1}{2}\Gamma t)\,(\langle \mathfrak{IC}^{(-)}\mathfrak{IC}^{(+)}(t)\rangle)_{\mathrm{av}}, \quad (5)$$

where $W(\mathbf{k})$ is the probability of observing a photon $\mathbf{k}$, $\mathfrak{IC}^{(+)}$ is the interaction between the nucleus and the electromagnetic field for emission of the photon $\mathbf{k}$, $\mathfrak{IC}^{(-)} = \mathfrak{IC}^{(+)\dagger}$, and Γ is the natural linewidth. The angular brackets $\langle\cdots\rangle$ denote an average over the occupation of the initial states of the nucleus, and the round brackets $(\cdots)_{\mathrm{av}}$ denote an average over the stochastic properties of the system Hamiltonian $\mathfrak{IC}(t)$ that governs the time dependence of $\mathfrak{IC}^{(+)}(t)$. This time dependence is given by

$$\mathfrak{IC}^{(+)}(t) = \exp\left[i\int_0^t \mathfrak{IC}(t')\,dt'\right]\mathfrak{IC}^{(+)} \times \exp\left[-i\int_0^t \mathfrak{IC}(t')\,dt'\right], \quad (6)$$

where the exponentiated operators are suitably time ordered. Our problem is the evaluation of this stochastic average when the Hamiltonian $\mathfrak{IC}(t)$ has the form (4). An expression similar to (5) arises in the treatment of nuclear magnetic resonance line shapes,[3] in the case of perturbed angular correlations of successive nuclear radiations[4] and in numerous other line-shape problems, so that the evaluation of the stochastic average given below will be of use in these other circumstances.

We consider, then, the calculation of

$$F(p) = \int_0^\infty dt\, e^{-pt}(\langle \mathfrak{IC}^{(-)}\mathfrak{IC}^{(+)}(t)\rangle)_{\mathrm{av}} \quad (7)$$

as a specific example. We may, as in Eq. (2.10) of Ref. 5, introduce a complete set of states for the evaluation of the correlation function in (7):

$$(\langle \mathfrak{IC}^{(-)}\mathfrak{IC}^{(+)}(t)\rangle)_{\mathrm{av}} = (2I_1+1)^{-1} \sum_{m_1 m_0, m_1' m_0'} \Big(\langle I_1 m_1 \mid \mathfrak{IC}^{(-)} \mid I_0 m_0\rangle \times \Big\langle I_0 m_0 \Big| \exp\Big[i\int_0^t \mathfrak{IC}(t')\,dt'\Big] \Big| I_0 m_0'\Big\rangle \langle I_0 m_0' \mid \mathfrak{IC}^{(+)} \mid I_1 m_1'\rangle \times \Big\langle I_1 m_1' \Big| \exp\Big[i\int_0^t \mathfrak{IC}(t')\,dt'\Big] \Big| I_1 m_1\Big\rangle\Big)_{\mathrm{av}}. \quad (8)$$

We must now evaluate the average of the product of the matrix elements of the time-ordered operators

$$\left(\left\langle I_0 m_0 \left| \exp\left[i\int_0^t \mathfrak{IC}(t')\,dt'\right] \right| I_0 m_0'\right\rangle \left\langle I_1 m_1' \left| \exp\left[-i\int_0^t \mathfrak{IC}(t')\,dt'\right] \right| I_1 m_1\right\rangle\right)_{\mathrm{av}}.$$

The evaluation of this expression is made difficult by the presence of two separate time-ordered series, since the stochastic average is most easily performed when all random functions are arranged in a single time-ordered sequence. It is convenient, for this purpose, to introduce the Liouville operator for the Hamiltonian, since this will allow the reordering of the two time-development operators in (8). A discussion of the Liouville operator is given, for convenience, in the Appendix, and we make use here of the results derived there. From Eq. (A8) we note that we may write

$$\exp\left[i\int_0^t \mathfrak{IC}(t')\,dt'\right]\mathfrak{IC}^{(+)}\exp\left[-i\int_0^t \mathfrak{IC}(t')\,dt'\right] = \exp\left[i\int_0^t \mathfrak{IC}^{\times}(t')\,dt'\right]\mathfrak{IC}^{(+)}, \quad (9)$$

where $\mathfrak{IC}^{\times}(t')$ is the Liouville operator for the Hamiltonian. Eq. (7) then becomes

$$F(p) = \int_0^\infty dt\, e^{-pt} \times \left\langle \mathfrak{IC}^{(-)}\left(\exp\left[i\int_0^t dt'\,\mathfrak{IC}^{\times}(t')\,dt'\right]\right)_{\mathrm{av}}\mathfrak{IC}^{(+)}\right\rangle, \quad (10)$$

so that our problem becomes the evaluation of the quantity

$$\left(\exp\left[i\int_0^t \mathfrak{IC}^{\times}(t')\,dt'\right]\right)_{\mathrm{av}}.$$

This average is a Liouville-type operator and is thus, according to Eq. (A2), labeled by four indices. Indeed, the

expansion (8) may be written as

$$(\langle H^{(-)}\mathcal{H}^{(+)}(t)\rangle)_{\rm av}=(2I_1+1)^{-1}\sum_{m_1m_0}\langle I_1m_1\mid\mathcal{H}^{(-)}\mid I_0m_0\rangle\left(\left\langle I_0m_0\;\middle|\;\left\{\exp\left[i\int_0^t\mathcal{H}^{\times}(t')\,dt'\right]\mathcal{H}^{(+)}\right\}\;\middle|\;I_1m_1\right\rangle\right)_{\rm av}$$
$$=(2I_1+1)^{-1}\sum_{m_0m_1,m_0'm_1'}\langle I_1m_1\mid\mathcal{H}^{(-)}\mid I_0m_0\rangle$$
$$\times\left\langle I_0m_0I_1m_1\;\middle|\;\left(\exp\left[i\int_0^t\mathcal{H}^{\times}(t')\,dt'\right]\right)_{\rm av}\;\middle|\;I_0m_0'I_1m_1'\right\rangle\langle I_0m_0'\mid\mathcal{H}^{(+)}\mid I_1m_1'\rangle. \quad (11)$$

Comparison with (8) shows that

$$\left\langle I_0m_0I_1m_1\;\middle|\;\left(\exp\left[i\int_0^t\mathcal{H}^{\times}(t')\,dt'\right]\right)_{\rm av}\;\middle|\;I_0m_0'I_1m_1'\right\rangle$$
$$=\left(\left\langle I_0m_0\;\middle|\;\exp\left[i\int_0^t\mathcal{H}(t')\,dt'\right]\;\middle|\;I_0m_0'\right\rangle\left\langle I_1m_1'\;\middle|\;\exp\left[-i\int_0^t\mathcal{H}(t')\,dt'\right]\;\middle|\;I_1m_1\right\rangle\right)_{\rm av}, \quad (12)$$

as is found from (A8). The introduction of the Liouville operator thus enables us to combine the two time-ordered sequences into a single one. Once we know the matrix elements of

$$\left(\exp\left[i\int_0^t\mathcal{H}^{\times}(t')\,dt'\right]\right)_{\rm av},$$

then we may calculate the line shape from (11), since the elements $\langle I_0m_0'\mid\mathcal{H}^{(+)}\mid I_1m_1'\rangle$ are expressible in terms of Clebsch-Gordan coefficients. [In the treatment of NMR line shapes $\mathcal{H}^{(+)}$ is replaced by I_x, and the matrix elements are well known.]

Let us turn, then, to the evaluation of

$$\left(\exp\left[i\int_0^t\mathcal{H}^{\times}(t')\,dt'\right]\right)_{\rm av}.$$

Introducing the notation

$$U(t)=\exp\left[i\int_0^t\mathcal{H}^{\times}(t')\,dt'\right], \quad (13)$$

we note that $U(t)$ satisfies the integral equation

$$U(t)=1+i\int_0^t dt'U(t')\mathcal{H}^{\times}(t'). \quad (14)$$

[This follows from the fact that $dU/dt=iU(t)\mathcal{H}^{\times}(t)$. Integrating this expression from zero to t and using $U(0)=1$ yields (14).] On substituting the form (4) for $\mathcal{H}(t)$, we obtain for (14)

$$U(t)=1+i\int_0^t dt'U(t')\sum_j V_j^{\times}f_j(t'), \quad (15)$$

where $V_j^{\times}$ is the Liouville operator associated with V_j. We wish to evaluate $(U(t))_{\rm av}$. If we were simply to take the average of (15) we would find that the right-hand side would contain terms of the form $(U(t)f_j(t))_{\rm av}$ which are more complicated than the simple average we seek. This occurrence of "higher-order" terms is similar to the Green's-function–type of analysis. In the present calculation, however, we do not proceed in this way. Instead, we introduce the notion of a *restricted* average[1,5,7] of $U(t)$, which we denote by $(a\mid\mathbf{U}(t)\mid b)$. This is the average of $U(t)$ over the restricted class of functions $f(t)$ such that $f(0)=a$ and $f(t)=b$, where a and b are two of the possible values taken on by $f(t)$. In detail: we take the ensemble of functions $f(t)$ and single out those functions with $f(0)=a$ and $f(t)=b$, discarding all others. We then average $U(t)$ over this restricted ensemble. The full average $(U(t))_{\rm av}$ which we require is then obtained by summing over all values b and averaging over all initial values a:

$$(U(t))_{\rm av}=\sum_{ab}p_a(a\mid\mathbf{U}(t)\mid b), \quad (16)$$

where p_a is the *a priori* probability of the occurrence of the initial value a. Hence the determination of $\mathbf{U}(t)$, which is a stochastic as well as a Liouville matrix, solves the problem.

We now take the average of Eq. (15), subject to the condition $f(0)=a$ and $f(t)=b$, and we consider each term in turn. The left-hand side becomes, of course, $(a\mid\mathbf{U}(t)\mid b)$. The average of unity, the first term on the right-hand side, is not, in this case, one, but is to be weighted by the probability that $f(t)=b$ *given* $f(0)=a$. We denote this quantity by $(a\mid\mathbf{P}(t)\mid b)$. In averaging the second term on the right, we make use (for the first time) of the stationary Markov property of the functions $f(t)$. We break the average into two parts; one over functions for which $f(0)=a$ and $f(t')=c$, and the other over functions for which $f(t')=c$ and $f(t)=b$. This is possible because probabilities in a Markov process depend only on the latest value assumed by the function. By summing over the values of the function at the intermediate time t', then, we obtain the restricted average. We find for the second term on the right in (15)

$$i\sum_{cd}\int_0^t dt'(a\mid\mathbf{U}(t')\mid c)$$
$$\times\sum_j V_j^{\times}(c\mid\mathbf{F}_j\mid d)(d\mid\mathbf{P}(t-t')\mid b),$$

where $\mathbf{F}_j$ is a diagonal matrix whose elements are the values assumed by $f_j(t')$. For example, if $f(t)=\pm1$ or 0,

and $f_j(t)=1-f^2(t)$, then

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

The factor $(d\,|\,\mathbf{P}(t-t')\,|\,b)$ is the probability that $f(t)=b$ given that $f(t')=d$. We may write the results of this partial averaging of Eq. (15) in matrix form. We have

$$\mathbf{U}(t)=\mathbf{P}(t)+i\int_0^t dt'\mathbf{U}(t')\sum_j V_j{}^{\times}\mathbf{F}_j\mathbf{P}(t-t'). \quad (16')$$

This averaged equation is now solvable, since the averaging process has introduced the factor $\mathbf{P}(t-t')$ on the right-hand side. We take the Laplace transform of (16'), and use the notation

$$\tilde{\mathbf{U}}(p)=\int_0^\infty dt\, e^{-pt}\mathbf{U}(t),$$

$$\mathbf{P}_l(p)=\int_0^\infty dt\, e^{-pt}\mathbf{P}(t),$$

so that

$$\tilde{\mathbf{U}}(p)=\mathbf{P}_l(p)+i\tilde{\mathbf{U}}(p)\sum_j V_j{}^{\times}\mathbf{F}_j\mathbf{P}_l(p), \quad (17)$$

since the Laplace transform of the convolution integral is equal to the products of the Laplace transforms of $\mathbf{U}$ and $\mathbf{P}$. The solution to (17) is

$$\tilde{\mathbf{U}}(p)=\mathbf{P}_l(p)[\mathbf{1}-i\sum_j V_j{}^{\times}\mathbf{F}_j\mathbf{P}_l(p)]^{-1}. \quad (18)$$

In order to obtain our final result in usable form we consider $\mathbf{P}(t)$. This matrix is given by[2,5]

$$\mathbf{P}(t)=\exp(\mathbf{W}t), \quad (19)$$

where $\mathbf{W}$ is a stochastic matrix whose off-diagonal elements $(a\,|\,\mathbf{W}\,|\,b)$ are equal to the probability per unit time that $f(t)$ makes a transition from a to b, and whose diagonal elements

$$(a\,|\,\mathbf{W}\,|\,a)=-\sum_{b(\neq a)}(a\,|\,\mathbf{W}\,|\,b)$$

are equal to the negatives of the "lifetime" of $f(t)$ in the value a. All of the physical information put into the model is in this matrix. From (19) we find that

$$\mathbf{P}_l(p)=\int_0^\infty dt\, e^{-pt}\exp(\mathbf{W}t)$$
$$=(p\mathbf{1}-\mathbf{W})^{-1}, \quad (20)$$

and, on substituting in (18) we obtain

$$\tilde{\mathbf{U}}(p)=[p\mathbf{1}-\mathbf{W}-i\sum_j V_j{}^{\times}\mathbf{F}_j]^{-1}. \quad (21)$$

This simple result gives the desired solution to the line-shape problem. We note that from (10), (13), and (16) only $\mathbf{U}(p)$ is required for the evaluation of the line shape, so that there is no need in this case to invert the Laplace transform to obtain $\mathbf{U}(t)$.

On combining (21), (16), (11), and (10), we find for $F(p)$:

$$F(p)=(2I_1+1)^{-1}\sum_{m_1m_0,m_1'm_0'}\langle I_1m_1\,|\,\mathfrak{IC}^{(-)}\,|\,I_0m_0\rangle\sum_{ab}p_a\langle I_0m_0I_1m_1a\,|\,[p\mathbf{1}-\mathbf{W}-i\sum_j V_j{}^{\times}\mathbf{F}_j]^{-1}\,|\,I_0m_0'I_1m_1'b\rangle\langle I_0m_0'\,|\,\mathfrak{IC}^{(+)}\,|\,I_1m_1'\rangle. \quad (22)$$

Let us consider in more detail the solution (21) for $\tilde{\mathbf{U}}(p)$. From (22) we see that this matrix is labeled by three indices, two quantum-mechanical corresponding to the excited and ground states of the emitter, and one stochastic index corresponding to the possible values of $f(t)$. The dimension of this matrix is then $(2I_1+1)(2I_0+1)n$, where I_1 is the spin of the excited state, I_0 the spin of the ground state, and n is the number of possible values of the stochastic function $f(t)$. In general, then, it is necessary only to invert a matrix of this size in order to solve the problem, and this inversion is easily performed numerically on a computer for any reasonably sized system. For example, the NMR line-shape problem for spin $\frac{1}{2}$ has $I_1=I_0=\frac{1}{2}$, and if the Hamiltonian jumps between eight different forms (e.g., if the nucleus is in a magnetic field that jumps between the eight [111] directions) the matrix will be 32×32, a size that presents no difficulties for a computer. It should be emphasized that $(2I_1+1)(2I_0+1)n$ is the *maximum* dimension for the matrix, since symmetry properties can be used to reduce this. If all of the operators V_j commute with one another they can be simultaneously diagonalized. In that case the $V_j{}^{\times}$ are simply numbers and an n-dimensional matrix must be inverted. This is of course the case for the original problem treated by Kubo and Anderson. We see therefore that (21) reduces to the solution found by Sack[6,3] for their problem if the $V_j{}^{\times}$ are c numbers and if $\mathbf{F}_j=\mathbf{F}$, the diagonal matrix of values assumed by $f(t)$. This incidentally illustrates mathematically the way in which the quantum-mechanical and stochastic aspects of the problem become separate when the Hamiltonian commutes with itself at different times. If, on the other hand, the different V_j operators cannot be simultaneously diagonalized the inversion of the matrix in (22) will cause a mixing of quantum-mechanical and sto-

TABLE I. Explicit evaluation of matrix $\langle I_0 m_0 I_1 m_1 a \mid p\mathbf{1}-\mathbf{W}-i\sum_j V_j^{\times}\mathbf{F}_j \mid I_0 m_0' I_1 m_1' b\rangle$ for the Hamiltonian given in Eq. (26). Notation: $I_0=I_1=\frac{1}{2}$, $h^{\pm}=h_x \pm ih_y$, $W_{++}=-W_{+-}$, $W_{--}=-W_{-+}$.

$m_0 m_1 a$ \ $m_0' m_1' b$	$\frac{1}{2}\ \frac{1}{2}\ 1$	$\frac{1}{2}\ \frac{1}{2}-1$	$\frac{1}{2}-\frac{1}{2}\ 1$	$\frac{1}{2}-\frac{1}{2}-1$	$-\frac{1}{2}\ \frac{1}{2}\ 1$	$-\frac{1}{2}\ \frac{1}{2}-1$	$-\frac{1}{2}-\frac{1}{2}\ 1$	$-\frac{1}{2}-\frac{1}{2}-1$
$\frac{1}{2}\ \frac{1}{2}\ 1$	$p-W_{++}$	$-W_{+-}$	$+\frac{1}{2}ih^+$	0	$-\frac{1}{2}ih^-$	0	0	0
$\frac{1}{2}\ \frac{1}{2}-1$	$-W_{-+}$	$p-W_{--}$	0	$-\frac{1}{2}ih^+$	0	$+\frac{1}{2}ih^-$	0	0
$\frac{1}{2}-\frac{1}{2}\ 1$	$+\frac{1}{2}ih^-$	0	$p-W_{++}-i(H+h_z)$	$-W_{+-}$	0	0	$-\frac{1}{2}ih^-$	0
$\frac{1}{2}-\frac{1}{2}-1$	0	$-\frac{1}{2}ih^-$	$-W_{-+}$	$p-W_{--}-i(H-h_z)$	0	0	0	$+\frac{1}{2}ih^-$
$-\frac{1}{2}\ \frac{1}{2}\ 1$	$-\frac{1}{2}ih^+$	0	0	0	$p-W_{++}+i(H+h_z)$	$-W_{+-}$	$+\frac{1}{2}ih^+$	0
$-\frac{1}{2}\ \frac{1}{2}-1$	0	$+\frac{1}{2}ih^+$	0	0	$-W_{-+}$	$p-W_{--}+i(H-h_z)$	0	$-\frac{1}{2}ih^+$
$-\frac{1}{2}-\frac{1}{2}\ 1$	0	0	$-\frac{1}{2}ih^+$	0	$+\frac{1}{2}ih^-$	0	$p-W_{++}$	$-W_{+-}$
$-\frac{1}{2}-\frac{1}{2}-1$	0	0	0	$+\frac{1}{2}ih^+$	0	$-\frac{1}{2}ih^-$	$-W_{-+}$	$p-W_{--}$

chastic indices, so that the effects of the rate of fluctuation on the quantum-mechanical problem occur as discussed in the Introduction.

III. EXAMPLE

In this section we consider in more detail the evaluation of the matrix $\tilde{\mathbf{U}}(p)$ and we present several illustrations as explicit examples of the mechanical procedures to be followed in using Eq. (22).

We wish to evaluate the inverse of the matrix

$$p\mathbf{1}-\mathbf{W}-i\sum_j V_j^{\times}\mathbf{F}_j.$$

To do this, we first construct this matrix, with each row and column labeled by three indices:

$$\langle I_0 m_0 I_1 m_1 a \mid p\mathbf{1}-\mathbf{W}-i\sum_j V_j^{\times}\mathbf{F}_j \mid I_0 m_0' I_1 m_1' b\rangle. \quad (23)$$

Clearly the purely stochastic matrices, such as $\mathbf{W}$, must be diagonal in the quantum-mechanical indices, while the Liouville operators $V_j^{\times}$ are diagonal in the stochastic indices. Hence,

$$\langle I_0 m_0 I_1 m_1 a \mid p\mathbf{1} \mid I_0 m_0' I_1 m_1' b\rangle = \delta_{m_0 m_0'}\delta_{m_1 m_1'}\delta_{ab}p, \quad (24a)$$

$$\langle I_0 m_0 I_1 m_1 a \mid \mathbf{W} \mid I_0 m_0' I_1 m_1' b\rangle = \delta_{m_0 m_0'}\delta_{m_1 m_1'}(a \mid \mathbf{W} \mid b), \quad (24b)$$

$$\langle I_0 m_0 I_1 m_1 a \mid V_j^{\times}\mathbf{F}_j \mid I_0 m_0' I_1 m_1' b\rangle = \langle I_0 m_0 I_1 m_1 \mid V_j^{\times} \mid I_0 m_0' I_1 m_1'\rangle (a \mid \mathbf{F}_j \mid a)\delta_{ab},$$

where, in the last expression, we have used the fact that the $\mathbf{F}_j$ are diagonal matrices. To complete these expressions we note that the definition of the elements of Liouville matrices, Eq. (A4), allows us to express these elements in terms of the matrix elements of ordinary operators:

$$\langle I_0 m_0 I_1 m_1 \mid V_j^{\times} \mid I_0 m_0' I_1 m_1'\rangle = \delta_{m_1 m_1'}\langle I_0 m_0 \mid V_j \mid I_0 m_0'\rangle - \delta_{m_0 m_0'}\langle I_1 m_1' \mid V_j \mid I_1 m_1\rangle.$$

We therefore have

$$\langle I_0 m_0 I_1 m_1 a \mid V_j^{\times}\mathbf{F}_j \mid I_0 m_0' I_1 m_1' b\rangle = (a \mid \mathbf{F} \mid a)\delta_{ab} \times[\delta_{m_1 m_1'}\langle I_0 m_0 \mid V_j \mid I_0 m_0'\rangle - \delta_{m_0 m_0'}\langle I_1 m_1' \mid V_j \mid I_1 m_1\rangle]. \quad (24c)$$

Hence, (23) can be evaluated in terms of the matrix elements of ordinary quantum-mechanical operators and the transition probabilities $(a \mid \mathbf{W} \mid b)$ by using (24a)–(24c). The resulting matrix may then be inverted to obtain $\tilde{\mathbf{U}}(p)$. Finally, we must specify the *a priori* probabilities p_a of the occurrence of a specific value a of $f(t)$. These are determined by the requirement that $f(t)$ be a *stationary* process, so that detailed balance holds for the transitions:

$$p_a(a \mid \mathbf{W} \mid b) = p_b(b \mid \mathbf{W} \mid a). \quad (25)$$

The p_a are determined from these relations and the normalizing condition

$$\sum p_a = 1.$$

The specification of W then provides sufficient information to perform the calculation.

To illustrate the construction of the matrix we consider the Hamiltonian

$$\mathcal{H}(t)=HI_z+\mathbf{h}\cdot\mathbf{I}f(t), \qquad (26)$$

where $f(t)=\pm 1$. If $\mathbf{h}$ is along the z axis we have the standard case of a fluctuating field parallel to a fixed field H. We will consider the case where $\mathbf{h}$ is in an arbitrary direction. We take $I_0=I_1=\frac{1}{2}$. This case is of interest in considering the NMR line shape of a spin-$\frac{1}{2}$ nucleus in a fixed field H along the z axis and a fluctuating field $\mathbf{h}$ in an arbitrary direction. We rewrite (26) in the form

$$\mathcal{H}(t)=HI_z+[\tfrac{1}{2}(h^+I_-+h^-I_+)+h_zI_z]f(t), \qquad (27)$$

where $h^{\pm}=h_x\pm ih_y$ and $I_{\pm}=I_x\pm iI_y$. The matrix to be inverted is then easily found, using (24a)–(24c), to be as in Table I. Note that if $h^+=h^-=0$, i.e., for $\mathbf{h}$ along the z axis, the 8×8 matrix is reduced to four 2×2 matrices, as in the original solution of Kubo and Anderson. In the general case, the full eight-dimensional matrix must be inverted and the quantum-mechanical and stochastic indices are intermixed. The NMR-absorption signal is given by an expression analogous to (5) (see p. 101 of Ref. 3). If the radio-frequency field of frequency ω is applied along the x axis the absorption is proportional to

$$I_x(\omega)=\mathrm{Re}\int_0^{\infty} dt\, e^{i\omega t}\ \mathrm{tr}\ (I_x(0)I_x(t))_{\mathrm{av}}, \qquad (28)$$

while for a rf field along the y axis it is proportional to

$$I_y(\omega)=\mathrm{Re}\int_0^{\infty} dt\, e^{i\omega t}\ \mathrm{tr}\ (I_y(0)I_y(t))_{\mathrm{av}}. \qquad (29)$$

In Fig. 1 we display the results of the evaluation of these expressions for the Hamiltonian (27) with $I=\frac{1}{2}$, using Eq. (21) to determine the stochastic average. In Figs. (1a) and (1b) we show the results for Eqs. (28) and (29), respectively. An imaginary part has been added to ω so that the spectrum will not collapse to δ-function peaks: $\omega\rightarrow\omega+0.5i$. The fluctuating field has been taken along the x axis, perpendicular to the applied field H, and the values $H=3$, $h=h_x=4$ have been used. In Fig. (1c) we show for comparison the same quantities (28) and (29) evaluated for a Hamiltonian in which the fluctuating field is along the z axis, i.e., parallel to the fixed field, with $H=3$ and $h=h_z=4$. In this case $I_x(\omega)=I_y(\omega)$. This situation corresponds to the simple adiabatic theory of Kubo and Anderson since here $[\mathcal{H}(t),\mathcal{H}(t')]=0$. The results illustrate the different effects produced by adiabatic and non-adiabatic fluctuations. In the case of very rapid fluctuation ($W=100$), the time varying term averages to zero, and the line shape is the same in the three cases. As the fluctuations slow down, differences appear. Case (c) is familiar from earlier discussions—in the limit of slow relaxation we find two lines corresponding to frequencies $H\pm h$, or for the parameters used here, at $\omega=1$ and $\omega=7$. The limiting case of slow relaxation is quite different when the fluctuating field is perpendicular to the fixed field, as in Fig. (1a) and (1b). The peak in $I_y(\omega)$, (1b), occurs at $\omega=(H^2+h^2)^{1/2}=5$. A similar peak occurs for $I_x(\omega)$, but there is, in addition, a large zero-frequency peak. This is a result of the component of the field along the x axis. The transition between the slow and fast relaxation regimes is shown for the intermediate values of W.

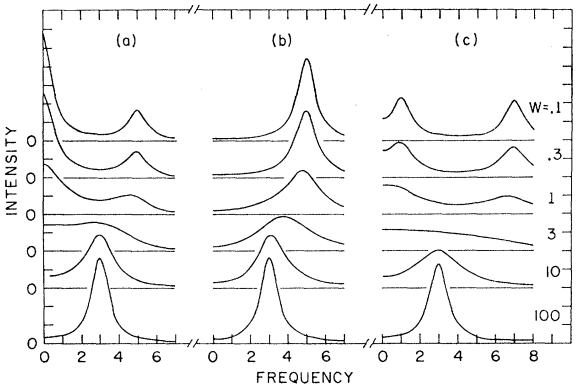

FIG. 1. NMR line shapes for a spin-$\frac{1}{2}$ nucleus in a fixed magnetic field along the z axis and also for a fluctuating field. W is the jump rate for the fluctuating field. (a) Fluctuating field along the x axis, resonant field along the x axis. $I_x(\omega)$ is calculated from Eqs. (28) and (20). (b) Same as (a), except $I_y(\omega)$ is shown. (c) Fluctuating field along the z axis, parallel to the fixed field. $I_x(\omega)=I_y(\omega)$ is shown.

The examples considered here have been treated to illustrate the utility of Eqs. (21) and (22) in constructing models for relaxation and in evaluating line shapes. In some future papers, a number of more complex models will be treated using those techniques. In particular, a model applicable to Mössbauer line shapes in thin films and to superparamagnetic particles, in which magnetic fields jump from one axis to another, will be considered.

Note added in proof. The time dependence of the density matrix of a system with a andomly varying Hamiltonian like those considered here has been treated by C. S. Johnson, Jr. [J. Chem. Physr **41,** 3277 (1964)] and applied to spin systems exchang.ing between two different environments [J. Magnetic Resonance (to be published)]. I am indebted to Dr. Johnson for a prepublication copy of the latter paper.

ACKNOWLEDGMENTS

I am indebted to J. A. Tjon and V. J. Emery for numerous helpful discussions.

APPENDIX

Liouville Operators

The quantum-mechanical Liouville operator was introduced by Kubo,[9] and exploited by Zwanzig.[10] The

[9] R. Kubo, J. Phys. Soc. Japan **12,** 570 (1957).
[10] R. Zwanzig, J. Chem. Phys. **33,** 1338 (1960).

line-shape problem has been discussed in terms of it by Fano.[11] We collect here, for convenience, some of the properties of this operator that are used in finding the solution (21). Briefly stated, with each quantum-mechanical operator A we may associate the Liouville operator $A^\times$ which acts on other quantum-mechanical operators B, so that $A^\times B$ gives the commutator of A with B

$$A^\times B = AB - BA = [A, B]. \tag{A1}$$

This appears to be no more than a notational device, and we might use it as such to simplify the mathematical problem, but there is also a physical significance to this concept that is discussed in Refs. (9–11), and that will be mentioned briefly below. First, in developing the mathematical properties of the Liouville operator, we note that a Liouville operator has the same relation to an ordinary linear operator as that ordinary operator has to a state vector. The ordinary operator acting on a state vector gives a different vector. Similarly, a Liouville operator acting on an ordinary operator gives a different operator. We may therefore write the matrix elements of the operator $A^\times B$ as a liner combination of the matrix elements of B:

$$\langle \mu \mid (A^\times B) \mid \nu \rangle = \sum_{\mu'\nu'} \langle \mu\nu \mid A^\times \mid \mu'\nu' \rangle \langle \mu' \mid B \mid \nu' \rangle, \tag{A2}$$

where the coefficients $\langle \mu\nu \mid A^\times \mid \mu'\nu' \rangle$ are labeled by four indices just as the elements of B are labeled by two. These coefficients can be expressed in terms of the matrix elements of the operator A, since from (A1) we find

$$\begin{aligned} \langle \mu \mid (A^\times B) \mid \nu \rangle &= \langle \mu \mid (AB - BA) \mid \nu \rangle \\ &= \sum_{\mu'} \langle \mu \mid A \mid \mu' \rangle \langle \mu' \mid B \mid \nu \rangle \\ &\quad - \sum_{\nu'} \langle \mu \mid B \mid \nu' \rangle \langle \nu' \mid A \mid \nu \rangle. \end{aligned} \tag{A3}$$

Comparing (A3) and (A2) shows that

$$\langle \mu\nu \mid A^\times \mid \mu'\nu' \rangle = \delta_{\nu\nu'} \langle \mu \mid A \mid \mu' \rangle - \delta_{\mu\mu'} \langle \nu' \mid A \mid \nu \rangle. \tag{A4}$$

This relation thus defines the four-index "matrix elements" of the Liouville operator in terms of the matrix elements of the ordinary operator with which it is associated.

The principal property of the Liouville operator which we use is the relation

$$e^A B e^{-A} = \exp(A^\times) B. \tag{A5}$$

To prove this we consider $e^{\lambda A} B e^{-\lambda A} = F(\lambda) B$, where $F(\lambda)$ is a four-index Liouville-type operator, and note that

$$(d/d\lambda) F(\lambda) B = e^{\lambda A} [A, B] e^{-\lambda A} = F(\lambda) A^\times B,$$

the formal solution of which is $F(\lambda) B = \exp(\lambda A^\times) B$. This reduces to (A5) for $\lambda = 1$. We may obtain some idea of the significance of (A5) by considering the particular case $A = i\mathcal{H}t$ where $\mathcal{H}$ is the system Hamiltonian. We find

$$\exp(i\mathcal{H}t)\, B \exp(-i\mathcal{H}t) = \exp(i\mathcal{H}^\times t)\, B = B(t). \tag{A6}$$

On expanding $\exp(i\mathcal{H}^\times t)$ in a power series we have

$$\begin{aligned} B(t) &= \sum_{n=0}^{\infty} \frac{t^n}{n!} (i\mathcal{H}^\times)^n B \\ &= \sum_{n=0}^{\infty} \frac{t^n}{n!} i^n [\mathcal{H}, [\mathcal{H}, \cdots [\mathcal{H}, B] \cdots]]. \\ &\qquad\qquad n \text{ commutators} \end{aligned} \tag{A7}$$

The nth commutator of the Hamiltonian with B is, however, the nth time derivative of B at $t=0$. (A7) is thus equivalent to

$$B(t) = \sum_{n=0}^{\infty} \frac{t^n}{n!} \frac{d^n B}{dt^n} \bigg|_{t=0},$$

which is the Taylor-series expansion for $B(t)$ about $t=0$. The Liouville-operator notation provides a compact way of writing the commutators in (A7). It should be noted that (A6) also holds if the operators are suitably time ordered. In particular we have

$$\begin{aligned} B(t) &= \exp_- \left[i \int_0^t \mathcal{H}(t')\, dt' \right] B \exp_+ \left[-i \int_0^t \mathcal{H}(t')\, dt' \right] \\ &= \exp_- \left[i \int_0^t \mathcal{H}^\times(t')\, dt' \right] B, \end{aligned} \tag{A8}$$

where the $-$ and $+$ subscripts on the exponential indicate negative and positive time-ordering, respectively. The proof is analogous to that for (A6).

The physical significance of the Liouville operator for the Hamiltonian $\mathcal{H}^\times$ may be seen by asking for its eigenvalues and eigenoperators. These are easily found in terms of the eigenvalues and eigenfunctions of the Hamiltonian itself. If we have $\mathcal{H} \mid \mu \rangle = E_\mu \mid \mu \rangle$, $\mathcal{H} \mid \nu \rangle = E_\nu \mid \nu \rangle$, then the transition operators $\mid \mu \rangle \langle \nu \mid$ are seen to be the "eigenoperators" of $\mathcal{H}^\times$:

$$\begin{aligned} \mathcal{H}^\times \mid \mu \rangle \langle \nu \mid &= \mathcal{H} \mid \mu \rangle \langle \nu \mid - \mid \mu \rangle \langle \nu \mid \mathcal{H} \\ &= (E_\mu - E_\nu) \mid \mu \rangle \langle \nu \mid. \end{aligned}$$

The eigenvalues of the Liouville operator $\mathcal{H}^\times$ are therefore the *differences* $E_\mu - E_\nu$ of all of the energy levels of the Hamiltonian. These are physically observable quantities, unlike the energy levels E_μ themselves, which contain an arbitrary zero of energy. The differences $E_\mu - E_\nu$ represent the possible spectral lines emitted by the system. Thus, it is not surprising that the operator $\mathcal{H}^\times$ is found useful (even if it is treated, as in Sec. II, simply as a convenient mathematical notation) in a discussion of the shape of spectral lines.

In the text, we sometimes use the term "Liouville operator" in a more general sense to refer to any four-index operator that acts to transform an ordinary operator. Such operators are functions of Liouville operators [such as $\exp(A^\times)$], and their matrix elements are of course not given by as simple a relation as (A4).

[11] U. Fano, Phys. Rev. **131**, 259 (1963).