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Note on the Stochastic Theory of Resonance Absorption

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The stochastic theory of magnetic resonance absorption developed recently by P. W. Anderson is examined here further in some details. The fundamental idea of the theory is that the resonating units suffer transitions among their possible states each of which is characterized by a proper frequency of the magnetic moment. The transition is assumed to be described by a Markoffian process. The fundamental equation for the auto-moment or the auto-correlation of the magnetic moment is rederived and transformed. Some general properties of the absorption spectrum are discussed on the basis of this equation. In particular, the narrowed spectrum for the case of rapid transition is proved to be Lorentzian with a half width determined by the equilibrium distribution of the units and the transition matrix of the Markoffian jumps. If the relaxation time of the transition is assumed to be completely degenerate, the resonance spectrum is given by

$$I(\omega)=\frac{1}{\pi}\mathrm{Re}\int\frac{P(\omega')d\omega'}{\omega_e+i(\omega-\omega')}\Big/\left\{1-\int\frac{\omega_e P(\omega')d\omega'}{\omega_e+i(\omega-\omega')}\right\}$$

where $P(\omega)$ is the intensity distribution in the limit of slow relaxation, $1/\omega_e$ being the relaxation time. Although this idealization is not quite physical, the result is useful for qualitative understanding of the changes in line shapes due to the motional effect. The limit of Gaussian-Markoff case is also discussed.

§ 1. Introduction

Recently P. W. Anderson[1] presented an interesting theory of the motional effect in magnetic resonance absorption. His model is that the resonance frequency is modulated randomly as a stochastic process. More specifically it is assumed that the resonating units make transitions between various states each of which has a characteristic resonance frequency. The transition process is assumed to be described as a Markoffian process. If the transition process is sufficiently slow, the observed spectrum of the resonance must be the set of those proper frequencies weighted by the relative probability of finding an unit in each of the frequencies. On the other hand, if the transition is extremely rapid, then the system will give rise to a sharp line the frequency of which is a certain average of the proper frequencies. Thus, the observed resonance spectrum will change between these two extremes as the transition rate varies. On this model, Anderson has developed a mathematical theory which affords at least qualitative understanding of such physical phenomena as the motional narrowing in nuclear magnetic resonance or the exchange effect in paramagnetic resonance absorption. The purpose of this note is to examine a little further some mathematical aspects of this model and to discuss certain problems which were left unsolved or untouched in Anderson's treatment.

§ 2. Fundamental Equations

Let us suppose that the possible states of the resonating unit are finite and numbered as $E_1, E_2\cdots E_r$. Our fundamental assumption is that the process in which the unit realizes in the course of time the various states is Markoffian, so that it is determined by the transition probabilities $P_{jk}(t)$. It is assumed further that this stochastic process is stationary, which means that the transition probabilities depend only on the time interval t. Furthermore, the following conditions are assumed[2].

1) $$P_{jj}(t)=1-c_j t+o(t)\,, \qquad (2.1)$$

2) $$P_{jk}(t)=c_j p_{jk} t+o(t)\,, \qquad (2.2)$$

where

$$p_{jj}=0, \text{ and } \sum_k p_{jk}=1\,. \qquad (2.3)$$

If the number of the states is infinite, we must assume that (2.2) holds uniformly with respect to j for every fixed k[3].

Under these assumptions, the Chapman-Kolmogorov equation

$$P_{jk}(t)=\sum_m P_{jm}(t-h)P_{mk}(h) \qquad 0<h<t,$$

can be transformed into the differential equations

$$\dot{P}_{jk}(t)=-c_kP_{jk}(t)+\sum_m P_{jm}(t)c_mp_{mk}\ , \qquad (2.4)$$

which is the so-called forward equation. This is a set of r equations for a fixed i. We may conveniently write this as

$$\dot{\varphi}_j(t)=-\varphi_jD\ ,$$

where φ_j is the row vector

$$\varphi_j=(P_{j1},\ P_{j2},\ \cdots\cdots\ P_{jr})\ , \qquad (2.5a)$$

and D the matrix

$$D_{mk}=c_k\delta_{km}-c_mp_{mk}\ . \qquad (2.5b)$$

Eq. (2.5) determines the matrix of transition probability ($P_{jk}(t)$) with the initial condition

$$P_{jk}(0)=\delta_{jk}. \qquad (2.6)$$

The adjoint equation of (2.5) is

$$\dot{\psi}(t)=-D\psi(t)\ , \qquad (2.7)$$

which corresponds to the backward equation, ψ being a column vector. Eq. (2.7) has an obvious solution

$$\psi_0=\begin{pmatrix}1\\1\\\cdot\\\cdot\\1\end{pmatrix}, \qquad D\psi_0=0\ , \qquad (2.8)$$

as one seems from the condition (2.3). Correspondingly Eq. (2.5) must have a stationary solution φ_0 which satisfies

$$\varphi_0D=0\ . \qquad (2.8a)$$

The eigenvector φ_0 must be unique and independent of j provided that our Markoffian process is ergodic, which we assume throughout the following treatment. The components of the eigenvector φ_0 are the stationary distribution or the equilibrium distribution to which the ensemble of our system must approach starting from any arbitrary distribution. The normalization of this equilibrium distribution is expressed by

$$\varphi_0\psi_0=1\ , \qquad (2.9)$$

which is

$$\sum_k P_k^0=1\ ,$$

where P_k^0 are the components of φ_0,

$$\varphi_0=(P_1^0,\ P_2^0,\cdots\cdots,\ P_r^0). \qquad (2.8b)$$

Now let the proper frequency of the resonating unit be denoted by ω_j in the state E_j. Thus the moment $M(t)$ of the resonating unit is assumed to be given by

$$M(t)=M(0)\exp i\int\omega(t')dt', \qquad (2.10)$$

where $\omega(t)$ is a stochastic variable assuming various values $\omega_1,\ \omega_2,\cdots\cdots,\ \omega_r$, as the unit jumps to and fro according to the basic process described by Eq. (2.4). Here we have neglected other possible complications coming from the variations in amplitudes and phases. It is also possible to construct a theory taking account of these, but we shall here employ the assumption (2.10) for the sake of simplicity. The problem we have now to solve is the calculation of the auto-moment of $M(t)$, which is the Fourier transform of the intensity distribution of the resonance absorption.

We shall here adopt a formulation which is a little different from that used by Anderson to derive the fundamental equation. Let us introduce a function $Q_{jk}(t)$ which is defined as the average of

$$\mu(t)=\exp i\int\omega(t')dt', \qquad (2.10a)$$

on the condition that the unit is in the state E_j at the time $t=0$ and is found in the state E_k at the time t. This definition yields, corresponding to the Chapman-Kolmogorov equation of $P_{jk}(t)$,

$$Q_{jk}(t+h)=\sum_m Q_{jm}(t)Q_{mk}(h)\ . \qquad (2.11)$$

We now see from the assumptions (2.1) and (1.2) that

$$Q_{jj}(h)=(1-c_jh)\,e^{ih\omega_j}+o(h)\ ,$$

$$Q_{jk}(h)=c_jp_{jk}h+o(h)\ .$$

Therefore, going to the limit of $h\to0$ in Eq. (2.11), we obtain the equation

$$\dot{Q}_{jk}(t)=(i\omega_k-c_k)Q_{jk}(t)+\sum_m Q_{jm}(t)c_mp_{mk}\ , \qquad (2.12)$$

which may be written as

$$\dot{Q}(t)=iQ\Omega-QD\ , \tag{2.13}$$

if we denote the matrix (Q_{jk}) by Q and the diagonal matrix $\omega_k\delta_{jk}$ by Ω. Eq. (2.12) has to be solved with the initial condition,

$$Q_{jk}(0)=\delta_{jk}\ .$$

The auto-moment of $M(t)$, Eq. (2.10), or that of $\mu(t)$, Eq. (2.10a) is now given from the fundamental solution of Eq. (2.13). Namely we first take the average of $Q_{jk}(t)$ with respect to the initial states distributed with the equilibrium probability (2.8b) and then sum up over all of the possible final states. Thus the auto-momemt of $\mu(t)$, or the correlation function of $M(t)$ is

$$g(t)=\varphi_0 Q(t)\psi_0\ . \tag{2.14}$$

Or, defining the vector function

$$u(t)=\varphi_0 Q(t)\ , \tag{2.15}$$

we may write (2.14) as

$$g(t)=u(t)\psi_0\ . \tag{2.14a}$$

For the function $u(t)$ we can set up the equation

$$\dot{u}(t)=iu(t)\Omega-u(t)D\ , \tag{2.16}$$

which is imposed by the initial condition,

$$u(0)=\varphi_0\ . \tag{2.17}$$

Eq. (2.16) is the fundamental equation of our treatment.

The formal solution of (2.16) is

$$u(t)=\varphi_0\exp\{-(D-i\Omega)t\}\ , \tag{2.18}$$

which gives

$$g(t)=\varphi_0\exp\{-(D-i\Omega)t\}\psi_0\ . \tag{2.19}$$

This is, of course, identical with the basic formula derived by Anderson[1].

Since simultaneous addition of ω_0 to all of the frequencies $\omega_1, \omega_2, \cdots, \omega_r$, gives to $u(t)$ only an extra factor $\exp i\omega_0 t$ we can choose the frequencies in such a way that

$$\sum_j P_j^0\omega_j=0 \tag{2.20}$$

or

$$\varphi_0\Omega\psi_0=0\ . \tag{2.20a}$$

This means that we are dealing with the spectrum the center of which is now arbitrarily chosen to zero. This particular choice is useful to simplify the calculation, so that we shall assume (2.20) in the following treatment.

§ 3. Some Direct Consequences of the Fundamental Equation

The auto-correlation, $g(t)$, and the normalized intensity distribution, $I(\omega)$, are mutually connected by the Fourer transforms,

$$g(t)=\int_{-\infty}^{\infty} I(\omega)e^{i\omega t}d\omega\ . \tag{3.1}$$

and

$$I(\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty} g(t)e^{-i\omega t}dt \tag{3.2}$$

Thus we must have

$$g(-t)=\overline{g(t)}\ . \tag{3.3}$$

Now the moments of the distribution $I(\omega)$ are generally given by the derivatives of $g(t)$ at $t=0$ provided that those derivatives uniquely exist. It is easy to see that the assumption of Markoffian process forbids the existence of the moments higher than the second. Expanding Eq. (2.29) one gets

$$\begin{aligned} g^{(n)}(+0)&=\varphi_0(\Omega+iD)^n\psi_0\\ &=\varphi_0\Omega(\Omega+sD)^{n-2}\Omega\psi_0, \end{aligned} \tag{3.4}$$

where we made the use of Eqs. (2.8) and (2.8a). Thus the second moment is

$$m_2=\varphi_0\Omega^2\psi_0=\sum_j P_j^0\omega_j^2, \tag{3.5}$$

whereas Eq. (3.3) and (3.4) show that the third derivative of $g(t)$ at $t=0$ cannot be uniquely defined, the right and left limits being generally different except when

$$\varphi_0\Omega D\Omega\psi_0=\sum P_j^0\omega_j D_{jk}\omega_k=0\ .$$

Thus, the third moment of $I(\omega)$ will not be convergent and the distribution falls off at infinity to allow only the existence the second moment, (3.5), which is independent of D, namely of the relaxation process. It is, however, to be remembered that the non-existence of higher moments just mentioned is utterly a mathematical consequence of our Markoffian assumption, which will certainly break down for very small time interval if our system is really a physical one. The dynamical coherence is always dominant for small time interval either in classical or quantum-mechanical systems so that the correlation function $g(t)$ must behave quite regularly in the neigh-

borhood of $t=0$. Therefore, the Markoffian theory as a physical theory is doomed to fail to describe correctly the wings of the resonance curves. But it is correct near the center and can give valuable conclusions if it covers the most of the frequency range which is practically important. The criterion of the validity or the usefulness of the Markoffian theory is actually pretty complicated depending on the dynamical nature of physical system of interest. Thus more detailed discussion of this point is beyond the scope of the present article.

The extreme limits of very slow and very rapid relaxation are, of course, to be seen at once from Eq. (2.19). If D is negligible, we have

$$g(t)=\sum_j P_j^0 e^{i\omega_j t} . \tag{3.6}$$

Thus, the spectrum is simply

$$I(\omega)=\sum_j P_j^0 \delta(\omega-\omega_j) , \tag{3.7}$$

as it ought to be. On the other hand, when D is so large that Ω can be neglected, Eqs. (2.19) and (2.8) or (2.8a) shows that $g(t)=1$, which gives

$$I(\omega)=\delta(\omega) . \tag{3.8}$$

The approximation from the side of weak relaxation can be made with the aid of perturbation method, which has been discussed by Anderson.

The approximation from the other side, that is from the limit of strong relaxation, needs somewhat more careful investigation. For this purpose and also for a general treatment of the problem, we may conveniently rewrite Eq. (2.16) as we shall see in the following section.

§ 4. Method of Solution of the Fnndamental Equation

Noticing that the operator D has the particular eigenvalue zero, we now want to elimi this particular eigen-space R_0 and set up the equation for the rest of the whole vector space. Let us put the solution $u(t)$ of Eq. (2.16) in the form

$$u(t)=c_0(t)\varphi_0+v(t) , \tag{4.1}$$

where $v(t)$ is orthogonal to the zero-eigenvector of D, namely,

$$v(t)\psi_0=\sum_j v_j(t)=0 . \tag{4.2}$$

Inserting (4.2) into Eq. (2.16) we get

$$\dot{c}_0(t)\varphi_0+\dot{v}(t)=ic_0(t)\varphi_0\Omega+iv(t)\Omega-v(t)D , \tag{4.3}$$

which can be separated into two equations:

$$c_0(t)=iv(t)\Omega\psi_0 , \tag{4.4a}$$

$$v(t)=ic_0\varphi_0\Omega+i(v\Omega-v\Omega R_0)-vD , \tag{4.4b}$$

where R_0 is the projection operator defined by

$$R_0=\psi_0\varphi_0 . \tag{4.5}$$

This is easily seen by making scalar product of the vector Eq. (4.3) with the eigen vector ψ_0 from the right. It gives Eq. (4.4a) by virtue of Eqs. (2.8), (2.9), and (2.20a). Eq. (4.4b) is obtained by subtracting (4.4a) from (4.3).

The most convenient way of treating Eq. (4.4) is the method of Laplace transformation. The Laplace transforms of $c_0(t)$ and $v(t)$ are defined as

$$C_0(s)=\int_0^\infty c_0(t)e^{-st}dt, \tag{4.6a}$$

$$V(s)=\int_0^\infty v(t)e^{-st}dt. \tag{4.6b}$$

Then Eqs. (4.4a) and (4.4b) are transformed into

$$sC_0(s)-1=iV(s)\Omega\psi_0 , \tag{4.7a}$$

$$sV(s)=iC_0(s)\varphi_0\Omega+iV(s)\Omega(1-R_0)-V(s)D , \tag{4.7b}$$

because, by the initial condition (2.17), we have

$$c_0(0)=1, \quad \text{and} \quad v(0)=0 .$$

Eliminating C_0 from Ex. (4.7a) we arrive at

$$V(s)\{s^2+sD-is\Omega(1-R_0)+\Omega R_0\Omega\}=i\varphi_0\Omega . \tag{4.8}$$

Since $V(s)$ and $i\varphi_0\Omega$ belong to the space $1-R_0$, we may write (4.8) in the form,

$$V(s)(1-R_0)\{s^2+sD-is\Omega(1-R_0)+\Omega R_0\Omega\}=i\varphi_0\Omega , \tag{4.8a}$$

using the relations,

$$R_0D=R_0=R_0\Omega R_0=0 .$$

The operators appearing on the left hand side of Eq. (4.8a) are essentially matrices in the spase $1-R_0$ with $r-1$ dimensions. Eq. (4.8) can also be written as

$$V(s)(s-i\Omega)[s(1-R_0)+(s-i\Omega)^{-1}sD+iR_0\Omega] = i\varphi_0\Omega\,, \qquad (4.8b)$$

or as

$$V(s)(1-R_0)(s-i\Omega)[s(1-R_0)+(s-i\Omega)^{-1}sD + iR_0\Omega]=i\varphi_0\Omega\,, \qquad (4.8c)$$

since

$$R_0(s-i\Omega)[s(1-R_0)+(s-i\Omega)^{-1}sD+iR_0\Omega]=0.$$

From Eq. (4.8c) we see easily that, in the limit of vanishing D, the solution of (4.8) becomes

$$V(s)=\varphi_0(s-i\Omega)^{-1}(1-R_0)\,, \qquad (4.9)$$

as it must be.

If Eq. (4.8) is solved after $V(s)$, Eq. (4.7a) gives $C_0(s)$ which is nothing but the Laplace transform of $g(t)$, i.e.,

$$C_0(s)=\int_0^\infty g(t)e^{-st}dt\,, \qquad (4.10)$$

because Eqs. (4.1) and (2.14a) give

$$g(t)=c_0(t)\,,$$

by virtue of (4.2). But the required intensity distribution is

$$\begin{aligned} I(\omega)&=\frac{1}{2\pi}\int_{-\infty}^{\infty} g(t)e^{-i\omega t}dt \\ &=\frac{1}{\pi}\,\mathrm{Re}\int_{-\infty}^{\infty} g(t)e^{-i\omega t}dt \\ &=\frac{1}{\pi}\,\mathrm{Re}\,[C_0(s)]_{s=i\omega}\,. \end{aligned} \qquad (4.11)$$

Therefore our problem is generally reduced to the solution of Eq. (4.8) or (4.8a) in the space $1-R_0$. With the obtained solution $V(s)$ the intensity distribution is given explicitly by

$$I(\omega)=(1/\pi)\,\mathrm{Re}\,(1+iV(i\omega)\Omega\psi_0)/(i\omega)\,. \qquad (4.12)$$

Perhaps it should be noticed here that the function $C_0(s)$ has no pole at $s=0$. This can be seen from Eq. (4.8), because for $s=0$ it becomes

$$V(s)\Omega\psi_0\varphi_0\Omega=i\varphi_0\Omega\,,$$

which gives $V(0)\Omega\psi_0=i$. Thus

$$[1+iV(s)\Omega\psi_0]_{s\to 0}=0\,.$$

§ 5. Narrowing for Rapid Relaxation

Eq. (4.8) can easily solved for the limit of strong narrowing, that is for the case where the relaxation effect is overwhelming. Let us denote the orders of magnitudes of D and Ω by τ_r^{-1} and ω_a. Then the orders of magnitudes of the four terms in the bracket on the left hand side of Eq. (4.8) are

$$\omega^2,\ \omega/\tau_r,\ \omega\omega_a,\ \text{and}\ \omega_a^2 \quad (s=i\omega)$$

respectively. Therefore, if we are interested in the frequencies satisfying the condition

$$\omega \lesssim \omega_a^2\tau_r\,, \qquad (5.1)$$

and if we assume that

$$\omega_a\tau_r \ll 1\,, \qquad (5.2)$$

the first and the third terms can be neglected, so that Eq. (4.8) becomes approximately

$$V(s)[sD+\Omega R_0\Omega]=i\varphi_0\Omega\,, \qquad (5.3)$$

or

$$V(s)D=s^{-1}\varphi_0\Omega(i-V\Omega\psi_0)\,. \qquad (5.4)$$

Here D is understood as $(1-R_0)D(1-R_0)$, which is an operator in the space $1-R_0$ and has no zero-eigenvalue. Thus the inverse D^{-1} of D can be defined in the space $1-R_0$. Eq. (5.4) now gives

$$V(s)\Omega\psi_0=s^{-1}\varphi_0\Omega D^{-1}\Omega\psi_0(i-V\Omega\psi_0)\,.$$

Hence we get

$$V\Omega\psi_0=\frac{is^{-1}\varphi_0\Omega D^{-1}\Omega\psi_0}{1+s^{-1}\varphi_0\Omega D^{-1}\Omega\psi_0}\,,$$

Inserting this into Eq. (4.12) we find

$$I(\omega)=\mathrm{Re}\,\frac{1}{\pi}\frac{1}{i\omega+\varphi_0\Omega D^{-1}\Omega\psi_0}\,, \qquad (5.5)$$

where both $\varphi_0\Omega$ and $\Omega\psi_0$ are vectors in the space $1-R_0$ so that the quantity $\varphi_0\Omega D^{-1}\Omega\psi_0$ has a definite meaning. If the eigenvalues of D in the space $1-R_0$ are all degenerate (see the next section), that is, if the relaxation time of the system is single, we have

$$D^{-1}=(1-R_0)\tau_r(1-R_0)\,,$$

and

$$\varphi_0\Omega D^{-1}\Omega\psi_0=\sum_j P_j{}^0\omega_j{}^2\tau_r=\overline{\omega^2}\tau_r\,. \qquad (5.6)$$

More generally we may write

$$\begin{aligned} \varphi_0\Omega D^{-1}\Omega\psi_0&=\int_0^\infty \varphi_0\Omega e^{-Dt}\Omega\psi_0 dt \\ &=\overline{\omega^2}\tau_{\mathrm{eff}}\,, \end{aligned} \qquad (5.7)$$

and express the intensity distribution as

$$I(\omega)=\frac{1}{\pi}\frac{\overline{\omega^2}\tau_{\mathrm{eff}}}{\omega^2+(\overline{\omega^2}\tau_{\mathrm{eff}})^2}\,. \qquad (5.8)$$

Thus the narrowed spectrum is generally a Lorentzian curve centered at the average frequency of the proper frequendies each of which is weighted by the equilibrium probability. The width of this Lorentzian curve is given by Eq. (5.7).

§ 6. Simple Relaxation

An interesting example which allows exact treatment is provided by the system with a single relaxation time. This is defined by a particular assumption for the elements of stochastic matrix involved in Eq. (2.2) such that

$$c_j=\omega_e(1-P_j^0)\ , \tag{6.1a}$$

and

$$p_{jk}=P_k^0(1-P_j^0)^{-1},\quad p_{jj}=0\ . \tag{6.1b}$$

with the condition

$$\sum_j P_j^0=1\ . \tag{6.2}$$

Thus the explicit form of D is

$$D_{jk}=\omega_e\delta_{jk}-\omega_e P_k^0\ . \tag{6.3}$$

With this matrix D one finds at once that any deviation from the equilibrium distribution (2.8b) relaxes as $\exp(-\omega_e t)$. This example was discussed by Anderson[1], but he did not give the complete solution of the problem. Although the model is not quite physical, it can still give qualitative understanding of the changes of line shapes as the rate of relaxation varies. Hence an exact solution of this model is not without physical interest.

For the sake of generality we shall consider here continuous cases rather than the discrete cases. Corresponding to Eq. (6.3) we may write the kernel of D as

$$D(\omega,\omega')=\omega_e\delta(\omega_e-\omega')-\omega_e P^0(\omega')\ , \tag{6.3a}$$

for continuous cases. In this expression $P^0(\omega)$ is normalized as

$$\int P^0(\omega)d\omega=1\ . \tag{6.2a}$$

More rigorously we may write

$$\varphi D\equiv\int\varphi(\omega)d\omega D(\omega,\omega')$$
$$=\omega_e\left\{\varphi(\omega')-P^0(\omega')\int\varphi(\omega)d\omega\right\}\ , \tag{6.4a}$$

$$D\psi\equiv\int D(\omega,\omega')d\omega'\psi(\omega')$$
$$=\omega_e\left\{\psi(\omega)-\int P^0(\omega')d\omega'\psi(\omega')\right\}\ , \tag{6.4b}$$

The equilibrium solution for D is provided by $P^0(\omega)$, that is

$$\int P^0(\omega)D(\omega,\omega')d\omega=0$$

and

$$\int D(\omega,\omega')\times\text{const.}\ d\omega'=0\ ,$$

Any function $f(\omega)$ which is orthogonal to the stationary solution, that is

$$\int f(\omega)d\omega=0\ ,$$

satisfies

$$fD=\omega_e f, \tag{6.5}$$

which means that any deviation from the equilibrium distribution decays with the relaxation time $1/\omega_e$.

Now the fundamental Eq. (2.16) is

$$(i\omega,t)=i\omega u(\omega,t)-\omega_e u(\omega,t)$$
$$+P^0(\omega)\int u(\omega',t)d\omega'. \tag{6.6}$$

Eqs. (4.4a) and (4.4b) are explicity written as

$$sC_0(s)-1=i\int\omega V(\omega,s)d\omega\ , \tag{6.7a}$$

and

$$(s+\omega_e-i\omega)V(\omega,s)$$
$$=iP^0(\omega)C_0(s)-\{sC_0(s)-1\}P^0(\omega). \tag{6.7b}$$

The latter equation gives

$$V(\omega,s)$$
$$=\{(i\omega-s)P^0(\omega)C_0(\omega)P^0(\omega)\}/(s+\omega_e-i\omega)$$
$$=-P^0(\omega)C_0(s)+\frac{\omega_e P^0(\omega)C_0(s)}{s+\omega_e-i\omega}+\frac{P^0(\omega)}{s+\omega_e-i\omega}\ . \tag{6.8}$$

Hence we get from Eq. (6.7b)

$$C_0(s)=\frac{1+\int\frac{i\omega P_0(\omega)d\omega}{s+\omega_e-i\omega}}{s-i\omega_e\int\frac{\omega P_0(\omega)d\omega}{s+\omega_e-i\omega}}\ . \tag{6.9}$$

We define the characteristic function of $P^0(\omega)$ by

$$Q^0(t)\equiv\int_{-\infty}^{\infty}P^0(\omega)e^{i\omega t}d\omega\ , \tag{6.10}$$

from which we find

$$\begin{aligned}R(s)&\equiv\int_0^{\infty}Q^0(t)\exp\{-(\omega_e+s)t\}dt\\&=\int_{-\infty}^{\infty}\frac{P^0(\omega)d\omega}{s+\omega_e-i\omega}\ ,\end{aligned} \tag{6.11}$$

and

$$\begin{aligned}&\int_0^{\infty}\frac{d}{dt}Q^0(t)\exp\{-(\omega_e+s)t\}dt\\&=\int\frac{i\omega P^0(\omega)\,d\omega}{s+\omega_e-i\omega}\\&=Q^0(t)\exp\{-(\omega_e+s)t\}\Big]_0^{\infty}\\&\quad+(\omega_e+s)\int_0^{\infty}Q^0(t)\exp\{-(\omega_e+s)t\}dt\\&=-1+(\omega_e+s)R(s)\ .\end{aligned} \tag{6.12}$$

Thus Eq. (6.9) can be written as

$$C_0(s)=\frac{R(s)}{1-\omega_eR(s)}\ . \tag{6.13}$$

This assures that the function $v(\omega, t)$ or $V(\omega, s)$ is zero when integrated over ω, because we get Eq. (6.13) from Eq. (6.8) if we integrate both sides of (6.8) over ω. Therefore Eq. (6.13) is the exact solution of our problem, from which we can find the spectrum $I(\omega)$ using Eq. (4.11):

$$I(\omega)=\mathrm{Re}\frac{1}{\pi}\frac{\int\frac{P^0(\omega')d\omega'}{\omega_e+i(\omega-\omega')}}{1-\omega_e\int\frac{P^0(\omega')d\omega'}{\omega_e+i(\omega-\omega')}}\ . \tag{6.14}$$

It is interesting to note here that the relaxation has no effect if the original distribution $P^0(\omega)$ is Lorentzian. Namely, a Lorentzian function

$$P^0(\omega)=(1/\pi)b/(\omega^2+b^2)\ ,$$

will give

$$Q^0(t)=\exp(-b|t|)\ ,$$

and

$$R(s)=1/(s+\omega_e+b)\ ,$$

which leads to

$$C_0(s)=(s+b)^{-1}\ ,\quad\text{and}\quad I(\omega)=P^0(\omega).$$

Thus the spectrum remains unchanged.

General expansion formulae of Eq. (6.14) for small ω_e and large ω_e can be derived as follows. For large ω_e, we expand $Q^0(t)\exp(-st)$ in power series of t to obtain

$$\begin{aligned}R(s)&=\sum_n\int_0^t\frac{t^n}{n!}\left[\frac{d^n}{dt^n}\{e^{-st}Q^0(t)\}\right]\exp(-\omega_et)dt\\&=\sum_n\frac{1}{\omega_e{}^{n+1}}\left[\left(\frac{d}{dt}-s\right)^nQ^0(t)\right]_{t=0}\\&=\sum(\omega_e)^{-n-1}\overline{(i\omega'-s)^n}\ .\end{aligned} \tag{6.15}$$

Inserting this into (6.13) an explicit expression of $I(\omega)$ can be obtained. Thus we have

$$R(i\omega)=\frac{1}{\omega_e}-i\frac{\omega}{\omega_e{}^2}-\frac{\overline{\omega^2}-\omega^2}{\omega_e{}^3}+\cdots\cdots,$$

so that

$$\begin{aligned}I(\omega)&=\frac{1}{\pi}\mathrm{Re}\frac{R(i\omega)}{1-\omega_eR(i\omega)}\\&=\frac{1}{\pi}\frac{\omega_e\overline{\omega^2}+\cdots\cdots}{(\omega^2+\omega^2)^2+\omega^2\omega_e{}^2+\cdots\cdots}\ ,\end{aligned}$$

which is simplified to

$$I(\omega)\simeq\frac{1}{\pi}\frac{\overline{\omega^2}/\omega_e}{\omega^2+(\overline{\omega^2}/\omega_e)^2}\ , \tag{6.16}$$

in accord to Eq. (5.8) for practically important frequencies

$$\omega\sim\overline{\omega^2}/\omega_e\ .$$

Next we shall derive an approximation for small ω_e assuming the distribution $P^0(\omega)$ to be continuous. Noticing that

$$R(i\omega)=\int_0^{\infty}Q^0(t)\,\mathrm{ext}\{-i(\omega-i\omega_e)t\}dt\ ,$$

(Eq. 6.11), we introduce

$$\int_0^{\infty}Q^0(t)e^{-i\omega t}dt=\pi(\chi_0{}''(\omega)-i\chi_0{}'(\omega))\ , \tag{6.17}$$

which means that

$$\chi_0{}''(\omega)=\mathrm{Re}\frac{1}{\pi}\int_0^{\infty}Q^0(t)e^{-i\omega t}dt=P^0(\omega),$$

and

$$\chi_0{}'(\omega)=\frac{1}{\pi}\mathrm{HW}\cdot\int\frac{P^0(\omega')d\omega'}{\omega'-\omega}\ ,$$

are the absorption and dispersion for the limiting case where $\omega_e=0$. Therefore we may write

$$R(i\omega)=\pi\{\chi_0{}''(\omega-i\omega_e)-i\chi_0{}'(\omega-i\omega_e)\}\ , \tag{6.18}$$

where we have assumed that the functions $\chi_0{}''$ and $\chi_0{}'$ can be analytically continued to complex values of the argument. These two

functions are mutually connected by the Kramers-Kronig relations, so that the knowledge of $P^0(\omega)$, for instance, allows us to construct its complementary part $\chi_0'(\omega)$. By the assumption of the regularity, we can then expand $R(i\omega)$ in powers of ω_e. Thus the intensity $I(\omega)$ can be calculated in power series of ω_e provided tha $\chi_0''(\omega)$ and $\chi_0'(\omega)$ are continuous and differentiable. To the first order of ω_e, we get

$$I(\omega)=P^0(\omega) + \omega_e\left[-\frac{d\chi_0'(\omega)}{d\omega}+\pi\{P^0(\omega)^2-\chi_0'(\omega)^2\}\right]+\cdots\cdots . \tag{6.19}$$

One finds easily that this first order term vanishes if $P^0(\omega)$ is Lorentzian. It would be interesting to examine the condition that the relaxation will result in the narrowing, or more roughly, in the enhancement of the peak. For this, let us assume the particular case where $P^0(\omega)$ has a single maximum at $\omega=0$ (which is the center of the gravity of the distribution $P^0(\omega)$) and further that $\chi_0'(0)=0$. Then

$$\omega_e\left[-\left\{\frac{d\chi_0'(\omega)}{d\omega}\right\}_{\omega=0}+\pi P^0(0)^2\right] =\frac{\omega_e}{\pi}\left\{\left[\int_0^\infty Q^0(t)\,dt\right]^2-\int_0^\infty tQ^0(t)dt\right\}, \tag{6.20}$$

is the first order change of the intensity at the peak. Evidently, this is equal to zero for the Lorentzian case, $Q^0(t)=\exp(-b|t|)$. If the decrease of $Q^0(t)$ is slower than the simple exponential decay for small values of t and faster for large t, then we may expect

$$\left\{\int_0^\infty Q^0(t)\,dt\right\}^2>\int_0^\infty tQ^0(t)dt ,$$

and the narrowing will take place as the result of the relaxation. If $Q^0(t)$ behaves in the opposite way, then we may except broadening rather than narrowing at least in the first order of ω_e. Thus, in a sense, the Lorentzian form is a stable distribution against the effect of random modulation of the resonating frequencies, which seems certainly of some physical interest.

§ 7. Remark on the Gaussian-Markoffian Limit

As we mentioned in § 2, the resonance frequency ω of a resonating unit is considered as a stochastic variable. If the random variable $\omega(t_1)$, $\omega(t_2)$, $\cdots\cdots$ $\omega(t_n)$ for any set of arbitrarily chosen n time points (n being arbitrary) are distributed with a Gaussian (normal) distribution function (naturally we assume here every $\omega(t)$ realizes continuous values),

$$f(\omega(t_1),\omega(t_2),\cdots\cdots,\omega(t_n)) =C\exp\left\{-\frac{1}{2}\sum_j\sum_k a_{jk}\omega(t_j)\omega(t_k)\right\},$$

$$\left(\int_{-\infty}^{\infty}\cdots\cdots\int_{-\infty}^{\infty} f(\omega(t_1),\cdots\cdots\omega(t_n))d\omega(t_1)\cdots\cdots d\omega(t_n) =1\right),$$

then the stochastic process of $\omega(t)$ is called a *Gaussian process*[3]. If the stochastic process $\omega(t)$, which is stationary, is Gaussian, it is easy to see that

$$g(t)=\exp\left\{-\int_0^t(t-\tau)\langle\omega(t'+\tau)\omega(t')\rangle d\tau\right\}, \tag{7.1}$$

as has been pointed out by Anderson and Weiss[4].

Now we shall remark here that under a certain conditions Markoffian process we have assumed in the above treatment approaches to a Gaussian-Markoffian process. Let us suppose that the resonance frequency of the resonating unit in each of its states is constructed from a number of small contributions. i.e.,

$$\omega(t)=\sum_n^N \Delta\omega_n(t) . \tag{7.2}$$

For instance, the resonance frequency of an unit can be conceived as determined by a local fied which is the resultant of small disturbances exerted by a number of surrounding atoms. The state of an unit is now characterized by the states of the surrounding atoms which are specified by set of numbers (j_1, j_2, $\cdots\cdots$ j_N). For simplicity we further assume that each of these atoms will realize its various states independently of the others. The stochastic process of the component $\Delta\omega_n(t)$ is thus assumed to be Markoffian which is due to random jumps of the n-th atom. Corresponding to our treatment in § 2, we describe this by the matrices D_n and $\Delta\Omega_n$. The zero-eigenvectors of D_n will be denoted by φ_{0n} and ψ_{0n}. Then we see at once that the

correlation function $g(t)$ for a resonating unit is given by

$$g(t)=\prod_{n=1}^{N} g_n(t)\ , \tag{7.3}$$

where

$$g_n(t)=\varphi_{0n}\exp\{-(D_n-i\Delta\Omega_n)t\}\psi_{0n}\ , \tag{7.4}$$

is the correlation function for the component $\Delta\omega_n(t)$. Now we expect there exists a generalization of the central limit theorem of probability theory which states that under some conditions the stochastic process of $\omega(t)$, (7.2), becomes Gaussian. A rigorous examination of this assertion is out of space, but we may say that if

$$\lim_{N\to\infty}\sum_{n=1}^{N}\langle(\Delta\omega_n-\langle\Delta\omega_n\rangle)^2\rangle=\lim_{N\to\infty}\sum_{n=1}^{N}\varphi_{0n}(\Delta\Omega_n)^2\psi_{0n}=\omega_p{}^2\ , \tag{7.5}$$

exists and if the distribution of every $\Delta\omega_n$ satisfies a certain condition such as the Lindeberg condition to prevent too wide a spread of its distribution function, the correlation function, (7.3) approaches to the form (7.1), for which we now have

$$\langle\omega(t'+\tau)\omega(t')\rangle=\lim_{n\to\infty}\sum_{n=1}^{N}\varphi_{0n}\Delta\Omega_n e^{-D_n\tau}\Delta\Omega_n\psi_{0n}=\lim_{N\to\infty}\varphi_0\Omega e^{-D\tau}\Omega\psi_0\ , \tag{7.6}$$

where Ω, D, φ_0 and ψ_0 now refer to the whole configuration space for all of the components.

With the use of the expansion formula for an exponential operator function,

$$e^{a+b}=e^a+\int_0^1 e^{(1-s)a}be^{sa}ds+\int_0^1\int_0^s e^{(1-s)a}be^{(s-s')a}be^{s'a}dsds'+\cdots,$$

we get

$$\begin{aligned}g_n(t)&=\varphi_{0n}\Big[e^{-D_nt}+\int_0^t e^{-D_n(t-t_1)}i\Delta\Omega_n e^{-D_nt_1}dt_1\\&\quad+\int_0^t\int_0^{t_1}e^{-D_n(t-t_1)}i\Delta\Omega_n e^{-D_n(t_1-t_2)}i\Delta\Omega_n e^{-D_nt_2}\\&\qquad\times dt_1dt_2+o(\Delta\omega^2)\Big]\psi_{0n}\\&=1+it\varphi_{0n}\Delta\Omega_n\psi_{0n}-\int_0^t(t-\tau)\varphi_{0n}\Delta\Omega_n e^{-D_n\tau}\\&\qquad\times\Delta\Omega_n\psi_{0n}d\tau+o(\Delta\omega^2)\\&=\exp\left\{-\int_0^t(t-\tau)\langle\Delta\omega_n(\tau)\Delta\omega_n(0)\rangle d\tau+o(\Delta\omega^2)\right\}\ ,\end{aligned}$$

where

$$\langle\Delta\omega_n\rangle=\varphi_{0n}\Delta\Omega_n\psi_{0n}=0\ ,$$

can be assumed without loss of generality.

Inserting the above expression into (7.3) and omitting the sum of the residual terms, we get

$$g(t)=\exp\left[-\int_0^t(t-\tau)\langle\omega(\tau)\omega(0)\rangle d\tau\right], \tag{7.7}$$

where $\langle\omega(\tau)\omega(0)\rangle$ is identical with (7.6). The correlation function (7.7) or (7.1) is equivalent to the Fourier transform of the absorption spectrum derived by Kubo and Tomita[5] with the use of second order perturbation theory. In particular, the strongly narrowed width of the spectrum is determined by

$$\int_0^\infty\langle\omega(\tau)\omega(0)\rangle d\tau=\int_0^\infty\varphi_0\Omega e^{-D\tau}\Omega\psi_0 d\tau\ ,$$

in agreement with Eq. (5.7). It should be noticed that this limit of strong narrowing is independent of the Gaussian assumption.

If the relaxation times or the eigenvalues of D (except the zero eigenvalue) are all degenerate (see § 6), we may write Eq. (7.7) as

$$\begin{aligned}g(t)&=\exp\left[-\omega_p{}^2\int_0^\infty\exp(-\omega_e\tau)(t-\tau)d\tau\right]\\&=\exp[-\omega_p{}^2(\exp(-\omega_et)-1+\omega_et)]\ .\end{aligned} \tag{7.8}$$

This should be compared with Eq. (7.25a) of Kubo and Tomita's paper. As was discussed by these authors (7.8) is a typical function to describe the narrowing process of a Gaussian spectrum with the second moment $\omega_p{}^2$ in the presence of a Markoffian motion characterized by the relaxation time $1/\omega_e$. This is the basis of the theory of motional narrowing of adiabatic broadening in nuclear magnetic resonance spectrum first discussed by Bloembergen, Purcell and Pound[6].

A particularly simple example of Eq. (7.8) is the case where every $\Delta\omega_n$ takes only two values ω_1 and $-\omega_1$ and the stochastic matrix of each component is

$$D_1=\begin{pmatrix}\frac{1}{2}\omega_e & -\frac{1}{2}\omega_e\\ -\frac{1}{2}\omega_e & \frac{1}{2}\omega_e\end{pmatrix}.$$

Then $g_1(t)$ is easily calculated to be

$$g_1(t)=\frac{1}{2\omega'}\left[\left(\frac{\omega_e}{2}+\omega'\right)\exp\left\{-\left(\frac{\omega_e}{2}-\omega'\right)t\right\}-\left(\frac{\omega_e}{2}-\omega'\right)\exp\left\{-\left(\frac{\omega_e}{2}+\omega'\right)t\right\}\right],$$

$$(\omega'^2=\omega_e^2/4-\omega_1^2)\ .$$

Taking the limit of $N\omega_1^2\to\omega_p^2$ as N increases indefinitely, it is easy prove directly Eq. (7.8).

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