Journal of the Physical Society of Japan Vol. 9, No. 3, May—June, 1954

A Mathematical Model for the Narrowing of Spectral Lines by Exchange or Motion*

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(Received January 11, 1954)

In this paper a simplified mathematical model of exchange and motional narrowing, which we call the "random frequency-modulation model," is developed, and, to a certain extent, justified. A number of cases are treated. The one general conclusion which is common to all is that in the case of extreme narrowing the central part of the line is resonance-shaped while the wings fall off more steeply than the resonance shape; the half-width is always of order of magnitude of the mean square frequency breadth divided by the rate of motion or exchange.

In two cases the model makes some quantitative approach to realism: first, the case of a single dipolar-broadened line with exchange, where the "Gaussian" assumption can be made and the results have been fitted to Van Vleck's fourth moment calculation to give satisfactory numerical answers; and second, the case of narrowing by diffusion in solids, where the "Markoffian" assumption is valid. The problem of narrowing of hyperfine structure is considered, and on this model it is found that before merging the lines draw together, a result which is confirmed by experiments.

§ 1. Introduction

Magnetic resonance spectroscopy, the study of absorption and dispersion of electromagnetic radiation by atomic or nuclear magnetic moments precessing about an external magnetic field, remains an active branch of physics. This may at first seem surprising: the magnetic resonance spectrum of an isolated atomic or nuclear moment consists of a single line at the Larmor frequency $\omega = g\beta/\hbar H$, and apparently there is only one parameter, g, to be measured for each atomic or nuclear species. However, when these moments are assembled into a piece of matter, their interactions affect this line, causing it to be shifted, or split up into components, and spread into a practically continuous band. We can learn about these interactions by studying the shape and breadth of this band, or by studying the related phenomenon of relaxation. Among other experimental and theoretical reasons, this very simplicity of the unperturbed spectrum has caused the study of line breadths, line shapes, and relaxation to assume a greater importance in magnetic resonance than in any other branch of spectroscopy. From its beginnings, magnetic resonance work has been deeply concerned with the line shape problem, and from the very first it has made great contributions through its line shape studies to our knowledge of the interactions and motions of atoms in matter.

The phenomenon of "narrowing" is a unique feature of magnetic resonance line breadths, and one of the most interesting and useful ones. It takes two forms: "motional narrowing", which is caused by the motions of the atoms themselves in gases, liquids, and even some solids; and "exchange narrowing", which is caused by exchange interactions (or exchange motions) of electronic magnetic moments. Exchange narrowing, although more complex, was apparently the first to be discussed, by Gorter and Van Vleck (1947)** and Van Vleck (1948), while motional narrowing was discussed by Bloembergen,

* Some of the work reported in this paper was also done independently by P. R. Weiss of Rutgers University, and discussions with Dr. Weiss have been most useful. A joint paper on this part has been published (Anderson and Weiss, 1953).

** References are found in a bibliography at the end of the paper, listed by year and author.

Purcell, and Pound (1948).

The mechanism is in principle the same in both motional and exchange narrowing. In order to understand this mechanism we must first have a clear understanding of what interactions can and cannot affect the magnetic resonance line directly. The line is a result of the precession of the magnetic moment of the sample, and therefore non-magnetic interactions cannot affect it directly. This is because these interactions (such as exchange, electric dipolar effects, etc.) are "unaware" of the direction of the magnetic moment, being magnetic scalars; in quantum language, they commute with the components of the magnetic moment and, by Heisenberg's equation of motion, cannot affect its motions. Only magnetic interactions, such as dipolar interactions, spin-orbit coupling, or hyperfine interactions of nuclei and electrons, can have a direct effect. These interactions, however, are themselves affected by non-magnetic interactions which cannot directly affect the line, and this produces the narrowing phenomenon.

Often the magnetic interactions are weak compared with the other interactions in the Hamiltonian. These other, non-magnetic interactions control the actual motions of electrons and atoms, and these motions may be quite rapid and completely independent of the magnetic phenomena. The magnetic interactions, since they depend on the positions of the electrons and atoms, will then vary in time in some way which is controlled by the electronic motions. It will be shown later that the magnetic resonance line experiences a time-averaged effect of the magnetic interactions. When the atomic or electronic motions are sufficiently rapid, this averaged effect may be much smaller than otherwise. Therefore the broadening effect of the magnetic interactions is reduced; the line is potentially narrowed and this is called the narrowing phenomenon.

The observed breadth of the line may contain two pieces of information: (1) the magnitude of the magnetic interactions; (2) the rate and magnitude of the motions of non-magnetic type. The second class of information may prove more interesting than the first. Unfortunately, while the breadth of the line in the absence of narrowing can be calculated in a rather rigorous manner (Van Vleck, 1948), no comparable treatment of the narrowing problem has appeared so far. There is a calculation of exchange narrowing by Van Vleck (1948) which, although perfectly rigorous, only shows that exchange narrowing occurs. At the same time it demonstrates that the actual line breadths and shapes are not calculable by the moment method.

Bloembergen, Purcell, and Pound (1948) attack the motional narrowing problem in a more physical way. They assume the basic mechanism explained above—that the broadening interactions vary in a random manner in time due to the non-magnetic interactions and motions—and estimate the line-breadth from this time variation. This estimate is very satisfactory. In the case of extreme narrowing (very rapid motions) it is

$$\Delta\omega \simeq \overline{\omega_p^2}/\omega_e\,, \qquad (1)$$

where $\overline{\omega_p^2}$ is the mean squared breadth in the absence of narrowing, and ω_e is an average rate of change of the broadening interactions. ω_e is equal to $1/\tau_c$, where τ_c is the "correlation time" of the motions.

In this paper we attack the narrowing problem (of either kind) by a method very similar to that of Bloembergen, Purcell, and Pound, in that we use a mathematical model which is also based on the above physical picture of the process. The model assumes that the precessing moments give rise to a radiated electromagnetic wave which is undergoing frequency-modulation, because the magnetic interactions act to change the frequency of the precession. The frequency-modulation is changing in a random way in time due to the effect of the non-magnetic motions on the magnetic interactions.

Only a qualitative justification for the model can be presented. However, there are good reasons for putting forward this method in spite of this. Most important is the fact that its simplicity and definiteness makes it possible to make much more complete calculations than have as yet been possible, and to treat more complex situations. Some of the resulting advantages are the following:

(a) The mathematics of the problem can be worked out in sufficient detail to give line-shapes as well as breadths. In all the variations of our model the line has the same general form: a Lorentz (resonance) line in the center with a more rapid decrease of intensity (a "cutoff") on the extreme wings. The fact that this shape is observed experimentally is valuable in giving confidence in the model; at the same time, the shape has become a useful tool in understanding experimental situations.

(b) An attempt is made to justify the use of one form of the model for the exchange narrowing problem. Van Vleck's calculations give numerical answers for two of the moments of the line shape, which can also be calculated by our model. However, as we have pointed out, his calculations cannot for fundamental reasons give the line-shape or breadth. We use the two moments computed by Van Vleck to fix the two adjustable constants in our line-shape (which are essentially $\overline{\omega_p{}^2}$ and ω_e as defined above), and then the observable breadth of the central peak can be related quantitatively to the dipolar interactions and the exchange integral. Thus we have used our method in this case essentially as an extrapolation method for Van Vleck's computation, and have obtained rather good agreement with experiment. This work was reported in an earlier paper (Anderson and Weiss, 1953); further details and some justification are included here.

(c) A particular model for the case of hyperfine structure can also be worked out in detail. The result is a qualitative indication of how the hyperfine structure peaks merge, which seems to be verified by a number of experiments.

(d) An extension of this model can be shown to be a fair approximation to the motional narrowing problem under diffusion in a solid. Here the random modulation of the frequency is "Markoffian", since the atomic jumps are very rapid compared to the length of time between them. In principle this problem is solvable in general, especially if the simplifying assumption is made that the jumps lead to a completely randomized frequency distribution. In this paper we give certain preliminary results for this problem.

§ 2. A General Discussion of Motional and Exchange Narrowing

In this section the justification from basic principles which is possible for the random frequency-modulation model is given and discussed. It can be made plausible that the general type of line-shape to be expected is derivable with this model; however, certainly one can make no exact quantitative theory.

It can be shown in general that the spectrum of the radiation from any quantum-mechanical system is given by*

$$I(\omega)=\mathrm{Trace}\left|\int_{-\infty}^{\infty}\mu(t)e^{-i\omega t}dt\right|^2, \qquad (2)$$

where $\mu(t)$ is the radiating dipole moment matrix in the Heisenberg representation:

$$i\hbar\frac{d\mu}{dt}=H\mu-\mu H. \qquad (3)$$

H is the complete Hamiltonian.

Now in any problem involving the type of narrowing we deal with here the Hamiltonian may be split up into three parts:

$$H=H_0+H_p+H_m. \qquad (4)$$

These three parts are: first, H_0, the "unperturbed Hamiltonian" which causes the energy-differences which lead to the observed spectral lines whose shapes we wish to study. Second is H_p, the "perturbing Hamiltonian"—generally just the dipolar interactions between the moments, although it may also involve other interactions, such as hyperfine splitting—which does not commute with H_0 and thus can change the frequencies radiated by the system over some more or less known range. H_p causes the broadening of the sharp single lines due to H_0 into broader lines or a fine structure. Finally, there is H_m, the "motional Hamiltonian", whose characteristic is that it commutes with both H_0 and μ, and thus can have no direct effect upon the radiation emitted or absorbed by the system. On the other hand, H_m does not commute with H_p, and thus, by the relation

$$i\hbar\dot{H}_p=[H,H_p]=[H_0,H_p]+[H_m,H_p], \quad (5)$$

H_m can cause a time-dependence of H_p. It is this time-dependence which "narrows out" the line-broadening which H_p otherwise would cause.

In the usual exchange narrowing case, H_0

* Anderson, 1949. A simple proof of equation (2) is given in Appendix I. The apparent lack of convergence is easily removed by convergence factors or by thinking of the integral as an average.

is the interaction of the magnetic moments μ of an assembly of atoms with the external field:

$$H_0=\sum_j \vec{\mu}_j\cdot\vec{H}=g\beta\sum_j \vec{S}_j\cdot\vec{H}\,. \qquad (6)$$

Here g is the Landé factor, β the Bohr magneton, $\vec{H}$ the external field, and $\vec{S}$ the spin.

H_p is the dipole-dipole interaction energy of the moments,

$$H_p=H_{dd}=g^2\beta^2\sum_{j,k}\frac{1}{r_{jk}^3}\left(\vec{S}_j\cdot\vec{S}_k-\frac{3(\vec{S}_j\cdot\vec{r}_{jk})(\vec{S}_k\cdot\vec{r}_{jk})}{r_{jk}^2}\right), \qquad (7)$$

which Van Vleck (1948) has shown can be simplified in some cases to

$$H_{dd}=g^2\beta^2\sum_{j,k}\frac{1}{r_{jk}^3}\left(\frac{3}{2}\cos^2\theta_{jk}-\frac{1}{2}\right)\times(\vec{S}_j\cdot\vec{S}_k-3S_{jz}S_{kz})\,. \qquad (8)$$

θ_{jk} is the angle between $\vec{r}_{jk}$ and the z-axis, along which we assume the external field to have been applied. It is assumed for the validity of (8) that $H_0 \gg H_p$; the terms omitted in (8) lead to the "satellite lines."

The "motional" Hamiltonian H_m in the ex change narrowing case is taken to be the Heisenberg exchange Hamiltonian,

$$H_m=H_{ex}=\sum_{j,k} J(\vec{r}_{jk})\vec{S}_j\cdot\vec{S}_k\,.$$

It can easily be shown that (9) commutes with the total spin vector of the system $\sum\vec{S}_j$, and thus both with its z-component, which is proportional to H_0 (6), and with its x or y component, which is the radiation dipole moment, $\mu(t)$, in (2). It does not commute with the dipole-dipole Hamiltonian H_{dd}, however.

In the case of motional narrowing H_0 and H_p ((6) and (7)) are of the same form as in exchange narrowing. Motion of the actual coordinates of the atoms can change H_{dd}, while neither H_0 nor $\mu=g\beta\sum_j S_{xj}$ are affected by physical motion, since they do not contain the spatial coordinates of the moments. In this case, H_m is the Hamiltonian of the translational and rotational motion of the molecules of the substance.

The random frequency-modulation picture of the narrowing process can be derived from the above physical assumptions:

(a) equation (2)
(b) equation (5)
(c) $H_m\mu-\mu H_m=0$
(d) $H_mH_0-H_0H_m=0$;
(e) and, in addition, the assumption that H_{dd} is small enough that it has no important matrix elements connecting different states $E_i^{(0)}$ and $E_j^{(0)}$ of the unperturbed energy H_0.

In any real substance assumption (e) will, of course, not be rigorously true, since there are many states of H_0 of equal energy (i.e. equal $S_z^{(0)}$) and therefore H_{dd} will obviously have important off-diagonal elements. However, we may look upon assumption (e) as an approximation—very like the "adiabatic approximation" of pressure broadening theory (Foley, 1946) which often, if carefully handled, leads to good quantitative results—which should not lead us too far astray. What is done is to use always a mean squared value of H_p which is computed without neglecting the off-diagonal elements, but to treat it as though it came only from diagonal ones. In other words, we do not neglect the magnitude of these elements but simply compute their effects non-rigorously whenever they are important.

Under assumptions (a–e), then, we wish to compute the spectral intensity (2). We realize first that we are only considering one spectral line, so that we only need to consider the element of $\mu(t)$ which connects two unperturbed levels of H_0, E_i and E_j. We can then say that for the spectral line under consideration,

$$\underset{i\to j}{I(\omega)}=\left|\int\mu_{ij}(t)\,e^{-i\omega t}\,dt\right|^2. \qquad (11)$$

Now we know part of the time-dependence of $\mu_{ij}(t)$, that due to the unperturbed Hamiltonian H_0. We express this fact by transforming to a new matrix element $\mu_{ij}'(t)$ which contains this time-dependence explicitly:

$$\mu_{ij}(t)=\mu_{ij}'(t)\exp(i\omega_{ij}^{(0)}t)\,, \qquad (12)$$

where

$$\hbar\omega_{ij}^{(0)}=E_i-E_j\,.$$

Now it is easily shown that the transformation (12) removes the terms of the time-equation (3) for μ which depend on H_0, so that now

$$i\hbar\frac{d\mu'}{dt}=[H_m+H_p,\mu]$$
$$=H_p\mu'-\mu'H_p\ , \qquad (13)$$

because of assumption (a).

Now, by the use of assumption (e) we can actually calculate $\mu_{ij}'(t)$, as follows:

$$i\hbar\dot{\mu}_{ij}'=[H_p\mu'-\mu'H_p]_{ij}$$
$$=(H_p)_{ii}\mu_{ij}'-\mu_{ij}'(H_p)_{jj}$$
$$\dot{\mu}_{ij}'(t)=i\Delta\omega_{ij}(t)\mu_{ij}'(t)\ . \qquad (14)$$

Here $\Delta\omega_{ij}(t)$ is defined as

$$\Delta\omega_{ij}(t)=\frac{H_p(t)_{ii}-H_p(t)_{jj}}{\hbar}\ . \qquad (15)$$

Equation (14) for the matrix element is easily integrated to give

$$\mu_{ij}'(t)=\mu_{ij}^{(0)}\exp\left(i\int_0^t\Delta\omega_{ij}(t')dt'\right). \qquad (16)$$

Inserting this into the intensity formula (11) gives us for the line shape (ignoring as usual constant or nearly constant factors since we wish only the shape function)

$$I_{ij}(\omega)\sim\left|\int_{-\infty}^{\infty}\exp\left(-i(\omega-\omega_{ij}^{(0)})t-i\int_0^t\Delta\omega_{ij}(t')dt'\right)\right|^2. \qquad (17)$$

$\Delta\omega_{ij}(t)$ is a random function of tlme; its value at any time depends on the values of the diagonal elements of H_p at that time, and these will change in a random way at a rate controlled by the motional Hamiltonian, H_m, as we see from the time equation (5) for H_p (there is no time dependence due to H_0 because these are diagonal elements):

$$i\hbar\dot{H}_p=[H_m,H_p]\ . \qquad (18)$$

The reason for assuming randomness is that in the important cases the effect of H_p back on H_m can be neglected, so that the motions embodied in H_m appear to the magnetic quantities to be uncorrelated. Equation (17), and the idea of $\Delta\omega_{ij}(t)$ as a random function of time whose rate of change is controlled by H_m according to (18), are the basic ideas of the random frequency-modulation model of narrowing phenomena.

In general, we will have no rigorous basis for giving $\Delta\omega_{ij}(t)$ any particular form. In the first place, because of the inaccuracy of assumption (e) $\Delta\omega_{ij}(t)$ is simply a construct, a single function which is meant to embody all of the broadening effects, diagonal as well as off-diagonal, of H_p. In the second place, even if we actually had a true expression for $\Delta\omega_{ij}(t)$ as a random function, we could probably not handle it mathematically in the present state of the theory of random functions.

What we know about $\Delta\omega_{ij}(t)$, or can usually find, is at least a good approximation to its probability distribution: the probability that at a given time it has a given value. In many cases Van Vleck (1948) gives us at least the mean second and fourth moments of this probability distribution (which, fortunately, seldom has the peculiarity of anomalously large wings); in other cases (Anderson 1950) the entire distribution is available.

Finding the random time properties of $\Delta\omega_{ij}(t)$ is another problem. It is likely that the problem of finding the line-shape is hopeless unless this function falls into one of the two simple cases, the Markoffian or the Gaussian, of random functions. (See Wang and Uhlenbeck, 1945) Even if we knew the exact properties of $\Delta\omega_{ij}(t)$, it would therefore be necessary to assume the best Gaussian or Markoffian fit to the real function before proceeding farther. For each of these two simple cases a solution for the intensity distribution (17) wiil be given in a later section of this paper. We shall show that the exchange narrowing problem probably is closely represented by a particular type of Gaussian random function. The problem of narrowing under diffusion in solids is a very close fit to the exact Markoffian case. Other cases must be arbitrarily assigned certain types of random functions.

Before going on with these detailed considerations, let us take a general look at the structure of the problem embodied in equations (17) and (18). The appearance of equation (17) may be simplified in the following way: let us redefine ω as

$$\omega=\omega-\omega_{ij}^{(0)}\ ; \qquad (19)$$

this is the frequency deviation from the line center. Also, let us introduce the phase deviation $\eta(t)$, which is of course simply the integral of the frequency deviation:

$$\eta(t)=\int^t\Delta\omega_{ij}(t')dt'\ . \qquad (20)$$

Then (17) becomes

$$I(\omega)=\left|\int_{-\infty}^{\infty}e^{-(\omega t-\eta(t))}\,td\right|^2, \qquad (21)$$

a form which is familiar from the "adiabatic theory" of pressure broadening. (See Anderson, 1949, or Foley, 1946.)

We shall find it very convenient to use the correlation-function form of the Fourier integral. By a well-known transformation one can show that

$$\left.\begin{aligned} I(\omega)&=\int_{-\infty}^{\infty} d\tau e^{i\omega\tau}\int_{-\infty}^{\infty} dt' \times e^{-i(\eta(t'+\tau)-\eta(t'))} \\ &\text{or,} \\ I(\omega)&=\int_{-\infty}^{\infty} d\tau e^{i\omega\tau}\varphi(\tau)\,. \end{aligned}\right\} \quad (23)$$

$\varphi(\tau)$ is called the "correlation (or autocorrelation) function" and can be written as:

$$\varphi(\tau)=\langle e^{i(\eta(t+\tau)-\eta(t))}\rangle \text{ave. over } t\,. \quad (24)$$

In view of equation (16), this is just the same as

$$\varphi(\tau)=\langle \mu_{ij}'^{*}(t+\tau)\mu_{ij}(t)\rangle \text{ave. over } t\,.$$

This represents the averaged "memory" of the function μ_{ij}' at the time $t+\tau$ for what its state was at a time τ earlier.

This theorem as a method of finding the line-breadth is much less sensitive to the exact line-shape than the moment method. A number of simple theorems showing this are given in Appendix II; however, we need, for present purposes, only the familiar one that the product of the frequency width of the spectrum of a function with the time-extension of this function is always roughly unity: $\Delta\omega\Delta t \simeq 1$. Thus we know that if $\varphi(\tau)$ falls off appreciably, say to $1/e$ of its value at $\tau=0$, by the time T, then the breadth of $I(\omega)$, its Fourier transform, is roughly

$$\Delta\omega \cong 1/T\,. \quad (25)$$

To find a rough estimate for T, let us go back to the definition (24) of $\varphi(\tau)$, remembering that η is given by (20).

Then

$$\varphi(\tau)=\left\langle \exp\left(i\int_t^{t+\tau}\Delta\omega_{ij}(t')dt'\right)\right\rangle \text{ave. over } t\,. \quad (26)$$

If $\omega_{ij}^{(0)}$ (i.e. H_0) was correctly chosen, there will be no tendency for $\eta(t)$ to change other than randomly with time; its swings may become larger but its average is zero. Then the question to be answered becomes: when on the average will the integral of $\Delta\omega_{ij}(t)$ take on a value of order of magnitude unity? This will make the real part of (26) small, and the imaginary parts will cancel because η is equally often positive or negative. Let us consider two cases:

I. The variation of $\Delta\omega_{ij}(t)$ with time is very slow. Then, for any given time t, $\Delta\omega_{ij}$ will have a nearly constant random value of order of magnitude

$$\Delta\omega_{ij} \simeq \sqrt{\overline{\Delta\omega_{ij}^2}}=\omega_p\,,$$

where we define ω_p as this value. Thus η will become appreciable in a time T satisfying $\omega_p T \cong 1$, so that the linebreadth is given by

$$\Delta\omega \cong \omega_p\,. \quad (27\text{–I})$$

Here we see that there has been no narrowing, as expected.

II. The time-rate of change of $\Delta\omega_{ij}(t)$ is greater than ω_p. In this case, although at any time $\Delta\omega_{ij}$ will be of roughly ω_p in magnitude, its value will change sign before the integral in (26) can become appreciable, and thus

$$\left.\begin{aligned} T &\gg 1/\omega_p \\ \Delta\omega &\ll \omega_p\,. \end{aligned}\right\} (27\text{–II})$$

Here we have narrowing, and we find that the criterion for "slow" vs. "rapid" motion is, correctly, that used by Bloembergen, Purcell and Pound (1948), namely a comparison with the line-breadth itself.

§ 3. The Spectrum for Gaussian Random Modulation; Exchange Narrowing

The case in which the random modulation of the frequency is Gaussian noise with an arbitrary spectrum is rather easily solved in general. The theorem which can be used in this case is the well-known one that any linear combination of values of a Gaussian random function is itself randomly distributed with a Gaussian probability curve. In the correlation function (26), the exponent

$$\int_t^{t+\tau}\Delta\omega_{ij}(t)dt=X(t,\tau) \quad (28)$$

is just such a linear combination. Thus we know that the probability distribution of X is simply

$$P(X)=\frac{1}{\sqrt{2\pi\overline{X^2}}}\exp\left(-\frac{X^2}{2\overline{X^2}}\right)\,. \quad (29)$$

Now we see that if we can find $\overline{X^2}$ we can find $\varphi(\tau)$, since

$$\left.\begin{aligned}\varphi(\tau)&=\int_{-\infty}^{\infty}e^{iX}P(X)dX\\ \varphi(\tau)&=\exp(-\overline{X^2}/2)\left[\frac{1}{\sqrt{2\pi\overline{X^2}}}\int_{-\infty}^{\infty}dy\right.\\ &\quad\left.\times\exp(-y^2/2\overline{X^2}\right]=\exp(-\overline{X^2}/2)\,.\end{aligned}\right\}\quad(30)$$

Now if $\varDelta\omega_{ij}(t)$ is a Gaussian random function it is completely characterized, aside from its mean square magnitude, by either its spectrum or its correlation function

$$\varphi_{\Delta\omega}(T)=\frac{\langle\varDelta\omega_{ij}(t)\varDelta\omega_{ij}(t+\tau)\rangle\text{ave.}}{\overline{\varDelta\omega_{ij}^2}}\,,\quad(31)$$

which are Fourier transforms of each other. Let

$$\omega_p^2=\overline{\varDelta\omega_{ij}^2}$$

be substituted for the mean square magnitude of the perturbation, for the sake of brevity. $\overline{X^2}$ can be found most easily in terms of the correlation function for $\varDelta\omega_{ij}$:

$$\begin{aligned}\overline{X^2}&=\left\langle\int_0^\tau dt\int_0^\tau dt'\varDelta\omega_{ij}(t)\varDelta\omega_{ij}(t')\right\rangle\text{ave.}\\ &=\omega_p^2\int_0^\tau dt\int_0^\tau dt'\varphi_{\Delta\omega}(t'-t)\,,\end{aligned}$$

the average being taken by the use of (31). The substitutlon of

$$x=t'-t$$
$$y=t'+t$$

as new variables leads to

$$\overline{X^2}=2\omega_p^2\int_0^\tau dx(\tau-x)\varphi_{\Delta\omega}(x)\,.$$

This gives us

$$\varphi(\tau)=\exp\left(-\omega_p^2\int_0^\tau dx(\tau-x)\varphi_{\Delta\omega}(x)\right).\quad(32)$$

Two extreme cases are now of interest. The first one corresponds to little or no narrowing. Here we assume that $\varDelta\omega_{ij}$ does not change appreciably during the time (about $1/\omega_p$) in which $\varphi(\tau)$ falls to a relatively low value. Then we can set $\varphi_{\Delta\omega}(x)=1$, so that

$$\varphi(\tau)_{\text{Case I}}=\exp(-\omega_p^2\tau^2/2)\,,\quad(33a)$$

and obviously the line shape is a Gaussian of second moment ω_p^2, which is of course precisely what we started out with. The more interesting case is Case II, in which we have a large narrowing. Then we can say that $\varphi_{\Delta\omega}(x)$ falls to a small fraction long before $\varphi(\tau)$ has changed appreciably. Let $1/\omega_e$ represent essentially the width of the $\varphi_{\Delta\omega}$ curve; this can be characterized by

$$\int_0^\infty\varphi_{\Delta\omega}(x)dx=\frac{1}{\omega_e}\,.\quad(34)$$

Then we can easily see that the contribution of the term in x in the integral is neglible, of order ω_p^2/ω_e^2, so that

$$\varphi(\tau)\cong\exp\left(-\omega_p^2\int_0^\tau dx\,\varphi_{\Delta\omega}(x)\right)$$

which, since most values of τ of interest are much greater than ω_e, gives

$$\varphi(\tau)_{\text{Case II}}\cong\exp(-\omega_p^2/\omega_e\cdot\tau)\,.\quad(33b)$$

This exponential correlation function corresponds to a lineshape of the resonance type, as is well-known. Thus at least the central portion of the line is of resonance shape; the wings are determined by $\varphi(\tau)$ for small τ, as we show in Appendix II, so that for these we need more detailed considerations. Note that this result is completely independent of the detailed shape of the correlation function $\varphi_{\Delta\omega}(\tau)$, and thus of the detailed spectrum of the random function $\varDelta\omega_{ij}(t)$; this is so unless this function has a correlation which falls off only as $1/\tau$ or less. Such a function would have a spectrum divergent at zero frequency, a possibility which seems very unlikely.

We shall give two explicit examples of the function $\overline{X^2}$. The first numerical example is the case of the Markoffian Gaussian process. A Markoffian process is a random process which proceeds in jumps, the probability of a jump to a given value of the function being dependent only upon the value of the function immediately before the jump. Such a process can be made Gaussian by letting the jumps become infinitesimally small. (See Wang and Uhlenbeck 1945). In this case the correlation function is exponential:

$$(\varphi_{\Delta\omega})_{\text{Mark.}}=e^{-\omega_e\tau}\,.\quad(35)$$

Here ω_e is the inverse of the correlation time τ_c for the process. Now

$$\begin{aligned}\overline{X^2}_{\text{Mark.}}&=2\omega_p^2\int_0^\tau dx(\tau-x)\exp(-\omega_e x)\\ &=2\omega_p^2\left[\frac{\tau}{\omega_e}-\frac{1}{\omega_e^2}(1-\exp(-\omega_e\tau))\right].\end{aligned}$$

This gives us for the correlation function

$$\begin{aligned}\varphi(\tau)_{\text{Mark.}}=\exp\Big\{&-\frac{\omega_p^2}{\omega_e}|\tau|\\ &+\frac{\omega_p^2}{\omega_e^2}(1-\exp(-\omega_e|\tau|))\Big\}\,.\quad(36)\end{aligned}$$

(We have inserted absolute value signs on τ because, of course, $\overline{X^2}$ is an even function of τ.) It can quickly be verified that our two limiting cases are true.

We should note that by either Theorem IV or V of the Appendix, the wings of the Gauss-Markoff spectrum fall off only as the fourth power of the frequency; it is easy to verify by those theorems, in fact, that the coefficient is

$$I(\omega)_{\omega\to\infty}\sim\frac{\omega_e\omega_p^2}{\omega^4}\,.$$

This means that, although it can be shown that in either limiting case the fourth power part is quite far on the wings, still it is true that the fourth moment is divergent. Van Vleck's calculations show that this is not a satisfactory model for exchange narrowing.

The second example we shall give is the Gaussian random noise with Gaussian spectrum. This should give results typical for the case in which the possible rate of change of frequency is severely limited. This is the situation one should expect to hold in exchange narrowing, where H_m can, after all, only change the frequency at a rate no greater than something of the order of $ZJ/\hbar$. Here we have a correlation function which is also Gaussian, and we define it as

$$\varphi_{\Delta\omega}(\tau)=\exp\left(-\frac{\pi}{4}\omega_e^2\tau^2\right). \qquad (37)$$

With this definition of $\varphi_{\Delta\omega}$ it is easy to see that ω_e agrees with the definition (34), and that therefore the limiting equation (33b) will hold. It is easily shown that in this case

$$\varphi(\tau)_{\text{Gauss}}=\exp\left\{-\frac{\omega_p^2\tau}{\omega_e}\int_0^{\omega_e\tau}\exp\left(-\frac{\pi}{4}x^2\right)dx+\frac{2\omega_p^2}{\pi\omega_e^2}\left(1-\exp\left(-\frac{\pi}{4}\omega_e^2\tau^2\right)\right)\right\}. \qquad (38)$$

For this case we should also like to have the second and fourth moments. These are most easily obtained through the theorems of the Appendix. By Theorem II,

$$\overline{\omega^2}=\omega_p^2\,. \qquad (39)$$

The fourth moment may be found either by Theorem I and taking the fourth derivative of (38), or by Theorem III of the Appendix. Using the latter method,

$$\omega^4=\langle\Delta\omega_{ij}^4\rangle_{\text{ave.}}+\left\langle\left(\frac{d}{dt}\Delta\omega_{ij}\right)^2\right\rangle_{\text{ave.}}\,.$$

The first term is easily found, since $\Delta\omega_{ij}$ is Gaussianly distributed; it is simply $3\omega_p^4$. A simple transformation based on the proof of theorem III given in the Appendix shows that

$$\left\langle\left(\frac{d}{dt}\Delta\omega_{ij}\right)^2\right\rangle_{\text{ave.}}=-\langle\Delta\omega_{ij}^2\rangle_{\text{ave.}}\left(\frac{d^2}{dt^2}\varphi_{\Delta\omega}(\tau)\right)_{\tau=0}=\frac{\pi}{2}\omega_p^2\omega_e^2\,.$$

Then

$$\overline{\omega^4}=3\omega_p^4+\frac{\pi}{2}\omega_p^2\omega_e^2\,. \qquad (40)$$

We see that now both moments (and in fact any further ones) are finite; the fourth moment, as discussed in Appendix III, has a form remarkably like that given by Van Vleck for the case of exchange narrowing.

For the comparisons with experiment which have as yet been made only these moments and the limiting cases of large and small narrowing are needed. The uncertainties caused by a number of experimental and theoretical complicating factors will make it hardly worthwhile, for these comparisons, to consider cases involving intermediate amounts of broadening. However, the line width has been computed approximately, for the sake of completeness, in the intermediate range where ω_p and ω_e are comparable. This material is therefore included in Appendix III.

The use of this Gaussian-Gaussian case as the model for exchange narrowing, and the comparison of its results with experiment, have been discussed in a previous paper (Anderson and Weiss, 1953). It is pointless to repeat this work here. The results are, in the main, very satisfactory; and indicate that the model is quite accurate and that no essentially new concepts need be introduced. The most interesting feature is the appearance of the "10/3 effect". The "satellite" (or non-secular) terms in the Hamiltonian (7) must be included when exchange is large, which can be understood from our model very easily.

§ 4. The Spectrum for Markoffian Random Modulation; Narrowing by Diffusion in Solids and Narrowing of Fine Structure

As has already been mentioned, the Markoffian is the second simple type of random function, and for this case too one can give a general method for finding the correlation function of the spectrum. The mathematics is considerably more complex than in the Gaussian case and in many cases the full solution cannot be carried out. We are, however, able to solve a few simple or limiting cases and get a general idea of the form of the solutions.

The problem is to find $\varphi(\tau)$ from equation (26)

$$\varphi(\tau)=\left\langle\exp\left(i\int_t^{t+\tau}\Delta\omega_{ij}(t')dt'\right)\right\rangle \text{av. over } t \tag{26}$$

under the assumption that $\Delta\omega_{ij}(t)$ is Markoffian. A Markoffian function $f(t)$ may be defined in a number of ways (see Wang and Uhlenbeck, 1945); the simplest is that the probability of a given value f_1 at the time t, if the value was f_2 at $t-\Delta t$, is independent of the value of the function at any earlier time than $t-\Delta t$. Thus the probability depends only on the value of the function at the earlier time, not on its slope, past history, etc.

An example of such a function is one which can take on the values ± 1, and whose probability of transition from one to the other in a given time interval dt is a constant, dt/τ. A more physical example is the momentum of a gas particle in a rarified gas of hard spheres. Collisions change the momentum by an amount independent of its earlier history, depending only on its present momentum.

The Markoffian process is characterized completely by its "second-order probabilities." In the case of a function of a continuous variable, the time, the second-order probabilities are written as

$$\left.\begin{array}{l}\text{Probability that value is } f_2 \text{ if}\\ \text{value is } f_1\ \Delta t \text{ seconds earlier}\end{array}\right\} = W(f_1|f_2,\Delta t). \tag{41}$$

If the function is not to vary in a senselessly rapid fashion it is known that W must be proportional to Δt for small Δt unless $f_1=f_2$; in fact, W may be written as

$$W(f_1|f_2,\Delta t)=\delta(f_1,f_2)+\Pi(f_1,f_2)\Delta t, \tag{42}$$

where now Π is the probability per unit time of a transition from f_1 to f_2. The δ-symbol is Kronecker if the f's form a discrete set, Dirac if the f's are continuous. Finally, since*

$$\int W df_2=1,$$

(stating that the function must have some value at every time) we see that

$$\int \Pi\, df_2=0, \tag{43a}$$

so that, since the transitions to values of $f_2 \neq f_1$ must always have positive probabilities, we have

$$\Pi(f_1,f_2)=-\omega_e(f_1)(\delta(f_1,f_2)-P(f_1,f_2)), \tag{44}$$

where the presumably non-singular function P is normalized:

$$\int P(f_1,f_2)df_2=1, \tag{43b}$$

and ω_e represents the total probability of transitions from the value f_1.

A few more words on Markoffian functions: There is for the usual case of "stationary" functions a "static distribution" or intrinsic probability distribution, $W_1(f)$, which is the probability distribution of f one gets if the function is left alone, for an indefinite period. Such a distribution has to be self-perpetuating, which means that it must satisfy the Smoluchowski equation embodying the condition that if the distribution W_1 holds at t it must hold at $t+\Delta t$:

$$W_1(f_2)=\int df_1 W_1(f_1)W(f_1|f_2,\Delta t), \tag{45}$$

or

$$0=\int df_1\,\Pi(f_1,f_2)W_1(f_1), \tag{45a}$$

or, finally,

$$\omega_e(f_2)W_1(f_2)=\int df_1 P(f_1,f_2)W_1(f_1)\omega_e(f_1). \tag{45b}$$

We see from comparing (45b) with (43b) that $P(f_1,f_2)$ is not symmetrical in its arguments. This could be avoided very easily by using

* All equations like the following can be written either as though f has a continuous range, in which case $\int df$ can be used, or as though f is discrete, in which case they are to be written as $\sum_f$. The one way of writing is generally obvious if the other is given, so that I shall not give both except where confusion might arise.

instead the function $\omega_e(f_1)W_1(f_1)P(f_1, f_2)$ which is symmetrical, at least in all cases we consider. This corresponds to defining a second-order probability $W'(f_1|f_2, \Delta t)$ which is the probability that the value is f_1 at t and f_2 at $t+\Delta t$, which is symmetrical unless the process violates microscopic reversibility.

With this brief introduction to Markoffian theory, let us see what can be done with (26) if $\Delta\omega_{ij}(t)$ is our Markoffian function $f(t)$. A matrix method of solution is used* in which we consider the probabilities $W(f_1, f_2)$ or $P(f_1, f_2)$ as two-dimensional matrices connecting the sets of indices f_1 to f_2; thus possibly for the following the assumption that $\Delta\omega$ has a discrete set of values will be more convenient.

The average in (26) may be written in the following way. We divide the interval τ into n equally spaced steps, such that τ/n is very small compared with the rate of change of $\Delta\omega$; then (42) will hold. The averagand is

$$\exp\left(i\sum_{m=1}^{n}\frac{\tau}{n}\Delta\omega\left(t+m\frac{\tau}{n}\right)\right) = \exp\left(i\int_t^{t+\tau}\Delta\omega(t')dt'\right). \quad (46)$$

Now we want to know the probability that $\Delta\omega$ takes on a certain set of values at the various instants in equation (46): i.e., that

$$\Delta\omega\left(t+\frac{\tau}{n}\right)=\Delta\omega_1, \quad \Delta\omega\left(t+2\frac{\tau}{n}\right)=\Delta\omega \quad \cdots\Delta\omega\left(t+\frac{m\tau}{n}\right)=\Delta\omega_m.$$

This is easily found (see, again, Wang and Uhlenbeck (1945)). The probability is

$$P(\Delta\omega_1\Delta\omega_2\cdots\Delta\omega_n)=W_1(\Delta\omega_1)\,W\left(\Delta\omega_1|\Delta\omega_2,\frac{\tau}{n}\right) \times W\left(\Delta\omega_2|\Delta\omega_3,\frac{\tau}{n}\right)\times\cdots\times W\left(\Delta\omega_{n-1}|\Delta\omega_n,\frac{\tau}{n}\right). \quad (47)$$

Now we can find (26) simply by summing the product of (46) and (47) over all the possible combinations of $\Delta\omega$'s, since these are respectively the value and the probability of a given averagand.

$$\varphi(\tau)=\sum_{\Delta\omega_1}\sum_{\Delta\omega_2}\sum_{\Delta\omega_3}\cdots\left(\exp\left(i\frac{\tau}{n}\sum_{m=1}^{n}\Delta\omega_m\right)\right) \times W_1(\Delta\omega_1)\prod_{m=2}^{n}W\left(\Delta\omega_{m-1}|\Delta\omega_m,\frac{\tau}{n}\right). \quad (48)$$

$$=\sum_{\Delta\omega_1}\sum_{\Delta\omega_2}\cdots\sum\prod_{m=1}^{n-1}\left(\exp\left(i\frac{\tau}{n}\Delta\omega_m\right) \times W\left(\Delta\omega_m|\Delta\omega_{m+1},\frac{\tau}{n}\right)\right)\exp\left(i\Delta\omega_n\frac{\tau}{n}\right).$$

Now the central product has the form of a matrix product. It will have this form exactly if we define the diagonal matrix $\underline{\underline{\Delta\omega}}$:**

$$(\underline{\underline{\Delta\omega}})_{\Delta\omega_1\Delta\omega_2}=\delta(\Delta\omega_1, \Delta\omega_2)\times\Delta\omega_1 \quad (49)$$

which has the effect in matrix multiplication simply of multiplying any matrix element $\underline{\underline{M}}_{\Delta\omega_1\Delta\omega_2}$ by $\Delta\omega_1$. The probability matrix has already been suggested:

$$\underline{\underline{W}}\left(\frac{\tau}{n}\right)_{\Delta\omega_1\Delta\omega_2}=W\left(\Delta\omega_1|\Delta\omega_2,\frac{\tau}{n}\right). \quad (50)$$

We also introduce $\underline{W_1}(\Delta\omega)$ as a row vector in $\Delta\omega$ space, and $\underline{1}(\Delta\omega)$, the vector all of whose components are unity, as a column vector.

Neglecting $\Delta\omega_n\cdot\tau/n$ at once compared to unity, we can write (48) as a matrix product multiplied on left and right by row and column vectors respectively:

$$\varphi(\tau)=\underline{W_1}\cdot\left(\exp\left(i\frac{\tau}{n}\underline{\underline{\Delta\omega}}\right)\underline{\underline{W}}\left(\frac{\tau}{n}\right)\right)^{n-1}\cdot\underline{1}. \quad (48a)$$

Now, since $\tau/n\cdot\Delta\omega$ can be made as small as we like, it is permissible to let

$$\underline{\underline{\exp\left(i\frac{\tau}{n}\Delta\omega\right)}}=\underline{\underline{1}}+i\frac{\tau}{n}\underline{\underline{\Delta\omega}}$$

while from (42) we can rewrite the matrix W in terms of a matrix $\underline{\underline{\Pi}}$:

$$\underline{\underline{W}}\left(\frac{\tau}{n}\right)=\underline{\underline{1}}+\underline{\underline{\Pi}}\frac{\tau}{n}.$$

This gives us for the product in (48a)

$$\left(\underline{\underline{\exp\left(i\frac{\tau}{n}\Delta\omega\right)}}\,\underline{\underline{W\left(\frac{\tau}{n}\right)}}\right)^{n-1} = \left(1+\frac{\tau}{n}(i\underline{\underline{\Delta\omega}}+\underline{\underline{\Pi}})\right)^{n-1}$$

which, letting n go to infinity, is

$$\underline{\underline{\exp(\tau(i\Delta\omega+\Pi))}}$$

so that (48) becomes

$$\varphi(\tau)=\underline{W_1}\cdot\underline{\underline{\exp(\tau(i\Delta\omega+\Pi))}}\cdot\underline{1}$$

or,

---

* The method was suggested by the Kramers-Wannier (1941) method in statistical mechanics.

** We shall underline vectors once, matrices twice in this vector space, the coordinates of which are numbers referring to the various possible values of $\Delta\omega$.

$$\varphi(\tau)=\sum_{\Delta\omega_1,\Delta\omega_2}\underline{W_1}(\Delta\omega_1)\{\underline{\underline{\exp(\tau(i\Delta\omega+\Pi))}}\}\Delta\omega_1,\Delta\omega_2 \tag{49}$$

Equation (49) is the general solution of our problem. It expresses $\varphi(\tau)$ in terms of the known matrices $\underline{\underline{\Pi}}$, defining the Markoffian process, and $\underline{\underline{\Delta\omega}}$, and the function $\underline{W_1}(\Delta\omega_1)$ (actually derivable from $\underline{\underline{\Pi}}$ by the integral equation (45b).)

We see now the form which the solution to this problem will take. The basic problem will be to diagonalize the matrix $(\underline{\underline{i\Delta\omega+\Pi}})$ by means of a transformation matrix $\underline{\underline{T}}$:

$$\underline{\underline{T}}^{-1}(\underline{\underline{i\Delta\omega+\Pi}})\underline{\underline{T}}=\underline{\underline{\Lambda}}\ ,$$

where $\underline{\underline{\Lambda}}$ is a diagonal matrix. If we can find $\underline{\underline{\Lambda}}$ and $\underline{\underline{T}}$, we can transform the two vectors $\underline{W_1}$ and $\underline{1}$ by means of $\underline{\underline{T}}$ into the coordinate system in which $\underline{\underline{i\Delta\omega+\Pi}}$ is diagonal. $\varphi(\tau)$ will then be a sum of exponentials $e^{-\Lambda_i\tau}$ in the eigenvalues* whose coefficients will depend on the extent to which their individual eigenvectors are contained in $\underline{W_1}$ and $\underline{1}$. Fourier transformation then shows us that $I(\omega)$ is a sum of resonance (Laplacian) distributions, with central frequencies given by the imaginary parts of the Λ_i, and widths by the negative real parts. In explicit form, we label the eigenvalues of $\underline{\underline{\Lambda}}$ with the subscript α, β etc. and the various $\Delta\omega$'s as before, and

$$\begin{aligned}\varphi(\tau)&=\sum_{\Delta\omega_1,\Delta\omega_2}(\underline{W_1})_{\Delta\omega_1}[\underline{\exp(\tau(i\Delta\omega+\Pi))}]_{\Delta\omega_1\Delta\omega_2}\\&=\sum_{\Delta\omega_1,\Delta\omega_2,\Delta\omega_3,\Delta\omega_4}\ \sum_{\alpha,\beta}(\underline{W_1})_{\Delta\omega_1}\underline{\underline{T}}_{\Delta\omega_1\alpha}\underline{\underline{T}}_{\alpha\Delta\omega_2}{}^{-1}\\&\quad\times[\underline{\underline{\exp(\tau(i\omega+\Pi))}}]_{\Delta\omega_2\Delta\omega_3}\underline{\underline{T}}_{\Delta\omega_3\beta}\underline{\underline{T}}_{\beta\Delta\omega_4}{}^{-1}\\&=\sum_{\Delta\omega_1,\Delta\omega_2,\alpha}(\underline{W_1})_{\Delta\omega_1}\underline{\underline{T}}_{\Delta\omega_1\alpha}\exp(\Lambda_\alpha\tau)\underline{\underline{T}}_{\alpha\Delta\omega_2}{}^{-1}\end{aligned} \tag{50}$$

so that the coefficient going with $\exp(\Lambda_\alpha\tau)$ is

$$\sum_{\Delta\omega_1,\Delta\omega_2}(\underline{W_1})_{\Delta\omega_1}\underline{\underline{T}}_{\Delta\omega_1\alpha}\underline{\underline{T}}_{\alpha\Delta\omega_2}{}^{-1}\ .$$

The two limiting cases of extreme narrowing and no narrowing come out of this formalism very easily. For little narrowing, we should be able to neglect transitions relative to the frequency differences, so that $\underline{\underline{i\Delta\omega}}\gg\underline{\underline{\Pi}}$. Then the matrix $\underline{\underline{i\Delta\omega+\Pi}}$ is already diagonal so that there is no necessity for using T (i.e. $T_{\alpha\Delta\omega}=\delta_{\alpha\Delta\omega}$) and the eigenvalues of $\underline{\underline{i\Delta\omega+\Pi}}$ are just $i\Delta\omega$. Equation (50) becomes

$$\varphi(\tau)=\sum_{\Delta\omega}W_1(\Delta\omega)e^{i\Delta\omega\tau}$$

which transforms into the spectrum

$$I(\omega)=\sum_{\Delta\omega}W_1(\Delta\omega)\delta_{\omega,\Delta\omega}=W_1(\omega)\ ,$$

which is just the spectrum we started with (since W_1 represents the normal stationary distribution of frequencies).

In the case of extreme narrowing, on the other hand, we can at first neglect $\underline{\underline{i\Delta\omega}}$ relative to $\underline{\underline{\Pi}}$. Now we really know without further specification only one eigenvalue of $\underline{\underline{\Pi}}$: namely, the eigenvalue zero, which corresponds to the right eigenvector $\underline{1}$, the left eigenvector $\underline{W_1}$. This is easily seen from the equations (43a) and (45a), which in sum notation read

$$\sum_{\Delta\omega_1}\underline{W_1}(\Delta\omega_1)\underline{\underline{\Pi}}_{\Delta\omega_1\Delta\omega_2}=(\underline{W_1}\cdot\underline{\underline{\Pi}})_{\Delta\omega_2}=0\ ,$$

and

$$\sum_{\Delta\omega_2}\underline{\underline{\Pi}}_{\Delta\omega_1\Delta\omega_2}=(\underline{\underline{\Pi}}\cdot\underline{1})_{\Delta\omega_1}=0\ .$$

This is a fortunate situation: it shows us that the vectors we actually happen to have in (49) for this case are the eigenvectors of the only eigenvalue we know exactly, so that the transformation matrix $\underline{\underline{T}}$ has non-vanishing coefficients only for this one eigenvalue, and

$$\varphi(\tau)=1\ .$$

This of course gives us an infinitely sharp line at the central frequency: $I(\omega)=\delta(\omega)$.

Next we consider the effect of including $\underline{\underline{i\Delta\omega}}$ in thc calculation to first or second order. In the first order, obviously all that happens is to change the eigenvalue by $\langle i\Delta\omega\rangle_{\text{ave.}}$: the center of our narrowed distribution is at the average frequency of the un-narrowed distribution. To second order, the other eigenvalues of $\underline{\underline{\Pi}}$ will begin to enter to some extent, but this is a minor effect, since the greater part of the line intensity will still be in the zero-eigenvalue line. This line, however, will also be affected, since the eigenvalue will be changed by an amount of order of magnitude $1/\Pi(i\Delta\omega)^2$. This can easily be shown to be a real negative contribution and means that the line has a breadth of order

* Note: For negative τ it may be easily verified that $\varphi(-\tau)=\varphi^*(\tau)$ so that, for negative τ, Λ_i must be replaced by $-\Lambda_i^*$. If this were not true the spectral intensity would take on complex values.

$(\Delta\omega)^2/\omega_e$, the usual "narrowed" breadth. Thus here again we see the basic features of the exchange narrowing phenomenon coming out.

It is of interest, both in clarifying the previous discussion and in bringing out further points, to actually work out some simple cases as far as possible. The simplest possible case is that in which we have only two possible frequency shifts, which we take (this is of course no specialization) to be $\pm\omega_0$, and these frequencies are equally probable so that $W_1(+\omega_0)=W_1(-\omega_0)$. The only possible "transition-matrix" $\underline{\underline{\Pi}}$ for this case is

$$\underline{\underline{\Pi}}=\begin{bmatrix}-\omega_e & \omega_e\\ \omega_e & -\omega_e\end{bmatrix}, \qquad (51)$$

where ω_e is an adjustable parameter specifying the rate at which jumping takes place back and forth between the two frequencies. The matrix we wish to diagonalize is then

$$\underline{\underline{(i\Delta\omega+\Pi)}}=\begin{bmatrix}i\omega_0-\omega_e & \omega_e\\ \omega_e & i\omega_0-\omega_e\end{bmatrix}. \qquad (52)$$

The secular equation is easily seen to be, (if λ is the eigenvalue)

$$(\omega_e+\lambda)^2+\omega_0^2-\omega_e^2=0,$$

or

$$\lambda=-\omega_e\pm\sqrt{\omega_e^2-\omega_0^2}. \qquad (53)$$

Defining

$$x=\omega_0/\omega_e, \qquad (54)$$

as the ratio of splitting to jump-rate,

$$\lambda=-\omega_e\,(1\pm\sqrt{1-x^2}). \qquad (53a)$$

Equation (53a) already says a great deal about the spectrum, since it gives the center frequencies and the breadths of the two component lines. For $x>1$ (splitting predominant) (53) reads

$$\lambda=\pm i\sqrt{\omega_0^2-\omega_e^2}-\omega_e, \qquad (53b)$$

which says that the two lines at $\pm\omega_0$ begin to draw together as the jump-rate increases but always have the breadth (half at half power) ω_e, given by the rate of jumping, so long as $x>1$. The breadth ω_e corresponds to the "exchange broadening" idea: lines separated by splittings large compared to the exchange frequency are broadened, not narrowed.

This tendency of the lines to draw closer together before being completely narrowed out seems to be experimentally confirmed by various measurements on hyperfine structure in dilute solutions of paramagnetic ions.* It seems to be a general property of the secular equations, although it can be less pronounced for larger numbers of lines, as we shall see.

In the case in which the jumping predominates, $x<1$, we have equation (53a), with no imaginary part of λ at all: both component lines are centered at the mean frequency. One line has a breadth of order of magnitude $2\omega_e$, the other a breadth (if $\omega_e\gg\omega_0$)

$$\Delta\omega=-\omega_e\left(1-\sqrt{1-\frac{\omega_0^2}{\omega_e^2}}\right)$$
$$\simeq\frac{\omega_0^2}{2\omega_e},$$

which exhibits the usual exchange narrowing form. This is the line which predominates: we shall see that the effect of the other line is simply to introduce a cutoff in the wings so that these fall off as $1/\omega^4$ rather than $1/\omega^2$. (Note that the fourth moment is infinite, as is to be expected from the theorems of Appendix I.)

Proceeding with the calculations of the explicit line shape, we define the two roots as

$$\left.\begin{aligned}\lambda_1&=-\omega_e(1-\sqrt{1-x^2})\\ \lambda_2&=-\omega_e(1+\sqrt{1-x^2})\end{aligned}\right\} \qquad (55)$$

The components of the transforming matrix $\underline{\underline{T}}$ must satisfy**:

$$\left.\begin{aligned}(i\omega_0-\omega_e-\lambda_1)T_{11}+\omega_eT_{21}&=0\\ (i\omega_0-\omega_e-\lambda_2)T_{22}+\omega_eT_{12}&=0\end{aligned}\right\} \qquad (56)$$

Now the correlation function is

$$\varphi(\tau)=\sum_{\lambda=\lambda_1,\lambda_2}\ \sum_{\Delta\omega_1,\Delta\omega_2=\pm\omega_0}\underline{\underline{T}}_{\Delta\omega_1\lambda}e^{\lambda\tau}\underline{\underline{T}}_{\lambda\Delta\omega_2}^{-1} \qquad (57)$$

so the coefficient of the λ_1 term, for instance, is

$$T_{11}T_{11}^{-1}+T_{21}T_{12}^{-1}+T_{21}T_{11}^{-1}+T_{11}T_{12}^{-1}.$$

We use the fact that $TT^{-1}=1$ to combine the first two terms, and using the orthogonality of T to effect further simplification it can eventually be shown that

* Schneider and England, 1951: they mention the effect on p. 225, and also it is evident in the $1N$ picture of their fig. 3. Garstens (1952) has also mentioned this effect.

** Note that this case involves a complex symmetric matrix $\underline{\underline{(i\Delta\omega+\Pi)}}$ so that a diagonalizing matrix can certainly be found. It can in fact be chosen to be a complex orthogonal matrix.

$$\varphi(\tau)=\left.\begin{array}{l}\exp\{-\omega_e\tau(1-\sqrt{1-x^2})\}\left(1+\dfrac{1}{\sqrt{1-x^2}}\right)\\ \quad+\exp\{(-\omega_e\tau(1+\sqrt{1-x^2})\}\left(1-\dfrac{1}{\sqrt{1-x^2}}\right)\end{array}\right\} \tag{58}$$

To obtain the spectrum from (58), we must separate the two cases $x>1$ and $x<1$. For $x>1$ (splitting predominant) we get

$$\begin{aligned}I(\omega)=\int_0^\infty e^{-\omega_e\tau}\Big[&\cos(\omega+\omega_e\sqrt{x^2-1})\tau\\ &+\frac{1}{\sqrt{x^2-1}}\sin(\omega+\omega_e\sqrt{x^2-1})\tau\\ &+\cos(\omega-\omega_e\sqrt{x^2-1})\tau\\ &-\frac{1}{\sqrt{x^2-1}}\sin(\omega-\omega_e\sqrt{x^2-1})\tau\Big]\end{aligned}$$

(the sine terms entering because, again, $\varphi(-\tau)=\varphi^*(\tau)$ so that the imaginary coefficients must change sign upon change of sign of τ.) This gives us

$$I(\omega)=2\left[\frac{2\omega_e+\omega/\sqrt{x^2-1}}{(\omega+\omega_e\sqrt{x^2-1})^2+\omega_e^2}+\frac{2\omega_e-\omega/\sqrt{x^2-1}}{(\omega-\omega_e\sqrt{x^2-1})^2+\omega_e^2}\right]. \tag{59a}$$

We note here that the spectrum is not exactly the sum of two resonance distributions, because of the imaginary terms which give us the odd terms in the numerator; but if $1\ll x$ or ω is not comparable with ω_0 (i.e. near the centers of the lines) the difference is small. However, as $x\to1$ these terms take on major importance in making the transition to the narrowed case, in which the signs of the two distributions are opposite. A summed form of (59a) will be of interest: It is

$$I(\omega)=\frac{8\omega_e^3x^2}{\omega^4+2\omega^2\omega_e^2(2-x^2)+\omega_e^4x^4}=\frac{8\omega_e\omega_0^2}{\omega^3+2\omega^2(2\omega_e^2-\omega_0^2)+\omega_0^4}. \tag{59b}$$

This is the same as the expression which has been obtained by Archer (1953) by an entirely different method. It is rather interesting that this summed expression is identical in the two cases $x<1$ and $x>1$, in spite of the apparent discontinuity in λ_1 and λ_2 between the two cases.

For $x<1$ the same procedure can be followed, although here the mathematics is a little simpler.

$$\begin{aligned}I(\omega)&=2\int_0^\infty\cos\omega\tau e^{-\omega_e\tau}\Big(\exp(+\omega_e\sqrt{1-x^2}\tau)\\ &\quad\times\left(1+\frac{1}{\sqrt{1-x^2}}\right)+\exp(-\omega_e\sqrt{1-x^2}\tau)\\ &\quad\times\left(1-\frac{1}{\sqrt{1-x^2}}\right)\Big)\\ &=\frac{2\omega_ex^2}{\sqrt{1-x^2}}\left[\frac{1}{\omega^2+\omega_e^2(1-\sqrt{1-x^2})^2}-\frac{1}{\omega^2+\omega_e^2(1+\sqrt{1-x^2})^2}\right].\end{aligned} \tag{59c}$$

Note the behavior of (59c) when $x\ll1$. Then the first term will far overshadow the second until $\omega\sim\omega_e$; at this point the two begin to be approximately equal, and thus the wings of the line fall off more rapidly than $1/\omega^2$ beyond this point.

The two terms of (59c) can be added together:

$$\begin{aligned}I(\omega)&=\frac{2\omega_ex^2}{\sqrt{1-x^2}}\frac{(4\omega_e^2\sqrt{1-x^2})}{\omega^4+\omega_e^4(1+1-x^2)-2\omega_e^4\sqrt{1-x^2}\times(\omega^2+\omega_e^2(1+1-x^2)+2\omega_e^2\sqrt{1-x^2})}\\ &=\frac{8\omega_e^3x^2}{\omega^4+2\omega^2\omega_e^2(2-x^2)+\omega_e^4x^4}\end{aligned}$$

and we get (59b), again in agreement with Archer.

Archer's form can be used to show that the "two-line" formulas such as (53) must not be taken too seriously: the imaginary part of λ does not give exactly the frequency of the maxima of the spectrum, nor do these maxima come together exactly at $x=1$; it gives rather a way of dividing the spectrum into two "lines". The actual maxima occur at the minima of the denominator in (59b) which come at

$$\left.\begin{array}{ll}\omega_{\max}=\pm\sqrt{\omega_0^2-2\omega_e^2} & x^2>2\\ \omega_{\max}=0 & x^2<2\end{array}\right\} \tag{60}$$

In figures 1 and 2 are plotted some of these results. Figure 1a shows both the imaginary part of λ (the nominal frequency of the lines) and the maxima (60) plotted against x (we plot ω/ω_0 to show the effect of narrowing). Figure 1b gives the nominal half-breadth, λ_{real} (divided by ω_e), as a function of x. There is not much point in finding the true half-breadth from (59b) since the line shape is not even approximately resonance in the intermediate region where corrections are important. In figure 2 a few of the complete line shapes are plotted for the inter-

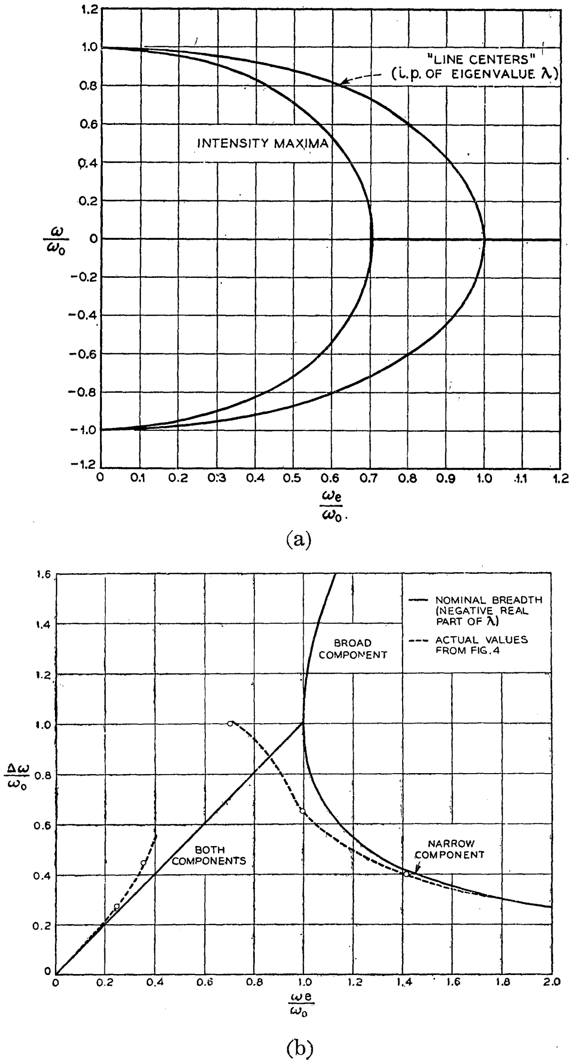

Fig. 1. Line breadths and frequencies for a pair of lines under exchange or motional narrowing.

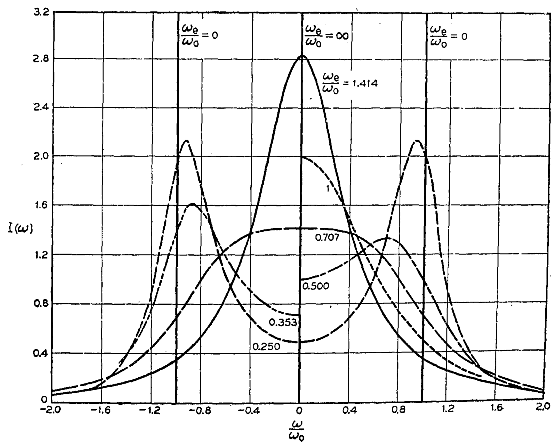

Fig. 2. Spectral intensity for a pair of lines with the ratio ω_e/ω_0 of jump-rate to splitting as parameter.

mediate region.

This very simple two-frequency case is the only one which is easily done exactly. It would be possible, but not very fruitful, to solve three- and four-line cases, which could of course be done in general. It seems to me more interesting to develop some fairly general perturbation methods for dealing with certain classes of cases involving many lines, so that we can get a rough idea of the behavior in the strong and weak narrowing regions.

The correct approach in the weak narrowing case is quite obvious: ordinary perturbation theory. Here the secular equation is nearly diagonal already, since we assume $i\Delta\omega \gg \Pi$. To first order, the j'th eigenvalue is just the j'th diagonal element:

$$\lambda_j^{(1)} = i\omega_j + \Pi_{jj} = i\omega_j - \omega_e(j)\,. \qquad (61)$$

This means that the individual lines are at first only broadened slightly by the frequency jumps. The second-order perturbation theory gives

$$\lambda_j^{(2)} = -\omega_e(j) + i\left(\omega_j - \sum_k \frac{\Pi_{jk}\Pi_{kj}}{\omega_j - \omega_k}\right). \qquad (62)$$

We see that there is a frequency-shift, of second order in Π (or ω_e) which, it is easily verified, is such as to shift the lines towards the center of the pattern. However, it is possible in some cases that the shift will not occur for all lines of a pattern, as we shall see, since it requires that there be more transition probability toward the center of the pattern than toward the edges *for each individual line,* which is not necessarily always the case.

We can give the expression for (62) for two simple cases which we shall consider as typical of two possible extremes. In each case we consider that the spectrum consists of a series of n equally spaced, equally strong lines, of frequencies

$$\omega_j = (n-1)i\omega_0,\ (n-3)i\omega_0 \cdots (-n+3)i\omega_0,\ (-n+1)i\omega_0\,. \qquad (63)$$

In case (a) we say that transitions are equally likely to all other lines of the spectrum (we assume a symmetrical Π-matrix) so that

$$\Pi_a=\begin{pmatrix} -\omega_e & \frac{\omega_e}{n-1} & \frac{\omega_e}{n-1} & - & - & - & \frac{\omega_e}{n-1} \\ \frac{\omega_e}{n-1} & -\omega_e & \frac{\omega_e}{n-1} & - & - & - & - \\ \frac{\omega_e}{n-1} & \frac{\omega_e}{n-1} & -\omega_e & - & - & - & - \\ \cdot & - & - & - & - & - & - \\ \cdot & - & - & - & - & - & - \\ \cdot & - & - & - & - & - & - \\ \frac{\omega_e}{n-1} & - & - & - & - & - & -\omega_e \end{pmatrix} \tag{64}$$

The transition probability *from* each line is ω_e. In case (b) we say that transitions occur only to the nearest lines, and so except for the end lines each line must have a probability for transition from it of ω_e, to each of its neighbors of $\omega_e/2$. This gives

$$\Pi_b=\begin{pmatrix} -\frac{\omega_e}{2} & \frac{\omega_e}{2} & 0 & 0 & - & - & - & 0 \\ \frac{\omega_e}{2} & -\omega_e & \frac{\omega_e}{2} & - & - & - & - & - \\ 0 & \frac{\omega_e}{2} & -\omega_e & - & - & - & - & - \\ 0 & 0 & \frac{\omega_e}{2} & - & - & - & - & - \\ 0 & - & - & - & - & - & - & - \\ \cdot & - & - & - & - & - & \frac{\omega_e}{2} & 0 \\ \cdot & - & - & - & - & - & -\omega_e & \frac{\omega_e}{2} \\ 0 & - & - & - & - & 0 & \frac{\omega_e}{2} & \frac{-\omega_e}{2} \end{pmatrix} \tag{65}$$

For case (a), (62) gives for the original line of frequency $m\omega_0$,

$$(\lambda_m)_a=-\omega_e +i\left(m\omega_0-\sum_{l=-n+1}^{n-1}{}' \omega_0\frac{\omega_e^2}{(n-1)^2}\times\frac{1}{m-k}\right).$$

(The prime, of course, means $k\neq m$). The pattern is symmetrical about 0, so pick $m>0$. Then

$$(\lambda_m)_a=-\omega_e +i\left(m\omega_0-\frac{\omega_e^2}{(n-1)^2\omega_0}\sum_{l=(n+1)-m}^{(n-1)+m}\frac{1}{l}\right). \tag{66}$$

(It must be remembered that all sums here are by steps of two.)

Case (b) is simpler. Clearly, all of the lines except the end ones are unshifted, as we suggested before could happen. The central lines have:

$$(\lambda_m)_b\big|_{|m|\neq n-1}=im\omega_0-\omega_e\,; \tag{67}$$

while the end lines obey

$$(\lambda_m)_b\big|_{m=\pm(n-1)}=-\frac{\omega_e}{2}+i\left((n-1)\omega_0-\frac{\omega_e^2}{8\omega_0}\right). \tag{68}$$

For the simple case of $n=4$ it might be useful to write down the various breadths and shifts, in Table I.

Table I

Line	Case a		Case b	
	breadth	shift	breadth	shift
$3\omega_e$	ω_e	$-\frac{11}{108}\frac{\omega_e^2}{\omega_0}$	$\frac{\omega_e}{2}$	$-\frac{\omega_e^2}{8\omega_0}$
ω_0	ω_e	$-\frac{\omega_e^2}{36\omega_0}$	ω_e	0
$-\omega_0$	ω_e	$+\frac{\omega_e^2}{36\omega_0}$	ω_e	0
$-3\omega_0$	ω_e	$+\frac{11}{108}\frac{\omega_e^2}{\omega_0}$	$\frac{\omega_e}{2}$	$+\frac{\omega_e^2}{8\omega_0}$

It is interesting to note that the shifts are rather small, and also that the sum of the shifts of the two lines on one side of the center is roughly the same in the two cases. The smallness is checked by experiment, in that the lines seem to shift only a very little before they merge and begin to narrow as a group.

Finally, it has been checked, in connection with these formulas and with Table II, that the change in the amplitudes with which the various components enter is of still higher order in ω_e/ω_0 and will probably not be noticeable until the perturbation treatment breaks down entirely.

The approximation from the opposite end of the scale, large narrowing, ($\Pi\gg i\Delta\omega$) is based on the observation we have already made, that the line-shape at this end is determined by the one eigenvalue λ near zero; all others represent broad, weak components of the line and can be neglected. Thus we can set λ nearly equal to zero; this implies that the large terms in the secular equation are those with low powers of λ, which we now set out to compute.

The constant term in the secular equation is the determinant, $|i\Delta\omega+\Pi|$. We note that $|\Pi|=0$, and that if the pattern is symmetrical there must be no imaginary terms so that the first terms here are of order ω_0^2. The term in λ in the secular equation is made up of the product of the various subdeterminants times λ:

$$(-\lambda)\sum_j |i\Delta\omega+\Pi|^{jj}$$

where this denotes the determinant with the j'th row and column omitted. If $\sum_j|\Pi|^{jj}\neq 0$, it certainly will overwhelm $i\Delta\omega$, so that this term is of order $\lambda\Pi\sim\omega_0^2$, as we shall see. The next term must be of order $\lambda^2\sim\omega_0^4$, so we can omit it. We have then

$$-\lambda\sum_j|\Pi|^{jj}+|i\Delta\omega+\Pi|=0$$

$$\lambda=\frac{|i\Delta\omega+\Pi|_{\omega_0^2\text{terms}}}{\sum_j|\Pi|^{jj}}. \qquad (69)$$

Examples will make this much clearer. We consider again the problems of Cases (a) and (b), defined by the transition matrices (64) and (65). In case (a)

$$\sum_j|\Pi|^{jj} = n\overbrace{\begin{vmatrix} -\omega_e & \frac{\omega_e}{n-1} & \frac{\omega_e}{n-1} & - & - & - & \frac{\omega_e}{n-1} \\ \frac{\omega_e}{n-1} & -\omega_e & & & & & \cdot \\ \cdot & \cdot & & & & & \cdot \\ \cdot & \cdot & & & & & \cdot \\ \frac{\omega_e}{n-1} & - & - & - & - & - & -\omega_e \end{vmatrix}}^{n-1\text{ columns}} \; n-1 \text{ rows}$$

This determinant can be evaluated to give

$$\sum_j|\Pi|^{jj}=\left(\frac{-n\omega_e}{n-1}\right)^{n-1}. \qquad (70)$$

Now we want to compute the ω_0^2 terms in $|i\omega+\Pi|$.

$$|i\omega+\Pi| = \begin{vmatrix} (n-1)i\omega_0-\omega_e & \frac{\omega_e}{n-1} & \frac{\omega_e}{n-1} \text{----} & \frac{\omega_e}{n-1} \\ \frac{\omega_e}{n-1} & (n-3)i\omega_0-\omega_e & \frac{\omega_e}{n-1} \text{--------} & \\ \frac{\omega_e}{n-1} & \frac{\omega_e}{n-1} & (n-5)i\omega_0-\omega_e \text{----} & \\ - & - & - & - \end{vmatrix}$$

The terms in $i\omega_0$, as already pointed out, vanish by cancellation between $+$ and $-\omega_j$. The terms in ω_0^2 can be picked out and are

$$|i\omega+\Pi|_{\omega_0^2}=\sum_{m<m'}(i\omega_0)^2mm'\left(\frac{\omega_e}{n-1}\right)^{n-2} \times \begin{vmatrix} 1-n & 1 & 1 & 1 & \cdots & 1 \\ 1 & 1-n & 1 & \cdots & 1 & \cdots \\ 1 & 1 & 1-n & \cdots & & \\ - & - & - & \cdots & & \end{vmatrix} \; (n-2 \text{ rows}) \qquad (71)$$

This determinant and the sum are easily evaluated. The result is

$$|i\omega+\Pi|_{\omega_0^2}=\frac{n^2-1}{3}\,\omega_0^2\left(\frac{-n\omega_e}{n-1}\right)^{n-2} \qquad (72)$$

and finally, the eigenvalue of interest is

$$\lambda=-\frac{\omega_0^2}{\omega_e}\,\frac{(n-1)^2(n+1)}{3n}. \qquad (73)$$

Note that this expression (which is the breadth of the narrowed line in this case) represents roughly the ratio of the square of the breadth of the pattern ($n\omega_0$) to the rate at which the frequency changes (ω_e).

Case (b) can also be done in general. $\sum_j|\Pi|^{jj}$ can be seen to be the sum of all the possible partitions into pieces of form

$$m \text{ rows} \overbrace{\begin{vmatrix} -\omega_e & \frac{\omega_e}{2} & 0 & - & - & - \\ \frac{\omega_e}{2} & -\omega_e & \frac{\omega_e}{2} & & & - \\ 0 & \frac{\omega_e}{2} & -\omega_e & & & - \\ & & & & -\omega_e & \frac{\omega_e}{2} \\ 0 & - & - & 0 & \frac{\omega_e}{2} & -\frac{\omega_e}{2} \end{vmatrix}}^{(m\text{ columns})} =\left[-\left(\frac{\omega_e}{2}\right)\right]^m \qquad (74)$$

by a simple computation. Adding the partitions together we get

$$\sum_j|\Pi|^{jj}=n\left(-\frac{\omega_e}{2}\right)^{n-1}. \qquad (75)$$

Now we must find $|i\omega+\Pi|_{\omega_0^2\text{terms}}$. The determinant $|i\omega+\Pi|$ is

$$|i\Delta\omega+\Pi| = \left|\begin{array}{ccccc} (n-1)i\omega_0-\dfrac{\omega_e}{2} & \dfrac{\omega_e}{2} & 0 & 0 & - \\ \dfrac{\omega_e}{2} & (n-3)i\omega_0-\omega_e & \dfrac{\omega_e}{2} & 0 & - \\ 0 & \dfrac{\omega_e}{2} & (n-5)i\omega_0-\omega_e & \dfrac{\omega_e}{2} & 0 \\ 0 & 0 & - & - & \\ \cdot & \cdot & & & \dfrac{\omega_e}{2} \\ \cdot & \cdot & & & \\ \cdot & \cdot & & & \\ 0 & - & - & \dfrac{\omega_e}{2} & \left(-(n-1)i\omega_0\dfrac{-\omega_e}{2}\right) \end{array}\right| \tag{76}$$

This may be broken up into a sum of terms containing $(im\omega_0)$ $(im'\omega_0)$ with $m>m'$. Multiplying these terms will be a product of three sub-determinants A, B, and C, with A being the part above $im\omega_0$. A and C will be of the form (74) with $(n-1-m)/2$ and $(n-1+m')/2$ rows and columns respectively.

$$A=\left(-\frac{\omega_e}{2}\right)^{((n-1)-m)/2}$$

$$C=\left(-\frac{\omega_e}{2}\right)^{(m'+(n-1))/2}.$$

The terms between $im\omega_0$ and $im'\omega_0$ give another type of determinant:

$$B=\left|\begin{array}{cccccc} -\omega_e & \dfrac{\omega_e}{2} & 0 & 0 & - & 0 \\ \dfrac{\omega_e}{2} & -\omega_e & \dfrac{\omega_e}{2} & & & - \\ 0 & \dfrac{\omega_e}{2} & -\omega_e & & & - \\ 0 & 0 & & & & - \\ - & & & -\omega_e & \dfrac{\omega_e}{2} & 0 \\ - & & & \dfrac{\omega_e}{2} & -\omega_e & \dfrac{\omega_e}{2} \\ 0 & - & - & 0 & \dfrac{\omega_e}{2} & -\omega_e \end{array}\right|$$

$$\times\left(\frac{m-m'}{2}-1 \text{ rows and columns}\right)$$

$$B=\left(\frac{\omega_e}{2}\right)^{(m-m')/2-1}\left(\frac{m-m'}{2}\right)(-1)^{(m-m')/2-1}$$

by another computation.

Thus, finally, we have

$$|i\Delta\omega+\Pi|_{\omega_0^2\text{terms}} = -\omega_0^2\left(\frac{-\omega_e}{2}\right)^{n-2}\sum_{m>m'} mm'\left(\frac{m-m'}{2}\right). \tag{77}$$

The summation in (77) can be evaluated by straightforward application of the various summation formulas for powers of integers, and the final result is

$$|i\Delta\omega+\Pi|_{\omega_0^2\text{terms}} = \left(\frac{-\omega_e}{2}\right)^{n-2}\omega_0^2\,\frac{n(n^4-1)}{30} \tag{78}$$

and

$$\lambda=-\frac{(n^4-1)}{15}\frac{\omega_0^2}{\omega_e}. \tag{79}$$

The fact that n^4 instead of n^2 (as in 73) appears in (79) for large n is reasonable on the following basis. The total width of the original pattern is $\sim n\omega_0$. This means that for λ to remain reasonable as $n\to\infty$ $\omega_e\sim n^2$; but this is correct, because this is the condition that the rate of diffusion remains reasonable. That is, the expression (79) is still the square of the band-width divided by the effective rate of change of frequency, which in this case of only short jumps is ω_e/n^2.

For such an unrealistic model further detailed study of particular discrete cases is hardly important. The next logical step is to consider continuous distributions of ω and, particularly, to consider a relatively realistic model of the effect of solid diffusion on unclear resonance breadths, which has been observed experimentally by Norberg and Slichter (1951). Diffusion in solids usually proceeds by jumps, short compared to the time between jumps. It is also true that a given atom nearly completely changes its magnetic environment with each jump (if the system is not dilute; diffusion in such a system as H in Pd or Na in NH_3 is quite a different thing, since there the perturbers are relatively far away compared to the jump distance, and there will be long-term correlation). If this is the case, we may assume that the new frequency to which a given atom jumps is unrelated to its old frequency.

Such a Markoff system can be set up, and integral equations found for the eigenvalues and eigenvectors. We shall do this, although we have not been able to solve the system in general, because of certain irregularities. However, the interesting case of extreme narrowing can be solved.

In the continuous case, the matrix $\underline{\underline{\Delta\omega}}$ can be written

$$(\underline{\underline{\Delta\omega}})_{\omega_1,\omega_2}=\omega_1\delta(\omega_1-\omega_2)\,. \qquad (80)$$

We assume that the frequencies are distributed according to some probability function $P(\omega)$. $P(\omega)$ (which we take to be normalized) is then the line shape in case the jump rate is slow. In accordance with our physical idea of what happens in the diffusion process, we assume that the probability of jumping *from* a given frequency per unit time is constant, $=\omega_e$. The probability of jumping *to* a given frequency ω_2 we assume unrelated to the previous frequency, so it can only be proportional to $P(\omega_2)$. These two criteria are satisfied if we set

$$\underline{\underline{\Pi}}(\omega_1,\,\omega_2)=\omega_e(-\delta(\omega_1-\omega_2)+P(\omega_2))\,. \qquad (81)$$

We could check that with $W_1(\omega)=P(\omega)$, the two Smoluchowski equations (43a) and (45a) are satisfied.

Now our problem is simply to diagonalize the matrix $(i\Delta\omega+\Pi)$, which gives us an integral eigenvalue equation. We introduce the eigenvector $\phi(\omega_2)$, and the integral equation is

$$\int d\omega_2(i\underline{\underline{\Delta\omega}}+\underline{\underline{\Pi}})(\omega_1,\,\omega_2)\underline{\phi(\omega_2)}=\lambda\underline{\phi(\omega_1)}\,. \qquad (82)$$

Equation (82) may be written out using (80) and (81), and we get

$$(\lambda+\omega_e-i\omega_1)\phi(\omega_1)=\omega_e\int P(\omega_2)\phi(\omega_2)d\omega_2\,. \qquad (83)$$

(83) can be solved in the two limiting cases of $\omega_e\to0$ and $\omega_e\to\infty$. In case $\omega_e\to0$, obviously

$$\phi(\omega_1)=\delta(\omega-\omega_1)$$

and

$$\lambda=i\omega\,.$$

Here the distribution is, of course, unchanged. In case $\omega_e\to\infty$, we may for practical purposes neglect $i\omega$ on the left, and then there are two possibilities: $\phi(\omega_1)=$constant, $\lambda=0$ or $\phi(\omega_1)=$any function orthogonal to $P(\omega_1)$, in which case both sides are zero and $\lambda=-\omega_e$. This reflects the fact that any distribution which is not $P(\omega)$ will decay according to $\exp(-\omega_e t)$ into $P(\omega)$; the eigenvalue $\lambda=0$ belongs to the stationary distribution. $\lambda=0$ means an infinitely narrow line, of course.

Mathematical difficulties immediately attend any perturbation approach from the side of $\omega_e=0$, because of the singularity of the eigenvectors; one easily sees that the perturbation of the eigenvector is also singular.

On the other end, a fairly satisfactory treatment of the eigenvalue coming from $\lambda=0$ can be done, as follows. The right-hand side of (83) is just a constant if it does not identically vanish; call this constant $\alpha\omega_e$, and we get

$$\phi(\omega_1)=\frac{\alpha\omega_e}{\lambda+\omega_e-i\omega_1}\,. \qquad (84)$$

But this must integrate to give α back again, so that

$$\int P(\omega)\frac{\alpha\omega_e}{\lambda+\omega_e-i\omega}=\alpha$$

$$1=\omega_e\int_{-\infty}^{\infty}\frac{P(\omega)}{\lambda+\omega_e-i\omega}d\omega.$$

Now we assume λ real and $P(\omega)$ an even function of ω. Then we get

$$1=\omega_e\int_0^{\infty}P(\omega)d\omega\left(\frac{1}{\lambda+\omega_e-i\omega}+\frac{1}{\lambda+\omega_e+i\omega}\right)$$

$$=2\omega_e\int_0^{\infty}P(\omega)d\omega\frac{\lambda+\omega_e}{(\lambda+\omega_e)^2+\omega^2}\,. \qquad (85)$$

This is a rigorous integral equation for the eigenvalue λ which, in principle, could be directly integrated at any time if we had the distribution $P(\omega)$.

Notice, however, that (85) will cease to furnish a real eigenvalue when ω_e becomes too small. For instance, imagine that $P(\omega)$ is a flat-topped distribution of width $2\omega_p$, height $1/2\omega_p$. Then the most the integral in (85) can give is $\pi/4\omega_p$, so the right-hand side is always less than $(\pi/2)\omega_e/\omega_p$. If ω_p is too large, this cannot equal 1.

We are, then, concerned primarily with the case in which the breadth of $P(\omega)$ is fairly small relative to ω_e. We can expand the integral, then, and get

$$1=\frac{2\omega_e}{\lambda+\omega_e}\int P(\omega)d\omega\left(1-\frac{\omega^2}{(\lambda+\omega_e)^2}\right)$$

or,

$$\lambda+\omega_e=\omega_e-\frac{\langle\omega^2\rangle_{\text{ave}}\omega_e}{(\lambda+\omega_e)^2}\,.$$

If ω_e is not too small, we can assume $\lambda\ll\omega_e$, and

$$\lambda\simeq-\frac{\langle\omega^2\rangle_{\text{ave}}}{\omega_e}\,. \qquad (86)$$

This is a very simple formula, and entirely in accordance with our expectations. It can be assumed that since all other eigenvectors will be approximately orthogonal to $P(\omega)$, only this eigenvalue will be important for large narrowing, and (86) may be taken to be the breadth of the line.

Further mathematical manipulations with the continuous case have not been successful, nor is it certain that they are of much help in solving problems. It would be of some interest to have a solution for the effect of correlation between the frequencies before and after a jump, but this has not been attempted. A sounder physical basis for the calculations in this section would also be desirable.

I am indebted to a number of my colleagues for helpful discussion, notably Drs. Lewis, Holden and Machlup. Professor Van Vleck kindly showed me Archer's results prior to publication.

Appendix I

Proof of the General Fourier Integral Equation for the Spectrum

The spectrum is given in more familiar form in the following way. We take the energy levels $E_1, \cdots E_m \cdots$ of the entire substance. The spectral intensity of the radiation or absorption of the substance, as it is most usually defined (we omit external factors) is given by

$$I(\omega)d\omega=\sum_{m,n}{}' |\mu_{mn}|^2\rho(m) \qquad (a)$$

where the prime on the sum means that we sum only over levels such that

$$E_m-E_n=\hbar\omega \qquad (b)$$

to within the interval $\hbar d\omega$. μ is the dipole moment matrix of the substance. $\rho(m)$ is essentially $\exp(-E_m/kT)$; it is practically constant in a paramagnet in normal circumstances and so will hereafter be omitted for brevity. The difficulty all comes from the restriction of the sum due to (b); but this can be avoided by the well-known trick of using the δ-function expansion

$$2\pi\delta(x)=\int_{-\infty}^{\infty}e^{ixt}dt\,. \qquad (c)$$

Then we get

$$I(\omega)=\sum_{m,n}\left|\int_{-\infty}^{\infty}dt\exp\left(-i\left(\omega-\frac{E_m-E_n}{\hbar}\right)t\right)\mu_{mn}\right|^2$$

where now the sum is unlimited. But

$$\exp\left(i\frac{(E_m-E_n)t}{\hbar}\right)\mu_{mn}=(\mu(t))_{mn}\,,$$

the time-dependent matrix element of the dipole moment, which satisfies equation (3) of the text. Thus we have,

$$I(\omega)=\sum_{m,n}\left|\int_{-\infty}^{\infty}dte^{-i\omega t}\mu(t)\right|^2_{mn}$$
$$=Tr\left|\int_{-\infty}^{\infty}dt\mu(t)e^{-i\omega t}\right|^2.$$

In case we want to include the density function $\rho(m)$, this can easily be done; the result is the more general formula given in the reference, Anderson (1949).

Appendix II

Some Useful Theorems About the Relationship Between $\varphi(\tau)$, $I(\omega)$ and $\Delta\omega_{ij}(t)$

Theorem I.

$$\frac{(-i)^n\dfrac{d^n\varphi}{d\tau^n}\Big|_{\tau=0}}{\varphi_{\tau=0}}=\frac{\int_{-\infty}^{\infty}d\omega\omega^nI(\omega)}{\int_{-\infty}^{\infty}d\omega I(\omega)}$$

or, if $\varphi(0)=1$ and $I(\omega)$ is normalized to unity,

$$(-i)^n\frac{d^n\varphi}{d\tau^n}\Big|_{\tau=0}=\int_{-\infty}^{\infty}d\omega\omega^nI(\omega)\,;$$

and conversely, the same theorem is true with $I(\omega)$ replaced by $\varphi(\tau)$ and vice versa, and the sign of i changed. The theorem is not new and is proved trivially by differentiating and setting $\tau=0$. The theorem means that the moments of $I(\omega)$ are determined by the behavior of $\varphi(\tau)$ very close to the origin, which may (as we shall see by the next theorem) have very little to do with its general course. On the other hand, we know intuitively that $I(\omega)$ will not be peculiar at the origin (unless it happens to have line structure, which case we shall ignore for the time being) so that we expect the moments of $\varphi(\tau)$ to be normal and manageable, and to be closely related to the line-breadth.

Theorem II.

The second moment of $I(\omega)$, in case it is of the form (21) of the text, is independent of whether or how $\varDelta\omega_{ij}(t)$ changes in time, but depends only on the probability distribution of $\varDelta\omega_{ij}(t)$; in fact, it is given by $\overline{(\varDelta\omega_{ij})^2}$.

This is easily proved from the first theorem. Starting with

$$\frac{d\varphi}{d\tau}=\langle i\varDelta\omega_{ij}(t+\tau)\exp\left(i\int_t^{t+\tau}\varDelta\omega_{ij}dt'\right)\rangle_{\text{ave.}}$$

we may shift the origin by an amount τ, so long as we leave the points equivalent to t and $t+\tau$ in the same relationship to each other. (This trick is not really necessary here, but will be useful for theorem III.) Thus we may write

$$\frac{d\varphi}{d\tau}=i\langle\varDelta\omega_{ij}(t)\exp\left(i\int_{t-\tau}^{t}\varDelta\omega_{ij}(t')dt'\right)\rangle_{\text{ave.}};$$

$$\frac{d^2\varphi}{d\tau^2}=-\langle\varDelta\omega_{ij}(t)\varDelta\omega_{ij}(t-\tau)\times\exp\left(i\int_{t-\tau}^{t}\varDelta\omega_{ij}(t')dt'\right)\rangle_{\text{ave.}}.$$

Clearly,

$$\left.\frac{d^2\varphi}{d\tau^2}\right|_{\tau=0}=-\langle(\varDelta\omega_{ij}(t))^2\rangle_{\text{ave. over } t},$$

and by theorem I we get our theorem. This theorem shows one of the many close analogies between our model and the real narrowing problem. Van Vleck (1948) shows the above relation to be true for the exchange narrowing problem—i.e. exchange cannot change the mean squared breadth—and it also can be shown for the motional narrowing problem, since it depends only on the assumption (a) of section II of this paper.

Another theorem showing the similarity of the model to the real problem is the following:

Theorem III.

$$\overline{\omega^4}=\left.\frac{d^4\varphi}{d\tau^4}\right|_{\tau=0}=\langle\varDelta\omega_{ij}^4\rangle_{\text{ave.}}+\langle\left(\frac{d}{dt}\varDelta\omega_{ij}\right)^2\rangle_{\text{ave.}}.$$

This is easily proved starting from the expression for $d^2\varphi/d\tau^2$ above. We get

$$\frac{d^3\varphi}{d\tau^3}=-\langle\varDelta\omega_{ij}(t)\left(\frac{d}{d\tau}\varDelta\omega_{ij}(t+\tau)+i\varDelta\omega_{ij}^2(t-\tau)\right)\exp\left(i\int_{t-\tau}^{t}\varDelta\omega_{ij}(t')dt'\right)\rangle_{\text{ave.}}$$

and now shifting the averaging variable back again to the original one by a change of τ, we get

$$\frac{d^3\varphi}{d\tau^3}=\langle\varDelta\omega_{ij}(t+\tau)\left(\frac{d}{dt}\varDelta\omega_{ij}(t)-i\varDelta\omega_{ij}^2(t)\right)\times\exp\left(i\int_t^{t+\tau}\varDelta\omega_{ij}(t')dt'\right)\rangle_{\text{ave.}}$$

$$\frac{d^4\varphi}{d\tau^4}=\langle\left(\frac{d}{dt}\varDelta\omega_{ij}(t+\tau)+i\varDelta\omega_{ij}^2(t+\tau)\right)\times\left(\frac{d}{dt}\varDelta\omega_{ij}(t)-i\varDelta\omega_{ij}^2(t)\right)\times\exp\left(i\int_t^{t+\tau}\varDelta\omega_{ij}(t')dt'\right)\rangle_{\text{ave.}}$$

$$\left.\frac{d^4\varphi}{d\tau^4}\right|_{\tau=0}=\overline{\omega^4}=\langle\varDelta\omega_{ij}^4\rangle_{\text{ave.}}+\langle\left(\frac{d}{dt}\varDelta\omega_{ij}\right)^2\rangle_{\text{ave.}}.$$

Now Van Vleck's result for $\overline{\omega^4}$ can be written in the following way;

$$\overline{\omega^4}=\langle[H,[H,\mu]]^2\rangle_{\text{ave.}}$$

which, in view of the facts that H_0 can be transformed out of all operators, and that H_m commutes with μ, gives us

$$\begin{aligned}\hbar^4\overline{\omega^4}&=\langle[H_p+H_m,[H_p,\mu]]^2\rangle_{\text{ave.}}\\&=\langle[H_p,[H_p,\mu]]^2\rangle_{\text{ave.}}\\&\quad+\langle[H_m,[H_p,\mu]]^2\rangle_{\text{ave.}}\\&\quad+2\langle[H_m,[H_p,\mu]][H_p,[H_p,\mu]]\rangle_{\text{ave.}}\end{aligned}$$

and he found that the last term on the right was always quite negligible. Thus he could write the fourth moment as the sum of the "normal" fourth moment, analogous to $\langle\varDelta\omega_{ij}^4\rangle_{\text{ave.}}$, which comes entirely from H_p, and another term coming-from the time rate of change of $[H_p,\mu]$.

Theorem IV.

Under certain limitations, the expansion of the spectrum on the wings in inverse powers of the frequency:

$$I(\omega)\sim\frac{A}{\omega^2}+\frac{B}{\omega^4}+\cdots$$

is controlled by the values of the successive odd derivatives of $\varphi(\tau)$ at the origin:

$$A=-\left.\frac{d\varphi}{d\tau}\right|_{\tau=0},\quad B=\left.\frac{d^3\varphi}{d\tau^3}\right|_{\tau=0},\quad\text{etc.}$$

This theorem is very closely related to theorem I: clearly, a finite $(2n-1)$ derivative is a singularity of $\varphi(\tau)$ at the origin which may be approximated by letting the $(2n$-th) derivative become infinite there. (e.g. a finite first derivative means that $\varphi(\tau)$ goes down on each side of zero with finite slope, so that we need an infinitely sharp curvature at the origin.) Thus we suspect that the $(2n)$th moment will be infinite, so that the spectrum falls off at least as slowly as $1/\omega^{2n+1}$ and possibly slower.

Any real physical $\varphi(\tau)$ will not have real singularities at the origin, but may approximate them because some process—e.g. the jumps in diffusion, or collisions in a gas—occurs very much faster than other processes. Thus eventually any $I(\omega)$ will fall off exponentially rather than in inverse powers of ω. (See, for an example, Anderson (1949a)).

Proof of the theorem. This is done by successive partial integrations. If $\varphi(\tau)$ is real it must be even; we assume it is since we always treat this case only. Therefore

$$I(\omega)=\int_0^\infty \cos \omega\tau\varphi(\tau)d\tau\ .$$

By a partial integration

$$I(\omega)=\frac{\varphi(\tau)}{\omega}\sin \omega\tau\Big|_0^\infty-\frac{1}{\omega}\int_0^\infty \frac{d\varphi}{d\tau}\sin\omega\tau\, d\tau\ ;$$

φ and all its derivatives which we use must be assumed to vanish at infinity, and none of the derivatives to be infinite at the origin (except, of course, when the series is found to have a term, as explained above). Then by another partial integration, after observing that the first term above is zero,

$$I(\omega)=-\frac{1}{\omega^2}\frac{d\varphi}{d\tau}\Big|_{\tau=0}-\frac{1}{\omega^2}\int_0^\infty \cos \omega\tau\frac{d^2\varphi}{d\tau^2}d\tau\ .$$

Further integrations give us

$$I(\omega)=-\frac{1}{\omega^2}\frac{d\varphi}{d\tau}\Big|_{\tau=0}+\frac{1}{\omega^4}\frac{d^3\varphi}{d\tau^3}\Big|_{\tau=0}-\frac{1}{\omega^6}\frac{d^5\varphi}{d\tau^5}\Big|_{\tau=0}+\frac{1}{\omega^7}\int_0^\infty \frac{d^7\varphi}{d\tau^7}\sin\omega\tau\, d\tau\ .$$

The process can be carried on until we find a nonvanishing term, so long as the derivatives are integrable and vanish at infinity. This proves the theorem.

Theorem V. If $\varphi_{\Delta\omega}(\tau)$—the correlation function of the random frequency modulation—has a finite first derivative at the origin, there is an inverse fourth power term in the expansion in theorem IV. This is easily proved from the expression for $d^3\varphi/d\tau^3$,

$$\frac{d^3\varphi}{d\tau^3}=\Big\langle \Delta\omega_{ij}(t+\tau)\Big(\frac{d}{dt}\Delta\omega_{ij}(t)-\Delta\omega_{ij}^2(t)\Big)\times\exp\Big(i\int^{t+\tau}\Delta\omega_{ij}(t')dt'\Big)\Big\rangle_{\text{ave.}}$$

We let $\tau\to 0$. $\overline{\Delta\omega_{ij}^3}$ is assumed to be zero; any term coming from this will be irrelevant to the theorem. The expression then becomes

$$\frac{d^3\varphi}{d\tau^3}\Big|_{\tau=0}=\Big\langle \Delta\omega_{ij}(t)\Big(\frac{d}{dt}\Delta\omega_{ij}(t)\Big)\Big\rangle_{\text{ave.}}$$

which is, in fact, just the same as

$$\frac{d}{d\tau}\overline{\Delta\omega_{ij}^2}\,\varphi_{\Delta\omega}(\tau)\Big|_{\tau=0}=\frac{d}{d\tau}\langle\Delta\omega_{ij}(t)\Delta\omega_{ij}(t+\tau)\rangle_{\text{ave.}}\ .$$

From this we can easily prove that if

$$\varphi_{\Delta\omega}(\tau)=e^{-\omega_e\tau}$$

$I(\omega)\sim\omega_e\omega_p^2/\omega^4$, as stated in the text.

Appendix III

Exchange Narrowing (Gaussian Modulation with Gaussian Spectrum) in the Intermediate Case.

Equation (38) of the main part of the paper gives an exact expression for the correlation function in the Gaussian-Gaussian case which we have assumed to correspond to true exchange narrowing. This is

$$\varphi(\tau)=\exp\Big[-\frac{\omega_p^2\tau}{\omega_e}\int_0^{\omega_e\tau}\exp\Big(-\frac{\pi}{4}x^2\Big)dx+\frac{2}{\pi}\frac{\omega_p^2}{\omega_e^2}\Big\{1-\exp\Big(-\frac{\pi}{4}\omega_e^2\tau^2\Big)\Big\}\Big]\ . \tag{A III-1}$$

In this Appendix we use this to find out how the line shape varies in the intermediate case in which ω_p is comparable with ω_e.

The fact that this function can be computed and tabulated is of little use, because the Fourier integral required to get the line shape would still have to be evaluated numerically, at considerable labor. Thus an approximate procedure might as well be used from the first, and since we know the limiting behaviors both for large and for small ω_e/ω_p, it seems most sensible to try to find correction terms at both ends and then fit the two curves together by interpolation in the intermediate range. To do this we need no more than approximate values of $\varphi(\tau)$ in the two ranges (A) $\omega_e\tau \gg 1$, and (B) $\omega_e\tau \ll 1$. The following values are easily derived from (A III-1).

Range A: $\omega_e\tau \gg 1$

$$\varphi(\tau)=\exp\left[-\left(\frac{|\tau|}{\omega_e}-\frac{2}{\pi\omega_e^2}\right)\omega_p^2\right] \quad \text{(A III-2)}$$

Range B: $\omega_e\tau \ll 1$

$$\varphi(\tau)\simeq\exp\left[-\left(\frac{\omega_p^2\tau^2}{2}-\frac{\pi}{48}\omega_e^2\omega_p^2\tau^4\right)\right]. \quad \text{(A III-3)}$$

Let us for simplification use dimensionless ratios as our variables. We define these as:

$$\left.\begin{aligned}\omega_e/\omega_p &= y\\ \omega_e\tau &= x\\ \omega/\omega_p &= \nu\ .\end{aligned}\right\} \quad \text{(A III-4)}$$

In terms of these the two approximations for $\varphi(\tau)$ are:

$$\text{A}: \quad \varphi(\tau)=\exp\left[-\frac{1}{y^2}\left(|x|-\frac{2}{\pi}+\cdots\right)\right] \times y\gg 1 \quad \text{(A III-2a)}$$

$$\text{B}: \quad \varphi(\tau)=\exp\left[-\frac{1}{y^2}\left(\frac{x^2}{2}-\frac{\pi x^4}{48}+\cdots\right)\right] \times y\ll 1\ . \quad \text{(A III-3a)}$$

How well these two expressions fit together is shown in fig. A1, in which is plotted the true expression for the coefficient of $-1/y^2$ in the exponent of φ as a function of x, as well as the two approximations (A III-2a and 3a).

The Fourier integral becomes

$$I(\nu)=\int_{-\infty}^{\infty}\exp\left(i\frac{\nu x}{y}-\frac{1}{y^2}f(x)\right)dx \quad \text{(A III-5)}$$

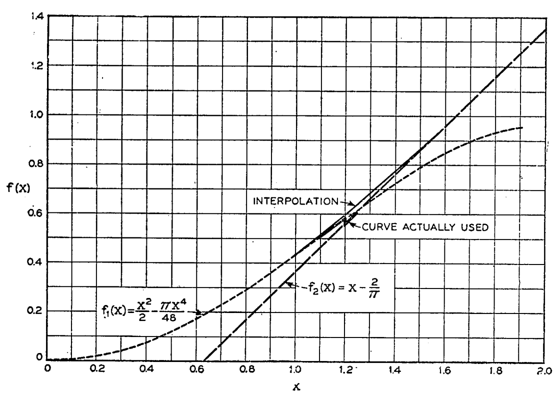

Fig. A-1. The function $f(x)$ from equation (A III-5).

where $f(x)$ is the function plotted in Fig. A1.

In computing line shapes, the easiest quantity to get is the central intensity, which, besides being of considerable experimental interest itself, is a fair measure of the line-breadth. This quantity, normalized on a scale of constant ω_p and varying $\omega_e/\omega_p=y$, is

$$I(0)=\frac{1}{y}\int_{-\infty}^{\infty}dx\exp\left(-\frac{1}{y^2}f(x)\right). \quad \text{(A III-6)}$$

This can rather easily be computed for the two limiting cases. For Case A we separate $f(x)$ into two parts:

$$f(x)=f_0+f_1=(x-2/\pi)+f_1(x) \quad \text{(A III-7)}$$

where

$$\begin{aligned}f_1(x)&=f(x)-\left(x-\frac{2}{\pi}\right)\\ &\simeq\frac{x^2}{2}-\frac{\pi x^4}{48}-\left(x-\frac{2}{\pi}\right) \quad x<1.2\\ &\simeq 0 \qquad\qquad x>1.2\end{aligned} \quad \text{(A III-8)}$$

f_1 is a function in any case which does not extend appreciably beyond $x=1$. This is a useful property.

Now,

$$\begin{aligned}I_A(0)&=\frac{2}{y}\int_0^{\infty}\exp\left(-\frac{f(x)}{y^2}\right)dx\\ &=\frac{2}{y}\int_0^{\infty}\exp\left(-\left(x-\frac{2}{\pi}\right)\frac{1}{y^2}\right)dx \times\exp\left(-\frac{f_1(x)}{y^2}\right)\end{aligned}$$

Changing variable,

$$I_A(0)=\exp(2/\pi y^2)(2y)\int_0^{\infty}e^{-u}du\exp(-f_1(y^2u)/y^2. \quad \text{(A III-9)}$$

This may be expanded into

$$I_A(0)=\exp(-2/\pi y^2)(2y)\int_0^{\infty}e^{-u}du \times\left(1-\frac{f_1(y^2u)}{y^2}+\cdots\right).$$

The appropriate approximation to the second term for large y is that unless u is very small $y^2u\gg 1$, so that e^{-u} is very close to unity. Thus

$$\begin{aligned}I_A(0)&\simeq 2y\exp(+2/\pi y^2)\left(1-\int_0^{\infty}\frac{f_1(y^2u)}{y^2}du\right)\\ &\simeq 2y\exp(+2/\pi y^2)\left(1-\frac{1}{y^4}\int_0^{\infty}f_1(x)dx\right).\end{aligned} \quad \text{(A III-10)}$$

Using the approximation A III-8 for $f_1(x)$, this gives

$$I_A(0)=2y\exp(+2/\pi y^2)\left(1-\frac{.299}{y^4}\right)$$
$$=2y\left(1+\frac{2}{\pi y^2}+\frac{.096}{y^4}\cdots\right). \qquad \text{(A III–11)}$$

The small y approximation (Case B) is more easily obtained. We get

$$I_B(0)=\frac{2}{y}\int_0^\infty \exp\left(-\frac{1}{y^2}\left(\frac{x^2}{2}-\frac{\pi x^4}{48}+\cdots\right)dx\right.$$
$$\cong\frac{2}{y}\int_0^\infty \exp(-x^2/2y^2)\,dx\left(1+\frac{\pi x^4}{48y^2}\right),$$

so

$$I_B(0)=2\sqrt{\frac{\pi}{2}}\left(1+\frac{\pi}{16}y^2\right). \qquad \text{(A III–12)}$$

(A III–11 and 12) as a function of y are plotted in figure A2, with an approximate interpolation drawn in to fit the two limiting cases together. This shows how the central intensity increases as a function of ω_e/ω_p, the "narrowing ratio".

The half-power width can also be estimated in a similar way. We start from the general expression for the ratio of intensity at a frequency ν to that at 0,

$$\frac{I(\nu)}{I(0)}=\frac{\int_0^\infty \cos\frac{\nu x}{y}\exp(-f(x)/y^2)\,dx}{\int_0^\infty \exp(-f(x)/y^2)\,dx}. \qquad \text{(A III–13)}$$

For the high narrowing case A we use (A III–7) for $f(x)$, and get

$$\frac{I(\nu)}{I(0)}=\frac{\int_0^\infty \cos\frac{\nu x}{y}\exp\left(-\frac{x}{y^2}-\frac{f_1(x)}{y^2}\right)dx}{\int_0^\infty \exp\left(-\frac{x}{y^2}-\frac{f_1(x)}{y^2}\right)dx}.$$

The half-width we assume to be close to that for the extreme case $y\to\infty$, which is $1/y$. Thus we set

$$\nu=\frac{1}{y}(1+\delta). \qquad \text{(A III–14)}$$

Then all quantities can be expanded, assuming as before that f_1/y^2 and δ are small. A straightforward calculation yields

$$\delta=-\frac{1}{2y^4}\frac{\int_0^\infty f_1(x)dx}{\int_0^\infty e^{-u}u\sin u\,du} \qquad \text{(A III–15)}$$
$$\cong-\frac{.299}{y^4}$$

$$(\Delta\nu_{1/2})_A\cong\frac{1}{y}\left(1-\frac{.299}{y^4}\right). \qquad \text{(A III–16)}$$

Note that the order of the change in half-width is smaller than that in $I(0)$; tnis indicates that the line-shape is less sensitive than the total scale to decreasing y, an interesting fact experimentally.

The approximation from the other end goes again from (A III–13), but here we set

$$f(x)\cong\frac{x^2}{2}-\frac{\pi x^4}{48},$$

and get

$$\frac{I(\nu)}{I(0)}\cong\frac{\int_0^\infty \cos\frac{\nu x}{y}\exp\left(-\frac{x^2}{2y^2}+\frac{\pi}{48}\frac{x^4}{y^2}\right)dx}{\int_0^\infty \exp\left(-\frac{x^2}{2y^2}+\frac{\pi}{48}\frac{x^4}{y^2}\right)dx}.$$

Here again we expand as in the case of $I(0)$, assuming $(\pi/48)(x^4/y^2)$ small as well as the difference

$$\delta\nu=\nu-\sqrt{2\,ln\,2}$$

between the true half-width and the one for $y=0$. To second order in y^2 we get

$$(\Delta\nu_{1/2})_B\cong\sqrt{2\,ln\,2}\left(1-\frac{\pi}{8}y^2\left(1-\frac{ln\,2}{3}\right)\right). \qquad \text{(A III–17)}$$

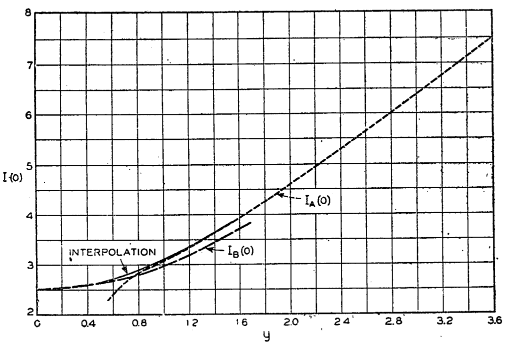

Fig. A–2. Central intensity I_0 in exchange narrowing as a function of the ratio $y=\omega_e/\omega_p$.

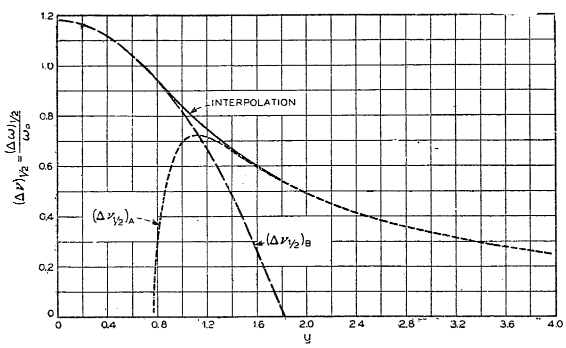

Fig. A–3. Half-power half-width (in units of ω_p) as a function of $y=\omega_e/\omega_p$.

The two approximations (A III-16 and 17) are plotted in figure A 3. It is seen that they fit fairly well together, and indicate an interpolation curve which one might well expect to be accurate to a few per cent. This curve then gives our best guess as to the half-width in the case of intermediate amounts of exchange narrowing.

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