PHYSICAL REVIEW VOLUME 131, NUMBER 1 1 JULY 1963

Pressure Broadening as a Prototype of Relaxation

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(Received 13 February 1963)

The theoretical results of Baranger, Kolb, and Griem on pressure broadening are rederived by a more compact and flexible procedure directly applicable to other relaxation processes. Pressure broadening is worked out to first order in the pressure, including previously disregarded corrections. The procedure adapts the concepts and techniques of scattering theory to the Liouville representation of density matrices. Its key quantity is a frequency-dependent relaxation operator $\langle M_c(\omega)\rangle$ introduced by Zwanzig.

1. INTRODUCTION

CONSIDERABLE progress has been made in the understanding and treatment of relaxation processes on a microscopic basis. However, the appreciation of this progress has been limited by the diversity and complexity of the formalisms that have been employed. Among these formalisms, the one developed by Zwanzig[1] recommends itself for its remarkable compactness and adherence to physical concepts. The present paper intends to illustrate and develop implications of the Zwanzig method with particular reference to the broadening and shift of spectral lines of a gas due to interaction among gas molecules.

This phenomenon, called "pressure broadening," is usually studied in the range where the observed effect is proportional to the gas pressure, i.e., to the collision frequency. Accordingly, it can be traced, in this range, to a sequence of separate elementary processes, namely collisions between pairs of molecules. Each elementary process is amenable—in principle and, to some extent, in practice—to detailed experimental and theoretical analysis. On the other hand, pressure broadening concerns the radiative properties of single molecules, irrespective of the effects of collisions on all other molecules. In fact, the surrounding gas acts merely as a thermal bath with respect to each molecule that emits or absorbs light. Thus, theory must express the macroscopic, thermal bath effect on spectral lines in terms of microscopic collision parameters integrated over the final state of perturbing molecules. Numerous other phenomena, such as the electric resistance due to impurities, belong the same class of relaxation effects which are amenable to rather detailed analysis.

A modern quantum theory of pressure broadening has been given by Baranger[2]; substantially equivalent results have been obtained independently by Kolb and Griem.[3] These authors were particularly concerned with ionized gases (plasmas) where long-range interactions raise special problems. We shall have in mind primarily neutral gases, where very accurate observations of rotational spectra under the influence of rare-gas buffer pressure have been performed.[4]

The principal content of this paper is a rederivation of the Baranger results by a procedure that emphasizes their general significance and applicability. This procedure may be described as an extension of the Lippman-Schwinger scattering theory to the Liouville representation, which is described in Sec. 2b and which is appropriate to the elimination of irrelevant variables. Like the scattering theory, the procedure of this paper emphasizes the physical quantities of experimental interest, the relationships among them and the equations which they obey, without facing yet the problem of their actual computation.

As a by-product, analytical formulas will be obtained in this paper that represent previously disregarded corrections. In particular, the treatment will be worked out completely to first order in the gas density, and the structure of the second-order terms will be described.

The following question seems worth mentioning because it is accessible to direct experimental investigation in pressure broadening and also in other phenomena. Pressure broadening replaces each atomic (or molecular) spectral frequency ω_{mn} with a modified frequency

$$\bar{\omega}_{mn}=\omega_{mn}+d_{mn}-iw_{mn}, \tag{1}$$

where d_{mn} is the shift and w_{mn} the pressure-induced half-width. According to the Rydberg-Ritz combination principle, whose experimental discovery led into the quantum theory of atoms, the two-index set of unperturbed frequencies ω_{mn} can be represented by $\omega_{mn}=\tau_m-\tau_n$ in terms of the single-index set of spectral terms τ_m, which correspond to the atomic energy levels. Now, does the Rydberg-Ritz principle still apply to the set of pressure-broadened line frequencies? That is, can we write

$$\bar{\omega}_{mn}=\bar{\tau}_m-\bar{\tau}_n{}^*,\quad \bar{\tau}_m=\tau_m+\delta_m-i\gamma_m? \tag{2}$$

Examination of the Baranger results[2] will show in Sec. 5b that (2) holds only in the approximation where each collision exerts a small perturbation on the radiating

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[1] R. Zwanzig, J. Chem. Phys. **33**, 1338 (1960); *Lectures in Theoretical Physics*, edited by W. E. Brittin (Interscience Publishers, Inc., New York, 1961), Vol. III, p. 106; Phys. Rev. **124**, 983 (1961).

[2] M. Baranger, Phys. Rev. **111**, 481, 494 (1958); **112**, 855 (1958), referred to here as "BI," "BII," and "BIII"; also in *Atomic and Molecular Processes*, edited by D. Bates (Academic Press Inc., New York, 1962), Chap. 13.

[3] A. C. Kolb and H. Griem, Phys. Rev. **111**, 514 (1958).

[4] See, e.g., A. Ben-Reuven, S. Kimel, M. A. Hirshfeld, and J. H. Jaffe, J. Chem. Phys. **35**, 955 (1961).

system. In this approximation the broadening is much smaller than the shift.

Validity of (2) would imply that the effect of molecular collisions upon the radiating system can be simply taken into account by adding a non-Hermitian term to the system's Hamiltonian. The eigenvalues of the perturbed Hamiltonian would be represented by $\hbar\bar{\tau}_m$. Such Hamiltonians have often been utilized for the phenomenological treatment of relaxation processes; experimental investigation of (2) provides a test of their validity. Also, the broadening of energy levels of an atomic system may be attributed to a fluctuating perturbation or to decay of the system into some channel or other. Validity of (2) implies then that the fluctuations or the decays of two levels m and n are uncorrelated; its breakdown implies the existence of correlations (i.e., interference effects) which are characteristic for each *pair of states*, that is, for the nonstationary radiating state represented by their superposition. These considerations are, of course, relevant to all quantum relaxation processes.

2. GENERAL TREATMENT

a. Initial Formulation

When a charged particle performs a motion described by $\mathbf{r}(\tau)$ and subject to statistical fluctuations, the spectrum of the radiation it emits or absorbs does not depend on the Fourier components of $\mathbf{r}(\tau)$ itself, because these vanish in general when averaged over the fluctuations. It is the correlation between successive positions $\mathbf{r}(\tau)$, $\mathbf{r}(\tau+t)$ at short intervals of time t which does not average out and determines the radiative behavior of the particle. The autocorrelation function $\langle\mathbf{r}(\tau)\cdot\mathbf{r}(\tau+t)\rangle$ is a statistical average (expectation value) over the fluctuations, and is independent of τ if the fluctuations are in a steady state. The radiative spectrum depends on the "power spectrum" of the fluctuating motion, that is, on the components of the Fourier analysis of the autocorrelation function with respect to the interval t, which may be evaluated for $\tau=0$ in a steady state. It suffices to consider separately the autocorrelation of each cartesian component of $\mathbf{r}$.

In accordance with these considerations, the spectral distribution emitted or absorbed by a molecule of interest under the influence of collisions with other gas molecules has been characterized [see, e.g., BII (8), (10)] in terms of the Fourier transform of a correlation function

$$F(\omega)=\pi^{-1}\,\mathrm{Re}\int_0^\infty e^{i\omega t}\,\mathrm{Tr}\{xx(t)\rho\}dt. \tag{3}$$

This formula should be understood in the sense that

$$\mathrm{Im}\omega=\epsilon>0 \tag{3a}$$

and that the limit $\epsilon\rightarrow 0$ should be taken eventually. The $\mathrm{Tr}\{\cdots\}$ in (3) represents the quantum-mechanical expectation value of the product of the dipole operator x and of the same operator in the Heisenberg representation evaluated after an interval t,

$$x(t)=e^{iHt}xe^{-iHt}. \tag{4}$$

Here H represents the total Hamiltonian of all interacting molecules divided by $\hbar$, i.e., measured in radian/sec rather than in ordinary energy units. The expectation value in (3) pertains to a state of the whole gas represented by its density matrix. It is usually—and rather reasonably—assumed that this state is time-independent (i.e., that ρ commutes with H) and in thermal equilibrium and that the correlations between the molecule of interest and the rest of the gas are negligible for our purpose in this state. We shall return to this assumption at the end of Sec. 2.

The practice of focusing from the outset on the analytic, even though formal, expression (3) of the observable quantity of interest has helped our understanding of statistical mechanics and other many-body problems. It is also characteristic for such formal expressions to involve time correlation functions.[5] Baranger's treatment of pressure broadening centers on the time evolution operators in (4) and specifically on the average of these operators over the irrelevant gas variables, to be taken in accordance with (3). For this reason the treatment is independent of the nature of the variables whose correlation is being considered (the dipole operators in our problem) and of all but a few features of the problem on hand.

Notice also the following alternative interpretation of

$$\mathrm{Tr}\{xx(t)\rho\}=\mathrm{Tr}\{xe^{-iHt}(\rho x)e^{iHt}\}. \tag{5}$$

The expression on the right represents the expectation value of the dipole moment x for a state that was characterized at $t=0$ by a density matrix (ρx) and has evolved from that time up to time t as specified by the Schrödinger equation for a density matrix. More specifically ρx represents the perturbation of ρ induced by an impulsive interaction with radiation at $t=0$; an unperturbed stationary ρ corresponds to a state with vanishing dipole moment.[6] Thus, the structural elements of the quantity of interest (3) are: A density matrix, of which only few characteristics will prove important, a pair of time evolution operators or, rather, its Fourier transform, and the dipole operator x of which it only matters that it pertains to one, or to a very few, among the very numerous variables of the whole gas.

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[5] See, e.g., the article by R. Kubo in *Lectures in Theoretical Physics*, edited by W. E. Brittin (Interscience Publishers, Inc., New York, 1959), Vol. I, p. 120; and W. Bernard and H. B. Callen, Rev. Mod. Phys. **32**, 1017 (1959).

[6] Non-Hermitian operators, such as ρx and $xx(t)$, appear in formulas (5) and (3) for economy of notation. Use of corresponding, physically significant, Hermitian operators is actually intended and their contribution is, in effect, selected out by the "real part" symbol in (3).

b. The Liouville Operator Representation

The pair of time evolution operators in (5) or (4) transforms the operator (ρx) or x. This role is emphasized by regarding[7] the whole set of elements of a matrix, e.g., the elements ρ_{mn} of ρ, as the set of components of a vector. The Schrödinger equation for a density matrix

$$d\rho/dt=-i(H\rho-\rho H) \tag{6}$$

represents then an infinitesimal orthogonal transformation (i.e., a "rotation"[8]) of this vector and is conveniently written in the form

$$d\rho/dt=-iL\rho, \tag{7}$$

where L is a Hermitian Liouville operator[9,10] defined by

$$(L\rho)_{mn}=\sum\nolimits_{m'n'} L_{mn,m'n'}\rho_{m'n'}, \tag{8}$$

$$\begin{aligned} L_{mn,m'n'}&=H_{mm'}\delta_{nn'}-\delta_{mm'}H_{n'n}\\ &=H_{mm'}\delta_{nn'}-\delta_{mm'}H_{nn'}{}^{*}. \end{aligned} \tag{8a}$$

This definition of L will be written more briefly

$$L=H-H^{*}, \tag{8b}$$

where the asterisk denotes complex conjugation and will recall that H and H^{*} operate on different variables; this property can be further stressed by writing in explicitly the unit operators of (8a) in the form

$$L=HI^{*}-IH^{*}. \tag{8c}$$

In terms of the Liouville operator, Eq. (5) becomes

$$\mathrm{Tr}\{xx(t)\rho\}=\mathrm{Tr}\{xe^{-iLt}(\rho x)\}. \tag{9}$$

The Fourier transformation in (3) can now be carried out formally to yield

$$F(\omega)=-\pi^{-1}\,\mathrm{Im}\,\mathrm{Tr}\left\{x\frac{1}{\omega-L}(\rho x)\right\}, \tag{10}$$

where $(\omega-L)^{-1}$ plays the role of the resolvent operator in the Liouville representation and embodies the complete dynamics of our problem.

c. Elimination of the Thermal Bath Variables

A main feature of the Zwanzig approach[1] is to make maximum use of the Liouville operator and to postpone as far as possible any specification of its structure for the problem under consideration. At this point it is important only to distinguish a radiating molecule (the "system" of interest), the rest of the gas (the thermal "bath") and their interaction. Accordingly, we write the Hamiltonian of the whole gas as

$$H=H_0{}^{(s)}+H_0{}^{(b)}+V, \tag{11}$$

where $H_0{}^{(s)}$ pertains to the molecule of interest exclusive of interaction with the other molecules, $H_0{}^{(b)}$ is a zero-approximation Hamiltonian for the other molecules and V the interaction between molecules. (The interaction between "other molecules" is included in V for convenience in the later expansion into powers of the gas density.) We call τ_μ, $\tau_\nu\cdots$ the eigenvalues of $H_0{}^{(s)}$ and $\tau_\alpha,\tau_\beta\cdots$ those of $H_0{}^{(b)}$. In accordance with (8b) and (11) we set then

$$L=L_0+L_1 \tag{12}$$

$$L_0=L_0{}^{(s)}+L_0{}^{(b)}=H_0{}^{(s)}-H_0{}^{(s)*}+H_0{}^{(b)}-H_0{}^{(b)*}, \tag{12a}$$

$$L_1=V-V^{*}. \tag{12b}$$

Each row or column of the matrix L is identified by a group of four indices in the scheme of eigenstates of H_0, because each of these eigenstates, say m, is an eigenstate μ of $H_0{}^{(s)}$ and α of $H_0{}^{(b)}$. The matrix elements of L_0 are then

$$\begin{aligned} (L_0)_{\mu\alpha,\nu\beta;\,\mu'\alpha',\nu'\beta'}&=[(\tau_\mu-\tau_\nu)+(\tau_\alpha-\tau_\beta)]\delta_{\mu\mu'}\delta_{\nu\nu'}\delta_{\alpha\alpha'}\delta_{\beta\beta'}\\ &=(\omega_{\mu\nu}+\omega_{\alpha\beta})\delta_{\mu\mu'}\delta_{\nu\nu'}\delta_{\alpha\alpha'}\delta_{\beta\beta'} \end{aligned} \tag{13}$$

We wish now to eliminate, at least formally, the thermal bath variables from (10), i.e., to carry out—or at least to condense in more suitable form—the summation over indices α, $\beta\cdots$ which is a part of the trace operation. To this end it is convenient to disentangle the interaction portion of L, namely L_1, from the rest of the resolvent operator $(\omega-L_0-L_1)^{-1}$. This is achieved by the operator identity

$$\frac{1}{\omega-L_0-L_1}=\frac{1}{\omega-L_0}\left[1+M(\omega)\frac{1}{\omega-L_0}\right], \tag{14}$$

where M is an operator with the equivalent expressions

$$\begin{aligned} M(\omega)&=\frac{1}{1-L_1(\omega-L_0)^{-1}}L_1=L_1\frac{1}{1-(\omega-L_0)^{-1}L_1}\\ &=L_1+L_1\frac{1}{\omega-L_0-L_1}L_1=L_1\sum_{n=0}^{\infty}\left[\frac{1}{\omega-L_0}L_1\right]^{n}, \end{aligned} \tag{14a}$$

which contains the interaction dynamics and vanishes in the weak-interaction limit $V=L_1=0$.

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[7] See, e.g., U. Fano, Rev. Mod. Phys. **29**, 74 (1957), to be referred to as "F," in particular Secs. 6 and 7.

[8] The Larmor precession of the mean magnetic moment of an atomic particle in a magnetic field is the special case where the representative space of this rotation coincides with the physical space. See F, Sec. 4a.

[9] The name "Liouville operator" derives from the classical mechanics analog, which represents the same transformation as a Poisson bracket. Classical statistical mechanics has utilized an equation identical with (7) except that ρ represents a classical distribution function. Equation (7) is introduced in reference 5. BII and BIII utilize a "doubled atom representation" equivalent to the one described here.

[10] It was stressed in F that the set of matrix elements ρ_{mn} can be replaced by any linearly independent set of variables $\rho_j=\Sigma_{mn}A_{j,mn}\rho_{mn}$. This replacement changes L into ALA^{-1}. The ρ_j are real if $A_{j,nm}=A_{j,mn}{}^{*}$, because ρ is Hermitian; in this case $\Omega=-iL$ is real and skew-symmetric and it represents an infinitesimal rotation of real cartesian coordinates. The use of variables ρ_j simplifies the notation because it replaces the double index (m,n) by the single j.

According to initial assumption, the density matrix ρ in (10) includes no significant correlation between the system and bath variables, and has, therefore, (F, Sec. 3h)[7] the product form[10a]

$$\rho=\rho^{(s)}\rho^{(b)}. \tag{15}$$

Moreover the distribution of gas molecules among the eigenstates of $H_0^{(b)}$ is stationary, so that

$$\rho_{\alpha\beta}{}^{(b)}=f_\alpha\delta_{\alpha\beta}, \tag{16}$$

this assumption being included in that of thermal equilibrium.

The factor $\delta_{\alpha\beta}$ in (16) causes the $L_0^{(b)}$ contribution to L_0 to vanish whenever L_0, being on the right side of (14), operates on (ρx) [see Eq. (13)]. The trace operation introduces the same factor $\delta_{\alpha\beta}$ on the left of (14). Therefore, both L_0 operators on the right-hand side of (14) reduce to $L_0^{(s)}$ and the trace operation over bath variables bears only on the product of $M(\omega)$ and $\rho^{(b)}$, thus generating the mean value

$$\langle M(\omega)\rangle=\mathrm{Tr}_b[M(\omega)\rho^{(b)}]. \tag{17}$$

This mean value is still a Liouville operator of the "system" variables, represented by the matrix

$$\langle M(\omega)\rangle_{\mu\nu,\mu'\nu'}=\textstyle\sum_{\alpha\alpha'} M_{\mu\alpha,\nu\alpha;\; \mu'\alpha',\nu'\alpha'}f_{\alpha'}. \tag{17a}$$

The operator $\langle M(\omega)\rangle$ represents the complete influence of the bath on the system of interest. The desired spectral distribution function (10) is now expressed as a trace over variables of the molecule of interest

$$\begin{aligned}F(\omega)=\pi^{-1}\,\mathrm{Im}\,\mathrm{Tr}_s\{&x(\omega-L_0^{(s)})^{-1}\\ &\times[1+\langle M(\omega)\rangle(\omega-L_0^{(s)})^{-1}](\rho^{(s)}x)\}.\end{aligned} \tag{18}$$

d. The Zwanzig Resolvent Operator

Zwanzig[1] constructed an equation of motion for the system of interest in which the effect of interaction with other variables is represented by a complement to the Liouville operator $L_0^{(s)}$ of the system. The resolvent of Zwanzig's equation is obtained by "re-entangling" $\langle M\rangle$ with $L_0^{(s)}$, applying (14) in reverse

$$\frac{1}{\omega-L_0^{(s)}}\left[1+\langle M(\omega)\rangle\frac{1}{\omega-L_0^{(s)}}\right]=\frac{1}{\omega-L_0^{(s)}-\langle M_c(\omega)\rangle} \tag{19}$$

with

$$\begin{aligned}\langle M_c(\omega)\rangle&=\frac{1}{1+\langle M(\omega)\rangle(\omega-L_0^{(s)})^{-1}}\langle M(\omega)\rangle\\ &=\langle M\rangle\sum_{n=0}^{\infty}\left[-\frac{1}{\omega-L_0^{(s)}}\langle M\rangle\right]^n.\end{aligned} \tag{20}$$

(The subscript "c" stands for "connected," for reasons explained in Sec. 3b-1.) Equation (18) becomes now

$$\begin{aligned}F(\omega)=-\pi^{-1}\,\mathrm{Im}\,\mathrm{Tr}_s\{x[\omega&-L_0^{(s)}\\ &-\langle M_c(\omega)\rangle]^{-1}(\rho^{(s)}x)\}.\end{aligned} \tag{21}$$

Zwanzig's equation of motion yields $M_c(\omega)$ directly, rather than as a function of M, in the form

$$\begin{aligned}M_c&=[1-L_1(1-P)(\omega-L_0)^{-1}]^{-1}L_1\\ &=L_1\sum_{n=0}^{\infty}[(1-P)(\omega-L_0)^{-1}L_1]^n,\end{aligned} \tag{22}$$

which differs from the definition (14a) of M by the insertion of the factor $(1-P)$. Here P represents a projection operator defined by[11]

$$PA\rho^{(b)}=\rho^{(b)}\,\mathrm{Tr}_b\{A\rho^{(b)}\}. \tag{23}$$

Equations (22) and (14a) imply

$$M_c=[1+MP(\omega-L_0^{(s)})^{-1}]^{-1}M, \tag{24}$$

which leads, in turn, to (20).

Equation (21) is analogous to BII(62), but the operator $\mathcal{H}$ in that reference, which corresponds to $\langle M_c\rangle$, was obtained only after simplifying assumptions relevant to the phenomenon of pressure broadening. Here it is stressed that (21) has very general significance, and that the determination of the properties of $\langle M_c\rangle$ and its evaluation for any specific problem can be taken up separately, as in the following sections of this paper.

Recall, at this point, that the only essential assumptions in the derivation of (21) are represented by (11), concerning the structure of the Hamiltonian, and by (15) and (16), concerning the structure of ρ. The assumptions about ρ are not quite consistent with the concept introduced in Sec. 2a that ρ also represents a thermal equilibrium state, because (16) requires ρ to be stationary with respect to $H_0^{(b)}$ whereas thermal equilibrium implies that it is stationary with respect to the complete Hamiltonian. Indeed, the interaction between molecules introduces correlations—probably minor ones—that are excluded by (15).

This difficulty is of no immediate concern when one intends, as in the present paper, to carry out a density expansion of the quantity of interest to lowest order in the gas density. The correlations introduced by the interaction between molecules in the equilibrium state ρ vanish to lowest order and would have to be included only in successive terms of the expansion.

Alternatively one might regard (15) and (16) as the definition of an initial state whose properties can, in principle, be assigned arbitrarily (provided only they are consistent with quantum mechanics). This matrix is perturbed by multiplication with x, which is not

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[10a] *Note added in proof.* The approximation implied by Eq. (15) is commented upon at the end of Sec. 2. While it is adequate to lowest order in the density, it would be of interest to sharpen its characterization and to treat the corrections neglected here systematically by successive approximations.

[11] The author is indebted to Dr. R. Zwanzig for the introduction of this operator.

relevant here, and then evolves in time in accordance with (9) and (10). The expression $[\omega-L_0{}^{(s)}-\langle M_c(\omega)\rangle]^{-1} \times(\rho^{(s)}x)$ in (21) represents the Fourier transform of $\mathrm{Tr}_b[\exp(-iHt)\rho x\exp(iHt)]$ which is the density matrix of the system of interest at the time t. Equation (21) itself represents the Fourier transform of the expectation value of x at t after the fixed initial time. From this point of view, correlations between system and bath are merely stated to vanish at $t=0$. Whatever correlations will build up at later times are taken into account implicitly in $\langle M_c(\omega)\rangle$. The correlation problem is thereby shifted to later consideration in the study of $\langle M_c(\omega)\rangle$.[12]

3. QUALITATIVE DISCUSSION OF $\langle M_c(\omega)\rangle$

A simple spectrum will occur in pressure broadening only when $\langle M_c(\omega)\rangle$ in (21) has suitable simple properties. The same remark applies to any other phenomena that lead to an equation of the same type. In fact, statements about experimental features of relaxation can be reduced to statements about properties of $\langle M_c(\omega)\rangle$. For purpose of orientation we indicate here the physical consequences of some possible properties of $\langle M_c(\omega)\rangle$ and then we shall try to trace back the origin of such properties.

a. Simple Situations

1. The Limiting Case of Zero Interaction

If $\langle M_c\rangle$ were to vanish, $L_0{}^{(s)}$ and $(\omega-L_0{}^{(s)})^{-1}$ would be diagonal, as seen from (13), and (21) would reduce to

$$F(\omega)=-\pi^{-1}\,\mathrm{Im}\sum\nolimits_{\mu\nu} x_{\mu\nu}{}^*(\omega-\omega_{\mu\nu})^{-1}(\rho x)_{\mu\nu}\rightarrow \sum\nolimits_{\mu\nu}x_{\mu\nu}{}^*\delta(\omega-\omega_{\mu\nu})(\rho x)_{\mu\nu}, \qquad (25)$$

where the last expression represents the limit for $\mathrm{Im}\omega=0+$. In this event, then, the spectrum reduces to the unperturbed line spectrum of the molecule of interest, as it should.

2. Possible Diagonalization of $L_0{}^{(s)}+\langle M_c(\omega)\rangle$

A line spectrum also arises whenever a linear transformation $S_{j,\mu\nu}$ is found such that

$$(S[L_0{}^{(s)}+\langle M_c(\omega)\rangle]S^{-1})_{jk}=\omega_j\delta_{jk}. \qquad (26)$$

The eigenvalues ω_j are generally complex because $\langle M_c\rangle$ is not Hermitian. The oscillations corresponding to the spectrum $F(\omega)$ would be damped provided $\mathrm{Im}\omega_j<0$, i.e., provided $i(\langle M_c\rangle-\langle M_c\rangle^\dagger)$ is a positive matrix (see 3b-3 below). The diagonalization succeeds only if $L^{(0)}+\langle M_c\rangle$ commutes with its Hermitian conjugate. Therefore, this commutability should be verified whenever a relaxation phenomenon is observed to proceed through damped-harmonic oscillations.

3. Non-Markoffian Behavior

The dependence of $\langle M_c(\omega)\rangle$ on ω implies that the rate of variation of the state of the system at the time t depends on the state at earlier times $t'<t$ through an integral "memory" operator, i.e., that the state evolution is non-Markoffian. In practice, the dependence of $\langle M_c\rangle$ on ω is often negligible over a limited frequency range of practical interest; we say, in this event, that the bath has a negligibly short memory.

4. Perturbation Treatment

Insofar as

$$|\langle M_c\rangle_{\mu\nu,\mu'\nu'}/(\omega_{\mu\nu}-\omega_{\mu'\nu'})|\ll 1, \quad \text{for} \quad (\mu,\nu)\neq(\mu',\nu'), \qquad (27)$$

$L_0{}^{(s)}+\langle M_c\rangle$ can be diagonalized approximately. Pressure broadening is often adequately treated in this manner in the lowest approximation in which off-diagonal elements are discarded altogether. The transformation S of (27) is then the identity and one simply replaces in (25) each eigenvalue $\omega_{\mu\nu}$ of $L_0{}^{(s)}$ by the corresponding displaced approximate eivenvalue

$$(L_0{}^{(s)}+\langle M_c\rangle)_{\mu\nu,\mu\nu}=\omega_{\mu\nu}+\langle M_c\rangle_{\mu\nu,\mu\nu}. \qquad (28)$$

The "shift" and "width" of the level are then

$$d_{\mu\nu}=\mathrm{Re}\langle M_c\rangle_{\mu\nu,\mu\nu},\ w_{\mu\nu}=-\mathrm{Im}\langle M_c\rangle_{\mu\nu,\mu\nu}. \qquad (29)$$

References 2 and 3 have been specifically concerned with situations where (27) breaks down for a group of narrowly spaced levels. The portion of the matrix $(\omega-L_0{}^{(s)}-\langle M_c\rangle)^{-1}$ in (21) that corresponds to these levels remains then nondiagonal and gives an aggregate contribution to $F(\omega)$ which departs from a Lorentz line shape.

5. Rydberg-Ritz Principle

A corollary of the preceding remarks is that, in the approximation (27), Eq. (2) holds if, and only if, $\langle M_c\rangle$ can be resolved in the form

$$\langle M_c\rangle_{\mu\nu,\mu\nu}=\langle T\rangle_\mu-\langle T\rangle_\nu. \qquad (30)$$

It will be seen in Sec. 5b that only a portion of $\langle M_c\rangle$ can be cast in the form (30).

b. Structure of $\langle M_c\rangle$

1. Connection Between $\langle M_c\rangle$ and $\langle M\rangle$

The appearance of operator $1-P$ in the perturbation expansion (22) of M_c shows it to have the character of a "linked diagram" expansion. This character is absent in the corresponding expansion (14a) of M. Observe also that the expansion of $\langle M\rangle$ into powers of $\langle M_c\rangle$, reciprocal to (20), namely,

$$\langle M(\omega)\rangle=[1-\langle M_c\rangle(\omega-L_0{}^{(s)})^{-1}]^{-1}\langle M_c\rangle = \langle M_c\rangle\sum_{n=0}^{\infty}[(\omega-L_0{}^{(s)})^{-1}\langle M_c\rangle]^n \qquad (31)$$

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[12] The present author pointed out in the past, Phys. Rev. **96**, 869 (1954), the opportunity of introducing at an early stage of the treatment an operator that, like $\langle M_c(\omega)\rangle$, represents the total action of the bath on the system of interest. However, this suggestion did not prove fruitful in the absence of the Liouville representation technique.

contains only positive terms and thus corresponds to the construction of a general operator as a sum of powers of linked-diagram or "connected" operators. Thus, $\langle M_c \rangle$ would appear to have a more fundamental character than $\langle M \rangle$. On the other hand, $\langle M \rangle$ will be seen to have simpler properties than $\langle M_c \rangle$.

2. *Equations Obeyed by M and M_c*

The expressions (14a) and (22) obey, respectively, the equations

$$M = L_1 + L_1 \frac{1}{\omega - L_0} M, \tag{32}$$

$$M_c = L_1 + L_1 \frac{1-P}{\omega - L_0} M_c. \tag{33}$$

As pointed out by Zwanzig,[1] these equations are of the type introduced by Lippman and Schwinger in scattering theory. In fact (32), which is independent of assumptions about the state of the system, is the exact analog of the Lippman-Schwinger equation in the Liouville representation. The convention (3a) about the sign of $\mathrm{Im}\omega$ characterizes both M and M_c as transition operators of the $T^{(+)}$ type.

3. *Expression of M in terms of Hermitian Operators*

As the Lippman-Schwinger transition operator or the scattering matrix can be expressed in terms of the reaction operator, which is Hermitian, so can we proceed here by resolving the propagator $(\omega - L_0)^{-1}$ according to the well-known formula

$$\lim_{\epsilon=0} \frac{1}{\omega - L_0} = \lim_{\epsilon=0} \frac{1}{\omega' + i\epsilon - L_0} = \mathcal{P} \frac{1}{\omega' - L_0} - i\pi\delta(\omega' - L_0), \tag{34}$$

where $\omega' = \mathrm{Re}\omega$ and $\mathcal{P}$ indicates that the Cauchy principal part is to be taken when integrating over the poles of $(\omega' - L_0)^{-1}$. Substitution of (34) into (14a) or (32) yields

$$M(\omega' + i0) = N(\omega')[1 + i\pi\delta(\omega' - L_0) N(\omega')]^{-1}, \tag{35}$$

where

$$\begin{aligned} N(\omega') &= L_1 \left[1 - \mathcal{P} \frac{1}{\omega' - L_0} L_1 \right]^{-1} \\ &= L_1 + L_1 \mathcal{P} \frac{1}{\omega' - L_0} N(\omega') \end{aligned} \tag{36}$$

is Hermitian, as seen, e.g., from its perturbation expansion. Equation (35) can also be expressed in the form

$$M(\omega' + i0) = M'(\omega' + i0) - i\pi M''(\omega' + i0), \tag{37}$$

$$M'(\omega' + i0) = N(\omega') \{1 + [\pi\delta(\omega' - L_0) N(\omega')]^2\}^{-1}, \tag{37a}$$

$$\begin{aligned} M''(\omega' + i0) &= N(\omega') \delta(\omega' - L_0) N(\omega') \\ &\quad \times \{1 + [\pi\delta(\omega' - L_0) N(\omega')]^2\}^{-1} \\ &= M(\omega' + i0)^{\dagger} \delta(\omega' - L_0) M(\omega' + i0), \end{aligned} \tag{37b}$$

where both M' and M'' are Hermitian and M'' is *nonnegative*, since it involves only even powers of N.

This result is a start to study the damping of the oscillations corresponding to the spectrum $F(\omega)$, i.e., to study under what conditions $i(\langle M_c \rangle - \langle M_c \rangle^{\dagger})$ is in fact positive (see Sec. 3a-2). It will be seen in Sec. 5b that the oscillations are indeed damped under the conditions of our treatment of pressure broadening. In general, however, we must consider that, even though M_c can be expressed in terms of an operator N_c analogous to N, this N_c would not be Hermitian owing to the presence of the non-Hermitian operator P in its definition. Alternatively, $\langle M_c(\omega' + i\epsilon) \rangle$ can be expressed in terms of $\langle M' \rangle$ and of $\langle M'' \rangle$ by means of (20), but these operators are themselves no longer Hermitian after the averaging.

4. *Short Memory Approximation*

The perturbation expansion of $\langle M_c \rangle$ or $\langle M \rangle$ into powers of the interaction L_1, as given in (22) or (14a), is probably relevant to numerous relaxation problems, though not to our treatment of pressure broadening. The first term of the expansion, $\langle M_c \rangle \sim \langle M \rangle \sim \langle L_1 \rangle$, does not contribute to relaxation because it represents the effect of the average potential exerted by the bath on the system and could be simply included in L_0. Therefore, the key term of the expansion is the second one, $\langle L_1 (1-P)(\omega - L_0)^{-1} L_1 \rangle$, if the expansion converges rapidly. Rapid convergence depends on the smallness of the effective (i.e., suitably averaged) value of $(1-P)(\omega - L_0)^{-1} L_1$. Since matrix multiplication of this operator by L_1 involves a summation over the continuous spectrum of eigenvalues of $L_0^{(b)}$, the effective value of $(\omega - L_0)^{-1} L_1$ will be small if a large range of $L_0^{(b)}$ is involved so that $(\omega - L_0)$ is, on the average, larger than L_1. This situation of broad spectral range is interpreted physically by the statement that the bath has a short memory so that the interaction L_1 can build up only a small cumulative effect during a single memory period. Over a long period of time, the interaction effect builds up as though it resulted from a long series of weak and short elementary processes, even though no such elementary processes are, in fact, identifiable on a microscopic time scale.[13]

4. EXPANSION INTO POWERS OF THE GAS DENSITY

In this section we expand $\langle M_c \rangle$, for the pressure broadening problem, into powers of the volume density of molecules that interact with the radiating molecule of interest. Following a familiar procedure, a finite volume, v, of gas containing n molecules will be considered initially, and then the limit will be taken for $v \to \infty$, $n \to \infty$, $n/v = \text{const}$. Our procedure and results

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[13] R. Zwanzig, reference 1, has been particularly concerned with the short memory type of approximation. The fact that a perturbation approach to relaxation implies a short memory had been emphasized in reference 12.

coincide in essence with those of Watson[14] and of Siegert and Teramoto.[15]

Set

$$V=\sum_{i=1}^{n} V_i+\sum_{i=2}^{n}\sum_{j=1}^{i-1} V_{ij}, \tag{38}$$

where V_i indicates the interaction between the molecule of interest and the ith "other molecule," and V_{ij} the interaction between the ith and jth "other molecules." Equation (12b) gives then

$$L_1=\sum_{i=1}^{n} L_i+\sum_{i=2}^{n}\sum_{j=1}^{i-1} L_{ij} \tag{39}$$

$$L_i=V_i-V_i^*,\quad L_{ij}=V_{ij}-V_{ij}^*. \tag{39a}$$

Because each matrix element of V_i contains the product of two wave functions of the motion of the ith molecule in the volume v, L_i is of order v^{-1}. For a similar reason V_{ij} is of order v^{-2}. Any power of L_i, say L_i^p, is also of order v^{-1} because the $(p-1)$-fold matrix product in L_i^p contains $p-1$ phase-space integrations, each of which yields a factor v. Similarly, any power of L_{ij} is of order v^{-2}. Products $L_i^pL_j^qL_{ij}^r$ are also of order v^{-2}. The product of any sequence of operators with m different indices is of order v^{-m}.

The expansion of $\langle M\rangle$ will be treated directly, that of $\langle M_c\rangle$ resulting from (20). (The first term is the same, of course, for both expansions.) Substitution of (39) into the last expression of (14a) yields a multiple sum of L_i and L_{ij} which can be organized in the form

$$M=\sum_{i=1}^{n} M_i^{(1)}+\sum_{i=2}^{n}\sum_{j}^{i-1} M_{ij}^{(2)} +\sum_{i}^{n}\sum_{j}^{i-1}\sum_{k}^{j-1} M_{ijk}^{(3)}+\cdots, \tag{40}$$

where $M_i^{(1)}$ is a sum of products of L_i and $(\omega-L_0)^{-1}$, $M_{ij}^{(2)}$ a sum of products of L_i, L_j, L_{ij} and $(\omega-L_0)^{-1}$, $M_{ijk}^{(3)}$ a sum of products of L_i, L_j, L_k, L_{ij}, L_{ik}, L_{jk} and $(\omega-L_0)^{-1}$, etc.

Upon carrying out the operation $\langle\ \rangle$, we see that $\langle M_i^{(1)}\rangle$ is independent of i, $\langle M_{ij}^{(2)}\rangle$ independent of i and j, etc., if all molecules are identical. If there are different kinds of molecules the result is more complicated but substantially equivalent for our purpose; we shall disregard this possibility in the following. Equation (40) yields, then,

$$\langle M\rangle=n\langle M_i^{(1)}\rangle+\tfrac{1}{2}n(n-1)\langle M_{ij}^{(2)}\rangle +\cdots+\binom{n}{p}\langle M_{ij\cdots l}^{(p)}\rangle+\cdots, \tag{41}$$

where the pth term is of order n^p, through $\binom{n}{p}$, of order v^{-p}, through $\langle M^{(p)}\rangle$, and therefore, of pth order in the gas density n/v. This term represents, of course, the effect on the radiating molecule of multiple collision processes involving p other molecules. Thus, (41) is the desired expansion and the remaining task consists of discussing the structure of its successive terms.

Each of the operators $M_{ij\cdots l}^{(p)}$ can be constructed by the following recursive procedure. Delete from (39) all terms with indices that are not included in the list $i, j\cdots l$, and substitute the residual L_1 into (14a). This yields, for $p=1, 2\cdots$,

$$[1-L_i(\omega-L_0)^{-1}]^{-1}L_i=m_i=M_i^{(1)} \tag{42}$$

$$[1-(L_i+L_j+L_{ij})(\omega-L_0)^{-1}]^{-1}(L_i+L_j+L_{ij}) =M_i^{(1)}+M_j^{(1)}+M_{ij}^{(2)}, \tag{42a}$$

etc. The symbol m_i has been introduced in (42) for later convenience.

In the expansion of (42a), or of analogous higher order expressions, into powers of the L_i and L_{ij}, each term consists of a product of "runs" of factors that contain only one of the operators, say L_j. Such a run of factors is equal to $[L_j(\omega-L_0)^{-1}]^{q-1}L_j$. The sum of all terms of the expansion which differ only in the length of a particular run is obtained by taking its lowest (run-of-one) term and replacing its single factor L_j by $\sum_{q=0}^{\infty}[L_j(\omega-L_0)^{-1}]^qL_j=m_j$. Similarly, the sum of all terms with a run of L_{ij} of varying length is expressed in terms of

$$[1-L_{ij}(\omega-L_0)^{-1}]^{-1}L_{ij}=m_{ij}. \tag{43}$$

It follows that each term of the expansion of M can be expressed in terms of the scattering operators m_i and m_{ij} rather than in terms of the corresponding interaction operators L_i and L_{ij}. The operator m_i pertains to collisions between the "radiating molecule" and one "other molecule," and m_{ij} to collisions between two "other molecules."

The expressions of (42a) and of the higher elements of the same set in terms of m_i and m_{ij} are quite complicated. This is to be expected in view of the nature of multiple collisions. As an example we give here the expression of (42a). To this end we define

$$D_{ij}=[1-(L_i+L_j)(\omega-L_0)^{-1}](L_i+L_j)$$

$$=\left(1+m_j\frac{1}{\omega-L_0}\right)m_i\left(1-\frac{1}{\omega-L_0}m_j\frac{1}{\omega-L_0}m_i\right)^{-1} +\left(1+m_i\frac{1}{\omega-L_0}\right)m_j\left(1-\frac{1}{\omega-L_0}m_i\frac{1}{\omega-L_0}m_j\right)^{-1}, \tag{44}$$

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[14] K. M. Watson, Phys. Rev. **103**, 493 (1956).

[15] A. J. F. Siegert and Ei Teramoto, Phys. Rev. **110**, 1232 (1958).

which contains only m_i and m_j. One finds, then,

$$M_i^{(1)}+M_j^{(1)}+M_{ij}^{(2)}=D_{ij}+\left(1+D_{ij}\frac{1}{\omega-L_0}\right)m_{ij}$$

$$\times\left(1-\frac{1}{\omega-L_0}D_{ij}\frac{1}{\omega-L_0}m_{ij}\right)^{-1}\left(1+\frac{1}{\omega-L_0}D_{ij}\right). \quad (45)$$

5. REDUCTION TO COLLISION AMPLITUDES

In this section we express the transition operator m_i, defined by (42), which pertains to a collision of the ith "other molecule" with the "molecule of interest" in the Liouville representation, in terms of the corresponding transition amplitude operator t_i of the ordinary wave function representation. The subscript i will be dropped for simplicity from m_i and t_i, from the interaction V_i and L_i and from $L_0^{(bi)}=H_0^{(bi)}-H_0^{(bi)*}$ which pertains to unperturbed states of the ith molecule.

The formal development will apply equally to m_i and to the complete operator M, even though m_i pertains to an elementary collision process and M does not. This difference would have a bearing on the discussion of the final results, but up to that point one may simply replace at each stage M for m_i, the full interaction V for V_i and an over all transition operator T for t_i.

In the explicitly time-dependent representation (5) the quantity corresponding to $m(\omega)$ is simply the direct product of two scattering operators that correspond to $\exp(-iHt)$ and $\exp(iHt)$ in the interaction representation. The analog of $m(\omega)$ is then, in essence, simply a product of the analogs of t and t^*. Accordingly, in our Fourier representation $m(\omega)$ will be expressed by a convolution integral.[16]

a. The Integral Representation

The operator $m(\omega)$ defined by (42) obeys the equation analogous to (32)

$$m(\omega)=L+L\frac{1}{\omega-L_0}m(\omega),\quad \mathrm{Im}(\omega)>0. \quad (46)$$

The corresponding transition amplitude operator obeys the Lippman-Schwinger equation

$$t(\psi)=V+V\frac{1}{\psi-H_0}t(\psi),\quad \mathrm{Im}(\psi)>0 \quad (47)$$

whose complex conjugate is

$$t^*(\psi^*)=V^*+V^*\frac{1}{\psi^*-H_0^*}t^*(\psi^*),\quad \mathrm{Im}(\psi^*)<0. \quad (47a)$$

We show that (46) is solved by[17]

$$m(\omega)=\frac{\omega-L_0}{2\pi i}\int_{-\infty+i\eta}^{\infty+i\eta}d\psi\left\{\frac{1}{\psi-H_0}t(\psi)\right.$$

$$+\frac{1}{\psi-\omega-H_0^*}t^*(\psi-\omega)+\frac{1}{\psi-H_0}\frac{1}{\psi-\omega-H_0^*}$$

$$\left.\times t(\psi)t^*(\psi-\omega)\right\}\frac{\omega-L_0}{(\psi-H_0)(\psi-\omega-H_0^*)}, \quad (48)$$

where

$$\epsilon=\mathrm{Im}\omega>\eta>0 \quad (48a)$$

so that $\mathrm{Im}(\psi-\omega)<0$.

The integrand of (48) has singularities on the axes $\mathrm{Im}\psi=0$ and $\mathrm{Im}\psi=\epsilon$ above and below the integration path. Singularities or cuts of $t(\psi)$ and $t^*(\psi-\omega)$ presumably cover each of these axes, respectively, but the singularities of $(\psi-H_0)^{-1}$ and $(\psi-\omega-H_0^*)^{-1}$ consist of a single pole corresponding to an eigenvalue of H_0 or H_0^*. Because the integrand converges at least as ψ^{-2} at infinity, the contributions of the first two terms in the braces of (48) can be obtained by looping the integration path around isolated poles on the axes $\mathrm{Im}\psi=\epsilon$ and $\mathrm{Im}\psi=0$, respectively. Therefore, and because $\omega-L_0=(\psi-H_0)-(\psi-\omega-H_0^*)$, (48) becomes

$$m(\omega)=t(\omega+H_0^*)-t^*(H_0-\omega)$$

$$+\frac{1}{2\pi i}\int_{-\infty+i\eta}^{\infty+i\eta}d\psi\left[\frac{1}{\psi-H_0}-\frac{1}{\psi-\omega-H_0^*}\right]$$

$$\times t(\psi)t^*(\psi-\omega)\left[\frac{1}{\psi-H_0}-\frac{1}{\psi-\omega-H_0^*}\right]. \quad (49)$$

To verify that (48) or (49) satisfy (46) we note that

$$1=(2\pi i)^{-1}\int_{-\infty+i\eta}^{\infty+i\eta}d\psi(\omega-L_0)/(\psi-H_0)(\psi-\omega-H_0^*), \quad (50)$$

and, therefore, from (48)

$$1+\frac{1}{\omega-L_0}m(\omega)=\int_{-\infty+i\eta}^{\infty+i\eta}d\psi\left[1+\frac{1}{\psi-H_0}t(\psi)\right]$$

$$\times\left[1+\frac{1}{\psi-\omega-H_0^*}t^*(\psi-\omega)\right]\frac{\omega-L_0}{(\psi-H_0)(\psi-\omega-H_0^*)}. \quad (51)$$

Multiplication of this formula from the left by $V-V^*$ and application of (47) and (47a) yields the right-hand

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[16] Since $L=V-V^*$ one could represent $m(\omega)$ by means of (44), replacing L_i by V, L_j by $-V^*$, m_i by t and m_j by $-t^*$. However, (44) is merely the condensed form of a geometric series. We can do better in our problem because V and V^* and, respectively, t and t^* operate on different variables and thus commute freely, whereas m_i and m_j do not.

[17] An analogous convolution has been used to combine contributions of unlinked diagrams, where the vertices of different diagrams commute and only the propagator variables have to be disentangled, as in our problem. See N. M. Hugenholtz, Physica **23**, 481 (1957).

side of (46) in the form

$$\frac{1}{2\pi i}\int_{-\infty+i\eta}^{\infty+i\eta} d\psi\left\{t(\psi)\left[1+\frac{1}{\psi-\omega-H_0{}^*}t^*(\psi-\omega)\right]\right.$$
$$\left.-\left[1+\frac{1}{\psi-H_0}t(\psi)\right]t^*(\psi-\omega)\right\}\frac{\omega-L_0}{(\psi-H_0)(\psi-\omega-H_0{}^*)}. \tag{52}$$

The procedure used to reduce (48) to (49) reduces also (52) to (49), which represents the left-hand side of (46), thus concluding our verification.

Consider now the expression (49) of $m(\omega)$, with the purpose of evaluating the integral within it. The integration path skirts the singularities of $1/(\psi-H_0)$ and $1/(\psi-\omega-H_0{}^*)$ leaving the former ones on its right and the latter ones on its left. The contributions to the integral arising from the skirting of singularities will be seen to vanish except when the path has to traverse a high saddle point between a singularity on the right and one on the left which happen to occur at equal values of $\mathrm{Re}\psi$. This contribution arises from the cross terms in the product of the braces in (49) and is very important for pressure broadening. All other contributions are nonsingular and will be seen to be small under conditions of simple pressure broadening.

Let us label the operators H_0 or $H_0{}^*$ with suffixes l or d, depending on whether they operate on the left or right of tt^* in (49), and write

$$\begin{aligned}&[(\psi-H_{0l})^{-1}-(\psi-\omega-H_{0l}{}^*)^{-1}][(\psi-H_{0r})^{-1}-(\psi-\omega-H_{0r}{}^*)^{-1}]\\&\quad=(H_{0l}-H_{0r})^{-1}[(\psi-H_{0l})^{-1}-(\psi-H_{0r})^{-1}]+(H_{0l}{}^*-H_{0r}{}^*)^{-1}[(\psi-\omega-H_{0l}{}^*)^{-1}-(\psi-\omega-H_{0r}{}^*)^{-1}]\\&\qquad+(H_{0l}-\omega-H_{0r}{}^*)^{-1}[(\psi-H_{0l})^{-1}-(\psi-\omega-H_{0r}{}^*)^{-1}]-(\omega+H_{0l}{}^*-H_{0r})^{-1}[(\psi-\omega-H_{0l}{}^*)^{-1}-(\psi-H_{0r})^{-1}].\end{aligned} \tag{53}$$

Equation (36) can now be applied in the limit

$$\eta=\mathrm{Im}\psi\rightarrow 0+,\quad \epsilon=\mathrm{Im}\omega\rightarrow 0+,\quad \epsilon-\eta\rightarrow 0+, \tag{54}$$

after which the integral over ψ in (49) resolves into contributions of the singularities and of principal parts. One finds

$$\begin{aligned}m(\omega'+i0)=\;&t(\omega'+H_0{}^*)-t^*(H_0-\omega')\\&+\frac{1}{2}\left\{-\frac{t(H_{0l})t^*(H_{0l}-\omega')-t(H_{0r})t^*(H_{0r}-\omega')}{H_{0l}-H_{0r}}+\frac{t(H_{0l}{}^*+\omega')t^*(H_{0l}{}^*)-t(H_{0r}{}^*+\omega')t^*(H_{0r}{}^*)}{H_{0l}{}^*-H_{0r}{}^*}\right.\\&+\mathcal{P}\frac{t(H_{0l})t^*(H_{0l}-\omega')+t(H_{0r}{}^*+\omega')t^*(H_{0r})}{H_{0l}-\omega'-H_{0r}{}^*}+2\pi i\delta(H_{0l}-\omega'-H_{0r}{}^*)t(H_{0l})t^*(H_{0r}{}^*)\\&-\mathcal{P}\frac{t(H_{0l}{}^*+\omega')t^*(H_{0l}{}^*)+t(H_{0r})t^*(H_{0r}-\omega')}{H_{0l}{}^*+\omega'-H_{0r}}+2\pi i\delta(H_{0l}{}^*+\omega'-H_{0r})t(H_{0r})t^*(H_{0l}{}^*)\\&\left.+\frac{g(H_{0l})-g(H_{0r})}{H_{0l}-H_{0r}}+\frac{g(H_{0l}{}^*+\omega')-g(H_{0r}{}^*+\omega')}{H_{0l}{}^*-H_{0r}{}^*}-\frac{g(H_{0l})-g(H_{0r}{}^*+\omega')}{H_{0l}-\omega'-H_{0r}{}^*}-\frac{g(H_{0l}{}^*+\omega')-g(H_{0r})}{H_{0l}{}^*+\omega'-H_{0r}}\right\},\end{aligned} \tag{55}$$

where $\omega'=\mathrm{Re}\omega$, $\mathcal{P}$ means "principal part," and

$$g(y)=\frac{1}{2\pi i}\int_{-\infty}^{\infty} d\psi'\mathcal{P}\frac{1}{\psi'-y}t(\psi'+i0)t^*(\psi'-\omega'-i0). \tag{55a}$$

The two δ-function singularities in (55) arise formally from the imaginary part of ω in the two factors $(H_{0l}-\omega-H_{0r}{}^*)^{-1}$ and $(\omega+H_{0l}{}^*-H_{0r})^{-1}$ on the right-hand side of (53). [The other two factors $(H_{0l}-H_{0r})^{-1}$ and $(H_{0l}{}^*-H_{0r}{}^*)^{-1}$ contain no such imaginary part.] In effect, the singularities are contributed by integration over a high saddle point as anticipated above.

b. Discussion

The result (55) is still complicated. In its further analysis one should recall that, for application to pressure broadening, one is actually interested in the diagonal matrix elements of the average m, namely $\langle M(\omega'+i0)\rangle_{\mu\nu,\mu\nu}$, to be entered in (28). (Recall from Sec. 4 that $\langle M_c\rangle\sim n\langle m\rangle$ to first order in the gas density n/v.) Moreover the values of ω' relevant to this matrix element is $\omega'\sim\omega_{\mu\nu}$ as seen in Sec. 3a; therefore, we are concerned with

$$\langle m(\omega_{\mu\nu}+i0)\rangle_{\mu\nu,\mu\nu}. \tag{56}$$

Each of the first two terms on the right-hand side of (55) operates on half of the variables. Their combined contribution to (56), calculated from (17a), is

$$\sum_\alpha[t(\tau_\mu+\tau_\alpha)_{\mu\alpha,\mu\alpha}-t^*(\tau_\nu+\tau_\alpha)_{\nu\alpha,\nu\alpha}]f_\alpha. \tag{57}$$

This expression consists of transition matrix elements for *forward scattering* (i.e., diagonal in α) evaluated *on the energy shell*. Its value can be obtained, at least in principle, from single scattering experiments. It obeys the Rydberg-Ritz principle, in accordance with (30).

The real and imaginary parts of (57) can be separated, the imaginary part being related to the total scattering cross section by the optical theorem (emphasized in BIII, p. 864). The separation can be performed in accordance with Sec. 3b-3, which yields

$$\begin{aligned} t(\omega'+i0) &= k(\omega')[1+i\pi\delta(\omega'-H_0)k(\omega')]^{-1} \\ &= [k(\omega')-i\pi k(\omega')\delta(\omega'-H_0)k(\omega')] \\ &\quad \times\{1+[\pi\delta(\omega'-H_0)k(\omega')]^2\}^{-1} \\ &= k(\omega')\{1+[\pi\delta(\omega'-H_0)k(\omega')]^2\}^{-1} \\ &\quad -i\pi t(\omega'+i0)^\dagger\delta(\omega'-H_0)t(\omega'+i0), \end{aligned} \tag{58}$$

where $k(\omega')$ is the Hermitian reaction matrix corresponding to $t(\omega'+i0)$. The two terms thus separated are, respectively, Hermitian and anti-Hermitian and contribute, respectively, the real and imaginary parts of (57) because the matrix elements in (57) are diagonal. These two parts contribute to the shift and width of the $\omega_{\mu\nu}$ line, according to (29). The imaginary part has negative sign, for the reason mentioned following (37b) taking again into account that we deal here with diagonal matrix elements, so that this contribution to the spectrum $F(\omega)$ corresponds to damped oscillations, as expected. The last term of (58) is clearly proportional to a total scattering cross section; the cross sections for the states μ and ν (initial and final states) contribute additively to the linewidth when (58) is entered in (57). Note also that when $k(\omega')$ is small, i.e., when the scattering phase shifts are small—which does not necessarily imply validity of the Born approximation—the real part of (57) is small of first order but the imaginary part is of *second order*. In this event, all additional terms of (55) are also small of second order, so that the only first-order effect is the line shift contributed by (57).

Consider now the singular terms, namely, the sixth and the eighth, on the right-hand side of (55). Setting $\omega'=\omega_{\mu\nu}$ and introducing the appropriate eigenvalues of H_0, we find the joint contribution of these terms to (56) to be

$$2\pi i \textstyle\sum_{\alpha\beta}\delta(\tau_\beta-\tau_\alpha)t(\tau_\alpha+\tau_\mu)_{\mu\beta,\mu\alpha}t^*(\tau_\alpha+\tau_\nu)_{\nu\beta,\nu\alpha}f_\alpha. \tag{59}$$

This contribution consists again only of transition matrix elements *on the energy shell*, such as may be obtained from scattering experiments. Clearly this contribution *does not obey the Rydberg–Ritz* principle. Its real and imaginary parts are a little more difficult to disentangle than for (57) because (59) involves off-diagonal matrix elements.

Baranger has shown (BIII, pp. 864, 865) how the imaginary part of (59) combines with the corresponding part of (57) to yield a characteristic quantum effect. (Note that the operator product tt^* appears both in (59) and in the last term of (58).) According to (57) the linewidth is proportional to the frequency of scattering of gas molecules by the molecule of interest, averaged over the states μ and ν of this molecule. Quantum mechanically, *elastic* scattering by these two states does not constitute a pair of distinguishable, mutually exclusive events. Therefore, the probability amplitudes for elastic scattering interfere and indeed would cancel out completely the contribution of elastic scattering to the linewidth if they happened to be equal, because in this event elastic scattering wouldn't perturb the molecular radiation process at all. That (59) relates only to elastic scattering is shown by the factor $\delta(\tau_\beta-\tau_\alpha)$.

The remaining terms of (55) depend entirely on transition matrix elements evaluated *off* the energy shell. Indeed their contribution would manifestly vanish if the transition operator $t(\psi)$ were independent of its energy parameter ψ. Therefore, this contribution represents the effect of transient stages of collisions whereas (57) and (59) depend only on characteristics of completed collisions. As Baranger has emphasized throughout,[2] the relative rate of variation of t as a function of ψ (an energy expressed in frequency units) represents a measure of the effective duration of a collision. Baranger left effects of this type out of consideration whenever they arose in the course of his calculations[2] in accordance with his assumption that each collision can be regarded as sufficiently short to be well separated from the others. The treatment of the present paper has provided in (55) an analytical representation of the transient effects, but additional research is required to analyze them and evaluate their significance in alternative conditions of interest.

As noted at the beginning of this section, the whole treatment leading to (55) could serve to express the operator $M(\omega)$, irrespective of any gas density expansion, in terms of a transition operator $T(\psi)=[1-V(\psi-H_0)^{-1}]^{-1}V$. The construction of matrix elements of $\langle M(\omega)\rangle$ in terms of matrix elements of T could also be carried out and the contribution of matrix elements on the energy shell discussed, as in the case of $\langle M(\omega_{\mu\nu})\rangle$, even though these elements no longer appear to pertain to recognizable separate elementary collision processes. However, there would seem to be no reason to disregard the transient effects.

ACKNOWLEDGMENT

The author is indebted to R. Zwanzig and to other colleagues for numerous discussions that have stimulated and helped materially the present work.