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A Kinetic Theory of Spectral Line Shapes

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The methods of kinetic theory are used to describe the radiation from an atom immersed in a gas of perturbing particles. It is shown that the line shape can be expressed in terms of a one-particle distribution function. The appropriate BBGKY hierarchy of equations is derived. This hierarchy is then truncated by assuming that only two-body collisions are important. The resulting equations are solved to obtain a non-Markovian kinetic equation which describes the combined effects of Doppler and pressure broadening. When the Markovian assumption is applied, a generalized linear Boltzmann equation is obtained which describes the line shape in the region where the impact limit is valid and which also describes the phenomenon of collisional narrowing.

KEY WORDS: Atomic and molecular line shapes; kinetic theory; BBGKY equations; collisional narrowing; pressure broadening; linear Boltzmann equation.

1. INTRODUCTION

It has been known for some time that the problem of describing the shape of a spectral line is intimately connected with the description of collisional processes in the gas one is observing. As a consequence, it should be no surprise that there is a close connection between atomic spectroscopy and kinetic theory. Some of the methods used by kinetic theorists have, in fact, been applied to the line shape problem. In particular, Popielawski and Rice[1] and Smith and Hooper[2] have used the Liouville operator formalism of Fano[3] and Zwanzig[4] to develop expressions for the line shape. On the other hand, Bezzerides[5] has applied the Green's function method to this problem. With the exception of the work of Smith and Hooper,[2] who were concerned with Stark broadening, these papers arrived at rather formal and not readily calculable results.

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The purpose of this paper is to show that the use of one of the simpler and more popular techniques of kinetic theorists, namely the BBGKY hierarchy approach,[6] leads very quickly to a relatively simple expression for the line shape which includes both the effects of collisions on the internal states of the radiator (pressure broadening) and on the center-of-mass motion of the radiator (Doppler narrowing). The collision integral can then be treated by means similar to those used for the ordinary Boltzmann equation.

The motivation for this is the phenomenon of Doppler narrowing of spectral lines, first discussed by Wittke and Dicke[7] and more recently by Rautian and Sobel'man,[8] who treated the problem by means of a phenomenological kinetic equation. It is of interest to note that a similar phenomenon occurs[9] in light scattering from liquids and plasmas,[10] where it has received considerable attention in recent years. In all of these problems, the usual approach is by means of a kinetic equation for an autocorrelation function. In the case of light scattering, this is the density autocorrelation function,[9,10] whereas in the case of spectral lines, it is the dipole autocorrelation function.

An interesting property of the autocorrelation functions is the fact that the kinetic equations turn out to be linear as opposed to the usual kinetic equations. This is an important and useful simplification.

We begin by writing the line shape in terms of a modified, one-particle, reduced density matrix. As is usually the case, this one-particle density matrix is coupled to two- and three-particle and higher density matrices through a hierarchy of equations. This hierarchy is truncated by assuming that only two-body collisions are important. It is then solved to yield a non-Markovian kinetic equation. For long times (small frequencies), the equation is approximately Markovian. Non-Markovian effects can become important on the wings of the line. A somewhat similar approach has been used recently by Pestov and Rautian.[11] However, they neglect all non-Markovian effects and use a Born approximation which is inappropriate for neutral particles.

In a separate paper,[12] we have used the more classical techniques of line shape theory to derive the same results. We feel that the derivation given here will be of interest to the kinetic theorist because it shows quite clearly and simply how the line shape problem can be cast into a kinetic theory problem. This connection between atomic and molecular spectroscopy and kinetic theory has important consequences for both fields. On the one hand, there are many new and useful techniques developed by kinetic theorists that can be applied to spectroscopy. On the other hand, spectroscopy offers an excellent way in which to test the assumptions used in kinetic theory. It is very interesting that a single line shape requires a kinetic equation which is valid for both long (line center) and short (line wings) times.

1.1. The Line Shape

If an atom or molecule is immersed in a gas of perturbing particles, the line shape of the dipole radiation emitted by the atom can be written approximately as [cf. Eq. (2.15) of Ref. 12]

$$I(\omega) = (1/\pi)\,\mathrm{Re}\int_0^\infty e^{i\omega t}C(t)\,dt \tag{1}$$

where

$$C(t) = \mathrm{Tr}\{\mathbf{d}(-\mathbf{k}, 0) \cdot \mathbf{D}(\mathbf{k}, t)\} \tag{2}$$

and

$$\mathbf{D}(\mathbf{k}, t) = \rho \mathbf{d}(\mathbf{k}, -t) \tag{3}$$

where ρ is the equilibrium density matrix for the system.

The quantity $\mathbf{d}(\mathbf{k}, t)$ is defined by

$$\mathbf{d}(\mathbf{k}, t) = [\exp(iHt/\hbar)]\, \mathbf{d}[\exp(i\mathbf{k} \cdot \mathbf{R})] \exp(-iHt/\hbar) \tag{4}$$

where $\mathbf{k} = (\omega/c)\hat{k}$, $\mathbf{d}$ and $\mathbf{R}$ are the atomic dipole moment operator and center-of-mass position operator, respectively, and H is the Hamiltonian for the system composed of the atom and the gas of perturbers.

The quantity $\mathbf{D}(\mathbf{k}, t)$ can be considered as a modified density matrix since it satisfies the quantum Liouville equation

$$i\hbar(\partial/\partial t)\mathbf{D} = [H, \mathbf{D}] \tag{5}$$

Since $\mathbf{d}(-\mathbf{k}, 0)$ operates only on radiator states, we can rewrite Eq. (2) as

$$C(t) = \mathrm{Tr}_e\{\mathbf{d}(-\mathbf{k}, 0) \cdot \mathbf{D}_1(\mathbf{k}, t)\} \tag{6}$$

where $\mathbf{D}_1$ is a modified one-particle, reduced density matrix for the radiator and Tr_e denotes the trace over radiator states. The quantity $\mathbf{D}_1$ can be defined by its matrix elements, which are given by

$$\begin{aligned} \langle a, \mathbf{P} \mid \mathbf{D}_1(\mathbf{k}, t) \mid b, \mathbf{P}' \rangle &= \sum_p \langle a, \mathbf{P}; p \mid \mathbf{D}(\mathbf{k}, t) \mid b, \mathbf{P}'; p \rangle \\ &= \langle a, \mathbf{P} \mid \mathrm{Tr}_p\, \mathbf{D}(\mathbf{k}, t) \mid b, \mathbf{P}' \rangle \end{aligned} \tag{7}$$

where p denotes a complete set of quantum numbers for the perturbers and Tr_p denotes the trace over all perturber states. Equation (6) then follows because $\mathbf{d}$ does not operate on the perturber states. We are labeling the atomic states by the internal quantum numbers a and b and the translational momentum $\mathbf{P}$.

We can write the expression for $C(t)$ in a more convenient and somewhat familiar form by using Eq. (3), the cyclic invariance of the trace, and the fact that $\mathbf{R}$ commutes with $\mathbf{d}$ to obtain

$$\begin{aligned} C(t) &= \mathrm{Tr}_e\{[\exp(-i\mathbf{k} \cdot \mathbf{R})]\, \mathbf{d} \cdot \mathbf{D}_1(\mathbf{k}, t)\} \\ &= \mathrm{Tr}_e\{[\exp(-i\mathbf{k} \cdot \mathbf{R}/2)]\, \mathbf{d} \cdot \mathbf{D}_1(\mathbf{k}, t) \exp(-i\mathbf{k} \cdot \mathbf{R}/2)\} \\ &= \sum_{a,b} \sum_{\mathbf{P}} \langle b \mid \mathbf{d} \mid a \rangle \cdot \langle a, \mathbf{P} + \tfrac{1}{2}\hbar\mathbf{k} \mid \mathbf{D}_1(\mathbf{k}, t) \mid b, \mathbf{P} - \tfrac{1}{2}\hbar\mathbf{k} \rangle \qquad (8) \\ &= \sum_{a,b} \sum_{\mathbf{P}} \langle b \mid \mathbf{d} \mid a \rangle \cdot \mathbf{F}_{ab}(\mathbf{k}, \mathbf{P}, t) \qquad (9) \end{aligned}$$

where

$$\mathbf{F}_{ab}(\mathbf{k}, \mathbf{P}, t) \equiv \langle a, \mathbf{P} \mid [\exp(i\mathbf{k} \cdot \mathbf{R}/2)]\, \mathbf{D}_1(\mathbf{k}, t) \exp(-i\mathbf{k} \cdot \mathbf{R}/2) \mid b, \mathbf{P} \rangle$$
$$= \langle a, \mathbf{P} + \tfrac{1}{2}\hbar\mathbf{k} \mid \mathbf{D}_1(\mathbf{k}, t) \mid b, \mathbf{P} - \tfrac{1}{2}\hbar\mathbf{k} \rangle \tag{10}$$

and we have use of the relation

$$\exp(i\mathbf{k} \cdot \mathbf{R}) \mid \mathbf{P} \rangle = \mid \mathbf{P} + \hbar\mathbf{k} \rangle \tag{11}$$

The quantity $\mathbf{F}_{ab}(\mathbf{k}, \mathbf{P}, t)$ is an off-diagonal matrix element of the one-particle, reduced density matrix corresponding to $\mathbf{D}$. It has a very close resemblance to the one-particle Wigner distribution function.[13] Indeed, if $a = b$, this quantity is the Fourier transform (in space) of a one-particle Wigner distribution function. We might, therefore, expect to find that $\mathbf{F}_{ab}$ approximately obeys something like a Boltzmann equation, at least for long times (or, in terms of frequency, near the line center).

This brings in the question of time scales. Since the Fourier transform of $\mathbf{F}$ gives rise to the line shape which is characterized by a halfwidth $\Delta\omega_{1/2}$ (among other things), the time scale on which $\mathbf{F}_{ab}$ changes is the inverse half-width $\tau_{1/2}$. Another characteristic time in the problem is the average duration of a collision (or correlation time) τ_d, which is of the order of the interaction range between atom and perturber divided by the thermal velocity. A third characteristic time will be the inverse of the frequency measured from the line center $\tau = 1/\Delta\omega$. If $\tau_d \ll \tau_{1/2}$ and we are interested in times $\tau \gg \tau_d$, then we expect that $\mathbf{F}_{ab}$ will be adequately described by a Markovian equation such as the Boltzmann equation. If, on the other hand, $\tau \leqslant \tau_d$, we would expect that non-Markovian effects would begin to appear.

2. THE KINETIC EQUATION: NEUTRAL PERTURBERS

There are, of course, many methods that can be used to obtain kinetic equations. These fall primarily into two classes, those which begin from the BBGKY hierarchy[6] and those which follow the Brussels school.[14] We will, in this case, use the hierarchy method, which seems to be the fastest and least complicated method for arriving at the first nontrivial approximation to the kinetic equation.

We consider a single atom or molecule which we call the emitter or radiator interacting with N perturbers in a volume $\mathcal{V}$.

In order to simplify notation, we will assume that the interaction between perturbers is negligible and that the internal states of the perturbers are not affected by their collisions with the emitters. These assumptions can be lifted without difficulty. Thus, we write the Hamiltonian as

$$H = H_0 + \sum_{i=1}^{N} H_p(i) + \sum_{i=1}^{N} V(i) \tag{12}$$

where H_0 is the unperturbed Hamiltonian for the emitter and has the eigenvalues

$$H_0 \mid a\mathbf{P} \rangle = [(P^2/2m) + \epsilon_a] \mid a\mathbf{P} \rangle \tag{13}$$

The quantity $H_p(i)$ is the Hamiltonian for a free perturber and $V(i)$ is the interaction potential between the radiator and the ith perturber.

We can obtain an equation of motion for $\mathbf{F}_{ab}$ from the Liouville equation by making use of the definition given in Eq. (10). We obtain

$$[(\partial/\partial t) + i(\omega_{ab} + \mathbf{k}\cdot\mathbf{P}/m]\,\mathbf{F}_{ab}(\mathbf{k},\mathbf{P},t) = -(in/\hbar)\cdot\sum_{\mathbf{p}_1}\langle a,\mathbf{P}+\tfrac{1}{2}\hbar\mathbf{k};\mathbf{p}_1 \mid [V(1),\mathbf{D}_2(k,1,t)] \mid b,\mathbf{P}-\tfrac{1}{2}\hbar\mathbf{k};\mathbf{p}_1\rangle \quad (14)$$

where

$$\omega_{ab} = \hbar^{-1}(\epsilon_a - \epsilon_b) \qquad \text{and} \qquad n = N/\mathscr{V} \quad (15)$$

The modified two-body reduced density matrix D_2 is defined by

$$\langle a,\mathbf{P};\mathbf{p}_1 \mid D_2(\mathbf{k},1,t) \mid a',\mathbf{P}';\mathbf{p}_1'\rangle = \mathscr{V}\sum_{p_2\cdots p_N}\langle a,\mathbf{P},\mathbf{p}_1,\mathbf{p}_2,\ldots,\mathbf{p}_N \mid \mathbf{D}(\mathbf{k},t) \mid a',\mathbf{P}';\mathbf{p}_1',\mathbf{p}_2,\ldots,\mathbf{p}_N\rangle \quad (16)$$

where $\mathbf{p}_1,\ldots,\mathbf{p}_N$ denote the momenta of the perturbers.

The next step is, of course, to obtain an expression for $\mathbf{D}_2$. In the usual manner,[6] one can generate a hierarchy of equations for $\mathbf{D}_1$, $\mathbf{D}_2$, etc. similar to the well-known BBGKY hierarchy. If the gas of neutral perturbers is sufficiently dilute, we expect the dominant contributions to arise from two-body collisions with the effects of three- and four-body and higher collisions smaller than those of two-body collisions by additional powers of the perturber density. Thus, we can "truncate" the hierarchy at the second level (i.e., the equation for $\mathbf{D}_2$) by treating the emitter and the perturbing particle as a simple two-body system (thus ignoring terms which are higher order in the perturber density). Then,

$$i\hbar(\partial/\partial t)\,\mathbf{D}_2(\mathbf{k},1,t) = [H_2(1),\mathbf{D}_2(\mathbf{k},1,t)] \quad (17)$$

where

$$H_2(1) = H_0 + V(1) + H_p(1) \quad (18)$$

is the two-body Hamiltonian for the system composed of emitter plus perturber. It is convenient to introduce the two-particle correlation operator

$$\mathbf{G}_2(1,t) = \mathbf{D}_2(\mathbf{k},1,t) - \mathscr{V}^{-1}\mathbf{D}_1(\mathbf{k},t)f_1(1) \quad (19)$$

where $f_1(1)$ is the Maxwell–Boltzmann distribution function for the perturbers. We are assuming here that the particles obey Boltzmann as opposed to Fermi or Bose statistics. This is valid in the ranges of density and temperature of experimental interest.

If we insert the above expression for $\mathbf{D}_2$ in terms of $\mathbf{D}_1$ and $\mathbf{G}_2$ into Eq. (14), we find that the $\mathbf{D}_1 f_1$ terms vanish because of spatial homogeneity (i.e., f_1 is diagonal in momentum states) and we are left with

$$[(\partial/\partial t) + i(\omega_{ab} + \mathbf{k}\cdot\mathbf{P}/m)]\,\mathbf{F}_{ab}(\mathbf{k},\mathbf{p},t) = -(in/\hbar)\sum_{\mathbf{p}_1,c_1}\langle a,\mathbf{P}+\tfrac{1}{2}\hbar\mathbf{k};\mathbf{p}_1 \mid [V(1),\mathbf{G}_2(\mathbf{k},1,t)] \mid b,\mathbf{P}-\tfrac{1}{2}\hbar\mathbf{k};\mathbf{p}_1\rangle \quad (20)$$

From Eq. (17), we obtain, to lowest order in the perturber density n,

$$i\hbar(\partial/\partial t)\,\mathbf{G}_2(\mathbf{k}, 1, t) = [H_2\,, \mathbf{G}_2(\mathbf{k}, 1, t)] + \mathscr{V}^{-1}[V(1), \mathbf{D}_1(\mathbf{k}, t) f_1(1)] \tag{21}$$

We can solve Eq. (21) in the form

$$\mathbf{G}_2(\mathbf{k}, 1, t) = e^{-iH_2 t/\hbar}\mathbf{G}_2(\mathbf{k}, 1, 0)\, e^{iH_2 t/\hbar} - (i/\mathscr{V}h)\int_0^t d\tau\, e^{-iH_2\tau/\hbar}[V(1), \mathbf{D}_1(\mathbf{k}, t-\tau) f_1(1)]\, e^{iH_2\tau/\hbar} \tag{22}$$

We will henceforth neglect any initial correlations between the atom and the perturbers. The effects of such correlations have been shown to be important only for short times τ or, alternatively, for $\hbar\,\Delta\omega > kT$,[15] which is often an uninteresting region of a line profile. One might also expect these contributions to vanish because of phase mixing, a common phenomenon in kinetic theory.[14] Substituting the resulting expression into Eq. (20), we obtain

$$\begin{aligned}[(\partial/\partial t) + i(\omega_{ab} + \mathbf{k}\cdot\mathbf{P}/m)]\,\mathbf{F}_{ab}(\mathbf{k}, \mathbf{P}, t) \\ = -(n/\hbar^2)\sum_{\mathbf{p}_1}\int_0^t d\tau \Big\langle a, \mathbf{P}, \mathbf{p}_1 \mid [\exp(-i\mathbf{k}\cdot\mathbf{R}/2)] \\ \times [V(1), U(0,-\tau)[\tilde{V}(1,-\tau), [\exp(-iH_0\tau/\hbar)] \\ \times \mathbf{D}_1(\mathbf{k}, t-\tau) f_1(1) \exp(iH_0\tau/\hbar)]\, U^{+}(0,-\tau)]\, \exp(-i\mathbf{k}\cdot\mathbf{R}/2) \mid b, \mathbf{P}, \mathbf{p}_1\Big\rangle\end{aligned} \tag{23}$$

where we have defined

$$U(0, -\tau) = e^{-iH_2\tau/\hbar}e^{iH_0\tau/\hbar} \tag{24}$$

and

$$\tilde{V}(1, \tau) = e^{iH_0\tau/\hbar}V(1)\, e^{-iH_0\tau/\hbar} \tag{25}$$

We define the operator $\mathbf{F}(\mathbf{k}, t)$,

$$\mathbf{F}(\mathbf{k}, t) = [\exp(-i\mathbf{k}\cdot\mathbf{R}/2)]\,\mathbf{D}_1(\mathbf{k}, t)\exp(-i\mathbf{k}\cdot\mathbf{R}/2) \tag{26}$$

so that

$$\mathbf{F}_{ab}(\mathbf{k}, \mathbf{P}, t) = \langle a\mathbf{P} \mid \mathbf{F}(\mathbf{k}, t) \mid b\mathbf{P}\rangle \tag{27}$$

We can then write Eq. (23) in the form

$$\begin{aligned}[(\partial/\partial t) + i(\omega_{ab} + \mathbf{k}\cdot\mathbf{P}/m)]\,\mathbf{F}_{ab}(\mathbf{k}, \mathbf{P}, t) \\ = -(n/\hbar^2)\sum_{\mathbf{p}_1, c_1}\int_0^t d\tau \Big\langle a, \mathbf{P}, \mathbf{p}_1 \mid [\exp(-i\mathbf{k}\cdot\mathbf{R}/2)] \\ \times [V(1), U(0,-\tau)[\tilde{V}(1,-\tau), [\exp(-iH_0\tau/\hbar)][\exp(i\mathbf{k}\cdot\mathbf{R}/2)] \\ \times \mathbf{F}(\mathbf{k}, t-\tau)[\exp(i\mathbf{k}\cdot\mathbf{R}/2)] f_1(1) \exp(iH_0\tau/\hbar)]\, U^{+}(0,-\tau)] \\ \times \exp(-i\mathbf{k}\cdot\mathbf{R}/2) \mid b, \mathbf{P}, \mathbf{p}_1\Big\rangle\end{aligned} \tag{28}$$

The above equation is a non-Markovian equation for $\mathbf{F}_{ab}(\mathbf{k}, \mathbf{P}, t)$ [or $\mathbf{F}(\mathbf{k}, t)$] which we can write in the form

$$(\partial/\partial t)\,\mathbf{F}(\mathbf{k}, t) + (i/\hbar)[H_0\,, \mathbf{F}] = \int_0^t d\tau\, \mathscr{B}(\tau)\,\mathbf{F}(\mathbf{k}, t-\tau) \tag{29}$$

Clearly when the Laplace transform is performed to obtain the line shape [cf. Eq. (1)], the Laplace transform $\mathscr{B}(\omega)$ of $\mathscr{B}(\tau)$ represents a width and shift operator.

3. THE MARKOVIAN OR IMPACT LIMIT

In many cases of interest, the duration of a collision is much smaller than the inverse half-width. In such cases, it is expected that for $t > \tau_d$, the kinetic equation becomes approximately Markovian. The process of obtaining the Markovian equation is quite analogous to that used to obtain the Boltzmann equation for neutral gases[16] and the Balescu–Lenard equation for plasmas.[17] In the context of line broadening theories, this approximation is known as the impact approximation.[15]

We begin by noting that Eq. (28) can also be written in the form

$$(\partial/\partial t)\,\mathbf{F}(\mathbf{k}, t) + (i/\hbar)[H_0\,, \mathbf{F}] = \int_0^t d\tau\, B(\tau)[e^{-iH_0\tau/\hbar}\mathbf{F}(\mathbf{k}, t-\tau)\, e^{iH_0\tau/\hbar}] \tag{30}$$

[$B(\tau)$ is not the same operator as $\mathscr{B}(\tau)$]. We then note from Eq. (28) that the kernel $B(\tau)$ becomes very small when $\tau > \tau_d$ [because of the operators $V(1)$ and $\tilde{V}(1,-\tau)$].

This behavior allows us to make a number of important simplifications. One of these is that we can neglect the factors $\exp(\pm i\mathbf{k}\cdot\mathbf{R})$ because they can be shown to lead to oscillating factors in the kernel of the form $\exp(i\mathbf{k}\cdot\mathbf{P}\tau/m)$, which are small when $\tau < \tau_D$ since $\mathbf{k}\cdot\mathbf{P}\tau/m$ is of the order of the range of the interaction potential divided by the wavelength of the observed radiation; we can neglect these oscillating factors.

Furthermore, if we confine ourselves to times of interest t larger than τ_d (the range where the Markovian approximation is expected to be valid), we can extend the upper limit of the τ integration to infinity, giving the result

$$(\partial/\partial t)\,\mathbf{F}(\mathbf{k}, t) + (i/\hbar)[H_0\,, \mathbf{F}] \simeq \int_0^\infty d\tau\, B_0(\tau)[e^{-iH_0\tau/\hbar}\mathbf{F}(\mathbf{k}, t-\tau)\, e^{iH_0\tau/\hbar}] \tag{31}$$

where $B_0(\tau)$ differs from $B(\tau)$ in not having the exponential factors $\exp(\pm i\mathbf{k}\cdot\mathbf{R})$.

The next crucial approximation involves the time dependence of $\mathbf{F}(\mathbf{k}, t)$. In the usual case, where one is considering the ordinary one-particle distribution function $f(t)$, one notes it changes on a time scale of the order of the relaxation time.[16,17] This allows the replacement of $f(t-\tau)$ by $f(t)$ in the collision integral. In this case, however, because of the presence of the second term on the right-hand side of Eq. (31), there is a rapid oscillation superimposed on the usual time behavior. Ignoring for the moment this additional time dependence, we note, as stated in the sentence following Eq. (29), that $\int_0^\infty d\tau\, B_0(\tau)$ is of the order of the half-width. If we remove the rapid oscillation by defining a new function

$$\mathbf{f}(t, \tau) = e^{-iH_0\tau/\hbar}\mathbf{F}(\mathbf{k}, t-\tau)\, e^{iH_0\tau/\hbar} \tag{32}$$

we find that $\mathbf{f}(t, \tau)$ as a function of τ will indeed vary on a time scale of the order of $\tau_{1/2}$ (the magnitude of the kernel is unchanged by the unitary transformation). Thus, since the values of τ for which $B(T)$ is nonzero are never larger than τ_d ($\ll\tau_{1/2}$), we can replace $\mathbf{f}(t, \tau)$ by $\mathbf{f}(t, 0)$. That is, for $\tau \ll \tau_{1/2}$ and $t \gg \tau_d$, we can write

$$e^{-iH_0\tau/\hbar}\mathbf{F}(\mathbf{k}, t-\tau)\, e^{iH_0\tau/\hbar} \simeq \mathbf{F}(\mathbf{k}, t) \tag{33}$$

The error made in this approximation is of the order of $\tau_d/\tau_{1/2} \ll 1$ which is the usual criterion of validity for the impact approximation.[15]

As a result of these approximations, the kinetic equation takes the form

$$\begin{aligned}[(\partial/\partial t) + i(\omega_{ab} + \mathbf{k}\cdot\mathbf{P}/m)]\, \mathbf{F}_{ab}(\mathbf{k}, \mathbf{P}, t) \\ = -(n/\hbar^2)\sum_{\mathbf{p}_1}\int_0^\infty d\tau\, \langle a, \mathbf{P}, \mathbf{p}_1 \mid [V(1), U(0, -\tau) \\ \times [\tilde{V}(1, -\tau), \mathbf{F}(\mathbf{k}, t) f_1(1)]\, U(0, -\tau)^\dagger] \mid b, \mathbf{P}, \mathbf{p}_1\rangle\end{aligned} \tag{34}$$

We then note that

$$\begin{aligned}(\partial/\partial\tau)U(0, -\tau)\, \mathbf{F}(\mathbf{k}, t) f_1(1) U(0, -\tau)^\dagger \\ = -(i/h)U(0, -\tau)[V(1, -\tau), \mathbf{F}(\mathbf{k}, t) f_1(1)]\, U(0, -\tau)^\dagger\end{aligned} \tag{35}$$

After performing the integration over τ, we finally arrive at the Markovian form

$$\begin{aligned}[(\partial/\partial t) + i(\omega_{ab} + \mathbf{k}\cdot\mathbf{P}/m)]\, \mathbf{F}_{ab}(\mathbf{k}, \mathbf{P}, t) \\ = -(in/\hbar)\sum_{\mathbf{p}_1, c_1} \langle a, \mathbf{P}, c_1, \mathbf{p}_1 \mid [T f_1(1)\, \mathbf{F}(\mathbf{k}, t)\, \Omega^{(+)\dagger} \\ - \Omega^{(+)} f_1(1)\, \mathbf{F}(\mathbf{k}, t)\, T^\dagger] \mid b, \mathbf{P}, c_1, \mathbf{p}_1\rangle\end{aligned} \tag{36}$$

where

$$\Omega^{(+)} = U(0, -\infty) \qquad \text{and} \qquad T = V\Omega^{(+)} \tag{37}$$

are the binary collision Möller operator and T-matrix, respectively.

Equation (36) is a generalized Boltzmann equation for the "modified" [cf. Eqs. (3) and (10)] radiator distribution function. Note that this equation is linear, as we might expect in analogy with the results pertaining to light scattering in liquids[9] and plasmas.[18] The reason for the linearity is that the modified density matrix $\mathbf{D}$ differs from the usual one by an operator which acts only on radiator states. This leads to the form $\mathbf{D}_2$ given by Eq. (19) and this form is responsible for the linearity of the final kinetic equation. When one is dealing with ordinary density matrices, the form of ρ_2 is given by[6]

$$\rho_2(1, 2) = \rho_1(1)\, \rho_1(2) + g_2(1, 2) \tag{38}$$

and this form gives rise to nonlinear kinetic equations.

The rather complicated form of this Boltzmann-like equation results from the fact that we have retained the effects of collisions on both the internal and translational

states of the radiator. We can remove the influence of the collisions on the internal states of the radiators by assuming that V, T, and $\Omega^{(+)}$ are diagonal in these states. In that case, as we might expect, the collision integral takes the usual Boltzmann form

$$[(\partial/\partial t) + i(\omega_{ab} + \mathbf{k}\cdot\mathbf{P}/m)]\,\mathbf{F}_{ab}(\mathbf{k},\mathbf{P},t) = \sum_{\mathbf{P}} A(\mathbf{P}',\mathbf{P})\,\mathbf{F}_{ab}(\mathbf{k},\mathbf{P}',t) - \nu(\mathbf{P})\,\mathbf{F}_{ab}(\mathbf{k},\mathbf{P},t) \tag{39}$$

where

$$A(\mathbf{P},\mathbf{P}') = \sum_{\mathbf{p}_1,\mathbf{p}_1'} (2n\pi/\hbar)\,|\langle \mathbf{P},\mathbf{p}_1 \mid T \mid \mathbf{P}',\mathbf{p}_1'\rangle|^2 \times f_1(\mathbf{p}_1')\,\delta[E(P) + E(p_1) - E(P') - E(p_1')] \tag{40}$$

and

$$\nu(\mathbf{P}) = \sum_{\mathbf{P}'} A(\mathbf{P},\mathbf{P}') \tag{41}$$

except, of course, that the collision integral is linear in $\mathbf{F}_{ab}$. This equation is therefore not the usual linearized Boltzmann equation.[19] This particular form also arises in the light scattering problem for the quantity

$$f_s(\mathbf{r},\mathbf{v},t;\mathbf{r}',\mathbf{v}',0) = \langle \delta(\mathbf{r} - \mathbf{r}_1(t))\,\delta(\mathbf{v} - \mathbf{v}_1(t)) \times \delta(\mathbf{r}' - \mathbf{r}_1(0))\,\delta(\mathbf{v}' - \mathbf{v}_1(0))\rangle \tag{42}$$

where $\mathbf{r}_1(t)$ and $\mathbf{v}_1(t)$ are the exact position and velocity of a given particle at time t. The quantity $\mathbf{F}_{ab}$ is very similar in form to f_s.

Equation (39) is the quantum generalization of the equation postulated by Rautian and Sobel'man[8] in their treatment of collisional narrowing of a pure Doppler profile. Equation (36) contains not only collisional narrowing, but also pressure broadening. It is fairly easy to show that the ordinary pressure broadening result can be obtained from Eq. (36) when the effects on translational motion are neglected.[12] In addition, as we will show in a separate paper,[12] there is a term which arises because of a correlation between the effects on internal and translational states as well as the customary pressure broadening and collisional narrowing terms.

4. DISCUSSION

We have used the well-known hierarchy approach to derive a non-Markovian kinetic equation which describes the line shape of radiation from an atom or molecule immersed in a gas of perturbers. In the longtime limit (provided $\tau_{\bar{a}} \ll \tau_{1/2}$), this equation becomes approximately Markovian and has the general appearance of a linear Boltzmann equation. The linearity arises because of the particular form of the one-particle distribution function we are dealing with. The kinetic equation yields the ordinary pressure broadening and collisional narrowing results and contains correlations between these two effects.

The fact that a single line shape encompasses the entire time (frequency) scale makes spectroscopy a potentially important and interesting application of kinetic

theory. Because of the range of times demanded, a single line shape can, in principle, be a test of several of the assumptions used in kinetic theory. In particular, because of the Boltzmann-like form of the kinetic equation derived here, line shapes can be used to find the ranges of validity of various models and approximate solutions of kinetic equations such as the BGK[20] and Fokker–Planck models.

NOTE ADDED IN PROOF

A paper by P. R. Berman and W. E. Lamb, Jr., in which they use an alternative approach, has recently appeared in *Phys. Rev. A* **4**:319 (1971). The general results of their formalism and ours are in agreement.

REFERENCES

1. J. Popielawski and S. A. Rice, *J. Chem. Phys.* **47**:2292 (1967).
2. E. W. Smith and C. F. Hooper, Jr., *Phys. Rev.* **157**:126 (1967).
3. U. Fano, *Phys. Rev.* **131**:259 (1963).
4. R. Zwanzig, *J. Chem. Phys.* **33**:1338 (1960).
5. B. Bezzerides, *Phys. Rev.* **181**:379 (1969).
6. N. N. Bogoliubov, in *Studies in Statistical Mechanics*, I. J. deBoer and G. E. Uhlenbeck, eds., North-Holland Publishing Co., Amsterdam (1962), Vol. I.
7. J. P. Wittke and R. H. Dicke, *Phys. Rev.* **103**:620 (1956).
8. S. G. Rautian and I. I. Sobel'man, *Soviet Phys.—JETP* **9**:701 (1967).
9. J. M. J. Van Leeuwen and S. Yip, *Phys. Rev.* **139**:A1138 (1965).
10. J. P. Dougherty and D. T. Farley, Jr., *J. Geophys. Res.* **68**:5473 (1963).
11. E. G. Pestov and S. G. Rautian, *Soviet Phys.—JETP* **29**:488 (1969).
12. E. W. Smith, J. Cooper, W. R. Chappell, and T. Dillon, *J.Q.S.R.T.*, in publication.
13. W. E. Brittin and W. R. Chappell, *Rev. Mod. Phys.* **34**:620 (1962).
14. I. Prigogine, *Non-Equilibrium Statistical Mechanics*, Interscience Publishers, New York (1962).
15. E. W. Smith, C. R. Vidal, and J. Cooper, *J. Res. Natl. Bur. Std. U.S.* **73A**:389, 405 (1969).
16. J. Weinstock, *Phys. Rev.* **132**:454 (1963).
17. R. Balescu, *Statistical Mechanics of Charged Particles*, Interscience Publishers, New York (1963).
18. N. Rostoker, *Phys. Fluids* **7**:479, 491 (1964).
19. K. Huang, *Statistical Mechanics*, John Wiley and Sons, New York, (1963), p. 132.
20. P. L. Bhatnagar, E. P. Gross, and M. Krook, *Phys. Rev.* **94**:511 (1954).

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