

Solving the line-shape problem with speed-dependent broadening and shifting and with Dicke narrowing. I. Formalism

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In this paper, we present a formalism for the exact calculation of spectral profile of an isolated line undergoing speed-dependent collisional broadening and shifting and Dicke narrowing. It is couched in the language of the density matrix as in the closely related fields of transport phenomena, laser physics, and nonlinear optics. The formalism is *ab initio* in spirit, permitting the calculation of the line shape starting only from a given interaction potential. The line shape is obtained by solving a transport/relaxation equation for the off-diagonal element of the density matrix, a macroscopic quantity. The collision operator in the transport/relaxation equation, which is determined from the (microscopic) interaction between the active molecule and the perturber, is presumed known.

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I. INTRODUCTION

Since the days of Boltzmann it has been recognized that the only viable treatment of systems that involve a large number of particles is in statistical terms. In this theory, a central role is played by a distribution function, which is a macroscopic quantity. For example, when one ignores the internal structure and describes the translational motion classically, the distribution function $f(t, \vec{r}, \vec{v})$ gives the probability of finding a molecule within a cell centered about a point at position \vec{r} and velocity \vec{v} at time t . The evolution of $f(t, \vec{r}, \vec{v})$ due to collisions is governed by the Boltzmann transport equation [1]

$$\frac{\partial}{\partial t} f(t, \vec{r}, \vec{v}) = -\vec{v} \cdot \vec{\nabla}_{\vec{r}} f(t, \vec{r}, \vec{v}) + \hat{S}_{VC} f(t, \vec{r}, \vec{v}), \quad (1)$$

where the velocity-changing collision operator

$$\begin{aligned} \hat{S}_{VC} f(t, \vec{r}, \vec{v}) = & - \int d^3 \vec{v}' A(\vec{v}' \leftarrow \vec{v}) f(t, \vec{r}, \vec{v}') \\ & + \int d^3 \vec{v}' A(\vec{v} \leftarrow \vec{v}') f(t, \vec{r}, \vec{v}') \end{aligned} \quad (2)$$

is given in terms of the collision kernel $A(\vec{v} \leftarrow \vec{v}')$, which describes the rate of transfer into the cell at \vec{v} from the cell centered at \vec{v}' . All microscopic aspects of the transport problem are contained in $A(\vec{v} \leftarrow \vec{v}')$ and may be calculated for a given interaction between the molecules. Equation (1), being an integral-differential equation, is very difficult to handle analytically even for an interaction described by a very simple function. On the other hand, Eq. (1) does not pose a

problem when solved numerically and there now exists a considerable literature involving a variety of techniques and approximations for the numerical treatment of transport problems in statistical mechanics (see Ref. [2], and references therein).

With the notable exceptions of neutron and Brillouin spectroscopy, all of spectroscopy involves particles with internal degrees of freedom. In such cases, the classical Boltzmann equation is inadequate and one must resort to the density-matrix formalism of quantum mechanics, where the equation of motion is

$$\frac{\partial}{\partial t} \hat{\rho}_{\text{entire}} = \frac{1}{i\hbar} [\hat{\mathcal{H}}, \hat{\rho}_{\text{entire}}], \quad (3)$$

where $\hat{\mathcal{H}}$ and $\hat{\rho}_{\text{entire}}$ are the Hamiltonian and density-matrix operator for the entire system: active molecules, perturbers (bath), and radiation field. For an example relevant to line shapes see Refs. [3,4]. Two approximations, (i) the translational motion is treated classically and (ii) the influence of the active molecules on the bath (perturbers) is treated as very weak, converts Eq. (3) to a Boltzmann-like transport/relaxation equation [5], where the Hamiltonian \hat{H} and the density matrix $\hat{\rho}$ apply only to the active molecules. \hat{H} contains the interaction with the electromagnetic field. The density matrix $\hat{\rho}$ is a continuous function of \vec{r} and \vec{v} and discrete in the internal degrees of freedom. The additional transport/relaxation terms that appear in Eq. (3) arise from “tracing” over the degrees of freedom of the perturbers. As in the Boltzmann equation, the transport/relaxation coefficients can and will, in general, depend upon the speed of the active molecule and may only be determined from microscopic calculations [6].

There are several historical forms to the revised Boltzmann equation, Eq. (3). It is referred to as the Wang-Chang-Uhlenbeck equation [7] if one ignores the degeneracy of the internal levels and restricts the treatment to the diagonal elements of the density matrix (populations). It is known as the

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Waldmann-Snider equation, if degeneracy is included [8,9]. This equation is also called the quantum-mechanical Boltzmann equation [9] or the quantum kinetic equation [10]. For the off-diagonal elements (optical coherence), it is known as the generalized Waldmann-Snider equation. Recently, one of us has discussed [5] what might be called the generalized Wang-Chang-Uhlenbeck equation. This captures all of the structure of the generalized Waldmann-Snider equation, but omits all polarization features. Polarization effects are intrinsically tied to the spatial degeneracy of the states of the active molecules or atoms.

A treatment similar to Refs. [3,5], but purely classical, was given much earlier by Rautian and Sobelman [11]. There is a clear advantage to using the density-matrix formalism. It permits a direct connection between the theoretical treatment of a range of subjects, such as the theory of spectral line shapes, the theory of mass transport, the theory of nonlinear optics, and the theory of gas lasers. This enlarges our understanding of physics and also allows us to borrow powerful techniques used in one area and use them constructively in another. Here, we adopt a numerical treatment used in transport phenomena, to the problem of determining the spectral line shape of an isolated line. Numerical solutions are required, since the new equation, like the Boltzmann equation is also an integral-differential equation and does not have an analytical solution without highly simplified assumptions or simple models for collision kernels (cf. [12,13]).

From the practical point of view it is important to use an efficient and flexible method in the numerical calculations. It is well known that Boltzmann-like operator equations can be solved using a complete set of orthogonal basis functions. This method, which is widely used in statistical physics [2] has already been applied to the line-shape problem [14,15]. Podivilov *et al.* [14] calculated the Dicke narrowed line shapes of ions in dense plasma. The shapes of spectral lines were calculated by Robert and Bonamy [15] in the case where collisional broadening and shifting is speed-dependent. They described the translational motion using the Keilson-Storer model [16] for the collision kernel, but ignored the Doppler shift. We treat the general problem using the same well-known method [2,14,15], in principle, starting from the intermolecular interaction. We focus on the macroscopic part of the problem, i.e., on a solution of the transport/relaxation equation for the off-diagonal elements of the density matrix assuming that the microscopic part of the problem has already been solved i.e., the collision operator in the transport/relaxation equation has already been calculated starting from the interaction between the active molecule and the perturber.

This paper is divided into a number of sections. In the second section, we present the fundamental transport/relaxation equation describing the off-diagonal element of the density matrix. We show its connection to the absorption coefficient and transform it in order to treat it in a manner parallel to the methods commonly used to handle mass transport in statistical mechanics. In the third section, we borrow further from the theory of mass transport and convert the transport/relaxation equation into a set of coupled linear equations that is generally applicable to the case of an iso-

lated line. In the fourth section, we specialize the formalism to the case where velocity changing collisions and dephasing collisions are statistically uncorrelated. This completes the formalism that, in principle, permits one to calculate the spectral profile of an isolated line with no adjustable parameters. We finish with a summary and conclusions.

II. TRANSPORT/RELAXATION EQUATION

As indicated above, the theory of the shape of an isolated absorption line can be formulated in terms of the density matrix [5]. For linear spectroscopy and an isolated line it is sufficient to consider a two-level system interacting with weak monochromatic electromagnetic radiation. To first order in the field E , the resonant part of the off-diagonal element of the density matrix for the active molecule ρ^- can be written [5] as $\rho^- = i\varrho(\omega, \vec{v})n_i\mu_{if}E \exp[-i(\omega t - \vec{k} \cdot \vec{r})]$, where n_i is the total population in the initial state i and μ_{if} is the matrix element of the dipole transition between the initial state i and the final state f . In our scalar treatment, we write the field as $E \exp[-i(\omega t - \vec{k} \cdot \vec{r})]$ where ω is the frequency and \vec{k} is the wave vector. In the rotating-wave approximation $\varrho(\omega, \vec{v})$ satisfies the following transport/relaxation equation

$$\varrho_0(\vec{v}) = -i(\omega - \omega_0 - \vec{k} \cdot \vec{v})\varrho(\omega, \vec{v}) - \hat{S}\varrho(\omega, \vec{v}), \quad (4)$$

where the ω_0 is the resonant frequency and $\varrho_0(\vec{v})$ describes the initial or zero-field velocity distribution of the molecules or atoms in state i . In this paper, we assume that the initial distribution is the normalized Maxwellian velocity distribution $f_m(\vec{v}) = (\pi v_m^2)^{-3/2} \exp(-v^2/v_m^2)$. Here $v_m = \sqrt{2k_B T/m_A}$ is the most probable speed of the absorber, m_A is the mass of the absorber, k_B is Boltzmann's constant, and T is the temperature of the gas. The collision operator \hat{S} describes the influence of the perturbers (bath) on the off-diagonal elements of the density matrix of the active molecules. It is proportional to the density of perturbers.

From a solution for the density-matrix operator $\hat{\rho}$, one can readily find the polarization, P , (dipole moment per unit volume) using $P = Tr[\hat{\rho}\hat{\mu}]$, where $\hat{\mu}$ is the dipole operator. With $\hat{\rho}$ known to the first order in E it follows that P can be written as χE , where χ is the complex susceptibility, the imaginary part of which is related to the absorption coefficient [5]. It follows that the line-shape function (normalized to unity) describing the dependence of the absorption on the frequency of absorbed radiation can be calculated as the real part of a velocity integral and written as

$$I(\omega) = \frac{1}{\pi} \text{Re} \int d^3\vec{v} \varrho(\omega, \vec{v}). \quad (5)$$

The imaginary part of this integral is related to the function describing the frequency dependence of the index of refraction [5].

As in the treatment of the diagonal element of the density matrix in statistical mechanics it is useful to express the off-diagonal element $\varrho(\omega, \vec{v})$ as

$$\varrho(\omega, \vec{v}) = f_m(v) h(\omega, \vec{v}) \quad (6)$$

and to define the operator \hat{S}^f (which is related to the collision operator \hat{S}) by the equation

$$\hat{S}^f f_m(v) h(\omega, \vec{v}) = f_m(v) \hat{S}^f h(\omega, \vec{v}). \quad (7)$$

If we insert Eq. (6) into Eq. (4) we obtain

$$1 = -i(\omega - \omega_0 - \vec{k} \cdot \vec{v}) h(\omega, \vec{v}) - \hat{S}^f h(\omega, \vec{v}), \quad (8)$$

which can be used to determine the function $h(\omega, \vec{v})$. A very similar equation was given much earlier and applied to investigate the dynamics of time-dependent processes in simple classical fluids [2,17]. Furthermore, if we define the scalar product (a, b) of functions $a(\vec{v})$ and $b(\vec{v})$ as [2]

$$(a, b) = \int d^3\vec{v} f_m(\vec{v}) a^*(\vec{v}) b(\vec{v}), \quad (9)$$

then Eq. (5) for the shape of line can be written as

$$I(\omega) = \frac{1}{\pi} \text{Re}(1, h(\omega, \vec{v})). \quad (10)$$

Thus, there is a direct connection between the solution of Eq. (8) and the spectral profile. However, as indicated above, there are no known analytical solutions to Eq. (8) for a collision operator containing speed-dependent effects and a physically realistic treatment of the translational motion. In this case, only a numerical approach to the line-shape problem is viable. The expression for the shape of a line, Eq. (10) is very close to the expression for the self-structure factor used in statistical physics [2].

III. SYSTEM OF COMPLEX LINEAR EQUATIONS

The complexity of the collision operator \hat{S} or \hat{S}^f dictates that we use an efficient numerical method for solving the transport/relaxation equation. It is well known in quantum and statistical mechanics that a solution to this kind of operator equation can be found using a complete set of orthogonal basis functions. Then the operator equation is replaced by an infinite system of (complex) linear equations.

Let us use an infinite set of orthonormal functions $\varphi_s(\vec{v})$, where $s=0,1,2, \dots$, in which $\varphi_0(\vec{v})=1$. It is useful to introduce the following ‘‘matrix element’’ notation

$$\langle s | s' \rangle = (\varphi_s, \varphi_{s'}) = \delta_{s,s'} \quad (11)$$

and

$$\langle s | \hat{A} | s' \rangle = (\varphi_s, \hat{A} \varphi_{s'}). \quad (12)$$

In terms of the basis functions, we can write the function $h(\omega, \vec{v})$ as

$$h(\omega, \vec{v}) = \sum_{s=0}^{\infty} c_s(\omega) \varphi_s(\vec{v}), \quad (13)$$

where the expansion coefficients $c_s(\omega)$ depend on the frequency, ω . Inserting Eq. (13) into Eq. (8), we obtain an infinite system of complex simultaneous linear equations for the coefficients $c_s(\omega)$. This set of equations can be written in matrix form as [15]

$$\underline{\mathbf{b}} = \mathbf{L}(\omega) \underline{\mathbf{c}}(\omega), \quad (14)$$

where the column vector $\underline{\mathbf{b}}$, contains one in the top position and zeros elsewhere, i.e., $[\underline{\mathbf{b}}]_s = \delta_{s,0}$. The column vector $\underline{\mathbf{c}}(\omega)$ consists of the coefficients $c_s(\omega)$, i.e., $[\underline{\mathbf{c}}(\omega)]_s = c_s(\omega)$. The matrix $\mathbf{L}(\omega)$ depends on the frequency ω and can be given in the following form

$$\mathbf{L}(\omega) = -i(\omega - \omega_0) \mathbf{1} + i\mathbf{K} - \mathbf{S}^f, \quad (15)$$

where $\mathbf{1}$ is the unit matrix, i.e., $[\mathbf{1}]_{s,s'} = \delta_{s,s'}$, \mathbf{K} is the matrix that represents the Doppler shift, i.e., $[\mathbf{K}]_{s,s'} = \langle s | \vec{k} \cdot \vec{v} | s' \rangle$, and \mathbf{S}^f is the matrix that represents the collision operator, i.e., $[\mathbf{S}^f]_{s,s'} = \langle s | \hat{S}^f | s' \rangle$. Note it follows directly from Eqs. (7) and (9) that

$$\langle s | \hat{S}^f | s' \rangle = \int d^3\vec{v} \varphi_s^*(\vec{v}) \hat{S}^f f_m(\vec{v}) \varphi_{s'}(\vec{v}). \quad (16)$$

This means that the matrix \mathbf{S}^f can be obtained directly from the operator \hat{S} . Inserting Eq. (13) into Eq. (10) we have [2,15]

$$I(\omega) = \frac{1}{\pi} \text{Re} c_0(\omega). \quad (17)$$

Thus, the line shape can be evaluated if the solution to the set of algebraic equations is known.

A variety of techniques [2] have been used in statistical mechanics to find approximate solutions to equations like Eq. (14). In this application to the line-shape problem, we simply limit the infinite set to the finite set $s = 0, 1, 2, \dots, s_{\max}$ and we represent all operators by matrixes defined in this subspace. Solving this finite set of algebraic equations yields an approximate spectral profile. The approximated shape of line tends to the exact profile as $s_{\max} \rightarrow \infty$. The quality of this approximation depends directly on the choice of the subset of functions $\varphi_s(\vec{v})$ and on the dimension, $s_{\max} + 1$. The dimension can be chosen relatively small if we find the basic set of functions with fast convergence. Thus, the general problem of determining a line shape is reduced to the art of choosing a set of basis functions and a practical value of s_{\max} .

As presented Eq. (14) is specific to each frequency ω so that the spectrum is evaluated point by point. As in line mixing [18] and Dicke narrowing [19], there is a way around this inconvenience, by applying a well-known diagonalization procedure to Eq. (14). For the sake of brevity we do not do that here.

IV. SPEED-DEPENDENT BROADENING AND SHIFTING, AND DICKE NARROWING

The expressions given above are general and could include such important effects as speed-dependent velocity-changing collisions, speed-dependent broadening and shifting, and correlation between the velocity-changing and dephasing collisions. However, we now limit the discussion to the case where velocity-changing and dephasing collisions are uncorrelated. In this case we can write

$$\hat{S} = \hat{S}_D + \hat{S}_{VC}, \quad (18)$$

where \hat{S}_{VC} is the velocity-changing collision operator and \hat{S}_D is the dephasing collision operator.

The real part of the dephasing collision operator is related to the speed-dependent collisional width $\Gamma(v)$ and the imaginary part is related to the speed-dependent collisional shift $\Delta(v)$. The operator \hat{S}_D is generally written as

$$\hat{S}_D = -\Gamma(v) - i\Delta(v), \quad (19)$$

where v is the speed of the active molecule. Only in the absence of speed dependence does Γ actually equal the Lorentzian width and Δ actually equal the collisional shift of an isolated line. We are interested in the case where the speed dependence may not be ignored. We assume that the microscopic scattering calculation (semiclassical or quantum) for the absorber/perturber system have been carried out so that $\Gamma(v)$ and $\Delta(v)$ are known. When speed dependence is significant it will almost certainly manifest itself in the spectral profile. For example, the line will not be Lorentzian [20,21], the width will not equal the thermal average of $\Gamma(v)$ and the shift will not equal the thermal average of $\Delta(v)$.

Equations (15)–(17) tell us that we need to evaluate the matrix elements of \hat{S}^f to determine the line shape. With \hat{S} given by Eq. (18) it follows that the matrix \mathbf{S}^f can be written

$$\mathbf{S}^f = \mathbf{S}_D^f + \mathbf{S}_{VC}^f, \quad (20)$$

where the matrix \mathbf{S}_D^f represents the dephasing collision operator, i.e., $[\mathbf{S}_D^f]_{s,s'} = \langle s | \hat{S}_D^f | s' \rangle$, and the matrix \mathbf{S}_{VC}^f represents the velocity-changing collision operator, i.e., $[\mathbf{S}_{VC}^f]_{s,s'} = \langle s | \hat{S}_{VC}^f | s' \rangle$.

We noted above that the matrix \mathbf{S}^f can be evaluated directly from the operator \hat{S} using Eq. (16). Nevertheless, we would like to illuminate the relation between the operators \hat{S} and \hat{S}^f . For the dephasing collisions it follows from Eq. (7) that $\hat{S}_D = \hat{S}_D^f$ and that the matrix element of \hat{S}_D^f may be evaluated if $\Gamma(v)$ and $\Delta(v)$ are known. However, in general, for velocity-changing collisions, \hat{S}_{VC} does not equal \hat{S}_{VC}^f . We illustrate this with a simple example. One of the most commonly used models for the velocity-changing collision operator is the Fokker-Planck operator, which describes

velocity-changing collisions in the soft or weak collision approach. This operator has the following form

$$\hat{S}_{VC} = \nu \left(\frac{v_m^2}{2} \Delta_v + \vec{\nabla}_v \cdot \vec{v} \right). \quad (21)$$

The corresponding operator \hat{S}_{VC}^f can be written as

$$\hat{S}_{VC}^f = \nu \left(\frac{v_m^2}{2} \Delta_v - \vec{v} \cdot \vec{\nabla}_v \right) \quad (22)$$

and differs from \hat{S}_{VC} . In some cases it may be more convenient to first derive \hat{S}_{VC}^f and to calculate its matrix elements directly rather than through the use of Eq. (16). Nevertheless, for given $\Gamma(v)$, $\Delta(v)$ and \hat{S}_{VC}^f or \hat{S}_{VC} , and a chosen set of basis functions it is always possible to evaluate the matrix $\mathbf{L}(\omega)$ and solve the set of equations Eq. (14), to find the shape of the line, numerically. We will show in the following paper that there are no practical limitations to this procedure.

V. SUMMARY

In this paper, we have considered the problem of an isolated line undergoing speed-dependent broadening and shifting and Dicke narrowing. We use a density-matrix approach in order to emphasize the connection to statistical mechanics (transport phenomena), laser physics, and nonlinear optics. The basic transport/relaxation equation was re-expressed using a nomenclature found in the treatment of transport phenomena and then, using a technique also found in that field, we converted the equation to a set of coupled linear equations. The connection between the solutions to this set of equations and the spectral profile is given. Thus, if the collision operator describing the speed-dependent broadening and shifting and translational motion is known as a result of microscopic calculations for a given intermolecular interaction, the numerical solution of the macroscopic part of the line-shape problem is available, i.e., an *ab initio* calculation of the spectral profile of an isolated line without any adjustable parameters is now possible. In the following paper, we show that calculations based on the formalism presented here can easily be carried out and we give, as an example, results for colliding rigid spheres of arbitrary mass ratio and with broadening or shifting that is speed dependent.

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