

Consequently, the dispersion relation may be written as

$$m\omega^2(k) = 3k^2\beta^{-1} + \sum_j {}^0\Phi_{ij} e^{-ik(R_i^0 - R_j^0)} \times \exp - \frac{1}{2}k^2\beta^{-1} \{ \Phi_{ii}^{-1} + \Phi_{jj}^{-1} + \Phi_{ij}^{-1} + \Phi_{ji}^{-1} \}, \quad (C14)$$

where Φ_{ij}^{-1} is the i th- j th element of the inverse of the matrix ${}^0\Phi$. For sufficiently small values of β^{-1} (i.e., for low temperatures), the usual phonon dispersion relation Eq. (C4) will follow from Eq. (C14).

The necessary limiting value of β is related to the lattice spacings and interparticle potential energies. For example, for a lattice of nearest-neighbor interactions, Eq. (C14) may be shown to be

$$m\omega^2(k) = 3\beta^{-1}k^2 + 2m\omega_D^2 \times \{1 - (\cos k\delta)e^{-k^2(2\beta\omega_D^2 m)^{-1}}\}, \quad (C15)$$

where, in the above expression, $m\omega_D^2$ equals the lattice force constant and δ is the lattice spacing. Thus, in this instance, in order to obtain the usual phonon dispersion relation, the inequalities $m\omega_D^2\beta\delta^2 \gg 1$ and $k^2/(m\beta\omega_D^2) \ll 1$ must be satisfied.

Let us now prove the assertion made in Ref. 9, viz., that the eigenfunction given by Eq. (2.14) reduces to zero when evaluated for a harmonic lattice. Indeed, for small k

$$\psi_7 \equiv [A_4(k) + |k|\omega^{-2}LA_3(k)] \sim -ik(MN/V)^{1/2}[q_k + \omega^{-2}\dot{p}_k]. \quad (C16)$$

Thus, in virtue of Eq. (C5), one has

$$\psi_7^{\text{lattice}}(k) \equiv 0. \quad \text{Q.E.D.}$$

Relaxation Theory of Spectral Line Broadening in Plasmas*

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In this theory of spectral line broadening in plasmas, the radiation process is treated as the relaxation of an excited atom, weakly coupled to a thermal bath, to a state of lower energy. The theory presented here emphasizes the Liouville-operator formalism, as developed by Zwanzig, and may be considered an extension of Fano's theory of pressure broadening in neutral gases. It may further be considered an illustration of a case in which an observable quantity can be expressed in terms of a well-defined correlation function, which can be evaluated without resorting to a microscopic analysis of the interactions. A comparison is made with the impact theories of Griem, Kolb, and Baranger; specifically, it is shown that the assumption of binary collisions and the impact approximation are not necessary in the relaxation theory. Of special importance are frequency-dependent "width" and "shift" operators which produce asymmetries in the intensity profile that are not predicted by the previous plasma-broadening theories. These asymmetries are illustrated in an application of the relaxation theory to the Lyman- α line. The line shape is calculated to second order in the weak-coupling potential, and a comparison is made with experimental observations of this line.

1. INTRODUCTION

THE shape of the broadened spectral lines emitted or absorbed by neutral and ionized gases is determined primarily by the interparticle forces present in the gas. Consequently, much effort has been devoted to the development of a theory which will accurately predict the shape of these lines. Such a theory would permit the observable characteristics of a given line (shift, width, etc.) to serve as noninterfering probes for a determination of the temperature, density, etc., of the gas.

The most successful line shape calculations have been obtained by the impact theories of Kolb,¹ Griem,² and Baranger.³ These theories use a time-dependent perturbation and employ an impact approximation that is based on a binary-collision model.

The application of these binary-collision-impact (BCI) theories to the Stark broadening in plasmas is plagued by the familiar divergences that result when a binary-collision model is used to treat long-range interactions. Attempts to avoid these divergences by means of impact-parameter cutoffs have led many BCI theories to neglect the long-range electron-atom interactions.

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† The work reported here is based on a dissertation submitted to the University of Florida in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

¹ A. C. Kolb and H. R. Griem, Phys. Rev. **111**, 514 (1958).

² H. R. Griem, *Plasma Spectroscopy* (McGraw-Hill Book Company, Inc., New York, 1964).

³ M. Baranger, *Atomic and Molecular Processes*, edited by D. Bates (Academic Press Inc., New York, 1962), Chap. 13.

The time-dependent perturbation methods used by the BCI theories require that complicated time integrals be performed; the explicit evaluation of these integrals requires certain simplifying assumptions. In particular, the impact approximation and additional approximations based on its assumed validity are used to replace the time-dependent perturbation by a constant effective interaction \mathcal{H} .

In a recent theoretical study of relaxation phenomena, Fano⁴ has shown that an important formal simplification of the line-broadening problem may be achieved by means of the Liouville operator formalism and the relaxation techniques developed by Zwanzig.⁵ Several authors^{4,6,7} have applied these techniques to the problem of pressure broadening in neutral gases; however, they have used the time-dependent “ t -matrix” formalism which is far too difficult to permit any practical calculations.

In this paper, the Liouville operator formalism and Zwanzig’s projection operator techniques are employed in the development of a relaxation theory for line broadening in plasmas. A time-independent perturbation theory is used and no time integration difficulties are experienced.

The model used by the relaxation theory contains a radiating atom weakly coupled to an electrically neutral gas of electrons and ions, which serves as a thermal bath for the atom. The primary broadening mechanism (i.e., the weak coupling) is the Stark interaction between the atom and the electric microfield produced by the electrons and ions. The effect of the ion broadening is approximated by assuming that the ions are stationary. The electric microfield is therefore composed of a rapidly fluctuating electron field plus the static ion component. The line shape of the atomic spectral radiation is obtained from a Laplace transform of the autocorrelation function, $\langle \mathbf{d} \cdot \mathbf{d}(t) \rangle$, of the atomic dipole vector. The autocorrelation function is obtained by taking an ensemble average of $\mathbf{d} \cdot \mathbf{d}(t)$ over the states of the atom and the thermal bath. It is shown that the ensemble average over the ion subsystem may be replaced by the familiar microfield average, in the static ion approximation.

The ensemble average over the electron subsystem is performed with a many-particle dilute gas treatment of the electron-atom interaction. The impact approximation and the binary-collision assumption, used by the BCI theories, are replaced by this dilute gas assumption, thus obviating the necessity for an impact parameter cutoff.

In the relaxation theory, the effects of the perturbing particles in the plasma are represented by a frequency-dependent effective-interaction operator $\mathcal{H}(\omega)$. This operator replaces the static operator \mathcal{H} obtained by the BCI theories. The frequency dependence of $\mathcal{H}(\omega)$ is shown to be a result of the time dependence of the quadratic Stark interaction between the electrons and the atom. This frequency dependence produces an asymmetry in the observed line shape. In order to illustrate this asymmetry, as well as the practical value of the relaxation formalism, a calculation of the Lyman (Ly) α line is made. This calculation shows an asymmetry on the order of 10%, and appears to be in agreement with a recent measurement⁸ of the Ly- α profile.

2. BASIC MECHANICS

A. The Liouville-Operator Representation

The time development of the density matrix is governed by the Liouville equation

$$i\hbar(\partial\rho/\partial t)=[H,\rho]. \quad (1)$$

In the Liouville representation this equation takes the form

$$i\hbar(\partial\rho/\partial t)=L\rho, \quad (2)$$

where L is the Liouville operator defined by

$$L\rho=[H,\rho] \quad (3)$$

or

$$(L\rho)_{mn}=\sum_{m'n'}L_{mn,m'n'}\rho_{m'n'}, \quad (4)$$

$$L_{mn,m'n'}=H_{mm'}\delta_{nn'}-\delta_{mm'}H_{n'n}. \quad (5)$$

These equations indicate that, if ρ is a matrix, the Liouville operator is a tetradic, or four-index, operator. The formal solutions of Eqs. (1) and (2) provide a useful identity for the time-development operator:

$$\rho(t)=e^{-itH/\hbar}\rho(0)e^{itH/\hbar}=e^{-itL/\hbar}\rho(0). \quad (6)$$

The Laplace transform of the time-development operator is frequently called its resolvent. In this paper, we will use a complex variable $\omega=\tilde{\omega}+i\epsilon$ ($\epsilon>0$) and the resolvent operator is defined by

$$K(\omega)=-i\int_0^\infty e^{i\omega t}e^{-itL/\hbar}dt=(\omega-L/\hbar)^{-1}. \quad (7)$$

B. Interacting Systems

Relaxation mechanics is concerned with a system a , in an excited state, relaxing to a state of lower energy by means of its interaction with another system b . In this paper, system a will be a radiating atom and system b will be a thermal bath composed of charged perturbers and a radiation field.

Following the treatment of Fano,⁹ we denote the density matrix for the composite system by $\rho^{(a,b)}$. Each

⁴ U. Fano, Phys. Rev. **131**, 259 (1963); *Lectures on the Many-Body Problem*, edited by E. R. Caianiello (Academic Press Inc., New York, 1964), Vol. II, p. 217.

⁵ R. Zwanzig, J. Chem. Phys. **33**, 1338 (1960); in *Lectures in Theoretical Physics*, edited by W. E. Downs and J. Down (Interscience Publishers, Inc., New York, 1961), Vol. III, p. 106; Phys. Rev. **124**, 983 (1961).

⁶ D. W. Ross, Ann. Phys. (N. Y.) **36**, 458 (1966).

⁷ A. Ben-Reuven, Phys. Rev. **141**, 34 (1966); **145**, 7 (1966).

⁸ R. C. Elton and H. R. Griem, Phys. Rev. **135**, A1550 (1964).

⁹ U. Fano, Rev. Mod. Phys. **29**, 74 (1957).

row or column of $\rho^{(a,b)}$ will be labeled by two indices (m,n) corresponding to eigenstates $\Psi_m^{(a)}$ and $\Psi_n^{(b)}$ of the individual subsystems; $\rho^{(a,b)}$ will thus have the form $\rho^{(a,b)}_{mn,m'n'}$.

An operator $Q^{(a)}$, pertaining to subsystem a , may be regarded as an operator of the composite system when it is multiplied (direct product) by the unit operator, $I^{(b)}$, of subsystem b . The ensemble average of $Q^{(a)}I^{(b)}$ is given by the trace of the matrix product $Q^{(a)}I^{(b)}\rho^{(a,b)}$. This trace is denoted by Tr_{ab} since it is a sum over states of both subsystems. If we define a reduced density matrix $\rho^{(a)}$ by

$$\rho^{(a)} = \text{Tr}_b\{\rho^{(a,b)}\}, \quad (8)$$

we obtain

$$\begin{aligned} \langle Q^{(a)}I^{(b)} \rangle &= \text{Tr}_{ab}\{Q^{(a)}I^{(b)}\rho^{(a,b)}\} \\ &= \text{Tr}_a\{Q^{(a)}\rho^{(a)}\}. \end{aligned} \quad (9)$$

The subsystems are statistically independent when the average of a quantity pertaining to one subsystem does not depend on the state of the other, that is, when

$$\langle Q^{(a)}Q^{(b)} \rangle = \langle Q^{(a)} \rangle \langle Q^{(b)} \rangle \quad (10)$$

for all operators $Q^{(a)}$ and $Q^{(b)}$. In this case, $\rho^{(a,b)}$ must have the direct product form

$$\rho^{(a,b)} = \rho^{(a)}\rho^{(b)}. \quad (11)$$

C. The Zwanzig Projection-Operator Technique

It is well known that a complete knowledge of the state of a system is not always necessary for the calculation of observable quantities pertaining to the system. A simple example of this is the case where the operator Q is diagonal in some representation; in that representation, we need only the diagonal part of the density matrix to calculate $\langle Q \rangle = \text{Tr}\{Q\rho\}$. Another example is found in problems involving interacting systems. According to Eq. (9), the only part of $\rho^{(a,b)}$ that is needed to compute the average of an operator $Q^{(a)}$, pertaining to subsystem a , is its projection $\rho^{(a)}$, in this subsystem.

Zwanzig⁵ has developed a formal procedure for obtaining an integro-differential equation which governs the time development of the "relevant" part of any operator satisfying Eqs. (1) and (2). The relevant part of the quantity $Q(t)$ is picked out by a projection operator P and is called $Q_1(t)$; the remainder of $Q(t)$ is the irrelevant part $Q_2(t)$. If $Q_2(0) = 0$, Zwanzig's equation is

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} Q_1(t) &= PLQ_1(t) - (i/\hbar) \\ &\times \int_0^t PL e^{-is(1-P)L/\hbar} (1-P)LQ_1(t-s) ds. \end{aligned} \quad (12)$$

In this paper we will not need $Q_1(t)$ itself, but rather its Laplace transform,

$$\mathcal{Q}_1(\omega) = \int_0^\infty e^{i\omega t} Q_1(t) dt. \quad (13)$$

The Laplace transform of Eq. (12) provides the following expression for $\mathcal{Q}_1(\omega)$:

$$\mathcal{Q}_1(\omega) = i\hbar [\hbar\omega - PL - PL(\hbar\omega - (1-P)L)^{-1} \times (1-P)L]^{-1} Q_1(0). \quad (14)$$

3. GENERAL TREATMENT

A. The Line Shape

The model which will be used to study plasma broadening contains a radiating atom weakly coupled to a radiation field and a macroscopically neutral gas of electrons and ions. The effect of the radiation field will be approximated by means of a damping factor which produces a Lorentzian "natural line." The plasma itself is regarded as three coupled subsystems: the atom, electrons, and ions. The initial expression for the shape of the atomic spectral radiation will be obtained by means of a slight modification of Baranger's³ derivation.

The power radiated when the plasma makes an atomic-dipole transition from the state $|m\rangle$ to the state $|n\rangle$, averaged over direction and polarization, is

$$P = (4\omega_{mn}^4/3c^3) \sum_j |\langle m|d_j|n\rangle|^2. \quad (15)$$

The vectors $|m\rangle$ and $|n\rangle$ represent states of the plasma (atom plus charged perturbers) and d_j are the components of the atomic dipole vector \mathbf{d} . The power spectrum is obtained by constructing an ensemble and summing (15) over all possible initial and final states, weighting the initial states by their probability of occurrence ρ_m . Baranger has written the power spectrum in terms of a series of delta function lines¹⁰:

$$P(\tilde{\omega}) = (4\tilde{\omega}^4/3c^3) \sum_{mnj} \delta(\tilde{\omega} - \omega_{mn}) |\langle m|d_j|n\rangle|^2 \rho_m. \quad (16)$$

In this paper, we will replace the delta-function spectrum by a series of very narrow Lorentzian lines centered about the frequencies ω_{mn} . For simplicity, each line will be assumed to have the same natural width ϵ and the natural shifts will be neglected. The power spectrum is then written

$$P(\tilde{\omega}) = (4\tilde{\omega}^4/3c^3) \sum_{mnj} \frac{(\epsilon/\pi)}{(\tilde{\omega} - \omega_{mn})^2 + \epsilon^2} |\langle m|d_j|n\rangle|^2 \rho_m. \quad (17)$$

The sum in Eq. (17) is called the line shape or line profile. In terms of the complex variable $\omega = \tilde{\omega} + i\epsilon$, the line shape is

$$\begin{aligned} I(\omega) &= -\pi^{-1} \text{Im} \sum_{nmj} \frac{|\langle m|d_j|n\rangle|^2}{(\omega - \omega_{mn})} \rho_m \\ &= \pi^{-1} \text{Re} \sum_{mnj} \int_0^\infty \exp\{i(\omega - \omega_{mn})t\} \\ &\quad \times dt |\langle m|d_j|n\rangle|^2 \rho_m. \end{aligned} \quad (18)$$

¹⁰ The frequency is denoted by $\tilde{\omega}$ in anticipation of the complex frequency variable $\omega = \tilde{\omega} + i\epsilon$.

The states $|m\rangle$ and $|n\rangle$ are chosen to be eigenstates of the system Hamiltonian H , and ρ_m are the matrix elements of an equilibrium density matrix. Making use of the Hermitian nature of \mathbf{d} and the completeness of the H eigenstates, we readily obtain

$$I(\omega) = \pi^{-1} \operatorname{Re} \int_0^\infty e^{i\omega t} \operatorname{Tr} \{ \mathbf{d} \cdot e^{-itH/\hbar} (\rho \mathbf{d}) e^{itH/\hbar} \} dt. \quad (19)$$

This line-shape function (with a complex frequency) is the same as that used by Fano,⁴ with the exception that the imaginary part of ω is now interpreted as a natural linewidth and the limit $\epsilon \rightarrow 0$ is not taken. The parameter ϵ produces the radiation damping, $\exp(-\epsilon t)$, which gives rise to the natural line shape. It should be noted that the radiation damping is included primarily as a mathematical convenience since it alters the line shape only in the region $|\bar{\omega} - \omega_{mn}| < \epsilon$ and, for problems of interest, it is not possible to study this region experimentally.

The trace in Eq. (19) is frequently called the relaxation function and is denoted by $\Phi(t)$:

$$\Phi(t) = \operatorname{Tr} \{ \mathbf{d} \cdot e^{-itH/\hbar} (\rho \mathbf{d}) e^{itH/\hbar} \}. \quad (20)$$

Thus, the line shape is expressed by the real part of the Laplace transform of $\Phi(t)$:

$$I(\omega) = \pi^{-1} \operatorname{Re} \int_0^\infty e^{i\omega t} \Phi(t) dt. \quad (21)$$

Equations (20) and (21) produce the entire line spectrum of radiation from the perturbed atom. In most practical cases however, one is interested in only one spectral line, or perhaps a group of very close, overlapping lines. In such cases, the lines of interest are obtained by restricting the operator \mathbf{d} to have matrix elements between only those atomic states which are relevant to the radiative transitions being studied. For example, if one is interested in the Ly- α line, \mathbf{d} will have matrix elements only between the hydrogen states having the principal quantum numbers 1 and 2.

B. Weak-Coupling Approximations

The Hamiltonian for the plasma is the sum of the unperturbed atomic Hamiltonian H_a , the electron and ion kinetic and potential energy operators ($K_e + V_{ee} + K_i + V_{ii}$), the electron-ion interaction V_{ei} , and the interaction between the atom and the gas of charged perturbers V_{ag} .

The coupling between the electron and ion subsystems is removed by assuming that it is possible to replace the potential energy operator ($V_{ee} + V_{ei} + V_{ii}$) by an effective potential of the form ($V_e + V_i$) in which V_e contains only electron coordinates and V_i contains only ion coordinates. The form of the potentials V_e and V_i is discussed in Sec. 3.D.

The coupling interaction V_{ag} will be approximated by the dipole term in a series expansion.¹¹ This term has the form $e\mathbf{R} \cdot (\boldsymbol{\varepsilon}_e + \boldsymbol{\varepsilon}_i)$, where $\boldsymbol{\varepsilon}_e$ and $\boldsymbol{\varepsilon}_i$ denote the electric microfields produced by the electrons and ions and \mathbf{R} is the coordinate position of the atomic electron.¹²

If we denote $(K_e + V_e)$ and $(K_i + V_i)$ by H_e and H_i , the total plasma Hamiltonian may be written:

$$H = H_a + H_e + H_i + e\mathbf{R} \cdot (\boldsymbol{\varepsilon}_e + \boldsymbol{\varepsilon}_i). \quad (22)$$

Most of the previous line-broadening theories have assumed that the atom, electron, and ion subsystems may be regarded as being statistically independent; this paper will also make this approximation. According to Eq. (11), this implies that the plasma density matrix must have the product form $\rho^{(a)}\rho^{(e)}\rho^{(i)}$. In order to achieve this product form, we neglect the interaction $e\mathbf{R} \cdot (\boldsymbol{\varepsilon}_e + \boldsymbol{\varepsilon}_i)$ in the Boltzmann factor, $\exp\{-H/kT\}$. With this approximation we obtain

$$\begin{aligned} \rho^{(a)} &= c_a \exp\{-H_a/kT\}, \\ \rho^{(e)} &= c_e \exp\{-H_e/kT\}, \\ \rho^{(i)} &= c_i \exp\{-H_i/kT\}. \end{aligned} \quad (23)$$

The constants c_a , c_e , and c_i are determined by normalizing $\operatorname{Tr}_a\{\rho^{(a)}\}$, $\operatorname{Tr}_e\{\rho^{(e)}\}$, and $\operatorname{Tr}_i\{\rho^{(i)}\}$ to unity.

The effect of ignoring the weak-coupling interaction V_{ag} , in the Boltzmann factor, should be quite small in the centers of most lines. It must be noted however, that this factor can give rise to asymmetries on the order of 10% in the wings of some lines. This approximation has been improved by the authors; however, the correction alters the Ly- α profile by less than 1%. Since the mathematics involved in this correction is somewhat lengthy, it will be included in a future paper.

C. The Relaxation Function

A brief study of the relaxation function [Eq. (20)] provides a framework in which we may understand the dynamic effects of the perturbing processes. Kubo¹³ has made an extensive study of such functions, and the following treatment of perturber dynamics is based on his methods.

The relaxation function for the line-broadening problem may be expressed as an autocorrelation function of the atomic dipole vector, $\langle \mathbf{d} \cdot \mathbf{d}(t) \rangle$. Baranger³ has shown that this may also be regarded as the autocorrelation of the light amplitude.

Relaxation functions, of the autocorrelation type, have a horizontal tangent at $t=0$, and fall smoothly to

¹¹ If the radiator is an ion, one must also consider its Coulomb interaction with the charged perturbers. Since this interaction does not depend on the state of the radiator, it may be included in the electron and ion potentials V_e and V_i .

¹² It should be noted that both \mathbf{d} and $-e\mathbf{R}$ are basically atomic dipole operators; however, it was shown in Sec. 3.A that the matrix elements of \mathbf{d} are frequently restricted in a manner that does not apply to $-e\mathbf{R}$, thus the separate notations.

¹³ R. Kubo, J. Math. Phys. **4**, 175 (1963); in *Lectures in Theoretical Physics*, edited by W. E. Downs and J. Down (Interscience Publishers, Inc., New York, 1959), Vol. I, p. 120.

zero as t increases. The width and shape of $\Phi(t)$ depend on the rate at which the light train loses the "memory" of its original phase.

Since the line shape $I(\omega)$ may be obtained by taking a Fourier transform of $e^{-i\omega t}\Phi(t)$, we expect that the observed width $\Delta\omega_{1/2}$ of a given spectral line, will be related to the width $\Delta t_{1/2}$ of $\Phi(t)$ by the well-known property

$$\Delta\omega_{1/2}\Delta t_{1/2} \simeq 1 \quad (24)$$

of Fourier transforms.¹⁴

Equation (24) implies that any process whose time of variation is much larger than $\Delta t_{1/2}$ may be regarded as static when calculating $\Phi(t)$ and $I(\omega)$. Similarly, a process whose duration time is much smaller than $\Delta t_{1/2}$ may be approximated as being instantaneous. These limits form the basis of the static and impact approximations used by most line-broadening theories.

In order to use Kubo's methods, we must determine a correlation time τ_c for the perturbing processes. This correlation time is a measure of the rate of change in the perturbation. We may define τ_c as follows: Starting with any time chosen at random, τ_c is the average length of time required for the potential to undergo an appreciable change from its value at the chosen starting time. The calculation of τ_c for the electron and ion microfields is discussed in Sec. 3.D.

Kubo has used two approximations to $\Phi(t)$, the $t \ll \tau_c$ asymptote $\Phi_0(t)$ and the $t \gg \tau_c$ asymptote $\Phi_\infty(t)$. In the region $t \ll \tau_c$ the wave train retains a "memory" of its original phase and $\Phi(t)$ is large. In the region $t \gg \tau_c$ the original phase has been "forgotten" and $\Phi(t)$ is small. If the correlation time τ_c is either much larger or smaller than $\Delta t_{1/2}$, we may represent $\Phi(t)$, over the times of interest, by the corresponding asymptote.¹⁵ These limits are called slow and fast modulation limits by Kubo; in line-broadening problems, they are called static and impact limits.

The static approximation, $\Phi(t) = \Phi_0(t)$, assumes that the coherence of the wave train persists for all times of interest; this assumption breaks down for the long times, $t > \tau_c$, which correspond to the center region, $\Delta\omega < \tau_c^{-1}$, on the line shape ($\Delta\omega$ is the frequency separation from the center of the natural line).

In the impact approximation, $\Phi(t) = \Phi_\infty(t)$, it is assumed that the perturbation varies so rapidly that the coherence of the wave train is quickly destroyed; this assumption is invalid for the small times, $t < \tau_c$, which correspond to the wings, $\Delta\omega > \tau_c^{-1}$, of the line.

If it is possible to find correlation times for the electron and ion fields, the methods of Kubo will permit a determination of the regions of validity of the static and impact approximations; this is the subject of the following section.

¹⁴ The width of $e^{-i\omega t}\Phi(t)$ is roughly the same as the width of $\Phi(t)$ since the natural width ϵ is much smaller than the observed width $\Delta\omega_{1/2}$.

¹⁵ The width $\Delta t_{1/2}$ is assumed to be known; it is obtained by inverting the experimentally observed width $\Delta\omega_{1/2}$ of the intensity profile.

D. Effective Potentials and the Correlation of Time

In Sec. 3.B, it was assumed that the potential energy operator ($V_{ee} + V_{ei} + V_{ii}$) could be replaced by $(V_e + V_i)$, where V_e and V_i contain only electron and ion coordinates, respectively. The effective potential $(V_e + V_i)$ must adequately represent the electron-ion gas for a length of time on the order of $\Delta t_{1/2}$. Since effective potentials are usually obtained from some type of ensemble or long-time average, the forms of V_e and V_i will depend critically on the change in the electron and ion distributions during the time $\Delta t_{1/2}$. In this length of time, a particle having a velocity $v_{av} = (3kT/m)^{1/2}$ will move a distance $\Delta r_{av} = v_{av}\Delta t_{1/2}$. Assuming that all particles of mass m move the same distance in the time $\Delta t_{1/2}$, it is possible to estimate the resulting change in the magnitude of the average electric field produced by these particles. In most plasma line-broadening problems, the ion field changes by less than 10% while the change in the electron field may be 50% or more.

Considerations such as these make plausible the representation of the electron-ion gas, over the times of interest, by a system of nearly stationary ions immersed in a rapidly fluctuating cloud of negative charge. In this model, the electron-charge distribution will be peaked about the slow moving ions, thus giving rise to a shield of negative charge for each ion. We therefore use a Debye-shielded potential for V_i and the ion microfield \mathcal{E}_i is the negative gradient of this potential¹⁶ (i.e., a Debye-shielded field).

Since the electron microfield is characterized by a rapid fluctuation over the times of interest, we may not use the (long-time averaged) Debye field to represent it.¹⁷

In the relaxation theory, the electrons are regarded as part of a thermal bath for the radiating atom. Since we do not expect the distribution of bath states to be too important in the calculation of atomic radiation, we will approximate the distribution of electron states by an ideal gas. The electron microfield \mathcal{E}_e will be taken to be the familiar Coulomb field due to N electrons.^{17,18} It should be noted that the electron-electron correlations thus neglected may be important for long times or small $\Delta\omega$. Lewis¹⁷ has studied this problem and his work indicates that these correlations may alter the line shape in the region $\Delta\omega \ll v_{av}/\lambda_D$, where λ_D is the Debye length.

It is a simple matter to find a correlation time for the ion field since a Debye-shielded field is not appreciably altered until the ions have moved a distance on the order of the Debye length. We therefore define τ_c for the ion field to be the time required for an ion, with a velocity $v_{av} = (3kT/m)^{1/2}$ to move this distance.

Since this paper does not use an impact or static approximation for the electron field, it is not necessary to define a correlation time for this field.

¹⁶ B. Mozer and M. Baranger, Phys. Rev. **118**, 626 (1960).

¹⁷ M. Lewis, Phys. Rev. **121**, 501 (1961).

¹⁸ M. Baranger and B. Mozer, Phys. Rev. **115**, 521 (1959).

E. The Line Shape in the Static Ion Approximation

The static ion approximation is made by assuming that the ions may be regarded as infinitely massive classical particles, during the time of interest. This assumption implies that the change in the potentials $e\mathbf{R} \cdot \boldsymbol{\varepsilon}_i$ and V_i due to the motion of the ions is negligible; that is, the commutators $[e\mathbf{R} \cdot \boldsymbol{\varepsilon}_i, K_i]$ and $[V_i, K_i]$ are inversely proportional to the ion mass, hence they vanish in the infinite mass limit.

In the static ion approximation, the time-development operator may be written in the form

$$\exp\{itH/\hbar\} = \exp\{itH'/\hbar\} \exp\{itH_i/\hbar\}, \quad (25)$$

where

$$H' = H_a + H_e + e\mathbf{R} \cdot (\boldsymbol{\varepsilon}_e + \boldsymbol{\varepsilon}_i). \quad (26)$$

The operator $\exp\{i(K_i + V_i)t/\hbar\}$ may be commuted with both the density matrix and the dipole operator; we therefore obtain the identity

$$e^{-itH/\hbar}(\rho\mathbf{d})e^{itH/\hbar} = e^{-itH'/\hbar}(\rho\mathbf{d})e^{itH'/\hbar}. \quad (27)$$

In a similar manner we commute the ion density matrix $\rho^{(i)}$ with $\exp\{-itH'/\hbar\}$ and obtain

$$e^{-itH/\hbar}(\rho\mathbf{d})e^{itH/\hbar} = \rho^{(i)}e^{-itH'/\hbar}(\rho^{(a)}\rho^{(e)}\mathbf{d})e^{itH'/\hbar}. \quad (28)$$

This relation is used in Eq. (20) to provide the following expression for the relaxation function:

$$\Phi(t) = \text{Tr}\{\mathbf{d} \cdot \rho^{(i)}e^{-itH'/\hbar}(\rho^{(a)}\rho^{(e)}\mathbf{d})e^{itH'/\hbar}\}. \quad (29)$$

The ion coordinates may be removed from H' in a manner similar to that used by Ohno.¹⁹ The relaxation function is written in terms of an integral containing a three-dimensional delta function:

$$\Phi(t) = \text{Tr}\left\{\rho^{(i)} \int \mathbf{d} \cdot e^{-itH''/\hbar}(\rho^{(a)}\rho^{(e)}\mathbf{d}) \times e^{itH''/\hbar} \delta(\boldsymbol{\varepsilon} - \boldsymbol{\varepsilon}_i) d^3\boldsymbol{\varepsilon}\right\}, \quad (30)$$

where

$$H''(\boldsymbol{\varepsilon}) = H_a + H_e + e\mathbf{R} \cdot (\boldsymbol{\varepsilon}_e + \boldsymbol{\varepsilon}). \quad (31)$$

The delta function in Eq. (30) will cause the integrand to vanish unless $\boldsymbol{\varepsilon}$ has the same magnitude and direction as the ion field $\boldsymbol{\varepsilon}_i$. We may therefore regard $\boldsymbol{\varepsilon}$ as the ion microfield even though it is not a function of ion coordinates. Similarly, the Hamiltonian $H''(\boldsymbol{\varepsilon})$ contains the influence of the ion field without being an explicit function of ion variables.

We commute the integral and the trace in Eq. (30), and factor the trace operations to obtain

$$\Phi(t) = \int Q(\boldsymbol{\varepsilon}) \text{Tr}_e\{\mathbf{d} \cdot e^{-itH''/\hbar}(\rho^{(a)}\rho^{(e)}\mathbf{d})e^{itH''/\hbar}\} d^3\boldsymbol{\varepsilon}, \quad (32)$$

where $Q(\boldsymbol{\varepsilon})$ is defined by

$$Q(\boldsymbol{\varepsilon}) \equiv \text{Tr}_i\{\rho^{(i)} \delta(\boldsymbol{\varepsilon} - \boldsymbol{\varepsilon}_i)\}. \quad (33)$$

¹⁹ Akiko Ohno, Quantum Chemistry Group, Uppsala University, Uppsala, Sweden, No. 109, 1963 (unpublished).

This is the familiar microfield function¹⁶ which gives the probability of finding an ion field $\boldsymbol{\varepsilon}$ at the atom. $Q(\boldsymbol{\varepsilon})$ will be regarded as a known function which is spherically symmetric,

$$Q(\boldsymbol{\varepsilon}) = Q(\varepsilon), \quad (34)$$

and is normalized to unity,

$$\int Q(\varepsilon) d^3\varepsilon = 1. \quad (35)$$

Since $Q(\varepsilon)$ is not a function of time, the line shape, in the static ion approximation, is given by

$$I(\omega) = \int Q(\varepsilon) J(\omega, \boldsymbol{\varepsilon}) d^3\varepsilon, \quad (36)$$

where

$$J(\omega, \boldsymbol{\varepsilon}) = \pi^{-1} \text{Re} \int_0^\infty e^{i\omega t} \text{Tr}_{ae} \times \{\mathbf{d} \cdot e^{-itH''/\hbar}(\rho^{(a)}\rho^{(e)}\mathbf{d})e^{itH''/\hbar}\} dt. \quad (37)$$

The function $J(\omega, \boldsymbol{\varepsilon})$ represents the line shape produced by the electron-atom interaction when an ion field $\boldsymbol{\varepsilon}$ is present at the atom.²⁰ The observed line shape is obtained, as indicated in Eq. (36), by averaging $J(\omega, \boldsymbol{\varepsilon})$ over all ion fields.

4. APPLICATION OF THE RELAXATION TECHNIQUES

A. The Effective Atomic Resolvent

In order to simplify the form of the line shape $J(\omega, \boldsymbol{\varepsilon})$, we introduce the Liouville operator $L(\boldsymbol{\varepsilon})$, corresponding to the Hamiltonian $H''(\boldsymbol{\varepsilon})$, and we define a vector operator $\mathbf{D}(t)$ by

$$\begin{aligned} \mathbf{D}(t) &= e^{-itH''/\hbar}(\rho^{(a)}\rho^{(e)}\mathbf{d})e^{itH''/\hbar} \\ &= e^{-itL/\hbar}(\rho^{(a)}\rho^{(e)}\mathbf{d}). \end{aligned} \quad (38)$$

Equation (37) may thus be written

$$J(\omega, \boldsymbol{\varepsilon}) = \pi^{-1} \text{Re} \int_0^\infty e^{i\omega t} \text{Tr}_{ae}\{\mathbf{d} \cdot \mathbf{D}(t)\} dt. \quad (39)$$

We now have a situation similar to that discussed in Sec. 2.C; the atomic dipole vector \mathbf{d} operates only in the atomic subsystem, hence, the only part of $\mathbf{D}(t)$ needed in Eq. (39) is its projection in this subsystem. We define a projection operator²¹ P by its operation on an arbitrary matrix M :

$$PM = \rho^{(e)} \text{Tr}_e\{M\}. \quad (40)$$

²⁰ It should be noted that $J(\omega, \boldsymbol{\varepsilon})$ depends on $\boldsymbol{\varepsilon}$ only through $\mathbf{R} \cdot \boldsymbol{\varepsilon}$; in the static ion approximation, the ion field may be used to define the z direction for the atom so that $\mathbf{R} \cdot \boldsymbol{\varepsilon}$ becomes $R^z\varepsilon$ and $J(\omega, \boldsymbol{\varepsilon})$ becomes $J(\omega, \varepsilon)$.

²¹ This operator was suggested by Zwanzig and used by Fano (see Ref. 4).

It is easily verified that this operator satisfies $P^2 = P$ as well as

$$\text{Tr}_{ae}\{\mathbf{d} \cdot \mathbf{D}(t)\} = \text{Tr}_{ae}\{\mathbf{d} \cdot P\mathbf{D}(t)\}. \quad (41)$$

We denote the relevant part $P\mathbf{D}(t)$ by $\mathbf{D}_1(t)$, and define its Laplace transform by

$$\mathfrak{D}_1(\omega) = \int_0^\infty e^{i\omega t} \mathbf{D}_1(t) dt. \quad (42)$$

Equation (39) is now written

$$J(\omega, \mathfrak{E}) = \pi^{-1} \text{Re} \text{Tr}_a\{\mathbf{d} \cdot \text{Tr}_e\{\mathfrak{D}_1(\omega)\}\}. \quad (43)$$

Zwanzig's technique provides an expression for $\mathfrak{D}_1(\omega)$ [Eq. (14)]; we then take the trace of $\mathfrak{D}_1(\omega)$, over electron states, and obtain

$$\text{Tr}_e\{\mathfrak{D}_1(\omega)\} = i[\omega - \mathcal{L}(\omega)]^{-1}(\rho^{(a)} \mathbf{d}), \quad (44)$$

where $\mathcal{L}(\omega)$ is defined by

$$\begin{aligned} \hbar \mathcal{L}(\omega) &= \langle L + L[\hbar\omega - (1-P)L]^{-1}(1-P)L \rangle \\ &= \langle L \sum_0^\infty [(1-P)L/\hbar\omega]^n \rangle. \end{aligned} \quad (45)$$

The notation $\langle M \rangle$ represents $\text{Tr}_e\{M\rho^{(e)}\}$, which is an operator in the atomic subsystem. Using Eq. (44), we may express $J(\omega, \mathfrak{E})$ in the form

$$J(\omega, \mathfrak{E}) = -\pi^{-1} \text{Im} \text{Tr}_a\{\mathbf{d} \cdot [\omega - \mathcal{L}(\omega)]^{-1}(\rho^{(a)} \mathbf{d})\}. \quad (46)$$

In analogy with Eq. (7), we regard the operator $K(\omega)$, defined by

$$K(\omega) \equiv [\omega - \mathcal{L}(\omega)]^{-1}, \quad (47)$$

as an effective atomic resolvent having a frequency-dependent, effective atomic Liouville operator $\mathcal{L}(\omega)$ (in frequency units).

B. Introduction of Perturbation Theory

Equation (45) gives $\mathcal{L}(\omega)$ in terms of a series in powers of L . It is possible to transform this into a perturbation series by expressing L as the sum of an unperturbed part L_0 and a perturbation L_1 . The operator L_0 corresponds to the Hamiltonian ($H_a + H_e$) and L_1 contains the weak-coupling interaction $e\mathbf{R} \cdot (\mathfrak{E}_e + \mathfrak{E})$. In Appendix B it is shown that L_0 may be commuted with the projection operator P . We use this commutativity property to transform Eq. (45) into the perturbation series

$$\hbar \mathcal{L}(\omega) = \langle L_0 \rangle + \langle L_1 \sum_0^\infty [(\hbar\omega - L_0)^{-1}(1-P)L_1]^n \rangle. \quad (48)$$

In terms of the unperturbed resolvent,

$$K^0(\omega) \equiv (\omega - L_0/\hbar)^{-1}, \quad (49)$$

Eq. (48) becomes the more familiar Green's-function

expansion

$$\hbar \mathcal{L}(\omega) = \langle L_0 \rangle + \langle L_1 \sum_0^\infty [K^0(\omega)(1-P)L_1/\hbar]^n \rangle. \quad (50)$$

The operator $\langle L_1 \sum [K^0(\omega)(1-P)L_1/\hbar]^n \rangle$ corresponds to the relaxation operator $\langle M_e(\omega) \rangle$ introduced by Fano. The general structure and symmetry properties of this operator have been discussed by Fano⁴ and by Ben-Reuven.⁷

Fano has pointed out that the first term $\langle L_1 \rangle$ in the $\langle M_e(\omega) \rangle$ series does not contribute to relaxation. This term represents an average, static perturbation of the atom and could therefore have been included in the unperturbed Hamiltonian. Something of this nature is done in the BCI theories in which the "unperturbed" radiator is an atom already perturbed by a linear Stark effect with a Debye-shielded ion field. Taking note of this fact, we write the operator $\mathcal{L}(\omega)$ in the form

$$\hbar \mathcal{L}(\omega) = \langle L_0 \rangle + \langle L_1 \rangle + \hbar \mathcal{H}(\omega), \quad (51)$$

where

$$\hbar \mathcal{H}(\omega) = \langle L_1 \sum_1^\infty [K^0(\omega)(1-P)L_1/\hbar]^n \rangle. \quad (52)$$

The operator $\mathcal{H}(\omega)$ contains all of the frequency dependence of the effective Liouville operator and therefore represents the relaxation effects of the "time-dependent" perturbation of the atom. In order to compare with previous theories, we must express the elements of the operator $[\omega - \mathcal{L}(\omega)]$ in terms of the eigenstates $|a\rangle, |b\rangle, |c\rangle, \dots$ of the unperturbed atomic Hamiltonian H_a . The matrix elements of L_0 and L_1 are given in Appendix A, assuming that \mathfrak{E} defines the z direction for the atom. We denote the z component of \mathbf{R} by R^z and use $\Delta\omega_{ab} = (\omega - \omega_{ab}) = \Delta\tilde{\omega}_{ab} + i\epsilon$ to obtain

$$\begin{aligned} [\omega - \mathcal{L}(\omega)]_{ab, a'b'} &= \Delta\omega_{ab} \delta_{aa'} \delta_{bb'} \\ &\quad - (e\mathfrak{E}/\hbar)(R^z_{aa'} \delta_{bb'} - R^z_{b'b} \delta_{aa'}) - \mathcal{H}(\omega)_{ab, a'b'}. \end{aligned} \quad (53)$$

A comparison of Eqs. (46) and (53) with Eqs. (10) and (32) of Ref. 22 shows that $\mathcal{H}(\omega)$ takes the place of the operator Φ_{ab} used by Griem. A similar comparison with Eq. (46) of Ref. 3 shows that it replaces the effective interaction \mathcal{H} used by Baranger. It is important to note that the effective interaction $\mathcal{H}(\omega)$, obtained in this paper, is frequency-dependent whereas the effective interaction in the BCI theories is not. This frequency dependence is due to a time dependence of the electron-atom interactions which was lost in the approximation made by the BCI theories. This point will be discussed in more detail in the following section, and it will be shown that the frequency dependence provides an asymmetry which is not present in the BCI theories. Finally, we note that the tetradic nature of $\mathcal{H}(\omega)$ is equivalent to the direct product, or "double-atom," representation used by the BCI theories.

²² H. R. Griem, A. C. Kolb, and K. Y. Shen, Phys. Rev. **116**, 4 (1959).

5. CALCULATIONS

A. A Second-Order Approximation

A calculation of the line shape requires a knowledge of the elements of the effective atomic resolvent $K(\omega)$. This, in turn, requires that the tetradic $[\omega - \mathcal{L}(\omega)]$ be inverted. An n th-order calculation of $K(\omega)$ is obtained by truncating the series for $\mathcal{L}(\omega)$ [Eq. (50)] after the n th-order term. The resulting tetradic, $[\omega - \mathcal{L}(\omega)]$, is represented by a matrix (just as the direct product of matrices is represented by a matrix²³) and the corresponding resolvent is obtained by a simple matrix inversion.

In this section, the results of a second-order evaluation of $K(\omega)$ are presented, and a comparison is made with the BCI theories. The third- and fourth-order corrections to $K(\omega)$ are readily obtained by a straightforward, but lengthy, calculation. In order to simplify the following calculations, we express the operator L_1 in the form $(L_1^e + L_1^i)$, where L_1^e corresponds to the electron-atom perturbation $e\mathbf{R} \cdot \mathbf{\mathcal{E}}_e$, and L_1^i corresponds to the ion-atom interaction $e\mathbf{R} \cdot \mathbf{\mathcal{E}}$. Since $e\mathbf{R} \cdot \mathbf{\mathcal{E}}$ does not operate in the electron subsystem, the projection operator [Eq. (40)] will commute with L_1^i . In the model we are using, $\mathbf{\mathcal{E}}_e$ is a rapidly fluctuating field; the average $\langle \mathbf{R} \cdot \mathbf{\mathcal{E}}_e \rangle$ will therefore vanish, thus causing $\langle L_1^e \rangle$ to vanish.²⁴

Using the commutativity of P with L_1^i and L_0 , the second-order term in Eq. (48) becomes

$$\begin{aligned} \langle L_1(\hbar\omega - L_0)^{-1}(1-P)L_1 \rangle &= \langle L_1^e(\hbar\omega - L_0)^{-1}(1-P)L_1^e \rangle \\ &= \langle L_1^e(\hbar\omega - L_0)^{-1}L_1^e \rangle - \langle L_1^e(\hbar\omega - L_0)^{-1} \rangle \langle L_1^e \rangle. \end{aligned} \quad (54)$$

Since $\langle L_1^e \rangle = 0$, the second term on the right-hand side vanishes and the second-order term contains only the electron-atom interaction,

$$\langle L_1^e(\hbar\omega - L_0)^{-1}L_1^e \rangle = \langle L_1^e K^0(\omega) L_1^e \rangle / \hbar. \quad (55)$$

The H_a eigenstates are denoted by $|a\rangle$, $|b\rangle$, $|c\rangle$, etc., and the H_e eigenstates by $|\alpha\rangle$, $|\beta\rangle$, $|\gamma\rangle$, etc. The electron-density matrix $\rho^{(e)}$ is diagonal in the states of H_e and we denote its diagonal elements by f_α . The tetradic operator $K^0(\omega)$ is diagonal between the composite state vectors $|a\alpha\rangle$, $|b\beta\rangle$, etc., and we denote its diagonal elements by $k^0(\omega)_{a\alpha, b\beta}$ (see Appendix A). The matrix elements of $\langle L_1^e K^0(\omega) L_1^e \rangle$ have the form

$$\begin{aligned} \langle L_1^e K^0(\omega) L_1^e \rangle_{ab, a'b'} &= \delta_{bb'} \sum_{\alpha\beta} \langle a\alpha | e\mathbf{R} \cdot \mathbf{\mathcal{E}}_e | c\beta \rangle \\ &\times \langle c\beta | e\mathbf{R} \cdot \mathbf{\mathcal{E}}_e | a'\alpha \rangle f_\alpha k^0(\omega)_{c\beta, b\alpha} \\ &+ \delta_{aa'} \sum_{\alpha\beta} \langle b'\alpha | e\mathbf{R} \cdot \mathbf{\mathcal{E}}_e | c\beta \rangle \langle c\beta | e\mathbf{R} \cdot \mathbf{\mathcal{E}}_e | b\alpha \rangle f_\alpha k^0(\omega)_{a\alpha, c\beta} \\ &- \sum_{\alpha\beta} \langle b'\beta | e\mathbf{R} \cdot \mathbf{\mathcal{E}}_e | b\alpha \rangle \langle a\alpha | e\mathbf{R} \cdot \mathbf{\mathcal{E}}_e | a'\beta \rangle f_\beta k^0(\omega)_{a\alpha, b'\beta} \\ &- \sum_{\alpha\beta} \langle a\alpha | e\mathbf{R} \cdot \mathbf{\mathcal{E}}_e | a'\beta \rangle \langle b'\beta | e\mathbf{R} \cdot \mathbf{\mathcal{E}}_e | b\alpha \rangle f_\beta k^0(\omega)_{a'\beta, b\alpha}. \end{aligned} \quad (56)$$

²³ E. P. Wigner, *Group Theory and Its Application to the Quantum Mechanics of Atomic Spectra* (Academic Press Inc., New York, 1959), p. 18.

²⁴ Mathematically, $\langle \mathbf{R} \cdot \mathbf{\mathcal{E}}_e \rangle$ vanishes because $\rho^{(e)}$ is a spherically symmetric function of electron coordinates and $\mathbf{R} \cdot \mathbf{\mathcal{E}}_e$ is antisymmetric.

Each of these terms is evaluated by a straightforward, but rather lengthy, procedure which we shall outline here (for more detail, the reader is referred to Appendices A, B, and C of Ref. 25). The matrix elements of $\mathbf{R} \cdot \mathbf{\mathcal{E}}$ are evaluated using unsymmetrized ideal gas wave functions for the electrons. The sums over electron states, in Eq. (56), are replaced by $3N$ -dimensional integrals over the N electron momenta. In evaluating these terms, it is found convenient to replace $k^0(\omega)$ by its integral representation [see Eqs. (7) and (A6)], and to commute this integral with the integrals over the electron momenta. The result of such an evaluation gives the following second-order expression for $\mathcal{K}(\omega)$:

$$\begin{aligned} \mathcal{K}(\omega)_{ab, a'b'} &= -\frac{2ie^4 n}{3\hbar^2} \left(\frac{8\pi m}{kT} \right)^{1/2} \\ &\times \left\{ \sum_c [\delta_{bb'} \mathbf{R}_{ac} \cdot \mathbf{R}_{ca'} G(\Delta\omega_{cb}) + \delta_{aa'} \mathbf{R}_{b'e} \cdot \mathbf{R}_{eb} G(-\Delta\omega_{ac}) \right. \\ &\quad \left. - \mathbf{R}_{aa'} \cdot \mathbf{R}_{b'b} [G(\Delta\omega_{ab'}) + G(-\Delta\omega_{a'b})] \right\}. \end{aligned} \quad (57)$$

$G(\Delta\omega_{ab})$ is an integral defined by

$$\begin{aligned} G(\Delta\omega) &= \int_0^\infty [s(s + i\hbar/kT)]^{-1/2} \exp\{is\Delta\omega\} ds \\ &= -\frac{i\pi}{2} \exp\{\hbar\Delta\omega/2kT\} H_0^{(2)}(-i\hbar\Delta\omega/2kT), \end{aligned} \quad (58)$$

where $H_0^{(2)}$ is a Hankel function of the second kind. Since $G(\Delta\omega)$ is a complex function of the complex variable $\Delta\omega = \Delta\tilde{\omega} + i\epsilon$, it is convenient to write

$$G(\Delta\omega) = G_r(\Delta\tilde{\omega}) - iG_i(\Delta\tilde{\omega}), \quad (59)$$

where G_r and G_i are real functions of the real variable $\Delta\tilde{\omega}$.

If we compare Eq. (57) with Eq. (4-45) of Ref. 2 or Eqs. (13-108) and (13-109) of Ref. 3, we see that the difference between the BCI theory and the relaxation theory lies in the integral $G(\Delta\omega)$.

B. The G Integral

The G integral in the BCI theory (for hydrogen lines) is given by Eq. (30) of Ref. 22 in the form

$$\int_{y_{\min}}^\infty e^{-y} dy / y \simeq -0.577 - \ln y_{\min}, \quad (60)$$

where y_{\min} is a temperature- and density-dependent cutoff parameter. This cutoff is a result of the impact parameter cutoffs which are necessary to avoid the logarithmic divergences in a binary collision theory.

The integral in Eq. (60) is real, hence we compare it with $G_r(\Delta\tilde{\omega})$. There is no analog for $G_i(\Delta\tilde{\omega})$ in the BCI theory for hydrogen lines. For most hydrogen lines in

²⁵ E. W. Smith, Ph.D. dissertation, University of Florida, 1966 (unpublished).

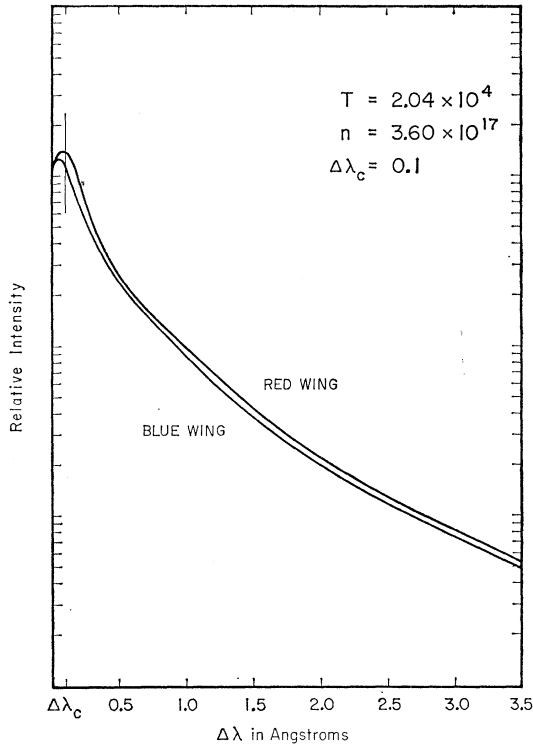


FIG. 1. Stark profile, Lyman- α line. Temperature is measured in degrees absolute, density in cm^{-3} , and $\Delta\lambda_c$ in angstroms.

the optical region, the condition $\hbar\Delta\tilde{\omega}/2kT \ll 1$ is satisfied. In particular, this condition is satisfied in the center of the Ly- α line. With Eqs. (58) and (59) one easily obtains

$$G_r(\Delta\tilde{\omega}) \approx -0.577 - \ln \left\{ \frac{\hbar}{4kT} (\Delta\tilde{\omega}^2 + \epsilon^2)^{1/2} \right\}. \quad (61)$$

In the relaxation theory, the frequency dependent function $(\hbar\Delta\tilde{\omega}/4kT)$ appears naturally, replacing the cutoff y_{\min} used in the BCI theories.

Griem²⁶ has pointed out that this is quite similar to the Lewis cutoff¹⁷ which replaces y_{\min} by $(\hbar\Delta\tilde{\omega}/nkT)$, where n is the principal quantum number. To study this similarity, we note that the usual binary-collision procedure replaces the time-development operator for the interval $(t, t+\Delta t)$ by a product of binary-collision transition operators¹ for those collisions whose time of closest approach falls in the chosen interval. Since the transition operator is essentially an S matrix, this procedure implicitly assumes that any collision whose time of closest approach lies in the interval $(t, t+\Delta t)$ is completed in that interval. Lewis has corrected this "completed collision assumption" by averaging over N electron-atom collisions at various stages of completion. This treatment allows all electrons to interact simultaneously with the atom, regardless of their times of closest approach. Since this is the essence of a many-particle

dilute gas treatment, it is not surprising that $G_r(\Delta\tilde{\omega})$ is similar to the Lewis cutoff. It should be noted, however, that our results [Eq. (59)] differ significantly from those of the impact theories by the presence of $G_r(\Delta\tilde{\omega})$.

Using Eq. (59) we may write Eq. (57) in the form

$$\mathcal{C}(\omega) = S(\Delta\tilde{\omega}) + iW(\Delta\tilde{\omega}). \quad (62)$$

Substituting this result in Eq. (53) we obtain

$$\begin{aligned} [\omega - \mathcal{L}(\omega)]_{ab,a'b'} &= \Delta\omega_{ab}\delta_{aa'}\delta_{bb'} \\ &\quad - (e\mathcal{E}/\hbar)(R^z_{aa'}\delta_{bb'} - R^z_{b'b}\delta_{aa'}) \\ &\quad - S(\Delta\tilde{\omega})_{ab,a'b'} - iW(\Delta\tilde{\omega})_{ab,a'b'}. \end{aligned} \quad (63)$$

Noting the role of this operator in the expression for the line shape [Eq. (46)], we may regard $S(\Delta\tilde{\omega})$ and $W(\Delta\tilde{\omega})$ as frequency-dependent shift and width operators.

In order to study the physical significance of this frequency dependence, we note that $\langle L_1^e K^0(\omega) L_1^e \rangle$ represents a second-order electron-atom interaction. In a perturbation expansion of the dipole-field interaction, the second-order correction to the energy has the form $\mathcal{E} \cdot \chi \cdot \mathcal{E}$, where $\chi \sim \mathbf{R}\mathbf{R}$ is the polarizability tensor. It is possible to show that $\langle L_1^e K^0(\omega) L_1^e \rangle$ can be expressed as the Laplace transform of four terms, all tetrads, of the form $\langle \mathcal{E}_e \cdot \chi(t) \cdot \mathcal{E}_e(t) \rangle$, where $\chi(t) \sim \mathbf{R} \exp\{itH_a/\hbar\} \mathbf{R}$ and $\mathcal{E}_e(t) = \exp\{-itL_0/\hbar\} \mathcal{E}_e$. We therefore interpret $\langle L_1^e K^0(\omega) L_1^e \rangle$ as an induced dipole interaction term whose frequency dependence is a result of the time dependence of the interaction. Physically, we expect that the electric field \mathcal{E}_e will induce an additional dipole moment and that, at any instant, the induced dipole will point in the same direction as \mathcal{E}_e . This interaction will lower the atomic energy levels, and, since the lower levels are more tightly bound, the energies of the final states will be less effected. This will reduce the energy separation of the initial and final states, resulting in a preference for lower energy, or longer wavelength transitions (as compared with the center of natural line). We therefore expect the quadratic electron-atom interactions to produce a small asymmetry which increases the intensity of the red wing relative to the blue wing. Such an asymmetry is indeed observed in the theoretical profile.

C. Numerical Results

Intensity profiles have been calculated for the Ly- α line of hydrogen. These calculations have used the microfield functions obtained by Mozer,¹⁶ which are tabulated up to a relative field strength of ten. This limit on the microfield average [Eq. (36)] imposes a limit on the range of frequency (or wavelength) separations for which realistic intensity profiles can be calculated. A more accurate method of calculating the microfield function has been developed by one of us,²⁷ and extensive calculations of the Ly- α line are now in progress.

²⁶ H. R. Griem (private communication).

²⁷ C. F. Hooper, Jr., Phys. Rev. **149**, 77 (1966).

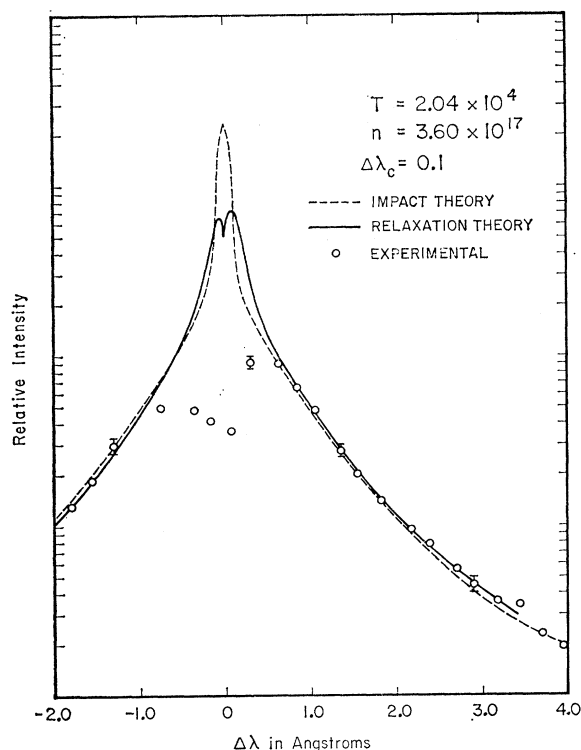


FIG. 2. A comparison of theoretical and experimental Lyman- α line shapes. Temperature is measured in degrees absolute, density in cm^{-3} , and $\Delta\lambda_c$ in angstroms.

A representative Ly- α profile is shown in Fig. 1, which plots relative intensity against the wavelength separation $\Delta\lambda$ measured from the center of the natural line. The critical wavelength $\Delta\lambda_c$ indicates the point where the static ion approximation breaks down (see Sec. 3.C). The region $|\Delta\lambda| \leq \Delta\lambda_c$ should not be regarded as accurate since it is not known how large a correction must be made for ion dynamics in this region. Lewis¹⁷ has estimated that electron-electron correlations, neglected in this paper, may be important in the region $|\Delta\omega| < v_{av}/\lambda_D$ (where v_{av} is the average electron velocity and λ_D is the Debye length). This corresponds to $|\Delta\lambda| < 5 \text{ \AA}$ in Fig. 2. However, we do not expect this effect to produce an appreciable alteration of the profile in the region $|\Delta\lambda| > \Delta\lambda_c$.

In order to compare the theoretical Stark profiles with experimental line shapes, we must consider the correction for Doppler broadening. This correction is usually made by folding the Doppler line into the Stark profile.² Doppler corrections have been applied to all of the Stark profiles which have been calculated by the authors, and the only observable alteration (between 1 and 10%) occurs in the region $|\Delta\lambda| < \Delta\lambda_c$. Since this region is not accurate, in the present theory, we will compare the Stark profiles directly with the experimental data and neglect the Doppler effects.

Figure 2 shows a comparison of the theoretical Stark profiles, obtained by the BCI theories and by this paper,

with an experimental profile measured by Elton and Griem.⁸ The experimental points are corrected for self-absorption. No correction has been made for boundary layer reabsorption however, and the data show a strong absorption dip at the center which is probably due to this effect.

In the region $|\Delta\lambda| > 0.5 \text{ \AA}$, the experimental profile shows an asymmetry on the order of 10% favoring the red wing; this is readily verified by noting that the experimental points lie slightly below the symmetric BCI profile on the blue wing and slightly above on the red wing. The relaxation profile also shows an asymmetry of about 10% and agrees quite well with the experimental data in these regions.

The asymmetry in the relaxation profile is due entirely to the quadratic electron-atom interactions since the ion broadening is symmetric about the unperturbed line (to the order of approximation used in this paper). While there are many other sources of asymmetry,^{2,28} we believe that these other sources contribute less than 1% to the asymmetry in this region of the Ly- α line. The quadratic electron-atom interaction should therefore account for asymmetry in this region and Fig. 2 seems to confirm this. We also suspect that this interaction will produce at least part of the unexplained asymmetry which has been found in the wings of this line.²⁸

6. CRITIQUE

The theory of plasma line broadening presented in this paper represents an initial approach to the problem using relaxation techniques. We feel that this method provides a more consistent treatment of the subject than do the previous theories. While approximations have been made, it should be possible to remove many of these in a systematic and practical manner. Some problems still to be considered are discussed in this section.

It has been noted that many sources of asymmetry have not been included in the present work; however, the other known asymmetries may be included in a manner similar to that used by Griem.^{2,28}

The absence of ion dynamics, in this theory and in other theories based on the static ion approximation, is not too serious because it casts doubt on a very small region at the line center. It should be noted, however, that some small unexplained shifts have been observed in the Ly- α and Ly- β lines.⁸ In order to study these shifts, a more accurate line-center theory is necessary.

A matter of some importance is the rather crude treatment of some correlations in this theory, and in most other Stark broadening theories. The electron-ion and ion-ion correlations are handled quite well by the present ion microfield theories. The electron-electron correlations and the correlations between the radiating atom and the charged perturbors are not treated as well, if they are considered at all.

²⁸ H. R. Griem, Phys. Rev. **140**, A1140 (1965).

The electron-electron correlations are neglected in this paper because an ideal gas Hamiltonian was used in evaluating Eq. (56). A method of correcting this approximation has recently been developed and numerical work is now in progress to determine the extent of this correction. Lewis¹⁷ has used a modified impact theory in order to test the influence of these correlations on the line shape. His work indicates that this effect is important in the region $|\Delta\omega| < v_{av}/\lambda_D$. Since this covers the entire profile in Fig. 2, the electron-electron correlations must be regarded as an important matter.

The correlations between the radiating atom and the charged perturbers are not considered by most Stark broadening theories. It is interesting to note, however, that it is the absence of such correlations which causes the factor $\langle \mathbf{R} \cdot \boldsymbol{\epsilon}_e \rangle$ to vanish (see Sec. 5.A). In this paper, $\langle \mathbf{R} \cdot \boldsymbol{\epsilon}_e \rangle$ vanishes because the operator $\mathbf{R} \cdot \boldsymbol{\epsilon}_e$ is averaged over a spherically symmetric electron distribution, $\rho^{(e)}$. One expects, however, that the existence of the atomic dipole \mathbf{R} will alter this spherical symmetry in the immediate vicinity of the atom. This would imply that there may be some $\langle \mathbf{R} \cdot \boldsymbol{\epsilon}_e \rangle$ contribution from the close electron-atom interactions. It is not known how large an effect, if any, this may have on the line shape.

Although many refinements are still necessary, the relaxation theory presented in this paper has some inherent advantages which are not found in the other modern Stark broadening theories. In particular, the impact approximation and the binary-collision approximation are not needed. The complicated time integrations, which necessitated approximations in the impact theories, are not found in the relaxation theory, thus allowing one to proceed further without approximation. Finally, the relaxation theory provides a more unified approach in that the electrons and ions are treated together as a perturbing gas. That is, Eqs. (36), (46), and (53) were explicitly derived.

The classical path approximation, which is made by most impact theories, assumes that the perturbers may be represented by wave packets of negligible spread and the trajectory of a given perturber is unaltered by the presence of the atom and the other perturbers. In most applications of this approximation a classical "point particle" is used to represent the perturber. This paper does not make the classical path approximation in the sense that no wave packets are formed; however, the statistical independence of the atom and the perturbers is assumed. It is interesting to note that the divergence which appears at small impact parameters in the classical path treatment does not occur in this paper. This divergence is not found in the relaxation theory because "point particles" are not used. This is more of a convenience than an improvement because a more rigorous quantum mechanical treatment of the interactions is necessary for such close collisions.

While we have by no means exploited all the advantages of the relaxation formalism, we feel that this

treatment provides a simple and unified framework for future improvements in the theory of Stark broadening.

Note added in proof. Recent calculations show that the inclusion of electron correlations removes the dip occurring at the center of the relaxation profile while not altering the rest of the profile appreciably [see Fig. (2)].

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APPENDIX A

In order to facilitate the evaluation of the elements of tetrads such as $L_{mn,m'n'}$, we use a direct product notation

$$L = H \otimes I - I \otimes H^*. \quad (A1)$$

If $|m\rangle$ and $|n\rangle$ are eigenvectors of H , we may use the basis $|m\rangle |n\rangle$ to obtain

$$\begin{aligned} L_{mn,m'n'} &= \langle m | \langle n | (H \otimes I - I \otimes H^*) | m' \rangle | n' \rangle \\ &= \langle m | H | m' \rangle \langle n | n' \rangle - \langle m | m' \rangle \langle n | H^* | n' \rangle \\ &= H_{mm'} \delta_{nn'} - \delta_{mm'} H_{n'n}, \end{aligned} \quad (A2)$$

which gives $L_{mn,m'n'}$ as defined by Eq. (5).

Since the ions are accounted for by the microfield average (36), it is necessary to calculate matrix elements between the basis vectors of only two subsystems (the atom and the electron gas). The basis vectors for the atomic subsystem are the H_a eigenvectors $|a\rangle$, $|b\rangle$, $|c\rangle$ having the energies E_a , E_b , E_c . The electron gas basis vectors are the H_e eigenstates $|\alpha\rangle$, $|\beta\rangle$, $|\gamma\rangle$ with energies E_α , E_β , E_γ . The composite vectors are $|a\alpha\rangle$, $|b\beta\rangle$, $|c\gamma\rangle$. A matrix operator, such as the density matrix, will have four subscripts, as discussed in Sec. 2.B. The density matrix, $\rho^{(a)}\rho^{(e)}$, has the elements [see Eq. (23)]

$$\begin{aligned} [\rho^{(a)}\rho^{(e)}]_{a\alpha b\beta} &= c_a c_e e^{-E_a/kT} e^{-E_\alpha/kT} \delta_{a\alpha} \delta_{b\beta} \\ &= f_a f_\alpha \delta_{a\alpha} \delta_{b\beta}, \end{aligned} \quad (A3)$$

where f_a and f_α denote $c_a \exp\{-E_a/kT\}$ and $c_e \exp\{-E_\alpha/kT\}$. A matrix operator, such as \mathbf{R} , which operates in only one subsystem, has the form

$$\mathbf{R}_{a\alpha, b\beta} = \mathbf{R}_{ab} \delta_{\alpha\beta}. \quad (A4)$$

A tetradic operator, such as $L_0 = (H_a + H_e) \otimes I - I \otimes (H_a + H_e)^*$, will have eight subscripts,

$$\begin{aligned} (L_0)_{a\alpha b\beta; a'\alpha' b'\beta'} &= [(E_a - E_b) + (E_\alpha - E_\beta)] \delta_{a\alpha'} \delta_{b\beta'} \delta_{a'\alpha'} \delta_{b'\beta'} \\ &= \hbar(\omega_{ab} + \omega_{\alpha\beta}) \delta_{a\alpha'} \delta_{b\beta'} \delta_{a'\alpha'} \delta_{b'\beta'}. \end{aligned} \quad (A5)$$

The resolvent $K^0(\omega)$, corresponding to L_0 [see Eq. (49)], will have the same diagonal form as L_0 ,

$$\begin{aligned} K^0(\omega)_{a\alpha b\beta; a'\alpha' b'\beta'} &= (\omega - \omega_{ab} - \omega_{\alpha\beta})^{-1} \delta_{a\alpha'} \delta_{b\beta'} \delta_{a'\alpha'} \delta_{b'\beta'} \\ &= k^0(\omega)_{a\alpha b\beta} \delta_{a\alpha'} \delta_{b\beta'} \delta_{a'\alpha'} \delta_{b'\beta'}; \end{aligned} \quad (A6)$$

we have defined the “matrix” of the diagonal elements of $K^0(\omega)$ by $k^0(\omega)$.

The operators L_1^e and L_1^i correspond to the interactions $e\mathbf{R} \cdot \boldsymbol{\varepsilon}_e$ and $e\mathbf{R} \cdot \boldsymbol{\varepsilon}$, respectively (Sec. 5.A); their elements are given by

$$(L_1^e)_{a\alpha b\beta; a'\alpha' b'\beta'} = \langle a\alpha | e\mathbf{R} \cdot \boldsymbol{\varepsilon}_e | a'\alpha' \rangle \delta_{bb'} \delta_{\beta\beta'} - \langle b\beta | e(\mathbf{R} \cdot \boldsymbol{\varepsilon}_e)^* | b'\beta' \rangle \delta_{aa'} \delta_{\alpha\alpha'} \quad (\text{A7})$$

and

$$(L_1^i)_{a\alpha b\beta; a'\alpha' b'\beta'} = e\boldsymbol{\varepsilon} \cdot (\mathbf{R}_{aa'} \delta_{bb'} - \mathbf{R}_{b'b} \delta_{aa'}) \delta_{\alpha\alpha'} \delta_{\beta\beta'}. \quad (\text{A8})$$

The elements of the operators $\langle L_0 \rangle$ and $\langle L_1^i \rangle$ are readily obtained from the above; they are

$$\begin{aligned} \langle L_0 \rangle_{ab, a'b'} &= \sum_{\alpha\beta} (L_0)_{a\alpha b\alpha; a'\beta b'\beta} f_{\beta} \\ &= \hbar\omega_{ab} \delta_{aa'} \delta_{bb'} \end{aligned} \quad (\text{A9})$$

and

$$\langle L_1^i \rangle_{ab, a'b'} = e\boldsymbol{\varepsilon} \cdot (\mathbf{R}_{aa'} \delta_{bb'} - \mathbf{R}_{b'b} \delta_{aa'}). \quad (\text{A10})$$

APPENDIX B

In order to show that P and L_0 commute, we consider the operation of P on an arbitrary matrix M . Equations (40) and (A3) give

$$(PM)_{a\alpha b\beta} = f_{\alpha} \delta_{\alpha\beta} \sum_{\alpha'} M_{a\alpha' b\alpha'}. \quad (\text{B1})$$

We next consider the operation of P on the matrix $(L_0 M)$,

$$\begin{aligned} [P(L_0 M)]_{a\alpha b\beta} &= f_{\alpha} \delta_{\alpha\beta} \\ &\times \sum_{\alpha', a'', a''', b'', \beta''} (L_0)_{a\alpha' b\alpha'; a''\alpha'' b''\beta''} M_{a''\alpha'' b''\beta''}. \end{aligned} \quad (\text{B2})$$

Using Eq. (A5) and noting that $\omega_{\alpha\alpha}=0$, we obtain

$$[P(L_0 M)]_{a\alpha b\beta} = \hbar f_{\alpha} \omega_{ab} \delta_{\alpha\beta} \sum_{\alpha'} M_{a\alpha' b\alpha'}. \quad (\text{B3})$$

In a similar manner, we obtain the matrix elements of $L_0(PM)$:

$$\begin{aligned} [L_0(PM)]_{a\alpha b\beta} &= \hbar \sum_{a'\alpha' b'\beta'} (\omega_{ab} + \omega_{\alpha\beta}) \\ &\times \delta_{aa'} \delta_{bb'} \delta_{\alpha\alpha'} \delta_{\beta\beta'} f_{\alpha'} \delta_{\alpha'\beta'} \sum_{\alpha''} M_{a'\alpha'' b'\alpha''} \\ &= \hbar f_{\alpha} \omega_{ab} \delta_{\alpha\beta} \sum_{\alpha'} M_{a\alpha' b\alpha'}. \end{aligned} \quad (\text{B4})$$

A comparison of Eqs. (B3) and (B4) indicates that

$$P(L_0 M) = L_0(PM); \quad (\text{B5})$$

the proof for a tetradic M is identical.