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Electron Correlations in Plasma
Line Broadening*


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Abstract

A method of including electron correlations in the relaxation theory for spectral line broadening plasmas is presented. The effect of these correlations in the relaxation theory is compared with the analogous results in the impact theory; specifically, it is shown that the impact parameter cutoff used in the impact theory constitutes a very good approximation to the effect of these correlations.

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1. INTRODUCTION

The spectral distribution of the radiation emitted by atoms in a plasma is determined primarily by perturbations which the charged particles exert on the atom. For neutral atoms, the dominant perturbation is a Stark effect with the electric microfield produced by the charged particles in the plasma. Since this is a "long range" type of interaction, one is forced to consider the simultaneous effect of many perturbing particles, that is, a many-body perturbation potential.

Over the times of interest in most line broadening problems, the distribution of ions does not vary appreciably. This fact has given rise to a static-ion approximation, in which it is assumed that the ions do not move at all. With this approximation, it is possible to treat the ions by means of an average over all possible static ion fields.¹ The many-body aspects of the ion-atom interaction are taken into account in the derivation of the ion field distribution function.^{2,3} In the static-ion approximation, the atom is perturbed by an electric field which has a static component due to the ions, and a rapidly fluctuating component due to the electrons.

In many line broadening theories, an attempt is made to reduce the electron-atom interaction to a binary collision between the atom and a single perturber. In these "one-electron" theories⁴, it is necessary to use an effective interaction which accounts for the many-body effects.

Since the usual effect of particle correlations is to introduce a shielding of the potential, one is at first tempted to use a Debye shielded field for the electron. Such arguments were indeed used in the early versions of the impact theory^{5,6} to justify cutting off the range of the electron-atom interaction at the Debye length. However, the validity of such a procedure is open

to question because a shielded field is a time-average effect whereas an important characteristic of the electron field, in this aspect of line broadening, is its rapid fluctuation in time. Lewis⁷ has approached this problem without the use of a shielded field assumption and without the "completed collision assumption" which had been made by the impact theories. His work indicates that the usual cutoff procedure is valid, in the line wings [see Eq.(19) of ref.(7)], if the frequency separation, $\Delta\omega$, from the center of the natural line is less than v_{av}/λ_D , where v_{av} is the average electron velocity and λ_D is the Debye length. For larger frequency separations, the cutoff at the Debye length is replaced by a cutoff at $v_{av}/\Delta\omega$.

In a recently developed relaxation theory for spectral line broadening in plasmas¹, an expression for the line profile was obtained, in the static-ion approximation, without the use of binary collision or impact approximations. In the relaxation theory, the electrons are treated as a many-particle dilute gas weakly coupled to the atom. The results of the relaxation theory are formally quite similar to those of the impact theories; the primary difference being in the form of the "effective interaction operator" which represents the influence of the electron perturbation on the atom. In the relaxation theory this operator, $\mathcal{K}(\omega)$, is a frequency-dependent complex operator whereas, in the impact theories (for hydrogen) this operator is not complex.

In ref.(1), calculations were made with the assumption that the distribution of electron states may be approximated by an ideal gas. It is the purpose of this paper to correct that ideal gas approximation and to compare the results of this correction with the corresponding work in the impact theory.

It will be shown that the electron correlations influence only the effective interaction operator, $\mathcal{K}(\omega)$, and their effect on the real part of this operator

is almost identical with the results obtained by Lewis⁷. It is also found that the strong electron-atom interactions, which have been given no special treatment in the relaxation theory, can influence $\mathcal{K}(\omega)$ in a significant manner.

2. INITIAL FORMULATION AND APPROXIMATIONS

In the relaxation theory, the system considered is an excited atom weakly coupled to a macroscopically neutral gas of electrons and ions. The weak coupling is provided by a dipole-field interaction of the form $e\mathbf{R} \cdot (\boldsymbol{\mathcal{E}}_e + \boldsymbol{\mathcal{E}}_i)$ in which \mathbf{R} denotes the position of the atomic electron while $\boldsymbol{\mathcal{E}}_e$ and $\boldsymbol{\mathcal{E}}_i$ represent the electric fields produced by the electrons and ions respectively.

The Hamiltonian for the plasma is the sum of the unperturbed atomic Hamiltonian, H_a , the electron and ion kinetic energy operators, K_e and K_i , the electron and ion internal potential energy operators, V_{ee} and V_{ii} , the electron-ion interaction, V_{ei} , and the weak coupling interaction $e\mathbf{R} \cdot (\boldsymbol{\mathcal{E}}_e + \boldsymbol{\mathcal{E}}_i)$:

$$H = H_a + K_e + V_{ee} + K_i + V_{ii} + V_{ei} + e\mathbf{R} \cdot (\boldsymbol{\mathcal{E}}_e + \boldsymbol{\mathcal{E}}_i). \quad (1)$$

It is assumed that the potential function $(V_{ee} + V_{ei} + V_{ii})$ can be replaced by an effective potential $(V_e + V_i)$ where V_e and V_i contain only electron and ion coordinates respectively. A Debye-Huckel effective potential is used for the ions; the electron potential will remain temporarily unspecified⁸. Using V_e and V_i , it is convenient to define electron and ion Hamiltonians, H_e and H_i , by

$$\begin{aligned} H_e &= K_e + V_e \\ H_i &= K_i + V_i. \end{aligned} \quad (2)$$

As in most line broadening theories, the ions are regarded as infinitely massive classical particles over the time of interest (static ion approximation). It is further assumed that the three subsystems are statistically independent and the plasma density matrix is given by a product of density matrices for the atom, electrons, and ions⁹, $\rho^{(a)} \rho^{(e)} \rho^{(i)}$. This approximation required that the coupling interaction, $eR \cdot (\underline{\mathcal{E}}_e + \underline{\mathcal{E}}_i)$, be neglected in the density matrix¹. By neglecting this coupling, the electron-atom and ion-atom correlations are removed. These correlations will be important for strong fields which will be discussed further in section (4).

With the above approximations, it is found that the line shape for dipole radiation is given by¹

$$I(\omega) = \int Q(\underline{\mathcal{E}}) J(\omega, \underline{\mathcal{E}}) d^3\mathcal{E} \quad (3)$$

where $Q(\underline{\mathcal{E}})$ is the probability of finding an ion field, $\underline{\mathcal{E}}$, at the atom and $J(\omega, \underline{\mathcal{E}})$ is the line shape resulting from the electron atom interaction in the presence of the static field $\underline{\mathcal{E}}$. In the relaxation theory, ω is a complex variable, $\omega = \tilde{\omega} + i\epsilon$, whose real part, $\tilde{\omega}$, is the true frequency and whose imaginary part, ϵ , represents the natural width for the line being studied. The Hamiltonian which appears in $J(\omega, \underline{\mathcal{E}})$ is

$$H' = H_a + H_e + eR \cdot (\underline{\mathcal{E}}_e + \underline{\mathcal{E}}) \quad (4)$$

where $\underline{\mathcal{E}}$ is a vector which has the same magnitude and direction as the ion field¹.

The microfield function, $Q(\underline{\mathcal{E}})$, is known^{2,3} and $J(\omega, \underline{\mathcal{E}})$, evaluated by means of the Zwanzig-Fano relaxation techniques, is given by¹:

$$J(\omega, \underline{\mathcal{E}}) = -\pi^{-1} \text{Im Tr}_a \{ d \cdot [\omega - \mathcal{L}(\omega)]^{-1} (\rho^{(a)}_d) \} \quad (5)$$

where \underline{d} is the atomic dipole operator¹⁰, $\mathcal{L}(\omega)$ is an effective Liouville operator for the atom, and the trace is over states of the atom. In ref.(1), $\mathcal{L}(\omega)$ is expanded in a perturbation series based on an unperturbed Liouville operator, L_0 , which corresponds to the Hamiltonian $(H_a + H_e)$, and a perturbation, L_1 , which corresponds to the interaction $e\mathbf{R} \cdot (\underline{\mathcal{E}}_a + \underline{\mathcal{E}}_e)$.

The H_a eigenstates $|a\rangle$, $|b\rangle$, $|c\rangle$ are used in evaluating the trace in Eq.(5) and the energy difference between the states $|a\rangle$ and $|b\rangle$ is denoted by ω_{ab} . Denoting the z component of \mathbf{R} by R^z and defining a variable $\Delta\omega_{ab} = \omega - \omega_{ab}$, the matrix elements of $[\omega - \mathcal{L}(\omega)]$ are given by¹

$$[\omega - \mathcal{L}(\omega)]_{ab, a'b'} = \Delta\omega_{ab} \delta_{aa'} \delta_{bb'} - (e\mathcal{E}/\hbar) (R_{aa'}^z \delta_{bb'} - R_{bb'}^z \delta_{aa'}) - \mathcal{K}(\omega)_{ab, a'b'} \quad (6)$$

where $\mathcal{K}(\omega)$ is an effective interaction operator which takes the place of the operator Φ_{ab} used by Griem et.al. [see Eqs.(10) and (32) of ref.(6)] or the operator \mathcal{K} used by Baranger [see Eq.(13-46) of ref.(11)]. Since the primary difference between the impact and relaxation theories lies in $\mathcal{K}(\omega)$, this operator will be studied in detail in the following sections.

3. THE EFFECTIVE INTERACTION OPERATOR

A. A Second Order Expression for $\mathcal{K}(\omega)$

In ref.(1), the perturbation operator L_1 was written in the form $(L_1^e + L_1^i)$ where L_1^e corresponds to $e\mathbf{R} \cdot \underline{\mathcal{E}}_e$ and L_1^i corresponds to $e\mathbf{R} \cdot \underline{\mathcal{E}}_a$. With these operators, the result of a second order evaluation of $\mathcal{K}(\omega)$ was found to be¹

$$\hbar^2 \mathcal{K}(\omega) = \langle L_1^e K^0(\omega) L_1^e \rangle \quad (7)$$

where $\langle \dots \rangle$ denotes an ensemble average over electron states and $K^0(\omega)$ is given by

$$\begin{aligned} K^0(\omega) &= (\omega - L_0 / \hbar)^{-1} \\ &= -i \int_0^\infty e^{i\omega t} e^{-iL_0 t / \hbar} dt. \end{aligned} \quad (8)$$

In order to write out an explicit expression for $\mathcal{K}(\omega)$, the H_a eigenstates $|a\rangle$, $|b\rangle$, $|c\rangle$ and the H_e eigenstates $|\alpha\rangle$, $|\beta\rangle$, $|\gamma\rangle$ will be used. In terms of the composite state vectors $|a\alpha\rangle$, $|b\beta\rangle$, $|c\gamma\rangle$, the operator $K^0(\omega)$ is diagonal:

$$\begin{aligned} K^0(\omega)_{\alpha\alpha\beta\beta; a'\alpha' b'\beta'} &= k^0(\omega)_{\alpha\alpha\beta\beta} \delta_{aa'} \delta_{bb'} \delta_{\beta\beta'} \delta_{\alpha\alpha'} \\ k^0(\omega)_{\alpha\alpha\beta\beta} &= -i \int_0^\infty \exp\{it(\omega - \omega_{ab} - \omega_{\alpha\beta})\} dt. \end{aligned} \quad (9)$$

The electron density matrix,

$$\rho^e = \exp(-H_e/kT) / \text{Tr}_e\{\exp(-H_e/kT)\}, \quad (10)$$

is also diagonal and its matrix elements are written in the form

$$\rho_{\alpha\alpha\beta\beta}^{(e)} = f_\alpha \delta_{\alpha\beta} \delta_{ab}. \quad (11)$$

With the above notation, $\mathcal{K}(\omega)$ may be written¹

$$\begin{aligned} \hbar^2 \mathcal{K}(\omega)_{\alpha\alpha\beta\beta; a'\alpha' b'\beta'} &= \delta_{bb'} \sum_{\alpha\beta c} \langle a\alpha | e \mathbf{R} \cdot \underline{\underline{\xi}}_e | c\beta \rangle \langle c\beta | e \mathbf{R} \cdot \underline{\underline{\xi}}_e | a'\alpha \rangle f_\alpha k^0(\omega)_{c\beta b\alpha} \\ &+ \delta_{aa'} \sum_{\alpha\beta c} \langle b'\alpha | e \mathbf{R} \cdot \underline{\underline{\xi}}_e | c\beta \rangle \langle c\beta | e \mathbf{R} \cdot \underline{\underline{\xi}}_e | b\alpha \rangle f_\alpha k^0(\omega)_{a\alpha c\beta} \\ &- \sum_{\alpha\beta} \langle b'\beta | e \mathbf{R} \cdot \underline{\underline{\xi}}_e | b\alpha \rangle \langle a\alpha | e \mathbf{R} \cdot \underline{\underline{\xi}}_e | a'\beta \rangle f_\beta k^0(\omega)_{a\alpha b'\beta} \\ &- \sum_{\alpha\beta} \langle a\alpha | e \mathbf{R} \cdot \underline{\underline{\xi}}_e | a'\beta \rangle \langle b'\beta | e \mathbf{R} \cdot \underline{\underline{\xi}}_e | b\alpha \rangle f_\beta k^0(\omega)_{a'\beta b\alpha}. \end{aligned} \quad (12)$$

These terms are evaluated in Appendix A using the classical limit of the Boltzmann factor and a linearized Debye-Huckel radial distribution function to describe the distribution of states in the electron gas; it is also assumed that the change in the internal electron potential, V_e , is negligible over the times of interest [see Eq.(A.15)]. The results of this evaluation provide the following expression:

$$\begin{aligned} \mathcal{K}(\omega)_{ab,a'b'} = & -(2ie^4 n / 3\hbar^2) (8\pi m / kT)^{1/2} \{ \sum_c [\delta_{bb'} R_{ac} \cdot R_{ca} G(\Delta\omega_{cb}) \\ & + \delta_{aa'} R_{cb'} \cdot R_{cb} G(-\Delta\omega_{ac})] - R_{aa'} \cdot R_{b'b} [G(\Delta\omega_{ab'}) + G(-\Delta\omega_{a'b})] \} \end{aligned} \quad (13)$$

where m and n denote the mass and density of electrons, and $G(\Delta\omega)$ is an integral discussed in the following sections.

B. Some Physical Properties of $\mathcal{K}(\omega)$

To second order, $\mathcal{K}(\omega)$ represents a quadratic Stark interaction between the atom and the fluctuating electron field. In order to study the meaning of the frequency dependence in $\mathcal{K}(\omega)$, we note that it is possible to interpret a quadratic Stark effect as an induced dipole interaction¹². The frequency dependence in $\mathcal{K}(\omega)$ is therefore a result of the time dependence in an induced dipole interaction; that is, as the microfield $\underline{\mathcal{E}}_e$ varies, the induced atomic dipole vector moves in such a way that it always points in the same direction as the field $\underline{\mathcal{E}}_e$. An interaction of this type will lower the atomic energy levels. Since the lower energy states are more tightly bound, the energies of the final states will be less affected, the net result being a reduction in the energy separation of the initial and final states. We therefore expect the quadratic electron-atom interactions to produce a small asymmetry in the line profile

which increases the intensity of the red wing relative to that of the blue wing; we also expect these interactions to shift the center of the line toward longer wavelengths¹³.

To explore the source of these shifts and asymmetries, we note that a simple Lorentzian line may be expressed by

$$\text{Im}[\omega - \omega_0 - (\omega_r + i\omega_i)]^{-1} = \omega_i / [(\Delta\omega - \omega_r)^2 + \omega_i^2] \quad (14)$$

where ω_r denotes a shift of the line center and ω_i provides the line width. The line shape $J(\omega, \mathcal{E})$, given by Eqs.(5) and (6), may be loosely compared with Eq.(14), and one may expect the real part of \mathcal{K} to produce a shift while the imaginary part adds to the line width. The frequency dependence of $\mathcal{K}(\omega)$ indicates that these "width" and "shift" operators may not be symmetric. The linear Stark effect in Eq.(6) produces a symmetric splitting and therefore contributes only to the width. These arguments are offered merely as plausibility arguments because, strictly speaking, one may not discuss the operators in $J(\omega, \mathcal{E})$ in the same manner as the scalars in Eq.(14). Nevertheless, this does give a rough idea of the roles played by the real and imaginary parts of \mathcal{K} in determining the line shape. It may be noted in passing that, in the numerical calculations made by the author, it is found that the line shift vanishes when the real part of \mathcal{K} is set to zero. Furthermore, when the shift vanishes, most of the asymmetry in the line center also vanishes; this indicates that the center region of the broadened line is roughly symmetric about the shifted frequency.

C. The Integral $G(\Delta\omega)$

From Eq.(13), it is clear that the integral $G(\Delta\omega)$ contains all of the frequency dependence in the effective interaction, $\mathcal{K}(\omega)$. In Appendix A, it

is shown that the influence of electron correlations is also contained in $G(\Delta\omega)$. Since this integral plays such an important role in the study of the electron-atom interaction, its derivation is presented in detail in that appendix. The results of this derivation are outlined and interpreted in this section.

The G integral which appears in the ideal gas case (no correlations) is given by Eq.(A38) [and also by Eq.(58) of ref.(1)] in the form

$$G_0(\Delta\omega) = \int_0^\infty \exp\{is\hbar\Delta\omega/kT\}(s^2+is)^{-1/2} ds. \quad (15)$$

When electron correlations are considered, it is found that a correction term is added to the integrand in Eq.(15). The corrected integral is given by Eq.(A38) in the form

$$G(\Delta\omega) = \int_0^\infty \exp\{is\hbar\Delta\omega/kT\} \left[(s^2+is)^{-1/2} - \sqrt{\pi}\alpha \exp\{\alpha^2(s^2+is)\} \text{Erfc}\{\alpha\sqrt{s^2+is}\} \right] ds, \quad (16)$$

where Erfc is the complimentary error function. The parameter α is defined by $\lambda/2\sqrt{\pi}\lambda_D$, where λ and λ_D are the thermal wavelength, $h/\sqrt{2\pi mkT}$, and the Debye length, $\sqrt{kT/4\pi ne^2}$, for electrons.

From Eq.(16) it is apparent that the parameter α is a measure of the importance of electron correlations. In the limit $\alpha \rightarrow 0$, the argument of the integrand in Eq.(15) becomes $1/\sqrt{s^2+is}$ hence $G(\Delta\omega)$ reduces to the ideal gas result, $G_0(\Delta\omega)$, in this limit. For any finite α however, the ideal gas term, $1/\sqrt{s^2+is}$, will dominate the Erfc term for sufficiently small values of s ; that is, the electron correlations are negligible for short times or large $\Delta\omega$. We note further that $1/\sqrt{s^2+is}$ is the large s asymptote of the Erfc term. This implies that the electron correlations will be important for long times or small $\Delta\omega$.

Further analysis of the integrand in Eq.(16) shows that the transition from the regime where correlations are important, to the ideal gas regime,

occurs for the values of s on the order of $1/\alpha$. Since $\alpha \approx \hbar \omega_p / kT$, where ω_p is the plasma frequency, we may use the well known property of Fourier transforms,

$$\Delta\omega \Delta t \gtrsim 1, \quad (17)$$

to infer that correlations will be important only for $|\Delta\omega| < \omega_p$. This also indicates that the transition from the correlated regime to the ideal gas regime occurs for values of $|\Delta\omega|$ on the order of ω_p or $v_{av.}/\lambda_D$ where $v_{av.}$ is the average electron velocity. This is exactly the point where the Lewis cutoff is applied in the impact theory⁷.

We therefore conclude that, for frequency separations (from the center of the natural line) less than $v_{av.}/\lambda_D$ many-particle effects are important and electron correlations must be considered. In the impact theory this is done by shielding the electron-atom interaction, or by cutting off the range of this interaction at the Debye length. When $|\Delta\omega|$ is larger than $v_{av.}/\lambda_D$ the correlations are negligible, hence the atom is perturbed through binary collisions with electrons and electron-atom interaction need not be shielded.

In order to illustrate the above conclusions graphically, it is convenient to express $G(\Delta\omega)$ in terms of real functions. It is possible to write $G(\Delta\omega)$ in the form

$$G(\Delta\omega) = G_r(\tilde{\Delta\omega}) - iG_i(\tilde{\Delta\omega}) \quad (18)$$

where G_r and G_i are real functions of the real variable $\tilde{\Delta\omega}$. The variable $\tilde{\Delta\omega}$, defined by $\Delta\omega = \tilde{\Delta\omega} + i\epsilon$, is the frequency separation from the center of the natural line. (Since the natural width, ϵ , is negligibly small, $|\Delta\omega| = |\tilde{\Delta\omega}|$ except at the line center when $|\tilde{\Delta\omega}| \approx \epsilon$.) There is no analog for G_i in the impact theories (for hydrogen), hence numerical comparisons will be made only for G_r .

The integral corresponding to G_r in the impact theory is given by Eq.(30) of ref.(6). The parameter y_{\min} used in that paper is just $2n^4\alpha^2/3$ where n is the principal quantum number and $\alpha=\lambda/2\sqrt{\pi}\lambda_D$. We therefore compare $G_r(\Delta\tilde{\omega})$ with

$$G_{\text{Impact}} = \frac{1}{2} \int_{y_{\min}}^{\infty} \frac{\exp(y)}{y} dy \quad (19)$$

$$\approx 0.08 - \log(\alpha) - 2\log(n)$$

This function is plotted in fig.(1) for $|\Delta\omega|$ smaller than the Lewis cutoff (LC). For larger values of $|\Delta\omega|$, Lewis obtains⁷

$$G_{\text{Lewis}} = 0.8 - \log(\hbar|\Delta\omega|/kT) - 2\log(n). \quad (20)$$

Fig.(1) shows that $G_r(|\Delta\tilde{\omega}|)$ and G_{Impact} differ by a constant over most of the correlated regime. To illustrate the source of this constant, it may be noted that

$$G_r(0) \approx 0.4 - \log(\alpha). \quad (21)$$

The significant difference between Eqs.(20) and (21) is in the factor $\log(n)$. In the impact theory this factor comes about because of a "strong-collision" cutoff which is not made in the relaxation theory. This point will be explored further in the next section.

For frequencies larger than the Lewis cutoff $G_r(\Delta\tilde{\omega})$ has the form

$$G_r(\Delta\tilde{\omega}) \sim \exp(\hbar\Delta\tilde{\omega}/2kT) [0.8 - \log(\hbar|\Delta\tilde{\omega}|/kT)]. \quad (22)$$

The factor $\exp(\hbar\Delta\tilde{\omega}/2kT)$ produces an asymmetry in G_r , which is observed in fig.(1), for large $|\Delta\tilde{\omega}|$. Since Lewis' results are symmetric, we may compare $[0.8 - \log(\hbar|\Delta\omega|/kT)]$

[dotted line in fig.(1)] with the expression for G_{Lewis} , Eq.(20). Again, we find a constant difference in which the factor $\log(n)$ plays a significant role.

Fig.(1) also shows the function $G_r(\Delta\tilde{\omega})$, calculated with only the ideal gas term Eq.(15). The corrected G_r goes into its ideal gas asymptote very rapidly at the Lewis cutoff(LC). While this transition is by no means as sharp as the change from G_{Impact} to G_{Lewis} , it does indicate that the cutoffs used in the impact theory provide a good approximation to the effects of electron correlations.

D. The Influence of Strong Collisions

In the previous section, it was noted that $G_r(\Delta\tilde{\omega})$ differs from its counterpart in the impact theories by a nontrivial constant. It was also noted that there is no analog for $G_i(\Delta\tilde{\omega})$ in the impact theories (for hydrogen) and it is this function which gives rise to a line shift in the relaxation theory. Since these are important points, it is appropriate to investigate the source of these disparities.

In the relaxation theory, the effective interaction operator may be written in the form

$$\mathcal{H}(\omega) = -(i/\hbar^2) \int_0^\infty \exp(it\Delta\omega) \langle VV(t) \rangle dt \quad (23)$$

[see Eqs.(A3) and (A4)] where $\langle \dots \rangle$ denotes an average over electrons and $V(t)$ is given by

$$V(t) = eR \cdot \underline{\xi}_e(t) \quad (24)$$

$$\underline{\xi}_e(t) = \exp\{itH_e/\hbar\} \underline{\xi}_e \exp\{-itH_e/\hbar\}. \quad (25)$$

If nonradiative transitions out of the initial states are neglected (no-quenching assumption), the $\Delta\omega$ which appears in Eq.(23) will be $(\omega-\omega_0)+i\epsilon$, where ω_0 is the unperturbed frequency. The radiation damping is not relevant to the following discussion, hence we may set ϵ to zero and the $\Delta\omega$ in Eq.(23) may be regarded simply as the frequency separation from the center of the natural line.

In the impact theory, the effective interaction operator corresponding to $\chi(\omega)$ is, to second order^{14,15},

$$i\phi = -(i/\hbar\Delta s) \left\langle \int_0^{\Delta s} V(t) \int_0^t V(t') dt' dt \right\rangle. \quad (26)$$

In the impact theory the electron-atom collisions are assumed to be instantaneous so that the limits on the integrals may be extended to infinity and Δs may be removed [see Eq.(4-44) of ref.(14)]. For purposes of comparison however, it is convenient to use

$$\begin{aligned} i\phi &= -\lim_{\tau \rightarrow \infty} (i/2\tau\hbar^2) \left\langle \int_{-\tau}^{+\tau} V(t) \int_{-\tau}^t V(t') dt' dt \right\rangle \\ &= -\lim_{\tau \rightarrow \infty} (i/2\tau\hbar^2) \left\langle \int_{-\tau}^{\tau} \int_0^{\tau} V(t) V(t+s) ds dt \right\rangle. \end{aligned} \quad (27)$$

In the impact theory, the average over the states of the electrons, denoted by $\langle \dots \rangle$ in Eq.(27), is called a "thermal average".

The perturbation is usually assumed to be a stationary random process (although this approximation is rarely stated explicitly), hence

$$\langle V(t)V(t+s) \rangle = \langle VV(s) \rangle. \quad (28)$$

This property is illustrated, in the impact theory, by Eq.(4A) of ref.(7).

With Eq.(28), the expression for ϕ may be written

$$i\phi = -(i/\hbar) \int_0^\infty \langle VV(t) \rangle dt. \quad (29)$$

Comparing Eqs.(23) and (29), it is apparent that the operators $\mathcal{K}(\omega)$ and $i\phi$ should be identical when $\Delta\omega=0$. Indeed, these operators should not differ appreciably for $\Delta\omega < 1/t_c$, where t_c is the correlation time for the electron field, because $\langle VV(t) \rangle$ should be negligible for $t > t_c$. Lewis⁷ has estimated t_c by λ_D/v_{av} ; using this estimate, we do not expect $\mathcal{K}(\omega)$ and $i\phi$ to differ until $\Delta\omega > v_{av}/\lambda_D$.

It has already been shown that these operators are not identical, even when $\Delta\omega=0$, hence the disparity between them must be due to differences in the methods of evaluating $\langle VV(t) \rangle$. Lewis⁷ has evaluated this operator in a manner which is similar to the derivation in this paper (Appendix A) and it is possible to make a fairly close step-by-step comparison. The essential difference in these derivations lies in the treatment of strong collisions. The term strong collisions refers to those interactions in which an electron comes close enough to the atom to produce an appreciable overlap of the electron and atom wave-packets. In the impact theory, an impact parameter cutoff removes these strong collisions from the average in $\langle VV(t) \rangle$.¹⁶ The resulting error in ϕ is estimated by a Lorentz-Weisskopf treatment of strong collisions and is found to be small⁶. Since no special treatment has been given for strong collisions in the relaxation theory, this is clearly the source of the disparity between $\mathcal{K}(\omega)$ and $i\phi$.

To test this assertion, the author has evaluated $\langle VV(t) \rangle$ using a cutoff which requires all electrons to remain outside a small spherical region around the atom (see Appendix B). The radius of this sphere may be taken to be $n^2\lambda/\sqrt{3\pi}$, the same as the cutoff in the impact theory [see Eq.(19) of ref.(6)].

Numerical calculations have been made with this cutoff, and it is found that $G_r(\Delta\tilde{\omega})$ is decreased as shown in Fig.(2). In Fig.(2), G_r and G_{Impact} agree to within the accuracy stated for the impact theory calculations. The function $G_r(\Delta\omega)$ still shows an asymmetry for large $|\Delta\omega|$ which does not appear in G_{Lewis} . This asymmetry is roughly equivalent to multiplying G_{Lewis} by $\exp(\hbar\Delta\tilde{\omega}/2kT)$.

A numerical calculation also shows that the strong collision cutoff reduces $G_i(\Delta\tilde{\omega})$ so much that the shift of the line center (for Ly- α) is reduced by a factor of 10. When line profile calculations are made, using the strong collision cutoffs, there is less than a 20% difference between the impact and relaxation theories.

4. RESULTS AND CONCLUSIONS

The role of electron correlations in plasma line broadening has been studied, within the framework of the relaxation theory, by the use of statistical techniques. This method provides a very accurate treatment of these correlations which is limited only by the choice of a radial distribution function for the electron gas. The linearized Debye-Huckel function which was used for this purpose is known to be quite adequate for the temperatures and densities encountered in most Stark broadening problems.

The results of this work indicate that the impact parameter cutoffs, which approximate the effects of electron correlations in the impact theories, are valid to within the accuracy stated by these theories. In the relaxation theory, an asymmetry is found for frequencies larger than the Lewis cutoff; this asymmetry may be included in the impact theory if Lewis' results [Eq.(20)] are multiplied by $\exp(\hbar\Delta\tilde{\omega}/2kT)$. The asymmetry and shift in the center region of the relaxation

theory profiles¹⁷ are primarily due to the real part of $\chi(\omega)$, for which there is no analog in the impact theory (for hydrogen). It has been found, however, that the real part of $\chi(\omega)$ is considerably reduced if the strong collision cutoff in the impact theory is also applied in the relaxation theory.

While the primary purpose of this paper is the study of electron correlations, the significant effects of a strong collision cutoff require some comment as well. The dipole interaction, which has been used to represent the electron-atom coupling, is certainly not valid when a perturber comes close enough to "penetrate" the atom. For these close contacts, the elementary Coulomb interactions between the perturber, the nucleus, and the bound electron should be used. In the relaxation theory there is no problem with the wave functions in a strong collision because one is free to choose any complete set of wavefunctions in evaluating a trace. There is a problem with the Boltzmann factors however; the electron-atom coupling which has been neglected in the density matrix [(sect.(2)] will become important in a strong collision. Tentative investigations indicate that it will be possible to treat strong collisions in the relaxation theory so that no cutoff will be needed. This work will be reported in a future paper.

In conclusion, it is noted that the relaxation theory does not require a binary collision approximation, an impact approximation, or a classical path assumption. When a strong collision cutoff is used, the results of the relaxation theory (for hydrogen) agree to within 20% with those of the impact theory, thus providing an independent verification of the approximations in the impact theory. The subject of strong collisions requires further investigation and it is felt that the formalism of the relaxation theory provides a promising framework in which to study this problem.

APPENDIX A: DERIVATION OF $G(\Delta\omega)$

A. Separation of Correlations

In Eq.(12), the effective interaction operator was expressed as the sum of four terms:

$$\hbar^2 \mathcal{K}(\omega)_{ab,a'b'} = [1] + [2] - [3] - [4] \quad (A1)$$

where

$$\begin{aligned} [1] &= \delta_{bb'} \sum_{\alpha\beta c} \langle a\alpha | e_{\mathbf{R}} \cdot \underline{\xi}_e | c\beta \rangle \langle c\beta | e_{\mathbf{R}} \cdot \underline{\xi}_e | a'\alpha \rangle f_{\alpha} k^0(\omega)_{c\beta b\alpha} \\ [2] &= \delta_{aa'} \sum_{\alpha\beta c} \langle b'\alpha | e_{\mathbf{R}} \cdot \underline{\xi}_e | c\beta \rangle \langle c\beta | e_{\mathbf{R}} \cdot \underline{\xi}_e | b\alpha \rangle f_{\alpha} k^0(\omega)_{a\alpha c\beta} \\ [3] &= \sum_{\alpha\beta} \langle b'\beta | e_{\mathbf{R}} \cdot \underline{\xi}_e | b\alpha \rangle \langle a\alpha | e_{\mathbf{R}} \cdot \underline{\xi}_e | a'\beta \rangle f_{\beta} k^0(\omega)_{a\alpha b'\beta} \\ [4] &= \sum_{\alpha\beta} \langle a\alpha | e_{\mathbf{R}} \cdot \underline{\xi}_e | a'\beta \rangle \langle b'\beta | e_{\mathbf{R}} \cdot \underline{\xi}_e | b\alpha \rangle f_{\beta} k^0(\omega)_{a'\beta b\alpha} \end{aligned} \quad (A2)$$

In order to illustrate the derivation of $G(\Delta\omega)$, the third term, [3], will be evaluated in detail; the remaining terms in Eq.(A2) are then obtained through simple transformations of the dummy variables.

Using Eq.(9) and the notations $V = e_{\mathbf{R}} \cdot \underline{\xi}_e$ and $\Delta\omega_{ab} = \omega - \omega_{ab}$, we have

$$\begin{aligned} [3] &= -i \sum_{\alpha\beta} \langle b'\beta | V | b\alpha \rangle \langle a\alpha | V | a'\beta \rangle f_{\beta} \int_0^{\infty} \exp\{i(\Delta\omega_{ab} - \omega_{\alpha\beta})t\} dt \\ &= -i \int_0^{\infty} \exp(i\Delta\omega_{ab}t) F(t)_{aa',b'b} dt. \end{aligned} \quad (A3)$$

where $F(t)_{aa',b'b}$ is given by

$$\begin{aligned} F(t)_{aa',b'b} &= \sum_{\alpha\beta} \langle \alpha | V_{aa,\rho}^{(e)} | \beta \rangle \langle \beta | \exp(itH_e/\hbar) V_{b'b} \exp(-itH_e/\hbar) | \alpha \rangle \\ &= \text{Tr}_e \{ V_{aa,\rho}^{(e)} \exp(itH_e/\hbar) V_{b'b} \exp(-itH_e/\hbar) \} \end{aligned} \quad (A4)$$

It is convenient to use $R_{aa'} = R_1, R_{b'b} = R_2$ and $F_{aa',b'b} = F_{12}$. Since any complete set of basis vectors may be used in evaluating a trace, we may use the eigenvectors of the N-electron position operator, X , to evaluate the trace in Eq.(A4). The eigenvectors of X are denoted by x ,

$$X|x\rangle = x|x\rangle \quad x = (x_1, x_2, \dots, x_N), \quad (A5)$$

where x is a 3N-vector whose components are the position vectors for each of the N electrons. In this notation, Eq.(A4) becomes

$$F(t)_{12} = \int \langle x | V_1 \rho^{(e)} \exp\{itH_e/\hbar\} V_2 \exp\{-itH_e/\hbar\} | x \rangle dx. \quad (A6)$$

In the classical limit, the density matrix for the canonical ensemble has the form¹⁸

$$\rho^{(e)} = \exp(-K_e/kT) \exp(-V_e/kT) / \text{Tr}_e \{ \exp(-K_e/kT) \exp(-V_e/kT) \} \quad (A7)$$

and

$$\begin{aligned} \text{Tr}_e \{ \exp[-K_e/kT] \exp[-V_e/kT] \} &= \int \langle x | \exp[-K_e/kT] | x \rangle \exp[-V_e(x)/kT] dx \\ &= \iint \langle x | p \rangle \langle p | \exp[-K_e/kT] | x \rangle \exp[-V_e(x)/kT] dx dp \\ &= \iint \langle x | p \rangle \langle p | x \rangle \exp[-K_e(p)/kT] \exp[-V_e(x)/kT] dx dp. \end{aligned} \quad (A8)$$

The 3N-vector $p = (p_1, p_2, \dots, p_N)$ is the N-electron momentum vector and is therefore an eigenvector of K_e with the eigenvalue $K_e(p) = p^2/2m$. In a position representation, the states $|p\rangle$ have the form

$$\langle x | p \rangle = \exp(ip \cdot x / \hbar) / h^{3N/2}, \quad (A9)$$

hence Eq.(A8) becomes

$$\begin{aligned} \text{Tr}_e \{ \exp[-K_e/kT] \exp[-V_e/kT] \} &= h^{-3N} \int \exp[-p^2/2mkT] dp \int \exp[-V_e(x)/kT] dx \\ &= \lambda^{-3N} \int \exp[V_e(x)/kT] dx \end{aligned} \quad (\text{A10})$$

where $\lambda = h/\sqrt{2\pi mkT}$ is the thermal wavelength for an electron. Using the N-electron probability function¹⁹

$$P(x) = \exp[-V_e(x)/kT] / \int \exp[-V_e(x)/kT] dx, \quad (\text{A11})$$

it is clear that

$$\rho^{(e)} |x\rangle = \exp(-K_e/kT) |x\rangle P(x) \lambda^{3N}. \quad (\text{A12})$$

The electron time-development operator will be treated in a similar manner; we first introduce the identity

$$\exp\{it(K_e + V_e)/\hbar\} = \exp\{itK_e/\hbar\} \exp\{(i/\hbar) \int_0^t \tilde{V}_e(t) dt\} \quad (\text{A13})$$

where

$$\tilde{V}_e(t) = \exp(itK_e/\hbar) V_e \exp(-itK_e/\hbar). \quad (\text{A14})$$

Since we do not expect the internal energy of the electrons, V_e , to vary appreciably, over the times of interest, we make the following approximation:

$$\exp\{(i/\hbar) \int_0^t \tilde{V}_e(t) dt\} \approx \exp\{itV_e/\hbar\}. \quad (\text{A15})$$

With this approximation we have

$$\exp(itH_e/\hbar) V_2 \exp(-itH_e/\hbar) \approx \exp(itK_e/\hbar) V_2 \exp(-itK_e/\hbar), \quad (\text{A16})$$

where V_e has been commuted with V_2 since they depend only on electron position operators.

Using Eqs.(A12) and (A16), and introducing the variable $s=tkT/\hbar$, we have

$$\begin{aligned}
 F_{12} &= \lambda^{3N} \int V_1(\mathbf{x}) P(\mathbf{x}) \langle \mathbf{x} | \exp\{-(1-is)K_e/kT\} V_2 \exp\{-isK_e/kT\} | \mathbf{x} \rangle d\mathbf{x} \\
 &= \lambda^{3N} \int V_1(\mathbf{x}) P(\mathbf{x}) \iint \langle \mathbf{x} | \mathbf{p} \rangle \langle \mathbf{p} | \exp\{-(1-is)K_e/kT\} | \mathbf{y} \rangle \\
 &\quad \times \langle \mathbf{y} | V_2 \exp\{-isK_e/kT\} | \mathbf{p}' \rangle \langle \mathbf{p}' | \mathbf{x} \rangle d\mathbf{p}' d\mathbf{p} d\mathbf{y} d\mathbf{x} \\
 &= \lambda^{3N} \int V_1(\mathbf{x}) P(\mathbf{x}) \iint \langle \mathbf{x} | \mathbf{p} \rangle \langle \mathbf{p} | \mathbf{y} \rangle \langle \mathbf{y} | \mathbf{p}' \rangle \langle \mathbf{p}' | \mathbf{x} \rangle V_2(\mathbf{y}) \\
 &\quad \times \exp\{-p^2/2mkT\} \exp\{is(p^2-p'^2)/2mkT\} d\mathbf{p}' d\mathbf{p} d\mathbf{y} d\mathbf{x}
 \end{aligned} \tag{A17}$$

where the K_e eigenvectors $|\mathbf{p}\rangle$ and $|\mathbf{p}'\rangle$ have been used [see Eq.(A9)]. Noting Eq.(9) it is apparent that

$$\langle \mathbf{x} | \mathbf{p} \rangle \langle \mathbf{p} | \mathbf{y} \rangle \langle \mathbf{y} | \mathbf{p}' \rangle \langle \mathbf{p}' | \mathbf{x} \rangle = h^{-9N/2} \langle \mathbf{y} - \mathbf{x} | \mathbf{p}' - \mathbf{p} \rangle. \tag{A18}$$

Changing variables from \mathbf{p}' to $\mathbf{q} = \mathbf{p}' - \mathbf{p}$ and noting further that $(p'^2 - p^2) = q^2 + 2\mathbf{p} \cdot \mathbf{q}$, the \mathbf{p} and \mathbf{q} integrals are performed in the following manner:

$$\begin{aligned}
 F_{12} &= \lambda^{3N} h^{-9N/2} \int V_1(\mathbf{x}) P(\mathbf{x}) \int V_2(\mathbf{y}) \langle \mathbf{y} - \mathbf{x} | \mathbf{q} \rangle \exp\{-isq^2/2mkT\} \\
 &\quad \times \int \exp\{-is\mathbf{p} \cdot \mathbf{q}/mkT\} \exp\{-p^2/2mkT\} d\mathbf{p} d\mathbf{q} d\mathbf{y} d\mathbf{x} \\
 &= h^{-3N/2} \int V_1(\mathbf{x}) P(\mathbf{x}) \int V_2(\mathbf{y}) \langle \mathbf{y} - \mathbf{x} | \mathbf{q} \rangle \exp\{-q^2(s^2 + is)/2mkT\} d\mathbf{q} d\mathbf{y} d\mathbf{x} \\
 &= \lambda^{-3N} (s^2 + is)^{-3N/2} \int V_1(\mathbf{x}) P(\mathbf{x}) \int V_2(\mathbf{y}) \exp\{-(\mathbf{y} - \mathbf{x})^2 \pi / \lambda^2 (s^2 + is)\} d\mathbf{y} d\mathbf{x}.
 \end{aligned} \tag{A19}$$

In order to simplify the following calculations we introduce the variable

$$A(s) = \sqrt{\pi} / \lambda \sqrt{s^2 + is}. \tag{A20}$$

The exponential appearing in the result of Eq.(A19) is expressed as a product involving the 3-vectors \mathbf{x}_j (electron position vectors),

$$\exp\{-(y-x)^2 A^2\} = \prod_j \exp\{-(y_j - x_j)^2 A^2\}, \quad (A21)$$

and a Coulomb field is used for the electrons,

$$V_2(y) = e R_2 \cdot \epsilon(y) = e^2 \sum_j R_2 \cdot y_j / y_j^3. \quad (A22)$$

With Eqs.(A20), (A21) and (A22), the y integral in Eq.(A19) is easily reduced to

$$\begin{aligned} & (A^2/\pi)^{3N/2} \int V_2(y) \exp\{-(y-x)^2 A^2\} dy \\ & = e^2 A \pi^{-3/2} \sum_j \int \exp\{-(y_j - x_j)^2 A^2\} \{R_2 \cdot y_j / y_j^3\} dy_j. \end{aligned} \quad (A23)$$

The remaining integral over y_j is evaluated in spherical coordinates, choosing x_j as the polar axis. The polar and azimuthal angles, between x_j and y_j are denoted by θ and ϕ while the corresponding angles between R_2 and x_j are denoted by θ_2^j and ϕ_2^j . The scalar product $R_2 \cdot y_j$ is expanded using the addition theorem for spherical harmonics of order 1,²⁰

$$R_2 \cdot y_j = R_2 y_j [\cos\theta \cos\theta_2^j + \sin\theta \sin\theta_2^j \cos(\phi - \phi_2^j)], \quad (A24)$$

and it is noted that the azimuthal integral of $\cos(\phi - \phi_2^j)$ vanishes. In this manner the y_j integral in Eq.(A23) is found to be

$$(A/\sqrt{\pi})^{3N} \int V_2(y) \exp\{-(y-x)^2 A^2\} dy = -e^2 R_2 \sum_j \cos\theta_2^j \frac{d}{dx_j} [\text{Erf}(x_j A)/x_j] \quad (A25)$$

Substituting this result into Eq.(A19) we obtain

$$F(t)_{12} = -e^4 R_1 R_2 \sum_{jk} x_k^{-2} \cos\theta_1^k \cos\theta_2^j \frac{d}{dx_j} [\text{Erf}(x_j A)/x_j] P(x) dx. \quad (A26)$$

Since $P(x_1, \dots, x_N)$ is symmetric with respect to an interchange of particle coordinates¹⁹, the form of the integrand in Eq.(26) indicates that only the one- and two-particle distribution functions,

$$P_1(x_j) = \int \cdots \int P(x) dx_1 \cdots dx_{j-1} dx_{j+1} \cdots dx_N \quad (A27)$$

$$P_2(x_j, x_k) = \int \cdots \int P(x) dx_1 \cdots dx_{j-1} dx_{j+1} \cdots dx_{k-1} dx_{k+1} \cdots dx_N,$$

will be needed. For a gas of N particles, these functions may be written¹⁹ in the form

$$P_1(x_j) = n/N \quad (A28)$$

$$P_2(x_j, x_k) = n^2 g_2(|x_j - x_k|)/N(N-1),$$

where n^2 is the density and g_2 is the radial distribution function for the gas. $F(t)$ is expressed as the sum of one- and two-body integrals in the following manner:

$$F(t)_{12} = F^0(t)_{12} + F^C(t)_{12} \quad (A29)$$

where

$$\begin{aligned} F^0(t)_{12} &= -e^4 R_1 R_2 \sum_j \int x_j^{-2} \cos \theta_1^j \cos \theta_2^j \frac{d}{dx_j} [\text{Erf}(x_j A)/x_j] P_1(x_j) dx_j \\ &= -ne^4 R_1 R_2 \int x_1^{-2} \cos \theta_1^1 \cos \theta_2^1 \frac{d}{dx_1} [\text{Erf}(x_1 A)/x_1] dx_1 \\ &= (8\pi ne^4 A/3\sqrt{\pi}) R_1 \cdot R_2 \end{aligned} \quad (A30)$$

and

$$\begin{aligned} F^C(t)_{12} &= -e^4 R_1 R_2 \sum_j \sum_{k \neq j} \int \int x_k^{-2} \cos \theta_1^k \cos \theta_2^j \frac{d}{dx_j} [\text{Erf}(x_j A)/x_j] P_2(x_j, x_k) dx_j dx_k \\ &= -n^2 e^4 R_1 R_2 \int \int x_1^{-2} \cos \theta_1^1 \cos \theta_2^2 \frac{d}{dx_2} [\text{Erf}(x_1 A)/x_1] g_2(|x_1 - x_2|) dx_1 dx_2 \end{aligned} \quad (A31)$$

The one-body integral, F^0 , will give rise to the usual ideal gas results, while the two-body term, F^C , represents the influence of electron correlations.

B. Evaluation of the Correlation Term

If there were no correlation between electrons, g_2 would be 1 and F^C would vanish (by virtue of the angle integrals). Since F^C vanishes if g_2 is replaced by 1, we may replace g_2 , in the integrand of Eq.(A31), by $(g_2-1) = -\tilde{g}_2$. In order to simplify the evaluation of F^C , we change variables to $y = x_1 - x_2$ and $x = x_2$ (the 3-vectors x and y used in this section should not be confused with the 3N-vectors $\underline{x} = (x_1, x_2, \dots, x_N)$ and y used in the previous section). With these variables, F^C becomes

$$\begin{aligned} F^C(t)_{12} &= n^2 e^4 R_1 R_2 \iint (x+y)^{-2} \cos\theta_2^x \cos\theta_1^{x+y} \frac{d}{dx} [\text{Erf}(xA)/x] \tilde{g}_2(y) dx dy \\ &= n^2 e^4 R_1 R_2 \int_0^\infty \int_0^\infty \Omega(x,y) \frac{d}{dx} [\text{Erf}(xA)/x] \tilde{g}_2(y) x^2 y^2 dx dy. \end{aligned} \quad (\text{A32})$$

where $\Omega(x,y)$ denotes the result of integrating over the solid angles Ω_x and Ω_y :

$$\begin{aligned} \Omega(x,y) &= \iint (x+y)^{-2} \cos\theta_2^x \cos\theta_1^{x+y} d\Omega_x d\Omega_y \\ &= \iint |R_1|^{-1} |x+y|^{-3} \cos\theta_2^x R_1 \cdot (x+y) d\Omega_x d\Omega_y \\ &= x \iint |x+y|^{-3} \cos\theta_1^x \cos\theta_2^x d\Omega_x d\Omega_y + y \iint |x+y|^{-3} \cos\theta_1^x \cos\theta_2^y d\Omega_x d\Omega_y \\ &= (16\pi/3x) \cos\theta_1^2 \begin{pmatrix} 0 \\ 1 \end{pmatrix} \begin{matrix} y > x \\ y < x \end{matrix} \end{aligned} \quad (\text{A33})$$

The final step in Eq.(A33) was made by integrating first over the y angles, choosing x as the polar axis, and then over the x angles with R_1 as the polar axis. Equation (A33) is substituted into (A32) and the x integral is performed with the result:

$$F^C(t)_{12} = -16\pi n^2 e^4 / 3 R_1 \cdot R_2 \int_0^\infty y \tilde{g}_2(y) \text{Erf}(yA) dy. \quad (\text{A34})$$

A linearized Debye-Huckel radial distribution function is used in the evaluation of Eq.(A34); this function has the form¹⁹

$$\tilde{g}_2(y) = 1 - g_2(y) = (e^2/kTy) \exp(-y/\lambda_D) \quad (A35)$$

where λ_D is the Debye length, $\sqrt{kT/4\pi ne^2}$, for electrons. Using Eq.(A35), F^c becomes

$$F^c(t)_{12} = -(4\pi ne^4/3\lambda_D) R_1 \cdot R_2 \exp(1/4\lambda_D^2 A^2) \text{Erfc}(1/2\lambda_D A) \quad (A36)$$

Combining Eqs.(A20), (A29), (A30) and (A36) and substituting in Eq.(A3) one obtains:

$$[3] = -(2ine^4/3)(8\pi m/kT)^{1/2} R_{aa'} \cdot R_{b'b} G(\Delta\omega_{ab'}) \quad (A37)$$

where $G(\Delta\omega)$ is an integral defined by

$$\begin{aligned} G(\Delta\omega) &= G_o(\Delta\omega) + G_c(\Delta\omega) \\ G_o(\Delta\omega) &= \int_0^\infty \exp\{i s \hbar \Delta\omega/kT\} (s^2 + is)^{-1/2} ds \\ G_c(\Delta\omega) &= -\alpha \sqrt{\pi} \int_0^\infty \exp\{i s \hbar \Delta\omega/kT\} \exp\{\alpha^2 (s^2 + is)\} \text{Erfc}(\alpha \sqrt{s^2 + is}) ds \end{aligned} \quad (A38)$$

and α is a constant defined by

$$\alpha = \lambda/2\sqrt{\pi}\lambda_D. \quad (A39)$$

The term denoted by [4] in Eq.(A2) is obtained by making the transformation $(a,b,a',b',\omega) \rightarrow (b,a,b',a',-\omega)$ plus complex conjugation on [3]. It is possible to write [1] in the form

$$\begin{aligned} [1] &= -i\delta_{bb'} \sum_c \int_0^\infty \exp(it\Delta\omega_{cb}) F(t)_{ca',ac} dt \\ &= -(2ine^4/3)(8\pi m/kT)^{1/2} \sum_c R_{ac} \cdot R_{ca'} G(\Delta\omega_{cb}) \end{aligned} \quad (A40)$$

where $F(t)$ is given by Eq.(A4). The second term [2], in Eq.(A1) is then obtained from [1] by the transformation $(a,b,a',b',\omega) \rightarrow (b,a,b',a',-\omega)$ plus complex conjugation. In this manner one obtains the result stated in Eq.(13).

APPENDIX B: STRONG COLLISION CUTOFF

A strong collision cutoff may be imposed in the relaxation theory by requiring that all electrons remain outside a small spherical region around the atom. The radius of this sphere is called x_0 ; the magnitude of x_0 will be on the order of the thermal wavelength for an electron²¹.

With a cutoff at x_0 , the ideal gas term, Eq.(A30), becomes

$$\begin{aligned} F_{12}^{oc} &= -(4\pi n e^4/3) R_1 \cdot R_2 \int_{x_0}^{\infty} \frac{d}{dx} [\text{Erf}(xA)/x] dx \\ &= -(4\pi n e^4/3) R_1 \cdot R_2 [\text{Erf}(x_0 A)/x_0] \end{aligned} \quad (B1)$$

Using Eq.(A33) in the correlation term, Eq.(A32), the cutoff gives rise to

$$F_{12}^{cc} = (16\pi^2 n^2 e^4/3) R_1 \cdot R_2 \int_{x_0}^{\infty} \frac{d}{dx} [\text{Erf}(xA)/x] \int_0^x y^2 \tilde{g}_2(y) dy dx \quad (B2)$$

Using the Dirichlet integral theorem we obtain the identity:

$$\begin{aligned} \int_{x_0}^{\infty} \int_0^x f(x,y) dy dx &= \int_{x_0}^{\infty} \int_0^{x_0} f(x,y) dy dx + \int_{x_0}^{\infty} \int_{x_0}^x f(x,y) dy dx \\ &= \int_0^{x_0} \int_{x_0}^{\infty} f(x,y) dx dy + \int_{x_0}^{\infty} \int_y^{\infty} f(x,y) dx dy \end{aligned} \quad (B3)$$

With this identity, Eq.(B2) becomes

$$F_{12}^{cc} = F_{12}^c - (16\pi^2 n^2 e^4/3) R_1 \cdot R_2 [x_0^{-1} \text{Erf}(x_0 A) \int_0^{x_0} y^2 \tilde{g}_2(y) dy - \int_0^{x_0} y \tilde{g}_2(y) \text{Erf}(yA) dy] \quad (B4)$$

where F_{12}^c is given by Eq.(A34).

Since F_{12}^c is the correlation term without a cutoff, the remaining terms on the right side of Eq.(B4) represent the strong collision effects on the electron correlations. It will be shown that strong collisions have a negligible

effect on these correlations. Using \tilde{g}_2 as given by Eq.(35), the first integral in Eq.(B4) is found to be:

$$\begin{aligned} & -(16\pi^2 n^2 e^4/3) R_1 \cdot R_2 [\text{Erf}(x_o A)/x_o] \int_0^{x_o} (e^2/kT) y \exp(-y/\lambda_D) dy \\ & = -(4\pi n e^4/3) R_1 \cdot R_2 [\text{Erf}(x_o A)/x_o] [1 - (1+x_o/\lambda_D) \exp(x_o/\lambda_D)] \end{aligned} \quad (B5)$$

Since (x_o/λ_D) is on the order of 10^{-2} or less, this term is 10^{-4} times smaller than F^{oc} [Eq.(B1)]. The remaining integral in Eq.(B4) is even smaller than the term in Eq.(B5); hence we see that strong collisions effects in the correlation term are negligible compared with their effects in the ideal gas term.

The strong collision cutoff may be included by subtracting $(F^{oc}-F^o)$ from the F given by Eq.(A29). This is equivalent to subtracting

$$G_{sc}(\Delta\omega) = \int_0^\infty \exp(ish\Delta\omega/kT) [(s^2+is)^{-1/2} - (\lambda/2x_o) \text{Erf}(\sqrt{\pi}x_o/\lambda\sqrt{s^2+is})] ds \quad (B6)$$

from the G integral given by Eq.(A38).

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8. The electron potential, V_e , is needed only to determine a radial distribution function, g_2 . It is therefore convenient to specify V_e through the choice of g_2 ; this is done in Eq.(A35) of Appendix A.
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10. It should be noted that, while both \underline{d} and $-e\mathbf{R}$ are basically dipole operators, the matrix elements of \underline{d} are frequently restricted in a manner that does not apply to $-e\mathbf{R}$. This is discussed further in sect.(3A) of ref.(1).
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15. Equation (21) is obtained by comparing Eqs.(5) and (6) with Eq.(4-35) of ref.(14) and then using Eq.(4-31) of ref.(14).
16. In the impact theory, $V(t)$ is a real classical potential function (classical path assumption), whereas, in the relaxation theory, the complex quantum mechanical operator is used [see Eq.(A6)]. This difference is not important when a strong collision cutoff is used because the classical path approximation is valid if the electron and atom wave packets do not overlap.

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21. The width of a wavepacket for an electron perturber is given by the thermal wavelength, λ . A cutoff whose magnitude is on the order of λ will prohibit a perturber wavepacket from overlapping the atomic nucleus. Most strong collision cutoffs, for low lying hydrogen lines, are therefore chosen to be some multiple of λ .

Figure Captions

Figure (1): G functions for the Lyman-alpha line at a temperature of 2×10^4 degrees. The Lewis cutoff (LC) denotes the separation of the ideal gas and correlated gas regimes.

Figure (2): G_r , calculated with a strong collision cutoff, for the Lyman-alpha line at a temperature of 2×10^4 degrees. The Lewis cutoff (LC) denotes the separation of the ideal gas and correlated gas regimes.

