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Unified Classical-Path Treatment of Stark Broadening in Plasmas

Earl W. Smith, J. Cooper,* and C. R. Vidal
National Bureau of Standards, Boulder, Colorado 80302
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A theoretical treatment of spectral line broadening in plasmas is developed using classical-path methods. This treatment unifies certain aspects of the familiar impact, one-electron, and relaxation theories to produce results which are valid from the line center to the far line wings where the electrons may behave quasistatically. Calculations of the Lyman-α line of hydrogen are used to illustrate the theory.

I. INTRODUCTION

A theoretical treatment of spectral line broadening in plasmas will be developed using classical-path methods[1,2] (Refs. 1 and 2 will henceforth be referred to as I and II). This treatment unifies certain aspects of the familiar impact,[2-4] one-electron,[2,3] and relaxation[5,6] theories to produce a more general theory which is correct from the line center to the far line wings.

In describing the center region of a line profile, most theories expand the time-development operator for the perturbed radiator to second order in the perturbation potential. The so-called "strong collisions," for which such a perturbation treatment breaks down, are usually treated by some type of strong collision cutoffs. This procedure works quite well, for example, in hydrogen where most of the broadening is done by the weaker interactions. For some isolated lines, however, the strong collisions may produce a large percentage of the broadening and it would be desirable to treat such interactions more accurately. This situation is also common in neutral gases (i.e., not plasmas) where essentially all of the broadening is due to strong collisions. In such cases one generally uses the impact theory which describes the collisions in terms of S matrices.

The unified classical-path approach developed in this paper is formally the same as the quantum-mechanical relaxation theory.[5,6] Since the latter is known to be valid in the line center when strong collisions are not too important (e.g., hydrogen lines), it is obvious that the unified approach will be similarly valid. For cases where strong collisions produce an appreciable percentage of the broadening, the collisions are treated by a time-development operator which is similar to the S-matrix treatment in the impact theory. In fact, the only essential difference between the impact theory and the unified theory is due to the fact that the unified theory does not make the "completed collision assumption."

The completed collision assumption assumes that any collision which occurs during the time of interest can be completed during that time.[2,7] It is this assumption which replaces the time-devel-

opment operator for a given collision by the S matrix for that collision. In the impact theory, this assumption is corrected by means of a frequency-dependent impact parameter cutoff (the Lewis cutoff[7]) which is used when calculating frequency separations $\Delta\omega$ (measured from the center of the natural line) greater than the plasma frequency ω_p for electrons. Since the derivation of the Lewis cutoff is based on an expansion which is valid only in the line wings, the application of this cutoff in the impact theory raised some doubts as to the validity of such a "modified" impact theory in the line center. These doubts were dispelled to some extent by the results of the relaxation theory which does not make a completed collision assumption; in Figs. 1 and 2 of Ref. 6 it is shown that the results of the relaxation theory essentially reproduce the behavior of a Lewis cutoff, and these results are not restricted to the line wings. Since the unified classical-path theory presented in this paper does not make a completed collision assumption, and since the results of this theory are identical with the results of the relaxation theory in the line center, we may regard these results as an additional verification of the Lewis cutoff procedure. In Sec. IV B, it will be shown that the difference between the present theory and the impact theory, with regard to the Lewis cutoff, lies in the treatment of the non-Markovian nature of the electron perturbation.

In the line wings, the present theory reproduces the results of the one-electron theory (as it was developed in II). Since the latter is known to be valid in the line wings, even if the electrons take on a quasistatic behavior, this indicates that the unified theory is correct both in the line center as well as the far line wings. The unified theory also has the advantage that the total line profile

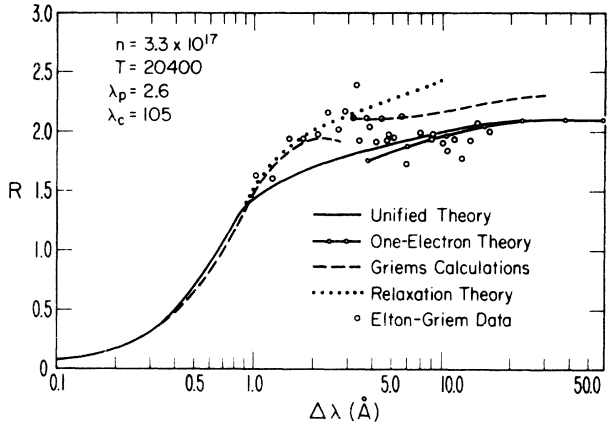

FIG. 1. Comparison of theoretical and experimental profiles relative to the asymptotic Holtsmark profile for $n = 3.3 \times 10^{17}$ cm^{-3} and $T = 20\ 400$ °K. The parameters λ_p and λ_c denote wavelengths (In Å) which correspond to the plasma frequency and the Weisskopf frequency, respectively.

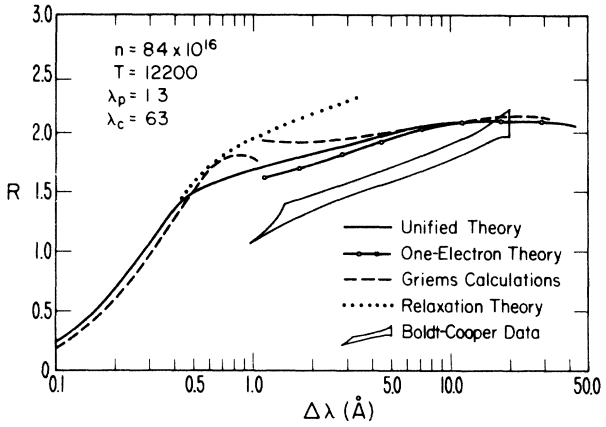

FIG. 2. Comparison of theoretical and experimental profiles relative to the asymptotic Holtsmark profile for $n = 8.4 \times 10^{16}$ cm^{-3} and $T = 12\ 200$ °K. The parameters λ_p and λ_c denote wavelengths (in Å) which correspond to the plasma frequency and the Weisskopf frequency, respectively.

is normalized; this cannot be done for the one-electron theory since it diverges in the line center.

The most restrictive approximation made in the derivation of the unified theory is the impact approximation (which we distinguish from the impact theory as discussed in Sec. VII B of II). The impact approximation assumes that two strong collisions never occur simultaneously and a weak collision occurring simultaneously with a strong one is negligible in comparison. This approximation should be valid when the duration time for strong collisions τ_s, is much less than the time between such collisions, $1/\nu_s$, where ν_s is the strong collision frequency. In Sec. VII B of II it was shown that $\tau_s \simeq 1/\Delta\omega_c$, where $\Delta\omega_c$ is the Weisskopf frequency for electrons. Therefore, we expect the unified theory to be valid over an entire line profile $0 \leq \hbar\Delta\omega < kT$ (the thermal energy kT provides an upper bound on classical-path methods) whenever $\nu_s \ll \Delta\omega_c$. Since $\nu_s \leq \Delta\omega_{1/2}$, where $\Delta\omega_{1/2}$ is the half-width of the observed line, this criterion is well satisfied for virtually all cases of interest.

To clearly illustrate the development of the unified theory and to avoid unnecessary mathematical complications, we will consider the case of the Lyman lines emitted by hydrogen atoms in a plasma. Calculations of the Lyman-α line are given to illustrate the results obtained by this method.

2. GENERAL THEORY

A. Basic Definitions

We will use the familiar quasistatic description of the ions in the plasma[3,4] and the Hamiltonian for an atom in a static ion field will be denoted by H_0. The plasma will contain N-electron perturb-

ers and the position and velocity of the jth perturber are denoted by $\vec{x}_j$ and $\vec{v}_j$, respectively. To simplify the mathematics, we will make use of the $6N$ vector

$$\vec{r} = (\vec{x}_1, \vec{v}_1, \vec{x}_2, \vec{v}_2, \ldots, \vec{x}_N, \vec{v}_N),$$

which denotes the positions and velocities of all electrons in the system. The Hamiltonian for the system is given by

$$H = H_0 + V(\vec{r}, t), \tag{1}$$

where $V(\vec{r}, t)$ denotes the electron-atom interaction which is produced when the electrons move past the atom on their classical trajectories (see Secs. VIII C and VIII D in I). This interaction potential can be expressed as a sum of terms containing an atomic operator multiplied by a function of electron variables. For example, the lowest-order approximation to the electron-ion interaction is the dipole term

$$V(\vec{r}, t) = e\vec{R} \cdot \vec{\mathcal{E}}(\vec{r}, t), \tag{2}$$

where $(-e\vec{R})$ is the atomic dipole operator and $\vec{\mathcal{E}}(\vec{r}, t)$ denotes the electric field generated by the electrons. This dipole expression is the most frequently used approximation to $V(\vec{r}, t)$ although for some problems one sometimes includes a quadrupole interaction. If the radiator should be an ion, the monopole term in the electron-ion interaction is included in the electron Hamiltonian when calculating the classical trajectory hence this term does not appear in $V(\vec{r}, t)$. To preserve generality, we will use the complete $V(\vec{r}, t)$ (without a monopole term) in the following derivation.

The time-development operator for the system may be written in an interaction representation defined by

$$T(\vec{r}, t) = \exp(-itH_0)U(\vec{r}, t), \tag{3}$$

where U is the solution of the differential equation (using $\hbar = 1$)

$$i\frac{\partial}{\partial t}U(\vec{r}, t) = \tilde{V}(\vec{r}, t)U(\vec{r}, t), \tag{4}$$

with the boundary condition $U(\vec{r}, 0) = 1$ and

$$\tilde{V}(\vec{r}, t) = \exp(itH_0)V(\vec{r}, t)\exp(-itH_0). \tag{5}$$

The only difference between the operator U defined above and the operator U_a defined by Eqs. (13) and (14) in II is in the no-quenching approximation which was used in conjunction with the latter; if this no-quenching approximation were applied to U, it would be identical to U_a.

We will consider radiative transitions from a group of initial states $|a\rangle$ to a group of final states $|b\rangle$ where $|a\rangle$ and $|b\rangle$ are H_0 eigenstates. For the Lyman lines of hydrogen (and for many other cases) the perturbation of the final state is negligible; that is, $\langle b|V|b'\rangle = 0$ or

$$\langle b|U|b'\rangle = \exp(-itE_b)\langle b|b'\rangle. \tag{6}$$

For cases where lower-state perturbation is not negligible this perturbation may be treated by means of the "doubled-atom" representation[3,4] or by tetradic notation.[5,8] Defining a frequency variable $\Delta\omega_{ab} = [\omega - (E_a - E_b)]$, the line shape is given by [2–4]

$$I(\omega) = (1/\pi)\mathrm{Re}\sum_{aa'b}(\vec{d}_{a'b}\cdot\vec{d}_{ba})\langle a|C(\Delta\omega_{ab})|a'\rangle\rho_{a'} \tag{7}$$

$$C(\Delta\omega_{ab}) = \int_0^\infty \exp(it\Delta\omega_{ab})F(t)dt, \tag{8}$$

where ρ is the atomic density matrix and $F(t)$ denotes the average of $U(\vec{r}, t)$ over perturber variables [except for the no-quenching approximation this function $F(t)$ is the same as the function $F(t)$ discussed in II]. Since H_0 is the Hamiltonian for an atom subjected to a static ion field, its eigenvalues E_a and E_b will depend on the ion field strength; the complete line profile is obtained by averaging $I(\omega)$ over ion fields in the usual manner.[2–5]

To make the function $F(t)$ more explicit, we define a normalized probability function $Q(\vec{r})$ for the electron perturbers and $F(t)$ is given by

$$F(t) = \int Q(\vec{r})U(\vec{r}, t)d\vec{r}. \tag{9}$$

This average over $\vec{r}$ denotes the average over electron positions and velocities; that is, $Q(\vec{r})$ may be given by

$$Q(\vec{r}) = P(\vec{x}_1, \ldots, \vec{x}_N)W(\vec{v}_1, \ldots, \vec{v}_N), \tag{10}$$

where $P(\vec{x})$ and $W(\vec{v})$ denote position and velocity distribution functions [compare Eq. (40) in II].

We next define a function $F(\vec{r}, t)$ by

$$F(\vec{r}, t) = Q(\vec{r})U(\vec{r}, t) \tag{11}$$

so that

$$F(t) = \int F(\vec{r}, t)d\vec{r}. \tag{12}$$

From Eq. (4) we obtain a dynamical equation for $F(\vec{r}, t)$

$$i\frac{\partial}{\partial t}F(\vec{r}, t) = \tilde{V}(\vec{r}, t)F(\vec{r}, t). \tag{13}$$

In Sec. 2B we will show how this differential equation may be transformed into a dynamical equation for $F(t)$.

B. Zwanzig Projection Operator Technique

In this section the projection-operator technique developed by Zwanzig[9] will be used to derive a dynamical equation for $F(t)$. To make use of this method, we define a projection operator $\mathcal{P}$ in terms of its operation on an arbitrary function, $f(\vec{r})$, of electron variables

$$\mathcal{P}f(\vec{r}) = Q(\vec{r})\int f(\vec{r}')d\vec{r}'. \tag{14}$$

From this definition we see that any operator which does not depend on electron variables (e.g., H_0, $\vec{R}$, etc.) will commute with $\mathcal{P}$. This projection operator is essentially the same as the projection operator used in the relaxation theory (see Sec. II C in Ref. 5) although it should not be confused with the projection operator P used in II.

We next define functions $F_1(\vec{r},t)$ and $F_2(\vec{r},t)$ by

$$F_1(\vec{r},t) = \mathcal{P}F(\vec{r},t), \quad F_2(\vec{r},t) = (1-\mathcal{P})F(\vec{r},t), \tag{15}$$

and $$F(\vec{r},t) = F_1(\vec{r},t)+F_2(\vec{r},t). \tag{16}$$

Operating on Eq. (13) with $\mathcal{P}$ and $(1-\mathcal{P})$ we obtain the differential equations

$$i\frac{\partial}{\partial t}F_1(\vec{r},t) = \mathcal{P}\tilde{V}(\vec{r},t)[F_1(\vec{r},t)+F_2(\vec{r},t)], \tag{17}$$

$$i\frac{\partial}{\partial t}F_2(\vec{r},t) = (1-\mathcal{P})\tilde{V}(\vec{r},t)[F_1(\vec{r},t)+F_2(\vec{r},t)]. \tag{18}$$

Equation (18) is easily solved to yield

$$F_2(\vec{r},t) = G(\vec{r};t,0)F_2(\vec{r},0) - i\int_0^t G(\vec{r};t,t')(1-\mathcal{P})\tilde{V}(\vec{r},t')F_1(\vec{r},t')dt', \tag{19}$$

where $$G(\vec{r};t,t') = \mathcal{O}\ \exp[-i\int_{t'}^{t}(1-\mathcal{P})\tilde{V}(\vec{r},s)ds], \tag{20}$$

and $\mathcal{O}$ is a time-ordering operator.[10] From Eq. (11) we see that $F(\vec{r},0)=Q(\vec{r})$ hence $F_2(\vec{r},0)=0$ and Eq. (19) becomes

$$F_2(\vec{r},t) = -i\int_0^t G(\vec{r};t,t')(1-\mathcal{P})\tilde{V}(\vec{r},t')F_1(\vec{r},t')dt'. \tag{21}$$

Substituting this result into Eq. (17) we obtain an integrodifferential equation for $F_1(\vec{r},t)$:

$$i\frac{\partial}{\partial t}F_1(\vec{r},t) = \mathcal{P}\,\tilde{V}(\vec{r},t)F_1(\vec{r},t) - i\int_0^t \mathcal{P}\tilde{V}(\vec{r},t)G(\vec{r};t,t')(1-\mathcal{P})\tilde{V}(\vec{r},t')F_1(\vec{r},t')dt'.$$

Integrating this equation over $\vec{r}$, and noting from Eqs. (12), (14), and (15) that $F_1(\vec{r},t)=Q(\vec{r})F(t)$, we obtain an equation for $F(t)$,

$$i\frac{\partial}{\partial t}F(t) = \langle\tilde{V}(t)\rangle F(t) - i\int_0^t \langle\tilde{V}(t)G(t,t')(1-\mathcal{P})\tilde{V}(t')\rangle F(t')dt', \tag{23}$$

where the bracket $\langle\cdots\rangle$ denotes the weighted average over $\vec{r}$; for example, for some arbitrary operator $A(\vec{r},t)$ we have

$$\langle A(t)\rangle = \int A(\vec{r},t)Q(\vec{r})d\vec{r}. \tag{24}$$

Note that $Q(\vec{r})$ must be written to the right of $A(\vec{r},t)$ in case $A(\vec{r},t)$ contains some $\mathcal{P}$ operators.

If the distribution of electrons described by $Q(\vec{r})$ is assumed to be spherically symmetric about the atom, then $\langle V(t)\rangle = 0$ (recall that for radiating ions, the monopole term, which does not have this property, is not included in V) and Eq. (23) becomes

$$\frac{\partial}{\partial t}F(t) = -\int_0^t \langle\tilde{V}(t)G(t,t')\tilde{V}(t')\rangle F(t')dt'. \tag{25}$$

This equation can be further simplified by means of the identity

$$\langle\tilde{V}(t)G(t,t')\tilde{V}(t')\rangle = \exp(it'H_0)\langle\tilde{V}(t-t')G(t-t',0)\tilde{V}(0)\rangle\exp(-it'H_0) \tag{26}$$

derived in Appendix A [see Eq. (A12)]. Using this identity and the notation $G(t-t',0)=G(t-t')$ we have

$$\frac{\partial}{\partial t}F(t) = -\int_0^t \exp(it'H_0)\langle\tilde{V}(t-t')G(t-t')\tilde{V}(0)\rangle\exp(-it'H_0)F(t')dt'. \tag{27}$$

This is a general equation for $F(t)$ which will be solved by Fourier transforms, in Sec. 2C to provide a general expression for the line shape. In later sections we will discuss some more useful approximate results.

C. General Expression for the Line Shape

To obtain a general expression for the line shape, it is convenient to consider an interaction representation defined by

$$\tilde{F}(t) = \exp(-itH_0)F(t). \tag{28}$$

Using this definition, Eq. (27) provides

$$i\frac{\partial}{\partial t}\tilde{F}(t) = H_0\tilde{F}(t) - i\int_0^t \exp[-i(t-t')H_0]\langle\tilde{V}(t-t')G(t-t')\tilde{V}(0)\rangle\tilde{F}(t')dt'. \tag{29}$$

To calculate the function $C(\Delta\omega_{ab})$ defined in Eq. (8), we note that

$$\langle a|C(\Delta\omega_{ab})|a'\rangle = \langle a|\int_0^\infty \exp\{it(\omega+E_b)\}\tilde{F}(t)dt|a'\rangle = \langle a|\mathfrak{F}(\omega+E_b)|a'\rangle, \tag{30}$$

where the transform $\mathfrak{F}(\omega+E_b)$ is thus defined. Multiplying Eq. (29) by $\exp\{it(\omega+E_b)\}$ and integrating over t we obtain

$$-i\tilde{F}(0)+(\omega+E_b)\mathfrak{F}(\omega+E_b) = H_0\mathfrak{F}(\omega+E_b)+\mathfrak{L}(\omega+E_b-H_0)\mathfrak{F}(\omega+E_b), \tag{31}$$

where

$$\mathfrak{L}(\omega+E_b-H_0) = -i\int_0^\infty \exp[it(\omega+E_b-H_0)]\langle\tilde{V}(t)G(t)\tilde{V}(0)\rangle dt. \tag{32}$$

Solving Eq. (31) for $\mathfrak{F}(\omega+E_b)$ and substituting this result, via Eq. (30), into Eq. (7) we obtain

$$I(\omega) = -(1/\pi)\,\mathrm{Im}\sum_{aa'b}(\vec{d}_{a'b}\cdot\vec{d}_{ba})\langle a|K(\omega)|a'\rangle\rho_{a'}, \tag{33}$$

where $K(\omega)$ is a resolvent operator defined by

$$K(\omega) = [(\omega+E_b-H_0)-\mathfrak{L}(\omega+E_b-H_0)]^{-1}. \tag{34}$$

To calculate a line profile using Eq. (33), it is first necessary to invert the matrix $[(\omega+E_b-H_0)-\mathfrak{L}(\omega+E_b-H_0)]$. In most cases it is sufficient to consider only initial states when performing this matrix inversion; that is, we need only invert a matrix whose matrix elements are given by

$$\langle a|[(\omega+E_b-H_0)-\mathfrak{L}(\omega+E_b-H_0)]|a'\rangle = \Delta\omega_{ab}\delta_{a,a'}-\langle a|\mathfrak{L}(\Delta\omega_{ab})|a'\rangle \tag{35}$$

for all initial states $|a\rangle$ and $|a'\rangle$. Since we are ignoring ground-state interaction this result is obtained by making the no-quenching approximation discussed in Secs. I B and VII B in II. The inverse of Eq. (35) will give the resolvent matrix $K(\omega)$ whose matrix elements are required by Eq. (33).

Equations (33) and (34) provide a very general expression for a line profile (to the extent that final-state perturbations are negligible) which would correctly describe the line profile from the line center to the quasistatic wings if we could evaluate the operator

$$\mathfrak{L}(\Delta\omega_{ab}) = -i\int_0^\infty \exp(it\Delta\omega_{ab})\langle\tilde{V}(t)G(t)\tilde{V}(0)\rangle dt \tag{36}$$

in all generality. It has not been possible to do this as yet and this is the purpose of the approximate treatment which follows.

3. UNIFIED LINE-SHAPE APPROXIMATION

The fundamental approximation which we shall use in deriving the unified line-shape expression is the impact approximation. This approximation was discussed in detail in Secs. III B and VII B of II and we will simply outline its properties as they pertain to the present problem.

The impact approximation as we use it simply states that (1) strong collisions do not overlap in time,

(2) a weak collision overlapping a strong one may be neglected in comparison, and (3) weak collisions may be treated by second-order perturbation theory. It should be noted that we make a distinction between the impact approximation and the impact theory; the impact theory contains the impact approximation as well as other approximations (e.g., the completed collision assumption).

The interaction potential $\tilde{V}(\vec{r},t)$ will in general be given by a sum of interactions $\tilde{V}(\vec{r}_j,t)$ where $\vec{r}_j$ refers to the position and velocity of the jth electron [compare Eq. (22) of II]

$$\tilde{V}(\vec{r},t)=\sum_j \tilde{V}(\vec{r}_j,t). \tag{37}$$

Using the impact approximation, the propagators $G(\vec{r};t,t')$ and $U(\vec{r};t,t')$ take a product form

$$G(\vec{r};t,t')=\mathcal{O}_0\Pi_j G(\vec{r}_j;t,t'), \tag{38}$$

$$U(\vec{r};t,t')=\mathcal{O}_0\Pi_j U(\vec{r}_j;t,t'), \tag{39}$$

where $$G(\vec{r}_j;t,t')=\mathcal{O}\exp[-i\int_{t'}^{t}(1-\mathcal{P})\tilde{V}(\vec{r}_j,s)ds], \tag{40}$$

$$U(\vec{r}_j;t,t')=\mathcal{O}\exp[-i\int_{t'}^{t}\tilde{V}(\vec{r}_j,s)ds], \tag{41}$$

and $\mathcal{O}_0$ is a time-ordering operator which keeps the interactions in chronological order; the proof of Eq. (39) is given in Sec. III B of II and the proof of Eq. (38) is an obvious extension.

We next assume that each interaction $V(\vec{r}_j,t)$ is statistically independent of the others. That is, the electrons will be replaced by shielded quasiparticles.[11] For most problems it is sufficient to use Debye shielded electrons although, if plasma oscillations have an influence on the broadening, one may have to use a dynamic shielding.[10,12]

In Appendix B it is shown that when these approximations are applied to the factor $\langle\tilde{V}(t)G(t,t')\tilde{V}(t')\rangle$ all of the projection operators vanish and this factor reduces to

$$\langle\tilde{V}(t)G(t,t')\tilde{V}(t')\rangle=\sum_j\langle\tilde{V}_j(t)U_j(t,t')\tilde{V}_j(t')\rangle, \tag{42}$$

where $\tilde{V}_j(t)$ and $U_j(t,t')$ refer to $\tilde{V}(\vec{r}_j,t)$ and $U(\vec{r}_j;t,t')$ under the average. Since each of these terms is the same under the average (i.e., $\vec{r}_j$ is just a dummy variable) we may write

$$\langle\tilde{V}(t)G(t,t')\tilde{V}(t')\rangle=N\langle\tilde{V}_1(t)U_1(t,t')\tilde{V}_1(t')\rangle, \tag{43}$$

where N denotes the total number of interactions. Substituting this result into Eq. (36) we obtain

$$\begin{aligned}\mathcal{L}(\Delta\omega_{ab})&=-iN\int_0^\infty\exp(it\Delta\omega_{ab})\langle\tilde{V}_1(t)U_1(t,0)\tilde{V}_1(0)\rangle dt\\&=N\int_0^\infty\exp(it\Delta\omega_{ab})\frac{d}{dt}\langle U_1(t,0)\tilde{V}_1(0)\rangle dt\\&=-i\Delta\omega_{ab}N\int_0^\infty\exp(it\Delta\omega_{ab})\langle U_1(t,0)\tilde{V}_1(0)\rangle dt.\end{aligned} \tag{44}$$

Using the results discussed in Appendix A, the matrix elements $\langle a|\mathcal{L}(\Delta\omega_{ab})|a'\rangle$, as required by Eq. (35), are obtained from

$$\begin{aligned}\mathcal{L}(\Delta\omega_{ab})&=-i\Delta\omega_{ab}N\int_0^\infty\exp(it\Delta\omega_{a'b})\langle U_1(0,-t)\tilde{V}_1(-t)\rangle dt\\&=\Delta\omega_{ab}N\int_0^\infty\exp(it\Delta\omega_{a'b})\frac{d}{dt}\langle U_1(0,-t)\rangle dt\\&=-\Delta\omega_{ab}N-i\Delta\omega_{ab}\Delta\omega_{a'b}N\int_0^\infty\exp(it\Delta\omega_{a'b})\langle U_1(0,-t)\rangle dt\\&=-i\Delta\omega_{ab}\Delta\omega_{a'b}N\int_0^\infty\exp(it\Delta\omega_{a'b})\langle U_1(0,-t)-1\rangle dt\\&=-i\Delta\omega_{ab}\Delta\omega_{a'b}N\int_0^\infty\exp(it\Delta\omega_{ab})\langle U_1(t,0)-1\rangle dt.\end{aligned} \tag{45}$$

Since the one-body spatial distribution function is given by $P_1(x_1)=n/N$ where n is the electron density,[13] $\mathfrak{L}(\Delta\omega)$ may now be given by

$$\langle a|\mathfrak{L}(\Delta\omega_{ab})|a'\rangle = -i\Delta\omega_{ab}\Delta\omega_{a'b}\int_0^\infty \exp(it\Delta\omega_{ab})\langle a|F^{(1)}(t)|a'\rangle\,, \tag{46}$$

where

$$F^{(1)}(t) = n\int d\vec{x}_1\int d\vec{v}_1 W(v_1)[U(\vec{x}_1,\vec{v}_1;t,0)-1]\,, \tag{47}$$

and $W(v_1)$ denotes a velocity distribution function [compare Eq. (10)].

If the influence of the ion field in $\tilde{V}(t)$ is treated in the approximate manner discussed in II, then the operator $F^{(1)}(t)$ is the same as the operator $F_1(t)$ discussed in II. This operator has been evaluated by numerical methods[8] (neglecting the time ordering in U_1) hence this operator may be regarded as known and the line shape may be obtained from Eqs. (33) and (34) by familiar matrix methods. The results of such a calculation will be discussed in Sec. V.

4. COMPARISON WITH OTHER THEORIES

A. Second-Order Results

Most line broadening theories provide expressions for the line shape which are formally the same as Eqs. (33) and (34). From the results of such work it is well established that a second-order (in $\tilde{V}$) approximation to $\mathfrak{L}(\Delta\omega_{ab})$ will generally be valid in the line center if strong collisions are properly treated by impact parameter cutoffs. Cases for which the second-order approximation is not sufficient will be discussed further in Sec. 4 B. For the present, we will consider a second-order approximation to $\mathfrak{L}(\Delta\omega_{ab})$ which may then be compared with the second-order results of the impact and relaxation theories. To obtain this expression we expand $U_1(t)$ in powers of $\tilde{V}_1$ [see Eq. (44)] and, since $\mathfrak{L}(\Delta\omega_{ab})$ is already second order in $\tilde{V}_1$, we retain only the zeroth-order term in the U_1 expansion; that is, U_1 is simply replaced by unity. It may be argued that strong collisions, for which U_1 may not be replaced by 1, cause U_1 to oscillate rapidly and $\mathfrak{L}(\Delta\omega_{ab})$ is effectively reduced to zero; this is the usual justification for strong collision cutoffs (compare Sec. VII C in I). When U_1 is replaced by 1, we obtain the second-order result

$$\mathfrak{L}(\Delta\omega_{ab}) \simeq \mathfrak{K}(\Delta\omega_{ab}), \tag{48}$$

where

$$\mathfrak{K}(\Delta\omega_{ab}) = -i\int_0^\infty \exp(it\Delta\omega_{ab})\langle\tilde{V}(t)\tilde{V}(0)\rangle dt\,. \tag{49}$$

Comparing with Eqs. (5), (6), and (23) of Ref. 6, we see that the above results are identical with the second-order results of the relaxation theory. However, note that in Eq. (23) of Ref. 6, $\tilde{V}(t)$ is replaced by $V(t)$; for the Ly-α line of hydrogen which was calculated in Ref. 6, the difference between $\tilde{V}(t)$ and $V(t)$ is unimportant. While this difference may be unimportant for some hydrogen lines, in general it is necessary to retain the exponentials in $V(t)$ as has been done in the present derivation. Since the relaxation theory is known to be valid in the line center when strong collisions are relatively unimportant this comparison indicates that the second-order results stated in Eqs. (48) and (49) are also valid for such cases. That is, when second-order calculations are appropriate, U_1 is simply replaced by unity.

B. Comparison with Impact Theory

Since the impact theory is the classical-path theory most frequently used in describing the line center, and since the second-order results derived in Sec. 4 A did not formally reproduce the results of the impact theory, we will next discuss a comparison with this theory.

If we substitute Eq. (43) into Eq. (25) or Eq. (27) we obtain an integrodifferential equation for $F(t)$ which will produce the results of the unified theory

$$\begin{aligned}\frac{\partial F(t)}{\partial t} &= -N\int_0^\infty \langle\tilde{V}_1(t)U_1(t,t')\tilde{V}_1(t')\rangle F(t')dt' \\ &= -N\int_0^t \exp(it'H_0)\langle\tilde{V}_1(t-t')U_1(t-t',0)\tilde{V}_1(0)\rangle\exp(-it'H_0)F(t')dt'.\end{aligned} \tag{50}$$

If this equation were solved by Fourier transforms we would obtain the results discussed in Sec. 3.

Changing variables from t' to $s=(t-t')$ in Eq. (50) we obtain

$$i\frac{\partial F(t)}{\partial t} = \exp(itH_0)\int_0^t h(s)\exp(-itH_0)F(t-s)ds\,, \tag{51}$$

where $$h(s) = -iN\exp(-isH_0)\langle\tilde{V}_1(s)U_1(s,0)\tilde{V}_1(0)\rangle\exp(isH_0)\,. \tag{52}$$

To obtain the results of the impact theory we first assume that there is some correlation time τ_p such that $\langle\tilde{V}_1(s)U_1(s,0)\tilde{V}_1(0)\rangle$ vanishes when $s>\tau_p$; for electron perturbers $\tau_p = 1/\omega_p$ (the average duration of a collision). We next assume that we need only consider times much longer than τ_p when calculating $F(t)$; that is, $t \gg \tau_p$. In this case $h(s)$ goes to zero long before s is on the order of t, hence we may replace $F(t-s)$ by $F(t)$ and the upper limit on the s integral may be extended to infinity. In this manner Eq. (51)

$$i\frac{\partial F(t)}{\partial t} = [\exp(itH_0)\mathcal{K}\exp(-itH_0)]F(t)\,, \tag{53}$$

where $$\mathcal{K} = -iN\int_0^\infty \exp(-isH_0)\langle\tilde{V}_1(s)U_1(s,0)\tilde{V}_1(0)\rangle\exp(isH_0)ds\,. \tag{54}$$

Using the results discussed in Appendix A, we have

$$\mathcal{K} = -iN\int_0^\infty\langle\tilde{V}_1(0)U_1(0,-s)\tilde{V}(-s)\rangle ds = N\int_0^\infty\frac{d}{ds}\langle\tilde{V}_1(0)U_1(0,-s)\rangle ds \tag{55}$$

$$= N\langle\tilde{V}_1(0)U_1(0,-\infty)\rangle = n\int\int d\vec{x}_1 d\vec{v}_1 W(v_1)V(\vec{x}_1,\vec{v}_1,0)U(\vec{x}_1\vec{v}_1;0,-\infty)\,,$$

where the one-body average is written explicitly in Eq. (47). We must now transform from $\vec{x}_1$ and $\vec{v}_1$ to the collision variables discussed in the Appendix to II. As in Sec. VI of II, we will denote the average over impact parameters, velocities, and angles by a subscript av, and Eq. (55) is written

$$\begin{aligned}\mathcal{K} &= n\int_{-\infty}^{\infty} dt_0[V_1(t_0)\mathcal{O}\exp\{-i\int_{-\infty}^{0}\tilde{V}_1(s+t_0)ds\}]_{\rm av}\\ &= n\int_{-\infty}^{\infty} dt_0[V_1(t_0)\mathcal{O}\exp\{-i\int_{-\infty}^{t_0}\tilde{V}_1(t)dt\}]_{\rm av}\\ &= in\int_{-\infty}^{\infty} dt_0(d/dt_0)[\mathcal{O}\exp\{-i\int_{-\infty}^{t_0}\tilde{V}_1(t)dt\}]_{\rm av}\\ &= in[\mathcal{O}\exp\{-i\int_{-\infty}^{\infty}\tilde{V}_1(t)dt\}-1]_{\rm av}\\ &= in[S_1-1]_{\rm av}\,,\end{aligned} \tag{56}$$

where S_1 denotes the S matrix for a binary collision.

Comparing Eqs. (53) and (56) with Eqs. (38), (42), and (43) of Ref. 3 we see that these results are exactly the results of the impact theory.

The relaxation equation for $F(t)$ in the unified theory, Eq. (50), is non-Markovian because the kernel $\langle\tilde{V}_1(t)U_1(t,t')\tilde{V}_1(t')\rangle$ exhibits a memory effect for $(t-t')<\tau_p$. That is, the state of the system at the time t depends on its state at some earlier times t'. Since the system has a relaxation time on the order of τ_p, this memory is lost after a time τ_p and the equation becomes Markovian. In deriving the results of the impact theory, the essential step was the "Markovianization" of Eq. (51), namely, the assumption that t would always be much larger than τ_p. This indicates that the impact and the unified theories will be identical for long times of interest $t>\tau_p$.

Since the Markov approximation breaks down when $t<\tau_p$ we may expect the impact theory to break down in the same region. This does in fact occur unless one modifies the impact theory with a Lewis cutoff (see Sec. VII C in II). The purpose of the Lewis cutoff is to put the non-Markovian behavior back into $F(t)$ in an approximate manner, thereby extending the region of validity of the impact theory.

The results of the impact theory could also have been obtained directly from $\mathfrak{L}(\Delta\omega_{ab})$ by setting $\Delta\omega_{ab}$ to zero in Eq. (44). This would be justified if $\tau_p\Delta\omega_{ab}\ll 1$ since the factor $\langle\tilde{V}_1(t)U_1(t,0)V_1(0)\rangle$ vanishes for $t>\tau_p$. If we take the "time of interest" as being $1/\Delta\omega_{ab}$ (or $1/\Delta\omega_{a'b}$), then this procedure is valid for times of interest longer than τ_p and it breaks down for shorter times of interest. Comparing Eqs. (44) and (54) we see that the matrix elements $\langle a|\mathfrak{L}(0)|a'\rangle$ are the same as $\langle a|\mathcal{K}|a'\rangle$ [the exponentials in Eq. (54) are unimportant when $t\Delta\omega_{ab}\ll 1$ and $t\Delta\omega_{a'b}\ll 1$]. We thus obtain $\mathfrak{L}(0) = in[S_1-1]_{\rm av}$ which is again the result of the impact theory.

From the above discussion we may conclude that the only essential difference between the impact theory

and the unified theory lies in the treatment of non-Markovian effects. The unified theory, and the quantum-mechanical relaxation theory, treat these effects without approximation by using a non-Markovian equation for $F(t)$; in the impact theory these effects are treated approximately by means of the Lewis cutoff. The close agreement between these two methods for hydrogen[6] indicates that the Lewis cutoff procedure provides a good approximation to these non-Markovian effects for cases where strong collisions are not too important.

If strong collisions dominate the broadening, and if the duration of the collisions is short compared to the time between collisions (validity criterion for the impact approximation), the S-matrix treatment should be quite good. The impact and the unified theories will be essentially identical for such cases.

The unified theory should also be useful for cases where both strong and weak collisions are equally important because the strong collisions are treated by a full exponential (essentially an S matrix) and, at the same time, the non-Markovian aspects of the weaker interactions are retained. The utility of the unified theory in such cases has yet to be demonstrated by practical calculations.

C. Line Wings

In this section we will consider $F(t)$ in the line wings where t is very small. For this purpose it is convenient to obtain a general expression for $F(t)$ which is then investigated in the $t \to 0$ limit. The general expression for $F(t)$ is obtained by first integrating Eq. (50) over t and using the Dirichlet integral formula (see p. 147 of Ref. 14),

$$\int_a^b \int_a^y f(x,y)\,dx\,dy = \int_a^b \int_x^b f(x,y)\,dy\,dx\,, \tag{57}$$

to obtain

$$F(t) = F(0) - \int_0^t \Gamma(t,t')F(t')\,dt'\,, \tag{58}$$

where

$$\Gamma(t,t') = N\int_{t'}^{t} \langle \tilde{V}_1(t'')U_1(t'',t')\tilde{V}_1(t')\rangle\,dt''\,. \tag{59}$$

Equation (58) is a Volterra integral equation of the second kind which has the unique solution[14]

$$F(t) = F(0)\Big[1 - \int_0^t \Gamma(t,t')\,dt + \cdots + (-1)^n \int_0^t \int_0^{t_1} \cdots \int_0^{t_{n-1}} \Gamma(t,t_1)\Gamma(t_1,t_2)\cdots\Gamma(t_{n-1},t_n)\,dt_n \cdots dt_1 + \cdots\Big]. \tag{60}$$

Since we are interested in $F(t)$ in the limit of small t, we will consider the lowest-order approximation to this general solution. Using $F(0) = 1$ we have, for small t,

$$\begin{aligned} F(t) &= 1 - N\int_0^t \int_0^{t'} \langle \tilde{V}_1(t')U_1(t',t'')\tilde{V}_1(t'')\rangle\,dt''\,dt' \\ &= 1 + iN\int_0^t \int_0^{t'} \frac{d}{dt''}\langle \tilde{V}_1(t')U_1(t',t'')\rangle\,dt''\,dt' \\ &= 1 - iN\int_0^t \langle \tilde{V}_1(t')U_1(t',0)\rangle\,dt' \\ &= 1 + N\int_0^t \frac{d}{dt'}\langle U_1(t',0)\rangle\,dt' \\ &= 1 + N\langle U_1(t,0) - 1\rangle\,. \end{aligned} \tag{61}$$

This is exactly the result obtained by the one-electron theory [see Eqs. (42) and (51) of II]. Since the one-electron theory is known to be valid in the wings, it is obvious that the unified theory is similarly valid.

5. CALCULATIONS

The Ly-α line of hydrogen was calculated for two temperature-density cases which correspond to experiments performed by Elton and Griem[15] and by Boldt and Cooper.[16] The operator $\mathfrak{L}(\Delta\omega_{ab})$ was calculated from Eq. (61) using the $F^{(1)}(t)$ functions discussed in Ref. 8 and the ion micro-

field average was performed using the distribution functions given by Hooper.[17] The results of these calculations are shown in Figs. 1 and 2 where we have plotted the ratio $R(\omega)$ between the Stark profile $I(\omega)$ and the asymptotic Holtsmark profile $I_H(\omega)$,

$$R(\omega) = I(\omega)/I_H(\omega) \tag{62}$$

$$I_H(\omega) = \sqrt{3}\,\pi n(\hbar/m)^{3/2}(1/\Delta\omega)^{5/2}, \tag{63}$$

against the wavelength separation $\Delta\lambda$ measured from the center of the natural line. In these figures we have also plotted calculations obtained by the relaxation theory,[5,6,18] impact theory, and line wing results obtained by Griem,[19] and the relevant experimental results.

Since the older impact-theory results which we have plotted do not agree with the unified theory in the vicinity of 1 Å, we have also made impact-theory calculations using the most recent work of Kepple and Griem[20]; these calculations have not been plotted because they lie precisely on top of the unified theory for $\Delta\lambda \lesssim 2\lambda_p$ (where λ_p is the wavelength which corresponds to the plasma frequency). The relaxation-theory profiles do not agree with the unified theory for $\Delta\lambda > 1$ Å because strong collisions were not treated properly in the relaxation theory. If a strong collision cutoff is made in the relaxation theory,[6] the resulting profile lies exactly on the unified theories results for $\Delta\lambda \lesssim 2\lambda_p$. This excellent agreement indicates that the unified theory is indeed correct in the line center, at least to the extent that the strong collision cutoff procedure is valid (in these calculations we have cut off at $\lambda = \hbar/mv$, the electron de-Broglie wavelength).

The results of the one-electron theory were included to show that the unified theory approaches the one-electron theory asymptotically in the line wings. We note in passing that both theories approach the asymptote $R = 2$ for $\Delta\lambda \gtrsim \lambda_C$ [λ_C is the wavelength which corresponds to the Weisskopf frequency defined in Eq. (85) of II].

There is some asymmetry between the red and blue wings of the line profile hence we have plotted an average of these wings in Figs. 1 and 2. We have not made any asymmetry studies because quadrupole interactions and quadratic ion Stark effect, which may influence asymmetries,[19] were not included in the calculations.

The agreement between theory and experiment is fair in Fig. 1 and rather poor in Fig 2. The agreement in Fig. 2 would be considerably improved if the experimental data were raised slightly as Griem has suggested.[19]

It should be noted that the unified theory calculations shown in Figs. 1 and 2 do not account for time ordering in $U_1(t, 0)$. This is due to the fact that we used $F^{(1)}(t)$ functions which were originally derived for use in the line wings where this ordering is negligible (see Sec. III C of II). This should not make any difference for hydrogen because it is known that a second-order theory is adequate in the line center and, as was shown in Sec. IV A, the second-order theory is obtained by setting U_1 to unity.

APPENDIX A

Since the perturbation described by $V(t)$ is a stationary process,[6,7] we have the familiar identity

$$\langle V(t)V(t_1+t)\cdots V(t_n+t)\rangle = \langle V(0)V(t_1)\cdots V(t_n)\rangle . \tag{A1}$$

That is, the average is invariant under time translation. If the above identity is applied to each member of a product of averages we obtain relations like

$$\langle V(t)V(t_1+t)\rangle\langle V(t_2+t)\cdots V(t_n+t)\rangle = \langle V(0)V(t_1)\rangle\langle V(t_2)\cdots V(t_n)\rangle . \tag{A2}$$

Using the projection operator $\mathcal{P}$ the above equation may be written

$$\langle V(t)V(t_1+t)\,\mathcal{P}\,V(t_2+t)\cdots V(t_n+t)\rangle = \langle V(0)V(t_1)\mathcal{P}V(t_2)\cdots V(t_n)\rangle . \tag{A3}$$

After a moments reflection it is also obvious that we may insert any function (or functions) of $\mathcal{P}$ among the V operators without altering this time translation invariance; for example,

$$\langle V(t)f(\mathcal{P})V(t_1+t)\,g(\mathcal{P})V(t_2+t)\cdots V(t_n+t)\rangle = \langle V(0)f(\mathcal{P})V(t_1)\,g(\mathcal{P})V(t_2)\cdots V(t_n)\rangle, \tag{A4}$$

where f and g are arbitrary functions of $\mathcal{P}$. In particular, we are interested in relations of the form

$$\langle V(t)(1-\mathcal{P})V(t_1+t)\,(1-\mathcal{P})V(t_2+t)\cdots(1-\mathcal{P})V(t_n+t)\rangle = \langle V(0)(1-\mathcal{P})V(t_1)(1-\mathcal{P})V(t_2)\cdots(1-\mathcal{P})V(t_n)\rangle . \tag{A5}$$

If we consider the interaction representation in which we have

$$\tilde{V}(t) = \exp(itH_0)V(t)\exp(-itH_0), \tag{A6}$$

the above identities are slightly altered. Since H_0 does not depend on electron variables, the exponentials $\exp(itH_0)$ are not influenced by the average and Eq. (A1) may easily be extended to

$$\langle \tilde{V}(t)\tilde{V}(t_1+t)\cdots\tilde{V}(t_n+t)\rangle = \exp(itH_0)\langle \tilde{V}(0)\tilde{V}(t_1)\cdots\tilde{V}(t_n)\rangle \exp(-itH_0). \tag{A7}$$

Since H_0 commutes with $\mathcal{P}$ we also have

$$\langle \tilde{V}(t)f(\mathcal{P})\tilde{V}(t_1+t)g(\mathcal{P})\tilde{V}(t_2+t)\cdots\tilde{V}(t_n+t)\rangle = \exp(itH_0)\langle \tilde{V}(0)f(\mathcal{P})\tilde{V}(t_1)g(\mathcal{P})\tilde{V}(t_2)\cdots\tilde{V}(t_n)\rangle \exp(-itH_0), \tag{A8}$$

where f and g are arbitrary functions of $\mathcal{P}$. The equation analogous to Eq. (A5) is

$$\langle \tilde{V}(t)(1-\mathcal{P})\tilde{V}(t_1+t)(1-\mathcal{P})\tilde{V}(t_2+t)\cdots(1-\mathcal{P})\tilde{V}(t_n+t)\rangle$$
$$= \exp(itH_0)\langle \tilde{V}(0)(1-\mathcal{P})\tilde{V}(t_1)(1-\mathcal{P})\tilde{V}(t_2)\cdots(1-\mathcal{P})\tilde{V}(t_n)\rangle \exp(-itH_0). \tag{A9}$$

The propagator $G(\vec{r};t,t')$ defined in Eq. (20) may, with a change of variables $s=s'+t'$, be written in the form

$$G(\vec{r};t,t') = \mathcal{O}\exp\Big[-i\int_0^{(t-t')}(1-\mathcal{P})\tilde{V}(s'+t')ds'\Big]$$
$$= 1+\sum_{n=1}^{\infty}\frac{(-i)^n}{n!}\int_0^{(t-t')}\int_0^{s_1}\cdots\int_0^{s_{n-1}}(1-\mathcal{P})\tilde{V}(s_1+t')\cdots(1-\mathcal{P})\tilde{V}(s_n+t')ds_n\cdots ds_1. \tag{A10}$$

If we consider the quantity $\langle \tilde{V}(t)G(t,t')\tilde{V}(t')\rangle$, we note that this quantity will be given by a sum of integrals over

$$\langle \tilde{V}(t)(1-\mathcal{P})\tilde{V}(s_1+t')(1-\mathcal{P})\tilde{V}(s_2+t')\cdots(1-\mathcal{P})\tilde{V}(s_n+t')\tilde{V}(t')\rangle$$

$$= \exp(it'H_0)\langle \tilde{V}(t-t')(1-\mathcal{P})\tilde{V}(s_1)(1-\mathcal{P})\tilde{V}(s_2)\cdots(1-\mathcal{P})\tilde{V}(s_n)\tilde{V}(0)\rangle \exp(-it'H_0), \tag{A11}$$

where we have used Eq. (A9). From this property of the terms in $\langle \tilde{V}(t)G(t,t')\tilde{V}(t')\rangle$ it is obvious that

$$\langle \tilde{V}(t)G(t,t')\tilde{V}(t')\rangle = \exp(it'H_0)\langle \tilde{V}(t-t')G(t-t',0)\tilde{V}(0)\rangle \exp(-it'H_0). \tag{A12}$$

APPENDIX B

Since the average interaction $\langle V(t)\rangle$ is assumed to vanish we have the identity

$$\langle \tilde{V}(t)G(t,t')V(t')\rangle = \langle \tilde{V}(t)G(t,t')(1-\mathcal{P})\tilde{V}(t')\rangle$$
$$= -i\frac{d}{dt'}\langle \tilde{V}(t)G(t,t')\rangle. \tag{B1}$$

We will henceforth concentrate on $\langle \tilde{V}(t)G(t,t')\rangle$ noting that $\langle \tilde{V}(t)G(t,t')\tilde{V}(t')\rangle$ is obtained from it by differentiation. Using Eqs. (37) and (38) we have

$$\langle \tilde{V}(t)G(t,t')\rangle = \sum_j \langle \tilde{V}_j \mathcal{O}_0 \prod_k G_k(t,t')\rangle, \tag{B2}$$

where $\tilde{V}_j(t)$ and $G_k(t,t')$ denote $\tilde{V}(\vec{r}_j,t)$ and $G(\vec{r}_k;t,t')$ under the average. Since each interaction is statistically independent of the others they may be averaged separately and we have

$$\langle \tilde{V}G\rangle = \sum_j \langle \tilde{V}_j \prod_{k<j}\langle G_k\rangle G_j \prod_{l>j}\langle G_l\rangle\rangle, \tag{B3}$$

where we have temporarily suppressed the time dependence for convenience of notation. In the series expansion of G_k we have 1 plus a series of terms each of which has a $(1-\mathcal{P})$ factor on the left. From the definition of $\mathcal{P}$ given in Eq. (13) it is obvious that

$$\langle (1-\mathcal{P})\text{factor}\rangle = \langle \text{factor}\rangle - \langle \text{factor}\rangle$$
$$= 0 \tag{B4}$$

hence
$$\langle G_k\rangle = 1 \tag{B5}$$

and Eq. (B3) becomes

$$\langle \tilde{V}G\rangle = \sum_j \langle \tilde{V}_j G_j\rangle$$
$$= N\langle \tilde{V}_1 G_1\rangle, \tag{B6}$$

where N denotes the total number of interactions (the average of $\tilde{V}_1 G_1$ is the same as the average of any other $\tilde{V}_j G_j$).

The factor G_1 still contains some projection op-

erators; to eliminate these we consider the second term in a series expansion of $N\langle \tilde{V}_1 G_1 \rangle$. This term has the form

$$N\langle \tilde{V}_1(1-\mathcal{P})\tilde{V}_1 \rangle = N\langle \tilde{V}_1\tilde{V}_1 \rangle - N\langle \tilde{V}_1 \rangle\langle \tilde{V}_1 \rangle . \quad \text{(B7)}$$

The one-body spatial distribution function is given by $P_1(x_1) = n/N$ where n is the electron density.[13] Using this function we have, for example,

$$\langle \tilde{V}_1(t)\tilde{V}_1(t') \rangle = (n/N)\int\int d\vec{x}_1 d\vec{v}_1 W(v_1) \times \tilde{V}(\vec{x}_1, \vec{v}_1, t)\tilde{V}(\vec{x}_1, \vec{v}_1, t'), \quad \text{(B8)}$$

where $W(v_1)$ is a velocity distribution function. It is thus apparant that $N\langle \tilde{V}_1\tilde{V}_1 \rangle \propto n$ whereas $N\langle \tilde{V}_1 \rangle\langle \tilde{V}_1 \rangle \propto n^2/N$, and in the limit $N \to \infty$ the second term is negligible. By an obvious extension of this argument one can show that the projection operators in G_1 produce terms which vanish in the limit $N \to \infty$ and, in this limit, we may replace $(1-\mathcal{P})\tilde{V}_1$ by $\tilde{V}_1$ in G_1. When this replacement is made we have

$$\langle \tilde{V}_1(t)G_1(t,t') \rangle = \langle \tilde{V}_1(t)U_1(t,t') \rangle \quad \text{(B9)}$$

and, using Eq. (B1),

$$\langle \tilde{V}_1(t)G_1(t,t')\tilde{V}_1(t') \rangle = \langle \tilde{V}_1(t)U_1(t,t')\tilde{V}_1(t') \rangle . \quad \text{(B10)}$$

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*And Joint Institute for Laboratory Astrophysics and Department of Physics and Astrophysics, University of Colorado, Boulder, Colo. 80302

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