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Charge-Density Fluctuations in Spectral Line Broadening*

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A method for describing the spectral line shapes for radiating atoms immersed in a plasma is developed without neglecting ion-electron interaction and without the static-ion assumption. Both the line center and the wings are investigated, and connection with previous work in these regions is made.

I. INTRODUCTION

The spectral lines of radiating atoms immersed in an equilibrium plasma are broadened due to the perturbation of the atom by both the ions and the electrons of the plasma (assuming for simplicity a two-component plasma). The problem of predicting the line shape for such radiation is difficult in general,[1] but is often simplified by reducing the calculation to one involving independent treatment of ion, electron, and atomic subsystems. Recent work[2-4] has accomplished this under the following assumptions: (i) ions may be considered as static, (ii) ion-electron interactions may be neglected, and (iii) electron-atom interactions may be treated by perturbation theory. The first two assumptions allow the introduction of an ion microfield function which yields the Stark broadening due to the average static ion field. This is not a weak interaction effect and may not be obtained by finite-order perturbation theory. The third assumption allows the electron broadening to be calculated from a "collision" operator, or "width and shift" operator calculated to second order in the atom-electron coupling. The ions and electrons are thus treated quite differently in their interaction with the atoms, since the strong static effect and weak dynamic, or "collisional" effect are two quite different approximations. In order for this description to be useful, the part of the line being described must be such that the radiation occurs in a time short compared to the time required for an ion to move significantly (i.e., across a Debye sphere). On the other hand, the time of radiation must be long compared to corresponding times for electron motion since static electron effects are not included in the collisional approximation. Fortunately, due to the large ratio of ion mass to electron mass, these conditions are met over an interesting portion of the line.

The description breaks down near the center of the line since this region corresponds to radiation over times long enough for the ions to move. Also, in the line wings the static electron effects begin to dominate, and again the theory fails. In the following, these two regions of failure are investigated. The line center and the wings are considered separately. Since the static-ion approximation is quite good from the wings to a region near the line center, it is desirable to retain the ion microfield function while obtaining corrections to the static broadening by including ion motion. This is accomplished without assumption on the ion-electron interactions. The result is formally similar to previous work with the difference that the collision operator depends on total field retarded and advanced autocorrelation functions rather than the corresponding electron field correlation functions. In addition, there is a term in the collision operator which tends to minimize the static effect very close to the center and maximize it farther from the center. Similar results are obtained in the line wings. There, however, the microfield function is that for the total field of the plasma, and therefore represents both static-ion and static-electron effects. Again the collision operator depends on the total field, retarded and advanced autocorrelation functions and a term which tends to adjust the total static effects. It is shown that the exact static result is obtained in the far wings.

The perturbation expansion for the collision operator is shown to be, in both cases, an expansion in the charge-density fluctuations. In terms of the charge-density fluctuations, it is found that the introduction of a microfield function leads to the subtraction of the corresponding static charge limit from the collision operator; that is, when the ion microfield is introduced, the static-ion part is subtracted out while in the case of the electron-ion microfield, the total static charge contribution to the collision operator is subtracted out. This is expected since the static charge contribution should not be counted both in the microfield and in the collision operator.

It is not known if the regions of validity of the two cases considered here overlap, and hence a form appropriate for some intermediate region may be required. In any case, these results generalize existing theories for the line center and wings to include ion-electron correlations, and ion motion, thereby extending their limits. The

real and imaginary parts of the collision operator are related to each other using Kramers-Kronig relations and to the exact dielectric constant for a two-component plasma. It is emphasized that practical calculations are possible in the random-phase approximation. If ion-electron correlations are neglected, the results here for the line center differ from those of Ref. 2 only by the ion-motion term which vanishes sufficiently far from the line center. (Strictly speaking, correlations are neglected in Ref. 2, but a uniform negative or positive background is assumed for each subsystem to maintain charge neutrality.)

II. LINE-SHAPE FUNCTION

The spectral line shape for dipole radiation from an atom in a bath of perturbers is given by[1]

$$I(\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty}dt\,e^{i\omega t}\langle\vec{d}\cdot\vec{d}(t)\rangle\ , \tag{2.1}$$

$$\langle dd(t)\rangle\equiv \mathrm{Tr}\rho\vec{d}\cdot\vec{d}(t)\ ,$$

where $d(t)$ is the Heisenberg operator $e^{iHt}\vec{d}e^{-iHt}$ (in units such that $\hbar=1$), and $\vec{d}=e\vec{R}$, the electric charge times the position of the atomic electron relative to the nucleus (we assume a hydrogenic atom).[5] The brackets indicate an equilibrium ensemble average over the system of atom and perturbers.[6] Since the average is invariant under time translations, and $\vec{d}$ is Hermitian, then

$$I(\omega)=\pi^{-1}\mathrm{Re}\int_0^{\infty}dt\,e^{i\omega t}\langle\vec{d}\cdot\vec{d}(t)\rangle\ . \tag{2.2}$$

We briefly summarize the basic ideas in existing work which is the basis for the generalization to be given here. Equation (2.2) may be expressed as

$$I(\omega)=\mathrm{Re}\frac{1}{\pi}\int_0^{\infty}dt\,e^{i\omega t}\langle\vec{d}\cdot\vec{D}(t)\rangle_a\ , \tag{2.3}$$

where now the brackets indicate an average over only the atomic subsystem. In passing from Eq. (2.2) to Eq. (2.3), it is assumed the ensemble is the product of a canonical ensemble for the atom and one for the perturbers.[7] The operator $\vec{D}(t)$ is the time-dependent atomic dipole operator, averaged over the perturbers

$$\vec{D}(t)\equiv\langle\vec{d}(t)\rangle_p. \tag{2.4}$$

The transform in Eq. (2.3) is performed, with the result

$$I(\omega)=\mathrm{Re}(1/\pi)\langle\vec{d}\vec{D}(\omega)\rangle_a\ , \tag{2.5}$$

where $D(\omega)$ satisfies an equation of the form[8]

$$[-i\omega+\mathfrak{L}(\omega)]\vec{D}(\omega)=\vec{d}\ . \tag{2.6}$$

The form of $\mathfrak{L}(\omega)$ is then obtained by some approximation procedure.

In the case of interest here, the perturbers constitute a two-component plasma with over-all charge neutrality. The coupling between the perturbers and atom is taken to be a dipole interaction,[9]

$$V_{ap}=\vec{d}\cdot\vec{E}_p\ , \tag{2.7}$$

and E_p is the total electric field at the atom due to all the charged perturbers

$$E_p=\sum_{i=1}^{N}\sigma_i\frac{\vec{q}_i}{|q_i|^3}\ . \tag{2.8}$$

A coordinate system with the atom at the origin has been chosen, and $\sigma_i=\pm e$ depending on the charge of the perturber. Usually the plasma consists of electrons and relatively heavy positive ions. The broadening of the atomic lines by the ions is then treated differently from that of the electrons. The reason for this is that the average velocity of the ions is much smaller than the average electron velocity, and, for frequencies greater than some minimum, the ions may be treated as static (i.e., the radiation occurs in a time short compared to the time necessary for the field to change). On the other hand, the same conditions are not met for the electrons except at considerably higher frequencies. The usual calculations therefore assume static ions but not static electrons, the electrons being treated in a collisional approximation. In addition, interaction of electrons and ions is neglected in order to factor the average over the perturbers into a product of averages over electrons and ions separately. This amounts to treating electron and ion broadening independently. The resulting form of the line shape is given in terms of an average ion microfield distribution function $Q(\vec{\mathcal{E}})$,

$$I(\omega)=-\mathrm{Im}\frac{1}{\pi}\int d^3\mathcal{E}\,Q(\vec{\mathcal{E}})J(\vec{\mathcal{E}},\omega)\ ,$$
$$Q(\vec{\mathcal{E}})=\langle\delta(\vec{\mathcal{E}}-\vec{E}_i)\rangle\ . \tag{2.9}$$

Here, $\langle\rangle_i$ denotes an average over the ion subsystem, and E_i is the electric field due to the ions. The line shape is essentially contained in $J(\vec{\mathcal{E}},\omega)$

$$J(\vec{\mathcal{E}},\omega)=\langle\vec{d}\cdot\vec{D}(\vec{\mathcal{E}},\omega)\rangle_a\ .$$

The equation for $D(\vec{\mathcal{E}},\omega)$, corresponding to Eq. (2.6), is obtained by expanding the operator $\mathfrak{L}(\omega,\vec{\mathcal{E}})$ to second order in the coupling between the atom and electrons.

In the following, the assumptions of static ions

and negligible ion-electron interaction will be eliminated. These assumptions arise in the procedure of introducing the ion microfield function $Q(\vec{\mathcal{E}})$. One might be tempted to eliminate the introduction of $Q(\vec{\mathcal{E}})$ altogether for this reason, but it is possible to show that, in the static limit, the use of $Q(\vec{\mathcal{E}})$ is equivalent to summing contributions to the line shape from all orders in an expansion of the operator $\mathfrak{L}(\omega)$ in terms of the atom-ion coupling . Therefore, it is desirable to express the line shape in a form which retains the features of the microfield function, yet does not require the above assumptions. Indeed, in treating the wings we shall enrich the ion microfield function to include the static-electron effects as well.

Returning to Eq. (2.5), we wish to calculate $D(\omega)$ in the form discussed,

$$\vec{D}(\omega) = \int_0^\infty dt\, e^{i\omega t} \langle \vec{d}(t) \rangle_p \ . \tag{2.10}$$

The most general approaches to the theory of spectral line shapes have made use of either Green's functions or Liouville operator techniques.[10] For the purposes here, the latter appears to be the most economical and transparent way to proceed, and will be used throughout. Briefly, the Liouville operator is defined by its action on an arbitrary operator of quantum mechanics[11]

$$Lf = i[H, f] \ ; \tag{2.11}$$

that is, the Liouville operator gives i times the commutator with the Hamiltonian H of the quantity on which it operates. Since $\partial d/\partial t = i[H, d]$, we have formally,

$$\vec{d}(t) = e^{Lt}\vec{d} \ . \tag{2.12}$$

For the system considered here, the Liouville operator is

$$L = L_0 + \lambda L_I, \quad L_0 \equiv L_a + L_p, \quad L_I \equiv L_{ia} + L_{ea} \tag{2.13}$$

corresponding to the decomposition of the Hamiltonian

$$H = H_a + H_p + \lambda H_I, H_p \equiv H_e + H_i, \quad H_I = V_{ia} + V_{ea} \tag{2.14}$$

A coupling constant λ has been introduced for convenience. The free atomic Hamiltonian is H_a,[12] and

$$H_e = \sum_{\alpha=1}^{N_e} \left(\frac{p_{e\alpha}^2}{2M_e} + \tfrac{1}{2} \sum_{\beta \neq \alpha}^{N_e} V(q_{e\alpha} - q_{e\beta}) + \tfrac{1}{2} \sum_{\beta=1}^{N_i} V(q_{e\alpha} - q_{i\beta}) \right) , \tag{2.15}$$

$$H_i = \sum_{\alpha=1}^{N_i} \left(\frac{p_{i\alpha}^2}{2M_i} + \tfrac{1}{2} \sum_{\beta \neq \alpha}^{Ni} V(q_{i\alpha} - q_{i\beta}) + \tfrac{1}{2} \sum_{\beta=1}^{N_e} V(q_{i\alpha} - q_{e\beta}) \right) .$$

Here, N_i and N_e are the ion and electron numbers ($N_i = N_e = \frac{1}{2}N$). It is important to note that electron-ion interactions have not been neglected in Eqs. (2.15) but have been shared equally between H_e and H_i. Finally, the potentials V_{ia} and V_{ea} are the dipole interactions, respectively, between ions and atom, and electrons and atom.

Equation (2.10) may now be written

$$D(\omega) = i \langle (\omega - iL_0 - i\lambda L_I)^{-1} \rangle_p \vec{d} \ . \tag{2.16}$$

According to the discussion above, we wish to express the line shape in the form

$$I(\omega) = -\,\mathrm{Im}\frac{1}{\pi} \int d^3\mathcal{E}\, Q(\vec{\mathcal{E}}) J(\vec{\mathcal{E}}, \omega),$$

or, using (2.16)

$$\mathrm{Re}(i/\pi) \langle \vec{d} \langle (\omega - iL_0 - i\lambda L_I)^{-1} \rangle_p \vec{d} \rangle_a$$

$$= -\,\mathrm{Im}\frac{1}{\pi} \int d^3\mathcal{E}\, Q(\vec{\mathcal{E}}) J(\vec{\mathcal{E}}, \omega) \ . \tag{2.17}$$

With this in mind, we define two operators $\mathfrak{K}^{(1)}(\lambda, \omega)$ and $\mathfrak{K}^{(2)}(\lambda, \omega)$ in the atomic subsystem by

$$\begin{aligned} \langle (\omega - iL_0 - i\lambda L_I)^{-1} \rangle_p &\equiv \langle [\omega - iL_a - i\lambda L_{ia} \\ &\quad - i\mathfrak{K}^{(1)}(\lambda, \omega)]^{-1} \rangle_p, \\ \langle (\omega - iL_0 - i\lambda L_I)^{-1} \rangle_p &\equiv \langle [\omega - iL_a - i\lambda L_I \\ &\quad - i\mathfrak{K}^{(2)}(\lambda, \omega)]^{-1} \rangle_p \ . \end{aligned} \tag{2.18}$$

The right-hand sides of these equations differ only in the occurrence of L_{ia} or L_I. The motivation for introducing these operators is that they allow the introduction of a microfield function without any approximation. Consider first the equation with $\mathfrak{K}^{(1)}$:

$$\langle [\omega - iL_a i\lambda L_{ia} - i\mathfrak{K}^{(1)}(\lambda, \omega)]^{-1} \rangle_p$$

$$= \int d^3\mathcal{E} \langle [\delta(\vec{\mathcal{E}} - E_i)(\omega - iL_a - i\lambda L_{ia} - i\mathfrak{K}^{(1)}(\lambda, \omega)]^{-1} \rangle_p$$

$$= \int d^3\mathcal{E} \langle [\delta(\vec{\mathcal{E}} - E_i)(\omega - iL_a - i\lambda L_{ia}(\vec{\mathcal{E}})$$

$$- i\mathfrak{K}^{(1)}(\lambda, \omega)]^{-1} \rangle_p,$$

or, recalling that $\mathcal{K}^{(1)}$ is defined to be an operator in the atomic subsystem

$$\langle[\omega - iL_a - i\lambda L_{ia} - i\mathcal{K}^{(1)}(\lambda,\omega)]^{-1}\rangle_p$$

$$= \int d^3\mathcal{E}\langle\delta(\vec{\mathcal{E}} - E_i)\rangle\rangle_p[\omega - iL_a - i\lambda L_{ia}(\vec{\mathcal{E}}) - i\mathcal{K}^{(1)}(\lambda,\omega)]^{-1}. \tag{2.19}$$

Here, $L_{ia}(\vec{\mathcal{E}})$ is obtained from L_{ia} by replacing $\vec{E}_i$ by $\vec{\mathcal{E}}$. The second equality follows from the fact that the ion field commutes with everything in L_a and $\mathcal{K}^{(1)}(\lambda,\omega)$. [Note that the presence of L_0 rather than L_a in the left-hand sides of Eq. 2.18) prevents the corresponding operation in $\langle(\omega - iL_0 - i\lambda L_I)^{-1}\rangle_p$.] A similar calculation is possible for the equation containing $\mathcal{K}^{(2)}$. Depending on which of the two definitions in Eq. (2.18) is used, the line shape is given by

$$I(\omega) = \mathrm{Im}\frac{1}{\pi}\int d^3\mathcal{E}Q^{(1)}(\vec{\mathcal{E}})J^{(1)}(\vec{\mathcal{E}},\omega),$$

$$Q^{(1)}(\vec{\mathcal{E}}) \equiv \langle\delta(\vec{\mathcal{E}} - \vec{E}_i)\rangle\rangle_p, \tag{2.20}$$

$$J^{(1)}(\vec{\mathcal{E}},\omega) \equiv \langle\vec{d}[\omega - iL_a - i\lambda L_{ia}(\vec{\mathcal{E}}) - i\mathcal{K}^{(1)}(\lambda,\omega)]^{-1}\vec{d}\rangle_a,$$

or $$I(\omega) = -\mathrm{Im}\frac{1}{\pi}\int d^3\mathcal{E}Q^{(2)}(\vec{\mathcal{E}})J^{(2)}(\vec{\mathcal{E}},\omega),$$

$$Q^{(2)}(\vec{\mathcal{E}}) \equiv \langle\delta(\vec{\mathcal{E}} - \vec{E}_i - \vec{E}_e)\rangle\rangle_p, \tag{2.21}$$

$$J^{(2)}(\mathcal{E},\omega) \equiv \langle\vec{d}[\omega - iL_a - i\lambda L_I(\vec{\mathcal{E}}) - i\mathcal{K}^{(2)}(\lambda,\omega)]^{-1}\vec{d}\rangle_a.$$

The results (2.20) and (2.21) are formally similar to previous results by construction. However, both Eqs. (2.20) and (2.21) are exact. The reason for obtaining two expressions for the line shape is that the first is amenable to perturbation theory near the line center, whereas Eq. (2.21) may be treated by perturbation theory in the line wings. This may be seen by noting that the microfield function $Q^{(1)}$ is an ion microfield function (although averaged over the entire plasma), while $Q^{(2)}$ is the corresponding total field (ion plus electron) function. Therefore, in the wings where static electron effects become important, they are accounted for in $Q^{(2)}$, whereas these same effects would have to be obtained from $\mathcal{K}^{(1)}$ to all orders in λ in the first formulation. We shall therefore determine $\mathcal{K}^{(1)}$ and $\mathcal{K}^{(2)}$ to second order in λ and use the formulation (2.20) in the line center and (2.21) in the line wings. It will be shown in Sec. III that $\mathcal{K}^{(2)}(\lambda,\omega) \to 0$ for large enough ω so that

$$\lim_{\omega\to\infty} I(\omega) = -\mathrm{Im}\frac{1}{\pi}\int d^3\mathcal{E}Q(\vec{\mathcal{E}})$$

$$\times\langle\vec{d}[\omega - iL_a - i\lambda L_I(\vec{\mathcal{E}})]^{-1}\vec{d}\rangle_a,$$

which is the exact static-ion–static-electron limit for the far wings (sufficiently high frequencies such that the radiation occurs in a time short compared to the time required for either electrons or ions to move significantly).

It remains to determine $\mathcal{K}^{(1)}$ and $\mathcal{K}^{(2)}$ from their definitions, Eqs. (2.18). As mentioned above, $\mathcal{K}^{(1)}(\lambda,\omega)$ is analytic in λ for ω near the line center, while $\mathcal{K}^{(2)}(\lambda,\omega)$ is analytic in the wings. These operators will be calculated here only to second order in λ, for comparison with previous work, although extension to higher order is straightforward. A direct expansion in λ of the left-and right-hand sides of the first of Eqs. (2.18) gives [recall, for an operator A, $(\partial A^{-1}/\partial\lambda) = A^{-1}(\partial A/\partial\lambda)A^{-1}$]:

$$\langle(\omega - iL_0 - i\lambda L_{ia})^{-1}\rangle_p$$

$$= (\omega - iL_a)^{-1} + i\lambda(\omega - iL_a)^{-1}\langle L_I\rangle_p(\omega - iL_a)^{-1}$$

$$- \lambda^2(\omega - iL_a)^{-1}\langle L_I(\omega - iL_0)^{-1}L_I\rangle_p(\omega - iL_a)^{-1} + O(\lambda^3)$$

and $$\langle[\omega - iL_a - i\lambda L_{ia} - i\mathcal{K}^{(1)}(\lambda,\omega)]^{-1}\rangle_p,$$

$$= [\omega - iL_a - i\mathcal{K}^{(1)}(0,\omega)]^{-1} + i\lambda\langle[\omega - iL_a - i\mathcal{K}^{(1)}(0,\omega)]^{-1}$$

$$\times\left(L_{ia} + \frac{\partial\mathcal{K}^{(1)}}{\partial\lambda}\Big|_{\lambda=0}\right)[\omega - iL_a - i\mathcal{K}^{(1)}(0,\omega)]^{-1}\rangle_p$$

$$+ \tfrac{1}{2}\lambda^2 i\langle[\omega - iL_a - i\mathcal{K}^{(1)}(0,\omega)]^{-1}\frac{\partial^2\mathcal{K}^{(1)}}{\partial\lambda^2}\Big|_{\lambda=0}$$

$$[\omega - iL_a - i\mathcal{K}^{(1)}(0,\omega)]^{-1}\rangle_p - 2\langle[\omega - iL_a - i\mathcal{K}^{(1)}(0)]^{-1}$$

$$\times\left(L_{ia} + \frac{\partial\mathcal{K}^{(1)}}{\partial\lambda}\Big|_{\lambda=0}\right)[\omega - iL_a - i\mathcal{K}(0)]^{-1}$$

$$\times\left(L_{ia} + \frac{\partial\mathcal{K}^{(1)}}{\partial\lambda}\right)[\omega - iL_a - i\mathcal{K}^{(1)}(0)]^{-1}\rangle_p + O(\lambda^3).$$

Comparing coefficients of λ determines $\mathcal{K}^{(1)}$ to second order in λ:

$$\mathcal{K}^{(1)}(\lambda,\omega) = i\lambda^2[\langle L_I K L_I\rangle_p - \langle L_{ia}K^a L_{ia}\rangle_p], \tag{2.22}$$

$$K \equiv (\omega - iL_0)^{-1}, \quad K^a \equiv (\omega - iL_a)^{-1}. \tag{2.23}$$

Use has been made of the fact that $\langle L_I\rangle = \langle L_{ia}\rangle = \langle L_{ea}\rangle = 0$. A similar analysis on the second of Eqs. (2.18) yields for $\mathcal{K}^{(2)}(\lambda,\omega)$ to second order in λ,

$$\mathcal{K}^{(2)}(\lambda,\omega) = i\lambda^2[\langle L_I K L_I\rangle_p - \langle L_I K^a L_I\rangle_p]. \tag{2.24}$$

The results (2.23) and (2.24) are similar to previous calculations. Here, however, the static-ion approximation has not been made, and since

the averages are taken over the entire plasma, no assumptions on the ion-ion, electron-electron, or ion-electron interactions have been made. Ion motion as well as electron motion is accounted for in $\langle L_I K L_I \rangle_p$. The operators $\mathcal{K}^{(1)}$ and $\mathcal{K}^{(2)}$ differ only in the subtracted term. It will appear that the subtracted term in each case removes from $\mathcal{K}(\lambda, \omega)$ the static part accounted for in the microfield function. Since the microfield functions are different in the two cases, the terms subtracted from $\mathcal{K}$ differ.

III. CHARGE-DENSITY FLUCTUATIONS

The form and analytic properties of $\mathcal{K}^{(1)}(\lambda, \omega)$ and $\mathcal{K}^{(2)}(\lambda, \omega)$, as given by Eqs. (2.23) and (2.24), will be considered in more detail. It will be found that these operators are determined from the advanced and retarded field-field autocorrelation functions. These in turn may be expressed in terms of the space- and time-dependent charge-density fluctuations in the system. It is convenient to discuss the operators in terms of these fluctuations since more general interactions between plasma and atom are also expressible in terms of them, and therefore the discussion is more general than the dipole approximation used here.[13] Also, as already pointed out, the microfield function and $J(\omega, \vec{\mathcal{E}})$ with $\mathcal{K}=0$ gives a static result, so it is natural to discuss deviations from the static result in terms of the intensity of the fluctuations in charge density.

First consider $\mathcal{K}^{(2)}(\lambda, \omega)$. The properties of this operator may be seen by its action on an arbitrary operator f in the atomic subsystem,

$$\begin{aligned}
&\mathcal{K}^{(2)}(\lambda,\omega)f = i\lambda^2\langle L_I[K-K^a]L_I\rangle f\,,\\
&\mathcal{K}^{(2)}(\lambda,\omega)f = -\lambda^2\int_0^\infty dt\, e^{i\omega t}\langle\langle H_I e^{iH_0t}H_I e^{-iH_0t}f\rangle\\
&-\langle H_I e^{iH_0t}fH_I e^{-iH_0t}\rangle - \langle e^{iH_0t}H_I f e^{-iH_0t}H_I\rangle\\
&+\langle e^{iH_0t}fH_I e^{-iH_0t}H_I\rangle\rangle + \lambda^2(\text{same with } H_0\to H_a).
\end{aligned} \tag{3.1}$$

The subscripts p have been left off the brackets with the understanding that all future averages are to be taken over the plasma, unless otherwise stated. A matrix representation may be obtained by taking matrix elements of Eq. (3.1) between two atomic eigenstates (of H_a), $|\mu\rangle$ and $|\nu\rangle$,

$$\langle\mu|\mathcal{K}^{(2)}(\lambda,\omega)|f|\nu\rangle = \sum_{\mu'\nu'}\mathcal{K}_{\mu\nu,\,\mu'\nu'}f_{\mu'\nu'}\,, \tag{3.2}$$

with $\mathcal{K}^{(2)}_{\mu\nu,\,\mu'\nu'} = \lambda^2\int_0^\infty dt\{e^{i\Delta\omega_{\mu'\nu'}t}\langle H_{I\mu\mu'}H_{I\nu'\nu}(t)\rangle$

$$\begin{aligned}
&+e^{i\Delta\omega_{\mu\nu'}t}\langle H_{I\mu\mu'}(t)H_{I\nu'\nu}\rangle - \sum_{\nu''}[e^{i\Delta\omega_{\nu''\nu}t}\\
&\times\langle H_{I\mu\nu''}H_{I\nu''\mu'}(t)\rangle f_{\nu\nu'} + e^{i\Delta\omega_{\mu\nu''}t}\langle H_{I\nu'\nu''}(t)H_{I\nu''\nu}\rangle]\}
\end{aligned}$$

- (same with $t=0$ in correlation functions.) (3.3)

Here $\Delta\omega_{\mu\nu}$ is the difference $\omega - (\epsilon_\mu - \epsilon_\nu)$; ϵ_μ is an eigenvalue of H_a.

The time dependence of $H_{\mu\mu'}(t)$ is determined by the Hamiltonian for the entire plasma; $H_I(t) = e^{iH_pt}H_I e^{-iH_pt}$. Using the dipole interaction, Eq. (2.7), we find

$$\begin{aligned}
\mathcal{K}^{(2)}_{\mu\nu,\,\mu'\nu'} &= \lambda^2\tfrac{1}{3}[\vec{d}_{\mu\mu'}\cdot\vec{d}_{\nu'\nu}[\int_0^\infty dt\, e^{i\Delta\omega_{\nu\mu'}t}\\
&\times(\langle\vec{E}\cdot\vec{E}(t)\rangle - \langle E^2\rangle) + \int_0^\infty dt\, e^{i\Delta\omega_{\nu'\mu}t}(\langle\vec{E}(t)\cdot\vec{E}\rangle - \langle E^2\rangle)]\\
&-\sum_{\nu''}[\delta_{\nu\nu'}\vec{d}_{\mu\nu''}\cdot\vec{d}_{\nu''\mu'}\int_0^\infty dt\, e^{i\Delta\omega_{\nu\nu''}t}(\langle\vec{E}\cdot\vec{E}(t)\rangle - \langle E^2\rangle)\\
&+\delta_{\mu\mu'}\vec{d}_{\nu'\nu''}\cdot\vec{d}_{\nu''\nu}\int_0^\infty dt\, e^{i\Delta\omega_{\nu''\mu}t}(\langle\vec{E}(t)\cdot\vec{E}\rangle - \langle\vec{E}^2\rangle)]\}\,.
\end{aligned} \tag{3.4}$$

The field $\vec{E}$ occurring here is the total field $\vec{E}=\vec{E}_i+\vec{E}_e$. It is clear from (3.4) that the subtracted term corresponds to a static effect. The corresponding expression for $\mathcal{K}^{(1)}_{\mu\nu,\,\mu'\nu'}$ differs only by replacing $\langle E^2\rangle$ in (3.4) by $\langle E_i^2\rangle$; i.e., only the static-ion part is subtracted out.

The field-field correlation functions, occurring in both $\mathcal{K}^{(1)}$ and $\mathcal{K}^{(2)}$, are of two types, the half transforms of $\langle\vec{E}(t)\cdot\vec{E}\rangle$ and $\langle\vec{E}\cdot\vec{E}(t)\rangle$. It is convenient to introduce the retarded and advanced correlation functions,

$$\begin{aligned}
G^R(\omega) &= \int_{-\infty}^\infty dt\, e^{i\omega t}\langle\vec{E}\cdot\vec{E}(t)\rangle\theta(t)\,,\\
G^A(\omega) &= \int_{-\infty}^\infty dt\, e^{i\omega t}\langle\vec{E}\cdot\vec{E}(t)\rangle\theta(-t)\,,
\end{aligned} \tag{3.5}$$

where $\theta(t)$ is the Heaviside step function,

$$\theta(t)=1,\quad t>0;\qquad \theta(t)=0,\quad t<0\,.$$

Making use of the fact that the correlation functions are invariant under time translations, it is easily shown,

$$\begin{aligned}
\int_0^\infty dt\, e^{i\omega t}\langle\vec{E}\cdot\vec{E}(t)\rangle &= G^R(\omega),\\
\int_0^\infty dt\, e^{i\omega t}\langle\vec{E}(t)\cdot\vec{E}\rangle &= G^A(-\omega)\,,
\end{aligned} \tag{3.6}$$

and Eq. (3.4) becomes

$$\mathcal{K}^{(2)}_{\mu\nu,\,\mu'\nu'}(\omega) = \lambda^2\tfrac{1}{3}\vec{d}_{\mu\mu'}\cdot\vec{d}_{\nu\nu'}\{[G^R(\Delta\omega_{\nu\mu'})$$

$$- G_\infty{}^R(\Delta\omega_{\nu\mu}'')] + [G^A(-\Delta\omega_{\nu'\mu}) - G_\infty{}^A(-\Delta\omega_{\nu'\mu})]\}$$

$$- \tfrac{1}{3}\lambda^2 \sum_{\nu''} \delta_{\nu\nu'} \vec{d}_{\mu\nu''} \cdot \vec{d}_{\nu''\mu'}$$

$$\times [G^R(\Delta\omega_{\nu\nu''}) - G_\infty{}^R$$

$$\times(\Delta\omega_{\nu\nu''})] + \delta_{\mu\mu'} \vec{d}_{\nu'\nu''} \cdot \vec{d}_{\nu''\nu} [G^A(-\Delta\omega_{\nu''\mu})$$

$$- G_\infty{}^A(-\Delta\omega_{\nu''\mu})]\} . \tag{3.7}$$

Here $\begin{Bmatrix} G_\infty{}^R(\omega) \\ G_\infty{}^A(\omega) \end{Bmatrix} \equiv \pm (i\omega)^{-1} \langle E^2 \rangle$,

a notation anticipating the result shown below that this is the asymptotic behavior of $G^{R,A}(\omega)$ for large ω. Again, the expression for $\mathcal{K}_{\mu\nu,\mu'\nu'}{}^{(1)}$ differs from Eq. (3.7) only in the replacement of $G_\infty{}^{R,A}(\omega)$ by

$$\begin{Bmatrix} G_{i\infty}{}^R(\omega) \\ G_{i\infty}{}^A(\omega) \end{Bmatrix} \equiv \pm (i\omega)^{-1} \langle E_i{}^2 \rangle .$$

The total field $\vec{E}$ occurring in Eq. (3.5) may be simply related to the charge density of the system,

$$\vec{E} = \sum_{i=1}^{N} \sigma_i \frac{\vec{q}_i}{q_i{}^3} = e\left(\sum_{i=1}^{N_i} \frac{\vec{q}_i}{q_i{}^3} - \sum_{i=1}^{N_e} \frac{\vec{q}_i}{q_i{}^3} \right) ,$$

where the first summation is over all ion coordinates and the second is over all electron coordinates. Further, we may write,

$$\vec{E} = \int d^3x \, \frac{\vec{x}}{x^3} \left(e \sum_{i=1}^{N_i} \delta(\vec{x} - \vec{q}_i) - e \sum_{i=1}^{N_i} \delta(\vec{x} - \vec{q}_i) \right)$$

$$= \int d^3x \, \frac{\vec{x}}{x^3} [e n_i(\vec{x}) - e n_e(\vec{x})] ,$$

$$E = \int d^3x \, \frac{\vec{x}}{x^3} \rho(\vec{x}) . \tag{3.8}$$

The charge density is $\rho(\vec{x}) = e[n_i(\vec{x}) - n_e(\vec{x})]$, where $n_i(\vec{x})$ and $n_e(\vec{x})$ are, respectively, the microscopic ion and electron number densities. The condition of charge neutrality requires $\int d^3x \rho(\vec{x}) = 0$, and since $\int d^3x \, (\vec{x}/x^3) = 0$, we may consider $\rho(\vec{x})$ as the deviation of the charge density from its equilibrium value. We note in passing that for interactions other than dipole, the integral in Eq. (3.8) is changed only by the form factor in front of the charge density.[13] In terms of the charge density, the field-field correlation function in Eq. (3.5) is

$$\langle \vec{E} \cdot \vec{E}(t) \rangle = \int d^3x \int d^3x' \frac{\vec{x} \cdot \vec{x}'}{x^3 x'^3} \langle \rho(\vec{x}) \rho(\vec{x}', t) \rangle . \tag{3.9}$$

Introducing Eq. (3.9) in (3.5), gives

$$\begin{Bmatrix} G^R(\omega) \\ G^A(\omega) \end{Bmatrix} = (4\pi)^2 \int \frac{d^3k}{(2\pi)^3} k^{-2} \begin{Bmatrix} G^R(\vec{k}, \omega) \\ G^A(\vec{k}, \omega) \end{Bmatrix} , \tag{3.10}$$

where the retarded and advanced functions $G^{R,A}(\vec{k}, \omega)$ are the transformed charge density space and time correlation functions,

$$G^R(\vec{k}, \omega) = \int_{-\infty}^{\infty} dt \, e^{i\omega t} \int d^3x \, e^{i\vec{k} \cdot \vec{x}} \langle \rho\rho(\vec{x}, t) \rangle \theta(t),$$

$$G^A(\vec{k}, \omega) = \int_{-\infty}^{\infty} dt \, e^{i\omega t} \int d^3x \, e^{i\vec{k} \cdot \vec{x}} \langle \rho\rho(\vec{x}, t) \rangle \theta(-t). \tag{3.11}$$

Use has been made of the invariance of $\langle \rho\rho(\vec{x}), t) \rangle$ under spatial translations.

The analytic properties of $\mathcal{K}(\omega)$ may therefore be obtained from those of $G^R(\vec{k}, \omega)$ and $G^A(\vec{k}, \omega)$. Before considering these latter, we first define their full-transformed counterpart

$$S(\vec{k}, \omega) = (2\pi)^{-1} \int d^3x \int_{-\infty}^{\infty} dt \, e^{i(\vec{k} \cdot \vec{x} + \omega t)} \langle \rho\rho(\vec{x}, t) \rangle . \tag{3.12}$$

It is easily shown that $S(\vec{k}, \omega)$ is real. The retarded and advanced charge density fluctuations may be expressed in terms of $S(\vec{k}, \omega)$ by noting that $G^R(\vec{k}, \omega)$ is analytic in the upper-half ω plane and $G^A(\vec{k}, \omega)$ is analytic in the lower-half plane. Therefore, we may write

$$G^R(\vec{k}, \omega) = -i \int_{-\infty}^{\infty} d\omega' \, \frac{S(\vec{k}, \omega')}{\omega' - \omega - i\epsilon} ,$$

$$G^A(\vec{k}, \omega) = i \int_{-\infty}^{\infty} d\omega' \, \frac{S(\vec{k}, \omega')}{\omega' - \omega + i\epsilon} , \tag{3.13}$$

where ϵ is an arbitrarily small positive constant. Taking the real and imaginary parts of Eq. (3.13) gives

$$\mathrm{Re}G^R(\vec{k}, \omega) = \pi S(\vec{k}, \omega) = \mathrm{Re}G^A(\vec{k}, \omega),$$

$$\mathrm{Im}G^R(\vec{k}, \omega) = -P \int_{-\infty}^{\infty} d\omega' \, \frac{S(\vec{k}, \omega')}{\omega' - \omega} = -\mathrm{Im}G^A(\vec{k}, \omega), \tag{3.14}$$

from which follows

$$G^A(\vec{k}, \omega) = [G^R(k, \omega)]^* . \tag{3.15}$$

The symbol P in Eq. (3.14) indicates the Cauchy-principal part should be taken. Equation (3.15) shows we need only consider $G^R(\vec{k},\omega)$.

It is now possible to justify the notation $G_\infty{}^{R,A}(\omega)$ for $\pm i\omega^{-1}\langle E^2\rangle$ in Eq. (3.7) for large ω, $\mathrm{Im}G^R(k,\omega)$ behaves as

$$\lim_{\omega\to\infty}\mathrm{Im}G^R(\vec{k},\omega)\to\omega^{-1}\int_{-\infty}^{\infty}d\omega' S(\vec{k},\omega') = \omega^{-1}\int d^3x e^{i\vec{k}\cdot\vec{x}}\langle\rho\rho(\vec{x},t=0)\rangle. \tag{3.16}$$

The existence of the integral over $S(\vec{k},\omega)$ implies $S(\vec{k},\omega)\to 0$ for large ω faster than ω^{-1}. Therefore, $\mathrm{Re}G^R(\vec{k},\omega)$ vanishes faster than the imaginary part. From Eq. (3.16) and Eq. (3.10), the behavior of $G^R(\omega)$ for large ω is

$$\lim_{\omega\to\infty}G^R(\omega)\to\omega^{-1}i(4\pi)^2\int\frac{d^3k}{(2\pi)^3}k^{-2}\int d^3x e^{i\vec{k}\cdot\vec{x}} \times\langle\rho\rho(\vec{x},t=0)\rangle = \frac{i}{\omega}\langle E^2\rangle \equiv G_\infty{}^R(\omega),$$

which was to be shown.

Finally, the real and imaginary parts of $G^R(\vec{k},\omega)$ are related by the Kramers-Kronig relations, which follow from Eq. (3.14)

$$\mathrm{Re}G^R(\vec{k},\omega)=\pi^{-1}P\int_{-\infty}^{\infty}d\omega'\frac{\mathrm{Im}G^R(\vec{k},\omega')}{\omega'-\omega}, \qquad \mathrm{Im}G^R(\vec{k},\omega)=-\pi^{-1}P\int_{-\infty}^{\infty}d\omega'\frac{\mathrm{Re}G^R(\vec{k},\omega')}{\omega'-\omega}, \tag{3.17}$$

which shows $G^R(\omega)$ can be neither pure real nor pure imaginary[14] (unless it vanishes everywhere). Equations (3.17) and (3.14) may now be used in the expression for $G^R(\omega)$, Eq. (3.10), to give the desired result,

$$G^R(\omega)=(4\pi)^2\left(\pi\int\frac{d^3k}{(2\pi)^3}k^{-2}S(\vec{k},\omega) - iP\int_{-\infty}^{\infty}d\omega'(\omega'-\omega)^{-1}\int\frac{d^3k}{(2\pi)^3}k^{-2}S(\vec{k},\omega')\right). \tag{3.18}$$

This form will be of use in Sec. IV, where $S(\vec{k},\omega)$ is related to the dielectric constant for the plasma.

The operators $\mathcal{K}^{(1)}$ and $\mathcal{K}^{(2)}$ are then

$$\mathcal{K}_{\mu\nu,\mu'\nu'}{}^{(1),(2)}(\omega)=\tfrac{1}{3}\lambda^2\vec{d}_{\mu\mu'}\cdot\vec{d}_{\nu'\nu} \times[\bar{G}_{1,2}{}^R(\Delta\omega_{\nu\mu'})+(\bar{G}_{1,2}{}^R(-\Delta\omega_{\nu'\mu}))^*]$$

$$-\tfrac{1}{3}\lambda^2\sum_{\nu''}[\delta_{\nu\nu'}\vec{d}_{\mu\nu''}\cdot\vec{d}_{\nu''\mu'}\bar{G}_{1,2}{}^R(\Delta\omega_{\nu\nu''}) +\delta_{\mu\mu'}\vec{d}_{\nu'\nu''}\cdot\vec{d}_{\nu''\nu}(\bar{G}_{1,2}{}^R(-\Delta\omega_{\nu''\nu}))^*]. \tag{3.19}$$

Here $\bar{G}_1{}^R(\omega)\equiv G^R(\omega)-G_{i\infty}{}^R(\omega)$, $\bar{G}_2{}^R(\omega)=G^R(\omega)-G_\infty{}^R(\omega)$. Recall that $\mathcal{K}^{(1)}$ is appropriate for the line center while $\mathcal{K}^{(2)}$ applies for the wings.

Before continuing, it is convenient at this point to compare with previous results. It has been shown that $\mathcal{K}^{(2)}(\omega)\to 0$ for large ω[since $\bar{G}^R(\omega)$ does] and therefore the formulation of Eq. (2.21) approaches the exact far-wing static limit. In the line center, it is easiest to compare with the results of Ref. 2. If electron-ion correlations are neglected, we have

$$\bar{G}_1{}^R(\omega)=\int_0^\infty dt\, e^{i\omega t}\langle\vec{E}_e\cdot E_e(t)\rangle_e + \int_0^\infty d\, e^{i\omega t}[\langle\vec{E}_i\cdot E_i(t)\rangle_i-\langle\vec{E}_i E_i\rangle_i].$$

The first term is the result of Ref. 2. The second term is strictly an ion term and represents the ion motion neglected there. To the extent that the time dependence of the ion field in the second integrand may be neglected, the static-ion result is obtained as expected. The role of the subtracted term $\langle E_i{}^2\rangle$ is therefore to eliminate the static contributions to $\mathcal{K}^{(1)}$. The relationship to the impact limit is discussed elsewhere.[2]

It may be disconcerting that $G_{i\infty}{}^R(\Delta\omega)$ diverges as $\Delta\omega\to 0$. However, this occurs only at the very line center in a region probably of little practical interest. It should be noted that such a divergence at the exact line center is present in any theory using a microfield function since for small enough frequencies the microfield function represents too much static effect. This may be seen in the work of Smith[15] where the divergent terms first occur at fourth order in the coupling constant.

IV. DIELECTRIC CONSTANT

It is evident from Sec. III that detailed knowledge of $S(\vec{k},\omega)$ is required. Often, it is more convenient to consider the (longitudinal) dielectric constant $\epsilon(\vec{k},\omega)$, for the plasma. A simple relationship exists between $S(\vec{k},\omega)$ and $\epsilon(\vec{k},\omega)$[16]:

$$\mathrm{Im}\epsilon^{-1}(\vec{k},\omega)=-(2\pi/k)^2n(\omega)^{-1}S(\vec{k},\omega), \tag{4.1}$$

where $n(\omega)\equiv(e^{\beta\omega}-1)^{-1}$.

In terms of the dielectric constant, Eq. (3.18) becomes

$$G^R(\omega)=4\pi\left(n(\omega)\int\frac{d^3k}{(2\pi)^3}\frac{\mathrm{Im}\epsilon(\vec{k},\omega)}{|\epsilon(\vec{k},\omega)|^2}\right.$$
$$\left.+\frac{iP}{\pi}\int_0^\infty d\omega'\frac{n(\omega')}{(\omega-\omega')}\int\frac{d^3k}{(2\pi)^3}\frac{\mathrm{Im}\epsilon(\vec{k},\omega')}{|\epsilon(\vec{k},\omega')|^2}\right). \quad (4.2)$$

Using Eq. (3.16), we obtain for $\bar{G}_2{}^R(\omega)$,

$$\bar{G}_2{}^R(\omega)=4\pi\left(n(\omega)\int\frac{d^3k}{(2\pi)^3}\frac{\mathrm{Im}\epsilon(\vec{k},\omega)}{|\epsilon(\vec{k},\omega)|^2}\right.$$
$$\left.+\frac{iP}{\pi}\int_{-\infty}^\infty d\alpha\frac{\alpha n(\alpha\omega)}{(\alpha-1)}\int\frac{d^3k}{(2\pi)^3}\frac{\mathrm{Im}\epsilon(\vec{k},\alpha\omega)}{|\epsilon(\vec{k},\alpha\omega)|^2}\right). \quad (4.3)$$

The expression for $\bar{G}_1{}^R(\omega)$ is

$$\bar{G}_1{}^R(\omega)=4\pi\left(n(\omega)\int\frac{d^3k}{(2\pi)^3}\frac{\mathrm{Im}\epsilon(\vec{k},\omega)}{|\epsilon(\vec{k},\omega)|^2}\right.$$
$$\left.+\frac{i}{\pi}P\int_{-\infty}^\infty d\omega'\frac{n(\omega')}{(\omega'-\omega)}\int\frac{d^3k}{(2\pi)^3}\frac{\mathrm{Im}\epsilon(\vec{k},\omega')}{|\epsilon(k,\omega')|^2}\right)$$
$$-\frac{i}{\omega}\langle E_i{}^2\rangle\,. \quad (4.4)$$

It is possible to express $\langle E_i{}^2\rangle$ also in terms of the dielectric constant and the electron and ion polarizabilities. However, it may be more convenient to calculate $\langle E_i{}^2\rangle$ directly, for example, using the microfield function $Q^{(1)}$.

Equations (4.3) and (4.4) in conjunction with (3.19) and (2.20) or (2.21) are the principal results of this paper. The real parts of $\bar{G}_{1,2}{}^R$ are formally the same as the results of Refs. 3 and 4, with the important difference that here the dielectric constant is that for the entire plasma rather than for the electron subsystem only. The presence of $|\epsilon(\vec{k},\omega)|^2$ in the integral is often used to describe results of this form in terms of effective atom interactions. In this terminology, we see that (4.3) and (4.4) represent an effective atom-plasma interaction which is dressed by both ions and electrons as opposed to just electrons.[17] For instance, the low-frequency limit of $|\epsilon(\vec{k},\omega)|^2$ yields a Debye shielding which is characterized by the sum of the electron and ion Debye lengths. In the random-phase approximation the dielectric constant is[18]

$$\epsilon(k,\omega)=1+\sum_\alpha\frac{2Z_\alpha{}^3\omega_{p\alpha}{}^2}{\beta\omega^3}\{\tfrac{1}{2}[(Z_\alpha+a/Z_\alpha)^{-1}\Phi(Z_\alpha-a/Z_\alpha)$$
$$-(Z_\alpha-a/Z_\alpha)^{-1}\Phi(Z_\alpha-a/Z_\alpha)]+\ i(\pi)^{1/2}e^{-\beta\omega/2}$$
$$\times(e^{\beta\omega}-1)e^{-Z^2{}_\alpha-a^2/Z^2{}_\alpha}\}, \quad (4.5)$$

where the sum over α indicates a sum over different species, here electrons and ions; $\Phi(x)$ is the plasma dispersion function $Z_\alpha\equiv(\omega/k)(\frac{1}{2}m_\alpha\beta)^{1/2}$, $\omega_{p\alpha}$ is the plasma frequency associated with the αth species, and $a\equiv\frac{1}{4}\beta\omega$. It may be shown that the ion contributions to (4.5) are small for $Z>0.1$. This occurs for either large ω, as expected, or small k. This latter fact shows that there are contributions to $\bar{G}_{1,2}{}^R$ from the ion-motion term even for frequencies larger than, say, the ion plasma frequency. Another way of stating this is that while $\epsilon(\vec{k},\omega)$ does approach the dielectric constant for the electron subsystem for large ω, it does not do so uniformly in k. A similar analysis holds for the imaginary part. It should also be noted that the simple form of Eq. (4.5) showing the dielectric constant as the sum of electron polarization and ion polarization holds only in the random-phase approximation. In general, electron and ion contributions to $\epsilon(\vec{k},\omega)$ are not additive. Also, the case in which electrons and ions are in quasiequilibrium at different temperatures may be described using (4.5) with β replaced by β_α.

V. DISCUSSION

Explicit calculation of a line shape based on the results here has not yet been carried out, so quantitative estimates of the regions of validity of $\mathcal{K}^{(1)}$ and $\mathcal{K}^{(2)}$ cannot be given. As pointed out the line center is improved over Refs. 2–4, and the far wings are exact (to the extent that the density matrix may be factored). The results here are the exact second-order perturbation calculations in the sense that no approximation was used in obtaining Eqs. (2.20) and (2.21). It is felt, therefore, that the region of failure of the results here represent the limitations of the usefulness of a microfield function in conjunction with finite-order perturbation theory. Also, in the past it has been found that ion-ion correlations and electron-electron correlations modify the line shape considerably. This would indicate that the ion-electron correlations included here may be significant. Even in the static-ion limit, $\bar{G}_1{}^R(\omega)$ does not go to $\int_0^\infty dt\,e^{i\omega t}\langle E_e E_e(t)\rangle_e$ but rather

$$\lim_{M_i\to\infty}\bar{G}_1{}^R(\omega)\to\int_0^\infty dt\,e^{i\omega t}\langle E_e E_e(t)\rangle_p-2\langle E_e E_i\rangle_p.$$

Not only is the average taken over the entire plasma but the time dependence of the electron field is generated by the plasma Hamiltonian.

It is felt that the generalization of existing methods[19] to calculate the new microfields occuring in Eqs. (2.20) and (2.21) will not prove too difficult. If it should, one can approximately factor the plasma average to obtain

$$\langle\delta(\vec{\mathcal{E}}-\vec{\mathrm{E}}_i-\vec{\mathrm{E}}_e)\rangle_p = \int d^3\mathcal{E}'\langle\delta(\vec{\mathcal{E}}'-\vec{\mathrm{E}}_i)\delta(\vec{\mathcal{E}}-\vec{\mathcal{E}}'-\vec{\mathrm{E}}_e)\rangle_p$$

$$\approx \int d^3\mathcal{E}'\langle\delta(\vec{\mathcal{E}}'-\vec{\mathrm{E}}_i)\rangle_i\langle\delta(\vec{\mathcal{E}}-\vec{\mathcal{E}}'-\mathrm{E}_e)\rangle_e$$

$$= \int d^3\mathcal{E}' Q_i(\vec{\mathcal{E}}') Q_e(\vec{\mathcal{E}}-\vec{\mathcal{E}}') ,$$

where Q_i and Q_e are the usual ion and electron microfields for which methods of calculation are already available. This approximation is strictly valid only if electron-ion correlations are neglected.

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[1]H. R. Griem, Plasma Spectroscopy, (McGraw-Hill Book Co., New York, 1964), and references therein.

[2]E. W. Smith and C. F. Hooper, Jr., Phys. Rev. 157, 126 (1967); E. W. Smith, Phys. Rev. Letters 18, 990 (1967); Phys. Rev. 166, 102 (1968).

[3]H. R. Zaidi, Phys. Rev. 173, 123 (1968); 173, 132 (1968).

[4]L. Klein, J. Quant. Spectry. Radiative Transfer 9, 199 (1969). The results of this reference are strictly valid only for noninteracting electrons, since the energies ϵ_α-ϵ_β in Eq. (17) arise only from the kinetic part of the electron Hamiltonian. In preparation of this work, the author received a preprint of a calculation by E. Smith, J. Cooper, and C. Vidal which purports to give good results over most of the line from far wings to line center. The author is grateful to Dr. E. Smith for sending this, and also to him and his co-workers for their comments on the present work.

[5]If there is more than one electron responsible for atomic transitions there must be a dipole associated with each.

[6]In general $d=\sum_\alpha eR_\alpha$; where the sum extends over all atoms in the system. To first order in the density (atomic) $\langle\vec{d}\cdot\vec{d}\rangle=\sum_\alpha e^2\langle\vec{R}_\alpha\cdot\vec{R}_\alpha\rangle=N_a e^2\langle\vec{R}_1\vec{R}_1\rangle$. Therefore, we consider only a single atom with the understanding that the line shape may require multiplication by N_a.

[7]This approximation neglects initial correlations of atom and plasma. However, it is an assumption quite independent of those to be considered here and will not be discussed further. It is also present in the above references.

[8]Strictly speaking the Green's function methods do not have an intermediate result of this form. However, the calculation of the self-energy part for the two-particle atomic Green's function as an atomic matrix operator amounts to the same thing.

[9]This is valid for all interactions except those for which $r/R \gg 1$ is not satisfied. (r is the distance of a perturber from the atom. See also Ref. 13).

[10]Liouville operator techniques, in the context here, have been discussed extensively by U. Fano, in Lectures on the Many-Body Problem, edited by E. R. Caianiello (Academic Press Inc., New York, 1964), Vol. 2.

[11]Liouville operator is not defined on the same space as the usual operators of quantum mechanics, but rather on one whose elements are themselves the usual operators. See Ref. 10.

[12]In the dipole approximation, the c.m. part of H_a responsible for c.m. motion commutes with the part of H_a describing the internal degrees of freedom. Therefore, there is no Doppler contribution in this approximation, and we consider H_a to be only internal degrees of freedom.

[13]In the general case, there is a Coulomb interaction between the perturbers and each constituent of the atom. This is still the sum of single-particle operators in the perturber subsystem and may be expressed as $V = \int d^3x V(\vec{x})\sum_\alpha\delta(\vec{x}-\vec{q}_\alpha)$, where $V(x)$ depends on atomic coordinates but not perturber variables. Therefore, the same calculation as in Eq. (3.8) may be carried out for the general case.

[14]Some confusion may arise from the fact that Refs. 3 and 4 consider only the real part of G^R. The agreement with results of Ref. 2 reported by H. R. Zaidi, Phys. Rev. 173, 132 (1968) holds only for the real part.

[15]The divergent term is $\langle L_{ea}KL_{ea}\rangle K^a\langle L_{ea}KL_{ea}\rangle$.

[16]A. G. Sitenko, Electromagnetic Fluctuations in Plasma, (Academic Press Inc., New York, 1967).

[17]A. A. Abrikosov, L. P. Gor'kov, and I. Ye Dzyaloshinskii, Quantum Field Theoretical Methods in Statistical Physics (Pergamon Press, Inc., New York, 1965), Sec. 22; W. Chappell, J. Cooper, and E. Smith, J. Quant. Spectry. Radiative Transfer 9, 149 (1969).

[18]This expression is obtained assuming a Boltzmann distribution for the free-particle occupation number density, and is valid if degeneracy effects are unimportant. It is easily checked that for temperatures of interest the deBroglie length is small compared to the average interparticle distance.

[19]C. F. Hooper, Phys. Rev. 149, 77 (1966).