Density-matrix correlations in the relaxation theory of electron broadening

T. A. Gomez,[1,*] T. Nagayama,[1] D. P. Kilcrease,[2] M. H. Montgomery,[3] and D. E. Winget[3]
[1]*Sandia National Laboratories, Albuquerque, New Mexico 87123, USA*
[2]*Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA*
[3]*Department of Astronomy, College of Natural Sciences, University of Texas at Austin, Austin, Texas 78712, USA*

(Received 17 May 2018; published 16 July 2018)

Spectral lines of radiating atoms are broadened by perturbations due to the surrounding plasma environment. In line-broadening calculations, the statistical average of the perturbation is weighted by the density matrix, which, in thermal equilibrium, contains correlations between the radiator and plasma. These correlations, however, have been neglected by all line-broadening theories except for the kinetic theory. The relaxation theory of line broadening is a mathematically exact derivation containing only one physical approximation: neglect of density-matrix correlations. We revisit this derivation and improve it by including the correlations. The line-broadening operator derived with the updated relaxation theory differs from that derived from the kinetic theory, though both derivations are considered to be exact. The kinetic theory derivation predicts that density-matrix correlations result a strong static shift of spectral lines. Our derivation, on the other hand, predicts that the correlations are a frequency-dependent effect that affects the line wings, and there is no shift of the line due to correlations. In addition, we predict that changes in the line shape due to correlations are only noticeable at extremely high densities. To distinguish the more appropriate model, we compare the shifts calculated with the relaxation and kinetic theory with data. The comparison shows support for the relaxation theory and casts into doubt the accuracy of the derivation of the kinetic theory of line broadening.

DOI: 10.1103/PhysRevA.98.012505

I. INTRODUCTION

The broadening of spectral lines is important for many applications, including diagnostics of laboratory and astrophysical plasmas [1,2] and modeling opacities [3–6]. Atomic lines are broadened because the radiating atom is perturbed by the charged particles (such as electrons and ions) in the surrounding plasma.

There are three primary methods for calculating electron broadening: the impact theory [7,8], the relaxation theory [9], and the kinetic theory [10]; the different methods all give slightly different functional forms for the electron-broadening operator. We will not discuss the impact theory further since it contains a number of simplifying assumptions. Since both the relaxation and kinetic theories are more mathematically rigorous, we will focus on the differences between them. There are two fundamental differences between the kinetic and relaxation theories: how the broadening is related to the electron-collision amplitude and the treatment of the density matrix. Here we will focus on the differences in the density-matrix treatment.[1]

The electron-broadening operator is closely related to the thermally-averaged collision amplitude, which is weighted by the density matrix [25]. The time dependence of the density matrix is governed by the time evolution of the total atom plus plasma-electron system

$$\rho(t) = e^{-iHt}\rho_0 e^{iHt}, \tag{1}$$

where $\rho_0 \equiv \rho(t=0)$ is the density matrix at a given initial time [9,25] and H is the Hamiltonian of the total system, consisting of radiator and plasma Hamiltonians (H_0^a and H_0^p, respectively) and the interaction (V^{rp}) between the radiator and plasma,

$$H = H_0^r + H_0^p + V^{rp}, \tag{2}$$

where the superscripts r and p denote the radiator of interest and perturbing plasma, respectively. The expected form of ρ_0 is that it is a thermal distribution of the total atom-plasma system

$$\begin{aligned}\rho_0 &= e^{-\beta H}/\mathrm{Tr}\{e^{-\beta H}\} \\ &= e^{-\beta(H_0^r+H_0^p+V^{rp})}/\mathrm{Tr}\{e^{-\beta(H_0^r+H_0^p+V^{rp})}\},\end{aligned} \tag{3}$$

where $\beta = 1/k_B T$. The presence of V^{rp} in the density matrix creates correlations between the radiator and the plasma. The kinetic theory is the only derivation that uses this form. The relaxation theory neglects V^{rp} in ρ_0 and the density matrix becomes the populations of the individual systems,

$$\rho_{0,\mathrm{relax}} \approx \rho_{r,u}\rho_{p,u}, \tag{4}$$

thus ignoring the correlations in ρ_0 between the atom and plasma; this is a common approximation when calculating the time evolution of the density matrix [7,11–14].

This is not to say that omitting correlations in ρ_0 neglects correlations entirely. According to Eq. (1), correlations will

*thogome@sandia.gov

[1]The density matrix is an important tool in calculating kinetics of quantum systems. Methods for solving for the time evolution of the density matrix vary, which include, but are not limited to, projection-operator techniques [11–15], solving the Bogoliubov-Born-Green-Kirkwood-Yvon hierarchy of differential equations [16–19], and Green's function methods [20–24].

build up in $\rho(t)$ as the plasma and radiator evolve in time and several collisions have taken place [7,9,11–15]. In other words, the relaxation theory [9] only neglects correlations at the initial time $t = 0$ and the correlations for $t \gg 0$ will be dominated by the collisions. In this picture, the correlations in ρ_0 will only be important for early-time evolution of $\rho(t)$, and for the application of spectral line broadening, this should only be important for the wings of the line (where $\Delta\omega$ is large). Both Baranger [7] and Fano [9] have predicted that the effect of the correlations in ρ_0 should only be important for plasma conditions where the coupling is high.

The kinetic-theory-based formalism that accounts for initial density-matrix correlations predicts a large frequency-independent shift of spectral lines [26]. Frequency-independent shifts imply that the correlations in $\rho(t)$ are always influenced by ρ_0 regardless of how much time has passed and how many collisions have occurred. This seems to contradict the above prediction of Fano [9] and Baranger [7] that the correlations in ρ_0 affect only the initial time evolution of $\rho(t)$.

In this paper, we investigate the prediction of the kinetic theory in two ways. First, we check it theoretically by including density-matrix correlations in another line-shape theory. Second, we check predictions of both the relaxation and kinetic theories against measured line shifts. In order to accomplish our first goal, we revisit the relaxation theory of line broadening, which is mathematically exact and the only physical approximation is Eq. (4). We do this with a straightforward step involving a specific definition of the identity operator. The corrections to the line shape in the formalism presented here differ from what is predicted in the kinetic theory of line broadening [10]. In the derivation here, the initial correlations have a frequency-dependent effect on the line shape, with the strongest changes in the wings and the smallest in the core; the overall change in the line shape due to initial correlations is a minor asymmetry. We then compare calculations using the relaxation and kinetic theory formulas with experiment [27] and show that the kinetic theory formulas overpredict the line shifts by several hundred percent. The differences in derivation and the comparison with experiment cast the kinetic theory results [10,26,28–30] into question.

The paper is organized as follows. We first show the reader Fano's derivation of the relaxation theory. We update the relaxation theory to include a more general density matrix. Then we perform a second-order evaluation of the line-shape operator and show terms that arise due to correlations. We then provide a means of evaluating these correlation terms. Finally, we compare our results with the kinetic theory and experiment.

II. FANO'S RELAXATION THEORY

The line shape is given by the real part of the Fourier transform of the dipole-dipole autocorrelation function [15,31]

$$I(\omega) = \frac{1}{\pi}\mathrm{Re}\int_0^\infty dt\, e^{i\omega t}\mathrm{Tr}\{\vec{D}\cdot\vec{D}(t)\rho_0\}, \tag{5}$$

where the trace is performed over all plasma and radiator states; the time evolution of the dipole moment is given in the Heisenberg picture

$$\vec{D}(t) = e^{iHt}\vec{D}e^{-iHt},$$

where H is the Hamiltonian of total radiator-plasma system [given in Eq. (2)] and ρ_0 is the density matrix. In the Heisenberg picture ρ_0 does not evolve in time; a cyclic permutation of the operators can include ρ_0 in the time evolution,

$$\begin{aligned} I(\omega) &= \frac{1}{\pi}\mathrm{Re}\int_0^\infty dt\, e^{i\omega t}\mathrm{Tr}\{D\cdot[e^{-iHt}\rho_0 D e^{iHt}]\} \\ &= \mathrm{Re}\int_0^\infty dt\, e^{i\omega t}\mathrm{Tr}\{D\cdot e^{-iLt}(\rho_0 D)\}, \end{aligned} \tag{6}$$

where the only difference between this and Eq. (1) is that the density matrix is multiplied by $\vec{D}$. In Eq. (6) we have used the Liouville notation as a shorthand,

$$L(\rho_0\vec{D}) = [H,(\rho_0\vec{D})] = H(\rho_0\vec{D}) - (\rho_0\vec{D})H$$

(see Ref. [9] or [15] for more details on the Liouville formalism). The line-shape formalism can be written as a function of frequency by moving the time integral inside the trace and performing the integral

$$I(\omega) = \frac{-1}{\pi}\mathrm{Im}\,\mathrm{Tr}\left\{D\frac{1}{\omega - L}(\rho_0 D)\right\}. \tag{7}$$

The total system can be separated into the radiator and the perturbing plasma coordinates, where we can split the trace accordingly,

$$I(\omega) = \frac{-1}{\pi}\mathrm{Im}\,\mathrm{Tr}_r\left[D\,\mathrm{Tr}_p\left\{\frac{1}{\omega - L}\rho_0\right\}D\right]. \tag{8}$$

The Liouville operator can be separated into the unperturbed and interaction Liouville operators, analogous to Eq. (2),

$$L = L_0^r + L_0^p + L_I, \tag{9}$$

where

$$L_0^r\rho_0 = \left[H_0^r,\rho_0\right], \tag{9a}$$

$$L_0^p\rho_0 = \left[H_0^p,\rho_0\right], \tag{9b}$$

$$L_I\rho_0 = [V^{r,p},\rho_0]. \tag{9c}$$

For simplicity in the derivation, we will contain all noninteracting Liouville operators into one operator $L_0 = L_0^r + L_0^p$. In order to evaluate the effect of the perturbers on the radiator's time evolution, it is convenient to isolate L_I. Fano rewrote the quantity inside the curly brackets of Eq. (8) as

$$\frac{1}{\omega - L_0 - L_I}\rho_0 = \frac{1}{\omega - L_0}\left[1 + T(\omega)\frac{1}{\omega - L_0}\right]\rho_0, \tag{10}$$

where

$$T(\omega) = L_I + L_I(\omega - L_0)^{-1}T(\omega) \tag{11a}$$

$$= \frac{1}{1 - L_I(\omega - L_0)^{-1}}L_I. \tag{11b}$$

Here $T(\omega)$ is the Liouville-generalized scattering T matrix (or collision amplitude) and contains the frequency-dependent interaction between the radiator and the perturbers. This is a particularly convenient form since the interaction between the radiator and plasma is isolated in $T(\omega)$ and is now linearized, so a density-matrix expansion can be performed, as Fano did in the

original publication. The density expansion permits everything to be written in terms of two- or three-particle interactions. Up to this point, Fano has not introduced any approximation and thus the expression is exact; Eq. (10) will be our starting point when we include a more general density matrix.

Fano introduced the approximation that the density matrix could be approximated as

$$\rho_0 \approx \rho_{r,u}\rho_{p,u}, \tag{12}$$

$$\rho_{r,u} = e^{-\beta H_0^r}/\mathrm{Tr}\{e^{-\beta H_0^r}\}, \tag{12a}$$

$$\rho_{p,u} = e^{-\beta H_0^p}/\mathrm{Tr}\{e^{-\beta H_0^p}\}, \tag{12b}$$

where $\rho_{r,u}$ is the density matrix of the isolated radiator and $\rho_{p,u}$ is the density matrix of the perturbers; the additional subscript u denotes uncorrelated density matrices, which is to distinguish these from the more general definition

$$\rho_r = \mathrm{Tr}_p\{\rho_0\}, \tag{13}$$

which contains the correlations. This assumes that correlations between the radiator and plasma are negligible. Equation (12) has the property that it commutes with $(\omega - L_0)^{-1}$. The perturber density matrix was moved to the other side of $(\omega - L_0)^{-1}$ so it is adjacent to the T matrix,

$$\frac{1}{\omega - L}\rho_{r,u}\rho_{p,u} = \frac{1}{\omega - L_0}\left[\rho_{p,u} + T(\omega)\rho_{p,u}\frac{1}{\omega - L_0}\right]\rho_{r,u}.$$

Then the trace in Eq. (8) can be rewritten as

$$\mathrm{Tr}_p\left\{\frac{1}{\omega - L}\rho_{r,u}\rho_p\right\} = \frac{1}{\omega - L_0^r}\left[1 + \langle T(\omega)\rangle_p\frac{1}{\omega - L_0^r}\right]\rho_{r,u}, \tag{14}$$

where

$$\langle T(\omega)\rangle_p = \mathrm{Tr}_p\{T(\omega)\rho_{p,u}\}. \tag{15}$$

The average $T(\omega)$ contains all the effects of the interaction of the radiator with the plasma.

It is desirable to connect Eq. (14) to a more commonly used expression for the line-shape function [7,31,32]

$$I(\omega) = \frac{-1}{\pi}\mathrm{Im}\,\mathrm{Tr}_r\left[D\frac{1}{\omega - L_0^r - \mathcal{H}(\omega)}\rho_{r,u}D\right], \tag{16}$$

where $\mathcal{H}(\omega)$ is the line-broadening operator and governs the time evolution of the radiator due to the average perturbation from the plasma. In other words, we need to find a functional form for $\mathcal{H}(\omega)$ that satisfies

$$\frac{1}{\omega - L_0^r - \mathcal{H}(\omega)} = \frac{1}{\omega - L_0^r}\left[1 + \langle T(\omega)\rangle_p\frac{1}{\omega - L_0^r}\right],$$

where the expression for $\mathcal{H}(\omega)$ that satisfies this equation is

$$\mathcal{H}(\omega) = \frac{1}{1 + \langle T(\omega)\rangle_p(\omega - L_0^r)^{-1}}\langle T(\omega)\rangle_p. \tag{17}$$

This is Fano's final expression for the electron-broadening operator and is valid for conditions when density-matrix correlations are not important.

III. INCLUDING OFF-DIAGONAL DENSITY-MATRIX TERMS

We now want to derive a line-broadening function that contains a density matrix that includes correlations; our starting point is Eq. (10). We need to manipulate Eq. (10) so that when we perform the trace, it becomes a form similar to Eq. (14),

$$\mathrm{Tr}_p\left\{\frac{1}{\omega - L_0}\left[1 + T(\omega)\frac{1}{\omega - L_0}\right]\rho_0\right\} = \frac{1}{\omega - L_0^r}\left[1 + \langle\mathfrak{T}(\omega)\rangle_p\frac{1}{\omega - L_0^r}\right]\rho_r, \tag{18}$$

where the unknown function $\mathfrak{T}(\omega)$ contains all of the radiator-perturber interactions (including the density matrix) and would replace $T(\omega)$ in evaluating the electron-broadening operator in Eq. (17); here ρ_r is defined according to Eq. (13).

When the trace is performed on the first term on the left-hand side of Eq. (18), it is similar in form to Eq. (14),

$$\mathrm{Tr}_p\{(\omega - L_0)^{-1}\rho_0\} = (\omega - L_0^r)^{-1}\rho_r.$$

To put the second term [on the left-hand side of Eq. (18)] in the desired form, we multiply on the right by the unit operator

$$I = \rho_r^{-1}(\omega - L_0^r)\frac{1}{\omega - L_0^r}\rho_r \tag{19}$$

so that

$$\begin{aligned}\frac{1}{\omega - L_0}T(\omega)\frac{1}{\omega - L_0}\rho_0 &= \frac{1}{\omega - L_0}T(\omega)\frac{1}{\omega - L_0}\rho_0\rho_r^{-1}(\omega - L_0^r)\frac{1}{\omega - L_0^r}\rho_r \\ &= \frac{1}{\omega - L_0}\mathfrak{T}(\omega)\frac{1}{\omega - L_0^r}\rho_r, \end{aligned}\tag{20}$$

$$\mathfrak{T}(\omega) = T(\omega)\frac{1}{\omega - L_0}\rho_0\rho_r^{-1}(\omega - L_0^r). \tag{21}$$

When we perform the trace over the plasma coordinates, this becomes the right-hand side of Eq. (18). Now the electron-broadening operator is defined as

$$\mathcal{H}(\omega) = \frac{1}{1 + \langle\mathfrak{T}(\omega)\rangle(\omega - L_0^r)^{-1}}\langle\mathfrak{T}(\omega)\rangle, \tag{22}$$

$$\mathfrak{T}(\omega) = L_I\frac{1}{1 - (\omega - L_0)^{-1}L_I}\frac{1}{\omega - L_0}\rho_0\rho_r^{-1}(\omega - L_0^r). \tag{23}$$

Use of Eq. (19) is required because ρ_0 no longer commutes with L_0. One property of Eq. (23) is that if ρ_0 is defined as in Ref. [9], then $\mathfrak{T}(\omega)$ reduces back to $T(\omega)$. We note that we have made no approximations about the structure of ρ_0, therefore this formula can be applied to a system with arbitrary initial conditions.

IV. SECOND-ORDER DENSITY-MATRIX CORRELATION CORRECTION

Calculations of the full N-body line-broadening problem are extremely difficult and would require a large amount of computing time; computer simulations can do this

numerically [33–36], but these line-broadening simulations are currently limited to classical particles. Some simplifying approximations for semianalytic evaluation include Taylor expanding the electron-broadening operator [and $\mathfrak{T}(\omega)$] to second order and collecting all terms that are second order in L_I. In addition, the line-broadening problem is often reduced to a binary-collision result [7,8], where the interactions between plasma particles are approximated with a screening factor [37–39]; these approximations are used by every semianalytic calculation. The second-order result for the electron broadening is [9,40]

$$\mathcal{H}(\omega) \approx \mathcal{H}^{(1)} + \mathcal{H}^{(2)}(\omega) - \mathcal{H}^{(1)}(\omega)\frac{1}{\omega - L_0^r}\mathcal{H}^{(1)}(\omega), \tag{24}$$

$$\mathcal{H}^{(1)}(\omega) = \mathrm{Tr}_p\{L_I G(\omega)\rho_0\}\rho_r^{-1}(\omega - L_0^r), \tag{24a}$$

$$\mathcal{H}^{(2)}(\omega) = \mathrm{Tr}_p\{L_I G(\omega) L_I G(\omega)\rho_0\}\rho_r^{-1}(\omega - L_0^r), \tag{24b}$$

where $G(\omega)$ is a Green's function, defined to be

$$G(\omega) = \frac{1}{\omega - L_0}.$$

In order to properly evaluate the density matrix, we need to define the Hamiltonian as explicit sums over the N plasma particles,

$$H_0^p = \sum_i^N H_0^i + \sum_i^N \sum_{j<i} V^{ij},$$

$$V^{rp} = \sum_i^N V^{r,i}$$

and insert this into Eq. (2) to get a total Hamiltonian

$$H = H_0^r + \sum_i^N H_0^i + \sum_i^N \sum_{j<i} V^{ij} + \sum_i^N V^{ri}. \tag{25}$$

We can write the density matrix in a slightly simplified form

$$\rho_0 \propto \exp\left\{-\beta\left(H_0^r + \sum_{i=1}^N H_0^i + \sum_{i=1}^N V^{ri}\right)\right\} \tag{26}$$

by assuming that we can account for the V^{ij} terms by screening V^{ri} [10,28,41]. Trying to solve for this density matrix explicitly is impractical, and a simpler method is required.

One of the goals of this section is to clearly show how the density-matrix correlations affect the line shape. We therefore use an integral expansion [7,15,26,29,42] of Eq. (26),

$$\begin{aligned}
&\exp\left[-\beta\left(H_0^r + \sum_i H_0^i + \sum_i V^{ri}\right)\right] \\
&= e^{-\beta H_0^r}\exp\left(-\beta\sum_i H_0^i\right) - e^{-\beta H_0^r}\exp\left(-\beta\sum_i H_0^i\right)\int_0^\beta d\tau \exp\left[\tau\left(H_0^r + \sum_j H_0^j\right)\right] \\
&\times \sum_k V^{rk}\exp\left[-\tau\left(H_0^r + \sum_{j'} H_0^{j'} + \sum_{k'} V^{rk'}\right)\right],
\end{aligned} \tag{27}$$

so that the first term is the same uncorrelated density matrix that Fano [9] used. We define the uncorrelated and correlated density matrices as

$$\rho_0 = [\hat{\rho}_{r,u}\hat{\rho}_{p,u} + \hat{\rho}_c]/\mathrm{Tr}\{\hat{\rho}_{r,u}\hat{\rho}_{p,u} + \hat{\rho}_c\}, \tag{28}$$

$$\hat{\rho}_{r,u} = e^{-\beta H_0^r}, \tag{28a}$$

$$\hat{\rho}_{p,u} = \exp\left(-\beta\sum_i H_0^i\right), \tag{28b}$$

$$\hat{\rho}_c = -e^{-\beta H_0^r}\exp\left(-\beta\sum_i H_0^i\right)\int_0^\beta d\tau\exp\left[\tau\left(H_0^r + \sum_j H_0^j\right)\right]\sum_k V^{rk}\exp\left[-\tau\left(H_0^r + \sum_{j'} H_0^{j'} + \sum_{k'} V^{rk'}\right)\right], \tag{28c}$$

where the density matrix with circumflexes denote unnormalized density matrices.

Since our goal is to calculate $\mathcal{H}(\omega)$ to second order in the interaction potential, we do not consider any density-matrix correlations for terms in Eq. (24) that are already second order in L_I; for these we will simply replace ρ_0 with $\rho_{r,u}\rho_{p,u}$ and they will become the original Fano [9] results. Therefore, the only second-order contribution from correlations will come from $\mathcal{H}^{(1)}(\omega)$. Using Eq. (28) to create uncorrelated and correlated terms, $\mathcal{H}^{(1)}(\omega)$ becomes

$$\begin{aligned}
\mathcal{H}^{(1)}(\omega) &= \mathrm{Tr}_p\{L_I(\omega - L_0)^{-1}\rho_0\}\rho_r^{-1}(\omega - L_0^r) \\
&= \left[\mathrm{Tr}_p\{L_I\hat{\rho}_{p,u}\hat{\rho}_{r,u}\}(\omega - L_0^r)^{-1}\rho_r^{-1}(\omega - L_0^r) + \mathrm{Tr}_p\{L_I(\omega - L_0)^{-1}\hat{\rho}_c\}\rho_r^{-1}(\omega - L_0^r)\right]/\mathrm{Tr}\{\hat{\rho}_{r,u}\hat{\rho}_{p,u} + \hat{\rho}_c\},
\end{aligned} \tag{29}$$

where commutation of $[L_0, \rho_{r,u}\rho_{p,u}] = 0$ has been used for the first term on the right-hand side; no further simplifications can be made to this equation without approximation. We desire to connect this first term to the original derivation of Fano; we therefore will approximate (though not entirely accurate) the inverse radiator density matrix as uncorrelated [10,26]

$$\rho_r^{-1} \approx \rho_{r,u}^{-1}.$$

This simplification allows us to take advantage of commutation relationships and remove the frequency dependence of this term; we will use this approximation for the rest of the paper. The uncorrelated line-broadening term approximately becomes the static shift as originally derived by Fano,

$$\mathrm{Tr}_p\left\{L_I\hat{\rho}_{p,u}\hat{\rho}_{r,u}\left(\omega - L_0^r\right)^{-1}\right\}\rho_r^{-1}\left(\omega - L_0^r\right)/\mathrm{Tr}\{\hat{\rho}_{r,u}\hat{\rho}_{p,u} + \hat{\rho}_c\} \approx \mathrm{Tr}_p\{L_I\hat{\rho}_p\}/\mathrm{Tr}\{\hat{\rho}_{r,u}\hat{\rho}_{p,u} + \hat{\rho}_c\}. \tag{30}$$

The second term then becomes the lowest-order correction for the density-matrix correlations

$$\mathrm{Tr}_p\{L_I(\omega - L_0)^{-1}\hat{\rho}_c\}\rho_r^{-1}\left(\omega - L_0^r\right)/\mathrm{Tr}\{\hat{\rho}_{r,u}\hat{\rho}_{p,u} + \hat{\rho}_c\}. \tag{31}$$

V. EVALUATION OF THE CORRELATION CORRECTION

To properly evaluate the correction, we first need to find the proper normalization factor for ρ_0, which requires evaluating the trace of the total density matrix [9,25]. The largest contribution to $\mathrm{Tr}\{\rho_0\}$ is $\hat{\rho}_{r,u}\hat{\rho}_{p,u}$ (see Appendix A); we therefore approximate the trace as

$$\mathrm{Tr}_{rp}\{e^{-\beta H}\} \approx \left[\sum_r e^{-\beta E_r}\right]\left(\frac{\mathcal{V}}{\lambda_D^3}\right)^N, \tag{32}$$

which will be accurate for the neutral hydrogen cases we explore here. The lowest-order correlated broadening term (31) becomes

$$\begin{aligned}&\mathrm{Tr}_p\{L_I(\omega - L_0)^{-1}\rho_c\}\rho_r^{-1}\left(\omega - L_0^r\right)\\ &\quad\approx -\mathrm{Tr}\left\{\sum_i\sum_k L_I^{ri}(\omega - L_0)^{-1}\left(\frac{\lambda_D^3}{\mathcal{V}}\right)^N \exp\left(-\beta\sum_j H_0^j\right)e^{-\beta H_0^r}\int_0^\beta d\tau\, e^{\tau(H_0^r + H_0^k)}V^{rk}e^{-\tau(H_0^r + H_0^k)}\right\}e^{\beta H_0^r}\left(\omega - L_0^r\right).\end{aligned} \tag{33}$$

The resulting interaction will have single-perturber ($i = k$) and two-perturber interactions ($i \neq k$), with the former of order N and the latter of order N^2. In addition, $\exp(-\beta\sum_j H_0^j)$ will give a factor of $\mathcal{V}/\lambda_D^3$ for every term where $j \neq k$ or $j \neq i$. Using u and k to denote radiator and free-perturber states, the lowest-order density-matrix-correlation correction to the line broadening is (upper-state broadening only)

$$\begin{aligned}&\mathrm{Tr}_p\{L_I(\omega - L_0)^{-1}\rho_c\}\rho_r^{-1}\left(\omega - L_0^r\right)\\ &\quad\approx -n_e^2\lambda_D^6\int_0^\infty d^3\vec{k}_1 e^{-\beta\frac{1}{2}k_1^2}\langle u\vec{k}_1|V^{r1}|u''\vec{k}_1\rangle(\omega - E_{u''} + E_l)^{-1}\int_0^\infty d^3\vec{k}_2 e^{-\beta\frac{1}{2}k_2^2}\langle u''\vec{k}_2|V^{r2}|u'\vec{k}_2\rangle\frac{1 - e^{-\beta(E_{u''} - E_u')}}{E_{u''} - E_{u'}}(\omega - E_{u'} + E_l)\\ &\qquad -n_e\lambda_D^3\int_0^\infty d^3\vec{k}_1\int_0^\infty d^3\vec{k}_1'\langle u\vec{k}_1|V^{r1}|u''\vec{k}_1'\rangle\left(\omega - E_{u''} + E_l - \tfrac{1}{2}k_1'^2 + \tfrac{1}{2}k_1^2\right)^{-1}\langle u''\vec{k}_1'|V^{r1}|u'\vec{k}_1\rangle e^{-\beta\frac{1}{2}k_1^2}\\ &\qquad\times\frac{1 - e^{-\beta(E_{u''} - E_{u'} + \frac{1}{2}k_1'^2 - \frac{1}{2}k_1^2)}}{E_{u''} - E_{u'} + \frac{1}{2}k_1'^2 - \frac{1}{2}k_1^2}(\omega - E_{u'} + E_l),\end{aligned} \tag{34}$$

where the superscripts on V denote on which particle the operator is acting. This formula can be reduced to radial integrals by performing a partial wave expansion and using Wigner $3j$ and $6j$ symbols [29,43–46], which is done in detail in Appendix B.

The inverse, $(\omega - L_0)^{-1}$, can be solved in the same way as in previous calculations where it is separated into its real and imaginary parts [9,43]

$$(\omega - L_0)^{-1} = \frac{\mathrm{P.V.}}{\omega - L_0} - i\pi\delta(\omega - L_0),$$

where P.V. is the principal value and δ is the Dirac delta function. There are multiple ways of evaluating these terms, such as the method in Ref. [43], and we will not discuss them further. Unfortunately, there is no simplification for the real part in Eq. (34), but there is considerable simplification for the imaginary part. The imaginary part of Eq. (34) can be evaluated in the same way as in [29,43,45], but with a correction factor (showing only upper-state broadening),

$$\begin{aligned}&\mathrm{Im}\,\mathrm{Tr}_p\left\{L_1(\omega - L_0)^{-1}\rho_c\rho_r^{-1}\left(\omega - L_0^r\right)\right\}\\ &\quad\approx -\mathrm{Im}\,\mathrm{Tr}_{k_1}e^{-\beta\frac{1}{2}k_1^2}\langle uk_1|V(\omega - L_0)^{-1}V|u'k_1\rangle\\ &\qquad\times[1 - e^{-\beta(\omega - E_{u'} + E_l)}].\end{aligned} \tag{35}$$

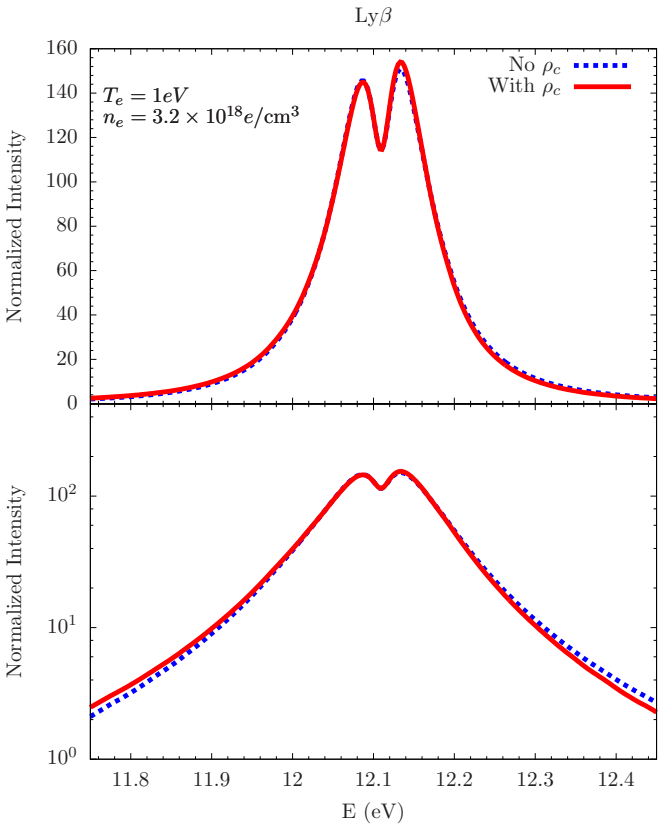

FIG. 1. Comparison of line profile with and without inclusion of the correlated density-matrix correction [the second term in Eq. (29)]. The example here is the Ly$_\beta$ transition of neutral hydrogen at $T_e =$ 1 eV and $n_e = 3.2 \times 10^{18}$ e/cm^3. The effect of the correlations is to slightly skew the wings of the profile.

This term does nothing to the center of the line, since the correction factor is zero when $\Delta\omega_{u'l} = \omega - E_{u'} + E_l = 0$. If $\Delta\omega_{u'l}$ becomes appreciable compared to β, the blue part of the wings of the line will become depressed due to the reduction in the broadening and the red wing, on the other hand, will become enhanced due to the increase of the broadening. In addition, the real part will also be zero at the line center due to the presence of $(\omega - L_0)$, but as the detuning becomes large, both the red and the blue sides of the profile exhibit a redshift, meaning that the depression of the blue wing and the enhancement of the red wing will become stronger. The overall effect, therefore, is to skew the wings of the profile toward the red, rather than being symmetric about the line center.

The effects of the density matrix are going to be most pronounced when the temperatures are small and the line shapes are wide. For typical laboratory conditions, such as those found in the Wiese *et al.* [27] experiment, the changes are not noticeable. Therefore, to illustrate how the density-matrix correlations change the line shape, we chose to compare line shapes at extremely high density. Figure 1 shows the line shape of Ly$_\beta$ neutral hydrogen with and without the density-matrix correlations (the details of the electron broadening are in [47] and repeated in Appendix B). As discussed above, the correlations skew the wings so that the red wing is enhanced and the blue wing is depressed. We can therefore conclude that, except for highly coupled plasmas, the correlations in the initial density matrix are not important.

VI. COMPARISON WITH KINETIC THEORY

First and foremost, we want to say that our derivation does not match the results of Hussey *et al.* [10]. The easiest way to see this is to write both results in the Lippmann-Schwinger [48] expansion. Hussey's electron broadening operator [Eq. (4.3) in [10]] is

$$\mathcal{H}_{\text{kin}}(\omega) = \text{Tr}_p\{\hat{\mathcal{H}}_{\text{kin}}(\omega)\rho_0\}\rho_r^{-1}, \tag{36}$$

where

$$\hat{\mathcal{H}}_{\text{kin}}(\omega)\rho_0 = L_I\rho_0 + \hat{\mathcal{H}}_{\text{kin}}(\omega)\rho_0 G_{\text{kin}}(\omega)\mathcal{L}_I, \tag{37}$$

$$G_{\text{kin}}(\omega) = \frac{1}{\omega - L_0^r - L_0^p - C_{r,p}(\omega)}, \tag{38}$$

where $\mathcal{L}_I$ is a screened interaction and $C_{r,b}(\omega)$ contains mean-field operators. The generalized relaxation theory results, which were derived in Appendix C, are

$$\mathcal{H}_{\text{relax}}(\omega) = \text{Tr}_p\{\hat{\mathcal{H}}_{\text{relax}}(\omega)\rho_0\}\rho_r^{-1}\big(\omega - L_0^r\big), \tag{39}$$

where

$$\hat{\mathcal{H}}(\omega)\rho = L_I\big(\omega - L_0^r - L_0^p\big)^{-1}\rho_0 + L_I\big(\omega - L_0^r - L_0^p\big)^{-1}[1-P]\hat{\mathcal{H}}(\omega)\rho_0, \tag{40}$$

where P is a projection operator [11],

$$PA\rho_0 = \rho_0\rho_r^{-1}Tr_p\{A\rho_0\};$$

this form is fundamentally different from the kinetic theory in two principle ways: how the density matrix affects the broadening and the presence of the projection operator.

The presence of the projection operator is unique to the relaxation theory of line broadening.[2] Hussey *et al.* [10] showed that [after using $C_{rp}(\omega)$ to screen L_I in frequency-dependent terms of $\mathcal{H}(\omega)$] that their derivation is formally identical to the unified theory of Smith *et al.* [38]. We point out that even though the final form of the unified theory does not contain a projection operator, it is formally present in the derivation and is thrown out, a point of criticism by Lee [49]. Therefore, because a projection operator is formally present in both the relaxation and unified theories of line broadening, the lack of one in the kinetic theory raises concerns. However, this is not the proper place to discuss or justify the presence of the projection operator in $\mathcal{H}(\omega)$. The rest of this section is devoted to comparing how the density-matrix correlations change the line broadening according to each prediction (kinetic or relaxation theory).

Both our work and the Hussey *et al.* [10] derivation established that the lowest-order corrections due to density-matrix correlations are in the first term of $\mathcal{H}(\omega)$, which we denote by $\mathcal{H}^{(1)}(\omega)$. Splitting the density matrix into its uncorrelated and correlated terms $\rho_0 = \rho_p\rho_r + \rho_c$, the $\mathcal{H}^{(1)}(\omega)$ for the relaxation

[2]Projection operators have never been included to calculate a line shape; they have always been ignored.

and kinetic theories are

$$\mathcal{H}^{(1)}_{\rm kin}(\omega) = {\rm Tr}_b\{L_I\rho_{p,u}\} + {\rm Tr}_p\{L_I\rho_c\}\rho^{-1}_{r,u}, \quad (41)$$

$$\mathcal{H}^{(1)}_{\rm rel}(\omega) = {\rm Tr}_b\{L_I\rho_{p,u}\} + {\rm Tr}_p\{L_I(\omega - L_0)^{-1}\rho_c\}\rho^{-1}_{r,u}(\omega - L^r_0). \quad (42)$$

Both theories have the same uncorrelated shift term, but the correlated-density-matrix correction is different: Kinetic theory is static (i.e., frequency independent), relaxation theory is frequency dependent.

Hussey *et al.* [10] predicts a static shift (meaning the whole line is shifted by this amount) that is second order in V (since both L_I and ρ_c contain a factor of V), which makes this term dipole allowed. For near-neutral one-electron atoms, dipole-allowed interactions are typically the strongest interactions, which means that this shift term can be quite large and similar in magnitude to the electron broadening. Interestingly, the first implementation of the Hussey *et al.* [10] results do not include the static shift [28], though it is implemented in later calculations [26,29,30].

In our derivation, the density-matrix correlations are a frequency-dependent effect. The far wings of the line are shifted by the amount predicted by Refs. [10,26], which is achieved by evaluating Eq. (42) at the limit where $\omega \to \infty$. The line core, on the other hand, does not have this shift; the presence of $(\omega - L^r_0)$ in Eq. (42) results in zero shift at the line core and a slight asymmetry of the spectral lines. This asymmetry will enhance the red wing of the profile and depress the blue wing of the profile (as shown in the preceding section).

There is experimental evidence that questions the accuracy of the kinetic-theory shift (41). The experiment by Wiese *et al.* [27] measured high-density hydrogen at temperatures of $\sim$1 eV and electron densities between 10^{16} and 10^{17} $e/{\rm cm}^3$; the scatter of the measured shifts for H_β are less than 0.1 Å. We computed $\mathcal{H}(\omega)$ according to the relaxation and kinetic theory formulas for H_β, the $n = 4$ to $n = 2$ transition; we use an expanded basis[3] to ensure the accuracy of our calculation. The shifts are compared in Fig. 2. At the highest-density conditions ($n_e = 10^{17}$ $e/{\rm cm}^3$), the shift from Eq. (41) overpredicts the measured value by 675%, while the relaxation theory underpredicts by 35%.

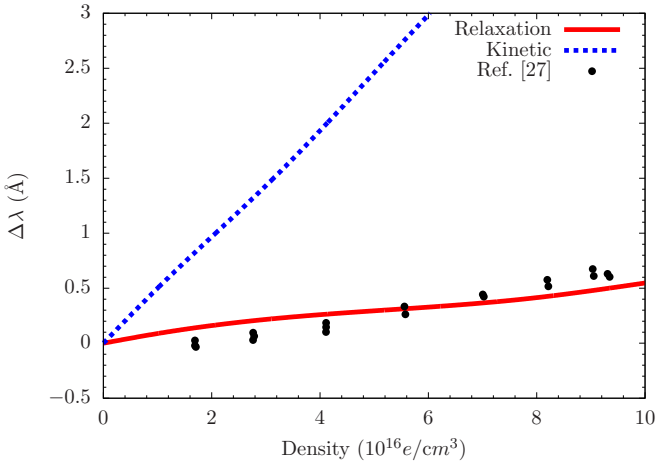

FIG. 2. Predictions of shifts for the relaxation theory and the kinetic theory compared to the measured shifts by Wiese *et al.* [27]. The shifts from the relaxation theory, while not perfect, agree fairly well with the measured values. The shifts from the kinetic theory, on the other hand, are several times larger than the measured values.

VII. CONCLUSION

Most line-broadening calculations assume that the density matrix which describes the radiator-plasma system is uncorrelated, meaning off-diagonal terms are neglected. Only the kinetic theory [10] of spectral line broadening has included these off-diagonal terms of the density matrix in its derivation. We have updated the mathematically rigorous relaxation theory of Fano [9] to include the off-diagonal terms of the density matrix. However, the line-broadening formulas we derive are different from that of the Hussey *et al.* [10] kinetic theory. The largest difference between our work and the kinetic theory is the appearance of a line shift in the latter. Comparison with experiment shows that the kinetic theory formalism overpredicts the shifts. This work questions the accuracy of the kinetic theory line-broadening derivation of [10], and closer inspection of the derivation is needed.

ACKNOWLEDGMENTS

We thank Dr. Carlos Iglesias, Dr. Stephanie Hansen, Dr. Andrew Baczewski, and Dr. Daniel Jensen for stimulating discussions. We also thank Marc Schaeuble for help with the manuscript. T.A.G. acknowledges support from the National Science Foundation Graduate Research Fellowship under Grant No. DGE-1110007. T.A.G. was also supported by the US Department of Energy, Office of Science Early Career Research Program, Office of Fusion Energy Sciences under Grant No. FWP-14-017426. M.H.M. and D.E.W. acknowledge support from the US Department of Energy under Grant No. DE-SC0010623, the Wooton Center for Astrophysical Plasma Properties under the US Department of Energy under Grant No. DE-FOA-0001634, and the National Science Foundation Grant No. NSF-AST 1707419. Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the US Department of Energy's National Nuclear Security Administration under Contract No. DE-NA-0003525. The views expressed in the article do not necessarily represent the views of the US Department of Energy or the United States Government.

APPENDIX A: NORMALIZING THE CORRELATED DENSITY MATRIX

The density matrix, by definition, needs to be normalized to unity [25],

$${\rm Tr}\{\rho_0\} = 1. \quad (A1)$$

Thus, whatever form the density matrix takes needs to be divided by the trace. In the discussion above, we have separated

[3]We include the $n = 5$ states in addition to the $n = 2$ and $n = 4$ states; see [50], [36], or [51] for a discussion of basis set accuracy.

the density matrix into its correlated and uncorrelated parts

$$\rho_0 = \rho_{r,u}\rho_{p,u} + \rho_c$$

and the trace is evaluated as the sum of both the uncorrelated and correlated parts of the density matrix. The trace of the uncorrelated density matrix was previously evaluated by Smith and Hooper [40] and O'Brien and Hooper [43],

$$\mathrm{Tr}_r\{\rho_{r,u}\} = \sum_i e^{-\beta E_i^r}, \tag{A2}$$

$$\mathrm{Tr}_p\{\rho_{p,u}\} = \left(\frac{\mathcal{V}}{\lambda_D^3}\right)^N, \tag{A3}$$

where $\mathcal{V}$ is the volume, λ_D is the thermal de Broglie wavelength, and N is the number of particles inside the volume. We use this section to evaluate the trace of the density matrix that includes correlations.

In the expansion of the density matrix given in Eq. (27), we obtain a first-order correction

$$\mathrm{Tr}\{\rho_c\} \approx \mathrm{Tr}\left\{e^{-\beta E_i^r}\exp\left(-\beta\sum_l H_0^l\right)\right.$$
$$\times\int_0^\beta d\tau\exp\left[\tau\left(H_0^r+\sum_j H_0^j\right)\right]$$
$$\left.\times\sum_i V^{ri}\exp\left[-\tau\left(H_0^r-\sum_k H_0^k\right)\right]\right\}. \tag{A4}$$

Because of the trace, and the properties of the single-particle operators in the matrix exponentials, the exponentials in the integral will vanish, so the trace reduces to

$$\mathrm{Tr}\{\rho_c\} \approx \left(\frac{\mathcal{V}}{\lambda_D^3}\right)^{N-1}\mathrm{Tr}\{e^{-\beta E_i^r}e^{-\beta H_0^1}NV^{r1}\beta\}. \tag{A5}$$

We can factor volume and de Broglie wavelength terms out of $\mathrm{Tr}\{\rho_c\}$ to make it proportional to $\mathrm{Tr}\{\rho_{r,u}\rho_{r,p}\}$,

$$\mathrm{Tr}\{\rho_0\} = \mathrm{Tr}\{\rho_{r,u}\rho_{p,u}\} + \mathrm{Tr}\{\rho_c\}$$
$$\approx \sum_i e^{-\beta E_i^r}\left(\frac{\mathcal{V}}{\lambda_D^3}\right)^N - \sum_i e^{-\beta E_i^r}\left(\frac{\mathcal{V}}{\lambda_D^3}\right)^N\lambda_D^3\frac{N}{V}\mathrm{Tr}\{e^{-\beta E_i^r}e^{-\beta H_0^i}V^{ri}\beta\}\left[\sum_i e^{-\beta E_i^r}\right]^{-1} \tag{A6}$$

so that we can write the trace of the total density matrix as

$$\mathrm{Tr}\{\rho_0\} \approx \mathrm{Tr}\{\rho_{r,u}\rho_{p,u}\}\left[1-\lambda_D^3\frac{N}{V}\mathrm{Tr}\{e^{-\beta E_i^r}e^{-\beta H_0^1}V^{r1}\beta\}\left(\sum_i e^{-\beta E_i^r}\right)^{-1}\right]. \tag{A7}$$

In most cases, the density is small compared to unity, meaning that the term in square brackets can almost always be approximated as unity,

$$\mathrm{Tr}\{\rho\} = \mathrm{Tr}\{\rho_{r,u}\rho_{p,u}\} + \mathrm{Tr}\{\rho_c\}$$
$$\approx \mathrm{Tr}\{\rho_{r,u}\rho_{p,u}\}, \tag{A8}$$

which is what we use as the normalization in Sec. V.

APPENDIX B: LINE-BROADENING DETAILS

This is an outline of the electron-broadening treatment that we use for calculation of the profiles in Fig. 1 and the shifts in Fig. 2. This was a code developed by Gomez [47] and we repeat the details here for the reader's convenience. Our electron-broadening calculation treats both the atomic and plasma electrons quantum mechanically. This was modeled after the quantum-mechanical treatments of Junkel *et al.* [29] and Woltz and Hooper [45], but differ in that we include exchange effects in our calculation. Since calculations of electron exchange in line broadening are not documented for a second-order line-broadening theory (in the same way that direct-only calculations are documented in [29,45]), we show the work here. The point here is not to open a discussion about exchange, but rather to inform the reader of our electron-broadening calculation.

For our electron-broadening treatment, we evaluate $\mathcal{H}(\omega)$ to second order in L_I, repeated from Appendix C,

$$\mathcal{H}(\omega) = \langle L_I G(\omega)\rho_0\rangle\rho_r^{-1}(\omega - L_0^r) + \langle L_I G(\omega)L_I G(\omega)\rho_0\rangle\rho_r^{-1}(\omega - L_0^r) - \langle L_I G(\omega)\rho_0\rangle\rho_r^{-1}\langle L_I G(\omega)\rho_0\rangle\rho_r^{-1}(\omega - L_0^r).$$

In the main text, we reduce this to a binary-collision approximation and we keep everything second order in the interaction, including terms with the density-matrix correlations. The resulting approximation for $\mathcal{H}(\omega)$ is

$$\mathcal{H}(\omega) = N\langle L_I\rho_p\rangle + N\langle L_I G(\omega)\rho_c\rangle\rho_r^{-1}(\omega - L_0^r) + N\langle L_I G(\omega)L_I G(\omega)\rho_p\rangle; \tag{B1}$$

we are not currently evaluating the third term. The reason for this is that $N\langle L_I\rho_p\rangle$ for neutral hydrogen is so small that the third term is negligible compared to $N\langle L_I G(\omega)L_I G(\omega)\rho_p\rangle$.

To calculate line shapes with the above, we use the same full-Coulomb treatment as Junkel *et al.* [29], where the individual terms are (showing only the upper-state broadening term)

$$\mathcal{H}_{u,u'}(\omega) = n_e\lambda_D^3\int_0^\infty e^{-\beta\frac{1}{2}k_1^2}\langle u\vec{k}_1|V|u'\vec{k}_1\rangle d^3\vec{k}_1 + n_e\lambda_D^3\int_0^\infty e^{-\beta\frac{1}{2}k_1^2}\int_0^\infty \langle u\vec{k}_1|V|u''\vec{k}_2\rangle G(\omega)\langle u''\vec{k}_2|\rho_c|u'\vec{k}_1\rangle d^3\vec{k}_1$$
$$+ n_e\lambda_D^3\int e^{-\beta\frac{1}{2}k_1^2}\int \langle u\vec{k}_1|V|u''\vec{k}_2\rangle G(\omega)\langle u''\vec{k}_2|V|u'\vec{k}_1\rangle d^3\vec{k}_1, \tag{B2}$$

where u denotes a set of atomic states and $\vec{k}$ denotes a set of free-electron states. Here we have neglected the two-electron term in Eq. (34), and all k subscripts denote the different states of only one electron (in the main text, the different subscripts were used to distinguish between electrons, but that is unnecessary here and the distinction between states becomes clearer).

As in Refs. [29,45], our interaction potential V is a Coulomb interaction and contains nuclear potential terms

$$V(r_1,r_2) = \left[\frac{1}{|\vec{r}_1-\vec{r}_2|} - \frac{1}{r_1}\right], \quad \frac{1}{|\vec{r}_1-\vec{r}_2|} = \sum_k\sum_q \frac{r_<^k}{r_>^{k+1}}\frac{4\pi}{2k+1}Y_{kq}^*(\hat{r}_1)Y_{kq}(\hat{r}_2), \tag{B3}$$

where the electron-electron repulsion is Taylor expanded for easy evaluation and $r_<$ and $r_>$ are the minimum and maximum of r_1 and r_2, respectively. To more simply evaluate the Coulomb matrix elements, we perform a partial-wave expansion of the free-electron states and assume that the atomic wave function can also be separable in radial and angular components [29,44,45,52]

$$\langle r|\vec{k}_1\rangle = \frac{2}{\pi}\sum_{l_1m_1} i^l\frac{1}{k_1 r}F_{l_1}(k_1,r)Y_{l_1m_1}^*(\hat{k}_1)Y_{l_1m_1}(\hat{r}), \quad \langle r|u\rangle = \frac{1}{r}R_uY_{lm}(\hat{r}), \tag{B4}$$

where the radial wave functions $F_l(k,r)$ are Coulomb waves (or plane waves for the case of neutral atoms). To evaluate the Coulomb matrix elements, it becomes convenient to couple the angular momentum together to a total angular momentum L with magnetic quantum number M. Coulomb matrix elements are independent of M and depend on m_1 only through a Clebsch-Gordan coupling coefficient [44]. We can evaluate the M and m_1 averaged interaction via a $3j$-symbol sum rule,

$$\langle uk_1l|\hat{\mathcal{H}}(\omega)|u'k_1l\rangle = \sum_L\langle ul_1k_1L|\hat{\mathcal{H}}(\omega)|u'lk_1L\rangle(2L+1)\sum_{m_1,M}\begin{pmatrix} l_u & l_1 & L\\ m_u & m_1 & -M\end{pmatrix}^2$$
$$= \sum_L\langle ul_1k_1L|\hat{\mathcal{H}}(\omega)|u'lk_1L\rangle\frac{(2L+1)}{2l_u+1}.$$

After inserting this into Eq. (B2), coupling the angular momentum of the atom and plasma electron, and then performing the sum over the magnetic quantum numbers, the electron-broadening operator becomes

$$\mathcal{H}_{u,u'}(\omega) = \sum_{L,S}\frac{(2L+1)(2S+1)}{(2l_u+1)(2s+1)}n_e\frac{\lambda_D^3}{2}\left\{\int_0^\infty e^{-\beta\frac{1}{2}k_1^2}A_{u,u'}(k_1)dk_1 + \int_0^\infty e^{-\beta\frac{1}{2}k_1^2}\int_0^\infty dk_2dk_1B_{u,u'',u'}(k_1,k_2)\right.$$
$$\left.\times\left[\frac{1-e^{-\beta(E_{u''}-E_{u'}+\frac{1}{2}k_2^2-\frac{1}{2}k_1^2)}}{E_{u''}-E_{u'}+\frac{1}{2}k_2^2-\frac{1}{2}k_1^2}(\omega-E_{u'}+E_l)+1\right]\left[\frac{PV}{\omega-E_{u''}+E_l-\frac{1}{2}k_2^2+\frac{1}{2}k_1^2} - i\pi\delta\left(\omega-E_{u''}+E_l-\frac{1}{2}k_2^2+\frac{1}{2}k_1^2\right)\right]\right\},$$

where the additional factor of $1/2$ is from the density matrix now including plasma-electron spin and s is the spin of the atomic electron. In addition, we have used, for shorthand [46],

$$A_{u,u'}(k_1) = \frac{2}{\pi}\delta_{l_ul_{u'}}\sum_{l_1}\left[\sum_k\langle ul_1k_1LS\|D^k\|u'l_1k_1LS\rangle + \langle ul_1k_1LS\|E^k\|u'l_1k_1LS\rangle\right], \tag{B5}$$

$$B_{u,u'',u'}(k_1,k_2) = \frac{4}{\pi^2}\delta_{l_u,l_{u''}}\frac{1}{2}\sum_{l_1,l_2}\left[\sum_k\langle ul_1k_1LS\|D^k\|u''l_2k_2LS\rangle + \langle ul_1k_1LS\|E^k\|u''l_2k_2LS\rangle\right]$$
$$\times\left[\sum_k\langle u''l_2k_2LS\|D^k\|u'l_1k_1LS\rangle + \langle u''l_2k_2LS\|E^k\|u'l_1k_1LS\rangle\right], \tag{B6}$$

$$\langle ul_1k_1LS\|D^k\|u''l_2k_2LS\rangle = (-1)^{L+l_u+l_{u''}}\begin{pmatrix} l_u & k & l_{u''}\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} l_1 & k' & l_2\\ 0 & 0 & 0\end{pmatrix}\begin{Bmatrix} l_u & l_1 & L\\ l_2 & l_{u''} & k\end{Bmatrix}$$
$$\times\int_0^\infty\int_0^\infty dr_2dr_1F_l(k_1,r_2)R_u(r_1)\left[\frac{r_>^k}{r_<^{k+1}} - \frac{\delta_{k,0}}{r_1}\right]R_{u'}(r_1)F_l(k_1,r_2),$$

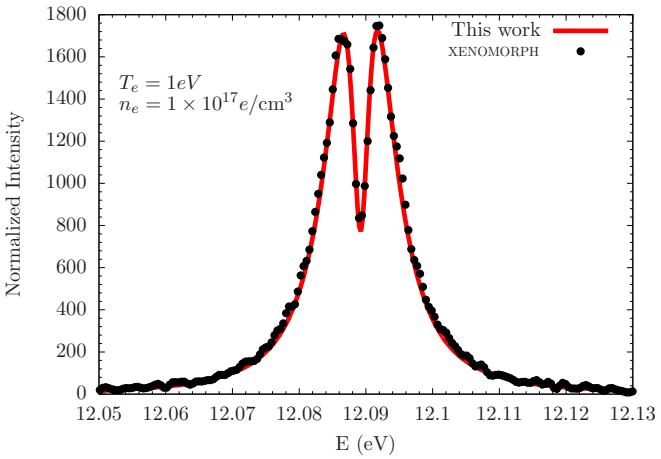

FIG. 3. Comparison of line profile calculated with the electron-broadening model here vs the XENOMORPH code [36]. For this comparison, the ion dynamics have been turned off in XENOMORPH [36]. The two calculations use the same ion microfields so the only difference between the codes is the electron broadening.

$$\langle u l_1 k_1 LS \| E^k \| u'' l_2 k_2 LS \rangle = (-1)^{S+l_u+l_{u''}} \begin{pmatrix} l_u & k & l_2 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & k' & l_{u''} \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} l_u & l_1 & L \\ l_{u''} & l_2 & k \end{Bmatrix}$$
$$\times \int_0^\infty \int_0^\infty dr_2 dr_1 F_l(k_1, r_2) R_u(r_1) \left[\frac{r_>^k}{r_<^{k+1}} - \frac{\delta_{k,0}}{r_1} \right] F_l(k_1, r_1) R_{u'}(r_2),$$

where we have labeled D for direct interaction and E for exchange interaction and we have used the $3j$ and $6j$ symbols [44] to perform the angular integrals. The factor of $1/2$ in B is due to the antisymmetrization operator and the structure of the scattering T matrix for hydrogenlike systems [53–56].

We want to present some level of validation of the electron-broadening model presented here. This code has compared well with other validated codes in Alexiou *et al.* [57]. In addition, we compare this calculation with that of Gomez *et al.* [36] (which has compared well with the Wiese *et al.* [27] experiment), which we show in Fig. 3 for typical laboratory conditions. To do a proper comparison, the two methods have the same static-ion broadening so that the only difference between this work and XENOMORPH [36] is the electron broadening. Also, as shown, in Fig. 3, the two calculations give near identical results.

APPENDIX C: DERIVATION OF THE LIPPMANN-SCHWINGER RECURSION RELATIONSHIP FOR THE ELECTRON-BROADENING OPERATOR

For purposes of comparison with the kinetic theory and to link this work back to the Lippmann-Schwinger [48] T-matrix form, we want to write the electron-broadening operator in a recursion-relationship form. The electron-broadening operator $\mathcal{H}(\omega)$ is given as a function of $\mathfrak{T}(\omega)$ and both can be Taylor expanded,

$$\begin{aligned} \mathcal{H}(\omega) &= \frac{1}{1 + \langle \mathfrak{T}(\omega) \rangle \left(\omega - L_0^r\right)^{-1}} \langle \mathfrak{T}(\omega) \rangle \\ &= \langle \mathfrak{T}(\omega) \rangle \sum_{k=0}^{\infty} \left[- \left(\omega - L_0^r\right)^{-1} \langle \mathfrak{T}(\omega) \rangle \right]^k, \\ \mathfrak{T}(\omega) &= L_I \frac{1}{1 - (\omega - L_0)^{-1} L_I} \frac{1}{\omega - L_0} \rho_0 \rho_r^{-1} \left(\omega - L_0^r\right) \\ &= L_I \sum_{k=0}^{\infty} [(\omega - L_0)^{-1} L_I]^k \frac{1}{\omega - L_0} \rho_0 \rho_r^{-1} \left(\omega - L_0^r\right). \end{aligned}$$

If we insert the Taylor-expanded definition for $\mathfrak{T}(\omega)$ into the Taylor-expanded definition for $\mathcal{H}(\omega)$ and collect all of the terms of the same L_I, the resulting equation for line-broadening is (out to third order)

$$\begin{aligned} \mathcal{H}(\omega) = & \langle L_I G(\omega) \rho_0 \rangle \rho_r^{-1} \left(\omega - L_0^r\right) \\ & + \langle L_I G(\omega) L_I G(\omega) \rho_0 \rangle \rho_r^{-1} \left(\omega - L_0^r\right) - \langle L_I G(\omega) \rho_0 \rangle \rho_r^{-1} \langle L_I G(\omega) \rho_0 \rangle \rho_r^{-1} \left(\omega - L_0^r\right) \\ & + \langle L_I G(\omega) L_I G(\omega) L_I G(\omega) \rho_0 \rangle \rho_r^{-1} \left(\omega - L_0^r\right) - \langle L_I G(\omega) \rho_0 \rangle \rho_r^{-1} \langle L_I G(\omega) L_I G(\omega) \rho_0 \rangle \rho_r^{-1} \left(\omega - L_0^r\right) \\ & - \langle L_I G(\omega) L_I G(\omega) \rho_0 \rangle \rho_r^{-1} \langle L_I G(\omega) \rho_0 \rangle \rho_r^{-1} \left(\omega - L_0^r\right) + \langle L_I G(\omega) \rho_0 \rangle \rho_r^{-1} \langle L_I G(\omega) \rho_0 \rangle \rho_r^{-1} \langle L_I G(\omega) \rho_0 \rangle \rho_r^{-1} \left(\omega - L_0^r\right), \end{aligned} \quad \text{(C1)}$$

where $G(\omega) = (\omega - L_0)^{-1}$. There is a common factor of $\rho_r^{-1}(\omega - L_0^r)$ on the right-hand side of all the terms; this can be factored out and we can seek a function $\hat{\mathcal{H}}(\omega)$ where

$$\mathcal{H}(\omega) = \mathrm{Tr}_b\{\hat{\mathcal{H}}(\omega)\}\rho_r^{-1}\left(\omega - L_0^r\right). \tag{C2}$$

Based on Eq. (C1), we can write

$$\hat{\mathcal{H}}(\omega) = L_I(\omega - L_0)^{-1}\rho_0 + L_I(\omega - L_0)^{-1}[1 - P]\hat{\mathcal{H}}(\omega), \tag{C3}$$

where P is a projection operator that performs a trace over the perturber coordinates

$$PA\rho_0 = \rho_0\rho_r^{-1}\mathrm{Tr}_p\{A\rho_0\}. \tag{C4}$$

This projection operator has slightly different properties than the one presented in Ref. [9] or [40]. Because of the lack of correlations, the projection operators there commuted with $(\omega - L_0)^{-1}$; ours does not.

[1] R. E. Falcon, G. A. Rochau, J. E. Bailey, T. A. Gomez, M. H. Montgomery, D. E. Winget, and T. Nagayama, Astrophys. J. **806**, 214 (2015).
[2] T. Nagayama, J. E. Bailey, R. C. Mancini, C. A. Iglesias, S. B. Hansen, C. Blancard, H. K. Chung, J. Colgan, P. Cosse, G. Faussurier, R. Florido, C. J. Fontes, F. Gilleron, I. E. Golovkin, D. P. Kilcrease, G. Loisel, J. J. MacFarlane, J.-C. Pain, G. A. Rochau, M. E. Sherrill, and R. W. Lee, High Energy Density Phys. **20**, 17 (2016).
[3] M. J. Seaton, J. Phys. B **23**, 3255 (1990).
[4] C. A. Iglesias, High Energy Density Phys. **18**, 14 (2016).
[5] I. Hubeny and D. Mihalas, *Theory of Stellar Atmospheres* (Princeton University Press, Princeton, 2014).
[6] P.-E. Tremblay and P. Bergeron, Astrophys. J. **696**, 1755 (2009).
[7] M. Baranger, Phys. Rev. **112**, 855 (1958).
[8] A. C. Kolb and H. Griem, Phys. Rev. **111**, 514 (1958).
[9] U. Fano, Phys. Rev. **131**, 259 (1963).
[10] T. Hussey, J. W. Dufty, and C. F. Hooper, Phys. Rev. A **12**, 1084 (1975).
[11] R. Zwanzig, J. Chem. Phys. **33**, 1338 (1960).
[12] K. Burnett, J. Cooper, R. J. Ballagh, and E. W. Smith, Phys. Rev. A **22**, 2005 (1980).
[13] V. L. Jacobs, J. Cooper, and S. L. Haan, Phys. Rev. A **50**, 3005 (1994).
[14] V. L. Jacobs, Phys. Rev. A **90**, 033841 (2014).
[15] R. Zwanzig, *Nonequilibrium Statistical Mechanics* (Oxford University Press, New York, 2001).
[16] N. N. Bogoliubov, J. Exp. Theor. Phys. **16**, 691 (1946).
[17] J. G. Kirkwood, J. Chem. Phys. **14**, 180 (1946).
[18] J. G. Kirkwood, J. Chem. Phys. **15**, 72 (1947).
[19] M. Born and H. S. Green, Proc. R. Soc. London Ser. A **188**, 10 (1946).
[20] D. W. Ross, Ann. Phys. (NY) **36**, 458 (1966).
[21] L. Klein, J. Quant. Spectrosc. Radiat. Transf. **9**, 199 (1969).
[22] B. Bezzerides, Phys. Rev. **159**, 3 (1967).
[23] R. Lee, J. Phys. A: Math. Gen. **5**, 950 (1972).
[24] R. W. Lee, J. Phys. B **5**, 1271 (1972).
[25] U. Fano, Rev. Mod. Phys. **29**, 74 (1957).
[26] D. B. Boercker and C. A. Iglesias, Phys. Rev. A **30**, 2771 (1984).
[27] W. L. Wiese, D. E. Kelleher, and D. R. Paquette, Phys. Rev. A **6**, 1132 (1972).
[28] T. W. Hussey, J. W. Dufty, and C. F. Hooper, Jr., Phys. Rev. A **16**, 1248 (1977).
[29] G. C. Junkel, M. A. Gunderson, C. F. Hooper, Jr., and D. A. Haynes, Jr., Phys. Rev. E **62**, 5584 (2000).
[30] M. A. Gunderson, G. C. Junkel-Vives, and C. F. Hooper, J. Quant. Spectrosc. Radiat. Transf. **71**, 373 (2001).
[31] P. W. Anderson, Phys. Rev. **76**, 647 (1949).
[32] H. R. Griem, *Spectral Line Broadening by Plasmas* (Academic, New York, 1974), Vol. 39.
[33] R. Stamm, E. W. Smith, and B. Talin, Phys. Rev. A **30**, 2039 (1984).
[34] M. A. Gigosos and V. Cardeñoso, J. Phys. B **29**, 4795 (1996).
[35] E. Stambulchik and Y. Maron, J. Quant. Spectrosc. Radiat. Transf. **99**, 730 (2006).
[36] T. A. Gomez, T. Nagayama, D. P. Kilcrease, M. H. Montgomery, and D. E. Winget, Phys. Rev. A **94**, 022501 (2016).
[37] P. Kepple and H. R. Griem, Phys. Rev. **173**, 317 (1968).
[38] E. W. Smith, J. Cooper, and C. R. Vidal, Phys. Rev. **185**, 140 (1969).
[39] C. R. Vidal, J. Cooper, and E. W. Smith, Astrophys. J. Suppl. **25**, 37 (1973).
[40] E. W. Smith and C. F. Hooper, Phys. Rev. **157**, 126 (1967).
[41] J. W. Dufty and D. B. Boercker, J. Quant. Spectrosc. Radiat. Transf. **16**, 1065 (1976).
[42] M. Baranger, Phys. Rev. **111**, 481 (1958).
[43] J. T. O'Brien and C. F. Hooper, Jr., J. Quant. Spectrosc. Radiat. Transf. **14**, 479 (1974).
[44] R. D. Cowan, *The Theory of Atomic Structure and Spectra* (University of California Press, Berkeley, 1981).
[45] L. A. Woltz and C. F. Hooper, Jr., Phys. Rev. A **30**, 468 (1984).
[46] H. Nguyen, M. Koenig, D. Benredjem, M. Caby, and G. Coulaud, Phys. Rev. A **33**, 1279 (1986).
[47] T. A. Gomez, Improving calculations of the interaction between atoms and plasma particles and its effect on spectral line shapes, Ph.D. thesis, University of Texas at Austin, 2017.
[48] B. A. Lippmann and J. Schwinger, Phys. Rev. **79**, 469 (1950).
[49] R. Lee, J. Phys. B **4**, 1640 (1971).
[50] E. Stambulchik, D. V. Fisher, Y. Maron, H. R. Griem, and S. Alexiou, High Energy Density Phys. **3**, 272 (2007).
[51] D. P. Kilcrease, R. C. Mancini, and C. F. Hooper, Jr., Phys. Rev. E **48**, 3901 (1993).

[52] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Academic, New York, 1957).

[53] D. H. Madison, I. Bray, and I. McCarthy, Phys. Rev. Lett. **64**, 2265 (1990).

[54] D. H. Madison, I. Bray, and I. E. McCarthy, J. Phys. B **24**, 3861 (1991).

[55] D. H. Madison, R. P. McEachran, and M. Lehmann, J. Phys. B **27**, 1807 (1994).

[56] M. L. Goldberger and K. M. Watson, *Collision Theory* (Wiley, New York, 1964).

[57] S. Alexiou, E. Stambulchik, T. Gomez, and M. Koubiti, Atoms **6**, 13 (2018).