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Second-order spectral line shifts formulae

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Disclaimer

Second-order spectral line shift comparisons

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Abstract

The second-order spectral line width formulae from the projection operator and kinetic theory methods were recently compared. It was shown that a systematic expansion of the projection operator width expression including initial correlations formally agrees with the second-order kinetic theory result. It is now shown that the second-order dynamic shifts are also formally the same. The static shifts, however, differ due to an ad hoc treatment of electron-electron correlations in the projection operator method. The approximation is necessary in order to screen the radiator-electron interactions. The differences, however, are expected to be small. The results suggest using the rigorous and more compact second-order width and shift expressions from the kinetic theory method as the starting point for spectral line shape calculations. At line center, however, the projection operator second-order expression for the width and shift without initial correlations is simpler and reduces to the kinetic theory result.

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1. Introduction

Spectral lines play an important role in plasma diagnostics [1]. By virtue of their practicality, second-order theories are extensively used to compute spectral line shapes [e.g., 2,3]. Recently, the second-order widths from the projection operator [4] and kinetic theory [5] methods were shown to be formally the same [6]. The agreement required including the often-neglected initial correlations [4] as well as introducing screened radiator-electron interactions in the projection operator approach. Such approximations are unnecessary in the kinetic theory method since it systematically treats initial and electron-electron correlations and justifies to a large degree replacing the perturbing electrons with ideal quasi-particles with screened radiator-electron interactions [5].

The present work extends the previous comparisons of line widths from the projection operator and kinetic theory methods [6] to line shifts. The analysis here is concise avoiding the lengthy algebra explicitly comparing matrix elements as previously done in [6]. In addition, it revisits the Kramers-Kronig relation between the dynamic shift and width [7].

Several factors motivated these comparisons. The projection operator or the kinetic theory methods are often the starting point for spectral line shapes calculations. Although the methods were developed about half a century ago, no formal comparisons exist in the literature. An exception is recent work [8] suggesting that there are significant differences between the two methods casting doubt on the kinetic theory approach. It is shown here, however, that the two methods yield essentially the same second-order expressions for the line widths and shifts.

2. Kinetic theory

The kinetic theory approach applies methods developed for time correlation functions to spectral line broadening in plasmas [5]. The line shape function is expressed in terms of a few-body problem by formally closing an infinite hierarchy of equations for the trace over perturbing electrons of the time dependent atomic dipole operator. No approximations are introduced resulting in the systematic treatment of initial correlations (no factorization of the density matrix) and electron-electron correlations (screening of radiator-perturber interaction).

In the kinetic theory method, the dipole radiation line shape function at photon energy $\hbar\omega$ is given by (suppressing quasi-static ion contributions to simplify notation) [5],

$$I(\omega) = \pi^{-1}\,\mathrm{Re}\int_o^\infty dt e^{i\omega t} Tr_{a,e}\left\{\rho(a,e)\vec{d}\cdot\vec{d}(t)\right\}$$
$$= -\pi^{-1}\,\mathrm{Im}\,Tr_a\left\{\vec{d}\cdot\frac{1}{\Delta\omega - B^{KT} - M^{KT}(\Delta\omega)} f(a)\vec{d}\right\} \tag{2.1}$$

where Tr_a and Tr_e respectively denote a trace over the radiator internal states and the electron gas degrees of freedom, $\vec{d}$ is the radiator dipole operator, and the detuning frequency

$$\Delta\omega = \omega - L(a) \tag{2.2}$$

$$L(a) = \hbar^{-1}\left[H(a),\cdots\right] \tag{2.3}$$

with $H(a)$ the Hamiltonian for the isolated radiator internal states and the square brackets a commutator. The reduced distribution functions are defined by

$$n_e^s f(a,1\cdots s) = N_e(N_e-1)\cdots(N_e-s+1)Tr_{s+1,\ldots,N_e}\rho(a,e) \tag{2.4}$$

where a and $1\cdots s$ denote radiator internal states and perturber electrons 1 through s, respectively, $Tr_{s+1,\ldots,N_e}$ denotes a trace over the electron gas degrees of freedom excluding electrons 1 through s, N_e and n_e are the total number and number density of perturber electrons, and $\rho(a,e)$ is the density matrix for the radiator-electron gas system. The operators $B^{KT} + M^{KT}(\Delta\omega)$ only depend on atomic variables (dependence is suppressed for clarity) and represent the electron gas effects on the radiator. The static or mean field term B^{KT} produces level shifts. The dynamic contributions $M^{KT}(\Delta\omega)$ describe momentum transfer between the radiator internal states and the perturbing electrons. The real and imaginary parts of $M^{KT}(\Delta\omega)$ yield the dynamic shifts and widths.

2.1 Static shifts

The term $\Delta\omega - B^{KT}$ in Eq. (2.1) is the exact short time (or far line wing) solution to the line shape function. It is given by [5]

$$B^{KT} = n_e Tr_1 L_1(a,1) f(a,1) f^{-1}(a) \tag{2.1.1}$$

where Tr_1 is a trace over a single perturber electron degrees of freedom and

$$L_1(a,1) = \hbar^{-1}\left[V_1(a,1),\cdots\right] \tag{2.1.2}$$

with $V_1(a,1)$ the bare interaction between a perturbing electron and the radiator internal states.

Expanding to first order in the radiator-electron interaction $V_1(a,1)$ yields

$$B_1^{KT} = n_e Tr_1 L_1(a,1) f_o(1) \tag{2.1.3}$$

where $f_o(1)$ is the perturbing electron reduced distribution function to zeroth order in $V_1(a,1)$. For the second-order term, use the first order expansions

$$\begin{aligned} \rho(a,e) &= f_o(a)\rho_0(e) + \rho_1(a,e) + O\left[V_1^2(a,1)\right] \\ f^{-1}(a) &= f_o^{-1}(a)\left[1 - Tr_e \rho_1(a,e) f_o^{-1}(a) + O\left[V_1^2(a,1)\right]\right] \end{aligned} \tag{2.1.4}$$

where $f_o(a)$ is the reduced distribution function for the isolated radiator internal states, $\rho_0(e)$ is the electron gas density matrix in the absence of the radiator, and $\rho_1(a,e)$ is the density matrix for the radiator-electron gas to first order in $V_1(a,1)$. Then,

$$B_2^{KT} = n_e Tr_1\left\{L_1(a,1) f_1(a,1)\right\} f_o^{-1}(a) - n_e^2 Tr_{1,2}\left\{L_1(a,1) f_o(1) f_1(a,2)\right\} f_o^{-1}(a) \tag{2.1.5}$$

where $f_1(a,1)$ is the first order correction to the reduced distribution function $f(a,1)$ [6,9]. The second term in Eq. (2.1.5) was neglected in [9] since it is of $O(n_e^2)$.

2.2 Dynamic contributions

The second-order dynamic contributions are given by [6],

$$M_2^{KT}(\omega) = n_e Tr_1\left\{L_s(a,1)\frac{1}{\Delta\omega - L(1)} f_o(a) f_o(1) L_s(a,1)\right\} f_o^{-1}(a) \tag{2.2.1}$$

The Liouville operator for the perturbing electron is

$$L(1) = \hbar^{-1}\left[H(1),\cdots\right] \tag{2.2.2}$$

with $H(1)$ the perturbing electron Hamiltonian, which includes the kinetic energy and the interaction with the net radiator charge, and

$$L_s(a,1) = \hbar^{-1}\left[V_s(a,1),\cdots\right] \tag{2.2.3}$$

with $V_s(a,1)$ a statically screened radiator-electron interaction [6].

The real and imaginary parts are obtained by letting $\Delta\omega \to \Delta\omega + i\varepsilon$ with ε a positive infinitesimal and Dirac's identity,

$$\lim_{\varepsilon\to 0}\frac{1}{x\pm i\varepsilon}=P\frac{1}{x}\mp i\pi\delta\left(x\right) \tag{2.2.4}$$

to give the dynamic shift

$$\Delta_2^{KT}\left(\omega\right)=\mathrm{Re}\,M_2^{KT}\left(\omega\right) \tag{2.2.5}$$

and width

$$\Gamma_2^{KT}\left(\omega\right)=\mathrm{Im}\,M_2^{KT}\left(\omega\right) \tag{2.2.6}$$

These satisfy the Kramers-Kronig relation [7]

$$\Delta_2^{KT}\left(\Delta\omega\right)=\pi^{-1}P\int_{-\infty}^{\infty}dz\frac{\Gamma_2^{KT}\left(z\right)}{z-\Delta\omega} \tag{2.2.7}$$

where P denotes the principal Cauchy part. The proof is given in Appendix A. A form of Eq. (2.2.7) more amenable to numerical evaluation is proposed in Appendix B.

3. Projection operator

The projection operator approach to spectral line broadening also uses methods developed for time correlation functions [4]. The premise is that complete knowledge of a system is not necessary for computing observable quantities; hence, a projection operator is devised to produce an integro-differential equation that governs the 'relevant' part. The method predates those in the kinetic theory method and as a result the radiator-electron interaction is not screened. In addition, initial correlations are typically neglected factoring the radiator-electron gas density matrix [4,8].

In the projection operator method, the line shape function in Eq. (2.1) is written as [4]

$$I\left(\omega\right)=-\pi^{-1}\,\mathrm{Im}\,Tr_a\left\{\vec{d}\cdot\frac{1}{\Delta\omega-H^{PO}\left(\Delta\omega\right)}f\left(a\right)\vec{d}\right\} \tag{3.1}$$

The operator $\mathrm{H}^{PO}\left(\Delta\omega\right)$ (dependence on atomic variables is again suppressed) represents the perturbing electron gas effects on the radiator and, including initial correlations, is given to second order by [6]

$$\mathrm{H}^{PO}\left(\Delta\omega\right)=B_1^{PO}+\mathrm{H}_2^{PO}\left(\Delta\omega\right)+O\left(V_s^3\right) \tag{3.2}$$

where the first order static shift is

$$B_1^{PO}=n_e Tr_1\left\{L_s\left(a,1\right)f_o\left(1\right)\right\} \tag{3.3}$$

and

$$\mathrm{H}_2^{PO}\left(\Delta\omega\right)=n_e Tr_1\left\{L_s\left(a,1\right)\frac{1}{\Delta\omega-L\left(1\right)}\left[L_s\left(a,1\right)f_o\left(1\right)+f_1\left(a,1\right)f_o^{-1}\left(a\right)\Delta\omega\right]\right\} \tag{3.4}$$

Note that $\mathrm{H}_2^{PO}\left(\Delta\omega\to\infty\right)\neq 0$ and the Kramers-Kronig derivation in Appendix A does not apply.

A second-order expansion explicitly separating the static shift is performed in Appendix C, which yields

$$\mathrm{H}^{PO}\left(\Delta\omega\right)=B_1^{PO}+B_2^{PO}+M_2^{PO}\left(\Delta\omega\right)+O\left(V_s^3\right) \tag{3.5}$$

where

$$B_2^{PO}=n_e Tr_1\left\{L_s\left(a,1\right)f_1\left(a,1\right)\right\}f_o^{-1}\left(a\right) \tag{3.6}$$

and

$$\begin{aligned} M_2^{PO}\left(\Delta\omega\right)&=n_e Tr_1\left\{L_s\left(a,1\right)\frac{1}{\Delta\omega-L\left(1\right)}f_o\left(a\right)f_o\left(1\right)L_s\left(a,1\right)\right\}f_o^{-1}\left(a\right)\\ &=M_2^{KT}\left(\Delta\omega\right)\end{aligned} \tag{3.7}$$

The last line used Eq. (2.2.1).

4. Discussion

It follows from Eq. (3.7) that the second-order dynamic shift and width contributions from the projection operator and kinetic theory methods are the same. Furthermore, the static shifts only have minor differences. First, in the kinetic theory the interaction $L_1\left(a,1\right)$ in Eq. (2.1.3) is not screened while in the projection operator $L_s\left(a,1\right)$ in Eq. (3.3) is screened. Note, however, that static shifts involve perturbing electrons overlapping with the radiator bound electron wavefunctions. In addition, screening effects are small at short distances. Thus, the combination should mitigate the difference. Second, the kinetic theory second-order static shift has a term of $O\left(n_e^2\right)$ absent in the projection operator method. The $O\left(n_e^2\right)$ term, however, should be negligible except at extreme high densites. Both differences are a consequence of the ideal quasi-particles approximation introduced in the projection operator method necessary to screened the radiator-electron interactions and obtain agreement for the second-order widths [6].

In the far line wing Eq. (3.2) or (3.5) lead to

$$\mathrm{H}^{PO}\left(\Delta\omega\to\infty\right)=B_1^{PO}+B_2^{PO}+O\left(V_s^3\right) \tag{4.1}$$

which based on the arguments above essentially agrees with second-order kinetic theory. On the other hand, Eqs. (3.2) and (3.4) yield near line center

$$\mathrm{H}^{PO}\left(\Delta\omega\approx 0\right)=B_1^{PO}+n_e Tr_1\left\{L_s\left(a,1\right)\frac{1}{\Delta\omega-L\left(1\right)}L_s\left(a,1\right)f_o\left(1\right)\right\}+O\left(V_s^3\right) \tag{4.2}$$

and the second-order static shift seems to vanish. As a result, it was erroneously suggested that the kinetic theory and projection operator methods would yield different line shifts [8]. The results in Eqs. (3.2) and (3.5) show, however, that using Eq. (3.7)

$$\begin{aligned}\mathrm{H}_2^{PO}\left(\Delta\omega\right)&=B_2^{PO}+M_2^{PO}\left(\Delta\omega\right)\\&=B_2^{PO}+M_2^{KT}\left(\Delta\omega\right)\end{aligned} \tag{4.3}$$

for all $\Delta\omega$. That is, in Eq. (3.5) the second-order static shift appears explicitly in the projection operator method and is implicit in Eq. (3.2).

Finally, most implementations of the projection operator formalism have neglected initial correlations and only kept the first term in Eq. (3.4). In other words, $\mathrm{H}_2^{PO}\left(\Delta\omega\right)$ has been approximated by an expression valid for $\Delta\omega\approx 0$ given by Eq. (4.2). It is readily shown that

$$\begin{aligned}\mathrm{H}^{PO}\left(\Delta\omega=0\right)&=B_1^{PO}+B_2^{PO}+M_2^{PO}\left(\Delta\omega=0\right)+O\left(V_s^3\right)\\&\approx B_1^{kt}+B_2^{KT}+M_2^{KT}\left(\Delta\omega=0\right)+O\left(V_s^3\right)\end{aligned} \tag{4.4}$$

Thus, essentially reducing to the kinetic theory results at line center.

5. Conclusion

It was shown that to second order the line shifts and widths from the projection operator and kinetic theory methods are basically the same. Furthermore, an apparent disparate treatment of static shifts between the two methods [8] was resolved. These comparisons required retaining intitial correlations as well as introducing ideal quasi-particles with screened radiator-perturber interactions in the projection operator method justified to a large degree by the kinetic theory results. Contrary to [6], the present approach avoids explicitly comparing atomic matrix elements of the width and shift operators. As previously suggested [6], the rigorous and more compact expressions from the kinetic theory method are recommended as the starting point for second-order spectral line shape calculations. Note that at line center the projection operator second-order expression for the width and shift without initial correlations is simpler and reduces to the kinetic theory result.

Credit authorship contribution statements

Carlos A. Iglesias: Writing – original draft, Validation, Investigation, Formal analysis, Conceptualization. **Thomas A. Gomez**: Validation, Investigation, Formal analysis.

Declaration of competing interest

The authors declare they have no known competing financial interests or personal relationship that could appear to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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Appendix A. Kramers-Kronig relation

The dynamic width and shift satisfy the Kramers-Kronig relation [7]. This Appendix provides a general proof and one specific for the second-order theory.

A.1 General proof

The general proof of these relations requires that a function $f(z)$ satisfy two conditions in the upper half of the complex plane: (1) it is analytic and (2) $f(z)\to 0$ for $|z|\to\infty$. Then [10],

$$\begin{aligned}\mathrm{Re}\, f_+(x_o) &= \frac{1}{\pi} P\int_{-\infty}^{\infty} dx \frac{\mathrm{Im}\, f_+(x)}{x-x_o}\\ \mathrm{Im}\, f_+(x_o) &= -\frac{1}{\pi} P\int_{-\infty}^{\infty} dz \frac{\mathrm{Re}\, f_+(x)}{x-x_o}\end{aligned} \tag{A.1.1}$$

where *P* denotes principal Cauchy part and the subscript + indicates how to distort the contour around a pole on the real axis; $x_o \to x_o + i0^+$.

The Fourier transform definition of $M^{KT}(\Delta\omega)$ in Eq. (2.23) of [5] is in effect an analytic continuation for $\Delta\omega$ into the upper half of the complex plane. In addition, $M^{KT}(\Delta\omega\to\infty)=0$ by construction [5]. Therefore, the results in Eq. (A.1.1) apply in general (not just second order) to the dynamic contributions of the kinetic theory method.

A.2 Specific proof

It was shown in [6] that the second-order dynamic contributions to the width and shift operator in the kinetic theory method can be written in the form

$$\begin{aligned}M_2^{KT}(\Delta\omega) &= -i\lim_{\varepsilon\to 0}\int_o^{\infty} dt e^{it[\Delta\omega+i\varepsilon]}\tilde{M}_2^{KT}(t)\\ &= -i\lim_{\varepsilon\to 0}\int_o^{\infty} dt e^{it[\Delta\omega+i\varepsilon]}\left\{\int_o^{\infty} dk_1\int_o^{\infty} dk_2 e^{i\left(E_{k_1}-E_{k_2}\right)t/\hbar}F(k_1,k_2)\right\}\end{aligned} \tag{A.2.1}$$

defining $\tilde{M}_2^{KT}(a,t)$ where $E_k=\hbar^2k^2/2m_e$ with m_e the electron mass, and ε a positive infinitesimal. All the time dependence is explicitly given in the integrand. The integrations over *k*'s are the result of a trace and identity operator over perturbing electron continuum states with

$F\left(k_1,k_2\right)$ a real function involving fundamental constants, the perturbing electron thermal distribution, and matrix elements of the radiator-electron interaction.

Performing the integration over time and applying Dirac's identity leads to

$$M_2^{KT}\left(\Delta\omega\right)=\Delta_2^{KT}\left(\Delta\omega\right)+i\Gamma_2^{KT}\left(\Delta\omega\right) \tag{A.2.2}$$

where

$$\begin{aligned}\Delta_2^{KT}\left(\Delta\omega\right)&=\mathrm{Re}\,M_2^{KT}\left(\Delta\omega\right)\\&=\hbar P\int_o^\infty dk_1\int_o^\infty dk_2\,\frac{F\left(k_1,k_2\right)}{\hbar\Delta\omega+\left(E_{k_1}-E_{k_2}\right)}\end{aligned} \tag{A.2.3}$$

and

$$\begin{aligned}\Gamma_2^{KT}\left(\Delta\omega\right)&=\mathrm{Im}\,M_2^{KT}\left(\Delta\omega\right)\\&=-\pi\hbar\int_o^\infty dk_1\int_o^\infty dk_2F\left(k_1,k_2\right)\delta\left(\hbar\Delta\omega+E_{k_1}-E_{k_2}\right)\end{aligned} \tag{A.2.4}$$

The proof of the Kramers-Kronig relation specific to second-order theory starts by introducing a heavy side function into Eq. (A.2.1),

$$\begin{aligned}\Theta\left(t\right)&=\begin{cases}1 & t>0\\0 & t<0\end{cases}\\&=-\frac{1}{2\pi i}\lim_{\eta\to0}\int_{-\infty}^\infty dz\,\frac{e^{-izt}}{z+i\eta}\end{aligned} \tag{A.2.5}$$

allowing extension of the time integral to minus infinity. Proceeding, get

$$\begin{aligned}M_2^{KT}\left(\Delta\omega\right)&=\lim_{\varepsilon\to0}\int_{-\infty}^\infty\frac{dt}{2\pi}\lim_{\eta\to0}\int_{-\infty}^\infty dx\,\frac{e^{i\left(\Delta\omega-x\right)t}}{x+i\eta}e^{-\varepsilon t}\tilde{M}_2^{KT}\left(a,t\right)\\&=\hbar\lim_{\eta\to0}\int_{-\infty}^\infty dx\,\frac{1}{x+i\eta}\int_o^\infty dk_1\int_o^\infty dk_2F\left(k_1,k_2\right)\delta\left(\hbar\Delta\omega-\hbar x+E_{k_1}-E_{k_2}\right)\\&=\pi^{-1}P\int_{-\infty}^\infty dx\,\frac{\Gamma_2^{KT}\left(x\right)}{x-\Delta\omega}+i\Gamma_2^{KT}\left(x\right)\end{aligned} \tag{A.2.6}$$

It follows that

$$\Delta_2^{KT}\left(\Delta\omega\right)=\pi^{-1}P\int_{-\infty}^\infty dz\,\frac{\Gamma_2^{KT}\left(z\right)}{z-\Delta\omega} \tag{A.2.7}$$

satisfying the Kramers-Kronig relation. It is emphasized that the manipulations in Eq. (A.2.6) requires changing the order of the $\varepsilon \to 0$ limit and the *t*-integration. This is possible since $M_{KT}^{(2)}\left(\Delta\omega \to \infty\right) = 0$ (equivalently $\tilde{M}_{KT}^{(2)}\left(t = 0\right) = 0$).

Appendix B. Computational form for $\Delta_2^{KT}\left(\Delta\omega\right)$

The dispersion relation for the dynamic shift in Eq. (2.2.7) avoids a double integral (see Eq. (A.2.4) in Appendix A) with a substantial increase in computational efficiency [7]. It is possible to simplify the principal part integration by first taking advantage of the detailed balance property [6],

$$\Gamma_2^{KT}\left(-\omega\right) = \exp\left(-\hbar\omega/T_e\right)\Gamma_2^{KT}\left(\omega\right) \tag{B.1}$$

to write

$$\Delta_2^{KT}\left(\omega\right) = \pi^{-1}P\int_o^\infty dz\,\frac{\Gamma_2^{KT}\left(z\right)}{z^2-\omega^2}\left\{\left(z+\omega\right)-\left(z-\omega\right)e^{-\hbar z/T}\right\} \tag{B.2}$$

To proceed, note that

$$\lim_{z\to\omega}\left\{\frac{\left[\left(z+\omega\right)-\left(z-\omega\right)e^{-\hbar z/T_e}\right]\Gamma_2^{KT}\left(z\right)-2\omega\Gamma_2^{KT}\left(\omega\right)}{z^2-\omega^2}\right\} = \frac{\Gamma_2^{KT}\left(\omega\right)}{2\omega}\left\{\left(1+e^{-\hbar\omega/T_e}\right)+O\left(\frac{z-\omega}{\omega}\right)\right\} \tag{B.3}$$

is finite and

$$P\int_o^\infty \frac{dz}{z^2-\omega^2} = 0 \tag{B.4}$$

Collecting results leads to

$$\Delta_2^{KT}\left(\omega\right) = \pi^{-1}\int_o^\infty dz\left\{\frac{\left[\left(z+\omega\right)-\left(z-\omega\right)e^{-\hbar z/T}\right]\Gamma_2^{KT}\left(z\right)-2\omega\Gamma_2^{KT}\left(\omega\right)}{z^2-\omega^2}\right\} \tag{B.5}$$

making the principal part unnecessary and simplifying numerical calculations.

Appendix C. Second-order expansion in projection operator method

The explicit separation of static and dynamic contributions in the projection operator method can be accomplished with minor modifications to Appendix C in [6]. That is, use the fact that in thermal equilibrium (required by the kinetic theory method [5]) the total system Hamiltonian and density matrix commute to extract the static terms [8].

To proceed, follow [6] and introduce the relation

$$Tr_a\vec{d}\cdot Tr_e\left(\frac{1}{\Delta\omega - L_e - L_I}\right)\rho(a,e)\vec{d} = Tr_a\vec{d}\cdot\left(\frac{1}{\Delta\omega - \mathrm{H}^{PO}(\omega)}\right)f(a)\vec{d} \tag{C.1}$$

The Liouville operators are defined as

$$\begin{aligned} L_e &= \sum_{j=1}^{N_e} L(j) = \hbar^{-1}\sum_{j=1}^{N_e}\left[H(j),\cdots\right] \\ L_I &= \sum_{j=1}^{N_e} L_s(a,j) = \hbar^{-1}\sum_{j=1}^{N_e}\left[V_s(a,j),\cdots\right] \end{aligned} \tag{C.2}$$

where N_e is the number of free electrons, $H(j)$ is the j[th] perturber Hamiltonian (recall ideal quasi-particles in the screened potential of the radiator net charge), and $V_s(a,j)$ is a screened interaction between the j[th] perturber and the radiator internal states. Rewrite Eq. (C.1) as

$$Tr_e\left(\frac{1}{\Delta\omega - L_e - L_I}\right)\rho(a,e)f^{-1}(a) = \left(\frac{1}{\Delta\omega - \mathrm{H}^{PO}(\omega)}\right) \tag{C.3}$$

The LHS of Eq. (C.3) can be rewrittten without approximation as

$$\begin{aligned} Tr_e\left\{R\rho(a,e)\right\} &= Tr_e\left\{R_o\rho(a,e)\right\} + Tr_e\left\{R_oL_IR\rho(a,e)\right\} \\ &= R_a\left[f(a) + Tr_e\left\{L_I\rho(a,e)R\right\}\right] \\ &= R_a\left[f(a) + Tr_e\left\{L_I\rho(a,e)\right\}R_a + Tr_e\left\{L_I\rho(a,e)R_oL_IR\right\}\right] \end{aligned} \tag{C.4}$$

where $R_a = \Delta\omega^{-1}$, $R_o = \left(\Delta\omega - L_e\right)^{-1}$, and

$$\begin{aligned} R &= \left(\Delta\omega - L_e - L_I\right)^{-1} \\ &= R_o + R_oL_IR \end{aligned} \tag{C.5}$$

defines the various resolvents.

C.1 LHS of Eq. (*C.3*)

Introduce the expansion parameter $L_I \to \lambda L_I$ and using the expansions in Eq. (2.1.4) (replacing V_1 with V_s) get for Eq. (C.4)

$$\begin{aligned} R_a^{-1}Tr_eR\rho(a,e)f^{-1}(a) &= 1 + \lambda Tr_e\left\{L_I\rho_0(e)\right\}R_a + \lambda^2\left[Tr_e\left\{L_I\rho_1(a,e)\right\}f_o^{-1}(a)R_a\right. \\ &\left. - Tr_e\left\{L_I\rho_0(e)\right\}R_aTr_e\left\{\rho_1(a,e)\right\}f_o^{-1}(a) + Tr_e\left\{L_I\rho_0(e)f_o(a)R_oL_If_o^{-1}(a)R_a\right\}\right] + O\left(\lambda^3\right) \end{aligned} \tag{C.1.1}$$

Here, $\rho_0(e)$ is the electron gas density matrix to zeroth order in $V_s(a,1)$ and $\rho_1(a,e)$ is the density matrix for the radiator-electron gas to first order in $V_s(a,1)$. Using the definition of the reduced distribution function in Eq. (2.4), Eq. (C.1.1) simplifies to second order in λ,

$$\begin{aligned} R_a^{-1}Tr_e R\rho(a,e) f^{-1}(a) R_a^{-1} &= 1+\lambda n_e Tr_1\left\{L_s(a,1) f_o(1)\right\} \\ &+\lambda^2 n_e Tr_1\left\{L_s(a,1)\left[f_1(a,1)+\frac{1}{\Delta\omega - L(1)} f_o(a) f_o(1) L_s(a,1)\right]\right\} f_o^{-1}(a) \\ &+\lambda^2 n_e^2 Tr_{1,2}\left\{L_s(a,1) f_o(1)\left[R_a f_o(a) f_o(2) L_s(a,2)+f_1(a,2)-R_a f_1(a,2)\Delta\omega\right]\right\} f_o^{-1}(a) \end{aligned} \tag{C.1.2}$$

where

$$f_o(1\cdots s)\to\prod_{j=1}^{s} f_o(j) \tag{C.1.3}$$

$$f_1(a,1\cdots s)\to\sum_{i=1}^{s} f_1(a,i)\prod_{\substack{j=1\\ j\neq i}}^{s} f_o(j) \tag{C.1.4}$$

for the assumed ideal quasi-particles [6].

C.2 RHS of Eq. (*C.3*)

Assuming the Taylor series expansion (temporarily suppressing frequency dependence),

$$\mathrm{H}^{PO} = \mathrm{H}_0^{PO} + \lambda \mathrm{H}_1^{PO} + \lambda^2 \mathrm{H}_2^{PO} + O(\lambda^3) \tag{C.2.1}$$

and taking advantage of the operator identity,

$$\frac{\partial A^{-1}}{\partial \lambda} = -A^{-1}\frac{\partial A}{\partial \lambda}A^{-1} \tag{C.2.2}$$

get to second order in λ

$$\left(\Delta\omega - \mathrm{H}^{PO}\right)^{-1} \approx \left(\Delta\omega - \mathrm{H}_0^{PO}\right)^{-1}\left\{1+\left[\lambda \mathrm{H}_1^{PO} + \lambda^2\left(\mathrm{H}_2^{PO} + \mathrm{H}_1^{PO} R_a \mathrm{H}_1^{PO}\right)\right]\left(\Delta\omega - \mathrm{H}_0^{PO}\right)^{-1}\right\} \tag{C.2.3}$$

Comparing Eqs. (C.1.2) and (C.2.3) shows that

$$\mathrm{H}_0^{PO} = 0 \tag{C.2.4}$$

and for the first order term

$$\begin{aligned} \mathrm{H}_1^{PO}(\Delta\omega) &= B_1^{PO} \\ &= n_e Tr_1\left\{L_s(a1) f_o(1)\right\} \end{aligned} \tag{C.2.5}$$

a static level shift independent of frequency. For the second order term get

$$
\begin{aligned}
\mathrm{H}_2^{PO}\left(\Delta\omega\right) &= n_e Tr_1\left\{L_s\left(a,1\right)f_1\left(a,1\right)\right\}f_o^{-1}\left(a\right)\\
&\quad + n_e Tr_1\left\{L_s\left(a,1\right)\frac{1}{\Delta\omega - L\left(1\right)}f_o\left(a\right)f_o\left(1\right)L_s\left(a,1\right)\right\}f_o^{-1}\left(a\right)\\
&\quad + n_e^2 Tr_1\left\{L_s\left(a,1\right)f_o\left(1\right)R_a Tr_2\left[f_o\left(a\right)f_o\left(2\right)L_s\left(a,2\right)f_o^{-1}\left(a\right) - L_s\left(a,2\right)f_o\left(2\right)\right]\right\}\\
&\quad + n_e^2 Tr_1\left\{L_s\left(a,1\right)f_o\left(1\right)Tr_2\left[f_1\left(a,2\right) - R_a f_1\left(a,2\right)\Delta\omega\right]\right\}f_o^{-1}\left(a\right)\\
&= B_2^{PO} + M_2^{PO}\left(\Delta\omega\right)
\end{aligned}
\tag{C.2.6}
$$

where the $O\left(n_e^2\right)$ terms cancel in agreement with [6]. That is, use

$$
Tr_e L\rho\left(a,e\right)f^{-1}\left(a\right) = Tr_e\rho\left(a,e\right)Lf^{-1}\left(a\right) \tag{C.2.7}
$$

with $L = L\left(a\right) + L_e + L_I$ the Liouville operator for the total radiator-electron gas system to show that after expanding to first order in λ,

$$
\begin{aligned}
&R_a Tr_2\left[f_o\left(a\right)f_o\left(2\right)L_s\left(a,2\right)f_o^{-1}\left(a\right) - L_s\left(a,2\right)f_o\left(2\right)\right]\\
&\quad + Tr_2\left[f_1\left(a,2\right) - R_a f_1\left(a,2\right)\Delta\omega\right]f_o^{-1}\left(a\right) = 0
\end{aligned}
\tag{C.2.8}
$$

References

[1] H. R. Griem, Spectral line broadening by plasmas, Academic Press, 1974.

[2] A. Calisti, F. Khelfaoui, R. Stamm, B. Talin, R.W. Lee, Model for the line shapes of complex ions in hot and dense plasmas, Phys. Rev. A42 (9) (1990) 5433–5440. doi: 10.1103/PhysRevA.42.5433.

[3] R.C. Mancini, D.P. Kilcrease, L.A. Woltz, C.F. Hooper, Calculational aspects of the Stark line broadening of multi-electron ions in plasmas, Computer Physics Communications 63 (1-3) (1991) 314-322. doi: 10.1016/0010-4655(91)90258-M.

[4] E. W. Smith, C. F. Hooper, Relaxation Theory of Spectral Line Broadening in Plasmas, Phys. Rev. 157 (1) (1967) 126–137. doi: 10.1103/PhysRev.157.126.

[5] T. Hussey, J. W. Dufty, C. F. Hooper, Kinetic theory of spectral line broadening, Phys. Rev. A12 (3) (1975) 1084–1093. doi: 10.1103/PhysRevA.12.1084.

[6] C.A. Iglesias, T.A. Gomez, Comparison of second-order spectral line width formulae, HEDP (*in press*). doi: 10.1016/j.hedp.2024.101080

[7] R. J. Tighe, C.F. Hooper, Stark broadening in hot, dense laser-produced plasmas, Phys. Rev. A14 (1976) 1514-1519. doi: 10.1103/PhysRevA.14.1514.

[8] T.A. Gomez, T. Nagayama, D.P. Kilcrease, M.H. Montgomery, D.E. Winget, Density-matrix correlations in the relaxation theory of electron broadening, Phys. Rev. A 98(2018) 012505. doi: 10.1103/PhysRevA.98.012505.

[9] D.B. Boercker & C.A. Iglesias, Static and dynamic shifts of spectral lines, Phys. Rev. A 30 (5) (1984), 2771-2774. doi: 10.1103/PhysRevA.30.2771

[10] H.W. Wyld, Mathematical Methods for Physics, Benjamin, Advanced Book Program, 1976.