On the Relationship Between Line Broadening and Second-Order Electron-Photon and Two-Photon Transitions in Hot, Dense Matter

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We demonstrate that second-order transitions, such as electron-photon and two-photon processes, arise exactly as the first term in an expansion of collisional and radiative line broadening. We suggest that this insight could form the basis for a new approach to improve calculations of opacity in hot, dense matter. Our findings imply that second-order processes should not be considered as an entirely new source of opacity, but could instead be incorporated into opacity calculations as an alternative limit to existing line broadening treatments.

The opacity of hot, high density material is important for both terrestrial and astrophysical applications, for example in modelling inertial confinement fusion [1–3], stellar physics [4, 5] and planetary interiors [6–8]. Predicted opacities, alongside equations of state and the abundances of heavy elements, are key inputs to solar models [9]. An increase in predicted opacities could help to reconcile discrepancies between solar models and helioseismic measurements that presently exist [10].

Some recent measurements of iron under solar conditions have yielded opacities in excess of predictions [11, 12]. In particular, increased opacity was observed in regions between characteristic absorption lines. Such regions make the strongest contribution to the Rosseland mean opacity, which encapsulates the influence of the opacity on radiation transport [13]. However, the measured opacities cannot be explained within the current theoretical consensus [14, 15] and are hard to reconcile with the upper limit for single-photon dipole absorption imposed by f-sum rules [16].

Such experimental findings have prompted recent interest in two-photon transitions as a possible source of opacity. Two-photon transitions are obtained from second-order perturbation theory and can be interpreted as the simultaneous absorption or emission of two photons. Since the energy required for the transition may be divided between the two photons in any ratio, two-photon processes yield a continuum of absorption reminiscent of the additional opacity seen experimentally. Furthermore, being at second-order in perturbation theory, two-photon opacity may exceed the limits of f-sum rules. However, published results have reached mixed conclusions, with the most detailed calculations finding that two-photon rates should be negligible under the relevant conditions [17, 19].

In a dense plasma, the two-photon process is not the only second-order process that may directly contribute to the opacity. Ions in dense plasmas are perturbed by both radiation and by collisions with electrons. We therefore expect an additional processes at second order, wherein a photon is absorbed simultaneously with an electron collision. This electron-photon process can be considered as the collisional analogue of the two-photon process. As in the two-photon case, a continuum of absorption should be expected. Such a process has been investigated theoretically and experimentally within the context of optical lasers and electron beams [20, 21].

The influence of the plasma environment on opacity is also studied in the context of line broadening. Within this picture, the influence of plasma electrons on radiative processes through collisional broadening has been widely explored [22, 23]. Since both collisional broadening and the second-order electron-photon process involve the influence of collisions on radiative processes, including facilitating the absorption or emission of off-resonant photons, it seems plausible that these two pictures might in some sense represent the same underlying physics. In fact, the appearance of certain satellite lines has been described as a second-order process [24, 25]. Likewise, it has been suggested that two-photon processes might be interpreted in terms of line broadening by background radiation fields [17]. This interpretation remains, however, relatively unexplored.

In this work, we firstly aim to elucidate the relationship between collisional line broadening and second-order electron-photon transitions. We then apply this analysis to the analogous case of radiation broadening and two-photon processes. This will allow us to determine to what extent second-order processes may already be accounted for within existing opacity calculations. Furthermore, it suggests a new perspective on opacity that may allow improved calculations in spectral regions highly relevant to stellar modelling.

We begin by considering line broadening by collisions and its relationship to the second-order electron-photon process. The overall lineshape is due to both the electrons and ions. It is often assumed that the ions can be treated statically, so that the lineshape can be written as [26, 27]:

$$I(\omega) = \int dF W(F) J(\omega, F),$$  \hspace{1cm} (1)
with

\[ J(\omega, \mathbf{F}) = -\frac{1}{\pi} \text{Im} \sum_{a,b,c,d} \langle b| \epsilon \cdot r|a \rangle \langle c| \epsilon \cdot r|d \rangle \]

\times \langle ab| \Delta \omega - \mathbf{r} \cdot \mathbf{F}/\hbar - \phi(\omega) \rangle^{-1} \rho_{cd}. \tag{2} \]

Here, \( \mathbf{F} \) represents the static ion microfield which introduces line shifts that, upon integration over the statistical distribution \( W(\mathbf{F}) \), become line broadening. Since this work is concerned with broadening by electrons, we can neglect \( \mathbf{F} \) for brevity without loss of generality. The sum runs over the atomic states, both bound and continuum, of which the density operator, \( \rho \), gives the statistical populations. Notably, this expression does not necessarily reduce to a form that would be bound by the \( f \)-sum rule.

In order to make a comprehensive comparison with the second-order electron-photon process, it is necessary to start with a general form for the broadening operator, \( \phi(\omega) \), where the matrix elements are given by \( [30] \)

\[ \phi_{ab,cd}(\omega) = \frac{1}{\hbar^2} \int \frac{d\mathbf{k}}{(2\pi)^3} \int \frac{d\Omega}{2\pi} \frac{S(k, \Omega)}{\omega_{ab} - \Omega + i\eta} \]

\times \left( \sum_{e} \frac{\delta_{ab} V_{ae}(\mathbf{k}) V_{ec}(\mathbf{k})}{\Delta \omega_{eb} - \Omega + i\eta} \rho_{e} \rho_{c}^{-1} + \sum_{e} \frac{\delta_{ac} V_{de}(\mathbf{k}) V_{eb}(\mathbf{k})}{\Delta \omega_{ae} - \Omega + i\eta} \right) . \tag{3} \]

The frequency detuning is defined as \( \Delta \omega_{ab} = (\omega_b - \omega_a) - \omega \).

In the limit \( (\Delta \omega \to 0) \), the broadening operator reduces to the form \( [23, 30] \)

\[ \gamma_{ab} = \left\langle \frac{n_e v}{2} \left[ \sigma_a + \sigma_b + \int d\Omega |F_a(\Omega) + F_b(\Omega)|^2 \right] \right\rangle_{AV} \tag{4} \]

where the \( \sigma \) are the inelastic contribution, which can be interpreted as lifetime broadening due to collisional rates, and \( F \) are the elastic contribution. This form for the broadening is widely used in practice and leads to a Lorentzian line shape, although the \( \Delta \omega \to 0 \) limit may be relaxed for the elastic contribution, for example using the approach of Lee \([25]\). The concept of lifetime broadening therefore represents an approximation that is strictly only valid in the line center and will break down in the line wings.

Next, we consider the opposite limit, where we are far from the line center. Making an expansion of Eq. 2 in orders of \( \phi/\Delta \omega \), we obtain \([27, 29]\)

\[ J(\omega) = -\frac{1}{\pi} \text{Im} \sum_{a,b,c,d} \langle b| \epsilon \cdot r|a \rangle \langle c| \epsilon \cdot r|d \rangle \]

\times \langle ab| \left( \frac{1}{\Delta \omega} + \frac{1}{\Delta \omega} \phi(\omega) \frac{1}{\Delta \omega} - O(\Delta \omega^{-3}) \right) \rho_{cd} \rangle . \tag{5} \]

Introducing Eq. 3 the lowest order contribution in this expansion is then given by

\[ J(\omega) = -\frac{1}{\pi} \sum_{a,b,c,d} \langle b| \epsilon \cdot r|a \rangle \langle c| \epsilon \cdot r|d \rangle \text{Im} \phi_{ab,cd}(\omega) \]

\[ \begin{array}{l}
\times \frac{1}{\hbar^2} \int \frac{d\mathbf{k}}{(2\pi)^3} \sum_{a,b,c,d,e} \left[ \frac{d_{ba} d_{cb} V_{ae}(\mathbf{k}) V_{ec}(\mathbf{k})}{\Delta \omega_{eb} \Delta \omega_{eb}} S(k, \Delta \omega_{eb}) \rho_{e} \\
+ \frac{d_{ba} d_{cd} V_{de}(\mathbf{k}) V_{eb}(\mathbf{k})}{\Delta \omega_{eb} \Delta \omega_{cd}} S(k, \Delta \omega_{eb}) \rho_{c} \\
- \frac{d_{ba} d_{cd} V_{ae}(\mathbf{k}) V_{db}(\mathbf{k})}{\Delta \omega_{eb} \Delta \omega_{cd}} S(k, \Delta \omega_{eb}) \rho_{a} \right].
\end{array} \tag{6} \]

where we have abbreviated the dipole matrix elements according to \( d_{ij} = \langle |e \cdot r| j \rangle \). We now compare this with the rate for an electron-photon transition, calculated using second-order perturbation theory \([31, 32]\):

\[ w_{\gamma n} = \frac{2\pi}{\hbar} \int \frac{d\mathbf{k}}{(2\pi)^3} \frac{S(k, \omega_{\gamma}) \epsilon^2 E_0^2(\omega_\gamma)}{\left| \sum_n \frac{\langle f| \epsilon \cdot r| n \rangle \langle n| V(\mathbf{k}) \rangle i}{E_n - E_f - i\hbar \omega_n} + (e \leftrightarrow \gamma) \right|^2} \times \delta (E_f - E_i - \hbar \omega_e - \hbar \omega_\gamma), \]

where the positions of the electron and photon are exchanged in the second term. We can use the delta function to express the collision energy in terms of the frequency detuning:

\[ \omega_{\epsilon} = (\omega_f - \omega_i) - \omega_\gamma = \Delta \omega_{if} \tag{7} \]

Now taking the total opacity due to electron-photon processes, and expanding the square modulus, we can obtain a quantity corresponding to \( J(\omega) \) of Eq. 6:

\[ J(\omega) = \frac{\hbar}{2\pi^2 \epsilon^2 E_0^2(\omega_\gamma)} \sum_{i,f} w_{\epsilon \gamma} \rho_i \]

\[ = \frac{\hbar}{2\pi^2 \epsilon^2 E_0^2(\omega_\gamma)} \sum_{i,f,m,n} \left[ \frac{d_{mf} d_{fn} V_{ni}(\mathbf{k}) V_{im}(\mathbf{k})}{\Delta \omega_{nf} \Delta \omega_{if}} \right. \]

\[ + \frac{d_{im} d_{nf} V_{im}(\mathbf{k}) V_{fn}(\mathbf{k})}{\Delta \omega_{nf} \Delta \omega_{if}} - \frac{d_{im} d_{nf} V_{im}(\mathbf{k}) V_{fn}(\mathbf{k})}{\Delta \omega_{nf} \Delta \omega_{if}} \right] S(k, \Delta \omega_{if}) \rho_i. \tag{8} \]
Comparing Eq. 6 and Eq. 8 we see that, with some relabelling of summation variables, the two expressions are identical. There is therefore exact equivalence between the electron-photon process and the first term in the line shape expansion. Thus, in the far line wings, the broadened transition can be expressed in terms of electron-photon transitions. Closer to the line center, it will become necessary to include further terms in the expansion. It is possible that such terms correspond to higher-order transitions involving a photon together with two or more electron collisions.

The two pictures yield identical analytic results for the total opacity. Yet, they do not agree if one attempts to artificially decompose the opacity into contributions from specific transitions. This does not in any way weaken our conclusions, as the total opacity is the physically measurable quantity. However, it is indicative of an ambiguity in identifying the initial and final states of a transition. For example, what might be considered the final state in a line-broadened transition could instead be viewed as an intermediate state in an electron-photon transition. This difference in interpretation is illustrated schematically in Fig. 1. Equivalently, one might say that line broadening occurs due to the possibility for a photon to be absorbed as one step of a higher-order process.

We now consider line broadening by background radiation. The broadening operator can be expressed in terms of the Fourier transform of the electric field autocorrelation [23]. The Wiener-Khinchin theorem then relates this autocorrelation function to the spectral energy density:

$$\int_{-\infty}^{\infty} dt e^{i\omega t} \langle E(\tau) E(\tau + t) \rangle = u(\omega). \quad (9)$$

Using this relation, we can then derive a broadening operator, analogous to Eq. 3 for broadening by background radiation:

$$\phi_{ab,cd}(\omega) = \frac{1}{\hbar^2} \int_{-\infty}^{\infty} \frac{d\Omega}{2\pi} 2\pi e^2 u(\Omega) \times \left( \sum_{c} \delta_{bd} \frac{d_{ac} d_{ec}}{\Delta\omega_{eb} - \Omega - i\eta} \rho_c \rho_e^{-1} + \sum_{c} \delta_{ae} \frac{d_{ac} d_{db}}{\Delta\omega_{ae} - \Omega - i\eta} \right). \quad (10)$$

Substituting this into the Eq. 5 just as in the collisional case, we can obtain the two-photon rate as the lowest-order contribution, with subsequent terms possibly corresponding to higher-order multiphoton processes. With an appropriate definition of the energy density, $u(\omega)$, the expansion includes not only stimulated two-photon processes but also processes incorporating spontaneous emission.

As in the case of collisional broadening, the radiation broadening reduces to the form of Eq. 4 in the limit $\Delta\omega \to 0$. The elastic term will disappear in this case as there are no zero-frequency photons, leaving only the lifetime broadening due to radiative rates. In particular, this includes the lifetime due to spontaneous emission, often referred to as the ‘natural’ width of the state. Away from the line centre, this approximation to the radiation broadening breaks down, and the two-photon approximation will become more appropriate. In the line wings, the concept of natural width should give way to two-photon transitions involving spontaneous emission.

For both radiative and collisional broadening, we can therefore identify two limits. Close to line centers, where $\Delta\omega \to 0$, a one-photon picture, with line widths determined by collisional and radiative lifetimes, is most appropriate. In the opposite limit, where $\Delta\omega^{-1} \to 0$, we should instead consider second-order electron-photon and two-photon processes.

The one-photon picture is, however, often applied across the whole line, particularly for radiative broadening. Where this is the case, the far wings of the Lorentzian represent an approximation, albeit poor, to the two-photon opacity. This approximate correspondence between two-photon processes and the one-photon
FIG. 3. The ratio of electron-photon to two-photon processes shown against detuning from the line center for typical solar conditions. The rates have been calculated in thermal equilibrium, using the RPA structure factor, which will be valid for a weakly-coupled plasma [34].

line width even extends to the case of two-photon transitions between states with no intermediate resonance, such as the 1s – 2s case. As illustrated in Fig. 2 the wings of the 3p (and higher np) states will extend into the region between 1s and 2s and represent a very rough approximation to the 1s – 2s two-photon opacity in this region. Such transitions had previously been thought of as a ‘pure’ two-photon contribution, with no equivalent in one-photon approaches [33]. As such, we should not consider two-photon transitions as an additional source of opacity, as this represents double-counting to some extent.

Although two-photon processes cannot be considered in simple addition to one-photon opacity, an approach to opacity calculations based on two-photon and electron-photon processes might yield improved results. This approach would be most accurate in the regions between lines, where the second-order contributions are dominant. Since these regions contribute strongly to the Rosseland mean opacity, this new approach would be particularly suited to opacity calculations for radiative transport.

By comparing Eqs. 3 and 10 in conjunction with the expansion in Eq. 5, we can determine the relative importance of electron-photon and two-photon processes. If both collisions and radiation are treated in the dipole approximation, then the ratio of the two processes can be written simply as a function of the detuning:

$$\frac{w_{e\gamma}}{w_{\gamma\gamma}} = \int \frac{dk}{(2\pi)^3} k^2 \left(\frac{4\pi e^2}{k^2}\right)^2 S(k, \omega)(2\pi e^2 u(\omega))^{-1}. \quad (11)$$

This expression has been evaluated for typical solar conditions in Fig. 3. We find that the electron-photon process dominates over the two-photon process for moderate detuning (\(\lesssim 100 \text{ eV}\)). This is consistent with calculations suggesting negligible two-photon contributions in the 6–10 Å range [19]. However, the two-photon process should become more important for larger detuning, for example between the K- and L-shells of heavier elements.

A preliminary calculation of opacity using an electron-photon approach is shown in Fig. 4. The calculation includes bound-bound electron-photon transitions, which correspond to a part of the bound-bound and bound-free opacity in the one-photon picture. We see that for intermediate distances from the line center there is good agreement between this approach and conventional line broadening. Closer to the line center the electron-photon approach diverges, however it is not expected to be appropriate in this region, where existing approaches will typically be most accurate. In the region between the lines, the electron-photon approach shows increased opacity at some photon energies and diminished opacity at others due to the frequency dependence of the collision rate. As such, it is possible that an electron-photon approach could lead to an increase in the Rosseland mean opacity, depending on the plasma conditions and the element under consideration. More comprehensive calculations, incorporating effects such as continuum lowering, may be able to reach a more definite conclusion in this regard.

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