

Contribution of Interband Transitions to Non-equilibrium Emission in Metals

Abstract

In conductors, free electrons play a central role in photoluminescence. Microscopic calculation of electronic transitions inside the conduction band (intraband transitions) at thermal equilibrium results in the famous Planckian emission [ref]. Transitions between the conduction and valence band (interband transitions) are shown to negligibly contribute to thermal emissions [ref?]. When illuminated by an external monochromatic source however, that is outside of thermal equilibrium, intraband contribution to emission has been shown to noticeably change [ref]. Our aim here is to quantify the contribution of interband transitions to non-equilibrium emission in metal nano-particles.

Tasks

1. Connection between the energy integral (constant eDOS) and the analytic expression at zero Kelvin.
2. Comparison between energy integral (variable eDOS) and the analytic expression at finite temperature. (subsection 2.2)
3. Comparison between energy integral (variable eDOS) and integration in momentum space (subsection 2.1).
1. See if in the $T = 0$ limit, the integral

$$\lim_{T \rightarrow 0} \int_0^{\infty} f^T(\mathcal{E} + \hbar\omega) [1 - f^T(\mathcal{E})] d\mathcal{E}$$

equals the analytic solution in the same limit

$$\lim_{T \rightarrow 0} \frac{\hbar\omega}{e^{\hbar\omega/k_B T} + 1}$$

In the zero temperature limit the above expression converges to zero. This is also the case for the full integral.

$$\lim_{T \rightarrow 0} f^T(\mathcal{E}) = 1 - H(\mathcal{E}) \quad (0.1)$$

Where H is the Heaviside step function. The integrand becomes

$$\lim_{T \rightarrow 0} f^T(\mathcal{E} + \hbar\omega) \left[1 - f^T(\mathcal{E}) \right] = \left[1 - H(\mathcal{E} + \hbar\omega) \right] H(\mathcal{E}) \quad (0.2)$$

Since the two complementary step functions overlap only when $\hbar\omega$ is negative, the product is always zero. The two expressions (the analytic and the integral) are identically equal to zero at zero Kelvin.

1 Introduction

The general emission integral, inspired by Yonatan's and Novotny's derivations [references], which gives the rate of emitted photons per unit energy can be attributed in certain cases to two separate contributions

$$\Gamma_{em}(\omega) = I_{ph}(\omega) \cdot I_e(\omega) \quad (1.1)$$

a photonic and electronic contributions respectively which are given by the following expressions

$$I_{ph}(\omega) = \frac{\hbar\omega}{2\epsilon_0} \rho_{ph}(\omega) \quad (1.2)$$

$$I_e(\omega) = \frac{2\pi V^2}{\hbar} \int_{BZ} \int_{BZ} \left| \mu(\mathbf{k}_i, \mathbf{k}_f) \right|^2 f(\mathbf{k}_i) \left[1 - f(\mathbf{k}_f) \right] \delta(\mathcal{E}(\mathbf{k}_f) - \mathcal{E}(\mathbf{k}_i) + \hbar\omega) d^3 k_i d^3 k_f \quad (1.3)$$

In this work we focus on the electronic aspect of emission. Photoluminescence in metals is predominantly generated by a collection of spontaneous emissions in which the recombination of an electron from an initial state $|k_i\rangle$ to a final state $|k_f\rangle$ is accompanied by a release of a photon of energy $\hbar\omega$. The rate for a single transition can be calculated using Fermi's golden rule, and integration over all initial and final states (through the consideration of the band structure) results in the total electronic contribution to the emission at a certain frequency (1.3)

We will investigate the electronic contribution in four distinct regimes

- Intraband transitions in thermal equilibrium (section 2). Electrons hop from one level of the conduction band to an energetically lower level of the same band in radiative transitions.
- Intraband transitions in non-equilibrium (section 3). The same intraband transitions for a system in steady state with a perturbing monochromatic light source which produces a non-equilibrium electronic distribution.
- Interband transitions in thermal equilibrium (section 4). We go back to thermal electronic distribution but now consider radiative transitions from the conduction into the valence band. Here electronic dispersion relation is no longer isotropic and we calculate the emission integral in momentum space.
- Interband transitions in non-equilibrium (section 5). Finally, we employ the non-equilibrium electronic distribution to the case of radiative transitions from the conduction to the valence band.

In all four cases, we assume that the transition dipole moment is a constant of integration, and for the sake of brevity, we henceforth neglect to explicitly write the prefactor $\frac{2\pi V^2}{\hbar}|\mu|^2$. Our primary expression is therefore

$$I_e(\omega) \propto \int_{BZ} \int_{BZ} f(\mathbf{k}_i) \left[1 - f(\mathbf{k}_f) \right] \delta(\mathcal{E}(\mathbf{k}_f) - \mathcal{E}(\mathbf{k}_i) + \hbar\omega) d^3 k_i d^3 k_f \quad (1.4)$$

For intraband calculations we also try to compare our numerical results to Yonatan's analytic expression for both equilibrium and non-equilibrium emissions.

2 Intraband Transitions (Equilibrium)

In the case of Drude metals, in which the density of conduction electrons is low, the free electron approximation is very good. Most importantly this means that the electronic dispersion relation is isotropic. Consequently our integration over 6 degrees of freedom (3 momentum directions for each of the initial and final states) reduces to 2 degrees of freedom (2 momentum magnitudes for the initial and final states) namely, equation (1.4) becomes

$$I_e \propto \int_{\text{BZ}} \int_{\text{BZ}} f^T(k_i) \left[1 - f^T(k_f) \right] \delta(\mathcal{E}(k_f) - \mathcal{E}(k_i) + \hbar\omega) (4\pi k_i^2 dk_i)(4\pi k_f^2 dk_f) \quad (2.1)$$

Note that we use a superscript T in the electronic distribution to denote that a thermal (Fermi-Dirac) distribution is being used.

Another benefit of the isotropy in the dispersion relation is the ability to simply change variables from momentum basis to energy basis using the electronic density of states (eDOS) $4\pi k_j^2 dk_j \rightarrow \rho_e^j(\mathcal{E}_j) d\mathcal{E}_j$. And because the transition takes place within the same band the eDOS functions are the same for the initial and final states $\rho_e^i = \rho_e^f \equiv \rho_e$. Integrating over energy allows us to simply resolve the delta function without resorting to more sophisticated approaches and further reduces the number of integration variables from 2 to 1. The integral takes the form

$$I_e \propto \int_0^\infty \int_0^\infty \rho_J(\mathcal{E}_i, \mathcal{E}_f) \delta(\mathcal{E}_f - \mathcal{E}_i + \hbar\omega) d\mathcal{E}_i d\mathcal{E}_f \quad (2.2)$$

$$= \int_0^\infty \rho_J(\mathcal{E}_f + \hbar\omega, \mathcal{E}_f) d\mathcal{E}_f \quad (2.3)$$

where we used the population-weighted joint density of pair states (JDOPS) given by the following

$$\rho_J(\mathcal{E}_i, \mathcal{E}_f) = f^T(\mathcal{E}_i) \rho_e(\mathcal{E}_i) \left[1 - f^T(\mathcal{E}_f) \right] \rho_e(\mathcal{E}_f) \quad (2.4)$$

with the expression for the eDOS (in 3-dimensions) is given by

$$\rho_e(\mathcal{E}) = \frac{m_e^{3/2}}{\pi^2 \hbar^3} \sqrt{2\mathcal{E}} = \frac{3n}{2\mathcal{E}_F} \left(\frac{\mathcal{E}}{\mathcal{E}_F} \right)^{1/2} \quad (2.5)$$

Where n is the density of conduction electrons.

2.1 Energy - Momentum Comparisons

We wish to solve the integral in both momentum and energy space. This might seem excessive since the (??) is simpler to compute and is more accurate. However, in later stages, transitioning to energy space might not be as trivial (perhaps not possible). Here we establish the viability of this approach.

In order to solve (2.1) numerically the delta function is approximated by a Gaussian with small enough standard deviation. (What does "small enough means")

$$I_e \propto \lim_{\sigma \rightarrow 0} \int_{\text{BZ}} \int_{\text{BZ}} f^T(k_i) \left[1 - f^T(k_f) \right] G_\sigma \left(\mathcal{E}(k_f) - \mathcal{E}(k_i) + \hbar\omega \right) (4\pi k_i^2 dk_i) (4\pi k_f^2 dk_f) \quad (2.6)$$

Where

$$G_\sigma = \frac{1}{\sigma \sqrt{2\pi}} \exp \left[-\frac{(\mathcal{E}(k_f) - \mathcal{E}(k_i) + \hbar\omega)^2}{2\sigma^2} \right] \quad (2.7)$$

plot the Gaussian as function of k1 k2

We expect this numerical integration to better converge to the energy space result as σ shrinks.

2.2 Comparison between numerical integration (energy basis) and analytic expression for emission

In 'Theory of "Hot" Photoluminescence from Drude Metals' two approximations are made that lead to an analytic result of the thermal intraband emission.

- Most intraband transitions take place close to the fermi energy and thus the eDOS $\rho_e(\mathcal{E}) \approx \rho_e(\mathcal{E} + \hbar\omega) \approx \rho_e(\mathcal{E}_F)$ is approximately constant.
- Chemical potential is much greater than electronic thermal energy at room temperature, namely $\mu >> k_B T$.

The first approximation enables to take the eDOS terms out of the integral and the second allows to analytically solve the integral. The application of the two approximations respectively is given below

$$I_e \approx \rho_e^2(\mathcal{E}_F) \int f^T(\mathcal{E} + \hbar\omega) [1 - f^T(\mathcal{E})] d\mathcal{E} \quad (2.8)$$

$$\approx \rho_e^2(\mathcal{E}_F) \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} \quad (2.9)$$

A in figure 1 of both (2.3) and (2.9) are plotted as well as their relative error, both in log scale.

In order to ascertain that the relative error has converged and is due to the discrepancy between the terms and not due to numerical inaccuracy, we progressively decreased the step size and calculated the mean relative error. Once a certain value has been reaches and is no longer noticeably fluctuating a desired integration step has been reached. Using that integration interval we can now draw conclusions about the relative errors between the two terms. Not only is the relative error quite high to begin with, it increases with larger emission energies.

We can estimate the relative error between the eDOS at the Fermi energy and the eDOS at an energy $\hbar\omega$ greater.

$$\delta\rho_e(\hbar\omega) = \frac{\rho_e(\mathcal{E}_F + \hbar\omega) - \rho_e(\mathcal{E}_F)}{\rho_e(\mathcal{E}_F)} = \sqrt{1 + \frac{\hbar\omega}{\mathcal{E}_F}} - 1 \quad (2.10)$$

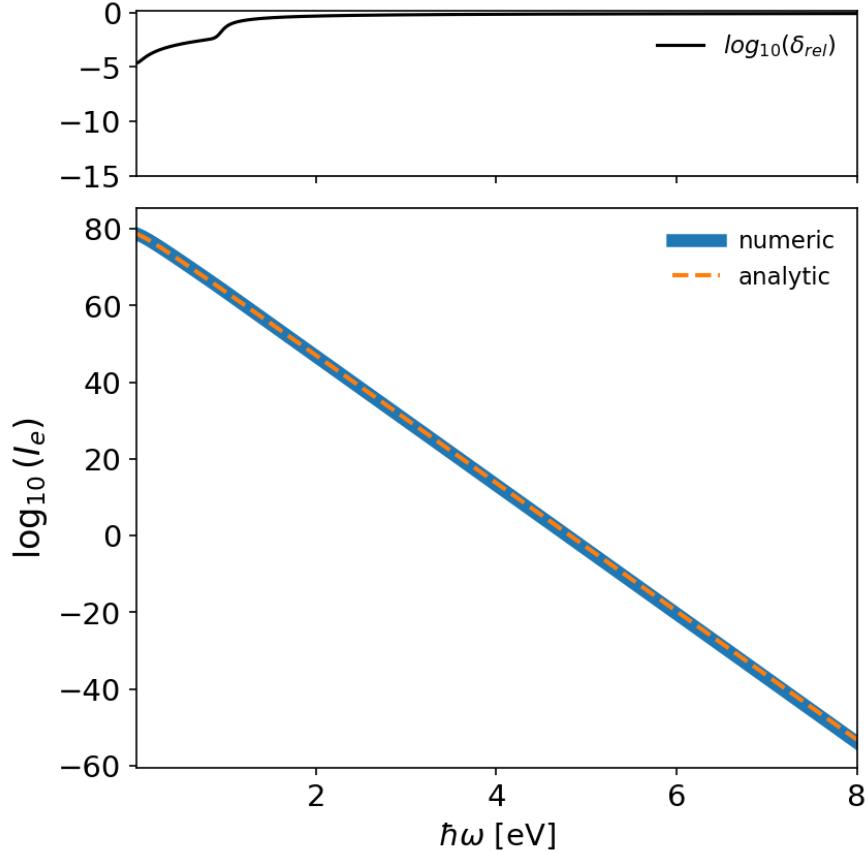


Figure 1: Comparison between the numerical solution in energy space for the electronic contribution to emissions and the analytic approximation. The log of both numeric and analytic solutions is given by the thick blue line and by the dashed orange line respectively as a function of emission energy. The log of the relative error between the two is given in the upper plot at each emission energy.

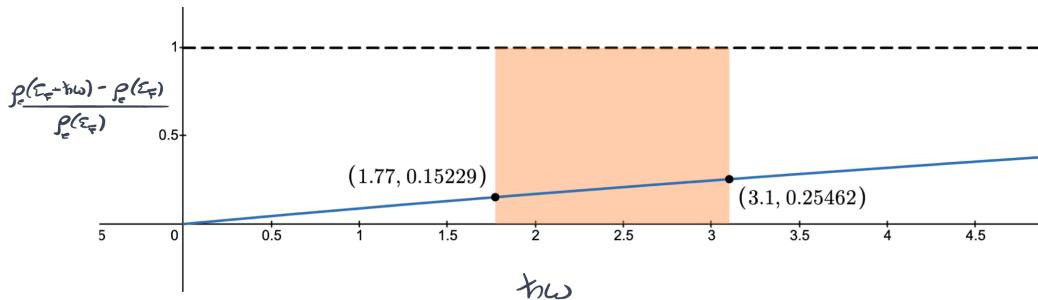


Figure 2: The relative error (blue line) in two eDOS around the Fermi energy with energetic separation of $\hbar\omega$. The relative error increases with emission energy and is quite significant even at optical frequencies (red region).

3 Intraband Transitions (Non-equilibrium)

4 Interband Transitions (Equilibrium)

5 Interband Transitions (Non-equilibrium)

6 Appendix

6.1 Thoughts about intraband transitions

A non-relativistic treatment of the energy/momentum conservation in the absorption process of a photon by an electron goes as follows