Second order divergence in the third order DC response of a cold semiconductor

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In this work, we present the analytical expression for the second order divergence in the third order DC response of a cold semiconductor, which can be probed by different electric field setups. Results from this expression were then compared, for the response of the gapped graphene monolayer, with numerical results from a velocity gauge calculation of the third order conductivity. The good agreement between the two validates our analytical expression.

I. INTRODUCTION

The existence of divergences in the nonlinear optical (NLO) conductivities of crystalline systems is a well-established result [1]. It dates back to the discovery of the second order injection current, whereby an elliptically polarized electric field generates a current that, in the absence of saturation and relaxation, has a finite and constant time derivative [2]. Shortly thereafter, two other effects, the two-color current and the current generated second harmonic generation, were described in terms of divergences of the third order NLO conductivity [2–5]. The first provided a valuable understanding of how the DC response of crystals could be controlled by dichromatic optical fields [2–4], while the second described the second harmonic generation in a material where a DC field breaks the inversion symmetry of the crystal [5]. The recent developments in two-dimensional materials [6–9] and their optical properties [10–18] have spurred a new interest in these divergences, with works focusing on effects such as the jerk current, the cross-phase modulation and the degenerate four-wave mixing [18–20]. Such a systematic study of the divergences of the NLO conductivities — that depend on both a frequency sum and a relaxation rate — is important as they describe, in principle, responses that can be expected to be large, i.e., responses that should be easily detectable and whose application can be useful in the field of nonlinear optics [21].

As the second order DC response of a cold semiconductor carries a divergence first in the inverse sum of frequencies and in the phenomenological inverse relaxation rate, one can expect the third order DC response to carry a divergence of second order — in the inverse of the sum of at least two of the frequencies, in the inverse relaxation rate or in the product of both. These can be probed by different setups of the electric field that have zero (or nearly zero) sum of frequencies. The jerk current, recently proposed in ref. [19], is the one associated to an electric field that has both a static and monochromatic component; in this case, the divergence is in the inverse square of the relaxation rate. Here, we shall also consider two additional setups of the electric field through which the divergence can be probed: one mixes the relaxation rate and a frequency sum and is associated to the response to a dichromatic field of frequencies $\omega$ and $\delta \ll \omega$; the other involves the product of two inverse frequency sums and is associated to the response to a trichromatic field of frequencies, $\omega + \delta_1 \sim \omega$, $\omega$ and $\delta_2 \ll \omega$. The three different setups involve output frequencies that are either zero, $\omega_{123} = 0$, or small, $\omega_{123} = \delta \ll \omega$, $\omega_{123} = \delta_1 + \delta_2 \ll \omega$, and therefore fall under the scope of a DC (or quasi-DC) response.

The main point of this work, however, is that, regardless of the setup, the divergence is always associated to the same coefficient, which is completely general and valid for a system with any number of bands, whether in two or three dimensions. We note that the coefficient derived here differs from the one derived in ref. [19]. A second point regarding this expression is that, with exception of the trichromatic setup, the pre-factor of the divergence depends on the type of phenomenology used to include relaxation; it is not the same when it is introduced via the equations of motion [21] or via adiabatic switching [17]. We use the latter one in this work.

Finally, a word concerning the type of materials at hand: cold semiconductors. Analytical calculations of NLO responses can be quite complicated, as the number and diversity of different contributions increases quite dramatically with the order of the calculation. These different contributions are, in general terms, either dependent on the difference between the occupation factors of two different bands, that is, a difference of Fermi functions, or a derivative with respect to a Fermi function. Cold semiconductors allow for a valuable simplification of this type of calculation: all terms involving derivatives of Fermi functions can be set to zero, while the occupation factors can be set to either one — in the valence bands — or zero — in the conduction bands.

This paper is organized as follows. In Sec.II, we derive the terms of the conductivity that carry the second order divergence in the DC (and quasi-DC) response. We also discuss how different electric field setups probe this divergence in different ways, as well as the role that phenomenology plays in the description of these divergent responses. In Sec.III, we present a comparison between the derived analytical results and results computed numerically in the velocity gauge, for the gapped graphene monolayer [17, 18]. The good agreement between the two validates the expressions that we have derived. A brief summary of the work is presented in Sec.IV.

II. THE THIRD ORDER RESPONSE OF A COLD SEMICONDUCTOR AND ITS SECOND ORDER DIVERGENCE IN THE DC RESPONSE

The nonlinear optical response of a crystalline system, which has been the subject of extensive work [1–5, 10–18, 22–25], can be described — at a given order in the electric field — in terms of certain response functions: susceptibilities, if the response...
is expressed by the electric polarization; and conductivities, if
the response is expressed by the electric current. If we choose
the latter procedure to determine the response, and noting
that the third order response is the subject of interest in this
work, one can write,

$$J^{(3)}_\beta(t) = \int \frac{d\omega_1}{2\pi} \frac{d\omega_2}{2\pi} \frac{d\omega_3}{2\pi} \sigma_{\alpha_1\alpha_2\alpha_3}(\omega_1, \omega_2, \omega_3) \times E^{\alpha_1}(\omega_1) E^{\alpha_2}(\omega_2) E^{\alpha_3}(\omega_3) e^{-i\omega_1 t},$$  \hspace{1cm} (1)

for the third order contribution to the electric current. The
derivation of $\sigma_{\beta_1\beta_2\beta_3}(\omega_1, \omega_2, \omega_3)$ is a technical and laborious
task that has been conducted in the aforementioned works,
for both the length [1–3, 5, 10–16, 22], and the velocity gauge
[17, 18, 23–25]. These gauge choices correspond to different
ways of treating the coupling between electrons in the crys-
tal and the electric field, and follow from the freedom that is
involved in the choice of representation of the electric field in
terms of the scalar and vector potentials. As we are interested
in obtaining expressions that can be used in analytical calcu-
lations, we choose to perform the calculations in the length
gauge. Moreover, we will carry over the notation that was
introduced in [16], as well as the notion that conductivities
can be fully determined by the energy bands, $\epsilon_{ks}$, and Berry
connections, $\xi_{ks,\gamma}$, of the electrons in the crystal [1].

The third order response is described by the following un-
symmetrized conductivity [16],

$$\frac{1}{i\epsilon^4} \sigma_{\beta_1\beta_2\beta_3}(\omega_1, \omega_2, \omega_3) = \int \frac{d^d k}{(2\pi)^d} \sum_{s'} s' \frac{1}{\hbar \omega_{123} - \Delta \epsilon_{ss'}} \left[ D^{\alpha_3}_{k}, \frac{1}{\hbar \omega_2 - \Delta \epsilon_k} \circ \left[ D^{\alpha_2}_{k}, \frac{1}{\hbar \omega_1 - \Delta \epsilon_k} \circ \left[ D^{\alpha_1}_{k}, \rho_k^{(0)} \right] \right] \right]_{ss'}.$$

Second order divergence in the third order DC response

We want to compute the second order divergence of Eq.(2)
in the case where the output frequency is either zero, $\omega_{123} = 0$, or is very small compared to the frequency of the optical com-
ponent of the field, $\omega_{123} \ll \omega$. To the second order divergence
of the third order DC conductivity we call $\Gamma_{\beta\alpha_1\alpha_2\alpha_3}$,

$$\sigma_{\beta_1\beta_2\beta_3}(\omega_1, \omega_2, \omega_3) = \Gamma_{\beta_1\beta_2\beta_3}(\omega_1, \omega_2, \omega_3) + (....),$$

the ellipsis represents all other contributions to the conductivity.

To isolate this contribution, it is first useful to manipulate the
expression in Eq.(2). We begin by exchanging the band
labels in the denominator that contains the total frequency,
$\omega_{123}$,

$$\frac{1}{\hbar \omega_{123} - \Delta \epsilon_{ss'}} \rightarrow \frac{1}{\hbar \omega_{123} + \Delta \epsilon_{ss'}},$$

which allows us to express Eq.(2) in the form

$$\frac{1}{i\epsilon^4} \sigma_{\beta_1\beta_2\beta_3}(\omega_1, \omega_2, \omega_3) =$$

$$= \int \frac{d^d k}{(2\pi)^d} \text{Tr} \left\{ \left( \epsilon_k^\beta \circ \frac{1}{\hbar \omega_{123} + \Delta \epsilon_k} \right) D^{\alpha_3}_{k}, A^{\alpha_2\alpha_1}_{k} (\omega_{12}, \omega_1) \right\}.$$
\[
\frac{1}{ie^2} \sigma_{\alpha_1 \alpha_2 \alpha_3}(\omega_1, \omega_2, \omega_3) = - \int \frac{d^3k}{(2\pi)^d} \sum_{s' \neq s} \left[ D^\alpha_{k^s}, v^\beta_{k^s} \circ \frac{1}{\hbar \omega_{123} + \Delta_{k^s}} \right]_{s's} A^{\alpha_1 \alpha_2 \alpha_3}_{k^s} k^s \left( \omega_{12}, \omega_1 \right) \tag{11}
\]

with

\[
A^{\alpha_1 \alpha_2 \alpha_3}_{k^s} k^s \left( \omega_{12}, \omega_1 \right) := \frac{1}{\hbar \omega_{12} - \Delta_{k^s}} \left[ D^\alpha_{k^s}, \frac{1}{\hbar \omega_1 + \Delta_{k^s}} \circ \left[ D^\alpha_{k^s}, \rho^{(0)}_{k^s} \right] \right]_{ss'}.
\]

We proceed to separate the conductivity into its \(s' \neq s\) and \(s' = s\) contributions.

1. \(s' \neq s\) contributions

For the \(s' \neq s\) contributions, the integrand in Eq.\((11)\) reads as,

\[
- \sum_{s' \neq s} \left[ D^\alpha_{k^s}, v^\beta_{k^s} \circ \frac{1}{\hbar \omega_{123} + \Delta_{k^s}} \right]_{s's} \\
\times \frac{1}{\hbar \omega_{12} - \Delta_{k^s}} \left[ D^\alpha_{k^2}, \frac{(-i)}{\hbar \omega_1 - \Delta_{k^s}} \circ \left[ \xi^\alpha_{k^s}, f^\beta_{k^s} \right] \right]_{ss'}.
\]

We will show that these terms do not contribute to second order divergences in the DC response. This requires expanding and manipulating the product of commutators contained in Eq.\((12)\), as shown in Appendix A. One term that follows from this procedure, Eq.\((A3)\), is,

\[
i \left[ D^\alpha_{k^s}, v^\beta_{k^s} \circ \frac{1}{\hbar \omega_{123} + \Delta_{k^s}} \right]_{s's} \\
\times \frac{\xi^\alpha_{k^s} \Delta f_{k's}}{\hbar \omega_{12} - \Delta_{k^s}} \left( \nabla^\beta \nabla^\alpha \xi_{k^s} \right) \frac{1}{\hbar \omega_1 - \Delta_{k^s}} \frac{1}{(\hbar \omega_{12} - \Delta_{k^s})^2}.
\]

Consider the product of denominators that are associated to it,

\[
\frac{1}{\hbar \omega_{12} - \Delta_{k^s}} \left( \hbar \omega_1 - \Delta_{k^s} \right)^2.
\]

It has been suggested that terms of this form contribute to the second order divergence in the third order DC response \([19, 20]\). That, however, cannot be the case, since taking the limit of \(\omega_2 \to 0\) in Eq.\((14)\) shows us that the product of denominators is not associated to any divergences,

\[
\frac{1}{\hbar \omega_{12}} \left( \hbar \omega_1 - \Delta_{k^s} \right)^2 \\
\frac{1}{(\hbar \omega_1 - \Delta_{k^s})^3} \\
= \frac{1}{2\hbar^2} \left( \nabla^\alpha \nabla^\beta \right) \frac{1}{\hbar \omega_1 - \Delta_{k^s}},
\]

and as such, the term in Eq.\((13)\) cannot contribute to \(\Gamma_{\alpha_1 \alpha_2 \alpha_3}\).

A careful analysis of all the other denominators contained in Eq.\((12)\) shows that no product of two divergent factors — a second order divergence — appears for the DC (or quasi-DC) response. The divergent factors in a conductivity with zero (or small) output frequency can only come about when the energy difference, \(\Delta_{k^s}\), in a denominator is zero, meaning that they only appear only when the two band indexes are the same. We thus turn to the \(s' = s\) contributions of Eqs.\((11)\).

2. \(s' = s\) contributions

For the \(s' = s\) contributions, the integrand in Eq.\((11)\) reads as,

\[
- \frac{1}{\hbar \omega_{123}} \frac{1}{\hbar \omega_{12}} \sum_{r \neq s} \left[ D^\alpha_{k^s}, v^\beta_{k^s} \circ \frac{1}{\hbar \omega_{123} + \Delta_{k^s}} \right]_{s's} \\
\times \frac{1}{\hbar \omega_{12} - \Delta_{k^s}} \left[ D^\alpha_{k^2}, \frac{(-i)}{\hbar \omega_1 - \Delta_{k^s}} \circ \left[ \xi^\alpha_{k^s}, f^\beta_{k^s} \right] \right]_{ss'},
\]

By expanding the two commutators, and after a careful treatment of the terms involved — presented in Appendix B — one can show that there is a single contribution involving the product of two divergent factors in the case of a DC response,

\[
\frac{1}{\hbar \omega_{123}} \frac{1}{\hbar \omega_{12}} \frac{1}{\hbar \omega_1} \sum_{r \neq s} \left( \nabla^\beta \nabla^\alpha \xi_{k^s} \right) \frac{1}{\hbar \omega_1 - \Delta_{k^s}} \left( \hbar \omega_{12} - \Delta_{k^s} \right)^2.
\]

Here, \(\Delta f_{k^r} = f_{k^r} - f_{k^s}\). By manipulating the band index sums and relabelling \(r \to s'\), we obtain

\[
\frac{1}{\hbar \omega_{123}} \frac{1}{\hbar \omega_{12}} \frac{1}{\hbar \omega_1} \sum_{s \neq s'} \left( \nabla^\beta \nabla^\alpha \xi_{k^s} \right) \frac{1}{\hbar \omega_1 - \Delta_{k^s}} \left( \hbar \omega_{12} - \Delta_{k^s} \right)^2.
\]

It is now clear how different frequency combinations of \(\omega_1, \omega_2\) and \(\omega_3\), that is, different electric field setups, correspond to different ways of probing the second order divergence in the DC (or quasi-DC) response:\([20]\)

- For \(\omega_{123} = \omega_{12} = 0\), i.e., \(\omega_1 = -\omega_2 = \omega_3 = 0\),

\[
\frac{1}{\hbar \omega_{123}} \frac{1}{\hbar \omega_{12}} \to \frac{1}{\hbar^2 (3i\gamma)(2i\gamma)} = \frac{1}{6\hbar^2} \gamma^{-2}.
\]

This corresponds to the jerk current: \(\Gamma_{\beta_1 \alpha_2 \alpha_3}(\omega, -\omega, 0)\).

- For \(\omega_{123} = \delta, \omega_{12} = 0\), i.e., \(\omega_1 = -\omega_2 = \omega\) and \(\omega_3 = \delta\), with \(\gamma \ll \delta \ll \omega\),

\[
\frac{1}{\hbar \omega_{123}} \frac{1}{\hbar \omega_{12}} \to \frac{1}{\hbar^2 (2i\gamma)} = -i \frac{1}{2\hbar^2} \gamma^{-1} \delta^{-1}.
\]

This corresponds to the dichromatic setup probe: \(\Gamma_{\beta_1 \alpha_2 \alpha_3}(\omega, -\omega, \delta)\).

- For \(\omega_{123} = \delta_1 + \delta_2, \omega_{12} = \delta_1\), e.g., \(\omega_1 = \omega + \delta_1, \omega_2 = -\omega\) and \(\omega_3 = \delta_2\), with \(\gamma \ll \delta_1, \delta_2 \ll \omega\),

\[
\frac{1}{\hbar \omega_{123}} \frac{1}{\hbar \omega_{12}} \to \frac{1}{\hbar^2 (\delta_1 + \delta_2)(\delta_2)} = \frac{1}{\hbar^2} (\delta_1 + \delta_2)^{-1} \delta_2^{-1}.
\]
This corresponds to the trichromatic setup probe: \( \Gamma_{\beta_1,\alpha_2,\alpha_3}(\omega + \delta_1, -\omega, \delta_2) \).

We can then express the denominator in its real and imaginary part and, as \( \hbar \gamma \) is the smallest energy scale in the integral, make the replacement,

\[
\frac{1}{\hbar \omega_1 - \Delta \epsilon_{kss'}} \rightarrow \frac{P}{\hbar \omega_1 - \Delta \epsilon_{kss'}} - i\pi \delta(\hbar \omega_1 - \Delta \epsilon_{kss'}).
\]  

(23)

and write the contribution to the conductivity that carries the second order divergence, \( \Gamma_{\beta_1,\alpha_2,\alpha_3} \), as,

\[
\frac{i e^4}{\hbar^3} \frac{(-1)}{\omega_{123}\omega_{12}} \int \frac{d^3k}{(2\pi)^3} \sum_{s \neq s'} (\nabla^\beta \nabla^\alpha_3 \Delta \epsilon_{kss'}) \xi_{kss'}^{\alpha_1} \xi_{kss'}^{\alpha_2} \Delta f_{kss'} \times \left[ \frac{P}{\hbar \omega_1 - \Delta \epsilon_{kss'}} - i\pi \delta(\hbar \omega_1 - \Delta \epsilon_{kss'}) \right].
\]  

(24)

Note that we have not yet symmetrized the conductivity. As we are interested in the terms that contribute to the second order divergence in the DC response, \( \Gamma_{\beta_1,\alpha_2,\alpha_3} \), there is a single relevant permutation, \((\alpha_1, \omega_1) \leftrightarrow (\alpha_2, \omega_2)\), that is to be taken into account. After a careful calculation — see Appendix C — one obtains a symmetrized \( \Gamma \), \( \Gamma_{\beta_1,\alpha_2,\alpha_3} \),

\[
\Gamma_{\beta_1,\alpha_2,\alpha_3}(\omega_1, \omega_2, \omega_3) = -\frac{e^4}{3\hbar^3} \frac{1}{\omega_{123} \omega_{12}} \Gamma_{\beta_1,\alpha_2,\alpha_3}(\omega_1),
\]  

(25)

with a coefficient, \( \iota_{\beta_1,\alpha_2,\alpha_3}(\omega_1) \), that is expressed in terms of a single integral involving a Dirac delta function,[27]

\[
\iota_{\beta_1,\alpha_2,\alpha_3}(\omega_1) = \pi \int \frac{d^3k}{(2\pi)^3} \sum_{s \neq s'} (\nabla^\beta \nabla^\alpha_3 \Delta \epsilon_{kss'}) \times \xi_{kss'}^{\alpha_1} \xi_{kss'}^{\alpha_2} \Delta f_{kss'} \delta(\hbar \omega_1 - \Delta \epsilon_{kss'}). \]  

(26)

Finally, we must comment on the numerical pre-factors in \( \Gamma_{\beta_1,\alpha_2,\alpha_3} \), Eq.(25). For the jerk current and the dichromatic setup probe to the divergence, different choices of phenomenology are associated to different numerical factors. If, for example, we were to consider the relaxation rate introduced via equations of motion, one would have \( \bar{\omega}_1 = \omega_1 + i\gamma \), \( \bar{\omega}_{12} = \omega_{12} + i\gamma \), and \( \bar{\omega}_{123} = \omega_{123} + i\gamma \), and factors of 1/6 and 1/2 would not appear in Eq.(20) and in Eq.(21), respectively. We will retain the use of the adiabatic switching approach, as we want to compare analytical results with results from a numerical calculation of the conductivity in the velocity gauge [17]. This phenomenological approach to introducing relaxation rates has recently gotten additional motivation [25].

### III. THE SECOND ORDER DIVERGENCE IN THE DC THIRD ORDER RESPONSE OF GAPPED GRAPHENE

Having determined the analytical expression for the second order divergence of the DC third order conductivity, we can compare this result with those that follow from a numerical calculation of the conductivity in the velocity gauge. The material to be considered here is the gapped graphene monolayer, described by a nearest neighbours tight-binding model with parameters \( \Delta = 300 \text{meV} \) and \( t = 3 \text{eV} \) [18]. For the analytical calculation, we consider an expansion of the tight-binding Hamiltonian around the band minima, \( \mathbf{k} = \mathbf{K}(\mathbf{K}') + \mathbf{q} \), Fig.(1), which renders the usual Hamiltonian,

\[
H_{\lambda}(\mathbf{q}) = \begin{bmatrix} \Delta/2 & \hbar v_F(\lambda q_x - iq_y) \\ \hbar v_F(\lambda q_x + iq_y) & -\Delta/2 \end{bmatrix}
\]  

(27)

where \( \lambda = \pm 1 \) for \( \mathbf{K} = 4\pi/3\sqrt{3}a_0 \hat{k}_x \) and \( \mathbf{K}' = -4\pi/3\sqrt{3}a_0 \hat{k}_x \), respectively, and \( \hbar v_F = 3t a_0/2 \), for \( a_0 = 1.42\AA \), the distance between two neighbouring atoms. Since this model has time reversal symmetry, one has \( \epsilon_{-\mathbf{k}s} = \epsilon_{\mathbf{k}s} \) and can choose the Berry connections such that \( \xi_{kss'}^{\alpha_1} = \xi_{kss'}^{\alpha_1} \). One can then show that the only relevant portion of Eq.(26) is the one involving the symmetric product of Berry connections — \( \xi_{kss'}^{\alpha_1} \xi_{kss'}^{\alpha_2} + \xi_{kss'}^{\alpha_2} \xi_{kss'}^{\alpha_1} \) — so that the \( \iota_{\beta_1,\alpha_2,\alpha_3}(\omega_1) \) coefficient is necessarily real.

The results for the three different probes to the divergence, Eqs.(20)–(22), are presented in the three plots of Figure 2. In the numerical computation, the relaxation rate \( \gamma \) is finite, as well as the frequency offsets \( \delta_1 \) and \( \delta_2 \); \( \delta_1 \) for the dichromatic field setup probe, plot (b), and both \( \delta_1 \) and \( \delta_2 \) for the trichromatic one, plot (c). So we compute \( \iota_{\beta_1,\alpha_2,\alpha_3}(\omega_1) \) by expressing it in terms of the conductivity, Eq.(8),

\[
\iota_{\beta_1,\alpha_2,\alpha_3}(\omega_1) \approx \frac{-3\hbar^3}{e^4} \omega_{123} \omega_{12} \sigma_{\beta_1,\alpha_2,\alpha_3}(\omega_1, \omega_2, \omega_3)
\]  

(28)

and replacing \( \bar{\omega}_{123} \), \( \bar{\omega}_{12} \) by the expressions given in Eqs.(20) to (22). There is good agreement between the analytical results that follow from Eq.(26), and the numerical results of a velocity gauge calculation of the full conductivity, for frequencies above the gap. This validates the analytical expression that we have derived here. In addition, the results themselves warrant two comments. First, we note that there are discrepancies between the analytical and numerical results for frequencies below the gap. These follow from the fact that the numerical calculation carries contributions other than \( \Gamma_{\beta_1,\alpha_2,\alpha_3} \) — the
terms represented by the ellipsis in Eq.(8) — which necessarily contribute to the response. That the differences between results are more noticeable in plots (b) and (c) of Figure 2 is due to the existence, in the full conductivity, of resonances at frequencies \( \omega \pm \delta \) and \( \omega \pm 2\delta \), respectively. Secondly, the analytical calculation gives us an expression for that \( \iota_{xxxx}(\Delta) \) that reads as,

\[
\frac{1}{a_0^2} \iota_{xxxx}(\Delta) = \frac{9t^2}{2\Delta^2}.
\]

(29)

The second order divergence in gapped graphene should be more pronounced when the band gap is smaller, which is consistent with the results of ref.[21] and similar to what was obtained for the second order response \[18\].

Finally, we present an estimation of the amplitude of the jerk current, \( J_{jerk} \), along the zig-zag direction in gapped graphene. For the values of the hopping parameter and band gap presented above and for \( \hbar\omega \sim \Delta, \tau = 1/\gamma \sim 100 \text{ fs}, E_x^r = 10^7 \text{ V/m} \) and \( E_0^r = 10^6 \text{ V/m} \), one obtains \( J_{jerk} \approx 12 \text{ A/m} \), which should be within experimental reach \[19\].

IV. SUMMARY

The study of divergences in nonlinear optical response functions provides us with the knowledge that some NLO responses can be made large simply by the choice of certain field setups, which is certainly relevant from the standpoint of nonlinear optics. It can also provide us with some valuable intuition concerning the physics that is associated to these processes, as it has been done in \[2, 5, 19\]. We have shown here that the leading order divergence in the third order DC (or quasi-DC) response of a cold semiconductor — first identified in ref.[19] — can be probed via three different electric field setups, and is described by a single coefficient, Eq.(26), that involves only one Dirac delta function, i.e., are localized contributions in the FBZ. The differences between the results of this calculation and that of ref.[19] were also addressed here. Finally, we compared, for the gapped graphene monolayer, the results that follow from Eq.(26) with results that follow from a numerical calculation of the conductivity in the velocity gauge: these are in clear agreement with each other.

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Figure 2. A comparison between the analytical result that follows from Eq.(26) — represented by the red dashed curve — and numerical results from a velocity gauge calculation of the conductivity \[17, 18\] — represented by the full curves — in gapped graphene, \( \Delta = 300 \text{ meV} \) and \( t = 3 \text{ eV} \), for the response along the zig-zag direction, \( \beta = \alpha_i = \alpha \), \( i = 1, 2, 3 \). The (a), (b) and (c) plots represent the second order divergence in the jerk current and the dichromatic and trichromatic field setup probes, respectively. In (a), we have also represented the analytical solution from ref.[19] — represented by the magenta dashed curve. This, we note, does not match with our numerical result. Note also that value of \( \iota \) at the gap, given by Eq.(29), reads as \( \iota_{xxxx}(\Delta)a_0^{-2} = 450 \).
Appendix A: \( s' \neq s \) terms

This appendix presents the intermediate steps of the derivation of the \( s' \neq s \) contribution that is considered in subsection II 1. It follows from Eq.(6) that the terms, \( s' \neq s \), Eq.(12), can be written as the sum of two contributions,

\[
(-1) \left[ D_{k_s}^{o_3}, v_{k_s}^{\beta} \circ \frac{1}{\hbar \omega_{123} + \Delta \epsilon_k} \right] s' s \left[ D_{k_s}^{o_2}, \frac{(-i)}{\hbar \omega_1 - \Delta \epsilon_k} \circ \left[ \xi_k^{o_1}, f_k \right] \right]_{s' s} = \\
i \left[ D_{k_s}^{o_3}, v_{k_s}^{\beta} \circ \frac{1}{\hbar \omega_{123} + \Delta \epsilon_k} \right] s' s \left[ D_{k_s}^{o_2} \left( \nabla_{k_s}^{o_1} \Delta f_{ks's} \right) \right] \left( \frac{1}{\hbar \omega_1 - \Delta \epsilon_k} \right)^2 \\
+ \left[ D_{k_s}^{o_3}, v_{k_s}^{\beta} \circ \frac{1}{\hbar \omega_{123} + \Delta \epsilon_k} \right] s' s \left[ \frac{1}{\hbar \omega_1 - \Delta \epsilon_k} \circ \left[ \xi_k^{o_1}, f_k \right] \right]_{s' s}. \tag{A1}
\]

Let us take the first term on the RHS of Eq.(A1) and further manipulate it. Since \( \nabla_k^{o_2} f_{ks} = 0 \) for a cold semiconductor, this term reads,

\[
i \left[ D_{k_s}^{o_3}, v_{k_s}^{\beta} \circ \frac{1}{\hbar \omega_{123} + \Delta \epsilon_k} \right] s' s \left[ \xi_k^{o_1} \Delta f_{ks's} \right] \left( \frac{1}{\hbar \omega_1 - \Delta \epsilon_k} \right)^2 \\
+ i \left[ D_{k_s}^{o_3}, v_{k_s}^{\beta} \circ \frac{1}{\hbar \omega_{123} + \Delta \epsilon_k} \right] s' s \left( \frac{1}{\hbar \omega_1 - \Delta \epsilon_k} \circ \left[ \xi_k^{o_1}, f_k \right] \right) \frac{1}{\hbar \omega_1 - \Delta \epsilon_k}. \tag{A2}
\]

We will take a look at the first contribution Eq.(A2), as it has been reported that terms like it — which involve the product of two denominators, one of them squared — contribute to the second order divergence of the third order DC conductivity [19, 20]. It reads as,

\[
i \left[ D_{k_s}^{o_3}, v_{k_s}^{\beta} \circ \frac{1}{\hbar \omega_{123} + \Delta \epsilon_k} \right] s' s \left[ \xi_k^{o_1} \Delta f_{ks's} \right] \left( \frac{1}{\hbar \omega_1 - \Delta \epsilon_k} \right)^2 \\
\tag{A3}
\]

We will show that these, in fact, do not contribute.

Appendix B: \( s' = s \) terms

This appendix presents the derivation of the \( s' = s \) contribution that is considered in subsection II 2. It follows from Eq.(6) that Eq.(17) can be expressed as,

\[
(-1) \sum_s \left[ D_{k_s}^{o_3}, v_{k_s}^{\beta} \circ \frac{1}{\hbar \omega_{123} + \Delta \epsilon_k} \right] s s \left[ D_{k_s}^{o_2}, \frac{(-i)}{\hbar \omega_1 - \Delta \epsilon_k} \circ \left[ \xi_k^{o_1}, f_k \right] \right]_{s s} = \\
\left[ D_{k_s}^{o_3}, v_{k_s}^{\beta} \circ \frac{1}{\hbar \omega_{123} + \Delta \epsilon_k} \right] s s \left( \frac{(-i)}{\hbar \omega_1} \left( \nabla_k^{o_2} \xi_k^{o_1} \Delta f_{ks} \right) + \frac{(-i)^2}{\hbar \omega_1 - \Delta \epsilon} \circ \left[ \xi_k^{o_1}, f_k \right] \right)_{s s} = \\
\frac{1}{\hbar \omega_1} \sum_s \left[ D_{k_s}^{o_3}, v_{k_s}^{\beta} \circ \frac{1}{\hbar \omega_{123} + \Delta \epsilon_k} \right] s s \left[ \xi_k^{o_2}, \frac{1}{\hbar \omega_1 - \Delta \epsilon} \circ \left[ \xi_k^{o_1}, f_k \right] \right]_{s s}. \tag{B1}
\]

In going from the second to the third line of Eq.(B1) we used \( \Delta f_{ks} := f_k - f_{ks} = 0 \). What remains can then be expressed as,

\[
\frac{1}{\hbar \omega_1} \sum_s \left( \frac{(-i)}{\hbar \omega_{123}} \left( \nabla_k^{o_2} v_{k_s}^{\beta} \right) - i \xi_k^{o_2} \right) \left( \frac{1}{\hbar \omega_1 + \Delta \epsilon} \circ \left[ \xi_k^{o_1}, f_k \right] \right)_{s} = \\
\sum_{r \neq s} \left( \frac{(-i)}{\hbar \omega_{123} + \Delta \epsilon_{rs}} \left( 1 - (s \leftrightarrow r) \right) \frac{1}{\hbar \omega_1 - \Delta \epsilon} \circ \left[ \xi_k^{o_1}, f_k \right] \right)_{s}. \tag{B2}
\]

It is now easy to identify the only term contributing to the second order divergence in the DC response. Since,

\[
\left[ \xi_k^{o_3}, v_{k_s}^{\beta} \circ \frac{1}{\hbar \omega_{123} + \Delta \epsilon} \right]_{s s} = \sum_r \left( \xi_k^{o_3} v_{k_s}^{\beta} \circ \frac{1}{\hbar \omega_{123} + \Delta \epsilon_{rs}} \right) \left( \frac{1}{\hbar \omega_1 - \Delta \epsilon} \circ \left[ \xi_k^{o_1}, f_k \right] \right)_{s r}, \tag{B3}
\]

does not carry a divergent factor. We are thus left with a single contribution,

\[
\frac{1}{\hbar \omega_1} \sum_s \left( \nabla_k^{o_3} \right) \left( \frac{1}{\hbar \omega_1 - \Delta \epsilon} \circ \left[ \xi_k^{o_1}, f_k \right] \right)_{s s} = \\
\frac{1}{\hbar \omega_1} \sum_{r \neq s} \left( \nabla_k^{o_3} \right) \left( \frac{1}{\hbar \omega_1 - \Delta \epsilon} \circ \left[ \xi_k^{o_1}, f_k \right] \right)_{s r}. \tag{B4}
\]

that can be written as,

\[
- \frac{1}{\hbar \omega_1} \sum_{r \neq s} \left( \nabla_k^{o_3} \epsilon_k \right) \left( \frac{1}{\hbar \omega_1 - \Delta \epsilon_{rs}} \circ \left[ \xi_k^{o_1}, f_k \right] \right)_{s r}. \tag{B5}
\]
Appendix C: Symmetrizing the third order DC conductivity in the context of a divergent response

The relevant physical object in a conductivity description of the response satisfies intrinsic permutation symmetry [28]:

\[
\tilde{\sigma}_{\beta\alpha\alpha_1\alpha_3}(\omega_1, \omega_2, \omega_3) = \frac{1}{3!} \left[ \sigma_{\beta\alpha_1\alpha_2\alpha_3}(\omega_1, \omega_2, \omega_3) + \sigma_{\beta\alpha_1\alpha_3\alpha_2}(\omega_1, \omega_2, \omega_3) + \sigma_{\beta\alpha_2\alpha_1\alpha_3}(\omega_1, \omega_2, \omega_3) \\
+ \sigma_{\beta\alpha_2\alpha_3\alpha_1}(\omega_3, \omega_2, \omega_1) + \sigma_{\beta\alpha_3\alpha_1\alpha_2}(\omega_3, \omega_1, \omega_2) + \sigma_{\beta\alpha_3\alpha_2\alpha_1}(\omega_2, \omega_3, \omega_1) \right]
\]  

(C1)

As we are interested in singling out the terms that have second order divergences, Eqs.(20)–(22) — when both \(\omega_{123}\) and \(\omega_{12}\) go to zero (or are much smaller than \(\omega\)) — we need only concern us with the first two terms in Eq.(C1); the remaining ones will only show have a first order divergences in \(\omega_{123}\). Symmetrizing Eq.(24) with respect to the frequencies and indexes \((\alpha_1, \omega_1) \leftrightarrow (\alpha_2, \omega_2)\), one obtains for the integrant,

\[
\sum_{s \neq s'} \frac{1}{6} (\nabla^\beta \nabla^\alpha \Delta \epsilon_{kss'}) \Delta f_{k's'} \left( \frac{1}{\hbar \omega_1 - \Delta \epsilon_{kss'}} - i \pi \delta(\hbar \omega_1 - \Delta \epsilon_{kss'}) \right) + \frac{1}{\hbar \omega_2 - \Delta \epsilon_{kss'}} + \frac{1}{\hbar \omega_2 + \Delta \epsilon_{kss'}} \right].
\]

(C2)

Note that the integration associated with the denominators is a principal value one. Swaping \(s' \leftrightarrow s\) in the terms with \(\omega_2\) gives us,

\[
\sum_{s \neq s'} \frac{1}{6} (\nabla^\beta \nabla^\alpha \Delta \epsilon_{kss'}) \Delta f_{k's'} \xi_{kss'}^{\alpha_1} \xi_{kss'}^{\alpha_2} \left[ -i \pi \delta(\hbar \omega_1 - \Delta \epsilon_{kss'}) - i \pi \delta(-\hbar \omega_2 - \Delta \epsilon_{kss'}) + \frac{1}{\hbar \omega_1 - \Delta \epsilon_{kss'}} + \frac{1}{\hbar \omega_2 + \Delta \epsilon_{kss'}} \right].
\]

(C3)

Now, let us consider the different cases in which we are interested. For the jerk current, Eq.(20) — \(\omega_1 = -\omega_2 = \omega, \omega_3 = 0\) — we can see that the terms with the Delta functions combine,

\[
-i \pi \delta(\hbar \omega - \Delta \epsilon_{kss'}) - i \pi \delta(-\hbar \omega - \Delta \epsilon_{kss'}) = -2i \pi \delta(\hbar \omega - \Delta \epsilon_{kss'}),
\]

(C4)

while those associated with principal value integrals cancel out,

\[
\frac{1}{\hbar \omega - \Delta \epsilon_{kss'}} + \frac{1}{-\hbar \omega + \Delta \epsilon_{kss'}} = 0.
\]

(C5)

The same is true in the case of the dichromatic setup, Eq.(21) — \(\omega_1 = -\omega_2 = \omega\) and \(\omega_3 = \delta\) — as only \(\omega_3\) changes. For the trichromatic setup, Eq.(22) — \(\omega_1 = \omega + \delta_1, \omega_2 = -\omega\) and \(\omega_3 = \delta_2\) — the resonances do contribute with additional terms, but, since we already isolated the terms that diverge as \(\delta_1 \rightarrow 0\) we can replace the term in square brackets in Eq.(C3) by its value at \(\delta_1 = 0\),

\[
-i \pi \delta(\hbar(\omega + \delta_1) - \Delta \epsilon_{kss'}) - i \pi \delta(-\hbar(\omega - \delta_3) - \Delta \epsilon_{kss'}) + \frac{1}{\hbar(\omega + \delta_1) - \Delta \epsilon_{kss'}} + \frac{1}{\hbar(-\omega + \Delta \epsilon_{kss'})} - 2i \pi \delta(\hbar \omega - \Delta \epsilon_{kss'}).
\]

(C6)

As before, the only relevant terms are those associated with a Dirac delta function in the frequency \(\omega\). We can thus write the symmetrized contribution to the second order divergence of the third order DC conductivity, \(\tilde{\Gamma}_{\beta\alpha\alpha_1\alpha_3}(\omega_1, \omega_2, \omega_3)\), as,

\[
\tilde{\Gamma}_{\beta\alpha_1\alpha_2\alpha_3}(\omega_1, \omega_2, \omega_3) = -\pi e^4 \frac{\hbar^3}{3 \omega_{123}^2} \int \frac{d^3k}{(2\pi)^3} \sum_{s \neq s'} (\nabla^\beta \nabla^\alpha \Delta \epsilon_{kss'}) \xi_{kss'}^{\alpha_1} \xi_{kss'}^{\alpha_2} \Delta f_{k's'} \delta(\hbar \omega - \Delta \epsilon_{kss'}).
\]

(C7)
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