Dynamic conductivity in graphene beyond linear response

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The independence of the dynamic conductivity of intrinsic graphene of frequency takes its origin in the compensation of the vanishing density of states by the diverging matrix element of the corresponding interband transition. The applicability of the linear response approach, however, breaks down when this matrix element becomes comparable with the inverse electron lifetime. We show that the physics of the ac conductivity in this regime is determined by Rabi oscillations and obtain it beyond the first order perturbation theory. Under strong applied electric fields the induced current eventually saturates at a value determined by the frequency and the lifetime. We also calculate the electromagnetic response of a graphene sheet and find that the optical transparency is increased by the non-linear effects and make experimental predictions.

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Introduction. Low-temperature dynamic conductivity \( (k_B T \ll \hbar \omega) \) of graphene was predicted to be of the order of the conductance quantum and independent of frequency, \( \sigma_0 = e^2/4\hbar \) \[1\], as long as the frequency \( \omega \) is small compared with the electron bandwidth \[2\]. This prediction has been verified experimentally \[3, 4, 5\]. Theoretical attempts to understand the role played by electron-electron interaction began even earlier \[6\]. Following the conclusion that the interactions do not modify the conductivity in the limit \( \omega \to 0 \) \[7, 8\] it was further predicted that even at non-vanishing frequencies the interband transitions are extremely small \[9, 10\] and should hardly be noticeable at all, the claim consistent with recent precision measurements of the optical transparency in the visible frequency range \[11\].

In this Letter we address a different aspect of the phenomenon of the minimal conductivity which has not been discussed before. We begin by pointing out that the minimal conductivity is essentially a linear response concept, which needs to be reevaluated in relation to Dirac fermions. For comparison, in a conventional metal the linear response formalism is reliable as long as the energy acquired in the external electric field over one period of its oscillation, \( eE v/\omega \), (or the mean free time, if disorder scattering can not be ignored) must be negligible compared with the Fermi energy \( E_F \) that is typically very large.

In contrast, in clean intrinsic graphene Fermi energy vanishes, \( E_F = 0 \), and the above reasoning fails. To gain a better understanding of the essential physics, let us take a closer look at the Golden rule derivation of the ac conductivity \( \sigma_0 \). Fig. 1 illustrates a vertical interband transition between the two states in the filled lower cone and the empty upper cone, which is responsible for the energy dissipation in electric field. The matrix element of this transition is of the order of the energy gained in external field, \( H_{12} \sim eE v/\omega \). The number of available electrons in the lower cone with energy \( \hbar \omega/2 \) is determined by the density of states which is linear in frequency, \( D(\omega) \sim \omega/v^2 \hbar \). Golden rule expression for the energy absorption rate in these transitions is simply, \( \dot{\mathcal{E}} \sim \omega |H_{12}|^2 D(\omega) \sim (e^2/\hbar) E^2 \). Recalling the usual Joule heat expression we arrive at the electric conductivity independent of frequency and of the order of the conductance quantum.

![FIG. 1: Interband transitions induced by external electric field of frequency \( \omega \). Dashed lines stand for a single transition (short lifetime \( 1/\Gamma \) or multiple Rabi oscillations (long lifetimes \( 1/\Gamma \)). Dotted lines illustrate energy dissipation from relaxation of electrons in the upper Dirac cone and holes in the lower cone.](image)

It is well-known, however, that the first order perturbation theory fails close to a resonance, i.e. when the matrix element becomes of the order of the detuning energy, which in our problem is \( \hbar \omega - 2ev \). Since available momenta are continuous there are always states with the vanishing detuning, in which case the inverse lifetime \( \Gamma \), calculated for a state with the corresponding momentum, must be used as a cut-off. This condition imposes the restriction upon the strength of electric field, \( eE \ll \hbar \omega \Gamma / v \). As frequency decreases, \( \omega \to 0 \), the amplitude of applied field must vanish significantly faster, at least as fast as \( \sim \omega^2 \) \[12\]. Here we concentrate on the response at the same frequency as the frequency of external field, disregarding possible effects of frequency multiplication. From the above arguments one can expect that the amplitude of induced current will be,

\[
j = \sigma_0 E \left( 1 + C \frac{e^2 E^2 v^2}{\hbar^2 \omega^2 \Gamma^2} + \ldots \right),
\]

(1)
and singular at low frequencies. In the present Letter we identify the leading terms in the series \(\sum_{n=0}^{\infty} f_n e^{-n\omega t} \) with the Rabi oscillations between states in the lower and upper cones with the same momentum.

The above analysis indicates that the lifetime \(\Gamma\) plays a central role in the calculation of ac conductivity. When \(\Gamma\) is small, or more precisely, when the dimensionless parameter
\[
\zeta = \frac{evE}{\hbar\omega\Gamma}
\]
is large, Rabi oscillations between states in the two cones persist for a long time and make energy dissipation less effective thus decreasing the conductivity. In the opposite limit, \(\zeta \ll 1\), fast relaxation ensures that the states in the upper cone are always empty and that no Rabi oscillations can occur, thus making first-order perturbation theory applicable. We find that a homogeneous external electric field applied along the \(x\)-axis within the plane of graphene
\[
E(t) = \hat{x}E\cos \omega t,
\]
induces the electric current which for arbitrary values of \(\zeta\) has the form \[13\],
\[
j = \hat{x}\frac{2\sigma_0 E \cos \omega t}{\sqrt{1 + \zeta^2} + 1}.
\]
We observe that the minimal conductivity is recovered when \(\zeta \to 0\), however for strong electric fields (or small frequencies), when \(\zeta \gg 1\), the current saturates at the value
\[
j_{\text{max}} = \left|\frac{e\omega \Gamma}{2v}\right|.
\]
This result can be qualitatively visualized as one electron being transferred per its lifetime \(1/\Gamma\) across each strip of graphene that has the width equal to the electron wavelength \(v/\omega\) corresponding to energy \(\hbar \omega\).

**Derivation.** Homogeneous external electric field is most conveniently incorporated in the electron dynamics with the help of the longitudinal gauge and vector potential
\[
A(t) = -\hat{x}e\cos \omega t.
\]
The Hamiltonian of graphene is the well-known Dirac Hamiltonian in the pseudospin (sublattice) space
\[
\hat{H} = v\sigma \cdot p + \frac{ev}{\omega} \hat{\sigma}_x E \sin \omega t.
\]
The crucial observation that allows the solution of the problem beyond first order perturbation theory is that the momentum \(p\) is an integral of motion. The external electric field therefore mixes only the two states with exactly the same momentum. Denoting by \(a_p(t)\) the amplitude to occupy state in the lower cone and by \(b_p(t)\) the same for the upper cone we write the total wave function as,
\[
\psi_p(t) = \frac{a_p(t)}{\sqrt{2}} \left( e^{-i\frac{\hbar\omega}{2}t} - e^{i\frac{\hbar\omega}{2}t} \right) e^{ivt} + \frac{b_p(t)}{\sqrt{2}} \left( e^{-i\frac{\hbar\omega}{2}t} - e^{i\frac{\hbar\omega}{2}t} \right) e^{-ivt},
\]
where \(\chi_p\) is the angle between the electron momentum \(p\) and the \(x\)-axis. Spinor Schrödinger equation \(i\hbar \partial \psi_p / \partial t = \hat{H} \psi_p\) reduces to a pair of equations (we assume for brevity that \(\hbar = 1\)),
\[
\begin{align*}
    i\dot{a}_p &= \frac{evE_0}{\omega} \sin \omega t \left( ib_p \sin \chi_p e^{-2ivt} - a_p \cos \chi_p \right), \\
    i\dot{b}_p &= \frac{evE_0}{\omega} \sin \omega t \left( b_p \cos \chi_p - ia_p \sin \chi_p e^{2ivt} \right).
\end{align*}
\]
In solving Eqs. (9) we follow the established route by keeping only the low-frequency resonant terms, \(\sim e^{\pm i(\omega-2vp)t}\), the approximation known in quantum optics as the rotating wave approximation. An additional modification of the equations of motion is needed, however. In the present form Eqs. (9) lack relaxation and describe undamped Rabi oscillations leading to the vanishing energy dissipation. To include energy relaxation we take into account the finite lifetime \(1/\Gamma_p\), which due to electron-hole symmetry is assumed to be the same for electrons in the upper cone and holes in the lower cone:
\[
\begin{align*}
    \dot{a}_p &= -i\Omega_p e^{i(\omega-2vp)t} b_p + \frac{\Gamma_p}{2} (1 - a_p), \\
    \dot{b}_p &= -i\Omega_p e^{-i(\omega-2vp)t} a_p - \frac{\Gamma_p}{2} b_p,
\end{align*}
\]
where we introduced the Rabi frequency \(\Omega_p = \frac{evE_0}{2\omega} \sin \chi_p\). While the relaxation is included into Eqs. (10) in a phenomenological way, it has an advantage of allowing analytical solution. After straightforward calculations,
\[
\begin{align*}
    a_p(t) &= \frac{\Gamma_p^2/4 - i\Gamma_p \Delta_p/2}{\Omega_p^2 + \Gamma_p^2/4 - i\Gamma_p \Delta_p/2} e^{i\Delta_p t/2 - \Gamma_p t/2} \\
    &\times \sum C_\pm \frac{\Delta_p^2 \pm \sqrt{\Omega_p^2 + \Delta_p^2}}{\Omega_p} e^{\pm i\sqrt{\Omega_p^2 + \Delta_p^2} t}, \\
    b_p(t) &= \frac{-i\Gamma_p \Omega_p/2}{\Omega_p^2 + \Gamma_p^2/4 - i\Gamma_p \Delta_p/2} e^{-i\Delta_p t} e^{i\Delta_p t/2 - \Gamma_p t/2} \\
    &\times \sum C_\pm \frac{\Delta_p^2 \pm \sqrt{\Omega_p^2 + \Delta_p^2}}{\Omega_p} e^{\pm i\sqrt{\Omega_p^2 + \Delta_p^2} t},
\end{align*}
\]
where \(\Delta_p = \omega - 2vp\) denotes the detuning between the frequency of electric field and the electron-hole excitation energy. The terms containing constants \(C_+\) and \(C_-\) depend on the initial conditions but decay with time and
thus are unimportant for the properties of a “stationary” state.

Expectation value of electric current carried by a pair with momentum \( p \) is given by, 
\[
\langle j^x_p \rangle = e u^x_p \tilde{\psi}_p(t) \bar{\psi}_p(t).
\]

Note that the vector potential term in Eq. (1) does not modify the expression for current since the former is independent of momentum. We obtain,
\[
j^x_p(t) = E e^2 v^2 \Gamma_p^2 \cos \omega t + 2 \Gamma_p^2 \Delta_p \sin \omega t \overline{(\Omega_p^2 + \gamma_p^2/4) + \Gamma_p^2 \Delta_p^2/4} \sin^2 \chi_p. \tag{11}
\]

The total current is found upon summation over all momenta, two spins directions and both Dirac points, 
\[
j = \sum_p j_p. \tag{12}
\]

For the first contribution, \( \sim \cos \omega t \), which is responsible for energy dissipation, it gives,
\[
j^x_1(t) = \cos \omega t \frac{e^2 E^2}{2 \pi^2 \omega} \int_{0}^{2 \pi} \int_{0}^{\infty} \frac{\Gamma_p \sin^2 \chi d \chi}{\left(2p - \omega \right)^2 + \beta^2(p, \chi)}. \tag{13}
\]

where we introduced the notation
\[
\beta(p, \chi) = \frac{\Gamma_p}{4v} + \frac{e^2 v E^2 \sin^2 \chi}{4 \omega^2 \Gamma^2}.
\]

Provided that \( \beta(p, \chi) \ll \omega/v \) the integrand is a sharply peaked function of \( p - \omega/2v \) and the integration over \( dp \) can be carried out easily. Two conditions must be satisfied in order to ensure this. The first one is essentially the condition that electrons are well-defined excitations, \( \Gamma \ll \omega \). The second condition imposes the restrictions on the upper value of electric field. In terms of the dimensionless parameter defined earlier, Eq. (2), this condition implies that \( \zeta \ll \omega/\Gamma \).

Integrating the sharply peaked Lorentian over \( dp \) and taking the subsequent integration over the angle we obtain,
\[
j^x_3(t) = \cos \omega t \frac{\omega \Gamma^2}{2v^2 E} \left( \sqrt{1 + \frac{e^2 v^2 E^2}{\omega^2 \Gamma^2}} - 1 \right). \tag{13}
\]

which is equivalent to Eq. (1). The lifetime in Eqs. (11) and (12) is taken at the value of momentum corresponding to frequency \( \omega \): \( \Gamma \equiv \omega/2v \).

The second term in the numerator of Eq. (11) describes the out-of-phase non-dissipative part of the current. This term is odd in \( \Delta_p = \omega - 2vp \) and thus vanishes after integration over the vicinity of resonant momenta. Note that the contribution of non-resonant momenta to the \( \sim \sin \omega t \) term though small is not necessarily zero, but is beyond the reach of the approximations employed in our analysis.

**Scattering mechanisms.** The dependence of the inverse lifetime \( \Gamma(\omega) \) on frequency determines the value of the saturation current \( I_0 \) and depends on the importance of various scattering mechanisms that could be present in graphene.

i) In case of short-range impurities (vacancies, non-charged substitutions) the electron lifetime in the first Born approximation is simply proportional to the density of states, \( \Gamma(\omega) \propto D(\omega) \propto \omega \) and the saturation current grows as the second power of the frequency of electric field.

ii) When charged impurities dominate, the amplitude of the bare Coulomb impurity potential is inversely proportional to the electron momentum, \( 2\pi e^2/q \propto 1/\omega \). Since the screening in intrinsic graphene does not modify this dependence, the lifetime \( \Gamma(\omega) \propto D(\omega)/\omega^2 \propto 1/\omega \) is inversely proportional to the frequency \( [14] \). Thus, the value of the saturation current is independent of frequency. In both cases of neutral and charged impurities \( j_{max} \) is inversely proportional to the concentration of impurities.

iii) Electron-phonon scattering at frequencies above the Debye frequency is quasi-elastic and follows the same linear dependence originating from the density of states as is the case for short-range disorder, \( \Gamma \propto 1/\omega [15] \).

**Implications for optical experiments.** Of particular significance for ongoing experiments \([3, 4, 5, 11]\) is the calculation of the response of a graphene layer to an incident electromagnetic wave in the nonlinear regime. Below we assume graphene suspended in vacuum (or air) and determine its optical transparency.

![FIG. 2: Dependence of the transmission coefficient \( T \) of suspended graphene on the effective intensity of the incident radiation, \( I = (eV_0)/(\hbar \omega \Gamma)^2 \equiv \zeta^2 \). At low intensities it starts from the value of 97.7% corresponding to the first order perturbation theory but increases sharply with the intensity \( I \), reaching 99% for \( \zeta \sim 3 \).](image-url)
Maxwell’s equations with the two-dimensional current provided by graphene sheet at \( z = 0 \) taken into account has the form,

\[
\frac{\partial^2 E}{\partial z^2} - \frac{1}{c^2} \frac{\partial^2 E}{\partial t^2} = -\frac{2\pi \sigma_0 \omega}{c^2} \frac{E_T \sin \omega t}{\sqrt{1 + \zeta^2}} \delta(z),
\]

(15)

where \( \zeta_T = \frac{e v E_T}{\hbar c} \) corresponds to the field acting in the graphene flake, \( E_T \). The first boundary condition requires the continuity of the electric field, \( E_0 + E_R = E_T \). The second condition is obtained from integrating Eq. (15) across the plane of graphene.

Solving for \( E_R \) and \( E_T \) we obtain the following algebraic equation for the transmission coefficient \( T = E_T^2/E_0^2 \),

\[
1 + \frac{\pi \alpha}{1 + \sqrt{1 + \Gamma}} = \frac{1}{\sqrt{T}},
\]

(16)

where \( \alpha = e^2/\hbar c \) stands for the fine structure constant, and the dimensionless intensity of the incident wave is introduced, \( I = (evE_0/\hbar cT)^2 \). Fig. 2 shows the dependence of the transmission coefficient on the magnitude of the incident wave. At low intensities, \( I \to 0 \) the transmission approaches the linear response value \( T = 97.7\% \), reported in the experiment [11]. As the intensity grows the transmission initially increases steeply, but eventually tends much more slowly towards \( T = 1 \) according to, \( T \approx 1 - 2\pi \alpha/\sqrt{T} \).

The modern experimental capabilities are well within the necessary means to resolve the nonlinear transmission, as predicted by Fig. 2. In particular, the precision reported in Ref. [11] was 0.1%. It is interesting to note the upward trend in \( T(\lambda) \) in the data presented in Ref. [11] for different wavelengths \( \lambda \). It is qualitatively reminiscent of the \( T(I) \) dependence predicted in the present Letter, if one assumes short-range impurities and/or phonons as the primary scattering mechanisms. Understandably, systematic and more detailed measurements of the intensity dependence are necessary before any comparisons could be made with the theory.

**Summary.** The conductivity of intrinsic graphene, \( e^2/4\hbar \), has been established to remains constant even when the frequency tends to zero despite the vanishing of the density of available states, \( D(\omega) \propto \omega \to 0 \). This celebrated result originates in the fact that the matrix element, \( evE/\omega \), for the corresponding interband transition between a filled state in the lower Dirac cone and an empty state in the upper cone diverges at low frequencies. This divergence implies the failure of the first order perturbation theory and, therefore inapplicability of the minimal conductivity at low frequencies for a fixed strength of applied electric field. The Golden rule approach is valid only if the magnitude of electric field vanishes at least as \( \omega^2 \), so that \( \zeta \ll 1 \). In this paper we extended the theory of electrical conductivity towards finite electric fields for arbitrary values of \( \zeta \), as long as \( \zeta \ll \omega/\Gamma(\omega) \). The key observation that allows a solution beyond perturbation theory is the fact that momenta are conserved since the important transitions are direct, see Fig. (1). The problem is therefore reduced to strong coupling within simple (and independent of each other) two-level systems. The electric conduction is largely determined by those states that are in the vicinity of the resonant transition, \( |\omega - 2\nu p| \sim \Gamma \). When the matrix element for the transition exceeds the inverse lifetime \( 1/\Gamma \) multiple Rabi oscillations develop that greatly reduce the probability of energy dissipation (Joule heat) and, hence, conductivity. As shown above this must result in the experimentally observable enhancement of the transparency of graphene.

The existing experiments have been performed in the infrared [3, 4, 5] and visible light [11] domains. Previously, however, nonlinear effects have not been systematically searched for. We expect that the stronger nonlinear signatures could be revealed for clean samples, strong intensities of incident radiation and lower frequencies (possibly infrared).

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