The Kubo-Greenwood formula as a result of the random phase approximation for the electrons of the metal

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Abstract. For calculation of short laser pulse absorption in metal the imaginary part of permittivity, which is simply related to the conductivity, is required. Currently to find the static and dynamic conductivity the Kubo-Greenwood formula is most commonly used. It describes the electromagnetic energy absorption in the one-electron approach. In the present study, this formula is derived directly from the expression for the permittivity expression in the random phase approximation, which in fact is equivalent to the method of the mean field. The detailed analysis of the role of electron-electron interaction in the calculation of the matrix elements of the velocity operator is given. It is shown that in the one-electron random phase approximation the single-particle conductive electron wave functions in the field of fixed ions should be used. The possibility of considering the exchange and correlation effects by means of an amendment to a local function field is discussed.

1. Introduction
At present, a large number of fundamental and applied problems are related to the physics of extreme states of matter (see, e.g., [1]). One way of obtaining a substance with a high energy density is the use of femtosecond laser radiation [2, 3]. At laser radiation intensities \( I \sim 10^{15} \text{ W/cm}^2 \), the behavior of a metal sample under the action of a femtosecond pulse can be qualitatively represented as follows. Laser radiation is absorbed by electrons in a thin near-surface layer. The electron temperature \( T_e \) increases sharply, the temperature of the \( T_i \) ions remains relatively small. The volume occupied by the substance is practically unchanged, that is, it can be assumed that the heating occurs isochorically. Later, by means of electronic thermal conductivity, the deeper layers of the sample are heated. As a result of electron-ion exchange, the ion temperature also increases. These phenomena are accompanied by the flow of complex hydrodynamic processes and phase transformations, in particular, shock-wave compression of matter to increased densities is possible. Depending on the design of the experiment, ablation or high-speed splitting is possible, due to a significant decrease in the density of matter. A two-temperature model is widely used for quantitative description of the phenomena described [3]. To describe propagation in matter and absorption of laser radiation, information is needed on the complex dielectric constant or dynamic conductivity, that is, the optical properties of metals. When analyzing the absorption of laser radiation, it is important to understand the optical properties of the metal, as well as the static conductivity or conductivity. Optical properties include complex dynamic conductivity, complex dielectric permeability, complex refractive index,
reflectivity and absorptivity A free electron does not absorb the energy of an alternating electric field either under classical or quantum considerations. In order to obtain a nonzero one, one must consider the interaction of an electron with other particles. The properties of matter in this state are significantly influenced by Coulomb interactions: between electrons and ions, electrons and electrons, ions and ions. One of the main methods for studying the optical properties of metals is the theory of linear response. An external electric field \( E(t) \) is superimposed on a system of interacting electrons and ions, which leads to a change in the dynamics of the electrons. This change can be calculated with the help of perturbation theory and obtain the current \( j(t) \), which then arises, and then the dynamic current. Information about the system in the theory of linear response is contained in the dynamics of the system in the absence of an electric field. This approach is based on the Kubo formalism [3], but the direct application of the Kubo formula is practically impossible

\[
\sigma_{\mu\nu} = \lim_{\alpha \to 0} \frac{1}{i\hbar} \int_{-\infty}^{0} dt \exp(-i\omega t + \alpha t) \int_{0}^{1/T} d\lambda \langle j_{\mu}(0) j_{\nu}(t - i\hbar\lambda) \rangle. 
\] (1)

Based on the approach of Kubo, Greenwood and other authors [6, 7], simpler formulas for the conductivity were obtained, based on the one-electron approximation. Spatial parts are calculated for electrons in the external ion potential. Wave functions that depend on time are obtained by multiplying the spatial parts by the corresponding time multipliers. Then, in the first order of the temporal perturbation theory, the current arising in the system under the action of an external electric field can be calculated. An alternative approach is to calculate the total energy absorbed by the electrons; From this energy can be calculated. With this consideration, the quantum Kubo-Greenwood formula is obtained. The Kubo-Greenwood formula includes only the spatial parts of the wave functions, and they contain all information about the system under consideration. It is the calculation by the Kubo-Greenwood formula that is used most often. In many works (see, for example, [7, 8]) (in the same papers some experimental data are also given), an even simpler Kubo-Greenwood formula for conductivity, obtained in [7], is used:

\[
\sigma_1(\omega) = \frac{2\pi \hbar^2}{3m^2\omega \Omega} \sum_{k,n,m} (f_0(E_{n,k}) - f_0(E_{m,k})) \times |\langle \Psi_{n,k} | \nabla_{\alpha} | \Psi_{m,k} \rangle|^2 \delta(E_{n,k} - E_{m,k} - \hbar\omega). 
\] (2)

The calculation by this formula is usually carried out as follows [9,10]. First, ion positions are set at a given ion temperature. Their position is usually determined by the methods of quantum or classical molecular-dynamic modeling. A computational cell can contain a lot of atoms, and then it repeats itself in space. Then the self-consistent Kohn-Shem equations for finding the electron wave functions are solved numerically. At the same time, the effective potential includes the Hartree potential and the exchange-correlation potential. Further, the matrix elements from the gradients are calculated and finally the sum or integral over. The delta function, as a rule, is replaced by some sharp analytic function. Often, further averaging is performed on the positions of the ions, which greatly increases the amount of computation. We will analyze such calculations. The most complexity of such an approach is the finding of one-electron wave functions. According to the very structure of the formula for the conductivity in this form, the connection with the imaginary part of the dielectric permittivity function in the random phase approximation (RPA) is clearly visible. Actually, the very derivation of these expressions is almost identical. The imaginary part of dielectric permittivity function \( \varepsilon'(\omega) \) is related to the conductivity \( \sigma(\omega) \) by the known relation

\[
\varepsilon'(\omega) = 1 + \frac{4\pi i \sigma(\omega)}{\omega}. 
\]
2. Dielectric Permittivity of Electrons in the Random Phase Approximation

We introduce the exact susceptibility \( \chi \)

\[
\rho_{\text{ind}} = \chi \cdot V_{\text{ext}}
\]

\[
\frac{1}{\varepsilon} = 1 + \frac{4\pi e^2}{q^2} \rho_{\text{ind}} V_{\text{ext}}.
\]

This function can be written in terms of the matrix elements from the density operator in terms of the exact many-particle wave functions of electrons and the exact many-particle energy values of \( E_\xi \), where \( \xi \) is the set of quantum numbers. Unfortunately, in this approach exact multiparticle energy values and wave functions are required, which cannot really be obtained. In this case, one can write down the formula for the inverse permittivity, for example, for the ground state of a system of electrons. From the expression obtained, one can obtain a rather cumbersome expression for the conductivity, which is unsuitable for further calculations.

\[
\frac{1}{\varepsilon(q, \omega)} = 1 - \frac{4\pi e^2}{\Omega q^2} \sum_\xi |\langle 0|\hat{\rho}(q)|\xi \rangle|^2 \left( \frac{1}{E_\xi - E_0 - \hbar \omega - i\delta} + \frac{1}{E_\xi - E_0 + \hbar \omega + i\delta} \right). \tag{3}
\]

If, on the other hand, the susceptibility of noninteracting electrons is applied to \( \chi_0 \),

\[
\rho_{\text{ind}} = \chi_0 \cdot V_{\text{ext}}
\]

this leads to fundamentally incorrect results for the electrons of the metal.

However, one can still use the susceptibility of noninteracting electrons to \( \chi_0 \), but the response of the electron system should be sought not on the external but on the total potential. In fact, it is the random phase approximation (RPA).

\[
\rho_{\text{ind}} = \chi_0 \cdot (V_{\text{ext}} + \frac{4\pi e^2}{q^2} \rho_{\text{ind}}). \tag{4}
\]

Going beyond RPA (accounting for exchange-correlation effects) is possible by introducing the local field correction function [12]

\[
\rho_{\text{ind}} = \chi_0 \cdot (V_{\text{ext}} + (1 - G)\frac{4\pi e^2}{q^2} \rho_{\text{ind}}). \tag{5}
\]

The random phase approximation for free electrons imaginary part of \( \varepsilon(q, \omega) \) is determined by a known equation [9]

\[
Im \varepsilon(q, \omega) = -\pi \frac{4\pi e^2}{\Omega q^2} \sum_k \left( f_0(\varepsilon^{(0)}_k) - f_0(\varepsilon^{(0)}_{k+q}) \right) \delta(\varepsilon^{(0)}_k - \varepsilon^{(0)}_{k+q} + \hbar \omega). \tag{6}
\]

When calculating the dielectric constant of an electron gas in the ion lattice potential [12], it suffices to introduce the square of the matrix element of the plane wave exp(iqr)

\[
\varepsilon(q, \omega) = 1 + \frac{4\pi e^2}{\Omega q^2} \sum_{k,n,m} \frac{(f_0(E_{n,k}) - f_0(E_{m,k+q}))|\langle n, k | e^{iqr} | m, k + q \rangle|^2}{\hbar \omega + E_{n,k} - E_{m,k+q} + i\delta}, \tag{7}
\]

where \( n, m \) - the numbers of Bloch functions. In the limit of small \( q \), the expression for the imaginary part \( \varepsilon(\omega) \) turns into
\[ Im \varepsilon(\omega) = \frac{4\pi^2e^2}{3\Omega} \sum_{k,n,m} (f_0(E_{n,k}) - f_0(E_{m,k})) |\langle n, k | r_\alpha | m, k \rangle|^2 \delta(h\omega + E_{n,k} - E_{m,k}). \quad (8) \]

By the very structure of the record of this formula, in this form, the apparent part of the permittivity function in the random phase approximation with the Kubo-Greenwood formula for the conductivity. The transition from matrix elements \( r_\mu \) to matrix elements \( \nabla_\mu \) is carried out with the aid of relation

\[ v_\mu = \frac{i}{\hbar} [H, r_\mu] = -\frac{i\hbar \nabla_\mu}{m}. \]

Then the matrix elements \( r_\mu \) can be expressed in terms of matrix elements \( \nabla_\mu \) as follows

\[ \langle \Psi_i | r_\mu | \Psi_j \rangle = \frac{\hbar^2}{2m} \langle \Psi_i | \nabla_\mu | \Psi_j \rangle (E_i - E_j), \]

below, because of the presence of the \( \delta \)-function, the energy difference in the denominator is replaced by \( \hbar \omega \). As a result, taking into account the connection between the imaginary part of \( \varepsilon(\omega) \) and the conductivity \( \sigma(\omega) \), we get

\[ \sigma_1(\omega) = \frac{2\pi e^2 \hbar^2}{3m^2\omega^2} \sum_{k,n,m} (f_0(E_{n,k}) - f_0(E_{m,k})) |\langle n, k | \nabla_\alpha | m, k \rangle|^2 \delta(E_{m,k} - E_{n,k} - \hbar\omega), \quad (9) \]

which exactly coincides with the Kubo-Greenwood formula.

3. Random phases approximation as a mean-field method

But the basic idea of the RPA method (in fact it is the mean-field method) is to find the response of a system of noninteracting electrons to a common (external plus induced) potential or field. When calculating conductivity, the Kubo-Greenwood method also looks for a response to a common (total) field. The interelectronic Coulomb interaction is taken into account both in the mean-field method and in the mean-field method. The response is sought not for the external, but for the general field.

\[ H = H_{\text{kin}} + H_{e-\text{ion}} + H_{e-e} + H_{\text{ext}} \]

\[ H_{\text{ext}} = \sum_q \hat{\rho}_e V_{\text{ext}}(q, \omega) \]

Further in the last formula, one of the electronic densities is averaged and a response is obtained to the common field

\[ H_{e-e} = \sum_q \frac{4\pi e^2}{q^2} \hat{\rho}_e(q)\hat{\rho}_e(-q) \]

\[ \tilde{H}_{e-e} = \sum_q \hat{\rho}_e(q) \left( V_{\text{ext}}(q, \omega) + \frac{4\pi e^2}{q^2} \langle \rho_e(q) \rangle \right). \quad (10) \]
4. Conclusions
Thus, in the pseudopotential approach, when conduction electrons are considered in the ion lattice, the wave functions of electrons and band energies and the matrix elements should apparently be calculated without allowance for the electron-electron interaction. A more accurate account of the interelectron interaction is possible through a correction to the local field.

\[ Im\varepsilon(\omega) = \frac{v_q Im\chi_0}{(1 + Gv_q Re\chi_0)^2 + (Gv_q Im\chi_0)^2}, \]  

where \( v_q = 4\pi e^2/q^2 \). In general, it is obvious that taking into account the electron-electron interaction should somewhat decrease the conductivity.

And, finally, we make a remark about the possible nonequilibrium of the electron subsystem itself in the process of absorption of a short laser pulse. In the Kubo-Greenwood formula, we mean the local equilibrium of the electrons at each instant of time. This means that the electronic processes of relaxation (the establishment of the electron temperature) occur much faster than the time of the action of the pulse. However, for femtosecond pulses this co-relation can be violated, and then the approach with energy absorption through conductivity of the Kubo-Greenwood type can turn out to be illegal.

5. References
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