An extension of the Kubo-Greenwood formula for use in molecular simulations

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Abstract

We discuss the foundations and extend the range of applicability of the widely used Kubo-Greenwood formula (KGF) for the electronic conductivity. The conductivity is derived from the current density, and only the probability amplitude rather than the transition probability is used. It is shown that the contribution to the conductivity from degenerate states in a low or zero frequency external electric field and the contribution from states near resonance with a finite frequency external field are finite. The improved conductivity expression does not include the familiar “energy conserving” delta function, and no artificial broadening parameter for delta function is required for the DC limit. We explored two methods of computing current density. We discuss the role of many-electron statistics in computing the conductivity in single-particle approximations, and we show that the conventional KGF is due to the contribution from single-particle excited states.

PACS numbers: 71.15.Pd, 72.10.Bg, 72.20.-i
I. INTRODUCTION

The Kubo-Greenwood formula (KGF) has been widely used with great success to calculate the electrical conductivity from first principles simulations.\textsuperscript{1,2,3,4,5,6} Despite the universal use of KGF, it is worth pointing out that it has certain limitations, and for some applications, improvements are possible. The aim of this paper is both to derive the KGF and more fundamental transport formulae from first principles, and to point out cases in which use of the KGF can be problematic, with a full explanation of the origins of the difficulty. New formulae are presented which circumvent some of these difficult cases.

Greenwood’s derivation of the conductivity used the transition probability between two single-electron states in an oscillating external field, in such a way that the interaction time must be long enough to assure that the transition probability is well-defined. On the other hand, to make perturbation theory applicable, the interaction time should be short.\textsuperscript{7,8,9,10} For a large system, in which the energy spectrum is continuous, these two conditions are in conflict. The usual time-dependent perturbation theory cannot be applied in two cases: (1) degenerate states and (2) if two groups of states are in resonance with an oscillating external field. Both circumstances are common in a macroscopic system. In addition, the energy conserving $\delta$ functions in KGF require an artificial broadening parameter when implemented numerically.

To avoid these difficulties, in Section II, both direct current (dc) conductivity and alternating current (ac) conductivity are derived from a new expression for the current density. Only the probability amplitude (not the probability itself) enters, and the $\delta$-function in the KGF disappears in the improved expression of conductivity. The new expression may be reduced to the well-known result for the conductivity by applying the Boltzmann equation with the relaxation-time approximation for a crystal. For a static field or oscillating field, the zeroth-order contribution from a group of degenerate states is shown to vanish, and the first-order contribution of degenerate states is finite (Appendix A). We also show that the zeroth-order contribution from two groups of states which are near or in resonance with an oscillating external field is zero. The first-order contribution of the two groups of resonant states is finite. (Appendix B). By invoking the single-particle approximation at different stages of the derivation, one is led to slightly different results. In section III, we use many-body perturbation theory to compute the conductivity for an intrinsic semiconductor, metal
and doped semiconductor. It is shown that at T=0K, the dc conductivity of an intrinsic semiconductor is zero, a well-known consequence of many-electron statistics.

II. THE CURRENT DENSITY

If the motions of nuclei are treated classically (as in most "ab initio" MD codes), the average energy of the electron + nuclei system in an electromagnetic field described by vector potential $\mathbf{A}$ and scalar potential $\varphi$ is given by

$$H = \int d\mathbf{r}_1 \cdots d\mathbf{r}_N \Lambda'_{\{\mathbf{w}_1, \ldots, \mathbf{w}_N\}}(\mathbf{r}_1 \cdots \mathbf{r}_N) H'_{e(\mathbf{w}_1, \ldots, \mathbf{w}_N)}(\mathbf{r}_1 \cdots \mathbf{r}_N)$$

(1)

$$+ \sum_\alpha \frac{1}{2M_\alpha} (P_\alpha - q_\alpha A(W_\alpha))^2 + \sum_\alpha q_\alpha \varphi(W_\alpha) + \sum_{\alpha, \beta(>\alpha)} V(W_\alpha, W_\beta)$$

where $q_\alpha$, $M_\alpha$, $P_\alpha$ and $W_\alpha$ are the effective charge, mass, canonical momentum and position vector of the $\alpha^{th}$ nucleus. $V(W_\alpha, W_\beta)$ is the interaction between the $\alpha^{th}$ nucleus and the $\beta^{th}$ nucleus.

$$H'_{e(\mathbf{w}_1, \ldots, \mathbf{w}_N)} = \sum_{j=1}^{N_e} \left[ \frac{1}{2m}(p_j - eA(r_j))^2 + e\varphi(r_j) \right] + \sum_{jk} V(r_j, r_k) + \sum_{j} V(r_j, W_\alpha)$$

(2)

is the electronic Hamiltonian in the external electromagnetic field. $V(r_j, r_k)$ is the interaction between an electron at $r_j$ and another electron at $r_k$, $V(r_j, W_\alpha)$ is the interaction between an electron at $r_j$ and the $\alpha^{th}$ nucleus at $W_\alpha$. The motion of the electrons is determined by

$$H'_{e(\mathbf{w}_1, \ldots, \mathbf{w}_N)} \Lambda'_{\{\mathbf{w}_1, \ldots, \mathbf{w}_N\}}(\mathbf{r}_1 \cdots \mathbf{r}_N) = E^e_{(\mathbf{w}_1, \ldots, \mathbf{w}_N)} \Lambda'_{\{\mathbf{w}_1, \ldots, \mathbf{w}_N\}}(\mathbf{r}_1 \cdots \mathbf{r}_N)$$

(3)

$\Lambda'_{\{\mathbf{w}_1, \ldots, \mathbf{w}_N\}}(\mathbf{r}_1 \cdots \mathbf{r}_N)$ is the many-electron wave function of $H'_{e(\mathbf{w}_1, \ldots, \mathbf{w}_N)}$ for a given nuclear configuration $\{\mathbf{w}_1, \ldots, \mathbf{w}_N\}$ belonging to eigenvalue $E^e_{(\mathbf{w}_1, \ldots, \mathbf{w}_N)}$. We use $H_e$ to denote $H'_{e(\mathbf{w}_1, \ldots, \mathbf{w}_N)}$ when external field does not appear, $\Lambda_{\{\mathbf{w}_1, \ldots, \mathbf{w}_N\}}$ is the eigenfunction of $H_e$ belonging to eigenvalue $E^e_{(\mathbf{w}_1, \ldots, \mathbf{w}_N)}$. Hereafter we use a symbol with prime to denote a quantity when external field appears, the corresponding symbol without prime to denote the quantity in zero field. The velocity of the $\gamma^{th}$ nucleus is determined by

$$\mathbf{V}_\gamma = \frac{\partial H}{\partial P_\gamma} = \frac{P^{\text{mech}}_\gamma}{M_\gamma} = \mathbf{V}_\gamma$$

(4)

where $\mathbf{V}_\alpha = P^{\text{mech}}_\alpha/M_\alpha$ is the velocity of the $\alpha^{th}$ nucleus, $P^{\text{mech}}_\alpha = P_\alpha - q_\alpha A(W_\alpha)$ is the mechanical momentum of the $\alpha^{th}$ nucleus. After some manipulations, $\dot{P}_\gamma = -\frac{\partial H}{\partial \mathbf{w}_\gamma}$ is read
as
\[ M_γ \dot{V}_γ = q_γ [E(W_γ) + V_γ \times B(W_γ)] - \sum_{α(≠γ)} \frac{\partial V(W_α, W_γ)}{\partial W_γ} - \frac{\partial E^{te}_{(W_1, W_α)}}{\partial W_γ} \] (5)

In the MD formulation, the positions of the nuclei are functions of 'time' (MD steps). The initial positions of nuclei are given from an initial configuration, the initial velocities of nuclei are assigned in some way. The electronic wave function \( Λ_{\{W_1, \cdots, W_N\}}(r_1, r_2, r_3, \cdots, r_N) \) is calculated from the configuration \( \{W_1, \cdots, W_N\} \), the forces on each nucleus is then calculated from \( Λ_{\{W_1, \cdots, W_N\}}(r_1, r_2, r_3, \cdots, r_N) \). The position and velocity of a nucleus in next step are calculated from the length of the time-step, acceleration and the velocity in last step.

According to the principle of virtual work, for a given state \( Λ' \), the microscopic electric current density \( j_m(r) \) at point \( r \) is

\[ j_m(r) = -\frac{\delta H}{\delta A(r)} \] (6)

\[ = N_e \frac{ihe}{2m} \int dr_2 dr_3 \cdots dr_N (Λ' \nabla_{r_1} A^{te} - A^{te} \nabla_{r_1} Λ') - \frac{e^2}{m} A(r) n^e_{\{W_1, \cdots, W_N\}}(r) + \sum_α q_α V_α δ(r - W_α) \]

where

\[ n^e_{\{W_1, \cdots, W_N\}}(r, t) = N_e \int dr_2 dr_3 \cdots dr_N A^{te}_{\{W_1, \cdots, W_N\}}(rr_2, r_3, \cdots, r_N) Λ'_{\{W_1, \cdots, W_N\}}(rr_2, r_3, \cdots, r_N) \] (7)

is the number density of electrons at \( r \) for a given nuclear configuration \( \{W_1, \cdots, W_N\} \).

Eq.(6) is the response of the electrons+nuclei system to the external field; the first two terms are due to electrons, and the last term is due to nuclei. The measured macroscopic current density at point \( r \) is a spatial average of Eq.(6) over a region \( Ω_r \) centered at \( r \):

\[ j(r) = \frac{1}{Ω_r} \int_{Ω_r} ds j_m(s) \] (8)

The linear size \( L \) of \( Ω_r \) satisfies: \( a << L << λ \), where \( a \) is a typical bond length, \( λ \) is the wavelength of external field or other macroscopic length scale. Eq.(8) is the usual current density defined for an infinitesimal area.

Using the single-electron approximation to separate variables in Eq.(3), we obtain the equation satisfied by the single-electron wave function \( χ'_l \):

\[ h'_a χ'_l(r) = E'_l χ'_l(r), \quad h'_a = \frac{1}{2m} (p - eA(r))^2 + eφ(r) + U(r, \{W_α\}) \] (9)
where $h'_a$ is the single-electron Hamiltonian in an external field, $U$ is the single-electron potential due to nuclear configuration $\{W_\alpha\}$, $h_a$, $\chi_l(\mathbf{r})$ and $E_\ell$ are the corresponding quantities when external field does not appear. They are the Hamiltonian, eigenfunctions and eigenvalues as in density functional theory (DFT), or other single particle theories.

The current density due to electrons can be computed as following. At finite temperature $T > 0$, the system can be in the ground or excited states. The electron current at temperature $T$ comes from both the various excited states and the ground state:

$$
j^e(\mathbf{r}) = \frac{i\hbar e N_e}{2m\Omega_r} \int_{\Omega_r} ds \int d\mathbf{r}_2 d\mathbf{r}_3 \cdots d\mathbf{r}_{N_e} \sum_{l_1l_2 \cdots l_{N_e}} W'_{l_1l_2 \cdots l_{N_e}} (A'_{l_1l_2 \cdots l_{N_e}} \nabla s A'_{l_1l_2 \cdots l_{N_e}} - A'_{l_1l_2 \cdots l_{N_e}} \nabla s A'_{l_1l_2 \cdots l_{N_e}})$$

where

$$
A'_{l_1l_2 \cdots l_{N_e}} = \frac{1}{\sqrt{N!}} \sum_{P} \delta_P P \chi'_{l_1}(s_1, s_{z1}) \chi'_{l_2}(s_2, s_{z2}) \cdots \chi'_{l_N}(s_N, s_{zN})
$$

is a $N_e$-electron state, $P$ is a permutation on $N_e$ objects $\{\mathbf{r}_1 s_{z1}; \mathbf{r}_2 s_{z2}; \mathbf{r}_3 s_{z3}; \cdots; \mathbf{r}_N s_{zN}\}$, $\delta_P = 1$ if $P$ is an even permutation, $\delta_P = -1$ if $P$ is odd. Of course $l_1, l_2, \cdots, l_{N_e}$ are distinct. Because any observable like $j^e$ is bilinear about $A'_{l_1l_2 \cdots l_{N_e}}$, the order of rows and the order of columns in $A'_{l_1l_2 \cdots l_{N_e}}$ do not matter. We only need to maintain a fixed order in all intermediate steps of calculation. The sum is over all possible choices of $N_e$ single-electron states. The arguments of $A'$ are $\{s, \mathbf{r}_2, \mathbf{r}_3, \cdots, \mathbf{r}_{N_e}\}$, to save space the spin variables are abbreviated.

$$
W'_{l_1l_2 \cdots l_{N_e}} = U'_{l_1l_2 \cdots l_{N_e}} / Z', \quad Z' = \sum_{l_1l_2 \cdots l_{N_e}} U'_0 = \exp[-(E'_{l_1l_2 \cdots l_{N_e}} - E'_{l_1l_2 \cdots l_{N_e}})/(k_B T)]
$$

is the appearing probability of state $A'_{l_1l_2 \cdots l_{N_e}}$. $E'_{l_1l_2 \cdots l_{N_e}}$ is the energy of $N_e$-electron ground state. When no field is applied on the system, macroscopic current does not appear in any state $A'_{l_1l_2 \cdots l_{N_e}}$. The current density from electrons reads:

$$
j^e(\mathbf{r}) = \frac{i\hbar e N_e}{2m\Omega_r} \int_{\Omega_r} ds \int d\mathbf{r}_2 d\mathbf{r}_3 \cdots d\mathbf{r}_{N_e} \sum_{l_1l_2 \cdots l_{N_e}} W'_{l_1l_2 \cdots l_{N_e}} [(A'_{l_1l_2 \cdots l_{N_e}} \nabla s A'_{l_1l_2 \cdots l_{N_e}} - A'_{l_1l_2 \cdots l_{N_e}} \nabla s A'_{l_1l_2 \cdots l_{N_e}})$$

$$
- (A_{l_1l_2 \cdots l_{N_e}} \nabla s A'_{l_1l_2 \cdots l_{N_e}} - A_{l_1l_2 \cdots l_{N_e}} \nabla s A'_{l_1l_2 \cdots l_{N_e}})](s\mathbf{r}_2 \mathbf{r}_3 \cdots \mathbf{r}_{N_e})
$$

For low temperatures, $\langle \chi_{l_1} | -\mathbf{e}\mathbf{E} \cdot \mathbf{r} | \chi_{l_1} \rangle << k_B T$ is not satisfied. Linearizing $W'_{l_1l_2 \cdots l_{N_e}}$ about field $\mathbf{E}$ is not legitimate (cf. Eq. [12]): current density is not necessary linear
about field, the dependence of conductivity on field is intrinsic at low temperature for semiconductors. If temperature is not too low \((\langle \chi l_1 \rangle - eE \langle r l_1 \rangle) \ll k_B T\), we may expand \(W'[\] \] in Eq. (13) to first order of field
\[
W'[\] \] = \(W[\]_{E=0} + \[\]_{E=0} \sum \alpha E_\alpha \frac{\partial W}{\partial E_\alpha} + W \sum \alpha E_\alpha \frac{\partial [\]}{\partial E_\alpha} = W \sum \alpha E_\alpha \frac{\partial [\]}{\partial E_\alpha} \quad (14)
\]
The last equal sign used the obvious fact \([\]_{E=0} = 0: no macroscopic current exist when external field vanishes. With the help of Eq. (14), Eq. (13) is simplified to
\[
\begin{align*}
\mathbf{j}(r) &= \frac{i \hbar e N_e}{2 m \Omega_r} \int d\mathbf{s} \int d\mathbf{r_2} d\mathbf{r_3} \cdots d\mathbf{r_N}\sum_{l_1 l_2 \cdots l_N} \frac{W_{l_1 l_2 \cdots l_N}}{Z, Z} \left[ (\Lambda'_{l_1 l_2 \cdots l_N} \nabla_s \Lambda'_{l_1 l_2 \cdots l_N} - \Lambda'_{l_1 l_2 \cdots l_N} \nabla_s \Lambda_{l_1 l_2 \cdots l_N}) \right] (\mathbf{s} \mathbf{r_2} \mathbf{r_3} \cdots \mathbf{r_N}) \quad (15)
\end{align*}
\]
where
\[
W_{l_1 l_2 \cdots l_N} = U_{l_1 l_2 \cdots l_N} / Z, \quad Z = \sum_{l_1 l_2 \cdots l_N} U_{l_1 l_2 \cdots l_N}, \quad U_{l_1 l_2 \cdots l_N} = \exp \left[ -(E_{l_1 l_2 \cdots l_N} - E_{v_1 v_2 \cdots v_N}) / (k_B T) \right]
\]
are the corresponding quantities without external field. In the single-particle approximation
\[
W_{l_1 l_2 \cdots l_N} = \prod_{\alpha=1}^{N_e} f(E_{l_{\alpha}}), \quad f(E_{l_{\alpha}}) = \frac{1}{e^{(E_{l_{\alpha}} - \mu) / k_B T} + 1} \quad (17)
\]
where \(\mu\) is chemical potential at given temperature and shape of the interested body.

The current density (15) and the conductivity deduced from it are just for one MD step. To include the thermal vibrations in a material, one must average the conductivity over many MD steps. Only the averaged conductivity may be compared to the experimental observations where the material changes its configurations with time through thermal vibrations. This observation is valid for solids, liquids and molecules.

The idea of linear response \(15\) can be applied in two different ways: (1) first express \(\Lambda'_{l_1 l_2 \cdots l_N}\) with single-electron wave functions \(\chi'\) and effect the multiple integral \(\int d\mathbf{r_2} d\mathbf{r_3} \cdots d\mathbf{r_N}\). Then view \(\chi'_{l_{\alpha}}\) as correction of \(\chi_{l_{\alpha}}\) under perturbation \(-e\mathbf{E} \cdot \mathbf{r}\). (2) view \(\Lambda'_{l_1 l_2 \cdots l_N}\) as correction of \(\Lambda_{l_1 l_2 \cdots l_N}\) under perturbation \(-\sum_{m=1}^{N_e} e\mathbf{E} \cdot \mathbf{r}_m\). Then effect multiple integral \(\int d\mathbf{r_2} d\mathbf{r_3} \cdots d\mathbf{r_N}\). Most discussion about the KGF \(7,8,9,10\) is based on method (1). The role of many-electron statistics is displayed more explicitly in method (2). Both schemes express the conductivity in terms of single-electron states and corresponding eigenvalues. In the remainder of this section, we will use method (1) and compare with previous result. Method (2) will be analyzed in the next section.
A. DC conductivity

Applying Eq. (11) and working out \( \int dr_2 dr_3 \cdots dr_{N_e} \), Eq. (15) leads to:

\[
 j^e(r) = \frac{i\hbar e}{2m\Omega r} \int_{\Omega_r} ds \sum_{l_1 l_2 \cdots l_{N_e}} W_{l_1 l_2 \cdots l_{N_e}} \left( \sum_{\alpha=1}^{N_e} \left( \chi'_{l_\alpha} \nabla_s \chi^*_{l_\alpha} - \chi^*_{l_\alpha} \nabla_s \chi'_{l_\alpha} \right) - \left( \chi_{l_\alpha} \nabla_s \chi^*_{l_\alpha} - \chi^*_{l_\alpha} \nabla_s \chi_{l_\alpha} \right) \right)
\]

(18)

the argument of all single-electron functions is \( s \).

In a static electric field, the nuclei and the bound electrons are pushed in opposite directions. These lead to a static deformation of the material. Since a static electric field does not produce any net velocities of nuclei, the 3rd term in Eq. (6) is zero. A static electric field is solely determined by scalar potential \( \varphi(r) \), which means \( A(r) = 0 \). The 2nd term in Eq. (6) vanishes. The interaction with an electron at \( r \) is

\[
 H_{fm} = e\varphi(r) = -eE \cdot r
\]

(19)

At this point, let us assume all the single-electron states in Eq. (18) are non-degenerate. The case of degenerate states will be discussed later. From first-order perturbation theory, the change \( \chi_c^{(1)} \) in the single electron wave function due to the external field is

\[
 \chi'_c = \chi_c + \chi_c^{(1)}, \quad \chi'_c^{(1)} = \sum_{d(\neq c)} \frac{\langle \chi_d| - eE \cdot r|\chi_c \rangle}{E_c - E_d} \chi_d
\]

(20)

\( \chi_c \) and \( E_c \) are the single electron wave function and the corresponding eigenvalue without external field. We should emphasize that voltage is proportional to the distance between two points, and so too is the interaction. The change in states cannot be described by the perturbation result Eq. (20). Except for very weak field, one must use WKB method rather than perturbation theory. In this work, let us limit ourselves to very weak field. Substituting Eq. (20) into Eq. (18), and only keeping the terms linear with external field, one has

\[
 j^e(r) = \frac{i\hbar e}{2m\Omega r} \int_{\Omega_r} ds \sum_{l_1 l_2 \cdots l_{N_e}} W_{l_1 l_2 \cdots l_{N_e}} \sum_{\alpha=1}^{N_e} \sum_{l(\neq l_\alpha)} \frac{1}{E_{l_\alpha} - E_l} \langle \chi_l|eE \cdot r|\chi_{l_\alpha} \rangle \langle \chi_{l_\alpha} \nabla_s \chi_l - \chi_l \nabla_s \chi_{l_\alpha} \rangle^*
\]

(21)

The sum over \( l(\neq l_\alpha) \) is not restrict to \( (l_1 l_2 \cdots l_{N_e}) \); it extends to all single particle states. By means of the definition of conductivity \( \sigma_{\mu\nu} \)

\[
 j_\mu = \sum_\nu \sigma_{\mu\nu} E_\nu, \quad \mu, \nu = x, y, z
\]

(22)
the dc conductivity is
\[
\sigma_{\mu\nu} = \frac{e^2 \hbar}{m\Omega} \sum_{l_1 l_2 \cdots l_{N_e}} W_{l_1 l_2 \cdots l_{N_e}} \sum_{\alpha=1}^{N_e} \sum_{l(l \neq l_\alpha)} \frac{1}{E_{l_\alpha} - E_l} \text{Im} \langle \chi_l | x_\mu | \chi_{l_\alpha} \rangle \int_{\Omega} d^3x (\chi_l \frac{\partial \chi^*_l}{\partial x_\mu} - \chi^*_l \frac{\partial \chi_l}{\partial x_\mu}) \tag{23}
\]
In a large system, the matrix element of position operator is not well defined. Making use of
\[
\langle \chi_d | x_\alpha | \chi_{l_\alpha} \rangle = \langle \chi_d | [\hat{h}_\alpha, x_\alpha] | \chi_{l_\alpha} \rangle = \frac{\hbar^2}{m} \langle \chi_d | \frac{\partial}{\partial x_\alpha} | \chi_{l_\alpha} \rangle = \frac{\hbar^2}{m} \langle \chi_d | \frac{\partial}{\partial x_\alpha} | \chi_{l_\alpha} \rangle \tag{24}
\]
one can change the matrix element of position operator into the matrix element of momentum operator.\[^{8}\]

Current use of the KGF is amounts to assuming that beside \( l_\alpha \), other single-electron states in \( \{ l_1 l_2 \cdots l_{N_e} \} \) are occupied. Only the factor \( f(E_{l_\alpha}) \) is left. Thus the sum over various choices of \( \{ l_1 l_2 \cdots l_{N_e} \} \) can be ignored if one extends the sum over \( \alpha \) to all possible single particle states.

In parallel with Greenwood’s work for ac field, Luttinger has derived an expression for static field by adiabatically introducing the interaction.\[^{16}\] Transition probability rather than the amplitude of probability was used. Eq.\[^{[23]}\] does not obviously display a feature of an intrinsic semiconductor: dc conductivity vanishes at zero temperature. In addition, due to the use of the single particle approximation before applying perturbation theory in Eq.\[^{[23]}\], one cannot exclude coupling between two occupied states. These faults can be cured in time-dependent perturbation theory or by applying perturbation theory directly to the many-electron wave function.

If there is only one group \( M \) degenerate single-electron states \( (\chi_{d_\sigma}, \sigma = 1, 2, \cdots, M) \) in \( \Lambda_{l_1 l_2 \cdots l_{N_e}} \), we first form correct zeroth order wave functions
\[
\chi^{(0)}_{d_\sigma} = \sum_{\sigma'} C_{d_\sigma d_{\sigma'}} \chi_{d_{\sigma'}} \, , \, \sigma, \sigma' = 1, 2, \cdots, M \tag{25}
\]
the secular equation satisfied by \( C_{d_\sigma d_{\sigma'}} \) is
\[
\sum_{\sigma'} (V_{d_\sigma d_{\sigma'}} - \varepsilon \delta_{d_{\sigma} d_{\sigma'}}) C_{d_{\sigma} d_{\sigma'}} = 0 \, , \, V_{d_\sigma d_{\sigma'}} = \int dr \chi^*_{d_{\sigma'}} (-e \mathbf{E} \cdot \mathbf{r}) \chi_{d_{\sigma'}} \tag{26}
\]
The perturbation matrix \( (V_{d_\sigma d_{\sigma'}}) \) is Hermitian, it can be diagonalized by a unitary transformation \( (C_{d_\sigma d_{\sigma'}}) \). Therefore
\[
\sum_{\sigma} (\chi_{d_\sigma}^{(0)} \nabla \chi^*_{d_\sigma} - \chi^*_{d_\sigma} \nabla \chi_{d_\sigma}^{(0)}) = \sum_{\sigma} (\chi_{d_\sigma} \nabla \chi^*_{d_\sigma} - \chi^*_{d_\sigma} \nabla \chi_{d_\sigma}) \tag{27}
\]
According to Eq. (18), the zeroth-order contribution of the degenerate states to conductivity is zero. This is consistent with usual experience: an electron is not accelerated along the direction of the field when it transits between states with same energy, and thus makes no contribution to the conductivity.

The first order correction to \( \chi_{d_\sigma}^{(0)} \) is:

\[
\chi_{d_\sigma}^{(1)} = \sum_k \frac{V_{k d_\sigma}}{E_{d_\sigma}^{(0)} - E_k^{(0)}} \chi_k + \sum_{\sigma'=1}^M \frac{1}{\varepsilon_{d_\sigma} - \varepsilon_{d_{\sigma'}}} \sum_k V_{d_{\sigma'} k} V_{k d_\sigma} \chi_{d_{\sigma'}}^{(0)}
\]

where

\[
\varepsilon_{d_\sigma} = \int d\mathbf{r} \chi_{d_\sigma}^{(0)^*}(-e\mathbf{E} \cdot \mathbf{r}) \chi_{d_\sigma}', \quad V_{k d_\sigma} = \int d\mathbf{r} \chi_k^{(0)^*}(-e\mathbf{E} \cdot \mathbf{r}) \chi_k
\]

\( k \) indexes non-degenerate states. The first sum in Eq. (28) runs over all states which are not degenerate with \( (\chi_{d_\sigma}, \sigma = 1, 2, \cdots, M) \).

Making use of Eq. (28), the macroscopic current density Eq. (18) becomes

\[
j' = \frac{e^2}{m} \sum_{l_1 l_2 \cdots l_{N_e}}^{N_e - M} W_{l_1 l_2 \cdots l_{N_e}} \left\{ \sum_{l \neq l_0} \sum_{\alpha = 1}^{N_e} \text{Im} \left( \frac{\chi_l \mathbf{E} \cdot \mathbf{r} \chi_{l_0}}{E_{l_0} - E_l} \right) \int_{\Omega_{l'}} ds \left( \chi_l \nabla_s \chi_{l_0}^* - \chi_{l_0}^* \nabla_s \chi_l \right) \right\}
\]

\[
+ \sum_{\sigma=1}^M \sum_{k} \text{Im} \left( \frac{\chi_k \mathbf{E} \cdot \mathbf{r} \chi_{d_\sigma}}{E_{d_\sigma}^{(0)} - E_k^{(0)}} \right) \int_{\Omega_{d_\sigma'}} ds \left( \chi_k \nabla_s \chi_{d_\sigma}^{(0)*} - \chi_{d_\sigma}^{(0)*} \nabla_s \chi_k \right)
\]

\[
+ \sum_{\sigma=1}^M \sum_{\sigma' \neq \sigma} \frac{1}{\varepsilon_{d_\sigma} - \varepsilon_{d_{\sigma'}}} \sum_k \frac{V_{d_{\sigma'} k} V_{k d_\sigma}}{E_{d_\sigma}^{(0)} - E_k^{(0)}} \int_{\Omega_{d_\sigma'}} ds \left( \chi_{d_\sigma}^{(0)*} \nabla_s \chi_{d_{\sigma'}}^{(0)} - \chi_{d_{\sigma'}}^{(0)} \nabla_s \chi_{d_\sigma}^{(0)*} \right)
\]

The sums over \( l \) and \( k \) are not restrict to \( (l_1 l_2 \cdots l_{N_e}) \). The first term in bracket is the contribution from coupling among non-degenerate states, the third term is contribution from coupling among M-fold degenerate states, the second term is contribution from coupling between member of non-degenerate states and the M-fold degenerate states. All denominators are non-zero.

Because \( \chi_{d_\sigma}^{(0)} \), \( \varepsilon_{d_\sigma} \) and \( V_{k d_\sigma} \) are functions of field, the 2\(^{nd}\) term and the 3\(^{rd}\) term in Eq. (30) do not exhibit a simple linear relation with field: each contribution to conductivity is field-dependent. The generalization to the situation in which there are several groups of degenerate states in \( \Lambda_{l_1 l_2 \cdots l_{N_e}} \) is straightforward.

The massive degeneracies in the \( N_e \)-electron states \( \Lambda_{l_1 l_2 \cdots l_{N_e}} \) do not cause any trouble: they are counted by the sum over all possible ways of picking up \( N_e \) single-electron states. In
a crystal, the degeneracies in the single-electron states may be caused by the high symmetry of the lattice. Sometimes accidental degeneracies (band crossing along a symmetry axis or a symmetry plane not compelled by symmetry) also occur\(^1\), as well as additional degeneracies produced by time reversal symmetry\(^18,19\). In a disordered system (liquid, amorphous solid and some molecules), only the degeneracies produced by time reversal symmetry are left. From the perspective of computing the conductivity, a disordered system has less degeneracy, and is simpler to treat than a crystal. Comparing the huge number of non-degenerate states (most of original degeneracies in the unit cell are removed by the interaction with first, second and third coordination shells), the number of degenerate states in each manifold is quite small. The third term in Eq. (30), the coupling among degenerate states, is small compared with the first two terms. If we neglect the field-dependence of \(\chi_d^{(0)}\) in the second term of Eq. (30) and use the original \(\chi_{dσ}\), one does not need to distinguish degenerate states and non-degenerate states. Eq. (23) could be used to compute conductivity by neglecting the coupling among degenerate states.

B. AC conductivity

The macroscopic current density in an oscillating field is

\[
j^\varepsilon(\mathbf{r}, t) = \frac{ie\hbar}{2m\Omega_\varepsilon} \int_{\Omega_\varepsilon} ds \sum_{l_1l_2\ldots l_{N_e}} W_{l_1l_2\ldots l_{N_e}}^{N_e} \sum_{\alpha=1}^{N_e} \left\{ \left[ \chi_{l_\alpha}(t) \nabla_s \chi_{l_\alpha}^{(1)*}(t) - \chi_{l_\alpha}^{(1)*}(t) \nabla_s \chi_{l_\alpha}(t) \right] + \left[ \chi_{l_\alpha}^{(1)}(t) \nabla_s \chi_{l_\alpha}^{(1)}(t) - \chi_{l_\alpha}^{(1)*}(t) \nabla_s \chi_{l_\alpha}(t) \right] \right\}
\]

In an ac electric field \(\mathbf{E} = E_0 \cos \omega t\), the interaction of an electron at \(\mathbf{r}\) with field is

\[
H_{fm}(t) = Fe^{-it\omega} + Fe^{it\omega}, \quad F = -\frac{1}{2}e\mathbf{r} \cdot \mathbf{E}_0
\]

Since the region \(\Omega_\varepsilon\) (employed to compute the spatial average) is much smaller than the wavelength of the field, the position dependence of field is ignored in Eq. (32). The wave function \(\chi_c'(t)\) in an external field can be computed from time-dependent perturbation theory

\[
\chi_c'(t) = \chi_c(t) + \sum_{d(\neq c)} a_d(t) \chi_d e^{-itE_d/\hbar}, \quad \chi_c(t) = e^{-itE_c/\hbar} \chi_c(\mathbf{r})
\]
where \( a_d(t) \) satisfies

\[
\frac{i\hbar}{\partial t} a_d(t) = \sum_{c_1} a_{c_1}(t) F_{dc_1} [e^{it(\omega_{dc_1} - \omega)} + e^{it(\omega_{dc_1} + \omega)}]
\]

(34)

where

\[
F_{dc_1} = \int d\mathbf{r} \chi_d^* F \chi_{c_1}, \quad \omega_{dc_1} = \frac{1}{\hbar} (E_d - E_{c_1})
\]

(35)

We assume initially only state \( \chi_c \) is occupied and other states are empty: \( a_{c_1}(t = -\infty) = \delta_{cc_1} \).

1. non-degenerate states

If all the states are not degenerate, Eq.\( (34) \) is simplified to

\[
\frac{\partial a_d(t)}{\partial t} = -\frac{i}{\hbar} F_{dc} e^{it(\omega_d - \omega)} - \frac{i}{\hbar} F_{dc} e^{it(\omega_d + \omega)}
\]

(36)

The solution of Eq.\( (36) \) is simply a time integral:

\[
a_d(t) = -\frac{F_{dc} e^{it(\omega_d - \omega)}}{\hbar(\omega_d - \omega - i\delta)} - \frac{F_{dc} e^{it(\omega_d + \omega)}}{\hbar(\omega_d + \omega - i\delta)}, \quad \delta \rightarrow 0^+
\]

(37)

The change in wave function \( \chi_c \) due to the ac field is

\[
\chi_c^{(1)}(t) = \sum_{d(\neq c)} (1 - n_d) a_d(t) \chi_d e^{-itE_d/\hbar}
\]

(38)

where \( n_d \) is the occupation probability of single-electron state \( \chi_d \). The “un-occupation” factor \( (1 - n_d) \) is implicitly assumed when we simplify Eq.\( (34) \) to Eq.\( (36) \): initially state \( \chi_d \) must be empty. In an intrinsic semiconductor at zero temperature, the valence band is fully occupied and conduction band is empty. Eq.\( (38) \) indicates that only conduction states can couple with the valence states. This implies that the dc conductivity of an intrinsic semiconductor at zero temperature is zero.

With the help of Eq.\( (33) \), Eq.\( (37) \) and Eq.\( (38) \), Eq.\( (31) \) becomes

\[
j^e(r', t) = \frac{i\hbar e}{2m \Omega_{e'}} \int_{\Omega_{e'}} ds \sum_{l_1 l_2 \cdots l_{N_e}} W_{l_1 l_2 \cdots l_{N_e}} \sum_{a=1}^{N_e} \sum_{d(\neq l_a)} (1 - n_d) e^{it(\omega_{d_0} + \omega)} (\chi_d \nabla_s \chi_d^* - \chi_d^* \nabla_s \chi_d)
\]

(39)
The semi-classical current density is given by

$$\sigma^{(1)}_{\mu\nu}(\omega) = \frac{e^2 \hbar}{2m\Omega} \sum_{l_1 l_2 \cdots l_{N_c}} W_{l_1 l_2 \cdots l_{N_c}} \sum_{\alpha=1}^{N_c} \sum_{d(\neq l_\alpha)} (1 - n_d)(\frac{1}{E_{l_\alpha} - E_d + \hbar\omega} + \frac{1}{E_{l_\alpha} - E_d - \hbar\omega})$$  \hspace{1cm} (40)

Im$$[\langle \chi_d | x_{\nu} | \chi_{l_\alpha} \rangle \int_{\Omega} d^3x (\chi_d^{*} \frac{\partial \chi_{l_\alpha}^{*}}{\partial x_\mu} - \chi_{l_\alpha}^{*} \frac{\partial \chi_d}{\partial x_\mu})]$$

When $$\omega = 0$$ Eq.(40) is reduced to Eq.(23) except for the factor $$(1 - n_d)$$, as it should be.

To compare with the result from Boltzmann equation, let us consider a crystalline metal. The semi-classical current density is given by

$$j_\mu^c = e \int \frac{2dk}{(2\pi)^3} v_\mu(k)g(k)$$  \hspace{1cm} (41)

where the integral is over the first Brillouin zone. $$g(k)$$ is the non-equilibrium distribution function under external field, in relaxation time approximation

$$g(k) = f(k) + \frac{\partial f}{\partial E} e \mathbf{E} \cdot \mathbf{v} \tau(E(k))$$  \hspace{1cm} (42)

where $$\tau(E(k))$$ is the energy-dependent relaxation time, $$f(k)$$ is the Fermi distribution function $$f(E(k))$$. The conductivity is read out from Eqs.(41) and (42):

$$\sigma_{\mu\nu} = \frac{e^2}{\Omega} \sum_{l_1 l_2 \cdots l_{N_c}} W_{l_1 l_2 \cdots l_{N_c}} \sum_{\alpha=1}^{N_c} \sum_{d(\neq l_\alpha)} (1 - n_d)(\frac{1}{E_{l_\alpha} - E_d + \hbar\omega} + \frac{1}{E_{l_\alpha} - E_d - \hbar\omega}) \frac{\hbar}{E_{l_\alpha} - E_d}$$  \hspace{1cm} (43)

Using Eq.(24) and the definition of velocity operator $$v_\mu = -\frac{im}{\hbar} \frac{\partial f}{\partial x_\mu}$$, Eq.(40) is changed into

$$\sigma^{(1)}_{\mu\nu}(\omega) = \frac{e^2}{\Omega} \sum_{l_1 l_2 \cdots l_{N_c}} W_{l_1 l_2 \cdots l_{N_c}} \sum_{\alpha=1}^{N_c} \sum_{d(\neq l_\alpha)} (1 - n_d)(\frac{1}{E_{l_\alpha} - E_d + \hbar\omega} + \frac{1}{E_{l_\alpha} - E_d - \hbar\omega}) \frac{\hbar}{E_{l_\alpha} - E_d}$$  \hspace{1cm} (44)

If we interpret $$\frac{\hbar}{E_{l_\alpha} - E_d}$$ as the energy-dependent relaxation time $$\tau(E_{l_\alpha})$$ caused by inelastic scattering of phonons (in a given MD step, scattering is caused by deviation from crystal; to reflect various vibration states and electron-phonon scattering, averaging over many MD steps is necessary), $$n_{l_\alpha}(1 - n_d)(\frac{1}{E_{l_\alpha} - E_d + \hbar\omega} + \frac{1}{E_{l_\alpha} - E_d - \hbar\omega})$$ as $$\frac{\partial f}{\partial E}$$, sum over states as integral over Brillouin zone: $$\frac{1}{\Omega} \sum_{l_1 l_2 \cdots l_{N_c}} W_{l_1 l_2 \cdots l_{N_c}} \sum_{\alpha=1}^{N_c} \sum_{d(\neq l_\alpha)} \int \frac{2dk}{(2\pi)^3}$$ (only in crystal, one can use $$k$$-points in the reciprocal space to characterize states), where $$n_{l_\alpha}$$ is removed from $$W$$. At $$\omega = 0$$, as expected, Eq.(44) is reduced to the semi-classical result (43).
The \( \sin \omega t \) terms in Eq. (39) lag 90\(^0\) behind the phase of external field. The contribution to the imaginary part of conductivity is

\[
\sigma^{(2)}_{\alpha\beta}(\omega) = \frac{e^2 \hbar}{2m\Omega} \sum_{l_1 l_2 \cdots l_{N_e}} W_{l_1 l_2 \cdots l_{N_e}} \frac{1}{N_e} \sum_{\alpha=1}^{N_e} \sum_{\ell(\neq l_\alpha)} (1 - n_d) \left[ \frac{1}{E_d - E_{l_\alpha} - \hbar \omega} - \frac{1}{E_d - E_{l_\alpha} + \hbar \omega} \right]
\]

\[
\text{Re}\left[ \langle \chi_d | x_\beta | \chi_{l_\alpha} \rangle \right] \int_{\Omega} d^3 x \left( \chi_d^* \frac{\partial \chi_{l_\alpha}}{\partial x_\alpha} - \chi_{l_\alpha}^* \frac{\partial \chi_d}{\partial x_\alpha} \right)
\]

(45)

it is interesting to notice that \( \sigma^{(2)}_{\alpha\beta}(0) = 0 \).

To first order in the field, the second term in Eq. (6) is

\[
-\frac{e^2}{m} A(r, t) n_e^{\text{e}} (w_1 \cdots w_N)(r, t) = \frac{e^2 E_0}{m\omega} n_e^{\text{e}} (w_1 \cdots w_N)(r) \sin \omega t
\]

(46)

From Eq. (5), to 1st order of field, the 3rd term in Eq. (6) is

\[
\sum_{\alpha} q_\alpha^2 e^{2} M_\alpha \omega \sin \omega t \delta(r - W_\alpha)
\]

(47)

Using Eq. (8), the imaginary part of conductivity of the electrons + nuclei is

\[
\sigma^I_{\alpha\beta}(\omega) = \sigma^{(2)}_{\alpha\beta}(\omega) + \frac{e^2 n_e^{\text{e}}}{m\omega} + \sum_{p} \frac{q_p^2 n_p^N}{M_p \omega}
\]

(48)

\( M_p, q_p \) and \( n_p^N \) are mass, effective charge and the number density of the \( p \)th species of nuclei. The last two terms are contributions from free charges.

We cannot use Eq. (37) in two situations: (1) degenerate states with low frequency field, \( \omega_{dc} = 0 \) and \( \omega \to 0 \); (2) external field and two groups of levels in resonance: \( \omega_{dc} - \omega = 0 \) or \( \omega_{dc} + \omega = 0 \). In these situations, Eq. (36) leads to \( a_d(t) \sim t \).

2. Interaction of degenerate states with a very low frequency external field

For a group of \( M \) degenerate states \((\chi_{d_\sigma}, \sigma = 1, 2, \cdots, M)\), the mutual coupling is much stronger than the coupling between one member and the states with different energy. The general evolution equation

\[
i\hbar \frac{da_j}{dt} e^{-iE_j t/\hbar} = \sum_k a_k V_{jk} e^{-iE_k t/\hbar}, \quad V_{jk} = \int d\mathbf{r} \chi_j^* H_{fm}(t) \chi_k
\]

(49)

is simplified to

\[
i\hbar \frac{da_j(t)}{dt} = \sum_k a_k(t) G_{jk} \cos \omega t, \quad G_{jk} = \int d\mathbf{r} \chi_j^*(-e \mathbf{E}_0 \cdot \mathbf{r}) \chi_k \quad j, k = d_1, d_2, \cdots, d_M
\]

(50)
Introduce new variable $s = \sin \omega t$, Eq. (50) becomes
\[ i\hbar \omega \frac{d a_j(s)}{ds} = \sum_k a_k(s) G_{jk}, \tag{51} \]

Notice $G_{jk}$ does not depend on time, taking Fourier transform
\[ a_j(s) = \int dp a_p e^{-ips}, \quad j = d_1, d_2, \ldots, d_M \tag{52} \]
in both sides of Eq. (51) leads to
\[ \sum_k a_p (G_{jk} - \hbar \omega p \delta_{jk}) = 0 \tag{53} \]

Because $(G_{jk})$ is Hermitian, its eigenvalues $p_1, p_2, \ldots, p_M$ are real and the matrix $(a_{p_\mu d_\alpha})$ is unitary. The $M$ special solutions of Eq. (50) are
\[ \chi_\mu^{r(0)}(t) = e^{-i p_\mu \sin \omega t} \sum_{\alpha=1}^M a_{p_\mu d_\alpha} \chi_{d_\alpha}, \quad \mu = 1, 2, \ldots, M \tag{54} \]

The matrix elements of perturbation $(-eE_0 \cdot r)$ relative to the new zero order wave functions are diagonal:
\[ \int dr \chi_\mu^{r(0)*}(t) \chi_\nu^{r(0)}(t) = G_{p_\mu p_\nu} \delta_{\mu \nu}, \quad \mu, \nu = 1, 2, \ldots, M \tag{55} \]

Because matrix $(a_{p_\mu d_\alpha})$ is unitary, one has
\[ \sum_{\mu=1}^M [\chi_\mu^{r(0)}(t) \nabla \chi_\mu^{r(0)*}(t) - \chi_\mu^{r(0)*}(t) \nabla \chi_\mu^{r(0)}(t)] = \sum_{\alpha=1}^M [\chi_{d_\alpha} \nabla \chi_{d_\alpha}^* - \chi_{d_\alpha}^* \nabla \chi_{d_\alpha}] = 0 \tag{56} \]

From Eq. (31), the zeroth order correction to degenerate states does not contribute to conductivity.

Unlike the KGF, where dc conductivity is obtained either by extrapolating from optical conductivity or by writing a separate code for zero frequency, the present ac expression includes dc expression in the obvious way. One may notice when $\omega = 0$, $j_c = 0$ and $j_x^e = 0$ (cf. Appendix A). Excepting the factor $(1 - n)$ which would not appear from single-electron stationary perturbation theory, when $\omega \to 0$, $j_c^e$ is reduced into the second sum of Eq. (30), $(j_c^e + j_{s2})$ is reduced into the third sum of Eq. (30) (cf. Appendix A).

In Appendix A, we show that the contributions to current density or conductivity from the degenerate states is finite. In the single-electron states, the number of degenerate states in each degenerate manifold is much smaller than the total number of non-degenerate states. The conductivity from the coupling among degenerate states can therefore be neglected. One can use Eqs. (40) and (45), in which only counts the coupling among non-degenerate states and the coupling between degenerate states and non-degenerate states.
3. Resonance with external field

Suppose in \((\chi_{I_1}, \chi_{I_2}, \cdots, \chi_{I_N})\) there is a \(M\)-fold degenerate manifold \((\chi_m^1, \chi_m^2, \cdots, \chi_m^M)\) and a \(M'\)-fold degenerate manifold \((\chi_n^1, \chi_n^2, \cdots, \chi_n^{M'})\) which are nearly in resonance with a finite frequency \(\omega\) external field: \(E_m^{(0)} - E_n^{(0)} = \hbar(\omega + \varepsilon)\), \(\varepsilon \ll \omega\) or \(\varepsilon = 0\). The coupling with other non-resonant states can be neglected. If we only consider the interaction with the smallest oscillating frequency,

\[
V_{mjnk}(t) \approx F_{mjnk} e^{it(\omega_{mjnk} - \omega)} = F_{mjnk} e^{ite}, \quad F_{mjnk} = \frac{1}{2} \int d\mathbf{r} \chi_{mj}^* (-eE_0 \cdot \mathbf{r}) \chi_{nk}
\]

the general evolution equation

\[
i\hbar \frac{da_{mj}}{dt} = \sum_{k=1}^{M'} V_{mjnk}(t) a_{nk}, \quad j = 1, 2, \cdots, M; \quad k = 1, 2, \cdots, M'
\]

is simplified to

\[
i\hbar \frac{da_{mj}}{dt} = \sum_{k=1}^{M'} F_{mjnk} e^{ite} a_{nk}
\]

Similarly if one only takes the interaction with smallest oscillating frequency

\[
V_{nkmj}(t) \approx F_{nkmj}^* e^{it(\omega_{nkmj} + \omega)} = F_{nkmj}^* e^{-ite}
\]

the general evolution equation

\[
i\hbar \frac{da_{nk}}{dt} = \sum_{j=1}^{M} V_{nkmj}(t) a_{mj}
\]

is simplified to

\[
i\hbar \frac{da_{nk}}{dt} = \sum_{j=1}^{M} F_{nkmj}^* e^{-ite} a_{mj}
\]

Introduce new functions \(b_{nk}: a_{nk} = b_{nk} e^{-ite}\) \((k = 1, 2, \cdots, M')\), Eq.\((59)\) becomes

\[
i\hbar \frac{da_{mj}}{dt} = \sum_{k=1}^{M'} F_{mjnk} b_{nk}
\]

Eq.\((62)\) becomes

\[
i\hbar b_{nk} = -\hbar \epsilon b_{nk} + \sum_{j=1}^{M} F_{mjnk}^* a_{mj}
\]

Eqs.\((63)\) and \((64)\) can be rearranged into

\[
i\hbar \frac{dV}{dt} = RV
\]
where
\[
R = \begin{pmatrix}
0_{M\times M} & B_{M\times M'} \\
(B_{M\times M'})^{\text{transpose}} & 0_{M'\times M'} - \hbar \epsilon I_{M'\times M'}
\end{pmatrix}
\]  
(66)

is a \((M+M')\times(M+M')\) matrix, 0 is zero matrix, \(I\) is the unit matrix, elements of matrix \(B\) are given by
\[
B_{jk} = F_{m_jn_k}, \quad j = 1, 2, \ldots, M; \quad k = 1, 2, \ldots, M'
\]  
(67)

\(V\) is a \((M+M')\) column vector, its transpose is
\[
V^{\text{transpose}} = (a_{m_1}, a_{m_2}, \ldots, a_{m_M}, b_{n_1}, b_{n_2}, \ldots, b_{n_{M'}})
\]  
(68)

We are looking for special solutions of Eq.\((63)\) in the form:
\[
a^{q}_{m_j}(t) = a^{q}_{m_j} e^{i\alpha_q t}, \quad j = 1, 2, \ldots, M; \quad b^{q}_{n_k}(t) = b^{q}_{n_k} e^{i\alpha_q t}, \quad k = 1, 2, \ldots, M'
\]  
(69)

The column vector \(V^{q}_0\) with
\[
(V^{q}_0)^{\text{transpose}} = (a^{q}_{m_1}, a^{q}_{m_2}, \ldots, a^{q}_{m_M}, b^{q}_{n_1}, b^{q}_{n_2}, \ldots, b^{q}_{n_{M'}})
\]  
(70)

is the eigenvector of \(R\) belonging to eigenvalue \(\hbar \alpha_q\). Then \((M+M')\) special solutions of the time-dependent single-electron Schrödinger equation are
\[
\chi^{(0)}_q(t) = \sum_{j=1}^{M} a^{q}_{m_j} e^{i\alpha_q t} \chi_{m_j} e^{-iE_{m_j} t/\hbar} + \sum_{k=1}^{M'} b^{q}_{n_k} e^{i(\alpha_q - \epsilon) t} \chi_{n_k} e^{-iE_{n_k} t/\hbar}, \quad q = 1, 2, \ldots, M + M'
\]  
(71)

and the general solution can be obtained from linear combinations. Because \(R\) is Hermitian, its eigenvalues \((\hbar \alpha_q, q = 1, 2, \ldots, M + M')\) are real, matrix \(C = (a^{q}_{m_1}, a^{q}_{m_2}, \ldots, a^{q}_{m_M}, b^{q}_{n_1}, b^{q}_{n_2}, \ldots, b^{q}_{n_{M'}})\) is unitary (\(q\) is index of row).

If we use Eq.\((71)\) and notice that \(C\) is unitary, one has
\[
\sum_{q=1}^{M+M'} (\chi^{(0)}_q \nabla \chi^{(0)}_q - \chi^{(0)}_q \nabla \chi^{(0)}_q) = \sum_{j=1}^{M} (\chi_{m_j} \nabla \chi_{m_{j+1}} - \chi_{m_{j+1}} \nabla \chi_{m_j}) + \sum_{k=1}^{M'} (\chi_{n_k} \nabla \chi_{n_{k+1}} - \chi_{n_{k+1}} \nabla \chi_{n_k})
\]  
(72)

From Eq.\((13)\), the contribution to current from two groups of states in resonance with an external field is zero. The artificial poles in the case of resonance in Eq.\((37)\) are removed. For a mechanical oscillator, if we input energy in a resonant way and do not take out energy, the amplitude of the oscillator will increase indefinitely. The situation for two groups of resonant levels is different; the system absorbs the external field while stimulated
emission also occurs. The material and field are in absorption-emission equilibrium, so that no singularity occurs. The two $\delta$ functions (they originate from first order correction of wave function) in Greenwood formula come from the long time limit, and are not caused by resonance. In Appendix B, we show that the contribution from resonant states is finite.

C. Comparison with Greenwood formula

Both the present work and the Greenwood derivation require the use of perturbation theory:

$$a_d(t) = -\frac{i}{\hbar} F_{dc} \int_{t_1}^{t_2} dt' \left[ e^{it'(\omega_{dc} - \omega)} + e^{it'(\omega_{dc} + \omega)} \right] \ll 1 \quad (73)$$

This means that the interaction time $\tau = (t_2 - t_1)$ cannot be too long:

$$\tau = (t_2 - t_1) \ll \frac{\hbar}{F} \quad (74)$$

The Greenwood derivation also requires that the transition probability per unit time be defined:

$$\lim_{\tau \to \infty} \frac{\sin^2 \frac{\tau (\omega_{dc} - \omega)}{2}}{\tau (\omega_{dc} - \omega)^2} = \pi \delta\left(\frac{\omega_{dc} - \omega}{2}\right) \quad \text{and} \quad \lim_{\tau \to \infty} \frac{\sin^2 \frac{\tau (\omega_{dc} + \omega)}{2}}{\tau (\omega_{dc} + \omega)^2} = \pi \delta\left(\frac{\omega_{dc} + \omega}{2}\right) \quad (75)$$

That is, the interaction time $\tau$ should be long enough

$$\tau >> \frac{2}{\omega_{dc} - \omega} \quad \text{and} \quad \tau >> \frac{2}{\omega_{dc} + \omega} \quad (76)$$

to allow the two limits in Eq. (75) to be taken. The law of conservation energy (of field + matter) can be verified by means of two measurements only to an accuracy of the order of $\hbar/\Delta t$, where $\Delta t$ is the time interval between the measurements, i.e. the interaction time $\tau$ between field and matter. Since in present work we do not need probability per unit time (i.e. long time limit), the energy conservation delta function will not appear.

For a large system with continuous energy spectrum, Eq. (76) contradicts Eq. (74) for close levels when $\omega \to 0$. Since a transition with small $\omega_{dc}$ makes a large contribution to conductivity, the dc conductivity obtained from the KGF is problematic. The derivation in this work does not need transition probability, therefore does not need condition (76), and is self-consistent. Numerically Eq. (40) and Eq. (48) get rid of the delta function, and do not require an artificial broadening.
III. ROLE OF MANY-ELECTRON STATISTICS

In this section, method (2), many-body perturbation theory, is used to compute the conductivity. We take a static field as example and apply to concrete examples.

A. Intrinsic semiconductor

1. K-electron excited state

Label the states in valence band from low energy to high energy as \( v_{N_e}, \ldots, v_2, v_1 \), the states in the conduction band from low energy to high energy as \( c_1, c_2, \ldots, c_{N_e} \). For an intrinsic semiconductor at \( T = 0 \)K, the valence band is full, and the number of states is the number of electrons. The system is in its ground state

\[
\Lambda_0 = \frac{1}{\sqrt{N_e!}} \sum_P \delta_P P_{r_1,s_{z1},r_2,s_{z2},r_{N_e},s_{zN_e}} v_1(r_1s_{z1})v_2(r_2s_{z2}) \cdots v_{N_e}(r_{N_e}s_{zN_e})
\]

(77)

At \( T > 0 \), various excited states appear. First consider one electron pumped into the conduction band from the valence band. A one-electron excited state \( \Lambda_{v_jc_k} \) is constructed from \( \Lambda_0 \) by replacing \( v_j \) with \( c_k \). There are \( N_e \) manners in choosing \( v_j \). There are \( N_e \) manners in choosing \( c_k \). The single-electron energy spectrum is very dense, there are many combinations of the choices of initial valence state and the final conduction state, the degeneracy among 1-electron excited states is high.

Since any observable, including current, are bilinear forms of a \( N_e \)-electron wave function, the order of \( N_e \) states in the Slater determinant \( \Lambda_{v_jc_k}^* \) does not matter provided that we maintain the same order in \( \Lambda_{v_jc_k}^* \). The probability of state \( \Lambda_{v_jc_k} \) relative to the ground state \( \Lambda_0 \) is

\[
U_{v_jc_k} = \exp\left\{ -\left[ (E_{v_1} - E_{v_j}) + (E_{c_k} - E_{c_1}) \right] / (k_B T) \right\}
\]

(78)

where \( E_g \) is the band gap.

If two electrons are pumped from valence band to conduction band, a 2-electron excited state \( \Lambda_{v_{j_1}v_{j_2}c_{p_1}c_{p_2}} \) is obtained from \( \Lambda_0 \) by replacing \( (v_{j_1}, v_{j_2}) \) with \( (c_{p_1}, c_{p_2}) \). The relative probability of state \( \Lambda_{v_{j_1}v_{j_2}c_{p_1}c_{p_2}} \) to ground state \( \Lambda_0 \) is

\[
U_{v_{j_1}v_{j_2}c_{p_1}c_{p_2}} = \exp\left\{ -\left[ (E_{v_1} - E_{v_{j_1}}) + (E_{v_1} - E_{v_{j_2}}) + 2E_g + (E_{c_{p_1}} - E_{c_1}) + (E_{c_{p_2}} - E_{c_1}) \right] / (k_B T) \right\}
\]

(79)
In $\Lambda_0$ if $K$ electrons are excited to the conduction band from valence band: state $v_{j_1}$ is replaced by state $c_{p_1}$, state $v_{j_2}$ is replaced by $c_{p_2}$, \ldots , state $v_{j_K}$ is replaced by state $c_{p_K}$, a K-electron excited state $\Lambda_{v_{j_1}v_{j_2}\ldots v_{j_K}c_{p_1}c_{p_2}\ldots c_{p_K}}$ is obtained. The probability of $\Lambda_{v_{j_1}v_{j_2}\ldots v_{j_K}c_{p_1}c_{p_2}\ldots c_{p_K}}$ relative to $\Lambda_0$ is

$$U_{v_{j_1}v_{j_2}\ldots v_{j_K}c_{p_1}c_{p_2}\ldots c_{p_K}} = \exp\left\{-\sum_{\alpha=1}^{K}(E_{v_{j_1}} - E_{v_{j_\alpha}}) + KE_g + \sum_{\alpha=1}^{K}(E_{c_{p_\alpha}} - E_{c_1})\right\}/(k_BT)$$ (80)

The absolute probability $W_{v_{j_1}c_k}$ of 1-electron excited state $\Lambda_{v_{j_1}c_k}$ is

$$W_{v_{j_1}c_k} = \frac{U_{v_{j_1}c_k}}{Z}, \quad Z = 1 + \sum_{j_k} U_{v_{j_k}c_k} + \cdots + \sum_{v_{j_1}v_{j_2}\ldots v_{j_K}c_{p_1}c_{p_2}\ldots c_{p_K}} U_{v_{j_1}v_{j_2}\ldots v_{j_K}c_{p_1}c_{p_2}\ldots c_{p_K}} + \cdots$$ (81)

It is easy to verify for low $T$ that $\exp\left(E_{v_{j_1}} - E_F\right) << 1$ and $\exp\left(E_{c_1} - E_F\right) >> 1$ (they are satisfied even in several thousand $K$), so that one has

$$W_{v_{j_1}c_k} = [1 - f(E_{v_{j_1}})]f(E_{c_k})$$ (82)

where

$$f(E_v) = \left[\exp\left(\frac{E_v - E_F}{k_BT}\right) + 1\right]^{-1} \quad \text{and} \quad f(E_c) = \left[\exp\left(\frac{E_c - E_F}{k_BT}\right) + 1\right]^{-1}$$ (83)

are Fermi distribution functions of valence states and conduction states.

The absolute probability $W_{v_{j_1}v_{j_2}c_{p_1}c_{p_2}}$ of 2-electron excited state $\Lambda_{v_{j_1}v_{j_2}c_{p_1}c_{p_2}}$ can be obtained similarly

$$W_{v_{j_1}v_{j_2}c_{p_1}c_{p_2}} = \frac{U_{v_{j_1}v_{j_2}c_{p_1}c_{p_2}}}{Z} = [1 - f(E_{v_{j_1}})][1 - f(E_{v_{j_2}})]f(E_{c_{p_1}})f(E_{c_{p_2}})$$ (84)

The absolute probability $W_{v_{j_1}v_{j_2}\ldots v_{j_K}c_{p_1}c_{p_2}\ldots c_{p_K}}$ of K-electron excited state $\Lambda_{v_{j_1}v_{j_2}\ldots v_{j_K}c_{p_1}c_{p_2}\ldots c_{p_K}}$ is

$$W_{v_{j_1}v_{j_2}\ldots v_{j_K}c_{p_1}c_{p_2}\ldots c_{p_K}} = \frac{U_{v_{j_1}v_{j_2}\ldots v_{j_K}c_{p_1}c_{p_2}\ldots c_{p_K}}}{Z} = \prod_{\alpha=1}^{K}[1 - f(E_{v_{j_\alpha}})]f(E_{c_{p_\alpha}})$$ (85)

2. Zero dc conductivity at $T=0K$

Because the interaction with a static field

$$H_{int} = -\sum_{m=1}^{N_e} eE \cdot r_m$$ (86)
is a single-particle operator (separable for coordinate of each particle), the ground state only couples with 1-electron excited states

$$\langle \Lambda_{v_jc_k} - \sum_{m=1}^{N_e} eE \cdot r_m | \Lambda_0 \rangle = \int d\mathbf{r}_1 c^*_k(\mathbf{r}_1)(-eE \cdot \mathbf{r}_1)v_j(\mathbf{r}_1)$$  \hfill (87)

The change in ground state $\Lambda_0$ by external field only includes 1-electron excited states

$$\Lambda_{0}^{(1)} = \sum_{jk} \frac{\langle \Lambda_{v_jc_k} - \sum_{m=1}^{N_e} eE \cdot r_m | \Lambda_0 \rangle}{E_0 - E_{v_jc_k}} \Lambda_{v_jc_k} = \sum_{jk} \frac{\langle c_k(1)|eE \cdot r_1|v_j(1) \rangle}{(E_{C_k} - E_{c_1}) + (E_{v_1} - E_{v_j}) + E_g} \Lambda_{v_jc_k}$$  \hfill (88)

If we take Eq. \((6)\) and effect the multiple integral, the current density is

$$j^e(\mathbf{r}) = \frac{ie\hbar N_e}{2m\Omega} \left\{ \sum_{jk} \frac{\langle c_k(1)|eE \cdot r_1|v_j(1) \rangle}{(E_{C_k} - E_{c_1}) + (E_{v_1} - E_{v_j}) + E_g} \int_{\Omega_\mathbf{r}} d\mathbf{s}(v_j(\mathbf{s})\nabla_\mathbf{s}c^*_k(\mathbf{s}) - c^*_k(\mathbf{s})\nabla_\mathbf{s}v_j(\mathbf{s})) \right. $$

$$+ \sum_{jk} \frac{\langle c_k(1)|eE \cdot r_1|v_j(1) \rangle}{(E_{C_k} - E_{c_1}) + (E_{v_1} - E_{v_j}) + E_g} \int_{\Omega_\mathbf{r}} d\mathbf{s}(c_k(\mathbf{s})\nabla_\mathbf{s}v_j^*(\mathbf{s}) - v_j^*(\mathbf{s})\nabla_\mathbf{s}c_k(\mathbf{s})) \right\}$$  \hfill (89)

Using Eq. \((22)\), one can read off conductivity. Because the external field is much weaker than the atomic field, the numerator is much smaller than the energy gap $E_g$ (this will become more obvious in next section), the change $\Lambda_{0}^{(1)}$ in wave function $\Lambda_0$ can be neglected, and the dc conductivity is negligible at $T=0$ in an intrinsic semiconductor. The coupling between 0-electron to 1-electron excited states can be viewed as a cross band transition, its probability is not exactly zero, but is extremely small. One may neglect the existence of conduction band: electron cannot be accelerated when valence band is full. To accelerate an electron in ground state, one has to go from valence band to conduction band. The probability is negligible for an external field which is much weaker than atomic field.

3. Conduction from one-electron excited states

Because $H_{int}$ is single-particle operator, a 1-electron excited state could couple with ground state, 1-electron excited states and 2-electron excited states. The energy difference between a 1-electron excited state and a 2-electron excited state is at least energy gap $E_g$. The contribution to current density from this coupling is small. So does the coupling between a 1-electron excited state and $\Lambda_0$. 

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Since $H_{int}$ is a single-particle operator, there are only two types of coupling between two different 1-electron excited states: $\Lambda_{c_k c_k} \leftrightarrow \Lambda_{c_k c_{k'}}$ or $\Lambda_{c_k c_k} \leftrightarrow \Lambda_{c_{k'} c_k}$. The energy difference between such pairs of 1-electron excited states can be small if states $c_{k'}$ and $c_k$ ($v_{j'}$ and $v_j$) are properly chosen. Their contribution will be much larger than the coupling between a K-electron excited state and a $(K \pm 1)$-electron excited state.

The change in $\Lambda_{c_k c_k}$ caused by a static field is

$$\Lambda_{c_k c_k}' = \sum_{k'} \frac{\langle c_{k'}(1)|c_{k}(1) \rangle}{E_{c_k} - E_{c_{k'}}} \Lambda_{c_k c_k} + \sum_{j'} \frac{\langle v_{j'}(1)|v_{j}(1) \rangle}{E_{v_{j'}} - E_{v_j}} \Lambda_{v_{j'} c_k}$$

By appealing to Eqs. (15), (22) and (24), the expression of conductivity in momentum representation is

$$\sigma_{\alpha \beta} = \frac{e^2 \hbar^2 N_e}{m^2 \Omega_r} \sum_{j k} W_{v_{j} c_k} \mathrm{Im}\left\{ \sum_{k'} \frac{\langle c_{k'}(1)|c_{k}(1) \rangle}{(E_{c_{k'}} - E_{c_k})^2} \int_{\Omega_{k'}} dr \left( c_{k'}(r) \partial c_{k}^*(r) / \partial x_{\alpha} - c_{k}(r) \partial c_{k'}^*(r) / \partial x_{\alpha} \right) \right\}$$

$$+ \sum_{j'} \frac{\langle v_{j'}(1)|v_{j}(1) \rangle}{(E_{v_{j'}} - E_{v_j})^2} \int_{\Omega_{v}} dr \left( v_{j'}(r) \partial v_{j}^*(r) / \partial x_{\alpha} - v_{j}(r) \partial v_{j'}^*(r) / \partial x_{\alpha} \right) \right\}$$

The accelerated hole in the valence band and the accelerated electron in conduction band contribute most to the conduction, the coupling between K-electron and $(K \pm 1)$-electron excited states contributes much less. We have proven that degenerate states act like non-degenerate states, cf. Eq.(30). All the denominators in Eq.(91) are not zero. Except delta functions, Eq.(91), the contribution from 1-electron excited states, corresponds to the ordinary Greenwood formula.

In the standard procedure applying KGF\(^{10}\)

$$\sigma(T) = \int_{-\infty}^{\infty} dE \sigma(E) \left[ -\frac{df}{dE} \right] , \quad \sigma(E) = \frac{\pi \hbar^2}{\Omega m^2} \sum_{mn} |\langle n|p_{s}|m \rangle|^2 \delta(E_n - E) \delta(E_m - E)$$

one broadens delta function by a Gaussian

$$\delta(E_n - E) \approx \frac{\exp\left[ -(E_n - E)^2 / (2\Delta^2) \right]}{\Delta \sqrt{2\pi}}$$

Numerically, this procedure is equivalent to replace whole series about $(E_{v_{j'}} - E_{v_j})^{-2}$ in Eq.(91) with several large terms, each of order of $\Delta^{-2}$. There are two relevant energy scales in the problem: $k_B T$, and characteristic energy level splittings near $E_F$. The choices of $\Delta$ is thus somewhat arbitrary. On one hand $\Delta$ should be order of $k_B T$ to reflect thermal environment. However $k_B T$ is a too small choice of $\Delta$ for room temperature but may be
too large for a high temperature. On the other hand, $\Delta$ should be order of or smaller than the eigenvalue splittings near $E_F$. This choice depends on the size of a structural model and also depends on how many k–points one wishes to use. Thus KGF depends on a fortunate choice of $\Delta$, or requires some other extrapolation scheme to $\omega = 0$. Eq. (91) or Eq. (40) does not suffer from this problem.

4. Conduction from 2-electron excited states

Although a 2-electron excited state may couple with a 1-electron excited state or a 3-electron excited state, the energy differences are at least energy gap $E_g$. Later, we only consider the matrix elements between two 2-electron excited states. The 1st order correction to $\Lambda_{v_{j1}v_{j2} c_{p1} c_{p2}}$ is

$$\Lambda_{v_{j1}v_{j2} c_{p1} c_{p2}}^{(1)} = \sum_{j_1} \frac{\langle v_{j_1}'(1)|e\mathbf{E} \cdot \mathbf{r}_1|v_{j_1}(1)\rangle}{E_{v_{j_1}'}} \Lambda_{v_{j1}v_{j2} c_{p1} c_{p2}} + \sum_{j_2} \frac{\langle v_{j_2}'(1)|e\mathbf{E} \cdot \mathbf{r}_1|v_{j_2}(1)\rangle}{E_{v_{j_2}'}} \Lambda_{v_{j1}v_{j2} c_{p1} c_{p2}}$$

$$+ \sum_{p_1} \frac{\langle c_{p_1}'(1)|e\mathbf{E} \cdot \mathbf{r}_1|c_{p_1}(1)\rangle}{E_{c_{p_1}'} - E_{c_{p_1}}} \Lambda_{v_{j1}v_{j2} c_{p1}'} c_{p_2} + \sum_{p_2} \frac{\langle c_{p_2}'(1)|e\mathbf{E} \cdot \mathbf{r}_1|c_{p_2}(1)\rangle}{E_{c_{p_2}'} - E_{c_{p_2}}} \Lambda_{v_{j1}v_{j2} c_{p1} c_{p2}}$$

where we keep the single-electron wave functions in each Slater determinant in a fixed order. Substitute Eq. (94) into Eq. (6) and effect the multiple integral, the macroscopic current density is then:

$$\mathbf{j}(r') = \frac{ieN_e}{2m\Omega'} \sum_{j_1,j_2,(>)j_1} \sum_{p_1,p_2,(>)p_1} W_{v_{j_1}v_{j_2} c_{p_1} c_{p_2}}$$

$$\times \left\{ \sum_{j_1(\neq j_1)} \frac{\langle v_{j_1}'(1)|e\mathbf{E} \cdot \mathbf{r}_1|v_{j_1}(1)\rangle^*}{E_{v_{j_1}'} - E_{v_{j_1}}} \int_{\Omega'} d\mathbf{r} (v_{j_1}(\mathbf{r})\nabla_r v_{j_1}^*(\mathbf{r}) - v_{j_1}^*(\mathbf{r})\nabla_r v_{j_1}(\mathbf{r})) \right\}$$

$$+ \sum_{j_2(\neq j_2)} \frac{\langle v_{j_2}'(1)|e\mathbf{E} \cdot \mathbf{r}_1|v_{j_2}(1)\rangle^*}{E_{v_{j_2}'} - E_{v_{j_2}}} \int_{\Omega'} d\mathbf{r} (v_{j_2}(\mathbf{r})\nabla_r v_{j_2}^*(\mathbf{r}) - v_{j_2}^*(\mathbf{r})\nabla_r v_{j_2}(\mathbf{r}))$$

$$+ \sum_{p_1(\neq p_1)} \frac{\langle c_{p_1}'(1)|e\mathbf{E} \cdot \mathbf{r}_1|c_{p_1}(1)\rangle^*}{E_{c_{p_1}'} - E_{c_{p_1}}} \int_{\Omega'} d\mathbf{r} (c_{p_1}(\mathbf{r})\nabla_r c_{p_1}^*(\mathbf{r}) - c_{p_1}^*(\mathbf{r})\nabla_r c_{p_1}(\mathbf{r}))$$

$$+ \sum_{p_2(\neq p_2)} \frac{\langle c_{p_2}'(1)|e\mathbf{E} \cdot \mathbf{r}_1|c_{p_2}(1)\rangle^*}{E_{c_{p_2}'} - E_{c_{p_2}}} \int_{\Omega'} d\mathbf{r} (c_{p_2}(\mathbf{r})\nabla_r c_{p_2}^*(\mathbf{r}) - c_{p_2}^*(\mathbf{r})\nabla_r c_{p_2}(\mathbf{r}))$$

$$+ \sum_{j_1(\neq j_1)} \frac{\langle v_{j_1}(1)|e\mathbf{E} \cdot \mathbf{r}_1|v_{j_1}(1)\rangle}{E_{v_{j_1}'} - E_{v_{j_1}}} \int_{\Omega'} d\mathbf{r} (v_{j_1}(\mathbf{r})\nabla_r v_{j_1}^*(\mathbf{r}) - v_{j_1}^*(\mathbf{r})\nabla_r v_{j_1}(\mathbf{r}))$$

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Using Eq. (22), one can pick off the conductivity from coupling between 2-electron excited states.

B. Metals

In a metal, the conduction band is partly filled. Relative to the Fermi surface, holes and electrons are in the same conduction band. The energy difference between hole and electron always can be taken as small. Beside the non-existent energy gap, the difference between a metal and a semiconductor is that the number of carriers \( \sim \frac{k_B T}{E_F} N_e \) in the former is greatly larger than that in the later. It is easy to check

\[
\int dr_1 dr_2 dr_3 \frac{1}{\sqrt{3!}} \begin{vmatrix}
  l'_1(1) & l'_1(2) & l'_1(3) \\
  l'_2(1) & l'_2(2) & l'_2(3) \\
  l'_3(1) & l'_3(2) & l'_3(3)
\end{vmatrix} (r_1 + r_2 + r_3) \frac{1}{\sqrt{3!}} \begin{vmatrix}
  l_1(1) & l_1(2) & l_1(3) \\
  l_2(1) & l_2(2) & l_2(3) \\
  l_3(1) & l_3(2) & l_3(3)
\end{vmatrix}
\]

\[
= \langle l'_1 | r | l_1 \rangle (\delta_{l'_2 l_2} \delta_{l'_3 l_3} - \delta_{l'_2 l_3} \delta_{l'_3 l_2}) + \langle l'_2 | r | l_2 \rangle (\delta_{l'_1 l_1} \delta_{l'_3 l_3} - \delta_{l'_1 l_3} \delta_{l'_3 l_1}) + \langle l'_3 | r | l_3 \rangle (\delta_{l'_1 l_1} \delta_{l'_2 l_2} - \delta_{l'_1 l_2} \delta_{l'_2 l_1})
\]

\[
+ \langle l'_2 | r | l_1 \rangle (\delta_{l'_3 l_3} \delta_{l'_2 l_2} - \delta_{l'_3 l_2} \delta_{l'_2 l_3}) + \langle l'_3 | r | l_2 \rangle (\delta_{l'_1 l_1} \delta_{l'_2 l_2} - \delta_{l'_1 l_2} \delta_{l'_2 l_1}) + \langle l'_1 | r | l_3 \rangle (\delta_{l'_2 l_2} \delta_{l'_1 l_1} - \delta_{l'_2 l_1} \delta_{l'_1 l_2})
\]

there are 9 terms, each term has 2 sub-terms (they form a determinant). By induction method, one finds

\[
\langle \Lambda_{l'_1 l'_2 \cdots l'_{N_e}} | e \mathbf{E} \cdot \sum_{m=1}^{N_e} \mathbf{r}_m | \Lambda_{l_1 l_2 \cdots l_{N_e}} \rangle = \sum_{j,k=1}^{N_e} (-)^{j+k} \langle \chi_{l'_j} | e \mathbf{E} \cdot \mathbf{r} | \chi_{l_k} \rangle D_{j,k}^{(l_1 l_2 \cdots l_{N_e} l'_1 l'_2 \cdots l'_{N_e})} \]

where \( D_{j,k}^{(l_1 l_2 \cdots l_{N_e} l'_1 l'_2 \cdots l'_{N_e})} \) is a \((N_e - 1) \times (N_e - 1)\) determinant, each element of \( D \) is a Kronecker delta symbol. The row indices are \((l_1 l_2 \cdots l_{N_e})\) in which \( l_k \) is removed, the column indices
are \((l'_1 l'_2 \cdots l'_{N_e})\) in which \(l'_j\) is removed. For example

\[
D^{(l_1 l_2 \cdots l_{N_e}; l'_1 l'_2 \cdots l'_{N_e})}_{l_1 l'_1} = \begin{vmatrix}
\delta_{l_1 l'_1} & \delta_{l_1 l'_2} & \cdots & \delta_{l_1 l'_{N_e}} \\
\delta_{l_2 l'_1} & \delta_{l_2 l'_2} & \cdots & \delta_{l_2 l'_{N_e}} \\
\vdots & \vdots & \ddots & \vdots \\
\delta_{l_{N_e} l'_1} & \delta_{l_{N_e} l'_2} & \cdots & \delta_{l_{N_e} l'_{N_e}}
\end{vmatrix}
\] (98)

The first order change in the \(N_e\)-electron wave function is

\[
\Lambda_n^{(1)} = \sum_{l_1 l'_1 \cdots l_{N_e}} \sum_{j} \sum_{k} (-)^{j+k} \left( \frac{\langle \chi_{l'_j} | - e \mathbf{r} | \chi_{l_k} \rangle}{E_{l_k} - E_{l'_j}} \right) \Lambda_{l_1 l'_1 \cdots l_{N_e}} D_{j k}
\] (99)

Next, substitute Eq. (99) into the expression of current density, one finds the dc conductivity:

\[
\sigma_{\mu \nu} = \frac{e^2 h}{m \Omega} \sum_{l_1 l_2 \cdots l_{N_e}} W_{l_1 l_2 \cdots l_{N_e}} \text{Im} \sum_{l_1 l'_1 \cdots l_{N_e}} \sum_{j,k=1}^{N_e} (-)^{j+k} \left( \frac{\langle \chi_{l'_j} | x_\mu | \chi_{l_k} \rangle^*}{E_{l_k} - E_{l'_j}} \right) D^{(l_1 l'_1 \cdots l_{N_e}; l'_2 \cdots l'_{N_e})}_{l_2 l'_2 \cdots l_{N_e} l'_1} \int d\mathbf{r} \left( \frac{\partial \chi_{l_p}^*}{\partial x_\mu} - \chi_{l_p} \frac{\partial \chi_{l_p}}{\partial x_\mu} \right)
\] (100)

where \(D^{(l'_1 l'_2 \cdots l'_{N_e}; l_1 l_2 \cdots l_{N_e})}_{l_2 l'_2 \cdots l_{N_e} l'_1}\) is a \((N_e - 1) \times (N_e - 1)\) determinant, each element of which is a Kronecker delta symbol. The row indices are \((l'_1 l'_2 \cdots l'_{N_e})\) in which \(l'_q\) is removed. The column indices are \((l_1 l_2 \cdots l_{N_e})\) in which \(l_p\) is removed.

\[
W_{l_1 l_2 \cdots l_{N_e}} = \prod_{j=1}^{N_e} f(E_{l_j}), \quad f(E_{l_j}) = \frac{1}{1 + \exp \left( \frac{E_{l_j} - E_F}{k_B T} \right)}
\] (101)

is the appearing probability of \(N_e\)-electron state \(\Lambda_{l_1 l_2 \cdots l_{N_e}}\). Using the definition of Fermi distribution, it is easy to check

\[
f(\varepsilon) = \frac{1}{e^{\beta \varepsilon} + 1} = 1 - f(-\varepsilon), \quad \varepsilon = E - E_F
\] (102)

introducing an electron in a state above Fermi surface \((E > E_F)\) is equivalent to introduce a hole below Fermi surface \((E < E_F)\). It is clear from Eq.(101), the states around Fermi surface contribute most to conductivity, as expected.

In a semiconductor, due to the energy gap \(E_g\), the appearing probability of a K-electron excited state includes a factor \(e^{-KE_g/k_B T}\). To calculate the conductivity, it is enough to restrict attention to the excited states with few electrons. In a metal, the conduction band is half-filled, and there exist many low-energy excited states. One must count all electrons although only a shell \(k_B T / E_F\) close to Fermi surface makes an important contribution.
C. Homogeneous doped semiconductor

In a weakly n-type doped semiconductor, there are substitutional atoms or interstitial atoms. The energy levels of the former lie just below the bottom of conduction band; the energy levels of the later lie above the Fermi level \( \mu_i \) of the intrinsic matrix. There are three contributions to conductivity: (1) electrons from substitutional donors, given by Eq. (100), \( E_F \) is the chemical potential of doped material in Eq. (101); (2) carriers from interstitial atoms; (3) carriers from intrinsic matrix. Parts (2) and (3) can be calculated by Eq. (91). Similar consideration is applicable to weakly p-type doped semiconductors.

IV. SUMMARY

We discussed some foundational issues with respect to computing the conductivity, and improved the Kubo-Greenwood formula by computing dc and ac conductivity from current density, in which only the amplitude of probability, and not the transition probability itself is used. Eqs. (40) and (48) are key new contributions of this paper. In this method, the expression of dc conductivity is extracted from the ac conductivity in a direct way. We found that (1) the contribution from the states which are near or in resonance with finite frequency external field is finite; (2) the contribution from degenerate states in low frequency or zero frequency external field is finite; (3) the energy conserving \( \delta \)-function does not appear in the improved expression, thus one can avoid artificial numerical broadening. In the formulation of many-body perturbation theory, i.e. “method (2)” for calculating the current density, the many-electron statistics is displayed explicitly. One example is that the dc conductivity of an intrinsic semiconductor at \( T=0K \) is zero. For an intrinsic semiconductor, Kubo-Greenwood formula is the contribution from 1-electron excited states.

V. APPENDICES

A. Conductivity from degenerate states in a low frequency external field

We first compute the first order correction to \( \chi_{P\nu}^{(0)}(t) \):

\[
\chi_{P\nu}^{(1)}(t) = \sum_j a^{(1)}_{P\nu j}(t) \chi_j e^{-itE_j/\hbar} + \sum_{\mu'} \sum_{P\nu' \rho \nu''} a^{(1)}_{P\nu' \rho \nu''}(t) \chi_{P\nu''}^{(0)} e^{-itE_{P\nu''}/\hbar} \tag{103}
\]
Now the zeroth order wave functions are

\[ \cdots \chi_k \cdots; \quad \chi^{(0)}_{p_1}, \chi^{(0)}_{p_2}, \cdots, \chi^{(0)}_{p_M} \]

At an initial moment, one electron is in state \( \chi^{(0)}_{p_0} \): \( a_{p_0}(-\infty) = 1 \) and other coefficients are zero. If the interaction time with field is not too long, \( a_{p_0}(t) \) is dominant. For a non-degenerate state \( \chi_j \), \( a^{(1)}_{p_j}(t) \) is determined by

\[
\frac{da_j(t)}{dt} = -\frac{i}{2\hbar} G_{jp_0}(e^{i\omega t} + e^{-i\omega t}) a_{p_0}(t) e^{i\omega_j t} 
\tag{104}
\]

The solution which satisfies initial condition \( a_j(-\infty) = 0 \) is

\[
a_{p_j}(t) = -\frac{1}{2\hbar} G_{jp_0} \left[ \frac{e^{i(\omega + \omega_{jp_0} + i\delta)t/\hbar}}{\omega_{jp_0} + \omega + i\delta} + \frac{e^{i(\omega_{jp_0} - \omega + i\delta)t/\hbar}}{\omega_{jp_0} - \omega + i\delta} \right], \quad \delta \to 0^+ 
\tag{105}
\]

For a member of the degenerate states \( \chi_{p_{\mu'}} (\mu' \neq \mu) \), \( a_{p_{\mu'}}(t) \) satisfies

\[
i\hbar \frac{da_{p_{\mu'}}(t)}{dt} e^{-itE_{p_{\mu'}/\hbar}} = \sum_k a_k(t) G_{p_{\mu'k}} e^{-itE_k/\hbar} \frac{e^{it\omega}}{2} + e^{-it\omega} 
\tag{106}
\]

and initial condition \( a_{p_{\mu'}}(-\infty) = 0 \). Index \( k \) in RHS of Eq.\( (106) \) runs over non-degenerate states only. Because Eq.\( (55) \), no coupling among \( \{ \chi^{(0)}_{p_{\mu}} \} \) in Eq.\( (106). \) \( a^{(1)}_{p_{\mu'p_{\mu'}}}(t) \) is given by

\[
a_{p_{\mu'p_{\mu'}}}(t) = \frac{1}{4\hbar^2} \sum_k G_{p_{\mu'k}} G_{kp_{\mu}} \left\{ \frac{1}{\omega_{kp_{\mu}} + \omega - \omega_{p_{\mu'}} - \omega_{p_{\mu'}} + i\delta} \right. \\
+ \left. \frac{1}{\omega_{kp_{\mu}} - \omega - \omega_{p_{\mu'}} + i\delta} \right. \\
+ \left. \frac{1}{\omega_{kp_{\mu}} - \omega + \omega_{p_{\mu'}} - \omega_{p_{\mu'}} + i\delta} \right. \\
+ \left. \frac{1}{\omega_{kp_{\mu}} + \omega + \omega_{p_{\mu'}} + i\delta} \right\} 
\tag{107}
\]

When \( \omega \to 0 \), all the denominators of Eqs.\( (105) \) and \( (107) \) are non-zero. For degenerate states in a zero frequency external field, the artificial singularity of perturbation formula \( (37) \) is removed.

Combining Eqs.\( (103), \ (105), \ (107) \) and \( (31) \), the macroscopic current density can be written as

\[
\vec{j}_e'(\vec{r}', t) = \vec{j}_{e_{\text{non}}}(\vec{r}', t) + \vec{j}^e_e(\vec{r}', t) + \vec{j}^e_s(\vec{r}', t) + \vec{j}^e_{c2}(\vec{r}', t) + \vec{j}^e_{s2}(\vec{r}', t) + \vec{j}^e_0(\vec{r}') 
\tag{108}
\]

where \( \vec{j}_{e_{\text{non}}}(\vec{r}', t) \) is the contribution from non-degenerate states, and is obtained by replacing \( \sum_{\alpha=1}^{N_e} \) by \( \sum_{\alpha=1}^{N_e-M} \) (sum over only non-degenerate states) in Eq.\( (39) \).

\[
\vec{j}^e_e(\vec{r}', t) = \cos \omega t \frac{e}{2m\Omega'_{r'}} \sum_{l_1l_2 \cdots l_{N_e}} W_{l_1l_2 \cdots l_{N_e}} \sum_{\mu=1}^{M} \sum_j (1 - n_j) 
\tag{109}
\]

\[ \]
\[
\frac{1}{\omega_{j\mu} + \omega} + \frac{1}{\omega_{j\mu} - \omega}\right] \text{Im} G_{j\mu} \int_{\Omega} ds (\chi_j \nabla s \chi_{\mu}^{(0)*} - \chi_{\mu}^{(0)*} \nabla s \chi_j)
\]
is the component with cos \(\omega t\) factor.

\[
j^c_2(r', t) = \sin \omega t \frac{e}{2m\Omega_r'} \sum_{l_1l_2 \cdots l_{Ne}} W_{l_1l_2 \cdots l_{Ne}} \sum_{\mu=1}^M \sum_{\mu'} (1 - n_{\mu'}) \sum_k \left( \frac{1}{\omega_{kp} + \omega_{p\mu'}\mp\omega} + \frac{1}{\omega_{kp} - \omega_{p\mu'}\mp\omega} - \frac{1}{\omega_{kp} - \omega_{p\mu'}\pm\omega} \right) \text{Im} G_{p\mu'k} G_{kp} \int_{\Omega} ds (\chi_{p\mu'}^{(0)*} \nabla s \chi_{p\mu}^{(0)} - \chi_{p\mu'}^{(0)} \nabla s \chi_{p\mu}^{(0)*})
\]
is the component with \(2\omega t\) factor.

\[
j^c_0(r') = \frac{e}{4\hbar m\Omega_r'} \sum_{l_1l_2 \cdots l_{Ne}} W_{l_1l_2 \cdots l_{Ne}} \sum_{\mu=1}^M \sum_{\mu'} (1 - n_{\mu'}) \sum_k \left( \frac{1}{\omega_{kp} + \omega_{p\mu'}\mp\omega} + \frac{1}{\omega_{kp} - \omega_{p\mu'}\mp\omega} - \frac{1}{\omega_{kp} - \omega_{p\mu'}\pm\omega} \right) \text{Im} G_{p\mu'k} G_{kp} \int_{\Omega} ds (\chi_{p\mu'}^{(0)*} \nabla s \chi_{p\mu}^{(0)} - \chi_{p\mu'}^{(0)} \nabla s \chi_{p\mu}^{(0)*})
\]
is the component without time variation factor. Using Eq. (22), one can easily identify the conductivity.

In Eqs. (109)-(113), the summation over \(j\) or \(k\) is not restricted to \((l_1l_2 \cdots l_{Ne})\): it extends to all single-electron states. \(j^c_2\), \(j^c_2\) and \(j^c_0\) come from indirect coupling among \(\{\chi_{p\mu}^{(0)} : \mu = 1, 2, \cdots, M\}\) through non-degenerate states. Interaction with external field appear twice in Eq. (107), three new time factors \(\cos 2\omega t\), \(\sin 2\omega t\) and \(1\), which are different from the original time factors \(e^{-it\omega}\) and \(e^{it\omega}\) of the external field, come from the 2nd order harmonic generations.
B. Conductivity from resonant states

To compute the contribution of two groups of resonant states to the current, we need the 1st order wave function

\[ \chi_q^{(1)}(t) = \sum_s a_s^{(1)} e^{-iE_s t/\hbar} \chi_s + \sum_k a_n^{(1)} e^{-iE_n t/\hbar} \chi_n + \sum_j a_m^{(1)} e^{-iE_m t/\hbar} \chi_m \]  

(114)

where \( s \) indicates the states which do not belong to the upper and lower degenerate groups. \( j \) scans over the upper group \((\chi_{m1}, \chi_{m2}, \ldots, \chi_{mJ})\); \( k \) scans over the lower group \((\chi_{n1}, \chi_{n2}, \ldots, \chi_{nJ})\). Suppose initially the system is in the \( q \)th mode of the resonance states, the first order evolution equation is then:

\[ i\hbar \frac{da_s^{(1)}}{dt} = \sum_j [F_{smj} e^{it(\omega_{smj} - \omega)} + F_{mj s}^* e^{it(\omega_{smj} + \omega)}]a_s^{(0)} + \sum_k [F_{slnk} e^{it(\omega_{slnk} - \omega)} + F_{lnk s}^* e^{it(\omega_{slnk} + \omega)}]a_l^{(0)} \]  

(115)

The solution of Eq.(115) is

\[ a_s^{(1)}(t) = -\frac{1}{\hbar} \sum_j \left[ \frac{F_{smj}}{\omega_{smj} - \omega + \alpha_q} e^{it(\omega_{smj} - \omega + \alpha_q)} + \frac{F_{mj s}^*}{\omega_{smj} + \omega + \alpha_q} e^{it(\omega_{smj} + \omega + \alpha_q)} \right] a_s^{(0)} \]  

(116)

\[ -\frac{1}{\hbar} \sum_k \left[ \frac{F_{slnk}}{\omega_{slnk} - \omega + \alpha_q - \epsilon} e^{it(\omega_{slnk} - \omega + \alpha_q - \epsilon)} + \frac{F_{lnk s}^*}{\omega_{slnk} + \omega + \alpha_q - \epsilon} e^{it(\omega_{slnk} + \omega + \alpha_q - \epsilon)} \right] b_l^{(0)} \]

For a member of the upper group, the first order probability amplitude is determined by:

\[ i\hbar \frac{da_m^{(1)}}{dt} = \sum_{k=1}^{M'} F_{nmj}^* e^{it(\omega + \epsilon)} a_n^{(0)} + \sum_{j'} \left[ F_{mj m'} e^{-i\omega t} + F_{m' m}^* e^{i\omega t} \right] a_m^{(0)} \]  

(117)

\[ + \sum_s \left[ F_{mjs} e^{it(\omega_{mjs} - \omega)} + F_{smj}^* e^{it(\omega_{mjs} + \omega)} \right] a_s^{(1)}, \quad j = 1, 2, \ldots, M \]

Using Eq.(116), the solution of eq.(117) is

\[ a_m^{(1)} = -\frac{1}{\hbar} \sum_{k=1}^{M'} \frac{F_{nmj}^*}{2\omega + \alpha_q - \epsilon} e^{it(\omega + \alpha_q)} a_n^{(0)} - \frac{1}{\hbar} \sum_{j'\neq j} \left[ \frac{F_{mj m'} e^{it(\alpha_q - \omega)}}{\alpha_q - \omega} + \frac{F_{m' m}^* e^{it(\alpha_q + \omega)}}{\alpha_q + \omega} \right] a_m^{(0)} \]  

(118)

\[ + \frac{1}{\hbar^2} \sum_s \left[ \sum_{j'} \frac{F_{smj'} e^{it(\alpha_q - 2\omega)}}{(\omega_{smj'} - \omega + \alpha_q)(\alpha_q - 2\omega)} + \frac{F_{mj s}^* e^{it\alpha_q}}{(\omega_{smj'} + \omega + \alpha_q)\alpha_q} \right] a_q^{(0)} \]

\[ + \sum_k \left\{ \frac{F_{slnk} e^{it(\alpha_q - \omega)}}{\omega_{slnk} - \omega + \alpha_q - \epsilon}(\alpha_q - \omega) + \frac{F_{lnk s}^* e^{it(\alpha_q + \omega)}}{\omega_{slnk} + \omega + \alpha_q - \epsilon}(\alpha_q + \omega) \right\} b_l^{(0)} \]
\[\sum_j [F^*_{m'j} e^{-it\omega_j} + F^*_{m'j} e^{i(\omega_j + \alpha_q)\omega}] \alpha_{m'j} + \sum_{k'} [F^*_{n'k} e^{-it\omega_k} + F^*_{n'k} e^{i(\omega_k + \alpha_q)\omega}] \beta_{n'k'}\]

For a member of the lower group, the first order probability amplitude is determined by:

\[\frac{im}{\hbar} \frac{da^{(1)}_{nk}}{dt} = \sum_{j=1}^{M} F_{nkj} e^{-it(2\omega_j + \epsilon)} a^{(0)}_{mj} + \sum_{k' \neq k} [F_{nk'k}\alpha_{nk'} + \beta_{nk'} \alpha_{nk'}]\]

Using Eq. (116), the solution of Eq. (119) is

\[a^{(1)}_{nk}(t) = -\frac{1}{\hbar} \sum_{j=1}^{M} F_{nkj} e^{i(\omega_j + \alpha_q)\omega} a^{(0)}_{mj} - \frac{1}{\hbar} \sum_{k' \neq k} [F_{nk'k}\alpha_{nk'} + \beta_{nk'} \alpha_{nk'}]b^{(0)}_{nk'}\]

\[\sum_j [F^*_{m'j} e^{-it\omega_j} + F^*_{m'j} e^{i(\omega_j + \alpha_q)\omega}] \alpha_{m'j} + \sum_{k'} [F^*_{n'k} e^{-it\omega_k} + F^*_{n'k} e^{i(\omega_k + \alpha_q)\omega}] \beta_{n'k'}\]

Substituting Eqs. (116), (118) and (120) into Eqs. (114), by means of Eq. (31), one can find current density. The full formula is too long to write out, we only write down the contribution from coupling between non-resonant states and resonant states: in Eq. (114) only keep the first term. The current density with time factor \(\cos \omega t\) is

\[j_{e}(r, t) = \frac{e}{m \Omega_{e}} \cos \omega t \int_{\Omega_{e}} ds \sum_{l_{1}l_{2}...l_{N_{e}}} W_{l_{1}l_{2}...l_{N_{e}}} \sum_{q_{s}} (1 - n_{s}) \]

\[\text{Im}\{\sum_{jj'} a^{0}_{m'j} a^{0*}_{m'j} (x_{mj} \nabla x_{s} - x^{*}_{sj} \nabla x_{mj}) [F^*_{m'j} e^{-i(\omega_{m'j} + \omega + \alpha_q)\omega}] + F^*_{m'j} e^{i(\omega_{m'j} + \omega + \alpha_q)\omega}] + \sum_{kk'} b^{0}_{n'k} b^{0*}_{n'k} (x_{nk} \nabla x_{s} - x^{*}_{js} \nabla x_{nk}) [F^*_{n'k} e^{-i(\omega_{n'k} + \omega + \alpha_q - \epsilon)\omega}] + F^*_{n'k} e^{i(\omega_{n'k} + \omega + \alpha_q - \epsilon)\omega}]\]

The current density with time factor \(\sin \omega t\) is
\[ \mathbf{j}_s(\mathbf{r}, t) = -\frac{ie}{m\Omega_r} \sin \omega t \int_{\Omega_r} ds \sum_{l_1l_2 \cdots l_N_e} W_{l_1l_2 \cdots l_N_e} \sum_{qs} (1 - n_s) \]  

\[ \text{Im} \left\{ \frac{\sum_{jj'} a^{q^s}_{m_j} a^{q^s}_{m'_j} (\chi_s \nabla \chi_{m_j}^* + \chi_{m_j}^* \nabla \chi_s) [F^*_{sm_j'}] \frac{1}{\omega_{sm_j'} - \omega + \alpha_q} - \frac{F^*_{m_j} \chi^*_{m_j} \chi \nabla \chi_s} {\omega_{sm_j'} + \omega + \alpha_q} \right\} + \sum_{k'k} \frac{b^{q^s}_{n_k} b^{q^s}_{n'_k} (\chi_s \nabla \chi_{n_k}^* + \chi_{n_k}^* \nabla \chi_s) [F_{sm_k'}] \frac{1}{\omega_{sm_k'} - \omega + \alpha_q - \alpha}} {\omega_{sm_k'} + \omega + \alpha_q - \alpha} \]  

The current density with time factor \( \cos 2\omega t \) is

\[ \mathbf{j}_c^2(\mathbf{r}, t) = -\frac{ie}{m\Omega_r} \cos 2\omega t \int_{\Omega_r} ds \sum_{l_1l_2 \cdots l_N_e} W_{l_1l_2 \cdots l_N_e} \sum_{qs} (1 - n_s) \sum_{jk} \]  

\[ \text{Re} \left\{ a^{q^s}_{m_j} b^{q^s}_{n_k} (\chi_s \nabla \chi_{m_j}^* + \chi_{m_j}^* \nabla \chi_s) F^*_{n_k} \frac{1}{\omega_{n_k} + \omega + \alpha_q - \alpha} \right\} + a^{q^s}_{m_j} b^{q^s}_{n_k} (\chi_{n_k}^* \nabla \chi_s + \chi_s \nabla \chi_{n_k}^*) F_{sm_j} \frac{1}{\omega_{sm_j} - \omega + \alpha_q} \]  

The current density with time factor \( \sin 2\omega t \) is

\[ \mathbf{j}_s(\mathbf{r}, t) = -\frac{ie}{m\Omega_r} \sin 2\omega t \int_{\Omega_r} ds \sum_{l_1l_2 \cdots l_N_e} W_{l_1l_2 \cdots l_N_e} \sum_{qs} (1 - n_s) \sum_{jk} \]  

\[ \text{Im} \left\{ a^{q^s}_{m_j} b^{q^s}_{n_k} (\chi_{m_j} \nabla \chi_s^* + \chi^*_s \nabla \chi_{m_j}) F_{n_k} \frac{1}{\omega_{n_k} + \omega + \alpha_q - \alpha} \right\} + a^{q^s}_{m_j} b^{q^s}_{n_k} (\chi_{n_k}^* \nabla \chi_s + \chi_s \nabla \chi_{n_k}^*) F_{sm_j} \frac{1}{\omega_{sm_j} - \omega + \alpha_q} \]  

The current density without time variation factor is

\[ \mathbf{j}_0(\mathbf{r}) = -\frac{ie}{m\Omega_r} \int_{\Omega_r} ds \sum_{l_1l_2 \cdots l_N_e} W_{l_1l_2 \cdots l_N_e} \sum_{qs} (1 - n_s) \sum_{jk} \]  

\[ \text{Re} \left\{ a^{q^s}_{m_j} b^{q^s}_{n_k} (\chi_{m_j} \nabla \chi_s^* + \chi^*_s \nabla \chi_{m_j}) F_{n_k} \frac{1}{\omega_{n_k} - \omega + \alpha_q - \alpha} \right\} + a^{q^s}_{m_j} b^{q^s}_{n_k} (\chi_{n_k}^* \nabla \chi_s + \chi_s \nabla \chi_{n_k}^*) F_{sm_j} \frac{1}{\omega_{sm_j} + \omega + \alpha_q} \]  

The contribution to current from two groups of resonant states is finite. Using Eq. (22), one can again read off conductivity.
VI. ACKNOWLEDGEMENTS

We thank the Army Research Office for support under MURI W91NF-06-2-0026, and the National Science Foundation for support under grants DMR 0600073 and 0605890. DAD thanks the Leverhulme Trust (UK) and the National Science Foundation for sabbatical support.

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