Electrical conductivity calculations: Structural disorder and the role of degenerate or resonant electron states

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Within a single-electron picture and perturbation theory, expressions for the electrical conductivity (exemplified by the Kubo-Greenwood formula) exhibit divergences for degenerate states and states which are near resonance with an ac field. In this paper, we obtain expressions for the conductivity starting with a many-particle approach, and we emphasize the importance of quantum statistics for the expression for the conductivity. For weak topological disorder, the new conductivity expression can be reduced to semiclassical Boltzmann expressions at various levels of approximation. We show that contributions to current from degenerate states in a low-frequency field and states near or in resonance with an ac field are finite. For the ac case, to the first-order change in the degenerate states caused by external field, new components of current with zero frequency and double frequency are predicted. To the first-order change in the states which are near or in resonance with field, zero-frequency, double-frequency and triple-frequency components of current appear. Zero dc conductivity at $T=0$ K in an intrinsic amorphous semiconductor can be directly demonstrated if we first calculate the change in many-electron wave functions caused by an external field. We show that for an intrinsic semiconductor, the conventional Kubo-Greenwood formula represents the contribution from single-particle excited states.

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I. INTRODUCTION

The theory of charge-carrier transport in materials is of the highest importance to modeling studies of devices and nanoscale electronics. Most often, the method of linear-response theory[1] is employed to forge links between experiments and computation. It has been implemented in the Green's function formalism,[2–4] in density-functional theory[5–8] and in time-dependent density-functional theory.[9–12] The Kubo-Greenwood formula (KGF) (Ref. 13) (as an example) has been used with great success to calculate the electrical conductivity from first-principles simulations.[14–19]

In connection with disorder and the scaling theory of localization, linear-response theory for the conductance has seen further development[20–28] since the 1980s. These investigations illustrated the significance of different geometries on the observed conductance. In the scattering formalism,[20–25,28] the effect of an external field on the system is factored out at an early stage: the linear dependence of current on external field is imposed at the outset. Consequently, the change in wave function caused by external field does not appear in the conductance. The direct current (dc) and alternating current (ac) conductances are expressed by the elements of the scattering matrix. The scattering matrix is determined by the disorder potential and the wave function outside the disorder region.

Conductivity of a substitutional alloy A_xB_{1-x} can be effectively computed using a combination of coherent potential approximation (CPA) and the muffin-tin potential model.[29–31] The full scattering operator is given by a standard series which prevents electrons from scattering twice in sequence on the same site.[29] CPA asserts that statistical correlations of single-atom t-matrices and corresponding effective wave of the effective medium are negligible. Then the vertex corrections of the current operator are a sum of single-site contributions. However the Green's function of the effective wave is not a property of the virtual crystal and has to use information from the fluctuating part of the potential.[29] With the muffin-tin potential model, the Green's function of the effective wave can be computed.[32] This labor can be saved if one first formulates transport coefficients in the muffin-tin potential model of alloy A_xB_{1-x}, and then applies CPA to simplify the scattering path operator.[30] In the "wave-vector" representation, the vertex correction of current operator takes a simpler form.[30] However, the method of CPA+muffin-tin potential is not easily applied to amorphous solids with topological disorder. In a first-principles simulation, one does not make a distinction between substitutional disorder and topological disorder. A large enough cell may be taken to represent the disorder present in an amorphous solid.[33]

Greenwood's derivation of the conductivity used the transition probability between two single-electron states caused by an oscillating external field,[13,34–36] in such a way that the interaction time must be long enough to assure that the transition probability is well defined. To make perturbation theory applicable, the interaction time should be short. For a large system, in which the energy spectrum is continuous, these two conditions are not always well satisfied. One well-known example is small-polaron hopping. Due to the quasicontinuity of the phonon spectrum, the resultant activation energy is very different from what is expected from the time integral of ordinary perturbation theory (the energy difference between two states).[37] In addition, the ordinary perturbation theory for nondegenerate states is not applicable to compute the contribution to current from the accidental degeneracy in some crystals,[38] from states which are in resonance with an ac external field and from degenerate localized states in amorphous semiconductors.

In this paper we first derive the expression for the current density from the principle of virtual work and coarse average

in Sec. II. Although the resulting expression for the current is equivalent to what was obtained from averaging the current operator with the time-dependent density matrix,[26,27] this approach makes it easier to include contributions from degenerate states and states which are in resonance with an ac field, which are ignored in previous work. If topological disorder is weak, the new conductivity formula can be reduced to semiclassical Boltzmann form.

For many practical calculations, the single-particle approximation must be invoked at some stage, and the mode in which this is carried out can produce different results. In earlier studies, workers applied the single-particle approximation to the many-electron wave function first and then considered the effect of an external field on the single-particle states. In Secs. III and IV, we also use this *ansatz*. In Sec. III, the dc conductivity is deduced from *stationary*-state perturbation theory. The expression is not quite correct, as the fermion "unoccupation" factor for the final state is lost. In previous work,[26,27,34–36] ordinary time-dependent perturbation theory was used to compute the change in wave function. In a low- or zero-frequency field, degenerate states lead to an artificial singularity in the expression for the current density. The dc conductivity is then obtained from ac conductivity by taking the zero-frequency limit. In Sec. IV, we separately calculate the contributions to ac conductivity from nondegenerate states, degenerate states, and states which are in resonance with a finite-frequency external field. Ordinary time-dependent perturbation theory is applied to nondegenerate states in Sec. IV A. This is the circumstance treated in previous work.[13,26,27,34–36] If the disorder in an amorphous solid is so small that a virtual crystal exists, we show in Sec. IV B that KGF reduces to Boltzman formulation at various levels of approximation. Comparison with Greenwood's formula is made in Sec. IV C. Because only the amplitude of transition probability caused by external field appears in the expression of current density, the long-time limit which is necessary to define transition probability per unit time is no longer needed.

In ordinary time-dependent perturbation theory, degenerate states in a low- or zero-frequency external field and states which are near or in resonance with a finite-frequency field create *artificial* poles in the wave function perturbed by external field. For degenerate states in a low- or zero-frequency field, one traditionally chooses a suitable integral contour to bypass the poles by adiabatically introducing the external field.[27,39] This procedure is not suited to localized states in an amorphous semiconductors. As we will explain later, localized states must be treated as discrete. Furthermore, the current density should be free of any singularity. In Sec. IV D, we develop time-dependent perturbation theory for degenerate states in a low-frequency external field. The zeroth-order contribution from degenerate states is shown to vanish and the first-order contribution of degenerate states is finite. In the new expression, the dc conductivity can be obtained from the ac conductivity by directly taking the value at $\omega=0$. In an ac field, the first-order corrections of the degenerate states lead to new components of current with complex field dependence. The components of current from direct coupling between degenerate states and nondegenerate states formally have linear dependence on field. But highly nonlinear field dependence enters through new zero-order eigenvalues and new zero-order wave functions of the degenerate states. The components of current from indirect coupling between two degenerate states mediated by a nondegenerate state have new time factors with double frequency and zero frequency. Formally they have second-order field dependence just as second-order nonlinear effect caused by nondegenerate states. However the nonlinear effect caused by nondegenerate states cannot exist in a system with inversion symmetry[40] while those caused by degenerate states are not sensitive to the symmetry of the system.

In Sec. IV E, we develop time-dependent perturbation theory for states which are near or in resonant with a finite-frequency external field. The zeroth-order contribution to conductivity is zero. The first-order contribution of these states is finite. The first-order correction of the states which are near or in resonance with an external field lead to new components of current at triple frequency, double frequency, and zero frequency. Some zero-frequency and double-frequency components formally associate with first-order field dependence. This is in contrast to usual second-order effect caused by nondegenerate states but also in contrast to the double-frequency components caused by degenerate states. At a finite-frequency monochromatic external field, RLC circuits with resonance frequencies 2ω and 3ω can detect new double-frequency and triple-frequency components of current, respectively.

In Sec. V, we compute the change in many-electron wave function induced by the external field and show that the dc conductivity can then be derived from stationary-state perturbation theory. In this analysis, the role of many-electron statistics on conductivity can be handled automatically. For an intrinsic semiconductor, we show that the KGF gives only the contribution from single-particle excitations, cf. Eq. (95).

II. CURRENT DENSITY

If the motion of nuclei are treated classically [as in *ab initio* molecular dynamics (MD) codes], the average energy $\bar{H}$ of the electron+nuclei system in an electromagnetic field described by vector potential $\mathbf{A}$ and scalar potential φ is given by

$$\bar{H} = \int d\mathbf{r}_1 \ldots d\mathbf{r}_{N_e} \Lambda'^{*}_{\{\mathbf{W}_1 \ldots \mathbf{W}_{\mathcal{N}}\}}(\mathbf{r}_1 \ldots \mathbf{r}_{N_e}) H'_e \Lambda'_{\{\mathbf{W}_1 \ldots \mathbf{W}_{\mathcal{N}}\}}(\mathbf{r}_1 \ldots \mathbf{r}_{N_e}) + \sum_\alpha \frac{1}{2M_\alpha}[\mathbf{P}_\alpha - q_\alpha \mathbf{A}(\mathbf{W}_\alpha)]^2 + \sum_\alpha q_\alpha \varphi(\mathbf{W}_\alpha)$$
$$+ \sum_{\alpha,\beta(>\alpha)} V(\mathbf{W}_\alpha, \mathbf{W}_\beta), \tag{1}$$

where q_α, M_α, $\mathbf{P}_\alpha$, and $\mathbf{W}_\alpha$ are the effective charge, mass, canonical momentum, and position vector of the αth nucleus. $V(\mathbf{W}_\alpha,\mathbf{W}_\beta)$ is the interaction between the αth nucleus and the βth nucleus. Here,

$$H'_e = \sum_{j=1}^{N_e}\left\{\frac{1}{2m}[\mathbf{p}_j - e\mathbf{A}(\mathbf{r}_j)]^2 + e\varphi(\mathbf{r}_j)\right\} + \sum_{jk} V(\mathbf{r}_j,\mathbf{r}_k) + \sum_{j\alpha} V(\mathbf{r}_j,\mathbf{W}_\alpha) \quad (2)$$

is the electronic Hamiltonian in the external electromagnetic field. $V(\mathbf{r}_j,\mathbf{r}_k)$ is the interaction between an electron at $\mathbf{r}_j$ and another electron at $\mathbf{r}_k$, $V(\mathbf{r}_j,\mathbf{W}_\alpha)$ is the interaction between an electron at $\mathbf{r}_j$ and the αth nucleus at $\mathbf{W}_\alpha$. The stationary state of electrons is determined by

$$H'_e\Lambda'_{\{\mathbf{W}_1\ldots\mathbf{W}_\mathcal{N}\}}(\mathbf{r}_1\ldots\mathbf{r}_{N_e}) = E'^{e}_{\{\mathbf{W}_1\ldots\mathbf{W}_\mathcal{N}\}}\Lambda'_{\{\mathbf{W}_1\ldots\mathbf{W}_\mathcal{N}\}}(\mathbf{r}_1\ldots\mathbf{r}_{N_e}), \quad (3)$$

where $\Lambda'_{\{\mathbf{W}_1\ldots\mathbf{W}_\mathcal{N}\}}(\mathbf{r}_1\ldots\mathbf{r}_{N_e})$ being the many-electron wave function of H'_e for a given nuclear configuration $\{\mathbf{W}_1\ldots\mathbf{W}_\mathcal{N}\}$ belonging to eigenvalue $E'^{e}_{\{\mathbf{W}_1\ldots\mathbf{W}_\mathcal{N}\}}$. We use H_e to denote H'_e when the external field does not appear, $\Lambda_{\{\mathbf{W}_1\ldots\mathbf{W}_\mathcal{N}\}}$ is eigenfunction of H_e belonging to eigenvalue $E^{e}_{\{\mathbf{W}_1\ldots\mathbf{W}_\mathcal{N}\}}$. Hereafter we use a primed symbol to denote a quantity in the presence of an external field, the corresponding symbol without the prime to denotes the quantity in zero field. In a MD formulation, the positions of the nuclei are provided as snapshots from MD time 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 $\Lambda_{\{\mathbf{W}_1\ldots\mathbf{W}_\mathcal{N}\}}(\mathbf{r}_1\mathbf{r}_2\mathbf{r}_3\ldots\mathbf{r}_{N_e})$ is calculated from the configuration $\{\mathbf{W}_1\ldots\mathbf{W}_\mathcal{N}\}$, the forces on each nucleus is then calculated from $\Lambda_{\{\mathbf{W}_1\ldots\mathbf{W}_\mathcal{N}\}}(\mathbf{r}_1\mathbf{r}_2\mathbf{r}_3\ldots\mathbf{r}_{N_e})$. The ionic time evolution is given by integrating Newton's second law.[33]

According to the principle of virtual work, for a given state Λ', the microscopic electric current density $\mathbf{j}_m(\mathbf{r}) = -\delta\bar{H}/\delta\mathbf{A}(\mathbf{r})$ at point $\mathbf{r}$ is[39]

$$\mathbf{j}_m(\mathbf{r}) = N_e\frac{i\hbar e}{2m}\int d\mathbf{r}_2 d\mathbf{r}_3\ldots d\mathbf{r}_{N_e}(\Lambda'\nabla_\mathbf{r}\Lambda'^{*} - \Lambda'^{*}\nabla_\mathbf{r}\Lambda') - \frac{e^2}{m}\mathbf{A}(\mathbf{r})n^e_{\{\mathbf{W}_1\ldots\mathbf{W}_\mathcal{N}\}}(\mathbf{r}) + \sum_\alpha q_\alpha\mathbf{V}_\alpha\delta(\mathbf{r}-\mathbf{W}_\alpha), \quad (4)$$

where

$$n^e_{\{\mathbf{W}_1\ldots\mathbf{W}_\mathcal{N}\}}(\mathbf{r},t) = N_e\int d\mathbf{r}_2 d\mathbf{r}_3\ldots d\mathbf{r}_{N_e}\Lambda'^{*}_{\{\mathbf{W}_1\ldots\mathbf{W}_\mathcal{N}\}}(\mathbf{r}\mathbf{r}_2\mathbf{r}_3\ldots\mathbf{r}_{N_e})\Lambda'_{\{\mathbf{W}_1\ldots\mathbf{W}_\mathcal{N}\}}(\mathbf{r}\mathbf{r}_2\mathbf{r}_3\ldots\mathbf{r}_{N_e}) \quad (5)$$

is the number density of electrons at $\mathbf{r}$ for a given nuclear configuration $\{\mathbf{W}_1\ldots\mathbf{W}_\mathcal{N}\}$. Equation (4) is the response of the electronic+nuclear system to an external field; the first two terms are due to electrons and the last term to nuclei. The measured macroscopic current density at point $\mathbf{r}$ is[41,42] a spatial average of Eq. (4) over a region $\Omega_\mathbf{r}$ centered at $\mathbf{r}$

$$\mathbf{j}(\mathbf{r}) = \frac{1}{\Omega_\mathbf{r}}\int_{\Omega_\mathbf{r}} d\mathbf{s}\mathbf{j}_m(\mathbf{s}). \quad (6)$$

The linear size L of $\Omega_\mathbf{r}$ satisfies: $a \ll L \ll \lambda$, where a is a typical bond length, λ is the wavelength of external field or other macroscopic length scale. Equation (6) is the usual current density defined for an infinitesimal area.[41,42]

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

$$h'_a\chi'_l(\mathbf{r}) = E'_l\chi'_l(\mathbf{r}), \quad h'_a = \frac{1}{2m}[\mathbf{p} - e\mathbf{A}(\mathbf{r})]^2 + e\varphi(\mathbf{r}) + U[\mathbf{r},(\mathbf{W}_\alpha)], \quad (7)$$

where h'_a is the single-electron Hamiltonian in an external field, U is the single-electron potential due to nuclear configuration $\{\mathbf{W}_\alpha\}$. h_a, $\chi_l(\mathbf{r})$, and E_l are the corresponding quantities when external field does not appear: they are the Hamiltonian, eigenfunctions, and eigenvalues of a single-particle theory.

For solids without translational invariance, one cannot define wave vectors to label single-electron states. The effect of static disorder arises from the single-electron potential U. One role of static disorder is to localize band tail states. Although extended states are eigenstates of h_a, the carriers in extended states are scattered by the disorder potential. This is in contrast to crystals, where Bloch waves are not scattered by static lattice. In an amorphous solid, carriers move in and out of the sample in a conduction process. Unlike the case of an isolated sample, the wave function of an extended state is no longer zero at the boundaries of a system carrying a current. Thus, carriers in extended states are still scattered by the disorder potential.[43] The electron-vibration coupling assists the hopping motion of localized carriers and scatters the carriers in extended states.

The current density due to electrons may be computed as follows. At temperature $T>0$, the system can be in the ground or excited states. The electron current at temperature T arises from various excited states and the ground state

$$\mathbf{j}^e(\mathbf{r}) = \frac{i\hbar e N_e}{2m\Omega_{\mathbf{r}}} \int_{\Omega_{\mathbf{r}}} d\mathbf{s} \int d\mathbf{r}_2 d\mathbf{r}_3 \ldots d\mathbf{r}_{N_e} \sum_{l_1 l_2 \ldots l_{N_e}} W'_{l_1 l_2 \ldots l_{N_e}} (\Lambda'_{l_1 l_2 \ldots l_{N_e}} \nabla_{\mathbf{s}} \Lambda'^{*}_{l_1 l_2 \ldots l_{N_e}} - \Lambda'^{*}_{l_1 l_2 \ldots l_{N_e}} \nabla_{\mathbf{s}} \Lambda'_{l_1 l_2 \ldots l_{N_e}}), \tag{8}$$

where

$$\Lambda'_{l_1 l_2 \ldots l_{N_e}} = \frac{1}{\sqrt{N_e!}} \sum_P \delta_P P \chi'_{l_1}(\mathbf{s}, s_{z1}) \chi'_{l_2}(\mathbf{r}_2, s_{z2}) \chi'_{l_3}(\mathbf{r}_3, s_{z3}) \ldots \chi'_{l_{N_e}}(\mathbf{r}_{N_e}, s_{zN_e}) \tag{9}$$

is a N_e-electron state. Here P is a permutation of N_e objects $(\mathbf{r}_1 s_{z1}; \mathbf{r}_2 s_{z2}; \mathbf{r}_3 s_{z3}; \ldots; \mathbf{r}_{N_e} s_{zN_e})$, $\delta_P = 1$ if P is an even permutation, $\delta_P = -1$ if P is odd. Of course $l_1, l_2, \ldots, l_{N_e}$ are all distinct. Because any observable like $\mathbf{j}^e$ is bilinear in $\Lambda'_{l_1 l_2 \ldots l_{N_e}}$, the order of rows and the order of columns in $\Lambda'_{l_1 l_2 \ldots l_{N_e}}$ do not matter. We only need to maintain a fixed order at intermediate steps of the calculation. The sum is over all possible choices of N_e single-electron states. The arguments of Λ' are $(\mathbf{s}, \mathbf{r}_2, \mathbf{r}_3, \ldots, \mathbf{r}_{N_e})$. To save space the spin variables are abbreviated. The occupancy probability of state $\Lambda'_{l_1 l_2 \ldots l_{N_e}}$ is $W'_{l_1 l_2 \ldots l_{N_e}} = U'_{l_1 l_2 \ldots l_{N_e}} / Z'$, where $Z' = \Sigma_{l_1 l_2 \ldots l_{N_e}} U'_{l_1 l_2 \ldots l_{N_e}}$ and $U'_{l_1 l_2 \ldots l_{N_e}} = \exp[-(E'_{l_1 l_2 \ldots l_{N_e}} - E'_0)/(k_B T)]$. E'_0 is the energy of N_e-electron ground state. When no field is applied to the system, the macroscopic current does not appear in any state $\Lambda_{l_1 l_2 \ldots l_{N_e}}$. The current density from electrons reads

$$\mathbf{j}^e(\mathbf{r}) = \frac{i\hbar e N_e}{2m\Omega_{\mathbf{r}}} \int_{\Omega_{\mathbf{r}}} d\mathbf{s} \int d\mathbf{r}_2 d\mathbf{r}_3 \ldots d\mathbf{r}_{N_e} \sum_{l_1 l_2 \ldots l_{N_e}} W'_{l_1 l_2 \ldots l_{N_e}} [(\Lambda'_{l_1 l_2 \ldots l_{N_e}} \nabla_s \Lambda'^{*}_{l_1 l_2 \ldots l_{N_e}} - \Lambda'^{*}_{l_1 l_2 \ldots l_{N_e}} \nabla_s \Lambda'_{l_1 l_2 \ldots l_{N_e}}) - (\Lambda_{l_1 l_2 \ldots l_{N_e}} \nabla_s \Lambda^{*}_{l_1 l_2 \ldots l_{N_e}} - \Lambda^{*}_{l_1 l_2 \ldots l_{N_e}} \nabla_s \Lambda_{l_1 l_2 \ldots l_{N_e}})](\mathbf{s} \mathbf{r}_2 \mathbf{r}_3 \ldots \mathbf{r}_{N_e}). \tag{10}$$

For very low temperatures, $\langle \chi_{l_1} | -e\mathbf{E} \cdot \mathbf{r} | \chi_{l_1} \rangle \ll k_B T$ is not satisfied, so that linearizing $W'_{l_1 l_2 \ldots l_{N_e}}$ about field $\mathbf{E}$ is not legitimate: the current density is not necessarily linear about field. If temperature is *not too low* such that $\langle \chi_{l_1} | -eEr | \chi_{l_1} \rangle \ll k_B T$, we may expand the expression following the summation symbol in Eq. (10) to first order in the field. Because no macroscopic current exists when external field vanishes, Eq. (10) is simplified to

$$\mathbf{j}^e(\mathbf{r}) = \frac{i\hbar e N_e}{2m\Omega_{\mathbf{r}}} \int_{\Omega_{\mathbf{r}}} d\mathbf{s} \int d\mathbf{r}_2 d\mathbf{r}_3 \ldots d\mathbf{r}_{N_e} \sum_{l_1 l_2 \ldots l_{N_e}} W_{l_1 l_2 \ldots l_{N_e}} [(\Lambda'_{l_1 l_2 \ldots l_{N_e}} \nabla_{\mathbf{s}} \Lambda'^{*}_{l_1 l_2 \ldots l_{N_e}} - \Lambda'^{*}_{l_1 l_2 \ldots l_{N_e}} \nabla_{\mathbf{s}} \Lambda'_{l_1 l_2 \ldots l_{N_e}}) - (\Lambda_{l_1 l_2 \ldots l_{N_e}} \nabla_{\mathbf{s}} \Lambda^{*}_{l_1 l_2 \ldots l_{N_e}} - \Lambda^{*}_{l_1 l_2 \ldots l_{N_e}} \nabla_{\mathbf{s}} \Lambda_{l_1 l_2 \ldots l_{N_e}})](\mathbf{s} \mathbf{r}_2 \mathbf{r}_3 \ldots \mathbf{r}_{N_e}), \tag{11}$$

where

$$W_{l_1 l_2 \ldots l_{N_e}} = U_{l_1 l_2 \ldots l_{N_e}} / Z, \quad Z = \sum_{l_1 l_2 \ldots l_{N_e}} U_{l_1 l_2 \ldots l_{N_e}},$$

$$U_{l_1 l_2 \ldots l_{N_e}} = \exp[-(E_{l_1 l_2 \ldots l_{N_e}} - E_{v_1 v_2 \ldots v_{N_e}})/(k_B T)] \tag{12}$$

are the corresponding quantities without external field. In the single-particle approximation

$$W_{l_1 l_2 \ldots l_{N_e}} = \prod_{\alpha=1}^{N_e} f(E_{l_\alpha}), \quad f(E_{l_\alpha}) = \frac{1}{e^{(E_{l_\alpha} - \mu)/k_B T} + 1}, \tag{13}$$

where μ is the chemical potential at temperature T. The conductivity tensor $\sigma_{\mu\nu}$ is defined by relation

$$j_\mu = \sum_\nu \sigma_{\mu\nu} E_\nu, \quad \mu, \nu = x, y, z, \tag{14}$$

where E_ν is the νth Cartesian component of electric field and $\sigma_{\mu\nu}$ can be read out from Eq. (11).

The current density [Eq. (11)] and the conductivity deduced from it are for one instantaneous configuration of the ions. To include the effect of thermal vibrations, one should average the conductivity over a number of MD steps.[14,16] In a fixed temperature, MD simulation samples various atomic configurations around a realistic structure. There are other ways to handle thermal vibration, for example, from a traditional electron-phonon approach. The electron-phonon coupling is particularly large for localized states in amorphous semiconductors.[44]

The single-particle approximation can be applied in two different ways: (1) first express $\Lambda'_{l_1 l_2 \ldots l_{N_e}}$ with single-electron wave functions χ' and carry out the multiple integral $\int d\mathbf{r}_2 d\mathbf{r}_3 \ldots d\mathbf{r}_{N_e}$. Then view χ'_{l_α} as correction of χ_{l_α} under perturbation $-e\mathbf{E}\cdot\mathbf{r}$, where $\mathbf{r}$ is the position of electron. (2) View $\Lambda'_{l_1 l_2 \ldots l_{N_e}}$ as correction of $\Lambda_{l_1 l_2 \ldots l_{N_e}}$ under perturbation $-\sum_{m=1}^{N_e} e\mathbf{E}\cdot\mathbf{r}_m$, then effect the integral $\int d\mathbf{r}_2 d\mathbf{r}_3 \ldots d\mathbf{r}_{N_e}$. Most discussion about the KGF (Refs. 13 and 34–36) 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 Secs. III and IV, we will use method (1) and compare with previous results. Method (2) will be analyzed in Sec. V.

III. STATIONARY PERTURBATION THEORY FOR ESTIMATING dc CONDUCTIVITY

In current density Eq. (11), if we first apply the single-particle approximation to Λ' and use stationary perturbation theory to compute χ', then we are *not* able to fully include the role of many-electron statistics in dc conductivity. However the expressions so obtained can be used to test the self-consistency of the corresponding results from time-dependent perturbation theory. By means of Eq. (9) and working out $\int d\mathbf{r}_2 d\mathbf{r}_3 \ldots d\mathbf{r}_{N_e}$, Eq. (11) leads to

$$\mathbf{j}^e(\mathbf{r}) = \frac{i\hbar e}{2m\Omega_{\mathbf{r}}} \int_{\Omega_{\mathbf{r}}} d\mathbf{s} \sum_{l_1 l_2 \ldots l_{N_e}} W_{l_1 l_2 \ldots l_{N_e}} \sum_{\alpha=1}^{N_e} [(\chi'_{l_\alpha} \nabla_{\mathbf{s}} \chi'^{*}_{l_\alpha} - \chi'^{*}_{l_\alpha} \nabla_{\mathbf{s}} \chi'_{l_\alpha}) - (\chi_{l_\alpha} \nabla_{\mathbf{s}} \chi^{*}_{l_\alpha} - \chi^{*}_{l_\alpha} \nabla_{\mathbf{s}} \chi_{l_\alpha})]. \quad (15)$$

In a static electric field, the nuclei and the bound electrons are pushed in opposite directions. This leads to a static deformation of the material. Since a static electric field does not produce net velocities of the nuclei, the third term in Eq. (4) is zero. At this point, let us assume that all the single-electron states in Eq. (15) are nondegenerate. The case of degenerate states will be discussed later. From stationary perturbation theory, the first-order change $\chi'^{(1)}_c$ in the single-electron wave function due to the external field is

$$\chi'_c = \chi_c + \chi'^{(1)}_c, \quad \chi'^{(1)}_c = \sum_{d(\neq c)} \frac{\langle \chi_d | -e\mathbf{E}\cdot\mathbf{r} | \chi_c \rangle}{E_c - E_d} \chi_d, \quad (16)$$

where χ_c and E_c are the single-electron wave function and the corresponding eigenvalue without external field. Substituting Eq. (16) into Eq. (15), and only keeping the terms linear with external field, the dc conductivity is

$$\sigma_{\mu\nu} = \frac{e^2\hbar}{m\Omega} \sum_{l_1 l_2 \ldots l_{N_e}} W_{l_1 l_2 \ldots l_{N_e}} \sum_{\alpha=1}^{N_e} \sum_{l(\neq l_\alpha)} \frac{1}{E_{l_\alpha} - E_l} \mathrm{Im} \langle \chi_l | x_\nu | \chi_{l_\alpha} \rangle \int_\Omega d^3x \left(\chi_l \frac{\partial \chi^*_{l_\alpha}}{\partial x_\mu} - \chi^*_{l_\alpha} \frac{\partial \chi_l}{\partial x_\mu} \right). \quad (17)$$

The sum over $l(\neq l_\alpha)$ is not restricted to $(l_1 l_2 \ldots l_{N_e})$; it extends to all single-particle states. In an infinite system, the matrix element of the position operator is not well defined. Making use of

$$\langle \chi_d | x_\alpha | \chi_{l_\alpha} \rangle = \frac{\langle \chi_d | [h_a, x_\alpha] | \chi_{l_\alpha} \rangle}{E_d - E_{l_\alpha}} = \frac{\hbar^2}{m} \frac{\langle \chi_d | \frac{\partial}{\partial x_\alpha} | \chi_{l_\alpha} \rangle}{E_{l_\alpha} - E_d}, \quad (18)$$

one can convert the matrix elements of position into the matrix elements of momentum.[34]

Current use of the KGF amounts to assuming that beside l_α, other single-electron states in $\{l_1 l_2 \ldots l_{N_e}\}$ are occupied, and only the factor $f(E_{l_\alpha})$ is retained. Thus the sum over various choices of $\{l_1 l_2 \ldots l_{N_e}\}$ can be ignored if one extends the sum over α to all possible single-particle states. Equation (17) does not obviously display an obvious feature of an intrinsic semiconductor: the dc conductivity should vanish at zero temperature. In addition, due to the use of the single-particle approximation before applying perturbation theory, 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 of M-fold degenerate single-electron states $(\chi_{d_\sigma}, \sigma = 1, 2, \ldots, M)$ in $\Lambda_{l_1, l_2, \ldots, l_{N_e}}$, we first form correct zeroth-order wave functions

$$\chi'^{(0)}_{d_\sigma} = \sum_{\sigma'} C_{d_\sigma d_{\sigma'}} \chi_{d_{\sigma'}}, \quad \sigma, \sigma' = 1, 2, \ldots, M \quad (19)$$

and the secular equation satisfied by $C_{d_\sigma d_{\sigma'}}$ is

$$\sum_{\sigma'} (V_{d_\sigma d_{\sigma'}} - \varepsilon \delta_{d_\sigma d_{\sigma'}}) C_{d_\sigma d_{\sigma'}} = 0,$$

$$V_{d_\sigma d_{\sigma'}} = \int d\mathbf{r} \chi^*_{d_\sigma} (-e\mathbf{E}\cdot\mathbf{r}) \chi_{d_{\sigma'}}. \quad (20)$$

The perturbation matrix $(V_{d_\sigma d_{\sigma'}})$ is Hermitian, it can be diagonalized by a unitary transformation $(C_{d_\sigma d_{\sigma'}})$. Therefore

$$\sum_{\sigma} (\chi'^{(0)}_{d_\sigma} \nabla \chi'^{(0)*}_{d_\sigma} - \chi'^{(0)*}_{d_\sigma} \nabla \chi'^{(0)}_{d_\sigma}) = \sum_{\sigma} (\chi_{d_\sigma} \nabla \chi^{*}_{d_\sigma} - \chi^{*}_{d_\sigma} \nabla \chi_{d_\sigma}). \quad (21)$$

According to Eq. (15), 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 of the same energy, and thus makes no contribution to the conductivity.

The first-order correction to $\chi'^{(0)}_{d_\sigma}$ is[39]

$$\chi'^{(1)}_{d_\sigma} = \sum_{k} \frac{V_{kd_\sigma}}{E^{(0)}_{d_\sigma} - E^{(0)}_{k}} \chi_k + \sum_{\sigma'=1}^{M} \left[\frac{1}{\varepsilon_{d_\sigma} - \varepsilon_{d_{\sigma'}}} \sum_{k} \frac{V_{d_{\sigma'}k} V_{kd_\sigma}}{E^{(0)}_{d_\sigma} - E^{(0)}_{k}} \right] \chi'^{(0)}_{d_{\sigma'}}, \quad (22)$$

where

$$\varepsilon_{d_\sigma} = \int d\mathbf{r} \chi'^{*}_{d_\sigma}(-e\mathbf{E}\cdot\mathbf{r})\chi'_{d_\sigma},$$

$$V_{kd_\sigma} = \int d\mathbf{r} \chi^{*}_{k}(-e\mathbf{E}\cdot\mathbf{r})\chi'^{(0)}_{d_\sigma},$$

$$V_{d_{\sigma'}k} = \int d\mathbf{r} \chi'^{(0)*}_{d_{\sigma'}}(-e\mathbf{E}\cdot\mathbf{r})\chi_k, \quad (23)$$

where k indexes nondegenerate states. The first sum in Eq. (22) runs over all states which are not degenerate with $(\chi_{d_\sigma}, \sigma = 1, 2, \ldots, M)$.

Making use of Eq. (22), the macroscopic current density Eq. (15) becomes

$$\mathbf{j}(\mathbf{r}') = \frac{e^2\hbar}{m\Omega_{\mathbf{r}'}} \sum_{l_1 l_2 \ldots l_{N_e}} W_{l_1 l_2 \ldots l_{N_e}} \left\{ \sum_{\alpha=1}^{N_e - M} \sum_{l(\neq l_\alpha)} \mathrm{Im} \frac{\langle \chi_l | \mathbf{E}\cdot\mathbf{r} | \chi_{l_\alpha} \rangle}{E_{l_\alpha} - E_l} \int_{\Omega_{\mathbf{r}'}} d\mathbf{s} (\chi_l \nabla_{\mathbf{s}} \chi^{*}_{l_\alpha} - \chi^{*}_{l_\alpha} \nabla_{\mathbf{s}} \chi_l) + \sum_{\sigma=1}^{M} \sum_{k} \mathrm{Im} \frac{\langle \chi_k | \mathbf{E}\cdot\mathbf{r} | \chi_{d_\sigma} \rangle}{E^{(0)}_{d_\sigma} - E^{(0)}_{k}} \right.$$
$$\left. \times \int_{\Omega_{\mathbf{r}'}} d\mathbf{s} (\chi_k \nabla_{\mathbf{s}} \chi'^{(0)*}_{d_\sigma} - \chi'^{(0)*}_{d_\sigma} \nabla_{\mathbf{s}} \chi_k) + \sum_{\sigma=1}^{M} \sum_{\sigma'(\neq\sigma)} \mathrm{Im} \left[\frac{1}{\varepsilon_{d_\sigma} - \varepsilon_{d_{\sigma'}}} \sum_{k} \frac{V_{d_{\sigma'}k} V_{kd_\sigma}}{E^{(0)}_{d_\sigma} - E^{(0)}_{k}} \right] \int_{\Omega_{\mathbf{r}'}} d\mathbf{s} (\chi'^{(0)*}_{d_\sigma} \nabla_{\mathbf{s}} \chi'^{(0)}_{d_{\sigma'}} - \chi'^{(0)}_{d_{\sigma'}} \nabla_{\mathbf{s}} \chi'^{(0)*}_{d_\sigma}) \right\}. \quad (24)$$

Equation (24) is the current density for a system that has one M-fold manifold of degenerate states in its energy spectrum. The sums over l and k are not restricted to $(l_1 l_2 \ldots l_{N_e})$. The first term in the bracket is the contribution from coupling among nondegenerate states, it leads to conductivity, Eq. (17). The third term is the contribution from indirect coupling among members of the M-fold degenerate states through nondegenerate states, the second term is a contribution from coupling between nondegenerate states and member of the M-fold degenerate states. Note that all denominators are nonzero. The generalization to the situation in which there are several groups of degenerate states in $\Lambda_{l_1, l_2, \ldots, l_{N_e}}$ is straightforward.

Usually linear-response theory means computing the response of system to first order in external field. This is realized by calculating *the first-order change in the state* (wave function or density matrix) of system. For nondegenerate states and states which are not in resonance with an ac external field, the first-order change in the state does depend linearly on the external field. However for degenerate states and states which are in resonance with an external field, the first-order changes in these states include a complicated nonlinear dependence on external field. Formally the second term of Eq. (24) is linear about field and the third term in Eq. (24) is second order in the field. Because $\chi'^{(0)}_{d_\sigma}$, ε_{d_σ}, and V_{kd_σ} are functions of field, the second term and third terms in Eq. (24) do not exhibit a simple linear relation with field: each contribution to conductivity is field dependent.

The order of magnitude of one term inside the second summation in Eq. (24) is the same as that of one term in the first summation. The order of magnitude of one term inside the third summation is the same as that of usual second-order nonlinear effect produced by nondegenerate states.

If we insist that conductivity is field independent, i.e., only keep the contributions to current to first order of external field, then we should discard the second term and the third term of Eq. (24). If we think current density should be formally linear in the field, then the second summation should be included. The conductivity thus defined is field dependent. If we interpret linear response as a consequence of the first-order change in states, the third summation should also be included. Whichever point of view we may adopt, the nonlinear components of current caused by degenerate states are a prediction. They are different from the second-order and higher order responses caused by nondegenerate states: (1) the latter does not depend on the existence of manifold(s) of degenerate states and states are in

resonance with external field, the nth($n \geq 2$)-order current density is a nth-order homogeneous polynomial of field components;[40] (2) the second-order current caused by nondegenerate states vanishes in a system with inversion symmetry.[40] The "second-order" nonlinear current [the third summation within curly brackets of Eq. (24)] caused by degenerate states is not sensitive to the symmetry of system.

IV. CONDUCTIVITY FROM TIME-DEPENDENT PERTURBATION THEORY

The macroscopic current density in an oscillating field is

$$\mathbf{j}^e(\mathbf{r},t) = \frac{i\hbar e}{2m\Omega_{\mathbf{r}}}\int_{\Omega_{\mathbf{r}}} d\mathbf{s} \sum_{l_1 l_2 \ldots l_{N_e}} W_{l_1 l_2 \ldots l_{N_e}} \sum_{\alpha=1}^{N_e} \{[\chi_{l_\alpha}(t)\nabla_{\mathbf{s}}\chi'^{(1)*}_{l_\alpha}(t) - \chi^*_{l_\alpha}(t)\nabla_{\mathbf{s}}\chi'^{(1)}_{l_\alpha}(t)] + [\chi'^{(1)}_{l_\alpha}(t)\nabla_{\mathbf{s}}\chi^*_{l_\alpha}(t) - \chi'^{(1)*}_{l_\alpha}(t)\nabla_{\mathbf{s}}\chi_{l_\alpha}(t)]\}. \tag{25}$$

In an ac electric field $\mathbf{E}=\mathbf{E}_0 \cos \omega t$, the interaction of an electron at $\mathbf{r}$ with field is

$$H_{fm}(t) = Fe^{-i\omega t} + Fe^{i\omega t}, \quad F = -\frac{1}{2}e\mathbf{r}\cdot\mathbf{E}_0. \tag{26}$$

Since the region $\Omega_{\mathbf{r}}$ (employed to compute the spatial average) is much smaller than the wavelength of the field, the position dependence of field is ignored in Eq. (26). The wave function $\chi'_c(t)$ in an external field can be computed from time-dependent perturbation theory as

$$\chi'_c(t) = \chi_c(t) + \sum_{d(\neq c)} a_d(t)\chi_d e^{-iE_d t/\hbar}, \quad \chi_c(t) = e^{-iE_c t/\hbar}\chi_c(\mathbf{r}), \tag{27}$$

where $a_d(t)$ satisfies

$$i\hbar\frac{\partial a_d(t)}{\partial t} = \sum_{c_1} a_{c_1}(t)F_{dc_1}[e^{i(\omega_{dc_1}-\omega)t} + e^{i(\omega_{dc_1}+\omega)t}] \tag{28}$$

and

$$F_{dc_1} = \int d\mathbf{r}\chi^*_d F \chi_{c_1} \quad \omega_{dc_1} = \frac{1}{\hbar}(E_d - E_{c_1}). \tag{29}$$

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

If one applies the current-field relation (14) in a macroscopic way, there are three equivalent but technically different approaches to estimating the conductance: (i) using the equality between Joule heating and the net absorption of the energy of external field;[13,24,34,35] (ii) the scattering matrix formalism;[21–23,25] and (iii) expressing the conductance by two-time velocity correlation function in accord with fluctuation-dissipation theorem.[28,45] In approach (ii), the effect of external field is factored out already. Only the effect of the disorder potential appears in the resulting form for the conductance. From a microscopic point of view, dissipation is due to the transitions between some states of the system induced by an external field. To make the transition probability well defined, a long-time limit is needed [cf. Eqs. (43)–(45)]. If the current-field relation (14) is used to the expression of current which is either ensemble averaged [cf. Eq. (19) of Ref. 27] or spatially averaged [cf. Eqs. (6) and (33)], the amplitude of transition probability caused by external field appears in the expression of conductivity [cf. Eqs. (25) and (32) in this work or Eqs. (14) and (19) in Ref. 27].

A. Nondegenerate states

If the states are nondegenerate, Eq. (28) is just

$$\frac{\partial a_d(t)}{\partial t} = -\frac{i}{\hbar}F_{\mathrm{dc}}e^{i(\omega_{\mathrm{dc}}-\omega)t} - \frac{i}{\hbar}F_{\mathrm{dc}}e^{i(\omega_{\mathrm{dc}}+\omega)t}\Big]. \tag{30}$$

The solution of Eq. (30) is a time integral

$$a_d(t) = -\frac{F_{\mathrm{dc}}e^{i(\omega_{\mathrm{dc}}-\omega)t}}{\hbar(\omega_{\mathrm{dc}}-\omega-i\delta)} - \frac{F_{\mathrm{dc}}e^{i(\omega_{\mathrm{dc}}+\omega)t}}{\hbar(\omega_{\mathrm{dc}}+\omega-i\delta)}, \quad \delta\to 0^+. \tag{31}$$

The external field is introduced adiabatically. The change in wave function χ_c due to the ac field is

$$\chi'^{(1)}_c(t) = \sum_{d(\neq c)}(1-n_d)a_d(t)\chi_d e^{-itE_d/\hbar}, \tag{32}$$

where n_d is the occupation probability of single-electron state χ_d. The unoccupation factor $(1-n_d)$ is implicitly assumed when we simplify Eq. (28) to Eq. (30): initially state χ_d must be empty. In an intrinsic semiconductor at zero temperature, the valence band is fully occupied and conduction band is empty. Equation (32) indicates that only conduction states can couple with the valence states. This implies that the dc conductivity of an intrinsic semiconductor at zero temperature vanishes.

With the help of Eqs. (27), (31), and (32), Eq. (25) becomes

$$\mathbf{j}^e(\mathbf{r}',t) = \frac{i\hbar e}{2m\Omega_{\mathbf{r}'}}\int_{\Omega_{\mathbf{r}'}} d\mathbf{s} \sum_{l_1 l_2 \ldots l_{N_e}} W_{l_1 l_2 \ldots l_{N_e}} \sum_{\alpha=1}^{N_e} \sum_{d(\neq l_\alpha)} (1-n_d)\frac{e}{2\hbar}\mathbf{E}_0\Bigg\{\langle\chi_d|\mathbf{r}|\chi_{l_\alpha}\rangle^*\left[\frac{e^{i\omega t}}{(\omega_{dl_\alpha}-\omega)} + \frac{e^{-i\omega t}}{(\omega_{dl_\alpha}+\omega)}\right] \times(\chi_{l_\alpha}\nabla_{\mathbf{s}}\chi^*_d - \chi^*_d\nabla_{\mathbf{s}}\chi_{l_\alpha}) + \langle\chi_d|\mathbf{r}|\chi_{l_\alpha}\rangle\left[\frac{e^{-i\omega t}}{(\omega_{dl_\alpha}-\omega)} + \frac{e^{i\omega t}}{(\omega_{dl_\alpha}+\omega)}\right](\chi_d\nabla_{\mathbf{s}}\chi^*_{l_\alpha} - \chi^*_{l_\alpha}\nabla_{\mathbf{s}}\chi_d)\Bigg\}. \tag{33}$$

By adiabatically introducing the external field in the evolution of density matrix, same result was obtained, cf. Eqs. (19) and (24) in Ref. 27.

Now, separate out $\cos \omega t$ terms in Eq. (33): they are in phase with the external field. The real part of conductivity then reads

$$\sigma_{\mu\nu}^{(1)}(\omega)=\frac{e^2\hbar}{2m\Omega}\sum_{l_1l_2\cdots l_{N_e}}W_{l_1l_2\cdots l_{N_e}}\sum_{\alpha=1}^{N_e}\sum_{d(\neq l_\alpha)}(1-n_d)\times\left(\frac{1}{E_{l_\alpha}-E_d+\hbar\omega}+\frac{1}{E_{l_\alpha}-E_d-\hbar\omega}\right)\times\mathrm{Im}\left[\langle\chi_d|x_\nu|\chi_{l_\alpha}\rangle\int_\Omega d^3x\left(\chi_d\frac{\partial\chi_{l_\alpha}^*}{\partial x_\mu}-\chi_{l_\alpha}^*\frac{\partial\chi_d}{\partial x_\mu}\right)\right]. \tag{34}$$

The sin ωt terms in Eq. (33) lag 90° behind the phase of external field. The contribution to the imaginary part of the conductivity is

$$\sigma_{\mu\nu}^{(2)}(\omega)=\frac{e^2\hbar}{2m\Omega}\sum_{l_1l_2\ldots l_{N_e}}W_{l_1l_2\ldots l_{N_e}}\frac{1}{N_e}\sum_{\alpha=1}^{N_e}\sum_{d(\neq l_\alpha)}(1-n_d)\times\left[\frac{1}{E_d-E_{l_\alpha}-\hbar\omega}-\frac{1}{E_d-E_{l_\alpha}+\hbar\omega}\right]\times\mathrm{Re}\left[\langle\chi_d|x_\nu|\chi_{l_\alpha}\rangle\int_\Omega d^3x\left(\chi_d\frac{\partial\chi_{l_\alpha}^*}{\partial x_\mu}-\chi_{l_\alpha}^*\frac{\partial\chi_d}{\partial x_\mu}\right)\right]. \tag{35}$$

Equation (35) indicates $\sigma_{\mu\nu}^{(2)}(0)=0$, as expected. To obtain $\sigma_{\mu\nu}^{(1)}(0)$, $\sigma_{\mu\nu}^{(2)}(0)$ and to avoid the difficulty of degenerate states in Eqs. (34) and (35), in previous method,[26,27] one needs to first take the adiabatic limit and then the zero-frequency limit.[27] Because we separately treat nondegenerate states and degenerate states, this artificial singularity does not appear and the dc conductivity is directly included in Eq. (34). What is more, when $\omega=0$, Eq. (34) reduces to Eq. (17) which is derived from stationary perturbation theory, except for the factor $(1-n_d)$, as one would expect.

To first order in the external field, the second term in Eq. (4) is

$$-\frac{e^2}{m}\mathbf{A}(\mathbf{r},t)n^e_{\{\mathbf{w}_1\ldots\mathbf{w}_\mathcal{N}\}}(\mathbf{r},t)=\frac{e^2\mathbf{E}_0}{m\omega}n^e_{\{\mathbf{w}_1\ldots\mathbf{w}_\mathcal{N}\}}(\mathbf{r})\sin\,\omega t \tag{36}$$

and the third term in Eq. (4) is

$$\sum_\alpha\frac{q_\alpha^2\mathbf{E}_0}{M_\alpha\omega}\sin\,\omega t\,\delta(\mathbf{r}-\mathbf{W}_\alpha). \tag{37}$$

Using Eq. (6), the imaginary part of the conductivity of the electrons+nuclei system is

$$\sigma_{\mu\nu}^I(\omega)=\sigma_{\mu\nu}^{(2)}(\omega)+\left(\frac{e^2n^e}{m\omega}+\sum_p\frac{q_p^2n_p^N}{M_p\omega}\right)\delta_{\mu\nu}, \tag{38}$$

where M_p, q_p, and n_p^N are mass, effective charge, and the number density of the pth species of nuclei. The last two terms are contributions from free charges.[42]

B. Connection to semiclassical Boltzmann formalism

In the weak scattering or dilute impurity limit, wave vector and band structure are approximately meaningful. Then, the KGF should reduce Boltzmann expressions for various levels of approximations.[46] The idea of Ref. 30 for A_xB_{1-x} can be applied to more general disorder (a mixture of substitutional and topological disorder). If no topological constraint exist, all local reference crystals will have matched orientations.[47] One then has an unified reference crystal. If the distortion is weak and localized states do not exist, wave vectors of the virtual crystal can be used to label states. The resistivity arises from scattering by disorder potential and by phonons. Using Eq. (18) and the definition of velocity operator $v_\mu=-i\hbar m^{-1}\partial/\partial x_\mu$, Eq. (34) is changed into

$$\sigma_{\mu\nu}^{(1)}(\omega)=\frac{e^2}{\Omega}\sum_{l_1l_2\ldots l_{N_e}}W_{l_1l_2\ldots l_{N_e}}\sum_{\alpha=1}^{N_e}\sum_{d(\neq l_\alpha)}(1-n_d)\left(\frac{1}{E_{l_\alpha}-E_d+\hbar\omega}+\frac{1}{E_{l_\alpha}-E_d-\hbar\omega}\right)\frac{\hbar}{E_{l_\alpha}-E_d}\mathrm{Im}\left\{\left[\int_\Omega d^3x\chi_d^*v_\nu\chi_{l_\alpha}\right]\times\left[\frac{1}{2}\int_\Omega d^3x(\chi_{l_\alpha}^*v_\mu\chi_d-\chi_dv_\mu\chi_{l_\alpha}^*)\right]\right\}. \tag{39}$$

When disorder is weak, the full single-particle wave function χ_d or χ_{l_α} in Eq. (39) is a linear combination of Bloch waves, and the expansion coefficients include information about disorder: substitutional and/or topological. In the Taylor series of disorder potential

$$(V_a-V_c)(\mathbf{r})=\sum_{\mathbf{n}}\frac{Ze^2}{4\pi\epsilon_0}\left(\frac{1}{|\mathbf{r}-\mathbf{R_n}|}-\frac{1}{|\mathbf{r}-\mathbf{R_n}-\mathbf{u_n}|}\right)-\sum_{\mathbf{n}}\frac{e^2}{4\pi\epsilon_0}\frac{Z_{\mathbf{n}}-Z}{|\mathbf{r}-\mathbf{R_n}-\mathbf{u_n}|}, \tag{40}$$

one can neglect the third and higher order terms in the small parameters $\{Z_{\mathbf{n}}-Z\}$ and $\{\mathbf{u_n}\}$, where $Z_{\mathbf{n}}$ is the effective nuclear charge of the atom at $\mathbf{R_n}+\mathbf{u_n}$, Z is the effective nuclear charge of the atoms in the virtual crystal. Using the more realistic potentials of density-functional theory or Hartree-Fock in Eq. (40) does not alter any essential point.

Since disorder is weak and it is assumed that a virtual crystal exists, the full single-particle wave functions can be viewed as perturbed Bloch waves. Clearly the matrix element of the current operator in Eq. (39) is fully dressed by the disorder potential. In the language of scattering, χ_{l_α} is the initial state and χ_d is the final state, and $\int_\Omega d^3x\chi_{l_\alpha}^*v_\mu\chi_d$ is the "scattering-in" term.[30] For static external field $\omega=0$, the energy denominators in Eq. (39) coalesce into $(E_{l_\alpha}-E_d)^{-2}$, which corresponds to $\mathrm{M}^{-1}\,\mathrm{M}^{-1}$ in Eq. (79) of Ref. 30. The initial state χ_{l_α} is occupied, $\frac{1-n_d}{E_{l_\alpha}-E_d}\to\frac{\partial f}{\partial E}$, where $f[E(\mathbf{k})]$ is the Fermi distribution function. Another $(E_{l_\alpha}-E_d)^{-1}$ produces an energy-dependent relaxation time $\tau[E(\mathbf{k})]=\hbar(E_{l_\alpha}-E_d)^{-1}$. To first order in the disorder potential (V_a-V_c), the relaxation time is $\hbar[E_{l_\alpha}^{(0)}-E_d^{(0)}+(V_a-V_c)_{l_\alpha^{(0)}l_\alpha^{(0)}}-(V_a-V_c)_{d^{(0)}d^{(0)}}]^{-1}$, where $(\chi_d^{(0)},\chi_{l_\alpha}^{(0)})$ and $(E_d^{(0)},E_{l_\alpha}^{(0)})$ are bare Bloch states and corresponding eigenvalues. If one neglects vertex corrections of

the current operator, i.e., replaces it by the matrix elements in bare Bloch states, $\int_\Omega d^3x\chi_d^* v_\nu \chi_{l_\alpha} \to \int_\Omega d^3x \chi_d^{(0)*} v_\nu \chi_{l_\alpha}^{(0)}$ as in Eq. (86) of Ref. 30. Then the scattering mechanism only appears in the factor $\frac{1-n_d}{(E_{l_\alpha}-E_d)^2}$ through energy eigenvalues E_{l_α} and E_d, i.e., corrections in the eigenvalues of Bloch states caused by disorder potential. The sum over states is converted into integral over Brillouin zone $\int \frac{2d\mathbf{k}}{(2\pi)^3}$. By dropping the scattering-in term, Eq. (39) is reduced to

$$\sigma_{\mu\nu} = e^2 \int \frac{2d\mathbf{k}}{(2\pi)^3} \frac{\partial f}{\partial E} \tau[E(\mathbf{k})] v_\mu(\mathbf{k}) v_\nu(\mathbf{k}), \quad \mu,\nu = x,y,z, \quad (41)$$

a result familiar from the relaxation-time approximation.[48]

The inelastic scattering of carriers with phonons is reflected in the average over many MD steps. In a given MD step, scattering is caused by the deviation of the given configuration from the reference crystal. For a given temperature, a sequence of MD steps sample various vibrational configurations around equilibrium. The electron-phonon scattering is described by the change in electronic energy spectrum by sampling different configuration.[15,16,33] In the relaxation-time approximation, inelastic scattering of carriers with phonons is also implied in factor $\frac{1-n_d}{(E_{l_\alpha}-E_d)^2}$ through energy eigenvalues E_{l_α} and E_d.

Now, for completeness imagine a *rigid crystalline* metallic material for which scattering with thermal vibration and disorder disappears. Partially filled band leads to that the energies of numerous available final states are quite close to the energy of initial state, so that the relaxation time $\hbar(E_{l_\alpha}-E_d)^{-1}$ is infinite. At the same time, the velocity matrix elements $\int_\Omega d^3x \chi_{l_\alpha}^* v_\mu \chi_d$ are finite. Therefore, rigid metallic crystal has infinite conductivity as expected.

One can obtain a systematic expansion about disorder potential and electron-phonon interaction beyond the relaxation-time approximation.[30] With bare Bloch states as zero-order approximation, the perturbation Hamiltonian is the sum of $(V_a - V_c)$ and the electron-phonon interaction. The full single-particle functions (χ_{l_α} and χ_d) and corresponding eigenvalues (E_{l_α} and E_d) can be calculated to arbitrary order in the stationary perturbation theory. Inserting the dressed states and eigenvalues back to Eq. (39), one obtains conductivity at various levels of approximation. We report this elsewhere.

C. Comparison to KGF

Both the present work and the Greenwood derivation require that perturbation theory be applicable

$$a_d(t) = -\frac{i}{\hbar} F_{\rm dc} \int_{t_1}^{t_2} dt' [e^{i(\omega_{\rm dc}-\omega)t'} + e^{i(\omega_{\rm dc}+\omega)t'}] \ll 1. \quad (42)$$

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

$$\tau = (t_2 - t_1) \ll \frac{\hbar}{F}. \quad (43)$$

The Greenwood derivation also requires that the transition probability *per unit time* be defined[13,35]

$$\lim_{\tau\to\infty} \frac{\sin^2 \frac{(\omega_{\rm dc}-\omega)\tau}{2}}{\tau\left(\frac{\omega_{\rm dc}-\omega}{2}\right)^2} = \pi\delta\left(\frac{\omega_{\rm dc}-\omega}{2}\right)$$

$$\text{or} \quad \lim_{\tau\to\infty} \frac{\sin^2 \frac{(\omega_{\rm dc}+\omega)\tau}{2}}{\tau\left(\frac{\omega_{\rm dc}+\omega}{2}\right)^2} = \pi\delta\left(\frac{\omega_{\rm dc}+\omega}{2}\right). \quad (44)$$

That is, the interaction time τ should be long enough

$$\tau \gg \frac{2}{\omega_{\rm dc}-\omega} \quad \text{or} \quad \tau \gg \frac{2}{\omega_{\rm dc}+\omega} \quad (45)$$

to allow the two limits in Eq. (44) to be taken. The law of conservation energy (of field+matter) can be verified by means of two measurements only to an *accuracy* on the order of $\hbar/\Delta t$, where Δt is the time interval between the measurements,[39] i.e., the interaction time τ between field and matter. For a large system with continuous energy spectrum, Eq. (45) contradicts Eq. (43) for close levels when $\omega \to 0$. Since a transition with small $\omega_{\rm dc}$ makes a large contribution to conductivity, the dc conductivity obtained from the KGF is problematic. The derivation in this work does not require the transition probability, therefore does not require condition in Eq. (45), and is self-consistent.

D. Degenerate states in a low-frequency external field

If the final state falls in continuous energy spectrum, the perturbed wave function is[39]

$$\chi_i' = \chi_i + \int d\nu_f \frac{\langle\chi_f| - e\mathbf{E}\cdot\mathbf{r}|\chi_i\rangle}{E_f - E_i - \hbar\omega + i\delta}\chi_f + \int d\nu_f \frac{\langle\chi_f| - e\mathbf{E}\cdot\mathbf{r}|\chi_i\rangle}{E_f - E_i + \hbar\omega + i\delta}\chi_f, \quad (46)$$

where ν_f is the set of quantum numbers characterizing state χ_f. The integral $\int d\nu_f$ is over all variables characterizing state χ_f, which include energy E_f and other continuous parameters used to distinguish degenerate states. The scattering states with several scattering centers and Bloch states in a crystal belong to a continuous energy spectrum. The wave vector which characterizes a Bloch state or a scattering state changes continuously, therefore the energy spectrum of a crystal or a scattering problem is highly degenerate.[39] $\langle\chi_f| - e\mathbf{E}\cdot\mathbf{r}|\chi_i\rangle$ is analytic about ν_f and approaches a definite limit when $\omega \to 0$ and $\mathbf{k}_f \to \mathbf{k}_i$. Thus the first integrals in Eq. (46) exists at pole $E_f = E_i + \hbar\omega$ in the meaning of principal value. One can use the formal relation

$$(E_f - E_i - \hbar\omega + i\delta)^{-1} = P(E_f - E_i - \hbar\omega)^{-1} - i\pi\delta(E_f - E_i - \hbar\omega) \quad (47)$$

to effect the integral.[27,39] Similar discussion is applicable to the second integral. Therefore for scattering states with several scattering centers and Bloch states in a crystal, one need not distinguish degenerate states and nondegenerate states. An extended state in an amorphous system can be viewed as

a wave packet formed by superposition of a primary Bloch state and several secondary Bloch waves. The secondary Bloch waves are generated by the scattering of primary Bloch wave with the disorder potential. The extended states can be labeled as the wave vector of the primary Bloch wave, thus Eq. (46) is suitable for the extended states in an amorphous solid.

For localized states in amorphous semiconductors, the two sums over final states in Eq. (46) are integrated about E_f and summed over discrete parameters distinguishing degenerate localized states for a given energy. An amorphous semiconductor is composed of many topologically similar atomic configurations. In different spatial regions, the degeneracy among localized states for a given energy is produced by similar structural conformations in different spatial regions. Even for $E_f \to E_i$, $\langle \chi_f | -e\mathbf{E}\cdot\mathbf{r} | \chi_i \rangle$ is different for each different member χ_f of a degenerate manifold of localized states. The two integrals in Eq. (46) do not exist even in a principal value sense. Although conduction tail states and valence tail states of an amorphous semiconductor belong to continuous spectrum, these localized states in a degenerate manifold act like discrete states.

If an energy spectrum is discrete, it is obvious that one cannot use Eq. (31) in two situations: (1) degenerate states $\omega_{\mathrm{dc}}=0$ in a dc field or near degenerate states in low-frequency field $\omega_{\mathrm{dc}}-\omega \to 0$; (2) states which are near or in resonance with external field: $\omega_{\mathrm{dc}} \pm \omega = 0$. In these situations, Eq. (30) leads to $a_d(t) \sim t$.

In this section, we will prove that the degenerate levels in the energy spectrum do not cause any singularity in response function such as conductance: the zero-order contribution to current is zero, cf. Eq. (53). The current components from first-order correction of degenerate states caused by external field is finite and has complicated field dependence, cf. Eqs. (60)–(65).

1. Zeroth-order contribution vanishes

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

$$i\hbar \frac{da_j(t)}{dt} = \sum_k a_k(t) G_{jk} \cos \omega t,$$

$$G_{jk} = \int d\mathbf{r} \chi_j^*(-e\mathbf{E}_0 \cdot \mathbf{r}) \chi_k,$$

$$j,k = d_1, d_2, \ldots, d_M. \tag{48}$$

Next, introduce a new "time" variable $s=\sin \omega t$, so that Eq. (48) becomes

$$i\hbar\omega \frac{da_j(s)}{ds} = \sum_k a_k(s) G_{jk}. \tag{49}$$

Then take the Fourier transform about s

$$a_j(s) = \int dp a_{pj} e^{-ips}, \quad j = d_1, d_2, \ldots, d_M, \tag{50}$$

where p is the "frequency" variable conjugate to s. Notice that G_{jk} does not depend on time and Eq. (49) becomes

$$\sum_k a_{pj}(G_{jk} - \hbar\omega p \delta_{jk}) = 0. \tag{51}$$

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. (48) are

$$\chi'^{(0)}_{p_\mu}(t) = e^{-ip_\mu \sin \omega t} \sum_{\alpha=1}^{M} a_{p_\mu d_\alpha} \chi_{d_\alpha}, \quad \mu = 1,2,\ldots,M. \tag{52}$$

The matrix elements of perturbation $(-e\mathbf{E}_0\cdot\mathbf{r})$ relative to the new zero-order wave functions are diagonal. Because the matrix $(a_{p_\mu d_\alpha})$ is unitary, one has

$$\sum_{\mu=1}^{M} [\chi'^{(0)}_{p_\mu}(t) \nabla \chi'^{(0)*}_{p_\mu}(t) - \chi'^{(0)*}_{p_\mu}(t) \nabla \chi'^{(0)}_{p_\mu}(t)] - \sum_{\alpha=1}^{M} [\chi_{d_\alpha} \nabla \chi^*_{d_\alpha} - \chi^*_{d_\alpha} \nabla \chi_{d_\alpha}] = 0. \tag{53}$$

From Eq. (25), the zeroth-order correction to degenerate states does not contribute to conductivity. Degenerate states do not cause any singularities in the conductivity.

2. New components of current from degenerate states

We first compute the first-order correction to $\chi'^{(0)}_{p_\mu}(t)$

$$\chi'^{(1)}_{p_\mu}(t) = \sum_j a^{(1)}_{p_\mu j}(t) \chi_j e^{-itE_j/\hbar} + \sum_{\mu'} a^{(1)}_{p_\mu p_{\mu'}}(t) \chi'^{(0)}_{p_{\mu'}} e^{-itE_{p_{\mu'}}/\hbar}. \tag{54}$$

Now the zeroth-order wave functions are nondegenerate states $\{\chi_k\}$ and new zero-order wave functions $\chi'^{(0)}_{p_1}, \chi'^{(0)}_{p_2}, \ldots, \chi'^{(0)}_{p_M}$ of degenerate states. At an initial moment, an electron is in state $\chi'^{(0)}_{p_\mu}: a_{p_\mu}(-\infty)=1$ and other coefficients are zero. If the interaction time with field is not too long, $a_{p_\mu}(t)$ is dominant. For a nondegenerate state χ_j, $a^{(1)}_{p_\mu j}(t)$ is determined by

$$\frac{da_j(t)}{dt} = -\frac{i}{2\hbar} G_{jp_\mu}(e^{i\omega t} + e^{-i\omega t}) a_{p_\mu}(t) e^{i\omega_{jp_\mu} t}. \tag{55}$$

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

$$a_{p_\mu j}(t) = -\frac{1}{2\hbar} G_{jp_\mu} \left[\frac{e^{i(\omega+\omega_{jp_\mu}+i\delta)t/\hbar}}{\omega_{jp_\mu}+\omega+i\delta} + \frac{e^{i(\omega_{jp_\mu}-\omega+i\delta)t/\hbar}}{\omega_{jp_\mu}-\omega+i\delta} \right], \quad \delta \to 0^+. \tag{56}$$

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

$$i\hbar \frac{da_{p_{\mu'}}(t)}{dt} e^{-itE_{p_{\mu'}}/\hbar} = \sum_k a_k(t) G_{p_{\mu'}k} e^{-itE_k/\hbar} \frac{e^{i\omega t} + e^{-i\omega t}}{2} \tag{57}$$

and initial condition $a_{p_{\mu'}}(-\infty)=0$. Index k in the rhs of Eq. (57) runs over nondegenerate states only. New zero-order

wave functions $\{\chi'^{(0)}_{p_\mu}\}$ do not couple to each other through external field. $a^{(1)}_{p_\mu p_{\mu'}}(t)$ is given by

$$a_{p_\mu p_{\mu'}}(t)=\frac{1}{4\hbar^2}\sum_k G_{p_{\mu'}k}G_{kp_\mu}\left\{\frac{1}{\omega_{kp_\mu}+\omega}\frac{e^{i(\omega_{p_{\mu'}p_\mu}+2\omega+i\delta)t}}{\omega_{p_{\mu'}p_\mu}+2\omega+i\delta}+\frac{1}{\omega_{kp_\mu}+\omega}\frac{e^{i(\omega_{p_{\mu'}p_\mu}+i\delta)t}}{\omega_{p_{\mu'}p_\mu}+i\delta}+\frac{1}{\omega_{kp_\mu}-\omega}\frac{e^{i(\omega_{p_{\mu'}p_\mu}+i\delta)t}}{\omega_{p_{\mu'}p_\mu}+i\delta}+\frac{1}{\omega_{kp_\mu}-\omega}\frac{e^{i(\omega_{p_{\mu'}p_\mu}-2\omega+i\delta)t}}{\omega_{p_{\mu'}p_\mu}-2\omega+i\delta}\right\}. \quad (58)$$

When $\omega\to 0$, all the denominators of Eqs. (56) and (58) are nonzero. For degenerate states in a zero-frequency external field, the artificial singularity of perturbation formula (31) is removed.

Combining Eqs. (25), (54), (56), and (58), the macroscopic current density can be written as

$$\mathbf{j}^e(\mathbf{r}',t)=\mathbf{j}^e_{non}(\mathbf{r}',t)+\mathbf{j}^e_c(\mathbf{r}',t)+\mathbf{j}^e_s(\mathbf{r}',t)+\mathbf{j}^e_{c2}(\mathbf{r}',t)+\mathbf{j}^e_{s2}(\mathbf{r}',t)+\mathbf{j}^e_0(\mathbf{r}'), \quad (59)$$

where $\mathbf{j}^e_{non}(\mathbf{r}',t)$ is the contribution from nondegenerate states and is obtained by replacing $\Sigma_{\alpha=1}^{N_e}$ by $\Sigma_{\alpha=1}^{N_e-M}$ (summing over only nondegenerate states) in Eq. (33). Two components $\mathbf{j}^e_c$ and $\mathbf{j}^e_s$ of current are produced by direct coupling between a member of degenerate states and a state with different energy

$$\mathbf{j}^e_c(\mathbf{r}',t)=\cos\,\omega t\frac{e}{2m\Omega_{\mathbf{r}'}}\sum_{l_1l_2\ldots l_{N_e}}W_{l_1l_2\ldots l_{N_e}}\sum_{\mu=1}^{M}\sum_j(1-n_j)\times\left[\frac{1}{\omega_{jp_\mu}+\omega}+\frac{1}{\omega_{jp_\mu}-\omega}\right]\times\mathrm{Im}\,G_{jp_\mu}\int_{\Omega_{\mathbf{r}'}}d\mathbf{s}(\chi_j\nabla_{\mathbf{s}}\chi'^{(0)*}_{p_\mu}-\chi'^{(0)*}_{p_\mu}\nabla_{\mathbf{s}}\chi_j) \quad (60)$$

is the component with cos ωt factor and

$$\mathbf{j}^e_s(\mathbf{r}',t)=\sin\,\omega t\frac{e}{2m\Omega_{\mathbf{r}'}}\sum_{l_1l_2\ldots l_{N_e}}W_{l_1l_2\ldots l_{N_e}}\sum_{\mu=1}^{M}\sum_j(1-n_j)\times\left[\frac{1}{\omega_{jp_\mu}+\omega}-\frac{1}{\omega_{jp_\mu}-\omega}\right]\times\mathrm{Re}\,G_{jp_\mu}\int_{\Omega_{\mathbf{r}'}}d\mathbf{s}(\chi_j\nabla_{\mathbf{s}}\chi'^{(0)*}_{p_\mu}-\chi'^{(0)*}_{p_\mu}\nabla_{\mathbf{s}}\chi_j) \quad (61)$$

is the component with sin ωt factor. Although formally $\mathbf{j}^e_c$ and $\mathbf{j}^e_s$ depend linearly on field E, they include more complicated field dependence through $\chi'^{(0)}_{p_\mu}$ and $E'^{(0)}_{p_\mu}$. For example, from Eq. (14), the contribution to conductivity from component $\mathbf{j}^e_c$ is

$$\sigma^e_{c\alpha\beta}(\omega;\mathbf{E}_0)=\frac{e^2}{2m\Omega_{\mathbf{r}'}}\sum_{l_1l_2\ldots l_{N_e}}W_{l_1l_2\ldots l_{N_e}}\sum_{\mu=1}^{M}\sum_j(1-n_j)\left[\frac{1}{\omega_{jp_\mu}+\omega}+\frac{1}{\omega_{jp_\mu}-\omega}\right]\mathrm{Im}\left[\left(\int d\mathbf{r}\chi^*_j x_\beta\chi'^{(0)}_{p_\mu}\right)\int_{\Omega_{\mathbf{r}'}}d\mathbf{s}\left(\chi'^{(0)*}_{p_\mu}\frac{\partial\chi_j}{\partial s_\alpha}-\chi_j\frac{\partial\chi'^{(0)*}_{p_\mu}}{\partial s_\alpha}\right)\right],\quad \alpha,\beta=x,y,z, \quad (62)$$

a function of the amplitude $\mathbf{E}_0$ of the ac field through $\chi'^{(0)}_{p_\mu}$ and $E'^{(0)}_{p_\mu}$.

Another three components of current formally have second-order field dependence. This is similar to the second-order nonlinear effect caused by nondegenerate states.[40]

$$\mathbf{j}^e_{c2}(\mathbf{r}',t)=\cos\,2\omega t\frac{e}{4\hbar m\Omega_{\mathbf{r}'}}\sum_{l_1l_2\ldots l_{N_e}}W_{l_1l_2\ldots l_{N_e}}\sum_{\mu=1}^{M}\sum_{\mu'}(1-n_{\mu'})\sum_k\left(\frac{1}{\omega_{kp_\mu}+\omega}\frac{1}{\omega_{p_{\mu'}p_\mu}+2\omega}+\frac{1}{\omega_{kp_\mu}-\omega}\frac{1}{\omega_{p_{\mu'}p_\mu}-2\omega}\right)\mathrm{Im}\,G_{p_{\mu'}k}G_{kp_\mu}\int_{\Omega_{\mathbf{r}'}}d\mathbf{s}(\chi'^{(0)*}_{p_\mu}\nabla_{\mathbf{s}}\chi'^{(0)}_{p_{\mu'}}-\chi'^{(0)}_{p_{\mu'}}\nabla_{\mathbf{s}}\chi'^{(0)*}_{p_\mu})] \quad (63)$$

is the component with cos $2\omega t$ factor.

$$\mathbf{j}^e_{s2}(\mathbf{r}',t)=\sin\,2\omega t\frac{e}{4\hbar m\Omega_{\mathbf{r}'}}\sum_{l_1l_2\ldots l_{N_e}}W_{l_1l_2\ldots l_{N_e}}\sum_{\mu=1}^{M}\sum_{\mu'}(1-n_{\mu'})\sum_k\left(\frac{1}{\omega_{kp_\mu}-\omega}\frac{1}{\omega_{p_{\mu'}p_\mu}-2\omega}-\frac{1}{\omega_{kp_\mu}+\omega}\frac{1}{\omega_{p_{\mu'}p_\mu}+2\omega}\right)\mathrm{Re}\,G_{p_{\mu'}k}G_{kp_\mu}\int_{\Omega_{\mathbf{r}'}}d\mathbf{s}(\chi'^{(0)}_{p_{\mu'}}\nabla_{\mathbf{s}}\chi'^{(0)*}_{p_\mu}-\chi'^{(0)*}_{p_\mu}\nabla_{\mathbf{s}}\chi'^{(0)}_{p_{\mu'}}) \quad (64)$$

is the component with sin $2\omega t$ factor. Equations (63) and (64) have similar structure as the corresponding current densities derived from second-order change in density matrix for nondegenerate states, cf. Eqs. (2–29) and (2–30) of Ref. 40. They are different in detail, however: (1) Eqs. (63) and (64) include more complex field dependence through $\chi'^{(0)}_{p_\mu}$ and $E'^{(0)}_{p_\mu}$, while the ordinary current density produced by second-order change in states only has E^2 field dependence; (2) the current density produced by degenerate states exits whatever the symmetry of system is, while the ordinary current produced by second-order change in nondegenerate states cannot exist in a system with inversion symmetry.

The current component

$$\mathbf{j}_0^e(\mathbf{r}') = \frac{e}{4\hbar m\Omega_{\mathbf{r}'}} \sum_{l_1 l_2 \ldots l_{N_e}} W_{l_1 l_2 \ldots l_{N_e}} \sum_{\mu=1}^{M} \sum_{\mu'} (1-n_{\mu'}) \sum_k \left(\frac{1}{\omega_{kp_\mu}+\omega} \frac{1}{\omega_{p_{\mu'}p_\mu}} + \frac{1}{\omega_{kp_\mu}-\omega} \frac{1}{\omega_{p_{\mu'}p_\mu}} \right)$$
$$\times \mathrm{Im}\left[G_{p_{\mu'}k} G_{kp_\mu} \int_{\Omega_{\mathbf{r}'}} d\mathbf{s} (\chi'^{(0)*}_{p_\mu} \nabla_{\mathbf{s}} \chi'^{(0)}_{p_{\mu'}} - \chi'^{(0)}_{p_{\mu'}} \nabla_{\mathbf{s}} \chi'^{(0)*}_{p_\mu}) \right] \tag{65}$$

is stationary. Equation (65) has both second-order field dependence and the complex field dependence through $\chi'^{(0)}_{p_\mu}$ and $E'^{(0)}_{p_\mu}$, while the ordinary current produced by the second-order change in nondegenerate states only has the second dependence of field, cf. Eqs. (1)–(8) of Ref. 40. The contribution to conductivity from $\mathbf{j}_0^e$ is

$$\sigma^e_{0\alpha\beta} = \frac{e^3}{4\hbar m\Omega_{\mathbf{r}'}} \sum_\gamma E_{0\gamma} \sum_{l_1 l_2 \ldots l_{N_e}} W_{l_1 l_2 \ldots l_{N_e}} \sum_{\mu=1}^{M} \sum_{\mu'} (1-n_{\mu'}) \sum_k \left(\frac{1}{\omega_{kp_\mu}+\omega} \frac{1}{\omega_{p_{\mu'}p_\mu}} + \frac{1}{\omega_{kp_\mu}-\omega} \frac{1}{\omega_{p_{\mu'}p_\mu}} \right)$$
$$\times \mathrm{Im}\left[\left(\int d\mathbf{r} \chi^*_{p_{\mu'}} x_\gamma \chi_k \right) \left(\int d\mathbf{r} \chi^*_k x_\beta \chi_{p_\mu} \right) \int_{\Omega_{\mathbf{r}'}} d\mathbf{s} \left(\chi'^{(0)*}_{p_\mu} \frac{\partial \chi'^{(0)}_{p_{\mu'}}}{\partial s_\alpha} - \chi'^{(0)}_{p_{\mu'}} \frac{\partial \chi'^{(0)*}_{p_\mu}}{\partial s_\alpha} \right) \right], \quad \alpha,\beta,\gamma = x,y,z. \tag{66}$$

It is easy to symmetrize indices β and γ. Except an implicit field dependence in $\{\chi'^{(0)}_{p_\mu}\}$ and $\{E'^{(0)}_{p_\mu}\}$, it depends on $E_{0\gamma}$ linearly.

In Eqs. (60)–(66), the summation over j or k is not restricted to $(l_1 l_2 \ldots l_{N_e})$: it extends to all single-electron states. $\mathbf{j}^e_{c2}$, $\mathbf{j}^e_{s2}$, and $\mathbf{j}^e_0$ arise from indirect coupling among $\{\chi'^{(0)}_{p_\mu}, \mu = 1,2,\ldots,M\}$ through nondegenerate states. The interaction with external field appears twice in Eq. (58). This leads to three new time factors $\cos 2\omega t$, $\sin 2\omega t$, and 1, which are different from the original time factors $e^{-i\omega t}$ and $e^{i\omega t}$ of the external field. $|\mathbf{j}^e_{s2}|/|\mathbf{j}^e_c|$ is about D^2/J, where D and J are, respectively, the average degree of degeneracy of states and the number of nondegenerate states in a band for a given size of sample. If one couples a piece of material in an oscillating field (frequency ω) to a RLC circuit with resonant frequency 2ω, the double-frequency components should be detectable.

One may notice when $\omega=0$, $\mathbf{j}^e_s=0$, and $\mathbf{j}^e_{s2}=0$. Excepting the factor $(1-n_j)$ which would not appear in single-electron stationary perturbation theory, when $\omega \to 0$, component $\mathbf{j}^e_c$ of current from coupling members of degenerate states and nondegenerate states is reduced to the second sum of Eq. (24). Similarly excepting the factor $(1-n_{\mu'})$, the sum of components $(\mathbf{j}^e_{c2}+\mathbf{j}^e_0)$ of current from indirect coupling among the members of degenerate states is reduced to the third sum of Eq. (24). The expression for current density derived from time-dependent perturbation theory for degenerate states is consistent with the expression of current derived from stationary perturbation theory for degenerate states.

Unlike the KGF, where dc conductivity is obtained either by extrapolating from optical conductivity[15] or by writing a separate code for zero frequency,[16,34,36] the present ac expression includes the dc expression as a special case.[31]

E. Resonance with finite-frequency external field

In previous work on ac conductivity, the resonance of an ac external field with two groups of states has been ignored. A rationale is that residual interactions such as electron-electron and/or electron-phonon interactions broaden single-particle levels, causing the resonance to be smoothed out.[49] This argument cannot be applied to molecular dynamics (MD) simulation of ac conductivity, where single-particle levels are well defined in each MD step, and averaging is carried out over the MD trajectory. The electron-electron interaction appears in Hartree-Fock or density-functional Hamiltonian, the electron-phonon interaction appears as the changes in configurations in consecutive MD steps. They do not appear as the residual interaction to broaden the energy levels. In this section, we show that the zero-order contribution to current from the states which are in resonance with external field is zero. The contribution from the first-order change in these states is finite.

1. Zeroth-order contribution to current vanishes

Suppose that in $(\chi_{l_1},\chi_{l_2},\ldots,\chi_{l_{N_e}})$ there is a M-fold degenerate manifold $(\chi_{m_1},\chi_{m_2},\ldots,\chi_{m_M})$ and a M'-fold degenerate manifold $(\chi_{n_1},\chi_{n_2},\ldots,\chi_{n_{M'}})$ which are nearly in resonance with an external field: $E_m^{(0)}-E_n^{(0)}=\hbar(\omega+\xi)$, where ω is the frequency of the external field and parameter $\xi \ll \omega$ or $\xi=0$ measures how close the frequency ω of external field is to resonance. For the zeroth-order correction of these states, the coupling with other nonresonant states may be neglected. If we only consider the interaction with the smallest oscillating frequency, the general evolution equations are simplified to

$$i\hbar\frac{da_{m_j}}{dt}=\sum_{k=1}^{M'}F_{m_jn_k}e^{i\xi t}a_{n_k},\quad F_{m_jn_k}=\frac{1}{2}\int d\mathbf{r}\chi_{m_j}^*(-e\mathbf{E}_0\cdot\mathbf{r})\chi_{n_k} \tag{67}$$

and

$$i\hbar\frac{da_{n_k}}{dt}=\sum_{j=1}^{M}F_{m_jn_k}^*e^{-i\xi t}a_{m_j}. \tag{68}$$

Introduce new functions $b_{n_k}: a_{n_k}=b_{n_k}e^{-it\xi}$ $(k=1,2,\ldots,M')$, Eq. (67) becomes

$$i\hbar\frac{da_{m_j}}{dt}=\sum_{k=1}^{M'}F_{m_jn_k}b_{n_k} \tag{69}$$

and Eq. (68) becomes

$$i\hbar\dot{b}_{n_k}=-\hbar\xi b_{n_k}+\sum_{j=1}^{M}F_{m_jn_k}^*a_{m_j}. \tag{70}$$

Equations (69) and (70) can be rearranged into

$$i\hbar\frac{d}{dt}V=RV, \tag{71}$$

where

$$R=\begin{pmatrix}0_{M\times M} & B_{M\times M'}\\ [(B_{M\times M'})^{\text{transpose}}]^* & 0_{M'\times M'}-\hbar\epsilon I_{M'\times M'}\end{pmatrix} \tag{72}$$

is a $(M+M')\times(M+M')$ matrix, 0 is zero matrix, I is the unit matrix, elements of matrix B are given by

$$B_{jk}=F_{m_jn_k},\quad j=1,2,\ldots,M;\quad k=1,2,\ldots,M'. \tag{73}$$

V is a $(M+M')$-column vector, its transpose is

$$V^{\text{transpose}}=(a_{m_1},a_{m2},\ldots,a_{m_M};b_{n_1},b_{n_2},\ldots,b_{n_{M'}}). \tag{74}$$

We are looking for special solutions of Eq. (71) in the form

$$a_{m_j}^q(t)=a_{m_j}^{q0}e^{i\alpha_q t},\quad j=1,2,\ldots,M;\quad b_{n_k}^q(t)=b_{n_k}^{q0}e^{i\alpha_q t},\quad k=1,2,\ldots,M'. \tag{75}$$

The column vector V_0^q with

$$(V_0^q)^{\text{transpose}}=(a_{m_1}^{q0},a_{m2}^{q0},\ldots,a_{m_M}^{q0};b_{n_1}^{q0},b_{n_2}^{q0},\ldots,b_{n_{M'}}^{q0}) \tag{76}$$

is the eigenvector of R belonging to eigenvalue $\hbar\alpha_q$. Then $(M+M')$ special solutions of the time-dependent single-electron Schrodinger equation are

$$\chi_q'^{(0)}(t)=\sum_{j=1}^{M}a_{m_j}^{q0}e^{i\alpha_q t}\chi_{m_j}e^{-iE_{m}t/\hbar}+\sum_{k=1}^{M'}b_{n_k}^{q0}e^{i(\alpha_q-\xi)t}\chi_{n_k}e^{-iE_{n}t/\hbar},\quad q=1,2,\ldots,M+M' \tag{77}$$

and the general solution can be obtained from linear combinations of the special solutions. Because R is Hermitian, its eigenvalues $(\hbar\alpha_q,q=1,2,\ldots,M+M')$ are real, matrix $C=(a_{m_1}^{q0},a_{m2}^{q0},\ldots,a_{m_M}^{q0};b_{n_1}^{q0},b_{n_2}^{q0},\ldots,b_{n_{M'}}^{q0})$ is unitary (q is index of row).

If we use Eq. (77) and notice that C is unitary, one has

$$\sum_{q=1}^{M+M'}(\chi_q'^{(0)}\nabla\chi_q'^{(0)*}-\chi_q'^{(0)*}\nabla\chi_q'^{(0)})=\sum_{j=1}^{M}(\chi_{m_j}\nabla\chi_{m_{j_1}}^*-\chi_{m_{j_1}}^*\nabla\chi_{m_j})+\sum_{k=1}^{M'}(\chi_{n_k}\nabla\chi_{n_{k_1}}^*-\chi_{n_{k_1}}^*\nabla\chi_{n_k}). \tag{78}$$

From Eq. (15), the contribution to the current from the states which are in resonance with an external field is zero. The artificial poles in the case of resonance in Eq. (31) are removed. For a mechanical oscillator, if we drive it at resonance and do not dissipate energy, the amplitude of the oscillator will increase indefinitely. The situation for two groups of resonant levels is different; the system absorbs quanta from the external field, stimulated emission also occurs. The material and field are in absorption-emission equilibrium, so that no singularity occurs. The two δ functions in Greenwood's formula come from the long-time limit and are not caused by resonance.

2. New components of current from resonant states

To compute the contribution to current from two groups of states which are in resonance with external field, we need the first-order corrected wave functions

$$\chi_q'^{(1)}(t)=\sum_s a_s^{q(1)}e^{-iE_st/\hbar}\chi_s+\sum_k a_{n_k}^{q(1)}e^{-iE_nt/\hbar}\chi_{n_k}+\sum_j a_{m_j}^{q(1)}e^{-iE_mt/\hbar}\chi_{m_j}, \tag{79}$$

where s indicates the states which do not belong to the upper and lower degenerate groups. j scans over the upper group $(\chi_{m_1},\chi_{m_2},\ldots,\chi_{m_M})$, k runs over the lower group $(\chi_{n_1},\chi_{n_2},\ldots,\chi_{n_{M'}})$. Suppose initially that the system is in the qth mode of the resonance states, for state χ_s which does not belong to the two group resonant states, the first-order evolution equation is then

$$i\hbar\frac{da_s^{(1)}}{dt}=\sum_j\left[F_{sm_j}e^{i(\omega_{sm_j}-\omega)t}+F^*_{m_js}e^{i(\omega_{sm_j}+\omega)t}\right]a^{(0)}_{m_j}+\sum_k\left[F_{sn_k}e^{i(\omega_{sn_k}-\omega)t}+F^*_{n_ks}e^{i(\omega_{sn_k}+\omega)t}\right]a^{(0)}_{n_k}. \quad (80)$$

The solution of Eq. (80) is

$$a_s^{(1)}(t)=-\frac{1}{\hbar}\sum_j\left[F_{sm_j}\frac{e^{i(\omega_{sm_j}-\omega+\alpha_q)t}}{\omega_{sm_j}-\omega+\alpha_q}+F^*_{m_js}\frac{e^{i(\omega_{sm_j}+\omega+\alpha_q)t}}{\omega_{sm_j}+\omega+\alpha_q}\right]a^{q0}_{m_j}-\frac{1}{\hbar}\sum_k\left[F_{sn_k}\frac{e^{i(\omega_{sn_k}-\omega+\alpha_q-\xi)t}}{\omega_{sn_k}-\omega+\alpha_q-\xi}+F^*_{n_ks}\frac{e^{i(\omega_{sn_k}+\omega+\alpha_q-\xi)t}}{\omega_{sn_k}+\omega+\alpha_q-\xi}\right]b^{q0}_{n_k}. \quad (81)$$

The first-order amplitude $a_s^{(1)}$ of probability comes from the qth mode of the resonance states.

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

$$i\hbar\frac{da^{(1)}_{m_j}}{dt}=\sum_{k=1}^{M'}F^*_{n_km_j}e^{i(2\omega+\xi)t}a^{(0)}_{n_k}+\sum_{j'(\neq j)}\left[F_{m_jm_{j'}}e^{-i\omega t}+F^*_{m_{j'}m_j}e^{i\omega t}\right]a^{(0)}_{m_{j'}}+\sum_s\left[F_{m_js}e^{i(\omega_{m_js}-\omega)t}+F^*_{sm_j}e^{i(\omega_{m_js}+\omega)t}\right]a^{(1)}_s,\quad j=1,2,\ldots,M. \quad (82)$$

Using Eq. (81), the solution of Eq. (82) is

$$\begin{aligned}a^{(1)}_{m_j}=&-\frac{1}{\hbar}\sum_{k=1}^{M'}F^*_{n_km_j}\frac{e^{i(2\omega+\alpha_q)t}}{2\omega+\alpha_q}b^{q0}_{n_k}-\frac{1}{\hbar}\sum_{j'(\neq j)}\left[F_{m_jm_{j'}}\frac{e^{i(\alpha_q-\omega)t}}{\alpha_q-\omega}+F^*_{m_{j'}m_j}\frac{e^{i(\alpha_q+\omega)t}}{\alpha_q+\omega}\right]a^{q0}_{m_{j'}}\\&+\frac{1}{\hbar^2}\sum_sF_{m_js}\left\{\sum_{j'}\left[F_{sm_{j'}}\frac{e^{i(\alpha_q-2\omega)t}}{(\omega_{sm_{j'}}-\omega+\alpha_q)(\alpha_q-2\omega)}+F^*_{m_js}\frac{e^{i\alpha_qt}}{(\omega_{sm_{j'}}+\omega+\alpha_q)\alpha_q}\right]a^{q0}_{m_{j'}}\right.\\&\left.+\sum_k\left[F_{sn_k}\frac{e^{i(\alpha_q-\omega)t}}{(\omega_{sn_k}-\omega+\alpha_q-\xi)(\alpha_q-\omega)}+F^*_{n_ks}\frac{e^{i(\alpha_q+\omega)t}}{(\omega_{sn_k}+\omega+\alpha_q-\xi)(\alpha_q+\omega)}\right]b^{q0}_{n_k}\right\}\\&+\frac{1}{\hbar^2}\sum_sF^*_{sm_j}\left\{\sum_{j'}\left[F_{sm_{j'}}\frac{e^{i\alpha_qt}}{(\omega_{sm_{j'}}-\omega+\alpha_q)\alpha_q}+F^*_{m_{j'}s}\frac{e^{i(\alpha_q+2\omega)t}}{(\omega_{sm_{j'}}+\omega+\alpha_q)(\alpha_q+2\omega)}\right]a^{q0}_{m'_j}\right.\\&\left.+\sum_k\left[F_{sn_k}\frac{e^{i(\alpha_q+\omega)t}}{(\omega_{sn_k}-\omega+\alpha_q-\xi)(\alpha_q+\omega)}+F^*_{n_ks}\frac{e^{i(3\omega+\alpha_q)t}}{(\omega_{sn_k}+\omega+\alpha_q-\xi)(3\omega+\alpha_q)}\right]b^{q0}_{n_k}\right\}. \quad (83)\end{aligned}$$

Because the average value of a mechanical quantity is bilinear in wave function, the common time factor $e^{i\alpha_qt}$ will disappear in current density. The first three terms are first order in field. Coupling with a member in the lower group produces a time factor $e^{i2\omega t}$. Coupling with another member in the upper group produces time factors $e^{i\omega t}$ and $e^{-i\omega t}$. The remain terms are second order about the field and come from indirect coupling through nonresonant state χ_s, i.e., the terms including $a_s^{(1)}$ in Eq. (82). Coupling with a member in upper group produces time factors $e^{-i2\omega t}$, 1, and $e^{i2\omega t}$. Coupling with a member in lower group produces time factor $e^{i3\omega t}$, $e^{-i\omega t}$, and $e^{i\omega t}$. The characterization of the first-order correction of resonant states are different from those of the first-order correction of the degenerate states. The time factors $e^{-i2\omega t}$, 1, and $e^{i2\omega t}$ caused by degenerate states are associated with formal second-order dependence of field.

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

$$i\hbar\frac{da^{(1)}_{n_k}}{dt}=\sum_{j=1}^{M}F_{n_km_j}e^{-i(2\omega+\xi)t}a^{(0)}_{m_j}+\sum_{k'(\neq k)}\left[F_{n_kn_{k'}}e^{-i\omega t}+F^*_{n_{k'}n_k}e^{i\omega t}\right]a^{(0)}_{n_{k'}}+\sum_s\left[F_{n_ks}e^{i(\omega_{n_ks}-\omega)t}+F^*_{sn_k}e^{i(\omega_{n_ks}+\omega)t}\right]a^{(1)}_s,\quad k=1,2,\ldots,M'. \quad (84)$$

Using Eq. (81), the solution of Eq. (84) is

$$\begin{aligned}a^{(1)}_{n_k}(t)=&-\frac{1}{\hbar}\sum_{j=1}^{M}F_{n_km_j}\frac{e^{i(\alpha_q-2\omega-\xi)t}}{\alpha_q-2\omega-\xi}a^{q0}_{m_j}-\frac{1}{\hbar}\sum_{k'(\neq k)}\left[F_{n_kn_{k'}}\frac{e^{i(\alpha_q-\omega-\xi)t}}{\alpha_q-\omega-\xi}+F^*_{n_{k'}n_k}\frac{e^{i(\alpha_q+\omega-\xi)t}}{\alpha_q+\omega-\xi}\right]b^{q0}_{n_{k'}}\\&+\frac{1}{\hbar^2}\sum_sF_{n_ks}\left\{\sum_j\left[F_{sm_j}\frac{e^{i(\alpha_q-3\omega-\xi)t}}{(\omega_{sm_j}-\omega+\alpha_q)(\alpha_q-3\omega-\xi)}+F^*_{m_js}\frac{e^{i(\alpha_q-\omega-\xi)t}}{(\omega_{sm_j}+\omega+\alpha_q)(\alpha_q-\omega-\xi)}\right]a^{q0}_{m_j}\right.\\&\left.+\sum_{k'}\left[F_{sn_{k'}}\frac{e^{i(\alpha_q-2\omega-\xi)t}}{(\omega_{sn_{k'}}-\omega+\alpha_q-\xi)(\alpha_q-2\omega-\xi)}+F^*_{n_{k'}s}\frac{e^{i(\alpha_q-\xi)t}}{(\omega_{sn_{k'}}+\omega+\alpha_q-\xi)(\alpha_q-\xi)}\right]b^{q0}_{n_{k'}}\right\}\end{aligned}$$

$$+\frac{1}{\hbar^2}\sum_s F^*_{sn_k}\left\{\sum_j\left[F_{sm_j}\frac{e^{i(\alpha_q-\omega-\xi)t}}{(\omega_{sm_j}-\omega+\alpha_q)(\alpha_q-\omega-\xi)}+F^*_{m_js}\frac{e^{i(\alpha_q+\omega-\xi)t}}{(\omega_{sm_j}+\omega+\alpha_q)(\alpha_q+\omega-\xi)}\right]a^{q0}_{m_j}\right.$$
$$\left.+\sum_{k'}\left[F_{sn_{k'}}\frac{e^{i(\alpha_q-\xi)t}}{(\omega_{sn_{k'}}-\omega+\alpha_q-\xi)(\alpha_q-\xi)}+F^*_{n_{k's}}\frac{e^{i(\alpha_q+2\omega-\xi)t}}{(\omega_{sn_{k'}}+\omega+\alpha_q-\xi)(\alpha_q+2\omega-\xi)}\right]b^{q0}_{n_{k'}}\right\}. \quad (85)$$

The common time factor $e^{i(\alpha_q-\xi)t}$ does not appear in any averaged quantity. Substitute Eqs. (81), (83), and (85) into Eq. (79), we find the first-order correction in the states which are in resonance with the external field. The current density is obtained by substituting Eq. (79) into Eq. (25). The full formula is too long to write out, we only write down the contribution from the first term in Eq. (79).

The current density involving the time factor $\cos\omega t$ is

$$\mathbf{j}_c(\mathbf{r},t)=\frac{e}{m\Omega_\mathbf{r}}\cos\omega t\int_{\Omega_\mathbf{r}}d\mathbf{s}\sum_{l_1l_2\ldots l_{N_e}}W_{l_1l_2\ldots l_{N_e}}\frac{1}{N_e}\sum_{qs}\mathrm{Im}\left\{\sum_{jj'}a^{q0}_{m_j}a^{q0*}_{m_{j'}}(\chi_{m_j}\nabla\chi^*_s-\chi^*_s\nabla\chi_{m_j})\left[F^*_{sm_{j'}}\frac{1}{\omega_{sm_{j'}}-\omega+\alpha_q}\right.\right.$$
$$\left.+F_{m_{j's}}\frac{1}{\omega_{sm_{j'}}+\omega+\alpha_q}\right]+\sum_{kk'}b^{q0}_{n_k}b^{q0*}_{n_{k'}}(\chi_{n_k}\nabla\chi^*_s-\chi^*_s\nabla\chi_{n_k})\left[F^*_{sn_{k'}}\frac{1}{\omega_{sn_{k'}}-\omega+\alpha_q-\xi}+F_{n_{k's}}\frac{1}{\omega_{sn_{k'}}+\omega+\alpha_q-\xi}\right]\left.\right\}. \quad (86)$$

The current density with time factor $\sin\omega t$ is

$$\mathbf{j}_s(\mathbf{r},t)=\frac{-ie}{m\Omega_\mathbf{r}}\sin\omega t\int_{\Omega_\mathbf{r}}d\mathbf{s}\sum_{l_1l_2\ldots l_{N_e}}W_{l_1l_2\ldots l_{N_e}}\frac{1}{N_e}\sum_{qs}\mathrm{Im}\left[\sum_{jj'}a^{q0*}_{m_j}a^{q0}_{m_{j'}}(\chi_s\nabla\chi^*_{m_j}+\chi^*_{m_j}\nabla\chi_s)\left[F_{sm_{j'}}\frac{1}{\omega_{sm_{j'}}-\omega+\alpha_q}\right.\right.$$
$$\left.-F^*_{m_{j's}}\frac{1}{\omega_{sm_{j'}}+\omega+\alpha_q}\right]+\sum_{kk'}b^{q0*}_{n_k}b^{q0}_{n_{k'}}(\chi_s\nabla\chi^*_{n_k}+\chi^*_{n_k}\nabla\chi_s)\left[F_{sn_{k'}}\frac{1}{\omega_{sn_{k'}}-\omega+\alpha_q-\xi}-F^*_{n_{k's}}\frac{1}{\omega_{sn_{k'}}+\omega+\alpha_q-\xi}\right]. \quad (87)$$

A typical term $a^{q0*}_{m_j}a^{q0}_{m_{j'}}(\chi_s\nabla\chi^*_{m_j})F_{sm_{j'}}$ in Eqs. (86) and (87) represents the coupling between two members χ_{m_j} and $\chi_{m_{j'}}$ in the upper group through a nonresonant state χ_s. Another typical term $b^{q0*}_{n_k}b^{q0}_{n_{k'}}(\chi_s\nabla\chi^*_{n_k})F_{sn_{k'}}$ in Eqs. (86) and (87) represents the coupling between two members χ_{n_k} and $\chi_{n_{k'}}$ in the lower group through a nonresonant state χ_s.

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

$$\mathbf{j}_{c2}(\mathbf{r},t)=\frac{-ie}{m\Omega_\mathbf{r}}\cos 2\omega t\int_{\Omega_\mathbf{r}}d\mathbf{s}\sum_{l_1l_2\ldots l_{N_e}}W_{l_1l_2\ldots l_{N_e}}\frac{1}{N_e}\sum_{qs}\sum_{jk}\mathrm{Re}\left[a^{q0*}_{m_j}b^{q0}_{n_k}(\chi_s\nabla\chi^*_{m_j}+\chi^*_{m_j}\nabla\chi_s)F^*_{n_ks}\frac{1}{\omega_{sn_k}+\omega+\alpha_q-\xi}+a^{q0}_{m_j}b^{q0*}_{n_k}(\chi^*_{n_k}\nabla\chi_s\right.$$
$$\left.+\chi_s\nabla\chi^*_{n_k})F_{sm_j}\frac{1}{\omega_{sm_j}-\omega+\alpha_q}\right]. \quad (88)$$

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

$$\mathbf{j}_{s2}(\mathbf{r},t)=\frac{-ie}{m\Omega_\mathbf{r}}\sin 2\omega t\int_{\Omega_\mathbf{r}}d\mathbf{s}\sum_{l_1l_2\ldots l_{N_e}}W_{l_1l_2\ldots l_{N_e}}\frac{1}{N_e}\sum_{qs}\sum_{jk}\mathrm{Im}\left[a^{q0}_{m_j}b^{q0*}_{n_k}(\chi_{m_j}\nabla\chi^*_s+\chi^*_s\nabla\chi_{m_j})F_{n_ks}\frac{1}{\omega_{sn_k}+\omega+\alpha_q-\xi}+a^{q0}_{m_j}b^{q0*}_{n_k}(\chi^*_{n_k}\nabla\chi_s\right.$$
$$\left.+\chi_s\nabla\chi^*_{n_k})F_{sm_j}\frac{1}{\omega_{sm_j}-\omega+\alpha_q}\right]. \quad (89)$$

The current density without time variation is

$$\mathbf{j}_0(\mathbf{r})=\frac{-ie}{m\Omega_\mathbf{r}}\int_{\Omega_\mathbf{r}}d\mathbf{s}\sum_{l_1l_2\ldots l_{N_e}}W_{l_1l_2\ldots l_{N_e}}\frac{1}{N_e}\sum_{qs}\sum_{jk}\mathrm{Re}\left[a^{q0}_{m_j}b^{q0*}_{n_k}(\chi_{m_j}\nabla\chi^*_s+\chi^*_s\nabla\chi_{m_j})F^*_{sn_k}\frac{1}{\omega_{sn_k}-\omega+\alpha_q-\xi}+a^{q0*}_{m_j}b^{q0}_{n_k}(\chi_{n_k}\nabla\chi^*_s\right.$$
$$\left.+\chi^*_s\nabla\chi_{n_k})F_{m_js}\frac{1}{\omega_{sm_j}+\omega+\alpha_q}\right]. \quad (90)$$

The contribution to current from two groups of resonant states is finite. In contrast with degenerate states, double-frequency and zero-frequency components of current are linked to the formal first-order dependence of field. If we look at a typical term $a_{m_j}^{q0} b_{n_k}^{q0*} (\chi_{n_k}^* \nabla \chi_s) F_{sm_j}$ in Eqs. (88)–(90), this is not surprise: a member χ_{n_k} in the lower group coupled with a member χ_{m_j} in the upper group couples to a member $\chi_{n_k}^*$ in the lower group through a nonresonant state χ_s. The coupling $\chi_{n_k}^* \nabla \chi_s$ originates from current operator, while F_{sm_j} comes from the field. It is different from the component of current with same frequency as the external field, where only the states in same group couple. We did not write out other contributions from coupling between nonresonant states and resonant states, i.e., the first three terms in $a_{m_j}^{(1)}$ and $a_{n_k}^{(1)}$, though they are also formal linear terms in the field. The aim here is to show the dramatic difference to the nonlinear effect caused by degenerate states.

In Eq. (25), the contribution to current from resonant states arises from

$$\sum_{q=1}^{M+M'} [\chi_q'^{(0)}(t) \nabla \chi_q'^{(1)*}(t) + \chi_q'^{(1)}(t) \nabla \chi_q'^{(0)*}(t) - \chi_q'^{(0)*}(t) \nabla \chi_q'^{(1)}(t) - \chi_q'^{(1)*}(t) \nabla \chi_q'^{(0)}(t)]. \quad (91)$$

By substituting Eqs. (77) and (79) into Eq. (91), it is easy to find the contributions to current density from the second term and the third term in Eq. (79). A typical term with time factor $e^{i3\omega t}$ is $\Sigma_{qjksk'} a_{m_j}^{q0*} b_{n_{k'}}^{q0*} (\chi_{m_j}^* \nabla \chi_{n_k}) F_{n_{k'}s}^* F_{sn_k}^* (\omega_{sn_{k'}} + \omega + \alpha_q - \xi)^{-1} (\alpha_q + 2\omega - \xi)^{-1}$, which comes from $\chi_q'^{(0)*} \nabla \chi_q'^{(1)}$. Formally this is a third process: state $\chi_{n_{k'}}$ in the lower group indirectly couples with another state χ_{n_k} in the lower group through a nonresonant state χ_s, state χ_{n_k} further couples with state χ_{m_j} in the upper group through current operator. But formally it only has second-order dependence on the field in $F_{n_{k'}s}^* F_{sn_k}^*$.

V. 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 the method to intrinsic semiconductors.

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

Let us label the single-particle states in the valence band from low to high energy as $v_{N_e}, \ldots, v_2, v_1$, the states in the conduction band from low 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, the system is in ground state Λ_0. At $T>0$, various excited states appear. A one-electron excited state $\Lambda_{v_j c_k}$ is constructed from Λ_0 by replacing v_j with c_k. Because the interaction with a static field

$$H_{int} = -\sum_{m=1}^{N_e} e\mathbf{E} \cdot \mathbf{r}_m \quad (92)$$

is a single-particle operator (separable for coordinate of each particle), the ground state only couples with one-electron excited states. The change in ground state Λ_0 by external field only includes one-electron excited states

$$\Lambda_0'^{(1)} = \sum_{jk} \frac{\langle c_k(1)|e\mathbf{E} \cdot \mathbf{r}_1|v_j(1)\rangle}{(E_{C_k} - E_{c_1}) + (E_{v_1} - E_{v_j}) + E_g} \Lambda_{v_j c_k}. \quad (93)$$

Substitute Eq. (93) into Eq. (4) and effect the multiple integral, one can read off conductivity from the current density Eq. (6) by using Eq. (14)

$$\sigma_{\mu\nu} = \frac{ie^2\hbar N_e}{2m\Omega} \sum_{jk} \left\{ \frac{\langle c_k(1)|r_{1\nu}|v_j(1)\rangle^*}{(E_{C_k} - E_{c_1}) + (E_{v_1} - E_{v_j}) + E_g} \int_{\Omega_\mathbf{r}} d\mathbf{s} \left[v_j(\mathbf{s}) \frac{\partial}{\partial s_\mu} c_k^*(\mathbf{s}) - c_k^*(\mathbf{s}) \frac{\partial}{\partial s_\mu} v_j(\mathbf{s}) \right] \right.$$
$$\left. + \frac{\langle c_k(1)|r_{1\nu}|v_j(1)\rangle}{(E_{C_k} - E_{c_1}) + (E_{v_1} - E_{v_j}) + E_g} \int_{\Omega_\mathbf{r}} d\mathbf{s} \left[c_k(\mathbf{s}) \frac{\partial}{\partial s_\mu} v_j^*(\mathbf{s}) - v_j^*(\mathbf{s}) \frac{\partial}{\partial s_\mu} c_k(\mathbf{s}) \right] \right\}, \quad \mu, \nu = x, y, z. \quad (94)$$

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 obvious in next section): the change $\Lambda_0'^{(1)}$ in wave function Λ_0 can be neglected, and the dc conductivity is negligible at $T=0$ in an intrinsic semiconductor. The coupling between zero-electron to one-electron excited states can be viewed as an interband transition, its probability is not exactly zero, but is exponentially small. One may neglect the existence of conduction band: the 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 that is much weaker than atomic field.

B. Conduction from one-electron excited states

Because H_{int} is single-particle operator, a one-electron excited state could couple with the ground state, one-electron excited states, and two-electron excited states. The energy

difference between a one-electron excited state and a two-electron excited state is at least the energy gap, E_g. The contribution to current density from this coupling is small. For the same reason, the coupling between a one-electron excited state and Λ_0 is also negligible.

Since H_{int} is a single-particle operator, there are only two types of coupling between two different one-electron excited states: $\Lambda_{v_j c_k} \leftrightarrow \Lambda_{v_j c_{k'}}$ or $\Lambda_{v_j c_k} \leftrightarrow \Lambda_{v_{j'} c_k}$. The energy difference between such pairs of one-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 $\Lambda_{v_j c_k}$ caused by a static field is easily computed. By appealing to Eqs. (11), (14), and (18), the expression for conductivity in the momentum representation is

$$\sigma_{\alpha\beta} = \frac{e^2\hbar^3 N_e}{m^2 \Omega_{\mathbf{r}'}} \sum_{jk} W_{v_j c_k} \mathrm{Im} \left\{ \sum_{k'} \frac{\langle c_{k'}(1)| \frac{\partial}{\partial x_{1\beta}} |c_k(1)\rangle}{(E_{c_{k'}} - E_{c_k})^2} \int_{\Omega_{\mathbf{r}'}} d\mathbf{r} \left[c_{k'}(\mathbf{r}) \frac{\partial c_k^*(\mathbf{r})}{\partial x_\alpha} - c_k^*(\mathbf{r}) \frac{\partial c_{k'}(\mathbf{r})}{\partial x_\alpha} \right] \right.$$
$$\left. + \sum_{j'} \frac{\langle v_{j'}(1)| \frac{\partial}{\partial x_{1\beta}} |v_j(1)\rangle}{(E_{v_{j'}} - E_{v_j})^2} \int_{\Omega_{\mathbf{r}'}} d\mathbf{r} \left[v_{j'}(\mathbf{r}) \frac{\partial v_j^*(\mathbf{r})}{\partial x_\alpha} - v_j^*(\mathbf{r}) \frac{\partial v_{j'}(\mathbf{r})}{\partial x_\alpha} \right] \right\}, \tag{95}$$

where

$$W_{v_j c_k} = [1 - f(E_{v_j})] f(E_{c_k}). \tag{96}$$

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 contribute less. All the denominators in Eq. (95) are nonzero. Except for δ functions, Eq. (95), the contribution from one-electron excited states, corresponds exactly to the ordinary Greenwood formula. The generalization to K-electron excited states and metals is straightforward.

In the standard application of the KGF (Ref. 36)

$$\sigma(T) = \int_{-\infty}^{\infty} dE \sigma(E) \left[-\frac{df}{dE} \right],$$

$$\sigma(E) = \frac{\pi\hbar^2}{\Omega m^2} \sum_{mn} |\langle n|p_x|m\rangle|^2 \delta(E_n - E) \delta(E_m - E), \tag{97}$$

one broadens δ function by a Gaussian

$$\delta(E_n - E) \approx \frac{\exp[-(E_n - E)^2/(2\Delta^2)]}{\Delta\sqrt{2\pi}}. \tag{98}$$

Numerically, this procedure is equivalent to replacing the whole series about $(E_{v_{j'}} - E_{v_j})^{-2}$ in Eq. (95) with several large terms, each of order of Δ^{-2}. There are three relevant energy scales in the problem: the step length of energy, $k_B T$, and characteristic energy level splitting near E_F. The choices of Δ is thus seen to be somewhat arbitrary. On one hand Δ should be order of $k_B T$ to reflect thermal environment. However $k_B T$ is a too small choice of Δ for room temperature but may be too large for a high temperature. On the other hand, Δ should be order of or smaller than the eigenvalue splitting 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 Δ or requires some other extrapolation scheme to $\omega=0$. Equation (95) or Eq. (34) does not suffer from this problem.

VI. SUMMARY

We derived an expression for the current density from the principle of virtual work and coarse graining. It includes the amplitude of transition probability caused by external field. This means that we do not require an assumption of long interaction time, that is unjustified for a large system. The result is equivalent to that derived from statistical average. But it is more convenient for complicated situations specially the cases of degenerate and resonant states. The key results of this paper are Eqs. (34), (35), (53), (63)–(65), (78), (83), (85), and (95).

The scattering states in the force field of several scattering centers and the Bloch states in a crystal form a continuous spectrum. When the final state of a transition (real or virtual) is a Bloch state or a scattering state, Eq. (47) is the standard procedure to bypass the poles in Eq. (46) introduced by degenerate states at $\omega=0$. This procedure does not work for localized states in an amorphous semiconductor and for degenerate states in a crystal caused by symmetry or accidental degeneracy.[38] These degenerate states for a given energy cannot be characterized by continuous parameters. They must be treated as degenerate states in a discrete spectrum. Ordinary perturbation theory used to derive the conductivity is only applicable to nondegenerate states and the states which are not in resonance with external field. In such a formulation, degenerate states and the states which are in resonance with external field cause a divergence. We designed time-dependent perturbation theories which are suitable for degenerate states in zero- or low-frequency field and

to the states which are in resonance with external field, respectively. With the help of these, zero-order contributions of these two cases vanishes, cf Eqs. (53) and (78). The current density from first-order change in degenerate states and resonant states are field dependent and finite, cf. Eqs. (24), (60)–(65), and (86)–(90). The dc conductivity is contained in the ac conductivity, no zero-frequency limit is needed.

If the disorder is small in an amorphous solid, single-particle states can be labeled by the wave vectors of the virtual crystal. One can obtain a systematic expansion of the conductivity expression in terms of disorder potential $(V_a - V_c)$. It corresponds to the semiclassical Boltzmann formalism at various levels of approximation.

In an oscillating field with time dependence $\cos \omega t$, in addition to two normal components of current with $\cos \omega t$ and $\sin \omega t$ time-dependence factors, three new components of current with time dependence of $\cos 2\omega t$, $\sin 2\omega t$, and 1 are produced by degenerate states. Formally they have second-order dependence on field. The first-order correction on the states which are in resonance with external field also produces components of current with time factors $\cos 2\omega t$, $\sin 2\omega t$, and 1. In this situation, the field dependence of these components is formally first order. In addition, the first-order correction of the resonant states also produces components of current with time-dependence $\cos 3\omega t$ and $\sin 3\omega t$, formally the field dependence of these components is second order. We hope that these predictions will be explored by experimentalists.

Fermi statistics cannot be properly reflected in the expression of dc conductivity if we first apply single-particle approximation to many-electron wave function and use stationary perturbation theory to calculate the change in single-electron states caused by dc field. The fault can be overcome if we use stationary perturbation theory on the change in many-electron wave function. Beside, one can explicitly display that the dc conductivity of an intrinsic semiconductor at $T=0$ K is zero. For an intrinsic semiconductor, the KGF is the contribution from one-electron excited states.

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