Transport calculations in complex materials: A comparison of the Kubo formula, the Kubo-Greenwood formula and the microscopic response method

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Recently we have introduced the microscopic response method (MRM) to compute the conductivity and Hall mobility for complex system with topological and thermal disorder, which is more convenient than the Kubo formula. We prove that for a canonical ensemble the MRM leads to the same expression as the Kubo formula. When the gradient of carrier density is small, the MRM reduces to the widely used Kubo-Greenwood formula.

Linear response theory[1, 2] is a rigorous and complicated procedure used to compute transport coefficients. It constructs the observable macroscopic response by averaging the operator of microscopic response over the density matrix of system. Then, to obtain transport coefficients, one has to calculate an imaginary time integral resulting from the commutator between the density matrix and microscopic response[3]. If a system has several types of elementary excitations and the interactions among elementary excitations are strong, it is difficult to fulfil the imaginary time integral with controllable approximations. For example, the imaginary time integral prevents researchers from computing all the important contributions in conductivity and Hall mobility of small polarons[4–9]. Amorphous semiconductors and semiconducting polymers require approximations beyond small polarons: the low-lying excited states often contain both localized states and extended states[10], and the electron-phonon interactions in localized states are much stronger than those in extended states[11, 12]. Even for the lowest order self-consistent approximation[13], it is difficult to apply the Kubo formula, and consistently include all important contributions for conductivity or Hall mobility.

To compute the transport coefficient for a mechanical perturbation, the microscopic response method (MRM) is more convenient[13, 14] than Kubo formula. A mechanical perturbation such as the coupling with an external field can be expressed via additional terms in the Hamiltonian[1, 2], and the wave function Ψ' of system in an external field at a later moment is determined by its initial value and the time-dependent Schrödinger equation. The microscopic response can be expressed in terms of the changes in wave function induced by the external field[13, 14]. The ensemble average and coarse-grained average needed to compute the macroscopic response (transport coefficient) can then be carried out at the final stage. Thus for a mechanical perturbation, we are able to avoid the imaginary time integral in the Kubo formula [13, 14].

The Kubo-Greenwood formula (KGF)[15] has been implemented in many *ab initio* codes to calculate the dielectric function and AC conductivity. However the KGF is based on a simplified expression for the current density,

which is borrowed from the kinetic theory of gas.

In this paper, we prove that for mechanical perturbations, the MRM is equivalent to the Kubo formula. To fulfil this aim, we first write out the observable macroscopic current density to first and second order in external field in the Kubo formulation.Then the same procedures are carried out with the MRM[14]. We see that the macroscopic response calculated in the two methods are the same. We discuss the connection between density matrix and transition amplitudes at different order of perturbation. We will see why the MRM allows easy classification of transport processes and expression for transport coefficient compared to the Kubo formulation[1]. We show that the current density used by Greenwood is justified only when the gradient of carrier density is small.

In this work, we use the Schrödinger picture. Consider a system with N electrons and $\mathcal{N}$ nuclei in an electromagnetic field with potentials $(\mathbf{A}, \phi)$, at time t, the many-electron state of system is described by $\Psi'(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N; t)$. To save space, we will not write out the nuclear coordinates explicitly. Ψ' satisfies the Schrödinger equation

$$i\hbar\partial\Psi'/\partial t = H'\Psi', \ H' = H + V(t), \qquad (1)$$

where $V(t)$ is the interaction between the system and external field. The time dependence in $V(t')$ comes from the external field. H is the Hamiltonian of the system without external field. We use $|m\rangle$ or Ψ_m and E_m to denote the mth stationary state and the corresponding eigenvalue of the N electrons $+ \mathcal{N}$ nuclei system: $H|m\rangle = E_m|m\rangle$. If the system is in a thermal bath at temperature T, then before introducing $V(t)$, the equilibrium density operator is

$$\widehat{\rho} = \sum_m |m\rangle P_m\langle m|, \ P_m = e^{-\beta E_m}/Z, \qquad (2)$$

where $Z = \sum_n e^{-\beta E_n}$ is the partition function. In an external electromagnetic field, the velocity operator $\mathbf{v}_i$ for the ith particle is[16]

$$\mathbf{v}_i = m^{-1}[\mathbf{P}_i - e\mathbf{A}(\mathbf{r}_i; t)], \qquad (3)$$

where $\mathbf{r}_i$ and $\mathbf{P}_i = -i\hbar\nabla_{\mathbf{r}_i}$ are the position and momentum operators of the ith particle, and e is the charge of electron. Because velocity and position cannot be simultaneously measured, one has to symmetrize the velocity and position operators in the current density operator. One may conjecture that the current density operator at point $\mathbf{r}$ is[17]:

$$\widehat{\mathbf{j}}(\mathbf{r}) = \frac{e}{2}\sum_{i=1}^{N}[\mathbf{v}_i\delta(\mathbf{r}-\mathbf{r}_i) + \delta(\mathbf{r}-\mathbf{r}_i)\mathbf{v}_i]. \quad (4)$$

In the MRM[13, 14, 18], we avoided $\widehat{\mathbf{j}}(\mathbf{r})$. Now we show that Eq.(4) leads to a proper microscopic current density[13, 14]. Because a mechanical perturbation can be expressed with additional terms in Hamiltonian, the states at time t can be described by a wave function which is determined by the initial conditions. The microscopic current density at time t and point $\mathbf{r}$ in state $\Psi'(\mathbf{r}_1,\mathbf{r}_2,\cdots,\mathbf{r}_N;t)$ is

$$\mathbf{j}_m(\mathbf{r};t) = \int d\tau \Psi'^{*}\widehat{\mathbf{j}}(\mathbf{r})\Psi', \quad (5)$$

where $d\tau = d\mathbf{r}_1 d\tau'$, and $d\tau' = d\mathbf{r}_2\cdots d\mathbf{r}_N$. Integrating by parts, one has

$$\mathbf{j}_m(\mathbf{r};t) = -\frac{e^2 N}{m}\mathbf{A}(\mathbf{r})\int d\tau' \Psi'^{*}\nabla_{\mathbf{r}}\Psi' \quad (6)$$

$$+\frac{i\hbar e N}{2m}\int d\tau'(\Psi'\nabla_{\mathbf{r}}\Psi'^{*} - \Psi'^{*}\nabla_{\mathbf{r}}\Psi'),$$

where the arguments of Ψ' in Eq.(6) are $(\mathbf{r},\mathbf{r}_2,\cdots,\mathbf{r}_N;t)$. Eq.(6) has been independently derived from the principle of virtual work[18], the continuity equation[14] and the polarization density[13]. The current operator given in Eq.(4) is correct, and it will bridge the Kubo formulation and the MRM.

To write out the macroscopic response in the Kubo formula, we notice that the time evolution for a system involving mixed states is included in the density matrix. The basis set should be a group of wave functions without any time dependence[19]. In the $|m\rangle$ representation, the matrix elements of $\widehat{\mathbf{j}}(\mathbf{r})$ are

$$\langle n|\widehat{\mathbf{j}}(\mathbf{r})|m\rangle = \frac{Nei\hbar}{2m}\int d\tau'[\Psi_m\nabla_{\mathbf{r}}\Psi_n^{*} - \Psi_n^{*}\nabla_{\mathbf{r}}\Psi_m]$$

$$-\frac{Ne^2}{m}\mathbf{A}(\mathbf{r})\int d\tau' \Psi_n^{*}\Psi_m, \quad (7)$$

where the arguments of Ψ_m and Ψ_n are $(\mathbf{r},\mathbf{r}_2,\cdots,\mathbf{r}_N)$. With ρ in Eq.(2) as the initial condition, one can use perturbation theory to solve the Liouville equation to any order in $V(t)$. The density matrix at time t is $\rho'(t) =$

$\rho + \rho^{(1)}(t) + \rho^{(2)}(t) + \cdots$. To first order in $V(t)$, the deviation $\rho^{(1)}(t)$ from ρ is[3]

$$\langle m|\rho^{(1)}(t)|n\rangle = \frac{1}{i\hbar}\int_{-\infty}^{t} dt' e^{i(t-t')(E_n-E_m)/\hbar} \quad (8)$$

$$\langle m|V(t')|n\rangle(P_n - P_m).$$

The conductivity can be read off from the macroscopic current density:

$$\mathbf{j}^{(1)}(\mathbf{r},t) = \sum_{mn}\langle m|\rho^{(1)}(t)|n\rangle\langle n|\widehat{\mathbf{j}}(\mathbf{r})|m\rangle. \quad (9)$$

To 2nd order in $V(t)$, the deviation $\rho^{(2)}(t)$ is

$$\langle m|\rho^{(2)}(t)|n\rangle = -\frac{1}{\hbar^2}e^{it(E_n-E_m)/\hbar}\sum_k\{ \quad (10)$$

$$(P_n\int_{-\infty}^{t} dt'\int_{-\infty}^{t'} dt'' + P_m\int_{-\infty}^{t} dt''\int_{-\infty}^{t''} dt')$$

$$e^{it''(E_k-E_n)/\hbar}e^{it'(E_m-E_k)/\hbar}\langle m|V(t')|k\rangle\langle k|V(t'')|n\rangle$$

$$-(\int_{-\infty}^{t} dt'\int_{-\infty}^{t'} dt'' + \int_{-\infty}^{t} dt''\int_{-\infty}^{t''} dt')$$

$$e^{it''(E_k-E_n)/\hbar}e^{it'(E_m-E_k)/\hbar}\langle m|V(t')|k\rangle P_k\langle k|V(t'')|n\rangle\},$$

The 2nd order macroscopic response $\mathbf{j}^{(2)}(\mathbf{r},t)$ is obtained from Eq.(9) by replacing $\langle m|\rho^{(1)}(t)|n\rangle$ with $\langle m|\rho^{(2)}(t)|n\rangle$. We are going to compare Eqs.(8,9,10) and $\mathbf{j}^{(2)}(\mathbf{r},t)$ with the corresponding quantities in the MRM.

In the MRM, the macroscopic response is given by [13, 14]:

$$\mathbf{j}(\mathbf{r},t) = \sum_n P_n\langle\Psi'_n(t)|\widehat{\mathbf{j}}(\mathbf{r})|\Psi'_n(t)\rangle. \quad (11)$$

If the initial state is Ψ_n, then the state $\Psi'_n(t)$ of a system at time t in an external field can be determined[19] by applying perturbation theory to Eq.(1):

$$\Psi'_n(t) = a^{(0)}(n,t)\Psi_n \quad (12)$$

$$+\sum_m a^{(1)}(mn,t)\Psi_m + \sum_m a^{(2)}(mn,t)\Psi_m,$$

where

$$a^{(0)}(n,t) = e^{-iE_n t/\hbar}, \quad (13)$$

and

$$a^{(1)}(mn,t) = -\frac{i}{\hbar}e^{-iE_m t/\hbar}\int_{-\infty}^{t} dt' \quad (14)$$

$$e^{i(E_m-E_n)t'/\hbar}\langle m|V(t')|n\rangle,$$

and

$$a^{(2)}(mn,t) = -\frac{1}{\hbar^2}e^{-iE_mt/\hbar}\sum_k\int_{-\infty}^t dt' e^{i(E_m-E_k)t'/\hbar}$$

$$\langle m|V(t')|k\rangle\int_{-\infty}^{t'}dt'' e^{i(E_k-E_n)t''/\hbar}\langle k|V(t'')|n\rangle. \quad (15)$$

To first order in $V(t)$, the macroscopic current density is

$$\mathbf{j}^{(1)}(\mathbf{r},t) = \sum_n P_n[\langle\Psi_n^{(0)}(t)|\widehat{\mathbf{j}}(\mathbf{r})|\Psi_n^{(1)}(t)\rangle \quad (16)$$

$$+\langle\Psi_n^{(1)}(t)|\widehat{\mathbf{j}}(\mathbf{r})|\Psi_n^{(0)}(t)\rangle].$$

Substituting Eqs.(12,13,14) into Eq.(16), and using the fact that $V(t')$ and $\widehat{\mathbf{j}}(\mathbf{r})$ are Hermitian operators, one finds the same result as Eqs.(8,9). To second order in $V(t)$, the macroscopic current density is

$$\mathbf{j}^{(2)}(\mathbf{r},t) = \sum_n P_n[\langle\Psi_n^{(0)}(t)|\widehat{\mathbf{j}}(\mathbf{r})|\Psi_n^{(2)}(t)\rangle \quad (17)$$

$$+\langle\Psi_n^{(2)}(t)|\widehat{\mathbf{j}}(\mathbf{r})|\Psi_n^{(0)}(t)\rangle + \langle\Psi_n^{(1)}(t)|\widehat{\mathbf{j}}(\mathbf{r})|\Psi_n^{(1)}(t)\rangle].$$

Substituting Eqs.(12,13,14,15) into Eq.(17), the first term of Eq.(17) is the same as the 1st term of $\mathbf{j}^{(2)}$ from Eq.(10), the 2nd term of Eq.(17) is the same as the 2nd term of $\mathbf{j}^{(2)}$ resulted from Eq.(10). One can see that the 3rd term Eq.(17) equals the sum of the 3rd term and the 4th term of $\mathbf{j}^{(2)}$ from Eq.(10), if one notices: (1) three integrands are the same; (2) the 3rd term in Eq.(17) is a two-dimensional integral in domain $[-\infty, t; -\infty, t]$; (3) the 3rd term of $\mathbf{j}^{(2)}$ is a successive integration $\int_{-\infty}^t dt'\int_{-\infty}^{t'}dt''$; (4) the 4th term of $\mathbf{j}^{(2)}$ is a successive integration $\int_{-\infty}^t dt''\int_{-\infty}^{t''}dt'$. The procedure is easy to proceed to any order in field. The equation (11) does not use any specific property of electromagnetic field, the procedure works for any mechanical perturbation. Introducing current density operator (4) is the key for the proof. In the original MRM, one does not need current density operator, the macroscopic response is obtained by averaging over the microscopic response (6) over canonical distribution. Eqs.(4,11) established a connection between two methods.

It is worthwhile to find the connection between the probability amplitudes in Eqs.(13-15) and the density matrices in Eqs.(8,10). The element of the density matrix is the average the product of two probability amplitudes over the $\mathcal{M}$ members in an ensemble[19]:

$$\rho_{mn} = \frac{1}{\mathcal{M}}\sum_\alpha a_\alpha^*(n,t)a_\alpha(m,t), \quad (18)$$

where α is the index of a member in the canonical ensemble. To the first order in $V(t)$,

$$\rho_{mn}^{(1)} = \frac{1}{N}\sum_\alpha a_\alpha^{*(0)}(n,t)a_\alpha^{(1)}(m,t) \quad (19)$$

$$+\frac{1}{N}\sum_\alpha a_\alpha^{*(1)}(n,t)a_\alpha^{(0)}(m,t),$$

where $a_\alpha^{(0)}(n,t)$ is the zero order transition amplitude from initial state $|n\rangle$ to final state $|n\rangle$, $a_\alpha^{(1)}(m,t)$ is the first order transition amplitude from initial state $|n\rangle$ to final state $|m\rangle$, $a^{(0)}(m;t)$ is the zero order transition amplitude from initial state $|m\rangle$ to final state $|m\rangle$, $a^{(1)}(n,t)$ is the first order transition amplitude from initial state $|m\rangle$ to final state $|n\rangle$. With these explanations, substituting Eqs.(13,14) into Eq.(19), one reaches Eq.(8), which was obtained from Liouville equation. To 2nd order in $V(t)$,

$$\rho_{mn}^{(2)} = \frac{1}{\mathcal{M}}\sum_\alpha\{a_\alpha^{*(0)}(n,t)a_\alpha^{(2)}(m,t) \quad (20)$$

$$+a_\alpha^{*(2)}(n,t)a_\alpha^{(0)}(m,t) + a_\alpha^{*(1)}(n,t)a_\alpha^{(1)}(m,t)\}.$$

In the 1st term of (20), the initial state is $|n\rangle$, $a_\alpha^{(2)}(m,t)$ is the 2nd order transition amplitude through intermediate states $|k\rangle$. By means of Eqs.(13,15), the first term of Eq.(20) is the same as the 1st term of Eq.(10). In the second term of (20), the initial state is $|m\rangle$, $a_\alpha^{(2)}(n,t)$ is the 2nd order transition amplitude through intermediate states $|k\rangle$ to final state $|n\rangle$. The second term of Eq.(20) is the same as the second term of Eq.(10). In the 3rd term of (20), two final states $|n\rangle$ and $|m\rangle$ come from a common initial state $|k\rangle$, all states $\{|k\rangle\}$ satisfy $k \neq n$ and $k \neq m$ can be taken as the initial state. In terms of the same trick in comparing the 3rd term in Eq.(17) and the sum of the 3rd and 4th terms of $\mathbf{j}^{(2)}(\mathbf{r},t)$ derived from Eq.(10), we can see that the 3rd term of (20) is the same as the sum of the 3rd term and the 4th term in Eq.(10).

We explain why the MRM is simpler than the Kubo formula for mechanical perturbations. To a given order in residual interactions, various transport processes contribute to a specific transport coefficient. In the MRM, each transport process is composed of several elementary transitions caused by external field and by residual interactions[13, 20]. Because the microscopic response is expressed by the wave function of system in external field rather than density matrix, each elementary transition appears as a transition amplitude[13]. According to Eq.(12), the state at t is a linear superposition of the various order changes induced by the external field. By means of Eqs.(6,16,17), gradient operator connects two components of the final state[13]. In addition, the transition amplitude of a higher order transition is constructed

by first making a product of the sequence of first order amplitudes of elementary transitions and then summing over all intermediate states. We can depict each transport process with a diagram, which has one line connecting two components of final state, and several other lines presenting elementary transitions. To a given order of residual interactions, the topology of diagrams can help us classify and construct all possible transport processes[13]. In the Kubo formulation, all time-dependence is included in density matrix, cf. Eqs.(9,7). To a given order in external field, the change in density matrix involves different members of the ensemble, cf. Eqs.(19,20). Besides, the density matrix is bilinear in transition amplitude. Therefore for a transport process with more than one elementary transitions, one cannot express it as a product of propagators.

Greenwood derived his conductivity expression from[15]

$$\mathbf{j}(t) = eTr\{\rho'(t)\mathbf{v}\}, \tag{21}$$

where $\rho'(t)$ is the density matrix of system in external field. We show that Eq.(21) is justified only when the fluctuation in the spatial distribution of carriers is small. Using Eq.(3) and the commutation relation between $\mathbf{r}_i$ and $\mathbf{P}_i$, Eq.(4) becomes

$$\widehat{\mathbf{j}}(\mathbf{r}) = e \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i)\mathbf{v}_i - \frac{i\hbar e}{2m} \sum_{i=1}^{N}[\nabla_{\mathbf{r}_i}\delta(\mathbf{r} - \mathbf{r}_i)]. \tag{22}$$

Averaging Eq.(22) over state $\Psi'(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N; t)$, Eq.(5) gives another expression for microscopic current density:

$$\mathbf{j}(\mathbf{r}; t) = \frac{i\hbar e}{2m}\nabla_{\mathbf{r}}n'(\mathbf{r}) \tag{23}$$

$$+eN \int d\tau' \Psi'^* m^{-1}[-i\hbar\nabla_{\mathbf{r}} - e\mathbf{A}(\mathbf{r})]\Psi',$$

where the arguments of Ψ' in Eq.(23) are $(\mathbf{r}, \mathbf{r}_2, \cdots, \mathbf{r}_N; t)$, $n'(\mathbf{r}) = N \int d\tau' \Psi'^* \nabla_{\mathbf{r}}\Psi'$ is the number density of electrons at point $\mathbf{r}$ in external field $(\mathbf{A}, \phi)$. The 1st term of Eq.(23) can be neglected only when the gradient of carrier density is small. Using the corresponding relation between the MRM and the Kubo formulation, the 2nd term of Eq.(23) reduces to Eq.(21). It is obvious that Eq.(21) and the consequent KGF are not suitable to the localized carriers in amorphous semiconductors and the d and f electrons in strong correlated systems. For a given error Δx of position, the error of velocity is $\Delta v \sim m^{-1}\hbar/\Delta x$. The error of current density is $n'e\Delta v \sim m^{-1}\hbar n'/\Delta x \sim m^{-1}\hbar\nabla_{\mathbf{r}}n'$. If the charge density is uniform like nearly electron gas, the uncertainty Δx of position is infinity, the momentum of electron is completely determined $\Delta p_x = 0$. One can use kinetic expression for current density $\mathbf{j} = 2e\sum_{\mathbf{k}} \mathbf{v}_{\mathbf{k}}f_{\mathbf{k}}$, where $f_{\mathbf{k}}$ is the distribution function.

In summary, we proved that for a mechanical perturbation the microscopic response method is equivalent to and simpler than Kubo formula. To compute transport coefficients for mechanical perturbations, the microscopic response method is advantageous because of the ease of obtaining expression to a given order of residual interactions consistently. When the gradient of carrier density is small, the strict current density Eq.(23) reduces to the kinetic expression (21).

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