Comparison of the Kubo formula, the microscopic response method, and the Greenwood formula

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For a mechanical perturbation, the microscopic response method is equivalent to and more convenient to use than the Kubo formula. When the gradient of the carrier density is small, the current density reduces to that used by Greenwood.

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 a collective variable over the density matrix of system [3,4]. However, it is difficult to apply the Kubo formula to systems which have several types of elementary excitations and for which the interactions among elementary excitations are strong. For example, the complexity of the imaginary time integral prevents researchers from computing all the important contributions in conductivity and Hall mobility of small polarons [5–8]. Amorphous semiconductors and semiconducting polymers require approximations beyond small polarons: the low-lying excited states often contain both localized states and extended states [9], and the electron-phonon interactions in localized states are much stronger than those in extended states [10]. Even for the lowest order self-consistent approximation [11], one cannot easily include all important contributions for conductivity or Hall mobility.

One hopes to find some alternative method for computing transport coefficients for various concrete external disturbances, which should be simpler than the original linear response theory [1] and still as rigorous as possible. To calculate the viscoelasticity of fluid, Evans *et al.* [12,13] introduced a nonequilibrium Hamiltonian to replace the nonequilibrium free energy, which significantly reduced the labor required in the linear response theory for a thermal disturbance [2]. Recently we have designed the microscopic response method (MRM) to compute the conductivity and Hall mobility for complex systems with topological and thermal disorder [11,14], which is more convenient than the Kubo formula (KF) for a "mechanical perturbation" [1]. A mechanical perturbation such as the coupling with an external field can be expressed *via* additional terms in the Hamiltonian [1,2], and the many-body 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 the many-body wave function induced by the external field [11,14]. The ensemble and coarse-grained average needed to compute the macroscopic response (the 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 KF [11,14]. The Greenwood formula (GF) [15] has been implemented in many *ab initio* codes to calculate the dielectric function and AC conductivity. However, the GF is based on a simplified expression for the current density, which is borrowed from the kinetic theory of gases.

In this Brief Report, we prove that for mechanical perturbations, the MRM is equivalent to the KF. We will use the many-body wave-function representation which is equivalent to the frequently used second quantized representation [16,17]. To prove the equivalence between the KF and the MRM, 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 [11,14]. We see that the macroscopic response calculated in the two methods is the same. We discuss the connection between density matrix and transition amplitudes at different orders of perturbation. The contribution for transport coefficient from each transport process can be easily read off from a diagrammatic rule [11,14]. We show that the current density used by Greenwood is justified only when the gradient of the carrier density is small in addition to invoking the single-particle approximation.

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

$$i\hbar \partial \Psi'/\partial t = H'\Psi', \quad H' = H + V(t), \tag{1}$$

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

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

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 [18]

$$\mathbf{v}_i = m^{-1}\big[-i\hbar \nabla_{\mathbf{r}_i} - e\mathbf{A}(\mathbf{r}_i; t)\big], \tag{3}$$

where $\mathbf{r}_i$ is the position operators of the ith electron 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. The current density operator at point $\mathbf{r}$ is [16]:

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

In the MRM [11,14], we avoided $\widehat{\mathbf{j}}(\mathbf{r})$. Now we show that Eq. (4) leads to a proper microscopic current density [11, 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

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

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

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

where the arguments of Ψ' in Eq. (6) are $(\mathbf{r}, \mathbf{r}_2, \cdots, \mathbf{r}_N; t)$. Equation (6) has been independently derived from the principle of virtual work [19], the continuity equation [14], and the polarization density [11]. The current operator given in Eq. (4) will bridge the KF and the MRM.

To write out the macroscopic response in the KF, 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 time dependence [20]. In the $|m\rangle$ representation, the matrix elements of $\widehat{\mathbf{j}}(\mathbf{r})$ are

$$\langle n|\widehat{\mathbf{j}}(\mathbf{r})|m\rangle = \frac{Nei\hbar}{2m} \int d\tau' [\Psi_m \nabla_{\mathbf{r}} \Psi_n^* - \Psi_n^* \nabla_{\mathbf{r}} \Psi_m]$$
$$- \frac{Ne^2}{m} \mathbf{A}(\mathbf{r}; t) \int d\tau' \Psi_n^* \Psi_m, \tag{7}$$

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 [1,4]

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

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

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

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

$$\langle m|\rho^{(2)}(t)|n\rangle$$
$$= -\frac{1}{\hbar^2} e^{it(E_n - E_m)/\hbar} \sum_k \left\{ \left(P_n \int_{-\infty}^{t} dt' \int_{-\infty}^{t'} dt'' + P_m \int_{-\infty}^{t} dt'' \int_{-\infty}^{t''} dt' \right) e^{it''(E_k - E_n)/\hbar} e^{it'(E_m - E_k)/\hbar} \langle m|V(t')|k\rangle \langle k|V(t'')|n\rangle \right.$$
$$\left. - \left(\int_{-\infty}^{t} dt' \int_{-\infty}^{t'} dt'' + \int_{-\infty}^{t} dt'' \int_{-\infty}^{t''} dt' \right) e^{it''(E_k - E_n)/\hbar} e^{it'(E_m - E_k)/\hbar} \langle m|V(t')|k\rangle P_k \langle k|V(t'')|n\rangle \right\}, \tag{10}$$

The second-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), and (10) and $\mathbf{j}^{(2)}(\mathbf{r}, t)$ with the corresponding quantities in the MRM.

In the MRM, the macroscopic response is given by [11,14]:

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

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 [20] by applying perturbation theory to Eq. (1):

$$\Psi_n'(t) = a^{(0)}(n,t)\Psi_n + \sum_m a^{(1)}(mn,t)\Psi_m + \sum_m a^{(2)}(mn,t)\Psi_m, \tag{12}$$

where

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

and

$$a^{(1)}(mn,t) = -\frac{i}{\hbar} e^{-iE_m t/\hbar} \int_{-\infty}^{t} dt' e^{i(E_m - E_n)t'/\hbar} \langle m|V(t')|n\rangle \tag{14}$$

and

$$a^{(2)}(mn,t) = -\frac{1}{\hbar^2} e^{-iE_m t/\hbar} \sum_k \int_{-\infty}^{t} dt' e^{i(E_m - E_k)t'/\hbar} \langle m|V(t')|k\rangle$$
$$\times \int_{-\infty}^{t'} dt'' e^{i(E_k - E_n)t''/\hbar} \langle k|V(t'')|n\rangle. \tag{15}$$

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

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

Substituting Eqs. (12), (13), and (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) and (9). To second order in $V(t)$, the macroscopic current density is

$$\mathbf{j}^{(2)}(\mathbf{r},t) = \sum_n P_n \big[\langle \Psi_n^{(0)}(t) | \widehat{\mathbf{j}}(\mathbf{r}) | \Psi_n^{(2)}(t) \rangle + \langle \Psi_n^{(2)}(t) | \widehat{\mathbf{j}}(\mathbf{r}) | \Psi_n^{(0)}(t) \rangle$$
$$+ \langle \Psi_n^{(1)}(t) | \widehat{\mathbf{j}}(\mathbf{r}) | \Psi_n^{(1)}(t) \rangle \big]. \quad (17)$$

Substituting Eqs. (12)–(15) into Eq. (17), the first term of Eq. (17) is the same as the first term of $\mathbf{j}^{(2)}$ from Eq. (10), the second term of Eq. (17) is the same as the second term of $\mathbf{j}^{(2)}$ resulting from Eq. (10). One can see that the third term Eq. (17) equals the sum of the third term and the fourth term of $\mathbf{j}^{(2)}$ from Eq. (10), if one notices (i) three integrands are the same, (ii) the third term in Eq. (17) is a two-dimensional integral in domain $[-\infty,t; -\infty,t]$, (iii) the third term of $\mathbf{j}^{(2)}$ is a successive integration $\int_{-\infty}^{t} dt' \int_{-\infty}^{t'} dt''$, (iv) the four term of $\mathbf{j}^{(2)}$ is a successive integration $\int_{-\infty}^{t} dt'' \int_{-\infty}^{t''} dt'$. The procedure is easy to carry out to any order in field. Equation (11) does not use any specific property of electromagnetic field; the procedure works for any mechanical perturbation. Introducing the current density operator (4) is the key to the proof. In the original MRM, one does not need the current density operator; the macroscopic response is obtained by averaging over the microscopic response (6) over the canonical distribution. Equations (4) and (11) established a connection between the two methods. The "nonequilibrium Hamiltonian" approach [12,13] can be viewed as a classical realization of the MRM for velocity gradient. Introducing a suitable "non-equilibrium Hamiltonian" [12] for the temperature gradient, one might calculate the Seebeck effect directly.

It is worthwhile to find the connection between the probability amplitudes in Eqs. (13)–(15) and the density matrices in Eqs. (8) and (10). The element of the density matrix is the average the product of two probability amplitudes over the $\mathcal{M}$ members in an ensemble [20]:

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

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

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

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 $|m\rangle$, and $a^{(1)}(n,t)$ is the first-order transition amplitude from initial state $|m\rangle$ to final state $|n\rangle$.

With these explanations, substituting Eqs. (13) and (14) into Eq. (19), one reaches Eq. (8), which was obtained from the Liouville equation. To second order in $V(t)$,

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

In the first term of (20), the initial state is $|n\rangle$, and $a_\alpha^{(2)}(m,t)$ is the second-order transition amplitude through intermediate states $|k\rangle$. By means of Eqs. (13) and (15), the first term of Eq. (20) is the same as the first term of Eq. (10). In the second term of (20), the initial state is $|m\rangle$, $a_\alpha^{(2)}(n,t)$ is the second-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 third 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. Using the same trick in comparing the third term in Eq. (17) and the sum of the third and fourth terms of $\mathbf{j}^{(2)}(\mathbf{r},t)$ derived from Eq. (10), we can see that the third term of (20) is the same as the sum of the third term and the fourth term in Eq. (10).

Now we explain why the MRM is simpler than the KF 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 the external field and by residual interactions [11,21]. Because the microscopic response is expressed by the wave function of the system in an external field rather than density matrix, each elementary transition appears as a transition amplitude [11]. According to Eq. (12), the state at time t is a linear superposition of the various changes induced by the external field. By means of Eqs. (6), (16), and (17), the gradient operator connects two components of the final state [11]. In addition, the transition amplitude of a higher-order transition is constructed by first forming a product of the sequence of first-order amplitudes of elementary transitions and then summing over all intermediate states. We can describe each transport process with a diagram, which has one line connecting two components of the final state, and several other lines representing the elementary transitions. To a given order of residual interactions, the topology of diagrams can help us classify and construct all possible transport processes [11]. In the Kubo formulation, all time dependence is included in density matrix, cf. Eqs. (9) and (7). To a given order in an external field, the change in density matrix involves different members of the ensemble, cf. Eqs. (19) and (20). Besides, the density matrix is bilinear in transition amplitude. Therefore for a transport process with more than one elementary transition, one cannot express it as a product of propagators.

It is interesting to note the semiclassical limit of Eq. (6). Using Eq. (3) and the commutation relation between $\mathbf{r}_i$ and $\mathbf{v}_i$, Eq. (4) becomes

$$\widehat{\mathbf{j}}(\mathbf{r}) = e \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) \mathbf{v}_i - \frac{i\hbar e}{2m} \sum_{i=1}^N \big[\nabla_{\mathbf{r}_i} \delta(\mathbf{r} - \mathbf{r}_i) \big]. \quad (21)$$

Averaging Eq. (21) over state $\Psi'(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N; t)$, Eq. (5) gives another expression for the microscopic current density:

$$
\begin{aligned}
\mathbf{j}_m(\mathbf{r}; t) = {} & \frac{i\hbar e}{2m} \nabla_{\mathbf{r}} n'(\mathbf{r}) \\
& + eN \int d\tau' \Psi'^* m^{-1} [-i\hbar \nabla_{\mathbf{r}} - e\mathbf{A}(\mathbf{r}; t)] \Psi', \quad (22)
\end{aligned}
$$

where the arguments of Ψ' in Eq. (22) are $(\mathbf{r}, \mathbf{r}_2, \cdots, \mathbf{r}_N; t)$, and $n'(\mathbf{r}) = N \int d\tau' \Psi'^* \Psi'$ is the number density of electrons at point $\mathbf{r}$ in external field $(\mathbf{A}, \phi)$. The first term of Eq. (22) can be neglected only when the gradient of the carrier density is small. It is consistent with qualitative reasoning based on the uncertainty principle: the smaller the gradient of the carrier density, the poorer the accuracy of carrier coordinate. If the position error of an electron in a state Ψ' is Δx, the error of velocity is $\Delta v \sim m^{-1} \hbar / \Delta x$. The error of current density is $n'e\Delta v \sim m^{-1} \hbar n' / \Delta x \sim m^{-1} \hbar \nabla_{\mathbf{r}} n'$. Under the single-particle

approximation and the semiclassical approximation [16], Eq. (22) is reduced to Eq. (28) of Ref. [15], the current density used by Greenwood.

In summary, we proved that for a mechanical perturbation the microscopic response method is equivalent to and simpler than the 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. (22) reduces to the kinetic expression of current density used by Greenwood [15].

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