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# The microscopic response method: Theory of transport for systems with both topological and thermal disorder

**Feature Article**

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In this paper, we review and substantially develop the recently proposed ''Microscopic Response Method,'' which has been devised to compute transport coefficients and especially associated temperature dependence in complex materials. The conductivity and Hall mobility of amorphous semiconductors (ASs) and semiconducting polymers are systematically derived, and shown to be more practical than the Kubo formalism. The effect of a quantized lattice (phonons) on transport coefficients is fully included and then integrated out, providing the primary temperature dependence for the transport coefficients. For higher-order processes, using a diagrammatic expansion, one can consistently include all important contributions to a given order and directly write out the expressions of transport coefficients for various processes.

**1 Introduction** The career of O. F. Sankey exemplifies the ideals of scientific exploration, and even adventure. His many contributions to semiconductor, materials, and biophysics are testimony to a man of ingenuity, energy, and integrity. He has also been a rigorous but patient mentor to many contributors to this volume, including D.A.D. This paper on transport in complex materials is offered with affection and gratitude on the occasion of his sixtieth birthday.

The Kubo formula[1] has been used to calculate the conductivity and Hall mobility of small polarons in molecular crystals [5–10]. The results obtained by different authors are inconsistent. The reasons are: (i) the imaginary time integral in the Kubo formula is complicated; and (ii) there is no systematic way to classify various transport processes induced by the external field and by the residual interactions. The small polaron model is inadequate for amorphous semiconductors (ASs) in two aspects: (i) the states at the fringes of valence and conduction bands are localized by topological disorder. At moderate temperature both localized and extended states are accessible to

electronic transport processes [11]. Figure 1 is a schematic energy spectrum of AS; (ii) a carrier in a localized state $\phi_A$ polarizes the nearby atoms: the static displacements $d_{p_A}$ of the atoms ($p_A$ is the index of atoms participating in localized state $\phi_A$) induced by the e–ph interaction is comparable to or even larger than $a_v$, the larger of the amplitudes of thermal
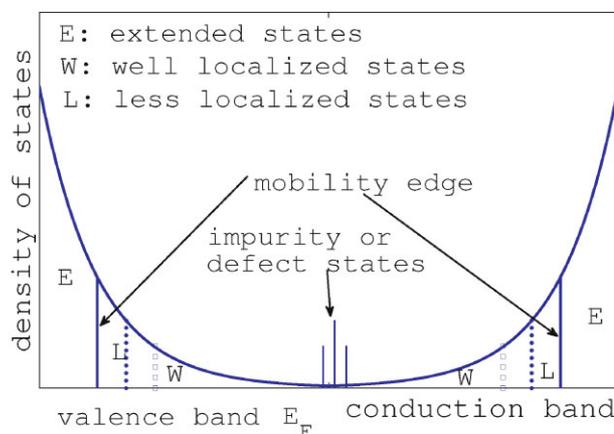


**Figure 1** (online colour at: www.pss-b.com) Schematic energy spectrum of amorphous semiconductors or semiconducting polymers.

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[1] In this paper the Kubo formula refers to the original treatment of Kubo [1], not the subsequent approximate form of Greenwood [2], which is discussed elsewhere [3, 4].

and zero point vibrations. In contrast, the static displacements of atoms caused by the carriers in extended states $\xi_B$ are negligible [12].

The imaginary time integral in the Kubo formula can be avoided in the microscopic response method (MRM) [3, 4, 13]. If an external perturbation on a system can be expressed via additional terms in the Hamiltonian (a "mechanical perturbation" [1], electromagnetic field is an example), the microscopic response can be obtained from the continuity equation for charge, the time-dependent Schrodinger equation and the initial conditions. The measured macroscopic response is a coarse-grained average, and an ensemble average of the microscopic response [13]. Thus one does not need to calculate the macroscopic response by averaging the response operator over density matrix, and the imaginary time integral is avoided [3]. The purpose of this paper is to review the MRM and to report the full formulae for the conductivity and Hall mobility.

The MRM is equivalent to and simpler than the Kubo formula [3]. Because the microscopic current density in a state is a bilinear form of the wave function of that state connected by the current operator, each transport process is a temporal evolution of a state under the driving force of the external field and the residual interactions which are time ordered in a specific way. The contribution to the microscopic current density from a process is a product of several transition amplitudes and a connector of the corresponding current operator. One may visualize the transport processes by a series of diagrams. The topology of diagrams gives us a systematic classification about various transport processes. It becomes easier to compute transport coefficients to a given order of residual interactions.

The consequence of strong polarization was first discussed by Marcus [14] for electron transfer in polar solvents and by Holstein [15] for small polarons in molecular crystals. Emin [16] have used small polaron theory to compute transport properties for well-localized carriers. However two related features in this model do not agree with the nature of ASs: (i) electronic localization in an AS is caused by the static positional disorder rather than the strong e–ph interaction; (ii) the localized states caused by the geometric disorder involve several atoms rather than one atom [17].

Miller and Abrahams studied the carrier hopping in a doped crystalline semiconductor. They assumed that the carriers are trapped in impurity or defect states close to the Fermi level, and the e–ph interaction is weak. Then the transitions between donor sites is mainly affected by the single-phonon absorption or emission [18].

Traditionally transport theory takes the zero order Hamiltonian $H_0$ as a sum of the vibrational part $H_v$ and the electronic part $H_e$ in the force field of fixed nuclei, and the e–ph interaction $H_{e-ph}$ is viewed as a small perturbation:

$$H_0 = H_e + H_{vib}, \qquad H = H_0 + H_{e-ph}. \tag{1}$$

We will use $h_e$ and $h_{e-ph}$ to denote the corresponding single-particle quantities. If the e–ph interaction is so weak that the static displacements of atoms induced by the e–ph interaction is negligible compared to $a_v$, partition (1) is reasonable. Both localized states and extended states are eigenstates of $h_e$, $H_{e-ph}$ is the unique residual interaction and induces [19] all four possible transitions among the eigenstates of $h_e$: (i) from a localized state to another localized state (LL), (ii) from a localized state to an extended state (LE), (iii) from an extended state to a localized state (EL), and (iv) from an extended state to another extended state (EE).

Both experiments and *ab initio* simulations show that in ASs the e–ph interaction for the well-localized tail states is strong $(d_{p_A} \gtrsim \alpha_v)$, while the e–ph interaction for the less localized states and for the extended states is weak [20, 21]. One has to adopt different Hamiltonian partitions for the two situations. For a well-localized state $A$ (we use $A$ with or without subscript to label a localized state), we take $h_{0e}^A = K + V_A$ as the single-particle Hamiltonian, where $V_A$ is the effective potential energy of the ions inside the region $D_A$ where $\phi_A^0$ (eigenfunction of $h_e$) is non-zero. One can easily show that $\phi_A \approx \phi_A^0$ even under perturbation $h_{e-ph}$, where $\phi_A$ is the ground state of $h_{0e}^A$ [12]. The zero order Hamiltonian is $h_0 = h_{0e}^A + (H_v + h_{e-ph})$. The attraction from other nuclei outside $D_A$ is taken as a perturbation. In this partition, LL and LE transitions are caused by the transfer integrals [12], cf. Section 6 of Ref. [22]. For an extended state $\xi_B$ (we use B with or without subscript to label an extended state), the zero order Hamiltonian was taken as $h_B = h_e + H_v$, $h_{e-ph}$ is the perturbation. EL and EE transitions are caused by the e–ph interactions [12].

In this paper, we apply the MRM to compute the conductivity and Hall mobility in ASs. In Section 2, the measured macroscopic response is obtained by taking a spatial and ensemble average over the microscopic current density. The required input is the many-body wave function $\Psi'(t)$ of $N$ electron $+ \mathcal{N}$ nuclei in an external field. By means of the single-electron approximation and the harmonic approximation for vibration, in Section 3, one can use a simplified many-body wave function $\psi'(t)$ to express the spatial averaged current density, $\psi'(t)$ describes the motion of single electron in coupling with the nuclear vibrations. Expanding $\psi'(t)$ with localized and extended states, the evolution equations of the transition amplitudes can be derived from the time-dependent Schrodinger equation. It is convenient to compute the transition amplitudes in normal coordinate representation. In Section 4, we outline how to obtain $\psi'(t)$ to required order in residual interactions and in external field. In Section 5, we compute the conductivity from both localized and extended states. With the help of a systematic diagrammatic perturbation expansion, one can determine conductivity to any order in external field and small parameters of residual interactions. We point out why some important contributions have been missed in previous calculations of small polarons based on the Kubo formula. The non-diagonal conductivity needed for Hall mobility is calculated in Section 6. To describe the Hall effect, one has to expand the current density to the 2nd order in the external

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field: one order is electric field, another is magnetic field. The MRM shows that: (i) there is a new type of term in the current density; (ii) there is an intrinsic interference effect between electric field and magnetic field. A new type temperature dependence is predicted. In the MRM, the atomic vibrations are described by quantum mechanics, the results obtained are correct for any temperature.

**2 Macroscopic current density** Consider an AS, with $N$ electrons and $\mathcal{N}$ nuclei in an electromagnetic field described by potentials $(\mathbf{A}, \phi)$. Denote the coordinates of the $N$ electrons as $\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N$, the coordinates of $\mathcal{N}$ nuclei as $\mathbf{W}_1, \mathbf{W}_2, \ldots, \mathbf{W}_{\mathcal{N}}$. The state $\Psi'(t)$ of the system is determined by the Schrödinger equation:

$$\frac{i\hbar\partial\Psi'}{\partial t} = H'\Psi', \tag{2}$$

where $H' = H + H_{\mathrm{fm}}$ is the total Hamiltonian, $H$ is the Hamiltonian of system, $H_{\mathrm{fm}}$ is the field-matter interaction. The arguments of $\Psi'$ are $(\mathbf{r}_1, \ldots, \mathbf{r}_N; \mathbf{W}_1, \ldots, \mathbf{W}_{\mathcal{N}}; t)$. In this work, we focus on the transport coefficients far below the frequency of infrared radiation. The direct contributions from nuclei will not be written out. For an ac field with higher frequency, especially in the infrared range, one has to take into account the direct contribution of the motion of atoms.

The microscopic current density $\mathbf{j}^{\Psi'}$ in state $\Psi'(t)$ is [3, 13]:

$$\begin{aligned}\mathbf{j}^{\Psi'}(\mathbf{r}; t) = &-\frac{e^2}{m}\mathbf{A}(\mathbf{r}; t)n'(\mathbf{r}; t) \\ &+ \frac{i\hbar e N}{2m}\int \mathrm{d}\tau'(\Psi'\nabla_{\mathbf{r}}\Psi'^* - \Psi'^*\nabla_{\mathbf{r}}\Psi'),\end{aligned} \tag{3}$$

where $n'(\mathbf{r}; t) = N\int \mathrm{d}\tau'\Psi'^*\Psi'$ is the carrier density in state $\Psi'(t)$, $\mathrm{d}\tau' = \mathrm{d}\mathbf{r}_2, \ldots, \mathrm{d}\mathbf{r}_N\mathrm{d}\mathbf{W}_1, \ldots, \mathrm{d}\mathbf{W}_{\mathcal{N}}$, the arguments of $\Psi'$ in Eq. (3) are $(\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_N; \mathbf{W}_1, \ldots, \mathbf{W}_{\mathcal{N}}; t)$. The first term of Eq. (3) expresses the oscillation of "free electrons." Comparing to the second term, its contribution to transport coefficients is negligible [23]. We will not discuss it further.

By averaging over a "physical infinitesimal" volume element [1, 24] $\Omega_s$ around point $s$, the coarse-grained current density $\tilde{\mathbf{j}}^{\Psi'}$ is:

$$\tilde{j}^{\Psi'}_\alpha(\mathbf{s}, t) = \Omega_s^{-1}\int_{\mathbf{r}\in\Omega_s}\mathrm{d}\mathbf{r}j^{\Psi'}_\alpha(\mathbf{r}, t), \quad \alpha = x, y, z. \tag{4}$$

For a mechanical perturbation, state $\Psi'(t)$ is determined by the initial condition $\Psi'(-\infty)$. Because one does not know what state the system was initially in, one must average $\tilde{j}^{\Psi'}_\alpha$ over all possible $\Psi'(-\infty)$ to compute the measured macroscopic current density $j_\alpha$:

$$j_\alpha(\mathbf{s}, t) = \sum_{\Psi'}P[\Psi'(-\infty)]\tilde{j}^{\Psi'}_\alpha(\mathbf{s}, t), \tag{5}$$

where $P[\Psi'(-\infty)]$ is the probability that the system is in state $\Psi'(-\infty)$ before the external field is adiabatically introduced. $P[\Psi'(-\infty)]$ depends only on the energy of state

$\Psi'(-\infty)$, and may be taken to be the canonical distribution [3, 13].

**3 Harmonic approximation and single-electron approximation** In the solid state, $\mathbf{W}_n = \mathcal{R}_n + \mathbf{u}_n$, where $\mathcal{R}_n = (X_{3(n-1)+1}, X_{3(n-1)+2}, X_{3n})$ and $\mathbf{u}_n = (x_{3(n-1)+1}, x_{3(n-1)+2}, x_{3n})$ are the equilibrium position vector and the vibrational displacement vector of the $n$th nucleus, respectively. In the harmonic approximation, the vibrational Hamiltonian is:

$$H_v = \sum_j -\frac{\hbar^2}{2M_j}\frac{\partial^2}{\partial x_j^2} + \frac{1}{2}\sum_{jk}k_{jk}x_jx_k, \tag{6}$$

where $(k_{ij})$ is the matrix of force constants.

Because in ASs the correlation between electrons is weak, one can use the single-electron approximation to $\Psi'(t)$. The arguments of the simplified single electron wave function $\psi'(t)$ include only the single electronic coordinate and the vibrational coordinates of nuclei. The state $\psi'$ of a carrier in an external field satisfies:

$$\frac{i\hbar\partial\psi'}{\partial t} = h'\psi'(\mathbf{r}, \{x_j\}, t), \tag{7}$$

where $\mathbf{r}$ is the coordinate of the carrier. $h' = h + h_{\mathrm{fm}}$ is the Hamiltonian of [system + external field]. In gauge $\nabla \cdot \mathbf{A}(\mathbf{r}, t) = 0$,

$$h_{\mathrm{fm}} = \left(\frac{i\hbar e}{m}\right)\mathbf{A}(\mathbf{r}) \cdot \nabla_{\mathbf{r}} + \frac{e^2\mathbf{A}^2(\mathbf{r})}{2m} + e\phi(\mathbf{r}), \tag{8}$$

is the coupling between the carrier and the external field. Here $h = h_e + H_v$ is the Hamiltonian without field, where:

$$h_e = \frac{-\hbar^2}{2m}\nabla_{\mathbf{r}}^2 + \sum_{n=1}^{\mathcal{N}}U(\mathbf{r} - \mathcal{R}_n - \mathbf{u}_n), \tag{9}$$

is the electronic Hamiltonian. $U(\mathbf{r} - \mathcal{R}_n - \mathbf{u}_n)$ is the effective potential energy between the electron at $\mathbf{r}$ and the $n$th nucleus. Denote the $3\mathcal{N}$ vibrational degrees of freedom as $\{x_j, j = 1, 2, \ldots, 3\mathcal{N}\}$, then the spatially averaged current density (4) at $\mathbf{s}$ is reduced to [13, 24]:

$$\begin{aligned}\tilde{\mathbf{j}}^{\psi'}(\mathbf{s}, t) = &\frac{i\hbar e N_e}{2m\Omega_s}\int_{\Omega_s}\mathrm{d}\mathbf{r}\int\left[\prod_{j=1}^{3\mathcal{N}}\mathrm{d}x_j\right] \\ &(\psi'\nabla_{\mathbf{r}}\psi'^* - \psi'^*\nabla_{\mathbf{r}}\psi').\end{aligned} \tag{10}$$

**4 Evolution equation in external field** The prime ingredient required for the conductivity and Hall mobility is the single particle state $\psi'(t)$ of the system in an external field [13]. To find $\psi'(t)$, we expand it using the approximate eigenstates of the single-particle Hamiltonian [12]:

$$\psi'(t) = \sum_A a_A(t)\phi_A + \sum_B b_B(t)\xi_B, \tag{11}$$

where the arguments of $\psi'$ are $(\boldsymbol{r}; x_1, x_2, \ldots, x_{3\mathcal{N}})$, $a_A(t)$ is the probability amplitude at time $t$ that the carrier is in a localized state $\phi_A$ while the vibrational displacements of $\mathcal{N}$ nuclei are $x_1, x_2, \ldots, x_{3\mathcal{N}}$. Here, $b_B(t)$ is the probability amplitude at time $t$ that the carrier is in an extended state $\xi_B$ while the vibrational displacements of $\mathcal{N}$ nuclei are $x_1, x_2, \ldots, x_{3\mathcal{N}}$. If the external field is not too strong, it is convenient to put the change in $\psi'$ caused by external field into the probability amplitudes rather than in the zero-order eigenstates. Substituting Eq. (11) into Eq. (7), the time variation of probability amplitudes under the external field are determined by [12]:

$$\left[i\hbar\frac{\partial}{\partial t} - h_{A_1}\right]a_{A_1} = \sum_A a_A J_{A_1 A}^{\mathrm{tot}} + \sum_B b_B K_{A_1 B}^{\prime\mathrm{tot}} \quad (12)$$

and

$$\left[i\hbar\frac{\partial}{\partial t} - h_{B_1}\right]b_{B_1} = \sum_A J_{B_1 A}^{\prime\mathrm{tot}} a_A + \sum_B K_{B_1 B}^{\mathrm{tot}} b_B, \quad (13)$$

where

$$J_{A_1 A}^{\mathrm{tot}} = J_{A_1 A} + J_{A_1 A}^{\mathrm{field}}, \qquad K_{A_1 B}^{\prime\mathrm{tot}} = K_{A_1 B}' + K_{A_1 B}^{\prime\mathrm{field}} \quad (14)$$

and

$$J_{B_1 A}^{\prime\mathrm{tot}} = J_{B_1 A}' + J_{B_1 A}^{\prime\mathrm{field}}, \qquad K_{B_1 B}^{\mathrm{tot}} = K_{B_1 B} + K_{B_1 B}^{\mathrm{field}}, \quad (15)$$

and

$$h_{A_1} = H_v + E_{A_1}, \quad h_{B_1} = H_v + E_{B_1}, \quad (16)$$

where $E_{A_1}$ is the eigen energy of localized state $A_1$ with the correction to first order of e–ph interaction, $E_{B_1}$ is the eigen energy of extended state $B_1$, transfer integral $J_{A_1 A} = \int d\boldsymbol{r}\phi_{A_1}^* \sum_{p\notin D_A} U(r-\mathcal{R}_p)\phi_A$ causes a transition from localized state $\phi_A$ to localized state $\phi_{A_1}$, the transfer integral $J_{B_1 A}' = \int d\boldsymbol{r}\xi_{B_1}^* \sum_{p\notin D_A} U(r-\mathcal{R}_p)\phi_A$ induces a transition from localized state $\phi_A$ to an extended state $\xi_{B_1}$. The e–ph interaction $K_{A_1 B}' = \int d\boldsymbol{r}\phi_{A_1}^* \sum_j x_j(\partial U/\partial x_j)\xi_B$ causes a transition from extended state $\xi_B$ to localized state $\phi_{A_1}$. The e–ph interaction $K_{B_1 B} = \int d\boldsymbol{r}\xi_{B_1}^* \sum_j x_j(\partial U/\partial x_j)\xi_B$ induces a transition from extended state $\xi_B$ to another extended state $\xi_{B_1}$. $J_{A_1 A}^{\mathrm{field}} = \int d\boldsymbol{r}\phi_{A_1}^* h_{\mathrm{fm}}\phi_A$ is the coupling between two localized states $\phi_A$ and $\phi_{A_1}$ caused by external field, etc.

The microscopic response is expressed by the state $\psi'(t)$ of [system + external field]. We replace the second line of Eq. (10) with $(\psi'\nabla_r\psi'^* - \psi'^*\nabla_r\psi') - (\psi\nabla_r\psi^* - \psi^*\nabla_r\psi)$, where $\psi(\boldsymbol{r}, \{x_j\}, t)$ satisfies $i\hbar\partial\psi/\partial t = h\psi$, is the state of system without external field. $(\psi\nabla_r\psi^* - \psi^*\nabla_r\psi)$ represents the microscopic current density when no external field is applied to the system. For carriers in localized states and in extended states (scattered by static disorder), the contribution to the coarse-grained current density $\tilde{\boldsymbol{j}}^\psi$ from $(\psi\nabla_r\psi^* - \psi^*\nabla_r\psi)$ is 0. The spatially averaged *microscopic*

current density to second order in the field is [13]:

$$\tilde{\boldsymbol{j}}^{\psi'}(\boldsymbol{s}, t) = -\frac{N\hbar e}{m\Omega_s}\int_{\boldsymbol{r}\in\Omega_s} d\boldsymbol{r}\int\left[\prod_{j=1}^{3\mathcal{N}} dx_j\right]$$
$$\times \{\mathrm{Im}(\psi^{(0)}\nabla_r\psi^{(1)*} - \psi^{(1)*}\nabla_r\psi^{(0)}) \quad (17)$$
$$+ \mathrm{Im}(\psi^{(0)}\nabla_r\psi^{(2)*} - \psi^{(2)*}\nabla_r\psi^{(0)}$$
$$+ \psi^{(1)}\nabla_r\psi^{(1)*})\},$$

where $\psi^{(1)}$ is the change in state to first order in field, and $\psi^{(2)}$ is the change in state to second order in field. $\psi^{(0)}$ is the state of carrier at time $t$ *without* an external field. Hereafter, the superscripts (0), (1), and (2) on $\psi$ indicate the order of external field, the order of residual interactions will be denoted as subscripts. For example, $\psi_J^{(1)}$ represents the change in state to first order of external field and to first order of $J$. If not explicitly stated, we understand that $\psi^{(0)}$, $\psi^{(1)}$, and $\psi^{(2)}$ are fully dressed by the residual interactions $J$, $J'$, $K'$, and $K$.

Unlike the nearly free carriers in crystalline materials or the extended states of an AS, the carriers in localized states cannot be accelerated by an external electric field. Because the force produced by the external field is much weaker than the binding force from static disorder, the quantum tunneling probability [25] $\Gamma = \exp\{-4(2m)^{1/2}\varepsilon_b^{3/2}/(3\hbar eE)\}$ produced by an external field is negligible, where $\varepsilon_b$ is the binding energy produced by static disorder. In addition, for a field of $10^5\,\mathrm{V\,cm}^{-1}$ and a typical distance $10\,\text{Å}$ between two neighboring localized states, the upper limit of the transition moment is $0.01\,\mathrm{eV}$, the same order as $J$ and $J'$. Denote $S$ as one of the small parameters $J$, $J'$, $K'$, $K$ from the residual interactions. One must calculate $\psi^{(0)}(t)$, $\psi^{(1)}(t)$, and $\psi^{(2)}(t)$ to order $S^0$ and $S^1$ and keep all possible order $S^0$ *and* $S^1$ contributions in current density $\boldsymbol{j}$.

To find $\psi'(t)$, it is convenient to transform the vibrational displacements $\{x\}$ of the atoms into normal coordinates $\{\Theta\}$ [12]. We expand probability amplitude $a_{A_1}(\cdots\Theta_\alpha\cdots; t)$ with the eigenfunctions of $h_{A_1}$:

$$a_{A_1} = \sum_{\cdots N_\alpha'\cdots} C^{A_1}(\cdots N_\alpha'\cdots; t)\Psi_{A_1}^{\{N_\alpha'\}} e^{-it\mathcal{E}_{A_1}^{\{N_\alpha'\}}/\hbar}, \quad (18)$$

where $C^{A_1}(\cdots N_\alpha'\cdots; t)$ is the probability amplitude at moment $t$ that the electron is in localized state $\phi_{A_1}$ while the vibrational state of the nuclei is characterized by occupation number $\{N_\alpha', \alpha = 1, 2, \ldots, 3\mathcal{N}\}$ in each mode. Similarly, we expand $b_{B_1}(\cdots\Theta_\alpha\cdots; t)$ with the eigenfunctions of $h_{B_1}$:

$$b_{B_1} = \sum_{\cdots N_\alpha'\cdots} F^{B_1}(\cdots N_\alpha'\cdots; t)\Xi_{B_1}^{\{N_\alpha'\}} e^{-it\mathcal{E}_{B_1}^{\{N_\alpha'\}}/\hbar}. \quad (19)$$

Equations (12) and (13) become the evolution equations for $C^A$ and $F^B$. Using perturbation theory, one can find the probability amplitudes $C^A$ and $F^B$ to any order of field for any initial conditions. Substitute $C^A$ and $F^B$ into Eqs. (18) and (19), and one obtains the probability amplitudes $a_A$ and $b_B$ in the normal coordinate representation. Substituting $a_A$ and $b_B$

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**Table 1** The origin of various conduction processes.

| order | expression | diagrams |
|---|---|---|
| $S^0$ | $(\psi_{S0}^{(0)}\nabla_r\psi_{S0}^{(1)*}-\psi_{S0}^{(1)*}\nabla_r\psi_{S0}^{(0)})$ | Figs. 2 and 6 |
| $S$ | $(\psi_S^{(0)}\nabla_r\psi_{S0}^{(1)*}-\psi_{S0}^{(1)*}\nabla_r\psi_S^{(0)})$ | Figs. 3 and 7 |
| $S$ | $(\psi_{S0}^{(0)}\nabla_r\psi_S^{(1)*}-\psi_S^{(1)*}\nabla_r\psi_{S0}^{(0)})$ | Figs. 4, 5, 8, and 9 |
| $K^2$ | $(\psi_{K^2}^{(0)}\nabla_r\psi_{S0}^{(1)*}-\psi_{S0}^{(1)*}\nabla_r\psi_{K^2}^{(0)})$ | Fig. 10a |
| $K^2$ | $(\psi_{S0}^{(0)}\nabla_r\psi_{K^2}^{(1)*}-\psi_{K^2}^{(1)*}\nabla_r\psi_{S0}^{(0)})$ | 10b–d |

back to Eq. (11), one determines the state $\psi'(t)$ of system in an external field. The results are listed in Section 1 of Ref. [22].

**5 Conductivity** For the conductivity, one needs only the first term in Eq. (17). To order $S^0$ and $S^1$, all possible contributions to $j$ are classified in Table 1. If the initial state is a localized state $\phi_A$, the expression for $j$ can be found by substituting the corresponding $\psi^{(0)}(t)$ and $\psi^{(1)}(t)$ into the first term in Eq. (17). There are 14 processes contributing to conductivity. This can be understood as follows. There are three terms in $\psi^{(0)}$: (i) the free evolution of state $\phi_A$ without external field and residual interactions; (ii) $J$ takes $\phi_A$ to another localized state; and (iii) $J'$ takes localized state $\phi_A$ to an extended state. As indicated in Eqs. (12) and (13), e–ph interactions $K$ and $K'$ do not couple a localized state to any other state. There are two order $S^0$ terms in $\psi^{(1)}$: the external field can bring $\phi_A$ to either another localized state or an extended state. There are eight order $S^1$ terms in $\psi^{(1)}$, they differ in the time ordering of the residual interaction $S$ and external field. The current density operator $(\psi^{(0)}\nabla_r\psi^{(1)*}-\psi^{(1)*}\nabla_r\psi^{(0)})$ links all components of $\psi^{(0)}$ to all components of $\psi^{(1)*}$.

We may use diagrams to visualize the 14 processes (cf. Figs. 2–5). The expression for the current density Eqs. (5) and (17) and the perturbative solution of Eqs. (12) and (13) suggest some rules to write out the contribution to $j$ for any process. $\psi^{(0)}(t)$ and $\psi^{(1)}(t)$ are two ingredients of $j$. In Eqs. (11), (18), and (19), $\psi^{(0)}(t)$ and $\psi^{(1)}(t)$ are expanded with the eigenfunctions of $h_{0e}^A+h_A$ and of $h_{0e}+h_B$. The expansion coefficients are transition amplitudes from a given initial state. The current density operator $(\psi^{(0)}\nabla_r\psi^{(1)*}-\psi^{(1)*}\nabla_r\psi^{(0)})$ links one component of $\psi^{(0)}$ to one component of $\psi^{(1)*}$ (connector). Thus $j$ is a sum of many terms, each term is a product of a connector and one or



a)         b)
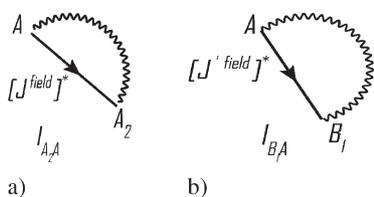
**Figure 2** Lowest order processes contributing to conductivity. Initial state is localized state $\phi_A$: order $J^0$ and $[J']^0$ contributions to conductivity (see text).



a)    b)    c)    d)
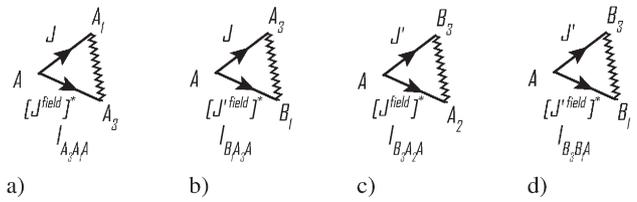
**Figure 3** Initial state is localized state $\phi_A$: order $J^1$ and order $[J']^1$ contributions to conductivity.



a)    b)    c)    d)
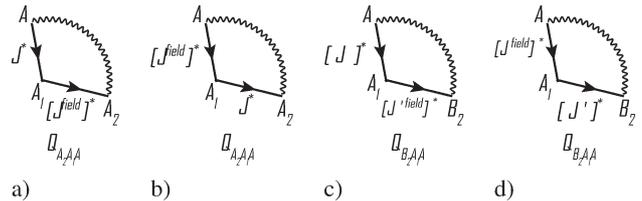
**Figure 4** Initial state is localized state $\phi_A$: order $[J']^1$ and order $J^1$ contributions to conductivity.



a)    b)    c)    d)
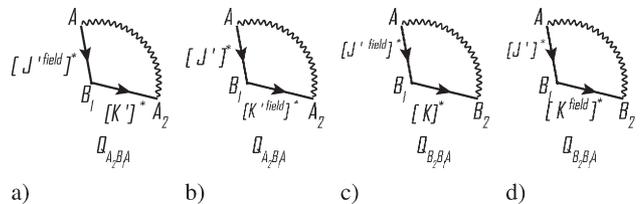
**Figure 5** Initial state is localized state $\phi_A$: order $[J']^1$, $K'$, and $K$ contributions to conductivity.

several transition amplitude(s). We draw a wavy line from one component of $\psi^{(0)}$ to one component of $\psi^{(1)*}$. The spatial average produces $\Omega_s^{-1}\int_{r\in\Omega_s}\mathrm{d}r$ before the microscopic current density, cf. the second to the fifth lines of Table 2. Because $\psi^{(0)}$ appears in $j$, the free evolution $\psi_{S0}^{(0)}(t)$ of the initial state or one of two final components in $\psi_{S1}^{(0)}(t)$ will appear in $j$. We use a solid arrow line upward (top right or top left) to express the transition amplitude in $\psi_{S1}^{(0)}(t)$ caused by one of residual interactions: the arrow points from initial state to final state. For a process in which $\psi_{S0}^{(1)*}$ appears in $j$, the complex conjugate (cc) of the transition amplitude(s) in $\psi_{S0}^{(1)}(t)$ will appear. We draw a solid arrow line downward (lower right or lower left) to express the cc caused by an external field: the arrow points from the initial state to the final state, see Table 3. For a process in which $\psi_{S1}^{(1)*}$ appears in $j$, the cc of two transition amplitudes in $\psi_{S1}^{(1)}(t)$ will appear. We draw two successive solid arrow lines downward, one represents the cc of the transition amplitudes caused by an external field, another expresses the cc of the transition amplitudes caused by a residual interaction, see Table 3. By retaining only order $S^0$ and $S^1$ terms in $j$, Figs. 2–5 describes all possible combinations. The two processes in Fig. 2a result from $\psi_{S0}^{(0)}$ and $\psi_{S0}^{(1)*}$. The four processes in Fig. 3 result from $\psi_{S1}^{(0)}$ and $\psi_{S0}^{(1)*}$. The eight processes in Figs. 4 and 5 result from $\psi_{S0}^{(0)}$ and $\psi_{S1}^{(1)*}$.

With the help of the diagrammatic rules listed in Tables 2 and 3, one can easily write out the corresponding

**Table 2** States coupled by the current operator.

| symbol | expression |
|---|---|
| $A \rightsquigarrow A_2$ | $\Omega_s^{-1} \int_{\Omega_s} d\mathbf{r}(\phi_A \nabla_{\mathbf{r}} \phi_{A_2}^* - \phi_{A_2}^* \nabla_{\mathbf{r}} \phi_A) \langle \Psi_{A_2}^{\{N''_\alpha\}} | \Psi_A^{\{N_\alpha\}} \rangle e^{it(\mathcal{E}_{A_2}^{\{N''\}} - \mathcal{E}_A^{\{N_\alpha\}})/\hbar}$ |
| $A \rightsquigarrow B_1$ | $\Omega_s^{-1} \int_{\Omega_s} d\mathbf{r}(\phi_A \nabla_{\mathbf{r}} \xi_{B_1}^* - \xi_{B_1}^* \nabla_{\mathbf{r}} \phi_A) \langle \Xi_{B_1}^{\{N'_\alpha\}} | \Psi_A^{\{N_\alpha\}} \rangle e^{it(\mathcal{E}_{B_1}^{\{N'_\alpha\}} - \mathcal{E}_A^{\{N_\alpha\}})/\hbar}$ |
| $B \rightsquigarrow A_2$ | $\Omega_s^{-1} \int_{\Omega_s} (\xi_B \nabla_{\mathbf{r}} \phi_{A_2}^* - \phi_{A_2}^* \nabla_{\mathbf{r}} \xi_B) \langle \Psi_{A_2}^{\{N''_\alpha\}} | \Xi_B^{\{N_\alpha\}} \rangle e^{it(\mathcal{E}_{A_2}^{\{N''_\alpha\}} - \mathcal{E}_B^{\{N_\alpha\}})/\hbar}$ |
| $B \rightsquigarrow B_1$ | $\Omega_s^{-1} \int_{\Omega_s} d\mathbf{r}(\xi_B \nabla_{\mathbf{r}} \xi_{B_1}^* - \xi_{B_1}^* \nabla_{\mathbf{r}} \xi_B) \langle \Xi_{B_1}^{\{N'_\alpha\}} | \Xi_B^{\{N_\alpha\}} \rangle e^{it(\mathcal{E}_{B_1}^{\{N'_\alpha\}} - \mathcal{E}_B^{\{N_\alpha\}})/\hbar}$ |
| $A_2 \dashrightarrow A_3$ | $\Omega_s^{-1} \int_{\mathbf{r} \in \Omega_s} d\mathbf{r} \phi_{A_2} \nabla \phi_{A_3}^* \langle \Psi_{A_3}^{\{N_\alpha\}} | \Psi_{A_2}^{\{N'''_\alpha\}} \rangle e^{it(\mathcal{E}'_{A_3}\{N_\alpha\} - \mathcal{E}'_{A_2}\{N'''_\alpha\})/\hbar}$ |

**Table 3** Transition amplitudes induced by the residual interactions and external field.

| symbol | expression |
|---|---|
| $A \xrightarrow{\text{field}} A_2$ | $\dfrac{i}{\hbar} \int_{-\infty}^{t} dt' [J_{A_2A}^{\text{field}}(t')]^* \langle \Psi_{A_2}^{\{N''_\alpha\}} | \Psi_A^{\{N_\alpha\}} \rangle e^{-it'(\mathcal{E}_{A_2}^{\{N''_\alpha\}} - \mathcal{E}_A^{\{N_\alpha\}})/\hbar}$ |
| $A \xrightarrow{\text{field}} B_1$ | $\dfrac{i}{\hbar} \int_{-\infty}^{t} dt' [J'^{\text{field}}_{B_1A}(t')]^* \langle \Xi_{B_1}^{\{N'_\alpha\}} | \Psi_A^{\{N_\alpha\}} \rangle e^{-it'(\mathcal{E}_{B_1}^{\{N'_\alpha\}} - \mathcal{E}_A^{\{N_\alpha\}})/\hbar}$ |
| $B \xrightarrow{\text{field}} A_2$ | $\dfrac{i}{\hbar} \int_{-\infty}^{t} dt''' [K'^{\text{field}}_{A_2B}(t''')]^* \langle \Psi_{A_2}^{\{N''_\alpha\}} | \Xi_B^{\{N_\alpha\}} \rangle e^{-it'''(\mathcal{E}_{A_2}^{\{N''_\alpha\}} - \mathcal{E}_B^{\{N_\alpha\}})/\hbar}$ |
| $B \xrightarrow{\text{field}} B_1$ | $\dfrac{i}{\hbar} \int_{-\infty}^{t} dt''' [K_{B_1B}^{\text{field}}(t''')]^* \langle \Xi_{B_1}^{\{N'_\alpha\}} | \Xi_B^{\{N_\alpha\}} \rangle e^{-it'''(\mathcal{E}_{B_1}^{\{N'_\alpha\}} - \mathcal{E}_B^{\{N_\alpha\}})/\hbar}$ |
| $A \xrightarrow{J} A_3$ | $-\dfrac{i}{\hbar} J_{A_3A} \langle \Psi_{A_3}^{\{N'''\alpha\}} | \Psi_A^{\{N_\alpha\}} \rangle \int_{-\infty}^{t} dt' e^{it'(\mathcal{E}_{A_3}^{\{N'''\alpha\}} - \mathcal{E}_A^{\{N_\alpha\}})/\hbar}$ |
| $A \xrightarrow{J'} B_3$ | $-\dfrac{i}{\hbar} J'_{B_3A} \langle \Xi_{B_3}^{\{N'''_\alpha\}} | \Psi_A^{\{N_\alpha\}} \rangle \int_{-\infty}^{t} dt' e^{it'(\mathcal{E}_{B_3}^{\{N'''\alpha\}} - \mathcal{E}_A^{\{N_\alpha\}})/\hbar}$ |
| $B \xrightarrow{K'} A_3$ | $-\dfrac{i}{\hbar} \langle \Psi_{A_3}^{\{N'''\alpha\}} | K'_{A_3B} | \Xi_B^{\{N_\alpha\}} \rangle \int_{-\infty}^{t} dt' e^{it'(\mathcal{E}_{A_3}^{\{N'''\alpha\}} - \mathcal{E}_B^{\{N_\alpha\}})/\hbar}$ |
| $B \xrightarrow{K} B_3$ | $-\dfrac{i}{\hbar} \langle \Xi_{B_3}^{\{N'''\alpha\}} | K_{B_3B} | \Xi_B^{\{N_\alpha\}} \rangle \int_{-\infty}^{t} dt' e^{it'(\mathcal{E}_{B_3}^{\{N'''\alpha\}} - \mathcal{E}_B^{\{N_\alpha\}})/\hbar}$ |

macroscopic current density for each conduction processes. Taking Fig. 3a as example, the contribution to $\mathbf{j}$ is:

$$
\left(-\frac{N_e e\hbar}{m}\right) \sum_{A\cdots N_\alpha \cdots} f(E_A) \prod_\alpha P(N_\alpha) \sum_{A_1 \cdots N'_\alpha \cdots} [1 - f(E_{A_1})]
$$

$$
\sum_{A_3 \cdots N'''_\alpha \cdots} [1 - f(E_{A_3})] \Omega_s^{-1} \int_{\Omega_s} d\mathbf{r}(\phi_{A_1} \nabla_{\mathbf{r}} \phi_{A_3}^* - \phi_{A_3}^* \nabla_{\mathbf{r}} \phi_{A_1})
$$

$$
\langle \Psi_{A_1}^{\{N'_\alpha\}} | \Psi_{A_3}^{\{N'''\}} \rangle e^{-it(\mathcal{E}_{A_1}^{\{N'_\alpha\}} - \mathcal{E}_{A_3}^{\{N'''\}})/\hbar}
$$

$$
\left(\frac{-i}{\hbar}\right) J_{A_1A} \int_{-\infty}^{t} dt'' \langle \Psi_{A_1}^{\{N'_\alpha\}} | \Psi_A^{\{N_\alpha\}} \rangle e^{it''(\mathcal{E}_{A_1}^{\{N'_\alpha\}} - \mathcal{E}_A^{\{N_\alpha\}})/\hbar}
$$

$$
\frac{i}{\hbar} \int_{-\infty}^{t} dt' [J_{A_3A}^{\text{field}}(t')]^* \langle \Psi_{A_3}^{\{N'''\alpha\}} | \Psi_A^{\{N_\alpha\}} \rangle e^{-it'(\mathcal{E}_{A_3}^{\{N'''\alpha\}} - \mathcal{E}_A^{\{N_\alpha\}})/\hbar},
\tag{20}
$$

where $P(N_\alpha) = \exp[-\beta(N_\alpha + 1/2)\hbar\omega_\alpha]/Z_\alpha$ is the probability that there are $N_\alpha$ phonons in the $\alpha$th mode, and $Z_\alpha = \sum_{N_\alpha} \exp(-\beta(N_\alpha + 1/2)\hbar\omega_\alpha)$. The second and third lines come from current operator, cf. the second line of Table 2. The fourth line of Eq. (20) is the transition amplitude induced by the transfer integral $J$, cf. the sixth line of Table 3. The fifth line of Eq. (20) is the cc of the transition amplitude induced by the external field, cf. the second line of Table 3. Because we transformed the vibrational displacements $\{x_j\}$ to normal coordinates $\{\theta_\alpha\}$, the integral over displacements $\int [\prod_{j=1}^{3\mathcal{N}} dx_j]$ in Eq. (17) becomes an integral over normal coordinates $\int [\prod_{\alpha=1}^{3\mathcal{N}} d\theta_\alpha]$ in $\langle \Psi_{A_1}^{\{N'_\alpha\}} | \Psi_{A_3}^{\{N'''\alpha\}} \rangle$. Because $A_1$ is the final state of the LL transition induced by the transfer integral $J$, $A_3$ is the final state of the LL transition induced by the external field, states $A_1$ and $A_3$ must not be occupied: one has factors $[1 - f(E_{A_3})]$ and $[1 - f(E_{A_3})]$. According to perturbation theory, one should (i) sum over all intermediate states; (ii) sum over all

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**Table 4** The conduction processes and conductivity: initial state is a localized state $\phi_A$.

| diagram | conductivity |
|---|---|
| 2a | $-\dfrac{Ne^2}{2\Omega_s}\sum_{AA_2}\mathrm{Im}(w^\alpha_{AA_2}-v^\alpha_{A_2A})i(E^0_A-E^0_{A_2})^{-1}(v^\beta_{A_2A})^*[I_{A_2A+}\pm I_{A_2A-}][1-f(E_{A_2})]f(E_A)$ |
| 2b | $-\dfrac{Ne^2}{2\Omega_s}\sum_{AB_1}\mathrm{Im}(w^\alpha_{AB_1}-v^\alpha_{B_1A})i(E^0_A-E^0_{B_1})^{-1}(v^\beta_{B_1A})^*[I_{B_1A+}\pm I_{B_1A-}][1-f(E_{B_1})]f(E_A)$ |
| 3a | $-\dfrac{Ne^2}{2\hbar\Omega_s}\mathrm{Im}\,i\sum_{A_3A_1A}(w^\alpha_{A_1A_3}-v^\alpha_{A_3A_1})i(E^0_A-E^0_{A_3})^{-1}(v^\beta_{A_3A})^*J_{A_1A}[I_{A_3A_1A+}\pm I_{A_3A_1A-}]f(E^0_A)[1-f(E^0_{A_1})][1-f(E^0_{A_3})]$ |
| 3b | $-\dfrac{Ne^2}{2\hbar\Omega_s}\sum_{AA_3B_1}\mathrm{Im}(w^\alpha_{A_3B_1}-v^\alpha_{B_1A_3})(E^0_A-E^0_{B_1})^{-1}(v^\beta_{B_1A})^*J_{A_3A}[I_{B_1A_3A+}\pm I_{B_1A_3A-}][1-f(E_{B_1})][1-f(E_{A_3})]f(E_A)$ |
| 3c | $-\dfrac{Ne^2}{2\hbar\Omega_s}\sum_{AA_2B_3}\mathrm{Im}(w^\alpha_{B_3A_2}-v^\alpha_{A_2B_3})(E^0_{A_2}-E^0_A)^{-1}(v^\beta_{A_2A})^*J'_{B_3A}[I_{B_3A_2A+}\pm I_{B_3A_2A-}][1-f(E_{B_3})][1-f(E_{A_2})]f(E_A)$ |
| 3d | $-\dfrac{Ne^2}{2\hbar\Omega_s}\sum_{AB_1B_3}\mathrm{Im}(w^\alpha_{B_3B_1}-v^\alpha_{B_1B_3})J'_{B_3A}(E^0_A-E^0_{B_1})^{-1}(v^\beta_{B_1A})^*[I_{B_3B_1A+}\pm I_{B_3B_1A-}][1-f(E_{B_3})][1-f(E_{B_1})]f(E_A)$ |
| 4a | $+\dfrac{Ne^2}{2\hbar\Omega_s}\sum_{A_2A_1A}\mathrm{Im}(w^\beta_{AA_2}-v^\beta_{A_2A})(E_{A_1}-E_{A_2})^{-1}(v^\alpha_{A_2A_1})^*J^*_{A_1A}(Q_{1A_2A_1A+}\pm Q_{1A_2A_1A-})f(E_A)[1-f(E_{A_2})]$ |
| 4b | $+\dfrac{Ne^2}{2\hbar\Omega_s}\sum_{A_2A_1A}\mathrm{Im}(w^\beta_{AA_2}-v^\beta_{A_2A})J^*_{A_2A_1}(E^0_A-E^0_{A_1})^{-1}(v^\alpha_{A_1A})^*(Q_{2A_2A_1A+}\pm Q_{2A_2A_1A-})f(E_A)[1-f(E_{A_2})]$ |
| 4c | $+\dfrac{Ne^2}{2\hbar\Omega_s}\sum_{B_2A_1A}\mathrm{Im}(w^\beta_{AB_2}-v^\beta_{B_2A})(E^0_{A_1}-E^0_{B_2})^{-1}(v^\alpha_{B_2A_1})^*J^*_{A_1A}(Q_{1B_2A_1A+}\pm Q_{1B_2A_1A-})f(E_A)[1-f(E_{B_2})]$ |
| 4d | $+\dfrac{Ne^2}{2\hbar\Omega_s}\sum_{A_2A_1A}\mathrm{Im}(w^\beta_{AB_2}-v^\beta_{B_2A})J'^*_{B_2A_1}(E^0_A-E^0_{A_1})^{-1}(v^\alpha_{A_1A})^*(Q_{2B_2A_1A+}\pm Q_{2B_2A_1A-})f(E_A)[1-f(E_{B_2})]$ |
| 5a | $+\dfrac{Ne^2}{2\hbar\Omega_s}\sum_{A_2B_1A}\mathrm{Im}(w^\beta_{AA_2}-v^\beta_{A_2A})(E^0_A-E^0_{B_1})^{-1}(v^\alpha_{B_1A})^*(Q^{K'}_{1A_2B_1A+}\pm Q^{K'}_{1A_2B_1A-})f(E_A)[1-f(E_{A_2})]$ |
| 5b | $+\dfrac{Ne^2}{2\hbar\Omega_s}\sum_{A_2A_1A}\mathrm{Im}(w^\beta_{AA_2}-v^\beta_{A_2A})(E^0_{B_1}-E^0_{A_2})^{-1}(v^\alpha_{A_2B_1})^*J'^*_{B_1A}(Q_{2A_2B_1A+}\pm Q_{2A_2B_1A-})f(E_A)[1-f(E_{A_2})]$ |
| 5c | $+\dfrac{Ne^2}{2\hbar\Omega_s}\sum_{B_2B_1A}\mathrm{Im}(w^\beta_{AB_2}-v^\beta_{B_2A})(E^0_A-E^0_{B_1})^{-1}(v^\alpha_{B_1A})^*(Q^K_{1B_2B_1A+}\pm Q^K_{1B_2B_1A-})f(E_A)[1-f(E_{B_2})]$ |
| 5d | $+\dfrac{Ne^2}{2\hbar\Omega_s}\sum_{B_2B_1A}\mathrm{Im}(w^\beta_{AB_2}-v^\beta_{B_2A})(E^0_{B_1}-E^0_{B_2})^{-1}(v^\alpha_{B_2B_1})^*J'^*_{B_1A}(Q_{2A_2B_1A+}\pm Q_{2A_2B_1A-})f(E_A)[1-f(E_{A_2})]$ |

the components of the final state. Because we do not know what the initial state is, we average over all possible initial states. At $t=-\infty$, the external field and various residual interactions ($J$, $J$, $K$, and $K'$) are not yet turned on, and the system is in equilibrium. The probabilities of $|A\cdots N_\alpha\cdots\rangle$ is $f(E_A)\prod_\alpha P(N_\alpha)$. The first sum comes from averaging over various initial states, the second sum comes from summing over the component of final state resulted from transfer integral, the third sum comes from summing over the component of final state caused by external field. The first factor has come from Eq. (17). One can similarly find the expressions of macroscopic density for other conduction processes.

In an electric field $\boldsymbol{E}=\boldsymbol{E}_0\cos\omega t$, the real part of conductivity tensor $\mathrm{Re}\sigma_{\alpha\beta}$ can be extracted from the component of $j_\alpha=\sum_\beta\sigma_{\alpha\beta}E_\beta$ with time factor $\cos\omega t$, the imaginary part $\mathrm{Im}\sigma_{\alpha\beta}$ is extracted from $j_\alpha$ with time factor $\sin\omega t$. For the conduction processes in which the initial state is a localized state, the expressions of $\mathrm{Re}\sigma_{\alpha\beta}(\omega)$ and $\mathrm{Im}\sigma_{\alpha\beta}(\omega)$ $(\alpha,\beta=x,y,z)$ are given in Table 4, the real part takes the upper sign, the imaginary part takes the lower sign.

We used

$$w^\alpha_{A_3A_2}=\frac{-i\hbar}{m}\int_{\Omega_s}\mathrm{d}\boldsymbol{r}\,\phi_{A_3}(\boldsymbol{r}-\boldsymbol{R}_{A_3})\frac{\partial}{\partial x_\alpha}\phi^*_{A_2}(\boldsymbol{r}-\boldsymbol{R}_{A_2})\quad(21)$$

and

$$v^\alpha_{A_2A_3}=\frac{-i\hbar}{m}\int_{\Omega_s}\mathrm{d}\boldsymbol{r}\,\phi^*_{A_2}(\boldsymbol{r}-\boldsymbol{R}_{A_2})\frac{\partial}{\partial x_\alpha}\phi_{A_3}(\boldsymbol{r}-\boldsymbol{R}_{A_3})\quad(22)$$

etc. to denote the matrix elements of velocity operator between single particle states. One can show that the integral over normal coordinates $\int[\prod_{\alpha=1}^{3\mathcal{N}}\mathrm{d}\theta_\alpha]$, i.e., the sum over final phonon states and averaging over initial phonon state can be carried out for all the contributions to the current density $\boldsymbol{j}$. The vibrational part of the current density $\boldsymbol{j}$ for each process becomes a time integral, cf. Section 2 of Ref. [22]. The time integrals $I_s$, $Q_s$, and $S_s$ are functions of temperature $T$ and the frequency $\omega$ of the external field, are listed in Section 3.1 of Ref. [22]. $\mathrm{Re}\sigma_{\alpha\beta}(\omega)$ and $\mathrm{Im}\sigma_{\alpha\beta}(\omega)$ satisfy the Kramers–Kronig relation. The reason that we list

**Table 5** The conduction processes and conductivity: initial state is an extended state $\xi_B$.

| diagram | conductivity |
|---|---|
| 6a | $-\dfrac{Ne^2}{2\Omega_s}\sum_{BA_2}\mathrm{Im}\, i(E^0_{A_2}-E^0_B)^{-1}v^\beta_{BA_2}(w^\alpha_{BA_2}-v^\alpha_{A_2B})[I_{A_2B+}(\omega)\pm I_{A_2B-}(\omega)][1-f(E_{A_2})]f(E_B)$ |
| 6b | $-\dfrac{Ne^2}{2\Omega_s}\sum_{BB_1}\mathrm{Im}\, i(E^0_{B_1}-E^0_B)^{-1}v^\beta_{BB_1}(w^\alpha_{BB_1}-v^\alpha_{B_1B})[I_{B_1B+}(\omega)\pm I_{B_1B-}(\omega)][1-f(E_{B_1})]f(E_B)$ |
| 7a | $-\dfrac{Ne^2}{2\hbar\Omega_s}\sum_{BA_3A_2}\mathrm{Im}(E^0_{A_2}-E^0_B)^{-1}v^\beta_{BA_2}(w^\alpha_{A_3A_2}-v^\alpha_{A_2A_3})[I_{A_3A_2B+}(\omega)\pm I_{A_3A_2B-}(\omega)][1-f(E_{A_3})][1-f(E_{A_2})]f(E_B)$ |
| 7b | $-\dfrac{Ne^2}{2\hbar\Omega_s}\sum_{BB_1A_3}\mathrm{Im}(E^0_{B_1}-E^0_B)^{-1}v^\beta_{BB_1}(w^\alpha_{A_3B_1}-v^\alpha_{B_1A_3})[I_{A_3B_1B+}(\omega)\pm I_{A_3B_1B-}(\omega)][1-f(E_{A_3})][1-f(E_{B_1})]f(E_B)$ |
| 7c | $-\dfrac{Ne^2}{2\hbar\Omega_s}\sum_{BB_3A_2}\mathrm{Im}(E^0_{A_2}-E^0_B)^{-1}v^\beta_{BA_2}(w^\alpha_{B_3A_2}-v^\alpha_{A_2B_3})[I_{A_2B_3B+}(\omega)\pm I_{A_2B_3B-}(\omega)][1-f(E_{A_2})][1-f(E_{B_3})]f(E_B)$ |
| 8a | $+\dfrac{Ne^2}{2\Omega_s\hbar}\sum_{A_2A_1B}\mathrm{Im}(w^\alpha_{BA_2}-v^\alpha_{A_2B})(E^0_{A_1}-E^0_{A_2})^{-1}(v^\beta_{A_2A_1})^*(S^{K'}_{1A_2A_1B+}\pm S^{K'}_{1A_2A_1B-})f(E_B)[1-f(E_{A_2})]$ |
| 8b | $+\dfrac{Ne^2}{2\Omega_s\hbar}\sum_{A_2A_1B}\mathrm{Im}(w^\alpha_{BA_2}-v^\alpha_{A_2B})J^*_{A_2A_1}(E^0_B-E^0_{A_1})^{-1}(v^\beta_{A_1B})^*(S_{2A_2A_1B+}\pm S_{2A_2A_1B-})f(E_B)[1-f(E_{A_2})]$ |
| 8c | $+\dfrac{Ne^2}{2\Omega_s\hbar}\sum_{A_2A_1B}\mathrm{Im}(w^\alpha_{BB_2}-v^\alpha_{B_2B})J'^*_{B_2A_1}(E^0_B-E^0_{A_1})^{-1}(v^\beta_{A_1B})^*(S_{1B_2A_1B+}\pm S_{1B_2A_1B-})f(E_B)[1-f(E_{B_2})]$ |
| 8d | $+\dfrac{Ne^2}{2\Omega_s\hbar}\sum_{B_2A_1B}\mathrm{Im}(w^\alpha_{BB_2}-v^\alpha_{B_2B})(E^0_{A_1}-E^0_{B_2})^{-1}(v^\beta_{B_2A_1})^*(S^{K'}_{2B_2A_1B+}\pm S^{K'}_{2B_2A_1B-})f(E_B)[1-f(E_{B_2})]$ |
| 9a | $+\dfrac{Ne^2}{2\Omega_s\hbar}\sum_{B_2A_1B}\mathrm{Im}(w^\alpha_{BA_2}-v^\alpha_{A_2B})(E^0_{B_1}-E^0_{A_2})^{-1}(v^\beta_{A_2B_1})^*(S^K_{1A_2B_1B+}\pm S^K_{1A_2B_1B-})f(E_B)[1-f(E_{A_2})]$ |
| 9b | $+\dfrac{Ne^2}{2\Omega_s\hbar}\sum_{A_2B_1B}\mathrm{Im}(w^\alpha_{BA_2}-v^\alpha_{A_2B})(E^0_B-E^0_{B_1})^{-1}(v^\beta_{B_1B})^*(S^{K'}_{2A_2B_1B+}\pm S^{K'}_{2A_2B_1B-})f(E_B)[1-f(E_{A_2})]$ |
| 10a | $+\dfrac{Ne^2}{2\Omega_s\hbar^2}\sum_{BB_1B_2B_3}\mathrm{Im}(w^\alpha_{B_3B_1}-v^\alpha_{B_1B_3})i(E^0_B-E^0_{B_1})^{-1}(v^\beta_{B_1B})^*[I_{B_3B_2B_1B+}(\omega)\pm I_{B_3B_2B_1B-}(\omega)][1-f(E_{B_1})][1-f(E_{B_3})]f(E_B)$ |
| 10b | $-\dfrac{Ne^2}{2\Omega_s\hbar^2}\sum_{B_3B_2B_1B}\mathrm{Im}(w^\alpha_{BB_3}-v^\alpha_{B_3B})i(E^0_B-E^0_{B_1})^{-1}(v^\beta_{B_1B})^*(K_{1B_3B_2B_1B+}\pm K_{1B_3B_2B_1B-})f(E_B)[1-f(E_{B_3})]$ |
| 10c | $-\dfrac{Ne^2}{2\Omega_s\hbar^2}\sum_{B_3B_2B_1B}\mathrm{Im}(w^\alpha_{BB_3}-v^\alpha_{B_3B})i(E^0_{B_1}-E^0_{B_2})^{-1}(v^\beta_{B_2B_1})^*(K_{2B_3B_2B_1B+}\pm K_{2B_3B_2B_1B-})f(E_B)[1-f(E_{B_3})]$ |
| 10d | $-\dfrac{Ne^2}{2\Omega_s\hbar^2}\sum_{B_3B_2B_1B}\mathrm{Im}(w^\alpha_{BB_3}-v^\alpha_{B_3B})i(E^0_{B_2}-E^0_{B_3})^{-1}(v^\beta_{B_3B_2})^*(K_{3B_3B_2B_1B+}\pm K_{3B_3B_2B_1B-})f(E_B)[1-f(E_{B_3})]$ |

both of them is to show that (i) they are symmetric about the positive and negative frequency time integrals and (ii) $\mathrm{Im}\,\sigma_{\alpha\beta}(0)=0$.

The conductivity from LL transitions [13] derives from the processes depicted in Figs. 2a, 3a, and 4a and b. For small polarons, the Kubo formula was used in both Refs. [5, 7] to obtain the second and fourth terms in Table 4, but not the eighth and ninth terms. The reason is the following. If one views both $J$ and $J^{\text{field}}$ as small parameters, the eighth and ninth terms in Table 4 result from a second order change in state, one in $J$ and one in $J^{\text{field}}$. To obtain conductivity in Kubo formulation, the change in the density matrix of system is computed to first order in external field. By substituting this first order change into the macroscopic current density, one obtains the conductivity by factoring out the external field [1]. In this way, the new combinations of $J$ and $J^{\text{field}}$ (Fig. 4a and b) are excluded. In the present work, we apply linear response to external field at the last step, so that there are various combinations between $S$ and $J^{\text{field}}$. From Eqs. (21), (25) and (27) of Ref. [22], we see that the $(\omega, T)$ dependence of the fourth term is different from those of the

eighth and ninth terms in Table 4. It will be interesting to see if new features of the eighth and ninth terms can be observed experimentally.

If the initial state is an extended state $\xi_B$, substituting the corresponding $\psi^{(0)}(t)$ and $\psi^{(1)}(t)$ into the first term of Eq. (17), one can similarly derive the corresponding relation between the contribution to $\boldsymbol{j}$ and the diagram of a conduction process, see Tables 2 and 3. There are 14 processes contributing to the conductivity, cf. Figs. 6–9. However
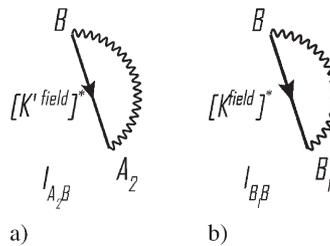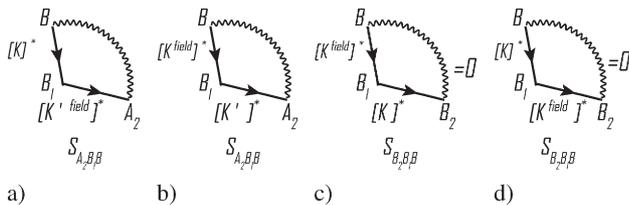


**Figure 6** Initial state is extended state $\xi_B$: order $[K']^0$ and order $K^0$ contributions to conductivity.
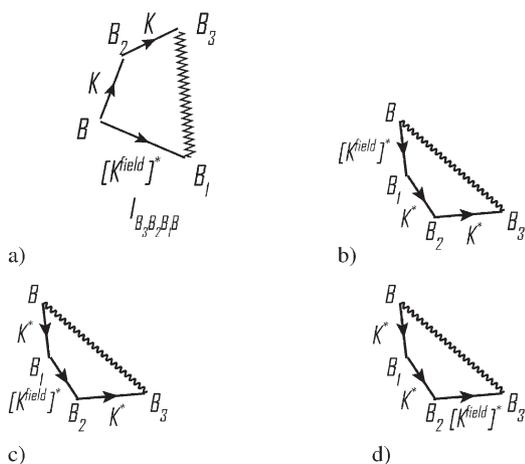
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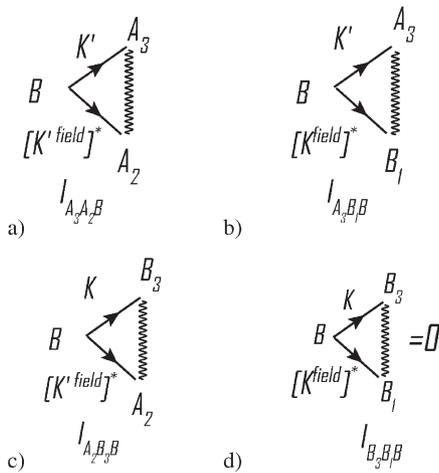
**Figure 7** Initial state is extended state $\xi_B$: order $[K']^1$ and order $K^1$ contributions to conductivity.
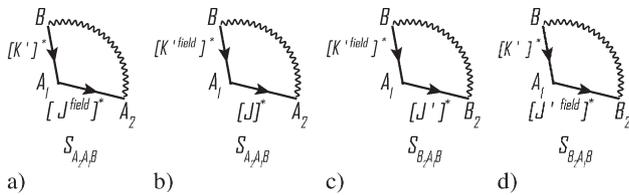


**Figure 8** Initial state is extended state $\xi_B$: order $K'$, $[J']^1$, and order $J^1$ contributions to conductivity.



**Figure 9** Initial state is extended state $\xi_B$: order $[K']^1$ and order $K^1$ contributions to conductivity.



**Figure 10** Initial state is extended state $\xi_B$: order $K^2$ contribution to conductivity.

three order $K^1$ EE transition processes (Figs. 7d and 9c and d) are 0 due to the e–ph interaction selection rule. For processes involving only extended states, order $K^2$ processes are the first non-zero contributions. The first term in Eq. (17) indicates there are four such terms (Fig. 10). Thus if the initial state is an extended state $\xi_B$, to lowest order self-consistent approximation, there are 15 conduction processes. The corresponding expressions for conductivity are listed in Table 5. The time integrals are given in Section 3.2 of Ref. [22].

For EE transition, the order $K^1$ contributions to conduction are 0 (Figs. 7d and 9c and d), so that one has to take into account order $K^2$ contribution (Fig. 10a–d). The time integrals are given in Section 3.3 of Ref. [22]. The conductivity from the pure EE transitions derives from the second (Fig. 6b: carriers are scattering by the static disorder), and the thirteenth to the sixteenth terms (Fig. 10: the carriers in extended states are inelastically scattered by phonons) in Table 5. This is consistent with the Boltzmann theory: in the lowest order approximation, the scattering probability is second order in the e–ph coupling constant $K$ while the distribution function $f^{(0)}$ is order $K^0$ (the non-interacting elementary excitations) [26]. Thus the collision integral is proportional to $K^2$ and the change $f^{(1)}$ in distribution function and the resulting conductivity is proportional to $K^2$.

The expression for the conductivity is a sum of 29 terms listed in Tables 4 and 5.

**6 Hall mobility** If an AS is placed in an external magnetic field, the conductivity is still defined through the current density $j_\alpha = \sum_\beta \sigma_{\alpha\beta} E_\beta$. If we apply a static electric field along the $x$-direction and a static magnetic field along the $z$-direction, the Hall voltage is along the $y$-direction and proportional to both $B_z$ and $E_x$. ASs are isotropic, and the Hall mobility is given by [8]:

$$\mu_H = \frac{B_z^{-1} \sigma_{yx}}{\sigma_{xx}}. \tag{23}$$

The non-diagonal conductivity in a magnetic field is described by the second term of Eq. (17).

In general, both the carriers in localized states and carriers in extended states contribute to the Hall effect. There are too many terms in the full expression for non-diagonal conductivity to reproduce here. We restrict ourselves to the LL transitions. This is a reasonable approximation for intrinsic and lightly doped ASs, where carriers in extended states are rare. At the end of this Section, we will indicate how to obtain the full expression of Hall mobility.

By substituting the corresponding $\psi^{(0)}$, $\psi^{(1)}$, and $\psi^{(2)}$ into the second term of Eq. (17), one finds the current density in a magnetic field and an electric field. Various contributions may be visualized by diagrams as for the conductivity: the transition amplitudes in Table 3 are still applicable. The expression for the two components connected by the current operator $(\psi^{(0)} \nabla_r \psi^{(2)*} - \psi^{(2)*} \nabla_r \psi^{(0)})$ is the same as that for two components connected by

$(\psi^{(0)}\nabla_r\psi^{(1)*}-\psi^{(1)*}\nabla_r\psi^{(0)})$ in the ordinary conductivity. We still use a wavy line to depict such a expression: it points from one component of $\psi^{(0)}$ to one component of $\psi^{(2)*}$. There is one order $J^0$ process and four order $J^1$ processes. In Table 7 we list the contributions from $(\psi^{(0)}\nabla_r\psi^{(2)*}-\psi^{(2)*}\nabla_r\psi^{(0)})$. If we exchange $\psi^{(0)}$ and $\psi^{(2)*}$, the current density changes sign. The new contribution to current density from $\psi^{(1)}\nabla_r\psi^{(1)*}$ does not include this exchange antisymmetry. We represent it by a dashed arrow line, cf. the last line of Table 2. The dashed arrow line points from one component in $\psi^{(1)}$ to one component in $\psi^{(1)*}$. There is one order $J^0$ process and four order $J^1$ processes. We list the contributions from $\psi^{(1)}\nabla_r\psi^{(1)*}$ in Table 6. Order $J^0$ contributions are illustrated in Fig. 11. Order $J$ contributions are illustrated in Figs. 12 and 13. In the symmetric gauge $A=(1/2)B\times r$, the coupling between two localized states by the external magnetic field becomes:

$$J^{\text{field}}_{A_2A_1}=-\frac{e}{2m}B_z L^z_{A_2A_1}-eE_x x_{A_2A_1}, \tag{24}$$

where $x_{A_2A_1}=\int dr\phi^*_{A_2}x\phi_{A_1}$, and $L_z^{A_2A_1}=\int dr\phi^*_{A_2}L_z\phi_{A_1}$ is the matrix element of the $z$ component of electronic orbital angular momentum. To compute the Hall mobility, we require only the terms which are proportional to $B_zE_x$. For example, in $(J^{\text{field}}_{A_3A_2})^*(J^{\text{field}}_{A_2A_1})^*$, we only keep:

$$\left(\frac{e^2}{2m}\right)B_zE_x(L^z_{A_3A_2}x_{A_2A_1}+x_{A_3A_2}L^z_{A_2A_1})^*. \tag{25}$$
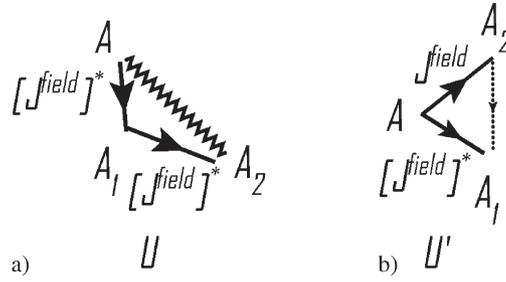
One can extract $\sigma_{yx}$ from $j_y$. The corresponding expressions for various processes are given in Table 8. The time integrals $U$, $U'$, $Z$, $Z'$, and $Y$ are given in Section 5 of Ref. [22], they are functions of temperature $T$. The non-diagonal conductivity $\sigma_{yx}$ is a sum of ten terms listed in Table 8. In the previous theory of the Hall effect [6–8], researchers introduced magnetic field dependent Wannier functions as the basis and expanded the magnetic field dependent phase in the final step. Such a method excludes the interference between the transition amplitudes caused by electric field and magnetic field. In the present work, we treat electric field and magnetic field on the same footing. A

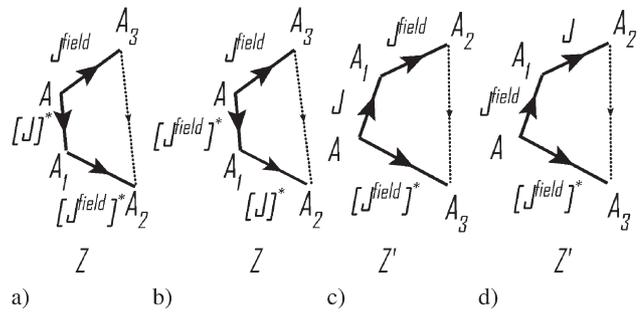**Table 6** Contributions to $\sigma_{yx}$ from $\psi^{(1)}\nabla_r\psi^{(1)*}$.

| $J^0$ | $\psi^{(1)}_{J^0}\nabla_r\psi^{(1)*}_{J^0}$ | Fig. 11b |
|---|---|---|
| $J$ | $\psi^{(1)}_{J^0}\nabla_r\psi^{(1)*}_J$ | 12a and b |
| $J$ | $\psi^{(1)}_J\nabla_r\psi^{(1)*}_{J^0}$ | 12c and d |

**Table 7** Contribution to $\sigma_{yx}$ from $(\psi^{(0)}\nabla_r\psi^{(2)*}-\psi^{(2)*}\nabla_r\psi^{(0)})$.
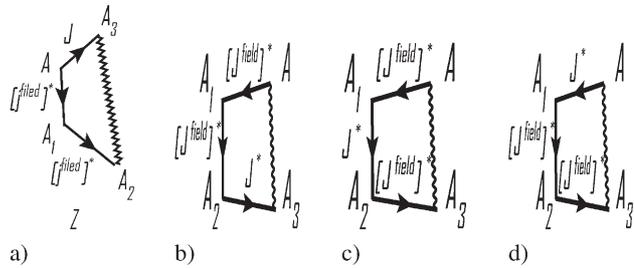
| $J^0$ | $\psi^{(0)}_{J^0}\nabla_r\psi^{(2)*}_{J^0}-\psi^{(2)*}_{J^0}\nabla_r\psi^{(0)}_{J^0}$ | Fig. 11a |
|---|---|---|
| $J$ | $\psi^{(0)}_J\nabla_r\psi^{(2)*}_{J^0}-\psi^{(2)*}_{J^0}\nabla_r\psi^{(0)}_J$ | Fig. 12a |
| $J$ | $\psi^{(0)}_{J^0}\nabla_r\psi^{(2)*}_J-\psi^{(2)*}_J\nabla_r\psi^{(0)}_{J^0}$ | 12b–d |



**Figure 11** Order $J^0$ contributions to $\sigma_{yx}$. (a) Results from $(\psi^{(0)}_{J^0}\nabla\psi^{(2)*}_{J^0}-\psi^{(2)*}_{J^0}\nabla\psi^{(0)}_{J^0})$. (b) Results from $\psi^{(1)}_{J^0}\nabla\psi^{(1)*}_{J^0}$.



**Figure 12** Order $J^1$ contributions to $\sigma_{yx}$: (a) results from $\psi^{(1)}_{J^0}\nabla\{\psi^{(1)}[A\xrightarrow{J^1}A_1\xrightarrow{J^{\text{field}}}A_2]\}^*$. (b) Results from $\psi^{(1)}_{J^0}\nabla\{\psi^{(1)}[A\xrightarrow{J^{\text{field}}}A_1\xrightarrow{J^1}A_2]\}^*$. (c) Results from $\psi^{(1)}[A\xrightarrow{J^1}A_1\xrightarrow{J^{\text{field}}}A_2]\nabla\psi^{(1)*}_{J^0}$. (d) Results from $\psi^{(1)}[A\xrightarrow{J^{\text{field}}}A_1\xrightarrow{J^1}A_2]\nabla\psi^{(1)*}_{J^0}$.



**Figure 13** Order $J$ contributions to $\sigma_{yx}$: (a) results from $(\psi^{(0)}_{J^1}\nabla\psi^{(2)*}_{J^0}-\psi^{(2)*}_{J^0}\nabla\psi^{(0)}_{J^1})$. (b–d) Result from $(\psi^{(0)}_{J^0}\nabla\psi^{(2)*}_{J^1}-\psi^{(2)*}_{J^1}\nabla\psi^{(0)}_{J^0})$.

mixing similar to Eq. (25) appears in each term of Table 8. In the application of Kubo formula [6–8], Figs. 11b, 12, and 13b–d are excluded. These new terms are of the same order as Figs. 11a and 13a, but the temperature dependence are different. To check the existence of these new term, it requires more experimental data points [13].

The full Hall effect from the carriers in localized states and in extended states can be found by eventually changing the states from A to B, and correspondingly changing the residual interaction and the transition amplitudes. For

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**Table 8** Diagrams and $\sigma_{yx}$.

| diagram | $\sigma_{yx}$ |
|---|---|
| 11a | $B_z \dfrac{Ne^3}{2m\hbar^2 \Omega_s} \sum_{AA_2A_1} \mathrm{Im}\{U_{AA_2A_1} f(E_A)[1-f(E_{A_2})]i(w_y^{AA_2}-v_y^{A_2A})(L_z^{A_2A_1}x_{A_1A}+x_{A_2A_1}L_z^{A_1A})^*\}$ |
| 11b | $-B_z \dfrac{Ne^3}{2m\hbar^2 \Omega_s} \sum_{AA_2A_1} \mathrm{Im}\{iw_y^{A_2A_1}(L_z^{A_1A}x_{A_2A}+x_{A_1A}L_z^{A_2A})^* U'_{AA_1A_2}(T)f(E_A)[1-f(E_{A_1})][1-f(E_{A_2})]\}$ |
| 12a | $B_z \dfrac{Ne^3}{2m\hbar^3 \Omega_s} \sum_{AA_1A_2A_3} \mathrm{Im} f(E_A)[1-f(E_{A_2})][1-f(E_{A_3})]w_y^{A_3A_2}(L_z^{A_3A}x_{A_2A_1}^* J_{A_1A}^* + x_{A_3A}(L_z^{A_2A_1})^* J_{A_1A}^*)Z_{AA_3A_2A_1}$ |
| 12b | $B_z \dfrac{Ne^3}{2m\hbar^3 \Omega_s} \sum_{AA_1A_2A_3} \mathrm{Im} f(E_A)[1-f(E_{A_2})][1-f(E_{A_3})]w_y^{A_3A_2}(x_{A_3A}J_{A_2A_1}^* (L_z^{A_1A})^* + L_z^{A_3A}J_{A_2A_1}^* x_{A_1A})Z_{AA_3A_2A_1}$ |
| 12c | $-B_z \dfrac{Ne^3}{2m\hbar^3 \Omega_s} \sum_{AA_1A_2A_3} \mathrm{Im} f(E_A)[1-f(E_{A_2})][1-f(E_{A_3})]w_y^{A_2A_3}(x_{A_3A}^* L_z^{A_2A_1} + (L_z^{A_3A})^* x_{A_2A_1})J_{A_1A}Z'_{AA_3A_2A_1}$ |
| 12d | $-B_z \dfrac{Ne^3}{2m\hbar^3 \Omega_s} \sum_{AA_1A_2A_3} \mathrm{Im} f(E_A)[1-f(E_{A_2})][1-f(E_{A_3})]w_y^{A_2A_3}(x_{A_3A}^* J_{A_2A_1}L_z^{A_1A} + (L_z^{A_3A})^* J_{A_2A_1}x_{A_1A})Z'_{AA_3A_2A_1}$ |
| 13a | $+B_z \dfrac{Ne^3}{2m\hbar^3 \Omega_s} \sum_{AA_1A_2A_3} \mathrm{Im} f(E_A)[1-f(E_{A_2})][1-f(E_{A_3})](w_y^{A_3A_2}-v_y^{A_2A_3})J_{A_3A}(L_z^{A_2A_1}x_{A_1A}+x_{A_2A_1}L_z^{A_1A})^*Z_{AA_3A_2A_1}$ |
| 13b | $\dfrac{Ne^3}{\Omega_s 2m^2\hbar^2} B_z \sum_{A_3A_2A_1A} \mathrm{Im}\, Y_{A_3A_2A_1A}f(E_A)[1-f(E_{A_3})]iJ_{A_3A_2}^* (w_{AA_3}^y - v_{A_3A}^y)[(L_{A_2A_1}^z)^*(x_{A_1A})^* + (x_{A_2A_1})^*(L_{A_1A}^z)^*]$ |
| 13c | $\dfrac{Ne^3}{\Omega_s 2m^2\hbar^2} B_z E_x \sum_{A_3A_2A_1A} \mathrm{Im}\, Y_{A_3A_2A_1A}f(E_A)[1-f(E_{A_3})]iJ_{A_2A_1}^* (w_{AA_3}^y - v_{A_3A}^y)[(L_{A_3A_2}^z)^*(x_{A_1A})^* + (x_{A_3A_2})^*(L_{A_1A}^z)^*]$ |
| 13d | $\dfrac{Ne^3}{\Omega_s 2m^2\hbar^2} B_z \sum_{A_3A_2A_1A} \mathrm{Im}\, Y_{A_3A_2A_1A}f(E_A)[1-f(E_{A_3})]iJ_{A_1A}^* (w_{AA_3}^y - v_{A_3A}^y)[(L_{A_3A_2}^z)^*(x_{A_2A_1})^* + (x_{A_3A_2})^*(L_{A_2A_1}^z)^*]$ |

example, there are seven more diagrams for each diagram in Fig. 13. Using Tables 2 and 3, one can easily write out the expressions for each Diagram [13].

**7 Conclusion** The MRM [3, 4, 13] is applied to systematically estimate the conductivity (Tables 4 and 5) and Hall coefficient (Table 8 and Eq. 23) in ASs. A diagrammatic representation of transport coefficients is introduced by inspecting the structure of the observed current density and the perturbation expansion of wave function about small parameters and about external field. From the topology of the diagrams, one can easily write down various contributions for a transport coefficient to a given order of small parameters. This is helpful for higher order processes. Comparing to the Kubo formula, all important conduction processes can be easily taken into account by the diagrammatic rules in Tables 2 and 3. Impressive advances have been made for computing transport properties from first principles using the Keldysh formalism [27–29]. The present method is complementary to that work as a means of computing temperature dependence of the transport coefficients rather than *I–V* curves.

The present work has two obvious advantages over the thermal average method of classical MD: (i) the vibrations of atoms are described by quantum mechanics, the results obtained are valid for arbitrary temperature (at least for which the harmonic approximation is valid), whereas the results of MD are correct only above the Debye temperature of a material; (ii) in the expressions for conductivity and Hall mobility, the e–ph interaction is already integrated out. To calculate the transport coefficients at a given temperature,

one only needs the eigenvectors and eigenvalues of the Kohn–Sham Hamiltonian and the dynamical matrix, and the e–ph coupling constants for each single electron state for one configuration. One does not need to compute the time-consuming MD trajectory or worry about proper equilibration. The method is ideally suited for *ab initio* simulation and is in the process of numerical implementation.

**References**

[1] R. Kubo, J. Phys. Soc. Jpn. **12**, 570 (1957).
[2] D. A. Greenwood, Proc. Phys. Soc. (London) **71**, 585 (1958).
[3] M.-L. Zhang and D. A. Drabold, Phys. Rev. E **83**, 012103 (2011).
[4] M.-L. Zhang and D. A. Drabold, J. Phys.: Condens. Matter **23**, 085801 (2011).
[5] I. G. Lang and Yu. A. Firsov, Zh. Eksp. Teor. Fiz. **43**, 1843 (1962) [Sov. Phys.-JETP **16**, 1301 (1963)].
[6] Yu. A. Firsov, Fiz. Tverd. Tela **5**, 2149 (1963) [Sov. Phys.-Solid State **5**, 1566 (1964)].
[7] J. Schnakenberg, Z. Phys. **185**, 123 (1965).
[8] T. Holstein and L. Friedman, Phys. Rev. **165**, 1019 (1968).
[9] A. Aldea, J. Phys. C, Solid State Phys. **5**, 1649 (1972).
[10] S. K. Lyo, J. Phys. C, Solid State Phys. **6**, 2158 (1973).
[11] N. F. Mott and E. A. Davis, Electronic Processes in Non-crystalline Materials (Clarendon Press, Oxford, 1971).
[12] M.-L. Zhang and D. A. Drabold, Eur. Phys. J. B **77**, 7–23 (2010).

[13] M.-L. Zhang and D. A. Drabold, Phys. Rev. Lett. **105**, 186602 (2010).

[14] R. A. Marcus, Rev. Mod. Phys. **65**, 599610 (1993).

[15] T. Holstein, Ann. Phys. **8**, 325, 343 (1959).

[16] D. Emin, Phys. Rev. Lett. **32**, 303 (1974); Adv. Phys. **24**, 305 (1975); Phys. Rev. B **43**, 11720 (1991).

[17] P. A. Fedders, D. A. Drabold, and S. Nakhmanson, Phys. Rev. B **58**, 15624 (1998).

[18] A. Miller and E. Abrahams, Phys. Rev. **120**, 745 (1960).

[19] P. Thomas, J. Non-Cryst. Solids **77&78**, 121 (1985).

[20] D. A. Drabold, P. A. Fedders, S. Klemm, and O. F. Sankey, Phys. Rev. Lett. **67**, 2179 (1991).

[21] R. Atta-Fynn, P. Biswas, and D. A. Drabold, Phys. Rev. B **69**, 245204 (2004).

[22] See supporting information at http://onlinelibrary.wiley.com/doi/10.1002/pssb.201147036/suppinfo.

[23] C. M. Van Vliet, Equilibrium and Non-equilibrium Statistical Mechanics (World Scientific, Singapore, 2008).

[24] M.-L. Zhang and D. A. Drabold, Phys. Rev. B **81**, 085210 (2010).

[25] D. Bohm, Quantum Theory (Prentice-Hall, New Jersey, 1951).

[26] E. M. Lifshitz and L. P. Pitaevskii, Physical Kinetics (Butterworth-Heinemann, Oxford, 1981).

[27] M. Brandbyge, N. Kobayashi, and M. Tsukada, Phys. Rev. B **60**, 17064 (1999).

[28] M. Brandbyge, K. Stokbro, J. Taylor, J. L. Mozos, and P. Ordejon, MRS Conf. Proc. **636**, D9.25 (2000).

[29] J. Taylor, J. Wang, and H. Guo, Phys. Rev. B **63**, 245407 (2001).

[30] D. Binosi and L. Theußl, Comput. Phys. Commun. **161**, 76 (2004).