Alternative approach to computing transport coefficients: application to conductivity and Hall coefficient of hydrogenated amorphous silicon

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We introduce a theoretical framework for computing transport coefficients for complex materials. As a first example, we resolve long-standing inconsistencies between experiment and theory pertaining to the conductivity and Hall mobility for amorphous silicon and show that the Hall sign anomaly is a consequence of localized states. Next, we compute the AC conductivity of amorphous polyaniline. The formalism is applicable to complex materials involving defects and band-tail states originating from static topological disorder and extended states. The method may be readily integrated with current ab initio methods.

The atomistic understanding of the electrical conductivity\textsuperscript{1, 2} and Hall coefficient\textsuperscript{3–7} are key unsolved problems in the physics of amorphous semiconductors\textsuperscript{8}. The challenge is due to two factors: (1) a complex array of localized states of varying physical origin; and (2) at moderate temperature, both localized states and extended states are accessible excited states\textsuperscript{9, 10}.

Previous work on the conductivity\textsuperscript{11, 12} and Hall coefficient\textsuperscript{13–17} of amorphous semiconductors has involved either Miller-Abrahams theory or small polaron models\textsuperscript{9}. Neither approach is ideal for amorphous semiconductors, with their complex manegerial of localized states due to defects, and tail states due to topological\textsuperscript{18} and chemical disorder\textsuperscript{8} and electron-phonon couplings strongly dependent upon carrier localization\textsuperscript{19}.

In this Letter, we first develop a novel formalism for the linear response to a mechanical perturbation\textsuperscript{20}. The method properly includes the four possible transitions between extended or localized initial and final states. The full results and many intermediate details are provided in Ref.\textsuperscript{21}; here we require only transitions between localized states. Our work resolves the puzzle of the sign anomaly of the Hall mobility in a-Si:H\textsubscript{2}, provides the temperature dependence of the transport coefficients, and accurately predicts the AC conductivity of polyaniline. The new formalism is expected to be applicable well beyond the examples of this Letter and lends itself to inclusion in current \textit{ab initio} schemes.

In the small polaron hopping regime, the Kubo linear response formula\textsuperscript{20} has been used to compute conductivity and Hall mobility\textsuperscript{12, 13, 17}. The key mathematical obstacle to computing the current-current correlation function is the imaginary time integral,\textsuperscript{12, 13, 17} which results from the commutator between the microscopic current and density matrix\textsuperscript{20}. For a “mechanical perturbation” (for which an external disturbance may be expressed with additional terms in the Hamiltonian\textsuperscript{20}), we can avoid this troublesome commutator, and within this picture the local density operator $\hat{\rho}$ of a quantity (charge, energy etc.) can be easily constructed\textsuperscript{22}.

We first average $\hat{\rho}$ over a state $\Psi(t)$ of the system with the mechanical perturbation, from which the microscopic local density $\rho(r, t) = \langle \Psi(t) | \hat{\rho} | \Psi(t) \rangle$ is obtained. Next we calculate $\partial \rho(r, t) / \partial t$ by means of the time-dependent Schrödinger equation $i\hbar \partial \Psi(t) / \partial t = H'(t) \Psi(t)$, where $H'(t)$ is the total Hamiltonian of [system + mechanical perturbation]. The third step is to apply the local density (charge density, energy density) continuity equation: $\partial \rho(r, t) / \partial t + \nabla \cdot j_m(r, t) = 0$; the microscopic response $j_m$ (current density, energy flux etc.) is then expressed in terms of $\Psi(t)$. Practically speaking, $\Psi(t)$ may be computed to the required order with perturbation theory. By substituting $\Psi(t)$ into the expression for $j_m(r, t)$, one can obtain the microscopic response to the required order of mechanical disturbance. Spatial and ensemble average are taken at the final stage. The desired transport coefficients can then be extracted from the ensemble average of the spatially averaged flux $\mathbf{j}$.

Since the state of the system is completely determined from the initial conditions, averaging over initial state can be delayed until the final stage. Thus we can avoid the commutator between flux and density matrix, \textit{i.e.} the integral over imaginary time.

Consider then, a system with $N_e$ electrons and $N$ nuclei in the presence of an electromagnetic field with potentials ($A, \phi$), the charge density of state $\Psi'$ at $r$ $\rho'(r, t) = \int d\tau \Psi'^* \hat{\rho}(r) \Psi'$, where the arguments of wave function $\Psi'$ are $(r_1 \cdots r_{N_e}; \mathbf{W}_1 \cdots \mathbf{W}_N; t)$, $\mathbf{W}_1$ is the position of the first nucleus, etc. $\hat{\rho}(r) = \sum_{e} \mathbf{e} \delta(r - r_e) - \sum_{l} Z_L e \delta(r - \mathbf{W}_L)$ is the charge density operator.

$$d\tau = d\tau_1 \cdots d\tau_{N_e} d\mathbf{W}_1 \cdots d\mathbf{W}_N$$

is the volume element in configuration space. The evolution of the state is determined by the time-dependent Schrödinger equation for which the total Hamiltonian includes the interaction between system and external field. The contribution from the electrons is:

$$j_m(r, t) = \frac{i e N_e}{2 m} \int d\tau' (\mathbf{\nabla} \Psi' \Psi'^* - \Psi'^* \mathbf{\nabla} \Psi') - \frac{e^2 N_e}{m} A(r, t) \int d\tau' \Psi'^* \Psi', \quad (1)$$

where the arguments of $\Psi'$ are
\[ (r, r_1, \cdots, r_{2N}; W_1, W_2, \cdots, W_N; t), \quad dr' = dr_1 \cdots dr_{N}\psi \cdot dW_1 \cdots dW_N. \] In Eq. (1), the anti-symmetry of \( \Psi' \) under exchange of particles was used, and the Coulomb gauge \( \nabla \cdot A(r, t) = 0 \) was adopted to simplify the expression. \( J_m(r, t) \) is gauge invariant \[14, 23\]. Without the nuclear coordinates, Eq. (1) is identical to the form used by BCS to compute paramagnetic and diamagnetic currents for superconductors in which Bloch states are not radially modified by the electron-phonon (e-ph) interaction \[23\]. Eq. (1) is a generalization to arbitrary strength of e-ph interaction, and may be used for the localized carriers in amorphous semiconductors or the polarons in ionic and molecular crystals.

We now apply Eq. (1) to compute the conductivity and Hall mobility of an amorphous semiconductor. The ratio of the second term to the first term is \( eA/p \) (\( p \) is electron momentum), so that the contribution from the 2nd term may be neglected. Since the carrier concentration is low in lightly-doped amorphous semiconductors, one can invoke the single-electron approximation, and \( \Psi'(t) \) for \( J_m \) may be replaced by the single-electron wave function \( \psi'(r; x_1, x_2, \cdots, x_{3N}; t) \), where \( r \) is the coordinate of the carrier, \( x_1, x_2, \cdots, x_{3N} \) are the displacements of \( 3N \) vibrational degrees of freedom.

Using perturbation theory, one can expand \( \psi'(t) \) to the required order of external field \[10, 21\]. We use \( A \) with subscripts to label localized states, denote the coupling between two localized states \( \phi_A \) and \( \phi_{A'} \) caused by external field as \( J_A^{field} = \int dr \phi_A^* \phi_{A'} h_{f \phi} \), where \( h_{f \phi} = (i\hbar c/m) \nabla \phi + e^2A^2(r)/(2m) + e \phi(r) \). The spatially averaged microscopic current density to second order of \( J^{field} \) is

\[
J(s, t) = -\frac{N_\alpha e^2}{\Omega_s} \int_{\Omega_s} dr \int [3N\prod_{j=1}^{3N} dx_j] \left\{ \text{Im} \left( \psi^{(0)} \nabla \psi^{(1)*} - \psi^{(1)} \nabla \psi^{(0)*} \right) \right. \\
+ \text{Im} \left( \psi^{(0)} \nabla \psi^{(2)*} - \psi^{(2)*} \nabla \psi^{(0)} + \psi^{(1)} \nabla \psi^{(1)*} \right) \left. \right\}, \quad (2)
\]

where \( \psi^{(1)} \) is change in state to order \( J^{field} \), and \( \psi^{(2)} \) is change in state to order \( J^{field} \), where \( \psi^{(0)}(t) \) is the state of carrier at time \( t \) without external field. \( \Omega_s \) is the "physical infinitesimal" volume of Kubo \[24\]. Because the initial state of the phonon-dressed carrier is unknown, we need to average \( j_k(k = x, y, z) \) over initial phonon distribution and single-electron states.

To compute the conductivity, we only require the order \( J^{field} \) term of Eq. (2). If one applies a voltage drop across the material, the potentials are \( A = 0 \) and \( \phi = -2E_0 \cdot r \cos \omega t \). Using perturbation theory, one can compute \( \psi^{(0)} \) and \( \psi^{(1)} \) to order \( J^3 \). Substitute \( \psi^{(0)} \) and \( \psi^{(1)} \) into the first term of Eq. (3), the conductivity from the LL transition is \[21\]:

\[
\text{Re} \left( \sigma_{\alpha\beta}(\omega) \right) = \frac{N_e^2}{\Omega_s} \text{Im} \int \sum_{A, A'} \left[ I_{A, A'} + I_{A', A} \right] \\
x f(E_A^*) \left[ 1 - f(E_{A'}^0) \right] y_{A, A'}^* \left( E_A^* - E_{A'}^0 \right)^{-1} (w_{A, A'} - v_{A, A'}) \\
+ \frac{N_e^2}{\Omega_s} \text{Im} \sum_{A, A'} f(E_A^*) \left[ 1 - f(E_{A'}^0) \right] \left[ 1 - f(E_{A'}^0) \right] \\
x \left( E_A^* - E_{A'}^0 \right)^{-1} h^{-1} J_{A, A'} \left[ I_{A, A'} + I_{A', A} \right] \\
+ \left( w_{A, A'} - v_{A, A'} \right) v_{A, A'}^* 
\]

\[
Q_{A, A'} \left[ I_{A, A'} + I_{A', A} \right] f(E_A^*) \left[ 1 - f(E_{A'}^0) \right] \\
+ \frac{N_e^2}{2\hbar \Omega_s} \sum_{A, A'} \left( w_{A, A'} - v_{A, A'} \right) J_{A, A'} \left( E_A^* - E_{A'}^0 \right)^{-1} (v_{A, A'}^*) \\
Q_{A, A'} \left[ I_{A, A'} + I_{A', A} \right] f(E_A^*) \left[ 1 - f(E_{A'}^0) \right]
\]

Re \( \sigma_{j_k}(\omega) \) takes the positive sign and \( \text{Im} \sigma_{j_k}(\omega) \) takes the negative sign. Unlike previous theories \[9\], the dc conductivity may be directly extracted from Eq. (3) without a limiting process. Here, \( v_{A, A'}^* = \int dr \phi_{A'}^* (p_{j, m}) \phi_A \) are the velocity matrix elements of a carrier. \( f(E_A^0) \) is the Fermi distribution. \( J_{A, A'} = \int dr \phi_{A'}^* \int_{\Omega_s} dE_A U(r - R_p) \phi_A \) is transfer integral from \( \phi_A \) to \( \phi_{A'} \). In Eq. (3), the first term is order \( J^0 \) contribution, the second term is order \( J^1 \) contribution. Here, \( I_{A, A'}(\omega, t) \) has dimension of time (denote its order as \( t_{A, A'}^z \)), and reflects the time evolution of \( \psi'(t) \) in a field-driven 2-site transition, cf. Eq. (C1) in \[21\]. The characteristic time \( t_{A, A'}^z \) may be interpreted as the mean free carrier time. Similarly the two-fold time integrals \( I_{A, A', A, A'} \), \( Q_{A, A', A, A'} \), and \( Q_{A, A', A, A'} \), have dimension \( \text{of time}^2 \), reflecting the time evolution of \( \psi'(t) \) in a 3-site transition induced by transfer integral \( J \); they have same order of magnitude \( v_{A, A'}^* \), cf. Eqs. (3), (7), (9) in \[21\]. At high temperatures \( k_B T > \hbar \omega \) (\( \omega \) is first peak in phonon spectrum), the time integrals \( I_s \) and \( Q_s \) can be approximated...
using the method of steepest descent (see Appendix D in [21]). For example:

\[ I_{A_1, A_1} = e^{-\beta \hbar (\omega'_{A_1, A_1} + \omega)/2 - \beta \lambda_{A_1, A_1}/4} \]

\[ \{C^{-1/2} \sum_{n=0}^{\infty} (-i)^n (\omega - \omega')^n / n!C_n^{1/2}\} \Gamma(n + 1/2) \]

\[ -i [\sum_{\alpha} \frac{1}{2} (\theta_{A_1} - \theta_{A_1}^2) \omega_\alpha \cosh \beta \omega_\alpha]^{-1}, \]

(4)

where \( \theta_{A_1} \) is the shift in origin of the \( \alpha \)th normal mode caused by a carrier in state \( \phi_{A_1} \). \( \lambda_{A_1, A_1} \) is the energy difference: \( t_{A_1, A_1}^{\pm} \sim \hbar^{-2} k_B T \lambda_{A_1, A_1} \). The mean free time decreases with increasing \( \lambda_{A_1, A_1} \) and energy difference: \( t_{A_1, A_1}^{\pm} \sim \hbar^{-2} k_B T \lambda_{A_1, A_1}^{-1} e^{-\beta \hbar (\omega'_{A_1, A_1} + \omega)/2 - \beta \lambda_{A_1, A_1}/4} \).

The average mobility \( \mu \) is defined by \( \sigma_{xx} = e^2 N_e / \hbar \mu \). From Eq. (3), one can see that \( \mu \) depends on the energy distribution and spatial distribution of localized states. A typical value of \( \mu \) can be estimated: \( \mu \sim v_{A_1, A_1}^2 \langle E_{A_1}^0 - E_{A_1}^0 \rangle^{-1} + v_{A_1, A_1} v_{A_1, A_1} \langle t_{A_1, A_1}^2 \rangle^{-1} \langle J_{A_1, A_1} \rangle \langle E_{A_1}^0 - E_{A_1}^0 \rangle^{-1} \).

As a test, we apply Eqs. (3) to the frequency dependence of the ac conductivity in polyvinyl alcohol at T = 300K [21]. The Austin-Mott \( \omega^{1.8} \) law [9] does not accurately fit experiments [20]. In Fig 1 we fit the data [25] with the first three terms (a quadratic polynomial of \( \omega \)) in Eq. (4). Because \( \omega_{\text{max}} = 10^9 \text{Hz} << T = 300K \), factors \( e^{\pm \beta \omega} \approx 1 \) do not play a role in the low frequency regime \( \omega \ll k_B T \).

To describe the Hall effect, one needs \( \psi (t) \) to second order of \( J^{\text{field}} \). One \( J^{\text{field}} \) includes electric field \( E_x \), and another includes magnetic field \( B_z \). After substituting \( \psi (0), \psi (1), \psi (2) \) into the second term in Eq. (2), and averaging over various initial conditions, \( \sigma_{yx} \) is determined from \( j_y \), see Eq. (49) in [21]. The primary temperature dependence of \( \sigma_{yx} \) is included in the time integrals which are obtained from integrating out vibrational states. The 3-site processes result to two-fold time integrals [21] which have dimension \([\text{time}]^2\). The time integrals have the same order of magnitude \( s_{A_1 A_1}^2 \), where \( s_{A_1 A_1} \) is the characteristic time for the 3-site processes. Similarly the 4-site processes result to three-fold time integrals [21], the order of magnitude is \( s_{A_1 A_1 A_1}^3 \), where \( s_{A_1 A_1 A_1} \) is the characteristic time for the 3-site processes. \( s_{A_1 A_1} \) (3-site processes) and \( [h^{-1} J_{A_1 A_1 A_1}]^{1/2} \) (4-site processes) may be explained as the mean free times in presence of magnetic field. Applying fields \( E_y \) and \( B_z \), \( \sigma_{yx} \) is inferred from \( j_y \). The order \( J \) contributions from various 4-site processes, their order is \( n_e e^2 \langle h^{-1} J_{A_1 A_1 A_1 A_1} \rangle^{-1} / m \) for \( A_1 A_1 A_1 \), where \( E_{A_1 A_1} = \int d \phi_{A_1} L_{A_1} \phi_{A_1} \), is the matrix element of the \( z \) component of electronic orbital angular momentum.

The widely used 3-site process in the literature [4, 7, 14–16] is a special case when \( A_1 = A_3 \). The order \( J \) contributions comes from 3-site processes. Their order is \( n_e e^2 \langle h^{-1} J_{A_1 A_1 A_1 A_1} \rangle^{-1} / m \). It roughly corresponds to the ‘inefficiency’ contribution (involving two sites) [16]. They are neglected in some other calculations [14, 17]. The ratio of the order \( J \) terms to \( J \) terms is \( \langle h^{-1} J_{A_1 A_1 A_1 A_1} \rangle / \langle h^{-1} J_{A_1 A_1 A_1 A_1} \rangle \sim 1 \).

Amorphous semiconductors are isotropic, so that one may estimate the Hall mobility as: \( \mu = B_z^{-1} \sigma_{xy} / \sigma_{xx} \sim \frac{e}{h} \), where \( \sigma_{A_1 A_1} = i e h \lambda_{A_1} (E_A^0 - E_A^0) \). For a-Si:H [8], \( \xi \) and \( R_{A_1 A_1} \sim 5 \sim 10 \), \( J = 0.02 \), one has \( \mu H \sim 0.1 \sim 0.2 \text{cm}^2 \text{V}^{-1} \text{sec}^{-1} \). The temperature dependence of \( \mu H \) may be obtained from those of \( \sigma_{xy} \) and \( \sigma_{xx} \):

\[ \mu H \sim e^{1 / \hbar T \sigma_{A_1 A_1}(t_{A_1 A_1}^{-1})} \exp \left\{ - \frac{E_{A_1 A_1}^3}{2 k_B T} \frac{3}{2} \right\} \]
R is the distance between two localized states for LL transition. The mean trapping time needed for a transition is determined by the reorganization energy for a localized carrier. The mean trapping time that a carrier spends in a localized state before making a transition to other states is

\[ \mu \sim \frac{\hbar}{m} \frac{d}{k_B T} \left( \Delta \phi \right) \]

where \( q \) is the charge of the carrier. If a system has only localized states, because the mean free time of a carrier is much larger than the effective interaction time with phonons and defects, the drift velocity is along the direction of \( qE \times B \), and the sign of the Hall voltage is normal. Because the force exerted on a carrier by the external \( E \) field is much weaker than the binding force of the disorder potential, the time average of \( m^{-1} \int \phi^*_{A_1} (-i \hbar \nabla_r - qA) \phi_{A_1} \) in a localized state is zero: no magnetic force acts on a localized carrier. The mean trapping time that a carrier spends in a localized state before making a transition to other states is

\[ m^{-1} \int \phi^*_{A_1} (-i \hbar \nabla_r - qA) \phi_{A_1} \sim \hbar J^{-2} (\Delta \phi_T) \]

(high temperature) or

\[ m^{-1} \int \phi^*_{A_1} (-i \hbar \nabla_r - qA) \phi_{A_1} \sim \hbar J^{-2} (\Delta \phi_L) \]

(low temperature), where \( \Delta \phi \) is the typical energy difference between the final and the initial states, and \( \lambda \) is the reorganization energy for a transition. The mean transition time needed for a transition event is

\[ m \frac{dR}{h} \]

where \( d \) is a typical bond length, \( R \) is the distance between two localized states for LL transition, \( R \) is localization length for localized-extended transition. The mean transition time is much shorter than the mean trapping time in a typical localized state. Comparing with the transition speed \( h/(md) \), the speed \( qE/dR/h \) obtained from external electric field \( E \) during the transition time is negligible. The magnetic force suffered by a carrier during a transition is along the direction of \( qV \times B \), where \( V \) is the transition velocity of the carrier. \( V \) does not have any relation to the direction of \( E \). If one applies \( E \) field along the \( x \) axis and \( B \) field along the \( z \) axis, a direction dependent Hall voltage should be detectable along any direction in the \( yz \) plane, not only along the \( y \) axis. Checking this prediction would be a critical test for this work. A recent experiment shows that the signs of Hall voltage in several a-Si:H films are not always reverse to those expected from \( qE \times B \), the present analysis seems to agree with this observation.

We show that localized states are responsible for the anomalous sign of the Hall voltage. The method has the potential to be implemented with current single-particle \( ab \) \( initio \) simulations, and requires only the eigenvalues and eigenvectors of the single-electron Hamiltonian, dynamical matrix, and quantities easily derived from these.

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