Simple Theory for Conductivity and Hall Mobility in Disordered Systems

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This Letter shows how the well-known expressions for conductivity and Hall mobility in crystalline semiconductors can be extended to disordered systems with a simple reinterpretation of the concepts of electronic mass, velocity, and lifetime based on the density matrix approach.

Electronic conduction in crystalline solids is commonly described using the Boltzmann equation. In disordered systems, where the wave number K is often not a good quantum number, I turn to a more fundamental theory with use of the density matrix and the Kubo formalism. The transport properties are then described in terms of electronic transitions between states closely spaced in energy. Depending on the nature of these states and of the transitions, the conduction process is classified into three regimes which we will refer to as the propagating, jumping, and hopping regimes. The *propagating* regime is the familiar one in crystalline solid theory; the electronic states are approximate velocity eigenstates with a mean lifetime determined by phonon and impurity scattering. The *hopping* regime is the other extreme where the electronic states are localized around particular atoms; the electrons can move only through phonon-assisted hopping, so that the conductivity goes to zero as the temperature tends to zero. In between these two is the regime encountered near mobility edges in amorphous solids where the electronic states are extended but there is no phase coherence from one atom to the next. The electron moves between nearest neighbors by quantum-mechanical tunneling depending on the overlap integral between neighboring states. However, because of disorder, alternative tunneling paths have random phases and do not interfere, unlike the propagating regime. On the other hand, the tunneling proceeds without the assistance of phonons and is temperature independent, unlike the hopping regime. To describe this regime, I will use the term *jumping* coined by Cohen.^{1}

The Hall effect in the propagating regime is well understood and is readily described by use of elementary kinetic arguments or the Boltzmann transport theory. In the jumping and hopping regimes, however, the Hall effect is much more complicated. No complete theory has emerged yet though our understanding has been advanced considerably through the works of various authors who have demonstrated that the Hall effect arises from the interference of transition amplitudes via alternative paths.$^{2-6}$

In this Letter I wish to show that with a straightforward and consistent redefinition of the parameters, the well-known expressions for conductivity and Hall mobility in the propagating regime may be applied to the jumping and the hopping regimes as well. The results obtained in this way agree (within a constant) with those derived by other authors using more rigorous arguments. This demonstration is not intended as a substitute for rigorous analysis; rather, the purpose is to point out a simple connection among the three regimes. I believe that such a unifying point of view will prove useful in gaining insights into this difficult problem.

I reproduce below the expressions for the dc conductivity σ_{xx}, the transverse conductivity σ_{xy} in a magnetic field H, the Hall mobility $\mu_{\rm H}$, and the Hall coefficient^7 $R_{\rm H}$:

$$\sigma_{xx} = e^2\langle v_x{}^2\tau\rangle N(E_{\rm F}), \tag{1a}$$

$$\sigma_{xy} = (e^2H/cm^*)\langle v_x{}^2\tau^2\rangle N(E_{\rm F}), \tag{1b}$$

$$\mu_{\rm H} = (c/H)\sigma_{xy}/\sigma_{xx}, \tag{1c}$$

and

$$1/R_{\rm H} = c\sigma_{xx}/\mu_{\rm H}, \tag{1d}$$

where $N(E_{\rm F})$ is the density of states at the Fermi level, v_x is the x-directed velocity of a state at the Fermi level, τ is the lifetime, m^* is the effective mass, and angular brackets denote the average value over the Fermi surface. An appropriate averaging is required when the lifetime τ is not constant.^{8} Equations (1) are true for conduction by electrons near the Fermi level. The results for conduction by electrons activated to a conduction band are obtained by replacing $N(E_{\rm F})$ with $N(E_c)\exp[(E_{\rm F}-E_c)/kT]$, where E_c is the conduction band edge. τ and v_x then refer to states around E_c.

I propose to show that Eqs. (1) may be used in the hopping and jumping regimes as well with an appropriate interpretation of v_x, τ, and m^*. In the next section I will discuss the basis for this interpretation.

Interpretation of v_x, τ, m^* in nonpropagating regimes.—Equations (1a) and (1b) are commonly derived from the Boltzmann equation. I present below a short derivation of Eq. (1a) with use of a density matrix formalism, for it illustrates the basis for the interpretation of v_x and τ in the jumping and hopping regimes.

An electric field E in the x direction produces a perturbation potential eEx. The change in the density matrix is obtained from perturbation theory,

$$\Delta\rho_{\alpha\beta} = eEx_{\alpha\beta}\frac{f(E_\alpha) - f(E_\beta)}{E_\beta - E_\alpha}, \tag{2}$$

where α and β denote two eigenstates of the unperturbed Hamiltonian and $f(E)$ denotes the equilibrium Fermi distribution function. The resulting current J in the x direction is obtained from the current operator

$$\begin{aligned} J &= (e/V)\sum_{\alpha,\beta}(v_x)_{\beta\alpha}\Delta\rho_{\alpha\beta} \\ &= \frac{e^2E}{V}\sum_\alpha\sum_\beta(v_x)_{\beta\alpha}x_{\alpha\beta}\frac{f(E_\alpha) - f(E_\beta)}{E_\beta - E_\alpha}, \end{aligned} \tag{3}$$

where V is the volume and v_x is the x-directed velocity operator.

I may now replace $x_{\alpha\beta}$ in terms of $(v_x)_{\alpha\beta}$ with use of the commutation relation $i\hbar v_x = [H,x]$. This yields

$$x_{\alpha\beta} = \frac{i(v_x)_{\alpha\beta}}{(E_\beta - E_\alpha)/\hbar + i\tau}, \tag{4}$$

where E_β and E_α are the energies of the states α and β, and the finite lifetime (2τ) of the states is treated as an imaginary part of the energy. It is apparent from Eqs. (3) and (4) that only pairs of states close together in energy $(E_\alpha \approx E_\beta)$ contribute to the real part of the conductivity. For such pairs I may set $x_{\alpha\beta} = (v_x)_{\alpha\beta}\tau$ and replace the last term in Eq. (3) by the derivative

$$\sigma_{xx} = (e^2/V)\textstyle\sum_\alpha(-df/dE_\alpha)\sum_\beta|(v_x)_{\alpha\beta}|^2\tau. \tag{5}$$

Equation (5) readily leads to Eq. (1a) if we note that in the propagating regime α and β are approximate velocity eigenstates and that $-df/dE_\alpha$ is a delta function at $E_\alpha = E_{\rm F}$ at low temperatures.

However, Eq. (5) is valid even when α and β are not velocity eigenstates, as in the nonpropagating regimes. To extend Eqs. (1) to these regimes we should use $\sum_\beta|(v_x)_{\alpha\beta}|^2$ in place of v_x^2 where α is a state at the Fermi level and β is any state to which electrons make transitions from α. τ is then the lifetime of the state α, to be determined appropriately for the different regimes.

I now come to the more difficult question of interpreting m^*. In crystalline solid theory the effective mass is commonly defined in terms of the curvature of the E-k plots—a definition which does not extend easily to disordered systems. However, I can define m^* more generally by calculating the expectation value of the x-directed acceleration operator a_x in response to an x-directed electric field E. With use of Eq. (2) for $\Delta\rho_{\alpha\beta}$,

$$\langle a_x\rangle = eE\sum_{\alpha,\beta}(a_x)_{\beta\alpha}x_{\alpha\beta}\frac{f(E_\alpha) - f(E_\beta)}{E_\beta - E_\alpha}. \tag{6}$$

Now, $(v_x)_{\alpha\beta}$ is related to $(a_x)_{\alpha\beta}$ the same way as $(x)_{\alpha\beta}$ is related to $(v_x)_{\alpha\beta}$ [Eq. (4)]; so

$$(a_x)_{\beta\alpha}(x)_{\alpha\beta} = |(v_x)_{\alpha\beta}|^2. \tag{7}$$

One may write Eq. (6) as

$$\langle a_x\rangle = 2eE\sum_\alpha f(E_\alpha)\sum_\beta\frac{|(v_x)_{\alpha\beta}|^2}{E_\beta - E_\alpha}, \tag{8}$$

assuming that $|(v_x)_{\alpha\beta}| = |(v_x)_{\beta\alpha}|$. Equation (8) suggests a definition of m^* for an electron in state α

$$\frac{1}{m^*} = 2\sum_\beta\frac{|(v_x)_{\alpha\beta}|^2}{E_\beta - E_\alpha}. \tag{9}$$

Here the β summation extends over all states to which the electron can make transitions from α.

To illustrate this definition of m^*, let us consider an electron at the bottom of a band in the tight-binding model. I know from the usual crystalline solid theory that

$$1/m^* = 2Ja^2/\hbar^2, \tag{10}$$

where J is the overlap integral between neighboring sites separated by a distance a. We get the same result if we consider the electron as making transitions from a site α to one of the nearest-neighbor sites β. I am assuming that the local site representation is an approximate eigenstate of the Hamiltonian so that Eq. (7) is valid. With use of the relation

$$i\hbar(v_x)_{\alpha\beta} = [H,x]_{\alpha\beta},$$

we have for this case

$$(v_x)_{\alpha\beta} = -iJa/\hbar. \tag{11}$$

Noting that there are two neighboring sites β, one on each side along the x direction, and that $E_\beta - E_\alpha = 2J$, I get Eq. (10) from Eq. (9). I also note that the sign of m^* for a state α as defined by Eq. (9) depends on whether there are more states β available immediately above α or below α. The effective mass is thus negative at the top of the band as in the usual crystalline solid theory.

To summarize, in order to extend the Eqs. (1) for conductivity and Hall mobility of crystalline solids to disordered systems one needs to interpret v_x, τ, and m^* appropriately, based on the density matrix approach. For an electron in a state α I interpret τ as the lifetime of the state, v_x^2 as the sum of the squares of the matrix elements of possible transitions $\sum_\beta |(v_x)_{\alpha\beta}|^2$, and m^* as defined by Eq. (9).

Conductivity and Hall Mobility in nonpropagating regimes.—I will now use this interpretation of τ, v_x, and m^* to calculate the conductivity and Hall mobility in the jumping and the hopping regimes from the familiar equations for the propagating regime [Eq. (1)]. The results are compared with Refs. 3 and 5. In either case I will assume a localized state to be an approximate eigenstate of the Hamiltonian, with a finite lifetime.

(a) Jumping regime: In the random-phase model for this regime the electron is pictured as jumping to nearest neighbors as in the tight-binding model of crystalline solids. The difference, however, is that phase coherence is lost after each jump; the lifetime τ is thus equal to the mean time for each jump. The expressions for m^* and v_x^2 remain the same as in the tight-binding model discussed in the last section:

$$1/m^* = 2Ja^2/\hbar^2 \tag{12a}$$

and

$$\textstyle\sum_\beta |(v_x)_{\alpha\beta}|^2 = 2J^2a^2/\hbar^2. \tag{12b}$$

The lifetime τ is the mean time for each jump, and can be written as

$$\tau \sim \hbar Z a^3 N(E_\mathrm{F}), \tag{12c}$$

where Z is the nearest-neighbor coordination number. This is because the approximate energy separation between nearest-neighbor states is $\sim[Za^3N(E_\mathrm{F})]^{-1}$. If conduction is by electrons activated to a conduction band rather than at the Fermi level, then $N(E_\mathrm{F})$ is replaced by $N(E_c)$. With use of Eq. (1) and (12) we thus have

$$\sigma_{xx} = (2e^2/\hbar) Z a^5 J^2 [N(E_\mathrm{F})]^2, \tag{13a}$$

$$\sigma_{xy} = (4e^2/\hbar)(eH/\hbar c) Z^2 a^{10} J^3 [N(E_\mathrm{F})]^3, \tag{13b}$$

and

$$\mu_\mathrm{H} = 2Z(ea^2/\hbar) a^3 J N(E_\mathrm{F}). \tag{13c}$$

Equation (13a) agrees with Ref. 3 within a factor of $\pi/3$. Equation (13b) also agrees with Ref. 3 except that Z^2 is replaced by $2\pi^2\bar{Z}\eta/3$ where $\bar{Z}$ and η are parameters depending on the nearest-neighbor arrangement. I believe that the differences arise from our approximate evaluation of τ, the mean time for a jump. The term τ^2 in σ_{xy} arises from a three-site jump and is not necessarily the square of the time τ for a two-site jump; a more accurate evaluation would require a consideration of nearest-neighbor configurations.

I also note that, with use of Eq. (1d),

$$1/R_\mathrm{H} = ecJN(E_\mathrm{F}). \tag{13d}$$

For activated electrons in a conduction band I replace the $N(E_\mathrm{F})$ in τ by $N(E_c)$ and the $N(E_\mathrm{F})$ in Eq. (1) by $N(E_c)\exp[(E_\mathrm{F}-E_c)/kT]$. Since the number of electrons in the conduction band is $kTN(E_c)\exp[(E_\mathrm{F}-E_c)/kT]$, it is clear from Eq. (13d) that R_H is changed by a factor kT/J from the free-electron value.

(b) Hopping regime: In this regime the electron makes transitions with the assistance of phonons; the mean time for a single-phonon hopping process is given by[7]

$$1/\tau = \nu_\mathrm{ph}\exp[-2\alpha R - W/kT], \tag{14a}$$

where ν_ph is a characteristic phonon frequency, R is the length of the hop and W is the energy difference between the final and initial states. In the hopping regime the spread in energies between different sites is large enough that the overlap integral cannot carry an electron from one site to another; rather it has to wait for a phonon to produce an energy fluctuation that brings the two energies within an overlap integral of each other. The first term in the exponential [Eq. (14)] comes from the overlap integral and the second is the Boltzmann factor, W being the energy fluctuation required to make the transition possible.

I will now evaluate v_x^2 and m^* for the process. For a hop of length R I have

$$\textstyle\sum_\beta |(v_x)_{\alpha\beta}|^2 \approx 2(R/\tau)^2. \tag{14b}$$

The factor of 2 accounts for the two neighboring sites β, one on each side along the x direction. The energy difference for each hop is twice the overlap integral, so that m^* is given by

$$\frac{1}{m^*} = \frac{2(R/\tau)^2}{J_0 e^{-\alpha R}}, \tag{14c}$$

where $J_0 e^{-\alpha R}$ is the overlap integral.

With use of Eqs. (14) and (1) I have

$$\sigma_{xx} = 2e^2R^2N(E_F)\nu_{ph}\exp[-2\alpha R - W/kT], \qquad (15a)$$

which is the same as the result in Mott and Davis.[9] Similarly for σ_{xy} we have

$$\sigma_{xy} = (e^3H/c)(4/J_0)R^4N(E_F)\nu_{ph}^2 \times \exp[-3\alpha R - 2W/kT]. \qquad (15b)$$

μ_H and R_H may then be obtained with use of Eqs. (1c) and (1d). The second term in the exponent in Eq. (15b) should actually be $4W/3kT$ rather than $2W/kT$. As mentioned previously, the term τ^2 in σ_{xy} is the mean time for a three-site hop; it has been shown[10] that this requires less activation energy than two uncorrelated two-site hops.

Equations (15a) and (15b) may be compared with Ref. 5, noting that the hop length R is given by[4]

$$R = \tfrac{1}{2}\eta N^{-1/3}, \qquad (16)$$

where N is the concentration of sites and η is a numerical factor ≈ 1.8. The exponential dependence of μ_H on R is in agreement with Ref. 5; however, a preexponential factor of $(\alpha N^{-1/3})^{-3}$ is not obtained in this simple analysis. I believe that this factor arises from the averaging over different values of R, which I have neglected here.

The results for multiphonon-assisted hopping are obtained with a slight modification in the expression for τ; ν_{ph} in Eq. (14a) is replaced by $J_0^2/\hbar(WkT)^{1/2}$.[11] The expressions obtained for σ_{xx} and μ_H then agree with those derived in Ref. 5 for the case of strong coupling with phonons.

This Letter shows how the well-known expressions for conductivity and Hall mobility in crystalline semiconductors can be used in disordered systems with a simple and consistent reinterpretation of the concepts of effective electronic mass, velocity, and lifetime based on the density matrix approach.

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