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Electrical conductivity for localized electrons M. Apostol Department of Theoretical Physics, Institute of Atomic Physics, Magurele-Bucharest MG-6, POBox MG-35, Romania email: apoma@theory.nipne.ro

Abstract

It is shown that a random lattice of localized electron states with an inter-site transfer matrix and a random distribution of on-site energies exhibits localized electron states without velocity. Nevertheless, these states may conduct the electrical current through the inter-site transfer matrices. The electrical conductivity is computed under such assumptions.

A random lattice. Let

$$\psi(\mathbf{r}) = \sum_{i} a_{i} \varphi_{i}(\mathbf{r}) \tag{1}$$

be the field operator for electrons localized on sites *i* with wavefunctions $\varphi_i(\mathbf{r})$. The wavefunctions are orthogonal and normalized, the a_i 's are destruction operators and spin is neglected. The hamiltonian is given by

$$H = \sum_{i} E_i a_i^+ a_i + \sum_{ij} V_{ij} a_i^+ a_j \tag{2}$$

where E_i are on-site energies and

$$V_{ij} = \int d\mathbf{r} \cdot \varphi_i^*(\mathbf{r}) (-\hbar^2 \Delta/2m) \varphi_j(\mathbf{r})$$
(3)

are the matrix elements of the kinetic (transfer) part of the hamiltonian ($V_{ii} = 0$). They may also include an external field. We assume that the energies E_i are distributed within some range W around zero. This hamiltonian was introduced by Anderson for localized electron states (or spin diffusion) in certain random lattices under the assumption that E_i are stochastic variables.¹ We show herein that this hypothesis is not necessary for the existence of the localized states, *i.e.* states without velocity. Nevertheless such states exhibit an electrical conductivity under the action of an external electric field. We compute herein such an electrical conductivity.

Electrical current. An external electric field F directed along, say, the z-axis has the effect of changing V_{ij} in equation (3) into $V_{ij} + \varphi_{ij}$ where

$$\varphi_{ij} = -eF \int d\mathbf{r} \cdot \varphi_i^*(\mathbf{r}) z \varphi_j(\mathbf{r})$$
(4)

-e being the electron charge. A constant on-site contribution may also be brought by the electric field, which is not relevant (it amounts to changing the energies E_i by a constant term). We assume

159 (2007)

¹P. W. Anderson, Phys. Rev. **109** 1492 (1958).

therefore $\varphi_{ii} = 0$. It is convenient to represent the matrix elements in (4) as $\varphi_{ij} = -eFas_{ij}$ where a is a mean inter-site distance and s_{ij} is the corresponding (dimensionless) integral. Similarly, the density of electrical current (along the field) is given by

$$j = \frac{e\hbar}{ma^4} \sum_{ij} t_{ij} a_i^+ a_j \tag{5}$$

where

$$t_{ij} = ia \int d\mathbf{r} \cdot \varphi_i^*(\mathbf{r}) (\partial/\partial z) \varphi_j(\mathbf{r})$$
(6)

and $t_{ii} = 0$.

Localized states. First, we solve the Schrödinger equation $(\hbar = 1)$

$$i\dot{a}_i = E_i a_i + \sum_j V_{ij} a_j \tag{7}$$

within the second-order of the perturbation theory with the initial conditions $a_i(0) = A_i = \delta_{i0}$. To this end it is convenient to use the Laplace transform

$$f_i(s) = \int dt \cdot e^{-st} a_i(t) \tag{8}$$

with the inverse

$$a_i(t) = -(i/2\pi) \int_{-i\infty}^{i\infty} ds \cdot e^{st} f_i(s)$$
(9)

where all the singularities are in the lhs of the integration contour. From (7) we get

$$f_{i} = \frac{iA_{i}}{is - E_{i}} + \frac{1}{is - E_{i}} \sum_{j} V_{ij} f_{j}$$
(10)

and, for $A_i = \delta_{i0}$,

$$f_i = \frac{1}{is - E_i} V_{i0} f_0 + \frac{1}{is - E_i} \sum_j \frac{1}{is - E_j} V_{ij} V_{j0} f_0 + \dots, \ i \neq 0$$
(11)

and

$$f_0 = \frac{i}{is - E_0} + \frac{1}{is - E_0} \sum_i \frac{1}{is - E_i} \left| V_{0i}^2 \right| f_0 \dots$$
(12)

From (12) we get

$$f_0 = \frac{i}{is - E_0 - \sum_i |V_{0i}|^2 / (is - E_i)}$$
 (13)

This is a dispersion equation which gives the well-known energy shift

$$E'_{0} = E_{0} + \sum_{i} \frac{|V_{0i}|^{2}}{E_{0} - E_{i}}$$
(14)

within the second-order of the perturbation theory. According to (9) the corresponding amplitude is $a_0 \simeq e^{-iE'_0 t}$..., where second-order terms $\sim e^{-iE_0 t}$ must be included. Similarly, the amplitudes a_i corresponding to equation (11) are

$$a_i \simeq \frac{V_{i0}}{E_i - E_0} \left(e^{-iE_i t} - e^{-iE_0} \right) + \dots , \ i \neq 0$$
(15)

to the lowest order. The localization probability

$$|a_i|^2 \simeq \frac{2|V_{i0}|^2}{(E_i - E_0)^2} \left[1 - \cos(E_i - E_0)t\right]$$
(16)

exhibits quantum beats. One can see that the amplitudes given above represent a localized state. The extent of localization depends on the range of the matrix elements V_{ij} and the order of the perturbation theory. The important thing is that such states do not have a velocity. They are not traveling waves, nor superpositions of travelling waves. In this sense they are localized. This phenomenon originates in the dependence of the energies E_i on the *i*-sites. It is easy to see that the perturbation theory does not apply for a degenerate state $E_i = E$. The wavepackets obtained by Anderson in the limit $s \to 0^2$ are not eigenstates of the hamiltonian (2), and the imaginary part of f_0 (denoted by $1/\tau$ by this author) is a spurios result arising from the $s \to 0$ -limit. The energy shift given by (14) cannot be obtained in the limit $s \to 0$. It is obtained by replacing (approximately) is in $(is - E_i)^{-1}$ in (13) by E_0 (which is different from zero).

Electrical conductivity. We pass now to computing the electrical conductivity. To the first-order of the perturbation theory equations (10) read

$$f_i = \frac{iA_i}{is - E_i} + \frac{1}{is - E_i} \sum_j V_{ij} \frac{iA_j}{is - E_j} + \dots$$
(17)

where the initial conditions A_i are not restricted now to the zeroth site and V_{ij} contain now the matrix elements φ_{ij} according to $V_{ij} \rightarrow V_{ij} + \varphi_{ij}$. The corresponding amplitudes are given by

$$a_{i} = A_{i}e^{-iE_{i}t} + \sum_{j} V_{ij}\frac{A_{j}}{E_{i} - E_{j}} \left(e^{-iE_{i}t} - e^{-iE_{j}t}\right) + \dots$$
(18)

Making use of these amplitudes in (5) we can compute the electrical current within this approximation (lowest-order of the perturbation theory). One can see that the products $A_i^*A_j$ entering the result are proportional to the elements of the density matrix at the initial moment. We assume that the ensemble of electrons are at equilibrium at that moment, so the density matrix is diagonal and $A_i^*A_j = \rho_i \delta_{ij}$. In addition we may take the occupation number ρ_i as given by $\rho_i = ne^{-\beta E_i}$ in the first approximation, where n is the electron density and $\beta = 1/T$ is the inverse of the temperature. With this assumption we get the electrical current

$$j = \frac{e\hbar}{ma^4} \sum_{ij} \left[\rho_j \frac{t_{ij} V_{ji}}{E_i - E_j} \left(e^{i(E_i - E_j)t} - 1 \right) + h.c. \right]$$
(19)

This is an adiabatic current, because the Joule heat, which is a second-order effect, is neglected.³

We average the above current over the oscillations periods, so the oscillating term in (19) disappears. Then, in order to simplify the discussion, we limit ourselves to the nearest neighbours, and put for them $t_{ij} = t$, $V_{ij} = V$ and $\varphi_{ij} = \varphi$ ($s_{ij} = s$ and $\varphi = -eFas$ in equation (4)).⁴ Then, the current becomes

$$j = \frac{2e\hbar}{ma^4} \sum_{\langle ij\rangle} t(V - eFas) \frac{\rho_i}{E_i - E_j}$$
(20)

²P. W. Anderson, *loc. cit.*

³See for instance W. Kohn and J. M. Luttinger, Phys. Rev. **108** 590 (1957).

⁴It is worth noting that t_{ij} must have a real part. If it is purely imaginary (as for instance for bound, localized, atomic orbitals in equation (6)), then the conductivity is vanishing. This requires $\varphi_i(\mathbf{r})$ to be of the form $e^{i\kappa\mathbf{r}}u_i(\mathbf{r})$, with κ real and localized (bound, atomic-like orbitals) $u_i(\mathbf{r})$.

and the electrical conductivity is given by

$$\sigma = -\frac{2e^2\hbar}{ma^3}st\sum_{\langle ij\rangle}\frac{\rho_i}{E_i - E_j}$$
(21)

(from $j = \sigma F$).

First, we note that, according to (20), there exists an electron current even in the absence of the electrical field. This is indeed a natural consequence of our assumption made above for ρ_i , which does not correspond to equilibrium of the ensemble with a non-vanishing transfer matrix V_{ij} . However, we may assume that the transfer matrix V_{ij} is very small, so the electron current is vanishing and the equilibrium is preserved. At the same time we assume that the electric field F is sufficiently strong in comparison with V in order to have an electrical conductivity as that given by (21). The conductivity given by (21) can also be writen as

$$\sigma = -\frac{e^2\hbar}{ma^3} st \sum_{\langle ij \rangle} \frac{\rho_i - \rho_j}{E_i - E_j}$$
(22)

or

$$\sigma = -\frac{2e^2\hbar}{ma^3}st\sum_i \left(\partial\rho_i/\partial E_i\right) \tag{23}$$

if ρ_i does not vary much from site to site. For $\rho_i = ne^{-\beta E_i}$ we get

$$\sigma = \frac{2e^2\hbar}{ma^3} st N_e \beta \tag{24}$$

where N_e is the number of electrons. It is worth noting that it goes like 1/T, which is known as the Bloch law⁵ (the equilibrium electrical conductivity for travelling electron wavepackets goes like $1/T^2$ in the high-temperature limit). In the limit of vanishing temperatures the Fermi-Dirac distribution employed in (23) leads to

$$\sigma = \frac{2e^2\hbar}{ma^3} st N_e / W \tag{25}$$

where W is the width of the uniform energy distribution.

Frequency-dependent conductivity. If the electrical field is of the form $F \sim e^{i\omega t}$ then equation (10) becomes

$$f_i(s) = \frac{iA_i}{is - E_i} + \frac{1}{is - E_i} \sum_j V_{ij} f_j(s) + \frac{1}{is - E_i} \sum_j \varphi_{ij} f_j(s - i\omega) .$$
(26)

This equation can be solved as above within the lowest order of the perturbation theory. Under the same assumptions as those employed before we get the frequency-dependent (ac) conductivity

$$\sigma(\omega) = -\frac{2e^2\hbar}{ma^3} st \sum_{\langle ij\rangle} \frac{\rho_i (E_i - E_j)^2}{(E_i - E_j)^2 - \omega^2}$$
(27)

where the frequency ω is assumed to be much smaller than the frequencies $E_i - E_j$. In the static limit $\sigma(0)$ coincides with the (dc) conductivity given by (21). We can have a representation of the form $\sigma(\omega) = \sigma(0)(1 + \omega^2/\Delta^2)$, where Δ is an energy cutoff such as $\omega \ll \Delta \ll W$. It depends on

⁵F. Bloch, Z. Phys. **59** 208 (1930).

the particular form of the distribution of the energies E_i for an energy scale comparable with ω . This requires additional hypotheses about such a distribution.

Approach to equilibrium. We leave aside the normalization factor and define the density matrix as $\rho_{ij} = a_i^+ a_j$. It satisfies the master equation

$$-i\frac{d}{dt}\rho_{ij} = \omega_{ij}\rho_{ij} + \sum_{k} \left(V_{ik}^*\rho_{kj} - V_{jk}\rho_{ik}\right)$$
(28)

corresponding to the hamiltonian given by (2), where $\omega_i = E_i - E_j$. One can see that ρ_{ij} is not diagonal in general, as for equilibrium. Conversely, if ρ is diagonal (in the energy representation) then it is constant in time and if it is constant in time then it is diagonal.

We solve this equation up to relevant contributions within the second-order of the perturbation theory. To this end, the most convenient way is to compute directly ρ_{ij} . We assume that the interaction is turned on adiabatically from $t = -\infty$ to t = 0, according to an exponential factor $e^{\alpha t}$, $\alpha \to 0$. Equation (10) remains valid, with $A_i = a_i(-\infty)$. It is easy to see that it leads to

$$f_i = \frac{iA_i + \sum_j V_{ij} \left[iA_j / (is - E_j) \right]}{is - E_i - \sum_j |V_{ij}|^2 / (is - E_j)} + O(V^2) .$$
⁽²⁹⁾

We can see that the energy is renormalized according to the well-known energy shift

$$E'_{i} = E_{i} + \sum_{j} \frac{|V_{ij}|^{2}}{\omega_{ij}}$$
(30)

within the second-order of the perturbation theory (see also (14)). Such corrections to the energy levels come from closed-loop (ladder) diagrams which contains products of the form $V_{ij}V_{jk}...V_{li}$. The amplitudes a_i corresponding to (29) are given by

$$a_{i} = A_{i}e^{-iE_{i}'t} + \sum_{j} V_{ij}\frac{A_{j}}{\omega_{ij}} \left(e^{-iE_{i}t} - e^{-iE_{j}t}\right) + O(V^{2}) .$$
(31)

We get the density matrix

$$\rho_{ij} = A_i^* A_j e^{i\omega'_{ij}t} + \sum_k V_{jk} \frac{A_i^* A_k}{\omega_{jk}} \left(e^{i\omega_{ij}t} - e^{i\omega_{ik}t} \right) + \sum_k V_{ik}^* \frac{A_k^* A_j}{\omega_{ik}} \left(e^{i\omega_{ij}t} - e^{i\omega_{kj}t} \right) + O(V^2) .$$

$$(32)$$

At t = 0 the V-terms in (32) are vanishing and we are left with a density matrix corresponding to a free ensemble of electrons with energy levels E'_i . Averaging the oscillating term $\exp(i\omega'_{ij}t)$ in (32) we get a diagonal density matrix constant in time as corresponding to the equilibrium. It is therefore justified to use ρ_i for equilibrium in computing the electrical current.

Let us assume now that we have equilibrium at t = 0, *i.e.* $A_i^* A_j = \rho_i^0 \delta_{ij}$. Then, from (32) we get

$$\rho_{ij} = \rho_i^0 \delta_{ij} - V_{ji} \frac{e^{i\omega_{ij}t} - 1}{\omega_{ij}} (\rho_i^0 - \rho_j^0) .$$
(33)

It is the solution of the equation of motion

$$i\frac{d}{dt}\rho_{ij} = V_{ji}e^{i\omega_{ij}t}(\rho_i^0 - \rho_j^0)$$
(34)

which agrees with (28) within the first-order of the perturbation theory. It is worth noting that the off-diagonal term in (33) is proportional to the corresponding term in the electrical current given by (19).

We average the oscillating terms in (33) and (34) over a time τ much longer than the periods E_i^{-1} according to

$$\left\langle e^{i\omega_{ij}t}\right\rangle = \frac{1}{i\omega_{ij}\tau} \left(e^{i\omega_{ij}\tau} - 1\right)$$
 (35)

Then we average again over τ and get

$$\left\langle e^{i\omega_{ij}t}\right\rangle = -\frac{1}{i\omega_{ij}\tau} \ . \tag{36}$$

Equations (33) and (34) become

$$\rho_{ij} = \rho_i^0 \delta_{ij} + \frac{V_{ji}}{\omega_{ij}} (\rho_i^0 - \rho_j^0)$$
(37)

and respectively

$$\frac{d}{dt}\rho_{ij} = \frac{V_{ji}}{\omega_{ij}\tau}(\rho_i^0 - \rho_j^0) \quad , \tag{38}$$

or

$$\frac{d}{dt}\rho_{ij} = \frac{1}{\tau}(\rho_{ij} - \rho_i^0 \delta_{ij}) .$$
(39)

This equation describes the evolution of the ensemble toward non-equilibrium. Making $t \to -t$ it will describe the approach to equilibrium. The diagonal term reads then

$$\frac{d}{dt}\rho_i = -\frac{1}{\tau}(\rho_i - \rho_i^0) ; \qquad (40)$$

it is the Boltzmann equation with the collisions term in its rhs. The solution is

$$\rho_i - \rho_i^0 = C_i^0 e^{-t/\tau} \tag{41}$$

where C_i^0 is the initial condition at the moment t = 0 of non-equilibrium. For $t \to \infty$ the density matrix approaches the equilibrium value $\rho_i \to \rho_i^0$. Similarly the off-diagonal terms in (39) give

$$\rho_{ij} = C_{ij}^0 e^{-t/\tau} . (42)$$

They are vanishing at equilibrium for $t \to \infty$.

The relaxation time τ remains undetermined. Its minimum value is of the order of E_i^{-1} ; it corresponds to the fluctuations regime.

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