Lagrange multiplier based transport theory for quantum wires

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We discuss how the Lagrange multiplier method of non-equilibrium steady state statistical mechanics can be applied to describe the electronic transport in a quantum wire. We describe the theoretical scheme using tight-binding model. The Hamiltonian of the wire is extended via a Lagrange multiplier to "open" the quantum system and to drive current through it. The diagonalization of the extended Hamiltonian yields the transport properties of wire. We show that the Lagrange multiplier method is equivalent to the Landauer approach within the considered model.

In recent years, several experimental groups have reported the measurements of the transport properties of carbon nanotubes, self-assembled monolavers of conjugated polymers and even individual molecules¹. This development has attracted much attention from theoreticians and most theoretical works reported so far are based on the Landauer type theory². Within the Landauer approach it is assumed that incoming electrons are scattered along the molecular wire and the conductance can be directly evaluated from the scattering T-matrix. The nonequilibrium Green's functions or Lipmann-Schwinger equation approaches have been used to compute T-matrix^{3,4,5}. This extensive calculation work on molecular junctions have provided basic understanding of the physical processes although the aim of the direct reproducing of experimental I-V characteristics is still elusive⁶. This current status of electron transport calculations in molecular wires requires that other, "non-Landauer-type" theoretical descriptions should also be properly explored.

A quantum wire with direct, static current is a nonequilibrium steady state system. This can be understood based upon the following qualitative discussion. Suppose that the left end of the wire works as a equilibrium source of the electrons and the right end works as a drain. The source and drain have different timeindependent chemical potentials ($\mu_s > \mu_d$). The source pumps electrons into the wire trying to establish the equilibrium, but at the same time the drain keeps pulling electrons out of it also trying to equilibrate the wire with itself. The equilibrium is never achieved as long as the chemical potentials μ_s and μ_d are kept fixed or if the current is constrained to be time-independent constant. The system stays in nonequilibrium steady state provided that there is the time-independent current through it.

Having established that a quantum wire with direct current is a steady state nonequilibrium quantum system, we can apply the powerful machinery of modern theoretical methods available in nonequilibrium steady state statistical mechanics to describe it. Recently, there have been considerable advances towards the formal understanding of nonequilibrium steady state open quantum systems on the basis of the Lagrange multiplier based method^{7,8,9,10}. The basic assumption of the Lagrange multiplier based method is that the origin of current is irrelevant to physics of the steady state or in other words that a homogeneous current-carrying state is the same whether it is introduced by the reservoirs, i.e. via boundary conditions, or by a bulk driving field. A nonequilibrium steady state can be produced by the following three-step "algorithm"^{7,10}:

- 1. Define the operator of current J via the continuity equation.
- 2. Extend the Hamiltonian by adding the term $(-\lambda J)$ where λ is a Lagrange multiplier.
- 3. Diagonalize the extended Hamiltonian.

The aim of this paper is to place electronic transport calculations into the general framework of the modern development of nonequilibrium steady state statistical mechanics. We begin with the model tight-binding Hamiltonian for an infinitely long quantum wire

$$H_0 = -t \sum_{n\sigma} (a^{\dagger}_{n+1\sigma} a_{n\sigma} + a^{\dagger}_{n\sigma} a_{n+1\sigma}) , \qquad (1)$$

where t is the hopping matrix element. The operators $a_{n\sigma}^{\dagger}(a_{n\sigma})$ create (annihilate) single electron on the site n, where $\sigma = \pm \frac{1}{2}$ is the spin of the electrons. Being fermionic operators the operators $a_{n\sigma}^{\dagger}(a_{n\sigma})$ obey the standard anticommutation relations:

$$\{a_{n\sigma}, a^{\dagger}_{m\sigma'}\} = \delta_{nm}\delta_{\sigma\sigma'} , \qquad (2)$$

$$\{a_{n\sigma}^{\dagger}, a_{m\sigma'}^{\dagger}\} = \{a_{n\sigma}, a_{m\sigma'}\} = 0.$$
 (3)

The left part of the wire is considered to be source for current and the right end serves as drain. We do not use any assumptions regarding the physical nature of the source/drain we merely assume they exist and are able to maintain a steady, i.e. time-independent, current through the wire.

As the first step, we define the operator of current via the continuity equation. The number of electrons on the site n is given by the expectation value of the operator

$$N_n = \sum_{\sigma} a^{\dagger}_{n\sigma} a_{n\sigma} \ . \tag{4}$$

By making use of Heisenberg representation the continuity equation can be written as the Heisenberg equationof-motion for the operator N_n :

$$\dot{N}_n = i [H_0, N_n]$$
 (5)

Given the standard anticommutation relations between electron creation and annihilation operators, the r.h.s. commutator (5) can be readily computed:

$$\dot{N}_{n} = -it \sum_{\sigma} (a^{\dagger}_{n+1\sigma} a_{n\sigma} - a^{\dagger}_{n\sigma} a_{n+1\sigma}) +it \sum_{\sigma} (a^{\dagger}_{n\sigma} a_{n-1\sigma} - a^{\dagger}_{n-1\sigma} a_{n\sigma}) .$$
(6)

Comparison of eq.(6) with the finite difference expression for continuity equation $\dot{N}_n = -(j_n - j_{n-1})$ yields the definition of the operator of current through the site n:

$$j_n = it \sum_{\sigma} (a_{n+1\sigma}^{\dagger} a_{n\sigma} - a_{n\sigma}^{\dagger} a_{n+1\sigma}) .$$

By making the sum of on-site currents along the wire we obtain the net current through the wire

$$J = it \sum_{n\sigma} (a_{n+1\sigma}^{\dagger} a_{n\sigma} - a_{n\sigma}^{\dagger} a_{n+1\sigma}) .$$
 (7)

The next step in our scheme is to fix the net current via a Lagrange multiplier λ . To this end the Hamiltonian H_0 is modified by adding the term which constraints the macroscopic current J:

$$H = H_0 - \lambda J = -t \sum_{n\sigma} (a^{\dagger}_{n+1\sigma} a_{n\sigma} + a^{\dagger}_{n\sigma} a_{n+1\sigma}) -\lambda it \sum_{n\sigma} (a^{\dagger}_{n+1\sigma} a_{n\sigma} - a^{\dagger}_{n\sigma} a_{n+1\sigma}) .$$

$$\tag{8}$$

The Hamiltonian (8) is hermitian although it is no longer a real operator. The term $(-\lambda J)$ breaks the symmetry between electrons moving along the wire in opposite directions. Now all physical properties of the system including transport characteristics should be obtained from the diagonalization of the Hamiltonian H not H_0 .

The final step is the diagonalization of the extended Hamiltonian. Using the periodic boundary conditions $a_{n\sigma} = a_{n+N\sigma}$ (N -the "length" of the box) the Hamiltonian (8) can be diagonalized via the Fourier transformation

$$a_{n\sigma} = \frac{1}{\sqrt{N}} \sum_{k} \exp(-ikn) a_{k\sigma} , \qquad (9)$$

where the sum over the k runs over the first Brillouin zone $(k = \frac{2\pi}{N}i \text{ with } i = 0, ..., N - 1)$. Furthermore, the operators $a_{k\sigma}^{\dagger}(a_{k\sigma})$ still obey the fermionic anticommutation relations. The transformation (9) brings the Hamiltonian (8) to the diagonal form

$$H = \sum_{k\sigma} E(k) a^{\dagger}_{k\sigma} a_{k\sigma} , \qquad (10)$$



FIG. 1: The current-dependent band energies of the one dimensional conductor for various current densities: solid line - zero current, dashed - 0.025 a.u. and dotted -0.05 a.u.

with the current-dependent dispersion relation for the quasiparticle energy (band energy):

$$E(k) = -2t(\cos(k) + \lambda\sin(k)) . \tag{11}$$

As we let the current tend to zero, i.e. $\lambda \to 0$, we recover the usual result for the band energy $E(k) = -2t\cos(k)$. The dispersion relation (11) is not yet in a form allowing for the energy to be computed as the Lagrange multiplier λ is not known yet. The additional equation for the Lagrangian multiplier λ is obtained if the density of the expectation value of the net current operator (7) over the ground state of the Hamiltonian (8)

$$\frac{1}{N}\langle J\rangle = \frac{4t}{N}\sum_{k}\sin(k)n_k \tag{12}$$

is required to yield the *a priori* known current density *I*. The occupation numbers n_k equals to 1 if the band energy $E(k) \leq 0$ and zero otherwise for half-occupied conductance band, i.e. $n_k = \theta(-E(k))$ where θ is the Heaviside step function.

We finally demonstrate application of the method with numerical and analytical examples. The numerical calculations were carried out for half-occupied conductance band with the box length N = 200. The value of the hopping integral t is chosen to be 2.5 eV which is the standard value for monoatomic metallic wires¹¹. The Lagrange multiplier λ is obtained via the numerical solution of the following nonlinear equation:

$$\frac{4t}{N}\sum_{k}\sin(k)n_{k} = I,$$
(13)

In Fig.1, the current-dependent band energies are shown for three different values of the current density.

$$J_k = \langle a_{k\sigma} J a_{k\sigma}^{\dagger} \rangle = 2t \sin(k). \tag{14}$$

It enables us to distinguish the electronic states by their negative or positive contributions to the net current. From Fig.1 we see that the current re-arranges the band structure in such a way that the part of the band which corresponds to states with positive current $(0 < k < \pi)$ has lower energy than the zero-current band while the energy of states with negative current are increased with respect to the zero-current solution. This selective to current alternation of the band energy splits the occupation numbers of states with positive and negative J_k .

Now we turn our attention towards how the voltage drop can be defined within the Lagrange multiplier based transport theory. For the most regimes observed in molecular wires the electrons are transmitted through the levels in the vicinity of the Fermi-energy E_f . Therefore to associate voltage with current we need to get clear physical picture of Fermi-energy response upon current. In the first Brillouin zone there are always two k which correspond to the Fermi-energy

$$E_f = -2t(\cos(k) + \lambda\sin(k)). \tag{15}$$

First solution of eq.(15), k_+ ($0 < k_+ \leq \pi$), gives a positive contribution to total net current while the second solution, k_- ($\pi < k_- \leq 2\pi$), contributes negatively. By turning off the current (i.e. in the limit of $\lambda = 0$) the energy of of k_+ -state is increased by the value of $(-2t\lambda\sin(k_+))$ while the energy of k_- -state goes down by $(-2t\lambda\sin(k_-))$. In the terminology of the Landauer theory for reflectionless contact¹², the energies of states originating from the source, i.e. k_+ states, are effectively decreased by voltage while the energies of states occupied by electrons from the drain, i.e. k_- states, are increased by voltage. Given that the voltage does the same job as the term $(-2t\lambda\sin(k_-))$ we arrive to the following equations:

$$E_f = -2t\cos(k_{\pm}) - 2t\lambda\sin(k_{\pm}))$$

$$\equiv -2t\cos(k_{\pm}) \mp \frac{1}{2}U,$$
 (16)

where U denotes the voltage drop. Eq.(15) yields the following expression for the voltage U:

$$U = 2t\lambda(\sin(k_+) - \sin(k_-)) \tag{17}$$

The voltage produces splitting (as in standard Landauer theory) the Fermi-Dirac occupation numbers of the the states with positive and negative J_k . The Fermi-Dirac occupation numbers are given in Fig.2 for two different values of the currents: I = 0.01 a.u. (the lower panel) and I = 0.025 a.u. (the upper panel). The Heaviside step function is smeared out as the corresponding Fermi-Dirac function taken at temperature T = 0.3 eV. The values of



FIG. 2: The Fermi-Dirac occupation numbers of current carrying states. The solid line is for the states with positive contribution to the net current $(J_k > 0)$. The dashed line is for the occupation probabilities of the states with negative J_k . $E_0(k) = -2t\cos(k)$ is the band energy of the zero-current wire.

the voltage computed by the formula (17) are also plotted on Fig.2. We would like to emphasize that the definition of voltage described above is applicable directly only if current J is an integral of motion for the Hamiltonian H_0 , i.e. $[H_0, J] = 0$. The commutator $[H_0, J]$ does not necessarily vanish exactly in general case and the occupation numbers of "upstream" and "downstream" electrons are tangled because the eigenstates of the extended Hamiltonian H are no longer uniquely characterized by value of the current in these states. Therefore it might be practically cumbersome to extract the voltage for a real molecular wire by looking at the populations of states carrying currents in the different directions. The rigorous definition of the applied voltage is generally a very controversial issue if one does not invoke to noninteracting electron reservoirs to represent boundary conditions and similar problems are encountered in ref.¹³. One can always resort to the exact definition of the voltage based upon the following physical picture: a voltmeter determines the voltage drop along the wire by measuring the work required to move a point unit charge from one side of the wire to the other. This brute force algorithm of calculating the work done on a test point charge can be always applied although it is not computationally the most tractable scheme. The evaluation of the different voltage definitions for the correlated electrons will be discussed elsewhere.

To demonstrate a compatibility with the Landauer

approach we re-derive the Landauer expression for the conductivity² using our formulae for the net current (12) and our definition of the voltage 17. Sum (12) can be replaced by the integral provided that for large N the spectrum E(k) can be considered as a quasi-continuum:

$$I = \frac{2t}{\pi} \int_{0}^{2\pi} dk \sin(k) n_k$$

= $\frac{2t}{\pi} \int_{0}^{\pi} dk \sin(k) (n_k - n_{k+\pi}).$ (18)

Assuming the small current, i.e. small λ , and by making use of the Taylor expansion the following expression for the occupation numbers difference can be found

$$n_k - n_{k+\pi} = \theta(\cos(k)) - \theta(\cos(k+\pi)) + 2\lambda \sin(k)\delta(\cos(k)).$$

Only the δ -function term gives a non-vanishing contribution to the integral (18) and the direct integration results into the following simple expression for the current density:

$$I = \frac{4t\lambda}{\pi} , \qquad (19)$$

To compute voltage by the formula (17) k_+ and k_- should be determined. For half-occupied band $E_f = 0$ and the eq.(15) can be straightforwardly resolved:

$$k_{+} = \pi - \arctan(\frac{1}{\lambda})$$
 $k_{-} = 2\pi - \arctan(\frac{1}{\lambda})$ (20)

Then eq.(17) yields the voltage

$$U = \frac{4t\lambda}{\sqrt{\lambda^2 + 1}} = 4t\lambda + O(\lambda^2) \tag{21}$$

Assuming again that the current is small and substituting the expressions for current (19) and voltage (21) into the definition of conductance G = I/U we obtain:

$$G = \frac{1}{\pi} , \qquad (22)$$

which is the Landauer value of G for a single transport channel of an ideal one-dimensional lead¹². Re-deriving the standard result we demonstrate that our method is equivalent to the Landauer approach within the considered model. It should be noted, however, that there is no guarantee that this formalism will exactly reproduce the Landauer results in more complicated cases.

Finally, we discuss how the Lagrange multiplier based transport theory can be applied to a molecular wire with inhomogeneous electron density. To describe this realistic scenario we specify the constraint on the current density distribution in the following form (constrained continuity equation):

$$\int dy \, dz \, j_x(\mathbf{r}) = I, \qquad (23)$$

where I is a desired value of the current through the wire. Within this description, net current flow is aligned along the x-axis and the net current flow across a cross section $\int dy dz j_x(\mathbf{r})$ is constrained, and this quantity is readily available experimentally. It leads to the following extended Hamiltonian:

$$H = H_0 - \int dx \lambda(x) \int \int dy \, dz \, j_x(\mathbf{r}), \qquad (24)$$

where $\lambda(x)$ is the pointwise Lagrange multiplier in the additional space- and current-dependent term. An inhomogeneous interacting electron gas has been considered based upon a variational analog of the Lagrange multiplier based transport theory and within the density functional theory one generally needs to solve the set of integral self-consistent equations for the pointwise Lagrange multiplier $\lambda(x)$ and the current-carrying Kohn-Sham orbitals¹⁵.

The final comment regarding the general applicability of the method is in due order. The common characteristic feature of all nonequilibrium steady state systems is the constant flux of a certain physical quantity, e.g. heat conduction (energy current), diffusion (particle current), electrical conductivity (charge current). We have discussed the scheme on an example of tight-binding Hamiltonian but it can be extended with a slight modification to any open steady state quantum system, e.g. the Ising model with the energy flux⁹. Constant current Hartree-Fock and Kohn-Sham approximations have also been recently formulated within the approach^{14,15}.

In this paper, we have given the Lagrange multiplier based formulation of electronic transport problem. We discussed the three-step practical algorithm to produce current carrying steady states in quantum wires. First, we defined the operator of macroscopic current via continuity equation. Next, tight-binding Hamiltonian was modified by the Lagrange multiplier term to account for the steady current. Then, the current-dependent bandenergies and the occupation numbers were obtained by the diagonalization of the extended Hamiltonian. The definition of the applied voltage which is compatible with the Landauer description was discussed. A sample calculation on an albeit simple model system produced exact agreement with results obtained from the Landauer theory. While the one-dimensional tight-binding model avoids a number of computational difficulties in using this approach, it shows how a Lagrange multiplier can be applied to describe electronic transport properties of quantum wires.

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