Many-Electron Systems with Constrained Current

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Abstract

A formulation for transport in an inhomogeneous, interacting electron gas is described. Electronic current is induced by a constraint condition imposed as a vector Lagrange multiplier. Constrained minimization of the total energy functional on the manifold of an arbitrary constant current leads to a many-electron Schrödinger equation with a complex, momentum-dependent potential. Constant current Hartree-Fock and Kohn-Sham approximations are formulated within the method and application to transport for quantum wires is developed. No appeal is made to near equilibrium conditions or other approximations allowing development of a general ab initio electronic transport formulation.

In recent years, there has been considerable advances towards the development of accurate theoretical models to deal with electron transport through atomic and molecular wires \cite{1}. This activity has been largely spurred on by development of experimental techniques to form atomic scale electrical contacts such as scanning tunneling microscopy \cite{2} and mechanically controllable break junctions \cite{3}. Measurement of current-voltage characteristics have been recently performed on a single benzene-1,4-dithiolate molecule \cite{4}, buckminsterfullerene \cite{5}, individual atoms \cite{6}, and DNA strands \cite{7}. The mechanisms for charge transport through these low-dimensional structures remain largely unexplored and unexplained. Several approaches have been developed on the basis of the extended Hückel \cite{8} and density functional theory within a Lippmann-Schwinger formalism \cite{9} or nonequilibrium Green’s functions \cite{10}. In these approaches, the system is partitioned into three parts: molecular device (or wire) and two electron reservoirs.

The interaction between contacts and wire represents the kernel for the Lippmann-Schwinger equation, and serves generally to define the non-interacting system for Green’s function approaches. Recent studies indicate the exact nature of the molecule-contact bonding are critical in predicting the correct order of magnitude for the currents with applied bias revealing that accurate electronic structure methods must be incorporated into quantum transport methods for accurate predictions and analysis of current-voltage relationships.

In this letter, we present a variational approach to charge transport in correlated electron systems. We begin by introducing a many-electron Schrödinger equation which provides exact wavefunctions on the manifold of a given current distribution. The many-electron Schrödinger equation is developed without any restrictions to the treatment of electron-electron correlations, whether as injected current or part of the molecular device. We next present specific approximations corresponding to the Hartree-Fock and configuration interaction treatments of
the many-electron problem. Next, the Kohn-Sham approximation to density functional theory is extended to the inhomogeneous electron gas with a fixed current at zero external magnetic field.

We begin by developing a general many-body theory for an inhomogeneous electron gas with arbitrary and static current density. For an inhomogeneous, interacting \( N \)-electron gas in an external potential \( v(\mathbf{r}) \), the ground state energy is given by the following energy functional (atomic units are employed throughout the paper unless otherwise mentioned):

\[
E[\rho, \Gamma] = \langle \Psi | H | \Psi \rangle = \int h_0(\mathbf{r}) \rho(\mathbf{r}, \mathbf{r}') \, d\mathbf{r} + \frac{1}{2} \int \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \Gamma(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2) \, d\mathbf{r}_1 \, d\mathbf{r}_2
\]  
(1)

where \( h_0(\mathbf{r}) \) is the one-body electron operator which includes the electronic kinetic energy and the one-body electron interactions with external potentials. We have introduced the one- and two-electron reduced density matrices:

\[
\rho(\mathbf{r}; \mathbf{r}') = N \int \Psi(\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_N) \Psi^*(\mathbf{r}', \mathbf{r}_2, \ldots, \mathbf{r}_N) \prod_{i=2}^N d\mathbf{r}_i
\]  
(2)

\[
\Gamma(\mathbf{r}, \mathbf{r}'; \mathbf{r}, \mathbf{r}') = N(N-1) \int \Psi(\mathbf{r}, \mathbf{r}', \ldots, \mathbf{r}_N) \Psi^*(\mathbf{r}, \mathbf{r}', \ldots, \mathbf{r}_N) \prod_{i=3}^N d\mathbf{r}_i,
\]  
(3)

where \( \Psi \) is the many-electron wave-function.

The fundamental quantity in our approach is the electron current density

\[
\mathbf{j}(\mathbf{r}) = \frac{1}{2i} \left[ \nabla_{\mathbf{r}} - \nabla_{\mathbf{r}'} \right] \rho(\mathbf{r}, \mathbf{r}')|_{\mathbf{r}=\mathbf{r}'}.
\]  
(4)

The current density is constrained to have specified values at prescribed points in position space, or more generally a functional \( G[\mathbf{j}](\mathbf{r}) \) is required to be zero at defined positions \( \mathbf{r} \). The task is to minimize the energy functional \( E[\rho, \Gamma] \) subject to the constraint \( G[\mathbf{j}](\mathbf{r}) = 0 \). Altho\( ugh \) the constraint formulated in this manner is nonholonomic, it may be included into a variational functional via pointwise vector Lagrange multipliers \( \mathbf{a}(\mathbf{r}) \). The constraint is explicitly achieved by introduction of an auxiliary functional

\[
\Omega[\rho, \Gamma, \mathbf{j}, \mathbf{a}] = E[\rho, \Gamma] - \mu \left( \int d\mathbf{r} \rho(\mathbf{r}) - N \right) + \Lambda[\mathbf{j}, \mathbf{a}]
\]  
(5)

The first two terms are standard in the variational formulation of quantum many-body theory with the first giving the total energy and the second is introduced to constrain particle number (or likewise, to introduce the orthonormality constraint for the wavefunction). The third term has been introduced to impose the current constraint. The functional \( \Lambda[\mathbf{j}, \mathbf{a}] \) depends linearly on \( \mathbf{a}(\mathbf{r}) \) and is designed to insure the following condition is maintained:

\[
\frac{\delta \Lambda[\mathbf{j}, \mathbf{a}]}{\delta \mathbf{a}(\mathbf{r})} = G[\mathbf{j}](\mathbf{r}).
\]  
(6)

Variation of \( \Omega[\rho, \Gamma, \mathbf{j}, \mathbf{a}] \) with respect to the Lagrange multiplier \( \mathbf{a} \) provides an additional constraint equation. One can view the \( \mathbf{a}(\mathbf{r}) \) as an infinite set of Lagrange multipliers, each associated with \( G[\mathbf{j}](\mathbf{r}) = 0 \) at a point \( \mathbf{r} \). The variation of \( \Lambda[\mathbf{j}, \mathbf{a}] \) over the current density \( \mathbf{j}(\mathbf{r}) \) yields a vector field:

\[
\mathbf{A}(\mathbf{r}) = \frac{\delta \Lambda[\mathbf{j}, \mathbf{a}]}{\delta \mathbf{j}(\mathbf{r})}.
\]  
(7)
Extrema of the auxiliary functional $\Omega[\rho, \Gamma, \mathbf{j}, \mathbf{a}]$ corresponds to the following many-electron Schrödinger equation

$$
\left( \sum_j \left\{ h_0(r_j) + \frac{1}{2i} [\nabla_j, \mathbf{A}(r_j)]_+ \right\} + \sum_{i<j} \frac{1}{|r_i - r_j|} \right) \Psi = E \Psi \quad \text{(8)}
$$

where we have defined the energy $E = N\mu$. The anti-commutator term,

$$
[\nabla, \mathbf{A}(r)]_+ = \nabla \mathbf{A}(r) + 2\mathbf{A}(r)\nabla,
$$

(9)
gives rise to an additional single-electron imaginary potential arising directly from the constraint on the current density. This additional constraint potential forces the many-electron wave function $\Psi$ to be irremovably complex and enforces the required current density distribution at extrema.

A physical interpretation of the vector field $\mathbf{A}(r)$ follows if we re-write the eq.(8) in the following form

$$
\left( \sum_j \left\{ \frac{1}{2} (-i\nabla_j + \mathbf{A}(r_j))^2 - \frac{1}{2} \mathbf{A}(r_j)\mathbf{A}(r_j) + v(r_j) \right\} + \sum_{i<j} \frac{1}{|r_i - r_j|} \right) \Psi = E \Psi. \quad \text{(10)}
$$

The current constraint has introduced terms equivalent to a vector potential of an external magnetic field $[\mathbf{A}]$, however, the vector field is a functional of the $\Psi$ and has to be determined self-consistently from the Eq.10 in our case.

The constrained many-electron Schrödinger equation is not yet in a form allowing for a solution to be found as the the Lagrange multiplier $\mathbf{a}(r)$ and the vector field $\mathbf{A}(r)$, which is a functional of $\mathbf{a}(r)$, for a specified current are not given. An expression for $\mathbf{a}(r)$ can not be found until an explicit form of constraint functional $\Lambda[j, \mathbf{a}]$ is first introduced. The motivation for the present study is to desire to develop the basic many-body formalism for the calculation of a direct current $I$ through a quantum wire. To achieve this aim, we specify the constraint on the current density distribution in the following form:

$$
\int dy dz j_x(r) = I_x \quad \text{(11)}
$$

Within this description, net current flow is aligned along the $x-$axis. This is a simple geometric arrangement to specify current flow for quantum wire and can be easily extended to more complex topologies. For the case specified, the functional $\Lambda[j, \mathbf{a}]$ takes the following form:

$$
\Lambda[j, \mathbf{a}] = \int dx a_x(x) \left( \int dy dz j_x(r) - I_x \right) \quad \text{(12)}
$$

The vector field induced by the presence of the constraint on the current density has spatial dependence and nonzero projection only along the $x$-axis:

$$
\mathbf{A}(r) = \frac{\delta \Lambda[j, \mathbf{a}]}{\delta j(r)} = (a_x(x), 0, 0) \quad \text{(13)}
$$

Therefore, for a quantum wire with a direct current the vector field $\mathbf{A}(r)$ coincides with the vector Lagrange multiplier $\mathbf{a}(r)$. Generally, if the constraint functional $\Lambda[j, \mathbf{a}]$ is a linear functional of $j(r)$, then the vector field $\mathbf{A}(r)$ and the Lagrange multiplier at each point $r$ are equivalent.
We next solve for the Lagrange multiplier $a_x(x)$ and obtain

$$a_x(x) = \frac{1}{2I_x} \left\{ \int dydz \int \prod_{i=2}^N dr_i \left[ \Psi^*H\Psi + \Psi H\Psi^* \right] - 2\mu \rho_x(x) \right\}, \quad (14)$$

where we have introduced the quantity

$$\rho_x(x) = \int dydz \rho(r). \quad (15)$$

Suppose now that the many-electron wave-function $\Psi$ is approximated as Slater determinant of $N$ orthonormal single-electron orbitals $\psi_i(r)$. The use of the Slater determinant enables us to write the electron current density $(4)$ as the sum of electron current through all occupied orbitals

$$j(r) = \frac{1}{2i} \sum_{i,occ} (\psi_i^*(r) \nabla \psi_i(r) - \psi_i(r) \nabla \psi_i^*(r)) \quad (16)$$

Likewise, as for the derivation of the exact many-electron Schrödinger equation, the current distribution is fixed via $G[j](r) = 0$. The constraint is included into Hartree-Fock minimization via an additional Lagrange multiplier $\Lambda[j,a] = \Lambda[\psi,\psi^*,a]$:

$$\Omega[\psi,\psi^*,a] = E[\psi,\psi^*] + \Lambda[\psi,\psi^*,a] \quad (17)$$

Minimization of eq. $(17)$ subject to the orthogonalization condition $\int dr \psi_i^*(r) \psi_j(r) = \delta_{ij}$ results in a Hartree-Fock equations with fixed current density distribution

$$\left( \hat{H}_{HF} + \frac{1}{2i} \left[ \nabla, A(r) \right]_+ \right) \psi_i(r) = E_i \psi_i(r), \quad (18)$$

where $\hat{H}_{HF}$ is the Hartree-Fock operator which contains the electron kinetic energy, external potential, Hartree potential and Fock exchange operator, $A$ is again an additional vector field induced by the current constraint. The configuration interaction (CI) representation follows directly if we substitute for the many electron wave function $\Psi$ a linear superposition of Slater determinants or spin coupled determinants. The CI expansion is substituted into eq. $(8)$ and variation with respect to the expansion coefficients yields a modified matrix eigenvalue problem, whereby the interaction matrix elements are supplanted with the additional one-body potential terms arising from the constraint potential $\frac{1}{2i} \left[ \nabla, A(r) \right]_+.$

We next turn to the task of incorporating the current constraint into the density functional theory (DFT) $(12)$. We describe an extension of the Kohn-Sham formulation of DFT $(13)$ to systems with a non-zero current density distribution. For an inhomogeneous, interacting electron gas in external potential $v(r)$, the ground state energy is given by the Hohenberg-Kohn energy functional $(12)$:

$$E_{HK}[\rho] = T_0[\rho] + \int dr v(r)\rho(r) + \frac{1}{2} \int \int \frac{\rho(r)\rho(r')}{|r-r'|} + E_{xc}[\rho] \quad (19)$$

The first term, $T_0$, is the kinetic energy functional of $N$ noninteracting electrons with given density and current density distribution. The second and third terms, are the interaction energy with external potential and the electrostatic interactions. The last term, $E_{xc}[\rho]$, is the exchange and correlation energy functional.
We follow closely to the derivation of the many-electron Schrödinger equation described in the beginning of this letter. The distribution for the current density vector is fixed through a functional $G[j](\mathbf{r}) = 0$ at certain points $\mathbf{r}$. The constraint is included into DFT variational determination of the charge density via a Lagrange multiplier $a(\mathbf{r})$:

$$
\Omega[\rho, j, a] = E_{HK}[\rho] - \mu \left( \int d\mathbf{r} \rho(\mathbf{r}) - N \right) + \Lambda[j, a]
$$

(20)

Following the Kohn and Sham approach [13], we introduce a reference fermion system with orthonormal single-particle orbitals $\psi_i(\mathbf{r})$ and occupation numbers $n_i$ to reproduce the charge and current densities:

$$
\rho(\mathbf{r}) = \sum_i n_i \psi_i^*(\mathbf{r}) \psi_i(\mathbf{r})
$$

(21)

$$
\mathbf{j}(\mathbf{r}) = \frac{1}{2} \sum_i n_i (\psi_i^*(\mathbf{r}) \nabla \psi_i(\mathbf{r}) - \psi_i(\mathbf{r}) \nabla \psi_i^*(\mathbf{r}))
$$

(22)

In analogy to the Kohn-Sham approach, we consider variation of the auxiliary functional $\Omega[\rho, j, a]$ eq. (20) with respect to the single-electron orbitals $\psi_i(\mathbf{r})$ to obtain the following single-electron self-consistent equations:

$$
\left[ \frac{1}{2} (-i \nabla + A(\mathbf{r}))^2 - \frac{1}{2} A(\mathbf{r}) A(\mathbf{r}) + v(\mathbf{r}) + \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \mu_{xc}[\rho](\mathbf{r}) \right] \psi_i(\mathbf{r}) = E_i \psi_i(\mathbf{r}),
$$

(23)

the desired result.

In order to get an indication of how our approach works, we solve the Kohn-Sham equation with fixed current (23) for the case of a uniform electron gas. Consider an electron gas in a cubical box of volume $V = L^3$, throughout which a background positive charge is uniformly spread out rendering the system neutral (jellium model). A direct current is applied along the x-axis $\mathbf{I} = (I_x, 0, 0)$. The classical Coulomb electron-electron interaction, the Hartree term, is completely compensated by the electron interaction with positive charge density and by the electrostatic energy of the positive background. The vector field is constant for the translationally invariant uniform electron gas yielding the following Kohn-Sham equation for the model:

$$
\left( -\frac{1}{2} \Delta + \mu_{xc} + i A(\mathbf{r}) \nabla \right) \psi_k(\mathbf{r}) = E_k \psi_k(\mathbf{r})
$$

(24)

with specification of the constraint taken in the form given by eq.(11). A dispersion relation which is coupled to the constraint equation for the current density may be obtained by inserting a plane-wave solution $\psi_k(\mathbf{r}) = \frac{1}{\sqrt{V}} \exp(i k \mathbf{r})$ into eq2.(24, 11), with the result

$$
E_k = \frac{k^2}{2} + \mu_{xc} + A_x k_x
$$

(25)

$$
\frac{1}{L} \sum_{k_x} k_x = I_x
$$

(26)

From the system of equations eqs.(25-26) the exact expression for the vector field $A$ can be deduced:

$$
A = -\frac{I_x}{\rho},
$$

(27)
with electron density $\rho = N/L$. Given the vector field, we can write the current density dependent dispersion relation of the uniform electron gas with applied direct current $I_x$:

$$E_k = \frac{k^2}{2} + \mu_{xc} - \frac{I_x}{\rho} k_x$$

(28)

The presence of the constrained current lifts the degeneracy of the $k$ and $-k$ states and results in the energy gap between the electron moving in the direction of net current flow, i.e. with positive $k_x$, and electrons moving in the opposite direction.

We finally demonstrate application of the method with a simple numerical example. We consider a one-dimensional system with current injection into a fixed, external potential. Trial states are taken to be pure plane wave states and these states are then allowed to relax to account for the presence of an external potential, taken to be a simple Gaussian form. In fig. 1, the solutions to the Schrödinger equation are shown with the current fixed by the constraint potential, i.e. no boundary conditions are imposed other than through the constraint condition. Within the figure, the changes in real and imaginary components of the wave function relative to a pure plane wave state are plotted. The constraint re-arranges the solution to the Schrödinger equation allowing for the changes due to the current encountering the external potential, while maintaining a constant current fixed at the value specified by the constraint condition.

In this letter, we have given a variational formulation of quantum electronic transport. There is no resort to any imposed conditions other than to constrain the current distribution. Thus the formulation is equally valid for highly correlated systems and for all nonequilibrium current regimes. The formulation has been specified for general many-body theory and cast into a form suitable for the Hartree-Fock and configuration interaction methods. We next showed how to introduce the constraints into density functional theory. The method as such is quite general and applicable to all common approaches to electronic structure theory.

For the case of one-dimensional transport in a two-terminal system, we have introduced a physical constraint which allows for an explicit determination of the Lagrange multipliers required to fix the current flow. With the Lagrange multipliers in hand, it is possible to determine the complex potential needed for solution of the many-body wavefunction, or electronic density, satisfying the physical boundary conditions introduced by a constant current flow in and out of a region. The formulation of the problem has been chosen for greatest compatibility with the methods in common use for electronic structure theory determination, and results in a completely variational formulation of the quantum electronic transport problem.

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Figure caption

Figure 1- Wave function shifts from an attractive Gaussian potential $V_{ext} = V_0 \exp(-(x-\mu)^2/\sigma^2)$ are shown as the difference in the wavefunction $\Psi = \phi + i\xi$ relative to a plane wave state $\Psi_0$ in box normalized units. All other quantities expressed in atomic units. Incident energy is $E = 2.0$ a.u., well depth $V_0 = -0.1$ a.u., well breadth $\sigma = 0.04\pi$. Shift in the real component $\phi - \phi_0$ are displayed with the heavy lines, shift in the imaginary component $\xi - \xi_0$ are displayed with the lighter lines.
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