Nonlinear electronic transport in nanoscopic devices: Nonequilibrium Green’s functions versus scattering approach

A. R. Hernández$^{1,2}$ and C. H. Lewenkopf$^3$

$^1$Laboratório Nacional de Luz Síncrotron, Caixa Postal 6192, 13083-970 Campinas, Brazil
$^2$Centro Brasileiro de Pesquisas Físicas, R. Dr. Xavier Sigaud 150, 22290-180 Rio de Janeiro, Brazil
$^3$Departamento de Física Teórica, Universidade do Estado do Rio de Janeiro, 20550-900 Rio de Janeiro, Brazil

(Dated: July 13, 2009)

We study the nonlinear elastic quantum electronic transport properties of nanoscopic devices using the Nonequilibrium Green’s function (NEGF) method. The Green’s function method allows us to expand the $I − V$ characteristics of a given device to arbitrary powers of the applied voltages. By doing so, we are able to relate the NEGF method to the scattering approach, showing their similarities and differences and calculate the conductance coefficients to arbitrary order. We demonstrate that the electronic current given by NEGF is gauge invariant to all orders in powers of $V$, and discuss the requirements for gauge invariance in the standard Density Functional Theory (DFT) implementations in molecular electronics. We also analyze the symmetries of the nonlinear conductance coefficients with respect to a magnetic field inversion and the violation of the Onsager reciprocity relations with increasing source-drain bias.

PACS numbers: 72.10.-d,73.23.-b,73.63.-b,85.65.+h

I. INTRODUCTION

There is a growing experimental and theoretical interest in quantum nonlinear electronic transport properties of nanoscopic devices. Experiments in mesoscopic semiconductors, such as quantum dots, quantum rings, and quantum wires, have focused on the investigation of rectification effects and violations of the Onsager-Casimir reciprocity relations. Similar issues have also been examined in the electronic transport through carbon nanotubes where considerable experimental effort has been put in showing that single molecules can be used as diodes, transistors, and switches.

The development of a comprehensive quantum nonlinear electronic transport theory, a non-equilibrium quantum many-electron problem, is still quite a challenge. Notwithstandingly, significant advances have been already achieved, particularly by restricting the theoretical analysis to elastic processes. Within this approximation, theoretical progress has mainly been achieved by pursuing two apparently very different paths, namely, the scattering approach put forward by Büttiker and collaborators and the nonequilibrium Green’s function method.

In both approaches the current-voltage $I − V$ characteristics is written in terms of transmission coefficients that account for the potential landscape built in the devices due to the applied bias. The scattering approach casts the current as a power series of the bias. The $S$-matrix serves not only to compute the transmission, like in the Landauer formula, but also to calculate the electrostatic potential built in the conductor by means of physical considerations. Those guarantee that the electrostatic potential is gauge invariant order by order in powers of $V$. Alternatively, NEGF has been used to investigate the linear and non-linear transport properties of mesoscopic and molecular systems. Here, the current and the electrostatic potential are calculated self-consistently to all orders at once. The formalism is quite powerful and robust but, as it is often the case in self-consistent calculations, different physical processes become inextricable making difficult to understand their role and importance for the electronic transport.

These considerations raise a natural question: To what extent are these approaches similar? One of the main purposes of this paper is to answer this question and explicitly show that both approaches are, in principle, equivalent. Furthermore, we show that differences appear depending on how the underlying many-body electronic problem is approximated.

To this end we use NEGF to write the current flowing through a multi-lead elastic conductor as a power series of the bias $V$, as done in Ref. 13. Treating the many-electron problem in the Hartree approximation we explicitly show that, in the Thomas-Fermi limit, the leading nonlinear correction in the $I − V$ characteristics reduces, almost exactly, to the scattering approach result. We discuss gauge invariance and the Onsager-Casimir reciprocity relations. At every step, we also analyze these symmetries beyond the Hartree term by addressing the standard Density Functional Theory (DFT) implementation for molecular electronics. We stress that, in contrast to the scattering approach, the NEGF formalism is not restricted to a local approximation. The many-body nature of NEGF allows one to extend its standard implementation in a variety of ways. To show this, we address the case where the many-body problem is treated in the Hartree-Fock approximation.

The presentation of the paper is organized as follows: In Sec.$^{1}$ we present the scattering approach highlighting its main elements and results for later comparison with the NEGF approach. In Sec.$^{11}$ we present the model Hamiltonian considered in this study. In Sec.$^{14}$
we calculate the transmission coefficients and the electrostatic potential using nonequilibrium Green’s functions. By these means, it is possible to systematically calculate the conductance coefficients and the characteristic potentials self-consistently to all orders in $V$, as discussed in Sec. [V]. The similarities between both approaches are discussed in Sec. [VI], where we also show how differences appear. The NEGF implementation of the Hartree-Fock approximation is described in Sec. [VII]. Finally, our conclusions are presented in Sec. [VIII].

II. THE SCATTERING APPROACH

Let us consider a conductor connected by leads to $\alpha = 1, \ldots, N$ electronic reservoirs at a temperature $T$. In the absence of an applied bias, the system is in thermal and chemical equilibrium, characterized by a chemical potential $\mu_0$. By applying voltages $\{V_\alpha\}$ to the reservoirs, the system is driven out of equilibrium and an electronic current flows.

According to B"uttiker, in the absence of inelastic processes, the current at the lead $\alpha$ is given by

$$I_\alpha = \frac{2e}{h} \sum_{\beta=1}^{N} \int_{-\infty}^{\infty} dE \, f_\beta(E) \, A_{\alpha\beta}(E, U(r)).$$

Here $f_\beta(E) = f_0(E-eV_\beta)$, where $f_0(E) = (e^{E/k_B T}+1)^{-1}$ is the Fermi distribution function and $k_B$ is the Boltzmann constant. For notational convenience, we consider $V_\beta$ as measured with respect to the equilibrium potential $\mu_0$, namely, $V_\beta \rightarrow V_\beta - \mu_0/e$. The transmission is identified with

$$A_{\alpha\beta}(E, U(r)) = \text{Tr} \{ 1_{\alpha} \delta_{\alpha\beta} - S_{\alpha\beta}(E, U(r)) \},$$

where $S_{\alpha\beta}(E, U(r))$ denotes the scattering matrix with lines and rows associated with the transversal modes at the contact $\alpha$ and $\beta$, respectively. $1_{\alpha}$ is the identity matrix whose rank is given by the number of propagating channels in the contact $\alpha$. The trace runs over open channels in $\alpha$ and $\beta$.

The transmission coefficient $A_{\alpha\beta}$ and the scattering matrix $S_{\alpha\beta}$ are functions of the electron energy and functionals of the electrostatic potential $U(r)$ in the conductor. In linear response, $A_{\alpha\beta}$ is computed at the equilibrium potential $U_{eq}(r)$ that is established when all reservoirs have the same chemical potential $\mu_0$. Beyond this regime, it is necessary to compute $U(r)$ self-consistently, as pointed out by Landauer.

To make analytical progress, it is convenient to expand all quantities in powers of $V$. The local electrostatic potential $U(r)$ reads

$$U(r) = U_{eq}(r) + \sum_{\alpha} u_\alpha(r)V_\alpha + \frac{1}{2} \sum_{\alpha\beta} u_{\alpha\beta}(r)V_\alpha V_\beta + O(V^3)$$

where $u_{\alpha\beta}(r)$ is the characteristic potential defined by

$$u_{\alpha\beta}(r) = \frac{\partial}{\partial V_\alpha} \frac{\partial}{\partial V_\beta} \bigg|_{\{V_\gamma\}=0}. \tag{4}$$

Here $\{V_\gamma\} = 0$ is a shorthand for $V_\gamma = 0$, for all $\gamma$.

Some properties of the characteristic potentials follow directly from simple physical considerations. For instance, $u_\alpha(r)$ has the following properties:

(a) Changes in the electro-chemical potential of the reservoir $\alpha$ should not affect $U(r)$ inside $\beta$, hence, $u_\alpha(r) = 0$, when $r$ is taken inside the reservoir $\beta \neq \alpha$. (b) For $r$ inside the reservoir $\alpha$, $U(r) = V_\alpha$ and, thus, $u_\alpha(r) = 1$. (c) A global change of the applied potentials, $V_\alpha \rightarrow V_\alpha + V_0$, makes $U(r) \rightarrow U(r) + V_0$, implying the sum rule $\sum_\alpha u_\alpha(r) = 1$ for all $r$.

The current $I_\alpha$, written as a power series of the applied voltages, is cast as a function of the coefficients $G_{\alpha\beta\gamma\delta}$, namely,

$$I_\alpha = \sum_\beta G_{\alpha\beta} + \sum_\beta \gamma \sum_\beta \gamma G_{\alpha\beta\gamma\delta} V_\gamma V_\delta + \sum_\beta \gamma \delta G_{\alpha\beta\gamma\delta} V_\delta V_\delta + \cdots. \tag{5}$$

In line with the standard notation, we do not write $I_\alpha$ as a Taylor series in $\{V_\alpha\}$. In Sec. [V] we will see how such notation determines the symmetrization of the indices $\alpha, \beta, \cdots$ in the conductance coefficients $G_{\alpha\beta\gamma\delta}$.

The coefficient $G_{\alpha\beta}$ corresponds to the linear conductance, as given by the Landauer formula

$$G_{\alpha\beta} = \frac{2e^2}{h} \int_{-\infty}^{\infty} dE \left( \frac{\partial f_0}{\partial E} \right) A_{\alpha\beta}(E, U_{eq}(r)). \tag{6}$$

Here $A_{\alpha\beta}(E, U_{eq}(r))$ is the multi-lead Landauer-B"uttiker transmission coefficient, with $S$ computed using $U_{eq}(r)$, as standard.

The first non-linear current correction, represented by $G_{\alpha\beta\gamma\delta}$ reads

$$G_{\alpha\beta\gamma\delta} = \frac{2e^3}{h} \int_{-\infty}^{\infty} dE \left( \frac{\partial f_0}{\partial E} \right) \times \int dr \left[ u_\gamma(r) - \frac{1}{2} \delta_{\gamma\delta} \right] \frac{\delta A_{\alpha\beta}}{\epsilon \delta U(r)} \bigg|_{\{V_\gamma\} = 0} \tag{7},$$

where the spatial integration is taken over the region where $\delta A_{\alpha\beta}/\delta U(r)|_{\{V_\gamma\} = 0}$ is non vanishing, namely, inside the conductor.

The above expression depends explicitly on the electrostatic potential via $u_\alpha(r)$. To determine $u_\alpha(r)$, the formalism has to be supplemented by a self-consistent microscopic electronic structure calculation, or by an adequate approximation. The latter was constructed in Ref. [8] by using the following argument: The potential $U(r)$ is related to the bias generated electronic density imbalance $\delta n(r)$ in the conductor. In turn, $\delta n(r)$ arises from the charge injected by the leads and the induced charge in the conductor, in response to the injected one.
The injection properties of the sample are given by the injectivity, which reads
\[
\frac{dn^s(r, \alpha)}{dE} = -\frac{1}{2\pi i} \int_{-\infty}^{\infty} dE \left( -\frac{\partial f_0}{\partial E} \right) \times \sum_{\beta} \text{Tr} \left[ S^\dagger_{\beta \alpha} \frac{\delta S_{\beta \alpha}}{\delta U(r)} - \frac{\delta S^\dagger_{\beta \alpha}}{\delta U(r)} S_{\beta \alpha} \right].
\] (8)
evaluated at \( \{V_r\} = 0 \). The superscript \( s \) labels quantities obtained within the scattering approach. Since \( dE^s/dE \) includes spin degeneracy, our definition differs from the one of Ref. [8] by a factor 2.

To linear order in \( V \), the induced charge density is given by
\[
dn_{\text{ind}}(r) = e \sum_{\alpha} \int d r' \Pi(r, r') u_\alpha(r') dV_\alpha.
\] (9)
where \( \Pi(r, r') \) is the Lindhard polarization function.\(^{22}\)
The scattering approach does not provide a recipe to obtain the later. However, by recalling the relation between the Wigner-Smith time delay and the conductor density of states, \( dn_{\text{ind}}(r) \) can be readily written in the Thomas-Fermi approximation as
\[
dn_{\text{ind}}(r) = e \sum_{\alpha} \frac{dn^s(r)}{dE} u_\alpha(r) dV_\alpha.
\] (10)

The local density of states \( dn^s/dE \) is
\[
\frac{dn^s(r)}{dE} = \sum_{\beta} \frac{dn^s(\beta, r)}{dE},
\] (11)
where \( dn^s(\beta, r)/dE \) is called emissivity and is given by
\[
\frac{dn^s(\beta, r)}{dE} = -\frac{1}{2\pi i} \int dE \left( -\frac{\partial f_0}{\partial E} \right) \times \sum_{\alpha} \text{Tr} \left[ S^\dagger_{\beta \alpha} \frac{\delta S_{\beta \alpha}}{\delta U(r)} - \frac{\delta S^\dagger_{\beta \alpha}}{\delta U(r)} S_{\beta \alpha} \right].
\] (12)
These elements render the Poisson equation
\[
-\nabla^2 u_\alpha(r) + 4\pi e^2 \frac{dn^s(r)}{dE} u_\alpha(r') = 4\pi e^2 \frac{dn^s(r, \alpha)}{dE}.
\] (13)
where both the density of states and the injectivity depend only on the scattering matrix.

Higher order conductance coefficients \( G_{\alpha \beta \gamma \ldots} \) can also be calculated in a straightforward way. Obtaining self-consistent equations for the characteristic potentials \( u_{\alpha \beta \gamma \ldots} \) becomes increasingly more involved, but is still possible within the Thomas-Fermi approximation.\(^{22}\)

In the next Sections we define a general model for a conductor and use the NEGF approach to show how to systematically obtain the coefficients \( G_{\alpha \beta \gamma \ldots} \) and the characteristic potentials \( u_{\alpha \beta \gamma \ldots} \) to arbitrary order.

### III. MODEL HAMILTONIAN

We separate the system in two regions, namely, the leads (L) and the conductor (C) to write the Hamiltonian as
\[
\mathcal{H} = \mathcal{H}_L + \mathcal{H}_C + \mathcal{H}_{LC}.
\] (14)
For definiteness, we introduce a surface \( S \) enclosing the conductor, to partition the model Hilbert space. The lead Hamiltonian reads
\[
\mathcal{H}_L = \sum_{k_{aa}s} E_{k_{aa}s} c_{k_{aa}s}^\dagger c_{k_{aa}s},
\] (15)
where \( k \) is the electron transversal wave number at the channel \( a (a = 1, \ldots, N_\alpha) \) in the lead \( \alpha (\alpha = 1, \ldots, N) \). The electron spin is \( s = \uparrow, \downarrow \) and the \( c_{k_{aa}s}^\dagger (c_{k_{aa}s}) \) are the usual fermionic creation (annihilation) operators, with \( \{c_{k_{aa}s'}, c_{k'a'\alpha's'}\} = \delta_{kk'}\delta_{\alpha\alpha'}\delta_{ss'} \delta_{s's'} \). The threshold energy to open the transversal propagation mode \( a \) in the lead \( \alpha \) is \( E_{k_{aa}s} \). We assume free motion in the direction along the leads. Hence, \( E_{k_{aa}s} = E_{\text{FAS}} + h^2 k^2/2m^* \), where \( m^* \) is the electron effective mass. The electrons at the lead \( \alpha \) are in thermal equilibrium with the reservoir at temperature \( T \) to which the lead is connected. This reservoir is characterized by a chemical potential \( \mu_\alpha \).

The conductor Hamiltonian reads
\[
\mathcal{H}_C = \sum_{\mu\nu,s} [H_C]_{\mu\nu} d_{\mu s}^\dagger d_{\nu s},
\] (16)
where \( d_{\mu s}^\dagger (d_{\mu s}) \) creates (annihilates) an electron at the \( \mu \)-th state of an arbitrary basis \( \{\nu\} \) that spans the conductor eigenstates. Since we consider \( \mathcal{H}_C \) as a bilinear operator, electron-electron interactions are only taken into account in the mean-field level. This is a good approximation, provided the system is open\(^{26}\) and hence neither charging nor electronic correlations effects are expected to play an important role.

The term that couples the leads to the conductor is
\[
\mathcal{H}_{LC} = \sum_{k_{aa},\mu,s} \left[ V_{k_{aa},\mu} c_{k_{aa}s}^\dagger d_{\mu s} + \text{H.c.} \right].
\] (17)

When there is a difference between the reservoirs’ electro-chemical potentials \( \mu_\alpha \), the system is driven out of equilibrium and a current flows. In the stationary regime a time-independent non-equilibrium self-consistent electrostatic potential \( U(r) \) is formed. It depends on the applied bias, as well as on the system geometry and material properties. In most of the paper, we assume \( U(r) \) to be local. A non-local \( U \) is discussed in Section [VII].

The Hamiltonian \( \mathcal{H}_L \) of Eq. (15) assumes free propagation in the leads. Alternatively, without significant increase in complexity, it can also represent periodic semi-infinite leads.\(^{26}\) In any of these events, the surface separating conductor and leads has to be chosen in such a way that, at any given lead \( \alpha \), \( U(r) \approx V_\alpha \). As a consequence, the spatial dependence of \( U(r) \) is entirely accounted for by \( \mathcal{H}_C \). This construction not only limits
the arbitrariness in defining the model Hilbert space, but also guarantees a simple prescription for computing the characteristic potentials $u_{\alpha \beta} \ldots (r)$, as we shall discuss in Section IV. In the standard DFT approach for molecular electronics, although not emphasized, this is the key notion behind defining an “extended molecule” and it is essential to ensure gauge invariance. 

There is a more basic principle behind the above construction than just simplifying calculations: The surface $S$ defines the leads region at a position where no electrical field lines penetrate its surface. Hence, the charge within the volume $V$ enclosed by $S$ is constant.

For the sake of simplicity we restrict our considerations to weak magnetic fields, or more precisely, to systems where we can neglect spin-orbit and Zeeman interactions and consider only orbital effects due to an external magnetic field. Hence, in what follows, except for Sec. VII we omit the spin index and replace the sums over spin projections by their degeneracy factors.

We also do not explicitly include the possibility of capacitive couplings in our model. In pumping experiments, such kind of coupling is likely to dominate the transport, as discussed in Refs. 22. In dc nonlinear transport, the effect of setting a fixed back gate voltage and, hence, defining bias mode, can be relevant in nonlinear conductance of quantum dots. We stress that both the scattering and the NEGF approaches can easily accommodate situations where the number of leads does not coincide with the number of gate voltages $\{V_{\alpha}\}$ and/or devices with more than one conductor.

IV. THE NEGF APPROACH

For elastic processes, the electronic current at the leads can be written in terms of the conductor Green’s functions, namely

$$I_{\alpha} = \frac{-2e}{\hbar} \int_{-\infty}^{\infty} \frac{dE}{2\pi} \text{Im Tr} \left\{ \Gamma_{\alpha} \left[ G^{<}(E) + f_{\alpha}(E)G^{r}(E) \right] \right\}, \quad (18)$$

where symbols in bold face correspond to matrices whose rows and columns are states of the conductor basis set $\{\mu\}$. The Green’s functions $G^{\mu\nu}_{\alpha\beta}(E)$ and $G^{<\mu\nu}_{\alpha\beta}(E)$ are the Fourier transforms of $G^{\mu\nu}(t - t') = -(i/\hbar)\delta(t - t')\langle \hat{d}_{\mu}(t), \hat{d}^\dagger_{\nu}(t') \rangle$ and $G^{<\mu\nu}(t - t') = (i/\hbar)\langle \hat{d}_{\mu}(t')\hat{d}_{\nu}(t) \rangle$ respectively, where $\langle \cdot \cdot \cdot \rangle$ is defined as standard. The decay width or line width matrix elements are given by

$$[\Gamma_{\alpha}]_{\mu\nu} = 2\pi \sum_{a,\alpha} V_{\mu,kaa} \rho_{kaa}(E) V^*_{\nu,kaa}, \quad (19)$$

where $\rho_{kaa}(E)$ is the density of states of mode $a$ at the $\alpha$ contact.

Since the conductor Hamiltonian $H_C$ is a bilinear operator, the exact conductor Green’s functions can be obtained in closed form using, for instance, the equations-of-motion method. (For a recent review, see Ref. 23.)

In the energy representation, the Green’s function $G^{r(a)}_{\mu\nu}$ is given by

$$G^{r(a)}(E) = \left[ EI - H_C - \Sigma^{r(a)}(E) \right]^{-1}. \quad (20)$$

The conductor lesser Green’s function $G^{<\mu\nu}_{\alpha\beta}$ follows directly from the Dyson equation

$$G^{<}(E) = G^r(E)\Sigma^{<}(E)G^a(E). \quad (21)$$

For the sake of definiteness the basis set is truncated and the matrices have rank $M$. $I$ is the identity matrix. (Later on we shall also use conductor Green’s functions in the coordinate representation and drop the boldface notation.)

The self-energy matrix elements read

$$\Sigma_{\mu\nu}(E) = \sum_{kaa} V_{\mu,kaa} g_{kaa}(E) V^*_{\nu,kaa}, \quad (22)$$

where $\Sigma^{r(a)}(E)$ and $\Sigma^{<}(E)$ are obtained by identifying the free electron Green’s function in the leads $g_{kaa}(E)$, with

$$g_{kaa}(E) = if_{\alpha}(E)\delta(E - E_{kaa}) \quad (23)$$

and

$$g^{r(a)}_{kaa}(E) = \mp i\pi \delta(E - E_{kaa}) + \frac{PV}{E - E_{kaa}}, \quad (24)$$

where PV stands for principal value integral.

The coupling matrix elements $V_{\mu,kaa}$ are, in general, smooth functions of the wave number $k$ and, hence, of $E_{kaa}$. Using (23) and assuming that $\rho_{\alpha\alpha}(E)$ has a broad band width and a smooth energy dependence, the matrix elements $\Sigma^{r(a)}_{\mu\nu}$ become energy independent and read

$$\Sigma^{r(a)}(E) \approx \mp \frac{i}{2} \Gamma = \mp \frac{i}{2} \sum_{\alpha} \left[ \Gamma_{\alpha} \right]. \quad (25)$$

For situations where the broad and flat band approximation does not hold, the results we obtain for the $I - V$ characteristics have to be modified in a straightforward way, as indicated later on.

In analogy, the self-energy matrix elements $\Sigma^{<\mu\nu}_{\alpha\beta}$ are given by

$$\Sigma^{<\mu\nu}_{\alpha\beta}(E) = \sum_{a=1}^{N} \sum_{ka} V_{\mu,kaa} g^{<\mu\nu}_{\alpha\beta}(E) V^*_{\nu,kaa} \approx \sum_{a=1}^{N} \left[ \Sigma^{<\mu\nu}_{\alpha}(E) \right]_{\mu\nu}. \quad (26)$$

Within the wide-band approximation, one arrives to

$$\Sigma^{<\mu\nu}_{\alpha}(E) \approx if_{\alpha}(E)\Gamma_{\alpha}. \quad (27)$$

Inserting $G^r$ from Eq. (20) and $G^<$ from Eq. (21) into Eq. (18), we write the current $I_{\alpha}$ as in Eq. (1),

$$I_{\alpha} = -\frac{2e}{\hbar} \sum_{\beta=1}^{N} \int_{-\infty}^{\infty} dE f_{\beta}(E) T_{\alpha\beta}(E, \{V_{\gamma}\}). \quad (28)$$
with transmission coefficients given by
\[ T_{\alpha\beta}(E, \{V_{\gamma}\}) = \text{Tr} \left[ \Gamma_{\alpha} G^r(E)(\Gamma_{\delta\alpha\beta} - \Gamma_{\beta}) G^a(E) \right]. \] (29)

By means of the useful relation
\[ G^a - G^r = iG^r \Gamma G^r = -iG^r \Gamma G^a, \] (30)
we obtain \( \sum_{\alpha=1}^{N} T_{\alpha\beta} = 0 \), and show that Eq. (28) satisfies current conservation,
\[ \sum_{\alpha=1}^{N} I_{\alpha} = 0. \]

As pointed out in Ref. 13, the current \( I_{\alpha} \) given by Eq. (28) is invariant under a global shift of the potential, that is, \( V_{\gamma} \rightarrow V_{\gamma} + V_0 \) for all \( \gamma \)'s and \( U \rightarrow U + V_0 \). This is not sufficient to prove that the formalism is gauge invariant. We still have to show that the same condition holds for the electron density \( n(r) \). This is done in what follows.

The applied voltages \( \{V_{\gamma}\} \) control the conductor charge distribution \( n(r) \) and the electrostatic potential \( U(r) \). The latter, in turn, enters the calculation of the conductor Green's functions. Both quantities, \( n(r) \) and \( G^r \), are related by
\[ n(r,t) = \sum_s \langle \psi_s^\dagger(r,t) \psi_s(r,t) \rangle = -2i\hbar \langle r| G^r(t,t) |r \rangle, \] (31)
where the factor 2 account for the spin degeneracy. By taking \( \psi_s(r,t) \) inside the conductor as \( \psi_s(r,t) = \sum_{\mu} d_{\mu s}(t)(|\mu\rangle r \rangle \), we obtain \( n(r,t) \) in matrix representation, namely,
\[ n(r,t) = -2i\hbar \sum_{\mu \nu} \langle \mu | G^r_{\mu \nu}(t,t) | \nu \rangle r \rangle. \] (32)

For stationary processes, where \( G^r(t,t) = G^r(0) \), the electronic density becomes
\[ n(r) = -2i \int_{-\infty}^{\infty} \frac{dE}{2\pi} \langle r| G^r(E) |r \rangle, \] (33)
with obvious matrix representation. In order to close the calculational procedure, a relation between \( n \) and \( U \) is needed. This can be done at different approximation levels.

In the Hartree approximation, the electronic density \( n(r) \) and \( U(r) \) are related by
\[ \nabla^2 U(r) = -4\pi e n(r) = 8\pi ie \int_{-\infty}^{\infty} \frac{dE}{2\pi} \langle r| G^r(E) |r \rangle, \] (34)
The boundary conditions are obtained by recalling that, by construction, \( U(r) \) is constant outside the conductor: \( U(r) = V_0 \) when \( r \) is taken at the lead \( \alpha \). In addition, the problem must be solved self-consistently, namely, \( U(r) \) enters the Hamiltonian \( \mathcal{H}_C \), which determines \( G^r(E) \), that in turn gives \( U(r) \).

Equation (33) leads to a local description of the electrostatic potential. In Section VII we show how NEGF deals with a non-local potential due to the exchange interaction.

Equation (33) also plays a key role in the standard implementations of the density functional theory (DFT) in molecular electronics (see, for instance, Ref. 14 for a review). In DFT, \( U(r) = U[n(r)] \) is considered as a functional of \( n(r) \), containing exchange and correlation interactions in addition to the Hartree one. Accordingly, the single-particle states \( \{\mu\} \) become Kohn-Sham orbital states. Although this is a very appealing construction, it is not as sound, from the conceptual point of view, as the derivation presented here: DFT is not a mean-field theory and a bilinear Hamiltonian, like Eq. (14), is not one of its underpinning elements. A good discussion about the shortcomings of the standard DFT approach to conductance can be found in Ref. 31.

We conclude this Section by stressing that in local approximation schemes Eq. (33) is manifestly gauge invariant, provided the partition given by Eq. (14) satisfies the conditions discussed in Section III. In this case, any global voltage shift can be absorbed by the energy integration, provided \( U(r) \) is calculated self-consistently. For systems where electronic correlations are built across the partition \( S \), gauge invariance calls for a more careful analysis. This is the case, for instance, in Kondo systems. In the mean field limit, discussed here, such correlations are absent. In DFT-NEGF, any semi-local functional of the exchange and correlation functional, \( U_{xc}[n(r)] \), allows for a partition \( S \) and hence preserves gauge invariance, as nicely discussed in Ref. 31. Nonlocal interactions present in the exact XC functional jeopardize the partition construction and spoil gauge invariance due to an XC contribution to the characteristic potentials in the contacts.\(^{31,33}\) In such situations, a partition free approach, like the one discussed in Ref. 32 is more suited.

V. Linear and Nonlinear Conductance Coefficients

In this Section we present a systematic approach to calculate the conductance coefficients \( G_{\alpha\beta\gamma...} \) and discuss some of their properties. For that purpose, we expand both \( f_\alpha(E) \) and \( T_{\alpha\beta}(E, U(r)) \), in Eq. (28), as powers of the voltages \( \{V_{\gamma}\} \).

We start writing the retarded (advanced) Green’s function as
\[ G^{r(a)}(E) = \frac{1}{E - H_0 - eU - \Sigma^{r(a)}(E)} \] (35)
without choosing a particular representation. Next we expand \( G^{r(a)} \) in terms of the differences between the non-equilibrium and equilibrium \( U \) and \( \Sigma \). As a result, we obtain the Dyson equation
\[ G^{r(a)} = G_0^{r(a)} + G_0^{r(a)} V_{\text{eff}} G^{r(a)} \] (36)
where the effective perturbation potential \( V_{\text{eff}} \) is given by
\[ V_{\text{eff}}(E) = eU - eU_{\text{eq}} + \]
and the equilibrium Green’s function by

\[ G_0^{(a)}(E) = \frac{1}{E - H_0 - eU_\text{eq} - \Sigma_r^{(a)}(E)} \]  

We now proceed by writing the self-energy

\[ \Sigma^{(a)}(E) = \sum_{\alpha} \sum_{a \in \alpha} \Sigma_r^{(a)}(E - eV_\alpha) \]

as

\[ \Sigma_r^{(a)}(E - eV_\alpha) = \Sigma_r^{(a)}(E) - eV_\alpha \frac{\partial \Sigma_r^{(a)}}{\partial E} \bigg|_{V_\alpha = 0} + e^2 V_\alpha \frac{\partial^2 \Sigma_r^{(a)}}{\partial E^2} \bigg|_{V_\alpha = 0} + \cdots \]  

where \( \Sigma_r^{(a)}(E) = \Sigma_r^{(a)}(E) \). From Eq. (40) we see that, in the flat band approximation, retarded and advanced self-energies do not depend on \( \{V_\alpha\} \), since

\[ \frac{\partial \Sigma_r^{(a)}}{\partial E} \bigg|_{V_\alpha = 0} \approx \frac{i}{2} \frac{\partial V_\alpha}{\partial E} = 0 \]  

Hence, \( V_{\text{eff}} \) depends only on the characteristic potentials, namely

\[ V_{\text{eff}} = e \sum_\alpha u_\alpha V_\alpha + \frac{1}{2} \sum_{\alpha \beta} u_{\alpha \beta} V_\alpha V_\beta + \cdots \]  

Inserting the above expression into (39) we formally obtain \( G^{(a)} \) to arbitrary order in \( V \).

We now turn our attention to the electronic density imbalance \( \delta n(r) = n(r) - n_\text{eq}(r) \), that ultimately allows us to calculate the characteristic potentials \( u_{\alpha \beta} \ldots \). To obtain \( \delta n(r) \), we expand \( G^\prec = G^\ast \Sigma^\prec G^a \) in powers of \( \{V_\alpha\} \) taking, as above, the wide flat band limit. In this approximation, the lesser self-energy \( \Sigma^\prec \), Eq. (20), reads

\[ \Sigma^\prec(E) = i \sum_\alpha f_0(E - eV_\alpha) \Gamma_\alpha \]

\[ = i \left( f_0 \Gamma - e \frac{\partial f_0}{\partial E} \sum_\alpha V_\alpha \Gamma_\alpha + \cdots \right) \]

Finally, \( G^\prec \) reads

\[ G^\prec = i f_0 G_0^\ast \Gamma G_0^a \]

\[ -e \sum_\alpha V_\alpha \left[ i e V_\alpha \Gamma_\alpha G_0^a + f_0 (G_0^\ast u_\alpha G_0^a - G_0^a u_\alpha G_0^\ast) \right] + O(V^2) \]

Close to equilibrium, when \( \{V_\alpha\} \to 0 \), \( G^\prec \to G_0^\prec = -2i f_0 \text{Im} G_0^\ast \), as given by the fluctuation-dissipation theorem. We use Eqs. (33) and (41) to write the electronic density as

\[ n(r) = \sum_{\ell} n^{(\ell)}(r) \]

where the \( \ell \)'s stand for the implicit powers of \( V^\ell \). Note that \( n^{(0)}(r) = n_\text{eq}(r) \).

We are now ready to identify the conductance coefficients \( G_{\alpha \beta \gamma} \ldots \) order by order: By plugging Eqs. (36) and (42) into (29) we obtain the transmission \( T_{\alpha \beta}(E) \) in terms of equilibrium Green’s functions and the characteristic potentials. The later can be computed from \( G^\prec \), as given by Eq. (44), with the help, for instance, of the Hartree equation (34).

### A. Linear conductance coefficients

To linear order in \( V \), the current at the contact \( \alpha \) is

\[ I_{\alpha}^{(1)} = \sum_\beta G_{\alpha \beta} V_\beta \]  

The conductance coefficients \( G_{\alpha \beta} \) are obtained from the linear expansion of the current (28) in the applied voltages \( V_\alpha \). They read

\[ G_{\alpha \beta} = -\frac{2e^2}{h} \int_{-\infty}^{\infty} dE \left( -\frac{\partial f_0}{\partial E} \right) T_{\alpha \beta}(E, \{V_\gamma\} = 0) \]  

which is identical to the multi-lead Landauer-Büttiker formula as it can be verified following, for instance, the path presented in Ref. 33.

Owing to physical considerations the linear conductance coefficients \( G_{\alpha \beta} \) follow some simple sum rules. Current conservation implies that \( \sum_\alpha G_{\alpha \beta} = 0 \). This sum rule is automatically satisfied by Eq. (48), since Eq. (28) does it to all orders in \( V \). Current invariance under a global voltage shift \( V_\alpha \to V_\alpha + V_0 \) leads to \( \sum_\beta G_{\alpha \beta} = 0 \). This is fulfilled, since \( \sum_\beta T_{\alpha \beta}(E, \{V_\gamma\} = 0) \).

Equations (33) and (44) give the electronic density as

\[ n_\text{eq}(r) = -\frac{2}{\pi} \int_{-\infty}^{\infty} dE f_0(E) \text{Im} \langle r | G_0^\ast(E) | r \rangle \]  

It is worth remarking that, even in the Hartree approximation, depending on the system, the computation of \( U_{\text{eq}}(r) \) can already be a formidable computational task. In mesoscopic physics, due to the chaotic and/or weakly disordered nature of the addressed systems, quantitative results can be obtained by a statistical treatment using random matrix theory or diagrammatic techniques. In molecular electronics a full electronic structure calculation is already necessary.
An important symmetry of linear transport is unveiled by considering an external magnetic field. The linear conductance coefficients fulfill the Onsager-Casimir reciprocity relations under magnetic field inversion. This is indeed the case of Eq. (48). Using “microreversibility”

\[ G_0^{(a)}(-B) = [G_0^{(a)}(B)]^T \]  

(50)

and the cyclic properties of the trace in (48), one can show that

\[ G_{\alpha\beta}(-B) = G_{\beta\alpha}(B) \]  

(51)

for \( \alpha \neq \beta \). For the diagonal coefficients, where \( \alpha = \beta \), one can either use current conservation and (51), or directly use Eq. (50) to show that \( G_{\alpha\alpha}(B) = G_{\alpha\alpha}(-B) \).

In the two-terminal case, the conductance itself is an even function of the applied magnetic field, namely,

\[ G_{12}(-B) = G_{12}(B), \]

(52)

which is a more stringent symmetry than the reciprocity relation for the general multi-lead case. In the scattering approach, Eq. (52) can be viewed as a consequence of the S-matrix unitarity \cite{24,32}, whereas using NEGF it follows from current conservation and from \( G_{\alpha\alpha}(B) = G_{\alpha\alpha}(-B) \).

The even symmetry of \( G \) with respect to \( B \) has been experimentally established \cite{28,39} and has important implications for interference experiments in two-terminal mesoscopic rings: It does not allow one to measure phase differences, since in the observed Aharonov-Bohm conductance oscillations the phase shift is locked either to 0 or to \( \pi \). \cite{28,39}

\section{Second order terms}

The next order current term, in powers of \( V \), is

\[ I^{(2)}_a = \sum_{\beta,\gamma} G_{\alpha\beta,\gamma} V_\beta V_\gamma. \]

(53)

The coefficient \( G_{\alpha\beta,\gamma} \), obtained by expanding \( \sum_{\beta} f_{\beta} T_{\alpha\beta} \) of Eq. (28), is formally given by Eq. (1):

\[ G_{\alpha\beta,\gamma} = \frac{2e^3}{h} \int_{-\infty}^\infty dE \left( -\frac{\partial f_0}{\partial E} \right) \sum_{\gamma} \Gamma_a G_0 \left( u_{\gamma}(r) - \frac{\delta_{\beta\gamma}}{2} \right) \left( G_0' \left( \Gamma_0 + \Gamma_0 \gamma_{\beta\gamma} - \Gamma_{\beta\gamma} \right) + \left( \Gamma_0 \gamma_{\beta\gamma} - \Gamma_{\beta\gamma} \right) G_0' \left( u_{\gamma} - \frac{\delta_{\beta\gamma}}{2} \right) \right) G_0' \right]. \]  

(55)

Its explicit expression in terms of equilibrium Green’s functions is\cite{13}

\[ G_{\alpha\beta,\gamma} = \frac{2e^3}{h} \int_{-\infty}^\infty dE \left( -\frac{\partial f_0}{\partial E} \right) \text{Tr} \left\{ \Gamma_a G_0 \left[ u_{\gamma}(r) - \frac{\delta_{\beta\gamma}}{2} \right] G_0' \left( \Gamma_0 + \Gamma_0 \gamma_{\beta\gamma} - \Gamma_{\beta\gamma} \right) + \left( \Gamma_0 \gamma_{\beta\gamma} - \Gamma_{\beta\gamma} \right) G_0' \left( u_{\gamma} - \frac{\delta_{\beta\gamma}}{2} \right) \right\}. \]

where

\[ \Pi(r, r') = -2i \int_{-\infty}^\infty \frac{dE}{2\pi} f_0 \left[ \langle r | G_0'(E) | r' \rangle \langle r' | G_0'(E) | r \rangle - \text{H.c.} \right] \]

is formally identified with the Lindhard function and

\[ \frac{dn(r, a)}{dE} = 2 \int_{-\infty}^\infty \frac{dE}{2\pi} \left( -\frac{\partial f_0}{\partial E} \right) \langle r | G_0' \Gamma_a G_0' | r \rangle \]

(58)

is a partial local density of states, called injectivity in the scattering approach. The compact form of (58) is due to the flat and wide band approximation. As discussed in Ref. \cite{13}, \( dn(r, a)/dE \) can be easily modified to account for a system specific energy dependence of self-energy \( \Sigma \). Such corrections are potentially important in molecular electronics, where the details of the contacts should matter.

In the Hartree approximation, the characteristic potentials \( u_{\alpha}(r) \) are determined by

\[ \nabla^2 u_{\alpha}(r) = 4\pi e^2 \left[ \int_{V} dr' \Pi(r, r')u_{\alpha}(r') - \frac{dn(r, \alpha)}{dE} \right]. \]  

(59)
with the boundary conditions discussed in Section III. The above equation has the same structure as Eq. (13). (We postpone a detailed comparison between both equations to the forthcoming Section.) Both terms in the r.h.s. of Eq. (59) stem from of the electronic charge imbalance $n^{(1)}(r)$.4

By using (59) and integrating by parts, the important relation

$$\sum_\alpha \frac{dn(r, \alpha)}{dE} = \int d\mathbf{r'} \Pi(r, \mathbf{r'})$$

(60)

is obtained. This relation holds also beyond the flat and wide band approximation.5

We now sum Eq. (59) over all leads $\alpha$ to write

$$\nabla^2 \sum_\alpha u_\alpha(r) = 4\pi e^2 \int d\mathbf{r'} \Pi(r, \mathbf{r'}) \left[ \sum_\alpha u_\alpha(r') - 1 \right].$$

(61)

Recalling the boundary conditions for $u_\alpha$, we find that $\sum_\alpha u_\alpha = 1$, formally recovering one of the sum rules put forward by Büttiker.6 This is a quite simple way to prove that, in the Hartree approximation, the NEGF formalism is manifestly gauge invariant. Conversely, the scattering approach uses $\sum_\alpha u_\alpha = 1$ to obtain (13).

Another way to picture the sum rule $\sum_\alpha u_\alpha = 1$ is by observing that it automatically guarantees that $n^{(1)}(r)$ remains invariant under the global shift $V_\alpha \to V_\alpha + V_0$ (as shown to all orders in the previous section).

As experimentally established1, 2, 3, 6 and theoretically discussed9, 15 the Onsager-Casimir reciprocity relations do not hold for non-linear conductance. In the formalism we present, this is manifest in Eq. (53). While $\delta T_{ab}/\delta U(r)$ computed at $\{V_\gamma\} = 0$ is even in magnetic field, in general $u_{a}(r, B) \neq u_{a}(r, -B)$. The later can be seen from Eq. (59): Albeit the Lindhard function is even in $B$

$$\Pi(r, \mathbf{r'}; B) = \Pi(r, \mathbf{r'}; -B),$$

(62)

as a consequence of the “micoreversibility” relation (50)

$$G^{(a)}(r, \mathbf{r'}; E, B) = G^{(a)}(r, \mathbf{r'}; E, -B),$$

in general

$$\frac{dn(r, \alpha, B)}{dE} \neq \frac{dn(r, \alpha, -B)}{dE}.$$  

(63)

C. Arbitrary order

Recent experiments measured higher order conductance coefficients, calling for a theoretical analysis of higher conductance coefficients. The general expression for $G_{\alpha\beta_1\ldots\beta_j}$ in terms of the “generating functional” $T_{\alpha\beta}$ is

$$G_{\alpha\beta_1\ldots\beta_j} = -2e^2 \hbar \int_{-\infty}^{\infty} dE \left( -\frac{\partial f_0}{\partial E} \right) \sum_{l=1}^{J-l} \sum_{n=0}^{\infty} \frac{(-1)^{l+1}}{l!} \delta_{\beta_1\beta_2} \delta_{\beta_2\beta_3} \ldots \delta_{\beta_{l-1}\beta_l} \times \prod_{i=1}^{l} \int d\mathbf{r}_i \cdots d\mathbf{r}_{l-1} \int d\mathbf{r}'_1 \cdots d\mathbf{r}'_n \frac{\delta T_{\alpha\beta_1}}{\delta U(\mathbf{r}_1)} \cdots \frac{\delta T_{\alpha\beta_l}}{\delta U(\mathbf{r}_{l-1})} \prod_{i=1}^{n} \frac{\delta U(\mathbf{r}'_i)}{\delta U(\mathbf{r}'_n)},$$

(64)

where $K^{(n)}$ is defined as

$$K^{(n)}_{\beta_1\ldots\beta_l}(r_1', \ldots, r_n') = \frac{1}{(J-l)! n!} \frac{\partial}{\partial V_{\beta_1}} \cdots \frac{\partial}{\partial V_{\beta_l}} \left[ U(r_1') \cdots U(r_n') \right] \bigg|_{\{V_\gamma\} = 0}$$

(65)

and related to the characteristic potentials by (1). For $n = 0$, we define $K^{(0)} = \delta H$.

Let us explain the structure of Eq. (64). We identify the term containing $V$ to the power $J$ in the $I-V$ characteristics Eq. (63), with the conductance coefficient $G_{\alpha, \beta_1\ldots\beta_j}$, and the V$^J$ term comes from the product of the expansions of $T_{\alpha\beta}$ and $f_0$ in (58). The first sum in Eq. (64) run over $l$, the power of $V$ that stem from the expansion of $f_0$. The $J-l$ derivatives of $T_{\alpha\beta}$ with respect to $V$ give raise to higher order characteristic potentials and functional derivatives of the kind $\delta T_{\alpha\beta}/\delta U(\mathbf{r}')$. The second sum in Eq. (64) run over $n$, that represent the number of derivatives $\partial U_{\alpha}$ that become $u_\alpha(\mathbf{r}')/\delta U(\mathbf{r}')$. The remaining $J-l-n$ derivatives are responsible for higher order characteristic potentials $u_{\beta_1,\beta_2}$. The expansion of $f_0$ is straightforward, but to factorize the $(-\partial E f_0)$ term, we have to integrate by parts. As a result, we obtain additional $l-1$ functional derivatives acting on $T_{\alpha\beta}$.

Note that, as discussed in Sec. II the indices $\beta_1 \ldots \beta_j$ are not symmetric. By combinatorial arguments it is not difficult to find the Taylor coefficients of the $J-V$ expansion.

Similar expressions have been obtained classically.25 The connection between the classical and quantum results is not clear yet.

The expression for the characteristic potential of order $J$ is obtained from the expansion of $G^{<}$ in Eq. (34)

$$\nabla^2 u_{\beta_1\ldots\beta_j}(r) = -8\pi e \int \frac{dE}{2\pi} \frac{\partial}{\partial V_{\beta_1}} \cdots \frac{\partial}{\partial V_{\beta_j}} \sum_{k=0}^{k \text{ terms}} \Gamma_{\alpha} G_0^{(0)} V_{\text{eff}} G_0^{(0)} \cdots V_{\text{eff}} G_0^{(0)} \sum_{\alpha} f(E - eV_\alpha) \Gamma_{\alpha}$$

(66)
For simplicity, we explicitly show the third order conductance coefficient, namely,

\[
\mathcal{G}_{\alpha\beta\gamma\delta} = -\frac{e^2}{\hbar} \int_{-\infty}^{\infty} dE \left\{ \int d\mathbf{r}_1 \frac{\delta T_{\alpha\beta}}{\delta U(\mathbf{r}_1)} u_{\gamma}(\mathbf{r}_1) \right. \\
\left. + \int d\mathbf{r}_1 \int d\mathbf{r}_2 \frac{\delta T_{\alpha\beta}}{\delta U(\mathbf{r}_1) \delta U(\mathbf{r}_2)} \left[ u_{\alpha}(\mathbf{r}_1) u_{\beta}(\mathbf{r}_2) - \delta_{\alpha\beta} u_{\delta}(\mathbf{r}_1) + \frac{1}{3} \delta_{\beta\gamma} \delta_{\alpha\delta} \right] \right\},
\]

(67)

and the corresponding equation for \( u_{\alpha\beta} \)

\[
\nabla^2 u_{\alpha\beta}(\mathbf{r}) = -4\pi e^2 \left[ -\frac{dn(\mathbf{r})}{dE} u_{\alpha\beta}(\mathbf{r}) + e \frac{d^2 n(\mathbf{r})}{dE^2} u_{\alpha}(\mathbf{r}) u_{\beta}(\mathbf{r}) + e \frac{d^2 n(\mathbf{r}, \beta)}{dE^2} \delta_{\alpha\beta} - e \frac{d^2 n(\mathbf{r}, \alpha)}{dE^2} u_{\alpha}(\mathbf{r}) - e \frac{d^2 n(\mathbf{r}, \alpha)}{dE^2} u_{\beta}(\mathbf{r}) \right].
\]

(68)

For simplicity, \( u_{\alpha\beta} \) is written in the Thomas-Fermi approximation. It is simple to explicitly show that \( \sum_{\alpha} u_{\alpha\beta} = 0 \), respecting gauge invariance.

**VI. CONNECTION WITH THE SCATTERING-MATRIX APPROACH**

We now establish the equivalence between the NEGF results for nonlinear elastic electronic transport and those obtained by the scattering approach, as formulated by Büttiker and collaborators, and summarized in Section II.

The underpinning elements of the scattering approach are: (a) The scattering matrix is viewed as a function of the electron energy and a functional of the non-equilibrium electrostatic potential in the conductor. \( S(E, U(\mathbf{r})) \) is used to construct a generating functional to obtain the nonlinear conductance coefficients. (b) Physical arguments are used to write a Poisson equation relating \( U(\mathbf{r}) \) with source terms expressed as functions of \( S \). Both \( S \) and \( U \) are solved self-consistently.

We begin by writing the standard (equilibrium) resonance scattering matrix

\[
S_{ba}(E) = \delta_{ba} - 2\pi i \sum_{\mu\nu} (\rho_{a}\rho_{b})^{1/2} V_{\mu b}^{*} G_{0}(E)_{\mu\nu} V_{\nu a} \, .
\]

(69)

where \( a \) and \( b \) label propagating modes in the leads and the conductor Green’s function is calculated for the equilibrium electrostatic potential \( U_{\text{eq}}(\mathbf{r}) \). As the bias is increased \( U(\mathbf{r}) \) is modified, as well as the conductor resonances and the channels thresholds. Provided that the applied bias does not add new physical processes to the transport problem, like for instance phonons, the “equilibrium” \( S \)-matrix can be generalized to

\[
S_{ba}(E, U(\mathbf{r})) = \delta_{ba} - 2\pi i \sum_{\mu\nu} (\rho_{a}\rho_{b})^{1/2} V_{\mu b}^{*} G^{r}(E)_{\mu\nu} V_{\nu a} \, .
\]

(70)

Here the non-equilibrium \( U(\mathbf{r}) \) is contained in the conductor Green’s function \( G^{r} \). By recalling the definition of the decay widths \( \Gamma \), we obtain

\[
A_{\alpha\beta} = \text{Tr} \left[ 1_{a} \delta_{\alpha\beta} - S_{\alpha\beta}^{\dagger} S_{\alpha\beta} \right] = -T_{\alpha\beta}
\]

(71)

and conclude that the scattering and the NEGF approaches formally give identical expressions for the current.

We now examine how \( U(\mathbf{r}) \) is treated in both approaches, namely, we compare Eqs. (13) and (59). We begin by comparing the injectivities. By making explicit the sums over channels, the scattering approach injectivity (5) becomes

\[
\frac{dn^{r}(\mathbf{r}, \alpha)}{dE} = -\frac{1}{2\pi i} \sum_{\beta} \int_{-\infty}^{\infty} \frac{dE}{2\pi} \left( -\frac{\delta f_{0}}{\delta E} \right) \times \sum_{\mu \in a, b \in \beta} \left[ S_{\mu b}^{\dagger} \delta S_{\mu a} \frac{\delta S_{ba}}{e\delta U(\mathbf{r})} - \frac{\delta S_{ba}^{\dagger}}{e\delta U(\mathbf{r})} \delta S_{\mu a} \right] ;
\]

(72)

evaluated at \( \{V_{\gamma}\} = 0 \). Equation (72) renders a quite amenable path to calculate the functional derivative \( \delta S_{ba}/\delta U(\mathbf{r}) \): First, we use \( G^{r} \delta[(G^{r})^{-1}] + (\delta G^{r})(G^{r})^{-1} = 0 \) to write

\[
\frac{\delta S_{ba}}{e\delta U(\mathbf{r})} = +2\pi i (\rho_{a}\rho_{b})^{1/2} \sum_{\mu \nu} V_{\mu b}^{*} G^{r}(E)_{\mu\nu} \delta \frac{G^{r}(E)^{-1}}{e\delta U(\mathbf{r})} \frac{G^{r}(E)_{\mu\nu} V_{\nu a}}{e\delta U(\mathbf{r})} .
\]

(73)

Second, noting that \( (G^{r})^{-1} = E - H_{0} - eU + i\Gamma/2 \) and \( U_{\mu\nu} = \int d\mathbf{r}' \langle \mu | \mathbf{r}' \rangle U(\mathbf{r}') \langle \mathbf{r}' | \nu \rangle \), we readily write

\[
\frac{\delta}{e\delta U(\mathbf{r})} [G^{r}(E)]_{\mu\nu} = -\langle \mu | \mathbf{r} \rangle \langle \mathbf{r} | \nu \rangle .
\]

(74)
Plugging Eqs. (69) and (73) into (72) and using (74) we show that \( d\pi^\alpha(r, \alpha)/dE \) exactly coincides with Eq. (58), obtained within the wide and flat band approximation.

Following the same steps, we also find that the scattering approach emissivity is given by

\[
\frac{dn(\alpha, r)}{dE} = 2\int_{-\infty}^{\infty} \frac{dE}{2\pi} \left( -\frac{\partial f_0}{\partial E} \right) (r|G_0^\alpha\Gamma_\alpha G_0|r). \tag{75}
\]

The Thomas-Fermi approximation is key to have a closed calculational scheme in terms of scattering matrix. As standard, it is assumed that \( u_\alpha(r) \) shows a slower coordinate dependence than \( \Pi(r, r') \) to write

\[
\int_\nu dr' \Pi(r, r') u_\alpha(r') \approx u_\alpha(r) \int_\nu dr' \Pi(r, r') \approx u_\alpha(r) \frac{dn(\alpha, r)}{dE} \tag{76}
\]

where we use (60). In this limit the NEGF Hartree equation (69) reduces to the scattering Poisson equation (13). It is interesting to note that the diagonal part of \( \Pi(r, r') \) can be written as

\[
\Pi(r, r) = -2i \int_{-\infty}^{\infty} \frac{dE}{2\pi} \left( -\frac{\partial f_0}{\partial E} \right) \left[ (r|G_0^\alpha(E) - G_0(E)|r) \right]
\]

which, integrating by parts and using (30), gives

\[
\Pi(r, r) = \sum_\alpha \frac{dn(\alpha, r)}{dE}. \tag{77}
\]

Note that Eq. (68) coincides with the corresponding one obtained in the scattering approach within the Thomas-Fermi approximation. This suggests that, within the approximations discussed in this Section, both approaches are equivalent to all orders.

\[
H^{HF}_{\text{int}} = \sum_{\mu\nu\gamma\delta} V_{\mu\nu\gamma\delta} \left( \langle d_{\mu s}^\dagger d_{\delta s'} \rangle d_{\nu s'}^\dagger d_{\gamma s'} - \langle d_{\mu s}^\dagger d_{\gamma s'} \rangle d_{\nu s'}^\dagger d_{\delta s'} + \frac{1}{2} \langle d_{\mu s}^\dagger d_{\gamma s'} \rangle \langle d_{\nu s'}^\dagger d_{\delta s'} \rangle - \frac{1}{2} \langle d_{\mu s}^\dagger d_{\delta s'} \rangle \langle d_{\nu s'}^\dagger d_{\gamma s'} \rangle \right). \tag{82}
\]

Since the \( H^{HF}_{\text{int}} \) is a bilinear operator, it is straightforward to obtain

\[
\tilde{G}^{(\alpha)}(E) = \left( [G^{(\alpha)}(E)]^{-1} - H^{HF}_{\text{int}} \right)^{-1}, \tag{83}
\]

where the \( H^{HF}_{\text{int}} \) matrix elements are

\[
[H^{HF}_{\text{int}}]_{\nu s', \gamma s''} = \delta_{s, s'} \sum_\mu \sum_{s''} V_{\mu\nu\gamma\delta} \left( \langle d_{\mu s}^\dagger d_{\delta s''} \rangle \langle d_{\nu s'}^\dagger d_{\gamma s''} \rangle - H_{\mu\delta\gamma} \delta_{s, s'} \langle d_{\mu s}^\dagger d_{\delta s''} \rangle \right). \tag{84}
\]

The lesser Green’s function is given by

\[
\tilde{G}^< (E) = \tilde{G}^{(\alpha)}(E) \Sigma^< (E) \tilde{G}^{(\alpha)}(E) \tag{85}
\]

and the self consistent equations reads

\[
\langle d_{\mu s}^\dagger d_{\nu s'} \rangle = -i \int \frac{dE}{2\pi} \tilde{G}^{<}_{\nu s', \mu s}(E) = -i \delta_{s, s'} \int \frac{dE}{2\pi} \tilde{G}^{<}_{\nu s'}(E). \tag{86}
\]
Gauge invariance is shown to hold by the same arguments used in Section IV.

Eqs. (83), (85) and (86) provide the elements to write a power expansion of $I_\alpha$, in analogy to Section V. The non-local nature of the exchange interaction is encoded in Eqs. (81) and (82), and leads to a more involved self-consist scheme than that of Section IV.

VIII. CONCLUSIONS

We studied the nonlinear phase coherent quantum electronic transport properties of nanoscopic devices using the Nonequilibrium Green’s function method. This method allows us to express the $I-V$ characteristics of a given system to arbitrary powers of the applied voltages in terms of equilibrium Green’s functions. We show that the formalism is gauge invariant, provided that $U(r)$ is calculated self-consistently and the induced charge is well localized. The latter condition is key to partition the system as in Eq. (14), the starting point of our discussion.

We explicitly establish a connection between the NEGF method and the scattering approach. This is done by analyzing the first nonlinear contributions to the current, namely, $I_\alpha^{(2)}$. We show that $I_\alpha^{(2)}$ obtained by NEGF at the Hartree level reduces to the scattering matrix result in the Thomas-Fermi limit (and by using the wide band approximation). It should be noted that while in the scattering approach gauge invariance is used to construct the Poisson equation, NEGF renders gauge invariance automatically. These observations suggest that NEGF provides a framework for treating the many-body problem at a more accurate level of approximation. In Sec. VII we discuss the Hartree-Fock approximation, very amenable to treat with NEGF, but clearly unsuited to the scattering approach, which is restricted to local potentials.

We also analyze the electronic transport symmetry with respect to magnetic field inversion. In particular, we discuss the consequences of “microreversibility” for the conductance coefficients $G_{\alpha\beta}$... using the NEGF method for the second order coefficients. The general conclusions are the same as the ones obtained from the scattering approach. We then generalize to the theory arbitrary order in $V$, which is useful to address nonlinear transport experiments, such as Ref. 1.

In general, as the bias is increased, very quickly inelastic channels are opened. The inclusion of inelastic processes in the formalism and the development of approximation schemes to solve such problem is one of the next main goals to pursue.

Acknowledgments

We thank A. Wasserman for useful discussions. This work was supported by CNPq (Brazil), CAPES(Brazil), FAPERJ (Brazil), and the Harvard’s Institute of Quantum Science and Engineering.

1. A. Löfgren, C. A. Marlow, I. Shorubalko, R. P. Taylor, P. Omling, L. Samuelson, and H. Linke, Phys. Rev. Lett. 92, 046803 (2004).
2. C. A. Marlow, R. P. Taylor, M. Fairbanks, I. Shorubalko, and H. Linke, Phys. Rev. Lett. 96, 116801 (2006).
3. D. M. Zumbühl, C. M. Marcus, M. P. Hanson, and A. C. Gossard, Phys. Rev. Lett. 96, 206802 (2006).
4. R. Leturcq, D. Sánchez, G. Götz, T. Ihn, K. Ensslin, D. C. Driscoll, and A. C. Gossard, Phys. Rev. Lett. 96, 126801 (2006).
5. L. Angers, E. Zakka-Bajjani, R. Deblock, S. Guérón, H. Bouchiat, A. Cavanna, U. Gennser, and M. Polianski, Phys. Rev. B 75, 115309 (2007).
6. J. Wei, M Shimogawa, Z. Wang, I. Radu, R. Dormaier, and D. H. Cobden, Phys. Rev. Lett. 95, 256601 (2005).
7. A. Nitzan and M. A. Ratner, Science 300, 1384 (2003).
8. M. Büttiker, J. Phys. Condens. Matter 5, 9361 (1993).
9. T. Christen and M. Büttiker, Europhys. Lett. 35, 523 (1996).
10. D. Sánchez and M. Büttiker, Phys. Rev. Lett. 93, 106802 (2004).
11. M. L. Polianski and M. Büttiker, Phys. Rev. Lett. 96, 156804 (2006).
12. M. L. Polianski and M. Büttiker, Phys. Rev. B 76, 205308 (2007).
13. B. Wang, J. Wang, and H. Guo, J. Appl. Phys. 86, 5094 (1999).
14. Y. Xue, S. Datta, and M. A. Ratner, Chem. Phys. 281, 151 (2002).
15. B. Spivak and A. Zvyuzin, Phys. Rev. Lett. 93, 226801 (2004).
16. E. Deyo, B. Spivak, and A. Zvyuzin, Phys. Rev. B 74, 104205 (2006).
17. P. S. Damle, A. W. Ghosh, and S. Datta, Phys. Rev. B 64, 201403(R) (2001).
18. J. Taylor, H. Guo, and J. Wang, Phys. Rev. B 63, 245407 (2001).
19. F. Evers, F. Weigend, and M. Koentopp, Phys. Rev. B 69, 235411 (2004).
20. S. H. Ke, H. U. Baranger, and W. Yang, Phys. Rev. B 70, 085410 (2004).
21. D. I. Golosov and Y. Gefen, Phys. Rev. B 74, 205316 (2006); S. E. Nigg, R. Lopez, M. Büttiker, Phys. Rev. Lett. 97, 206804 (2006).
22. R. Landauer, in Nonlinearity in Condensed Matter, Ed. R. Bishop et al., (Springer, Berlin, 1987).
23. H. Bruus and K. Flensberg, Many-Body Quantum Theory in Condensed Matter Physics: An Introduction (Oxford University Press, 2004).
24. Z.-s. Ma, J. Wang, and H. Guo, Phys. Rev. B 57, 9108 (1998).
25. I. L. Aleiner, P.W. Brouwer, and L.I. Glazman, Phys. Rep.
26 A. Hernández, V. M. Apel, F. A. Pinheiro, and C. H. Lewenkopf, Physica A \textbf{385}, 148 (2007).
27 L. DiCarlo, C. M. Marcus, and J. S. Harris, Phys. Rev. Lett. \textbf{91}, 246804 (2003); M. Switkes, C. M. Marcus, K. Campman, and A. C. Gossard, Science \textbf{283}, 1905 (1999).
28 P. W. Brouwer, Phys. Rev. B \textbf{63}, 121303(R) (2001); M. Martínez-Mares, C. H. Lewenkopf, and E. R. Mucciolo, Phys. Rev. B \textbf{69}, 085301 (2004).
29 Y. Meir and N. S. Wingreen, Phys. Rev. Lett. \textbf{68}, 2512 (1992).
30 H. Haug and A.-P. Jauho, \textit{Quantum Kinetics in Transport and Optics of Semiconductors} (Springer, New York, 1996).
31 M. Koentopp, C. Chang, K. Burke, and R. Car, J. Phys.: Condens. Matter \textbf{20}, 083203 (2008). M. Koentopp, K. Burke and F. Evers, Phys Rev B \textbf{73}, 121403(R) (2006).
32 M. Cini, Phys. Rev. B \textbf{22}, 5887 (1980)
33 G. Stefanucci and C.-O. Almbladh, Europhys. Lett. \textbf{67}, 14 (2004).
34 M. Büttiker, IBM J. Res. Dev. \textbf{32}, 317 (1988).
35 D. S. Fisher and P. A. Lee Phys. Rev. B \textbf{23}, 6851 (1981).
36 L. Onsager, Phys. Rev. \textbf{38}, 2265 (1931); H. B. G. Casimir, Rev. Mod. Phys. \textbf{17}, 343 (1945).
37 M. Büttiker, Phys. Rev. Lett. \textbf{57}, 1761 (1986).
38 A. D. Benoit, S. Washburn, C. P. Umbach, R. B. Lai- bowitz, and R. A. Webb, Phys. Rev. Lett. \textbf{57}, 1765 (1986).
39 A. Yacoby, M. Heiblum, D. Mahalu, and H. Shtrikman, Phys. Rev. Lett. \textbf{74}, 4047 (1995); A. Yacoby, R. Schuster, and M. Heiblum, Phys. Rev. B \textbf{53}, 9583 (1996).
40 A. L. Yeyati and M. Büttiker, Phys. Rev. B \textbf{52}, R14 360 (1995).
41 I. B. Levinson, Sov. Phys. JETP \textbf{68}, 1257 (1989).
42 D. Andrieux and P. Gaspard, J. Stat. Mech. P02006 (2007); J. Chem. Phys. \textbf{121} 6167 (2004).
43 C. Mahaux and H. A. Weidenmüller, \textit{Shell-model Approach to Nuclear Reactions} (North Holland, Amsterdam, 1969).
44 We adopt the convention that a trace in an expression involving $S$-matrices refers to sums over channels $a \in \alpha$ and $b \in \beta$, whereas traces over Green’s functions are taken over the conductor states \{\mu\}.