



# Non-equilibrium linear-response transport through quantum dot beyond time homogeneity at Hartree–Fock level

Miloš S. Dražić\*, Viktor Z. Cerovski, and Radomir Žikić

Institute of Physics Belgrade, University of Belgrade, Pregrevica 118, 11080 Belgrade, Serbia

Received 30 September 2013, revised 9 March 2014, accepted 15 April 2014

Published online 31 May 2014

**Keywords** Hartree–Fock approximation, linear response, non-equilibrium Green's functions, quantum transport, time homogeneity

\* Corresponding author: e-mail milosdrazic@gmail.com, Phone/Fax: +381 11 2691 773

The expression for current, induced by finite bias with additional time-dependent (TD) external perturbation, through a molecule/dot is derived using the non-equilibrium Green's function (GF) formalism in the standard two-probe geometry. The GFs as well as self energies (SEs) are split into time-homogeneous (TH) and time-inhomogeneous (TIH) contributions, where the former are obtained as a result of zeroth-order expansion of the full, two-time corresponding quantities and the latter we find as linear corrections. The TD charge in the dot consists of a charge that is injected from the electrodes and the charge that is induced in the dot. The TD potential, induced in the dot due to dot TD charge, was treated self consistently at Hartree–Fock (HF) level as a TIH part of Coulomb interaction related SE. It is assumed that TH quantities are solved either exactly or approximately, i.e., using density functional theory (DFT). The theory is charge conserving and its gauge invariance is explicitly shown. The contribution of TD

HF potential to the total Coulomb interaction energy vanishes in the case of one-electron existence, i.e., the self-interaction error (SIE), beyond the one associated with the DFT, was not introduced. Known results in a special case of time homogeneity are recovered and extended to TIH transport. The issues of current partitioning and the displacement current are resolved naturally, without any additional assumptions about any of quantities, due to explicit inclusion of dot potential. The special cases of wide-band limit, zero bias, and zero-bias wide-band limit are also considered and in each case the corresponding expression for the TD current is derived. The theory is particularly suitable for use in connection with DFT when it provides a first-principle microscopic linear-response description of the non-equilibrium TIH quantum transport useful for calculation of TD current through quantum dots, molecules, junctions, or devices at the nano-scale.

© 2014 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

**1 Introduction** One of the main challenges of the microscopic description of current flow through a quantum system is how to treat Coulomb interaction. Since the pioneering work of Landauer [1], the scattering formalism was used to formulate the theory of transport through quantum-coherent systems coupled to electronic reservoirs. In the equilibrium case, the transport is described using the concept of conducting channels, directly related to the conductance of the system [2, 3]. In the non-equilibrium case, the approach was extended to the non-equilibrium quantum-coherent case in the mesoscopic regime using the scattering formalism in the presence of a time-dependent (TD) potential of small frequency for quantum dots, which intra-dot

interaction is treated at the Hartree (random phase approximation, RPA) level [4], leading to the recent experimental finding of the quantization of conductance in the alternating current regime [5]. The quantum mesoscopic system in the presence of the incoherent scattering was studied as well, extending results to the case of dephasing processes, using the formalism of non-equilibrium Green's functions (NEGFs) [6], which was also used to formulate a current-conserving gauge-invariant theory without explicit treatment of TD potential induced by TD injected charge [7]. The connection between the scattering and NEGF results for electronic current in the Hartree case has been established as well [8].

The treatment of non-equilibrium transport in the finite-bias stationary state by combining NEGFs and density functional theory (DFT) has also been used to numerically compute conductance and direct current [9–11], by expressing electronic density through NEGFs and treating Coulomb interaction at the DFT level, through Hartree and (semi-)local exchange-correlation (XC) functionals.

The DFT can be used so that GFs are associated directly with the effective one-particle, Kohn–Sham (KS) Hamiltonian. From the equations of motion of the GFs, the treatment of interaction also includes an expansion of the two-particle GF to obtain the interaction self energy (SE) [12], while the conservation relations [13, 14] provide a specific form of the SE. All higher orders of the two-particle GF expansion beyond the Hartree contribution lead to the spatially non-local SE, which is furthermore time non-local beyond the Fock contribution [15]. Our approach is to make a connection between time-homogeneous (TH) and time-inhomogeneous (TIH) parts of GFs and consequently TH and TIH parts of all relevant quantities derived from GFs using the Keldysh technique [15, 16] applied to the Kadanoff–Baym (KB) formalism [12–14]. Assuming that the ratio between amplitude of the TD voltage and frequency is much smaller than  $\hbar/e$ , where  $\hbar$  is Planck's constant and  $e$  elementary charge, it is possible to neglect the voltage-nonlinear contribution to the current [6, 17]. We adopted the picture in Ref. [18], where it was assumed that due to good screening properties of the electrodes, a time-varying field causes a spatially homogeneous shift of energy levels in the electrodes. This picture is spoiled when the driving frequency exceeds the metallic plasma frequency. For this reason, the sudden application of the TD voltage cannot be described properly within our approach. The TD voltage rise time has to be slower than the plasma frequency period. The coupling of DFT and NEGFs is achieved through the DFT treatment of the TH contribution of the GFs, while the KB/NEGF approach provides the TIH part of the interaction SE, which is just the TD potential in the dot, calculated self consistently at the Hartree–Fock (HF) level. The starting point is the standard partitioning scheme where the Hamiltonian of the whole system is represented by separate Hamiltonians of electrode, dot, and junction regions [18, 19].

It is not necessary to consider the equation of motion of GFs in order to describe the steady-state regime, where it is possible to work directly with the matrix equation in the energy domain. The GF of the whole system is the resolvent of the total Hamiltonian; the connection between block matrices, associated with subsystems and contained in the equation, provides relevant equations for the dot, electrode, and junction regions; and, the junction SE is obtained as a function of surface (isolated electrode) GF, hopping, and mixed overlap matrices [9, 11]. In the non-steady regime working with the equation of motion is very useful because it facilitates computations with two-particle GFs [12, 15], and for this reason we use creation/annihilation operators of orthogonal states in the second quantization [6, 7, 18].

Working with two-particle GFs allows us to trivially demonstrate the current conservation, i.e., validity of the continuity equation, using the GF equation of motion. In order to satisfy the request of current conservation (as well as momentum and energy conservation), the approximate SE, stemming from two-particle GF expansion, has to take particular forms [13, 14]. Therefore, some basic physics was preserved, and the need for current-conserving theory was the motive for introducing the DFT, coupled with NEGFs, in our description. Namely, combining the two methods, treating the steady state in one way (DFT) and the TD contribution in another way, i.e., using HF expansion of the two-particle GFs and keeping its TIH part, provides the current conservation, as we will demonstrate explicitly. In addition to being current conserving, our approach is advantageous compared with Hartree self-consistent treatment of the TD internal potential, because the HF potential does not introduce a self-interaction error (SIE). Namely, the energy of the Coulomb interaction, within the linear-response description of TD systems, consists of contributions associated with time-independent and TD charge density that interact via TH, Coulomb interaction related, SE and contributions due to time-independent charge density that interact via TIH, Coulomb interaction related, SE. Within the proposed scheme, TH GFs are treated in the DFT manner, while the linear TIH corrections are adopted from perturbation expansion in the HF approximation. The consequences of such approximation are a replacement of TH SE by the Hartree plus exchange-correlation (H + XC) part of the KS Hamiltonian. In the one-electron case, the first two contributions are not zero (constant), which is the intrinsic DFT property, i.e., SIE, but the third term goes to zero, due to cancelation of Hartree and Fock contributions. The need for the current-conserving description, as well as the possibility of self-interaction-free TD transport theory, was a motivation for us to propose this hybrid approach.

The rest of the paper is organized as follows: in Section 2, the model and notation are introduced; the equation of motion of GFs in the presence of an external TD potential is discussed; in Section 3, the connections between TIH and TH quantities are established and a set of equations for their determination is derived, while the use of DFT to calculate TH quantities is discussed in Section 3.1; in Section 3.2, we point out the SIE problem as well as the benefit of our method associated with SIE reduction; in Section 4, expressions for both direct (Section 4.1) and alternating (Sections 4.2 and 4.3) currents are derived, and the solution to the current-partitioning problem within the theory is also given; gauge invariance of the obtained expressions is shown in Section 4.3; special cases of wide-band limit (WBL), zero bias, and zero-bias WBL are considered in Section 5, where corresponding expressions for TD current in each of the three cases are derived; and, Section 6 summarizes the main results of the paper.

**2 Hamiltonian** The standard model of two probes with TD energy levels coupled to a quantum dot (molecule),

described by the Hamiltonian

$$H = H_L + H_{LD} + H_D + H_{RD} + H_R, \quad (1)$$

is considered, where  $H_{L/R}$  are Hamiltonians of the left/right lead,  $H_D$  is the dot Hamiltonian, and  $H_{LD/RD}$  are Hamiltonians describing the interaction of the left/right lead and the dot, which in the second quantization take the following forms:

$$H_\alpha = \sum_{k\alpha} \epsilon_{k\alpha}(t) c_{k\alpha}^\dagger c_{k\alpha}, \quad (2)$$

$$H_D = \sum_{nm} \epsilon_{nm} d_n^\dagger d_m + \frac{1}{2} \sum_{mnkl} W_{mn,kl} d_m^\dagger d_n^\dagger d_l d_k, \quad (3)$$

$$H_{\alpha D} = \sum_{k\alpha,n} (V_{k\alpha,n} c_{k\alpha}^\dagger d_n + \text{h.c.}), \quad (4)$$

where  $k$  is a wave vector such that  $k\alpha$  counts eigenstates of the probe  $\alpha = L, R$ ; the index  $n$  labels basis vectors of the dot, the Hamiltonian  $H_D$  is assumed to be Hermitian, represented in a basis  $\{\phi_n(\mathbf{r})\}$ , with particles interacting via two-particle interaction described by the matrix  $W$ , while the spin indices are not written since it is assumed that the system is non-magnetic. Creation and annihilation operators in the dot,  $d_n(t)$  and  $d_n^\dagger(t)$ , respectively, as well as creation and annihilation operators in the leads,  $c_{k\alpha}(t)$  and  $c_{k\alpha}^\dagger(t)$ , respectively, all satisfy fermionic commutation relations, while operators of the dot and leads anti-commute, i.e.,  $\{c_{k\alpha}^\dagger(t), d_n^\dagger(t)\} = 0$ . We set  $\hbar = 1$  hereafter to simplify notation without loss of generality. One-particle, kinetic with additional external potential, energy matrix elements are

$$\epsilon_{nm} = \int d\mathbf{r} \phi_n^*(\mathbf{r}) \left( -\frac{1}{2m} \Delta_{\mathbf{r}} + u(\mathbf{r}) \right) \phi_m(\mathbf{r}) \quad (5)$$

and the Coulomb repulsion of electrons is represented via matrix elements of  $W$  as

$$W_{mn,kl} = e^2 \int d\mathbf{r} \int d\mathbf{r}' \frac{\phi_m^*(\mathbf{r}) \phi_n^*(\mathbf{r}') \phi_k(\mathbf{r}) \phi_l(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (6)$$

It is furthermore adopted that the standard assumption is that the two probes do not interact one with another and that the only interaction between the probes and the dot is through the coupling  $V_{k\alpha,n}$ , typically representing tunneling amplitudes across the junction between lead  $\alpha$  and the molecule D.

**3 Time dependence** An externally applied voltage in the lead  $\alpha$ ,  $V_\alpha(t)$ , induces time dependence of probe energy levels  $\epsilon_{k\alpha} = \epsilon_{k\alpha}(t)$ , thus making  $H$  time dependent as well. As a consequence, the first concern is how this introduces TD potential in the dot, and it is analyzed by using Dyson's equation. The GF of  $H_D$  is

$$G_{nm}(t, t') = -i \langle T_C d_n(t) d_m^\dagger(t') \rangle, \quad (7)$$

where  $d_n$  ( $d_m^\dagger(t')$ ) is an annihilation (creation) operator in the Heisenberg picture, and the time ordering  $T_C$  is on the Keldysh contour  $C$ , where also lie time arguments [15, 16]. The equation of motion of  $d_n$  is

$$i \dot{d}_n(t) = [d_n(t), H(t)]. \quad (8)$$

The evaluation of the commutator is simplified because  $[d_n(t), H_\alpha] = 0$  due to  $\{d_n(t), c_{k\alpha}(t)\} = 0$ . The commutator  $[d_n(t), H_{\alpha D}(t)]$  gives a contribution to the SE of the junction, while  $[d_n(t), H_D(t)]$  gives SE coming from the interaction part of  $H_D$  (the second sum of Eq. (3)). The junction SE,  $\Sigma^{\text{jnc}}$ , comes from its surface GF [18],

$$g_{k\alpha}(t, t') = -i \langle T_C c_{k\alpha}^{(H_\alpha)}(t) c_{k\alpha}^{(H_\alpha)\dagger}(t') \rangle, \quad (9)$$

where operators are in the Heisenberg picture according to the electrode Hamiltonian  $H_\alpha(t)$ , while the dot-interaction SE time dependence comes from the two-particle GF [12]

$$G_2(nt, mt', n_1 t_1, m_1 t'_1) = (-i)^2 \langle T_C d_n(t) d_m(t') d_{m_1}^\dagger(t'_1) d_{n_1}^\dagger(t_1) \rangle. \quad (10)$$

The last GF can be in principle represented as a one-particle GF multiplying the dot-interaction SE  $\Sigma^{\text{int}}$  that is generally difficult to calculate. The standard assumption of non-interacting electrons in the leads is used, while the dot interaction remains Coulomb. Therefore, TD potential will exist in the dot due to potentials in electrodes coupled to the dot, which can be in principle found knowing  $\Sigma^{\text{int}}$ . It is important to emphasize that, due to the coupling of the dot and probes, the TD potential introduced in the probes will make the dot-interaction GF and the SE time dependent. Therefore, the problem is approached by decomposing all quantities into TH and TIH parts [6], expanding the two-particle GF up to the Hartree–Fock level [12], and then treating the TH parts of the obtained expressions using a different theory, in this case DFT [20–22], which solves, in principle exactly or in practice approximately, ground-state properties of interacting electrons in the dot through KS single-particle solutions. In other words, a perturbative technique is used to find the TD potential in the dot (related to TIH  $\Sigma^{\text{int}}$ ), while DFT deals with the Coulomb interaction in the dot (related to TH  $\Sigma^{\text{int}}$ ).

The TH part of  $\Sigma^{\text{int}}$  can be taken into account by decomposing it into the HF local part and the non-local remainder [15]:

$$\Sigma^{\text{int}}(t, t') = \Sigma^{\text{int, HF}}(t, t') \delta(t - t') + \Sigma^{\text{int, >}}(t, t') \theta(t - t') + \Sigma^{\text{int, <}}(t, t') \theta(t' - t), \quad (11)$$

obtained from the expansion of the two-particle GF, where the lowest-order term gives the HF part, and the remaining two terms contain the contribution from the two-particle interaction.

The concern is with the linear-response regime, where Dyson's equation for the TIH part is derived assuming that the



TIH contribution is small and depends on time-varying voltage up to the linear term [6, 8], giving the following equation of motion of the GF, written in matrix form as

$$i \frac{\partial G(t, t')}{\partial t} = \delta(t - t') I + \varepsilon G(t, t') + \int_C dt_1 \Sigma(t, t_1) G(t_1, t'), \quad (12)$$

where  $I$  is the unity matrix, and  $\Sigma$  is the total SE, which can be split into the interaction and junction parts,  $\Sigma = \Sigma^{\text{int}} + \Sigma^{\text{jnc}}$ , with the following equations for each contribution:

$$\begin{aligned} \sum_l \int_C dt_1 \Sigma_{nl}^{\text{int}}(t, t_1) G_{lm}(t_1, t') \\ = -i \sum_{jkl} W_{njl} G_2(kt, lt; mt', jt'), \end{aligned} \quad (13)$$

$$\Sigma_{nl}^{\text{jnc}}(t, t_1) = \sum_{k\alpha} V_{k\alpha, n}^* g_{k\alpha}(t, t_1) V_{k\alpha, m}, \quad (14)$$

where Eq. (13) describes the intra-dot Coulomb interaction of electrons, Eq. (14) describes the coupling between the dot and leads, and  $g$  is the surface GF, Eq. (9). The time argument  $t^+$  means  $t + \delta$  for infinitesimal  $\delta > 0$ , and the time integration is along the Keldysh contour  $C$ . Similarly, both  $G$  and  $\Sigma$  are decomposed into TH and TIH parts:

$$G(t, t') = G^h(t - t') + G^i(t, t'), \quad (15)$$

$$\Sigma(t, t') = \Sigma^h(t - t') + \sigma(t, t'). \quad (16)$$

Equation (15) allows separation of the equation of motion of the GF, Eq. (12), into two equations, for TH and TIH parts,

$$\begin{aligned} i \frac{\partial G^h(t - t')}{\partial t} = \delta(t - t') I + \varepsilon G^h(t - t') \\ + \int_C dt_1 \Sigma^h(t - t_1) G^h(t_1 - t'), \end{aligned} \quad (17)$$

$$\begin{aligned} i \frac{\partial G^i(t, t')}{\partial t} = \varepsilon G^i(t, t') + \int_C dt_1 \Sigma^h(t - t_1) G^i(t_1, t') \\ + \int_C dt_1 \sigma(t, t_1) G^h(t_1 - t') \end{aligned} \quad (18)$$

with the following particular solution for the TIH part:

$$G^i(t, t') = \int_C dt_1 \int_C dt_2 G^h(t - t_1) \sigma(t_1, t_2) G^h(t_1 - t'). \quad (19)$$

The TIH SE of the junction,  $\sigma^{\text{jnc}}(t, t')$ , directly follows from Eq. (14),

$$\sigma_{mn}^{\text{jnc}}(t, t') = \sum_{k\alpha} V_{k\alpha, m}^* g_{k\alpha}^i(t, t') V_{k\alpha, n}, \quad (20)$$

where the TIH part is now contained in the surface GF. Evolution of  $g$  in the Heisenberg picture of  $H_\alpha$  is given by

$$\begin{aligned} g_{k\alpha}(t, t') = \theta(t - t') (-i) \langle c_{k\alpha} c_{k\alpha}^\dagger \rangle e^{-i(\epsilon_{k\alpha}(t - t') + \int_{t'}^t d\tau V_\alpha(\tau))} \\ + \theta(t' - t) i \langle c_{k\alpha}^\dagger c_{k\alpha} \rangle e^{-i(\epsilon_{k\alpha}(t' - t) + \int_t^{t'} d\tau V_\alpha(\tau))} \end{aligned} \quad (21)$$

with retarded, advanced, and lesser GFs given by

$$\begin{aligned} g_{k\alpha}^R(t, t') &= -i\theta(t - t') d^{-i\epsilon_{k\alpha}(t - t')} \\ &\quad - i\theta(t - t') d^{-i\epsilon_{k\alpha}(t - t')} \sum_{n=1}^{\infty} \frac{(-i)^n}{n!} \left( \int_{t'}^t d\tau V_\alpha(\tau) \right)^n, \\ g_{k\alpha}^A(t, t') &= i\theta(t' - t) e^{-i\epsilon_{k\alpha}(t - t')} \\ &\quad + i\theta(t' - t) e^{-i\epsilon_{k\alpha}(t - t')} \sum_{n=1}^{\infty} \frac{(-i)^n}{n!} \left( \int_t^{t'} d\tau V_\alpha(\tau) \right)^n, \\ g_{k\alpha}^<(t, t') &= i \langle c_{k\alpha}^\dagger c_{k\alpha} \rangle e^{-i\epsilon_{k\alpha}(t - t')} \\ &\quad + i \langle c_{k\alpha}^\dagger c_{k\alpha} \rangle e^{-i\epsilon_{k\alpha}(t - t')} \sum_{n=1}^{\infty} \frac{(-i)^n}{n!} \left( \int_{t'}^t d\tau V_\alpha(\tau) \right)^n. \end{aligned} \quad (22)$$

Within the linear-response regime, we keep only the first term ( $n = 1$ ) of each series, which gives the TIH part of SE, Eq. (14), expressed through the TH part

$$\sigma^\gamma(t, t') = -i \sum_\alpha \int_{t'}^t d\tau V_\alpha(\tau) \Sigma_\alpha^{\gamma h}(t - t'), \quad (23)$$

where  $\gamma$  stands for R, A, or  $<$ . Furthermore, assuming that the leads contain non-interacting fermions, we can associate a Fermi distribution with the average number of electrons in a single-particle state  $k\alpha$ :

$$\langle c_{k\alpha}^\dagger c_{k\alpha} \rangle = f_\alpha(\epsilon_{k\alpha}). \quad (24)$$

Now that TIH junction SEs are expressed in the linear-response approximation, attention is paid to  $\Sigma^{\text{int}}$ . As announced, it will be treated in the HF approximation [12],

$$\begin{aligned} G_2(kt, lt; mt', jt') &\approx G_{km}(t, t') G_{lj}(t, t') \\ &\quad - G_{kj}(t, t') G_{lm}(t, t'), \end{aligned} \quad (25)$$

where two terms on the right-hand side represent, respectively, the Hartree and the Fock terms. Inserting this approximate expression into Eq. (13), we get the interaction

SE in the HF approximation

$$\Sigma_{nl}^{\text{int}}(t, t_1) = \delta(t - t_1) \sum_{jk} (2W_{njlk} - W_{njkl}) \langle d_j^\dagger(t) d_k(t_1) \rangle. \quad (26)$$

The result is time local, as expected within the HF approximation, and can be conveniently expressed as

$$\Sigma_{nl}^{\text{int}}(t, t) = -i \sum_{jk} (2W_{njlk} - W_{njkl}) G_{kj}^<(t, t). \quad (27)$$

Prior to the further derivation, a remark about Eq. (19) will be made. It is a linear TD correction to the zeroth-order TH GF due to external TD perturbation  $\sigma^{\text{jnc}}$  and induced field  $\sigma^{\text{int}}$ , and the total TD SE can be recognized as the effective field in the dot. This is analogous to the random phase approximation (RPA) [23], the difference being that the explicit external potential influences the dot through the junction TIH SE, Eq. (23), and that the induced field is TD HF while in the RPA it is TD Hartree potential. The induced field can be understood as a shielding potential that screens the particle interaction [23]. Then, non-inclusion of short-range effects in RPA leads to the overestimation of the screening.

Our aim is to find the TIH part of the HF SE, using the decomposition  $G^<(t, t') = G^{<\text{h}}(t - t') + G^{<\text{i}}(t, t')$ . Obviously, the TIH part of the interaction SE is related to the TIH lesser GF through

$$\sigma_{nm}^{\text{int}}(t, t) = -i \sum_{jk} (2W_{njmk} - W_{njkm}) G_{kj}^{<\text{i}}(t, t), \quad (28)$$

while another connection is provided by applying Langreth rules [16] on Eq. (19), leading to

$$\begin{aligned} G^{<\text{i}}(t, t) = & \iint dt_1 dt_2 [G^{\text{Rh}}(t - t_1) \sigma^{\text{R}}(t_1, t_2) G^{<\text{h}}(t_2 - t) \\ & + G^{\text{Rh}}(t - t_1) \sigma^{<}(t_1, t_2) G^{\text{Ah}}(t_2 - t) \\ & + G^{<\text{h}}(t - t_1) \sigma^{\text{A}}(t_1, t_2) G^{\text{Ah}}(t_2 - t)] \\ & + \int dt_1 [G^{\text{Rh}}(t - t_1) \sigma^{\text{int}}(t_1, t_1) G^{<\text{h}}(t_1 - t) \\ & + G^{<\text{h}}(t - t_1) \sigma^{\text{int}}(t_1, t_1) G^{\text{Ah}}(t_1 - t)]. \end{aligned} \quad (29)$$

The first term can be interpreted as the contribution to the TD charge density in the dot due to charge injection, as a consequence of the external TD potentials, while the second term is the charge density induced as a response, which depends on the internal, screening HF potential. Finally, lesser TH GFs are expressed through the Keldysh equation [16, 18], valid for a non-interacting system

$$G^{<}(t - t') = \iint dt_1 dt_2 G^{\text{R}}(t - t_1) \Sigma^{<}(t_1 - t_2) G^{\text{A}}(t_2 - t'). \quad (30)$$

From the expressions derived so far, it is possible to formulate a self-consistent scheme for deriving the dot potential, Eq. (28): what is needed is the TIH part of the lesser GF, Eq. (29), which depends on TH retarded, advanced, and lesser GFs, TIH retarded, advanced, and lesser junction SEs as well as TIH interaction SE, i.e., the TD dot potential. This brings us back to Eq. (28) as the new input for Eq. (29). The TH expression for SE, Eq. (23), as a consequence of the linear-response approximation, provides the TIH junction SE, contained in Eq. (29), and the TH lesser GF, also included in Eq. (29), is through Eq. (30) described in terms of TH retarded and advanced GFs, and TH lesser junction SE.

### 3.1 Time-homogeneous quantities of the dot

The set of equations derived in the previous section forms the basis for alternating current calculation, where TIH quantities are reduced to TH quantities. Now the TH quantities, that is, TH dot's GF and TH isolated electrode's GF, are addressed, where the latter will provide the TH junction SE.

Fourier transformation (FT) of the equation of motion of the TH GF, Eq. (17), gives the well-known result

$$G(E) = (E - \varepsilon - \Sigma^{\text{jnc}} - \Sigma^{\text{int}})^{-1}. \quad (31)$$

At this point, DFT can be used to provide an effective single-electron Hamiltonian, the so-called KS Hamiltonian, of the system in the ground state, by mapping an interacting to an effective non-interacting, KS electronic system. This system is influenced by a (semi-)local potential generated from the electron density. The potential consists of external, Hartree, and exchange-correlation (XC) contributions. The key point here is that the GF related to  $H_{\text{eff}}$  and the GF related to the KS Hamiltonian provide densities that are equal. This feature has a benefit as it allows the use of the GF related to the KS Hamiltonian to find the density, Eq. (55). At the same time, a determinantal (Slater) shape of the many-electron function can be used due to an effectively non-interacting description.

The KS states, which build the Slater determinant, are solutions of the following eigenproblem [20]:

$$\left(-\frac{1}{2m} \Delta + u[n] + v_{\text{H}}[n] + v_{\text{XC}}[n]\right) \phi_{\mu}^{\text{KS}}(\mathbf{r}) = \varepsilon_{\mu}^{\text{KS}} \phi_{\mu}^{\text{KS}}(\mathbf{r}), \quad (32)$$

where  $n$  is the electron density  $n(\mathbf{r}) = \sum_{\mu} |\phi_{\mu}^{\text{KS}}(\mathbf{r})|^2$ , with corresponding GF

$$G = (E - \varepsilon^{\text{KS}} - \Sigma^{\text{jnc}})^{-1}. \quad (33)$$

The KS matrix elements in the dot basis are

$$\varepsilon_{nm}^{\text{KS}} = \int d\mathbf{r} \phi_n^*(\mathbf{r}) \left(-\frac{1}{2m} \Delta_{\mathbf{r}} + u + v_{\text{H}} + v_{\text{XC}}\right) \phi_m(\mathbf{r}). \quad (34)$$

KS orbitals can be expanded in an orthonormal basis  $\{\phi_n(\mathbf{r})\}$  of the dot,

$$\phi_\mu^{\text{KS}}(\mathbf{r}) = \sum_n C_{n\mu} \phi_n(\mathbf{r}), \quad (35)$$

where orthonormality provides the constraint that expansion coefficients in Eq. (35) have to satisfy [24]:

$$\sum_{nm} C_{n\beta}^* \varepsilon_{nm}^{\text{KS}} C_{m\alpha} = \varepsilon_{\alpha\beta}^{\text{KS}} \delta_{\alpha\beta}, \quad \sum_n C_{n\beta}^* C_{n\alpha} = \delta_{\alpha\beta}. \quad (36)$$

What remains is to find a description of the junction SE, which depends on the isolated electrode's GF. In practice, this is the first step in obtaining the dot GF [25]. The iterative procedure developed in Ref. [9] then finds the initial electron density from the electric field between the electrodes at the Hartree level, providing the initial KS Hamiltonian matrix, Eq. (32). The matrix and junction SE determine the initial GF, Eq. (33), which is then used to calculate the density matrix  $D$  and from it the electron density  $n = \text{Tr } D$ . The process is then iteratively repeated until the convergence of  $n$ . The scheme remains valid in the present theory as well, insofar as it solves the Hartree part of the problem and with it the associated direct current, to which we will return in Section 4.1.

**3.2 Self interaction** The reducing of SIE will be demonstrated. It is necessary to find the Coulomb interaction related potential energy. By observing Eqs. (17) and (18), it is possible to find the total energy by taking the trace of the time derivative of lesser GFs over the first time argument, repeating the same procedure with the time derivative over the second time argument, and finding the difference of the obtained derivatives [12]. The total energy will include kinetic, lead-dot interaction, and Coulomb interaction energies. For the last, it can be found that

$$E_{\text{int}}(t) \sim \text{Tr} \int dt' [(\Sigma^{\text{int}}(t, t') G(t', t))^< + (G(t, t') \Sigma^{\text{int}}(t', t))^<]. \quad (37)$$

Decomposing both  $G$  and  $\Sigma^{\text{int}}$  into TH and TIH parts, Eqs. (15) and (16), adopting the DFT description of TH GF and SE, and treating the TIH SE at the HF approximation, it can be observed that Eq. (37) consists of the following parts: (i) a contribution due to stationary (obtained from lesser TH GF) charge interacting via effective H + XC potential

$$\text{Tr}[(\varepsilon_{\text{H}}^{\text{KS}} + \varepsilon_{\text{XC}}^{\text{KS}}) G^<],$$

(ii) a contribution due to dynamic (obtained from lesser TIH GF) charge interacting via effective H + XC potential

$$\text{Tr}[(\varepsilon_{\text{H}}^{\text{KS}} + \varepsilon_{\text{XC}}^{\text{KS}}) G^<^{\text{i}}(t, t)],$$

(iii) a contribution due to stationary charge interacting via internal HF time-dependent potential

$$\text{Tr}[\sigma^{\text{int}}(t, t) G^<].$$

Taking the existence of one electron only, it is, recalling Eq. (28), possible to straightforwardly see that the third contribution is zero (the prefactor 2 at the Hartree term came because of spin summation, but in the single-electron case this summation does not exist). The problem of SIE remains due to the fact that in DFT, moving of a single electron is influenced by the external potential, i.e., the junction SE, but also to a certain extent by H + XC potential. This is in contrast to the physical picture, in which this potential would have to be constant (there should be no Coulomb force acting on the single electron), namely,

$$\begin{aligned} v_{\text{eff}}(\mathbf{r}) &= v_{\text{H}}(\mathbf{r}) + v_{\text{X}}(\mathbf{r}) + v_{\text{C}}(\mathbf{r}); \\ v_{\text{H}}(\mathbf{r}) + v_{\text{X}}(\mathbf{r}) &= \text{const.}; \\ v_{\text{C}}(\mathbf{r}) &= 0. \end{aligned} \quad (38)$$

If this were satisfied, then the first two contributions to the interaction energy would be

$$\text{const.} \sum_{n,m} \delta_{nm} G^<(t, t)_{mn} = \text{const.}, \quad (39)$$

where the unity value of the trace of the total lesser GF was taken, according to the existence of one electron only. In order to avoid the problem of SIE, the DFT SIC scheme [26, 27] (SIC – self-interaction correction) has to be adopted. In that case, the first and the second contributions could be zero (constant), and this is what knowing the exact functionals guarantees. However, it is important to point out that even in the case of DFT that is free of SIE, the linear-response, time-dependent theory would be free of SIE only within the proposed HF treatment of the time-dependent internal potential. Throughout the rest of the paper the symbol for SE (TH, TIH, or total) means junction SE, unless otherwise noted.

**4 Current** Electrical current originates in the leads that are kept at a finite potential difference, the externally controlled bias  $V$ , where additionally the potential  $V_\alpha$  of lead  $\alpha$  changes in time. The standard adopted assumption is of non-interacting Fermi-distributed electrons in the leads when the difference in chemical potentials between the left and the right electrodes is due to the bias, i.e.,  $\mu_L - \mu_R = eV$ . At some time, assumed to be in the remote past, reservoirs providing electrons to the leads are exposed to the influence of time-dependent potential. The total electron flow through the system then is the sum of the time-independent currents due to the finite bias and the time-dependent currents due to the varying potential, which were each determined separately, starting from the definition of the electrical current in

the lead  $\alpha$ :

$$I_\alpha(t) = -e \frac{d}{dt} \langle N_\alpha(t) \rangle = -ie \langle [H(t), N_\alpha(t)] \rangle, \quad (40)$$

where  $N_\alpha(t) = \sum_{k\alpha} c_{k\alpha}^\dagger(t) c_{k\alpha}(t)$  is the total number of electrons in the lead  $\alpha$ . The evaluation of the commutator in Eq. (40) gives

$$I_\alpha(t) = ie \sum_{kn} (V_{k\alpha,n} \langle c_{k\alpha}^\dagger(t) d_n(t) \rangle - V_{k\alpha,n}^* \langle d_n^\dagger(t) c_{k\alpha}(t) \rangle). \quad (41)$$

The last sum can be expressed with the lesser form of the mixed GF, which involves analytical continuation on the real-time axis [16], transforming Eq. (41) into

$$I_\alpha(t) = 2e \int_{-\infty}^t dt' \text{Tr} [G^R(t, t') \Sigma_\alpha^<(t', t) + G^<(t, t') \Sigma_\alpha^A(t', t) - \Sigma_\alpha^R(t, t') G^<(t', t) - \Sigma_\alpha^<(t, t') G^A(t', t)]. \quad (42)$$

Double counting, due to spin summation, is included in the above equation. Partitioning of GFs and SEs into TH and TIH parts done in Section 3 gives two contributions to the total current  $I_\alpha(t)$ , namely a time-independent direct current (DC)  $I_\alpha$  and a time-dependent alternating current (AC)  $i_\alpha(t)$ , respectively, as follows:

$$I_\alpha(t) = I_\alpha + i_\alpha(t), \quad (43)$$

$$I_\alpha = 2e \int dt' \text{Tr} [G^R(t-t') \Sigma_\alpha^<(t'-t) + G^<(t-t') \Sigma_\alpha^A(t'-t) - \Sigma_\alpha^R(t-t') G^<(t'-t) - \Sigma_\alpha^<(t-t') G^A(t'-t)], \quad (44)$$

$$i_\alpha(t) = 2e \int dt' \text{Tr} [G^R(t, t') \Sigma_\alpha^<(t'-t) + G^R(t-t') \sigma_\alpha^<(t', t) + G^<(t-t') \sigma_\alpha^A(t', t) - \Sigma_\alpha^R(t-t') G^<(t', t) - \sigma_\alpha^R(t, t') G^<(t'-t) - \Sigma_\alpha^<(t-t') G^A(t', t) - \sigma_\alpha^<(t, t') G^A(t'-t)], \quad (45)$$

where the index  $\alpha$  denotes the contribution from the lead  $\alpha$ . Langreth rules [16] provide the retarded and advanced forms of the TIH contribution of the dot GF, Eq. (19), as

$$G^{\gamma i}(t, t') = \iint dt_1 dt_2 G^{\gamma h}(t-t_1) [\sigma^{\gamma}(t_1, t_2) + \sigma^{\text{int}}(t_1, t_2) \delta(t_1 - t_2)] G^{\gamma h}(t_2 - t'), \quad (46)$$

where  $\gamma$  stands for R or A. Note that in this expression all one- and two-time quantities correspond to TH and TIH terms, respectively, which remains true for all the expressions in the rest of the paper, and thus explicit writing of 'h' and 'i' hereafter is omitted.

**4.1 Direct current** After FT of the expression for DC, Eq. (44), it is obtained that

$$I_\alpha = \frac{e}{\pi} \int \text{Tr} [G^R \Sigma_\alpha^< + G^< \Sigma_\alpha^A - \Sigma_\alpha^R G^< - \Sigma_\alpha^< G^A] dE, \quad (47)$$

where, to simplify the notation, explicit dependence of quantities under the integral on  $E$  is omitted. From Eq. (20), it follows that

$$\Sigma_\alpha^\gamma = V_{\alpha D}^\dagger g_\alpha^\gamma V_{\alpha D}, \quad \gamma = R, A, < \quad (48)$$

and, from Eqs. (22) and (24), SE matrices describing the influence of electrodes are obtained as follows:

$$\Sigma_\alpha^A - \Sigma_\alpha^R = i \Gamma_\alpha, \quad (49)$$

$$\Sigma_\alpha^< = i f_\alpha \Gamma_\alpha, \quad (50)$$

where the bandwidth  $\Gamma$  is defined as

$$\Gamma = \sum_\alpha \Gamma_\alpha; \quad \Gamma_\alpha(E) = 2\pi V_{\alpha D}^\dagger \Delta_\alpha(E) V_{\alpha D} \quad (51)$$

and  $\Delta_\alpha(E)$  is the density of states matrix of the isolated electrode  $\alpha$ .

From Eq. (49), it follows that

$$\Gamma_\alpha(E) = -2\text{Im} \Sigma_\alpha^R(E) \quad (52)$$

and, recalling Eqs. (33) and (49), it is straightforward to show that

$$[G^R]^{-1} - [G^A]^{-1} = \Sigma^A - \Sigma^R, \quad i(G^R - G^A) = G^R \Gamma G^A, \quad (53)$$

which, together with the TH part of the Keldysh equation (30), gives the expression for DC, Eq. (47), in the well-known Caroli form [19]

$$I_\alpha = \frac{e}{\pi} \int dE (f_\alpha - f_\beta) \text{Tr} [\Gamma_\beta G^R \Gamma_\alpha G^A], \quad \alpha \neq \beta. \quad (54)$$

This equation was obtained before using the scattering formalism of Büttiker [28, 29], where particle interaction in the dot was treated up to the elastic one-particle interaction level, the connection between S-matrix and GF was established via the Fisher–Lee relation [3], and the transmission



recognized in the term  $\text{Tr}[\Gamma_\alpha G^R \Gamma_\beta G^A]$ . Beyond elastic mean-field potential scattering, however, equality between this expression and the transmission coefficient does not hold any longer.

The expressions for the TH lesser GF, Eq. (30), and the lesser SE, Eq. (50), together with Eq. (53), determine the electron density matrix as

$$D = -iG^<(t - t^+) = \frac{1}{2\pi i} \int dE G^<(E). \quad (55)$$

The Fourier-transformed Keldysh equation (30), together with Eq. (49), expresses the lesser TH GF as

$$\begin{aligned} G^< &= G^R \Sigma^< G^A \\ &= G^R \sum_\beta i f_\beta \Gamma_\beta G^A \\ &= i f_\beta G^R \Gamma G^A + i(f_\alpha - f_\beta) G^R \Gamma_\alpha G^A. \end{aligned} \quad (56)$$

It is assumed here that  $\mu_\alpha > \mu_\beta$  for definiteness, two terms of the TH lesser GF, respectively, are the equilibrium density matrix associated with lead states  $k\beta$  up to  $\mu_\beta$  and the non-equilibrium part with the energy values between chemical potentials. Due to Eq. (53), the equilibrium part is simply

$$i f_\beta G^R \Gamma G^A = -2i f_\beta \text{Im} G^R, \quad (57)$$

which is analytical in the complex upper half-plane except at poles of the Fermi distribution at the imaginary axis, and the integral can be calculated by contour integration [9, 10]. The non-equilibrium part of the density matrix is not analytical due to the presence of both retarded and advanced GFs, so the integration is done along the real axis [9–11].

The DC is conserved, which can be demonstrated by taking the sum over left and right current contributions, Eq. (47), to obtain

$$\sum_{\alpha=R,L} I_\alpha = \frac{e}{\pi} \int \text{Tr}[(G^R - G^A)\Sigma^< + (\Sigma^A - \Sigma^R)G^<] dE. \quad (58)$$

The first rows of Eqs. (53) and (56) then trivially lead to the DC conservation.

**4.2 Alternating current** The expression for the alternating current, Eq. (45), can be transformed recalling Eqs. (29), (28), (23), and (46), to obtain an expression involving only TH quantities. To this end, first the double FT is applied to all two-times quantities, which transforms the expression for AC, Eq. (45), into a sum of four contributions

$$\begin{aligned} i_\alpha(\omega) &= \frac{e}{\pi} \int dE \text{Tr}[i_\alpha^{(1)} + i_\alpha^{(2)} + i_\alpha^{(3)} + i_\alpha^{(4)}], \\ i_\alpha^{(1)} &= [G^R(E_+) - G^A(E)]\sigma_\alpha^<(E_+, E), \end{aligned}$$

$$\begin{aligned} i_\alpha^{(2)} &= [\Sigma_\alpha^A(E) - \Sigma_\alpha^R(E_+)]G^<(E_+, E), \\ i_\alpha^{(3)} &= G^R(E_+, E)\Sigma_\alpha^<(E) - \Sigma_\alpha^<(E_+)G^A(E_+, E), \\ i_\alpha^{(4)} &= G^<(E_+)\sigma_\alpha^A(E_+, E) - \sigma_\alpha^R(E_+, E)G^<(E), \end{aligned} \quad (59)$$

where  $E_+$  stands for  $E + \omega$  (notation adopted from Ref. [6]). The first three terms agree with the results previously obtained by Anantram and Datta (see Eq. (22) of Ref. [6]), who provided also their interpretation – the first term,  $i_\alpha^{(1)}$ , corresponds to the correlated injection of electrons from electrode  $\alpha$  at energies  $E$  and  $E_+$ , while the second,  $i_\alpha^{(2)}$ , describes the correlated injection of the electrons in the other direction, from the dot into the lead; the third term,  $i_\alpha^{(3)}$ , corresponds to the injection of the electron from one energy from the leads to the changing density of states in the dot.

The fourth term,  $i_\alpha^{(4)}$ , also presented in Refs. [7, 8], can be interpreted by tracing back its origin to the expression for the TIH junction SE, Eq. (60) – if, for the sake of simplicity,  $\Sigma(E)$  changes linearly with  $E$ , then  $\sigma_\alpha(E_+, E) = (-\partial\Sigma_\alpha(E)/\partial E)V_\alpha$ , i.e., TIH SE is produced by the change of the TH junction SE with energy. The change of the real part is associated with the shifting of energy levels in the dot, while the change of the imaginary part with the change of width of dot levels. Since these changes originate in the leads, the fourth term describes the process that is the third process reversed, namely an injection of the electron from the dot into the lead due to the altering density of states in the leads. This term gives the contribution beyond the WBL approximation, which is discussed later (Section 5.1) considering it a special case of the general expression (59).

Subsequently, the four contributions to the current can be grouped into two types of processes:  $i^{(1)} + i^{(3)}$  corresponds to the transfer of the electron from the leads into the dot, while  $i^{(2)} + i^{(4)}$  corresponds to the transfer of the electron from the dot into the leads.

**4.3 Expression for current** Now, what follows is the derivation of the final expression for the dynamical current starting with the FT of Eq. (23):

$$\sigma_\alpha^\gamma(E_+, E) = \frac{V_\alpha(\omega)}{\omega} [\Sigma_\alpha^\gamma(E) - \Sigma_\alpha^\gamma(E_+)], \quad (60)$$

where  $\gamma$  stands for A, R, or  $<$ . The FT of Eq. (46) is

$$G^\gamma(E_+, E) = G^\gamma(E_+)[U(\omega) + \sigma^\gamma(E_+, E)]G^\gamma(E), \quad (61)$$

where  $\gamma$  stands for A or R, and  $U$  is the time-dependent potential at the HF level

$$U_{nm}(\omega) = \frac{1}{2\pi} \int dE \sigma_{nm}^{\text{int}}(E_+, E), \quad (62)$$

determined self consistently. The FT of the TIH contribution of the lesser GF of the dot, Eq. (29), is

$$\begin{aligned} G^<(E_+, E) &= G^R(E_+)\sigma^R(E_+, E)G^<(E) \\ &+ G^R(E_+)\sigma^<(E_+, E)G^A(E) \\ &+ G^<(E_+)\sigma^A(E_+, E)G^A(E) \\ &+ G^R(E_+)U(\omega)G^<(E) \\ &+ G^<(E_+)U(\omega)G^A(E). \end{aligned} \quad (63)$$

The self-consistent set of equations now involves the use of Eqs. (60), (62), and (63) to express TIH quantities through TH ones, resulting in the expression for the current where all the quantities are functions of either  $E$  or  $E + \omega$ . For this reason, to simplify notation, the writing of explicit dependence on  $E$  is dropped, while the explicit dependence on  $E + \omega$  is indicated by the subscript  $+$ , while  $V$  and  $U$  depend on  $\omega$  only, which is also not explicitly written. Using this notation, the derivation of the expression for dynamical current at the frequency  $\omega$  is given in the Appendix, with the following result:

$$\begin{aligned} i_\alpha(\omega) &= \frac{e}{\pi} \int dE \operatorname{Tr} (G_+^R \tilde{U}_\alpha^R G^R \Sigma_\alpha^< - \Sigma_{\alpha+}^< G_+^A \tilde{U}_\alpha^A G^A) \\ &+ \frac{e}{\pi} \int dE \operatorname{Tr} \{ [\Sigma_\alpha^A - \Sigma_{\alpha+}^R] [G_+^R \tilde{U}_\alpha^R G^< \\ &+ G_+^< \tilde{U}_\alpha^A G^A + G_+^R \frac{V_\beta - V_\alpha}{\omega} (\Sigma_\beta^< - \Sigma_{\beta+}^<) G^A] \}, \end{aligned} \quad (64)$$

$$\tilde{U}_\alpha^\gamma = \frac{V_\beta - V_\alpha}{\omega} (\Sigma_\beta^\gamma - \Sigma_{\beta+}^\gamma) + U - V_\alpha; \quad \gamma = R, A; \beta \neq \alpha, \quad (65)$$

where  $\tilde{U}_\alpha$  can be perceived as an effective potential that includes TIH self energy as well as the induced dot potential, all shifted by the potential of the corresponding lead.

The first integral of Eq. (64) contains the AC contribution from leads-to-dot processes  $i_\alpha^{(1,3)}$ . Presence of the in-scattering rate  $\Sigma^<$  in the integral shows that the described process is not only due to external potentials but also due to internal ones [30]. The second integral of Eq. (64), corresponding to the contribution of dot-to-leads processes  $i_\alpha^{(2,4)}$ , is due to the presence of the dissipative term  $G^<$  [30].

The gauge-invariant current theory is the one where simultaneous shift of all potentials by the same amount has no observable effect on current, i.e., the current depends only on voltage differences [4, 7, 8, 28, 31]. Both of these contributions to the total AC show that the current depends on potential differences, which is the hallmark of gauge invariance, and clearly point out the necessity of the explicit introduction of internal potential in order to preserve gauge invariance.

**4.3.1 Admittance** Although expressions for AC and DC have been derived and the scheme for the calculation

of all relevant quantities developed, no connection to the conductance has been made so far. Büttiker established a connection between time-dependent Hartree potential and electrode potentials via conductance using the formalism of characteristic potentials [4], and proved the gauge invariance with respect to constant potential shifts of  $V$ . To better understand the obtained result, Eq. (64), especially the role of the displacement current, the expression can be formally rewritten in terms of the transport coefficient, the particle current associated admittance  $\tilde{G}^p(\omega)$ , and the displacement current  $i_\alpha^d$  as

$$i_\alpha(\omega) = \sum_{\alpha\beta} \tilde{G}_{\alpha\beta}^p(\omega) V_\beta(\omega) + i_\alpha^d(\omega) \quad (66)$$

or, in matrix form, as

$$\begin{bmatrix} i_L \\ i_R \end{bmatrix} = \begin{bmatrix} \tilde{G}_L^p & \tilde{G}_{LR}^p \\ \tilde{G}_{RL}^p & \tilde{G}_R^p \end{bmatrix} \begin{bmatrix} V_L \\ V_R \end{bmatrix} + \begin{bmatrix} i_L^d \\ i_R^d \end{bmatrix}, \quad (67)$$

where corresponding components of the admittance matrix can be easily extracted from Eq. (64). The obtained expression appears non-homogeneous in  $V_\alpha$  due to the displacement-current term  $i_\alpha^d(\omega)$ , equal to the contribution of the first four terms in Eq. (64) containing all the contributions of the TD potential in the molecule  $U(\omega)$ . This potential, however, is determined self consistently and therefore also indirectly depends on  $V_\alpha$ . This can be seen by considering first the limit of vanishing amplitudes of electrode potentials  $V_\alpha$ . In this case, for small frequencies the response of the dot to the external field will also be small, and expansion of  $U$  in  $V_\alpha$  would provide a constant term in the lowest order, which can be removed by choosing a suitable gauge, and terms linear in  $V_\alpha$  as the largest non-trivial corrections, thus making the displacement current also linearly dependent on  $V_\alpha$ ,

$$i_\alpha^d = \sum_\beta \tilde{G}_{\alpha\beta}^d V_\beta.$$

Therefore, the main effect of the displacement current is the renormalization of the total admittance of the molecule,

$$i_\alpha(\omega) = \sum_{\alpha\beta} \tilde{G}_{\alpha\beta}(\omega) V_\beta(\omega), \quad \tilde{G}(\omega) = \tilde{G}^p(\omega) + \tilde{G}^d(\omega). \quad (68)$$

In this limit of vanishing  $V_\alpha(\omega)$ , the current will be vanishing as well so long as  $\omega$  is smaller than the molecular gap. When the two energies are comparable, however, there is a possibility of forming transient excited states, which are not well described in the formalism of linear response [16]. This sets the upper limit for the frequency of the driving field to about the (effective) level spacing near the Fermi energy of the dot or, alternatively, the HOMO–LUMO gap of the molecule.

In general, if  $V(\omega)$  is non-vanishing,  $U(\omega)$  does not have to be linear in  $V_\alpha(\omega)$  even when all TIH quantities are, where the source of nonlinearities is the intra-dot Coulomb

interaction. Then, due to TH contributions of  $U$  nonlinear in  $V_\alpha$ , a simple relation (68) is only an approximation and would acquire additional nonlinearity in  $V_\alpha$  terms, which are taken into account with the presented formalism and already included in the expression for dynamical current, Eq. (64).

**4.3.2 Current partition** When talking about the electron injection between the dot and the lead, it should be stated that the four terms in Eq. (59) include not only the particle current, but also the current due to charge accumulation in the dot induced by the external potential, the displacement current  $i_d$ . This is due to the fact that the system of equations developed in Section 3 includes also the intra-dot interaction, whose TIH contribution is exactly the TD potential in the dot. The left and right AC contributions to Eq. (59) are

$$i(\omega) = i_L(\omega) + i_R(\omega). \quad (69)$$

Taking the GFs in a Kohn–Sham form, Eq. (33), the above sum is

$$\begin{aligned} \sum_{\alpha=R,L} i_\alpha(\omega) = & -e \frac{\omega}{\pi} \int dE \operatorname{Tr} [G_+^R \sigma^<(E_+, E) G^A \\ & + G_+^< \sigma^A(E_+, E) G^A + G_+^R \sigma^R(E_+, E) G^<] \\ & - e \frac{\omega}{\pi} \int dE \operatorname{Tr} [G_+^< U(\omega) G^A + G_+^R U(\omega) G^<], \end{aligned} \quad (70)$$

where  $U$  is the HF time-dependent potential, Eq. (62). The above result is easy to obtain if the sum of left and right contributions of the second term of Eq. (59) is transformed:

$$\begin{aligned} & (\Sigma^A - \Sigma_+^R) G^<(E_+, E) \\ & = -\omega G^<(E_+, E) + ([G_+^R]^{-1} - [G^A]^{-1}) G^<(E_+, E). \end{aligned} \quad (71)$$

Using Eq. (63), in the second term on the right-hand side, it can be found that this term is canceled by the left and right sums of the first, third, and fourth terms of Eq. (59), giving Eq. (70). The right-hand side of Eq. (70) also equals

$$-2ei\hbar \frac{\partial}{\partial t} \operatorname{Tr} G^<(t, t).$$

Equation (70) consists of two contributions: the current associated with injected charge where the external potential was recognized in the TIH junction SE, and the current associated with induced charge with corresponding internal potential, Eq. (62). The displacement current density is the divergence of the time derivative of the electric field generated by charge density. This charge density is composed from injected and induced charge densities in the dot.

The molecule–lead coupling affects both the molecule and the leads. For metallic leads, effects of this coupling are expected to be screened at the depth of the Thomas–Fermi length, which is at most a few lattice constants, with bulk-

like properties deeper in the conductor, which in the case of finite bias means the uniform electro-chemical potentials in the bulk. This is then used to impose the correct boundary conditions: the system is divided into the central region, the so-called extended molecule (EM), containing the molecule and parts of the electrodes, with the requirements that its potential and non-equilibrium distribution match with those in both electrodes. Due to the screening of field lines, the charge neutrality is maintained in the central region if sufficiently large parts of the leads are included [9, 11, 32].

This approach is extended to the TD transport in Hartree approximation by the introduction of characteristic potentials [4, 8, 17, 31].

At the HF level studied in this research, inclusion of the internal potential  $U$  into the system of equations determining the current does not require use of characteristic potentials and, since inclusion of the exchange through the Fock term results in the reduced interaction of half of the electrons [33, 34], the screening is expected to be slightly weakened compared to the Hartree case. As a consequence, the size of the central region, where charge neutrality is maintained, should be larger than in the RPA description. As far as our model is concerned, the exchange contribution to the internal potential is localized within the EM. With this in mind, the proper boundary conditions thus should include: matching of the TD Hartree potential, vanishing TD Fock contribution, and imposing the EM charge-neutrality condition,  $\operatorname{Tr}[G^<(t, t)] = 0$ .

It can be stated that the right-hand side of Eq. (70) is a time derivative of the volume integral of the TD charge density, which is, due to EM charge neutrality, zero. In other words [4, 17, 31], field lines, stemming from the charge density, do not penetrate the surface which encloses the EM. The charge neutrality of the central region, besides providing boundary conditions, means that the voltages of contacts are well defined [35]. Therefore, Eq. (70) represents the current conservation as well as the current partition on left and right terms. The effects of the displacement current are self-consistently included during the determination of the time-dependent dot potential via implicit inclusion of the Coulomb interaction (which is responsible for the displacement current [4, 8, 17, 31] in the first place).

**5 Wide-band limit and zero bias** Generally, whenever the leads are connected to the electronic reservoir and good featureless conductors, one may expect fast screening of the external electric field by a large electronic density of states at the leads' surface, effectively creating a capacitor-like system with the dot/molecule in the middle and approximately constant density of states at the surface. In this case one expects the wide-band-limit approximation to be adequate, simplifying the derived expressions. Another interesting case is that of voltage without any bias, corresponding to a time-dependent-only driving voltage on the leads. We therefore consider these cases separately and derive the appropriate expressions for  $i_\alpha$ .

**5.1 Current in the WBL** As discussed earlier (Section. 4.2), the fourth contribution  $i^{(4)}$  of the dynamical current, Eq. (59), corresponds to the charge injection from the dot into the changing density of states in the leads.

The WBL consists then in the assumption that there is no such density change, so, in this case, the alternating current is Eq. (59) without the fourth term, which leads to the result as in Ref. [6], with a caveat that the here derived expression for the current is more general due to the self-consistent inclusion of dot interaction. To derive the expression for AC in WBL, we start with the TH self energy, Eq. (14), which after FT can be written in matrix form as

$$\Sigma_{\alpha}^{\gamma}(E) = V_{\alpha}^{\dagger} g_{\alpha}^{\gamma}(E) V_{\alpha}, \quad \gamma = R, A.$$

The  $k$  index labelling the wave vector, can be expressed via the density of states, with explicitly separated real and imaginary parts of the above equation,

$$\Sigma_{\alpha}^{\gamma}(E) = \int_{-W}^W d\epsilon \Delta_{\alpha}(\epsilon) V_{\alpha}^{\dagger}(\epsilon) [\text{Re } g_{\alpha}^{\gamma}(E, \epsilon) + \text{Im } g_{\alpha}^{\gamma}(E, \epsilon)] V_{\alpha}(\epsilon),$$

where  $W$  is the band half-width. After finding of separate contributions to the SE from the real and imaginary parts of the isolated electrode TH retarded GF, Eq. (9), and using the standard principal value (PV) representation of the Fourier-transformed GF

$$g_{\alpha}^{R/A}(E, \epsilon) = \frac{1}{E - \epsilon \pm i\delta} = \text{PV} \left( \frac{1}{E - \epsilon} \right) \mp i\pi\delta(E - \epsilon),$$

we obtain

$$\Sigma_{\alpha}^{R/A}(E) = \mp i\pi V_{\alpha}^{\dagger}(E) \Delta_{\alpha}(E) V_{\alpha}(E) + \text{PV} \int_{-W}^W d\epsilon \Delta_{\alpha}(\epsilon) V_{\alpha}^{\dagger}(\epsilon) \frac{1}{E - \epsilon} V_{\alpha}(\epsilon). \quad (72)$$

The imaginary part is associated with the dot bandwidth, Eq. (51), assumed within WBL to be energy independent throughout the band, thus giving

$$\Sigma_{\alpha}^{R/A}(E) = \left( \frac{1}{2\pi} \ln \left| \frac{W+E}{W-E} \right| \mp \frac{i}{2} \right) \Gamma_{\alpha}. \quad (73)$$

When it is furthermore assumed that the electrode bandwidth is much larger than any other relevant energy scale, such as amplitudes of time-dependent potentials and the dot bandwidth  $\Gamma$ , the real part of SE goes to zero.

As mentioned in the introduction, the TIH SE acts as a TD external perturbation. By its construction, Eq. (14), the junction SE is expected to vanish in leads away from the molecule. In general, the evolution of the EM is non-unitary due to interaction and junction self energies. The

continuity equation for closed systems is preserved by the current-conservation condition. In the case of the open system, this condition affects only the interaction SE, while the presence of junction SE breaks the continuity equation as a consequence of boundaries where particles emerge or disappear.

The WBL approximation significantly overestimates the electrode density of states and consequently screening effects, which leads to the neglect of the external perturbing potential, i.e., changes of the TIH junction SE. Besides the vanishing  $i_{\alpha}^{(4)}$ , WBL reduces the changes of the density of states within the EM (without self-consistent potential inclusion, there would be no changes at all), and affects the correlated electron injection from the dot to the leads by removing the effects of external potentials on the electron correlation function  $G^<$ . The expression for AC in the WBL again consists of two contributions, due to the particle current, associated with terms containing external potentials only, and the displacement current containing the internal potential only,

$$i_{\alpha}(\omega) = \frac{e}{\pi} \int dE \text{Tr} \{ i f_{\alpha} G_{+}^R (U - V_{\alpha}) G^R - i f_{\alpha+} G_{+}^A (U - V_{\alpha}) G^A - \sum_{\gamma=L,R} G_{+}^R [f_{\gamma} (U - V_{\alpha}) G^R \Gamma_{\beta} + f_{\gamma+} \Gamma_{\gamma} G_{+}^A (U - V_{\alpha})] G^A \Gamma_{\alpha} - (f_{\beta} - f_{\beta+}) \frac{V_{\beta} - V_{\alpha}}{\omega} G_{+}^R \Gamma_{\beta} G^A \Gamma_{\alpha} \}.$$

Once again, it can be observed that the inclusion of displacement current through the self-consistent introduction of the internal field preserves the gauge invariance. The Fermi distributions come from Eq. (50). The first two terms under the integral are due to charge-correlated charge injection as well as injection with corresponding changing density of states within the dot, i.e., the EM, while the remaining terms correspond to correlated charge injections into the leads without changing their density of states. To the best of our knowledge, this expression has not been derived before.

**5.2 Current in the zero-bias regime** Another important special case is that of the zero bias, when the molecule is exposed to the AC only. In this case chemical potentials of the leads are equal and Fermi distributions therefore unshifted, leading to the zero direct current and simplifying the expression for the dynamical current, Eq. (64), to obtain

$$i_{\alpha} = \frac{e}{\pi} \int dE \text{Tr} \left[ (f \tilde{U}_{\alpha}^R - f_{+} \tilde{U}_{\alpha}^A) G^A (\Sigma_{\alpha}^A - \Sigma_{\alpha+}^R) G_{+}^R + f_{+} \tilde{U}_{\alpha}^A G^A (\Sigma_{\alpha}^A - \Sigma_{\alpha+}^A) G_{+}^A - f \tilde{U}_{\alpha}^R G^R (\Sigma_{\alpha}^R - \Sigma_{\alpha+}^R) G_{+}^R + \frac{V_{\beta} - V_{\alpha}}{\omega} G_{+}^R (i f \Gamma_{\beta} - i f_{+} \Gamma_{\beta+}) G^A (\Sigma_{\alpha}^A - \Sigma_{\alpha+}^R) \right]. \quad (74)$$



To the best of our knowledge, this result has also not been obtained yet.

**5.3 Current in the zero-bias WBL** Finally, we consider the case of applied AC only in the WBL, which greatly further simplifies the current expression, Eq. (64), to obtain

$$i_\alpha(\omega) = \frac{e}{\pi} \int dE \text{Tr} \{ (f - f_+) \Gamma_\alpha G_+^R \times \left[ i(U - V_\alpha) + \frac{V_\alpha - V_\beta}{\omega} \Gamma_\beta \right] G^A \}. \quad (75)$$

To compare the obtained expression with the zero-bias result, Eq. (27) of Ref. [6], it is convenient to work in a gauge corresponding to the experimental setup from the reference (which is in our case possible due to the gauge invariance), by setting  $V_\alpha \mapsto V_\alpha - V_\beta$  and  $V_\beta \mapsto 0$ , i.e., by shifting external potentials of both electrodes by  $V_\beta$ . In this gauge, and by neglecting the TD potential in the dot,  $U$ , the two expressions agree.

**6 Conclusions** In conclusion, we have derived a set of equations describing non-equilibrium charge-conserving gauge-invariant transport through a quantum dot/molecule, including the time-dependent dot potential and with it the associated displacement current, at the Hartree–Fock level, and derived the expression for the frequency dependence of the dynamical current. The gauge invariance of the theory was explicitly shown and special cases of the wide-band limit, zero bias, as well as the zero-bias wide-band limit considered and corresponding expressions for the current derived. The theory is particularly suitable for use with the DFT, where the latter can provide the time-homogeneous contribution of the Coulomb interaction to the dot potential, thus providing a theoretical basis for the first-principle microscopic description of the non-equilibrium quantum transport in linear response and calculation of electronic current in molecules, dots, junctions, or nano-scale devices beyond the time homogeneity. Coupled with SIC DFT, the theory is free of a self-interaction error and suitable for the time-dependent transport description in the cases where the single-charge effects, for example in the regime of weak coupling between electrodes and the molecule, could be of interest. The current conservation based on the DFT coupling with GFs relies on the fact that the time-dependent internal potential was approximated at the mean-field level. Therefore, within our scheme, the possible systematic expansion of TIH interaction SE, with the aim to include time non-local contributions, would not provide current conservation. However, it does not mean that the description based on time local potentials was exhausted. It is our opinion that the mean-field approximation introduced in Ref. [34] leaves room for further progress.

**Appendix** In this appendix we will derive the expression for the dynamical current. We start with its expression,

Eq. (59), and separately consider two contributions: the first one describing the charge injection,

$$i_\alpha^{\text{inj}} = \frac{e}{2\pi} \int dE \text{Tr} (i_\alpha^{(1)} + i_\alpha^{(3)}) \quad (76)$$

and the second one related to charge emission,

$$i_\alpha^{\text{emi}} = \frac{e}{2\pi} \int dE \text{Tr} (i_\alpha^{(2)} + i_\alpha^{(4)}). \quad (77)$$

Equation (76) is transformed using Eqs. (59), (60), (61), and (63) to obtain

$$i_\alpha^{\text{inj}} = \frac{e}{2\pi} \int dE \text{Tr} \left[ \frac{V_\alpha}{\omega} (G_+^R - G^A) (\Sigma_\alpha^< - \Sigma_{\alpha+}^<) + G_+^R \sigma^R G^R \Sigma_\alpha^< - \Sigma_{\alpha+}^< G_+^A \sigma^A G^A + G_+^R U G^R \Sigma_\alpha^< - \Sigma_{\alpha+}^< G_+^A U G^A \right]. \quad (78)$$

Since the integration is over all energies, we can transform the first-term contribution on the right-hand side:

$$\begin{aligned} & \int dE \text{Tr} [(G_+^R - G^A) (\Sigma_\alpha^< - \Sigma_{\alpha+}^<)] \\ &= \int dE \text{Tr} [(G_+^R - G^R) \Sigma_\alpha^< - \Sigma_{\alpha+}^< (G_+^A - G^A)]. \end{aligned} \quad (79)$$

The expressions

$$G_+^\gamma - G^\gamma, \quad \gamma = A, R, \quad (80)$$

can be transformed by recalling the definition of the KS GF, out of which directly follows

$$(G_+^\gamma)^{-1} - (G^\gamma)^{-1} = \omega + \Sigma^\gamma - \Sigma_+^\gamma, \quad (81)$$

which, after multiplying with  $G_+^\gamma$  from the left and with  $G^\gamma$  from the right, gives

$$G^\gamma - G_+^\gamma = \omega G_+^\gamma G^\gamma + G_+^\gamma (\Sigma^\gamma - \Sigma_+^\gamma) G^\gamma. \quad (82)$$

Finally, recalling Eq. (60), we obtain

$$\frac{V_\alpha}{\omega} (G_+^\gamma - G^\gamma) = -G_+^\gamma \left( V_\alpha + \sigma_\alpha^\gamma + \frac{V_\alpha}{V_\beta} \sigma_\beta^\gamma \right) G^\gamma, \quad (83)$$

where  $\alpha \neq \beta$ . This result is inserted on the right-hand side of Eq. (79) and the obtained expression is added to the rest of Eq. (78) to obtain

$$i_\alpha^{\text{inj}} = \frac{e}{2\pi} \int dE \text{Tr} (G_+^R \tilde{U}_\alpha^R G^R \Sigma_\alpha^< - \Sigma_{\alpha+}^< G_+^A \tilde{U}_\alpha^A G^A), \quad (84)$$

where  $\tilde{U}$  is the effective potential, Eq. (65). A similar procedure applied to Eq. (77) gives

$$i_{\alpha}^{\text{emi}} = \frac{e}{2\pi} \int dE \text{Tr}[(\Sigma_{\alpha}^{\text{A}} - \Sigma_{\alpha+}^{\text{R}})(G_{+}^{\text{R}}UG^{\text{<}} + G_{+}^{\text{<}}UG^{\text{A}} + G_{+}^{\text{R}}\sigma^{\text{R}}G^{\text{<}} + G_{+}^{\text{<}}\sigma^{\text{A}}G^{\text{A}} + G_{+}^{\text{<}}\sigma^{\text{<}}G^{\text{A}} + G_{+}^{\text{<}}\sigma_{\alpha}^{\text{A}} - G^{\text{<}}\sigma_{\alpha}^{\text{R}})]. \quad (85)$$

The contribution from the last line is transformed as was done with Eq. (79),

$$\begin{aligned} & \int dE \text{Tr}[G_{+}^{\text{<}}(\Sigma_{\alpha}^{\text{A}} - \Sigma_{\alpha+}^{\text{A}}) - G^{\text{<}}(\Sigma_{\alpha}^{\text{R}} - \Sigma_{\alpha+}^{\text{R}})] \\ &= \int dE \text{Tr}[(G_{+}^{\text{<}} - G^{\text{<}})(\Sigma_{\alpha}^{\text{A}} - \Sigma_{\alpha+}^{\text{R}})]. \end{aligned} \quad (86)$$

In order to find a suitable expression for lesser GFs, we use the Keldysh equation (30). In the case of  $G_{+}^{\text{<}}$ , Eq. (82), where  $\gamma$  stands for advanced functions, will be useful. Taking the product of both sides of this equation with  $V_{\alpha}/\omega$  and then with  $G_{+}^{\text{R}}\Sigma_{+}^{\text{<}}$  acting from the left, we obtain

$$\frac{V_{\alpha}}{\omega}G_{+}^{\text{<}} = \frac{V_{\alpha}}{\omega}G_{+}^{\text{R}}\Sigma_{+}^{\text{<}}G^{\text{A}} - G_{+}^{\text{<}}(V_{\alpha} + \sigma_{\alpha}^{\text{A}} + \frac{V_{\alpha}}{V_{\beta}}\sigma_{\beta}^{\text{A}})G^{\text{A}}. \quad (87)$$

We follow the same route for  $G^{\text{<}}$ , with those differences that in Eq. (82),  $\gamma$  stands for retarded functions, and that we take the both sides product with  $\Sigma^{\text{<}}G^{\text{A}}$  acting from the right. This leads to

$$\frac{V_{\alpha}}{\omega}G^{\text{<}} = \frac{V_{\alpha}}{\omega}G_{+}^{\text{R}}\Sigma^{\text{<}}G^{\text{A}} + G_{+}^{\text{R}}(V_{\alpha} + \sigma_{\alpha}^{\text{R}} + \frac{V_{\alpha}}{V_{\beta}}\sigma_{\beta}^{\text{R}})G^{\text{<}}. \quad (88)$$

The insertion of Eqs. (87) and (88) into the right-hand side of (86), and the obtained result into Eq. (85), leads to

$$\begin{aligned} i_{\alpha}^{\text{emi}} &= \frac{e}{2\pi} \int dE \text{Tr}\{[\Sigma_{\alpha}^{\text{A}} - \Sigma_{\alpha+}^{\text{R}}] \\ &\times [G_{+}^{\text{R}}\tilde{U}_{\alpha}^{\text{R}}G^{\text{<}} + G_{+}^{\text{<}}\tilde{U}_{\alpha}^{\text{A}}G^{\text{A}} \\ &+ G_{+}^{\text{R}}(V_{\beta} - V_{\alpha})\frac{\Sigma_{\beta}^{\text{<}} - \Sigma_{\beta+}^{\text{<}}}{\omega}G^{\text{A}}]\}. \end{aligned} \quad (89)$$

Taking the sum of Eqs. (84) and (89), we arrive at Eq. (64).

**Acknowledgements** M. S. Dražić thanks Nenad Vukmirović for discussions. The authors acknowledge support by the European Union Project FP7 nanoDNAsequencing and the Ministry of Science and Education of the Republic of Serbia, Project No. 171033.

## References

- [1] R. Landauer, IBM J. Res. Dev. **1**, 223 (1957).
- [2] M. Büttiker, Y. Imry, R. Landauer, and S. Pinhas, Phys. Rev. B **31**, 6207 (1985).
- [3] D. S. Fisher and P. A. Lee, Phys. Rev. B **23**, 6851 (1981).
- [4] M. Büttiker, J. Phys.: Condens. Matter **5**, 9361 (1993).
- [5] J. Gabelli, G. Feve, J.-M. Berroir, B. Placais, A. Cavanna, B. Etienne, Y. Jin, and D. C. Glattli, Science **313**, 499 (2006).
- [6] M. P. Anantram and S. Datta, Phys. Rev. B **51**, 7632 (1995).
- [7] B. Wang, J. Wang, and H. Guo, Phys. Rev. Lett. **82**, 398 (1999).
- [8] Y. Wei and J. Wang, Phys. Rev. B **79**, 195315 (2009).
- [9] M. Brandbyge, J.-L. Mozos, P. Ordejón, J. Taylor, and K. Stokbro, Phys. Rev. B **65**, 165401 (2002).
- [10] J. Taylor, H. Guo, and J. Wang, Phys. Rev. B **63**, 121104 (2001).
- [11] A. R. Rocha, V. M. Garcia-Suarez, S. Bailey, C. Lambert, J. Ferrer, and S. Sanvito, Phys. Rev. B **73**, 085414 (2006).
- [12] L. P. Kadanoff and G. Baym, Quantum Statistical Mechanics: Green's Function Methods in Equilibrium and Nonequilibrium Problems (W. A. Benjamin, Inc., New York, 1962).
- [13] G. Baym, Phys. Rev. **127**, 1391 (1962).
- [14] U. von Barth, N. E. Dahlen, R. van Leeuwen, and G. Stefanucci, Phys. Rev. B **72**, 235109 (2005); C.-O. Almbladh, U. von Barth, and R. van Leeuwen, Int. J. Mod. Phys. B **13**, 535 (1999).
- [15] P. Danielewicz, Ann. Phys. **152**, 239 (1984).
- [16] H. Haug and A.-P. Jauho, Quantum Kinetics in Transport and Optics of Semiconductors, 2<sup>nd</sup> ed. (Springer, Berlin, 2008).
- [17] M. Büttiker, A. Prêtre, and H. Thomas, Phys. Rev. Lett. **70**, 4114 (1993).
- [18] A.-P. Jauho, N. S. Wingreen, and Y. Meir, Phys. Rev. B **50**, 5528 (1994).
- [19] C. Caroli, R. Combescot, P. Nozieres, and D. Saint-James, J. Phys. C, Solid State Phys. **4**, 916 (1971).
- [20] W. Kohn, Rev. Mod. Phys. **71**, 1253 (1999).
- [21] H. Eschrig, The Fundamentals of Density Functional Theory, Teubner-Texte zur Physik (Teubner, Stuttgart, 1996).
- [22] R. M. Dreizler and E. K. U. Gross, Density Functional Theory: An Approach to the Quantum Many-Body Problem (Springer, Berlin, 1990).
- [23] G. Rickayzen, Green's Functions and Condensed Matter (Academic Press, London, 1980).
- [24] A. R. Williams, P. J. Feibelman, and N. D. Lang, Phys. Rev. B **26**, 5433 (1982).
- [25] M. P. Lopez Sancho, J. M. Lopez Sancho, and J. Rubio, J. Phys. F, Met. Phys. **14**, 1205 (1984).
- [26] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
- [27] C. Toher, A. Filippetti, S. Sanvito, and K. Burke, Phys. Rev. Lett. **95**, 146402 (2005).
- [28] M. Büttiker, Phys. Rev. B **46**, 12485 (1992).
- [29] V. Mihajlo, Ph.D. thesis, University of Basel (2008).
- [30] S. Datta, Electronic Transport in Mesoscopic Systems (Cambridge University Press, Cambridge, 1995).
- [31] M. Büttiker, Il Nuovo Cimento B **110**, 509 (1995).
- [32] Y. Xue, S. Datta, and M. A. Ratner, Chem. Phys. **281**, 151 (2002).
- [33] J. Hubbard, Proc. R. Soc. Lond. A **243**, 336 (1958).
- [34] K. S. Singwi, M. P. Tosi, and R. H. Land, Phys. Rev. **176**, 589 (1968).
- [35] M. H. Pedersen and M. Büttiker, Phys. Rev. B **58**, 12993 (1998).