PHYSICAL REVIEW B **79**, 195315 (2009)

Current conserving nonequilibrium ac transport theory

Yadong Wei[1] and Jian Wang[2,*]

[1]*Department of Physics and Institute of Computational Condense Matter Physics, Shenzhen University, Shenzhen 518060, China*
[2]*Department of Physics and Center of Theoretical and Computational Physics, The University of Hong Kong, Pokfulam Road, Hong Kong, China*

(Received 8 December 2008; revised manuscript received 6 March 2009; published 15 May 2009)

We develop a microscopic theory for ac transport using nonequilibrium Green's-function theory. By including the self-consistent Coulomb interaction, the current conserving and gauge-invariant conditions are satisfied. On the theoretical side, our theory can be used to calculate nonlinear ac transport properties order by order at finite frequency when the system is driven far from equilibrium. In addition, the nonlinear ac charge response such as ac electrochemical capacitance can also be calculated. On the application side, our theory can be coupled to the density-functional theory to numerically predict the ac transport properties of nanodevices.

DOI: 10.1103/PhysRevB.79.195315 PACS number(s): 73.23.−b, 72.10.Bg

I. INTRODUCTION

Quantum transport in nanostructures under ac bias has been the subject of intense studies both experimentally and theoretically.[1–11] Ac response is of fundamental interest because it can probe the charge distribution and the dynamics of the system. In addition, the frequency introduces another energy scale into the problem which plays a role quite different from temperature. So far, ac has been studied for a variety of systems including normal quantum dot systems[1,3,8] as well as normal superconducting hybrid systems.[6] When the strongly electron-electron interaction is included, an exactly solution of ac has been obtained in the Kondo regime.[5] In addition to frequency-dependent current, transient ac,[4] as well as photon-assisted shot noise[2,7] have also been investigated. At low frequencies, the dynamic response of a quantum capacitor can be described by a quantum capacitance in series with a charge-relaxation resistance.[9] For a conductor that allows single-channel transmission, the charge-relaxation resistance was predicted to be half of the resistance quanta[9,10] and was recently confirmed experimentally.[11] Due to the existence of quantum inductance, the current accumulates a phase and lags behind the voltage leading to a negative capacitance.[12]

In the theoretical treatment, the current is usually defined in terms of conduction current, i.e., $I_\alpha^c = dq_\alpha/dt$, where q_α is the charge flowing in the α lead. From the continuity equation $\Sigma_\alpha I_\alpha^c + dQ/dt = 0$ we see that the conduction current I_α^c is a conserved quantity in the steady state. Under the ac bias, however, the conduction current is not a conserved quantity anymore. The displacement current I_α^d due to the charge pileup dQ/dt inside the scattering region becomes important and must be considered. The problem of current conserving can be solved by partitioning the total displacement current $\Sigma_\alpha I_\alpha^d = dQ/dt$ into each leads giving rise to a conserving total current $I_\alpha = I_\alpha^c + I_\alpha^d$. The current partition at small bias was achieved by Buttiker *et al.*[13] using the scattering matrix approach. This approach has been extended to the situation far from equilibrium using nonequilibrium Green's-function (NEGF) method.[14] Physically, the displacement current is due to the long-range Coulomb interaction.[9] At low-frequency limit, a microscopic current conserving theory was developed using the scattering matrix theory[9] where the dynamic conductance to the first order in frequency was studied. A linear-response theory was developed later to predict weakly nonlinear ac conductance order by order in bias voltage.[15] By including Coulomb interaction, the problem of gauge invariance can also be solved. As we know, the current of a two-probe device should be a function of bias difference only. The gauge-invariant condition says that the current of a multiprobe system remains the same if all the bias are shifted by a constant amount. By including the Coulomb potential to the linear order in bias voltage, the second-order nonlinear dc conductance satisfied the gauge-invariant condition.[9] This scattering approach has been generalized to predict higher-order-weakly nonlinear dc conductance.[16] Despite of all the success in the current conserving and gauge-invariant formulations, the dynamic conductance at general frequency $G_{\alpha\beta}(\omega)$ was only treated at level of current partition.[17] This is because only a formal definition of $G_{\alpha\beta}(\Omega)$ was presented in the linear-response theory[16] and an operational expression of $G_{\alpha\beta}(\Omega)$ is clearly needed. It is known that the scattering matrix theory and linear-response theory are suitable when the system is near equilibrium. When the system is far away from equilibrium, a general current conserving and gauge-invariant ac transport theory is yet to be developed.

It is the purpose of this paper to fill this gap. Using the nonequilibrium Green's-function theory, we have developed a microscopic theory for ac transport. Treating Coulomb interaction at Hartree level, our theory satisfies the current conserving and gauge-invariant conditions. In particular, we have demonstrated our method by calculating the frequency-dependent dynamic conductance, frequency-dependent electrochemical capacitance, and various frequency-dependent density of states. It has been recognized that in the first-principle transport calculation, the NEGF is a better candidate to couple with the density-functional theory (DFT) (Ref. 18) to predict transport properties in nanodevices. With this approach, quantitative comparison can be made between numerical results and experimental results. For instance, in charge transport through oligophenylene[19] and alkanethiol[20] molecular wires in contact with Au leads the currents were found to decrease exponentially with wire length which is in quantitative agreement with experimental data. Quantitative analysis of nonequilibrium spin injection from Ni contacts to the octanethiol molecular spintronic system has also been carried out and compared with experimental data.[21] In view of the recent success of the first-principle approach using NEGF+DFT formalism in treating dc transport in nanostructures,[18,22–25] our theory provides an important framework for the NEGF+DFT formalism in dealing with ac transport.

The rest of the paper is organized as follows. The basic formulation is presented in Sec. II where the frequency-dependent characteristic potential and frequency-dependent density of states are introduced. As an illustration, the frequency-dependent current to the first order in bias voltage is calculated with Coulomb interaction including. Section III provides some relations among frequency-dependent density of states and Onsager-Casimir relations. Discussions and summary are given in Sec. IV.

II. THEORETICAL FORMULATION

We start with the model Hamiltonian ($\hbar=1$),

$$H(t)=H_{\rm lead}+H_{\rm dot}+H_T.$$

Here $H_{\rm lead}$ is the Hamiltonian of leads given by

$$H_{\rm lead}=\sum_{k\alpha}\epsilon_{k\alpha}(t)\hat{C}^\dagger_{k\alpha}\hat{C}_{k\alpha},$$

where $C^\dagger_{k\alpha}$ creates an electron in lead α, $\epsilon_{k\alpha}(t)=\epsilon_k^0+qv_\alpha\cos(\omega t)$ with $\epsilon^{(0)}_{k\alpha}$ the energy levels in lead α, and v_α is the ac bias on the lead α. The second term $H_{\rm dot}$ is the Hamiltonian of the isolated quantum dot,

$$H_{\rm dot}=\sum_n\epsilon_n d_n^\dagger d_n+\sum_{nm}V_{nm}d_n^\dagger d_n d_m^\dagger d_m, \tag{1}$$

where $d_n^\dagger$ creates an electron in the quantum dot. Note that we have included the electron-electron interaction into the second term in $H_{\rm dot}$ where V_{nm} is the matrix element of the Coulomb potential. In real space the Coulomb interaction is

$$V(x,x')=q/|x-x'|. \tag{2}$$

In the Hartree approximation, Eq. (1) becomes

$$H_{\rm dot}=\sum_n(\epsilon_n+U_n)d_n^\dagger d_n,$$

where the self-consistent (on the Hartree level) Coulomb potential U_n inside the quantum dot is defined as[26]

$$U_n=\sum_m V_{nm}\langle d_m^\dagger d_m\rangle. \tag{3}$$

Here we only considered the Coulomb interaction, the exchange and correlation interactions can be treated in a similar fashion. From the definition of the lesser Green's function, one has $G^<_{nn}=i\langle d_n^\dagger d_n\rangle$. Using the lesser Green's function, Eq. (3) in real space becomes

$$U(x)=-i\int dx'\,V(x,x')G^<(x',x').$$

From Eq. (2) we have $\nabla_x^2V(x,x')=-4\pi q\delta(x-x')$. Hence Eq. (3) is equivalent to the following self-consistent Poisson equation (we have included time explicitly),

$$\nabla^2U(x,t)=-4\pi\rho(x,t)=4\pi iq[G^<(t,t,U)]_{xx}, \tag{4}$$

where $\rho(x,t)$ is the charge density and x labels the position. Since the lesser Green's function is related to the retarded Green's function and depends on time, we have put time index explicitly in Coulomb potential and the charge density. The boundary condition of the Poisson equation is such that $U=V_\alpha$ at probe α. The third term H_T is the Hamiltonian describing the coupling between quantum dot and the leads with the coupling constant $t_{k\alpha n}$,

$$H_T=\sum_{k\alpha n}[t_{k\alpha n}C^\dagger_{k\alpha}d_n+t^*_{k\alpha n}d_n^\dagger C_{k\alpha}]. \tag{5}$$

The current from lead α can be calculated according to the Heisenberg equation of motion,

$$I_\alpha(t)=-\sum_{kn}[t_{k\alpha n}G^<_{n,k\alpha}(t,t)]+\text{H.c.}$$

After analytic continuation, the current is written as[4]

$$\begin{aligned}I_\alpha(t)=-\int dt_1\,\mathrm{Tr}[&G^r(t,t_1)\Sigma^<_\alpha(t_1,t)+G^<(t,t_1)\Sigma^a_\alpha(t_1,t)\\&-\Sigma^<_\alpha(t,t_1)G^a(t_1,t)-\Sigma^r_\alpha(t,t_1)G^<(t_1,t)],\end{aligned} \tag{6}$$

where,

$$\Sigma^\gamma_\alpha(t,t')=\sum_k t^*_{k\alpha m}g^\gamma_{k\alpha}(t,t')t_{k\alpha n} \tag{7}$$

and $\gamma=r,a,<$. Here

$$g^{r,a}_{k\alpha}(t,t')=\mp i\theta(\pm t\mp t')\exp\left[-i\int_{t'}^{t}dt_1\epsilon_{k\alpha}(t_1)\right], \tag{8}$$

$$g^<_{k\alpha}(t,t')=if(\epsilon^{(0)}_{k\alpha})\exp\left[-i\int_{t'}^{t}dt_1\epsilon_{k\alpha}(t_1)\right]. \tag{9}$$

The retarded Green's function G^r satisfies the following Dyson equation:

$$G^r=G_0^r+G_0^rUG^r+G_0^r\Sigma^rG^r. \tag{10}$$

Note that Eq. (10) is a matrix equation with G^r, G_0^r, and Σ^r being matrices in both space and time dimensions. For instance G_0^r is the Green's function of the isolated scattering region with the matrix elements $G_0^r(x,x',t,t')$ defined as

$$\left(i\frac{\partial}{\partial t}-H_0+i\eta\right)G_0^r(x,x',t,t')=\delta(t-t')\delta(x-x'), \tag{11}$$

where $H_0=\Sigma_n\epsilon_n d_n^\dagger d_n$. Here the Coulomb potential U is a diagonal matrix with the matrix element $U(x,t)$. Expanding $U(t)$ in terms of the *amplitude* of external bias $v_\alpha(0)=v_\alpha$, we have[9,16]

$$\begin{aligned}U(t)&=U_{\rm eq}+U_1+U_2+\cdots=U_{\rm eq}+\sum_\alpha u_\alpha(t)v_\alpha\\&\quad+\frac{1}{2}\sum_{\alpha\beta}u_{\alpha\beta}(t)v_\alpha v_\beta+\cdots,\end{aligned} \tag{12}$$

where $U_{\rm eq}$ is the equilibrium potential when there is no external bias, $U_1(t)=\Sigma_\alpha u_\alpha(t) v_\alpha$ is the first-order correction, and $u_\alpha(t)$ and $u_{\alpha\beta}(t),\ldots$ are the characteristic potentials.[9,16] Here $u_\alpha(t)$ describes the first-order internal response due to the Coulomb interaction and $u_{\alpha\beta}(t)$ corresponds to the second-order correction. Following sum rules on the characteristic potential can be derived from the requirement of current conserving and gauge invariance: $\Sigma_\alpha u_\alpha(t)=\cos\omega t$ and $\Sigma_\alpha u_{\alpha\beta}(t)=\Sigma_\beta u_{\alpha\beta}(t)=0$.[27] For instance, if all the bias $v_\alpha(t)$ are shifted by a constant amount v_0, the potential landscape will shift by the same amount. Applying this statement in the equation $U_1(t)=\Sigma_\alpha[u_\alpha(t)/\cos(\omega t)]v_\alpha(t)$ leads to $\Sigma_\alpha u_\alpha(t) = \cos(\omega t)$.

A. Characteristic potential at small bias

We now derive the equations governing the characteristic potentials at finite frequency. In Eq. (4) the lesser Green's function $G^<(t,t,U)$ can be expressed in terms of retarded and advanced Green's function using the Keldysh equation,

$$G^<(t,t,U) = \int dt_1 dt_2 G^r(t,t_1,U)\Sigma^<(t_1,t_2)G^a(t_2,t,U). \tag{13}$$

Expanding $G^<(t,t,U)$ in power series of external bias v_α, we can derive the equations for all the characteristic potentials. To illustrate, we calculate ac in the small bias limit. Higher-order terms can be calculated perturbatively. Expanding Green's function G^γ and self-energy Σ^γ_α to the first order in the bias v_α, we have[14,32]

$$G^\gamma(t,t_1) = G^\gamma_0(t,t_1) + g^\gamma(t,t_1)$$

and

$$\Sigma^\gamma_\alpha(t,t_1) = \Sigma^\gamma_{0\alpha}(t,t_1) + \sigma^\gamma_\alpha(t,t_1),$$

where $G^\gamma_0(t,t_1)$ is the equilibrium Green's function and $g^\gamma(t,t_1)$ is the first-order correction. Note that equilibrium Green's function $G^\gamma_0(t_1,t_2)$ and self-energy $\Sigma^\gamma_0(t_1,t_2)$ depend only on the time difference t_1-t_2, while nonequilibrium parts depend on double-time indices t_1 and t_2. In energy representation, the Green's function is written as

$$G^r_0(E) = \frac{1}{E - H_0 - U_{\rm eq} - \Sigma^r_0(E)}. \tag{14}$$

The first-order correction for the retarded, advanced, and lesser Green's function $g^{r,a,<}$ are found by iterating Eq. (10),

$$g^{r,a} = G^{r,a}_0[\sigma^{r,a} + U_1]G^{r,a}_0$$

and

$$g^< = g^r\Sigma^<_0 G^a_0 + G^r_0\sigma^< G^a_0 + G^r_0\Sigma^<_0 g^a.$$

Taking the double-time Fourier transform on the first-order correction of Green's function $g^\gamma(t,t_1)$ and self-energy $\sigma^\gamma_\alpha(t,t_1)$ with $\gamma = <, r, a$, we find

$$g^{r,a}(E_+,E) = \bar{G}^{r,a}_0[\sigma^{r,a}(E_+,E) + U_1(\Omega)]G^{r,a}_0,$$

$$g^<(E_+,E) = \bar{G}^r_0\sigma^<(E_+,E)G^a_0 + g^r(E_+,E)\Sigma^<_0 G^a_0 + \bar{G}^r_0\bar{\Sigma}^<_0 g^a(E_+,E), \tag{15}$$

and[32]

$$\sigma^\gamma_\alpha(E_+,E) = qv_\alpha(\Omega)(\Sigma^\gamma_{0\alpha} - \bar{\Sigma}^\gamma_{0\alpha})/\Omega,$$

where $v_\alpha(\Omega)=\pi v_\alpha[\delta(\Omega+\omega)+\delta(\Omega-\omega)]$. Here ω is the driving frequency and Ω is the response frequency. We have used the abbreviations $\bar{G}^r_0 = G^r_0(E_+)$ and $\bar{\Sigma}^\gamma_{0\alpha}=\Sigma^\gamma_{0\alpha}(E_+)$, with $E_+ = E + \hbar\Omega$. In the linear bias, anticipating only first harmonics are involved, we have $u_\alpha(t)=\Sigma_{m=\pm1}\exp[im\omega t]u_\alpha(m\omega)$. The Fourier transform of $u_\alpha(t)=\int d\Omega \exp(-i\Omega t)u_{\alpha\Omega}/(2\pi)$ gives $u_{\alpha\Omega}=u_\alpha(\Omega)\pi[\delta(\Omega+\omega)+\delta(\Omega-\omega)]$. Note that in the Fourier space, the sum rule for $u_\alpha(t)$ becomes

$$\sum_\alpha u_\alpha(\Omega,x) = 1. \tag{16}$$

To simplify the notation, from now on we will drop the subscript and use G^r instead of G^r_0. To make discussion simple, we will use the wideband limit where the linewidth function is taken to be independent of energy. In this case,

$$\sigma^{r,a}_\alpha(E_+,E) = 0,$$

$$g^{r,a}(E_+,E) = \bar{G}^{r,a}U_1(\Omega)G^{r,a}, \tag{17}$$

and

$$\sigma^<_\alpha(E_+,E) = iq\Gamma_\alpha v_\alpha(\Omega)\frac{f-\bar{f}}{\Omega}, \tag{18}$$

where Γ_α is the linewidth function and $\bar{f}=f(E_+)$. In the wide-band limit, Eq. (15) becomes

$$g^<(E_+,E) = iq\sum_\alpha v_\alpha(\Omega)\frac{f-\bar{f}}{\Omega}\bar{G}^r\Gamma_\alpha G^a + i\bar{G}^r U_1(\Omega)G^r\Gamma G^a f + i\bar{G}^r\Gamma\bar{G}^a U_1(\Omega)G^a\bar{f}. \tag{19}$$

The Fourier transform of the dynamic charge distribution $\rho(t)=iqG^<(t,t)-iqG^<_{\rm eq}$ is given by

$$\rho(\Omega) = iq\int\frac{dE}{2\pi}g^<(E_+,E). \tag{20}$$

Substituting Eqs. (12) and (20) into Eq. (4), the Poisson equation becomes

$$\nabla^2 u_\alpha(\Omega,x) = -4\pi q^2\frac{dn_\alpha(\Omega,x)}{dE} + 4\pi q^2\int dx'\Pi(\Omega,x,x')u_\alpha(\Omega,x'), \tag{21}$$

where we have introduced the frequency-dependent injectivity matrix [its physical meaning will be discussed after Eq. (30)],

$$\frac{dn_\alpha(\Omega)}{dE} = \int \frac{dE}{2\pi}\frac{f-\bar{f}}{\Omega}[\bar{G}^r\Gamma_\alpha G^a], \tag{22}$$

with its diagonal matrix element being the local frequency-dependent injectivity $dn_\alpha(\Omega,x)/dE$ that is related to the frequency-dependent local density of states

$$\frac{dn(\Omega,x)}{dE} = \sum_\alpha \frac{dn_\alpha(\Omega,x)}{dE}. \tag{23}$$

The frequency-dependent partial global density of states[10,12] can also be obtained

$$\frac{dN_\alpha(\Omega)}{dE} = \int \frac{dE}{2\pi}\frac{f-\bar{f}}{\Omega}\mathrm{Tr}[\bar{G}^r\Gamma_\alpha G^a]. \tag{24}$$

For later use, we also introduce the frequency-dependent emissivity matrix $d\bar{n}_\alpha(\Omega)/dE$ defined as

$$\frac{d\bar{n}_\alpha(\Omega)}{dE} = \int \frac{dE}{2\pi}\frac{f-\bar{f}}{\Omega}[G^a\Gamma_\alpha \bar{G}^r], \tag{25}$$

with its diagonal matrix element being frequency-dependent emissivity $d\bar{n}_\alpha(\Omega,x)/dE$. In Eq. (21), $\Pi(\Omega,x,x')$ is the frequency-dependent Lindhard function defined as

$$\Pi(\Omega,x,x') = -i\int \frac{dE}{2\pi}[(f-\bar{f})\bar{G}^r_{xx'}G^a_{x'x} + \bar{G}^a_{xx'}G^a_{x'x}\bar{f} - \bar{G}^r_{xx'}G^r_{x'x}f]. \tag{26}$$

Expanding $dn_\alpha(\Omega,x)/dE$ and Eq. (26) in powers of Ω, it is not difficult to show that

$$\int dx'\Pi(\Omega,x,x') = dn(\Omega,x)/dE \tag{27}$$

and

$$\int dx'\Pi(\Omega,x',x) = d\bar{n}(\Omega,x)/dE, \tag{28}$$

where $d\bar{n}(\Omega,x)/dE = \Sigma_\alpha d\bar{n}_\alpha(\Omega,x)/dE$. From Eqs. (27) and (28), we have,

$$\sum_\alpha \mathrm{Tr}\left[\frac{d\bar{n}_\alpha(\Omega)}{dE}\right] = \sum_\alpha \mathrm{Tr}\left[\frac{dn_\alpha(\Omega)}{dE}\right]. \tag{29}$$

Note that Eq. (27) is also consistent with the gauge-invariant condition $\Sigma_\alpha u_\alpha(\Omega,x)=1$ which can be seen by summing Eq. (21) over α.

In the Thomas-Fermi approximation,[9] we assume $\Pi(\Omega,x,x') = \delta(x-x')dn(\Omega,x)/dE$.[28] This means that only local response is considered. With this approximation, the Poisson equation becomes

$$\nabla^2 u_\alpha(\Omega,x) = -4\pi q^2\frac{dn_\alpha(\Omega,x)}{dE} + 4\pi q^2\frac{dn(\Omega,x)}{dE}u_\alpha(\Omega,x). \tag{30}$$

The physics of Eq. (30) is clear. The frequency-dependent charge distribution on the right-hand side of Eq. (30) consists of two parts: (1) $\rho(\Omega) = \rho_{\mathrm{inj}}(\Omega) + \rho_{\mathrm{ind}}(\Omega)$, where $\rho_{\mathrm{inj}}(\Omega) = dn_\alpha(\Omega,x)/dE$ is the injected charge distribution. For this reason $dn_\alpha(\Omega,x)/dE$ is called frequency-dependent injectivity. (2) $\rho_{\mathrm{ind}}(\Omega) = [dn(\Omega,x)/dE]u_\alpha(\Omega)$ is the induced charge distribution due to the injected charge. In solving Eq. (21) and (30), the following boundary condition must be used: the total charge enclosed in the whole scattering region is zero, i.e.,

$$\mathrm{Tr}\left[\frac{dn_\alpha(\Omega)}{dE} - \Pi(\Omega)u_\alpha(\Omega)\right] = 0, \tag{31}$$

or for the Thomas-Fermi approximation,

$$\mathrm{Tr}\left[\frac{dn_\alpha(\Omega)}{dE} - \frac{dn(\Omega)}{dE}u_\alpha(\Omega)\right] = 0. \tag{32}$$

In Eqs. (31) and (32), $dn_\alpha(\Omega)/dE$ is the frequency-dependent injectivity matrix and $u_\alpha(\Omega)$ and $dn(\Omega)/dE$ are diagonal matrices with matrix element $u_\alpha(\Omega,x)$ and $dn(\Omega,x)/dE$, respectively.

B. Ac at small bias

In the following, we shall calculate the ac in the presence of Coulomb interaction and show that the boundary condition Eq. (31) and (32) leads to the conservation of current.

The ac to the linear order in external voltage can be calculated similar to the lesser Green's function. Expanding Green's functions up to linear order in bias, we have

$$I_\alpha(t) = -q\int dt_1\, \mathrm{Tr}[G^r(t,t_1)\sigma^<_\alpha(t_1,t) + g^r(t,t_1)\Sigma^<_\alpha(t_1,t) + G^<(t,t_1)\sigma^a_\alpha(t_1,t) + g^<(t,t_1)\Sigma^a_\alpha(t_1,t)] + \mathrm{H.c.},$$

where the equilibrium terms cancel to each other because the current is zero when the external voltage is absent. Taking the Fourier transform, we have,

$$\begin{aligned} I_\alpha(\Omega) = -q\int \frac{dE}{2\pi}\mathrm{Tr}[&G^r_0(E_+)\sigma^<_\alpha(E_+,E) + g^r(E_+,E)\Sigma^<_{0\alpha}(E) \\ &+ G^<_0(E_+)\sigma^a_\alpha(E_+,E) + g^<(E_+,E)\Sigma^a_{0\alpha}(E) \\ &- \Sigma^<_{0\alpha}(E_+)g^a(E_+,E) - \sigma^<_\alpha(E_+,E)G^a_0(E) \\ &- \Sigma^r_{0\alpha}(E_+)g^<(E_+,E) - \sigma^r_\alpha(E_+,E)G^<_0(E)]. \end{aligned}$$

In the wideband limit, we find with the help of Eqs. (17)–(19)

$$I_\alpha(\Omega) = q^2\int \frac{dE}{2\pi}\frac{f-\bar{f}}{\Omega}\mathrm{Tr}\left[i(\bar{G}^r - G^a)\Gamma_\alpha v_\alpha(\Omega) - \bar{G}^r\sum_\beta \Gamma_\beta v_\beta(\Omega)G^a\Gamma_\alpha + i\Omega\Gamma_\alpha\bar{G}^r U_1(\Omega)G^a\right]. \tag{33}$$

Equations (30) and (33) are main results of this paper. Note that in Eqs. (30) and (33) all the quantities have been expanded in terms of equilibrium Green's function. In calculating linear ac transport properties in nanodevices, one has to compute two Coulomb potentials: (1) equilibrium Coulomb potential U_{eq} appeared in Eq. (12). With U_{eq} obtained, the Green's function is given by Eq. (14). (2) Nonequilibrium Coulomb potential u_α in the presence of ac bias. The potential u_α determines the contribution from the displacement current.

1. Current conservation

Now we examine the current conservation condition. It is easy to see that

$$\sum_\alpha I_\alpha = iq^2 \int \frac{dE}{2\pi} \mathrm{Tr}\left[\bar{G}^r \sum_\alpha \Gamma_\alpha v_\alpha(\Omega) G^a - \bar{G}^r U_1(\Omega) G^a \Gamma \right] \times (\bar{f} - f).$$

Using the relation (in the wideband limit)[29]

$$\int \frac{dE}{2\pi} \mathrm{Tr}[\bar{G}^a U_1(\Omega) G^a \bar{f} - \bar{G}^r U_1(\Omega) G^r f] = \int \frac{dE}{2\pi} \mathrm{Tr}[(\bar{G}^r - G^a) U_1(\Omega)] \frac{f - \bar{f}}{\Omega}, \qquad (34)$$

we have

$$\sum_\alpha I_\alpha = - \Omega q^2 \sum_\alpha \mathrm{Tr}\left[\frac{dn_\alpha(\Omega)}{dE} - \Pi(\Omega) u_\alpha(\Omega) \right] v_\alpha(\Omega).$$

Note that in obtaining $u_\alpha(\Omega)$ Eq. (31) must be satisfied. Hence we see that the current is conserved up to the first order in bias if the Coulomb interaction $U_1(t)$ is included. From the definition of dynamic conductance $I_\alpha(\Omega) = \Sigma_\beta G_{\alpha\beta}(\Omega) v_\beta(\Omega)$, we find

$$G_{\alpha\beta}(\Omega) = q^2 \int \frac{dE}{2\pi} \mathrm{Tr}[- i(\bar{G}^r - G^a)\Gamma_\alpha \delta_{\alpha\beta} + \bar{G}^r \Gamma_\beta G^a \Gamma_\alpha + i\Omega \Gamma_\alpha \bar{G}^r u_\beta(\Omega) G^a] \frac{f - \bar{f}}{\Omega}, \qquad (35)$$

where $u_\beta(\Omega)$ is the solution of Eq. (21). It is clear that the dynamic conductance consists of two contributions: particle current (terms that does not involve u_β) and displacement current. Note that the current conservation condition gives $\Sigma_\alpha G_{\alpha\beta} = 0$. It is easy to show that $\Sigma_\beta u_\beta(\Omega) = 1$ gives $\Sigma_\beta G_{\alpha\beta} = 0$. In deriving Eq. (35) we have used the wideband limit, it is straightforward to go beyond this limit.

2. Dynamic conductance

We now examine the dynamic conductance in more detail. We introduce an unscreened local dynamic conductance matrix

$$g_{\alpha\beta}(\Omega) = \int \frac{dE}{2\pi} \frac{f - \bar{f}}{\Omega} [i\Omega \bar{G}^r \Gamma_\alpha G^a \delta_{\alpha\beta} - G^a \Gamma \bar{G}^r \Gamma_\alpha \delta_{\alpha\beta} + G^a \Gamma_\alpha \bar{G}^r \Gamma_\beta], \qquad (36)$$

such that q^2 Tr$[g_{\alpha\beta}]$ is equal to the particle current in Eq. (35). Using the Fisher-Lee relation,[30] it is straightforward to show that

$$\mathrm{Tr}[g_{\alpha\beta}] = \int \frac{dE}{2\pi} \frac{f - \bar{f}}{\Omega} \mathrm{Tr}[\delta_{\alpha\beta} - s^\dagger_{\alpha\beta} \bar{s}_{\alpha\beta}], \qquad (37)$$

which agrees with the scattering matrix approach.[13] In addition, if we set $U_1 = 0$ in Eq. (33) it recovers the frequency-dependent current derived by Buttiker *et al.*[13]

In terms of $g_{\alpha\beta}$ and the frequency-dependent emissivity, Eq. (35) can be written in a more compact form similar to the linear-response theory[15]

$$G_{\alpha\beta}(\Omega) = q^2 \ \mathrm{Tr}\left[g_{\alpha\beta}(\Omega) + i\Omega \frac{d\bar{n}_\alpha(\Omega)}{dE} u_\beta(\Omega) \right]. \qquad (38)$$

Note that the frequency-dependent injectivity and emissivity satisfy

$$\sum_\alpha g_{\alpha\beta}(\Omega) = - i\Omega \frac{dn_\beta(\Omega)}{dE} \qquad (39)$$

and

$$\sum_\beta \mathrm{Tr}[g_{\alpha\beta}(\Omega)] = - i\Omega \ \mathrm{Tr}\left[\frac{d\bar{n}_\alpha(\Omega)}{dE} \right]. \qquad (40)$$

As will be clear in Sec. III that in the absence of magnetic field, Eq. (40) is also valid without the trace and therefore makes it symmetric between Eqs. (39) and (40).

In Eq. (38), the second term is a matrix multiplication. In the Thomas-Fermi approximation, it becomes

$$G_{\alpha\beta}(\Omega) = q^2 \ \mathrm{Tr}\left[g_{\alpha\beta}(\Omega) + i\Omega \frac{d\bar{n}_\alpha(\Omega,x)}{dE} u_\beta(\Omega,x) \right], \qquad (41)$$

where the trace is over position x. Now we consider the quasineutrality approximation, i.e., when the local charge is zero at any point $\rho(\Omega,x) = 0$. From Eq. (30) we have $dn_\alpha(\Omega,x)/dE - [dn(\Omega,x)/dE] u_\alpha(\Omega,x) = 0$. Hence, in the quasineutrality approximation, the dynamic conductance is given by

$$G_{\alpha\beta}(\Omega) = q^2 \ \mathrm{Tr}\left[g_{\alpha\beta}(\Omega) + i\Omega \frac{d\bar{n}_\alpha(\Omega,x)}{dE} \frac{dn_\beta(\Omega,x)}{dE} \Big/ \frac{dn(\Omega,x)}{dE} \right].$$

From Eqs. (29), (39), and (40), it is easy to show that $\Sigma_\alpha G_{\alpha\beta}(\Omega) = \Sigma_\beta G_{\alpha\beta}(\Omega) = 0$.

In terms of emissivity, another frequency-dependent partial global density of states can be defined,

$$\frac{d\bar{N}_\alpha(\Omega)}{dE} = \mathrm{Tr}\left[\frac{d\bar{n}_\alpha(\Omega)}{dE} \right] = i \int \frac{dE}{2\pi} \frac{f - \bar{f}}{\Omega^2} \sum_\beta \mathrm{Tr}[\delta_{\alpha\beta} - s^\dagger_{\alpha\beta} \bar{s}_{\alpha\beta}]. \qquad (42)$$

C. Electrochemical capacitance

To discuss electrochemical capacitance, we assume that the scattering region of a two-probe system can be roughly divided into two regions Ω_{I} and Ω_{II} with total charge $Q_{\mathrm{I}}(\Omega)$

and $Q_{\mathrm{II}}(\Omega)$, respectively. The general electrochemical capacitance coefficients can be defined by[15]

$$Q_\alpha(\Omega)=\sum_\beta C_{\alpha\beta}(\Omega)v_\beta(\Omega)+\frac{1}{2}\sum_{\beta\gamma}C_{\alpha\beta\gamma}v_\beta(\Omega)v_\gamma(\Omega)+\cdots. \tag{43}$$

Charge neutrality condition Eq. (31) in the scattering region ensures that $\Sigma_\alpha Q_\alpha(\Omega)=0$. The general bias dependent of Q_α can be obtained by expanding Eq. (13) in terms of bias. To the lowest order in bias, the charge Q_α is given by

$$Q_\alpha(\Omega)=-q^2\int_{\Omega_\alpha}dx\sum_\beta\left[\frac{dn_\beta(\Omega,x)}{dE}v_\beta(\Omega)-\int dx'\Pi(\Omega,x,x')u_\beta(\Omega,x')v_\beta(\Omega)\right], \tag{44}$$

from which we obtain the frequency-dependent electrochemical capacitance,

$$C_{\alpha\beta}(\Omega)=-q^2\int_{\Omega_\alpha}dx\left[\frac{dn_\beta(\Omega,x)}{dE}-\int dx'\Pi(\Omega,x,x')u_\beta(\Omega,x')\right]. \tag{45}$$

In the discrete potential approximation,[31] we use U_{I} and U_{II} to represent the Coulomb potential in regions I and II, respectively. The classical capacitance C_0 can be defined as

$$Q_{\mathrm{I}}(t)=C_0[U_{\mathrm{I}}(t)-U_{\mathrm{II}}(t)] \tag{46}$$

or

$$Q_{\mathrm{I}}(\Omega)=C_0[U_{\mathrm{I}}(\Omega)-U_{\mathrm{II}}(\Omega)]. \tag{47}$$

In the absence of magnetic field and dc transport, Eq. (44) is

$$Q_\alpha(\Omega)=-q^2\left[\frac{dn_\alpha(\Omega)}{dE}v_\alpha(\Omega)-\frac{dn_\alpha(\Omega)}{dE}U_\alpha(\Omega)\right]. \tag{48}$$

From Eq. (44), (46), and (48), we obtain[12]

$$\frac{q^2}{C_{\mathrm{II}}(\Omega)}=\frac{q^2}{C_0}+\frac{1}{dn_{\mathrm{I}}(\Omega)/dE}+\frac{1}{dn_{\mathrm{II}}(\Omega)/dE}. \tag{49}$$

III. RELATIONS AMONG FREQUENCY-DEPENDENT DENSITY OF STATES

A. Orthogonal systems

In the absence of magnetic field and spin-orbit interaction, the system belongs to the orthogonal ensemble and the Hamiltonian H is a real symmetric matrix with $H=H^T$. So the Green's function (inversion of $EI-H+i\eta I$) is also a symmetric matrix. From the fact that $[\bar{G}^r\Gamma_\alpha G^a]^T=[G^a\Gamma_\alpha\bar{G}^r]$, we have

$$\frac{dn_\alpha(\Omega)}{dE}=\left[\frac{d\bar{n}_\alpha(\Omega)}{dE}\right]^T, \tag{50}$$

or

$$\frac{dn_\alpha(\Omega,x)}{dE}=\frac{d\bar{n}_\alpha(\Omega,x)}{dE}, \tag{51}$$

and

$$\Pi(\Omega,x,x')=\Pi(\Omega,x',x), \tag{52}$$

i.e., frequency-dependent Lindhard function is symmetric. If spin-orbit interaction is present while magnetic field is absent, the Hamiltonian is a real quaternion matrix. If we are only interested in the charge transport, Eq. (51) is still valid where the trace over spin is implied.

B. Unitary systems

In the presence of magnetic field B, the system belongs the unitary ensemble. Due to the microreversibility of the scattering matrix, we have

$$s_{\alpha\beta}(B)=s_{\beta\alpha}(-B), \tag{53}$$

the following relation is valid from Eq. (37),

$$\mathrm{Tr}[g_{\alpha\beta}(B)]=\mathrm{Tr}[g_{\beta\alpha}(-B)]. \tag{54}$$

From Eqs. (39) and (40), we arrive at

$$\frac{dN_\alpha(\Omega,B)}{dE}=\frac{d\bar{N}_\alpha(\Omega,-B)}{dE}. \tag{55}$$

To prove the relation for local frequency-dependent injectivity and emissivity, we note that Eq. (53) together with the Fisher-Lee relation implies

$$G^r(B)=[G^r(-B)]^T \tag{56}$$

and similarly $\Gamma_\alpha(B)=[\Gamma_\alpha(-B)]^T$. Hence

$$\frac{dn_\alpha(\Omega,-B)}{dE}=\int\frac{dE}{2\pi}\frac{f-\bar{f}}{\Omega}[\bar{G}^r(-B)\Gamma_\alpha G^a(-B)]=\int\frac{dE}{2\pi}\frac{f-\bar{f}}{\Omega}[G^a(B)\Gamma_\alpha\bar{G}^r(B)]^T \tag{57}$$

or

$$\frac{dn_\alpha(\Omega,B)}{dE}=\left[\frac{d\bar{n}_\alpha(\Omega,-B)}{dE}\right]^T \tag{58}$$

with its diagonal matrix element satisfying

$$dn_\alpha(\Omega,x,-B)/dE=d\bar{n}_\alpha(\Omega,x,B)/dE \tag{59}$$

which is the generalization of the static case.[9] Similarly, for the frequency-dependent Lindhard function we have

$$\Pi(\Omega,x,x',B)=\Pi(\Omega,x',x,-B). \tag{60}$$

Now we will show that when the Coulomb interaction is included the dynamic conductance $G_{\alpha\beta}(\Omega)$ still satisfies a similar relation as that of Eq. (53). To proceed, we first note that the first term in Eq. (38) obeys $\mathrm{Tr}[g_{\alpha\beta}(\Omega,B)]=\mathrm{Tr}[g_{\beta\alpha}(\Omega,-B)]$. For the second term, we introduce the Green's function for $u_\alpha(\Omega)$ as follows:[9]

$$\nabla^2 g(\Omega,x,x') = 4\pi q^2 \int dx'' \Pi(\Omega,x,x'') g(\Omega,x'',x') - 4\pi q^2 \delta(x - x'). \tag{61}$$

From Eqs. (60) and (61) we have

$$g(\Omega,x,x',B) = g(\Omega,x',x,-B). \tag{62}$$

In terms of the Green's function $g(\Omega)$, Eq. (38) is

$$G_{\alpha\beta}(\Omega) = q^2 \,\mathrm{Tr}\left[g_{\alpha\beta}(\Omega) + i\Omega \frac{d\bar{n}_\alpha(\Omega)}{dE} g(\Omega) \frac{dn_\beta(\Omega)}{dE} \right]. \tag{63}$$

Using Eqs. (57) and (62), we finally have

$$G_{\alpha\beta}(\Omega,B) = G_{\beta\alpha}(\Omega,-B). \tag{64}$$

For a two-probe system, the current conserving and gauge-invariant conditions give rise to

$$G_{11}(\Omega) = -G_{12}(\Omega) = G_{22}(\Omega) = -G_{21}(\Omega). \tag{65}$$

From Eqs. (64) and (65) we conclude that $G_{\alpha\beta}(\Omega)$ is an even function of magnetic field for two-probe systems.

IV. DISCUSSION AND SUMMARY

So far, we have demonstrated the current conserving and gauge-invariant formalism in the small bias limit. Higher-order corrections to the current can be obtained perturbatively order by order. Here we give a general proof of the current conserving formalism, i.e., $\Sigma_\alpha I_\alpha(V,U)=0$ if the Coulomb potential is included. To proceed, we make double Fourier transform on Eq. (13) and obtain

$$\int dt G^<(t,t,U)\exp(i\Omega t) = \int (dE/2\pi) G^<(E_+,E,U), \tag{66}$$

where $E_+=E+\Omega$. Hence Eq. (4) becomes

$$\nabla^2 U(\Omega,x) = 4\pi i q \int (dE/2\pi)[G^<(E_+,E,U)]_{xx}. \tag{67}$$

In solving this Poisson equation, we use the following boundary condition:

$$\int (dE/2\pi)\mathrm{Tr}[G^<(E_+,E,U)] = 0, \tag{68}$$

to make sure the total charge conservation in the scattering region [see discussion below Eq. (70)]. Making double Fourier transform on Eq. (6), we have

$$\begin{aligned} I_\alpha(\Omega) = -q \int \frac{dE}{2\pi} \int \frac{dE'}{2\pi} \mathrm{Tr}[&G^r(E+\Omega,E')\Sigma_\alpha^<(E',E) \\ &+ G^<(E+\Omega,E')\Sigma_\alpha^a(E',E) - \Sigma_\alpha^<(E+\Omega,E')G^a(E',E) \\ &- \Sigma_\alpha^r(E+\Omega,E')G^<(E',E)]. \end{aligned} \tag{69}$$

In the Appendix, we shall show that

$$\sum_\alpha I_\alpha(\Omega) = q\Omega \int (dE/2\pi)\mathrm{Tr}[G^<(E_+,E)]. \tag{70}$$

Using Eq. (66), Eq. (70) becomes

$$\sum_\alpha I_\alpha(\Omega) + iq\Omega Q(\Omega) = 0, \tag{71}$$

where $Q(\Omega)$ is the Fourier transform of the total charge accumulation inside the scattering region. Equation (71) is clearly the Fourier transform of the continuity equation with the second term in Eq. (71) being the charge accumulation in the scattering region. Obviously, if the Coulomb interaction is not considered the current given in Eq. (69) is only the particle current. Once the displacement current is included by solving Poisson equation Eq. (67) with the condition Eq. (68), the second term in Eq. (71) is zero and the current is conserved or charge is conserved.

In summary, we have developed a microscopic theory for the time-dependent quantum transport using nonequilibrium Green's-function theory. The theory is current conserving and gauge invariant. The key to this formalism is the inclusion of the self-consistent Coulomb interaction. We have derived the expression for the ac in the small bias limit. At finite bias, one can include the Coulomb interaction by including higher order of characteristic potential order by order. Our theory can be useful in the nonequilibrium situation and can be used in the first-principle transport calculation where the nonequilibrium Green's function is coupled with the density-functional theory.

ACKNOWLEDGMENTS

We gratefully acknowledge support by a RGC grant from the HKSAR under Grant No. HKU 704607P. We thank Y. X. Xing for helpful discussions.

APPENDIX

From Ref. 32, we have the following relation:

$$E_1 G^r_{E_1E_2} - \int dE H_E G^r_{E_1-E,E_2} - (\Sigma^r G^r)_{E_1E_2} = 2\pi\delta(E_1 - E_2), \tag{A1}$$

where we have assumed that the Hamiltonian may depend on time and used the abbreviation $G(E,E')=G_{EE'}$. Here H_E is the Fourier transform of $H(t)$. Multiplying Eq. (A1) by $[G^r]^{-1}_{E_2E'}$ and summing over E_2, we have

$$([G^r]^{-1})_{E_+E'} = 2\pi E_+ \delta(E_+ - E') - H_{E_+-E'} - \Sigma^r_{E_+E'},$$

$$([G^a]^{-1})_{EE'_-} = 2\pi E \delta(E - E'_-) - H_{E-E'_-} - \Sigma^a_{EE'_-},$$

where $E_+=E+\Omega$ and $E'_-=E'-\Omega$. From which we obtain

$$([G^r]^{-1})_{E_+E'} - ([G^a]^{-1})_{EE'_-} = 2\pi\Omega\,\delta(E_+ - E') - (\Sigma^r_{E_+E'} - \Sigma^a_{EE'_-}). \qquad \text{(A2)}$$

Multiplying Eq. (A2) by $G^a(E_1,E)$ from the left and $G^r(E',E_2)$ from the right, one finds,

$$G^a_{E_1E_{2-}} - G^r_{E_{1+}E_2} = 2\pi\Omega\int dE G^a_{E_1E}G^r_{E_+E_2} - \int dEdE' G^a_{E_1E}[\Sigma^r_{E_+E'} - \Sigma^a_{EE'_-}]G^r_{E'E_2}.$$

Therefore,

$$\int\frac{dE}{4\pi^2}\mathrm{Tr}[G^r\Sigma^< - \Sigma^<G^a]_{E_+E} = \int\frac{dE_1dE_2}{4\pi^2}\mathrm{Tr}[G^r_{E_{1+}E_2}(\Sigma^<)_{E_2E_1} - (\Sigma^<)_{E_2E_1}G^a_{E_1E_{2-}}] = -\int\frac{dE}{4\pi^2}(2\pi\Omega G^<_{E_+E} - [(\Sigma^rG^<)_{E_+E} - (G^<\Sigma^a)_{EE_-}]),$$

which is equivalent to Eq. (70).

---

*jianwang@hkusub.hku.hk

[1] T. H. Oosterkamp, L. P. Kouwenhoven, A. E. A. Koolen, N. C. van der Vaart, and C. J. P. M. Harmans, Phys. Rev. Lett. **78**, 1536 (1997); T. H. Oosterkamp, T. Fujisawa, W. G. van der Wiel, K. Ishibashi, R. V. Hijman, S. Tarucha, and L. P. Kouwenhoven, Nature (London) **395**, 873 (1998).

[2] G. B. Lesovik and L. S. Levitov, Phys. Rev. Lett. **72**, 538 (1994).

[3] C. Bruder and H. Schoeller, Phys. Rev. Lett. **72**, 1076 (1994).

[4] A. P. Jauho, N. S. Wingreen, and Y. Meir, Phys. Rev. B **50**, 5528 (1994).

[5] A. Schiller and S. Hershfield, Phys. Rev. Lett. **77**, 1821 (1996).

[6] J. C. Cuevas, A. Martin-Rodero, and A. Levy Yeyati, Phys. Rev. B **54**, 7366 (1996).

[7] R. J. Schoelkopf, A. A. Kozhevnikov, D. E. Prober, and M. J. Rooks, Phys. Rev. Lett. **80**, 2437 (1998).

[8] Q. F. Sun, J. Wang, and T. H. Lin, Phys. Rev. B **61**, 12643 (2000).

[9] M. Buttiker, J. Phys.: Condens. Matter **5**, 9361 (1993).

[10] S. E. Nigg, R. Lopez, and M. Buttiker, Phys. Rev. Lett. **97**, 206804 (2006).

[11] J. Gabelli, G. Feve, J. M. Berroir, B. Placais, A. Cavanna, B. Etienne, Y. Jin, and D. C. Glattli, Science **313**, 499 (2006).

[12] J. Wang, B. G. Wang, and H. Guo, Phys. Rev. B **75**, 155336 (2007).

[13] M. Buttiker, A. Pretre, and H. Thomas, Phys. Rev. Lett. **70**, 4114 (1993).

[14] B. G. Wang, J. Wang, and H. Guo, Phys. Rev. Lett. **82**, 398 (1999).

[15] Z. S. Ma, J. Wang, and H. Guo, Phys. Rev. B **59**, 7575 (1999).

[16] Z. S. Ma, J. Wang, and H. Guo, Phys. Rev. B **57**, 9108 (1998).

[17] The frequency-dependent electrochemical capacitance is an exception (Ref. 12).

[18] J. Taylor, H. Guo, and J. Wang, Phys. Rev. B **63**, 245407 (2001); **63** 121104 (2001).

[19] C. C. Kaun, B. Larade, and H. Guo, Phys. Rev. B **67**, 121411(R) (2003).

[20] C. C. Kaun and H. Guo, Nano Lett. **3**, 1521 (2003).

[21] Z. Y. Ning, Y. Zhu, J. Wang, and H. Guo, Phys. Rev. Lett. **100**, 056803 (2008).

[22] P. S. Damle, A. W. Ghosh, and S. Datta, Phys. Rev. B **64**, 201403(R) (2001).

[23] M. Brandbyge, J.-L. Mozos, P. Ordejón, J. Taylor, and K. Stokbro, Phys. Rev. B **65**, 165401 (2002).

[24] Y. Xue, S. Datta, and M. A. Ratner, Chem. Phys. **281**, 151 (2002).

[25] E. Louis, J. A. Vergés, J. J. Palacios, A. J. Pérez-Jiménez, and E. SanFabián, Phys. Rev. B **67**, 155321 (2003).

[26] L. P. Kadanoff and G. Baym, *Quantum Statistical Mechanics* (Benjamin, London, 1962), p. 21.

[27] When $\omega=0$, it recovers the sum rules given in Refs. 9 and 16 in the static case.

[28] In the presence of magnetic field, one has to be careful on the Thomas-Fermi approximation.

[29] This equation can be proved by expanding the integrand in powers of Ω.

[30] D. S. Fisher and P. A. Lee, Phys. Rev. B **23**, 6851 (1981).

[31] T. Christen and M. Buttiker, Phys. Rev. Lett. **77**, 143 (1996).

[32] M. P. Anantram and S. Datta, Phys. Rev. B **51**, 7632 (1995).