Asymptotic self-consistency in quantum transport calculations

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Ab initio simulations of quantum transport commonly focus on a central region which is considered to be connected to infinite leads through which the current flows. The electronic structure of these distant leads is normally obtained from an equilibrium calculation, ignoring the self-consistent response of the leads to the current. We examine the consequences of this, and show that the electrostatic potential $\Delta\phi$ is effectively being approximated by the difference between electrochemical potentials $\Delta\mu$, and that this approximation is incompatible with asymptotic charge neutrality. In a test calculation for a simple metal-vacuum-metal junction, we find significant errors in the nonequilibrium properties calculated with this approximation, in the limit of small vacuum gaps. We provide a scheme by which these errors may be corrected.

I. INTRODUCTION

The last 15 years have seen considerable progress in the simulation of nonequilibrium many-electron nanoscale systems[1–7] typically using the local density approximation (LDA) to density functional theory[8,9] (DFT) within either a scattering-states-based approach[1,2,10,11] or the framework of nonequilibrium Green's functions (NEGFs).[3–7,12] In the latter simulations the systems under study consist of two electrodes (or leads), placed to the left and to the right of an active central region which contains a molecule and parts of the left and right electrode. Starting from the unconnected electrode–central-region–electrode system with each of the electrodes itself in equilibrium but not in equilibrium with each other,[13] the NEGF formalism then provides the formal apparatus to switch on the contacting terms of the Hamiltonian adiabatically, causing a current to flow through the system. Associated with this current and related to the resistance of the molecule there is a "resistivity dipole" arising from the newly induced charge density, which causes the electrostatic potential to drop in the neighborhood of the central region. The magnitude of the drop in the self-consistent electrostatic potential is essentially fixed by a charge neutrality condition, i.e., the fact that the asymptotic electrode regions must themselves be charge neutral since a net charge would cause the electrostatic potential to diverge. In the case of jellium electrodes, this charge neutrality condition acquires a strict local form[14] since, asymptotically, the electron density exactly cancels the background density at any point. The relationship between electrostatic potential drop and asymptotic charge neutrality has been addressed in earlier work.[10,11,15,16] In this paper we place this into the context of NEGFs, including a discussion of how to incorporate the response of the leads to the passing current within the partitioned-NEGF formalism, and a numerical estimate, based on a simple model system, of the errors induced by ignoring this response. It should be pointed out that any practical implementation of the NEGF formalism based on static DFT cannot, strictly speaking, properly take into account the drop in the electrostatic potential between the leads, since the

adiabatic switching of the contacting terms of the Hamiltonian (i.e., the time-dependent perturbation) changes the density, and the response to that change cannot be described inside the realm of static DFT.[17,18] Furthermore, the lead self-energies, which describe the coupling between the leads and the central region, are commonly obtained from an equilibrium calculation.[4,5] At the level of the Hartree approximation and in the nonequilibrium regime, this means that the leads do not respond to the flow of charge induced by the applied bias voltage; the electrochemical potentials remain fixed to their equilibrium values and the drop in the self-consistent electrostatic potential $\Delta\phi$ is, as discussed below, effectively being approximated by the difference between electrochemical potentials $\Delta\mu$.[1,4,5,19] At the level of the Hartree-Fock approximation this lack of asymptotic self-consistency also implies that the nonequilibrium Fock operator deep inside the leads would be equal to the equilibrium one, which is clearly not the case since the Fock operator depends on the nonequilibrium occupancies of the current-carrying states, which are different from the equilibrium ones everywhere. However, we will not further discuss the effects of the lack of asymptotic self-consistency in the Fock operator. The most severe effects appear already in the self-consistent Hartree potential which we will use as an illustration in our paper. We would like to note that nonpartitioned NEGF approaches, as suggested by Cini[20] and later elaborated by Stefanucci and Almbladh,[21,22] are in theory free from these objections as they focus on the evaluation of the nonequilibrium Green's function in the whole transporting system.

The relation between the electrostatic drop and asymptotic charge neutrality is already implicit in the original form of the Landauer formula[23,24] $I = (2e^2 T / hR)\Delta\phi$, and has been explored by some authors over the years[15,16] until very recently.[25] In Ref. 25 the authors further clarify the distinction between the difference between the electrochemical potentials of the left and right electrodes $\Delta\mu$ and the drop in the electrostatic potential $\Delta\phi$ as well as the role played by the geometry. However they do not discuss in detail the validity of the approximation $\Delta\mu = \Delta\phi$.

To fix ideas consider a biased system that is translationally invariant in two of the three spatial directions and has some localized inhomogeneity along the z direction. Since left- and right-going scattering states are occupied up to two different electrochemical potentials μ_L and μ_R, respectively, a current flows along z, and therefore there is an electrostatic potential drop $\Delta\phi$. *If we assume* that $\Delta\mu = \mu_R - \mu_L = \Delta\phi$, then it is easy to show that in the asymptotic electrode regions the electronic density ρ is in the case of jellium electrodes given by[15,16,26]

$$\rho(z \to \pm\infty) = \rho_B(z \to \pm\infty) \pm \int_0^{+\infty} dk_\pm T(E_z)[f_R(E_z) - f_L(E_z)],$$
(1)

where $\rho_B(z)$ is the background density, $k_\pm$ are the magnitudes of the z components of the momentum in the asymptotic right (+) and left (−) electrode regions, respectively, $E_z(k_\pm) = k_-^2/2 = k_+^2/2 - \Delta\phi$ is the energy associated with the motion in the direction of the current, $T(E_z)$ are the usual transmission probabilities, and f_R and f_L are the equilibrium Fermi-Dirac distributions for right- and left-going electrons averaged over the components of the momentum perpendicular to the direction of the current, each of which is characterized by an electrochemical potential $\mu_{R(L)}$. The latter, as functions of k_-, are given by[15,16,26]

$$f_{L,R}(k_-) = \frac{1}{(2\pi)^2}(k_{L,R}^2 - k_-^2)\Theta(k_- - k_{L,R}),$$
(2)

where $k_{L,R}$ are the asymptotic Fermi wave vectors for left- and right-going electrons, respectively, in the left asymptotic region. Therefore, when imposing $\Delta\mu = \Delta\phi$, associated with the presence of a current from, say, left to right, there is a charge depletion in the asymptotic left-electrode region and a charge accumulation in the asymptotic region of the right electrode.[15,16,25,26] Therefore it is clear that the drop in the *self-consistent* electrostatic potential is necessarily different from $\Delta\mu$. It is then surprising that in many state-of-the-art *ab initio* quantum transport simulations the approximation $\Delta\mu = \Delta\phi$ is used without further explanation or comments on its validity.[1,4,5,19] Of the few that have considered this problem let us mention Pötz,[15] who introduces a drift in the electronic distribution functions of left- and right-going electrons so that the asymptotic electrode regions remain neutral, Bokes and Godby,[16] whose proposed method is applied in this work, and Lang[10] and Di Ventra and Lang,[11] who renormalize the electron densities deep in the jellium electrodes. Even though the effects discussed here are general they may be minimized by particular device geometries such as the quantum point contact geometry where for sufficiently wide electrodes the current density drops to zero and therefore $\Delta\mu \approx \Delta\phi$ asymptotically.

From the above given discussion it should be clear that asymptotic self-consistency (i.e., the *full* nonequilibrium Green's function of the leads) is generally needed in order to describe the drop in the electrostatic potential correctly. The lack of asymptotic self-consistency naturally leads to the approximation $\Delta\mu = \Delta\phi$ which is incompatible with charge neutrality in the asymptotic lead regions. The rest of this paper is organized as follows. In Sec. II we show explicitly the effect that the lack of asymptotic self-consistency has in the calculated nonequilibrium properties of a simple jellium metal-vacuum-metal junction. In Sec. III we express these ideas in the language of NEGFs, showing which terms are commonly neglected and providing a simple recipe to incorporate them for the case of jellium electrodes. We conclude in Sec. IV.

II. EXAMPLE: ASYMPTOTIC CHARGE NEUTRALITY IN A JELLIUM METAL-VACUUM-METAL INTERFACE

Neglecting the nonequilibrium contributions to the Green's function of the leads results, at the level of the Hartree or DFT LDA approximations, in the approximation $\Delta\mu = \Delta\phi$, which in turn is incompatible with asymptotic charge neutrality in the leads. We now show the effects of this approximation in the calculated properties of a nonequilibrium metal-vacuum-metal junction. Even though we will use a scattering-state-based approach its equivalence with the NEGF formalism may be noted.

The jellium model of the metal-vacuum-metal interface[1,27,28] is defined in terms of the background density:

$$\rho_B(z) = n_0[\theta(-z) + \theta(z - L)],$$
(3)

where $n_0 = 3/4\pi r_s^3$ and L is the length of the vacuum gap. For this system we solve the Kohn-Sham equations self-consistently using the Perdew-Zunger[29] parametrization of the LDA exchange-correlation potential. Historically this system was the first to be studied using conventional *ab initio* techniques in a nonequilibrium regime,[1,28] and, for our purposes, constitutes a simple system for which the electrostatic effects under study arise in the most transparent manner.

In order to ensure charge neutrality in the asymptotic electrode regions, for a given value of $\Delta\phi$ we need to find k_R and k_L in Eqs. (2) such that

$$n_0 = \rho(z \to \pm\infty)$$
(4)

are satisfied. k_R and k_L are related to the electrode electrochemical potentials simply by

$$\mu_R - \mu_L = \frac{k_R^2 - k_L^2}{2}.$$
(5)

Therefore, at each step of the self-consistency cycle, we solve the Poisson equation with Dirichlet boundary conditions, fixing $\Delta\phi$ and calculating the corresponding $\Delta\mu$ that ensures that the asymptotic left- and right-electrode regions remain neutral. Strictly speaking this procedure is only justified in the case (such as the metal-vacuum-metal junction) that there is a one-to-one correspondence between $\Delta\mu$ and $\Delta\phi$, i.e., there is a one-to-one correspondence between the applied bias and the current. For this particular case our method is equivalent to the alternative one of fixing $\Delta\mu$ and calculating $\Delta\phi$ by solving the Poisson equation with von Neumann boundary conditions.[7]

When studying the influence of asymptotic charge neutrality on the calculated nonequilibrium properties we solve
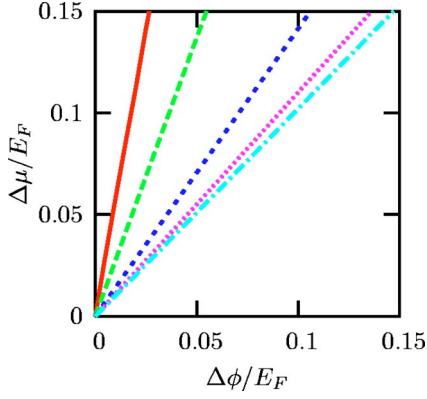
FIG. 1. (Color online) The figure shows the difference between electrochemical potentials $\Delta\mu$ as a function of the drop in the electrostatic potential $\Delta\phi$, in units of the equilibrium Fermi energy, for different values of the electrode-electrode distance L. $L=0.25r_s$ (solid line), $0.5r_s$ (dashed), $1r_s$ (short dashes), $1.5r_s$ (dots), and $2r_s$ (dot-dashed). $\Delta\mu\approx\Delta\phi$ only for large electrode-electrode spacings. For reference $E_F=3.131$ eV.

the Kohn-Sham equations self-consistently using the procedure described by McCann and Brown,[1] with the approximation $\Delta\mu=\Delta\phi$ and without it, using the asymptotic neutrality condition Eq. (4). In particular the Poisson equation is solved using Nieminen's method,[1,19,27] which greatly stabilizes the iterative process and speeds up the convergence.

We next present a set of results for a symmetric metal-vacuum-metal junction with electrodes characterized by $r_s=4$,[30] focusing on the differences between $\Delta\phi$ and $\Delta\mu$ as functions of the electrode-electrode distance and the effect that the lack of asymptotic neutrality has in the calculated resistivity dipoles and current densities.[31] Figure 1 shows a linear relation between $\Delta\mu$ and $\Delta\phi$ for different lengths of the vacuum gap. All the lines fall between two limiting ones: $\Delta\phi=0$ for $L=0$ and $\Delta\phi=\Delta\mu$ for $L\to\infty$ as expected. For $L=0$ the system is homogeneous along the z direction and hence there is no electrostatic drop. As the distance between electrodes increases the transmission coefficient $T(E_z)$ decreases, the current decreases, and $\rho(z\to\pm\infty)\to n_0$; therefore the electrostatic drop and the difference between electrochemical potentials are approximately equal in that limit. In fact $\Delta\mu\approx\Delta\phi$ for $L>2r_s$. However, one should note that there are no molecular conducting channels present in our model. If these were present and open, then the deviation from $\Delta\mu=\Delta\phi$ should, according to Eq. (1), be larger at a fixed value of the electrode-electrode separation. Figure 2 shows the calculated resistivity dipoles defined as

$$\delta\rho(z) = \rho(z,\Delta\phi\neq 0) - \rho(z,\Delta\phi=0) \qquad (6)$$

for different values of the applied bias. In Fig. 2(a) the dipoles were calculated within the approximation $\Delta\mu=\Delta\phi$. Enforcing this boundary condition when solving the Poisson equation leads to the appearance of unphysical charges which are placed at the edges of the numerical grid used in the calculations. These spurious contributions to the induced density disappear as $\Delta\mu\to 0$ or $L\to\infty$, since in these limits $\Delta\mu=\Delta\phi$. In Fig. 2(b) we show the calculated resistivity di-
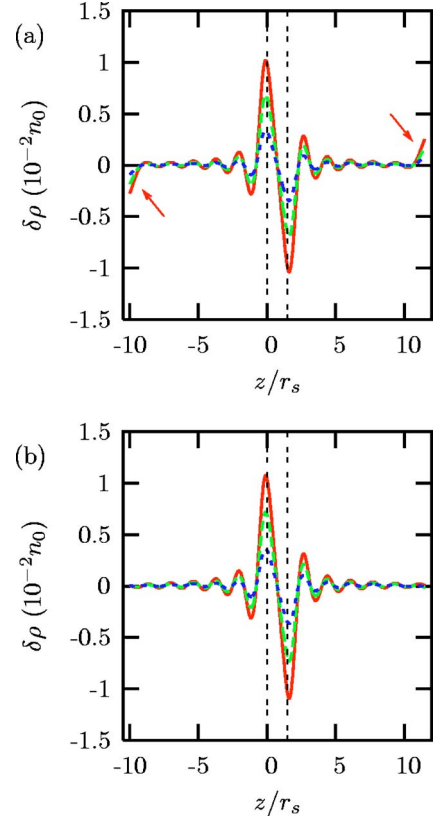

FIG. 2. (Color online) (a) Resistivity dipoles calculated for different values of $\Delta\phi$ with $L=1.5r_s$, using $\Delta\phi=\Delta\mu$. The arrows indicate the presence of unphysical charges at the edges of the numerical grid. (b) Same as in (a) but calculated using our neutrality scheme. Solid line $\Delta\phi/E_F=0.075$, dashed $\Delta\phi/E_F=0.05$, dotted $\Delta\phi/E_F=0.025$. The vertical lines indicate the positions of the edges of both jellium surfaces.

poles by choosing k_L and k_R so that Eqs. (4) are satisfied. The induced density goes smoothly to zero as $z\to\pm\infty$ even at small values of L and relatively large values of $\Delta\phi$. Finally in Fig. 3 we present calculated J-ΔV curves (with ΔV equal to $\Delta\mu$ or $\Delta\phi$ depending on the pair of curves being compared) for different electrode-electrode spacings. A large difference between the J-$\Delta\phi=\Delta\mu$ curve and any of the other two is present at small electrode-electrode separations. As argued above, as the separation between the electrodes becomes larger all three curves converge into a single one. Table I contains numerical values of the ratios between linear response conductances (calculated at a small but finite bias) with and without the approximation $\Delta\mu=\Delta\phi$. The performance of this approximation is poorer for larger values of the conductance, as expected.

III. RELATION TO THE PARTITIONED NEGF APPROACH

Even though the problem of asymptotic charge neutrality for jellium electrodes is clear and directly solvable through the scattering states as is done in this paper, the issue becomes more involved within the partitioned NEGF approach. We proceed to show explicitly the terms that are usually
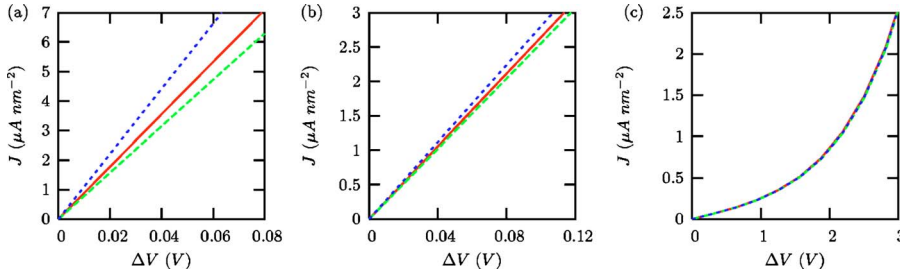
FIG. 3. (Color online) J-ΔV characteristics for different electrode-electrode spacings. L=(a) $1r_s$; (b) $1.5r_s$; (c) $3r_s$. For the solid lines $\Delta V=\Delta\phi=\Delta\mu$, for the dotted lines $\Delta V=\Delta\phi$, and for the dashed lines $\Delta V=\Delta\mu$.

neglected in practical implementations and to provide a simple scheme by which asymptotic self-consistency may be easily implemented.

Let us consider a system's Hamiltonian partitioned into two semi-infinite leads [left (L) and right (R)] and finite central region (C). The Green's functions we consider below are all defined on the Keldysh contour with the complex time variable[32] τ and are meant to represent matrices with two indices m, n belonging to some complete set of spatially localized basis functions. Each of these can belong to any of the above introduced regions L, R, or C. We employ the notation

$$[G_\alpha]_{nm} \equiv -i\langle T_\tau\{\hat{c}_{n\in\alpha}(\tau)\hat{c}^\dagger_{m\in\alpha}(\tau')\}\rangle, \quad \alpha=L,R,C, \quad (7)$$

for the disconnected systems and

$$[G_{\alpha\beta}]_{nm} \equiv -i\langle T_\tau\{\hat{c}_{n\in\alpha}(\tau)\hat{c}^\dagger_{m\in\beta}(\tau')\}\rangle, \quad \alpha,\beta=L,R,C, \quad (8)$$

for the contacting ones. We also use $1 \equiv \delta_{nm}\delta(\tau-\tau')$.

Before we turn on the contacting between L and C and C and R the unconnected Green's functions satisfy the equations of motion

$$(i\partial_\tau - H_L)G_L = 1, \quad (9)$$

$$(i\partial_\tau - H_C)G_C = 1, \quad (10)$$

$$(i\partial_\tau - H_R)G_R = 1. \quad (11)$$

This can be also written in a block form as

$$\left[i\partial_\tau\mathbf{1} - \begin{pmatrix} H_L & 0 & 0 \\ 0 & H_C & 0 \\ 0 & 0 & H_R \end{pmatrix}\right]\begin{pmatrix} G_L & 0 & 0 \\ 0 & G_C & 0 \\ 0 & 0 & G_R \end{pmatrix} = \mathbf{1}, \quad (12)$$

or more concisely as

$$(i\partial_\tau - \mathbf{H})\mathbf{G}^0 = \mathbf{1}. \quad (13)$$

TABLE I. Ratios between the calculated linear response conductances per unit area $G_{2P}=J/\Delta\mu$, $G_{4P}=J/\Delta\phi$, and $G_{\Delta\mu=\Delta\phi}=J/\Delta V$ with $\Delta V=\Delta\mu=\Delta\phi$, together with their corresponding values of the transmission coefficient evaluated at $E_z=E_F$.

L/r_s	$G_{2P}/G_{\Delta\mu=\Delta\phi}$	$G_{4P}/G_{\Delta\mu=\Delta\phi}$	T ($E_z=E_F$)
1.0	0.89	1.24	0.675
1.5	0.97	1.06	0.347
3.0	1.00	1.00	0.006

Next we turn on the interaction terms that couple the left and central and the right and central parts, written as V_L and V_R, respectively. The coupling, however, induces also a change in Hamiltonians via the change of the density in the Hartree and exchange-correlation potentials which we together write as δH_α for $\alpha=L,C,R$. Due to the self-consistent screening $\delta H_{L/R}$ will attain the periodicity of the bulk crystalline electrode far from the central region. Using the block Green's functions we have

$$(i\partial_\tau - \mathbf{H} - \delta\mathbf{H} - \mathbf{V})\mathbf{G} = \mathbf{1}, \quad (14)$$

where

$$\mathbf{H} + \delta\mathbf{H} = \begin{pmatrix} H_L^0 + \delta H_L & V_L & 0 \\ V_L^\dagger & H_C + \delta H_C & V_R \\ 0 & V_R^\dagger & H_R + \delta H_R \end{pmatrix}$$

and

$$\mathbf{G} = \begin{pmatrix} G_{LL} & G_{LC} & G_{LR} \\ G_{CL} & G_{CC} & G_{CR} \\ G_{RL} & G_{RC} & G_{RR} \end{pmatrix}.$$

The solution of Eq. (14) can be written using Eq. (13) in the form of the Dyson equation as

$$\mathbf{G} = \mathbf{G}^0 + \mathbf{G}^0[\delta\mathbf{H} + \mathbf{V}]\cdot\mathbf{G}, \quad (15)$$

where $\cdot$ stands for the integral along the Keldysh contour over an internal time variable.

The Green's function of the central region corresponds to the finite system and is usually solved numerically in a self-consistent manner. It solves the Dyson equation

$$G_{CC} = G_C + G_C\delta H_C\cdot G_{CC} + G_C V_L\cdot G_{LC} + G_C V_R\cdot G_{RC} \quad (16)$$

which can be found as the "CC" component of Eq. (15). To have a closed system of equations we need to find G_{LC} and G_{RC}. These are similarly given as "LC" and "RC" components of Eq. (15) as

$$G_{LC} = G_L V_L\cdot G_{CC} + G_L\delta H_L\cdot G_{LC} \quad (17)$$

and

$$G_{RC} = G_R V_R\cdot G_{CC} + G_R\delta H_R\cdot G_{RC}. \quad (18)$$

The latter two can be formally inverted (in m, n as well as in τ) to give

$$G_{LC} = [1 - G_L\delta H_L]^{-1}\cdot G_L V_L\cdot G_{CC}, \quad (19)$$

$$G_{RC} = [1 - G_R \delta H_R]^{-1} \cdot G_R V_R \cdot G_{CC}. \tag{20}$$

Combining Eqs. (16), (19), and (20) we finally obtain

$$G_{CC} = G_C + G_C(\delta H_C + \Sigma_{CC}) \cdot G_{CC}, \tag{21}$$

$$\Sigma_{CC} = V_L[1 - G_L \delta H_L]^{-1} \cdot G_L V_L + V_R[1 - G_R \delta H_R]^{-1} \cdot G_R V_R \tag{22}$$

$$= V_L \widetilde{G}_L V_L + V_R \widetilde{G}_R V_R, \tag{23}$$

where we have introduced the self-energy Σ_{CC} representing the leads for the central region and defined new auxiliary Green's functions $\widetilde{G}_{L/R}$ that satisfy the equations of motion

$$(i\partial_\tau - H_\alpha - \delta H_\alpha)\widetilde{G}_\alpha = 1, \quad \alpha = L, R. \tag{24}$$

The surface Green's functions $\widetilde{G}_\alpha$ need to be such that they correspond to the equilibrium situation with $\delta H_{L/R}$ being turned on but with chemical potentials (or Fermi-Dirac occupation factors f_L and f_R) kept the same as in $G_{L/R}$. For this reason the only significance of the auxiliary Green's functions is their presence in the expression for the self-energy Σ_{CC}; they have no other direct physical meaning.[33] Using the calculated G_{CC} in Eq. (19) one can now employ the usual derivation of the expression for the current in terms of $G_{LC}^<$ (Ref. 34)

$$I = \frac{2e}{\hbar} \text{Re}\{\text{Tr}[VG_{LC}^<]\}. \tag{25}$$

The usual treatments[3,5,6] do not consider the change in the lead Hamiltonians due to the change in density $\delta H_{L/R}$ that arises in the nonequilibrium regime. This results in a simplification of our equations since the resolvent operators $[1 - G_R \delta H_R]^{-1}$ and $[1 - G_L \delta H_L]^{-1}$ do not have to be calculated in the nonequilibrium regime. We note that the evaluation of these would require a complete calculation of G_{LL} and G_{RR} for the contacting system since these give the nonequilibrium density which in turn determines the changes $\delta H_{L/R}$. This can be most easily achieved for semi-infinite jellium electrodes, which is equivalent to the calculations presented in the previous section of this paper (see also Ref. 22 for model one-dimensional cases treated directly using the nonpartitioned NEGF formalism). In this case the change in the potential is just a constant shift, i.e., $\delta H_{L/R} = \delta U_{L/R}$, which ensures the asymptotic charge neutrality. As can be seen from Eq. (24), this shift moves the bottoms of the bands in the lead densities of states, which are the only characteristics of the leads that eventually enters into the final expression for the current Eq. (25). The relation between the drop in the chemical potentials, the drop in the induced potential, and these shifts is simply

$$\Delta\phi + \delta U_L - \delta U_R = \mu_R - \mu_L. \tag{26}$$

Here we have three unknowns $\Delta\phi$ and $\delta U_{L/R}$. $\delta U_{L/R}$, or even the full $\delta H_{L/R}$ for the case of atomistic calculation, can be determined iteratively from the central region Hamiltonian. To describe the implementation of asymptotic self-consistency into the usual *ab initio* NEGF calculations we first consider a central region of converged size which includes parts of the atomic layers of the left and right electrodes. One could start the iterative cycle by calculating the the Kohn-Sham Hamiltonian in the central region with the initial guess $\Delta\phi = \Delta\mu$ (i.e., $\delta H_{L/R} = 0$). Due to the self-consistent screening in the central region we expect its Hamiltonian to be a good approximation to the actual one except in regions that are close to the edges of the partition. By including enough of the electrode's atomic layers into the central region one can infer the change $\delta H_{L/R}$, or its average over one unit cell $\delta U_{L/R}$, from the shape of the self-consistent potential inside the included atomic layers within the central region. In order to complete the iteration we need an updated estimate of the central region self-energy Σ_{CC} which involves inverting the semi-infinite matrix in Eq. (24), a task that can be done using conventional techniques.[35,36]

IV. CONCLUSIONS

We have shown that in an exact time-dependent density functional formulation of the partitioned Keldysh-NEGF approach the changes in the Hamiltonian of the leads due to the contact need to be included. It is important for a correct description of the electrostatic potential profile at large currents or junctions with transmission close to 1. Using a simple jellium model of a biased metal-vacuum-metal junction we have examined quantitatively the effects of fixing $\Delta\mu = \Delta\phi$. Significant differences between the nonequilibrium properties calculated using this approximation and using a more reasonable treatment of the electrostatic problem based on asymptotic charge neutrality arise in the limit of small electrode-electrode separation. These effects would be even more pronounced for resonant molecular junctions where both electrostatics and high conductance acting simultaneously may significantly influence the *I-V* characteristics of the system.

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