

First-Principles Electrostatic Embedding for Dielectric and Capacitance Analysis in Nonequilibrium 2D Devices

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Abstract— As semiconductor devices approach the atomic-scale limit, reliable modeling of device electrostatics requires a first-principles description of non-equilibrium electronic structure. While density functional theory (DFT) combined with the nonequilibrium Green's function formalism has been widely used for quantum transport, key electrostatic quantities such as interfacial capacitance and local permittivity under non-equilibrium conditions remain difficult to define due to the ambiguity in partitioning quantum-mechanically hybridized systems. Herein, we introduce an electrostatic potential embedding method within multi-space constrained-search DFT to enable atomistic analysis of dielectric properties of devices under non-equilibrium conditions. The method allows consistent partitioning of a device into subsystems through an embedding potential derived from the full nonequilibrium solutions, enabling direct evaluation of geometric and quantum capacitances as well as spatially resolved permittivity. This approach provides a rigorous first-principles route to characterize interfacial electrostatics in nanoscale devices.

Keywords— Dielectric, Capacitance, Interface, Device

I. INTRODUCTION

As semiconductor devices are pushed toward nanometer-scale dimensions, their characteristics become increasingly dependent on atomic-scale details. Technology computer-aided design (TCAD) has long been a key framework for the analysis and optimization of semiconductor devices, particularly through continuum-level descriptions that are essential for practical device design. For regimes in which quantum-mechanical and atomistic effects strongly influence carrier transport, density functional theory combined with the non-equilibrium Green's function formalism (DFT-NEGF) serves as a powerful framework for describing nanoscale devices at an atomistic, quantum-mechanical level [1].

Within the DFT-NEGF formalism, the non-equilibrium electronic structure of an atomic-scale device is described from the Landauer viewpoint, in which the central scattering region is treated as an open system coupled to semi-infinite electrodes under an applied bias. However, this Landauer viewpoint intrinsically imposes several limitations on standard DFT-NEGF. In particular, since the DFT-NEGF formalism describes the electrodes as grand-canonical macroscopic reservoirs repeated semi-indefinitely along the transport direction, standard DFT-NEGF is not naturally applicable to finite-sized or low-dimensional electrodes, such as graphene, where the electrostatic potential alone may not uniquely determine the

electrochemical state due to its low density of states (DOS). More importantly, the variational total energy and Kohn-Sham wave functions, which are central quantities in conventional DFT and provide much of its microscopic interpretability, are not directly available within DFT-NEGF. As a result, several device properties beyond quantum transport are inaccessible or difficult to evaluate within standard DFT-NEGF.

In particular, interfacial properties, which are essential for determining device characteristics, are difficult to understand because their interpretation typically requires partitioning the electronic structure into different device components. At the atomic scale, such partitioning is inherently ambiguous, as quantum-mechanical hybridization at the interface hinders the separation of the total electronic structure into individual electrode, interface, and channel contributions [Fig. 1(a)]. In conventional DFT, wave-function projection onto local atomic or orbital bases can partially resolve this ambiguity by providing microscopic information. In this respect, standard DFT-NEGF does not provide direct access to a comparable wave-function-level description that can separately resolve the material, interface, and electrostatic contributions to the non-equilibrium device response.

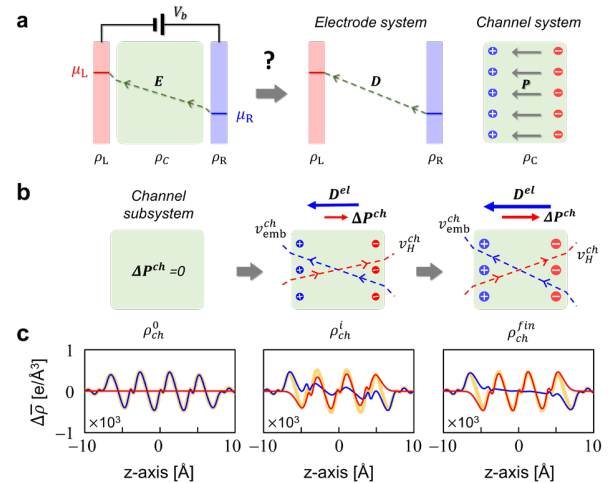


Fig. 1. Schematic of (a) nanoscale device simulations, where the decomposition for electronic densities of electrode and channel system is ambiguous. (b) Electrostatic potential embedding method as an example for channel as target system. (c) Self-consistent partitioning process for the electronic densities in electrostatic potential embedding for channel (red) and electrode (blue) sub-system.

Recently, multi-space density functional theory (MS-DFT) [2, 3] has been developed that replaces the Landauer picture with the multi-space excitation viewpoint and adopts a microcanonical ensemble analogous to conventional DFT. As a result, MS-DFT provides a variational description of non-equilibrium electronic states while retaining access to variational non-equilibrium total energies, Kohn–Sham wave functions, and local chemical-potential information, such as quasi-Fermi-level distributions in the channel region, which enables general device analysis at the atomic level. Another key distinction from DFT–NEGF is the electrode boundary condition, as MS-DFT is applicable to finite-sized electrodes and uses the electrochemical potential difference rather than the electrostatic potential difference that enables reliable calculations of finite-capacitance device models.

We develop an electrostatic-potential embedding method within the MS-DFT framework for analyzing non-equilibrium quantum-mechanical subsystems in nanoscale devices. In this approach, the device is partitioned into a target subsystem and its surrounding environment, and the target subsystem is embedded in the electrostatic potential generated by the remaining part of the device. This formulation enables the practical decomposition of the subsystem electron density retaining the electrostatic influence of the full device, and thus allows the extraction of device properties. By utilizing the chemical- and electrostatic-potential information available in MS-DFT, the method provides the total capacitance and its decomposition into geometric and quantum capacitance contributions. It also enables the analysis of local interface properties under non-equilibrium conditions, including polarization and local dielectric responses such as static and optical permittivities. The method is validated by extracting the capacitance and dielectric properties of a two-dimensional nanocapacitor and comparing them with experimental results.

II. METHODS

A. MS-DFT formalism

We first summarize the MS-DFT formalism, which adopts a microcanonical picture and maps the finite-bias quantum transport process onto a multi-space excitation. For a junction composed of the left electrode (L), channel (C), and right electrode (R) regions, the nonequilibrium Kohn–Sham wave functions, (ψ_i) are classified according to their dominant spatial character. Specifically, the states predominantly associated with the L , C , R regions are denoted as ψ_i^L , ψ_i^C and ψ_i^R , respectively. This classification can be efficiently implemented within a localized atomic-orbital basis representation.

To impose non-equilibrium condition, the occupation of L and R states in the electrode regions are assigned electrochemical potentials μ_L and μ_R , respectively. The C states in the scattering channel region on the other hand, are assigned to either μ_L or μ_R according to their spatial proximity to the left or right electrode. Under this construction, the nonequilibrium Kohn–Sham Hamiltonian of the L – C – R system can be formulated, and the corresponding total energy is minimized variationally under the constraint of an applied bias, $eV_b = \mu_L - \mu_R$, imposed on the occupations of the electronic states.

We note that the electrochemical-potential difference can be further decomposed $eV_b = e\Delta\phi + \Delta\delta\mu$, where $\Delta\phi = \phi_L - \phi_R$

is the electrostatic potential drop, and $\Delta\delta\mu = \delta\mu_L - \delta\mu_R$ is the chemical potential shift. In contrast to the conventional DFT–NEGF formalism, which typically imposes boundary conditions on $e\Delta\phi$, MS-DFT constrains the full electrochemical-potential difference between μ_L and μ_R including chemical potential contributions $\delta\mu$, allowing reliable description for the electrochemical interface.

B. Electrostatic potential embedding

Although MS-DFT provides a well-defined classification of nonequilibrium Kohn–Sham states according to their dominant spatial character, directly using the classified states to construct regional densities, $\rho^{L/C/R} = \sum_{i \in occ} |\psi_i^{L/C/R}|^2$, does not generally yield a proper subsystem density for evaluating device properties. This is because the nonequilibrium states remain quantum mechanically coupled across the electrode–channel interfaces and are typically spatially extended along the junction. Therefore, for the analysis of bias-induced interfacial polarization, capacitance, and dielectric response in atomistic device structures, a spatial decomposition of the total electron density into electrode and channel contributions is required, rather than a decomposition based solely on the wave functions.

To this end, the total electron density of the device system is decomposed into target-subsystem and environment-subsystem contributions as, $\rho^{tot}(\mathbf{r}; V_b) = \rho^S(\mathbf{r}; V_b) + \rho^{S'}(\mathbf{r}; V_b)$. Here, S and S' denote the target and environment subsystems, respectively. In this work, we choose the channel as the target subsystem, $S = ch$, and the electrodes as the environment, $S' = el$. Although the opposite assignment is, in principle, admissible, the dependence of the results on the choice of target subsystem will be examined in future work.

For a device under an applied bias V_b , the nonequilibrium MS-DFT calculation provides the total electron density of the full device, $\rho^{tot}(\mathbf{r}; V_b)$, and the corresponding electrostatic potential, $v_H^{tot}(\mathbf{r}; V_b)$. Given a trial density $\rho^{ch}(\mathbf{r}; V_b)$ for the target subsystem, the electrostatic embedding potential acting on ch is defined as $v_{emb}^{ch}(\mathbf{r}; V_b) = v_H^{tot}(\mathbf{r}; V_b) - v_H^{ch}(\mathbf{r}; V_b)$, where v_H^{ch} is the Hartree potential generated by ρ^{ch} [Fig 2b]. The embedding potential is incorporated into the Kohn–Sham Hamiltonian of ch , and the embedded Kohn–Sham equations are solved until ψ_i^{ch} and the corresponding ρ^{ch} converge. The resulting ρ^{ch} and ρ^{el} are thereby effectively separated and become consistent with those of the corresponding spatial regions in the full MS-DFT calculations [Fig 2c].

C. Capacitance and dielectric properties

Applying the electrostatic-potential embedding scheme to the capacitor models, the total self-consistent density can be decomposed into electrode and channel contributions, denoted by ρ^{el} and ρ^{ch} , respectively. These subsystem densities provide a direct route to the electrostatic, quantum, and dielectric response of the device.

For the capacitance analysis, we first define the bias-induced charge density in the electrodes as $\Delta\rho^{el}(\mathbf{r}, V_b) = \rho^{el}(\mathbf{r}, V_b) - \rho^{el}(\mathbf{r}, 0)$. The excess charge accumulated on the left and right

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electrodes is then given by $Q^{L/R}(V_b) = e \int_{\Omega_{L/R}} \Delta\rho^{el}(\mathbf{r}, V_b) d\mathbf{r}$, where $\Omega_{L/R}$ denotes the spatial domain of the left or right electrode, excluding the channel region. For a two-terminal capacitor under charge-neutral biasing, the excess charges satisfy $Q(V_b) = Q^L(V_b) = -Q^R(V_b)$. The corresponding free charge density and electric displacement are $\sigma(V_b) = Q(V_b)/A$ and $D(V_b) = 4\pi\sigma(V_b)$, respectively, where A is the cross-sectional area of the device. The differential total capacitance is then defined as

$$C_{tot}(V_b) = \frac{dQ(V_b)}{dV_b} \quad (1)$$

Using the decomposition of the electrochemical potential difference, $eV_b = e\Delta\phi + \Delta\delta\mu$, the inverse total capacitance can be separated into geometrical and quantum contributions, $C_{tot}^{-1} = C_{geo}^{-1} + C_q^{-1}$. Here, the geometrical capacitance is

$$C_{geo}(V_b) = \frac{dQ(V_b)}{d\Delta\phi} \quad (2)$$

and quantum capacitance is

$$C_q(V_b) = e \frac{dQ(V_b)}{d\Delta\delta\mu} \quad (3)$$

We next evaluate the local dielectric response of the channel. The bias-induced channel charge density is defined as $\Delta\rho^{ch}(\mathbf{r}, V_b) = \rho^{ch}(\mathbf{r}, V_b) - \rho^{ch}(\mathbf{r}, 0)$. Introducing the planar average along the direction z normal to the capacitor plates, the induced polarization profile is obtained as $\Delta\bar{P}(z, V_b) = \int_{z_0}^z \Delta\rho^{electrode}(\mathbf{r}, V_b) dz$, where z_0 is a reference position at which the induced polarization is set to zero. The local dielectric response is then evaluated as [4],

$$\bar{\epsilon}(z, V_b) = \frac{D(V_b)}{D(V_b) - 4\pi\Delta\bar{P}(z, V_b)} \quad (4)$$

The spatial profile of $\bar{\epsilon}(z, V_b)$ thus resolves the inhomogeneous dielectric screening of the channel region under finite bias.

III. RESULTS AND DISCUSSION

Having established the electrostatic-potential embedding scheme within MS-DFT, we now apply it to the first-principles evaluation of dielectric and capacitance properties in model nanocapacitors. We consider vdW nanocapacitor models consisting of three-layer (3L) hBN sandwiched between gold (Au) or graphene (G) electrodes [Fig. 2a]. MS-DFT calculations are performed for both capacitor models under an applied bias V_b between the left and right electrodes. Then, and applying the electrostatic potential embedding, we evaluate the excess charges (Q) accumulated at the electrodes as a function of V_b [Fig. 2b], and obtain the corresponding total, geometrical, and quantum capacitances, denoted by, $C_{geo}(V_b)$, and $C_q(V_b)$, respectively [Fig. 2c]. For the Au-electrode capacitor, $C_{tot}(V_b)$ is nearly equivalent to $C_{geo}(V_b)$, whereas for the graphene electrode capacitor, $C_{tot}(V_b)$ deviates from the $C_{geo}(V_b)$ due to the lower magnitudes of $C_q(V_b)$ which increases approximately linearly with V_b reflecting the linear density of states of graphene electrode's near the Dirac point [5].

We further analyze the effect of channel thickness on the capacitance of the G/multilayer-hBN/G and Au/multilayer-hBN/Au capacitor models. Specifically, we calculate the inverse

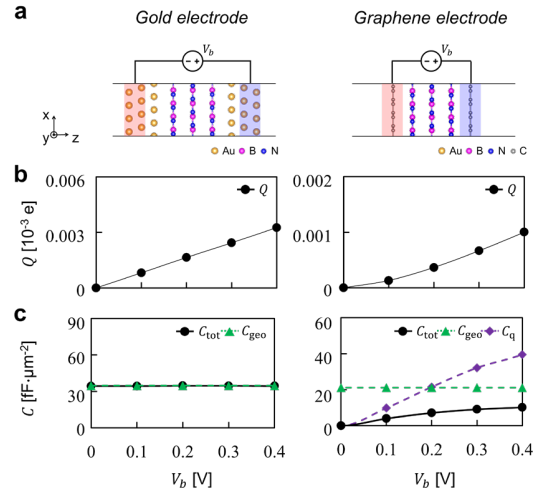


Fig. 2. (a) Atomic models of Au/3L-hBN/Au (left) and G/3L-hBN/G nanocapacitor models (right). (b) Calculated excess charge (Q) and (c) C_{tot} , C_{geo} , and C_q as a function of V_b for the Au/3L-hBN/Au (left) and G/3L-hBN/G (right).

geometrical capacitance as a function of the thickness d , of the hBN slab, where d is defined as the distance between the outermost hBN layers, and d_{int} denotes the interlayer distance between electrode and [Fig. 3a]. The thickness dependence can be analyzed using $1/C_{geo} = (d/\epsilon_{bulk} + d_{int}/\epsilon_{int})/A$, which separates the bulk and interfacial contributions to the geometrical capacitance. From this analysis, we extract the out-of-plane interfacial and bulk optical dielectric constants, ϵ_{int}^∞ and ϵ_{bulk}^∞ , respectively [black diamond, Fig. 3b]. For both Au- and graphene-electrode capacitors, the extracted bulk dielectric constants show $\epsilon_{bulk}^\infty = 2.9$, which is in good agreement with theoretical result (3.0) [6]. However, for ϵ_{int}^∞ , we observe that the Au/hBN interface exhibits a significantly larger value than the G/hBN interface, which is attributed to the stronger electronic screening effect of gold [7].

To further analyze ionic contributions to the dielectric response, we additionally relax the atomic geometries of the hBN layers under finite bias within the MS-DFT framework. This provides the corresponding static dielectric parameters, $\epsilon_{int}^0 = 4.9$ and $\epsilon_{int}^0 = 3.2$ for the Au-electrode capacitor, and $\epsilon_{int}^0 = 3.6$ and $\epsilon_{int}^0 = 3.2$ for the graphene-electrode capacitor [grey diamond, Fig. 3b]. We note that the obtained static dielectric constants are larger than the corresponding optical values, reflecting the additional ionic-polarization contribution. The extracted bulk static value, however, is smaller than the previously reported value of 3.8 for the bulk condition [6]. This reduction can potentially be attributed to the confined junction geometry, which also appears in electrode/water/dielectric geometries [8].

To obtain an atomistic picture of the interfacial dielectric response, we evaluate the local permittivity profiles $\bar{\epsilon}(z)$ for both graphene- and Au-electrode models with 3L- and 5L-hBN channels under $V_b = 1.0$. As shown in Fig. 3c, the $1/\bar{\epsilon}(z)$ obtained from the electrostatic-potential embedding approach agrees well with that derived from the external field method. In both capacitor models, the dielectric response in the inner region

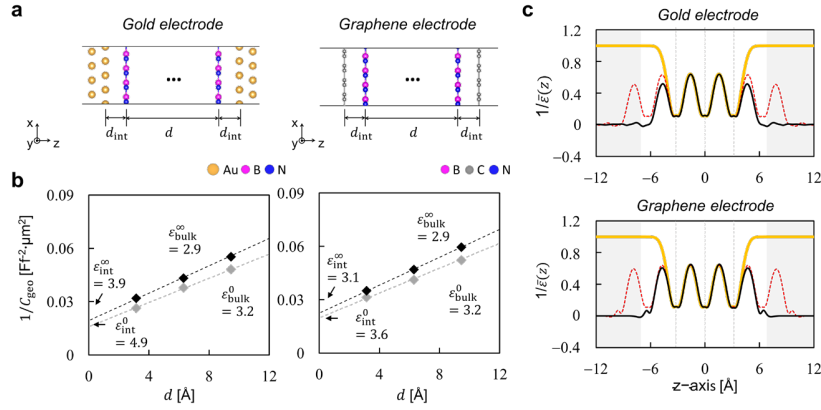


Fig. 3. (a) Atomic model of Au/hBN/Au (left) and G/hBN/G (right). (b) $1/C_{geo}$ of Au/hBN/Au (left) and G/hBN/G (right) as a function of channel distance d . (c) $1/\epsilon(z)$ profiles of Au/3L-hBN/Au (top) and G/3L-hBN/G (bottom). The black solid and red dotted lines represent permittivity profiles for the 3L- (black solid) and 5L-hBN (red dotted) capacitor models, respectively, whereas the yellow line indicate the result from the external field approach.

of the hBN slab remains nearly unchanged. Near the interface, however, the Au-electrode capacitor exhibits a larger local permittivity than the graphene-electrode capacitor, consistent with the capacitance analysis. These results demonstrate that the electrostatic-potential embedding approach captures both the macroscopic capacitance and the atomistic details of interfacial dielectric screening in vdW nanocapacitors.

IV. CONCLUSION

To summarize, we have developed an electrostatic-potential embedding scheme within the MS-DFT framework to decompose the nonequilibrium electron density of nanoscale devices under applied bias into channel and electrode contributions. By applying this scheme to two-dimensional hBN-dielectric-based nanocapacitors with Au or graphene electrodes, we evaluate the capacitance and dielectric properties from first principles.

For the capacitance properties, the Au-electrode capacitor shows a total capacitance nearly identical to the geometrical capacitance, whereas the graphene-electrode capacitor exhibits a finite quantum-capacitance contribution associated with the low density of states near the Dirac point. We have also demonstrated that thickness-dependent capacitance analysis separates the bulk and interfacial dielectric contributions, revealing stronger interfacial screening at the Au/hBN interface than at the G/hBN interface. Ionic relaxation of the hBN layers under applied bias further enhances the static dielectric response.

To further capture the atomistic dielectric properties of the interface, we have also analyzed the local permittivity profiles. The dielectric response in the inner hBN layers agrees well with fixed-field calculations, whereas clear differences appear near the interface depending on the electrode. In particular, the Au-electrode capacitor shows a larger interfacial permittivity than the graphene-electrode capacitor, consistent with the capacitance analysis. These results demonstrate that the present approach captures both macroscopic capacitance and atomistic interfacial dielectric screening. They also provide a useful first-principles framework for designing nanoscale energy-storage

and electronic devices, including supercapacitors and gate dielectrics.

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