



Atomistic Modeling of Metal-Nanotube Contacts

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Abstract. The scaling-down of devices to the atomistic scale lets them operate close to their ballistic limit. At these dimensions the resistance of the entire system is dominated by the contacts. In this paper we describe a simulation tool by which the metal-nanotube heterostructure is modeled atomistically in its entirety, so that contact properties and the associated contact resistances can be explored for different contact materials. We show results for a self-consistently calculated current-voltage (I-V) for an armchair tube with its open ends contacted to gold-[111] surface.

Keywords: carbon-nanotubes, contacts, quantum transport, NEGF, molecular electronics

1. Introduction

The study of transport through molecules attached to surfaces, and nanoscale devices such as metal-nanotube heterostructures is of high technological and fundamental interest. Since the size of the devices are continuously shrinking to atomistic scales, quantum mechanical effects dominate and control the performance of the device. On these scales the physical and chemical properties of the interface region between the device and the contacts become particularly important, especially when the central device operates close to its ballistic limit. Under these conditions the effective resistance of the entire system is dominated by the interface, which extends only a few atomic layers.

Near-ballistic transport of carbon-nanotube FETs (CNT-FETs) has been experimentally reported at low temperatures, where CNTs show Schottky-barrier type behavior. On the other hand, ohmic behavior has also been reported, with Pd contacts, for example [1]. It is therefore important to develop an atomistic description of the metal-CNT interface.

To understand transport through metal-nanotube contacts on an atomistic scale, different modeling and simulation techniques, each well-established in separate communities, have to be merged. One has to ac-

count for the electronic structures of both the metal and the tube, along with the local bonding chemistry, charge transfer and bandlineup at their interfaces, the 3D electrostatics, and finally non-equilibrium quantum transport under bias—all at the same time.

In this article we describe a self-consistent Poisson-NEGF scheme that accounts for the above using Extended-Hückel-theory (EHT) [2] to model the metal-nanotube system atomistically, cf. Fig. 1.

2. Choice of Model Hamiltonian

The first step within the modeling process is to specify an appropriate Hamiltonian for each sub-system, namely for the device (tube) and the contacts. For an atomistic description we choose EHT, which is a non-orthogonal, semi-empirical electronic structure scheme well-known in quantum chemistry [2], and which has been extended to describe bulk-properties of solids such as bandstructures [3].

In contrast to empirical tight-binding, where the Hamiltonian matrix elements are directly used as fitting parameters, in EHT only the diagonal (onsite) matrix elements of the Hamiltonian H and the orbital basis-functions are fitted. The prescription to construct the

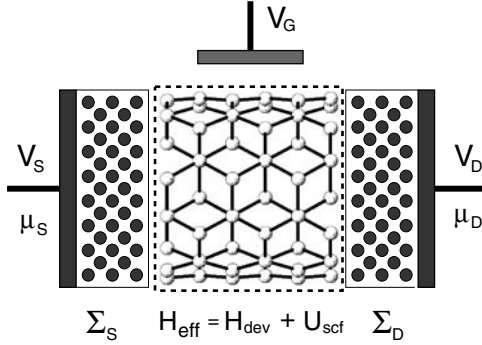


Figure 1. Sketch of a typical device geometry for a CNT connected to metallic contacts such as gold in [111]-orientation. H_{eff} corresponds to the effective device Hamiltonian incorporating the Hamiltonian of the isolated device H_{dev} , and the self-consistent potential U_{scf} . The self-energy matrices $\Sigma_{S,D}$ are introduced to account for the device-contact couplings. V_S , V_D , and V_G are the source, drain, and gate terminal potentials, respectively.

EHT-matrix elements is

$$H_{\mu\mu} = E_{\mu\mu} \text{ (fit)}, \quad (1)$$

$$H_{\mu\nu} = \frac{1}{2} K_{\text{eht}} S_{\mu\nu} (H_{\mu\mu} + H_{\nu\nu}), \quad (2)$$

$$S_{\mu\nu} = \int d^3\mathbf{r} \phi_{\mu}^*(\mathbf{r}) \phi_{\nu}(\mathbf{r}), \quad (3)$$

where $S_{\mu\nu}$ is the overlap matrix between the atomic wavefunction $\phi_{\mu,v}$ of orbital μ and ν , respectively [2]. K_{eht} is an additional fitting parameter, typically set to 1.75 for molecules and 2.3 for solids [2,3].

Employing the parametrization due to Cerda et al. [3] ensures, that the chosen model Hamiltonian reproduces the correct bulk physics by means of the $E - k$ relation, cf. Fig. 2. This is an important step within the benchmarking of the individual sub-systems, since the bulk-bandstructure of the contacts enter indirectly into the self-energy Σ , which accounts for the open boundary condition of the device Green's function, as will be discussed further below.

3. Laplace Potential

The Laplace equation, $\Delta\Phi_L(\mathbf{r}) = 0$ is solved using the Finite Element Method employing Dirichlet boundary conditions for the potential at the source, drain, and gate. The source is taken as reference and is grounded. The Laplace solution at each carbon-atom position $\{\mathbf{R}_i\}$

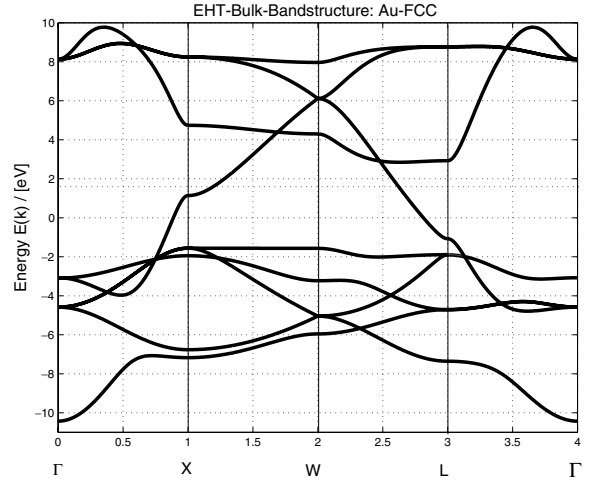


Figure 2. Calculated bulk-bandstructure for gold within Extended-Hückel theory using the parametrization due to Cerda [3].

is obtained using linear superposition

$$\begin{aligned} \Phi_L(\mathbf{R}_i) = & V_D \Phi_{L,D}(\mathbf{R}_i) + V_G \Phi_{L,G}(\mathbf{R}_i) \\ & + V_S \Phi_{L,S}(\mathbf{R}_i), \end{aligned} \quad (4)$$

where we set $\Phi_{L,S}(\mathbf{R}_i) = 0$ by grounding the source. We solve for $\Phi_{L,D}$ and $\Phi_{L,G}$ separately using $\Delta\Phi(\mathbf{r}) = 0$ with unit voltage applied only to the corresponding plate and grounding the rest. The electrostatic energy is then given by $U_L(\mathbf{R}_i) = -q\Phi_L(\mathbf{R}_i)$ with $q = |e|$ the charge of the electron.

4. Poisson Potential in CNDO

In order to obtain the electrostatic potential due to the charge distribution in the device, we solve the integral form of Poisson's equation in orbital space. The interaction energy between electrons is given by [2,4]

$$H_{\sigma\delta}^{ee} = \sum_{\alpha\beta} \rho_{\alpha\beta} \left[(\sigma\delta|\alpha\beta) - \frac{1}{2}(\sigma\alpha|\delta\beta) \right], \quad (5)$$

where $(\sigma\delta|\alpha\beta)$ is the two-center integral for electron-repulsion, and ρ is the density-matrix. The second term to the right of Eq. (5) is the Fock-(exchange) term, which we will discard. The first term describes the classical Coulomb (Hartree) interaction.

The two-center electron-integrals can be calculated within the CNDO-approximation (Complete Neglect

of **Differential Overlap**). Within this scheme the two-center integral is approximated by $(\sigma\delta|\alpha\beta) = 0$ except for $(\sigma\sigma|\delta\delta) = \gamma_{\sigma\delta}$. A further simplification can be made if the integrals for all valence orbitals of the same atom are identical, $\gamma_{\sigma\delta} \equiv \gamma_{ij}$, $\forall \sigma \in i, \delta \in j$, where i, j are atomic indices [4]. This means that electron-electron interactions are not orbital resolved. In this case the electrostatic energy at site \mathbf{R}_i is given by the Poisson term

$$U_{i,P} = \gamma_{ii}\rho_i + \sum_{j \neq i} \rho_j \gamma_{ij}, \quad \text{with} \quad (6)$$

$$\rho_i = \sum_{\sigma} \rho_{\sigma\sigma}^i, \quad (7)$$

$$\gamma_{ij} = e^2 / \left(4\pi\epsilon_0 R_{ij} + \frac{2e^2}{\gamma_{ii} + \gamma_{jj}} \right), \quad (8)$$

and R_{ij} the distance between atom i and j . The electrostatic interaction between two electrons located at atom i and j , respectively, is calculated via Eq. (8) within the Mataga-Nishimoto approximation [4].

The values for the one-center two-electron integrals γ_{ii} are taken from experimental data for the ionization energies and electron affinities for each atom species i . Due to non-orthogonality, the atomic Poisson-term also contains an off-diagonal contribution $U_{ij,P} = \frac{1}{2} S_{ij}(U_{i,P} + U_{j,P})$ with S_{ij} the overlap between atom i and j .

5. Non-Equilibrium Transport

The transport of electrons through the nanotube under bias is described by means of the Non-Equilibrium Green's Function formalism (NEGF) [5–7]. The central quantity within this formalism is the retarded Green's function G which formally corresponds to the retarded response due to a local excitation.

Within the coupled Poisson-NEGF solver the retarded Green's function of the device is given by

$$G = (ES - H_{dev} - U_{scf}(\rho) - \Sigma_S - \Sigma_D)^{-1} \quad (9)$$

which includes the matrix elements S, H of the isolated device, the effective self-consistent potential $U_{scf} = U_L + U_P(\rho)$ consisting of the Laplace and Poisson potentials, and the self-energy matrices $\Sigma_{S,D}$.

The self-energy matrices account for the open boundary conditions for the device region due to the source and drain contacts. Each contact is assumed to be in equilibrium, characterized by the Fermi-Dirac

distribution $f_i(E) = 1/(1 + \exp[\beta(E - \mu_i)])$, $i = S, D$ and $\beta = (k_B T)^{-1}$ with k_B the Boltzmann constant, T the temperature, and μ_i the chemical potential of contact i . The self-energy matrices are given by $\Sigma = \tau G_s \tau^\dagger$, where τ corresponds to the coupling matrix describing the chemical bonding between the tube and the gold-[111] surface. G_s is the surface Green's function of the contacts, which is energy dependent, and contains all information about the bulk-bandstructure of the leads projected on the gold-[111] surface. The contacts are assumed to be semi-infinite leads along the transport axis, and infinite in the transverse direction. As described in [8] the surface Green's function can be calculated iteratively along the transport axis using periodic boundary conditions in the transverse direction.

Figure 3 shows the bulk (DOS) and surface (SDOS) density of states of the gold-contact modeled in EHT. The Fermi-energy is at $E_F = -10.0$ eV and the DOS per atom per spin is roughly ≈ 0.18 eV $^{-1}$, which agrees very well with the published data for the total DOS of ≈ 0.34 eV $^{-1}$ including spin [9]. The non-equilibrium part enters into the formalism when calculating the correlation function $G^<$ [7], which specifies the non-equilibrium occupancy of the device states. The state filling is determined both by the contact chemical potentials and their couplings strength to the device.

The strength of the coupling is determined by the broadening matrices $\Gamma_{S,D} = i(\Sigma_{S,D} - \Sigma_{S,D}^\dagger)$, which characterizes the life-time of an electron in each device state. The electron correlation and the respective

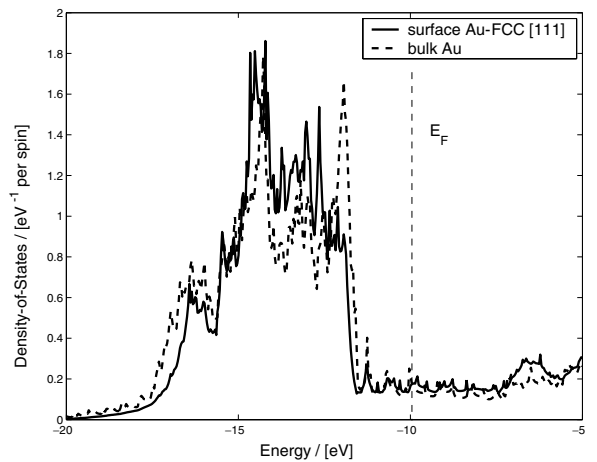


Figure 3. Calculated bulk (green) and surface density-of-states (blue) for gold-[111] determined by means of the recursive technique as described in Ref. [8].

density matrix at energy E are given by [7]

$$G^<(E) = iG(f_1\Gamma_1 + f_2\Gamma_2)G^\dagger \quad (10)$$

$$\rho = \frac{i}{2\pi} \int_{-\infty}^{\infty} dE G^<(E) . \quad (11)$$

The calculation has to be done self-consistently, since ρ depends on U (ρ) through the retarded Green's function G . The self-consistently converged Green's function is used to calculate the bias-dependent transmission, $T(E) = \text{Tr}[\Gamma_S G \Gamma_D G^\dagger]$, and the source-drain current, $I = \frac{2e}{h} \int_{-\infty}^{\infty} dE T(E) [f_S(E) - f_D(E)]$ [7].

6. Results and Discussion

We now apply the above scheme to calculate the I-V characteristics for a metallic, armchair (5,5)-tube connected to a gold-[111] surface, cf. Fig. 4. The I-V is linear within the bias voltage range of ± 1 V. For ideal CNT-CNT junctions, we get a conductance of $2G_0 = 4e^2/h$ coming from two degenerate valleys and a factor of 2 due to spin. With Au-contacts, however, the conductance of the CNT is reduced to $G \approx G_0 = 2e^2/h$, implying that only one of the two metallic bands conducts around the Fermi level. This agrees with equilibrium ab-initio calculations of Palacios et al. [11], who considered different metals such as Al and Au. Choi et al. [10] argued that the decrease of the conductance from $2G_0$ to G_0 can be explained in terms of the different coupling strengths

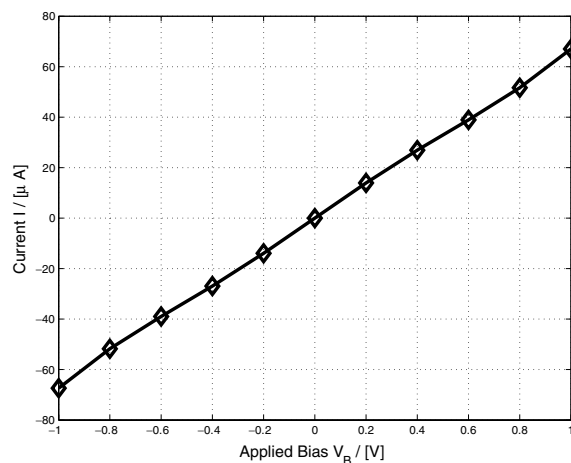


Figure 4. Self-consistently calculated I-V as function of the bias voltage V_B for a metallic (5,5)-CNT connected to bulk-Au contacts.

of the extended π and π^* states of the tube due to their different angular momenta. At present, it is not clear if this is the operating mechanism in our calculations, and the theory therefore needs further investigation.

7. Summary

We have described a self-consistent solution scheme based on NEGF within Extended-Hückel theory. This theory is capable of capturing the bulk-contact physics as well as the chemical bonding at the interface. The scheme was applied to calculate the I-V for a metallic tube connected to Au-[111] surface, where the conductance was reduced to $G \approx G_0$, consistent with other calculations.

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