

Transport Simulations with Density-Matrix-Based Real-Time Time-Dependant Density Functional Theory

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Abstract—This paper compares the results of two different ab-initio approaches to simulate electronic transport through nanostructures. The first one is real-time time-dependant density functional theory, the second one the Non-Equilibrium Green's Function formalism. Both methods are applied here to the computation of the channel resistance of a carbon nanotube placed between two Pd electrodes. A remarkably good agreement between them is found.

I. INTRODUCTION

Real-time time-dependant density functional theory (RT-TDDFT) is a powerful method to simulate electronic processes from first principles. The method is based on the integration of the time-dependant Schrödinger equation at the DFT^[1, 2] level of accuracy. It is non-perturbing and does not need a steady electronic state, thus allowing for the investigation of a wide range of phenomena such as transient regimes. Furthermore, RT-TDDFT can be expanded to Ehrenfest molecular dynamics (EMD), which generalizes this technique to include atomic core movements.

In this paper, after briefly introducing the approach, we compute the transport properties of a metallic carbon nanotube (CNT) embedded between two Pd contacts with RT-TDDFT and compare the results with those obtained via the Non-equilibrium Green's function (NEGF)^{[3]–[5]} formalism combined with DFT. NEGF is a well-established method in the field of device simulation^[6], contrary to TDDFT, which usually finds application in the computation of absorption spectra. A good agreement between both simulation methods is demonstrated when considering the channel resistance of the considered CNT device in the ballistic limit of transport. To the best of our knowledge such a comparison^[7, 8] as well as RT-TDDFT simulations for the purpose of transport in general^{[9]–[13]} have so far only been done for small systems, not realistic CNT structures composed of more than 1000 atoms.

II. METHODS

RT-TDDFT explicitly propagates the electronic wave-function of the inspected structure over time. The equation describing the propagation is^[14]:

$$\dot{a}_a^j = - \sum_{\beta\gamma} iS_{\alpha\beta}^{-1} H_{\beta\gamma} a_\gamma^j, \quad (1)$$

with S being the overlap matrix, a^j the coefficients of the j th molecular orbital when the wave-function is expressed as a linear combination of atomic orbitals, here contracted Gaussian-type orbitals (GTO), i.e.

$$\psi^j(r, t) = \sum_a a_\alpha^j \phi_\alpha(r - R_{A_\alpha}), \quad (2)$$

finally, in Eq.(1), H is the Kohn-Sham Hamiltonian^[2]:

$$E_{KS}[\rho[\{\psi_j\}]] = T_s[\{\psi_j\}] + E_{ext}[\rho] + E_{Coul}[\rho] + E_{xc}^{ALDA}[\rho], \quad (3)$$

where $T_s[\{\psi_j\}]$ is the kinetic, $E_{ext}[\rho]$ the external, $E_{Coul}[\rho]$ the Coulomb, and $E_{xc}^{ALDA}[\rho]$ the exchange-correlation energy within the adiabatic local density approximation (ALDA).

As an illustration of the method, electron transport through the metallic carbon nanotube placed between two palladium contacts of Fig. 1 is investigated. For the RT-TDDFT calculation a voltage is applied through two planes of fixed electrostatic potential^[15], one on each side of the system. This potential difference induces a current from one side to the other. It has been shown that such closed boundary conditions can correctly produce a temporary steady-state^[16, 17].

RT-TDDFT and EMD have been implemented in the CP2K DFT package^[18, 19]. The software has been recently expanded to exploit sparsity by propagating the density matrix instead of the wave-function itself. This allows for a better scaling of the computational time for large atomic systems^[20]. The NEGF calculations have been performed at the DFT level via the coupling of

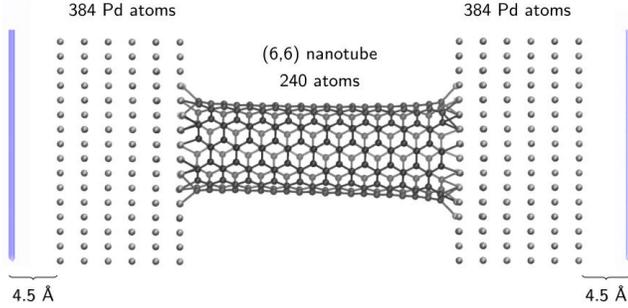


Fig. 1. Simulation Setup for the calculation of the current through a metallic (6,6) carbon nanotube. The planes on the side of the system are constraints for the Poisson equation solver, where the potential is fixed. The palladium contacts serve as a reservoir from which electrons are taken away from/added to the system, during the simulation. The length of the nanotube is approximately 2.5 nm and the width of the contacts about 1.3 nm each. The structure is composed of a total of 1008 atoms, which corresponds to a Hamiltonian and overlap matrix of size 22320 x 22320.

CP2K and the OMEN^{[21]–[23]} quantum transport code. In both cases, a DZVP basis set was used with 25 GTO per Pd atom and 13 GTO per C atom. Goedecker-Teter-Hutter (GTH) pseudopotentials^[24] were used to simulate the atomic cores and the inner electrons. The exchange-correlation energy was calculated through the Perdew-Burke-Ernzerhof (PBE)^[25] GGA functional. The plane-wave cutoff for the calculation of the electrostatic and the exchange-correlation energy was set to 300 Rydberg. The time step for the RT-TDDFT simulation was limited to five attoseconds per step, and the wave-function was propagated using the enforced time-reversible symmetry (ETRS) propagator^[26]. The filtering threshold for the Hamiltonian, the overlap, and the density matrices was 10^{-12} .

III. RESULTS

At the beginning of the RT-TDDFT simulation the ground-state density is calculated and used as starting point for the electronic wave-function. During the evolution of the system, following the application of a bias of 0.25 V, three stages are observed (Figs 2 and 3). Initially the field is constant across the system, which causes a uni-directional current across both the contacts and the tube. After approximately 100 attoseconds the field in the metallic contacts vanishes as a result of the contact polarization. At this point, the current inside the contacts is rather chaotic, but it is uniformly distributed in the nanotube, as the electric field. The current leads to an accumulation of charges at the boundaries of the device. These charges shield the applied voltage and therefore the field across the tube slowly decreases, followed by

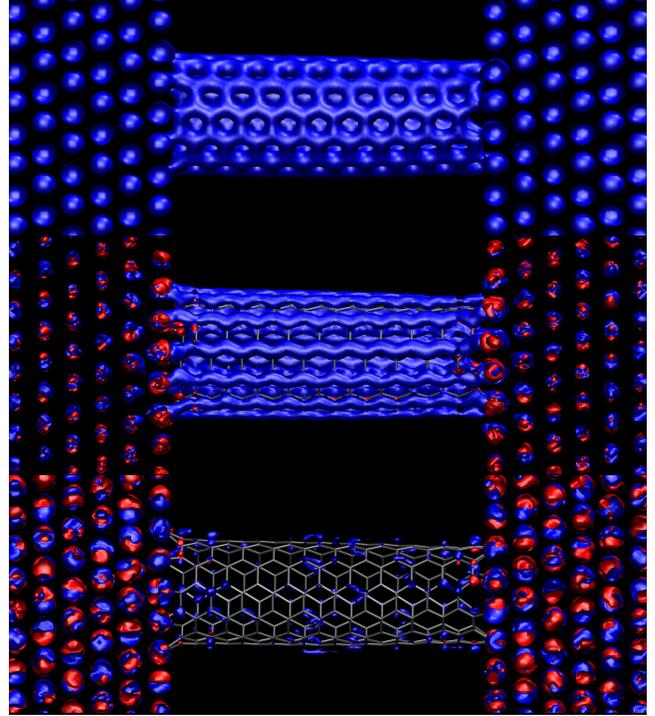


Fig. 2. Visualization of the current through the CNT structure, taken at 25, 500 and 5000 (top to down) attoseconds simulation time. The color indicates the direction of the current, blue for right to left propagation, red for left to right.

the current intensity. In the final stage the system reaches an equilibrium. The accumulated charges completely hide the potential difference and no effective current or field remains inside the CNT.

The resistivity of the nanotube can be extracted from the change in charges on the contacts as a function of the time. We used two methods (Fig. 4) to calculate the resistivity and derived a value of 10.1 and 11.4 $k\Omega$, respectively, which is close to the resistance of 12.9 $k\Omega$, which is obtained at quantum conductance. The first method focuses on the initial phase of the simulation, while the second extracts the resistance from the total simulation, through an equivalent circuit model. The good agreement between both methods is interesting, since the simulation is longer than the time it takes for backscattering to occur inside the contacts. The dependence of the resistivity on the voltage has been carefully analysed by performing simulations at different applied voltages and the system was found to be ohmic, as expected from a metallic nanotube.

For the NEGF simulations the contacts must be expanded with more layers of palladium atoms to allow for the introduction of open boundary conditions. The initial wave-function is obtained from a CP2K energy

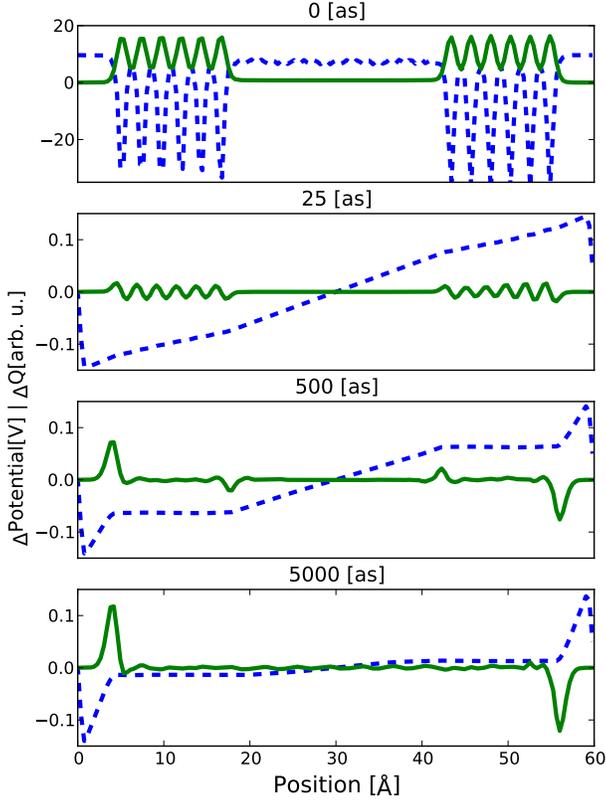


Fig. 3. Evolution of the electrostatic potential (dashed blue lines) and electronic density (solid green line) over time. Initial state ($t=0$) (top). Changes in electrostatic potential and electronic density between the initial state and the one after at 25 (middle-top), 500 (middle-bottom), and 5000 (bottom) attoseconds.

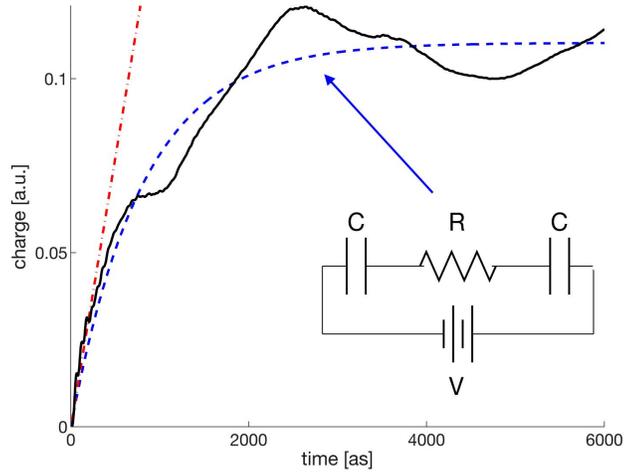


Fig. 4. Extraction methods for the device resistance based on the electric charge that moves from one metal contact to the other as a function of time. (solid black line) First method: The resistance is calculated from a linear fit of the charge transfer at $t=0$ (dash-dotted red). Second method: The resistance is estimated from a circuit model, as illustrated in the inset (dashed blue line). The circuit is composed of two capacitors that account for the coupling between the planes with a fixed potential and the Pd contacts and of a resistor that corresponds to the nanotube channel. The analytical solution of the circuit is an exponential function of the form $n(t) = \frac{CV}{2}(1 - \exp^{-\frac{2t}{RC}})$.

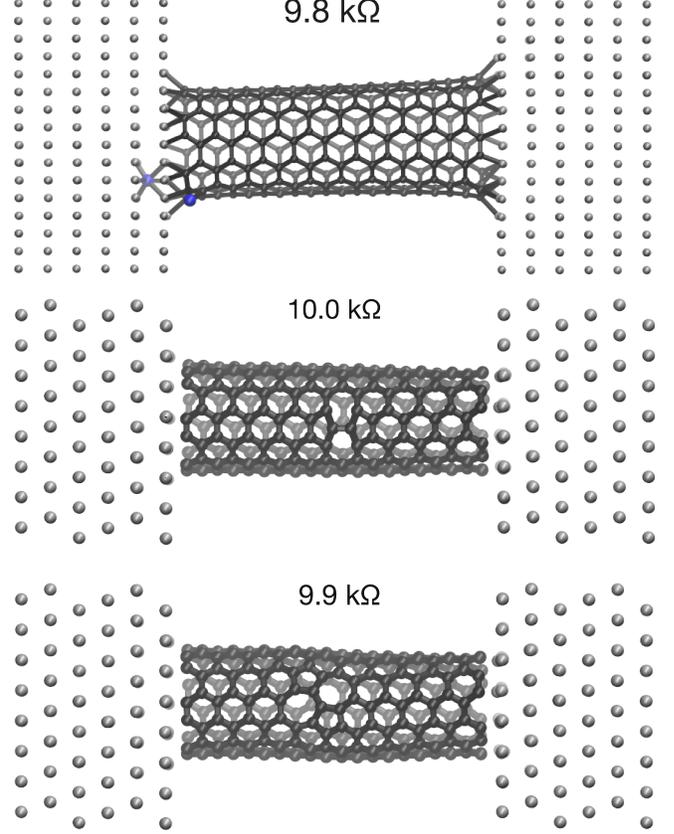


Fig. 5. Nanotube structure with various defects introduced. The resistances have been calculated with the first method from Fig. 4 (time step: 1 as, potential: 1 V) (top) Hydrogen atoms added at the Pd/nanotube interface. (middle, bottom) Stone-Wales defects inside the nanotube in two different orientations.

minimization. The transmission probability through the CNT structure is then calculated semi-self-consistently at zero bias (low-field approximation) and 300 Kelvin in the post-SCF phase. The obtained NEGF resistance is equal to $11.1 \text{ k}\Omega$, a result very close to the one derived from RT-TDDFT, thus confirming the validity of the latter approach for transport calculations.

Furthermore, the impact of several defect types (e.g. hydrogen atoms at the metal/CNT interface or Stone-Wales defects ^[27]) (Fig. 5), in the nanotube and the contact regions, was studied. None of the considered configurations was found to significantly alter the resistance.

IV. CONCLUSION

We have determined the electric resistance of a carbon nanotube connecting two metallic contacts using two different approaches, RT-TDDFT and NEGF. The calculated electric resistances are in good agreement. This supports the usage of RT-TDDFT/EMD as an efficient alternative to NEGF for the simulation of electronic processes from

first-principles, RT-TDDFT also has the advantage that it can be applied to non-steady-state cases, such as transient regimes. In the future, larger and semiconducting instead of metallic systems will be investigated.

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