Time-dependent QM/EM Simulation Method Applied to Carbon Nanotube

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***Abstract*—A hybrid method based on quantum mechanics and electromagnetics is used for simulation of the real time dynamics. The scalar and vector potentials are used to integrate Maxwell's equations in the time domain. The TDDFT-NEGF-EOM method is employed to simulate the electronic dynamics in the quantum mechanical region. When a classical electromagnetic wave penetrates into the quantum mechanical region, the entire system can be solved with Maxwell's equations.**

Keywords—quantum mechanics; electromagnetics; hybrid; time domain

I. INTRODUCTION

Quantum mechanical calculations are limited to the computational costs of small system. While, Maxwell's equation coupled with the drift-diffusion equation for charge transport ignores the quantum effects and atomistic details. To simulate the entire system, there has been found a hybrid method which combines quantum mechanics (QM) and electromagnetics (EM), the QM/EM method. The core region is modeled with quantum mechanics considered quantum effects and atomistic details, the rest of the system is modeled with Maxwell's equation and the drift-diffusion equation. We exert the method to time domain which QM region are modeled by time-dependent density-functional theory (TDDFT) and Maxwell's equations are employed to simulate the electromagnetic response. This method is a good guarantee of accuracy and efficiency.

II. METHODS

A. Electromagnetics Simulation

Maxwell's equations are employed to describe the temporal and spatial evolution of the EM fields. Maxwell's equations in Differential forms are as follows:

$$\begin{aligned}\nabla\cdot\vec{E} &= -\frac{\partial}{\partial t}\vec{B}\\ \nabla\cdot\vec{H} &= \vec{J}+\frac{\partial}{\partial t}\vec{D}\\ \nabla\cdot\vec{B} &= 0\\ \nabla\cdot\vec{D} &= \rho\end{aligned} \tag{1}$$

where $\vec{E}$, $\vec{H}$, $\vec{D}$, and $\vec{B}$ denote the electric field, the magnetic field, the electrical induction, and the magnetic induction, respectively. And ρ and $\vec{J}$ denote the charge and current densities, respectively.

By employing the constitutive relations and an alternative scalar and vector potentials, we can simplify the Maxwell's equation as

$$\begin{aligned}&\nabla\cdot\left[\varepsilon\left(-\nabla V-\frac{\partial}{\partial t}\vec{A}\right)\right]-\rho=0\\ &\nabla\times\left[\frac{1}{\mu}\left(\nabla\times\vec{A}\right)\right]-\left[\vec{J}+\frac{\partial}{\partial t}\left(\varepsilon\left(-\nabla V-\frac{\partial}{\partial t}\vec{A}\right)\right)\right]=0\end{aligned} \tag{2}$$

The constitutive equation connected the current $\vec{J}$ with the electric field. The free carrier densities are also considered in the EM region.

For the conductor in the system, $\vec{J}$ is given by Ohm's law:

$$\vec{J}=\sigma\vec{E} \tag{3}$$

where σ is the conductivity of the conductor. And the current continuity equation is given as followed:

$$\nabla\cdot\vec{J}+\frac{\partial}{\partial t}\rho=0 \tag{4}$$

As for the semiconductors, the current due to electrons (or holes) is split into drift and diffusion terms:

$$\begin{aligned}\vec{J}_n &= q\mu_n n\vec{E}+k_B T\mu_n\nabla n\\ \vec{J}_p &= q\mu_p p\vec{E}-k_B T\mu_p\nabla p\end{aligned} \tag{5}$$

where n and p represent the electron and hole density, respectively. $\mu_{n(p)}$ denotes the mobility of the electron(hole). k_B is Boltzmann constant and T is temperature. The continuity equations for the electrons and holes are

$$\begin{aligned}\nabla\cdot\vec{J}_n-q\frac{\partial}{\partial t}n-qR(n,p)=0\\ \nabla\cdot\vec{J}_n+q\frac{\partial}{\partial t}p+qR(n,p)=0\end{aligned} \tag{6}$$

where R is the charge carrier generation rate. Finally, the total charge density is given as

$$\rho = q(p - n + N_D - N_A) \tag{7}$$

The EM part is solved by the finite volume method (FVM).

B. Quantum Mechanics Simulation

For QM calculation, the TDDFT-NEGFEOM method is employed. To improve the computational efficiency, the AWBL approximation and the density functional tight-binding (DFTB) is adopted for the electronic dynamics.

An electronic device is considered to connect with left and right electrodes. We simulate the current through the central device region with a time-dependent bias potential, and follow the equation of motion of the reduced single electron density matrix of the device region, given as

$$i\sigma_D(t) = [h_D(t), \sigma_D(t)] - i\sum_{\alpha=L,R} Q_\alpha(t) \tag{8}$$

where h_D and σ_D denote the fock and density matrix of the device, respectively. Q stands for the influence of electrodes or gates.

Based on the framework of the NEGF formalism, $Q(t)$ can be written in a form only related to the dimension of the device region

$$\begin{aligned} Q_\alpha(t) = &\int_{-\infty}^{\infty} d\tau \left[\sum\nolimits_\alpha^r (t,\tau) G^<(\tau,t) + \sum\nolimits_\alpha^< (t,\tau) G^a(\tau,t) \right] \\ &- \int_{-\infty}^{\infty} d\tau \left[G^<(t,\tau) \sum\nolimits_\alpha^a (\tau,t) + G^r(t,\tau) \sum\nolimits_\alpha^< (\tau,t) \right] \end{aligned} \tag{9}$$

This equation involved with Green's function is of great difficulties to solve. Therefore, an AWBL approximation is adopted to reduce the complexity of the calculation.

III. Numerical Results

The time-domain QM/EM method has been applied to a carbon nanotube device with two electrodes embedded in a silicon substrate, and the device has a dimension of $8\times5\times5$ nm^3. The carbon nanotube constructed of 144 carbon atoms with hydrogenation saturation on both sides can be analysed for its own transport properties.

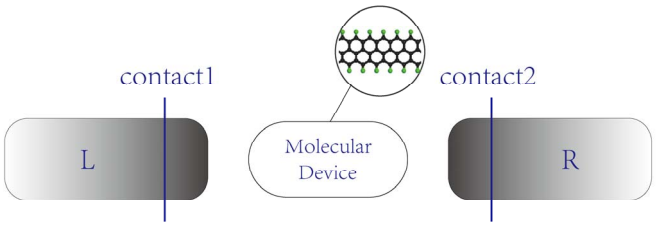

Fig. 1. Diagram of an electronic device. L and R are regarded as infinit leads under an external bias potential. The contact1 and contact2 represent the interface of QM and EM region and the area between them denotes the QM computational region.

An exponential increasing bias voltage with time constant $a = 1\ fs$ is given as follows

$$V(contact1) = V_{dc} + V_{ac}(1 - e^{-t/a}) \tag{10}$$

where $V_{dc} = 0.0V$ and $V_{ac} = 1mV$.

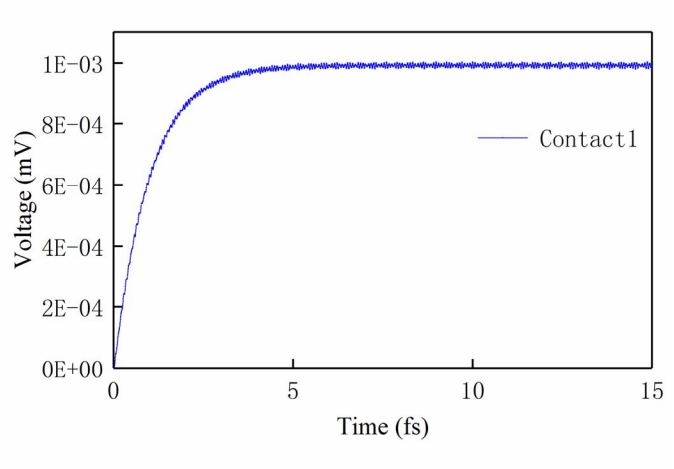

Fig. 2. The voltage of the contact1 which denotes the left lead potential.

Considering the coupling in the system, a tiny vibration of the voltage is reasonable.

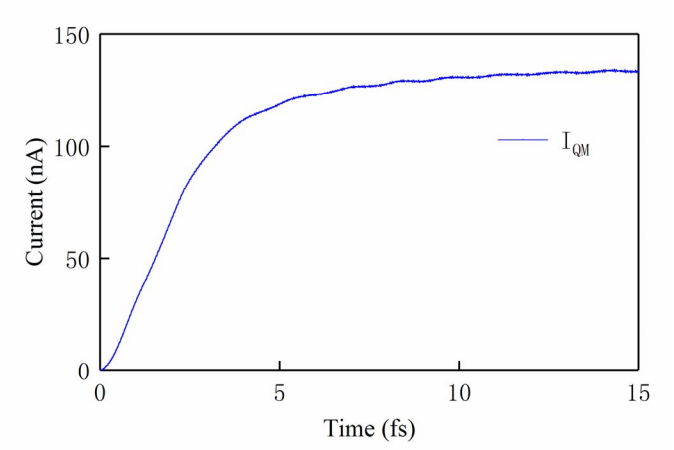

Fig. 3. The current computed in the QM region.

An undoped silicon substrate with a relative permittivity of 11.9 is adopted in this case. The maximum time step has to be less than $0.5\times10^{-3}\ fs$ which is quite efficient according to the courant stability condition. This method guarantees both the accuracy and efficiency. The QM current increasingly reaches its steady state at about 10fs.

IV. Conclusion

A time-domain QM/EM method is proposed and extended to study the dynamic electrical response of a carbon nanotube based upon molecular device. The drift-diffusion equation and NEGF formalism coupled with Maxwell's equations are solved to determine the interaction between charge particles and electromagnetic field at different temporal and spatial scales.

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