Quantum Wavepacket Ab-initio Molecular Dynamics Formalism for Calculating Electron Transport in Molecular Wires

Alexander B. Pacheco and Srinivasan S. Iyengar
Department of Chemistry, Indiana University, Bloomington, IN 47405

Abstract

We present a mixed basis, time-dependent formalism for electron transport through molecular wires. The simultaneous dynamics of electrons and nuclei in the wire is coupled to the dynamics of the tunneling electron (described here as a wavepacket) within the framework of the recently developed Quantum Wavepacket - Ab-initio Molecular Dynamics treatment [1,2,3]. The motion of the classical nuclei in response to the tunneling electron is accounted for in detail. The electronic structure is partitioned as follows. The flux of electrons flowing through the wire is treated using a grid representation as a wavepacket. The electrons within the wire are written as a density matrix using gaussian basis representation. To account for the non-equilibrium conditions due to external applied bias or the electrodes, the dynamical operators are adjusted to include adiabatic potentials connected to the Non-Equilibrium Green's Function approach. As a example, we present preliminary results for electron conduction in the Au-S6-C6H4-S-Au molecule.

Introduction

Investigation of the current-voltage characteristics for electron transport in organic molecules has received considerable attention recently. Such studies involve treatments which account for a non-equilibrium open system compared to the closed systems in standard quantum chemistry. Non-Equilibrium Green’s Function (NEGF) and Time-Dependent Density Function Theory treatments are common tools for studying such systems. The system consists of a molecular wire system sandwiched between two semi-infinite metal electrodes at dc chemical potentials with respect to each other. Due to the difference in potential between the two electrodes, electrons tunnel through the molecular wire from the electrode at negative bias potential, called the Source (S) electrode, to the electrode at positive bias potential, called the Drain (D) electrode. In NEGF treatments, the Green’s function describes the dynamics of the electrodes inside the wire.

The tunneling electron interacts with the electrodes and nuclei of the molecular wire resulting in interesting dynamics which can be looked into from a time-dependent perspective. The method we present of the simultaneous dynamics of electrons and nuclei of the molecular wire with the tunneling electron can also be applied to systems where such dynamics is important such as quantum-mechanical scattering, ab initio, etc. We consider a molecular wire device which interacts with the electrodes only at the contact and assume that there is no interaction between the electrodes. The e-e’ Hamiltonian arising from the interaction between the electron and the contacts is described by the self energy, $\Sigma$, of the electrodes. To properly account for the interaction of the contacts, we include a portion of the electrodes in the wire device.

We present our method as follows. First we give a brief overview of the standard NEGF treatment to obtain the self energy of the electrodes and obtain the Green’s function for the wire. Next, we make a connection of the NEGF with the evolution operator of time-dependent treatments. This connection permits us to create a formalism similar to the NEGF treatment of a mixed basis approach to a time dependent quantum system interacting with the molecular wire device. We also make an assumption that the non-equilibrium condition due to the voltage bias interacts directly with the tunneling electron and through it indirectly with the wire.

Non-Equilibrium Green’s Function Formalism for Molecular Electronics

• Partition the system into source and drain electrodes and the molecular wire device. Solve the time-independent Schrödinger equation for the system to obtain the self energy of the electrode in terms of the Green’s function of the isolated electrode or surface green function’s solution.

The Green’s function for molecular wire device is given by

$$\Sigma = \Sigma_{S} + \Sigma_{D}$$

where $\Sigma$ is the self energy due to the two electrodes and $\Sigma_{S}$ is the self energy of the source electrode. The Non-Equilibrium Green’s function and the evolution operator in the time-dependent Schrödinger equation are related by

$$\frac{d}{dt} \psi(t) = i\left(\mathbf{H} - \mathbf{\Delta}\right) \psi(t)$$

where $\mathbf{H}$ is an applied external bias.

Theory

Quantum Wavepacket Ab-initio Molecular Dynamics

• To model open system boundary conditions and non-equilibrium conditions, we split the general schematic into four stages: Stage I, propagation of an initial electron wavepacket in the semi-infinite electrode at higher potential; Stage II, Stage III, and Stage IV consist of propagating the wavepacket in the right and (back into the) left electrodes respectively.

Stage II is the region of primary interest consisting of the electron tunneling through the molecular wire contact interfaces.

The total wavefunction $\psi(t)$ is partitioned as follows:

$$\psi(t) = \psi_{S}(t) + \psi_{D}(t) + \psi_{QW}(t)$$

satisfying the time-dependent Schrödinger equation,

$$\frac{d}{dt} \psi(t) = \left[\mathbf{H} + \mathbf{\Delta}\right] \psi(t)$$

The goal in Stage I is to create an electron wavepacket that tunnels through the contact(molecular)-contact region in Stage II with the appropriate coupling between the molecular wire and the electrode. To realize this goal, we propagate a wavepacket through the semi-infinite electrode, truncated by negative imaginary absorbing potentials, $V_{A}$, at the molecular wire end in the presence of an external bias, $\mathbf{\Delta}$.

• Stage II contains the region of primary interest, i.e., the molecular wire and contact regions. The accumulated wavepacket density from the previous step in the absorbing region, is treated as the initial wavepacket for propagation through the molecular wire and wire/electrode interface region. Here the negative imaginary potential included in the previous step, is rigorously canceled through a positive imaginary potential in the current step and the associated time-dependent Schrödinger equation for Stage II is

$$\frac{d}{dt} \psi = \left[\mathbf{H} + \mathbf{\Delta} - V_{A}\right] \psi$$

Introducing the relations, $V_{F} / 2 = V_{A} - V_{T} / 2$, and $V = V_{T} + V_{F}$, we obtain the time-dependent version of the equation commonly used in NEGF theory,

$$\frac{d}{dt} \psi = \left[\mathbf{H} + \mathbf{\Delta} + V_{F}\right] \psi$$

• If the imaginary potentials are assumed to be diagonal, we can write the time evolution of $\psi(t)$ in real space, then the time evolution of $\sigma(\mathbf{R}, \mathbf{q}, t)$ is approximated using the symmetric split operator approach.

$$\sigma(\mathbf{R}, \mathbf{q}, t) = \frac{1}{\pi} \int_{-\infty}^{\infty} e^{i\mathbf{K} \cdot \mathbf{R}} \mathcal{K}(\mathbf{K}, \mathbf{q}, \Delta t) \mathcal{R}(\mathbf{K}, \mathbf{q}, \Delta t) d\mathbf{K}$$

where $\mathcal{K}(\mathbf{K}, \mathbf{q}, \Delta t)$ is the free propagator $\mathcal{K}(\mathbf{K}, \mathbf{q}, \Delta t)$ represented using distributed approximating functions (DAFs) [1]

$$\sigma(\mathbf{R}, \mathbf{q}, t) = \frac{1}{\pi} \int_{-\infty}^{\infty} e^{i\mathbf{K} \cdot \mathbf{R}} \mathcal{K}(\mathbf{K}, \mathbf{q}, \Delta t) \mathcal{R}(\mathbf{K}, \mathbf{q}, \Delta t) d\mathbf{K}$$

where $\mathcal{K}$ and $\mathcal{R}$ are even Hermite polynomials.

The energy functional $E(\mathbf{R}, \mathbf{p})$ in the QM/QM interaction terms between the electron flux and the molecular wire. For convenience, $\mathbf{p}$ is on one-electron character. We currently include the electrostatic interaction between the electrons and nuclei of the wire but future versions will include, polarization, and exchange repulsion.

• We can quantify the flow of electrons through the molecular wire in Stage II by computing the flux (or current) correlation function

$$\sigma(\mathbf{R}, \mathbf{q}, t) = \frac{1}{\pi} \int_{-\infty}^{\infty} e^{i\mathbf{K} \cdot \mathbf{R}} \mathcal{K}(\mathbf{K}, \mathbf{q}, \Delta t) \mathcal{R}(\mathbf{K}, \mathbf{q}, \Delta t) d\mathbf{K}$$

where the wavepacket flux, $\mathbf{j}(t) \equiv \nabla \psi^* \psi$. Here $\mathbf{R}$ represents the real part of the complex number in square parenthesis.

Conclusions

• The method we present considers the explicit treatment of the tunneling electron and simultaneously treats the e-e’ setting of the tunneling electron on the electrodes and nuclei of wire device.

• Our formalism provides (a) a physically consistent representation for the self energy of the electrodes analogous to that of Geyer et al. [4] and (b) a method to quantify flow of electrons through the wire.

• Exchange interactions between tunneling electron and the electrodes in the wire are important and will be accounted for later.

• QM-AIMD has proven to provide good description of vibrational spectra in clusters. In systems where nuclear motions are important, this method can be used to obtain accurate vibrational spectra.

References


Preliminary Results and Discussion

• We have carried out calculations for the electronic dynamics on $\text{Ar} \rightarrow \text{S}_{6} \rightarrow \text{Au}$ with an potential of $1 \text{~V}$ between the $\text{Au}$-atoms.