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

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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 on the electrodes, the dynamical operators are adjusted to include absorbing potentials connected to the Non-Equilibrium Green's Function approach. As a example, we present preliminary results for electron conduction in the Au-S-C_6H_4-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 or 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 system.

- The system consists of a molecular wire system sandwiched between two semi-infinite metal electrodes at different 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 electron inside the wire.

- The tunneling electron interacts with the electrons 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/may be important such as electron-molecule scattering, solvated electron, 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 effective Hamiltonian arising from the interaction between the wire and the contacts is described by the self energy, Σ of the electrodes. To properly account for the interaction at the contacts, we include a portion of the electrode in the wire device.

- We present our method as follows: We first give a brief overview of the standard NEGF treatment to obtain the self energy of the electrodes and obtain the Green's function for 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 where *we treat the injection of charge from the sink as 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.
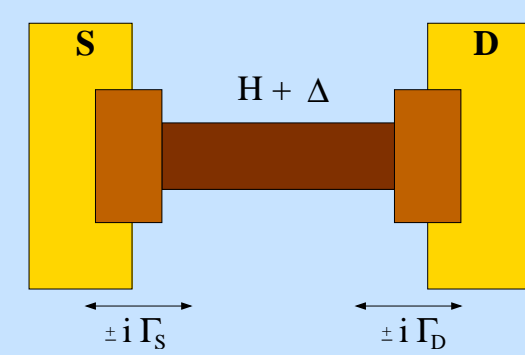
Theory

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's function

- Self energies for the source and drain are given in terms of the surface green's function,

$$\Sigma_S = \tau_S^\dagger g_S \tau_S \;\; ; \;\; \Sigma_D = \tau_D^\dagger g_D \tau_D$$

where τ is the wire-electrode coupling and g is the green's function for an isolated electrode given in terms of the electrode Hamiltonian as

$$g_{S(D)} = (E - H_{S(D)})^{-1}$$

- The Green's function for molecular wire device is given by

$$G(E) = (E - H - \Sigma)^{-1}$$

where $\Sigma = \Sigma_S + \Sigma_D$

- The Green's function allows us to replace an infinite open system with a finite one, consisting of just the molecular wire device with the self energy describing the effect of the electrodes on the molecular wire.

- The Non-Equilibrium Green's function and the evolution operator in the time-dependent Schrödinger equation are related by

$$(E - H - \Sigma)^{-1} = \lim_{\epsilon \to 0} -\frac{i}{\hbar} \int_0^\infty dt \exp\left\{\frac{i}{\hbar} Et\right\}$$
$$\left[\exp\left\{-\frac{i}{\hbar}(H + \Sigma)t\right\}\right] \exp\left\{i\frac{i}{\hbar}\epsilon t\right\}$$

Quantum Wavepacket *Ab-initio* Molecular Dynamics

- To model open system boundary conditions and non-equilibrium conditions, we split the general schematic into four stages named I-IV separated by absorbing or emitting potentials.

- Stage I consists of propagation of an initial electron wavepacket in the semi-infinite electrode at higher potential

- Stages III and IV consists of propagating the wavepacket in the right and (back into the) left electrodes respectively. Stage III and IV thus propagate the transmitted and reflected wavepacket respectively.

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

- The total wavefunction $\Psi(t)$ is partitioned as follows

$$\Psi(t) = \Psi_I(t) + \Psi_{II}(t) + \Psi_{III}(t) + \Psi_{IV}(t)$$

satisfying the time-dependent Schrödinger equation,

$$i\hbar\frac{\partial}{\partial t}\Psi(t) = (H + \Delta)\Psi(t)$$
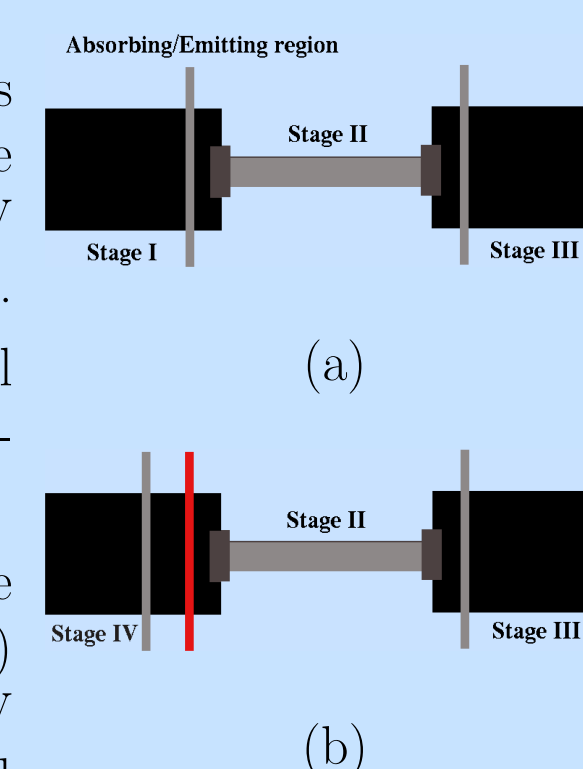
where Δ is an applied external bias.

FIGURE 1: (a) Schematic for Stages I-III. The light grey vertical lines represent absorbing potentials introduced between the various Stages. (b) Schematic for Stages II, III and IV.

- The goal in Stage I is to create an electron wavepacket that tunnels through the contact/molecule/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_{I-II} at the molecular wire end in the presence of an external bias, Δ.

$$i\hbar\frac{\partial}{\partial t}\Psi_I = [H_I + \Delta - iV_{I-II}]\Psi_I$$

- Stage II contains the region of primary interest, viz 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

$$i\hbar\frac{\partial}{\partial t}\Psi_{II} = [H_{II} + \Delta - iV_{II-III} - iV_{II-IV}]\Psi_{II} + iV_{I-II}\Psi_I$$

- Introducing the relations, $V'\Psi_{II} = V_{I-II}\Psi_I$, $\Gamma_l = V' - V_{II-IV}$ and $\Gamma_r = -V_{II-III}$, we obtain the time-dependent version of the equation commonly used in NEGF theory,

$$i\hbar\frac{\partial}{\partial t}\Psi_{II} = [H_{II} + \Delta + i\Gamma]\Psi_{II}$$

where $\Sigma = \Delta + i\Gamma$ is the self energy due to the two electrodes and $\Gamma = \Gamma_l + \Gamma_r$.

- If the imaginary potentials are assumed to be diagonal[4] in real space, then the time evolution of $\Psi_{II}(R_{QW}, t)$ is approximated using the symmetric split operator approach

$$\Psi_{II}(R_{QW}^i; t + \Delta t) = \sum_j \exp\left\{-\frac{iV(R_{QW}^i)\Delta t}{2\hbar}\right\} K(R_{QW}^i, R_{QW}^j; \Delta t)$$
$$\exp\left\{-\frac{iV(R_{QW}^i)\Delta t}{2\hbar}\right\} \Psi_{II}(R_{QW}^i; t)$$

and the free propagator $K(R_{QW}^i, R_{QW}^j; \Delta t)$ represented using distributed approximating functionals (DAFs)[5]

$$K(R_{QW}^i, R_{QW}^j; \Delta t) = \frac{1}{\sigma(0)}\exp\left\{-\frac{(R_{QW}^i - R_{QW}^j)^2}{2\sigma(\Delta t_{QW})}\right\}\sum_{n=0}^{M/2}$$
$$\left(\frac{\sigma(0)}{\sigma(\Delta t_{QW})}\right)^{2n+1}\left(\frac{-1}{4}\right)^n \frac{1}{n!}(2\pi)^{-1/2}H_{2n}\left(\frac{R_{QW}^i - R_{QW}^j}{\sqrt{2}\sigma(\Delta t_{QW})}\right)$$

where H_{2n} are even order Hermite polynomials.

- The quantity $V(R_{QW}^i)$ is the potential experienced by the electron flux,

$$V(R_{QW}^i) = E(\{\mathbf{R}_c, \mathbf{P}_c\}, R_{QW}^i) + \Delta(R_{QW}^i) + i\Gamma(R_{QW}^i)$$

- The energy functional, $E(\{\mathbf{R}_c, \mathbf{P}_c\}, R_{QW}^i)$ is the QM/QM interaction term between the electron flux and the molecular wire. For convenience, it is one-electron in 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-flux (or current-current) correlation function

$$\sigma(\omega) \propto \int_{-\infty}^{+\infty} dt e^{[-i\omega t]}\langle \mathbf{J}(t)\mathbf{J}(0)\rangle$$

where the wavepacket flux, $\mathbf{J}(t) = \mathcal{R}\left[\left\langle\psi(t)\left|\frac{-i\hbar}{m}\nabla\right|\psi(t)\right\rangle\right]$. Here $\mathcal{R}[\cdots]$ represents the real part of the complex number in square parenthesis.

- In Stages III and IV, the collected wavepacket from Stage II is propagated to give the transmitted and reflected wavepacket respectively,

$$i\hbar\frac{\partial}{\partial t}\Psi_{III/IV} = \left[H_{III/IV} + \Delta\right]\Psi_{III/IV} + iV_{II-III/IV}\Psi_{II}$$

- To compute conductance, we obtain scattering matrix elements from the wavepacket propagation

$$S(III/IV) \propto \left\{\int_0^\infty dt \exp\left\{iEt/\hbar\right\}\left\langle\xi_{III/IV}\middle|\Psi(t)\right\rangle\right\}$$

where S represents the probability of the wavepacket in regions III or IV; the probability in IV being the reflection coefficient and III being the transmission coefficient.

- The current through the wire is calculated as

$$I = \frac{2e^2}{h}\int_{-\infty}^\infty T(E, \Delta)[f_S(E) - f_D(E)]dE$$

where $T(E, \Delta)$ is the transmission coefficient for energy E and bias voltage Δ, and $f(E)$ is the Fermi distribution function of the electrodes.

Preliminary Results and Discussion

- We have carried out calculations for the electron dynamics on $Au - S - C_6H_4 - S - Au$ with a potential of 1 eV between the Au atoms.
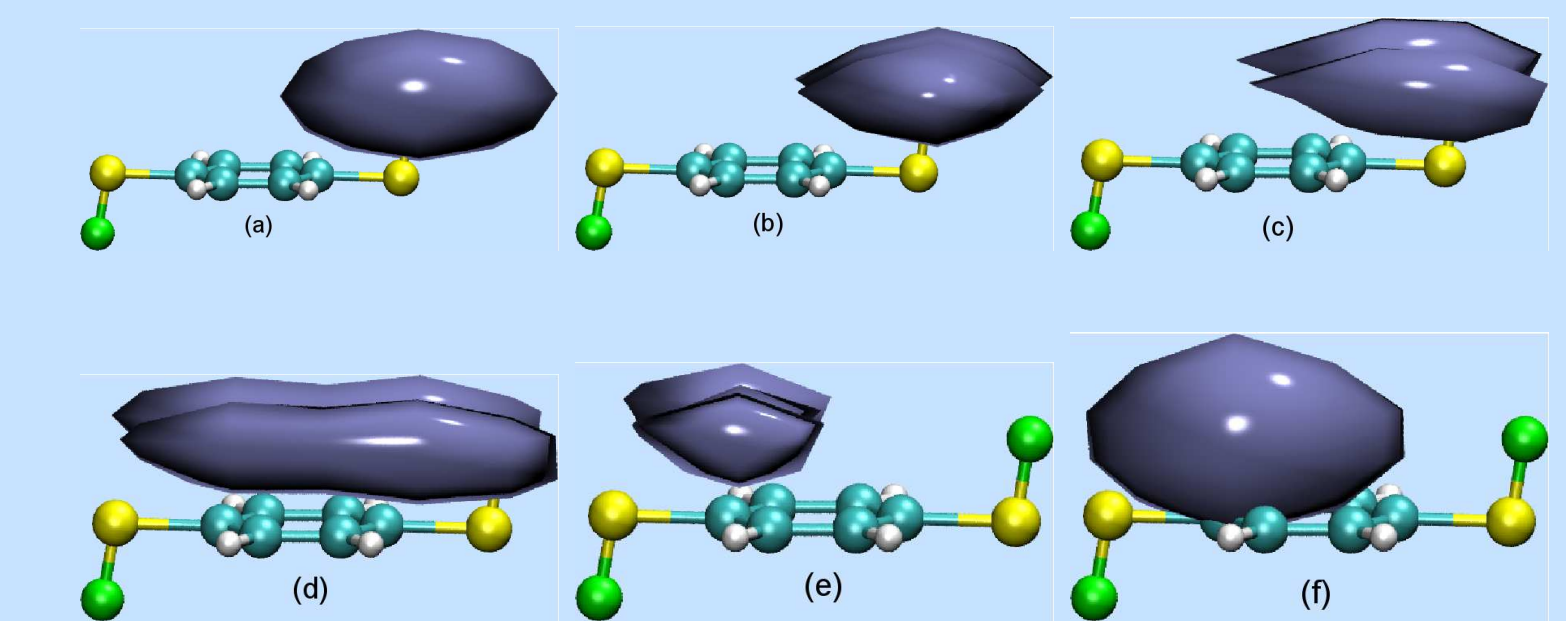
FIGURE 2: Snapshots of the Electron Wavepacket at (a) initially, (b) 0.05fs, (c) 0.1fs, (d) 0.15fs, (e) 0.2fs and (f) 0.25fs.

Conclusions

- The method we present considers the explicit treatment of the tunneling electron and simultaneously treats the effect of the tunneling electron on the electrons and nuclei of wire device.

- Our formalism provides (a) a physically consistent representation for the self energy of the electrodes analogous to that of Goyer *et al.*[6] and (b) a method to quantify flow of electrons through the wire.

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

- QW-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

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