

Objectives

- Goal: Model transmittance and I-V properties of molecular systems
- Methodology (Landauer description): Implement TDDFT and non SC-NEGF⁴ methods
- Modeling: Self-energy convergence and reliability
- Applications:
 - Iron-Porphyrin as molecular switch or spin-valve.
 - Tunnel junctions and chemical sensors.
 - Molecular junctions as transistors.

NOTE:

All geometry optimizations and single point calculations of the necessary Hamiltonian were performed with QChem 3.0.

Modeling

Define Converged Self-Energy Model

Methodology

Strong-coupling bulks
NEGF Implementations: use TDDFT (freq-domain) electronic-structure information

Implement an active-space TDDFT formalism

Applications

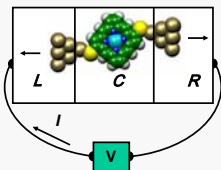
Molecular switch
Porphyrin based or other system

Nanoscale Transistors

Molecular Sensors based on specialized Tunnel junction

Electrical Devices Composed of Single molecules

The structure is a device (C) sandwiched between two semi-infinite metallic gold leads (L,R).



Inputs: one electron Hamiltonian (H) and overlap (S) matrices.

Parse H and S, into device and lead regions (lead-lead interactions are neglected).

$$H = \begin{pmatrix} H_{LL} & H_{LC} & 0 \\ H_{CL} & H_{CC} & H_{CR} \\ 0 & H_{RC} & H_{RR} \end{pmatrix} \quad S = \begin{pmatrix} S_{LL} & S_{LC} & 0 \\ S_{CL} & S_{CC} & S_{CR} \\ 0 & S_{RC} & S_{RR} \end{pmatrix}$$

GF based Landauer Formalism

Landauer formalism describes the current passing through the device in terms of transmittance. GF methodology casts the transmittance in terms of a Green function / Self Energy picture:

$$I = \frac{2e}{h} \int_{-\infty}^{+\infty} T_C(E) \left[f_L(E, \frac{eV}{2}) - f_R(E, \frac{eV}{2}) \right] dE$$

$$T_C(E) = \text{Tr}(\Gamma_L G_C^r \Gamma_R G_C^a)$$
 (transmittance)

$$\Sigma_{(L,R)}^{(r,a)} = (ES_{CL} - H_{CL}) g_{(LL,RR)}^{(r,a)} (ES_{LC} - H_{LC})$$

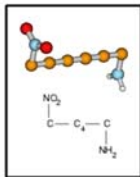
(self-energy: describes bulk-molecule interaction)

$$G_C^{(r,a)} = (ES_{CC} - H_{CC} - \Sigma_{(L,R)}^{(r,a)} - \Sigma_{(L,R)}^{(r,a)})^{-1}$$
 (molecule GF)

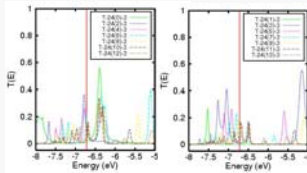
$$\Gamma_{(L,R)} = i[\Sigma_{(L,R)}^{(r)} - \Sigma_{(L,R)}^{(a)}]$$
 (broadening function)

$$g_{(LL,RR)}^{(r,a)} = \lim_{\eta \rightarrow 0^+} [ES_{(LL,RR)} - H_{(LL,RR)} \pm i\eta]^{-1}$$
 (bulk GF)

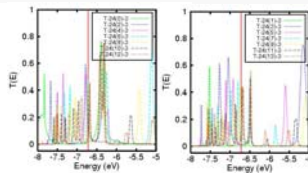
Model Benchmarking and Method Development



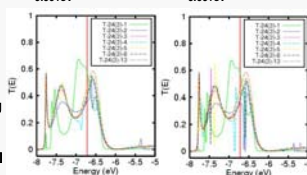
Wide Band Limit:
Device Smear Factor of 0.01eV



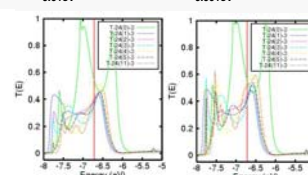
Wide Band Limit:
Device Smear Factor of 0.01eV



Full Periodic Method:
Bulk Smear Factor of 0.026eV (room temperature.)
Device Smear Factor of 0.001eV



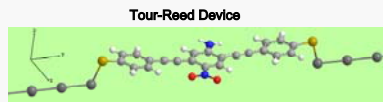
Full Periodic Method:
Bulk Smear Factor of 0.026eV (room temperature.)
Device Smear Factor of 0.001eV



- Conclusions:
 - Convergence of transmission difficult to achieve (possibly due to non-negligible interactions between distant neighbors in bulk Au Hamiltonian.
 - Using 'clean' bulk → bulk convergence vs. device convergence
 - Increasing smear factors eliminates numerical noise and helps converge transmission.
- Goals:
 - Introduce strong coupling effects into the formalism
 - Apply TDDFT and linear response theory to model weak field perturbations

Single Molecule Transistors:

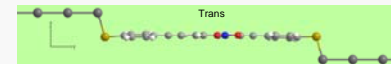
Gating Fields and Cis/Trans Conformational Switching



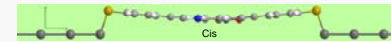
-Gating fields in the x direction (parallel to the rings) has little little to no effect on the transmission function (and thus the current flow)

-Gating fields in the z direction (perpendicular to the rings), however, has a marked effect on the transmission function, and thus shows promise as a mechanism for transistor-like behavior of single molecules.

-Gating fields of various magnitudes have little effect on the transmission, when the device is in a trans conformation

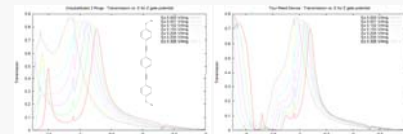


-Gating fields can have a substantial effect when the device is in a cis conformation

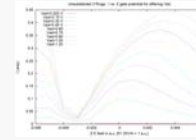


-Gating fields along the z-direction for a cis conformation device give rise to different affects on the transmission function when they have a positive or negative magnitude.

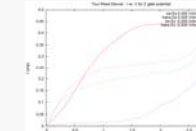
-Transistor-like behavior (switching) can be induced in the Tour-Reed device or the unsubstituted 3 ring system by changing the magnitude of a z-directed electric field, or by switching between a cis and trans conformation of the device



Transmission of Tour-Reed device and unsubstituted corollary vs. E (eV) for Z gating fields

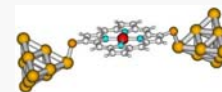


Current vs. z gating field – each curve is for a constant source drain voltage

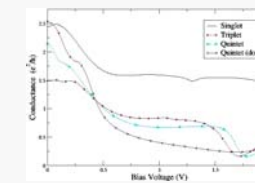
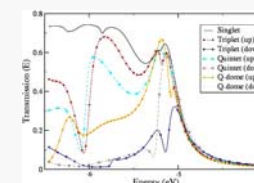


Current vs. source drain voltage for the cis and trans conformations

Conductance Switching Properties of Molecular Devices



- Spin-dependent transmission of an iron ligated porphyrin.
- Molecular conductance reduction upon excitation of the spin state of Fe(II)-Porphyrins.



Transmission through chemical sensors

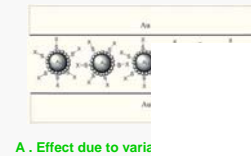
A. Effect on transmission due to variation of Au-Au-S angle

transmission at different tunnel junctions

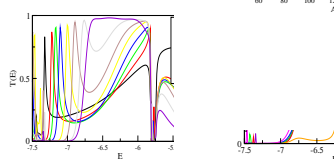
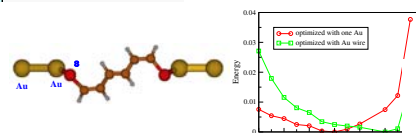
B. Swelling effect upon exposure to analyte molecule

Symmetric junction (ene-ene)

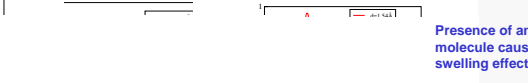
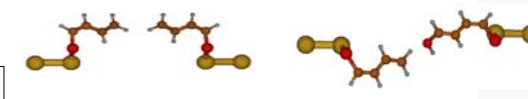
Asymmetric junction (ene-ol)



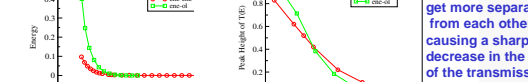
A. Effect due to vari



Transmission peak is dependent on Au-Au-S angle and gets broadened at an angle 130



Presence of analyte molecule causes the swelling effect



The tunnel junctions get more separated from each other causing a sharp decrease in the height of the transmission peaks.