Modelling molecular field effect transistor using non-equilibrium Green function method

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Abstract. In this paper, we introduce a model of molecular field effect transistor (MFET). Because of the small size of these devices (about 1 nm), and the near one-dimensional nature of charge transport within them, MFET modelling demands a rigorous quantum-mechanical basis. This is achieved in this model by using non-equilibrium Green function method to compute transport function and ultimately, the current-voltage (I-V) characteristics. The programme is written by using graphic user guide (GUI) in Matlab. The effects of material, temperature, and bias on I-V characteristics of the MFET have been considered.

Keywords: Molecular transistor, molecular field effect transistor, molecular electronic device.

1. Introduction
Current interest in molecular electronics is largely driven by expectations that molecules can be used as nanoelectronic components able to complement or replace standard silicon CMOS technology on the way down to 10 nm circuit components. The first speculations about molecular electronic devices (diodes, rectifiers) were apparently made in the mid-1970s [1]. That original suggestion of a molecular rectifier has generated a large interest in the field and a flurry of suggestions of various molecular electronic components.

The theoretical description of electron transport through molecular electronics (ME) systems is a complex many-particle problem, where the full solution is not possible in practice. The available approaches use certain approximations, however, the basis for transport calculations is the description of the ME device itself, which implies that approaches to the simulation of transport and structure cannot be chosen independently. A diverse spectrum of approaches to the transport calculations was developed to study the whole spectrum of problems ranging from exact many-particle problem treatment within some simplified models (e.g., the two-barrier potential) for the system, to semi-empirical models for transport through quite realistic structures consisting of a few hundred atoms. Although some of these methods were developed for purposes apparently different from the ME design, like intra-molecular donor–acceptor charge transfer or scanning tunnelling microscopy (STM) image calculation, they are often applicable to ME systems.

Two distinct approaches to the transport calculations are suitable for proper accounting of the full chemical structure of the system: the Green function (GF) method and the density functional (DF) method. The conceptual difference is that in the GF approach the interactions within the system are treated in the phenomenological way, in the sense that transport calculations and calculations of system properties are separated, thus enabling any level of input to be used. The range of examples
varies from semi-empirical models to discrete tight-binding or continuous DF descriptions. Within the DFT framework, the charge carrier density is the unique parameter, hence the current is naturally calculated simultaneously with other system properties that depend on or constitute the density. Consequently, at least in theory, the system could be seamlessly restructured under the bias, but neither the tight-binding nor semi-empirical level of the description is naturally allowed within the DF method. Hence, GF is often used in a semi-empirical way to fit the experimental data. The fitting parameter is usually the shape of the voltage drop over the system.

In this work, we introduce a model of MFET, review the transport calculation using NEGF, and use graphic user interface (GUI) in Matlab to compute current-voltage characteristics of MFET. This is achieved in this model by using non-equilibrium Green function method to compute transport function and ultimately, the current-voltage (I-V) characteristics. As examples, typical simulations of MFET are presented. The effects of material, temperature, and bias on I-V characteristics of the MFET are also considered.

2. Simulation results

The central focus of this work is to introduce a model of a three-terminal molecular devices, namely the molecular field effect transistor (MFET). MFET is a promising alternative candidate of traditional MOSFET in future due to its small size, low power and high speed. The structure of the MFET is in shape like traditional MOSFET, but its conductive channel is replaced by a benzene-1,4-dithiolate molecule.

A schematic view of a molecule coupled to gold source (S) and drain (D) contacts is shown in figure 1. As an example we use the benzene-1,4-dithiol molecule which consists of a phenyl ring with thiol (-SH) end groups. A gate terminal may be used to modulate the conductance of the molecule. The coupling between the gate and the molecule is purely capacitive – there is no gate current.

The molecular energy levels consist of a set of occupied levels separated by a gap from a set of unoccupied levels. At equilibrium, the Fermi energy is typically located in the gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), but when a bias is applied, the Fermi energy in the source contact ($\mu_1$) floats up by $qV_D$ relative to the Fermi level in the drain contact ($\mu_2$). The molecule conducts when the bias is large enough that one or more of the molecular energy levels lie between $\mu_1$ and $\mu_2$.

![Figure 1](image.png)

**Figure 1.** a) Schematic view of a molecule coupled to source and drain contacts. b) The molecule is described by a Hamiltonian $H$ and a self-consistent potential $U_{SC}$. The effect of the large contacts is described using self-energy matrices $\Sigma_{1,2}$. Scattering processes may be described using another self-energy matrix $\Sigma_p$. The source and drain contacts are identified by their respective Fermi levels $\mu_1$ and $\mu_2$.

2.1. The non-equilibrium Green function formalism (NEGF)

The source and drain contacts are identified by their respective Fermi levels $\mu_1$ and $\mu_2$. If a positive voltage $V_D$ is applied externally to the drain contact with respect to the source contact, then the drain...
has Fermi energy level lower than that of the source by $qV_D$: $\mu_1 - \mu_2 = qV_D$. The source and drain contacts thus have different Fermi functions and each seeks to bring the molecule into equilibrium with itself. The source keeps pumping electrons in hoping to establish equilibrium. But equilibrium is never achieved as the drain keeps pulling electrons out in its bid to establish equilibrium. The molecule is thus forced into a balancing act between two reservoirs with different agendas which sends it into a non-equilibrium state intermediate between what the source would like to see and what the drain would like to see [2-5]. To describe this balancing process we need a kinetic equation that keeps track of the input and output from each of the reservoirs as shown in figure 2.

**Figure 2.** Current flows through a single energy level. One contact keeps filling it up and the other keeps emptying it causing a net current flow from one contact to the other.

### 2.2. Current through single energy level

We treated the energy level $\varepsilon$ as discrete, ignoring the broadening $\gamma = \gamma_1 + \gamma_2$ that arises due to the coupling with the source and drain contacts. To take the broadening into account we may replace the discrete level with a Lorentzian density of state (DOS) $D(E)$:

$$D_\varepsilon(E) = \frac{\gamma/2\pi}{(E - \varepsilon)^2 + (\gamma/2)^2}, \quad \gamma = \gamma_1 + \gamma_2 .$$

Let us model a nano-transistor by writing the DOS as:

$$D_\varepsilon(E) = \frac{m^*WL}{\pi h^2} \theta(E - E_C) ,$$

where $E_C$ is the energy of the conduction band edge, $W$ is the width of the molecule channel, $L$ is the length of the molecule channel.

The self-consistent potential is:

$$U = U_L + \frac{q^2}{C_E} (N - N_0) ,$$

where $U_L = \frac{C_G}{C_E} (- qV_G) + \frac{C_D}{C_E} (- qV_D) ,$

is the Laplace potential and $C_E = C_S + C_G + C_D ,$ is the total capacitance.

The effect of the self-consistent potential $U$ is to raise the density of state (DOS) in energy and can be included in our expressions for the number of electrons $N$ and the current $I_D$ which include the effect of broadening.

The number of electrons $N$ is accounted for the broadened DOS:

$$N = \int_{-\infty}^{\infty} dE \frac{D_\varepsilon(E-U) \gamma_1 f_1(E) + \gamma_2 f_2(E)}{\gamma_1 + \gamma_2 ,}$$

and the current $I_D$ is given as

$$I_D = \frac{2q}{h} \int_{-\infty}^{\infty} dE \frac{2\pi D_\varepsilon(E-U) \gamma_2 f_2(E)}{\gamma_1 + \gamma_2} ,$$

$$\gamma_1 f_1(E) - f_2(E) \right] .$$
We could write it in the form

\[ I_D = \frac{2e}{h} \int_{-\infty}^{\infty} \mathcal{T}(E-U)[f_1(E) - f_2(E)] \, dE, \quad (8) \]

where the transmission function is defined as follows

\[ \mathcal{T}(E) = 2\pi D(E) \frac{\gamma_1 \gamma_2}{\gamma_1 + \gamma_2} = \frac{\gamma_1 \gamma_2}{(E-\epsilon)^2 + (\gamma/2)^2}. \quad (9) \]

2.3. NEGF equation as multi-level generalization

We use a simple semi-empirical Hamiltonian \( H \) and a self-consistent potential \( U_{SC} \) to describe the molecule. The effect of the source and drain contacts are taken into account using self-energy functions \( \Sigma_1 \) and \( \Sigma_2 \). Scattering processes may be described using another self-energy matrix \( \Sigma_p \). However, in this work we focus on coherent or ballistic transport \( \Sigma_p = 0 \). The source and drain contacts are identified with their respective Fermi levels \( \mu_1 \) and \( \mu_2 \). Our simulation consists of iteratively solving a set of coupled equations and the self-consistent potential \( U_{SC} \). Given \( H, U_{SC}, \Sigma_1, \Sigma_2, \mu_1 \) and \( \mu_2 \), the NEGF formalism has clear prescriptions to obtain the density matrix \( \rho \) from which the electron and current may be calculated. Once the electron density is calculated we solve the Poisson’s equation to obtain the self-consistent potential \( U_{SC} \, [5, 6] \).

Self-energy formally arises out of partitioning the molecule-contact system into a molecule subsystem and a contact subsystem. The contact self-energy matrix \( \Sigma \) is calculated knowing the contact surface Green’s function \( G \) and the coupling between the molecule and contact \( \tau \). For a molecule coupled to two contacts (source and drain) the molecular Green’s function at an energy \( E \) is written as follows:

\[ G(E) = [EI - H - U_{SC} - \Sigma_1 - \Sigma_2]^{-1}, \quad (10) \]

where, \( I \) is the identity matrix, \( H \) is the molecule Hamiltonian and \( U_{SC} \) is the self-consistent potential. The contact self-energy matrices are

\[ \Sigma_{1,2}(E) = \tau_{1,2} g_{1,2} \tau^\dagger_{1,2}. \quad (11) \]

Given \( H, \Sigma_{1,2}, \) contact Fermi energies \( \mu_{1,2} \) and the self-consistent potential \( U_{SC} \), NEGF has clear prescriptions to obtain the density matrix \( \rho \). The density matrix can be expressed as an energy integral over the correlation function – \( iG^<(E) \), which can be viewed as an energy-resolved density matrix:

\[ \rho = \int dE \left[ -iG^<(E) / 2\pi \right]. \quad (12) \]

The correlation function is obtained from the Green’s function \( G \) and the broadening function \( \Gamma_{1,2} \):

\[ -iG^<(E) = G(f_1\Gamma_1 + f_2\Gamma_2)G^+. \quad (13) \]

Unlike the Hamiltonian, the self-energy matrices are non-Hermitian. The anti-Hermitian part of the self-energy is also known as the broadening function

\[ \Gamma_{1,2} = i \left( \Sigma_{1,2} - \Sigma^+_{1,2} \right), \quad (14) \]

where \( f_{1,2}(E) \) are Fermi functions with energy Fermi levels \( \mu_{1,2} \):

\[ f_{1,2}(E) = \frac{1}{e^{(E-\mu_{1,2})/k_BT}+1}. \quad (15) \]

The density matrix so obtained can be used to calculate the electron density \( n(\vec{r}) \) expressed in terms of the eigenvectors \( \Psi_q(\vec{r}) \) of the Hamiltonian.
\[ n(\vec{r}) = \sum_{\alpha, \beta} \Psi_\alpha(\vec{r})^* \Psi_\beta(\vec{r}) \rho_{\alpha\beta}. \] (16)

The Poisson’s equation relates the real space potential distribution \( U(\vec{r}) \) in a system to the charge density \( n(\vec{r}) \). The Poisson’s equation is then solved for the change in the charge density \( n - n_0 \) from the nominal value:

\[ \nabla^2 U(\vec{r}) = -q^2 \left( n(\vec{r}) - n_0(\vec{r}) \right). \] (17)

Figure 4. Model for a multi-level conductor with \( n \) energy levels is presented. General matrix model is based on the non-equilibrium Green’s function (NEGF) formalism. A channel is connected to two contacts (source and drain). The “s-contact” distributed throughout the channel, describes incoherent scattering processes. In general, this contact cannot be described by Fermi function, unlike the real contacts.

The total number of electrons \( N \) may be obtained from the density matrix

\[ N = \text{Trace} (\rho). \] (18)

The density matrix may also be used to obtain the terminal current. For coherent transport, we can simplify the calculation of current by using the transmission formalism, where the transmissions function

\[ T(E) = \text{Trace} \left[ \Gamma_1 G \Gamma_2 G^+ \right] \] (19)

is used to calculate the terminal current

\[ I_D = \frac{2q}{h} \int_{-\infty}^{\infty} dE \ T(E) \left[ f_1(E) - f_2(E) \right]. \] (20)

In this work the program is written by using graphic user guide (GUI) in Matlab. We have found difference of I-V characteristics between traditional MOSFET and MFET. In addition, effects of type of materials, temperature, and bias on I-V characteristics of the MFET have been considered. Using GUI in Matlab, simulation results are intuitively displayed.

Current–voltage (I-V) characteristics of the molecular field effect transistor (MFET) at different values of bias voltage are shown in figure 5.
Figure 5. Current – voltage characteristics of the MFET: (a) $I_D = f(V_{DS})$ for different values of the gate voltage and (b) $I_D = f(V_{GS})$ for different values of the drain voltage.

Figure 6. Voltage – current characteristics of MFET for different materials of conductive channel:
(a) $I_D = f(V_{DS})$ and (b) $I_D = f(V_{GS})$.

Current–voltage (I-V) characteristics of the molecular field effect transistor (MFET) for different values of the length (L) and the width (W) of the conductive molecule channel are shown in figure 6. Benzene-1,4-dithiol molecules have different values of the length (L) and the width (W) (table 1).

Table 1. Benzene-1,4-dithiol molecules have different values of the length (L) and the width (W).

| Molecules | $C_6H_4S_2$ | $C_6H_4I_2$ | $C_6H_4Br_2$ | $C_6H_4F_2$ | $C_6H_4Cl_2$ |
|-----------|--------------|--------------|--------------|--------------|--------------|
| Length L (nm) | 0.8460 | 1.0321 | 1.0025 | 0.7957 | 0.9340 |
| Width W (nm) | 0.6542 | 0.6637 | 0.6714 | 0.7460 | 0.7365 |

The effects of temperature on I-V characteristics of the MFET are shown in figure 7. When temperature increased, the drain current is also increased. The change of drain current in temperature is $10^{-10}$ A/K.
2.4. Analytical expression of drain current

From figure 8 we find out that the curves of drain current-voltage characteristics of the MFET can be divided into two regions: linear and saturation areas with evolution point as

\[ V_{DS(sat)} = V_{GS} - V_T. \]  

(21)

Drain current in linear area (i.e. \( V_{DS} \leq V_{DS(sat)} \)) is

\[ I_D = \frac{W}{L} \mu_{Ball} \frac{C_G}{2} \left[ 2(V_{GS} - V_T) V_{DS} - V_{DS}^2 \right]. \]  

(22)

The gate capacitance of the MFET is given by

\[ C_G = \frac{\varepsilon_0 \varepsilon_r W L}{t_{ox}}, \]  

(23)

where \( t_{ox} \) is the thickness of insulator SiO₂, \( \varepsilon_0 = 8.854 \times 10^{-12} \text{ F/m} \) is dielectric constant in a vacuum, \( \varepsilon_r = 3.9 \) is relative dielectric constant of SiO₂. For very small drain-source voltage, \( V_{DS} \), equation (22) becomes

\[ I_D = \frac{W}{L} \mu_{Ball} C_G (V_{GS} - V_T) V_{DS}. \]  

(24)

For higher drain-source voltages (i.e. \( V_{DS} \geq V_{DS(sat)} \)), equation (22) (i.e. saturation drain current) becomes

\[ I_{D(sat)} = \frac{W}{L} \mu_{Ball} \frac{C_G}{2} (V_{GS} - V_T)^2 + \alpha V_{DS}^2, \]  

(25)

where \( \alpha \) is the slope: \( \alpha = dI_D/dV_{DS} \).
3. Conclusions
We use non-equilibrium Green’s function method to compute transport function of charges and ultimately, the current-voltage (I-V) characteristics. The program is written by using graphic user guide (GUI) in Matlab. We have found difference of I-V characteristics between MOSFET and MFET. In addition, effects of type of material, temperature, and bias on I-V characteristics of the MFET have been considered. Using GUI in Matlab, obtained results of simulations are intuitively displayed.

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