Politecnico
di Torino

NANOELECTRONIC SYSTEMS
LABORATORIES

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Lab 2 - Theory

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Electron transport in molecular transistor

1.1 Introduction

In this lab exercise you will investigate transport properties of molecules used as transistors. We will use for this purpose a numerical model that describes the molecules behavior under the impact of external voltages and taking into account the most important technological parameters. The most accurate way to perform this study is via atomistic simulators (e.g. QuantumATK). However, they are extremely computationally intensive. When dealing with applications it is very important to be reduce the time required for simulation, still taking into account the physics and the technological parameters. Obviously results obtained by the model must be compared to the ab-initio simulation and their range of validity assessed. However, a model of this kind allows to simulate several devices at the same time, or devices in several possible conditions. This characteristic is essential in a phase in which the device is studied and designed from the application point of view.

The model that we are using in this lab is called EE-BESD (Molecular FET Modeling for Efficient and Effective Nanocomputing Design). It is based on other similar numerical models presented in literature and modified in order to obtain higher accuracy without loosing efficiency. However, the objectives of this lab are not to evaluate the model, but *i) to use it to understand the transport behavior in molecular transistors* and *ii) to appreciate how a complex physical phenomenon as transport at the nanoscale can simplified and numerically described* and *iii) to have an example of how accuracy and efficiency can be traded-off depending on the necessities.*

1.2 Molecules suited for molecular transistors

Here follows a short description of the molecules type analyzed in this lab.

1.2.1 Thiophene (1TT)

The first molecule is the thiophene molecule, a simple molecule that is the starting block for a set of conductive molecules called *oligothiophene*. Since this molecule is a basic block for many applications and molecular systems, usually its structure can be find in atomistic software databases ready to be used.

The thiophene formulation is C_4H_4S and its structure and symbol are in Figure 1.1.

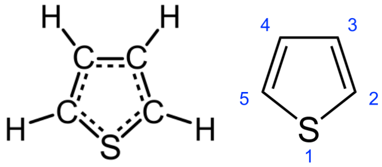

Figure 1.1: Thiophene molecule

Thiophene is a π-conjugated molecule having novel electrical properties which make them a good candidate for making electronic devices such as light emitting diodes, molecular wires, field effect transistors, solar cells. These molecules are stable in conducting and non-conducting states. They have also ability for making dense monolayer. The decay constant of these π conjugated oligothiophene is $0.1(A)^{-}1$ which is much smaller then sigma-conjugated molecules, which makes them suitable for longer molecular wires. Injection and tunneling of charged carriers are possible in these molecules because of their smaller HOMO-LUMO gap. Thus the conduction of molecule can be controlled by electrochemical gate voltages. All these properties make thiophene a promising candidate for future molecular scale electronics.

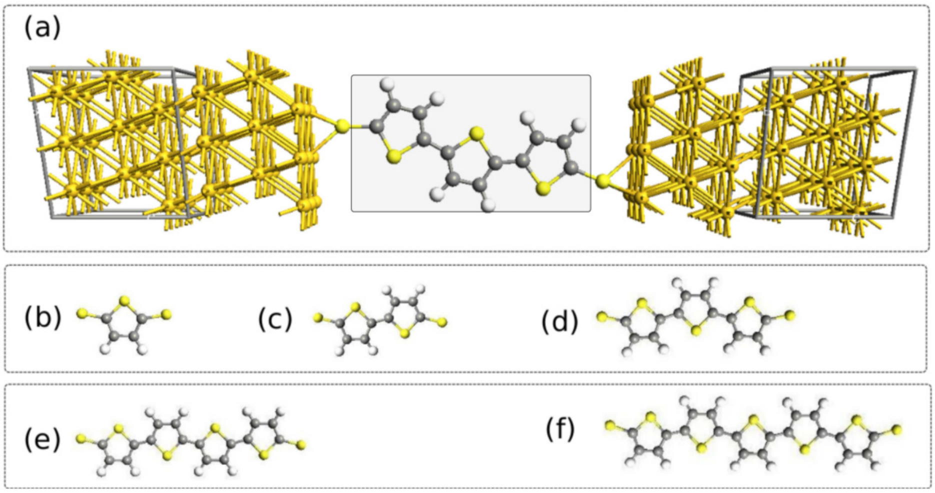

Figure 1.2: Thiophene Molecule: (a) A structure of thiophene molecule bounded to gold molecule. (b)-(f) Different length of Thiophene molecules.

This molecule will be used as conductive molecule, so you need to add two thiols for further bonding to the gold electrodes. Figure 1.2 depicts different versions of Thiophene molecules, with or without gold electrodes. The basic molecule is called 1TT, adding further molecules to the chain different types of Thiophene molecules are generated (2TT, 3TT, 4TT and 5TT).

1.2.2 Oligo Phenylene Ethynylene (OPE)

Oligo Phenylene Ethynylene (OPE) derivative are molecules in which the repeating unit is composed of a phenylene (i.e. a benzene which were subtracted two hydrogen atoms) and an ethynylene (-C≡C-, derivable from ethyne for removal of H atoms), as depicted in Figure 1.3. These are fully conjugated molecules and electrons are delocalized over the length of molecule. Due to their large delocalized structure and spine, OPE presents a greater efficiency in the charge transport compared with a saturated molecule. Indeed, in OPE molecule the energy gape between HOMO-LUMO is smaller than that of saturated molecules. The conductance of molecular chains depends on its length. In fact, current decreases with increasing length of the molecule. The conduction property of these molecules also depends on the type of anchoring group between molecule and electrodes.

1.2.3 Oligo Phenylene Vinylene (OPV)

Oligo Phenylene Vinylene (OPV) are similar to OPE, as the repetitive unit is still phenylene, but the aromatic rings are linked by vinylene (-C = C-, obtained from ethene by removal of two atoms hydrogen). Its basic structure is depicted in Figure 1.4. The difference between OPE and OPV lies in the type of multiple bond which greatly affects the electrical characteristics of the molecule. The structure of vinylene has a double bond, with respect to that ethynylene which has one triple. The presence of vinylene double bond opposes greater resistance to rotation of the aromatic rings, which makes OPV molecule more planar than the OPE molecule. In OPE, alternating single and double bonds is blocked by the triple bond of ethynylene, while in the case of OPV molecule the bonds between the carbon atoms are shorter. This leads to a decrease in the energy gap between HOMO

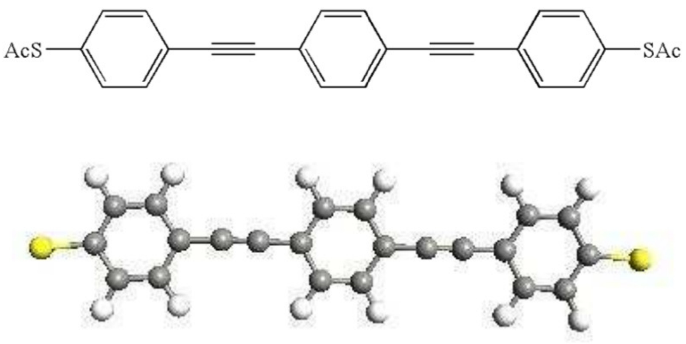

Figure 1.3: Oligo Phenylene Ethynylene (OPE) molecule.

and LUMO(3,5eV in case of the OPE, 3.1eV in case of OPV). For these reasons, the conductance of this molecular structure is about one order of magnitude higher than that of the OPE.

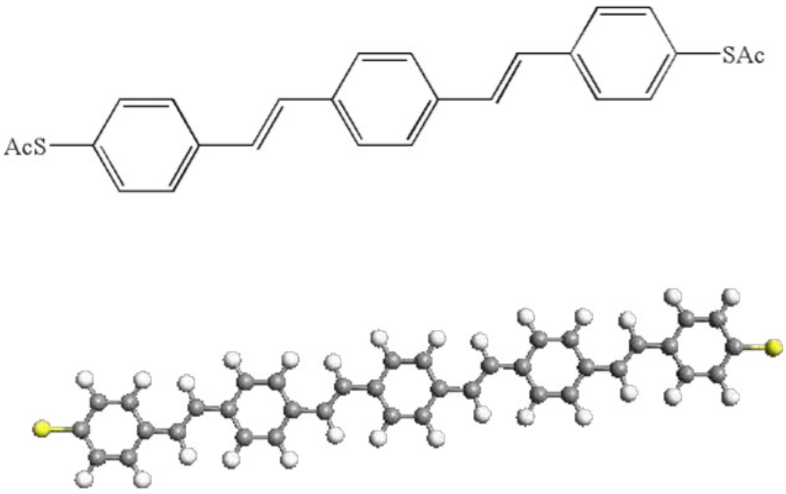

Figure 1.4: Oligo Phenylene Vinylene (OPV) molecule.

1.3 EE-BESD: Molecular FET Modeling for Efficient and Effective Nanocomputing Design

In this lab you will use an accurate and at the same time computationally efficient method, named **ee-besd** to calculate the electron transport characteristics of molecular transistors. The transmission spectrum is used to estimate the transport properties of the molecular transistor in presence of applied bias and gate voltages. The transmission spectrum represents the probability that, for each energy level, there is a “transmission” of electrons through the molecule. The transmission spectrum is evaluated with ATK, and models parameters are extracted from it to be used with EE-BESD algorithm. The accuracy of the model is evaluated considering several molecules (OPV, OPE, 3TT, 4TT and 5TT) and using the ATK simulation results as reference.

1.3.1 General description

Figure 1.5 shows the algorithm flow of our proposed model for the calculation of current in molecular transistor. Hereinafter we will refer to it as **ee-besd**; the acronim derives from the types of approximations and methods used and will be clear after a thorough explanation at the end of this section.

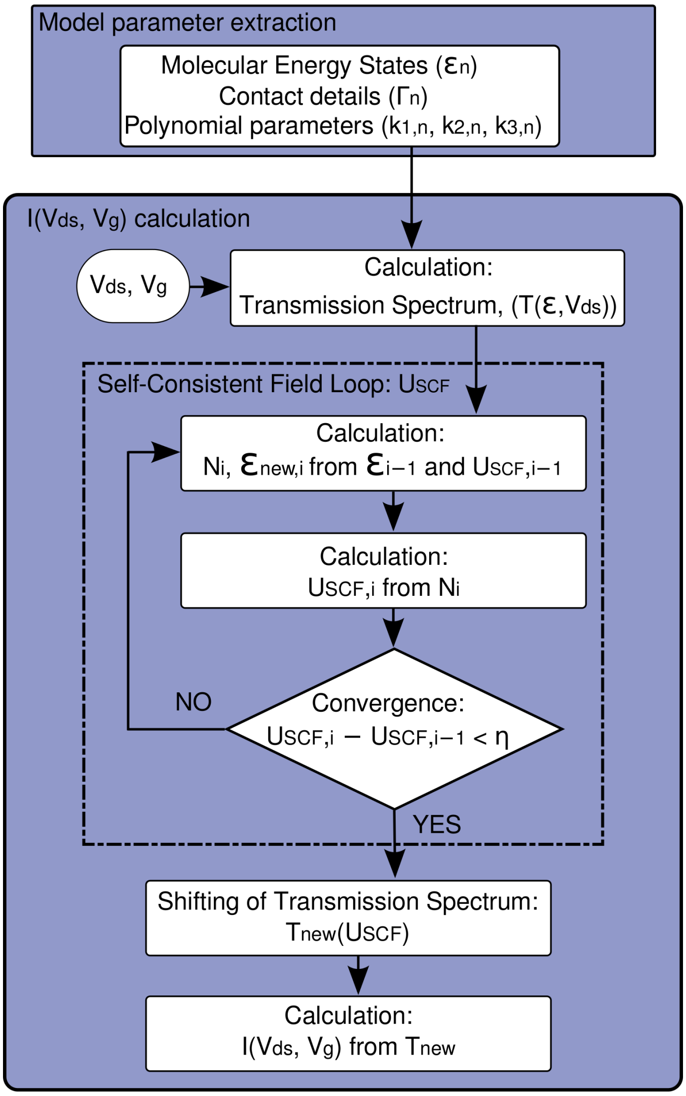

Figure 1.5: Algorithm for calculating the current with the proposed model **ee-besd**: the preliminary step is the extraction of some parameters from atomistic simulations, that will be provided as inputs to the current calculation flow. This flow is mainly divided in three phases: the calculation of the transmission spectrum ($T(\mathcal{E}, V_{ds})$), the SCF loop and, finally, the calculation of current ($I(V_{ds}, V_g)$).

The proposed algorithm requires the preliminary extraction of some parameters for a specific molecule suitable for MolFET technology obtained by atomistic simulations.

As depicted in the *Model parameters extraction* box (Figure 1.5, top rectangle), these parameters are: the molecular energy states ($\mathcal{E}_n$, where n is a reference to the n_{th} orbital), the coupling strength (Γ_n) of the two metal-molecule contacts and the polynomial coefficients ($k_{1,n}, k_{2,n}, k_{3,n}$).

Afterwards, the extracted parameters become inputs for the $I(V_{ds}, V_g)$ *calculation* phase (Figure 1.5, main gray rectangle) and they are used to find voltage dependent transmission spectrum ($T(E, V_{ds})$).

Then, the self-consistent-field (SCF) loop is involved in the algorithm (inner dash-dotted rectangle in the figure). The necessity of this loops derives from the fact that the electrons, when moving from one electrode to the other, influence the potential energy of the metal-molecule-metal system, leading to a shift of the transmission spectrum. This loop, thus, with this successive approximation approach, estimates the correct potential energy U_{SCF} with an approximation level that can be decided by the user.

In addition, the algorithm computes the effect of the gate voltage (V_g) on the transmission spectrum. Thus, finally, the current $I(V_{ds}, V_g)$ is calculated as function of the bias conditions and the obtained transmission spectrum.

1.3.2 Model parameters extraction

For sake of simplicity, this task has been already performed for you. The five molecule have been first simulated with ATK at the equilibrium. Data obtained by these simulations are used to set important parameters adopted in the proposed algorithm to define the transmission spectrum for different bias voltages. They include: four molecular orbitals $\mathcal{E}_n$ near to Fermi level and their coupling strengths for L (left contact) and R (right contact) $\Gamma_{L/R}$. The $I - V$ characteristics mainly depend on the contribution of these four molecular orbitals for the applied voltage range (in this lab defined as $V_{ds} = -3 \div +3V$).

We assumed that right R and left L contacts are symmetrical, thus their coupling strengths Γ_R and Γ_L are the same. Γ is the width of the broadened energy level.

All the extracted parameters have been included in the input data file named *Molc_Inputs_name-ot-the-molecule.m*.

1.3.3 Calculation of transmission spectrum

For each $\mathcal{E}_n$ and given the extracted parameters, the transmission spectrum $T(\mathcal{E} - \mathcal{E}_n)$ of molecular orbitals is obtained by equation 1.1:

$$T(\mathcal{E} - \mathcal{E}_n) = \frac{\Gamma_{L_n}\Gamma_{R_n}}{(\mathcal{E} - \mathcal{E}_n) + (\Gamma_n/2)^2} \tag{1.1}$$

The phenomenon of change in transport properties after applying voltages can be viewed in terms of evolution of transmission spectrum. The applied voltage affects the transmission spectrum in two ways: 1) changing the position of molecular orbitals relative to the Fermi level of electrode and 2) broadening of molecular orbitals. Moreover, also a variation of V_G changes the energy levels w.r.t. the Fermi value. This influence is analyzed in section 3.E, while herein and in the following subsection the first two effects are discussed.

The applied bias voltages affect the area of the transmission spectrum of the molecular system: the change of the transmission peaks with applied bias in **ee-besd** is approximated with a quadratic polynomial. This choice is a trade-off between accuracy and computational efficiency.

1.3.4 Self-Consistent-Field loop (SCF)

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As mentioned above one of the effect of the bias voltage is a shifting of the transmission spectrum. In our model, the relative position of peaks in energy (e.g. the position of one peak w.r.t. the other) is not affected by bias voltages. As a consequence, in **ee-besd** the complete transmission spectrum is always rigidly shifted in energy, and the shift depends on V_{ds}, V_g and on the charge hosted by molecular levels (charging effect).

Charging effect produces a shift of transmission spectrum and it is accounted for in the self-consistent field (SCF) loop in the algorithm (the inner dash-dotted rectangle in the algorithm flow). The shifting depends on the Self consistent-field energy (U_{SCF}) related to the charge hosted in the molecular orbitals. At each step of the loop, the energies of molecular orbitals $\mathcal{E}_{n,i}$ are re-calculated by adding self-consistent field energy U_{SCF} as in the following equation

$$\mathcal{E}_{n,i} = \mathcal{E}_{n,i-1} + U_{SCF} \tag{1.2}$$

The self-consistent field energy is computed from electron population using

$$U_{SCF} = U_0(N - N_0) \tag{1.3}$$

where U_0 is charging energy for a single electron. N_0 is the total number of electrons hosted by the energy levels of the molecular system at the equilibrium. N is the sum of the electrons hosted by all the energy levels involved in the conduction and it is expressed by equation 1.4:

$$N = 2\sum_n \frac{\Gamma_{L_n} f_{L_n}(\mathcal{E}_{n,i}) + \Gamma_{R_n} f_{R_n}(\mathcal{E}_{n,i})}{\Gamma_{L_n} + \Gamma_{R_n}} \tag{1.4}$$

where f_{L_n} and f_{R_n} are the Fermi-Dirac functions of left and right electrodes, respectively.

Equations (1.4) and (1.3) are calculated iteratively until the convergence is achieved. In particular, defined the desired accuracy η, the iterations end when:

$$U_{SCF,i} - U_{SCF,i-1} < \eta \tag{1.5}$$

The value N obtained as mentioned above is related to the discrete energy levels D_L of the spectrum. However, if we consider the broadening of the energy levels as well, the number of electrons N should take also into account, in theory, the occupancy of each energy level given by the Density Of States (DOS). This is done in the Atomistic ToolKit (ATK) simulations.

In this lab you will compare the results obtained by ATK simulations (DOS) and EE-BESD model.

1.3.5 Calculation of Current

Finally, referring to the last step of the flow diagram, the new current I is calculated using the modified transmission spectrum and the Landauer formula in equation 1.6:

$$I(V_{ds}) = \frac{2q}{h}\int T(\mathcal{E}, V_{ds})(f_L(\mu_L) - f_R(\mu_R))d\mathcal{E} \tag{1.6}$$

where f_L and f_R are again the Fermi-Dirac functions of left and right electrodes, respectively, while μ_L and μ_R are the chemical potential of the same electrodes.

1.3.6 Gate voltage effect

In three terminal device, the gate voltage also shifts the molecular energy levels relative to E_f. For each energy level, the effect of the shifting can be accounted as in eq.(1.7)

$$\mathcal{E}'_n = \mathcal{E}_n - q\alpha V_g \tag{1.7}$$

where α is the gate coupling factor. This factor can be measured from Fowler-Nordheim plot of $I - V$ characteristic of molecular transistor. The obtained $\mathcal{E}'_n$ are then used in the self-consistent field loop.