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Semi-empirical Study of Modeling of Molecule Based Single Electron Transistor

Preferencial Kala C[1]*, ArunaPriya P[2] and John Thiruvadigal D[1]

[1]Department of Physics and Nano Technology, Center for Materials Science and Nanodevices, SRM University, Kattankulathur - 603 203. India.
[2]Department of Electronics and Communication Engineering, Center for Materials Science and Nanodevices, SRM University, Kattankulathur - 603 203. India.

Abstract : We present the semi-empirical studies based on extended huckel theory (EHT) and nonequilibrium greens function formalism (NEGF) for calculating the charging energies of molecular systems weakly coupled to the single electron transistor environment. This approach is applied to phenyldithiol and borazine molecules, which is lying flat on gate dielectric between the source and drain electrodes. The calculated values of charging energies for isolated phenyldithiol and borazine molecules are in good agreement with experimental values. The charging energy of these molecules is reduced in a considerable manner in an SET environment due to the renormalization of molecular energy levels. Further, the charge stability diagram of molecule based single-electron transistor (SET) has been obtained by calculating the charging energies as a function of an external gate potential,the result shows the dependence of SET conductance on the gate voltage and the source-drain bias. Our implementation is intended to predict the charging energies of the phenyldithiol and borazine-based SETs that reveals further scope in realization of the devices at nanoscale.

1. Introduction

The use of non-equilibrium Greens functions (NEGF) in connection with density-functional theory (DFT)[1,2], or semi-empirical models[3,4,5], has been highly successful in modelling coherent transport in various types of molecular junctions. However, in the case of molecular single-electron transistors (SET), the transport is incoherent,[6], and another approach is needed. [7]introduced a semi-empirical model for simulating the properties of molecular SETs. In particular they showed the importance of including renormalization of the molecular charge states due to the polarization of the environment. There have been a lot of discoveries dealing with experimental studies, recently experimental investigations on single-molecule SET constructing from bottom up approach[8,9]using organic molecule as an active component shows its applicability towards future nanoelectronic systems.

Theoretically, two limiting regimes can be distinguished, namely coherent transport (CT) for strong coupling between the molecule and the source/drain electrodes and coulomb blockade (CB) for weak coupling.

Calculations for CT regime have been successfully performed by First principle approach or semi-empirical approach. However, in the case of single-molecule SET operating in CB regime,the transport is incoherent [10].

Therefore,the approach based on semi-empirical model for simulating the properties of single-molecule single-electron transistors (SETs) has been recently introduced by [7], and showed the importance of renormalization of molecular charge states due tothe polarization of the environment. To understand the concept of CT and CB clearly a morerealistic and quantitative theoretical description is needed.

In this study, we have adopted semi-empirical approach to calculate the charging energy of phenyldithiol and borazinemolecules weakly coupled to an SET environment. Thus, we obtain the charge stability diagram of phenyldithiol and borazinebased SET by calculating the charging energies as the function of external gate potential. Specifically, the influence of the SET environment on the positions of the molecular energy levels of phenyldithiol and borazine has been demonstrated.

2. Computational method

In this section we will discusses the semi-empirical approach for calculating the charging energies of phenyldithiol and borazine moleculesin electrostatic SET environment. For this purpose the total energies are evaluated by performing selfconsistent calculations for different charge states of the molecule, i.e., with varying number of electrons on the molecule. The molecular ionization potential (IP) and the electron affinity(EA) are given by the differencein total energy between the neutral and singlycharged states of the molecule, i.e.,

$$IP = E^{N-1} - E^{N} \quad (1)$$

And $$EA = E^{N} - E^{N+1} \quad (2)$$

Here, N denotes the number of electrons in the neutralstate of the molecule. The charged states with one electronadded (N + 1) and removed (N-1) correspond to the anionand cation, respectively. The addition energy is given bythe difference between IP and EA.

$$E_{add} = IP - EA = E^{N-1} + E^{N+1} - 2E^{N} \quad (3)$$

All calculations are performed based on Extended Huckel theory combined with NEGF formalism using AtomistixToolKit (ATK)[11]. The semi-empirical approach in ATK is based on pseudopotentials with numerical localized basis functions. In this framework, a compensation charge is introduced for each atomic site. The compensation charge has the same charge as the pseudopotential, and is used to screen the electrostatic interactions.

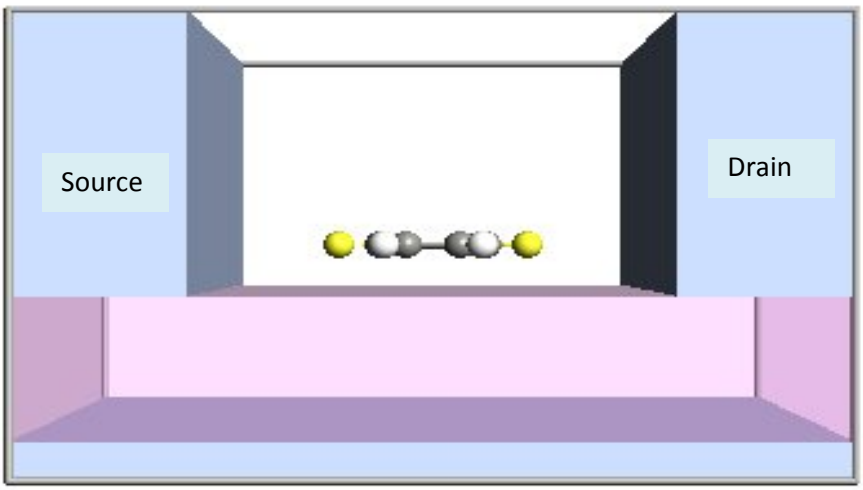

Figure.1 phenyldithiolmolecule in the SET environment

At first the structure of the isolated molecule is optimized based on density functional theory (DFT) using ATK, similar to our earlier work [12]. Using the optimized isolated molecule the single electron transistor geometry was formed. Figure 1 represents a typical molecular single electron transistor geometry where a phenyldithiol molecule is positioned on top of a dielectric material and surrounded by metallic

electrodes. Within the metallic regions the potential is fixed to the applied voltage on each respective electrode.Tothe left and the right of the molecule, there are metallicsource-drain electrodes and the system consists of a metallic back-gate, above the gate there is a dielectric material with dielectric constant 10 ε_0.

3. Result and Discussion

To obtain some reference energies, we first calculate the charging energies of the molecules in gas phase denoted as 'isolated' molecules. For isolated case, our calculated values of charging energy for phenyldithiol and borazine molecules are reported in table 1. The charging energy for phenyldithioland borazine molecules is in good agreement with that of experimental values. While in electrostatic SET environment, the charging energy is strongly reduced as compared to its gas phase values. The reduction in the charging energy arises from the screening of the charged molecule by the surrounding dielectric and metal electrodes.

Table 1. The calculated and experimental values of ionization (I) and affinity (A) energies (all are in eV) for phenyldithiol and borazine in gas phase and in SET environment

Phenyldithiol	E_I^+	E_I	E_A	E_A^+
Experiment		9.25		
Isolated	14.873	9.078	-3.041	-6.60
SET	11.23	7.314	-1.404	-3.17

(a)

Borazine	E_I^+	E_I	E_A	E_A^+
Experiment		12.35		
Isolated	19.64	14.17	2.57	0.11
SET	15.29	13.02	-1.50	-2.50

(b)

After that, we calculate the total energy of the different charge states in SET environment as a function of gate voltage (V_G), it is represented in Figure 2. Figure 2 shows, the neutral molecule has the lowest energy and hence it is a stable charge state. Negative charge states lower energy by positive gate voltage, while positive charge states lower energy at negative gate potentials. This is in agreement with HOMO and LUMO levels following $-eV_G$, thus, at positive gate voltage the LUMO level gets below the electrode Fermi level and therefore attracts an electron and the molecule gets negatively charged. At negative bias, the HOMO level gets above the electrode Fermi level, hence, an electron escapes from phenyldithiol and borazine molecules and the molecule becomes positively charged.

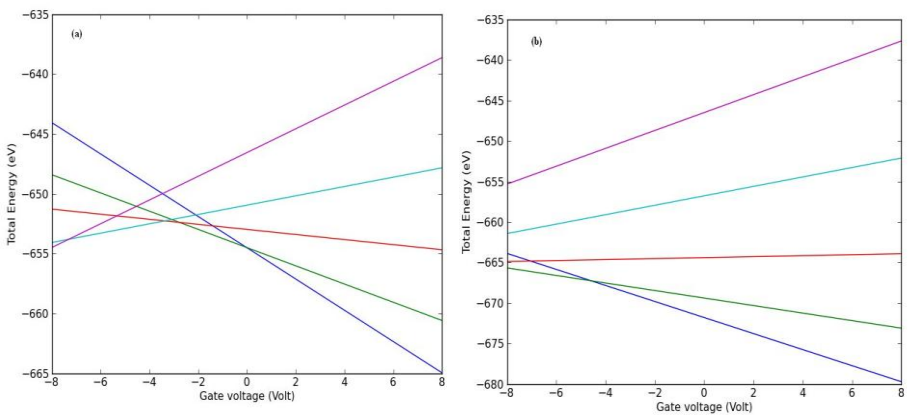

Figure. 3 The total energy as a function of gate voltage for (a) phenyldithiol (b) borazine in the SET environment , Different curves for different charge states of naphthalene, blue (-2), green (-1), red (0), turquoise (1), violet (2)

For a single-molecule SET operating in the coulomb blockade regime, charge transfer through molecule is possible when either the ionization potential (IP) or the electron affinity (EA) is positioned within the bias window. If on the other hand, no levels are present in the bias window, current is blocked and the molecule remains in a fixed charged state. To reach the regime where transport is possible, one can either shift the IP and EA levels with the gate voltage or apply a sufficiently large source-drain bias.

We next calculate the charge stability diagram for phenyldithiol and borazine based SET as shown in Figure. 4 by evaluating total energies of these molecules as a function of gate and source-drain bias. The different colors in this diagram show the number of molecular levels inside the bias window for given values of the gate and source-drain bias. The conductance is directly related to the number of energy levels inside the bias window and hence this diagram indicates an indirect measure of the current level for a given gate and source-drain voltage. It can also be noted that charge stability diagram depends only on the difference in energies between charge states and is independent of charge states and hence in charge stability diagram, the non-linear dependence of the total energy on gate voltage is not observed. The present study reveals that that the SET environment renormalizes the molecular energy levels by changing the charging energies of these molecules and also insights into the properties of single-molecule SET operating in coulomb blockade regime.

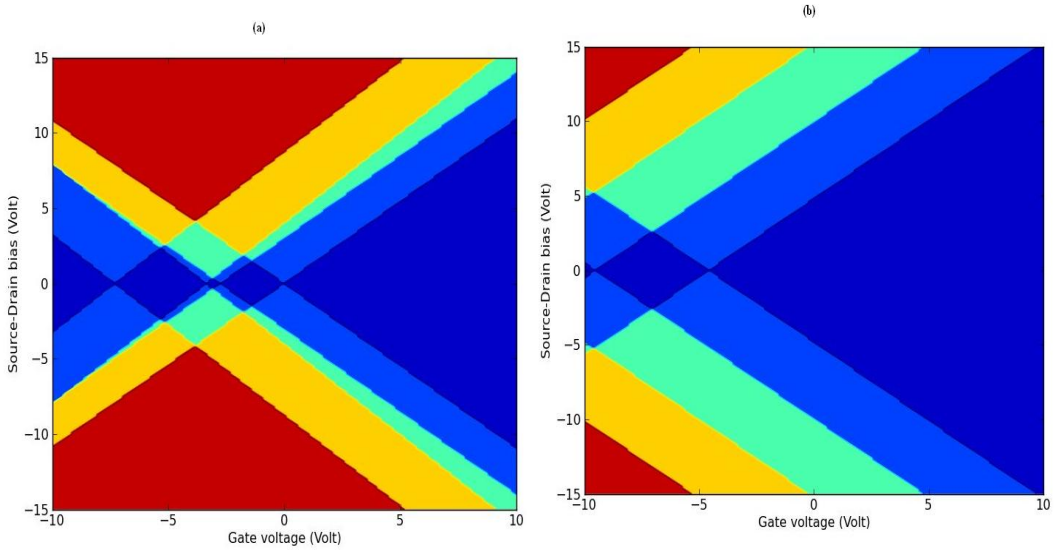

Figure.4 Charge stability diagram for (a) phenyldithiol (b) borazine in the SET environment. The color shows the number of charge states dark blue (-2), blue (-1), red (0), green (1), yellow (2) within the bias window for a given gate voltage and source-drain bias

4. Conclusion

We have demonstrated the use of semi-empirical approach for calculating the charging energy of a phenyldithiol and borazine molecules in a metallic environment that models the geometry of a molecular single-electron transistor. We observed that the SET environment reduce the charging energies in a considerable value and the charging energies of isolated molecule is in good agreement with the experimental value.Further, it is alsoobserved that the SET environment renormalizes themolecular energy levels and hence reduces the chargingenergies for the phenyldithiol and borazine molecules. The present investigationfurther demonstrates the use of semi-empirical approach togain new insights into the properties of single-moleculeSET operating in coulomb blockade regime.

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