

Renormalization of Molecular Energy Levels in Single-Molecule Nanojunctions: An Ab-initio Approach

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Abstract. Using first-principle calculations based on Density Functional Theory (DFT) in conjunction with the Non-Equilibrium Greens Functions (NEGF) technique, we have studied the effect of electrostatic environment in molecular energy levels of single-molecule transistors. This approach is applied to three polycyclic aromatic hydrocarbons (PAHs) anthracene, tetracene and pentacene, for calculating charging energies of molecular systems weakly coupled to an electrostatic environment. The result shows renormalization of molecular energy levels in an electrostatic environment. Further, it is observed that on increasing the number of aromatic rings, the addition energy value decreases which increases the conductivity of the system. Subsequently charge stability diagram for PAHs has been obtained.

1. Introduction

The dimensions of conventional silicon-based electronic devices will soon be so small that quantum effect, such as electron tunneling and energy quantization will begin to influence and eventually limits the device functionality. On the other hand, molecular Single-electron transistor (SET) constructing from the bottom up approach using organic molecules as active component have been considered as potential building block for future nanoelectronic systems [1-3]. Aviran and Ratner in 1974, first proposed theoretically the concept of electron transport in single molecule devices [4] and attracted significant interest due to its recent progress in experimental characterization [5-8]. Theoretically, electron transport can be generally distinguished within two limiting regimes, namely, coherent transport (CT) for strong coupling between the molecule and electrodes and coulomb blockade (CB) for weak coupling. However, in case of molecular SET, transport is incoherent [9].

First principle calculations usually based on Non-Equilibrium Green's Function (NEGF) methods in combination with Density Functional Theory (DFT) [10, 11] have been successfully applied in CT regime. However, in the CB regime, ab-initio approach renewed interest recently [12, 13]. Transport in CB regime is characterized by the so called charge stability diagram indicating frontiers between low and high conductivity domains in the source/drain bias gate voltage co-ordinates [14, 15]. Key quantities in this charge stability diagram is addition energy defined here as the difference between molecular ionization potential (IP) and electron affinity (EA) of single molecule.

Despite the great progress achieved, outstanding questions about fundamental issues such as energy levels, influence of electrodes are still not fully explored. Therefore, a more realistic and quantitative theoretical description is needed. Also, Martin-Lasanta et al recently found that on



increasing the number of rings in polycyclic aromatic hydrocarbons (PAHs) will give higher conductivity as well as mechanical and current stability [16]. Motivated by this, we use the model to calculate charging energy of three PAHs namely anthracene, tetracene and pentacene of acene series in the SET environment. The purpose of the present study is to examine the influence of electrostatic environment on the positions of molecular energy levels of PAHs. Further, the effect of number of aromatic rings on addition energy has been demonstrated. Thus, we obtain charge stability diagram in the SET environment by calculating the charging energies as the function of external gate potential.

2. Computational method

All the calculations are carried out by using DFT based NEGF formalism which is implemented in Atomistix ToolKit [17]. For the calculations we use non-polarized DFT in the local density approximation (LDA) and expand the wave functions in double-zeta polarized (DZP) basis set. We setup benzene, anthracene, tetracene and pentacene molecule in the SET geometry as shown in the Figure 1. It consists of a metallic back-gate, and above the gate there is 3.8 Å of dielectric material with dielectric constant $10 \epsilon_0$. The molecule is positioned 1.2 Å above the dielectric. To the left and the right of the molecule, there are metallic source-drain electrodes respectively. Moreover, the distance between the molecule and the electrode is kept 2.8 Å.

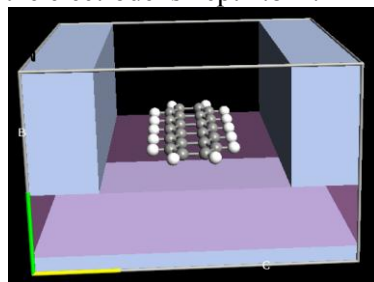


Figure 1. A pentacene molecule lying flat on the top of dielectric substrate between source and drain electrodes with metallic back-gate resembling SET environment at zero gate and source-drain bias

3. Results and Discussion

Initially, DFT calculations have been performed in gas phase and in SET environment for benzene molecule. The gas phase values denoted as “isolated” in the Table 1 are obtained from the total energies of the charged isolated molecule. While the “SET” values are obtained by calculating the total energies of the charged molecule in the electrostatic surrounding at zero gate and drain bias. The calculated charging energies for benzene are in excellent agreement with available results [9].

Table 1. The calculated and experimental values of IP and EA for anthracene, tetracene and pentacene

Anthracene	E_I^{+1} (eV)	E_I (eV)	E_A (eV)	E_A^{-1} (eV)
Experiment ^a	-	7.439	0.530	-
isolated	11.56	6.86	0.05	-4.48
SET	7.18	5.68	2.02	0.62
Tetracene	E_I^{+1}	E_I	E_A	E_A^{-1}
isolated	10.46	6.29	0.69	-3.37
SET	6.39	5.20	2.56	1.44
Pentacene	E_I^{+1}	E_I	E_A	E_A^{-1}
isolated	9.68	5.89	1.14	-2.58
SET	5.95	4.91	2.90	1.91

^aNIST server (<http://cccbdb.nist.gov/>)

Further, we apply the same approach to anthracene, tetracene and pentacene. Table 1 show the calculated values of charging energies for anthracene in isolated case that are in good agreement with experimental results [18]. These energies are also evaluated for tetracene and pentacene. While in SET environment, the charging energies of all the three molecules are strongly reduced as compared to its gas phase values. The reduction in the charging energy is caused by screening of the charged molecule by surrounding dielectric and metal electrodes [19].

We have compared our findings with the GW calculations [20]. They found gas phase values $E_{\text{LUMO}} - E_{\text{HOMO}} = 6.91$ eV and absorbate gap values $E_{\text{LUMO}} - E_{\text{HOMO}} = 4.29$ eV for anthracene. Similarly, these values are $E_{\text{LUMO}} - E_{\text{HOMO}} = 6.09$ eV and $E_{\text{LUMO}} - E_{\text{HOMO}} = 3.62$ eV for tetracene and $E_{\text{LUMO}} - E_{\text{HOMO}} = 5.24$ eV and $E_{\text{LUMO}} - E_{\text{HOMO}} = 2.88$ eV for pentacene respectively. These results are comparable with our values $E_{\text{I}} - E_{\text{A}} = 6.81$ eV, $E_{\text{I}} - E_{\text{A}} = 3.66$ eV for anthracene, $E_{\text{A}} = 5.60$ eV, $E_{\text{I}} - E_{\text{A}} = 2.64$ eV for tetracene and $E_{\text{I}} - E_{\text{A}} = 4.75$ eV, $E_{\text{I}} - E_{\text{A}} = 2.01$ eV for pentacene in gas phase and in SET environment respectively. Thus, we conclude that the addition energy in an electrostatic environment is heavily reduced compared to their corresponding gas phase values. It can also be noted that in SET environment, on increasing the number of aromatic rings, the addition energy value reduces which indirectly affect the conductivity of the system. This is in correspondence with HOMO-LUMO gap. Since the barrier of electron transfer is approximately proportional to the HOMO-LUMO gap [21], therefore in SET environment, the current increased with increasing the number of aromatic rings.

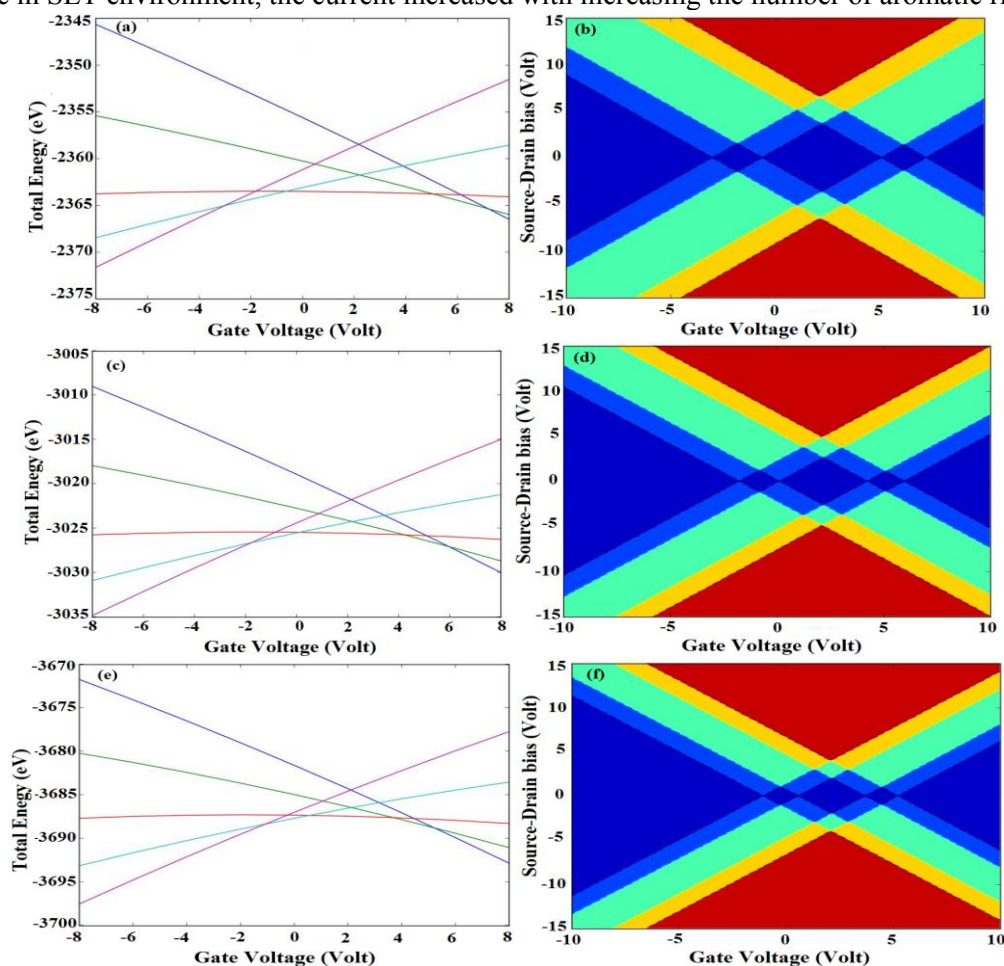


Figure 2. The total energy as function of gate voltage for anthracene (a), tetracene (c), and pentacene (e) in the SET environment. Different colors for different charge states: blue (-2), green (-1), red (0), turquoise (1), violet (2). The charge stability diagram for anthracene (b), tetracene (d), and pentacene (f) in SET environment. The color shows the number of charge states dark blue (-2), blue (-1), red (0), green (1), orange (2) within the bias window for a given gate voltage and source-drain bias

We next calculate the total energy of different charge states in SET environment as a function of gate voltage as shown in Figure 2. (a), (c), (e). The total energy includes reservoir energy qW , where q represents charge of organic molecule and W ($=5.28\text{eV}$) is the work function of gold electrode. At zero gate voltage, the neutral molecule has the lowest energy and hence it is stable charge state. Negative charge states lowers energy by positive gate voltage while positive charge states lowers energy at negative bias. This is in agreement with HOMO and LUMO levels follow $-eV_G$, thus, at positive voltage the LUMO level gets below the electrode Fermi level therefore attracts an electron and the molecule gets negatively charged. At negative bias, the HOMO level gets above the electrode Fermi level hence electron escapes organic molecule and the molecule become positively charged.

Further, we calculate the charge stability diagram for anthracene, tetracene and pentacene molecules by evaluating total energies as shown in Figure 2. (b), (d), (f). The different color shows the number of molecular energy levels inside the bias window for given values of gate and source-drain bias. As we know that the height of central diamond related to the addition energy [20], reduces on increasing the number of aromatic rings which indirectly increase the conductivity of the system. This effect is also observed in recently reported results [16]. It can also be noted that, charge stability diagram depends only on the difference in energies between charge states and hence in charge stability diagram the non-linear dependence of the total energy on gate voltage is not observed.

4. Conclusions

We performed an ab-initio calculation to obtain the charge stability diagram of anthracene, tetracene and pentacene in the coulomb blockade regime by calculating the charging energies as a function of external gate potential. We found that the electrostatic environment reduces the charging energies of the molecule. Further, it is also observe that number of rings in PAHs decrease the addition energy and hence increase the conductance of the system.

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