First-Principles Modeling of the Smallest Molecular Single Electron Transistor

Research Article

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Abstract. Using first-principles method the charging energy has been calculated; of the smallest *Single Electron Transistor* (SET) consisting of only two carbon atoms while operating in coulumb blockade regime. The ethyne (C_2H_2) molecule is acting like a quantum dot (with discrete energy levels) and is weakly coupled to the gold electrodes (continuum). The quantum effects are significant and the conduction of current takes place through incoherent method via electron tunneling. The electronic levels of the molecule determine the electron transport properties. The molecule may be in several charged states from +2 to −2. It has been observed that the HOMO-LUMO gap is strongly reduced in solid state environment with metallic electrodes, as compared to the vacuum. This reduction is attributed to the image charges generated in the source and drain electrodes. This results in strong localization of charges in the molecule, a phenomenon addressed earlier. The charging energy has been calculated in vacuum and in SET environment. The interaction between molecule and the electrodes is treated self-consistently through Poisson equation. The charge stability diagram of the smallest molecular SET has been obtained.

Keywords. Single electron transistor; Incoherent transport; Ethyne; Coulomb blockade; Quantum tunneling; Charge stability diagram

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1. Introduction

Modern day computer microprocessor integrated circuit has billions of transistors on a single chip, with a clock period of a billionth of a second [1]. The trend of decreasing dimensions and clock speed has been maintained since the transistors came into existence, and still continuing. As the packing density of transistors (gates, memory elements) increases, the energy signal has to be reduced in order to keep the energy dissipation low. Even though the size of a transistor reached nm range (presently few hundreds of nm) the operational principle of today's transistor remains classical (as in MOSFETs). As technology is moving towards building the ultimate limit size (molecular or atomic size! transistors) the quantum effects starts becoming significant. Thus electrons starts behaving as wave and the principle of operations has to be redefined in the quantum domain. In quantum optics it is possible to detect a single particle like electron or photon moving in vacuum efficiently; by using photomultiplier tubes or devices based on it. But for detection of electrical signal generated by a moving single electron, the amplifier has to be an excellent energy sensor and simultaneously possess outstanding electrical characteristics. A device which possesses characteristics is *Single Electron Transistor* (SET). Its principle of operation is based on quantum tunneling and it controls the movement of single electrons. SET has applications in quantum optics [2, 3], metrology [4], DNA sequencing [5, 6, 7] and many other areas. The idea of electronic transport through molecule was first described theoretically by Aviram and Ratner [8]. Generally the coherent transport in various types of molecular junction has been studied using *Non Equilibrium Greens Functions* (NEGF) coupled with semiemperical [9, 10] or *Density Functional Theory* (DFT) [11, 12]. As the transport mechanism is different in SET being incoherent [13], the molecule is not physically connected to the source and drain. Thus the existing method will not work and one has to deal with it differently. Kaasbjerg [14] and Stokbro [15] suggested the semiempirical and DFT models respectively to deal with the incoherent transport properties in SET. In fact, the idea of renormalization of energy levels in SET as suggested by Kaasbjerg, was later incorporated by Stokbro in his DFT model. Using DFT model, Stokbro calculated the charging energy as a function of gate potential and obtained the charge stability diagram of benzene (consisting 6 carbon atoms) a planar two dimensional and C60 (consisting 60 carbon atoms) a three dimensional spherical molecule. In the present work, we have applied Stokbro DFT model to the simplest one dimensional system ethyne (C_2H_2) consisting of two carbon atoms. Due to relatively small size of molecules the level spacing and charging energy of single molecule SET are considerably higher than quantum dots or metallic islands. The peculiar size and one dimensional structure of this molecule will further reduce the transistor size thereby enabling enhanced packing of SETs on a given surface area.

2. Formal Expression for Charging Energy in SET

The following expression for charging energy has been derived by Stokbro [15]. In SET weak coupling regime where the transport is described by sequential tunneling, we will define energy as a function of number of electrons; for source electrode, island and drain electrode. Let $E^S(M)$, $E^I(N)$ and $E^D(K)$ are the total energies of source, island and drain of the SET, where M, N and K are the number of electrons on them respectively. The electron will hop from source to

island if the island has lower energy i.e.

$$E^S(M) + E^I(N) \geq E^S(M-1) + E^I(N+1). \tag{2.1}$$

Similarly the electron will hop from island to drain if the drain has lower energy

$$E^D(K) + E^I(N+1) \geq E^I(N) + E^D(K+1), \tag{2.2}$$

where M, K and N are the initial number of electrons on source, island and drain respectively. From eqn. (2.1)

$$E^S(M) - E^S(M-1) \geq E^I(N+1) - E^I(N). \tag{2.3}$$

The maximum energy in the source electrode is $(-W + eV)$, where W is the work function of the electrode and V is the applied bias, hence

$$-W + eV/2 \geq \Delta E^I(N). \tag{2.4}$$

Similarly from eqn. (2.2), one gets

$$E^I(N+1) - E^I(N) \geq E^D(K+1) - E^D(K),$$

$$\Delta E^I(N) \geq -W - eV/2, \tag{2.5}$$

where $\Delta E^I(N) = E^I(N+1) - E^I(N)$ or

$$eV/2 \geq W + \Delta E^I(N) \geq -eV/2. \tag{2.6}$$

Here $\Delta E^I(N)$ is the charging energy of the island and one may calculate this charging energy of C_2H_2 SET to obtain the charge stability diagram. The diagram shows the number of charge states inside the bias window as a function of the gate and source drain voltage. As shown in Fig. 1 the C_2H_2 molecule is present in electrostatic environment. Here we have used ATOMISTIX TOOLKIT (ATK) [16] program to perform the calculations.

3. Results and Discussion

Fig. 1 shows the optimized structure of the molecule, a cartoon of the SET and the actual SET considered in the calculations. It consists of a metallic back-gate and above the gate is a dielectric slab with thickness 3.8 Å. The parameter $\epsilon_r = 10$ which corresponds to the dielectric Al_2O_3. The high dielectric constant ensures reasonable coupling between the gate and molecule. The molecule is placed on the top of gate at a distance of 1 Å. The gate electrode and its capacitive coupling to the molecule is essential for functionality of SETs. It allows the shift of molecular levels by mild electrostatic means and there by the current is turned on and off. Table 1 shows the calculated energy values of various charge states in isolated and SET environment, with zero potential at gate electrode. The HOMO and LUMO of the neutral molecule do not give the correct values of ionization potential and electron affinity because when the molecule become charged, there is an additional charging energy which is not included in a calculation pertaining to neural molecule. The values of first and second IP and E_A associated ethyne
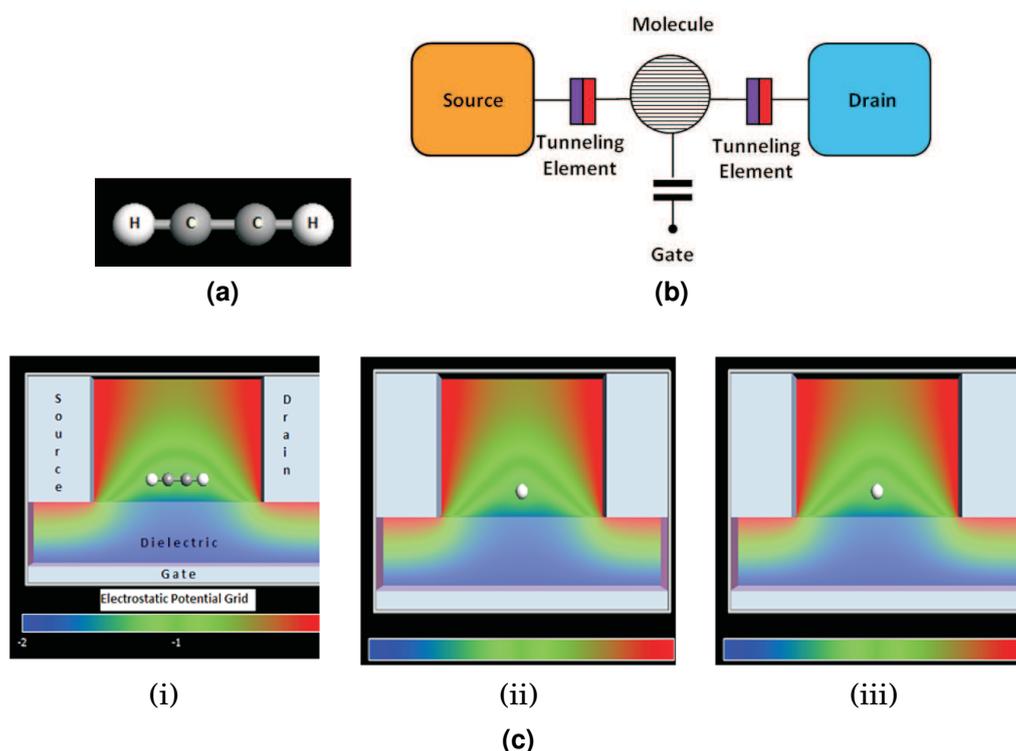
Figure 1. (a) Optimized structure of C_2H_2 molecule. (b) Cartoon of single electron transistor. (c) Different orientation of molecule in SET (flat along the gate (i), flat perpendicular to gate (ii) and vertical perpendicular to gate (iii)). The contour shows the induced electrostatic potential for $V_g = 2\,V$ and $V_{s-d} = 0\,V$.

molecule in isolated and SET environment are displayed in Table 2. In the first column the calculated value of IP^1 matches very well with the experimental value justifying the level of accuracy of theoretical calculations. These values are greatly reduced in SET environment due to stabilization of the charge on the molecule by electrostatic surroundings. For the molecule on the substrate, the charge on the molecule is mainly stabilized by the dielectric substrate. Fig. 2 shows the total energy of the different charge states of the SET system as a function of gate potential. The total energy includes the source energy $q\varphi$ where q is the charge on the molecule and φ is work function of the gold electrode (5.28 eV).

Table 1. Calculated energy (eV) values of neutral and ionized C_2H_2 molecule in vacuum and SET environment

| C_2H_2	E^0	E^{1+}	E^{2+}	E^{1-}	E^{2-}
Isolated	−343.17	−331.73	−309.83	−338.58	−326.30
SET [i]	−343.21	−333.26	−316.19	−340.48	−333.26
SET [ii]	−343.17	−332.99	−314.81	−339.84	−331.85
SET [iii]	−343.19	−333.43	−316.89	−340.51	−316.89

Table 2. Ionization and electron affinity values of different charge states in vacuum and SET environment (all values are in (eV)).

C_2H_2	$IP^1 = E^{1+} - E^0$	$IP^2 = E^{2+} - E^{1+}$	$E_A^1 = E^0 - E^{1-}$	$E_A^1 = E^{1-} - E^{2-}$
Expt.	12.3[a]/11.4[b]	-	-	-
Isolated	11.44	22.90	−5.15	−12.28
SET [i]	9.95	17.00	−2.73	−7.22
SET [ii]	10.18	18.18	−4.33	−7.99
SET [iii]	9.76	16.54	−2.68	−7.05

[a]: Ref. [17];   [b]: Ref. [18]
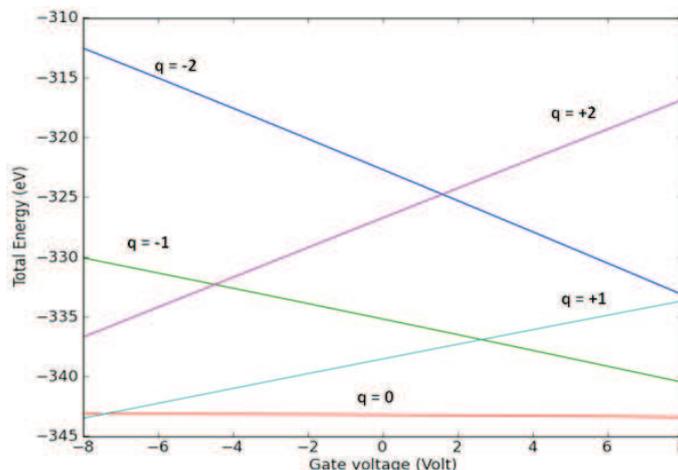
Figure 2. Total energy as a function of gate potential for ethyne molecule in SET environment. Different charge state ($q = 0, +1, +2, -1, -2$) plots are shown with different colors.
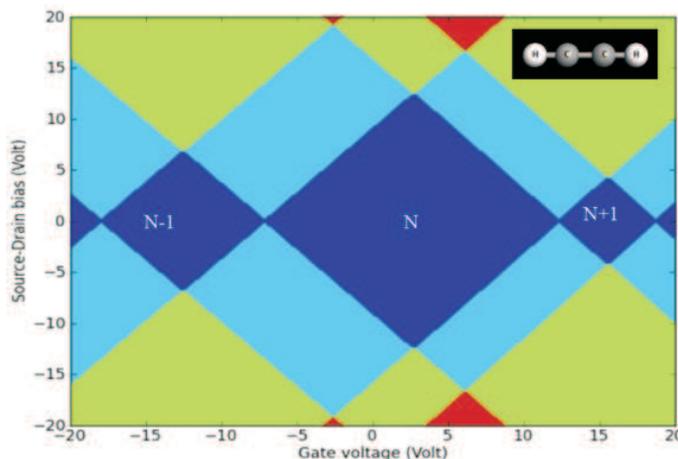
Figure 3. Diamond plot of Ethyne SET. The colour shows the energy states within the bias window for a given V_g and V_{s-d}. Dark blue (0), light blue (1), green (2) and red (3). Middle diamond for neutral molecule and the smaller diamonds on left and right for cation and anion. N denotes the total number of electrons.

The neutral molecule ($q = 0$) has the lowest energy (most stable) and is same at all values gate potentials. Negative voltages stabilize positive ions and positive gate voltages stabilize negative ions. At positive voltages, the LUMO goes below the electrode Fermi level and attracts an electron. The molecule becomes a negative ion. On the other hand, at negative voltages; the HOMO goes above the Fermi level. As an electron moves out from the molecule, it becomes positive ion.

The diamond plots or charge stability diagrams are very useful for studying the properties of a given SET device. The quantitative information about the addition energy and gate coupling can be inferred from these plots. Alternatively from the total energy versus gate potential graph, the coupling can be obtained. The gate coupling (α) has been calculated in three cases with differing molecule orientation in SET (see Fig. 1(c) (i), (ii), (iii)). The values are 0.63, 0.57 and 0.19, respectively. Thus the molecule is strongly coupled when it is lying flat along the gate; this value is slightly greater than the value 0.62 reported by Stokbro [15] for benzene SET. The ethyne molecule under investigation is much smaller having only two carbon atoms so a much smaller SET can be constructed.

Competing Interests

The authors declare that they have no competing interests.

Authors' Contributions

Both the authors contributed equally and significantly in writing this article. Both the authors read and approved the final manuscript.

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