Scientia Iranica F (2015) 22(6), 2752–2756

Sharif University of Technology
Scientia Iranica
Transactions F: Nanotechnology
www.scientiairanica.com

Electronic transmission of benzene metallic junctions: Reliability range of perturbation values

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Received 6 January 2015; received in revised form 23 July 2015; accepted 5 October 2015

KEYWORDS
Electronic transport;
Benzene;
Metallic junctions;
Perturbation theory.

Abstract. In this paper, the electronic transmission of an electrode-benzene-electrode system using equilibrium Green's and first order perturbation theory is investigated. The effect of different values of perturbation on substitution of the electrode into the different atomic sites is presented. The range of the perturbation values are from zero to the energy gap between the highest occupied and the lowest unoccupied molecular orbitals. Our calculations indicate that increasing the perturbation value does not greatly affect the case where the connection is with maximum transmission (para), whereas, doing likewise for the case of minimum transmission (ortho), we find a much more sensitive transmission response.

1. Introduction

The new era of miniaturized circuits has paved the way towards molecular electronics. Aviram and Ratner, in 1974, were the first people to calculate electronic transmission through a molecular bridge [1]. This bridge, in a donor-spacer-acceptor structure, may behave as a diode [2]. Electronic transmission through a variety of different molecules has been studied, and this has paved the way for investigating the electronic behavior of molecules and organic materials, and their applications in the technology of microelectronics [3] and biosensors [4]. In between molecules, benzene with non-localized π orbitals represents a noble conductivity. Interference effects in transport through aromatic systems in general and through benzene in particular have been studied both experimentally [5,6] and theoretically [7-18]. The mechanism of molecular transmission calculation in this paper is by first calculating the Green's function of an isolated molecule. Here, we are working with a model Hamiltonian at the Hückel level of electronic structure and then locating the molecule between two metal electrodes. The effect of connection to the electrodes is then added to the Hückel Hamiltonian as a perturbation [7]. The value of this perturbation affects the transmission, and the range of its variation is between chemical potential reactivity, Highest Occupied Molecular Orbital (HOMO), and Lowest Unoccupied Molecular Orbital (LUMO). Here, the effect of different values of perturbation on different substitution via two pathways is studied.

2. Method

The Hückel Hamiltonian governing π orbitals of benzene is [7]:

$$H = \sum_{i=1}^{6} \alpha \,|i\rangle\langle i| + \sum_{i=1}^{6} \beta \Big(|i\rangle\langle i+1| + |i+1\rangle\langle i| \Big), \qquad (1)$$

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where $|i\rangle$ represents π orbital on atom i, α is the onsite energy, which is usually set to zero, and β is the energy of jumping to the nearest neighboring atomic site. The Green's function of an isolated molecule derived from the Hamiltonian [7] is:

$$G_0 = (E - H_0 + i\eta)^{-1}, \tag{2}$$

where η is an infinitesimal loading of the retarded Green's function, and E is the energy eigenvalue. The connection to two metal electrodes is represented by an imaginary part added to each atomic energy site [7]:

$$\alpha \rightarrow \alpha - i\Gamma, \tag{3}$$

where Γ is a spectral density and the negative shift is reminiscent of a retarded Green's function. In this study, we have used a wide band approximation in which the effect of connection is imaginary. So, the effective Hamiltonian of a connected molecule using the Lowdin partitioning technique is [7]:

$$H_{eff} =$$

$$\begin{bmatrix} \alpha - i\Gamma/2 + \sum_{aa}^{A} + \sum_{aa}^{B} & \sum_{ab}^{A} + \sum_{ab}^{B} \\ \sum_{ba}^{A} + \sum_{ba}^{B} & \alpha - i\Gamma/2 + \sum_{bb}^{A} + \sum_{bb}^{B} \end{bmatrix}, \tag{4}$$

where $\sum_{ab}^{A,B}$ is the self-energy from pathways A and B; a is the atomic site, to which the first electrode is connected, and the second electrode b connects to atomic site 2, 3 or 4. Different substitutions result from coupling the electrodes to different atomic sites (Figure 1). The Green's function of a perturbed molecule via the off-diagonal element of the Green's function is evaluated using Dyson's equation as shown in Box I [7]. The molecular transmission is evaluated with [7]:

$$T(E) = \Gamma^2 \left|G(E)\right|^2. \tag{6}$$

In this paper, the effect of different Γ's on molecular transmission is investigated.

3. Results and discussions

The studied system is demonstrated in Figure 1. The first electrode is fixed at atomic site 1 and the second connection can be substituted on different atomic sites,

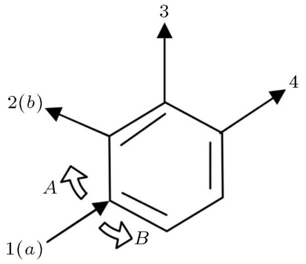

Figure 1. Different pathways (A and B) and electrode substitution patterns (1 → 2, 1 → 3 and 1 → 4) in the benzene molecule.

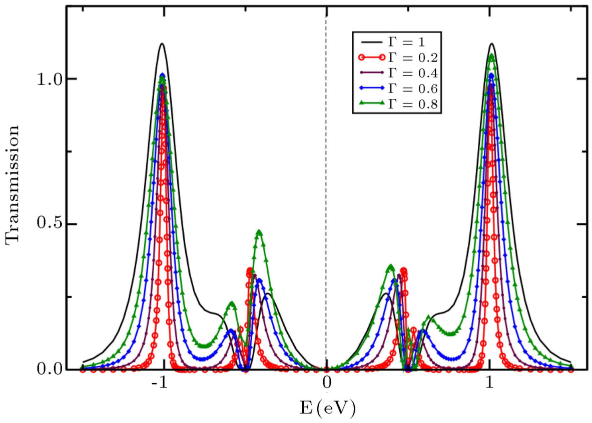

Figure 2. Transmission function $T(E)$, for different perturbation values on ortho substitution. The red dashed-dot is for $\Gamma = 0.2$, blue $\Gamma = 0.4$, black $\Gamma = 0.6$, green $\Gamma = 0.8$, and solid red $\Gamma = 1$.

2, 3 or 4, to form, respectively, ortho (1 → 2), meta (1 → 3) and para (1 → 4) substitutions. Transmission of ortho substitution is plotted in Figure 2. The graphs for $\Gamma = 0.2$ in all figures are calculated transmissions and they are in agreement with [7]. Very small values of perturbation (0.01) result in the δ-function, like peaks in a transmission plot. If the perturbation value increases, the width of peaks in the transmission plot increases. When the perturbation had a real section, the peaks shifted. In an unperturbed molecule, there are no anti-resonances, which can be seen in all plots of the transmission. The reason is the interference of two different spatial pathways (A and B) [7]. Increasing the value of perturbation broadens the width of peaks.

We have varied the value of perturbation (Γ) between 0.2 and 1, where 0.2 is the calculated transmis-

$$G_{ba} = \frac{\sum_{ba}^{A} + \sum_{ba}^{B}}{\left(E - \alpha + i\frac{\Gamma}{2} - \sum_{aa}^{A} - \sum_{aa}^{B}\right)\left(E - \alpha + i\frac{\Gamma}{2} - \sum_{bb}^{A} - \sum_{bb}^{B}\right)\left(\sum_{ba}^{A} + \sum_{ba}^{B}\right)\left(\sum_{ab}^{A} A + \sum_{ab}^{B}\right)}. \tag{5}$$

Box I

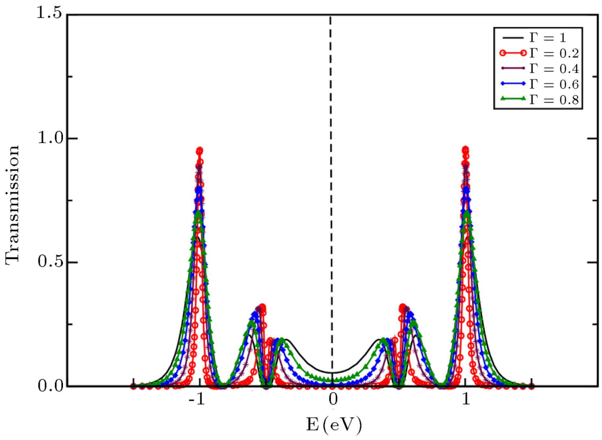

Figure 3. Transmission function, $T(E)$, for different perturbation values on meta substitution. The red dashed-dot line is for $\Gamma = 0.2$, blue $\Gamma = 0.4$, black $\Gamma = 0.6$, green $\Gamma = 0.8$, and solid red $\Gamma = 1$.

sion in [7] and 1 is the energy gap between HOMO and LUMO orbitals. As Γ increases, the peaks broaden, but, we see no shift in peak positions, as the perturbation value is purely imaginary. The validity of the first order perturbation is in the range of Γ, being much smaller than 1. In Figure 2, different values of T on ortho substitution are illustrated. This variation has influenced this substitution more than that of the two others because of electron richness and the spatial symmetry of substituting the two electrodes into the nearest neighbor of each.

In Figure 3, meta substitution, meaning location of the second electrode on atomic site 3, is presented. It reflects the fact that increasing perturbation has less effect than in the ortho situation. In Figure 4, para substitution, meaning location of the second electrode on atomic site 4, is shown. As it has the maximum transmission between these three substitutions, increasing the value of perturbation does not change the width of the peaks too much. As a result, moving further from the first electrode increases transmission and decreases the effect of perturbation.

The behavior of the electron with a scattering region (here, a benzene molecule) is like a potential barrier. The smallest barrier width is when the electrodes are connected in a symmetric position (para substitution). As the connection gets far from the symmetry, the barrier width increases and, therefore, reduces the probability of electron tunneling. As a result, full symmetric substitution results in maximum transmission. From the molecular orbitals point of view, when para substitution is used, the overlap of molecular orbitals is in better agreement with the atomic orbitals of electrodes.

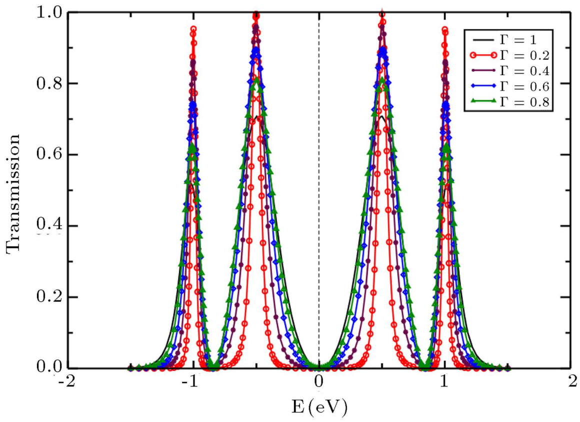

Figure 4. Transmission function, $T(E)$, for different perturbation values on para substitution. The red dashed-dot line is for $\Gamma = 0.2$, blue $\Gamma = 0.4$, black $\Gamma = 0.6$, green $\Gamma = 0.8$, and solid red line $\Gamma = 1$.

The effect of electron-electron interaction. In order to investigate the effect of electron-electron interaction, we have placed the molecule between two Au electrodes. The first principle calculation of electronic transport, based on Density Functional Theory (DFT) [19], has been used to calculate the transmission (or the conductance) of nano-junctions. In this approach, we are treating the junction as a many body problem with electron-electron interactions. Transport properties are calculated using Non-Equilibrium Green's Function (NEGF) [20]. Using this approach, which is implemented in the Smeagol (non-equilibrium electronic transport) package [21], we are not considering the approximations mentioned in the analytical approach. The results are depicted in Figure 5. In this figure, we have plotted the Projected Density Of States (PDOS) of the carbon atom, which is connected to the right (or left) lead, and the peaks of the PDOS are in agreement with the peaks of transmission. We have also revealed both broadening and shifting in the peaks of transmission, in comparison with Figure 4, which are the results of eliminating the approximations. Moreover, it should be noted that in Figure 4, four peaks are the results of two different pathways. However, in Figure 5, there is only one pathway and, therefore, the comparison is only between the positive sides of Figures 4 and 5. Adding electron-electron interaction changes our junction to a scattering region with many body interactions.

4. Conclusions

In this paper, we have studied the transmission of an electrode-benzene-electrode system. Different substitution of electrodes results in different transmissions. The greatest transmission is when the electrode is on para substitution, and, the interference of different pathways (A, B) results in new anti-resonances in the transmission plot. The effect of the connection to

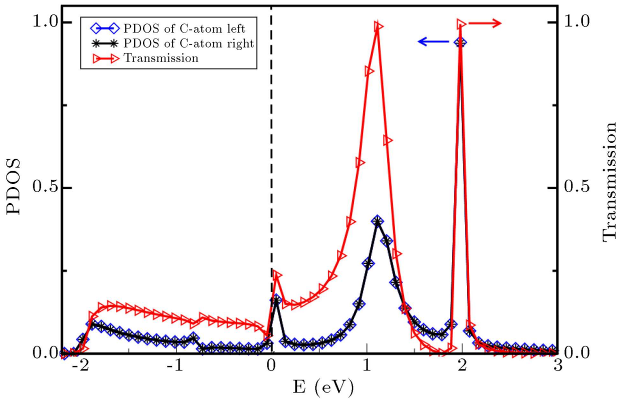

Figure 5. The effect of electron-electron interaction on the para substitution. The black and blue lines (that are on top of each other) are PDOS of right and left carbon atom connected to the electrodes, respectively. The red line is related transmission function.

the electrodes is an imaginary perturbation on the Hamiltonian of an isolated molecule. So, increasing this perturbation value broadens the peaks in the transmission plot until the time at which this perturbation value reaches the gap between HOMO and LUMO orbitals. As the perturbation value touches this energy gap, first order perturbation is invalid. We have also endeavored to indicate that whether electrode substitution with maximum transmission is less affected by increasing perturbation. Increasing perturbation has more influence on ortho substitution, which has less transmission.

Acknowledgment

The authors would like to thank Dr. Alan Evans (University of Kent, Canterbury, UK) for helping with the manuscript.

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