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The effect of different electrodes on the electronic transmission of benzene junctions: Analytical approach

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ABSTRACT

In this paper we have investigated the electronic transmission of systems electrode–benzene–electrode using the Landauer approach. The effect of different electrodes made of metal (Au) and semiconductors (Si, TiO_2) is investigated. These three electrodes are compared between them and the results show that the electronic transmission of benzene junctions, when using semiconductor electrodes, is associated to a gap in transmission which is due to the electrodes band gap. As a consequence, a threshold voltage is necessary to obtain conducting channels.

1. Introduction

Molecular junctions have attracted an immense interest, for its various potential applications, from the capability of miniaturizing electronic circuits to the adsorption of molecules on the surface of dye sensitized solar cells [1,2], and in the interaction of tip with the surface in scanning tunnel microscopy experiments [3].

In all these processes there is a charge transfer between a molecule and the bulk substrate. The mechanism governing this charge transfer can be treated in two general ways: computational approaches based on electronic structure, ab-initio studies [2,4–7], and analytical approaches [3,8,9]. By using ab-initio studies we do increase the complexity with the aim of more realistic results. Although the complexity of such approaches brings us closer to the experimental results, namely in what concerns the quantitative accuracy, we lose on the other hand the qualitative physical insight of the phenomena. This provides an appropriate motivation for applying the analytical description presented in this study. In this way, we establish a physical description of the charge transfer mechanisms far from the computational complexity.

Among organic molecules, benzene with non-localized π orbitals depicts interesting electronic properties [3]. Many theoretical and experimental studies on benzene molecule adsorbed to the surface of semiconductors like Si and TiO_2 and metals have been done [5,10–12]. Charge separation that takes place at the interface of dye molecules and titanium dioxide nanoparticles in dye sensitized solar cells [4,13] and electrochemical processes at the metal surface convinced us to use some models [3,14–16] for a better understanding of the physics behind fundamental applications.

In this study we first introduce the three different electrodes (Au, Si, TiO_2). The self-energy is specific of each electrode. The effect of the electrodes on the electronic transmission of benzene junction is then investigated and the transmission functions are evaluated and depicted. By starting from Au–benzene–Au system for a clear comparison, we then switch to the Si–benzene–Si system and finally TiO_2–benzene–TiO_2 junction.

2. Methods

The studied system is displayed in Fig. 1 with the electrodes in the para substitution which corresponds to the maximum conductance in the benzene molecule junction [8,10].

We first treat the isolated benzene molecule with tight binding Hamiltonian [3]:

$$H = \sum_{i=1}^{6} \alpha |i><i| + \sum_{i=1}^{6} \beta (|i><i+1| + |i+1><i|) \quad (1)$$

In this Hamiltonian i is the atomic site on benzene molecule, α is the onsite energy and β is the hopping energy to the nearest neighbor. The method consists to use equilibrium Green's function for zero bias. So Green's function for the isolated molecule according to the above Hamiltonian is [3]

$$G^{ret}(E) = (E - H + i\delta)^{-1} \quad (2)$$

where δ is a positive infinitesimal value for satisfying retarded Green's function.

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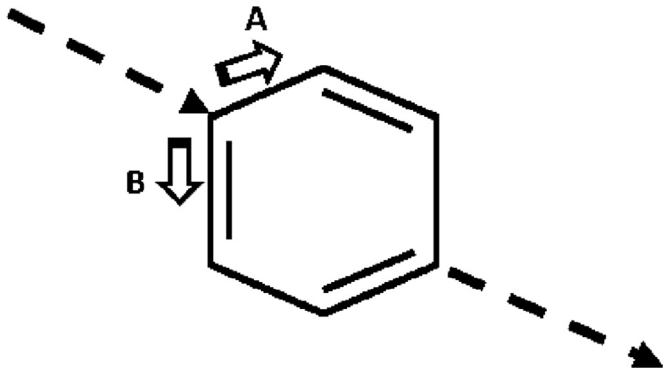

Fig. 1. Benzene junctions with different pathways (A,B) and maximum transmission substitution.

The effect of connecting the electrodes to the molecule is treated as a perturbation to the Hamiltonian of the isolated molecule. This part is called self-energy. For different electrode types we have different self-energies of the form [10]:

$$\Sigma(E) = \Lambda(E) - i/2\Gamma(E) \tag{3}$$

The self-energy is composed of two parts. It includes a real part and an imaginary part, called spectral density. The real part in the metal–molecule–metal just shifts the transmission peaks due to hybridization with the electrodes, while in the semiconductor–molecule–semiconductor it reveals interesting effects. The imaginary part causes the broadening of the transmission peaks in both cases. Starting from the self-energies, the transmission is calculated using the Landauer relation [3]:

$$T(E) = \mathrm{Tr}[\Gamma^{L}G^{ret}(E)\Gamma^{R}G^{adv}(E)] \tag{4}$$

$\Gamma^{L(R)}$ is the spectral density for the Left (Right) electrode respectively and $G^{adv}(E)$ is the advanced Green's function [18,19]. We first discuss the approach by calculating the electrodes self-energies. We put the molecule in the same electrodes, i.e. both electrodes are either metal or semiconductor simultaneously. Newns derived a simple analytical model for the self-energy of an interface between a molecule and a one-dimensional, tight binding metal electrode [14], according to the earlier work by Anderson [15]. Several perturbations of the Newns–Anderson metal model have been used for modeling semiconductors [16]. According to a model introduced by Koutecky [17] and Davison (KD) [6,17], which is used in this paper, each atom is considered as a unit cell, with two site states corresponding to s and p orbitals. The coupling between s and p orbitals in the same unit cell describes their overlap and the coupling across unit cells describes the inter-atomic bonding. The s–s and p–p overlap is neglected in the tight binding Hamiltonian. Assuming $2N$ atomic sites in the system, the Hamiltonian for this system is [10]

$$H_{KD} = \alpha\sum_{j=1}^{N}|\chi_{2j-1}><\chi_{2j-1}| - \alpha\sum_{j=1}^{N}|\chi_{2j}><\chi_{2j}| + \left[\beta_1\sum_{j=1}^{N}|\chi_{2j-1}><\chi_{2j}| + \beta_2\sum_{j=1}^{N-1}|\chi_{2j+1}><\chi_{2j}| + h.\,c.\right] \tag{5}$$

$|\chi_{>}$ is the atomic level, β_1, β_2 are the hopping energies due to the orbital hybridization (meaning that s and p orbitals become degenerate). The KD model has three important limits. First, $\alpha \to 0$ and $\beta 1 \to \beta 2 = \beta$ which results in Newns–Anderson model for metals. Second, $\beta 1 \to \beta 2 = \beta$ this alternating site (AS) model has been used to describe titanium dioxide electrode [10]:

$$H_{AS} = \alpha\sum_{j=1}^{N}|\chi_{2j-1}><\chi_{2j-1}| - \alpha\sum_{j=1}^{N}|\chi_{2j}><\chi_{2j}| + \left[\beta\sum_{j=1}^{2N-1}|\chi_{j}><\chi_{j+1}| + h.\,c.\right] \tag{6}$$

Finally, the limit $\alpha \to 0$ which is the limit of alternating bond (AB) model [10]

$$H_{AB} = \beta_1\sum_{j=1}^{N}|\chi_{2j-1}><\chi_{2j}| + \beta_2\sum_{j=1}^{N-1}|\chi_{2j+1}><\chi_{2j}| + h.\,c. \tag{7}$$

Using these three limits of Koutecky–Davison (KD) Hamiltonian through solving the Hamiltonian eigensystem, we can calculate spectral density [10].

The AB model is a simplification of Newns–Anderson model which is applied for the metal model (Au electrode) [10]. The introduction of alternating site energies has opened new avenues for using semiconductor models which yield to a band gap in the density of states of models [6,7,16]. In the Newns–Anderson model [15] which is used for the metal electrodes, the real part of self-energy is [10],

$$\Gamma_{NA}(E) = \gamma^2/\beta^2\sqrt{4\beta^2 - E^2} \tag{8}$$

and the spectral density is as follows [10]:

$$\frac{\Lambda_{NA}(E)}{\gamma^2} = \frac{E}{2\beta^2} + \Theta_{NA}(E)\frac{\sqrt{E^2-4\beta^2}}{2\beta^2} \tag{9}$$

where

$$\Theta_{NA}(E) = \Theta(-2|\beta| - E) - \Theta(E - 2|\beta|) \tag{10}$$

$\Theta_{NA}(E)$ specifies the sign choices. The result for the AS (Alternating Site) model is used for titanium dioxide electrodes with the real and imaginary parts of self-energy as:

$$\frac{\Gamma_{AS}(E)}{\gamma^2} = \frac{1}{\beta^2}\sqrt{\frac{(\alpha^2+4\beta^2-E^2)(E+\alpha)}{E-\alpha}} \tag{11}$$

For $|\alpha| < |E| \le \sqrt{\alpha^2+4\beta^2}$ and $\Gamma_{As}(E) = 0$ otherwise. And similarly [10]

$$\frac{\Lambda_{AS}(E)}{\gamma^2} = \frac{E^2-\alpha^2+\Theta_{AS}(E)\sqrt{(E^2-\alpha^2)(E^2-\alpha^2-4\beta^2)}}{2\beta^2(E-\alpha)} \tag{12}$$

with

$$\Theta_{AS}(E) = \Theta(\alpha^2 - E^2) - \Theta(E^2 - \alpha^2 - 4\beta^2) \tag{13}$$

In this calculations, $2|\alpha|$ is the band gap and $\sqrt{\alpha^2+4\beta^2} - |\alpha|$ is the valence (conductance) band width. The bulk band edges have extended to $\pm\alpha$ as in Koutecky [16] and the poles in $E{=}\alpha$ indicate the surface states.

In the AB (Alternating Bond) model, which is used for the Si electrode, the spectral density is [10]

$$\frac{\Gamma_{AB}(E)}{\gamma^2} = \frac{1}{\beta_2^2}\sqrt{\frac{[(\beta_1+\beta_2)^2-E^2][E^2-(\beta_1-\beta_2)^2]}{E^2}} \tag{14}$$

for $|\beta_1 - \beta_2| \le |E| \le |\beta_1 + \beta_2|$ and $\Gamma_{AB}(E) = 0$ otherwise, additionally [10]

$$\frac{\Lambda_{AB}(E)}{\gamma^2} = \frac{E^2-\beta_1^2+\beta_2^2+\Theta_{AB}(E)\sqrt{(E^2-(\beta_1+\beta_2)^2)(E^2-(\beta_1-\beta_2)^2)}}{2\beta_2^2E} \tag{15}$$

where

$$\Theta_{AB}(E) = \Theta((\beta_1-\beta_2)^2 - E^2) - \Theta(E^2 - (\beta_1+\beta_2)^2) \tag{16}$$