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Quantum transport through organic molecules

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Abstract

We investigate the electronic transport for the model of benzene-1, 4-dithiolate (BDT) molecule and some other geometric models of benzene molecule attached with two semi-infinite metallic electrodes by the use of Green's function technique. An analytic approach for the electronic transport through the molecular bridges is presented, based on the tight-binding model. Transport of electrons in such molecular bridges is strongly affected by the geometry of the molecules and their coupling strength with the electrodes. Conductance (g) shows resonance peaks associated with the molecular energy eigenstates. In the weak molecule-to-electrodes coupling limit current (I) passing through the molecules shows staircase-like behavior with sharp steps, while, it varies quite continuously in the limit of strong molecular coupling with the applied bias voltage (V). In presence of the transverse magnetic field conductance gives oscillatory behavior with flux ϕ, threaded by the molecular ring, showing $\phi_0 (= ch/e)$ flux-quantum periodicity. Though conductance changes with the application of transverse magnetic field, but the current–voltage characteristics remain same in presence of this magnetic field for these molecular bridge systems.

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Keywords: Green's function; Organic molecules; Conductance; I–V characteristic and magnetic field

1. Introduction

Molecular electronics is an essential technological concept of fast-growing interest since molecules constitute promising building blocks for future generation of electronic devices. Understanding of the fundamental processes of electron conduction through individual molecules is a most important requirement for the purposeful design of molecules for electronic functionalities. The electron transport through molecules was first studied theoretically in 1970 [1]. Since then several numerous experiments [2–4] have been performed through molecules placed between two electrodes with few nanometer separation. Transport properties in such small molecular systems cannot be studied by using the conventional procedure done in electronics [5] i.e., by solving the Boltzmann's equation. Full quantum mechanical treatment is required to characterize the transport through molecules. The operation of such two-terminal devices is due to an applied bias. Current passing across the junction is strongly nonlinear function of applied bias voltage and its detailed description is a very complex problem. The full knowledge of the conduction mechanism in this scale is not well understood yet, but the transport properties of these systems are associated with some quantum effects, like as quantization of energy levels and quantum interference effects [27] of electron waves. A quantitative understanding of the physical mechanisms underlying the operation of nanoscale devices remains a major challenge in nanoelectronics research. Here we focus onto the molecular transport that are currently the subject of substantial experimental, theoretical and technological interest. These molecular systems can act as gates, switches, or transport elements, providing new molecular functions that need to be well characterized and understood. In an experiment Reed et al. [6] have

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investigated the conductance and current–voltage characteristics of benzene-1, 4-dithiolate molecule in a two terminal geometry which is highly reproducible. This motivates us to calculate the electronic transport properties through benzene molecules attached with two semi-infinite metallic electrodes.

Here we describe theoretically the electronic transport properties for the model of benzene-1, 4-dithiolate (BDT) molecule and also for different other geometric models of benzene molecule, attached with two metallic electrodes, by the use of Green's function technique. An analytic approach for the electron transport through the molecular bridge systems is presented based on the tight-binding model. Transport through a molecule strongly depends on the geometry of the molecule, coupling strength between the molecule with two side attached electrodes. Based on the scanning probe technique measurement, conductance of such molecular systems is directly measured [7–12]. Theoretically there exist several formulations [25,26] for the calculation of conductance by using the Landauer formula and the seminal 1974 paper of Aviram and Ratner [1]. At very low temperatures and low bias voltages the electron transport becomes coherent through the molecule. Here we assume that the dissipation and equilibration processes occur only in the two contacting electrodes and this approximation enables to describe the propagation of an electron by means of single particle Green's function. This theory is much more flexible than any other theoretical approach and also applicable to any system described by a Hamiltonian with a localized orbital basis. By using this method the electronic transport of any system can be studied very easily with a few computational cost. In that case we have to know only the Hamiltonian matrix for the molecule but no need to know anything about the electronic wave function.

In this article we reproduce an analytic approach based on the tight-binding model to investigate the electronic transport properties for the molecules taken into consideration. There exist some *ab initio* methods for the calculation of conductance [13–18], but yet it is needed the simple parametric approaches [19–24] for this calculation. The parametric study is motivated by the fact that the *ab initio* theories are computationally too expensive and here we do attention on the qualitative effects rather than the quantitative ones. This is why we restrict our calculations only on the simple analytical formulation of the transport problem.

The plan of this paper is as follows. In Section 2, we describe the formulation of conductance g by calculating the transmission probability T and current I for any finite size conducting system attached with two semi-infinite metallic electrodes by the use of Green's function method. Section 3 describes conductance–energy and current–voltage characteristics for single benzene molecules with different geometries, while, in Section 4, we investigate the same for an array of benzene molecules. The effect of transverse magnetic field on electronic transport through a single benzene molecule is investigated in Section 5. Finally, we draw our conclusions in Section 6.

2. Formulation of g, T and I : Green's function method

Here we give a brief description for the calculation of transmission probability (T), conductance (g) and current (I) through a finite size conducting system attached with two semi-infinite electrodes by means of Green's function technique.

Let us first consider a one-dimensional conductor with N number of sites (array of filled circles) connected with two semi-infinite electrodes, the source and drain as shown in Fig. 1. The conducting system in between the two electrodes can be an array of few quantum dots, or a single molecule, or an array of few molecules etc. At the low voltage and low temperature limit the conductance of the conductor can be written by using the Landauer conductance formula

$$g = \frac{2e^2}{h} T \tag{1}$$

where g is the conductance and T is the transmission probability of an electron through the conductor. This transmission probability can be expressed in terms of the Green's function of the conductor and the coupling of the conductor with the two electrodes through the expression

$$T = \mathrm{Trace}\left[\Gamma_S G_c^r \Gamma_D G_c^a\right] \tag{2}$$

where G_c^r and G_c^a are respectively the retarded and advanced Green's function of the conductor. Γ_S and Γ_D are the coupling terms of the conductor due to the coupling with the source and drain, respectively. For the complete system i.e., the conductor with the two electrodes, the Green's function is defined as

$$G = (\epsilon - H)^{-1} \tag{3}$$

where $\epsilon = E + i\eta$. E is the injecting energy of the source electron and η is a very small number which can be put as zero in the limiting approximation. The above Green's function corresponds the inversion of an infinite matrix which consists of the finite conductor and two semi-infinite electrodes. It can be partitioned into different sub-matrices that correspond the individual sub-systems.

The Green's function for the conductor can be written as

$$G_c = (\epsilon - H_c - \Sigma_S - \Sigma_D)^{-1} \tag{4}$$

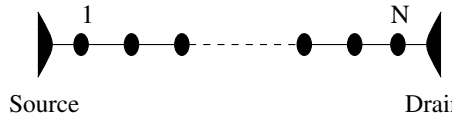

Fig. 1. Schematic view of a one-dimensional conductor with N number of sites (filled circles) attached with two electrodes. The first and the last sites are labeled by 1 and N respectively.