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Theoretical verification of experimentally obtained conformation-dependent electronic conductance in a biphenyl molecule

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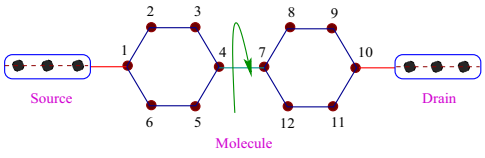
HIGHLIGHTS

- Conformation-conductance correlation is studied in a biphenyl molecule.
- A tight-binding framework is given to describe the molecular system.
- Two-terminal conductance is calculated using Green's function technique.
- Theoretical results are in good agreement with experimental observations.

GRAPHICAL ABSTRACT



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ABSTRACT

The experimentally obtained (Venkataraman et al. [1]) cosine squared relation of electronic conductance in a biphenyl molecule is verified theoretically within a tight-binding framework. Using Green's function formalism we numerically calculate two-terminal conductance as a function of relative twist angle among the molecular rings and find that the results are in good agreement with the experimental observation.

1. Introduction

In a glorious experiment Venkataraman et al. [1] have established that electronic conductance of a molecular wire does not depend only on the chemical properties of the molecule used, but also on its conformation. It has been examined that for the biphenyl molecule where two benzene rings are connected by a single C–C bond, electronic conductance varies significantly with the relative twist angle among these molecular rings. The conductance reaches a maximum for the planar conformation, while it gets reduced with increasing the twist angle and eventually drops to zero when the molecular rings are perpendicular to each other. The experimental results suggest a clear correlation between junction conductance and molecular conformation which predicts that the conductance of the biphenyl molecule decreases with increasing twist angle obeying a *cosine squared relation*.

In this present communication we essentially verify theoretically this conformation dependent molecular conductance and prove that our numerical results agree well with the experimental realization. A simple tight-binding (TB) Hamiltonian is given to describe the model quantum system and we numerically compute molecular conductance using Green's function approach based on the Landauer conductance formula [2]. Within a non-interacting electron picture this framework is well applicable for analyzing

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electron transport through a molecular bridge system, as illustrated by Aviram and Ratner [3] in their work where they have first described two-terminal electron transport through a molecule coupled to two metallic electrodes. Later several works [4–35] have been done to explore electron transfer through different bridging molecular structures. A full quantum mechanical approach is needed [36] to study electron transport in such molecular bridge systems where transport properties are characterized by several key factors like, quantization of energy levels, quantum interference of electronic waves associated with the geometry of bridging system adopts within the junctions and other several parameters of the Hamiltonian that are used to describe a complete system.

Here we use a simple parametric approach [37–42] rather than *ab initio* methods to describe conformation-dependent electron conductance in a biphenyl molecule. The physical picture about conformation-conductance correlation that emerges from our present study based on the single band TB model is exactly the same as obtained in the experiment [1] and provides a very good insight to the problem.

The structure of the paper is as follows. In Section 2, we describe the molecular model and theoretical formulation for the calculations. The essential results are analyzed in Section 3. Finally, in Section 4, we summarize our main results.

2. Molecular model and theoretical formulation

Let us refer to Fig. 1 where a biphenyl molecule is connected to two semi-infinite one-dimensional (1D) non-interacting electrodes, commonly known as source and drain. The single particle Hamiltonian for the entire system which describes the molecule and side-attached electrodes becomes

$$H = H_{\rm M} + H_{\rm ele} + H_{\rm tun}. \tag{1}$$

The first term $H_{\rm M}$ represents the Hamiltonian of the biphenyl molecule coupled to source and drain electrodes. Within a nearest-neighbor hopping approximation, the TB Hamiltonian of the molecule containing 12 ($N=12$) atomic sites gets the form,

$$\begin{aligned} H_{\rm M} = & \sum_i \epsilon c_i^\dagger c_i + \sum_i v[c_{i+1}^\dagger c_i + c_i^\dagger c_{i+1}] \\ & + \sum_j \epsilon c_j^\dagger c_j + \sum_j v[c_{j+1}^\dagger c_j + c_j^\dagger c_{j+1}] \\ & + v_{4,7}[c_4^\dagger c_7 + c_7^\dagger c_4] \end{aligned} \tag{2}$$

where the index i is used for the left ring and for the right ring we use the index j. ϵ represents the site energy of an electron at i-(j-)th site and v gives the nearest-neighbor coupling strength between the molecular sites. $c_i^\dagger(c_j^\dagger)$ and $c_i(c_j)$ are the creation and annihilation operators, respectively, of an electron at the i-(j-)th site. The last term in the right-hand side of Eq. (2) illustrates the coupling among the molecular rings and in terms of the relative twist angle θ between these two rings, the coupling strength $v_{4,7}$ is written as $v_{4,7} = v\cos\theta$.

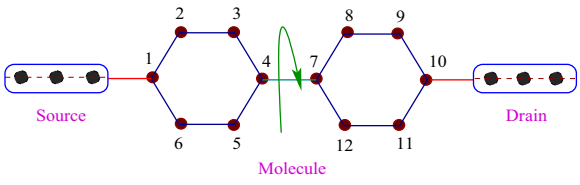

Fig. 1. A biphenyl molecule attached to source and drain electrodes. The relative twist among the molecular rings is described by the green arrow. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this paper.)

Similarly the second and third terms of Eq. (1) denote the TB Hamiltonians for the two semi-infinite 1D electrodes and their couplings to the molecule. They are expressed as follows.

$$\begin{aligned} H_{\rm ele} &= H_{\rm S} + H_{\rm D} \\ &= \sum_{\alpha={\rm S,D}} \left\{ \sum_n \epsilon_0 d_n^\dagger d_n + \sum_n t_0 [d_{n+1}^\dagger d_n + h.c.] \right\}, \end{aligned} \tag{3}$$

and,

$$\begin{aligned} H_{\rm tun} &= H_{\rm S,mol} + H_{\rm D,mol} \\ &= \tau_{\rm S}[c_p^\dagger d_0 + h.c.] + \tau_{\rm D}[c_q^\dagger d_{N+1} + h.c.]. \end{aligned} \tag{4}$$

The parameters ϵ_0 and t_0 correspond to the site energy and nearest-neighbor hopping integral in the source and drain electrodes. $d_n^\dagger$ and d_n are the creation and annihilation operators, respectively, of an electron at the site n of the electrodes. The hopping integral between the source and the molecule is $\tau_{\rm S}$, while it is $\tau_{\rm D}$ between the molecule and the drain. The source and drain are attached to the biphenyl molecule via the sites p and q, respectively, those are variable.

To calculate two-terminal conductance (g) we use the Landauer conductance formula $g = (2e^2/h)T$, where the transmission function $T = {\rm Tr}[\Gamma_{\rm S} G_{\rm M}^r \Gamma_{\rm D} G_{\rm M}^a]$ [36]. Here, $G_{\rm M}^r$ and $G_{\rm M}^a$ are the retarded and advanced Green's functions, respectively, of the molecule including the effects of the electrodes. $G_{\rm M} = (E - H_{\rm M} - \Sigma_{\rm S} - \Sigma_{\rm D})^{-1}$, where $\Sigma_{\rm S}$ and $\Sigma_{\rm D}$ are the self-energies due to coupling of the chain to the source and drain, respectively, while $\Gamma_{\rm S}$ and $\Gamma_{\rm D}$ are their imaginary parts.

3. Results and discussion

Throughout the analysis we choose the site energies in the molecule and side-attached electrodes to zero, $\epsilon = \epsilon_0 = 0$. The nearest-neighbor hopping integral in the electrodes (t_0) is set at 2 eV, while in the molecule (v) it is fixed at 1 eV. The hopping integrals of the molecule to the source and drain electrodes ($\tau_{\rm S}$ and $\tau_{\rm D}$) are also set at 1 eV. Here, we consider that the entire voltage drop takes place across the molecule–electrode interfaces and it is a very good approximation for smaller size molecules. We also restrict ourselves at absolute zero temperature and choose the units where $c = e = h = 1$. The energy scale is measured in unit of v.

Fig. 2 describes the variation of electronic conductance of the biphenyl molecule for a typical energy as a function of twist angle θ when the source and drain electrodes are attached to the molecular sites 1 and 10, respectively. The results are shown for two different energy values. In (a) we set $E = 0.25$ eV, while in (b) it is fixed at 1.65 eV. The red dotted curves in the spectra are generated from the numerical results and they are superimposed on the blue dotted curves those are plotted from the cosine squared relation $A\cos^2(\theta)$, where A is the conductance amplitude for the planar conformation of the molecule. We evaluate this amplitude A numerically. Very interestingly we notice that for $E = 0.25$ eV the red dotted curve sharply coincides with the blue one, and even for the other case i.e., when $E = 1.65$ eV the results are surprisingly close to each other. We also carry out extensive numerical work for other possible energies within the allowed energy band and find that the molecular conductance determined from the Landauer conductance formula agrees well with the cosine squared relationship. Thus we can emphasize that our numerical results can well fit the experimental data and provide a detailed information of the behavior of the molecular conductance on its conformation. Now the reduction of electronic conductance with the molecular twist can be clearly understood from the following interpretation. The degree of π-conjugation between the molecular rings decreases with the rise of twist angle θ which