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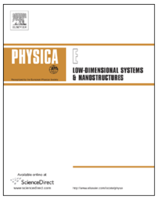

Model of electron tunneling coupled to torsional vibrations: Exact solution and study of performance of approximation methods

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HIGHLIGHTS

- A 2D model of the electron interaction with molecular vibrations is solved.
- Various transmission functions are calculated accurately numerically.
- The exact results are compared with various approximations.
- The validity of approximations is discussed.
- The excitation of the vibrational degree of freedom is detailed.

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ABSTRACT

A two dimensional model for the electron interaction with molecular vibrations in molecular junctions is proposed. Alternatively the model can be applied to tunneling through a cylindrical nano-structure. The transmission function is calculated accurately numerically. The exact results are then compared with various approximations: (1) completely frozen vibrations for very light molecule, (2) Chase approximation for very heavy molecule, and (3) discrete-state-in-continuum model in resonant regime. The validity of these approximations is discussed in terms of the characteristic time-scales and coupling strengths. The excitation of the vibrational degree of freedom and the emergence of prominent threshold structures in the strong coupling regime are discussed in more details.

1. Introduction

Molecular electronics is promising field of research that may lead not only to ultimate miniaturization of the electronic devices but also to complete change of paradigm in the chip production [1]. Prototypical device for study of the conductive properties of individual molecules is represented by molecular junction, which consists of two microscopic electrodes bridged by single molecule, covalently bonded to the electrodes. First such device has been constructed in late 90s [2]. Since then this field of research substantially advanced considering both the experimental techniques and theoretical methods to describe such devices (see for example [3,4] for recent reviews).

Calculation of the current conduction properties of a molecular junction represents a great challenge for the theory (see for example [5–7] for reviews). The theory is even more challenging when the vibrational degrees of freedom of the molecule are taken into account (see for example [8–13]).

One of the key difficulties is the many-particle nature of the current conduction in the junction due to the presence of Fermi sea of electrons. It is usually treated with the nonequilibrium-Green's function formalism considering the electron–vibrational coupling as a perturbation [8]. We take different point of view by considering the current conduction as a sequential scattering of individual electrons through the junction [14,15]. Although this approximation does not take into account the coupling of electrons within the Fermi sea correctly it allows us to concentrate on the difficulties due to the coupling of the electronic and the vibrational motion. In our model, we do not have to restrict neither to a small values of vibrational coupling nor to harmonic vibrations like in the most of the studies of molecular junctions.

This approximation also links the problem of theoretical description of the molecular junction to the theory of electron scattering from the molecules in gas phase [16,17].

There are number of approximations used to treat the problem of vibrations of the molecules in the molecular junction and their interaction with electronic degrees of freedom. First, in many calculations the vibrations are completely ignored. The authors just assume that the atoms in the molecule are sitting in their equilibrium positions and do not move. This may be good approximation if the

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electron-transport properties of the molecule are not much influenced by the position of the atoms. The simplest approximation including vibrations takes the positions of the atoms fixed on the first place, but then averages the transmission function of the junction over vibrational wave-functions of the molecules. In the context of electron-molecule scattering this approach is known as Chase or adiabatic-nuclei approximation [18,16]. The same approach is also used in the molecular electronics calculations (see for example [19]).

Another frequently used approach is based on the projection-operator formalism of Feshbach [20,16]. It assumes that the electron can only get through the junction through a localized state, which is usually called the discrete state. The electron dynamics is thus reduced to a model of the discrete state in continuum which is coupled to vibrational dynamics. This is very powerful approach in some cases [16], but it is rarely used in the full form, because it leads to nonlocal, energy-dependent effective term in the effective interaction. This nonlocal term is often replaced by local complex potential (LCP) [16,21], which is computationally much easier to handle. This approximation is usually called wide band limit in context of solid state physics.

In this paper we propose simple exactly solvable model for the transmission of an electron through a molecular junction, where it can interact with one vibrational degree of freedom. The model is introduced in the following paragraph. The method of exact solution of the dynamics and the formula for the transmission function are presented in Section 2. Section 3 is devoted to discussion of resulting transmission function. We stress the understanding of the physics behind the structures observed in the transmission functions and their description in various approximation methods mentioned above. Since we have exact solution in our model the present paper can serve as a benchmark for the performance of the approximation methods in various transport regimes. We conclude with Section 4 summarizing the results and suggesting further extension of the present approach in the future.

1.1. Description of the model

A simple model to mimic the behavior of an inelastic electron tunneling through a molecular junction is introduced here. The system we have in mind is schematically represented in Fig. 1. A molecule capable of the torsional vibrational motion is captured between two electrodes. We consider a motion of a single electron, which is freely moving inside the electrodes. It can also jump to the molecule through a potential barrier either from the left or from the right electrode. The strength of the barrier is assumed to depend on the orientation of the molecule in the junction. Such system is described with the model hamiltonian

$$H = -\frac{1}{2m_e}\frac{\partial^2}{\partial x^2} - \frac{1}{2I}\frac{\partial^2}{\partial \varphi^2} + \lambda_L(\varphi)\delta(x+a) + \lambda_R(\varphi)\delta(x-a), \qquad (1)$$

where the coordinate x describes the linear motion of the electron through the junction and the coordinate φ is the torsional angle for the molecule. The mass of the electron m_e and the offset of the barriers a can be eliminated by scaling of the coordinate x and the energy. We thus set $m_e = a = 1$. The coordinate $\varphi \in (0, 2\pi)$ cannot be scaled and the moment of inertia of the molecule I is an important parameter influencing the character of the behavior of the system.

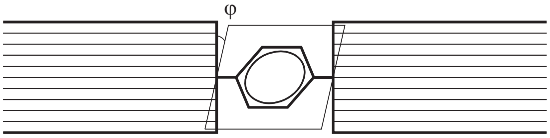

Fig. 1. A schematic representation of the molecular junction with a torsional vibrational mode.

The strength of the barrier between the molecule and the left/right electrode is $\lambda_L(\varphi)$ and $\lambda_R(\varphi)$ respectively. Its φ-dependence drives the coupling of the electronic and the vibrational motion.

To keep the model simple we assume that the φ-dependence is given by two lowest terms in the Fourier series expansion

$$\lambda_l = \alpha_l + \beta_l \cos(\varphi - \varphi_l), \qquad (2)$$

where $l = L, R$ and α_l, β_l, φ_l are real constants. The constant α thus controls the strength of the barrier, the ratio $v = \beta/\alpha$ the strength of the electron–vibration coupling and the difference $\varphi_0 = \varphi_R - \varphi_L$ the asymmetry of the junction (we can set $\varphi_L = 0$ without loss of generality). The assumption (2) is motivated by the behavior of the coupling in the molecules consisting of several benzyl rings. The cosine term results from the overlap of two π-orbital systems [22–25]. The suggested coupling functions λ_l correspond to the situation, where the part of the molecule undergoing the torsional motion is connected to the electrodes through additional benzyl rings.

There is an alternative interpretation of the model just described. The same model hamiltonian describes a motion of an electron on the surface of a cylinder with two barriers that break the axial symmetry. The coordinates x and φ parameterize the surface of the cylinder. The moment of inertia $I = m_e R^2$ depends on the radius R of the cylinder. The hamiltonian (1) can thus be understood as the description of the electron tunneling through a cylindrical nano-structure with double barrier. This alternative interpretation of the model is schematically represented in Fig. 2.

Before explaining the method of the solution of the electron scattering through the junction, we would like to discuss briefly the relevant parameter ranges. The parameter I gives the moment of inertia in units $m_e a^2$. In realistic molecular junctions we expect the values of the order of $10^3 - 10^4$. If the model is interpreted as an electron tunneling through the nano-structure (Fig. 2), the value of I can be tuned arbitrarily depending on the aspect ratio of the device. Another important parameters are the strength of the barriers α_l and the vibrational coupling strength $v = \beta/\alpha$. Since the nature of the bonding of a molecule to the electrodes can vary from strong covalent bond to very loose or no bonding (tunneling setup), these values can also be tuned quite freely to investigate different transport regimes.

2. Full numerical solution of the problem

The problem of the single electron transmission through the double barrier described by model hamiltonian (1) can be solved by applying the scattering boundary conditions to a corresponding stationary Schrodinger equation. We will rather employ the scattering theory formalism based on the splitting of the Hamiltonian (1) into the kinetic and the potential energy terms

$$H = H_0 + V,$$

$$H_0 = -\frac{1}{2}\frac{\partial^2}{\partial x^2} - \frac{1}{2I}\frac{\partial^2}{\partial \varphi^2},$$

$$V = \lambda_L(\varphi)\delta(x+1) + \lambda_R(\varphi)\delta(x-1).$$

The general stationary state for the hamiltonian H_0 can obviously be written as a linear combination of separable terms $|k\rangle|m\rangle$, where

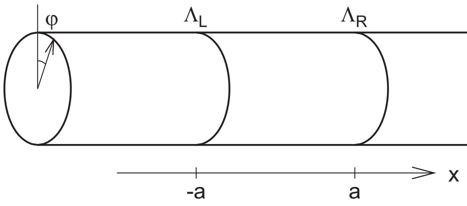

Fig. 2. Alternative interpretation of the model – electron motion on a surface of a cylinder with double barrier.