Model of Electron Tunneling through Molecular Junction: Numerically Exact Solution and Performance of Approximation Methods

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Abstract. We propose a model of the electron tunneling through a molecular junction, with torsional vibrational motion of the molecule coupled to the electron. The quantum dynamics for this two dimensional model is solved numerically by expansion of the wave-function in the Fourier series in the vibrational coordinate and the inversion of the system of equations resulting from the integral Lippmann-Schwinger equation. The fast convergence of this spectral method is observed and essentially exact solution is obtained. The resulting transmission functions are discussed in different regimes and the performance of some common approximation techniques (frozen vibrations, Chase (adiabatic) approximation, method of the local complex potential) is tested.

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INTRODUCTION OF THE MODEL

Contacting of the individual organic molecules with metal electrodes has been demonstrated experimentally in late 90's [1]. Since then the number of experimental techniques has been developed to achieve and study this setup called single molecule junction or just molecular junction [2]. This setup has great potential for various possible technological applications in electronics, precision measurement, sensors etc [3]. One of the interesting aspects of the molecular junctions is the possibility of the interactions of the current carrying electrons (or holes) with molecular vibrations [4, 5]. The theoretical description of phenomena related to such coupling is very difficult subject, since it involves non-equilibrium states of many electrons coupled nonadiabatically to the vibrations.

In this paper we suggest a simple model for the molecular junction, consisting of two conducting leads connected to a molecule with one active internal degree of freedom describing the torsional vibrations of part of the molecule (see Figure 1 for the schematic representation of the junction). Such molecules are know from both experimental and theoretical ab initio studies ([6] are references there). They are also envisioned to function as a molecular motor [7].

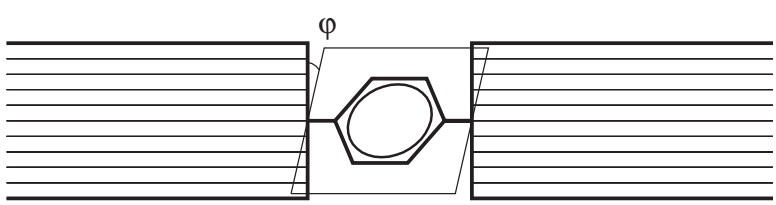

FIGURE 1. Schematic representation of the junction. The shaded areas represent the conduction leads. The leads are connected by molecule with a group capable of torsional vibrations.

The model hamiltonian that contains the key features of the dynamics of such junction can be written as

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

where x is the coordinate of the electron along the junction (with the middle of the molecule being at $x = 0$), φ is the torsional angle, i. e. the vibrational coordinate, m_e is the effective mass of the electron in the leads, I is the moment of

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inertia of the molecule. First two terms thus describe the kinetic energy of the electron and the torsional vibrations. The last two term give the barriers that the electron must overcome to jump on the molecule. They are idealized by delta function terms placed in $x = \pm a$. We can set $a = 1$ and $m_e = 1$ without loss of generality, just by choice of the units of the length and the energy. The size of the barrier depends on the torsional angle. This dependence is responsible for the coupling of the vibrational and electronic motion in our model. Both the experimental and the ab initio studies of the realistic molecular junctions [6] show that a reasonable assumption for the shape of this dependence is

$$\lambda_l = \alpha_l + \beta_l \cos(\varphi - \varphi_l), \tag{2}$$

where α_l, β_l and φ_l are model parameters of the $l = L, R$ (left and right) barriers.

While this model gives rather simplified picture of the molecular junction, it is capable to describe the key features of the coupled electron-vibrational dynamics and unlike more realistic many-body description it allows numerically exact solution (see the next section). We can thus study the dynamics of the junction described by this model very precisely and then we will investigate the performance of some approximations which are frequently used in more realistic calculations.

FULL NUMERICAL SOLUTION OF THE PROBLEM

The goal of this section is to calculate the transmission probability for the electron coming with the energy E from the left lead through the junction to the right lead. The torsional vibrations of the junction can be excited during the transmission, which we have to take into account. This problem can be formulated in standard way using the multichannel scattering theory. The wave function $\psi(x, \varphi)$ of the stationary scattering state can be obtained by solving the two dimensional Schrodinger equation with the appropriate boundary conditions or from the unique solution of the integral Lippmann-Schwinger equation. Here we follow the later alternative, i. e. we solve

$$|\psi\rangle = |k\rangle|m_i\rangle + G_0(E)V|\psi\rangle, \tag{3}$$

where $G_0(E) = (E + i\varepsilon - H_0)^{-1}$ is the Green operator for the hamiltonian H_0 consisting of the first two terms in (1) and V is the interaction, i. e. the last two terms in (1). The inhomogeneous term $|k\rangle|m_i\rangle$ describes the incoming electron (plane wave) with energy $k^2/2$ and the initial state of the junction with the angular momentum m_i. The total energy of this state is $E = k^2/2 + m_i^2/2I$. Thanks to the structure of the interaction term V, the whole wave function is known if we know its values at $x = \pm a$. We expand these values in the Fourier series in φ. The integral equation (3) thus reduces to system of linear equations for the Fourier coefficients. Solving this system we obtain the wave function. The transmission probability T is then calculated using standard expressions of scattering theory (i.e. from the corresponding elements of the T-matrix). Similarly we can also calculate the probability for the reflection of the electron back to the left lead.

The only approximation in the above method for the calculation of the transmission function $T(E)$ is the termination of the infinite Fourier series to finite number of terms. We have studied the convergence of this procedure (the details will be shown in the full paper). For the typical model parameters used later in this paper we achieve the precision of at least 10 decimal digits with typically 50 terms of the Fourier series. The fast convergence of this spectral method for the solution of the integral equation (1) was expected since the method is based on the expansion of the smooth functions $\psi(\pm a, \varphi)$.

APPROXIMATION METHODS

The full numerical solution presented above has limited applicability. The numerical method of solution is designed specifically to the present model. The extension for more complicated systems is not possible. It also provides little insight into the dynamics itself. It is therefore important to introduce some approximation methods. The advantage of the present approach is that we can both get insight from these methods and we can also test their performance against the exact solution at the same time. The approximations are introduced in the following sections.

Fixed Vibrational Coordinate

The most simple approximation is to ignore the vibrations at all. The kinetic energy term in the hamiltonian (1) is thus ignored and the functions $\lambda_l(\varphi)$ are replaced by their angularly averaged values $\overline{\lambda}_l$. The transmission function can then be obtained easily in closed form

$$P_T = \left| \frac{k^2}{\overline{\lambda}_L \overline{\lambda}_R e^{4ik} - (\overline{\lambda}_L - ik)(\overline{\lambda}_R - ik)} \right|^2 . \tag{4}$$

We expect that this result will approximate the full transmission function well if the function $\lambda_l(\varphi)$ is close to its average value $\overline{\lambda}_l$, i. e. if it is approximately constant. The validity of this assumption is characterized by the size of the ratio $v = \beta/\alpha$. In Figure 2 (left), we show the 1D transmission (4) together with the full transmission function for several values of v. We observe that for small value of $v = 0.2$ the full transmission follows closely the 1D model. The agreement gets worse for the larger values of v.

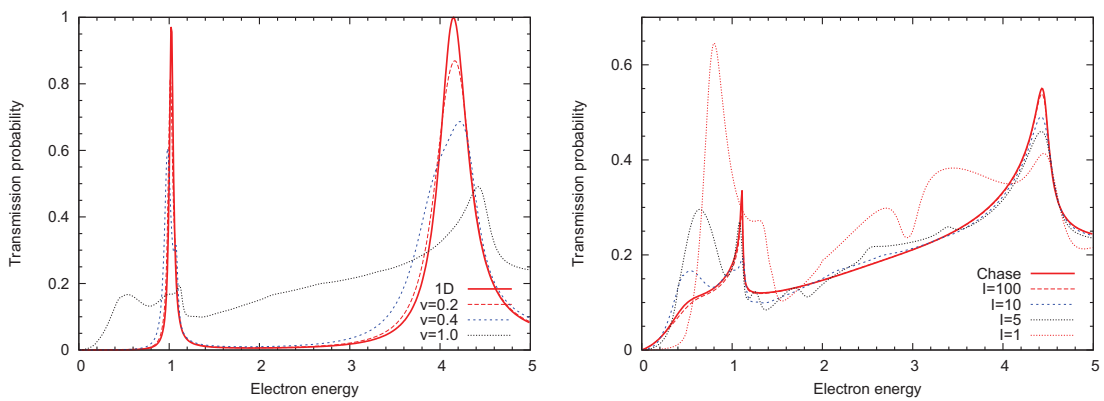

FIGURE 2. Performance of 1D (left) and Chase (right) approximation for the transmission function.

Chase Approximation

The next step in understanding the transmission data is to include the angular dependence of $\lambda_l(\varphi)$ into 1D model approximately. This can be done by taking the angle φ fixed and using 1D model for each angle separately. The resulting transmission is than obtained by averaging the individual probabilities over all angles. This approximation has been suggested for the description of the vibrational excitation of the molecules by Chase [8] and it can also be used in molecular electronics. More detailed analysis shows that its validity is based on the separation of the time scales for the electronic and vibrational motion. The general wisdom says that the slower the vibrational motion is the better this approximation works. We show this in Figure 2 (right). The speed of vibrations is controlled by the moment of inertia I. For heavy molecule $I = 100$ the approximation is almost perfect, but it gets worse with smaller I. Notice also that, in general, the Chase approximation works better for broader resonance at $E \simeq 4.4$. This is related to the above mentioned separation of the time scales. For narrower resonance the electron spends more time in the interaction region and the molecule has to be heavier if the vibrations are to be slower that this electronic motion.

Approximation of the Local Complex Potential and Beyond

The Chase approximation thus breaks for very narrow resonances, even for heavy molecules. This is demonstrated in Figure 3. The transmission function from the full calculation (full line) has a peak shape, with a shoulder related to the vibrational levels of the junction. The Chase approximation (dotted line) works well outside the resonance peak, but it is more that factor of 2 wrong at the resonance peak. This deficiency can be cured using the local complex

potential (LCP) approximation (see [9] and references therein) to describe the vibrational dynamics due to resonance coupling of the electronic and vibrational degrees of freedom. We will explain this approximation in more details. The resulting transmission function (dashed line) gives correct shape of the resonance peak, including the shoulder structure. It can also be used to describe the heating of the junction.

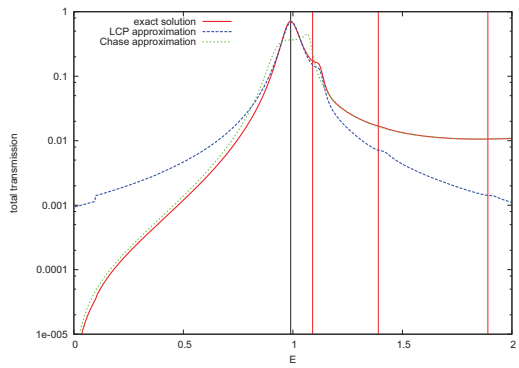

FIGURE 3. Chase and LCP approximations for narrow resonance. Transmission function is now plotted in logarithmic scale.

CONCLUSIONS

The proposed model of the molecular junction has been solved numerically by expansion of the wave function in the Fourier basis, substitution of the expansion into integral Lippmann-Schwinger equation and solution of the resulting system of equations. The resulting transmission functions were analyzed in different regimes. In the case of weak vibrational coupling the transmission function exhibits resonance peaks typical for resonant tunneling. The shape of the function can be understood using the 1D model and the Chase approximation, providing that the tunneling does not involve resonances with lifetime larger than typical vibrational times. The difficult case of the strong vibrational coupling and the large resonance lifetime can be treated to some degree using the local-complex potential approximation.

In the full paper we will also discuss the possibility to go beyond the local-complex-potential approximation with the tools of the nonlocal resonance theory [9]. We will also discuss in more detail other quantities of interest for the tunneling through the junction like the average heating of the junction after the tunneling and the possibility to control the unidirectional rotation of the molecule by controlling the current [7].

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