Charge transport through a flexible molecular junction*)

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Vibrationally inelastic electron transport through a flexible molecular junction is investigated. The study is based on a mechanistic model for a biphenyl molecule between two metal electrodes. Employing methods from electron-molecule scattering theory, which allow a numerically exact treatment, we study the effect of vibrational excitation on the transmission probability for different parameter regimes. The current-voltage characteristic is analyzed for different temperatures, based on a Landauer-type formula. Furthermore, the process of electron assisted tunneling between adjacent wells in the torsional potential of the molecule is discussed and the validity of approximate methods to describe the transmission probability is investigated.

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1 Introduction

The field of molecular electronics, which may represent the ultimate limit of the miniaturization of electronic devices, has received much interest in the last decade (see for example [1, 2] and references therein). Although the basic idea to use molecules as active elements in electronic circuits is not new [3], only recently it became possible to study the conduction of single molecules experimentally ([4, 5, 6, 7]). In contrast to metal or semiconductor devices, in molecular electronics the complex structure of a single molecule may be utilized to obtain the functionality of the device. For example, switching behavior and negative differential conductivity [8, 9] have recently been demonstrated experimentally and are believed to be a consequence of geometry changes in the conducting molecule.

The tremendous experimental progress has stimulated great interest in the theory and *ab initio* modeling of charge transport through single molecules (see for example [1, 2] and references therein). In particular, non-equilibrium Green's function methods in combination with state-of-the art electronic structure calculations have been employed to study the conductivity of metal-molecule-metal junctions with fixed nuclear geometry. The dependence of the conductive properties on the binding geometry of the molecular bridge has also been investigated [10, 11].

*) This paper is dedicated to Jiří Horáček our friend and scientific mentor of one of us (MČ) on the occasion of his sixtieth birthday

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The role of the vibrational degrees of freedom of the molecular bridge in the conduction process and and their effect on the functionality of the device are less well understood. The "static" influence of the internal vibrational modes has been studied by averaging the elastic transmittance over the probability distribution of the vibrational degrees of freedom [12, 13, 14]. The dynamical impact of the vibrational degrees of freedom on the tunneling current in molecular junctions has been investigated within, e.g., nearest neighbor tight-binding models [15, 16, 17, 18, 19]. These studies have demonstrated that the vibrational motion of the molecular bridge may result in additional (vibrational) resonance structures in the transmission probability which can alter the current-voltage characteristic significantly. Dynamical effects of nuclear motion on the conductivity have also been observed experimentally. For example, in experiments on electron transport through H_2 molecules between two platinum electrodes [6] as well as C_{60} molecules connected to gold electrodes [20], indications for an influence of the center-of-mass motion of the respective molecule on the conductivity have been found. Moreover, the excitation of the vibrational degrees of freedom of the molecule provides a mechanism for heating of the molecular junction and thus is a possible source of instability [21, 22].

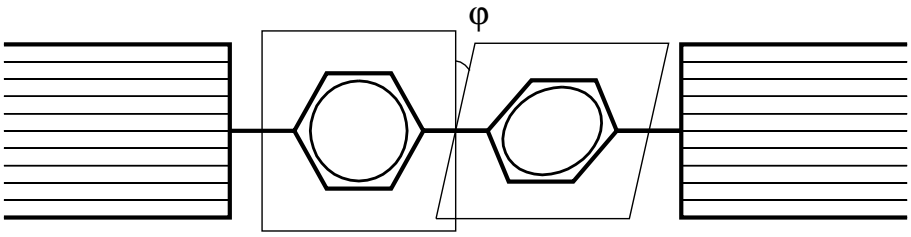

Fig. 1. Schematic illustration of the molecular junction studied.

Recently, we have demonstrated [23] that methods developed in the field of resonant electron-molecule scattering [24] can be advantageously applied to study vibrationally inelastic effects on electron transport. In this study, the vibrational degrees of freedom of the molecular bridge were described within the harmonic approximation. As an extension of this work, we investigate in this paper the influence of large-amplitude motion of a flexible molecular bridge on charge transport through a molecular junction. Specifically, we consider a mechanistic model for electron conduction through a biphenyl molecule, schematically shown in Fig. 1. In biphenyl and similar molecules (such as bypiridine [25] or biphenyl dithiol [26]), the torsion of the two benzene rings is expected to have a strong effect on the conductivity. Ratner, Datta and coworkers have considered this effect for a static nuclear bridge [27] as well as in the adiabatic approximation [14]. *Ab initio* calculations of equilibrium geometries of neutral molecules and anions for several related molecules [8] also indicate that the torsional motion is presumably rather strongly coupled

to the tunneling electron. Dynamical effect of vibrations beyond the harmonic approximation have been studied for similar systems based on molecular dynamics simulations [28], where the nuclear motion was treated classically and the electronic structure was described by a density-functional tight-binding Hamiltonian. The purpose of this paper is to study the dynamical effect of the torsional motion on the transport through the bridge within a fully quantum mechanical treatment.

This paper is organized as follows: In section 2.1 we introduce a generic model Hamiltonian to describe charge transport through a flexible molecular junction schematically shown in Fig. 1. The torsional angle between the two benzene rings is thereby treated as a dynamical variable. The model parameters are chosen in accordance with available *ab initio* data for the biphenyl molecule. The methods employed to calculate the inelastic transmission probability and the current for this model are presented in section 2.2. In section 3 we discuss the results of the model study for different parameter regimes and analyze the performance of approximate methods, in particular the purely elastic calculation of the transmission probability and the adiabatic-nuclei approximation.

2 Theory

2.1 Model

We describe charge transport through the molecular junction schematically depicted in Fig. 1 in the single particle approximation as the subsequent transmission of single electrons from a state $|\phi_k\rangle$, $k \in \mathrm{L}$, in the conduction band of the left lead into state $|\phi_k\rangle$, $k \in \mathrm{R}$ in the right lead. We assume that the conduction electron can cross the junction only through a π-orbital $|\phi_1\rangle$ associated with the benzene ring which is coupled directly to the left lead and through a π-orbital $|\phi_2\rangle$ associated with the second benzene ring that is coupled to the right lead. The torsional angle φ of the two benzene rings is explicitly taken into account as a dynamical variable, since it modulates the overlap of the π-orbitals of the benzene rings and this will have an important effect on the conductivity of the molecular junction. The influence of the other vibrational modes is neglected in the present study. The Hamiltonian of the model thus reads

$$\begin{aligned} H &= T_\varphi + V_0(\varphi) \\ &\quad + |\phi_1\rangle\epsilon_1\langle\phi_1| + |\phi_2\rangle\epsilon_2\langle\phi_2| + |\phi_1\rangle\beta(\varphi)\langle\phi_2| + |\phi_2\rangle\beta(\varphi)^*\langle\phi_1| \\ &\quad + \sum_{k\in L,R}\left\{|\phi_k\rangle\epsilon_k\langle\phi_k| + \sum_{j=1,2}\left[|\phi_j\rangle V_k^j\langle\phi_k| + |\phi_k\rangle V_k^{j*}\langle\phi_j|\right]\right\} \end{aligned} \tag{1}$$

The first line of Eq. (1) describes the torsional dynamics of the two benzene rings in the absence of an excess electron, the second line describes the electronic resonance states corresponding to the situation when the excess electron is located on the molecular bridge, and the last line represents the free electrons in the leads and the coupling between the leads and the two $\pi-$orbitals. The kinetic energy operator

for the torsional motion is given by

$$T_\varphi = -\frac{1}{2I}\frac{\mathrm{d}^2}{\mathrm{d}\varphi^2}, \tag{2}$$

where $I = \frac{1}{2}Md^2$ is the moment of inertia, M denotes the mass of the carbon atom and d is the diameter of the benzene ring. The potential energy $V_0(\varphi)$ for the torsional motion of the isolated biphenyl molecule can be calculated by standard methods of quantum chemistry. In this study, we approximate the potential in form of a three-term Fourier series

$$V_0(\varphi) = C_0 + \sum_{i=2,4,6} \tfrac{C_i}{2}[1 - \cos(i\varphi)], \tag{3}$$

where the parameters C_i have been adopted from Ref. [29]. We furthermore consider a symmetric molecular junction with $\epsilon_1 = \epsilon_2 \equiv \epsilon_0$, $V_{k\in\mathrm{L}}^{j=1} = V_{k\in\mathrm{R}}^{j=2} \equiv V_k$ and $V_{k\in\mathrm{L}}^{j=2} = V_{k\in\mathrm{R}}^{j=1} = 0$. The electronic coupling between the two rings is assumed to be of the form

$$\beta(\varphi) = \beta_0 \cos(\varphi). \tag{4}$$

The parameters ϵ_0 and β_0 can in principle be determined from electronic-structure calculations of the potential-energy surface of the molecular anion. The vertical and adiabatic electron affinities of biphenyl have been calculated, e.g., in Ref. [30] yielding slightly different result for different levels of electron structure theory. Since the molecular electronic structure is modified by the coupling of the biphenyl to the leads, we cannot directly adopt these data, but they can guide us to select the parameters in a reasonable range of values. Within our model, the adiabatic potential-energy curves of the molecular anion can be obtained by diagonalization of the first two lines of the Hamiltonian (1) for fixed nuclear geometry (i.e. $T_\varphi \approx 0$). This way, we obtain two potential energy curves

$$V_\mathrm{d}^{(\pm)}(\varphi) = V_0(\varphi) + \epsilon_0 \pm |\beta_0 \cos(\varphi)|, \tag{5}$$

corresponding to the ground and excited electronic state of the molecular anion, respectively. To determine the parameters ϵ_0 and β_0, we impose the following requirements as motivated by the results of the electronic structure calculations [30] mentioned above: We require the equilibrium geometry of the anion to be planar, i.e. $\varphi = 0$, with a small, but positive, adiabatic electron affinity and, furthermore, assume a negative vertical electron affinity of the order of -0.1eV at the equilibrium geometry of the neutral molecule ($\varphi_0 = 42°$). These requirements are fulfilled for $\epsilon_0 = 0.9$eV and $\beta_0 = 1$eV. The corresponding potential-energy functions $V_0(\varphi)$ (full line) and $V_\mathrm{d}^{(-)}(\varphi)$ (dashed line) are shown in Fig. 2. The upper of the two adiabatic molecular-anion potentials, $V_\mathrm{d}^{(+)}(\varphi)$, which exhibits an avoided crossing with $V_\mathrm{d}^{(-)}(\varphi)$, is too high in energy to be seen in Fig. 2.

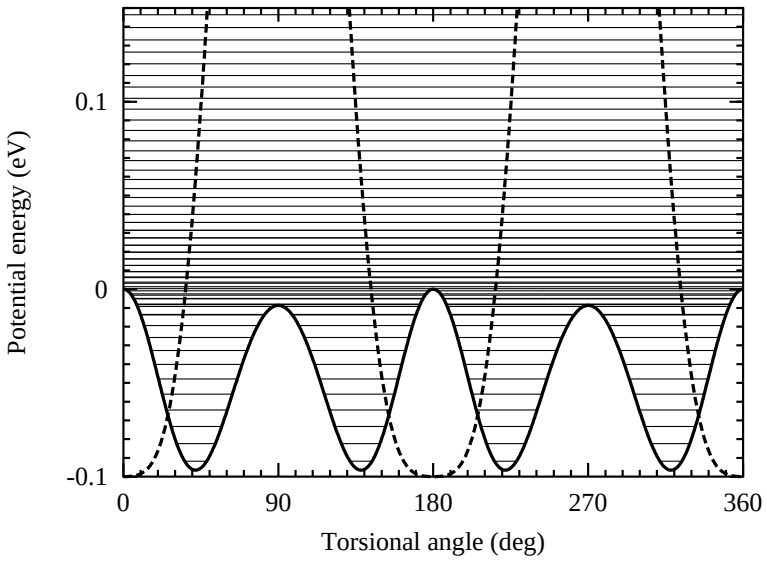

Fig. 2. Potential-energy curves for the model (for details see text). The energy levels of the hindered torsional motion of the neutral molecule are also shown as horizontal lines. Note that the states with energies well below and well above zero are nearly degenerate (four-fold degenerate below and two-fold degenerate above zero energy, respectively).

As is well known (see for example Ref. [31]), the effect of the electronic coupling to the leads is fully described by specifying the self-energy functions

$$\Sigma_{ij}(\epsilon) \equiv \sum_k \langle \phi_i | H | \phi_k \rangle \frac{1}{\epsilon^+ - \epsilon_k} \langle \phi_k | H | \phi_j \rangle = \delta_{ij} \Sigma_j(\epsilon). \tag{6}$$

The presence of the factor δ_{ij} is a consequence of the fact that we neglect the direct coupling of the right benzene ring to the left lead and the coupling of the left ring to the right lead. As in our previous work [23], we assume that the self-energies are proportional to the Hubbard Green's function [32]

$$\Sigma_j(z) = \frac{2\alpha^2}{z - \mu_j + \sqrt{(z-\mu_j)^2 - 4\beta^2}}, \tag{7}$$

which is the exact self-energy for a one dimensional semi-infinite atomic chain with nearest-neighbor tight-binding interaction. Within this model, the energy of an electron in state $|\phi_k\rangle$ in lead j reads

$$\epsilon_k = \mu_j + 2\beta \cos k. \tag{8}$$

The nearest-neighbor coupling parameter β determines the width of the conduction band, which is 4β, and α is the coupling strength between the last atomic site of the

lead and the π-orbital $|\phi_j\rangle$ of the adjacent benzene ring. For simplicity we assume this coupling to be the same for both leads and independent of the angle φ. The chemical potential μ_j is different for both leads, the difference $eV = \mu_{\rm L} - \mu_{\rm R}$ being the bias voltage across the junction. By analytic continuation we obtain the real and imaginary parts of the self-energy $\Sigma_j = \Delta_j - \frac{i}{2}\Gamma_j$ on the real energy axis. The imaginary part (which is sometimes also called 'energy-dependent decay width of the resonance state') is given by

$$\Gamma_j(\epsilon) = \frac{\alpha^2}{\beta^2}\sqrt{4\beta^2 - (\epsilon - \mu_j)^2} \tag{9}$$

inside the conduction band ($|\epsilon - \mu_j| < 2\beta$) and $\Gamma_j = 0$ otherwise. In our model studies we use a value $\beta = 1$eV, which corresponds to a conduction-band width of 4 eV. The strength α of the coupling between the molecule and the leads is varied as described below.

2.2 Calculation of transmission probability and current

Employing scattering theory, the transmission probability for scattering of a conduction electron from the initial state $|\phi_{k_{\rm i}}\rangle$ in the left lead to the final state $|\phi_{k_{\rm f}}\rangle$ in the right lead, accompanied by a vibrational transition of the molecule from initial state $|\chi_{v_{\rm i}}\rangle$ to final state $|\chi_{v_{\rm f}}\rangle$ is given by

$$t_{\rm L\to R}(\epsilon_{\rm i}, v_{\rm i}, \epsilon_{\rm f}, v_{\rm f}) = \delta(E_{v_{\rm f}} + \epsilon_{\rm f} - E_{v_{\rm i}} - \epsilon_{\rm i})\Gamma_1(\epsilon_{\rm i})\Gamma_2(\epsilon_{\rm f})\left|\langle\chi_{v_{\rm f}}|[E - H_d - F(E)]^{-1}_{21}|\chi_{v_{\rm i}}\rangle\right|^2. \tag{10}$$

Thereby, the Dirac delta function accounts for energy conservation

$$E \equiv E_{v_{\rm i}} + \epsilon_{\rm i} = E_{v_{\rm f}} + \epsilon_{\rm f}, \tag{11}$$

with $\epsilon_{\rm i}$ ($\epsilon_{\rm f}$) and $E_{v_{\rm i}}$ ($E_{v_{\rm f}}$) being the initial (final) electron and vibrational energies, respectively. H_d is a 2×2 matrix in the electronic basis $\{|\phi_1\rangle, |\phi_2\rangle\}$ given by

$$H_d = \begin{pmatrix} T_\varphi + V_0(\varphi) + \epsilon_0 & \beta(\varphi) \\ \beta(\varphi) & T_\varphi + V_0(\varphi) + \epsilon_0 \end{pmatrix}, \tag{12}$$

where each matrix element is a vibrational operator. Similarly, $F(E)$ is a diagonal 2×2 matrix with matrix elements

$$F_j(E) \equiv \Sigma_j(E - T_\varphi - V_0(\varphi)) = \sum_v |\chi_v\rangle\Sigma_j(E - E_v)\langle\chi_v|. \tag{13}$$

Since the operator $T_\varphi + V_0(\varphi)$ does not commute with $\beta(\varphi)$, the transmission probability cannot be obtained in a closed analytical formula. However, the expression (10) can rather easily be evaluated numerically adopting, for example, the free-rotor basis for the theoretical treatment of the torsional motion of the bridge.

Based on the transmission probability (10), the current through the molecular bridge is calculated employing the generalized Landauer formula [14]

$$I = \frac{1}{\pi}\sum_{v_\mathrm{i},v_\mathrm{f}} p_{v_\mathrm{i}} \int \mathrm{d}\epsilon_\mathrm{i} \int \mathrm{d}\epsilon_\mathrm{f} \left\{ f_L(\epsilon_\mathrm{i})[1-f_R(\epsilon_\mathrm{f})] t_{\mathrm{L}\to\mathrm{R}}(\epsilon_\mathrm{i}, v_\mathrm{i}, \epsilon_\mathrm{f}, v_\mathrm{f}) - f_R(\epsilon_\mathrm{i})[1-f_L(\epsilon_\mathrm{f})] t_{\mathrm{R}\to\mathrm{L}}(\epsilon_\mathrm{i}, v_\mathrm{i}, \epsilon_\mathrm{f}, v_\mathrm{f}) \right\}. \quad (14)$$

Here,

$$p_{v_\mathrm{i}} = \exp(-E_{v_\mathrm{i}}/kT)/Z \quad (15)$$

denotes the Maxwell-Boltzmann distribution of the initial vibrational states for a given temperature T and

$$f_j(E) = \frac{1}{1+\exp[(E-\mu_j)/kT]} \quad (16)$$

is the Fermi-Dirac distribution for the conduction-electrons in the leads. The bias voltage enters the formula through the chemical potentials $\mu_\mathrm{L} = eV/2$ and $\mu_\mathrm{R} = -eV/2$ for the left and right leads, respectively, and is thus also present in the transmission function through the dependence of $\Gamma_j(\epsilon)$ on the chemical potentials μ_j.

3 Results and discussion

3.1 Transmission probability

The transmission probabilities $t_{\mathrm{L}\to\mathrm{R}}(\epsilon_\mathrm{i}, v_\mathrm{i}, \epsilon_\mathrm{f}, v_\mathrm{f})$ for zero bias have been calculated according to formula (10) employing a free rotor basis with typically 200 basis functions. To illustrate the results, we average $t_{\mathrm{L}\to\mathrm{R}}$ over the lowest four vibrational energy levels $v_\mathrm{i} = 0, 1, 2, 3$ (which are nearly degenerate due to the symmetry of the torsional potential), sum over all final states v_f and integrate over the final energy of the electron ϵ_f. The resulting transmission probability is shown for three values of the coupling strength ($\alpha = 0.05$ eV, 0.1 eV and 0.2 eV) in figure 3. It is seen that the transmission is essentially nonzero only in the region where the molecular resonance is located. The process can thus be understood as resonant tunneling of the electron from the left lead to the right lead through the eigenstates of H_d. These states coincide (in the relevant energy region) with the torsional eigenstates in the potential $V_\mathrm{d}^{(-)}(\varphi)$ (shown as dashed line in Fig. 2). In the transmission probability, the individual states are resolved only for the smallest value of the coupling $\alpha = 0.05$ eV. For larger values of α, the individual peaks are wiped out due to the stronger coupling with the leads.

It is also interesting to compare the full transmission probability with the elastic one, calculated for frozen vibrations

$$t^{(\mathrm{el})}_{\mathrm{L}\to\mathrm{R}}(\epsilon_\mathrm{i}, \epsilon_\mathrm{f}, \varphi) = \delta(\epsilon_\mathrm{f}-\epsilon_\mathrm{i})\Gamma_1(\epsilon_\mathrm{i})\Gamma_2(\epsilon_\mathrm{f}) \frac{\beta(\varphi)^2}{\left\{[\epsilon_\mathrm{i}-\epsilon_0-\Sigma_1(\epsilon_\mathrm{i})][\epsilon_\mathrm{f}-\epsilon_0-\Sigma_2(\epsilon_\mathrm{f})] - \beta(\varphi)^2\right\}^2}. \quad (17)$$

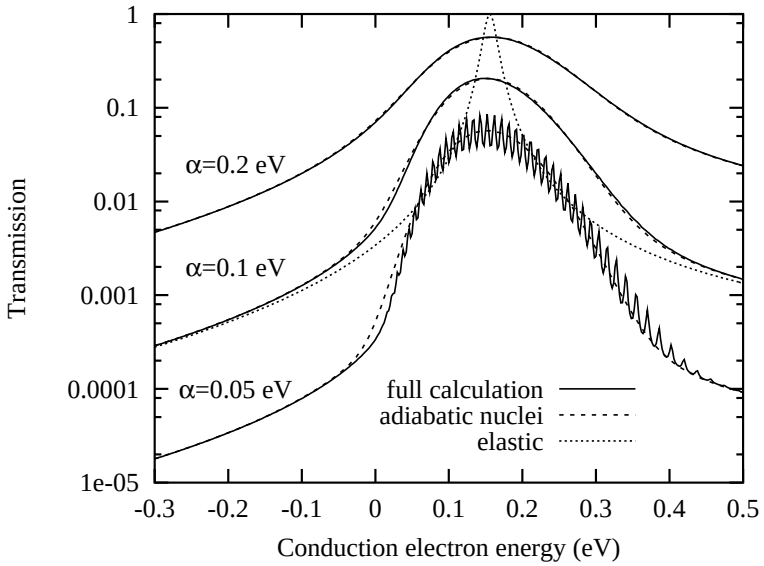

Fig. 3. Energy dependence of the averaged transmission probability (see text) for three coupling strengths α and temperature $T = 0$. The adiabatic nuclei approximation (dashed lines) is compared with the full nonadiabatic calculation (full lines). The elastic transmission calculated at the equilibrium geometry of the neutral molecule is also shown for one case (dotted line).

The elastic transmission function $t^{(\mathrm{el})}_{\mathrm{L}\to\mathrm{R}}$ depends on the instantaneous value of the torsional angle φ. Fig. 3 shows this function (dotted line) at the equilibrium geometry of the neutral molecule ($\varphi_0 = 42°$), integrated over the final energy of the electron ϵ_f for one value of the electronic coupling ($\alpha = 0.1$ eV). It is seen that the elastic transmission is much narrower than the full inelastic transmission, thus demonstrating the pronounced broadening effect of the torsional degree of freedom. To investigate if this is a truly dynamical effect or rather the result of the distribution of torsional angles which contribute to the quantum-mechanical initial state $|\chi_{v_\mathrm{i}}\rangle$, we have averaged $t^{(\mathrm{el})}_{\mathrm{L}\to\mathrm{R}}$ over the initial distribution of the torsional angle φ for temperature T. Integrating furthermore over the final energy of the electron, we obtain the expression

$$t^{(\mathrm{AN})}_{\mathrm{L}\to\mathrm{R}}(\epsilon,\varphi) = \sum_v p_v \int \mathrm{d}\varphi \int \mathrm{d}\epsilon_\mathrm{f} |\chi_v(\varphi)|^2 t^{(\mathrm{el})}_{\mathrm{L}\to\mathrm{R}}(\epsilon,\epsilon_\mathrm{f},\varphi), \tag{18}$$

which in the context of electron-molecule scattering is also called the adiabatic-nuclei approximation [33]. As the results in Fig. 3 show, the adiabatic-nuclei approximation works very well for the system under consideration except for extremely small coupling to the leads where individual vibrational states of the molecular

anion are resolved, which is not reproduced in adiabatic-nuclei approximation.

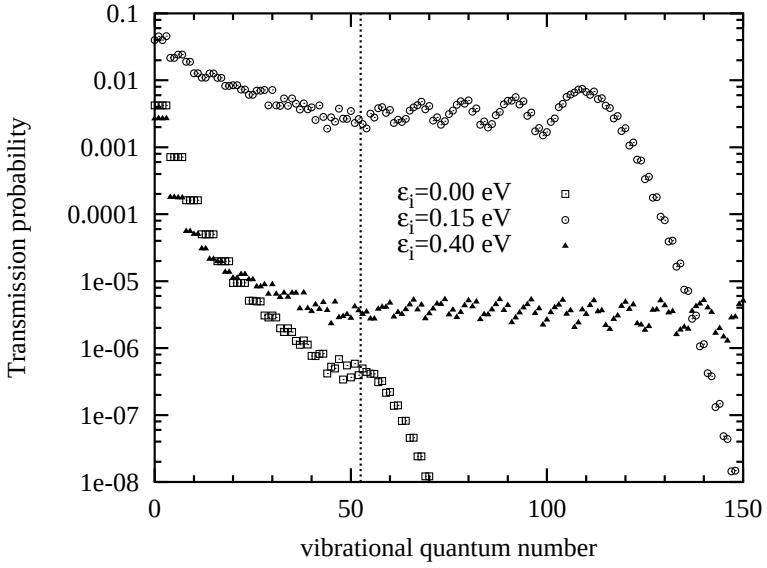

Fig. 4. Dependence of the transmission probability on the final torsional state for three different initial energies of the electron: below resonance ($\epsilon_\mathrm{i} = 0$), on resonance ($\epsilon_\mathrm{i} = 0.15$ eV) and above resonance ($\epsilon_\mathrm{i} = 0.4$ eV). The vertical dotted line shows the position of the state with energy $E_v = 0$ (onset of freely rotating states) (cf. Fig. 2).

Being based solely on elastic transmission mechanisms, however, the adiabatic-nuclei approximation cannot describe the vibrational excitation of the molecular bridge accompanying the transmission of the electron. This information, which is important to characterize the possible heating of the molecular bridge, is contained in the full transmission probability (10). As an illustration, Fig. 4 shows the dependence of the inelastic transmission probability (integrated over the final electron energy) on the final torsional state for a coupling strength of $\alpha = 0.1$ eV and three different initial energies of the electron. The results exhibit a substantial vibrational excitation of the bridge in the case of resonant electron transmission. The effect of the electronic coupling strength α on this resonant heating process is studied in Fig. 5. It is seen that highly excited torsional states are not populated for strong coupling to the leads (corresponding to a broad resonance), although in this case the total transmission probability is larger than for small values of α (cf. Fig. 3). This result is due to the fact that for strong coupling between molecular bridge and leads the residence time of the electron on the molecular bridge is too short to allow efficient electron-nuclear interaction and thus the total transmission is dominated by the elastic contribution.

In the context of electron transport through molecular bridges, vibrational ex-

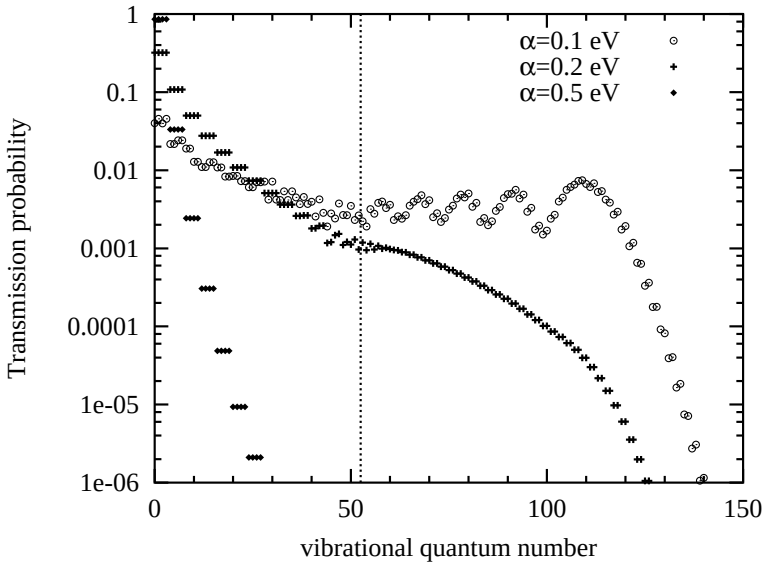

Fig. 5. Dependence of the transmission probability on the final torsional state for three different strengths of the coupling of the molecule to the leads and an initial energy of the electron, $\epsilon_\mathrm{i} = 0.15$ eV.

citation (and possibly dissociation) of the molecular bridge is presumably the most important process induced by the coupling between electron and vibrational degrees of freedom. Another interesting process is electron assisted tunneling between the wells of the torsional potential $V_0(\varphi)$. To study this process, we consider torsional states which are localized in the wells of the potential $V_0(\varphi)$. The potential $V_0(\varphi)$ has four equivalent equilibrium geometries $\varphi_{0,1} = \pm\varphi_0$ and $\varphi_{2,3} = \pi \pm \varphi_0$ (see Fig. 2). As a consequence, combinations of the four nearly degenerate states with lowest energy can be used to obtain states which are localized in the four wells. Due to the near-degeneracy, these states are close to stationary states. In Fig. 6 we show the transmission probability of the electron starting from a torsional state located at φ_0 and ending up in the same state (upper two curves) or in a torsional state that is localized in the adjacent potential well at φ_1 (lower two curves). It is seen that the resonance peak for both processes is located at the same position, the width of the peak, however, is significantly narrower for the lower two curves, i. e. for current-induced tunneling between the potential wells. This can be understood as suppression of the electron transmission due to (assisted) tunneling through the torsional barrier. Another interesting result is that the transmission probabilities for the two different processes at energies close to the resonance peak become very similar for smaller coupling ($\alpha = 0.05$ eV, full lines). This is a consequence of the long-lived character of the molecular anion in the case of small coupling to the

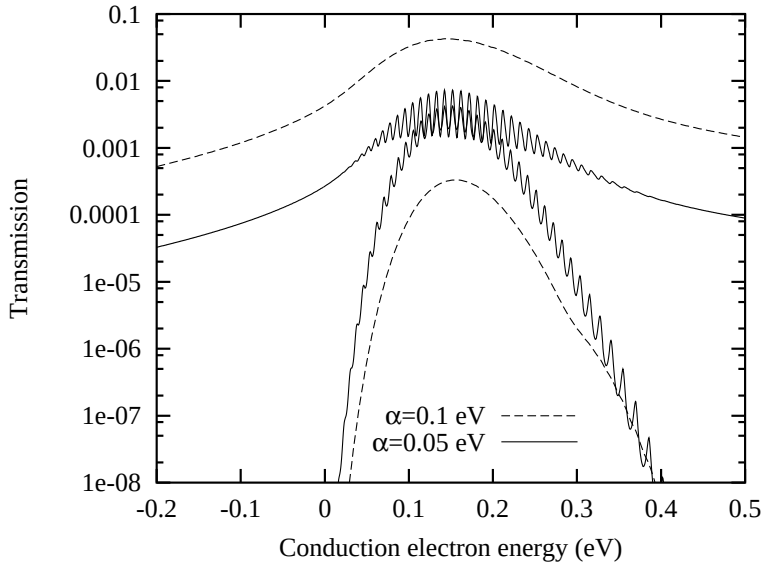

Fig. 6. Electron-assisted tunneling between adjacent wells in the torsional potential. Shown is the energy dependence of the electron transmission probability starting from a torsional state which is localized around φ_0 with (lower two curves) and without (upper two curves) transition to another, equivalent torsional state in the neighboring well.

leads. For sufficiently long lifetimes of the molecular anion, the torsional state in the potential $V_{\mathrm{d}}^{(-)}$ has the same probability to decay to both neighboring wells in the neutral potential V_0.

3.2 Current-voltage characteristic

Finally, we consider the current-voltage characteristic for our model. To obtain the current for a given voltage via Eq. (14), we have calculated the transmission coefficients (10) for a series of bias voltages on a dense energy grid. Fig. 7 shows results for different temperatures T. The $I-V$ characteristics exhibit a step-like structure. Due to thermal broadening, the width of the step increases with increasing temperature. It should be emphasized, that this thermal broadening is mainly a result of the thermal excitation of the torsional degree of freedom (i.e. Eq. (15)), whereas the thermal effect of the electrons (in Eq. (16)) is almost negligible.

The adiabatic-nuclei approximation (data not shown) follows the full calculation closely. For voltages above 0.3 V, the difference is not noticeable. It becomes more apparent close to zero bias. For example, for $T = 100$ K the zero-bias conductivity is 4.5×10^{-4}, whereas the adiabatic nuclei approximation gives 6.7×10^{-4}. This difference is a consequence of the energy loss during the transmission process which is correctly described in the full calculation, but not in the adiabatic-nuclei

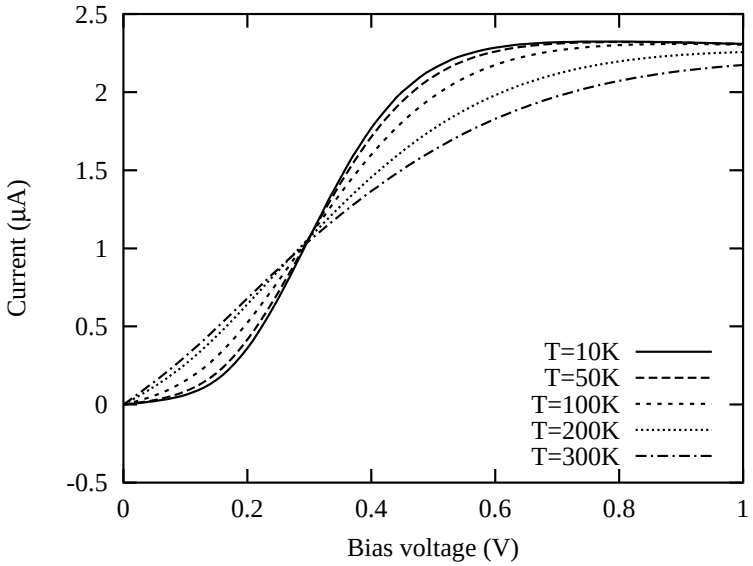

Fig. 7. Current-voltage characteristics for different temperatures (see legend) and an electronic coupling strength $\alpha = 0.1$eV.

approximation.

4 Conclusions

We have analyzed vibrationally inelastic electron transport through a molecular junction in the presence of an anharmonic large-amplitude motion of the molecular bridge. The study was based on a mechanistic model for a biphenyl molecule between two metal electrodes. The results of the study demonstrate the effects of electron-vibrational coupling on the transmission probability and the current through the junction. While for small coupling between the molecule and the leads the torsional degree of freedom gives rise to well resolved structures in the transmission function, for stronger coupling it mainly results in a broadening, which increases significantly for higher temperature. We have, furthermore, studied the vibrational excitation process accompanying the transmission of the electron through the molecular bridge, which is particularly pronounced for electron energies close to the molecular resonance state and/or small to moderate electronic coupling strength. A correct description of the vibrational excitation process is also important to characterize the heating of the molecule caused by the electron transport. To investigate this heating process in more detail, the coupling to the other vibrational degrees of freedom of the molecule (which were neglected in the present study) and the environment has to be taken into account [21, 22, 23].

Another interesting process, which is not related directly to vibrational excitation of the molecular bridge, are structural changes of the bridge, in particular electron assisted tunneling between different wells of the torsional potential. Our studies show that electron assisted tunneling becomes particularly important when narrow resonances are present.

We have also investigated the validity of approximate methods, in particular the purely elastic description of the transmission process and the adiabatic nuclei approximation. As was found in our previous study for models with small amplitude motion [23], the purely elastic calculation typically predicts much too narrow transmission probabilities. The adiabatic nuclear approximation, on the other hand, which takes into account the 'static' effect of the vibrational degrees of freedom due to their initial distribution, can describe the average transmission probability rather well, but it is not capable of describing the vibrational excitation accompanying the electron transport. Furthermore, it is also expected to fail if the density of states of the leads varies quickly in the energy range of interest. This aspect, which is expected to be of particular importance if the molecular bridge is bound to semiconductor instead of metal electrodes will be the subject of future work.

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