

# Theory of Vibrationally Inelastic Electron Transport through Molecular Bridges

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## Abstract

Vibrationally inelastic electron transport through a molecular bridge that is connected to two leads is investigated. The study is based on a generic model of vibrational excitation in resonant transmission of electrons through a molecular junction. Employing methods from electron-molecule scattering theory, the transmittance through the molecular bridge can be evaluated numerically exactly. The current through the junction is obtained approximately using a Landauer-type formula. Considering different parameter regimes, which include both the case of a molecular bridge that is weakly coupled to the leads, resulting in narrow resonance structures, and the opposite case of a broad resonance caused by strong interaction with the leads, we investigate the characteristic effects of coherent and dissipative vibrational motion on the electron transport. Furthermore, the validity of widely used approximations such as the wide-band approximation and the restriction to elastic transport mechanisms is investigated in some detail.

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## I. INTRODUCTION

The experimental demonstration of the possibility to connect two electrodes by a single molecule and to measure a current through such a molecular junction [1–3] has stimulated increasing theoretical efforts to elucidate the basic mechanisms of electron transport in such systems (see, for example, [4–7] and references therein). Most of the theoretical work in recent years has been devoted to the determination of the electronic structure of molecular junctions, employing a variety of methods that include extended Hückel approaches [8–13], *ab initio* quantum-chemistry methods [14–16], and density functional theory [17–21]. The majority of these studies have focused on elastic mechanisms for electron transport, where the current through the molecular junction can be obtained from the single-electron transmission probability using the Landauer formula [22–24]. These studies have demonstrated the importance of the electronic energy level structure of the molecular bridge: the tunneling of electrons through occupied and unoccupied levels of the molecule results in resonance structures in the transmission probability which in turn may cause strongly nonlinear current-voltage characteristics.

Much less is known about the effect of vibrationally inelastic processes, associated with the vibrational motion of the molecular bridge, on the electron transport. In experiments on electron transport through H<sub>2</sub> molecules between two platinum electrodes [2] as well as C<sub>60</sub> molecules connected to gold electrodes [25], indications for an influence of the center-of-mass motion of the respective molecule on the conductivity have been found. Effects of the internal vibrational motion of the molecular bridge on the current through the junction, on the other hand, have (to our knowledge) not yet been reported. Such effects have, however, been predicted in a variety of theoretical studies. For example, the "static" influence of the internal vibrational modes has been studied by averaging the transmittance over the probability distribution of the vibrational degrees of freedom [26–28]. 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 [29–33]. 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. Furthermore, 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 [34,35].

The effect of vibrationally inelastic processes on electron transport has also been investigated for a variety of closely related problems including the tunneling of electrons through long polymer chains (molecular wires) [36,37], electron transport through quantum dots and heterostructures [38–42], as well as the theoretical description of single-molecule vibrational spectroscopy in scanning tunneling microscopy (STM) experiments [43–50].

Another closely related process is vibrationally inelastic electron-molecule scattering. Here, it is well established that the resonant scattering of a low-energy electron from a molecule can result in strong vibrational excitation. This process has been studied in great detail experimentally (see, for example, the reviews [51,52]). Furthermore, efficient theoretical methods have been developed to describe the interaction of electronic and vibrational degrees of freedom in resonant collision processes of low-energy electrons with molecules [53]. As a result, inelastic electron scattering from diatomic molecules is now well understood from first principles [54]. Due to the close similarities between the process of vibrational excitation induced by electron scattering from a molecule and vibrationally inelastic electron transmission through a molecular junction, it is to be expected that the methods and concepts developed in the former field can advantageously be used in the latter field. An example is the so-called wide-band approximation, where the energy dependence of the coupling between the molecule and the leads is neglected. This approximation, which has been adopted in most of the theoretical studies of vibrationally inelastic electron transport in molecular junctions (for exceptions, see Refs. [29,37,39,40,55]) has been tested in detail for resonant electron-molecule scattering [53]. It has been shown that the wide-band approximation breaks down at energies close to thresholds and often does not accurately describe vibrational excitation processes.

In this paper we study vibrationally inelastic effects on electron transport through a molecular junction beyond the wide-band approximation. To this end, we consider a generic model for vibrational excitation in resonant electron transmission processes through a molecular junction. The model includes the coupling of an electronic resonance state, located at the molecular bridge, to the continuum of electronic lead states as well as the coupling of the electronic degrees of freedom to a vibrational reaction mode of the molecule. Employing projection-operator techniques [56] well-known from electron-molecule scattering [53], the transmission probability through the molecular junction can be evaluated numerically exactly within this model. The current through the bridge is obtained employing a generalized Landauer formula [57]. Based on numerical results for models in different parameter regimes, we study the importance of inelastic effects on molecular conductance as well as the validity of the wide-band approximation.

Furthermore, we investigate how vibrationally inelastic effects on electron transport are altered if the vibrational motion has dissipative character. Dissipative vibrational processes (such as, for example, vibrational dephasing and relaxation) are expected to be of importance in larger molecules or in molecular bridges that are embedded in an environment. To describe dissipative vibrational motion, we consider the coupling of the reaction mode to a vibrational bath. The various observables are then obtained employing an expansion with respect to the number of quanta in the final state of the bath. This technique, which has been proposed some years ago in the context of electron scattering from large molecules [58], allows us to describe the effect of vibrational relaxation in an approximate, yet controlled, way, without invoking Markov-type approximations. Moreover, it is shown that in the case of identical left and right leads and zero bias voltage a unitarity condition can be exploited, which allows a numerically exact evaluation of the transmission probability, including the effects of a dissipative vibrational bath.

This paper is organized as follows: After an introduction of the model and the observables of interest, Sec. II outlines the theoretical methods used to describe the transmission probability and the current through the molecular bridge. In particular, we discuss var-

ious levels of the theoretical treatment: a theoretical description based on purely elastic transport mechanisms, the incorporation of vibrationally inelastic processes (coherent and dissipative), as well as the wide-band approximation. Sec. III presents model studies of vibrationally inelastic electron transport for different parameter regimes, comprising both the case of a molecular bridge that is weakly coupled to the leads, resulting in narrow resonance structures, and the opposite case of a broad resonance caused by strong interaction with the leads. Furthermore, the various levels of theory are critically compared. Finally, Sec. IV gives a summary and concludes.

## II. THEORY

### A. Model Hamiltonian

To investigate the influence of vibrational motion on the transmission of electrons through a molecular bridge, we consider a situation where two metallic leads, which serve as a reservoir of electrons, are connected to a molecule through which electrons can be transferred from one lead to the other. As has been demonstrated in previous work on elastic electron transport (see, for example, [59]), the transmission of electrons through molecular junctions is typically characterized by resonances which correspond to the various electronic orbitals of the bridging molecule. From the theoretical point of view, the situation is thus characterized by a set of resonance states which are embedded in the continuum of lead states. In this paper, we will consider, for simplicity, a situation where only a single electronic resonance, corresponding (in the limit of vanishing coupling to the leads) to a molecular anion, contributes to the transmission process.

From the theory of resonant electron-molecule scattering, it is well known that the influence of vibrational motion on the electron transmission can be advantageously described by choosing a basis of diabatic electronic states consisting of a discrete state  $|\phi_d\rangle$ , which represents the resonance (i.e. the situation where the transmitting electron is situated at the

bridging molecule) and a set of orthogonal continuum states,  $|\phi_{k\alpha}\rangle$ ,  $\alpha = \text{L,R}$ , describing the electron in the left and right lead, respectively. Accordingly, the Hamiltonian reads

$$H_S = |\phi_d\rangle\tilde{H}_d\langle\phi_d| + \sum_{k,\alpha=L,R} \left\{ |\phi_{k\alpha}\rangle(\epsilon_{k\alpha} + \tilde{H}_0)\langle\phi_{k\alpha}| + |\phi_d\rangle V_{dk\alpha}\langle\phi_{k\alpha}| + |\phi_{k\alpha}\rangle V_{dk\alpha}^*\langle\phi_d| \right\}, \quad (1)$$

where  $\tilde{H}_0$  denotes the vibrational Hamiltonian of the neutral molecule in the electronic ground state and  $\tilde{H}_d$  the vibrational Hamiltonian in the discrete electronic state  $|\phi_d\rangle$ . The electronic coupling between the leads and the molecule is specified by the coupling matrix elements  $V_{dk\alpha}$ .

The electronic parameters of the model Hamiltonian (1) can in principle be determined by electronic structure calculations [60]. In the model studies considered below, we have adopted a parameterization which is based on a simple tight-binding model schematically shown in Fig. 1. The central site corresponds to the electron in the discrete state  $|\phi_d\rangle$  and the states  $|l\rangle$ ,  $l = \pm 1, \pm 2, \dots$  represent the atomic sites of the left ( $-$ ) and right ( $+$ ) lead, respectively. The nearest-neighbor coupling constants between two lead sites and between the leads and the central site are specified by  $\beta$  and  $v$ , respectively, and  $\mu_{\text{L/R}}$  denotes the chemical potential in the leads. The stationary continuum states in the right lead are given by

$$|\phi_k\rangle = \sum_l \frac{\sin(kl)}{\sqrt{\pi\beta \sin k}} |l\rangle, \quad (2)$$

and similar for the left lead. The energy  $\epsilon$  of the electron satisfies the dispersion relation

$$\epsilon = \epsilon_{k\alpha} = \mu_\alpha + 2\beta \cos k, \quad (3)$$

in the left and right lead,  $\alpha = \text{L/R}$ , respectively. Using this particular model for the leads we obtain

$$V_{dk\alpha} \equiv \langle\phi_d|H_{\text{el}}|\phi_{k\alpha}\rangle = v\sqrt{\frac{\sin k}{\pi\beta}}. \quad (4)$$

As we will see in Sec. II C, the electronic structure of the leads enters the expressions for the observables of interest only through the energy-dependent width function of the leads (atomic units with  $e = \hbar = 1$  are used throughout the paper unless stated otherwise)

$$\Gamma_\alpha(\epsilon) \equiv 2\pi \sum_k \delta(\epsilon - \epsilon_{k\alpha}) |V_{dk\alpha}|^2. \quad (5)$$

The width function  $\Gamma_\alpha(\epsilon)$  is the imaginary part of the self-energy function

$$\Sigma_\alpha(\epsilon) = \sum_k \frac{|V_{dk\alpha}|^2}{\epsilon^+ - \epsilon_{k\alpha}} \equiv \Delta_\alpha(\epsilon) - \frac{i}{2}\Gamma_\alpha(\epsilon), \quad (6)$$

where  $\epsilon^+ = \epsilon + i\gamma$ ,  $\gamma$  being a positive infinitesimal. The real part of the self-energy function, the level-shift function  $\Delta_\alpha(\epsilon)$ , is related to the width function via Hilbert transformation, i.e.

$$\Delta_\alpha(\epsilon) = \frac{1}{2\pi} \text{P} \int \frac{\Gamma_\alpha(\epsilon')}{\epsilon - \epsilon'} d\epsilon', \quad (7)$$

where P denotes the principal value of the integral.

For the nearest-neighbor tight-binding model of the leads introduced above, the self-energy function  $\Sigma(z)$  is given by the Hubbard Green's function [61,62], multiplied by the coupling strength  $v$  between the last atomic site in the leads and the bridge,

$$\Sigma_\alpha(z) = \frac{2v^2}{z - \mu_\alpha + \sqrt{(z - \mu_\alpha)^2 - 4\beta^2}}. \quad (8)$$

Here, the width of the conduction band is given by  $4\beta$ . Analytic continuation in the complex energy ( $z$ ) plane gives the real part

$$\Delta_\alpha(\epsilon) = \begin{cases} \frac{v^2}{2\beta^2}(\epsilon - \mu_\alpha) & \text{for } |\epsilon - \mu_\alpha| < 2\beta \\ \frac{v^2}{2\beta^2} \left[ (\epsilon - \mu_\alpha) \mp \sqrt{(\epsilon - \mu_\alpha)^2 - 4\beta^2} \right] & \text{for } \pm(\epsilon - \mu_\alpha) > 2\beta \end{cases} \quad (9)$$

and the imaginary part

$$\Gamma_\alpha(\epsilon) = \begin{cases} \frac{v^2}{\beta^2} \sqrt{4\beta^2 - (\epsilon - \mu_\alpha)^2} & \text{for } |\epsilon - \mu_\alpha| < 2\beta \\ 0 & \text{for } |\epsilon - \mu_\alpha| > 2\beta \end{cases} \quad (10)$$

As will be demonstrated in Sec. III, the inclusion of the energy dependence of the width function  $\Gamma_\alpha(\epsilon)$  and thus of the coupling matrix elements  $V_{dk\alpha}$ , which complicates the theoretical treatment significantly, is crucial in order to account correctly for inelastic effects, in particular for energies close to the edge of the conduction band.

To study vibrationally inelastic effects on the transmission through the molecular bridge, we consider a single vibrational (reaction) mode, along which the equilibrium geometry of the discrete electronic state is shifted with respect to the continuum states due to the presence of the additional electron at the molecule. Within the harmonic approximation, this situation is described by the vibrational Hamiltonians

$$\tilde{H}_0 = \omega_S a^\dagger a \quad , \quad \tilde{H}_d = \omega_S a^\dagger a + \lambda(a + a^\dagger) + \epsilon_d = \omega_S a_d^\dagger a_d + \epsilon_d - \frac{\lambda^2}{\omega_S}. \quad (11)$$

Here,  $\omega_S$  is the vibrational frequency of the reaction mode, and  $a^\dagger$  and  $a$  denote the creation and annihilation operators for the reaction mode which are related to the corresponding operators in the discrete electronic state by the shift in equilibrium geometry,  $\lambda/(\sqrt{2}\omega_S)$ , i.e.  $a_d = a + \lambda/\omega_S$ .

Most of the experimental studies of electron transport through molecular bridges conducted so far have considered relatively large molecules with many vibrational degrees of freedom. In large molecules the coupling of reaction coordinates (which are strongly coupled to the electronic degrees of freedom) to the remaining (inactive) vibrational modes of the molecule results in the process of intramolecular vibrational redistribution, which is well known from the spectroscopy of large molecules [63–69]. To study the effect of vibrational relaxation on the electron transmission, we adopt a linear response model for vibrational relaxation [58] in the discrete state, where the reaction mode is coupled to a bath of harmonic oscillators. Thus the Hamiltonian of the overall system is given by

$$H = H_S + H_B + H_{SB}, \quad (12)$$

where the 'system' Hamiltonian  $H_S$  is given by Eq. (1), the bath Hamiltonian reads

$$H_B = \sum_j \omega_j b_j^\dagger b_j, \quad (13)$$

and the coupling between the reaction coordinate and the bath is given by

$$H_{SB} = |\phi_d\rangle \sum_j c_j (a_d b_j^\dagger + a_d^\dagger b_j) \langle \phi_d|. \quad (14)$$



Here,  $b_j^\dagger$  and  $b_j$  denote creation and annihilation operators for the bath mode with frequency  $\omega_j$  and  $c_j$  is the corresponding system-bath coupling constant.

As is well known [70,71], all properties of the vibrational bath which influence the dynamics of the system are characterized by the bath spectral density

$$J(\omega) = \sum_j c_j^2 \delta(\omega - \omega_j). \quad (15)$$

In the numerical calculations reported below, it will be modeled by a continuous Ohmic bath with exponential cutoff [70,71]

$$J(\omega) = \eta \omega e^{-\omega/\omega_c}. \quad (16)$$

Here, the characteristic frequency  $\omega_c$  defines the maximum of the spectral density and the overall strength of the system-bath coupling is measured by  $\eta$ .

## B. Observables of Interest

Various observables are of interest when investigating the influence of vibrational motion on the electron transport through a molecular bridge. The most detailed information on the transmission process of a single electron is comprised in the initial- and final-state resolved scattering probability. Employing scattering theory, it is straightforward to show that the probability for scattering of an electron with the energy  $\epsilon_i$  from lead  $\alpha_i$  into a state with energy  $\epsilon_f$  in the lead  $\alpha_f$ , accompanied by a vibrational transition from state  $|v_i\rangle|\mathbf{v}_i\rangle$  to state  $|v_f\rangle|\mathbf{v}_f\rangle \neq |v_i\rangle|\mathbf{v}_i\rangle$  (we denote the bath vibrations with bold face letters and the system mode vibrations with italic letters) is given by [53]

$$t_{\alpha_f \leftarrow \alpha_i}(\epsilon_f, v_f, \mathbf{v}_f, \epsilon_i, v_i, \mathbf{v}_i) = \delta(\epsilon_i + E_{\mathbf{v}_i} + E_{v_i} - \epsilon_f - E_{\mathbf{v}_f} - E_{v_f}) \Gamma_{\alpha_i}(\epsilon_i) \Gamma_{\alpha_f}(\epsilon_f) \\ \times \left| \langle \mathbf{v}_f | \langle v_f | \langle \phi_d | (\epsilon_i^+ - H)^{-1} | \phi_d \rangle | v_i \rangle | \mathbf{v}_i \rangle \right|^2, \quad (17)$$

where  $E_{\mathbf{v}_i}$ ,  $E_{v_i}$  and  $E_{\mathbf{v}_f}$ ,  $E_{v_f}$  are the initial and final vibrational energies of the bath and system modes, respectively. Writing the transition probability in the form (17), we have

assumed, for simplicity, that the coupling element  $V_{dk\alpha}$  does not depend on the vibrational degrees of freedom. The generalization of the formula to include such effects is straightforward (see, for example, Ref. [53]).

While Eq. (17) describes the most detailed information on the scattering process, in experiments typically more averaged observables are measured. It is thus expedient to introduce the integral transmission probability from lead  $\alpha_i$  into lead  $\alpha_f$  (summed over all possible final vibrational states)

$$t_{\alpha_f \leftarrow \alpha_i}(\epsilon_f, \epsilon_i) \equiv \sum_{v_f, \mathbf{v}_f} t_{\alpha_f \leftarrow \alpha_i}(\epsilon_f, v_f, \mathbf{v}_f, \epsilon_i, v_i, \mathbf{v}_i), \quad (18)$$

and the total transmission probability, integrated over the final energy of the electron,  $\epsilon_f$ ,

$$t_{\alpha_f \leftarrow \alpha_i}(\epsilon_i) = \int t_{\alpha_f \leftarrow \alpha_i}(\epsilon_f, \epsilon_i) d\epsilon_f. \quad (19)$$

The most important observable for the study of electron transport through a molecular bridge is, of course, the current which is induced when a finite voltage is applied to the molecular junction. To calculate the current through the bridge, we employ the generalized Landauer formula [5]

$$I = \frac{1}{\pi} \int d\epsilon_i \int d\epsilon_f \{t_{R \leftarrow L}(\epsilon_f, \epsilon_i) f_L(\epsilon_i) [1 - f_R(\epsilon_f)] - t_{L \leftarrow R}(\epsilon_f, \epsilon_i) f_R(\epsilon_i) [1 - f_L(\epsilon_f)]\}, \quad (20)$$

where  $f_\alpha(E)$ ,  $\alpha = L, R$ , denotes the Fermi-Dirac distribution for the left and right lead, respectively.

In principle the basis states  $|\phi_d\rangle$ ,  $|\phi_{k\alpha}\rangle$ , and therefore also the functions  $\Gamma_\alpha(\epsilon)$  and vibrational Hamiltonian  $H_d$ , depend on the bias voltage  $V$  across the bridge. Here, we assume for simplicity that the bias voltage  $V$  enters Eq. (20) only through the Fermi distribution of the leads and the width function  $\Gamma_\alpha(\epsilon)$  [cf. Eq. (3), (5)] via the chemical potentials of the leads  $\mu_{L/R} = \pm V/2$ . Moreover, in this paper we will not consider thermal effects on the electron transport, i.e. in all numerical calculations reported below we have taken  $T = 0$  K. Thus, the initial state of the vibrational degrees of freedom is the ground state of the system and bath modes, respectively,  $|v_i = 0\rangle |\mathbf{v}_i = \mathbf{0}_B\rangle$  and the Fermi-Dirac distribution  $f_\alpha(E)$  in Eq. (20) reduces to the Heaviside step function.

The validity of the formula (20) for calculating currents including inelastic effects has been discussed controversially in the literature. The current formula is sometimes used without the Pauli exclusion principle factors  $[1 - f(\epsilon)]$  (see for example the discussion in Refs. [24,72]). It has been argued, however, that for weak metal-bridge coupling the expression (20) is appropriate [5]. Employing nonequilibrium Greens-function theory and the second quantized version of the Hamiltonian (1), it can be shown that Eq. (20) gives the correct description of the current in the limit where many-electron processes are negligible for the dynamics [73]. It should also be mentioned that the use of Eq. (20) implicitly assumes that the bridge relaxes into the ground vibrational state  $|v_i = 0\rangle |v_i = \mathbf{0}_B\rangle$  before each subsequent transmission event. In view of the low currents observed experimentally, this should be a reasonable assumption (for a similar discussion in the case of STM currents, see, for example, Ref. [46]).

### C. Method of Solution

#### 1. Elastic transmission

Let us first consider the case without coupling to the vibrational degrees of freedom [i.e.  $\lambda = \eta = 0$  in Eqs. (11),(16)]. In this case, only elastic processes contribute to the electron transport, and the total transmission probability is given by

$$t_{R \leftarrow L}(\epsilon_i) = t_{L \leftarrow R}(\epsilon_i) = \frac{\Gamma_R(\epsilon_i)\Gamma_L(\epsilon_i)}{[\epsilon_i - \epsilon_d - \Delta_L(\epsilon_i) - \Delta_R(\epsilon_i)]^2 + [\Gamma_L(\epsilon_i) + \Gamma_R(\epsilon_i)]^2/4}, \quad (21)$$

which is the well-known result for elastic resonant tunneling transmission. The Landauer formula (20) for the current is exact in this case (see, for example, Ref. [74]) and the evaluation of the current reduces to a simple numerical integration.

#### 2. Inelastic transmission without dissipation

Let us next consider the influence of the coupling to the vibrational degrees of freedom on the transmission of the electron, i.e. vibrationally inelastic transmission through the

molecular bridge. If we exclude dissipative processes induced by the coupling to the bath, the dynamics is described by the system Hamiltonian  $H_S$ , Eq. (1). The probability for transmitting an electron with energy  $\epsilon_i$  from the left lead into a state with energy  $\epsilon_f$  in the right lead, accompanied by a vibrational transition from the state  $|v_i = 0\rangle$  to the state  $|v_f\rangle$  is given by

$$t_{R\leftarrow L}(\epsilon_f, \epsilon_i) = \sum_{v_f} \delta(\epsilon_i - \epsilon_f - E_{v_f}) \Gamma_R(\epsilon_f) \Gamma_L(\epsilon_i) \left| \langle v_f | G_d^{(S)}(\epsilon_i) | 0 \rangle \right|^2, \quad (22)$$

where

$$G_d^S(E) \equiv \langle \phi_d | (E^+ - H_S)^{-1} | \phi_d \rangle \quad (23)$$

denotes the Green's function projected on the resonance state. Employing projection operator techniques well known from the theory of resonant electron-molecule scattering (see [53] and references therein),  $G_d^S(E)$  can be recast in the form

$$G_d^S(E) = \left[ E^+ - \tilde{H}_d - \Sigma_L(E - \tilde{H}_0) - \Sigma_R(E - \tilde{H}_0) \right]^{-1}. \quad (24)$$

This form has the advantage that the electronic continuum has been formally eliminated and only vibrational dynamics in the discrete electronic space has to be evaluated. Efficient techniques have been developed [75,76] to evaluate the matrix elements of the Green's function (24). In the present case, where  $\tilde{H}_0$  and  $\tilde{H}_d$  describe harmonic oscillators, the Green's function (24) can be obtained, e.g., by inverting a basis representation of the operator  $E^+ - \tilde{H}_d - \Sigma_L(E - \tilde{H}_0) - \Sigma_R(E - \tilde{H}_0)$  for each energy  $E$ , employing efficient algorithms for the inversion of tridiagonal matrices [77].

### 3. Wide-band approximation

While the expressions discussed so far take full account of the energy dependence of the width function  $\Gamma(\epsilon)$ , in the majority of previous work on the effect of vibrational motion on electron transmission, the so-called wide-band (WB) approximation has been invoked, where the width function is assumed to be constant, i.e.  $\Gamma(\epsilon) = \text{const}$ . In this approximation, the

level-shift function vanishes [cf. Eq. (7)],  $\Delta(\epsilon) = 0$ , and the transmission probability, Eq. (22), can be written as

$$t_{\text{R}\leftarrow\text{L}}^{(\text{WB})}(\epsilon_f, \epsilon_i) = \Gamma_{\text{R}}\Gamma_{\text{L}} \sum_{v_f} \delta(\epsilon_i - \epsilon_f - E_{v_f}) \left| \sum_n \frac{\langle v_f | n \rangle \langle n | 0 \rangle}{\epsilon_i - E_n + \frac{i}{2}(\Gamma_{\text{R}} + \Gamma_{\text{L}})} \right|^2, \quad (25)$$

which yields after integration over the final energy of the electron the total transmission probability

$$\begin{aligned} t_{\text{R}\leftarrow\text{L}}^{(\text{WB})}(\epsilon_i) &= \Gamma_{\text{R}}\Gamma_{\text{L}} \sum_n \frac{|\langle n | 0 \rangle|^2}{(\epsilon_i - E_n)^2 + \frac{1}{4}(\Gamma_{\text{R}} + \Gamma_{\text{L}})^2} \\ &= \Gamma_{\text{R}}\Gamma_{\text{L}} \sum_n \frac{\frac{1}{n!} \left(\frac{\lambda^2}{2\omega_{\text{S}}}\right)^n e^{-\frac{\lambda^2}{2\omega_{\text{S}}}}}{(\epsilon_i - E_n)^2 + \frac{1}{4}(\Gamma_{\text{R}} + \Gamma_{\text{L}})^2}. \end{aligned} \quad (26)$$

In Sec. III, we will study the validity of the wide-band approximation based on the comparison of Eq. (26) with the full inelastic transmission probability given by Eq. (22).

#### 4. Inelastic transmission including vibrational relaxation

Finally, we consider the case of inelastic transmission of an electron through the molecular bridge in the presence of vibrational relaxation. The theoretical treatment of this problem is considerably more complicated than the cases considered above, because we have to deal with two qualitatively different continua: the electronic scattering continuum describing the leads and the dissipative vibrational mode continuum of the bath. In principle, it is possible to start from the general formula for the transition probability (17) and derive formal expressions as in Eqs. (22), (24) with the bath modes included in  $\tilde{H}_0$  and  $\tilde{H}_d$ . However, with increasing number of bath modes it becomes difficult to perform the matrix inversion in Eq. (24) and, therefore, such an approach is limited to very few bath modes.

To circumvent this problem, we adopt an approach that has been proposed to describe the effect of vibrational relaxation in the context of resonant electron scattering from large molecules [58]. The basic idea of this method is to express the transmission probability, Eq. (18), as a sum

$$t_{\text{R}\leftarrow\text{L}}(\epsilon_f, \epsilon_i) = \sum_{m=0}^{\infty} t_{\text{R}\leftarrow\text{L}}^{(m)}(\epsilon_f, \epsilon_i), \quad (27)$$

where  $t_{\text{R}\leftarrow\text{L}}^{(m)}(\epsilon_f, \epsilon_i)$  describes transmission processes with  $m$  quanta of excitation in the final state of the bath. In the parameter regime where the vibrational relaxation rate is small compared to the electronic decay rate of the resonance, only the first few terms in the expansion will contribute to the overall transmission probability. The first two terms in the expansion, which correspond to processes where the final state of the bath contains zero or one quantum of excitation, respectively, read

$$t_{\text{R}\leftarrow\text{L}}^{(0)}(\epsilon_f, \epsilon_i) = \sum_{v_f} \delta(\epsilon_i - \epsilon_f - E_{v_f}) \Gamma_{\text{R}}(\epsilon_f) \Gamma_{\text{L}}(\epsilon_i) |\langle v_f | G_{\text{d}}(\epsilon_i) | 0 \rangle|^2, \quad (28a)$$

$$t_{\text{R}\leftarrow\text{L}}^{(1)}(\epsilon_f, \epsilon_i) = \sum_{v_f} J(\epsilon_i - \epsilon_f - E_{v_f}) \Gamma_{\text{R}}(\epsilon_f) \Gamma_{\text{L}}(\epsilon_i) |\langle v_f | G_{\text{d}}(\epsilon_f + E_{v_f}) a_{\text{d}} G_{\text{d}}(\epsilon_i) | 0 \rangle|^2, \quad (28b)$$

with the Green's function

$$\begin{aligned} G_{\text{d}}(E) &\equiv \langle \phi_{\text{d}} | \left( E^+ - H_{\text{S}} - |\phi_{\text{d}}\rangle a_{\text{d}}^\dagger \langle \phi_{\text{d}} | \int d\omega \frac{J(\omega)}{E^+ - H_{\text{S}} - \omega} |\phi_{\text{d}}\rangle a_{\text{d}} \langle \phi_{\text{d}} | \right)^{-1} | \phi_{\text{d}} \rangle \\ &= \langle \phi_{\text{d}} | \left( E^+ - H_{\text{S}} - |\phi_{\text{d}}\rangle a_{\text{d}}^\dagger \int d\omega J(\omega) G_{\text{d}}^{\text{S}}(E - \omega) a_{\text{d}} \langle \phi_{\text{d}} | \right)^{-1} | \phi_{\text{d}} \rangle. \end{aligned} \quad (29)$$

The expressions for higher order terms ( $m > 1$ ) can be found in Ref. [58]. The Green's function  $G_{\text{d}}(E)$  can be evaluated either as the unique solution of the Lippmann-Schwinger equation

$$G_{\text{d}}(E) = G_{\text{d}}^{\text{S}}(E) + G_{\text{d}}^{\text{S}}(E) \left[ a_{\text{d}}^\dagger \int d\omega J(\omega) G_{\text{d}}^{\text{S}}(E - \omega) a_{\text{d}} \right] G_{\text{d}}(E) \quad (30)$$

using the iterative Schwinger-Lanczos method [76,78] (which converges with only few iterations) or employing matrix inversion techniques as described in Ref. [58].

In general situations where the left and right lead are not identical, e.g., due to a non-zero bias voltage, the expansion in Eq. (27) has to be terminated for practical reasons at a certain order  $m$  and is thus only applicable in the case of a weakly damped system mode. We would like to emphasize, though, that the electronic coupling of the molecule to the leads is treated exactly in the approach outlined above and it can thus be arbitrarily strong.

Furthermore, the treatment of the dissipation described by Eq. (28) does not invoke Markov-type approximations and is, therefore, not limited to situations where the bath-correlation time is short compared to the system dynamics.

In the case of identical left and right leads and zero bias, however, one can exploit the unitarity condition to express the sum of all higher order corrections, i.e.  $t_{R\leftarrow L}^{(m)}$  with  $m > 0$ , in terms of the elastic (with respect to the bath) terms  $t_{R\leftarrow L}^{(0)}$  and  $t_{L\leftarrow L}^{(0)}$ . To see this, it is noted that in the symmetric case we have  $t_{R\leftarrow L}^{(m)} = t_{L\leftarrow L}^{(m)}$  for all  $m > 0$ . For  $m=0$ , the total transmission probabilities are given by

$$t_{R\leftarrow L}^{(0)}(\epsilon_i) = \sum_{v_f=0}^{\infty} \Gamma_R(\epsilon_i - E_{v_f}) \Gamma_L(\epsilon_i) |\langle v_f | G_d(\epsilon_i) | 0 \rangle|^2, \quad (31a)$$

$$t_{L\leftarrow L}^{(0)}(\epsilon_i) = |1 - i\Gamma_L(\epsilon_i) \langle 0 | G_d(\epsilon_i) | 0 \rangle|^2 + \sum_{v_f=1}^{\infty} \Gamma_L(\epsilon_i - E_{v_f}) \Gamma_L(\epsilon_i) |\langle v_f | G_d(\epsilon_i) | 0 \rangle|^2. \quad (31b)$$

The difference between the transmissions probabilities from the left to the right lead and from the left back to the left lead is due to the special role of the transition amplitude with the same initial and final state which only contributes in the latter case. Together with the unitarity condition

$$t_{L\leftarrow L}^{(0)}(\epsilon) + \sum_{m>0} t_{L\leftarrow L}^{(m)}(\epsilon) + t_{R\leftarrow L}^{(0)}(\epsilon) + \sum_{m>0} t_{R\leftarrow L}^{(m)}(\epsilon) = 1, \quad (32)$$

this yields

$$t_{R\leftarrow L}(\epsilon_i) = \frac{1}{2} \left( 1 + t_{R\leftarrow L}^{(0)}(\epsilon_i) - t_{L\leftarrow L}^{(0)}(\epsilon_i) \right) = -\Gamma_L(\epsilon_i) \text{Im} \langle 0 | G_d(\epsilon_i) | 0 \rangle. \quad (33)$$

Eq. (33) is an exact formula for the total transmission of the electron through the molecular bridge, including the bath to all orders in the system-bath coupling. Moreover, it can easily be evaluated numerically. Although it is limited to symmetric leads, and thus cannot be applied directly to calculate the current, it is very helpful for checking the convergence properties of the expansion (27) for zero bias or in the linear response regime.

### III. RESULTS AND DISCUSSION

In this section we present the results of a model study of the influence of vibrational motion and vibrational dissipation on the transmission probability and the current-voltage characteristics of a molecular bridge. To obtain a comprehensive picture of the various mechanisms, we shall consider models in different parameter regimes. In particular, we will consider both the case of a molecular bridge that is weakly coupled to the leads, resulting in narrow resonance structures, and the opposite case of a broad resonance, caused by strong interaction with the leads. The parameters specific to the different models are collected in Table I. The nearest-neighbor coupling strength in the leads is  $\beta = 1$  eV in all models considered (this parameter is an overall energy scaling factor). The characteristic frequency of the bath is chosen to coincide with the frequency of the system mode, i.e.  $\omega_C = \omega_S$ , and we will consider a relatively weak coupling between the system mode and the bath,  $\eta = 0.1$ .

#### A. Tunneling through a narrow resonance

First, we consider the resonant transmission of electrons in the tunneling regime, which is characterized by a relatively weak coupling of the electronic state localized at the bridge to those in the leads. We have chosen a coupling strength of  $v = 0.2$  eV, which corresponds to a fifth of the nearest-neighbor hopping amplitude  $\beta$  in the leads. We will, furthermore, consider a localized state that is situated well inside the conduction band with an energy of  $\epsilon_d = 0.5$  eV (for zero voltage, the conduction band extends over the range  $[-2$  eV,  $2$  eV]).

We start with Model A, which is characterized by a relatively weak coupling between the electronic degrees of freedom and the vibrational motion of the system mode,  $\lambda = 0.3$  eV. Fig. 2 depicts the transmission probability for model A obtained for zero voltage using the different levels of theory introduced in Sec. II C: the elastic transmission probability, Eq. (21), the vibrationally inelastic transmission probability integrated over the final electron energy, Eq. (22), the wide-band approximation of the vibrationally inelastic transmission



probability, Eq. (26), and the transmission probability in the presence of vibrational relaxation, Eq. (33). The elastic transmission probability (dotted line) exhibits a rather narrow peak at the position of the discrete electronic state. Including the coupling of the electronic degrees of freedom to the vibrational motion of system mode (vibrationally inelastic transmission, thick dashed line), this peak is seen to become split into several sub-peaks which correspond to the different vibrational levels in the discrete electronic state. This effect is well known from previous studies [41,42]. The comparison between the elastic and inelastic transmission probability in Fig. 2 demonstrates that even in the case of relatively weak electronic-vibrational coupling a theoretical treatment which only includes elastic processes provides a rather poor description. The wide-band approximation (thin dashed line), on the other hand, which takes the vibrational excitation into account but neglects the energy dependence of the width function, is seen to give an excellent description of the transmission probability. This is due to the fact that in model A the resonance is situated well inside the conduction band and, therefore, threshold effects are negligible.

The inclusion of the coupling to the vibrational bath (solid line) causes a further broadening and slight shift of the peaks belonging to the first and second excited vibrational level in the discrete electronic state. The main peak, which corresponds to tunneling through the ground vibrational state of  $\tilde{H}_d$ , on the other hand, remains almost unaffected. This is due to the fact that (in a zero-order picture without electronic coupling) the ground vibrational state of  $\tilde{H}_d$  is a stationary state, while all excited vibrational states decay into the ground state.

The result for the inelastic electron transmission including vibrational relaxation depicted in Fig. 2 has been obtained employing Eq. (33) which is only valid for zero bias. For situations with non-zero bias (in particular, to evaluate the current through the bridge), we will use the expansion of the total transmission probability in terms of the number of excitations in the final states of the bath, Eq. (27). It is therefore important to study the validity of this expansion. The results in Fig. 3 demonstrate that for the present example the expansion (27) is well converged if bath states with zero and one quantum of excitation ( $m = 0, 1$ ) are

taken into account.

Fig. 4 shows the current through the bridge as a function of the applied voltage for model A. The results have been obtained employing Eq. (20). As has been discussed in detail by other authors [79,80], each resonance peak in the transmission probability has its counterpart in a step in the current-voltage curve. Thereby, the steps occur in the order as they appear in the transmission probability counted from the zero-voltage Fermi energy (which is set to zero). Accordingly, the current based on the elastic treatment of the transmission (dotted line) exhibits only a single broad maximum corresponding to the position of the discrete electronic state. The inelastic current (thick dashed line), on the other hand, exhibits several steps which belong to the different vibrational peaks in the transmission probability. The wide-band approximation (thin dashed line) is seen to give very good results except at high voltages, where the resonances are closer to the edge of the conduction band and, therefore, the energy dependence of the width function becomes important.

Although there is a pronounced effect of the vibrational motion on the current in model A, the influence of the coupling to the bath (thick solid line) is rather small. This is a consequence of the location of the discrete electronic state, which is situated 0.5 eV above the Fermi energy in this model. As a result, the current for low voltages (0 – 1V) is almost exclusively due to tunneling of electrons via the resonance corresponding to the ground state of  $\tilde{H}_d$ , which is hardly affected by dissipation (cf. the discussion above).

If we change the discrete state energy to  $\epsilon_d = -0.5$  eV (Model B), the transmission functions, depicted in Fig. 5, remain virtually unchanged except for a shift in energy by 1 eV. In contrast, the current-voltage characteristic for Model B, shown in Fig. 6, is qualitatively different from that of Model A (cf. Fig. 4). The reason is that the order of the peaks as counted from the Fermi energy is reversed and therefore the low-voltage region of the current is influenced by tunneling through excited vibrational states of  $\tilde{H}_d$  which are more strongly affected by the presence of the bath. The current with and without vibrational relaxation thus differs by more than 50 % for voltages in the range 0.5 – 1 V.

The differences between the various levels of the theoretical treatment become more significant if we consider a model with larger coupling between the electronic and vibrational degrees of freedom. Such a situation is described by model C, where the vibrational frequency is chosen as  $\omega_S = 0.4$  eV and the vibronic coupling strength as  $\lambda = 0.7$  eV. The location of the discrete state is the same as in model A,  $\epsilon_d = 0.5$  eV. The transmission probability for model C is shown in Fig. 7. It is seen that the stronger vibronic coupling results in a pronounced vibrational progression in the transmission probability. In contrast to the cases considered above, the wide-band approximation essentially fails to describe the transmission probability. It predicts an amplitude which is too small by about a factor of two. Furthermore, the position of the peaks is not correctly described in the wide-band approximation due to the neglect of the level-shift function  $\Delta(E)$ , and the individual peaks in the numerically exact results are narrower than in the wide-band approximation. This effect of 'vibrational narrowing' is well-known from resonant electron-molecule scattering [77] and results from the interference between overlapping resonances.

The effect of vibrational relaxation on the transmission probability, illustrated in Fig. 8, also is much more pronounced in this model than in model A. Except for the lowest two peaks, the vibrational resonances are smeared into a broad hump, when vibrational dissipation is included. This is due to the fact that the vibrational relaxation process becomes more effective for higher excited vibrational states. Also shown in Fig. 8 is the expansion of the total transmission probability in terms of the number of excitations in the final state of the bath, Eq. (27). As a result of the importance of higher vibrational states and the relatively small electronic coupling to the leads, the expansion is seen to converge much slower than in the models considered above.

Let us next consider the current-voltage characteristic for model C, depicted in Fig. 9. It is seen that the coupling to the vibrational motion has a rather strong effect on the current through the bridge. In particular, the current-voltage characteristic exhibits step-like structures corresponding to the different vibrational levels in the discrete electronic state. As expected from the discussion of the transmission probability above, both the

elastic treatment and the wide-band approximation fail severely in the description of the current. Fig. 10 demonstrates that the coupling to the bath has a strong effect on the current-voltage characteristic in model C. In particular, the step-like structure is washed-out and the magnitude of the current decreases by more than a factor of two. Also shown in Fig. 10 is the contribution of the different terms in the expansion (27) to the total current. In contrast to the transmission probability, the expansion for the current converges relatively fast for this model. The reason for this at first sight surprising finding is that, due to the Pauli principle exclusion factors in the formula for the current, terms with a higher number of excitations in the final state of the bath are suppressed at lower voltage.

### B. Transmission through a bridge strongly coupled to the leads

All models considered so far were characterized by a relatively weak coupling of the discrete electronic state to the leads, which results in narrow resonance structures. In this section we shall consider the opposite limit of a localized state that is strongly coupled to the leads. Such a situation is realized in model D, where the coupling strength between the discrete electronic state and the leads is chosen as  $v = 1$  eV. The position of the discrete state is in the upper part of the conduction band,  $\epsilon_d = 1.6$  eV. All other parameters are the same as in Model C. We mention that if the coupling to the bath is not considered, model D is essentially equivalent to a model studied by Gelfand et al. [55] in the context of inelastic tunneling in heterostructures.

The results for the transmission probability are depicted in Fig. 11. The strong coupling to the leads results in a rather broad transmission probability, which is qualitatively well described taking into account only elastic processes. Vibrationally inelastic contributions to the transmission probability manifest themselves in various cusp structures. Thereby, each cusp indicates the opening of a new vibrational channel. It is well-known from the theory of electron-molecule scattering that the wide-band approximation is not at all applicable in this case. The effect of the coupling to the bath, which is well described including the

two lowest term in the expansion (27), is very small. This is a consequence of the strong electronic coupling which results in a very short residence time of the electron on the bridge.

Fig. 12 displays the current-voltage characteristic for model D. As to be expected from the transmission probabilities, the differences among the various levels of theory are small with the exception of higher bias voltages. For higher voltages, the elastic current vanishes due to the empty overlap of the left and right conduction bands. Inelastic transmission processes, however, which are accompanied by an energy loss of the electron, are still allowed.

Although there are no structures in the transmission probability in Fig. 11 which are obviously related to the position of the discrete electronic state, the location of this state does play an important role. This is demonstrated in Fig. 13, which shows the transmission probability for Model E, which differs from Model D only in a lower energy of the discrete electronic state,  $\epsilon_d = -0.7$  eV. This different location of the discrete state results in pronounced peaks and minima in the transmission function, which are somewhat smoothed, but not destroyed, by the coupling to the bath. To facilitate the interpretation of these structures, Fig. 14 shows the potential-energy curve of the discrete state (corresponding to  $\tilde{H}_d$ ) together with the energies of the vibrational states. In addition, the potential energy of  $\tilde{H}_0$  is shown, shifted by  $\pm 2$  eV, respectively, to indicate the energy which electrons coming from the conduction band may carry into the bridging molecule. Though the localized state is strongly coupled to the continuum, due to the shift of the two potential curves, the ground vibrational state in  $\tilde{H}_d$  has only a small overlap with the respective ground state in  $\tilde{H}_0$ . Consequently the coupling between the two states is effectively small and sharp resonances may be observed. If the discrete state is localized higher in energy (as in model D), the potential energy curve of  $\tilde{H}_d$  is shifted up. Then, the ground state of  $\tilde{H}_d$  still has a small overlap with the ground state of  $\tilde{H}_0$  but the decay into higher vibrational states becomes energetically possible. The sharp resonances thus "dissolve" in the continuum. As is demonstrated in Fig. 15, the sharp structures close to the bottom of the conduction band have no significant effect on the current, and the overall appearance of the current-voltage characteristic is similar as in model D.

## IV. CONCLUSIONS

In this paper we have studied vibrationally inelastic effects on electron transport through a molecular bridge that is connected to two metal leads. The study was based on a generic model for vibrational excitation in resonant electron transmission processes through a molecular junction. Employing projection-operator methods well-known from resonant electron-molecule scattering, we have outlined how the transmission probability can be evaluated numerically exactly within this model, without invoking the wide-band approximation or perturbation theory with respect to the coupling between the bridging molecule and the leads. Furthermore, the influence of dissipative vibrational processes was investigated by considering the coupling of a vibrational reaction mode to a dissipative bath.

The results of the model study can be summarized as follows: In the case of tunneling through a molecular bridge which is weakly coupled to the leads, the transfer of an electron may result in strong vibrational excitation, which manifests itself in pronounced vibrational resonance structures in the transmission probability and in a step-like appearance of the current-voltage characteristic. Since in this case the residence time of the electron on the molecular bridge is relatively long, dissipative processes such as vibrational relaxation can have a significant effect on the dynamics. In particular, they result in a broadening of the resonance peaks in the transmittance and of the step-like structures in the current-voltage characteristic. Furthermore, vibrational relaxation may result in this case in a significant reduction of the overall magnitude of the current. Due to the pronounced effects of the vibrational degrees of freedom, a theoretical treatment which only includes elastic processes is not appropriate in this parameter regime. Our studies also show that the wide-band approximation can only be applied if the electronic resonance state is situated well within the conduction band and the electron-vibrational coupling is weak.

In the opposite case of a molecular bridge that is strongly coupled to the leads, the transmission probability is typically characterized by a broad distribution, which in turn results in a rather structureless current-voltage characteristic. Nevertheless, the vibrational

motion may manifest itself in cusp structures in the transmittance. Furthermore, sharp resonance structures may occur in the transmission probability, if the energy of the discrete electronic state is low enough and the electronic-vibrational coupling sufficiently strong, such that the vibrational ground state of  $\tilde{H}_d$  has some overlap with lower-lying vibrational states of  $\tilde{H}_0$ . Except for the latter case, the effect of vibrational relaxation is very small in this parameter regime. The comparison of the results obtained at different levels of theory shows that methods which only include elastic processes can give a rather good qualitative description of the electron transport in this case, although they miss the detailed cusp and resonance structures. The wide-band approximation, on the other hand, is not valid in this parameter regime; due to the strong molecule-lead coupling, threshold effects become important which are neglected in the wide-band approximation.

To study the basic mechanisms of vibrationally inelastic electron transport, we have focused in this work on relatively simple models with a single harmonic reaction coordinate and a single electronic resonance state. It should be noted, however, that the methods employed in this work are not limited to these models. The extension of the theory to an anharmonic reaction coordinate, several reaction coordinates, and several resonance states is relatively straightforward. Also, it should be emphasized that the potential-energy surfaces of such models can in principle be determined *ab initio* by electronic structure calculations. In this way, for example, the possibility of dissociation of the molecular bridge induced by a strong current can be studied.

Finally, it is noted that in the present work the current through the molecular junction was obtained with the generalized Landauer formula, Eq. (20). Although this formula gives the correct description in the limit of weak coupling between molecule and leads as well as in the situation when only single-electron processes are important, it needs to be extended for applications where these assumptions are not fulfilled. A theoretical treatment of inelastic processes without these limitations is possible within the framework of non-equilibrium Green's function theory [74]. The combination of this formalism with the methods employed in this paper is a challenging subject for future research.

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## REFERENCES

- [1] M. A. Reed *et al.*, Science **278**, 252 (1997).
- [2] R. H. M. Smit, Y. Noat, C. Untiedt, N. D. Lang, M. C. van Hemert, and J. M. van Ruitenbeek, Nature **419**, 906 (2002).
- [3] J. Reicher, R. Ochs, H.B. Weber, M. Mayor, and H. von Lohneysen, Phys. Rev. Lett. **88**, 176804 (2002).
- [4] C. Joachim, J. K. Gimzewski, and A. Aviram, Nature **408**, 541 (2000).
- [5] A. Nitzan, Annu. Rev. Phys. Chem. **52**, 681 (2001).
- [6] F. Grossmann, R. Gutierrez, and R. Schmidt, Chem. Phys. Chem. **3**, 650 (2002).
- [7] A. Nitzan and M. A. Ratner, Science **300**, 1384 (2003).
- [8] S. Datta *et al.*, Phys. Rev. Lett. **79**, 2530 (1997).
- [9] E. G. Emberly and G. Kirczenow, Phys. Rev. B **58**, 10911 (1998).
- [10] W. Tian *et al.*, J. Chem. Phys. **109**, 2874 (1998).
- [11] M. Magoga and C. Joachim, Phys. Rev. B **56**, 4722 (1997).
- [12] M. Magoga and C. Joachim, Phys. Rev. B **57**, 1820 (1997).
- [13] M. Magoga and C. Joachim, Phys. Rev. B **59**, 16011 (1997).
- [14] F. Faglioni, C. L. Claypool, N. S. Lewis, and W. A. Goddard, J. Phys. Chem. **101**, 5996 (1997).
- [15] S. Larsson and A. Klimkans, Theochem. J. Mol. Struc. **464**, 59 (1999).
- [16] S. N. Yaliraki *et al.*, J. Chem. Phys. **111**, 6997 (1999).
- [17] N. D. Lang, Phys. Rev. B **52**, 5335 (1995).
- [18] K. Hirose and M. Tsukada, Phys. Rev. B **51**, 5278 (1995).

- [19] N. D. Lang and P. Avouris, Phys. Rev. Lett. **84**, 358 (2000).
- [20] M. Di Ventra, S. T. Pantelides, and N. D. Lang, Phys. Rev. Lett. **84**, 979 (2000).
- [21] V. Mujica, A. E. Roitberg, and M. A. Ratner, J. Chem. Phys. **112**, 6834 (2000).
- [22] R. Landauer, IBM J. Res. Dev. **1**, 223 (1957).
- [23] R. Landauer, Phys. Lett. A **85**, 91 (1981).
- [24] S. Datta, *Electric Transport in Mesoscopic Systems* (Cambridge University Press, 1995).
- [25] H. Park *et al.*, Nature **407**, 57 (2000).
- [26] M. Olson *et al.*, J. Phys. Chem. **B 102**, 941 (1998).
- [27] W. Schmickler, Chem. Phys. **289**, 349 (2003).
- [28] A. Troisi, M. A. Ratner, and A. Nitzan, J. Chem. Phys. **118**, 6072 (2003).
- [29] E. G. Emberly and G. Kirczenow, Phys. Rev. B **61**, 5740 (2000).
- [30] K. Walczak, arXiv: cond-mat/0306174 1 (2003).
- [31] D. Boese and H. Schoeller, Europhys. Lett. **54**, 668 (2001).
- [32] D. Fedorets, L. Y. Gorelik, R. I. Shekhter, and M. Jonson, Europhys. Lett. **58**, 99 (2002).
- [33] K. D. McCarthy, N. Prokof'ev, and M. T. Tuominen, Phys. Rev. B **67**, 245415 (2003).
- [34] D. Segal and A. Nitzan, J. Chem. Phys. **117**, 3915 (2002).
- [35] D. Segal, A. Nitzan, and P. Hänggi, J. Chem. Phys. **119**, 6840 (2003).
- [36] Z. G. Yu, D. L. Smith, A. Saxena, and A. R. Bishop, Phys. Rev. B **59**, 16001 (1999).
- [37] H. Ness and A. J. Fisher, Phys. Rev. Lett. **83**, 452 (1999).
- [38] F. I. Dalidchik, Sov. Phys. JETP **60**, 795 (1984).

- [39] J. A. Stovneng, E. H. Hauge, P. Lipavský, and V. Špička, Phys. Rev. B **44**, 13595 (1991).
- [40] K. Haule and J. Bonča, Phys. Rev. B **59**, 13087 (1999).
- [41] N. S. Wingreen, K. W. Jacobsen, and J. W. Wilkins, Phys. Rev. Lett. **61**, 1396 (1988).
- [42] N. S. Wingreen, K. W. Jacobsen, and J. W. Wilkins, Phys. Rev. B **40**, 11834 (1989).
- [43] B. N. J. Persson and A. Baratoff, Phys. Rev. Lett. **59**, 339 (1987).
- [44] N. Lorente and M. Persson, Phys. Rev. Lett. **85**, 2997 (2000).
- [45] C. Spataru and P. Budau, J. Phys.: Condensed Matter **9**, 8333 (1997).
- [46] M. A. Gata and P. R. Antoniewicz, Phys. Rev. B **47**, 13797 (1993).
- [47] A. Bringer, J. Harris, and J. W. Gadzuk, J. Phys.: Condensed Matter **5**, 5141 (1993).
- [48] M. Brandbyge and P. Hagedgaard, Phys. Rev. Lett. **72**, 2919 (1994).
- [49] S. Gao, M. Persson, and B. I. Lundqvist, Phys. Rev. B **55**, 4825 (1997).
- [50] M. A. Gata and P. R. Antoniewicz, Phys. Rev. B **60**, 8999 (1999).
- [51] G. J. Schulz, Rev. Mod. Phys. **45**, 423 (1973).
- [52] M. Allan, J. El. Spectrosc. **48**, 219 (1989).
- [53] W. Domcke, Phys. Rep. **208**, 97 (1991).
- [54] M. Čížek, J. Horáček, M. Allan, and W. Domcke, Czech. J. Phys. **52**, 1057 (2002).
- [55] B. Y. Gelfand, S. Schmitt-Rink, and A. F. J. Levi, Phys. Rev. Lett. **62**, 1683 (1989).
- [56] H. Feshbach, Ann. Phys. **19**, 287 (1962).
- [57] See, for example Ref. [5], page 724.
- [58] M. Thoss and W. Domcke, J. Chem. Phys. **109**, 6577 (1998).

- [59] C. Kerqueris *et al.*, Phys. Rev. B **59**, 12505 (1999).
- [60] M. Berman, C. Mündel, and W. Domcke, Phys. Rev. A **31**, 641 (1985).
- [61] E. N. Economou, *Green's Functions in Quantum Physics* (Springer-Verlag, 1983).
- [62] D. S. M C Desjonquères, *Concepts in Surface Physics* (Springer-Verlag, 1993).
- [63] J. B. Hopkins, D. E. Powers, and R. E. Smalley, J. Chem. Phys. **72**, 5093 (1980).
- [64] S. Mukamel and R. E. Smalley, J. Chem. Phys. **73**, 4156 (1980).
- [65] K. F. Freed and A. Nitzan, in: *Energy Storage and Redistribution in Molecules*, ed. J. Hinze (Plenum, New York, 1983), p. 467.
- [66] D. Gruner and P. Brumer, J. Chem. Phys. **94**, 2848 (1991).
- [67] T. Uzer, Phys. Rep. **199**, 124 (1991).
- [68] A. H. Zewail, *Femtochemistry—Ultrafast Dynamics of the Chemical Bond*, (World Scientific, Singapore 1994), Vol. II, p. 703.
- [69] D. J. Nesbitt and R. W. Field, J. Phys. Chem. **100**, 12735 (1996).
- [70] A. J. Leggett, S. Chakravarty, A. T. Dorsey, M. P. A. Fisher, A. Garg, and W. Zwerger, Rev. Mod. Phys. **59**, 1 (1987).
- [71] U. Weiss, *Quantum Dissipative Systems* (World Scientific, Singapore, 1999).
- [72] M. Wagner, Phys. Rev. Lett. **85**, 174 (2000).
- [73] M. Čížek, unpublished.
- [74] H. Haug and A. P. Jauho, *Quantum Kinetics in Transport and Optics of Semiconductors* (Springer-Verlag, 1998).
- [75] J. Horáček, J. Phys. B **28**, 1585 (1995).
- [76] M. Čížek, J. Horáček, and H.-D. Meyer, Comput. Phys. Communications **131**, 41 (2000).

- [77] W. Domcke and L. S. Cederbaum, *J. Phys. B* **14**, 149 (1980).
- [78] H.-D. Meyer, J. Horáček, and L. S. Cederbaum, *Phys. Rev. A* **43**, 3587 (1991).
- [79] A. Baratoff and B. N. J. Persson, *J. Vac. Sci. Technol. A* **6**, 331 (1988).
- [80] L. I. Glazman and R. I. Shekhter, *Sov. Phys. JETP* **67**, 163 (1988).

TABLES

Model	$\epsilon_d$	$v$	$\omega_S$	$\lambda$
A	0.5	0.2	0.5	0.3
B	-0.5	0.2	0.5	0.3
C	0.5	0.2	0.4	0.7
D	1.6	1	0.4	0.7
E	-0.7	1	0.4	0.7

TABLE I. Parameters for the different models considered. We have set  $\beta = 1$  eV in all cases, and  $\eta = 0.1$ ,  $\omega_C = \omega_S$  if the coupling to the dissipative bath is taken into account. Furthermore, the center of the conduction band is equal to Fermi energy  $\mu_{L/R} = \pm \frac{1}{2}V = \epsilon_F$  for the left and right lead respectively

## FIGURES

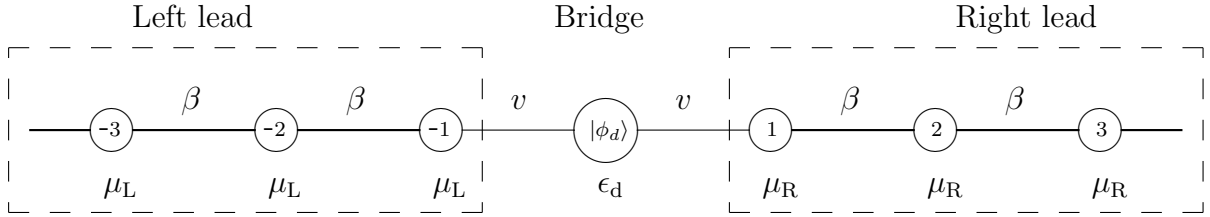


FIG. 1. Schematic representation of the tight-binding model used to parameterize the Hamiltonian, Eq. (1). The circles depict the atomic sites for the leads and the molecular site for the bridge (with energy written below) and the lines indicate the nonzero hopping amplitudes (written above).

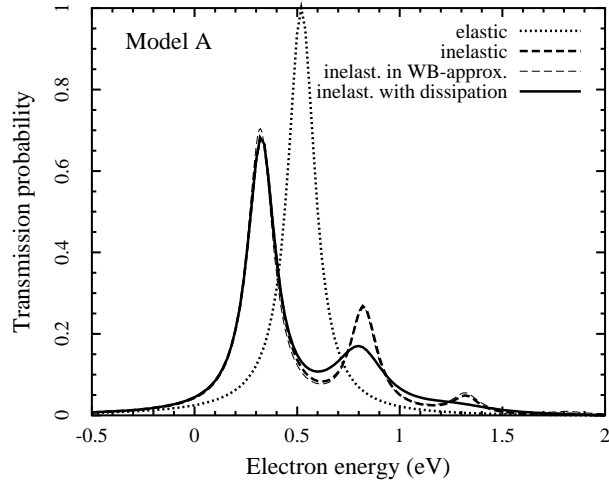


FIG. 2. Transmission probabilities for Model A at zero bias voltage. The results shown have been obtained at different levels of theory: purely elastic transmittance (dotted line), numerically exact inelastic transmittance (thick dashed line), inelastic transmittance in the wide-band approximation (thin dashed line). The full line depicts the inelastic transmission probability including vibrational relaxation.

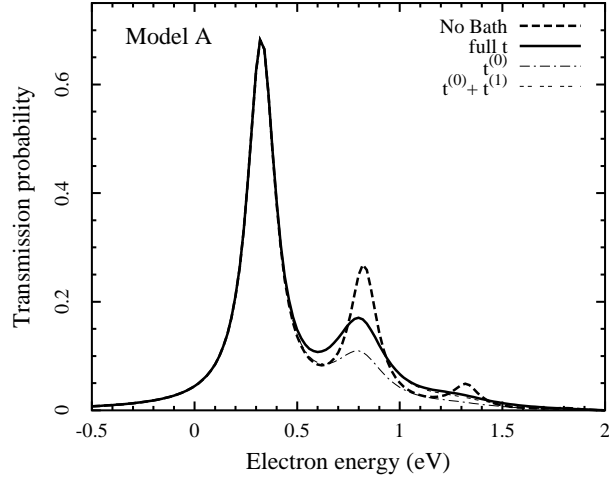


FIG. 3. Transmission probability for Model A as in Fig. 2. The different levels of approximation for the treatment of bath are shown together with exact result (solid line) and the result obtained without coupling to the bath (thick dashed line). The result including up to one quantum in the final state of the bath ( $t^{(0)} + t^{(1)}$ ) is indistinguishable from the exact result (full  $t$ ).

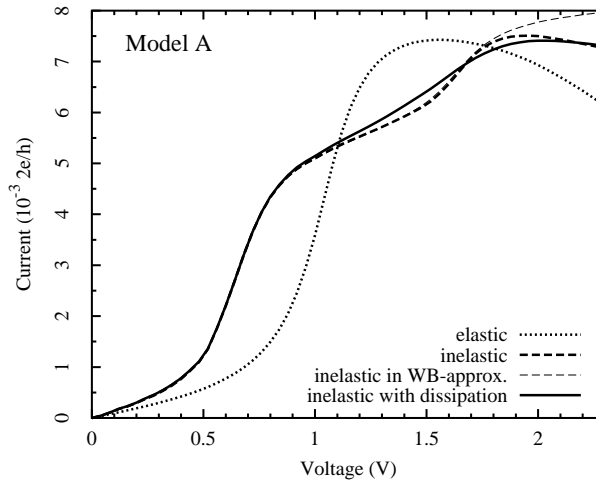


FIG. 4. Current-voltage characteristic for Model A obtained at different level of theory.



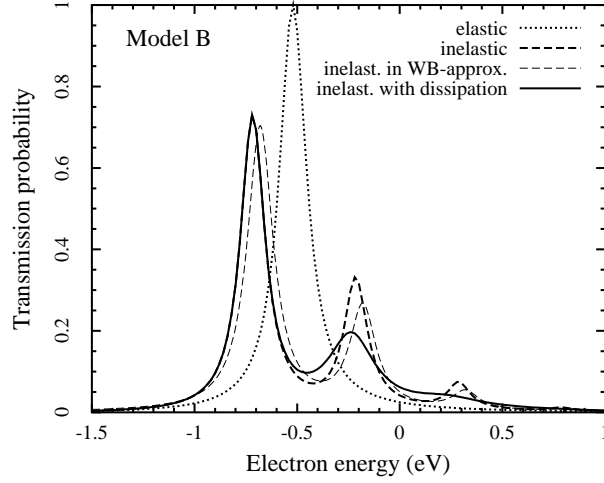


FIG. 5. Transmission probabilities for Model B at zero bias voltage. Shown are results obtained at different levels of theory as explained in the caption of Fig. 2.

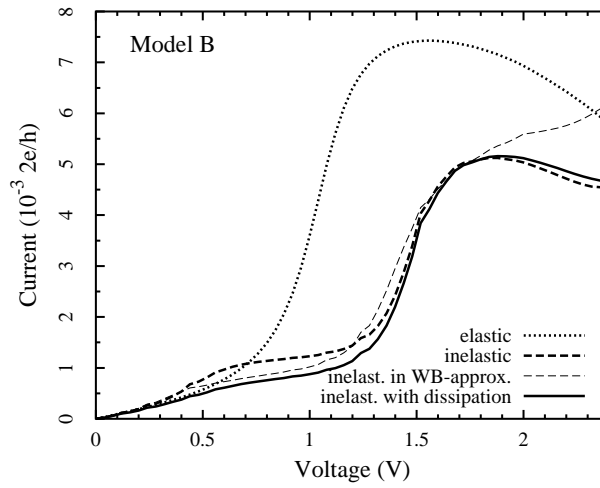


FIG. 6. Current-voltage characteristic for Model B. Shown are results obtained at different levels of theory.

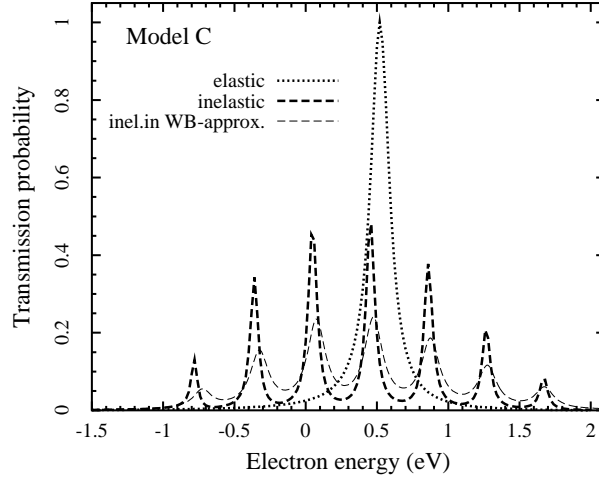


FIG. 7. Transmission probabilities for Model C at zero bias voltage. Shown are results obtained at different levels of theory.

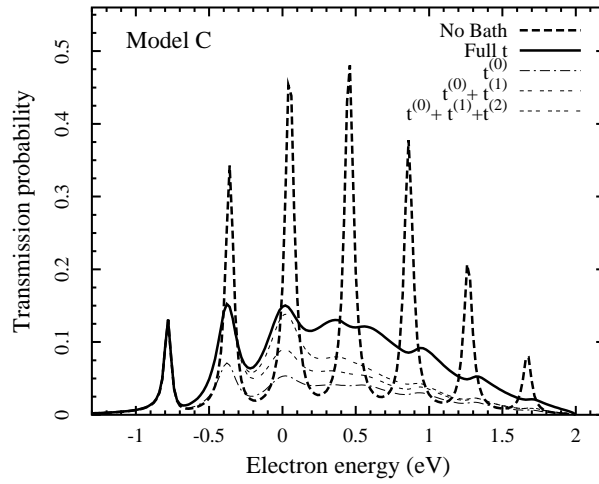


FIG. 8. Transmission probabilities for Model C at zero bias voltage. Shown are the numerically exact results for the inelastic transmittance with (thick dashed line) and without (full line) vibrational relaxation, as well as the convergence of the expansion with respect to the number of quanta in the final state of the bath (thin lines).

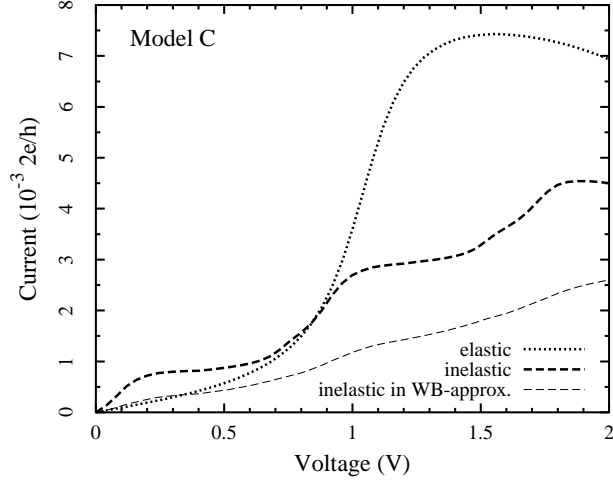


FIG. 9. Current-voltage characteristic for Model C. Shown are results obtained at different levels of theory as explained in the legend.

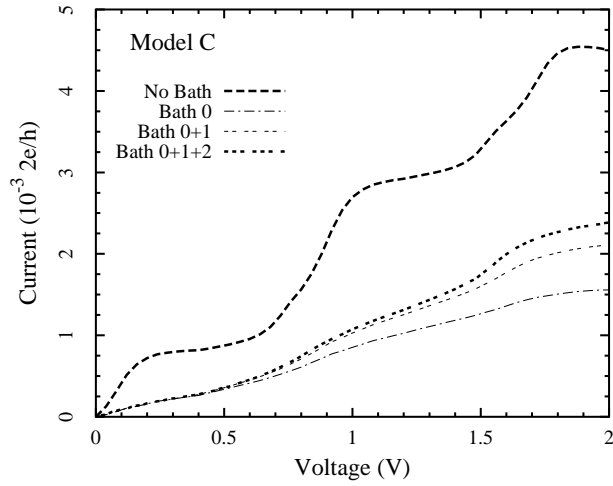


FIG. 10. Current-voltage characteristic for Model C. Shown are results that illustrate the convergence of the expansion with respect to the number of quanta in the final state of the bath, as well as the result without vibrational relaxation (thick dashed line)

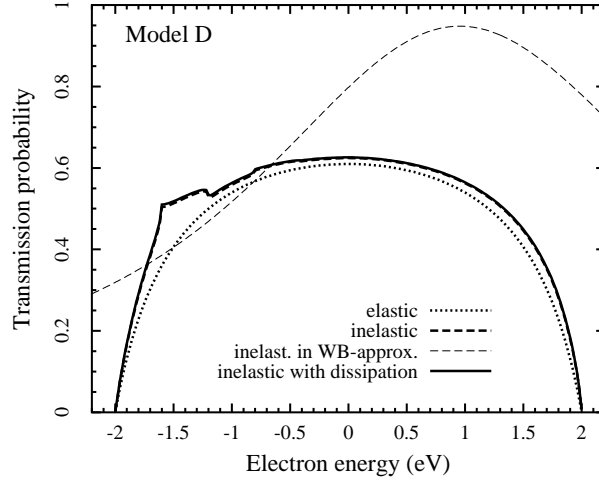


FIG. 11. Transmission probabilities for the case of a bridge strongly coupled to the leads (Model D) at zero bias voltage.

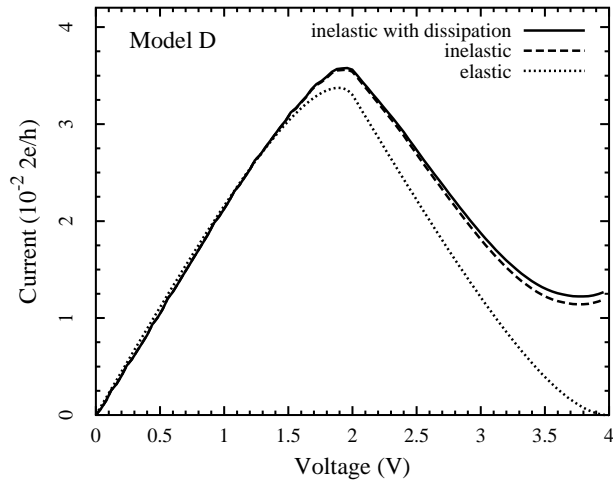


FIG. 12. Current-voltage characteristic for Model D.

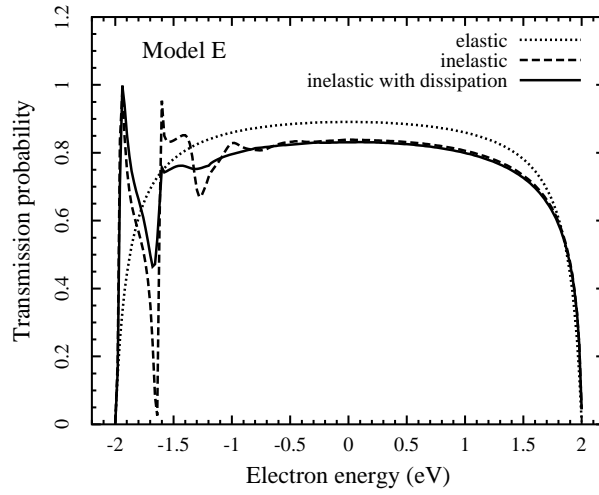


FIG. 13. Transmission probabilities for the case of a bridge strongly coupled to the leads (Model E) at zero bias voltage.

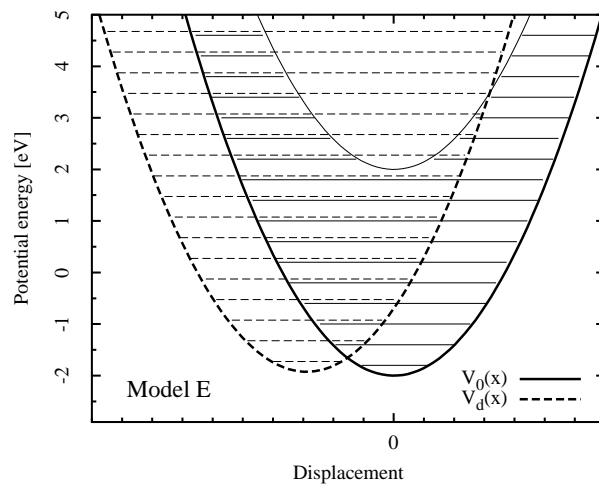


FIG. 14. Potential-energy curves for the interpretation of the vibrational structures in Model E (as explained in the text).

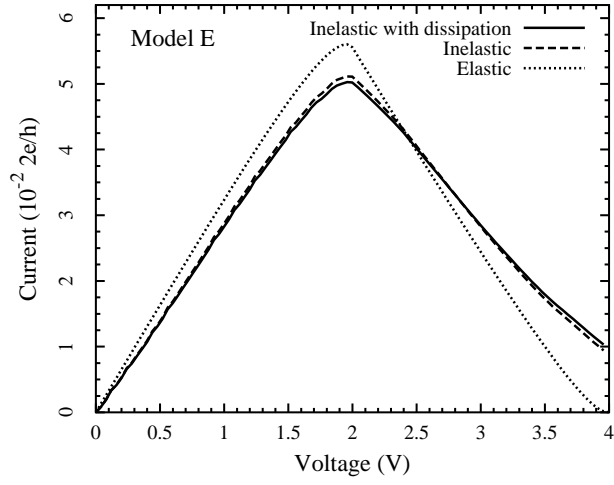


FIG. 15. Current-voltage characteristic for Model E