

Electron–vibration interaction in tunneling processes through single molecules

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Abstract. It is shown how effective Hamiltonians are constructed in the framework of the adiabatic approach to the electron–vibration interaction in electron tunneling through single molecules. Methods for calculating tunneling characteristics are discussed and possible features resulting from the electron–vibration coupling are described. The intensity of vibrations excited by a tunneling current in various systems is examined.

1. Introduction

There are various experimental systems for studying a tunneling current flowing through single molecules. First, this is true in regard to the investigation of molecules adsorbed on a surface of various materials by the scanning tunneling microscopy/spectroscopy (STM/STS) methods [1–3]. Second, the experiments are being conducted in which molecules are deposited from gas of very low density onto the area of a break tunneling junction [4, 5]. Third, recently it has become possible to ‘drag’ metal atomic chains through the contact from one lead to another [6, 7]. Such an atomic chain

can also be considered a linear molecule which carries a tunneling current.

When a current flows in such systems, their current–voltage characteristics exhibit peculiarities at voltages equal to the energies of vibrational modes.

In one of first studies on inelastic effects in molecules adsorbed on a surface by the STM/STS methods, peculiarities of the tunneling conductance spectra of $^{16}\text{O}_2$ and $^{18}\text{O}_2$ molecules were observed. In Fig. 1 taken from Ref. [1], one can see that for different isotopes the peculiarities arise at different voltages, and for $^{18}\text{O}_2$ the peculiarities are shifted to lower energies. Such a shift is additional evidence that the peculiarities are related precisely to oxygen atom vibrations in a molecule.

The shape of peculiarities observed in tunneling conductance is not a universal characteristic. It may vary upon changing the contact parameters, which has been demonstrated in a series of experiments. In Ref. [8], copper phthalocyanine molecules deposited onto varied-thickness oxide layers grown on an NiAl surface were studied by the STM method. The variation of the oxide layer thickness resulted in a relative change in the rates of the molecule–substrate and molecules–STM tip tunneling transitions. In this case, the shape of the peculiarities related to molecular vibrations noticeably changed.

In relatively recent study [9] on another organic molecule on a silver surface, the tunneling spectra were recorded by means of STM/STS for various distances between the tip of the tunneling microscope and the molecule. One can see in Fig. 2 taken from this study that the peculiarities related to different molecular vibrations (indicated by different letters in the figure) change shape when contact parameters vary (in the figure, different distances between the tip and molecule correspond to different values of current at a certain reference voltage). The positions of peculiarities very well

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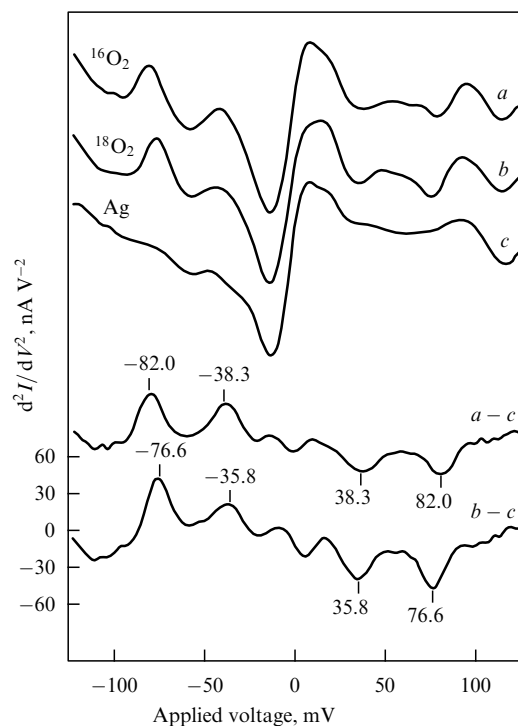


Figure 1. Spectra of the tunneling conductance from Ref. [1] for molecules $^{16}\text{O}_2$ ($a-c$ —with subtracted background) and $^{18}\text{O}_2$ ($b-c$ —with subtracted background) studied by the STM/STS method. The peculiarities corresponding to molecular vibrations are marked.

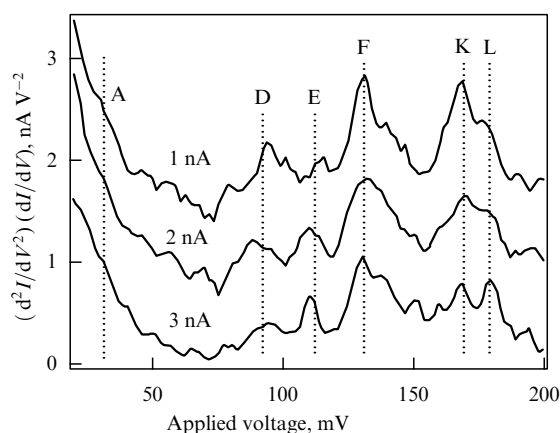


Figure 2. Tunneling spectra from Ref. [9] for various distances between the tip of a tunneling microscope and an organic molecule. The peculiarities related to various molecular vibrations (marked by letters) change shape when varying the contact parameters.

agreed with the corresponding vibration frequencies of the molecule, obtained by the EELS (Electron Energy Loss Spectroscopy) method.

In electron tunneling through atomic chains between two contact leads, an electron–phonon interaction usually results in a reduction in the tunneling conductance. It is manifested by a ‘step-down’ arising in the tunneling spectra at those voltages corresponding to the chain phonon frequencies. One such typical characteristic [7] is shown in Fig. 3. The position of the peculiarity shifted as the chain, made from gold atoms, was stretched (different curves correspond to different stretching), which reveals the frequency change under stretching.

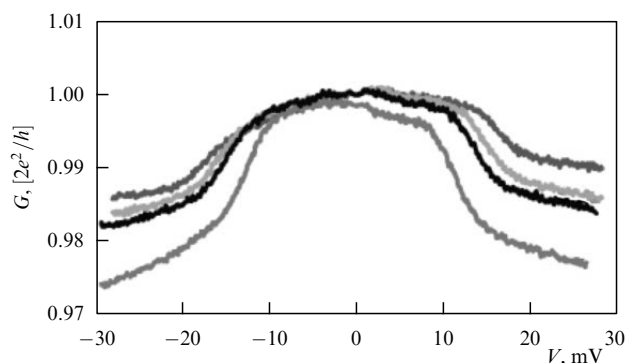


Figure 3. Tunneling conductance of an atomic chain (taken from Ref. [7]).

Due to electronic–vibrational interaction, current flow is also accompanied by the excitation of vibrations—that is, nonequilibrium heating of the system. Since the system is strongly nonequilibrium, the most appropriate theoretical description of all such phenomena leans upon the diagram technique for nonequilibrium processes. The technique allows considering, on a common basis, both the tunneling current variation and the excitation of molecular vibrations due to interaction. To apply the nonequilibrium diagram technique ‘automatically’, first it is necessary to determine what is the operator of electron–vibrational mode interaction in such problems? Generally, the choice of the most appropriate model depends on the particular system under consideration. However, the adiabatic approach to separation of a complete Hamiltonian into the parts describing the electronic and vibrational degrees of freedom and their interaction remains to be, in our opinion, the most consistent. The difficulties arising in realizing this program we shall consider by the example of the simple model [10–13] in which only one electron energy level of a small molecule (an electronic state) is taken into account under the assumption that the rest are far away in energy and do not fit into the voltage range of interest.

It should be noted that we shall sometimes call vibrational degrees of freedom in molecules phonons, and an interaction of electrons with vibrational modes will be referred to as an electron–phonon interaction.

2. Interaction of electrons with vibrational modes in the model of a molecule with a single electronic state

For simplicity, let us consider a diatomic molecule residing between the two leads of a tunneling contact (see Fig. 4). The complete description of all states in such a molecule in the framework of the adiabatic approach [14] is made in two stages. First, the electronic states should be found, which are determined by the Hamiltonian dependent on the interatomic separation (ion positions) as a parameter.

The energies $\varepsilon_i(R)$ of these electronic states are functions of interatomic separation R (assuming that the Coulomb interaction inside the molecule is implicitly included in the definition of electron energy $\varepsilon_i(R)$, and electron spin is insignificant for the electron interaction with vibrational modes). If the occupation of only a certain electronic state ε_1 in the molecule is changed in the process of tunneling, then the Hamiltonian of an isolated molecule in the interaction representation can be written out in the form (hereinafter

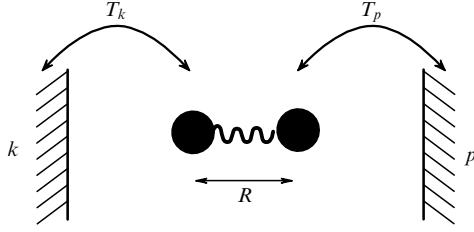


Figure 4. Schematic diagram of a tunneling contact with a diatomic molecule.

the Planck constant is assumed to be unity, $\hbar = 1$):

$$\hat{H} = a_1^\dagger a_1 \left[-\frac{1}{2M} \frac{\partial^2}{\partial R^2} + W_1(R) \right] + (1 - a_1^\dagger a_1) \left[-\frac{1}{2M} \frac{\partial^2}{\partial R^2} + W_0(R) \right], \quad (1)$$

where a_1 is the electron annihilation operator for the localized molecular state with the energy ε_1 , $W_1(R)$, and $W_0(R)$ are the effective potentials of ions, corresponding to the occupied and empty electronic state ε_1 , respectively:

$$W_1(R) = V_{\text{ion}}(R) + E_e(R) + \varepsilon_1(R), \\ W_0(R) = V_{\text{ion}}(R) + E_e(R). \quad (2)$$

Here, $V_{\text{ion}}(R)$ is the potential energy for the direct (Coulomb) interaction of ions, and $E_e(R)$ is the energy of all occupied electron states except for the state ε_1 . In the harmonic approximation, atoms vibrate around the equilibrium state determined by a minimum of effective potential $W(R)$. Since we have two different potentials for the occupied and empty states, two sets of oscillatory wave functions arise, which describe the atomic vibrations around *different* equilibrium positions with, generally speaking, *different* frequencies. At a small number of electrons, a change in the occupation of even a single electronic state may substantially affect both the nucleus equilibrium positions and vibrational frequencies. For the occupied (empty) state ε_1 , the equilibrium position $R_{1(0)}$ is determined by the condition $\partial W_{1(0)}(R)/\partial R|_{R_{1(0)}} = 0$, and the square of a vibrational frequency is $\omega_{1(0)}^2 \propto \partial^2 W_{1(0)}(R)/\partial R^2|_{R_{1(0)}}$. The eigenfunctions $\Phi_v^{1(0)}(R) = \Phi_v(R - R_{1(0)})$ are conventional wave functions for an oscillator with frequencies $\omega_{1(0)}$.

We may introduce in the usual way the creation and annihilation operators b^+ and b^- for describing the motion of nuclei in the potential W_0 , corresponding to the state for unoccupied level ε_1 , in the harmonic approximation:

$$R - R_0 = \sqrt{\frac{1}{2M\omega_0}} (b + b^+), \quad \frac{\partial}{\partial R} = \sqrt{\frac{M\omega_0}{2}} (b - b^+),$$

where $M\omega_0^2 = \partial^2 W_{(0)}(R)/\partial R^2|_{R_{(0)}}$.

When describing an oscillatory motion of atoms in the potential W_1 in the language of secondary quantization, it is necessary to employ other operators b_1^+ and b_1 :

$$R - R_1 = \sqrt{\frac{1}{2M\omega_1}} (b_1 + b_1^+), \quad \frac{\partial}{\partial R} = \sqrt{\frac{M\omega_1}{2}} (b_1 - b_1^+),$$

where $M\omega_1^2 = \partial^2 W_{(1)}(R)/\partial R^2|_{R_{(1)}}$.

It turns out that unified operators can also be introduced, which describe a creation and annihilation of vibrational

quanta in both cases in the following way. Let us introduce the transformation of the b^+ and b operators by means of the unitary operator U :

$$\tilde{b} = UbU^{-1}, \quad \tilde{b}^+ = Ub^+U^{-1}, \quad (3)$$

where

$$U = \exp [\lambda a_1^\dagger a_1 (b - b^+)] \exp [\theta a_1^\dagger a_1 (bb - b^+b^+)]. \quad (4)$$

The new \tilde{b}^+ and \tilde{b} operators (3) coincide with operators b^+ and b in their action on the state with $n_1 = 0$, and with operators b_1^+ and b_1 in their action on the state with $n_1 = 1$ if the parameters λ and θ are chosen as follows:

$$\lambda = \sqrt{\frac{M\omega_0}{2}} (R_0 - R_1), \quad \theta = \frac{1}{2} \ln \beta, \quad \beta^2 = \frac{\omega_1}{\omega_0}. \quad (5)$$

Transformation U (4) has a clear physical meaning in the language of transformations of oscillatory wave functions. The first exponent in formula (4), $\exp [(R_1 - R_0) \partial/\partial R] \times \Phi_v^0(R)$, describes a shift of a wave function from the equilibrium position R_0 to the position R_1 . The second part of the transformation is responsible for coordinate contraction or expansion in the wave function due to the changed curvature of potential W_1 as compared to potential W_0 :

$$\Phi_v^1(R) = \sqrt{\beta} \exp \left[(R_1 - R_0) \frac{\partial}{\partial R} \right] \times \exp_x \left[(\beta - 1)(R - R_0) \frac{\partial}{\partial R} \right] \Phi_v^0(R), \quad (6)$$

where $\beta = \sqrt{\omega_1/\omega_0}$, and the notation \exp_x means that in expanding the exponent in a power series all the differential operators should be placed to the right of the coordinate operators.

In an explicit form, transformation (3) is given by

$$\tilde{b} = v_1 b + v_2 b^+ + \beta \lambda a_1^\dagger a_1, \quad (7)$$

where

$$v_1 = (1 - a_1^\dagger a_1) + \cosh(2\theta) a_1^\dagger a_1, \quad v_2 = \sinh(2\theta) a_1^\dagger a_1. \quad (8)$$

In order to independently describe electronic and vibrational degrees of freedom (by commutative operators), it is necessary to pass on to new electron coordinate operators by using the same transformation U simultaneously with the introduction of the \tilde{b} operators:

$$\tilde{a}_1 = U a_1 U^{-1}. \quad (9)$$

Since $a_1^\dagger a_1$ commute with the transformation operator U , this combination remains invariant: $\tilde{a}_1^\dagger \tilde{a}_1 = a_1^\dagger a_1$. Thus, we can immediately express the electron operators in initial Hamiltonian (1) in terms of the new operators $\tilde{a}_1^\dagger \tilde{a}_1$ and describe nucleus vibrational motion by introducing in a unified manner the operators \tilde{b} for both the occupied and empty electronic states.

In this way, the Hamiltonian of an isolated molecule in the secondary quantization representation can be expressed in the form

$$H_0 = \varepsilon_1 \tilde{a}_1^\dagger \tilde{a}_1 + \omega_0 \tilde{b}^+ \tilde{b} + (\omega_1 - \omega_0) \tilde{a}_1^\dagger \tilde{a}_1 \tilde{b}^+ \tilde{b}, \quad (10)$$

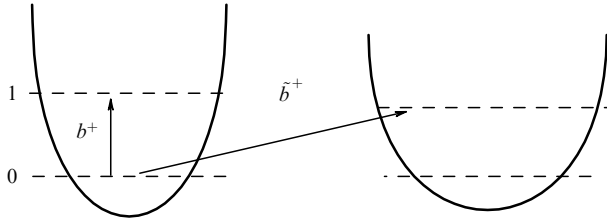


Figure 5. Definition of the creation operators for the vibrational quantum of an ordinary oscillator (b^+) and of an oscillator with a changed equilibrium position and frequency (\tilde{b}^+).

where the energy of an electronic state, $\tilde{\varepsilon}_1 = W_1(R_1) - W_0(R_0) + (\omega_1 - \omega_0)/2$, does not coincide in the general case with $\varepsilon_1(R_1)$ (the constant contribution $W_0(R_0) + \omega_0/2$ was omitted).

Notice that the term comprising the product of electron and phonon occupation numbers in Hamiltonian (10) has no meaning with regard to electron–phonon interaction, i.e., it does not lead to phonon emission or absorption. It only reflects the fact that the vibrational frequencies vary with a change in electron occupation numbers.

The description in terms of transformed operators has a clear physical meaning. Whereas operator b^+ was responsible for the transition to the next excited state in the initial oscillator, operator \tilde{b}^+ describes the transition to the next excited state even if the oscillator equilibrium position and its frequency have changed. It is schematically shown in Fig. 5. Thus, operator \tilde{b}^+ , in contrast to b^+ , describes just the oscillator excitation, regardless of whether the oscillator and its frequency have shifted or not. This is a ‘correct’ operator governing the excitation of a molecule vibrational subsystem.

As for the new electron creation operator \tilde{a}_1^+ , its action results in the origin of an electron in the state with the wave function $\psi_1(R, r)$ and the simultaneous *change of an ion subsystem wave function*. If the initial state comprised neither electron nor excited vibrations, then the wave function of the state was $\Phi_0^0(R)$. The action of operator \tilde{a}_1^+ transfers the initial state to another: $\Phi_0^0(R) \rightarrow \Phi_0^1(R) \psi_1(R, r)$. That is, in multiplying the system wave function by the wave function of the electron in state ‘1’, the oscillator wave function simultaneously is transferred to the wave function of a shifted oscillator. An action of the ‘correct’ operator \tilde{a}_1^+ results in the appearance of the electron *keeping the vibrational system on the same oscillatory level* regardless of the oscillator displacement due to the added electron.

In the presence of tunneling transitions between the molecular electronic states and contact leads, the part of the Hamiltonian describing the electron transitions from the molecule to a contact lead has the form

$$H_{\text{tun}} = T_{k,1}(R) c_k^+ a_1 + \text{h.c.} \quad (11)$$

The operators c_k correspond to the electronic states at the contact leads, and $T_{k,1}(R)$ is the overlap integral between the electron state with the momentum k at the contact lead and the molecular electronic state, which, naturally, depends on the positions of the atoms in the molecule. Hence, with allowance made for molecular vibrations, the tunneling matrix element will also be modulated with these vibrations. To describe this modulation, we may expand the matrix element $T_{k,1}(R)$ in a power series of displacement $R - R_1$ from the equilibrium position R_1 (we shall show in the

Appendix that the expansion in a power series of displacement $R - R_0$ from another equilibrium position R_0 results in the same final formulae for the tunneling Hamiltonian):

$$\begin{aligned} T_{k,1}(R) &= \exp \left[(R - R_1) \frac{\partial}{\partial R} \right]_{R_1} T_{k,1}(R) \\ &= T_{k,1}(R_1) + (R - R_1) \frac{\partial}{\partial R} \bigg|_{R_1} T_{k,1}(R) + \dots \quad (12) \end{aligned}$$

By expressing the displacement $R - R_1$ in the standard way via the creation and annihilation operators of vibrational quanta, we obtain one type of interaction between electrons and phonons in tunneling transitions. In addition, since the number of electrons in the molecule changes under the action of Hamiltonian (11), the state of the whole electron–ion system also changes, and we have to express the electron operators a_1 in Hamiltonian (11) via ‘correct’ electron operators (9). The complete Hamiltonian for the interaction between electrons and phonons in the tunneling process is thoroughly derived in the Appendix. A general cumbersome expression comprises three parameters which in many cases may be assumed to be small: θ , λ (5), and the parameter $\alpha_{k,p}$ defined as follows:

$$\alpha_{k,p} = \sqrt{\frac{\hbar}{2M\omega_1}} \frac{1}{T_{k,p}} \frac{\partial}{\partial R} T_{k,p} \bigg|_{(R_1+R_0)/2}.$$

Assuming all three parameters are small, we may restrict ourselves to only the first terms in expanding all the quantities in general formula (86) (see the Appendix) in a power series of these parameters. Then, the first-order tunneling Hamiltonian with respect to all the parameters takes the form

$$\begin{aligned} H_{\text{tun}} &= T_{\mathbf{k}}(c_{\mathbf{k}}^+ a_1 + \text{h.c.}) + T_{\mathbf{p}}(c_{\mathbf{p}}^+ a_1 + \text{h.c.}) \\ &+ \alpha_{\mathbf{k}} T_{\mathbf{k}}(b^+ + b)(c_{\mathbf{k}}^+ a_1 + a_1^+ c_{\mathbf{k}}) + (\mathbf{k} \rightarrow \mathbf{p}) \\ &+ \lambda \beta T_{\mathbf{k}}(b - b^+)(c_{\mathbf{k}}^+ a_1 - a_1^+ c_{\mathbf{k}}) + (\mathbf{k} \rightarrow \mathbf{p}) \\ &+ \theta T_{\mathbf{k}}(bb - b^+ b^+)(c_{\mathbf{k}}^+ a_1 - a_1^+ c_{\mathbf{k}}) + (\mathbf{k} \rightarrow \mathbf{p}), \quad (13) \end{aligned}$$

where the tunneling matrix element corresponds to the position of atoms at the distance $(R_1 + R_0)/2$, namely, $T_{\mathbf{k}} = T_{\mathbf{k}}((R_1 + R_0)/2)$.

The three contributions to an electron–phonon interaction arising in tunneling are responsible for different physical effects. The contribution connected with the term $\alpha_{k,p}$ describes the processes of phonon (vibration) emission or absorption when the electron tunnels between the contact leads and the molecule due to the modulation of the tunneling matrix elements with atomic vibrations. At the same time, the part related to the constant λ arises due to the adiabatic change of the distance between atoms in the molecule, which transfer to new positions corresponding to a minimum energy at different electron densities. It should be noted that these two interaction types do not act ‘additively’ and cannot be combined to a single interaction with a summarized coupling constant. The interaction with the constant θ describes those effects related to changes in molecular vibrational frequency under a changed number of electrons in the molecule.

In order to determine the limits of applicability for the power series expansion of the general expression for the tunneling Hamiltonian, it is necessary to estimate how small the constants θ , λ , and α are. In real molecules, the constant θ

can always be considered a small parameter because, even if the vibrational frequency changes twice in adding an electron, one has $\theta \simeq 0.15$ [see definition (5)]. This parameter is the smallest one, and in what follows we shall not make allowance for the interaction related with the last term in Hamiltonian (13).

For the constant $\alpha_{k,p}$, the following estimate is valid. Assuming an exponential dependence of tunneling matrix elements on the distance, viz. $T(R) \simeq T_0 \exp(-\delta R/a)$, we obtain $\alpha_{k,p} \simeq (m/M)^{1/4}(a_0/a)$, where a_0 is the Bohr radius. The characteristic value of this constant equals approximately 0.1. To find the constant λ , it is necessary to estimate the equilibrium distance variation $\Delta R_{10} = R_1 - R_0$. In view of initial expressions (1) and (2), we arrive at the estimate

$$\Delta R_{10} \simeq \frac{\partial \varepsilon_1 / \partial R}{\partial^2 (V_{\text{ion}}(R) + E_c(R)) / \partial R^2} \simeq \frac{a_{\text{int}}^2}{Z a_0},$$

where a_{int} is the characteristic scale of localization for inner electronic states, a_0 is the radius of the state ε_1 , and Z is the number of occupied electronic states. This yields the estimate for the constant $\lambda \simeq (M/m)^{1/4} a_{\text{int}}^2 / (Z a_0^2)$. For light molecules like H_2 , the constant is $\lambda > 1$. For such molecules, a passage considered to a simple first-order expression in terms of the interaction constants (13) is inapplicable. It is necessary to use the exact expression for the tunneling Hamiltonian (see formula (86) in the Appendix). Nevertheless, expression (13) can be applied to the molecules comprising at least 6–8 electrons.

Thus, the Hamiltonian of an isolated molecule is given by formula (10), and the electron transitions between the molecule and contact leads are described by Hamiltonian (13). In Section 3, we shall consider the case where tunneling transitions weakly affect the electronic states of the molecule.

3. Influence of electron–vibrational mode interaction on tunneling characteristics

To completely describe the whole tunneling system, we should add the Hamiltonian describing the electrons in the contact leads to the Hamiltonian of the molecule. In the former Hamiltonian, the voltage V applied to the contact is included in the shift of the chemical potential of electrons in a contact lead:

$$\hat{H}_0 = \sum_{\mathbf{k}} (\varepsilon_{\mathbf{k}} - \mu) c_{\mathbf{k}}^{\dagger} c_{\mathbf{k}} + \sum_{\mathbf{p}} (\varepsilon_{\mathbf{p}} - \mu - eV) c_{\mathbf{p}}^{\dagger} c_{\mathbf{p}}. \quad (14)$$

The tunneling current operator is determined in the standard way from the continuity equation:

$$I = e \dot{N}_k = -ie [N_k, H_{\text{tun}}],$$

where N_k is the number of electrons in a contact lead. In the subsequent calculations, a current will be measured as the number of electrons per second — that is, the electron charge will be assumed to be unity ($e = 1$). For Hamiltonian (13), the tunneling current is determined by the following expression

$$I = iT_{\mathbf{k}} \sum_{\mathbf{k}} (\langle c_{\mathbf{k}}^{\dagger} a_1 \rangle - \langle a_1^{\dagger} c_{\mathbf{k}} \rangle) + iT_{\mathbf{k}} \sum_{\mathbf{k}} \left[\left\langle \left((\alpha_{\mathbf{k}} + \lambda) b + (\alpha_{\mathbf{k}} - \lambda) b^{\dagger} \right) c_{\mathbf{k}}^{\dagger} a_1 \right\rangle - \text{h.c.} \right]. \quad (15)$$

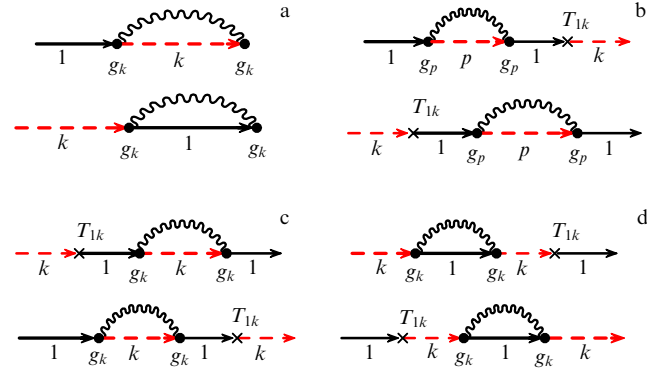


Figure 6. Diagrams determining first-order tunneling current with respect to g^2 , where $g = (\lambda, \alpha)$. Dashed lines correspond to the Green functions of contact leads, and solid lines correspond to the Green functions of electrons in a molecule. Wavy lines depict the specially defined phonon Green functions.

A conventional tunneling current is given by the first contribution to formula (15) if allowance is only made for direct tunneling processes without atomic vibrations. However, if the electron–phonon interaction is taken into account, this contribution also changes and results in a change in total current, as does the contribution from the second group of terms which comprise the electron–phonon interaction constants λ and α in an explicit form. In calculating the current by formula (15) according to the perturbation theory with respect to electron–phonon interaction (13) for a lower-order interaction we arrive at the set of diagrams shown in Fig. 6. The diagrams describe a set of appropriate Green functions with the index ‘<’ in the Keldysh diagram technique and are calculated by ordinary rules. The only distinction from the standard rules is that we have to modify the standard definition of the phonon Green function. Since the phonon operators enter into two interaction terms in Hamiltonian (13) in different combinations, it is convenient to define two phonon Green functions in the following way:

$$\begin{aligned} D^{(-)}(t, t') &= -i \langle T b(t) b^{\dagger}(t') \rangle, \\ B^{(-)}(t, t') &= -i \langle T b(t) b(t') \rangle, \\ B^{+(-)}(t, t') &= -i \langle T b^{\dagger}(t) b^{\dagger}(t') \rangle. \end{aligned} \quad (16)$$

The function B^+ is not independent because it is related with the function B by an obvious relationship:

$$B^+(t, t') = -[B(t', t)]^*,$$

which holds true for all Keldysh components. These anomalous functions, as well as the functions D , satisfy all standard relationships between different components, such as the followings:

$$\begin{aligned} B^{--}(t, t') &= B^{<}(t, t') + B^r(t, t'), \\ B^{<}(\Omega) &= iN(\Omega) \text{Im} B^r(\Omega) \end{aligned} \quad (17)$$

(the superscript ‘r’ stands for ‘retarded’). In averaging over the equilibrium state, the functions B become zero, but as soon as a current arises or the system is disturbed from a thermodynamic equilibrium in some other way, these averages become nonzero.

In the general case, the equilibrium functions D_0 determined by Hamiltonian (10) take into account a variation of vibrational frequency in changing the number of electrons on a molecule:

$$D^r(\Omega) = \frac{1 - n_1}{\Omega - \omega_0 + i\delta} + \frac{n_1}{\Omega - \omega_1 + i\delta}, \quad (18)$$

$$D^<(\Omega) = 2iN(\Omega) \operatorname{Im} D^r(\Omega) \\ = -i2\pi N(\Omega) [(1 - n_1)\delta(\Omega - \omega_0) + n_1\delta(\Omega - \omega_1)]. \quad (19)$$

Each vertex in the diagrams shown in Fig. 6 comprises the sum over the interaction types (α, λ) with the same combination of electron operators. This results in the following effective phonon Green function which should be put into correspondence to each wavy line in the diagrams:

$$\begin{aligned} \tilde{D}(t, t') &= \alpha^2 [D(t, t') + D(t', t) + B^+(t, t') + B(t, t')] \\ &+ \lambda^2 [D(t, t') + D(t', t) - B^+(t, t') - B(t, t')] \\ &- 2\alpha\lambda [D(t, t') - D(t', t)] \\ &= (\alpha - \lambda)^2 D(t, t') + (\alpha + \lambda)^2 D(t', t) \\ &+ (\alpha^2 - \lambda^2) (B^+(t, t') + B(t, t')), \end{aligned} \quad (20)$$

where α equals α_p or α_k , depending on which tunneling vertices the phonon line connects to. This is the most general expression in the nonequilibrium case. However, it was shown in paper [15] that the contribution from anomalous functions can be neglected in most cases when studying characteristic properties of a current.

In this case, relationship (20) shows that effective phonon functions may be introduced, which are specific in the interaction with each lead of the contact. Such a function is defined in the Fourier representation as follows:

$$\begin{aligned} \tilde{D}_p^r(\Omega) &= (\alpha_p - \lambda)^2 D^r(\Omega) + (\alpha_p + \lambda)^2 D^a(-\Omega), \\ \tilde{D}_p^<(\Omega) &= (\alpha_p - \lambda)^2 D^<(\Omega) + (\alpha_p + \lambda)^2 D^>(-\Omega) \end{aligned} \quad (21)$$

(the superscript ‘a’ stands for ‘advanced’). We may do the same with D_k . Using the expressions for equilibrium functions (18) we conclude that functions $\tilde{D}^<$ and \tilde{D}^r are again interrelated by the standard relationships

$$\tilde{D}^<(\Omega) = 2iN(\Omega) \operatorname{Im} \tilde{D}^r(\Omega).$$

From expressions (21) one can see that if a certain type of electron–phonon interaction prevails, i.e., $\lambda \ll \alpha$ or $\lambda \gg \alpha$, then we again return to the standard definition of the Green functions for electron–phonon interaction, based on the symmetric mean: $\mathcal{D} = -i\langle T(b(t) + b^+(t))(b(t') + b^+(t')) \rangle$. In the general case, an interference between two interaction channels (with the constants λ and α) leads to new expressions.

The addition to a tunneling current, arising due to an electron–phonon interaction, can be divided into two parts: the first one is determined by the variations of the electron spectral function due to interaction, and the second part is related to the inelastic processes of phonon emission or absorption. For the sake of brevity, we shall call these contributions elastic and inelastic, respectively.

Expression (15) describing the current flowing from a contact lead to a molecule looks asymmetric with respect to another contact lead. At first glance, the diagrams shown in Fig. 6 are also asymmetric. However, these diagrams include the electron Green functions for the molecule, calculated with allowance made for all tunneling transitions (without phonons). Hence, the symmetry with respect to contact leads in the explicit expression for a tunneling current is recovered. Let us consider this issue in more detail.

For this purpose we shall calculate the expression corresponding to the diagrams in Fig. 6b. Since it describes the contribution to a current made by the interaction with the ‘p’ lead, this part of the current will be designated I_p . Omitting the integral over ω , we can rearrange the terms entering into I_p in the following way:

$$\begin{aligned} I_p &= T_k^2 \operatorname{Re} [G_1^{(1)<} G_k^a + G_1^{(1)r} G_k^<] \\ &= T_k^2 \operatorname{Re} [(G_1^< \Sigma_p^a G_1^a - G_1^r \Sigma_p^< G_1^a + G_1^r \Sigma_p^r G_1^<) G_k^a \\ &+ G_1^{(1)r} G_k^<] = T_k^2 \operatorname{Re} \{ n_1 [(G_1^a - G_1^r) \Sigma_p^a G_1^a \\ &+ G_1^r \Sigma_p^r (G_1^a - G_1^r)] G_k^a + G_1^{(1)r} G_k^< - G_1^r \Sigma_p^< G_1^a G_k^a \} \\ &= T_k^2 \operatorname{Re} \{ [n_1 (G_1^{(1)a} - G_1^{(1)r}) G_k^a + G_1^{(1)r} G_k^<] \\ &+ [n_1 G_1^r (\Sigma_p^r - \Sigma_p^a) G_1^a - G_1^r \Sigma_p^< G_1^a] G_k^a \}, \end{aligned} \quad (22)$$

where Σ_p with different superscripts are the corresponding irreducible parts shown in Fig. 6. The Green function of electrons on a molecule, entering into this expression with allowance made for the tunneling transitions, has the form

$$G_1^r(\omega) = \frac{1}{\omega - \varepsilon_1 + i(\gamma_p + \gamma_k)}.$$

The electron energy level of the molecule broadens due to the tunneling transitions, and the tunneling rates are determined by the standard expression

$$\gamma_k = iT_k^2 \sum_k G_k^r, \quad \gamma_p = iT_p^2 \sum_p G_p^r.$$

The occupation numbers for the state ε_1 become non-equilibrium due to a tunneling current:

$$n_1(\omega) = \frac{\gamma_p n_p^0(\omega) + \gamma_k n_k^0(\omega)}{\gamma_p + \gamma_k}. \quad (23)$$

In rearranging expressions (22) we used the relationship $G_1^< = n_1(G_1^a - G_1^r)$, and defined the first interaction-assisted correction to the retarded Green function as follows: $G_1^{(1)r} = G_1^r \Sigma_p^r G_1^r$.

The first part of expression (22) looks exactly like an ordinary tunneling current but, due to the interaction, with a changed spectral function of electrons, $\operatorname{Im} G_1^r$. As we shall see later, the second part of the terms in Eqn (22) is responsible for an inelastic current — that is, the current related to a real emission of phonons.

A contribution similar to expressions (22) is made to the elastic part of the current by the diagrams describing in Fig. 6 the interaction with another lead of the contact. These diagrams make contributions which differ in that the subscript p is replaced by subscript k in the first group of terms for

I_p (22). By adding up these two contributions and taking into account the relationship $T_k^2 \sum_k G_k^< = 2i\gamma_k n_k(\omega)$, we obtain the final expression for the elastic part of the current, which is symmetric with respect to the contact leads:

$$I_1 = \int \left[4 \frac{\gamma_k \gamma_p}{\gamma} \text{Im} G^{(1)r}(\omega) \right] (n_p(\omega) - n_k(\omega)) \frac{d\omega}{2\pi}. \quad (24)$$

Here, n_k and n_p are the Fermi electron occupation numbers for the contact leads, differing in the chemical potential shift by the value of applied voltage, namely, $n_p(\omega + eV) = n_k(\omega)$, $\gamma = \gamma_p + \gamma_k$. Expression (24) is similar to the ordinary formula for tunneling current except that the initial spectral function of a localized state in Eqn (24) is replaced by the first correction to the spectral function $\text{Im} G^{(1)r}(\omega)$:

$$\text{Im} G^{(1)r}(\omega) = \text{Im} [G_0^{(1)r}(\omega) \Sigma^r(\omega) G_0^{(1)r}(\omega)], \quad (25)$$

where the eigenenergy part Σ^r is determined by the interaction with phonons:

$$\begin{aligned} \Sigma_{11}^r(\omega) = & i T_k^2 \int \sum_k [\tilde{D}_k^r(\Omega) G_k^<(\omega - \Omega) \\ & + \tilde{D}_k^>(\Omega) G_k^r(\omega - \Omega)] d\Omega \\ & + i T_p^2 \int \sum_p [\tilde{D}_p^r(\Omega) G_p^<(\omega - \Omega) \\ & + \tilde{D}_p^>(\Omega) G_p^r(\omega - \Omega)] d\Omega. \end{aligned} \quad (26)$$

It should be noted that the diagrams in Fig. 6d correspond to the eigenenergy corrections to the Green functions of electrons in the contact leads. These diagrams contribute a higher-order correction to the current compared to $(\lambda, \alpha)^2 \gamma^2$ and are neglected here.

The inelastic part of the current for the diagrams plotted in Fig. 6c [the second group of terms in Eqn (22)] can be transformed into the form

$$\begin{aligned} I_p^{\text{inel}} = & \gamma_k \int \frac{d\omega}{2\pi} \text{Im} [\Sigma_p^<(\omega) - n_1(\omega) 2i \text{Im} \Sigma_p^r(\omega)] |G_1^r(\omega)|^2 \\ = & -\gamma_k \gamma_p \int \frac{d\omega}{2\pi} |G_1^r(\omega)|^2 \int \frac{d\Omega}{2\pi} \left\{ 2n_1(\omega) \right. \\ & \times [\text{Im} \tilde{D}^a(\Omega) 2n_p(\omega - \Omega) - i\tilde{D}^>(\Omega)] \\ & \left. + 2n_p(\omega - \Omega) i\tilde{D}^>(\Omega) \right\} \\ = & 4 \frac{\gamma_k \gamma_p}{\gamma} \int \frac{d\omega}{2\pi} \text{Im} G_1^a(\omega) \int \frac{d\Omega}{2\pi} \text{Im} \tilde{D}_p^a(\Omega) \\ & \times \left\{ n_1(\omega) [1 + N(\Omega) - n_p(\omega - \Omega)] \right. \\ & \left. - n_p(\omega - \Omega) N(\Omega) \right\} \\ = & 4 \frac{\gamma_k \gamma_p}{\gamma} \int \frac{d\omega}{2\pi} \text{Im} G_1^a(\omega) \int \frac{d\Omega}{2\pi} \text{Im} \tilde{D}_p^a(\Omega) \\ & \times \left\{ \frac{\gamma_k}{\gamma} (n_k(\omega) - n_p(\omega)) [1 + N(\Omega) - n_p(\omega - \Omega)] \right. \\ & \left. + [n_p(\omega) - n_p(\omega - \Omega)] [N(\Omega) - N_0(\Omega)] \right\}. \end{aligned} \quad (27)$$

This part is also obviously asymmetric with respect to the contact leads. To derive the contribution to an inelastic

current, in which the parameters of another contact lead are included in a similar way, it is necessary to add up the expressions corresponding to two diagram types, namely, the diagrams presented in Figs 6a and 6c. Both the diagram types give the same functional expression, which is included, however, with the factor γ_k for the diagrams from Fig. 6a, and factor $-\gamma_k^2/\gamma$ for the diagrams from Fig. 6c. By summing these two expressions we recover the symmetry with respect to the subscripts k and p : $\gamma_k - \gamma_k^2/\gamma = \gamma_k \gamma_p/\gamma$.

Thus, by adding up all the contributions we arrive at the following final expression for the inelastic current

$$\begin{aligned} I^{\text{inel}} = & 4 \frac{\gamma_k \gamma_p}{\gamma^2} \int \frac{d\omega}{2\pi} \text{Im} G_1^a(\omega) \int \frac{d\Omega}{2\pi} \\ & \times \left\{ (n_k(\omega) - n_p(\omega)) [\gamma_k \text{Im} \tilde{D}_p^a(\Omega) [1 + N(\Omega) \right. \\ & - n_p(\omega - \Omega)] + \gamma_p \text{Im} \tilde{D}_k^a(\Omega) [1 + N(\Omega) \\ & - n_k(\omega - \Omega)] \right\} + \gamma [N(\Omega) - N_0(\Omega)] \\ & \times \left(\text{Im} \tilde{D}_p^a(\Omega) (n_p(\omega) - n_p(\omega - \Omega)) \right. \\ & \left. + \text{Im} \tilde{D}_k^a(\Omega) (n_k(\omega - \Omega) - n_k(\omega)) \right). \end{aligned} \quad (28)$$

Formula (28) also holds true in the case where the phonon distribution function $N(\Omega)$ becomes nonequilibrium. Anyway, the current addition tends to zero with decreasing voltage, as it must because $N(\Omega) - N_0(\Omega) \rightarrow 0$ for $V \rightarrow 0$.

Recall again that a correct calculation of tunneling current does not necessitate the artificial symmetrization of initial expressions [like Eqns (15), (22)] with respect to the subscripts k and p , which was done in paper [16], because the final expression for a current always satisfies the symmetry relationships in their transposition (the change in voltage polarity).

In the case of weak excitation of a phonon subsystem, where $N(\Omega) \approx N_0(\Omega)$, formula (28) is simplified. Using the explicit form of the functions $\tilde{D}_{p,k}^a$ (21), we arrive at the expression comprising two additive contributions related to the excitation of vibrations at the frequencies ω_0 and ω_1 :

$$I^{\text{inel}} = (1 - n_1) I_0 + n_1 I_1, \quad (29)$$

where

$$\begin{aligned} I_0 = & 4 \frac{\gamma_k \gamma_p}{\gamma^2} \int \frac{d\omega}{2\pi} \text{Im} G_1^a(\omega) (n_k(\omega) - n_p(\omega)) \\ & \times \left\{ \gamma_k [(\lambda - \alpha_p)^2 [1 + N(\omega_0) - n_p(\omega - \omega_0)] \right. \\ & + (\lambda + \alpha_p)^2 [N(\omega_0) + n_p(\omega + \omega_0)]] \\ & + \gamma_p [(\lambda - \alpha_k)^2 [1 + N(\omega_0) - n_k(\omega - \omega_0)] \\ & \left. + (\lambda + \alpha_k)^2 [N(\omega_0) + n_k(\omega + \omega_0)]] \right\}. \end{aligned} \quad (30)$$

The expression for I_1 is obtained from I_0 by making the substitution $\omega_0 \rightarrow \omega_1$.

An inelastic current is proportional to the difference between the occupation numbers, $n_p(\omega) - n_k(\omega)$; hence, as usual the contribution is only made by those states from the domain of width V between the Fermi levels of the contact leads. In addition, for moderate temperatures $T \ll \omega_0$ the

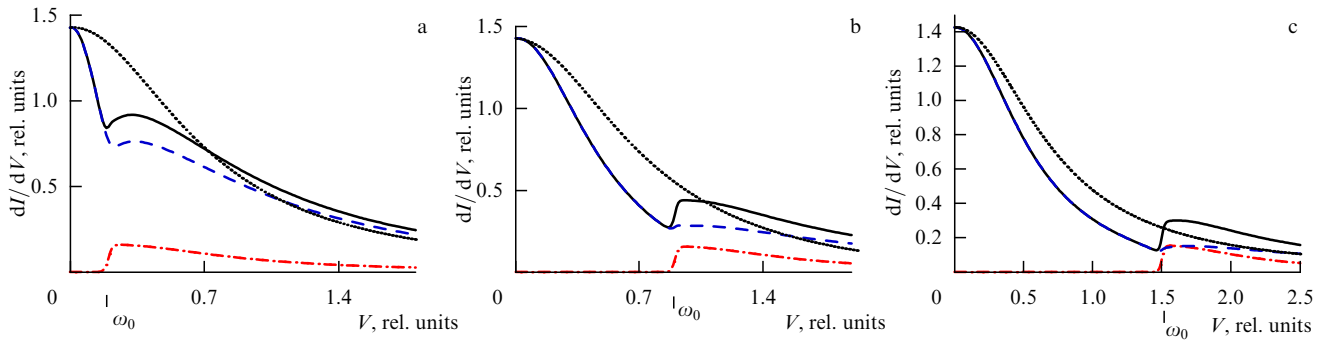


Figure 7. Variation of the tunneling conductance versus the frequency of a vibrational mode at a fixed position and width of the electronic level: $\varepsilon_1 = 0$, $\gamma = 0.7$. Dashed lines show the ‘elastic’ contribution to a current, dashed-dotted lines depict the ‘inelastic’ contribution, and solid lines show the total current. For comparison, the tunneling conductance neglecting interaction with the vibrational mode is depicted by a dotted line.

Fermi factors turn the integral to zero until the voltage becomes greater than $\omega_0(\omega_1)$. This contribution to a current only exists when the processes of real phonon emission start, which are related to a loss of energy $\omega_0(\omega_1)$ by the electron in tunneling from one contact lead to another.

Notice also that the magnitude of an inelastic current is always determined by the ‘cross’ products of the rates (like $\alpha_k \gamma_p$, $\alpha_p \gamma_k$) of the direct tunneling transition from one contact lead to a molecule and the tunneling transition with phonon emission from the molecule to another contact lead. For real phonon emission to occur, an electron should complete the tunneling from one lead to another with a loss of energy. At the same time, the change in the density of states, which is the reason for the appearance of an ‘elastic’ additive to current (24), is described by irreducible parts (26) which are nonzero in equilibrium as well. This change in the density of states is determined by the interaction with each of the contact lead independently.

In the general case, the tunneling conductance may exhibit three features. One of them is related to a passage of voltage through the electronic level of an impurity. At such voltages, a current may grow due to inelastic processes; however, the effect is weak against the background of a sharp change in total tunneling current at the same voltages. The second feature arises at voltages equal to the phonon frequency (energy); both elastic and inelastic parts of a current contribute to this effect. The third feature arises upon a further increase in the voltage (in absolute value) to the magnitude of $eV = \varepsilon_1 + \omega_0$. This additional peak in the tunneling conductance is mainly related to an inelastic current; it may be well resolved only if the condition $\gamma \ll \omega_0$ holds true.

The structure and specific form of the features of tunneling characteristics related to electron–phonon interaction are similar for the contributions both to current I_0 and to I_1 . Under the condition of a very weak broadening of electronic levels in the molecule due to tunneling processes, two sets of similar features should arise for molecular vibrations with the frequencies ω_0 and ω_1 . Nevertheless, in most experiments the level broadening γ is much greater than the difference between ω_0 and ω_1 . In this case, there is no reason in distinguishing between the frequencies ω_0 and ω_1 . Hence, below we shall only consider those features associated with vibrations at the single frequency ω_0 .

If an electronic level resides close to the Fermi level of the contact leads and is strongly broadened due to the tunneling hybridization with the states of a continuous spectrum in contact leads, then the feature on the tunneling conductance

may look like a peak or dip, depending on the parameters of the contact. Such a situation is illustrated in Fig. 7.

In the literature it is asserted that the passage from one type of the feature to another is related to the initial contact conductance with neglected electron–phonon interaction at $eV = \omega_0$ being either greater or less than a conductance quantum. Actually, the relationship between the feature type and the value of the initial conductance is only qualitative. Indeed, in Fig. 7 one can see that, at a high initial conductance and voltages $eV = \omega_0$, the feature more closely resembles a dip in the tunneling characteristics, and at low initial conductance there is a rise (step-up). However, the feature in Fig. 7b looks like a step, although on the whole the contact conductance falls. In addition, there is no definite threshold value of the conductance at which one feature type transfers to another.

Nevertheless, qualitatively the change in feature appearance versus the initial contact conductance at the voltage $eV = \omega_0$ is actually noticeable, which is clearly observed in the conductance derivative with respect to voltage, shown in Fig. 8.

In a strongly asymmetric contact, i.e., in the contact in which the rates of the tunneling transitions from the molecule to different contact leads substantially differ, the conventional tunneling current is symmetric with respect to the

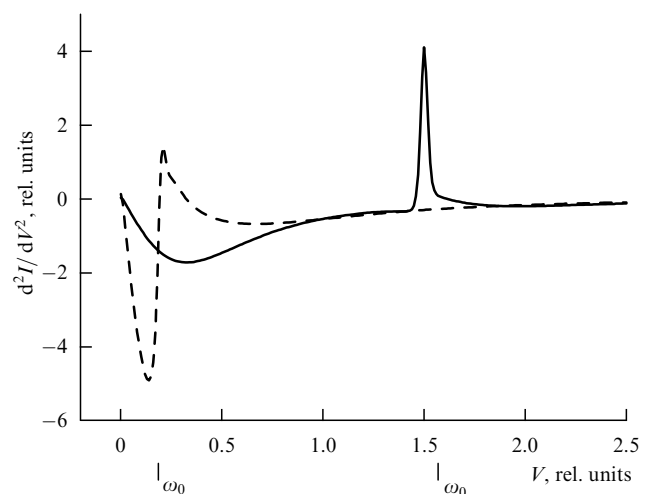


Figure 8. The derivative of the tunneling conductance for the same contact as in Fig. 7: plots 7a (dashed line), and 7c (solid line).

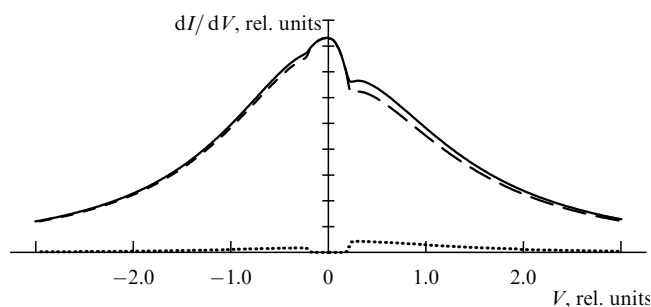


Figure 9. Conductance of the asymmetric contact with the parameters: $\varepsilon_1 = 0$, $\omega_0 = 0.2$, $\gamma_k = 0.2$, and $\gamma_p = 0.9$ at different voltage polarities. The dashed line shows the ‘elastic’ contribution to the current, the dotted line refers to the ‘inelastic’ contribution, and the solid line presents the total current.

change in voltage polarity. However, in such a contact the features related to the interaction with vibrational modes would noticeably differ in intensity for different voltage polarities, which makes the current–voltage characteristics asymmetric. Depending on contact parameters, it may occur that the features considered do not actually reveal themselves at a certain voltage polarity, whereas at the opposite polarity they are well distinguished (see Fig. 9). It worth noting that the appearance and intensity of the features are determined by the kinetics of the whole tunneling process.

If tunneling coupling with contact leads is weak and the electronic level in the molecule constitutes a sufficiently narrow resonance shifted from the Fermi level of the leads, then a tunneling conductance derivative would have, in addition to the feature at ω_0 , an additional feature at $eV = \varepsilon_1 + \omega_0$. The latter is mainly related to the abrupt increase in the inelastic contribution to a current at such voltages. Such characteristics are demonstrated in Figs 10a and 11b.

The shape of features at the same level position and phonon frequency would vary with a change in the degree of tunneling coupling with leads. From Fig. 10b one can see that the feature shape in the dependence dI/dV at the voltage $eV = \omega_0$ has changed from a ‘step’ to an asymmetric peak at stronger tunneling coupling with leads, and the tunneling

conductance feature at the voltage $eV = \varepsilon_1 + \omega_0$ has completely disappeared (become invisible).

When the impurity level lies at a little depth under the Fermi level, the feature may be strongly revealed, which is connected with the origin of an inelastic current – that is, with the onset of phonon emission. From Fig. 11b one can see that it is the origin of an inelastic contribution to the tunneling current that mainly determines the feature at ω_0 . The figure gives a clear understanding of the difference in feature shapes at ω_0 and at $\varepsilon_1 + \omega_0$. Both features are explained by the electron interaction with phonons, the first feature looking like a step, and the second one the peak in the tunneling conductance curve. Correspondingly, the feature shapes in the dependence d^2I/dV^2 are also well distinguished. However, these features may overlap at other values of the parameters, resulting in substantial shape distortions, which is illustrated in Fig. 11a.

It is evident that the shape of features depends on the proportion between elastic and inelastic contributions to the current, and on the ratio between different tunneling transition rates. Hence, the feature shape carries information concerning contact parameters. The problem of varying feature shape under the changed proportion between the elastic and inelastic parts of a current was considered in Ref. [12] in the single-level ‘polaron’ model of interaction between electrons and a vibrational mode.

In large tunneling contacts, the peculiarities of tunneling characteristics are mainly related to the change in the density of electronic states, connected only with the behavior of the eigenenergy parts like those of formula (26) due to electron–phonon interaction [17], i.e., with the elastic part of the current. At the same time, it is seen that in small-dimension systems these features may not be so substantial as compared to the tunneling current variations due to inelastic tunneling channels arising.

If the constant λ is the greatest parameter in a system, i.e., the main mechanism of the electron interaction with vibrational modes consists in the displacement of atoms to some other equilibrium position under the varying number of electrons on the molecule, then it is reasonable to use another approximation. The approximation has a simple form if a vibrational frequency variation can be neglected. In the

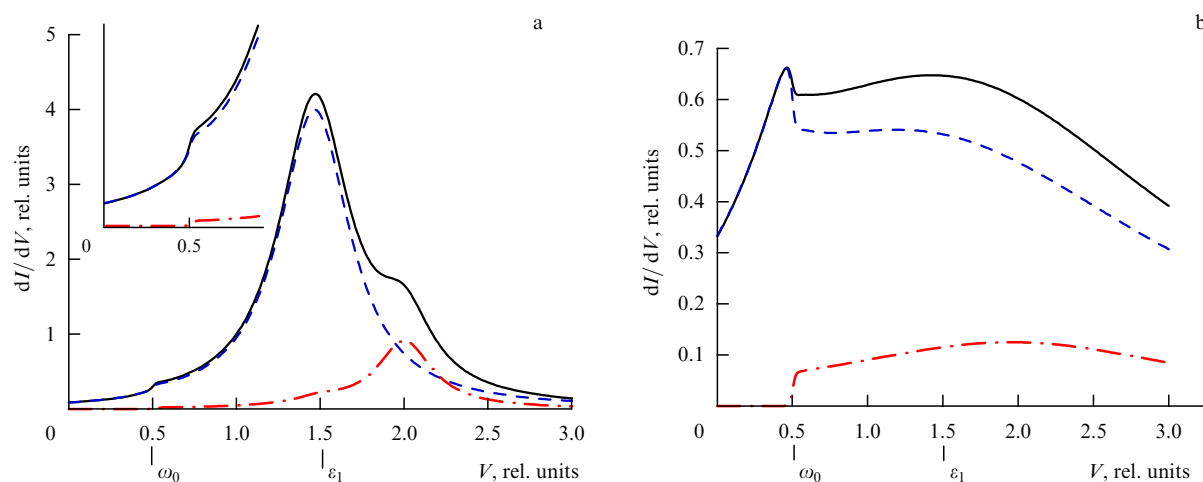


Figure 10. Contact conductance: (a) for weak hybridization of the electronic level in a molecule with the states of leads, $\gamma = 0.2$, and (b) for strong hybridization, $\gamma = 1.5$. The dashed curve depicts the ‘elastic’ contribution to current, the dashed-dotted curve shows the ‘inelastic’ contribution, and the solid curve corresponds to the total current.

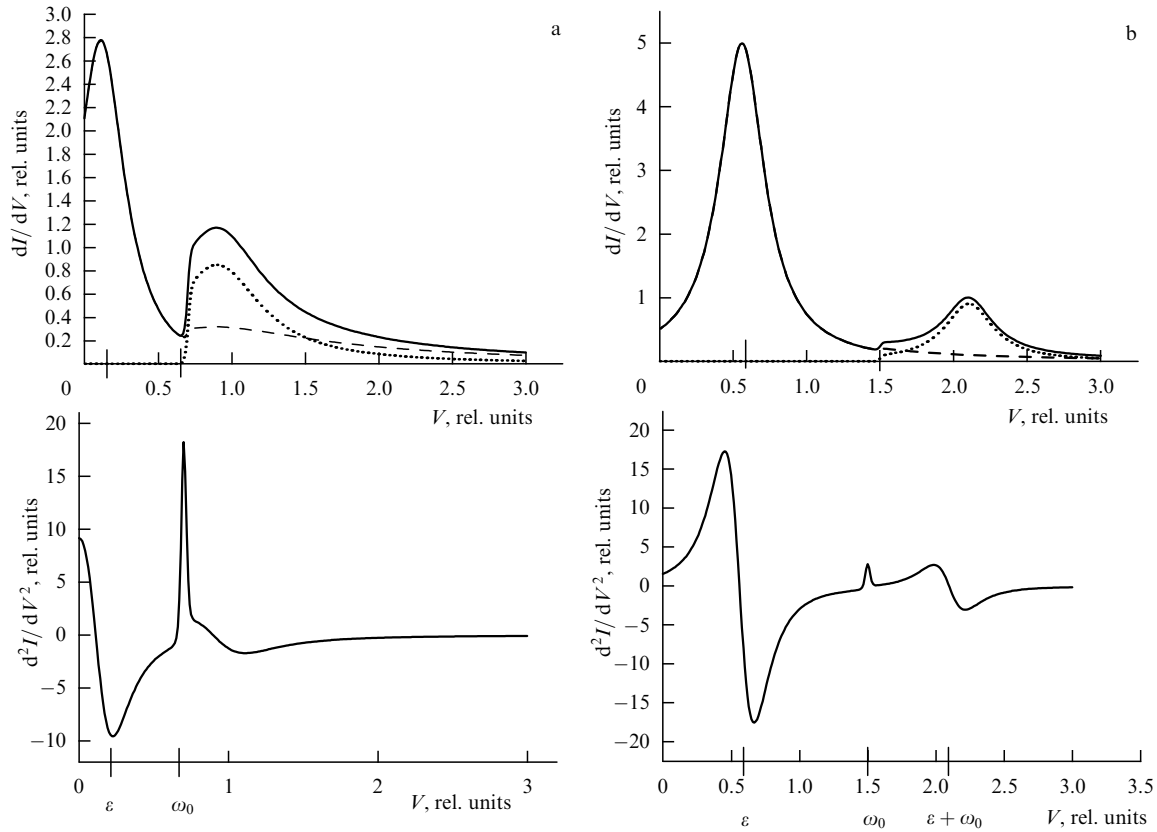


Figure 11. A tunneling conductance and its derivative for the case of $\varepsilon_1 < \omega_0$: (a) $\varepsilon_1 = 0.2$, $\omega_0 = 0.7$, $\alpha_k = 0.35$, $\alpha_p = 0.30$, and (b) $\varepsilon_1 = 0.6$, $\omega_0 = 1.5$, $\alpha_k = 0.35$, $\alpha_p = 0.45$. The parameters $\gamma_p = \gamma_k = 0.1$ and $\lambda = 0.15$ did not change. A dashed curve shows the elastic contribution into current, dotted curve depicts the inelastic contribution, and solid curve refers to a total tunneling current.

expression for tunneling Hamiltonian (90) (see the Appendix), we should retain only the term

$$H_{\text{tun}} = c_k^+ \tilde{a}_1 \exp[\lambda(\tilde{b} - \tilde{b}^+)] T_{k,1} \left(\frac{R_1 + R_0}{2} \right) + \text{h.c.} \quad (31)$$

One can see that the phonon operators $\tilde{b} - \tilde{b}^+$ are replaced by the operators $\exp[\lambda(\tilde{b} - \tilde{b}^+)]$. Hence, all the calculations of the tunneling current in this case are performed similarly to the previous case, with the exception that the ordinary Green function for phonons is replaced with the function F constructed from operators $\exp[\lambda(\tilde{b} - \tilde{b}^+)]$ rather than $\tilde{b} - \tilde{b}^+$:

$$F^{(--)}(t, t') = -i \langle T \exp[\lambda(\tilde{b}(t) - \tilde{b}^+(t))] \times \exp[\lambda(\tilde{b}(t') - \tilde{b}^+(t'))] \rangle. \quad (32)$$

The function of this type can be easily expressed in terms of ordinary phonon Green functions D (18) (in which one should set $\omega_0 = \omega_1$):

$$\begin{aligned} F^{(>)}(t) &= \exp[-\lambda^2(-iD^{>}(t) - iD^{<}(t) + 2N + 1)], \\ F^{(<)}(t) &= F^{(>)}(-t), \\ F^{(r)}(t) &= \theta(t)(F^{(>)}(t) - F^{(<)}(t)). \end{aligned} \quad (33)$$

From Eqn (33) one can see that the function F with the exponent expanded in a power series comprises all the harmonics of an initial vibrational frequency; hence, the peculiarities in the tunneling characteristics arise at all the multiple phonon frequencies [18]. We shall not dwell on this issue because this case still seems to have only theoretical meaning.

4. Strong hybridization of the states of an adsorbed molecule (atom) with a contact lead

We considered in Section 3 the case where a hybridization of molecular electronic states with contact leads was not strong; hence, in the zero approximation it was possible to take the vibrational states determined for an isolated molecule. However, one more type of vibrations exists in the tunneling systems comprising adsorbed molecules, namely, the vibrations of a molecule as a whole. The frequencies and characteristics of such vibrations are determined, in turn, by the degree of hybridization of molecular electronic states with the states of a substrate; therefore, such vibrational degrees of freedom cannot be determined independently by neglecting electron tunneling transitions. Since we are discussing the vibrations of a molecule as a whole, there is no difference between considering a molecule or a single atom adsorbed on a surface. Hence, consider the system illustrated in Fig. 12. A hybridization of the atomic states with a surface, determined by the matrix elements T_k , is assumed sufficiently strong and cannot be taken into account by means of the perturbation theory. At the same time, the tunneling matrix elements T_p describing the transitions of electrons to another contact lead (for example, to the tip of a tunneling microscope) are assumed small and the perturbation theory can be applied to them in the ordinary way.

To find vibrational modes, it is necessary to use the expression for the total electronic energy of a system with an adsorbed atom. The dependence of this energy on the distance R between the atom and surface is determined by a variation

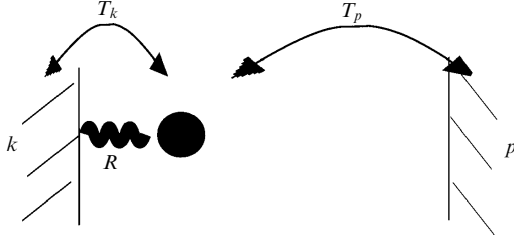


Figure 12. Schematic diagram of the contact with an adsorbed atom which is strongly coupled to a contact lead: $T_k \gg T_p$.

of hybridization matrix elements $T_k(R)$ versus the distance:

$$E_c(R) = \int \frac{d\omega}{2\pi} \omega n_k(\omega) \left[\text{Im } G_d^a(R, \omega) + \sum_k \text{Im } G_{kk}^a(R, \omega) \right].$$

The Green functions in this expression can be exactly calculated as in the Andersen problem on an impurity hybridized with the states of a continuous spectrum. This energy constitutes the potential energy of ion motion, which determines the vibrational frequencies of atoms near the surface. In order to determine the electronic–vibrational interaction correctly, we should again start with the exact wave functions $\Psi_n(r, R)$ of the whole system. In terms of such exact states, the interaction is described by the Hamiltonian

$$H_{\text{int}} = \sum_{n,m} \left[\int dr \Psi_n^*(r, R) \frac{\partial}{\partial R} \Psi_m(r, R) \right] \left(-\frac{1}{M} \frac{\partial}{\partial R} \right). \quad (34)$$

In order to pass to a secondary quantization representation, we may expand the wave functions into the states ‘ k ’ of a continuous spectrum and into the state ‘ d ’ of an adsorbed atom (for simplicity, we consider only one electronic level in an atom):

$$\begin{aligned} \Psi_n(r, R) &= \beta_d^n(R) \Psi_d(r - R) + \sum_k \beta_k^n(R) \Psi_k(r), \\ c_n^+ &= \beta_d^n(R) d^+ + \sum_k \beta_k^n(R) c_k^+. \end{aligned} \quad (35)$$

By using the orthonormality conditions having the form

$$\begin{aligned} \sum_n \beta_k^n(R) \beta_d^{n*}(R) &= \int \frac{d\omega}{2\pi} \text{Im } G_{kd}^a(R, \omega) = 0, \\ \sum_n \beta_d^n(R) \beta_d^{n*}(R) &= \int \frac{d\omega}{2\pi} \text{Im } G_{dd}^a(R, \omega) = 1, \end{aligned} \quad (36)$$

we arrive at

$$\begin{aligned} \sum_n \Psi_n(r, R) c_n^+ &= \Psi_d(r - R) d^+ + \sum_k \Psi_k(r) c_k^+, \\ \sum_m \frac{\partial}{\partial R} \Psi_m^*(r, R) c_m &= \sum_k (g_{dk} \Psi_d(r) c_k + g_{kd} \Psi_k(r) d) \\ &\quad + \sum_{kk'} g_{kk'} \Psi_k(r) c_{k'}, \end{aligned} \quad (37)$$

where $g_{dk} = \sum_m (\partial \beta_d^m / \partial R) \beta_k^{m*}$. The rest of the coupling constants are determined in a similar way. Unfortunately,

these constants cannot be obtained in an explicit form, because we know all the Green functions for the impurity problem, but do not know the explicit form of the exact wave functions of the whole system. By retaining only the interaction related to the electron transitions between an atom and a substrate, we arrive at the Hamiltonian in the form

$$H_{\text{int}} = \sum_k (\alpha_{kd} c_k^+ d + \alpha_{dk} d^+ c_k) (b^+ - b) \quad (38)$$

with the coupling constants $\alpha_{kd} = \sqrt{\omega_0 / (2M)} g_{kd}$. By differentiating expression (36) with respect to R , we easily obtain the expression $g_{kd} + g_{dk}^* = 0$, from which it follows that the Hamiltonian obtained exhibits the same interaction type as the interaction determined by the constant λ for inner molecular vibrations:

$$H_{\text{int}} = \sum_k \alpha_d (c_k^+ d - d^+ c_k) (b^+ - b) \quad (39)$$

(the constants α_d are real quantities). Hamiltonian (39) describes the interaction of electrons with the vibrations of the adsorbed atom if its electronic states are strongly hybridized with the states of the substrate. If the tunneling coupling with the second contact lead is noticeably weaker, then, similarly to the previous case, the second channel of the electron interaction with the vibrations of the atom (or the molecule as a whole) arises, being related to a modulation of the tunneling matrix element $T_p(R)$ in atomic vibrations:

$$H_{\text{int}} = \sum_p \alpha_p (c_p^+ d + d^+ c_p) (b^+ + b). \quad (40)$$

The tunneling current is determined by the diagrams (Fig. 13) that exhibit the same type as in Fig. 6.

In contrast to Section 3, here all possible Green functions for electrons in the strongly coupled system ‘atom plus substrate’ are included as ‘zero’-approximation Green functions. In calculating these functions, the hybridization $T_k(R)$ is exactly taken into account; hence, in addition to the diagonal functions G_{kk} and G_{dd} , the diagrams in Fig. 13 also include the off-diagonal functions G_{kd} and G_{dk} .

Due to a strong hybridization of atomic states with the lead k , the electron occupation numbers for an adsorbed atom actually coincide with the occupation numbers of substrate states, $n_d(\omega) \simeq n_k(\omega)$, even in the presence of a tunneling current. Hence, the inelastic part of the current is only contributed from the first diagram in Fig. 13. This contribution is described by formula (28) in which one should put $\gamma_k \gg \gamma_p$:

$$\begin{aligned} I^{\text{inel}} &= 4\gamma_p \alpha_p^2 \int \frac{d\omega}{2\pi} \text{Im } G_1^a(\omega) \int \frac{d\Omega}{2\pi} \text{Im } D^a(\Omega) \\ &\quad \times \left\{ (n_k(\omega) - n_p(\omega)) [1 + N(\Omega) - n_p(\omega - \Omega)] \right. \\ &\quad \left. + [N(\Omega) - N_0(\Omega)] (n_p(\omega) - n_p(\omega - \Omega)) \right\}. \end{aligned} \quad (41)$$

In formula (41), the phonon Green function is determined now in the ordinary way [in contrast to that in formula (28)].

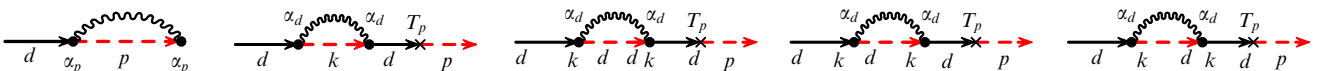


Figure 13. Diagrams describing the tunneling current through an adsorbed atom.

All the expressions are given under the assumption of a weak dependence of electronic–vibrational interaction constants on the momentum k .

The Green functions G_{kd} and $G_{kk'}$ entering into the diagrams presented in Fig. 13 can always be expressed in terms of the functions G_{dd} and G_{kk}^0 by using the Dyson equation, for example,

$$\sum_k T_k G_{kd}^r = -i\gamma_k G_{dd}^r, \quad \sum_{k,k'} T_k G_{kk'}^r T_{k'} = \gamma_k^2 G_{dd}^r. \quad (42)$$

In view of relationships (42), the correction to a current, arising due to the interaction determined by the constant α_d , can be presented in the same form as for the case of a molecule weakly coupled with contact leads:

$$I_k = \gamma^p \int \text{Im} [G_d^r(\omega) \Sigma_{\text{eff}}^r(\omega) G_d^r(\omega)] (n_p(\omega) - n_k(\omega)) \frac{d\omega}{2\pi}. \quad (43)$$

However, a strong hybridization of atomic (molecular) states with a contact lead is specific in that the eigenenergy part is unusual here:

$$\begin{aligned} \Sigma_{\text{eff}}^r(\omega) = & i\alpha_d^2 \int \sum_k [D^r(\Omega) G_k^<(\omega - \Omega) + D^>(\Omega) \\ & \times G_k^r(\omega - \Omega)] \frac{d\Omega}{2\pi} + 4\pi i\gamma_k v_k \alpha_d^2 \\ & \times \int \sum_p [D^r(\Omega) n_k(\omega - \Omega) \\ & \times G_d^r(\omega - \Omega) - D^>(\Omega) G_d^r(\omega - \Omega)] \frac{d\Omega}{2\pi}. \end{aligned} \quad (44)$$

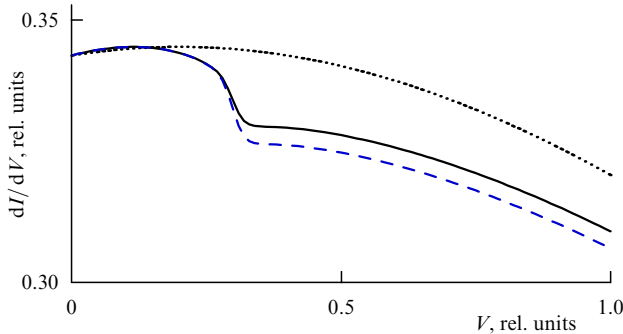


Figure 14. Typical behavior of a tunneling conductance at a substantially broadened electronic level of an adsorbed atom, $\omega_0 = 0.3$. A dashed curve shows the elastic contribution into a current, solid curve depicts the total current, and dotted curve presents the tunneling conductance ignoring the interaction with a vibrational mode.

The voltage dependences of a tunneling conductance calculated by these formulae show that if the electronic level of an atom resides closely to the Fermi level of a substrate, then for large values of hybridization T_k (γ_k) the peculiarities related to atomic vibrations have the shape of a ‘step-down’ (the conductance falls). Such a rather general behavior of a tunneling conductance is displayed in Fig. 14. In this case, the shape of the peculiarity is mainly determined by the elastic contribution to a current, which is clear from the figure.

If the electronic level is separated from the Fermi level by an energy value comparable to level broadening due to hybridization, the shape of the peculiarity changes. The shape is substantially different depending on whether the atomic energy level is higher or lower than the Fermi level. In Fig. 15, such changes in feature shape are shown versus the varied position of the electronic level in an atom relative to the Fermi level of contact leads.

If the atomic level resides above the Fermi level, the peculiarity looks like a sharp dip; if it is essentially below the Fermi level, the peculiarity looks like a peak. In Fig. 15, the inelastic current contribution is also given, but for strong hybridization with a contact lead ($T_k \gg T_p$) this contribution is small and has actually no influence on the behavior of tunneling conductance.

5. Tunneling conductance of atomic chains

In a series of studies, tunneling contacts were produced by various methods, with their conductance being determined by isolated atomic chains [6, 7]. In the tunneling conductance of such chains peculiarities were revealed at certain voltages and associated with the excitation of vibrational modes in the atomic chains. Theoretical models were suggested for describing such features with allowance made for the influence of electron–phonon interaction in atomic chains on tunneling characteristics [19, 20]. However, although the peculiarities are described qualitatively by these theories, they often employ an initially wrong definition of the parameters of electron–phonon interaction in such systems.

It is easiest to develop the theories for atomic chains based on the strongly coupled electron method. In this case, the electronic states of isolated atoms are first determined, and the states of the whole chain are described by the Hamiltonian

$$H = \sum_i \varepsilon_i c_i^\dagger c_i + \sum_{i,j} T_{i,j} (R_{i,j}) (c_i^\dagger c_j + c_j^\dagger c_i), \quad (45)$$

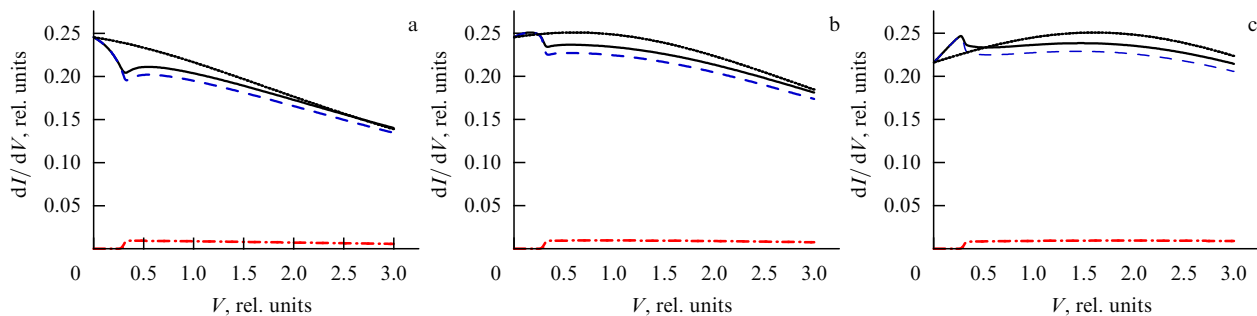


Figure 15. Shape variation of a peculiarity in the tunneling conductance upon changing the electronic level position in an atom. The vibrational frequency is $\omega_0 = 0.3$, and level broadening is $\gamma = 3.8$. A dashed curve refers to the elastic contribution to a current, a dash-and-dot curve shows the inelastic contribution, a solid curve depicts the total current, and a dotted curve presents the tunneling conductance ignoring the interaction with a vibrational mode; (a) $\varepsilon_1 = -0.6$, (b) $\varepsilon_1 = 0.6$, and (c) $\varepsilon_1 = 1.6$.

where ε_i are the energies of the electronic states in individual atoms, and $T_{i,j}(R_{i,j})$ is the amplitude of a transition from one atom to another. In this approach, the change of electronic states of the whole chain due to a variation of atomic positions is determined by introducing a dependence of the matrix element for electron transitions between atoms as a function of the interatomic distance. Such a method allows one to escape solving the exact Schrödinger equation for electrons of the whole chain at fixed positions of atoms.

Usually, a naive approach is realized in constructing an electron–phonon interaction, which implies a simple expansion of $T_{i,j}(R_{i,j})$ in the displacements of atoms from the equilibrium position in their vibrations. The first term of the expansion, $\partial T_{i,j}/\partial R_{i,j}(R - R_0)(c_i^\dagger c_j + c_j^\dagger c_i)$, is considered as the Hamiltonian of electron–phonon interaction after substituting the corresponding operators of phonon creation and annihilation for the atomic displacements $R - R_0$. However, in a consistent separation of states of the whole electron–ion system into vibrational and electronic degrees of freedom in the adiabatic approach, the variation of $T_{i,j}(R_{i,j})$ under changes of atomic positions makes a contribution to the effective potential for ion motion. A correct procedure again implies using the exact wave functions $\Psi_n(r, R)$ of the whole system, by analogy with formula (34). For electrons in the strong coupling model (45), the exact interaction (34) can be expressed in terms of the quantity $\partial T_{i,j}/\partial R_{i,j}$ in the following way. By using the exact eigenfunctions for Hamiltonian (45), we may write out the derivative:

$$\left\langle \Psi_n \left| \frac{\partial}{\partial R_i} H \right| \Psi_m \right\rangle = E_m \left\langle \Psi_n \left| \frac{\partial}{\partial R_i} \right| \Psi_m \right\rangle, \quad (46)$$

which entails

$$\begin{aligned} & \left\langle \Psi_n \left| \sum_j \frac{\partial T_{i,j}}{\partial R_i} (c_i^\dagger c_j + c_j^\dagger c_i) \right| \Psi_m \right\rangle \\ &= (E_m - E_n) \left\langle \Psi_n \left| \frac{\partial}{\partial R_i} \right| \Psi_m \right\rangle + \frac{\partial}{\partial R_i} E_m \delta_{n,m}. \end{aligned} \quad (47)$$

In view of the appearance of Hamiltonian (45), the interaction in terms of the creation and annihilation operators for electrons in exact states c_n^\dagger , c_n can be written in the form

$$\begin{aligned} H_{\text{int}} &= \sum_i \sum_{n \neq m} \left[\frac{\sum_j (\beta_i^{n*} \beta_j^m \beta_k^{m*} \beta_l^n + \beta_i^{n*} \beta_j^m \beta_k^{m*} \beta_l^n) \partial T_{i,j}/\partial R_i}{E_m - E_n} \right] \\ &\times c_n^\dagger c_m \left(-\frac{1}{M_i} \right) \frac{\partial}{\partial R_i}, \end{aligned} \quad (48)$$

where we again expressed the electron creation operators in the exact states Ψ_n in terms of the creation operators on the i -chain atoms, similarly to the case of the adsorbed atom considered above [see formulae (35)–(37)]. The coefficients of this expansion are as follows:

$$c_n^\dagger = \sum_i \beta_i^n(R) c_i^\dagger. \quad (49)$$

By using relationship (49) again, we can bring the complete interaction operator to the form

$$\begin{aligned} H_{\text{int}} &= \sum_{l,k,i} \sum_{n \neq m,j} \left[\frac{(\beta_i^{n*} \beta_j^m \beta_k^{m*} \beta_l^n + \beta_i^{n*} \beta_j^m \beta_k^{m*} \beta_l^n) \partial T_{i,j}/\partial R_i}{E_m - E_n} \right] \\ &\times c_l^\dagger c_k \left(-\frac{1}{M_i} \right) \frac{\partial}{\partial R_i}. \end{aligned} \quad (50)$$

And finally, by expressing atomic displacements in terms of the operators of vibrational modes in the chain, viz.

$$\frac{\partial}{\partial R_i} = \sqrt{\frac{M\omega_v}{2}} e_i^v (b^v - b^{v\dagger}),$$

we obtain

$$H_{\text{int}} = \sum_{l,k,v} g_{l,k}^v c_l^\dagger c_k (b^v - b^{v\dagger}), \quad (51)$$

where the coupling constant $g_{l,k}^v$ is rather complicated:

$$\begin{aligned} g_{l,k}^v &= \sum_{n \neq m,j,i} \left[\frac{(\beta_i^{n*} \beta_j^m \beta_k^{m*} \beta_l^n + \beta_i^{n*} \beta_j^m \beta_k^{m*} \beta_l^n) \partial T_{i,j}/\partial R_i}{E_m - E_n} \right] \\ &\times \sqrt{\frac{M\omega_v}{2}} e_i^v. \end{aligned} \quad (52)$$

If we start with the naive expression $\partial T_{i,j}/\partial R_{i,j}(R - R_0) \times (c_i^\dagger c_j + c_j^\dagger c_i)$ as the operator of the interaction of electrons and atomic vibrations, we will obtain an expression similar to Eqn (51) but with the coupling constant

$$g_{i,j}^v = \frac{\partial T_{i,j}}{\partial R_i} \sqrt{\frac{2}{M\omega_v}} e_i^v \quad (53)$$

which differs from exact expression (52).

Due to different symmetries of chain vibrational modes and coefficients β_i^n for electronic states, the total constant of the interaction of electrons with certain vibrational modes may be very small (in the ideal case it turns to zero). Hence, not all the vibrational modes will give rise to peculiarities in the tunneling conductance [20].

The general expression for current flowing through an atomic chain, also valid for an electron–phonon interaction, takes the form [21]

$$\begin{aligned} I(V) &= 2 \int |T_{1k}|^2 v_k(\omega) \\ &\times [2\text{Im} G_{11}^r(\omega) n_k^0(\omega) - iG_{11}^<(\omega)] \frac{d\omega}{2\pi}, \end{aligned} \quad (54)$$

or

$$I(V) = \frac{2}{\pi} \int |T_{1k}|^2 v_k(\omega) \text{Im} G_{11}^r(\omega) [n_k^0(\omega) - n_1(\omega)] d\omega, \quad (55)$$

where v_k is the density of states at the end of a contact lead, and G_{11} is the Green function for the first chain atom closest to the lead. If we neglect the interaction of electrons with chain atom vibrations, then expressions for current (54) can be put in the form symmetrical with respect to the contact leads:

$$\begin{aligned} I(V) &= \frac{2}{\pi} \int |T_{1k}|^2 |T_{Np}|^2 v_k(\omega) v_p(\omega - eV) |G_{1N}^r(\omega)|^2 \\ &\times [n_k^0(\omega) - n_p(\omega)] d\omega, \end{aligned} \quad (56)$$

where the subscript N corresponds to the last chain atom closest to the other lead of the contact.

The electron–phonon interaction yields corrections to the Green functions G_{11} in initial formulae (54). The appropriate current variations may again be divided into two parts, which we may call elastic and inelastic contributions to a tunneling current from the interaction effects. The elastic contribution to the current is described by the same formula (56) as in the absence of interaction, but with the function $|G_{1N}^r(\omega)|^2$ changed due to the involvement of interaction; in other words, it is only related to the change of the spectral function $\text{Im } G_{11}^r(\omega)$ in formula (55). An inelastic contribution is related to the change of the electron occupation numbers $n_1(\omega)$ entering into the Green function $G_{11}^<(\omega)$ (54) due to the electron interaction with vibrations. By substituting the corresponding change of $G_{11}^<(\omega)$, viz.

$$\delta G_{11}^< = \sum G_{1i}^r \Sigma_{ij}^< G_{j1}^a, \quad (57)$$

into formula (54), we arrive at the following expression for the inelastic part of the current [22]:

$$I_{\text{inel}}(V) = 2 \int |T_{1k}|^2 v_k(\omega) \times \left[-i \sum_{i,j} G_{1i}^r(\omega) \Sigma_{ij}^<(\omega) G_{j1}^a(\omega) \right] \frac{d\omega}{2\pi}, \quad (58)$$

where the sum over i, j runs over all the chain atoms. This contribution, in contrast to the elastic case, cannot be written out in the standard form (56) that is valid for a system without interaction. The irreducible part Σ in the first order with respect to electron–phonon interaction is expressed as

$$\Sigma_{ij}^<(\omega) = \int \frac{d\Omega}{2\pi} \sum_{k,l,v} g_{ik}^v g_{lj}^v G_{kl}^<(\omega - \Omega) D_v^<(\Omega). \quad (59)$$

In a series of studies [23–25], attempts were made to calculate the current–voltage characteristics for particular atomic chains by formulae similar to Eqn (54) (although with an incorrectly defined electron–phonon interaction). In all the calculations, the characteristics obtained exhibit an abrupt fall in conductance at the voltages equal to the frequencies of vibrational modes. The shapes of these characteristics are similar to those in Fig. 15. Such a behavior of current–voltage characteristics testifies to the fact that the main role in interactions with vibrations is played by the ‘elastic’ contribution to a current variation, which always reduces the conductance. The ‘inelastic’ contribution increasing the total conductance through the system is small in this case.

6. Vibrational excitation by a tunneling current

In order to quantitatively describe the degree of phonon subsystem heating, it is necessary to calculate the nonequilibrium phonon occupation numbers for a flowing tunneling current. The nonequilibrium phonon occupation numbers are determined from the Green function

$$D^<(t, t') = -i \langle b^+(t') b(t) \rangle. \quad (60)$$

In a stationary state, this function in a Fourier representation satisfies the following relationship

$$D^<(\Omega) = 2iN(\Omega) \text{Im } D^r(\Omega). \quad (61)$$

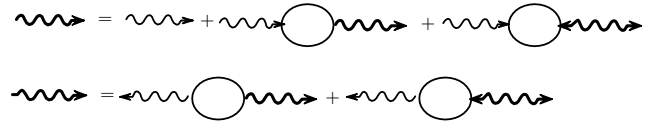


Figure 16. Dyson equation for vibrational modes.

A nonequilibrium diagram technique provides a calculation of functions $D^<(\Omega)$ and $D^r(\Omega)$, thus giving the possibility of determining the occupation numbers $N(\Omega)$ (in the model of ‘polaron’ interaction at a single electronic level, such a theory was developed in Ref. [11]). Notice that in the nonequilibrium case, the ‘anomalous’ phonon averages are also nonzero, which results in Green functions having the form $B^<(t, t') = -i \langle b(t) b(t') \rangle$. Hence, in the nonequilibrium, albeit stationary, case at a fixed current flowing through the contact, an exact system of Dyson equations is slightly complicated, as shown in Fig. 16.

The Dyson equation for vibrational modes in a Fourier representation assumes the form

$$\begin{aligned} D^{\alpha\beta}(\Omega) &= D_0^{\alpha\beta}(\Omega) + D_0^{\alpha\gamma}(\Omega) \\ &\times \left\{ \Pi_{dd}^{\gamma\delta}(\Omega) D^{\delta\beta}(\Omega) + \Pi_{db}^{\gamma\delta}(\Omega) B^{\delta\beta}(\Omega) \right\}, \\ B^{\alpha\beta}(\Omega) &= D_0^{\alpha\gamma}(-\Omega) \\ &\times \left\{ \Pi_{bd}^{\gamma\delta}(\Omega) D^{\delta\beta}(\Omega) + \Pi_{bb}^{\gamma\delta}(\Omega) B^{\delta\beta}(\Omega) \right\}, \end{aligned} \quad (62)$$

where D_0 is the equilibrium Green function for phonons, namely

$$\begin{aligned} D_0^r(\Omega) &= \frac{1}{\Omega + i\delta - \omega_0}, \\ D_0^<(\Omega) &= -2\pi i N_0(\omega_0) \delta(\Omega - \omega_0), \end{aligned} \quad (63)$$

with N_0 being the Bose distribution. The form of the polarization operators Π depends on the particular system under consideration. Prior to concretizing the form of these operators, we shall make the following general remark.

In many cases (both in theory and experiments), it is important to determine the amplitudes of atomic vibrations in a molecule excited by a tunneling current. In the equilibrium case, the root-mean-square amplitude of atomic vibrations is completely determined by the occupation numbers for vibrational modes. In the nonequilibrium case, however, an r.m.s. displacement of atoms is determined as follows:

$$\begin{aligned} \langle \delta R^2 \rangle &= \frac{\hbar}{2M\omega_0} \langle (b + b^+)(b + b^+) \rangle \\ &= \frac{\hbar}{2M\omega_0} [2iD^<(t, t) + 1 + iB^<(t, t) + iB^{+<}(t, t)]. \end{aligned} \quad (64)$$

In addition to the ordinary displacements that are similar to the equilibrium thermal fluctuations of atoms, additional displacements arise which are proportional to $-2\text{Im } B^<$. In some cases, this additional contribution may be not very small [15].

Nevertheless, the situation is noticeably simplified in most cases. The corrections related to the allowance made for the

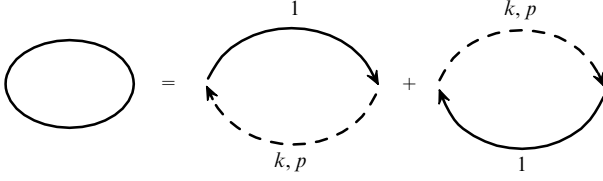


Figure 17. Polarization operator in tunneling through a single electronic level of a molecule.

anomalous function B are usually small quantities of the order Γ^2/ω_0^2 , where Γ is the broadening of a vibrational level due to interaction [15]. If Γ is small, the main contribution to the nonequilibrium excitation of atomic vibrations is related to the ‘normal’ polarization operator Π_{dd} .

In the case of electron tunneling through a single electronic level of a molecule, considered in Section 2, the operator Π_{dd} is expressed in the form

$$\Pi_{dd} = (\alpha_k - \lambda_k)^2 \Pi_{1k} + (\alpha_k + \lambda_k)^2 \Pi_{k1} + (k \rightarrow p). \quad (65)$$

The polarization operators in the first-order with respect to electron–phonon interaction are shown in Fig. 17. The corresponding analytical expression has the form

$$\begin{aligned} \Pi_{1k}^r(\Omega) &= -iT_k^2 \sum_k \int \frac{d\omega}{2\pi} \\ &\times [G_1^r(\omega) G_k^<(\omega - \Omega) + G_1^<(\omega) G_k^a(\omega - \Omega)], \\ \Pi_{1k}^<(\Omega) &= iT_k^2 \sum_k \int \frac{d\omega}{2\pi} [G_1^<(\omega) G_k^>(\omega - \Omega)]. \end{aligned} \quad (66)$$

Electron Green functions in contact leads ($G_{k(p)}$) and at the level ε_1 (G_1) are calculated taking into account all the tunneling transitions without inference from phonons [26]. Due to the tunneling transitions, the level ε_1 acquires the width $\gamma = \gamma_k + \gamma_p$, where $\gamma_{k(p)} = \pi T_{k(p)}^2 v_{k(p)}$ are the rates of tunneling transitions to contact leads ($v_{k(p)}$ is the density of states in the contact leads). The remaining functions Π_{k1} , Π_{p1} , and Π_{1p} are determined similarly to Eqn (66). In the wide band approximation for contact leads, the maximum values of real and imaginary parts of these operators are of the same order: $\text{Im } \Pi_{1k}^r \simeq \text{Re } \Pi_{1k}^r \simeq \gamma_k$. The electron–phonon interaction is assumed sufficiently weak, so that $\alpha^2 \gamma \ll \omega_0$ and $\lambda^2 \gamma \ll \omega_0$. Then variations of phonon frequencies may be neglected, and we may allow for only the imaginary parts of polarization operators, which determine the broadening of phonon lines: $\text{Im } \Pi_{dd}^r \equiv \Gamma$. From Dyson equation (62) one can easily deduce that within the accuracy of the order of Γ^2/ω_0^2 the spectral function of phonons may be replaced by the delta-function in all the integrals:

$$\text{Im } D^r(\Omega) \simeq \frac{\Gamma(\Omega)}{(\Omega - \omega_0)^2 + \Gamma(\Omega)^2} \simeq -\pi \delta(\Omega - \omega_0). \quad (67)$$

By using Dyson equation (62), we obtain the expression for $D^<$:

$$D^<(\Omega) = -D^r(\Omega) \Pi_{dd}^<(\Omega) D^a(\Omega). \quad (68)$$

From this evidence and formula (61), it follows that the nonequilibrium phonon occupation numbers are given by

$$N(\Omega) = \frac{i\Pi_{dd}^<(\Omega)}{2\text{Im } \Pi_{dd}^r(\Omega)}. \quad (69)$$

By substituting into formula (66) the explicit expressions for the Green function and integrating over momenta k and p , we obtain the following expressions for the functions $\Pi_{dd}^<(\Omega)$ and $\text{Im } \Pi_{dd}^r(\Omega)$:

$$\begin{aligned} \text{Im } \Pi_{dd}^r(\Omega) &= 2 \int \frac{d\omega}{2\pi} \text{Im } G_1^a(\omega) \\ &\times \left\{ [\gamma_k(\alpha_k - \lambda)^2 (n_k(\omega) - n_k(\omega - \Omega)) + (k \rightarrow p)] \right. \\ &+ [\gamma_k(\alpha_k + \lambda)^2 (n_k(\omega + \Omega) - n_k(\omega)) + (k \rightarrow p)] \\ &+ 4 \frac{\gamma_p \gamma_k}{\gamma} \lambda(\alpha_p - \alpha_k) (n_p(\omega) - n_k(\omega)) \left. \right\}, \end{aligned} \quad (70)$$

$$i\Pi_{dd}^<(\Omega) = 2\text{Im } \Pi_{dd}^r(\Omega) N_0(\Omega) + P^<(\Omega),$$

where

$$\begin{aligned} P^<(\Omega) &= 4 \frac{\gamma_p \gamma_k}{\gamma} \int \frac{d\omega}{2\pi} \text{Im } G_1^a(\omega) \\ &\times \left\{ [(\alpha_k - \lambda)^2 (n_k(\omega - \Omega) - 1) + (\alpha_k + \lambda)^2 n_k(\omega + \Omega) \right. \\ &- (k \rightarrow p)] + 4\lambda N_0(\Omega)(\alpha_k - \alpha_p) \left. \right\} (n_p(\omega) - n_k(\omega)). \end{aligned} \quad (71)$$

The formula for phonon occupation numbers (69) can be presented as a sum of an equilibrium occupation number and the nonequilibrium additive caused by the tunneling current: $N(\Omega) = N_0(\Omega) + \Delta N(\Omega)$, where

$$\Delta N(\Omega) = \frac{P^<(\Omega)}{2\text{Im } \Pi_{dd}^r(\Omega)}. \quad (72)$$

Nonequilibrium phonon occupation numbers are always proportional to the difference between electron occupation numbers in contact leads, $n_p(\omega) - n_k(\omega)$, and turn to zero in the absence of a tunneling current.

Analysis of formulae (70)–(72) permits establishing the conditions under which the phonon emission is high or, conversely, low. A low phonon emission is observed if the degrees of molecular tunneling hybridization with the different contact leads noticeably differ, for example, for $\Gamma_p \gg \Gamma_k$, $\gamma_p \gg \gamma_k$. The nonequilibrium occupation numbers of a vibrational mode to an order of magnitude will be equal to $\Delta N \simeq (\Gamma_k/\Gamma_p + \gamma_k/\gamma_p)$. The least heating will occur if the intermediate energy level ε_1 lies near the Fermi level of the lead p , to which it is bounded more strongly, so that $E_F^p - \varepsilon_1$ and ω_0 are on the order of γ . Then, even for voltages $eV \gg \varepsilon_1$ the perturbation of a phonon subsystem is small: $\Delta N \ll 1$.

Strong phonon emission will occur if the level ε_1 initially lies deep enough beneath E_F , so that $E_F^p - \varepsilon_1 \gg \omega_0$, and the state ε_1 is approximately equally hybridized with both the leads: $\Gamma_p \simeq \Gamma_k$, $\gamma_p \simeq \gamma_k$. In this case, as soon as the voltage across the contact reaches ε_1 , strong atomic vibrations are excited. The maximum possible occupation numbers at high voltages can also be easily estimated: $\Delta N \simeq \varepsilon_1^2/(\gamma\omega_0)$.

The calculated phonon occupation numbers as functions of voltage are compared in Fig. 18 for a symmetric tunneling system and a system in which the tunneling coupling with one contact lead is much stronger than with another. In the case of a symmetric contact, the number of phonons barely rises in the wide range of voltages from ω_0 to $\omega_0 + \varepsilon_1$, and then the excitation sharply increases. In an asymmetric contact, the number of phonons rises not so rapidly, and phonon emission at high voltages is noticeably weaker.

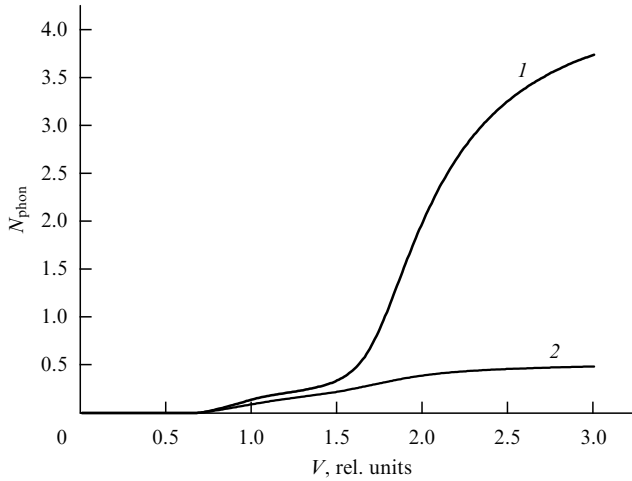


Figure 18. The phonon occupation numbers versus voltage for a system with $\varepsilon_1 = 1$, $\omega_0 = 0.7$, and $\lambda = 0.15$. Curve 1 depicts a strong generation of phonons in a symmetric system with $\gamma_p = \gamma_k = 0.1$, $\alpha_p = 0.55$, and $\alpha_k = 0.65$; curve 2 fits a suppressed generation in an asymmetric system with $\gamma_p = 0.3$, $\gamma_k = 0.05$, $\alpha_p = 0.55$, and $\alpha_k = 0.25$.

An important property of the model considered is the interference between two tunneling processes with phonon participation. A small variation of the proportion between the different constants α and λ results in substantial suppression or amplification of phonon emission. This evidence is illustrated in Fig. 19, where a variation of nonequilibrium phonon occupation numbers is plotted versus a small variation of constants α_k and α_p . Such a difference in system's behavior is mainly determined by the last term in formula (70) which is proportional to the product $\lambda(\alpha_p - \alpha_k)$. At a sufficiently large difference in the rates of tunneling with phonon contribution to the different leads of a contact, a very intense generation of phonons may develop due to the denominator which tends to zero in formula (72). To adequately describe the phenomenon, it is necessary to take into account nonlinear processes limiting system excitation in a way similar to that in Ref. [26].

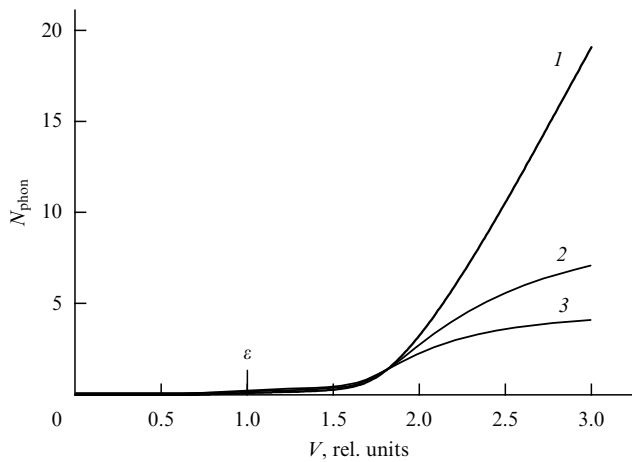


Figure 19. Degree of system excitation at small relative variations of the parameters α_p , α_k . The parameters are as follows: $\varepsilon_1 = 1$, $\omega_0 = 0.7$, $\lambda = 0.15$, and $\gamma_p = \gamma_k = 0.1$. Curve 1 corresponds to $\alpha_k = 0.55$, $\alpha_p = 0.65$; curve 2 refers to $\alpha_k = \alpha_p = 0.55$, and curve 3 corresponds to $\alpha_k = 0.65$, $\alpha_p = 0.55$.

From the viewpoint of the general laws of a vibrational mode excitation in flowing tunneling current, the excitation of vibrations of an adsorbed atom is similar to the case of a strongly asymmetric tunneling contact, where the vibrational modes are weakly excited.

In studying the problem of exciting vibrations in a chain of atoms, it is easier to start with the interaction Hamiltonian written out in terms of the exact electronic states for the whole chain (48):

$$H_{\text{int}} = \sum_{n,m} g_{n,m}^v c_n^+ c_m (b_v^+ + b_v). \quad (73)$$

Then the nonequilibrium occupation numbers for vibrational modes are given by general formula (69) [26]:

$$N_v(\Omega) = \frac{i\Pi^<(\Omega)}{2\text{Im}\Pi^r(\Omega)}, \quad (74)$$

and the polarization operators take the form

$$\begin{aligned} \text{Im}\Pi^r(\Omega) &= 2 \sum_{n,m} (g_{n,m}^v)^2 \int \frac{d\omega}{2\pi} \left[\text{Im}G_n^a(\omega) \text{Im}G_m^a(\omega - \Omega) \right. \\ &\quad \times (n_n(\omega) - n_m(\omega)) + \text{Im}G_m^a(\omega) \text{Im}G_n^a(\omega - \Omega) \\ &\quad \left. \times (n_m(\omega) - n_n(\omega)) \right], \\ i\Pi^<(\Omega) &= \sum_{n,m} (g_{n,m}^v)^2 \int \frac{d\omega}{2\pi} \left[-G_n^<(\omega) G_m^<(\omega - \Omega) \right. \\ &\quad + 2iG_n^<(\omega) \text{Im}G_m^a(\omega - \Omega) + 2iG_m^<(\omega) \text{Im}G_n^a(\omega - \Omega) \\ &\quad \left. - G_m^<(\omega) G_n^<(\omega - \Omega) \right]. \end{aligned} \quad (75)$$

In deriving expressions (75), we neglected the interaction due to modulation of the tunneling matrix elements, which bind the molecule and the contact leads, with vibrations of outermost atoms. This interaction, generally speaking, should be added similarly to the above case.

In the general case of long atomic chains in which many electronic states and vibrational eigenmodes exist, general expressions are cumbersome and may only be estimated numerically. Nevertheless, one can follow some regularities of chain vibrational excitation, even for the simple example of a diatomic chain, which can be considered analytically.

In a diatomic chain (comprising two similar atoms) there are two electronic eigenstates: symmetric (s), and anti-symmetric (as). The Green functions corresponding to the eigenstates and needed for determining the excitation of atomic vibrations can be expressed via the Green functions of the first and second atoms in the chain:

$$G_{s,a}^<(\omega) = \frac{1}{2} (G_{11}^<(\omega) + G_{22}^<(\omega)) \pm i \text{Im}G_{12}^<(\omega). \quad (76)$$

Taking advantage of the formulae for functions $G_{11}^<(\omega)$, $G_{22}^<(\omega)$, and $G_{12}^<(\omega)$ given in Ref. [27], we obtain

$$\begin{aligned} G_{s,as}^<(\omega) &= -i \frac{\gamma_k n_k [(\omega - \varepsilon_0 \pm T_{12})^2 + \gamma_p^2] + \gamma_p n_p [(\omega - \varepsilon_0 \pm T_{12})^2 + \gamma_k^2]}{[(\omega - \varepsilon_0)^2 - T_{12}^2 - \gamma_p \gamma_k]^2 + (\gamma_p + \gamma_k)^2 (\omega - \varepsilon_0)^2}, \end{aligned} \quad (77)$$

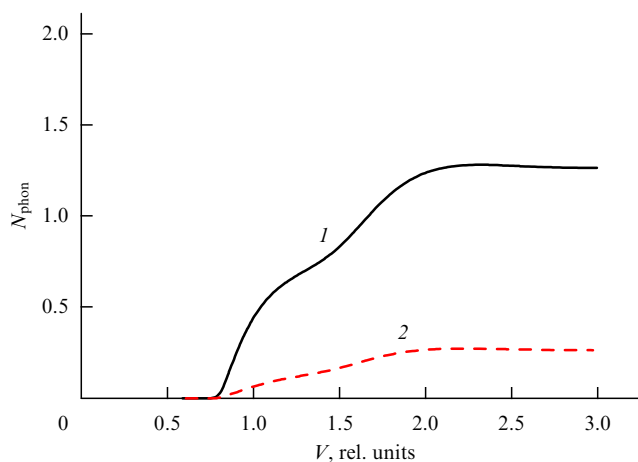


Figure 20. Nonequilibrium occupation numbers for vibrational modes of a diatomic chain at various couplings with contact leads: curve 1 corresponds to $\gamma_p \gg \gamma_k$, and curve 2 corresponds to $\gamma_p \ll \gamma_k$.

$$\text{Im } G_{s,as}^I(\omega) = -\frac{1/2(\gamma_p + \gamma_k)[(\omega - \varepsilon_0 \pm T_{12})^2 + \gamma_p \gamma_k]}{[(\omega - \varepsilon_0)^2 - T_{12}^2 - \gamma_p \gamma_k]^2 + (\gamma_p + \gamma_k)^2(\omega - \varepsilon_0)^2}. \quad (78)$$

Formulae (77), (78) permit us to determine how the degree of vibrational excitation changes with the variation of the chain tunneling coupling with contact leads—that is, under changes of γ_p and γ_k . In Fig. 20, the nonequilibrium occupation numbers for a vibrational mode (i.e., the intensity of phonon emission) are shown at various ratios between the tunneling rates γ_p and γ_k .

The physical reason for such intensity variation is that in inverting the proportion between γ_p and γ_k , the character of energy occupation of states of the first and second atoms changes. In a certain energy range, an inversion arises of the nonequilibrium occupation numbers for the ground and excited states in the diatomic chain, which substantially affects the vibrational excitation probability. However, the total number of electrons in the upper level is always less than in the lower level. In Fig. 21, the variation of nonequilibrium occupation numbers for upper and lower levels is shown versus energy under changes of the ratio between γ_p and γ_k .

7. Conclusion

We have shown that in small tunneling contacts, as well as in bulky material, a description of the interaction between electrons and vibrational modes should start with a successive separation of the vibrational and electronic degrees of freedom and with constructing the Hamiltonian of their interaction in the framework of the adiabatic approach. In the general case, the electron–phonon interaction in the process of electron tunneling through single molecules may be contributed by various mechanisms: modulation of the tunneling matrix elements with vibrating atoms in a molecule, the change of equilibrium atomic positions and vibrational frequencies in electron transitions between a molecule and contact leads, and phonon emission or absorption in electron transitions between the energy levels of a molecule itself. If several different mechanisms make comparable contributions, interesting effects may arise connected with the interference of the interactions of different types. As was

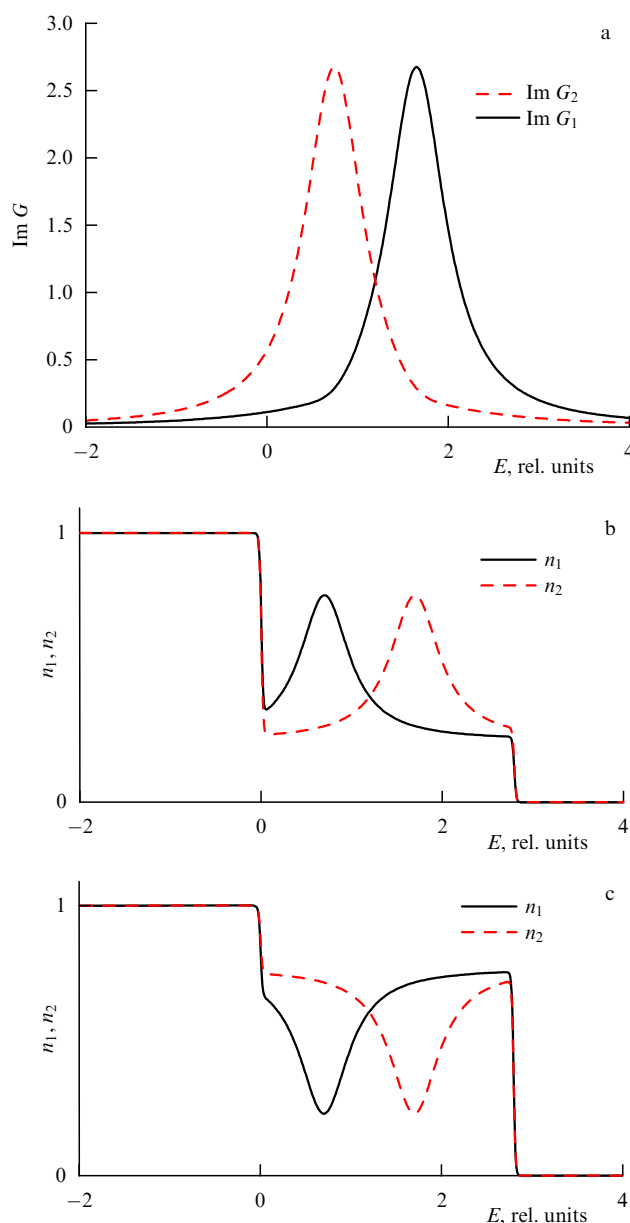


Figure 21. (a) Density of states for a ground and an excited state of a diatomic chain. (b, c) Occupation numbers for the states. One can see how the character of occupation of upper and lower electronic levels changes in reversing the ratio between the rates of tunneling transition to the contact leads.

shown above by the example of electron tunneling through a single electronic level of a small molecule, an interference of two interaction channels in different conditions results in either amplification or suppression of molecular vibrations when the tunneling current flows. The expressions obtained for the intensity of vibrational excitation by a tunneling current in various systems permitted us to determine the general conditions which influence the generation intensity. The generation of atomic vibrations is stronger in symmetric contacts where the tunneling coupling of a molecule with different contact leads is approximately equal. In contrast, the generation is suppressed in an asymmetric contact with noticeably different rates of tunneling transitions to the different leads of the contact.

Due to the interaction of electrons with molecule vibrational modes, the tunneling characteristics acquire peculia-

rities whose positions are related to the energies (frequencies) of vibrational modes. The shape of these peculiarities is not universal: it depends on the system type and particular parameters of the tunneling contact. Qualitatively, we may say that the peculiarity shape depends on the ratio between the ‘elastic’ and ‘inelastic’ contributions into the tunneling current due to an electron–phonon interaction. The elastic addition relates to the change in the density of electronic states caused by the interaction. The inelastic addition arises when real processes of phonon emission start in the contact. The elastic contribution always deteriorates the contact conductance, whereas the inelastic contribution provides a conductance increase due to the emergence of an additional channel for electron transport.

The theory makes it possible to determine a peculiarity shape at various contact parameters. Hence, the tunneling spectroscopy may principally allow not only finding the frequencies of molecular vibrations, but also obtaining information on tunneling contact parameters, for example, on the ratio of tunneling transition rates.

In small molecules with a large energy separation between electronic levels that are still well resolved despite tunneling broadening, the peculiarity may appear as a peak or ‘step-up’ due to a large contribution from an inelastic current. In such systems weakly bounded to contact leads with discrete electronic levels, the tunneling conductance exhibits peculiarities not only at voltages corresponding to the vibrational energies, but also at voltages separated from the electron energy level by the phonon energy.

According to experiments and the theoretical calculations of some authors, an elastic contribution prevails over an inelastic one for large molecules and long atomic chains. This results in the tunneling conductance in such systems reducing as the voltage reaches the energy of a certain vibrational mode (the peculiarity looks like a ‘step-down’).

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8. Appendix.

Derivation of the complete Hamiltonian describing electron interaction with vibrational modes in tunneling processes

Initially, tunneling transitions are described by Hamiltonian (11):

$$H_{\text{tun}} = T_{k,1}(R) c_k^+ a_1 + \text{h.c.} \quad (79)$$

The operators c_k correspond to the electronic states in contact leads, and $T_{k,1}(R)$ is the overlap integral between the electronic state with momentum k in the contact lead and the electronic state of the molecule. Since $T_{k,1}(R)$ depends on the positions of the atoms in the molecule, tunneling matrix element will be modulated with the atomic vibrations in the molecule. For describing the modulation we may expand the matrix element $T_{k,1}(R)$ in a power series of displacement $R - R_1$ from the equilibrium position R_1 :

$$\begin{aligned} T_{k,1}(R) &= \exp \left[(R - R_1) \frac{\partial}{\partial R} \right]_{R_1} T_{k,1}(R) \\ &= T_{k,1}(R_1) + (R - R_1) \frac{\partial}{\partial R} \Big|_{R_1} T_{k,1}(R) + \dots \quad (80) \end{aligned}$$

Below we shall show that an expansion in a power series of displacement $R - R_0$ from another equilibrium position R_0 would give the same final formulae for the tunneling Hamiltonian; consequently, there is no actual arbitrariness in choosing the point of expansion for the tunneling matrix element $T_{k,1}(R)$. The displacement $R - R_1$ is expressed in the standard way through the creation and annihilation operators of vibrational quanta, b_1^+ and b_1 , and, in view of relationship (7), can be expressed in terms of new operators \tilde{b}^+ and \tilde{b} :

$$\begin{aligned} \sqrt{2M\omega_1} (R - R_1) &= b_1 + b_1^+ \\ &= \beta(1 - \tilde{a}_1^+ \tilde{a}_1)(\tilde{b} + \tilde{b}^+ + 2\lambda) + \tilde{a}_1^+ \tilde{a}_1(\tilde{b} + \tilde{b}^+). \quad (81) \end{aligned}$$

In formula (79) it is also necessary to express the initial electron operators a_1 in terms of the operators \tilde{a}_1 corresponding to true electronic excitations of the whole molecule under changes of the number of electrons. The inverse transformation to that in formula (9), which expresses the initial operators a_1 in terms of new operators \tilde{a}_1 , has an explicit form

$$\begin{aligned} a_1 &= \tilde{a}_1 \exp [\beta\lambda(\tilde{b} - \tilde{b}^+)] \\ &\times \exp \left\{ \theta [\tilde{b}\tilde{b} - \tilde{b}^+ \tilde{b}^+ - 2\beta\lambda(\tilde{b} - \tilde{b}^+)] \right\}. \quad (82) \end{aligned}$$

In further transformations it is convenient to employ the fact that the momentum and coordinate operators for oscillators ω_1 and ω_0 suit the relationships

$$\begin{aligned} a_1^+ a_1 (b - b^+) &= \beta a_1^+ a_1 (\tilde{b} - \tilde{b}^+), \\ a_1^+ a_1 (\tilde{b} + \tilde{b}^+) &= \beta a_1^+ a_1 (b + b^+ + 2\lambda). \quad (83) \end{aligned}$$

We now substitute expressions (80)–(82) into tunneling Hamiltonian (79):

$$\begin{aligned} H_{\text{tun}} &= c_k^+ \tilde{a}_1 \exp [\beta\lambda(\tilde{b} - \tilde{b}^+)] \\ &\times \exp \left\{ \theta [\tilde{b}\tilde{b} - \tilde{b}^+ \tilde{b}^+ - 2\beta\lambda(\tilde{b} - \tilde{b}^+)] \right\} \\ &\times \exp \left[\frac{1}{\sqrt{2M\omega_1}} [\beta(1 - \tilde{a}_1^+ \tilde{a}_1)(\tilde{b} + \tilde{b}^+ + 2\lambda) \right. \\ &\quad \left. + \tilde{a}_1^+ \tilde{a}_1(\tilde{b} + \tilde{b}^+)] \frac{\partial}{\partial R} \right]_{R_1} T_{k,1}(R) + \text{h.c.} \\ &= c_k^+ \tilde{a}_1 \exp [\beta\lambda(\tilde{b} - \tilde{b}^+)] \\ &\times \exp \left\{ \theta [\tilde{b}\tilde{b} - \tilde{b}^+ \tilde{b}^+ - 2\beta\lambda(\tilde{b} - \tilde{b}^+)] \right\} \\ &\times \exp \left[\frac{1}{\sqrt{2M\omega_1}} (\tilde{b} + \tilde{b}^+) \frac{\partial}{\partial R} \right]_{R_1} T_{k,1}(R) + \text{h.c.} \quad (84) \end{aligned}$$

It should be noted that, because the tunneling matrix element $T(R)$ in initial expression (79), naturally, commutes with electron operators and may reside either to the right or to the left of the operators $c_k^+ a_1$, Hamiltonian (84) can be written out in the equivalent form in which $T(R)$ is to the right of the electron operators. These two forms are entirely equivalent, though in final form (84) such a transposition is not obvious at first glance. Expression (84) can be simplified by using the

relationships

$$\begin{aligned} & \exp [\beta \lambda (\tilde{b} - \tilde{b}^+)] \exp \left\{ \theta [\tilde{b} \tilde{b} - \tilde{b}^+ \tilde{b}^+ - 2\beta \lambda (\tilde{b} - \tilde{b}^+)] \right\} \\ & \times \exp [-\beta \lambda (\tilde{b} - \tilde{b}^+)] = \exp [\theta (\tilde{b} \tilde{b} - \tilde{b}^+ \tilde{b}^+)], \\ & \exp [\beta \lambda (\tilde{b} - \tilde{b}^+)] \exp \left[\frac{1}{\sqrt{2M\omega_1}} (\tilde{b} + \tilde{b}^+) \frac{\partial}{\partial R} \right]_{R_1} \\ & = \exp \left[\beta \lambda (\tilde{b} - \tilde{b}^+) + \frac{1}{\sqrt{2M\omega_1}} (\tilde{b} + \tilde{b}^+) \frac{\partial}{\partial R} \right]_{R_1} \\ & \times \exp \left[\frac{1}{2} (R_0 - R_1) \frac{\partial}{\partial R} \right]_{R_1}. \end{aligned} \quad (85)$$

In addition, taking into account that the action of the operator

$$\exp \left[\frac{1}{2} (R_0 - R_1) \frac{\partial}{\partial R} \right]_{R_1}$$

reduces to a coordinate shift from R_1 to $(R_1 + R_0)/2$, we arrive at the final expression for the tunneling Hamiltonian

$$\begin{aligned} H_{\text{tun}} &= c_k^+ \tilde{a}_1 \exp [\theta (\tilde{b} \tilde{b} - \tilde{b}^+ \tilde{b}^+)] \exp \left[\beta \lambda (\tilde{b} - \tilde{b}^+) \right. \\ & \left. + \frac{1}{\sqrt{2M\omega_1}} (\tilde{b} + \tilde{b}^+) \frac{\partial}{\partial R} \right]_{(R_1+R_0)/2} T_{k,1}(R) + \text{h.c.} \end{aligned} \quad (86)$$

Let us now show that if expression (80) is expanded about R_0 , then the final form (86) is not changed:

$$\begin{aligned} T_{k,1}(R) &= \exp \left[(R - R_0) \frac{\partial}{\partial R} \right]_{R_0} T_{k,1}(R) \\ &= T_{k,1}(R_0) + (R - R_0) \frac{\partial}{\partial R} \bigg|_{R_0} T_{k,1}(R) + \dots \end{aligned} \quad (87)$$

By expressing $R - R_0$ in terms of operators b^+ and b and the new operators \tilde{b}^+ and \tilde{b} , namely

$$\begin{aligned} \sqrt{2M\omega_1} (R - R_0) &= b + b^+ \\ &= \left[(1 - \tilde{a}_1^+ \tilde{a}_1) (\tilde{b} + \tilde{b}^+) + \tilde{a}_1^+ \tilde{a}_1 \frac{1}{\beta} (\tilde{b} + \tilde{b}^+ - 2\beta \lambda) \right], \end{aligned} \quad (88)$$

we obtain instead of formula (84) the following expression

$$\begin{aligned} H_{\text{tun}} &= c_k^+ \tilde{a}_1 \exp [\beta \lambda (\tilde{b} - \tilde{b}^+)] \\ & \times \exp \left\{ \theta [\tilde{b} \tilde{b} - \tilde{b}^+ \tilde{b}^+ - 2\beta \lambda (\tilde{b} - \tilde{b}^+)] \right\} \\ & \times \exp \left[\frac{1}{\sqrt{2M\omega_1}} (\tilde{b} + \tilde{b}^+ - 2\beta \lambda) \frac{\partial}{\partial R} \right]_{R_0} T_{k,1}(R) + \text{h.c.} \end{aligned} \quad (89)$$

By using relationships (85) once more, we arrive at

$$\begin{aligned} H_{\text{tun}} &= c_k^+ \tilde{a}_1 \exp [\theta (\tilde{b} \tilde{b} - \tilde{b}^+ \tilde{b}^+)] \\ & \times \exp \left[\beta \lambda (\tilde{b} - \tilde{b}^+) + \frac{1}{\sqrt{2M\omega_1}} (\tilde{b} + \tilde{b}^+) \frac{\partial}{\partial R} \right]_{R_0} \\ & \times \exp \left[\frac{1}{2} (R_1 - R_0) \frac{\partial}{\partial R} \right]_{R_0} T_{k,1}(R) \\ & = c_k^+ \tilde{a}_1 \exp [\theta (\tilde{b} \tilde{b} - \tilde{b}^+ \tilde{b}^+)] \exp [\beta \lambda (\tilde{b} - \tilde{b}^+)] \\ & + \frac{1}{\sqrt{2M\omega_1}} (\tilde{b} + \tilde{b}^+) \frac{\partial}{\partial R} \bigg|_{(R_1+R_0)/2} T_{k,1}(R) + \text{h.c.}, \end{aligned} \quad (90)$$

i.e., the same expression as Eqn (86). This confirms that the appearance of the interaction Hamiltonian is independent of the point at which the tunneling matrix element is expanded in a power series.

General expression (86) comprises three parameters of electron–phonon interaction. The parameter $\alpha_{k,p}$ is added to the parameters θ and λ (5), which can be determined from Eqn (86) in the following way:

$$\alpha_{k,p} = \sqrt{\frac{\hbar}{2M\omega_1}} \frac{1}{T_{k,p}} \frac{\partial}{\partial R} T_{k,p} \bigg|_{(R_1+R_0)/2}.$$

By expanding general expression (86) to a first order in all three parameters, we arrive at interaction Hamiltonian (13).

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