Calculation of Electronic Lifetimes in Molecular Junctions

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Abstract: *We study the electronic lifetimes in molecular junctions using the Keldysh nonequilibrium Green function (NEGF) model. It is found that two characteristic time scales which govern the electron tunneling phenomena. One is the electronic lifetime in which electronic energy in the molecular electronic state dissipates into the right/left electrode or vibrational mode, the other is the residence time due to virtual excitation of electrons between the two electrodes and the molecular electronic state. And using a set of the parameters which characterize the molecular junction, we show that the molecular vibrational frequency, the position of the electronic state of the molecule, the strength of electron-vibration coupling (via the electron-phonon interaction) and the distance between the molecule and the electrodes (via the molecule-electrode coupling) represent substantial contributions that affect the electronic lifetime in molecular junctions, as result all are represent important parameters to determine the nature and the mechanisms of electron transport in molecular junctions.*

Keywords: *Molecular junctions, green function method, inelastic electron tunneling, vibrational excitation, electron-phonon interaction, electronic lifetimes.*

I.   Introduction

In recent years, electron transport via molecules put among electrodes has been attracting increasing attention because it may forms fundamental nano and molecular electronics devices. These devices provide an ideal test ground for the study of basic physics including the nano size [1-5]. Molecular junctions are the simplest components of molecular electronics, and are structures in which a single molecule forms a stable electrically conducting bridge between two metal and/or semiconductor electrodes have been studied intensively experimentally and theoretically due to their potential device applications [6-8]. However, the evidence for quantum nature of electron transport properties has been observed in the differential conductance for the molecular system by several experimental groups [9-12]. Theoretically, a lot of effort has been focused on the study of current-voltage characteristics of molecular systems [1, 13-15]. They found that the electron transport is nondissipative up to a finite voltage threshold corresponding to the excitation of the molecular vibrations. This threshold showed the evidence of inelastic current accompanied by excitation of vibrational mode. And a sudden drop in the conductance was attributed to the excitation of an intramolecular vibrational mode. A common characteristic of the molecular systems is an inelastic electron transport accompanied by vibrational excitation. In these and other studies the electronic lifetimes had not calculated, in spite of its importance and its role in determining the change in conductance and inelastic electron tunneling spectroscopy (IETS) [16-18].

In this work, we use the Keldysh nonequilibrium Green function model to calculate the electronic lifetimes in molecular junction and to present a study to elucidate how the parameters important for molecular junctions affects on the electronic lifetimes. It is found that the parameters which characterize molecular junction are important parameters to determine the nature and the mechanisms of electron transport in molecular junctions.

II.   Theoretical Model

The model system under consideration is illustrated in Fig. 1. It consists of a single molecule connected with two electrodes. The electrons in the molecule are also coupled to a single phonon mode. When electron tunnels into the unoccupied state of the molecule from the left/right electrode, this electron form a temporal negative ion state. Then the electron hops to the right/left electrode and the molecule returns to the electronic ground state, but may be left in a vibrational excited state. The vibrational excited state can decay via the excitation of an electron-hole pair [19, 20].
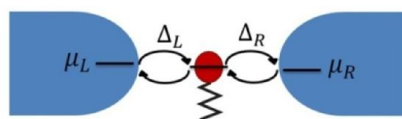
Figure 1: (Color online) Schematic representation of a molecular junction. The molecule is connected to two leads with couplings Δ_L and Δ_R. The electrons in the molecule are also interacting with a single phonon mode.

This system is described by the Hamiltonian [21-25]

$$H = H_m + H_L + H_R + H_X + H_T .$$ (1)

The first three terms denote the Hamiltonian for electrons in the independent molecule, the left and right non-interacting metallic electrodes, respectively [21, 24],

$$H_m = \sum_m [E_0 + \lambda(a + a^\dagger)] d_m^\dagger d_m ,$$ (2)

often use a single-level molecular model that corresponds to the molecular orbital of energy E_0 to represents the molecular electronic system. λ is the coupling constant between the molecule electrons and the phonon mode, $a^\dagger(a)$ and $d_m^\dagger (d_m)$ are creation (annihilation) operators of phonon and molecule electrons, respectively. And [22, 25],

$$H_L + H_R = \sum_{k \in L,R} E_k C_k^\dagger C_k ,$$ (3)

where $C_k^\dagger(C_k)$ is the electron creation (annihilation) operator in the electrodes, and E_k is the single particle energy of conduction electrons. The fourth term describes the phonon mode,

$$H_X = \hbar\Omega \, a^\dagger a ,$$ (4)

where Ω is the frequency of the single phonon mode. The last term represents the coupling of the molecule to the electrodes,

$$H_T = \sum_{k \in L,R} (V_{km} C_k^\dagger d_m + h.c.) ,$$ (5)

where the tunneling matrix elements V_{km} give rise to transfer electrons through an insulating barrier out of the molecule.

The current operators from the electrodes to the molecule are defined as [22]

$$I_{L(R)} = \sum_{k \in L(R)} (V_{km} C_k^\dagger d_m - h.c.).$$ (6)

The net current is given by $I = (\langle I_L \rangle - \langle I_R \rangle)/2$. Using the Keldysh nonequilibrium Green function formalism, the net current can be obtained as [21, 22, 25]

$$I = \frac{2e}{\hbar} \frac{\Delta_L \Delta_R}{\Delta} \int dE \, \mathrm{Im} G^r(E) [f_L(E) - f_R(E)],$$ (7)

where $f_{L(R)}$ are the Fermi distribution functions of the left and right electrodes, which has different chemical potential upon a voltage bias $eV = \mu_L - \mu_R$, the coupling of the molecule to the electrodes is characterized by the parameter [21, 22, 25]

$$\Delta_{L(R)}(E) = \pi \sum_{k \in L(R)} V_{km} V_{mk} \, \delta(E - E_k) ,$$ (8)

which is the level-width matrix, and the full width of the resonance is just the sum $\Delta = \Delta_L + \Delta_R$. The retarded Green's function $G^r(E)$ is given by [22, 24],

$$G^r(E) = [E - E_m - i\Delta(E) - \Sigma^r(E)]^{-1}.$$ (9)

The imaginary part of the retarded self-energy $\Sigma^r(E)$ is calculated to the second-order of λ as [17, 22, 24]

$$\mathrm{Im}\Sigma^r(E) = \pi\lambda^2 \int d\omega \, \rho_{ph}(\omega) \times \{f_{ph}(\omega)[\rho_m(E - \omega) + \rho_m(E + \omega)] + [1 - f_m(E - \omega)]\rho_m(E - \omega)$$
$$+ f_m(E + \omega)\rho_m(E + \omega)\},$$ (10)

the real and imaginary parts of $\Sigma^r(E)$ represent the energy-dependent energy shift and the broadening of the molecular electronic states due to the electron-phonon coupling, respectively. Eq. (10) indicates the processes in which an electron (hole) with energy E emits (absorbs) a vibrational energy ω, and transition of an electron (hole) from energy E to energy $E - \omega$ $(E + \omega)$ accompanied with emission (absorption) of a vibrational phonon. These the processes give main contribution to energy dissipation. $\rho_{ph}(\omega)$ and $\rho_m(E)$ are the density of states (DOS) for phonons and electrons, respectively,

$$\rho_{ph}(\omega) = (\Gamma_{eh}(\omega)/\pi)/[(\omega - \hbar\Omega)^2 + \Gamma_{eh}^2(\omega)] ,$$ (11)

$$\rho_m(E) = (\Delta/\pi)/[(E - E_m)^2 + \Delta^2] .$$ (12)

The vibrational damping rate $\Gamma_{eh}(\omega)$ due to electron-hole excitation is given by [22, 24]

$$\Gamma_{eh}(\omega) = 2\pi\lambda^2 \int dE \, [f_m(E) - f_m(E + \omega)] \, \rho_m(E)\rho_m(E + \omega) ,$$ (13)

the stationary distribution function for electrons f_m and the stationary distribution function for phonons f_{ph} in the localized state are, respectively, given by [17, 22, 24]

$$f_m(E) = [\Delta_L f_L(E) + \Delta_R f_R(E)]/\Delta,$$ (14)

$$f_{ph}(\omega) = \left[\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1\right]^{-1} + \frac{\pi\lambda^2}{\Gamma_{eh}(\omega)}\frac{\Delta_L \Delta_R}{\Delta^2} \times \int dE\, \rho_m(E+\omega)\rho_m(E)$$
$$\times [f_L(E+\omega) - f_R(E+\omega)] \times [f_L(E) - f_R(E)]. \tag{15}$$

There are two different time scales which govern the electron tunneling process. One is the electronic lifetime given by

$$T_{\text{life}}(E) = (\hbar/\Delta) - \text{Im}\Sigma^r(E), \tag{16}$$

in which electronic energy in the localized state of molecule dissipates into the right/left electrode or vibrational mode. The other is the residence time given by

$$T_{\text{res}}(E) = \hbar/|E_o - \text{Re}\Sigma^r(E) - \mu_{L/R}|, \tag{17}$$

in which the virtual transition from the Fermi levels in the left and right electrodes to the molecular electronic state. Inclusion of multiple electron-phonon scattering in Eq. (1) by replacing the denominator of Δ with $\Delta - \text{Im}\Sigma^r(E)$ in the resonant case, it is found that the electronic lifetime plays important roles in various features of the tunneling phenomena, for example the change in conductance and inelastic electron tunneling spectroscopy (IETS) [17, 24].

III.   Results And Discussion

In what follows the numerical calculations are performed to study and calculate the electronic lifetime T_{life} from Eq. (16) as a function for a set parameters important for molecular junction, which are the bias voltage $\emptyset$, the electron-vibration coupling λ, the level-width with the two electrodes Δ_L and Δ_R, the vibrational frequency Ω, the position of the molecular electronic state E_0, and the temperature T. The molecular junction is assumed to be in thermal equilibrium at the same temperature T, and the molecule has electronic resonance above the Fermi level. The Fermi levels (which are the equilibrium chemical potential) of the two electrodes were taken to be zero in the unbiased junction. Depending on the wide-band limit we use Δ_L, Δ_R and Δ as constants and the electrodes have broad and flat density of states. We consider the coupling of the molecule to the two electrodes to be symmetric $\Delta_L = \Delta_R$, and $\hbar = 1$ and $e = 1$ with the atomic mass unit. In our calculations, we use as a representative set of molecular junction parameters the values $\Delta_L(= \Delta_R) = 500$ meV, $\Omega = 50$ meV, $E_0 = 0.0$ meV, $\lambda = 100$ meV and $\emptyset = 60$ mV with taking interesting the change in the parameter value used as a variable of T_{life}. The temperature is taken $T = 10$ K; however, we find that the result of T_{life} is independent of T up to room temperature.

Figure 2(a-f) display our result to show the dependence of the electronic lifetime T_{life} to the parameters which characterize molecular junction. Figure 2(a) shows the bias voltage dependence. Physically meaningful values of T_{life} correspond to the threshold voltage, $e\emptyset = \hbar\Omega$, at which the vibrational feature is observed due to the broadening of the vibrational density of states. Where T_{life} almost constant below the threshold because of the missing the vibrational excitation, then T_{life} decreases after the threshold due to the vibrational excitation and open the electron-phonon interaction. In Fig. 2(b), T_{life} decreases with increasing strong electron-phonon interaction, this means increasing the dispersion rate of electronic energy in the localized state of the molecule in junction. Figures 2(c) and 2(d) display the dependence of T_{life} to Δ_L and Δ_R. We primarily consider two situations that are distinguished by the choice of molecule-electrodes couplings. In one that corresponds to strong chemisorption to both electrodes we take $\Delta_L = \Delta_R = 500$ meV. In the other, more akin to an STM geometry, we take Δ_L ($or\ \Delta_R$) < 500 meV and Δ_R ($or\ \Delta_L$) $= 500$ meV, where the more weakly coupled electrode represents physisorption. The level-width reflects the distance between the molecule and the electrodes, so that T_{life} decreases with increases the distance between the molecule and the electrodes as a result increasing the dispersion rate of electronic energy into the right/left electrode or vibrational mode. In Fig. 2(e), there are increases in T_{life} with increasing Ω of the molecule which determines the vibrational excitation threshold and open the electron-phonon interaction. Finally, Fig. 2(f) shows the effect the position of the resonance energy E_0 on T_{life}. In the limit $|\mu_{L/R} - E_0| \gg \Delta_L + \Delta_R$, T_{life} increases due to the low of the transmission probability of electrons in the tunneling process.

IV.   Conclusions

The Keldysh Green's function model has been employed to study the electronic lifetime. Using a set of the parameters which characterize molecular junction and depending on our results, the following points are noteworthy: (1) The electronic lifetime decreases upon an opening of the inelastic channel at $e\emptyset = \hbar\Omega$. (2) The variation of the electronic lifetime with the electron-phonon coupling changes from a rapid decrease at small λ to a relatively mild dependence when λ increases beyond order of magnitude of Δ_L/Δ_R. (3) The electronic lifetime depends mildly on the molecule-electrode coupling, a parameter that may be varied by changing the molecule-electrode distance. (4) The electronic lifetime increases with increasing the molecular vibrational frequency. (5) The electronic lifetime increases with increasing spacing between the Fermi energy of unbiased

junction and the electronic resonance energy of the molecule. (6) The electronic lifetime is only very weakly sensitive to the temperature.
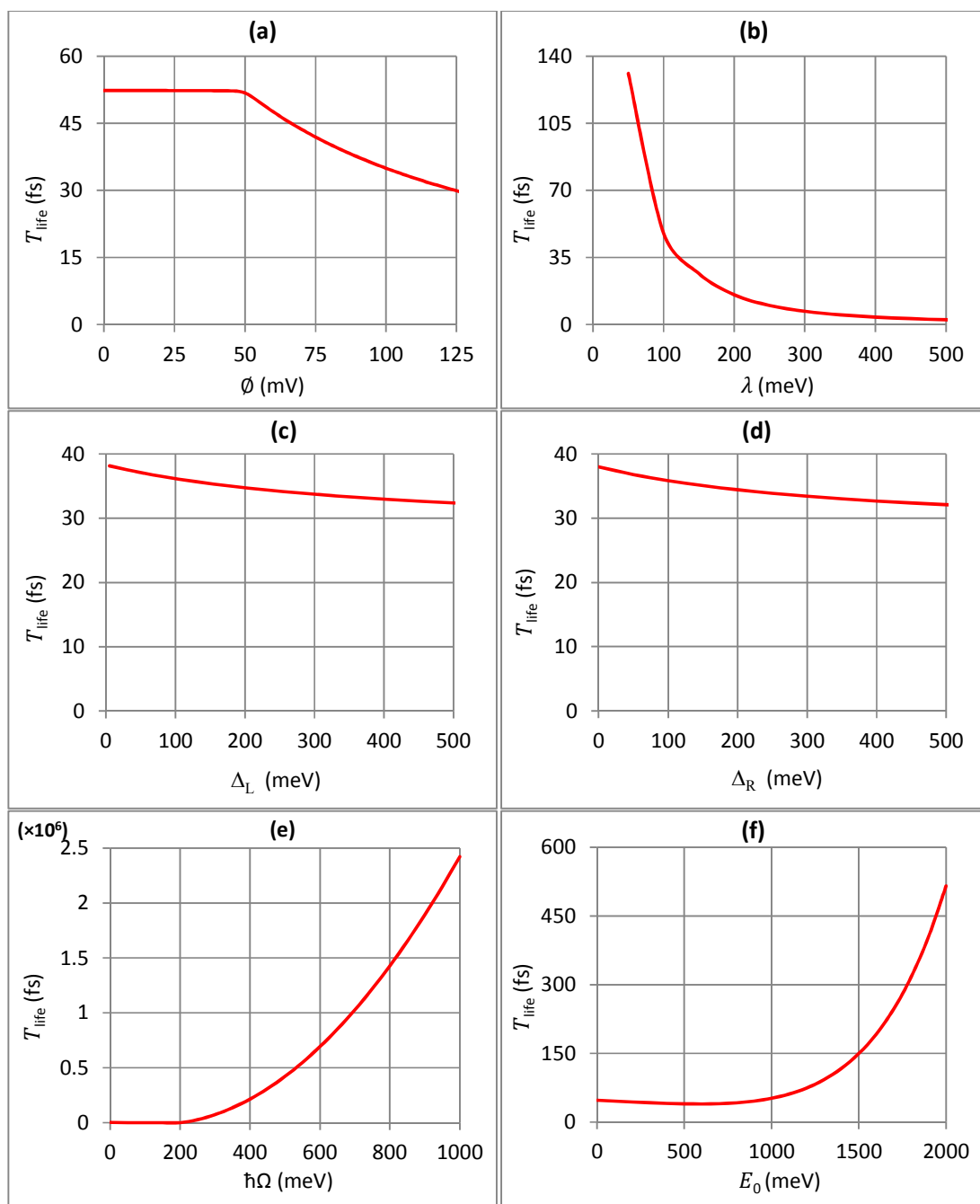
Figure 2: (Color online) Numerical calculations of the electronic lifetimes (T_{life}) in molecular junction for a set of parameters: the bias voltage $\emptyset$, the electron-phonon coupling λ, the level-width with the two electrodes Δ_L and Δ_R, the vibrational frequency Ω and the position of the molecular electronic state E_0 at the temperature 10 K (See the parameters in text).

Acknowledgements

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