Theory of Inelastic Electric Current through Single Molecules

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An electronic structure theory has been developed for an inelastic electric current of electron-intramolecular vibration coupling origin in terms of the Keldysh Green function method and the self-consistent Born approximation. Numerical calculations were made for the benzenedithiol molecule linking the two Au(111) electrodes. The calculations successfully reproduce typical features commonly observed in inelastic tunneling spectroscopy. The vibrational excitation energy due to the inelastic current was estimated. The inelastic electric current is quite important for the structural stability and the switching possibility of the molecular device.

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Single molecules linked to macroscopic electrodes have been studied extensively both theoretically and experimentally in the hope that they might be useful for building up the smallest electric device in history. The field called molecular electronics, which is one of the most exciting fields in nanotechnology, is a growing and interdisciplinary field between many branches of physics, chemistry, and engineering [1]. It is often supposed without justification in the analysis of experimental results and also in theoretical investigations that electric conduction in a molecule takes place in a ballistic manner. Inelastic scattering effects have been neglected so far [2]. Without a special effect such as the Berry phase effect in a carbon nanotube to cancel out the electron-phonon umklapp scattering process, such a premise is quite questionable. Organic molecules are so floppy that one may expect a large inelastic scattering effect of electron-intramolecular vibration (*e*-mv) origin. The *e*-mv coupling effects have long been studied in bulk organic conductors composed of molecular aggregates and biological molecules [3,4].

In a closely related field of surface chemistry, both single molecule chemistry by scanning tunneling microscope (STM) and inelastic STM current have been receiving much attention [5–7]. Small negative differential resistance was observed in a STM current of a pyrrolidine molecule adsorbed on a Cu(001) surface. The adsorbate is supposed to have two local minimum conformations on the surface, one of which is highly conducting and another is less conducting. It was suggested that due to inelastic electric current, the vibrational state is excited and hence the molecular conformation changes. This suggests that a molecular switching device may be realized by dosing electric current. Inelastic electric current has been observed by careful STM experiments on many organic molecules adsorbed on various metallic surfaces. The mechanism of the inelastic current has been studied by using simple models. Theoretical studies have succeeded in explaining the threshold behavior of the inelastic current against the bias voltage, where the threshold value corresponds to the molecular vibrational energy [8–10]. Because the phenomenon is largely dependent on structures of adsorbed molecule and surface, development of a theoretical method based on electronic structure theory that takes care of structural dependencies of molecules and surfaces such as band theory and/or quantum chemistry is highly desirable.

Here we propose an electronic structure theory of inelastic electric current through single molecules between semi-infinite electrodes, based on *e*-mv coupling. We combine the Keldysh Green function method [2,11,12], electronic structure theory, theory of the *e*-mv coupling, and the embedding potential method for the surface state into our theory [13–15]. Self-consistent calculation enables us to take into account (i) the effect of opening the inelastic channel back to the elastic one, (ii) higher order phonon processes relevant for the transport, and (iii) the effect of the surface state such as the evanescent mode close to the contact region. They have not been taken into account in previous theoretical studies using simple models [8–10]. In particular, the contact effect between the molecule and electrodes expressed in the embedding potential method should play an important role in a quantitative description of the inelastic current. It has been noticed that the contact effect from electrodes is indispensable in obtaining the correct temperature dependence of conductance of nanowire in the Tomonaga-Luttinger regime and also the correct size dependence of the conductance. There has been significant progress in the theory of ballistic conductance of molecules. However, as far as the author knows, there is no realistic electronic structure calculation of inelastic conductance of the molecule. The present work may be the first one that goes beyond the ballistic regime.

Denoting current density by $\vec{J}(\vec{r}, E)$, its divergent is written in terms of the molecular Hamiltonian H_{mol} and the electron correlation function $G^n = -iG^<(\vec{r}, \vec{r}')$ as follows [2,16]:

$$\nabla \cdot \vec{J}(\vec{r}, E) = \frac{e}{h}[\{H_{\mathrm{mol}}(\vec{r}) - H^*_{\mathrm{mol}}(\vec{r}')\}G^<(\vec{r}, \vec{r}')]_{\vec{r}=\vec{r}'}. \quad (1)$$

The total current is calculated by taking a surface integral surrounding the molecule (S) between the two electrodes [2,16];

$$\oint_S \nabla \cdot \vec{J}(\vec{r}, E)d\vec{r} = \frac{e}{h}\mathrm{Tr}[\Sigma^< G^> - \Sigma^> G^<], \quad (2)$$

where $G^p = iG^>$, $\Sigma^{\mathrm{in}} = -i\Sigma^<$, and $\Sigma^{\mathrm{out}} = i\Sigma^>$ are the hole correlation function, inscattering function, and outscattering function, respectively. Here, we have adopted the "standard" notations [11,12,16,17] for the correlation functions and scattering functions instead of the notations used in the Ref. [2,18]. The interrelation between these notations and their nomenclature was clearly summarized in these references. The inscattering function $-i\Sigma^<$ is decomposed into that of e-mv coupling origin $-i\Sigma^<_\varphi$ and the contribution from the pth electrode $-i\Sigma^<_p$; $-i\Sigma^< = -i\Sigma^<_\varphi - i\sum_p \Sigma^<_p$. Similarly, $i\Sigma^> = i\Sigma^>_\varphi + i\sum_p \Sigma^>_p$, where p denotes L (the left electrodes) or R (the right electrodes), respectively. Hence the total current is written as follows:

$$\oint_S \nabla \cdot \vec{J}(\vec{r}, E)d\vec{r} = i_\varphi(E) + \sum_p i_p(E), \quad (3)$$

where $i_p(E) = \frac{e}{h}\mathrm{Tr}[\Sigma^<_p G^> - \Sigma^>_p G^<]$ and $i_\varphi(E) = \frac{e}{h}\mathrm{Tr}[\Sigma^<_\varphi G^> - \Sigma^>_\varphi G^<]$. If we use an atomic orbital representation rather than the coordinate representation, the matrix elements of $\mathbf{\Sigma}^>_\varphi(E)$ and $\mathbf{\Sigma}^<_\varphi(E)$ are written as follows:

$$\Sigma^<_{\varphi,rs}(E) = \lambda_{rs}\int d\omega D(\omega)G^<_{rs}(E - \omega), \quad (4)$$

$$\Sigma^>_{\varphi,rs}(E) = \lambda_{rs}\int d\omega D(\omega)G^>_{rs}(E + \omega), \quad (5)$$

where $D(\omega)$ is the boson correlation function for the molecular vibration; $D(\omega) = N_{ph}\delta(\omega - \omega_0) + (N_{ph} + 1) \times \delta(\omega + \omega_0)$, $N_{ph} = \frac{1}{\exp(\beta\omega_0) - 1}$ is the Bose distribution function, ω_0 is the molecular vibrational frequency, and $\beta = \frac{1}{k_B T}$ (k_B is the Boltzmann constant and T is the temperature). The e-mv coupling constant λ is given in terms of the normal coordinate Q derivative of the single particle molecular Hamiltonian h, atomic orbitals χ, and molecular orbital coefficients u;

$$\lambda_{rs} = \frac{1}{\sqrt{2\omega_0}}\sum_k \left\langle \chi_r \,\middle|\, \frac{\partial h}{\partial Q} \,\middle|\, \chi_s \right\rangle u^*_{kr} u_{ks}. \quad (6)$$

k is the molecular orbital suffix and r and s are atomic orbital suffices. In the steady state, $\mathbf{G}^> \approx \mathbf{G}^R \mathbf{\Sigma}^> \mathbf{G}^A$ and $\mathbf{G}^< \approx \mathbf{G}^R \mathbf{\Sigma}^< \mathbf{G}^A$, where the retarded and the advanced Green function are given as follows: $\mathbf{G}^R(E)^{-1} = E \cdot \mathbf{1} - \mathbf{H}_{\mathrm{mol}} - \mathbf{\Sigma}^R_\varphi(E) - \sum_p \mathbf{\Sigma}^R_p(E) + i\eta \cdot \mathbf{1}$, $\mathbf{G}^A(E)^{-1} = E \cdot \mathbf{1} - \mathbf{H}_{\mathrm{mol}} - \mathbf{\Sigma}^A_\varphi(E) - \sum_p \mathbf{\Sigma}^A_p(E) - i\eta \cdot \mathbf{1}$. The inscattering (outscattering) function of contact origin is given in terms of the retarded and advanced self-energy and the local fermion distribution function $f_p(E)$ defined on the pth electrode;

$$-i\mathbf{\Sigma}^<_p(E) = f_p(E)\mathbf{\Gamma}_p(E), \quad (7)$$

$$i\mathbf{\Sigma}^>_p(E) = [1 - f_p(E)]\mathbf{\Gamma}_p(E), \quad (8)$$

$$\mathbf{\Gamma}_p(E) = i[\mathbf{\Sigma}^R_p(E) - \mathbf{\Sigma}^A_p(E)], \quad (9)$$

where $f_p(E) = \frac{1}{\exp^{\beta(E-\mu_p)} + 1}$ and μ_p is the local chemical potential at the pth electrode. The terminal current i_p is decomposed into the elastic $i_{p,\mathrm{ela}}$ and the inelastic $i_{p,\mathrm{inela}}$ components:

$$i_{p,\mathrm{ela}}(E) = \frac{e}{h}\sum_q \mathrm{Tr}[\mathbf{\Gamma}_p \mathbf{G}^R \mathbf{\Gamma}_q \mathbf{G}^A][f_p(E) - f_q(E)], \quad (10)$$

$$i_{p,\mathrm{inela}}(E) = -\frac{ie}{h}\mathrm{Tr}[\mathbf{\Sigma}^<_p \mathbf{G}^R \mathbf{\Gamma}_\varphi \mathbf{G}^A - \mathbf{\Gamma}_p \mathbf{G}^R \mathbf{\Sigma}^<_\varphi \mathbf{G}^A], \quad (11)$$

respectively. The formula for $i_{p,\mathrm{ela}}(E)$ is equivalent formally to the linear response formula for the ballistic current. It should be noticed, however, that $\mathbf{G}^R$ and $\mathbf{G}^A$ in that formula includes the self-energy of the e-mv coupling origin $\mathbf{\Sigma}^R_\varphi$ and $\mathbf{\Sigma}^A_\varphi$ which do not appear in the ballistic case. The retarded and advanced contact self-energies $\mathbf{\Sigma}^R_p$ and $\mathbf{\Sigma}^A_p$ are derived by using the embedding potential method [14,15], and a self-consistent loop is formed between $\mathbf{\Sigma}^<$ and $\mathbf{G}^<$ ($\mathbf{\Sigma}^>$ and $\mathbf{G}^>$). The self-consistent Born approximation for the e-mv problem is employed. Using the formalism presented above, I have calculated the elastic and inelastic components of the electric current through the single benzenedithiol (BDT) molecule placed between the two semi-infinite Au(111) electrodes in a top site adsorption manner. Here for simplicity the extended Hückel approximation has been adopted to evaluate all the matrix elements necessary to calculate the electric current [19]. The structure, vibrational frequencies, and normal coordinate were calculated by using a cluster model of the singlet ground state of Au-BDT-Au, the *ab initio* Hartree-Fock method, and the MINI basis set [20,21]. The lamp model has been adopted for the chemical potential [2]: $\mu_L = E_F + (1 - \eta)$ eV and $\mu_R = E_F - \eta$ eV, where E_F is the Fermi level of the electrodes, V is the applied bias voltage, and η is the voltage division factor which gives the ratio of the voltage drop at the two contacts and takes a value between 0 and 1. In the present case $\eta = 0.5$, because the two electrodes are equivalent and the BDT molecule is

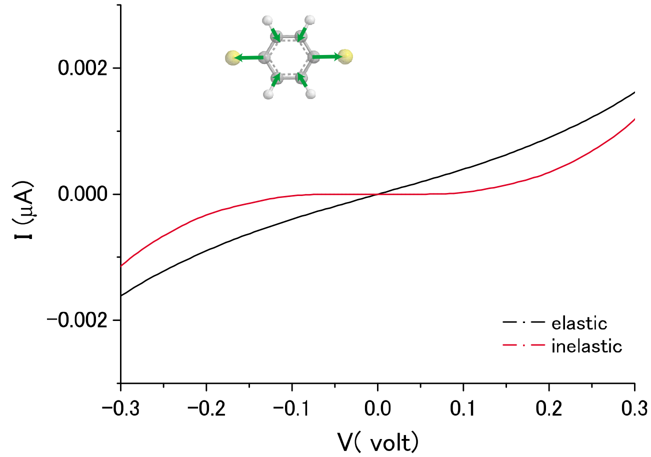

FIG. 1 (color). Voltage (V) dependence of electric current (I) that flows through the BDT molecule. The black line denotes elastic current, while the red line denotes inelastic current. The frequency of the molecular vibration is 815.2 cm^{-1}. The vibrational mode is one of the A_g modes of the BDT molecule, which is depicted schematically in the inset. The inelastic current starts to grow above a threshold voltage, 0.101 V, that corresponds to the vibrational frequency.

symmetric. The Fermi level of the Au(111) electrodes is put $E_F = -5.31$ eV, which is close to the bulk value found in the literature [22]. All these shortcomings limit us to cases (i) the low bias region and (ii) the high frequency intramolecular vibrational modes. Despite these shortcomings, semiquantitative arguments are still useful, if we limit ourselves to the two cases.

The elastic and inelastic electric currents $I_{p,\mathrm{ela}} = \int_{-\infty}^{\infty} i_{p,\mathrm{ela}}(E)dE$ and $I_{p,\mathrm{inela}} = \int_{-\infty}^{\infty} i_{p,\mathrm{inela}}(E)dE$ were calculated, and they are plotted in Fig. 1. The mode is one of the A_g modes of the BDT molecule. The vibrational frequency was calculated to be $\omega_0 = 0.1011$ eV. A clear increase of $I_{p,\mathrm{inela}}$ is found at the threshold energy, i.e., vibrational energy ω_0. $\frac{dI}{dV}$ and $\frac{d^2I}{dV^2}$ as a function of V are shown in Fig. 2, where the threshold behavior across the vibrational energy can be seen more clearly. The peaks of $\frac{d^2I}{dV^2}$ are symmetrically located at the positive and the negative branches of the voltage (V) axis. The threshold behavior has been found in STM experiments on various molecules adsorbed on surfaces. It is a general feature of inelastic tunneling spectroscopy and the calculation is successful in reproducing this feature. The inelastic currents were calculated for all the vibrational modes whose energies are larger than 450 cm^{-1}. $\frac{d^2I}{dV^2}$'s are plotted in Fig. 3, which shows strong mode dependencies on the magnitude of $\frac{d^2I}{dV^2}$. A propensity rule, which is often observed in experiments and a matter of current theoretical interests [23], may apply for the vibrational modes. The vibrational mode ($\omega_0 = 0.1011$ eV) used in Fig. 1 is one of the most strongly coupled modes to the electric current. The power loss $-\frac{2}{e}\int_{-\infty}^{\infty} E i_{\varphi}(E)dE$ due to the coupling to this vibrational mode was calculated and was plotted in Fig. 4. At $V = 0.3$ V, the power loss was estimated to be 0.3×10^{-9} W, which may amount to 0.2 eV, if the electric current dosing is done without relaxation for 0.1 ns. The period was estimated from a typical value of the half-width of the molecular vibrational spectrum. The estimated energy is close to the vibrational two quanta for that mode. The energy may be transferred to low frequency phonon modes, which are closely related to bonding between the BDT molecule and the Au(111) surface. The energy value is not small for low frequency modes, and it is likely that either the desorp-

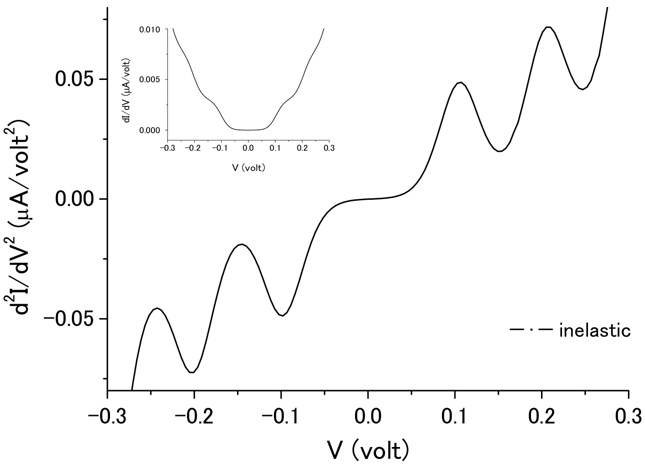

FIG. 2. The second derivative $\frac{d^2I}{dV^2}$ of the inelastic component of the electric current. The vibrational mode is the same as that used in Fig. 1. The threshold behavior is more clearly seen. The peak structure and the line shape are symmetric against the sign change of the voltage. The inset is the first derivative $\frac{dI}{dV}$ of the inelastic component of the electric current.

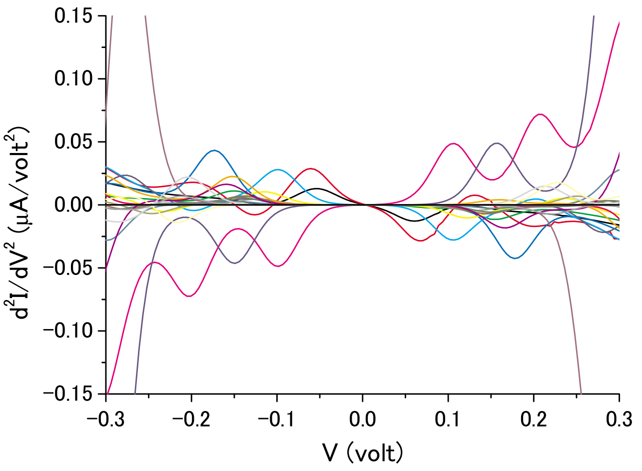

FIG. 3 (color). The vibrational mode dependencies of the second derivative $\frac{d^2I}{dV^2}$ of the inelastic component of the electric current. In all, six $\frac{d^2I}{dV^2}$s are much larger than the others.

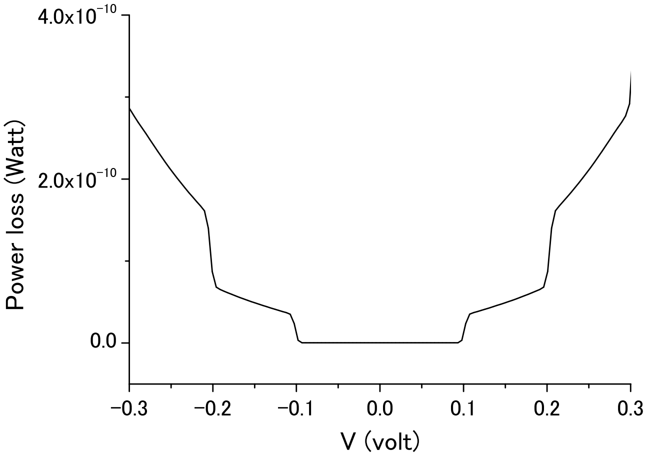

FIG. 4. Power loss (in unit of watts) due to the *e*-mv coupling. The vibrational mode is the same as that used in Fig. 1.

tion process or the conformational change occurs. The inelastic electric current calculated here is quite important for the structural stability and the switching possibility of the molecular device.

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Note added.—After the submission of this work, the author came to notice the existence of the literature [24–26], where the primary importance of the longitudinal vibrational modes of molecules for the inelastic currents in some molecular junction systems was concluded. This conclusion does not contradict the results obtained here.

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