Current-induced quantum friction of nano-linked molecular vibration

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Abstract. Current-induced energy dissipation of nano-linked molecule vibration is studied from a microscopic viewpoint. The equation of motion for the vibration is derived based on the quantum mechanical calculations. It is shown that the current between molecule and electrode promotes quantum friction for the vibration. Moreover, we demonstrate that the damping of vibration is very sensitive to energy-level position of molecule and the electronic correlation in molecule.

1. Introduction

Electron transports through nano-scale molecule systems have attracted intensive studies during last ten years. Since the molecule systems are often linked with outer systems like metal electrodes by a limited number of atomic bonds, the energy accumulation and dissipation in molecule vibration occur originating from the electronic current that flows through such bond connection. For example, it has often been observed that the electronic current easily excites the molecule vibration, rotation and movement by way of the inelastic scattering of electrons [1]. In this work, we consider the opposite process; the molecule vibration induces the electronic current between the molecule and metal electrodes and such current dissipates the vibration energy. The purpose of this work is to clarify how fast the molecule vibration damps by the electronic current at nano-contact interfaces from a microscopic viewpoint.

2. Model and Formulation

2.1. Model System

In this work, we consider the simplest model schematically shown in Fig. 1(a); the nano-scale molecule having a single energy level links with an external electrode and the vibration occurs at this linkage bond. The vibration is represented by a harmonic oscillator, while the electronic correlation in molecule is realized by the so-called Anderson’s sd Hamiltonian. Thus, the Hamiltonian of the present system is described as

\[ \hat{H} = \frac{\hat{p}^2}{2M} + \frac{M\nu^2}{2}x^2 + \sum_\sigma \epsilon_0 \hat{c}_0^\dagger \hat{c}_{0\sigma} + U \sum_{0\tau} \epsilon_0^\dagger \hat{c}_0^\dagger \hat{c}_{0\tau} + U \sum_{\sigma k\tau} \epsilon_k \hat{c}_{k\sigma}^\dagger \hat{c}_{k\tau} + V(x) \sum_{k\sigma} \hat{c}_{k\sigma}^\dagger \hat{c}_{k\sigma} + \sum_{\sigma} \hat{c}_{0\sigma}^\dagger \hat{c}_{0\sigma} + \hat{c}_{0\sigma} \hat{c}_{0\sigma}^\dagger \]

Here, the fast and second terms represent the vibration energies of a linked molecule, where the displacement and the corresponding momentum are expressed by \(x\) and \(\hat{p}\), respectively. \(M\) is an
effective mass of a molecule, and $\omega$ is the vibration frequency. The third and forth terms are energies of electrons in the molecule, where $\hat{c}_{0\sigma}^+$ and $\hat{c}_{0\sigma}$ are creation and annihilation operators of $\sigma$-spin electrons in the molecule ($\sigma = \pm 1$). $\varepsilon_0$ is a molecule-site energy, while $U$ the repulsion energy between electrons. The fifth term is energies of electrons in an electrode, where the energy $\varepsilon_k$ is characterized by the wave number $k$. The last term corresponds to the electron transfer between the molecule and the electrode. Since the transfer energy depends on the displacement of molecule as $v(x)$, the last term induces the electron-vibration interaction.

2.2. Derivation of effective action

The equation of vibration motion is obtained from the action integral of the system based on the principle of least action. Thus, we first derive the effective action integral for the vibration. When we adopt the Wick rotation by replacing the real time with the imaginary time as $\tau = i t$, the time-evolution of the system is equivalently described by the partition function of the system, $Z = \text{Tr} \, e^{-\beta \hat{H}}$, as [2]

$$Z = \int Dx Dc^+ Dc \exp \left[ -\int_0^\beta dt (L_{\text{vib}} + L_{\text{mol}} + L_{\text{elc}} + L_{\text{vib-el}}) \right],$$

$$L_{\text{vib}} = \frac{M}{2} \dot{x}^2 (\tau) + \frac{M \omega^2}{2} x(\tau)^2,$$

$$L_{\text{mol}} = \sum_{\sigma} \epsilon_{0\sigma} (\tau) (\partial_\tau + \epsilon_0 - \mu) c_{0\sigma} (\tau) + U c_{0\uparrow}^+ (\tau) c_{0\downarrow} (\tau) c_{0\downarrow}^+ (\tau) c_{0\uparrow} (\tau),$$

$$L_{\text{elc}} = \sum_{k\sigma} \epsilon_{k\sigma}^e (\tau) (\partial_\tau + \epsilon_k - \mu) c_{k\sigma}^e (\tau),$$

$$L_{\text{vib-el}} = v(x(\tau)) \sum_{k\sigma} (c_{k\sigma}^e (\tau) c_{0\sigma}^e (\tau) + c_{0\sigma}^e (\tau) c_{k\sigma}^e (\tau)).$$

Here, we used the path integral representation, where $c^+$ and $c$ are Grassmann numbers representing electron freedom. $L_{\text{vib}}$, $L_{\text{mol}}$, $L_{\text{elc}}$, and $L_{\text{vib-el}}$ are Lagrangeans corresponding to the molecule vibration, electrons in molecule, electrons in electrode, and vibration-electron interaction, respectively.

Next, we introduce an auxiliary field, $\varphi$, and employ the Stratonovich-Hubbard transformation to artificially delete the electron-electron interaction [3, 4]. In this case, the partition function can be written as

$$Z = \int Dx D\varphi Dc^+ Dc \exp \left[ -\int_0^\beta dt (\tilde{L}_{\text{vib}} + \tilde{L}_{\text{mol}} + \tilde{L}_{\text{el}} + \tilde{L}_{\text{vib-el}}) \right],$$

Fig. 1. (a) Schematic picture of model system studied in this work. (b) Electronic states realized in molecule. There are four states corresponding to electron occupation. Two states have spin polarization.
\[ \mathcal{L}_{\text{mol}} = \frac{U}{2} \varphi(\tau)^2 + \sum_{\sigma} c_{\sigma 0}^\dagger(\partial_{\tau} + \varepsilon_0 - \mu + \sigma U \varphi(\tau))c_{\sigma 0}(\tau). \] (8)

When a mean-field approximation is adopted for the electron-electron interaction, the auxiliary field represents the spin polarization, \( \varphi = -\text{Tr}(c_{01}^\dagger c_{01} - c_{0+}^\dagger c_{0+}) \).

Then, we eliminate electronic freedoms in Eq.(7) by the simple integration of \( c^\dagger \) and \( c \) variables. As a result of integration, one obtain the effective action as

\[ Z = \int D\varphi \exp[-S_{\text{eff}}], \]

\[ S_{\text{eff}} = \int_0^\beta dt (L_{\text{vib}} + \frac{U}{2} \varphi(\tau)^2) - \ln(\text{det } M), \]

where the matrix elements of \( M \) are defined by

\[ \langle k, i\omega, \sigma | M | k', i\omega', \sigma' \rangle = \delta_{\sigma\sigma'} \left[ (-i\omega + \varepsilon_k - \mu)\delta_{kk'} + \sigma U \varphi(i\omega_i - i\omega')/\sqrt{\beta} \right] \delta_{\omega\omega'} \delta_{kk'}, \]

\[ v_{\delta\delta'}(i\omega_i - i\omega')/\sqrt{\beta}. \] (11)

Here, \( \omega_i \) and \( \omega_n \) are Matsubara frequencies, \( \omega_i = (2l+1)\pi/\beta \) and \( \omega_n = 2\pi n/\beta \), respectively. \( \varphi(i\omega_i) \) and \( v(i\omega_i) \) are Fourier transforms of \( \varphi(\tau) \) and \( v(\tau) \), defined as

\[ \varphi(i\omega_i) = \int_0^\beta d\tau \varphi(\tau) e^{-i\omega_i \tau}/\sqrt{\beta} \] and \( v(i\omega_i) = \int_0^\beta d\tau v(\tau) e^{-i\omega_i \tau}/\sqrt{\beta}. \) (12)

Hereafter, for simplicity, we assume that the electron transfer energy is sufficiently small as \( v(x) \ll |\mu - \varepsilon_0| \), where \( \mu \) is the Fermi energy of the electrode. Moreover, since the vibration is sufficiently slow compared to the ordinary electronic motion, we can adopt the adiabatic approximation and ignore the time-evolution change of the auxiliary field, \( \varphi \). This treatment is exactly correct within the second order of \( (i\omega_i \neq 0) \) when the action is expanded by \( \varphi(i\omega_i \neq 0) \). In this case, applying the second-order perturbation of \( v(x) \) to Eq.(10) and expanding the \( M \) matrix, we obtain the effective action \( S_{\text{eff}} \) as

\[ S_{\text{eff}} \approx \int_0^\beta dt (L_{\text{vib}} + \frac{U}{2} \varphi^2) - \text{Tr}[- \ln(G_0^{-1})] + \frac{1}{2} \int_0^\beta dt \int_0^\beta d\tau v(x(\tau))v(x(\tau'))K(\tau - \tau'), \]

\[ K(\tau - \tau') = -\frac{1}{\beta} \sum_{k\sigma} \sum_{i\omega} e^{i\omega_k(\tau - \tau')} \left( \frac{f(\varepsilon_k) - f(\varepsilon_{k\sigma})}{\varepsilon_{0\sigma} - \varepsilon_k - i\omega_{\sigma}} + \frac{f(\varepsilon_{k\sigma}) - f(\varepsilon_k)}{\varepsilon_k - \varepsilon_{0\sigma} - i\omega_{\sigma}} \right), \]

where \( f(\varepsilon) \) is Fermi distribution function and \( \varepsilon_{0\sigma} = \varepsilon_0 + \sigma U \varphi \). \( G_0 \) is Green’s function which matrix elements are defined by the first term of Eq.(11). \( K(\tau - \tau') \) is the two-time Fourier transform of polarization function. \( f(\varepsilon_k) \) and \( f(\varepsilon_{0\sigma}) \) in the numerator of Eq. (35) appear due to the electron motions from electrode to molecule and from molecule to electrode, respectively. When we assume that the system temperature is sufficiently low as \( |\beta(\varepsilon_0 - \mu)| >> 1 \), \( K(\tau - \tau') \) can be approximated by

\[ K(\tau - \tau') \approx -\frac{2}{(\tau - \tau')^2} \sum_{k\sigma} -\frac{\partial f(\varepsilon_k)}{\partial \varepsilon_k} \delta(\varepsilon_k - \varepsilon_{0\sigma}). \] (15)

The energy derivative of Fermi distribution function in this equation originates from the difference of electron-transfer motions into and out-of the molecule, thus representing the electronic current between molecule and electrode.
2.3. Equation of vibration motion

The equation of vibration motion is obtained by applying the variational principle for the vibration freedom, \( x(\tau) \), to the effective action in Eq.(13) and performing inverse Wick rotation (\( \tau \rightarrow it/\hbar \)). The result is written as

\[
M\ddot{x} + \frac{\partial \tilde{V}(x)}{\partial x} + \eta(x) \dot{x} = 0, \\
\]

where \( \tilde{V}(x) \) is the renormalized potential and \( \eta(x) \) the Ohmic-like friction coefficient, both of which are defined by

\[
\eta(x) = 2\pi \left( \frac{dv(x)}{dx} \right)^2 \sum_{k\sigma} -\frac{\partial f(\varepsilon_k)}{\partial \varepsilon_k} \delta(\varepsilon_k - \varepsilon_0 - \sigma U \phi), \\
\]

\[
\tilde{V}(x) = \frac{M\omega^2 x^2}{2} - \nu(x)^2 \sum_{k\sigma} \frac{f(\varepsilon_k) - f(\varepsilon_0 + \sigma U \phi)}{\varepsilon_0 + \sigma U \phi - \varepsilon_k}. \\
\]

The physical meaning of the \( \eta(x) \) formula is apparent; the friction occurs due to the electron transfer between molecule and electrode. Thus, the friction is proportional to both the square of electron-vibration coupling, \( dv(x)/dx \), and the density of states in electrode, \( \sum \delta(\varepsilon_k - \varepsilon_{\sigma}) \). Similarly, the equation of motion for \( \phi \) is obtained by the variation, \( \partial S_{eff} / \partial \phi = 0 \), as

\[
U\phi + \sum_{\sigma} \sigma U f(\varepsilon_0 + \sigma U \phi) + \frac{1}{2\beta} \int d\tau \nu(x(\tau))^2 = 0. \\
\]

Although the vibration motion is determined by the coupled equations, (17) and (19), these equations can not be solved analytically. Thus, in this work, for simplicity, we neglect the third term of Eq.(19). This treatment is equivalent to assuming that the spin polarization does not change largely during the vibration. We consider the specified cases with respect to the magnitude of the electronic repulsion, \( U \), in the next section.

3. Result and Discussion

3.1. In case of weak repulsion

We first consider the case when the electronic repulsion is sufficiently small; \( U \ll |\varepsilon_0 - \mu| \). In this case, Eq.(19) has only a single stable solution, \( \phi = 0 \), which corresponds the electronic states having no spin polarization in molecule. Therefore, the friction becomes independent of the vibration,
x(t), and becomes sensitive to only the energy level position of molecule, \( \varepsilon_0 \). Figure 2 shows the friction coefficient as a function of \( \varepsilon_0 \). It is seen that the friction becomes large when \( \varepsilon_0 \) approaches the Fermi energy of electrode, \( \mu \).

Figure 3(a) and 3(b) illustrate the schematic pictures explaining the variation of friction seen in Fig.2. When \( \varepsilon_0 \) is located far below \( \mu \) as in Fig.3(a), since the molecule level and electrode levels having \( \varepsilon_0 \) energy are always fully occupied by electrons, it is difficult to produce electronic current between molecule and electrode. As a result, the dissipation of vibration energy by the current is highly suppressed. The similar scenario is also applied to the case when \( \varepsilon_0 \) is located far above \( \mu \). However, when \( \varepsilon_0 \) is located near \( \mu \) as in Fig.3(b), since both the molecule level and electrode levels having \( \varepsilon_0 \) energy are partially occupied, large current can flows between molecule and electrode and promotes large energy dissipation.

3.2. In case of large repulsion

Then, we consider the opposite case where the electronic repulsion in molecule is sufficiently large; \( U > |\varepsilon_0 - \mu| \). In this case, Eq.(19) has five solutions. Among them, the full-polarization \( \varphi = \pm 1 \) solutions become most stable. On the other hand, as seen in Eq.(17), the friction becomes largest when \( \mu \approx \varepsilon_0 + \sigma U \varphi \). However, this equation contradicts to the assumption of large repulsion. Thus, we can expect that the friction becomes small compared to the case of small repulsion. This result is physically reasonable because, as the repulsion increases, the electron transfer is suppressed and thus the current decreases.

3.3. Evaluation of friction magnitude

Finally, we evaluate the friction and current magnitude expected in experiments, in the case of weak repulsion. To characterize the friction, we consider the relaxation time by the friction, \( \tau_f \), which is defined by \( \tau_f^{-1} = \eta(x = 0) / M \). When \( \varepsilon_0 \) is located near \( \mu \) and the system temperature is sufficiently low, the friction becomes largest and \( \tau_f^{-1} \) is written as

\[
\tau_f^{-1} \approx 2\pi\hbar / M \left( d\eta / dx \right)_{x=0}^2 D(\varepsilon_0) \left( -d\varepsilon / d\varepsilon_0 \right)_{x=0}.
\]

(20)

Here \( D(\varepsilon_0) \) is the density of states in electrode, which is typically 0.5 eV\(^{-1}\) for electrodes made of normal metals and doped semiconductors, while the energy derivative of Fermi distribution function is
about 600 eV when T=5 K. The transfer energy is often represented in an exponential form as 
\[ v(x) = v_0 \exp(-x/\lambda), \]
where \( x \) is the displacement of a linked molecule. \( v_0 \) and \( \lambda \) are the electron transfer energy and the overlap length of wavefunctions, respectively, which are typically 0.05 eV and 2 Å for the molecule adsorbed on the electrode. Using these values and assuming that the molecule is a naphthalene with the mass of \( M = 2 \times 10^{-25} \) kg, the relaxation time is estimated more than \( \tau_f \approx 20 \) psec. This value is reasonably larger than the typical oscillation period of molecular vibration around 1 psec. On the other hand, the current flowing between the molecule and electrode is evaluated as 
\[ \frac{2\pi e}{h} \nu^2 (x = 0) D(v_0) \] [5, 6], when we use the similar approximation to the present case of friction. Thus, using the typical values mentioned above, we can expect the reciprocating current around 100 nA between the molecule and electrode during the damping of molecular vibration.

4. Conclusions
We have theoretically derived the equation of motion for nano-linked molecule vibration for the case of small electronic transfer and low temperature, by evaluating the effective action based on the path integral formalism. It is shown that the electronic current at the molecule/electrode interface works as a friction for vibration. The friction becomes large when the energy of molecule approaches the Fermi energy of electrode. This is because such energy resonance promotes frequent electron transfer motion between molecule and electrode and induces large energy dissipation. In addition, we have shown that the electronic correlation in molecule decreases this type of friction.

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References
[1] Y.Kim, T.Komeda, M.Kawai, Phys.Rev.Lett. 89 (2002) 126104, *ibid.* 95, (2005) 246102.
[2] R. P. Feynman and A. R. Hibbs, *Quantum Mechanics and Path Integrals* (McGraw-Hill, New York, 1965).
[3] R. L. Stratonovich, Dokl. Akad. Nauk SSSR 115, (1957) 1907 [Sov. Phys. Dokl. 2, (1958) 416].
[4] J. Hubbard, Phys. Rev. Lett. 3, (1959) 77.
[5] H. Ishii, T. Nakayama, Phys. Rev. B73, (2006) 235311-1-11.
[6] H. Ishii, Y. Tomita, T. Nakayama, phys. Stat. sol. (c) 4, (2007) 481.