Transient Current Behavior through Molecular Bridge Systems; Effects of Intra-Molecule Current on Quantum Relaxation and Oscillation

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Transient current behavior through two-site molecular bridge systems is studied using density-matrix calculations in order to clarify the multi-site effects in molecule. It is shown that, as increasing the number of energy-level sites in molecule, the relaxation speed becomes slow and the period of current oscillation increases reflecting the change of electronic states in molecule. Moreover, we found that the intra-molecule quantum electron motion often induces a new oscillation and largely modulates the transient current behavior. This motion is also expected seen as a spike-like vibration in steady-state current when a molecule changes its structure such as by the adsorption and desorption of another molecule. [DOI: 10.1380/ejssnt.2009.606]

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I. INTRODUCTION

Electronic transport through nanoscale systems, such as molecular bridges [1–3], semiconductor quantum-point contacts [4], and quantum dots [5–7], has attracted intensive investigations in these days. From these studies, the unique transport properties, such as the resonant tunneling, the quantization of conductance, the Kondo effects, the molecule persistent current, and the strange anisotropic currents in artificial lattices, have been revealed [8–15]. All these are concerned with steady-state properties. However, to employ these systems as practical devices, it is essential to understand the transient-current behavior responding to a sudden switching or an applied pulse voltage because the relaxation speed to the steady state and the deformation of input pulse voltage determine the device efficiency. Recently, the real-time measurements of electronic current have become possible [16, 17], thus increasing our attention to the transient behavior of current through nanoscale systems.

There have been many theoretical studies of time-dependent transport through nanoscale systems, mainly by using the time-dependent nonequilibrium Green’s function method [18–20] and the time-dependent density matrix formalism [21–24]. In most of these studies, the calculated transient current often shows the relaxation and oscillation [25–28]. In order to clarify the physical origins of such transient behavior, in our previous paper [24], we employed the density-matrix method and showed that the relaxation occurs due to the energy dissipation into a number of electronic states in electrodes, thus the relaxation speed depending on the density of states in electrode and the electron transfer energy between the electrode and nanoscale system. On the other hand, the oscillation originates from the time-dependent electron transitions between the electrode and nanoscale system, thus its period depending on the Fermi-energy position and the bandwidth of electrodes.

In most these studies so far, however, the nanoscale system is simply modeled having the single energy-level site. In this view, it is interesting to study how the transient-current behavior changes when the nanoscale system is made of not a single site but multi sites. In this work, we study the transient current through the two-site molecular bridge systems and clarify the effects of such multi sites, comparing to the results of the single-site system. In Sec. II, we explain the model system considered in this work and present our calculation method of time-dependent current. Then, in Sec. III, we show the calculated transient currents and discuss new features that are induced by the existence of multi sites in molecule. In addition, we consider what occurs in steady-state current when the number of molecule sites suddenly changes, corresponding to the change of molecule structures. Section IV is devoted to the conclusions.

II. MODEL AND METHOD

In order to study the transient current in the multi-site molecule system, in this paper, we adopt the simplest molecule made of two sites. We call these sites the C and c sites, hereafter. Depending on the arrangement of these sites, there exist two types of molecules, as shown in Figs. 1(a) and 1(b). One is the branch-type molecule, where only the C site is connected to left (L) and right (R) electrodes and the c site is coupled only with this C site as a branch site. The other is the straight-type molecule, where the C and c sites are connected to left and right electrodes, respectively, and both sites are coupled with each other in a straight array between two electrodes. The
Hamiltonian for these types of systems is written as

\[ \hat{\mathcal{H}} = \mathcal{H}_0 + \mathcal{H}_1 = \varepsilon_C \hat{C}^\dagger \hat{C} + \varepsilon_c \hat{c}^\dagger \hat{c} + v' (\hat{C}^\dagger \hat{c} + \hat{c}^\dagger \hat{C}) + \sum_{k, \alpha = L, R} \varepsilon_{k\alpha} \hat{a}_{k\alpha}^\dagger \hat{a}_{k\alpha} + \hat{H}_1, \]

where \( \varepsilon_C \) and \( \varepsilon_c \) are on-site energies of electrons at the C and c sites, respectively, while \( \varepsilon_{k\alpha} \) is an electron energy in the \( \alpha = \) L or R electrode with the wavenumber, \( k \). \( v' \) is the intra-molecule electron transfer energy between the C and c sites. \( \hat{c}^\dagger \) , \( \hat{c} \), and \( \hat{a}_{k\alpha}^\dagger \) are electron-creation operators of these states. Here, we assume that the electron is represented by a spinless fermion for simplicity. \( \hat{H}_1 \) represents the coupling between molecule sites and electrodes, thus having the different forms between the branch and straight-type molecules. They are respectively written as

\[ \hat{\mathcal{H}}_1^{(b)} = \sum_k v_L (\hat{C}^\dagger \hat{a}_{kL} + \hat{a}_{kL}^\dagger \hat{C}) + \sum_k v_R (\hat{C}^\dagger \hat{a}_{kR} + \hat{a}_{kR}^\dagger \hat{C}), \]

\[ \hat{\mathcal{H}}_1^{(s)} = \sum_k v_L (\hat{C}^\dagger \hat{a}_{kL} + \hat{a}_{kL}^\dagger \hat{C}) + \sum_k v_R (\hat{c}^\dagger \hat{a}_{kR} + \hat{a}_{kR}^\dagger \hat{c}). \]

Here, \( v_\alpha \) is the electron transfer energy between the molecule site and \( \alpha \) electrode.

It should be noted here that we consider only the two-site molecules in this paper, instead of considering the general \( N \)-site molecules. This is because, when the number of sites in molecule is larger than three, there appear a variaty of site configurations such as not only the simple combinations of the branch and straight types but also the combinations with the ring-skeleton types, which all are often seen in organic molecular systems. The number of such combinations rapidly increases as the number of sites in molecule increases. Therefore, to analyze the effects of essential elements in such combinations, we select the simplest cases, i.e., the two-site molecules, as the first step of our study.

Time dependence of current is evaluated using the density-matrix formalism based on the Liouville equation, which was developed by Ishii et al.\[24\] The basic equation that should be solved is written as

\[ \frac{\partial \sigma(t)}{\partial t} = i \dot{\mathcal{L}}_0 \sigma(t) + T_{LR} \dot{\mathcal{L}}_1 \int_{t_0}^t d\tau e^{-i\varepsilon_C(t-\tau)} \dot{L}_1 \hat{\rho}_L \hat{\rho}_R \sigma(\tau), \]

where \( \sigma(t) \) is the density matrix of molecule system at time, \( t \). \( \hat{\rho}_L \) and \( \hat{\rho}_R \) are density matrices of left and right electrodes, respectively, which are assumed to obey the grand-canonical distribution having chemical potentials, \( \mu_L \) and \( \mu_R \). \( T_{LR} \) and \( T_{RL} \) are trace operations for electronic freedoms in left and right electrodes, respectively. \( \dot{\mathcal{L}}_0 \) is the Liouville super operator corresponding to the Hamiltonian, \( \mathcal{H}_0 \), while \( \dot{L}_1 \) is that corresponding to \( \mathcal{H}_1 \). They operate such as \( \mathcal{L}_0 \bullet \equiv -i/\hbar [\mathcal{H}_0, \bullet] \) for any operator, \bullet.

In general case of \( N \)-site molecule systems, the density matrix, \( \sigma(t) \), becomes \( 2^N \times 2^N \) matrix, thus it being \( 4 \times 4 \) matrix in the present study. We choose that the four components of this matrix correspond to the states, \( |1\rangle \equiv \hat{C}^\dagger |0\rangle \), \( |2\rangle \equiv \hat{C}^\dagger |0\rangle \), \( |3\rangle \equiv \hat{c}^\dagger |0\rangle \), and \( |4\rangle \equiv |0\rangle \), where \( |0\rangle \) is the vacant state. Thus, the diagonal elements, \( \sigma_11, \sigma_{22}, \sigma_{33}, \) and \( \sigma_{44} \) represent the probabilities of these state, while the electron occupations at the C and c sites are obtained as \( n_C = \sigma_11 + \sigma_{22} \) and \( n_c = \sigma_{33} + \sigma_{44} \), respectively. On the other hand, the off-diagonal elements such as \( \sigma_{23} \) represent the transition amplitude between two electronic states. The equations of these matrix elements are summarized in the Appendix.

It should be noted here that the first term in the right side of Eq. (4) is propotional to the intra-molecule transfer, \( v' \), which reflects the quantum-mechanical intra-molecule motion of electrons in the molecule. On the other hand, the second term is propotional to the square of the transfers between the molecule and electrodes, \( v_\alpha \), which reflects that the electronic quantum motion is ther-mally equilibrated in electrodes once the electrons are transferred into electrodes because the electrodes normally have the macroscopic degrees of freedom \[24\]. In this way, Eq. (4) describes both the intra-molecule quantum motion of electrons and the energy-dissipation process of electrons in electrodes.

We solve the Eq. (4) by the numerical calculation adopting the standard finite difference method \[24\]. There are various parameters in the present systems. Since we are interested in the multi-site effects on the transient current, in the numerical simulation, we change only the magnitude of intra-molecule transfer energy, \( v' \), and employ the same values for the other parameters as the typical values in case of the single-site molecule \[24\]. They are \( \varepsilon_C = \varepsilon_c = 0.0, v = v_L = v_R = 0.1, \) and \( D = D_L = D_R = 1, \) where \( D \) is the density of states in...
electrodes. The applied voltage is represented by $\mu_L = 1.0$ and $\mu_R = -1.0$. Moreover, we assumed that the electrode has an infinite band width and the temperature is zero. These parameterization indicates that we choose the unit of energy as $\mu_L - \varepsilon_C = 1.0$ and the corresponding unit of time as $\hbar/(\mu_L - \varepsilon_C)$.

Similar to the case of the single-site molecule, we first connect the molecule and electrodes at the time, $t_0 = 0$, and then apply the voltage at $t = 30$. We adopted the first connection at $t_0 = 0$, experimentally because most nano-contact measurements are performed after connecting the molecule with electrodes and theoretically because such connection induces the quantum hybridization between energy states of the molecule and electrodes and promotes unintentional transient currents. It is noted here that, as described in Ref. [24], we consider the case when the molecule-electrode transfer, $v_\alpha$, is smaller than the applied voltage, $\mu_L - \mu_R$, we obtain Eq. (4) for the density matrix by adopting the second-order approximation of $v_\alpha$. This approximation is known to induce the level broadening of molecule electronic state in the steady state [21]. On the other hand, the current oscillation seen just after $t = 0$ in Fig. 2(a) corresponds to the time-dependent production of such level broadening in the time domain. Other calculational details are described in ref. [24].

**III. RESULTS AND DISCUSSION**

**A. Branch-type molecule**

In this subsection, we consider the branch-type molecule. Three cases are simulated for the transient behavior; (i) $v' = 0.5$, (ii) $v' = 0.1$, and (iii) $v' = 0.02$, which correspond to the large, same, and small intra-molecule transfer energies, respectively, compared to the transfer energy between the molecule and electrodes, $v = 0.1$. The calculated results of the left and right-contact currents, $I_L$ and $I_R$, are shown as a function of time, in Figs. 2(a), 3(a), and 4(a) for these three cases. On the other hand, the corresponding time dependence of electron occupations at the C and c sites, $n_C$ and $n_c$, and the total number of electrons in the molecule, $n = n_C + n_c$, are displayed in Figs. 2(b), 3(b), and 4(b). In these figures, the results for the single-site molecule are also shown as thin lines for reference, where the number of electrons in the single-site molecule is doubled in order to make the comparison easy.

It is noted that these quantities apparently obey the charge conservation; $I_L + I_R = \partial n/\partial t$. To realize the current conservation picture as in an electronic circuit, one has to consider the displacement currents at left and right contacts, $I_L^d$ and $I_R^d$ [29–31]. In this sense, the present $I_L$ and $I_R$ are sometimes called as particle currents. In case of the same electron-transfer energies for left and right contacts and the infinite band width of electrodes considered in this paper, $I_L^d$ and $I_R^d$ have the same values as shown by Wang et al. [32] and are given by $I_L^d = I_R^d = 1/2 \cdot \partial n/\partial t = (I_L + I_R)/2$. Therefore, the total current in the present circuit becomes $I = I_L - I_L^d = -I_R + I_R^d = (I_L + I_R)/2$, which is also shown in Figs. 2(a), 3(a), and 4(a). Since the characteristics observed are similar among $I_L$, $I_R$, and $I$, hereafter, we mainly concentrate on the left-contact current, $I_L$.

First, we consider the case (i). It is seen in Fig. 2(a) that the left-contact current shows the oscillation and relaxation, and reach the steady-state values, similar to the case of the single-site molecule. However, we note that there exist definite different features in the two-site molecule; (a) although the steady-state current has the same magnitude, the relaxation time to the steady state is around 15, which is about twice long compared to that of the single-site molecule. Here, we defined the relaxation time as the time necessary to realize the half value of the peak. This relaxation feature can be easily recognized in the time evolution of the number of electrons shown in Fig. 2(b). (b) The oscillation period is also around 15, about twice longer than the single-site molecule case. In addition, one can see another small oscillation with half period overlapping on this oscillation.

In order to explain the reasons of these features, we first analyze the electronic states in molecule. When the intramolecule transfer energy, $v'$, is larger than the molecule-electrode one, $v$, it becomes a reasonable approximation to diagonalize the molecule electronic states at first. In
FIG. 3: Calculated transient behavior of (a) the left and right-contact currents, \( I_L \) and \( I_R \), and the total current, \( I \), and (b) the electron occupations, \( n_C \), \( n_c \), and \( n \), in the two-site branch-type molecule for the case of \( v' = v = 0 \). As in Figs. 2(a) and 2(b), the results for the single-site molecule are shown by thin lines.

In this case, we have two electronic states, which have eigen energies, \( \varepsilon_1 = \varepsilon_C + v' = 0.5 \) and \( \varepsilon_2 = \varepsilon_C - v' = -0.5 \), and the wavefunction amplitude of \( \pm 1/\sqrt{2} \) at both C and c sites. Since these energies are in the range between Fermi energies of left and right electrodes as \( \mu_L > (\varepsilon_1, \varepsilon_2) > \mu_R \), both states contribute to flow the current as independent channels.

Then, we explain the steady-state values of electron number and currents. Since there are two sites in the present molecule and both these sites are half occupied, the number of electrons in molecule becomes one as shown in Fig. 2(b), which is twice compared to the case of the single-site molecule. On the other hand, in our previous work on the single-site molecule [24], it was shown that the electronic current is proportional to the square of transfer energy between the molecule and electrodes, \( v^2 \). In the present case of the two-site molecule, because of the diagonalization described above, each channel is connected to the electrodes with the renormalized transfer energy of \( \pm v/\sqrt{2} \) and thus promotes the current with the half magnitude of the single-site molecule. However, since there exist two channels, the total current becomes \( 2 \times (v/\sqrt{2})^2 = v^2 \) and has the same magnitude as the single-site molecule.

It is noted here that, as shown in the textbook by Datta [33], the steady current is written by \( I = e/\hbar \cdot \gamma/2 \int_{\mu_L}^{\mu_R} dE \, D(E) \), where \( D(E) \) is the density of states in molecule, which includes the effect of level broadening by the molecule-electrode coupling, and \( \gamma \) is the level broadening given by \( 2\pi v^2 D \), which corresponds to the life time of the electronic state in molecule [20, 21, 24, 26]. When the effective molecule-electrode coupling, \( 2\pi v^2 D \), is larger than the applied voltage between left and right electrodes, \( eV = \mu_L - \mu_R \), the steady-state current is approximately calculated as \( I = e^2/\hbar \cdot V \), which reproduces the conductance by the Landauer’s formula, \( G_0 = I/V = e^2/\hbar \). However, the present simulations correspond to the opposite cases where the effective molecule-electrode coupling is smaller than the applied voltage as \( 2\pi v^2 D = 0.06 << eV = 2 \). In this case, the integral is approximately calculated to be an unity and the current becomes as \( I = e^2/h \cdot \gamma/2 = e^2/h \cdot \pi v^2 D \), which is proportional to the effective molecule-electrode coupling as shown in Ref. [21] and coincides with the steady-state current value obtained in Ref. [24]. This current can be written as \( I = e^2/h \cdot V \cdot (2\pi v^2 D)/eV \), indicating that the steady-state current is much smaller than the value expected by the Landauer’s formula.

Then, we consider the relaxation feature. It was shown in the previous work that the relaxation time of tran-

FIG. 4: Calculated transient behavior of (a) the left and right-contact currents, \( I_L \) and \( I_R \), and the total current, \( I \), and (b) the electron occupations, \( n_C \), \( n_c \), and \( n \), in the two-site branch-type molecule for the case of small intra-molecule transfer as \( v' = 0.02 < v = 0.1 \). As in Figs. 2(a) and 2(b), the results for the single-site molecule are shown by thin lines.
sient current is propotional to the inverse of the quantum transition probability of electrons between the molecule and electrode, i.e., the inverse of the square of transfer energy as \( v^2 \) [24]. In the present case of the two-site molecule, since the transfer energies are renormalized, both two eigen-state channels have the same relaxation time, \( (\sqrt{2}/v)^2 = 2 \cdot v^2 \), which is twice compared to the case of the single-site molecule. If one goes back from the diagonalized eigen-state picture to the site-representation picture of electronic states, this relaxation feature can be represented in other words; since there are two sites in the present molecule, it takes twice time to relaxate the current compared to the case of the single-site molecule.

Then, we consider the oscillation. The oscillation period was shown propronional to the inverse of the energy difference between \( \varepsilon_C \) and \( \mu_L \), as \( h/(\mu_L - \varepsilon_C) \) [24], which is \( h/1.0 \) in the present parametrization of the single-site molecule. In case of the two-site molecule, however, due to the diagonalization, \( \varepsilon_C \) is replaced by \( \varepsilon_1 = \varepsilon_C + v^2 \), thus the period becoming \( h/(\mu_L - \varepsilon_1) = h/0.5 \), i.e., twice long to the case of the single-site molecule. On the other hand, the origin of another small oscillation is understood by observing the time evolution of \( n_C \) and \( n_c \) in Fig. 2(b). It is seen that the electron occupations at the C and c sites oscillate with showing alternative peaks. This oscillation apparently reflects the go-and-back quantum motion of electrons between the C and c sites caused by the intramolecule transfer energy. This motion has the period of \( h/2v^2 = h/1.0 \), thus having the half period of the principal oscillation.

Next, we consider the case (ii). In the short interval of \( t = 30 \sim 35 \) after the voltage application, the current \( I_L \) shows almost the same magnitude and variation as the case of the single-site molecule. After \( t = 35 \), however, the current shows quite different behavior; it has the large values and the plateau shape. This unique behavior also reflects the quantum oscillating motion of electrons between the C and c sites, which is clearly seen in the variation of electron occupations in Fig. 3(b). Since \( v^2 = 0.1 \) and thus the period of such intra-molecule oscillation becomes around \( h/0.2 \), comparable to that of the molecule-electrode oscillation of \( h/0.1 \), the transient current between electrodes is largely modulated by the intramolecule electron motion in case of (ii).

Finally, we consider the case (iii) shown in Figs. 4(a) and 4(b). The transient behaviors of both \( I_L \) and \( I_R \) are same as the case of the single-site molecule for a initial interval of \( t = 30 \sim 60 \). This is because the c site is so weakly coupled to the C site that the system looks like a single-site molecule having the relaxation caused by only the transfer, \( v \). On the other hand, after \( t = 60 \) when the C site is sufficiently occupied, the c site starts to be occupied by electrons and reaches the steady state till \( t = 400 \) with showing an extremely slow relaxation. This relaxation is caused by the transfer, \( v^2 \). Therefore, one can say that the relaxation processes caused by \( v \) and \( v^2 \) are clearly separated in time with each other in case of (iii). With respect to the oscillation, however, the period caused by \( v^2 \) is so long, around \( h/0.04 \), that the corresponding variation becomes slow and the oscillation feature is not apparently seen in the time evolution of current and occupation.

![FIG. 5: Calculated transient behavior of (a) the left and right-contact currents, \( I_L \) and \( I_R \), and the total current, \( I \), and (b) the electron occupations, \( n_C \), \( n_c \), and \( n \), in the two-site straight-type molecule for the case of \( v^2 = v = 0.1 \). As in Figs. 2(a) and 2(b), the results for the single-site molecule are shown by thin lines.](http://www.sssj.org/ejssnt)
\(v\) in case of (ii). On the other hand, one can see the qualitatively different feature in the right-contact current and the occupation at \(c\). For example, as seen in Figs. 6(a) and 6(b) in case of (iii), just after the voltage is applied at \(t = 30\), the left-contact current suddenly flows and the electron occupation at the \(C\) site sharply increases, while the right-contact current and the electron occupation at the \(c\) site are considerably small. After the \(C\) site is sufficiently occupied around \(t = 60\), the electron occupation at the \(c\) site increases and the right-contact current starts to flow. This result indicates that the electron transfer between the \(C\) and \(c\) sites becomes the limiting process for the current between electrodes. Correspondingly, reflecting the small value of \(v'\), the steady-state current is much smaller than that of the single-site molecule.

Finally, we shortly comment on the steady-state electron occupations at the \(C\) and \(c\) sites. In most studies on the electron transport through nanoscale systems such as molecular bridges and quantum dots [18–24], the Fermi-Dirac grand-canonical equilibrium distribution is often assumed for the electronic states in electrodes. Therefore, the electron occupation at low temperature is assumed to be 1.0 and 0.0 at the edge points of left and right electrodes, respectively. In case of (iii) in the present system, i.e., when \(v' < v\), one can approximately regard the \(C\) and \(c\) sites not as the sites in molecule but as edge points of left and right electrodes. In fact, as seen in Fig. 6(b), the electron occupations of these sites are about 0.86 and 0.14, respectively, similar values to 1.0 and 0.0 at the edge points of electrodes. However, they are definitely different from 1.0 and 0.0. In case of the present two-site straight-type molecule with the small intra-molecule transfer, i.e., \(v' << v\), for example, by employing the steady-state conditions that the time is infinity and all the density-matrix elements in equations shown in Appendix have constant values, the transition probabilities become independent of time\[^{24}\] In this case, the electron occupations at the \(C\) and \(c\) sites are written by

\[
n_C = \frac{1 + 2\delta}{1 + 4\delta} \quad \text{and} \quad n_c = \frac{2\delta}{1 + 4\delta},
\]

where \(\delta = \left(\frac{v'}{v}\right)^2/\left(4\pi^2e^2D^2\right)\), indicating that the ratio of \(\left(\frac{v'}{v}\right)^2\) becomes the rough measure for the rationality of electron distribution in electrodes. In any case, the present fractional values at the \(C\) and \(c\) sites indicate that the assumption of Fermi-Dirac distribution around the edge region of electrodes should be examined when the electron transfer energies in electrodes have similar magnitude to those in the molecule.

C. Sudden switching of intra-molecule coupling

In previous subsections, we have studied the transient current behavior when the molecule has two independent
sites from the beginning. In this subsection, we consider the case when the number of molecule sites suddenly changes between one and two in the steady current state. This case is realized, for example, by the adsorption/desorption of a molecule to/from the molecular bridge system. Figures 7(a) and 7(b) show the transient currents and the electron occupations as a function of time, respectively, when the voltage is applied to a single-site molecule, C, at $t = 30$, then an additional single-site molecule, c, attaches to this molecule at $t = 80$, and then the c molecule leaves the C molecule at $t = 180$. Here, we used the parameters, $v' = 0.5$ and $\varepsilon_c = 0.0$ for the c molecule.

It is seen in this figure that the current suddenly increases at $t = 80$ and then shows the oscillation and relaxation. Since the c-site molecule is not occupied by electrons before $t = 80$, the connection to the C-site molecule promotes the net electron flow from the C to c sites and increases the current between electrodes. The oscillation is caused by the quantum electron motion between the C and c sites, which is clearly seen in Fig. 7(b), while the relaxation is realized by the electronic coupling to the electrodes.

Most interesting feature of current is seen in the case of molecule desorption at $t = 180$. Before the desorption, the C and c sites are occupied by electrons and reach the steady state. When the c molecule departs from the C molecule at $t = 180$, there is no change of electron occupations in these sites, thus no displacement current. However, we can observe a spike-like vibration of both left and right-contact currents around $t = 180$. This occurs due to the quantum electron motion between two molecules. Even when the steady state is realized, the quantum electron motion proceeds between two molecules, which is examined by the non-zero values of off-diagonal density-matrix elements, $\sigma_{23}(t)$ and $\sigma_{32}(t)$. Thus, the breakdown of the molecule connection induces the current changes. In this way, we expect that the quantum electron motion in molecule can be seen in the current variation when the molecule changes its structure.

IV. CONCLUSIONS

In this paper, we have studied how the transient current behavior in molecular bridge system changes when the number of energy-level sites in molecule increases. It was shown that the relaxation speed to the steady state in general becomes slow as increasing the energy-level sites. This is because there exist multi sites in molecule and thus it needs more time to fulfill all the sites by electrons. Moreover, we found that the intra-molecule current often becomes the limiting process and promotes the extreme prolongation of relaxation time when the intra-molecule coupling is small. On the other hand, as increasing the energy-level sites, the oscillation in transient current changes the period due to the change of eigen energies of electronic states in molecule. In addition, we found that the intra-molecule quantum electron motion often induces a new oscillation and largely modulates the transient current behavior. It was demonstrated that such quantum motion can be observed when the molecule changes its structure, such as by the molecule desorption.

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Appendix

In this Appendix, we list the equations of motion for density matrix elements. These equations are derived by the similar calculations to the case of single-site molecule shown in our previous paper[24]. However, as explained in the text, the two-site molecule promotes the quantum intra-molecule transitions, which are represented by the off-diagonal density-matrix elements such as $\sigma_{23}$ not present in the case of the single-site molecule, and thus the equations have different structures. Moreover, it is noted that the projection operation to equilibrium distribution loses the quantum coherence and does not commutate with the time evolution operation of electronic states in molecule due to the molecule-electrode couplings. Thus, the approximate treatment of independent channels discussed in case of (i) in Sec. 3 does not apply to the cases of small intra-molecule couplings, which indicates that the equations of motion have different forms depending on the site configurations in molecule. Therefore, we arranged this Appendix.

In case of the branch-type molecule, the equations become as follows;

$$\frac{\partial \sigma_{11}(t)}{\partial t} = \sum_{k,\alpha=L,R} \left( \frac{v_\alpha}{\hbar} \right)^2 \int_{t_0}^{t} d\tau \left\{ (1 - f_{k\alpha}) \left( \cos \left( \frac{\varepsilon_{k\alpha} + v'}{\hbar} (t-\tau) \right) + \cos \left( \frac{\varepsilon_{k\alpha} - v'}{\hbar} (t-\tau) \right) \right) \sigma_{11}(\tau) - f_{k\alpha} \left( \cos \left( \frac{\varepsilon_{k\alpha} + v'}{\hbar} (t-\tau) \right) + \cos \left( \frac{\varepsilon_{k\alpha} - v'}{\hbar} (t-\tau) \right) \right) \sigma_{33}(\tau) - f_{k\alpha} \frac{1}{2} \left( e^{-i\frac{\tau}{\hbar} (\varepsilon_{k\alpha} + v')(t-\tau)} - e^{-i\frac{\tau}{\hbar} (\varepsilon_{k\alpha} - v')(t-\tau)} \right) \sigma_{23}(\tau) - f_{k\alpha} \frac{1}{2} \left( e^{i\frac{\tau}{\hbar} (\varepsilon_{k\alpha} + v')(t-\tau)} - e^{i\frac{\tau}{\hbar} (\varepsilon_{k\alpha} - v')(t-\tau)} \right) \sigma_{32}(\tau) \right\} \right(5)$$
\[
\frac{\partial \sigma_{22}(t)}{\partial t} = \left(\frac{1}{i\hbar}\right)(\sigma_{32}(t) - \sigma_{23}(t))v' \\
+ \sum_{k,\alpha=L,R} \left(\frac{v_0}{i\hbar}\right)^2 \int_0^t d\tau \left\{ -f_\alpha \left( \cos \left( \frac{(\varepsilon_{k\alpha} + v')'(t - \tau)}{\hbar} \right) + \cos \left( \frac{(\varepsilon_{k\alpha} - v')'(t - \tau)}{\hbar} \right) \right\} \sigma_{22}(\tau) \\
- f_\alpha \left( \cos \left( \frac{(\varepsilon_{k\alpha} + v')'(t - \tau)}{\hbar} \right) + \cos \left( \frac{(\varepsilon_{k\alpha} - v')'(t - \tau)}{\hbar} \right) \right) \sigma_{44}(\tau) \\
- (1 - f_\alpha) \frac{1}{2} \left( e^{-i\frac{h}{\tau}(\varepsilon_{k\alpha} + v')'(t - \tau)} - e^{-i\frac{h}{\tau}(\varepsilon_{k\alpha} - v')'(t - \tau)} \right) \sigma_{23}(\tau) \\
- (1 - f_\alpha) \frac{1}{2} \left( e^{i\frac{h}{\tau}(\varepsilon_{k\alpha} + v')'(t - \tau)} - e^{i\frac{h}{\tau}(\varepsilon_{k\alpha} - v')'(t - \tau)} \right) \sigma_{32}(\tau), \\
\]  
(6)

\[
\frac{\partial \sigma_{33}(t)}{\partial t} = \left(\frac{1}{i\hbar}\right)(\sigma_{23}(t) - \sigma_{32}(t))v' \\
+ \sum_{k,\alpha=L,R} \left(\frac{v_0}{i\hbar}\right)^2 \int_0^t d\tau \left\{ f_\alpha \left( \cos \left( \frac{(\varepsilon_{k\alpha} + v')'(t - \tau)}{\hbar} \right) + \cos \left( \frac{(\varepsilon_{k\alpha} - v')'(t - \tau)}{\hbar} \right) \right\} \sigma_{33}(\tau) \\
- (1 - f_\alpha) \left( \cos \left( \frac{(\varepsilon_{k\alpha} + v')'(t - \tau)}{\hbar} \right) + \cos \left( \frac{(\varepsilon_{k\alpha} - v')'(t - \tau)}{\hbar} \right) \right) \sigma_{11}(\tau) \\
+ f_\alpha \frac{1}{2} \left( e^{-i\frac{h}{\tau}(\varepsilon_{k\alpha} + v')'(t - \tau)} - e^{-i\frac{h}{\tau}(\varepsilon_{k\alpha} - v')'(t - \tau)} \right) \sigma_{23}(\tau) \\
+ f_\alpha \frac{1}{2} \left( e^{i\frac{h}{\tau}(\varepsilon_{k\alpha} + v')'(t - \tau)} - e^{i\frac{h}{\tau}(\varepsilon_{k\alpha} - v')'(t - \tau)} \right) \sigma_{32}(\tau), \\
\]  
(7)

\[
\frac{\partial \sigma_{23}(t)}{\partial t} = \left(\frac{1}{i\hbar}\right)(\sigma_{33}(t) - \sigma_{22}(t))v' \\
+ \sum_{k,\alpha=L,R} \left(\frac{v_0}{i\hbar}\right)^2 \int_0^t d\tau \left\{ -(1 - f_\alpha) \frac{1}{2} \left( e^{-i\frac{h}{\tau}(\varepsilon_{k\alpha} + v')'(t - \tau)} - e^{-i\frac{h}{\tau}(\varepsilon_{k\alpha} - v')'(t - \tau)} \right) \sigma_{11}(\tau) \\
- (1 - f_\alpha) \frac{1}{2} \left( e^{-i\frac{h}{\tau}(\varepsilon_{k\alpha} + v')'(t - \tau)} - e^{-i\frac{h}{\tau}(\varepsilon_{k\alpha} - v')'(t - \tau)} \right) \sigma_{22}(\tau) \\
+ f_\alpha \frac{1}{2} \left( e^{-i\frac{h}{\tau}(\varepsilon_{k\alpha} + v')'(t - \tau)} - e^{-i\frac{h}{\tau}(\varepsilon_{k\alpha} - v')'(t - \tau)} \right) \sigma_{33}(\tau) \\
+ \frac{1}{2} \left( e^{-i\frac{h}{\tau}(\varepsilon_{k\alpha} + v')'(t - \tau)} + e^{-i\frac{h}{\tau}(\varepsilon_{k\alpha} - v')'(t - \tau)} \right) \sigma_{23}(\tau), \\
\]  
(8)

\[
\frac{\partial \sigma_{32}(t)}{\partial t} = \left(\frac{1}{i\hbar}\right)(\sigma_{22}(t) - \sigma_{33}(t))v' \\
+ \sum_{k,\alpha=L,R} \left(\frac{v_0}{i\hbar}\right)^2 \int_0^t d\tau \left\{ -(1 - f_\alpha) \frac{1}{2} \left( e^{i\frac{h}{\tau}(\varepsilon_{k\alpha} + v')'(t - \tau)} - e^{i\frac{h}{\tau}(\varepsilon_{k\alpha} - v')'(t - \tau)} \right) \sigma_{11}(\tau) \\
- (1 - f_\alpha) \frac{1}{2} \left( e^{i\frac{h}{\tau}(\varepsilon_{k\alpha} + v')'(t - \tau)} - e^{i\frac{h}{\tau}(\varepsilon_{k\alpha} - v')'(t - \tau)} \right) \sigma_{22}(\tau) \\
+ f_\alpha \frac{1}{2} \left( e^{i\frac{h}{\tau}(\varepsilon_{k\alpha} + v')'(t - \tau)} - e^{i\frac{h}{\tau}(\varepsilon_{k\alpha} - v')'(t - \tau)} \right) \sigma_{33}(\tau) \\
+ f_\alpha \frac{1}{2} \left( e^{i\frac{h}{\tau}(\varepsilon_{k\alpha} + v')'(t - \tau)} - e^{i\frac{h}{\tau}(\varepsilon_{k\alpha} - v')'(t - \tau)} \right) \sigma_{44}(\tau) \\
+ \frac{1}{2} \left( e^{i\frac{h}{\tau}(\varepsilon_{k\alpha} + v')'(t - \tau)} + e^{i\frac{h}{\tau}(\varepsilon_{k\alpha} - v')'(t - \tau)} \right) \sigma_{32}(\tau), \\
\]  
(9)

Here, we used the Fermi-Dirac distribution, \( f_\alpha = 1/(1 + \exp(\beta(\varepsilon_{k\alpha} - \mu_\alpha))) \), where \( \beta = 1/k_B T \) is the inverse temperature.

In case of the straight-type molecule, the equations of motion for the density-matrix elements become as follows;

http://www.sssj.org/ejssnt (J-Stage: http://www.jstage.jst.go.jp/browse/ejssnt/) 613
\[
\frac{\partial \sigma_{11}(t)}{\partial t} = \sum_k \left( \frac{v_k}{\hbar} \right)^2 \int_{t_0}^{t} d\tau \left\{ (1 - f_{KL}) \left( \cos \left( \frac{(E_{KL} + \nu')(t - \tau)}{\hbar} \right) + \cos \left( \frac{(E_{KL} - \nu')(t - \tau)}{\hbar} \right) \right) \right\} \sigma_{11}(\tau) \\
- f_{KL} \left( \cos \left( \frac{(E_{KL} + \nu')(t - \tau)}{\hbar} \right) + \cos \left( \frac{(E_{KL} - \nu')(t - \tau)}{\hbar} \right) \right) \sigma_{33}(\tau) \\
- \frac{1}{2} f_{KL} \left( e^{-i\frac{\hbar}{2}(E_{KL} + \nu')(t - \tau)} - e^{-i\frac{\hbar}{2}(E_{KL} - \nu')(t - \tau)} \right) \sigma_{23}(\tau) \\
- \frac{1}{2} f_{KL} \left( e^{i\frac{\hbar}{2}(E_{KL} + \nu')(t - \tau)} - e^{i\frac{\hbar}{2}(E_{KL} - \nu')(t - \tau)} \right) \sigma_{32}(\tau) \\
+ \sum_k \left( \frac{v_k}{\hbar} \right)^2 \int_{t_0}^{t} d\tau \left\{ (1 - f_{KR}) \left( \cos \left( \frac{(E_{KR} + \nu')(t - \tau)}{\hbar} \right) + \cos \left( \frac{(E_{KR} - \nu')(t - \tau)}{\hbar} \right) \right) \right\} \sigma_{11}(\tau) \\
- f_{KR} \left( \cos \left( \frac{(E_{KR} + \nu')(t - \tau)}{\hbar} \right) + \cos \left( \frac{(E_{KR} - \nu')(t - \tau)}{\hbar} \right) \right) \sigma_{22}(\tau) \\
- \frac{1}{2} f_{KR} \left( e^{-i\frac{\hbar}{2}(E_{KR} + \nu')(t - \tau)} - e^{-i\frac{\hbar}{2}(E_{KR} - \nu')(t - \tau)} \right) \sigma_{23}(\tau) \\
- \frac{1}{2} f_{KR} \left( e^{i\frac{\hbar}{2}(E_{KR} + \nu')(t - \tau)} - e^{i\frac{\hbar}{2}(E_{KR} - \nu')(t - \tau)} \right) \sigma_{32}(\tau) \right) \\
\]

\[
\frac{\partial \sigma_{32}(t)}{\partial t} = \left( \frac{1}{i\hbar} \right) (\sigma_{32}(t) - \sigma_{23}(t)) \nu' \\
+ \sum_k \left( \frac{v_k}{\hbar} \right)^2 \int_{t_0}^{t} d\tau \left\{ (1 - f_{KL}) \left( \cos \left( \frac{(E_{KL} + \nu')(t - \tau)}{\hbar} \right) + \cos \left( \frac{(E_{KL} - \nu')(t - \tau)}{\hbar} \right) \right) \right\} \sigma_{22}(\tau) \\
- f_{KL} \left( \cos \left( \frac{(E_{KL} + \nu')(t - \tau)}{\hbar} \right) + \cos \left( \frac{(E_{KL} - \nu')(t - \tau)}{\hbar} \right) \right) \sigma_{44}(\tau) \\
- (1 - f_{KL}) \left( e^{-i\frac{\hbar}{2}(E_{KL} + \nu')(t - \tau)} - e^{-i\frac{\hbar}{2}(E_{KL} - \nu')(t - \tau)} \right) \sigma_{23}(\tau) \\
- (1 - f_{KL}) \left( e^{i\frac{\hbar}{2}(E_{KL} + \nu')(t - \tau)} - e^{i\frac{\hbar}{2}(E_{KL} - \nu')(t - \tau)} \right) \sigma_{32}(\tau) \right) \\
+ \sum_k \left( \frac{v_k}{\hbar} \right)^2 \int_{t_0}^{t} d\tau \left\{ (1 - f_{KR}) \left( \cos \left( \frac{(E_{KR} + \nu')(t - \tau)}{\hbar} \right) + \cos \left( \frac{(E_{KR} - \nu')(t - \tau)}{\hbar} \right) \right) \right\} \sigma_{11}(\tau) \\
+ f_{KR} \left( \cos \left( \frac{(E_{KR} + \nu')(t - \tau)}{\hbar} \right) + \cos \left( \frac{(E_{KR} - \nu')(t - \tau)}{\hbar} \right) \right) \sigma_{22}(\tau) \\
+ f_{KR} \left( e^{i\frac{\hbar}{2}(E_{KR} + \nu')(t - \tau)} - e^{i\frac{\hbar}{2}(E_{KR} - \nu')(t - \tau)} \right) \sigma_{23}(\tau) \\
+ f_{KR} \left( e^{-i\frac{\hbar}{2}(E_{KR} + \nu')(t - \tau)} - e^{-i\frac{\hbar}{2}(E_{KR} - \nu')(t - \tau)} \right) \sigma_{32}(\tau) \right) \\
\]

\[
\frac{\partial \sigma_{33}(t)}{\partial t} = \left( \frac{1}{i\hbar} \right) (\sigma_{23}(t) - \sigma_{32}(t)) \nu' \\
+ \sum_k \left( \frac{v_k}{\hbar} \right)^2 \int_{t_0}^{t} d\tau \left\{ f_{KL} \left( \cos \left( \frac{(E_{KL} + \nu')(t - \tau)}{\hbar} \right) + \cos \left( \frac{(E_{KL} - \nu')(t - \tau)}{\hbar} \right) \right) \right\} \sigma_{33}(\tau) \\
- (1 - f_{KL}) \left( \cos \left( \frac{(E_{KL} + \nu')(t - \tau)}{\hbar} \right) + \cos \left( \frac{(E_{KL} - \nu')(t - \tau)}{\hbar} \right) \right) \sigma_{11}(\tau) \\
+ f_{KL} \left( e^{-i\frac{\hbar}{2}(E_{KL} + \nu')(t - \tau)} - e^{-i\frac{\hbar}{2}(E_{KL} - \nu')(t - \tau)} \right) \sigma_{23}(\tau) \\
+ f_{KL} \left( e^{i\frac{\hbar}{2}(E_{KL} + \nu')(t - \tau)} - e^{i\frac{\hbar}{2}(E_{KL} - \nu')(t - \tau)} \right) \sigma_{32}(\tau) \right) \\
\]
\[
\frac{\partial \sigma_{23}(t)}{\partial t} = \left( \frac{1}{\hbar} \right) (\sigma_{22}(t) - \sigma_{33}(t)) v'
\]

\[
+ \sum_k \left( \frac{v_k}{\hbar} \right)^2 \int_{t_0}^t dt' \left[ - f_{KR} \left( \cos \left( \frac{(\varepsilon_{KR} + v')(t - \tau)}{\hbar} \right) + \cos \left( \frac{(\varepsilon_{KR} - v')(t - \tau)}{\hbar} \right) \right) \sigma_{44}(\tau) \\
+ (1 - f_{KR}) \left( \cos \left( \frac{(\varepsilon_{KR} + v')(t - \tau)}{\hbar} \right) + \cos \left( \frac{(\varepsilon_{KR} - v')(t - \tau)}{\hbar} \right) \right) \sigma_{33}(\tau) \\
- (1 - f_{KR}) \left( e^{i \frac{\hbar}{\tau} (\varepsilon_{KR} + v')(t-\tau)} - e^{-i \frac{\hbar}{\tau} (\varepsilon_{KR} - v')(t-\tau)} \right) \sigma_{23}(\tau) \\
- (1 - f_{KR}) \left( e^{-i \frac{\hbar}{\tau} (\varepsilon_{KR} + v')(t-\tau)} - e^{i \frac{\hbar}{\tau} (\varepsilon_{KR} - v')(t-\tau)} \right) \sigma_{32}(\tau) \right] \\
\]

\[
\frac{\partial \sigma_{32}(t)}{\partial t} = \left( \frac{1}{\hbar} \right) (\sigma_{22}(t) - \sigma_{33}(t)) v'
\]

\[
+ \sum_k \left( \frac{v_k}{\hbar} \right)^2 \int_{t_0}^t dt' \left[ - f_{KL} \left( \cos \left( \frac{(\varepsilon_{KL} + v')(t - \tau)}{\hbar} \right) + \cos \left( \frac{(\varepsilon_{KL} - v')(t - \tau)}{\hbar} \right) \right) \sigma_{44}(\tau) \\
+ (1 - f_{KL}) \left( \cos \left( \frac{(\varepsilon_{KL} + v')(t - \tau)}{\hbar} \right) + \cos \left( \frac{(\varepsilon_{KL} - v')(t - \tau)}{\hbar} \right) \right) \sigma_{33}(\tau) \\
- (1 - f_{KL}) \left( e^{i \frac{\hbar}{\tau} (\varepsilon_{KL} + v')(t-\tau)} - e^{-i \frac{\hbar}{\tau} (\varepsilon_{KL} - v')(t-\tau)} \right) \sigma_{23}(\tau) \\
- (1 - f_{KL}) \left( e^{-i \frac{\hbar}{\tau} (\varepsilon_{KL} + v')(t-\tau)} - e^{i \frac{\hbar}{\tau} (\varepsilon_{KL} - v')(t-\tau)} \right) \sigma_{32}(\tau) \right] \\
\]