Transport through the single-molecular dots in an external irradiation

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We present a fully nonequilibrium calculation of the low-temperature transport properties of a single molecular quantum dot coupled to local phonon mode when an ac field is applied to the gate. The resonant behavior is shown in the time-averaged differential conductance as the ac frequency matches the frequency of the local phonon mode, which is a direct consequence of the satellite-phonon-peak structure in the dot electron spectral function. The different step structures with and without the external irradiation is found in the I-V curves, and the oscillation behavior is found in the step height as a function of the irradiation intensity.

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Recent advances in nanotechnology have allowed the fabrication of very small molecular quantum dots weakly coupled to the macroscopic charge reservoirs (leads). In contrast to the semiconductor dot, which is quite rigid in space, the molecules involved in the electron tunneling process naturally possess the vibrational degrees of freedom which will inevitably react to the transform of electrons through the molecular quantum dots. In addition to the importance in molecular-scale electronics from the application point of view, these artificial, tunable devices are potentially important for understanding the basic physics including the many-body effect. Theoretically, a lot of effort has been focused on the quantum conductance of molecular systems based on the kinetic equation approach, the rate equation approach, the correlation effects, the nonequilibrium quantum theory, and the strong coupling to environment. So far, the stationary quantum transport through the molecular dots has been considered, while the influence of a time-dependent ac field on the current has not been well addressed. Irradiation of a quantum dot with an ac field offers a new way of affecting its dynamics, which enables one to study the effect of electron-phonon interaction on the transport phenomenon of molecular dots in essentially nonequilibrium condition.

In this Letter, we use the Keldysh nonequilibrium Green’s function technique to study the nonlinear ac transport through a single-molecular quantum dot coupled to a local phonon mode with the external irradiation applied to the gate, for the first time. After a canonical transformation, we obtain a formula for the time-dependent current in general terms of bias, temperature, the intensity and frequency of the external ac field, and the electron-phonon coupling. We show that the satellite-peak structure due to the electron-phonon interaction can be probed by imposing on top of gate bias an ac bias voltage. The satellite-peak structure in the dot electron spectral function gives rise to resonant behavior in the time-averaged current as the ac frequency matches the frequency of local phonon mode, which can be observed directly in experiments. The calculated I-V curves also show the different step structures with and without the external irradiation, and the step height shows the Bessel-type oscillation behavior as a function of irradiation intensity.

In this work we consider a simplest Holstein-type model with a single phonon mode is employed to address the vibrational degrees of freedom in the molecular dot. All other complexity of real molecular devices, apart from interaction with phonon mode, is ignored. Then the system Hamiltonian can be written as

\[ H = H_{\text{leads}} + H_X + H_D + H_T, \]

where

\[ H_{\text{leads}} = \sum_{k, \eta, \sigma} \epsilon_{k\eta} c_{k\eta\sigma}^\dagger c_{k\eta\sigma}, \]

\[ H_X = \omega_0 a_{\sigma}^\dagger a_{\sigma}, \]

\[ H_D = \sum_{\alpha} \left[ \epsilon_0(t) + \lambda (a + a^\dagger) \right] d_{\alpha}^\dagger d_{\alpha}, \]

\[ H_T = \sum_{k, \eta, \sigma, \alpha} \left[ V_{\sigma, \alpha}^\eta c_{k\eta\sigma}^\dagger d_{\alpha} + \text{H. C.} \right]. \]

\( c_{k\eta\sigma}^\dagger (c_{k\eta\sigma}) \) are creation (annihilation) operators for the noninteracting electrons with momentum \( k \) and spin index \( \sigma \) in the left (\( \eta = L \)) or right (\( \eta = R \)) metallic leads. \( \omega_0 \) is the frequency of the single phonon mode, and \( a^\dagger \) (\( a \)) is the phonon creation (annihilation) operator. \( H_D \) describes the electron in the quantum dot coupled to the local phonon mode with the coupling constant \( \lambda \), where \( d_{\alpha}^\dagger (d_{\alpha}) \) is the dot-electron creation (annihilation) operator, and \( \epsilon_0(t) \) is the single energy level of the dot which can be tuned by the external irradiation, \( \epsilon_0(t) = \epsilon_0 + V_r \cos(\omega_r t) \) for harmonic bias. Here we assume that the metallic leads are dc biased, neglecting the possible “leakage” of the irradiating ac field to the leads. The generalization onto the case of nonzero ac bias is straightforward. \( H_T \) describes the tunneling coupling between the dot and the leads, where the tunneling matrix elements \( V_{\sigma, \alpha}^\eta \) transfer electrons through an insulating barrier out of the dot.
Based on the Keldysh nonequilibrium Green’s function formalism\cite{12}, the time-dependent current from the \( \eta \) lead to the dot is given by\cite{10}

\[
J_\eta (t) = - \frac{2e}{\hbar} \sum_\alpha \int_{-\infty}^t dt' \int \frac{d\epsilon}{2\pi} \text{Im} \left\{ e^{i\epsilon(t-t')} \Gamma_\alpha^\eta \times \left[ G_{\alpha\alpha}^{\lessgtr}(t, t') + f_\eta (\epsilon) G_{\alpha\alpha}^r (t, t') \right] \right\},
\]

(3)

where \( f_{L(R)} (\epsilon) \) are the Fermi distribution function of the left (right) leads, which have different chemical potentials upon a dc bias voltage \( \mu_L - \mu_R = eV \). \( \Gamma_\alpha^\eta = 2\pi \rho_\alpha (0) \left| V_{k_\alpha\alpha}^\eta \right|^2 \) characterizes the coupling between the dot and the leads, and \( \rho_\alpha (0) \) is the spin-\( \alpha \) band density of states in the leads. Here we assume that the leads give rise to a flat, energy independent, density of states (i.e., the wide-band limit). \( G^{r(c)} \) is the retarded (lesser) Green’s function of the dot.

In order to compute the time-dependent current, one has to compute the dot electron Green’s functions in the presence of both the electron-phonon interaction and the tunneling coupling between dot and leads. The Green’s function can be calculated by performing the canonical transformation \( S = (\lambda/\omega_0) \sum_\alpha d_\alpha^\dagger d_\alpha (a^\dagger - a) \)\cite{12}, and then the dot level is renormalized to \( \epsilon_0 - \Delta \), where \( \Delta = \lambda^2/\omega_0 \), and the tunneling coupling term is also renormalized as \( V_{\alpha\alpha}^\eta \sum_{k,n,s} \left\{ V_{k_{\alpha\alpha}}^\eta c_{k_{\alpha\alpha}}^\dagger d_\alpha X + H.C \right\} \), where \( X = \exp \left\{ - (\lambda/\omega_0) (a^\dagger - a) \right\} \). Ignoring the effects of narrowing the bands of leads due to the phonons\cite{14}, the dot-electron Green’s function can be decoupled as \( G_{\alpha\alpha}^r (t, t') = \tilde{G}_{\alpha\alpha}^r (t, t') \langle X (t) X^\dagger (t') \rangle_{ph} \), where \( \tilde{G}_{\alpha\alpha}^r (t, t') = -i\Theta (t-t') \left\langle \left\{ \tilde{d}_\alpha (t), \tilde{d}_\alpha^\dagger (t') \right\} \right\rangle_{el} \), \( \tilde{d}_\alpha (t) = e^{i\Phi (t)} d_\alpha e^{-i\Phi (t)} \), \( \Phi (t) = \frac{(\lambda/\omega_0)^2}{2} \left[ N_{ph} (1 - e^{-i\omega_0 t}) + (N_{ph} + 1) (1 - e^{-i\omega_0 t}) \right] \), and \( N_{ph} = 1/| \exp (\beta \omega_0) - 1 \|. \) The retarded Green’s function can be easily obtained by the standard Dyson equation approach\cite{12}, and the result is

\[
G_{\alpha\alpha}^{r}(t, t') = -i\delta_{\alpha\alpha} \Theta (t-t') e^{-iJ_0} \int dt'' V_{\alpha} \cos (\omega \tau) \times e^{-i\epsilon_0 \Delta - i\Phi (t-t')},
\]

(4)

where \( \Gamma_\alpha = \Gamma_\alpha^L + \Gamma_\alpha^R \) is the total tunneling coupling to the leads. Following the operational rules\cite{12} to the Dyson equation for the contour-ordered Green’s function, the Keldysh Green’s function is found to be

\[
G_{\alpha\alpha}^{<}(t, t') = \delta_{\alpha\alpha} \int dt_1 \int dt_2 \tilde{G}_{\alpha\alpha}^r (t_1, t_2) \times \Sigma_\alpha^{<} (t_1, t_2),
\]

(5)

with the less self-energy

\[
\Sigma_\alpha^<(t_1, t_2) = i \sum_\eta \int \frac{d\epsilon}{2\pi} \Gamma_\alpha^\eta e^{-\eta [-\epsilon (t_1-t_2)]} f_\eta (\epsilon) e^{-i\epsilon (t_1-t_2)}.
\]

(6)

Without electron-phonon interaction, the above result fully agrees with that for time-dependent transport through noninteracting quantum dot\cite{10}.

Substitution of the Green’s functions into Eq. (3) gives

\[
J_\eta (t) = - \frac{e}{\hbar} \sum_\alpha \int d\omega \left\{ 2f_\eta (\omega) \text{Im} \left[ A_\alpha (\omega, t) \right] ight\}
\]

\[
-2 \left( \sum_\eta \Gamma_\alpha^\eta f_\eta (\omega) \right) \times \int_{-\infty}^t dt_1 e^{-\Gamma_\alpha (t-t_1)} \text{Im} \left[ A_\alpha (\omega, t_1) \right],
\]

(7)

with \( A_\alpha (\omega, t) = \int_{-\infty}^t dt_1 e^{i\omega (t-t')} G_{\alpha\alpha}^r (t, t') \). Obviously, in the time-independent case, \( A_\alpha (\omega) \) is just the Fourier transform of the retarded Green’s function \( G_{\alpha\alpha}^r (\omega) \). After some algebra, we find that for this model,

\[
A_\alpha (\omega, t) = e^{-g(2N_{ph}+1)} \sum_{l,m,n} (-1)^{l+m} e^{i(l-m)\omega t} e^{n\omega_0 \beta/2}
\]

\[
\times J_l (V_{\alpha\alpha}) J_m (V_{\alpha\alpha}) I_n \left\{ 2g [N_{ph} (N_{ph}+1)]^{1/2} \right\}
\]

\[
\times \frac{1}{\omega - (\epsilon_0 - \Delta) + m \omega_0 - n \omega_0 + \frac{1}{2} \Gamma_\alpha},
\]

(8)

where \( J_m (z) \) is the Bessel function of the \( m \)-th order, \( I_n (z) \) is the Bessel function of complex argument, and \( l, m, n = 0, \pm 1, \pm 2 \ldots \). Eq. (8) together with the current expression Eq. (7) provides the complete solution to the time-dependent transport of molecular quantum dot coupled to local phonon mode in the ac field. Experimentally what is interest is the current on a time scale long compared to \( 2\tau/\omega \). Here we discuss the time-averaged current \( \langle J (t) \rangle \), which could be directly relevant to experiment. For this model, we then obtain

\[
\langle J_L (t) \rangle = - \langle J_R (t) \rangle
\]

\[
= \frac{2e}{\hbar} \left( \frac{1}{2} \right) e^{-g(2N_{ph}+1)} \sum_\alpha \Gamma_\alpha^L \Gamma_\alpha^R \int d\omega \left\{ f_L (\omega) - f_R (\omega) \right\} \sum_{m,n} J_m \left( \frac{V_{\alpha\alpha}}{\omega} \right)
\]

\[
\times I_n \left( 2g [N_{ph} (N_{ph}+1)]^{1/2} \right) e^{n\omega_0 \beta/2}
\]

\[
\times \frac{1}{\omega - (\epsilon_0 - \Delta) + m \omega_1 - n \omega_0 + \frac{1}{2} \Gamma_\alpha}.
\]

(9)

In the absence of external irradiation, i.e., \( V_{r} = 0 \), Eq. (9) fully agrees with the result of dc current in Refs.
The contribution of the external irradiation to the transport becomes significant when the argument of the Bessel function, $V_r/\omega_r$, is of the order of unity. Another important consequence is that the time-averaged current under irradiation is proportional to $J_m^2$. As a result, one should expect the change in current due to the external irradiation to depend on the intensity of irradiation.

For simplicity, we consider the tunneling coupling between the molecular dot and the two leads to be symmetric and independent of the spin index, i.e., $\Gamma^L = \Gamma^R = \Gamma^L = \Gamma^R = \Gamma$. In Fig. 1, we plot the zero-temperature differential conductance as a function of the Fermi energy measured relative to the single level $\epsilon_0$ of the dot in the external ac field with frequency $\omega_r = \omega_0$ and different values of irradiation intensities. For comparison, we also plot the differential conductance in the absence of ac field. At zero ac bias voltage, our results agrees well with that in Refs. [7, 8], where the electron-phonon coupling can lead to the satellite resonant peaks. Fig. 1 shows that the ac field with frequency $\omega_r = \omega_0$ can lead to the enhancement of satellite resonant peaks in the positive energy region and the appearance of new peaks in the negative energy region. One can also see that the main peak is suppressed by the irradiation while increasing the intensity. In Fig. 2, we plot the zero-temperature differential conductance as a function of the frequency of ac field for different values of irradiation intensities by fixing the Fermi energy of the leads $E_F$ as $E_F - (\epsilon_0 - \Delta) = 0$ to avoid unnecessary complications. As the intensity of ac field increases, resonant signals are clearly shown when the frequency of ac field satisfies $m\omega_r = n\omega_0$. The satellite-phonon-peak structure in the dot electron spectral function, as shown in Refs. [7, 8] and also in Fig. 1 of this Letter, gives rise to resonant behavior in the conductance as the irradiating ac frequency matches the frequency of local phonon mode, and can be observed directly in experiments. Fig. 2 also shows that more resonant signals can be observed while increasing the irradiation intensity. Fig. 3 shows the calculated zero-temperature current-voltage curves with and without the external ac irradian...
Here we assume the leads to be symmetrically voltage biased, i.e., $+V/2$ on the left lead and $-V/2$ on the right one, to avoid unnecessary complications. In the absence of external ac field, clear steps appear at roughly $2\omega_0$ intervals in the weak tunneling coupling limit, corresponding to $eV/2 = \pm n\omega_0$, with $n = 0, 1, 2 \ldots$, and the height of the $N$-th step decreases with $N$, which can be easily understood from Eq. (10) [see below] by taking $V_r = 0$ for small electron-phonon interaction. In the presence of ac field with frequency $\omega_r = \omega_0$, steps appear at the same intervals $2\omega_0$ as those in the zero ac field, while the step height is modulated by Bessel function due to the irradiation [see Eq. (11) in below]. Fig. 3 also shows that more steps appear at the leads $\omega_0$ in the case of $\omega_r = 0.5\omega_0$, corresponding to $eV/2 = m\omega_r - n\omega_0$ with $m = 0, \pm 1, \pm 2 \ldots$. The zero-temperature $N$-th step's height in an external ac field with frequency $\omega_r = \omega_0$ can be analytically obtained from Eq. (11) at the fixed Fermi energy $E_F$ as $E_F - (\epsilon_0 - \Delta) = 0$,

$$\Delta J_N = \pi \left( \frac{2e}{h} \right) e^{-g} \sum_{\alpha} \frac{\Gamma_\alpha^L \Gamma_\alpha^R}{\Gamma_\alpha^L + \Gamma_\alpha^R} \times \sum_{n=0}^{\infty} \frac{g^n}{n!} \left[ J_{2n+N}^2 \left( \frac{V_r}{\omega_r} \right) + J_{2n-N}^2 \left( \frac{V_r}{\omega_r} \right) \right]$$  \hspace{1cm} (10)$$

In Fig. 4, we plot the height of the $N$-th step, where $N = 0$ and 1, as a function of the irradiation intensity for different values of the electron-phonon coupling constant. The oscillation behavior of the step height is clearly observed for the small electron-phonon interaction due to the external irradiation [see Eq. (11)], while this oscillation smears out for large electron-phonon interaction. The large electron-phonon interaction enhances the processes of absorption and emission of many ($n > 1$) phonons when electron tunnels through the dot, and then the summation of Bessel function with large values of indices $n \pm N$ results in the smearing of the oscillation behavior [see Eq. (11)].

Summarizing, using the Keldysh nonequilibrium Green’s function technique, we have studied in this work, to the best of our knowledge, for the first time the time-dependent transport through a single molecular quantum dot coupled to a local phonon mode in the presence of an external ac field. We show that the external irradiation provides another important experimental tool where both the equilibrium and out of equilibrium transport phenomenon can be probed. In particular, resonant behavior as the ac frequency matches the frequency of local phonon mode is shown to exist as a result of the satellite-phonon-peak structure in the dot electron density of states. The nonlinear I-V curves exhibit new structure caused by the external irradiation, which can be investigated experimentally.

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