Interplay of Electron-Electron and Electron-Phonon Interactions in Molecular Junctions

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(Dated: December 19, 2018)

In this work we consider a current carrying molecular junction with both electron-phonon and electron-electron interactions taken into account. After performing Lang-Firsov transformation and considering Markov approximations in accordance to weak coupling to the electronic leads, we obtain the master equation governing the time evolution of the reduced density matrix of the junction. The steady state of the density matrix can be used to obtain I-V characteristic of the junction in several regimes of strengths of the interactions. Our results indicate that the system can show negative differential conductance (that is, the current decreases by increasing the applied bias voltage) in some regimes as an interplay between the electron-phonon and Coulomb interactions.

The paper is organized as follow. In Sec II the Hamiltonian of our system is introduced and the corresponding ME is derived. Moreover, the formula to obtain the electrical current through the MJ is obtained. In Sec III we present our numerical results and discussions, and finally, Sec IV concludes our work.

II. MODEL AND METHOD

Our model consists of a single level MJ which connects two leads. This level can be populated by two opposite spin electrons which repel each other according to Coulomb interaction. Moreover, electrons on the MJ are coupled to a single frequency phonon mode. The Hamiltonian of this system is

$$\hat{H} = \hat{H}_d + \hat{H}_{leads} + \hat{H}_{ph} + \hat{H}_{tun} + \hat{H}_{e-ph}.$$  (1)

$$\hat{H}_d = \sum_{\sigma=\uparrow,\downarrow} \epsilon_{\sigma} \hat{n}_\sigma + U_0 \hat{n}_\uparrow \hat{n}_\downarrow,$$  (2)

$$\hat{H}_{leads} = \sum_{k,\sigma,\alpha \in \{R,L\}} \epsilon_{k,\alpha} \hat{a}_{k\sigma\alpha}^\dagger \hat{a}_{k\sigma\alpha},$$  (3)

$$\hat{H}_{ph} = \Omega \hat{b}^\dagger \hat{b},$$  (4)

$$\hat{H}_{tun} = \sum_{k,\sigma,\alpha \in \{R,L\}} V_{k\alpha} \hat{c}^\dagger_{\sigma} \hat{a}_{k\sigma\alpha} + h.c.,$$  (5)

$$\hat{H}_{e-ph} = \sum_{\sigma} \lambda \Omega \hat{n}_\sigma \left( \hat{b} + \hat{b}^\dagger \right),$$  (6)

where $\hat{c}_{\sigma}$ ($\hat{c}_{\sigma}^\dagger$) is the annihilation (creation) operator of an electron with spin $\sigma$ on MJ, $\hat{n}_\sigma = \hat{c}_{\sigma}^\dagger \hat{c}_{\sigma}$ is the number operator, $\epsilon_0$ is the on-site energy of electrons on the MJ and $U_0$ is the strength of Coulomb repulsion. $\hat{b}$$\hat{b}^\dagger$ is the annihilation (creation) operator of phonons on MJ, $\Omega$ is the phonon frequency and $\lambda$ determines electron-phonon coupling. Moreover, $\hat{a}_{k\sigma\alpha}$ ($\hat{a}_{k\sigma\alpha}^\dagger$) annihilates (creates) an electron on the MJ.
electron with spin $\sigma$ in the state $k$ of the lead $\alpha$ ($\alpha = R, L$), and $V_{k,\alpha}$ determines the electron hopping between MJ and the leads.

Performing the Lang-Firsov transformation as $\epsilon^{\delta} \hat{H} e^{-\delta}$ (where $\delta = \sum_{\alpha} \lambda \alpha (b^\dagger - b)$), the e-ph part disappears and the leads and bare phonon parts remain unchanged. $H_d$ retains its form provided that we renormalize the on-site energy and e-e interaction strength to

$$\epsilon = \epsilon_0 - \lambda^2 \Omega$$

and

$$U = U_0 - 2\lambda^2 \Omega,$$

respectively.

Following the standard steps for deriving a Markovian ME in the limit of weak lead to MJ coupling, would result in the dynamics of the density matrix (DM), $\rho$, of the system (where by system we mean MJ electrons and phonons). In order to do these calculations, we work in the many-body Fock space, spanned by the number states of the form $|t_\uparrow, n_+ m\rangle$, where $n_+ = 0, 1$ is the number of electrons and $m = 0, 1, 2, \ldots$ is the number of phonons. As in our former work\cite{23}, it is straightforward to show that when the initial DM is diagonal, it would remain diagonal for all times. So, it suffices to just obtain the time evolution of the diagonal elements of $\rho$, $\langle n_\uparrow, m| \rho| n_\uparrow, m\rangle$, which we show by $P_{n_\uparrow, m}$.

The master equation of the system results in

$$\frac{d}{dt} P_{00m} = \sum_{m',\alpha} \Gamma_\alpha \left( [1 - f_\alpha (\Omega (m' - m) + \epsilon)] |\hat{X}_{mm'}|^2 P_{10m'} + \right.$$

$$+ [1 - f_\alpha (\Omega (m' - m) + \epsilon)] |\hat{X}_{mm'}|^2 P_{01m'} - 2f_\alpha (\Omega (m' - m) + \epsilon) |\hat{X}_{mm'}|^2 P_{00m'} \right),$$

$$\frac{d}{dt} P_{10m} = \sum_{m',\alpha} \Gamma_\alpha \left( f_\alpha (\Omega (m' - m) + \epsilon)|\hat{X}_{mm'}|^2 P_{00m'} + \right.$$

$$+ [1 - f_\alpha (\Omega (m' - m) + U + \epsilon)] |\hat{X}_{mm'}|^2 P_{01m'} - [1 - f_\alpha (\Omega (m' - m) + \epsilon)] |\hat{X}_{mm'}|^2 P_{10m'} -$$

$$- f_\alpha (\Omega (m' - m) + U + \epsilon)|\hat{X}_{mm'}|^2 P_{10m} \right),$$

$$\frac{d}{dt} P_{11m} = \sum_{m',\alpha} \Gamma_\alpha (f_\alpha (\Omega (m' - m) + U + \epsilon)$$

$$|\hat{X}_{mm'}|^2 (P_{10m'} + P_{01m'}) - 2[1 - f_\alpha (\Omega (m' - m) + U + \epsilon)] |\hat{X}_{mm'}|^2 P_{11m} \right).$$

where $\hat{X} = \exp[\lambda (\hat{b}^\dagger - \hat{b})]$ and $f_\alpha (\omega) = \frac{\sin(\frac{\omega}{\lambda})}{\pi \omega}$ is the Fermi distribution of lead $\alpha$, in which $\mu_\alpha$ is chemical potential of the lead and $\beta_\alpha$ is its inverse temperature. $\Gamma_\alpha$ determines the tunneling rate of electrons between MJ and lead $\alpha$, which is defined to be $\Gamma_\alpha (\omega) = \sum_k 2|V_{k,\alpha}|^2 \delta(\epsilon_{k\alpha} - \omega)$. In wide band limit (WBL), we take $\Gamma_\alpha$ to be independent of $\omega$. Moreover, it should be noticed that according to spin symmetry in our model, $P_{01m_0} = P_{01m_1}$.

The number of electrons in MJ is $N_e = \sum_m = (P_{10m} + P_{01m} + 2P_{11m}).$ The electrical currents from the leads to the MJ determine the range of change of electron population, i.e., $dN_e/dt = \sum_\alpha I_\alpha$. Comparison with Eqs.\cite{7} the relation for current from lead $\alpha$ to the MJ is obtained as

$$I_\alpha = 2\Gamma_\alpha \sum_{mm'} \left( f_\alpha (\Omega (m' - m) + \epsilon) |\hat{X}_{mm'}|^2 P_{00m'} - \right.$$

$$- [1 - f_\alpha (\Omega (m - m') + \epsilon)] |\hat{X}_{mm'}|^2 P_{10m'} + f_\alpha (\Omega (m' - m) + U + \epsilon) |\hat{X}_{mm'}|^2 P_{10m'} -$$

$$\left. - [1 - f_\alpha (\Omega (m - m') + U + \epsilon)] |\hat{X}_{mm'}|^2 P_{11m} \right),$$

and the total current passing through the MJ is $I = (I_L - I_R)/2$.

In the next section, we numerically compute the current as a function of the applied bias voltage and investigate the situation when e-e and e-ph interactions coexist.

### III. NUMERICAL RESULTS

In this section we represent our numerical results. We work in a system of units in which $\hbar = 1$. Also, the Boltzmann constant, $k_B$, is taken to be 1. We set the phonon frequency to be our energy unit, i.e., $\Omega = 1$. These automatically set our units of time, bias voltage and electrical current. Moreover, the bias voltage is applied symmetrically, so that $\mu_L = -\mu_R = V/2$, and we consider $\epsilon = -0.25$. In this work, we don’t consider the temperature gradient between the leads and set both leads to be at zero temperature. Finally, the tunneling rates between MJ and the leads are assumed to be $\Gamma_L = \Gamma_R = 0.1$.

In fig.\cite{4} the current through MJ as a function of bias voltage is depicted for different values of e-ph coupling, $\lambda$, ranging from 0 to 1. In all of these curves, the electrical current starts when the chemical potential of the right lead reaches $\epsilon$, that is, when the bias voltage is $V = 2\epsilon = 0.5$. For the case where $\lambda$ vanishes, there is just one more step in the $I$-$V$ curve, and that is when $V/2 = \epsilon + U$, as is expected in Coulomb blockade regime.

When $\lambda$ is not zero, all of the steps in the electrical current occur at the side-band energies, that is, every step is at a bias voltage of the form $\left( V = 2\epsilon + n \Omega + m U \right)$, where $m$ is integer and $n = 0, 1$. The most interesting ones of these steps, are those that show NDC, which in fig.\cite{4} are at the bias voltage of $V = 2(\epsilon + \Omega)$.

As it is seen in the curves, by increasing the e-ph coupling strength, this NDC increases at first, and then gradually disappears. In order to understand this behavior, we note that before this bias voltage, non of the phonon side-bands lie in the bias window. At $V = 2(\epsilon + \Omega)$,
FIG. 1. The current as a function of bias voltage, for different values of $\lambda$, while $U = 2.7$ and $\epsilon = -0.25$. It is seen that by increasing the e-ph coupling strength, NDC first appears at the bias voltage of $V = 2(\epsilon + \Omega)$, and then disappears.

Another transport channel is opened and phonons get excited. As a result, we have two opposing phenomena. Since a new transport channel is opened the current tends to increase. On the other hand, tunneling electron couples to the phonons and spends more time in the junction (this results in the increasing of electron population on the MJ, as can also be seen in a spin-less model, like what we used in our former work [23]). Because of Coulomb interaction, the increased population of electrons with one spin blocks opposite spin electrons to pass through, which reduces the current (it should be noticed that at this bias voltage, double occupancy is prohibited). The relative strength of e-e and e-ph interactions determines which effect would win. For small $\lambda$s, the transport channel is of less importance than the Coulomb repulsion, however, when the $\lambda$ gets strong enough, the new opened channel becomes more important. Moreover, by increasing e-ph coupling the current before the step also reduces. This current which is for bias voltages $\epsilon < V/2 < \epsilon + \Omega$, can be computed analytically to be (in this voltage range no phonons are exited and $P_{n_1,n_1,m}$ vanishes unless $m = 0$)

$$I_0 = \frac{2}{3} \Gamma e^{-\lambda^2},$$

(9)

In fig. 2 we have depicted the current as a function of bias voltage, for $U = 1.5$ and 6, while $\lambda = 0.5$ and $\epsilon = -0.25$. The curves show that for small values of e-e interaction we don’t have NDC, however, if the Coulomb repulsion is strong enough, NDC appears at more than one bias voltages.

$U = 1.5$ the system does not show NDC. On the other hand, for strong $U$s, we can have several bias voltages corresponding to different phonon side-bands, at which NDC appears. As it is shown in the figure, for $U = 6$, we have NDC at two bias voltages.

IV. CONCLUSIONS

In conclusion, we considered an open MJ at zero temperature with both e-e and e-ph interactions. We performed polaron transformations and traced out the lead degrees of freedom in the total density matrix of the system. Using Markov approximation, we obtained the ME that describes the time evolution of our MJ. This ME can be used to obtain the steady state of the system and compute electrical current.

The most important result we obtained was that the system would show NDC as the interplay between e-e and e-ph interactions. For strong enough e-e interactions, this NDC would appear when the bias voltage reaches some of phonon side-bands. This phenomena can be understood by noting that at these side-bands the phonons get excited. Even though this opens a new transport channel, because of electron-phonon coupling, tunneling electrons would spend more time on the junction, which in-

FIG. 2. The current as a function of bias voltage, for $U = 1.5$ and 6, while $\lambda = 0.5$ and $\epsilon = -0.25$. The curves show that for small values of e-e interaction we don’t have NDC, however, if the Coulomb repulsion is strong enough, NDC appears at more than one bias voltages.
creases the Coulomb blockade of opposite spin electrons. It should be noted that in a spin-less model one can see the increase of electron population on the MJ, however there are no electrons with different spin to be blocked.

From the preceding discussion it is clear that this NDC can only be seen if the e-e interaction is strong enough. However, the e-ph coupling strength should also be in an appropriate range. Very small e-ph interaction would result in negligible current difference which is not useful. On the other hand, for very strong e-ph couplings NDC disappears completely. The reason is at this regime the opened transport channel is more effective and wins the competition. Moreover, the current before the step, $I_0$, also reduces exponentially by increasing e-ph couplings.

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