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It is shown that the “hysteresis” in a polaron model of electron transport through the molecule found by M. Galperin et al. [Nano Lett. 5, 125 (2005)] is an artefact of their “mean-field” approximation. The reason is trivial: after illegitimate replacement $\hat{n}^2 = \hat{n}n_0$, where $n_0 = \langle c_0^\dagger c_0 \rangle \leq 1$, the average molecular level occupation Galperin et al obtained non-physical dependence of a renormalized molecular energy level on the non-integer mean occupation number $n_0$ (i.e. the electron self-interaction) and the resulting non-linearity of current. The exact theory of correlated polaronic transport through molecular quantum dots (MQDs) that we proposed earlier [Phys. Rev. B67, 235312 (2003)] proved that there is no hysteresis or switching in current-voltage characteristics of non-degenerate, $d = 1$, or double degenerate, $d = 2$, molecular bridges, contrary to the mean-field result. Switching could only appear in multiply degenerate MQDs with $d > 2$ due to electron correlations.

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Although the correlated electron transport through mesoscopic systems with repulsive electron-electron interactions received considerable attention in the past, and continues to be the focus of intensive studies \cite{1}, much less has been known about a role of electron-phonon correlations in MQD. Recently we have proposed a negative–$U$ Hubbard model of a $d$-fold degenerate quantum dot \cite{2} and a polaron model of resonant tunneling through a molecule with $d$–degenerate level \cite{2}. We found that the attractive electron correlations caused by any interaction within the molecule could provide a molecular switching effect where the current-voltage (I-V) characteristic has two branches with high and low current at the same voltage. This prediction has been confirmed by our theory of the correlated transport through degenerate MQDs with a full account of both the Coulomb repulsion and realistic electron-phonon (e-ph) interactions \cite{3}. We have shown that while the phonon side-bands significantly modify switching in comparison with the negative-$U$ Hubbard model (appearance of phonon ladder on the I-V curve), switching is robust. It shows up when the effective interaction of polarons is attractive and the state of the dot is multiply degenerate, $d > 2$, while there is no switching in a non-degenerate ($d = 1$) or a double degenerate ($d = 2$) MQD.

Surprisingly, later on Galperin et al. \cite{4} neglected these results (there is no citation of our polaron transport theory through the molecule \cite{3}) claiming that even a non-degenerate electronic level coupled to a single vibrational mode provides an I-V curve with the hysteresis, switching, and negative differential resistance. Here we show that these findings are artefacts of their mean-field approximation that neglects the Fermi-Dirac statistics of electrons.

First, we will illustrate the failure of the mean-field approximation of Ref. \cite{4} on a simplest model of a single atomic level coupled with a single one-dimensional oscillator using the first quantization representation for its displacement $x$,

\[
H = \varepsilon_0\hat{n} + fx\hat{n} - \frac{1}{2M}\frac{\partial^2}{\partial x^2} + \frac{kx^2}{2},
\]

Here $M$ and $k$ are the oscillator mass and the spring constant, $f$ is the interaction force, and $\hbar = c = k_B = 1$. This Hamiltonian is readily diagonalized with the exact displacement transformation of the vibration coordinate $x$,

\[
x = y - \hat{n}f/k,
\]

to the transformed Hamiltonian without electron-phonon coupling,

\[
\hat{H} = \varepsilon\hat{n} - \frac{1}{2M}\frac{\partial^2}{\partial y^2} + \frac{ky^2}{2},
\]

where we used $\hat{n}^2 = \hat{n}$ because of the Fermi-Dirac statistics. It describes a small polaron at the atomic level $\varepsilon_0$ shifted down by the polaron level shift $E_p = f^2/2k$, and entirely decoupled from ion vibrations. The ion vibrates near a new equilibrium position, shifted by $f/k$, with the “old” frequency $(k/M)^{1/2}$. As a result of the local ion deformation, the total energy of the whole system decreases by $E_p$ since a decrease of the electron energy by $-2E_p$ overruns an increase of the deformation energy $E_p$. It
becomes clear that the major error of the mean-field approximation of Ref. [4] originates in illegitimate replacement of the square of the occupation number operator \( \hat{n} = c_\mu^\dagger c_\mu \) by its “mean-field” expression \( \hat{n}^2 = \hat{n} \hat{n}_0 \) with the average population of a single molecular level, \( \hat{n}_0 \), in disagreement with the exact identity, \( \hat{n}^2 = \hat{n} \). This leads to a spurious self-interaction of a single polaron with itself \([\varepsilon = \varepsilon_0 - \delta U \xi \varepsilon_{\text{reorg}} n_0] \) instead of Eq. (11), and a resulting non-existent nonlinearity in the rate equation.

The correct procedure should be as follows, see Ref. [3]. The appropriate molecular Hamiltonian includes the Coulomb repulsion, \( U^{C} \), and the electron-vibron interaction as

\[
H = \sum_\mu \varepsilon_\mu \hat{n}_\mu + \frac{1}{2} \sum_{\mu \neq \mu'} U^{C}_{\mu \mu'} \hat{n}_\mu \hat{n}_{\mu'} + \sum_{\mu} \hat{n}_\mu \omega_q (\gamma_{\mu q} d_q + H.c.) + \sum_{q} \omega_q (d_q^\dagger d_q + 1/2) \sum_{\mu} \omega_q (d_q^\dagger d_q + 1/2) \sum_{\mu} \omega_q (d_q^\dagger d_q + 1/2)
\]

Here \( d_q \) annihilates phonons, \( \omega_q \) is the phonon (vibron) frequency, and \( \gamma_{\mu q} \) are the e-ph coupling constant \( (q \) enumerates the vibron modes). This Hamiltonian conserves the occupation numbers of molecular states \( \hat{n}_\mu \).

One can apply the canonical unitary transformation \( e^S \), with \( S = -\sum_q \gamma_{\mu q} \hat{n}_\mu (\gamma_{\mu q} d_q - H.c.) \) integrating phonons out. The electron and phonon operators are transformed as

\[
\hat{c}_\mu = c_\mu X_\mu, \quad X_\mu = \exp \left[ \sum_q \gamma_{\mu q} d_q - H.c. \right]
\]

and

\[
\hat{d}_q = d_q - \sum_\mu \gamma_{\mu q}^* \hat{n}_\mu,
\]

respectively. This Lang-Firsov transformation shifts ions to new equilibrium positions with no effect on the phonon frequencies. The diagonalization is exact:

\[
\bar{H} = \sum_i \varepsilon_i \hat{n}_i + \sum_q \omega_q (d_q^\dagger d_q + 1/2) + \frac{1}{2} \sum_{\mu} \sum_{\mu'} U^{C}_{\mu \mu'} \hat{n}_\mu \hat{n}_{\mu'},
\]

where

\[
U^{C}_{\mu \mu'} = U^{C}_{\mu \mu'} - 2 \sum_q \gamma_{\mu q}^* \gamma_{\mu q} \omega_q,
\]

is the renormalized interaction of polarons comprising their interaction via molecular deformations (vibrongs) and the original Coulomb repulsion, \( U^{C}_{\mu \mu'} \). The molecular energy levels are shifted by the polaron level-shift due to a deformation created by the polaron,

\[
\bar{\varepsilon}_\mu = \varepsilon_\mu - \sum_q \left| \gamma_{\mu q} \right|^2 \omega_q,
\]

Applying the same transformation to the retarded Green’s function, one obtains the exact MQD spectral function \( \mathcal{F} \) for a \( d \)-fold degenerate MQD (i.e. the density of molecular states, DOS) as

\[
\rho(\omega) = Z d \sum_{r=0}^{d-1} Z_r(n) \sum_{l=0}^{\infty} I_l (\xi)
\]

\[
\times \left[ e^{\beta \omega_0/2} \left[ (1 - n) \delta(\omega - rU - l\omega_0) + n \delta(\omega - rU + l\omega_0) \right] + (1 - \delta_{l0}) e^{-\beta \omega_0/2} \left[ n \delta(\omega - rU - l\omega_0) + (1 - n) \delta(\omega - rU + l\omega_0) \right] \right],
\]

where

\[
Z = \exp \left[ -|\gamma|^2 \coth \frac{\beta \omega_0}{2} \right],
\]

is the polaron narrowing factor \( \mathcal{F} \), \( \xi = |\gamma|^2 / \sinh(\beta \omega_0 / 2) \), \( I_l (\xi) \) the modified Bessel function, \( \beta = 1/T \), and \( \delta_{lk} \) the Kroneker symbol. To simplify our discussion, we assume that the Coulomb integrals do not depend on the orbital index, i.e. \( U_{\mu \mu'} = U \), and consider a coupling to a single vibrational mode, \( \omega_q = \omega_0 \).

The important feature of DOS, Eq. (11), is its nonlinear dependence on the average electronic population \( n = \langle c_\mu^\dagger c_\mu \rangle \) which leads to the switching, hysteresis, and other nonlinear effects in I-V characteristics for \( d > 2 \) \( \mathcal{F} \). It appears due to correlations between different electronic states via the correlation coefficients

\[
Z_r(n) = \frac{(d - 1)!}{r!(d - 1 - r)!} n^r (1 - n)^{d-1-r}.
\]

There is no nonlinearity if the dot is nondegenerate, \( d = 1 \), since \( Z_0(n) = 1 \), contrary to Ref. [4]. In this simple case the DOS, Eq. (11), is a linear function of the average population that can be found as a textbook example of an exactly solvable problems \( \mathcal{F} \). As a result, the rate equation for \( n \) \( \mathcal{F} \) yields only a single solution [see Eq. (43) in Ref. \( \mathcal{F} \)] and no switching in the whole voltage range.

However, their “mean-field” approximation led the authors of Ref. [4] to the opposite conclusion. Indeed, Galperin et al. [4] have replaced the occupation number operator \( \hat{n} \) in the e-ph interaction by the average population \( n_0 \) [Eq. (2) of Ref. [4]] and found the average steady-state vibronic displacement \( (d + d^\dagger) \) proportional to \( n_0 \). Then, replacing the displacement operator \( d + d^\dagger \) in the bare Hamiltonian, Eq. (1), by its average, Galperin et al. obtained a new molecular level, \( \bar{\varepsilon}_0 = \varepsilon_0 - 2 \varepsilon_{\text{reorg}} n_0 \) shifted linearly with the average population of the level. This is in stark disagreement with the conventional constant polaronic level shift, Eq. (11) \( (\varepsilon_{\text{reorg}} = |\gamma|^2 \omega_0 in our notations). Their spectral function turned out to be highly nonlinear as a function of the population, e.g. for the weak-coupling with the leads \( \rho(\omega) = \delta(\omega - \varepsilon_0 - 2 \varepsilon_{\text{reorg}} n_0) \), see Eq. (17) in Ref. [4]. As a result, the authors of Ref. [4] have found multiple solutions for the steady-state population, Eq. (15) and Fig. 1,
and switching, Fig. 4 of Ref. [3], which actually do not exist. Taking into account the coupling with the leads (Γ in Ref. [3,4]) beyond the second order and the coupling between the molecular and bath phonons does not provide any non-linearity of the non-degenerate DOS either, because these couplings do not depend on the electron population.

Different from the non-degenerate dot, the rate equation for a multi-degenerate dot, \( d > 2 \), has multiple physical roots in a certain voltage range and a hysteretic behavior due to correlations between different electronic states of MQD [3]. We conclude that Galperin et al. [4] have found a non-existent hysteresis in a model already exactly solved well before their work in Ref. [3].