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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 [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 [2] and a polaron model of resonant tunneling through a molecule with \( d \)-degenerate level [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 [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. [4] neglected these results (there is no citation of our polaron transport theory through the molecule [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. [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 \( x \),

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

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 $\hat{n}^2 = \hat{n}_0$ with the average population of a single molecular level, $n_0$, in disagreement with the exact identity, $\hat{n}^2 = \hat{n}$. This leads to a spurious self-interaction of a single polaron with itself [$\varepsilon = \varepsilon_0 - n_0 E_c$ instead of Eq. (1)], 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

$$H = \sum_\mu \varepsilon_\mu \hat{n}_\mu + \frac{1}{2} \sum_{\mu \neq \mu'} U_{\mu \mu'} \hat{n}_\mu \hat{n}_{\mu'} + \sum_{\mu\gamma} \omega_\gamma (\gamma_{\mu \gamma} \hat{d}_\gamma + H.c.) + \sum_q \omega_q (d_\gamma^\dagger d_\gamma + 1/2|5|)$$

Here $d_\gamma$ annihilates phonons, $\omega_q$ is the phonon (vibron) frequency, and $\gamma_{\mu \gamma}$ 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 $e^{\hat{S}}$, with $\hat{S} = -\sum_q \hat{\mu}_\gamma (\gamma_{\mu \gamma} \hat{d}_\gamma - H.c.)$ integrating phonons out. The electron and phonon operators are transformed as

$$\hat{c}_\mu = c_\mu X_\mu, \quad X_\mu = \exp \left( \sum_q \gamma_{\mu \gamma} \hat{d}_\gamma - H.c. \right)$$

and

$$\hat{\tilde{d}}_\gamma = d_\gamma - \sum_\mu \hat{\tilde{n}}_{\mu\gamma} \gamma_{\mu \gamma}^*,$$

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

$$\hat{H} = \sum_i \tilde{\varepsilon}_i \hat{n}_i + \sum_q \omega_q (\hat{d}_\gamma^\dagger \hat{d}_\gamma + 1/2) + \frac{1}{2} \sum_{\mu \neq \mu'} U_{\mu \mu'} \hat{n}_\mu \hat{n}_{\mu'},$$

where

$$U_{\mu \mu'} = U_{\mu \mu'}^C - 2 \sum_q \gamma_{\mu \gamma}^* \gamma_{\mu' \gamma} \omega_q,$$

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

$$\tilde{\varepsilon}_\mu = \varepsilon_\mu - \sum_q |\gamma_{\mu \gamma}|^2 \omega_q.$$

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

$$\rho(\omega) = Z d \sum_{r=0}^{d-1} \sum_{\gamma} \sum_{l=0}^{\infty} I_l(\xi) \times e^{\beta \omega_{\gamma}/2} \left[ (1 - n) \delta(\omega - rU - l\omega_0) + n \delta(\omega - rU + l\omega_0) \right] + (1 - \delta_{l0}) e^{-\beta \omega_{\gamma}/2} \left[ n \delta(\omega - rU - l\omega_0) + (1 - n) \delta(\omega - rU + l\omega_0) \right],$$

where

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

is the polaron narrowing factor, $\xi = |\gamma|^2 / \sinh(\beta \omega_0/2)$, $I_l(\xi)$ 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 $d > 2$. 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. [3]. 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 problem [3]. As a result, the rate equation for $n$ yields only a single solution [see Eq. (43) in Ref. [3]] 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 ($d + d'$) proportional to $n_0$. Then, replacing the displacement operator $d + d'$ in the bare Hamiltonian, Eq. (1), by its average, Galperin et al. obtained a new molecular level, $\tilde{\varepsilon}_0 = \varepsilon_0 - 2 \varepsilon_{\text{reorg}} n_0$ shifted linearly with the average population of the level. This is in stark disagreement with the conventional constant polaronic level shift, Eq. (1) (the latter $\varepsilon_{\text{reorg}}$ is $|\gamma|^2 \omega_0$ 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. [3]. 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. [4], 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].

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