Comment on Hysteresis, Switching, and Negative Differential Resistance in Molecular Junctions: a Polaron Model, by M. Galperin, M.A. Ratner, and A. Nitzan, Nano Lett. 5, 125 (2005)

A. S. Alexandrov$^1$ and A.M. Bratkovsky$^2$

$^1$Department of Physics, Loughborough University, Loughborough LE11 3TU, United Kingdom
$^2$Hevlett-Packard Laboratories, 1501 Page Mill Road, MS 1123, Palo Alto, California 94304

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 $n_0 = \langle \hat{c}_f^\dagger \hat{c}_f \rangle \leq 1$ the average molecular level occupation Galperin et al obtained non-physical dependence of a non-degenerate 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 theory of correlated polaronic transport through molecular quantum dots (MQDs) that we proposed earlier [Phys. Rev. B 67, 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. Most of the molecular quantum dots are in the regime of weak coupling to the electrodes addressed in our formalism.

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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.[3] 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. [3] neglected these results, 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. [3] on a simplest model of a single atomic level coupled with a single one-dimensional oscillator using the first quantization representation for its displacement $x$,

$$H = \varepsilon_0 \hat{n} + fx \hat{n} - \frac{1}{2M} \frac{\partial^2}{\partial x^2} + \frac{kx^2}{2}. \quad (1)$$

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 $x$,

$$x = y - \hat{n}f/k, \quad (2)$$

to the transformed Hamiltonian without electron-phonon coupling,

$$\hat{H} = \varepsilon \hat{n} - \frac{1}{2M} \frac{\partial^2}{\partial y^2} + \frac{ky^2}{2}, \quad (3)$$

$$\varepsilon = \varepsilon_0 - E_p, \quad (4)$$

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 \( \hat{n} = c_\mu^d c_\mu \) by its “mean-field” expression \( \hat{n}^2 = \hat{n} n_0 \) 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 [\( \varepsilon = \varepsilon_0 - n_0 E_p \) instead of Eq. (1)], and a resulting non-existent nonlinearity in the rate equation.

The correct procedure should be as follows, see Ref. [5]. The appropriate molecular Hamiltonian includes the Coulomb repulsion, \( U^C \), and the electron-vibron interaction as

\[
H = \sum_{\mu} \varepsilon_{\mu} \hat{n}_\mu + \frac{1}{2} \sum_{\mu \neq \mu'} U_{\mu \mu'} \hat{n}_\mu \hat{n}_{\mu'} + \sum_{\mu, q} \hat{n}_\mu \omega_q (\gamma_{\mu q} \hat{d}_q + H.c.) + \sum_q \omega_q (\hat{d}_q^\dagger \hat{d}_q + 1/2). \tag{5}
\]

Here \( \hat{d}_q \) 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 \( S = -\sum_{q, \mu} \hat{n}_\mu (\gamma_{\mu q} \hat{d}_q - H.c.) \) integrating phonons out. The electron and phonon operators are transformed as

\[
\tilde{c}_\mu = c_\mu X_\mu, \quad X_\mu = \exp \left( \sum_q \gamma_{\mu q} \hat{d}_q - H.c. \right) \tag{6}
\]

and

\[
\tilde{d}_q = d_q - \sum_\mu \hat{n}_{\mu'} \gamma^*_{\mu q}, \tag{7}
\]

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

\[
\tilde{H} = \sum_i \tilde{\varepsilon}_i \tilde{n}_i + \sum_q \omega_q (\hat{d}_q^\dagger \hat{d}_q + 1/2) + \frac{1}{2} \sum_{\mu \neq \mu'} U_{\mu \mu'} \tilde{n}_\mu \tilde{n}_{\mu'}, \tag{8}
\]

where

\[
U_{\mu \mu'} = U^C_{\mu \mu'} - \frac{1}{2} \sum_q \gamma^*_{\mu q} \gamma_{\mu' q} \omega_q, \tag{9}
\]

is the renormalized interaction of polarons comprising their interaction via molecular deformations (vibrons) 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,

\[
\tilde{\varepsilon}_\mu = \varepsilon_{\mu} - \sum_q |\gamma_{\mu q}|^2 \omega_q. \tag{10}
\]

Applying the same transformation to the retarded Green’s function, one obtains the exact MQD spectral function [3] for a \( d \)-fold degenerate MQD (i.e. the density of molecular states, DOS) as

\[
\rho(\omega) = Z d \sum_{r=0}^{d-1} \sum_{n=0}^{\infty} I_n (\varepsilon)(\omega) \times e^{\beta \omega_0 / 2} [(1 - n) \delta(\omega - rU - \omega_0) + n \delta(\omega - rU + \omega_0)] + (1 - \delta_0) e^{-\beta \omega_0 / 2} \rbracket \varepsilon(\omega - rU + \omega_0), \tag{11}
\]

where

\[
Z = \exp \left(-|\gamma|^2 \coth \frac{\beta \omega_q}{2} \right), \tag{12}
\]

is the polaron narrowing factor [3], \( \xi = |\gamma|^2 / \sinh(\beta \omega_0 / 2) \), \( I_n (\varepsilon) \) 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 \( n = \langle c_\mu^d c_\mu \rangle \) which leads to the switching, hysteresis, and other nonlinear effects in I-V characteristics for \( d > 2 \) [3]. It appears due to correlations between different electronic states via the correlation coefficients

\[
Z_r(n) = \frac{r!}{r!} \frac{(d - 1)!}{(d - 1 - r)!} n^r (1 - n)^{d-1-r}. \tag{13}
\]

There is no nonlinearity if the dot is nondegenerate, \( d = 1 \), since \( Z_0(n) = 1 \), contrary to Ref. [5]. 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 [5]. As a result, the rate equation for \( n \) [3] 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. [1] 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 \( \langle d + d^\dagger \rangle \) proportional to \( n_0 \) (this is an explicit neglect of all quantum fluctuations on the dot accounted for in the exact solution [3]). 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, \( \tilde{\varepsilon}_0 = \varepsilon_0 - 2 \varepsilon_{\text{reorg}} n_0 \) shifted linearly with the average population of the level. This is in stark disagreement with the conventional constant polaronic level-shift, Eq. (11) (\( \varepsilon_{\text{reorg}} \) 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. [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. [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.

Note that the mean-field solution by Galperin et al. [4] applies at any ratio Γ/ω₀, including the limit of interest to us, Γ ≪ ω₀, where their transition between the states with n₀ = 0 and 1 only sharpens, but none of the results change. Therefore, they do predict a current bistability in the system where it does not exist at d = 1. Results in Ref. [4] are plotted for Γ > ω₀, Γ ≈ 0.1 – 0.3 eV, which corresponds to molecular bridges with a resistance of about a few 100 kΩ. Such model ‘molecules’ are rather ‘metallic’ in their conductance and could hardly show any bistability because carriers do not have time to interact with vibrons on the molecule. This obvious conclusion for molecules strongly coupled to the electrodes can be reached in many ways, see e.g. a very involved derivation in Ref. [3]. The current hysteresis does not occur in their model, it remains a single-valued function of bias with superimposed noise. In any case, it certainly has nothing to do with our result that applies to molecular quantum dots (Γ ≪ ω₀) with d > 2.

As a matter of fact, most of the molecules are very resistive, so the actual molecular quantum dots are in the regime we study, see Ref. [8]. For example the resistance of fully conjugated three-phenyl ring Tour-Reed molecules chemically bonded to metallic Au electrodes [6] is larger than 1GΩ. Different from the non-degenerate dot, the rate equation for a multi-degenerate dot, d > 2, weakly coupled to the leads 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 solved well before their work in Ref. [8].

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