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)

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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 $n_0 = \left\langle c_0^\dagger c_0 \right\rangle \leqslant 1$ 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. 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.

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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,

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

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,

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

to the transformed Hamiltonian without electron-phonon coupling,

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

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

where we used $\hat{n}^2 = \hat{n}$ because of the Fermi-Dirac statistics. It describes a small polaron at the atomic level ε_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 $\hat{n} = c_0^\dagger c_0$ 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.(4)], 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 [3]

$$H = \sum_\mu \varepsilon_\mu \hat{n}_\mu + \frac{1}{2} \sum_{\mu \neq \mu'} U_{\mu\mu'}^C \hat{n}_\mu \hat{n}_{\mu'}$$
$$+ \sum_{\mu,q} \hat{n}_\mu \omega_q (\gamma_{\mu q} d_q + H.c.) + \sum_q \omega_q (d_q^\dagger d_q + 1/2) \quad (5)$$

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

$$\tilde{c}_\mu = c_\mu X_\mu, \qquad X_\mu = \exp\left(\sum_q \gamma_{\mu q} d_q - H.c.\right) \quad (6)$$

and

$$\tilde{d}_q = d_q - \sum_\mu \hat{n}_\mu \gamma_{\mu q}^*, \quad (7)$$

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

$$\tilde{H} = \sum_i \tilde{\varepsilon}_\mu \hat{n}_\mu + \sum_q \omega_q (d_q^\dagger d_q + 1/2) + \frac{1}{2} \sum_{\mu \neq \mu'} U_{\mu\mu'} \hat{n}_\mu \hat{n}_{\mu'}, \quad (8)$$

where

$$U_{\mu\mu'} \equiv U_{\mu\mu'}^C - 2 \sum_q \gamma_{\mu q}^* \gamma_{\mu' q} \omega_q, \quad (9)$$

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,

$$\tilde{\varepsilon}_\mu = \varepsilon_\mu - \sum_q |\gamma_{\mu q}|^2 \omega_q. \quad (10)$$

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

$$\rho(\omega) = \mathcal{Z} d \sum_{r=0}^{d-1} Z_r(n) \sum_{l=0}^\infty I_l(\xi)$$
$$\times \left[e^{\beta\omega_0 l/2} [(1-n)\delta(\omega - rU - l\omega_0) + n\delta(\omega - rU + l\omega_0)] \right.$$
$$+ (1 - \delta_{l0}) e^{-\beta\omega_0 l/2} [n\delta(\omega - rU - l\omega_0)$$
$$\left. + (1-n)\delta(\omega - rU + l\omega_0)] \right], \quad (11)$$

where

$$\mathcal{Z} = \exp\left[-|\gamma|^2 \coth \frac{\beta\omega_0}{2}\right], \quad (12)$$

is the polaron *narrowing factor* [5], $\xi = |\gamma|^2 / \sinh(\beta\omega_0/2)$, $I_l(\xi)$ the modified Bessel function, $\beta = 1/T$, and δ_{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 $d > 2$ [3]. It appears due to *correlations* between *different* electronic states via the correlation coefficients

$$Z_r(n) = \frac{(d-1)!}{r!(d-1-r)!} n^r (1-n)^{d-1-r}. \quad (13)$$

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 [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. [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 $\langle d + d^\dagger \rangle$ 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, $\tilde{\varepsilon}_0 = \varepsilon_0 - 2\varepsilon_{reorg} n_0$ shifted linearly with the average population of the level. This is in stark disagreement with the conventional constant polaronic level shift, Eq. (4,10) (ε_{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 $\rho(\omega) = \delta(\omega - \varepsilon_0 - 2\varepsilon_{reorg} n_0)$, 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.

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].

[1] For recent reviews, see: *Molecular Nanowires and Other Quantum Objects*, eds. Alexandrov, A. S.; Demsar, J. and Yanson, I. K; Kluwer: Dodrecht, 2004.

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[5] Mahan, G. D. *Many-Particle Physics (*2nd edition*)*; Plenum: New York, 1990.