Title

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Reply to Comment by Alexandrov and Bratkovsky [cond-mat/0603467]

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The submitted Comment is based on using an isolated quantum dot approach to discuss the situation where the coupling to the leads is considerable (not negligible). This finite lead coupling is the situation in most molecular transport junctions. In such situations the population on the molecule is not static and dynamical effects (fluctuations) are crucial. While the discussion in Ref. 2, and in the Comment may well apply for an isolated molecule, it is simply irrelevant for the very different transport situation analyzed in our original contribution.

In their preceding comment on our earlier paper,[1] Alexandrov and Bratkovsky (AB) bring up the following claims:

1. A previous work by AB[2] that discusses bistability in correlated transport through a degenerate molecular quantum dot was "surprisingly" not cited in our paper.[1]

2. The mean field approximation used in Ref. 1 is invalid.

3. The bistability and hysteresis phenomenon discussed in Ref. 1 is an artifact of this invalid mean field approximation.

Indeed, while we have cited the paper on bistable tunneling current by AB,[3] we indeed overlooked the paper 2 by these authors. In retrospect we believe (for reasons given below) that the paper is only marginally relevant to our work, however discussing it at the time would have make some issues clearer and could have saved the present exchange, so we regret our failing to do so. In what follows we address issues (2) and (3).

Consider first the mean field approximation. Let two coupled subsystems a and b of system s be described by the Hamiltonian $H_s = H_a + H_b + V_{ab}$ and let system a be characterized by two states, $|1_a >$ and $|2_a >$. Assume furthermore that an additional process causes a rapid interchange between states $|1_a >$ and $|2_a >$, and that this process by itself would bring subsystem a to equilibrium with probability P_1 to be in state $|1_a >$ and P_2 to be in state $|2_a >$. How good is an approximation by which the dynamics of system b is assumed to be governed by the Hamiltonian $H_b+ < V_{ab} >_a$ where $< \ldots >_a$ denotes an average over the state of a, and in particular when can $< V_{ab} >_a$ be represented by $P_1 < 1_a|V_{ab}|1_a > +P_2 < 2_a|V_{ab}|2_a >$?

Describing the motion of subsystem b by the Hamiltonian $H_b+ < V_{ab} >_a$ (while deriving the dynamics of a from the frozen instantaneous state of b) is the essence of the adiabatic (Born-Oppenheimer) approximation used in quantum molecular dynamics, and relies on the assumption that system a is much faster than system b. The correct identification of $< V_{ab} >_a$ depends on details of this assumption. In particular, in the example constructed above, identifying $< V_{ab} >_a$ as given by $P_1 < 1_a|V_{ab}|1_a > +P_2 < 2_a|V_{ab}|2_a >$ (rather than, e.g. moving system b under the potential $< 1_a|V_{ab}|1_a >$ when a is in state $|1_a >$ and under $< 2_a|V_{ab}|2_a >$ when a is in state $|2_a >$) is valid *provided that the dynamics of the $|1_a > \leftrightarrow |2_a >$ is fast on the timescale that characterizes the dynamics of system b.*

In the present problem system b is the vibration of frequency ω_0 and system a is the molecule, which is characterized by two states

- occupied and unoccupied. The process that interchanges between the two states is the molecule-leads electron exchange, whose characteristic timescale is $\Gamma^{-1} = 2\pi V^2 \rho$ where V is the molecule-lead coupling and ρ - the electronic density of states in the lead. From the above discussion it is clear that the condition for the validity of the mean-field approximation as applied in Ref. 1 is $\Gamma > \hbar\omega_0$. In molecular junctions with chemical binding between the electrodes and the molecular bridge Γ is of the order $0.1 - 1$ eV while typical vibrational frequencies span the range $0.001 - 0.3$ eV. There is thus a wide regime in which this approximation is valid.

In the preceding comment, AB illustrate the failure of the mean field approximation for a model in which $\Gamma = 0$. Clearly this illustration is irrelevant for the problem at hand. They then proceed to discuss, under what they call "the correct procedure", a different model (a recast of Ref. 2) in which bistability stems from electron-electron interaction in a d-fold degenerate molecule. Again, analysis of this model is done by neglecting the molecule-leads coupling and, furthermore, disregarding the effect of the electron-vibration interaction on the state of the vibration - two principal ingredients of the model of Ref. 1. While we have no objections to this model and its consequences, it can hardly be regarded as a "correct procedure" with respect to our model, or, indeed, to the molecular junction problem that we analyzed. We note that similar models, with similar conclusions about the inherent bistability in the system (though with different views about its consequence - see below) have been recently discussed by several authors.[4–7]

Next consider the consequences of the bistable nature of the nuclear potential surface obtained in the mean field approximation. Obviously, as emphasized by Mitra et al,[6] this bistability does not imply any phase transition property. The observation of hysteresis or, instead, switching behavior (telegraphic noise) depends on the timescale of changing the external control parameter (e.g. the bias or the gate potential) relative to the rates of transitions between locally stable states.[7] Both phenomena are observed in molecular junctions, and the question whether they are accounted for by the present mechanism should be settled by determining these rates. This issue has not been raised or discussed in the preceding comment by AB.

We end our reply with several comments:

1. For an isolated molecule (MQD in the AB language) the molecular level is well defined, and is shifted from ε_0 to $\varepsilon_0 - M^2/\omega_0$ by the electron-vibration interaction (reorganization energy). Coupling to the leads gives rise to electronic level population that fluctuates on the characteristic timescale Γ^{-1}. The observation that for $\Gamma > \hbar\omega_0$ the electronic energy shift does depend on the average population of molecular level, was first made in Refs. 8, 9. The isolated MQD consideration of 2 misses the physics of this situation, which is physically relevant to molecular transport junctions.

2. The AB Comment refers to the approximation $\hat{n}^2 = n_0\hat{n}$ as "a spurious self-interaction of a single polaron with itself". In fact, this term represents the interaction of a tunneling electron at a particular time with the polarization charge established in response to electrons (many tunneling events) which traversed the junction at earlier times. This "self-interaction" is legitimate in the (physically relevant) case where coupling to the leads (disregarded in the AB treatment) is taken into account.

3. The treatment of Ref. 7 of the same one-level model, which goes beyond the mean-field approximation, also leads to multistability in agreement with our treatment. The statement in Ref. 2 that "the Born-Oppenheimer approximation does not apply to nondegenerate level, since there are no fast (compared to the characteristic phonon time $1/\omega_0$) electron transitions within the dot" holds for the isolated MQD. In molecular wires the molecule-metal electron exchange with timescale Γ^{-1} provides this fast process.

4. Contrary to statements made in the AB Comment, taking into account the coupling with the

leads (after the Lang-Firsov transformation applied to the Hamiltonian as is done in Ref. 2) does provide nonlinearity, since the effective couplings do depend on the electron population on the bridge. Confusion here is due to the approximation made in 2 which neglects the effect of the electron-vibration coupling on the vibration state. For detailed discussion see 10.

In conclusion, while the discussion in Ref. 2, and in the AB Comment apply for an isolated molecule, it is simply irrelevant for the very different transport situation analyzed in our original contribution.

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