Molecular switching with strong electron-phonon interaction

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Abstract. We have shown that the attractive electron correlations caused by a strong electron-phonon interaction (EPI) in molecular quantum dots (MQDs) weakly coupled with the leads provide a switching effect, when the current-voltage characteristics show two branches with high and low current for the same voltage. Key features of polaronic correlated transport in degenerate MQDs are briefly reviewed fully taking into account both the Coulomb repulsion and EPI. Switching shows up when the effective interaction of polarons is attractive and the state of the dot is multiple degenerate.

1. Introduction
Polarons in low-dimensional semiconductor structures and quasi-zero-dimensional systems like individual molecules have received significant attention in recent years. Quite generally confinement enhances EPI and the tendency to polaron formation. While correlation effects in transport through metallic quantum dots with repulsive electron-electron interactions received considerable attention in the past, and continue to be the focus of intense investigations, much less has been known about a role of attractive correlations between small polarons mediated by EPI in MQD. Recently a switching phenomenon of MQD has been theoretically predicted with a full account of both the Coulomb repulsion and EPI [1, 2]. Ref. [1] has shown that while the phonon side-bands significantly modify the shape of hysteretic I-V curves the switching is robust showing up at sufficiently low temperatures, if the effective interaction of polarons in MQD is attractive and the molecular level is multiple degenerate. Here the theoretical prediction of a switching behaviour of many-fold degenerate molecular quantum dots is briefly reviewed referring the reader to more comprehensive reviews and books [3, 4, 5].

2. Short-range attraction of small polarons in MQD
Molecular vibronic deformations strongly affect the interaction between electrons. In bulk ionic crystals polarons repel each other at large distances, but their Coulomb repulsion is substantially reduced owing to the ion polarization. When a short-range deformation potential and molecular EPIs (e.g. of the Jahn-Teller type) are taken into account together with the long-range Fröhlich interaction, EPI can overcome the Coulomb repulsion, so that the resulting interaction becomes attractive at a short distance of about a lattice constant [6]. Then two small polarons readily form a bound state in bulk semiconductors, i.e. a small bipolaron, which is quite mobile in particular lattice structures like cuprate superconductors [6, 7].
Figure 1. Two localised electrons shift the equilibrium position of the ion (3). As a result two electrons on neighboring sites 1 and 2 attract each other.

The origin of the attractive force between two small polarons can be readily understood using a toy model [3], Fig.1, with two electrons on neighbour sites 1,2 interacting with an ion nearby, on site 3. If we assume that the ion 3 is a three-dimensional oscillator described by a displacement vector $u$ and the mass $M$, then the Hamiltonian of the model is

$$H = E_a(n_1 + n_2) + u \cdot (f_1 \hat{n}_1 + f_2 \hat{n}_2) - \frac{\hbar^2}{2M} \left( \frac{\partial}{\partial u} \right)^2 + \frac{ku^2}{2},$$

(1)

where $f_{1,2} = Ze^2 \mathbf{e}_{1,2}/a^2$ is the Coulomb force, $a$ is the equilibrium distance between sites in the absence of electrons, $\mathbf{e}_{1,2}$ are units vectors connecting sites 1,2 and site 3, $\hat{n}_{1,2}$ are the occupation number operators at sites 1,2, respectively and $k$ is the oscillator spring constant. This Hamiltonian is readily diagonalised by the displacement transformation of the vibronic coordinate $u$, $u = v - (f_1 \hat{n}_1 + f_2 \hat{n}_2)/k$. The transformed Hamiltonian has no electron-phonon coupling,

$$\tilde{H} = (E_a - E_p)(n_1 + n_2) + V_{ph} \hat{n}_1 \hat{n}_2 - \frac{\hbar^2}{2M} \left( \frac{\partial}{\partial v} \right)^2 + \frac{kv^2}{2},$$

(2)

and describes two small polarons at their atomic levels, $E_a$, shifted by the polaron level shift, $E_p = f_{1,2}^2/2k$, which are entirely decoupled from ion vibrations. As a result, the lattice deformation caused by two electrons leads to an effective interaction between them, $V_{ph} = -f_1 \cdot f_2/k$, which should be added to their Coulomb repulsion, $V_c$. When $V_{ph}$ is negative and large compared with positive $V_c$ the full interaction becomes negative.

Small polarons with their attractive correlations are quite feasible also in molecular nanowires and quantum dots (MQD) used as the “transmission lines” and active molecular elements in molecular-scale electronics. In such devices a molecule is placed between two metallic leads. When electrons from the lead tunnel to the molecular orbits they deform the molecule, and tunnel via molecular sites as small polarons with effective inter-polaron attraction.

3. Polaronic switching

Attractive polaron-polaron correlations in molecules cause a fast switching in the I-V characteristics of certain molecular bridges, which could be the basis of future oscillators, amplifiers and other important circuit elements.

With some assumptions the current through MQD is given by the Landauer-type expression [1] as

$$I(V) = I_0 \int_{-\infty}^{\infty} dE \left[ f_1(E) - f_2(E) \right] \rho(E),$$

(3)
Figure 2. The bistable I-V curves for tunneling through the 4-fold degenerate molecular quantum dot with the electron-vibron coupling constant $\gamma^2 = 11/13, \hbar \omega_0/\Delta = 0.2$, and $V_c = 0$. The up arrows show that the current picks up at some voltage when it is biased, and then drops at lower voltage when the bias is being reduced. The bias dependence of current basically repeats the shape of the level occupation $n$ (right column). Steps on the curve correspond to the changing population of the vibron side-bands (after [1]).

allowing for a transparent analysis of essential physics of the switching phenomenon. Here $I_0$ is a constant, $f_{l(2)}(E) = 1/\{\exp[(E + \Delta \mp eV/2)/k_B T] + 1\}$ is the electron distribution function in left (1) and right (2) metallic leads, respectively, $T$ is the temperature, $\Delta$ is the position of the lowest unoccupied molecular level with respect to the chemical potential, and $V$ is the voltage drop in MQD. The density-of-states (DOS), $\rho(E)$, of a $d$-fold degenerate dot is given by

$$
\rho(E) = \mathcal{Z} d \sum_{r=0}^{d-1} Z_r(n) \sum_{l=0}^{\infty} I_l(\xi) \\
\times \left[ e^{\frac{\hbar \omega_0}{2}} \left[ (1 - n) \delta(E - rU - l\hbar \omega_0) + n \delta(E - rU + l\hbar \omega_0) \right] + (1 - \delta_{0l}) e^{-\frac{\hbar \omega_0}{2}} \left[ n \delta(E - rU - l\hbar \omega_0) + (1 - n) \delta(E - rU + l\hbar \omega_0) \right] \right].
$$

Here a second-order perturbation theory in powers of the molecular-lead hopping integral $t$ is applied, using $t/\hbar \omega \ll 1$ as a small parameter but keeping all orders of the Coulomb repulsion and EPI with the vibronic mode of the frequency $\omega_0$, and the coupling constant $\gamma$. $\mathcal{Z} = \exp \left[ -|\gamma|^2 \coth(\beta \hbar \omega_0/2) \right]$ accounts for the familiar polaronic renormalisation of the hopping integrals, $\xi = |\gamma|^2/\sinh(\beta \hbar \omega_0/2)$, $I_l(\xi)$ is the modified Bessel function, $\delta_{lk}$ is the Kronecker symbol ($l, k = 0, 1, 2, ...$), and $\beta = 1/k_B T$ is the inverse temperature. The resulting polaron-polaron interaction, $U = V_c - 2|\gamma|^2\hbar \omega_0$, comprises the Coulomb repulsion, $V_c$, and the vibron-
mediated attraction. An important feature of DOS is its nonlinear dependence on the molecular occupation number \( n \), owing to correlation side-bands with the spectral weight
\[
Z_r(n) = \frac{(d-1)!}{r!(d-1-r)!} n^r (1-n)^{d-1-r}.
\]

The DOS, Eq.(4), contains full information about all possible correlations in transport, in particular, the vibron and correlation side-bands. It is derived by solving the finite system of coupled equations for \( N \)-particle Green’s functions, as described in Ref. [1].

Equating incoming and outgoing numbers of electrons in MQD per unit time one obtains the self-consistent equation for the molecular level occupation \( n \) as [1]
\[
2nd = \int dE \rho(E) [f_1(E) + f_2(E)],
\]
which automatically satisfies \( 0 \leq n \leq 1 \). There is only one physical root of this equation for \( n \), and hence there is no switching, if the dot is nondegenerate, \( d = 1 \), or double-degenerate, \( d = 2 \). Remarkably, the switching appears for \( d > 2 \), as illustrated in Fig.2 for \( d = 4 \) using Eqs.(3,4).

4. Conclusions

The actual mechanisms of molecular switching are of the highest current experimental and theoretical value [8]. The further progress will depend upon finding molecules and understanding intrinsic mechanisms for their reversible switching from low to high current state. Here we have reviewed the multi-polaron theory of the current controlled switching mechanism. The degenerate MQD with a strong electron-vibron coupling shows the hysteretic volatile memory, if the degeneracy of the molecular level is larger than two, \( d > 2 \). The hysteretic behavior strongly depends on the electron-vibron coupling and characteristic vibron frequencies. The current bistability vanishes above some critical temperature.

Importantly, the switching does not exist in non- and two-fold degenerate MQDs [1, 9]. Among potential candidates for the negative \( U \) quantum dot are a single \( C_{60} \) molecule (\( d = 6 \)), where the electron-vibronic coupling can be particularly strong, or other carbon nanostructures including short nanotubes (\( d \gg 1 \)) connected to metal electrodes. There should be no retardation of the switching on the time scale above the inverse vibron (phonon) frequency, which is \( 10^{-14} \) s or less in carbon-based compounds. Electronic transport measurements of some single-molecule transistor devices [10] suggest that also alternative switching mechanisms rather than (bi)polaronic effects may be involved in certain measurement configurations (see also [4, 5]).

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