Fast polaron switching in degenerate molecular quantum dots

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Abstract

Devices for nano- and molecular size electronics are currently a focus of research aimed at an efficient current rectification and switching. Current switching due to conformational changes in the molecules is slow, of the order of a few kHz. Fast switching ($\sim$1 THz) may be achieved, at least in principle, in a degenerate molecular quantum dot with strong coupling of electrons with vibrational excitations. We show that the mean-field approach fails to properly describe intrinsic molecular switching and present an exact solution to the problem.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

For many applications one needs an *intrinsic* molecular 'switch', i.e. a bistable voltage-addressable molecular system with very different resistances in the two states that can be accessed very quickly [1]. There is a trade-off between the stability of a molecular state and the ability to switch the molecule between two states with an external perturbation (we discuss an electric field; switching involving absorbed photons is impractical at a nanoscale). Indeed, the applied electric field, of the order of a typical breakdown field $E_b \leqslant 10^7$ V cm^{-1}, is much smaller than a typical atomic field $\sim 10^9$ V cm^{-1}, characteristic of the energy barriers. A small barrier would be a subject for sporadic thermal switching, whereas a larger barrier $\sim$1–2 eV would be impossible to overcome with the applied field. One may only change the relative energy of the minima by an external field and, therefore, redistribute the molecules statistically slightly inequivalently between the two states. An intrinsic disadvantage of the conformational mechanism [2], involving motion of an ionic group, exceeding the electron mass by many orders of magnitude, is a slow switching speed ($\sim$kHz). In the case of supramolecular complexes like rotaxanes and catenanes [3] there are two entangled parts which can change mutual positions as a result of redox reactions (in solution). Thus, for rotaxane-based memory devices a slow switching speed of $\sim 10^{-2}$ s was reported.
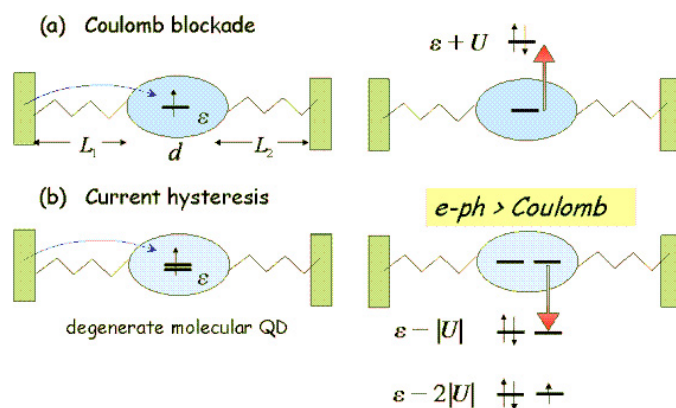
Figure 1. Schematic diagram of a molecular quantum dot with central conjugated unit separated from the electrodes by wide-band insulating molecular groups. The first electron tunnels into the dot and occupies an empty (degenerate) state there. If the interaction between the first and second incoming electron is repulsive, $U > 0$, then the dot will be in a Coulomb blockade regime (a). If the electrons on the dot effectively attract each other, $U < 0$, the system will show current hysteresis (b).

We have, therefore, explored the possibility for a fast molecular switching where switching is due to strong correlation effects on the molecule itself, the so-called molecular quantum dot (MQD). The molecular quantum dot consists of a central *conjugated* unit (containing half-occupied, and, therefore, extended π-orbitals); see figure 1. Frequently, they are formed from the p-states on carbon atoms, which are not *saturated* (i.e. they do not share electrons with other atoms forming strong σ-bonds, with typical bonding–antibonding energy difference about 1 Ryd). Since the π-orbitals are half-occupied, they form HOMO–LUMO states. The size of the HOMO–LUMO gap is then directly related to the size of the conjugated region d, figure 1, by a standard estimate $E_{\mathrm{HOMO-LUMO}} \sim \hbar^2/md^2 \sim$ 2–5 eV. It is worth noting that in the conjugated linear polymers like polyacetylene $(-\overset{|}{C}=\overset{|}{C})_n$ the spread of the π-electron would be $d = \infty$ and the expected $E_{\mathrm{HOMO-LUMO}} = 0$. However, such a one-dimensional metal is impossible: Peierls distortion (C=C bond length dimerization) sets in and opens up a gap of about $\sim$1.5 eV at the Fermi level [4–6]. In a molecular quantum dot the central conjugated part is separated from electrodes by insulating groups with saturated σ-bonds, like for example the alkane chains; see figure 1. Now, there are two main possibilities for carrier transport through the MQD. If the length of at least one of the insulating groups $L_{1(2)}$ is not very large (the conductance $G_{1(2)}$ is not much smaller than the conductance quantum $G_0 = 2e^2/h$), then the transport through the MQD will proceed by resonant tunnelling processes. If, on the other hand, both groups are such that the tunnel conductance $G_{1(2)} \ll G_0$, the charge on the dot will be quantized. Then we will have another two possibilities: (i) the interaction of the extra carriers on the dot is *repulsive*, $U > 0$, and we have a Coulomb blockade [7], or (ii) the effective interaction is *attractive*, $U < 0$, then we would obtain current *hysteresis* and switching [8] (see below). Coulomb blockade in molecular quantum dots has been demonstrated in [9]. In these works, and in [10], three-terminal active molecular devices have been fabricated and successfully tested.

Much faster switching compared to the conformational one may be caused by coupling to the vibrational degrees of freedom, if the vibron-mediated attraction between two carriers on the molecule is stronger than their direct Coulomb repulsion; see figure 1(b). The attractive

energy (i.e. a negative 'Hubbard' U) is the difference of two large interactions, the Coulomb repulsion and the phonon-mediated attraction, of the order of 1 eV each; hence $|U| \sim 0.1$ eV.

2. Failure of mean field model of polaron molecular switching

Although the correlated electron transport through mesoscopic systems with repulsive electron–electron interactions has received considerable attention in the past, and continues to be the focus of current studies, much less has been known about the role of electron–phonon (e–ph) correlations in 'molecular quantum dots' (MQDs). Some while ago we have proposed a negative-U Hubbard model of a d-fold degenerate quantum dot [11] and a polaron model of resonant tunnelling through a molecule with a degenerate level [8]. We found that the *attractive* electron correlations caused by any interaction within the molecule could lead to a molecular *switching* effect where the I–V characteristics have two branches with high and low current at the same bias voltage. This prediction has been confirmed and extended further in our theory of *correlated* transport through degenerate MQDs with a full account of both the Coulomb repulsion and realistic e–ph interactions. We have shown that while the phonon side-bands significantly modify the shape of hysteretic I–V curves in comparison with the negative-U Hubbard model, the switching remains robust. It shows up when the effective interaction of polarons is attractive and the state of the dot is multiply degenerate, $d > 2$.

Nevertheless, later on Galperin *et al* [12] argued, without discussing the discrepancies with the prior work, that even a non-degenerate electronic level ($d = 1$) coupled to a single vibrational mode produces a hysteretic I–V curve, a current switching, and a negative differential resistance. Here we explicitly calculate I–V curves of the nondegenerate ($d = 1$) and two-fold degenerate ($d = 2$) MQDs to show that these findings are artefacts of the mean-field approximation used in [12] that neglects the Fermi–Dirac statistics of electrons.

We start with a simple model that illustrates an absence of switching in a molecular quantum dot, which has a non-degenerate ($d = 1$) or doubly degenerate ($d = 2$) level [13]. First, we shall illustrate the failure of the mean-field approximation on the simplest model of a single atomic level coupled with a single one-dimensional oscillator with a displacement, x, described by a simple Hamiltonian,

$$H = \varepsilon_0 \hat{n} + f x \hat{n} - \frac{1}{2M} \frac{\partial^2}{\partial x^2} + \frac{k x^2}{2}. \tag{1}$$

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,

$$x = y - \hat{n} f / k, \tag{2}$$

to the transformed Hamiltonian without e–ph coupling,

$$\tilde{H} = \varepsilon \hat{n} - \frac{1}{2M} \frac{\partial^2}{\partial y^2} + \frac{k y^2}{2}, \tag{3}$$

$$\varepsilon = \varepsilon_0 - E_p, \tag{4}$$

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. The major error of the mean-field approximation of [12] originates in illegitimate replacement of the square of the occupation number operator
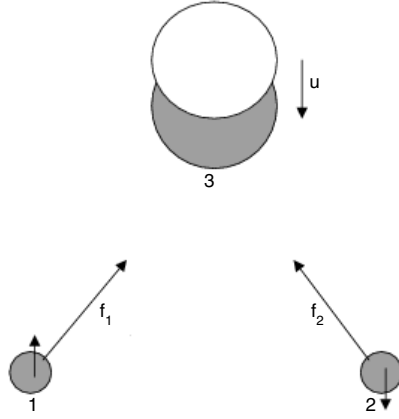
Figure 2. Two localized electrons at sites **1** and **2** shift the equilibrium position of the ion at site **3**. As a result, the two electrons *attract* each other.

$\hat{n} = c_0^\dagger c_0$ by its 'mean-field' expression $\hat{n}^2 = n_0 \hat{n}$ which contains 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 (i.e. the term $\varepsilon = \varepsilon_0 - n_0 E_\mathrm{p}$ instead of equation (4)), and a resulting non-existent nonlinearity in the rate equation.

Lattice deformation also strongly affects the interaction between electrons. When a short-range deformation potential and molecular e–ph interactions are taken into account together with the long-range Fröhlich interaction, they can overcome the Coulomb repulsion. The resulting interaction becomes attractive at a short distance comparable to a lattice constant. The origin of the attractive force between two small polarons can be readily understood from a similar Holstein-like toy model as above [14], but with two electrons on neighbouring sites **1**, **2** interacting with an ion **3** between them; see figure 2. For generality, we now assume that the ion is a three-dimensional oscillator described by a displacement vector $\mathbf{u}$, rather than by a single-component displacement x as in equation (1).

The vibration part of the Hamiltonian in the model is

$$H_\mathrm{ph} = -\frac{1}{2M}\frac{\partial^2}{\partial \mathbf{u}^2} + \frac{k\mathbf{u}^2}{2}. \tag{5}$$

Electron potential energies due to the Coulomb interaction with the ion are about

$$V_{1,2} = V_0(1 - \mathbf{u}\cdot\mathbf{e}_{1,2}/a), \tag{6}$$

where $\mathbf{e}_{1,2}$ are unit vectors connecting sites **1**, **2** and site **3**, respectively. Hence, the Hamiltonian of the model is given by

$$H = E_a(\hat{n}_1 + \hat{n}_2) + \mathbf{u}\cdot(\mathbf{f_1}\hat{n}_1 + \mathbf{f_2}\hat{n}_2) - \frac{1}{2M}\frac{\partial^2}{\partial \mathbf{u}^2} + \frac{k\mathbf{u}^2}{2}, \tag{7}$$

where $\mathbf{f_{1,2}} = Ze^2\mathbf{e}_{1,2}/a^2$ is the Coulomb force, and $\hat{n}_{1,2}$ are occupation number operators at every site. This Hamiltonian is also readily diagonalized by the same displacement transformation of the vibronic coordinate $\mathbf{u}$ as above,

$$\mathbf{u} = \mathbf{v} - \left(\mathbf{f_1}\hat{n}_1 + \mathbf{f_2}\hat{n}_2\right)/k. \tag{8}$$

The transformed Hamiltonian has no e–ph coupling,

$$\tilde{H} = (\varepsilon_0 - E_\mathrm{p})(\hat{n}_1 + \hat{n}_2) + V_\mathrm{ph}\hat{n}_1\hat{n}_2 - \frac{1}{2M}\frac{\partial^2}{\partial \mathbf{v}^2} + \frac{k\mathbf{v}^2}{2}, \tag{9}$$

and it describes two small polarons at their atomic levels 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}, which should be added to their Coulomb repulsion, V_c,

$$V_{ph} = -\mathbf{f_1} \cdot \mathbf{f_2}/k. \tag{10}$$

When V_{ph} is negative and larger by magnitude than the positive V_c, the resulting interaction becomes attractive. That is V_{ph} rather than E_p, which is responsible for the hysteretic behaviour of MQDs, as discussed below.

3. Exact solution of polaron switching

The procedure, which fully accounts for all correlations in MQDs, is as follows; see [8]. The molecular Hamiltonian includes the Coulomb repulsion, U^C, and the electron–vibron interaction as

$$H = \sum_{\mu} \varepsilon_\mu \hat{n}_\mu + \frac{1}{2} \sum_{\mu \neq \mu'} U^C_{\mu\mu'} \hat{n}_\mu \hat{n}_{\mu'} + \sum_{\mu,q} \hat{n}_\mu \omega_q (\gamma_{\mu q} d_q + \text{H.c.}) + \sum_q \omega_q (d_q^\dagger d_q + 1/2). \tag{11}$$

Here d_q annihilates phonons, ω_q is the phonon (vibron) frequency, and $\gamma_{\mu q}$ are the electron–vibron 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

$$S = -\sum_{q,\mu} \hat{n}_\mu \left(\gamma_{\mu q} d_q - \text{H.c.} \right)$$

integrating phonons out. The electron and phonon operators are transformed as

$$\tilde{c}_\mu = c_\mu X_\mu, \qquad X_\mu = \exp\left(\sum_q \gamma_{\mu q} d_q - \text{H.c.} \right) \tag{12}$$

and

$$\tilde{d}_q = d_q - \sum_\mu \hat{n}_\mu \gamma_{\mu q}^*, \tag{13}$$

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

$$\tilde{H} = \sum_i \tilde{\varepsilon}_\mu \hat{n}_\mu + \sum_q \omega_q (d_q^\dagger d_q + 1/2) + \frac{1}{2} \sum_{\mu \neq \mu'} U_{\mu\mu'} \hat{n}_\mu \hat{n}_{\mu'}, \tag{14}$$

where

$$U_{\mu\mu'} \equiv U^C_{\mu\mu'} - 2 \sum_q \gamma_{\mu q}^* \gamma_{\mu' q} \omega_q, \tag{15}$$

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 the deformation created by the polaron,

$$\tilde{\varepsilon}_\mu = \varepsilon_\mu - \sum_q |\gamma_{\mu q}|^2 \omega_q. \tag{16}$$

If we assume that the coupling to the leads is weak, so that the level width $\Gamma \ll |U|$, we can find the current from [15]

$$I(V) = e\Gamma \int_{-\infty}^{\infty} d\omega \left[f_1(\omega) - f_2(\omega) \right] \rho(\omega), \tag{17}$$

$$\rho(\omega) = -\frac{1}{\pi} \sum_\mu \text{Im}\, \hat{G}_\mu^R(\omega), \tag{18}$$

where $|\mu\rangle$ is a complete set of one-particle molecular states, and $f_{1(2)}(\omega) = \left(\exp\frac{\omega+\Delta\mp eV/2}{T} + 1\right)^{-1}$ is the Fermi function. Here $\rho(\omega)$ is the molecular density of states (DOS), $\hat{G}^R_\mu(\omega)$ is the Fourier transform of the Green's function (GF) $\hat{G}^R_\mu(t) = -\mathrm{i}\theta(t)\langle\{c_\mu(t), c^\dagger_\mu\}\rangle$, $\{\cdots,\cdots\}$ is the anticommutator, $c_\mu(t) = \mathrm{e}^{\mathrm{i}Ht}c_\mu\mathrm{e}^{-\mathrm{i}Ht}$, and $\theta(t) = 1$ for $t > 0$ and zero otherwise. We calculate $\rho(\omega)$ *exactly* for the Hamiltonian (14), which includes both the Coulomb U^C and electron–vibron interactions.

The retarded GF becomes

$$G^R_\mu(t) = -\mathrm{i}\theta(t)\left[\langle c_\mu(t)c^\dagger_\mu\rangle\langle X_\mu(t)X^\dagger_\mu\rangle + \langle c^\dagger_\mu c_\mu(t)\rangle\langle X^\dagger_\mu X_\mu(t)\rangle\right]. \tag{19}$$

The phonon correlator is simply

$$\langle X_\mu(t)X^\dagger_\mu\rangle = \exp\sum_q \frac{|\gamma_{\mu q}|^2}{\sinh\frac{\beta\omega_q}{2}}\left[\cos\left(\omega t + \mathrm{i}\frac{\beta\omega_q}{2}\right) - \cosh\frac{\beta\omega_q}{2}\right], \tag{20}$$

where the inverse temperature $\beta = 1/T$, and $\langle X^\dagger_\mu X_\mu(t)\rangle = \langle X_\mu(t)X^\dagger_\mu\rangle^*$. The remaining GFs, $\langle c_\mu(t)c^\dagger_\mu\rangle$, are found from the equations of motion *exactly*. For the simplest case of a coupling to a single mode with the characteristic frequency ω_0, $\gamma_q \equiv \gamma$ and $U_{\mu\mu'} = U$ one obtains [8]

$$\begin{aligned}
G^R_\mu(\omega) = \mathcal{Z}\sum_{r=0}^{d-1} C_r(n)\sum_{l=0}^{\infty} I_l(\xi) \\
\times\left[\mathrm{e}^{\frac{\beta\omega_0 l}{2}}\left(\frac{1-n}{\omega - rU - l\omega_0 + \mathrm{i}\delta} + \frac{n}{\omega - rU + l\omega_0 + \mathrm{i}\delta}\right) + (1-\delta_{l0})\mathrm{e}^{-\frac{\beta\omega_0 l}{2}}\right. \\
\left.\times\left(\frac{1-n}{\omega - rU + l\omega_0 + \mathrm{i}\delta} + \frac{n}{\omega - rU - l\omega_0 + \mathrm{i}\delta}\right)\right],
\end{aligned} \tag{21}$$

where

$$\mathcal{Z} = \exp\left(-\sum_{\mathbf{q}}|\gamma_q|^2\coth\frac{\beta\omega_q}{2}\right) \tag{22}$$

is the familiar *polaron narrowing* factor, the degeneracy factor

$$C_r(n) = \frac{(d-1)!}{r!(d-1-r)!}n^r(1-n)^{d-1-r}, \tag{23}$$

$\xi = |\gamma|^2/\sinh\frac{\beta\omega_0}{2}$, $I_l(\xi)$ is the modified Bessel function, and δ_{lk} is the Kronecker symbol.

Then using equation (18) the exact spectral function for a d-fold degenerate MQD (i.e. the density of molecular states, DOS) is found as

$$\begin{aligned}
\rho(\omega) = \mathcal{Z}d\sum_{r=0}^{d-1} C_r(n)\sum_{l=0}^{\infty} I_l(\xi)[\mathrm{e}^{\beta\omega_0 l/2}[(1-n)\delta(\omega - rU - l\omega_0) + n\delta(\omega - rU + l\omega_0)] \\
+ (1-\delta_{l0})\mathrm{e}^{-\beta\omega_0 l/2}[n\delta(\omega - rU - l\omega_0) + (1-n)\delta(\omega - rU + l\omega_0)]].
\end{aligned} \tag{24}$$

The important feature of the DOS, equation (24), is its nonlinear dependence on the average electronic population $n = \langle c^\dagger_\mu c_\mu\rangle$, which leads to the switching, hysteresis, and other nonlinear effects in the I–V characteristics for $d > 2$. It appears due to *correlations* between *different* electronic states via the correlation coefficients $C_r(n)$. There is no nonlinearity if the dot is nondegenerate, $d = 1$, since $C_0(n) = 1$. In this simple case the DOS, equation (24), is a *linear* function of the average population that can be found as a textbook example of an exactly solvable problems [16].

　　　In the present case of an MQD weakly coupled with leads, one can apply the Fermi–Dirac golden rule to obtain an equation for n. Equating incoming and outgoing numbers of electrons in the MQD per unit time we obtain the self-consistent equation for the level occupation n as

$$(1 - n) \int_{-\infty}^{\infty} d\omega \, \{\Gamma_1 f_1(\omega) + \Gamma_2 f_2(\omega)\} \, \rho(\omega)$$
$$= n \int_{-\infty}^{\infty} d\omega \, \{\Gamma_1 [1 - f_1(\omega)] + \Gamma_2 [1 - f_2(\omega)]\} \, \rho(\omega), \tag{25}$$

where $\Gamma_{1(2)}$ are the transition rates from the left (right) leads to the MQD, and $\rho(\omega)$ is found from equation (24). For $d = 1, 2$ the kinetic equation for n has only one physical root, and the switching is *absent*. Switching appears for $d \geqslant 3$, when the kinetic equation becomes nonlinear. Taking into account that $\int_{-\infty}^{\infty} \rho(\omega) = d$, equation (25) for the symmetric leads, $\Gamma_1 = \Gamma_2$, reduces to

$$2nd = \int d\omega \, \rho(\omega)(f_1 + f_2), \tag{26}$$

which automatically satisfies $0 \leqslant n \leqslant 1$. Explicitly, the self-consistent equation for the occupation number is

$$n = \tfrac{1}{2} \sum_{r=0}^{d-1} Z_r(n)[n a_r + (1 - n) b_r], \tag{27}$$

where

$$a_r^+ = \mathcal{Z} \sum_{l=0}^{\infty} I_l(\xi) \Big(e^{\frac{\beta \omega_0 l}{2}} [f_1(rU - l\omega_0) + f_2(rU - l\omega_0)]$$
$$+ (1 - \delta_{l0}) e^{-\frac{\beta \omega_0 l}{2}} [f_1(rU + l\omega_0) + f_2(rU + l\omega_0)] \Big), \tag{28}$$

$$b_r^+ = \mathcal{Z} \sum_{l=0}^{\infty} I_l(\xi) \Big(e^{\frac{\beta \omega_0 l}{2}} [f_1(rU + l\omega_0) + f_2(rU + l\omega_0)]$$
$$+ (1 - \delta_{l0}) e^{-\frac{\beta \omega_0 l}{2}} [f_1(rU - l\omega_0) + f_2(rU - l\omega_0)] \Big). \tag{29}$$

The current is expressed as

$$j \equiv \frac{I(V)}{I_0} = \sum_{r=0}^{d-1} Z_r(n)[n a_r^- + (1 - n) b_r^-], \tag{30}$$

where

$$a_r^- = \mathcal{Z} \sum_{l=0}^{\infty} I_l(\xi) \Big(e^{\frac{\beta \omega_0 l}{2}} [f_1(rU - l\omega_0) - f_2(rU - l\omega_0)]$$
$$+ (1 - \delta_{l0}) e^{-\frac{\beta \omega_0 l}{2}} [f_1(rU + l\omega_0) - f_2(rU + l\omega_0)] \Big), \tag{31}$$

$$b_r^- = \mathcal{Z} \sum_{l=0}^{\infty} I_l(\xi) \Big(e^{\frac{\beta \omega_0 l}{2}} [f_1(rU + l\omega_0) - f_2(rU + l\omega_0)]$$
$$\times (1 - \delta_{l0}) e^{-\frac{\beta \omega_0 l}{2}} [f_1(rU - l\omega_0) - f_2(rU - l\omega_0)] \Big), \tag{32}$$
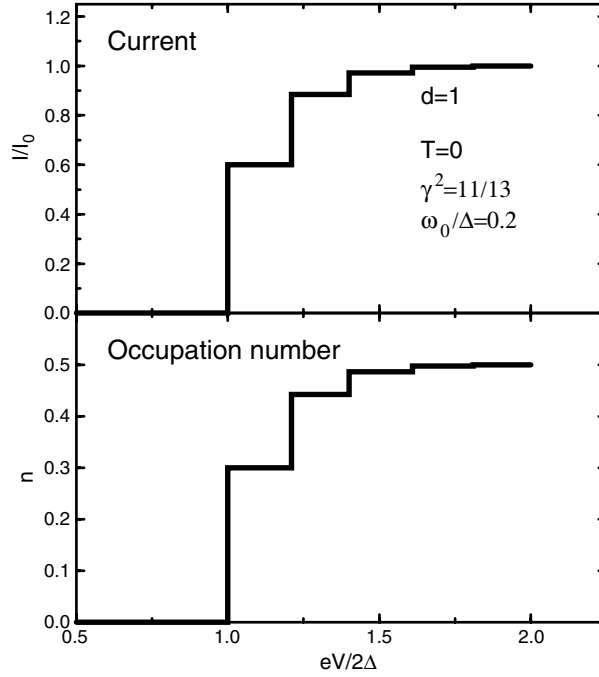
and $I_0 = ed\Gamma$.

Figure 3. Current–voltage characteristic of the nondegenerate ($d = 1$) MQD at $T = 0$, $\omega_0/\Delta = 0.2$, and $\gamma^2 = 11/13$. There is a phonon ladder in I–V, but no hysteresis.

4. Absence of switching of singly or doubly degenerate MQDs

If the transition rates from electrodes to the MQD are small, $\Gamma \ll \omega_0$, the rate equation for n and the current, $I(V)$, are readily obtained by using the exact molecular DOS, equation (24), and the Fermi–Dirac Golden rule. In particular, for a nondegenerate MQD and $T = 0$ K the result is

$$n = \frac{b_0^+}{2 + b_0^+ - a_0^+}, \tag{33}$$

and

$$j = \frac{2b_0^- + a_0^- b_0^+ - a_0^+ b_0^-}{2 + b_0^+ - a_0^+}. \tag{34}$$

The general expressions for the coefficients equations (28), (29) and equations (31), (32) at arbitrary temperatures in [8] are simplified in the low-temperature limit as

$$a_0^\pm = \mathcal{Z} \sum_{l=0}^\infty \frac{|\gamma|^{2l}}{l!} [\Theta(l\omega_0 - \Delta + eV/2) \pm \Theta(l\omega_0 - \Delta - eV/2)], \tag{35}$$

$$b_0^\pm = \mathcal{Z} \sum_{l=0}^\infty \frac{|\gamma|^{2l}}{l!} [\Theta(-l\omega_0 - \Delta + eV/2) \pm \Theta(-l\omega_0 - \Delta - eV/2)], \tag{36}$$

where Δ is the position of the MQD level with respect to the Fermi level at $V = 0$, and $\Theta(x) = 1$ if $x > 0$ and zero otherwise. The current is single valued, figure 3, with the familiar steps due to phonon side-bands.
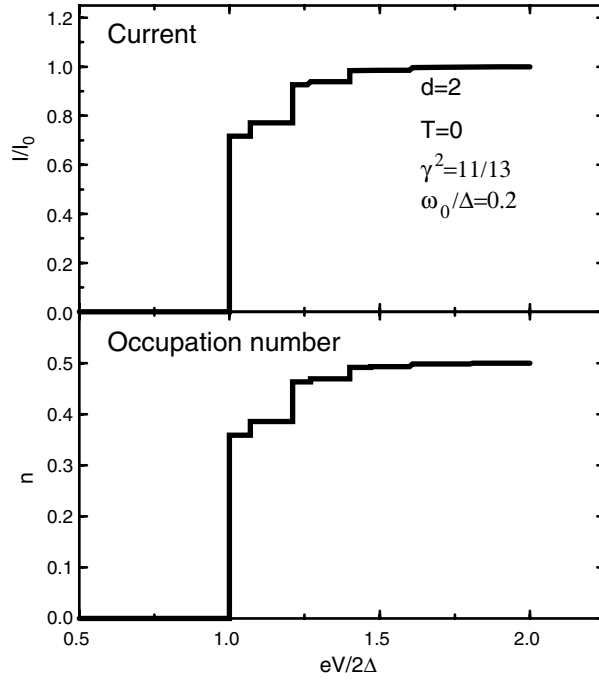
Figure 4. The current–voltage characteristic of two-fold degenerate MQDs ($d = 2$) does not show hysteretic behaviour. The parameters are the same as in figure 3. The larger number of elementary processes for conductance compared to the nondegenerate case of $d = 1$ generates more steps in the phonon ladder in comparison with figure 3.

In contrast, the mean-field approximation (MFA) leads to the opposite conclusion. Galperin *et al* [12] have replaced the occupation number operator $\hat{n}$ in the e–ph interaction by the average population n_0 (equation (2) of [12]) and found the average steady-state vibronic displacement $\langle d + d^{\dagger} \rangle$ to be proportional to n_0 (this is an explicit *neglect of all quantum fluctuations* on the dot accounted for in the exact solution). Then, replacing the displacement operator $d + d^{\dagger}$ in the bare Hamiltonian, equation (11), by its average, [12], they obtained a new molecular level, $\tilde{\varepsilon}_0 = \varepsilon_0 - 2\varepsilon_{\mathrm{reorg}}n_0$ shifted linearly with the average population of the level. This is in stark disagreement with the conventional constant polaronic level shift, equations (4), (16) ($\varepsilon_{\mathrm{reorg}}$ is $|\gamma|^2\omega_0$ in our notations). The MFA spectral function turned out to be highly nonlinear as a function of the population, e.g. for the weak-coupling with the leads $\rho(\omega) = \delta(\omega - \varepsilon_0 - 2\varepsilon_{\mathrm{reorg}}n_0)$; see equation (17) in [12]. As a result, the authors of [12] have found multiple solutions for the steady-state population, equation (15) and figure 1, and switching, figure 4 of [12], which actually do not exist, being an artefact of the approximation.

In the case of a doubly degenerate MQD, $d = 2$, there are two terms, which contribute to the sum over r, with $C_0(n) = 1 - n$ and $C_1(n) = n$. The rate equation becomes a quadratic one [8]. Nevertheless there is only one physical root for any temperature and voltage, and the current is also single-valued. The doubly degenerate level provides more elementary processes for conductance reflected in larger number of steps on phonon ladder compared to $d = 2$ case, figure 4.

Note that the mean-field solution by Galperin *et al* [12] applies at any ratio Γ/ω_0, including the limit of interest to us, $\Gamma \ll \omega_0$, where their transition between the states with $n_0 = 0$ and 1 only sharpens, but none of the results change. Therefore, the MFA predicts a current

bistability in the system where it does not exist at $d = 1$. Reference [12] plots the results for $\Gamma \geqslant \omega_0$, $\Gamma \approx 0.1$–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 at all because carriers do not have time to interact with vibrons on the molecule. Indeed, taking into account the coupling with the leads beyond the second order and the coupling between the molecular and bath phonons could hardly provide any nonlinearity because these couplings do not depend on the electron population. This rather obvious conclusion for molecules strongly coupled to the electrodes can be reached in many ways; see e.g. the derivation in [17, 18]. While [17, 18] do talk about telegraph current noise in the model, there is no hysteresis in the adiabatic regime, $\Gamma \gg \omega_0$, either. This result certainly has nothing to do with our mechanism of switching [8] that applies to molecular quantum dots ($\Gamma \ll \omega_0$) with $d > 2$. Such a regime has not been studied in [17–19], which have applied the adiabatic approximation, as being 'too challenging problem'. Nevertheless, Mitra *et al* [19] have misrepresented our formalism [8], claiming that it 'lacks of renormalization of the dot–lead coupling' (due to electron–vibron interaction), or 'treats it in an average manner'. In fact, the formalism [8] is exact, fully taking into account the polaronic renormalization, phonon side-bands and polaron–polaron correlations in the exact molecular DOS, equation (24).

In fact, most of the molecules are very resistive, so the actual molecular quantum dots are in the regime we study; see [20]. For example, the resistance of fully conjugated three-phenyl-ring Tour–Reed molecules chemically bonded to metallic Au electrodes [2] exceeds 1 GΩ. Therefore, most of the molecules of interest to us are in the regime that we discussed, not that of [17, 18].

5. Nonlinear rate equation and switching

The switching appears only for $d > 2$. For example, for $d = 4$ the rate equation (27) is of the fourth power in n,

$$2n = (1 - n)^3[na_0^+ + (1 - n)b_0^+] + 3n(1 - n)^2[na_1^+ + (1 - n)b_1^+]$$
$$+ 3n^2(1 - n)[na_2^+ + (1 - n)b_2^+] + n^3[na_3^+ + (1 - n)b_3^+]. \tag{37}$$

In contrast to that for the non-degenerate or doubly degenerate MQD, the rate equation for $d = 4$ has two stable physical roots in a certain voltage range and the current–voltage characteristics show a hysteretic behaviour. Our numerical results [8] for $\omega_0 = 0.2$ (in units of Δ, as are all the energies in the problem), $U^C = 0$, and for the coupling constant, $\gamma^2 = 11/13$ are shown in figure 5. This case formally corresponds to a negative Hubbard $U = -2\gamma^2\omega_0 \approx -0.4$ (we selected those values of γ^2 to avoid accidental commensurability of the correlated levels separated by U and the phonon side-bands). The threshold for the onset of bistability appears at a voltage bias $eV/2\Delta = 0.86$ for $\gamma^2 = 11/13$ and $\omega_0 = 0.2$. The steps on the I–V curve, figure 5, are generated by the phonon side-bands originating from correlated levels in the dot with the energies $\Delta, \Delta + U, \ldots, \Delta + (d - 1)U$. Since ω_0 is not generally commensurate with U, we obtain a quite irregular picture of the steps in I–V curves. The bistability region reduces with temperature.

Note that switching required a degenerate MQD ($d > 2$) and weak coupling to the electrodes, $\Gamma \ll \omega_0$. In contrast to that for a 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 behaviour due to *correlations* between different electronic states of the MQD.
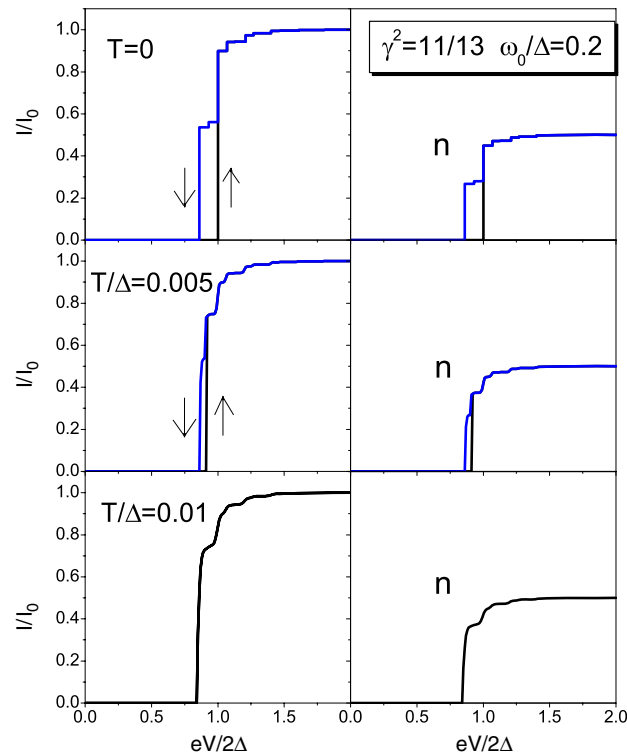
10

Figure 5. The bistable I–V curves for tunnelling through a molecular quantum dot with the electron–vibron coupling constant $\gamma^2 = 11/13$ and $\omega_0/\Delta = 0.2$. 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 phonon side-bands.

6. Summary

We have calculated the I–V characteristics of non-degenerate ($d = 1$) and two-fold degenerate ($d = 2$) molecular quantum dots showing no hysteretic behaviour of current, and concluded that the mean field approximation [12] leads to a non-existent switching in a model that was solved exactly in [8]. In contrast to those for non-degenerate and two-fold degenerate dots, the rate equation for a multi-degenerate dot, $d > 2$, weakly coupled to the leads, has multiple physical roots in a certain voltage range showing hysteretic behaviour due to *correlations* between different electronic states of the MQD [8]. Pair tunnelling is also allowed in our model, though it should only result in tiny peaks on the background of the main current contributed by single-polaron tunnelling. Our conclusions are important for searching for current-controlled polaronic molecular-size switches. Incidentally, C_{60} molecules have a degeneracy $d = 6$ of the lowest unoccupied level, which makes them one of the most promising candidate systems, if the weak coupling with leads is secured.

Acknowledgments

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