

# Dynamical symmetry breaking in transport through molecules

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We analyze the interplay between vibrational and electronic degrees of freedom in charge transport across a molecular single-electron transistor. We focus on the wide class of molecules which possess quasi-degenerate vibrational eigenstates, while no degeneracy occurs for their anionic configuration. We show that the combined effect of a thermal environment and coupling to leads, involving tunneling events charging and discharging the molecule, leads to a dynamical symmetry breaking where quasi-degenerate eigenstates acquire different occupations. This imbalance gives rise to a characteristic asymmetry of the current versus an applied gate voltage.

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Molecular electronics is a promising answer to the demand of miniaturization, reproducibility and flexibility of electronic devices. Starting with the pioneering work of Aviram and Ratner [1], and especially with the first single-molecule measurement by Reed *et al.* [2], molecular electronics has become an active research field both experimentally and theoretically [3]. Still, fundamental questions on the peculiar nature of single-molecule junctions and their novel functionalities remain open. Among others they involve the unique electromechanical properties of molecular junctions which render these distinctly different from, e.g., semiconductor quantum dots.

Recent research on this particular topic has revealed a number of interesting effects such as shuttling instabilities [4, 5, 6], Franck-Condon blockade [7, 8] and, more generally, conformational [9, 10, 11] or vibronic [12, 13, 14, 15] signatures in the electron transport characteristics. In this respect, however, the role of coherences in transport due to quasi-degenerate levels has not been highlighted.

In this Letter we consider charge transport through a molecular junction weakly contacted to two leads and capacitively coupled to a gate electrode, with focus on the interplay between the vibrational and electronic degrees of freedom. In particular, we address molecules characterized by eigenstate doublets in the neutral configuration and non-degenerate anionic states, or vice versa, as sketched in Fig. 1. It represents, e.g., the adiabatic potential energy surfaces of biphenyl as a function of the dihedral angle between the phenyl rings [15], to mention just one prominent system, which has also been studied in recent state-of-the-art transport experiments [16].

We show that dynamical symmetry breaking (DSB), where quasi-degenerate eigenstates are differently occupied, may occur and affect transport, while in the absence of couplings to the leads these states are equally populated at finite temperature, and hence the system does not prefer a definite parity. Temperature, on the other hand, should not exceed a critical value above which DSB is lost due to dephasing, caused by a thermal bath. Solving the master equation for the reduced density matrix

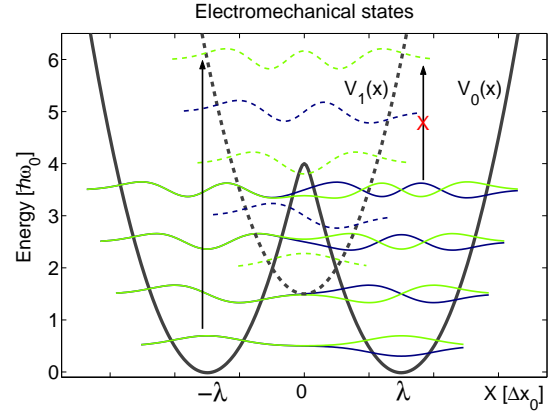


FIG. 1: (color online) Electromechanical states of the molecule. Thick black lines indicate the adiabatic potentials  $V_0$  and  $V_1$  for the neutral (solid) and singly-charged (dashed) molecule. Thin green (blue) lines denote the even (odd) vibrational eigenfunctions (for the two potentials) displayed with a vertical shift equal to their corresponding energy eigenvalue. Energies are given in units of  $\hbar\omega_0$  and lengths in terms of the zero-point motion  $\Delta x_0 = \sqrt{\hbar/m\omega_0}$ . The arrows mark examples of allowed and forbidden transitions.

including coherences, we demonstrate the possibility of detecting DSB in the current through the molecule under different bias and gating conditions.

To address transport in the single-electron regime, where only the electronic ground states  $|0\rangle$  of the neutral and  $|1\rangle$  of the anionic configuration are involved, we describe the molecule through the Hamiltonian

$$H_S = \frac{p^2}{2m} + |0\rangle\langle 0| V_0(x) + |1\rangle\langle 1| V_1(x) \quad (1)$$

in terms of the corresponding adiabatic potential energy surfaces  $V_0(x)$ ,  $V_1(x)$  associated with the softest mode coordinate  $x$ . The adiabatic potentials and the related vibrational eigenfunctions are sketched in Fig. 1. The neutral molecule is characterized by the double well potential  $V_0$  with minima located at  $\pm\lambda$ . For large enough barriers, i.e. exponentially small tunnel splitting, the low-lying eigenstates are organized in pairs of (quasi-)degenerate

wave functions. The anion is modelled by a single harmonic potential  $V_1$  with frequency  $\omega_1$ , centered at the origin of the coordinate system (dashed line in Fig. 1).

We express the system coupled to leads and in contact with a thermal bath through the Hamiltonian

$$H = H_S + H_L + H_R + H_B + V_T + V_{SB}. \quad (2)$$

The leads are described as reservoirs of non-interacting quasi-particles in terms of  $H_L + H_R = \sum_{k;\alpha=L,R} (\epsilon_{k\alpha} - \mu_\alpha) c_{k\alpha}^\dagger c_{k\alpha}$ , where  $\mu_{L,R} = \pm \Delta V/2$  accounts for the effects of a symmetrically applied bias voltage and  $c_{k\alpha}^\dagger$  ( $c_{k\alpha}$ ) creates (destroys) an electron in the lead  $\alpha$ . Transfer of electrons is mediated by the tunneling Hamiltonian  $V_T = v \sum_{k;\alpha=L,R} (|0\rangle\langle 1| c_{k\alpha}^\dagger + |1\rangle\langle 0| c_{k\alpha})$ . Finally,  $H_B$  describes a thermal bath of harmonic oscillators coupled linearly to the displacement coordinate  $x$  via the system-bath Hamiltonian  $V_{SB} = \hbar \tilde{g} x \sum_q (d_q^\dagger + d_q)$ , where  $d_q^\dagger$  and  $d_q$  are bosonic creation and destruction operators associated with the oscillator with energy  $\hbar \omega_q$ .

Since we are interested only in the low-energy states, we approximate  $V_0(x)$  by two harmonic wells centered at  $\pm \lambda$  and with frequency  $\omega_0$ . Formally, this is achieved by projecting the Hamiltonian  $H$  on a smaller Hilbert space in which we can define the identity operator as

$$\mathbb{1} = |1\rangle\langle 1| + |0\rangle\langle 0| (\mathcal{P}_+ + \mathcal{P}_-). \quad (3)$$

Here  $\mathcal{P}_\pm = \sum_{n=0}^N |n, \pm\rangle\langle n, \pm|$  are projection operators on the states right/left to the barrier. They are defined in terms of the shifted harmonic oscillator eigenvectors  $|n, \pm\rangle \equiv \exp(\mp i \lambda p / \hbar) |n\rangle$ . The condition of negligible overlap between these eigenfunctions reads  $\mathcal{P}_+ \mathcal{P}_- = \mathcal{P}_- \mathcal{P}_+ = 0$ . In the Hilbert space defined by identity (3) we obtain as effective system Hamiltonian

$$H_S^{\text{eff}} = |0\rangle\langle 0| \sum_{\tau=\pm} [\mathcal{P}_\tau (\frac{1}{2} + d_\tau^\dagger d_\tau) \mathcal{P}_\tau] \hbar \omega_0 + |1\rangle\langle 1| [(\frac{1}{2} + d^\dagger d) \hbar \omega_1 + eV_g - \epsilon_a], \quad (4)$$

where  $d_\pm^\dagger$  and  $d^\dagger$  are operators for the neutral and charged configurations,  $V_g$  is the gate voltage, and  $\epsilon_a$  the electron affinity. Along similar lines we find for the effective tunneling and system-bath Hamiltonians

$$V_T^{\text{eff}} = v \sum_{k;\alpha=L,R} \left[ |0\rangle\langle 1| c_{k\alpha}^\dagger (\mathcal{P}_+ + \mathcal{P}_-) + h.c. \right], \\ V_{SB}^{\text{eff}} = \hbar g \sum_q (d_q + d_q^\dagger) \left\{ \delta |1\rangle\langle 1| (d + d^\dagger) + |0\rangle\langle 0| \sum_{\tau=\pm} [\mathcal{P}_\tau (d_\tau + d_\tau^\dagger + \tau 2\lambda) \mathcal{P}_\tau] \right\}, \quad (5)$$

with  $g = \tilde{g} \sqrt{2\hbar/(m\omega_0)}$  and  $\delta = \sqrt{\omega_1/\omega_0}$ . For transport, we seek stationary solutions of the Liouville equation

$$\dot{\sigma}(t) = -\frac{i}{\hbar} \text{Tr}_{\text{leads+bath}} \{ [H^{\text{eff}}, W(t)] \} \quad (6)$$

for the reduced density matrix (RDM)  $\sigma(t) := \text{Tr}_{\text{leads+bath}} \{ W(t) \}$ , where  $W(t)$  is the total density matrix associated with the effective Hamiltonian corresponding to that in Eq. (2). Treating the interactions  $V_T^{\text{eff}}$  and  $V_{SB}^{\text{eff}}$  as perturbations, we rewrite Eq. (6) in terms of three contributions:  $\dot{\sigma}(t) = \mathcal{L}\sigma(t) = (\mathcal{L}_{\text{coh}} + \mathcal{L}_{\text{tun}} + \mathcal{L}_{\text{damp}}) \sigma(t)$ . The coherent part of the differential equation has the usual form  $\mathcal{L}_{\text{coh}} \sigma(t) = -(i/\hbar) [H_S^{\text{eff}}, \sigma(t)]$  describing the evolution of the isolated molecule. The coupling to the leads/bath gives rise to the driving/damping terms  $\mathcal{L}_{\text{tun}} \sigma(t)$  and  $\mathcal{L}_{\text{damp}} \sigma(t)$ .

We now perform the following standard approximations: we treat the leads as thermal reservoirs at equilibrium temperature  $T$ , consider the coupling to the leads up to second order in  $V_T^{\text{eff}}$  and, being interested in the stationary solution, neglect non-Markovian contributions to the equation of motion. Furthermore, neglecting off-diagonal elements of the RDM between anionic and neutral configurations, as well as between non-degenerate eigenstates, and disregarding non-energy conserving contributions, the anionic and neutral state components read

$$(\mathcal{L}_{\text{tun}} \sigma)_{11} = \sum_{\alpha=L,R;\tau=\pm} \left[ 2(\Gamma_{\text{in}}^\alpha \sigma_{00} \mathcal{P}_\tau + \mathcal{P}_\tau \sigma_{00} \Gamma_{\text{in}}^{\alpha\dagger}) - (\mathcal{P}_\tau \Gamma_{\text{out}}^\alpha \sigma_{11} + \sigma_{11} \Gamma_{\text{out}}^{\alpha\dagger} \mathcal{P}_\tau) \right], \\ (\mathcal{L}_{\text{tun}} \sigma)_{00}^{\tau\tau'} = \sum_{\alpha=L,R} \mathcal{P}_\tau \left[ \Gamma_{\text{out}}^\alpha \sigma_{11} + \sigma_{11} \Gamma_{\text{out}}^{\alpha\dagger} - 2(\Gamma_{\text{in}}^\alpha \sigma_{00} + \sigma_{00} \Gamma_{\text{in}}^{\alpha\dagger}) \right] \mathcal{P}_{\tau'}, \quad (7)$$

with rate matrices for tunneling into/out of the molecule

$$\Gamma_{\text{in}}^\alpha = \frac{\Gamma_\alpha}{2} \sum_{m,n,\tau=\pm} |m\rangle\langle n, \tau| f(eV_g + \epsilon_{nm}) \langle m|n, \tau\rangle, \\ \Gamma_{\text{out}}^\alpha = \frac{\Gamma_\alpha}{2} \sum_{m,n,\tau=\pm} |n, \tau\rangle\langle m| - \Gamma_{\text{in}}^{\alpha\dagger}. \quad (8)$$

Here  $f(\epsilon)$  is the Fermi function, and  $\Gamma_\alpha = (2\pi/\hbar) D_\alpha |v|^2$  is the bare electronic rate, with  $D_\alpha$  the density of states in lead  $\alpha$  at the Fermi energy. For convenience we assumed equal frequencies  $\omega_0 = \omega_1$  of the neutral and anionic potential, and hence  $\epsilon_{nm} = \hbar \omega_0 (m - n)$ ; calculations for  $\omega_0 \neq \omega_1$  yielded no qualitative changes. Furthermore we shifted the electrochemical potential  $eV_g - \epsilon_a \rightarrow eV_g$  in the argument of the Fermi function. The overlap matrix elements  $\langle m|n, \tau\rangle$  of the vibrational states of the neutral and charged configurations, known as Franck-Condon factors, determine, together with energy resonance conditions, the transition rates (8) and thus the transport characteristics of the junction. While the Franck-Condon factors are fixed by the adiabatic potentials, the bias and gate voltages influence the resonance conditions.

To describe relaxation and dephasing, we consider the case of an Ohmic bath with spectral density  $J(\omega) =$

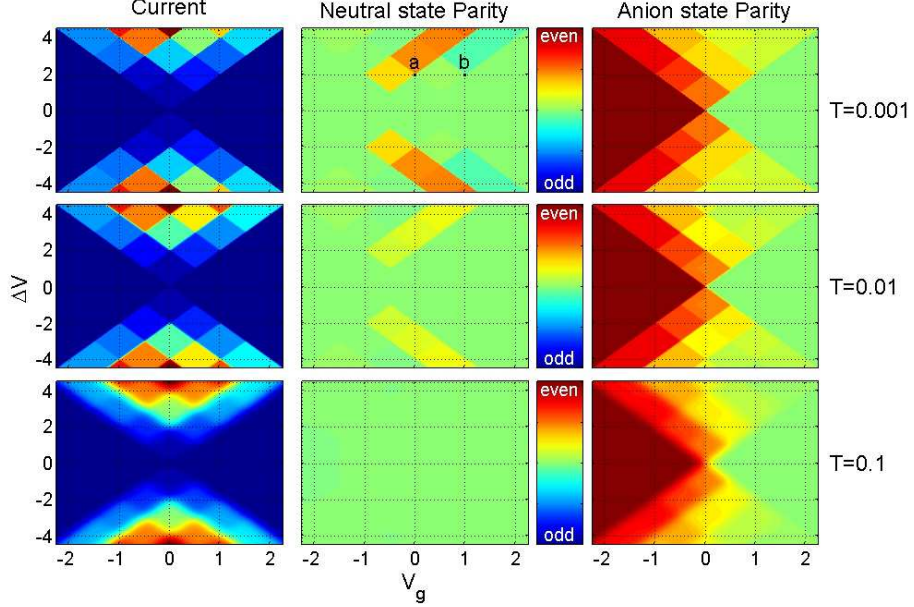


FIG. 2: (color online) Onset of the dynamical symmetry breaking with decreasing temperature (in units of  $\hbar\omega_0/k_B$ ) from bottom to top. The columns show the stationary current and the parity of the neutral and ionic state as a function of the gate voltage  $V_g$  and the bias  $\Delta V$  across the molecular junction, both in units of  $\hbar\omega_0/e$ . The dots in the central column indicate the even (a) and odd (b) parity transitions described in Fig. 3.

$m\gamma\omega$ , where  $\gamma$  is the damping coefficient [17]. Along the same lines as for the tunneling term we find

$$\begin{aligned}
 (\mathcal{L}_{\text{damp}} \sigma)_{11} &= -\frac{i\gamma}{2\hbar}[x, \{p, \sigma_{11}\}] - \\
 &\quad -\frac{\gamma m\omega_0}{\hbar}(\bar{N} + \frac{1}{2})[x, [x, \sigma_{11}]], \\
 (\mathcal{L}_{\text{damp}} \sigma)_{00}^{\tau\tau'} &= -\frac{i\gamma}{2\hbar}\mathcal{P}_\tau[x, \{p, \sigma_{00}^{\tau\tau'}\}]\mathcal{P}_{\tau'} - \\
 &\quad -\frac{\gamma m\omega_0}{\hbar}(\bar{N} + \frac{1}{2})\mathcal{P}_\tau[x, [x, \sigma_{00}^{\tau\tau'}]]\mathcal{P}_{\tau'} - \\
 &\quad -8\gamma\frac{k_B T}{\hbar\omega_0}\lambda^2(\mathcal{P}_+ \sigma_{00}^{\tau\tau'} \mathcal{P}_- + \mathcal{P}_- \sigma_{00}^{\tau\tau'} \mathcal{P}_+),
 \end{aligned} \tag{9}$$

where  $\bar{N}(\omega)$  is the Bose distribution function. Note the occurrence of a term responsible for pure inter-well dephasing and proportional to  $T$  and  $\lambda^2$  in the expression for  $(\mathcal{L}_{\text{damp}} \sigma)_{00}$ . Since we are interested in the long-time properties, we look for solutions of the stationary problem  $\mathcal{L}\sigma^{\text{stat}} = 0$ . Given the stationary RDM  $\sigma^{\text{stat}}$  we calculate the stationary current as the trace over the system degrees of freedom of the left/right current operators,  $I^{\text{stat}} = \text{Tr}_{\text{mech}}[\sigma^{\text{stat}} \hat{I}_L] = \text{Tr}_{\text{mech}}[\sigma^{\text{stat}} \hat{I}_R]$ , with, e.g.,

$$\begin{aligned}
 \hat{I}_L &= \sum_{\tau=\pm} \left[ 2|0\rangle\langle 0|(\mathcal{P}_\tau \Gamma_{\text{in}}^L + \Gamma_{\text{in}}^{L\dagger} \mathcal{P}_\tau) - \right. \\
 &\quad \left. - |1\rangle\langle 1|(\mathcal{P}_\tau \Gamma_{\text{out}}^L + \Gamma_{\text{out}}^{L\dagger} \mathcal{P}_\tau) \right].
 \end{aligned} \tag{10}$$

We stress that not only populations but also coherences of the RDM in the  $(\pm)$  basis contribute to  $I^{\text{stat}}$ .

In the first column of Fig. 2 we present the results of our calculation of the gate- and bias-dependent current for increasing temperature (from bottom to top). Besides the evidence of a Franck-Condon blockade [7, 8] (where due to an exponential suppression of the Franck-Condon factors  $\langle m|n, \tau \rangle$  transport is blocked and the Coulomb diamonds no longer close), Fig. 2 shows an increasing asymmetry in the gate voltage  $V_g$  with decreasing temperature. To understand the origin of this asymmetry, we depict in the second and third column of Fig. 2 the parities of the neutral and anionic state defined as

$$\begin{aligned}
 P_0 &= \sum_{n=0}^N \left[ \langle 0, e, n | \sigma | 0, e, n \rangle - \langle 0, o, n | \sigma | 0, o, n \rangle \right], \\
 P_1 &= \sum_{n=0}^{\infty} \left[ \langle 1, 2n | \sigma | 1, 2n \rangle - \langle 1, 2n+1 | \sigma | 1, 2n+1 \rangle \right],
 \end{aligned} \tag{11}$$

where the even/odd states of the neutral molecule are

$$|0, e/o, n\rangle = \frac{1}{\sqrt{2}}(|n, +\rangle \pm (-1)^n |n, -\rangle). \tag{12}$$

In the parameter region where the current becomes asymmetric with respect to  $V_g$ , degenerate states are *differently* populated, i.e., a dynamical symmetry breaking (DSB) in the occupation of the even/odd states occurs. In the regions of defined parity (warm colors for even, cold for odd) the system exhibits spatial coherences in the  $(\pm)$  basis, cf. Eqs. (8),(9). In contrast, we find that in

the even/odd basis coherences are decoupled from populations and vanish for the stationary density matrix. The onset of this even/odd parity regions in the gate-bias voltage plane can be understood in terms of transition rates between the different vibrational states of the molecule (see Fig. 3). At zero bias, energy conservation prevents any transition *from* the neutral (even or odd) or anionic ground states to occur. These states are thus blocking states. In particular for positive gate voltages the molecule is neutral and dephasing ensures equilibration of the even and odd populations of the degenerate ground state ( $P_0 = 0$ ). At negative gate voltages the molecule is charged and dissipation ensures relaxation predominantly to the anionic ground state ( $P_1 \approx 1$ ).

The situation changes for combinations of bias and gate voltages that allow current to flow: the electromechanical system is maintained out of equilibrium by the applied voltage. Now the parity of the anionic state fluctuates due to population of the higher excited states, and the distribution of the populations no longer corresponds to the thermal distribution in equilibrium with the bath.

The sign of the neutral-state parity depends on the particular rate configuration. Though a quantitative prediction relies on the solution for  $\sigma^{\text{stat}}$ , it is possible to understand the sign of the neutral state parity with simple arguments. In Fig. 3 a representation of the electromechanical rates for two specific cases is reported. Despite the complexity of the scheme, only few lines are crucial: these are the two red dashed arrows representing the rates which lift the blocking character of the neutral ground states. In the case (a) the neutral odd ground state can be depopulated resulting in an even parity of the stationary state. In case (b) the neutral even ground state is involved leading to an odd parity of the stationary state. These unblocking rates represent the bottle-neck in the DSB and are competing with the dephasing generated by the heat bath (wavy line joining the even and odd sector of the neutral state). The intensity of the unblocking rates depends on the Franck-Condon factors of the vibrational wave functions involved. A comparison with the dephasing rate allows to estimate the transition temperature  $T_{\text{tr}}$  as  $k_B T_{\text{tr}} = \hbar\omega_0\Gamma_{\text{ub}}/(4\lambda^2\gamma)$ , where  $\Gamma_{\text{ub}}$  is the unblocking rate (i.e. the *depopulation* rate of the relevant neutral ground state). The even transition (a) involves a larger  $\Gamma_{\text{ub}}$ : it is more robust and occurs at higher  $T$  (compare first and second panel in the central column of Fig. 2).

To summarize, we analyzed the dynamics of a molecular junction in the single-electron transport regime. The molecule possesses quasi-degenerate vibrational eigenstates in the neutral configuration and no degeneracy in the anionic case. Tunneling processes charging and discharging the molecule preserve the parity of the wavefunctions. As a consequence, unequal occupation of degenerate molecular neutral states occurs. An explanation of this effect in terms of unblocking rates is given. We

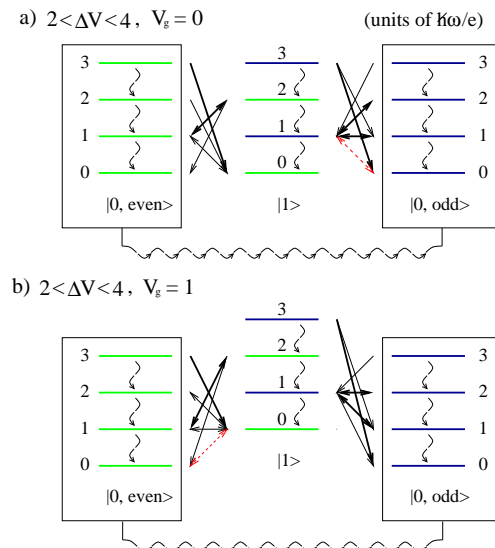


FIG. 3: (color online) Rates scheme at the even (a) and odd (b) transition points (see Fig. 2). The horizontal lines mark the electromechanical states of the neutral and anionic configuration with green (blue) color representing the even (odd) parity. Straight arrows represent transitions due to the coupling to the leads: the rate is qualitatively expressed by the thickness of the line. Red dashed arrows show transitions lifting the blocking character of the ground states and are crucial for the understanding of the symmetry breaking transition. Wavy arrows represent the effect of the phononic bath.

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