Voltage induced conformational changes and current control in charge transfer through molecules

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Transport through molecular contacts with a sluggish intramolecular vibrational mode strongly coupled to excess charges is studied far from equilibrium. A Born-Oppenheimer approximation in steady state reveals voltage dependent energy surfaces which cause abrupt conformational changes of the molecular backbone. These are directly related to transitions between current plateaus which are relatively robust against thermal fluctuations. In a regime accessible in experiments this allows to operate a molecular junction as a current switch or as a molecular machine in form of a valve controlled by time dependent bias and gate voltages.

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I. INTRODUCTION

In recent years impressive progress has been achieved in fabricating, functionalizing and controlling molecular junctions for charge transfer \[1,2\] and as nano-machines \[4\]. This includes advanced techniques to link molecular structures to metallic electrodes and gates, to design molecular rectifiers or to induce rotary molecular motion. Particularly fascinating is the interplay of charge transfer and conformational dynamics.

Theoretically, density functional calculations (DFT) in combination with non-equilibrium Greens function techniques as well as model based descriptions in terms of master equations have elucidated fundamental aspects of single molecule contacts. A particular challenge is to capture electromechanical properties of these devices where injected charges drive internal molecular degrees of freedom such as vibrational or rotational modes far from equilibrium which in turn back-act on the transport channels. A well-established procedure is to determine energy surfaces for these modes from the conformation of the molecular backbone. These are directly related to transitions between current plateaus which in steady state reveals voltage dependent energy surfaces. Notably, stable molecular conformations can be controlled by bias and gate voltage which are directly related to a robust quantization of current transfer. This opens the possibility for realizations of molecular machines \[11,14\] as e.g. switches and valves.

For charge transfer through molecular contacts BOs in steady state have been discussed previously in several contexts. In \[15\] a type of self-consistent treatment for a contact with a single electronic level coupled to single harmonic intramolecular degree of freedom revealed the appearance of hysteresis and negative differential conductance. Greens functions methods have been used in conjunction with a BO to extract effective potential surfaces for nearly harmonic vibronic modes in \[16\]. However, both treatments exploit that the driven dynamics of an harmonic oscillator is analytically known. Instead, in the sequel a methodology for substantial anharmonicity of intramolecular modes and/or Coulomb interaction between excess charges on several molecular electronic levels is studied.

II. MODEL

The biphenyl molecule (Fig.1) consists of two benzene rings which can be twisted by an angle \(\phi\). Each of the rings may carry one excess electron and the tunnel coupling between left ring (L) and right ring (R) depends on...
this torsional angle as the dominant intramolecular mode with respect to transport properties. The total molecule Hamiltonian then reads \[ H_0 = -\frac{1}{2I} \frac{\partial^2}{\partial \phi^2} + V(\phi) + T(\phi)(d_L^\dagger d_R + d_R^\dagger d_L) + E_c(n_L + n_R) + U_0 n_L n_R + \frac{V_S}{2}(n_L - n_R) \] where the first line describes the dynamics of the torsional angle and tunneling between the rings, i.e., \[ V(\phi) = V_0 \cos^2(2\phi), \quad T(\phi) = T_0 \cos \phi, \] and the second line captures the charging energy \( E_c \) for individual excess charges on the molecule and the Coulomb repulsion \( U_0 \) for double occupancy, respectively. Following microscopic calculations \[11] we also incorporate a Stark energy shift \( V_S \) of the molecular sites due to an external electric field. It turns out that this Stark shift has substantial impact on the molecular conformations and transport properties. Further we have the local electron densities \( n_\alpha = d_\alpha^\dagger d_\alpha, \alpha = L, R \), where operators \( d_L^\dagger (d_R^\dagger) \) create excess electrons on the left (right) subunit. Crucial for the charge transfer across this structure is the separation of energy scales with a small height \( V_S = 0.5 eV \) for the rotational barrier of the neutral molecule, a large hopping element \( T_0 = 0.5 eV \), and a large inertial moment \( I = 20000 eV^{-1} \) \[17,18]. As it is typical for conjugated organic molecules, orbitals are thus delocalized throughout the molecular backbone. Accordingly, it is appropriate to introduce the molecule’s charge energy eigenstates as linear combinations of the left and right localized states: \( d_\alpha^\dagger = \cos \theta d_L^\dagger + \sin \theta d_R^\dagger \) and \( d_\alpha = -\sin \theta d_L^\dagger + \cos \theta d_R^\dagger \). The mixing angle \( \theta \in [-\pi/2, \pi/2] \) depends on the torsional degree of freedom \[ \theta(\phi) = \arctan \left( \frac{T(\phi)}{\lambda(\phi) + \frac{V_S}{2}} \right), \] with the eigenenergies of the one-electron Hamiltonian \( \lambda(\phi) = \sqrt{\pi(\phi)^2 + V_S^2/4} \). As one can see, for vanishing Stark shift, we have \( \theta = \pm \pi/4 \) (the sign of \( \theta \) jumps at \( \phi = \pi \) where the hopping matrix element crosses zero) and the energy eigenstates become the symmetric and antisymmetric combinations of localized states, which couple symmetrically (except for a sign) to the right and left leads. For large Stark shift we instead get \( \theta = 0 \) and the eigenstates become the localized ones that only couple to a single lead each.

In eigenstate representation the molecule Hamiltonian is

\[
H_0 = -\frac{1}{2I} \frac{\partial^2}{\partial \phi^2} + E_0(\phi) |0\rangle \langle 0| + E_+(\phi) |+\rangle \langle +| + E_-(\phi) |--\rangle \langle -| + E_D(\phi) |D\rangle \langle D|.
\]

Here, \( |0\rangle \) denotes the neutral molecule, \( |\pm\rangle \) the two one-particle eigenstates, and \( |D\rangle \) is the doubly occupied state. The torsional dependent energies of these states are given by: \( E_0(\phi) = V(\phi), E_\pm(\phi) = V(\phi) \pm \lambda(\phi) + E_c, \) and \( E_D(\phi) = V(\phi) + 2E_c + U_0 \).

The molecular junction is now modeled by the Hamiltonian \( H = H_0 + H_I + H_L + H_R \) with \( H_\alpha = \sum_k (\epsilon_{k\alpha} - \mu_{\alpha}) c_{k\alpha}^\dagger c_{k\alpha}, \alpha = \{L, R\} \) describing left (L) and right (R) lead, respectively, as reservoirs of non-interacting quasi-particles with creation (annihilation) operators \( c_{k\alpha}^\dagger (c_{k\alpha}) \). The chemical potentials \( \mu_{L/R} = V_S \pm V_b/2 \) are fixed by the bias voltage \( V_b \) and the gate voltage \( V_g \). The Stark-shift varies with the bias according to \( V_S = \kappa V_b \) with a parameter \( \kappa < 1 \). Coupling of the left (right) lead to the left (right) ring is described by

\[
H_I = \gamma_L d_L^\dagger \psi_L + \gamma_R d_R^\dagger \psi_R + h.c.
\]

\[
= \gamma_L (\cos \theta d_L^\dagger - \sin \theta d_R^\dagger) \psi_L + \gamma_R (\sin \theta d_L^\dagger + \cos \theta d_R^\dagger) \psi_R + h.c.
\]

with \( \psi_\alpha = \sum_k c_{\alpha,k} \). Charge transfer into/out of the molecule is determined by rates \( \Gamma_\alpha = D_\alpha \gamma_\alpha^2 / 2 \hbar \) where electrodes are taken in the wide band limit with a density of states \( D_\alpha \). Apparently, the coupling of the molecular states depends on the mixing angle \( \theta \) which itself depends sensitively on the Stark-field according to \[4\]. For instance, the coupling of the \( |+\rangle \) state to the left (right) lead is given by \( 2\Gamma_L \cos^2(\theta) \approx 2\Gamma_L \sin^2(\theta) \). As shown in Fig. \[2\] for \( \Gamma_L = \Gamma_R = \Gamma \) these couplings are identical only for vanishing electric field, i.e. \( V_S = 0 \) and \( \theta(\phi) = \pi/4 \). For finite values of \( V_S \) this symmetry is immediately broken, e.g. around \( \phi = \pi/2 - \delta \) with small deviations \( \delta \), one has \( \theta(\pi/2 - \delta) \approx (T_0/V_S)\delta \) so that \( 2\Gamma \cos(\theta) \approx 2\Gamma \Rightarrow 2\Gamma \sin^2(\theta) \approx 2\Gamma(T_0\delta/V_S)^2 \).

In the remainder we are particularly interested in the steady state current \( \langle I_\alpha \rangle = e\text{Tr}\{W_0 N_\alpha(t \rightarrow \infty)\} = e\text{Tr}\{N_\alpha W(t \rightarrow \infty)\} \) where \( N_\alpha = \sum_k c_{\alpha,k}^\dagger c_{\alpha,k} \) is the number operator in lead \( \alpha \) and \( W(t) \) is the density operator of the junction. With electrodes residing in thermal equilibrium the reduced density operator \( \rho(t) = \text{Tr}_{\text{Leads}}\{W(t)\} \) provides the relevant transport information. A standard procedure is to derive from the Liouville-von Neumann equation \( \dot{\rho}(t) = (-i/\hbar)\text{Tr}_{\text{Leads}}\{H, W(t)\} \) a master equation by treating \( H_I \) as a perturbation (weak coupling). This way, upon employing the usual Born-Markov approximation one arrives at \( \dot{\rho}(t) = (-i/\hbar)[H_0, \rho(t)] + \mathcal{R}\rho(t) \).
FIG. 2: Frank-Condon-factor $\cos^2 \theta(\phi)$ as a function of $\phi$ and $V_s$. As described in the text, a finite electric field breaks the symmetry of the one-electron eigenstates ($\theta(\phi) = \pi/4$) and induces a preference for angles $\phi \approx \pi/2$ in the coupled system.

with the Redfield tensor\cite{19,21}

$$\dot{R}(t) = -\frac{1}{\hbar^2} \int_0^\infty d\tau \text{Tr}_{\text{Leads}}[H_I, [H_I(-\tau), W(t)]] \tag{6}$$

Positively definite steady-state solutions are only obtained if a secular approximation is applied to $\Theta$ so that couplings between populations (diagonal elements) and coherences (off-diagonal elements) of non-degenerate states are dropped\cite{21}. The corresponding Redfield tensor $R$ determines the steady state density due to $R \rho_{st} = 0$. Further, from $\Theta$ one has

$$\langle I_\alpha \rangle = -\frac{1}{h} \lim_{t \to \infty} \int_0^t d\tau \text{Tr}(W(t)[I_\alpha, H_I(-\tau)]) \tag{7}$$

with the current operator $I_\alpha = (ie/\hbar)[N_\alpha, H_I] = (ie/\hbar) \sum_k (d_\alpha^c c_k^\alpha - d_\alpha c_{k\alpha})$. Of course, in steady state $I_R = -I_L$.

### III. STEADY STATE OBSERVABLES

For low voltages ($|V_0|, |V_0' < V_0|$) and very weak couplings, transport properties are restricted to the low energy sector. Thus a representation of $\rho(t)$ in the basis $\{0, m\}, \{-, n\}$ is appropriate, with vibrational modes $\{m, n\}$ probing only the vicinity of $\phi = 0$ on surfaces $E_0(\phi), E_{-}(\phi)$, respectively\cite{10,11} (see Fig. 3).

In regime of higher voltages, however, this scheme poses severe difficulties. On surfaces $E_0, E_{\pm}$ the density of torsional eigenstates (typical level spacings $\sqrt{V_0/T} \approx meV$) strongly increases such that they should more accurately be described in terms of coherent states. This necessitates the inclusion of coherences in $\Theta$ also for non-degenerate eigenstates which typically leads to negative populations and thus to a breakdown of the perturbative treatment. A separation of time scales between the sluggish motion of the dihedral angle and a faster charge transfer through the contact suggests an alternative approach though which avoids this deficiency. In the spirit of a BO one first calculates steady-state solutions $\rho_{st}(\phi)$ for the electronic system at any fixed value of the rotational angle and then uses this solution to extract an effective steady-state potential for the torsional mode. Within the basis $\{0, \{\pm\}, \{D\}\}$ and for given $\phi$ corresponding energies are not degenerate [apart for $V_S = 0$ at $\phi = \pi/2 \mod \pi$ (Fig. 3)\cite{10}]. A secular approximation applied for fixed $\phi$ to $\Theta$ leads thus in steady state to $R(\rho_{00}, \rho_{++}, \rho_{--}, \rho_{DD}) = 0$ with

$$R = \begin{pmatrix}
\sigma_{00} & -\Sigma_{0+} & -\Sigma_{0-} & 0 \\
-\Sigma_{+0} & \sigma_{++} & 0 & -\Sigma_{out}^{out} \\
-\Sigma_{-0} & 0 & \sigma_{--} & -\Sigma_{out}^{out} \\
0 & -\Sigma_{D+} & -\Sigma_{D-} & \sigma_{DD}
\end{pmatrix} \tag{8}
$$

Here, transition rates read $\sigma_{00} = \Sigma_{in}^{in} + \Sigma_{out}^{in}, \sigma_{\pm \pm} = \Sigma_{2+}^{in} + \Sigma_{2-}^{out},$ and $\sigma_{DD} = \Sigma_{D+}^{out} + \Sigma_{D-}^{out},$ where incoming self-energies are given by

$$\Sigma_{in}^{ab} = \sum_\alpha \Gamma_{ab, \alpha} f_\alpha [E_\alpha(\phi) - E_\beta(\phi)] \tag{9}$$

and outgoing ones by $\Sigma_{out}^{ab} = \int d\tau \langle I_\alpha \rangle \rho_{\alpha \beta}(\phi)$. Further, we have introduced Fermi distributions $f_\alpha(E) = 1/[1 + \exp(\beta(E - \mu_\alpha))]$ and coupling rates: $\Gamma_{ab, \alpha} = 2\Gamma_\alpha |\langle a|d_\alpha+d_\alpha^\dagger|b\rangle|^2$. As noted above, these coupling rates are proportional to $\sin^2 \theta(\phi)$ and $\cos^2 \theta(\phi)$, respectively, and reduce to $\Gamma_\alpha$ in absence of a Stark-shift ($V_S = 0 : \theta = \pi/4$).

The angle dependent steady state density determines all relevant quantities such as the Born-Oppenheimer surface (BOS) for the torsional mode

$$V_{eff}(\phi) = \sum_{j \in \{0, +, -\}} E_j(\phi) \rho_{jj}(\phi) \tag{10}$$

(red line in Fig. 3) and the angle dependent current through lead $\alpha$ [see $\Theta$]

$$I_\alpha(\phi) = -\rho_{00}(\Sigma_{in} + \Sigma_{in}^{out}) + \rho_{++}(\Sigma_{in} + \Sigma_{in}^{out}) + \rho_{--}(\Sigma_{in}^{out} - \Sigma_{in}) + \rho_{DD}(\Sigma_{in}^{out} + \Sigma_{in}) \tag{11}$$

(red line in Fig. 3) Eventually, the Schrödinger equation for the torsional degree of freedom with the effective potential $\bar{V}_{eff}(\phi)$ is solved providing eigenfunctions $\Psi_{\phi}(\phi)$ and energies $\epsilon_{\phi}$. Note that these depend on the electronic steady state of the junction and thus on bias and gate voltage as well as temperature. Angle-averaged expectation values of observables $X(\phi)$ are obtained from $\langle X(\phi) \rangle = \int d\phi \sum_{\phi} X(\phi) |\Psi_{\phi}(\phi)|^2 \exp(-\beta \epsilon_{\phi})$ $Z$ with partition function $Z$. A thermal equilibrium state of the torsional sector is not in conflict with steady-state solutions of the electronic sector far from equilibrium due to the coupling of the former one to a heat bath environment of residual vibronic modes. Note that this in turn
FIG. 3: Energy surfaces of the bare molecular states $|0\rangle, |\pm\rangle$ and the BOS $V_{\text{eff}}$ vs. the torsional angle $\phi$ for $V_b = 0.5V$, $V_g = 0.5V$. In upper part bare molecular eigenstates are used, in the lower one a Stark shift between the left and right site of $V_S = 0.3V_b$ is assumed.

suppresses any possible bistability of the system, e.g. in Fig. 3 (top) a bistability between the global minimum situated at $\phi = 0$ and the local one around $\phi = \pi/2$. With typical energy barriers in $V_{\text{eff}}$ of order $eV$ (Fig. 3), the mean angle $\langle \phi \rangle$ is dominated over a broad temperature range mostly by torsional states well localized around the minima of $V_{\text{eff}}$ (green lines in Fig. 4). Finite angle-averaged currents $\langle I(\phi) \rangle$ result from sufficient overlap of angle dependent currents (11) with these states.

Before we proceed, let us specify the constraints for the above scenario. It is based on a time scale separation between electronic passage through the molecule and torsional motion (adiabaticity) and on a separation between electronic transition energies and electrode-molecule couplings $\hbar \Gamma$ (perturbation theory). Specifically, this means $\epsilon_\nu \ll \hbar \Gamma \ll E_+ - E_-$ which should be accessible in experimental set-ups due to $\epsilon_\nu \sim meV \ll E_+ - E_- \sim eV$.

IV. TRANSPORT PROPERTIES

Let us now discuss the steady state properties in more detail. We start with the case of a vanishing intramolecular field $\kappa = 0$. In Fig. 5 (bottom) the twist angle displays stability plateaus which reveal conformational changes with increasing bias and gate voltage, respectively. In a central diamond (low bias voltage, $V_g > 0$) the molecule resides in an almost planar configuration ($\langle \phi \rangle / \pi \approx 0$), while outside it is found mainly out of plane with $\langle \phi \rangle / \pi \approx 1$ or $\langle \phi \rangle / \pi \approx \frac{1}{3}$. One additional plateau appears with $\langle \phi \rangle / \pi \approx \frac{1}{10}$ when four transition channels are accessible: $|0\rangle \rightarrow |\pm\rangle, |\pm\rangle \rightarrow |D\rangle$. This step-wise snapping leaves its imprint on the current as seen in Figs. 5 (top) and 6. According to (11) and (9) transport channels open when $eV$ exceeds transition energies between molecular states which lie in the conduction window determined by $V_g$. The current exhibits distinct plateaus with $\langle I \rangle / (e\Gamma) = 0, \frac{1}{2}, \frac{2}{3}, \frac{3}{4}, 1$ which can be individually activated by the gate voltage. An asymmetric response to $V_g$ is also seen with a central Coulomb diamond shifted towards positive voltages [11].

FIG. 4: Angle dependent current and probability density for the $T = 80K$ rotational state. Parameters are the same as in Fig. 3.

FIG. 5: Net current in units of $e\Gamma$ (top) and mean torsional angle (degrees, bottom) in steady state vs. gate voltage $V_g$ and bias voltage $V_b$ (in units of $V$) with $V_S = 0$. 

FIG. 6: Angle dependent current and probability density for the $T = 80K$ rotational state. Parameters are the same as in Fig. 3.
In realistic junctions the presence of an intramolecular field (according to [11] we set $\kappa = 0.3$) breaks the symmetry, thus opening a gap between the $E_+$ and the $E_-$ surfaces (Fig. 3) and decreasing the HOMO ($E_0$)–LUMO ($E_-$) separation [11]. While for the mean twist angle and the net current (Fig. 7) the general appearance of the central diamond survives, new wedge-like structures appear with $\langle \phi \rangle / \pi = 1/2$ and thus $\langle I \rangle \approx 0$ due to $T(\pi/2) = 0$. Namely, for finite Stark shifts the effective coupling between the leads and the one-particle eigenstates becomes highly asymmetrical and peaked near $\phi = \pi/2$. This effect is surprisingly robust and dominates the conduction properties even at very low internal fields ($\kappa = 0.01$). The fully symmetric situation for $V_S = 0$ turns thus out to be extremely unstable and not applicable to actual junctions. A cut through the $V_b$-$V_g$ plane at a fixed bias voltage (Fig. 8) reveals the details of the opening and closing of transitions between molecular states upon sweeping $V_g$ from negative to positive values and the simultaneous snapping of the dihedral angle. In contrast, previous treatments where the torsion angle is considered to be fixed [6,8,12] provide conductances $\propto \cos^2(\phi)$. Here, transitions between current plateaus occur rather abruptly with simultaneous switchings of the molecular backbone. Notably, this behavior is very insensitive to temperature fluctuations; the system showed just the same plateaus (albeit slightly rounded) for $T = 300K$. Of particular interest are sequences $\langle I \rangle / e\Gamma \approx 1 \leftrightarrow 0 \leftrightarrow 1/2$ in the regime $V_g = 0 \ldots 4$ with substantial conformational changes $\langle \phi \rangle / \pi \approx 1/4 \leftrightarrow 1/2 \leftrightarrow 0$. This could be exploited as a molecular switch (current on/off) with the benefit of being insensitive against variations of temperature and internal fields in contrast to alternative proposals. In another application the voltage dependence of the molecular conformation could be used by operating the biphenyl as a molecular motor [14]. More specifically, in a first version a slowly varying time periodic gate voltage at a fixed bias voltage induces a valve-like behavior (e.g. open for $\phi = 0$, closed for $\phi = \pi/2$). The state of the rotor is directly read off from the variations of the dc-current. In an extended set-up side-groups are attached to each of the biphenyl rings to break in an additional static electric field the $\pi$-symmetry. A time-dependent gate voltage may then generate left- resp. right-handed rotations of the individual rings. This situation will be explored in a subsequent work.

V. SUMMARY

We have analyzed charge transfer through conjugated organic molecules contacted to metallic electrodes where a single sluggish vibrational degree of freedom strongly couples to excess charges. In the regime of higher voltages and molecule-electrode couplings large compared to vibrational excitations, but small compared to intramolecular electronic level spacings, voltage dependent
energy surfaces are determined. Bias and gate voltage allow to activate current plateaus that correspond to specific molecular conformations under steady state conditions. Applications may include non-linear junctions robust against thermal fluctuations and molecular motors.

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