Charge transfer dynamics in driven molecular ratchets: quantum Monte Carlo results and rate models

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Abstract. Charge transfer dynamics is studied in a ratchet-type molecular wire subject to finite frequency driving. Numerically exact data are obtained within the path integral Monte Carlo approach over the full transient time regime until a stationary net population imbalance has been established. This allows for a quantitative comparison with the master equation approaches and, in particular, underlines the usefulness of these rate models.

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1. Introduction

The nonequilibrium dynamics in ratchet potentials has been the subject of substantial research for more than a decade now [1]. One reason for this interest originates from the counter-intuitive behavior of these systems when they are driven by unbiased time-dependent forces and embedded in a dissipative environment. Due to the broken spatial symmetry asymptotically a finite flux emerges, thus allowing for transport without applied net forces, a situation that may be realized in various native systems [2] and has been observed in properly designed mesoscopic circuits [3, 4]. Most of the theoretical work has focused on the classical regime and moderate to strong dissipation. The quantum mechanical problem carries one fundamental complication: the fact that a simple analog to the classical Langevin or Fokker–Planck equation does not exist. A formally exact expression of the time-dependent reduced density matrix has been derived in terms of path integrals, but explicit evaluations are restricted to simple model systems [5]. Hence, progress has been made mainly in the adiabatic limit, where the external force reduces to a periodic ‘up’ and ‘down’ switch [6]–[8]. In the two latter works, the dynamics in infinite tight-binding lattices has been investigated, which has the advantage that the exact path integral expression can be cast in a retarded master equation that reduces to a time-local equation of motion in the Markovian limit [9]. Central ingredients are transition rates calculated within the NIBA (non-interacting blip approximation) type of approximations, which was originally developed for the spin-boson model [5, 9]. An approximation similar in spirit has been employed to study the net flux in spatially extended ratchets, where for driving by moderate frequencies a reduction to the lowest lying energy bands applies [10]. Interestingly, charge transfer through molecular structures [11] has been shown to be accurately captured by this type of tight-binding model, where the transition rates reduce (for time-independent systems) to the well-known Marcus rates in the classical regime [12]. In [13], it was demonstrated that also a driven coherent molecular wire coupled to fermionic leads instead of a bosonic heat bath exhibits ratchet features.

A particularly powerful approach to providing numerically exact results for quantum diffusion in tight-binding systems is the path integral Monte Carlo (PIMC) method [14], which has seen substantial extensions recently comprising larger systems [15, 16], correlated charge transfer [17], and even structures contacted with voltage biased leads [18]. In the present work, we apply it to study charge transfer dynamics in a finite tight-binding lattice subject to finite frequency driving. As a possible realization we think about a properly synthesized molecular wire with the charge dynamics initiated by a pump pulse which excites a charge from a dark state to a donor site and pushes residual molecular degrees of freedom out of equilibrium. Coherent motion of collective vibronic modes may thus occur [20] and directly trigger the diffusive charge transfer. The question then is how a population imbalance in the ratchet-type of wire is built upon changing parameters such as driving frequency, amplitude and background bath temperature. The PIMC data allow for a detailed comparison with the above-mentioned master equations over sufficiently long times and in regimes that have been not accessible so far.

The paper is organized as follows: we start in section 2 with a description of the tight-binding model and introduce the basic notation. Since the PIMC methodology has been presented in detail previously, we give here only some specific features for driven systems in section 3. In section 4, analytical treatments are discussed including master equations (section 4.1) and a simplified ratchet model (section 4.2) to understand the PIMC data represented and discussed in section 5. Final conclusions are presented in section 6.
Figure 1. A ratchet consisting of two segments with \( L = 3 \).

2. System

We restrict our model to a set of \( 2L + 1 \) (orthonormal) localized electronic states \(|l\rangle\), \(-L \leq l \leq L\), with nearest-neighbor coupling. That is, electronic motion is facilitated through tunneling which occurs only between adjacent states with real valued tunneling amplitudes that, for the sake of simplicity, we set to a uniform value \( \Delta \) (the extension of both the analytical as well as the numerical results presented below to the case on non-uniform amplitudes is straightforward). The electronic coordinate can then be expressed as

\[
q(t) = a \cdot l(t),
\]

where \(-L \leq l(t) \leq L\). The position operator thus is equivalent to the spin \( L \) operator

\[
a S_z |l\rangle = a |l\rangle.
\]

In terms of electron transfer, \(|-L\rangle\) and \(|L\rangle\) represent the donor and acceptor \(|D\rangle\) and \(|A\rangle\), respectively, while the other states are referred to as the bridge states.

The free \( 2L + 1 \)-level system Hamiltonian can then be written as

\[
H_0 = \hbar E - \hbar S_x,
\]

where \( E \) describes the energetic distribution of the electronic sites according to

\[
E|l\rangle = \epsilon_l |l\rangle,
\]

while \( S_x \) governs the nearest-neighbor tunneling,

\[
S_x |l\rangle = \Delta (|l-1\rangle + |l+1\rangle), \quad \text{for} \ |l| \neq L,
\]

\[
S_x |\pm L\rangle = \Delta | \pm (L - 1)\rangle.
\]

Here, we focus on electronic levels with a ratchet-type topology as shown in figure 1: a finite number of segments with linear ramp structure is combined into a single molecule ratchet.

This electronic system is embedded in an environment of solvent and/or vibronic degrees of freedom. We assume here that it consists of one pronounced environmental mode, which displays coherent motion on timescales relevant for the charge transfer, and a continuous background. The interaction with this environment is then modeled within the framework of a system-plus-reservoir model, leading to the total Hamiltonian

\[
H = H_0 + H_I + H_B + H_f(t)
\]

\[
= H_0 - a S_z \sum_a c_a X_a + (a S_z)^2 \sum_a \frac{c_a^2}{2m_a \omega_a^2} + \sum_a \left( \frac{P_a^2}{2m_a} + \frac{1}{2} m_a \omega_a^2 X_a^2 \right) + H_f(t).
\]
Here, the residual degrees of freedom are archetypically modeled as a harmonic bath coupling bilinearly to the position of the electron \((H_t)\) [5]. As discussed in detail in [5, 21, 22], this provides a reasonably accurate description of reality for the great majority of electron transfer systems. The influence of the coherent mode or external field is described by

\[ H_f(t) = f(t) S_z, \]  

with the ‘force’ \(f(t) = A \cos(\Omega t + \phi)\) acting as an external oscillatory driving source with amplitude \(A\), frequency \(\Omega\) and phase shift \(\phi\). To rationalize this form one could think of the charge transfer as initiated by exciting an electron from a dark state to a donor state (e.g. \(|0\rangle\) in figure 1) at \(t = 0\), which also includes a nonequilibrium preparation of the environmental degrees of freedom [19]. It has been experimentally observed [20] that in this case collective vibronic motion may occur triggering the charge transfer over relatively long times. Another realization would be a true external driving source, e.g. a laser field.

3. PIMC

As the starting point for deriving a real-time PIMC scheme we use the path integral representation of the dynamics of the full system (6). Accordingly, for a factorizing initial condition \(W_0\) the time-dependent populations of the localized electronic states \(|l\rangle\) can be expressed as [5]

\[ P_l(t) = \text{tr}\{W_0 e^{-iHt/\hbar} |l\rangle \langle l| e^{iHt/\hbar}\}, \]  

where \(\tilde{I}(t)\), consisting of a forward and backward path \(l(t)\) and \(l'(t)\), respectively, denotes a closed path along the Kadanoff–Baym contour, \(S_0\) is the bare action of the free system, and the Feynman–Vernon influence functional \(\Phi[\tilde{I}]\) describes the influence of the traced-out bath [23],

\[ \Phi[\tilde{I}] = \Phi_B[\tilde{I}] + \Phi_f[\tilde{I}]. \]  

Here,

\[ \Phi_B[\tilde{I}] = \int_0^t ds' \int_0^{s'} ds'' [I(s') - I'(s'')] [L(s' - s'') + i\hat{\mu}/2] \]  

summarizes the continuous solvent background, characterized by its complex-valued auto-correlation function

\[ L(t) = \frac{1}{\pi} \int_0^\infty d\omega J(\omega) \frac{\cosh[\omega(\hbar \beta/2 - it)]}{\sinh(\hbar \omega \beta/2)}, \]  

with \(\beta = 1/k_B T\) and \(\hat{\mu} = (2/\pi) \int_0^\infty d\omega J(\omega)/\omega\), given in terms of the spectral density

\[ J(\omega) = \frac{\pi a^2}{2\hbar} \sum_a \frac{c_a^2}{m_a \omega_a} \delta(\omega - \omega_a). \]
\( \Phi_f \), on the other hand, describes the influence of the dominant mode onto the electronic system. Since the eigenstates of \( H_f(t) \) are given by the (time-independent) pointer basis \( \{|l\}\rangle \), \( \Phi_f \) takes the rather simple form

\[
\Phi_f[\hat{l}] = \frac{i}{\hbar} \int_0^t ds \; [l(s) - l'(s)] f(s).
\]  

Combining equation (8) with a proper discretization description for the real-time axis then yields an efficient scheme for performing real-time PIMC simulations, as described in detail in [14]–[16]. The dynamical sign problem, a major nuisance in stochastic real-time methods, can be significantly reduced by exploiting symmetries in the influence functional, originating from the decoherent influence of the environment. Again, we refer to [14]–[16] for further details.

### 4. Analytical treatments

In this section, we present, on the one hand, a rate model that has been shown to follow directly from the exact path integral expression of the reduced density matrix in the limit of short memory times of the bath (Markovian limit) and, on the other hand, give arguments that show that the relevant timescales of an adiabatically driven ratchet system allow one to understand finite frequency data.

#### 4.1. Rate model

For single charge transfer along one-dimensional tight-binding lattices, a description of the population dynamics in terms of retarded master equations is completely equivalent to the path integral representation even in the presence of time-dependent forces [9]. In addition, for sufficiently strong dissipation and/or high temperatures, phase coherence is lost after each jump between adjacent sites, and the transfer occurs as a sequential diffusive process. In this case, the exact dynamics obeys approximately

\[
\frac{d\tilde{P}(t)}{dt} = \mathbf{R}(t) \; \tilde{P}(t),
\]

where \( \tilde{P} \) collects the single particle populations and the matrix \( \mathbf{R}(t) \) contains the transition rates between adjacent sites. For driven systems, these rates are time dependent and do not obey a detailed balance relation as in the time-independent situation. Explicitly, one finds for a transition from site \( l \) to site \( m \) with energy difference being \( \epsilon_{lm} = \epsilon_l - \epsilon_m \) (forward rate)

\[
\Gamma_{l,m}(t) \equiv \Gamma(t; \epsilon_{lm}, f)
\]

\[
= \Delta^2 \int_0^\infty d\tau \; e^{-Q(\tau)} \cos \left[ Q'(\tau) + \epsilon_{lm}\tau + \zeta(t, \tau) \right],
\]

where

\[
\zeta(t, \tau) = \int_{t-\tau}^t ds \; f(s).
\]

The corresponding backward rate follows as \( \Gamma_{m,l} = \Gamma(t; -\epsilon_{lm}, -f) \). Further, \( Q(t) = Q'(t) + iQ''(t) \) is the twice-integrated bath force–force autocorrelation function (11)

\[
Q(t) = \frac{1}{\pi} \int_0^\infty d\omega \frac{J(\omega)}{\omega^2} \left[ \coth(\hbar \beta \omega/2) \right] \left[ 1 - \cos(\omega t) \right] \left[ 1 - \sin(\omega t) \right].
\]
Note that the particular form of $f(s < 0)$, which should be irrelevant for the case of a charge excited from a dark state at $t = 0$, only enters into equation (15) for times $t$ which are smaller than the timescale over which $e^{-Q(t)}$ practically decays to 0. This timescale, however, also determines the lifetime of quantum coherences after a hopping process [5], such that $f(s < 0)$ only matters for times that lie beyond the validity of the overall rate picture (14). Alternatively, the ambiguity regarding the form of $f(s < 0)$ can also be avoided by setting $f(s < 0) = 0$ without restricting the general physical model.

In the absence of the external driving $f$ the rates are time independent and reduce in the classical high-temperature limit to the well-known Marcus rate expression. The above rate equations are then simply solved by diagonalizing the rate matrix $R$, where $2L$-negative eigenvalues describe the relaxation dynamics, while the vanishing eigenvalue corresponds to the stationary populations in thermal equilibrium. For an oscillatory driving with frequency $\Omega_1$ the rates are periodic, $\Gamma_{l,m}(t + n2\pi/\Omega_1) = \Gamma_{l,m}(t)$, where $n$ is an integer, so that according to (14) for sufficiently long times the populations reach a ‘stationary state’ periodic in time, i.e. $\bar{P}_a(t + n2\pi/\Omega_1) = \bar{P}_a(t)$.

4.2. Simplified ratchet system

In order to obtain an understanding of the mechanism that determines the population dynamics in a driven tight-binding ratchet, it is instructive to consider an elementary segment of the finite lattice in figure 1 subject to a force which switches adiabatically between $+A$ (up tilt) and $-A$ (down tilt). In the present case such an elementary unit that already displays the essential features of the transport contains four sites, i.e. two boundary sites with identical on-site energies (in figure 1 corresponding, e.g., to sites $|−3⟩$ and $|0⟩$) connected by a ramp-like bridge of two sites (e.g. $|−2⟩$ and $|−1⟩$ in figure 1). For this system three non-vanishing eigenvalues $|\gamma_1^{(v)}| \geq |\gamma_2^{(v)}| \geq |\gamma_3^{(v)}|$, $v = \pm$, exist for each of the two static rate matrices $R_{+A}$ and $R_{-A}$. For a system initially prepared with probability 1 on either the right-most ($|0⟩$) or the left-most ($|−3⟩$) site, the relaxation dynamics is governed by these eigenvalues for $v = +$ (i.e. $+A$) or $v = -$ (i.e. $-A$), respectively. In figure 2, we display the ratios $r_i = \gamma_i^{(+)} / \gamma_i^{(−)}$ as functions of the amplitude $\Delta$ at a higher and a lower temperature, $\hbar\beta\Delta = 0.1$ (a) and 0.4 (b) as a function of the driving amplitude $A$. See text for details.
bath parameters used in section 5, quantum mechanical coherences do influence the population dynamics below temperatures $\hbar \beta \Delta \gtrsim 0.5$, thus causing the sequential transfer to break down. One observes that in the high-temperature case the ratio $r_1 < 1$ so that on the corresponding (short) timescales the population transfer $|-3\rangle \rightarrow |0\rangle$ for down tilt (denoted by $P_0^{(-)}(t)$) is faster than that from $|0\rangle \rightarrow |-3\rangle$ for up tilt. This scenario may change for longer times when processes on the timescales $\gamma_2^{(\pm)}, \gamma_3^{(\pm)}$ come into play. Namely, at higher temperatures $r_2, r_3 > 1$ so that on these longer timescales population transfer happens to be faster from $|0\rangle \rightarrow |-3\rangle$ for up tilt than vice versa. However, at the lower temperature $r_2$ becomes smaller than 1, while still $r_3 > 1$, so that the described changeover occurs at longer times. For the adiabatic switching, one thus has a transient population imbalance between state $|-3\rangle$ for up tilt and state $|0\rangle$ for down tilt depending on the ratios of these eigenvalues. Of course, for this finite system, this imbalance vanishes for long times as a thermal equilibrium is approached.

Based on this simple model, we expect the following scenario for driving with finite frequencies: population transfer to the right exceeds that to the left for all frequencies $\Omega$ which are larger than or of the order of $\min\{|\gamma_1^{(\pm)}|\}$ with $r_1 < 1$. For slower driving, however, slower rate processes tend to play a role, and a changeover occurs to a situation where population transfer to the left exceeds that to the right. In this sense, external driving ‘probes’ the intrinsic charge dynamics and gives direct information about relevant transient timescales. For instance, for $\hbar \beta \Delta = 0.1$, where $r_1 < 1$ while $r_2, r_3 > 1$, the rates $|\gamma_1^{(\pm)}|$ are of order 1 and the rates $|\gamma_2^{(\pm)}|$ are about 0.6. Hence, one expects a changeover to appear for driving frequencies in the range $0.6 \lesssim \Omega \lesssim 1$. For $\hbar \beta \Delta = 0.4$, one has $r_1, r_2 < 1$ ($A$ not too large) while $r_3 > 1$ with $|\gamma_2^{(\pm)}|$ about 0.5 and $|\gamma_3^{(\pm)}|$ about 0.06 so that the changeover should happen at smaller frequencies $0.06 \lesssim \Omega \lesssim 0.5$. We will see in the next section that these predictions are indeed verified by the full dynamical calculation.

5. Results and discussion

In the following, we present results for an electronic system consisting of a ratchet-like molecular structure with $2L + 1 = 7$ sites (see figure 1). It is thus a combination of two ramp-like linear chains such that the elementary unit discussed in the previous section has four sites. The environment is characterized by an ohmic-type spectral density

$$J(\omega) = 2\pi \alpha \omega e^{-\omega/\omega_c},$$

(18)

with the cut-off frequency $\omega_c$ and coupling parameter $\alpha$. These latter parameters remain fixed and are taken as $\omega_c/\Delta = 5$ and $\alpha = 0.25$, a parameter regime at which the influence of quantum coherences is weak enough for the dynamics of the undriven system to strictly follow a rate description but strong enough for the corresponding rates to be given by quantum instead of classical expressions [15, 16]. For the PIMC simulations, the bath temperature has been chosen as $\hbar \beta \Delta = 0.1$, while for the analytical treatment also the somewhat lower temperature $\hbar \beta \Delta = 0.4$ has been considered. We recall that electronic coherences start to prevail for inverse temperatures beyond $\hbar \beta \Delta \approx 0.5$. Since in the long time limit the phase of the external driving does not play an important role, we set $\phi = 0$.

In figure 3, PIMC results for the population dynamics of the left-most state $P_{-3}(t)$ and of $P_{-1}(t)$ are shown for two sets of external driving parameters ($A = 1.25\hbar \Delta$, $\Omega = \Delta$ and $A = 2.5\hbar \Delta$, $\Omega = 2.8\Delta$) together with the corresponding results of the rate equation (14). We mention that the time evolution of the initially populated state $P_0(t)$ shows basically no signs
of oscillations and relaxes almost monotonically. The rate model gives a quite good qualitative description and its predictions quantitatively deviate from the numerically exact data by at most about 10%. This is in agreement with our previous findings for static charge transfer and can be attributed to adiabatic effects in the bath dynamics not captured by the golden rule rate (15). Of course, the rate model can cover the time evolution to much longer times until oscillating quasi-stationary states are reached. However, the PIMC simulations are able to describe almost the complete transient time interval of the dynamics and can thus be used, in principle, to retrieve all timescales of the problem. The general conclusion is that the rate description (14) together with (15) gives a sufficiently accurate picture of the exact quantum dynamics. For this sequential process electronic nearest-neighbor tunneling is accompanied by tunneling of collective vibronic modes.

An interesting observable for this finite size system is the population imbalance \( \delta P(t) = P_{-3}(t) - P_3(t) \), which for the undriven situation relaxes towards zero in thermal equilibrium. The rate model reproduces again quite satisfactorily the PIMC data with finite mean population imbalances

\[
\langle \delta P \rangle = \lim_{t \to \infty} \frac{\Omega}{2\pi} \int_t^{t+2\pi/\Omega} d\tau \delta P(\tau).
\]

From the simplified ratchet model discussed in the previous section, we attribute such finite population imbalances to the fact that \( \Omega > |\gamma_{2,3}^{(\pm)}| \) (see section 4.2) in the considered parameter range. More insight is provided by analyzing \( \langle \delta P \rangle \) for varying driving amplitude \( A \) (at fixed frequency) and for varying frequency \( \Omega \) (fixed amplitude). Results for the former case obtained within the rate model for very long times are depicted in figure 4(a). At higher temperatures the averaged population imbalance increases quadratically for small amplitudes, then crosses over to an almost linear growth, before a saturation sets in for large amplitude driving. This behavior is reminiscent of the amplitude dependence of the time-averaged escape rate out of a metastable well subject to periodic driving in the case of strong dissipation [25]. Namely, the ratchet-type setup of electronic levels can effectively also be seen as a potential well located at \( \ket{0} \) separated from two adjacent wells at \( \ket{-3} \) and \( \ket{3} \) by asymmetric potential barriers. In this picture the population imbalance is related to different time-averaged forward and backward rates out of.
the central well. Since each of these rates exhibits the mentioned dependence on $A$, the same is true for the time-averaged population imbalance. We note in passing that a quadratic growth for small driving amplitudes has also been found for the net current through a driven coherent wire contacted to fermionic leads [13]. At the lower temperature a similar behavior can be found for small to intermediate amplitudes, while for large amplitudes the population imbalance decreases again so that a pronounced minimum appears. This strong temperature dependence reflects the substantial impact of vibronic tunneling during the charge transfer.

In the second case we fix $A$ to 2.5$\hbar\Delta$ and investigate the rate model for the time-averaged population imbalance as a function of the driving frequency (see figure 4(b)). As suggested by the simplified ratchet model, one finds a changeover exactly in the range where $\Omega \approx |\gamma_2^{(\pm)}| \approx 0.6\Delta$ for the smaller inverse temperature $\hbar\beta\Delta = 0.1$, and for $|\gamma_3^{(\pm)}| < \Omega \approx 0.1\Delta < |\gamma_2^{(\pm)}|$ for the larger inverse temperature $\hbar\beta\Delta = 0.4$. For faster driving the population imbalance increases towards a minimum and tends to zero for very fast driving in accordance with the results obtained for the stationary current for infinite classical ratchets [1]. The width of this extremum shrinks with decreasing temperature, while at the same time the absolute value of the population imbalance substantially grows. In contrast, when the bosonic heat bath is replaced by fermionic leads as in [13], sharp resonance-like structures appear in the net current.

6. Conclusions

We have presented both an analytical and a numerical investigation of the dynamics of a dissipative tight-binding system, which is subject to periodic external driving, with emphasis on the (incoherent) net charge transfer across a quantum ratchet. Therefore, we have extended, on the one hand, a rate-model approach based on exact master equations, which has been shown to yield an adequate picture of the dynamics of the corresponding system in the absence of external influence [15, 16], to incorporate the effects of the time-dependent external driving force. On the other hand, a numerically exact PIMC scheme was obtained by combining a path-integral expression for the influence of the external force with efficient strategies to soothe the dynamical sign problem in dissipative quantum systems. Both approaches can, in principle, be applied for
arbitrary spectral densities of the dissipative environment, finite driving frequencies $\Omega$, outside the thermodynamic limit (i.e. for finite system sizes), and in parameter regions where quantum effects play a decisive role. For charge transport, which is dominated by incoherent hopping processes, the results from the time-dependent rate picture are compared with the numerically exact PIMC data, which cover the full transient regime. Both qualitative as well as quantitative agreement is achieved as long as the external driving is governed by timescales smaller than those needed by the environment to destroy quantum coherences (i.e. for $\Omega < \omega_c$). By extending the predictions of the rate picture to the quasi-stationary regime, we observe a finite net charge transfer across the ratchet, which is nonmonotonic with respect to the driving amplitude and frequency and strongly enhanced in the quantum regime.

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