Non-Equilibrium Dynamics of Correlated Electron Transfer in Molecular Chains

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The relaxation dynamics of correlated electron transport (ET) along molecular chains is studied based on a substantially improved numerically exact path integral Monte Carlo (PIMC) approach. As archetypical model we consider a Hubbard chain containing two interacting electrons coupled to a bosonic bath. For this generalization of the ubiquitous spin-boson model, the intricate interdependence of correlations and dissipation leads to non-Boltzmann thermal equilibrium distributions for many-body states. By mapping the multi-particle dynamics onto an isomorphic single particle motion this phenomenon is shown to be sensitive to the particle statistics and due to its robustness allows for new control schemes in designed quantum aggregates.

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Recent progress in engineering and manufacturing of nanoscopic electronic devices enabled to tackle the long standing problem of contacting single molecules \cite{1,2,3}. This remarkable achievement not only opens a way for building the ultimate transistor on the molecular basis, but is also expected to become an important tool for investigating electron transport (ET), which is one of the most fundamental processes in chemistry and biology \cite{4}, the best known example being photosynthesis \cite{5}. Likewise, in semiconductors charge transfer plays a key role and most recently studied arrays of few electron quantum dots may be seen as artificial molecular structures which, in contrast to their native counterparts, allow for a completely controllable ET \cite{6}.

The most successful paradigm for the description of ET is the donor–acceptor model. In its simplest form it is represented by a two-site chain where a single electron is transferred between the sites via tunneling hybridization. However, irreversible transfer can only take place in presence of an environment consisting e.g. of residual vibronic degrees of freedom or electromagnetic fluctuations. In the past, the Caldeira–Leggett model \cite{7} has been shown to capture the relevant features of dissipative ET, where the electronic system is coupled to a bath of harmonic oscillators \cite{8}. In case of only two sites and one single charge this is the famous spin–boson model, which, together with its generalizations to multi-site geometry, is a paradigmatic model on its own comprising e.g. quantum Brownian motion, Kondo physics, Luttinger liquids \cite{9}, and atomic quantum dots \cite{10}. Despite its simplicity the associated phenomenology is extremely rich showing different sorts of quantum phase transitions \cite{11}.

With the advent of fully tunable quantum structures a fundamental constraint has to be relaxed though, namely, the restriction to single particle dynamics. Multi-particle correlation effects may undoubtedly have a potential to considerably alter the simple ET physics and open the door for new control mechanisms \cite{11,12}. Of course, correlated ET in a dissipative reservoir is a formidable task, mainly due to the fact, that a quantum reservoir leads to strong retardation effects. So far virtually all studies made use of perturbative approaches focusing on either completely coherent transfer with no dissipation \cite{13,14}, or completely sequential transfer with very strong Coulomb repulsion \cite{15}, which effectively reduces to a single particle ET problem. The inclusion of both correlations and dissipation has been attacked only recently in \cite{16}, where equilibrium properties of a two site spinful system filled with two electrons has been analyzed with the help of numerical renormalization group (RG) technique. However, being intrinsically an equilibrium technique, this method cannot reveal any information about dynamical properties of these systems. In addition, finite temperature effects are usually quite difficult to access in the framework of the RG. In this Letter we close this gap and, based on a numerically exact path integral Monte Carlo (PIMC) scheme, we present results for the real-time dynamics of two correlated fermions in a dissipative environment. This model can be seen as the simplest generalization of the single particle spin-boson model to include many-body effects. It may thus reveal archetypical properties of correlated dissipative quantum dynamics.

The system is modeled by an open Hubbard chain with \( N \) sites of spacing \( a \)

\[
H_S = \sum_{i=1,\sigma=\uparrow,\downarrow}^{N} E_i d_{i\sigma}^\dagger d_{i\sigma} + \frac{U_i}{2} d_{i\uparrow}^\dagger d_{i\uparrow} d_{i\downarrow}^\dagger d_{i\downarrow} + \sum_{i=1,\sigma=\uparrow,\downarrow}^{N-1} \Delta_i \left( d_{i\sigma} d_{i+1\sigma} + h.c. \right),
\]

(1)

where \( d_{i\sigma} \) are annihilation operators for electrons with spin \( \sigma \) on the site \( i \). \( E_i \) are the bare energies of the levels, \( U_i \) the corresponding interaction strengths and \( \Delta_i \) are the tunneling matrix elements. The interaction with the bosonic bath given by the Hamiltonian \( H_B = \sum_{\alpha} \left( P_{\alpha}^2/2m_\alpha + m_\alpha \omega_\alpha^2 X_\alpha/2 \right) \) is accomplished via a standard dipole coupling

\[
H_I = -aP \sum_{\alpha} c_\alpha X_\alpha + a^2P^2 \sum_{\alpha} \frac{c_\alpha^2}{2m_\alpha \omega_\alpha^2},
\]

(2)
where
\[ P = \sum_{i=1,\sigma}^{N} [i - (N + 1)/2] d_{i\sigma}^\dagger d_{i\sigma} \] (3)
is the polarization operator of the Hubbard chain.

We are interested in the reduced dynamics of the fermionic system determined by the density operator \( \rho(t) = \text{Tr}_B \{ \exp(-iHt/\hbar) W(0) \exp(iHt/\hbar) \} \), where \( W(0) \) specifies the initial state of the compound. Here the trace over the bosonic bath degrees of freedom can be done exactly within the path integral approach by representing the density operator in the site representation of the chain in terms of a pseudo-spin-\((N - 1)/2\) operator \( \tilde{S}^\sigma \). Accordingly, the eigenvalues of \( \tilde{S}^\sigma \) represent the density operator in the site representation with \( \tilde{S}^\sigma = \sigma^\sigma |\sigma^\sigma \rangle \langle \sigma^\sigma | \). Then, the corresponding many-body basis \( \{|s^\uparrow, s^\downarrow \rangle \} \) follows from properly anti-symmetrized single particle states. The relevant dynamical observables are the populations \( P_\lambda(t) = \text{Tr}_S \{ \lambda \rho(t) \} \) where \( \lambda \) denotes a projection operator either onto a certain site and spin or onto a certain many-body state. Initially, the system is prepared in a specific many-body state with the bosonic reservoir equilibrated to that state.

This way, the reduced density operator is expressed as a double path integral along a Keldysh contour with forward \( s^\sigma \) and backward \( \tilde{s}^\sigma \) paths. The impact of the dissipative environment appears as an influence functional introducing arbitrarily long-ranged interactions in time between the paths. It is convenient to switch to the combinations \( \eta^\sigma = s^\sigma + \tilde{s}^\sigma \) and \( \xi^\sigma = s^\sigma - \tilde{s}^\sigma \) so that one arrives at the exact expression
\[ P_\lambda(t) = \int D\eta D\xi \lambda(\eta, \xi) A[\eta, \xi] \exp(-\Phi[\eta, \xi]) \] (4)
where \( \eta = (\eta^\uparrow, \eta^\downarrow) \) and \( \xi = (\xi^\uparrow, \xi^\downarrow) \). Here, \( A \) is the bare action factor in absence of a reservoir and the influence functionals reads
\[
\Phi[\eta, \xi] = \int_{0}^{\tau} \int_{0}^{s} du \left\{ \xi(s) \cdot \vec{e} \right\} L'(s-u) \left[ \xi(u) \cdot \vec{e} \right] \\
+ i \left\{ \xi(s) \cdot \vec{e} \right\} L''(s-u) \left[ \eta(u) \cdot \vec{e} \right] \\
+ i \frac{\mu}{2} \int_{0}^{s} ds \left\{ \xi(s) \cdot \vec{e} \right\} \left[ \eta(s) \cdot \vec{e} \right]
\]
with \( \vec{e} = (1, 1) \). The kernel \( L(t) = L'(t) + iL''(t) \) is related to the force-force auto-correlation function of the bath and is completely determined by the spectral density of its modes. Further, \( \mu = \lim_{\beta \to 0} \hbar \beta L(0) \). The immediate advantage of the representation is that formally it looks like the dynamics of a single particle in a two-dimensional plane. We shall discuss this point in more detail below. Note further, that even in absence of a direct Coulomb interaction the two charges are correlated due to the coupling to the heat bath.

An analytical treatment of the expression \( \Phi \) is in general not feasible, mainly due to the retardation in the influence functional which grows with decreasing temperature. In this situation PIMC methods have been shown to be very powerful numerically exact means to explore the non-perturbative range. Our starting point is a PIMC scheme \( \textsuperscript{17} \) which exploits the linear dependence of \( \Phi[\eta, \xi] \) on the quasi-classical paths \( \eta(t) \), so that in \( \textsuperscript{18} \) the corresponding summations can be expressed as a series of simple matrix multiplications and therefore be carried out explicitly. These matrices include the bare short time propagators of the system and phase factors stemming from the \( \eta \)-dependent part of \( \Phi \). Consequently, the number of MC variables is reduced by a factor of two, which leads to a significant soothing of the dynamical sign problem \( \textsuperscript{18} \). Previous simulations were restricted to single particle transport on up to three sites and for shorter times only, because the standard MC-weight requires to perform the full series of matrix multiplications for each MC-step due to the retardation of the \( \eta \)-dependent phase factor. A breakthrough is gained by neglecting the long-time retardations during the propagation of the MC trajectory. Since they are fully accounted for during the final accumulation process, the numerical exactness of the MC scheme is not impaired. This way, one achieves a strong decoupling of quasi-classical \( (\eta) \) and quantum \( (\xi) \) coordinates, which allows to calculate and store products of short time propagators independent of the MC-sampling. Eventually a speed-up with respect to the original method \( \textsuperscript{18} \) by a factor of about 100 is gained.

The simplest non-trivial system which is able to accommodate two electrons and thus the simplest many-body generalization of the spin-boson model is a two-site chain. The proper representation of a corresponding many-body basis is given by
\[ \mathcal{B} = \{|\uparrow\downarrow, 0\rangle, |\downarrow\uparrow, 0\rangle, |\uparrow, \downarrow\rangle, |0, \downarrow\rangle\} \] (5)
where the left(right) argument of the ket represents the spin occupation of site \(-1/2(1/2)\). For these localized spin states the relevant observables are the site populations and the populations \( P_\psi \) occupying one of the states \( |\psi\rangle \in \mathcal{B} \). In particular, the latter ones give detailed insight into the intimate relation between correlations and dissipation during the relaxation from an initial non-equilibrium state. For very long times, the expectation is that the system reaches a thermal equilibrium, where all four many-body states are populated according to a Boltzmann distribution. Thus, in case of vanishing Coulomb interaction \( U_1 = 0 \) and energetically completely degenerated sites \( E_i = 0 \), one anticipates, no matter how the system is prepared at \( t = 0 \), a final probability of \( 1/4 \) for each state in \( \mathcal{B} \), whereas both sites of the chain have to be half-filled. While the latter expectation turns out to be true, remarkably, the former one cannot be confirmed by our simulations (see Fig. \textsuperscript{14}). Not only do
the populations \(P_\psi(t)\) saturate at different values, but these also depend on the initial preparation. This at first startling dynamics leading to a non-Boltzmann distributed steady state in the many-body basis \(|\psi_i\rangle\), can be understood in terms of decoherence free states (DFS) \([9]\). These states are simultaneous eigenstates of \(H_S\) and of the polarization operator \(\mathcal{P}\). Accordingly, after being prepared in such a state the system stays there forever and no relaxation into the equilibrium can occur. While DFS have been studied for very weakly damped systems in the context of quantum information processing, where the generic basis is the eigenbasis of \(H_S\), in strongly condensed phase systems the site representation is the proper one. Hence, for correlated ET the impact of DFS onto transport properties is important and leads to completely new and unexpected phenomena. In the case considered here, there is only one such state, namely

\[
|\phi_1\rangle = (|\downarrow, \uparrow\rangle - |\uparrow, \downarrow\rangle)/\sqrt{2},
\]

which corresponds to zero dipole moment and apparently is a delocalized spin state. An alternative basis set of the electronic Hilbert space is thus given by

\[
\{|\phi_i\rangle\}_{i \leq 4} = \{|\phi_1\rangle, |\phi_2\rangle, \frac{1}{\sqrt{2}}(|\downarrow, \uparrow\rangle + |\uparrow, \downarrow\rangle), |\uparrow, 0\rangle, |0, \downarrow\rangle\}
\]

consisting of both delocalized (\(|\phi_1\rangle, |\phi_2\rangle\)) and localized (\(|\phi_3\rangle, |\phi_4\rangle\)) spin states. Obviously, \(|\phi_1\rangle\) does not participate in the relaxation process, such that equilibration is restricted to the sub-space spanned by \(|\phi_i\rangle, i = 2, 3, 4\), leading for an energetically degenerate system to

\[
P_{\phi_i}(t \rightarrow \infty) = [1 - P_{\phi_i}(t = 0)]/3, \quad i = 2, 3, 4
\]

Now, due to \(P_{\downarrow, \downarrow}(t = 0) = P_{\uparrow, \uparrow}(t = 0)\) and \(P_{\downarrow, \uparrow}(t = 0) + P_{\uparrow, \downarrow}(t = 0) = P_{\downarrow, \downarrow}(t = 0) + P_{\uparrow, \uparrow}(t = 0)\), and \(P_{\downarrow, \downarrow}(t = \infty) = P_{\uparrow, \uparrow}(t = \infty) = P_{\downarrow, \uparrow}(t = \infty) = P_{\uparrow, \downarrow}(t = \infty)\) for \(t \rightarrow \infty\) due to symmetry, one easily understands from \([9]\) both the non-Boltzmann distribution of the localized states as well as their dependence on the initial preparation. Imagine that initially the electronic sub-system is prepared in one of the states in \([9]\), which experimentally is the typical situation. Then, for the non-equilibrium dynamics two different scenarios are possible: If both electrons initially occupy the same site, i.e. \(P_{\downarrow, \downarrow}(0) = 1\) or \(P_{\uparrow, \uparrow}(0) = 1\), one always has \(P_{\phi_1}(0) = 0\) so that the final equilibrium distributions read \(P_{\downarrow, \downarrow}(t = \infty) = P_{\uparrow, \uparrow}(t = \infty) = 1/3\) and \(P_{\downarrow, \uparrow}(t = \infty) = P_{\uparrow, \downarrow}(t = \infty) = 1/6\). If, however, both sites are initially occupied, i.e. \(P_{\downarrow, \downarrow}(0) = 1\) or \(P_{\uparrow, \uparrow}(0) = 1\), so that \(P_{\phi_1}(0) = 1/2\), the final distributions become \(P_{\downarrow, \downarrow}(t = \infty) = P_{\uparrow, \uparrow}(t = \infty) = 1/6\) and \(P_{\downarrow, \uparrow}(t = \infty) = P_{\uparrow, \downarrow}(t = \infty) = 1/3\). Therefore, the system, after having been prepared in one of the states \([9]\), always remembers, whether this state had a vanishing or non-vanishing dipole moment. This phenomenon crucially depends on the symmetry of the operators mediating the interaction with the bosonic baths. However, since the dipole coupling specified in \([2]\) is generic for a variety of native and artificial molecular structures, the above dynamics can be expected to be typical. In most native molecules ET is triggered by exciton-polariton phenomena \([10]\) and \([11]\) so that correlated ET is difficult to observe. In contrast, e.g. in synthetic aggregates, which are very weakly coupled to external leads \([12][13]\), or in arrays of quantum dots \([14]\) the excess charge can be better controlled. Then, starting e.g. from a totally unpolarized ensemble, after equilibration only 1/3 of its constituents would be polarized and 2/3 of them unpolarized. This is an example of a non-Boltzmann type of thermal distribution, which for the generic form of system-bath coupling is a signature of: (i) the topology of the tunneling couplings in \(H_S\) \([15]\) and (ii) Fermi-Dirac statistics. Let us analyze these two points in more detail.

To address (i), one first realizes that the existence of a common eigenstate \(|\phi_1\rangle\) of \(H_B\) and \(\mathcal{P}\) is completely independent of the electronic energies \(E_i\), the Coulomb interaction strengths \(U_i\), temperature and the spectral density of the bath modes. Accordingly, the described phenomena can also be observed for non-degenerate systems \((E_1 \neq E_2 \neq 0\) and/or \(U_1 \neq U_2 \neq 0\)). In this case,
FIG. 3: Same as in Fig. 1 but for $\hbar \beta \Delta = 0.5$. Inset: Dynamics for a system with $\hbar \beta \Delta = 0.1$, Coulomb interaction $U_1 = U_2 = 4 \hbar \Delta$, and $E_1 = E_2 = 0$, i.e. $\langle \downarrow \uparrow, 0 | H_S | \downarrow \uparrow, 0 \rangle = \langle \downarrow \uparrow, 0 | H_S | \uparrow \downarrow, 0 \rangle = 4 \hbar \Delta$, $\langle \downarrow \uparrow | H_S | \downarrow \uparrow, 0 \rangle = \langle \uparrow \downarrow | H_S | \uparrow \downarrow, 0 \rangle = 0$.

FIG. 4: Same as in Fig. 1 but for two identical bosons on a chain with $N = 3$. Shown are the populations for states $|n_{-1}, n_0, n_1\rangle$ with occupation $n_i$ on site $i$: $|2, 0, 0\rangle$ (circles), $|1, 1, 0\rangle$ (squares), $|1, 0, 1\rangle$ (triangles up), $|0, 2, 0\rangle$ (triangles down), $|0, 1, 1\rangle$ (diamonds), and $|0, 0, 2\rangle$ (triangles right). Inset: Dynamics for $N = 2$ with states $|n_{-1/2}, n_{1/2}\rangle$; $|2, 0\rangle$ (circles), $|1, 1\rangle$ (squares), $|0, 2\rangle$ (triangles).

one even arrives at the counter-intuitive situation that in thermal equilibrium the occupations of energetically higher lying states exceed those of energetically lower lying ones (cf. inset in Fig. 5). Moreover, effects tied to the DFS also survive the coherent–incoherent transition, its typical signature being the onset of oscillations in the population dynamics (cf. Fig. 3). Thus, they prevail in two distinct dynamical regimes. However, DFS crucially depend on the topology of the tunneling couplings in $H_S$. They always exist for isotropic couplings, but can be easily destroyed e.g. by appropriately adding or removing couplings between the localized states (3). For example, interchanging the coupling according to Fig. 2b so that spin flips and two-particle tunneling are allowed, the Boltzmann equilibrium is restored (see inset in Fig. 1).

To discuss (ii), one easily deduces a mapping of the dissipative dynamics of two correlated fermions on two sites onto a single particle motion along the edges of a two-dimensional square, spanned by the many body states $|0, 0\rangle$, see Fig. 2. This mapping has two immediate consequences that will be studied in details elsewhere: First, it allows to adapt perturbative approaches like the NIBA and the NICA (8) developed for ordinary spin-boson models to capture also correlated many-body dynamics; on the other hand, the dynamics along any $N$-site chain with an arbitrary number of electrons can be mapped onto a dissipative single particle ET on a higher-dimensional square [29]. For indistinguishablebosons such a mapping is also found leading though to a triangular lattice. Then one derives from the geometry of the mapping that for a Hubbard chain only one DFS exists whereas for the similar bosonic model such states are only possible for odd $N$. This is illustrated in Fig. 4 for chains with $N = 3$ and $N = 2$. In the former case one has final populations of $1/5$ vs. $1/10$, while in the latter one they all saturate at $1/3$. Note that the $N = 3$ fermionic system exhibits smaller equilibrium values of $1/8$ vs. $1/12$ due to the larger number of accessible many-body states. Of course, DFS never exist in one-dimensional single particle systems.

To summarize, we have developed a PIMC technique which opens the door for a reliable modeling of the nonequilibrium dynamics of correlated ET even on longer time scales. As a remarkable many-body effect, related to the existence of a DFS, a non-Boltzmann steady state was predicted. A mapping onto an isomorphic single particle model reveals its sensitivity to the particle statistics. Experimentally, this phenomenon may lead to new control schemes for fermionic or bosonic transport in tight-binding systems like synthesized molecular chains, quantum dot arrays, or optical lattices.

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