Effective electronic dynamics in organic charge-transfer salts

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Abstract

We derive the finite temperature effective dynamics of electrons coupled to in-phase boson modes of a crystal lattice in the long wavelength limit. We extend current literature results, showing their validity domain, and incorporate nonunitary and thermal effects. © 1997 Published by Elsevier Science B.V.

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The two-site Hubbard model has proven to be an adequate tool to investigate optical properties of the organic salts for which the ion radical molecules are quasi-isolate dimers \cite{1-3}. In the case that the fermionic degrees of freedom are coupled to their internal molecular vibrations, an effective Hamiltonian has been proposed by Kozlov et al. \cite{2} in the context of a mean field approximation using the two-site Hubbard model \cite{4}.

The aim of the present contribution is to investigate how the electron dynamics is affected by coupling with bosonic degrees of freedom, assumed in thermal equilibrium. Recently van Kampen \cite{5} proposed an exactly solvable model which allows one to obtain an exact analytical solution of the reduced dynamics of the system of interest when coupled to a set of bosonic modes in thermal equilibrium. This is always possible provided the coupling term commutes with the free Hamiltonian of the subsystem to be described. A physically relevant realization of such situation for the organic charge-transfer salts is the following.

The microscopic model to describe the one-electron states of the ion-radical dimer of the CT salts interacting with the collective modes of internal vibration of the molecule is given by the Hamiltonian

\begin{equation}
\hat{H} = \hat{H}_e + g\hat{N} \sum_{i=1}^{M} (\hat{b}_i^\dagger + \hat{b}_i) + \sum_{i=1}^{M} \hbar \omega_i \hat{b}_i^\dagger \hat{b}_i,
\end{equation}

where \(\hat{H}_e\) is the fermionic Hamiltonian in the presence
of an external magnetic field chosen in the $z$ direction,
\[
\hat{H}_e = \sum_{i=1}^{2} \sum_{\sigma=\pm 1} (E + \sigma \lambda B_z) \hat{n}_{i\sigma} + \sum_{\sigma=\pm 1} T(\hat{a}_{i\sigma}^\dagger \hat{a}_{2\sigma} + \hat{a}_{2\sigma}^\dagger \hat{a}_{1\sigma}) + U \sum_{i=1}^{2} \hat{n}_{i\uparrow} \hat{n}_{i\downarrow},
\]
(2)

$E$ is the diagonal part of the kinetic energy, $T$ is the so-called hopping integral, $U$ is the effective intraatomic Coulomb interaction, $\lambda = -g \mu_B / 2$, where $g$ is the Landé factor, and $\mu_B$ is the Bohr magneton. The fermionic operator $\hat{a}_{i\sigma}^\dagger$ (a) creates (destroys) an electron at site $i$ and spin $\sigma$ and satisfies the anticommutation relations
\[
\{ \hat{a}_{i\sigma}, \hat{a}_{j\sigma}^\dagger \} = \delta_{ij} \delta_{\sigma\sigma'} \mathbf{1}, \quad \{ \hat{a}_{i\sigma}, \hat{a}_{j\sigma} \} = 0.
\]
(3)

The bosonic operator $\hat{b}_{i\sigma}^\dagger$ ($\hat{b}_{i\sigma}$) creates (destroys) a vibronic mode with frequency $\omega_i$. We are assuming that there are $M$ distinct vibronic modes. The bosonic operators satisfy the commutation relations
\[
\{ \hat{b}_{i\sigma}, \hat{b}_{j\sigma}^\dagger \} = \delta_{ij} \mathbf{1}, \quad \{ \hat{b}_{i\sigma}, \hat{b}_{j\sigma} \} = 0.
\]
(4)

In Eq. (1), $\hat{N}$ is the total number of fermions operator,
\[
\hat{N} = \sum_{i=1}^{2} \sum_{\sigma=\pm 1} \hat{n}_{i\sigma}.
\]
(5)

We obtain the coupling term in Hamiltonian (1) from the Hamiltonian of Ref. [1] when the wavelength associated with the vibronic modes is much larger than the distance between the monomers.

The Hamiltonian $\hat{H}_e$ commutes with the total Hamiltonian $\hat{H}$, as required to obtain an exact analytical expression for the reduced dynamics of the electronic subsystem.

Let us first consider the case of uncorrelated initial condition, i.e.,
\[
\rho(0) = \left( \sum_{n,n'} f_{n,n'} |n\rangle \langle n'| \right) \otimes \prod_{i=1}^{M} \frac{e^{-\beta \hbar \omega_i \hat{b}_{i \downarrow}}} {Z},
\]
(6)

where
\[
Z = \text{Tr}[e^{-\beta \hbar \omega_i \hat{b}_{i \downarrow}}].
\]

The basis for the electronic system has four labels corresponding to the number of the space site $i$ of the electron, $i = 1, 2$, and the spin $\sigma$, $\sigma = \uparrow, \downarrow$; $\hat{n} \equiv (n_{1\uparrow}, n_{1\downarrow}, n_{2\uparrow}, n_{2\downarrow})$.

The time evolution of the initial density operator given by Eq. (6), under the dynamics of Eq. (1), is
\[
\rho(t) = e^{(i/\hbar) \hat{H}t} \rho(0) e^{-(i/\hbar) \hat{H}t},
\]
(7)

where $\hat{H}$ is the Hamiltonian (1) of the whole system.

Using Lie algebraic techniques [6] we compute the electronic effective density at a later time by taking the trace over the oscillator degrees of freedom,
\[
\rho_S(t) = \mathcal{U}(t) \left( \mathcal{D}(\rho_S(0)) \right),
\]
(8)

where $\mathcal{U}(t)$ represents unitary evolution and $\mathcal{D}(\cdot)$ is essentially nonunitary. $\mathcal{U}(t)$ represents a time dependent Hamiltonian contribution
\[
\mathcal{U}(t) = \exp \left( -\frac{i}{\hbar} \int_{0}^{t} \sigma \left[ \hat{H}_S - \hbar \hat{N}^2 R(\sigma), \cdot \right] \right),
\]
(9)

where we have employed the same notation convention as in Ref. [7] for superoperators. Thus the unitary part of the time evolution of the fermionic subsystem, acquires a new contribution due to the dynamics of the bosonic modes, given by
\[
\hat{H}_{\text{eff}}(t) = \hat{H}_e - R(t) \hat{N}^2,
\]
(10)

with
\[
R(t) = \sum_{i=1}^{M} \frac{c_i^2}{\omega_i} (1 - \cos \omega_i t).
\]

Note that $R(t)$ depends on the coupling constants $c_i$ and the frequencies $\omega_i$ of the vibronic modes. Since we have a finite number of vibronic modes, the function oscillates in time within the interval
\[
\left[ 0, 2 \sum_{i=1}^{M} \frac{c_i^2}{\omega_i} \right].
\]

The time-dependent term that appears in the effective Hamiltonian (10) leaves a shift in the energy spectrum of the Hamiltonian $\hat{H}_e$ which is proportional to the square of the total number of fermions. This justifies the mean field assumption of Ref. [2]. It shows moreover that the shift in the energy spectrum is different for each Fock subspace, and it is characterized by the total number $\hat{N}$ of electrons in the electronic
subsystem. Also, although the effect of this unitary evolution on the spectrum is the addition of a constant, there will be a new process in the Hamiltonian operator, since $\hat{N}^2 = \hat{n}_1 + \hat{n}_2 + 2\hat{n}_1 \cdot \hat{n}_2$. We are using the definition $\hat{n}_i = \sum_{\alpha=1,2} \hat{a}_{\alpha i}$. The last term will give a contribution to a process involving different sites and the same spin. The second term on the r.h.s. of Hamiltonian (10) gives a nontrivial contribution to the dynamics when the quantum state of the electronic subsystem is not restricted to a single Fock subspace.

The nonunitary contribution $D(t)$ is responsible for the decoherence and recoherence of the subsystem of interest. It is given by

$$D(t) = \exp\{-\lambda(t) (\hat{N}^2 - 2\hat{N} \cdot \hat{\hat{N}} + \hat{\hat{N}}^2)\}.$$  \hspace{1cm} (11)

where

$$\lambda(t) = \sum_{i=1}^{M} \frac{c_i^2}{\omega_i} (1 - \cos \omega_i t) \coth(\frac{1}{2} \beta \hbar \omega_i).$$

For a finite number of vibronic modes, the function $\lambda(t)$ has an oscillatory behavior and varies in the interval

$$\left[0, 2 \sum_{i=1}^{M} \frac{c_i^2}{\omega_i} \coth(\frac{1}{2} \beta \hbar \omega_i)\right].$$

The discussion of the coupling of the electronic modes to lattice phonons is entirely analogous to the case of vibronic modes. The main difference between these two cases is that the latter presents a continuous distribution of frequencies. The Hamiltonian that describes this system is similar to Hamiltonian (1). In this case, the operator $\hat{b}_i (\hat{b}_i^\dagger)$ destroys (creates) a lattice phonon and the sum over $i$ is replaced by an integral. The previous results continue to be valid, but now it is meaningful to split $\lambda(t)$ as $\lambda(t) = \lambda^0(t) + \lambda^\beta(t)$, as in Ref. [9], with

$$\lambda^0(t) = \int_0^\infty \frac{D(\omega)}{\omega} (1 - \cos \omega t)$$ \hspace{1cm} (12)

and

$$\lambda^\beta(t) = \int_0^\infty \frac{D(\omega)}{\omega} \frac{1 - \cos \omega t}{e^{\beta \hbar \omega} - 1},$$ \hspace{1cm} (13)

where $D(\omega)$ corresponds to the spectral density of the lattice [8]. The first of these terms, Eq. (12), corresponds to zero temperature and the second, Eq. (13), to finite temperature $\beta$. Their behavior is qualitatively different as can be verified in Ref. [9]. These parameters control the rate at which the off diagonal (correlations) elements vanish. The vanishing of the off-diagonal elements in the $N$ representation justifies the usual assumption of a unitary evolution within each of these subspaces. The functions $R(t)$, $\lambda^0(t)$ and $\lambda^\beta(t)$ present well-defined asymptotic ($t \rightarrow \infty$) behaviors, that are not oscillatory and depend on the low frequency part of the spectral density $D(\omega)$.

We next turn to a class of correlated initial conditions for which it is still possible to find analytical results for the effective subsystem’s dynamics. We assume that the full system is in equilibrium at a given temperature and after this state is reached the electronic density is, by some external process, taken to a nonequilibrium state. This situation can be mathematically implemented by the following class of initial conditions,

$$\rho(0) = e^{\beta H/2} \rho^0(0) e^{\beta H/2}.$$ \hspace{1cm} (14)

Taking the trace over the bosonic modes leaves the following mixed state for the fermions,

$$\rho^f(0) = A e^{-\beta H_{\text{eff}}(0)}$$ \hspace{0.5cm} \times \{\exp[-\lambda'(\infty) (\hat{N}^2 - 2\hat{N} \cdot \hat{N} + \hat{N}^2)\} \rho^f(0)\} \hspace{0.5cm} \times e^{-\beta H_{\text{eff}}(0)},$$ \hspace{1cm} (15)

where $A$ is a normalization constant and

$$\lambda'(\infty) = \sum_i \frac{c_i^2}{\omega_i} \tanh(\frac{1}{2} \beta \hbar \omega_i).$$

$H_{\text{eff}}(0)$ is the effective Hamiltonian (10) at $t = 0$.

Proceeding as before, we can obtain the effective dynamics for this class of initial conditions and show that the decoherence process is now slower as compared to the first one, since the initial system is already a mixed state. The time evolution of $\rho^f(0)$ is given by

$$\rho^f(t) = A e^{-iH_{\text{eff}}(0)/\hbar} \exp\{-[\lambda(t) - \lambda'(t)]$$ \hspace{1cm} \times (\hat{N}^2 - 2\hat{N} \cdot \hat{N} + \hat{N}^2)\} \rho^f(0) e^{iH_{\text{eff}}(0)/\hbar},$$ \hspace{1cm} (16)

$\lambda(t)$ is given by Eqs. (12) and (13) and
\[ \lambda'(t) = \sum_i \frac{\omega_i^2}{\omega_i} (1 - \cos \omega_i t) \tanh \left( \frac{1}{4} \beta \hbar \omega_i \right). \]

Note that \( \lambda(t) > \lambda'(t) \), so that their difference is positive for all \( t \). A comparison between Eqs. (8) and (11) and Eq. (16) shows that the rate at which thermal equilibrium is achieved is slower for the correlated initial conditions. The decoherence process is sensitive to the lattice’s spectral density too and therefore experiments measuring relaxation time scales can be useful to unveil various aspects of the intricate dynamics of organic charge-transfer salts.

We should say that when we have few bosonic degrees of freedom coupled (vibronic modes) to the electronic subsystem, we have a quasi-periodic decoherence–recoherence oscillatory behavior the amplitude of which will be smaller than that of the factorized initial state.

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References