A STUDY OF ELECTRON TRANSFER USING A THREE-LEVEL SYSTEM COUPLED TO AN OHMIC BATH

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Abstract

Electron transfer is studied using a multi-level system coupled to a bosonic bath. Two-body correlation functions are obtained using both exact enumeration of spin paths and Monte Carlo simulation. We find that the phase boundary for the coherent-incoherent transition lies at a smaller friction in the asymmetric two-level model than in the symmetric two-level model. A similar coherent-incoherent transition is observed for three-level system.

1 Introduction

Electron transfer in liquids is an important phenomenon in chemistry and physics. Following Marcus' picture [1], we use the spin boson model, which is a multi-level system coupled to a harmonic bath. The case of symmetric two-level model has been studied by many people, in the context of the Kondo problem and electron transfer in liquids[2]. It is not an exactly solvable model, except for the case of an adiabatic bath. In Section 3, we analyze the model with Feynman path integral which we evaluate with the exact enumeration of spin paths and Monte Carlo simulation. In Section 4, we present the results for an asymmetric two-level system and compare the results with the symmetric two-level system [3, 4, 5]. We also discuss the results for a three-level system. Finally, in Section 5, we summarize our results.

2 Model Hamiltonian

The Hamiltonian which defines our system is given by:

$$H = H_0 + H_B + H_{int}. \tag{1}$$

Here H_0 is the the Hamiltonian for the free three-level system,

$$H_0 = \begin{pmatrix} E_1 & J_{12} & J_{13} \\ J_{12} & E_2 & J_{23} \\ J_{13} & J_{23} & E_3 \end{pmatrix}, \tag{2}$$

where E_i gives the energy for an electron localized on site i, and J_{ij} gives the electronic coupling between sites i and j. H_B is the Hamiltonian of the harmonic bath. H_{int} is the coupling between the three-level system and the bath, and is given by

$$H_{int} = \mathcal{E}_{12}\sigma_{12} + \mathcal{E}_{23}\sigma_{23} + \mathcal{E}_{13}\sigma_{13}. \tag{3}$$

Here σ_k $(k = (12), (23), (13))$ is defined by

$$\sigma_{12} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \sigma_{23} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}, \sigma_{13} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \tag{4}$$

and the field $\mathcal{E}_k$ is a linear combination of the bath modes, $\mathcal{E}_k = \sum_j c_j^k x_j$. Harmonic baths linearly coupled to spin systems can be defined by the spectral density:

$$J^{kl}(\omega) = \frac{\pi}{2} \sum_j \frac{c_j^k c_j^l}{m_j \omega_j} \delta(\omega - \omega_j). \tag{5}$$

Here, k and l are the pairs, (12), (23) or (13). For electron transfer in a liquid, an Ohmic spectral density gives a good model for the environment surrounding the electron. [2, 4]

$$J^{kl}(\omega) = \eta^{kl} \omega \exp(-\omega/\omega_c^{kl}) \tag{6}$$

3   Numerical Methods

The quantity we are interested in is the following two-body time correlation function.

$$< n_1(0) n_1(t) > = \frac{1}{Z} Tr \exp(-\beta H) n_1 \exp(iHt/\hbar) n_1 \exp(-iHt/\hbar), \tag{7}$$

where n_1 is the population operator for being on site 1. Since H_{int} does not commute with H_0 and H_B, we use the following Suzuki-Trotter formula to do the path integral evaluations.

$$\exp(-\beta H) = \lim_{p \to \infty} \{\exp(-\beta H_0/p) \exp(-\beta H_B/p) \exp(-\beta H_{int}/p)\}^p. \tag{8}$$

Expanding this equation in a path integral representation and performing the Gaussian bath integrals analytically leads to:

$$< n_1(0) n_1(t) > = \frac{1}{Z} \sum_{\{\sigma_i\}} \exp(\varphi(\{\sigma_i\})) n_1(\sigma_{p+1}) n_1(\sigma_{p+q+1}), \tag{9}$$

where p and q, sometimes called Trotter numbers, are the numbers of partitions the path has been divided into the thermal and real time part of the path. The sum goes over 3^N states of S=1 Ising system, where N is the total Trotter number, $N = p + 2q$. The action φ in Eq. 9 consists of two parts,

$$\varphi = \varphi_0 + \varphi_{int}. \tag{10}$$

The first part, φ_0, comes from the free three-level system Hamiltonian, and second part, φ_{int}, results from the interaction between the system and the bath which we have already integrated out. The action φ_{int} is given by:

$$\varphi_{int} = \frac{1}{2} \sum_{ij} \sum_{kl} f_k(\sigma^i) f_l(\sigma^j) \chi_{ij}^{kl}, \tag{11}$$

where $f_k(\sigma^i)$ is a quadratic function of σ^i, and the χ_{ij}^{kl} is expressed by the spectral density $J^{kl}(\omega)$ as follows.

$$\chi_{ij}^{kl} = \frac{\hbar}{\pi} \int_0^\infty J^{kl}(\omega) \cosh \frac{\omega}{2} (\Delta_{ij} - \Delta_{ji}). \tag{12}$$

Here,

$$\Delta_{ij} = \sum_{k=i}^{j-1} \Delta_k, \tag{13}$$

where $\Delta_k = \beta/p$, $-it/q$ or it/q, depending on the location of σ^k on the path.

Thus, the original three-level system coupled to a bath is now transformed into a S=1 Ising model with infinite-range interactions. This model is exactly solvable for the case of an adiabatic bath[6]. This case corresponds to Ising magnets in a very slow Gaussian field. In the general case, the analytic solution of this model is unknown.

To do the numerical calculation on this model for small Trotter number, we used the exact enumeration of the path integral by adding all the 3^N states of the Ising spin system. For example, exact enumeration of N=17 spins (1.29×10^8 states) takes 3 minutes on a Cray X-MP.

We also used Monte Carlo simulation. Some filtering method[5] was necessary to overcome the so-called sign-problems [7, 8, 9, 10, 11, 12], which is often seen in quantum calculations of fermionic systems or spin models.

4 Results

To check the validity of our calculations, we have studied a free three-level system (i.e., coupling between the spin system and the bath is turned off), and a three-level system coupled to an adiabatic bath. For these systems, we computed the following correlation functions.

$$C_1(t) = Re < n_1(0)n_1(t) >, C_2(t) = Re < n_1(0)n_2(t) >, C_3(t) = Re < n_1(0)n_3(t) > \tag{14}$$

Our results give good agreement with analytic results in these limits.

For the special case of an asymmetric two-level system, we have calculated the time-correlation functions, and compared the results with the symmetric case[4]. Figure 1 shows the results for an asymmetric case with the parameters $E_1 = 0$, $E_2 = 2K$, $E_3 = \infty$, and $J_{12} = -K$, $J_{13} = J_{23} = 0$. We find from Figure 1 that the coherent-incoherent transition occurs around

$\eta/\hbar = 0.4$, or $\alpha = 2\eta/\hbar\pi = 0.25$. For a symmetric two-level system[4], the phase boundary for this temperature was at $\alpha = 0.4$. Thus, the whole phase boundary is expected to lie at smaller α for the asymmetric case than for the symmetric case. In the asymmetric case, the symmetry is already broken, thus the coherence is easier to break than in the symmetric case.
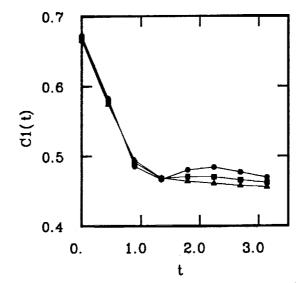

FIG. 1 The correlation function $C_1(t)$ for an asymmetric two-level model of $E_2 = 2K$, $\beta K = 2.5$, with $\eta/\hbar = 0.3$ (circles), 0.4(squares), 0.5 (triangles) obtained by exact enumeration of spin paths with p=2 and q=7.
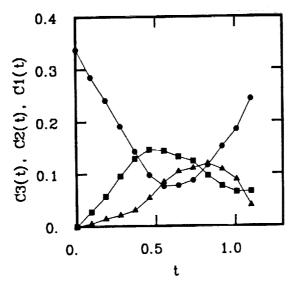

FIG. 2 The correlation functions $C_1(t)$ (circles), $C_2(t)$ (squares) and $C_3(t)$ (triangles) for a three-level system in the coherent region, $J_{12} = J_{23} = -2K$, $J_{13} = -K$, $E_1 = 0.5K$, $E_2 = K$, $E_3 = 0$, $\beta K = 0.25$, $t_c^{13} = 2$, $t_c^{12} = t_c^{23} = 0$, $(t_c = K/\omega_c)$, $\eta^{13}/\hbar = 1$, $\eta^{12}/\hbar = \eta^{23}/\hbar = 0$.

Figures 2 and 3 show results for a three-level system. The calculations were done by Monte Carlo simulation, with the Trotter numbers p=2 and q=10. As has been found in quantum Monte

Carlo simulation of spin systems[8], for systems having sign problems, it is usually more efficient to define 1 Monte Carlo step (MCS) to be a small subset of all the possible flips than to define it as all the possible flips. In our simulation, we define 1 MCS as 1 single spin-flip, 1 double spin-flip, 1 global spin-flip (i.e., flips all the spins), and 1 spin-flip of random length. We determine whether the spins should be flipped by the standard Metropolis algorithm, using the modulus of the complex weight $\exp(\varphi)$ for the transition probability. In this way, we have carried out simulation of 10^6 MCS, taking about 14 minutes on the Cray X-MP. To estimate the degree of sign cancellation, we measured the quantity r, the remaining ratio (related to the negative ratio defined in [8]).

$$r = \frac{Z_+ - Z_-}{Z_+ + Z_-} \tag{15}$$

Here Z_+ denotes the sampled sum of the positive real parts of the weights, and Z_- denotes the same for absolute values of negative real parts of the weights. If r is small, the cancellation of the signs is large, leading to inaccuracy in the data. If r is large, the cancellation is small, thus giving more accurate results. In this definition, we are ignoring the effect of the cancellation due to the imaginary parts of the weights.
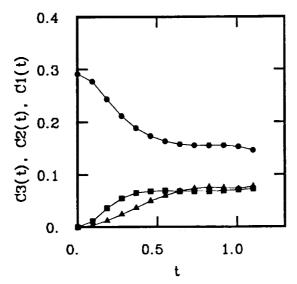

FIG. 3 The correlation functions $C_1(t)$, $C_2(t)$ and $C_3(t)$ for a three-level system in the incoherent region. J_j, E_j and β are same as in Fig. 2. $t_c^{13} = 2$, $t_c^{12} = t_c^{23} = 1$, $\eta^{13}/\hbar = 1$, $\eta^{12}/\hbar = \eta^{23}/\hbar = 2$.

For the free three-level Hamiltonian H_0, we assume the parameters, $J_{12} = J_{23} = -2K$, $J_{13} = -K$, $E_1 = 0.5K$, $E_2 = K$, $E_3 = 0$. This could correspond to a system of redox-sites 1, 2 and 3, where distance between states 1 and 2, or 2 and 3 is shorter than the distance between 1 and 3. The correlation function $< n_1(0)n_2(t) >$ approximately tells the rate of the electron transfer starting at state 1 and reaching 2 after time t. The energy of the state 2, E_2, is assumed to be highest, followed by the energy of the state 1, E_1. Starting from the state 1, the electron moves to state 2, since the exchange J_{12} is stronger than J_{13}, then gradually goes to state 3. In Fig. 3, the bath has the role of dephasing the coherence, preventing the electron population from going back to the

original state. This is a very brief picture of electron transfer over 3 states, with the intermediate state strongly coupled to the initial and terminal states.

As for the effect of the sign cancellations, the remaining ratio r defined in Eq. 15 is 3% for Fig.2 and 13% for Fig.3. The magnitude of error is about 0.1 in Fig.2 and 0.02 in Fig.3 The incoherent case has less effect of the exchange K, thus leading to less sign cancellations.

5 Summary

We have briefly described the numerical calculations of the time-correlation functions of an asymmetric two-level system and a three-level system. For an asymmetric two-level system, we find that the coherent-incoherent transition occurs at smaller friction η than for the symmetric case. For a three-level system, we calculated the population transfer of the electron when there is an intermediate high-energy state. We observed a coherent-incoherent transition similar to the two-level system. Further application of this model will be discussed elsewhere.

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VI.   GROUP REPRESENTATIONS