Spin–spin model for two-level system/bath problems: A numerical study

Cite as: J. Chem. Phys. **111**, 9918 (1999); https://doi.org/10.1063/1.480346
Submitted: 22 July 1999 . Accepted: 15 September 1999 . Published Online: 23 November 1999

Andrei A. Golosov, Stefan I. Tsonchev, Philip Pechukas, Richard A. Friesner, et al.

Spin–spin model for two-level system/bath problems: A numerical study

Andrei A. Golosov, Stefan I. Tsonchev,[a] Philip Pechukas,[b] and Richard A. Friesner
Department of Chemistry, Columbia University, New York, New York 10027

(Received 22 July 1999; accepted 15 September 1999)

We study a new model for treating quantum dissipative systems, in which the bath is modeled as a collection of spins coupled to the system of interest. We develop a quasiclassical method to study this model, approximating the quantum Heisenberg equations by the classical ones, supplemented with stochastic initial conditions carefully chosen so that the results obtained from the classical equations are as close as possible to the quantum results. Using this method we compare the dynamics of such a spin–spin system with that of a spin–boson system, in which the bath is modeled as a collection of harmonic oscillators. We verify numerically that when the system-bath coupling is spread over many bath spins (the Brownian motion limit), the spin–spin model can be mapped on the spin–boson model (although with a temperature dependent spectral density). We also demonstrate that the two dissipative models are qualitatively very different in a non-Brownian motion regime. © *1999 American Institute of Physics.* [S0021-9606(99)51446-3]

I. INTRODUCTION

Dynamical simulation of quantum dissipative systems is a challenging problem in condensed matter physics and chemistry.[1] Such systems consist of a few relevant degrees of freedom coupled to the environment, or bath, whose number of degrees of freedom tends to infinity. Usually it is the properties of the open dissipative system that are of interest. Quantum dissipative systems serve as models for condensed phase dynamical processes such as charge-transfer reactions,[2] vibrational relaxation,[3,4] macroscopic tunneling,[5] etc.

The most commonly used microscopic model of a dissipative system is that of a two- (or a few-) level system linearly coupled to an infinite set of harmonic oscillators. The problem is naturally called the spin–boson problem. This model is convenient to use because the harmonic bath can be integrated out analytically,[6] leading to a path integral expression[7] which is the basis of the quantum Monte Carlo (QMC) method, the only feasible exact method available so far.

Recently, a new model for treating quantum dissipative systems has been developed.[8–10] In it, instead of consisting of harmonic oscillators, the bath is modeled as a collection of spins coupled to the system of interest. Thus, we can naturally call this model the spin–spin model for quantum dissipation. A spin bath naturally arises[9,11] in the problems of magnetic resonance and quantum tunneling of magnetization. It has been shown[12] that the spin–boson model can be viewed as a particular case of the spin–spin model. In the limit of infinite number of bath degrees of freedom weakly coupled to the system (the Brownian motion limit) the two models lead to identical equations of motion, and therefore to identical results. Thus, in that limit, the two models can be mapped into each other. This observation was recently made by Makri[13] as well.

In this paper we consider the dynamics of the simplest dissipative system, a two-level system interacting with a bath. For a harmonic bath there are a number of methods available: semiclassical approximation,[14,15] tensor multiplication algorithm,[16,17] a memory equation approach,[18] and the celebrated noninteracting blip approximation (NIBA).[5] Methods for a spin bath are not so well developed. In this paper we develop a quasiclassical method to treat the dynamics of the spin–spin system. Using this method, we show explicitly—by comparing with the reference data for a spin–boson model—that the correspondence between spin–spin and spin–boson models holds in the Brownian motion limit. On the other hand, we show that outside the Brownian motion regime the two dissipative models are qualitatively very different.

The rest of the paper is organized in the following way. In Sec. II, spin–spin and spin–boson models are discussed. For these models we derive a quasiclassical method in Sec. III. Numerical results are presented in Sec. IV, followed by a discussion in Sec. V, and Sec. VI contains concluding remarks and sketches future directions.

II. SPIN–BOSON AND SPIN–SPIN MODELS

In its simplest form, the spin–boson model represents a two-level system (TLS) linearly coupled to an infinite set of harmonic oscillators which mimic the environment (bath) within the regime of validity of linear response theory. This model has been used extensively to describe chemical reactions at low temperature when tunneling from reactants to products is the major contributor to the reaction rate. The Hamiltonian for this model, for a bath consisting of total of M modes, is[5]

$$H=\epsilon\sigma_z+K\sigma_x+\frac{1}{2}\sum_j^M (p_j^2+\omega_j^2 q_j^2)+\sigma_z\sum_j^M g_j q_j, \qquad (1)$$

[a]Present address: Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260.
[b]Electronic mail: pechukas@chem.columbia.edu

where σ_z and σ_x are Pauli matrices of the TLS, ϵ is a bias, K is a tunneling element between two sites, q_j is the position of the jth bath mode with conjugate momentum p_j and frequency ω_j, and g_j is the coupling strength of the jth bath mode to the TLS. The constant $\hbar$ is assumed to be unity throughout the paper. All information about the bath that is essential for the dynamics of the system can be captured in the compact form of the spectral density function[5]

$$J(\omega)=\frac{\pi}{2}\sum_j \frac{g_j^2}{\omega}\delta(\omega-\omega_j). \tag{2}$$

The Hamiltonian for the simplest spin–spin problem, a TLS coupled to a heat bath of M two-level systems (spin 1/2), is

$$H=\epsilon\sigma_z+K\sigma_x+\sum_j^M \frac{\lambda_j}{2}S_{jx}\sigma_z+\sum_j^M \frac{\omega_j}{2}S_{jz}, \tag{3}$$

where S_{jx} and S_{jz} are the Pauli matrices for the jth bath spin, with Larmor frequency ω_j and coupling strength λ_j. This form of the Hamiltonian naturally arises as a linear coupling simplification of the Hamiltonian presented in the fundamental articles.[10,12]

In the limit of a small λ_j and a large number of bath spins (the so-called Brownian motion limit), the spin–spin system can be mapped onto the spin–boson system.[10,12] The correspondence between two models for the above Hamiltonians is given by the following:[10]

$$\lambda_j^2=\frac{g_j^2}{\frac{\omega_j}{2}\tanh\frac{\beta\omega_j}{2}}, \tag{4}$$

where the $\{\omega_j\}$ are the same for both models.

III. QUASICLASSICAL METHOD

In this section we describe the method we have used in order to obtain results for the dynamics of the quantum dissipative TLS. We will use the Heisenberg equations for the system and bath operators, and we will approximate the quantum Heisenberg equations by the classical ones, supplemented with carefully chosen stochastic initial conditions such that the results obtained from the classical equations are as close as possible to the quantum ones.

The Heisenberg equations for the spin–boson model are

$$\begin{aligned}
\dot\sigma_x&=-2\sum_j g_jq_j\sigma_y-2\epsilon\sigma_y,\\
\dot\sigma_y&=-2K\sigma_z+2\sum_j g_jq_j\sigma_x+2\epsilon\sigma_x,\\
\dot\sigma_z&=2K\sigma_y,\\
\dot q_j&=p_j,\quad j=1,\ldots,M,\\
\dot p_j&=-\omega_j^2q_j-g_j\sigma_z,
\end{aligned} \tag{5}$$

and the same equations for the spin–spin model are

$$\begin{aligned}
\dot\sigma_x&=-\sum_j \lambda_jS_{jx}\sigma_y-2\epsilon\sigma_y,\\
\dot\sigma_y&=-2K\sigma_z+\sum_j \lambda_jS_{jx}\sigma_x+2\epsilon\sigma_x,\\
\dot\sigma_z&=2K\sigma_y,\\
\dot S_{jx}&=-\omega_jS_{jy},\\
\dot S_{jy}&=-\lambda_jS_{jz}\sigma_z+\omega_jS_{jx},\quad j=1,\ldots,M,\\
\dot S_{jz}&=\lambda_jS_{jy}\sigma_z.
\end{aligned} \tag{6}$$

We will average the spin operators $\sigma_x(t)$, $\sigma_y(t)$, and $\sigma_z(t)$ of the system according to $\langle\sigma_z(t)\rangle=\mathrm{Tr}\,\sigma_z(t)\rho(0)$, etc., where $\rho(0)$ is the system-bath density matrix at the initial moment. For a factorized initial density matrix we have

$$\rho(0)=\rho_s(0)\otimes\frac{e^{-\beta H_{\mathrm{bath}}}}{Z}, \tag{7}$$

which corresponds to switching on interactions between the system and a bath which is in equilibrium at the initial time (here H_{bath} is the bath Hamiltonian and Z is its partition function). The most commonly used initial preparation for the system is complete occupation of the ''spin up'' site, so that

$$\langle\sigma_z(0)\rangle=1\quad\text{and}\quad\langle\sigma_{x,y}(0)\rangle=0. \tag{8}$$

In the classical Heisenberg equations, operators are replaced by numbers which can be thought of as the average values of the operators with respect to the initial reduced density matrix. Thus, in the case of the spin–boson problem the quasiclassical approximation amounts to using the initial conditions $(\sigma_x,\sigma_y,\sigma_z)=(0,0,1)$ and sampling the initial coordinates and momenta of the bath oscillators from a Wigner distribution (in the spirit of Stock[14]) obtaining $\langle\sigma_z(t)\rangle$ as an average over classical trajectories. This approach is valid in the adiabatic regime, when the bath dynamics is very slow compared to that of the system and the temperature is high enough that the bath is almost classical.[14]

We may try to make an analogous approximation for the spin–spin problem, so that the averages over trajectories $\langle\sigma_x(t)\rangle_{\mathrm{traj}}$, $\langle\sigma_y(t)\rangle_{\mathrm{traj}}$, and $\langle\sigma_z(t)\rangle_{\mathrm{traj}}$ are as close as possible to the corresponding quantum-mechanical values. To see how to proceed, consider the example of the unbiased two-state system ($\epsilon=0$) coupled to a bath that consists of only one spin with frequency ω and coupling strength λ. For the initial conditions (7) and (8) we can express the averages $\langle\sigma_x(t)\rangle$, $\langle\sigma_y(t)\rangle$, and $\langle\sigma_z(t)\rangle$ as a Taylor series expansion in t,

$$\langle\sigma_\alpha(t)\rangle=\sum_{j=0}^{\infty}\frac{\overline{\sigma_\alpha^{(j)}}t^j}{j!},\quad\alpha=x,y,z. \tag{9}$$

The coefficients $\overline{\sigma_\alpha^{(j)}}$ involve the averages $\langle\sigma_\alpha(0)\rangle$ ($\alpha=x,y,z$).

Let us consider the coefficients $\overline{\sigma_z^{(j)}}$ up to the sixth order. From the quantum-mechanical calculations we obtain [all odd coefficients are zero due to initial conditions (8)]

$$\overline{\sigma_z^{(0)}}=1,$$

$$\overline{\sigma_z^{(2)}} = -\kappa^2,$$
$$\overline{\sigma_z^{(4)}} = \kappa^2(\kappa^2+\lambda^2), \tag{10}$$
$$\overline{\sigma_z^{(6)}} = -\kappa^2(\kappa^4+2\kappa^2\lambda^2+\lambda^4+\omega^2\lambda^2),$$

where $\kappa = 2K$. The reader might be surprised that the expansion coefficients for σ_z do not explicitly depend on temperature, except through the temperature dependence of the parameter λ. (The temperature dependence would appear in the expansion coefficients for σ_x. It would enter there through $\langle S_z(0)\rangle$.) It can be shown through direct diagonalization that the coefficients for σ_z do not depend on temperature only for the case of a single bath spin.

Consider the classical expression for the expansion coefficients. In it we *leave out* all terms containing odd powers of σ_x, σ_y, S_x, and S_y. We do so because these terms will cancel out under the initial conditions that we specify later. The fact that we keep only terms containing even powers of σ_x, σ_y, S_x, and S_y is represented by replacing the ''='' sign with ''→''

$$\overline{\sigma_z^{(0)}} \to \sigma_z,$$
$$\overline{\sigma_z^{(2)}} \to -\kappa^2\sigma_z,$$
$$\overline{\sigma_z^{(4)}} \to \kappa^2(\kappa^2+\lambda^2 S_x^2)\sigma_z, \tag{11}$$
$$\overline{\sigma_z^{(6)}} \to -\kappa^2(\kappa^4+2\kappa^2\lambda^2 S_x^2+\lambda^4 S_x^4+9\omega^2\lambda^2 S_x^2 - 8\omega^2\lambda^2 S_y^2)\sigma_z,$$

where S_α and σ_z denote $S_\alpha(0)$ and $\sigma_z(0)$, respectively.

Comparing Eqs. (10) and (11), we see that if we choose the initial conditions for S_x, S_y to take random values ± 1 with the proper initial averages $\langle S_x\rangle = \langle S_y\rangle = 0$, and if we take $\sigma_z(0) = 1$, the quantum and the classical expansions for $\langle\sigma_z(t)\rangle$ agree through seventh order; the first difference appears in eighth order. (Indeed, if $\omega = 0$ it can be shown that this approach is *exact* to all orders.) In order to get the other components of the spin polarization we apply the same strategy to S_z: $S_z = \pm 1$ with $\langle S_z\rangle = \langle S_z\rangle_{\rm eq}$. As for the system spin σ, it turns out that ''randomization'' of the (x,y) components—$\sigma_{x,y} = \pm 1$ with $\langle\sigma_{x,y}\rangle = 0$—does not improve the results and takes four times as long as a ''standard'' quasiclassical calculation, $\sigma_{x,y} = 0$, so our calculations were done with this standard assignment for the system spin. Generalization of this approach to the case of many bath particles is straightforward.

Note that our classical description of the bath spin is *different* from the conventional one. Our bath spin obeys classical equations of motion but its length is $\sqrt{3}$, *not* one. This is due to the initial conditions for the trajectories: $S_{x,y,z}(0) = \pm 1$.

It is interesting to note that if we make an expansion analogous to (10) and (11) for the harmonic bath case, using the trick of the Wigner distribution for q_j and p_j leads to an expression for the classical $\langle\sigma_z(t)\rangle$ that agrees with the quantum result also through seventh order.

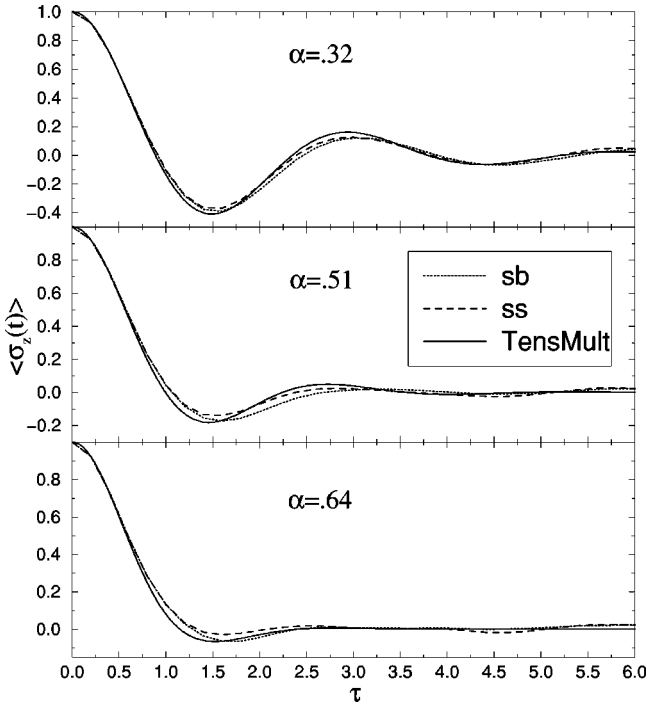

FIG. 1. The transition from the coherent to the incoherent regime at $T = 0.625$, $\omega_c = 2.5$, $K = 1$ (parameters from Ref. 23). Quasiclassical calculations for spin–boson (sb) and spin–spin (ss) models are compared with tensor multiplication results (TensMult). The time step for the quasiclassical calculations was 0.05.

IV. NUMERICAL DETAILS

In this section we calculate the dynamics of a spin–spin system by the method described in the preceding section and compare it with results for the spin–boson system. First we consider the Brownian motion limit, where the spin–spin and spin–boson models are equivalent. We show that our results are in excellent agreement with the ones obtained by QMC[19] or by the tensor multiplication algorithm of Makarov and Makri.[16,17] Then we demonstrate that the two dissipative models are qualitatively very different in a non-Brownian motion regime.

We have applied the quasiclassical method to the spin–spin model in the Brownian motion limit with ohmic spectral density

$$J(\omega) = \frac{\pi}{2}\alpha\omega\exp(-\omega/\omega_c), \tag{12}$$

where α is a Kondo parameter and ω_c is a cutoff frequency. This form of $J(\omega)$ has been used frequently in the literature because a compact analytical solution given by NIBA can be obtained, and in addition, the spin–boson system with this spectral density exhibits interesting behavior,[5] such as a transition from coherent to incoherent dynamics with increasing α, symmetry breaking at zero temperature, etc.

We have calculated the population dynamics $P(t) = \langle\sigma_z(t)\rangle$, which is of the most interest for the study of the chemical reaction dynamics. The results have been compared with QMC[19] and tensor multiplication[16,17] calculations. We have tested our method for several sets of parameters spanning the transition from coherent to incoherent dynamics at

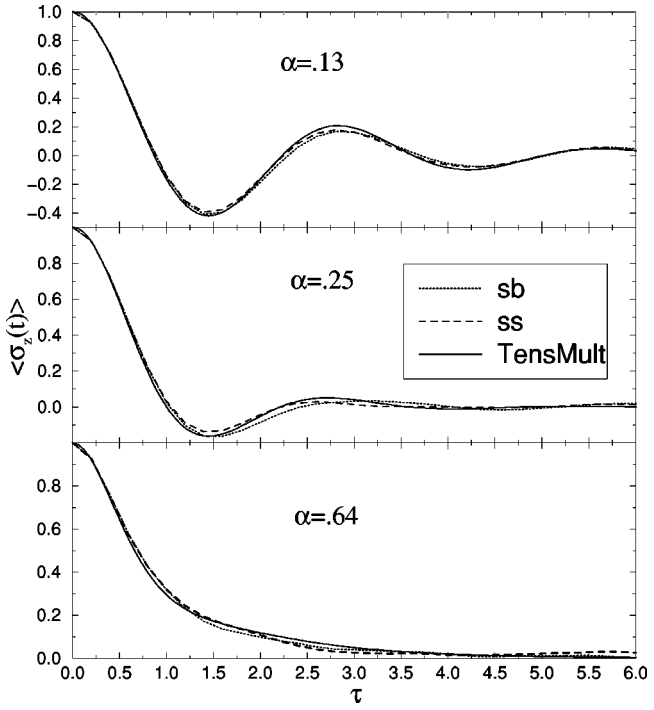

FIG. 2. The transition from the coherent to the incoherent regime at $T=2.5$, $\omega_c=2.5$, $K=1$ (parameters from Ref. 23). Quasiclassical calculations for spin–boson (sb) and spin–spin (ss) models are compared with tensor multiplication results (TensMult). The time step for the quasiclassical calculations was 0.05.

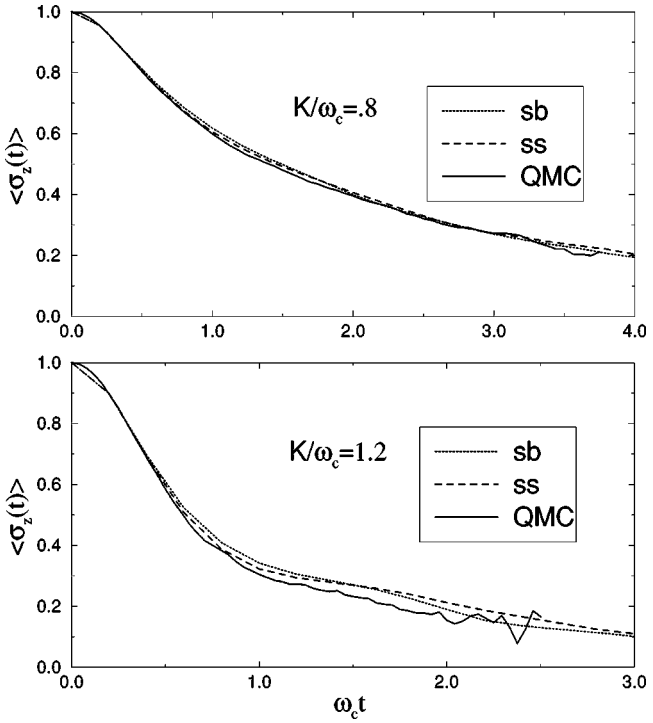

FIG. 3. Simulations for strong system-bath coupling $\alpha=2$, $T/\omega_c=4.0$. Quasiclassical calculations for spin–boson (sb) and spin–spin (ss) models are compared with the ones obtained by QMC (from Ref. 19). The time step for the quasiclassical calculations was 0.01.

both low and high temperatures (Figs. 1 and 2) and including strong system-bath coupling ($\alpha=2$) (Fig. 3).

The harmonic bath was discretized with $M=400$ harmonic modes with frequencies uniformly distributed between 0 and $10\omega_c$ and couplings g_j obtained from integration of both sides of Eq. (2) by the trapezoidal rule and assignment of g_j to the term containing $J(\omega_j)$. After that the frequencies for the spin bath were taken to be the same as the ones for the harmonic one and the couplings λ_j for the spin–spin model were obtained from relation (4). In addition, in the study of the non-Brownian motion regime (see below), the number of discretization modes was varied. The classical Heisenberg equations with appropriate initial conditions (see preceding section) were solved by the third-order Runge–Kutta method. We ran 2500 trajectories in order to obtain converged results, which took about 2–10 minutes of CPU time on PowerPC (604e/200 MHz) under AIX 4.1. The parameters for the calculation by the tensor multiplication scheme are given elsewhere.[18]

V. DISCUSSION

From the figures we see that, overall, the results of the spin–spin model are excellent. In most cases they practically coincide with the exact QMC or tensor-multiplication scheme. This is both a confirmation that the relation (4) is valid and a demonstration that the quasiclassical method works quite well. The latter is probably due to the randomization of nuclear phases, as was studied in detail by Stock.[14] (In fact, Fig. 3 presents calculations for the same parameter regimes as in Fig. 3 of Stock.[14] Our results are in much better agreement with exact calculations, even though for a spin–boson model our quasiclassical method is equivalent to his self-consistent-field approach. This discrepancy is due to[20] a choice of initial conditions in Ref. 14 different from the product initial condition 7; that is, we suspect that Stock's results are better than he claimed.)

In a non-Brownian motion regime, the nature of the bath becomes very important. In order to see that, consider the adiabatic limit where the quasiadiabatic method is expected to work best. By decreasing the number of discretization modes, we can see that the difference in dynamics of the system spin due to the difference in the nature of baths (spins or harmonic oscillators) becomes more and more apparent (Fig. 4), especially for a single-particle bath (Fig. 5). For example (Fig. 5), while polarization of the spin coupled to a harmonic bath reaches quasiequilibrium (the term ''quasi'' will be explained below), the dynamics of the spin coupled to a spin bath does not exhibit decay at all. Instead, we observe a so-called ''spin-locking,'' when the dynamics of the main spin is ''slaved'' by the dynamics of the bath spin. In the case of very strong coupling, this ''slavery'' results in the localization of the spin polarization in the vicinity of its original value. This property could perhaps be useful for the construction of storage devices.

Let us analyze the adiabatic limit more closely for a spin coupled to a bath consisting of one particle (spin or harmonic oscillator). Consider the strict adiabatic limit, with $\omega\to 0$, so that the classical solvation energy[21] $S_{\mathrm{eff}}=(1/\pi)\int d\omega\,[J(\omega)/\omega]=\mathrm{const}$. In that limit, the correspondence relation (4) becomes $\lambda^2=8S_{\mathrm{eff}}/\beta$. If the popula-

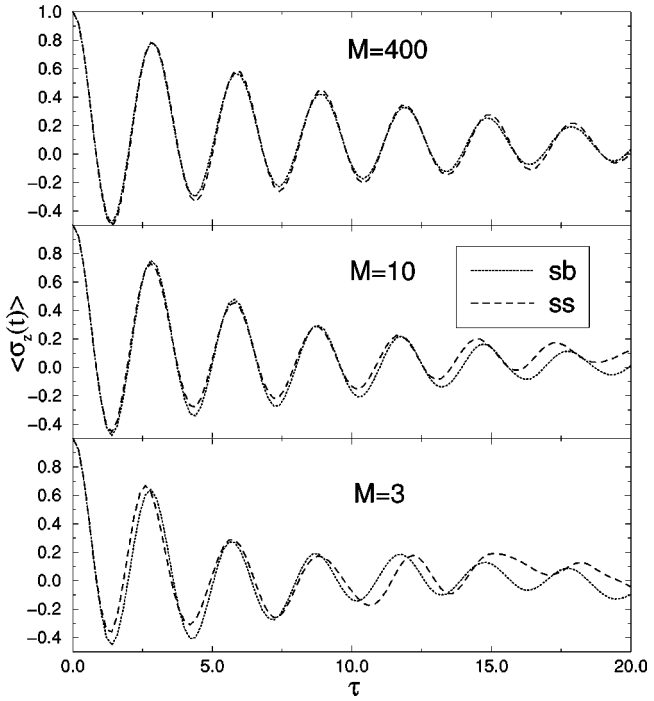

FIG. 4. The population dynamics of spin–spin (ss) and spin–boson (sb) models ($\alpha=20$, $T=0.2$, $K=1$, $\omega_c=0.1$) compared for various bath particle numbers M. The time step for the quasiclassical calculations was 0.05.

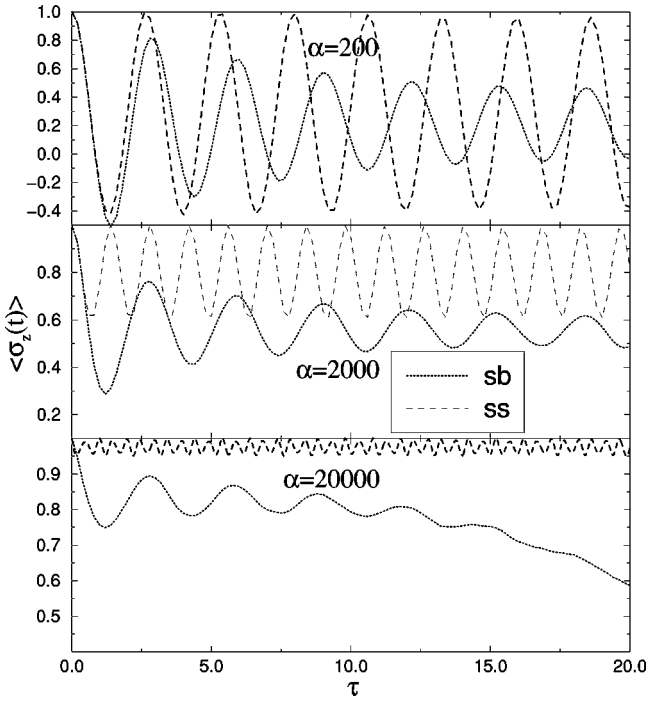

FIG. 5. The population dynamics of spin–spin (ss) and spin–boson (sb) models in the near-adiabatic limit ($T=0.2$, $K=1$, $\omega_c=0.01$) compared for various values of the coupling strength α. The time step for the quasiclassical calculations was 0.05.

tion dynamics of a bare two-level system ($H=K\sigma_x+\epsilon\sigma_z$) is given by $P(t;\epsilon)$,

$$P(t;\epsilon)=\frac{K^2\cos(2\sqrt{K^2+\epsilon^2}t)+\epsilon^2}{K^2+\epsilon^2}, \tag{13}$$

then it can be easily shown (by direct diagonalization) that in the strict adiabatic limit the population dynamics of the spin coupled to a bath spin with the coupling strength λ will be given by

$$P_{\rm ss}(t)=P(t;\lambda/2). \tag{14}$$

The analogous expression for a spin–boson model is[21,22]

$$P_{\rm sb}(t)=\frac{1}{\sqrt{\pi}}\int_{-\infty}^{\infty}dx\,e^{-x^2}P\left(t;\sqrt{\frac{4S_{\rm eff}}{\beta}}x\right). \tag{15}$$

From Eqs. (13) and (14) we see that the reduced dynamics for the spin–spin model is just restricted oscillations around some value. As the system-bath coupling increases, the oscillations get more and more suppressed, so that in the limit of infinite coupling the system spin becomes localized in its initial state.

From the analogous expression (15) for a spin–boson model we see that, due to averaging over a Gaussian distribution, the amplitude of oscillations decay over time, so that the system reaches *quasi*equilibrium. This is a pure dephasing decay, since there is no energy loss in this case and therefore not true dissipation. Hence the system reaches not the equilibrium in thermodynamical sense, but rather *quasi*-equilibrium. Distributing the system-bath coupling among many bath spins leads to a dephasing as well (Fig. 4).

VI. CONCLUSIONS

In this paper we have studied a new model for quantum dissipative systems, in which the bath is by spins instead of harmonic oscillators. This bath model naturally arises in problems of magnetic resonance, quantum tunneling of magnetization, quantum computing, etc.

We have studied the case of a single spin coupled to a spin bath, and we have developed a quasiclassical method for calculating the reduced dynamics of the spin–spin system. Using this method we have compared the dynamics of a spin–spin system with that of a spin–boson system.

We have confirmed numerically that when the system-bath coupling is spread over many bath spins (the Brownian motion limit), the spin–spin model can be mapped on the spin–boson model (although with a *temperature dependent* spectral density). Also, the comparison in the Brownian motion limit shows that the quasiclassical method works quite well for the cases studied here.

We have also considered a non-Brownian motion regime where the difference between the two bath models is expected to matter. For example, when the system-bath coupling is no longer diluted among many bath spins, the dynamics of a spin coupled to a few spins does not exhibit dephasing, in contrast with that of a spin coupled to a few harmonic modes. Instead, the reduced dynamics of a spin–spin system with very few bath spins exhibits ''spin–locking:'' the dynamics of the system spin is ''slaved'' by the dynamics of the bath spins. In the case of strong system-bath coupling the system becomes more and more localized in its initial state. This could be of practical importance in the construction of storage devices.

Although the model presented here uses very simple type of coupling, it can be generalized to include hyperfine or dipole–dipole interactions. These interactions are at the heart of NMR and EPR and are also thought to be important[9] in recent experiments on quantum tunneling of magnetization.

Finally, we would like to emphasize that the quasiclassical methodology described here—a way of obtaining proper initial distributions for classical variables of motion in order to reproduce a quantum-mechanical result—is not restricted to only spin–spin or spin–boson models.

ACKNOWLEDGMENTS

We thank Goran Krilov for proofreading of the paper and Chi Mak for his QMC raw data. This work was supported by DOE Grant No. DE-FG02-90ER14162 to R.A.F. and NSF Grant No. CHE-9633796 to P.P.

[1] U. Weiss, *Quantum Dissipative Systems* (World Scientific, Singapore, 1993).
[2] J. Ulstrup, *Charge Transfer Processes in Condensed Media* (Springer, New York, 1979).
[3] S. A. Egorov and J. L. Skinner, J. Chem. Phys. **105**, 7047 (1996), and references therein.
[4] J. S. Bader and B. J. Berne, J. Chem. Phys. **100**, 8359 (1994).
[5] A. J. Leggett, S. Chakravarty, A. T. Dorsey, M. P. A. Fisher, A. Garg, and W. Zwerger, Rev. Mod. Phys. **59**, 1 (1987).
[6] R. P. Feynman and A. R. Hibbs, *Quantum Mechanics and Path Integrals* (McGraw-Hill, New York, 1965).
[7] R. P. Feynman and F. L. Vernon, Ann. Phys. (N.Y.) **24**, 118 (1963).
[8] N. D. Mermin, Physica A **177**, 561 (1991).
[9] P. C. E. Stamp, in *Tunneling in Complex Systems* (World Scientific, Singapore, 1998), and references therein.
[10] S. I. Tsonchev, Ph.D. thesis, Columbia University (1997). This thesis introduces a novel binary-collision model for quantum Brownian motion and shows that it is equivalent to a particle/spin bath problem.
[11] C. P. Slichter, *Principles of Magnetic Resonance* (Springer, New York, 1990), third ed.
[12] S. I. Tsonchev and P. Pechukas, Phys. Rev. E (submitted).
[13] N. Makri, J. Phys. Chem. B **103**, 2823 (1999).
[14] G. Stock, J. Chem. Phys. **103**, 1561 (1995).
[15] X. Sun and W. H. Miller, J. Chem. Phys. **106**, 916 (1997).
[16] N. Makri and D. E. Makarov, J. Chem. Phys. **102**, 4600 (1995).
[17] N. Makri and D. E. Makarov, J. Chem. Phys. **102**, 4611 (1995).
[18] A. A. Golosov, R. A. Friesner, and P. Pechukas, J. Chem. Phys. **110**, 138 (1999).
[19] R. Egger and C. H. Mak, Phys. Rev. B **50**, 15210 (1994).
[20] G. Stock (personal communication).
[21] B. Carmeli and D. Chandler, J. Chem. Phys. **82**, 3400 (1985).
[22] A. Lucke, C. H. Mak, R. Egger, J. Ankerhold, J. Stockburger, and H. Grabert, J. Chem. Phys. **107**, 8397 (1997). In Eq. (6) of this reference, substitute the distribution function from Eq. (4) which corresponds to the product initial preparation.
[23] C. H. Mak and D. Chandler, Phys. Rev. A **44**, 2352 (1991).