9360 J. Phys. Chem. A **1998,** *102,* 9360−9366

# Semigroup Representations, Site Couplings, and Relaxation in Quantum Systems

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*Received: March 2, 1998; In Final Form: June 29, 1998*

The semigroup formalism permits a general description of relaxation processes in quantum mechanical systems coupled to Markovian baths. From its definition, the semigroup formalism should be expressed in terms of the dissipative and relaxation coupling of the eigenstates of the quantum system to the bath modes. Often, for convenience both in calculation and in physical interpretation, it is more straightforward to couple local states of the quantum mechanical system to the bath. Within a simple two-site system, we examine the generalities of these two different coupling schemes, noting situations in which they are the same and situations for which substantial differences occur.

## I. Introduction

Quantum mechanical systems in which the states are few in number generally exhibit multiply periodic dynamics and do not show irreversible approaches to equilibrium. When such systems interact with dense, multilevel environments (classical or quantal), irreversible behavior is seen, and equilibrium is approached. Many formulations exist for describing this bath-related relaxation.[1−3] The various theoretical models for evaluating the properties of this coupled quantum mechanical system−bath problem involve a rich and varied list of techniques. The early theories of relaxation developed by Wangsness and Bloch[4,5] and later extended by Redfield[6,7] grew out of applications of time-dependent perturbation theory to the density matrix formalism. Over the last 20 years, the sophistication and breadth of relaxation theories has blossomed to include techniques such as Feynman path integrals,[8,9] Brownian oscillator models,[10,11] generalized master equations,[12,13] and projection operator techniques.[14] Each of these theories has its own inherent rigor, range of applicability, and interpretation.

Of these relaxation models, perhaps the most widely utilized in the chemical literature has been Redfield theory. For instance, in condensed phase electron transfer (ET), Redfield theory has demonstrated the appropriate regime in which Fermi's Golden Rule is applicable[15] and also predicted some intriguing manifestations of quantum coherences in ultrafast optical spectra.[16] While new advances in Redfield theory have expanded the number of states in the quantum system that can be included in the reduced density matrix,[17,18] there still exist several difficulties in applying it to real chemical systems, including serious concerns about how to partition properly the degrees of freedom included in the system from those in the bath.[17] Relying on the smallness of the system−bath coupling parameters has inherent dangers, including nonphysical behaviors such as negative elements in the propagated density matrix.[19]

One of the more flexible and easily applied theories of relaxation applied to chemical systems is the semigroup methodology.[20−22] The development of semigroup methods relies on the fact that the time evolution operator of the quantum mechanical system generates a completely positive dynamical semigroup.[23−25] Semigroup methods are general enough that they are easily extended to include several different kinds of system−bath interactions at once; these might include relaxation, dissipation, energy dephasing, binary collisions, or energy transfer. Usually, semigroup theory is expressed so that the equations of motion involve the system operators, instead of the elements of the reduced density matrix.[26]

The very rapid growth in the sophistication of pump/probe and multiple-wave mixing methods in optical spectroscopy[27] has led to important developments in the formal analysis of quantal systems interacting with a dissipative environment. Most of this work has focused on the harmonic oscillator and the two-level system as simple but illustrative examples.[28] Significant differences among the various approaches to this problem have been noted. The focus, in the semigroup approach, on positivity (physically, this means that populations can never become negative) implies that, for the harmonic oscillator, either the solution must fail to approach equilibrium properly or it cannot be translationally invariant.[28,29] On the other hand, other approaches, including Redfield theory, have other drawbacks including loss of complete positivity (negative populations are not physical!). Therefore, it is important to understand the applicability and general behavior of the different approaches to quantum dissipation if a useful, general method for quantum dissipative dynamics is to be obtained.

To be rigorous in applying semigroup techniques, the operators describing the time evolution of the quantum mechanical system should be expressed in their eigenstate representation.[30] However, for many chemical systems, working in a noneigenstate basis is often advantageous for several reasons:

(1) For systems with more than two coupled fields and sites, solving the system eigenvalue problem may be very difficult, or even impossible analytically. Examples include the spin/boson picture broadly used for electron-transfer problems[12,16,17,27,28] and anharmonic multimode molecular vibrational Hamiltonians.

(2) Working in a noneigenstate basis often makes the comparison between theoretical and experimental results easier, since many chemists visualize complex systems or molecules as being made up of unique pieces whose isolated properties are known. These same concerns arise when applying other relaxation theories, such as Redfield theory, where the reduced

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10.1021/jp9813544 CCC: $15.00

density matrix of the system is most conveniently expressed in the eigenstate basis.

This leads to the purpose of this paper, namely an investigation of when semigroup techniques can be applied directly to quantum mechanical systems expressed in terms of operators relating to a local set of sites rather than to eigenstates. In particular, the quantum mechanical system of interest consists of a coupled fermion two-site model, which is allowed to interact with an external thermal bath. The two-site model has become one of the workhorses of quantum chemistry, having been used previously to model systems such as coupled spins, coupled bosons, and intervalence electron transfer.

Although this issue, namely coupling to the environment via eigenstates or local states, might seem merely a formal exercise, it has substantial physical significance. In the spin/boson situation, for example, the obvious physical approximation is to permit dissipation independently in the vibrational and electronic manifolds (not in the eigenstates, which are not analytically obtainable).[29] We study the very simple case of the two-level system because the local states and eigenstates can be trivially interconnected, and their relaxation dynamics can be found from the semigroup equation without further approximation. Thus this simple system provides an ideal example for the study of the effect of local state versus eigenstate relaxation.

This paper is organized as follows. In section II the semigroup formalism is introduced and then applied to the two-fermion site model, expressed first in the local site basis and then in the eigenstate basis. The equations of motion arising in section II are evaluated, and the results of these calculations investigated in section III. Finally, section IV summarizes the results of this work, and some conclusions are given.

## II. Theory

**A. Semigroup Formalism.** The semigroup approach is applicable to a quantum mechanical system undergoing relaxation, dissipation, or sudden perturbations arising from coupling with an external bath. Semigroup techniques are valid for all situations where the system−bath interaction is Markovian; i.e., the decay of memory effects is instantaneous. The total Hamiltonian can be written as eq 2.1, where $\mathbf{H}_S$, $\mathbf{H}_{SB}$, and $\mathbf{H}_B$

$$\mathbf{H} = \mathbf{H_S} + \mathbf{H_{SB}} + \mathbf{H_B} \tag{2.1}$$

stand for the system, system−bath, and bath Hamiltonians, respectively. Just as in density matrix theory,[1,4−7,33] the semigroup analysis transforms the full dynamics to a picture of reduced dynamics within the space of the quantum system. The equations of motion are expressed using the Heisenberg representation of the system operators instead of the density matrix of the system. Since the expectation values of these operators correspond to experimental observables, the results of the semigroup analysis are amenable to direct comparison with experimental results.

The influence of $\mathbf{H}_{SB}$ and $\mathbf{H}_B$ on the quantum mechanical system is included in the Heisenberg equation as additional relaxation-type terms for the system operators. Thus, the Heisenberg equation of motion becomes

$$\frac{\mathrm{d}\Omega}{\mathrm{d}t} = \frac{\mathrm{i}}{\hbar}[\mathbf{H}_S,\Omega] + \frac{\partial\Omega}{\partial t} + \mathbf{L}_D(\Omega) \tag{2.2}$$

In eq 2.2 $\Omega$ is an arbitrary quantum mechanical system operator, and the first two terms on the right correspond to the normal Heisenberg evolution terms. In the remainder of this communication, the system operators will be time-independent and the second term on the right will be ignored. The last term is a Liouville operator which formally describes dissipation due to the influence of the bath and the system−bath coupling. The system−bath coupling is further assumed to be of the form

$$H_{SB} = \sum_i \Gamma_i \mathbf{V}_i \mathbf{B}_i \tag{2.3}$$

where $\mathbf{V}_i$ is a system operator, $\mathbf{B}_i$ is a bath operator, and $\Gamma_i$ is an interaction strength.

From the assumption that eq 2.3 is valid for the system of interest, semigroup theory derives the following equation for the relaxation terms:[25]

$$\mathbf{L}_D(\Omega) = \sum_i \gamma_i \left( \mathbf{V}_i \Omega \mathbf{V}_i^\dagger - \frac{1}{2}[\mathbf{V}_i \mathbf{V}_i^\dagger, \Omega]_+ \right) \tag{2.4}$$

Here the $\gamma_i$ values are positive, real relaxation amplitudes whose magnitude can be estimated using perturbation theory, provided the bath correlation functions are known.[31−33] Equation 2.4 holds in general for both Hermitian and non-Hermitian system operators. In the specific case where $\mathbf{V}_i$ is Hermitian, then eq 2.4 simplifies to[22]

$$\mathbf{L}_D(\Omega) = -\sum_i \frac{\gamma_i}{2}[\mathbf{V}_i,[\mathbf{V}_i,\Omega]] \tag{2.5}$$

where the double commutator form is standard for relaxation processes.

**B. Local Basis: Relaxation Terms and Dynamical Equations.** The model system of interest has two fermion sites, of energy $\pm\Delta$, coupled to one another with an interaction strength mediated by the tunneling matrix element $J$. Expressing the system operators using second quantization allows the system Hamiltonian to be written as

$$\mathbf{H}_S = \Delta(a_1^\dagger a_1 - a_2^\dagger a_2) + J(a_1^\dagger a_2 + a_2^\dagger a_1) \tag{2.6}$$

The relaxation in this system is included by defining the following form for $\mathbf{L}_D(\Omega)$

$$\mathbf{L}_D(\Omega) = -\frac{\gamma_1}{2}[a_1^\dagger a_1,[a_1^\dagger a_1,\Omega]] - \frac{\gamma_1}{2}[a_2^\dagger a_2,[a_2^\dagger a_2,\Omega]] + \gamma_2\left\{a_1^\dagger a_2 \Omega a_2^\dagger a_1 - \frac{1}{2}[a_1^\dagger a_2 a_2^\dagger a_1,\Omega]_+\right\} + \gamma_3\left\{a_2^\dagger a_1 \Omega a_1^\dagger a_2 - \frac{1}{2}[a_2^\dagger a_1 a_1^\dagger a_2,\Omega]_+\right\} \tag{2.7}$$

The first two terms in eq 2.7 correspond to pure dephasing terms, and the last two terms describe the population relaxation of the two sites; in the language of magnetic resonance or vibrational relaxation theories these correspond to $T_2$* and $T_1$ processes, respectively.

The four coupled operators whose time-dependent expectation values describe the dynamics of this two-site system are most conveniently expressed as the Hermitian operators

$$\Omega_1 = a_1^\dagger a_1$$

$$\Omega_2 = a_2^\dagger a_2$$

$$\Omega_3 = a_1^\dagger a_2 + a_2^\dagger a_1$$

$$\Omega_4 = i(a_1^\dagger a_2 - a_2^\dagger a_1) \tag{2.8}$$

Using these system operators and the fermion commutation relations

$$[a_i^\dagger, a_j^\dagger]_+ = [a_i, a_j]_+ = 0 \tag{2.9}$$

$$[a_i^\dagger, a_j]_+ = \delta_{i,j} \tag{2.10}$$

the equations of motion become

$$\frac{\mathrm{d}}{\mathrm{d}t}\begin{pmatrix}\Omega_1\\ \Omega_2\\ \Omega_3\\ \Omega_4\end{pmatrix} = \begin{pmatrix} -\gamma_2 & \gamma_3 & 0 & -J \\ \gamma_2 & -\gamma_3 & 0 & J \\ 0 & 0 & -\gamma_1 - \dfrac{(\gamma_2+\gamma_3)}{2} & 2\Delta \\ 2J & -2J & -2\Delta & -\gamma_1 - \dfrac{(\gamma_2+\gamma_3)}{2} \end{pmatrix}\begin{pmatrix}\Omega_1\\ \Omega_2\\ \Omega_3\\ \Omega_4\end{pmatrix} \tag{2.11}$$

In any relaxation theory of the system/bath type, the system should approach, asymptotically in time, the appropriate thermal equilibrium population distribution (physically, the system should assume the temperature of the bath). Within the system's own evolution, this temperature dependence must be required, usually via proportionality requirements on the relaxation parameters. These requirements arise, physically, because it is the dynamics of the bath ($\mathbf{H}_{\mathrm{SB}}$ and $\mathbf{H}_{\mathrm{B}}$ in eq 2.1) that determine this dependence (a simple case occurs for competitive first-order chemical kinetics schemes, where $\exp(-\Delta G°/RT) = k_{\mathrm{f}}/k_{\mathrm{b}}$, with $\Delta G°$, $R$, $k_{\mathrm{f}}$, and $k_{\mathrm{b}}$ respectively the free energy difference, gas constant, and forward and backward first-order rate constants).

Within the semigroup approach, it can be useful to require thermal equilibration, and in previous work, thermal effects have been introduced in a variety of ways. One example is the ad hoc addition of constant terms to the equations of motion, so at long times the expectation values approach their Boltzmann averages.[20,29] In this work, temperature will be included via the relaxation coefficients. At a sufficiently long time, a steady state between sites 1 and 2 should be established, so that $\mathrm{d}\Omega_1/\mathrm{d}t = 0$. Hence, from eq 2.11

$$-\gamma_2\Omega_1 + \gamma_3\Omega_2 - J\Omega_4 = 0 \tag{2.12}$$

Averaging eq 2.12 over a canonical ensemble, and realizing that $\langle\Omega_4\rangle = 0$ gives the following relationship between $\gamma_2$ and $\gamma_3$

$$\gamma_3 = \frac{\langle\Omega_1\rangle}{\langle\Omega_2\rangle}\gamma_2 \tag{2.13}$$

If we now require a Boltzmann distribution in $\langle\Omega_1\rangle/\langle\Omega_2\rangle$, this yields

$$\gamma_3 = \gamma_2\,\mathrm{e}^{-2\beta\Delta} \tag{2.14}$$

where $\beta = (k_{\mathrm{B}}T)^{-1}$ and $k_{\mathrm{B}}$ is the Boltzmann constant.

**C. Eigenvector Basis: Relaxation Terms and Dynamical Equations.** The eigenvalues of eq 2.6 are denoted as $\pm E = (\Delta^2 + J^2)^{1/2}$, and the system Hamiltonian becomes, in the eigenvector basis,

$$\mathbf{H}_{\mathrm{S}} = E(a_+^\dagger a_+ - a_-^\dagger a_-) \tag{2.15}$$

Here the labels + and − refer to the eigenstates with eigenvalues $+E$ and $-E$, respectively. Denoting the quantum mechanical system operators in this basis with the label $\theta$ and including the same types of relaxation terms as were present in the local basis gives an $\mathbf{L}_{\mathrm{D}}(\theta)$ of

$$\mathbf{L}_{\mathrm{D}}(\theta) = -\frac{\epsilon_1}{2}[a_+^\dagger a_+,[a_+^\dagger a_+,\theta]] - \frac{\epsilon_1}{2}[a_-^\dagger a_-,[a_-^\dagger a_-,\theta]] + \epsilon_2\left\{a_+^\dagger a_-\theta a_-^\dagger a_+ - \frac{1}{2}[a_+^\dagger a_- a_-^\dagger a_+,\theta]_+\right\} + \epsilon_3\left\{a_-^\dagger a_+\theta a_+^\dagger a_- - \frac{1}{2}[a_-^\dagger a_+ a_+^\dagger a_-,\theta]_+\right\} \tag{2.16}$$

At this point the equations of motion in the eigenstate basis could be written down by defining an analogous set of system operators as in eq 2.8 and just inspecting the equations of motion in the local basis. However, since the results from doing the relaxation in the eigenstate basis must be transformed back to the local basis for comparison with eq 2.11, it is actually advantageous to work with a non-Hermitian set of system operators in the eigenstate basis. The exact procedure followed for doing these basis transformations is outlined in the Appendix, with the result given as follows

$$\frac{\mathrm{d}}{\mathrm{d}t}\begin{pmatrix}\Omega_1\\ \Omega_2\\ \Omega_3\\ \Omega_4\end{pmatrix} = \begin{pmatrix} A-B & A+B & C & -J \\ -A+B & -A-B & -C & J \\ D+C & D-C & F+G & 2\Delta \\ 2J & -2J & -2\Delta & G-F \end{pmatrix}\begin{pmatrix}\Omega_1\\ \Omega_2\\ \Omega_3\\ \Omega_4\end{pmatrix} \tag{2.17}$$

where

$$A = \frac{\Delta}{2E}(\epsilon_3 - \epsilon_2)$$

$$B = \left(\frac{\Delta^2}{2E^2} + \frac{J^2}{4E^2}\right)(\epsilon_3 + \epsilon_2) + \frac{J^2}{2E^2}\epsilon_1$$

$$C = -\frac{J\Delta}{4E^2}(\epsilon_3 + \epsilon_2) + \frac{J\Delta}{2E^2}\epsilon_1$$

$$D = \frac{J}{2E}(\epsilon_3 - \epsilon_2)$$

$$F = -\frac{J^2}{4E^2}(\epsilon_3 + \epsilon_2) + \frac{J^2}{2E^2}\epsilon_1$$

$$G = -\left(\frac{\Delta^2}{4E^2} + \frac{J^2}{2E^2} + \frac{1}{4}\right)(\epsilon_3 + \epsilon_2) - \left(\frac{\Delta^2}{2E^2} + \frac{1}{2}\right)\epsilon_1 \tag{2.18}$$

The procedure for introducing thermal equilibrium into these equations of motion is similar to that in eq 2.14 and is outlined in the Appendix with the final result

$$\epsilon_3 = \epsilon_2\,\mathrm{e}^{-2\beta E} \tag{2.19}$$

## III. Computations and Results

From the form of the eigenvalues in this two-site system, it seems reasonable that the magnitude of the tunneling integral $J$ will control how well the local site relaxation equations model the "exact" or transformed eigenstate equations. When $J$ is small compared to $\Delta$, then the two sets of equations should yield similar results since as $J \rightarrow 0$ the local sites and local site energies become the eigenstates and eigenvalues of the two-

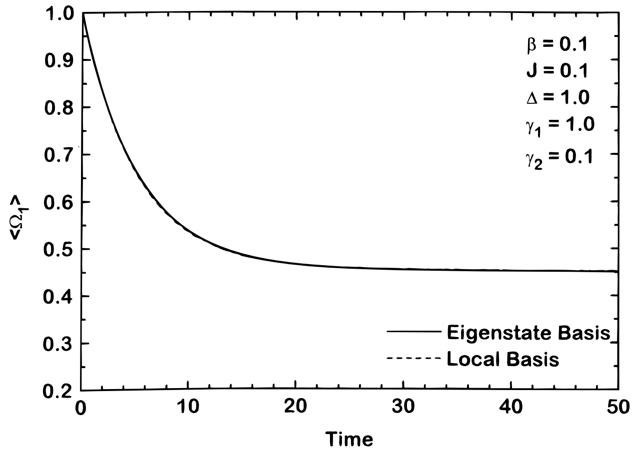

**Figure 1.** Time dependence of the population located on site 1, in the nonadiabatic regime, as predicted by relaxation applied in the two different system bases. The parameters for the two models have the unitless values $\beta = 0.1$, $\Delta = 1.0$, $J = 0.1$, $\gamma_1 = 1.0 = \epsilon_1$, and $\gamma_2 = 0.1 = \epsilon_2$. Notice that the dynamics are the same in the two bases.

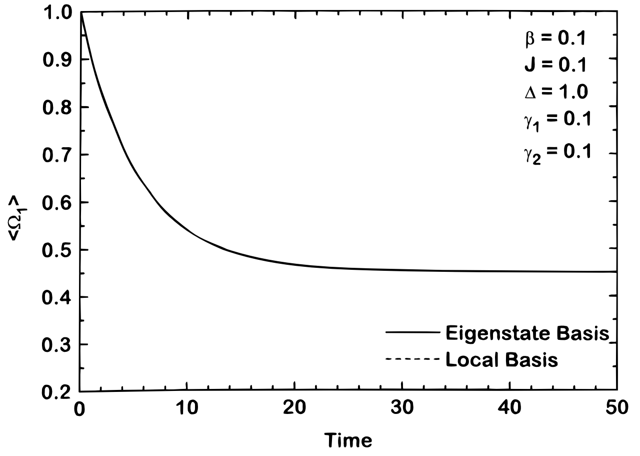

**Figure 2.** A plot similar to Figure 1, except $\gamma_1$ and $\epsilon_1$ have decreased by an order of magnitude to 0.1. There is no discernible $T_2$* dependence of the population dynamics in the low *J* regime.

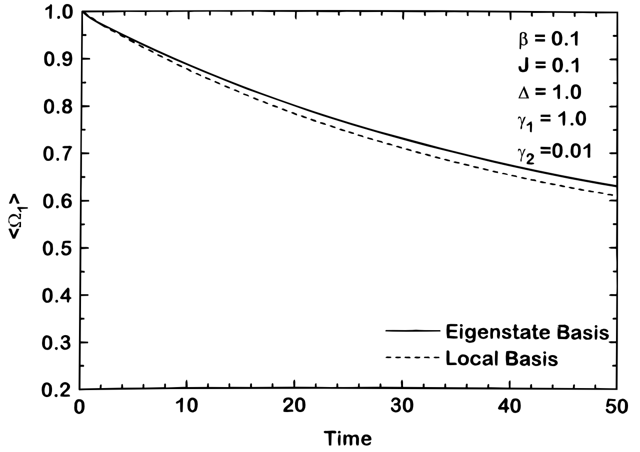

**Figure 3.** The evolution of the model two-site system when $\gamma_2 = \epsilon_2 = 0.01$, with all other parameters as in Figure 1. Note the slower rate of thermalization when the $T_1$-type fluctuations are decreased.

site system. As *J* increases, clearly the local sites and the eigenstates begin to differ and the corresponding expectation values of the system operators should begin to diverge between the two equations of motion.

The equations of motion, eqs 2.11 and 2.18, are solved numerically using the fourth-order Runge–Kutta algorithm supplied with the software package MathCad.[34] It is found that convergence of the results over a period of 50 arbitrary time units requires a 5000-point grid and consumes 30–45 s of real time on a 75 MHz pentium processor. A system of arbitrary units is used for all variables in the equations of motion, since only the qualitative behavior of these two models is of concern here.

The initial conditions of the quantum system are always $\langle \Omega_1 (t{=}0)\rangle = 1.0$ and $\langle \Omega_n(t{=}0)\rangle = 0.0$ for $n = 2$, 3, or 4, corresponding to all of the fermion population located on site 1 at the beginning of the dynamics. Since neither of the model Hamiltonians includes terms which remove population from the quantum system into a fermion "sink", then the total population is conserved and $\langle \Omega_1\rangle + \langle \Omega_2\rangle = 1.0$ at all times.

**A. Weak Coupling Regime.** When $2J$ is much less than $k_BT$ (and other relevant parameters), an ET system is in a nonadiabatic regime. In nonadiabatic ET, the rate is proportional to the squared electron tunneling matrix element between the donor and acceptor potential wells, so (if the bath coupling is effective) the site populations are usually monotonically decaying with time and lack the oscillatory structure that can characterize adiabatic ET. Figure 1 shows the time-dependent population of site 1, and the smooth, monotonic decay is evident in both the eigenstate and local site relaxation calculations. More importantly, the evolution of the population on site 1 is essentially identical for the two relaxation schemes. Decreasing the magnitude of the eigenstate and local site energy fluctuation relaxation ($\gamma_1$ and $\epsilon_1$) does little to the population dynamics of $\Omega_1$ (Figure 2). However, lowering $\gamma_2$ and $\epsilon_2$ dramatically lengthens the decay time of $\Omega_1$ (Figure 3); essentially, the $T_1$-type process reduces the effective strength of the coupling *J*. Again, the dynamics from introducing relaxation in the eigenstate basis and the local site basis are the same, with a minor difference in the population distributions due to slightly different thermal factors, when the coefficients $\gamma_2$ and $\epsilon_2$ are decreased.

**B. Strong Coupling Regime.** As the magnitude of *J* increases, the coupled fermion system begins to resemble an adiabatic ET model. In underdamped adiabatic ET, the system dynamics resembles simple tunneling with the electron population undergoing damped oscillations across the barrier repeatedly until a steady state is established between the donor and acceptor populations. An analogous population fluctuation shows up in both the local and eigenstate relaxation models as *J* increases, as seen in Figure 4. The period of the fluctuations is slightly longer in the local site basis (as measured by the peak to peak separation), and $\Omega_1$ reaches thermal equilibrium faster. The damping of the coherent transfer of population between sites 1 and 2 is stronger in the eigenstate basis, since the expectation value of $\Omega_1$ becomes a smooth function earlier than in the local basis. The thermal equilibrium population on site 1 for the two relaxation models varies because of the large difference between the eigenvalues and the local site energies in this regime.

Not only can there be a discrepancy in the population transfer dynamics in the eigenstate versus the local bases, but the phase information carried in the operators $\Omega_3$ and $\Omega_4$ can also be very different. Figure 5A is a plot of the expectation value of $\Omega_3$ versus time in the same parameter regime as was used in Figure 4. Evolution under local basis coupling displays damped oscillations, which return to zero after each recurrence, at short times, followed by longer time asymptotic decay. In the eigenstate basis, $\langle \Omega_3\rangle > 0$ until $t > 9$, followed by an asymptotic approach to a negative value. $\langle \Omega_3\rangle$ in the eigenstate basis does not asymptotically approach zero because it is simply the difference in the eigenstate thermal equilibrium populations. Figure 5B shows the corresponding results for $\langle \Omega_4\rangle$. For this

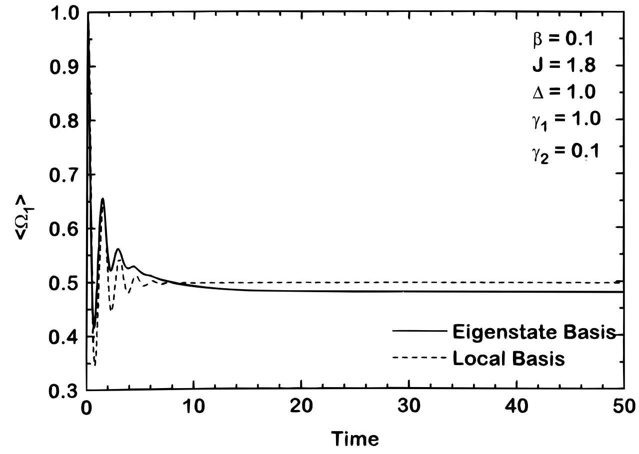

**Figure 4.** Comparison of the results from relaxation applied in the local state basis versus the eigenstate basis in the strong coupling regime. The parameters in this plot were given the values $\beta = 0.1$, $\Delta = 1.0$, $J = 1.8$, $\gamma_1 = \epsilon_1 = 1.0$, and $\gamma_2 = \epsilon_2 = 0.1$.

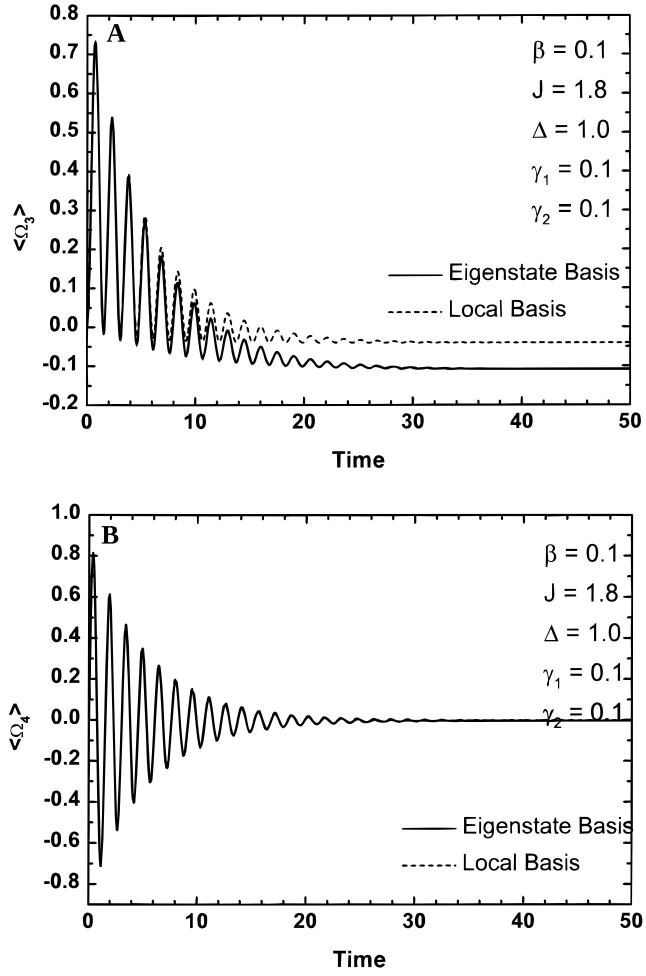

**Figure 5.** Evolution of the expectation values of the operators which convey phase information for our two-site model, $\Omega_3$ (A) and $\Omega_4$ (B). The model parameters have the same values as in Figure 4.

operator, both coupling regimes lead to similar dynamics, displaying dampened oscillations at short times and a constant value close to zero at longer times. The main difference between the local and eigenstate results for this operator is the larger amplitudes of successive recurrences in the local basis.

The influence of the relaxation coefficients on the system dynamics, in the strong coupling regime, is shown in Figures 6 and 7. When the system−bath coupling becomes weaker for the eigenstate and the local site population damping (a decrease in $\epsilon_1$ or $\gamma_1$, respectively), the oscillations in both bases become significantly more underdamped; this behavior is a direct manifestation of the pure dephasing nature of $\epsilon_1$ and $\gamma_1$. When the system−bath coupling of the transfer matrix element is decreased, there is little change in the local site dynamics, whereas there is an increase in the lifetime of the eigenstate basis decay. Notice that in the strong coupling regime $\epsilon_2$ and $\gamma_2$ have a much weaker effect on the population evolution than they did in the weak coupling limit, but their influence still manifests itself in the dynamics of the eigenstate basis results.

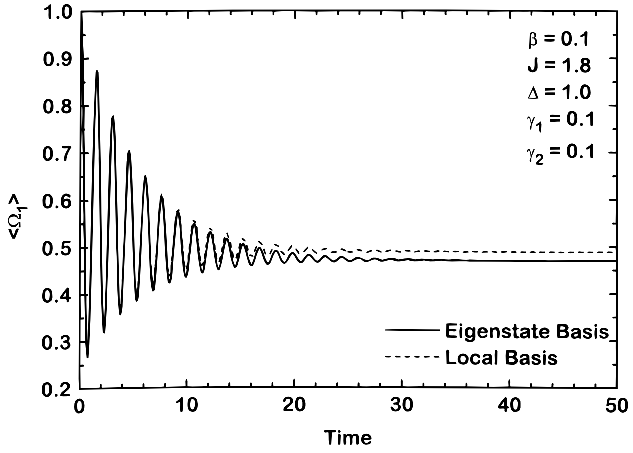

**Figure 6.** The results for the strongly coupled two-site model when $\gamma_1$ and $\epsilon_1$ are decreased from 1.0 to 0.1. The decrease in these relaxation coefficients results in significant underdamping of the site−site population fluctuations. Also, the dynamics arising from the two models become very similar in the high-temperature regime where the coupling coefficients are of the same magnitude.

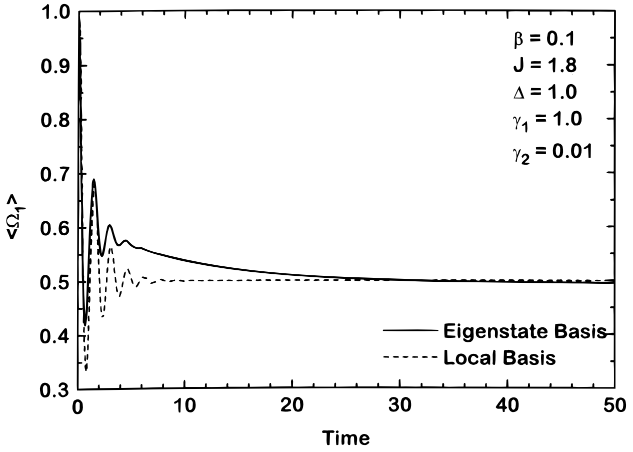

**Figure 7.** Effect of lowering the site/eigenstate energy dephasing by an order of magnitude when $J = 1.8$. The results are less dramatic in the strong coupling limit than in the low $J$ regime (Figure 3).

In Figures 4 and 7, it is evident that the dynamics of fermion transfer are different when relaxation is imposed in the eigenstate basis or in the local site basis. In Figure 6, however, the two sets of equations seem to give rise to similar dynamics, with a slight offset between the two decay curves arising from different thermal factors. The cause of the agreement between the two relaxation treatments is not the decrease in the magnitude of the energy relaxation coefficients, as seen in Figure 8 where $\epsilon_1$ and $\gamma_1$ are reduced to 0.5 and the relaxation dynamics are still dissimilar between the two models. The identical dynamics arise in a regime where the system is placed in the high temperature (small $\beta$) limit, and the two independent relaxation coefficients in each basis ($\gamma_1$ and $\gamma_2$ or $\epsilon_1$ and $\epsilon_2$) are of

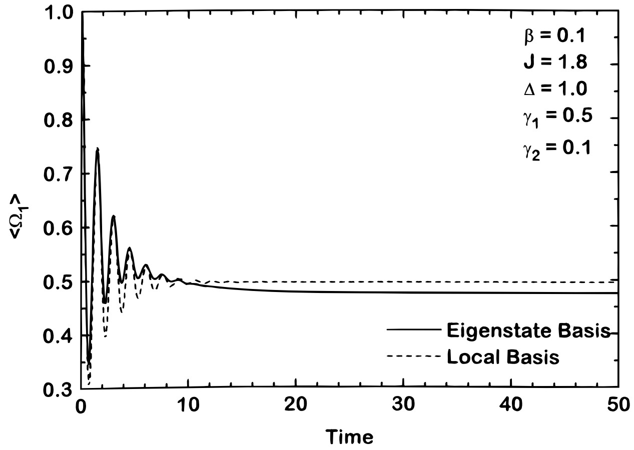

**Figure 8.** Coupled two-site model when $J = 1.8$, $\beta = 0.1$, $\Delta = 1.0$, $\gamma_1 = 0.5 = \epsilon_1$, and $\gamma_2 = 0.1 = \epsilon_2$. These results illustrate that it is not simply the decrease in $\gamma_1$ and $\epsilon_1$ which is responsible for the relaxation in the two bases yielding similar dynamics in Figure 5.

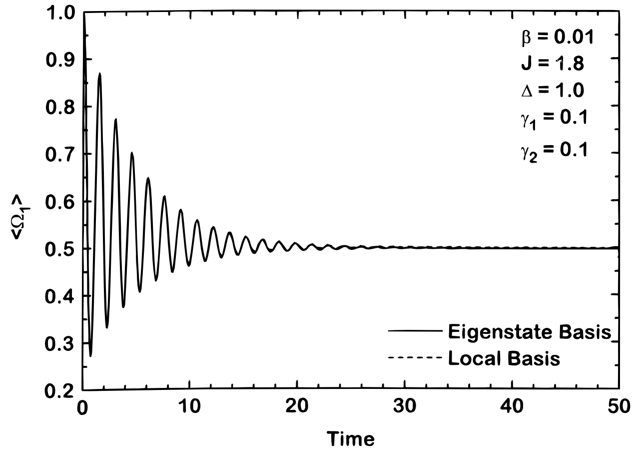

**Figure 9.** The decrease of $\beta$ from 0.1 to 0.01 (with all other parameters as in Figure 5) results in the local site basis and the eignestate basis giving the exact same dynamics, even though the two-site model is in the strong coupling regime.

comparable magnitude. As $\beta \to 0$, then $\epsilon_2 = \epsilon_3$ and $\gamma_2 = \gamma_3$. Also, if $\epsilon_2 = \epsilon_1$, then the elements in the relaxation matrix of eq 2.17 become $B = \epsilon_1$, $G = -2\epsilon_1$, and $A = C = D = F = 0$. A comparison of these equations of motion with eq 2.11, when $\gamma_2 = \gamma_1$, shows that the two approaches will have an identical population evolution. In Figure 9, $\beta$ has been lowered from 0.1 to 0.01, and one can see that the eigenstate and local basis results are identical.

## IV. Conclusions

The semigroup analysis offers an attractive way to discuss relaxation dynamics in a quantum mechanical system. It fits easily within a Heisenberg description of the evolution of the system operators, whose average can then be used to deduce actual dynamical observables.

The formal derivation of the semigroup holds for a diagonal operator set, corresponding to the eigenstates of the quantum system, coupled to a Markovian bath. As long as one deals with a simple system, finding these eigenstates is straightforward and therefore the relaxation can be carried out in a rigorous fashion. For more complex systems (such as the spin-boson system), however, finding the system's eigenstates is itself a major task. Moreover, those system eigenstates are not necessarily easily interpreted in an intuitive fashion. It then becomes relevant to consider how large the error might be if operators diagonal in the local states, rather than in the eigenstates, are coupled to the Markovian bath using the semigroup analysis.

We have analyzed a simple two-site model and have examined the systematics of the relaxation and thermalization processes. We find two conditions under which the dissipative and relaxation coupling to the local states is a good approximation to the coupling to the eigenstates. The first and more obvious of these is when the intersite coupling parameter, which we call $J$, is small. Under this condition, the system eigenstates essentially are local states, and therefore one is not surprised to find similar relaxation behavior. The other, less intuitive situation occurs in the high-temperature limit when the site energy dephasings are roughly equal to the dephasings of the transfer element itself. Then, essentially, all dynamical variables relax uniformly, and the relaxation/evolution equations become identical.

Like the Redfield analysis, to which it is closely related,[28] the semigroup analysis in principle makes no arguments about the perturbative nature of the substate coupling within the system. Indeed, if one can solve for the eigenstates of this system, one has a general analysis of the dynamics, including both causal evolution within the system and bath-induced relaxation.

As a practical matter, it is still probably most appropriate to minimize the interactions between subsystems within the quantum mechanical space and then to use quantum or semiclassical propagation[35] to describe the evolution; the semigroup can then completely and appropriately describe the relaxation processes.

**Acknowledgment.** We are grateful to the Chemistry Division of the National Science Foundation for support of this work and to David Tannor for helpful discussions. M.R. thanks John Jean for remarks on the general subject of relaxation dynamics. This note is dedicated, with affection and with respect, to Raphy Levine, on his sixtieth birthday.

## Appendix

By using the non-Hermitian operator basis

$$\theta_1 = a_+^\dagger a_+, \quad \theta_2 = a_+^\dagger a_-, \quad \theta_3 = a_-^\dagger a_+, \quad \theta_4 = a_-^\dagger a_- \qquad \text{(A1)}$$

the equations of motion in the eigenstate operator basis become

$$\frac{\mathrm{d}}{\mathrm{d}t}\begin{pmatrix}\theta_1\\ \theta_2\\ \theta_3\\ \theta_4\end{pmatrix} = \begin{pmatrix} -\epsilon_2 & 0 & 0 & \epsilon_3 \\ 0 & 2\mathrm{i}E - \epsilon_1 + \dfrac{(\epsilon_2 + \epsilon_3)}{2} & 0 & 0 \\ 0 & 0 & -2\mathrm{i}E - \epsilon_1 + \dfrac{(\epsilon_2 + \epsilon_3)}{2} & 0 \\ \epsilon_2 & 0 & 0 & -\epsilon_3 \end{pmatrix} \begin{pmatrix}\theta_1\\ \theta_2\\ \theta_3\\ \theta_4\end{pmatrix} \equiv \hat{A}\begin{pmatrix}\theta_1\\ \theta_2\\ \theta_3\\ \theta_4\end{pmatrix} \qquad \text{(A2)}$$

Introducing the requirement that the expectation values of $\theta_1$ and $\theta_4$ approach thermal equilibrium at long times is done in an analogous way as in the local site basis. At steady state $\mathrm{d}\theta_1/\mathrm{d}t = 0$, and averaging the equation of motion for $\theta_1$ over a canonical ensemble yields the following relationship for $\epsilon_2$ and

$\epsilon_3$

$$\epsilon_3 = \epsilon_2\, e^{-2\beta E} \tag{A3}$$

The transformations between the local basis operators and the eigenstate basis operations have the following forms

$$\begin{pmatrix}\Omega'_1\\ \Omega'_2\\ \Omega'_3\\ \Omega'_4\end{pmatrix} = \begin{pmatrix} \cos^2\frac{\alpha}{2} & -\sin\frac{\alpha}{2}\cos\frac{\alpha}{2} & -\sin\frac{\alpha}{2}\cos\frac{\alpha}{2} & \sin^2\frac{\alpha}{2}\\ \sin\frac{\alpha}{2}\cos\frac{\alpha}{2} & \cos^2\frac{\alpha}{2} & -\sin^2\frac{\alpha}{2} & -\sin\frac{\alpha}{2}\cos\frac{\alpha}{2}\\ \sin\frac{\alpha}{2}\cos\frac{\alpha}{2} & -\sin^2\frac{\alpha}{2} & \cos^2\frac{\alpha}{2} & -\sin\frac{\alpha}{2}\cos\frac{\alpha}{2}\\ \sin^2\frac{\alpha}{2} & \sin\frac{\alpha}{2}\cos\frac{\alpha}{2} & \sin\frac{\alpha}{2}\cos\frac{\alpha}{2} & \cos^2\frac{\alpha}{2} \end{pmatrix} \begin{pmatrix}\theta_1\\ \theta_2\\ \theta_3\\ \theta_4\end{pmatrix} \equiv \hat{B}\begin{pmatrix}\theta_1\\ \theta_2\\ \theta_3\\ \theta_4\end{pmatrix} \tag{A4}$$

$$\begin{pmatrix}\theta_1\\ \theta_2\\ \theta_3\\ \theta_4\end{pmatrix} = \begin{pmatrix} \cos^2\frac{\alpha}{2} & \sin\frac{\alpha}{2}\cos\frac{\alpha}{2} & \sin\frac{\alpha}{2}\cos\frac{\alpha}{2} & \sin^2\frac{\alpha}{2}\\ -\sin\frac{\alpha}{2}\cos\frac{\alpha}{2} & \cos^2\frac{\alpha}{2} & -\sin^2\frac{\alpha}{2} & \sin\frac{\alpha}{2}\cos\frac{\alpha}{2}\\ -\sin\frac{\alpha}{2}\cos\frac{\alpha}{2} & -\sin^2\frac{\alpha}{2} & \cos^2\frac{\alpha}{2} & \sin\frac{\alpha}{2}\cos\frac{\alpha}{2}\\ \sin^2\frac{\alpha}{2} & -\sin\frac{\alpha}{2}\cos\frac{\alpha}{2} & -\sin\frac{\alpha}{2}\cos\frac{\alpha}{2} & \cos^2\frac{\alpha}{2} \end{pmatrix} \begin{pmatrix}\Omega'_1\\ \Omega'_2\\ \Omega'_3\\ \Omega'_4\end{pmatrix} \equiv \hat{C}\begin{pmatrix}\Omega'_1\\ \Omega'_2\\ \Omega'_3\\ \Omega'_4\end{pmatrix} \tag{A5}$$

where

$$\Omega'_1 = a_1^\dagger a_1, \quad \Omega'_2 = a_1^\dagger a_2, \quad \Omega'_3 = a_2^\dagger a_1, \quad \Omega'_4 = a_2^\dagger a_2 \tag{A6}$$

and

$$\tan \alpha = J/\Delta \tag{A7}$$

So, to transform the equations of motion given in eq A2, the matrix $\hat{B}\hat{A}\hat{C}$ is evaluated and then rearranged into the Hermitian local site basis of eq 2.6.

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