The interaction representation and nonadiabatic corrections to adiabatic evolution operators. II. Nonlinear quantum systems

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This paper reports further applications of the recently developed interaction representation form of infinite order operator corrections to adiabatic evolution operators. Previous work derived the form of the correction, and applied the methodology to a bilinearly coupled system bath model. In this paper we present results on coupled quantum systems in which the coupling is highly nonlinear. The method is both easy to implement and numerically accurate. © 1996 American Institute of Physics. [S0021-9606(96)01320-7]

I. INTRODUCTION

The solution of the quantum dynamics of multiple degree of freedom problems remains a major challenge to theoretical chemical physics. Over the past few years, we have developed an operator theoretic approach to the solution of coupled problems. Application of operator theoretic methods have allowed us to derive infinite order corrections\(^{1,1b}\) to the adiabatic approximation; and then to analytically resum an infinite subset of these corrections.\(^{1c}\) Corrections to various orders have been computed.\(^{1d}\) This work has been successful in describing varied physical phenomena such as chemical reaction rates,\(^{1e}\) and vibrational energy transfer.\(^{1e,1f}\) Most recently, we have developed a new form of the resummed correction that casts the corrections in terms of an interaction representation.\(^2\) This approach is useful for a number of reasons. First, as described in Ref. 2, the physics of corrections to the adiabatic approximation is especially transparent in the interaction representation form. Second, numerical application of the correction is quite simple. The operator form of the correction in all previous work is \(e^{tH}\), and \(H\) is time dependent and not in a form easily diagonalizable. As a result, in the past corrections have either been calculated by expanding the exponential, or by cumulant methods. In Ref. 2 we developed a method that allowed direct application of the full correction without any further approximation. We then applied the interaction representation approach to a standard test problem of a double well bilinearly coupled to a bath oscillator. We found the correction easy to implement; yielding results that were essentially exact. In this paper we extend application of this method to nonlinear systems. Aside from the purely intellectual question as to whether the accuracy of the method was due to the linear form of the coupling, it has also been shown in recent work that nonlinear couplings of reaction coordinates to bath modes can actually have significantly different effects on rates of reaction in condensed phases as compared to a linear bath\(^3\) in classical systems. There has been recent work\(^4\) discussing how to use the Path Integral Centroid\(^5\) method to investigate quantum activated rate theory. The method described in Ref. 2 and in this paper can present another approach to similar problems along with general problems of quantum dynamics in nonlinear systems.

The structure of this paper is as follows: The next section briefly reviews the interaction representation form of infinite order corrections to adiabatic evolution operators. For details, the reader is referred to Ref. 2. Following this we present models in which the coupling between a double well (the reaction coordinate) and a bath oscillator is highly nonlinear. The paper then concludes.

A. Review of the theory

As in the previous work we recall from elementary quantum mechanics that

\[ e^{A+B} \neq e^A e^B. \]  

(1)

Lie algebraic methods allow one to find exponential corrections which produce equality\(^6\)

\[ e^{A+B} = e^A e^B e^{C_1} e^{C_2} \ldots. \]  

(2)

With the \(\{C_n\}\) given by \(n\)-th order commutators of \(A\) and \(B\). For instance, \(C_1 = -[A, B]\). For clarity of presentation we work with a two-dimensional system represented by the Hamiltonian,

\[ H = H_a + H_b + f(a, b). \]  

(3)

Here, \(H_a\) is the quantum Hamiltonian operator representing the isolated \(a\) subsystem, and we have a similar definition for \(H_b\). The operator \(f(a, b)\) can be of any form for the following discussion. With minor modifications to what appears below it can be time dependent. We emphasize that it need not be linear in either coordinate and can also be a function of momentum. In fact actual use of the method described below is not much simpler for linear couplings!

The evolution of the entire system is given by the evolution operator,

\[ \Psi(t) = U(t)\Psi(0) = e^{-itH}\Psi(0). \]  

(4)

If this equation is placed in phase space then the evolution operator may be evaluated as a Feynman Path integral.\(^7\) Now if we group the coupling with the \(b\) subsystem and separate the exponentials of the evolution operators into an uncoupled
a subsystem and a coupled b subsystem, but with the a degree of freedom held fixed in the b evolution operator we obtain an operator version of the adiabatic approximation,

$$U(t)_{\text{adiabatic}} = e^{-iH_a t} e^{-i[H_b + f(a,b)] t},$$

(5)

Makri has used quite successfully the Feit and Fleck symmetrization of the adiabatic evolution operator in numerical evaluation of Feynman path integrals. We have shown an infinite order resummation of the corrections in Eq. (2) results in the following form of the approximate evolution operator:

$$U(t)_{\text{resum}} = U(t)_{\text{adiabatic}} e^{\sigma(t)},$$

(6)

where

$$\sigma(t) = -\int_0^t dt' \int_0^{t'} dt'' e^{iH_a t''} [H_a, f(a,b)] e^{-iH_a t''}.$$  

(6a)

In the past we have evaluated the commutator in Eq. (6a) using standard forms for the commutator of functions of position operators (the coupling potential) and functions of momentum (the kinetic energy operator). Following Ref. 2 we take a different approach. Using the Heisenberg Equation we may write the correction $\sigma(t)$ as

$$\sigma(t) = i \int_0^t dt' \int_0^{t'} dt'' \frac{d}{dt''} e^{iH_a t''} f(a,b) e^{-iH_a t''}.$$  

(7)

Now the argument of the integrals in Eq. (7) will be recognized as the time evolved derivative of the coupling, where both the derivative and the time evolution are with respect to the uncoupled Hamiltonian subsystem. This will in turn be recognized to be the derivative of the coupling in the interaction representation of the Hamiltonian subsystem. We write the full evolution operator as

$$U(t)_{\text{tot}} = U(t)_0 U(t)' ,$$

(8)

Then $U(t)_0$ is the evolution operator due to $H_0$, and $U(t)'$ is in fact the interaction propagator. Then without repeating the details contained in Ref. 2, we obtained a form for our infinite order corrected propagator,

$$U(t)_{\text{resum}} = U(t) H_a U(t) H_b + f(a,b) U(t) H_a^{-1} f(a,b) U(t) H_a.$$  

(9)

As discussed in Ref. 2, this form is obtained when a constant zero time phase factor is dropped. The interpretation of Eq. (9) is that the two outer propagators are uncoupled subsystem propagators. The two inner propagators are, respectively, the adiabatic b subsystem with the coupling holding a fixed; and the inverse of the adiabatic a subsystem holding this time b fixed. As described in detail, the interpretation of this equation does not require that one switch which degree of freedom is considered “fast.” The original adiabatic approximation contained in the first two operators on the right-hand side of Eq. (9) is valid in the limit that a is slow compared to b. (Rigorously that commutators of the coupling with the uncoupled a Hamiltonian are vanishingly small.) The second two operators are the mathematical form of an infinite order correction to this approximation.

This equation is easy to evaluate, because only one dimensional propagators (adiabatic or uncoupled) need to be found. The propagators can be evaluated in any fashion we choose—basis set expansion, numerical Feynman path integral, etc. In addition, each further bath mode, as long as it is only strongly coupled to the reaction coordinate and not to other bath modes, increases the computational complexity linearly. Note, this is independent of the form of the coupling. The coupling need not be linear.

**B. Application**

Following Ref. 2, the specific problem we address is that of a double well potential coupled to an oscillator. Nonlinear couplings have been shown to yield significant influence on activated rate processes in classical systems, and so a quantum approach to study nonlinear couplings is of great use. Application of the approach described in this paper to quantum activates rate processes problem is currently under way. The Hamiltonian we wish to investigate is

$$H = \frac{p_x^2}{2m_x} + V(s) + \frac{p_q^2}{2m_q} + V(q) + cf(q,s),$$

(10)

where $c$ is a coupling constant. $V(s)$ is $c_1 s^4 - c_2 s^2$, the standard double well. We choose the same set of parameters used in our previous work: $c_1 = 0.0035$ and $c_2 = 0.003$. The mass of the coupled bath mode is 2000 atomic units and that of the double well is 1837. Because we wish to investigate the application of the method to nonlinear quantum systems we have studied cases in which $V(q)$ is a harmonic oscillator, and a Morse oscillator. As expected the methodology works equally well for both cases. In the Morse oscillator case, exact results are hard to obtain by direct diagonalization of the two dimensional Hamiltonian—a great many states are needed. In general the results for the Morse oscillator case are very similar to the Harmonic case with frequency equal to that of the bottom of the Morse well. Following Voth et al. the coupling potentials we consider are nonlinear in the system degree of freedom. As in our previous work we calculate the tunnel splitting in the double well as it is affected by coupling to the environment. Because our method yields a propagator, we do this by calculating a survival probability for a wave packet centered on one side of the double well at time $t = 0$.

The evolution operators in Eq. (9) were all evaluated using basis set expansions. In other words uncoupled or adiabatic Hamiltonians were diagonalized using the EISPACK routines to yield the eigenfunctions $\phi_i$ and eigenvalues $E_i$, and the appropriate propagator was formed as

$$K(x',x;t) = \sum_i \phi_i^*(x') \phi_i(x) e^{-iE_i t}.$$  

(11)

Survival probabilities were calculated and lowest state splittings were extracted for three forms of the coupling,

$$f(s,q) = csq^* (2 - e^{-s^2}),$$  

(12a)
posed to the linear coupling evaluated using the Gaussian–Hermite quadrature as needed. Matrix elements of the adiabatic Hamiltonian are coupled system degree of freedom, an extra numerical step is error. In calculating the propagator for the adiabatically we tend to feel that this spread is in fact due to numerical

c~lower values as a function of the coupling constant

b~tanh

coupling 1 resum coupling 1 exact

coupling 2 resum coupling 2 exact

coupling 3 resum coupling 3 exact

coupling 1 exact

coupling 2 exact

coupling 3 exact

coupling constant

c = 0.005 0.01 0.015 0.02 0.025 0.03 0.035 0.04

decay time (a.u.)

FIG. 1. This figure shows the decay time of the survival probability for a wave packet started in the left well of the double well potential. The coupled oscillator has a frequency of 0.0136 a.u. Three coupling potentials are used; coupling 1 = f(s, q) = csq × (2 − e−t^2), coupling 2 = csq × (2 − 2e−t^2), and coupling 3 = (cq/2) × tanh(s/0.5).

\[
f(s, q) = csq^* (2 - 2e^{-s^2}), \quad (12b)
\]

\[
f(s, q) = cq^* 0.5^* \tanh \left( \frac{s}{0.5} \right). \quad (12c)
\]

Figure 1 shows a graph of decay times for all three couplings for an harmonic bath oscillator of frequency 0.0135 a.u. The results are quite good. There does seem to be a bit more spread between the exact results (calculated by diagonalizing the full Hamiltonian) and the results obtained by the present method. There seems to be no general trend (i.e., higher or lower values as a function of the coupling constant c); and so we tend to feel that this spread is in fact due to numerical error. In calculating the propagator for the adiabatically coupled system degree of freedom, an extra numerical step is needed. Matrix elements of the adiabatic Hamiltonian are evaluated using the Gaussian–Hermite quadrature as opposed to the linear coupling (or any polynomial coupling) in which these matrix elements can be evaluated analytically. Subsequent diagonalization of this matrix to yield the adiabatic eigenfunctions and eigenvalues can tend to exacerbate small numerical errors in the matrix elements of the Hamiltonian. In addition, double numerical integrals must be calculated for the exact diagonalization. We again point out that the operator resummation methodology needs to correct very large errors. The adiabatic calculation is terrible; with decay results very little different for all values of the coupling constant.

II. CONCLUSIONS

We have presented in this paper further calculations employing our new interaction representation form for resummed operator corrections to adiabatic evolution operators. The results were shown to be accurate, and the method was easy to implement. In fact, the only difference in application in this nonlinear case and the previous linear investigations is in finding the eigenfunctions of the adiabatic Hamiltonians. Here numerical overlaps must be calculated —when the coupling is linear (or polynomial) overlaps between harmonic oscillator states are, of course, analytic. It is well known that nonlinear couplings can yield very different results in a variety of problems of chemical interest than the corresponding linearized couplings. For this reason, we feel that any general quantum method that allows incorporation of nonlinearities in coupled systems of multiple degrees of freedom is of significant use.

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