Time-dependent self-consistent field (TDSCF) approximation for a reaction coordinate coupled to a harmonic bath: Single and multiple configuration treatments

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This paper explores the usefulness of the time-dependent self-consistent field (TDSCF) approximation for treating the dynamics of a reaction coordinate coupled to a bath of harmonic degrees of freedom. The reaction coordinate is a one-dimensional double well potential, typical of a hydrogen atom isomerization process. The standard (i.e., one configuration) TDSCF approximation is found to provide a very poor description of the effect of coupling to the bath on the isomerization rate. A multiconfiguration (MC-TDSCF) treatment is thus developed and found to provide a much improved description.

I. INTRODUCTION

Dynamical processes in polyatomic molecules can often be described as a “system” of one or two “interesting” degrees of freedom which characterize the process of interest, plus a “bath” of the many remaining degrees of freedom which, though coupled to the system, do not play a principal role. Very often the bath is taken to be a set of harmonic modes (with perhaps variable frequencies, functions of the system coordinates). An example of such a model is the reaction path (or surface) Hamiltonian, where the system is the reaction coordinate (i.e., the distance along the minimum energy reaction path through the transition state), and the bath are local harmonic vibrations orthogonal to the reaction path. Since it is not possible, in general, to deal accurately with more than three or so degrees of freedom by brute force quantum mechanical methods, all strategies for treating the dynamics of system–bath models involve eliminating the bath degrees of freedom, after taking account of their effect on the system as best as possible, and then dealing with the few degrees of freedom of the system by straightforward means.

Feynman path integral methodology is, in principle, the most powerful and attractive tool for dealing with system–bath problems. Its efficiency lies in the fact that it can be used to integrate out the harmonic bath exactly. After this has been done, however, the quantum mechanics for the system corresponds to a nonlinear Schrödinger equation so that one must treat the system dynamics also by path integral methods. Because path integrals are many-dimensional integrals, even for one degree of freedom, Monte Carlo methods are the only feasible numerical approach, but this is far from straightforward because the integrand of the path integral expression for the propagator, $e^{-iHt/\hbar}$, is oscillatory. (In contrast, the integrand of the path integral expression for the Boltzmann operator $e^{-\beta H}$ is real and positive, so that equilibrium statistical mechanical calculations are comparatively easy.) There have recently been several very promising new approaches to Monte Carlo path integration for the propagator, but whether these actually turn out to be feasible for practical calculations awaits further developments.

Because of these difficulties inherent in path integral approaches, there is thus interest in simpler and more accurate, though approximate, models for incorporating the effect of the bath on the dynamics of the system. Recently, for example, we have shown $11$ that a simple basis set method provides quite a good description of the effect of bath coupling on tunneling in a symmetric double well potential (the system). The key to the accuracy of this model is that one uses a localized basis set for the system, and a basis set for the harmonic bath that has its equilibrium position shifted to incorporate the average effect of the coupling. One needs only to diagonalize a Hamiltonian matrix whose dimension is that of the number of basis functions of the system. The principal limitation of this model—at least in its zeroth-order version which is computationally the simplest—is that it is not able to describe energy transfer between system and bath, a feature that would clearly be important in many asymmetric double well problems, e.g., exothermic isomerizations.

The purpose of this paper is to explore another class of approximate models for treating system–bath dynamics, namely the time-dependent self-consistent field (TDSCF) approximation. $12-15$ Its potential advantage over the zeroth-order basis set method noted above is that it can describe energy transfer between system and bath. Though a fully quantum mechanical method, the TDSCF approach has a very semiclassical character to it, especially with regard to the harmonic bath. Since several different groups $16-18$ are currently advocating these “quantum system” plus “classical bath” approaches, it is of interest to see how useful they are for describing the effect of bath coupling on isomerizations.

We first consider the standard (single configuration) TDSCF scheme, noting that for this problem $19$ it is identical to the semiclassical Ehrenfest model, i.e., quantum system plus classical bath. Unfortunately, this model is totally inadequate for our test problem, a double well potential coupled to a harmonic bath. The essential difficulty, which is inherent to this approximation, is that the bath responds only to the average force exerted on it by the system, rather than a force that is different for different values of the system coordinate.

We have therefore generalized the TDSCF procedure to
a multiconfiguration treatment. Specifically, the wave function for the double well system is divided into two components, with a different bath wave function for each component. The time dependence of all the wave functions is determined from the time-dependent variational principle. This multiconfiguration TDSCF (MC-TDSCF) model is seen to provide a much better description of the effect of coupling on tunneling in the double well system.

Section II gives the formal development of the single and multi- (two-) configuration treatment of the system-bath problem, and results of application to the double well system coupled to a harmonic bath are presented in Sec. III. Section IV concludes.

II. THE TDSCF EQUATIONS FOR THE SYSTEM–BATH MODEL

The model under consideration is described by the Hamiltonian

\[
\hat{H}(p, s, P, Q) = \frac{p^2}{2m} + V_0(s) + \sum_k \left( \frac{p_k^2}{2m} + \frac{1}{2} m \omega_k^2 Q_k \right) - \sum_k Q_k f_k(s) = H_s + \sum_k H_{Q_k} - \sum_k Q_k f_k(s). \tag{1}
\]

Here \(s\) is the reaction coordinate and \(Q_1, Q_2, ..., Q_N\) are the harmonic degrees of freedom that constitute the bath, which is linearly coupled to the system. For the specific examples treated in this paper \(V_0(s)\) is a double well potential function corresponding roughly to motion of a hydrogen atom with a barrier of 6 kcal/mol.

A. Single configuration TDSCF

Consider first the standard TDSCF scheme, with the wave function represented by a single Hartree product:

\[
\Psi(s, Q; t) = \chi(s; t) \prod_k \phi_{n_k}(Q_k; t) . \tag{2}
\]

Substitution of Eq. (2) into the time-dependent Schrödinger equation

\[
\hbar \frac{\partial}{\partial t} \chi(s; t) = \left[ H_s - \sum_k \left( \frac{\langle \phi_{n_k} | Q_k | \phi_{n_k} \rangle}{\langle \phi_{n_k} | \phi_{n_k} \rangle} f_k(s) \right) + \sum_k \left( \frac{\langle \phi_{n_k} | H_{Q_k} | \phi_{n_k} \rangle}{\langle \phi_{n_k} | \phi_{n_k} \rangle} - i \hbar \frac{\langle \phi_{n_k} | \dot{\phi}_{n_k} \rangle}{\langle \phi_{n_k} | \phi_{n_k} \rangle} \right) \chi(s; t) \right] , \tag{3}
\]

while projection onto \(\langle \chi | \Pi_{\neq k} \phi_{n_k} \rangle\) gives the TDSCF equation for \(\phi_{n_k}\):

\[
\hbar \frac{\partial}{\partial t} \phi_{n_k}(Q_k; t) = \left[ H_{Q_k} - \frac{\langle \chi | \dot{\phi}_{n_k} \rangle}{\langle \chi | \phi_{n_k} \rangle} \phi_{n_k} + \frac{\langle \chi | H_{Q_k} \phi_{n_k} \rangle}{\langle \chi | \phi_{n_k} \rangle} - \frac{\langle \chi | H_s \phi_{n_k} \rangle}{\langle \chi | \phi_{n_k} \rangle} \right] \phi_{n_k}(Q_k; t) . \tag{4a}
\]

Equations (4a) and (4b) can be simplified by defining the functions \(X\) and \(\Phi_{n_k}\) that include appropriate phase factors:

\[
X(s; t) = \chi(s; t) \exp \left( i \int_0^t dt' \sum_k \frac{\langle \phi_{n_k} | H_{Q_k} | \phi_{n_k} \rangle}{\langle \phi_{n_k} | \phi_{n_k} \rangle} \right) , \tag{5a}
\]

\[
\Phi_{n_k}(Q_k; t) = \phi_{n_k}(Q_k; t) \exp \left( i \int_0^t dt' \frac{\langle \chi | H_{Q_k} \phi_{n_k} \rangle}{\langle \chi | \phi_{n_k} \rangle} - \frac{\langle \chi | H_s \phi_{n_k} \rangle}{\langle \chi | \phi_{n_k} \rangle} - i \hbar \int_0^t dt' \sum_k \frac{\langle \phi_{n_k} | \dot{\phi}_{n_k} \rangle}{\langle \phi_{n_k} | \phi_{n_k} \rangle} \right) . \tag{5b}
\]

Then the equations to be solved become

\[
\hbar \frac{\partial}{\partial t} X(s; t) = \left[ H_s - \sum_k \left( \frac{\langle \phi_{n_k} | Q_k | \phi_{n_k} \rangle}{\langle \phi_{n_k} | \phi_{n_k} \rangle} f_k(s) \right) - \sum_k \frac{\langle \phi_{n_k} | H_{Q_k} | \phi_{n_k} \rangle}{\langle \phi_{n_k} | \phi_{n_k} \rangle} \frac{\langle \chi | f_k(s) \rangle}{\langle \chi | \phi_{n_k} \rangle} \right] X(s; t) , \tag{6a}
\]

\[
\hbar \frac{\partial}{\partial t} \Phi_{n_k}(Q_k; t) = \left[ H_{Q_k} - \frac{\langle \chi | \dot{\phi}_{n_k} \rangle}{\langle \chi | \phi_{n_k} \rangle} - \frac{\langle \chi | H_{Q_k} \phi_{n_k} \rangle}{\langle \chi | \phi_{n_k} \rangle} \right] \Phi_{n_k}(Q_k; t) . \tag{6b}
\]

The TDSCF scheme proceeds by solving the \(N + 1\) differential equations, one for each mode. Thus the time evolution of each mode is governed by a time-dependent potential which is the average of the full interaction potential over all other modes. Notice that the TDSCF equations are not linear and therefore the rate depends on the initial conditions.

In the present application, where the bath consists of only harmonic degrees of freedom linearly coupled to the system, one can actually solve Eqs. (6b) analytically; this is because they have the form of uncoupled, linearly forced harmonic oscillators. Specifically, the time-dependent bath wave functions \(\Phi_{n_k}(Q_k; t)\), the solution of Eq. (6b), are given by
\[
\Phi_n(Q_\xi; t) = \int_{-\infty}^{\infty} dQ_k \ K(Q_k, Q_\xi; t) \Phi_n(Q_\xi; 0),
\]
with
\[
S_k = \frac{m \omega_k}{2 \sin \omega_k t} \left[ (Q_\xi^2 + Q_k^2) \cos \omega_k t - 2 Q_k Q_\xi + \frac{2Q_k}{m \omega_k} \int_{0}^{t} dt' f_k(t') \sin \omega_k t' + \frac{2Q_k}{m \omega_k} \int_{0}^{t} dt' f_k(t') \sin \omega_k (t-t') \right],
\]
\[
f_k(t) = \frac{\langle X(t) | f_k(t) | X(t) \rangle}{\langle X(t) | X(t) \rangle},
\]
It is then straightforward to show that the expectation value of \(Q_\xi\) that appears in Eq. (6a) is given by
\[
\langle \Phi_n(t) | Q_\xi | \Phi_n(t) \rangle = \frac{\langle \Phi_n(0) | Q_\xi | \Phi_n(0) \rangle \sin \omega_k t}{m \omega_k}
+ \frac{\langle \Phi_n(0) | Q_\xi | \Phi_n(0) \rangle \cos \omega_k t}{m \omega_k}
+ \frac{1}{m \omega_k} \int_{0}^{t} dt' \sin \omega_k (t-t') \langle X(t') | f_k(t') | X(t') \rangle \frac{\langle X(t) | f_k(t') | X(t') \rangle}{\langle X(t') | X(t') \rangle}.
\]
Equation (9) is the same as the classical expression for the position of a forced oscillator at time \(t\), in terms of the initial position \(\langle \Phi_n(0) | Q_\xi | \Phi_n(0) \rangle\) and initial momentum \(\langle \Phi_n(0) | P_{\xi} | \Phi_n(0) \rangle\).

Thus, the problem reduces to the solution of only one differential equation, namely Eq. (6a), which is closed by virtue of Eq. (9). This result has been obtained previously, where it was emphasized that Eq. (6a) plus Eq. (9) is essentially the Schrödinger equation analog of the classical generalized Langevin equation; i.e., Eqs. (6a) and (9) have memory effects \([\dot{X}(t)\text{ depends on }X(t')\text{ for }t'<t\) and a "random force" that involves initial conditions of the bath. The full quantum mechanical solution can be easily obtained by expanding \(X(s; t)\) in a basis set.

It is easy to show that Eqs. (4a) and (4b) conserve the norm of the wave function for each mode, as well as the average total energy, i.e.,
\[
\langle X(t) | X(t) \rangle = \langle \Phi_n(t) | \Phi_n(t) \rangle = 1
\]
and
\[
\frac{d}{dt} \langle \Psi(t) | H | \Psi(t) \rangle = 0.
\]

B. Multiconfiguration TDSCF

As noted in the Introduction (and vide infra), the standard single configuration TDSCF is completely inadequate

\[
\begin{align*}
\hat{H} \frac{\partial}{\partial t} \chi_a &= \left[ H_c - \langle \phi_a | Q | \phi_a \rangle f(s) + \frac{\langle \phi_a | H_c | \phi_a \rangle}{\langle \phi_a | \phi_a \rangle} - i\hbar \frac{\langle \phi_a | \phi_a \rangle}{\langle \phi_a | \phi_a \rangle} \chi_a \right] \chi_a \\
&+ \left[ \frac{\langle \phi_a | \phi_a \rangle}{\langle \phi_a | \phi_a \rangle} H_c - \frac{\langle \phi_a | Q | \phi_a \rangle}{\langle \phi_a | \phi_a \rangle} f(s) + \frac{\langle \phi_a | H_c | \phi_a \rangle}{\langle \phi_a | \phi_a \rangle} - i\hbar \frac{\langle \phi_a | Q | \phi_a \rangle}{\langle \phi_a | \phi_a \rangle} \chi_a \right] \chi_a \\
&= \frac{\chi_a}{\chi_a} \chi_a \chi_a + \frac{\chi_a}{\chi_a} \chi_a \chi_a - i\hbar \frac{\langle \phi_a | \phi_a \rangle}{\langle \phi_a | \phi_a \rangle} \chi_a \\
\hat{H} \frac{\partial}{\partial t} \phi_a &= \left[ H_c - \langle \phi_a | Q | \phi_a \rangle f(s) + \frac{\langle \phi_a | H_c | \phi_a \rangle}{\langle \phi_a | \phi_a \rangle} - i\hbar \frac{\langle \phi_a | \phi_a \rangle}{\langle \phi_a | \phi_a \rangle} \chi_a \right] \phi_a \\
&= \frac{\chi_a}{\chi_a} \chi_a \chi_a + \frac{\chi_a}{\chi_a} \chi_a \chi_a - i\hbar \frac{\langle \phi_a | \phi_a \rangle}{\langle \phi_a | \phi_a \rangle} \chi_a
\end{align*}
\]
and similarly for \(\chi_b, \phi_b\).
Because of the presence of the $\langle \Phi_a | \Phi_a \rangle$ term in Eq. (11a) and the $\langle \Phi_b | \Phi_b \rangle$ term in Eq. (11b), it is difficult to solve these equations simultaneously. One would have to evaluate $\langle \phi_a | \phi_a \rangle$ of Eq. (11a) using Eq. (11b), which contains $\langle \chi_a | \chi_a \rangle$, so that $(\partial / \partial t) \chi_a$ would be expressed in terms of $\langle \chi_a | \chi_a \rangle$. This problem can be overcome by introducing appropriate phase factors:

$$X_a (s; t) = \chi_a (s; t) e^{\alpha(t)},$$  

$$X_b (s; t) = \chi_b (s; t) e^{\beta(t)},$$  

$$\Phi_a (Q; t) = \phi_a (Q; t) e^{\gamma(t)},$$  

$$\Phi_b (Q; t) = \phi_b (Q; t) e^{\delta(t)}.$$  

(12a)
(12b)
(12c)
(12d)

It is easily verified that with the choice

$$\gamma(t) = -\alpha(t), \quad \delta(t) = -\beta(t)$$  

(13)

any diagonal coordinate-independent term in Eq. (11a) (plus the corresponding equation for $\chi_b$), or in Eq. (11b) (plus the corresponding equation for $\phi_b$), but not in both pairs, can be eliminated. Specifically, by defining

$$\gamma(t) = \frac{1}{\hbar} \int_0^t dt' \left[ \frac{\langle \chi_a | H_s | \chi_a \rangle}{\langle \chi_a | \chi_a \rangle} - i\hbar \frac{\langle \chi_a | \chi_a \rangle}{\langle \chi_a | \chi_a \rangle} \right],$$  

$$\delta(t) = \frac{1}{\hbar} \int_0^t dt' \left[ \frac{\langle \chi_b | H_s | \chi_b \rangle}{\langle \chi_b | \chi_b \rangle} - i\hbar \frac{\langle \chi_b | \chi_b \rangle}{\langle \chi_b | \chi_b \rangle} \right].$$  

(14a)
(14b)

Equations (11a) and (11b) reduce to

$$i\hbar \frac{\partial}{\partial t} X_a = \left[ H_s - \frac{\langle \Phi_a | Q | \Phi_a \rangle}{\langle \Phi_a | \Phi_a \rangle} f(s) + \frac{\langle \Phi_a | H_s | \Phi_a \rangle}{\langle \Phi_a | \Phi_a \rangle} - i\hbar \frac{\langle \Phi_a | \Phi_a \rangle}{\langle \Phi_a | \Phi_a \rangle} \right] X_a +$$

$$+ \left[ \frac{\langle \Phi_a | \Phi_b \rangle}{\langle \Phi_a | \Phi_a \rangle} H_s - \frac{\langle \Phi_a | Q | \Phi_b \rangle}{\langle \Phi_a | \Phi_a \rangle} f(s) + \frac{\langle \Phi_a | H_s | \Phi_b \rangle}{\langle \Phi_a | \Phi_a \rangle} - i\hbar \frac{\langle \Phi_a | \Phi_b \rangle}{\langle \Phi_a | \Phi_a \rangle} \right] X_b - i\hbar \frac{\langle \Phi_a | \Phi_a \rangle}{\langle \Phi_a | \Phi_a \rangle} X_b,$$

$$i\hbar \frac{\partial}{\partial t} X_b = \left[ H_s - \frac{\langle X_a | Q | X_a \rangle}{\langle X_a | X_a \rangle} Q \right] \Phi_a + \left[ \frac{\langle X_a | H_s | X_a \rangle}{\langle X_a | X_a \rangle} - \frac{\langle X_a | Q | X_b \rangle}{\langle X_a | X_a \rangle} Q \right] \Phi_b,$$

(15a)
(15b)

and similarly for $X_b$ and $\Phi_b$. Equations (15a) and (15b) conserve the total energy.

So far, the MC-TDSCF equations, Eq. (15), involve no approximations [other than the MC-TDSCF ansatz for the wave function, Eq. (10)]. Unlike the single configuration TDSCF equations, however, here it is not possible to solve Eq. (15b) analytically for the oscillator wave functions $\Phi_a (Q; t)$ and $\Phi_b (Q; t)$; this is because there are now two oscillator wave functions (for each bath mode), rather than just one, and the equations for the two are coupled to each other. For a problem with $N$ bath modes, the complete quantum mechanical solution of the $2(N + 1)$ equations that are involved in this method is still a relatively simple calculation for $N$ not too large, especially if this is compared to a full basis set calculation.

Nevertheless, it would clearly be a considerable simplification if one could solve the equations for the bath modes analytically and thus eliminate them from the problem. This can be done approximately by neglecting the terms in Eq. (15b) that couple $\Phi_a$ and $\Phi_b$. Thus Eq. (15b) is approximated by

$$i\hbar \frac{\partial}{\partial t} \Phi_b = \left[ H_s - \frac{\langle X_a | Q | X_a \rangle}{\langle X_a | X_a \rangle} Q \right] \Phi_b,$$  

(16)

which, like Eq. (6b), can be solved analytically by using the Feynman kernel; a similar approximate equation holds for $\Phi_a$. In the case of zero coupling, Eq. (16) is exact. For non-zero coupling, the physical meaning of this approximation, Eq. (16), is that the time-dependent force that the bath wave function $\Phi_a$ experiences is determined by averaging the force $f(s)$ only over the region of well $a$, i.e., with respect to the wave function $X_a (s; t)$:

$$\frac{\langle X_a (t) | f_s (X_a (t)) \rangle}{\langle X_a (t) | X_a (t) \rangle} = f_a (t),$$

(16)

rather than averaging it over both wells as happens in single configuration TDSCF. Note here that $X_a (s; t)$ is itself not normalized to 1, but rather $\langle X_a (t) | X_a (t) \rangle$ is the probability that the system is in well $a$ at time $t$.

Therefore, with Eq. (16) approximating Eq. (15b), $\Phi_a$ is given by Eqs. (7) and (8), and similarly for $\Phi_b$. It is then possible to evaluate analytically the overlap quantities $\langle \Phi_a | \Phi_a \rangle$ and $\langle \Phi_b | Q | \Phi_b \rangle$ that appear in Eq. (15a) for $X_a$; these expressions are

$$\langle \Phi_a (t) | \Phi_a (t) \rangle = \langle \Phi_a (Q - q; 0) | \exp \left[ \frac{iQ}{\hbar} \int_0^t dt' [f_a (t') - f_a (t') \cos \omega t'] \right] | \Phi_a (Q; 0) \rangle.$$
\[
\begin{align*}
\langle \Phi_d(t)|Q|\Phi_b(t) \rangle &= \begin{bmatrix}
\langle \Phi_d(Q = 0)| Q \exp \left( i Q \int_0^t dt' \left[ f_a(t') - f_a(t') \right] \cos \omega t' \right) \Phi_b(Q = 0) \rangle \\
\times \exp \left( \frac{-i m \omega}{2 \hbar \sin \omega t} \int_0^t dt' \left[ f_a(t') - f_a(t') \right] \cos \omega t' \right) \\
\times \frac{\sin \omega t}{m \omega} \int_0^t dt' \left[ f_a(t') - f_a(t') \right] \cos \omega t' \\
\times \frac{\sin \omega t}{m \omega} \int_0^t dt' \left[ f_a(t') - f_a(t') \right] \cos \omega t' \\
\times \frac{\sin \omega t}{m \omega} \int_0^t dt' \left[ f_a(t') - f_a(t') \right] \cos \omega t'
\end{bmatrix},
\end{align*}
\]

where

\[
q(t) = \frac{1}{m \omega} \int_0^t dt' \left[ f_a(t') - f_a(t') \right] \sin \omega t'.
\]

With this approximation [Eq. (16)] for the bath dynamics, the problem has thus been reduced to only the two coupled equations for \( X_a(s) \) and \( X_b(s) \), i.e., Eq. (15a) with Eq. (17) for \( X_a \) and a similar one for \( X_b \).

### III. NUMERICAL APPLICATION: TUNNELING RATES IN A SYMMETRIC DOUBLE WELL

To test the various TDSCF schemes presented in Sec. II, calculations were carried out for a symmetric double well potential \( V_0(s) \) coupled to a bath consisting of one harmonic oscillator. (The limitation to one or two bath modes for these tests is necessary in order to be able to generate exact results for comparison.) The specific form of \( V_0(s) \) is

\[
V_0(s) = -\frac{1}{2}a_0 s^2 + c_0 s^4,
\]

where the two constants are chosen so that (with the mass \( m \) equal to that of an H atom) the frequency at the local minima is 1530 cm\(^{-1}\) and the height of the barrier is 6.3 kcal/mol, roughly typical of an H atom transfer process. The frequency of the bath mode is 2980 cm\(^{-1}\). The time evolution of a state initially localized in well \( a \) of the double well potential, as determined by TDSCF, was studied and compared to the exact time evolution, obtained by basis set calculations.

The potential surface of Eq. (1) for the case of one bath mode and \( f(s) = c_s \) (linear coupling) is shown in Fig. 1. The wave function for the initial state was chosen to be of the form

\[
\Psi(s,Q;0) = \tilde{\chi}_0(s) \tilde{\phi}_0(Q - \lambda).
\]

Here \( \tilde{\chi}_0 \) is a Gaussian that is centered at the minimum of well \( a \) and corresponds to the lowest eigenstate of the locally harmonic potential \( \lambda \):

\[
\lambda = \frac{\langle \tilde{\chi}_0|\tilde{\chi}_0 \rangle}{m \omega^2}.
\]

is the shift in the \( Q \) coordinate from \( Q = 0 \) due to the coupling, and \( \tilde{\phi}_0 \) is the ground state harmonic oscillator function of frequency \( \omega \).

Consider first the single configuration TDSCF approach. Equation (6a), with Eq. (9), is solved by expanding \( X(s,t) \) in an orthonormal basis set:

\[
X(s,t) = \sum c_i(t)s_i(t);
\]

\[
\langle x_i|x_j \rangle = \delta_{ij},
\]

thereby converting the equation for \( X(s,t) \) into a set of \( m \) first-order ordinary differential equations for the coefficients \( \{ c_i(t) \} \). The basis functions \( x_i(s) \) are chosen to be localized about grid points \( s_i \); specifically, they are the orthogonalized distributed Gaussians used recently by Hamilton and Light, and here they are distributed over the region encompassing both potential wells (and the barrier between them). The survival probability

\[
P(t) = |\langle X(0)|X(t) \rangle|^2
\]

FIG. 1. Contour plot of the potential \( V(s,Q) = V_0(s) + f(s)Q \) with \( f(s) = c_s \), with \( c_s = 0.39 \) mdyne/Å for \( \omega = 2980 \) cm\(^{-1}\). The numbers labeling the curves indicate the height of the potential surface in kcal/mol.
is plotted as a function of the time \(t\), and from this the tunneling period is obtained for a given coupling constant. If \(\tau\) is the time at which \(P(t)\) decays to zero, the tunneling splitting in the ground state is given by

\[
\Delta E = \frac{\pi R}{\tau}.
\]

Figure 2 shows the survival probability [Eq. (20)] for \(c = 0\). The high frequency beats are due to the mixing of other eigenstates of the double well (mainly the third and fourth) besides the lowest two in the wave function at \(t = 0\). The single configuration TDSCF calculation is obviously exact in the case of zero coupling. Figure 3, however, which shows how \(\Delta E\) varies as the coupling constant \(c\) is increased from zero, shows that this single configuration TDSCF approximation is extremely poor for essentially any nonzero value of \(c\). It greatly overestimates the degree to which the coupling diminishes the tunneling splitting.

We thus move on to the two configuration MC-TDSCF model. The functions \(X_a\) and \(X_b\) of Eqs. (12a) and (12b) are expanded as follows:

\[
X_a (s, t) = \sum_{i} c_{i a}(t) x_i (s), \tag{22a}
\]

\[
X_b (s, t) = \sum_{j} c_{j b}(t) x_j (s), \tag{22b}
\]

where \(\{x_i (s)\}\) are the localized basis functions noted above; \(x_i (s)\) is localized in well \(a\) for \(i < m/2\) and in well \(b\) if \(i > m/2\). Note that, by construction, \(\langle X_a | X_b \rangle = 0\) at all times.

The exact TDSCF equations [Eqs. (15a) and (15b)] are solved numerically by expanding \(\Phi_a (Q,t)\) and \(\Phi_b (Q,t)\) in another basis set:

\[
\Phi_a (Q,t) = \sum_{i} d_{i a}(t) \phi_i (Q), \tag{23a}
\]

\[
\Phi_b (Q,t) = \sum_{j} d_{j b}(t) \phi_j (Q), \tag{23b}
\]

where \(\{\phi_i (Q)\}\) is also an orthogonalized distributed Gaussian basis. Note that here \(\langle \Phi_a | \Phi_b \rangle \neq 0\) in the special case of zero coupling, \(\langle \Phi_a | \Phi_b \rangle = 1\).

The results of this MC-TDSCF calculation, as seen in Fig. 3, are orders of magnitude better than the one-configuration results. Also shown in Fig. 3 are the results of the approximate MC-TDSCF model [where the exact equation for the bath wave function, Eq. (15b), is replaced by the approximate, analytically solvable Eq. (16)], and they are seen to be only slightly less accurate than the values from the exact MC-TDSCF calculation.

Thus the MC-TDSCF model (two configurations for this example) is seen to be a dramatic improvement over the standard, single configuration TDSCF description for this model of an isomerization process. It is encouraging, too, that the approximate version of the MC-TDSCF approach is almost as accurate as the exact version, for the former allows one to eliminate the bath degrees of freedom completely analytically and thus be left with only the two coupled equations for the two configurations of the reaction coordinate.

Finally, though, even the exact version of the MC-TDSCF model does not give results for this example that are as accurate as the shifted oscillator basis set model employed by us earlier. For the coupling strengths shown in Fig. 3, the results given by the latter approach are indistinguishable from the exact values shown there.

IV. CONCLUDING REMARKS

Perhaps the most striking result of this work is how poorly the standard, single configuration TDSCF model works for describing the effect of system-bath coupling on the isomerization rate. This is particularly disturbing because for this system, this treatment is equivalent to the quantum system plus classical bath model that many workers hope will be sufficient to describe the effect of a bath on a system of interest. Our results thus suggest caution in
this regard. (It is worth pointing out that one could improve the single configuration TDSCF results by defining new coordinates that are linear combinations of the system coordinate and the bath coordinates. This is not desirable for these system–bath problems, though, because it would prevent one from integrating out the bath degrees of freedom.)

The multiconfiguration TDSCF description, however, is seen to correct the major shortcoming of the single configuration model. Here each configuration, or component, of the system wave function has its own separate bath wave function, and each bath wave function responds only to the force averaged over its associated configuration of the system. The equations of Sec. II B can clearly be extended to deal with more than two configurations. The MC-TDSCF equations are more complicated than the standard TDSCF, but with the approximate version—which was seen to be almost as accurate as the exact MC-TDSCF—the number of coupled equations to be solved numerically is only the number of configurations of the system.

The MC-TDSCF approach should thus find considerable utility for treating the dynamics of these system–bath problems.

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22This procedure is what results from using the Dirac time-dependent variational principle, i.e., requiring that the functional $\int dt [\langle \psi(t) | \partial \psi(t) / \partial t \rangle - H(\psi(t))]$ be stationary with respect to variation of $\psi$.