

## TIME-DEPENDENT SELF-CONSISTENT FIELD APPROXIMATION WITH EXPLICIT TWO-BODY CORRELATIONS

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A new quantum mechanical time propagation method is described, which is best suited for studying the dynamics of a system strongly coupled to a bath. The method makes use of the time-dependent self-consistent field (TDSCF) idea and thus scales linearly with the number of degrees of freedom, but explicitly incorporates in the wave function two-body correlations between strongly coupled modes. Test applications on a three-degree-of-freedom reaction-path-type model show the method to be extremely accurate over a variety of conditions and with very strong coupling, even in cases where the traditional TDSCF approach is completely incapable of describing the dynamics.

### 1. Introduction

In recent years, much effort has been devoted toward developing numerical techniques for calculating the time evolution of many-body quantum systems. The difficulty in studying the evolution of a quantum mechanical system (as opposed to that of a classical one) arises because of the non-local character of the Schrödinger equation. Brute-force fully-quantum basis set or grid-based calculations require storage space and computational effort that grows exponentially with the number of coupled degrees of freedom involved. The most efficient time-dependent grid method, the split propagator fast Fourier transform (FFT) technique [1], requires computer time that scales almost linearly with the number of grid points, which in turn grows exponentially with the dimensionality of the system.

Path integral methods [2] appear in principle as the most attractive approach, because they reduce the problem to the evaluation of an integral whose dimension grows *linearly* with the number of degrees of freedom. Monte Carlo integration algorithms [3] are specifically designed for computing high-dimensional integrals of smooth functions; thus, importance sampling techniques are ideally suited for calculating path integrals in imaginary time (which corresponds to inverse temperature), and therefore for studying finite temperature equilibrium properties of large systems. However, straightforward generalization of these techniques to the study of real time dynamics is not possible, because of the rapidly oscillatory nature of the time evolution operator. A number of methods for dealing with this problem have been developed in the past three years [4–6]. The success of test calculations performed with these Monte Carlo path integral methods is encouraging, but further refinement of the techniques will be necessary before they can be successfully used to simulate dynamical properties of many-particle systems.

On the other hand, a wide variety of approximate quantum, semiclassical, or mixed quantum–classical propagation schemes are known. Unfortunately, computational efficiency and numerical accuracy are properties which are hard to satisfy simultaneously when dealing with large systems that involve strong interactions. Gaussian wave packet techniques [7] are sufficiently accurate and easy to use for short time propagation; however, the simplest version of the wave packet propagation method is not capable of obtaining longer time dynamical

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information, and curing its shortcomings requires substantial increase in complexity [8].

The time-dependent self-consistent field (TDSCF) approximation [9–15] appears to be a very attractive candidate as a propagation technique for a variety of problems. The method maintains full mode separability and thus scales linearly with the number of degrees of freedom, while it allows the flow of energy between coupled modes through the introduction of time-dependent mean field potentials. The TDSCF scheme is generally successful when the coupling terms in the Hamiltonian are small, and/or when only average properties are to be calculated; for example, it is often used to study energy transfer rates in molecules with weak bonds such as van der Waals complexes. However, the TDSCF approximation is known to fail completely when the dynamics depends on the specific character of the interaction potential [12]. To make the method applicable in these more demanding cases, the TDSCF approximation has been generalized [12,13] to include multiple configurations (MC-TDSCF), which are usually chosen on the basis of physical intuition. Even though the MC-TDSCF treatment succeeds in remedying the basic limitation of the single configuration TDSCF, it is not capable of producing quantitatively accurate results (at least with a small number of physically relevant configurations) when the coupling terms in the Hamiltonian are strong [12].

The purpose of this paper is to present another approximate mean field propagation scheme, best suited for (but not limited to) system–bath problems, which is capable of achieving high accuracy while requiring computational effort and storage that grow *linearly* with the number of degrees of freedom. Unlike standard TDSCF, which requires the wave function to be fully separable at all times, the present approach *explicitly includes in the wave function two-body correlations between strongly coupled modes*.

The basic formalism, as well as some numerical techniques appropriate for solving the differential equations that result, are described in section 2. In section 3 the method is applied to a strongly coupled three-degree-of-freedom model reaction-path-type Hamiltonian. Numerical examples presented in that section illustrate the quantitative features of the approach. Finally, some concluding remarks and suggestions for interesting future applications of this technique are given in section 4.

## 2. TDSCF equations with two-body correlations for a system coupled to a bath

### 2.1. Formalism

Consider a system consisting of one physically important coordinate  $s$ , which is strongly coupled to  $N$  bath degrees of freedom  $\{Q_k\}$ . We assume that the bath degrees of freedom do not interact directly (or interact weakly) with one another. Such systems occur in many areas of chemistry and physics, both in gas phase and in condensed matter systems. An important class of such problems are chemical processes that involve large amplitude motion in polyatomic molecules, which can be studied using the reaction path Hamiltonian formalism [16]. According to the latter,  $s$  represents the reaction coordinate, i.e. the coordinate along the steepest descent path that connects the saddle point of the potential energy surface with the minima, and  $\{Q_k\}$  are orthogonal locally harmonic vibrational degrees of freedom which are linearly coupled to the reaction coordinate.

The method proposed in this paper is not restricted to a quadratic bath; we will therefore consider a more general Cartesian system–bath Hamiltonian of the form

$$H(s, \mathbf{Q}) = H_s(s) + \sum_{k=1}^N H_k(Q_k) + \sum_{k=1}^N f_k(s) g_k(Q_k), \quad (1a)$$

where

$$H_s(s) = \frac{p_s^2}{2m} + V_0(s), \quad (1b)$$

$$H_k(Q_k) = \frac{P_k^2}{2m} + V_k(Q_k), \quad k=1, \dots, N, \quad (1c)$$

and we have suppressed the momentum dependence of the Hamiltonians. For simplicity of notation we consider the case of only two bath degrees of freedom,  $N=2$ , below. The multidimensional generalization of the method is straightforward and is given at the end of this section.

The basic limitation of the standard TDSCF approach arises essentially because the bath responds to the *average* force exerted on it by the system, rather than a force that is different for different values of the reaction coordinate. To eliminate this problem, we introduce the following TDSCF-type ansatz for the time-dependent wave function, which explicitly incorporates system-bath correlation:

$$\Phi(s, Q_1, Q_2; t) = \phi_1(s, Q_1; t) \phi_2(s, Q_2; t). \quad (2)$$

The advantage of allowing the wave function to have this particular form, over the conventional fully separable TDSCF function, should already be clear. Even when the initial wave function is fully separable, one expects the system-bath separability assumption to break down after a short time propagation when the system is strongly coupled to the bath. Incorporating time-dependent system-bath correlation explicitly in the wave function allows the effect of the coupling to be quantitatively accounted for, resulting in a dramatic improvement in accuracy over traditional TDSCF. On the other hand, bath-bath correlation is induced only *indirectly* as the time progresses through coupling of the bath to the reaction coordinate, and is therefore a higher order effect. Thus, the omission in eq. (2) of explicit correlation between different bath modes is not expected to constitute a severe approximation. The validity of these points is very clearly demonstrated by the numerical calculations presented in section 3.

To proceed, we wish to obtain self-consistent equations that govern the evolution of  $\phi_1$  and  $\phi_2$ . By substituting eq. (2) in the time-dependent Schrödinger equation

$$i\hbar \frac{\partial \Phi}{\partial t} = H\Phi, \quad (3)$$

multiplying on the left by  $\phi_2^*(s, Q_2; t)$  and integrating over  $Q_2$ , we obtain the following differential equation for  $\phi_1(s, Q_1; t)$ :

$$i\hbar \dot{\phi}_1(s, Q_1; t) = H_{1,\text{eff}}(s, Q_1; t) \phi_1(s, Q_1; t), \quad (4a)$$

where

$$H_{1,\text{eff}}(s, Q_1; t) = \langle \phi_2 | \phi_2 \rangle_2^{-1}(s; t) [ \langle \phi_2 | H | \phi_2 \rangle_2(s, Q_1; t) - i\hbar \langle \phi_2 | \dot{\phi}_2 \rangle_2(s; t) ]. \quad (5a)$$

Here the subscript 2 indicates that integration over  $Q_2$  alone is to be performed; for example,

$$\langle \phi_2 | H | \phi_2 \rangle_2(s, Q_1; t) \equiv \int dQ_2 \phi_2^*(s, Q_2; t) H(s, Q_1, Q_2) \phi_2(s, Q_2; t).$$

Similarly, the evolution of  $\phi_2(s, Q_2; t)$  is found to be determined by the equation

$$i\hbar \dot{\phi}_2(s, Q_2; t) = H_{2,\text{eff}}(s, Q_2; t) \phi_2(s, Q_2; t), \quad (4b)$$

where

$$H_{2,\text{eff}}(s, Q_2; t) = \langle \phi_1 | \phi_1 \rangle_1^{-1}(s; t) [ \langle \phi_1 | H | \phi_1 \rangle_1(s, Q_2; t) - i\hbar \langle \phi_1 | \dot{\phi}_1 \rangle_1(s; t) ]. \quad (5b)$$

The existence of the time derivative terms in the effective Hamiltonians appears to complicate the numerical evaluation of the latter. Notice, however, that by multiplying eq. (4a) on the left by  $\phi_1^*(s, Q_1; t)$  and integrating over  $Q_1$ , we obtain

$$i\hbar \left( \frac{\langle \dot{\phi}_1 | \dot{\phi}_1 \rangle_1}{\langle \phi_1 | \phi_1 \rangle_1} + \frac{\langle \dot{\phi}_2 | \dot{\phi}_2 \rangle_2}{\langle \phi_2 | \phi_2 \rangle_2} \right) = \frac{\langle H \rangle_{12}}{\langle \phi_1 | \phi_1 \rangle_1 \langle \phi_2 | \phi_2 \rangle_2}, \quad (6)$$

where  $\langle H \rangle_{12}$  denotes the Hamiltonian averaged over the bath coordinates,

$$\langle H \rangle_{12}(s; t) = \int dQ_1 \int dQ_2 \phi_1^*(s, Q_1; t) \phi_2^*(s, Q_2; t) H(s, Q_1, Q_2) \phi_1(s, Q_1; t) \phi_2(s, Q_2; t). \quad (7)$$

Making the symmetric choice

$$i\hbar \frac{\langle \dot{\phi}_1 | \dot{\phi}_1 \rangle_1}{\langle \phi_1 | \phi_1 \rangle_1} = i\hbar \frac{\langle \dot{\phi}_2 | \dot{\phi}_2 \rangle_2}{\langle \phi_2 | \phi_2 \rangle_2} = \frac{1}{2} \frac{\langle H \rangle_{12}}{\langle \phi_1 | \phi_1 \rangle_1 \langle \phi_2 | \phi_2 \rangle_2} \quad (8)$$

allows these terms to be easily calculated and guarantees that the effective Hamiltonians shall remain Hermitian at all times. The time evolution of the initial state is thus obtained by integrating the coupled differential equations for  $\dot{\phi}_1$  and  $\dot{\phi}_2$ .

Eqs. (4), with the effective Hamiltonians given by eqs. (5), conserve the normalization of the total wave function, as well as the mean energy. The norm conservation can be easily shown by writing

$$\begin{aligned} \frac{d}{dt} \langle \Phi | \Phi \rangle &= \int ds (\langle \phi_1 | \dot{\phi}_1 \rangle_1 \langle \phi_2 | \phi_2 \rangle_2 + \langle \phi_1 | \phi_1 \rangle_1 \langle \phi_2 | \dot{\phi}_2 \rangle_2 + \text{complex conjugate}) \\ &= \int ds [(i\hbar)^{-1} \langle H \rangle_{12} + \text{complex conjugate}] = 0, \end{aligned}$$

where use was made of eq. (6) as well as of the hermiticity of the Hamiltonian. The energy conservation property can be established in a similar fashion. Finally, because eqs. (4) fully incorporate the correlation effects due to direct system-bath coupling, the above equations are exact if only one of the bath modes is coupled to the reaction coordinate.

All equations derived above are straightforward to generalize to the case where the bath consists of  $N$  degrees of freedom. Thus, eqs. (2), (4) and (5) become

$$\Phi(s, \mathbf{Q}; t) = \prod_{k=1}^N \phi_k(s, Q_k; t), \quad (9)$$

$$i\hbar \dot{\phi}_k(s, Q_k; t) = H_{k,\text{eff}}(s, Q_k; t) \phi_k(s, Q_k; t), \quad (10)$$

$$\begin{aligned} H_{k,\text{eff}}(s, Q_k; t) &= \left( \prod_{k' \neq k}^N \int dQ_{k'} \phi_{k'}^*(s, Q_{k'}; t) \phi_{k'}(s, Q_{k'}; t) \right)^{-1} \\ &\times \prod_{k' \neq k}^N \int dQ_{k'} \phi_{k'}^*(s, Q_{k'}; t) H(s, Q_1, \dots, Q_N) \phi_{k'}(s, Q_{k'}; t) - i\hbar \sum_{k' \neq k}^N \frac{\int dQ_{k'} \phi_{k'}^*(s, Q_{k'}; t) \dot{\phi}_{k'}(s, Q_{k'}; t)}{\int dQ_{k'} \phi_{k'}^*(s, Q_{k'}; t) \phi_{k'}(s, Q_{k'}; t)}, \end{aligned} \quad (11)$$

and the time derivative terms are easily obtained according to

$$i\hbar \frac{\int dQ_k \phi_k^*(s, Q_k; t) \dot{\phi}_k(s, Q_k; t)}{\int dQ_k \phi_k^*(s, Q_k; t) \phi_k(s, Q_k; t)} = \frac{1}{N} \frac{\prod_{k'=1}^N \int dQ_{k'} \phi_{k'}^*(s, Q_{k'}; t) H(s, Q_1, \dots, Q_N) \phi_{k'}(s, Q_{k'}; t)}{\prod_{k'=1}^N \int dQ_{k'} \phi_{k'}^*(s, Q_{k'}; t) \phi_{k'}(s, Q_{k'}; t)}. \quad (12)$$

The evolution of each function  $\phi_k(s, Q_k; t)$  is therefore governed by the average of the Hamiltonian over all other bath modes  $Q_{k'}$ ,  $k' \neq k$ . *No averaging over the strongly coupled system coordinate is performed.* The time propagation is performed by integrating numerically  $N$  two-dimensional coupled differential equations of the form of eq. (10), with the effective Hamiltonians given by eq. (11).

## 2.2. Numerical procedure

Perhaps the most straightforward scheme for propagating a wave function according to the idea described in section 2.1 is to discretize each  $\phi_k$  on a two-dimensional grid, evaluate the right-hand side of eq. (10) at each grid point, and use some differential equation solver to integrate the resulting first-order coupled differential equations by one time step. The number of grid points required can be minimized by performing all kinetic energy operations in the momentum representation, in which the kinetic energy operator is local. The transformation between the position and the momentum representation is performed very efficiently with the FFT algorithm. Evaluating the effective Hamiltonians reduces essentially to computing two-dimensional integrals, and scales linearly with  $N$ . Another alternative [12] is to expand each system-bath wave function  $\phi_k$  in a basis set with time-dependent coefficients, and integrate numerically the coupled differential equations which determine the evolution of the expansion coefficients. Note that split propagator algorithms [1] cannot be used for the time propagation, because the effective Hamiltonian operators involved mix position and momentum for the  $s$  degree of freedom in a non-additive sense.

The choice of the most appropriate differential equation integrator will generally depend on the particular problem and involves a compromise between speed and numerical accuracy. The simple second-order differencing (SOD) scheme [17] requires a single evaluation of the Hamiltonian (which is the most time-consuming part of the calculation) per time step; the local error of the method per time step  $\Delta t$  scales as  $\Delta t^3$ , but the global error grows as  $\Delta t^2$  and often becomes unacceptably large after a few hundred propagation steps. Higher-order predictor-corrector or extrapolation [18] based algorithms are usually accurate and efficient. A sixth-order Gear integrator [19] (which requires two Hamiltonian operations per time step) with fourth-order Runge-Kutta [20] initiation procedure was found quite satisfactory in terms of speed and precision.

## 3. Applications

We demonstrate the high accuracy of the method described in section 2 by applying it to a model three-degree-of-freedom system-bath Hamiltonian,

$$H = \frac{p_s^2}{2m} + V_0(s) + \sum_{k=1}^2 \left( \frac{P_k^2}{2m} + \frac{1}{2} m \omega_k^2 Q_k^2 - f_k(s) Q_k \right). \quad (13)$$

To provide a challenge to the method, we choose  $V_0(s)$  to be a symmetric double well potential, in view of the difficulty that the standard single-configuration TDSCF approximation has been found to face in that case [12]. The parameters are taken such that eq. (13) describes tunneling of a hydrogen atom between two equilibrium configurations which for  $c_1 = c_2 = 0$  are separated by a distance of 1.1 Å and by a barrier of 7.8 kcal/mol. The two bath degrees of freedom represent normal-mode-type vibrations and are strongly coupled to the reaction coordinate  $s$ . Two different forms of the coupling functions, which give rise to different symmetry properties of the global potential [21], are considered: (a) linear coupling,  $f_k(s) = c_k s$ , and (b) quadratic coupling,  $f_k(s) = c_k s^2$ .

In the calculations presented below the time evolution of the initial states was obtained with the method described in section 2; each of the two-dimensional wave functions  $\phi_1$  and  $\phi_2$  was discretized on a two-dimensional grid, and the corresponding amplitudes were propagated according to eqs. (4) using a sixth-order Gear integrator routine (see also section 2.2). To compare with exact calculations, the same initial states were propagated using Feit and Fleck's split propagator algorithm [1]. The single configuration TDSCF scheme was also tried and compared.

For the first example  $f_1(s) = c_1 s$  and  $f_2(s) = c_2 s^2$ , with  $c_1 = 0.1$  and  $c_2 = 0.05$  in atomic units, while  $\omega_1 = \omega_2 = 3000 \text{ cm}^{-1}$ . Fig. 1 shows contour plots of the corresponding potential energy surface. It is obvious from the extent of the distortion of the potential from the uncoupled ( $c_1 = c_2 = 0$ ) fully symmetric potential that the effect

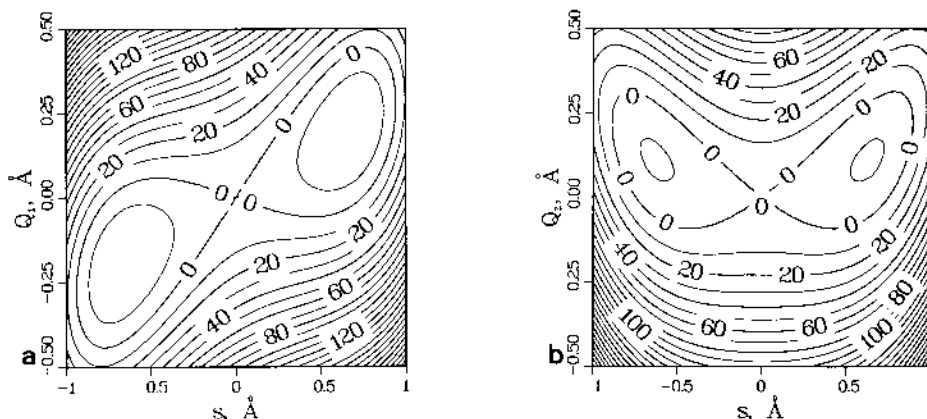


Fig. 1. Contour plots of the potential used in the first calculation of section 3 (cf. eq. (13)). The parameters are given in the text. The numbers labeling the curves indicate the height of the potential surface in kcal/mol. (a) Plot of the potential as a function of  $s$  and  $Q_1$  at fixed  $Q_2=0$ . (b) Plot of the potential as a function of  $s$  and  $Q_2$  at fixed  $Q_1=0$ .

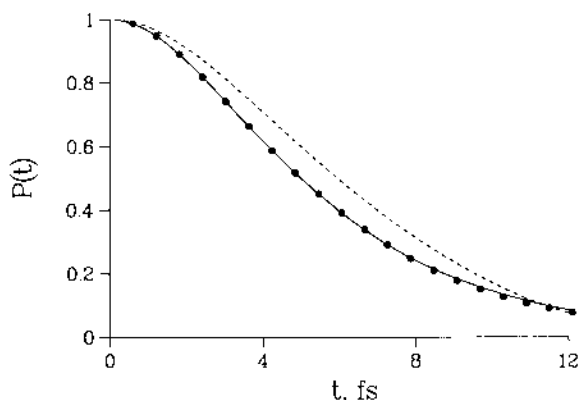


Fig. 2. The survival probability, eq. (15), as a function of time, for the first calculation discussed in section 3. The circles indicate results obtained with the method presented in this paper. Exact results are shown by the solid line. The dashed line shows the survival probability as calculated with the standard single configuration TDSCF approach.

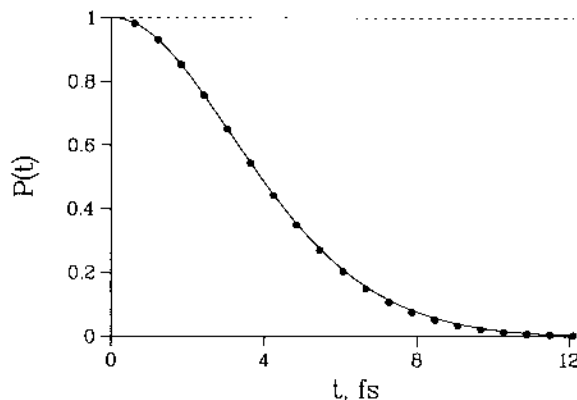


Fig. 3. The survival probability, eq. (15), as a function of time, for the second example discussed in section 3. The circles indicate results obtained with the method presented in this paper. Exact results are shown by the solid line. The dashed line shows the survival probability as calculated with the standard single configuration TDSCF approach.

of the coupling on the dynamics should be very significant. The initial wave function is chosen to be a three-dimensional Gaussian of the form

$$\Phi(s, Q_1, Q_2; 0) = \psi_0(s) \psi_1(Q_1) \psi_2(Q_2), \quad (14)$$

centered at the saddle point ( $s=Q_1=Q_2=0$ ) of the potential;  $\psi_1$  and  $\psi_2$  have widths equal to the widths of the lowest energy eigenstates of the harmonic  $Q_1$  and  $Q_2$  potentials, respectively, while the  $s$  function  $\psi_0$  is chosen to resemble the ground state of the quadratic fit to  $V_0$  about either one of the two potential minima.

Fig. 2 shows the survival probability,

$$P(t) = |\langle \Phi(t) | \Phi(0) \rangle|^2, \quad (15)$$

as a function of the time  $t$ , as obtained with the present method, and compares with the exact results. The agreement is seen to be excellent (error  $<0.5\%$ ) at all times. Also shown is the survival probability as given by the standard TDSCF approximation; this is seen to deviate considerably from curve showing the exact results, as anticipated.

In the second test calculation the double well is coupled linearly to both of the bath oscillators, which have frequencies  $\omega_1 = 300 \text{ cm}^{-1}$  and  $\omega_2 = 1000 \text{ cm}^{-1}$ ; the coupling constants are  $c_1 = 0.006$  and  $c_2 = 0.02$  atomic units. Strongly coupled low frequency bath modes have been found [21] to affect the dynamics in a very dramatic way, and most known approximations are unable to treat such problems successfully. The initial state has the form of eq. (14) and uses the same  $\psi_1$  and  $\psi_2$  Gaussian functions as in the previous example; the  $s$  wave function  $\psi_0$ , though, is chosen as the ground state of the one-dimensional double well  $V_0$ . Thus, the initial state is an eigenstate of the uncoupled potential, and any non-trivial time evolution results merely from system-bath coupling.

In this case the standard TDSCF approximation breaks down completely, as it fails to obtain any time evolution of the initial state. This is so because the average forces  $\langle f_k \rangle$  and bath positions  $\langle Q_k \rangle$  over the symmetric one-dimensional initial wave functions are *zero*, and therefore the effective potentials are independent of the coupling. The coupling terms drop out from the TDSCF equations at subsequent times as well, as the wave function remains an eigenstate of the uncoupled Hamiltonian and is thus symmetric at any time. On the contrary, the method presented in this paper yields very accurate time evolution because it explicitly takes into account the effects of direct system-bath coupling. The survival probability is shown in fig. 3, where it is also compared with numerically exact results. The quantitative agreement (error  $<0.5\%$ ) shows the power of the present approach; the TDSCF result is  $P(t) = 1$  for any time, as explained above.

#### 4. Concluding remarks

The idea described in this paper constitutes a major step forward in the direction of exploring the dynamics of strongly coupled multidimensional systems. The method should be most useful for problems that involve strong coupling or one physically important coordinate to several "bath" degrees of freedom. The novel feature of the present approach is that it is based on the time-dependent mean field idea and therefore requires numerical effort which grows *linearly* with the number of degrees of freedom, while at the same time it explicitly incorporates two-body correlation between strongly coupled modes, thus achieving very high accuracy.

Apart from direct use to study the time evolution of systems initially prepared in a non-stationary state, an important application of the technique presented in section 2 involves calculation of reaction rates in polyatomic molecules according to the flux correlation function [22] formalism, and this work is in progress.

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#### References

- [1] M.D. Feit, J.A. Fleck Jr. and A. Steiger, *J. Comput. Phys.* 47 (1982) 412; M.D. Feit and J.A. Fleck Jr., *J. Chem. Phys.* 78 (1983) 301.
- [2] R.P. Feynman, *Rev. Mod. Phys.* 20 (1948) 367; R.P. Feynman and A.R. Hibbs, *Quantum mechanics and path integrals* (McGraw-Hill, New York, 1965).

- [3] N. Metropolis, A.W. Rosenbluth, M.N. Rosenbluth, H. Teller and E. Teller, *J. Chem. Phys.* 21 (1953) 1087;  
J.P. Valleau and S.G. Whittington, in: *Modern theoretical chemistry*, Vol. 5, ed. B.J. Berne (Plenum Press, New York, 1977) pp. 137-168.
- [4] V.S. Filinov, *Nucl. Phys. B* 271 (1986) 717.
- [5] N. Makri and W.H. Miller, *Chem. Phys. Letters* 139 (1987) 10; *J. Chem. Phys.* 89 (1988) 2170;  
N. Makri, *Chem. Phys. Letters* 159 (1989) 489
- [6] J.D. Doll and D.L. Freeman, *Advan. Chem. Phys.* 73 (1988) 120;  
J.D. Doll, D.L. Freeman and M.J. Gillan, *Chem. Phys. Letters* 143 (1988) 277;  
J.D. Doll, T.L. Beck and D.L. Freeman, *J. Chem. Phys.* 89 (1988) 5753;  
T.L. Beck, J.D. Doll and D.L. Freeman, *J. Chem. Phys.* 90 (1989) 3181.
- [7] E.J. Heller, *J. Chem. Phys.* 62 (1975) 1544; 65 (1976) 4979; 67 (1977) 3339; 68 (1978) 3891;  
M.J. Davis and E.J. Heller, *J. Chem. Phys.* 71 (1979) 3383;  
N. DeLeon, M.J. Davis and E.J. Heller, *J. Chem. Phys.* 80 (1984) 794.
- [8] D. Huber and E.J. Heller, *J. Chem. Phys.* 87 (1987) 5302;  
D. Huber, E.J. Heller and R.G. Littlejohn, *J. Chem. Phys.* 89 (1988) 2003.
- [9] R.B. Gerber, V. Buch and M.A. Ratner, *J. Chem. Phys.* 77 (1982) 3022; *Chem. Phys. Letters* 91 (1982) 173;  
V. Buch, R.B. Gerber and M.A. Ratner, *Chem. Phys. Letters* 101 (1983) 44;  
G.C. Schatz, V. Buch, M.A. Ratner and R.B. Gerber, *J. Chem. Phys.* 79 (1983) 1808.
- [10] R.B. Gerber, V. Buch and M.A. Ratner, in: *Intramolecular Dynamics, Proceedings of the 15th Jerusalem Symposium on Quantum Chemistry and Biochemistry*, eds. J. Jortner and B. Pullman (Reidel, Dordrecht, 1982).
- [11] R. Harris, *J. Chem. Phys.* 72 (1980) 1776.
- [12] N. Makri and W.H. Miller, *J. Chem. Phys.* 87 (1987) 5781.
- [13] Z. Kotler, A. Nitzan and R. Kosloff, *Chem. Phys. Letters* 153 (1988) 483;  
R. Kosloff, *J. Phys. Chem.* 92 (1988) 2087.
- [14] J. Kucar, H.D. Meyer and L.S. Cederbaum, *Chem. Phys. Letters* 140 (1987) 525;  
H.D. Meyer, J. Kucar and L.S. Cederbaum, *J. Math. Phys.* 29 (1988) 1417.
- [15] D. Kumamoto and R. Silbey, *J. Chem. Phys.* 75 (1981) 5164.
- [16] W.H. Miller, N.C. Handy and J.E. Adams, *J. Chem. Phys.* 72 (1980) 99;  
W.H. Miller, *J. Phys. Chem.* 87 (1983) 3811; in: *The theory of chemical reaction dynamics*, ed. D.C. Clary (Reidel, Dordrecht, 1986) pp. 27-45;  
W.H. Miller, B.A. Ruf and Y.T. Chang, *J. Chem. Phys.* 89 (1988) 6298.
- [17] A. Askar and A.S. Cakmak, *J. Chem. Phys.* 68 (1978) 2794.
- [18] W.H. Press, B.P. Flannery, S.A. Teukolsky and W.T. Vetterling, *Numerical recipes* (Cambridge Univ. Press, Cambridge, 1986).
- [19] C.W. Gear, *Math. Comput.* 21 (1967) 146.
- [20] C.E. Gerald, *Applied numerical analysis*, 2nd Ed. (Addison-Wesley, Reading, 1980).
- [21] N. Makri and W.H. Miller, *J. Chem. Phys.* 86 (1987) 1451.
- [22] W.H. Miller, S.D. Schwartz and J.W. Tromp, *J. Chem. Phys.* 79 (1983) 4889.