

# Continuous configuration time-dependent self-consistent field method for polyatomic quantum dynamical problems

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A new continuous configuration time-dependent self-consistent field method has been developed to study polyatomic dynamical problems by using the discrete variable representation for the reaction system, and applied to a reaction system coupled to a bath. The method is very efficient because the equations involved are as simple as those in the traditional single configuration approach, and can account for the correlations between the reaction system and bath modes rather well. © 2005 American Institute of Physics. [DOI: 10.1063/1.1869496]

The last decade has witnessed significant progress in quantum mechanical studies of dynamical chemical processes at the molecular level. The development of the time-dependent wave packet (TDWP) method has made it possible to perform exact quantum mechanical calculations for four-atom systems.<sup>1-4</sup> The recent report on the state-to-state integral cross sections for the H+H<sub>2</sub>O reaction suggests that we are close to solving four-atom reactive scattering problems completely.<sup>2</sup>

The grand challenge in the field of quantum dynamics now is to develop practical yet accurate methods to study polyatomic dynamical problems involving many atoms. However, due to the fact that computational effort grows exponentially with dimensionality, it is impractical at present to study polyatomic dynamical processes exactly in full dimensions although there has been some progress in this direction.<sup>5</sup> Naturally, one has to resort to the reduced dimensionality approach to cut down the number of degrees of freedom included in dynamical studies, or some computational approximate methods to overcome the scaling of effort with dimensionality.

A promising approach is the time-dependent self-consistent field (TDSCF) method.<sup>6-15</sup> In the simplest version, i.e., the single configuration time-dependent self-consistent field (SC-TDSCF) approach, the wave function of the system is written as a direct product of the wave functions for subsystems.<sup>7-10,12</sup> A principal drawback of SC-TDSCF is that it replaces exact interaction between subsystems by mean-field coupling, resulting in the lack of correlations between subsystems. One way to account for the important correlations neglected in SC-TDSCF is to add wave functions with different configurations to give more flexibility to the wave function of the system, resulting in the so-called multiconfiguration time-dependent self-consistent field (MC-TDSCF)

method.<sup>6,13-15</sup> Wave functions with different configurations are usually constructed by imposing orthogonal condition explicitly, making it hard to use more than a few configurations in numerical implementation. Furthermore, the resulting equations for MC-TDSCF are very complicated compared to those in SC-TDSCF method. For these reasons, MC-TDSCF has only been applied to some model problems. The closely related multiconfiguration time-dependent Hartree method (MCTDH) generalizes MC-TDSCF in a systematic way, thus eliminating the need for choices of the TDSCF states.<sup>16,17</sup> It has successfully been applied to study various realistic and complex quantum dynamical problems (see Ref. 17 for references). However, the general application of MCTDH method to strongly correlated systems yields a numerical method wherein the number of possible TDSCF configuration grows exponentially with the number of degrees of freedom, again confining practical use of the method to relatively small systems.

Here, we propose a new and efficient scheme for MC-TDSCF. Very often dynamical processes in polyatomic systems can be described as a system of a few strongly coupled degrees of freedom which characterize the process of interest, coupled with clusters of bath modes. Bath modes inside a cluster may be coupled to each other, but the coupling between bath modes in different clusters is negligible. The basic idea for our new method is to use discrete variable representation (DVR)<sup>18</sup> for the system and then to each DVR point of the system we associate a configuration of wave function in terms of direct product wave functions for different clusters of the bath modes. In this way, the correlations between the system and bath modes, as well as the correlations between bath modes in each individual cluster can be described properly, while the correlations between bath modes in different clusters are neglected. Since DVR used

for the system are orthogonal, the resulting equations are as simple in structure as those for SC-TDSCF. The dimensionalities of the equations are determined by the number of degrees of freedom in the system and in each individual cluster of bath modes. In this approach the configuration can change continuously with system coordinates, hence we denote this method as continuous-configuration time-dependent self-consistent field (CC-TDSCF) method to differentiate it from other MC-TDSCF methods.

For clarity, let us first use a one-dimensional system coupled to some one-dimensional bath modes to derive the equations of motion,

$$H = \frac{P_s^2}{2M} + V_0(s) + \sum_{k=1}^N \left[ \frac{p_k^2}{2m_k} + v(x_k) \right] - \sum_{k=1}^N f_k(s, x_k) \\ = H_s + \sum_{k=1}^N h_k(x_k) - \sum_{k=1}^N f_k(s, x_k), \quad (1)$$

where  $s$  is the system coordinate and  $x_i$  ( $i=1, \dots, N$ ) are bath modes each of which is coupled to the system.

The CC-TDSCF *ansatz* for the total wave function is written as follows:

$$\Psi(s, x_1, \dots, x_N, t) = \sum_{i=1}^M C_i(t) |s_i\rangle \Phi_i(x_1, \dots, x_N, t), \quad (2)$$

where  $|s_i\rangle$  denotes DVR points for the system coordinate  $s$ ;  $\Phi_i(x_1, x_2, \dots, x_N, t)$ , which depends on the DVR point  $s_i$ , is written as a product of single-mode functions as in the single configuration TDSCF,

$$\Phi_i(x_1, \dots, x_N, t) = \prod_{k=1}^{k=N} \phi_i^k(x_k, t), \quad (3)$$

where  $\phi_i^k(x_k, t)$  is the time-dependent wave function for the  $x_k$  bath coordinate at the  $i$ th DVR point in the system coordinate with the constraints

$$\langle \phi_i^k(t) | \frac{\partial}{\partial t} \phi_i^k(t) \rangle = 0, \quad \text{and} \quad \langle \phi_i^k(0) | \phi_i^k(0) \rangle = 1, \quad (4)$$

for  $k=1, 2, \dots, N$ . These constraints will guarantee that the single-mode functions are normalized at any time  $t$ .

For simplification in writing, we introduce the "single-hole function:"

$$\Phi_i^{(k)} = \phi_i^1 \cdots \phi_i^{(k-1)} \phi_i^{(k+1)} \cdots \phi_i^N, \quad (5)$$

then  $\Phi_i$  in Eq. (3) can be written as

$$\Phi_i = \phi_i^k \Phi_i^{(k)}. \quad (6)$$

Employing the Dirac-Frenkel variational principle,<sup>19</sup> we obtain

$$i\dot{C}_i = \sum_j \langle s_i \Phi_i | \hat{H} | \Phi_j s_j \rangle C_j, \quad \text{for } i = 1, \dots, M; \quad (7)$$

$$i[\dot{C}_i \phi_i^k + C_i \dot{\phi}_i^k] = \sum_j \langle s_i \Phi_i^{(k)} | \hat{H} | s_j \Phi_j^{(k)} \rangle [C_j \phi_j^k], \\ \text{for } k = 1, 2, \dots, N. \quad (8)$$

At this stage, substituting Eq. (7) into Eq. (8) will result in complicated equations for  $\phi^k$ . To avoid this problem, we define a new function,

$$\varphi_i^k = C_i \phi_i^k. \quad (9)$$

Then Eq. (8) can be rewritten as

$$i\dot{\varphi}_i^k = \sum_j \langle s_i \Phi_i^{(k)} | \hat{H} | s_j \Phi_j^{(k)} \rangle \varphi_j^k, \quad k = 1, \dots, N. \quad (10)$$

The resulting equations for  $\varphi_i^k$  are extremely simple and can be solved by using the split-operator method as in the regular time-dependent wave packet approach.

Finally, the single-mode function  $\phi_i^k$  can be obtained by multiplying  $C_i^*$  on both sides of Eq. (9) and resorting the normalization conditions for the single-mode functions,

$$C_i^* \varphi_i^k = |C_i|^2 \phi_i^k, \Rightarrow \phi_i^k = \frac{C_i^* \varphi_i^k}{\|C_i^* \varphi_i^k\|}, \quad (11)$$

where  $\|f\| = \sqrt{\langle f | f \rangle}$  denotes the modulo of a function.

We can see from Eq. (7) and Eq. (10) that the evolution of  $C_i$  in Eq. (7) is governed by a one-dimensional effective Hamiltonian arising from averaging the total Hamiltonian over all the bath modes at each DVR point in the system coordinate, while the evolution of the  $k$ th bath mode wave function is governed by a two-dimensional effective Hamiltonian arising from averaging the total Hamiltonian over all the bath modes except itself ( $k$ th mode) on each DVR point in the system coordinate. Hence one needs to solve a single one-dimensional equation and  $N$  two-dimensional equations to propagate the total wave function.

Although Eq. (7) and Eq. (10) are derived here for a one-dimensional system coordinate  $s$  and one-dimensional bath modes, these two equations can be generalized to a system with  $\alpha$  degrees of freedom coupled to  $N$  bath clusters with the  $k$ th bath cluster comprised of  $\beta_k$  degrees of freedom. Under this generalization, one needs to solve one  $\alpha$  dimensional equation for the system, plus  $N$  equations for the bath clusters with a dimension of  $\alpha \times \beta_k$  for  $k$ th bath cluster.

Now we test the CC-TDSCF method for the model system of a one-dimensional double well linearly coupled to a harmonic bath.<sup>20-22</sup> This system has been used extensively in recent years to test new quantum dynamics methodologies, in particular for those semiclassical theory based methodologies.<sup>23,24</sup> In order to compare with exact quantum dynamics results easily, we limit the number of bath modes in our test to 5. The frequency for the  $k$ th mode,  $\omega_k$ , ( $k=1, 2, \dots, 5$ ) is simply taken as  $\omega_k = k \times 500 \text{ cm}^{-1}$  by choosing the frequency density to be  $\rho(\omega) = 1/500 \text{ cm}^{-1}$  and the maximum cut-off frequency  $\omega_m = 5\omega_c = 2500 \text{ cm}^{-1}$ , where  $\omega_c = 500 \text{ cm}^{-1}$  is the cut-off frequency for the Ohmic spectral density for the bath modes,

$$J(\omega) = \eta \omega e^{-\omega/\omega_c}. \quad (12)$$

For such a system, the thermal rate constant,  $k(T)$ , can be calculated from the time integral of a flux-flux autocorrelation function<sup>23–25</sup>

$$k(T) = Q_r(T)^{-1} \int_0^\infty dt C_{ff}(t), \quad (13)$$

where  $Q_r(T)$  is the reactant partition function,

$$C_{ff}(t) = \text{tr}[\hat{F}e^{i\hat{H}t_c}\hat{F}e^{-i\hat{H}t_c}] = \sum_{n=0} C_{ff}^n(t), \quad (14)$$

and  $t_c = t - i\beta/2$  with  $\beta = (k_B T)^{-1}$ .  $C_{ff}^n$  is defined as the autocorrelation function for the  $n$ th transition state wave packet.<sup>25</sup> Here, we will focus on the flux-flux autocorrelation function for its ground transition state wave packet,<sup>25</sup>

$$C_{ff}^0(t) = \langle \psi(t) | \hat{F} | \psi(t) \rangle, \quad (15)$$

where

$$|\psi(t)\rangle = e^{-i\hat{H}t} e^{-\hat{H}\beta/2} \sqrt{|\lambda|} |+\rangle |g_1(x_1) \cdots g_N(x_N)\rangle, \quad (16)$$

$|+\rangle$  is the eigenfunction for the system coordinate flux operator at  $s=0$  with an eigenvalue of  $\lambda$ , and  $|g_k(x_k)\rangle$  ( $k=1, 2, \dots, N$ ) is the ground state wave function for  $h_k(x_k)$ . From Eq. (16), one can see that we first propagate each transition state wave packet in imaginary time to  $\beta/2$ , and then propagate it in real time.

Figure 1 shows  $C_{ff}^0$  as a function of real time propagation,  $t$ , for the ground transition state at  $T=300$  K for  $\eta = 0.2, 1.0, 4.0$ . [see Eq. (12)]. When  $\eta=0.2$ , the coupling between system coordinate and bath mode is weak. Re-crossing of  $C_{ff}^0$  (autocorrelation function  $C_{ff}^0$  crosses through zero) will occur as found in previous studies,<sup>22–24</sup> due to the fact that energy in the system coordinate cannot be dissipated effectively into the bath modes. Because of weak coupling between system and bath modes, we also expect the SC-TDSCF to work quite well for a short time  $t$ . Figure 1(a) does show these features. As can be seen from the exact quantum results, a negative recrossing occurs starting from  $t=2200$  a.u., following a small positive recrossing starting from 1600 a.u. Then at  $t=3800$  a.u., another positive recrossing occurs. (As shown by Topaler and Makri,<sup>22</sup>  $C_{ff}^0$  will decay to zero after the negative recrossing if one includes sufficient number of bath modes instead of 5 bath modes in this test study.) The CC-TDSCF  $C_{ff}^0$  precisely follows the exact  $C_{ff}^0$  from  $t=0$  up to  $t=1500$  a.u. The perfect agreement between the exact  $C_{ff}^0$  and the CC-TDSCF  $C_{ff}^0$  at  $t=0$  indicates that the CC-TDSCF approximation is sufficiently accurate to describe the wave function of the system during imaginary time propagation. At  $t > 1500$  a.u., one can see that the CC-TDSCF  $C_{ff}^0$  begins to oscillate rapidly about the exact  $C_{ff}^0$ . Figure 1(a) also shows  $C_{ff}^0$  based on the SC-TDSCF approach. At  $t=0$ , the SC-TDSCF  $C_{ff}^0$  is very close to the exact  $C_{ff}^0$ , indicating that the SC-TDSCF approximation is quite good for imaginary time propagation because of weak coupling between the system coordinate and bath modes. Up to  $t=1500$  a.u., the SC-TDSCF  $C_{ff}^0$  follows the exact  $C_{ff}^0$  quite well, decaying to a very small value. As real

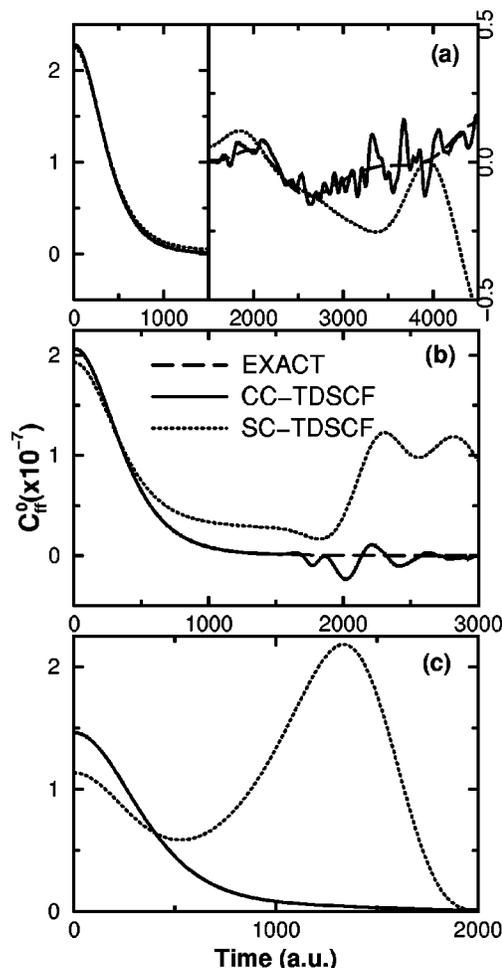


FIG. 1.  $C_{ff}^0$  as a function of real time propagation calculated by using exact wave packet propagation, CC-TDSCF, and SC-TDSCF methods for (a)  $\eta = 0.2$  in Eq. (12); (b)  $\eta=1.0$ ; (c)  $\eta=4.0$ . Note the change of y scale on the right half of (a).

time propagation continues, the discrepancy between the SC-TDSCF and exact  $C_{ff}^0$  begins to build up, in particular after  $t=4000$  a.u.

In Fig. 1(b) and 1(c), we show  $C_{ff}^0$  as a function of real time propagation,  $t$ , for  $\eta=1.0$  and  $4.0$ , corresponding to intermediate and strong coupling regions, respectively. The exact  $C_{ff}^0$  for both  $\eta=1.0$  and  $4.0$  show very simple behavior: decay to zero essentially without any recrossings. For  $\eta=4.0$  the CC-TDSCF  $C_{ff}^0$  exactly follows the exact  $C_{ff}^0$ , decaying to zero without any recrossings, while for  $\eta=1.0$  the CC-TDSCF  $C_{ff}^0$  exactly follows the exact  $C_{ff}^0$  only up to  $t=1600$  a.u. After that, one can see some small oscillations around the CC-TDSCF  $C_{ff}^0$  which is equal to zero in the region. As expected, the SC-TDSCF approximation begins to deteriorate and finally breaks down as the coupling between the system coordinate and bath modes increases. For  $\eta=4.0$ , one can see that the SC-TDSCF  $C_{ff}^0$  is considerably smaller than the exact  $C_{ff}^0$  at  $t=0$  after imaginary time propagation, and it incorrectly blows up after  $t=500$  a.u.

As we know  $C_{ff}^0$  is measured at  $s=0$ , hence it may not give a complete picture for the whole wave functions. In Fig. 2, we show the wave functions calculated by using different methods as a function of  $s$  after integrating over bath coor-

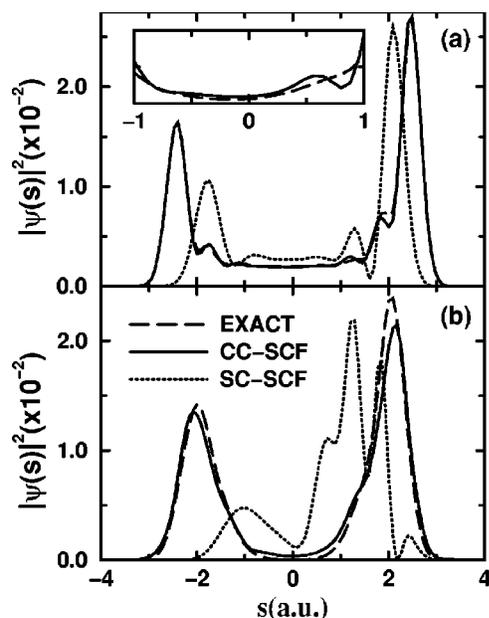


FIG. 2. Wave functions calculated by using different methods as a function of  $s$  after integrating over bath coordinates at (a)  $t=1500$ ; (b)  $t=3000$  a.u. for  $\eta=1.0$ .

ordinates at  $t=1500$  and  $3000$  a.u. for  $\eta=1.0$ . We see from Fig. 1 that the value  $C_{ff}^0$  predicted by the CC-TDSCF method does not agree perfectly with the exact  $C_{ff}^0$  at  $t > 1500$  a.u. for  $\eta=1.0$ . However, at  $t=1500$  a.u., the overall agreement between the exact wave function and the CC-TDSCF result is remarkable. Around  $s=0$ , we can see from the insert in Fig. 2(a) that the CC-TDSCF wave function is not as smooth as the exact wave function, resulting in the oscillatory behavior in  $C_{ff}^0$  for  $t > 1600$  a.u. Even at  $t=3000$ , the CC-TDSCF wave function agrees with the exact one quite well. The SC-TDSCF wave function is only slightly smaller than the exact one at  $t=0$ . But as the time increases, the discrepancy becomes more severe. At  $t=3000$ , the SC-TDSCF wave function differs totally from the exact wave function, except qualitatively for both wave functions being separated into two parts around  $s=0$ .

Thus to this model harmonic bath system, the CC-TDSCF approach is much more accurate than the traditional SC-TDSCF method, because it allows the bath wave function to change continuously along the system coordinate, in contrast to the SC-TDSCF method which just uses one bath

wave function. For this model problem, the CC-TDSCF approach is capable of producing semiquantitative, or even quantitative results. Also, the equations used in this approach are as simple in structure as those in the SC-TDSCF method, except that the number of dimensions involved is higher than in SC-TDSCF. But by choosing the system and bath modes carefully, one can always keep the number of dimensions in CC-TDSCF within the computational power one has.

Finally, the methodology used in this study to obtain a set of linear equations by defining a new wave function in Eq. (9) can also be applied to the multiconfiguration time-dependent Hartree (MCTDH) method.<sup>17</sup> The results will be reported soon.<sup>26</sup>

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