Nonadiabatic dynamics with the help of multiconfigurational Ehrenfest

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Abstract

This article proposes an improved version of recently developed Multiconfigurational
Ehrenfest approach to quantum dynamics. The idea of the approach is to use Frozen
Gaussians (FG) guided by Ehrenfest trajectories as a basis set for fully quantum
propagation. The method is applied to simulation of nonadiabatic dynamics of pyrazine
and shows that nonadiabatic dynamics on two coupled electronic states S₂ and S₁, which
determines pyrazine absorption spectrum, can be simulated with the help of a basis
comprised of very small number of trajectory guided basis functions. For the 24D model
good results were obtained with the basis of only 250 trajectory guided FG per electronic
state. The efficiency of the method makes it particularly suitable for future application
together with direct dynamics, calculating potentials on the fly.

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1. Introduction

Developing methods capable of treating quantum systems with many degrees of freedom (DOF) is the key problem of computational chemistry and physics. Due to exponential scaling of basis sets size $N=I^M$ with the number of degrees of freedom $M$ standard grid or basis set techniques are limited to only few DOF. New techniques push the limits of quantum mechanics much further. Although still suffering from exponential scaling Multiconfigurational Time Dependent Hartree method (MCTDH) [1-3] is capable of treating 20-30 DOF. Even larger systems are accessible for multilayer MCTDH [4]. MCTDH reduces the base of exponent by combining modes into groups and using small number of very flexible configurations per group. Many numerically accurate results have been obtained with the MCTDH technique. The method has been critically reviewed from the point of view of pure mathematics in [5].

Another group of methods of multidimensional quantum dynamics relies on trajectory guided basis sets [6-19]. The basis functions are often chosen to be Frozen Gaussian Coherent States (CS) and the existing trajectory based approaches differ in their prescriptions for guiding the basis. The main advantage of the trajectory based methods is that they sample only dynamically important regions of the phase space thus minimising the basis set size. Another attractive feature is that the basis can be selected randomly, which avoids exponential growth of the basis set size and therefore can be particularly useful in many dimensions.

The method of Multiple Spawning [11-15] (MS) has been developed for treating nonadiabatic dynamics, which involves more than one potential energy surface. The central feature of the MS approach is the use of adaptive basis sets. New basis functions are generated continuously in the process called spawning [14,15]. When a Gaussian
approaches the region of strong nonadiabatic coupling between the two electronic states
an elegant but somewhat ad hoc procedure called spawning is used to generate new basis
function on another surface. The main problem with the MS method is that the Gaussians
on two different potential energy surfaces quickly run away from each other and become
decoupled. This was highlighted in the recent article [15] which shows that in order to
keep significant coupling the basis set must be continuously increased quickly becoming
rather large.

Similar to MS the method of variational Multiconfigurational Gaussians (vMCG)
[16] represents the wave function as a superposition of Frozen Gaussian Coherent States.
The difference is that their trajectories are determined from full variational principle
applied simultaneously to all parameters of the wave function (i.e. phase space positions
of the Coherent States and their amplitudes). The trajectories are therefore nonclassical
and can go into classically forbidden regions. Gaussian MCTDH (G-MCTDH) method
[17] uses MCTDH approach and regular basis for few most important modes and
Gaussian CS for the rest of the degrees of freedom (DOF). The central common feature
of vMCG and G-MCTDH is that both use a fully variational equations for the parameters
of the wave function. Variational principle is a powerful tool of quantum mechanics.
However finding fully variational vMCG and G-MCTDH trajectories can be rather
expensive because it requires a solution of the system of linear equation for time
derivatives of all wave function parameters at each time step of the propagation. This is a
common feature of many variational techniques [18]. Nevertheless, the variational
trajectories follow the dynamics of the wave packet and the hope is that this benefit will
out-weight their high computational cost.
The method of Coupled Coherent States (CCS) [6-9] is somewhat in between MS and vMCG. CCS uses trajectories which are driven by the Hamiltonian averaged over the Gaussians. This brings quantum corrections into the Hamiltonian and changes trajectories allowing some of them into the classically forbidden regions. Thus, CCS trajectories account for some quantum effects, although to a lesser extent than fully variational trajectories do. On the other hand the CCS trajectories are independent from each other, just like classical trajectories. CCS equations for the Coherent States amplitudes are similar for those of MS and therefore much cheaper than those of vMCG. A number of multidimensional systems have been simulated with the CCS method [6-10]. For example it has been shown that accurate propagation for a 10D problem can be achieved with the basis of only 100 trajectory guided Gaussian Coherent States [10]. Even a basis of only 10 CS was able to provide a semiquantitative description of the dynamics in 10D system [10].

In the recent paper [19] a new Multiconfigurational Ehrenfest (MCE) method has been suggested, which is a generalisation of CCS for nonadiabatic processes occurring on two or more electronic potential energy surfaces. The idea is to use Ehrenfest trajectories on a potential which is an average between the two electronic states to guide the quantum basis set of Frozen Gaussian CS. The Hamiltonians for all trajectories are quite close and the hope is that the trajectories diverge less than in the MS method, when they move on two different potential energy surfaces. Comparably to fully variational trajectories the Ehrenfest trajectories are much less expensive to calculate. The analysis of variational trajectories shows that in a truly multidimensional system after some time they run away from each other and fully variational equations become those of the Ehrenfest approach. The power of the MCE method has been demonstrated in [19], where well converged
results were obtained for Spin-Boson model with up to 2000 DOF using no more than 200 basis functions.

In this paper an improved version of the MCE method is reported and tested by calculating the absorption spectrum of pyrazine, which has served as a benchmark for a number of methods of multidimensional quantum mechanics. Pyrazine adsorption spectrum has been simulated previously by MCTDH [3], the matching pursuit algorithm [20], and with relatively low accuracy by CCS and MS methods [7,13]. Recently the same system has been used to test G-MCTDH [17]. Also pyrazine has served as a benchmark for number of approximations such as semiclassical Herman-Kluck propagator and single switch surface hopping [21,22]. The most accurate calculations of pyrazine nonadiabatic dynamics [3,17] is based on the MCTDH wave functions with more than 10 million coupled variational parameters and huge basis sets. It will be shown in this paper that the MCE technique reproduces the main features of absorption spectrum of pyrazine with only few hundreds of time dependent coefficients of Ehrenfest basis configurations describing the wave function in 24 dimensions. Thus, this paper demonstrates that a fully trajectory based quantum method can treat nonadiabatic dynamics in multidimensional systems rather accurately. An analytical potential energy surfaces have been used in this work, but relatively small number of basis trajectories employed by the MCE method suggests that in future it can perhaps be implemented together with \textit{ab initio} “on the fly” electronic structure calculations for direct dynamics.
2. Theory

2.1 Working equations

Multitrajectory Ehrenfest approach has been proposed in the article [19] to describe the dynamics on two coupled potential energy surfaces $|1\rangle$ and $|2\rangle$

\[
\hat{H} = \begin{pmatrix}
\hat{H}_{11} & \hat{H}_{12} \\
\hat{H}_{21} & \hat{H}_{22}
\end{pmatrix}
\]  

(1)

Everywhere in this article we assume only two electronic PES. The generalisation to several PES or any type of electronic wave function other than simple linear combination $a_1|1\rangle + a_2|2\rangle$ is trivial. The derivation of working equations begins by working out those of the Ehrenfest approximation introduced by Billing in his semiclassical coupled states method [23-25]. Here we first assume the wave function in the form of a single Frozen Gaussian wave packet “shared” between the two potential energy surfaces

\[
|\phi(t)\rangle = |\phi_{elec}(t)\rangle |\phi_{nuc}(t)\rangle = (a_1(t)|1\rangle + a_2(t)|2\rangle) |p(t),q(t)\rangle = (a_1(t)|1\rangle + a_2(t)|2\rangle) |z(t)\rangle
\]  

(2)

In (2) the kets $|1\rangle$ and $|2\rangle$ describe the electronic states and the Frozen Gaussian $|p(t),q(t)\rangle$ describes the nuclear wave function. Often FG $|p(t),q(t)\rangle$ is called Coherent State $|z(t)\rangle$ and is labeled by the single complex vector

\[
z = \frac{\gamma^{1/2} q + i \gamma^{-1/2} h^{-1} p}{2^{1/2}}
\]

which includes coordinate $q$ and momentum $p$ into its real and imaginary part. In coordinate representation a 1D CS is a Frozen Gaussian:

\[
\langle x|z\rangle = \left(\frac{\gamma}{\pi}\right)^{1/4} \exp\left(-\frac{\gamma}{2}(x-q)^2 + \frac{ip(x-q)}{h} + \frac{ipq}{2h}\right)
\]  

(3)
where \( \gamma \) is the Gaussian width, which for Frozen Gaussian is assumed to be constant. In
\[
|p(t), q(t)\rangle \text{ notations the CS } \langle x|p,q\rangle = \left(\frac{\gamma}{\pi}\right)^{1/4} \exp\left(-\frac{\gamma}{2}(x-q)^2 + \frac{ip(x-q)}{\hbar}\right)
\]
differs from Eq.(3) by a phase factor, which leads to the definition of action (7) different from standard action \( S = \int (p\dot{q} - H) dt \). See ref. [7] for more details about two systems of notations (\( |p(t), q(t)\rangle \) vs. \( |z(t)\rangle \)). A multidimensional CS in M dimensions
\[
|z(t)\rangle = |z^{(1)}(t)\rangle |z^{(2)}(t)\rangle \cdots |z^{(M)}(t)\rangle
\]
is a product of M 1D Coherent States. The overlap of two 1D CS is
\[
\langle z'|z''\rangle = \exp\left(z'^*z'' - \frac{z'^*z' - z''*z''}{2}\right)
\]
and the overlap of two multidimensional CS is the product of their 1D components, which can be written as
\[
\langle z'|z''\rangle = \exp\left(z'^*z'' - \frac{z'^*z' - z''*z''}{2}\right)
\]

In ref [19] the equation for time dependent parameters of the wave function (2) have been derived from variational principle showing that the evolution of the wave function (2) is given by the trajectories of the CS
\[
\dot{i}z = -\frac{\partial H^{Ehr}}{\partial z^*}
\]  
(4)
(or equivalently \( \dot{p} = -\frac{\partial H^{Ehr}}{\partial q} \), \( \dot{q} = \frac{\partial H^{Ehr}}{\partial p} \)) where
\[
H^{Ehr} = \langle \phi |\dot{H}|\phi \rangle = \\
\langle z|\dot{H}_{11}|z\rangle a_1^* a_1 + \langle z|\dot{H}_{12}|z\rangle a_2^* a_1 + \langle z|\dot{H}_{12}|z\rangle a_1^* a_2 + \langle z|\dot{H}_{21}|z\rangle a_2^* a_1 + \langle z|\dot{H}_{21}|z\rangle a_1^* a_2
\]
(5)
is the Ehrenfest average Hamiltonian. The amplitudes $a_1$ and $a_2$ of the two PES evolve according to the coupled equations. If the coefficients are written as a product of smooth preexponential factor and oscillating exponent of the classical action

$$ a_{1,2} = d_{1,2} \exp(iS_{1,2}) $$

where

$$ S_{1,2} = \int \frac{z z^* - z^* z}{2} - \langle z | H | z \rangle \ dt $$

is the classical CS action, then the coupled equations become

$$ \dot{a}_1 = -i \langle z | \hat{H}_1 | z \rangle a_2 \exp(i(S_2 - S_1)) $$
$$ \dot{a}_2 = -i \langle z | H_2 | z \rangle a_1 \exp(i(S_1 - S_2)) $$

Equations (4-8) are similar to those in the Ehrenfest-Billing semiclassical coupled states approach [23-25].

The Equations (4-8) are not more expensive than those of classical mechanics and very easy to solve. However, the Ehrenfest-Billing wave function (2) is not flexible enough to represent accurately the quantum dynamics. The proposal of the Ref[19] and here is to use a set of the wave functions (2) as a basis for exact quantum propagation. In this paper the exact wave function is represented as a superposition of Ehrenfest-Billing configurations as follows

$$ |\Psi(t)\rangle = \sum_{k=1,N} D_k(t) |\phi_k(t)\rangle = \sum_{k=1,N} D_k(t) (a_{1k}(t)|1\rangle + a_{2k}(t)|2\rangle) |\bar{z}_k(t)\rangle $$

where now the wave function is described not by a single configuration (2), but by linear combination of several configurations $ (a_{1k}(t)|1\rangle + a_{2k}(t)|2\rangle|\bar{z}_k(t)\rangle $. The basis CS $ |\bar{z}_k(t)\rangle $ differ by their initial conditions. Unlike (2) the wave function (9) can (at least in principle) be converge to the numerically exact result.
Everywhere in this article we use “~” in CS $|\tilde{z}_j(t)\rangle$ to indicate that this CS is part of a basis which is used to represent a wave function which initially can be a CS itself $|\Psi(0)\rangle = |z_0\rangle$. Evolution of each $|\Psi\rangle$ is described by the motion of its own basis of CS $|\tilde{z}_j(t)\rangle$ and the time dependence of their amplitudes $a_{j}(t), a_{z_j}(t), D_j(t)$ in (9). Therefore the wave packet $|\Psi\rangle$ is a simple Gaussian only initially. The basis Coherent States $|\tilde{z}_j(t)\rangle$ remain “frozen”, i.e. the shape of CS $|\tilde{z}_j(t)\rangle$ does not change.

Time evolution of $a_{j_k}(t), a_{z_k}(t), \tilde{z}_k(t)$ is given by the Eqs.(4-8) and the equations for the coefficients $D_k(t)$ can easily be obtained simply by substituting (9) into the Shrödinger equation $\frac{d}{dt}|\Psi(t)\rangle = -i\hat{H}|\Psi(t)\rangle$. A rather trivial but lengthy derivation described in the appendix yields a set of linear equations for $D_k(t)$

$$\sum_i \langle \varphi_j(t) | \varphi_i(t) \rangle \frac{dD_i(t)}{dt} = -i \sum_j \Delta^2 \langle H \rangle_{ji} D_j(t)$$  (10)

where

$$\langle \varphi_j(t) | \varphi_i(t) \rangle = \langle \tilde{z}_j(t) | \tilde{z}_i(t) \rangle (a_{j}^{(1)} * a_{i}^{(1)} + a_{j}^{(2)} * a_{i}^{(2)})$$  (11)

is the overlap matrix of the Ehrenfest basis wave functions and the elements of the matrix $\Delta^2 \langle H \rangle$ are

$$\Delta^2 \langle H \rangle_{ji} = \mathrel{\rlap{\langle \varphi_j(t)|H|\varphi_i(t)\rangle}} - \mathrel{\rlap{\langle \tilde{z}_j(t)|\tilde{z}_i(t)\rangle H_{ji}}} - i \mathrel{\rlap{\langle \varphi_j(t)|\varphi_i(t)\rangle}} \langle \tilde{z}_j^{*} - \tilde{z}_i^{*} \rangle \tilde{z}_i$$  (12)

In (12)
\[ \langle \varphi_j(t)|\hat{H}|\varphi_i(t)\rangle = \langle \tilde{z}_j|\hat{H}_{11}|\tilde{z}_i\rangle a_j^{(1)}a_i^{(1)} + \langle \tilde{z}_j|\hat{H}_{22}|\tilde{z}_i\rangle a_j^{(2)}a_i^{(2)} + \langle \tilde{z}_j|\hat{H}_{12}|\tilde{z}_i\rangle a_j^{(1)}a_i^{(2)} + \langle \tilde{z}_j|\hat{H}_{21}|\tilde{z}_i\rangle a_j^{(2)}a_i^{(1)}. \]  

(13)

and the matrix \( \langle z_j(t)|z_i(t)\rangle \hat{H}_{\mu}\) is given as

\[ \langle \tilde{z}_j(t)|\tilde{z}_i(t)\rangle \hat{H}_{\mu} = a_j^{(1)}\langle \tilde{z}_j|\hat{H}_{11}|\tilde{z}_i\rangle a_i^{(1)} + a_j^{(2)}\langle \tilde{z}_j|\hat{H}_{22}|\tilde{z}_i\rangle a_i^{(2)} + a_j^{(1)}\langle \tilde{z}_j|\hat{H}_{12}|\tilde{z}_i\rangle a_i^{(2)} + a_j^{(2)}\langle \tilde{z}_j|\hat{H}_{21}|\tilde{z}_i\rangle a_i^{(1)}. \]  

(14)

The elements of coupling matrix \( \Delta^2\langle \hat{H} \rangle \) are always small. The matrix is sparse, and has zero diagonal. In the case of single PES the equations (10-14) for the amplitudes become those of the CCS theory [7]. Therefore the current approach represents an extension of the CCS technique to nonadiabatic multisurface dynamics. See appendix for more details.

The equations (4-8,10), which describe the evolution of the Multiconfigurational Ehrenfest wave function, represent the main result of this paper. The difference between the current approach and that of ref[19] is that here the trajectories of configurations \( \phi_k(t) = (a_{1k}(t)|1\rangle + a_{2k}(t)|2\rangle)\tilde{z}_k(t) \) are completely independent from each other.

Previously in [19] the ansatz for the wave function was written as

\[ |\Psi(t)\rangle = \sum_{k=1,N}(a_{1k}(t)|1\rangle + a_{2k}(t)|2\rangle)\tilde{z}_k(t) \]  

(15)

Although the trajectories were determined by exactly the same equations as (4,5) the coefficients \( a_{1k} \) and \( a_{2k} \) were coupled not only within the same configuration (same k) but also across configurations with different k, which made the trajectories effectively coupled as well. Now the configurations in (9) are weighted with the coefficients D which are coupled by the Eq.(10) but the trajectories \( |\tilde{z}_k(t)\rangle \) (and \( a_{1k}(t), a_{2k}(t) \) in (9)) no longer interact with those of other configurations. The Ehrenfest trajectories become
more stable and also can be run prior to quantum simulation, i.e. the solution of expensive equation (10). The independent nature of the Ehrenfest trajectories makes current version of the MCE approach convenient for future “on the fly” direct dynamics calculations.

2.2 Basis set sampling and initial value representation

Since the current MCE technique is a generalisation of the CCS method many tricks developed in CCS can be adopted to enhance the efficiency. For example if initial wave function is a Gaussian wave packet itself \( |\Psi(t = 0)\rangle = |\psi_0\rangle \) then the initial conditions of basis \( |\tilde{z}_k(t)\rangle \) can be biased to the center of initial wave packet and chosen from a compressed initial distribution.

\[
F(\tilde{z}_k) \propto e^{-\alpha_{comp}[\tilde{z}_k-z_0]^2}
\]

(16)

where \( \alpha_{comp} \) is a compression parameter (unrelated to the CS width \( \gamma \)), which is adjusted such that the initial bath function \( |\Psi(t = 0)\rangle \) is well represented on a small grid of basis CS \( |\tilde{z}_k\rangle \) (k=1,...,N). The higher is the compression parameter the smaller is the number of basis CS \( |\tilde{z}_k\rangle \) required for a good representation of the initial wave function. Small and initially compact basis only works well for some time (perhaps rather short), which however can be sufficient in many physical situations. The quality of a compressed basis can systematically be improved by increasing its size and decreasing simultaneously its compression. See ref [10] and Appendix 2 in ref [19] for more details.

Compressed CS basis sets are particularly efficient when the propagating wave packet is initially a Gaussian CS itself. Fig 1a shows such basis set biased to the initial wave function. The basis set follows the wave function evolution, thus economizing the basis
set size. It also has been shown in [10] that the compression can vary from mode to mode and good results can be achieved for the so called pancake sampling with larger compression for less important DOF [10].

Often multidimensional wave function is complicated and can not be easily represented on a small basis of CS. One however can decompose it into a superposition of a number of CS by inserting the CS identity operator $I = \int |z_0\rangle \frac{d^2z_0}{\pi^2} \langle z_0|$ as follows

$$\Psi(0) = \int |z_0\rangle \frac{d^2z_0}{\pi^2} \langle z_0 | \Psi(0)\rangle$$

where $d^2z_0 = \frac{dp_z dq_z}{2\pi^2}$. After that one can propagate each CS $|z_0\rangle$ individually and represent the total time dependent wave function as a superposition

$$e^{-iHt} |\Psi(0)\rangle = \int e^{-iHt} |z_0\rangle \frac{d^2z_0}{\pi^2} \langle z_0 | \Psi(0)\rangle$$

The advantage is that a Gaussian wave packet $|z_0\rangle$ can be efficiently propagated on a small compressed basis $|\tilde{z}_k\rangle$ initially biased to $|z_0\rangle$ as described above. This idea, which is very similar to the semiclassical initial value representation [26-28], has been previously used for quantum propagation in Ref. [29] and in the previous version of MCE in ref [19]. Initial value representation is illustrated at the Fig 1b. First multidimensional wave function is represented as a superposition of several $|z_0\rangle$, then each one of them is propagated on a small compressed basis $|\tilde{z}_k\rangle$ initially biased to $|z_0\rangle$. Therefore, IVR (18) implements a useful strategy of decomposing complicated problem into a number of relatively simple tasks, which can be performed in parallel. Although IVR and basis set bias do not constitute any formal approximations in practice for any finite basis set size N
the procedure is accurate only for some time (perhaps rather short) which nevertheless can be sufficient for reproducing physical properties of the system.

3. Results

In this paper, the new version of MCE approach is tested on the benchmark of multidimensional vibronic-coupling dynamics at the $S_2$-$S_1$ conical intersection of the pyrazine molecule. This system has been the subject of previous investigations using the MCTDH method, notably the benchmark calculations by Raab et al. [3] for a second-order vibronic-coupling model, which will be used here as well. The aim of the present study is to illustrate the performance of the MCE method for this model system.

The parameters of 4D and 24D model potential energy surfaces (PES) were supplied by Burghardt and they are similar to those used previously in [3,17]. The Frank-Condon absorption spectrum was calculated as a real part of the Fourier transform of the autocorrelation function

$$I(E) = \text{Re} \int e^{iEt} \left< \Psi(0) | e^{-iEt} | \Psi(0) \right>$$

(19)

The autocorrelation function is obtained by propagating the wave packet initially moved vertically from the ground state $S_0$ to the surface $S_2$ and evolving on two coupled surfaces ($S_2$ and $S_1$). Thus, the initial wave packet is itself a Gaussian located at the origin. The electronic states and initial wave packet are sketched at the Fig.2.

Figure 3 shows absorption spectrum obtained for the 4D model with the basis of 250 and 500 CS per electronic state sampled from the Gaussian distribution (16) around the center of the initial wave packet with the compression parameter $\alpha = 1$, which mimics the shape of the initial wave function. The initial conditions for the amplitudes of the basis CS localised at the surface $S_2$
\begin{align}
a_{1k}(0) &= 0 \\
ad(0) &= 1
\end{align}

and the initial conditions for \(D\) were obtained by applying the basis set identity operator

\[ \hat{I} = \sum_{j,k=1}^{N} \langle \tilde{z}_j \mid \Omega_{jk}^{-1} \mid \tilde{z}_k \rangle \]

(21)

to the initial wave function

\[ |\Psi(0)\rangle = \sum_{j=1}^{N} D_j |\tilde{z}_j \rangle = \hat{I}|\Psi(0)\rangle = \sum_{j,k=1}^{N} \langle \tilde{z}_j | \Omega_{jk}^{-1} | \tilde{z}_k \rangle |\Psi(0)\rangle \]

(22) so that

\[ D_j = \sum_{k=1}^{N} \Omega_{jk}^{-1} | \tilde{z}_k \rangle |\Psi(0)\rangle \]

(23)

where \(\Omega_{jk}^{-1}\) are the matrix elements of the inverse of the overlap matrix \(\Omega_{jk} = \langle \tilde{z}_j | \tilde{z}_k \rangle\).

For the CS localized initially at the surface \(S_1\) \(a_{1k}(0) = 1\), \(a_{2k}(0) = 0\) and \(D_1 = 0\) After setting the initial conditions the equations for Ehrenfest configurations (4-8) and eq.(10) for their coupled amplitudes were solved and the autocorrelation function was obtained.

Fig 3 shows the spectrum obtained with MCE method for the 4D model, which is almost indistinguishable from the results of G-MCTDH and MCTDH techniques.

Calculation for the 24D model is more difficult. However 20 out of 24 modes of the pyrazine molecule are essentially the “bath” modes. The initial wave function was represented as a product of the 4 modes system and 20 modes bath

\[ |\Psi(0)\rangle = |\Psi_{\text{stem}}(0)\rangle |\Psi_{\text{bath}}(0)\rangle \]

(24) and the bath modes wave function was represented as IVR superposition

\[ |\Psi_{\text{bath}}(0)\rangle = \int |z_{\text{bath}}^{0}\rangle |\psi_{\text{bath}}(0)\rangle \frac{d^2z_{\text{bath}}}{\pi M_{\text{bath}}} \]

(25)

\[ = \int \frac{|z_{\text{bath}}^{0}\rangle}{|\psi_{\text{bath}}(0)\rangle} \frac{d^2z_{\text{bath}}}{\pi M_{\text{bath}}} \]
Then instead of propagating the total wave function (24) a number of wave packets $|\Psi_z(0)\rangle = |\Psi_{stem}(0)\rangle |z_{bath}^{\prime}\rangle$ was propagated and the autocorrelation function was calculated as their average

$$\langle \Psi(0)|e^{-iHt}|\Psi(0)\rangle = \int \frac{\langle \Psi(0)|e^{-iHt}|\Psi_{stem}(0)\rangle |z_{bath}^{\prime}\rangle}{\langle \Psi_{bath}(0)|z_{bath}^{\prime}\rangle} \langle z_{bath}^{\prime}|\Psi_{bath}(0)\rangle^2 \frac{d^2z_{bath}}{\pi M_{x=0}} \quad (26)$$

If $|z_{bath}^{\prime}\rangle$ is sampled from the square modulus wave function distribution $F(z_{bath}) = |\langle z_{bath}|\Psi_{bath}(0)\rangle|^2$ then the autocorrelation function is a simple sum over a number $N_{z_{bath}}$ of bath initial states

$$\langle \Psi(0)|e^{-iHt}|\Psi(0)\rangle = \frac{1}{N_{z_{bath}}} \sum_{z_{bath}} \frac{\langle \Psi(0)|e^{-iHt}|\Psi_{stem}(0)\rangle |z_{bath}^{\prime}\rangle}{\langle \Psi_{bath}(0)|z_{bath}^{\prime}\rangle} \quad (27)$$

For each $|\Psi_z(0)\rangle = |\Psi_{stem}(0)\rangle |z_{bath}^{\prime}\rangle$ the basis of several hundred 24D CS has been chosen from the so called pancake distribution [7] with low compression of the 4 “system” modes and large compression of the 20 bath modes. Although for each propagation the compressed basis does not sample the whole initial 24D wave function the initial value representation compensates for that. Frame (a) of the Fig. 4 shows the spectrum of the autocorrelation function for the standard 24 D model of pyrazine [3]. The calculations were performed with the basis size of 250 and 500 per state and were repeated 50 times ($N_{z_{bath}} = 50$) to estimate the sum (27). Even 20 repetitions were sufficient. The spectrum was obtained by Fourier transforming the autocorrelation function truncated after the first 200 fs. MCE autocorrelation function for 24 D model decays smoothly and the spectrum is not sensitive to the truncation time. Fig.4b compares the MCE result with that of
MCTDH. The MCE method is accurate enough to reproduce correctly all major features of the spectrum.

4. Discussion and comparison with other techniques

4.1 Comparison with other trajectory based methods of quantum dynamics

The proposed MCE technique is related to a number of known methods used previously. First of all it originates from the approach suggested first by Billing who in his method of semiclassical coupled states proposed to use a single Ehrenfest trajectory (very similar to that of Eq. (4,5)) to describe the dynamics of classical subsystem and coupled equations (8) for the amplitudes of quantum subsystem [23-25]. Independently similar mean-field method has also been suggested in the ref.[30] approximately at the same time. The Ehrenfest dynamics is not limited to the description of coupled electronic states. For instance it has also been used to simulate proton tunneling [31]. In refs [32,33] a multi-trajectory approach was proposed to improve the Ehrenfest approximation by replacing single trajectory with an ensemble of the Ehrenfest trajectories with initial conditions mimicking the initial wave function. The multi-configurational approach proposed in [19] and here also uses an ensemble of Ehrenfest trajectories (4-8) but with the difference that their quantum amplitude are coupled with each other (by equations (10) in this article) and unlike [32-33] contributions of configurations change with time. This makes the MCE approach formally exact and allows at least in principle to converge it to the exact quantum result. Just like in the CCS theory [6-10] the coupling matrix $\Delta^\lambda \langle H \rangle_\mu$ in (10) is sparse small and has zero diagonal. Multi-trajectory Ehrenfest approach [32,33] naturally comes as an approximation to MCE by disregarding completely the small right hand side, which gives trivial approximate solution $D(t) = const$. 
It is important to discuss the connection between the MCE technique and the vMCG and G-MCTDH approach of Burghardt and coworkers [16,17]. vMCG and G-MCTDH use different representations for the wave function but the common feature is that all parameters of the wave function are determined from the variational principle. For the ansatz (9), which includes large number of parameter $D$, $a$ and $z$, all of them would have been coupled together within a fully variational approach approach. In the case of 500 configurations in 24 degrees of freedom the wave function includes 500 parameters $D$, 1000 amplitudes $a$ and $24 \times 500$ phase space points $z$. In a fully variational approach, a system of linear equations for 13500 derivatives of all the parameters must be solved at each propagation time step. Even if variational approach would require fewer configurations still it will be expensive. Using the trajectory (4-8) other than that of full variational principle results into huge savings in computational costs. The equations (4-8) for the evolution of $a$ and $z$ are almost free in comparison with those of fully variational method. Coupled equations (10) must be solved only for small number of coefficients $D$.

In any method based on trajectory guided Gaussian the initial conditions for the trajectories must be close to each other in order to represent well the initial wave function. In a truly multidimensional system the trajectories will always run away from each other rather quickly. After that, as has been shown in [34] for the dynamics on a single potential energy surface, the equations for fully variational trajectories become identical to those of CCS, because the forces with which variational trajectories “push” each other decay with their overlap. Similarly it can be demonstrated that the equations for variational trajectories for the wave function (9) soon become those of the Ehrenfest trajectories. Therefore it is likely that an ensemble of Ehrenfest trajectories will likely
stay in the same region of the phase space as its variational counterpart for the whole time of propagation.

As has been shown in the recent article [15] the MS trajectories diverge rather quickly. The spawning generates new Gaussian basis CS on a different Potential Energy Surface. The basis CS run away from each other, quickly becoming uncoupled. As a result it is difficult for the MS to keep coupling between the basis functions without increasing rapidly their numbers. This problem is less severe for the MCE technique. Multiple Spawning is very much an extension of the elegant and very intuitive surface hopping picture. However in a strongly quantum regime our intuition can be misleading and variational trajectories may follow the wave packet motion more closely, providing better convergence. This article shows that cheap Ehrenfest trajectories also can follow wave packet well and locate the basis in the right place.

Finally, it is important to point out one more time that the current version of the MCE approach differs from that of ref [19] in using of the ansatz (9) instead of (15). Unlike (15) all configurations in (9) are independent and Ehrenfest trajectories (4-8) do not affect each other. The trajectories (4,5) now can be run prior to quantum simulation (i.e. the solution of the Eq.(10)) thus giving a chance to employing the strategy of growing PES [35,36], a technique well established in classical dynamics. Thus, the new version is particularly suitable for the use together with direct dynamics, i.e. “on the fly” electronic structure calculations. Calculation of an independent Ehrenfest trajectory (4-8) is not more expensive than that of a classical trajectory. As has been shown here only few hundreds of Ehrenfest configurations is required for accurate quantum propagation, which is not an unsurmountable task for direct dynamics.
4.2 Accuracy and computational cost

As has been shown here and in Ref [19] MCE method is capable of performing quantum dynamics in multidimensional systems. In [19] Spin-Boson model with thousands of degrees of freedom was accurately described by MCE with no more than 200 basis configurations. Here a complicated dynamics of 24D pyrazine on two model potential energy surfaces with conical intersection has been described with the help of only 250 basis CS per electronic state and therefore only 500 variational parameters. An attractive feature of current implementation is that MCE can be combined with IVR, which replaces a large problem with a number of relatively simple tasks. Another useful feature of the MCE approach is that it relies on completely random basis sets and is run in a manner similar to classical Molecular Dynamics.

As has been discussed in [19] and also is known from previous CCS work, the downside of any Monte-Carlo based approach including MCE is that its quality deteriorated with time and it is accurate only for short time propagation. However, as has been pointed out in [19] many multidimensional systems require only short time propagation. Fig. 5 shows that for pyrazine the autocorrelation function decays very quickly, particularly for the 24D model. Therefore short time propagation is sufficient for reproducing the physical properties such as experimental absorption spectrum.

Fig 5 also illustrates the comparison between MCE with MCTDH. As has already being mentioned the MCE includes very few quantum parameters. Costly coupled equations (10) for only few hundred coefficients $D_i$ in front of the Ehrenfest configurations $\phi_i$ are to be solved. The parameters $a_{ik}$, $a_{2k}$, $z_k$ of the Ehrenfest configuration $|\phi_k(t)\rangle = (a_{ik}(t)|1\rangle + a_{2k}(t)|2\rangle)|z_k(t)\rangle$ come from very cheap equations (4-8). MCTDH [1-3], G-MCTDH [16,17] and particularly multilayer MCTDH [4] wave
functions are much more detailed. Of course MCE propagation based on just a few randomly selected basis functions can not be as accurate as MCTDH at longer times, which is illustrated by the figure 5. For 24D model fine features of the autocorrelation function at long times can not be reproduced by MCE with small random basis. Also the convergence of MCE is slow. Fig.4 shows that the spectrum obtained with 500 CS per state is not much closer to that of MCTDH than the one obtained with 250 CS per state in the region near 2eV where the discrepancy between MCE and MCTDH spectrum is the largest. Nevertheless, reproducing the spectrum requires only short time dynamics, which apparently can be done by MCE with sufficient accuracy.

For the results shown by the figure 4 a single propagation with 250 basis CS per state required 4.2 hours of the CPU time on Intel Xeon 2.0 GHz processor. The main broad feature of the spectrum between 2 and 3 eV is well reproduced with only half of the basis put initially only on the S$_2$ state. This reduces the CPU time by the factor of 4 and brings it to just about 1 hour per single propagation. It also must be mentioned that the current MCE code did not have many simple features previously used to optimise the performance of the CCS method. If implemented these improvements should reduce the CPU time by approximately 30%. In order to obtain the spectrum shown at the Fig. 4a the propagation was repeated several times (between 20 and 50). Therefore altogether the CPU time is comparable with what would be required by initial MCTDH simulation [3] on a modern processor. Additional efforts can be made to minimise the number of configurations and the CPU time in MCTDH [37]. However the advantage of MCE is that the repetitions can be run in parallel and the actual waiting time is quite small. Another advantage is that MCE is a fully trajectory based technique suitable for direct dynamics.
4.3 Potential of applications with ab initio direct dynamics

So far direct dynamics has been used predominantly with the Multiple Spawning [12-15] and to a lesser extent with fully variational vMCG [38,39]. Both have developed many useful techniques to calculate matrix element ab initio “on the fly”. All this experience can be used within the new MCE approach. The independence of MCE trajectories from each other and their relatively slow divergence suggests that a small number of them can be run “on the fly” prior to actual quantum simulation in order to calculate and parameterise the PES. After that an expensive quantum simulation can be done on the analytical PES.

5. Conclusions

This article proposes an improved version of recently developed Multiconfigurational Ehrenfest approach to quantum dynamics. The idea of the approach is to use wave packets guided by Ehrenfest trajectories as a basis set for fully quantum propagation. The method is applied to simulation of nonadiabatic dynamics of pyrazine and shows that the absorption spectrum can be simulated with the help of a basis comprised of very small number of trajectory guided basis functions. For 24D model good results were obtained with only 250 trajectories per state. The paper demonstrates that rather accurate high dimensional quantum propagation in electronically nonadiabatic system can be obtained with the fully trajectory based MCE technique. The efficiency of the method makes it
particularly suitable for future application together with *ab initio* direct dynamics, calculating potentials “on the fly”.

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Appendix

Derivation of working equations

In this work the ansatz for the wave function is

\[ |\Psi\rangle = \sum_i D_i(t) |\phi_i(t)\rangle = \sum_i D_i(t) \left( a^{(1)}_i(t) |1\rangle + a^{(2)}_i(t) |2\rangle \right) \bar{z}_i(t) = \sum_i D_i(t) \left( d^{(1)}_i(t) e^{i \delta_1} |1\rangle + d^{(2)}_i(t) e^{i \delta_2} |2\rangle \right) \bar{z}_i(t) \]  \hspace{1cm} (A.1)

Now let us derive the equations for the parameters of the wave function (A1). First let us assume that the equations for \( d, S \) and \( z \) come from the Ehrenfest-Billing theory for a single configuration. As we know from the previous work [19] they are yielded by variational principle applied to a single “configuration” \( |\phi_i\rangle = \left( a^{(1)}_i(t) |1\rangle + a^{(2)}_i(t) |2\rangle \right) \bar{z}_i(t) \).

The equations for the amplitudes obtained previously are

\[
\frac{da^{(1)}}{dt} = i \left( i \frac{\ddot{\bar{z}}^* - \dot{\bar{z}}^* \bar{z}}{2} - \langle \bar{z} | \hat{H}_{11} | \bar{z} \rangle \right) a^{(1)} - i \langle \bar{z} | \hat{H}_{12} | \bar{z} \rangle a^{(2)} \\
\frac{da^{(2)}}{dt} = i \left( i \frac{\ddot{\bar{z}}^* - \dot{\bar{z}}^* \bar{z}}{2} - \langle \bar{z} | \hat{H}_{22} | \bar{z} \rangle \right) a^{(2)} - i \langle \bar{z} | \hat{H}_{21} | \bar{z} \rangle a^{(1)} \]  \hspace{1cm} (A.2)

More conveniently, they can be written as equivalent equations for \( d \) and \( S \), the amplitude prefactor and actions \( a = d e^{i S} \)
\[
\dot{d}^{(1)} = -i \langle \bar{z} | \dot{\hat{H}}_{11} | \bar{z} \rangle \ d^{(2)} \exp \left( i \left( S^{(2)} - S^{(1)} \right) \right) \\
\dot{d}^{(2)} = -i \langle \bar{z} | \dot{\hat{H}}_{21} | \bar{z} \rangle \ d^{(1)} \exp \left( i \left( S^{(1)} - S^{(2)} \right) \right)
\] (A.3)

\[
S^{(1)} = \int \left[ i \frac{\bar{z} \dot{\bar{z}}^* - \dot{\bar{z}}^* \bar{z}}{2} - \langle \bar{z} | \dot{\hat{H}}_{11} | \bar{z} \rangle \right] dt
\] (A.4)

\[
S^{(2)} = \int \left[ i \frac{\bar{z} \dot{\bar{z}}^* - \dot{\bar{z}}^* \bar{z}}{2} - \langle \bar{z} | \dot{\hat{H}}_{22} | \bar{z} \rangle \right] dt
\]

The trajectories \( \bar{z}(t) \) are

\[
\dot{\bar{z}} = \frac{\partial H_{Ehr}}{\partial \bar{z}^*}
\] (A.5)

where the Ehrenfest Hamiltonian is

\[
H_{Ehr} = \langle \hat{H} \rangle = \langle \varphi | \hat{H} | \varphi \rangle = \\
\frac{\langle \bar{z} | \dot{\hat{H}}_{11} | \bar{z} \rangle a^{(1)*} a^{(1)} + \langle \bar{z} | \dot{\hat{H}}_{22} | \bar{z} \rangle a^{(2)*} a^{(2)} + \langle \bar{z} | \dot{\hat{H}}_{12} | \bar{z} \rangle a^{(1)*} a^{(2)} + \langle \bar{z} | \dot{\hat{H}}_{21} | \bar{z} \rangle a^{(2)*} a^{(1)}}{a^{(1)*} a^{(1)} + a^{(2)*} a^{(2)}}
\] (A.6)

Unlike original MCE, in this new version the norm \( a^{(1)*} a^{(1)} + a^{(2)*} a^{(2)} = 1 \) is conserved within single configuration and the trajectories are now completely independent from each other. The Ehrenfest configurations \( |\varphi_i\rangle = (a^{(1)}_i(t)|1\rangle + a^{(2)}_i(t)|2\rangle) \bar{z}(t) \) form a time dependent basis. The basis functions \( |\varphi_i\rangle \)
are normalized (i.e. \( \langle \varphi | \varphi \rangle = a^{(1)} * a^{(1)} + a^{(2)} * a^{(2)} = 1 \)) but not orthogonal. Any wave function can in principle be expanded in this basis.

The equations for the amplitudes \( D_i(t) \) can be obtained from variational principle but it is easier to achieve exactly the same result simply by substituting (A.1) with time dependence of \( a \) and \( z \) given by (A2-A5) into the Schrödinger equation

\[
\frac{d|\Psi\rangle}{dt} = -i\hat{H}|\Psi\rangle \tag{A.7}
\]

Then

\[
\sum_i \frac{dD_i(t)}{dt} |\varphi_i(t)\rangle = -i\sum_i D_i(t)\hat{H}|\varphi_i(t)\rangle - \sum_i D_i(t) \left| \frac{d\varphi_i(t)}{dt} \right| \tag{A.8}
\]

and

\[
\sum_i \langle \varphi_i(t) | \varphi_i(t) \rangle \frac{dD_i(t)}{dt} = -i\sum_i \langle \varphi_i(t) | \hat{H} | \varphi_i(t) \rangle D_i(t) - \sum_i \langle \varphi_i(t) | \frac{d\varphi_i(t)}{dt} \rangle D_i(t) = -i\sum_i \left[ \langle \varphi_i(t) | \hat{H} | \varphi_i(t) \rangle - i\hbar \langle \varphi_i(t) | \frac{d\varphi_i(t)}{dt} \rangle \right] D_i(t) \tag{A.9}
\]

In equation (A9)

\[
\langle \varphi_i(t) | \varphi_i(t) \rangle = \langle \tilde{Z}_i(t) | \tilde{Z}_i(t) \rangle \left( a_i^{(1)} * a_i^{(1)} + a_i^{(2)} * a_i^{(2)} \right) = \Omega_i \tag{A.11}
\]

\[
\langle \varphi_j(t) | \hat{H} | \varphi_i(t) \rangle = a_j^{(1)} * a_j^{(1)} \langle \tilde{Z}_j(t) | \hat{H}_{11} | \tilde{Z}_i(t) \rangle + a_j^{(2)} * a_j^{(2)} \langle \tilde{Z}_j(t) | \hat{H}_{12} | \tilde{Z}_i(t) \rangle + a_j^{(1)} * a_j^{(2)} \langle \tilde{Z}_j(t) | \hat{H}_{21} | \tilde{Z}_i(t) \rangle + a_j^{(2)} * a_j^{(1)} \langle \tilde{Z}_j(t) | \hat{H}_{22} | \tilde{Z}_i(t) \rangle \tag{A.12}
\]
\[
\langle \varphi_j(t) \mid \frac{d\varphi(t)}{dt} \rangle = \langle \vec{z}_j(t) \mid \vec{z}_i(t) \rangle (a_j^{(1)} * a_i^{(1)} + a_j^{(2)} * a_i^{(2)}) + \\
\langle a_j^{(1)} * a_i^{(1)} + a_j^{(2)} * a_i^{(2)} \rangle \langle \vec{z}_j(t) \mid \vec{z}_i(t) \rangle = \\
= \langle \vec{z}_j(t) \mid \vec{z}_i(t) \rangle (a_j^{(1)} * a_i^{(1)} + a_j^{(2)} * a_i^{(2)}) + \\
\langle \varphi_j(t) \mid \varphi_i(t) \rangle \left( \vec{z}_j * - \vec{z}_i * \right) \vec{z}_i + \frac{\vec{z}_j * \vec{z}_i - \vec{z}_i * \vec{z}_j}{2}
\]

(A.13)

To obtain (A.13) we must remember that

\[
\langle \vec{z}_j(t) \mid \vec{z}_i(t) \rangle = \\
\frac{\exp\left( \vec{z}_j * (\vec{z}_i + \Delta \vec{z}_i) \right) - \frac{(\vec{z}_i * \Delta \vec{z}_i)(\vec{z}_i + \Delta \vec{z}_i)}{2} - \exp\left( \vec{z}_j * \vec{z}_i - \frac{\vec{z}_j * \vec{z}_i}{2} - \frac{\vec{z}_j * \vec{z}_i}{2} \right) }{\Delta t}
\]

\[
= \exp\left( \vec{z}_j * \vec{z}_i - \frac{\vec{z}_j * \vec{z}_i}{2} - \frac{\vec{z}_j * \vec{z}_i}{2} \right) \exp\left( \vec{z}_j * \Delta \vec{z}_i - \frac{\vec{z}_j * \Delta \vec{z}_i + \Delta \vec{z}_i * \vec{z}_i}{2} \right) - 1 = \\
= \exp\left( \vec{z}_j * \vec{z}_i - \frac{\vec{z}_j * \vec{z}_i}{2} - \frac{\vec{z}_j * \vec{z}_i}{2} \right) \exp\left( \vec{z}_j * \Delta \vec{z}_i - \frac{\vec{z}_j * \Delta \vec{z}_i + \Delta \vec{z}_i * \vec{z}_i}{2} \right) \Delta t = \\
= \langle \vec{z}_j(t) \mid \vec{z}_i(t) \rangle \left( \vec{z}_j * - \vec{z}_i * \right) \vec{z}_i + \frac{\vec{z}_j * \vec{z}_i - \vec{z}_i * \vec{z}_j}{2}
\]

(A.14)

Also we can write
\[
\langle \tilde{z}_j(t) | \tilde{z}_i(t) \rangle (a^{(1)}_j \ast a^{(1)}_i + a^{(2)}_j \ast \dot{a}^{(2)}_i) = \\
\langle \tilde{z}_j(t) | \tilde{z}_i(t) \rangle (a^{(1)}_j \ast d^{(1)}_i e^{i\phi}_i + a^{(2)}_j \ast a^{(1)}_i (i\dot{\tilde{S}}_j^{(1)}) + a^{(2)}_j \ast \dot{a}^{(2)}_i e^{i\phi}_i + a^{(2)}_j \ast a^{(2)}_i (i\dot{\tilde{S}}_j^{(2)})) = \\
\langle \tilde{z}_j(t) | \tilde{z}_i(t) \rangle (a^{(1)}_j \ast (-i)\langle z_i(t) | \tilde{H}_{12} | z_i(t) \rangle d^{(2)}_i e^{i\phi}_i - i\dot{\tilde{S}}_j^{(1)} e^{i\phi}_i + a^{(2)}_j \ast a^{(1)}_i (i\dot{\tilde{S}}_j^{(1)}) + \\
a^{(2)}_j \ast (-i)\langle \tilde{z}_i(t) | \tilde{H}_{12} | \tilde{z}_i(t) \rangle d^{(2)}_i e^{i\phi}_i - i\dot{\tilde{S}}_j^{(2)} e^{i\phi}_i + a^{(2)}_j \ast a^{(2)}_i (i\dot{\tilde{S}}_j^{(2)})) = \\
\langle \tilde{z}_j(t) | \tilde{z}_i(t) \rangle (a^{(1)}_j \ast (-i)\langle \tilde{z}_i(t) | \tilde{H}_{12} | \tilde{z}_i(t) \rangle a^{(1)}_i) + a^{(2)}_j \ast (-i)\langle \tilde{z}_i(t) | \tilde{H}_{12} | \tilde{z}_i(t) \rangle a^{(2)}_i \\

\text{where}
\]
\[
\langle \tilde{z}_j(t) | \tilde{z}_i(t) \rangle \tilde{H}_{ji} = (a^{(1)}_j \ast \langle \tilde{z}_i(t) | \tilde{H}_{12} | \tilde{z}_i(t) \rangle a^{(2)}_i + a^{(2)}_j \ast \langle \tilde{z}_i(t) | \tilde{H}_{12} | \tilde{z}_i(t) \rangle a^{(1)}_i) \\
+ a^{(1)}_j \ast \langle \tilde{z}_i(t) | \tilde{H}_{12} | \tilde{z}_i(t) \rangle a^{(1)}_i + a^{(2)}_j \ast \langle \tilde{z}_i(t) | \tilde{H}_{12} | \tilde{z}_i(t) \rangle a^{(2)}_i
\]  

(A.15)

Therefore substituting (A.15) into (A.13) we get:

\[
\langle \varphi_j(t) | d\varphi_i(t) dt \rangle = \\
\langle \tilde{z}_j(t) | \tilde{z}_i(t) \rangle (a^{(1)}_j \ast a^{(1)}_i + a^{(2)}_j \ast \dot{a}^{(2)}_i) + \\
\langle a^{(1)}_j \ast a^{(1)}_i + a^{(2)}_j \ast \dot{a}^{(2)}_i \rangle \langle \tilde{z}_j(t) | \tilde{z}_i(t) \rangle = \\
i \langle \varphi_j(t) | \varphi_i(t) \rangle \left( i\frac{\tilde{z}_j \ast \dot{\tilde{z}}_i - \dot{\tilde{z}}_j \ast \tilde{z}_i}{2} - \langle \varphi_j(t) | \tilde{H} | \varphi_i(t) \rangle \right) + \\
\langle \varphi_j(t) | \varphi_i(t) \rangle \left( (\tilde{z}_j \ast -\tilde{z}_i)^{\dagger} \dot{\tilde{z}}_j + \frac{\tilde{z}_j \ast \dot{\tilde{z}}_i - \dot{\tilde{z}}_j \ast \tilde{z}_i}{2} \right) = \\
\langle \varphi_j(t) | \varphi_i(t) \rangle \left( (\tilde{z}_j \ast -\tilde{z}_i)^{\dagger} \dot{\tilde{z}} - i\langle \varphi_j(t) | \tilde{H} | \varphi_i(t) \rangle \right)
\]  

(A.17)
Finally the equations for the amplitudes $D$

\[
\sum_i \langle \phi_j(t) | \phi_0(t) \rangle \frac{dD_i(t)}{dt} = -\frac{i}{\hbar} \sum_i \langle \phi_j(t) | \hat{H} | \phi_0(t) \rangle D_i(t) - \sum_i \langle \phi_j(t) | \frac{d\phi_0(t)}{dt} \rangle D_i(t) \\
- \frac{i}{\hbar} \sum_i \left[ \left( \langle \phi_i(t) | \hat{H} | \phi_0(t) \rangle - i\hbar \langle \phi_i(t) | \frac{d\phi_0(t)}{dt} \rangle \right) D_i(t) \right] = \\
- i \sum_i \left[ \langle \phi_i(t) | \hat{H} | \phi_0(t) \rangle - i\langle \phi_i(t) | \phi_0(t) \rangle \left( \bar{\mathbf{z}}_j^* - \mathbf{z}_j^* \right) \right] \mathbf{z}_i - i \langle \phi_i(t) | \phi_0(t) \rangle \left( \bar{\mathbf{z}}_j^* - \mathbf{z}_j^* \right) \mathbf{z}_i D_i(t) = \\
- i \sum \Delta^2 \langle H \rangle_{\mu_{ij}} D_i(t) 
\]

(A.18)

can be written in a very compact form

\[
\sum_i \langle \phi_j(t) | \phi_0(t) \rangle \frac{dD_i(t)}{dt} = -i \sum \Delta^2 \langle H \rangle_{\mu_{ij}} D_i(t) 
\]

(A.19)

which is very similar to the working equation as in the CCS approach (see Ref.[7] for details). The difference is that this time

\[
\Delta^2 \langle H \rangle_{\mu_{ij}} = \\
\langle \phi_j(t) | \hat{H} | \phi_0(t) \rangle - \langle \bar{\mathbf{z}}_j(t) | \bar{\mathbf{z}}_i(t) \rangle \mathbf{H}_\mu - i\langle \phi_j(t) | \phi_0(t) \rangle \left( \bar{\mathbf{z}}_j^* - \mathbf{z}_j^* \right) \bar{\mathbf{z}}_i 
\]

(A.20)

includes the nondiagonal matrix elements of the Ehrenfest Hamiltonian

\[
\langle \phi_j(t) | \hat{H} | \phi_0(t) \rangle = \\
\langle \bar{\mathbf{z}}_j | \hat{H}_{11} | \mathbf{z}_i \rangle a_{j_{1}}^{(1)} a_{i_{1}}^{(1)} + \langle \bar{\mathbf{z}}_j | \hat{H}_{22} | \mathbf{z}_i \rangle a_{j_{2}}^{(2)} a_{i_{2}}^{(2)} \\
+ \langle \bar{\mathbf{z}}_j | \hat{H}_{12} | \mathbf{z}_i \rangle a_{j_{1}}^{(1)} a_{i_{2}}^{(2)} + \langle \bar{\mathbf{z}}_j | \hat{H}_{21} | \mathbf{z}_i \rangle a_{j_{2}}^{(2)} a_{i_{1}}^{(1)} 
\]

(A.21)

and the matrix $\langle \bar{\mathbf{z}}_j(t) | \bar{\mathbf{z}}_i(t) \rangle \mathbf{H}_\mu$ given by (A.16). The diagonal of the $\Delta^2 \langle H \rangle_{\mu_{ij}}$ is zero. If the trajectory is defined by Eq.(A.5) then the expansion of $\Delta^2 \langle H \rangle_{\mu_{ij}}$ with respect to
\((\tilde{z}_j^* - \tilde{z}_i^*)\) begins with the second order term proportional to \((\tilde{z}_j^* - \tilde{z}_i^*)^2\). The configurations, which include CS \(z\) close to each other, are uncoupled. Those which are far away are uncoupled as well due to the lack of overlap. Therefore coupling is almost always small.

In case of a single PES the equations (A.19, A.20) become exactly those of the CCS theory.
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The centers of the basis CS, shown by black circles, are sampled from a distribution which is biased to the initial position of the wave function. They follow the dynamics thus economizing the basis set size.
Fig 1b

The sketch of initial value representation. First the initial wave function is represented on a set of CS $|z_0\rangle$ shown by dot lines, which in turn are represented on a basis of $|\tilde{z}_k\rangle$ (black circles). Each of $|z_0\rangle$ is then propagated independently.
Fig. 2

Sketch of Potential Energy Surfaces and wave packet dynamics of pyrazine.
Fig 3

The absorption spectrum for 4D model obtained with a basis of 500 four dimensional CS per state (solid line). The MCTDH spectrum is almost indistinguishable.
**Fig 4a**

The absorption spectrum for the 24D model of pyrazine obtained with the basis of 250 (dashed line) and 500 24D Gaussian Coherent States per electronic state (solid line). Initial Value Representation with averaging over $N_{\text{bath}} = 50$ initial states if the bath modes has been used.
Fig. 4b

Same as 4a but comparison is made comparison with MCTDH (dotted line)
Fig. 5a

Absolute value of rapidly decaying autocorrelation function for the 4D model obtained with the basis of 500 (solid line) 4D Gaussian CS per electronic state.
Fig. 5b

Absolute value of rapidly decaying autocorrelation function for the 24D model obtained 500 (solid line) 24D Gaussian CS per electronic state compared with MCTDH (dots). Initial Value Representation and averaging over 50 initial states if the bath modes has been used.