Optimal Coordinates for Separable Approximations in Quantum Dynamics of Polyatomic Systems: Coordinate Choice Criteria and Error Estimates

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Abstract

A considerable effort has been recently directed towards developing separable (mean-field) approximations for quantum molecular dynamics, such as the Time-Dependent Self-Consistent Field (TDSCF) or the Classical Separable Potential (CSP) methods. Unlike numerically exact solutions of the time-dependent Schrödinger equation, the accuracy of separable quantum dynamical simulations crucially depends on the choice of the coordinate frame. Since the approximate methods replace exact interactions between individual degrees of freedom by mean-field couplings the goal is to work with coordinates which separate modes as well as possible. Unfortunately, for larger system no practical way to optimize coordinates for mean-field quantum dynamics exists. Here, we suggest a simple and practical method for estimating the error of separable simulations, which allows to select from a given set the optimal

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coordinate frame, or to identify modes the couplings between which have to be treated more accurately. In the spirit of the CSP method, the time-dependent error estimate is based on differences between the exact and mean-field Hamiltonians along a swarm of classical trajectories. This makes it possible to very simply determine optimal coordinates for CSP or TDSCF propagation before actually performing any quantum simulation. The present methodology is applied to realistic and experimentally relevant systems, namely to the ultrafast relaxation following electron photodetachment in I^-Ar_n (n=2 and 12) and Cl^-H_2O clusters. It is shown that the accuracy of separable quantum methods is strongly system and coordinate dependent. Comparison with numerically exact results shows that the suggested error measure correlates well with the actual error of the approximate quantum propagation, the accuracy of which can be consequently improved significantly, practically without additional computational effort. Finally, the feasibility of the proposed method for simulations of large polyatomic systems is demonstrated.

I. INTRODUCTION

For small atomic and molecular systems techniques for a numerically exact propagation of the time-dependent Schrödinger equation are well established[1−9] and, provided the underlying potentials are known sufficiently well, give usually accurate results in good agreement with experiment. Unfortunately, standard quantum propagation methods scale exponentially with system size and can at present be applied to at most tri-atomic or tetra-atomic systems. In order to simulate dynamics of large polyatomics approximations have to be employed. A widespread approach, the Time-Dependent Self-Consistent Field (TDSCF) method,[10−18] aims at finding the best time-dependent wavefunction having the form of a simple product of single mode functions (Hartree approximation) using the time-dependent variational principle.[19−20] Unlike the time-independent problem which leads to a self-consistent iterative cycle, the time-dependent solution is obtained by propagating single mode functions along the Hartree effective Hamiltonians.[15] TDSCF simulations have been successfully applied to various fast processes in moderately sized systems.[21] The bottleneck of the method lies in the evaluation of effective single mode Hamiltonians which for large systems requires multidimensional quadratures. Several methods employing to some extent classical mechanics, such as the classical-quantum TDSCF,[22] the semiclassical TDSCF,[13] or the Classical Separable Potentials (CSP),[23] have been developed to overcome this bottleneck making simulations for large systems practical.

A principle drawback of separable approaches is that they replace exact interactions between modes by mean-field couplings, lacking thus the intermode correlations. This makes the choice of coordinates a very important issue. While the exact solution does not, of course, depend on a particular coordinate frame, the accuracy of a mean-field propagation can be significantly improved by choosing modes in which the non-separable part of the Hamiltonian is as small as possible. Even with an optimal coordinate choice the separable propagation is not numerically exact and the remaining correlations can only be accounted for by going beyond the mean-field approximation e.g., via the Configuration Interaction[24−25] or Multi-Configuration[14,26–29] TDSCF, both being computationally rather demanding and exponentially scaling with system size. The goal of the present paper is different: To remove within computationally simple separable propagations the 'artificial' correlations connected with a non-optimal coordinate choice.

For mean-field propagations the best coordinate frame, which can actually be time-dependent, depends on the particular system and process under study. For systems moving close to the bottom of the potential surface normal modes usually represent a good choice. On the other hand, highly energetic (e.g., dissociation) processes are likely to be better described in some kind of atom-atom distance or Cartesian coordinates. Quite generally, at each instant it should in principle be possible to determine the best modes for the process under study by including the coordinate optimization into the time-dependent variational procedure. Despite early attempts to find variationally optimal modes both in the time-dependent and time-independent frameworks which have been successful on small or model systems,[30–40] currently no algorithm exists that would not for large systems lead to computational schemes of the same complexity as the numerically exact solution, loosing thus all the numerical advantage of mean-field propagations.

In order to obtain a computationally practical scheme, we restrict ourselves in the present study to a less general goal. First, we develop a very simple semiclassical time-dependent error measure which allows us to asses very easily the quality of a given mean-field propagation within a particular coordinate frame. Next, we apply this scheme to a set of important ultrafast processes, namely to the vibrational relaxation following electron photodetachment in I^-Ar_n (n=2 and 12) and Cl^-H_2O clusters. Photoelectron or ZEKE spectra for these systems have been recorded experimentally[41–43] and these processes have also been modeled by several theoretical groups.[44–49] In this paper, we explore different coordinate systems, such as normal modes, Cartesian or Radau coordinates and, using the present error estimate, suggest for each case an optimal choice within the above set. We also use the error estimate for determining strongly coupled modes the description of which should go beyond the separable mean-field approximation.

The rest of the paper is organized as follows. In the next section we develop the semiclassical error measure and discuss the different coordinates employed. Section III concentrates on the atomic and molecular clusters under investigation and on the underlying potential energy surfaces. Details concerning the classical and quantum mean-field CSP propagations are presented in in the end of this section. Section IV contains results and discussion and the concluding remarks are in Section V.

II. ERROR ESTIMATES AND COORDINATE FRAMES FOR SEPARABLE QUANTUM DYNAMICS

Separable approximations to quantum dynamics start with factorizing the total wavefunction Ψ into a product of single mode functions

$$\Psi(q_1, ..., q_N, t) = \prod_{j=1}^{N} \phi_j(q_j, t) \tag{1}$$

where the multiplication runs over all modes. Straightforward application of the time-dependent variational principle[19−20] to the the above wavefunction *Ansatz* leads to the following set of one-dimensional Schrödinger equations for the individual degrees of freedom

$$i\hbar \frac{\partial \phi_j(q_j, t)}{\partial t} = [-\frac{\hbar^2}{2m_j}\frac{\partial^2}{\partial q_j^2} + \bar{V}_j(q_j, t)]\phi_j(q_j, t) \tag{2}$$

where the effective TDSCF single mode potentials $\bar{V}_j$ are defined as

$$\bar{V}_j(q_j, t) = \langle \prod_{l \neq j} \phi_l(q_l, t) | V(q_1, ..., q_N) | \prod_{l \neq j} \phi_l(q_l, t) \rangle + \frac{1-N}{N} \langle \prod_{l=1}^{N} \phi_l(q_l, t) | V(q_1, ..., q_N) | \prod_{l=1}^{N} \phi_l(q_l, t) \rangle \tag{3}$$

The first term in Eq. 3 is the actual mean-field potential for mode j obtained by integrating out all the remaining degrees of freedom, while the second term is just a time-dependent energy normalization factor which defines the overall phase of the wavefunction.

Seemingly, the TDSCF method linearizes the quantum dynamical problem, however, we are left with the construction of the effective potentials involving for large systems multidimensional quadratures. A principal computational advantage of the mean-field CSP method is that it replaces the numerically tedious evaluation of the single mode effective TDSCF potentials defined in Eq. 3 by computationally simple averages over a swarm of Wigner trajectories[23]

$$V_j^{CSP}(q_j,t) = \sum_{\alpha=1}^{n_T} V(q_1^{(\alpha)}(t),...,q_{j-1}^{(\alpha)}(t),q_j,q_{j+1}^{(\alpha)}(t),...,q_N^{(\alpha)}(t))\omega_\alpha + \frac{1-N}{N}\sum_{\alpha=1}^{n_T} V(q_1^{(\alpha)}(t),...,q_j^{(\alpha)}(t),...,q_N^{(\alpha)}(t))\omega_\alpha \quad (4)$$

where α is the trajectory index running from 1 to the total number of trajectories n_T, $q_l^{(\alpha)}(t)$ is the value of the lth coordinate at time t for a trajectory α, and ω_α is the weight of a trajectory α following from the Wigner mapping of the initial wavefunction onto a classical phase space.[23,50–51]

A standard way of testing approximate mean-field quantum dynamical methods is to compare their predictions to a numerically exact propagation for a low-dimensional model system, where the latter calculations are feasible.[52–57] Despite the usefulness of these test, such comparisons are of a limited value since one tests a method tailored to large polyatomics on small systems, and the physics of the two can differ significantly. For example, it has been recognized earlier that large systems with many modes tend to behave more statistically than the corresponding more strongly correlated low-dimensional analogues, therefore, mean-field approximations tend to work better upon increasing the number of degrees of freedom.[57] For the above reasons, it would be highly desirable to have in hand an error measure which would indicate how reliable a given approximate quantum propagation is directly for the polyatomic system under study.

In a search for such an error measure, we have to leave aside all definitions which lead to computations infeasible for large polyatomic systems. Obviously, we cannot use the most straightforward error estimate - the overlap between the numerically exact and the approximate separable wavefunctions since we simply do not know the exact wavefunction for a system with more than three or four atoms. A remedy lies in moving from studying deficiencies of wavefunctions to estimating mean deviations of effective mean-field potentials from exact ones. Clearly, errors in wavefunctions are caused by the use of approximate effective Hamiltonians and, as it is also demonstrated later on practical examples, there is a direct correspondence between the two.

On a first sight, an appealing possibility seems to be to monitor the following mean deviation: The square root of the expectation value of the square of the difference between the exact, fully correlated potential V and the sum over all modes of the mean field potentials V_i^{approx}

$$\varepsilon(t) = \sqrt{\langle \prod_{l=1}^{N} \psi_l^{approx}(q_l,t) | (V(q_1,...,q_N) - \sum_{j=1}^{N} V_j^{approx}(q_j,t))^2 | \prod_{l=1}^{N} \psi_l^{approx}(q_l,t) \rangle} \tag{5}$$

The problem with this definition is that it involves N-dimensional quadratures which become extremely hard to evaluate when the size of the system exceeds several atoms.

The principle idea of this paper is to apply the CSP methodology also to the error estimate and replace the numerically tedious integral expression in Eq. 5 by a simple trajectory average

$$\varepsilon^{CSP}(t) = \sqrt{\sum_{\alpha=1}^{n_T} (V(q_1^{(\alpha)}(t),...,q_N^{(\alpha)}(t)) - \sum_{l=1}^{N} V_l^{CSP}(q_l^{(\alpha)},t))^2 \omega_\alpha} \tag{6}$$

A relative error measure can be then defined as

$$\varepsilon_{rel}^{CSP}(t) = \frac{\varepsilon^{CSP}(t)}{\sum_{\alpha=1}^{n_T} V(q_1^{(\alpha)}(t),...,q_N^{(\alpha)}(t))\omega_\alpha} \times 100\% \tag{7}$$

Eq. 7 represents a practical error estimate for mean-field quantum propagations of large systems. The computational simplicity of this expression is due to the fact that it contains no multidimensional quadratures over wavefunctions. As a matter of fact, it does not involve any quantum propagation, all one needs is to propagate a swarm of Wigner trajectories.

It might seem strange to estimate the error of a mean-field wavepacket propagation without actually performing any quantum simulation. However, the experience gained with the CSP method shows that for moderately quantal systems the TDSCF and CSP effective potentials practically coincide and the error of the method is not due to the introduction of classical trajectories but due to the neglect of intermode correlations resulting from the separable *Ansatz* for the wavefunction.[23,58] In other words, unless the system is very strongly quantal, error estimates given by Eqs. 5 and 6 will be very similar to each other (after all we are postulating error measures where order of magnitude rather than many digit accuracy is required) and will reflect the deficiency of the separable approximation. Thus, we are taking advantage of the fact that, on one hand, the swarm of classical trajectories evolves according to the exact potential V and is, therefore, fully correlated and can serve for estimating the error of a separable propagation. On the other hand, classical propagation of hundreds to thousands of trajectories necessary for a converged error estimate (see Results) does not represent a major computational challenge even for relatively large systems.

The principal goal of the present work is to use the error estimate defined by Eq. 7 to improve separable quantum propagations. It has been stressed in the previous section that the quality of mean-field methods strongly depends on the choice of coordinates. Indeed, a wrong choice of the coordinate frame can lead to a failure of a mean-field methods even in cases when the wavefunction in the 'right' coordinates is separable. This issue has attracted a considerable interest in the time-independent framework where the quality of the mean-field vibrational energies and eigenstates of small model systems has been significantly improved using an optimization of the coordinates.[33–40] The situation for the time-dependent problem is more difficult since the optimal coordinate frame can evolve in time, and very little has been done so far. The Time-Dependent Rotated Hartree approach[30–32] aims at a rotation of the wavefunction rather than coordinates. It has been successfully applied to model low-dimensional systems, however, it is not computationally feasible for more than three degrees of freedom. Thus, the simple error estimate derived here represents a first practical scheme leading to an improvement of the choice of coordinates for large polyatomics.

With the error measure given in Eq. 7 in hand we aim at two issues. The first is to select, for particular systems and processes under study, the best coordinates from a given set. Second, for cases where even using the 'best' coordinates the mean-field propagation is not satisfactory due to strong intermode couplings, to identify (if possible) a small subset of strongly correlated modes which have to be treated beyond the separable approximation. In both cases, we utilize the error estimate developed above which involves no quantum propagation. This effectively makes the computational complexity of the optimization problem comparable to classical molecular dynamics. Among all possible coordinate systems we consider those which are practical for propagations of large systems and in this sense we talk about coordinate optimization. This mainly means that we restrict ourselves to orthogonal coordinate frames in which the kinetic energy operator is diagonal. Among these the most widely used are the Cartesian, normal, Jacobi, and Radau coordinates.[59] For the quantum time-independent problem of small molecules (water in particular) these coordinates and the optimal choice among them have been widely discussed.[60–65] Here, we extend the discussion to quantum dynamics of large systems.

III. SYSTEMS AND SIMULATIONS

The methodology described in the previous section is applied to modeling the ultrafast dynamics following electron photodetachment in heterogenous anionic clusters. Such quantum simulations probe motions on neutral surfaces of these clusters and directly correlate with experimental photoelectron or ZEKE spectra[41–43] providing at the same time interpretation in terms of the underlying dynamics.[45–46] In this paper, we simulate using the CSP method[23] the dynamics following photodetachment in a small I^-Ar_2 cluster (where comparison with numerically exact results is possible), in a large I^-Ar_{12} cluster, and in a medium-size Cl^-H_2O complex.

The potential energy surface of the anionic Cl^-H_2O cluster has been adopted from Ref. 47. The system has a planar geometry with a nearly collinear O-H-Cl^- arrangement. In the vicinity of this potential minimum, which is the important part of the surface necessary for generating the initial harmonic vibrational wavefunction and the corresponding normal modes, the empirical potential agrees very well with recent Coupled-Cluster *ab initio* calculations.[66] For geometries considered here, the interaction both in the anionic and neutral systems are dominated by electrostatic forces. While in the anion the leading terms are the (chlorine) charge - (oxygen and hydrogen) partial charges and polarization interactions, in the neutral complex the most important interaction is the (chlorine) quadrupole-(oxygen and hydrogen) partial charges term.

Until recently, no reliable description of the three low-lying potential surfaces of the neutral Cl...H_2O complex existed. Therefore, we have very recently performed an extended *ab initio* scan of these surfaces, arising from three different orientations of the unpaired *p*-orbital of the chlorine atom, and we have fitted the Coupled-Cluster points to a semi-empirical Diatomics-in-Molecule (DIM) model.[66–68] The non-pairwise DIM potential, a detailed description of which is given in Ref. 66, is constructed from diatomic Cl-O and Cl-H fragments which have a spherically symmetric part and an asymmetric part depending on the orientation of the unpaired *p*-orbital of the chlorine atom. The three electronic states are then obtained by diagonalizing the DIM matrix in the basis of spherical harmonics $(Y_{1,-1}, Y_{1,0}, Y_{1,1})$. The DIM formulation also allows for a simple inclusion of the spin-orbit coupling.[64–66] The only two differences between the potential employed here and the one given in Ref. 66 is that in the present work we use a refined 4-site model of water with the negative partial charge placed slightly away from the oxygen atom[69] and that the value Q=2.33 DÅ of the quadrupole moment on chlorine is no more a fitting parameter but has been obtained by an *ab inito* Coupled-Cluster calculation. These changes involved a re-fitting the *ab initio* points resulting in a new DIM potential with the mean deviation from the Coupled-Cluster points reduced to 50% compared to the old fit. The new potential parameters are listed in Table I and have exactly the same meaning as those given in Ref. 66.

The theoretical calculations predict a significant difference between the anionic and neutral potentials. For example, the lowest neutral state, the dynamics on which is investigated in this paper, has an out-of-plane minimum with a short Cl-O distance of 2.7 A and hydrogens pointing away from the Cl atom.[66] A vertical transition initiated by the photodetachment process places the system around the dissociation threshold invoking large amplitude (partially dissociative) motions.

The potential surfaces for the I^-Ar_n clusters and the corresponding neutral species have been constructed in a similar fashion. The anionic and low-lying diatomic I-Ar potential curves have been extracted from ZEKE experiments and expressed as Morse-Morse-switching function-van der Waals functions.[41] For the polyatomic clusters, the anionic potentials have been constructed in a pairwise manner, while the neutral surfaces have been obtained using the DIM scheme described above. The I^-Ar_2 cluster has a geometry of an isosceles (nearly equilateral) triangle, while the I^-Ar_{12} complex has a slightly bent icosahedral structure with the argons forming a nearly complete solvation shell around the iodine anion.[45] Unlike the previous case, the difference between the anionic and neutral surfaces is rather small in these clusters. Even when excited to the most repulsive second neutral surface, which is the process studied here, the cluster remains well below the dissociation threshold and a spatially confined dynamics is observed.

Evaluation of the error measure defined in Eq. 7 requires a propagation of a swarm of trajectories. Initial coordinates and momenta have been generated by a Wigner mapping[50−51] of the initial (anionic) harmonic vibrational ground state of the system under study. Depending on the particular system, hundreds to thousands of trajectories have been propagated using a standard Gear routine[70] with a timestep of 0.5 fs for the $I...Ar_n$ and 0.05 fs for the $Cl...H_2O$ clusters. Approximate quantum dynamical simulations have been performed by the CSP method[23] employing the Fourier approach for the evaluation of the action of the kinetic energy operator[71] and using the split-operator propagator [72] with the same time-step as the corresponding classical simulation.

IV. RESULTS AND DISCUSSION

A. Photodetachment in the I^-Ar_2 cluster

The small I^-Ar_2 cluster has been chosen both for its experimental relevancy[42] and for the fact that numerically exact propagation is still feasible in this system.[46,58] Thus, we can directly demonstrate that the error estimate proposed here correlates well with the quality of the method and apply it then with confidence to larger systems where exact calculations are infeasible. Four orthogonal coordinate sets have been tested - normal modes corresponding to the anionic and neutral $I3/2$ surfaces, Cartesian and Radau coordinates. The last set of 'heliocentric' Radau coordinates has been included since it is supposed to work well for a heavier atom surrounded by lighter particles.[59] From previous quantum simulations of the dynamics following photodetachment in this system we have learned that mean-field methods are excellent for the first 500 fs (which is roughly the vibrational period) after which they start to deteriorate.[46,58] There is no good separation of frequencies between the three vibrational modes (42 cm^{-1} symmetric stretch, 34 cm^{-1} asymmetric stretch, and 25 cm^{-1} bend), therefore, the system represents a particular challenge for mean-field methods. Figure one shows the plot of the error estimate $\varepsilon_{rel}^{CSP}(t)$ (see Eq. 7) for the four different coordinate frames. We see, that for about 500 fs the error is below 5% in all cases indicating that separability hold on this timescale. However, significant correlations build up later and the four coordinate frames lead to very different errors. Quite surprisingly, the anionic normal modes, employed in previous studies,[45,46,58] are the worst. A much better performance is seen for the neutral normal modes, and the Radau and Cartesian coordinates work even better. The last two sets are, however, rather impractical for such a small system with only three normal modes compared to six Radau and nine Cartesian coordinates.

We can immediately use the knowledge gained above to improve mean-field quantum simulations for the system under study by simply switching from anionic to neutral normal modes. The only remaining problem is that the initial state is expressed as a separable wavefunction in the anionic mode, which is actually one of the reasons why earlier simulations employed these coordinates. In any other coordinate frame the initial wavefunction is generally non-separable, however, mean-field methods can only propagate separable wavepackets. A remedy lies in employing the linearity of quantum mechanics and expanding the initial wavepacket into a sum of separable functions each of which being propagated separately.[18] Provided the change of coordinates is large, such an expansion can be quite long and a practical method to truncate it without a significant loss of accuracy still remains to be developed. In our case, the difference between the anionic and neutral normal modes is small since the corresponding potential energy surfaces have a similar shape. Therefore, already the zero order term of such an expansion based on the rotation between the two normal frames has a 98% overlap with the anionic initial wavefunction. Including the first order (linear) terms, this overlap reaches 99.5% which is fully satisfactory.

We have performed, for the system under study, CSP simulation using the neutral normal modes and compared it to numerically exact propagation and CSP calculation with anionic normal modes.[58] It has been shown earlier that one of the most sensitive qualities is the autocorrelation function,[23,58] which is also directly related to the absorption or photoelectron spectra via a Fourier transform.[73] Fig. 2 shows the autocorrelation function, i.e. the overlap between the wavefunction at time t and the initial wavepacket, for CSP simulations with neutral and anionic normal modes, compared to the numerically exact result.[58] Two curves are presented for the neutral normal mode propagation, one resulting from taking only the leading zero order term in the expansion of the initial wavefunction, the other corresponding to the inclusion of the first order terms, too. We see that these two curves practically coincide indicating that the employed expansion of the initial wavepacket, separable in the anionic modes, in the neutral normal modes is converged. It follows from Fig. 2 that that agreement with the numerically exact autocorrelation function is significantly improved by moving from anionic to neutral normal modes. This demonstrates a direct correlation between the proposed error estimate and the quality of the corresponding mean-field propagation.

Photodetachment spectra, obtained as Fourier transforms of corresponding autocorrelation functions, are depicted in Fig. 3. Since the photodetachment process under study is a bound-to-bound transition, ideally all the spectral features should be infinitely narrow. The non-zero widths arise from Fourier transforming finite time-signals. Quantum simulation of more than 20 ps is necessary to resolve all the spectral features (see Fig. 3d). Unfortunately, mean-field wavepackets cannot be reliable propagated for more than several picoseconds due to accumulation of errors. Therefore, we show in Fig. 3a-b spectra obtained from 3 ps CSP propagations using anionic and neutral normal modes which should be compared to the result of an exact propagation of the same length (see Fig. 3c). Due to the short propagation time, these spectra are significantly broadened, however, the main spectral features corresponding to the $0 \leftarrow 0$, $1 \leftarrow 0$, ..., vibrational progression, are still resolved. We see, that also for the spectra CSP with neutral modes does better than CSP with anionic normal modes bringing the peak positions closer to the numerically exact values.

Fig. 4 shows convergence of the error estimate with the number of Wigner trajectories for the system under study using anionic normal modes. It immediately follows from Eq. 7 that using just one trajectory the error measure would be by definition zero - a single trajectory is separable and only a swarm of trajectories can recover intermode correlations. The speed of convergence of course depends on the particular process and on the duration of the simulation. For our system, about 1000 trajectories are necessary for achieving convergence for 2 ps, while 100 trajectories suffices during the first picosecond.

B. Photodetachment in the I^-Ar_{12} cluster

Dynamics following electron photodetachment in the large I^-Ar_{12} cluster[42,45] with a nearly complete argon solvation shell differs significantly from that in the small I^-Ar_2 complex discussed in the previous subsection. Since the photodetachment processes switches only the I-Ar potentials leaving the Ar-Ar interaction practically intact, effectively a smaller change in interactions and consequently lower amplitude dynamics is expected in the larger system. Indeed, the small cluster has two I-Ar interactions and only one Ar-Ar interaction, while in the large cluster, there are 12 I-Ar interactions compared to 66 pair Ar-Ar interactions. This fact results in an opposite behavior of the error measure as a function of the coordinate frame compared to the previous system. This is demonstrated on Fig. 5 showing the error of CSP propagation for I...Ar_{12} using four different coordinates, which should be compare to the analogous Fig. 1. Unlike the small cluster, here both the anionic and neutral normal modes perform very well, while the Cartesian and Radau coordinates are clearly inferior. This demonstrates that normal modes are suitable for the description of bound processes with little kinetic energy resulting in motions close to the bottom of the potential well, while Cartesian or Radau coordinates describe better more 'thermalized' processes with a higher amount of kinetic energy.

Convergence of the error estimate with the number of Wigner trajectories for anionic normal modes is depicted in Fig. 6. Interestingly, only about 100 trajectories suffice to provide a converged error estimate which is significantly less than in the previous case. The reason for this is that the system moves closer to the bottom of the potential and the dynamics is more separable than in the case of the smaller cluster. Therefore, a smaller number of trajectories is necessary to recover the intermode correlations. One can generalize by stating that the dynamics in large systems tends to be more separable and couplings more of a mean-field character compared to an analogous process in a small system.

C. Photodetachment in the Cl^-H_2O cluster

The dynamics following electron photodetachment in the Cl^-H_2O complex is much more vigorous than that for the I^-Ar_n clusters. This is due to the fact that in the former complex there is a large difference between the anionic and neutral potential energy surfaces and a vertical photodetachment process places the system around (mostly slightly above) the dissociation threshold of the neutral complex.[66] Thus, the system explores a highly anharmonic regions of the intermolecular potential where intermode correlations play an important role and mean-field approximation breaks very early. This is demonstrated on Fig. 7 which shows the time evolution of the error measure for three different coordinate frames - anionic normal modes, Cartesians, and mixed water normal modes with three Cartesian coordinates of the Cl species. Neutral normal modes have not been included since the minimum on the neutral surface is very different from the optimal initial anionic structure.[66]

First, note the timescale of 10 fs compared to a picosend timescale for the previous system demonstrating a much faster dynamics and consequent break up of mean-field description for the Cl...H_2O complex. Second, unlike the I^-Ar_2 cluster, Cartesians are a very bad choice here. This is due to the fact, that the intramolecular water vibrations preserve their normal mode character (the accessible energy in the system does not suffice to significantly excite the water modes) and cannot be described in a separable Cartesian framework. Therefore, we have tried to employ a mixed water normal mode plus chlorine Cartesian description, which however, does not lead to any significant improvement (see Fig. 7). This mixed framework is even worse than the anionic normal modes due to an inadequate description of the initial state. This is because in the relatively strongly bound anionic complex the water molecule is slightly distorted[66] and there is a non-negligible mixing between intra- and intermolecular modes. As a result of this and of the fact that there are, as discussed below, strong correlations mainly among the intermolecular modes, the error of the mixed description is shifted up and essentially parallel to that arising from a mean-field description using anionic normal modes. Finally, we have found that 100 trajectories provide a converged error estimate at the 10 fs timescale.

The basic problem for the Cl...H_2O system is that there are no 'good' coordinates for separable quantum dynamics. Certain modes (especially intermolecular) are so strongly coupled with each other that a mean-field description is simply inadequate. Here we show, how one can efficiently use the present error estimate to identify these strongly coupled modes which have to be treated beyond mean-field approximation. For pairs of modes, the idea is to use in Eq. 7 instead of the single mode V_l^{CSP} potentials two-dimensional V_{lk}^{CSP2}

effective potentials, which have been derived in Refs. 58 and 74 and which explicitly couple modes l and k. A similar procedure can be also done for triples or higher number of modes. In the limit of this procedure, one would in principle fully couple all modes of the system recovering thus the exact dynamics, and by definition the error measure would equal to zero.

For the Cl...H_2O cluster we have tried to explicitly correlate all pairs of modes. It turns out that on the studied timescale there is only a single pair of strongly coupled modes, namely the intermolecular Cl...H_2O stretch (mode 4) and the intermolecular out-of-plane bend (mode 5). This is demonstrated on Fig. 8 which shows the error measure for anionic normal modes with explicit coupling between modes 4 and 5. It immediately follows from this figure that explicit inclusion of correlations between these two modes improves the quality of the propagation dramatically. On the other hand, Fig. 8 also shows that it does not further help to include explicitly also the third intermolecular mode (in-plane bend - mode 6) within an explicit three-mode treatment. In a forthcoming study, this observation will be directly used for a construction of an optimal computationally feasible wavefunction *Ansatz* for the Cl...$(H_2O)_n$ (n=1,2,...) complexes with partial separability and explicit treatment of important pairs of modes.

V. CONCLUSIONS

A computationally simple semiclassical error measure has been developed for optimizing coordinates for separable quantum molecular dynamics. This error estimate involves only classical propagation and is thus easily applicable to large polyatomic systems where no other practical method for estimating the error of approximate mean-field propagations, arising from the neglect of intermode correlations, exists. Test calculations of ultrafast dynamics following photodetachment in several anionic clusters demonstrate that the quality of separable propagation is strongly coordinate and system dependent. It has been shown that the proposed error measure correlates well with the quality of the mean-field propagations and it can assist in improving the simulation by selecting the best coordinate frame from a given set or by explicitly coupling a small subset of strongly interacting modes. Finally, the results suggest a possible future extension of separable propagations. The optimal coordinates are in many cases time-dependent and it should be possible to develop a coordinate switching approximation where one starts with one set of coordinates and during the dynamics makes one or several coordinate switches in order to minimize the error of the separable quantum dynamics.

Acknowledgment

We wish to thank Burkhard Schmidt and Nimrod Moiseyev for valuable discussions. Support from the Granting agency of the Academy of Sciences of the Czech Republic via a grant No. A4040706 (to PJ) is gratefully acknowledged. The work in Irvine was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society (to RBG). The research in Jerusalem was supported in part by the Israel National Science Foundation (to RBG).

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FIGURES

FIG. 1. Time evolution of relative errors of mean-field CSP propagations for the I...Ar_2 cluster using four different coordinate frames.

FIG. 2. Autocorrelation functions for the I...Ar_2 cluster. Mean-field CSP propagations using anionic and neutral (taking the zero or including also first order terms in the expansion of the initial wavefunction) normal modes are compared to numerically exact results. using four different coordinate frames.

FIG. 3. Vibrationally resolved photoelectron spectra for the I...Ar_2 cluster obtained from 3 ps CSP propagations using anionic and neutral normal modes, compared to spectra following from 3 and 24 ps numerically exact propagations. using four different coordinate frames.

FIG. 4. Convergence of the time-dependent error estimate defined in Eq. 7 with the number of Wigner trajectories for the I...Ar_2 complex. using four different coordinate frames.

FIG. 5. Time evolution of relative errors of mean-field CSP propagations for the I...Ar_{12} cluster using four different coordinate frames.

FIG. 6. Convergence of the time-dependent error estimate defined in Eq. 7 with the number of Wigner trajectories for the I...Ar_{12} complex. using four different coordinate frames.

FIG. 7. Time evolution of relative errors of mean-field CSP propagations for the Cl...H_2O cluster using three different coordinate frames.

FIG. 8. Time evolution of relative errors of quantum propagations for the Cl...H_2O cluster using anionic normal modes and assuming full separability, explicit coupling between modes 4 and 5, or explicit coupling between modes 4, 5, and 6.

Table 1

Optimal values of fitting parameters (defined in Ref. 66) for the three low-lying neutral surfaces of the Cl...H_2O complex.

a_H	5.92×10^2 kcal mol^{-1}
b_H	2.40 Å^{-1}
A_H	1.16×10^3 kcal mol^{-1}
B_H	2.79 Å^{-1}
a_O	7.76×10^4 kcal mol^{-1}
b_O	3.29 Å^{-1}
c_O	3.40×10^3 kcal mol^{-1} Å^6
A_O	5.23×10^4 kcal mol^{-1}
B_O	3.07 Å^{-1}
C_O	1.70×10^3 kcal mol^{-1} Å^6

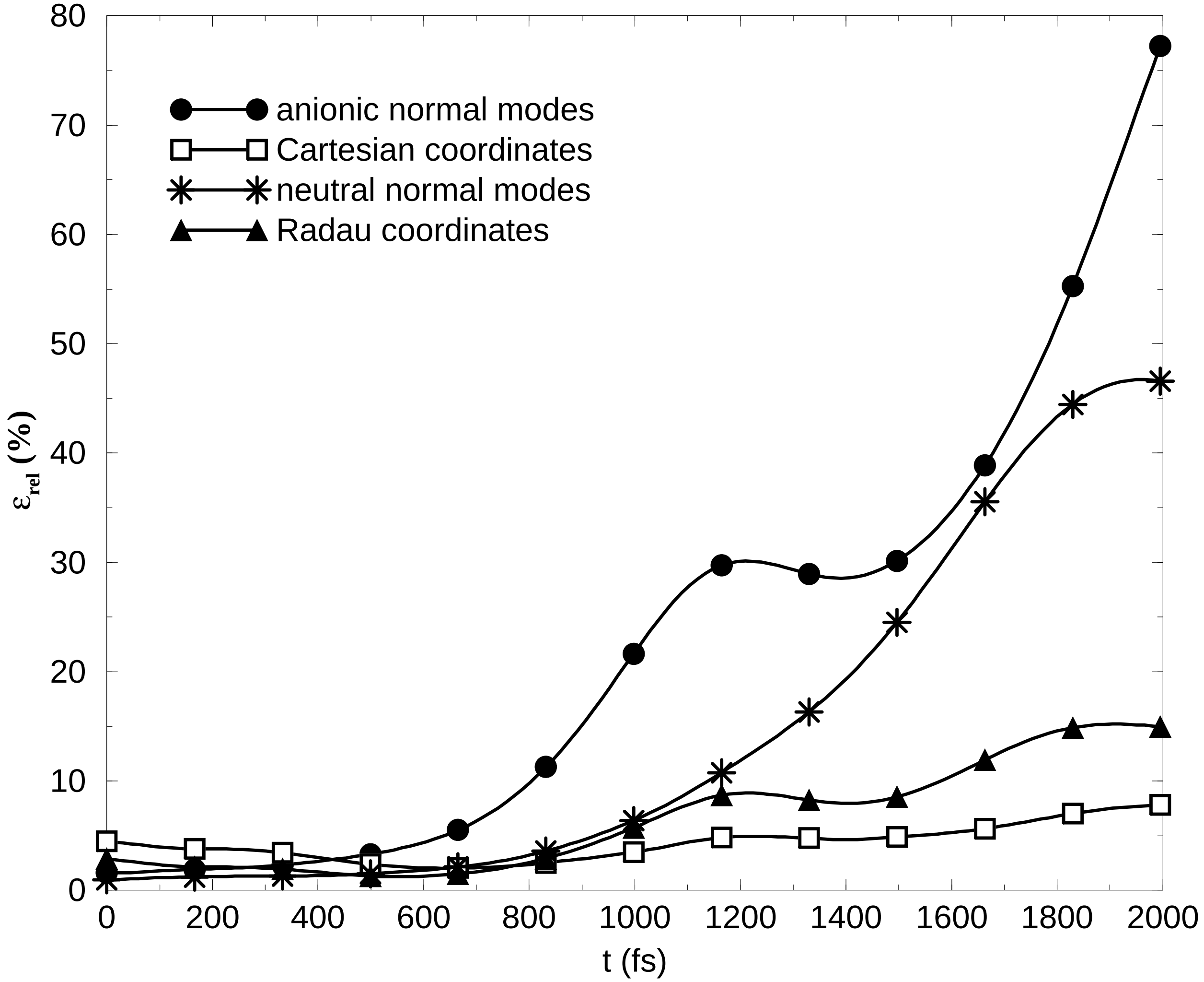

Figure 1 (Jungwirth, Roeselova, Gerber)

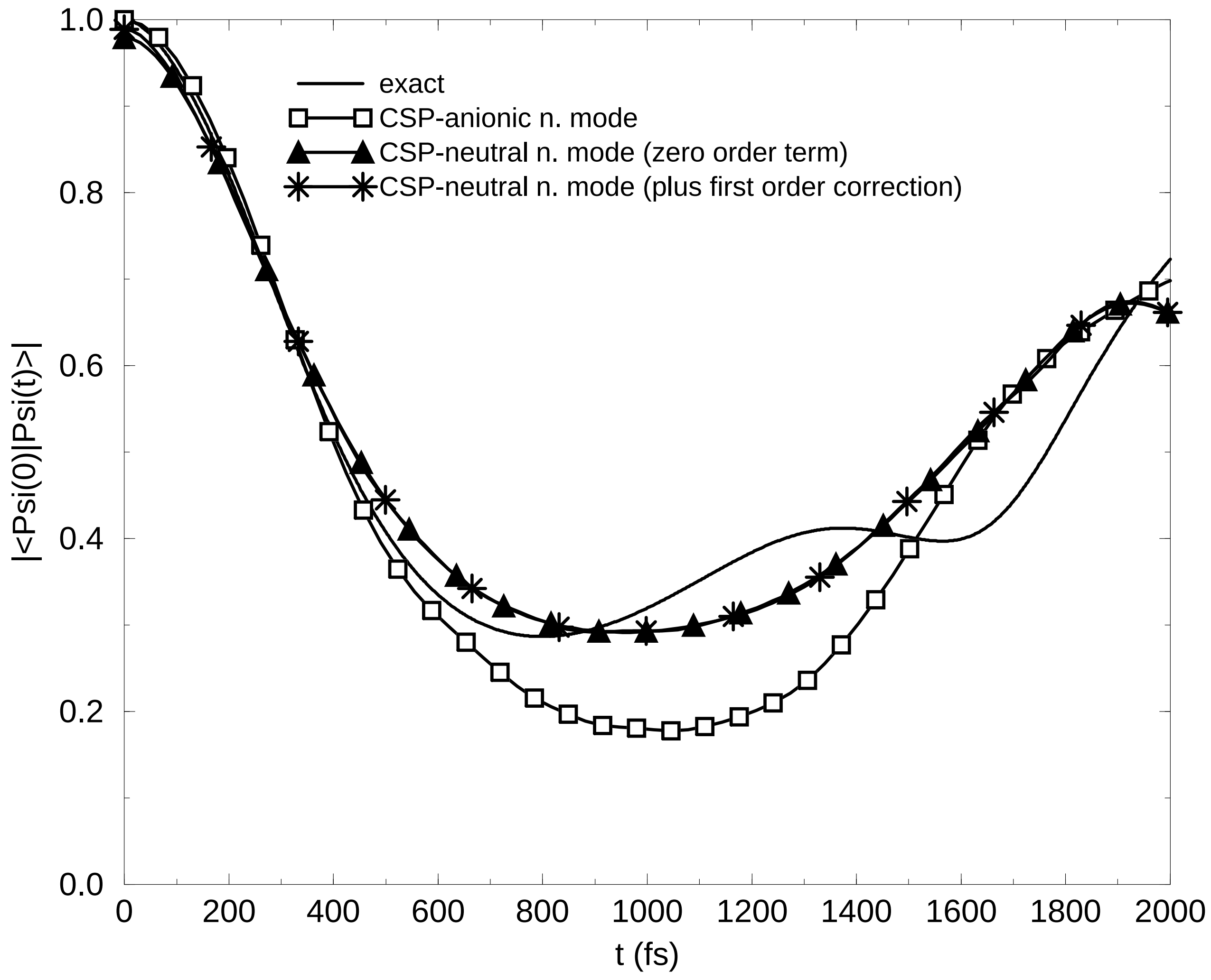

Figure 2 (Jungwirth, Roeselova, Gerber)

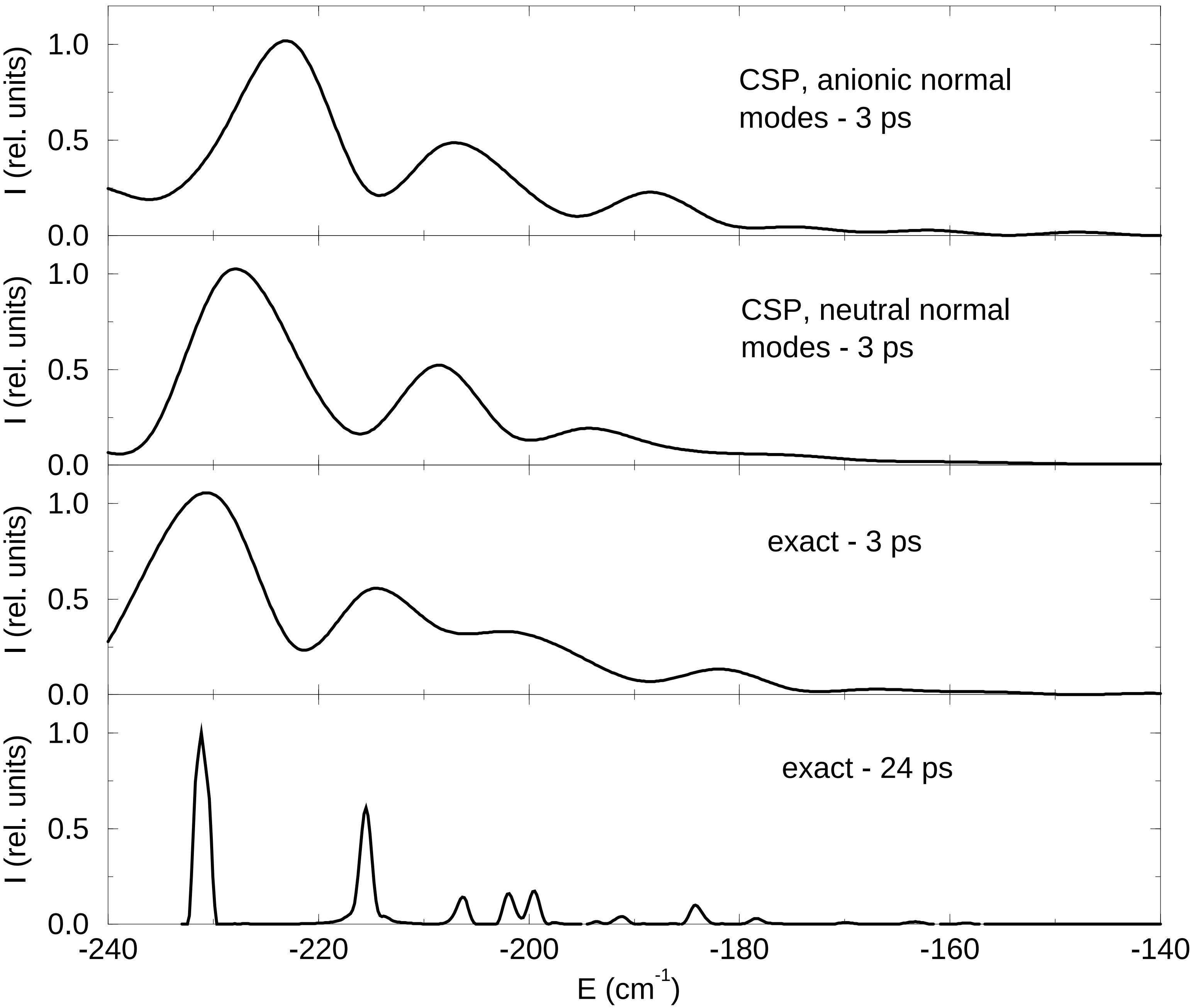

Figure 3 (Jungwirth, Roeselova, Gerber)

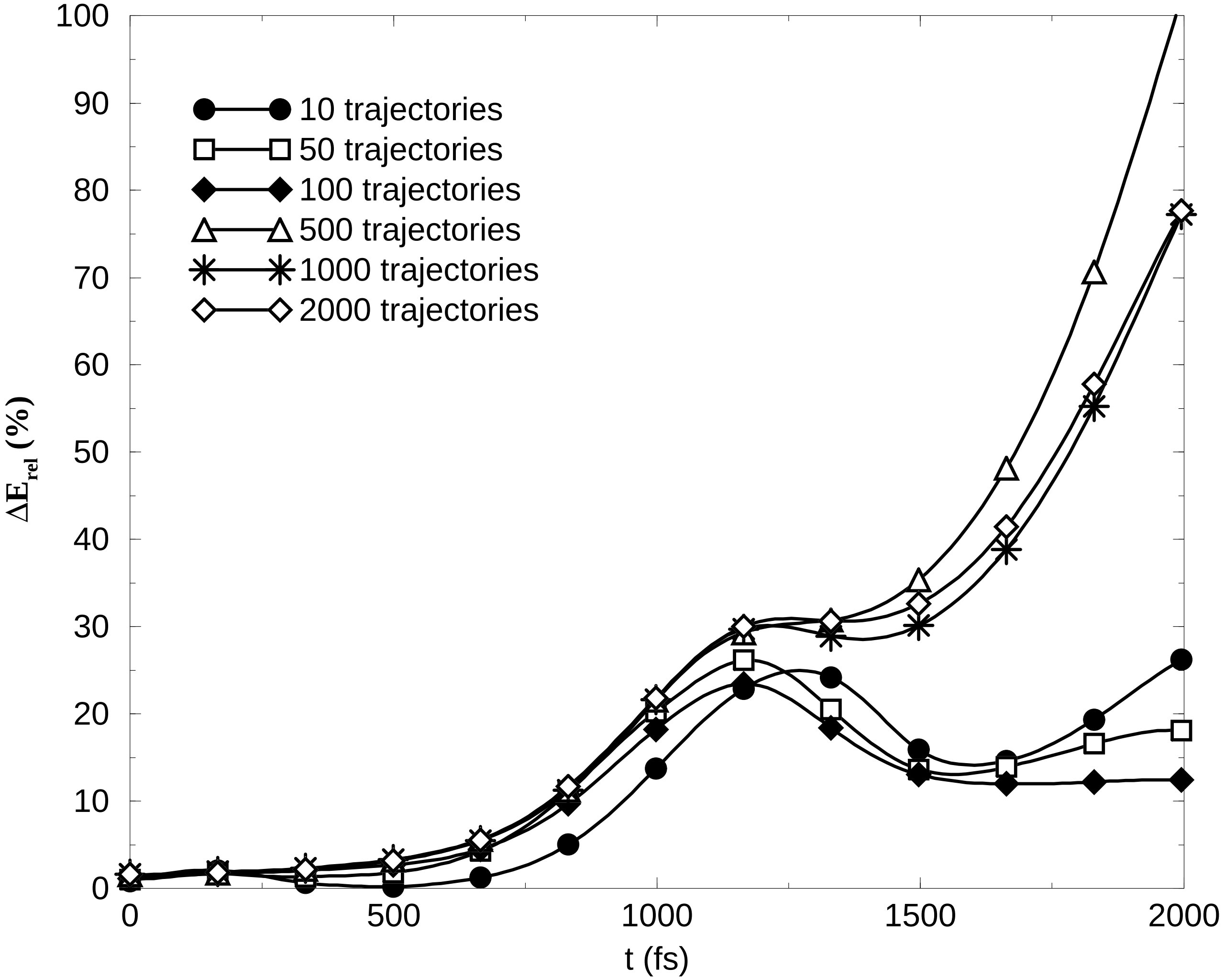

Figure 4 (Jungwirth, Roeselova, Gerber)

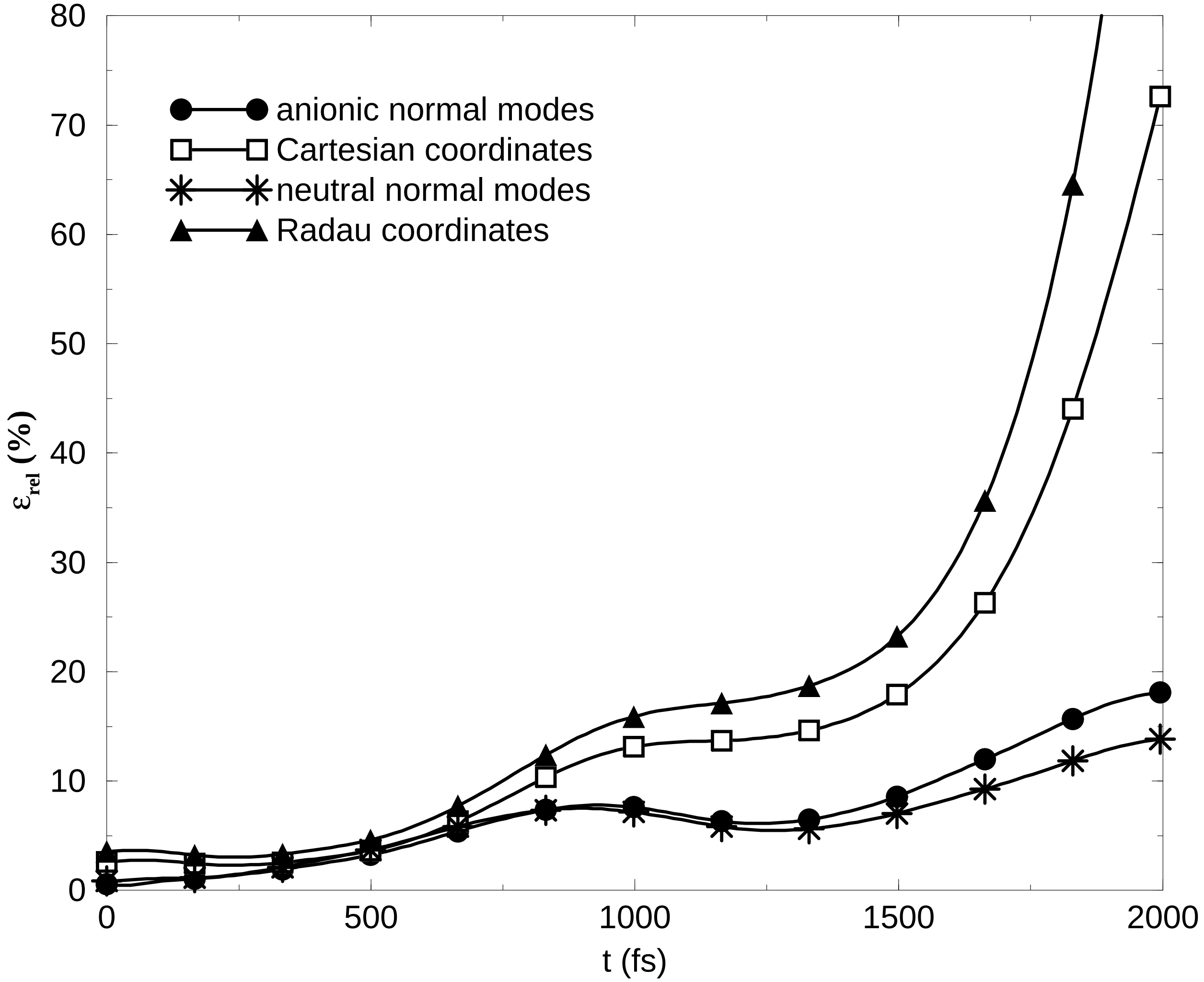

Figure 5 (Jungwirth, Roeselova, Gerber)

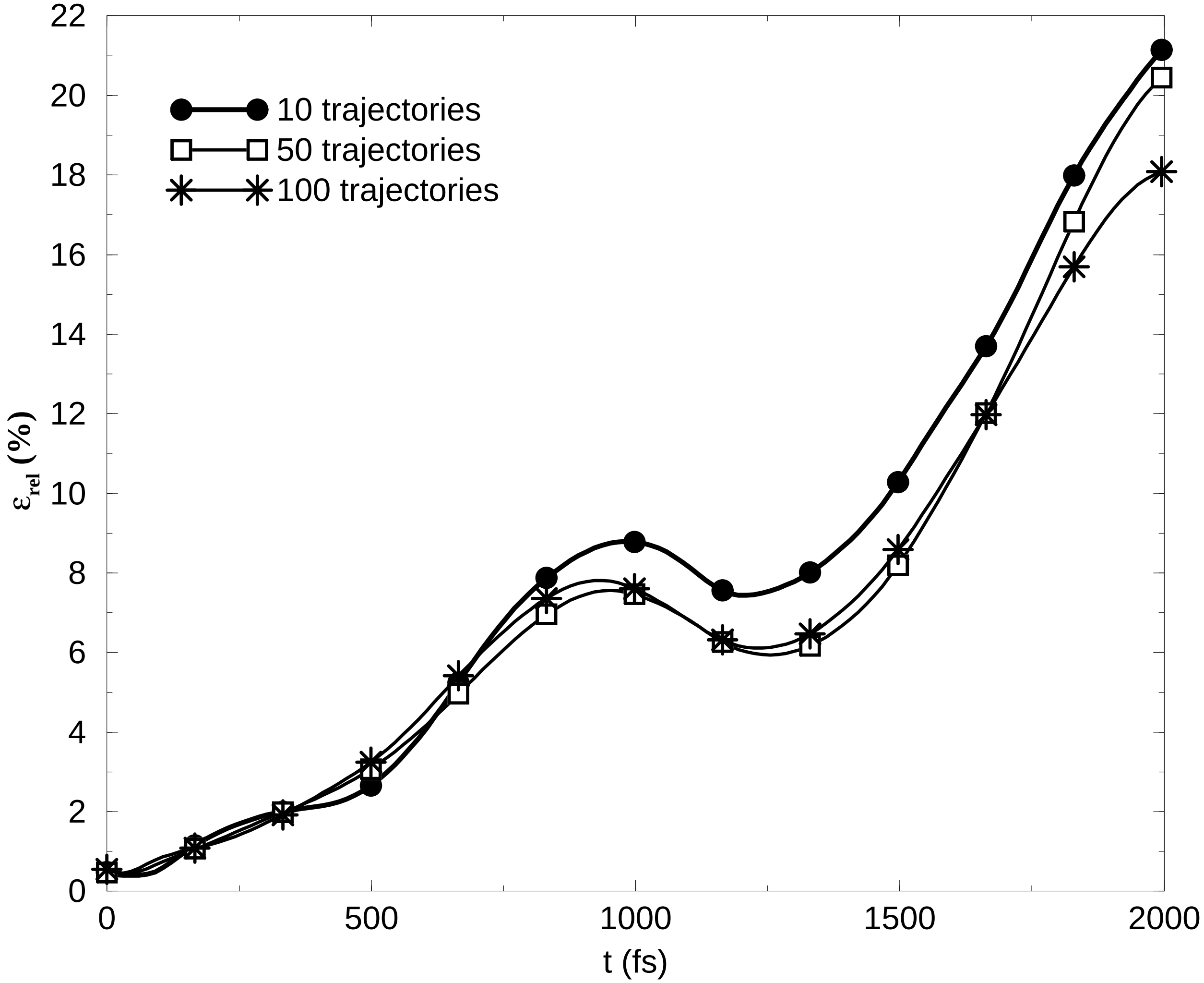

Figure 6 (Jungwirth, Roeselova, Gerber)

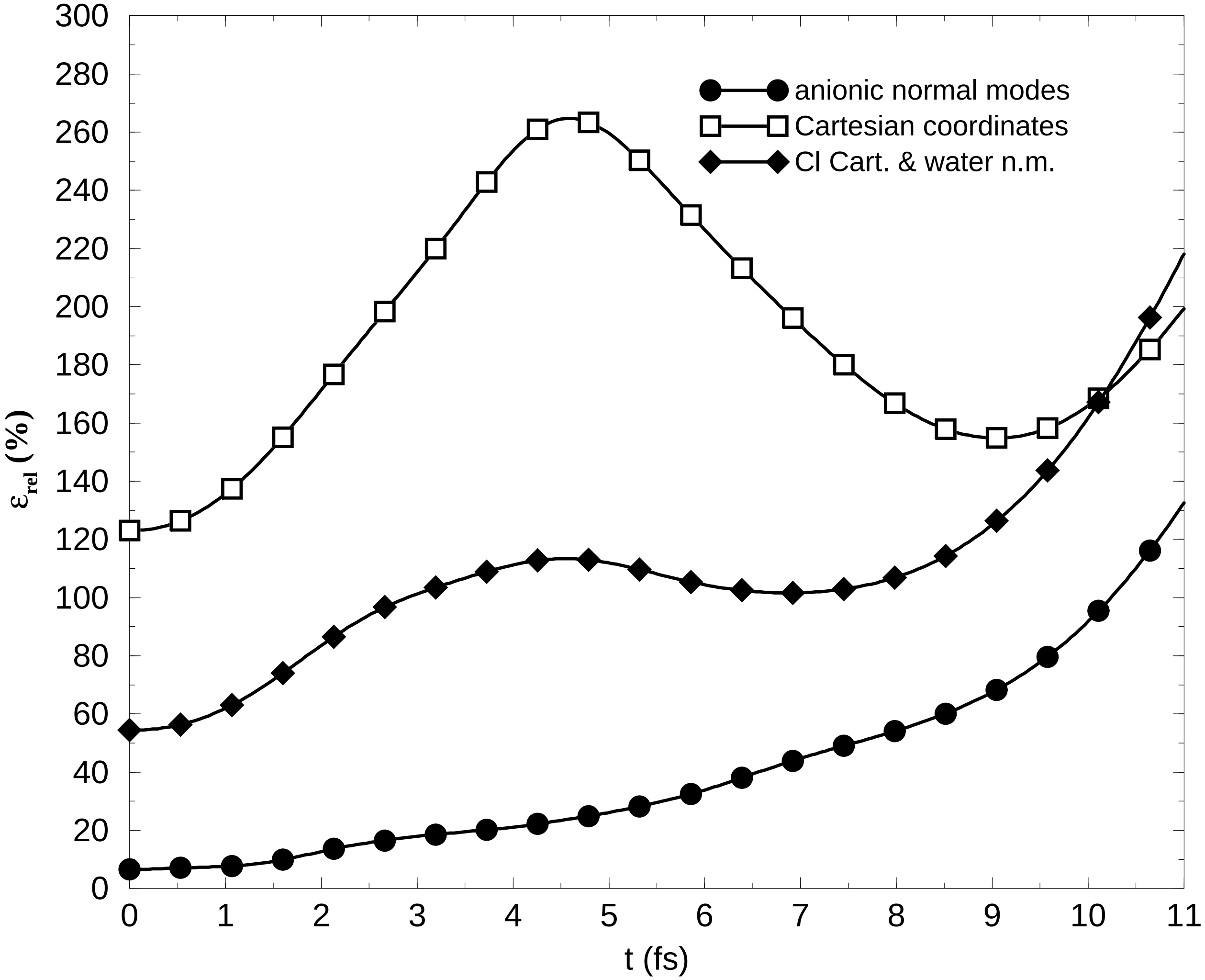

Figure 7 (Jungwirth, Roeselova, Gerber)

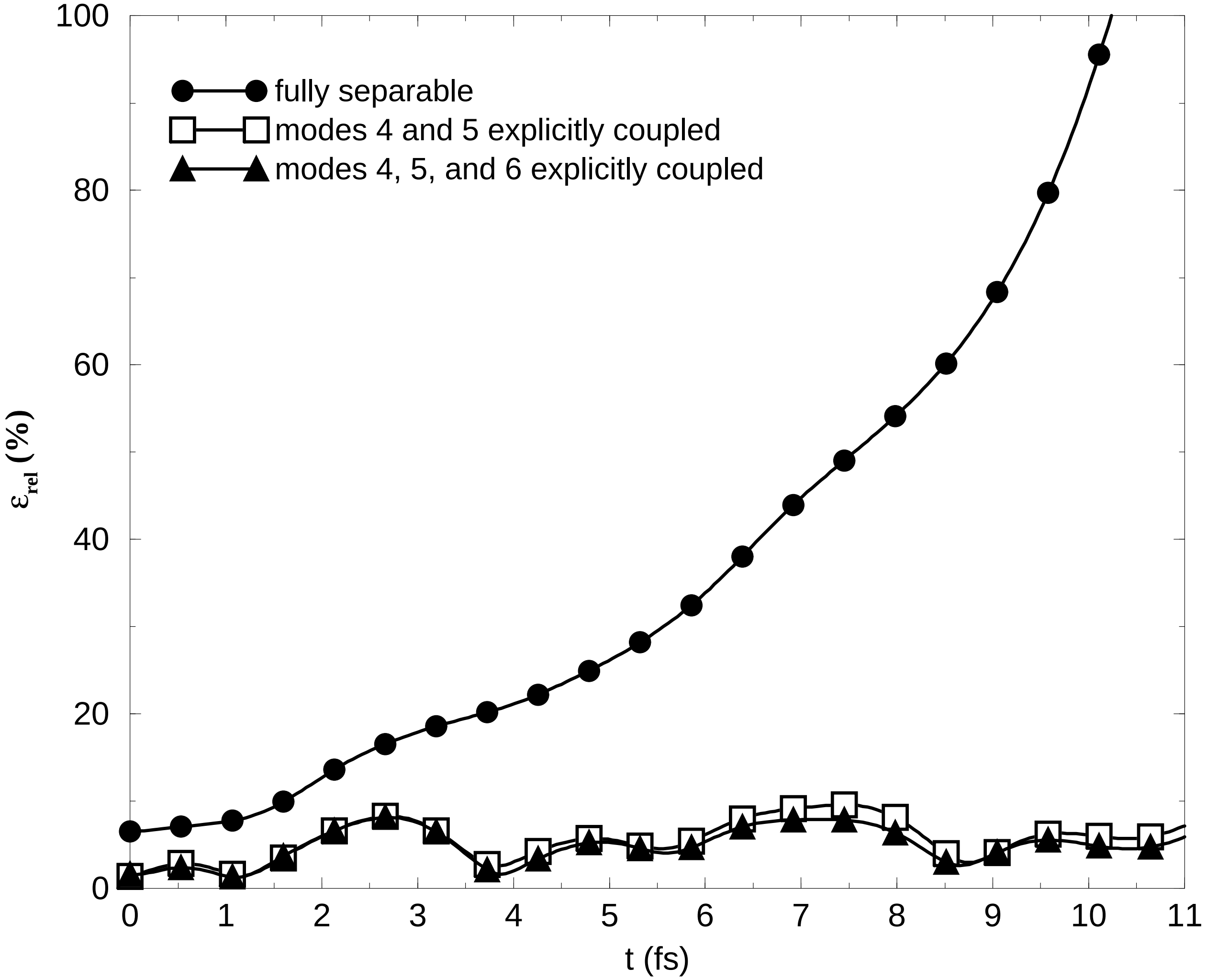

Figure 8 (Jungwirth, Roeselova, Gerber)