Quantum molecular dynamics of large systems beyond separable approximation: The configuration interaction classical separable potential method

Pavel Jungwirth,[a] Erick Fredj,[b,c] and R. Benny Gerber[b,c]

a) J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3, 18223 Prague 8, Czech Republic.

b) Department of Physical Chemistry and The Fritz Haber Center for Molecular Dynamics, The Hebrew University of Jerusalem, Jerusalem 91904, Israel.

c) Department of Chemistry, University of California, Irvine, CA 92717, USA.

Abstract

A non-separable method for time-dependent quantum simulations of large polyatomic systems is presented and applied to the dynamics of the I_2Ar_{17} cluster, following electronic excitation of the iodine molecule. The new method is an extension of the Classical Separable Potential (CSP) approximation, in which the evolution of each mode is governed by a time-dependent mean potential due to the other modes and the total wavepacket is a product of single mode wavefunctions. The computational effectiveness of the CSP approach stems from the use of classical Molecular Dynamics (MD) trajectories, carried out at the outset of the procedure, for obtaining the effective single-mode potentials. The present method generalizes the CSP scheme by a Configuration Interaction (CI) treatment, in which the total wavepacket is represented as a linear combination of separable terms, with coefficients determined from the time-dependent Schrodinger equation. The single mode wavefunctions for each configuration are propagated along effective potentials that are generated using individual classical trajectories. The classical MD simulation is also used for simplifying the dynamical equations for the CI coefficients. Thus, the selection of correlations that are included quantum mechanically is guided by classical mechanics, which is the basis for the computational efficiency of this approach. The CI wavepacket for the I_2Ar_{17} system with 51 vibrational degrees of freedom was propagated for 500 fs following $I_2(B \leftarrow X)$ excitation. About 1500 configurations proved sufficient for convergence of the CI series. The separable approximation to the wavefunction holds for 60 fs and begins to break down upon the first collision of the iodine atoms with argons. After the second iodine-argon collision this breakdown is almost complete, and at t=500 fs the CSP term represents less than 5 % of the correlated wavepacket. Both absorption and resonance Raman spectra are, however, well described by the separable CSP method, since they are dermined within the first 60 fs.

The CI-CSP method offers very good accuracy due to inclusion of important correlation effects between different modes, while remaining computationally feasible for systems up to a hundred degrees of freedom and more.

I. Introduction

Solving the time-dependent Schrodinger equation for nuclear motions can be viewed as the ultimate goal of molecular dynamics. Unfortunately, this goal can currently only be achieved for diatomic, triatomic, and, with great effort, for certain tetraatomic systems. This is due to a very unfavorable (exponential) scaling of the computational effort with system size. For this reason numerically exact quantum wavepacket propagations for large polyatomic systems will most probably remain unfeasible also long into the future, at least if attempted by the present-day methods. The usual way out of this dilemma is to retreat to classical Molecular Dynamics (MD). Standard methods allow today for classical propagation of coupled motions of many thousands of atoms. The price of course is to give up on description of quantum effects connected with zero point motions, tunneling, resonant quantum energy transfer, etc. Also, in the realm of pure classical mechanics it is not possible to account for nonadiabatic interaction of nuclear with electronic motions and there are principal problems with spectra modeling.

If quantum effects in large systems are to be explored, new approaches must be developed. Recently, methods based on the path integral method[1,2] and semiclassical centroid approximation[3,4] appeared, which are, however, still confined to small or model systems, Vast simplification of the quantum dynamical problem in N degrees of freedom is achieved by assuming separability of the quantum wavepacket. Indeed, approximating the total wavepacket by a product of single mode terms leads to a set of one-dimensional Schrodinger equations with single mode self-consistent potentials. Unfortunately, the evaluation of these effective potentials involves N-1 dimensional quadratures which makes the time-dependent self-consistent field (TDSCF) method[5−10] impractical for large systems unless further simplifications are done. One can e.g., try to expand the full potential into a truncated Taylor series in normal coordinates or to use some kind of mixed semiclassical approximation. The latter means treating only part of the systems quantally and the rest classically or using Heller's semiclassical gaussians.[11,12] Recently, we developed a different approach called Classical Separable Potential (CSP) method,[13,14] in which a separable quantum wavepacket is propagated for the multidimensional system, while the effective potentials are constructed as a weighted average over classical trajectories. This calculation of effective potentials is very efficient since it does not involve multidimensional quadratures. In this way, couplings between the modes are first build in mean-field potentials using classical trajectories, followed by fully quantum propagation of a separable wavepacket. By overcoming the bottleneck of the TDSCF method it became possible to propagate wavepackets for systems with more than a hundred of degrees of freedom.[15]

From the quantum dynamical point of view quantum-classical molecular dynamics methods suffer both from the separability *ansatz* and the partial use of classical mechanics. It has been recently shown[16] that, in most cases, separability and not the use of classical trajectories is the main source of error of mixed quantum-classical schemes, which is in perfect accord with our experience with the CSP method applied to moderately quantal chemical systems.[13] Separable approximations are generally not valid for longer time propagations for which the effects of intermode correlations are important. The principal aim of this study is to overcome this problem by extending the CSP method beyond separability, in the direction of Configuration Interaction (CI). We build on the experience with TDSCF that has been extended along several lines. These include multiconfiguration and configuration interaction extensions of the TDSCF methods, utilizing basis set expansions,[17–19] time-dependent perturbation series[20] and TDSCF factorization into more than one-dimensional factors.[21] No matter how useful and elegant these approaches are they still remains prohibitively expensive for more than several atoms. Therefore, we follow here a different strategy, namely we use the individual classical trajectories to generate quantum wavepackets (configurations) which are then mixed with the CSP wavepacket in a CI-CSP scheme carried up to single and double excitations. In this we rely on the fact that classical trajectories propagated using the fully coupled potential 'know' about correlations. Therefore, they can guide us in the choice of the CI space and in evaluation of the intermode coupling terms. It should be stressed that after the choice of the CI space is accomplished, a fully quantal propagation of the CI wavepacket is performed. In this way, where we refrain from evaluation of multidimensional integrals, it becomes possible to propagate non-separable quantum wavepackets for systems with more than a hundred degrees of freedom, which represents one to two orders of magnitude jump compared to existing methods. Due to the necessarily approximate nature of the CI-CSP approach it is very important to perform test calculations on realistic but small systems where numerically exact propagations are still computationally feasible. Such tests of the CI-CSP method against numerically exact calculation for a simple threedimensional problem are very encouraging and show a significant increase of accuracy upon inclusion of intermode correlations.[22]

Using the CI-CSP method we investigate the subpicosecond dynamics following B $\leftarrow$ X photoexcitation of I_2 in a double icosahedral Ar_{17} cluster representing the first solvation shell. Photochemistry of the iodine molecule in chemically inert solvents as well as in the gas phase has been in the focus of numerous experimental and theoretical studies including many experiments sensitive to quantum effects.[23−50] In our previous work,[15] where we also gave a more detailed introduction to this system and process, we studied using the CSP method the early (< 100 fs) dynamics with emphasis on absorption and resonance Raman spectra. The CI-CSP approach allows us here to propagated further when strong correlations between the modes develop due to collisions of the iodine atoms with the argon 'wall', and investigate the dynamics connected with the quasioscillatory I-I motion in the expanding argon cage.

The paper is organized as follows. In Section II the CSP scheme is briefly reviewed and the CI-CSP method is derived in detail. Section III describes the system under investigation and details concerning the CI-CSP propagation. Results and discussion are to be found in Section IV and Section V contains conclusions. Finally, the Appendix gives the complete set of the CI equations.

II. Method

A. Classical separable potential method

We first briefly review the principles of the separable CSP approach[13] which is the starting point for the configuration interaction extension described in the next subsection. The basic concept of the CSP method lies in simplifying the multidimensional coupled quantum dynamical problem by constructing an effective time-dependent separable mean-field potential for each degree of freedom using classical trajectories. This is done by carrying out first a classical MD simulation. Using the ensemble of trajectories, an effective potential for each mode is computed. Subsequently, the system is 'quantized', and a one-dimensional quantum propagation is performed for each mode using the above separable potentials.

The CSP scheme starts with mapping the initial quantum state of the system onto a set of classical coordinates and momenta which serve as initial values for MD simulations using Wigner distribution. For cases, where Wigner distribution becomes negative in certain regions of the configuration space (e.g., for higher states of harmonic oscillators) one can use Husimi distribution, which is always positive.[51] A set of n_T classical trajectories $\{q_1^{(\alpha)}(t), q_2^{(\alpha)}(t), ..., q_N^{(\alpha)}(t), \alpha = 1, ..., n_T\}$ started from Wigner coordinates and momenta is generated by solving the classical equations of motion and used to construct a separable time-dependent effective potential $\mathrm{V}_j(\mathrm{q}_j,\mathrm{t})$ for each mode l $(j = 1, 2, ..., N)$ in the following way:

$$V_j(q_j,t) = \sum_{\alpha=1}^{n_T} V(q_1^{(\alpha)}(t),...,q_{j-1}^{(\alpha)}(t),q_j,q_{j+1}^{(\alpha)}(t),...,q_N^{(\alpha)}(t))w_\alpha + \frac{1-N}{N}\overline{V}(t). \tag{1}$$

Here, V is the fully coupled potential and the summation runs over all MD trajectories and w_α is the Wigner weight of trajectory α calculated using the initial wavepacket. Energy transfer between the modes is implicitly accounted for in the CSP method through the time-dependence of the effective separable potentials. The coordinate-independent constant $\overline{V}$

$$\overline{V}(t) = \sum_{\alpha=1}^{n_T} V(q_1^{(\alpha)}(t),...,q_{j-1}^{(\alpha)}(t),q_j^{(\alpha)}(t),q_{j+1}^{(\alpha)}(t),...,q_N^{(\alpha)}(t))w_\alpha \tag{2}$$

which does not influence the dynamics ensures that the single-mode potentials sum up approximately to the total potential energy of the system. The replacement of the N-1 dimensional quantum quadratures by a weighted average over a few hundred trajectories is the key trick of the CSP method which allows for quantum dynamical description of very large systems.

Finally, the time-dependent Schrödinger equation in the separable approximation is solved for each mode j

$$i\hbar\frac{\partial\psi_j(q_j,t)}{\partial t} = (\hat{T}_j + V_j(q_j,t))\psi_j(q_j,t), j=1,...,N. \tag{3}$$

Here, normal mode coordinates are used, $\hbar$ represents the Plank's constant, and $\hat{T}_j$ is the kinetic energy operator of mode j. The total wavepacket for the system under study is then given as a product of the single-mode wavefunctions

$$\Psi(q_1,...,q_N,t) = \prod_{j=1}^{N}\psi_j(q_j,t). \tag{4}$$

For separable initial wavepacket the time propagation is straightforward. Provided that at t=0 the wavepacket cannot be represented as a product of single mode wavefunctions it is in principle possible to to expand it into a series of separable terms and, taking advantage of the linearity of the Schrodinger equation, propagate each term separately using the CSP method.

B. Configuration interaction extension of the CSP method

The CSP method involves two kinds of approximations - one resulting from the use of classical trajectories for the construction of effective single mode potentials, the other being connected with the separable nature of the quantum wavepacket. It is our experience gained from a variety of photochemical systems and processes that the former approximation does not usually cause significant loss of accuracy, and the Classical Separable Potentials are practically identical to the quantum self-consistent field potentials for cases where the latter calculation is computationally feasible.[13] The only exceptions, where the above 'rule' is unlikely to apply, are extremely quantum mechanical systems. On the other hand, it has been shown that the accuracy of separable methods decays rapidly in time due to cumulative errors resulting from the difference between mean-field and exact couplings between the modes. The method we propose here for including the correlation effects between the modes is based on a CI approach. Again, classical MD is used to overcome the unfavorable scaling of the computational effort with the system size. More specifically, classical trajectories, which describe a fully correlated dynamics, are used to guide the selection of important CI terms and to enable evaluation of coupling terms without multidimensional quadratures. The CI method is based on the time-dependent variational principle which ensures superiority of the CI results to the CSP ones. The degree of improvement over the separable CSP method crucially depends on the right choice of the CI terms. In our approch we rely on the fact that classical mechanics is fully correlated and that in moderately quantal systems modes that are strongly correlated classically will also exhibit this property in quantum mechanics.

For the CI method built on the Classical Separable Potential scheme we propagate separable wavepackets $\Psi^{(\alpha)} = \psi_1^{(\alpha)} \times ... \times \psi_N^{(\alpha)}$ along individual classical trajectories α, i.e. using potentials of the type

$$V_j^{(\alpha)}(q_j,t) = V(q_1^{(\alpha)}(t),...,q_{j-1}^{(\alpha)}(t),q_j,q_{j+1}^{(\alpha)}(t),...,q_N^{(\alpha)}(t)) + \frac{1-N}{N}\overline{V}^{(\alpha)}(t) \tag{5}$$

together with the CSP wavepacket guided by the CSP potential (see Eq.1). The coordinate-independent constants $\overline{V}^{(\alpha)}$

$$\overline{V}^{(\alpha)}(t) = V(q_1^{(\alpha)}(t),...,q_j^{(\alpha)}(t),...,q_N^{(\alpha)}(t)) \tag{6}$$

again do not influence the dynamics and are only added for energy normalization.

The CI-CSP *ansatz* for the wavepacket is as follows:

$$\Psi^{CI-CSP}(q_1,...,q_N,t) = c_0(t)\psi_1^0(q_1,t)...\psi_N^0(q_N,t) + \sum_{j,\alpha}^{N,M_j} s_{j\alpha}(t)\psi_1^0(q_1,t)...\psi_j^{(\alpha)}(q_j,t)...\psi_N^0(q_N,t)$$

$$+\sum_{j(<j'),\alpha,j',\beta}^{N,M_j,N,M_{j'}} d_{j\alpha j'\beta}(t)\psi_1^0(q_1,t)...\psi_j^{(\alpha)}(q_j,t)...\psi_{j'}^{(\beta)}(q_j',t)...\psi_N^0(q_N,t). \tag{7}$$

Here, ψ_j^0 are the CSP functions, $\psi_j^{(\alpha)}$ denote j-mode wavefunctions propagated along trajectory α. These 'excited' wavefunctions are included into the CI space when the overlap between ψ_j^0 and $\psi_j^{(\alpha)}$ drops bellow a certain threshold. The choice of this threshold is to a certain extend arbitrary but for numerical stability of the algorithm the CI functions must be included early, typically when the overlap drops below 99%. On the other hand choice of this large overlap criterion results in including also many terms the contribution of which is negligible - an issue which is further dealt with in the end of this section. To make the CI problem computationally tractable the excited wavefunctions in Eq.7 are orthogonalized with respect to the CSP wavefunctions and each other using standard Schmidt orthogonalization procedure. By the use of the overlap threshold the CI space is steadily growing and thus accomodates the evolution of correlations between the modes. Also, in this way we avoid numerical singularities connected with orthogonalization of (nearly) identical functions. N is the number of modes and M_j is the number of (included into the CI space) trajectories for mode j. Finally, c_0 is the CSP coefficient, $s_{j\alpha}$ are single excitations coefficients, and $d_{j\alpha j'\beta}$ are coefficients corresponding to double excitations. The notion of excitations is borrowed from electronic structure CI and within this analogy the above *ansatz* corresponds to configuration interaction with single and double excitations (neglecting higher excitations). From a physical point of view one should rather talk about changes of single mode orbitals (polarizations) instead of single excitations and of two-mode mutual correlations instead of double excitations but we conform to the nomenclature used in the time-independent context.

There is no unique way how to construct the 'nuclear orbitals' $\psi_j^{(\alpha)}$ using classical trajectories. In the current version a wavepacket is propagated along each trajectory. In some cases it might turn out to be more advantageous to opt for a slightly different possiblity, namely to propagate separable wavepackets along differents subsets of the full set of classical trajectories. In this way, which remains to be explored, all the wavepackets would be guided by averaged potentials, either over all or selected subsets of trajectories.

Next, the CI-CSP wavepacket (Eq. 7) is substituted into the time-dependent Schrodinger equation:

$$i\hbar\frac{\partial\Psi^{CI-CSP}(1,...,N,t)}{\partial t} = (\sum_{j=1}^{N}\hat{T}_j + V(1,...,N))\Psi^{CI-CSP}(1,...,N,t), \tag{8}$$

where $\hat{T}_j$ is the kinetic energy operator for mode j and and V is the total (fully coupled) potential. To get working equations we make the following approximations:

(a) Let us first assume that the initial state is separable. Then, $c_0 = 1$ and all other CI coefficients equal to zero at t=0. In a short time approximation we take into account only couplings between the CSP function and doubly excited functions (it can easily be shown that coupling between CSP and singly excited functions is always zero, which is a time-dependent analogy of the Brillouin theorem). This approximation grossly simplifies the equations of motion. It is, however, possible to derive the full set of equations without the above approximation, and this is done in the Appendix. If the initial state is not separable, it can always be expanded as a linear combination of separable states, and the above tretmnent can be applied to each of them.

- whenever in an integral $< \Psi|V|\Phi >$ Ψ and Φ differ in two modes j and j' we approximate it by $< \psi_j\psi_{j'}|V^{CSP2}_{jj'}|\phi_j\phi_{j'} >$, where

$$V^{CSP2}_{jj'}(q_j, q_{j'}, t) = \sum_{\alpha=1}^{n_T} V(q_1^{(\alpha)}(t), ..., q_j, ..., q_{j'}, ...q_N^{(\alpha)}(t))w_\alpha \tag{9}$$

is a two dimensional analogue of the CSP.

Multiplying Eq. 6 by $< \psi_1^0...\psi_N^0|$ and $< \psi_1^0...\psi_j^{(\alpha)}...\psi_{j'}^{(\beta)}...\psi_N^0|$ we get, using the above approximations, the following equations for the time evolution of the CI coefficients c_0 (CSP) and $d_{j\alpha j'\beta}$ (double excitations):

$$i\hbar\frac{\partial c_0}{\partial t} = \sum_{j(<j'),\alpha,i',\beta}^{N,M_j,N,M_{j'}} d_{j\alpha j'\beta} < \psi_j^0\psi_{j'}^0|V^{CSP2}_{jj'}|\psi_j^{(\alpha)}\psi_{j'}^{(\beta)} >, \tag{10}$$

$$i\hbar\frac{\partial d_{j\alpha j'\beta}}{\partial t} = c_0 < \psi_j^{(\alpha)}\psi_{j'}^{(\beta)}|V^{CSP2}_{jj'}|\psi_j^0\psi_{j'}^0 > . \tag{11}$$

Finally, at this level of approximation the single excitation terms can be set to zero at all times.

In order to make the propagation computationally less demanding we restrict the CI space by omiting unimportant contributions. This is done by including only those double excitations for which $< \psi_l^m\psi_{l'}^{m'}|V^{CSP2}_{ll'}|\psi_l^0\psi_{l'}^0 > \geq \epsilon$, where ϵ is an empirically adjusted threshold. Since the magnitude of the CI integrals varies in time, in practice we take ϵ as a fraction of the averaged value of these integrals (for already included terms) at a given time. The ultimate size of the CI space can be either fixed from the outset of the procedure or is given by the choice of the parameter ϵ. Finally, a significant speedup in calculations is achieved by evaluating the above two-dimensional CI integrals using a collocation scheme.[18]

III. System and Simulation

Iodine molecule embedded in different environments ranging from clusters to liquid and solid phases has served as a model and benchmark system for studying photochemistry of a 'solvated' diatomic chromophore,[23−50] which is, of course, due to the spectroscopic convenience and richness of this molecule. Investigations of clusters are especially appealing since they allow to model solvent effects in systems with finite number of degrees of freedom possesing already many features of the condensed phases. Simulations in this work were performed for the I_2 molecule surrounded with 17 argon atoms representing the double icosahedral first solvation shell. More precisely, due to their larger size the iodine atoms slightly distort the perfect D_{5h} symmetry of the double icosahedron towards lower C_{2v} symmetry. The graphical representation of the geometry of the system under study is to be found in our previous paper[15] and in Section IV of this work.

The ground state and excited states potential energy surfaces were taken as sums of I-I, I-Ar, and Ar-Ar pair contributions. The potential functions were the same as in our earlier study.[15] Namely, the I-I (ground state) X potential was modeled by a simple Morse function.[37] The B($^3\Pi_{0u^+}$) state on which, after photoexcitation, the dynamics takes place was constructed using the RKR points[52] adding a long range attractive dispersion and a short-range repulsive exponential terms.[47] This excited state potential is asymptotically shifted by the value of iodine spin-orbit splitting of 0.943 eV. The Ar-Ar potential was taken from the work of Aziz and Slaman[53] and a Lennard-Jones potential for the Ar-I interaction[37] was adopted. Though used in most of the previous theoretical studies, these potentials do not go beyond pair additivity and do not take into account other excited I-I potential surfaces.[54, 55] We use them mainly since their simple form speeds up the computationally demanding quantum calculations and still they proved to give results of near-quantitative accuracy.[15]

Quantum propagation was performed using the split-operator method[56, 57] with time-step of 0.2 fs. Classical equations of motion were integrated using a standard fourth order predictor-corrector Gear scheme[58] and the CI coefficients were propagated using the Adams predictor-corrector technique.[59] Equidistant grid of 128 points was adopted for all (ground state) normal modes except for the I-I mode where 256 points were used. Converged results for 500 fs dynamics were obtained with 150 classical trajectories and 1517 CI functions and the corresponding simulation took less than a CPU day on a HP Apollo 735 workstation.

IV. Results and Discussion

A. Dynamical Correlations

In our previous study[15] we investigated the early (< 100 fs) quantum dynamics following I_2 ($B \leftarrow X$) photoexcitation in large rare gas clusters. Here, we extend the dynamical study in the Ar_{17} cluster to 500 fs which covers two succesive collisions of the vibrating $I_2(B)$ species with the argon wall. Fig. 1 which shows the time evolution of the CI-CSP coefficients clearly demonstrates that such an extension is only possible in the realm of a method which goes beyond separability. A quantitative measure of the separable character of the total wavepacket is the value of the square of the c_0 coefficient connected with the CSP wavepacket. For the first 60 fs which cover the first passage of the I-I wavepacket along the effective potential (due to the iodine and the argon atoms) when the absorption and Resonance Raman spectra are fully determined, this value is larger than 0.95. This brings further evidence for our earlier findings that separability is an excellent approximation on this relatively extended time scale. As a results, absorption and resonance Raman spectra can be nearly quantitatively reproduced at the separable CSP level.[15]

The onset of correlated regime coincides with the first collision with the argon wall (starting around 80 fs) when correlations start to strongly build up and separable approximation looses validity. Another event connected with important correlations between the modes is the second collision with the argons starting after 300 fs, after which the square of the c_0 coefficient further decreases and finally drops bellow 0.1 after 400 fs. At this point the short time approximation which assumes that c_0 is the dominant coefficient starts to fail and to propagate correctly further we would have to include also couplings among the excited functions. Work in this direction, which will allow for propagation for at least several picoseconds, is in progress. Certainly, the wavepacket which bears all the physical information is the most demanding quantity to be reproduced and around 500 fs separability turns out to be a poor approximation to it. As shown in the following subsections, many 'semiclassical' observables (such as mean interatomic distances) are, however, still very well reproduced using the separable CSP approach at these time scales. Although definitely not perfect, the above results provide first estimates of the deterioration of separability and buildup of correlations in realistic large polyatomic systems.

It is interesting to investigate which modes are responsible for the correlation couplings. As can be seen from Fig. 1, the loss of separability is not due to a single or a few CI functions but rather a result of many small contributions to correlation. Still, some modes play important and some only a marginal role and, consequently, among the 1517 CI functions there are major and minor contributors. One may expect that it is the energetically rich I-I mode which will most strongly couple with other modes but this turns out not to be exactly true. First and most important correlations appear between 'cage modes' where the patterns of atomic motions and the vibrational frequencies are similar. A typical example is the strong coupling between mode 16 (representing a collinear elongationg and shrinking of the cage) and mode 13 (corresponding to cage breathing), responsible for some 7% of the decay of the CSP wavepacket. Fig. 2 depicts these two normal modes together with the I-I mode. It can be deduced from Fig. 2 that strong couplings develop between modes where argon atoms mostly involved in the vibrations exhibit very similar motions.

Only later, around the first collision with argons, couplings between the I-I and cage modes build up. Not surprisingly, the most important cage modes in this respect involve axial motions of the two 'polar' argons and argons in the adjacent argon rings, which are mostly being affected by the I-I expansion. As can be seen in Figs. 2, the above mentioned modes 13 and 16 fall into this class and actually couple most strongly with the I-I mode. Alltogether, couplings of the I-I mode with cage modes are responsible only for some 15% of the CSP wavepacket decay, the rest being due to cage-cage correlations. This is both due to the fact that the strongest correlations are of the cage-cage type and due to the number factor - there are N(N-1)/2 cage mode-cage mode pairs but only N-1 I-I mode-cage mode pairs.

B. Wavefunctions

One of the advantages of the configuration interaction method is that while going beyond separability it expresses the total wavepacket as a sum of separable terms, and therefore still allows to a certain extent interpretation in terms of single-mode wavefunctions. For example, due to mutual orthogonality of the CI functions it is easy to intergate the CI wavepacket over all but one degree of freedom j and obtain projected CI 'single mode' functions $P_j(j,t) =< \Psi(1,...,N,t)|\Psi(1,...,N,t) >_j$, where symbol $<>_j$ means ommiting mode j in the integration. Fig. 3 shows the time evolution of the projected CI I-I wavepacket during the first 500 fs. The dynamics involves a quasiperiodic motion in an effective potential formed by the iodines and surrounding argons accompanied with reshaping of the wavepacket during the first two collisions with the solvent wall. Comparisons of the CI functions with CSP wavepackets for the I-I mode and modes 13 and 16 (which are most strongly involved in the CI mixing) after 500 fs are depicted in Figs. 4-6. It can readily be seen from Fig. 4 that the I-I mode is only moderately involved in couplings and even after 500 fs to a large extend preserves the CSP character. Note that the most strongly contributing I-I mode CI function (propagated along the 9th classical trajectory) is very different from the CSP one, however, the corresponding CI coefficients are small, and therefore this function causes only small changes between the CSP and CI-CSP wavepacket.

On the other hand, modes 13 and 16 (and some other cage modes) get strongly involved in cage-cage and also in I-I mode-cage correlations. Figs. 5-6 shows how different the CI-CSP wavepackets are from the CSP ones for modes 13 and 16. Several wavepackets propagated along individual trajectories (e.g. trajectories No. 28 and 2) contribute importantly to the CI function. As a result, the overlap between the CI-CSP and the CSP wavepackets decreases significantly. Also, the CI-CSP function develops 'shoulders' practically not present in the CSP wavepacket. This indicates that the separable approximations tend to some extend artificially preserve the initial gaussian shape of the wavefunction and only after correlations are taken into account via CI significant non-gaussian features unravel. In other words, it is hard to reproduce the breaking up of the initial gaussian shape of the wavepacket by separable methods such as CSP (which itself goes beyond the gaussian approximation) since correlations obviously play an important role in this effect.

C. Observable quantities

In this subsection we investigate how the inclusion of correlations via CI influences quantities such as the mean interatomic distance between two atoms A and B, defined as $<\Psi|r_{AB}|\Psi>$, mean single mode kinetic energies $<\Psi|T_j|\Psi>$, and Resonance Raman intensities. A qualitative picture of the 500 fs dynamics can be gained from Fig. 7, which shows a series of snapshots of the mean CI-CSP atomic positions. It can be seen that the I-I motion mainly influences the 'polar' argons which get a major kick, together with the two adjacent argon rings. More quantitatively, Fig. 8 shows the time evolution of the mean I-I distance during the first 500 fs. As discussed in previous subsection, the I-I mode only mildly couples with the cage modes, therefore the separable CSP approximation already reproduced very well the oscillatory I-I motion during the first two collisions with argons. Quantitatively, compared to the CSP results, the CI-CSP oscillations are slightly more dumped on the argon wall side indicating a more efficient energy transfer to cage modes. This is in agreement with a general observation that separable methods tend to underestimate energy transfer between the modes since energy transfer often involves a relatively large contribution from correlated motions of modes. The deviations caused by inclusion of correlations are more pronounced for the mean distance between iodine and adjacent argon atoms (see Fig. 9). This is due to the fact that these quantities depend not only on the mildly correlated I-I motion but also on the cage modes correlations. Still, CSP results are qualitatively correct for all interatomic distances. The differences between CSP and CI-CSP are more pronounced for energetic quantities such as the mean single mode kinetic energy. The oscillatory behavior of the I-I kinetic energy becomes more dumped when correlations are included (see Fig. 10). Figs. 11-12 demonstrate that this effect is even more pronounced for modes 13 and 16 which gets strongly involved in cage-cage and I-I mode-cage correlations.

The results of calculations discussed in this subsection are in accord with experimental trends. Direct comparison with measurements is available, e.g. via absorption and Resonance Raman spectra.[39,40,44,45,60] Fig. 13 shows comparison of the CI-CSP Resonace Raman spectrum of the I_2Ar_{17} cluster with experimental Raman progressions in an argon matrix[40] and in the gas phase.[45,60] The strong environmental effect, both inthe cluster and in the matrix, is due to the dephasing of the cage modes which results in dumping of the erratic structure of the gas phase overtone intensities and in the fact that the Raman process is finished in less than 80 fs. The CI-CSP spectrum (which practically coincide with the CSP one) is in a very good agreement with the experiment. For a longer time dynamics, questions concerning intermode energy transfer can be addressed via pump-probe spectroscopy. Fig. 14 depicts time evolution of the kinetic energy of the I-I mode together with solvent modes. The oscillations of the I-I curve reflect the dumped vibrational motion of the chromophore. From the difference of the first two peaks on this curve we can get a 0.2 eV energy transfer during the first collision with the argon cage. Another estimate of 0.15 eV can be obtained from the difference of the whole cage kinetic energy before and right after the collision (see Fig. 14). The first number is an upper bound since some kinetic energy also goes to the potential energy of the I-I mode (the wavepacket broadens) while the second number represents a lower bound since the cage also absorbs potential energy during the collision. This predicted strong energy transfer from the chromophore to the cage can be verified using time-resolved spectroscopy. Importantly, we note that there is a strong cage mode selectivity in the collisional energy tranfer with modes involving strong motions of the 'polar' argons (e.g., no. 12, 13, and 16) being most efficient. Let us stress at this point the importance of quantum mechanical description of the nuclear motions. Although the system under study does not consists of very light nuclei the cryogenic temperatures involved make the zero point effects on the dynamics and energy transfer non-negligible (it is know that to describe at least qualitatively very cold argon clusters in a classical framework it is necessary to artificially heat the cluster by tens of Kelvins[29,30]). Moreover, spectroscopic quantities tend to be very sensitive to the phase relations of the quantum wavepacket which can hardly be reproduced by classical mechanics.

D. Convergence

An important quality of the results is their convergence with respect to the number of classical trajectories and number of CI functions. The necessary number of classical trajectories depends on the concrete system and lengths of propagation. Certainly, the number of classical trajectories should be sufficient to mimic the spreading of the quantum wavepacket so that the classical separable potentials are close to the quantum TDSCF ones. From the configuration interaction point of view the more trajectories we include the more likely we are to recover the 'fluctuations' from the mean potentials, which give rise to intermode correlations. In all cases studied so far convergence was very fast with only several hundreds of trajectories needed, and for a 500 fs quantum dynamics in I_2Ar_{17} 150 trajectories provide converged CSPs.

The issue of convergence with respect to the number of CI functions has two parts. The first one concerns the convergence of the CI series in terms of single, double, triple, etc. excitations. Similarly to electronic structure theory, CI calculations for large systems are tractable only when this series is truncated very early, namely at double excitations. Unless we succeed to formulate a computationally practical theory including higher excitations we have to rely on general experience that double excitations recover most of the correlations and that the excitation series converges rather fast. CI with double excitations may be said to represent a model in which not more than two modes are correlated at a given time. An interesting question connected with this issue is what kind of correlations are we recovering by our method. Do they arrise because the ground state normal modes cease to be good coordinates after the iodine-argon collision or are they inherent correlations which will remain even with the ideal choice of the coordinate frame? Despite notable attempts to find optimal coordinates for separable approximations[14,61] no practical scheme exists for large realistic systems and we are, as for now, left with speculations.

The second part of the question is about convergence within the doubly excited CI space. For our system there are millions of doubly excited functions and it is both impossible and unnecessary to include them all. Indeed, only a small fraction of these functions contribute significantly to the configuration interaction and, as described in previous sections, we devised methods how to gradually include the important terms. By changing the acceptance criteria we can modify the final size of the CI space. Convergence with respect to the number of included doubly excited functions can be assessed from Fig. 15, which shows the time evolution of the leading c_0 CI coefficient for four different simulations with 657, 1052, 1246, and 1517 CI functions. It follows from our calculations that 1517 selected CI functions provide reasonably well converged results.

V. Conclusions

In this work we presented a configuration cnteraction extension of the classical separable potential method and applied it to the quantum dynamics following B $\leftarrow$ X photoexcitation of I_2 embedded in a double icosahedral Ar_{17} cluster. We showed mainly that:

i) quantum dynamical calculations going beyond separable *ansatz* are feasible for systems with 10-100 degrees of freedom,

ii) separability is a very good approximation for early dynamics ($<$ 60 fs) and provides absorption and resonance Raman spectra with satisfactory agreement with experiment,

iii) buildup of correlations in the system under study is connected with solute-solvent collisions. Eventually, however, the numerous cage-cage couplings are more effective in dismantling separability than I-I mode-cage couplings,

iv) after the first collision (80-200 fs) the separable approximation ceases to quantitatively, and after the second collision (350-500 fs) even qualitatively represent the correlated wavepacket. Still, many averaged 'semiclassical' quantities remain to be reasonably well described at the separable level.

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VI. Appendix

In the Appendix we give the full set of the CI-CSP equations without the short time approximation, which means including also the single-single, single-double and double-double interaction terms. The final set of equations for the time evolution of the CI coefficients c_0 (CSP), $s_{j\alpha}$ (single excitations), and $d_{j\alpha j'\beta}$ (double excitations) reads:

$$i\hbar\frac{\partial c_0}{\partial t} = \sum_{j(<j'),\alpha,j',\beta}^{N,M_j,N,M_{j'}} d_{j\alpha j'\beta} < \psi_j^0\psi_{j'}^0|V_{jj'}^{CSP2}|\psi_j^{(\alpha)}\psi_{j'}^{(\beta)} >, \tag{12}$$

$$\begin{aligned} i\hbar\frac{\partial s_{j\alpha}}{\partial t} &= -s_{j\alpha}\sum_{k(\neq j)}^{N} < \psi_k^0|\hat{T}_k + V_k^{CSP}|\psi_k^0 > + \sum_{\gamma}^{M_j} s_{j\gamma} < \psi_j^{(\alpha)}|\hat{T}_j + V_j^{CSP}|\psi_j^{(\gamma)} > \\ & - i\sum_{\gamma}^{M_j} s_{j\gamma} < \psi_j^{(\alpha)}|\frac{\partial\psi_j^{(\gamma)}}{\partial t} > + \sum_{k(\neq j),\gamma}^{N,M_k} s_{k\gamma} < \psi_j^{(\alpha)}\psi_k^0|V_{jk}^{CSP2}|\psi_j^0\psi_k^{(\gamma)} > \\ & + \sum_{k(>j),\gamma,\delta}^{N,M_j,M_k} d_{j\gamma k\delta} < \psi_j^{(\alpha)}\psi_k^0|V_{jk}^{CSP2}|\psi_j^{(\gamma)}\psi_k^{(\delta)} > \\ & + \sum_{k(<j),\gamma,\delta}^{N,M_k,M_j} d_{k\gamma j\delta} < \psi_j^{(\alpha)}\psi_k^0|V_{jk}^{CSP2}|\psi_j^{(\delta)}\psi_k^{(\gamma)} > \\ & + \sum_{k(<l),\gamma,l,\delta}^{N,M_k,N,M_l} d_{k\gamma l\delta} < \psi_j^{(\alpha)}\psi_k^0\psi_l^0|V_{jkl}^{CSP3}|\psi_j^0\psi_k^{(\gamma)}\psi_l^{(\delta)} >, \end{aligned} \tag{13}$$

$$\begin{aligned} i\hbar\frac{\partial d_{j\alpha j'\beta}}{\partial t} &= -i\sum_{\gamma}^{M_j} d_{j\gamma j'\beta} < \psi_j^{(\alpha)}|\frac{\partial\psi_j^{(\gamma)}}{\partial t} > -i\sum_{\gamma}^{M_{j'}} d_{j\alpha j'\gamma} < \psi_{j'}^{(\beta)}|\frac{\partial\psi_{j'}^{(\gamma)}}{\partial t} > \\ & + c_0 < \psi_j^{(\alpha)}\psi_{j'}^{(\beta)}|V_{jj'}^{CSP2}|\psi_j^0\psi_{j'}^0 > \\ & + s_{j\alpha} < \psi_{j'}^{(\beta)}|\hat{T}_{j'} + V_{j'}^{CSP}|\psi_{j'}^0 > + s_{j'\beta} < \psi_j^{(\beta)}|\hat{T}_j + V_j^{CSP}|\psi_j^0 > \\ & + \sum_{\gamma(\neq\alpha)}^{M_j} s_{j\gamma} < \psi_j^{(\alpha)}\psi_{j'}^{(\beta)}|V_{jj'}^{CSP2}|\psi_j^{(\gamma)}\psi_{j'}^0 > \\ & + \sum_{\gamma(\neq\beta)}^{M_{j'}} s_{j'\gamma} < \psi_j^{(\alpha)}\psi_{j'}^{(\beta)}|V_{jj'}^{CSP2}|\psi_j^0\psi_{j'}^{(\gamma)} > + \sum_{k(\neq j,j'),\gamma}^{N,M_j} s_{j\gamma} < \psi_j^{(\alpha)}\psi_{j'}^{(\beta)}\psi_k^0|V_{jj'k}^{CSP3}|\psi_j^0\psi_{j'}^0\psi_j^{(\gamma)} > \\ & + d_{j\alpha j'\beta}(< \psi_j^{(\alpha)}|\hat{T}_j|\psi_j^{(\alpha)} > + < \psi_{j'}^{(\beta)}|\hat{T}_{j'}|\psi_{j'}^{(\beta)} > \\ & + < \psi_j^{(\alpha)}\psi_{j'}^{(\beta)}|V_{jj'}^{CSP2}|\psi_j^{(\alpha)}\psi_{j'}^{(\beta)} > - \sum_{k\neq j,j'}^{N} < \psi_k^0|V_k^{CSP}|\psi_k^0 >) \\ & + \sum_{\gamma(\neq\alpha)}^{M_j} d_{j\gamma j'\beta}(< \psi_j^{(\alpha)}|\hat{T}_j|\psi_j^{(\gamma)} > + < \psi_j^{(\alpha)}\psi_{j'}^{(\beta)}|V_{jj'}^{CSP2}|\psi_j^{(\gamma)}\psi_{j'}^{(\beta)} >) \end{aligned}$$

$$+\sum_{\gamma(\neq\beta)}^{M_{j'}} d_{j\alpha j'\gamma}(<\psi_{j'}^{(\beta)}|\hat{T}_{j'}|\psi_{j'}^{(\gamma)}> + <\psi_j^{(\alpha)}\psi_{j'}^{(\beta)}|V_{jj'}^{CSP2}|\psi_j^{(\alpha)}\psi_{j'}^{(\gamma)}>)$$

$$+\sum_{\gamma(\neq\alpha),\delta(\neq\beta)}^{M_j,M_{j'}} d_{j\gamma j'\delta} <\psi_j^{(\alpha)}\psi_{j'}^{(\beta)}|V_{jj'}^{CSP2}|\psi_j^{(\gamma)}\psi_{j'}^{(\delta)}>$$

$$+\sum_{k(<j',\neq j),\gamma,\delta}^{N,M_k,M_{j'}} d_{k\gamma j'\delta} <\psi_j^{(\alpha)}\psi_{j'}^{(\beta)}\psi_k^0|V_{jj'k}^{CSP3}|\psi_j^0\psi_{j'}^{(\delta)}\psi_k^{(\gamma)}>$$

$$+\sum_{k(>j,\neq j'),\gamma,\delta}^{N,M_j,M_k} d_{j\gamma k\delta} <\psi_j^{(\alpha)}\psi_{j'}^{(\beta)}\psi_k^0|V_{jj'k}^{CSP3}|\psi_j^{(\gamma)}\psi_{j'}^0\psi_k^{(\delta)}>$$

$$+\sum_{k(<l,\neq j,j'),\gamma,l(\neq j,j'),j'}^{N,M_k,N,M_l} d_{k\gamma l\delta} <\psi_j^{(\alpha)}\psi_{j'}^{(\beta)}\psi_k^0\psi_l^0|V_{jj'kl}^{VCSP4}|\psi_j^0\psi_{j'}^0\psi_k^{(\gamma)}\psi_l^{(\delta)}> .$$

Here, $V_{jj'}^{CSP2}$,$V_{jj'k}^{CSP3}$, and $V_{jj'kl}^{CSP4}$ represent two-, three-, and four-dimensional potentials defined in analogy to CSPs:

$$V_{jj'}^{CSP2}(q_j, q_{j'}, t) = \sum_{\alpha=1}^{n_T} V(q_1^{(\alpha)}(t), ..., q_j, ..., q_{j'}, ..., q_N^{(\alpha)}(t))w_\alpha \tag{14}$$

$$V_{jj'k}^{CSP3}(q_j, q_{j'}, q_{jj'k}, t) = \sum_{\alpha=1}^{n_T} V(q_1^{(\alpha)}(t), ..., q_j, ..., q_{j'}, ..., q_k, ..., q_N^{(\alpha)}(t))w_\alpha \tag{15}$$

$$V_{jj'kl}^{CSP4}(q_j, q_{j'}, q_k, q_l, t) = \sum_{\alpha=1}^{n_T} V(q_1^{(\alpha)}(t), ..., q_j, ..., q_{j'}, ..., q_k, ..., q_l, ..., q_N^{(\alpha)}(t))w_\alpha \tag{16}$$

It can readily be seen that solving the full set of CI equations involves numerical evaluation of up to four dimensional integrals. This is computationally rather demanding but feasible, especially when using a collocation method.[18]

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Figure Captions

Figure 1: Time evolution of the CSP and doubly excited CI coefficients.

Figure 2: I-I mode and cage modes No. 13 and 16. Spheres connected by a bond represent iodine atoms, the rest are argons.

Figure 3: Time evolution of the I-I mode wavepacket. Plotted is the CI wavefunction integrated over all but the I-I coordinate at different times.

Figure 4: Comparison of the projected CI-CSP, CSP, and 9th trajectory I-I wavepacket at 500 fs.

Figure 5: Comparison of the projected CI-CSP, CSP, and 28th trajectory mode 13 wavepacket at 500 fs.

Figure 6: Comparison of the projected CI-CSP, CSP, and 2th trajectory mode 16 wavepacket at 500 fs.

Figure 7: Series of snapshots of mean CI-CSP atomic positions covering first 500 fs of the dynamics.

Figure 8: Mean CI-CSP and CSP I-I distance.

Figure 9: Mean CI-CSP and CSP iodine-adjacent argon distance.

Figure 10: Mean CI-CSP and CSP I-I mode kinetic energy.

Figure 11: Mean CI-CSP and CSP mode 13 kinetic energy.

Figure 12: Mean CI-CSP and CSP mode 16 kinetic energy.

Figure 13: I_2 resonance Raman overtone intensities in cluster, matrix, and gas phase.

Figure 14: Single mode CI-CSP kinetic energies. Insert shows the three most important cage mode with finer energy scale.

Figure 15: Time evolution of the leading CI coefficient for 657, 1052, 1246, and 1517 CI functions.