New Methods in Quantum Molecular Dynamics of Large Polyatomic Systems

Pavel Jungwirth[1] and R. Benny Gerber[2,3]

[1] J. Heyrovsky Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejskova 3, 18223 Prague 8, Czech Republic
[2] Department of Physical Chemistry and The Fritz Haber Research Center, The Hebrew University, Jerusalem 91904, Israel
[3] Department of Chemistry, University of California, Irvine, CA 92697-2025, U.S.A.

Abstract. We present new methods for time-dependent quantum mechanical simulations of large polyatomic systems and their applications to photochemical processes in clusters. Two related approaches are discussed: The Classical Separable Potential (CSP) approach, and its extension towards Configuration Interaction (CI-CSP). The former scheme assumes separability of the vibrational modes of the system, and describes each mode as moving in a mean field due to the other modes. The basic idea, which allows for quantum simulations of hitherto unaccesibly large systems, is that the effective single-mode potentials are obtained from a classical MD simulation that precedes the quantum calculation. The second approach represents an improvement that corrects for correlations between different modes, resulting in a scheme of good accuracy. Applications of the methods are presented for dynamics following photodetachment in a small $I^{-}(Ar)_2$ cluster (where comparison with numerically exact calculation is possible) and for photoexcitation dynamics and spectroscopy of atomic and molecular impurities in large clusters, such as $I_2(Ar)_{17}$ and $I_2(Ar)_{47}$. Future directions of method development are suggested in the light of the algorithmic aspects and the applications.

1 Introduction

The preferable theoretical tools for the description of dynamical processes in systems of a few atoms are certainly quantum mechanical calculations. There is a large arsenal of powerful, well established methods for quantum mechanical computations of processes such as photoexcitation, photodissociation, inelastic scattering and reactive collisions for systems having, in the present state-of-the-art, up to three or four atoms, typically.[1−9] Both time-dependent and time-independent "numerically exact" algorithms are available for many of the processes, so in cases where potential surfaces of good accuracy are available, excellent quantitative agreement with experiment is generally obtained. In addition to the full quantum-mechanical methods, sophisticated semiclassical approximations have been developed that for many cases are essentially of near-quantitative accuracy and certainly at a level sufficient for the interpretation of most experiments.[10−13] These methods also are computationally applicable in the present state-of-the-art, to systems of several atoms only.

As far as methodology is concerned, the situation for large polyatomic systems and for condensed phases is very different. Quantum mechanical simulation methods of quantitative accuracy have not been available for dynamical processes in systems of many coupled degrees of freedom. Classical Molecular Dynamics (MD) simulations have been the prime theoretical tool for interpretation, analysis and comparison with experiment. They are computationally feasible in the present state-of-the-art for systems having up to tens of thousands of atoms, and have been extensively applied to processes in biomolecules, large molecular aggregates and condensed phases. However, many physical properties cannot be treated classically, at least not quantitatively. Resonance Raman spectroscopic intensities in condensed phases, and state-to-state transitions in atom scattering from large molecules are only two examples in a virtually endless list of observable properties for which classical calculations are not adequate.[14] To this one must add the need to describe quantum effects such as zero-point motions, nonadiabatic transitions and tunneling events in the dynamics of many large systems. The need for a quantitative quantum-mechanical description of large polyatomic systems is thus well recognized, but hitherto suitable methods for this purpose have not been at hand. The situation in this respect for some time-independent properties is much better: For instance, methods such as the Diffusion Quantum Monte Carlo (DQMC) and related techniques have been used very effectively to compute ground-state energies and structural properties of large quantum clusters and solids.[15−18] Likewise, Feynman Path Integral methods were very successfully applied to the calculation of thermodynamic and structural properties of such systems at thermal equilibrium.[19−21] Another example are the ground and the low-lying vibrational eigenfunctions of large polyatomic molecules, that were recently calculated for several such systems by the Vibrational Self-Consistent Field (VSCF) method and its extensions.[22−24] Thus, calculations of the ground and of the fundamental excited vib-rotational states were reported for the protein BPTI.[24]

Within the time-dependent framework, the Time-Dependent Self-Consistent Field (TDSCF) approximation is known, in the context of electronic structure theory, from the early years of quantum theory,[29] but its applications to problems of molecular dynamics are much more recent.[30−42,23] Methods of much improved accuracy were developed on the basis of the TDSCF approximation.[34−42] Also, some technical hurdles in applying the method for larger systems were overcome in the last few years at least for some types of interaction potentials, so recently calculations have been reported for problems of significantly increased number of degrees of freedom.[16,37] Different methods for time-dependent quantum simulations of large systems were pursued vigorously by several research groups, and much progress was made. Some of the novel methods proposed are still confined to models or special systems, while for a few of the others realistic applications are already at hand. Examples of such recent methods are the Path Integral approach developed by Makri and coworkers[25,26] and the semiclassical centroid density approximation of Voth *et al.*[27,28]

The paper discusses two related recent methods for time-dependent quantum simulations of many-atom systems in which the present authors have been involved, the Classical Separable Potential (CSP) method and its Configuration Interaction extension (CI-CSP). While by no means developed to completion or general in applicability yet, these methods provide already practical working algorithms for a wide range of applications. Indeed, in the very short time since the introduction of the CSP method, many applications to large realistic systems were already made, showing that the method is already a "production tool" for extensive simulations of systems with tens to hundreds of degrees of freedom.

The CSP method involves approximations that separate the different modes, and treats each mode as moving in the average field of all the other modes. The effective single-mode potentials are determined from independent classical Molecular Dynamics simulations carried out at the outset, and then used in the quantum calculation. The CI-CSP extension goes beyond the separability approximation by expanding the multidimensional time-dependent wavepacket into a sum of separable terms with variationally determined coefficients. The choice of the CI terms is guided by the individual classical trajectories. In this way, the number of CI terms is grossly reduced and due to a favorable (non-exponential) scaling with the number o degrees of freedom the method is applicable to large polyatomic systems. The applications that will be mentioned in the present paper are all for cluster systems. This seems to us a natural choice: In trying to develop simulation methods ultimately applicable to condensed phase problems, large clusters offer physical properties similar to these phases, while still retaining the simplicity of finite systems.

Sec. 2 presents the CSP method, while an improved approach built on it (CI-CSP) is described in Sec. 3. Sec. 4 gives some examples of applications of the CSP and CI-CSP methods to the photochemical ultrafast dynamics in clusters. Directions for future progress and improvements are discussed in Sec. 5.

2 The Classical Separable Potential (CSP) Method

The principal idea behind the CSP approach is to use input from Classical Molecular Dynamics simulations, carried out for the process of interest as a first preliminary step, in order to simplify a quantum mechanical calculation, implemented in a subsequent, second step. This takes advantage of the fact that classical dynamics offers a reasonable description of many properties of molecular systems, in particular of average quantities. More specifically, the method uses classical MD simulations in order to determine effective potentials such that by the use of the latter a subsequent quantum calculation becomes far simpler$^{(43)-(48)}$.

Here, we give here a brief outline of the methods as introduced in Refs. 43, 44, and 47. Suppose that the initial state of the system is $\psi_0(q_1, ..., q_N)$. From ψ_0, the Wigner phase-space distribution $D(q_1, ..., q_N; p_1, ..., p_N)$ is computed. This distribution is used to sample initial positions and momenta $q_1^{(\alpha)}$, ... , $q_N^{(\alpha)}; p_1^{(\alpha)}, ..., p_N^{(\alpha)}$, for a classical trajectory simulation of the process of interest. The set of trajectories $q_1^{(\alpha)}(t), ..., q_N^{(\alpha)}(t)$, for $\alpha = 1, ..., n_T$, can be used to generate in the classical framework any quantity of interest at each time point t. From the trajectories, we compute the average potential acting on each mode j:

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

where $V(q_1, ..., q_N)$ is the full potential function of the system, and the summation in (24) extends over all MD trajectories. ω_α is the weight of the α trajectory in the initial state distribution (as determined from the Wigner distribution). Note that in (24), all the coordinates q_l are evaluated at trajectory points, except the q_j for which the mean potential $\bar{V}_j(q_j, t)$ is evaluated. The j-th coordinate is kept as in the full potential function. $\bar{V}(t)$ in (24) is a coordinate-independent function of time given by:

$$\bar{V}(t) = \sum_{\alpha=1}^{n_T} V(q_1^{(\alpha)}(t), ..., q_j^{(\alpha)}(t), ..., q_N^{(\alpha)}(t))\omega_\alpha \quad (2)$$

The inclusion of the second term on the right-hand-side of (24) is convenient, because in this way the average (over the trajectories) of the sum of the single-mode potentials, $\sum_{j=1}^{n} \bar{V}(q_j, t)$, equals to the average of the full potential function $V(q_1, ..., q_N)$. Using the single-mode effective potentials $\bar{V}_j(q_j, t)$, one can solve a time-dependent Schrödinger equation for each mode:

$$i\hbar \frac{\partial \phi_j(q_j, t)}{\partial t} = [T_j + \bar{V}_j(q_j, t)]\phi_j(q_j, t) \quad (3)$$

where T_j is the kinetic energy operator for mode j. A separable approximation for the total wavepacket of the system is given by

$$\psi(q_1, ..., q_N, t) = \prod_{j=1}^{N} \phi_j(q_j, t) \quad (4)$$

With the above definitions, there is no additional overall phase factor to be included in (27). Eqs. (24)-(27) are the CSP approximation.[43–47] Like TDSCF, CSP is a separable approximation, using a time-dependent mean potential for each degree of freedom. However, the effective potentials in CSP are obtained from classical MD, and their evaluation is computationally very easy, not involving multidimensional integrals as in the case of TDSCF. This gives CSP a computational advantage that for large systems is enormous, especially for systems where the potential function cannot be simplified to reduce the dimensionality of the TDSCF integrals.

The accuracy of the CSP approximation is, as test calculations for model systems show, typically very similar to that of the TDSCF.[43] The reason for this is that for atomic scale masses, the classical mean potentials are very similar to the quantum mechanical ones. CSP may deviate significantly from TDSCF in cases where, e.g., the dynamics is strongly influenced by classically forbidden regions of phase space. However, for simple tunneling cases it seems not hard to "fix" CSP, by running the classical trajectories slightly above the barrier. In any case, for typical systems the classical estimate for the mean potential functions works extremely well.

It should be noted that due to the use of classical trajectories to evaluate the time-dependent single-mode potentials, the quantum CSP energy is not strictly conserved (TDSCF conserves energy, since the single-mode potentials are obtained self-consistently with the single-mode wavefunctions). The extent of the non-conservation is, however, small and it does not seem to create significant difficulties. The smaller the difference between the TDSCF and the CSP single-mode potentials, the smaller is the CSP energy non-conservation. The more near-classical a system is, the smaller is the non-conservation effect. In general, CSP is expected to be less accurate than TDSCF, although only slightly so, because the quantum effects are not included in the evaluation of the single-mode potentials. In special cases, however, CSP may give slightly better results than TDSCF, because the CSP mean-potentials are calculated from an approach that includes correlation effects between the modes (classical MD). In summary: TDSCF and CSP give very similar results in most cases, but for systems with appreciable quantum effects, TDSCF is more accurate than CSP, while the latter may prove somewhat accurate when correlation effects are quite important.

It is obvious that CSP depends, as does TDSCF, on the choice of coordinates. As pointed out in Sec. 2.2, numerical convenience often limits the choice of the coordinates. CSP may, however, offer practical prospects for the choice of physically optimal modes. The deviation of the true potential from CSP separability is given by:

$$\Delta V_{corr}(q_1,...,q_N,t) \equiv V(q_1,...,q_N) - \sum_{j=1}^{N} \bar{V}_j(q_j,t) \tag{5}$$

ΔV_{corr} can be evaluated readily from the classical MD simulation for any choice of coordinate system, and it may be possible to determine the modes that give the smallest ΔV_{corr}. These should be optimal CSP modes. Work along these lines is in progress in our group. So far, however, the coordinate choices in the CSP applications were all straightforward and based on qualitative physical consideration.

3 Configuration Interaction extension of the CSP method

The main extension hitherto introduced for the CSP approximation is referred to as the Configuration Interaction CSP (CI-CSP) method.[48] This approach represents the full non-separable wavepacket as a linear combination, with time-dependent coefficients, of terms that are each separable. The applications of this method are very encouraging. The method can provide major improvements over CSP, and can probably be pursued at a level of high accuracy, while still being computationally feasible for large systems.[48] The method is flexible, and allows for the use of physical considerations to optimize it. The most important advantage is that within CI-CSP, the classical MD simulations greatly simplify the determination of the terms or configurations, that play the most important role in the total wavefunction. The approach is based on the following: The CSP wavepacket is obtained from mean single-mode potentials, computed as an average over all the trajectories. To include correlation effects, it is necessary to include also wavefunction terms computed from potentials that represent "fluctuations" from the average. Such potentials can be computed along a limited set of trajectories, even individual trajectories (rather than as an average over all trajectories). In the version of CI-CSP discussed here, we start with propagating separable wavepackets using effective potentials obtained from individual trajectories:

$$\bar{V}_j^{(\alpha)}(q_j,t) = V(q_1^{(\alpha)}(t),..,q_{j-1}^{(\alpha)}(t),q_j,q_{j+1}^{(\alpha)}(t),..,q_N^{(\alpha)}(t)) + \frac{1-N}{N}\bar{V}^{(\alpha)}(t) \quad (6)$$

The coordinate-independent quantities $\bar{V}^{(\alpha)}(t)$ are given by:

$$\bar{V}^{(\alpha)}(t) = V(q_1^{(\alpha)},...,q_j^{(\alpha)}(t),...,q_N^{(\alpha)}(t)) \quad (7)$$

In addition to wavepackets propagated along effective potentials corresponding to individual trajectories, we also propagate in CI-CSP the CSP wavefunctions, governed by the average potentials $\bar{V}_j(q_j,t)$ of Eq. (24). The CI-CSP *ansatz* for the total wavepacket of the system is then as follows:[48]

$$\Psi(q_1,...,q_N,t) = c_o(t)\prod_{j=1}^{N}\phi_j(q_j,t) + \sum_{j,\alpha}^{N,M_j} s_j^{(\alpha)}(t)\phi_1...\phi_j^{(\alpha)}...\phi_N +$$

$$+\sum_{j<j\prime,\alpha,\beta}^{N,M_j,N,M} d_{j\alpha j\prime\beta}(t)\phi_1...\phi_j^{(\alpha)}...\phi_{j\prime}^{(\beta)}...\phi_N \quad (8)$$

Here $\phi_j(q_j,t)$ are the CSP functions, $\phi_j^{(\alpha)}(q_j,t)$ denotes the q_j-mode wavefunction propagated on the effective potential generated from the α trajectory. These wavefunctions are orthogonalized and included in the CI expansion when the overlap between ϕ_j and $\phi_j^{(\alpha)}$ drops below a certain threshold (typically 99%). In this way, the CI space grows in the course of the dynamical evolution, corresponding to the increase of correlation between the modes. In the above expansion, M_j is the number of trajectories actually included in the CI expansion (with respect to functions of the mode j), $c_o(t)$ is the CSP coefficient, $s_j^\alpha(t)$ are single mode excitation coefficients, while $d_{j\alpha j\prime\beta}(t)$ are coefficients corresponding to two-mode excitations. The language of excitation is borrowed from time-independent CI in electronic structure theory,[80] with which the present formulation has strong analogies. Within this analogy, the *ansatz* (31) corresponds to configuration interaction with single and double excitations (neglecting higher-order excitations). From a physical point of view one should rather talk about mode-mode correlations instead of double excitations and mode 'polarization' terms instead of single excitations but we stay with the usual notation. To obtain equations of motion for the coefficients $c_o(t), s_j^\alpha(t), d_{j\alpha j\prime\beta}(t)$ of the wavefunction expression (31), we substitute the *ansatz* into the time-dependent Schrödinger equation of the system, Eq. (1), with the fully coupled potential. To get practical working equations we make several approximations:

(i) Consider for simplicity the case when the initial state is separable (extension to a non-separable initial state is straightforward, though technically more complicated). Then at $t=0, c_o=1$ and all the other CI coefficients are zero. In a short-time approximation we then take into account only coupling between the CSP state, and doubly excited states (it can be shown that coupling between CSP and singly excited states is always zero - this is a time-dependent analogue of the Brillouin theorem, familiar from electronic structure theory[80]). In this way we neglect very small (at least initially) single-single, single-double, and double-double excitation couplings.

(ii) Consider an integral $\langle\Phi|V|\hat{\Phi}\rangle$ where Φ and $\hat{\Phi}$ differ in two modes j and $j\prime$ only. We approximate this integral by $\langle\phi_j\phi_{j\prime}|V_{jj\prime}^{CSP2}|\hat{\phi}_j\hat{\phi}_{j\prime}\rangle$, where

$$V_{jj\prime}^{CSP2}(q_j,q_{j\prime},t)=\sum_{\alpha=1}^{n_T}V(q_1^{(\alpha)}(t),...,q_j,...,q_{j\prime},...,q_N^{(\alpha)}(t))\omega_\alpha \tag{9}$$

where n_T is the total number of trajectories.

Substitution of the *ansatz* (31) into the Schrödinger equation (1) for the full system, together with the above approximations, yields the following equations for the coefficients $c_o(t), d_{j\alpha j\prime\beta}(t)$ of the CI expansion (31):

$$i\frac{\partial c_o}{\partial t}=\sum_{j,\alpha,j\prime,\beta}^{N,M,N_j,M_{j\prime}}d_{j\alpha j\prime\beta}(t)\langle\phi_j\phi_{j\prime}|V_{jj\prime}^{CSP2}|\hat{\phi}_j^{(\alpha)}\hat{\phi}_{j\prime}^{(\beta)}\rangle \tag{10}$$

$$i\frac{\partial d_{j\alpha j'\beta}(t)}{\partial t} = c_o(t)\langle\hat{\phi}_j^{(\alpha)}\hat{\phi}_{j'}^{(\beta)}|V_{jj'}^{CSP2}|\phi_j\phi_{j'}\rangle \tag{11}$$

For separable initial states the "single excitation" terms can be set to zero at all times at this level of approximation. Eqs. (32),(33),(34) together with the CSP equations and with the *ansatz* (31) for the total wavefunction are the working equations for the approach. This form, without further extension, is valid only for short time-domains (typically, a few picoseconds at most). For large times, higher correlations, i.e. interactions between different singly and doubly excited states must be included.

An important computational advantage of CSP and CI-CSP for large systems is that the methods can be applied to any potential function without any need to simplify the latter by expansion, assumption of pairwise interactions, etc., as is the case for TDSCF. Applications of CSP for systems having up to $\sim 10^3$ degrees of freedom, and of CI-CSP for systems of up to ~ 100 modes are not computationally extremely demanding, and were indeed carried out on quite modest scalar workstations, of the type of SGI Indigo, HP Appollo, etc. Finally, implementation of CSP on a parallel computer is straightforward and almost ideal in efficiency. Recently, there has been extensive work on application of the CSP method on parallel computer systems with very encourageing results.[46,47,83]

4 Applications of CSP and of CI-CSP

Almost from the introduction of the CSP and CI-CSP methods, applications to large systems with realistic potential functions became possible. A general CSP code was written and is available.[47] The applications of CSP so far include a study of electron photodetachment dynamics for $I^-(Ar)_n, n = 2, ..., 12$,[44,83] a study of the dynamics following electronic excitation of $Ba(Ar)_n$ for $n = 10,\ n = 20$,[45] and a study of electronic excitation, cage effects and vibrational dephasing and relaxation dynamis for I_2 in $I_2(Rg)_n$, for $Rg = Ar$, Xe and $n = 17, 47$ (corresponding respectively to complete first and complete first two solvation layers around the iodine).[47] The dynamics of $Ba(Ar)_n$ following the excitation of the Ba in this cluster involves nonadiabatic transitions, since there are three quasidegenerate p-states of the Ba atom, and the system is then governed by three potential energy surfaces corresponding to these state, with possible non-adiabatic transitions between them. The simulations of Ref. 45 thus went beyond simple CSP, and were in fact a three-configuration CI-CSP, with a separable term in the CI wavefunction for each adiabatic electronic state. This approach, while not a converged quantum treatment, is expected already to be more reliable than semiclassical "surface hopping" methods that treat nuclear motions classically.[81] Comparison of the CI-CSP with semiclassical "surface hopping" simulations for $Ba(Ar)_{10}$

and $Ba(Ar)_{20}$, suggests that the "surface hopping" results for properties such as population ratios of the electronic states at, say, $t \approx 1$ ps after excitation, can differ from quantum results by a significant factor, of the order of ~ 2 in this case.[45]

The small $I^-(Ar)_2$ complex serves as a benchmark system since numerically exact calculation is still possible here. By numerically exact calculation we mean here a 3-dimensional wavepacket propagation using the time-dependent vibrational Schrödinger equation with the fully coupled interaction potential. The experimentally observed vibrationally resolved photoelectron spectrum can be modeled as a Fourier transform of the calculated autocorrelation function, i. e. the overlap of the initial total wavepacket with the wavepacket at time t. At the same time the complex autocorrelation function is a very sensitive quantity for testing the quality of approximate approaches since it depends not only on the amplitude but also on the phase of the wavepacket. Fig. 1 depicts the short time CSP and CI-CSP autocorrelation functions, compared to exact and TDSCF results. First, we note that there is qualitative agreement among all four approaches indicating that mean-field methods represent a reasonable approximation even though there is no significant separation in mode frequencies in this system. The excellent agreement between CSP and TDSCF demonstrates that only minor errors are introduced by replacing the quantum mean-field integrals by averages over classical trajectories. Finally, inclusion of two-mode correlations significantly improves the autocorrelation funcion and brings it closer to the exact one.

For $I_2(Ar)_{17}$, an extensive CI-CSP simulation was carried out,[48] and the results were compared with those of the simple CSP approximation.[46] Both calculations are for the ultrafast dynamics following excitation of the I_2 into the B state. We found that the CI-CSP calculation, including "doubly excited configurations", is close to converged for times up to $t \sim 500$ fs, when 1500 configurations are included. Fig. 2 shows $|c_o(t)|^2$, the coefficient of the CSP term and the doubly excited terms $|d_{j\alpha j'\beta}|^2$ in the full CI-CSP wavefunction, versus time.

It turns out that the CSP approximation dominates the full wavefunction, and is therefore almost exact till $t \approx 80$ fs. This timescale is already very useful: The first ≈ 20 fs are sufficient to determine the photoadsorption lineshape and, as turns out, the first ≈ 80 fs are sufficient to determine the Resonance Raman spectrum of the system. Simple CSP is almost exact for these properties. As Fig. 3 shows, for later times the accuracy of the CSP decays quickly: for $t \approx 500$ fs in this system, the contribution of the CSP approximation to the full CI wavefunction is almost negligible. In addition, this wavefunction is dominated not by a few specific terms of the CI expansion, but by a whole host of configurations. The "decay" of the CSP approximation was found to be due to "hard collisions" between the iodine atoms and the "surrounding wall" of argons. Already the first hard collision brings a major deterioration of the CSP approximation, but also the role of the second collision can be clearly identified. As was mentioned, for $t < 80$ fs, the CSP

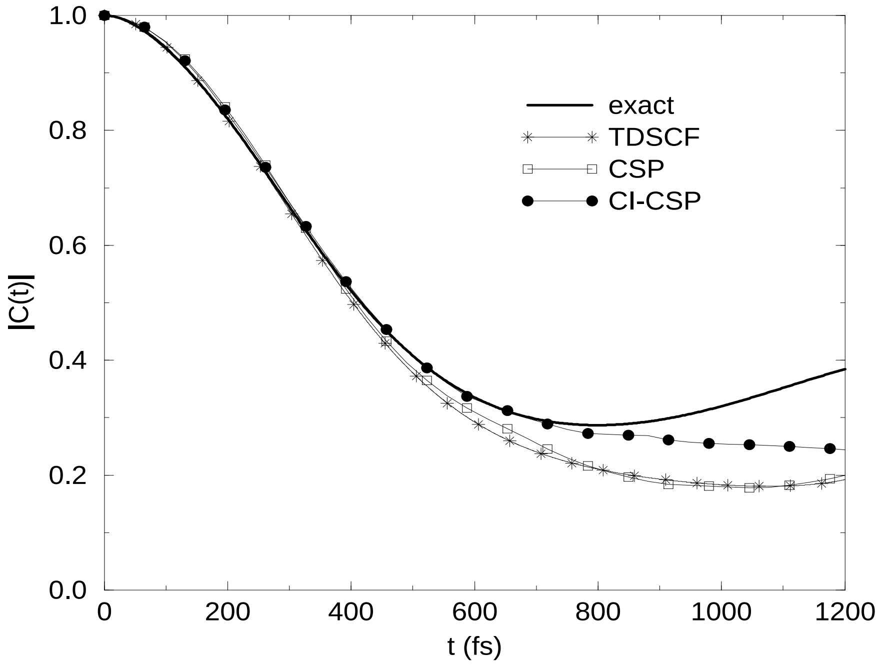

Fig. 1. Comparison between the CID-CSP, CSP, TDSCF, and the numerically exact autocorrelation functions.

is essentially of quantitative accuracy. Fig. 3 shows the Resonance Raman spectrum for $I_2(Ar)_{17}$.[46]

The intensities are plotted vs. v, the final vibrational quantum number of the transition. The CSP results (which for this property are almost identical with CI-CSP) are compared with experimental results for I_2 in a low-temperature Ar matrix.[82] The agreement is excellent. Also shown is the comparison with gas-phase, isolated I_2. The "solvent effect" on the Raman intensities is clearly very large and qualitative. These show that CSP calculations for short timescales can be extremely useful, although for later times the method breaks down, and CI-CSP should be used.

5 Concluding Remarks

Two methods for time-dependent quantum simulations of many-atom systems are examined in this article: the CSP-based and the CI-CSP-based algorithms. The CSP method begins with a separable approximation for

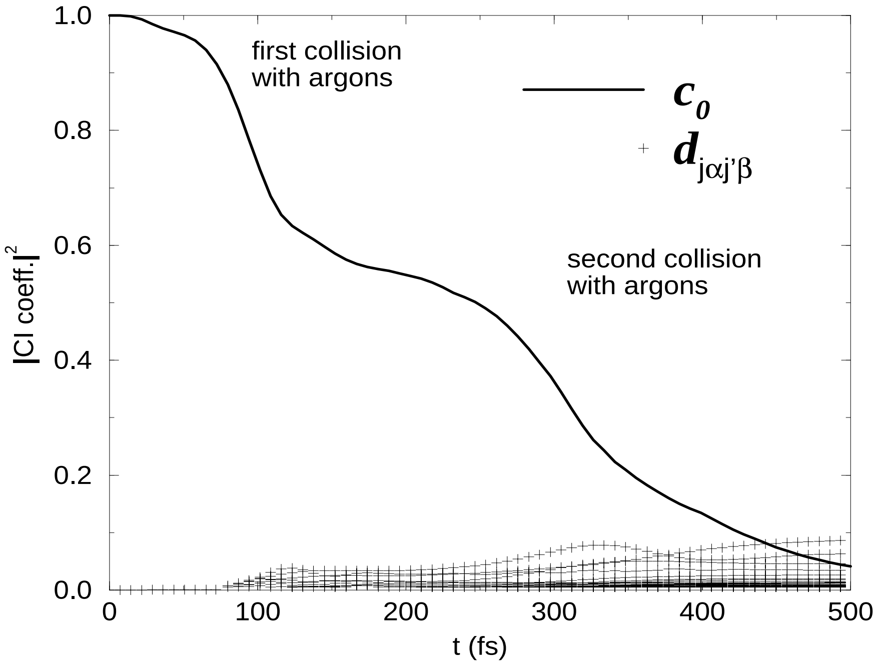

Fig. 2. The contribution c_o of the CSP approximation to the CI wavefunction and the correlation coefficients d $_{j\alpha j'\beta}$ versus time.

the wavefunction, and describes each mode as governed by a mean time-dependent potential due to the other modes, the effective potentials being determined from classical MD simulations. Correlations are included within the CI-CSP approach by expanding the total wavepacket into a sum of separable terms. Classical MD calculation assist in the selection of important terms and in the evaluation of CI coupling terms. Both methods can and have already been applied to systems of substantial sizes, and are thus already practical simulation tools. Applications of CSP and CI-CSP to systems having of the order of $\sim$ 100 degrees of freedom are already at hand, and CSP calculations for biomolecules of 10^4 degrees of freedom are in advanced stages of progress. Clearly, the introduction of correlation effects between modes is computationally the most demanding aspect of the approach. In our belief, a search for simplified methods for correlation corrections should be one of the most useful directions to be followed in the future. An efficient treatment of important correlation effects will benefit in particular processes involving, e.g., chemical (substitution) reactions and nonadiabatic processes, in which

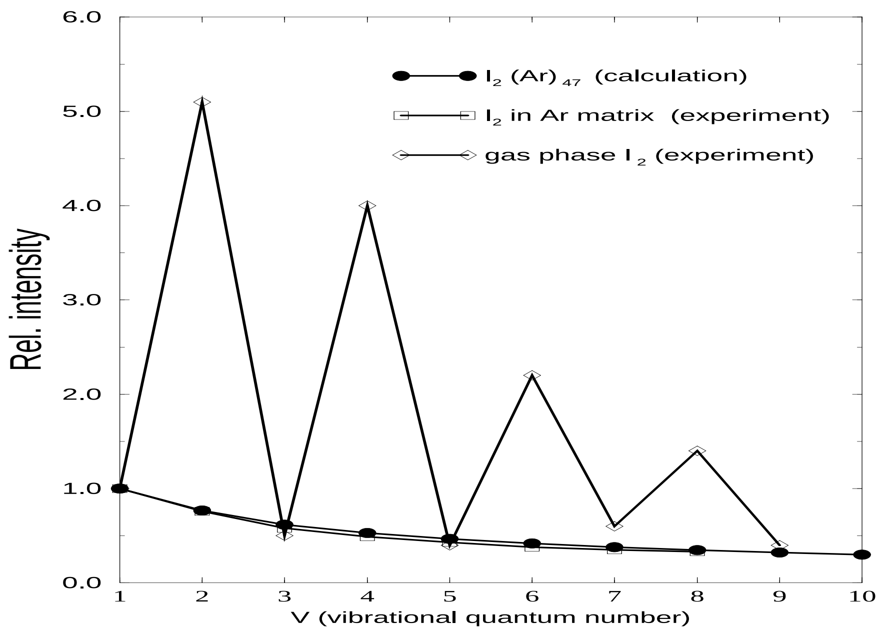

Fig. 3. Resonance Raman Intensities for I_2 $(Ar)_{47}$

the role of dynamical correlations is both extremely important and hard to handle computationally.

The computational efficiency is a major advantage of CSP and CI-CSP, and we expect that in the forthcoming few years CSP-based methods will be extensively used as practical tools for the study of an increased range of dynamical processes in large systems.

Acknowledgement

We thank Dr. B. Schmidt, E. Fredj, Prof. M. A. Ratner, and Dr. A. Marks for helpful discussions and suggestions. The research described here was supported by the Chemistry Division of the NSF (grant CHE-9503258 to R.B.G.) and by the Granting Agency of the Academy of Sciences of the Czech Republic (grant A4040706 to P.J.).

6 References

1. G.C. Schatz, *J. Phys. Chem.* **100**, 12839 (1996).

2. R. Kosloff, *Ann. Rev. Phys. Chem.* **45**, 145 (1994).

3. J.Z.H. Zang and W.H. Miller, *J. Chem. Phys.* **92**, 1811 (1990).

4. U. Manthe, T. Seideman and W.H. Miller, *J. Chem. Phys.* **92**, 10078 (1990).

5. D. Neuhauser, *J. Chem. Phys.* **9272** (1994).

6. U. Peskin and N. Moiseyev, *J. Chem. Phys.* **99**, 4590 (1993).

7. D.J. Kouri, Y. Houng, W. Zhu and D.K. Hoffman, *J. Chem. Phys.* **100**, 3362 (1994).

8. D.H. Zang and J.Z.K. Zang, *J. Chem. Phys.* **100**, 2679 (1994).

9. R. Schinke, *Photodissociation Dynamics* (Cambridge University Press, Cambridge, 1993).

10. W.H. Miller, *Adv. Chem. Phys.* **30**, 77 (1975).

11. E.J. Heller, *J. Chem. Phys.* **94**, 2723 (1994).

12. B.W. Spath and W.H. Miller, *J. Chem. Phys.* **104**, 95 (1996).

13. J.G. Kay and W.H. Miller, *J. Chem. Phys.* **104**, 95 (1996).

14. G.C. Schatz and M.A. Ratner, *Quantum Mechanics in Chemistry* (Prentice Hall, New Jersey, 1993).

15. J.B. Anderson, *J. Chem. Phys.* **63**, 1499 (1975).

16. M.A. Suhm and R.O. Watts, *Phys. Rep.* **204**, 293 (1991).

17. M.A. McMahan, R.N. Barnet and K.B. Whaley, *J. Chem. Phys.* **99**, 8816 (1993).

18. S. Broude and R.B. Gerber, *Chem. Phys. Lett.* **258**, 416 (1996).

19. D. Scharf, G.J. Martyna and M.L. Klein, *J. Chem. Phys.* **99**, 8997 (1993).

20. V. Buch, *J. Chem. Phys.* **100**, 7610 (1994).

21. D. Scharf, G.J. Martyna, D. Li, G.A. Voth and M.L. Klein, *J. Chem. Phys.* **99**, 9013 (1993).

22. J.M. Bowman, *Acc. Chem. Res.* **19**, 202 (1986).

23. R.B. Gerber and M.A. Ratner, *Adv. Chem. Phys.* **70**, 97 (1988).

24. A.E. Roitberg, R.B. Gerber, R. Elber and M.A. Ratner, *Science* **268**, 1319 (1995).

25. N. Makri, *Chem. Phys. Lett.* **193**, 435 (1992).25. N. Makri, *Chem. Phys. Lett.* **193**, 435 (1992).

26. M. Topaler and N. Makri, *Chem. Phys. Lett.* **210**, 285 (1993).

27. J. Cao and G.A. Voth, *J. Chem. Phys.* **100**, 5106 (1994).

28. J. Cao and G.A. Voth, *J. Chem. Phys.* **101**, 6168 (1994).

29. P.A.M. Dirac, *Proc. Camb. Phil. Soc.* **26**, 376 (1930).

30. E.J. Heller, *J. Chem. Phys.* **64**, 63 (1976).

31. R.B. Gerber, V. Buch and M.A. Ratner, *J. Chem. Phys.* **77**, 3022 (1982).

32. Z. Li and R.B. Gerber, *J. Chem. Phys.* **99**, 8637 (1993).

33. E. Fredj, R.B. Gerber and M.A. Ratner, *J. Chem. Phys.* **105**, 1121 (1996).

34. N. Makri and W.H. Miller, *J. Chem. Phys.* **87**, 5781 (1987).

35. H.-D. Meyer, U. Manthe and L.S. Cederbaum, *Chem. Phys. Lett.* **165**, 73 (1990).

36. U. Manthe, H.-D. Mayer and L.S. Cederbaum, *J. Chem. Phys.* **97**, 3199 (1992).

37. G.A. Worth, H.-D. Mayer and L.S. Cederbaum, *J. Chem. Phys.* (in press).

38. J.-Y. Fang and H. Guo, *J. Chem. Phys.* **101**, 5831 (1994).

39. J.-Y. Fang and H. Guo, *J. Chem. Phys.* **102**, 2404 (1995).

40. Z. Kotler, E. Neria and A. Nitzan, *Comput. Phys. Commun.* **63**, 243 (1991).

41. J. Campos-Martinez and R.D. Coalson, *J. Chem. Phys.* **93**, 4740 (1990).

42. A.D. Hammerich, R. Kosloff and M.A. Ranter, *Chem. Phys. Lett.* **171**, 97 (1990).

43. P. Jungwirth and R.B. Gerber, *J. Chem. Phys.* **102**, 6046 (1995).

44. P. Jungwirth and R.B. Gerber, *J. Chem. Phys.* **102**, 8855 (1995).

45. P. Jungwirth and R.B. Gerber, *J. Chem. Phys.* **104**, 5803 (1996).

46. P. Jungwirth, E. Fredj and R.B. Gerber, *J. Chem. Phys.* **104**, 9932 (1996).

47. P. Jungwirth, E. Fredj, P. Zdanska and R.B. Gerber, *Computers&Chemistry* **21**, 419 (1997).

48. P. Jungwirth, E. Fredj and R.B. Gerber, *J. Chem. Phys.* **107**, 8963 (1997).

49. D.J. Thouless, *The Quantum Mechanics of Many-Body Systems* (Academic Press, New York, 1961) pp. 88-93.

50. P. Bonche, S.E. Koonin and J.W. Negele, *Phys. Rev.* **C13**, 1226 (1976).

51. S. Lent, *Phys. Rev.* **C21**, 1594 (1980).

52. J.W. Negele, *Physics Today* **38**, 24 (1985).

53. K. Goeke and P.-G. Reinhard, *Time-Dependent Hartree-Fock and Beyond*, Lecture Notes in Physics, Vol. 171 (Springer-Verlag, Berlin, 1982).

54. V. Buch, M.A. Ratner and R.B. Gerber, *Chem. Phys. Lett.* **101**, 44 (1983).

55. R.B. Gerber, R. Kosloff and M. Berman, *Comput. Phys. Reports* **5**, 59 (1986).

56. M.D. Feit, J.A. Fleck and A. Steiger, *J. Comp. Phys.* **47**, 412 (1982).

57. U. Peskin, R. Kosloff and N. Moiseyev, *J. Chem. Phys.* **99**, 4590 (1993).

58. T.R. Horn, R.B. Gerber and M.A. Ratner, *J. Chem. Phys.* **91**, 1813 (1989).

59. T.R. Horn, R.B. Gerber, J.J. Valentini and M.A. Ratner, *J. Chem. Phys.* **94**, 6728 (1991).

60. R.H. Bisseling, R. Kosloff, R.B. Gerber, M.A. Ratner, L. Gibson and C. Cerjan, *J. Chem. Phys.* **87**, 2760 (1987).

61. A. Garcia-Vela, *J. Chem. Phys.* **104**, 1047 (1996).

62. R. Alimi, R.B. Gerber, A.D. Hammerich, R. Kosloff and M.A. Ratner, *J. Chem. Phys.* **93**, 6484 (1990).

63. A. Garcia-Vela and R.B. Gerber, *J. Chem. Phys.* **103**, 3463 (1995).

64. A.B. McCoy, R.B. Gerber and M.A. Ratner, *J. Chem. Phys.* **101**, 1975 (1994).

65. A.B. McCoy, *Mol. Phys.* **85**, 965 (1995).

66. Z. Li and R.B. Gerber, *Chem. Phys. Lett.* **104**, 5803 (1996).

67. J.O. Jung and R.B. Gerber, *J. Chem. Phys.* (in press).

68. A.Y. Rom and R.B. Gerber, *J. Chem. Phys.* (submitted).

69. A. Jäckle and H.-D. Meyer, *J. Chem. Phys.* **104**, 7974 (1996).

70. A. Jäckle and H.-D. Meyer, *J. Chem. Phys.* **102**, 5605 (1995).

71. G.D. Billing and G. Jolicard, *Chem. Phys. Lett.* **221**, 75 (1994).

72. J.R. Waldeck, J. Campos-Martinez and R.D. Coalson, *J. Chem. Phys.* **94**, 2773 (1991).

73. N.P. Blake and H. Metiu, in *Femtosecond Chemistry*, ed. J. Manz and L. Wöste (VCH, Weinheim, 1995) p. 532.

74. J. Kucar, H.-D. Meyer and L.S. Cederbaum, *Chem. Phys. Lett.* **140**, 525 (1987).

75. R.B. Gerber and A. Alimi, *Chem. Phys. Lett.* **184**, 69 (1991).

76. J. Campos-Martinez and R.D. Coalson, *J. Chem. Phys.* **99**, 9629 (1993).

77. E. Fredj, R.B. Gerber and M.A. Ratner (to be published).

78. E.J. Heller, *J. Chem. Phys.* **62**, 1544 (1975).

79. M.P. Allen and D.J. Tildesley, *Computer Simulation of Liquids*, (Clarendon, Oxford, 1987).

80. R. McWeeny, *Methods of Molecular Quantum Mechanics*, 2nd edition (Academic Press, San Diego, 1992).

81. A.I. Krylov, R.B. Gerber, M.A. Gaveau, J.M. Mestdagh, B. Schilling and J.P. Visticot, *J. Chem. Phys.* **104**, 3651 (1996).

82. J.F. Grzykowski and L. Andrews, *J. Raman Spectros.* **4**, 99 (1975).

83. P. Jungwirth and B. Schmidt, *Chem. Phys. Lett.*, 275 (1997) 127.

83. R. B. Gerber, P. Jungwirth, E. Fredj, and A. Y. Rom *Modern methods for multidimensional dynamics computations in chemistry*, ed. D. L. Thompson (World Scientific, River Edge, NJ, 1998).