Photochemistry from first principles — advances and future prospects

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Abstract

Detailed simulation of photochemistry poses considerable challenges because quantum mechanical effects are important in determining both the electronic potential energy surfaces and the subsequent nuclear dynamics. We provide a brief overview of the ab initio multiple spawning (AIMS) method which addresses the problem by solving both the electronic and nuclear Schrödinger equations simultaneously. We discuss our recent AIMS simulations of *cis–trans* photoisoimerization in ethylene as an example application. The prospects of the method for modeling of photochemistry in large organic molecules and condensed phases are assessed. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

The previous presentations in this workshop [1–3] have focused on the importance of conical intersections in photodynamics and means of locating these special points on the potential energy surface. The realization that conical intersections could exist and that these could be important in photochemistry was made already in the 1930s [4]. However, it was generally believed that these points were pathological and would tend to occur only at very high energies, far above the Franck–Condon point on S_1. The demonstration that energetically accessible intersections are commonly occurring [5] has led to the recasting of our theoretical pictures of photodynamics in terms of pathways leading from the Franck–Condon region to an intersection, with possible barriers on the way. In this context, it is very tempting to postulate that the important information can be obtained in the spirit of transition state theory, just by knowing the relative energetics of a few distinguished points along these pathways (the Franck–Condon point, conical intersections and barriers separating these). In such a cartoon, one would assume ultrafast and ultraefficient decay when a conical intersection is encountered. The pathway approach of Fuss et al. builds on these ideas [6].

However, there are a few stumbling blocks. Firstly, the time scale for photodynamics is often found to be very short, in the realm of femtoseconds [7–9]. This is far too fast to jus-

tify the high-friction viewpoint which would guarantee the perfect funneling at an intersection implied by the naïve picture. If the details of the distribution of vibrational energy are important, it will be possible to skirt a conical intersection, leading to decay probabilities which may deviate significantly from unity. Secondly, the prediction of which products arise from decay through a given intersection is not straightforward. As Haas has pointed out, any conical intersection necessarily connects at least three basins, i.e. possible products, on S_0 [2]. Determining the partitioning between these products requires detailed knowledge of the way in which the molecules approach the conical intersection. Again, the distribution of the vibrational energy is critical. The conclusion from these observations is that a complete theoretical picture of photochemistry must address both the conical intersection geometries and also the way in which these intersections are accessed, i.e. the detailed molecular dynamics. Previous work addressing such dynamical considerations has generally focused on highly accurate solution of the nuclear Schrödinger equation [10–12]. While these studies have been very instructive, the use of nearly-exact quantum dynamics has restricted them to reduced dimensionality and model (often harmonic) potential energy surfaces. A notable recent study removes the reduced dimensionality approximation to study nonadiabatic effects on the electronic absorption spectrum of pyrazine [13]. In this contribution, we summarize our progress in developing a theory that encompasses both of these areas, using an approximate quantum dynamical method which was developed to avoid reduced dimensionality approximations and

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also to maintain compatibility with on-the-fly solution of the potential energy surfaces and their couplings using ab initio quantum chemistry. We aim to persuade the reader that our approach is already applicable to paradigmatic gas-phase organic photochemistry and we will point out the directions that we are pursuing to go beyond this to larger molecules and condensed phases.

2. Ab initio multiple spawning (AIMS) photodynamics

Photochemical reactions often give rise to many products, some with unexpected bond rearrangements. For example, irradiation of gas-phase butadiene leads to double bond isomerization, bicyclo[1·1·0]butane, cyclobutene, and 1-methylcyclopropene [14,15]. Describing such extensive bond rearrangement demands extreme flexibility in the potential energy surfaces, which is typically difficult to achieve using parameterized functional forms. Hence, one would like to generate the potential energy surfaces by direct solution of the electronic Schrödinger equation, in the spirit of the Car–Parrinello method [16] and earlier direct dynamics approaches [17]. At the same time, one must recognize that the nuclear dynamics is intrinsically quantum mechanical. Since more than one electronic state is involved, classical mechanics is not strictly applicable. This leads to an apparent paradox — while quantum chemistry can provide energies and gradients at a single nuclear configuration, quantum dynamics requires global knowledge of the potential energy surfaces at each time step. We have reconciled these considerations through the development of the multiple spawning method for quantum dynamics [18–22]. This method is designed to be compatible with direct solution of the electronic Schrödinger equation by building the nuclear wavefunction from a set of semi-local nuclear basis functions, complex frozen Gaussians [23]. A schematic description is provided

in Fig. 1, which shows a simplified picture of the dynamics that results when a molecule encounters a conical intersection. The individual basis functions move according to classical mechanics, but each also carries a complex prefactor whose evolution is determined by the nuclear Schrödinger equation. In this way, the correct branching ratios between different possible outcomes can be determined. Notice that the individual basis functions differ from classical trajectories in that they obey Heisenberg's uncertainty principle but are otherwise quite localized. Every time the conical intersection is approached, new basis functions are created (i.e. spawned) and the amplitudes corresponding to these are determined by solving the nuclear Schrödinger equation. The width and shape of the nuclear basis functions is not allowed to vary in time, and any changes in the shape of the nuclear wavefunction must come from the complex coefficients that are determined variationally. Detailed equations and information about the numerical implementation are available in our past publications [18–22] and we focus only on the conceptual framework here. While Fig. 1 is restricted to a two-dimensional representation of the nuclear dynamics, we emphasize that the calculations are carried out in the full dimensionality of the molecule degrees of freedom all vibrational and are included.

When the multiple spawning method for quantum dynamics is combined with direct solution of the electronic Schrödinger equation, we refer to the method as ab initio multiple spawning or AIMS. Because of the great difficulty in computing reasonable approximations to excited state potential energy surfaces, the bottleneck in AIMS dynamics generally lies in the quantum chemistry, solving the electronic part of the problem. Given current computational resources, this limits the AIMS method to molecules with fewer than 20 atoms. While this is not as large as one might like, it certainly lies in the realm where fundamental paradigms in gas-phase organic photochemistry can be
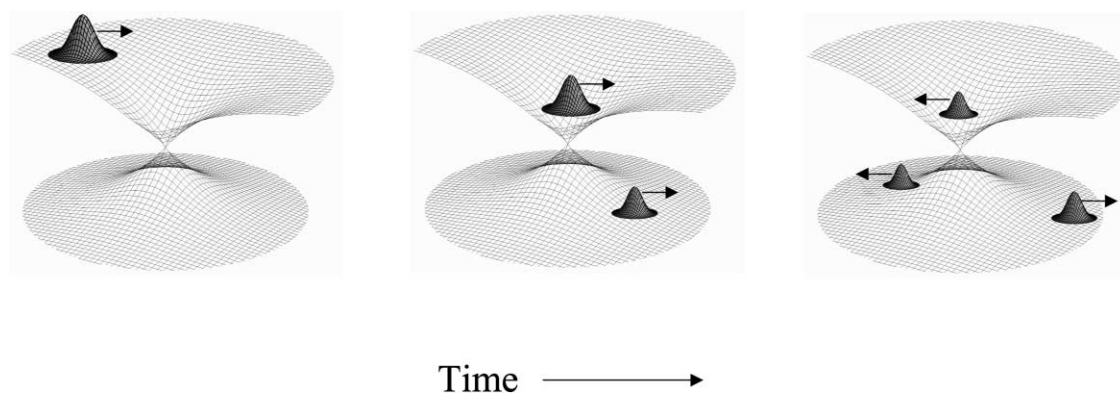

Fig. 1. Cartoon diagram demonstrating the basic principles of the multiple spawning method for dynamics around a conical intersection. The three panels represent the nuclear probability density at three successive points in time. Initially (left panel), the wavepacket describing the molecule moves toward the conical intersection. For simplicity, we only show a single nuclear basis function representing the wavepacket. On the first encounter with the conical intersection (middle panel), new basis functions are spawned (created) to represent the electronic quenching. The nuclear Schrödinger equation is solved to determine the relative populations of the old and new basis functions (represented schematically by the heights of the various wavepackets). The portion of the nuclear wavepacket that remains on the excited state may rattle around, spawning more basis functions (right panel).

explored. For example, we have investigated the photoisomerization and photofragmentation of ethylene, [22,24] a prototype for *cis–trans* isomerization of unsaturated hydrocarbons, and the ring-opening of cyclobutene, [25] a prototype for photochemically-allowed Woodward–Hoffmann reactions. Using ethylene as an example, we illustrate the type of information that can be obtained from the AIMS method.

3. AIMS simulation of ethylene photodynamics

The photochemistry of ethylene is interesting as a paradigm for photoinduced *cis–trans* isomerization in unsaturated hydrocarbons. However, some special features should be expected. The combination of large excitation energy and small number of vibrational modes implies that fragmentation as well as isomerization will be observed. Indeed, photoexcitation of ethylene in the gas-phase leads to acetylene, and atomic and molecular hydrogen [26]. The simplest possible mechanism for photoinduced isomerization identifies torsion about the C=C double bond as the reaction coordinate and focuses on the π^2 and $\pi \rightarrow \pi^*$ electronic states. Computation of the S_0 and S_1 potential energy surfaces along this coordinate shows that this view is considerably oversimplified (regardless of the detailed way in which the bond stretch and angle coordinates are allowed to vary). In particular, the minimal S_0–S_1 energy gap that results is approximately 60 kcal/mol, implying a long excited state lifetime and significant fluorescence. Yet there is no detectable fluorescence from photoexcited ethylene.

Briefly, our AIMS simulations have used multi-reference configuration interaction (MRCI) electronic wavefunctions within a double zeta basis set. We do not include Rydberg basis functions and hence the Rydberg states of ethylene will not be discussed in the following. Thus, we will use the labels S_1 and $\pi \rightarrow \pi^*$ interchangeably even though we realize that a more accurate treatment would show that the S_1 state of ethylene is of Rydberg $\pi \rightarrow 3s$ character ([27] and references therein). The nuclear dynamics is followed for 0.5 picoseconds, and the total dynamics is represented by averaging over results obtained using 10 different representations of the initial wavefunction. Overall, approximately 100 nuclear basis functions are spawned during the simulation time. A more complete description of the technical details is available in our previous reports on the subject [22,24].

The first dynamical question to ask concerns the excited state lifetime. In Fig. 2, we show the AIMS results for the population on S_1 as a function of time following photoexcitation of the gas-phase molecule at $t = 0$. The solid line depicts the theoretically predicted result and the lighter dashed lines are the outcome for each of the 10 different initial conditions. The results shown in Fig. 2 have been used to compare with the recent ultrafast pump-probe experiment of Radloff and coworkers [28]. The observed excited state lifetime extracted from these simulations (35 ± 2 fs) agrees
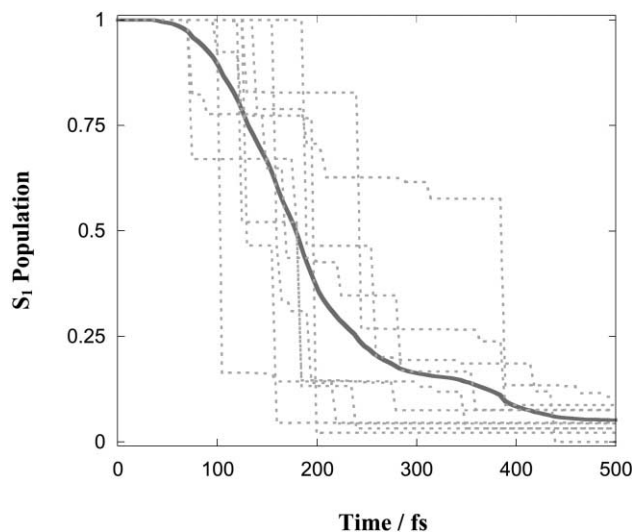

Fig. 2. Excited state population in ethylene as a function of time. The solid line denotes the theoretically predicted result, obtained by averaging over different representations of the initial state. The dashed lines denote the traces of S_1 population for each of the different initial conditions. Notice the short lifetime and the non-exponential decay.

well with the experimental [22] one (30 ± 15 fs). Notice that the population transfer for each of the localized initial conditions occurs very quickly, but one can see that it is continuous if the time axis is greatly expanded (not shown). Such ultrafast decay is the signature expected when accessing a conical intersection. However, notice that the decay is not perfectly efficient, the height of the steps in the light dashed lines of Fig. 2 varies considerably. This is a reflection of the influence of dynamics — the nuclear wavepacket has a finite width and is of greater dimensionality than the conical intersection. Hence, only a portion of the wavepacket actually traverses the intersection. Furthermore, the way in which the intersection is accessed influences the nonadiabatic coupling experienced by the wavepacket, and thus the decay probability.

The early dynamics of the ethylene molecule on S_1 is best described as follows, first the C–C bond stretches, then the molecule begins to twist about the C–C bond, and subsequently one of the methylene units pyramidalizes (indicating a hybridization change about one of the carbon atoms from sp^2 to sp^3.) In Fig. 3, we show a schematic of the wavepacket dynamics emphasizing the torsion and pyramidalization coordinates. Notice that the global minimum on S_1 is not at a twisted D_{2d} geometry, but rather at a twisted, mono-pyramidalized geometry. That pyramidalization of one of the methylene units is energetically favorable after $\pi \rightarrow \pi^*$ excitation was first noticed by Salem and coworkers, [29,30] who emphasized the sudden polarization which would ensue. By symmetry, the planar and twisted forms of ethylene have no dipole moment, but a significant dipole moment is generated when one of the methylene units pyramidalizes. The original speculation that the electrical
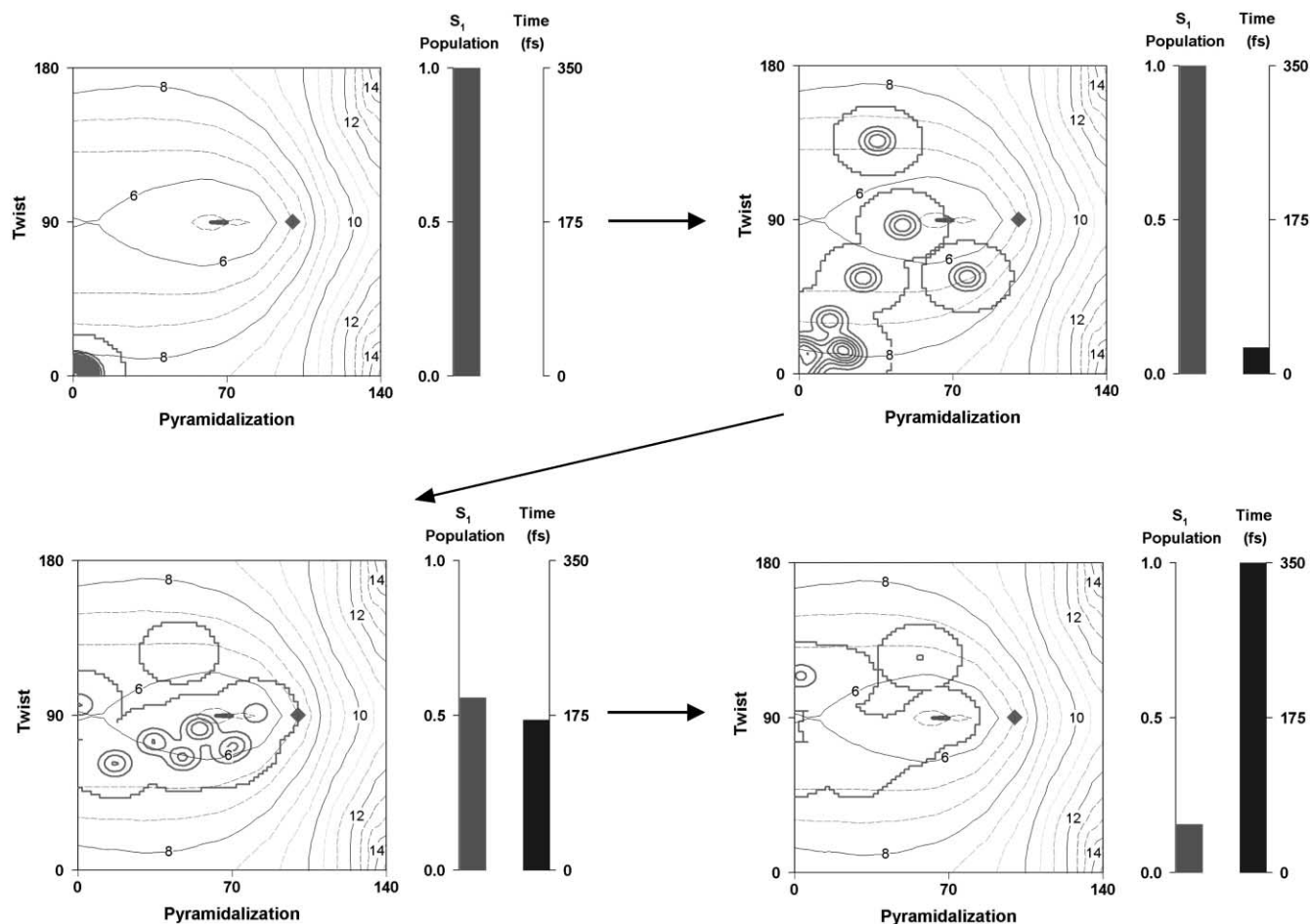
Fig. 3. Schematic description of nuclear wavepacket dynamics for photoexcited ethylene, superimposed on a contour plot of the S_1 electronic state potential energy surface (contours are in eV relative to the ground state minimum). The location of the conical intersection is denoted with a diamond. In order to clearly show how the nuclear wavepacket is constructed as a sum of Gaussian basis functions, arbitrary widths are used for the nuclear basis functions (the basis functions in the calculation are Gaussians expressed in Cartesian coordinates). The initially excited molecule is clearly planar (upper left panel), but quickly begins to twist and pyramidalize (upper right panel). By the time half of the population has quenched to S_0 and thereafter, the wavepacket spends most of its time twisted with varying degrees of pyramidalization (lower panels).

signal thus generated might trigger conformational change in the visual pigment proteins [29] was abandoned when it was shown that proton transfer was required for vision [31]. Irrespective of its importance in the retinal protonated Schiff base chromophore of the visual pigments and in spite of the crude electronic structure treatment which originally led to the observation, pyramidalization is an important part of ethylene dynamics on the S_1 state. Most importantly, pyramidalization is not only energetically favorable, but it leads directly to a conical intersection (the diamond on the excited state potential energy surface contour plots in Fig. 3). In fact, it is not even clear that there exists a true global minimum on S_1 — most of our calculations predict that the conical intersection is the lowest energy point [22,24,27].

These features are emphasized in Fig. 4, where we show the S_0 and S_1 potential energy surfaces as a function of twist and pyramidalization. This surface is computed using the CASPT2 method, which is one of the most reliable methods available for excited electronic states. Comparison with

similar plots using other electronic structure methods shows that the features we emphasize are not strongly dependent on either the detailed treatment of electron correlation or the flexibility of the electronic basis set [24,27].

One of the advantages of AIMS is the ability to describe bond rearrangement without any special treatment. In Fig. 5, we show a sample of the kinds of reactive events that we observe in the simulations. In both panels we show the time-evolution of individual (frozen Gaussian) basis functions that are used to construct the time-dependent basis set. We emphasize that the time-evolution of individual basis functions should not be confused with time-dependent position expectation values, these are equivalent only when the basis function shown has unit weight. Expectation values of position or any other observable can be evaluated using the AIMS wave function and the appropriate operator. The right and left panels correspond to the same initial conditions, and this is a representative example in that one usually sees more than one reactive outcome from a particular set of
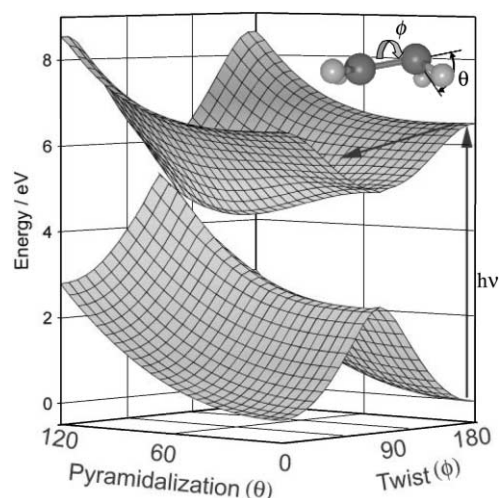
Fig. 4. Ground and first excited potential energy surfaces for ethylene, plotted in the coordinates that are most important as judged by the dynamics simulations. The remaining internal coordinates are fixed, with the C–C bond elongated slightly compared to the planar ground state equilibrium geometry. These surfaces are obtained from a CASPT2 treatment of electron correlation with a 6-31G* basis set. The global minimum on S_1 is at a twisted and pyramidalized geometry, and is nearly coincident with a conical intersection.

acetylene formation within our simulation time window of 0.5 ps. This is not unexpected since there are significant barriers to be overcome from any of the transient products that we do observe, vinyl radical, ethylidene, and vinylidene. For example, CCSD(T) calculations [32] and kinetics experiments [33] agree on a barrier of 1.66 eV for decomposition of vinyl radical to acetylene and atomic H. The barrier heights for the decomposition of ethylidene and vinylidene are calculated [32,34,35] to be in the ranges 1.46–1.52 and 0.06–0.13 eV, respectively. Notice that the bond rearrangement occurs on the ground state, this is what we typically find for ethylene, although we have also observed occasional bond rearrangment on S_1. There are experimental results available for H_2 product internal and translational energy distributions, as well as the branching between atomic and molecular hydrogen products [36–39]. Comparison to these experiments will require either longer simulation times or the use of statistical assumptions to extrapolate from $t = 0.5$ ps to ∞ results.

4. Conclusions and future prospects

In summary, the AIMS method provides a powerful new means of elucidating photochemical mechanism. We have demonstrated that it is feasible for gas-phase photochemistry of small organic molecules and we have also shown that it is quantitatively accurate for certain cases where ultrafast experiments are available for comparison [22]. There remain clear avenues for improvement that we are pursuing. These are naturally presented under two headings, improvements in the quantum mechanical nuclear dynamics, i.e. the multiple spawning method, and improvements in the quantum chemistry, i.e. the solution of the electronic Schrödinger equation to generate potential energy surfaces and their couplings. It is important to realize that any improvements made

initial conditions. In each case, the time trace of the C–H bond distances (all coordinates are included in the simulation, although we only show a subset here) begins when the depicted basis function is spawned from the excited state, and both originate from the same family of conical intersections (there are many different types of intersections in ethylene [27], as classified by the electronic states involved and the qualitative geometrical parameters). In both panels, the final products shown are expected to further decompose to acetylene. However, this decomposition occurs on a longer time scale and we have only rarely observed
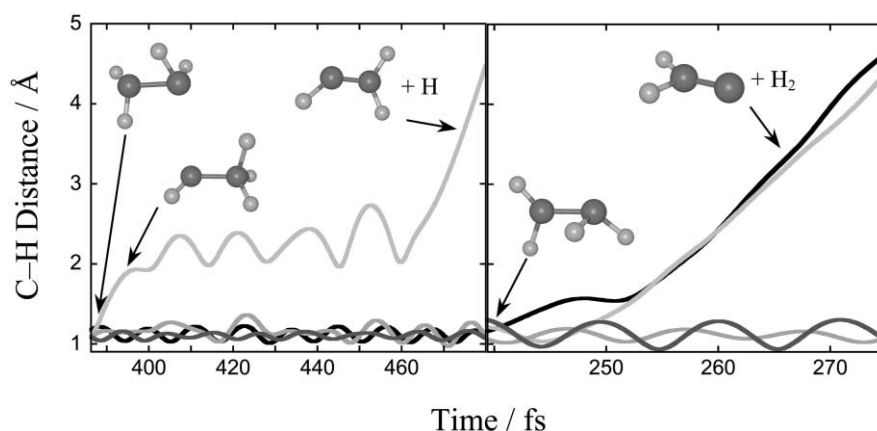

Fig. 5. Sample reactive outcomes of ethylene photochemistry. Left and right panels represent different basis functions originating from the same initial conditions, with final populations of 15 and 56%, respectively. Traces denote the C–H bond lengths as a function of time for one of the nuclear basis functions evolving on the ground state, after quenching through the twisted/pyramidalized conical intersection. The left panel shows a case which forms vinyl radical and atomic hydrogen and the right panel shows a case where H_2 is eliminated in concerted fashion to give vinylidene. Both of these products are expected to be transient, ultimately decomposing to acetylene.

under one heading must always take into account the other. Thus, one can expect a further blurring of the dividing line between dynamics and electronic structure in the future. We mention just a few of the avenues that we are exploring.

In the context of the nuclear dynamics, it remains to characterize the performance of multiple spawning dynamics in large molecules. How fast does the method converge? To some extent, this clearly depends on the questions that are being asked. With respect to the broad outlines of photochemical mechanism, convergence seems to be quite rapid. However, this becomes less clear as one demands more detailed mechanistic information and/or as the molecules being studied become larger. We have shown that multiple spawning dynamics (using parameterized force fields to describe the ground and excited potential energy surfaces) is feasible for protein molecules with more than 3000 atoms [40]. Although these calculations are useful and provide insight into protein function, one certainly cannot claim that they are completely converged. As a further example, we do not yet know whether we can correctly predict the precise branching ratio between atomic and molecular hydrogen in the photofragmentation of ethylene. In general, questions of branching ratios in products will involve relatively long time dynamics, greater than 1 ps, with correspondingly greater demands on the method used to represent the quantum mechanical features of the dynamics. Although we have shown that electronic absorption and resonance Raman spectra may be computed with the AIMS method, [41] these are clearly applications that demand the use of many nuclear basis functions — the detailed phase interference effects must be treated correctly over the time scale which determines the spectrum. New ways of increasing the size of the nuclear basis set without significantly increasing the number of potential energy surface evaluations [42] will be critical in efforts to answer these questions about the accuracy of the underlying dynamical approximations. We have also expanded multiple spawning dynamics to treat tunneling effects explicitly, [43] as may be important in photoinduced excited state proton transfer reactions.

From the vantage point of quantum chemistry, there are two major problems. Firstly, how can the AIMS method be extended to gas-phase photochemistry of larger molecules, such as stilbene and $Fe(CO)_5$? Secondly, how can the AIMS method be extended beyond the gas-phase to encompass photoactive proteins and solution phase photochemistry? We believe that excited state density functional theory methods [44–46] provide an attractive possible avenue with regards to the first question, but we have also shown that current implementations do not provide the global accuracy that is required to answer mechanistic photochemical questions, at least for ethylene [22]. Another avenue includes hybrid strategies which use empirical potential energy functions for parts of the potential energy surface, for example, near known previously-characterized reactant and product minima, and reserve direct solution of the electronic structure problem for the part of configuration space which is poorly

described by these empirical forms. This strategy combines potential energy surface interpolation with ab initio molecular dynamics and attempts to avoid the situation where one discards valuable information about the potential energy surface only to recompute it shortly thereafter. Both Thompson and Martínez [47] and others [48,49] have explored this approach, although it has not yet proven generally applicable for large molecules where all vibrational degrees of freedom are included.

In the case of condensed phase photochemistry, it is apparent that a mixed quantum mechanical/molecular mechanics approach, as has often been used for ground state reactions, [50–52] will be advantageous. The primary challenge here lies in extending these approaches to the case of multiple electronic states in the solute, which demands more detailed consideration of the nature of the quantum/classical boundary than has been presented so far. We have shown how an approach which avoids any solute-dependent parameterization can be formulated for the special, but common, case of closed-shell solvents [53]. Extension of this approach to excited state solutes is in progress.

We hope that we have convinced the reader of the impact that the AIMS method can have in its current state of development on such fundamental problems as photoinduced *cis–trans* isomerization. We also hope that the reader shares with us the excitement at what will be possible in the near future, as the AIMS method is expanded to address photobiological problems and condensed phase photochemistry.

Acknowledgements

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