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Review

Overview of theoretical research in France on ultrafast processes in molecules

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Abstract Ultrafast processes initiated in molecules by light or collision are extremely widespread. The intrinsic timescale of nuclear motion is the femtosecond (1 fs $= 10^{-15}$ s) and the one of electrons, lighter particles, is the attosecond (1 as $= 10^{-18}$ s). Dynamics simulations are essential for understanding the mechanism, rate and yield of ultrafast processes. In this article, we review recent theoretical works, performed in France, to describe photon-induced or collision-induced ultrafast processes in molecules. In particular, we discuss recent studies on quantum dynamics of small molecules or Hamiltonian models, and works focused on "on-the-fly" mixed quantum-classical dynamics of molecules. Both state-of-the-art applications and method developments towards overcoming current bottlenecks are presented.

1 Introduction

Two of the most fundamental and widespread processes in chemistry and physics are the absorption of light and the collision with atomic or molecular systems to excite electrons of matter and potentially induce a rearrangement of the nuclei [1]. The intrinsic timescale of nuclear motion is the femtosecond (1 fs $= 10^{-15}$ s) while the intrinsic timescale of the motion of electrons, lighter particles, is the attosecond (1 as $= 10^{-18}$ s). As a result of excitation into an electronic excited state, the distribution of electrons and thus the reactivity of a molecule differ significantly from the ones in the ground state. We distinguish photochemistry, when the absorption of light causes a chemical reaction, from photophysics— otherwise. The most common photon-induced or collision-induced chemical reactions are isomerization, pericyclic reaction, dissociation and electron transfer. Although the applications of these processes cover many fields today, their practical use is limited by the quantum yield of the desired process, the latter almost always competing with other processes. A challenge for chemists is therefore to design more efficient molecular systems and optical control methods. The idea of understanding the behaviour of a molecule upon light absorption or molecular collision has thus motivated, and continues to motivate researchers in the field of physical chemistry.

From the late 1980s, the development of femtosecond lasers has allowed the experimental study of the structure and dynamics of atoms in molecules [2]. By using a light pulse that is shorter than the characteristic time for nuclear motion, it is possible to promote the system in a localised region on an excited electronic potential energy landscape. The subsequent nuclear motion could then be probed as a function of the time delay between pump and probe pulses. In 2001, the "femtosecond barrier" was broken with the first generation of attosecond pulses [3, 4]. This generation relies on the time-energy uncertainty principle: $\Delta E \Delta t \geq \hbar$. By collecting together coherent light sources with a large energy bandwidth ΔE of several eV, one can obtain an ultrashort pulse with duration $\tau \approx \hbar/\Delta E$ of few attoseconds. The emergence of attosecond measurement tools opened up the possibility to experimentally observe and control electrons, on their intrinsic timescale. Attosecond pulses were first applied to atoms [5] and then condensed-matter [6] and polyatomic molecules [7], the latter giving birth to the field of "attochemistry". One could finally investigate changes in the electronic distribution during a chemical reaction, until now considered as instantaneous.

From a theoretical perspective, in order to understand the behaviour of a molecule upon photon- or collision-induced excitation, one needs to evaluate the importance of the different relaxation pathways. Only a dynamic strategy, which simulates the evolution of the molecular wavepacket over time, provides a complete and intuitive image of the electronic states and nuclear structures visited by the system after excitation, and

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of the different relaxation pathways. Describing the time evolution of an electronically-excited molecule implies going beyond the Born-Oppenheimer approximation [8]. Huge advances have been made and different flavours of non-adiabatic dynamics methods have been developed over the last decades to model, from first principles, the chemical properties and dynamics of molecules in their electronic excited states [9, 10].

The scope of the present article is to review and illustrate the recent advances made in France in theoretical chemistry and physics, to describe ultrafast processes in molecules, both in terms of applications and method developments. We chose to limit ourselves to several French theoretical studies published in the last few years, investigating the ultrafast coupled electron-nuclear dynamics in molecules (two atoms or more). In Sect. 2, we present recent studies of quantum dynamics on small molecules or Hamiltonian models. In Sect. 3, works focused on state-of-art "on-the-fly" mixed quantum-classical dynamics are reported. Section 4 concludes this article with a summary of the recent advances and some perspectives for the future of this field.

2 Quantum dynamics of small molecules and model systems

The most accurate quantum nuclear dynamics methods are either grid-based simulations or using the Multi-Configuration Time-Dependent Hartree (MCTDH) method [11]. These imply a fully quantum treatment of the molecular dynamics. As will be seen from the cited examples, grid-based quantum dynamics simulations are often limited to few nuclear coordinates. Using the MCTDH method and extensions of it, one can afford more nuclear coordinates. In the following, we first detail several state-of-the-art applications of such methods. We then present works focused on developments to improve the practical use of these methods.

2.1 From applications...

Using grid-based calculations with the resolvent-operator method [12], Catoire et al. studied the dynamics of the He_2^{2+} diatomic ion induced by a strong IR laser pulse [13]. They investigated in particular the role of electronic excited states in the dissociation dynamics. Cornaggia and co-workers studied nuclear dynamics of H_2 laser-induced double ionization using one-dimensional grid-based simulations [14].

A typical illustration of theoretical work of nuclear quantum dynamics by the same group is the study of molecular reorientation during photo-ionization using a two-dimensional model [15, 16]. Alignment of linear molecules induced by light leads to time-dependent observables. The latter can be analysed in terms of spectral periodic components A_{2l}, with l being a positive integer. Using available calculated ionization yields

of fixed-in-space molecules of CO_2—a symmetric linear molecule, they performed numerical calculations of laser-induced impulsive alignment and tunnel ionization. Figure 1 shows, for $l = 1$ and $l = 2$, four fractional revivals within each rotational period τ_{2l}. The revivals exhibit constant successive phase shifts that depend on the parity of the initial rotational states. This analysis provides an alternative explanation for the so-called high-order revivals.

Using the MCTDH method, Lasorne, Lauvergnat and co-workers studied the ozone photolysis induced by deep ultraviolet radiation [17]. Upon excitation to the B state of ozone by a 10-fs pulse, the quantum dynamics simulations show an early splitting of the wavepacket at an inflection point of the potential energy surface between a path leading to dissociation and an oscillating path revolving around the Franck–Condon region at around 20 fs. As the non-dissociative part of the wavepacket oscillates between the Franck–Condon region and the inflection point, both revivals around the Franck–Condon region and dissociation occur periodically, approximately every 20 fs. The same collaboration also studied the ultrafast internal conversion in 4-aminobenzonitrile upon UV light absorption, from a charge-transfer state to a locally-excited state [18]. Using the multi-layer (ML) version of the MCTDH method, the Hamiltonian model constructed included three diabatic electronic states and all nuclear coordinates, i.e. 39 dimensions. They showed that the relaxation occurs sequentially along an extended seam of conical intersections, with planar geometries dominating at early times ($t < 20$ fs). Using two singlet and four triplet electronic states, and 63 vibrational modes, Huix-Rotllant and co-workers studied the ultrafast intersystem crossing in xanthone [19]. Their ML-MCTDH quantum dynamics simulations provided a sequential mechanism, consistent with the El Sayed's
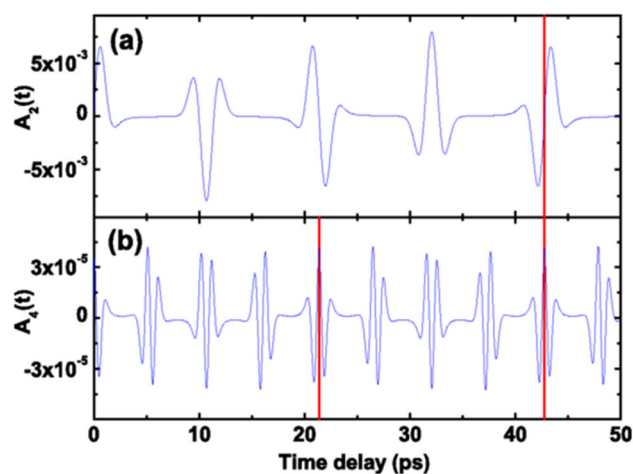

Fig. 1 A_{2l} components of the ion signal CO_2^+ as a function of time. **a** $l = 1$ and **b** $l = 2$. For each l value, the period τ_{2l} and its multiples are represented by vertical red lines. Reprinted figure with permission from [15]. Copyright (2015) by the American Physical Society

rule for intersystem crossing: from the second singlet excited state, (i) an internal conversion between singlets $^1\pi\pi^* \rightarrow\ ^1n\pi^*$ occurs on a timescale of 85 fs, (ii) an intersystem crossing $^1n\pi^* \rightarrow\ ^3\pi\pi^*$ on a 2.0 ps timescale, and (iii) an internal conversion between triplets $^3\pi\pi^* \rightarrow\ ^3n\pi^*$ on a timescale of 602 fs. The unusually fast transition was explained by the absence of barriers in the paths to the conical intersections and the proximity of the latter with the minimum energy structures. With a similar approach (but in reduced dimensionality), the same group simulated, for a heme-CO complex, the photolysis and spin-crossover reactions happening concurrently on a femtosecond timescale [20]. Using the MCTDH method as well, Gatti and co-workers simulated the collision reactions between an atom and small molecules [21–23]. Using a two-level spin-boson Hamiltonian model, the same group studied the role of initial bath conditions in the photo-induced electron transfer and electronic coherence in plant cryptochromes [24]. A spin-boson model has also been used by Mangaud et al. [25] with the hierarchical equations of motion method, to describe the time evolution of an open quantum system strongly coupled to a bath.

Another typical example of MCTDH quantum dynamics study is the work on transition metal carbonyl α-diimine complexes by Fumanal et al. [26]. Using a reduced-dimensional Hamiltonian model (15 normal modes) of [M(imidazole)(CO)$_3$(phenanthroline)]$^+$ (M = Mn, Re), they studied the competition between luminescence, electron transfer, and photoinduced CO release, with a focus on the role of the metal atom on the branching ratio between these paths. Figure 2 shows the diabatic populations of [Re(imidazole)(CO)$_3$(phenanthroline)]$^+$ (left) and [Mn(imidazole)(CO)$_3$(phenanthroline)]$^+$ (right). In the rhenium complex, the intersystem crossing occurs readily in the S2 state to the long-lived lowest triplet state T1 within 100 fs while, in contradiction with the Kasha's rule, the lowest singlet state S1 is not populated. In contrast, in the manganese complex, the lowest S1 state is efficiently populated within 50 fs from S2, and the low-lying triplet states remain marginally populated because of modest spin-orbit coupling strength. In other works, the same group studied in detail the CO release pathway [27] and the effects of ligand substitution and conformers [28]. For a review on ultrafast processes in transition metal complexes, the reader is referred to the review by Daniel [29].

2.2 ...to method developments

A key ingredient to quantum dynamics simulations is the choice of system of nuclear coordinates. Physically well-adapted curvilinear coordinates have the advantage to lead to a Hamiltonian operator as separable as possible and thus simplifies the resolution of the time-dependent Schrödinger equation. The corresponding curvilinear expression of the kinetic energy operator can be used either analytically or numerically, the

memory requirement for the latter approach becoming often extremely demanding. Nauts et al. [30] develop an on-the-fly algorithm to reduce the memory storage bottleneck. They tested it recently on a three-dimensional model of the *cis-trans* photoisomerisation of part of the retinal chromophore [31].

The MCTDH method involves the development of a model Hamiltonian often based on harmonic potentials and, typically, a reduced number of nuclear coordinates. The development of a model Hamiltonian implies a heavy work of calculating the potential energy surfaces and relevant couplings on a grid and fitting them, prior to any dynamics simulations. Due to computational cost, the coupling constants are sometimes approximated from excited-state energies. Fumanal et al. [32] developed a protocol to calculate more accurate interstate vibronic coupling constants at the time-dependent density functional theory level through the overlap integrals between excited-state adiabatic auxiliary wavefunctions. To address the same problem, Yalouz et al. [33] work on a variational quantum eigensolver to estimate analytically non-adiabatic couplings between electronic states (and gradients for excited states).

Another important point is that electronic structure quantities needed to construct the model are calculated in the adiabatic basis, while the quantum dynamics is simulated in a (quasi-)diabatic basis. The diabatisation (procedure to convert the adiabatic data into diabatic ones) is not straightforward. Lasorne and co-workers develop strategies to perform this step. They for instance showed how a pseudofragmentation scheme can be used to define relevant diabatic representations, and illustrated it with small oligomers [34]. They also develop a "black-box" valence-bond-based automatic diabatization method [35]. The idea is to first reduce the full Hamiltonian to a low rank matrix that preserves the target eigensubspace. This is followed by a sequence of Householder transformations. The diabaticity criterion is implemented in a way that maximizes the diversity of valence bond structure weights between different diabatic states. They also proposed a pointwise phase correction scheme [36]. They illustrated their approach on several prototypical examples. For instance, Fig. 3 shows a two-dimensional description of the cyclopentadienyl radical Jahn-Teller conical intersection spanned by 2-fold degenerate displacements Q(a) and Q(b). Figure 3A displays the adiabatic potential energy surfaces of the ground and first excited states, with a typical Mexican hat shape. Figure 3B and C display the diabatic potential energy surfaces and the phase-corrected diabatic coupling, respectively: the developed approach produces a smooth crossing, with no cusp in the diabatic coupling. Along Q(a), the two diabatic states appear degenerate and the diabatic coupling is a nonzero quasi-linear function; along Q(b), the diabatic potentials are close to the adiabatic ones and the diabatic coupling is near zero.

To overcome the bottleneck of constructing and fitting the model before simulating the dynamics, Panadés-Barrueta et al. develop an automated methodology for the generation of global potential energy

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Fig. 2 Time evolution of the diabatic electronic populations of (left) [Re(imidazole)(CO)$_3$(phenanthro and (right) [Mn(imidazole)(CO)$_3$(phenanthro Adapted with permission from [26]. Copyright 2018 American Chemical Society
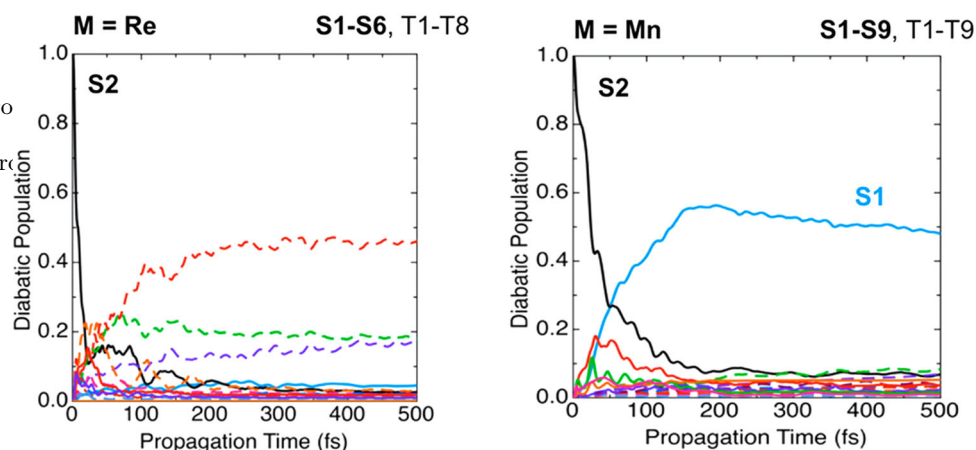
surfaces and molecular properties surfaces [37]. Their approach includes, in particular, a tensor decomposition algorithm to turn an automatically generated surface into sum of products (Tucker) form, as required in the MCTDH method. They tested their methodology on the *cis-trans* isomerisation reactions in HONO in full dimensionality (6 dimensions).

3 "On-the-fly" mixed quantum-classical dynamics of molecules

To address the different issues of quantum dynamics, "on-the-fly" dynamics methods have been developed. In these, the potential energy surfaces are calculated as needed along nuclear trajectories, the latter serving as a basis to describe the nuclear wavepacket motion. The nuclear trajectories are most of time moving classically in all nuclear dimensions, according to Newton's equations of motion. Similarly to the previous section, we first detail several state-of-the-art applications of such mixed quantum-classical dynamics methods. We then present works focused on the impact of the approximations of these methods and on developments to improve their accuracy.

3.1 From applications...

The most popular on-the-fly mixed quantum-classical method is surface hopping: it uses an ensemble of independent classical trajectories, and a quantum propagation of the electronic wavepacket inducing stochastically jumps between electronic states. To illustrate such a method, one can present the work of Vacher and co-workers on the *cis-to-trans* photoisomerisation of azobenzene [38]. One of the most interesting properties of azobenzene is the dependence of the measured quantum yield on the wavelength of the incident light used to trigger the photo-isomerisation. While there have been numerous works focusing on the *trans-to-cis*

isomerisation of azobenzene, the *cis-to-trans* photoisomerisation has been much less investigated. Their surface hopping simulations of the dynamics in full dimensionality (33 dimensions) provided the quantum yields of *cis-to-trans* isomerisation upon excitation to the $n\pi^*$ (S$_1$) and $\pi\pi^*$ (S$_2$) states, which occur on the timescale of several hundred of fs. They reproduced the decrease in quantum yield of 0.10 measured recently when exciting to the higher energy state and suggested a mechanism for it, different from the one accepted for the *trans-to-cis* direction. Figure 4 summarises the major relaxation pathways accessible to *cis*-azobenzene, and the fraction of trajectories which follow each pathway in both excitation cases. Two factors explain the quantum yield reduction: (i) a potential well that, after $\pi\pi^*$ excitation, traps photochromes which under $n\pi^*$ excitation would have exclusively formed *trans*-azobenzene and (ii) photochromes in this well excited initially to the $\pi\pi^*$ state are more likely to reform *cis*-azobenzene upon leaving the well than those excited to the $n\pi^*$ state.

Vacher and co-workers also simulated with the surface hopping method the competition between several relaxation pathways in furanone and derivatives [39]: ring-puckering spreads the excited state wavepacket quickly enough to influence the outcome of an otherwise expectedly direct ring-opening reaction in less than 50 fs. The same group also simulated the intersystem crossing that occurs within 1 ps in thiopyridone [40], and studied the role of conical intersection topography in the non-adiabatic transition probability [41]. Using the surface hopping method as well, Huix-Rotllant and co-workers simulated the behaviour of photoexcited thymine [42]: their dynamics explained the unusual long excited-state lifetime by an ultrafast ($\approx$ 30 fs) S$_2$ $\rightarrow$ S$_1$ internal conversion, followed by a trapping in S$_1$ state from which the decay to the ground state is slow ($\approx$ 6.1 ps). The same group simulated the ultrafast internal conversion on porphine [43]: the dominant mechanism demonstrated by the dynamics is sequential involving a set of dark states populated within $\approx$ 20 fs from the initially excited B band, and which then populate the Q band within $\approx$

Fig. 3 Potential energy surfaces of the cyclopentadienyl radical around the conical intersection along Q(a) and Q(b) distortions: **A** Adiabatic energies. **B** Diabatic diagonal energies (H11 and H22). **C** Phase-corrected diabatic coupling (H12). Reproduced with permission from [36]. Copyright 2021 American Chemical Society
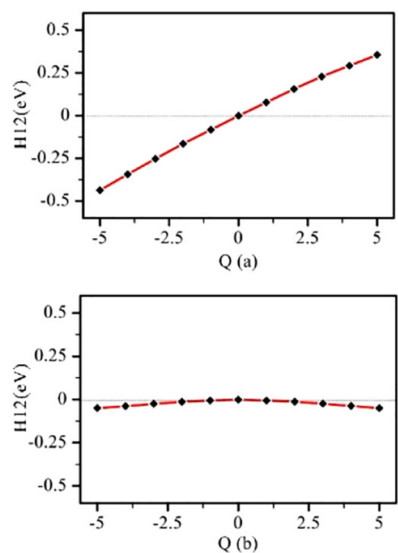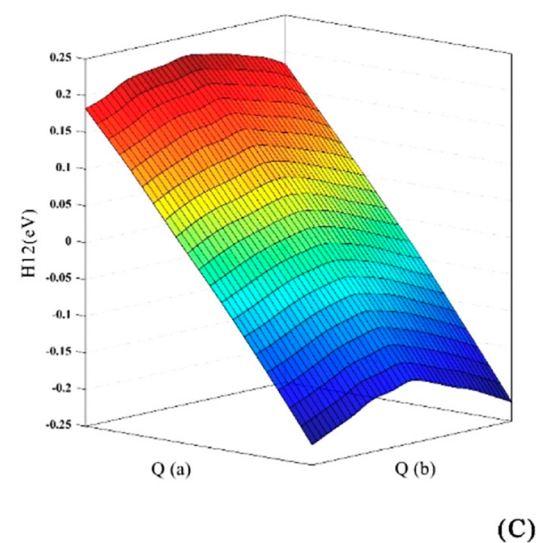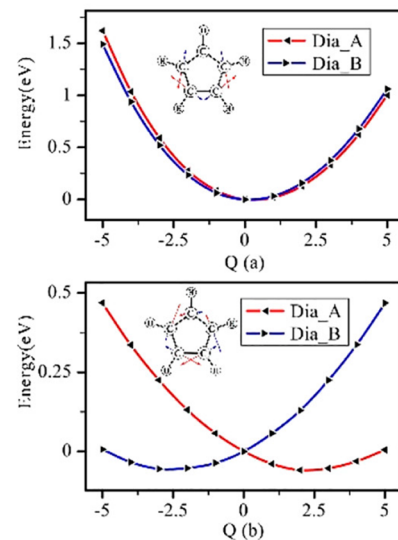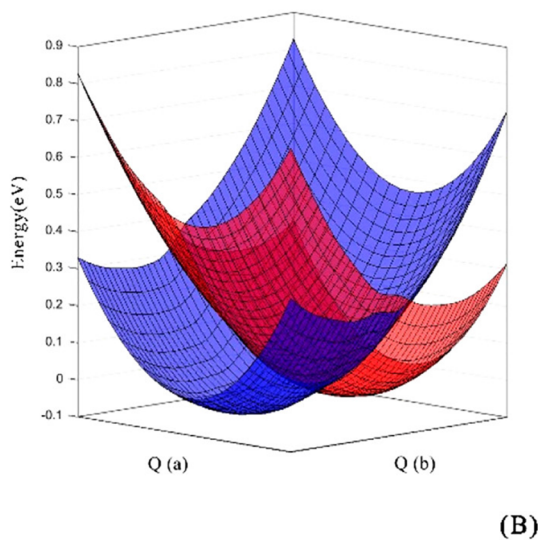
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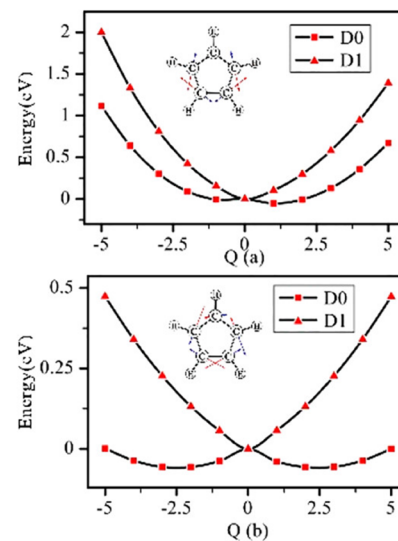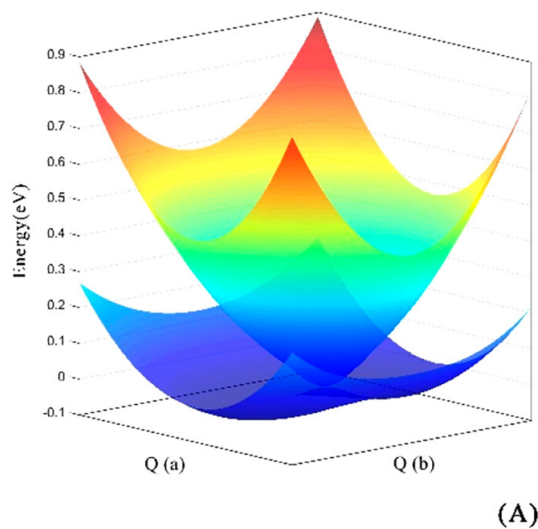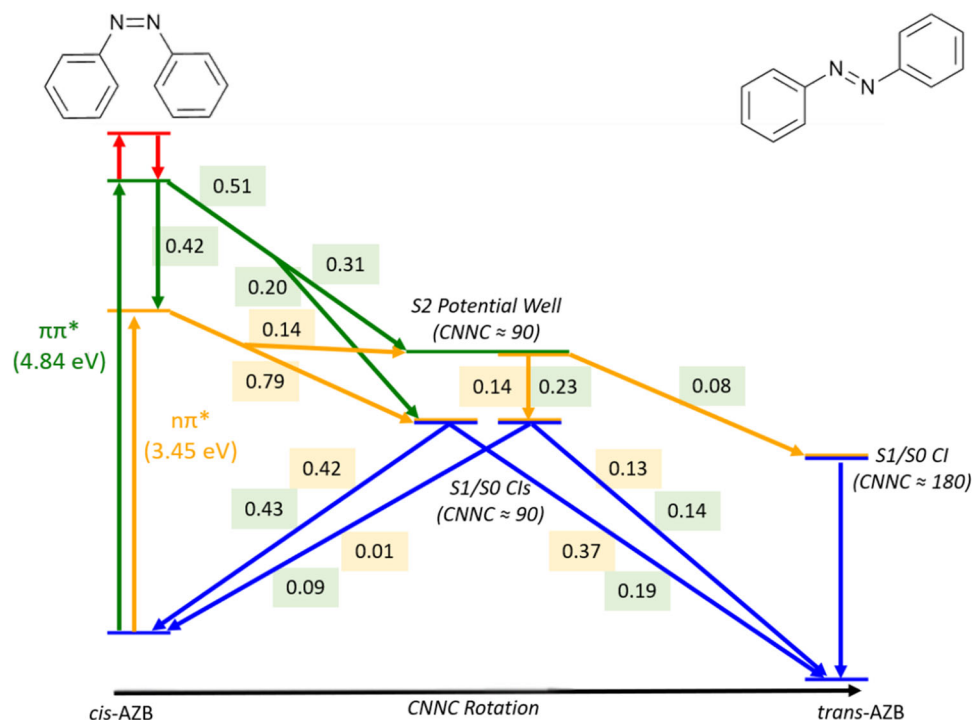Eur. Phys. J. Spec. Top. (2023) 232:2069–2079

Fig. 4 Major pathways, and the fraction of trajectories which follow each pathway, accessible to *cis*-azobenzene upon excitation to the $n\pi^*$ (numbers in yellow) and $\pi\pi^*$ (numbers in green) states. Reproduced from [38] with permission from the PCCP Owner Societies

100 fs. Barbatti and co-workers studied the photodynamics of coumaryl Meldrum and sinapoyl Meldrum [44, 45]. The fast (<1 ps) and efficient nonradiative decay to repopulate the electronic ground state upon UV absorption makes these molecules good candidates for sunscreen applications. The same group also simulated the dynamics of benzene excimer formation in 2 ps after S_1 excitation [46], the photoinduced formation of hydrogen-bonded ion pair in hydrochlorofluorocarbon-133a in the sub-ps timescale [47], and the photoisomerization of a macrocyclic cyclobiazobenzene molecule in less than 100 fs [48]. Monari and co-workers studied and compared the intersystem crossing rate for formyluracil and formylcytosine, i.e. oxidative lesions and epigenetic intermediates possibly acting as intrinsic DNA photosensitizers [49]. The same group investigated the importance of hydrogen transfer in photoexcited curcumin which happens in the sub-ps regime and compete with the intersystem crossing channel [50], and the photophysics of phenanthrene [51].

3.2 ...to method developments

A key ingredient to the mixed quantum-classical dynamics simulations are the initial conditions. Barbatti and co-workers worked on their definition and impact on the subsequent dynamics, in particular trying to take into account the effect of temperature [52], or when a reaction is initiated by thermal light [53]. Another important choice in the surface hopping method is how to adjust the velocity after a jump between electronic states in order to conserve total energy. The several options are for instance the nonadiabatic coupling vector, the momentum, and the energy

gradient difference. Barbatti studied the impact of this choice on time constants and structural evolution of photoexcited ethylene, and the comparison did not show any significant differences [54]. The same group extended the surface hopping method to describe irreversible decay mechanism using an imaginary potential [55]. They employed to survey the relaxation mechanisms of the shape resonant anions of iodoethene. The main bottleneck of such mixed quantum-classical dynamics simulations remain the electronic structure calculations. Barbatti and co-workers develop machine-learned potentials to be used in dynamics [56] to drastically reduce the cost of the simulations and allow to reach longer timescales [57]. The aim is to generate accurate machine-learned models of potential energy surfaces with no more than 10,000 points while conventional on-the-fly mixed quantum-classical simulations would typically require 100 trajectories with a time step of 0.5 fs for 1 ps, i.e. 200,000 electronic structure calculations.

The limits of these on-the-fly mixed quantum-classical methods like surface hopping are the classical treatment of the motion of nuclei and the non-exact description of electronic coherence. To address these points, the strategy is to couple the trajectories to recover some "quantumness". Along those lines, Agostini and co-workers develop a coupled-trajectory mixed quantum-classical algorithm, based on the exact factorization equations [58]. In the latter approach, instead of using the Born-Huang expansion, the total molecular wavefunction is exactly expressed as a single product of an electronic wavefunction and a nuclear wavefunction [59]. There, the electronic wavefunction is of course not an eigenfunction (nor a superposition of eigenfunctions)
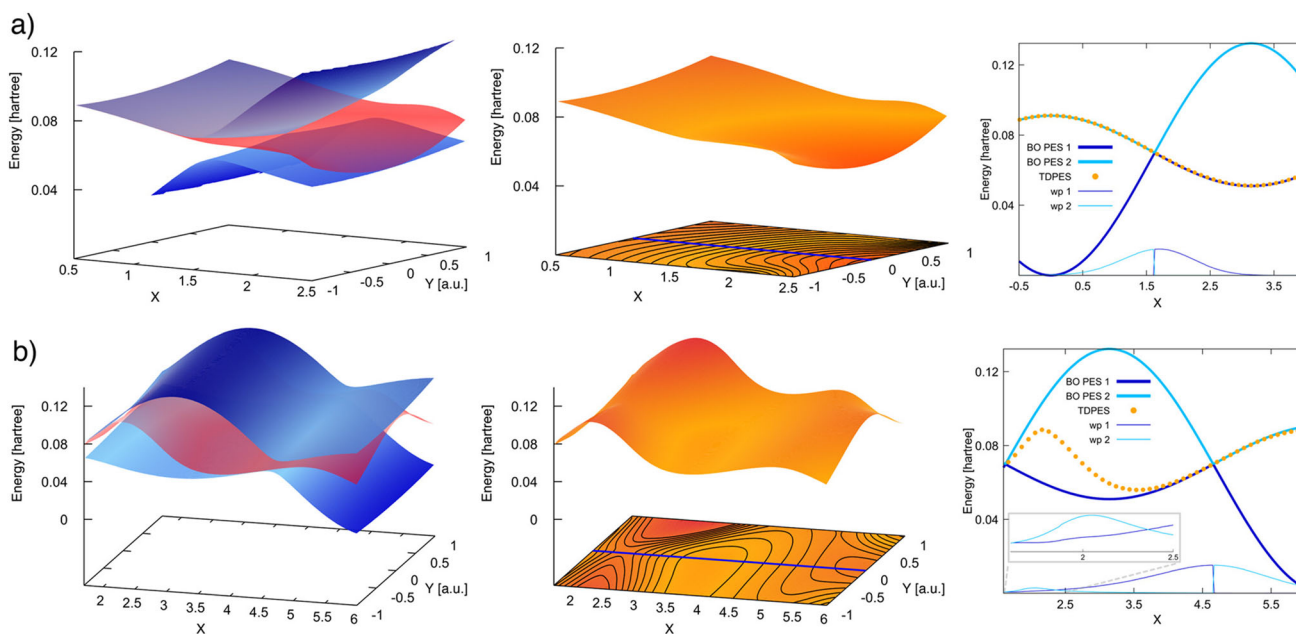
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Fig. 5 At two different times of the simulation **a** $t = 295$ au and **b** $t = 675$ au: comparison of the adiabatic potential energy surfaces (left and right, in blue) with the time-dependent one (left in red, middle and right in orange) and (right) nuclear densities in states 1 and 2 along a cut in the X direction. Reproduced with permission from [61]. Copyright 2017 American Chemical Society

of the traditional Born–Oppenheimer electronic Hamiltonian, but that of a somewhat more involved electronic Hamiltonian which depends on the nuclear wavefunction itself. An important feature of the exact factorization formalism is that dynamics occurs on a time-dependent potential energy surface, as in the Ehrenfest method. But, in contrast to Ehrenfest, an additional "coupled-trajectory" term appears in both the electronic and nuclear equations [60]. To illustrate the fundamental difference between Born-Huang and exact factorization formalisms, in particular in the vicinity of a conical intersection, dynamics was simulated on a two-state two-dimensional model [61]. Initial conditions were chosen so that once promoted from state 1 to state 2, the molecular wavepacket rapidly approaches a first conical intersection region ($t = 295$ au), and almost fully transfers back to state 1 non-radiatively with a small portion remaining in state 2 after passing through the conical intersection ($t = 675$ au). The molecular wavepacket enters then a second coupling region. Figure 5a compares the adiabatic and exact factorization representations of the dynamics at $t = 295$ au. The conical shape formed by the adiabatic surfaces is absent from the time-dependent potential energy surface. The latter shows a smooth character bridging the two adiabatic surfaces diabatically, as confirmed by the initially pure diabatic behaviour of the molecular wavepacket. However, at $t = 675$ au (Fig. 5b), the time-dependent potential energy surface continues to follow the adiabatic surfaces diabatically at large X on either side of the second conical intersection but it also exhibits additional features at smaller X. This is a signature of part of the molecular wavepacket that has remained in state

2 after the first conical intersection. In other words, the splitting of the molecular wavepacket enforces a step in the time-dependent potential energy surface. The exact factorization method has recently been extended to describe for instance spin-forbidden intersystem crossings [62, 63], quantum nuclear effects [64], mass and inertia effects of all molecular particles (i.e. electrons as well) [65], and electron dynamics in the Floquet formalism [66].

Another promising on-the-fly method with quantum accuracy is the direct-dynamics variational multiconfigurational Gaussian (DD-vMCG) method, based on the propagation of variationally coupled Gaussian wavepackets following quantum trajectories [67]. Vacher and co-workers applied it to simulate the very early nuclear dynamics induced in benzene induced upon tunnel ionization and measured using high harmonic spectroscopy [68].

4 Summary and perspectives

In this article, we reviewed and illustrated several recent studies, performed in France, dedicated to the theoretical description of ultrafast processes in molecules induced by light or collision, both in terms of state-of-the-art applications and method development works.

We first highlighted studies simulating quantum dynamics of systems ranging from diatomic molecules using grid-based methods, to transition metal complexes using the MCTDH method and Hamiltonian

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models. We then presented works focused on developments to improve the practical use of fully quantum dynamics methods, including for instance on-the-fly algorithms to overcome memory storage bottleneck, diabatisation strategies, automated methodologies to generate global potential energy surfaces.

We then turned our attention toward studies focusing on on-the-fly mixed quantum-classical dynamics of molecules. In particular, we illustrated applications of the popular surface hopping method on several medium-sized organic molecules. Moreover, we presented works focused on the impact of the approximations intrinsic to these methods (initial conditions, velocity rescaling, etc.) and we highlighted the recent efforts made to go beyond the classical treatment of the nuclear motion in on-the-fly dynamics methods.

A common bottleneck of all dynamics methods is the electronic structure calculations, either for the generation and fitting of global potential energy surfaces for quantum dynamics or in an on-the-fly manner for direct dynamics methods. Not only potential energy but also quantities such as energy derivatives and non-adiabatic couplings are required. To overcome this bottleneck, novel technologies such as machine learning [37, 56, 57] or quantum computing [33] are being developed and could be adapted to the theoretical description of ultrafast processes in molecules. These would really revolutionize the application of the current state-of-the-art dynamics methods. This would allow describing more complex and realistic systems, treating for instance the environment of molecules in solvent or in biological medium. This would also allow the simulation of dynamics over longer times bridging the processes happening on ultrafast timescales to those happening on longer ones. All of this will help us pushing the current limits of the fundamental understanding about the behaviour of molecules upon light absorption.

Data availability No data associated in the manuscript.

References

1. X. Ma, H. Tian, Photochemistry and photophysics. Concepts, research, applications. By Vincenzo Balzani, Paola Ceroni and Alberto Juris. Angew. Chem. Int. Ed. **53**(34), 8817–8817 (2014). https://doi.org/10.1002/anie.201405219

2. A.H. Zewail, Femtochemistry: atomic-scale dynamics of the chemical bond. J. Phys. Chem. A **104**(24), 5660–5694 (2000). https://doi.org/10.1021/jp001460h

3. P.M. Paul, E.S. Toma, P. Breger, G. Mullot, F. Augé, P. Balcou, H.G. Muller, P. Agostini, Observation of a train of attosecond pulses from high harmonic generation. Science **292**(5522), 1689–1692 (2001). https://doi.org/10.1126/science.1059413

4. M. Hentschel, R. Kienberger, C. Spielmann, G.A. Reider, N. Milosevic, T. Brabec, P. Corkum, U. Heinzmann, M. Drescher, F. Krausz, Attosecond metrology. Nature **414**(6863), 509–513 (2001). https://doi.org/10.1038/35107000

5. M. Drescher, M. Hentschel, R. Kienberger, M. Uiberacker, V. Yakovlev, A. Scrinzi, T. Westerwalbesloh, U. Kleineberg, U. Heinzmann, F. Krausz, Time-resolved atomic inner-shell spectroscopy. Nature **419**(6909), 803–807 (2002)

6. A.L. Cavalieri, N. Müller, T. Uphues, V.S. Yakovlev, A. Baltuska, B. Horvath, B. Schmidt, L. Blümel, R. Holzwarth, S. Hendel, M. Drescher, U. Kleineberg, P.M. Echenique, R. Kienberger, F. Krausz, U. Heinzmann, Attosecond spectroscopy in condensed matter. Nature **449**, 1029 (2007). https://doi.org/10.1038/nature06229

7. L. Belshaw, F. Calegari, M.J. Duffy, A. Trabattoni, L. Poletto, M. Nisoli, J.B. Greenwood, Observation of ultrafast charge migration in an amino acid. J. Phys. Chem. Lett. **3**(24), 3751–3754 (2012). https://doi.org/10.1021/jz3016028

8. M. Born, K. Huang, *Dynamical Properties of Crystal Lattices* (Clarendon, Oxford, 1968)

9. F. Agostini, B.F. Curchod, Different flavors of nonadiabatic molecular dynamics. Wiley Interdisciplinary Rev. Comput. Mol. Sci. **9**(5), 1417 (2019)

10. R. Crespo-Otero, M. Barbatti, Recent advances and perspectives on nonadiabatic mixed quantum-classical dynamics. Chem. Rev. **118**(15), 7026–7068 (2018). https://doi.org/10.1021/acs.chemrev.7b00577. (**PMID: 29767966**)

11. G.A. Worth, M.H. Beck, A. Jäckle, H.-D. Meyer, The MCTDH package, Version 8.3. See http://www.pci.uni-heidelberg.de/tc/usr/mctdh/ (2003)

12. F. Catoire, R.E.F. Silva, P. Rivière, H. Bachau, F. Martín, Molecular resolvent-operator method: electronic and nuclear dynamics in strong-field ionization. Phys. Rev. A **89**, 023415 (2014). https://doi.org/10.1103/PhysRevA.89.023415

13. F. Catoire, H. Bachau, Study of the he_2^{2+} dynamics induced by a strong IR field by means of the resolvent technique. J. Phys. B: At. Mol. Opt. Phys. **47**(12), 124028 (2014). https://doi.org/10.1088/0953-4075/47/12/124028

14. S. Saugout, C. Cornaggia, A. Suzor-Weiner, E. Charron, Ultrafast electronuclear dynamics of h_2 double ionization. Phys. Rev. Lett. **98**, 253003 (2007). https://doi.org/10.1103/PhysRevLett.98.253003

15. C. Cornaggia, Temporal analysis of fractional revivals of molecular observables following impulsive alignment. Phys. Rev. A **91**, 043426 (2015). https://doi.org/10.1103/PhysRevA.91.043426

16. L. Quaglia, M. Brewczyk, C. Cornaggia, Molecular reorientation in intense femtosecond laser fields. Phys. Rev. A **65**, 031404 (2002). https://doi.org/10.1103/PhysRevA.65.031404

17. T. Latka, V. Shirvanyan, M. Ossiander, O. Razskazovskaya, A. Guggenmos, M. Jobst, M. Fieß, S. Holzner, A. Sommer, M. Schultze, C. Jakubeit, J. Riemensberger, B. Bernhardt, W. Helml, F. Gatti, B. Lasorne, D. Lauvergnat, P. Decleva, G.J. Halász, A. Vibók, R. Kienberger, Femtosecond wave-packet revivals in ozone.

Phys. Rev. A **99**, 063405 (2019). https://doi.org/10.1103/PhysRevA.99.063405

18. P.J. Castro, A. Perveaux, D. Lauvergnat, M. Reguero, B. Lasorne, Ultrafast internal conversion in 4-aminobenzonitrile occurs sequentially along the seam. Chem. Phys. **509**, 30–36 (2018). https://doi.org/10.1016/j.chemphys.2018.03.013 (**High-dimensional quantum dynamics (on the occasion of the 70th birthday of Hans-Dieter Meyer)**)

19. M. Alías-Rodríguez, C. de Graaf, M. Huix-Rotllant, Ultrafast intersystem crossing in xanthone from wavepacket dynamics. J. Am. Chem. Soc. **143**(51), 21474–21477 (2021). https://doi.org/10.1021/jacs.1c07039

20. K. Falahati, H. Tamura, I. Burghardt, M. Huix-Rotllant, Ultrafast carbon monoxide photolysis and heme spin-crossover in myoglobin via nonadiabatic quantum dynamics. Nat. Commun. **9**(1), 4502 (2018). https://doi.org/10.1038/s41467-018-06615-1

21. C.H. Yuen, D. Lapierre, F. Gatti, V. Kokoouline, V.G. Tyuterev, The role of ozone vibrational resonances in the isotope exchange reaction 16o16o + 18o -> 18o16o + 16o: the time-dependent picture. J. Phys. Chem. A **123**(36), 7733–7743 (2019). https://doi.org/10.1021/acs.jpca.9b06139. (**PMID: 31408343**)

22. Z. Zhang, F. Gatti, D.H. Zhang, Full dimensional quantum mechanical calculations of the reaction probability of the h + nh3 collision based on a mixed jacobi and radau description. J. Chem. Phys. **150**(20), 204301 (2019). https://doi.org/10.1063/1.5096047

23. Z. Zhang, F. Gatti, D.H. Zhang, Full-dimensional quantum mechanical calculations of the reaction probability of the h + ch4 reaction based on a mixed jacobi and radau description. J. Chem. Phys. **152**(20), 201101 (2020). https://doi.org/10.1063/5.0009721

24. D. Mendive-Tapia, E. Mangaud, T. Firmino, A. de la Lande, M. Desouter-Lecomte, H.-D. Meyer, F. Gatti, Multidimensional quantum mechanical modeling of electron transfer and electronic coherence in plant cryptochromes: The role of initial bath conditions. J. Phys. Chem. B **122**(1), 126–136 (2018). https://doi.org/10.1021/acs.jpcb.7b10412. (**PMID: 29216421**)

25. E. Mangaud, R. Puthumpally-Joseph, D. Sugny, C. Meier, O. Atabek, M. Desouter-Lecomte, Non-markovianity in the optimal control of an open quantum system described by hierarchical equations of motion. New J. Phys. **20**(4), 043050 (2018). https://doi.org/10.1088/1367-2630/aab651

26. M. Fumanal, E. Gindensperger, C. Daniel, Ultrafast intersystem crossing vs internal conversion in α-diimine transition metal complexes: quantum evidence. J. Phys. Chem. Lett. **9**(17), 5189–5195 (2018). https://doi.org/10.1021/acs.jpclett.8b02319. (**PMID: 30145893**)

27. M. Fumanal, C. Daniel, E. Gindensperger, Excited-state dynamics of [mn(im)(co)3(phen)]+: photocorm, catalyst, luminescent probe? J. Chem. Phys. **154**(15), 154102 (2021). https://doi.org/10.1063/5.0044108

28. M. Fumanal, E. Gindensperger, C. Daniel, Ligand substitution and conformational effects on the ultrafast luminescent decay of [re(co)3(phen)(l)]+ (l = imidazole, pyridine): non-adiabatic quantum dynamics. Phys. Chem. Chem. Phys. **20**, 1134–1141 (2018). https://doi.org/10.1039/C7CP07540E

29. C. Daniel, Ultrafast processes: coordination chemistry and quantum theory. Phys. Chem. Chem. Phys. **23**, 43–58 (2021). https://doi.org/10.1039/D0CP05116K

30. A. Nauts, D. Lauvergnat, Numerical on-the-fly implementation of the action of the kinetic energy operator on a vibrational wave function: application to methanol. Mol. Phys. **116**(23–24), 3701–3709 (2018). https://doi.org/10.1080/00268976.2018.1473652

31. E. Marsili, F. Agostini, A. Nauts, D. Lauvergnat, Quantum dynamics with curvilinear coordinates: models and kinetic energy operator. Philos. Trans. Roy. Soc. A: Math. Phys. Eng. Sci. **380**(2223), 20200388 (2022). https://doi.org/10.1098/rsta.2020.0388

32. M. Fumanal, F. Plasser, S. Mai, C. Daniel, E. Gindensperger, Interstate vibronic coupling constants between electronic excited states for complex molecules. J. Chem. Phys. **148**(12), 124119 (2018). https://doi.org/10.1063/1.5022760

33. S. Yalouz, E. Koridon, B. Senjean, B. Lasorne, F. Buda, L. Visscher, Analytical nonadiabatic couplings and gradients within the state-averaged orbital-optimized variational quantum eigensolver. J. Chem. Theory Comput. **18**(2), 776–794 (2022). https://doi.org/10.1021/acs.jctc.1c00995. (**PMID: 35029988**)

34. E.K.-L. Ho, B. Lasorne, Diabatic pseudofragmentation and nonadiabatic excitation-energy transfer in meta-substituted dendrimer building blocks. Comput. Theor. Chem. **1156**, 25–36 (2019)

35. Y. Zhang, P. Su, B. Lasorne, B. Braïda, W. Wu, A novel valence-bond-based automatic diabatization method by compression. J. Phys. Chem. Lett. **11**(13), 5295–5301 (2020). https://doi.org/10.1021/acs.jpclett.0c01466. (**PMID: 32521163**)

36. Y. Zhang, W. Wang, B. Lasorne, P. Su, W. Wu, Diabatization around conical intersections with a new phase-corrected valence-bond-based compression approach. J. Phys. Chem. Lett. **12**(7), 1885–1892 (2021). https://doi.org/10.1021/acs.jpclett.0c03506. (**PMID: 33587630**)

37. R.L. Panadés-Barrueta, E. Martínez-Núñez, D. Peláez, Specific reaction parameter multigrid potfit (srp-mgpf): automatic generation of sum-of-products form potential energy surfaces for quantum dynamical calculations. Front. Chem. (2019). https://doi.org/10.3389/fchem.2019.00576

38. I.C.D. Merritt, D. Jacquemin, M. Vacher, cis → trans photoisomerisation of azobenzene: a fresh theoretical look. Phys. Chem. Chem. Phys. **23**, 19155–19165 (2021). https://doi.org/10.1039/D1CP01873F

39. O. Schalk, J. Galiana, T. Geng, T.L. Larsson, R.D. Thomas, I. Fdez Galván, T. Hansson, M. Vacher, Competition between ring-puckering and ring-opening excited state reactions exemplified on 5h-furan-2-one and derivatives. J. Chem. Phys. **152**(6), 064301 (2020). https://doi.org/10.1063/1.5129366

40. J. Norell, M. Odelius, M. Vacher, Ultrafast dynamics of photo-excited 2-thiopyridone: theoretical insights into triplet state population and proton transfer pathways. Struct. Dyn. **7**(2), 024101 (2020). https://doi.org/10.1063/1.5143228

41. I. Fdez Galván, A. Brakestad, M. Vacher, Role of conical intersection seam topography in the chemiexcitation of 1,2-dioxetanes. Phys. Chem. Chem. Phys.

24, 1638–1653 (2022). https://doi.org/10.1039/D1CP05028A

42. W. Park, S. Lee, M. Huix-Rotllant, M. Filatov, C.H. Choi, Impact of the dynamic electron correlation on the unusually long excited-state lifetime of thymine. J. Phys. Chem. Lett. **12**(18), 4339–4346 (2021). https://doi.org/10.1021/acs.jpclett.1c00712. (**PMID: 33929858**)

43. K. Falahati, C. Hamerla, M. Huix-Rotllant, I. Burghardt, Ultrafast photochemistry of free-base porphyrin: a theoretical investigation of b → q internal conversion mediated by dark states. Phys. Chem. Chem. Phys. **20**, 12483–12492 (2018). https://doi.org/10.1039/C8CP00657A

44. T.T. Abiola, N.N. Rodrigues, C. Ho, D.J.L. Coxon, M.D. Horbury, J.M. Toldo, M.T. do Casal, B. Rioux, C. Peyrot, M.M. Mention, P. Balaguer, M. Barbatti, F. Allais, V.G. Stavros, New generation uv-a filters: understanding their photodynamics on a human skin mimic. J. Phys. Chem. Lett. **12**(1), 337–344 (2021). https://doi.org/10.1021/acs.jpclett.0c03004

45. J.M. Toldo, M.T. do Casal, M. Barbatti, Mechanistic aspects of the photophysics of uva filters based on meldrum derivatives. J. Phys. Chem. A **125**(25), 5499–5508 (2021). https://doi.org/10.1021/acs.jpca.1c03315

46. T.M. Cardozo, A.P. Galliez, I. Borges, F. Plasser, A.J.A. Aquino, M. Barbatti, H. Lischka, Dynamics of benzene excimer formation from the parallel-displaced dimer. Phys. Chem. Chem. Phys. **21**, 13916–13924 (2019). https://doi.org/10.1039/C8CP06354K

47. G. Pereira Rodrigues, T.M. Lopes de Lima, R.B. de Andrade, E. Ventura, S.A. de Monte, M. Barbatti, Photoinduced formation of h-bonded ion pair in hcfc-133a. J. Phys. Chem. A **123**(10), 1953–1961 (2019). https://doi.org/10.1021/acs.jpca.8b12482

48. T.-S. Zhang, Z.-W. Li, Q. Fang, M. Barbatti, W.-H. Fang, G. Cui, Stereoselective excited-state isomerization and decay paths in cis-cyclobiazobenzene. J. Phys. Chem. A **123**(29), 6144–6151 (2019). https://doi.org/10.1021/acs.jpca.9b04372. (**PMID: 31246461**)

49. A. Francés-Monerris, M. Lineros-Rosa, M.A. Miranda, V. Lhiaubet-Vallet, A. Monari, Photoinduced intersystem crossing in dna oxidative lesions and epigenetic intermediates. Chem. Commun. **56**, 4404–4407 (2020). https://doi.org/10.1039/D0CC01132K

50. R. Losantos, A. Pasc, A. Monari, Don't help them to bury the light. The interplay between intersystem crossing and hydrogen transfer in photoexcited curcumin revealed by surface-hopping dynamics. Phys. Chem. Chem. Phys. **23**, 24757–24764 (2021). https://doi.org/10.1039/D1CP03617C

51. M. Nazari, C.D. Bösch, A. Rondi, A. Francés-Monerris, M. Marazzi, E. Lognon, M. Gazzetto, S.M. Langenegger, R. Häner, T. Feurer, A. Monari, A. Cannizzo, Ultrafast dynamics in polycyclic aromatic hydrocarbons: the key case of conical intersections at higher excited states and their role in the photophysics of phenanthrene monomer. Phys. Chem. Chem. Phys. **21**, 16981–16988 (2019). https://doi.org/10.1039/C9CP03147B

52. F. Kossoski, M. Barbatti, Nuclear ensemble approach with importance sampling. J. Chem. Theory Comput. **14**(6), 3173–3183 (2018). https://doi.org/10.1021/acs.jctc.8b00059. (**PMID: 29694040**)

53. M. Barbatti, Simulation of excitation by sunlight in mixed quantum-classical dynamics. J. Chem. Theory Comput. **16**(8), 4849–4856 (2020). https://doi.org/10.1021/acs.jctc.0c00501. (**PMID: 32579345**)

54. M. Barbatti, Velocity adjustment in surface hopping: ethylene as a case study of the maximum error caused by direction choice. J. Chem. Theory Comput. **17**(5), 3010–3018 (2021). https://doi.org/10.1021/acs.jctc.1c00012. (**PMID: 33844922**)

55. F. Kossoski, M. Barbatti, Nonadiabatic dynamics in multidimensional complex potential energy surfaces. Chem. Sci. **11**, 9827–9835 (2020). https://doi.org/10.1039/D0SC04197A

56. P.O. Dral, M. Barbatti, W. Thiel, Nonadiabatic excited-state dynamics with machine learning. J. Phys. Chem. Lett. **9**(19), 5660–5663 (2018). https://doi.org/10.1021/acs.jpclett.8b02469. (**PMID: 30200766**)

57. S. Mukherjee, M. Pinheiro, B. Demoulin, M. Barbatti, Simulations of molecular photodynamics in long timescales. Philos. Trans. Roy. Soc. A: Math. Phys. Eng. Sci. **380**(2223), 20200382 (2022). https://doi.org/10.1098/rsta.2020.0382

58. F. Agostini, An exact-factorization perspective on quantum-classical approaches to excited-state dynamics. Eur. Phys. J. B **91**(7), 143 (2018). https://doi.org/10.1140/epjb/e2018-90085-9

59. A. Abedi, N.T. Maitra, E.K.U. Gross, Exact factorization of the time-dependent electron-nuclear wave function. Phys. Rev. Lett. **105**, 123002 (2010). https://doi.org/10.1103/PhysRevLett.105.123002

60. G.H. Gossel, F. Agostini, N.T. Maitra, Coupled-trajectory mixed quantum-classical algorithm: a deconstruction. J. Chem. Theory Comput. **14**(9), 4513–4529 (2018). https://doi.org/10.1021/acs.jctc.8b00449. (**PMID: 30063343**)

61. B.F.E. Curchod, F. Agostini, On the dynamics through a conical intersection. J. Phys. Chem. Lett. **8**(4), 831–837 (2017). https://doi.org/10.1021/acs.jpclett.7b00043. (**PMID: 28151670**)

62. F. Talotta, S. Morisset, N. Rougeau, D. Lauvergnat, F. Agostini, Spin-orbit interactions in ultrafast molecular processes. Phys. Rev. Lett. **124**, 033001 (2020). https://doi.org/10.1103/PhysRevLett.124.033001

63. F. Talotta, S. Morisset, N. Rougeau, D. Lauvergnat, F. Agostini, Internal conversion and intersystem crossing with the exact factorization. J. Chem. Theory Comput. **16**(8), 4833–4848 (2020). https://doi.org/10.1021/acs.jctc.0c00493

64. F. Agostini, I. Tavernelli, G. Ciccotti, Nuclear quantum effects in electronic (non)adiabatic dynamics. Eur. Phys. J. B **91**(7), 139 (2018). https://doi.org/10.1140/epjb/e2018-90144-3

65. A. Scherrer, F. Agostini, D. Sebastiani, E.K.U. Gross, R. Vuilleumier, On the mass of atoms in molecules: beyond the born-oppenheimer approximation. Phys. Rev. X **7**, 031035 (2017). https://doi.org/10.1103/PhysRevX.7.031035

66. M. Schirò, F.G. Eich, F. Agostini, Quantum-classical nonadiabatic dynamics of floquet driven systems. J. Chem. Phys. **154**(11), 114101 (2021). https://doi.org/10.1063/5.0043790

67. M. Vacher, M.J. Bearpark, M.A. Robb, Direct methods for non-adiabatic dynamics: connecting the single-set variational multi-configuration gaussian (vmcg) and ehrenfest perspectives. Theoret. Chem. Acc. **135**(8), 1–11 (2016). https://doi.org/10.1007/s00214-016-1937-2

68. D.R. Austin, A.S. Johnson, F. McGrath, D. Wood, L. Miseikis, T. Siegel, P. Hawkins, A. Harvey, Z. Mašín, S. Patchkovskii, M. Vacher, J.P. Malhado, M.Y. Ivanov, O. Smirnova, J.P. Marangos, Extracting sub-cycle electronic and nuclear dynamics from high harmonic spectra. Sci. Rep. **11**(1), 2485 (2021). https://doi.org/10.1038/s41598-021-82232-1