Ultrafast Molecular Dynamics in Excited States Using Mixed Quantum-Classical Approaches

(Ultraschnelle Molekulardynamik in angregten Zuständen mit gemischte Quanten-Klassischen Methoden)

HABILITATIONSSCHRIFT
zur Erlangung der venia docendi
für das Fach Theoretische Chemie
an der Institut für Theoretische Chemie
der Universität Wien

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Wien 2007
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Summary

Quantum chemical modeling of electronically-excited molecular systems is an important area in Theoretical Chemistry providing information on ultrafast processes occurring in electronically excited states. In particular, this kind of investigations is important for the analysis of femtosecond time-resolved spectroscopic data, when they cannot provide details on the occurring reaction mechanisms. In addition to conventional static quantum chemical approaches, dynamics simulations constitute key tools able to provide information on interesting time-dependent aspects, such as excited-state lifetimes.

The main strategy followed here is based on the usage of the mixed quantum-classical dynamics (MQCD) methods, in which the nuclei are propagated classically, while the behavior of the electrons are quantum-mechanically treated by solving the time-dependent Schrödinger equation. Using an on-the-fly approach, this procedure allows the straightforward inclusion of all nuclear degrees of freedom in the dynamics. This type of methods also permits to go beyond the Born-Oppenheimer approximation, by recoupling the nuclear and electronic motions. This is specially required in ultrafast processes showing radiationless deactivation. A new software implementation of MQCD methods, the NEWTON-X program package, has been developed. The program is written in a flexible, modular and general way and new dynamics and quantum chemical methods and interfaces can be directly implemented.

A large variety of systems, from small substituted ethylenes to systems formed by up to three aromatic rings, has been investigated combining static and MQCD methods, as to shed light on mechanistic aspects of their photodynamics. Particular attention has been given to the determination of the factors that contribute to the efficiency of the different excited-state reaction paths.
Zusammenfassung


Eine große Vielfalt von Systemen, beginnend mit kleinen substituierten Ethylenverbindungen bis hin zu Molekülen, die bis zu drei aromatische Ringe enthalten, wurde mit der Kombination konventioneller und MQCD Methoden untersucht, um Aufschluss über die mechanistischen Aspekte der Photodynamik zu erhalten. Besondere Aufmerksamkeit wurde auf die Bestimmung der Faktoren gelegt, die einen Beitrag zur Effizienz der verschiedenen Reaktionswege in angeregten Zuständen haben.
1. The molecular photoactivation

1.1 Femtochemistry phenomenology

The molecular photoactivation results in photophysical and photochemical transformations that may end up in the conversion of the excess of electronic energy into either mechanical energy or photoemission.\textsuperscript{1,2} In the first case, phenomena involving the breakdown of the Born-Oppenheimer approximation play a role that can hardly be overestimated.\textsuperscript{3} The occurrence of avoided crossings and degeneracies between two or more electronic states plays a crucial role in the determination of the radiationless channels driving the photoreactions.\textsuperscript{4,5} In particular, when the energy surfaces of states of the same multiplicity cross in form of conical intersections,\textsuperscript{6} the switching of electronic states may take place at the femtosecond time scale.

In the context of the photobiologic phenomena, the solar radiation as the primary energy source left several fundamental marks in the evolutionary history of the Earth. Most different organisms have used this radiation not only to directly or indirectly activate their own metabolic processes, but also to collect information about the environment.\textsuperscript{7-9} Moreover, they also had to develop mechanisms of protection against photochemical degradation caused by UV irradiation.\textsuperscript{10-12} Processes occurring in the excited states of organic molecules underlie phenomena, such as the stabilization of nucleic acids,\textsuperscript{10-15} photosynthesis,\textsuperscript{16,17} the molecular mechanism of vision,\textsuperscript{18-20} photocontrol of acidity,\textsuperscript{21} and general biological response to UV exposure.\textsuperscript{8,13} Despite the biological complexity of all these subjects, the initial steps usually involve the photoactivation of particular chromophore sites of proteins and nucleic acids triggering excited-state isomerization processes, which can be treated in the domain of the theoretical photochemistry.

Although this thesis is mainly dedicated to organic and biological aspects of the molecular photoactivation, it is worth noting that this kind of phenomenon naturally extends over many other fields. Besides being an interesting subject on its own for basic sciences,\textsuperscript{1,2} the immediate chemical and physical transformations of photoexcited molecules is an ubiquitous subject in science and technology, being particularly important for investigations on material photodegradation,\textsuperscript{22,23} photo-switch developments,\textsuperscript{24,25} induced reactions in environmental sciences,\textsuperscript{26,27} and molecular synthesis in astrophysics.\textsuperscript{28}
With the development of ultrafast laser pulses and of the time-resolved femto- and attosecond spectroscopy, the molecular and even atomic transient changes occurring in the excited states can be experimentally monitored while they take place. Even more impressive are techniques like the 4D ultrafast electron microscopy (UEM), which can provide images of the 3D structures with Å resolution as snapshots captured with femtosecond resolution, and the 2D femtosecond spectroscopy, which can provide direct information on the vibrational and electronic couplings. Nevertheless, the most commonly used techniques, such as pump-probe or transient absorption, heavily rely on theoretical modeling for the deconvolution of the raw data, formed by several overlapped instrumental and molecular component signals. For this reason, the same set of data can be subject to different interpretations and the quantum-chemistry calculations play a fundamental role for determining and predicting the underlying processes.

1.2 Theoretical and computational methods

The main source of theoretical information in photochemistry comes from quantum-chemical approaches, which can provide excited-state properties such as energies, wave-function characters, dipole transition moments, spin-orbit couplings, non-adiabatic couplings, etc., along specific cuts on the potential energy surfaces connecting different minima, saddle points and conical intersections. For the theoretician, this field is challenging, since the most advanced, costly and difficult methods of quantum chemistry must be employed to deal with the complexity of the excited-state surfaces, which commonly violates the chemical intuition. In this context, the development of the minimum energy path (MEP) approaches applied for excited states can be considered as an important addition to the investigation of the molecular photodynamics and have revealed possible pathways for the relaxation and the localization of regions of non-adiabatic transition for several systems.

Moreover, since time is an intrinsically important variable in these phenomena, conventional static approaches can only provide a limited amount of information and dynamics simulations in excited states are an important complementary tool. Different from dynamics simulations in the ground state, which are well established being applied even to macromolecules due to the extraordinary computational efficiency of the semi-empirical and force-field approaches, excited-state dynamics can be considered as the next frontier in the advances of the computational chemistry. These simulations applied to systems of biological interest are becoming feasible with present computational capabilities and constitute a new area still under development.
The ideal scenario would be to perform complete time-dependent quantum mechanical treatment of the systems. Unfortunately, such approaches\textsuperscript{3,5,40,41} are only applicable either to very small molecular systems or to a very restricted subset of nuclear coordinates of large molecules. If the “important coordinates” can be selected and are relatively isolated from the other degrees of freedom, the results of the full quantum-mechanical treatment are of outstanding precision, as can be attested in the brief collection of applications discussed in Refs. \textsuperscript{3,42-45} of the multi-configuration time-dependent Hartree (MCTDH) method. Nevertheless, the selection of the “important coordinates” can also introduce bias whose effect is of difficult evaluation. The extension of these methods to the full set of coordinates is limited by two factors, the computational cost of the integration of the time-dependent Schrödinger equation and by intrinsic impossibility of producing multi-dimensional potential energy surfaces for relatively large systems.

Mixed quantum-classical dynamics (MQCD) approaches\textsuperscript{46,47}, in which the nuclei are treated classically whereas the electrons are treated quantum mechanically, represent an effective gain in terms of reduction of computational effort in comparison with the full quantum-mechanical methods. Besides that, since the classical time-evolution of the nuclei depend only on local forces, these approaches are naturally fitted to on-the-fly algorithms, in which the energy gradients and other needed properties are computed in the course of the dynamics. Thus, MQCD methods allow the investigation of the full set of coordinates at the cost of neglecting non-local phenomena such as energy quantization and tunneling. Non-local features can be further incorporated by coupling the classical trajectories, as for example in the family of Velocity Coupling Approximation methods.\textsuperscript{48} Another way to circumvent the limitations of the local approach is to treat the nuclei also quantum mechanically but making usage of approximations motivated by the classical limit of quantum mechanics, as done in the Multiple Spawning method.\textsuperscript{9,49,50}

Since the integration of the classical equations in the independent trajectory approaches is obtained practically “for free”, the bottleneck for the MQCD simulations rests on the cost of computing electronic properties \textit{on-the-fly}. Moreover, the electronic-structure method should allow the analytical computation of energy gradients for the excited states and, eventually, non-adiabatic coupling vectors. Due to the development of efficient algorithms to compute these quantities at the multireference configuration interaction level (MRCI),\textsuperscript{51,52} we can currently perform half-picosecond dynamics simulations with single excitations (MR-CIS) for systems as large as adenine\textsuperscript{53} and with single and double excitations (MR-CISD) for systems as large as pyrrole.\textsuperscript{54}
In selecting methods for performing dynamics, the usage of semi-empirical methods, mainly those developed within the framework of multiconfigurational wavefunctions, pays off for their extremely high computational efficiency. These methods, however, have as major limitation the unpredictable quality of the potential energy surfaces in regions not spanned by the fitting of the parameters. Some methods such as the time-dependent density functional theory (TD-DFT) or the coupled-cluster-based RI-CC2 and EOM-CC allow the computation of analytical gradients, but lack the multireference character. Attempts of calculating non-adiabatic coupling vectors at the TD-DFT and at the restricted open-shell Kohn-Sham (ROKS) levels have been reported, although it is not fully clear how their performance degrades close to conical intersections. Others, such as the DFT/MRCI or the family of multireference perturbation theory methods can adequately describe the energies close to multireference regions, but do not allow the computation of analytical gradients. It is worth noting that analytical gradients computed with the complete active space second-order perturbation theory (CASPT2) have been recently developed and this constitutes a promising fact for the near future. As already mentioned, although substantial progress has been made by the development of analytic energy gradients and non-adiabatic coupling vectors for MRCI and state-averaged multiconfiguration self-consistent field (SA-MCSCF) approaches, these methods are still rather expensive and their usage limited.

Therefore, since there is no ideal electronic-structure method that conjugates quality and efficiency, the decision about which one to use will depend on each particular case. Thus, while in the usage of ground-state dynamics for UV-absorption spectrum simulations it might be worth using a semiempirical method, in the simulation of excited-state proton transfer a single-reference method, such as TD-DFT, can be the best option. In ab initio simulations of radiationless deactivation through conical intersections the usage of either MCSCF or MRCI methods is mandatory. In order to have sufficient flexibility to choose among all these variety of methods and still perform dynamics without needing extensive code changes, we considered necessary to develop a program package oriented to MQCD dynamics simulations, which was modular enough to allow the easy interfacing to other programs and methods. This has been accomplished in the NEWTON-X package.

Along this thesis, we are going to discuss all these phenomenological and methodological issues in some detail. The discussion will be mainly based on our MQCD implementation into the NEWTON-X program package and on several investigations that we have carried out, so far encompassing almost twenty different molecular systems (see Table 1), employing conventional quantum-chemical methods and dynamics simulations.
Table 1 - Systems that we have investigated using the excited-state dynamics methods described in this thesis.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Subject</th>
<th>Level</th>
<th>Ref.</th>
<th>Paper</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene</td>
<td>Internal conversion</td>
<td>FOMO/AM1</td>
<td>75,76</td>
<td>9</td>
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<tr>
<td>Methaniminium cation</td>
<td>Internal conversion</td>
<td>MR-CISD</td>
<td>77</td>
<td>5</td>
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<tr>
<td></td>
<td>Internal conversion</td>
<td>CASSCF</td>
<td>78</td>
<td>7</td>
</tr>
<tr>
<td>Sylaethylene</td>
<td>Internal conversion</td>
<td>MR-CISD</td>
<td>79</td>
<td>8</td>
</tr>
<tr>
<td>6-Aminopyrimidine</td>
<td>Internal conversion</td>
<td>MR-CISD</td>
<td>78</td>
<td>7</td>
</tr>
<tr>
<td>9H-Adenine</td>
<td>Internal conversion</td>
<td>CASSCF</td>
<td>53</td>
<td>3</td>
</tr>
<tr>
<td>PSB3</td>
<td>Internal conversion</td>
<td>MR-CISD</td>
<td>77</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Internal conversion</td>
<td>MR-CISD</td>
<td>82,83</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Internal conversion</td>
<td>CASSCF</td>
<td>81</td>
<td>4</td>
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<tr>
<td>Isomerization</td>
<td>RI-CC2</td>
<td>77</td>
<td>5</td>
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<td>Isomerization</td>
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<td>MR-CISD</td>
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<td></td>
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<td>Internal conversion</td>
<td>CASSCF</td>
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<td>Internal conversion</td>
<td>MR-CISD</td>
<td>54</td>
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<td></td>
<td>Hot ground state</td>
<td>CASSCF</td>
<td>38</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Hot ground state</td>
<td>GVB-PP</td>
<td>38</td>
<td>1</td>
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<tr>
<td>Formamide</td>
<td>Internal conversion</td>
<td>CASSCF</td>
<td>85,86</td>
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<td>Protonated formamide</td>
<td>Internal conversion</td>
<td>CASSCF</td>
<td>87</td>
<td></td>
</tr>
<tr>
<td>Butatriene cation</td>
<td>Internal conversion</td>
<td>CASSCF</td>
<td>77</td>
<td>5</td>
</tr>
<tr>
<td>HBT</td>
<td>ESIPT</td>
<td>TD-DFT</td>
<td>34,88</td>
<td>3</td>
</tr>
<tr>
<td>HBQ</td>
<td>ESIPT</td>
<td>TD-DFT</td>
<td>34</td>
<td>3</td>
</tr>
<tr>
<td>BP(OH)$_2$</td>
<td>ESIPT</td>
<td>TD-DFT</td>
<td>89</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ESIPT</td>
<td>RI-CC2</td>
<td>89</td>
<td></td>
</tr>
<tr>
<td>Pyrazine</td>
<td>Spectrum</td>
<td>CASSCF</td>
<td>77</td>
<td>5</td>
</tr>
<tr>
<td>Biphenyl</td>
<td>Spectrum</td>
<td>TD-DFTB</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>Terphenyl</td>
<td>Spectrum</td>
<td>TD-DFTB</td>
<td>90</td>
<td></td>
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ESIPT – Excited-state intramolecular proton transfer; FOMO – Fractional-occupation of molecular-orbitals method; GVB-PP – perfect-pairing generalized valence bond; PSB$n$ – protonated Schiff base with $n$ double bonds; HBT – 2-(2'-hydroxyphenyl)benzothiazole, HBQ – 10-hydroxybenzo[h]quinoline; BP(OH)$_2$ – 2,2'-bipyridyl-3,3'-diol.
2. Methods and Programs

2.1 Mixed quantum-classical dynamics methods

The core of all MQCD methods\textsuperscript{46,47,93} is to treat the nuclei classically by solving the Newton’s equation for each nucleus \( I \)

\[
- \nabla_R E = M_j \frac{d^2 R_I}{dt^2},
\]

where \( E \) is the potential energy surface, which will depend on the specific MQCD method as discussed below. The electrons are at same time quantum-mechanically treated by solving the time-dependent electronic Schrödinger equation

\[
\frac{i \hbar}{\partial t} \psi = H_e \psi,
\]

where \( \psi \) is the electronic wave function and \( H_e \) the electronic Hamiltonian.

To go beyond the adiabatic approximation and recover the coupling between the electronic states, we proceed by expanding \( \psi \) in the orthonormal basis \( \{ \psi_i \} \)

\[
\psi(r, R, t) = \sum_i c_i(R, t) \psi_i(r; R(t)).
\]

where the electronic wavefunctions \( \psi_i = \psi_i(r; R) \) depend on the electronic coordinates \( r \) and parametrically on the nuclear coordinates \( R \).

Substituting Eq. (3) in (2), multiplying from the left by \( \psi_k^* \), and integrating over the electronic coordinates we get a set of differential equations for the coefficients \( c_k \)

\[
\dot{c}_k = -\sum_i c_i \left( \frac{i}{\hbar} H_{ki} + \left\langle \psi_k^* \left| \frac{\partial}{\partial t} \psi_i \right. \right\rangle \right).
\]

These equations couple the electronic states \( k \) and \( i \) through the non-diagonal Hamiltonian term \( H_{ki} = \langle \psi_k^* | H_e | \psi_i \rangle \) and the time-derivative coupling term \( \langle \psi_k^* | \dot{\psi}_i \rangle \). The time-derivative coupling term can be conveniently written as\textsuperscript{94}
\[
\begin{align*}
\left\langle \psi_k, \frac{\partial}{\partial t} \psi_i \right\rangle &= \mathbf{R} \cdot h_{ki},
\end{align*}
\]  

(5)

where \( \mathbf{R} \) is the nuclear velocity vector and \( h_{ki} \) is the non-adiabatic coupling vector between the electronic states \( k \) and \( i \), defined for each atom \( I \) as

\[
h_{ki}^I \equiv \left\langle \psi_k^I \left| \nabla_{\mathbf{R}_I} \psi_i^I \right. \right\rangle.
\]

(6)

Here, the gradient operator acts on the nuclear coordinates \( \mathbf{R}_I \).

Eq. (4) can be further simplified depending on the specific representation of \( \psi_i \). In particular, in the diabatic representation \( h_{ki} = 0 \) and in the adiabatic representation \( H_{ki} = 0 \). In our current MQCD implementation, only the adiabatic representation is used and the final result for the electronic time evolution is

\[
\dot{c}_k = -\sum_i c_i \left( \mathbf{R} \cdot h_{ki} \right).
\]

(7)

A formulation of the MQCD dynamics in terms of local-diabatic representation can be found in Ref. \cite{95} and comparisons between the results obtained under both representations can be found in Ref. \cite{46}.

In the Newton’s equations [Eq. (1)], we assume that the nuclei move on the electronic surface \( E = \left\langle \phi \left| H \right| \phi \right\rangle \). Substituting the electronic wavefunction given in Eq. (3) into \( E \) and inserting the result into the Newton’s equations, we obtain

\[
-\nabla_{\mathbf{R}_I} \sum_k |c_k|^2 E_k = M \frac{d^2 \mathbf{R}_I}{dt^2},
\]

(8)

Here the adiabatic representation was assumed and, therefore, \( E_k \) is the Born-Oppenheimer energy \( \left\langle \psi_k \left| H \right| \psi_k \right\rangle \). According to Eq. (8), the nuclei move classically in the average potential weighted by the state populations \( |c_k|^2 \). If this averaged potential is used, the MQCD method is called Ehrenfest or Mean Field approach.\cite{47} In the Surface Hopping approach instead, a swarm of independent trajectories is run, each one moving always in a single state \( k = l \). (\( l \) can change along the trajectory, as will be explained below.) The effect of the population \( |c_k|^2 \) appears not in one trajectory, but statistically in the swarm of trajectories. To guarantee the correct distribution of trajectories among the states, Eq. (4) is integrated for each time step and the \( c_k \)'s are obtained. The transition probability between each pair of electronic states is evaluated and a stochastic algorithm decides whether the system remains on the same
electronic surface or hops to another one. Therefore, if a swarm of trajectories with the same initial condition is started, they start to diverge soon due to the stochastic nature of the algorithm and the fraction of trajectories in each state (occupation) develops toward the average value of $|k_i|^2$ over all trajectories.

There are several recipes for computing the transition probabilities.\textsuperscript{94,96,97} Probably the most common is the Fewest-switches algorithm proposed by Tully.\textsuperscript{94} In this algorithm, the number of hoppings within one time step $\Delta t$ is minimized. Under this condition, the hopping probability between states $k$ and $j$ is

$$P_{k \rightarrow j} = \max \left[ 0, 2 \text{Re} \left( c_k^* c_j \right) \mathbf{R} \cdot \mathbf{h}_{jk} |c_k|^2 \Delta t \right].$$

The main assumption underlying the Surface Hopping methods is that the results of a large number of independent trajectories do correspond to the full quantum result. Naturally, it is not expected that the method could reproduce non-local features like recurrences of the wavepacket. Nevertheless, it is desirable that the occupation of each state, defined as the fraction of trajectories at each state as a function of time, corresponds to the evolution of the quantum population of each state, as stated above. Direct comparisons between Surface Hopping, Multiple Spawning and full quantum treatments have shown the existence of cases with both excellent and very bad agreement.\textsuperscript{48,50,94,98} Since the full quantum result is normally unavailable, one common test is the comparison between the occupation and the population

$$a_j(t) = \left\langle |c_j(t)|^2 \right\rangle,$$

where the average is performed over all trajectories.

It has been shown that the divergence between occupation and average population can occur in cases where the number of frustrated hoppings (hoppings that cannot take place because there is not enough available energy) is particularly large.\textsuperscript{47,99} Granucci and Persico\textsuperscript{100} have recently shown that the origin of the problem is connected to the lack of decoherence in the Surface Hopping. As usual, a quantum-mechanical system coupled to external degrees of freedom is expected to evolve from a pure state to a statistical mixture.\textsuperscript{2} This phenomenon is governed by the evolution of the density matrix, with the non-diagonal terms quickly dropping down to zero. The fact that this is not take into account in the MQCD methods is a general problem, which can be corrected in an ad hoc way.\textsuperscript{100,101}

As a summary, the methodological basis of the MQCD methods involves three different steps:

1. To find the new nuclear arrangement by integrating the Newton’s Equations for one time step.
2. To solve the time-independent electronic Schrödinger equation at a given time step in the nuclear frame of step 1 and to compute electronic energies, energy gradients, nonadiabatic couplings, etc.

3. Still in the same nuclear frame, to use the information from step 2 to integrate the time-dependent electronic Schrödinger equation and to use the information of steps 2 and 3 to restart step 1.

Practical issues for the implementation of these methods will be discussed in the next section.

2.2 The NEWTON-X program package

We have developed the NEWTON-X package\textsuperscript{73,74} (see detailed description of the program in Paper 5) as a general tool for dynamics simulations, easy and practical to use, allowing the user to choose among the most common options and algorithms. At the best of our knowledge, the NEWTON-X package is the first publicly available general program oriented to MQCD methods. The package works interfaced to third-party electronic-structure programs and its modular architecture allows for the easy development of new interfaces and the inclusions of new methods. NEWTON-X results from the collaboration between our group in Vienna and M. Persico and G. Granucci in Pisa. The surface-hopping routines were rewritten from previous programs developed by the Italian group\textsuperscript{95} and integrated in a large frame of other programs, which have been mainly planned and developed by the author, providing the tools for tasks ranging from the input generation, over the dynamics propagation, to the statistical analysis of the results.

The program is designed to execute two main tasks:

1) Mixed quantum-classical dynamics simulations.

2) Semi-classical simulation of electronic spectra (absorption and emission).

In the dynamics simulation module, the nuclear motion is represented by classical trajectories computed by numerical integration of Newton’s equations using the velocity-Verlet algorithm.\textsuperscript{102} Temperature influence can be added by means of the Andersen thermostat.\textsuperscript{103} The molecule is considered to be in some specific electronic state at any time and the nuclear trajectory is driven by the gradient of the potential energy surface of this state.

Imposing the electronic wavefunction to obey the time-dependent Schrödinger equation, the transition probability to jump from one potential surface to another can be obtained on the
basis of either Tully's fewest switches algorithm\textsuperscript{46,94} or the modified fewest-switches algorithm proposed by Hammes-Schiffer and Tully.\textsuperscript{96} In either case the decoherence correction developed by Granucci and Persico\textsuperscript{100} can be applied. These algorithms statistically decide in which electronic state the system will stay in the next time step. There is no limitation on the number of states that can be simultaneously propagated.

In the module for simulation of spectra, the program prepares an adequate ensemble of nuclear geometries and momenta in the ground or excited state and the spectra are simulated employing a similar approach as described in Refs. \cite{2,104}. The ensemble can be generated either by using some previously performed dynamics or by random sampling according to harmonic oscillator distributions. Oscillator strengths and energy gaps are then evaluated for each point of the ensemble (post-Condon approach). After that, the spectrum is obtained by computing the electronic contribution for the electronic transition probability according to the Einstein coefficients for absorption or emission. Further planned development work for this module includes time-dependent simulation of the spectra and simulation of pump-probe spectra.\textsuperscript{2}

As already mentioned before, NEWTON-X has been developed in a highly modular way, with several independent program modules (Perl and Fortran 90) communicating via files. At each integration step of Newton’s equations, NEWTON-X invokes a suitable external quantum chemistry program and obtains the necessary quantities, such as electronic energies, energy gradients, and non-adiabatic coupling vectors. In principle, any program that can supply analytical energy gradients and eventually analytical non-adiabatic couplings is eligible. For the time being, interfaces are provided for the quantum chemistry packages COLUMBUS\textsuperscript{105,106}, TURBOMOLE,\textsuperscript{107} and DFTB.\textsuperscript{108} Interfaces to the ACES II package\textsuperscript{109} and GAUSSIAN\textsuperscript{110} are under development and some others are planned. A summary of the available and planned interfaces is given in Table 2.

Normally, the adiabatic and non-adiabatic simulation of photochemical or photophysical processes requires the execution of a rather large number of trajectories. In the current implemented approaches, each trajectory is completely independent of the others. Nevertheless, after having all trajectories completed, the data must be retrieved and stored in such a way that all quantities of interest, such as quantum yields, state populations, and internal coordinates can be computed as averages over all trajectories. NEWTON-X provides routines to generate ensembles of initial conditions for initiating several independent
trajectories, to control the input and output of multiple trajectories, and to perform the required statistical analysis.

Table 2 - Interfaces between NEWTON-X and other third-party programs.

<table>
<thead>
<tr>
<th>Method</th>
<th>Third-Party program</th>
<th>Dynamics</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Classical</td>
<td>MQCD</td>
<td></td>
</tr>
<tr>
<td>MRCl</td>
<td>COLUMBUS</td>
<td>Implemented</td>
<td>Implemented</td>
<td></td>
</tr>
<tr>
<td>MCSCF</td>
<td>COLUMBUS</td>
<td>Implemented</td>
<td>Implemented</td>
<td></td>
</tr>
<tr>
<td>(TD)DFT</td>
<td>TURBOMOLE</td>
<td>Implemented</td>
<td>x</td>
<td></td>
</tr>
<tr>
<td>RI-CC2</td>
<td>TURBOMOLE</td>
<td>Implemented</td>
<td>x</td>
<td></td>
</tr>
<tr>
<td>(TD)DFTB</td>
<td>DFTB</td>
<td>Implemented</td>
<td>x</td>
<td></td>
</tr>
<tr>
<td>Analytical models</td>
<td>Pre-built/User provided</td>
<td>Implemented</td>
<td>Implemented</td>
<td></td>
</tr>
<tr>
<td>MCSCF</td>
<td>GAUSSIAN</td>
<td>Under tests</td>
<td>Under tests</td>
<td></td>
</tr>
<tr>
<td>FOMO-AM1</td>
<td>MOFPAC</td>
<td>Under tests</td>
<td>Under tests</td>
<td></td>
</tr>
<tr>
<td>EOM-CC</td>
<td>ACES II</td>
<td>Under tests</td>
<td>Planned</td>
<td></td>
</tr>
<tr>
<td>QM/MM</td>
<td>QMMM</td>
<td>Planned</td>
<td>Planned</td>
<td></td>
</tr>
<tr>
<td>(TD)DFTB</td>
<td>DFTB+</td>
<td>Planned</td>
<td>x</td>
<td></td>
</tr>
<tr>
<td>MCSCF</td>
<td>MOLPRO</td>
<td>Planned</td>
<td>Planned</td>
<td></td>
</tr>
<tr>
<td>CASPT2</td>
<td>MOLPRO</td>
<td>Planned</td>
<td>x</td>
<td></td>
</tr>
<tr>
<td>MCSCF</td>
<td>MOLCAS</td>
<td>Planned</td>
<td>x</td>
<td></td>
</tr>
</tbody>
</table>

Besides the new interfaces, the development and implementation of new algorithms is planned as well. A number of them are schematically shown in Table 3 together with already implemented methods. Due to the modularity features, some of these methods correspond to simple technical modifications of the current code, as in the case of the Andersen-Lowe thermostat. Other methods demand more extensive extension of the code, as is the case of the local diabatization method, which should solve problems related to the dynamics very close to the singularities caused by conical intersections.

Note that the calculation of the probabilities according to Eq. (9) requires the computation of the non-adiabatic coupling vector $h_{jk}$. This quantity is particularly demanding and, in principle, it should be computed for every pair of electronic states, which means that for a problem involving $K$ states, $K(K-1)/2$ couplings vectors should be computed. The computational cost can be alleviated by specific algorithms to skip the coupling vector computation when the energy gap is larger than some pre-determined threshold or between non-consecutive states. A number of these algorithms are already implemented in NEWTON-X.

In the near future, we intend also to implement the “adiabatic hopping” algorithm, an inexpensive method for computing the hopping probabilities, although probably not so precise as the fewest-switches approach. In collaboration with J. Pittner (Prague), the direct computation of the time-derivative couplings in terms CI-vector overlaps is being implemented. This has the potential to speed up the calculations mainly in the MCSCF
dynamics. The possibility of implementation of a surface-hopping algorithm allowing the computation of transition probabilities between states of different multiplicities is also being considered. Finally, the decoherence-corrected Mean-Field (Ehrenfest) approach will also be implemented.101

Table 3 - Hierarchy of main methods and algorithms implemented in the NEWTON-X program. Gray cells indicate methods whose implementation is planned.

<table>
<thead>
<tr>
<th>Dynamics</th>
<th>Classical</th>
<th>MQCD</th>
<th>DC-Surface-hopping</th>
<th>Fewest-switches</th>
<th>EDA</th>
<th>Andersen-Lowe Thermostat</th>
<th>Time-derivat. couplings</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MQCD</td>
<td>DC-Surface-hopping</td>
<td>Fewest-switches</td>
<td>EDA</td>
<td>Andersen-Lowe Thermostat</td>
<td>Time-derivat. couplings</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Classical</td>
<td>MQCD</td>
<td>DC-Surface-hopping</td>
<td>Fewest-switches</td>
<td>EDA</td>
<td>Andersen-Lowe Thermostat</td>
<td>Time-derivat. couplings</td>
</tr>
<tr>
<td>Spectrum / Initial conditions</td>
<td>Classical HOD</td>
<td>Quantum HOD</td>
<td>Previous dynamics</td>
<td>Random velocities</td>
<td>Absorption</td>
<td>Emission</td>
<td>TD spectrum</td>
</tr>
</tbody>
</table>

MQCD – Mixed quantum-classical dynamics; HOD – Harmonic oscillator distribution; DC – Decoherence corrected;100,101 S/T – singlet/triplet hoppings; EDA – Essential dynamics analysis.112

Typical photochemical reactions proceed in specific environments in condensed phase (external fields, solvents, crystal matrices, protein pockets) and the effect of such environments should be included in the dynamics simulations. This influence in the non-adiabatic deactivation is still not sufficiently understood and it has only recently started to be addressed.12,57,91,113-116 Since it is out of question to treat thousands of atoms quantum mechanically, the inclusion of the environmental effects in the investigations is mainly done by means of hybrid methods, such as the QM/MM approach.117-119 The implementation of hybrid methods is possibly the most important development planned for NEWTON-X in the near future. They will not only extend the range of applications, but also allow more realistic simulations. An electrostatic embedding approach is currently being developed in our group by M. Ruckenbauer and it will allow performing the dynamics of the chromophore at a quantum-mechanical level while treating the solvent as point charges. An important step further will be the implementation of full QM/MM approaches. Since our focus is on excited-state dynamics, the approach must be based on additive schemes.117-119 There are several QM/MM implementations available and we are studying to interface NEWTON-X with one of them. A promising possibility is to use the QMMM program developed in the Truhlar’s group.120 The modularity of this program as well as the large set of options for treating the
boundary between the QM and MM regions make it a good candidate for the kind of applications that we are aiming at.
3. Applications to photochemical and photobiological problems

The application of conventional quantum-chemistry and of dynamics methods to the investigation of several systems along the last years has allowed us to understand in great detail many different aspects of photophysical and photochemical processes in organic molecules. In this Chapter, some of these aspects will be highlighted. This general discussion is a survey of the work published in Papers 1 and 2.

In a simple way, conical intersections happen when the upper state is stabilized, the lower state is destabilized or, more usually, when both situations occur. Conical intersections between the ground and the first excited state occur at strongly deformed nuclear geometries. The reason for that is that the initial stabilization of excited system usually finds a local minimum in the excited state still close to the Franck-Condon (FC) region. At this “spectroscopic minimum”1 the destabilization of the ground state is not strong enough to cause the degeneracy. Additional relaxation of the excited state is necessary to reach the region of crossing between the states.

In our work, we have made a large effort to find similarity patterns in the set of molecules that we have investigated. This kind of approach has paid off by first showing that, as we shall discuss in the Section 3.1, it seems that only few different stabilization mechanisms are responsible for driving the dynamics towards the conical intersections. And second, by showing that these mechanisms are in competition among themselves and, as we shall see in Section 3.2, the efficiency of each one of them will deeply depend on the particular features of the excited state surface of the investigated system.

3.1 Mechanisms giving rise to conical intersections

Supposing that the main character of the excited-state wavefunction is a single excitation, the stabilization of the excited state can be simply rationalized as the minimization of the electrostatic repulsion of these two aligned but non-bonded electrons. This is simple to understand in ethylene and substituted ethylenes. There, the stabilization of the $\pi\pi^*$ state is given by the torsion around the main axis. Along the torsion, however, the closed-shell (CS) configuration is destabilized because it is pulling apart aligned and bonded electrons.
Assuming the main contribution for the ground state is the CS configuration, this means that along the torsional path the excited state is stabilized and the ground state destabilized, as expected for the formation of conical intersections.

Normally, after the full 90° torsion, there is still an energy gap between the states. As has been analytically demonstrated by Michl, Bonačič-Koutecký, and Koutecký,\textsuperscript{1,121} this energy gap depends on the difference of the electronegativities between the two atoms of the main axis. For a non-polar system, the gap can be as large as 3 eV as it is in the case of ethylene (see Fig. 4 in Paper 10), while it is very small for \( \text{CH}_2\text{NH}_2^+ \) (see Fig. 2 in Paper 7). Since the gap depends on the electronegativity difference, it can be modified by the application of external electromagnetic fields\textsuperscript{122}, by solvation effects\textsuperscript{123}, or – what is the most important case for the current discussion – by activation of other internal modes simultaneously to the torsion. In ethylene for instance this happens by activating the pyramidalization, hydrogen migration, and scissoring modes.\textsuperscript{1,49,124-127}

Fig. 1. Examples of conical intersections for various systems and the relation with the primitive conical intersections (thick lines). (a) HBT\textsuperscript{88}: twisted; (b) Pyrrole\textsuperscript{128}: stretched-bipyrimalized; (c) 4MCF\textsuperscript{129}: twisted-pyramidalized; (d) Pyridone\textsuperscript{84} and (e) formamide\textsuperscript{86}: out-of-plane O.
Besides torsion, our dynamics simulations have revealed another mechanism that can have similar influence for the decrease of the $S_1-S_0$ energy gap in substituted ethylenes, the stretching of the main bond\textsuperscript{77-79} (see also Papers 7 and 8). In this case, however, although the strong destabilization of the ground state is observed for the same reason as before, the excited state is not stabilized to a large extent because of the breaking of the $\sigma$ bond. As before, the activation of other modes, in particular, the bi-pyramidalization, can still bring the system to the conical intersection (see Fig. 2 in Paper 1).

Table 4 - Primitive conical intersections.

<table>
<thead>
<tr>
<th>Conical intersection</th>
<th>Structure</th>
<th>Examples</th>
</tr>
</thead>
</table>
| Twisted                       | \[
\begin{array}{c}
R_1 \\
X \\
C \\
R_3 \\
R_4 \\
R_2 \\
\end{array}
\] | Polar substituted ethylenes (e.g. CH$_2$NH$_2$\textsuperscript{78,130}) PSB$_3$, PSB$_4$\textsuperscript{127} HBT\textsuperscript{36} |
| Twisted-pyramidalized         | \[
\begin{array}{c}
R_1 \\
X \\
C^* \\
R_4 \\
R_3 \\
R_2 \\
\end{array}
\] | Ethylene\textsuperscript{124,125,127} 6-membered rings (e.g. aminopyrimidine\textsuperscript{38}) 4MCF\textsuperscript{129} Stilbene\textsuperscript{131} |
| Stretched-bipyramidalized     | \[
\begin{array}{c}
R_1 \\
X \\
\text{C} \\
R_3 \\
R_4 \\
R_2 \\
\end{array}
\] | Polar substituted ethylenes\textsuperscript{78,130} Formamide\textsuperscript{86} 5-membered rings (e.g. pyrrole\textsuperscript{128}) |
| H-migration/carbene           | \[
\begin{array}{c}
R_1 \\
C \\
\text{H} \\
R_3 \\
R_2 \\
\end{array}
\] | Ethylidene\textsuperscript{124,125,127} Cyclohexene\textsuperscript{132} |
| Out-of-plane O                | \[
\begin{array}{c}
R_1 \\
\text{C} \\
\text{O} \\
R_3 \\
R_2 \\
\end{array}
\] | Formamide\textsuperscript{86} Pyridone\textsuperscript{38} Cytosine\textsuperscript{133,134} |
| Bond breaking                 | \[
\begin{array}{c}
R_1 \\
\text{X} \\
\text{Y} \\
R_2 \\
\end{array}
\] | Heteroaromatic rings (e.g. pyrrole\textsuperscript{135}, adenine\textsuperscript{136}) |
| Proton transfer               | \[
\begin{array}{c}
X \\
\text{H} \\
R_1 \\
R_2 \\
\end{array}
\] | Watson-Crick base pairs\textsuperscript{11,12} |

Sobolewski, Domcke and co-workers\textsuperscript{135-141} have shown the existence and discussed in details the existence of an important basic mechanism producing conical intersections, the H-detachment. Different from the previous two mechanisms, which involve either the $\pi\pi^*$ or the
π\* states, along the H-detachment path the πσ\* state is stabilized until crossing the ground state. Recently, examples of πσ*/S0 conical intersections for the N-C and S-C bond breakings have been reported for adenine\(^{140}\) and thiophene\(^{142}\), showing that this kind of mechanism is rather general and it is not limited to the hydrogen atom detachment.

Sobolewski and Domcke have also discussed how the hydrogen transfer mechanism can produce conical intersections by means of the stabilization of the charge-transfer ππ\* state. In several examples of excited-state proton transfer such process is not enough to cause degeneracy of states\(^{34,143,144}\). Nevertheless, in the particular case of the Watson-Crick base pairs the energy gap can be substantially reduced to bring the system to a region close to the conical intersection or at least to a region with high internal conversion rates\(^{11,12,14}\).

There are still two other basic mechanisms leading to conical intersections. One is the hydrogen migration, which gives rise to carbene formation like in the ethylidene isomer of ethylene (\(:\text{CHCH}_3\)\(^{127}\). The second is the out-of-plane deformation of the oxygen atom in aldehyde and carboxyl groups\(^{84,86,133,134}\).

The resulting structures of each one of these mechanisms compose a set of “primitive conical intersections”, in the sense that if a conical intersection is found for a large and complex system, one of these primitive conical intersections will be the underlying structure causing the degeneracy. They are shown in Table 4 and some examples are given in Fig. 1. This set is certainly not complete and somewhat arbitrary. New primitive conical intersections could be added to it and eventually some primitive conical intersections, such as the stretched-bipyramidalized and the bond-breaking, could perhaps be grouped together. The importance of this set is, however, to provide a general tool-kit for searching and characterizing conical intersections in large systems. In this context, puckered conical intersections in six-membered rings, for example, can be identified with the torsional primitive conical intersection\(^{38,80}\) (see also Paper 4). The ring-puckered conical intersection in pyrrole, can be identified with the stretched-bipyramidalized primitive conical intersection\(^{128}\) (see Figs. 1.7 and 1.8 in Paper 2). The H-migration conical intersection in cyclohexene is an example of a carbene primitive intersection\(^{132}\). Some of the conical intersections in formamide\(^8\), pyridone\(^{38}\), and cytosine\(^{133,134}\) for example, show the out-of-plane oxygen atom primitive conical intersection structure.

These excited-state stabilization mechanisms may co-exist for the same system. The question that arises is how they are selected in the course of the dynamics. We are going to discuss this point in the next section.
3.2 Efficiency of multiple mechanisms

In general, the molecular system has several available reaction paths in the excited state. There are many factors contributing to the efficiency of a number of these paths over the others. Some of these factors, such as the relation between initial energy and the energy of the conical intersection or the existence of barriers along the path, are obvious and are largely explored in the literature. Other factors also influencing in the efficiency of the path are the shape of the surface near the crossing seam region beyond the linear approximation, the initial slope of the path at the Franck-Condon region, and the distance between the Franck-Condon region and the conical intersection.

During the dynamics on the excited-state surface, the molecule follows different pathways until eventually finding the region of the intersection seam. From a classical point of view, the swarm of trajectories can either form a narrow distribution along a minimum energy path or can diverge and broadly spread in the configuration space. Our investigations on a variety of systems have shown that both situations may occur depending not only on the system, but also on the initial surface and occasional restrictions to the motion.

To illustrate this point, consider the dynamics of the methaniminium cation (CH$_2$NH$^+$). When the dynamics starts in the S$_1$ state, the torsional motion is the main mechanism driving the trajectories. This characterizes the first situation in which the trajectories are concentrated in a small region of the configuration space. If, however, the dynamics starts in the S$_2$ state, the trajectories split in two types, those showing torsional motion and those showing stretching-bipyramidalization (see Fig. 4 in Paper 5). This means that the trajectories are now distributed over a larger region of the configuration space. The same kind of splitting of trajectories between the torsional and the stretching-bipyramidalization mechanism has been also observed in the dynamics of silaethylene starting in the S$_1$ state. (See animations at homepage.univie.ac.at/mario.barbatti, CSiH4 movies.)

When the excited state isomerization occurs through different mechanisms this implies that the molecular system may end up in different regions of the crossing seam. In substituted ethylenes, with the splitting between torsional and stretching-bipyramidalized types of trajectories, this correlation is direct. For instance, torsional trajectories normally return to the ground state at the twisted conical intersection. But the type of trajectory does not entirely determine the type of conical intersection that will be accessed. We have observed that to reach the conical intersection, the molecule needs to hold a very specific set of internal coordinates. For example, when the CH$_2$NH$^+$ reaches 90° its CN distance is not that leading
to a degeneracy, it can just move to other regions of the configuration space and deactivate in a different conical intersection later. (See animation at homepage.univie.ac.at/mario.barbatti, CNH4+ stating in the S1 state movie.) For this reason, the shape of the potential energy surface around the conical intersection plays a very important role.

![Diagram](image)

Fig. 2. Characterization of one single trajectory in the dynamics simulation of adenine in terms of the Cremer-Pople parameters $\theta$ and $\phi$. The conical intersections of adenine are indicated by crosses. The dots are 0.5 fs apart. The geometry at the hopping time is also shown.

In aminopyrimidine, for example, the trajectories remain “trapped” a long time around out-of-plane deformations about $C_4$ (see Figure 9 in Paper 1 and the discussion there) and this gives the system time to find the “right” coordinates that tune the conical intersection. If the shape is not favorable, the molecule can quickly move near the conical intersection and exit to other regions of the configuration space before deactivating. This “trapping effect” can be observed in Fig. 2. The Cremer-Pople parameters $^{145}$ $\theta$ and $\phi$ are given along a single trajectory for 9H-adenine starting in the $S_3$ state. $^{53}$ The $\theta$ and $\phi$ parameters describe the type of puckering in the pyrimidine ring. In the $\theta$-$\phi$ space there are several different conical intersections and in this particular trajectory, adenine moves along a sequence of conformations with conical intersections ($^{3}S_4$, $^{3}H_4$, …) without hopping. The reason for this behavior is the lack of “right” coordinates. When adenine is in the half-chair $^{3}H_2$ conformation, for example, the degree of puckering (not shown) is relatively small, $Q \approx 0.2 \text{ Å}$, and the energy gap is not significantly
reduced until having $Q \approx 0.5$ Å. If the shape of the $S_1$ surface were such that adenine remained trapped near the $3H_2$ conformation, it could eventually tune the right value for the conical intersection and decay there. What occurs, however, is that adenine does not remain time enough in the $3H_2$ conformation and changes to the $E_2$ envelope conformation. As can be seen in Fig. 2, adenine is trapped in this last conformation and moves there until the hopping to the ground state takes place. (See animation at homepage.univie.ac.at/mario.barbatti, adenine movie.)

Fig. 8 of Paper 1 shows the distribution of the $\theta$ and $\phi$ parameters for aminopyrimidine at the hopping time. Taking for example the dynamics starting in the $S_2$ state, we can see that the hopping can occur at any part of the crossing seam between the $2E$ and $4E$ envelope conformations. We also see that conical intersections with the $1S_6$ screw-boat conformation are simply not accessed although the barrier between the minimum in the excited state and this intersection seam is only about 0.1 eV. This means that several possible pathways in the excited state are in competition, which can have important consequences for the photoproducts. We can extract two main methodological implications from this fact. First, dynamics simulations can provide a type of information that conventional determination of surface extremes and reaction paths can barely touch. Second, the necessity of simulation of multiple trajectories goes beyond the requirement of the non-adiabatic dynamics expressed in Eq. (8): the simple adiabatic dynamics in the excited state demands multiple trajectories in order to access the information on the efficiency of the multiple paths.

Up to now, we have investigated the efficiency of the mechanisms based on concepts like the tuning of right coordinates or the trapping effect in some regions of the surface, as discussed above. We have designed specific new research subjects to deal with other aspects of the efficiency of multiple paths. The competition between the H-detachment path and the ring-opening path is being explored now for pyrrole. The effect of the distance between the FC region and the conical intersection has been investigated in aminopyrimidine and adenine. The effect of energy barriers has been investigated using “biased” dynamics simulations for pyridone. The influence of the initial slope has been investigated in the dynamics of protonated formamide. With the exception of pyrrole, whose work is still in progress, these other examples should appear in the next months.
4. Description of the selected papers

A set of ten papers was selected to compose this thesis. They are representative of the work that the author has developed in Vienna in the last years. A brief description of each one (in reverse chronological order) is given below.

As required by the regulations for Habilitation in the University of Vienna, a statement about the effective participation of the author of this thesis in each publication is also given. This is accomplished by the following color code:

<table>
<thead>
<tr>
<th>Color code</th>
<th>Description</th>
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<tbody>
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In this invited paper, a comprehensive review about non-adiabatic processes in substituted ethylenes, protonated Schiff bases and heteroaromatic rings is given. We have made an effort to generalize the results of several different dynamics investigations to rationalize the common mechanistic aspects shared by all these different systems. The result is surveyed in the discussions of Section 3.1 and 3.2 above.

**Contributions of M.B.**

<table>
<thead>
<tr>
<th>Research design</th>
<th>Calculations</th>
<th>Data analysis</th>
<th>Writing</th>
<th>Corresp. author</th>
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In this book chapter, the dynamics of heteroaromatic systems is discussed focusing on different aspects: excited state relaxation, S_1-S_0 deactivation, and dynamics in the hot ground state. By investigating these different aspects we tried to illustrate how MQCD methods can be applied to the investigation of nucleobases.

**Contributions of M.B.**

<table>
<thead>
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</table>

This work presents the first results of the collaboration with the experimental group of E. Riedle (Munich). Classical dynamics (Vienna), wavepacket dynamics (Munich) and time-resolved spectroscopy (Munich) are combined to explain the proton transfer in HBT and HBQ. A detailed picture of the ESIPT process in HBT and HBQ is given, showing how the distortions in the molecular frame trigger the transfer. A second theoretical/experimental paper is being prepared to discuss the torsional dynamics of HBT after the ESIPT.

**Contributions of M.B.**

<table>
<thead>
<tr>
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<th>Writing</th>
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The similarities between aminopyrimidine (6AP) and adenine (Ade) are explored to gain insight on the deactivation of the nucleobase. We have shown that the excited 6AP deactivates in about 400 fs. The conical intersections used, however, are not energetically available in Ade because of the imidazole group restrictions. By imposing mechanical restrictions at two H atoms to simulate the presence of the imidazole, the lifetime increases to 1 ps and occurs by puckering at the C_2 atom, which is consistent with Ade deactivation.

**Contributions of M.B.**

<table>
<thead>
<tr>
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The NEWTON-X program is presented in this paper. To illustrate the capabilities of the program, several different examples are presented using MR-CISD, CASSCF, TD-DFT and RI-CC2 methods not only in dynamics but also in absorption spectra simulations.

**Contributions of M.B.**

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In this paper, a new deactivation path involving ring puckering has been found for pyrrole. It is discussed how this new path competes with the H-detachment path to explain the pyrrole photofragmentation. As sequence of this work, we have performed dynamics simulations for pyrrole to investigate the excited-state relaxation\(^{54}\) and the hot ground-state behavior.\(^{38}\)

**Contributions of M.B.**

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The influence of the initial excited state in determining completely different outcomes for the dynamics is discussed for the methaniminium cation. We have shown that when the dynamics starts in the S$_1$ state, the system follows torsional trajectories, while when it starts in the S$_2$ state it follows stretched-bipyramidalized trajectories. The reason for this difference is related to the momentum acquired in the initial motion in the S$_2$ state.

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In this work we observed the splitting of trajectories of silaethylene starting in the S$_1$ state into two types, torsional and stretched-bipyramidalized, similarly to that described in Paper 7 for methaniminium cation. The reason now is an extreme sensitivity to the initial conditions, which suggest the existence of chaotic behavior. The importance of the tuning of the “right” coordinates for the deactivation (see Section 3.2 above) is also discussed.

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Semi-empirical Surface Hopping dynamics was carried out to investigate the ethylene deactivation. In a previous work (Paper 10) we had mapped a large portion of the crossing seam of ethylene, showing that the twisted-pyramidalized, the H-migration and the ethylidene minima on the crossing seam were connected. In this paper, we performed a careful analysis of how important each one of these regions of the crossing seam really is for the deactivation process.

Contributions of M.B.

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High level quantum chemistry calculations were employed to characterize the potential energy surfaces of ethylene, including an extensive mapping of the crossing seam connecting several different minima on the crossing seam.

Contributions of M.B.

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5. Conclusions

Excited-state dynamics simulations in general and MQCD methods in particular are very powerful tools to design specific investigations and to shed light on the mechanistic aspects of the processes following the molecular photoexcitation. This has been our procedure in the last years in investigation of systems ranging from ethylene to molecules containing up to three aromatic rings.

These dynamics simulations are not in any sense a substitute for conventional quantum chemistry calculations. They are rather a complementary method to be used with caution to solve very specific problems in which the time is an essential variable. The MQCD methods using ab initio electronic-structure information are naturally limited to phenomena happening in the range of few picoseconds and to the quantum-mechanical treatment of only few dozen atoms. The limitations are not only due to the extremely high computational costs, but also connected to methodological limitations. In the course of dynamics, the system visits very different regions of the configuration space. It is hard to devise any method that can describe the wavefunctions and potential energy surfaces for all these regions with the same level of quality. For reasons like that, the conventional quantum chemistry approach, with determination of the extremes, cuts and optimized paths on the potential energy surfaces is still the first and mandatory step in any investigation.

The fundamental step of our research project was the development of the NEWTON-X program package. The flexibility of the program has given us the possibility of exploring photochemical processes in a very systematic and standardized way, allowing easy comparison between results obtained for different systems. As discussed in this thesis, the NEWTON-X project is far from being concluded and several important developments are planned or being implemented. The most important of them will be the possibility of include the environment effects in the excited-state dynamics.

Although the theoretical basis and model applications of the MQCD methods are available for more than twenty years, their application to systems of chemical and biological interest in their full dimensionality is a relatively new area that called for the current computational capabilities. With the very notable exception of Warshel performing mean-field dynamics for retinal as early as the middle seventies,19 most of applications date to less than ten years, and
even groups with a large experience in photochemical investigations employing conventional methods are still trying to solve basic routine problems like how to avoid undesired transformations of the CAS orbitals or how far can one go with the less than modest 3-21G basis set.

Performing dynamics for systems as big as adenine is remarkably challenging in the delicate balance between cost and quality. In this experience, we have learned for instance how to save computational time by avoiding the unnecessary computation of certain coupling vectors or how to treat the huge amount of data coming from the dynamics simulations by developing algorithms to make automatic recognition and classification of structures and trajectories. The most fascinating lessons, however, have been taught by the results themselves showing, for example, that the extremely counter-intuitive structures like the strong ring puckering in heterocycles are really responsible for the non-radiative deactivation in the sub-picosecond time scale. It is amazing to realize that this deactivation can be connected to some of the most basic facts of our evolutionary history, the selection of the nucleobases that would be part of our genetic code.
References


Acknowledgments

For the past four years I have had the pleasure of working with Hans Lischka. His active and rigorous mind, always prone to challenge you, is exactly the necessary stimulus to go beyond the routine. I have repeated to any new aspirant in our group that, different from many other places, in Vienna he will not meet the boss only in the Christmas party. On the contrary, he would get into trouble if he did not knock Lischka’s door to have a good discussion at least a couple of times a week. Hans knows how much I have knocked his door these years and I know how much I owe him.

For the stimulating and intelligent coffee-based environment I have to thank Bernhard Sellner, Daniel Tunega, Felix Passler, Jaroslav J. Szymczak, Hasan Pasalic, and Matthias Ruckenbauer. And these are only the current people in our group. I miss many others that have been with us in the last years, in particular Mario Vazdar.

There is a person in our group that deserves my special thanks: Adélia Aquino. Her skills to deal with people’s emotions together with her natural wish of helping everyone have been crucial not only for me, but, I am sure, for all of us there.

I am glad I have had the chance of collaborating with high level scientists like Giovanni Granucci, Mauricio Persico (Pisa), Jiri Pittner (Prague); with the groups of Mirjana Eckert-Maksić (Zagreb), of John Manz (Berlin), and of Eberhard Riedler (Munich). I am in debt with Christel Marian for the kind support that she has given me during my stays in Düsseldorf.

I am grateful for the technical support of Frau Jakubetz and Herr König. I also thank people in the Schrödinger II and III clusters of the University of Vienna, where the calculations have partially run.

***

Finally, Carla: she was in the “Acknowledgments” of my Master thesis ten years ago. And she was also in there in my PhD thesis six years ago. Something tells me that I would not be writing a new “Acknowledgment” now if she was not in there. Some people are blessed for having the emotional support of the partner. I could say I am doubly blessed for having from my wife’s emotional and intellectual support.

***

My work in Vienna was supported in the first year by the Brazilian Agency CNPq. In the last three years, the work has been supported by the Austrian Science Fund within the framework of the Special Research Program F16 (Advanced Light Sources) and Project P18411-N19. Additional support has been provided by the COST actions D26 and D37.
Selected papers