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FACOLTÀ DI SCIENZE MATEMATICHE, FISICHE E NATURALI

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DEVELOPMENT OF MODELS FOR QUANTUM DYNAMICAL
SIMULATIONS OF PHOTOEXCITED MOLECULES. APPLICATION TO
THE $\pi\pi^*/n\pi^*$ INTERNAL CONVERSION IN THYMINE

Tesi di Laurea Magistrale

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Corso di Laurea Magistrale in CHIMICA
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Sessione di Laurea 16 Luglio 2012

Anno Accademico 2011-2012

To Dylan Dog

Summary

This work illustrates the theoretical modeling and the results of quantum and mixed quantum-classical dynamical simulations of the $\pi\pi^* \rightarrow n\pi^*$ internal conversion in the thymine molecule. The importance of this process in the fields of photochemistry and photobiology is related to the photostability of nucleic acids. In fact, nucleobases strongly absorb UV light, undergoing electronic transitions to excited reactive $\pi\pi^*$ states, leading to potentially mutagenic effects. However, time-resolved experiments show that the $\pi\pi^*$ state is depopulated in an ultrafast (< 500 fs) time scale, and the relevance, in pyrimidine nucleobases, of its deactivation via an internal conversion to a $n\pi^*$ state, closely lying in energy, is strongly debated in literature.

For the purposes of this work, a novel methodology for the quantum dynamical study of semirigid photoexcited nonadiabatic (i. e. with electronic states close in energy) chromophores was developed and is presented here. As an original result, it is proven that, if the excited state Potential Energy Surfaces (PES) are described within the harmonic approximation, it is possible to find effective coordinates partitioned into blocks, defining a hierarchical sequence of reduced-dimensionality effective Hamiltonians to compute quantum dynamics, where the members of the hierarchy depend on a growing number of coordinates. A procedure is presented to build up this sequence of Hamiltonians, that has the property that the larger the number of effective coordinates, the longer the time scale to which the dynamics is reproduced accurately.

This is a new approach, generally applicable to the study of the excited state dynamics of semirigid molecular systems, and improves a pre-existing hierarchical model for harmonic PESs, valid only in the limit where the excited state has the same frequencies and normal modes of the ground state (in practice, quite 'rigid' assumptions, even according to the chemical intuition).

The procedure is applied here to the simulation of the $\pi\pi^* \rightarrow n\pi^*$ nonradiative transfer in thymine, exploiting different levels of accuracy for constructing the quadratic PESs of the excited states involved in the dynamics, and discussing the differences between such different approaches. The results show that the transfer is effective ($\approx 80\%$) and occurs in a time scale of ≈ 100 fs; therefore the $n\pi^*$ state is involved in the dynamics from the very beginning. The nonadiabatic absorption spectra are also computed and compared with experimental measurements.

Moreover, the convergence of the predicted population transfer and the absorption spectra, with respect to the number of coordinates included is tested and proved, so that the theoretical methodology developed reveals to be very satisfactory.

List of frequently used acronyms (alphabetical order)

| | |
|------|---|
| AH | Adiabatic Hessian. Scheme for the construction of the quadratic Potential Energy Surface for an excited state, computing its Hessian at its own equilibrium geometry |
| AS | Adiabatic Shift. Scheme for the construction of the quadratic Potential Energy Surface for an excited state, where the equilibrium geometry is reported exactly and it is assumed that the frequencies and normal modes are the same of the ground state |
| BO | Born-Oppenheimer. Approximation relative to systems where the nuclear motion can be considered separated to that of the electrons. At each geometry, the electronic states are considered isolated |
| CoI | Conical Intersection. Feature of (at least) two adiabatic Potential Energy Surfaces, which exhibit a conical topology in correspondence of a degeneration |
| CDQ | Create and Destroy Quanta. Potential terms in a second-quantized vibrational Hamiltonian which create or destroy couples of quanta ($a_i a_j$ and $a_i^\dagger a_j^\dagger$) |
| EQ | Exchange Quanta. Potential terms in a second-quantized vibrational Hamiltonian which move an excitation from a mode to another ($a_i^\dagger a_j$ and $a_i a_j^\dagger$) |
| FC | Franck-Condon. Approximation relative to an excitation process from the ground to an excited state, which considers the excitation instantaneous. Soon after the photoexcitation the molecule maintains the ground state equilibrium structure (Franck-Condon geometry) |
| LVC | Linear Vibronic Coupling. Model for the Hamiltonian of a system of coupled diabatic states, where the Potential Energy Surfaces are harmonic with the same frequencies and normal modes of the ground state, and the diabatic coupling is a linear function of the coordinates |
| PES | Potential Energy Surface. Eigenvalue of the electronic Hamiltonian. Since this latter is parametrized by the nuclear geometry, the PES is a multi-dimensional function of the nuclear coordinates |
| QVC | Quadratic Vibronic Coupling. Model for the Hamiltonian of a system of coupled diabatic states, where the Potential Energy Surfaces and the diabatic coupling are generic quadratic functions of the coordinates |
| TDSE | Time-Dependent Schrödinger Equation In this work it is solved to determine the evolution of vibrational wave packets after a photoexcitation |
| VG | Vertical Gradient. Scheme to construct the quadratic Potential Energy Surface for an excited state, computing its gradient at the Franck-Condon point, and using the same frequencies and normal modes of the ground state |
| VH | Vertical Hessian. Scheme to construct the quadratic Potential Energy Surface for an excited state, computing its gradient and Hessian at the Franck-Condon point |

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INTRODUCTION

*Anche questa sera la luna è sorta,
affogata in un colore troppo rosso e vago,
Vespero non si vede, si è offuscata,
la punta dello stilo si è spezzata.
Che oroscopo puoi trarre questa sera, Mago?*

F. GUCCINI

The interest of the chemical research in organic molecular photochemistry is rapidly growing, being related, to a large extent, to the modern technologies (photonics), the bio-medical applications (e. g. the fluorescent biosensors) and the solar energy utilization.[1]

Light-driven reactions are ubiquitous even in biological systems. Clearly, the most common process of this kind is the photosynthesis occurring in plants, by which they are able to produce glucose to feed themselves; besides, many other everyday examples of photochemical processes can be found in nature: the luminescence in fireflies, the phototropism in sunflowers and, of course, the process of vision in animals' eyes.

In addition, the photodegradation reactions which may occur in biomolecules are of great importance in the field of photobiology. In fact, many molecular 'building blocks' of life, nucleobases and amino-acids, once UV-excited, become potentially reactive toward reactions of dissociations or dimerizations, leading to possible mutagenic effects in nucleic acids or interfering with the activity of the proteins . However, as a result of molecular evolution, all these biomolecules show efficient, ultrafast internal conversion channels, which, in some cases, can depopulate the photoreactive excited states in a sub-picosecond time scale ($< 10^{-12}$ s).[2]

Experimental and theoretical approaches

In many cases, the complex molecular systems of interest, naturally or artificially designed to have tailored properties, exhibit closely-lying electronic states, like when they feature large aromatic rings. In this sense, they are nonadiabatic systems, meaning that their excited-state properties are governed by the degeneration among electronic energy levels (conical intersections).[3][4]

Most of the excited-state phenomena occurring in such molecules are vividly debated in the current literature, and routinely investigated by the experimentalists by means of steady-state UV-absorption and fluorescence.

In addition to these spectroscopic techniques, a wide range of time-resolved pump-probe experiments have been recently developed, many of them are still under development, and three-pulses spectroscopies are also becoming customary in some laboratories.[5] Briefly, a pump-probe spectroscopy requires a first pulse which excites electronically the molecule. The photoexcited system is subsequently interrogated by a second pulse that can be either sent to the sample (for example to probe its UV or IR absorption) or generated by the sample itself, for example as spontaneously emitted light. The results of these experiments are two-dimensional time-frequency spectra or correlation frequency-frequency spectra.[6]

However, although the results of time-resolved measurements are in principle richer of information, the interpretation of the multi-dimensional spectra is not straightforward at all. For this reason, such experiments need to be interplayed with theoretical studies, which should help to connect the complex spectroscopic signals with the microscopic molecular excited state dynamics which gives rise to those signals.

There are two different levels of computational methodologies for the study of the excited state phenomena: i) 'static' approaches, focused on the computation of potential energy paths, frequencies, excitation energies, reorganization energies, single-state UV vibronic spectra, and so on; ii) 'dynamical' approaches, concerning the simulation of the evolution of the photoexcited molecule in time. The essence of the latter methods is the calculation of the motion of the nuclei of a molecule, once it has undergone an electronic excitation. This motion is then reflected into steady-state and time-resolved spectra, and the nuclear dynamics can be used to compute such signals (on the contrary, it is very hard to extract information about nuclear motion from the spectra).

In this respect, many quasi-classical and semi-classical approaches for the description of the nuclear motion have been proposed in literature.[7][8] In these methods the quantum phenomenon

of internal conversion is described in terms of ‘hoppings’ between potential energy surfaces, being the probability of the hopping, at each time, proportional to the strength of the nonadiabatic couplings among the electronic states at the current geometry.

Quantum dynamical description of excited states and reduced-dimensionality models

A full quantum description of the phenomena occurring around a conical intersection is desirable for a number of aspects. First, a nonadiabatic transition is intrinsically a pure quantum phenomenon; second, the experimental counterpart to the excited-state calculations is the electronic spectroscopy, where the presence (or absence) of specific vibronic features, like vibrational progressions in steady-state and time-resolved spectra, can be very informative on the system and the process under investigation.[4][9] Even such vibronic features arise from the quantum nature of the nuclear motion and can therefore be properly described only within a full quantum mechanical computation scheme.

The quantum mechanical description of the excited-state dynamics of a molecule requires two fundamental steps:

1. **The definition of the Hamiltonian.** It requires ‘static’ calculations, whose purpose is to define the functional form and the parameters of the potential where the nuclear motion takes place. From a classical viewpoint this means to describe the nature and the entity of the forces acting on the nuclei.
2. **The wave packet evolution.** Since the motion is described at a quantum level, it is associated to the time-propagation of a wavefunction depending on the nuclear degrees of freedom. This wavefunction evolves in time according to the time-dependent Schrödinger equation.

In this work the models and the related computations are referred to *semirigid* molecules, whose motion, once they have been put out of equilibrium by the photoexcitation, has essentially a vibrational nature. Indeed, the semirigid organic molecules constitute a large class of systems of photophysical interest (for example in the field of the design of organic solar cells), usually including all the molecules featuring small cycles, single or condensed aromatic rings.

For what concerns the computational aspects, the potential of such system is usually described at the harmonic level of approximation, i. e. with a quadratic function of the coordinates. The determination of harmonic force constants for the ground and the excited states (the step 1 above) is now at hand even for large molecules (hundreds of normal modes), for instance at the Time-

Dependent Density Functional Theory (TD-DFT) level. However, the computational cost for the quantum dynamical simulations (step 2) grows heavily with the number of degrees of freedom. Therefore, when treating sizeable systems, it is necessary to establish reduced dimensionality models of the system. This means that the real, *full-dimensionality* system, should be replaced by a fictitious *reduced-dimensionality effective* system, whose Hamiltonian depends only on few effective coordinates and it should be determined in such a way to reproduce the dynamical results (population transfer, UV spectra, etc.) we would obtain if we could compute the dynamics with the complete Hamiltonian.

In some cases, the effective coordinates to define the reduced Hamiltonian can be determined empirically, on the basis of the physics and the chemistry which these coordinates are expected to represent (see, for example, Refs. [10] and [60]).

Before this work, a rigorous *exact* definition of such reduced-dimensionality models was found just for a particular case within the harmonic approximation, namely the Linear Vibronic Coupling (LVC) model,[11]-[14] where the excited states have the same normal modes and frequencies of the ground state, and the coupling between the states, responsible for the internal conversion, is proportional to the linear displacement along the normal modes. Thus, quadratic cross-terms (kQ_iQ_j) do not appear in the potential. Within this model, it is possible to define a *hierarchy* of reduced models to perform quantum dynamics. The members of this hierarchy are effective Hamiltonians, depending on a growing number of coordinates, such that a higher dimensionality corresponds to a longer time-scale to which the dynamics is reproduced *exactly*. In particular, the short-time dynamics (first 30-50 fs) is recovered by the first reduced Hamiltonian, which depends on just three effective coordinates, in the case of two coupled states.

The LVC model is expected to have a poor physical meaning in many cases, since the only effect it takes into account is the change of the molecular geometry following the excitation; however, according to the chemical intuition, once a molecule has been electronically excited, some of its bonds will weaken and thus their frequencies will decrease; moreover (as a consequence), considering the equilibrium geometry of the excited state, the small rectilinear nuclear oscillations around this position (identified by the normal modes) will slightly misaligned with the corresponding oscillations for the ground state, the ones being related to the others by a sort of 'rotation', named *Duschinsky mixing*.

A more realistic description of the photophysics of a semirigid molecule releases the constraints of the LVC model, and requires a generic quadratic Hamiltonian (including cross-terms), which takes into account both the frequency changes and the Duschinsky rotation in going from the

ground to the excited state. This kind of model is denoted Quadratic Vibronic Coupling (QVC) Model.

One of the purposes of this work is to develop a practical numerical procedure to define the hierarchy of effective reduced-dimensionality Hamiltonians for the LVC model, and to formulate an extension of this procedure to cover also the QVC case. In both cases, the effectiveness of these reduced-dimensionality models will be tested by quantum dynamical simulations, and these approaches will be employed for the studies described below.

Finally, the possibility to include the remaining degrees of freedom (not included in the reduced-dimensionality models) as *classical* coordinates will be tested and discussed.

Application: investigation of the photostability of the nucleobases

The nucleobases of the nucleic acids, DNA and RNA, strongly absorb UV light. They are extensively studied because of their important role in the fields of photochemistry and photobiology. In fact, the photoexcited nucleobases are the precursors of reactions culminating in DNA photodamage. The most common of these reactions is the cyclobutane occurring between two photoexcited pyrimidine bases, adjacent in the same DNA strand (Fig. 1.1).[2]

If the bases are properly oriented during UV absorption, this process can occur on a picosecond ($1 \text{ ps} = 10^{-12} \text{ s}$) time-scale.[16] After the dimerization, energetically costly enzymatic repairs must be activated, preventing complex biological consequences, such as apoptosis, immune suppression and photocarcinogenesis.

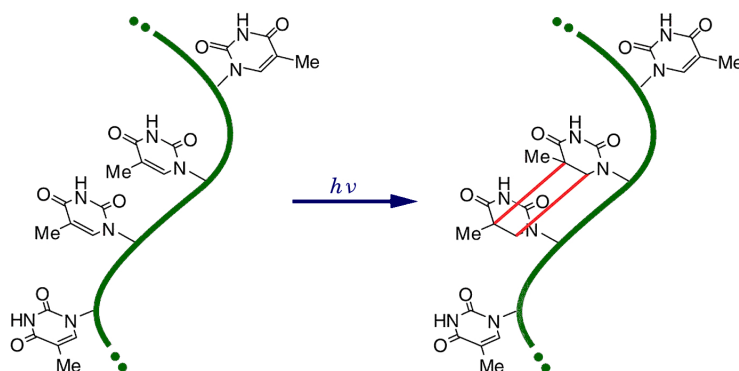


Figure 1.1: $[2 + 2]$ cycloaddition between two thymine molecules, leading to the formation of a dimer within the same nucleotide strand.

Sunlight, essential for the life on Earth, contains significant quantities of harmful UV radiation. Actually, the photons with wavelength $\lambda < 400$ nm are among the most powerful environmental carcinogenic agents.

The genetic information encoded into the nucleic biopolymers has always been under this extra-terrestrial photochemical attack. Therefore, it is not surprising that the more relevant DNA chromophores, the nucleobases, are highly stable with respect to the possible photochemical lesions, probably as a result of a long process of molecular evolution.

This stability is related to the presence of efficient non-radiative decay channels, whose experimental study has begun very recently, by means of femtosecond time-resolved spectroscopies (1 fs = 10^{-15} s), since before 2000 the techniques achieving the proper time resolution were scarcely available.

The nature of the initial photoexcitation on a single or double polynucleotide strand is not completely clarified, but experimental and theoretical studies suggest that possible mechanisms can involve both a collective excitation of a group of five to ten bases,[17] or excitations localized on the single monomers.[2] The following evolution can give rise to intermonomeric charge transfer[18][19] or proton transfer states[20][21] or also decays localized on a single monomer.

For what concerns the decay pathways for the single monomers, the time-resolved transient absorption and fluorescence upconversion signals, which are sensitive, in some sense, to the excited state population, show a multi-exponential, usually bi-exponential, decay[23][24]. Even if the two time constants depend on the experiment performed and the nature of the solvent used, and slightly change in the gas-phase, for pyrimidine bases, the shortest time constant usually is in the sub-picosecond time scale, whereas the longest one is about 5-10 ps.

The mechanism of the deactivation process of pyrimidine bases is strongly debated in literature.[2] In the manifold of singlet electronic states, the process may occur at the conical intersections between the ground state, and a $\pi\pi^*$ state, which is initially populated after the photoexcitation. However, the $\pi\pi^*$ state is close in energy to a 'dark' $n\pi^*$ state, which could participate in the excited state dynamics. Thus, other additional decay channels are possible: the excited molecule could decay via an internal conversion to the $n\pi^*$ state. Alternatively, a fraction of molecules could populate the $n\pi^*$ state on an ultrafast time-scale, and afterwards come back to the $\pi\pi^*$ state and decay to the ground state by an internal conversion.[25]

Actually, the more discussed point is whether the $n\pi^*$ state has a role in the dynamics or not and, eventually, what the time scale for it to be populated is. In the second part of this work the methods developed in the first part will be adopted to model the $\pi\pi^* \rightarrow n\pi^*$ transfer in

photoexcited gas-phase thymine, and it will be shown that this process is relevant and occurs on a femtosecond time scale.

The thesis is organized as follows: in Chapter 2 an overview of the main concepts necessary for the description of the photophysics and photochemistry of a molecular system are given; Chapter 3 illustrates the method to build up a hierarchic sequence of reduced-dimensionality models; in Chapter 4 the methods for the wave packet evolution are presented; Chapter 5 reports the results of the quantum dynamical simulations on the excited states of thymine.

Some preliminary results about this work were reported in Ref. [10], and a large part of the theoretical and computational achievements given here was published very recently.[36]