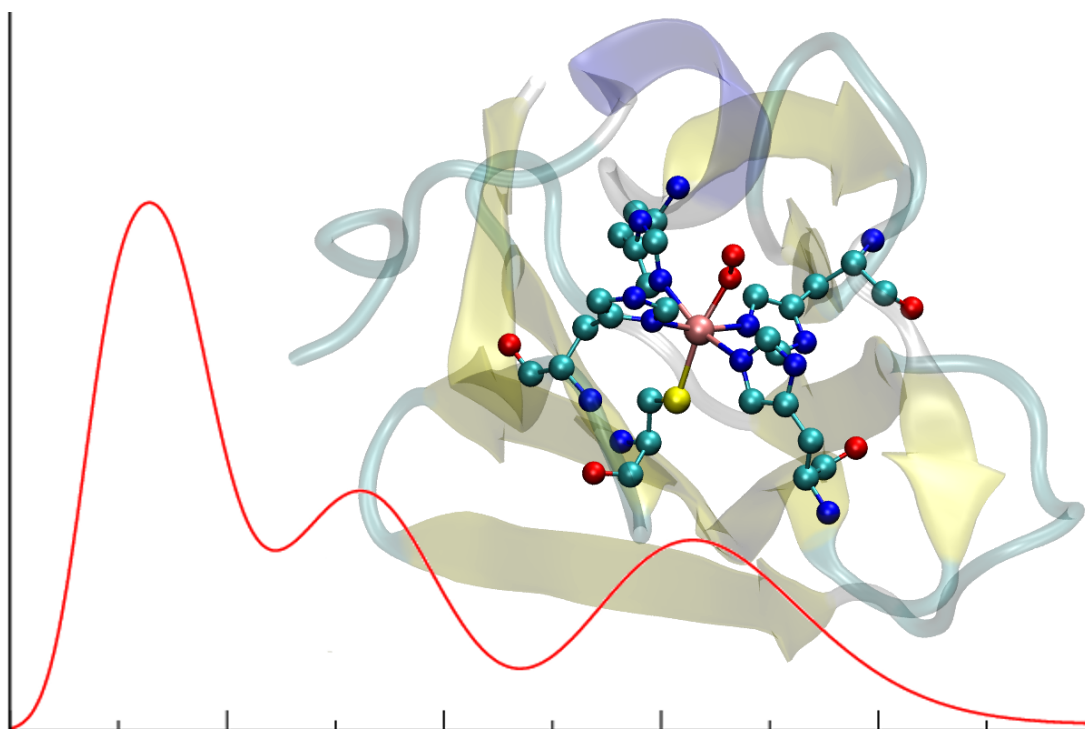# New QM/MM opportunities for in silico macromolecular spectroscopy

February 28, 2012 - March 02, 2012,
Centre Blaise Pascal, ENS Lyon, France

1 Description

Sunlight is the predominant energy on Earth, and a key factor in photosynthesis. It is intimately related to life. The in-depth understanding of the nature of electronic excited states in biological or other complex systems is uncontestedly one of the key subjects in present days chemical and physical sciences.

Interaction between light and matter has indeed many important consequences in biological process or in advanced materials elaboration. From the comprehension of physiological process (for instance vision) to the development of phototherapeutic drugs, from the elaboration of molecular photoelectronic devices to the design of efficient solar cells.

In all these cases, the interplay of the molecular and macromolecular environment should be taken into account as precisely as possible to get a meaningful description and hence to allow for a predictive approach and molecular design.

New and more powerful techniques, both theoretical and experimental, have emerged. Hybrid QM/MM methodologies have proven to be capable to provide such a description to reproduce experimental data and to give them a deeper insight.

In this workshop, the state of the art of the different approaches will be presented, their limitation and the need of of development will be underlined, the interaction between theory and experience will especially be considered.

2 Organization

Organizing committee

Elise Dumont
 Ecole Normale Supérieure de Lyon, France

Nicolas Ferré
 University of Aix-Marseille, France

Antonio Monari
 University of Lorraine-Nancy, France

Yohann Moreau
 University Joseph Fourier, Grenoble, France

Scientific commitee

Ursula Röthlisberger
Ecole Polytechnique Fédérale de Lausanne, Switzerland

Massimo Olivucci
University of Siena, Italy and B.G.U. Ohio, U.S.A.

Philipe Sautet
Ecole Normale Supérieure de Lyon, France

Stéphane Ménage
CEA Grenoble, France

3 Program

Day 1 - February, 28 2012

From light to bio, advanced methods for advanced applications
- 14:00 to 14:30 - Welcome

- 14:30 to 15:10 - **Luca Frediani**
One- and two-photon spectroscopy in solution by polarizable methods: DFT/MM and DFT/MM/PCM studies

- 15:10 to 15:30 - **Isabelle Navizet**
Light emission in firefly: a QM/MM study

- 15:30 to 16:00 - Poster Session

- 16:00 to 16:30 - Coffee Break

- 16:30 to 16:55 - **Tatiana Domratcheva**
Computational spectroscopy of light-sensing flavoproteins

- 16:55 to 17:20 - **Pablo Campomanes**
Spectral tuning in rhodopsin early photointermediates

- 17:20 to 17:40 - **Anikó Udvarhelyi**
Photoinduced electron transfer in a flavin-binding blue light photoreceptor – a CASSCF-POCAS study

Day 2 - February, 29 2012

Advanced materials and molecular design what theory can provide
- 9:00 to 9:40 - **Leticia Gonzalez**
Photochemistry and control from first principles: from quantum dynamics to molecular dynamics and back.

- 9:40 to 10:00 - **Marie-Laure Bonnet**
Local disorder in lithium imide characterized by ab initio molecular dynamics simulations and NMR spectroscopy

- 10:00 to 10:30 - Coffee Break
- 10:30 to 10:50 – **Hossam Elgabarty**
Xray-structure versus in-situ structure of c-phycocyanin: insight from first-principles NMR calculations.

- 10:50 to 11:15 - **Marcus Boeckmann**
Ab initio molecular dynamics (AIMD) tailored for probing photoswitchable smart materials

- 11:15 to 12:00 - **Massimo Olivucci**
From computational photobiology to the development of biomimetic molecular devices

- 12:00 to 14:30 - Poster Session and Buffet Lunch

From light to bio: we need to talk about the environment
- 14:30 to 15:15 - **Anna Krylov**
Quantum chemistry behind bioimaging: insights from ab initio studies of fluorescent proteins and their chromophores

- 15:15 to 15:35 - **Thibaut Very**
Treatment of the environment: effect on UV-visible spectra of ruthenium complex

- 15:35 to 16:00 - **Marco Garavelli**
Retinal chromophores and rhodopsins photophysics: a computational perspective

- 16:00 to 16:30 - Coffee Break

- 16:30 to 16:55 - **Bernard Levy**
Interplay between the chromophore and the protein dynamics in fluorescent proteins

- 16:55 to 17:15 - **Christoph Allolio**
Unraveling the molecular origin of the time-dependent stokes shift via ab initio molecular dynamics simulations

- 17:15 to 17:40 - **Jean-Philip Piquemal**
Coupling hybrid QM/MM methods and quantum interpretative techniques.

Day 3 - March, 1 2012

Experimental wishlist
- 9:00 to 10:00 - **Olivier Maury**
Lanthanides for nonlinear optics, from old complexes to new concepts…

- 10:00 to 10:30 - Coffee Break

- 10:30 to 11:15 - **Gregory Scholes**
Quantum mechanisms for light harvesting in photosynthesis

- 11:15 to 12:00 - **Guido Pintacuda**
Structure and dynamics of proteins by high-resolution solid-state NMR

- 12:00 to 14:10 - Poster Session and Buffet Lunch

TDDFT and beyond: the right methods for the right system
- 14:10 to 14:55 - **Kenneth Ruud**
QM/MM calculations of chiroptical properties: a utopia ?

- 14:55 to 15:15 - **Hélène Jamet**
QM and QM/MM studies of the magnetic properties for inhibitors of tyrosinase

- 15:15 to 15:40 - **Chantal Daniel**
Spectroscopy and photophysics of ruthenium(II) polypyridyl complexes used as DNA intercalators

- 15:40 to 16:00 - **Kristian Sneskov**
  The polarizable embedding coupled cluster method

- 16:00 to 16:30 - Coffee Break

- 16:30 to 16:55 - **Denis Jacquemin**
  Ab initio models for multi-photochromic entities

- 16:55 to 17:20 - **Gilles Frison**
  Modeling the one-electron reduction of diprotonated peptides

- 17:20 to 17:40 - **Miquel Huix-Rotllant**
  A hybrid exchange-correlation kernel with double excitation configurations for linear-response time-dependent density-functional theory

Day 4 - March, 2 2012

Going further and think different: original methods and architectures

- 9:00 to 9:40 - **Vincenzo Barone**
  The QM/MM/PCM approach for absorption and fluorescence spectra

- 9:40 to 10:00 – **A word on new architectures** (Bull)

- 10:00 to 10:30 - Coffee Break

- 10:30 to 10:55 - **Michel Caffarel**
  Coupling QMC with MM or MD: a few remarks and perpectives

- 10:55 to 11:15 - **Emanuele Coccia**
  Quantum Monte Carlo / molecular mechanics (QMC/MM): relaxed geometries of retinal in gas phase and in rhodopsin

- 11:15 to 12:00 - Closing word

4 Plenary Lectures

One- and two-photon spectroscopy in solution by polarizable methods: DFT/MM and DFT/MM/PCM studies

Luca Frediani
 Center for Theoretical and Computational Chemistry, University of Tromsoe, Norway

The experimental investigation of molecular systems is most often carried out at the liquid state for obvious practical reasons. The focus on biomolecules and material science makes also the size of the molecular system itself a challenge for quantistic methods: despite the development in linear scaling methods, a large macromolecule immersed in solvent is still beyond reach of current QM methods. Moreover well defined concepts for a small gas-phase molecule such as a polarizability or an optimized geometry loose their meaning for large systems. It is therefore important to be able to account for the environment in an accurate yet efficient way. Thanks to the fact that a large number of properties and chemical processes are localized -- in other words they can be ascribed to a relatively small substrate -- it is possible to limit the size of the QM system; the remainder can be conveniently represented by polarizable MM units: they can reproduce well the interaction of the substrate with the environment without generating a significant overhead to the calculation. A further step can also be taken by surrounding the QM/MM system with a continuum dielectric which accounts for long range effects in averaged way. We have implemented a massively parallel implementation of DFT/MM and applied it to the Two-Photon Absorption of DFT. We have further combined the DFT/MM method with the Polarizable Continuum Model and applied it to the computation of excitation energies of small chromophores.

Photochemistry and control from first principles: from quantum dynamics to molecular dynamics and back.

Leticia Gonzalez
 Universität Wien · Institut für Theoretische Chemie

Understanding photochemistry and its eventual control means calculating electronic excited states but also following the reaction mechanisms that molecules undergo after light irradiation. Only after the natural dynamics is unveiled it is even possible to manipulate light-induced processes using coherent light. Quantum chemistry, e.g. based on CASPT2/CASSCF methods, can provide a very accurate picture of photochemistry. However, a more detailed comprehension is only obtained with a time-dependent analysis. Two extreme approaches to do that can be considered. One is to employ quantum dynamics and propagate accurate wavepackets on potential energy surfaces, albeit of reduced dimensionality. The other is to use ab initio molecular dynamics, where the electronic structure is treated quantum mechanically but the nuclear motion is subject to classical mechanics and then full-dimensional calculations are affordable. The advantages and disadvantages of both extremes will be discussed and illustrated with examples, as fundamental as cis/trans isomerization [1], excited state hydrogen transfer [2] and the photostability of DNA nucleobases [3]. Moreover, a recently developed an ab initio molecular dynamics method (SHARC), which allows treating on the same footing non-adiabatic and spin-orbit couplings as well as transitions induced by laser fields [4] will be presented.

[1] D. Kinzel, J. González-Váquez, and L. González. H-abstraction is more efficient than cis-trans isomerization in (4-methylcyclohexylidene) fluoromethane. An ab initio molecular dynamics study. Phys. Chem. Chem. Phys. (in press), DOI: C1CP22646K, (2012).
[2] A. Migani, V. Leyva, F. Feixas, T. Schmierer, P. Gilch, I. Corral, L. González, and L. Blancafort. Ultrafast Irreversible Phototautomerization of ortho-Nitrobenzaldehyde. Chem. Commun., 47, 6383 (2011)
[3] J. González-Vázquez and L. González, Chem. Phys. Chem. 11, 3617 (2010)
[4] M. Richter, P. Marquetand, J. González-Vázquez, I. Sola, and L. González. SHARC - ab initio molecular dynamics with surface hopping in the adiabatic representation including arbitrary couplings. J. Chem. Theory Comput., 7,1253 (2011)

From computational photobiology to the development of biomimetic molecular devices

Massimo Olivucci
  Chemistry Department, University of Siena, 53100 Siena, Italy and Chemistry Department, Bowling Green State University, USA

During the last few years QM/MM computations based on the CASPT2//CASSCF approach have been employed to investigate spectroscopic and photochemical properties of light-sensitive proteins. In this lecture we will show how the same technology could be used to design light-driven molecular devices. In our lab we are exploring the possibility of designing and synthesizing molecules that could mimic the photoisomerization of the visual pigment Rhodopsin and, in particular its low-temperature photochromism [1]. When embedded in the opsin cavity the Rhodopsin chromophore displays an ultrafast and stereoselective photoisomerization with high quantum yield. In order to design a chromophore displaying a similar efficiency in common solvents we have been looking at diverse alkylated Schiff bases featuring a single isomerizable double bond.

In this lecture we show that the indanylidene-pyrroline (NAIP) framework [2-4] provides a computationally and synthetically viable prototype for the development of systems that reproduce the excited state electronic structure and photoisomerization dynamics of Rhodopsin in methanol. We will also show that, on the basis of these studies we have been able to achieve systems that, in perspective, can be used as mechanical or electrostatic switches capable of inverting, reversibly, a ca. 15 D dipole moment upon double bond photoisomerization [5].

[1] Shapiro I., Ryazantsev M. N., Frutos L.-M., Ferré N., Lindh R. & Olivucci M. (2011) J Am Chem Soc 133:3354-3364.
[2] Lumento F., Zanirato, V., Fusi, S., Busi, E., Latterini, L., Elisei, F., Sinicropi, A., Andruniów, T., Ferré, N., Basosi, R. & Olivucci, M. (2007) Angew Chem Int Ed Engl 46:414-420.
[3] Sinicropi A., Martin, E., Ryasantsev, M., Helbing, J., Briand, J., Sharma, D., Léonard, J., Haacke, S., Cannizzo, A., Chergui, M., Zanirato, V., Fusi, S., Santoro, F., Basosi, R., Ferré, N. & Olivucci, M. (2008) Proc. Nat. Acad. Sci. USA 105:17642-17647.
[4] Briand J., Bräm, O., Réhault, J., Léonard, J., Cannizzo, A., Chergui, M., Zanirato, V., Olivucci, M., Helbing, J. & Haacke, S. (2010) Phys Chem Chem Phys 12:3178 - 3187.
[5] Melloni A., Rossi Paccani, R., Donati, D., Zanirato, V., Sinicropi, A., Parisi, M. L., Martin, E., Ryazantsev, M., Ding, W. J., Frutos, L. M., Basosi, R., Fusi, S., Latterini, L., Ferré, N. & Olivucci, M. (2010) J Am Chem Soc 132:9310-9319

Quantum chemistry behind bioimaging: insights from ab initio studies of fluorescent proteins and their chromophores

Anna Krylov
  U. Southern California

The unique properties of green fluorescent protein (GFP) have been harnessed in a variety of bioimaging techniques, revolutionizing many areas of the life sciences. Molecular-level understanding of the underlying photophysics provides an advantage in the design of new fluorescent proteins (FPs) with improved properties; however, because of its complexity, many aspects of the GFP photocycle remain unknown. This lecture will discuss computational studies of FPs and their chromophores that provide qualitative insights into mechanistic details of their photocycle and the structural basis for their optical properties. Methodological aspects will also be highlighted.

An interesting feature of several anionic FP chromophores in the gas phase is their low electron detachment energy. For example, the bright excited $\pi\pi^*$ state of the model GFP chromophore (2.6 eV) lies above the electron detachment continuum (2.5 eV). Thus, the excited state is metastable with respect to electron detachment. This autoionizing character needs to be taken into account in interpreting gas-phase measurements and is very difficult to describe computationally. Solvation (and even microsolvation by a single water molecule) stabilizes the anionic states enough such that the resonance excited state becomes bound. However, even in stabilizing environments (such as protein or solution), the anionic chromophores have relatively low oxidation potentials and can act as light-induced electron donors. Protein appears to affect excitation energies very little (<0.1 eV), but alters ionization or electron detachment energies by several electron volts. Solvents (especially polar ones) have a pronounced effect on the chromophore's electronic states; for example, the absorption wavelength changes considerably, the ground-state barrier for cis–trans isomerization is reduced, and fluorescence quantum yield drops dramatically. Calculations reveal that these effects can be explained in terms of electrostatic interactions and polarization, as well as specific interactions such as hydrogen bonding.

The results of sophisticated first-principle calculations (using QM/MM in combination with high-level electronic structure methods) can be interpreted in terms of simpler, qualitative molecular orbital models to explain general trends. In particular, an essential feature of the anionic GFP chromophore is an almost perfect resonance (mesomeric) interaction between two Lewis structures, giving rise to charge delocalization, bond-order scrambling, and, most importantly, allylic frontier molecular orbitals spanning the methine bridge. We demonstrate that a three-center Hückel-like model provides a useful framework for understanding properties of FPs. It can explain changes in absorption wavelength upon protonation or other structural modifications of the chromophore, the magnitude of transition dipole moment, barriers to isomerization, and even non-Condon effects in one- and two-photon absorption.

K.B. Bravaya, B.L. Grigorenko, A.V. Nemukhin, and A.I. Krylov; Acc. Chem. Res., in press (2012).

Lanthanides for nonlinear optics, from old complexes to new concepts…

Olivier Maury

Laboratoire de chimie, UMR5182 CNRS – Université de Lyon 1 - ENS Lyon

In the last decade lanthanide complexes have been extensively used for their catalytic, magnetic, luminescence properties for applications ranging from material sciences (laser, color screen, telecommunication devices) to biological imaging (MRI contrast agent, bioassay…). By contrast, the study of the nonlinear optical (NLO) properties of lanthanide remains in its infancy and becomes currently an emerging field of research. In this context, we reported the contribution of f-electrons to the second order NLO activity,[1] and this discovery prompted us to revisit the classical description of f-electrons using a combined crystallography/theory approach.[2] More recently, the proof-of-concept of lanthanide luminescence sensitisation by a two-photon antenna effect - a third order NLO phenomenon - has been achieved, [3] opening the way for the design of new europium, terbium or ytterbium containing bio-probes (molecular complexes or nanoparticles) for biphotonic confocal microscopy imaging. [4] During the course of this study, we serendipity discovered a new class of compounds exhibiting very strong supramolecular interactions with amino-acid, able to co-crystallize with a large variety of proteins and acting as valuable auxiliaries for proteins X-rays structures determination. [5]
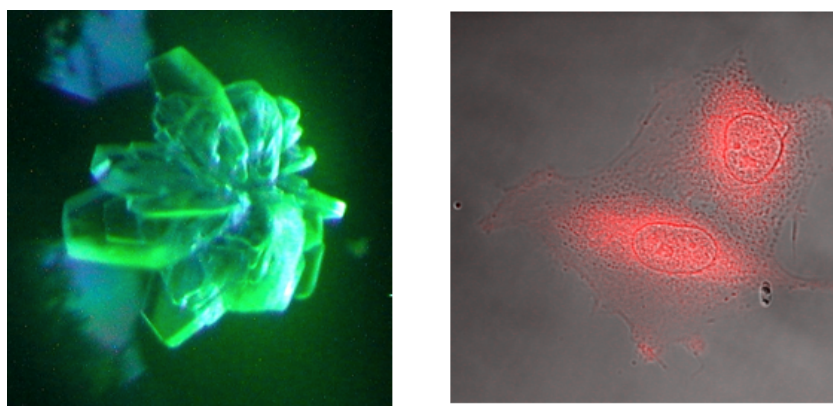
Nonlinear microscopy imaging of cancer cell doped with europium complexes (right), [4] luminescence imaging of lysozyme crystal co-crystallized with a terbium complex (left) [5]

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4 Picot, A.; D'Aléo, A.; Baldeck, P. L.; Grichine, A.; Duperray, A.; Andraud, C.; Maury, O., J. Am. Chem. Soc. 2008, 130, 1532-1533. . Philippot, C. ; Bourdolle, A. ; Maury, O. ; Dubois, F. ; Boury, B. ; Brustlein, S. ; Brasselet, S. ; Andraud, C. ; Ibanez A. J. Mater. Chem. 2011, 21, 18613-18622.
5 G. Pompidor, A. D'Aléo, J. Vicat, L. Toupet, N. Giraud, R. Kahn, O. Maury Angew. Chem. Int. Ed., 2008, 47, 3388 –3391.

Quantum mechanisms for light harvesting in photosynthesis

Gregory Scholes
  Department of Chemistry, University of Toronto

More than 10 million billion photons of light strike a leaf each second. Incredibly, almost every red-coloured photon is captured by chlorophyll pigments and initiates steps to plant growth. In recent work we have been investigating marine algae that use quantum mechanics in order to optimize light harvesting [1]. In a recent review [2] we described the principles learned from studies of various natural antenna complexes and suggested how to utilize that knowledge to shape future technologies. We forecast the need to develop ways to direct and regulate excitation energy flow using molecular organizations that facilitate feedback and control—not easy given that the energy is only stored for a billionth of a second. In this presentation I will report some new examples of coherent energy transfer, I will discuss what coherence means for the description of the dynamics, and I will identify some challenges for future work.

[1] Elisabetta Collini, Cathy Y. Wong, Krystyna E. Wilk, Paul M. G. Curmi, Paul Brumer, and Gregory D. Scholes, "Coherently wired light-harvesting in photosynthetic marine algae at ambient temperature" Nature 463, 644–648 (2010).
[2] Gregory D. Scholes, Graham R. Fleming, Alexandra Olaya-Castro and Rienk van Grondelle, "Lessons from nature about solar light harvesting" Nature Chem. 3, 763–774 (2011).

Structure and dynamics of proteins by high-resolution solid-state NMR

Guido Pintacuda
  CRMN, ENS Lyon

Solid-state NMR spectroscopy has significantly grown in recent years, and is rapidly becoming a powerful structural tool in chemistry and biology. Steadily ongoing methodological developments combined with tremendous engineering advances in probe and spectrometer hardware, along with notably increased magnetic field strengths, have paved the way for studying the structure and dynamics of solid chemical and biological samples at atomic resolution spanning a broad atlas of structures ranging from materials to protein aggregates or membrane proteins.

This communication presents an outline of this experimental technique, of its recent progress, and of its immense potential. As a case study, the structural and dynamical determination of a paramagnetic human enzyme, the Cu(II),Zn(II)-superoxide dismutase, in microcrystalline form will be presented.

QM/MM calculations of chiroptical properties: a utopia ?

Kenneth Ruud
  Centre for Theoretical and Computational Chemistry, Department of Chemistry, University of Tromsoe, Norway

I will present the results of calculations of different molecular properties using a QM/MM methodology with polarizable force fields. Particular focus will be on the perspectives for calculating molecular chiroptical properties, such as circular dichroism and multiphoton circular dichroism spectroscopies, but also ground-state based spectroscopic techniques such as Raman Optical Activity. This perspective will be based on the results obtained for QM/MM calculations of molecular magnetic properties, such as nuclear magnetic resonance (NMR) shielding constants and molecular magnetizabilities for describing solvent effects on magnetic properties. I will reflect on the possibility of obtaining reliable estimates for magnetic properties of solvated molecules using QM/MM methods, in view of our emerging understanding of quantum effects on the magnetic properties of weakly interacting systems as obtained from a visualization and analysis of magnetically induced currents.

The QM/MM/PCM approach for absorption and fluorescence spectra

Vincenzo Barone
Scuola Normale Superiore, piazza dei Cavalieri 7, 56126 Pisa, Italy

The subtle interplay of several different effects still makes the interpretation and analysis of experimental spectra in terms of structural and dynamic characteristics a very challenging task. In this context theoretical studies can be very helpful and this is the reason behind the rapid evolution of computational spectroscopy from a highly specialized research field toward a versatile and widespread tool. However, in the case of electronic spectra (UV–vis, fluorescence, ECD) the most popular approach still relies on computation of vertical excitation energies, which are further convoluted to simulate line-shapes. Such a treatment completely neglects the effect of nuclear motions, despite the well-recognized notion that proper account of vibrational effects is often mandatory in order to interpret correctly experimental findings. In this respect, recent implementations of effective approaches rooted into a time-independent model, allow feasible yet reliable simulations of spectra line-shape, including vibronic contributions even for large systems. Of course, these phenomena do not involve only isolated chromophores, but are tuned by their environment. The notion of "chemical environment" is fairly versatile, and can be applied to a complex biomolecular structure (e.g. a protein), or to a macromolecular matrix, which not necessarily behaves as a passive medium, but can instead profoundly affect the spectroscopic properties of a molecular probe. The huge dimensionality and the complexity of the problem make traditional approaches either unfeasible or not precise enough to model a specific property. However, it is possible to address the problem by simplified models ranging from atomistic quantum description, through appropriately tailored FFs and finally a continuum description of boundaries. Mutual polarization effects between QM and MM regions can be included by means of polarizable FFs (MMPol) and bulk solvent effects by the polarizable continuum model (PCM). Recently, a combined QM/MMPol/PCM approach has been proposed by our group to describe excited states in solution with a fully polarizable treatment of the environment. This model accurately describes the spectroscopic properties of chromophores in complex environments with specific interactions. Some specific examples will be sketched to illustrate our recent integrated approach.

5 Communications

Light emission in firefly: a QM/MM study

Isabelle Navizet

  University of the Witwatersrand, Johannesburg

The emitting light in fireflies arises from the electronic relaxation of oxyluciferin, an organic compound resulting from the oxidation of the D-luciferin substrate inside an enzyme called luciferase. The bioluminescence process results from three moities of the luciferin-luciferase system: the chemiluminophore, which opens the path to the excited state surface, the electon-donating fragment, which lowers the activation energy of the reaction of a charge transfer mechanism and a charge transfer controlling group which modulate the color emission, depending on the interactions between this moiety and the protein.[1]

In such systems, the use of quantum mechanical/molecular mechanical (QM/MM) methods is required. Accurate QM level is needed for dealing with charge transfer phenomena and taking into account the surrounding protein at the MM level is essential in order to understand the color modulation. The present lecture will discuss some of the results obtained on this system with calculations done with the coupling of the programs MOLCAS (CASPT2/CASSCF) and TINKER (AMBER force field).

Our systematic theoretical investigation of all the possible light emitter structures of firefly shows that the phenolate-keto form of oxyluciferin is responsible for the light emission.[2] Our theoretical results[3] on the oxyluciferin-luciferase complex shows in agreement with recent experimental observations that the wavelength of the emitted light depends on the polarity of the microenvironment at the phenol/phenolate terminal of the benzothiazole fragment of oxyluciferin. Some last results show that even in the protein the molecule is almost planar like in the fluorescent molecule, this behaviour being different from the one in the bioluminescent coelenterate system.[4]

[1] I Navizet, YJ Liu, N Ferré, D Roca-Sanjuan, R Lindh Chem. Phys. Chem., 2011, 12, pp 3064-3076.
[2] SF Chen, YJ Liu, I Navizet, N Ferré, W.-H. Fang, R Lindh, J. Chem. Theory Comput., 2011, 7 (3), pp 798-803.
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[4] D Roca-Sanjuan , M Delcey, I Navizet, N Ferré, YJ Liu, R Lindh, J. Chem. Theor. Comp., 2011, 7 (12), pp 4060-4069.

Computational spectroscopy of light-sensing flavoproteins

Tatiana Domratcheva
MPI for Medical Research, Heidelberg

Flavoproteins mediate physiological responses to light conditions by undergoing a variety of photoreactions in which photoinduced electron transfer plays a key role. The flavin photochemistry constitutes a sequence of electron-transfer and proton-transfer reactions and involves redistribution of the electrostatic charges in the core of the protein. The accurate estimates of the energies of the charged/(ionic) and radical species in the electronic ground and excited states are absolutely essential for the conclusive studies of the photoreaction mechanisms and for interpretation of the molecular-spectroscopy data. The QM/MM calculations for those species will be presented and the proposed mechanistic models explaining the spectroscopy data will be discussed.

Spectral tuning in rhodopsin early photointermediates

Pablo Campomanes
  Ecole Polytechnique Fédérale Lausanne, CH-1015, Lausanne, Switzerland

In this contribution, I will show how a combined strategy based on the computation of absorption energies, using the ZINDO/S semi-empirical method, for a statistically relevant number of thermally sampled configurations extracted from QM/MM trajectories can be used to establish a one-to-one correspondence between the structures of the different intermediates involved in the very early steps of the rhodopsin photocycle and their optical spectra. The analysis of the results clarify the role played by some of the residues located in the protein-binding pocket as well as the importance of the structural features and conformation of the chromophore on the spectral shifts observed between the intermediates. They also permit the identification of some chromophore structural parameters as good descriptors for the different transitions leading from dark- to lumi-rhodopsin, therefore allowing the characterization of the distinct states.

Photoinduced electron transfer in a flavin-binding blue light photoreceptor – a CASSCF-POCAS study

Anikó Udvarhelyi[1], Massimo Olivucci[2] and Tatiana Domratcheva[1]
[1]Computational Photobiology Group, Department of Biomolecular Mechanisms, Max-Planck-Institute for Medical Research,Heidelberg,Germany
[2]Dipartimento di Chimica, Università di Siena, Italy and Department of Chemistry and Biochemistry, Ohio State University, USA

Flavoproteins mediating various light responses in different organisms have been extensively studied in the several past years. The bacterial photoreceptor BLUF (blue light sensing using FAD) has a unique photocycle that is characterized by slight spectral shifts of the chromophore absorption. The photoreaction involves the highly conserved glutamine and tyrosine residues of the chromophore binding pocket. The tyrosine residue serves as electron donor to the electronically excited flavin. The photoinduced electron transfer is followed by proton transfer reactions resulting in an altered hydrogen bonding network around the chromophore. The molecular details of the hydrogen bonding rearrangements, which is observed as a small red-shift of the flavin absorption, are still a subject of much controversy.

We study the electron transfer coupled to proton transfer reactions occurring at the BLUF chromophore site. To uncover the mechanisms implicated in light-activation, two types of electronic excited states are of interest: the local excitations of the flavin chromophore as well as electron transfer between two different molecular fragments (e.g. from aromatic amino acids to the flavin). In order to compute wave functions, energies and energy gradients of the excited states of different character, we use the CASSCF/PT2 methodology. However, we find that the "conventional" way of constructing the CASSCF wave function is impractical and it is possible to define the active space in a physical way: Rather than trying to include all π molecular orbitals (MOs) into the active space (which would be computationally impossible for our case anyway), we only consider the principal MOs describing each electronic state of interest. The states of interest can be identified by using independent configuration-interaction (CI) calculations. Thus, the proposed principle orbital CASSCF (POCAS) approach relies on spectral calculations rather than a "chemical intuition". The POCAS wave function accounts merely for the static correlation, and the dynamic correlation is included by using multi-reference perturbation theory. We obtain good energies and geometries with the POCAS active space as we show by extensive benchmark calculations.

To study BLUF photoactivation, we use XMCQDPT2//CASSCF/DZV(P) calculations with the POCAS active space on a supra-molecular cluster including the flavin chromophore and the conserved tyrosine and glutamine residues. In addition, hybrid QM/MM calculations were employed to study the effect of the protein environment of the Slr-BLUF protein on the electronic properties of the chromophore site. We computed the entire photoreaction pathway by taking into consideration four low-lying electronic states (two locally excited $\pi\pi^*$ states of the flavin chromophore and the tyrosine π - flavin π^* electron transfer state). Photon absorption generates a locally excited $\pi\pi^*$ singlet state of the flavin that decays along a non-adiabatic pathway involving the intersection with the tyrosine π - flavin π^* electron transfer state. The latter is stabilized by subsequent proton transfer steps from the electron donor to the acceptor. We mapped different proton transfer pathways which all result in a tautomeric form of glutamine.

The computed relaxation pathways reveal that the hydrogen bonds involving glutamine control BLUF photoefficiency. Our results are consistent with the hypothesis that the BLUF photoreceptor is activated via proton-coupled electron transfer (PCET) which is one of the main photochemical and redox mechanisms identified in biomolecules.

Local disorder in lithium imide characterized by ab initio molecular dynamics simulations and NMR spectroscopy

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The decreasing availability and increasing (energetic) mining costs of fossil fuels will soon impose a shift in the type of primary energy sources and energy carriers on which our society relies. In particular, we must find a technologically suitable way to sustain mobility and transportation. Hydrogen (H_2) as a fuel is considered one of the most promising energy carrier for vehicles and can potentially achieve zero CO_2 emission. The most convenient method is to stock H2 is via physisorption or chemisorption [1] within solid state host structures. In order to have a good ratio between cargo load and the weight of the host structures, alkali imide/amide systems are a very interesting system. In particular, $LiNH_2$ is a promising material and it could stock 10.6 wt% with the reaction: [2] $Li_2NH+H_2 \rightarrow LiNH_2+LiH$. A lot of experimental studies were performed on this system, but a detailed understanding of local structural and dynamical features is still missing. The structural picture of Lithium Imide compounds is critically revised on the atomic scale. The local conformation of this system is crucial for understanding their microscopic hydrogen uptake and release processes. We have performed First-Principles molecular dynamics simulations and calculations of ^{1}H, ^{7}Li, and ^{15}N NMR parameters in order to elucidate local hydrogen bonding structure as well as the degree of ordering within the Li sublattice with CP2K software [3]. Our results provide evidence for a considerable disorder of the Li positions in Li_2NH, which is in surprising contrast to experimental X-ray results. We have observe that this disorder is associated with the reorientation of the NH bonds. Our NMR results compare to the X-ray structure and other theoretical [4-5] ones show a quite good fitting with experimental NMR [6].

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Xray-structure versus in-situ structure of c-phycocyanin: insight from first-principles NMR calculations.

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We present hybrid ab initio QM/MM MD simulations and theoretical NMR chemical shift calculations of the bilin chromophore phycocyanobilin (PCB) bound to the alpha subunit of C-phycocyanin. The possibility of bond breaking and formation in ab initio simulations allows us to address questions related to the protonation state of PCB and its stability. The computed NMR chemical shifts point to a discrepancy between the reported X-ray structure and the experimental solution-state NMR spectrum. Our calculations suggest the presence of a strong hydrogen bond acceptor close to ring A. Our combined MD/NMR calculations suggest that this missing hydrogen bond acceptor might be a water molecule that is only present inside the binging pocket in solution, but not in the crystal structure.

Ab initio molecular dynamics (AIMD) tailored for probing photoswitchable smart materials

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Ab initio molecular dynamics is traditionally used to sample the accessible configuration space in the electronic ground state in order to apply the machinery of statistical physics in the, e.g, NVE or NVT ensemble to derive the desired physical quantities. Here, in the context of density functional theory (DFT) the restricted open-shell Kohn-Sham (ROKS) formalism provides a means for describing the first excited singlet state from first principles. We employ our nonadiabatic QM/MM molecular dynamics technique to investigate the fate of a most prominent reversible photoswitch, the azobenzene chromophore, after photoexcitation in different chemicalenvironments. Application results will be presented together with a general description of the method.

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Treatment of the environment: effect on UV-Visible spectra of ruthenium complex

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Nowadays applications of transition metal complexes cover a large range of fields. As an example, new generation photovoltaic cells use ruthenium complexes as dye-sensitisers. Moreover, platinum complexes such as the well-known cisplatin are being used daily for the treatment of cancers.

Here we are interested by potential alternatives based on ruthenium which seem to show fewer cytotoxicity. We show here results for a ruthenium complex with a ligand dipyri-dophenazine, which is able to intercalate between DNA base pairs, and two ancillary bipyridine ligands (Rdb2). The UV-Visible emission spectra of Rdb2 is very sensitive to the environment in which it is embedded. While the emission spectra in water is very weak, it is very intense when Rdb2 is in interaction with DNA[1].

We present the UV-Visible absorption spectra of Rdb2 computed at TD-DFT/QM:MM level for the complex intercalated at several positions of a DNA double strand. The environment plays a crucial role to reproduce the experimental spectra. The classical force field we use to describe the environment uses point charges for the atoms. As a consequence, during the transition, the electronic response of the surroundings (ERS) is not taken into account by the computation. To overcome this problem, we add a polarizable continuum with a dielectric constant extrapolated at infinite frequency that allows the system to react to the modification of the electronic cloud of Rdb2 induced by the transition. TD-DFT results are analysed by the mean of Natural Transition Orbitals (NTO) [2] thanks to an utility developped in our group [3].

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Retinal chromophores and rhodopsins photophysics: a computational perspective

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Visual perception is one of the most fascinating processes devised by nature. Through ultrafast (200 fs) photoinduced stereoselective isomerisation of its 11-cis retinal chromophore, the visual protein rhodopsin (Rh) converts the energy of a single photon into chemical energy with remarkable efficiency (65% quantum yield). This paradoxically fast and efficient but one-way photoactivated reaction calls for a primary event that is mediated by a strongly "peaked" conical intersection (CI) [1-2]. However, isorhodopsin (isoRh), a visual pigment analog containing a 9-cis retinal chromophore, isomerizes around the 9=10 double bond with a surprisingly lower quantum yield (22%) and slower rate [3], suggesting a different topography in its excited state and/or S1/S0 crossing seam. Thus, Rh and isoRh appear as the ideal systems to study and address how the topography around a seam affects the dynamics of transitions between electronic states at CIs.

In this talk we compare the photophysical and photochemical behaviour of retinal chromophores in the gas phase and within the visual rhodopsin proteins (Rh and isoRh), providing a review of the latest achievements in this field and next forthcoming challenges. A hybrid QM(CASSCF)/MM(Amber) approach to compare the CI dynamics of Rh with that of isoRh is employed. In agreement with the experiments, we find a longer excited state lifetime in isoRh with pulsed stimulated emission decay and photoproduct formation. A mechanistic interpretation is provided.

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Interplay between the chromophore and the protein dynamics in fluorescent proteins

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Fluorescent proteins (FPs) are efficient sensors for a variety of physico-chemical properties and they are extensively used as markers in living cells imaging [1,2]. The fluorescence lifetime t is directly related to the interaction between the chromophore and the protein [3,4] and the comparison with experimental values of t in different FPs provide good tests of the theoretical description of that interaction. From the theoretical point of view, one is faced with three difficulties for predicting t : the size of the system (~30 000 atoms including a water box), the time scale required (> 8 ns) ruling out QM/MM approaches and the coupling between several internal coordinates of the chromophore in the excited state ruling out standard force fields.We have developed a new 'non additive dihedral angle' (NADiA) potential specifically designed to overcome these difficulties and we have implemented it in a parallel version of the AMBER suite.The NADiA potential as allowed to reproduce the fluorescence life time of the green FP with a good accuracy (2.2 ns, exp : 3.0 ns) [5]. Then it has also allowed to demonstrate that the fluorescence quenching in the yellow and the photoactivable FP Padron results from a spontaneous internal twist of the chromophore occurring when the protein moves in a very specific way in the vicinity of the chromophore. This critical protein motion requires a small amount of energy but it is very specific and occurs with a low probability.In other words, the fluorescent life time of this type of FPs is not limited by an energy barrier (related for instance to the volume required for the chromophore twist) but rather to an entropic barrier leading to an unusual temperature dependence. It allows to explain qualitatively that the chromophore may undergo a photo-isomerisation even at low temperature (100 K) in Padron FP [6]

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Unraveling the molecular origin of the time-dependent stokes shift via ab initio molecular dynamics simulations

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The molecular probe N-methyl-6-quinolone (MQ) gives access to the local infrared spectrum via its time dependent Stokes shift.[1] Using ab-initio molecular dynamics, we have simulated the excited state solvation of MQ[2] and the time evolution of its Stokes shift in aqueous solution. Results are in good agreement with experimental data obtained using femtosecond spectroscopy. The effect of electronic excitation is discussed in terms of the actual atomistic coupling to the surrounding hydrogen bond network and dipolar relaxation. Our understanding of the time dependent aqueous solvation around MQ is then used to investigate hydrogen bonding dynamics in complex biophysical systems available to experimentalists.[3]

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Coupling hybrid QM/MM methods and quantum interpretative techniques.

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In this talk, I will show how quantum interpretative techniques such as Atoms in Molecules, the Electron Localization Function (ELF) or the NCI (Non Covalent Interaction) approach can be used in connection with QM/MM computations allowing to open a quantum window on large complex systems. Perspectives towards the analysis of molecules beyond their ground state will be discussed in the framework of the Electron Pair Localization Function (EPLF).

QM and QM/MM studies of the magnetic properties for inhibitors of tyrosinase

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Tyrosinases (Ty) are copper-containing metalloenzymes, which catalyze the oxidation of phenolic compounds into catechols (phenolase activity) and catechol into o-quinone (catecholase activity) successively. After further chemical transformations the formed quinones lead to the formation of melanin pigments. Tyrosinase inhibition is a well-known strategy to control the over production and accumulation of melanins. In this context, theoretical chemistry can give molecular–levels insights into inhibition mechanisms through the determination of the binding mode for the inhibitors on the dicopper catalytic centers of the enzyme. In this work we consider one inhibitor, the well-known acid kojic [1].

Scheme 1

$X = O$ $Y_{,} = N$ ou C
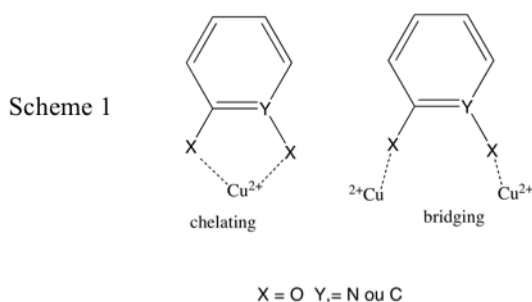
Two different binding modes (see scheme 1) were investigated. Calculations were done on biomimetic model complexes but also on the met form of one bacterial Ty[2] using the LSCF/MM scheme at ab-initio level. [3] Because these systems feature two unpaired electrons carried by the copper centers, magnetic properties were studied. To our knowledge it is the first QM/MM calculations of magnetic properties of such systems. Our results show a good agreement with experimental data. [4]

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Spectroscopy and photophysics of ruthenium(II) polypyridyl complexes used as DNA intercalators

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The purpose of this lecture is to illustrate the complexity of the mechanisms that govern the photophysics and the activity of Ru(II) complexes when intercalated in DNA on the basis of two well studied systems, namely $[Ru(phen)_2dppz]^{2+}$ and $[Ru(tap)_2dppz]^{2+}$ (phen=1,10-phenanthroline; tap=1,4,5,8-tetraazaphenanthrene; dppz=dipyridophenazine). After a short review of the theoretical tools available nowdays for such complicated studies, the results obtained for the two representative complexes will be presented and discussed. The aim of the theoretical study, based on DFT, TD-DFT and QM/MM methods, is to understand and to rationalize the different photophysical behaviours of the two complexes when intercalated in DNA, namely a luminescence process, highly efficient in the case of the phen substituted molecule, process which is quenched by fast or ultra-fast electron transfer from the guanine to the Ru(II) complex in the case of $[Ru(tap)_2dppz]^{2+}$. It is shown that the character of the lowest ^{3}MLCT states ($d_{Ru} \rightarrow \pi^*_{phen}$, $d_{Ru} \rightarrow \pi^*_{tap}$, $d_{Ru} \rightarrow \pi^*_{dppz}$) and their position with respect to the ^{3}IL ($\pi_{dppz} \rightarrow \pi^*_{dppz}$) state will control the photophysics of these molecules in various media or when intercalated in polynucleotides. Whereas the main features of the electronic absorption spectra depend strongly on the solvent corrections and on the mode of intercalation in DNA they have little influence on the observed processes, namely luminescence or electron transfer.

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The polarizable embedding coupled cluster method

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Coupled cluster (CC) theory is often acknowledged as one of the most sophisticated methods of solving the Schrödinger equation for the electronic ground state. With the advent of response theory[1] it became possible to transfer the accuracy, simplicity, and black-box nature of standard CC methods to the study of excited state phenomena [2]. Recently, we introduced the so-called Polarizable Embedding -Coupled Cluster (PE-CC) approach [3] that in a comparatively simple manner extends the computational reach of CC response theory to excited state phenomena of large molecular systems. Here, we shall present the general concepts of PE and important insight gained by applying both PE-CC as well as its Density Functional Theory variant (PE-DFT) to some relevant molecular systems such as photoactive proteins as well as solvatochromism for a variety of solvents. Further, we shall advocate the need to explicitly incorporate the effects of polarization especially when excited state properties such as one- and two-photon absorption are explored[4] and accuracy in comparison with experiment is strived for.

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Ab initio models for multi-photochromic entities

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Photochromic entities may undergo a light-induced reversible transformation between two isomers presenting distinct structural and electronic features. Obviously, if the properties of the two forms are significantly different, like in diarylethenes (DA), photochromes may act as the main building blocks in on/off nano-devices. To store more complex information than a "simple" 0/1 pattern, one can couple several photochromes in one molecule. However, such entities present experimental limitations e.g. switching on one part of the compound may interfere with the photoreactivity of other fragments. In addition, the current operative systems only demonstrate increased contrast rather than emergent properties. In that framework, Density Functional Theory and its Time-Dependent counterpart (DFT & TD-DFT) are useful tools for investigating the origin of these limitations. In this presentation, we will consider a series of diarylethene dimers and trimers, proposing a three-step approach to understand the photochromism of multi-DA systems. Both the successes and the failures of standard TD-DFT simulations will be illustrated.
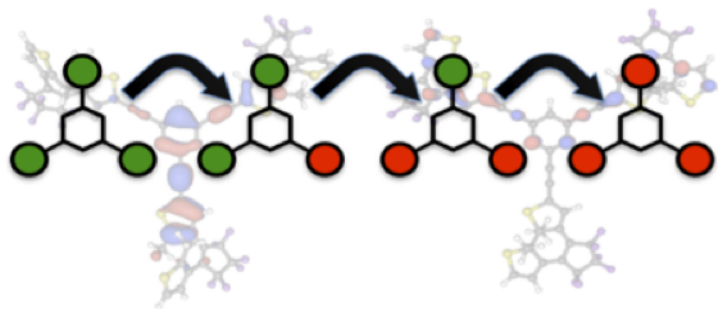
Modeling the one-electron reduction of diprotonated peptides

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Electron-based methods of mass spectrometry rely on partial reduction of multiply charged biomolecular ions. These recent techniques, such as electron capture dissociation (ECD), have become increasingly popular because they have shown much utility and promise for sequencing peptides and proteins due to extensive backbone fragmentation. However, the precise mechanism(s) by which the attached electron induces the bond cleavages needs to be better understood to optimize the usefulness of these techniques. Previous computational studies based on conventional DFT schemes have concluded that the first step of these processes, the attachment of the electron, leads to extensive delocalization of the spin density in the intermediate radical cation. In this lecture, we will focus on the ability of a variety of computational methods to describe accurately the energetics of single-electron reduction of ammonium groups and various models of protonated peptides. In contrast with the spin delocalization over several charge sites that was previously proposed in the literature, we will show that the question of where the electron goes in the electronic ground state of the reduced radical cation can be estimated by assigning the unpaired electron to the group with the largest electronic affinity in the precursor cation. Our results highlight the shortcomings of conventional DFT methods to describe properly radical protonated peptides. They suggest that range separated functionals drastically improve the description of these peptides, at least for the simplest molecular systems.

A hybrid exchange-correlation kernel with double excitation configurations for linear-response time-dependent density-functional theory

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Time-dependent density-functional theory (TDDFT) is a promising method for representing efficiently electron dynamics of medium to large sized systems [1]. TDDFT is formally exact [2], although in practice the exchange-correlation functional has to be approximated. The most popular approximation is the so-called adiabatic approximation (AA),

$$f_{xc}^{AA}(\mathbf{r}, \mathbf{r}', t - t') \approx \delta(t - t') \frac{\delta v_{xc}[\rho_t](\mathbf{r})}{\delta \rho_t(\mathbf{r}')}.$$

which supposes that the density reacts instantaneously to changes during the time evolution. The AA works remarkably well for low-energy valence excited states which are well described by a mixture of single excitation configurations. This is too restrictive for applications in which double excitation configurations become important, such as in bond dissociation or some conical intersections [3].To extend the application of TDDFT, there is a need to develop more sophisticated functionals beyond the AA. In this talk, we present a recently developed exact correlation kernel which can include all double excitations [4]. This exact kernel allows a simple generalization of the dressed TDDFT model of Maitra et al. [5], including double excitations in the AA by mixing the adiabatic kernel with a portion of the many-body kernel [6]. The result of this mixture is a hybrid TDDFT kernel, which includes double excitations and keeps most of the efficiency of adiabatic TDDFT [7].

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Coupling QMC with MM or MD: a few remarks on perpectives

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Quantum Monte Carlo (QMC) methods are powerful stochastic methods to solve the Schrodinger equation. In the recent years a number of applications have shown that realistic chemical systems involving hundreds of electrons can be treated and that a precision comparable to that obtained with the best post-Hartree-Fock approaches or DFT schemes can been achieved. Having to our disposal such an accurate ab initio quantum-mechanical method and in order to develop an effective modeling tool to study very large molecular systems (including environment) it is quite natural to combine QMC with various schemes such as Molecular Dynamics (QM/MD), Molecular Mechanics (QM/MM), or simplified QM methods (QM/QM') as it is done with standard methods of quantum chemistry. In the last years several attempts have been done in this direction. Let us cite for example the Coupled Electron-Ion Monte Carlo (CEIMC) method of Pierloni and co-workers for thermodynamical properties,[1] the QMC/ab initio MD approach of Grossman and Mitas[2] and that of Attaccalite and Sorella for describing the dynamics of nuclei.[3] In this talk I will discuss a number of aspects, limitations, and perspectives related to the development of such hydrid methodologies.

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Quantum Monte Carlo / Molecular Mechanics (QMC/MM): relaxed geometries of retinal in gas phase and in rhodopsin

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Membrane protein Rhodopsin is responsible for the light capture of rod cells in retina. A complete understanding of the spectral tuning of the photoactive moiety, the Retinal Protonated Schiff Base (RPSB), triggering the signal transmission mechanism, is still elusive [1]. The geometrical features of RPSB, such as the bond length alternation (BLA) and the twist of the -ionone ring, play an important role in the spectral tuning of the chromophore [2]. An accurate description of such ground state properties still represents a challenge for high level quantum chemistry calculations; for instance, several levels of theory (HF, CC, CASSCF, CASPT2, DFT) give different estimates for the ground state BLA for the prototypical case of polyene chains [3] and for RPSB [2].

Here we propose a multiscale Quantum Monte Carlo/Molecular Mechanics (QMC/MM) approach to calculate the ground state S0 relaxed geometry of large chromophores, like RPSB, within the protein binding pocket. The approach is based on recent developments of geometry optimization techniques using Variational Monte Carlo [4] with a Jastrow-Antisymmetrised Geminal wavefunction [5]. Recent works on energy, geometry and electrical properties of small molecules in gas phase reveal that this compact variational wavefunction is able to correctly catch correlation effects with an affordable computational cost [6-7].We have initially used the gas phase Minimal Model ($C_5H_6NH_2^+$) as benchmark for the setup of the QMC optimization, with a specific attention to the wavefunction definition and to the convergence of structural parameters like the BLA. QMC *cis/trans* isomerisation energies are in excellent agreement with CASPT2 and CASSCF results [8]; the corresponding QMC BLA is 0.088(1) for the cis isomer and 0.0850(7) for the trans one, close to the CASPT2 estimates of 0.076 [9] and 0.075 [10], respectively. Starting from previous QM/MM calculations [11] we present preliminary results on the QMC full geometry relaxation of RPSB in gas phase and within the protein environment of Bovine Rhodopsin.

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6 Posters

UV-Vis absorption properties of a solvated Ru(II) complex. How to take into account the environment. [P1]

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Ruthenium organometallic complexes are now well recognized as key components of dye sensitized solar cells [1], efficient DNA probes upon intercalation as well as possible candidates for use in antitumoral drugs [2]. Understanding the so called light-switching effect observed when the complexes are allowed to interact with DNA necessitates the elucidation of the involved photophysical processes [3].

The focus of the present study is on the theoretical determination of the UV-Vis spectrum of the dication Ruthenium di-bipyridinlyl (bipy), dipyridophenazine (dppz) (Ru(bipy$_2$dppz)$^{2+}$) in aqueous solution. The UV-Vis spectra were calculated using the TD-DFT formalism at the B3LYP/LANL2DZ level of theory. We have followed two methodologies: a) treating the complex quantum mechanically while representing the solvent by a continuum infinite dielectric characterized by its dielectric constant (PCM model) and b) treating the complex quantum mechanically while retaining the discrete nature of the solvent which is treated at the molecular mechanics (QM/MM) level. In methodology b) the dynamic nature of the solvent has been taken into account by performing a classical molecular dynamics (MD) simulation to compute the trajectories of the solvent molecules. Subsequent statistical analysis using randomly sampled snapshots of the solvent molecule configurations yielded the theoretically predicted UV-Vis spectrum. In order to take into account the fact that the solvent molecules' charge distribution responds to the sudden redistribution of the solute's charge density following the vertical transition, we have followed the ERS formalism (Electrostatic Response of the Surroundings) [4] combined with methodology b), which avoids the use of an explicitly polarized force field for the solvent molecules. The results obtained with methodologies a) and b) (with and without the inclusion of polarization) have been analyzed and compared while an NTO (Natural Transition Orbitals) analysis (*http://nancyex.sourceforge.net/*) of the most important transitions was performed to obtain a qualitative understanding of the nature of the transitions.

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Solvent induced isomerization of phycocyanobilin [P2]

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Phytochromes belong to the family of photoreceptors that trigger reactions of biological systems to light. Upon excitation with light, the photocycle is initialized by an isomerization of the central chromophore. Recent NMR experiments on the isolated chromophore phycocyanobilin show differing spectroscopic properties for different solvents. We investigate the underlying conformational space by means of ab-initio molecular dynamics and free energy calculations as well as ab-initio NMR spectroscopy. In our simulations, we observe specific spectroscopic properties depending on the conformation of the chromophore. By linking our results to the actual experiments, we can identify preferences for different conformations as a function of the solvents ability to form hydrogen bonds. This effect can be traced back to a change in the equilibrium between intra- and intermolecular hydrogen bonds of the chromophore and the solvent.

Two-photon absorption in fluorescent proteins using an advanced polarizable embedding - DFT scheme [P3]

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We will present a QM/MM study of the two-photon absorption (TPA) in the green fluorescence protein (GFP) chromophore embedded in the full protein environment. The protein is described by an advanced quantum mechanically derived polarizable force field, and TPA is calculated by using the polarizable embedding density functional theory (PE-DFT) method [1], which is fully parallelized. The method includes a self-consistent treatment of the environmental polarization at the ground- and excited-state level, in order to faithfully model the TPA properties of the GFP chromophore in its native environment. The importance of treating the protein environment explicitly with a polarizable force field and higher-order multipoles will be demonstrated, as well as the importance of including water molecules close to the chromophore in the protein barrel.

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TD-DFT study of absorption spectrum of photoisomerizable iron complexes [P4]

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Over the past decades dye-sensitized solar cells (DSSCs) have attracted remarkable attention as one of the most promising technologies toward cost-effective solar energy conversion. One of the main disadvantage of DSSCs is related to the use of Ruthenium, a rare and expensive metal. Because of this, a lot of research is focused to find cheapest dyes, as full organic, polymeric or cheap metal-based complexes.In some recent works Welter and co-workers [1] synthesized two complexes of iron with salicyloylhydrazono dithiolane ligand, which showed interesting properties and potential applications as dye sensitizers for solar cells. The complexes are strongly colored and undergo spontaneous photo-reduction and photo-isomerisation following a rather complex mechanism. The fine rationalization of the excited state mediated reduction process is fundamental to enhance the properties of the complexes and to maximize the possibility to store and convert solar light. Excited states have been computed at the Time Dependent Density Functional Theory (TD-DFT), that has showed to be reliable in reproducing with good accuracy UV-Vis absorption spectra. The solvatochromic effects have been taken into account using PCM models. A rather systematic benchmark of different functionals, in particular long-range corrected ones is also performed. We will show that we are able to reproduce experimental results correctly and the nature of excited states is analyzed using natural transition orbitals (NTO) [2], allowing a rationalization of their nature and the possibility to enhance the spectroscopic feature of the complexes by a rational modification of ligands.

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SEBOMD: Semi-Empirical Born-Oppenheimer molecular dynamics. Techniques and applications to biological systems [P5]

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Theoretical modelling through classical Molecular Mechanics (MM) is widely used in theoretical chemistry and biochemistry. However, some important chemical phenomena (bond making/breaking, charge transfer, exited states etc.) are in general not accessible by these means, since the quantum chemical nature of the system is involved. On the other hand, ab initio Quantum Mechanics (QM) or Density Functional Theory require large computational costs to study molecular dynamics (MD), thus mixed QM/MM methods are often used to describe a small part of the system at a QM level, while the rest is treated at the MM level. When the portion of the system to be treated at a QM level is large, and/or when it is important to sample the dynamics of the system along reasonable time scales, even such a hybrid approach becomes computationally prohibitive. To overcome this issue, a satisfactory compromise is represented by the use of a QM semiempirical NDDO Hamiltonian (AM1, PM3, etc.) within the Born-Oppenheimer approximation to perform MD simulations (SEBOMD: SemiEmpirical Born-Oppenheimer Molecular Dynamics). At each time step of the simulation, the energy and the gradient of the whole system are computed after a full SCF convergence. The SEBOMD approach has been implemented into a local version of the AMBER 9 suite of programs[1]. MD runs can be performed using periodic boundary conditions, at finite temperature or in the microcanonical ensemble, and long-range electrostatic interactions are treated through the Ewald scheme. A linear scaling Divide & Conquer version of the code is available to tackle large molecular systems.

SEBOMD has already been successfully applied to study molecules in the condensed phase, including liquid water[1] and N-methyl acetamide in water [2]. In this work we focus on its application to small organic molecules, which provide model systems to test the ability of this method to reproduce the solvent effect (solute-solvent hydrogen bond, hydrophilicity/hydrophobicity) on the amino-acids side chains.

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DNA photorepair mechanism by (6-4) photolyase: a QM/MM study [P6]

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When exposed to UV light (200-400 nm), DNA can be damaged, forming covalent bonds between adjacent pyrimidine bases. The most common forms of DNA damage are the cyclobutane pyrimidine dimers (CPD) and pyrimidine-pyrimidone (6-4) photoproducts. Theselesions in the DNA cause difficulty in replication as well as in transcription. If left unrepaired, they can lead to cell death or cancer. DNA photolyase and (6-4) photolyase are two enzymesthat catalyze the reformation of the initial monomers as part of the DNA repair mechanism, by using visible light. The repair of CPD lesion by CPD photolyase is well studied and known. However the repair mechanism of (6-4) lesion by (6-4) photolyase is less known and unclear.In this direction, several hypothetical models for the repair mechanism based on experimental and theoretical methods have been proposed1,2,3,4. However, non of them have been able to fully explain the current observations. Our work aims to develop consistent reliable theoretical models for the repair process by means of a hybrid quantum mechanics/molecular mechanics (QM/MM) computational strategy based on CASSCF geometry optimization and CASPT2 energy corrections. Thereby, outline the energetics of the repair mechanism to discriminate against the various hypotheses, solving both experimental and theoretical discrepancies.This poster will illustrate some of the key factors that influence the complicated DNA repair mechanism and events that occur when the damaged DNA reacts with the (6-4) photolyaseupon light radiation. We outline the excited-state and spectroscopic properties of chemically active chromophore (FADH-) along with the lesion in the (6-4) photolyase system. The effects of protonation of the key amino acid residue (HIS365), and the DNA counter ions (Na^+), which are predicted to play important role in defining the mechanism of enzyme action will also be highlighted.

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How the picture of interactions and conformations in the ethane and small molecules could help for biological systems [P7]

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Non-covalent interactions are very important to understand many molecular, supramolecular and biological systems (eg. protein folding). The NCIPLOT software [1] is based on electronic density and its derivatives. It is developed in order to detect non-covalent interactions but it could be used for some covalent interactions. Thanks to this smart graphical tool, we can reveal, localize and classify all the interactions by just an insight on a picture. The nature of the leading interaction controlling the conformation of ethane is still a question for modern chemistry and thus a challenge for NCIPLOT. As a matter of fact it was evidenced that stabilizing interactions (hyperconjugation) of the staggered conformation plays a more important role than steric repulsion in the eclipsed conformation [2]. The examination NCIPLOT confirms the balance of these both effects. Nevertheless this balance appears to depend strongly on the system considered as it could be seen on the example of hexafluoroethane.

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Generalisation of the vibronic coupling hamiltonian model: application to ethylene [P8]

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The pi-to-pi* photo-excitation of CC bonds and subsequent cis-trans photo-isomerisation is one of the most fundamental processes in organic photochemistry. For example, electronically excited ethylene experiences large-amplitude deformations thateventually lead to ground-state regeneration through a conical intersection. Despite the apparent simplicity of this system, there still remain unanswered questions about the photo-absorption spectrum and the radiationless decay mechanism of this prototypemolecule.
We show here [1] that the lowest manifold of excited electronic states of ethylene can be described correctly with a selected active space of 17 quasi-diabatic configurations built on state-averaged orbitals. This space is stable upon large-amplitudedeformations, such as torsion, pyramidalisation, CC stretching and HCH bending. The properties of the nuclear coordinates and valence and Rydberg electronic states are investigated within the framework of nuclear-permutation-inversion group theory. Thissystematic analysis is compared to a previous model of the valence states of ethylene [2, 3]. Our approach is intended to be generalised to the non-adiabatic photochemistry of organic molecules where large-amplitude deformations require global vibronic Hamiltonian models to be expressed in terms of simple functions of polyspherical valence coordinates.

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An investigation of the photochemical ring-opening of benzopyran [P9]

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Photochemical reaction control with laser pulses is becoming feasible with the ongoing progress of femtochemistry. Those experimental and theoretical advances now allow us to have a better understanding of photochemical phenomena. In most cases,such processes are governed by strong quantum mechanical effects. A correct description thus implies theoretical approaches based on quantum mechanics.
We are interested in cis-trans photoisomerisations. We focus in particular on the conversions of spirobenzopyrans into merocyanins. Some experimental evidences show that benzopyran is a good model for the ring-opening that occurs before the isomerisation [1]. This photoisomerisation involves a conical intersection, which allows an ultrafast radiationless decay of the excited to the ground electronic state after photoexcitation [2]. This means that it is possible to control the process by changing how the excitation energy is distributed among the vibrational modes of the system.
The final aim of our study is to explain and predict photochemical phenomena with quantum dynamics simulations using the multi-configuration time-dependent Hartree (MCTDH) method [3]. Thus, an analytical model for the potential energysurfaces (PES) and interstate couplings is required to perform this kind of calculations.The main issue remains the production of fitted PES

within a reasonable amount of calculations. In addition, chemical processes often imply many large-amplitude motions over which the PES can take very complicated shapes. The present work is devoted to defining a general strategy for producing fitted PES and couplings as simple functions of large-amplitude coordinates. The various steps involved can be summarised as follows.

First, we analyse the geometries and gradients of the stationary and crossing points to determine a reduced set of active coordinates. Finding the most relevant coordinates for describing the reaction path will lead to simpler expressions of the PES. Second, we analyse the electronic structure of the different states involved. We use the complete active space self-consistent field (CASSCF, and a second order perturbation treatment, CASPT2) method to get a good understanding of the problem in terms of dominant electronic configurations. Finally, we build an analytical model for the PES and couplings where the electronic configurations are approximate quasidiabatic states.

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Action of secondary ions on biomolecules: anisotropy and radiosensitization properties [P10]

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Action of high energy radiations, as UV radiations may induce severe damage on biological medium. However, it has been shown that important damage is due to the secondary particles which are generated along the track after interaction of an ionizing radiation with the biological medium [1]. In particular, low-energy secondary ions have been widely investigated recently [2,3]. In such ion-biomolecule collisions, charge transfer and fragmentation mechanisms have to be considered. From a theoretical point of view, the charge transfer process may be studied in the molecular framework and requires the determination of potential energy surfaces of the different states involved in the reaction, as well as the non-adiabatic couplings between these levels. The dynamical treatment may be performed in the keV energy range using semi-classical methods. However, we have extended recently our approach to low-collision energies, still almost unexplored, and specific features have been pointed out.

Such an approach has been developed for the study of charge transfer between carbon ions and uracil, thymine and halouracil targets [4-6]. The radiosensitisation properties can be investigated between uracil or thymine and halouracil targets. The anisotropy of the processes is analyzed in correlation with steric effects and non-adiabatic interactions. Some general features are exhibited.

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