Laser control - an overview

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Starting with some historical notes on laser control, I will discuss examples of laser control in the weak-field as well as strong-field regimes.

Laser Control of quantum dynamics in dissipative environments: a Non-Markovian master equation approach

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Using laser pulses to steer the dynamics of quantum systems opens far reaching possibilities in many areas ranging from reactivity in chemical physics to quantum information processing. However, in most relevant cases, the quantum systems cannot be considered as isolated, and the interaction with an environment alters the dynamics and control scenario.

Here, we present a theoretical approach which is based on the Nakajima-Zwanzig projector formalism combined with an efficient density matrix propagation approach, first proposed in [1]. This method has the specificity of treating dissipation correctly even in the presence of strong external fields, since it explicitly includes the effect of external fields in the dissipative operator kernel. It is thus ideally suited to study dissipative effects in the strong driving regime, and is moreover suited to be combined with theories of coherent control. It thus allows to treat strong field control of non-isolated quantum systems.

Specifically, in this presentation, two examples of strong field control under dissipation are given: the first is a model of Cope's isomerization of the methyl-cyclopentadienylcarboxylate dimer [2], described as the motion along a one-dimensional reaction path, and the second example is devoted to the study of strong field excitations of single quantum dots [3]. In the case of the latter, a systematic analysis of non-Markovian dynamics of excitons generated in an embedded InAs/GaAs quantum dot has is given, for which several experimental results are reported [4,5,6] . These experiments have shown the interplay of acoustic phonon mediation and external driving in the dephasing of the exciton dynamics. The presented theoretical simulations are in good agreement with experimental results, and clearly shows effects of field-dependent relaxation mechanisms.

In the case of the isomerization of the methyl-cyclopentadienylcarboxylate dimer, the non-Markovian master equation is combined with optimal control theory. As major result we find that including dissipation at the design stage is crucial for an effective control, and the underlying mechanisms on how the control field copes with the dissipation is presented [2].

[1] C. Meier and D. J. Tannor *J. Chem. Phys.* 111, 3365 (1999), A. Pomyalov, C. Meier, D. Tannor, Chem. Phys. 370, 98 (2010)
[2] A. Chenel, G. Dive, C. Meier and M. Desouter-Lecomte, *Phys. Chem. A*, J. Phys. Chem. A, 116, 11273 (2012)
[3] A. Debnath, C. Meier, B. Chatel, T. Amand, *Phys. Rev. B*, Phys. Rev. B 88, 201305 (2013)
[4] A. J. Ramsay, A. V. Gopal, E. M. Gauger, A. Nazir, B. W. Lovett, A. M. Fox, and M. S. Skolnick, *Phys Rev Lett.* 104,017402 (2010).
[5] C.-M. Simon, T. Belhadj, B. Chatel, T. Amand, P. Renucci, A. Lemaitre, O. Krebs, P. A. Dalgarno, R. J. Warburton, X. Marie, and B. Urbaszek, *Phys Rev Lett.* 106,166801 (2011).
[6] Y. Wu, I. M. Piper, M. Ediger, P. Brereton, E. R. Schmidgall, P. R. Eastham, M. Hugues, M. Hopkinson, and R. T. Phillips, *Phys Rev Lett.*106,067401 (2011).

Photodetachment of deprotonated chromophore anions: electronic structure and dynamics

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Nature has developed a myriad of highly efficient photoactive proteins for gathering energy for chemical processes and initiating specific actions. A particularly well-known example is the green fluorescent protein (GFP) that was first found in the jellyfish *Aequorea victoria*. Not only is GFP used extensively in cell biology and biomedical research as a fluorescent marker but it also acts as a light-induced electron donor with the potential to monitor and manipulate redox processes in cells.

Studies of the deprotonated chromophore anion in the gas-phase have revealed that the electronic absorption spectrum of the deprotonated chromophore anion in the gas phase is remarkably similar to that in the protein.[1] However, in the gas phase, the deprotonated chromophore anion does not fluoresce[2,3] and its excited state lifetime[4] has been found to be very similar to that in solution.[5]

In this presentation, we will describe competing electron emission processes following photoexcitation in the range 350–315 nm.[6,7] As well as direct electron detachment from S_0, we observe resonant excitation of the $2^1\pi\pi^*$ state of the anion followed by autodetachment. The experimental photoelectron spectra are found to be significantly broader than the photoelectron spectrum calculated using the Franck-Condon method and we attribute this to rapid ($\sim$ 10 fs) vibrational decoherence, or intramolecular vibrational energy redistribution, within the neutral radical. We demonstrate that the competition between direct and indirect electron emission can be controlled by the substitution of electron-donating or electron-withdrawing groups on the phenol ring or increasing the conjugation of the chromophore.

REFERENCES

[1]S. B. Nielsen, A. Lapierre, J. U. Andersen, U. V. Pedersen, S. Tomita, and L. H. Andersen, Phys. Rev. Lett. **87**, 228102 (2002).

[2]M. W. Forbes and R. A. Jockusch, J. Am. Chem. Soc **131**, 17038 (2009).

[3]M. W. Forbes, A. M. Nagy, and R. A. Jockusch, J. Int. J. Mass. Spec. **308**, 155 (2011).

[4]C. R. S. Mooney, D. A. Horke, A. S. Chatterley, A. Simperler, H. H. Fielding, and J. R. R. Verlet, Chem. Sci. **4**, 921 (2013).

[5]D. Mandal, T. Tahara, and S. R. Meech, J. Phys. Chem. B **108**, 1102 (2004).

[6]C. R. S. Mooney, M. E. Sanz, A. R. McKay, R. J. Fitzmaurice, A. E. Aliev, S. Caddick, and H. H. Fielding, J. Phys. Chem. A **116**, 7943 (2012).

[7]C. R. S. Mooney, M. E. Parkes, L. Xhang, H. C. Hailes, A. Simperler, M. J. Bearpark, and H. H. Fielding, J. Chem. Phys. , submitted (2014).

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Glimpse into the excited state dynamics of biochromophores

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Non-adiabatic molecular dynamics is an efficient method for simulating photochemical and photophysical processes by propagating classical nuclear trajectories along multiple electronic potential energy surfaces constructed "on the fly"[1,2]. We have used this technique in combination with time dependent density functional theory to elucidate the mechanisms of radiationless excited-state deactivation in biological chromophores. Specific examples include: the deactivation mechanism of kynurenines, UV filters found in the human ocular lens which protect the retina from radiation damage; studies of ultrafast non-radiative deactivation mechanisms of electronically excited peptides, such as N-acetylphenylalaninylamide (NAPA); and the all-trans to 13-cis photoisomerization of the protonated Schiff base of retinal (SBR^+) in solution. The photoisomerization of SBR^+ in bacteriorhodopsin is one of the fastest photochemical reactions in nature. In solution, the efficiency, speed and selectivity of the reaction are all drastically reduced due to the presence of competing non-reactive mechanisms. The origins of the non-reactive channels active in SBR^+ will be discussed.

[1] J. C. Tully, J. Chem. Phys. 93 (1990) 1061
[2] B. F. E. Curchod, U. Rothlisberger, I. Tavernelli, ChemPhysChem 14 (2013) 1314
[3] M. Mališ, Y. Loquais, E. Gloaguen, H. S. Biswal, F. Piuzzi, B. Tardivel, V. Brenner, M. Broquier, C. Jouvet, M. Mons, N. Došlić, I. Ljubić, J. Am. Chem. Soc. 134 (2012) 20340
[4] M. Mališ, Y. Loquais, E. Gloaguen, C. Jouvet, V. Brenner, M. Mons, I. Ljubić, N. Došlić, Phys. Chem. Chem. Phys. 16 (2014) 2285

Diabatic Strategies for Photochemical Quantum Dynamics

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Quantum dynamics simulations applied to ultrafast photoinduced processes often require an adiabatic-to-diabatic transformation (diabatisation) of the data produced from quantum chemistry calculations. The vibronic coupling Hamiltonian (VCH) quasidiabatic model developed by Köppel and coworkers is a fruitful strategy that has been used for calculating photoabsorption and photoelectron spectra with the multiconfiguration time-dependent Hartree (MCTDH) quantum dynamics approach. We present here a set of strategies to generalise the VCH model to the treatment of photochemical reactions whereby large-amplitude nuclear motions occur along complicated reaction pathways connecting several potential energy wells through transition barriers. This is illustrated on the photoisomerisation of ethylene [1] and the ring opening of benzopyran [2]. A global model based on local information at critical points is being developed for high-dimensional quantum dynamics simulations using the novel multilayer formulation of MCTDH termed ML-MCTDH. Alternatively, the direct dynamics variational multiconfiguration Gaussian (DD-vMCG) wavepacket method frees simulations from this preliminary step by calculating the potential energy and its derivatives on the fly [2]. The quasidiabatic Hamiltonian is currently generated from a regularisation method, and work is in progress to implement a local diabatisation procedure.

1. J. Jornet Somoza, B. Lasorne, M. A. Robb, H.-D. Meyer, D. Lauvergnat, and F. Gatti, J. Chem. Phys. 137 (2012) 084304
2. L. Joubert Doriol, B. Lasorne, D. Lauvergnat, H.-D. Meyer, and F. Gatti, “A generalised vibronic-coupling Hamiltonian model for benzopyran”, J. Chem. Phys. 140 (2014) 044301
3. D. Mendive-Tapia, B. Lasorne, G. A. Worth, M. A. Robb, and M. J. Bearpark, J. Chem. Phys. 137 (2012) 22A548

Laser-induced electron and nuclei localization

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Three examples for localization phenomena in quantum systems are presented. Regarding a simple model for coupled electron-nuclei motion, we investigate the influence of non-adiabatic couplings on the asymmetry of time-resolved photoelectron momentum distributions [1]. In the second case, the control of localization in a double-well potential via the carrier envelope phase of a laser pulse is studied [2]. Finally, exciton localization in a molecular aggregate subject to an external perturbation is discussed [3].

[1] M. Falge, V. Engel, S. Grfe Fingerprints of adiabatic versus diabatic vibronic dynamics in the asymmetry of photoelectron momentum distributions J. Phys. Chem. Lett. 3, 2617-2620 (2012).

[2] K. Hader, K. Renziehausen, V. Engel Carrier envelope phase effects induced by weak multicycle pulses: Localized quantum dynamics in double well potentials Chem. Phys. Lett. 579, 23-27 (2013)

[3] J. Wehner, A. Schubert, V. Engel Vibronic energy localization in weakly coupled small molecular aggregates Chem. Phys. Lett. 541, 49 (2012).

Light-controlled nuclear and electron dynamics in (and sometimes without) an environment

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Optical control of nuclear or electronic dynamics in an environment, *i.e.*, at a surface, in a solvent, or for a chromophore in a large molecule, is typically hampered by two effects: Energy relaxation and dephasing.

In this presentation, in a first part a general introduction into "system plus bath" or "dissipative" dynamics will be given. Methods which rest on either a full description based on wavefunctions and the time-dependent Schrödinger equation, or on reduced models based on open-system density matrices and Liouville-von Neumann equations will be presented. Some basics of optical control by rational laser pulses and of optimal control theory will also provided, both for isolated and open quantum systems.

In a second part, selected applications will be presented:

- State- and mode-selective IR-laser pulse control of adsorbate vibrations at surfaces, such as hydrogen on Si(100) [1] or CO on Cu(100) [2]. A related example is IR-induced subsurface adsorption of H atoms at Pd(111) by laser distillation [3].
- Optically controlled electronic motion in molecules [4] and atoms [5], with the goal to either enforce selective state-to-state transitions, or to control "properties" such as non-linear responses or electron correlation.

[1] G.K. Paramonov, S. Beyvers, I. Andrianov, and P. Saalfrank, Phys. Rev. B **75**, 045405 (2007); G.K. Paramonov, I. Andrianov, and P. Saalfrank, J. Phys. Chem. C **111**, 5432 (2007); I. Andrianov und P. Saalfrank, Chem. Phys. Lett. **433**, 91 (2006); F. Lüder, M. Nest, and P. Saalfrank: Theor. Chem. Accts. **127**, 183-193 (2010).

[2] S. Beyvers, Y. Ohtsuki, and P. Saalfrank, J. Chem. Phys. **124**, 234706 (2006); J.C. Tremblay, S. Beyvers, and P. Saalfrank, J. Chem. Phys. **128**, 194709 (2008). S. Beyvers and P. Saalfrank, J. Chem. Phys. **128**, 074104 (2008).

[3] J.C. Tremblay and P. Saalfrank, J. Chem. Phys. **131**, 084716 (2009); J.C. Tremblay, S. Monturet, and P. Saalfrank, Phys. Rev. B **81**, 125408 (2010).

[4] J.C. Tremblay and P. Saalfrank, Phys. Rev. A **78**, 063408 (2008); J.C. Tremblay, P. Krause, T. Klamroth, and P. Saalfrank, Phys. Rev. A **81**, 063420 (2010).

[5] M. Nest, I. Ulusoy, T. Klamroth, and P. Saalfrank, J. Chem. Phys. **138**, 164108 (2013).

Optimal control of ultrafast dynamics in small atoms and molecules.

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We discuss possibilities to control strong-field dynamics such as ionization and high-harmonic generation in atoms and molecules. The emphasis is on quantum optimal control theory (OCT) as formulated in the 1980s by Rabitz, Kosloff, Tannor et al. We review the basic principles of OCT and demonstrate how it can be used for various purposes by reformulating the target functional. Then we present different applications including controlled excitations, enhanced ionization, suppressed ionization, and high-harmonic generation. The main focus is on single-electron control, but examples and ongoing work in the multielectron regime are described as well.

Intra-Molecular Charge Generation and Control with Ultrashort Laser Pulses

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The ability of strong laser pulses to shape the multi-dimensional landscape of molecules has for some time been recognised as a means for controlling molecular bonds and hence chemical reactivity. However, even with optimally shaped femtosecond laser pulses, the degree of control can be limited as some pathways require very strong fields to induce dissociation when non-resonant transition are not readily available. With the advent of few-cycle optical pulses and XUV attosecond pulses, alternatively the chemistry could be controlled by directing the ultrafast electron dynamics. I will begin by looking at how charge can be localised in dissociation of H2+ using the carrier-envelope phase of few-cycle pulses, before moving onto how the formation and migration of a hole in amino acids and small peptides influences the resulting molecular fragmentation. New attosecond pump-probe observations of charge migration within an amino acid will also be presented and the potential for control of these intramolecular electron wavepackets discussed.

Strong field ionization, laser control and dynamics of small molecules

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We study the strong-field control of a vibrational wavepacket created by multiphoton ionization [1,2]. Two control schemes are employed: reshaping of the wave packet via strong field population transfer ("hole burning"), and redirecting its trajectory by dressing the potential energy surface on which the wavepacket evolves ("photon locking"). As test systems, we use small polyatomic molecules, in particular the halogenated methanes CH_2XY (X, Y = I, Br), where different effects like non-adiabatic coupling and spin-orbit coupling play a role. It is shown, how simulations including such interactions can be extended taking more degrees of freedom into account by looking at the excited-state dynamics of SO_2 [4]. Finally, a simple model for the computation of the initial multiphoton ionization step is shortly introduced [5,6]. For all simulations, a close comparison to experimental measurements is highlighted.

[1] D. Geißler, T. Rozgonyi, J. González-Vázquez, L. González, P. Marquetand, T. C. Weinacht. *Phys. Rev. A*, **84**, 053422 (2011).
[2] D. Geißler, P. Marquetand, J. González-Vázquez, L. González, T. Rozgonyi, T. Weinacht. *J. Phys. Chem. A*, **116**, 11434–11440 (2012).
[3] P. Marquetand, T. Weinacht, T. Rozgonyi, J. González-Vazquez, D. Geißler, L. González in: Advances in Multiphoton Processes and Spectroscopy, Vol. 21, World Scientific, Singapore (2013).
[4] S. Mai, P. Marquetand, L. González, submitted (2014). arxiv.org/abs/1302.1438
[5] M. Ruckenbauer, T. Rozgonyi, M. Pötzlberger, T. Weinacht, P. Marquetand, in preparation.
[6] W. Lunden, P. Sandor, T. Weinacht, T. Rozgonyi, submitted.

Coherent electronic motion in femtoscale: creating and controlling giant molecular antennas

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Attophysics deals with electron dynamics. In this talk we propose different schemes that employ ultrafast (attosecond) pulses and/or static fields or slow oscillating pulses in order to create and manipulate oscillating electric dipoles in homonuclear diatomic cations. We argue that any working control mechanism needs i) to break the symmetry of the system and ii) to sustain highly correlated electronic and nuclear motion, thus pushing the period of oscillation of the dipoles from the electronic (attosecond) timescale to the nuclear (femtosecond) timescales.

Using reduced dimensionality models with regularized soft-core Coulomb potentials for the Hydrogen molecular cation we show that one can create dipoles as large as 40 Debyes oscillating in the far-infrared regime, that act as molecular antennas.

Photophysics of fulvene under the non-resonant Stark effect. Shaping the conical intersection seam

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A new mechanistic strategy to control the excited state lifetimeof fulvene is introduced. It's based on shaping the topography of an extended seam of intersection with the non-resonant Stark effect. Fulvene has a very short excited state lifetime due to an energetically accessible seam of intersection which lies along the methylene torsion coordinate, and the initial decay occurs at the seam segment around the planar conical intersection structure. Starting from our previous[1] model for the excited state dynamics, we have followed a three-step approach to simulate the control. First, we have calculated the effect of a non-resonant electric field on the potential energy surface at the *ab initio* level, including the field in a self-consistent way. We find that the relative energy of the planar segment of the seam is increased by the non-resonant field. In the second step we simulate the control with a static field to derive the main control mechanisms. At moderately intense fields ($\varepsilon \leq 0.03$ a.u.) the decay is faster compared to the field free case because the vibrational overlap between the excited and ground state vibrational functions is increased. However, at more intense fields ($\varepsilon = 0.04$ a.u.) the planar conical intersection is energetically inaccessible and the decay occurs at a slower time scale, at the segment of the seam with more twisted geometries. In the third step, the control is exerted with a non-resonant dynamic field. The acceleration of the decay due to the improved vibrational overlap does not occur, but the decay can be made slower with a dynamic field of 0.08 a.u. The results show the viability of our approach to control the photophysics shaping the topology of the conical intersection seam, and they prove that the extended nature of the seam is crucial to simulate and understand the control.

1 L. Blancafort, F. Gatti, H. Meyer, J.Chem.Phys., 2011, 135

The Time-resolved Photoelectron Spectrum of Toluene

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In order to model the time-resolved photoelectron spectra of aromatic molecules, we use a first-order perturbation expansion to generate the total ion yield as a function of the time of the ionising pulse relative to the pump pulse[1]. This is achieved by combining the overlaps of wavepackets from a series of quantum dynamics calculations carried out using the MCTDH package, where the wavepacket in the pumped state is projected onto the ionic potential energy surface and allowed to propagate thereon. Summing the contributions, moderated with the laser pulse strength, from projections performed at a range of times after the pump pulse we get the total ion yield. Results for the toluene molecule are compared to calculations performed using discretised continua[2] to represent the free-electron wavefunction and also to experimental data[3].

[1] V. Engel, Chem. Phys. Lett., 1991, 178, 130.
[2] M. Seel and W. Domcke, J. Chem. Phys., 1991, 95, 7806.
[3] J. A. Davies, A. M. Green and K. L. Reid, Phys. Chem. Chem. Phys., 2010, 12, 9872.

Effects of Intersystem Crossing on Photoexcited Nucleobases an *ab initio* MD Study using SHARC

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Singlet-triplet transitions in organic molecules are commonly believed not to compete with femtosecond processes such as internal conversion[1]. A recently developed mixed quantum-classical dynamics method called SHARC[2,3], that allows treating non-adiabatic couplings and spin-orbit couplings on the same footing was used to study the deactivation of the DNA/RNA nucleobases cytosine [4,5], uracil and thymine after absorption of UV light involving both, singlet and triplet states. The results, obtained at the CASSCF level of theory, reveal the presence of substantial intersystem crossing taking place in the first picoseconds, thus competing with internal conversion to the ground state. The direct comparison of dynamics including only singlet states to dynamics that take into account possible intersystem crossing to the triplet states shows a qualitative different relaxation behaviour. Thus, the possibility for ultrafast intersystem crossing in biologically relevant systems that lack heavy atoms opens a new view on the importance of these processes in general.

[1] D. A. McQuarrie, and J. D. Simon, *Physical Chemistry: A Molecular Approach* (1997).
[2] M. Richter, P. Marquetand, J. González-Vázquez, I. Sola, and L. González, *J. Chem. Theory Comput.* 7 (2011) 1253-1258.
[3] P. Marquetand, M. Richter, J. González-Vázquez, and L. González, *Faraday Discuss.* 153 (2011) 261-273.
[4] M. Richter, P. Marquetand, J. González-Vázquez, I. Sola, and L. González, *J. Phys. Chem. Lett.* 3 (2012) 3090-3095.
[5] S. Mai, P. Marquetand, M. Richter, J. González-Vázquez, and L. González, *ChemPhysChem.* 14 (2013) 2920-2931.

Financial Support: FWF (P 25827-N28)

Simulations of ultrafast x-ray scattering experiments

Adam Kirrander, School of Chemistry, University of Edinburgh, UK

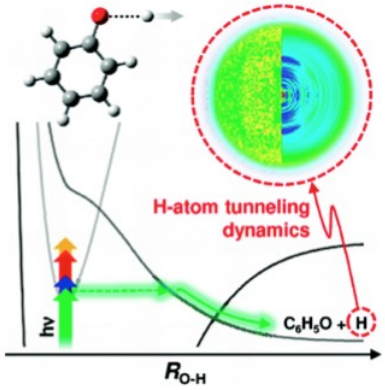
New x-ray free electron lasers provide ultrashort, high-intensity, pulses of coherent x-ray photons that can be used to study ultrafast photochemical processes. In this talk, we will present quantum simulations of electron dynamics in Ar atoms and of the ring-opening reaction of 1,3-cyclohexadiene, and discuss how the x-ray elastic scattering from the systems may be calculated efficiently. On-going work towards accounting for the inelastic contribution will be outlined.

Title: Towards manipulating photodissociation in biological molecules

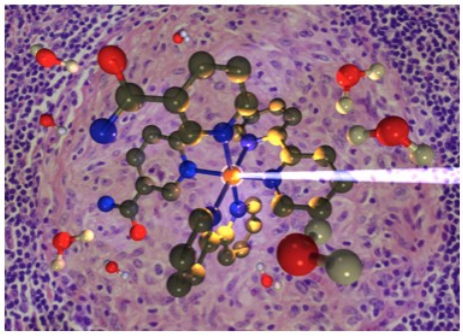
Vasilios Stavros, University of Warwick, UK

Abstract: Through evolution, molecular function has been finely tuned such that even the most complex of chemical processes occurring in humans takes place with exceptional efficiency. One example relates to the origins of resistance to photochemical damage, or *photoprotection*, following absorption of UV radiation of DNA bases, amino acids and their subunits. However, even when photochemical damage occurs, the use of transition metal anti-cancer complexes activated through absorption of UV radiation, termed *photoactivation*, can be used, for example, to destroy cancer cells. This talk will discuss our work into the underlying mechanisms of photoprotection in subunits of biomolecules (a) and more recently our endeavours into photoactivation mechanisms in transition metal complexes (b), both involving photodissociation events.

(a)



(b)



Optimal Control of high-harmonic generation spectra

Jorge Budagosky, Inst. for Biocomputation and Physics of Complex Systems, University of Zaragoza, Spain

We examine computationally the possibility of optimizing the high-harmonic generation (HHG) spectrum of Hydrogen atoms by shaping a laser pulse in the THz range. The spectra are computed with a fully quantum mechanical description, by explicitly computing the time-dependent dipole moment of the systems, which are modeled in one dimension. Specifically, by the quantum optimal control theory (OCT), we studied the possibility of arbitrarily adjusting the plateau extension in the high-harmonic spectra. The cutoff extension of the plateau can be controlled not only by using a frequency window or by increasing the pulse intensity, but increasing the length of this

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Describing Resonance-enhanced Strong-field Ionization with Shaped Laser Pulses Using a Simple Model

Tamás Rozgonyi, Inst. of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Siences, Budapest, Hungary.

A simple model for simulating resonantly enhanced strong field ionization will be presented. The model combines the adiabatic elimination of off-resonant neutral electronic states with the continuum discretization method. In the poster the effect of dynamic Stark-shifts on the photoelecton spectrum will be discussed and pulse shape dependent strong field ionization yields will be interpreted. A comparison of the computed and measured photoelectron spectra distinguishes between a single intermediate resonance leading to multiple continua and multiple intermediate resonances each leading to a separate continuum.

High-harmonic generation by nonlinear resonant excitation of surface plasmon in metallic nanoparticles

Jérôme Hurst, Institut de physique et chimie des matriaux de strasbourg (IPCMS), University of Strasbourg, France

The collective electron dynamics in metal clusters is described using a semiclassical approach based on a quantum hydrodynamic model that incorporates the principal quantum many-body effects, such as the Hartree potential and exchange and correlation effects. Through a variational method, the hydrodynamic equations are reduced to a simple set of differential equations, which are used to determine the ground state and linear-response properties of the cluster. The nonlinear regime is explored by means of numerical simulations. We show that, by exciting the electron dynamics with a chirped laser pulse with slowly varying frequency (autoresonance), it is possible to completely ionize the cluster on a timescale of the order of 100 fs. The accompanying radiated power spectrum is significantly broad.

Ultrafast photodynamics of pyrrole: a comparative TDDFT and ADC(2) study

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Biological chromophores are characterized by efficient excited state relaxation, termed photo-stability. A high degree of photo-stability appears to be an evolutionary adaptation to life on Earth, as the mechanism minimizes the occurrence of potentially harmful reactions in the excited electronic states. In this context a key protective role has been attributed to excited state proton transfer and elimination reactions.

Here we will present a photodynamics study of pyrrole, a prototype biological chromophore, using full-dimensional nonadiabatic dynamics simulations based on the Tully surface hopping algorithm [1]. We compared the performance of two electronic structure methods: time dependent density functional theory and the algebraic diagrammatic construction to second order (ADC(2)) method.

For medium sized molecules, calculations using the ADC(2) scheme are sufficiently fast for use in nonadiabatic dynamics simulations, and in most cases give a good description of the excited states. Unlike coupled-cluster methods, ADC(2) is also numerically stable in regions near conical intersections where excited states become degenerate.

We compare our results with recent experimental measurements with the goal of reducing the existing gap between theory and experiment [2,3].

[1] S. Hammes-Schiffer, J.C. Tully, J. Chem. Phys. 101 (1994), 4657

[2] Mario Barbatti J. Pittner, M. Pederzoli, U. Werner, R. Mitric, V. Bonacic-Koutecký, H. Lischka, Chem. Phys. 375 (2010) 26

[3] G. M. Roberts, C. A. Williams, H. Yu, A. S. Chatterley, J. D. Young, S. Ullrich, V. G. Stavros, Faraday Discuss, 163 (2012) 95-116

A time and velocity resolved study of alkali atoms desorbing from helium nanodroplets

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With temperatures in the cold regime (0.38 K) and only weak interaction, doped Helium Nanodroplets are interesting environments to study pertubations of atoms and molecules induced by many particle interaction. Within this context, we will present results concerning the desorption dynamics of the heavy alkali atoms Rb and Cs from helium droplets. Both dopants are weakly attached to the droplet surface. By resonance enhanced multiphoton-ionization via low lying pseudodiatomic Σ- and Π-states and subsequent ion and electron imaging, we observe dissociation dynamics similar to that of a diatomic molecule and an energy transfer to the droplet during the desorption process, suggesting substantial He-droplet excitation. In addition, the desorption process has been studied in a fs-pump probe scheme. By detecting either the bare Rb-ions or the whole ionized droplet, we observed submersion dynamics occuring within 1 ps. Besides that, the formation dynamics of exciplexes has been investigated.

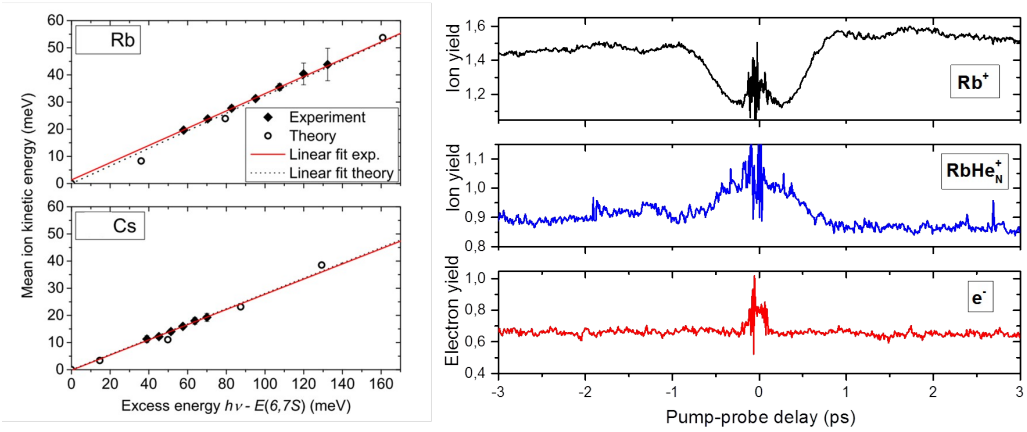

Figure 1: Left: Mean kinetic energy of the desorbing Rb- and Cs-atoms as a function of laser excitation via pseudodiatomic sΣ-states. Right: fs pump probe scans for bare Rb ions, ionized doped droplets and electrons.

Strong laser field control of the direct photodissociation of methyl iodide in the A band

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Strong field control scenarios are investigated in the CH_3I ultrafast dissociation dynamics in the A band. This process, that takes place in a timescale of tens of femtoseconds, generates $CH_3(\nu)$ and I through two possible channels. If the reaction evolves adiabatically in the state firstly excited ($^3Q_0$), spin-orbit excited $I^*(^2P_{1/2})$ and low kinetic energy methyl fragments are generated. The second channel yielding ground $I(^2P_{3/2})$ and high kinetic energy methyl fragments is the result of population transfer to the $^1Q_1$ state through a conical intersection [1].

In our work, we show how moderately strong ($\sim 5TWcm^{-2}$) NIR laser pulses can be used to modify the outcome of the reaction by creating a light induced conical intersection (LICI)[2] between the $^3Q_0$ and the ground states. This allows us to alter the photofragmentation process in two different ways by changing different parameters of the control laser pulses: it is possible to modify the ratio between the ground and spin-orbit excited I atoms generated in the photodissociation and the kinetic energy of the fragments resulting from the dissociation through the light induced conical intersection.

[1] R. de Nalda, J. Durá, A. García-Vela, J. G. Izquierdo, J. González-Vázquez, L. Bañares, J. Chem. Phys. 128, 244309–20 (2008)
[2] J. González-Vázquez, L. González, I. R. Solá, J. Santamaría, J. Chem. Phys. 131, 104302–5 (2009)