

Twentieth International Workshop on

**Quantum Systems in Chemistry,
Physics and Biology**

14-20 September 2015
Varna, Bulgaria

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The Previous Workshops

- **QSCP-XIX 2014 Taipei**, Taiwan (Main organizer: Chao-Ping Hsu)
- **QSCP-XVIII 2013 Paraty** [Rio de Janeiro], Brazil (Main organizer: Marco Antonio Chaer Nascimento)
- **QSCP-XVII 2012 Turku**, Finland (Main organizer: Matti Hotokka)
- **QSCP-XVI 2011 Kanazawa**, Japan (Main organizer: Kiyoshi Nishikawa)
- **QSCP-XV 2010 Cambridge** (Main organizer: Philip Hoggan)
- **QSCP-XIV 2009 Madrid** [El Escorial] (Main organizer: Gerardo Delgado-Barrio)
- **QSCP-XIII 2008 Lansing** [MI, USA] (Main organizer: Piotr Piecuch)
- **QSCP-XII 2007 Windsor** [Royal Holloway] (Main organizer: Stephen Wilson)
- **QSCP-XI 2006 St Petersburg** [Pushkin] (Main organizer: Oleg Vasyutinskii)
- **QSCP-X 2005 Tunis** [Carthage] (Main organizer: Souad Lahmar)
- **QSCP-IX 2004 Grenoble** [Les Houches] (Main organizer: Jean-Pierre Julien)
- **QSCP-VIII 2011 Athens** [Spetses] (Main organizer: Aristides Mavridis)
- **QSCP-VII 2002 Bratislava** [Casta Paprinicka] (Main organizer: Ivan Hubac)
- **QSCP-VI 2001 Sofia** (Main organizer: Alia Tadjer)
- **QSCP-V 2000 Uppsala** (Main organizer: Erkki Brändas)
- **QSCP-IV 1999 Paris** [Marly-le-Roi] (Main organizer: Jean Maruani)
- **QSCP-III 1998 Granada** (Main organizer: Alfonso Hernandez-Laguna)
- **QSCP-II 1997 Oxford** (Main organizer: Stephen Wilson)
- **QSCP-I 1996 Pisa** [San Miniato] (Main organizer: Roy McWeeny)

Scientific and Social Program of QSCP-XX – Varna, Bulgaria
September 14–20, 2015

Monday 14-09	Tuesday 15-09	Wednesday 16-09	Thursday 17-09
	<i>Session : CMQC</i> <i>Chair: Moiseyev</i>	<i>Session : MSDS</i> <i>Chair: Levine</i>	<i>Session : CMQC</i> <i>Chair: Cederbaum</i>
	09:00 Levine	09:00 Cederbaum	09:00 Lefebvre
	09:40 Savin	09:30 Michl	09:30 Herbert
	10:10 Mukherjee	10:00 Bacchus	10:00 Witek
	10:40 Coffee	10:30 Coffee	10:30 Coffee
	<i>Session : MSDS</i> <i>Chair: Michl</i>	<i>Session : AMSF</i> <i>Chair: Maruani</i>	<i>Session : CMQC</i> <i>Chair: Mukherjee</i>
	11:00 Champagne	11:00 Glushkov	11:00 Maruani
	11:30 Maitra	11:30 Surauud	11:30 Sanchez
	12:00 Kuleff	12:00 Demekhin	12:00 Wasserman
	12:30 Lunch	12:30 Lunch	12:30 Lunch
	13:30-16:00 Tour of the complex and beach	13:30 Visit to Pobiti Kamani (Stone Forest), Varna Museum and Thracian Treasures	13:30 Visit to Balchik and Aladzha Monastery
14:00 Registration opens	<i>Session : RCCR</i> <i>Chair: Delgado-Barrio</i>		
	16:00 Klaiman		
	16:30 Wu		
	17:00 Jiang		
17:00 Opening Session Conference Lectures	17:30 Coffee	17:00 Coffee	17:00 Coffee
17:20 Tonev	<i>Session : RECQ</i> <i>Chair: Glushkov</i>	<i>Poster Session</i> <i>Chair: Champagne</i>	<i>Poster Session</i> <i>Chair: Kuleff</i>
17:40 Todorov	18:00 Karwowski 18:30 Khetselius	17:30 Flash presentations	17:30 Flash presentations
18:20 Moiseyev	19:00 Svinarenko	18:30-19:30 Poster session	18:30-19:30 Poster session
19:00 Welcome Party	19:30 Music Party		

Scientific and Social Program of QSCP-XX – Varna, Bulgaria
September 14–20, 2015

Friday 18-09		Saturday 19-09	Sunday 20-09	
<i>Session : CMQC</i> <i>Chair: Gross</i>		<i>Session : CCPB</i> <i>Chair: Galabov</i>	<i>Session : CCPB</i> <i>Chair: Yu Chin-Hui</i>	
09:00 Brändas		09:00 Gross	09:00 Drakova	
09:30 Nascimento		09:30 Canuto	09:30 Shigeta	
10:00 Szabados		10:00 Yu Chin-Hui	10:00 Yu Jen-Shiang	
10:30 Coffee		10:30 Coffee	10:30 Coffee	
<i>Session : MSDS/CCPB</i> <i>Chair: Brändas</i>		<i>Session : RCCR</i> <i>Chair: Jenkins</i>	<i>Session : CCPB</i> <i>Chair: Tadjer</i>	
11:00 Császár		11:00 Delgado-Barrio	11:00 Millot	
11:30 Averbukh		11:30 Galabov	11:30 Jaziri	
12:00 Frutos		12:00 Gonzalez-Lezana	12:00 Wang	
12:30 Lunch		12:30 Lunch	12:30 Closing Session	
<i>Session : CMQC/MNEB</i> <i>Chair: Nascimento</i>		13:15 Visit to Euxinograd Palace and Winery	13:00 Lunch	
14:00 Jenkins				
14:30 Hsu				
15:00 Banacky				
15:30 Chatterjee		<i>Session : CCPB</i> <i>Chair: Wang</i>	14:00 Departures See you next year at ... (to be announced at the Banquet)	
16:00 Coffee		16:15 Sheka		
<i>Session : CCPB/MNEB</i> <i>Chair: Hsu</i>		16:45 Guskova		
<i>Session : MSDS</i> <i>Chair: Császár</i>		17:15 Castaño		
16:30 Temprado		16:30 Rashev		17:45 Coffee
17:00 Georgiev		17:00 Takahashi		<i>Session : MSDS</i> <i>Chair: Averbukh</i>
17:30 Mirzaei		17:30 Nenov		
18:00 Romanova		18:00 Mejia		
18:30 Makhoute		18:30 Kuo		
		19:00 Mehandzhiyski		
19:30 Conference Banquet				

INRNE Achievements in the Field of Experimental Research

D. Tonev

Institute for Nuclear Research and Nuclear Energy, Bulgarian Academy of Sciences, Sofia 1784, Bulgaria

- The Institute for Nuclear Research and Nuclear Energy (INRNE) at the Bulgarian Academy of Sciences (BAS) has been working since 2012 on the project “Cyclotron laboratory of INRNE–BAS”. The project was launched in 2012 at the initiative of the Council of Ministers of the Republic of Bulgaria and the management of INRNE-BAS to solve a very old problem of the country – the lack of domestic production of short lived medical cyclotron radioisotopes.
- The project envisions a new cyclotron laboratory as a part of INRNE-BAS consisting of: a specialized building that meets the regulatory requirements in the field of radiation safety and good manufacturing practices in the pharmaceutical industry; a bunker with a TR-24 cyclotron; a sector for nuclear physics and applied research and development in radiopharmacy with enhanced educational functions; a sector for the production of radiopharmaceuticals.
- One of the main objectives of the project is within five years to allow for regular supply of ¹⁸F-FDG to 8 regional PET/CT centres at a low price, providing “full cost recovery”, with a small profit margin used to sustain the laboratory. This will allow the examination of 16,000 patients a year in the regional PET/CT centres. The wider access to PET/CT will improve the health and extend the life of the patients suffering from cancer. The revenue from the sale of radioisotopes and radiopharmaceuticals will be fully reinvested in the research program and in the development of the laboratory
- The TR-24 cyclotron of INRNE-BAS has the following characteristics: accelerates negatively charged hydrogen ions; variable energy of the proton beam; minimum energy of the proton beam of 15 MeV; maximum energy of the proton beam of 24 MeV; proton beam current of 400 μ A, upgradeable to 1000 μ A; simultaneous extraction of two proton beams; external CUSP ion source.
- The cyclotron parameters have been selected in such a way that in the next twenty years INRNE–BAS will be able to produce a wide range of radioisotopes with applications in medicine with a relatively low initial investment and moderate maintenance costs. At these proton energies and beam current it is possible to produce commercial quantities of radioisotopes with traditional and expected future applications in medicine as: PET radioisotopes – ¹⁸F, ¹²⁴I, ⁶⁴Cu, ⁶⁸Ge/⁶⁸Ga; SPECT radioisotopes – ¹²³I, ¹¹¹In, ⁶⁷Ga, ^{99m}Tc; alpha-emitters for therapy – ²²⁵Ac/²¹³Bi, ²³⁰U/²²⁶Th. Some part of the equipment for the production of radioisotopes will be designed and constructed in INRNE–BAS with the help of the Design and Production Workshop – Physics and will be sold on the international market subsequently.
- **Acknowledgments:** We thank for the generous contributions of our first financial donors – the United States Department of Energy and NPP “Kozloduy”

Pythagorean Trends in Quantum Field Theory(?)

I. Todorov

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Feynman amplitudes in perturbative quantum field theory are being expressed in terms of a family of functions – extending the familiar logarithms, and associated numbers – *periods*. The study of these functions (including hyperlogarithms) and numbers (like multiple zeta values), that dates back to the time of Leibniz and Euler, has attracted anew the interest of algebraic geometers and number theorists during the last decades. The two originally independent developments are recently coming together in an unlikely but rather healthy collaboration between what is regarded as the most abstruse domain of mathematics and particle physics.

Complex Potential Energy Surfaces for Cold Collision Experiments

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In cold molecular collision experiments molecular resonances (auto-ionizing and pre-dissociative metastable states) are generated and their finger prints are observed in the measured cross sections.

The evaluation of the cross sections for cold collision experiments requires the calculation of complex potential energy surfaces (CPES). However, the computation of CPES is difficult since it requires a severe modification of the standard codes and methods developed for the electronic structure calculations.

Here we show how CPES can be calculated by using the standard electronic structure codes without the need to modify them. The “trick” is to carry out analytical continuations to the complex energy plane of the real eigenvalues obtained by the standard method using the fact that the basis set is not complete. For complete (infinite) basis set it has been proved that such analytical continuations are not possible.

In the talk the motivation for calculating CPES, the difficulties to compute them, and our solution to this problem will be explained in a simple illustrative way.

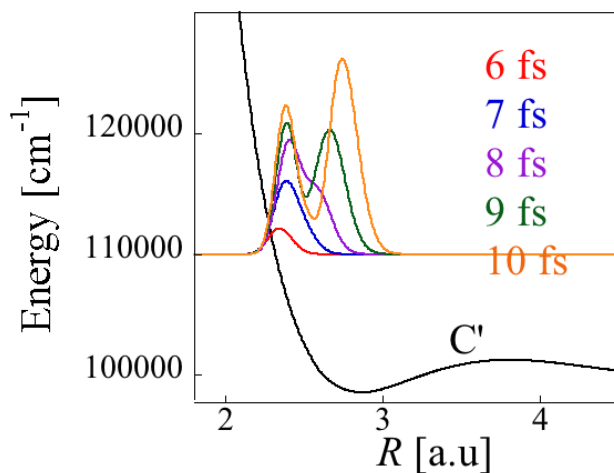
Pumping Ultrafast Nonequilibrium Electron Dynamics and Probing by the Induced Nuclear Motion

R.D. Levine

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An ultrashort pulse spans coherently a range of frequencies and, if short enough, the pulse can excite a superposition of electronic states. Such a coherent superposition is not a stationary state [1]. This opens up a variety of post Born Oppenheimer dynamics that are not possible when the electrons are equilibrated with the instantaneous configuration of the nuclei. Here we specifically discuss the probing of the electron dynamics upon excitation. An experimental setup for producing an ultrafast pump can also produce an ultrafast probe that is delayed with respect to the pump. The probe can ionize the non stationary electronic state, for example [2].

A different scheme is to probe the non equilibrated electrons by the response of the nuclei. We have discussed, Figure 1, [3] prompt dissociation as such a probe. The figure shows a computation for N_2 where the ultrafast pulse is included in the Hamiltonian and the atoms are allowed to move. Very shortly the excited molecule reaches the repulsive dissociative C' state. In the talk we will provide also other potential signatures of the electronic reorganization as seen through the motion of the nuclei.



- References:** [1] F. Remacle and R.D. Levine, *An electronic time scale in chemistry*, Proceedings of the National Academy of Sciences **103**(18), p. 6793–6798 (2006).
[2] B. Mignolet, R.D. Levine, and F. Remacle, *Electronic Dynamics by Ultrafast Pump Photoelectron Detachment Probed by Ionization: A Dynamical Simulation of Negative-Neutral-Positive in LiH*, Journal of Physical Chemistry A **118**(33), p. 6721–6729 (2014).
[3] B.H. Muskatel, F. Remacle, and R.D. Levine, *AttoPhotoChemistry. Probing ultrafast electron dynamics by the induced nuclear motion: The prompt and delayed predissociation of N-2*, Chemical Physics Letters **601**, p. 45–48 (2014).

Spectrum Conserving Modified Coulomb Operators?

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The divergence of the Coulomb operator is eliminated by choosing:

$$\frac{1}{r} \rightarrow \frac{\operatorname{erf}(\mu r)}{r} + c \exp(-\alpha^2 r^2)$$

It is shown that for a certain range of the parameter μ , the parameters c and α can be chosen such that the bound spectrum of the hydrogen atom can be reproduced with an accuracy better than 1 mhartree.

Its extension to more than one-particle is discussed, for

1. the harmonium with two electrons, and
2. the uniform electron gas

Finally, speculations about its use in density functional, and in perturbation theory are presented.

Unitary Group Adapted MRCC and MRPT Theories: SU vs SS Approaches

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In this talk we will undertake a comparative study of the formulations and implementations of State-Specific (SS) and State-Universal (SU) Multi-reference Coupled Cluster (MRCC) theories, which are explicitly unitary group-adapted (UGA) and thus do not suffer from spin-contamination. We will refer to them as UGA-SSMRCC [1] and UGA-SUMRCC [2,3] respectively. We shall also discuss the perturbative analogue of the SS version which we call UGA-SSMRPT2 [4].

These formulations involve a new normal ordered multi-exponential type cluster Ansatz analogous to but different from the one suggested by Jeziorski and Monkhorst (JM). Unlike the JM Ansatz, we define our cluster operators with spin-free generators of the Unitary Group. The excitation operators are noncommuting in general, and this is why we invoked the normal ordered multi-exponential Ansatz to simplify the working equations. The UGA-SUMRCC follows from the Bloch equation involving a suitable active space, while the UGA-SSMRCC theory requires suitable sufficiency conditions to arrive at a well-defined set of equations for the cluster amplitudes. A comparative study of the performance of the projection equations and the amplitude equations will also be touched upon.

UGA-SSMRPT2 [4], a perturbative approximant to the UGA-SSMRCC, is explored as a worthwhile undertaking since it has the potentiality of describing the PES of large systems in a size-extensive, size-consistent and intruder-free manner. The perturbative approximation to any MRCC presents a unique set of challenges with regard to maintaining the desirable characteristics of the corresponding CC theory and including the essential physics in a compact manner. Analyzing size-consistency for an orbitally non-invariant multi-reference theory, such as our UGA-SSMRPT, is also subject to special hurdles which we try to analyze in a systematic manner [5].

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Challenges in the Prediction of the Nonlinear Optical Properties of Small Molecules and Molecular Switches

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Notwithstanding continuous methodological developments, predicting and interpreting the nonlinear optical (NLO) properties of molecules remains a challenge for quantum chemistry, owing to the many different aspects that need to be taken into account: i) slow basis set convergence, ii) huge electron correlation effects, iii) strong frequency dispersion, iv) vibrational contributions, and v) impact of the surrounding. In this talk, several of these issues will be illustrated by considering small reference molecules and molecular switches. In the case of small molecules, the focus will be on the description of frequency dispersion at correlated levels by addressing the performance of approximate schemes and by assessing the reliability of density functional theory [1,2]. Moreover, since these molecules are typically used as internal references for experimental hyperpolarizability evaluations, comparisons with experiment will be presented. Then, in the case of molecular switches, *i.e.* molecules that can commute between two or more forms displaying contrasts in their NLO properties, the presentation will discuss design rules to achieve large hyperpolarizability contrasts [3]. For these systems, the effects of the surrounding will also be discussed: solvent effects [4], chromophores in biological environments [5], surface functionalization [6], and solid state effects.

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Electron-Electron and Election-Ion Correlation Potentials in Strong Field Dynamics

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The study of electron dynamics far from the ground-state is of increasing interest today in many applications: attosecond control and manipulation of electron and consequent ion dynamics, photovoltaic design, photoinduced processes in general. Time-dependent density functional theory has had much success in the linear response regime for calculations of excitation spectra and response, but its reliability in the fully non-perturbative regime is less clear, although increasingly used. By studying some exactly-solvable models of charge-transfer dynamics and strong-field processes, we find that the exact correlation potential of time-dependent density functional theory develops stark features in time that are missed by the currently available approximations. We discuss these features and their implications for charge transfer dynamics and time-resolved spectroscopy. In the second part of the talk, we broaden our focus to the description of coupled electron-ion motion. When the coupling to quantum nuclear dynamics is accounted for, we find additional terms in the potential acting on the electronic subsystem, that fully account for electron-nuclear correlation, and that can yield significant differences to the traditional potentials used when computing coupled electron-ion dynamics. We study such potentials for the phenomena of field-induced electron localization, and charge-resonance enhanced ionization, within the exact-factorization approach to coupled electron-ion dynamics.

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Controlling Ultrafast Charge Migration in Molecules

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Exposing molecules to ultrashort laser pulses can trigger pure electron dynamics in the excited or ionized system. In the case of ionization, these dynamics may manifest as an ultrafast migration of the initially created hole-charge throughout the ionized molecule and were termed charge migration [1]. Charge migration is solely driven by electron correlation and appeared to be a rich phenomenon with many facets that are rather characteristic of the molecule studied [2]. All this increasingly attracts the attention of the scientific community from both theoretical and experimental sides. Due to the coupling between the electronic and the nuclear motion, the control over the pure electron dynamics offers the extremely interesting possibility to steer the succeeding chemical reactivity by predetermining the reaction outcome at a very early stage. A way to control the charge migration [3] by appropriately tailored [4] femtosecond laser pulses will be presented and the consequences of the application of such a scheme will be discussed.

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Barrierless Single-Electron-Induced *Cis–Trans* Isomerization

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Lowering the activation energy of a chemical reaction is an essential part in controlling chemical reactions. By attaching a single electron, a barrierless path for the *cis–trans* isomerization of maleonitrile on the anionic surface is formed. The anionic activation can be applied in both reaction directions, yielding the desired isomer. We identify the microscopic mechanism that leads to the formation of the barrierless route for the electron-induced isomerization. The generalization to other chemical reactions is discussed.

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Density Functional Theory Studies on Electronic and Photocatalytic Properties of Some Heavy-Metal Containing Compounds

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The consumption of traditional fossil-fuel energy resources cause the increasingly serious environmental problems resulting in the crisis of human sustaining development. The clean and renewable energy has attracted much attention over the past decade. Hydrogen energy and solar energy belong to this category. Photocatalysis is an environmentally-friendly technology that can split water to produce clean hydrogen energy and convert CO₂ to hydrocarbon fuel using the most abundant renewable resource, solar light. In this abstract we present the recent results of our research group on computational studies on the electronic structures and photocatalytic properties of a series of heavy-metal containing compounds. For example, the theoretical results demonstrated that Ag₃PC₄^{VI} (C = S, Se) both are potential candidates for the photocatalytic hydrogen generation from water. AgSb_{0.8125}Bi_{0.1875}O₃ solid-solution is a promising candidate for solar light absorption makes for the production of oxygen in a Z-scheme water-splitting system with the combination of a strong oxidizing potential and an optimal band gap.

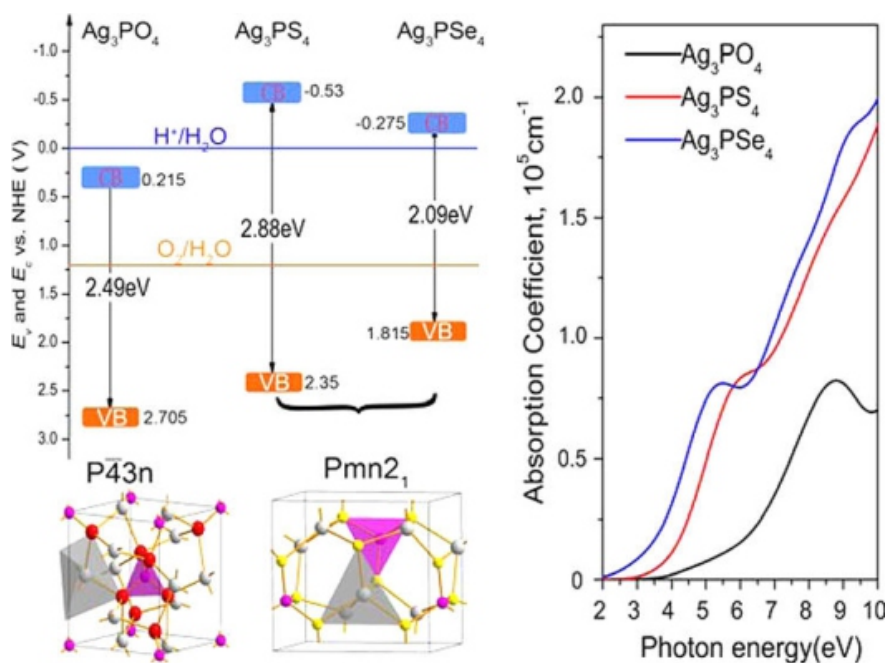


Figure: Electronic and Photocatalytic Properties of the silver compound Ag₃PC₄^{VI} (C = O, S, Se).

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Theoretical Study of Methane Adsorption and Reaction on IrO₂ (110) Surface

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The capability to activate methane at mild temperature and facilitate all elementary reactions on the catalyst surface is an important issue, especially for the direct conversion of methane to ethylene. In my talk, I will present the catalytic characteristic of an IrO₂ (110) surface for methane activation. The energetics and mechanism for methane dehydrogenation reactions, as well as C–C coupling reactions on the IrO₂ (110) surface, are investigated by using van der Waals-corrected density functional theory calculations. The results indicate that a non-local interaction significantly increases the binding energy of a CH₄ molecule with an IrO₂ (110) surface by 0.35 eV. Such an interaction facilitates a molecular-mediated mechanism for the first C–H bond cleavage with a low kinetic barrier of 0.3 eV which is likely to occur under mild temperature conditions. Among the dehydrogenation reactions of methane, CH₂ dissociation into CH has the highest activation energy of 1.19 eV, making CH₂ the most significant monomeric building block on the IrO₂ (110) surface. Based on the DFT calculations, the formation of ethylene could be feasible on the IrO₂ (110) surface via selective CH₄ dehydrogenation reactions to CH₂ and a barrierless self-coupling reaction of CH₂ species. The results provide an initial basis for understanding and designing an efficient catalyst for the direct conversion of methane to ethylene under mild temperature conditions.

Dirac Operator in Quantum Chemistry: A Bumpy Way to Understanding

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The energy spectrum of the free Dirac operator corresponding to an electron is composed of two continua: the positive one from mc^2 to $+\infty$ and the negative one from $-mc^2$ to $-\infty$ separated by the energy gap $(-mc^2, +mc^2)$. The Dirac operator in an external field may have discrete eigenvalues in the gap. These very eigenvalues and the corresponding eigenfunctions, in cases of external potentials of physical significance, correspond to physically observed states and are interesting from the point of view of both physics and chemistry. The variational description of the discrete spectrum of the Dirac operator is governed by a theorem known as the mini-max principle [1]. There are many different modes of implementation of this principle, ranging from simple approximations and numerical prescriptions to strict models which, in principle, can lead to a numerically exact reproduction of both the discrete part of the spectrum and the corresponding wavefunctions.

Generalizations to a many-electron case create new challenges related to the complicated structure of the continuous parts of the spectrum and the degeneracy of the discrete and continuous spectra leading to the so called Brown-Ravenhall disease. Here, a clean distinction between mathematical structures resulting from defining the many-electron Hilbert space as a tensor product of one-electron Hilbert spaces and models directly describing physically observed phenomena is essential but not trivial [2].

The diagnostics of the results obtained within models based on discrete representations of the Dirac operator, in particular the assignment of a computed energy level to the discrete spectrum or to one of the continua is, in many cases, difficult (probably the best known example are the so called ‘spurious roots’). A very general and powerful tool for such a diagnostics is offered by the complex coordinate rotation (CCR) method in which a simple separation of the discrete and the continuous parts of the discretized spectra is possible [3].

The evolution of our understanding of the consequences of the unusual properties of the Dirac operator over the nine decades which passed since this operator was defined is strongly coupled with the construction of specific computational models and, most important, with establishing links between the results of calculations and the physical reality. The aim of this presentation is a discussion of these topics.

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Hyperfine and Electroweak Interaction and Parity Violation in Heavy Finite Fermi-System

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Nowadays, the parity non-conservation effect in heavy atomic, nuclear and molecular systems has a potential to probe a new physics beyond the Standard Model. In our paper we systematically apply the formalism of the nuclear-QED many-body perturbation theory [1–3] to precise studying a parity violation effect in heavy atoms with account for the relativistic, nuclear and radiation QED corrections. The nuclear block of theory is presented by the relativistic mean field model (the Dirac–Woods–Saxon model). As a test, we present the results of computing the energy levels, hyperfine structure intervals, $E1$, $M1$ radiation transitions amplitudes in the heavy atoms such as ^{133}Cs , ^{173}Yb , ^{205}Tl . Further we have computed the parity violation radiative amplitudes for a number of the atomic and nuclear systems, namely: ^{133}Cs , ^{173}Yb , ^{205}Tl (atomic parity violation) and $^{119,121}\text{Sn}$ (nuclear parity violation). Accuracy of accounting for the inter electron exchange-correlation corrections, the Breit and weak e – e interactions, radiation & nuclear (magnetic moment distribution, finite size, neutron “skin”) effects, nuclear spin dependent corrections due to an anapole moment, Z -boson [$(A_n V_e)$ current] exchange, the hyperfine- Z boson exchange [$(V_n A_e)$ current] have been analysed. Besides, the weak charge has been calculated for the ^{133}Cs , ^{205}Tl atoms and firstly ^{173}Yb and comparison of the theoretical results with the Standard Model data has been done. Using the experimental parity non-conservation parameter value $\Delta E_1^{PNC}/\beta = 39$ mV/cm (Berkeley, 2009; Tsigutkin *et al.*) and our value $9.707 \cdot 10^{-10} e a_B$, it is easily to determine the weak charge value $Q_W = -92.31$ for ^{173}Yb ($Z = 70$, $N = 103$) that should be compared with the Standard Model value $Q_W = -95.44$.

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Theoretical Studying Spectra of Lanthanides Atoms on the Basis of Relativistic Many-Body Perturbation Theory

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The talk is devoted to application of the a relativistic many-body perturbation theory [1] with the Dirac-Kohn-Sham (DKS) zeroth approximation to studying spectra of heavy atoms, in particular, spectra of lanthanides (Yb, Tm) atoms. The wave function zeroth basis is computed from the Dirac equation with potential, which includes ab initio (the optimized DKS potential, the electric potential of a nucleus). All correlation corrections of the second order and dominated classes of the higher orders diagrams (electrons screening, particle-hole interaction, mass operator iterations) are taken into account. As example, in Table 1 we list our selected data and experimental (compilation) and other theoretical data for energies (accounted from the ground state: $4f^{14}6s^2\ ^1S_0$) of some YbI singly excited states: MCHF-BP – data, obtained on the basis of multiconfiguration Hartree-Fock method, HFR – data, obtained on the basis of Cowan's code of the relativistic Hartree-Fock method; MBPT-data by Ivanov *et al.* obtained on the basis of the model many-body perturbation theory (from Refs. [2]).

Table 1: The Yb singly excited states energies (cm^{-1}).

Conf.	J	MCHF	HFR	MBPT	Exp.	Our data
$6s_{1/2}6p_{1/2}$	0	17262	17320	17400	17288	17310
$6s_{1/2}6p_{3/2}$	1	26667	25069	25500	25068	25094
$6s_{1/2}6p_{3/2}$	2	18249	19710	19800	19710	19715
$6s_{1/2}5d_{3/2}$	1	28871	24489	23900	24489	24410
$6s_{1/2}5d_{5/2}$	2	29633	27677	26100	27678	26970
$6s_{1/2}5d_{5/2}$	3	29374	25271	24900	25271	25098

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On Systems with and without Excess Energy in Environment ICD and Other Interatomic Mechanisms

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How does a microscopic system like an atom or a small molecule get rid of the excess electronic energy it has acquired, for instance, by absorbing a photon? If this microscopic system is isolated, the issue has been much investigated and the answer to this question is more or less well known. But what happens if our system has neighbors as is usually the case in nature or in the laboratory? In a human society, if our stress is large, we would like to pass it over to our neighbors. Indeed, this is in brief what happens also to the sufficiently excited microscopic system. A new mechanism of energy transfer has been theoretically predicted and verified in several exciting experiments. This mechanism seems to prevail “everywhere” from the extreme quantum system of the He dimer to water and even to quantum dots. The transfer is ultrafast and typically dominates other relaxation pathways.

Can there be interatomic/intermolecular processes in environment when the system itself (again, an atom or small molecule) does not possess excess energy? The answer to this intriguing question is yes. The possible processes are introduced and discussed. Examples and arguments are presented which make clear that the processes in question play a substantial role in nature and laboratory.

Work on the interatomic processes discussed can be found in the Bibliography:

<http://www.pci.uni-heidelberg.de/tc/usr/icd/ICD.refbase.html>

Toward New Materials for Singlet Fission: Structural Design Rules

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Singlet fission is a photophysical process in which a singlet excited molecule transfers some of its energy to a nearby ground state molecule to produce the triplet excited state of each. The two triplets are initially coupled into an overall singlet, making this mode of converting singlets to triplets in a dimer, aggregate, or solid spin-allowed and often ultrafast. Singlet fission is of potential interest for solar energy conversion since it promises an increase of the maximum theoretical efficiency of an inexpensive single-junction solar cell from the Shockley-Queisser limit of 1/3 to nearly 1/2. A serious obstacle to its practical utilization is the very tiny number of materials that are known to perform the process efficiently. Most are related to tetracene or pentacene and none of them seem to be very practical. It therefore appears important to formulate qualitative structural design rules for additional materials that perform singlet fission efficiently. This has been accomplished using a diabatic quantum mechanical treatment of a simple model in which only the frontier molecular orbitals of the two partners are considered. The rules have two parts: (i) selection of a chromophore, and (ii) identification of an optimal spatial relation between two chromophores.

Influence of Nanohydration of Uracil on Proton-Induced Charge Transfer

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Understanding how the solvent alters the properties of a solute at the molecular level is of great importance in science and technology and of fundamental interest in the gas-phase where the specific features of the solute and of solute-solvent interactions can be disentangled from one another. Compounds of biological interest and in contact with a controlled number of water molecules are of particular relevance in the context of radiation damage, where the contribution of the solvent could be critical. Besides primary radiation, secondary particles generated along the track of the environment can also produce strong excitations, possibly leading to charge transfer, ionization, and eventually fragmentation of the molecule [1].

The problem of charge transfer in collisions of energetic protons on hydrated uracil has been addressed here using a combination of theoretical modeling techniques. Low-energy structures have been determined by a systematic exploration based on force fields and replica-exchange molecular dynamics, and further optimized at different levels of quantum chemical methods. The results indicate segregated solvation patterns with a possible formation of a water cluster next to the ARN building block, at variance with all previous computational literature on the subject [2]. At finite temperature, entropy effects become important and stabilize different structures in which solvation proceeds closer to the uracil plane.

Charge transfer cross sections upon collision with protons have been calculated by determining potentials and non-adiabatic couplings for the different states involved in the reaction. A dynamical treatment was performed in a wide collision energy range using semi-classical methods already used for isolated molecules [3]. The charge transfer efficiency is surprisingly found to be enhanced all the more than the number of surrounding molecules is low. Our calculations also indicate a strong dependency of the cross sections on the molecular conformation, suggesting possibly strong temperature effects.

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Relativistic Energy Approach to Heavy Fermi-Systems in a Strong Field: Autoionization and Multi-Photon Resonances

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It is presented an advanced combined relativistic operator perturbation theory (PT) and energy approach [1,2] and its application to studying interaction of the finite Fermi systems (heavy atoms, nuclei, molecules) with a strong external (DC electric and laser) field. It is based on the Gell-Mann and Low adiabatic formalism and method of the relativistic Green's function for the Dirac equation with complex energy. Results of the calculation for the multi-photon resonance and ionization profile in Na, Cs, Ba atoms are listed [2]. We have studied the cases of single-, multi-mode, coherent, stochastic laser pulse shape. New data on the DC, AC strong field Stark resonances, multi-photon and autoionization resonances, ionization profiles for a few heavy atoms (Eu, Tm, Gd, U) are presented. It has been firstly studied a giant broadening effect of the autoionization resonance width in a sufficiently weak electric (laser) field for uranium. It is declared that probably this effect is universal for optics and quantum chemistry of lanthanides and actinides and superheavy elements.

The direct interaction of super intense laser field ($I \sim 10^{25} - 10^{35} \text{ W/cm}^2$) with nuclei is studied within the operator PT and the relativistic mean-field (plus Dirac-Woods-Saxon) model [2,3]. We present the results of AC Stark shifts of single proton states in the nuclei ^{16}O , ^{168}Er and compared these data with available data. New data are also listed for the ^{57}Fe and ^{171}Yb nuclei. Shifts of several keV are reached at intensities of roughly 10^{34} W/cm^2 for ^{16}O , ^{57}Fe and 10^{32} W/cm^2 for heavier nuclei. It is firstly presented a consistent relativistic theory of multiphoton-resonances in nuclei and first estimates of energies and widths for such resonances are presented for ^{57}Fe and ^{171}Yb nuclei.

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Probing Electron Dynamics in Clusters and Molecules: A Theoretical Contribution

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The analysis of the dynamical response of clusters and molecules subject to electromagnetic perturbations remains a challenging issue. Particularly rich information can be obtained from measuring the properties of emitted electrons. Such analysis of electron signals cover observables at various levels of detail, from net ionization to Photo-Electron Spectra (PES), Photo-electron Angular Distributions (PAD), and ideally combined PES/PAD. Recent progress in the design of new light sources (high intensity, high frequency, ultra short pulses) has opened a wealth of new possibilities for measurements. This, in turn, has motivated numerous theoretical investigations of the dynamics of electron emission up to such a complex and interesting system as C₆₀ [1]. Time Dependent Density Functional Theory (TDDFT) propagated in real time provides here an ideal tool of investigation. It allows to access a pertinent, robust, and efficient description of electronic emission including the detailed pattern of PES and PAD, which in turn allows direct comparisons with experiments.

We present the theoretical approaches we have developed on the basis of real time TDDFT to address the analysis of electronic emission following irradiation of clusters and molecules [2]. Following a brief experimental survey we present the available theoretical tools focusing on TDDFT and detailing the methods used to address ionization observables. We then present illustrative results: total ionization in pump and problem scenarios for tracking the ionic dynamics of clusters; PES and PAD to address more directly electronic dynamics itself. When possible the results will be directly compared to experiments [2]. We also discuss the information content of PES in case of excitation by swift and highly charged ions rather than lasers [5]. We conclude by discussing future directions of investigations, in particular the account of dissipative effects at the side of TDDFT [3, 4] in order to consider longer laser pulses where the competition between direct electron emission and thermalization is known to play a role as, *e.g.*, in experiments with C₆₀.

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Light-Induced Conical Intersections in Polyatomic Molecules

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Conical intersections in polyatomic molecules are known to play a central role in many processes in nature from photochemistry to biophysics. These CIs are determined by nature and are hard to manipulate. Recently, it was shown that employing intense laser pulses it is possible to induce CIs not available in nature, even in diatomic molecules [1]. When the carrier frequency of a laser pulse fits to the energy difference between two electronic states of a molecule, the potential energy surfaces of these states dressed by the field become energetically close and the states can couple strongly to each other. For diatomic molecules, these surfaces may exhibit a conical intersection induced by the laser light in the space of the nuclear internal and external coordinates [1–3]. Light-induced conical intersections (LICIs) can give rise to dramatic non-adiabatic effects between the electronic, vibrational, and rotational degrees of freedom of a diatomic molecule exposed to resonant laser pulses [3–6].

Here, we report a general theory of the light-induced conical intersections emerging in polyatomic molecules where additional internal degrees of freedom are involved in the dynamics [7]. Freely rotating and also fixed-in-space arbitrary polyatomic molecules exposed to differently polarized optical laser pulses of resonant carrier frequency are considered. Detailed analysis of the theory shows how the light-induced conical intersections can be controlled by molecular orientation and by the carrier frequency, polarization, strength, and duration of the laser pulse. This opens the possibility to also control the ensuing non-adiabatic dynamics. Different strategies of exploitation of the light-induced conical intersections are proposed. The present theory is exemplified by utilizing the light-induced conical intersections to control photodissociation of the second electronically excited state S_2 of the fixed-in-space cis-methyl nitrite CH_3ONO .

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Exact Factorization of the Molecular Wave Function: Which Future?

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The Born-Oppenheimer (BO) approximation is an essential tool in the study of molecular processes. The wave function is written as a product of an electronic factor (the wave function of the electrons with frozen nuclei) and a factor describing the nuclear motion with the nuclear-dependent electronic energy as a potential. However a condition is necessary for the scheme to be valid: The electronic energies must be well separated. Many situations do not fulfill this condition. For instance if two electronic potentials cover the same energy range, this may affect the positions of the vibrational energies calculated separately for the two states. The BO method consists in writing the total wave function as a combination of Born-Oppenheimer products. It has been argued (see for example [1,2]) that even in cases where the traditional BO approach is failing, the exact molecular wave function can still be written as the product of an electronic wave function depending parametrically on nuclear positions by a nuclear factor. An example of the failure of the BO approximation is the study of the perturbations in the N₂ vibrational spectrum. We use [3,4] the supposedly exact wave functions for the treatment of these perturbations to determine the ingredients necessary to write the wave functions of the new scheme, that is as single products. This does not mean solving the basic equations of this scheme. However this proves the existence of these functions. We then use these functions to build the potentials which determine the vibrational states. The wave equation with these potentials is solved to show that we recover the correct energies.

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Improving the Efficiency of DFT and Time-Dependent DFT for Excited States

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Time-dependent density functional theory (TDDFT) is one of the most widely-used methods for describing excited states of large systems. This talk will describe our efforts to increase the efficiency and utility of TDDFT-based methods along several lines. This includes analytic derivative coupling vectors for TDDFT and its spin-flip variant, [1, 2] which facilitate efficient optimization of minimum-energy crossing points along conical seams. A low-cost local orbital approximation has been developed that is highly efficient for including explicit solvent molecules in a TDDFT calculation [3]. Finally, an *ab initio* version of the Frenkel-Davydov exciton model [4] provides a good way to describe collective excited states and energy transfer in multi-chromophore systems.

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Analytical Form of Helium Wave Function

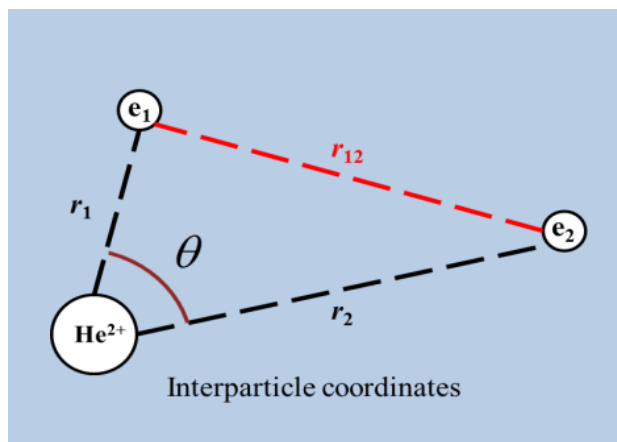
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Implicit analytical form of the ground state wave function for helium

$$\Psi(r_1, r_2, r_{12}) = \sum_{n=0}^{\infty} (r_1^2 + r_2^2)^{\frac{n}{2}} \sum_{p=0}^{\lfloor \frac{n}{2} \rfloor} (\ln(r_1^2 + r_2^2))^p \cdot f_{np} \left(\underbrace{\frac{r_1^2 - r_2^2}{r_1^2 + r_2^2}}_{\cos \alpha}, \underbrace{\frac{r_1^2 + r_2^2 - r_{12}^2}{2r_1 r_2}}_{\cos \theta} \right)$$

was proposed by Fock in 1954 [1]. Explicit determination of the angular Fock coefficients $f_{np}(\alpha, \theta)$ turned out to be a complex task; only few of them are found up to date [1–6]. The Fock series can be considered as an extended Taylor series of the exact wave function in the coordinates $(r = \sqrt{r_1^2 + r_2^2}, \ln r, \cos \alpha, \cos \theta)$ around the triple coalescence point $r = 0$. The current talk will show how the Fock series emerges. In particular, it will show how the logarithmic terms appear in low-order Fock coefficients in order to guarantee physical behavior (continuity and finiteness) of the resulting wave function. We will address also the question of Fock expansion for helium in states with non-zero angular momentum.



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The Dirac Equation as a Privileged Road to Understanding Quantum Systems

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The Dirac equation, which was derived by combining, in a consistent manner, the relativistic invariance condition and the quantum probability principle, has shown its fecundity by explaining the half-integer spin of fermions and predicting antiparticles [1], the former resulting from a wave beat between a particle and its antiparticle [2]. In our previous papers [3–5], it was conjectured that the spinning motion of the electron was that of a *massless charge* at *light speed*, this internal motion being responsible for the *rest mass* measured in external motions and interactions. Implications of this concept on such basic properties as time, mass, electric charge, and magnetic moment were considered. The present paper is a recollection of these ideas aimed at a general understanding of quantum matter.

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The Cosmos as a Quantum System

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Arthur Haas explained the Hydrogen spectra, 3 years before Niels Bohr, by extending the virial theorem to the Planck energy formula. This suggests the *holographic coherence principle*: energy conservation means frequency unicity, *i.e.* the coherence condition for Holography. This is applied to an Hydrogen molecule model, in a black-hole sphere of horizon $R = 2GM/c^2$: this critical condition being seen as a *general holographic conservation*, and tied to the Kotov cosmic period t_{cc} . So R/c appears as a period $2G_F t_{cc}^2 / \hbar \lambda_e^3 \approx 13.8123(1)$ Gyr, while $R = 2\hbar^2 / Gm_e m_p m_H \approx 13.812(1)$ Glyr confirms Eddington's statistical formula. These two formulas displays a G – G_F symmetry between Newton and Fermi constants and are compatible with the so-called 'Universe age' 13.81(5) Gyr of standard cosmology.

The *cosmic microwave background (CMB)* wavelength enters an associated special holographic conservation, confirming a come-back to the steady-state cosmology, for which the factor 3/10 for matter density is trivial, eliminating the 'dark energy problem', and confirming the Eddington prediction $M/m_H = 136 \times 2^{256}$, while the *real* Hydrogen density is found to be $\sqrt{(m_e/m_H)} \approx 0.0233$, compatible with the Helium density and *CMB* temperature. From Sanchez-Maruani matter-antimatter vibration viewpoint, dark matter would be seen as *usual matter vibrating in quadrature*. A Hydrogen atom model relates directly R , λ_e and the Bohr radius r_B with $R' = 2r_e^3/l_P^2 \approx 4R/3$, seen as the radius of a sphere representing a Grandcosmos. This rules out several common conjectures: 1) the Primordial Big-Bang, 2) the Planck wall concept, 3) the Cosmic Anthropic Principle, 4) the Multiverse hypothesis.

The holographic relations can be represented in a *topological axis*, involving a double exponential function, and showing the special *string dimension* series $n = 2 + 4p$. It yields R and r_B for the canonic values $n = 26$ and 10, with a non-standard Gluon mass for $p = 1$. The Grandcosmos is the lacking concept in 1) the CMB interpretation (no more a fossil radiation) 2) the steady-state model (no more any need for an internal thermostat) 3) the lacking point $p = 7$. The physical parameters are shown to connect with music numbers, economic numbers and biological parameters, pointing to a *Grand Theory*.

Partition Density Functional Theory

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I will discuss recent developments on density-based fragmentation methods for ground-state and time-dependent molecular calculations, with an emphasis on Partition Density Functional Theory (PDFT) [1–3]. Using the simplest possible systems where the various methods can be transparently compared, I will emphasize subtle but important differences between alternative approaches [4]. I will also highlight some of the challenges involved with density partitioning through explicit examples on diatomic molecules. I will discuss: (1) the meaning of partition potentials, which represent the density for a given choice of partitioning; (2) the connection between charge-transfer and electronegativity equalization between fragments; (3) different ways of treating fractional fragment charges and spins; and (4) a general strategy based on PDFT for overcoming delocalization and static-correlation errors in density-functional calculations.

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A First Principle Representation of Autaptic Neurons

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We present a quantum-based model of the autaptic neuron, commonly found in the circuits of the cerebral cortex. Trehub [1], originally proposed the autapse, *i.e.* a synapse formed by an array of neurons devised for visual perceptions, in his celebrated work on the so-called retinoid system. Within our integrated thermal quantum thermal formulation we transform the generic symmetries of the reduced neuronal dynamics as the projection of the abstract degrees of freedom onto 3D space. In particular the spatio-temporal portrait suggests a universal mirroring interpretation of the autaptic network as self-organised trajectories matching retinal stimuli. Two columns, corresponding to the visual processing information are displayed in Figure 1, reflecting the mirroring spatio-temporal symmetry, where the column d_1 (straight arrows) relates to the actual communication between neurons of the direct processing pathway and d_6 , (curly arrows) the dual parity pathway. The present representation prompts a motive for the abundance of chemical synapses of a neuron onto itself and imparts a simple explanation of the phi phenomenon and the Necker cube optical illusion [2].

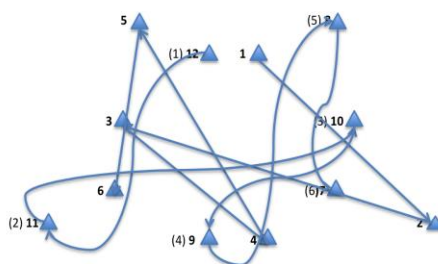


Figure 1: Actual set of columns d_1 and d_6 .

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Permutation Symmetry and Correlation Energy

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From the expression of the hamiltonian for a many-electrons system (atom or molecule) it is clear that a permutation among identical particles will leave it unchanged. This was first recognized by Heisenberg who expressed this fact by saying that, for quantum systems, **the permutation among identical particles is a fundamental constant of motion**:

$$HP_{ij} = P_{ij}H, \quad \forall i, j \text{ particles}$$

Wigner put this statement in a more rigorous basis by saying that **physically acceptable** wave functions for quantum systems of N identical particles must transform as irreducible representations (IR) of the symmetric (or permutation) S_N group. As a consequence, the wave function for quantum systems must be symmetric or antisymmetric under the permutation of any two identical particles of the system. Examining two electrons systems (He and Li^+) Heisenberg concluded that for many-fermion systems (particles with half-integer spin) the total wave function must be antisymmetric (antisymmetry principle).

Slater, in an attempt at constructing many-electron wave functions avoiding the use of group theory (the gruppen pest) proposed the determinant form of the wave function (Slater determinants) which is indeed antisymmetric by construction but not a basis for S_N . This type of wave function served as the basis for the development of the Hartree-Fock (HF) method for atoms and molecules and this method was elected as the reference independent particle model (IPM) to compute electronic correlation energy.

In this talk we will examine some of the consequences of the lack of permutation symmetry in the HF wave functions. In particular we will discuss the problem of doubly occupancy of orbitals, the unphysical effect known as “non-dynamic” correlation energy and how HF overestimates the correlation energy.

Spin Symmetry and Size Consistency of Strongly Orthogonal Geminals

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Geminal based theories work with two-electron units as building block and construct the total wavefunction as an antisymmetrized product, in a manner analogous to Hartree-Fock. The geminal based approach results a conceptually simple multireference framework, retaining the efficiency of the mean-field description regarding inter-geminal interactions. Intra-geminal correlation is accounted for exactly, offering the advantage of breaking covalent bonds correctly. Restricting geminal spins as singlet produces qualitatively correct potential curves when dissociating isolated single bonds. Triplet geminals have been known to be important for non-isolated (*e.g.* multiple) bond dissociation. The role of triplet geminals in such processes has recently been characterized numerically. [1]

This study presents an overview of a class of geminal functions, exploiting the so-called strong orthogonality condition, and allowing for singlet-triplet mixing at the level of the two-electron units. Spin-contamination of the total wavefunction is restored by spin-projection. Full variation after projection is examined for two models. One is the well known spin-projected Extended Hartree-Fock (EHF). The other is a yet unexplored function, termed spin-projected Extended Antisymmetized Product of Strongly orthogonal Geminals (EAPSG). A formal case study on size consistency is presented for both models. Numerical performance of EHF and EAPSG is compared on small test systems, H_4 and H_8 . [2]

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The Fourth Age of Quantum Chemistry

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In the fourth age of quantum chemistry [1] properties of unusual molecules and of unusual high-resolution molecular spectra can be studied in considerable detail. Examples from recent efforts of our research group will be given in the talk.

The examples include the case of the molecular ion H_3^+ , for which the introduction of motion-dependent and coordinate-dependent mass surfaces is investigated [2]. The background experimental information about rotational-vibrational energy levels of H_3^+ is provided by our MARVEL (Measured Active Rotational-Vibrational Energy Levels) data [3]. Another interesting case is the astructural H_5^+ molecular cluster ion and its deuterated analogues [4–6]. The coupling of several large-amplitude motions present a challenge to theory to model rotation-vibration-tunneling energy levels. A third example concerns the effect nuclear motions, that is rotations and vibrations, have on the tunneling splittings characterizing $^{14}\text{NH}_3$ [7]. Here again the experimental data are supplied by a MARVEL analysis of all available experimental high-resolution transitions [8]. It is shown how internal motions can promote and (almost completely) inhibit tunneling through the effective double-well potential of $^{14}\text{NH}_3$.

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***Ab Initio* Green's Function Methods for Molecular Bound-Free Transitions**

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Traditional methods of *ab initio* quantum chemistry relying on L2 single-electron bases have been instrumental in predicting the energies and properties of bound electronic states of molecules. In contrast, theoretical description of bound-free electronic transitions, *e.g.* of photoionisation and autoionisation type, proved to be more difficult. While application of L2 methods to these phenomena is possible within a number of computational approaches, such as complex scaling, introduction of complex absorbing potentials, stabilisation method, *etc.*, such *ab initio* calculations are rather tedious and the underlying methods are far from being available to a non-specialist as a black box tool. In this talk I will review our recent progress on efficient implementation and application of one of such L2 approaches, Stieltjes-Chebyshev moment theory in conjunction with many-electron Green's function methods of the algebraic diagrammatic construction (ADC) type. Applications to photoionisation, Auger decay and inter-atomic decay in polyatomic molecules and clusters will be discussed. I will also discuss the major limitations of the L2 approach and show how these can be overcome by introduction of the B-spline single electron basis set in the framework of the B-spline ADC.

A Mechanochemical Viewpoint of Substituent Effect

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Substituents play a significant role in controlling the chemical reactivity of a given substrate. Usually substituents are not directly involved in a given chemical reaction, and they affect the reactivity in a “soft” way (*e.g.* by modifying the reaction rate rather than affecting the reaction mechanism). Additionally, the reactivity of a chemical system can also be strongly affected when it is subjected to some kind of mechanical forces, being possible to predict this effect relying on the principles of covalent mechanochemistry. [1]

The effect of a substituent is usually rationalized by chemists in terms of electronic properties, *e.g.* inductive or conjugative effects. Nevertheless, this conception of the substituent effect can be replaced by a quantitative mechanochemical formulation: substituents affect the substrate as they induce some forces on it. These forces alter a given energy profile in the same way as an external mechanical force could do, eventually affecting different properties as equilibrium constant or reaction rates, photophysical properties [2,3] or conical intersection topology in photochemical processes. [4]

Here we develop a general formulation and the corresponding computational procedure to quantify the forces induced by a substituent and its effect on chemical reactivity. A remarkable result of this substituent effect mechanochemical formulation is the derivation of the well-known Hammett equation where σ and ρ parameters are no longer empirical.

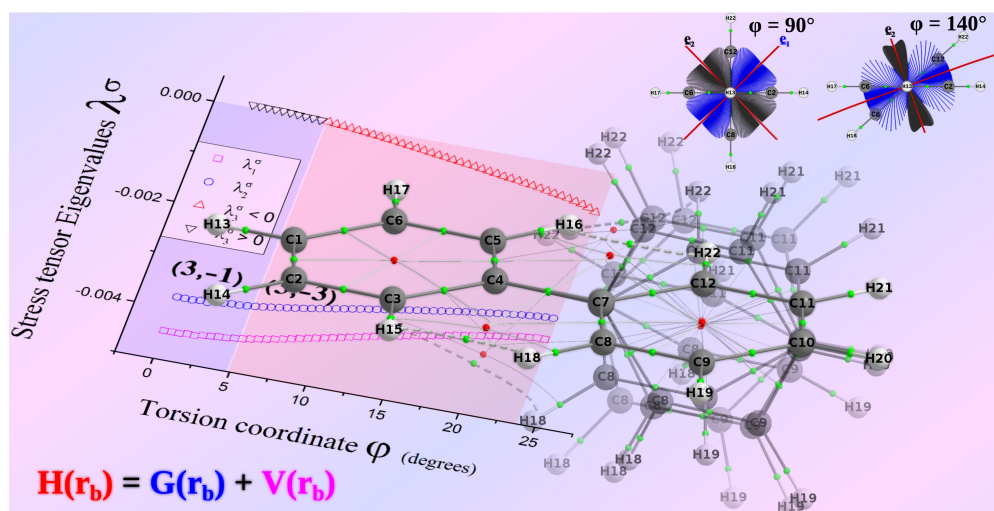
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Biphenyl: A Stress Tensor and Vector-Based Perspective Explored within the Quantum Theory of Atoms in Molecules (QTAIM)

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We use QTAIM and the stress tensor topological approaches to explain the effects of the torsion φ of the C-C bond linking the two phenyl rings of the biphenyl molecule on a bond-by-bond basis using both a scalar and vector-based analysis. Using the total local energy density $H(\mathbf{r}_b)$ we show the favorable conditions for the formation of the controversial H---H bonding interactions for a planar biphenyl geometry. In addition, the $H(\mathbf{r}_b)$ analysis showed that *only* the central torsional C-C bond indicated a minimum for a torsion φ value coinciding with that of the conventional global energy minimum. The H---H bonding interactions are found to be topologically unstable for any torsion of the central C-C bond away from the planar biphenyl geometry. Conversely, we demonstrate that for $0.0^\circ < \varphi < 39.95^\circ$ there is a resultant increase in the topological stability of the C nuclei comprising the central torsional C-C bond. Evidence is found of the effect of the H---H bonding interactions on the torsion φ of the central C-C bond of the biphenyl molecule in the form of the QTAIM response β of the total electronic charge density $\rho(\mathbf{r}_b)$. Using a vector-based treatment of QTAIM we confirm the presence of the sharing of chemical character between adjacent bonds. In addition we present a QTAIM interpretation of hyper-conjugation and conjugation effects, the former was quantified as larger in agreement with MO theory. The stress tensor and the QTAIM H atomic basin path set areas are independently found to be new tools relevant for the incommensurate gas to solid phase transition occurring in biphenyl for a value of the torsion reaction coordinate $\varphi \approx 5^\circ$.



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Singlet Fission and Charge Transfer in Photovoltaics

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Organic photovoltaic (OPV) devices have great potential in harvesting solar energy. In organic solar cells, the role of the donor-acceptor heterojunction is critically important, where an optical excitation leads to charge separation (CS) and subsequently, photocurrent generation. Charge recombination (CR) may also happen, which reduces the efficiency of the device. In a pentacene-C₆₀ OPV, the singlet excitation of a pentacene can achieve CS at the interface, or it may also undergo singlet fission and produce two triplet excitons, which may further undergo CS at the interface. We studied the charge transfer processes at the pentacene-C₆₀ interface, including CS rates in both singlet and triplet surfaces, and the CR rate back to the ground state. We found that the electron transfer couplings have a systematic preference on the configurations. In estimating the electron transfer rates, we found that the interfacial energy shift has a determining effect. When an interfacial energy derived from experimental results is included, we found that the calculated triplet CS rate can reach 10^{13} s^{-1} , while the singlet CS rates are only 10^5 s^{-1} . The CR rate was calculated to be 10^{11} s^{-1} for a singlet ion pair. Since triplet CS can proceed after singlet fission, with its immediate recombination being spin-forbidden, it is important to photovoltaic performance in the pentacene-C₆₀ system.

The singlet fission coupling in pentacene is also studied. With a singlet exciton split into two triplet excitons, singlet fission has a great potential to increase the efficiency of solar cells. The Fragment Spin Difference (FSD) scheme was generalized to calculate the singlet fission coupling. Without manually including the CT components, the largest coupling strength obtained was 14.8 meV for two pentacenes in a crystal structure, or 33.7 meV for a transition-state structure, which yielded singlet fission lifetime of 239 or 37 fs, generally consistent to experimental result (80 fs). We found that the charge on one fragment in the S₁ diabatic state correlates well with FSD coupling, indicating the importance of the CT component. The FSD approach is a useful first-principle method for singlet fission coupling, without the need to include the CT component explicitly.

Single and Multi-Wall Nanotubes of Boron and Metal-Borides: Stability, Electronic Structure and Aspects of Superconductivity

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Control of the chirality of carbon nanotubes (CNT) is an unresolved problem, and the production of CNTs with the required electronic properties, *i.e.*, metallic or semiconducting with a medium or small gap, is unrealistic. Large differences in the conductivities of these forms yields nonuniformity in their emissions and restrict application, especially in the area of field emission. Under these circumstances, a more robust material with a nanotubular form, that does not suffer from these problems, is desired. Boron nanotubes (BNT) or metal borides nanotubes (MeBNT) should not only provide an alternative to CNTs, but also be more efficient.

Here we present results of our theoretical studies of boron-based nanostructures. Calculations are based on helical symmetry of nanotubular structures, in roto-translation modification which enables irreducible unit cell of parent 2D sheet to remain also the unit cell of tubular structure [1,2]. This gives rise to a possibility to treat tubular system as pseudo 2D with minimal unit cell, instead of large translation-unit cell as it follows from the standard chiral treatment of tube formation.

Based on this treatment, we were able to study not only large diameter single-wall boron and metal borides nanotubes, but also large diameter multi-wall nanotubes. Results show that these nanotubes are all metallic, irrespective of chirality. Moreover, some structures are superconductors and the electronic band structures of MgB₂-multiwall nanotubes (MgB₂MWNT) correspond to the band structure character and topology of superconducting bulk MgB₂.

The results confirm that the quasi-1D superconductor MgB₂MWNT is a stable structure (stability of 25-wall NT is on the level of bulk structure [2]), can be synthesized and, moreover, it should be superior material for nanoelectronics and in form of single-photon detector should become the key-element for development of quantum computing technologies with fast optical response at relatively high operating temperature.

Acknowledgements

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Molecular Electronic Correlation Described by Natural Orbitals Geminal Theories

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Predicting electronic structure is one of the most important tasks in quantum chemistry and geminal theories based on natural orbitals have become a useful tool. One of the possible geminal-based ansätze for the wave-function are antisymmetrized product of strongly orthogonal geminals (APSG) and its simpler variant – general valence bond (GVB) which is equivalent to one of the natural orbital functionals – PNOF5 [1]. Contribution of only two orbitals to each geminal in GVB functional makes its computational cost lower than APSG functional in price of accuracy. GVB functional energy is always considerably higher than that of APSG.

Performance of these geminal-based wave-functions in describing ground states of molecules has been explored extensively and it is known they cannot provide a uniformly accurate description of dynamic and static correlation. In this study, we proposed ERPA-GVB method, based on the general valence bond (GVB) theory and the recently proposed extended random phase approximation (ERPA) [2] intergeminal correlation correction [3], which is capable of accounting for both dynamic and static correlation. ERPA-GVB yields excellent results comparing to CCSD, CCSD(T), CCSDTQ, FCI, DMRG at modest computational cost.

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Structures, Thermochemistry and Mechanism of the Reaction of Pd(0) Biscarbenes with Molecular Oxygen

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Pd(0) biscarbenes, Pd(NHC)₂ (NHC = *N*-heterocyclic carbene, react with O₂ to yield side-on monoperoxo complexes, (η²-O₂)Pd(NHC)₂ [1]. However, when a bulky NHC were used, it was possible to isolate and structurally characterize the corresponding end-on bis-superoxo complex (η¹-O₂)₂Pd(NHC)₂ [2]. DFT calculations have been performed to study the influence of the NHC on the structures of the oxygenated complexes formed and on the thermochemistry of O₂ addition reactions. Finally, a detailed mechanistic investigation has been carried out to understand the striking reactivity observed for the IPr derivative as compared with that previously reported for other NHC complexes.

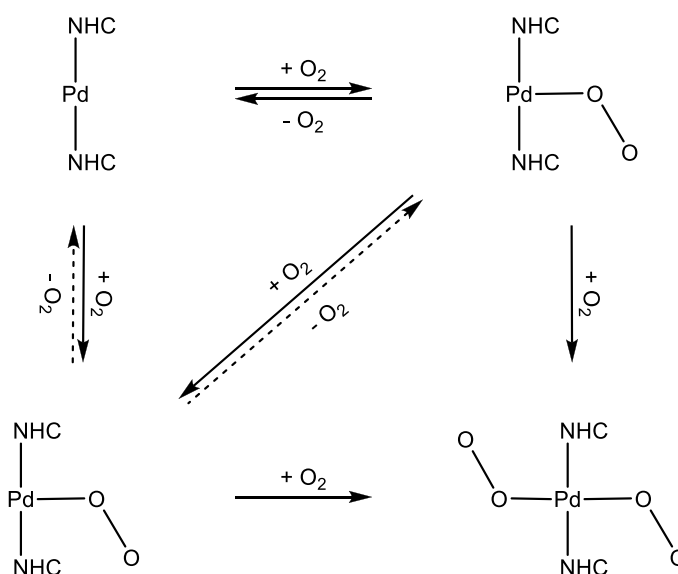


Figure: General mechanism for reaction of a Pd(NHC)₂ complex with O₂.

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Topological Quantum Computation with Non-Abelian Anyons in Fractional Quantum Hall States

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We review the general strategy of topologically protected quantum information processing with non-Abelian anyons in which information is encoded using the fusion channels and fusion paths in two-dimensional quantum Hall systems while quantum gates are implemented by braiding of these anyons.

As an example we consider the Pfaffian topological quantum computer based on the fractional quantum Hall state with filling factor $\nu = 5/2$.

The elementary qubits are constructed by localizing Ising anyons on fractional quantum Hall antidots and various quantum gates, such as the Hadamard gate, phase gates and CNOT, are explicitly realized by braiding. We also discuss the appropriate experimental signatures which could eventually be used to detect non-Abelian anyons in Coulomb blockaded quantum Hall islands.

Detections of Weak Hydrogen Bonds in Nucleobases through Quantum Chemical Computations

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Hydrogen bonds (HBs) electrostatic interactions play major roles in chemical and biological systems especially in the nucleobase, which are the building blocks of nature [1]. Strong HBs make two-strand nucleobases in DNA whereas weak HBs could determine the 3D shapes [2]. Weak HBs are not easily detected because of low concentrations of shared electrons between the atomic counterparts; therefore, their recognition is important to predict and interpret the 3D structures in biological systems [3]. Performing atomic-level quantum chemical computations on biological systems could reveal insightful information about the existing HBs [4]. Evaluations of optimized structures and nuclear magnetic resonance (NMR) properties including chemical shielding (CS) and electric field gradient (EFG) tensors could help to better achieve the purpose [5] Uracil nucleobase and its derivatives are all capable of contributing to both types of strong (N...N, O...O, and F...F) and weak (N...C or O...C) HBs interactions [6]. Evaluations of CS and EFG tensors for the atoms of optimized structures could help to detect the various types of HBs for the uracil pairs. The results based on density functional theory (DFT) computations showed that presence of the weak HBs interactions, confirmed by CS and EFG properties, could make different 3D structures for uracil pairs. Triplet or quartet uracil systems could be also constructed based on strong and weak HBs interactions as detected by computations [7].

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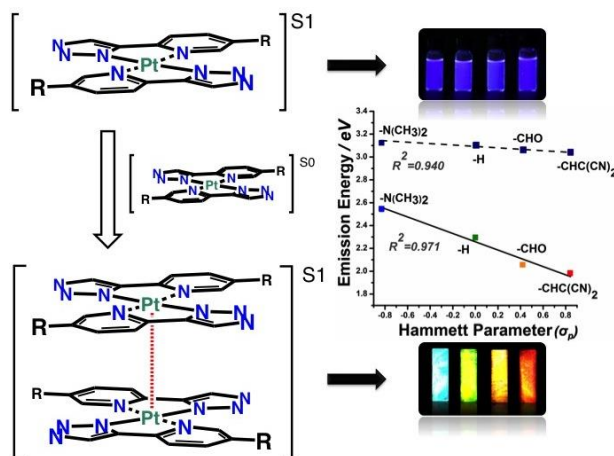
The Role of Substituent Effects in Tuning Metallophilic Interactions and Emission Energy of bis-4-(2-Pyridyl)-1,2,3-triazoloplatinum(II) Complexes [1]

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Four novel 5-substituted-pyridyl-1,2,3-triazolato Pt(II) homoleptic complexes with intriguing photoluminescence properties were recently designed and synthesized in our laboratory. Despite the broad range of the donor/acceptor strength of the substituents at 5-position, the series of complexes is characterized with weak absorption tunability in diluted and highly concentrated solutions, as well as in thin films. However, emission tunability changes from weak at low concentration (397–408 nm) to strong at high concentration and solid state (487–625 nm). In addition, emission maxima in concentrated solution and solid-state depend linearly on the donor/acceptor strength of the substituents.

In order to gain a deeper insight into the unusual concentration and substituent dependence, we have performed DFT/TDDFT investigation on the absorption and emission properties of the compounds. For this purpose, the ground (S_0), the first excited singlet (S_1) and triplet (T_1) states of the homoleptic Pt(II) complexes and of their dimers were optimized in implicit solvent environment by using the PBE0 functional. Theoretical results attribute the “turn-on” emission tunability to the formation of excimers with strong Pt(II)—Pt(II) metallophilic interactions and to a change in the excited state character going from isolated complexes (1MLCT) to dimers (1MMLCT). Moreover, the simulations reveal that due to the excimerization process the S_1 - T_1 energy difference decreases and varies as a function of the donor/acceptor strength of the substituent (from 0.25 to 0.1 eV at 0 K). This result suggests that the substituents modification could affect the intersystem crossing rate constants at supramolecular level and hence demonstrates a promising approach for the molecular design of luminescence materials [2].



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Laser-Assisted (e, 2e) Collisions in Atoms

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Second-order Born calculations have been performed to investigate the triple differential cross sections of coplanar asymmetric laser-assisted (e, 2e) collisions for hydrogen and helium targets. The incident electron is considered to be dressed by the laser field in a nonperturbative manner by choosing the Volkov solutions in both the initial and final channels. Detailed calculations of the scattering amplitudes are performed by using the Sturmian basis expansion. The state of the ejected electron is described by a Coulomb-Volkov wave function. Two geometries are investigated in which the laser polarization vector is either parallel to the incident momentum of the projectile or parallel to the transfer momentum. Our numerical results show that, in the low energy range, these two laser polarization orientations give the same shape and order of magnitude of laser-assisted ionization cross sections of helium and hydrogen targets.

Large Scale Vibrational Calculations on IVR in S₀ Thiophosgene

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In the present work, using our recently developed vibrational variational method, we carry out a detailed theoretical study on the vibrational level structure of S₀ thiophosgene, both in the lower as well as in the very highly excited vibrational energies domain. We provide a detailed description of our method of calculations and the associated programming code, called TPG_vibcalc. First, a full quartic potential field for thiophosgene was generated with the nwchem suite of ab initio programs. Next, using our vibrational method, we carried out large scale converged variational calculations on S₀ thiophosgene (Cl₂CS), in order to determine a refined set of force constants for the molecular potential energy surface, that gives a good coincidence of the calculated with the experimentally measured vibrational frequencies [1].

We also explore the vibrational spectral structure and level density at very high vibrational excitation energies (up to $\sim 20000\text{ cm}^{-1}$), in order to establish the characteristics and extent of vibrational level mixing and intramolecular vibrational energy redistribution (IVR) at the dissociation limit of the ground electronic state S₀.

We compare the results from our calculations with the recent high resolution spectral data by McKellar *et al.* [2], as well as with the very extensive spectral measurements by M. Gruebele *et al.* [3].

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How Many Water Molecules Contribute to Atmospherically Relevant Carbonyl Oxide Water Reaction?

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Atmospherically relevant carbonyl oxide R_1R_2COO , so-called Criegee intermediates (CIs), can have many different forms depending on the substituents R_1 and R_2 . These strong oxidizing species are the key intermediate in the ozonolysis of different kinds of alkenes in the atmosphere. Due to CI's active participation in atmospheric chemistry, such as aerosol formation and OH radical production, the atmospheric fate of this very reactive species is a very important topic. However, presently there are no effective methods to measure the CI concentration in the atmosphere. Thus the only way to know the CI concentration is through the rate of its production and removal. Considering the abundance of water in the atmosphere, the reaction of CI's and water vapor is very important to accurately model the removal rate of CI. However, the accurate rates for even the simplest CH_2OO was not measured experimentally until very recently. With experimental difficulties to observe the rate for larger species, we turn to theoretical simulations. We considered the reaction of $CI+H_2O$ and $CI+(H_2O)_2$, to model the process.

Based on our calculation result, we find that for room temperatures $CI+(H_2O)_2$ reaction is nearly 100 times faster than $CI+H_2O$ for CH_2OO . Furthermore, we found that the reaction rate has a negative temperature dependence for the water dimer reaction. Thus the reactivity increases with decreasing temperature allowing the water dimer reaction to dominate the reaction of $CI +$ water vapor in cold upper troposphere layer even though the concentration of the water dimer, $[(H_2O)_2]$, is much lower than $[H_2O]$. On the other hand, the water monomer reaction has a normal temperature dependence, thus increasing reactivity with increase in temperature. From the different trend in reactivity $CIs+H_2O$ reactions originally regarded very slow in room or lower temperature, actually play significant roles at high temperatures. The alkyl substituted species such as CH_3CHOO , CH_3CH_2CHOO , and $(CH_3)_2COO$ show interesting trends in reactivity toward water compared to the CH_2OO ; and will also be discussed in the conference.

Spectral Lineshape in Nonlinear Electronic Spectroscopy: A Practical Approach Based on a Single Trajectory

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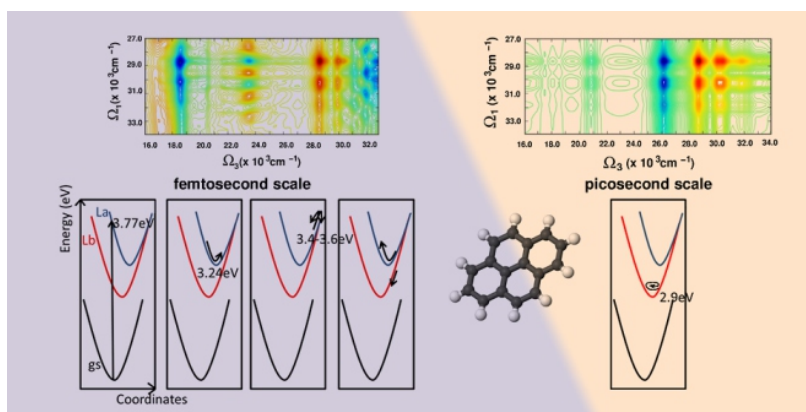
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We outline a computational approach for generating nonlinear spectra, which accounts for the electronic fluctuations due to nuclear degrees of freedom, thereby explicitly considering the fluctuations of higher excited states, induced by the dynamics in the photoactive state(s) [1]. The approach is based on mixed quantum-classical dynamics simulations, tedious averaging over multiple trajectories is avoided by introducing the linearly displaced Brownian harmonic oscillator model. The presented strategy couples accurate computations of the high-lying excited state manifold within the SA-CASSCF/CASPT2 framework to dynamics simulations. The protocol is applied to generate nonlinear 3rd order bi-dimensional electronic spectra of pyrene, a polycyclic aromatic hydrocarbon characterized by an ultrafast decay from the bright S₂ state to a dark S₁ state on a time scale of few tens of femtoseconds. Comparison of theoretical and experimental [2] spectra for different waiting times shows remarkable agreement allowing to unambiguously assign the detected signals.



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Understanding the Azeotropic Diethyl Carbonate–Water Mixture by Structural and Energetic Characterization of DEC(H₂O)_n Heteroclusters

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Diethyl carbonate (DEC) is an oxygenated fuel additive. During its synthesis through a promising green process, a DEC-water azeotrope is formed, which decreases DEC production efficiency in the gas phase [1]. Molecular information about this system is scarce [2] but could be of benefit in understanding (and potentially improving) the synthetic process. Therefore, we report a detailed computational study of the conformers of DEC, and their microsolvation with up to four water molecules, with the goal of understanding the observed 1:3 DEC:H₂O molar ratio. The most stable DEC conformers (with mutual energy differences < 1.5 kcal mol⁻¹) contribute to the energetic and structural properties of the complexes. An exhaustive stochastic exploration of each potential energy surface of DEC-(H₂O)_n, (where $n = 1, 2, 3, 4$) heteroclusters discovered 3, 8, 7, and 4 heterodimers, heterotrimers, heterotetramers, and heteropentamers, respectively, at the MP2/6-311++G(d,p) level of theory. DEC conformers and energies of the most stable structures at each heterocluster size were refined using CCSD(T)/6-311++G(d,p). Energy decomposition, electron density topology, and cooperative effects analyses were carried out to determine the relationship between the geometrical features of the heteroclusters and the non-covalent interaction types responsible for their stabilization. Our findings show that electrostatic and exchange energies are responsible for heterocluster stabilization, and also suggest a mutual weakening among hydrogen bonds when more than three water molecules are present. All described results are complementary and suggest a structural and energetic explanation at the molecular level for the experimental molar ratio of 1:3 (DEC:H₂O) for the DEC-water azeotrope.

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Vibrational Motion of Zundel Form of Proton

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Structure of hydrate proton is typically classified into Eigen (H_3O^+) and Zundel (H_5O_2^+) forms. While this is a textbook knowledge, it remains very challenging to keep track of their vibrational signatures. Gas-phase ionic spectra collected over the last two decades have provided plenty of experimental vibrational spectra that allow us to examine the vibrational motion of proton in H-bonded cations. In this talk, we will present our recent systematic theoretical studies on a range of Zundel form of H-bonded cation ranging from H_4O_2^+ , $\text{H}^+(\text{MeOH})_2$, $\text{H}^+(\text{EtOH})_2$ to $\text{H}^+(\text{Me}_2\text{O})_2$. Our theoretical studies engage *ab initio* treatment on a selected set of quantum degrees of freedom and treat their vibrational anharmonicity/coupling explicitly. We will also access the performance of a few approximate treatments on vibrational coupling/anharmonicity using these molecular systems.

The Superconducting Order Parameter in Real Space and Its Relation to Chemical Bonds

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Density functional theory for superconductors (SCDFT) [1] allows one to make accurate predictions [2–4] of the critical temperature and the gap of phonon-driven superconductors. In SCDFT, the exchange-correlation free-energy is a functional not only of the electron density but also of the superconducting order parameter. As a consequence, any Kohn-Sham calculation of SCDFT yields the order parameter as a natural output. In this lecture we shall investigate the structure of the superconducting order parameter in real space [5]. Being a function of two position vectors, the superconducting order parameter, $\chi(r, r')$, is best analysed as function of the coordinates $R = (r + r')/2$ and $s = (r - r')$, the center-of-mass and the relative coordinate of the Cooper pair. As function of R , the order parameter reveals the symmetry of the underlying crystal structure. Figure 1 below shows $\chi(R, s = 0)$ for MgB_2 . The σ -bonds in the hexagonal boron planes are clearly visible.

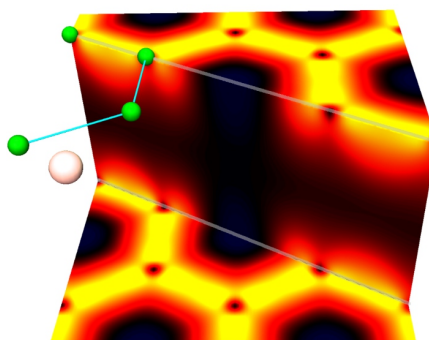


Figure 1: The superconducting order parameter $\chi(R, s = 0)$ for MgB_2 (from Ref. [5]).

As function of the relative coordinate, s , the order parameter reveals the internal symmetry of the Cooper pair, representing, *e.g.*, s-wave, p-wave, or d-wave pairing. The order parameter may exhibit regions of negative sign. Those are indicative of strong Coulomb renormalization. This will be demonstrated with the example of a superconducting monolayer of Pb on a Si(111) substrate. Finally, for the class of MgB_2 -type superconductors, we demonstrate that the localisation of the sigma bonds correlates with the critical temperature of the material [6].

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Quantum Systems and Properties along the Phase Diagram

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The combination of quantum mechanics with molecular modeling is a powerful tool for studies of simple and complex liquids [1]. This is generally called QM/MM method, because both classical and quantum methodologies are employed. As long as the thermodynamic condition can be imposed this opens a large avenue for applications in other parts of the phase diagram. Hence, we have also addressed the technologically and environmental friendly condition of supercritical fluids. Several applications will be shown indicating the accuracy of the calculated results. In particular we discuss the structural aspects of supercritical CO₂ and its role on the spectrum of para-nitroaniline as obtained from Born-Oppenheimer Molecular Dynamics [2]. More recently we have pointed our focus to the vicinities of the critical point. Theoretical studies of the critical behavior of fluids have been conducted mostly by universal scaling functions and renormalization theories. We have given the first explicitly calculated values of the dielectric constant in the close vicinity of the critical point ($T > T_c$). Thus, the behavior of the dielectric constant, only slightly above the critical point, is determined using first-principle quantum mechanical calculations. Our multi-scale results [3] obtained by combining statistical mechanics and first-principle quantum mechanics indicate that the dielectric constant of Ar only 2 K above T_c and around the critical isochoric (0.531 g/cm³) becomes density-independent (Figure 1).

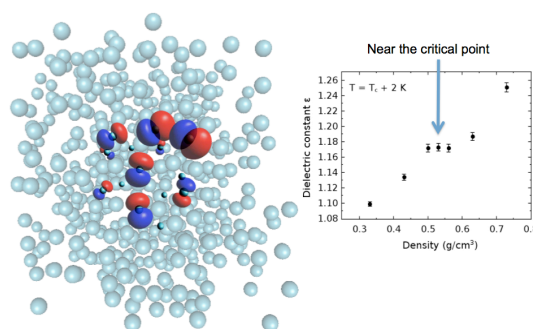


Figure 1: Variation of the dielectric constant of Ar with the density.

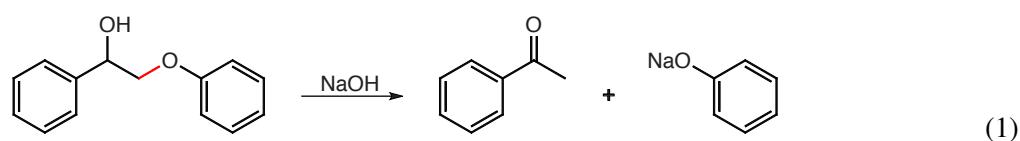
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Theoretical Study of Base Catalysed Hydrolysis of 2-Phenoxy-1-Phenylethanol for Lignin Degradation

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The degradation of lignin into small molecules as an alternative feedstock becomes increasingly important in times of dwindling resources. 2-phenoxy-1-phenylethanol is used as model for the β -O-4 link in lignin and its decay in alkaline solutions [1] as model for the base catalysed hydrolysis of lignin.



M06/6-31G(d,p) quantum calculations show that the hydrolysis follows a thermodynamically driven E2 mechanism. The chemical environment is of great importance for this reaction. The electric field caused by the surrounding solvent molecules (simulated with a polarisable continuum model) generally stabilises the intermediate carbanion while hydrogen bonds between solvent molecules and ether oxygen atom favour the formation phenoxide and destabilise the carbanion. The Na⁺ counterions to the catalytic OH⁻ ions are likely to have only a vanishingly small influence on the overall kinetics of the reaction.

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Reactive Scattering Calculations for $^{87}\text{Rb} + ^{87}\text{RbHe} \rightarrow \text{Rb}_2 ({}^3\Sigma_u^+, v) + \text{He}$ from Ultralow to Intermediate Energies

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We investigate atom-diatom reactive collisions, as a preliminary step, in order to assess the possibility of forming Rb_2 molecules in their lowest triplet electronic state by cold collisions of rubidium atoms on the surface of helium nanodroplets. A simple model related to the well-known Rosen treatment of linear triatomic molecules [N. Rosen, J. Chem. Phys. **1**, 319 (1933)] in relative coordinates is used, allowing to estimate reactive probabilities for different values of the total angular momentum. The best available full dimensional potential energy surface [Guillon *et al.*, J. Chem. Phys. **136**, 174307 (2012)] is employed through the calculations. Noticeable values of the probabilities in the ultracold regime, which numerically fulfill the Wigner threshold law, support the feasibility of the process. The rubidium dimer is mainly produced at high vibrational states, and the reactivity is more efficient for a bosonic helium partner than when the fermion species is considered [1].

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Elucidation of Reaction Mechanisms: Combining Theory and Experiment

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Application of theoretical quantum chemistry methods have become an invaluable approach in evaluating fine details of chemical reaction pathways. Nevertheless, the outcomes of computational modeling may depend on the level of theory applied, how the reaction medium is simulated, and other factors. Additionally, multiple pathways are possible for many processes and theory cannot always resolve satisfactorily which mechanism dominates. On the experimental side, spectroscopy has proved the method of choice in kinetic studies. In favorable cases, spectroscopic methods may also provide information on key reaction intermediates. In this talk, the combined application of quantum chemical modeling and spectroscopic (IR, UV, NMR) methods in evaluating the mechanisms and quantifying reactivity for several organic reactions will be discussed. The following organic reactions are considered: aminolysis of esters, aminolysis of carbamates, alkaline hydrolysis of amides, S_N2 reactions, and electrophilic aromatic substitution (halogenation, nitration) [1–6].

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Low Temperature Dynamics of Atom-Diatom Collisions

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The dynamics of some atom-diatom reactions at low temperature can be investigated by means of statistical approaches, thus suggesting the possibility of complex-forming pathways. In particular the $D^+ + H_2$ reaction has been recently studied [1–3] by means of a statistical quantum method [4,5] and exact quantum and experimental rate coefficients in terms of the energy have been reproduced down to collision energies of $E_c \sim 10^{-3}$ eV. A similar analysis performed for the $Li + YbLi$ reaction [6] suggests the existence of a intermediate complex-mediated dynamics at the low energy regime.

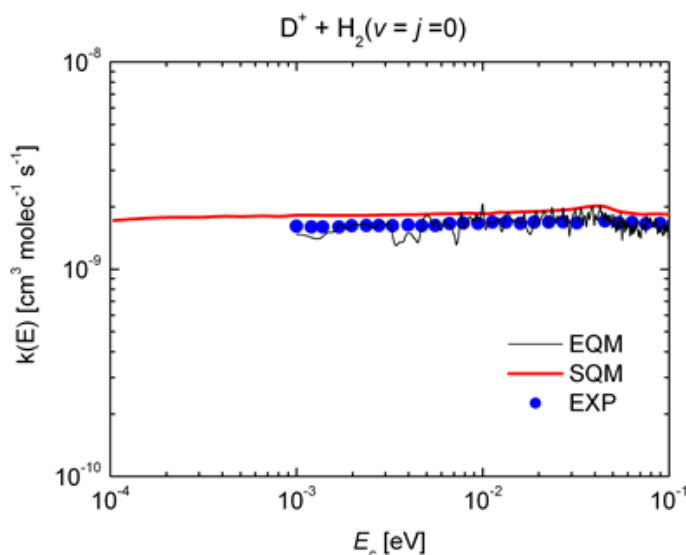


Figure 1: Rate coefficient as a function of the collision energy for the $D^+ + H_2$ reaction. Comparison between theoretical (statistical and exact quantum mechanical) and experimental results.

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Theoretical Chemical Physics of Graphene

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The interdisciplinary nature of chemical physics, which led by cross-fertilization to a lot of fascinating results, has been considerably strengthened during last decades owing to incorporation of the theoretical domain that included principal applications from quantum chemistry to material science, biochemistry, biophysics and even medicine. As a result of this commitment, the theoretical chemical physics (TCP) has become an indispensable resource for carrying out fundamental scientific research. In view of this, one of the points of the proposed report is to demonstrate a real forthfulness of the resource. Evidently, graphene best suits the goal owing to its dualistic crystalline-molecular nature due to which the chemical physics is the environment of its existence.

The report is concentrated on molecular essence of graphene and its effect on graphene physics. Such main characteristics of graphene chemical physics as graphene chemistry and its influence on graphene electronics, graphene mechanics, graphene magnetism, and graphene optical properties are the main topics. Molecular theory of sp^2 nanocarbons, suggested by the author and previously successfully applied to fullerenes [1], was led the foundation of the consideration. Whichever was possible, the theoretical conclusions and predictions were supported by experimental data thus creating a self-consistent view of graphene chemical physics.

According to its interdisciplinary nature, TCP can not be built on single individual computations but should be constructed as a result of a series of numerical experiments, done in the same manner. The TCP of graphene presented in the paper is based on experiments of such kind. Wherever possible, the conclusions and predictions of the suggested approach have been supported with available empirical and computational data.

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Supramolecular Organization and Solid-State Order in Small-Molecule-Based Materials for Organic Electronics

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Self-assembly of small conjugated molecules has attracted considerable attention from physicists, chemists and materials scientists working towards a common goal: to design conducting components on the nanometer-range scale for materials with optimized transport properties. In order to understand how functional organic architectures are formed and how the molecules are packed within the supramolecular assemblies, different computer models have been proposed to tackle a wide range of intra- and intermolecular interactions involved in the molecular self-organization.

In this talk we will start by characterizing some aspects of 2D-bottom-up assembly in different organic materials. First of all, the morphology of the thin solid films probed with all-atom molecular dynamics simulations will be demonstrated to highlight the impact of systematic structural variation on the self-assembly and stacking interaction of crystalline oligothiophenes. Secondly, the strong tendency to form ordered monomolecular layers of quaterthiophenes carrying electron-withdrawing groups on silica surface will be discussed, indicating a close similarity with experimental findings for the majority of compounds.

In addition, the structural and electronic properties of a donor-acceptor polymer semiconductor having diketopyrrolopyrrole and quaterthiophene units will be scrutinized. In focus will be the high density and low energy crystal structures for the corresponding monomer, predicted using Monte Carlo simulation annealing technique, as well as all the parameters for the charge transfer process in this material via quantum chemical calculations.

Finally, the last part of the talk will highlight the overall themes which pertain to self-organization motifs of small π -conjugated molecules in confined geometries, e.g. on surfaces and at the interfaces, and in the bulk phase.

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A Theoretical Study of All-cis-[10]Annulene C¹³-NMR Spectra

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In 1970 Masamune *et al.* [1] isolated two crystalline [10]-annulenes (**A** and **B**) by chromatography on alumina at -80°C . They proposed that **A** and **B** consisted of mono-trans and all-cis configurations respectively, on the basis of experimental data. The theoretical works released so far [2,3] have studied the conformational exchange of mono-trans conformers and the mechanism obtained at correlated levels match the one proposed by Masamune, although MP2 and DFT fail in order to calculate the relative energy between C₂ and C_s conformations. On the contrary, MP4 and CCSD render C₂ conformation as the more stable one, consistent with the five peaks showed by the C¹³-NMR spectrum below -100°C . As Masamune *et al.* checked, this mechanism explains the dependence of the spectrum on temperature. However, it remains to be elucidated all-cis conformational exchange mechanism, which will be the aim of our work.

We have calculated the pathways of that mechanism at CASSCF level using 10 electrons in an active space constituted by 10 π orbitals. Subsequently, dynamic electronic correlation has been taken into account by CCSD in order to refine the energy barriers between the conformers, but the pathways have remained unchanged. The obtained mechanism looks like the one proposed by Masamune *et al.*, but it includes going through a C_s conformation to rotate the binary axis of C₂ conformers along the ring and a pathway through a D₂ transition state for shifting double bonds. Using this mechanism, the Bloch equations have been written and solved in order to compare to the C¹³-NMR measured for **B** at different temperatures and confirm if the Masamune's hypothesis is right.

We acknowledge the financial support of the Spanish Ministerio de Economía y Competitividad under grant CTQ2012-36966 and of the University of Alcalá, under grants CCG2013/EXP-089 and CCG2014/EXP-083.

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Resonant-Auger – ICD Cascade in Rare-Gas Dimers

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Interatomic (intermolecular) Coulombic decay (ICD) is an important source of reactive slow electrons and radical cations in radiation chemistry. A mechanism for controlling both the generation site and the kinetic energies of the emitted slow electrons was recently proposed [1]. It utilizes core excitation of specific atoms in a cluster to trigger a two-step electronic decay cascade, the resonant-Auger – ICD cascade, at a desired location. The functioning of the proposed control mechanism has been experimentally confirmed in a variety of systems such as molecular [2] and rare-gas dimers [3–5].

The aim of this study is to provide a detailed understanding of the origins of the peaks in the spectra and also to explain how the spectra depend on the neighboring atom. For this purpose, the ICD electron and kinetic energy release spectra produced following $2p_{3/2} \rightarrow 4s$, $2p_{1/2} \rightarrow 4s$, and $2p_{3/2} \rightarrow 3d$ core excitations of Ar in Ar₂ and ArKr were computed fully *ab initio* and compared with available experimental data. Our findings show that the manifold of ICD states populated in the resonant Auger process can be divided into fast and slow decaying states. ICD spectra in good agreement with the experiment can be obtained only if nuclear dynamics in the slow decaying states is taken into account. We also demonstrate that by substituting the neighboring Ar atom with the “softer” Kr, one can not only tune the energies of the emitted slow ICD electrons, but also control the ICD yield. The thorough understanding of the cascade in dimers is of importance for larger systems in which the full *ab initio* investigation of the cascade is impossible.

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Dynamics of Energy Transfer Driven by Ultrafast Localization in Perylene Based Molecules

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Light-harvesting and intramolecular energy funneling are fundamental processes in natural photosynthetic systems, biosensors, and a large variety of organic photovoltaic devices. Perylene based molecules can be used as artificial light-harvesting molecules possessing unique architectures that allow the efficient energy funneling through the molecular system without significant losses. In this work we have studied the energy transfer mechanism over two dendrimer molecules: 2G1m-Eper and 2G2m-Eper as well as two Perylene-Tetrapyrrole dyads. The dendrimers are Poly(Phenylene Ethynylene) based molecule composed of two monodendrons and a perylene trap.

To unravel the kinetics and intramolecular energy redistribution mechanism after the photoexcitation for these molecules, we have employed Nonadiabatic Excited State Molecular Dynamics. [1] We found that the electronic energy transfer mechanism involves the ultrafast collapse of the photoexcited wavefunction due to non-adiabatic electronic transitions. The localization of the wavefunction is driven by the efficient coupling to high-frequency vibrational modes leading to ultrafast excited state dynamics and unidirectional efficient energy funneling. [2]

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***Ab Initio* Molecular Dynamics Study on the Interactions between Propanoate Ion and Metal Ions in Water**

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The interaction between propanoate ion and the divalent – Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} and the monovalent Na^{+} metal ions is studied via Born-Oppenheimer molecular dynamics (Figure 1a). The main focus of the study is the selectivity of the propanoate ion - metal ion interaction in aqueous solution [1]. The interaction is modelled by explicitly accounting for the solvent molecules on a DFT level. The hydration energies of the metal ions along with their diffusion and mobility coefficients is determined and a trend correlated with their ionic radius is found. Subsequently, a series of 16 constrained molecular dynamics simulations for every ion are performed and the interaction free energy (Figure 1b) is obtained from thermodynamic integration of the forces between the metal ion and the propanoate ion. The results indicate that the magnesium ion interacts most strongly with the propanoate ion, followed by calcium, strontium, barium and sodium. Since the interaction free energy is not enough to explain the selectivity of the reaction observed experimentally, more detailed analysis is performed on the simulation trajectories in order to understand the steric changes in the reaction complex during dissociation. The solvent dynamics appear to play important role during the dissociation of the complex and also in the observed selectivity behaviour of the divalent ions.

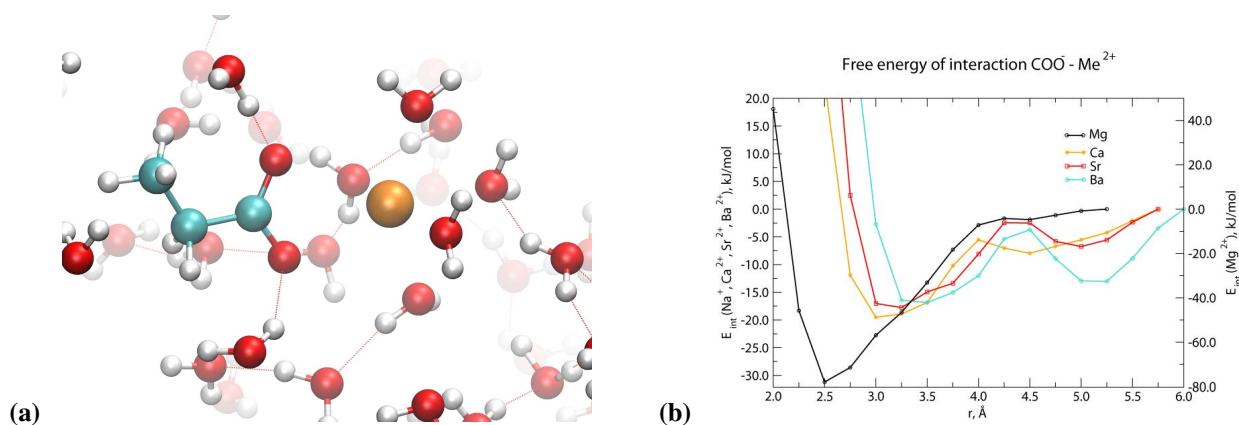


Figure 1: (a) Snapshot of the simulated system; (b) Interactions free energies.

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How Can the Green Sulphur Bacteria in the Depths of the Black Sea Use Quantum Computing for Light Harvesting?

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When in 2007 the New York Times published an article suggesting that plants were quantum computers, quantum information scientists exploded into laughter [1]. Their concern was, of course, decoherence which is believed to be one of the fastest and most efficient processes in nature. The laughter is over and quantum biology is firmly established, but the mechanism which sets decoherence apart is still under debate. Correspondingly extensive experiments have demonstrated quantum behavior in the long-time operation of the D-Wave quantum computer. The decoherence time of D-Wave's qubits is, however, reported to be on the order of nanoseconds, which is comparable to the time for a single operation and much shorter than the time required to carry out a computation, which is on the order of seconds. Explanations for the factor of 10^9 discrepancy between the single qubit decoherence time and the long-time quantum behaviour are hard to imagine. We suggested an explanation where the qubits are coupled to a high density environment of particles called gravonons [2]. The entanglement with the environment suppresses the spin flip effectively and coherent evolution continues which is, however, a coherent evolution in high dimensional spacetime and cannot be understood as a solution of Schrödinger's time-dependent equation in 4-dim spacetime. The properties of our model reflect correctly the experimentally found behaviour of the D-Wave machine and explain the factor of 10^9 discrepancy between decoherence time and quantum computation time.

Explanations for the quantum beats observed in 2D spectroscopy of the Fenna–Matthews–Olson (FMO) protein complex in the green sulphur bacteria are presently sought in constructing transport theories based on quantum master equations where 'good' molecular vibrations ('coloured noise') in the chlorophyll and the surrounding protein scaffold knock the exciton oscillations back into coherence [3]. These 'good' vibrations are claimed to have developed in three billion years of natural selection. These theories, however, face the disconcerting experimental observation that "attempts to scramble vibrational modes or to shift resonances with isotopic substitution miserably failed to affect the beating signals" [4]. As a possible way out of this dilemma we adopted the formalism of the quantum computation to the quantum beats in the FMO protein complex.

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An Integrated Approach for Analyzing Mutational Effects on Enzymatic Reactions of Nylon Oligomer Hydrolase (NylB)

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⁴IPCMS/CNRS, France

We carried out *in silico* mutational analyses on the enzymatic processes of Nylon oligomer hydrolase (NylB) from induced-fit in substrate binding to acylation of the substrate by using integrated theoretical methodologies to elucidate how NylB acquires a hydrolytic activity to a non-biological amide bond. To solve this question, we investigated the mutational effects of Y170F and D181G mutants, which were important amino acid residues suggested from previous experimental studies [1]. According to results obtained by the first-principles molecular dynamics accelerated with a Metadynamics approach both for wild type (WT) and for Y170F, we found that Tyr170 keeps a direction of NH group in non-biological amide bond pointing always toward a proton donor to accept a proton and an absence of Tyr170 results in elevation of the activation energy [2,3]. On the other hand, despite a lack of a hydrogen bond between substrate and Tyr170 in the Y170F mutant, the highest free energy barrier of Y170F during the induced-fit is similar to that of WT [4]. This means that kinetics of the induced-fit process is little affected by the mutation. Results obtained by Fragment molecular orbital method indicate that a role of Asp181 is not to decrease the activation energy, but to enhance the substrate specificity [3,5]. Finally, we performed structural homology analyses on enzymes with the same family and discovered the new one. According to the homology analyses, we suggested that a natural selection of Tyr170 attributes *Arthrobacter* sp. KI72 to acquire the hydrolytic activity on the non-biological amide bond.

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Theoretical Study on the Sulfur Transfer in Mercaptopyruvate Sulfurtransferases

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The reaction mechanism of sulfur transfer in human mercaptopyruvate (**mp**) sulfurtransferases [1] is investigated using a two-layer methodology combining DFT of B3LYP/6-31G(d) and Amber99sb force field. The thiolate of C248 residue, surrounded by a C248-G249-S250-G251-V252-T253-A254 (CGSGVTA) loop, reacts with **mp** and produces persulfide and pyruvate. Calculations show that sulfur transfer in the thiolate form (scheme 2) is kinetically more favorable than that in the thiol form (scheme 1), as demonstrated in Figure 1. The —NH/—OH groups of the CGSGVTA loop tends to stabilize the persulfide group with electrostatic interactions, and the hydroxyl group of S250 in the Asp/His/Ser triad forms hydrogen bond with the carbonyl oxygen atom of **mp** during the sulfur transfer, stabilizing the substrate in the enolate form. Electrostatic potential analyses suggest that in the product, an electron-deficient σ -hole exists on the top side along the S—S bond, while the periphery of the terminal sulfur is relatively electron-rich. Its HOMO involving the π^* of the persulfide group is enclosed by the CGSGVTA loop whereas the LUMO composed of the σ^* is axial toward the substrate. These results indicate that the characteristic CGSGVTA loop structure facilitates electrophilic attack from the front top along the S—S axis instead of nucleophilic attack.

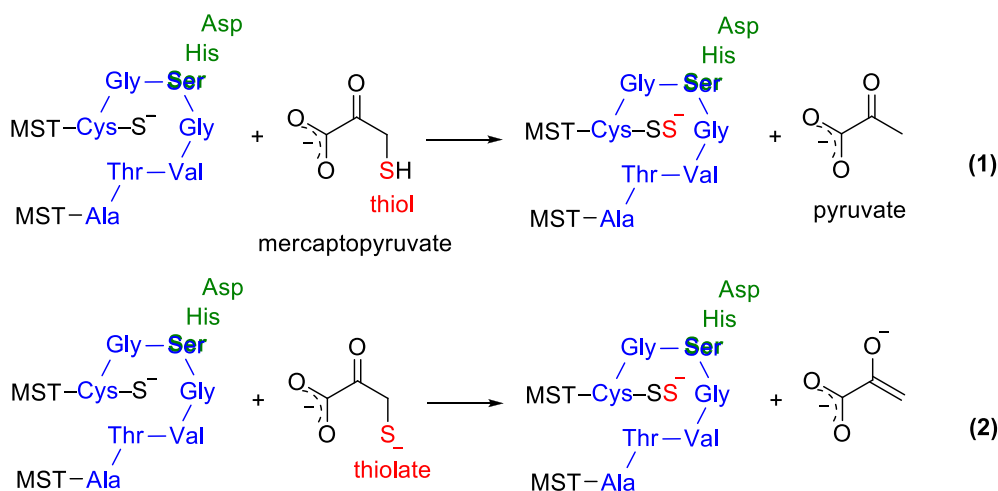


Figure 1: Possible sulfur transfer processes involving **mp** in the 1) thiol and 2) thiolate forms.

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Towards an Accurate *Ab Initio* Force Field for Modelling Water Using Quantum Simulations

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Modelling water in clusters and condensed phases is one of the main challenges of computational physics and chemistry. Quantum properties of nuclear motions can be important and quantum simulations using an accurate potential energy function are extremely useful. [1] Accurate potentials are calibrated on high quality quantum calculations of monomer, dimer and small clusters potential energy surfaces (PES) but most of them are extremely complicated and unpractical for use in Molecular Dynamics (MD) simulations of condensed phases. Our aim is to develop such an accurate potential but remaining practical for quantum simulation of liquid water and ice. Our potential is designed to have an analytical form easily generalizable to other systems and will keep the number of interaction site per molecule equal to the number of atoms. To develop such a model potential, we start from the recent CC-pol-8s and CC-pol-8sf potentials proposed by Szalewicz and coworkers, [2] representing two of the most accurate potentials available for modelling rigid and flexible water dimer respectively. Using CCSD(T) calculations, we then examine a re-parametrization of those potentials by reducing the number of sites per molecule from 25 to 3. An accurate modelling of the (ab initio) molecular dipole moment and polarizability dependence on the monomer geometry has been obtained using distributed-multipoles and -polarizabilities models similar to those already used in Molecular Dynamics simulations of liquid water. [3] Each component of the interaction energy (electrostatic, induction, repulsion, dispersion) is reparametrized and the results for dimer properties are compared with others potentials. [1,2]

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***Ab Initio* Calculations of the Electronic Structure and Optical Properties of MoS₂ Monolayer**

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In the recent years, layered two-dimensional materials have received a lot of interest because of their potential applications in the next generation low-cost solar cells and as possible candidate for replace traditional semiconductors in the next generation of nanoelectronic device. The current semiconductor technology requires new materials with definite advantages over traditional silicon, and even grapheme. Transition Metal Dichalcogenides (TMDs) build a new class of layered 2D materials, Molybdenum disulfide (MoS₂) is a widely known TMD with strong molecular intralayer bonds, and Van der Waals interaction enables stacking of the layers. The purpose of this work is to present a detailed characterization of the electronic band structure and optical properties of MoS₂ as function of layers number, via first-principles calculations (in the frame work of Density Functional Theory (DFT) based on Linearized Augmented Plane Wave (LAPW) as implemented in WIEN2k code). The 2D excitonic states can be explained by the dielectric screening effect of the Coulomb potential.

Computational Studies of Heteroatom-Doped Single-Walled Carbon Nanotubes

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Owing to their unique mechanical and electrical properties, carbon nanotubes (CNTs) have numerous prominent applications including chemical sensors, nanobioelectronics, and hydrogen storage. Past research has investigated the external doping of transition metal atoms into the supramolecular carbon framework and suggested a resulting higher conductivity and reactivity of the system. However, the internal doping of CNTs has not been extensively studied but is of great interest due to the predicted reactivity differences on the internal face of the nanotubes. Thus, this project studies the exo- and endo-doping of transition metal and main group atoms into single-walled CNTs (SWCNTs) and the resulting energy gap using density functional theory (DFT). Chiral SWCNTs are heavily emphasized due to the strong electrical dependence of the nanotubes on chirality. Moreover, since the computational costs increase dramatically with the size of the nanotube systems, the most accurate theories are far beyond affordable, even with the rapid growth of computing resources. Therefore, this project includes the search for suitable approximation models to allow for the study of large CNT systems at low computational costs.

Electronic Structure, Natural Bond Analysis and Spectroscopy of Glyphosate: Theoretical Approach

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The aim of this work is the theoretical study of T N-(phosphonomethyl) glycine or Glyphosate, which is currently the most widely used pesticide. It is a non-selective broad-spectrum herbicide [1]. Detailed calculations of molecular structure and spectroscopy analysis were executed using Gaussian 09W package. The molecular geometry including bond lengths, bond angles and vibrational wavenumbers of this organophosphorus compound have been calculated in the ground state by density functional theory (DFT) with 6-31G (d) and LANL2DZ basis set [2]. The theoretical spectrum and electronic properties, such as HOMO and LUMO energies have been interpreted by time dependent DFT approach. The computed HOMO and LUMO energies claim that charge transfer occurs within the molecules. Atomic Mullikan and natural charge obtained allow an understanding of atomic theory. The theoretical spectra were compared with experimental spectra and good agreements were obtained between the results.

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Design of Highly Effective Squaraines and Croconines for Photonic Application

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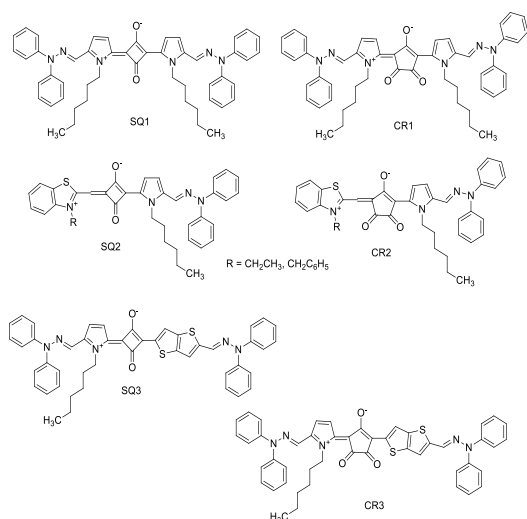
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Organic Photovoltaics (OPVs) have attracted a great deal of research interest as they are potentially low-cost, lightweight, and flexible sources for renewable energy. Exploring new materials is one of the paramount approaches to achieve high-performance OPVs.

Squaraine dyes are described as highly efficient absorbers for OPV applications. Squaraines are 1,3-derivatives of squaric acid, a condensation product of squaric acid and electron-rich aromatics or heterocycles. Squaraine dyes feature sharp and intense absorption in the red to near infrared (NIR) region of the solar spectrum. More importantly, squaraine film absorption is quite broad, which is highly beneficial for sunlight absorption.

The eventual use of a squaraine dye (SQ1) as electron donor component in bulk heterojunction organic solar cells (BHJ) has been studied from the optical point of view [1]. The soluble n-type fullerene, (6,6)-phenyl C61 butyric acid methyl ester (PC₆₀BM) has been used as acceptor.



Optical modelling based on transfer matrix method has been carried out to predict and improve photovoltaic performance of a BHJ device with blended SQ1/PC₆₀BM active layer. The geometry, electronic structure and absorption spectrum of SQ1 have been theoretically investigated by using density functional theory (DFT) and time-dependent DFT (TDDFT).

An efficient electron donor component in organic photovoltaic bulk heterojunction solar cell should possess some favorable properties – large absorption coefficient, low band gap, high charge mobility, environmental stability, suitable HOMO/LUMO level and solubility. A set of 3 squaraines and 3 croconines with different substituents has been designed to screen dyes with desired properties. The results indicate that SQ2 unsymmetrical squaraines with ethyl or benzyl group in the benzothiazole ring will be more efficient squaraine than SQ1.

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Design of D-D⁺ Cation-Based Nonlinear Optical Chromophores

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Dipolar push-pull organic chromophores, in which a conjugated π -system contains asymmetrically positioned electron-donor and electron-acceptor substituents, are typical second-order NLO chromophores [1]. The multipolar and multidimensional (nD) structures offer challenging possibilities in the design of molecules with enhanced NLO responses [2,3]. The design of NLO chromophores relies on information provided by theoretical and experimental investigations into relationships between (hyper)polarizability and donor-acceptor strength, nature and length of π -conjugation, molecular architecture, *etc.* The goal of the study is to relate the linear and nonlinear optical responses to the molecular structure/architecture of the model compounds by using theoretical calculations. The objects chosen for the study are 1D (D-A⁺)/2D (D-A⁺-D, D- π -A⁺- π -D) quinolizinium-based nonlinear optical chromophores. The impact of the structural modifications on the linear and nonlinear optical properties of the studied objects has been summarized and discussed. The study is expected to be valuable in the development of new 1D and 2D NLO chromophores with high molecular hyperpolarizability, β .

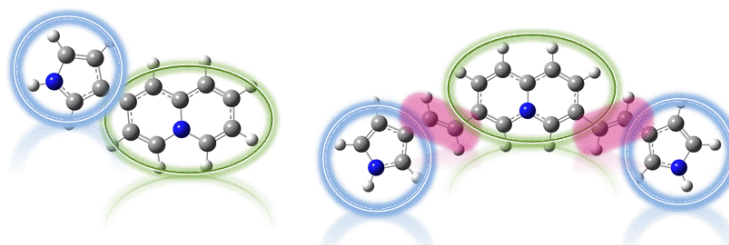


Figure: Examples of 1D (D-A⁺) and 2D (D- π -A⁺- π -D) chromophores based on heteroaromatic cations as acceptor units.

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Stacking Interaction and the Four-Body Term Non-Additivity in Adenine-Thymine Base-Pair Step in the B-DNA: A Quantum Monte Carlo Study

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Stacking is a non-covalent interaction in a molecular system. Non-additivity is often neglected but contributes towards B-DNA molecule dynamism. Understanding the contribution of the four-body term in the DNA molecule is important both to basic biological knowledge and to useful applications in biotechnology and biomedical research. Previous ab initio studies have shown substantial challenge to predict accurately the stacking interactions since they are inherent quantum mechanical phenomena that are as a result of the electron correlation effects in the DNA molecular system. However, recent studies have shown that the Quantum Monte Carlo (QMC) approaches can accurately describe stacking interaction through the inclusion of the correlation effects which is absent in methods such as Hartree-Fock and conventional functionals in Density Functional Theory (DFT) [1]. The QMC approach was adopted for this research as it recently predicted stacking interactions. Results indicated the AA:TT four-body term is positive and less than 1.76 kcalmol⁻¹. In AA:TT, DFT_{BSE} reports -10.17 kcalmol⁻¹ while QMC reports -4.23 kcalmol⁻¹. The results agrees with the previous work on the contribution of inter-strand and intra-strand to stacking stability. There is need to account for many-body contributions in a molecular system.

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Ligand Shell Effects on the Properties of Gold Nanoclusters

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Nanosized gold clusters have become key building blocks with a wide variety of applications in biology, catalysis and nanotechnology [1]. In this poster, we theoretically report the structural, electronic and optical properties of mixed functionalized undecagold-based clusters within the framework of DFT. We show that, compared to hydrogen and phenyl substituents, the presence of ethane chains on phosphine ligands gives rise to a highly negative charged shell that strongly distorts the metallic core. Additionally, optical absorption profiles computed at the TD-DFT level show that while the lowest energy transitions in $[\text{Au}_{11}(\text{PPh}_3)_8\text{Cl}_2]^{+1}$ involve mostly the gold core, a significant contribution from ethane ligands is observed in the case of $[\text{Au}_{11}(\text{PCH}_2\text{CH}_3)_8\text{Cl}_2]^{+1}$. Also, we find a considerable enhancement of the electron-donor character of phosphines in the presence of phenyl substituent. As a whole, our investigation shows that the electronic and optical properties, core morphology and charge distribution are noticeably affected by the ligand shell [2,3]. This may help to design complex structures to eventually obtain advanced materials.

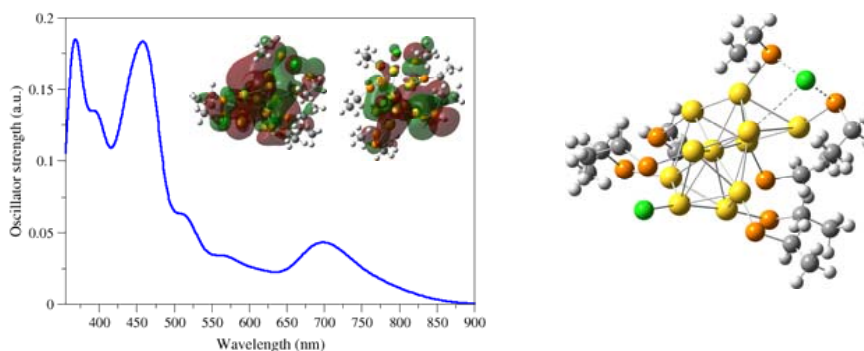


Figure: Computed optical absorption spectrum of the $[\text{Au}_{11}(\text{PCH}_2\text{CH}_3)_8\text{Cl}_2]^{+1}$ cluster.

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High Temperature Superconductivity and Long-Range Order in Strongly Correlated Electronic Systems

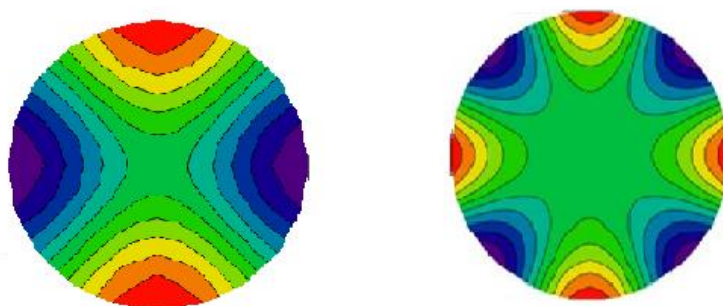
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This poster presentation concerns high temperature superconductivity from repulsive electronic correlations on alternant cuprate [1] and iron-based lattices [2]. It contains further a short introduction and review of conventional superconductors, from BCS to Yang's notable concept of Off-Diagonal Long-Range Order, ODLRO [3], the common denominator being that all pairs have the same macroscopic condensate wavefunction. In short repulsive electronic correlations will keep electron pairs out of the short-range repulsive region allowing an electron pair to reside with higher probability in the attractive part of the potential.



$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots) = \left(\sum_l (-1)^l (a_{lpx\uparrow}^\dagger a_{lpx\downarrow}^\dagger - a_{lpy\uparrow}^\dagger a_{lpy\downarrow}^\dagger) \right)^M |0\rangle$$

Figure: Shape of cuprate condensate wavefunction in k -space (left) and shape of iron-based condensate wavefunction in k -space (right).

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Multi-Photon Spectroscopy of the Many-Electron Atoms and Ions in a Laser Field with Accounting for the Debye Plasma Effects

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A great number of physically different effects occur in atomic systems (ensembles) in dependence upon a intensity, frequency, multi-colority of laser field, energy spectrum structure of an atomic system etc. In the last decade a considerable interest has attracted studying of the elementary atomic processes in plasma environments because of the plasma screening effect on the plasma-embedded atomic systems. In this paper one- and two-color multi-photon spectroscopy of a number of transitions in a hydrogen, lithium and caesium atoms and ions (free and immersed in a Debye plasmas) is studied theoretically. The theoretical approach is based on the relativistic operator perturbation theory (PT) and relativistic energy approach [1]. The energy shift and width of the multiphoton resonances are calculated within an energy approach, which is based on the Gell-Mann and Low adiabatic formalism [2]. The plasmas medium effects are taken into account by introducing the Yukawa-type electron-nuclear attraction and electron-electron repulsion potentials into the electronic Hamiltonian for N-electron atom (ion) in a plasma [3]. There is studied a plasmas with typical corresponding parameters: the Debye lengths $\lambda_D = 5$ a.u. (solar core: temperature $T = 10^7$ K; density 10^{32} m^{-3}) and 25 a.u. (inertial confinement: temperature $T = 10^4$ K; density 10^{28} m^{-3}). It has been quantitatively determined a variation of the multi-photon resonance enhancement frequencies in dependence upon the plasmas parameters (the Debye length). For example, the corresponding values for the resonance enhancement frequencies ω_{r_1} , ω_{r_2} and ω_{r_3} for the 1s–4f transition in the hydrogen for different Debye lengths ($\lambda_D = 5 - 50$ a.u.) are between 0.009 and 0.023 a.u. The H-plasma data are compared with available other data [2].

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Atomic Ensemble in a Laser Pulse of the Nonrectangular Shape: Resonant Dynamics, Optical Bi-Stability, Noise and Chaos Effects

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The work is devoted to studying the temporal dynamics of atomic ensemble in a laser pulse of the nonrectangular form and searching a possibility for observation of the strengthen internal optical bi-stability and chaos effects. The master system includes the modified Bloch equations, which describe an interaction of resonance radiation with ensemble of the two-level atoms subject to dipole-dipole interaction of atoms:

$$\frac{dn}{d\tau} = \frac{i2\mu T_1}{\hbar}(E^*P - P^*E) + (1 - n)$$

$$\frac{dP}{d\tau} = \frac{i2\mu T_1 n}{\hbar} - PT_1 \frac{1 - i(\delta + bn)}{T_2},$$

where $n = N_1 - N_2$ are the populations' differences for resonant levels, P is an amplitude of the atom's resonance polarization, E is an amplitude of effective field, $b = 4\pi\mu^2 N_0 T_2 / 2\hbar$ is the constant of dipole-dipole interaction, T_1 is the longitudinal relaxation time, $\delta = T_2(\omega - \omega_{21})$ is the offset of the frequency ω of effective field from the frequency of resonance transition ω_{21} , N_0 is the density of resonance atoms, μ is the dipole moment of transition, $\tau = t/T_1$.

We present new data on the population's dynamics for the resonant levels of atoms in a laser pulse of the non-rectangular (gauss or soliton-like) form. Our data shows that there are three stationary states n_i (two from them with maximal and minimal value of n are at that stable) under the assumption of $b > 4$ and $b < |\delta|$ with $\delta < 0$ (the long-wavelength offset of incident light frequency is less than Lorenz frequency $\omega_L = b/T_2$) and if the intensity of light field has certain value ($I_0 = 4|E_0|^2\mu^2 T_1 T_2 / \hbar^2$). We have found for a case of the nonrectangular laser pulse that there is a strengthen possibility of manifestation of the internal optical bi-stability effect; besides, an addition of a noise leads to quantitative changing dynamics.

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New Nonlinear Optics and Dynamics of Quantum and Laser Systems with Elements of a Chaos

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The work is devoted to carrying out new approaches to the universal quantum-dynamic and chaos-geometric modelling, analysis and prediction of a chaotic dynamics of nonlinear processes in molecular systems in intense electromagnetic fields and quantum-generator and laser systems. The latter include a single-modal laser with an absorbing cell, a fiber laser, a semiconductor laser coupled with feedback with delay, the system of semiconductor quantum generators, combined through a general cavity. The computing code includes a set of numerical quantum-dynamic models and such non-linear analysis methods as the correlation integral approach, multi-fractal analysis, average mutual information, surrogate data, false nearest neighbours algorithms, the Lyapunov's exponents and Kolmogorov entropy approach, spectral methods and nonlinear prediction (predicted trajectories, neural network etc) algorithms [1].

We present the results of the complete numerical investigation of a chaos generation in the low- and high-attractor time dynamics of the semiconductor GaAs/GaAlAs laser system with delayed feedback (the governing parameter: feedback strength or current injection). It has been numerically shown that firstly arising periodic states of the system transform into individual chaotic states and then global chaotic attractor with a chaos generation scenario through period-doubling bifurcation, which is significantly modified. We present firstly computed original data on the Lyapunov's exponents (+, +), correlation (chaos – 2.2; hyperchaos – 7.4), embedding (correspondingly 4 and 8), Kaplan-York (correspondingly 1.8 and 7.1) dimensions, the Kolmogorov entropy (0.15–0.71). It's firstly presented new model of forecasting the low-attractor time dynamics.

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Relativistic Quantum Chemistry of Heavy Hadronic Multi-Electron Atoms

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The gauge-invariant relativistic many-body perturbation theory approach [1] to consistent computing hadronic atomic systems ions with an account of relativistic, correlation, nuclear, radiative effects and strong interaction contribution is presented. The wave functions zeroth basis is found from the Klein-Gordon-Fock (pionic and kaonic atoms) equation. The potential includes the core ab initio potential, the electric and polarization potentials of a nucleus (the Gauss and Fermi models for charge distribution in a nucleus is used). The vacuum polarization radiative contribution is calculated in the generalized Uehling-Serber approximation. It is developed a precise theory for calculating energy levels shifts and widths, provided by a strong π^- -N interaction (“strong” width) and the interaction of the pion with QED vacuum (radiation width) within the model optimized optical complex π^- -N interaction potential and relativistic energy approach based on the Gell-Mann and Low formalism with complex relativistic e-e interaction potential.

It has been carried out computing energy (electromagnetic) contributions (Coulomb correction, radiation corrections, including basic contribution for polarization of the vacuum, the Breit-Rosenthal-Crawford-Schawlow effect etc.) to the different (for example: 5g-4f, 4f-3d) transition energies for ^{133}Cs , ^{165}Ho , ^{169}Tm , ^{173}Yb , ^{203}Tl , ^{208}Pb , ^{238}U . It is shown that the electromagnetic corrections to the transition energies, in particular due to radiation effect, are up to ~ 5 keV, nuclear ones – up to ~ 0.2 keV and correction for electronic shielding due to the presence of the survived 2[He], 4[Be], [Ne] electron shells is ~ 0.07 keV.

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Molecular Dynamics Assessment of the Interactions between Doxorubicin and a Drug-Binding Peptide

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A promising approach towards more efficient delivery of pharmaceuticals for cancer treatment is their attachment to various carriers. Doxorubicin (DOX) is an anthracycline antibiotic often used for treating leukemia and solid tumors. As a first step of constructing a complex system for its improved delivery to neoplastic cells, the non-covalent interactions between DOX and a tailored drug-binding peptide (DBP) are explored. The formation of the drug-peptide complex and the structural changes that occur during binding are explored via classical molecular dynamics simulations in aqueous solution at room and at body temperature. Characteristic dihedral angles in DOX and DBP, the intermolecular separation, and hydrogen bonds are analyzed. The binding energy is calculated at the DFT quantum-chemical level or using a hybrid ONIOM method. Higher flexibility of the complex is observed at body than at room temperature and there is difference between the preferred positions of the drug with respect to the peptide in the populated structures. From the dihedral angles analysis it is apparent that both molecules change their geometries when forming the complex. DOX and DBP interact mostly via π -stacking but hydrogen bonding plays an important role in stabilizing some of the structures at both temperatures. Drug-peptide binding is predominantly attractive and in some cases DOX even intercalates between two tryptophan residues. Binding energy varies strongly with drug-peptide orientation. Several peptide binding sites are identified, outlining the DOX-DBP complex as a prospective drug-carrying unit.

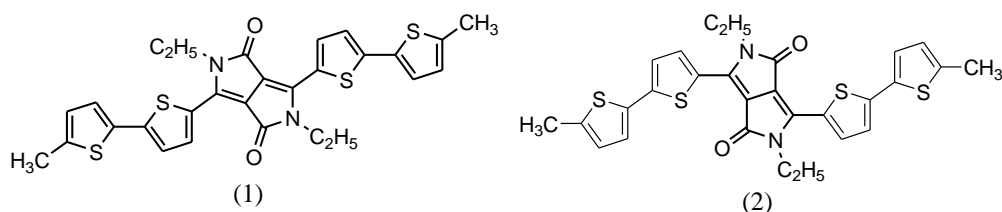
Transport Properties of Diketopyrrolopyrrole-Thiophene Polymer: A Computational Study

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Charge transport properties of diketopyrrolopyrrole-thiophene polymer, a promising semiconductor material, are studied using oligomer approach. We performed QM calculations of relative and reorganization energies, ionization potentials, electron affinities and intermolecular couplings of two conformers in the gas phase, *o*-dichlorobenzene solution and medium with the value of dielectric constant $\varepsilon = 3$, which is typical for organic semiconductors. Calculations are carried out by M06-2X/cc-pVDZ method and PCM model in GAUSSIAN09. Crystal structure predictions are performed using BIOVIA Materials Studio 8.0.



It is found, that the energetically favorable conformer (1) possesses slightly better electron donor and electron acceptor properties. The conformer (2) has larger reorganization energies for both electron and hole transport as compared to conformer (1) in all the considered media.

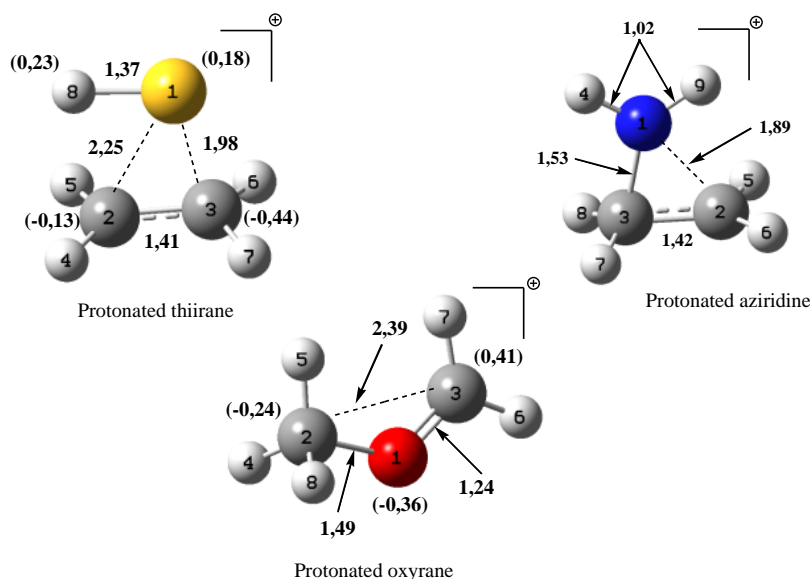
For several predicted high density and low energy crystal structures with the most common space groups for diketopyrrolopyrrole derivatives, the charge transfer couplings between adjacent molecules are estimated. The largest value of coupling defines the most preferential transport pathway of a charge carrier. Using the reorganization energy values in combination with the HOMO and LUMO orbital splittings (ESID method) in the various packing motifs, hole and electron transfer rates at 298 K are computed in the framework of Marcus theory for the self-exchange reaction.

Theoretical Study of Hydrotreating Process in Small Heterocyclic Rings

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A theoretical investigation has been realized by use of DFT-B3lyp/cc-pvdz calculation levels, to clarify at the atomic scale the hydrotreating process which depends on the remove of sulfur, nitrogen and oxygen atoms from the small heterocyclic rings such as thiirane, aziridine and oxirane. Activation of C-S, C-N and C-O bonds has been done via a simple and a double protonation followed by a full optimization of geometry. Critical points on the potential energy surface, of the protonated systems, were located by use of the frequency calculation. Our results indicate that the small protonated heterocyclic rings have revealed a carbocationic system as organic reactive intermediates presented by a complex with a weak interaction. In addition, proton affinities and charge delocalizations based on NBO analysis have been taken to check the ability of the lone pair of heteroatoms to participate in the formation of H-S, H-N or H-O bonds.



- References:** [1] D.D. Withurts, T. Isoda, I. Mochida, *Adv. Catal* **42**, 345 (1998).
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Performance of Some DFT Functionals with Dispersion on Modeling of the Translational Isomers of a Solvent-Switchable [2]rotaxane

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Computational methods (MM and DFT) were used to study the translational isomers of a solvent switchable fullerene-stoppered [2]rotaxane (**1**) manifesting unexpected behavior, namely that due to favorable dispersion interactions the fullerene stopper becomes the second station upon change of the solvent. For comparison, another system, a pH switchable molecular shuttle (**2**), was also examined as an example of prevailing electrostatic interactions. Tested for **1** were five global hybrid GGA functionals (B3LYP, B3LYP-D3, B3LYP-D3BJ, PBEh1PBE and APFD), one long-range corrected, range-separated functional with D2 empirical dispersion correction, ω B97XD, the hybrid meta-GGA functional M06-2X, and a pure functional, B97, with the Grimme's D3BJ dispersion (B97D3). The MM method qualitatively correctly reproduced the behavior of the [2]rotaxanes, whereas the DFT models, except for M06-2X to some extent, failed in the case of significant dispersion interactions with participation of the fulleropyrrolidine stopper (rotaxane **1**). Unexpectedly, the benzylic amide macrocycle tends to adopt preferentially 'boat'-like conformation in most of the cases.

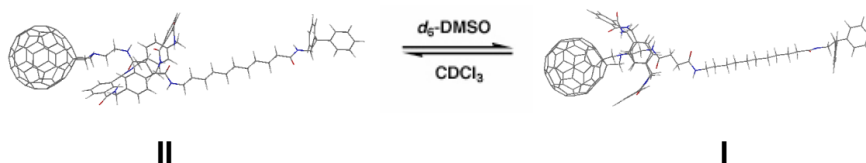


Figure: Instead of moving from station **II** to the station close to the right-end stopper, the macrocyclic ring is located over the succinamide template (**II**) or the fulleropyrrolidine portion (**I**).

The electrostatic interactions in **2** have the decisive contribution both when the macrocyclic ring is positioned at the dipeptide residue for the neutral form, and at the N-benzylalanine fragment after protonation, and the observed behavior of the [2]rotaxane is correctly reproduced by the methods used.

Conical Intersection – a Feasible Route of the Photoisomerization of a Candidate for Molecular Memory

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2,2',4'-Trihydroxychalcone is a modern candidate for an active unit in molecular devices [1,2]. Its rather unique photochemistry is responsible for various potential logic networks, including for memory with ultrafast write, nondestructive read and discrete deep/shallow states. Previous theoretical research on the photoreactivity of this molecule is not known.

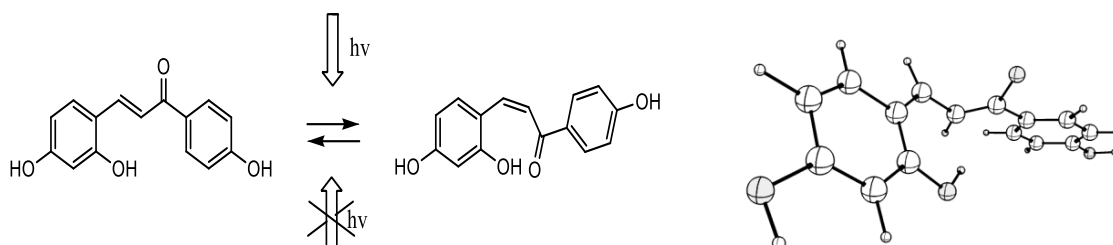


Figure: (Left) Only the E conformers are photoreactive; (right) geometry at MECP with reaction coordinate (dihedral angle) ca. -100° .

The most stable isomer in vacuum is selected after an extensive conformational analysis (AMBER), re-ordered by total energy with mpw1mp91/6-31g*. Its E/Z isomerization is modeled at SA-CASSCF/STO-3G level of theory. Careful selection of critical orbitals was made, based on energy and CIS correspondence, orbital shape and molecular symmetry. Rationalization of the changes in density matrix, geometry, NBO charges and total energy for S_0 and S_1 PES at the E minima, FC geometry, Z minima and the conical intersections (CIs) is done, the active space reevaluated at each of these steps. PES scans along the reaction coordinate in the ground and first excited states give energy profiles and barriers of the modeled process. Implicit CPCM model is used to account for solvent effects. The quantitative differences with the experimental data are explained. The minimal correct active space is confirmed by two real CIs, relevant to the E/Z isomerization path. Their characterization is used for rationalization of the observed chemical behavior.

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Relativistic Theory of Excitation and Ionization of the Heavy Rydberg Atoms in a Black-Body Radiation Field

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The accurate radiative transitions probabilities, ionization rates are needed in astrophysics, the ultracold plasma diagnostics etc. We present an advanced relativistic model potential method to computing the spectra, radiation amplitudes for the K, Cs, Tl Rydberg atoms (RA), the ionization rates of states in the field of blackbody radiation (BBR). The master method is the combined energy approach [1] and relativistic many-body perturbation theory with the zeroth model potential approximation [2]. It provides sufficiently correct and simultaneously simplified numerical procedure to determination of the corresponding radiative transition and ionization properties. Interaction of the Rydberg atom $A(nL)$ with the BBR induces transitions to the bound states and states of continuum: $A(nL) + \hbar\omega_{BBR} \rightarrow A^+ + e^-$, where $\hbar\omega_{BBR}$ – an energy of the BBR photon; A^+ is the corresponding ion. Probability of induced BBR transition between the nlj and $n'l'j'$ states is determined by the radiative matrix element and number of photons for ω_{nm} . A rate of ionization in the initial bound Rydberg state nl is determined by an intergral (integration is carrying out on the BBR frequency) $\sim \int_{|E_{nl}|}^{\infty} \sigma_{nl}(\omega)\rho(\omega, T)d\omega$, where E_{nl} is the threshold frequency of ionization of the Rydberg atom state. The energy parameters, radiation amplitudes for RA K, Cs, Tl their ionization rates of states with $n = 10 - 100$ in the BBR field ($T = 300 - 600$ K) are presented and compared with available experimental and the alternative theories data [3].

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Theoretical Studies on Some Organic Reactions Catalyzed by Cinchona Alkaloids

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The reaction mechanisms catalyzed by cinchona alkaloids (See Figure 1) are investigated by DFT methods. (1) Results of Michael addition of malononitrile to α,β -unsaturated ketones show that ketone substrates could be activated by generating reactive iminium ion intermediates through primary amine group of quinidine and the tertiary amine in quinidine promotes the activation of malononitrile and deprotonation. The rate-determining step was the transfer of H atom from quinoline unit to C atom of ketone. (2) The mechanism of Michael addition of malononitrile to cinnamylideneacetophenones shows that the reaction proceeds through a dual activation mechanism. The steric repulsion between the phenyl group attached to the carbonyl group in the ketone and the quinuclidine ring of cinchona alkaloid plays an important role for the control of stereoselectivity. (3) The mechanism and origin of the selectivity of asymmetric Diels-Alder reactions of 2,4-dienones by trienamine catalysis shows that one-step cycloaddition was adopted for *N*-phenylmaleimide, while a stepwise process was used for benzylidenecyanoacetate dienophile. The combination of a hydrogen bond and steric repulsion makes the dienophile substrates approach the trienamine from the one preferred face. The orbital factors define the most favored alignment of the trienamine and dienophile to realize the *endo*-selectivity of the product. These results are in agreement with experimental observations.

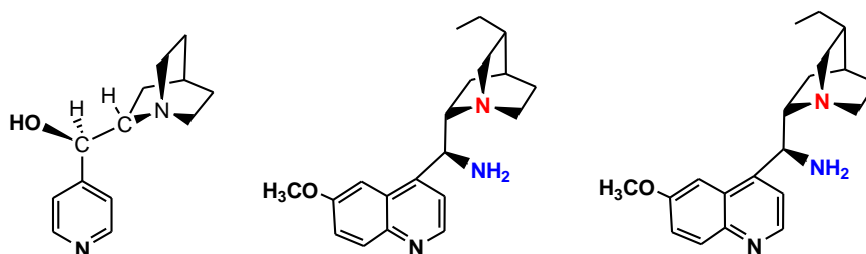


Figure 1: Three cinchona alkaloids used in the asymmetric syntheses.

- References:** [1] Zhishan Su, Hai Whang Lee, Chan Kyung Kim, *Org. Biomol. Chem.* **9**, 6402–6409 (2011).
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Anharmonic Vibrational State Analyses of Polyatomic Molecules with Quantum Monte Carlo Method

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Quantum Monte Carlo (QMC) method, especially Diffusion Monte Carlo (DMC) method, is one of the most accurate *ab initio* method to solve the Schrödinger equations of atoms, molecules, and solids [1]. The DMC method has, however, unavoidable problems known as the population control bias, the difficulty to compute the expectation values of the non-commutative operators with Hamiltonian, and troublesome tasks of the extrapolation of expectation values with respect to an imaginary-time step. In order to improve these problems and difficulties, we developed a new QMC method that combines Reptation Monte Carlo (RMC) method [2] with Multi-product (MP) expansion method [3] providing a very accurate imaginary-time propagator, and applied our method to anharmonic vibrational state analysis of polyatomic molecules.

Table 1 shows fundamental frequencies of H₂O molecule and its isotopologues (D₂O and HOD) obtained with the harmonic approximation (HA) and RMC-MP method. The mean absolute deviation (MAD) from corresponding experimental values are also given. The RMC method well reproduces the fundamental frequencies of all molecules (MAD is 2 ~ 3 cm⁻¹), while the HA significantly overestimates the frequencies (MAD is 72 ~ 137 cm⁻¹). More results for other molecules and the application to the analysis of H/D isotope effect on nuclear magnetic shielding will be presented on the day.

Table 1: The fundamental frequencies (cm⁻¹) of H₂O and its isotopologues.

Molecule	Method				
H ₂ O		HOH bend.	OH sym. str.	OH asym. str.	MAD
	HA	1641	3838	3942	137
	RMC-MP	1591(1)	3662(1)	3753(1)	3(1)
	Exptl.[4]	1594.6	3657.1	3756.0	
D ₂ O		DOD bend.	OD sym. str.	OD asym. str.	MAD
	HA	1200	2767	2888	72
	RMC-MP	1175(1)	2676(1)	2785(1)	3(1)
	Exptl.[5]	1178.3	2671.7	2788.0	
HOD		HOD bend.	OD str.	OH str.	MAD
	HA	1437	2826	3892	106
	RMC-MP	1401(1)	2725(1)	3709(1)	2(1)
	Exptl.[6]	1403.3	2723.7	3707.5	

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***Ab Initio* Molecular Modeling of Novel Potent Curcumin Derivatives for Treating Alzheimer's Diseases**

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Alzheimer's disease (AD) is developed in relation to the accumulation of amyloid- β ($A\beta$) peptides in a brain. $A\beta$ peptides are produced from the cleavage of amyloid precursor protein (APP) by both β - and γ -secretases. Among the produced $A\beta$ peptides species, $A\beta_{40}$ and $A\beta_{42}$ have a large population, and the amount of $A\beta_{42}$ is larger than $A\beta_{40}$ in the brains of the AD patients. To suppress the production of $A\beta$ peptides, it is effective to inhibit the APP cleavage process by the secretases. However, the secretases also play key roles in production of other vital proteins, so secretase inhibitors have an increased side effect risk. Therefore, it has been desired to develop novel compounds which bind specifically to the cleavage site of APP and inhibit the γ -secretase attacks.

In the present study [1], to propose new agents for suppressing the generation of $A\beta$ peptides, we investigated the mechanism of interactions between a short APP peptide and derivatives of curcumin, a constituent of turmeric, which is a spice used in Indian cuisine. We performed molecular simulations based on protein-ligand docking as well as *ab initio* fragment molecular orbital (FMO) methods to propose some potent curcumins effective for inhibiting the production of $A\beta_{42}$.

We determined curcumin I, curcumin II and curcumin III are more stable than their derivatives and docked these compounds to APP. Subsequently, we added solvating water molecules with in a 8 Å distance from the surface of APP+curcumin complexes, and solvated structures were fully optimized by classical molecular mechanics calculations. Finally, the most stable structure of these complexes was determined accurately by *ab initio* FMO calculations. The specific interactions between the residues of APP and curcumin were also elucidated from the interaction energies obtained by the FMO calculations.

The results simulated reveals that curcumin I binds to APP in a way as it covers over the γ -secretase cleavage site of APP. It is thus expected that curcumin I can suppress the cleavage of APP by γ -secretase. In addition, the binding energy between APP and curcumin I evaluated by FMO is the largest. We thus designed some novel compounds based on curcumin I, which are expected to be potent inhibitors for the production of $A\beta$ peptides.

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Dynamics of Ligand Exchange on Nanometer Size Gold Clusters: A Theoretical Investigation

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The physicochemical characterization of small gold clusters (SGC) represents a big challenge. Here, we analyze the optical, electronic and structural properties of several phosphine, chloride and thiolate ligated SGC with Au_{38} , Au_{28} , Au_{25} and Au_{13} metallic cores at the DFT level in the gas phase. Comparison of the UV – visible absorption profiles computed at the TD – DFT level shows that it is possible to shift the position of the lowest optical absorption band by controlling the electron density in the metallic core through the design of the ligand layer protecting the cluster. In all cases we found that *the more negative the metallic core the more the lowest optical absorption band is red shifted* [1]. On the other hand, *n* – heterocyclic carbenes (NHC) have been proved to be good candidates in the synthesis of SGC [2]. We found that compared to phosphine, a single NHC is strongly absorbed on the Au_{38} surface and significantly distorts the metallic core. Finally, our results show that the nature and organization of ligands on the SGC surface have a significant impact on their properties [3]. and motivate the study of these nanosystems in order to understand and tune their properties.

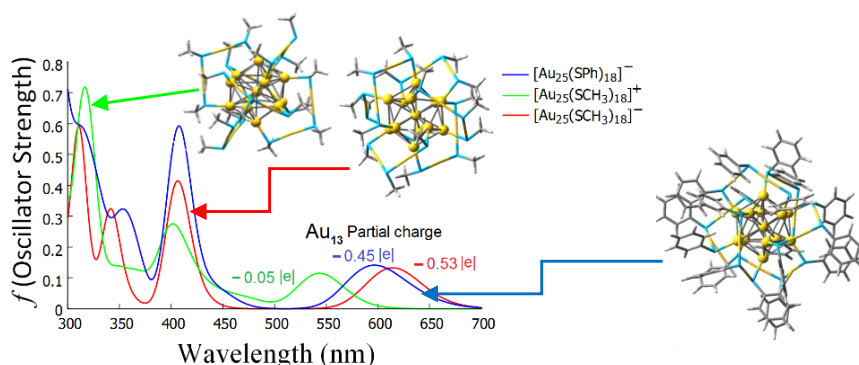


Figure: Computed optical absorption spectra of the ligated anions $[\text{Au}_{25}(\text{SCH}_3)]^-$, $[\text{Au}_{25}(\text{SC}_6\text{H}_5)]^-$ and the cation $[\text{Au}_{25}(\text{SCH}_3)]^+$ SGC at the TD–DFT level.

- References:** [1] G. Lugo, V. Schwanen, B. Fresch, F. Remacle, J. Phys. Chem. C. **119** (20), 10969-10980, (2015).
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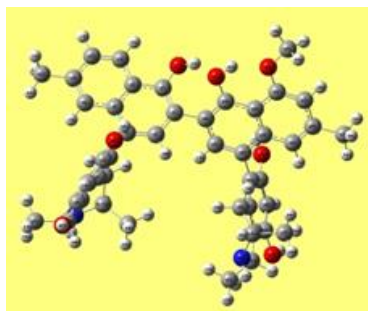
Computational Study of Michellamines – Naphtylisoquinoline Alkaloids with Anti-HIV Activity

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Michellamine A, B and C are naphtylisoquinoline alkaloids isolated from the leaves of *Ancistrocladus korupensis* from Cameroun and exhibiting anti-HIV activity [1–4], with michellamine B being the most active. The three molecules have the same structure and differ only by being atropisomeric. Each molecule consists of two units, each containing an isoquinoline moiety and a naphtylene moiety.

A thorough conformational study was performed *in vacuo* and in three solvents with different polarities and different hydrogen bonding abilities (chloroform, acetonitrile and water), using two levels of theory, HF/6-31G(d,p) and DFT/B3LYP/6-31+G(d,p). Frequency calculations were performed to verify that the identified stationary points are true minima and to get indications about the strength of intramolecular hydrogen bonds from the red shifts they cause. Potential energy profiles for the rotation of single bonds between moieties were calculated to identify preferences for their mutual orientations. Conformational preferences are influenced by the presence and patterns of intramolecular hydrogen bonds (having the major stabilizing effect) and by the mutual orientations of the isoquinoline and naphtyl moieties, which prefer to be perpendicular to each other. Other relevant molecular properties (dipole moments, HOMO-LUMO gaps, solvent effect, *etc.*) are also analyzed and discussed.



Michellamine A

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Conformational Preferences of Euglobals G6 and G7 – Two Acylphloroglucinols Differing by Their Acyloxy Groups Positions

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Euglobals are acylphloroglucinol-terpene adducts isolated from several *Eucalyptus* species. They can inhibit the Epstein–Barr virus (EBV) activation induced by the tumor promoter 12-*O*-tetradecanoylphorbol-13-acetate (TPA) [1]. Being polyhydroxyphenols, their potentialities as antioxidants and chemopreventives of diseases caused by free radicals are also interesting. The current study focuses on two euglobals with anticancer activities – euglobal G6 (E-G6, Figure 1) and euglobal G7 (E-G7, Figure 2). These molecules differ only by the positions of the two acyloxy chains (formyl and isovaleryl chains) with respect to the terpene moiety. The study (which follows a previous study of euglobals G1 and G2 [2]) aims at identifying patterns in the conformational preferences and molecular properties of E-G6 and E-G7. The influence of the positions of the acyloxy chains and intramolecular hydrogen bonding (IHB) patterns are given particular attention. IHBs play important roles in the stabilization of acylphloroglucinols [3] and only conformers of E-G6 and E-G7 having two IHB are significantly populated. Calculations were performed at the HF/6-31G(d,p) and DFT/B3LYP/6-31+G(d,p) levels *in vacuo* and in three solvents with different polarities and H-bonding abilities – chloroform, acetonitrile and water. Frequency calculations were performed to verify the nature of identified stationary points and also for the indications that the red-shifts of the donor OHs can provide about the relative strengths of IHBs.

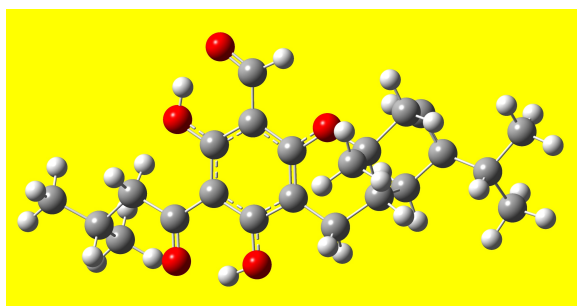


Figure 1: Euglobal G6.

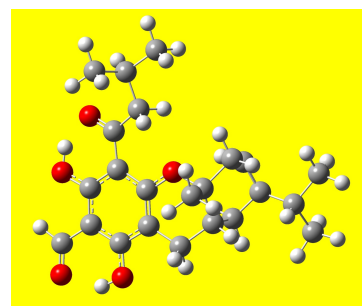


Figure 2: Euglobal G7.

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Reactions of Hydrated Electron in Water Nanoparticles: Sodium Pickup on Pure and N₂O-Doped Water Clusters

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Hydrated electron is a long-known and still poorly understood species. The formation of hydrated electron upon sodium pickup on water particles is accompanied by a decrease in ionization energy which can be used for sizing of water nanoparticles as well as for measuring their vibrational properties [1]. Hydrated electron is considered to be a mere spectator which can be utilized for investigating the nanoparticles. For more complex particles the situation is more complicated as the hydrated electron can react with some of the molecules. We show here that this is the case for N₂O-doped water clusters [2].

We have studied these processes using quantum chemistry DFT methods on (H₂O)₁₅ and N₂O (H₂O)₁₅ sample systems. Determining energetics and structure gave basis to *ab initio* molecular dynamics simulation of interaction between sample systems and sodium atom. These simulations showed two types of reactions. Pure water clusters act as an electron sink for sodium and form Na⁺...(H₂O)₁₅⁻, while in N₂O-doped clusters electron preferably reacts with N₂O forming Na⁺...(N₂O)⁻(H₂O)₁₅. Nitrous oxide anion eventually decays to N₂ and O⁻ and in the second stage oxygen anion reacts with water molecule to create OH radical and OH⁻. On top of that, evaporation of several molecules due to excess energy was observed in some of performed simulations.

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Prêt-à-Porter: Biscoumarine Outfits of Tb(III)

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Complexes of lanthanides with derivatives of 4-hydroxy-coumarins have potential as photosensors [1], anti-HIV agents [2,3], and antibiotics [4], and have been researched intensely during the past few years. In the present study, three biscoumarin derivatives are investigated as ligands, for which the optimised geometries, the IR, and UV/vis spectra in vacuum and in several solvents are computed and compared to experimental results. In addition, Tb(III) complexes are modelled with one of the ligands, characterised by IR and UV/vis spectra. Comparison between simulated and recorded IR spectra sheds light on the type of coordination or at least allows clarifying of the bands nature. These complexes have been synthesized and show promising biological activity,. Design of the ligand substituents aims at formulation of complexes with higher activity, lower toxicity, and fewer side effects.

The geometries of the ligand and the complexes are optimised with DFT in gas phase. The spatial structure of the free ligands permits two different orientations of the coumarin fragments denoted as parallel and antiparallel, depending on whether the carbonyl groups are closest or farthest apart. The antiparallel conformation of the ligands is more stable due to intramolecular H-bonds, which reproduces well the experimental X-ray and spectroscopic data [5], thus validating our computational protocol. Upon deprotonation, the more stable form of the ion becomes the parallel one. Interconversion between the antiparallel and the parallel conformation is feasible due to the low energy barrier that can be easily overcome. Thus, three types of coordination are modelled: to the hydroxyl oxygens (P1) or the carbonyl oxygens (P2) of the deprotonated parallel form, and mixed coordination with the deprotonated antiparallel ligand. The results show that the order of stability is $P1 > A > P2$.

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Modelling Liquid Photoemission Spectra via Non-Empirically Tuned Long Range Corrected Functionals

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Despite the structural simplicity of the H₂O molecule, the electronic structure of liquid water is still not fully understood. In the present work we focus on the valence orbital structure of liquid water based on realistic modelling of photoelectron spectra of liquid water using the extended Koopmans theorem. The performed realistic simulations of the photoelectron spectrum require (i) an accurate protocol for simulation of the spectral broadening and (ii) correct calculations of the ionization energies. We suggest an efficient and accurate approach based on the reflection principle combined with path-integral molecular dynamics with GLE thermostat PI+GLE [1] (for i), and direct calculations of the ionization energies enabled by the emerging GPU technology (for ii). We also show the application of the extended Koopmans theorem with optimally tuned range-separated hybrid functionals [2] to achieve the whole set of the ionization energies (*i.e.* HOMO, HOMO-1 *etc.*). We compare the direct approach to the cluster-continuum schemes using the concept of non-equilibrium polarizable continuum models.

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Landau Quantization and Neutron Emissions by Nuclei in the Crust of a Neutron Star

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At the end point of stellar evolution, neutron stars are not only the most compact stars in the universe, but also the strongest magnets. In particular, magnetic fields of the order of 10^{14} – 10^{15} G have been measured at the surface of soft gamma-ray repeaters and anomalous x-ray pulsars, thus dubbed *magnetars*. On the other hand, numerical simulations have shown that the internal magnetic field could be even stronger, up to about 10^{18} G. The outermost layer of a neutron star is thought to consist of a solid crust, whose atoms are fully ionized by the huge pressure. With increasing depth, nuclei become progressively more neutron rich by capturing electrons until at some point, neutrons start to drip out of nuclei. The presence of a neutron liquid in the inner crust of a neutron star is expected to leave its imprint on various observed astrophysical phenomena like sudden spin-ups and spin-downs, quasiperiodic oscillations detected in the giant flares from soft gamma-ray repeaters, and cooling.

We study the effects of a strong magnetic field on the neutron-drip transition in the crust of a magnetar. We show that the neutron-drip density and pressure increase almost linearly with the magnetic field strength in the strongly quantizing regime for which electrons lie in the lowest Landau level. In the weakly quantizing regime, the variations of the neutron-drip density with magnetic field strength exhibit typical quantum oscillations. The neutron-drip transition in a magnetar, as compared to unmagnetized neutron stars, can thus be shifted to either higher or lower densities depending on the magnetic field strength. For weaker magnetic fields, the neutron drip density can be either increased or decreased. The results suggest that the region of a magnetar crust where a neutron liquid is present, may change with time as the magnetic field decays. These results may have important implications for the interpretation of various astrophysical phenomena.

Water: A Walk-on or a Supporting Actor?

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In quantum-chemistry calculations solvents are usually introduced implicitly utilizing some of the traditional continuum models (PCM, COSMO, SMx). Yet very often the solvent molecules bind to the solute and persist upon drying. In these cases they are not just a medium and have to be treated discretely. The conducting form of polyaniline, the emeraldine salt (ES), is known to retain water upon drying and to lose crystallinity when thoroughly dried [1]. On the other hand, crystalline ES absorbs water which turns it into mesophase and drastically affects the absorption spectrum [2].

In order to study the effect of water molecules on the structural characteristics and the charge distribution in ES, model chains in the presence of an explicit solvent molecule immersed in implicit solvent medium are considered. The polaronic and the bipolaronic forms of the oligomer (corresponding to different configurations of the chloride counterions) are simulated and the water molecule is placed at various positions tangentially and vertically along the chain. The geometry is optimised with B3LYP and the structural deformation invoked by the water molecule is discussed. The redistribution of charges (NBO) is analysed. The binding energy is estimated and the type of bonding between chain and water is commented.

It is shown that the solvent polarity is a stabilising factor for ES. The structural deformation of polarons is local and more expressed while in bipolarons it is non-local. Water seams the chains tangentially, providing 2D structures (films), whereas π -stacking governs the aggregation in vertical direction, water penetrating in the stacks more efficiently in the presence of strongly hydrophilic counterions. Water enhances the redistribution of charges between chain and counterions and depending on its position either accepts electron density from the counterions or donates density to the chain.

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Modelling of Porous Hydrocarbon Materials for Facile Ion Migration

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Nowadays, Li-ion batteries are an indispensable attribute of our life – every wristwatch, smartphone, laptop, and tablet utilises them. Compact and durable, they are an attractive power source for other appliances and even for electric vehicles but the cost of lithium is prohibitively high. Therefore, scientists are investigating and optimising systems in which lithium is replaced by or mixed with sodium. Due to the difference in atomic radii, electrode materials, particularly graphitic anodes used in Li-ion batteries, are not suitable for intercalation of the larger Na atoms.

Polycyclic aromatic hydrocarbons (PAHs) are promising candidates for anode materials, since they possess low-lying vacant orbitals that can accommodate electrons. However, these compounds are mostly planar and tend to aggregate in closely packed stacks. To avoid stacking, structures containing five- and eight-membered rings are chosen – the former being typically electron-accepting fragments, often invoking deviation from planarity, and the latter known for pronounced out-of-plane deformation due to the Jahn-Teller effect.

In this research we are modelling the interaction of sodium atoms with non-planar hydrocarbons to be used as anode materials. The geometry optimisation is performed with different methods – MP2, LC-BLYP and wB97XD and compared in search of balance between accuracy and computational effort. The charge transfer between Na and the hydrocarbon molecules and the binding energy are estimated. The deviation from planarity and the effect of the metal-substrate interaction on the geometry is assessed.

Relationship between Metallophilic Interaction and Luminescent Properties in Pt(II) Complexes: TD-DFT Guide for the Molecular Design of Light-Responsive Materials

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The ground-, singlet and triplet excited-states of a series of bis-pyridyl-triazolato platinum (II) complexes and their intermolecular dimers are obtained with the DFT/TD-DFT approaches and the PBE0 functional. The molecular complexes are structurally similar and differ only in the type of substituent attached to the pyridine ring: $-\text{N}(\text{CH}_3)_2$, $-\text{H}$, $-\text{CHO}$ or $-\text{CHC}(\text{CN})_2$ group. [1] The simulations reveal that in ground-state the intermolecular dimers result from weak metallophilic interaction, while in excited state the metal-metal attraction is strong and causes excimer formation. The energy of the intermolecular interaction in ground-state is estimated with the PBE0, as well as with the dispersion-corrected version of the functional PBE0-D3. The electronic structure, molecular geometry, absorption and emission properties of the monomers and dimers are presented and discussed in details. It is demonstrated that at monomer level the substituent modification does not result in substantial changes in the optical properties. However, the substituent has an impact on the ground- and mainly on the excited-state metallophilic interaction and its modification can be successfully used for the tuning of emission wavelengths at supramolecular level. The theoretical results are interpreted in the light of the ligand (substituent) effect and in respect to available experimental data. Structure-properties relationships obtained with the DFT and TD-DFT approaches are applied in the formulation of guidelines for the molecular design of platinum-based organic luminescent materials.

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Theoretical Study of Charge Separation through Hot States in Organic Photocell

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Organic solar cells utilizing π -conjugated oligomers and polymers have been gathering much attention as one of renewable natural power resources. The manufacturing of organic semiconductors does not require for high-temperature processes unlike inorganic semiconductors such as poly- and amorphous- silicon materials. Low-temperature processes help to reduce the production costs of organic solar cells. In addition, the unique features of organic semiconductors, such as versatility of functionalization, thin film flexibility, and easy processing, are attractive from not only scientific but also industrial viewpoints. However, at present the conversion efficiency of organic solar cells remains lower compared with inorganic photocells. In order to improve the efficiency, the mechanisms of photocurrent generation in organic semiconductors have been actively investigated. The dissociation of electron-hole pair (exciton) generated by adsorbed photon energy is one of important processes in the mechanisms of organic photocells.

We theoretically study the dissociation process of geminate electron-hole pair (excitation) through vibrational hot states at the donor-acceptor interface of organic solar cell. [1] We modify the formalism of Rubel *et al.* (Phys. Rev. Lett. **100**, 196602 (2008)), and employ the theoretical concept of Arkhivov *et al.* (Phys. Rev. Lett. **82**, 1321 (1999)) to take into account the hot states. Effects of the band offset and the excess energy dissipation on the exciton dissociation process are presented through theoretical calculations of the escape probability of hot electron. We will show that the hot states and delocalization of exciton are effective to raise the probability to separate electron-hole pair.

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Assessment of the DFT Functionals with Non-Empirically Tuned Range-Separation Parameter for Calculating the Chiroptical Properties of Heptahelicenes

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From the theoretical and computational points of view, optical rotation (OR) and circular dichroism (CD) spectra are challenging to predict. It has been demonstrated that Time-Dependent Density Functional Theory (TDDFT) is able to reproduce most of the experimental features and can help in interpreting the CD spectra of several helicenes and substituted helicenes [1]. To remedy the wrong asymptotic behavior of the exchange-correlation (XC) potentials of conventional density functionals at large interelectronic distances, the Long Range Correction (LC) scheme has been proposed. The key improvement consists in a smooth separation of DFT and nonlocal Hartree-Fock (HF) exchange interactions through the so-called range-separation parameter μ . This parameter can be non-empirically tuned so that in the Kohn-Sham density functional calculations the highest occupied molecular orbital (HOMO) energy of the N-electron system is equal to the opposite of the ionization potential (IP). As it has been shown, this parameter is system-specific and property-dependent [2].

The goal of the study is to assess the importance of optimizing the range-separation parameter on the predicted OR, UV/visible and CD spectra of a set of heptahelicenes. This tuning scheme has been applied at LC-BLYP level. The optimized range-separation parameter value varies between 0.19 and 0.24 (Bohr⁻¹) and is significantly decreased compared to the typical default values of 0.33 or 0.47. Additional computations using three LC-DFT functionals: CAM-B3LYP, ω B97XD, and LC- ω PBE were also performed and compared and discussed to the results obtained by the three hybrid functionals with a constant fraction of HF exchange. *e.g.*, B3LYP, BHandHLYP, PBE0, as well as to the available experimental data. The computational results show a strong dependence of the calculated optical rotation and CD spectra on the range-separation parameter. The increase of μ in the range 0.1–0.6 (Bohr⁻¹) leads to a significant decrease of the optical rotation. For some compounds the two low energy transitions exchange at certain μ (reordering of states) resulting in a change of the sign of the Cotton effect.

The conclusion that “the tuning procedure can be cautiously recommended for applications to electronic optical activity” drawn by M. Srebro and J. Autschbach [3] concerns also the UV/vis and CD spectra within the tuned LC-DFT scheme.

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Relativistic and Mass Corrections on the Ground State Energy in Few and Multiply Charged Heliumoid Ions

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Relativistic spinless corrections of the ground state effective **Breit-Pauli Hamiltonian** for helium isoelectronic series with atomic numbers from $Z = 2$ to $Z = 118$, for the main nuclides and existing isotopes are investigated. The calculations of non-relativistic ground state energies are performed using trial explicitly correlated generalized Hylleraas-type wave functions. The calculations are made with and without taking into account the mass correlation effects, by including the mass polarisations operator into the main Hamiltonian in the developed variational perturbation approach. Using the variational perturbation procedure allows solving the two-particle Schrodinger equation. The inclusion of the mass polarisation effects in the minimisation procedure, as a correction of a lower order in respect to the relativistic corrections, allows for the correct account of the later. Velocity corrections of the kinetic energy, the contact correction to the potential energy, the correction of Darwin and the orbit-orbit corrections are calculated. These corrections are calculated: i) without taking in to account the mass corrections; ii) with the mass correction, without their inclusion in the minimisation procedure; iii) and after their inclusion in the minimisation procedure.

The spinless relativistic corrections behaviour for atomic number Z , their dependence on the mass number A versus Z , as well as the influence of the mass polarization effects on their forming are studied.

The high accuracy of the results allows for their use in different precise theoretical approaches for analysis of astrophysical and laboratory plasma. The method and the results are a basis for the study of the spin-relativistic and QED effects.

Quantifying the Hospitality of Cucurbiturils

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Cucurbit[*n*]urils (CB[*n*]) are a family of macrocyclic compounds with remarkable properties as host molecules for various guests. Their high binding affinity, high selectivity and recent advances in their synthesis and chemical functionalization allow them to compete with cyclodextrins as platforms of choice for fundamental and applied molecular recognition and self-assembly studies [1]. So far, CB[*n*] complexes have mostly been studied experimentally and very few theoretical works attempt to elucidate the nature of their exceptionally strong binding potential or to predict the binding affinity of CB[*n*] towards new guest molecules [2–4]. In the present study we try to establish a reasonably accurate and inexpensive computational protocol to predict the properties, such as geometry and binding affinity, of complexes of CB[*n*]. We also attempt to clarify the structure of the complex between 1-butyl-3-methylimidazole and CB[7], and of the ternary complex between methyl viologen, 2,6-dihydroxynaphthalene and CB[8], both of which have been studied experimentally [5,6].

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Spectroscopy of Cooperative Laser Electron- γ -Nuclear Processes in Diatomics, Multiatomic Molecules and Clusters

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In the modern molecular spectroscopy it is intensively studied a new class of problems, connected with modelling the cooperative laser-electron- γ -nuclear processes, computing the mixed γ -optical transitions in molecules *etc.* The first qualitative estimates of the cooperative effects parameters were earlier presented (see [1–3] and refs. therein). We present an advanced quantum approach to calculation of laser-electron- γ -transition spectra (e-vibration satellites) of nucleus in diatomic and multiatomic molecules, based on the density functional formalism and energy approach [3]. Decay and excitation probability are linked with imaginary part of the molecule – field system. As example, in Figure 1 the theoretical emission and absorption spectrum of the nucleus ^{127}I in the diatomic molecule H^{127}I is presented. New data on the electron-nuclear γ -transition spectra of the nucleus in some multiatomics are presented for a number of molecules: 3-atomic XY_2 ($\text{D}_{\infty h}$), 4-atomic XY_3 (D_{3h}), 5-atomic XY_4 (T_d), 7-atomic XY_6 (O_h) ones.

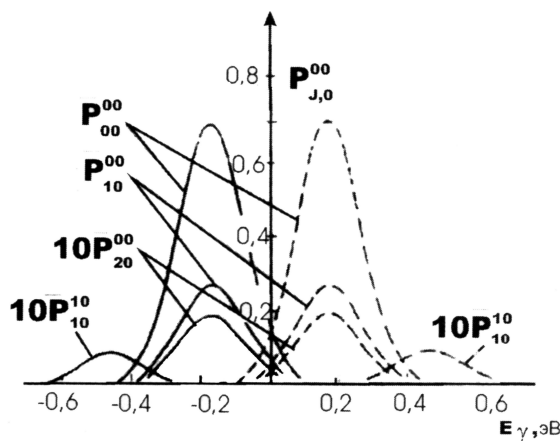


Figure 1: Emission and absorption spectra of ^{127}I in the H^{127}I (mol. init. state: $\nu_a = 0$, $J_a = 0$).

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Advanced Relativistic Energy Approach to Computing the Radiation Transition Probabilities for Heavy Rydberg Atoms

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In this present work we present an advanced version of the relativistic energy approach [1] to computing the radiation transition probabilities (oscillator strengths) in spectra of heavy Rydberg neutral atoms and multicharged ions. The approach is based on S-matrix Gell-Mann and Low formalism [1] and relativistic many-body perturbation theory with optimized model potential zeroth approximation [3]. The key feature of the presented basis theory is an implementation of the optimized one-particle representation [1] into the frames of the S-matrix energy formalism. It provides a consistent method to minimization of the gauge-non-invariant contributions to the radiation transition (radiation decay width) probability and thus it makes our approach significantly more advantageous in comparison with standard methods to calculating radiative transition parameters. The important exchange-correlation effects are accounted with using relativistic Kohn-Sham-like density functionals.

We present the results of computing energies, radiation transition probabilities, oscillator strengths in spectra of the heavy Li-like multicharged ions ($Z > 55$), neutral tantalum and thulium (in particular, transitions to the $4f_{7/2,5/2}^{13}6s_{1/2}(3,2)ns,np$ and $4f_{5/2}^{13}6s_{1/2}(2)nsp_{1/2}[3/2]$ states, $n = 15 - 40$). We have compared the obtained results with the experimental results and other theoretical data, obtained on the basis of the Coulomb approximation with the Coulomb gauge of the photon propagator, the multiconfiguration Hartree-Fock and Dirac-Fock methods (see [2,4] and refs. therein). We have checked that the results for oscillator strengths, obtained within our approach in different photon propagator gauges (Coulomb, Babushkin, Landau), are practically equal (difference $\sim 0.1-0.3\%$).

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Relativistic Quantum Chaos in the Heavy Rydberg Atoms in an Electromagnetic Field and Backward-Wave Oscillators

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The work is devoted to theoretical modelling, analysis and forecasting chaotic dynamics of nonlinear processes in relativistic systems: heavy Rydberg atoms in an microwave field and backward-wave tubes (RBWT). For the first time it has been performed quantitative modelling, analysis, forecasting dynamics RBWT, as well as the relativistic atoms in a microwave field with accounting relativistic effects ($\gamma_0 = 1.5\text{--}6.0$), dissipation, a presence of space charge, reflection of waves at the end of deceleration system etc on the basis of the methods [1,2]. There are computed the temporal dependences of the normalized field amplitudes (power) in a wide range of variation of the controlling parameters which are characteristic for distributed relativistic electron-waved self-oscillator systems: electric length of an interaction space N , bifurcation parameter proportional to (\sim current I) Pirse one $L(J)$: 2.7–3.9 and relativistic factor $\gamma_0 = 1.5\text{--}6.0$). There are computed the dynamic and topological invariants of the RBWT dynamics in auto-modulation(AUM)/chaotic regimes, correlation dimensions values (3.1; 6.4), embedding, Kaplan-York dimensions, Lyapunov's exponents (LE: +, +) Kolmogorov entropy (KE = 0.74). It's developed new non-perturbative relativistic approach to computing, analysis of chaotic dynamics of relativistic atomic systems in microwave field, which is based on quasi-energy method, relativistic operator perturbation theory, complex coordinates rotation algorithm; it's firstly carried out computing relativistic ionization dynamics of Rydberg atoms Rb (test), Fr, Tm ($n > 55$; $F > 3 \cdot 10^{-9}$ a.u.). It's firstly given description of new relativistic chaos phenomenon and listed data on correlation, embedding, Kaplan-York dimensions, LE (+, +) KE and conditions for transition from chaotic mode to stabilization.

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QTAIM and Stress Tensor Interpretation of the $(\text{H}_2\text{O})_5$ Potential Energy Surface

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We use the Quantum theory of Atoms in Molecules (QTAIM) and the stress tensor topological approaches to interpret the $(\text{H}_2\text{O})_5$ potential energy surface (PES). We firstly take an overview using the recently formulated Quantum Topology Phase Diagram (QTPD) [1]. This enables us to make *directed* QTPDs to create a link between the QTAIM and the PES. The total local energy density $H(\mathbf{r}_b)$ is used to demonstrate the presence and extent of the two- way coupling and exchange of chemical character between the hydrogen bonding H–O and covalent (sigma) O–H bonding. We then track the QTAIM and stress tensor bond critical point (*BCP*) properties along the entire intrinsic reaction coordinate (IRC) from the transition state down to the associated pair of minima. We find a smooth variation in the QTAIM and stress tensor *BCP* properties for a range of traditional QTAIM properties such as ellipticity ε , bond-path curvature and the total local energy density $H(\mathbf{r}_b)$. In addition, we use recently introduced and physically intuitive properties such as the *BCP* stiffness S . We explain the role of the O—O *BCPs* in facilitating the path to the transition state for high energy barriers. Next, we introduce, using the vector character of QTAIM and the stress tensor an eigenvector following formulation to track the changes in the topology along the IRC. Finally, we attempt to use the vector character of QTAIM and the stress tensor to correctly predict the path up the IRC.

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A Comparative MD Study of Water Structuring

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The structuring of water at the water/vapour interface has been an object of lasting scientific interest in the past several decades. Ever since the first successful attempts to investigate liquid water using the methods of theoretical chemistry were made [1, 2], the number of studies on water structure increased continuously. Most of them are focused on bulk water or ices, while surface water still needs more detailed research.

In the present study several atomistic water models were chosen – non-polarisable (SPC [3], TIP3P and TIP4P [4]) and polarisable (SW-RIGID-ISO [5], SWM4-NDP [6] and COS/G2 [7]) and classical molecular dynamics (MD) simulations of bulk and surface water were carried out. All systems were kept at 298 K and 1 atm. Structural features of bulk and surface layers were examined using radial distribution functions and Voronoi analysis; some electric properties – dipole moments and dielectric constants, were also evaluated. In addition, MD simulations of the water/octane interface were carried out utilizing the non-polarisable (TIP4P) and polarisable (COS/G2) water models and the structural properties were compared. The systems are to be enriched with surface active substances in order to determine their influence on the studied characteristics.

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Real-Time Detection of *Cis-Trans* Photoisomerization in New Metal Styryl Azacrown Ether Complexes

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A series of novel styryl azacrown ether dyes has been synthesized [1,2] and their chemical structures and photophysical properties [3] in presence and in absence of different metal cations have been elucidated. The real-time *cis-trans* photoisomerization of the dyes has been measured by a diode – pumped frequency doubled solid state laser (emitting at $\lambda = 532$ nm, *cw*, up to 80 mW) using a series of logarithmic – scaled ND (neutral optical density filters, Thorlabs Inc.) allowed to change the laser power smoothly. Quantum-chemical calculations at DFT level have been performed in order to determine the stability, absorption and associated emission of the *cis-trans* ligands and metal complexes in gas phase and in solution.

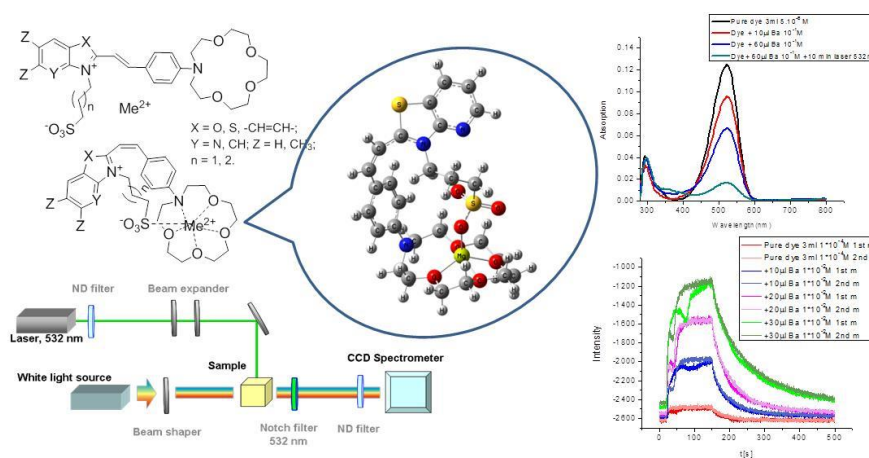


Figure: Laser induced real-time *cis-trans* photoisomerization in novel 15-aza-crown-5 containing styryl dyes.

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