



ITN-EJD: Theoretical Chemistry and Computational Modelling

Second Annual Meeting, Supervisory Board Meeting and Training Workshop "Project Management Course", Leuven, Belgium, 17 – 21 July 2017. <https://quantchem.kuleuven.be/ejdtccm/index.html>. Local Organizers: Jeremy Harvey and Arnout Ceulemans

Program

A pdf document containing the abstracts of all oral presentations is available on the webpage. The speakers who are Early Stage Researchers within the ITN are labeled below as 'ESR' with the number of their project. All activities take place within the Maria Theresia College of KU Leuven.

Mon 17	09:30 - 12:30	Supervisory Board Meeting*
	12:30 - 13:30	Lunch
	13:30 - 16:00	Supervisory Board Meeting*
	16:30 - 16:35	Conference Opening
	16:35 - 17:20	Shirin Faraji "Insights into light-driven DNA repair by photolyases"
	17:20 - 17:45	Neus Aguilera-Porta "In silico modelling insight into assessing NSAIDS excited states deactivation mechanisms" ESR 8
	17:45 - 18:10	Martina De Vetta "Photosensitizers for photodynamic therapy: from photophysics to assisted delivery" ESR 7
	18:10	Welcome reception
Tue 18	09:00	Opening of Scientific Session 2
	09:00 - 09:45	Stijn De Baerdemacker "When two is better than one: new wavefunctions from the seniority scheme"
	09:45 - 10:10	Giovanna D'Angelo "Knockout driven reactions in porphyrin molecules and butadiene clusters" ESR 9
	10:10 - 10:35	Meilani Wibowo "Electronic coupling calculations for a potential singlet fission chromophore" ESR 3
	10:35 - 11:05	Coffee break
	11:05 - 11:30	Dmytro Ivashchenko "Improvement of methods for the structural characterisation of drug metabolites based on collisional cross sections" ESR 10
	11:30 - 11:55	Enrico Skoruppa "DNA elasticity from coarse-grained simulations: the effect of groove asymmetry"
	11:55 - 12:20	Tommaso Francese "Magnetic fingerprint of planar bistable molecule-based magnets" ESR 13
	12:20 - 14:00	Lunch
	14:00	Opening of Scientific Session 3
	14:00 - 14:45	Martin Paterson "Development and Applications of Monte Carlo Configuration Interaction"
	14:45 - 15:10	Andi Cuko "Structure predictions of technologically and environmentally relevant oxide nanoparticles" ESR 11
	15:10 - 15:35	Carles Martí "Ab initio modelling the chemical storage of renewable energy" ESR 4
	15:35 - 16:00	Coffee break
	16:00 - 18:00	ESR and experts meeting + TCCM discussion*

Wed 19	09:00	Opening of Scientific Session 4
	09:00 - 09:45	Celine Chizallet " <i>Insight from ab initio calculations into the structure and reactivity of complex catalysts: the case of platinum-based subnanometric particles supported on alumina</i> "
	09:45 - 10:10	Ewa Szlapa " <i>Kinetics and selectivity in hydroformylation of propene</i> " ESR 12
	10:10 - 10:35	Francesco Talotta " <i>A theoretical investigation of the trans-[RuC(NO)(Py)₄]²⁺ photochemistry</i> " ESR 6
	10:35 - 11:05	Coffee break
	11:05 - 11:30	Stefano Battaglia " <i>Electronic structure properties of [n]Cyclacenes: semi-empirical and wave function approaches</i> " ESR 5
	11:30 - 11:55	Eliot Boulanger " <i>Improved Lennard-Jones Parameters for Accurate Molecular Dynamics Simulations</i> "
	11:55 - 12:20	Maria Izquierdo " <i>Charge transfer in bulk heterojunction organic solar cells</i> " ESR 2
	12:20 - 15:30	Lunch + poster session
	15:30	Opening of Scientific Session 5 – in honour of Arnout Ceulemans
	15:30 - 15:40	Session opening remarks
	15:40 - 16:25	Tohru Sato " <i>Vibronic coupling density and its applications</i> "
	16:25 - 16:40	Daryna Smyrnova " <i>An exciting life of fluorescent proteins</i> "
	16:40 - 16:55	Athanasios Arvanitidis " <i>Valence bonds in elongated boron clusters</i> "
	16:55 - 17:40	Patrick Fowler " <i>Some current work on currents</i> "
17:40 - 18:10	Arnout Ceulemans " <i>Symmetry: unquestioned answers - unanswered questions</i> "	
19:00	Conference Dinner	

Thu 20	09:00	Opening of Scientific Session 6
	09:00 - 09:45	Julien Michel " <i>Molecular simulation methods for ensemble-based drug design</i> "
	09:45 - 10:10	Gabriele dalla Torre " <i>Computational approach to aluminum biochemistry</i> " ESR 14
	10:10 - 10:35	Maximilian F.S.J. Menger " <i>Excited state gradients in polarizable QM/MM models: an induced dipole formulation</i> " ESR 1
	10:35 - 11:05	Coffee break
	11:05 - 11:50	Robert Deeth " <i>Computational Coordination Chemistry: Harnessing Quantum Chemistry to Build Better Force Fields</i> "
	11:50 - 12:15	Jelle Vekeman " <i>Adsorption of methane on graphene</i> " ESR 15
	12:15 - 12:20	Closing Remarks of the Conference
	12:20	Lunch and end of the public sessions
	14:00	ESR training event: Workshop "Project Management Course" - for ESRs only. Session organizer: Berta Herrero.

Fri 21	09:00 - 12:20	Continuation of the Project Management Course
	12:20	Lunch and end of the workshop

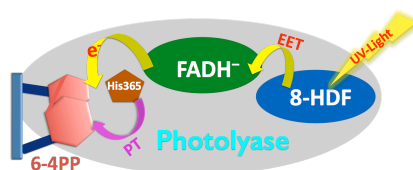
Mon 17 16:35-17:20

Insights into Light-driven DNA Repair by Photolyases

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UV radiation triggers various chemical reactions in DNA such as intra-strand cross-linking between adjacent pyrimidines, causing genetic mutations. In fact, pyrimidine dimers are supposed to be the major players in the formation of skin cancer. DNA photolyases are enzymes initiating cleavage of mutagenic pyrimidine (6-4) pyrimidone photolesions by a photo-induced electron transfer from flavin adenine dinucleotide to the lesion.



Using hybrid quantum mechanical/molecular mechanical (QM/MM) dynamics, we have carried out series of simulations to completely map out the entire evolution of functional processes involved in the molecular mechanism of this important biological system. We have demonstrated that the electron catalyzing the repair is generated via an intermolecular Coulombic decay (ICD) process [1]. In fact, this is the first example for ICD as operating mechanism in a real biological system. We have presented the most energetically feasible electron-induced splitting mechanism in which the initial step is electron-coupled proton transfer from the protonated Histidine to the lesion, which proceeds simultaneously with intramolecular OH transfer along an oxetane-like transition state [2]. Our theoretical findings are in agreement with experimental time-resolved measurements [3]. The experimental spectroscopic signature of the detected 6-4PP intermediate is assigned theoretically to a specific molecular structure determining the operating molecular mechanism of the electron-induced restoration of (6-4) photolesions. Thereby, all pieces of the (6-4) photolesion repair puzzle are finally put together [4].

[1] P. Harbach, M. Schneider, S. Faraji, A. Dreuw, *J. Phys. Chem. Lett.* 4, 943 (2013).

[2] S. Faraji and A. Dreuw, *J. Phys. Chem. Lett.* 3, 227 (2012), S. Faraji, G. Groenhof and A. Dreuw, *J. Phys. Chem. B.* 117, 10071 (2013)

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[4] S. Faraji, D. Zhong, and A. Dreuw, *Angew. Chem. Int. Ed. Engl.* 55, 5175 (2016). S. Faraji, A. Dreuw. *Photochem. Photobiol.* 93, 37 (2017).

**In silico modelling insight into assessing NSAIDs
excited states deactivation mechanisms**

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Drugs' light exposure, either in the visible (Vis) or ultraviolet (UV) range, along the pharmaceutical chain is inevitable. Thus, it is crucial to investigate the photophysics and the photoreactive paths that can be activated upon photon absorption [1]. The International Council of Harmonization (ICH) S10 guidance (and the associated ICH M3 guidance) suggests the characterization of the UV-Vis absorption spectrum as the initial assessment because it can obviate any further photosafety evaluation.

Thus, we have computed the absorption spectra of a set of eleven NSAIDs (piroxicam, carprofen, indomethacin, benoxaprofen, naproxen, diclofenac, suprofen, tiaprofenic acid, ketoprofen, ibuprofen and aspirin) in gas phase as well as in solution. Multistate second order perturbation theory on state average complete active space self-consistent field wavefunctions MS-CASPT2//SA-CASSCF (for aspirin and ibuprofen) and time dependent density functional theory (TD-DFT) (for all the NSAIDs set) were the computational protocols used for this purpose [2,3,4].

Besides, we have also considered the presence of triplet states close in energy to the singlet spectroscopic states at the Franck-Condon (FC) region. In fact, triplet excited states might be involved in the diversion of the excited population to pathways different from the return of the population back to the original ground state. Understanding the complexity of the deactivation mechanism, however, requires the in-detail mapping of the potential energy landscape for the ground and excited states. The accessibility of lower lying singlet electronic states and the coupling to the triplet excited states are key to explain the photostability or photoreactivity of these systems. Calculations exploring the topography of the potential energy surfaces of singlet and triplet multiplicity for the NSAIDs ibuprofen and aspirin are in course.

In a next stage, within the mechanistic scenario provided by the static calculations, the most probable photophysical deactivation mechanism of the excited molecules will be determined with the help of semi-classical dynamics simulations, performed with the surface-hopping algorithm incorporating spin orbit coupling, recently developed by Granucci et al. in Pisa [5]. These results are expected to shed light on the lifetime of the excited state. Our final aim is to generate a model phototoxicity alert that will improve the assessment of the photophysical properties of drugs.

Acknowledgments: ITN-EJD: TCCM: This project is possible thanks to the funding from the European Union's Horizon 2020 research and innovation programme under the Marie Curie Skłodowska-Curie grant agreement No.642294.

References

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- [5] G. Granucci, et al., *J. Chem. Phys.* **137**, 22A501 (2012).

Photosensitizers for photodynamic therapy: from photophysics to assisted delivery.

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Theoretical studies have been employed in photodynamic therapy to predict and understand the optical and photophysical properties of photosensitizers. This is particularly helpful, when a new class of compounds is considered as photosensitive drug, such as BODIPYs. Insights on the deactivation mechanism, upon radiation, could suggest substitution patterns to enhance their efficacy as photosensitizers. [1] The overall efficacy of the treatment, though, is not only due to the light-response of the drug, but arise from the effectiveness of the different stages represented in Figure 1.

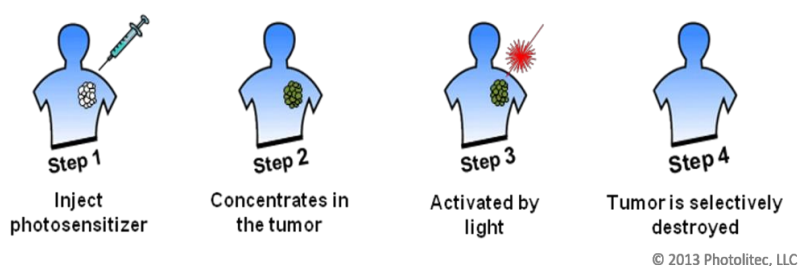


Figure 1. Schematic representation of photodynamic therapy treatment stages.

The hydrophobicity of porphyrin derivative photosensitizers, such as Temoporfin, prevents an easy administration of the drug. This problem has been addressed engaging nano-carriers, such as liposomes, for an assisted delivery. Calorimetric measurements showed that the thermal stability of the liposome is enhanced when the photosensitizer is embedded inside it. [2] In order to explain this behaviour, all-atom classical molecular dynamics simulations have been performed. Specifically, the disaggregation process of the drug/bilayer structure induced by high temperatures has been modelled. These challenging simulations, which involve half a million of atoms and simulation times of hundreds of nanoseconds, are feasible thanks to the use of GPU-based hardware. Understanding the nature of the interactions responsible for the altered stability of the carrier, when loaded with the drug, is expected to help formulating improved nano-carriers for extremely hydrophobic drugs.

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Tue 18 09:00-09:45

When two is better than one: new wavefunctions from the seniority scheme

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"Strong quantum correlation" is one of the unsolved problems of electronic structure theory. It was recently observed [1] that the seniority scheme offers a much better partitioning of the Hilbert space than the conventional particle-hole scheme to capture strong static correlations. This scheme organizes the electron configurations into electron pairs, rather than in single-particle excitations on top of a reference state. Full Configuration Interaction (fCI) calculations limited to the fully paired space only (or Doubly-Occupied Configuration Interaction) are able to describe bond-breaking processes with very high accuracy. Unfortunately, as a fCI method, the computational scaling of DOCI remains exponential, and hence impractical for large systems.

The mean-field picture associated with electron pairing is known as the theory of Antisymmetric Product of Interacting Geminals (APIG)[2]. This ties in with the intuitive Lewis picture of chemical bonding, however the exponentially scaling computational cost of an APIG wavefunction is hardly better than DOCI. A recent breakthrough in APIG theory came with the connection with Richardson-Gaudin (RG) integrable systems [3,4], in which we have identified a new family of APIG states with mean-field like computational cost and the same accuracy as DOCI.

In this presentation, I will discuss recent research from the Ghent-McMaster collaboration on the seniority scheme, APIG theory and its connection to Richardson-Gaudin integrability [5,6,7].

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[5] Van Raemdonck M, Alcoba D R, Poelmans W, De Baerdemacker S, Torre A, Lain L, Massaccesi G E, Van Neck D, and Bultinck P, 2015 J. Chem. Phys. 143 104106

[6] Claeys P, Van Neck D and De Baerdemacker S, 2017 arXiv:1706.05511

[7] Claeys P, Caux J-S, Van Neck D and De Baerdemacker S (in preparation)

Knockout driven reactions in porphyrin molecules and butadiene clusters

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Recent studies on collisions between energetic ions/atoms and PAHs, fullerenes or their clusters have demonstrated the importance of prompt atom knockout in Rutherford-like scattering for molecular processing [1]. Such processes may lead to molecular growth, due to the formation of highly reactive fragments that very efficiently form new covalent bonds with surrounding molecules [1]. This type of energetic processing can be of importance for, e.g., the origin and evolution of complex molecules in space [2].

Here we present the modeling of keV-ion impact on butadiene clusters [3] and of collisions between tetraphenyl-porphyrin (TPP) ions and Ne or He atoms at 50-80 eV center-of-mass collision energies [4]. We have performed classical Molecular Dynamics simulations to model entire collision sequences, i.e. the initial knockout event and the subsequent fragmentation or molecular growth processes inside molecular clusters. Figure 1 shows a comparison between experimental and simulated mass spectra for collisions with butadiene clusters. The spectra clearly suggest the presence of molecular growth within the clusters and that this is driven by prompt carbon knockouts. We are currently investigating possible secondary fragmentation pathways, specific to collisions with atoms or ions, by means of density functional theory based methods.

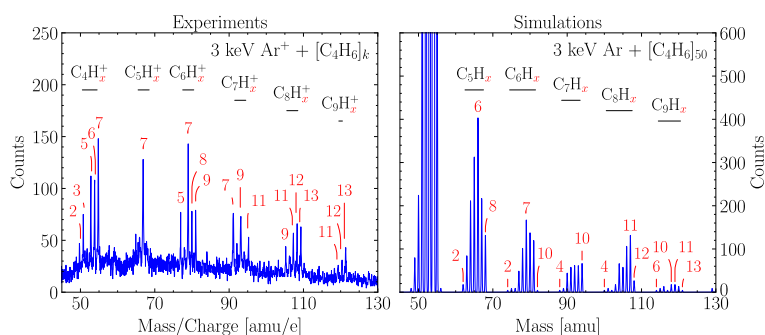


Fig.1 Experimental (left) and simulated (right) mass spectra for collision of C_4H_6 cluster with Ar^+ .

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Electronic coupling calculations for a potential singlet fission chromophore

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The singlet fission process converts an excited singlet state into two (local) triplets that are coupled into a singlet (¹TT). This process exploits a high-energy photon to generate multiple electron-hole pairs that are capable for charge separation, which ultimately can improve the efficiency of organic solar cells. For an efficient singlet fission process, one has to ensure that for the chromophore the condition of $E(T_2) > E(S_1) \cong 2E(T_1)$ is met in order to have a significant rate [1]. In the Fermi's golden rule approximation, the singlet fission rate depends on the electronic coupling between the initial and final states and the density of final states. Here, we describe the calculation of the electronic coupling based on a nonorthogonal configuration interaction approach and the effect of intra molecular vibrations on this coupling [2,3]. This approach will be applied to a potential singlet fission chromophore, the biradicaloid molecule (see Figure 1), which has been previously reported to fulfil the energetic condition [4].

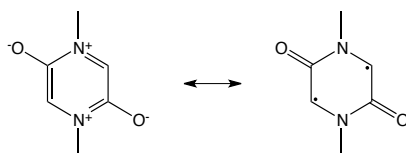


Figure 1. The resonance structures of the biradicaloid molecule

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§ **Improvement of methods for the structural characterisation of drug metabolites based on collisional cross sections**

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Ion Mobility Mass Spectrometry (IM/MS) is a technique that allows separation of isomeric species based on differences in their collision cross sections (CCSs) in the gas-phase, thus providing specific information on the potential structure of a compound [1]. In combination with Molecular Modelling, it is considered as a potential tool for small molecule identification by measuring their gas-phase CCSs and comparing them to theoretically derived CCS databases. A protocol for theoretical determination of CCS has been introduced in [2] and its improvement is at the core of this project.

In the initial stage of the project we have developed a script – an extensive automation of the protocol, which allows all the routine and necessary steps of the algorithm to be performed automatically. It minimises human intervention and saves valuable time. Further research is aimed at investigating deeper possible sources responsible for the differences between the theoretical and experimental CCS values.

In the present work, new atomic parameters employed in the CCS determination software (MOBCAL [3]) have been introduced: the protocol has been modified to be able to distinguish between different atom types and to assign appropriate parameters. Other modifications include an additional step in the protocol that calculates root-mean-square deviation (RMSD) of the found conformations and performs filtering based on the level of similarity among structures. Extensive tests of the protocol with the introduced changes are to be made in order to assess the performance of the new script. Additionally, the calculation of the partial charges used by MOBCAL to calculate the ion-induced part of the potential is to be included in the protocol. Further research includes the study of the possible effect of the dipole moment on the CCS of a metabolite and the assessment of the possible use of QSAR in the protocol.

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Tue 18 11:30-11:55

DNA elasticity from coarse-grained simulations: the effect of groove asymmetry

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(Dated: 11 July 2017)

It is well-established that many physical properties of DNA at sufficiently long length scales can be understood by means of simple polymer models. These models neglect most of the chemical details of DNA and reduce it to a continuous inextensible rod that exhibits resistance to bending and twisting deformations. The simplest such model is the twistable worm-like chain (TWLC) that treats those deformations independently. However, recently it was shown that some discrepancies between experimental results and theoretical predictions obtained with the TWLC can be resolved by introducing a twist-bend coupling into the energy functional of the TWLC. This coupling was predicted to be a direct consequence of a molecular asymmetry of the DNA duplex, but due to the notorious difficulty of its experimental exploration very little information about its strength relative to the more explored bending and torsional stiffnesses is available in the literature. In the present work the origin of this coupling is explicitly explored by means of molecular dynamics simulations of oxDNA, a coarse-grained model of double stranded DNA. It is shown that solely the molecular asymmetry without any further assumptions gives rise to a very substantial contribution of twist-bend coupling in this model. Our analysis is based on the calculation of the covariance matrix of equilibrium deformations, from which the stiffness parameters are obtained. Furthermore, it is shown how the introduction of twist-bend coupling can naturally explain the large variations on experimental estimates of the intrinsic torsional stiffness performed in the past.

Keywords: DNA, oxDNA, twist-bend coupling, molecular dynamics, coarse-graining

Magnetic Fingerprint of Planar Bistable Molecule-Based Magnets

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Theoretical predictions of magnetic properties of bistable purely organic molecule-based magnets have experienced an incredible development during the last years. Some of these compounds present peculiarities that cannot yet be explained with the *state-of-the-art* theoretical models. Our attention is devoted to dithiazolyl (DTA, see Figure 1a)-based compounds, namely TTTA¹, PDTA, TDPDTA, and 4NCBDTA². They are, in principle, the best candidates for potential technological applications, like storage devices, sensors and quantum computers. The study addresses three main issues. First, to evaluate by means of FPBU working strategy³ which pairs of radicals are magnetically non-negligible in order to identify the magnetic topology of the molecule-based crystals. Second, to assess whether structural (geometrical) as well as the electronic (DTA-ring, substituent interactions) factors affect the magnitude of the overall radical···radical J_{AB} magnetic coupling. Finally, we aim at providing a magneto-structural map as a function of the substituents of the DTA-moiety to highlight which is the static ferromagnetic fingerprint region. At this point, we would like to stress that this magneto-structural map could be used as a practical tool to help experimentalists to design more stable and efficient purely organic radicals with ferromagnetic properties in the solid state.

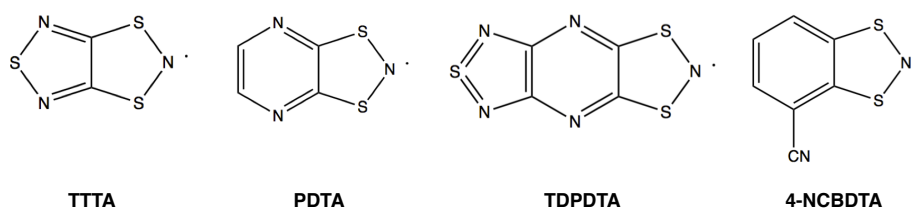


Figure 1. DTA-based compounds investigated.

¹ Brusso et al., *J. Am. Chem. Soc.* 2004, 126, 8256-8265² Vela et al., *Chem. Eur. J.* 2017, 23, 3479 – 3489³ Vela et al., *Phys.Chem.Chem.Phys.*, 2015, 17, 16306

Tue 18 14:00-14:45

Development and Applications of Monte Carlo Configuration Interaction

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While Full Configuration Interaction (FCI) is numerically exact it is computationally too demanding for all but the smallest of systems. Monte Carlo configuration interaction (MCCI) involves a stochastic search through the electronic Hilbert space to produce highly compact wavefunctions that are capable of representing full configuration interaction for both energies and properties, but at only a very small fraction of the state size.[1] MCCI treats static and strongly correlated systems in a *blackbox* manner, and is capable of generating diagnostics detailing the nature of a system's true correlated wavefunction.[2] The basics of the methodology will be introduced alongside details of its scope and accuracy. Examples from our recent work to be discussed will include studies of reactive potential energy surfaces,[3] static and frequency-dependent molecular electric properties,[4-5] electronic excitation energies and transition moments,[6] core-hole excited states,[7] and strongly correlated metal-metal bonding interactions.[8] Extensions of the basic methodology will also be discussed, including MCCI-PT2,[9] natural orbital approximations,[2,9,10] and application to mixed electronic/positronic systems.[11]

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Structure predictions of technologically and environmentally relevant oxide nanoparticles

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Nanotechnology in recent years is playing a very important role in such diverse field as catalysis, electronics, optics, etc. The key role of the success of these classes of materials is the structure-property relationship. Moreover, several nanoparticles properties can be tuned by varying its size. There are several experimental techniques such as electron spectroscopies, that have been successfully applied to determine nanoparticles structure with high resolution. Nevertheless, theoretical structure predictions are still needed especially in an ultra small size regime (i.e. size ≤ 1 nm) which usually is below the experimental resolution. At this size regime it is possible to predict the atomic structure of nanoparticles applying global optimization techniques such as Monte Carlo basin hopping (MCBH). This is a power tool that provide realistic models in order to elucidate the structure-property relationship.

We applied MCBH on titania (TiO_2) nanoclusters in order to predict the crystalline-to-amorphous crossover size¹. At size of 2.0 – 2.5 nm we predict a crossover in energetic stability between photoactive anatase bulk-like (> 2.5 nm) and amorphous inactive TiO_2 nanoparticles (< 2.0). We studied as well titanosilicates systems which are industrial catalyst widely used for oxidation of organic molecules in mild conditions. These catalysts are based on crystalline zeolitic silica framework in which it is disperse a very low fraction of 4-coordinated titanium active centres. Only a very low fraction of titanium is included in the framework due to its low miscibility, however, at nanoscale we predicted a high miscibility between silica and titania at a wide range of compositions. Here we provide as well useful informations such as calculated harmonic IR spectra which contain “signatures” of mixed titanosilicates in order to help experimentalists characterize these structures². Our next studies are focus on using MCBH on hydroxylated systems such as silica³ and titania to better understand the influence of water on oxides clusters stability. Here, we are developing new strategies and methods to predict stable hydroxylated nanoparticles.

¹ Lamiel-Garcia, O.; Cuko, A.; Calatayud, M.; Illas, F.; Bromley, S. Predicting Size-Dependent Emergence of Crystallinity in Nanomaterials: Titania Nanoclusters versus Nanocrystals. *Nanoscale* **2016**, *9*, 1049–1058.

² Cuko, A.; Calatayud, M.; Bromley, S. Size dependency of stability and structure in mixed-oxide titanosilicates: from nanocluster to bulk. In preparation

³ Cuko, A.; Maciá, A.; Calatayud, M.; Bromley, S. Global Optimisation of Hydroxylated Silica Clusters: A Cascade Monte Carlo Basin Hopping Approach. *Comput Theor Chem* **2017**, *1102*, 38–43.

ESR 4, Tue 18 15:10-15:35

Networked computing for ab-initio modeling the chemical storage of renewable energy

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Université Toulouse III – Paul Sabatier

After the reactive scattering probabilities obtained for the OH + H₂ system using the Quantum-Classical method, the research has continued by investigating the non reactive scattering processes. The conditions needed for the inelastic analysis of the non reactive scattering processes, have evidenced the inability of the until then used PES in order to describe correctly the intermolecular long range potential. A Potential energy tail based on the Improved Lennard Jones potential and the electrostatic quadrupole-dipole interaction have been developed and added to the until then used Potential energy surface. Reactive and inelastic rate constants have then been calculated by simulating the scattering processes with the new PES. The comparison of the results obtained with the experimental ones available in literature showed an excellent agreement and a clear increase in accuracy of the obtained results. Its success encouraged the development of a more general approach, a Potential Energy fitting method able to intrinsically predict the long range behaviour. The Bond Order expansion fitting method has thus been started to develop in order to reach that goal.

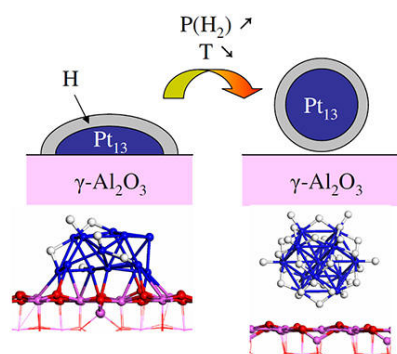
Ru nanoparticles acting as Sabatier catalyst have been started to study by means of DFTB method. Validation of the parameters used in the calculations have been carried out by comparing DFTB results with the ones obtained from DFT method for small nanoparticles. The excellent agreement will allow to perform calculations on bigger nanoparticles, performing global optimization using Parallel Tempering method and run the dynamics to see the Role of the Ru nanoparticles acting as Sabatier reaction catalysts. After the failure of the kinetic study using data from literature, calculations of the energy barriers of the steps composing an extended mechanism for the Sabatier reaction have also been performed.

INSIGHT FROM *AB INITIO* CALCULATIONS INTO THE STRUCTURE AND REACTIVITY OF COMPLEX CATALYSTS: THE CASE OF PLATINUM-BASED SUBNANOMETRIC PARTICLES SUPPORTED ON ALUMINA

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Most efficient heterogeneous catalysts used industrially are generally very complex systems. Computational chemistry is of great help to unravel their atomic-scale structures and understand their roles in the catalytic reaction. Very often however, simple structural models are proposed to understand catalytic reactions. In the present talk, we will show how Density Functional Theory (DFT) calculations were used to provide an original information about the structure for active sites of complex catalytic systems of industrial relevance, as a function of their environment, to assign spectroscopic observations and to quantify the kinetics of multi-step reactions they can catalyze.[1] The focus will be put on catalytic reforming heterogeneous catalysts. Catalytic reforming is a very important process in the refinery, at the core of the production of gasoline with high octane number, and also providing hydrogen. Catalysts are composed of sub-nanometric platinum particles dispersed on a gamma-alumina support. The nature of the active sites and their catalytic behavior remains a matter of debate. We will show the contribution of *ab initio* calculations to elucidate the physical-chemistry of these systems,[2] revealing original cluster morphologies in this size range (about 13 atoms),[3] which also depend on the level of hydroxylation,[4] possibly chlorination,[5] of the surface. The reactive environment-dependent (hydrogen and hydrocarbons) morphology of subnanometric platinum and platinum-tin clusters was also revealed,[6] and employed for a state-of-the-art assignment of XANES spectra.[7] The effect of platinum alloying with other metals is also addressed.[8] Finally, we show how these feature impact the reactivity of the particles for alkane dehydrogenation,[9] paving the way for the introduction of *ab initio* kinetic data in kinetic models, to access macroscopic predictions thanks to a multiscale approach.[10]



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Kinetics and Selectivity in Hydroformylation of Propene

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Homogenously catalysed hydroformylation, used in industrial synthesis of aldehydes from alkenes and syngas (hydrogen and carbon monoxide), is one of the most extensively studied reaction both experimentally and theoretically [1-2]. One of the crucial aspects of the reaction is the selectivity of the catalyst towards the desired product. In this studies we employ the computational approach in order to investigate the kinetics and selectivity of unmodified cobalt-catalysed propene hydroformylation. In this chemical process a propene substrate reacts at a high temperature with hydrogen and carbon monoxide producing two aldehyde isomers: linear n-butylaldehyde and branched iso-butylaldehyde. The product ratio depends on the reaction conditions (temperature, initial catalyst and propene concentrations and pressure of gases). Density functional theory and explicitly correlated coupled-cluster methods are used to accurately compute potential energy surfaces of the catalysis leading to both products. Coupling the computationally resolved mechanism with kinetic modelling gives an important insight into the detailed mechanism of the investigated reaction. The proper designation of symmetry numbers [3] is essential in order to reproduce the experimental selectivity [4-5].

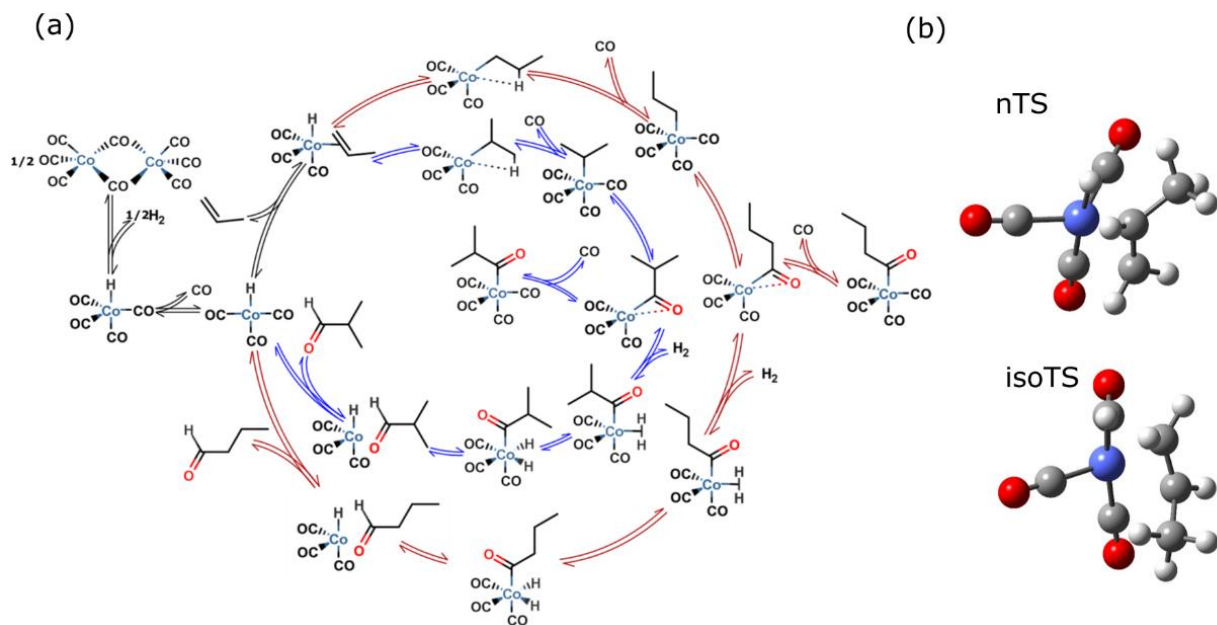


Figure 1 (a) Catalytic cycle of propene hydroformylation reaction indicating elementary steps and pathways leading to two distinct products. The red cycle leads to formation of linear n-butylaldehyde, while a blue cycle to branched iso-butylaldehyde. b) The pathway separates at bifurcation step and depends on the orientation of propene while it is inserted into Co-H bond

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ESR 6, Wed 19 10:10-10:35

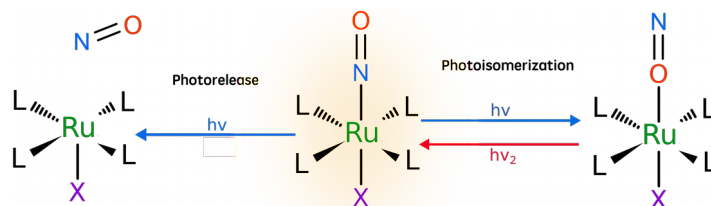
A THEORETICAL INVESTIGATION OF THE TRANS-[RuCl(NO)(py)₄]²⁺ PHOTOCHEMISTRY

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Ruthenium nitrosyl complexes have found utility in a variety of applications, such as optical switches, data storage, and medicine. Depending on the ancillary ligands, environment, and irradiation wavelength, these complexes can undergo either intramolecular NO linkage photoisomerization or NO photorelease (Figure 1). In the last two years, DFT studies of both the NO linkage photoisomerization and photorelease process in the trans-[RuCl(NO)(py)₄]²⁺ complex revealed a complex two-step photoisomerization mechanism involving a sequential two-photon absorption.[1,2] This mechanistic picture has been confirmed experimentally recently.[3] The DFT study was based on the exploration of the lowest singlet and triplet potential energy surfaces, assuming efficient decay via intersystem crossing (ISC) from the first singlet excited state to the lowest triplet state. Further ab initio CASSCF/CASPT2 calculations performed during last year, supported and completed the DFT and experimental findings. In particular, the spin-orbit coupling outcomes helped to uncover the first steps of the photoisomerization process, suggesting an efficient singlet to triplet intersystem crossing after light absorption. At the same time, the topology of the CASPT2 potential energy surfaces highlighted the possibility of several photoisomerization pathways. It would therefore be desirable to verify these hypotheses, by determining the most probable pathways along with the spin-orbit couplings responsible for radiationless transitions. In addition, the role of the excited states in the NO photorelease process has not been investigated so far, and it is interesting to know what is their potential role. It is important to verify that a single-configuration-based method such as DFT can be reliable to describe complex photochemical mechanisms such as the ones studied here.[4] Thus, in my presentation I will present the results of ab initio and DFT calculations on the trans-[RuCl(NO)(py)₄]²⁺ complex that describe i) the absorption spectra of the involved isomers. ii) the complete ab initio photoisomerization pathways. iii) the preliminary results for the NO photorelease mechanism. iv) the assessment of the DFT and TD-DFT results.



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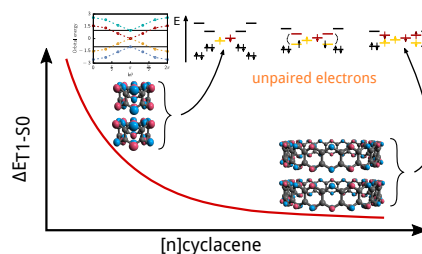
Electronic Structure Properties of $[n]$ Cyclacenes: Semi-Empirical and Wave Function Approaches

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Cyclacenes have been subject of studies for the last 30 years and are still under active investigation because of their complicated electronic structure and their potential applications[1, 2]. Similarly to their "cousins" systems, the linear polyacenes, theoretical investigations have been proved difficult from a methodological perspective, which resulted in contradicting results. In this contribution, the investigation of different properties such as the total position spread tensor (TPS) and the singlet-triplet energy gap (ST gap) as a function of the system size will be presented at different levels of theory, namely by a semi-empirical Hückel approach and by wave function theory[2, 3]. The obtained results show a decreasing ST gap and an increasing radical character with increasing system size, which is in agreement with the most recent results obtained using TAO-DFT[1].



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Improved Lennard-Jones Parameters for Accurate Molecular Dynamics Simulations

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The outcome of classical molecular dynamics simulations highly depends on the accuracy of the force field. While bonded and electrostatic parameters can be determined from quantum mechanical computations, the Lennard-Jones parameters associated with the core repulsion and van der Waals dispersive attraction often need to be empirically adjusted in order to match experimental liquid phase data. Predictive models require a global optimization of the Lennard-Jones parameters for a large training set of molecules.

We compiled a database of enthalpy of vaporization, density and free energy of solvation for 531 molecules encompassing all kind of atom types which are liquid at reasonable temperatures. Our starting point was GAFF[1] Lennard-Jones parameters and we refined charges and dihedral parameters using GAAMP.[2] The optimization was made for molecular volume and enthalpy of vaporization using the least square method and the free energy of solvation was used for validation. We build pure liquid boxes of around 20x20x20 Å³ and equilibrated them. Gradients for the objective function were obtained in a perturbative manner using short molecular dynamics (0.5 – 2ns).

Comparing our results to the original GAFF parameters, we could maintain a very good molecular volume and significantly improve the prediction of the heat of vaporization. Our parameters systematically underestimate the free energy of solvation and we proposed to rescale the water-compound interaction.

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Charge Transfer States in Bulk Heterojunction Organic Solar Cells

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Organic solar cells (OSCs), unlike inorganic ones, lead to an exciton or strongly bound electron-hole pair after absorption of a photon. The generation of free charges then depends on the exciton binding energy and the absorption properties of the materials used [1]. In the modelling of more efficient OSCs, we have combined a conjugated polymer with a fullerene derivative in bulk heterojunction architectures (see Figure 1). In such architectures, the excitons formed on the absorber polymer are separated through electron transfer process that lead to Charge Transfer (CT) states at the interface of the polymer and fullerene based molecule. We have computed the CT energies in bulk heterojunctions by using Density Functional Theory and its Time Dependent extension, coupled with the Discrete Reaction Field method as implemented in the Amsterdam Density Functional modeling suite [2]. Our preliminary results suggest that organic-photovoltaic blends should perform better when polarizable groups as triethylene glycol chains (TEG) are added to the backbone. Furthermore, our results indicate that the environment stabilizes the charge separation process.

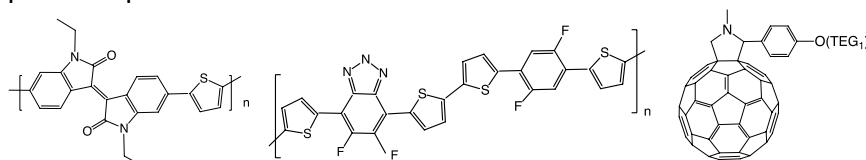


Figure 1. Molecular structure of potential photovoltaic materials used in the modeling of charge transfer and charge separated states. Left, electron-rich type conjugated polymers; (a) polyisindigothiophene (P1TI), (b) polythiophenefluorobenzene (PTFB). Right, acceptor C60 based molecule (PTEG1).

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Vibronic Coupling Density and Its Applications

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Vibronic couplings play important roles in various properties of molecules. In a light-emitting molecule, for instance, off-diagonal vibronic couplings give rise to nonradiative transitions, and a diagonal vibronic coupling is a driving force of the vibrational relaxation from a vertical excited state. A large vibrational relaxation results in small Franck-Condon factors which give rise to a small rate constant of the radiative transition. Therefore, small diagonal and off-diagonal vibronic couplings are crucial in designing of an efficient emitting molecule[1].

We have proposed a concept of vibronic coupling density (VCD) to analyze and control diagonal and off-diagonal vibronic couplings[2,3]. On the basis of VCD analysis, we designed efficient emitting molecules by the suppression of vibronic couplings in anthracene[4] and triphenylamine[5], and we observed the increase of quantum yields of the designed molecules[6,7]. It should be noted that triphenylamine is a non-emitting molecule. We can make a non-emitting molecule fluorescent by the molecular design on the basis of VCD analysis.

Thermally-activated delayed fluorescence (TADF) has attracted much attention as a highly-efficient emitting mechanism for organic light-emitting diodes[8]. In this mechanism, both T_1 and S_1 excitons which are generated by electrical excitations are utilized for light emission. Thermally excited T_1 excitons are converted to S_1 excitons via reverse intersystem crossing (RISC). We will discuss that highly-efficient light-emission via RISC from T_n states higher than T_1 is possible by suppressing non-radiative transitions from T_n based on the concept of vibronic coupling density[9,10].

We will also discuss a design principle of carrier-transporting molecules using the VCD concept, and VCD as a chemical reactivity index.

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An exciting life of fluorescent proteins

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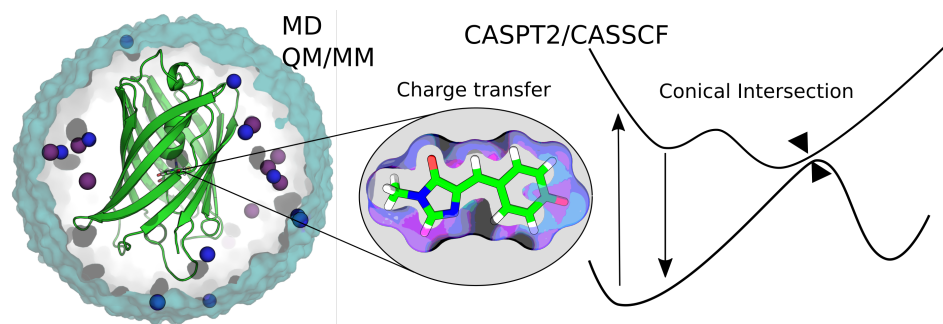
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Reversibly-switchable fluorescent proteins (RSFPs) are widely used in super-resolution microscopy. Fluorescence time decorrelation is used in order to break diffraction limit. In other words RSFPs should switch between fluorescent and non-fluorescent states on different timescales.

A rational approach to a study of an excited state reaction pathway is one of the key solution to understanding of their photo-switching mechanism. A set of five proteins based on Dronpa[1], one of the most commonly used RSFPs, was scrutinized in our study. Combination of MD simulations and QM/MM calculations was used to assess major reasons controlling the spectral tuning and photophysical properties of a consistent model set. On the basis of the RSFPs models, which are based on a CASPT2//CASSCF level of QM theory we reproduce an experimental absorption/emission trend. Then we show how protein environment controls chromophore's isomerization and spectral tuning. Furthermore, we identify how the conical intersection topography correlates with protein's photoswitching speed.



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Wed 19 16:40-16:55

Valence bonds in elongated boron clusters

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Analyzing bonding patterns in complex systems remains a challenge. While chemists are used to the Lewis-type localized bonding, this approach works mainly for simple cases. As a result, resonance introduced as a concept to explain any further difficulties. A tool, the Adaptive Natural Density Partitioning (AdNDP)[1, 2], which reconciles both types of localized and delocalized bonding, will be presented. This method is an extension of the Natural Bond Analysis (NBO)[3] and performs search for up to $nc-2e$ bonds, where n ranging up to the total number of atoms in a system. It provides a quantitative picture of bonding in many non-classical chemical structures such as boron clusters. Further, a well defined class of planar or quasi-planar elongated boron clusters, of type B_{7+3n}^{q-} , will serve as a basis to identify the valence bond picture of delocalized boron networks. Specific electron counting rules will be used for both π and σ -multi-center bonding. The analysis supports $4c-2e$ bonds as an alternative to the common $3c-2e$ bonds. The results are validated by symmetry induction and *ab initio* calculations[4].

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Wed 19 16:55-17:40

Some current work on currents

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Currents within and through molecules are of interest in chemistry and physics for several reasons. For example, circulations induced by a magnetic field (ring currents) are related to experimental NMR signatures of aromatic molecules and the vexed question of how to define aromaticity. On the other hand, ballistic currents induced by potential differences are related to molecular electronics.

This talk will describe some of our recent work on modelling molecular currents at various levels of theory, with emphasis on the construction of very simplest models, cast in terms of chemical concepts.

Thu 20 09:00-09:45

Molecular simulation methods for ensemble-based drug design

Julien Michel, Edinburgh University

Our group develops computational methodologies to enable rational modulation of protein dynamics for ligand design purposes. In this talk I will present molecular simulation methodologies we have used to characterise cryptic ligand binding sites in proteins. I will also discuss our efforts to develop robust alchemical free energy protocols and software for predicting protein-ligand binding energetics. I will present results obtained on diverse proteins that were the subject of retrospective studies, blinded predictions, and joint computational/experimental efforts.

Computational approach to aluminum biochemistry

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In the last century, human intervention has made aluminum highly bioavailable^[1]. However, there is increasing evidence that aluminum could be behind of a variety of toxic effects in biological systems, with significant risks for human health. Indeed, aluminum is not involved in any biological cycle and it has been associated with some neurodegenerative diseases, such as the Alzheimer Disease^[2].

In this context, the goal of chelation therapy is the removal of toxic metal ions from human body or attenuation of their toxicity by transforming them into less toxic compounds^[3].

Such a situation led several groups to focus the attention and to make efforts toward the identification of aluminum-specific chelating agents, with a need to rationalize the effect of different substituents in the modulation of the Al(III)-ligand binding affinity. Accordingly, we think that a computational approach, using *state-of-the-art* theoretical tools, would provide valuable insights toward the development of new powerful aluminum chelators.

In the present work, we have assessed the affinity of aluminum for two families of bidentate chelating agents (salicylic acids and catechols^[4]) bearing different substituents, for which rigorous experimental data are available^[5]. Binding energies calculated in aqueous solution at the B3LYP-D3(BJ)/6-311++G(3df,2p) level of theory show very good agreement with respect to experimental stability constants, thus validating our theoretical protocol.

Besides, we have characterized geometrical features and different physico-chemical quantities for the Al-O interactions, by means of the Bader's Quantum theory of Atoms in Molecules (QTAIM), Natural Bond Orbital (NBO) theory and the Energy Decomposition Analysis (EDA) scheme by Ziegler and Rauk.

Interestingly, we found that there is a small but significant degree of covalency in these mainly electrostatic closed-shell Al-O interactions, which provides an explanation for the different modulation of the binding affinity by Electron Donating Groups (EDGs, CH₃, OCH₃) and Electron Withdrawing Groups (EWGs, NO₂ and CF₃).

The present findings would provide a valuable help in the design and tuning of new, suitable Al(III) chelating agents.

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Excited state gradients in polarizable QM/MM models: an induced dipole formulation

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Charge and structural properties of electronically excited states in embedded systems are strongly affected by the environment. Multiscale approaches where different levels of theory are combined in a single calculation, have shown to properly describe such effects combining accuracy with computational efficiency.

Here we present an extension of a fully polarizable QM/MM scheme to analytic excited state gradients following a Lagrangian approach [1, 2]. Time-dependent density functional theory is used as the QM method of choice, whereas the classical environment is treated in terms of a polarizable force-field, where the polarization is included through induced dipoles [3]. The method is applied to study of formation and relaxation of the bright excited state of an organic dye (DAPI) intercalated in a DNA pocket. The results indicate the non negligible effect of polarization between the DAPI and DNA pocket, in determining the fluorescence properties of the embedded dye [4].

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Thu 20 11:05-11:50

Computational Coordination Chemistry: Harnessing Quantum Chemistry to Build Better Force Fields

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Abstract

Coordination complexes of transition metal ions are frequently paramagnetic with complicated electronic structures. These appear to demand complex, multi-reference quantum mechanical (QM) methods but such calculations can be extremely expensive. In contrast, ligand field theory (LFT) provides a far simpler, albeit parametric, approach to the multi-determinant states of predominantly d-orbital parentage. However, LFT alone is an insufficient basis for molecular modelling since it only generates an electronic energy without any nuclear contributions. The latter require some additional treatment, the simplest of which is classical molecular mechanics (MM). The ligand field/molecular mechanics (LFMM) combination efficiently captures the important structural and energetic consequences of d-electron effects such as Jahn-Teller distortions and spin-state changes. The challenge now is the recognition that a MM force field (FF) is only as good as its parameters. In this talk, using the spin states of d^6 Fe(II) complexes as exemplars, the basis of the LFMM approach will be outlined and we will explore how to harness DFT and/or wavefunction methods to generate selective data upon which an accurate LFMM FF may be trained and then deployed to generate quantum-level accuracy at a tiny fraction of the cost of any QM-based method.

ESR 15, Thu 20 11:50-12:15

METHANE AND HYDROGEN ADSORPTION ON GRAPHENE

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Graphene is widely investigated for its ability to adsorb small molecules through van der Waals interactions, possibly leading to new ways of natural gas storage. Given the environmental issues of our time, hopes are that graphene could play an important role in capture and separation of greenhouse gases from gas mixtures. From those greenhouse gases methane is one of the most abundant and most active gases around. Diminishing its emissions is therefore of utmost importance. One way to lower the emissions is by filtering CH₄ from gas mixtures before releasing the mixture into the atmosphere. The aforementioned qualities of graphene make the material a good candidate for the proposed tactics. Furthermore, graphene has shown promise as a material for energy storage. The adsorption and controlled release of gases like methane and hydrogen may lead to efficient clean energy technologies.

In this work interaction energies for graphene-X and X-X (X being CH₄ or H₂) were calculated using the DFT-method with the B97D functional and a TZV2P basis set. The basis set superposition error was minimized by means of the counter-poise correction. The results were fitted to Improved Lennard-Jones[1] type potentials in order to get a set of parameters describing the dispersion interactions of interest. Aside from this, the parameters were also calculated from correlation formulae[2] at DFT, CC2, CC3 and CCSD level. The influence of inclusion of the Coulombic sum has also been investigated. This way we obtained numbers from different levels of theory to ensure parameters describing an accurate potential energy. We aim at producing potentials that are on one hand very accurate, but on the other easily compatible with molecular dynamics. The resulting potentials were compared with energies from highly correlated ab initio methods in order to assure accuracy. The created force fields are applied in molecular dynamics and grand canonical Monte Carlo dynamics to calculate adsorption isotherms, diffusion coefficients and other relevant characteristics.

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