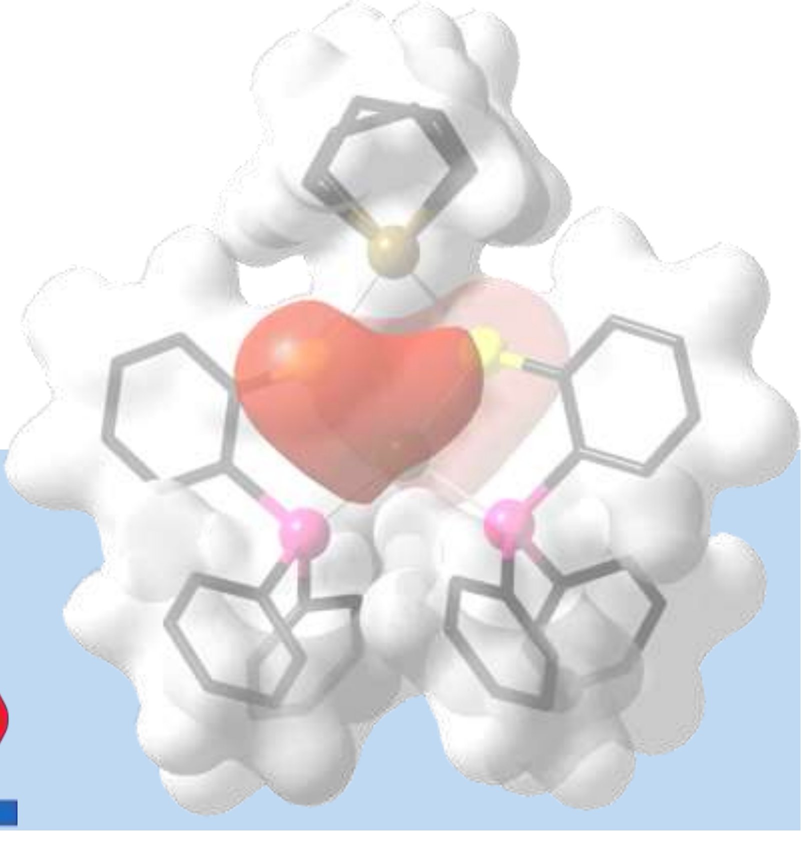
BABEȘ-BOLYAI UNIVERSITY
FACULTY OF CHEMISTRY AND CHEMICAL ENGINEERING

Molecular Modeling in Chemistry and Biochemistry
28-30 October 2018, Cluj-Napoca, Romania

BOOK OF ABSTRACTS



MOLD

MOLECULAR MODELING IN CHEMISTRY AND BIOCHEMISTRY

Faculty of Chemistry and Chemical Engineering, Babes-Bolyai University

Mon 28 OCT – ROOM 88

08.30-09.00 Registration, poster set-up

09.00-09.10 Opening remarks

09.10-09.50 Paul Mezey, Memorial University of Newfoundland, Canada – Symmorphy of molecular shapes, a generalization of symmetry groups

09.50-10.30 Mihail V. Vener, Mendeleev University of Chemical Technology, Russia – Inhibiting low-frequency vibrations explains exceptionally high electron mobility in 2,5-Difluoro-7,7,8,8-tetracyanoquinodimethane (F2-TCNQ) single crystals

10.30-10.50 Coffee break, poster viewing

10.50-11.30 Snezana Zaric, University of Belgrade, Serbia & Texas A&M University at Qatar – Stacking interactions of metal-chelate rings and hydrogen-bridged rings

11.30-12.00 Attila Bende, National Institute for Research and Development of Isotopic and Molecular Technologies, Romania – DFT modeling of singlet-triplet spin transitions in Ni(II)-based macrocyclic-ligand supramolecular complexes

12.00-12.40 Valera Veryazov, Lund University, Sweden – Symmetric or antisymmetric? Electronic structure of dimers with even and odd numbers of electrons

12.40-14.30 Lunch

14.30-15.10 Fanica Cimpoesu, Institute of Physical Chemistry, Bucharest, Romania – Bond. Chemical Bond! Spying the secrets of molecular structure with state-of-the-art and revisited computation method

15.10-15.40 Mihai V. Putz, West University of Timisoara, Romania – Bondonic theory of chemical interactions. Applications on graphenic systems

15.40-15.55 Andrei Neamtu, Iasi University of Medicine and Pharmacy, Romania – Antibody structure prediction and epitope mapping by molecular dynamics simulations

15.55-16.10 Szilard Fejer, Ab Initio Research Services Ltd & Provitam Foundation, Romania – Coarse-grained models for self-assembling hollow shells from colloidal building blocks

16.10-16.25 Dragos Isac, Petru Poni Institute of Macromolecular Chemistry, Romania – A new pathway of azobenzene interconversion assisted by DFT and ab initio methods

16.25-16.50 Poster Session / coffee

16.50-17.05 Mihai Medeleanu, Polytechnical University of Timisoara, Romania – Novel staffane-like structures, topological and quantum chemical characterization

17.05-17.20 Lorentz Jantschi, Technical University of Cluj-Napoca, Romania – The eigenproblem for alignment of molecules

17.20-17.35 Janos Szoverfi, Provitam Foundation, Romania – Molecular dynamics studies of CCMV capsid protein oligomers

17.35-17.50 Adrian Branzanic, Babes-Bolyai University, Romania – Role of siroheme and the Fe_4S_4 cluster in the active site of sulfite reductase

17.50-18.05 Octav Caldararu, Lund University, Sweden – Quantum refinement of X-ray and neutron protein crystal structures

18.05-18.35 Power-poster presentations

19.00-21.00 Conference cocktail/dinner (Universitas complex of the Babes-Bolyai University)

TUE 30 OCT – ROOM 88

09.00-09.40 Peter Szalay, Eotvos Lorand University, Hungary – Characterization of the excited states of DNA building blocks: a coupled cluster computational study
09.40-10.20 Andreas Savin, CNRS & Sorbonne University, France – On choosing the "best" density functional...or any computational method in chemistry. Probabilistic estimators
10.20-10.35 Alexandru Lupan, Babes-Bolyai University, Romania – Density functional theory investigation of carbalane polyhedra

10.35-11.00 Coffee break

11.00-11.30 Paul Nicu, Lucian Blaga University of Sibiu, Romania – Implications of the generalized coupled oscillator mechanism for the interpretation and calculation of Vibrational Circular Dichroism spectra
11.30-12.10 Dragos Horvath, Louis Pasteur University, France – The mapping of conformational space
12.10-12.50 Henning Henschel, University of Oulu, Finland – Water and proton dynamics from semi-empirical QM/MM Simulations

12.50-14.30 Lunch

14.30-15.10 Marilena Ferbinteanu, University of Bucharest, Romania – On the use of time-dependent density functional methods in the account of ligand field-type spectra of the coordination compounds
15.10-15.25 Claude Millot, Université de Lorraine, France – Modeling electric properties of hexahalobenzenes
15.25-15.40 Istvan Horvath, Ab Initio Research Services Ltd, Romania - A modified adjustable density matrix Assembler approach for fast computation of ab initio quality electron densities of complete proteins
15.40-16.10 Titus Beu, Babes-Bolyai University, Romania – Coarse-grained modeling of polyethyleneimine
16.10-16.25 Ionut-Tudor Moraru, Babes-Bolyai University, Romania – On the possible presence of carbides in the Fischer-Tropsch process catalyzed by ruthenium nanoparticles: a DFT study
16.25-16.40 Dennis Dinu, Institute of General, Inorganic and Theoretical Chemistry, LFU Innsbruck, Austria – Anharmonic Vibrational Spectroscopy of Small Organic Compounds
16.40-16.55 Radu Silaghi-Dumitrescu, Babes-Bolyai University, Romania – TBA
16.55- Closing remarks

POSTER PRESENTATIONS:

1. **Reka-Anita Domokos, Babes-Bolyai University, Romania – Adsorption of the two isomers of resveratrol on Graphene**
2. **Luana Radu, Babes-Bolyai University, Romania – Reversible complexation of ammonia by breaking a manganese-manganese bond in a manganese carbonyl ethylenedithiolate complex**
3. **Alina Matei, Babes-Bolyai University, Romania – The high affinity of small-molecule antioxidants for hemoglobin and myoglobin**
4. **Adrian Branzanic, Babes-Bolyai University, Romania – DFT benchmarking for the correct description of spin states in bioinorganic centers. Heme vs. siroheme models of the sulfite reductase active site**
5. **Raluca Septelean, Babes-Bolyai University, Romania – Density functional theory investigation of hypoelectronic eight-vertex metallaboranes**
6. **Adrian Branzanic, Babes-Bolyai University, Romania – Dimetallaborane Analogues of the Octaboranes: Structural Variations with Changes in the Skeletal Electron Count**
7. **Alex-Adrian Farcas, NIRDIMT and Babes-Bolyai University, Romania – Intersystem crossing in metal-ligand coordination complexes with pyramidal-planar and octahedral coordination configurations**
8. **Hussein Unver, Ankara University, Turkey – DFT Calculations, Green synthesis and biological applications of methanesulfonamide functionalized graphene quantum dots**
9. **Donatella Balint, Babes-Bolyai University, Romania – Comparison of geometry optimization methods on amino acid structures**
10. **Teodor-Lucian Biter, INCDTIM Cluj-Napoca, Romania – Theoretical study of phenylene- and biphenyl-linked porphyrin layers**
11. **Tudor Vasiliu, Petru Poni Institute of Macromolecular Chemistry, Romania – Functionalized β-cyclodextrin as trans-membrane channel**
12. **Cristina Maria Buta, Institute of Physical Chemistry Bucharest, Romania – Through-space and Through-solvent Interactions between Nitroxide-based Stable Radicals**
13. **Alice Mischie, Institute of Physical Chemistry Bucharest, Romania – Hybrids and Bond Angles in Small Prototypic Hydrocarbon Molecules**
14. **Ana-Maria Toader, Institute of Physical Chemistry Bucharest, Romania – Reshaping the principles and techniques of Gaussian-type basis sets in computational chemistry**
15. **Larisa-Milena Timbolas, Babes-Bolyai University, Romania – Photophysical properties of perylene derivatives**
16. **Florin Teleanu, Babes-Bolyai University, Romania – Antiaromaticity comes in six: A HOMA/NICS study of [n]helicenes (n = 6 - 24)**
17. **Artiom Gaina Gardiuta, Babes-Bolyai University, Romania – Linkage isomerism in complexes of cobalamin with cysteine sulfenic, sulfinic and sulfonic acids**
18. **Roxana Pasca, Babes-Bolyai University, Romania – Thermodynamic properties of ethylenimine and ethylene glycol polymers**
19. **Mircea Nasui, Technical University of Cluj-Napoca, Romania – Challenges in designing nanoceria for antioxidant therapy**
20. **Dragos Isac, Petru Poni Institute of Macromolecular Chemistry, Romania – Computational studies of silicon-containing benzoic acid derivatives: 4–((Trimethylsilyl)methoxy) and 4–(3–(trimethylsilyl)propoxy)benzoic acid**
21. **Szabolcs Jako, Babes-Bolyai University, Romania – Data processing: dull or fun task?**
22. **Ionut-Tudor Moraru, Babes-Bolyai University, Romania – Towards a unitary description of E-O and E-N bonds (E = Si, Ge, Sn); from inorganic ethers to amines and isoelectronic species**
23. **Amr A.A. Attia – Nickel-substituted iron dependent cysteine dioxygenase: implications for the dioxygenation activity of nickel model compounds**
24. **Augustin Mot – Chemometric methods applied in questing phytoglobins roles in plant stress conditions**

ORAL PRESENTATIONS

Symmorphy of molecular shapes, a generalization of symmetry groups

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Symmorphy is a generalization of symmetry, where the symmetry operators, as linear transformations of the 3D space which leave all the metric properties of all point pairs of an object (such as a molecule) invariant, are replaced by continuous transformations which leave the appearance of the morphology of an object invariant. The latter family of transformations also forms an algebraic group, the symmorphy group of the object [1-3], that is characteristic to the shape of the object, providing a far more detailed shape characterization than the point symmetry group. The actual point symmetry group of any molecule is a subgroup of the symmorphy group of the given molecule. The complexity of symmorphy groups can be reduced by considering subgroups with specific fixed points for all elements of the subgroup, and alternative simplifications are also possible. Some of these advances in molecular shape analysis are reviewed.

References:

[1] P.G. Mezey, Topology of Molecular Shape and Chirality, in "New Theoretical Concepts for Understanding Organic Reactions", Eds. J. Bertran and I.G. Csizmadia, Nato ASI Series, Kluwer Academic Publishers, Dordrecht, 1989, pp 77-99.

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[3] P.G. Mezey, Fuzzy Measures of Molecular Shape and Size, in "Fuzzy Logic in Chemistry", Ed. D.H. Rouvray, Academic Press, San Diego, 1997, pp 139-223.

Inhibiting Low-frequency vibrations explains exceptionally high electron mobility in 2,5-difluoro-7,7,8,8-tetracyanoquinodimethane (F2-TCNQ) single crystals

Chernyshov I.Yu. [1], Vener M.V. [1], Feldman E.V. [2], Paraschuk D.Yu. [2], Sosorev A.Yu. [2], (

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Organic electronics requires materials with high charge mobility. Despite decades of intensive research, charge transport in high-mobility organic semiconductors has not been well understood. In this Letter, we address the physical mechanism underlying the exceptionally high band-like electron mobility in F2-TCNQ (2,5-difluoro-7,7,8,8-tetracyanoquinodimethane) single crystals among a crystal family of similar compounds Fn-TCNQ (n = 0, 2, 4) using a combined experimental and theoretical approach. While electron transfer integrals and reorganization energies did not show outstanding features for F2-TCNQ, Raman spectroscopy and solid-state DFT indicated that the frequency of the lowest vibrational mode is nearly twice higher in F2-TCNQ crystal than in TCNQ and F4-TCNQ ones [1]. This phenomenon is explained by specific packing motif of F2-TCNQ with only one molecule per primitive cell so that electron-phonon interaction decreases and the electron mobility increases. We anticipate that our findings will encourage investigators for the search and design of organic semiconductors with one molecule per primitive cell and/or the poor low-frequency vibrational spectrum.

References:
1. I.Yu. Chernyshov, M.V. Vener, E.V. Feldman, D.Yu. Paraschuk, A.Yu. Sosorev, *J. Phys. Chem. Lett.* **2017**, *8*, pp 2875–2880

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Stacking interactions of metal-chelate rings and hydrogen-bridged rings

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Stacking interactions are ubiquitous in many chemical and biological systems, and they are of great interest in the areas of crystal engineering and materials science. Stacking interactions are typically referred to as the interactions of aromatic molecules. However, there are moieties that frequently form stacking interactions that are stronger than stacking interactions of aromatic molecules. Two examples are metal-chelate rings [1] and hydrogen-bridged rings [2].

The searching of the Cambridge Structural Database (CSD) showed that metal-chelate rings can form both chelate-aryl and chelate-chelate stacking interactions [1]. The analysis of crystal structures also showed that C_6 aromatic rings prefer stacking with chelate ring than with other C_6 aromatic rings. Quantum chemical calculations explained this preference by showing that chelate-aryl stacking interactions (-6.39 kcal/mol) are stronger than stacking interactions between benzene molecules (-2.73 kcal/mol). Chelate-chelate stacking interactions are even stronger (-9.70 kcal/mol). It was shown that the nature of both chelate-benzene and chelate-chelate stacking depends on the metal [1,3].

The analysis of the CSD crystal structures showed that planar five-membered hydrogen-bridged rings frequently form stacking interactions, both with other hydrogen-bridged rings [2] and with C_6 aromatic rings [4]. Quantum chemical calculations showed that stacking interactions between hydrogen-bridged rings can be as strong as -4.89 kcal/mol, while stacking between benzene and hydrogen-bridged ring can be as strong as -4.38 kcal/mol.

References:
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DFT modeling of singlet-triplet spin transitions in Ni(II)-based macrocyclic-ligand supramolecular complexes

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Abstract

Intersystem crossings in different Ni(II) macrocyclic ligand complexes with square-pyramidal and octahedral ligand-metal coordination have been investigated by means of static (DFT) and time-dependent density functional theory (TD-DFT) calculations. Considering the several exchange-correlation (XC) functionals together with the def2-TZVP basis set, the adiabatic singlet-triplet energy gaps, and the Ni···N ligand bond distances are compared and the origin of their discrepancies are discussed. Using the TD-DFT method, the stability of the light–mediated reversible ligand coordination and the switching of magnetic properties have been characterized by identifying the active electronic excited states both in singlet and triplet spin configuration involved in the light-induced excited spin-state trapping. The intersystem crossing point on the potential energy hyper-surface have been located on one hand by considering the minimum path technique along the Ni···N ligand bond and on the other hand by using the "Penalty Function" gradient method for singlet and triplet energies. Finally, different singlet-triplet transition pathways for the mechanism of the reversible intersystem crossing are proposed both for the square-pyramidal and octahedral ligand-metal coordination configuration cases.

Symmetric or antisymmetric?
Electronic structure of dimers with even and odd numbers of electrons.

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The symmetry of the wavefunction can be different from the symmetry of nuclei. For example, for a dimer (formed by two atoms or two molecular fragments) adding or removing one electron can lead to two different solutions: symmetric wavefunction, or locatization of this extra electron on one centre.

Density functional theory is known to have problems with such systems (H_2^+, Li_2^+), containing one extra electron, which can be localized in different positions. One has to apply multiconfigurational theory [1] in order to get proper electronic structure at dissociation limit. We studied two systems: fullerene dimer and chromium dimer with different numbers of electrons by using multiconfigurational theory, and considered both symmetric and antisymmetric solutions.

Symmetry can influence the systems with electronic spin. For instance, metal-oxide framework (MOF) materials contains metallic atoms, connected by organic bridges. MIL53(Cr) is one of the most popular examples of MOFs. Using symmetry the electronic structure of a cluster with two Cr atoms, representing MIL53(Cr), is septet. However, if symmetry is not enforced, the more stable spin configuration is singlet. [2]

The chromium dimer is a benchmark molecule to evaluate the performance of different computational methods. The multiconfigurational perturbation theory (CASPT2 and RASPT2) was shown to be able to reproduce the details of the the potential energy surface of the chromium dimer [3]. Increase of the active space reduces the dependence of the results on the computational details, in particular to the choice of zeroth-order Hamiltonian in the perturbation theory. The cation, Cr_2^+, is even more complicated system due to the odd number of electrons. The recent study of Cr_2^+ [4] by CCSD(T) method suggests a binding ground state structure with very short interatomic distance. Our investigation shows that this result is an artefact due to the symmetry restrictions used in the calculations. Multiconfigurational theory predicts the ground state to be of high-spin nature (S=11/2) with a lower energy, with a potential energy curve with much more shallow minimum near 3Å, with significant charge disproportionation between the two Cr sites.

Fullerenes, C_{60}, can hold some negative charge, and creates stable crystals with a composition $C_{60}K_n$. We studied the electronic structure of a dimer formed by two fullerenes, with variation of negative charge (n=1,2,3,4,5,6) [5]. Calculations were performed within multiconfigurational theory CASSCF/CASPT2 with two sets of active spaces: 8 and 11 orbitals. With even numbers of electrons the obtained wavefunction is symmetric, and with odd number of electrons it is asymmetric.

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3. Y. Yamada, K. Hondo, K. Egashira, Y. Kita, U. Nagashima, M. Tachikawa, *Chem. Phys. Letter*, *555*, 84 (2013)
4. F. Naderi, V. Veryazov, *AIP Conference Proceedings* 1906, 030024 (2017)

Bond. Chemical Bond! Spying the secrets of molecular structure with state-of-the-art and revisited computation methods

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We propose a walk through the borders of theoretical chemistry with related domains, such as the junction between calculation techniques and the realm of heuristic meanings and chemical intuition.

A somewhat serendipitous recent finding, done with the occasion of writing a intentionally didactical modulus about basis sets,[1] is that the Gaussian Type Orbitals (GTOs) have major flaws. The weak point is not the exponential part, as everyone may believe, but a very poor and wrong design in the polynomial cofactors of the standard Gaussian-type primitives. We started a tedious incursion in the attempt to change the bases and even the codes. The computational peoples are helping themselves with the GTOs from available data bases, but this “fast food”-alike choice, practically imposed by the available market, has some dangers because of the hidden “unhealthy” ingredients.

Since several modern analyses of the chemical bond mechanisms were based on the existent GTO infrastructure, we try to revisit this issue, through the prism of alleviated basic ingredients of the computation methods.

Other part of our discussion is based on comparing the qualitative and elusive perception of concepts like hybridization and aromaticity, dear to chemical colloquial language, with their technical counterpart. Such notions are mirrored in quantum chemistry in different ways: hybrids and resonance structures are technical elements in Valence Bond (VB) calculations,[2] while in other methods are retrieved in post-computational manner, trough of Natural Bond Orbitals (NBO) theory [3]. We find that NBO is a reasonable surrogate for VB in the respect of hybrid functions, while the subsequent Natural Resonance Theory (NRT) does not mimic well the VB equivalent. Being adepts of the rather rarely used nowadays VB methods, we try to restore the insight power of this method with the phenomenological side of the Heisenberg spin-coupling Hamiltonian, which helps in regarding in a semi-quantitative respects the chemical bond as electron pairing.

A third part of our discourse is dedicated to the coordination bonding, bringing new ideas and conclusions in the structural chemistry of d-type and f-type coordination compounds (i.e. transition metal ions and lanthanide complexes). Here we face the cases of partly covalent bonding (d systems) and the ionic nature of chemical affinities (in the case of f compounds).

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[1] Mihai V. Putz, Fanica Cimpoesu, Marilena Ferbinteanu, “*Structural Chemistry. Principles, Methods, and Case Studies*”, Springer, Cham, **2018**.

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Bondonic theory of chemical interactions. Applications on graphenic systems

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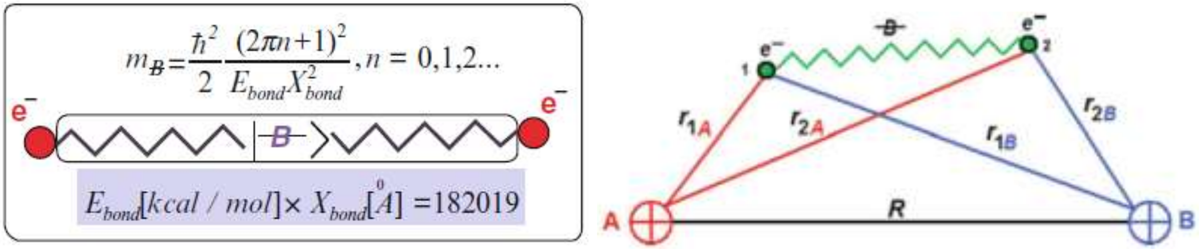
The bond is becoming again a central intellectual arena, and one can even find allusions to the bond as an elementary particle of chemistry, so-called ‘‘bondon’> was recently stated in the first paragraph of the authoritative book on Chemical bonding, edited by Profs. Frenking & Shaik [1], while referring to the ”missing link” of chemical boning – the bosonic bondon [2-7]. The “missing link” since the quantum chemistry remains somehow in orphanage from the closed circle of quantum wave-particle duality, since it was stopped (eventually by the computational fascination and advances) to the almost exclusive electronic molecular orbitals (and even under the density aggregation) in bonding: one starts from electrons (particles), associates their atomic orbitals (waves), then applies the quantum interference (the bonding) and produces the molecular orbitals (again the waves) – but where it is the associated particle of bonding (at least by the universal de Broglie first quantization)? One knows the free electrons interact by photons (bosons), and in general that the fermions interchange through the bosonic fields – so alike the electros in the atomic nucleus baths, in molecules, should “communicate” by means of bosonic particles; the bosonic bondon rises as the necessity the chemical bond be quantum complete. The bondonic reality is therefore advanced [2-4] and explored [5-7], from its physical origins [2], to its prediction on the graphenic systems [5], from the graphenic Raman spectra [6], and with the entangled properties [7], yet to be confirmed by challenging quantum measurements.

Figure 1: *The bondonic bosonic mass quantification in a chemical bond, as it is driven by the Heisenberg’s like relationship of bonding energy and action radius [2,4].*



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Antibody structure prediction and epitope mapping by molecular dynamics simulations

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Epitope mapping consist in identifying antigen amino acid residues that are involved in binding the complementary paratope residues on the antibody. *In silico* epitope prediction is a structural approach aiming to find epitope residues based on computer generated models of antibody/antigen complexes. This approach is particularly useful when used in conjunction with experimental identification techniques such as epitope excision and epitope extraction. Here we present a new *in silico* approach, based on Hamiltonian replica exchange molecular dynamics simulations (REST2)[1], that improves the antibody structure prediction and epitope mapping as an alternative to refine knowledge-based prediction methods. Ten experimentally determined antibody structures from Protein Data Bank (PDB) were selected as targets for the calculations. The study was performed in a step-wise manner starting with construction of antibodies variable region (Fv) from sequence data using dedicated software tools (RosettaAntibody) [2], followed by REST2 molecular dynamics simulations of the predicted models. For the prediction of antibody (Fv)/antigen complexes, standalone protein/protein docking software or online services were used. Results indicated an improvement of the antibody predicted structures with an average root mean square deviation (RMSD) from the native conformations of 1.27 Å (Figure 1). By applying REST2 methodology the RMSD of antibody/antigen prediction reaches ~ 2 Å compared with ~ 5 Å obtained by conventional protein-protein docking calculations.

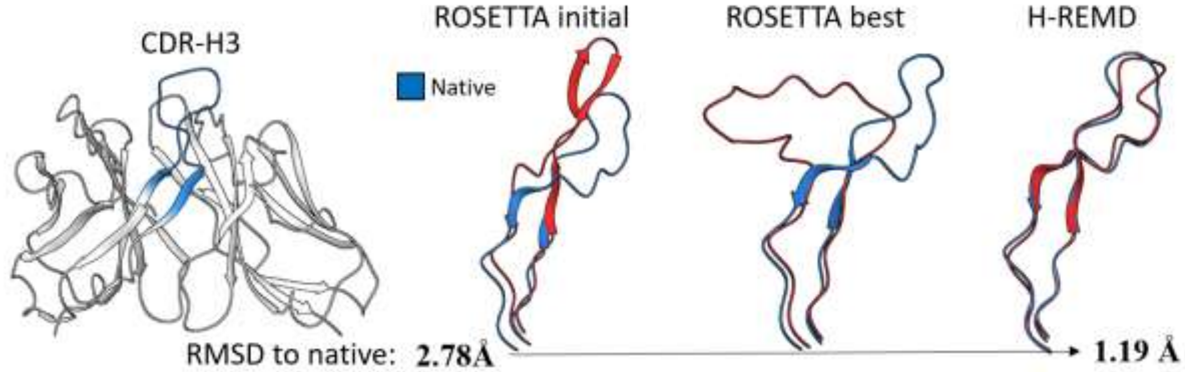

Figure 1. Improvement of antibody structure prediction by REST2 molecular dynamics simulations

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Coarse-grained models for self-assembling hollow shells from colloidal building blocks

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Recent experimental advances on creating colloidal building blocks with specific shape and/or interaction anisotropies created a whole new field, that of ‘colloidal molecules’. Computational methods can guide experimentalists by showing what minimal interactions are necessary that allow self-assembly of colloidal building blocks into complex structures. One such system, containing palladium(II) ions complexed with bidentate ligands, has been shown to form hollow shells with exotic symmetries (Goldberg polyhedra) [1]. Here we present a minimalistic model that allows assembly of different types of Goldberg polyhedra from colloidal building blocks, and study their dynamics *in silico*. The building blocks have only pairwise ionic and excluded volume interactions, yet their behaviour is extremely complex.

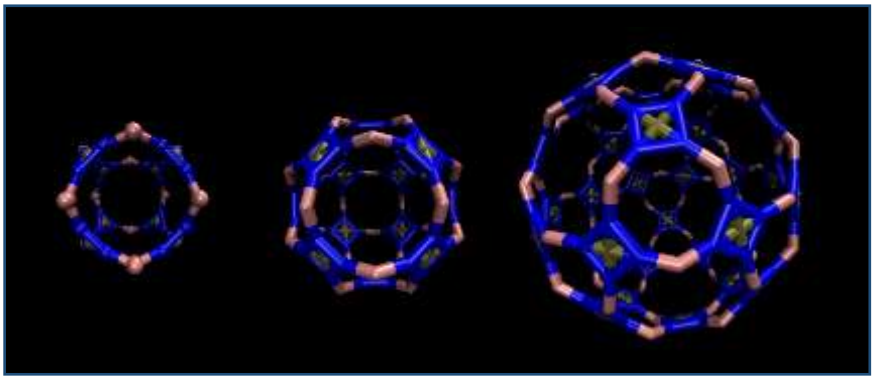

Figure 1. Examples of colloidal Goldberg polyhedra obtained with global optimization

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A new pathway of azobenzene interconversion assisted by DFT and ab initio methods

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Azobenzene molecule (AB), structurally can be activated by photoirradiation making it a part of the photochromic molecular systems family[1]. Photoisomerization that acts as effect of photoirradiation can interconvert the AB structure between its trans (E)- and cis (Z)- isomers via UV light irradiation. This process of isomerization is reversible by two pathways, namely when the molecule is irradiated with visible light or thermal isomerization occurs in the darkness[2]. Each isomer presents electronic distinct spectral and geometric properties that allow these molecules to serve as ideal model systems for molecular motors or into the optical switch devices[1,2]. However, some aspects concerning the electronic structures, spectra and the interconversion mechanism of AB systems after isomerization remain questionable and open for discussion[2]. Two most commonly mechanisms for isomerization process were proposed: rotation and inversion. The rotational pathway involves torsion around the -N1=N1'- bond of dihedral angle -C2-N1=N1'-C2'-, while in the inversion pathway the -N1=N1'-C2'- angle increases to 180°, resulting in a semi-linear transition state which leads to change the hybridization of the nitrogen atom from sp^2 at the *sp*. In addition, other two mixed mechanisms, such as the concerted inversion or the inversion-assisted rotation have also been considered as possible pathways for the photoisomerization of azobenzene. But these mechanisms are still not consensual. In the present work, a possible mechanism of interconversion was analyzed in detail using the DFT (PBE0, B3LYP) and ab initio (MP2) calculations. Theoretical results showed a new possible pathway of interconversion can be considered.

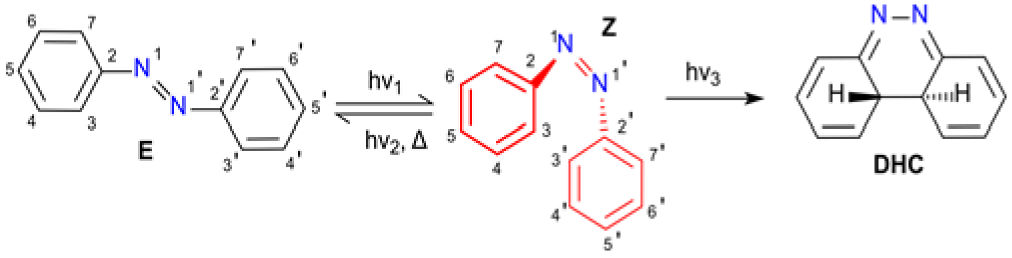

Figure 1. E - Z conversion, Z - E reverse process and irreversible conversion Z – DHC.

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Novel staffane-like structures, topological and quantum chemical characterization

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Derivatives of **[n]staffanes** are end-functionalized telomers or polymers obtained from [1,1,1]propellane, Figure 1. The name was proposed by the authors [1] for the hydrocarbon that should be obtained.

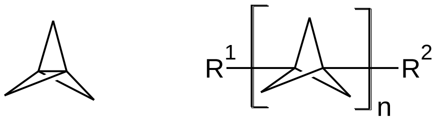

Figure 1 [1,1,1]propellane and a [n]staffane structure

The compounds were largely characterized by spectroscopic methods, physico-chemical properties, geometric properties etc. [1,2].
We propose in this paper some similar structures based on hexahydroxy cyclohexane (all axial) and adamantane [3] as building blocks Figure 2.

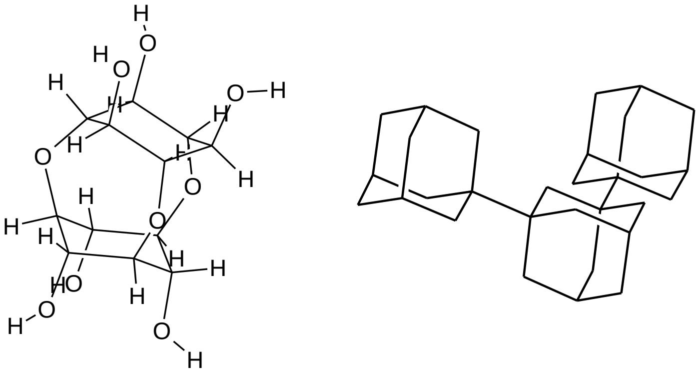

Figure 2 Examples of building blocks

The proposed structures are characterized by topological methods (graph energy, remote adjacency matrices, eigenvalues of adjacency matrices, topological indices) and by quantum chemical descriptors (geometry, energy) obtained by DFT methods.

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The eigenproblem for alignment of molecules

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Abstract

The molecular conformation as subproblem of geometrical shaping of the molecules is essential for expressing the biological activity. It is well known that from the series of all possible sugars, the ones most naturally occurring and usable by the living organisms as source of energy because it can be phosphorylated by hexokinase, the first enzyme in the glycolysis pathway are D- (from latin dextro), and for the most naturally occurring amino acids in the living cells the situation is exactly opposed, are L- (from latin laevo).

The most difficult problem dealing with the conformers is their comparison. One alternative is the molecular alignment.

Here, a solution to the eigenproblem of the molecular alignment is communicated. The Cartesian system is rotated, and eventually translated and reflected until the molecule arrives in a position characterized by highest absolute values of the eigenvalues taken on the Cartesian coordinates. The rotation alone can provide eight alternate positions relatively to the reflexes by each coordinate.

Molecular dynamics studies of CCMV capsid protein oligomers

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In our work we studied *in silico* the behaviour of the Cowpea Chlorotic Mottle Virus (CCMV) capsid protein. The self-assembly of the virus capsid is a hierarchical process through the formation of dimers and pentamers of dimers [1]. The connection of the subunits is established through three types of known binding interfaces. Global optimization of protein dimers showed that type I and type II interfaces play a significant role in the capsid formation process [2]. A better understanding of these interactions gives us the opportunity to find factors that influence the stability of the capsid.

We performed molecular dynamics simulations for type I and type II dimers on 300 K and 350 K, using implicit and explicit solvent. The type I dimer proved to be stable through a long, one microsecond simulation, therefore a pentamer of dimers containing predominantly type I interfaces was selected for further simulations. The trajectories were compared for the type I and type II dimers with that of the pentamer.

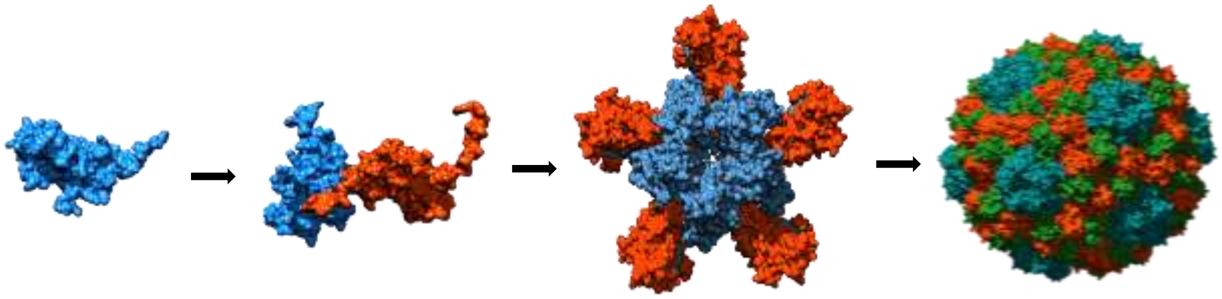

Figure 1 Steps of the hierarchical self-assembly of the CCMV virus capsid. The last step probably proceeds through the sequential addition of dimers to the pentamer of dimers.

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Role of siroheme and the Fe_4S_4 cluster in the active site of sulfite reductase

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The active site of sulfite reductase (SiR) consists of an unusual siroheme–Fe_4S_4 assembly (where the siroheme is connected to the iron–sulfur cluster via a cysteinate sulfur) and serves for multi-electron redox reactions. The electronic details of the siroheme–cluster interactions have not been explored so far to a major extent. Density functional calculations (DFT) have previously been reported on the catalytic cycle of SiR mostly using a simple iron-porphyrin model, without accounting directly for the role of the iron–sulfur cluster and with little attention to the importance of the special variant of heme employed in SiR.

Reported here are theoretical investigations carried out on bioinorganic models derived from the active site of sulfite reductase in which differences in terms of electron transfer are emphasized between the biologically occurring siroheme-[Fe4S4] system and the synthetic heme-[Fe4S4] system in order to give more insights on nature's preferences for the former system over the latter.

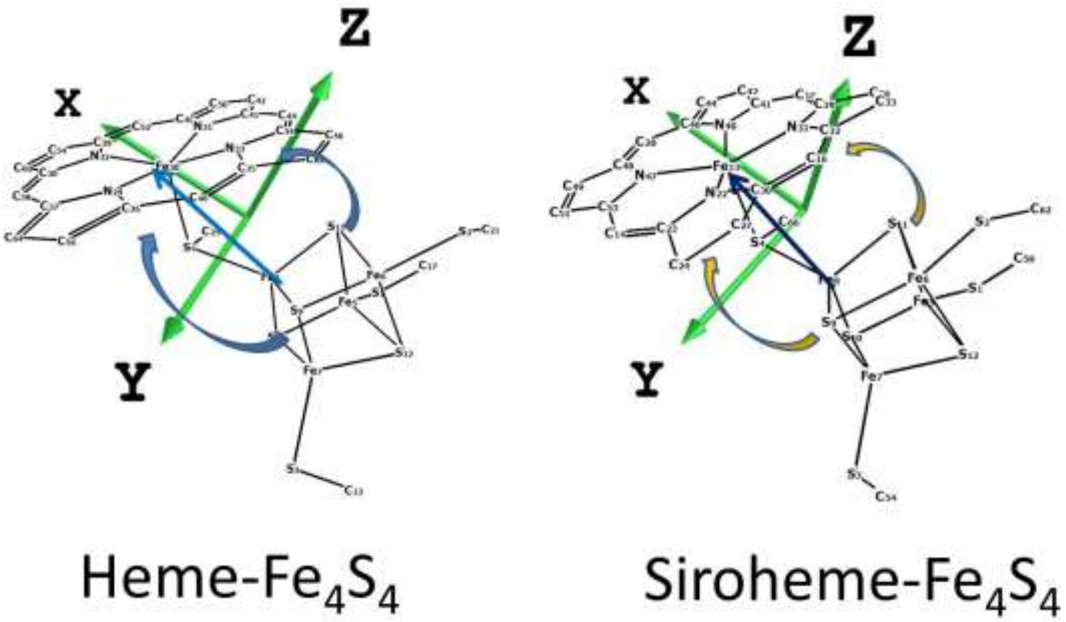

Figure 1. Possible electron route transfers from the cubane to the (siro)heme cofactor.

Quantum refinement of X-ray and neutron protein crystal structures

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Combining quantum mechanics and molecular mechanics (QM/MM) is one of the most important methods of studying the structure and function of proteins. This approach can also be applied in crystallographic refinement, as the geometry restraints used in refinement are in the form of an MM force-field. Thus, the MM potential for a small part of the molecule (for example, the active site of an enzyme or the binding pocket of a ligand) can be replaced by a QM potential, which can result in local improvement of protein crystal structures. We have developed such a method, *quantum refinement*, implemented in the ComQum-X program, which integrates a quantum chemical software with a crystallographic refinement software. Furthermore, this method can be applied in neutron crystallography by interfacing quantum mechanical calculations with joint X-ray—neutron refinement. This has been implemented in the more recent ComQum-U program[1].

We present several recent applications of quantum refinement on both X-ray and neutron protein crystal structures. Mainly, we show how quantum refinement can help in determining the composition and geometry of the active site in metalloenzymes. For example, quantum refinement supports a model of particulate methane monooxygenase (pMMO) with only one copper atom in the active site instead of the two that the structure deposited in the PDB contains.[2] We also show a protonation study of the active site of nitrogenase. Quantum refinement predicts the correct protonation state of the homocitrate residue[3] and suggests that the MoFe-cluster is fully unprotonated in the ground-state crystal structure. Finally, we applied the newly developed ComQum-U on the active site of lytic polysaccharide monooxygenase.

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Characterization of the excited states of DNA building blocks: a Coupled Cluster computational study

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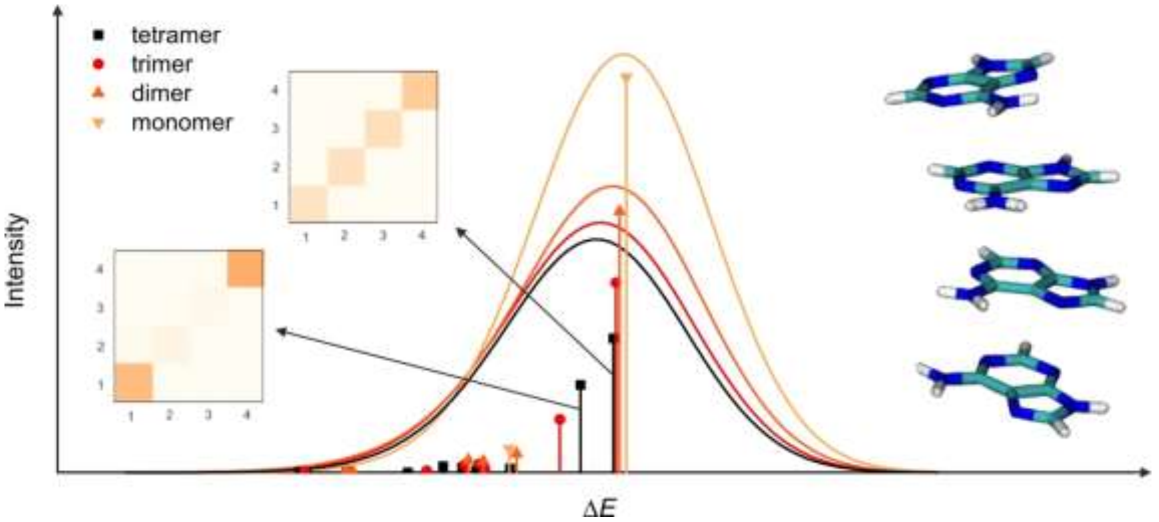
What happens with the DNA after UV irradiation? This question is asked not only by scientist, but even public interest is high due to health risks related to increased UV impact on earth surface. To understand all details of this process, the most logical route, both theoretically and experimentally, should start with the investigation of the nucleobases, the principal building blocks of DNA responsible for the absorbance of UV photons, and then continue with a systematic build-up of the natural DNA with hydrogen-bonded Watson-Crick pairing, π stacking, solvent effects, etc. If DNA is split in to small building blocks, even the highest level methods of quantum chemistry can be used to understand the basic processes.

In this study DNA building blocks consisting of up to four nucleobases are investigated with the EOM-CCSD and CC2-LR methods in two B-DNA-like arrangements of a poly-adenine:poly-thymine (poly-A:poly-T) system. The main interest was the character of the excited states with emphasis on the location of the hole and particle and the change of the spectrum with the growing size of the complex. Excitation energies and oscillator strengths are presented along with densities and density changes. The results show somewhat different behavior for poly-A and poly-T systems. We also investigate the effect of the H-bonds connecting the strands and found that breaking of these does not alter the spectral intensity considerably, it only causes a redshift of the absorption band. Thus it is unable to explain the experimentally observed DNA hyperchromism on its own, and stacking interactions need to be considered for the description of this effect as well.



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On choosing the “best” density functional
...or any computational method in chemistry
Probabilistic estimators

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Methods in computational chemistry do not provide useful bounds for the properties calculated. However, data are available and used in benchmarking, by comparing with experimental results, or calculations considered more reliable.

The present talk questions some of the criteria used in benchmarks found in literature[1-3], and recommends using probabilistic estimators such as the empirical cumulative distribution function[4].

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DOI:10.3390/computation4020020
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Density functional theory investigation of carbalane polyhedra

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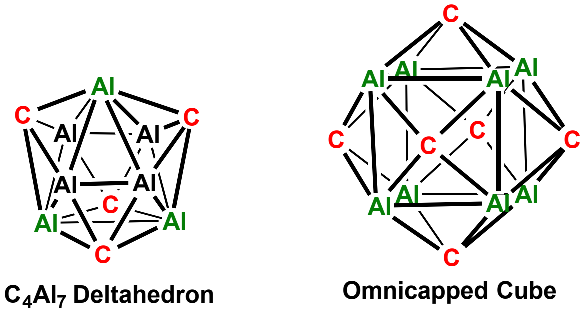
Organoaluminum compounds are important as ingredients in catalytic systems for olefin polymerization and related processes.[1] In this connection new types of organoaluminum compounds having central mixed aluminum-carbon clusters exhibiting unusual polyhedral structures have been reported (figure 1).[2,3] In order to understand the structures and bonding in such clusters, the $C_mAl_{n-2}Me_n$ ($m = 2, 4, 6$; $n = 7$ to 14; Me = methyl) systems have been studied by density functional theory.[4-6]

The strong preference of the carbon atoms for degree 4 vertices leads to some polyhedra not found in borane chemistry such as 12-vertex deltahedra having two degree 4 vertices, two degree 6 vertices, and eight degree 5 vertices in all of the low-energy structures of the 12-vertex dicarbalane $C_2Al_{10}Me_{12}$ rather than the regular icosahedron having exclusively degree 5 vertices. For the tetracarbalanes, the experimentally observed C_4Al_7 deltahedron with carbon atoms at the four degree 4 vertices is found in the lowest energy 11-vertex $C_4Al_7Me_{11}$ structure but severely distorted from ideal C_{2h} to Cs symmetry. The low-energy hexacarbalane structures no longer resemble polyhedral borane structures because of the high concentration of carbon atoms. They have the MeAl vertices within bonding distance of four carbon vertices to give the aluminum atom the 8-electron argon configuration.



C_4Al_7 Deltahedron **Omnicapped Cube**

Figure 1. (left) The C_4Al_7 deltahedron found in $(AlEt)_7(CCH_2Ph)_4(CCH_2Ph)_4(C{\equiv}CPh)H$; (right) The C_6Al_8 omnicapped cube found in $(AlMe)_8(CCH_2Ph)_5(C{\equiv}CPh)$. Degree 4, 5, 6 vertices are in red, black, and green.

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Implications of the generalized coupled oscillator mechanism for the interpretation and calculation of Vibrational Circular Dichroism spectra

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Vibrational Circular Dichroism (VCD) spectroscopy, the differential absorption of left and right circularly polarized light during a vibrational transition, is one of the very few spectroscopic techniques able to discriminate between the enantiomers of chiral compounds. When using VCD, the assignment of the absolute configuration is based on comparisons of simulated and experimental spectra. The advancements made in the last decade in computational and experimental techniques have made VCD the most versatile chiroptical technique available today. In spite of this, interpretation of the VCD spectra is still cumbersome. One of the main complications is the interpretation of the vibrational magnetic dipole transition moment, which by definition is origin dependent.

In this presentation, a simple and intuitive procedure for the interpretation of VCD spectra is demonstrated for two real-life molecules, i.e., dehydroquinidine[1] and benzyl-(2,3,4,6-tetra-O-acetyl-ß-D-glucopyranosyl) disulfide[2]. This new approach is based on the recently introduced generalized coupled oscillator (GCO) mechanism[3]. As will be shown, the GCO analysis allows one to identify on-the-fly the VCD-active/-inactive sites of a molecule. This in turn, allows one to perform faster and more accurate calculations of VCD spectra.

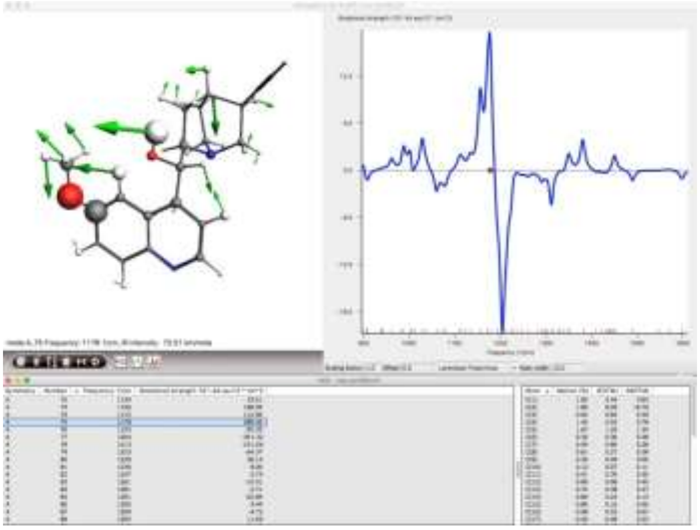

Figure 1: Generalized coupled oscillator analysis of dehydroquinidine.

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The Mapping of Conformational Space

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Generative Topographic Mapping (GTM)[1] was challenged to produce planar projections of the high-dimensional conformational space of complex molecules. Conformers of dipeptides, but also of large peptides (1LE1) can be successfully projected on relevant 2D maps. GTM is a probability-based mapping strategy, and its capacity to support property prediction models serves to objectively assess map quality (in terms of regression statistics). The properties to predict were total, non-bonded and contact energies, surface area and fingerprint darkness. Map building and selection was controlled by a previously introduced evolutionary strategy allowed to choose the best-suited conformational descriptors, options including classical terms and novel atom-centric autocorrellograms. The latter condensate interatomic distance patterns into descriptors of rather low dimensionality, yet precise enough to differentiate between close favorable contacts and atom clashes. In case of dipeptides, the conformation space of which can be exhaustively visited within reasonable amounts of computing time, the maps served to monitor the convergence of the S4MPLE[2]-driven evolutionary conformational sampling tool. Dipeptide maps[3] are able to host predictive energy landscapes, and may serve to compare sampled conformers to native ones, as seen in PDB geometries.
For the complex structure of 13-aminoacid 1LE1, a subset of 20K conformers, randomly selected from a pool of 2M geometries (generated by the S4MPLE tool) was employed for map building and cross-validation of property regression models[4]. The GTM build-up challenge reached robust three-fold cross-validated determination coefficients of Q^2=0.7…0.8, for all modeled properties. Mapping of the full 2M conformer set produced intuitive and information-rich property landscapes. Functional and folding subspaces appear as well-separated zones, even though RMSD with respect to the PDB structure was never used as a selection criterion of the maps.

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Water and proton dynamics from semi-empirical QM/MM simulations

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The long-term goal of our research is the development of novel magnetic resonance imaging (MRI) methodologies for the characterization of musculoskeletal tissues (in particular articular cartilage). One central strategy for this is the development of parameters derived from the dispersion of the longitudinal relaxation time in the rotating frame ($T_{1\rho}$). While these parameters show promise for detecting degenerative changes in cartilage, the underlying mechanisms are only poorly understood. One of the mechanisms most likely contributing to the dispersion of $T_{1\rho}$ dispersion in many tissue types is the chemical exchange of protons between biomacromolecules and water. We have now performed an extensive benchmark study of a large set of modern semi-empirical methods, concerning their ability to realistically describe proton transfers between fragments of biomacromolecules and water in QM/MM simulations.

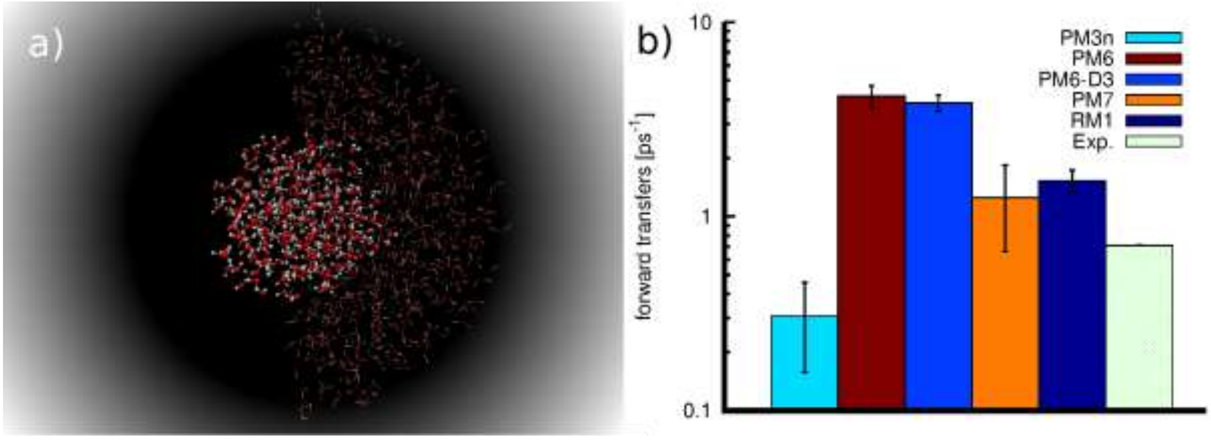

Figure 1. a) Schematic QM/MM system setup for both bulk water and excess hydrated proton simulations. b) Obtained proton forward transfer rates for the excess hydrated proton compared to experiment.

In this presentation we are focusing on the correct description of the properties of bulk water and the representation of proton transfer processes between water molecules. Figure 1a illustrates the general system setup used for these calculations. The QM layer of the model consists of ~250 water molecules, which are surrounded by an ~10 Å MM layer containing ~1500 TIP3P water molecules. For the studies of the proton transfer rate, one excess proton is added to the QM layer. Figure 1b shows the results for the proton transfer rates for a selection of the methods tested. All of the methods shown here give a proton transfer rate within one order of magnitude from the experimental value. On the other hand, we have found that two hydrogen bond corrections for PM6, which give superior results for small water clusters, entirely break down when applied to bulk water (independent of the presence of an excess proton).

We thank the Academy of Finland (project 297033), and the Jane and Aatos Erkko foundation for funding, and CSC-IT Center for Science in Espoo, Finland, for computational resources.

On the use of time-dependent density functional methods in the account of ligand field-type spectra of the coordination compounds

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For a chemist oriented towards the experimental sides of structural chemistry, such as the characterization of coordination compounds by spectroscopic, magnetic and X-ray diffraction methods, the practicing of routine level of nowadays user-friendly computer codes offers valuable complements to grasp causal relationships between structure and properties. The Time-Dependent (TD) method, subsequent to DFT (Density Functional Theory) calculations, is a very convenient route toward the optical properties, since it demands the simple TD keywords, with the specification of the desired number of states, aside to the other minimal ingredients triggering the calculation: Cartesian coordinates, charge and multiplicity, the DFT and basis set chosen from standard *à la carte* options. [1]

However, being limited to single-electron excitations, the TD procedures cannot describe all the possible states, recommending its use with caution in a Ligand Field (LF) problem with d or f type of molecular orbitals. For instance, the TD treatment skips the double excitations in the LF spectrum of a complex with d^8 configuration. On the other hand, the TD is reliable in problems where the LF excitations are taking the one-particle appearance. For transition metal complexes, the TD-DFT can be applied to systems whose central ion has a D-type ground spectral term, namely the d^1, d^9, high-spin d^4 or d^6 configurations. To the best of our knowledge, this technical aspect was not yet debated in the literature dedicated to the spectral modeling.

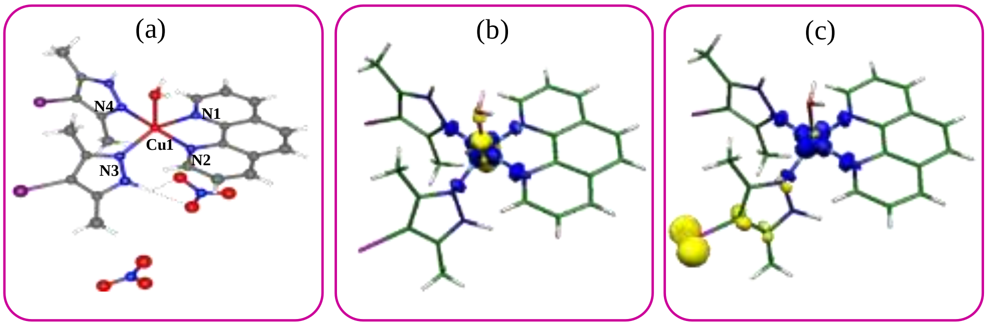

Figure 1. Illustration of the TD-DFT treatment of a copper(II) complex, $[(L)_2Cu(H_2O)(phen)](NO_3)_2$, where L= 3,5-dimethyl-4-iodopyrazole and phen =1,10 phenanthroline. (a) The X-ray determined molecular structure. (b) The density-difference map for a d-d transition. (c) The example of a charge-transfer transition, given as density-difference map. The blue surfaces correspond to density accumulation, while the yellow coloring describes the depletion zones.

In previous instances, we probed the utility of TD-DFT in the case of the d^4 configuration, for Mn(III) complexes.[2] Now we focus on a series of copper(II) systems, synthesized with pyrazole- based ligands, characterized by X-ray diffraction as belonging to a rather large structural diversity: mononuclears, tetranuclears and chains. The Figure 1 illustrates the case of a mononuclear compound.

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Modeling electric properties of hexahalobenzenes

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The development of accurate intermolecular potentials is an important application of quantum chemistry and remains a challenging task. It is usual to design force fields based on a selection of interaction sites per molecules located on atoms and/or on additional extra sites in order to partition the interaction energy between components having a physical and chemical meaning. Concerning the electrostatic energy component, rigorous methods to obtain distributed electric mulipoles and polarizabilities from the wave function exist (1-3) but they lead to very complicated models which are difficult and expensive to use in computer simulation. An alternative is to fit relatively simple and compact models of distributed multipoles and polarizabilities in order to reproduce the electrostatic potential and the induction energy of a polarized molecule (4-8).

Such fitting strategies based on MP2/aug-cc-pVTZ (and pseudopotential for the bromine atom) calculations have been applied in this work to get atomic distributed multipoles of hexahalobenzene molecules C_6X_6 (X= F, Cl, Br) including up to atomic quadrupoles reproducing as accurately as possible the electrostatic potential around a molecule. Distributed polarizability models are also discussed. The described models can be useful, for example, for the development of force fields of hexahalobenzene molecules interacting with ions.

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A modified Adjustable Density Matrix Assembler approach for fast computation of *ab initio* quality electron densities of complete proteins

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The ADMA (Adjustable Density Matrix Assembler)[1] approach is a method that can be used to calculate the electron densities of large molecules such as proteins. It consists of the division of the studied molecule into smaller nuclear families, for which the density matrix and electron density can be calculated easily using QM methods, and these fragments can be assembled to obtain the electron density for the whole molecule with a certain accuracy.[2] The accuracy can be improved by including more atoms in each nuclear family.[3] The block-ADMA method developed by us is based on the ADMA approach, only differing in the selection of the density matrix elements at assembly. This approach decreases drastically the necessary computation time, with an acceptable loss of accuracy.

The calculation time of the electron density from the assembled density matrix and the basis functions can be further decreased by massive parallelization, coding parts of the procedure for graphical processing units. With the use of 80 CPUs for Gaussian calculations and a single GPU for the electron density calculation, we were able to compute an *ab initio* quality electron density of the avidin-biotin complex on a 0.5 a.u. resolution grid, at a B3LYP/6-31G(d) level of theory, in approximately 3 hours.

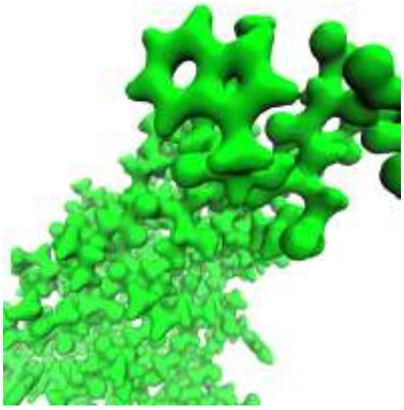

Figure 2: 0.1 a.u. electron density isosurface of the avidin-biotin complex, created with the block-ADMA method.

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Coarse-grained modeling of polyethyleneimine

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In simulating modern drug delivery protocols, the massive computational effort can be significantly reduced by adopting coarse-grained (CG) models. Provided they are realistic enough, they offer insight into processes which, at all-atom (AA) level, are barely accessible. Considering polyethyleneimine (PEI) as gene delivery vector, we present a novel CG force field (FF) for linear PEI chains. The parametrization procedure of the CG FF is based on AA molecular dynamics (MD) simulations carried out employing our recently published atomistic FF for PEI [1] which complies with the CHARMM standard [2]. Essentially, we employed the AA FF in MD simulations of PEI chains of various sizes and protonation patterns to produce probability distributions for the distances, angles, and dihedral angles formed by the centers of mass of adjacent residues. The probability distributions were then used to extract CG parameters for a MARTINI-type FF [3] by means of the Boltzmann inversion technique [3]. Furthermore, we studied the structural and dynamical properties of the CG PEI chains in aqueous solutions, which we matched against their atomistic equivalents in order to fine-tune the FF. The developed CG FF is a promising candidate for large-scale simulations of DNA-PEI polyplexes, of current interest to drug delivery mechanisms.

Keywords: cationic polymers, polyethyleneimine, force fields, coarse-graining.

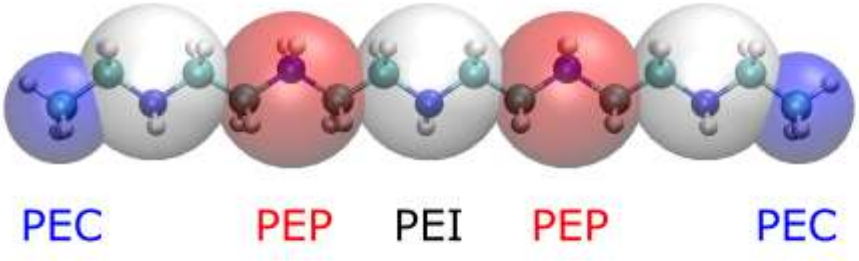

Figure 1: Definition of the CG beads for an alternatively protonated PEI pentamer.

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On the possible presence of carbides in the Fischer-Tropsch process catalyzed by ruthenium nanoparticles: a DFT study

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The predicted exhaustion of fossil energy resources represents the foremost factor that led in the last years to an intensification of the research on renewable energy. Green fuels, with H_2 being the main candidate, are obtained in several types of reactions including the hydrogen evolution reaction (HER) or the water gas shift (WGS), while conversion of biomass or coal into fuels is performed during the Fischer-Tropsch synthesis (FTS). Thus, developing highly active catalysts with reasonable costs remains a great challenge for the scientists working in the field.

FTS[1] involves syngas (CO and H_2) transformation into liquid hydrocarbons. Ruthenium catalysts lead to high selectivity and long-chain alkanes, the high cost usually restricting their applications to fundamental research. Nevertheless, for a comprehensive overview, Ru species may represent ideal candidates, as Fe and Co involve more complex architectures during FTS. A longstanding issue of FT process relies on the CO bond-breaking, three main routes being generally accepted (Figure 1).

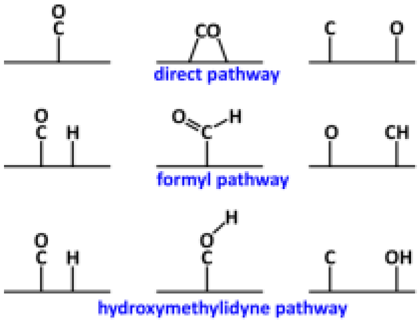

Figure 1. Main pathways proposed for the CO bond cleavage during Fischer-Tropsch synthesis

According to our previous work[2], Ru carbides can be achieved during CO hydrogenation *via* hydroxymethylidyne (COH) pathways, and stabilized in the presence of water. Within the actual study, carbide formation was assessed by DFT calculations under realistic FTS conditions. The direct and the hydroxymethylidyne mechanisms were investigated for several sites on a Ru_{55} model nanoparticle, including both terraces and defective sites.

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Anharmonic Vibrational Spectroscopy of Small Organic Compounds

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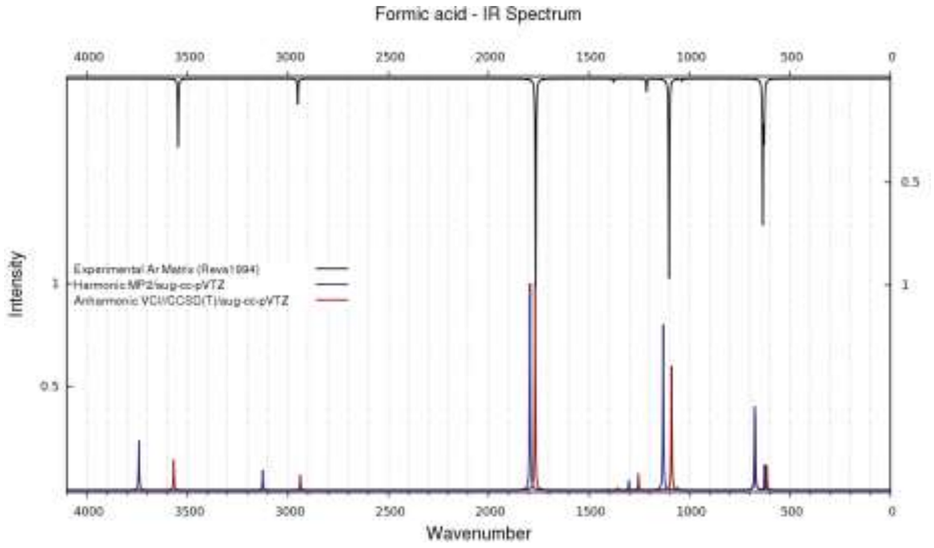
Numerous recent developments in the generation of potential energy surfaces (PES) at a high level of electronic structure theory promise an economic yet flexible and accurate access to quantum chemistry calculations beyond the harmonic approximation. These developments aim for approximate PES of polyatomic molecular systems, where the design of a global PES is cumbersome and expensive. A prominent field of application is the calculation of vibrational states of molecular systems by variational methods for solving the time-independent nuclear Schrödinger equation, i.e. vibrational self-consistent field (VSCF) and vibrational configuration interaction (VCI). Hence, these methods are commonly developed hand-in-hand, and in best case together with improvements in electronic structure theory. Within a variety of authors working on these methods, we find the most versatile implementations in the Molpro software package [1].

We employed PES generator and VSCF/VCI tools by Rauhut et al. [2,3] to compute anharmonic vibrational spectra of small organic compounds. In order to validate the theoretical prediction, we performed argon and neon matrix-isolation infrared spectroscopy. This technique suppresses rotation and thus yields vibrational spectra with very high resolution [4]. The compounds in this study are supposed to be important anchor-points in reaction mechanisms of the selective activation of carbon dioxide and water, making their precise characterization highly relevant for contemporary scientific research of renewable energy.



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Linkage isomerism in bioinorganic centers

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Linkage isomerism, understood as the competing occurrence of two or more linkage isomers at the same coordination centers, is an expanding topic in bio-inorganic chemistry. We were the first to document linkage isomerism in an enzyme, i.e. nitro/nitrito in nitrite reductases and then also in a range of related proteins, at centers consisting of heme *b*, heme d_1, copper or molybdenum. Subsequently, other cases were identified/explored, which include bioinorganic complexes of enzyme active sites with nitric oxide and derivatives thereof (e.g., HNO, hydroxylamine), peroxynitrite, chlorine oxides/oxyanions, sulfur oxides/oxyanions, sulfenic/sulfinic acids, thiocyanate. An overview of these cases, as examined by DFT data, will be given.

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POSTER PRESENTATIONS

P-1

Adsorption of the two isomers of resveratrol on graphene

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Resveratrol (3,5,4'- trihydroxystilbene- RESV) has a strong antioxidant activity which renders this compound very interesting for the biomedical field.

As a stilbenoid molecule, RESV contains two phenolic rings connected by an olefin C=C bond with three hydroxyl groups, which facilitates two isomeric forms, called *trans* (E)- and *cis* (Z)-RESV and they differ by the relative orientation of the hydroxyl groups.[1, 2] The biological activity of this molecule is primary due to its *trans*-isomers, whereas the *cis* conformer is naturally obtained by UV-irradiation of the *trans*-resveratrol.[3] However, the low aqueous solubility is a limiting factor for its bioavailability. For practical applications as a drug or nutraceutical, RESV needs to be transported by nanocarriers like, for instance, graphene materials.

In this work we explored the possibility of adsorbing the RESV isomers on graphene materials and to check the possible discrimination between enantiomers by such surfaces.

The interaction between the resveratrol's (*trans*- and *cis*-) isomers and graphene oxide are investigated by using UV-Vis spectroscopy and zeta potential measurements. Quantum chemical calculations based on density functional theory (DFT) are used to get insights into the geometries of adsorption and interaction energies between resveratrol and graphene.

Both isomers of resveratrol were successfully adsorbed onto the grapheme oxide surface and the experimental and computational data suggest a better stability of the complexes of *trans* isomer with graphene compared to the c*is* partner.

Our results show that experimental results coupled with quantum chemical calculations would help to discriminate the enantiomers and to develop nanocarriers of resveratrol for various biomedical applications.

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P-2

Reversible complexation of ammonia by breaking a manganese-manganese bond in a manganese carbonyl ethylenedithiolate complex

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The reaction of $Mn(CO)_5Br$ with sodium ethylenedithiolate was reported in 1968[1] to give a dark red volatile binuclear $H_2C_2S_2Mn_2(CO)_6$ complex possessing the property of complexing reversibly with ammonia to give a yellow $H_2C_2S_2Mn_2(CO)_6 \cdot NH_3$ adduct. We performed density functional studies on the $H_2C_2S_2Mn_2(CO)_n$ ($n = 4$ to 8) systems as well as their relevant ammonia and trimethylphosphine adducts. These theoretical studies strongly indicate reaction of $H_2C_2S_2Mn_2(CO)_6$ with ammonia to involve a unusual type of reversible rupture of manganese-manganese bond by ligand coordination. Complexation of $H_2C_2S_2Mn_2(CO)_6$ with NH_3 or Me_3P preserves the complexed C=C double bond of the ethylenedithiolate ligand but lengthens the Mn$\cdots$Mn distance to a non-bonding ~3.6 Å. Thus $H_2C_2S_2Mn_2(CO)_6$ represents an unusual type of Lewis acid where reversible complexation with Lewis bases involves rupture of a metal-metal bond. The thermodynamics of CO dissociation in the series $H_2C_2S_2Mn_2(CO)_n$ ($n = 8$ to 5) accounts for the formation of the hexacarbonyl $H_2C_2S_2Mn_2(CO)_6$ upon reaction of $Mn(CO)_5Br$ with sodium ethylenedithiolate.

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P-3

The high affinity of small antioxidants for hemoglobin and myoglobin

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It has previously been shown that hemoglobin displays ascorbate and urate peroxidase activity with low Km values – lower than the concentration of these antioxidants in blood.[1, 2] A direct interaction between hemoglobin and ascorbate was shown by ^{1}H-NMR spectroscopy.[3] Reported here are Michaelis-Menten data according to which hemoglobin also has high affinity for a wide range of exogenous small-molecule antioxidants such as caffeate, gallate, rutin, quercetin, epicatechin, luteolin, 3-hidroxiflavone and 3,6-dihydroxiflavone. Furthermore, ^{1}H-NMR and ^{13}C-NMR spectra reveal a fast dynamic effect or the existence of multiple binding sites of these antioxidants on myoglobin. Fluorescence and ICT measurements also suggest high-affinity dynamic binding with a key role for hydrogen bonding and van der Waals forces. Docking calculations allow for identification of binding sites on globins for the antioxidants investigated here, in all cases with affinities in the sub-millimolar range, in good agreement with the experimental data. As was proposed before [4], Tyr42 is shown to be involved in the binding of three substrates studied here. Additionally, Tyr 145, Tyr 35 and other redox-active aminoacids (mainly Trp) are found at the binding sites of antioxidants on hemoglobin and/or myoglobin. These data may bear physiological relevance in terms of the increasingly versatile dietary patterns of humans on non-endogenous small antioxidants, as well as in understanding the manners in which the effect of oxidative stress may be reduced in cases where the stress-related reactivity of globins is important, such as in hemoglobin-based oxygen carriers (HBOC).

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P-4

DFT benchmarking for the correct description of spin states in bioinorganic centers. heme vs. siroheme models of the sulfite reductase active site

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A test set of models that describe bioinorganic centers was employed to benchmark the performance of several density functional methods for the accurate description of overall spin states of these centers. The set comprises four models derived from biological active sites that possess different ground state multiplicities (high-spin, low-spin and intermediate-spin state), as depicted in Figure 1.

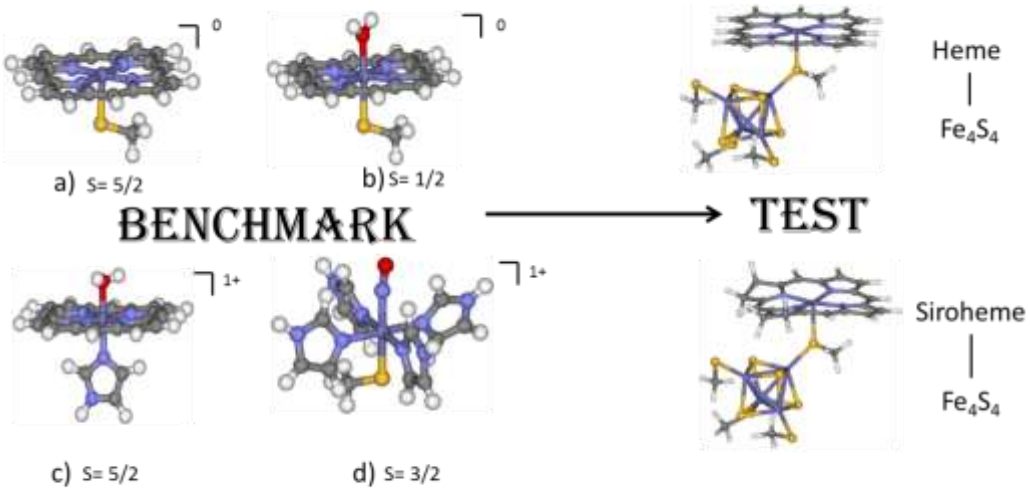

Figure 1. Left: Bioinorganic models derived from the active sites of the following proteins: ferric cytochrome P450 with a vacant distal position (a) and aqua-bound (b), ferric haemoglobin (c) and ferrou-nitrosyl Superoxide Reductase (d). Right: heme-[Fe4S4] and siroheme-[Fe4S4] systems

In general, when conducting quantum chemical calculation on open-shell systems using the framework of density functional theory, it is observed that hybrid functionals tend to overestimate high-spin states, while pure functionals overestimates low-spin states. Thus, finding a functional that performs acceptable in all spin state situations encountered in bioinorganic molecules is not a trivial task. In this study, we engage in such a quest, by choosing a set of functionals that use a different amount of exact Hartree-Fock exchange in their evaluation of the exchange integrals.

Further theoretical investigations are carried out with the best performing functionals on bioinorganic models derived from the active site of sulfite reductase in which differences in terms of energetics, bonding, spin coupling are emphasized between the biologically occurring siroheme-[Fe4S4] system and the fictive heme-[Fe4S4] system in order to give more insights on nature's preferences for the former system over the latter.

P-5

Density functional theory investigation of hypoelectronic eight-vertex metallaboranes

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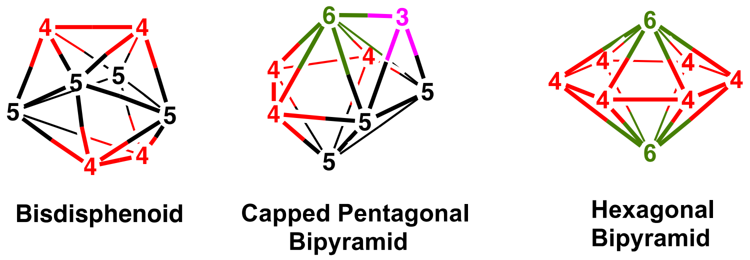
The BH vertices in polyhedral boranes can be replaced by transition metal units. Each such vertex is a donor of a specific number of so-called skeletal electrons thus influencing the geometry and the properties of the cluster. Thus a BH vertex as well as CpCo, $Fe(CO)_3$, and $HRh(PMe_3)_2$ vertices become donors of two skeletal electrons. Similarly a CH vertex as well as CpNi and $Co(CO)_3$ vertices become donors of three skeletal electrons. Examples of metallaborane vertices donating fewer skeletal electrons include CpM (M = Fe, Ru) as donors of a single skeletal electron as well as $M(CO)_3$ (M = Cr, Mo) and CpM´(M = Mn, Re) as donors of zero skeletal electrons. The 8- and 9-vertex closo deltahedra have non-degenerate frontier orbitals and thus can serve as a basis for structures with only 2n skeletal electrons rather than the 2n + 2 skeletal electrons suggested by the Wade-Mingos rules.

We have performed a density functional theory study on various 8-vertex metallaborane systems having 16 skeletal electrons (= 2n for n = 8). Such systems were neglected in some of our earlier theoretical studies that were limited to structures having 9 to 12 vertices. The lowest energy structures for all of the eight-vertex $[M]CB_6H_7$ {[M] = CpFe, CpRu. $Co(CO)_2$, $Rh(CO)_2$, $(Me_3P)_2Fe(H)$, $(Me_3P)_2Ru(H)$}, $[M]C_2B_5H_7$ {[M] = CpMn, CpRe, $Cr(CO)_3$, $Mo(CO)_3$}, and $[M]_2C_2B_4H_6$ ([M] = CpFe, CpRu) systems having 16 skeletal electrons are all capped pentagonal bipyramids providing a degree 6 vertex for a metal atom. Thus the capped pentagonal bipyramid plays a similar role for these 8-vertex metallaboranes with 16 (= 2n for n = 8) as the isocloso deltahedra play for the 9- and 10-vertex metallaboranes with 2n skeletal electrons. In the lowest energy structures the carbon atoms occupy degree 4 vertices and the metal atoms normally occupy the highest degree vertices including the unique degree 6 vertex of the capped pentagonal bipyramid (Figure 1).



Bisdisphenoid

Capped Pentagonal Bipyramid

Hexagonal Bipyramid

Figure 1. Structural 8-vertex units encountered in low-energy metallaborane clusters.

P-6

Dimetallaborane analogues of the octaboranes: structural variations with changes in the skeletal electron count

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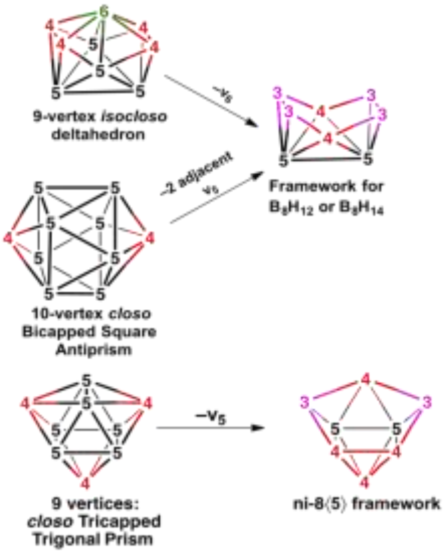
The structures and energetics of the complete series of hydrogen-rich dimetallaboranes $Cp_2M_2B_6H_{10}$ ($Cp=\eta5-C_5H_5$; M = Pd, Pt; Rh, Ir; Ru, Os; Re; Mo, W; Ta), related to the experimentally known $Cp^*{}_2Rh_2B_6H_{10}$[1], and $Cp^*{}_2W_2B_6H_{10}$[2] ($Cp^*= \eta5-Me_5C_5$), have been investigated by density functional theory[3]. The lowest energy structures of the hyperelectronic $Cp_2M_2B_6H_{10}$ (M= Pd, Pt; Rh, Ir) systems have central M_2B_6 frameworks with a hexagonal open face similar to the B_8 networks in arachno-B_8H_{14} and nido-B_8H_{12}. The two lowest energy structures for $Cp_2Rh_2B_6H_{10}$, lying within 1 kcal/mol of energy, differ only in the locations of the bridging hydrogen atoms around the hexagonal hole consistent with the experimentally observed fluxionality of the related $Cp^*{}_2Rh_2B_6H_{10}$. Most of the lowest energy
$Cp_2M_2B_6H_{10}$ (M = Ru, Os) structures also have a central M_2B_6 framework similar to B_8H_{12}, typically with such additional features as an additional metal-metal bond or a formal metal-metal double bond. A common motif for the low-energy structures of the hypoelectronic $Cp_2M_2B_6H_{10}$ (M=Re; Mo, W; Ta) systems, including the experimentally known $Cp^*{}_2W_2B_6H_{10}$, is a central M_2B_4 octahedron with its two M_2B faces capped by the remaining boron atoms and with four M–B edges bridged by hydrogen atoms. Such structures can also be derived from the experimentally known 9-vertex oblatocloso $Cp^*{}_2Re_2B_7H_7$ structure by removal of the unique degree 4 vertex atom.



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P-7

Intersystem crossing in metal-ligand coordination complexes with pyramidal-planar and octahedral coordination configurations

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Materials with "spin crossover" or "spin transition" properties are of major interest through their potential applications such as molecular memory, sensors or molecular switches[1,2].

We have obtained results about the equilibrium geometry optimization and about the searching of intersystem crossing (ISC) points on the potential energy surfaces of the electronic states with singlet and triplet spin states in the case of Ni-Tetrakis(pentafluorophenyl)-porphyrin functionalized with azopiridine (Ni-TPP-AP) as well as in the case of Ni-porphyrin functionalized with two azopiridines (Ni-P-biAP) molecular complexes. The first 30 electronic excited states have been computed at MN12-SX/def2-TZVP level of theory. We have tailored eight different supramolecular complexes for the studying the spin crossover efficiency.

Using the algorithm called "Penalty Function" we have identified the possible intersection points on the hyper-surface of the potential energies for the two singlet and triplet spin configurations. In order to make efficient the searching procedure we have developed a home-made Python code (PyISC) which is able to perform both intersystem crossing and conical intersection point searches either for the ground or the excited state electronic configuration.

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P-8

DFT Calculations, Green synthesis and biological applications of methanesulfonamide functionalized graphene quantum dots

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Nanotechnology is a newly emerging field in many interdisciplinary research fields. Therefore, nanoparticle research continues today with the fields of synthesis, characterization and biotechnological application [1,2]. Methanesulfonamide functionalized highly luminescent (Fig. 1) graphene quantum dots (GQDs) was synthesized using a hydrothermal reaction between citric acid and methane sulfonamide [3]. Graphene quantum dots have been characterized by UV-Vis, FT-IR spectroscopy, TEM, EDX spectroscopy and DLS, which were in good agreement with the structure predicted by the theoretical calculations using density functional theory (DFT) [4].

The biological applications of the GQDs were studied. The antimicrobial activity of the nanoparticles was investigated for its minimum inhibitory concentration (MIC) to bacteria and yeast cultures. The interactions of the compound with DNA were studied by the Ultraviolet-visible spectra and gel electrophoresis method. The experimental results indicated that methanesulfonamide based GQDs could bind to DNA via an electrostatic mode and showed that the compound cleaved DNA without the need for external agents. In addition, antioxidant activity of GQDs was measure using the DPPH method [5]. As the concentration of the compound increased, the antioxidant activity also increased.

Figure 1. Luminescent graphene quantum dots (GQDs)

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P-9

Comparison of geometry optimization methods on amino acid structures

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Diverse methods (Hartree-Fock methods, Semi-empirical methods, Density Functional Theory, Molecular Mechanics) employed in order to optimize a molecule structure have the same basic approach but differ in the mathematical approximations used. Using the 3D structures collected from PubChem Database, 20 amino acid geometry optimization calculations were performed with several methods. The purpose of the study was to analyze these methods so as to find the relationship between them and determine which one to use under certain circumstances. Cluster analysis and principal component analysis were performed in order to evaluate the similarity between different methods.

P-10

Theoretical study of phenylene- and biphenyl-linked porphyrin layers

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By means of DFT we have tackled the mono- and bilayer structures consisting of porphyrin covalently linked through phenylene- and biphenyl-linkers. We have conducted a bond analysis in both cases and constructed the Wannier functions [1] for the phenylene-linked porphyrin in the attempt to analyze the rotation characteristics of the linkers. The formation and energetics of the bilayer has also been studied.

Although covalently biphenyl-linked porphyrin has already been successfully synthesized [2,3], to the best of our knowledge, the on surface synthesis of phenylene-linked networks has yet to be achieved and thus, among our goals was to give those who wish to synthesize these structures a starting point in their endevour.

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P-11

Functionalized β-cyclodextrin as trans-membrane channel

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It is well known that cyclodextrine has the ability to auto-assemble in a tube like structures. Coining on this ability, we tried to find a functionalized β-cyclodextrin (figure 1A) that would insert in a lipid bilayer and stack in a tubular structure. In this work we present some molecular dynamics studies done on such a cyclodextrine. In order for the cyclodextrine to insert itself in a membrane the OH groups on the small rim where functionalized with para-phenil n-imino-octil. The parameters for the cyclodextrine where taken from Christine Cézard et.al [1] and the parameters for para-phenil n-imino-octil were determined using ambertools and the GAFF forcefield. The charges were determined using RED-tools. Two types of simulations where done in order to determine the viability of β-cyclodextrin as a trans-membrane channel. Firstly, auto-assembly of a lipid bilayer in the presence of β-cyclodextrin was computed, that showed the ability of the β-cyclodextrin to embed in the membrane. Secondly, the cyclodextrine where stacked (Figure 1B) and inserted in a preformed membrane. The simulation showed that the β-cyclodextrin tube maintained its structure for 750 ns. In order to validate the theoretical computations, the membrane permeability must be determined experimentally.

A) B)

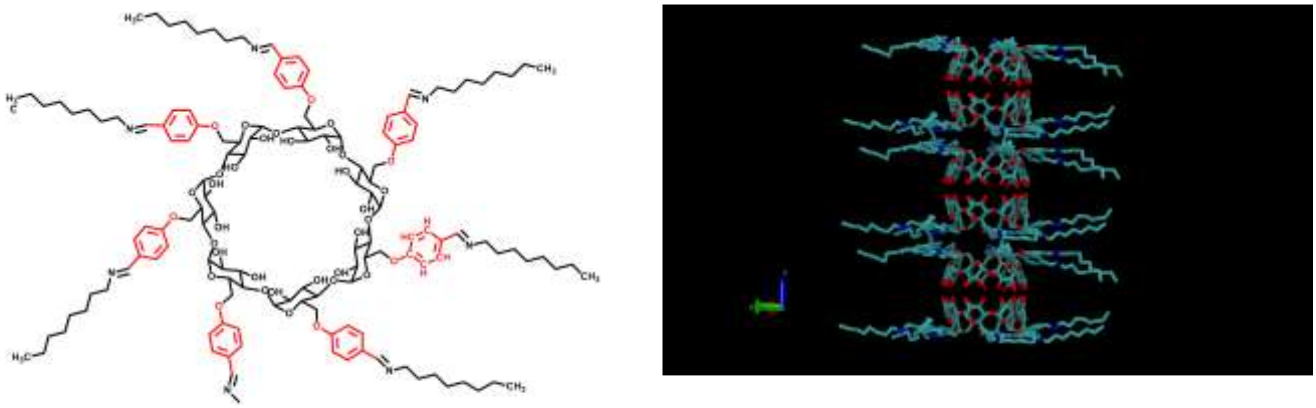

Figure 1 A) the structure of the functionalzied cyclodextrine and B) the channel structure of the cyclodextrine tube inserted in the membrane

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P-12

Through-space and through-solvent interactions between nitroxide-based stable radicals

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According to our interests in the spin chemistry of stable organic radicals, [1] we approached systems containing the (2,2,6,6-tetramethylpiperidin-1-yl)-oxyl unit, known as TEMPO. Idealized systems, containing couples of TEMPO or related systems in different mutual placements can be well rationalized with the help of the orbital paradigms of the exchange coupling [2] using numeric experiments based on state-of-the art Density Functional Theory (DFT) methods, within the specific Broken-Symmetry (BS) treatments.

Acknowledging that the real behavior of the systems, as recorded in the course of electronic paramagnetic resonance (EPR) experiments, is made much more complicate by the role of the solvent, we investigated this aspect, from different sides.

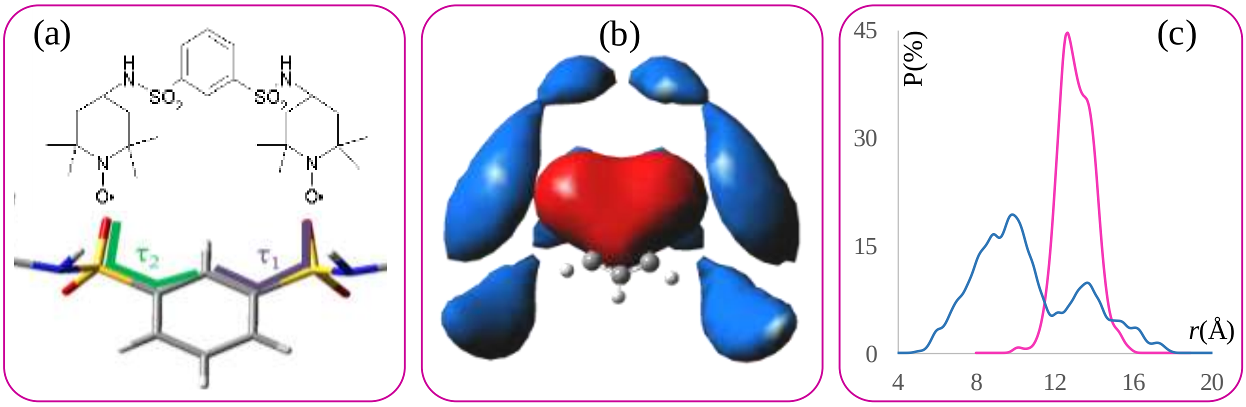

Figure 1. Synopsis of the molecular dynamics experiments performed on a selected biradical, shown in the panel (a). The panel (b) shows the density of probability for the placement of the barycenters of the two NO bonds (blue isosurfaces) and of the middle point between the two NO groups (red isosurface), as resulted from molecular dynamics (MD) in the CH_2Cl_2 solvent. The panel (c) compares the distance between the NO barycenters in MD trajectories taken in solvent (pink curve) vs. vacuum (blue line).

Taking relevant mutual placements of two TEMPO units, we analyzed the exchange coupling in the pristine dimer, versus idealized complexes containing a CH_2Cl_2 molecule at the midpoint between the two oxygen atoms. We found sensible changes, strongly dependent on the orientation of the solvent. At the same time, the exchange-coupling estimated with the Self Consistent Reaction Field (SCRF) method, built in the used Gaussian code, yields only incremental changes, assessing then that such treatments are not appropriate for the ab initio account of the Spin Hamiltonian parameters. The complexity of phenomena in solution was approached doing molecular dynamics on the TEMPO-$NHSO_2$-C_6H_4-SO_2NH-TEMPO biradical, at approximated level of molecular mechanics, realizing statistics over the conformations adopted by the biradicals in a box of solvent molecules (see Figure 1).

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P-13

Hybrids and Bond Angles in Small Prototypic Hydrocarbon Molecules

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The hybridization concept belongs to the basic language of chemistry, in principle, unnecessary at the technical level of computational chemistry. However, grace to its heuristic virtues, this paradigm deserves to be safeguarded, the most coherent approach being realized by the body of post-computational analyses belonging to the Natural Bond Orbital (NBO) theory and code [1]. At the same time, the hybrid orbitals are the legitimate objects of a proper setting in Valence Bond (VB) calculations. Although there are modern codes for this computation method [2], the VB is rarely used nowadays.

Reviving previous investigations advocating for hybridization as a valuable complement of state of the art calculations,[3] because it offers an adequate account for the local character of the electronic correlation, we present here new analyses on this line. We analyze and discuss relevant organometallic systems as well as several prototypic hydrocarbon molecules. The left panel of the synoptic Figure 1 suggests some puzzling issues, finding that experimental structures obey well a simple model based on bond angles correlated by hybridization, while optimized geometries are deviant (probably due to hidden intrinsic problems with basis functions and non-covalent effects). In turn, the NBO-based hybrid bond angles are obeying the ideal pattern.

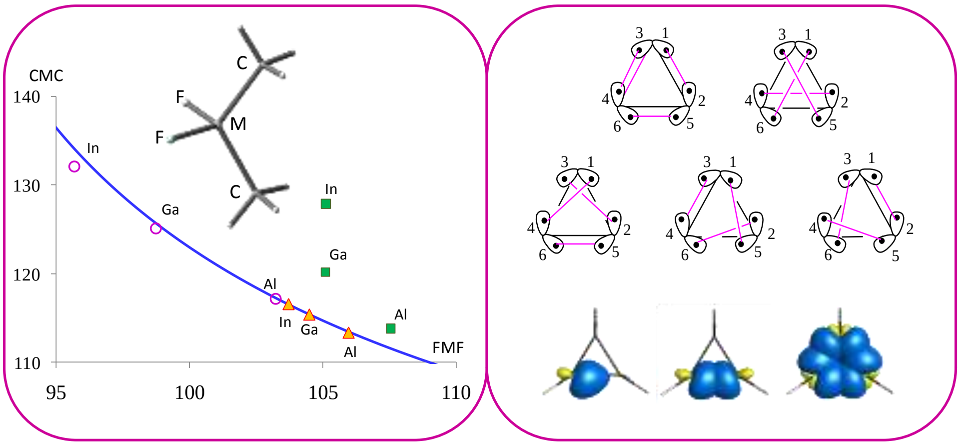

Figure 1. Synopsis of the numeric experiments on hybrids as computational objects. Left panel: the correlation of FMF vs. CMC angles in the [MF$_2$Me$_2$]- organometallic anions, with M=Al, Ga, In; the line-is our phenomenological model, the circles correspond to experimental geometries, the squares to structures optimized by b3lyp/AQZP, the triangles describe the NBO hybrids resulted from the same method. Right side panel: the case of hybrids in strained rings; the bottom line shows the VB optimized functions (one, a pair and all six of bent C-C bonds), the upper part showing the VB resonance structures.

Another part is devoted to molecules with ring strain, such as cyclopropane, spirane and other polyciclic congeners, where the hybrids cannot be perfectly aligned, measuring the ring strain with the help of a heuristic model of the hybridization, complemented with state-of-the art calculations, in the frame of Density Functional and Valence Bond theories.

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P-14

Reshaping the principles and techniques of Gaussian-type basis sets in computational chemistry

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The computational chemistry is a distinct branch of modern chemistry and a valuable counterpart of the applied sciences, from materials to biomolecules, providing valuable explanations and predictions, as guidelines for achieving desired properties. The majority of quantum chemical calculations is based on the so-called Gaussian Type Orbitals (GTOs), which represent the "concrete and steel" of the actual development in this field. [1]

It is well acknowledged that the GTOs are not natural primitives to build approximations of the atom electronic structure, first of all, because of the $\exp(-\zeta r^2)$ pattern, while Slater Type Orbitals (STOs), with $\exp(-\zeta r)$ exponential components, are more appropriate to this goal. However, the biggest problem, a hidden drawback, stays in the fact that the standardized GTO bases have drastic limitations in the radial polynomial cofactors. [2]

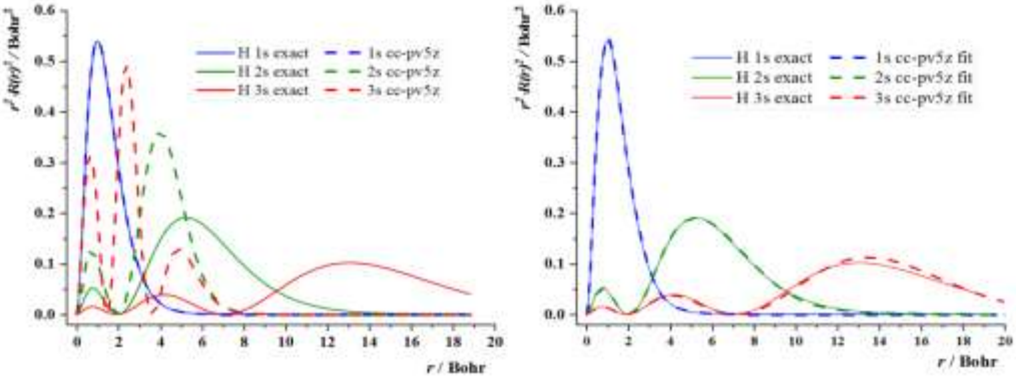

Figure 1. The $r^2R(r)^2$ vs. r profiles for the eigenfunctions corresponding to 1s-3s orbitals of hydrogen, resulted from exact Schrödinger solution (solid line) in comparison with the cc-pv5z GTOs (dash line) (in left side) and improved when r and r^2 factors are introduced (in right side).

An important test of basis sets is given by the case of hydrogen atom, for which correct analytical solutions are known (see Figure 1). Confined to the non-relativistic Schrödinger equation, the eigenvalues are, simply, $E_n = -Z/(2n^2)$, for a given n main quantum number. Most of the bases are reproducing well eigenvalues close to -0.5 Hartree for the ground level, while many are in difficulty in accounting the -0.125 Hartree expectation value of 2s. Very few are approaching the value of 3s, i.e. -0.055 Hartree. Actually, in many situations, the 2s and 3s levels are positive eigenvalues, which, of course, is a faulted result. We alleviate this situation introducing general $r^k\exp(-\zeta r^2)$ primitives, in analogy to known exact solutions for hydrogen case.

Focusing the hydrogenic atom, we find that rebuilding the basis with primitives spanning the $\exp(-\zeta r^2)$, $r\cdot\exp(-\zeta r^2)$ and $r^2\cdot\exp(-\zeta r^2)$ patterns one reaches a drastic improvement in orbital energies and radial profiles even with a moderate number of components. Detailed analyses were performed on the hydrogen standard, advancing with preliminary results towards the other elements in the periodic table.

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P-15

Photophysical properties of perylene derivatives

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Understanding and characterization of the electronic excited states (ESs) of molecules is crucial for their industrial applications in dyeing and chemical colors, energy conversion, but also in biological and medical processes and organic molecular electronics. Being short-lived, highly reactive and often coupled together, the electronically excited-states are computationally much more demanding than their ground state counterparts.

During the last decade, Time-Dependent Density Functional Theory (TD-DFT) has become the method of choice for modeling ESs, yet remaining much more affordable than the electron-correlated wave function approaches. It is now able to provide not only the vertical transition energies, but also geometries and other properties of the excited states, like: electronic densities, polarizabilities, vibronic structures of optical spectra, dipole moments, emission wavelengths, as well as radiative lifetimes of ESs.

Fluorescence lifetimes is an extremely important parameter for the electronically excited states. It is used in the Fluorescence Lifetime Imaging Spectroscopy, providing increased resolution for the fluorescence imaging technique.

The key objective of the work is to address the performance of TD-DFT in the linear response regime for describing the electronically ESs of three perylene derivatives (perylene, PTCDI and PTCDA) . We were particularly interested in the vertical absorption and emission energies, geometries of the emitting structures, adiabatic energies, 0-0 transition energies and the radiative lifetimes.

Using adequate models and proper computation methodologies we were able to reproduce or to predict the radiative lifetime of the investigated molecules.

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P-16

Antiaromaticity comes in six
A HOMA/NICS study of [n]helicenes (n = 6 - 24)

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Helicenes are organic molecules made of condensed benzene rings in a spring-like fashion. They display interesting physical properties like non-linear optical properties and apparently asymptotical optical activity[1]. Their extended π-system was shown to display (anti)aromatic behavior resembling the analogous system of the [n]phenacenes derivatives[2]. The previous computational studies conducted only NICS(0) analysis in order to assess the local aromaticity of individual rings. It was shown by different aromaticity indices that the external rings are more aromatic than the internal ones. In order to treat the aromatic character of the systems as a whole, we calculated the chemical shielding along the central axis for each [n]helicene (n = 6 -24). Also, we investigated the difference in bond lengths of the internal and external spirals via HOMA method.

All structures were optimized at the same DFT level of theory. For this purpose, we employed the PBE0 hybrid functional along with double-zeta basis set (Def2-SVP). In order to calculate the magnetic properties of the ghost atoms, we used the GIAO method and selected the on-axis component of the magnetic shielding tensor.

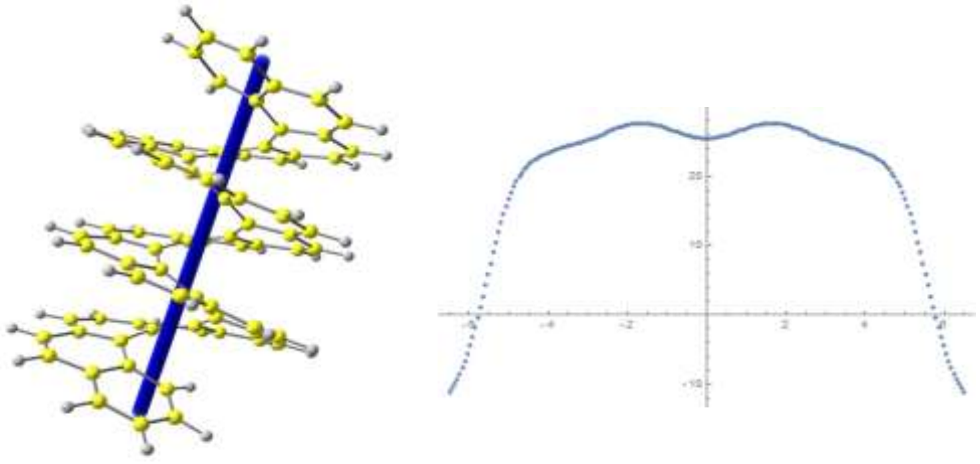

Figure 1. The optimized geometry of [19]helicene with 201 ghost atoms aligned on the central Z axis (left); ZZ component of the magnetic shielding tensor for each ghost atom as a function of distance (right).

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P-17

Linkage isomerism in complexes of cobalamin with cisteine sulfenic, sulfinic and sulfonic acids

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Linkage isomerism is an expanding topic in bio-inorganic chemistry. Examples include the complexes of metal centers in proteins with nitrite, nittric oxide, peroxynitrite, or with chlorine or sulfur oxidess/oxyanions. Reported here are DFT data regarding tautomerism and linkage isomerism in cysteine and in its sulfenic, sulfonic and sulfinic acids, as well as in their complexes with cobalamin, providing a new class of ligands that can exhibit linkage isomerism in bioinorganic chemistry.

As a free molecule/ion, the sulfoxide/sulfone forms are less stable than their tautomers, the sulfenic/sulfinic acids. Moreover, the sulfinate group is more acidic than the carboxylate => under physiological conditions the S-oxidized cysteines are probably deprotonated at the SO_n (n=1-3) group

Cysteine sulfenate/sulfinate/sulfonate generally ligates to cobalamin via the sulfur-bound oxygen. However, at neutral pH this isomer is essentially degenerate with the one bound via carboxylate. Also, at low pH sulfenate binds essentially equally via the S and the O atom of its SO group. Sulfonate always binds via the S-bound oxygen, except at high pH when the amino and carboxylato groups outperform the SO_3.

P-18

Thermodynamic properties of ethylenimine and ethylene glycol polymers

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The design of gene carriers is essential to modern gene delivery protocols. Among them, polymers such as polyethylenimine, are widely used as non-viral gene vectors [1], so it is very important to know their behavior in terms of thermodynamic stability.

Polyethylenimine or polyaziridine [–(NH – CH2–CH2)n–] has repeating NH and methylene groups and appears in linear or branched configurations [2].

Another key polymer is polyethylene glycol or polyethylene oxide has repeating ether groups $[H-(O-CH_2-CH_2)_n-OH]$, also existing both in linear or non-linear configurations.

The two biopolymers, namely polyethylenimine (PEI) and polyethylene glycol (PEG) in linear configurations, with a different range of polymerization, containing between 3 and 25 repeat units (mers), have been studied by means of 3 functions of state (internal energy, enthalpy and Gibbs free energy) using the Gaussian 09W package at the DFT PBEPBE 6-311G (d,p) level of theory.

Preliminary results show that the stability of the two polymers decreases with their degree of polymerization, with the increasing of their chain length.

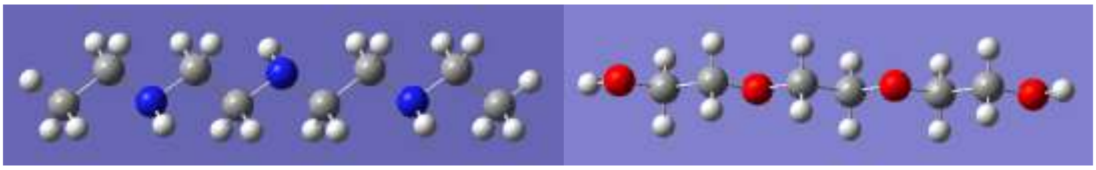

Figure 1. PEI (left) and PEG (right) containing 3 monomers

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P-19

Challenges in designing nanoceria for antioxidant therapy

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Cerium oxide (IV) nanoparticles offer high redox ability, while maintaining nontoxicity and high stability. Due to the unique property of cerium to easily switch oxidation states between Ce^{3+} and Ce^{4+} in CeO_2, cerium oxide has gained a considerable interest in the field of biomedicine as potential antioxidant agent exerting neuroprotective effects, as well. Thus, dispersed nanoCeria is a promising candidate as antioxidant material for human cells. It was reported recently that ceria nanoparticles do not show antioxidant property at acidic pH. Subsequently, the catalyst mimetic activity of nanoCeria was also demonstrated via H_2O_2 treated ceria nanoparticles suspension ($H_2O_2 + 2Ce^{3+} + 2H^+ \rightarrow H_2O + 2Ce^{4+}$ and $H_2O_2 + Ce^{4+} \rightarrow O_2 + 2H^+ + 2Ce^{3+}$).

The main objective of this work is to produce nanoparticles and to combine an experimental study with molecular modeling in order to study their behavior as antioxidant agents. The structure and morphology of the particles were investigated.

A series of data regarding the behavior of Cerium (III) oxide in the presence of oxygenated water were collected (oxygen detector) and were analyzed with regard of the kinetic of the changing of the oxidation state of Ce process. A model with two exponentials has been identified as the best fit for the process. The model can be further interpreted as a complex process involving a Michaelis-Menten mechanism.

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P-20

Computational Studies of Silicon-Containing Benzoic Acid Derivatives: 4–((Trimethylsilyl)methoxy) and 4–(3–(Trimethylsilyl)propoxy)Benzoic Acids

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Benzoic acid derivatives are important compounds that can be employed as chemicals, pharmaceuticals, agrochemicals and consumer products [1]. Therefore, it is essential to reveal the structural-electronic insights of this type of molecules.

Herein, we report theoretical outcomes related to computer-aided molecular modeling of two benzoic acid derivatives containing trimethylsilyl tails, namely, 4–((trimethylsilyl)methoxy) (**1**) and 4–(3–(trimethylsilyl)propoxy) (**2**) benzoic acids. Theoretical studies of these two molecules were performed by using the quantum chemical techniques, such as Density Functional Theory (DFT B3LYP/6–31+G**), Hartree–Fock (HF/6–31+G**) and semiempirical methods (PM3, PM6 and PM7). The optimized molecular geometries were found to be in good agreement with observed structures resulted from X–ray diffraction patterns. Maximum electronic absorption bands noticed at 272–287 nm (UV–vis spectra) were attributed to $\pi \rightarrow \pi^*$ transitions. These absorption bands were in reasonable agreement with the time dependent density functional theory (TD–DFT) outcomes (Fig.1). Calculated vibrational frequencies by DFT method were assigned and compared with experimental infrared spectra. The mapped electrostatic potentials disclosed the most important reactive sites that were correlated with the observation of the dimer supramolecular structures formed in the crystals by hydrogen–bonding. In addition, we computed (for titled molecules) the energies of frontier molecular orbitals (HOMO and LUMO), energy gap, dipole moment and other molecular descriptors, thereby providing structural-electronic insights.

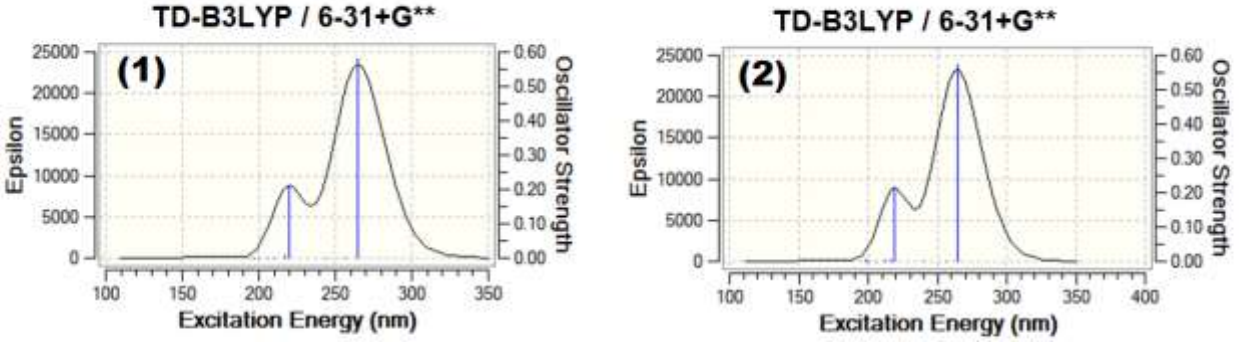

Figure 1. Theoretical electronic absorption spectra for compounds **1** and **2** (in $CHCl_3$ implicit solvent).

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P-21

Data processing: dull or fun task?

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Computers and software, as we know them, are around us for nearly 50 years, and we use them to ease up our daily work or for entertainment.

In the field of science we need them to perform complex calculations. Calculations that would normally take great amount of time solving them by hand, with a computer it can be performed in a heartbeat.

However performing computation is not the only field where a piece of software (code) can help us in our work. Handling files (scanning them, creating new files with specific instructions for input data) it can be a tedious work, especially when you have to deal with thousands of them.

This work presents a small software that simplifies the task, by creating input files for back end quantum chemistry programs like Gaussian[1], or by analyzing the *.log files which are the output result from these type of calculations.

As described above the software has two main parts: input file generation and analysis. The input file generation consists of processing the files with spinput, gjf and xyz extension. In these files the software recognizes the coordinate system and writes it to new file with specified rout card, title and charge/spin multiplicity (these are given by the user). The analysis is fully automated. The program decompresses the tar/tgz files, reads through every log record and separates the ones containing errors from the ones having imaginary frequencies. The files with imaginary frequencies are then converted with the help of Xvibs[2] and (M)AWK[3] to the new input data with the new coordinate system.

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2. Copyright 1999, 2000 Bradley A. Smith; 2007, 2010 Kun Attila-Zsolt (locally modified version)
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P-22

Towards a unitary description of E-O and E-N bonds (E = Si, Ge, Sn); from inorganic ethers to amines and isoelectronic species

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The chemistry of siloxanes was widely developed in the last decades, as they represent the backbone of silicon-based polymer industry. Nevertheless, their peculiar structural features led to further investigations by theoretical means, opening thus a debate on the nature of Si-O bond. Recent studies[1,2] shed more light on the phenomena, stressing the influence of vicinal hyperconjugative interactions on the molecular geometry of the disiloxane molecule. Previous data[3] published by our group revealed that similar patterns can be extended for the heavier analogues with Ge and Sn, and further emphasized that *p→d* interactions dictate to a lesser extent the structures of E-O-E species (E =Si, Ge, Sn).

The present study aimes to extend the theoretical model developed for inorganic ethers towards $(ER_3)_3N$ amines (E = Si, Ge, Sn; R = H, Me) and other isoelectronic species, in which the central N atom was replaced by Oxygen, Carbon or Boron. All these derivatives (Figure 1) were investigated at the DFT level of theory. Natural Bond Orbital (NBO) analyses were performed on the optimized structures, in order gain insight on the electronic effects occurring within them.

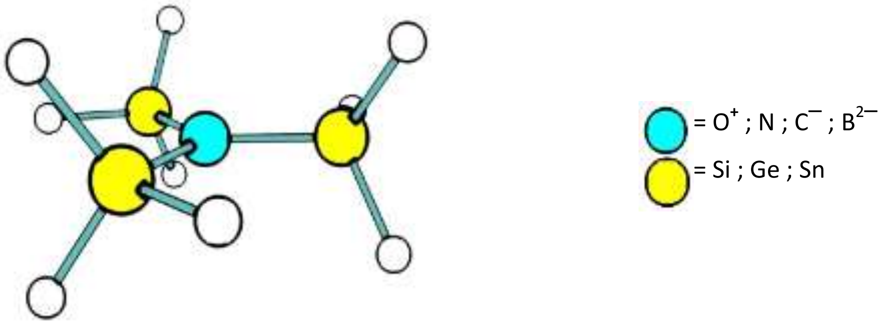

Figure 1. Structural model of the investigated inorganic amines of the type $(ER_3)_3N$ (E = Si, Ge, Sn) and related isoelectronic species with O, C and B

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P-23

Nickel-substituted iron dependent cysteine dioxygenase: implications for the dioxygenation activity of nickel model compounds

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A DFT study was carried out to investigate the ability of Ni-substituted iron-dependent cysteine dioxygenase (CDO) to catalyze the oxidation of cysteine to cysteine sulfinic acid. The first steps of the commonly accepted mechanism for CDO, the O_2 activation mechanism, suggests the binding of O_2 to the metal ion, converting O_2 to O_2^-, followed by the attack of the distal oxygen atom on the cysteine sulfur. An alternative mechanism entailing the attack of the cysteine sulfur on the proximal oxygen atom of the dioxygen moiety to form a persulfenate intermediate without any redox exchange between the metal ion and the O_2 ligand, is supported by an X-ray crystal structure showing a CDO with a bound cysteine persulfenate, and also supported by data on the oxidation of thiols catalyzed by Ni(II) compounds. Our results show that the O_2 activation mechanism with a Ni-substituted active site follows the same pattern as native CDOs albeit with much higher energy barriers for the formation of the intermediates suggesting that the reaction might not be biologically feasible. Conversely, the immediate cleavage of the persulfenate S-O bond in the alternative mechanism suggests that cysteine persulfenate might not be a true intermediate in catalytic cycle of CDOs. [1]

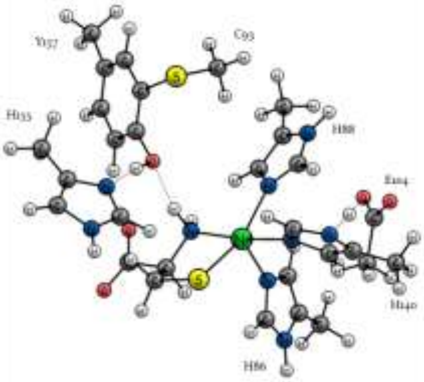

Figure 1. The optimized X-ray crystal structure of Ni substituted CDO (pdb id 4IEV) including truncated first and second shell residues.

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P-24

Chemometric methods applied in questing phytoglobins roles in plant stress conditions

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Untargeted metabolomics, at a given development stage, at a certain tissue level is an approach that is more and more popular nowadays due to this comprehensive analysis of metabolites that reveal what processes take place in a tissue and thus allow physiological interpretation in given conditions [1]. However, this approach is very challenging and difficult due to the vast array of metabolites that are evaluated and their different chemical properties. This difficulty of handling a great amount of data can be faced using accurate advance analytical tools coupled with robust chemometric methods that are able to extract the core information and lead to clues and better understanding of how plants respond in this stress conditions [2]. Several phenolic compounds belonging to different classes were comparatively analyzed for their ability to reduce oxidized forms of the three non-symbiotic phytoglobins which were generated *in situ*. The kinetic profiles of the substrates oxidation were evaluated using principal component analysis (PCA) and cluster analysis (CA). The three globins were different both in terms of kinetic profiles and also in mechanism. The electron donor ability of the studied phenolics depended upon phytoglobins type and did not depend only upon their chemical structure but also upon presumptive binding pocket environment. Hardly any metabolomic information is known about the nsHbs and nitrosative stress, although, the globins in general are known to be involved in RNS regulation.

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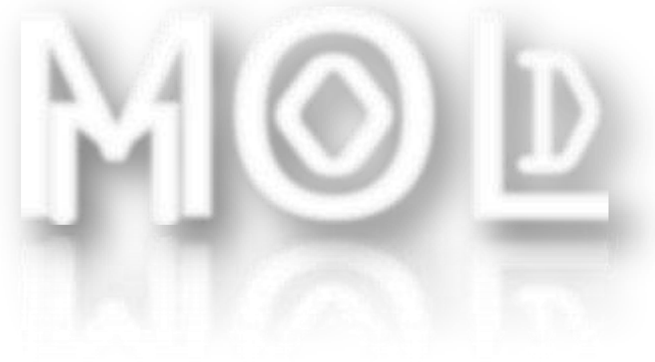

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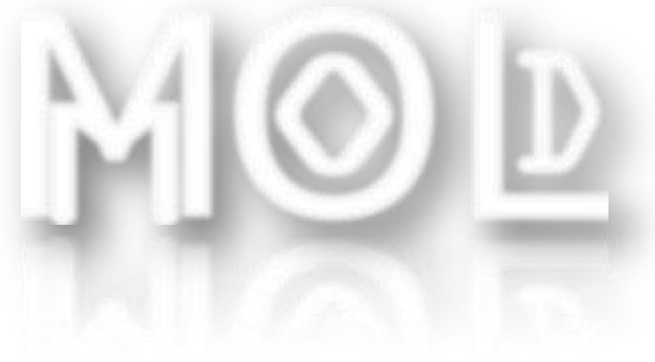

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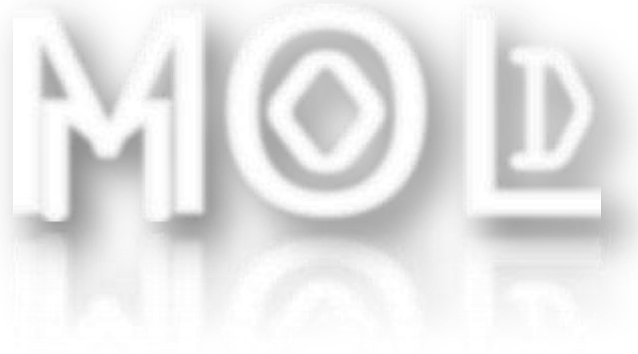

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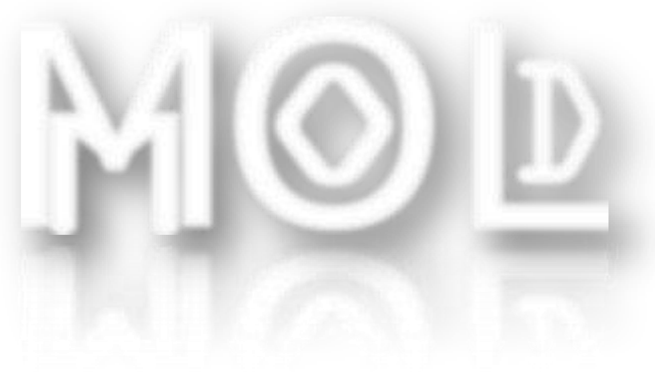

MolMod 2018 locations:
Presentations: Faculty of Chemistry and Chemical Engineering, 11, Arany Janos Street
Cocktail Party: Universitas Student House, 7, Pandurilor Street