19th deMon developers workshop

deMon2k density of Montréal deMon-nano

Fréjus, France
May 26-30 2019

Organizing committee

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Carine Clavaguéra (CNRS, Université Paris Sud, Orsay)
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Tzonka Mineva (CNRS Institut Charles Gerardth, Montpellier)
Mathias Rapacioli (CNRS, Université Paul Sabatier, Toulouse)

Acknowledgments

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Réseau Français de Chimie Théorique (RFCT)
Laboratoire d'Excellence NEXT (Toulouse, France)
Institut de Recherche sur les Systèmes Atomiques et Moléculaires Complexes (Toulouse, France)
CECAM nodes Grand Sud-Ouest and Rhône-Alpes

We kindly thank Natacha Gillet and Xiaojing Wu for their demoniac representations of the Fréjus' demons.

WELCOME

We are very glad to welcome you in Fréjus for the 19th deMon developers workshop.

Since 2000 the "deMon developers workshops" serve to discuss the program evolutions. It has become a good custom to make it a scientific forum for discussions with scientists who are familiar with other methods, algorithms and programs, not common to the deMon developer's community. Previous "deMon developers" workshops were held in Canada 2000, Mexico 2001, Switzerland 2002, Sweden 2003, Italy 2004, Germany 2005, Canada 2006, France 2007, India 2009, Brazil 2010, Germany 2011, China 2012, France 2013, Mexico 2014, Bulgaria 2015, China 2016, Canada 2017, Mexico 2018.

We are sure you will contribute to make the 19th workshop an enthralling event with several exiting discussions, and hopefully new collaborations. We wish you all good moments spent together in the meeting room and around drinks and diners.

Website of deMon2k: http://demon-software.com
Website of deMon-Nano: http://demon-nano.ups-tlse.fr

You can download the electronic version of the booklet there:

Sunday, May 26th

18:00 – 20:00 arrival

Monday, May 27th

8:00 - 8:45 : registration
8:45 : welcoming words
Morning Session, Chairs: Aurélien de la Lande and Olga Malkina

Time	Speaker	Title
9:00–9:30	Dennis Salahub	deMon Quo Vadis?
9:30–10:00	Andreas Köster	Development Report on deMon2k Version 6.x
10:00–10:30	Patrizia Calaminici	Mixed second and third energy derivatives from Auxiliary Density Functional Theory
10:30–11:00	Coffee break	
11:00–11:30	Elfi Kraka	Exploiting vibrational spectra - the local vibrational mode analysis
12:00-12:30	Maximilien Levesque	Embedding by molecular density functional theory
12:30 – 13:00	Fernand Louisnard	Parallel-Tempering Path-Integral Molecular Dynamics approach to water clusters simulations
13:00 – 14:30	Lunch	

Afternoon Session, Chair: Andreas Köster and Patrizia Calaminici

Time	Speaker	Title
14:30 – 15:00	Emmanuel Fromager	A many-weight-dependent approach to excited states in density-functional theory for ensembles
15:00 –15:30	Luis Hernández-Segura	Linear response time dependent auxiliary density functional theory in deMon2k: Current development and perspectives
15:30 – 16:00	Adèle Laurent	Shedding Light on new Photochrome
16:00 – 16:30	Coffee break	
16:30-17:00	Lars Pettersson	Storing Solar Energy in Chemical Bonds
17:00-17:30	Henry Chermette	Coordination chemistry of Zn2+ with sal(ph)en ligands: Tetrahedral coordination vs penta-coordination. A conceptual DFT analysis.
17:30 – 18:30	Round Table: Chair: J. Cuny, A. de la Lande, T. Mineva	QMMM and Free Energy Sampling in deMon.6.0.2: Accomplishments & Further actions
18:30 - 20:00	Welcoming cocktail & POSTER SESSION	

20:00	Diner

Tuesday, May 28th

Morning Session, Chairs: Natacha Gillet, Mark Casida

Time	Speaker	Title
9:00–9:30	Evgeni Posenitskiy	Implementation of non-adiabatic dynamics and its application to the relaxation of excited polyacenes
9:30–10:00	Mark Casida	Comparison of TD-DFTB with and without long-range correction for modeling energy and charge transfer times
10:00–10:30	Thomas Niehaus	Range-separated functionals in DFTB for ground and excited states
10:30–11:00	Coffee break	
11:00–11:30	Natacha Gillet	Recent development of DFTB/MM for transfer mechanisms in proteins
12:00-12:30	Elise Dumont	QM/MM investigations of DNA lesions: what can we learn so far ?
12:30 – 13:00	Luigi Genovese	Potentialities of Wavelet formalisms for large-scale DFT calculations and beyond
13:00 – 14:30	Lunch	

Afternoon Session, Chair: Bernardo Antonio Zúñiga Gutiérrez and Xiaojing Wu

Time	Speaker	Title
14:30 – 15:00	Bernardo Antonio Zúñiga Gutiérrez	Recent advances in the magnetic property calculation with deMon2k
15:00 –15:30	Olga Malkin	A mystery of a through-space indirect spin-spin coupling between two hydrogen atoms
15:30 – 16:00	Maylis Orio	Computational study of magnetic properties of polynuclear transition metal complexes
16:00 – 17:00	Coffee break	
17:00-17:30	Vladimir Malkin	Visualization of EPR Hyperfine Structure Coupling Pathways
17:30-18:00	Ismail Can Oguz	Spin polarization of Fe-N-C catalysts: deMon2k vs VASP calculations
18:00-18:45	Round Table (Chair: D.R. Salahub)	Integration of new modules in deMon2k and deMon nano, version control, experience-sharing with K. Hasnaoui (*Institut du développement et des ressources en informatique scientifique*)

19:30	Workshop Diner

Wednesday, May 29th

Morning Session, Chairs: Jérome Cuny and Tzonka Mineva

Time	Speaker	Title
9:00–9:30	Léo Dontot	Theoretical insight into the dissociation of PAH clusters
9:30–10:00	Aurelio Alvarez-Ibarra	Implementation of Ehrenfest MD for efficient electron/nuclear coupled dynamics
10:00–10:30	Adrian Amor Martínez Carranza	Symmetry adapted Density Fitting
10:30–11:00	Coffee break	
11:00–11:30	Andreas Savin	Judging density functionals using databases
12:00-12:30	Jiri Hostas	Towards modelling of oil upgrading – Conformational search of molybdenum disulfide nanoparticles
12:30 – 13:00	deMon Action Items - Chair : D.R. Salahub	
13:00 – 14:30	Lunch	

Afternoon Session, Chair: Fabien Cailliez

Time	Speaker	Title
14:30 – 15:00	Xiaojing Wu - Karim Hasnaoui	Implementation of Real-Time Propagation of the Electronic Density with Scalapack library
15:00 –15:30	Angela Parise	Ultrafast energy relaxation following interaction of biomolecules with ionizing radiations

20:00	Diner

Thursday, May 30th

Morning Session, Chair: Karim Hasnaoui

Time	Speaker	Title
9:00–9:30	Luis Lopez Sosa	Constraint optimization on a hypersphere
9:30–10:00	Aurélien de la Lande	Multicomponent DFT with density fitting
10:00–10:30		
10:30–11:00	Fabien Cailliez	
11:00–11:30	Nohad Gresh	Recent validation of the ab initio-grounded SIBFA molecular mechanics/dynamics potential.
12:00	Lunch and departure	

ORAL PRESENTATIONS

deMon Quo Vadis ?

Dennis Salahub*[1]

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I will give a brief update of the main functionalities of deMon2k and deMonNano and go over the Action Items from last year's workshop in Guadalajara, in order to start the creative juices flowing.

Development Report on deMon2k Version 6.x

Andreas M. Köster[1,2*]

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In this presentation, I will report about current developments, merges and bug fixes in the deMon2k developer version 6.x [1]. After a general overview, the presentation will focus on the stabilization of the self-consistent field (SCF) procedure. Particular attention will be given to the numerical stability of the Lee-Yang-Parr (LYP) correlation functional, the use of very large extended basis sets with small exponents, the combination of large basis sets with relative small auxiliary function sets and the auxiliary density functional theory (ADFT) gradient calculation with effective and model core potentials. The discussed SCF problems may arise in specific hybrid functional (B3LYP, Becke H&H) and range-separated [2] hybrid functionals and in ADFT perturbation theory applications [3]. Most often, they arise from the ADFT specific use of the auxiliary density for the calculation of exchange-correlation energies and potentials. I will present the problem analysis along with possible solutions [4]. The talk will finish with some perspectives about new theoretical developments of fitted exact exchange currently under investigation in my research group at Cinvestav.

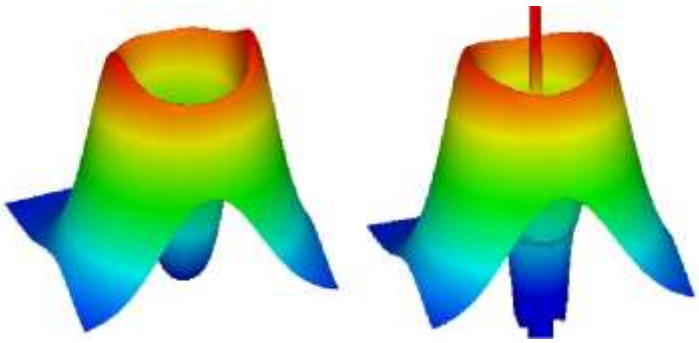

Figure 1: Comparison of Kohn-Sham density (left) and ADFT density (right) at a Cerium atom employing a small core effective core potential.

References
(1) http://www.demon-software.com
(2) Delesma, F.A.; Geudtner, G.; Mejía-Rodríguez, D.; Calaminici, P.; Köster, A.M., Range-Separated Hybrid Functionals with Variational Fitted Exact Exchange. *J. Chem. Theor. Comput.* 2018, 14, 5608.
(3) Delgado-Venegas, R.I.; Calaminici, P.; Köster, A.M., Mixed Second and Third Energy Derivatives from Auxiliary Density Functional Theory. *Mol. Phys.* in press.
(4) Pedroza-Montero, J.N.; Morales, J.L.; Geudtner, G.; Álvarez-Ibarra, A.; Calaminici, P.; Köster, A., Variational Density Fitting with a Krylov Subspace Method. to be submitted.

Mixed second and third energy derivatives from auxiliary density perturbation theory

Rogelio I. Delgado-Venegas[1], Patrizia Calaminici*[1], Andreas M. Köster[1]

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The working equations for the calculation of mixed second- and third-order energy derivatives in the framework of auxiliary density functional theory are presented. The perturbations with respect to nuclear displacements and external homogeneous electric field components are calculated with auxiliary density perturbation theory. The presented energy derivative working equations were implemented in deMon2k and validated by vibrational spectra simulations within the double harmonic approximation (1). The effect of the auxiliary functions on the IR and Raman spectra simulation were analyzed for the C_{60} fullerene. As applications, the results of vibrational spectra of icosahedral carbon fullerenes with up to 540 atoms calculated without employing symmetry constraints will be presented and discussed.

References

(1) Delgado-Venegas, R.I.; Calaminici, P.; Köster A.M., Mixed second and third energy derivatives from auxiliary density perturbation theory. *Mol. Phys. 2019*, in press.

Exploiting vibrational spectra - the local vibrational mode analysis

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Information on the electronic structure of a molecule, the strength of its bonds, its geometry, and its conformational flexibility is encoded in the normal vibrational modes. However, normal vibrational modes are generally delocalized caused by electronic and mass coupling, hindering the direct access to this information. The electronic coupling can be suppressed by solving the Wilson equation, which involves the diagonalization of the force constant matrix. Konkoli and Cremer (1) showed that the remaining mass coupling can be eliminated by solving a mass-decoupled equivalent of the Wilson equation leading to local vibrational modes, which are associated with internal coordinates such as bond lengths, bond angles, and dihedral angles. Zou, Kraka and Cremer (2) verified that there is a one-to-one relationship between the local and the normal vibrational modes through an adiabatic connection scheme, allowing a normal mode decomposition into local mode contributions, and as such the detailed analysis of a vibrational spectrum. This is of particular value, given the fact that the local mode analysis can be applied to both calculated and measured spectra.

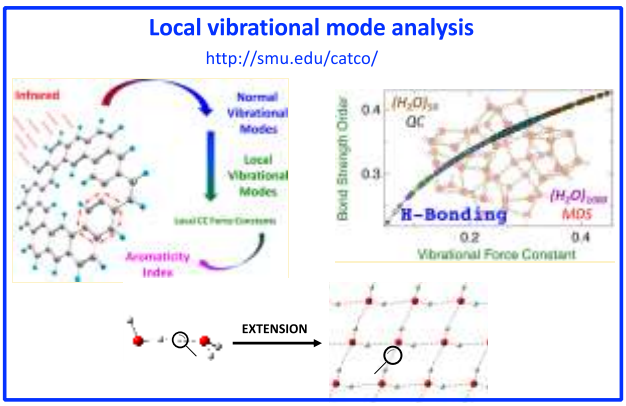

Figure 2: Some successful applications of the local vibrational

The local stretching force constants obtained from local vibrational modes provide a direct measure of the intrinsic strength of a chemical bond or weak chemical interaction, reflecting all electronic effects influencing the strength of the bond under consideration. (3)

We will highlight successful applications of the local mode analysis i) to systematically excel our current knowledge about weak chemical interactions, stretching form halogen, chalcogen, pnicogen to tetrel bonding; ii) to substantially deepen our understanding of the complexity of hydrogen bonding networks; iii) to exploit a new way to characterize metal ligand bonding and iv) how to extend the local mode analysis to periodic systems and solids. (4) Finally we will discuss how the local mode analysis can be interfaced with the DeMon2K program.

References

(1) Konkoli, Z; Cremer, D., A New Way of Analyzing Vibrational Spectra I. Derivation of Adiabatic Internal Modes. *Int. J. Quant. Chem.* 1998, *67*, 1-11.

(2) Zou, W.; Kalescky, R.; Kraka, E.; Cremer. D, Relating Normal Vibrational Modes to Local Vibrational Modes with the help of an Adiabatic Connection Scheme. *J. Chem. Phys.* 2012, *137*, 084114.

(3) Zou, W.; Cremer. D. C_2 in a Box: Determining its Intrinsic Bond Strength for the $X^1\Sigma^+_g$ Ground State. *Chem. Eur. J.* 2016, *22*, 4087-4097.

(4) Tao, Y.; Zou, Sethio, D.; Verma, N.; Qui, Y.; Tian, C.; Cremer, D.; Kraka, E. In Situ Measure of Intrinsic Bond Strength in Crystalline Structures: Local Vibrational Mode Theory for Periodic Systems. *J. Chem. Theory Comput.*, 2019, DOI: 10.1021/acs.jctc.8b01279

Embedding by molecular density functional theory

Maximilien Levesque[1]*

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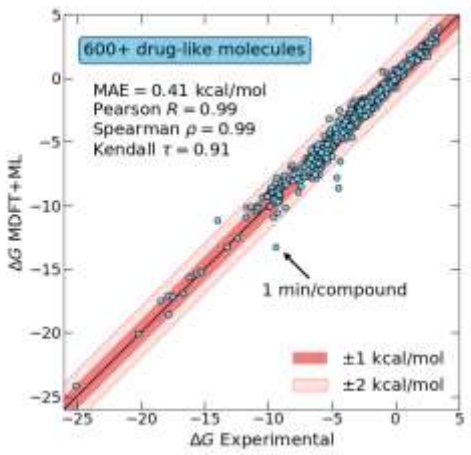

Chemistry often happens in a solvent made of a large number of molecules like water. To take into account this embedding medium, several methods are available to *in silico* experimentalists:

(i) One can forget about the molecular nature of the solvent: no hydrogen bonding, no crowding effect ... Those primitive models, like the polarizable continuums, focus on macroscopic properties of the solvent like its dielectric permittivity. It's a crude approximation but is numerically cheap, fast, and arbitrarily configurable.

(ii) One can use atomistic simulations like molecular dynamics. The numerical cost increases by 4 to 5 orders of magnitude with respect to solution (i) but you gain insight into all the molecular details... If it fits into your computers.

(iii) I will present the molecular density functional theory (MDFT). I will show how MDFT computes rigorously and within minutes some equilibrium properties of complex solutes like a protein or many small molecules. I will focus on free energies, solvation profile, and so-called water-maps.

I will discuss advantages of MDFT (fast, rigorous, systematically improvable), its drawbacks (it's a theory and thus rely on approximations), and how we use machine learning to improve its predictability. I will give perspectives on the coupling between ab initio calculations and MDFT.

Parallel-Tempering Path-Integral Molecular Dynamics approach to water clusters simulations

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The path-integral (PI) molecular dynamics approach based on Feynman's formalism allows to include nuclear quantum effects (NQEs) within classical molecular dynamics simulations (1,2). In turn, parallel-tempering (PT) simulations allow to achieve a complete exploration of the potential energy surfaces of complex molecular systems (3) Combining both approaches is thus important to achieve accurate MD simulations of water clusters. The research group of Michelle Ceriotti recently released a python code (i-PI v 2.0) that performs molecular dynamics using this PT-PIMD approach. i-PI can be plugged to any external code that computes energies and forces, deMonNano or deMon2k in the present case (4)

In my presentation, I will introduce the implementation of the socket interface between i-PI and both deMonNano and deMon2k and discuss applications of the PT-PIMD approach to small water clusters. Besides, to improve computational efficiency, we would like to have this PI-PTMD approach natively implemented in both deMonNano and deMon2k. PTMD has already been implemented in deMonNano a few years ago and I will now present and discuss its recent implementation in deMon2k. I will also give some preliminary PTMD results obtained with deMon2k.

References

1 S. Habershon, D. E. Manolopoulos, T. E. Markland, T. F. Miller III *Annu. Rev. Phys. Chem.* 2013, 64, 387-413.

2 M. Ceriotti, W. Fang, P. G. Kusalik, R. H. McKenzie, A. Michaelides, M. A. Morales, T. E. Markland *Chem. Rev.* 2016,116, 7529–7550.

3 Y. Wang, V. Babin, J. M. Bowman, F. Paesani *J. Am. Chem. Soc.* 2012, 134, 11116–11119.

4 R. Petraglia, A. Nicolaï, M. D. Wodrich, M. Ceriotti, C. Corminboeuf *Journal of computational chemistry*, 2016, 37, 83-92.

A many-weight-dependent approach to excited states in density-functional theory for ensembles

Emmanuel Fromager*[1]

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I will discuss the calculation of excited-state energy levels in the context of (time-independent) ensemble density-functional theory (eDFT). A many-weight-dependent generalization of the original Gross-Oliveira-Kohn formulation of eDFT (1) will be introduced. I will show that, if the many-weight dependence of the ensemble exchange-correlation functional is known, then it becomes possible to extract from a single eDFT calculation the energies of all the states within the ensemble (2). The extraction procedure, which is in principle exact, is expected to pave the way towards the calculation of excited-state properties within eDFT. Exact and approximate results will be shown for the prototypical asymmetric Hubbard dimer (2-4). The construction of *ab-initio* weight-dependent density-functional approximations will also be discussed.
If time permits, I will show how the formalism can be generalized to charged excitations, thus giving access to ionization potentials and electron affinities (5).

References

(1) E. K. U. Gross, L. N. Oliveira, and W. Kohn, Phys. Rev. A 37, 2809 (1988).
(2) K. Deur and E. Fromager, J. Chem. Phys. (2019). [preprint: arXiv:1812.02461]
(3) K. Deur, L. Mazouin, and E. Fromager, Phys. Rev. B 95, 035120 (2017).
(4) K. Deur, L. Mazouin, B. Senjean, and E. Fromager, Eur. Phys. J. B 91, 162 (2018).
(5) B. Senjean and E. Fromager, Phys. Rev. A 98, 022513 (2018).

Linear response time dependent auxiliary density functional theory in deMon2k: Current development and perspectives

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Current developments of Linear Response Time Dependent Auxiliary Density Functional Theory (TDADFT) within deMon2k and perspectives for future work are presented. All implementations discussed are extensions of previous works from Ipatov *et al.* [1] and Carmona *et al.* [2]. They are collected in a local developer version of deMon2k that is now working with the 6.x version of deMon2k. Improvements include the parallelization of Davidson steps [2], implementation of ERIS DIRECT [2] and MIXED for the matrix vector operations, implementation of the Davidson algorithm for Spin-Flip Linear Response Time Dependent Auxiliary Density Functional Theory (SF-TDADFT) and optimization of the full matrix diagonalization. We also present a validation of the Davidson algorithm. As options for the future development we will discuss the implementation of the Lanczos shift and invert eigensolver from ARPACK [3] and the implementation of hybrid functionals for both, TDADFT and SF-TDADFT, calculations.

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \omega \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix}$$

Referencess

[1] Ipatov, A. *et al. J. Mol. Struct. (THEOCHEM)* 2006, 762(1-3), 179-191.

[2] Carmona-Espíndola, J. *et al. Can. J. Chem.* 2013, 91(9), 795-803.

[3] Sorensen, D. C. *et al.* https://www.caam.rice.edu/software/ARPACK/.

Shedding Light on new Photochrome

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The majority of organic photochromic materials employ azobenzenes (AZ), spiropyrans (SP), or diarylethenes (DA) due to their excellent performances (large conformational changes and high fatigue resistance). However, they are often triggered by high-energy irradiation, which can cause photodamage of healthy cells or photodegradation of the studied materials. Within that framework, two new classes of photochromes have recently highlighted and display highly interesting photochemical properties, named donor–acceptor Stenhouse adducts (1-3) and Iminothioindoxyl (4).

In those works performed in collaboration with Feringa's and Foggi's groups, we will present the recent investigations on new photochrome, i.e. photomechanism and solvent effects. We will show how theoretical tools (DFT and TD-DFT) succeed to get deeper insights into ultrafast time-resolved pump-probe spectroscopy in both the visible and IR regions.

Reference (ACS Style)

(1) Helmy, S. ; Oh, S. ; Leibfarth, F. A. ; Hawker, C. J.; de Alaniz, J. R., Design and synthesis of donor–acceptor stenhouse adducts: a visible light photoswitch derived from furfural. *J. Org. Chem.* 2014, 79 (23), 11316-11329.

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(3) Lerch, M. M.; Di Donato, M.; Laurent, A. D.; Medved, M.; Iagatti, A.; Bussotti, L., ... & Feringa, B. L., Solvent Effects on the Actinic Step of Donor–Acceptor Stenhouse Adduct Photoswitching. *Angew. Chem. Int. Ed.* 2018, 57 (27), 8063-8068.

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Storing Solar Energy in Chemical Bonds

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Global climate change requires that we not only build a closed carbon cycle in terms of energy use, but also develop efficient means to capture and store intermittent solar energy. In one part of the project we thus work on electrochemical and photochemical CO_2 conversion back into fuels and chemicals to close the cycle, thus storing energy in chemical bonds. In another, we work on generating hydrogen from waste products, such as glycerol from biodiesel production and black liquor, which is a waste product from pulp production. Using alcohols or sugar acids can reduce the energy cost by 60-70% over traditional water splitting, but requires efficient and low-cost electrocatalysts to be practically useful. Our task is to computationally screen for such electrode candidates that will then be synthesized and tested experimentally.

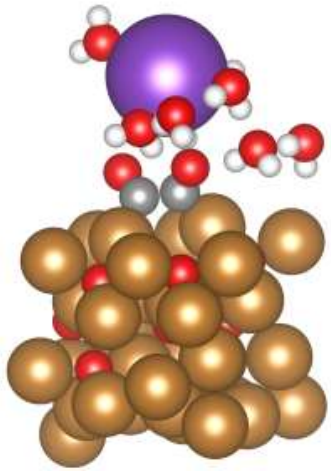

Figure 3: Periodic model of final state in electrochemical C-C coupling from two CO on amorphous copper with subsurface oxygen.

Here I will describe our work on oxide-derived copper catalysts for highly selective electrochemical CO_2 reduction into ethylene (1) as well as a descriptor-based approach to transferring a complete reaction path from one catalyst to any other (2) which we will use when screening electrocatalysts for hydrogen production.

References

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2. Yu, L.; Vilella, L.; Abild-Pedersen, F., Generic approach to access barriers in dehydrogenation reactions. *Comms. Chem.* 2018, *1*, 2.

Coordination chemistry of Zn^{2+} with sal(ph)en ligands: Tetrahedral coordination vs penta-coordination. A conceptual DFT analysis.

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The Lewis acidic character within a series of Zn-Sal(ph)en complexes is reviewed and revisited. Besides traditional analyses found in the literature, conceptual density functional theory descriptors are used to assess this acidic character. Using these tools, we highlight how the nature of the bridging diamine linker in the Schiff base ligand controls this feature mainly responsible of the coordination geometry of these complexes. This Lewis acidic behavior is addressed first by application of the usual dual descriptor to a prototypical complex, namely $ZnCl_4^{2-}$. However, the usual dual descriptor exhibits significant weaknesses to retrieve the electrophile part on the metal cation of sal(ph)en complexes. The inclusion of the densities of the electronic excited states by the so-called state specific dual descriptor allows us to recover successfully the appropriate reactivity of these chosen complexes with different diamine bridges in flexible to semi-rigid then to rigid ranges. The relaxation of the orbitals through the excitation processes are discussed.

Size dependence of the time-resolved electronic relaxation of polyacenes

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The Tully's fewest-switches trajectory surface hopping algorithm (1) is implemented within the framework of the Time-Dependent Density Functional based Tight Binding method (TD-DFTB) (2) in the deMon-Nano code to simulate the energy relaxation following absorption of a UV photon by Polycyclic Aromatic Hydrocarbons (PAHs). We first report some implementation details related to the surface hopping scheme.

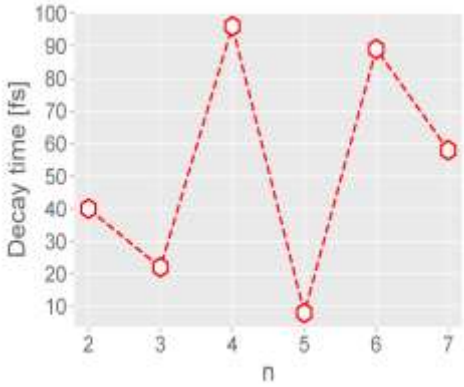

Figure 4: Decay time of the brightest singlet excited state (red hexagons) as a function of number of aromatic cycles in the polyacene.

The approach is further applied to study the size effect on the ultrafast dynamics in excited states for a special class of PAH species called polyacenes. We determine the dynamical relaxation times and discuss the underlying mechanisms. Our results show that there is a striking alternation (see Fig. 1) in decay times of the brightest singlet state for neutral polyacenes with 3 to 6 aromatic cycles. The alternation corresponds to an order-of-magnitude variation between roughly 10 and 100 fs and is correlated with a qualitatively similar alternation of energy gaps between the brightest state and the state lying just below in energy.

We acknowledge the support of the European Union (EU) and Horizon 2020 funding awarded under the Marie Skłodowska-Curie action to the EUROPAH consortium, grant number 722346 and HPC resources from CALMIP (Grant 2018-P18019).

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Comparison of YD-DFTB With And Without Long-Range Correction For Modeling Energy And Charge Transfer Times

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The implementation of time-dependent (TD) density-functional tight binding (DFTB) and TD long-range corrected (lc) DFTB in the DFTBaby (1) fewest-switches surface hopping (FSSH) program is tested out for a particularly difficult problem, namely for the investigation of energy transfer (ET) and charge transfer (CT) times in a model organic heterojunction consisting of a single buckminsterfullerene (C_{60}) molecule in contact with a single pentacene (Pent) molecule. Second-order algebraic diagrammatic construction [ADC(2)] and second-order coupled cluster (CC2) *ab initio* calculations of the singlet excitation manifold with and without spin scaling reveal an average of more than one state every 0.1 eV. State assignments remain roughly invariant among the different *ab initio* methods. This is too much to expect for more approximate methods such as TD density-functional theory (TD-DFT) and TD-DFTB, but we may hope to get either the general shape of the absorption spectrum or the general energy range of the absorption spectrum. TD-B3LYP and TD-DFTB spectra are red shifted compared to the ADC(2) and CC2 spectra by about 0.5 eV. In contrast, TD-CAM-B3LYP and TD-lc-DFTB spectra are correctly centered around the main absorbtion peaks in the spin-scaled *ab initio* calculations. Although an accurate description of the character and ordering of the individual states in the dense manifold of singlet excited states is not possible, we find it encouraging that the TD-lc-DFTB method centers this manifold where we expect it should be. TD-DFTB and TD-lc-DFTB FSSH calculations of ET and CT times are reported (2).

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Range-separated functionals in DFTB for ground and excited states

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In this contribution, we summarize recent advances in the development of the density functional based tight-binding method (DFTB) (1). We first present a generalization of the method for the use with range-separated exchange correlation functionals (LC-DFTB) (2). In contrast to the traditional DFTB scheme, the density matrix is used as basic variable in an expansion of the energy functional in generalized Kohn-Sham theory. The theory provides access to hybrid functionals in DFTB as a special case. Implementation issues and numerical aspects of the new scheme are also covered. We present results for quasiparticle gaps in organic molecules and discuss polaron formation in polymers (3). We also present the recent time-dependent extension of LC-DFTB to treat electronic excited states, which overcomes the notorious problem of local functionals with charge-transfer excitations in very large systems with thousands of atoms (4,5).

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Recent development of DFTB/MM for transfer mechanisms in proteins

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For decades, the multiscales QM/MM approaches have proven their relevance in the study of the reactivity of biological molecules. To reach a balance between the computational cost of the description of the quantum part and the sampling of the environment structure and dynamics, several strategies such as biased simulation or use of specific QM/MM coupling can be used. One can also play with the level of theory of the quantum part, which often constitutes the limiting part in term of simulation time. In this view, semi-empirical methods (AM1, PM6, DFTB…) constitute a good alternative to DFT to decrease the computational cost. In the Pr. Elstner's group, we are developing DFTB[1] (Tight Binding DFT) and DFTB/MM methods to describe biological transfers of charge, proton or exciton. Our Fragment Orbital (FO)-DFTB/MM protocol[2] , dedicated to the study of long-range charge transfer, can be used for the determination of driving forces and electronic coupling and to propagate the additional charge over several redox partner at the nanosecond timescale in an unbiased fashion. [3] DFTB/MM protocol have been also use to treat proton transfer and we propose a new coordinate for charge transfer coupled to proton motion in biased protocol such as metadynamic.[4] Finally, the recent development of long-range corrected DFTB[5] allows the calculation of excitation in proteins and a protocol similar to the FO-DFTB/MM scheme for electron transfer will be proposed for exciton propagation in photosensitive protein.

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QM/MM investigations of DNA lesions: what can we learn so far ?

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Whereas DNA is conceptually simpler than proteins, as a polymer with 4 constitutive nucleobases *vs.* 20 residues, it presents a rich oxidatively-induced and photoinduced chemistry that gives rise to potentially more than 70 lesions identified by spectrometry HPLC-MS/MS. Some intermediates are known to be central in the oxidation cascade, such as the radical cation of guanine, but the mechanisms leading to DNA lesions are poorly identified. Analogously, the triplet state of thymine is the hotspot for photolesions, and generated widely through photosensitization (2). I will present our recent and ongoing QM/MM efforts to investigate the mechanistic pathways for important lesions (1), stressing the need for new efficient computational schemes. I will also exemplify the combinatorial nature of DNA lesions induction that calls for efficient hybrid schemes, with the need to describe the dynamic nature of DNA lesions.

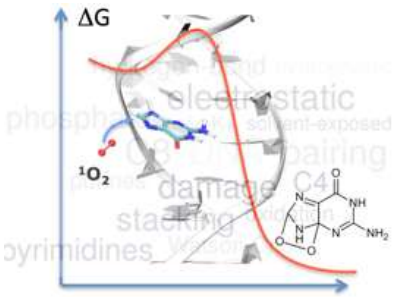

Figure 5: Reaction profile for the formation of a transient guanine endoperoxide within B-DNA.

This work was performed within the framework of the LABEX PRIMES (ANR-11-LABX-0063) of Université de Lyon.

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Potentialities of Wavelet formalisms for large-scale DFT calculations and beyond

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The increasing power of massively parallel machines offers new opportunities for first principles materials simulations, providing software can be developed to effectively exploit new hardware. Density functional theory has enjoyed widespread success for systems of up to a few hundred atoms, but is limited by the cubic scaling with the number of atoms of standard approaches. However, in recent years various linear scaling (LS) approaches have been developed, enabling simulations on tens of thousands of atoms. Since the parallel scalability is related to the number of atoms, such methods are also well suited to exploit supercomputers. One key factor influencing the accuracy and cost of DFT is the choice of basis set, where minimal, localized basis sets compete with extended, systematic basis sets. However, wavelets offer both locality and systematicity and are thus ideal for representing an adaptive local orbital basis which may be exploited for LS-DFT [1]. One may also make further approximations, e.g. dividing a system into fragments [2] or exploiting underlying repetition of local chemical environments [3], where each approximation may be controlled and quantified. This ability to treat large systems with controlled precision offers the possibility of new types of materials simulations [4]. We will demonstrate the advantages of wavelets as a basis for large scale DFT calculations, as implemented in BigDFT code. We will illustrate our discussion by presenting some case-studies among which the example of materials for organic LEDs, showing how our approach may be used to account for environmental and statistical effects on excited state calculations of disordered supramolecular materials [5].

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Recent advances in the magnetic property calculations with deMon2k

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In this presentation, the working equations and implementation details of an extension of the magnetic property calculation module within deMon2k for computing magnetic shielding tensors employing hybrid functionals are shown. Before this development, the module was capable of calculating shielding tensors employing only LDA, GGA and mGGA type of exchange-correlation functionals (1). The validation calculations show that a better agreement with experimental magnetic shielding constants is achieved with the PBE0 hybrid functional. Furthermore, the induced current density due to the presence of an external magnetic field is now available for plotting, which can help to rationalize the measured chemical shifts on a particular system. These developments are applied for the theoretical prediction of the hydrogen chemical shifts of the system bipyridine-CH_2-CH_2-bipyridine^{+2} and the results are also shown. Calculations of these chemical shifts employing GGA functionals have failed to provide a good qualitative and quantitative agreement with respect to available experimental data.

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A mystery of a through-space indirect NMR spin-spin coupling between two hydrogen atoms

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Indirect nuclear spin-spin coupling constants are amongst the most important magnetic resonance parameters, invaluable in establishing molecular structure from NMR spectroscopy. Their detailed understanding in terms of molecular and electronic structure is thus of central importance in many fields of research and has been pursued since the beginnings of NMR spectroscopy. Nowadays quantum-chemical calculations can offer a variety of tools for the interpretation of couplings including visualization of spin-spin coupling pathways by real-space functions (1).
In this presentation we will show how visualization of NMR spin-spin coupling pathways has been used for interpretation of the experimentally detected "through-space" indirect spin-spin couplings between protons formally separated by 18 covalent bonds (2,3).

Acknowledgment. This work received funding from the Slovak Research and Development Agency (grant APVV-15-0726).

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Computational study of magnetic properties of polynuclear transition metal complexes

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Polynuclear transition-metal complexes with magnetically interacting open-shell ions are a focal topic of research in chemistry and physics owing to their central importance in fields as diverse as molecular magnetism and bioinorganic catalysis. The challenge of understanding the structure and behaviour of these systems can be addressed by the complementary study of their magnetic and spectroscopic properties; these intimately connected aspects offer insight into the global and local electronic structure of the clusters, as well as their structural features. Current research on the magnetic properties of such systems has focused on understanding the key structural and electronic factors that control the exchange interactions between metal centers. Theoretical approaches based on density functional theory (DFT), particularly in its broken-symmetry (BS) implementation, are a meeting point for the treatment of magnetic and spectroscopic properties because they offer ways to evaluate both within a common framework. These methods are especially important in the study of magnetic exchange interactions in oligonuclear complexes, and in principle they can provide a more detailed picture of the interactions than that achievable by analysis of experimental data.(1) Focusing this presentation on the case of a tetranuclear copper complex that was recently synthetized and characterized in our lab, we will show how BS-DFT was used to provide a rational of the magnetic behaviour of this cluster as well as an estimate of the energy of specific non-covalent interactions.(2)

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Visualization of EPR Hyperfine Structure Coupling Pathways

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Paramagnetic compounds represent an important class of technologically relevant materials. They can be used as contrast agents for enhancing NMR imaging, molecular magnets, materials for spintronics and advanced information storage, transition-metal battery materials and many others. Paramagnetic NMR spectra contain a wealth of information about paramagnetic compounds but their interpretation is often challenging. In the past few years significant progress in relativistic and nonrelativistic quantum-chemical methods for calculations of pNMR shifts has been achieved, bringing new opportunities for interpretation of experimental results. One of the most interesting questions in the analysis of pNMR shifts concerns the pathways of the contact and pseudocontact shifts which help to understand the structure-property relations for paramagnetic compounds.

In the present work we propose a new tool for visualization of hyperfine coupling pathways based on our experience with visualization of NMR indirect spin–spin couplings (1). The plotted 3D-function is the difference between the total electron densities when the magnetic moment of the nucleus of interest is parallel and antiparallel to the external magnetic field and as such is an observable from the physical point of view. In contrast to the widely used visualization of spin density, our new approach depicts only the part of the electron cloud of a molecule that is affected by the interaction of the unpaired electron(s) with the desired nuclear magnetic moment.

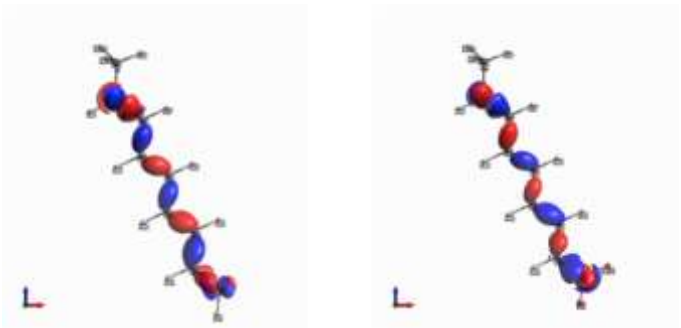

Figure 6: The coupling pathways for a) $^{7}A(C_1\text{-}C_8)$ (cutoff 0.00025) b) $^{7}J(C_1\text{-}C_8)$ (cutoff 0.002).

Acknowledgment.
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Spin State Changes in the Zigzag Edge of Graphene Embedded Fe-N-C Catalysts: VASP and deMon2K results

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As a pristine graphene nanostructure, zigzag graphene nanoribbons (ZGNRs) has embarked considerable excitement over the past decade due to the presence of polarizable edge states (1). It has also been employed as a model system for non-precious metal catalysts since it can host a variety of ORR active sites (2). Among explored catalyst formations, iron and nitrogen co-doped graphene has been emerging as promising electrocatalysts. Furthermore, it has also been shown that Fe embedded porphyrin-like vacancy is more stable at edges than in bulk graphene (3). In light of those recent studies the change of spin states on the edge and in the bulk, caused by Fe and N co-doping, is an essential factor to tune the electronic and magnetic states on graphene. Therefore, unraveling spin interactions between co-doped metal-nitrogen complex and edge states (illustrated in Fig. 1) can lead to control the electronic conductivity of the Fe-N-C materials, which is essential for their applications in electrocatalysts.

In this talk, the effect of nitrogen-metal and vacancies in the bulk and edge configurations on the spin polarization on graphene materials will be presented as obtained from two computational methodologies: plane waves and atomic-centered Gaussian functions. There are some drawbacks on each DFT code regarding magnetic calculations. Sensitivity of the value of total magnetic moment in VASP obtained from Bravais lattice depends on k-point sampling, smearing parameters and stress applied to unit cell. On the other hand, the initial spin moment guess on each atom is not implemented on deMon2k to be able to obtain anti-ferromagnetic states of graphene.

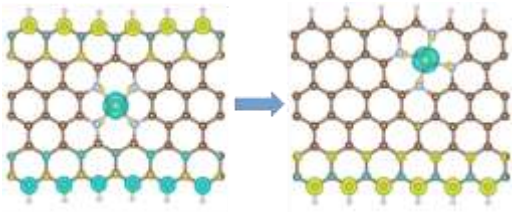

Figure 7: Suppression of spin polarization in edge modification by FeN4

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Theoretical insights into the dissociation of PAH clusters

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Astrophysical observations suggest that PAH are produced by photoevaporation of very small grains which could be PAH clusters stabilized by van der Waals and electrostatics interactions or by charge resonance between the PAH units in the case of ions. Containing tens to few thousands of atoms, such systems can hardly be approached via traditional ab initio schemes at the moment. Density functional based tight binding method (DFTB, an approximate DFT scheme) allows to deal with systems of this size range. Unfortunately, it inherits from DFT the difficulties to describe the typical interactions met in molecular clusters, in particular charge resonance in ions. This presentation will give an overview of how DFTB can be modified to become a realistic and efficient tool to investigate the structural, electronic and energetic properties of PAH clusters. We will compare the computed observables with recent experimental results and will use the theoretical electronically excited potential energy surfaces to propose mechanisms involved in photo-dissociation experiments.

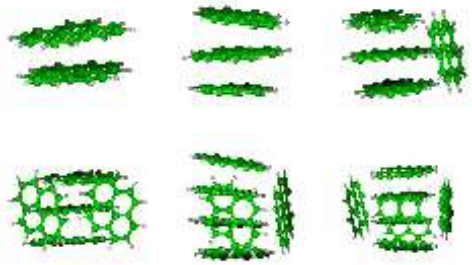

Figure 8 Most stable structures obtained for cationic clusters

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Implementation of Ehrenfest MD for efficient electron/nuclear coupled dynamics

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Simulation of important chemical phenomena including charge transfer, photochemical reactions and radiolysis do not follow the assumptions of the widely applied Born-Oppenheimer molecular dynamics (MD). In these situations, so-called non-adiabatic MD simulations are required in order to follow the evolution in time of the coupled electronic and nuclear motions. The method implemented in deMon2k is the Ehrenfest molecular dynamics, which consist in solving the equations of motion of one type of particle in an effective potential given by the other type of particle. This results in an averaged-path evolution for the system under treatment. While the nuclei are considered classical particles and thus characterized by Newton equations of motion, electrons evolve via a Liouville-von Neumann equation using a Magnus propagation scheme. Challenges remaining to solve involving the calculation of the coupled equations of motion will be presented, along results of ionizing radiation effects on small molecules.

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Symmetry adapted Density Fitting

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The working equations for the symmetry adapted density fitting in auxiliary density functional theory are derived and discussed. The symmetry blocking of the Kohn-Sham equation systems for the point groups (1) C_n ,C_{nv}, C_{nh}, D_n, D_{nd}, D_{nh}, C_i, C_s, S_4, S_6, $C_{\infty v}$, $D_{\infty h}$, T, T_d, T_h, O, O_h, I and I_h *with* n = 2 to 6, is validated with and without symmetry adapted density fitting. The symmetry relation between the Kohn-Sham density (2) and auxiliary density in point groups with degenerated irreducible representations is analyzed in more detail.

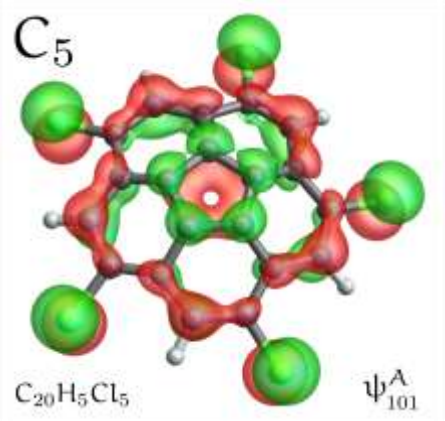

Figure: Last occupied molecular orbital belonging to the A irreducible representation

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Judging density functionals using databases.

Comments on using statistics

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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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Towards modelling of oil upgrading – Conformational search of molybdenum disulfide nanoparticles

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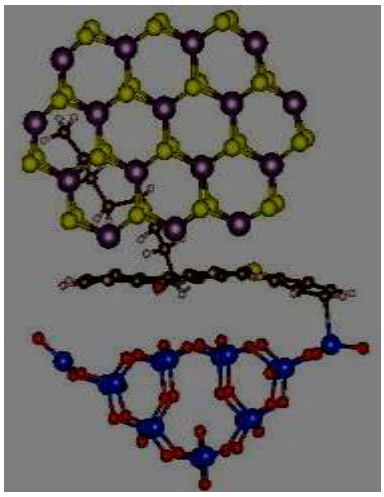

Along with its many **industrially interesting** properties utilized in hydrodesulfurization processes, molybdenum disulfide (MoS_2) is being developed in the Prof. Pereira group as a hydrogenation and coke - prevention catalyst. Catalyst is manufactured using an original and very distinctive preparation method. In order to model its reactions later on, we have performed DFT Born–Oppenheimer molecular dynamics and minima hopping simulations for starting-structure determination, using the Local Density Approximation and severely-pruned auxiliary function sets as a fast methodology for exploring the potential-energy surface to find local minima. The implications for catalysis are currently under discussion and the project is being extended to machine learning.

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Implementation of Real-Time Propagation of the Electronic Density with Scalapack library

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The interest for electronic dynamics has been growing in recent years due to the continuous progress in optics and laser technologies that made the realization of pump-probe probe experiments on the attosecond regime a reality. Such techniques have started to shed unprecedented light on the details of the electronic dynamics in intimate relationship with chemical structure and dynamic**.** The propagation of time-dependent Kohn-Sham equations provides a mean to access the realm of attosecond electron dynamics (1). We have implemented in deMon2k a real time time dependent-density-functional (RT-TDDFT) module (2). In this presentation we will present the details of this efficient implementation thanks to the used of fitted densities and Scalapack library.

The Magnus propagation involves the exponentiation of a (generally) complex matrix without any special properties, posing a computational bottleneck for the electron dynamics. In order to alleviate the computational cost, a parallel implementation based on the ScaLAPACK/MPI library has been implemented for the Taylor expansion within a cyclic-cyclic distribution of the data. Matrix products based on the existing MPMULMAT subroutine have been also optimized with ScaLAPACK. Benchmark tests as function of the system size, the topology of the chosen grid and the number of CPU used will be presented. The memory print and MPI communication optimizations for the Magnus propagation will be also presented

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Ultrafast energy relaxation following interaction of biomolecules with ionizing radiations

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The transient collision (10^{-17} s) of high-energy-transfer particles with biological matter results in ionization or excitation of its constituent molecules. Huge amounts of energy are deposited locally, typically several tens of eV. These early physical events produce a myriad of reactive radical species that are at the source of cascades of chemical processes spanning several spatial and temporal scales. The physical chemistry of these ultrafast processes are not well understood at the present time.

Our group is developping dedicated first principles approaches to simulate the physical stage of radiolysis of matter. They are based on so-called Real-Time Time-Dependent Auxiliary DFT (1,2). In this presenttation I will show how to estimate the cross-section of the first ionization of water molecule in the gaseous phase and comparing it with the experimental data (3). I will show first examples with deMon2k of effect induced by radiation to the electron cloud on protein back-bone. With this purpose have been studied some model systems formed by molecules of glycine, focusing on energy profiles and the redistribution of charge that taking place in the first femtoseconds of the interaction between a fast charge particle and bio-molecules.

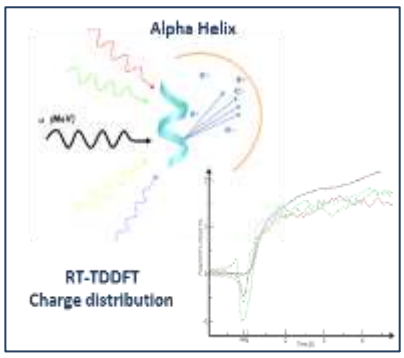

Figure 9: schematic representation of induced ionization on an alpha-helix by alpha-particle radiation.

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Constraint optimization on a hypersphere

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Constrained and unconstrained geometry optimization in Cartesian coordinates employing the internal degrees of freedom of molecular systems was developed, implemented and validated in deMon2k. In this new methodology the external degrees of freedom (infinitesimal translations and rotations) of the molecule are eliminated by a projection matrix P in each optimization step. To build the projection matrix, a Gram-Schmidt orthogonalization to the external degrees of freedom is employed to generate *3M-5* or *3M-6* vectors, depending if the molecule is linear or not, respectively. With P at hand the external degrees of freedom can be then projected out from the Cartesian gradient vector and Hessian matrix. As a result, the optimization step is calculated in a reduced space of *3M-5* or *3M-6* dimensionality. Furthermore, a new algorithm for constrained optimizations on a hypersphere[(1,2)] with two restrictions was developed and tested. This new algorithm was incorporated into the Saddle interpolation[(3)] and intrinsic reaction coordinate[(4)] (IRC) calculation. Illustrative examples will be presented and discussed.

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Multicomponent DFT with density fitting

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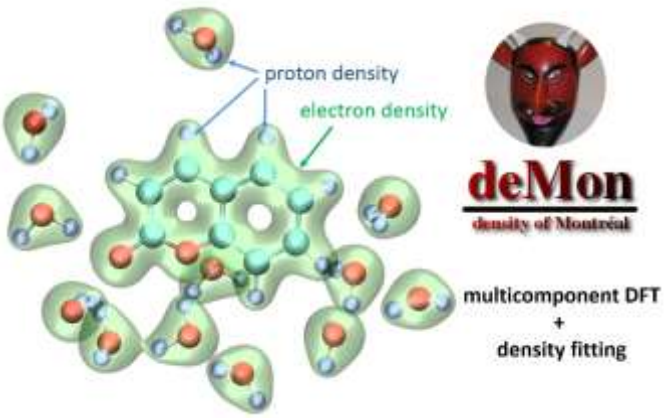
Multicomponent Density Functional Theory (MDFT) is a promising methodology to incorporate nuclear quantum effects, such as zero-point energy or tunneling, or to simulate other types of particles such as muons or positrons using particle densities as basic quantities. As for standard electronic DFT, a still ongoing challenge is to achieve the most efficient implementations. We introduce a multicomponent DFT implementation within the framework of auxiliary density functional theory, focusing on molecular systems comprised of electrons and quantum protons. We introduce a dual variational procedure to determine auxiliary electron and proton densities which leads to a succession of approximate energy expressions. Electronic and protonic fitted densities are employed i) in electron-electron, proton-proton and electron-proton classical Coulomb interactions, ii) in electron exchange-correlation, proton-proton exchange, and electron-proton correlation potentials. If needed, exact exchange among electrons or among protons are computed by the variational fitting of the corresponding Fock potential. The implementation is carried out in deMon2k. We test various electron proton correlation functionals on proton affinities. We find that auxiliary densities can be safely used in electron-electron, proton-proton, and electron-proton classical Coulomb interactions as well as in electron-proton correlation, albeit with some precautions related to the choice of the electronic auxiliary basis set that must be flexible enough. Computational tests reported in the last section indicate that introduction of density fitting in MDFT is clearly advantageous in terms of computational effort with good scaling properties with respect to the number of electron and protons treated at the DFT level.



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Tyrosine oxidation studied using QM/MM approaches

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Oxidative stress in living cells is at the origin of various diseases, due to the reaction of highly reactive species with biomolecules (DNA, RNA, or proteins) that degrades their function. Understanding the mode of action of radicals with proteins is thus of paramount importance.
Centrin is a ubiquitous protein that plays an essential role in the organization of the centrosome. It has been shown that this protein is highly sensitive to oxidation by radicals (1,2). The oxidation by N_3° radicals (more specific than OH° radicals) leads to the formation of oligomers of centrin, covalently bound through their C-terminal tyrosine residues. Surprisingly, the yield of oligomerization of centrin is higher than that of isolated tyrosine in the same condition, showing the importance of the protein environment. The structuration of the protein has also been shown to play a role for the oligomerization (3).
In this work, we have used a combination of classical molecular dynamics simulations and QM/MM single point calculations in order to get insight into the reactivity of the C-terminal Tyrosine residue of centrin towards oxidation. As a step towards rigorous computation of redox potential of tyrosine in the protein environment, we have computed redox potentials of isolated tyrosine. We have used various cappings for the tyrosine in order to imitate various positions of Tyrosine within a peptide chain (at the N-terminus, C-terminus, or in the middle).

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Recent validations of the ab initio-grounded SIBFA polarizable molecular mechanics/dynamics potential. Perspectives for large-scale, massively parallel, molecular dynamics simulations.

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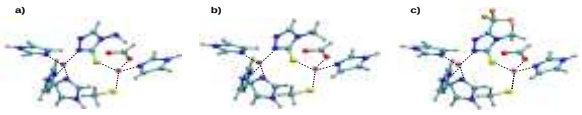
In the SIBFA polarizable molecular mechanics/dynamics procedure, the interaction energy is formulated as a sum of five distinct contributions: electrostatic, short-range repulsion, polarization, charge-transfer and dispersion, formulated, calibrated and validated on the basis of ab initio QC energy decomposition analyses (EDA) [1, 2]. We present validation tests in two cases: cation channeling along the vertical axes of two stacked guanine tetramers [3], and the complexes of anionic triazole thione derivatives to the Zn(II)-binding sites of L1 and VIM-2 metallo-β-lactamases, which are responsible for the acquired resistance of bacteria to antibiotics [4]. ΔE(SIBFA) can closely match the numerical values ΔE(QC) and its trends over a wide range of variations.. We then present refinements on the basis of SAPT EDA. Thus, for a given constitutive fragment, we leveraged a procedure automatically optimizing the parameters of each the five energy contributions by least-square minimization of it difference with respect to its QC counterpart in training sets encompassing 20-150 complexes of this fragment with a dipolar and with a dicationic 'probe', namely water and Zn(II). SIBFA is being ported into the massively parallel 'Tinker-HP' code [5]. Perspectives for large-scale molecular dynamics simulations in this context are discussed.

Figure 1. Complexes of triazole thione inhibitors in the dizinc recognition site of VIM-2 MBL



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POSTERS

Theoretical study of Ebselen, a powerful Covalent inhibitor of the New-Delhi metallo-ß-lactamase (NDM-1)

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The hydrolysis of the ß-lactam core, typical of some antibiotics such as penicilins, cephalosporins and carbapenems, is caused by enzymes belonging to ß-lactamases family present in some bacteria. Specifically, the New-Delhi metallo-ß-lactamase (NDM-1) is able to hydrolyze the four-membered structure of the ß-lactam ring thanks to the help of two zinc ions that share the coordination of a bridge water molecule. Most recently, the discovery of a promising NDM-1 inhibitor, ebselen, was reported (1). Spectroscopic analysis suggested that ebselen could bind to NDM-1 by forming a S-Se bond with the Cys-166 residue coordinated to a zinc ion, Zn2 (Figure 1). Computational methods can be used to accelerate the long and costly drug discovery process. Molecular simulations, in fact are critical for understanding enzymatic catalysis and unveil mechanistic insights potentially useful for designing better drugs. In particular, the knowledge of the inhibition mechanism of enzyme by ebselen can be helpful to drive a rational design of most efficient inhibitors. In our investigation, starting from the crystallographic structure of the NDM-1 alone enzyme (ID: 3SPU) docking and classical molecular dynamics (MD) simulations have been undertaken in order to obtain a starting enzyme-inhibitor complex for the next mechanistic investigation at quantum mechanical level. To do this the metal center parameter builder MCPB (2) was applied to generate parameters useful to describe the unusual coordination of the metal centers. MD simulations were deeply analyzed in terms of RMSD, RMSF and H-bonds on both apo-enzyme and enzyme-inhibitor systems.

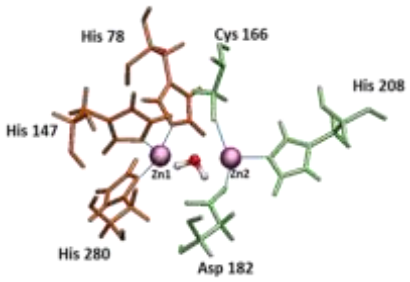

Figure 10: Active site of the New-Delhi metallo-ß-lactamase.

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Inverse surface Pd segregation on Pd/Au(001) under CO reactive gas: effect on CO oxidation

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Alloys often exhibit catalytic properties superior than their constituent metals. Au-Pd alloy, for instance, have a higher reactivity in CO oxidation at low temperature (1) compared to pure Au and Pd surfaces. In order to unravel the catalytic properties of the alloy, one should first characterize and control the atomic surface arrangement under the reactive gas conditions. In our work, we developed a theoretical methodology to predict the change occurring on the surface of Au-Pd alloy under CO pressure. We begin by describing a method for using density function theory calculations to construct Ising-like Hamiltonians for use in Monte Carlo simulations. Furthermore, we use Monte Carlo simulations to obtain segregation isotherms and to exploit the evolution of the Pd surface concentration as a function of the CO coverage. Then we report and discuss the results of these simulation in terms of different adsorption sites of AuPd (100) surface. Briefly, Pd segregation into Au (001) surface induced by the presence of CO gas leads to two ordered configuration states, Pd chain (figure1a) and Pd checkerboard formation (figure1b). Next, the stability of both ordered phases is analyzed by using DFT calculations. Pd chain formation is found more stable than the other ordered phase. Experimental studies (1) also attributed the observed enhanced CO oxidation to the formation of this configuration on the AuPd(001) surface. Furthermore, we present the theoretical phase diagrams of the CO adsorption-induced equilibrium surface structures as a function of temperature and CO pressure (2). CO oxidation reaction patterns on these ordered configurations have been compared in terms of reactivity and stability (3).

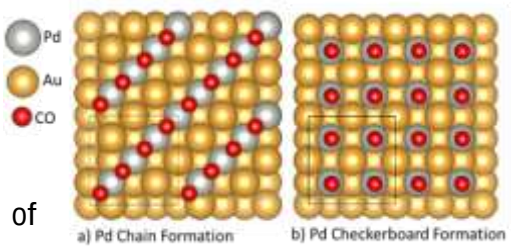

Figure 11: CO Adsorption-induced Surface Segregation and Formation of Pd chain and

Reference

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Implementation of zero order regular approximation (ZORA) in deMon2k

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The relativistic effects are important for studying many chemical and physics properties of atoms and molecules containing heavy elements (Z > 50). The Dirac equation describes these effects. However, the Dirac equation is much more difficult than the resolution of the non-relativistic Schrödinger equation. One approximation for the Dirac Hamiltonian is ZORA which has been proven that it yields accurate results in atomic calculations. The aim of this project is to implement ZORA in the deMon2k code. The first step after the implementation is to calculate ionization potentials for different elements and to compare them with experimental results. The PW91 exchange-correlation functional as well as ANO-RCC basis sets were used for these calculations. The next step is to calculate ionization potentials, bound distances and HUMO-LUMO gap in gold nanoparticles with 2 to 8 atoms (3). A comparison of the results obtained with an all electron basis set (DZVP), and electronic core potentials (aug-cc-DZVT) as well as calculations including ZORA approach is shown. Our calculations show that the predicted ionization potentials on heavy atoms have a reasonable good agreement with experiment, except for gold that yields a deviation of around 60%. The expectations for this project are to fixed error for gold, formulate a GGA for exchange and correlation potential and to optimize a basis set specific for ADFT calculations including relativistic effects.

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Theoretical, experimental and molecular docking calculations of Alvocidib (2-(2-chlorophenyl)-5, 7-dihydroxy-8-[(3$, 4R)-3-hydroxy-1-methyl-4-piperidinyl]-4-chromenone) study by Density Functional Theory

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The experimental and theoretical DFT study of the structural, vibrational and electronic properties of Alvocidib is presented using B3LYP exchange-correlation functional with 6-31G**++basis set [1, 2]. The molecular electrostatic potential surface (MEPS), HOMO-LUMO energy gap and natural bond orbitals (NBOs) were also calculated and compared with available X-ray data of Alvocidib. A transition for UV spectrum for the structure was assigned and the calculated bands showed good agreement with the measured experimental data. The comparative IR studies showed intermolecular hydrogen bonds that stabilize the molecule and revealed characteristic vibrations for the structure. Molecular docking studies with cyclin-dependent kinase 9 [3] complex showed binding free energy 7.89 kcal/mol, which indicates the better potential inhibitor for this receptor.

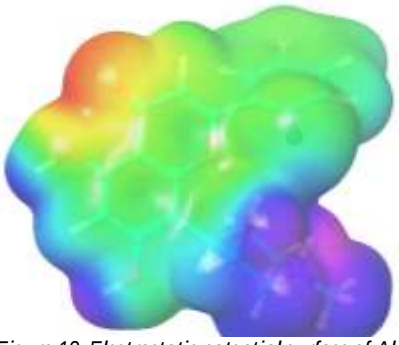

Figure 12: Electrostatic potential surface of Alvocidib

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Density functional theory studies on molecular structure, vibrational spectra and docking studies of Docetaxel® (DTX)

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Docetaxel® (DTX) is one of the standard first-line **β**-tubulin inhibitor for the treatment of metastatic cancers [1,2]. However, theoretical and experimental description of their structural, electronics, spectroscopic properties and molecular docking studies still lacking in the literature. Therefore, density functional theory (DFT) with 6-31G**++ basic set was implemented to calculate the molecular geometries and electronic structures of DTX [3]. Initially, the number of global and local reactivity descriptors was calculated to predict the reactive sites in the molecules. In addition, the electronic properties includes frontier orbitals highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbitals (LUMO), molecular geomtry, electron-affinity and ionization potential were examined to deep insight of molecular properties. Further, the molecular electrostatic potential (MEP) were calculated to assess the nucleophilic or electrophilic reactivity. The results of molecular docking studies indicated that DTX as a potential inhibitor for **β**-tubulin.

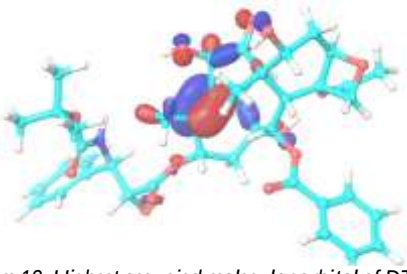

Figure 13: Highest occupied molecular orbital of DTX.

References

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DFT/B3LYP Calculations and Combined Study of Molecular Docking for Suggesting Therapeutically Potent PLA2 Inhibitors

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Abstract: The quantum chemical density functional method at B3LYP/6-31G**++ basis set level was used to obtain the equilibrium geometries of the molecules. The quantum theory of atoms-in-molecule approach was employed to study various intra-molecular C-H…O interactions within the molecules. Further, the molecular geometry and the electronic properties such as highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) energy gaps were investigated to get a better insight of the molecular properties. Molecular electrostatic potential (MEP) for the compounds were determined to check their electrophilic or nucleophilic reactivity. Molecular docking study was performed to elucidate the binding interaction between the active sites of PLA2.

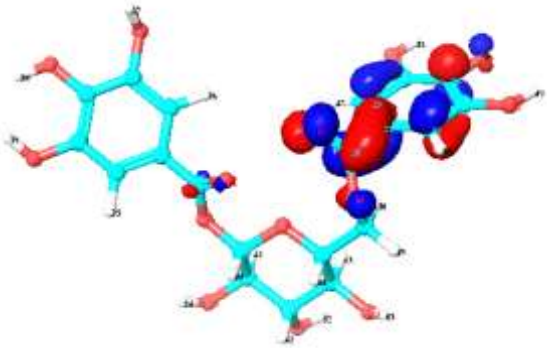

Figure 14: Plots of the highest unoccupied molecular orbital.

Reference

(1) Salahub, D.R.; Noskov, S.Y.; Lev, B.; Zhang, R, Ngo, V.; Goursot, A.; Calaminici, P.; Köster, A.M.; Alvarez-Ibarra, A.; Mejía-Rodríguez, D.; Řezáč, J.; Cailliez, F.; de la Lande, A., QM/MM calculations with deMon2k. *Molecules*. 2015,16;20(3):4780-812.
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New functionalities of deMon2k for user-friendly QM/MM simulations

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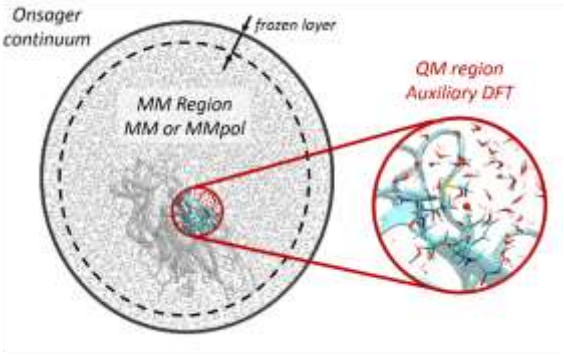
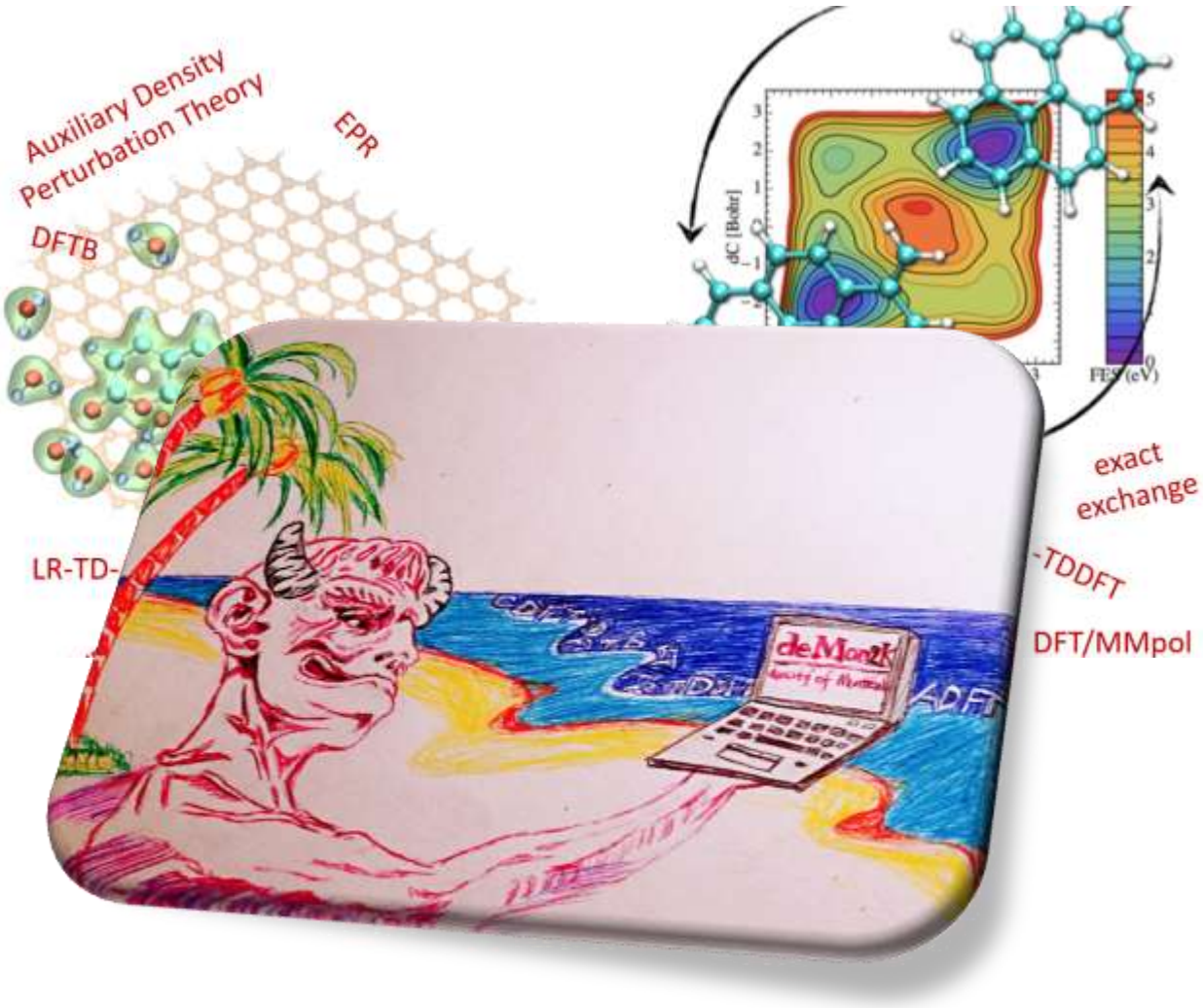
deMon2k implements a so-called "in-deMon2k" QM/MM implementation of hybrid quantum mechanics/Molecular Mechanics method. In the last two years we implemented several key functionalities to make QM/MM simulations user-friendly and useful for actual researches. These include the coding of link atoms to deal with QM/MM frontiers cutting covalent bonds, the inclusion of Onsager polarizable continuum model for long range electrostatic effects, the inclusion of user defined restraints on geometrical parameters. The Amberff02 polarizable force field has been implemented. Interface to the PLUMED library has been incorporated to enable metadynamics simulations. Last but not least tools have been created to help user to easily switch from standard MM packages (AMBER, CHARMM, Gromacs) to deMon2k for QM/MM simulations.
We review on this poster the that are readily available in the 6.0.2 deMon2k developer version (contact the authors)



Reference:
Aurélien de la Lande, Aurelio Alvarez-Ibarra, Karim Hasnaoui, Fabien Cailliez, Xiaojing Wu, Tzonka Mineva, Jérôme Cuny, Patrizia Calaminici, Luis López-Sosa, Gerald Geudtner, Isabelle Navizet, Cristina Garcia Iriepa, Dennis R. Salahub and Andreas M. Köster, *Molecules*, 2019, 24, 1643.



Hope to see you at the 20th Workshop !