



# The 11th OpenMolcas Developers' Workshop

Bologna, 14-16 June 2023



## Book of Abstracts

# Sponsors



**Hewlett Packard  
Enterprise**



# PROGRAM

click on the speaker name for a link to the abstract

	Wednesday 14	Thursday 15	Friday 16
Chair		<i>S. Coriani</i>	<i>I. Fdez. Galván</i>
9:00 - 9:30	Check-in	<b>P. O. Dral</b>	<b>K. Pernal</b>
9:30 - 10:30		V. Veryazov	F. Plasser
		D. De Chavez	G. Li Manni
	M.-B. Lepetit	F. Aleotti	
10:30 - 11:00	<b>coffee and opening</b> M. Garavelli	<b>coffee break</b>	<b>coffee break</b>
Chair	<i>G. Li Manni</i>	<i>A. Nenov</i>	<i>R. Lindh</i>
11:00 - 11:30	<b>M. G. Delcey</b>	<b>P. Altoè &amp; P. Masera</b>	<b>A. F. Izmaylov</b>
11:30 - 12:30	<i>I. Fdez. Galván</i>	F. Fasulo	M. Mörchen
	S. Battaglia	J. Staab	A. A. Safari
	L. M. Frutos*	M. Huix-Rotllant	O. Weser
12:30 - 14:00	<b>welcome lunch</b>	<b>lunch break</b>	<b>lunch break</b>
Chair	<i>I. Conti</i>	<i>M. Garavelli</i>	<i>F. Plasser</i>
14:00 - 14:30	<b>G. Cerullo</b>	Discussion	<b>K. Bravaya*</b>
14:30 - 15:30	R. E. Daoud		S. Ghosh*
	L. Cupellini		S. Coriani
	S. Alessandrini	M. Lundberg	
15:30 - 16:00	<b>coffee break</b>	<b>coffee break</b>	<b>concluding notes</b> R. Lindh
16:00 - 19:00	flash talks & poster session	Bologna sightseeing	<b>goodbye coffee break</b>
19:00 onwards		<b>gala dinner</b>	

Link to website: <https://eventi.unibo.it/openmolcas-workshop-2023>

## Variational optimization of multiconfigurational pair-density functional theory

Mickael G. Delcey<sup>1</sup>, M. Scott<sup>2</sup>, G. L. S. Rodrigues<sup>2</sup>

<sup>1</sup> Lund University, Sweden

<sup>2</sup> KTH Royal Institute of Technology, Sweden

Pair-density functional theory (PDFT) has been suggested in the 90s as an alternative to the current spin-density formulation of density functional theory.<sup>[1]</sup> The idea was to have a formulation that gives identical results to spin-density functional theory for a single determinant wavefunction but with improved properties for multiconfigurational (MC) wavefunctions. The idea grew in popularity after a MC-PDFT implementation was made available in 2014.<sup>[2]</sup> This implementation demonstrated an accuracy on-par or better than multireference perturbation theory on several examples.<sup>[3]</sup> However, it has shortcomings, both in the treatment of low-spin open-shells and in the fact that the implementation is not variational, complicating property evaluations and arguably deteriorating its results. Here we present a fully variational optimization of MC-PDFT. First, we demonstrate the proper translation of spin-density functionals for the treatment of low-spin open-shells, and then we present the gradient expressions and how they can easily be implemented in a standard MCSCF code. We illustrate how the method is not only more accurate and reliable than the non-variational one, but also significantly more efficient, with a cost on-par with standard DFT for small to medium active spaces. We also discuss the question of double-counting of the electronic correlation due to the use of functionals designed for standard Kohn-Sham DFT, with preliminary tests being very encouraging.

[1] Becke, A. D., Savin, A., Stoll, H., *Theoretica chimica acta* 91 (1995), 147.

[2] Li Manni, G., Carlson, R. K., Luo, S., Ma, D., Olsen, J., Truhlar, D. G., Gagliardi, L., *J. Chem. Theory Comput.* 10 (2014), 3669–3680.

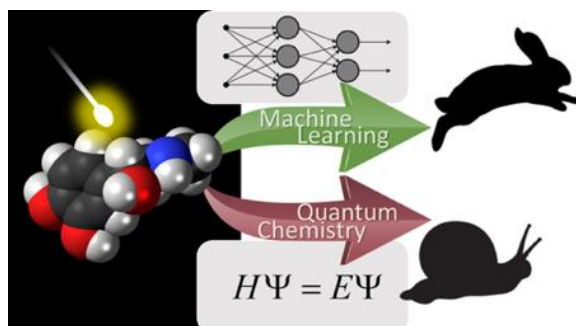
[3] Hoyer, C. E., Ghosh, S., Truhlar, D. G., Gagliardi, L., *J. Phys. Chem. Lett.* 7 (2016), 586–591.

## Making quantum chemistry more accessible with machine learning

Pavlo O. Dral

Xiamen University, China

I will present our efforts in making accurate quantum chemical calculations more accessible with the help of machine learning. One of main results of these efforts is the general-purpose, artificial intelligence-enhanced quantum mechanical method 1 (AIQM1).<sup>[2]</sup> It approaches the CCSD(T)/CBS accuracy for closed-shell, neutral organic molecules in their ground state at the speed of semiempirical quantum mechanical methods, while also being able of performing simulations at the MRCI level with reasonable accuracy. We also develop methods to accelerate the simulation of one-<sup>[3]</sup> and two-photon<sup>[4]</sup> absorption spectra as well as nonadiabatic dynamics by learning expensive CASSCF energies and gradients<sup>[5]</sup>. Our implementations are made available via our open-source *MLatom* program for user-friendly atomistic machine learning simulations which can be run for free online using our MLatom@XACS (Xiamen atomistic computing suite) cloud-based service.<sup>[6]</sup>



[1] Dral, P. O., Barbatti, M., *Nat. Rev. Chem.* 5 (2021), 388–405.

[2] Zheng, P., Zubatyuk, R., Wu, W., Isayev, O., Dral, P. O., *Nat. Commun.* 12 (2021), 7022.

[3] Xue, B.-X., Barbatti, M., Dral, P. O., *J. Phys. Chem. A* 124 (2020), 7199–7210.

[4] Su, Y., Dai, Y., Zeng, Y., Wei, C., Chen, Y., Ge, F., Zheng, P., Zhou, D., Dral, P. O., Wang, C., *Adv. Sci.* 10 (2023), 2204902.

[5] Chen, W.-K., Liu, X.-Y., Fang, W., Dral, P. O., Cui, G., *J. Phys. Chem. Lett.* 9 (2018), 6702–6708.

[6] Dral, P. O., Ge, F., Xue, B.-X., Hou, Y.-F., Pinheiro Jr, M., Huang, J., Barbatti, M., *Top. Curr. Chem.* 2021 379, 27. See MLatom.com @ XACScloud.com.

## Quantum Computing for Quantum Chemistry: How to bring quantum advantage sooner

Artur F. Izmaylov

University of Toronto, Canada

Quantum chemistry problem is one of the attractive targets for demonstrating quantum advantage of quantum computing technology. Having strongly correlated systems as the main target, I would like to discuss what new classical computing techniques need to be developed to help quantum computing algorithms to solve the electronic structure problem. Encoding the electronic Hamiltonian in the second quantized form on a quantum computer is not a trivial problem, and its efficiency can become a bottleneck for the entire quantum solution. Dealing with this Hamiltonian can be facilitated by partitioning it into a sum of fragments diagonalizable using rotations from either small Lie groups or the Clifford group. These fragments are convenient for performing various algebraic manipulations required in circuit compiling and quantum measurement. I will illustrate how the Hamiltonian partitioning can be used to improve performance of several quantum algorithms for quantum chemistry (e.g. Variational Quantum Eigensolver and Quantum Phase Estimation).

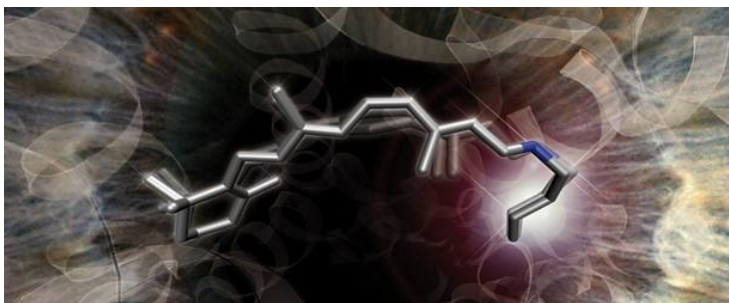
## Real-time observation of conical intersection in biomolecules

Giulio Cerullo

Politecnico di Milano, Italy

Conical intersections (CIs) are regions of the potential energy landscape of a molecule where the electronic and nuclear degrees of freedom become strongly mixed and the Born–Oppenheimer approximation breaks down. CIs are ubiquitous features in the photophysics and photochemistry of molecules and can be considered as “doorways” through which the photoexcited wavepacket is efficiently funneled to a lower-energy electronic state. CIs play a dual role in the interaction of biomolecules with light: either to promote efficient conversion from a reactant to a product state in a photochemical reaction or to enable efficient dissipation of excess electronic energy, preventing a potentially harmful photochemical reaction.<sup>[1]</sup> An example of the first case are visual opsin proteins, in which the photoexcited retinal chromophore exploits a CI to promote ultrafast photoisomerization to a ground-state photoproduct which triggers visual transduction. An example of the second case are nucleobases, the building blocks of DNA, for which CIs are used to promote rapid dissipation of excited state energy, preventing photoreactions which could damage the genetic code.

Given the extreme speed of the processes leading to CIs, ultrafast optical spectroscopy is the elective tool for their observation. However, the direct visualization of a wavepacket passing through a CI is challenging, because the energy gap between the interacting levels changes very rapidly over a short time, calling for the combination of high temporal resolution and broad spectral coverage. In this talk I will present examples of real-time visualization of CIs in biomolecules (opsin proteins<sup>[2]</sup> and nucleobases<sup>[3,4]</sup>) using a specially developed ultrafast transient absorption spectroscopy system combining sub-20-fs time resolution with broad frequency tunability, from the UV to the infrared.<sup>[5]</sup> I will also discuss the potential of X-ray free-electron lasers to open new spectroscopic windows for the detailed study of the CI dynamics, via element-specific probing of ultrafast electronic and structural dynamics.



[1] Cerullo, G., Garavelli, M., *PNAS* 117.43 (2020), 26553-26555.

[2] Polli, D. et al., *Nature* 467.7314 (2010), 440-443.

[3] Borrego-Varillas, R. et al., *J. Am. Chem. Soc.* 140.47 (2018), 16087-160-93.

[4] Borrego-Varillas, R. et al., *Nature Commun.* 12.1 (2021), 7285.

[5] Manzoni, C., Cerullo, G., *Journal of Optics* 18.10 (2016), 103501.

## Multireference methods for electronic resonances

Ksenia Bravaya

Boston University, USA

Electronic metastable states or resonances are states that lie energetically above ionization/detachment threshold and, therefore, have a finite lifetime. Owing to the scattering nature of the states they cannot be treated with conventional quantum chemistry methods developed for bound states. In this talk I will present the recent developments in theory for electronic resonances with the focus on extending multireference methods implemented in OpenMolcas to metastable electronic states. The calculations of resonance energies and widths are enabled through interface between OpenCAP software<sup>[1]</sup> that accounts for the resonant character of the states using projected Complex Absorbing Potential (CAP) approach<sup>[2]</sup> and the multireference methods infrastructure available in OpenMolcas. The performance of the approach will be discussed by considering several representative examples of resonances in molecular systems.

[1] <https://github.com/gayverjr/opencap>

[2] Gayvert, J. R., Bravaya, K. B., *J. Chem. Phys.* 156 (2022), 094108.



## An accurate and efficient adiabatic connection method with Cholesky decomposition for dynamic correlation energy of strongly correlated systems

Katarzyna Pernal

Lodz University of Technology, Poland

Strong correlation can be essentially captured with multireference wavefunction methods such as complete active space (CAS) or, if dozens of active electrons are involved, with density matrix renormalization group (DMRG) technique. Accurate description of electronic structure of strongly correlated systems requires accounting for the dynamic electron correlation, which CAS and DMRG largely miss. In my talk a new method for the correlation energy based on the adiabatic connection (AC)<sup>[1]</sup> will be presented. It is rigorously size-consistent, free from instabilities and intruder states. AC has been combined with CASSCF and DMRG to treat ground states and spin states.<sup>[2,3]</sup> It employs the particle-hole multireference random phase approximation and the Cholesky decomposition technique,<sup>[4]</sup> which leads to a computational cost growing with the fifth power of the system size. Thanks to AC depending solely on one- and two-electron CAS reduced density matrix, the method is more efficient in treating large active space than multireference perturbation theory methods. I will show applications for singlet-triplet organic biradicals.<sup>[4]</sup>

[1] Pernal, K., *Physical review letters* 120.1 (2018), 013001

[2] Pastorczak, E. et al., *J. Phys. Chem. Lett.*, 10.16 (2019): 4668-4674

[3] Beran, P. et al., *J. Chem. Theory and Comput.*, 17.12 (2021): 7575-7585

[4] Drwal, D. et al., *J. Phys. Chem. Lett.*, 13.20 (2022): 4570-4578.

## Acceleration on GPU of quantum chemistry applications

Piero Altoè<sup>1</sup>, Paolo Masera<sup>2</sup>

<sup>1</sup> Nvidia Corporation

<sup>2</sup> Hewlett Packard Enterprise Italia

Nvidia and HPE present the recent porting and development of quantum and molecular mechanics applications. The adoption of advanced programming languages in conjunction with modern computer architectures allow unprecedented speedups. We introduce Grace-Hopper<sup>[1]</sup>, a CPU-GPU tightly integrated HPC system, and the advantages of programming it with standard Fortran<sup>[2]</sup> and C++<sup>[3]</sup>. The last part of the talk is dedicated to the introduction of AI techniques for scientific data analysis.

[1] <https://resources.nvidia.com/en-us-grace-cpu/nvidia-grace-hopper>

[2] <https://developer.nvidia.com/blog/accelerating-fortran-do-concurrent-with-gpus-and-the-nvidia-hpc-sdk/>

[3] <https://developer.nvidia.com/blog/accelerating-standard-c-with-gpus-using-stdp>

## Polishing the foundation of [Open]Molcas infrastructure

Valera Veryazov

Lund University, Sweden

The Molcas/OpenMolcas package is highly regarded for its scientific capability and computational capabilities. But what makes this package truly special is its robust code infrastructure, including scripts, tools, input language and output structure. Some components of the Molcas/OpenMolcas infrastructure have evolved organically, while others were created in a rush and have not been updated in years. But now is the time to take a closer look at these components, to identify areas where improvements can be made. This talk will provide an overview of programming solutions in OpenMolcas, with a focus on key components of the infrastructure related to code development and user interface, including input, formatted output and integration with other codes.

## Detecting ionic states in CASSCF calculations

Felix Plasser

Loughborough University, UK

It is a long-known problem that  $\pi\pi^*$  states in organic molecules are often very poorly described by CASSCF producing errors of well above 1 eV. More specifically, CASSCF struggles in describing states that are classified as ionic within a valence bond picture whereas covalent states are often described without a problem.<sup>[1]</sup> This problem can severely hamper the applicability of CASSCF and related multireference wavefunction models. It is the purpose of this contribution to explain the physics of ionic and covalent states and why only the former cause problems for CASSCF. In particular, we highlight the importance of  $\sigma$ -correlation in reducing the energies of ionic singlet states.<sup>[2]</sup> An intuitive explanation based on the transition density is presented.<sup>[3]</sup> We proceed by suggesting a few diagnostics, based on the transition density, that can be used to detect ionic states. The relevance of these diagnostics in predicting CASSCF errors is highlighted.

[1] Roos, B. O., Andersson, K., Fülischer, M. P., *Chem. Phys. Lett.* 192.1 (1992), 5–13.

[2] Kimber, P., Plasser, F., *J. Chem. Theory Comput.* 19 (2023), 2340-2352.

[3] Kimber, P., Plasser, F., *Physical Chemistry Chemical Physics* 22.11 (2020), 6058–6080.

## Correcting One-Centered Two-Electron Integrals in Inner Projection based Integral Approximations

Danjo De Chavez, Roland Lindh

Uppsala University, Sweden

One well-known bottleneck in computational chemistry is the computation of four indexed integrals which easily becomes prohibitive. Existing inner projection techniques which includes resolution-of-identity (RI) and Cholesky decomposition (CD) of the two-electron integrals are often used to efficiently evaluate these two-electron integrals. Under these formalisms, an auxiliary basis set serving as a means to reduce size scaling is present. The two approaches are closely related, and this has led to recent advancements in the methods for systematically derived unbiased auxiliary basis sets – the atomic CD (aCD) and atomic compact CD (acCD) auxiliary basis sets – which are distinct from precomputed auxiliary basis sets – the Karlsruhe family of auxiliary basis sets. The primary goal of this study is to determine whether an explicit correction of the one-centered two-electron integrals may further increase the quality of these approximations in the RI technique. With the proposed linear scaling correction, it can be used to gain faster convergence towards the conventional treatment of the two-electron integrals, or as a mean to design smaller auxiliary basis sets while maintaining the same accuracy as that of the uncorrected approach. Since CD and RI scales  $O(N^3)$  while our proposed correction only scales  $O(N)$ , this becomes easily negligible in larger systems while offering a more accurate and homogeneous approximations.

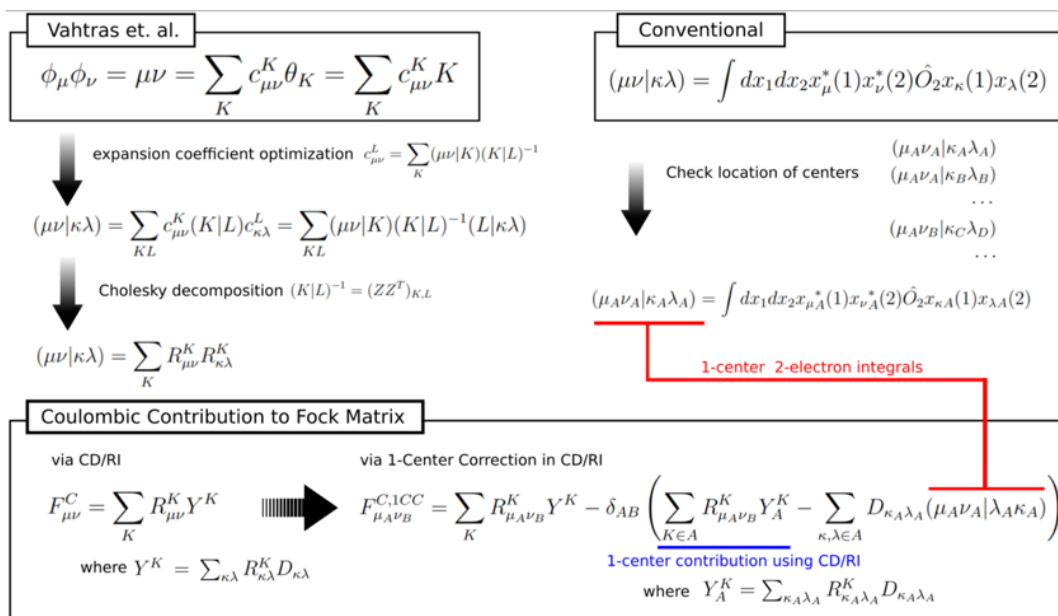


Figure 1: One-centered Correction Scheme for CD/RI-based Integral Evaluations

## Explicit Correlated F12 Composite Schemes for Noncovalent Systems: Interaction Energy and Geometry

Silvia Alessandrini<sup>1</sup>, Jacopo Lupi<sup>2</sup>, Vincenzo Barone<sup>3</sup> and Cristina Puzzarini<sup>1</sup>

<sup>1</sup> Università di Bologna, Bologna, Italy

<sup>2</sup> Trinity College Dublin, Ireland

<sup>3</sup> Scuola Normale Superiore, Pisa, Italy

A new model for the computation of the interaction energy (IE) in the case of noncovalent molecular complexes has been developed using explicit correlated F12 methodologies.<sup>[1]</sup> The starting point for this new model is the “cheap composite scheme” (ChS),<sup>[2,3]</sup> which is based on the coupled cluster singles and doubles approach augmented by a perturbative treatment of triple excitations, namely CCSD(T), in conjunction with a triple-zeta basis set. This first computation is then corrected to take into account (i) the extrapolation to the complete basis set (CBS) limit and (ii) the effect of core-valence (CV) correlation. These terms are obtained as follows: (i) the CBS correction is computed using second order Møller-Plesset perturbation theory (MP2) within the frozen-core (fc) approximation, the extrapolation being carried out with the n-3 formula by Helgaker et al.<sup>4</sup> (basis sets of triple- and quadruple-zeta quality are employed); (ii) the CV correction is evaluated as energy difference between all-electron and frozen-core MP2 calculations in conjunction with the cc-pwCVTZ basis set. Starting from the outlined scheme, its explicit correlated variant has been developed employing the F12 counterparts of the above-mentioned methods, i.e., the CCSD(T)-F12 and the MP2-F12 methods. To this aim, the convergence to the CBS limit of both methodologies has been analyzed in detail, addressing two critical aspects of the CBS extrapolation: the exponential formula and the family of basis set to employ. Based on the previous results, the best approach for the determination of equilibrium geometries for noncovalent molecular complexes was also investigated. In this case, several *ab initio* approaches have been considered, involving both standard and explicit correlated methods, but also double-hybrid density functionals. All the results have been obtained using the A14 dataset as reference<sup>5,6</sup> shown in Fig.1 and will be illustrated during my contribution.

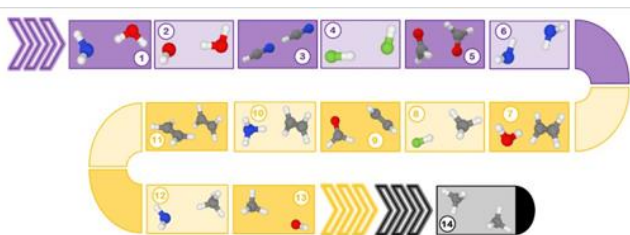


Figure 1. Schematic Representation of the A14 data set

[1] Lupi, J., Alessandrini, S., Puzzarini, C., Barone, V. *J. Chem. Theory Comput.* 17 (2021), 6974.

[2] Puzzarini, C. et al., *Phys. Chem. Chem. Phys.* 15 (2013), 16965.

[3] Alessandrini, S.; Barone, V.; Puzzarini, C., *J. Chem. Theory Comput.* 13 (2020), 988.

[4] Helgaker, T., Klopper, W., Koch, H., Noga, J., *J. Chem. Phys.* 106 (1997), 9639.

[5] Řezáč, J., Hobza, P., *J. Chem. Theory Comput.* 9 (2013), 2151.

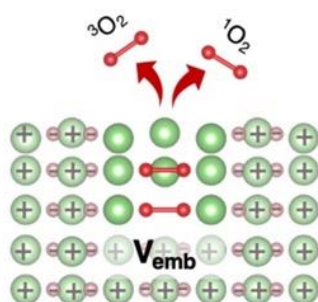
[6] Řezáč, J., Dubecký, M., Jurečka, P., Hobza, P. *Phys. Chem. Chem. Phys.* 17 (2015), 19268.

## Unveiling Singlet Oxygen Release at Lithium Peroxide Interface via an Embedded-Cluster CASPT2 Approach

Francesca Fasulo, Arianna Massaro, Ana B. Muñoz-García and Michele Pavone

University of Naples Federico II, Italy

Upon Li-air battery charge, several recent experiments have shown that singlet oxygen ( $^1\text{O}_2$ ) is formed, and such highly reactive species undermine the performance and the long-term stability of these devices.<sup>[1,2]</sup> The formation mechanism of singlet oxygen is still not fully clear, and studying this elusive process represents a challenging task for both experiments and theory.<sup>[3]</sup> Here, comparing two computational strategies, a periodic DFT and an embedded cluster approach at the CASPT2 level of theory, we address the release of triplet- and singlet- oxygen species from the most exposed facet of lithium peroxide ( $\text{Li}_2\text{O}_2$ ) nanoparticles.<sup>[4]</sup> The application of embedding approaches in materials sciences is helpful to describe the elusive chemistry of highly correlated species at heterogeneous interface.<sup>[5]</sup> We find that high-accuracy calculations by means of embedded-cluster CASPT2 allow the identification of a stable superoxide along the potential energy surface (PES) for  $^1\text{O}_2$  release. DFT is not able to find this intermediate. Moreover, our results show that the relative stability of superoxide species can affect the  $\text{Li}_2\text{O}_2$  oxidation. This surface process can occur via two possible pathways: (i) the two-step one-electron peroxide oxidation leading to a stable superoxide, which acts as reaction intermediate, and low amount of  $^1\text{O}_2$ ; (ii) the one-step two-electron peroxide oxidation via an unstable superoxide, that favors the singlet oxygen release. Overall, fine-tuning of the relative stability of superoxide species can enable the control of detrimental singlet oxygen release, thus enabling the deployment of Li-air batteries. Beyond these specific results, our study paves the route for future applications of embedded-cluster methods for advanced investigations on electrocatalytic processes at heterogeneous interfaces.



[1] Wandt, J. et al., *Angew. Chem. Int. Ed.* 55.24 (2016), 6892–6895.

[2] Mahne, N. et al., *Nat. Energy* 2.5 (2017), 1–9.

[3] Schürmann, A. et al., *Chem. Rev.* 121.20 (2021), 12445–12464.

[4] Mo, Y., Ong, S. P., Ceder, G., *Phys. Rev. B* 84.20 (2011), 205446.

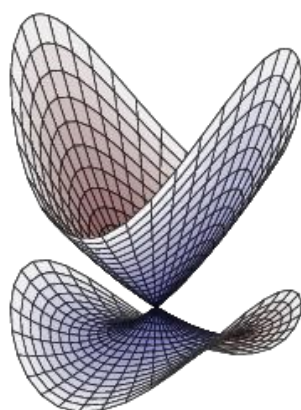
[5] Fasulo, F., Muñoz-García, A. B., Massaro, A., Crescenzi, O., Huang, C., Pavone, M., *J. Mater. Chem. A* 11.11 (2023), 5660–5669.

## A diabatic model for conical intersection optimizations

Ignacio Fdez. Galván, Roland Lindh

Uppsala University, Sweden

Structure optimizations are routine in computational chemistry. Their comparative easiness of set up and interpretation should not, however, hide the fact that it is a complex task: finding specific points in a high-dimensional space in as few iterations as possible, with only local information. Typical (and robust and successful) optimization methods are often based on a second-order Taylor expansion of the potential energy surface, that becomes more and more accurate as the optimization reaches convergence.<sup>[1]</sup> Recently, a number of methods have been proposed that use machine learning techniques to construct a surrogate model that goes beyond the second-order expansion and are thus able to better utilize all the information generated during the optimization process to find the target more efficiently. One such method is the restricted variance optimization (RVO),<sup>[2]</sup> based on a Gaussian process regression surrogate model aided by chemical heuristics. In a conical intersection, two adiabatic potential energy surfaces are exactly degenerate, and the degeneracy is broken linearly along two independent structural distortions.<sup>[3]</sup> This results in surfaces that have cusps (forming a double cone, hence the name “conical intersection”) and are therefore not differentiable. Additionally, optimization methods to locate conical intersections work better when they can make use of the nonadiabatic coupling vector, which is not directly obtainable from the potential energy surfaces only. Hence, creating a surrogate model for RVO capable



of describing the cusps of conical intersections and of providing nonadiabatic coupling predictions requires some effort. This report shows a possible way to construct a model consisting of three smooth, differentiable surfaces that when combined can accurately reproduce the potential energy surfaces and nonadiabatic couplings at and around a conical intersection.<sup>[4]</sup> Using this model together the RVO method reduces the computational effort needed for locating minimum energy conical intersections with respect to a state-of-the-art conventional second-order method.

[1] Schlegel, H. B., "Wiley Interdiscip." *Rev.: Comput. Mol. Sci* 1.5 (2011): 790-809.

[2] Raggi, G., Fdez. Galván, I., Ritterhoff, C. L., Vacher, M., Lindh, R., *J. Chem. Theory Comput.* 16 (2020), 3989–4001.

[3] Fdez. Galván, I., Delcey, M. G., Pedersen, T. B., Aquilante, F., Lindh, R., *J. Chem. Theory Comput.* 12 (2016), 3636–3653.

[4] Fdez. Galván, I., Lindh, R., *J. Chem. Theory Comput.* (2023), in press.doi:10.1021/acs.jctc.3c00389



## Towards a FCIQMC implementation of Complete Active Space Second Order Perturbation Theory

Arta A. Safari, Robert J. Anderson, Giovanni Li Manni

Max-Planck-Institute for Solid State Research, Germany

The last decade has seen much progress in developing sparse Full Configuration Interaction solvers such as FCIQMC.<sup>[1]</sup> Nevertheless, the requirement for a large one-particle basis to converge dynamic correlation effects on top of these reference wave functions continues to fuel research in perturbation theory, for instance Complete Active Space Second Order Perturbation Theory (CASPT2).<sup>[2]</sup> A prior attempt to couple FCIQMC to CASPT2 was hampered by difficulties in sampling the inverse of the three-particle density matrix (3RDM) used to orthogonalise the perturber functions.<sup>[3]</sup> In this contribution, we present the prototype of a new approach for accurately calculating higher order RDMs in FCIQMC which consists of: (1) restricting the sampling of the corresponding excitations to a deterministic subspace, (2) averaging RDMs from statistically independent runs and (3) projecting the averaged 3RDM onto the closest positive semi-definite matrix. The Chromium dimer CASSCF(12,12)/CASPT2 binding curve is computed as a proof of concept.

[1] Booth, G. H., Thom, A. J. W., Alavi, A., *J. Chem. Phys.* 131 (2009), 054106.

[2] Andersson, K., Roos, B. O. in *Advanced Series in Physical Chemistry* vol. 2 55–109 (World Scientific Publishing Company, 1995).

[3] Anderson, R. J., Shiozaki, T., Booth, G. H., *J. Chem. Phys.* 152 (2020), 054101.

## Spin-phonon coupling calculations in crystalline molecular magnetic materials

Jakob Staab, Rizwan Nabi and Nicholas Chilton

The University of Manchester, UK

Single-molecule magnets (SMMs) are an interesting research subject due to their potential applications in high density data storage and spintronic devices. Finite temperature spin dynamics driven by energy exchange between thermal vibrational energy present in the environment is detrimental to many of their desired properties, and harnessing the coupling of phonons to the electronic states is crucial to the design of the next generation SMMs. The computational modeling of crystalline molecular magnetic materials is an important cornerstone in understanding relaxation and decoherence pathways on the atomic level,<sup>[1,2]</sup> but the treatment of extended, infinitely periodic environments poses major challenges to contemporary quantum chemical protocols: (i) The efficient derivation of spin-phonon coupling parameters along tens of thousands of nuclear degrees of freedom; and (ii) The consistent inclusion of the long range electrostatic potential into correlated wave function methods. Recently, we implemented the fully analytical, single-shot linear vibronic coupling method which enables the efficient and accurate evaluation of spin-phonon couplings in extended systems, where the environment is described by point charges, at the cost of the gas phase calculation.<sup>[3]</sup> Using a finite cluster expansion of point charges coupled with a reaction field approach to recover the long-range electrostatics, we obtain the true Ewald potential to be employed for single point and gradient calculations alike exploiting infrastructure readily available in OpenMolcas, and compute temperature dependent magnetic relaxation rates in a Dy(III) based SMM in the solid state which show close agreement with experiment.

[1] Briganti, M., Santanni, F., Tesi, L., Totti, F., Sessoli, R., Lunghi, A., *J. Am. Chem. Soc.* 134 (2021), 13633–13645.

[2] Mondal, S., Lunghi, A., arXiv preprint arXiv:2212.11705 (2022)

[3] Staab, J. K., Chilton, N. F., *J. Chem. Theory Comput.* 18 (2022), 6588–6599.

## Exploiting locality in FCIQMC for fast excitation generation

Oskar Weser<sup>1</sup>, Ali Alavi<sup>1,2</sup>, and Giovanni Li Manni<sup>1</sup>

<sup>1</sup> Max-Planck-Institute for Solid State Research, Germany

<sup>2</sup> University of Cambridge, UK

We propose an improvement of the excitation generation algorithm in the full configuration interaction quantum monte carlo (FCIQMC) method, which is particularly effective for systems described by localised orbitals. The method is an extension of the precomputed heat-bath (PCHB) strategy of Holmes et al., with an improved sampling of double excitations and a novel approach for non-uniform sampling of single excitations. We demonstrate the effectiveness of the algorithm for a chain of 30 hydrogen atoms with atom-localised orbitals, a stack of benzene molecules, an Fe-porphyrin model complex, whereby we show an overall efficiency gain by a factor of two to four, as measured by variance reduction per wall-clock time.

## Autonomous Active Space Calculations through AutoCAS

Maximilian Mörchen, Moritz Bensberg, and Markus Reiher

ETH Zürich, Switzerland

In order to describe strongly correlated systems correctly, the choice of an active space imposes one of the greatest problems in multi-configurational quantum chemistry. In the AutoCAS algorithm, concepts from quantum information theory are exploited in order to automatically and consistently select orbitals for an active space. We present our Python-based AutoCAS<sup>[1-4]</sup> module, which can be employed in existing workflows to streamline multi-configurational calculations in a black-box manner. The Python module enables streamlining of active space methods,<sup>[5]</sup> as well as the customization of existing AutoCAS workflows. With our latest addition of consistent orbital spaces along reaction coordinates,<sup>[6]</sup> post-active space methods like Tailored Coupled Cluster<sup>[7-9]</sup> or second order perturbation theory<sup>[10]</sup> can be routinely applied to chemical reactions.

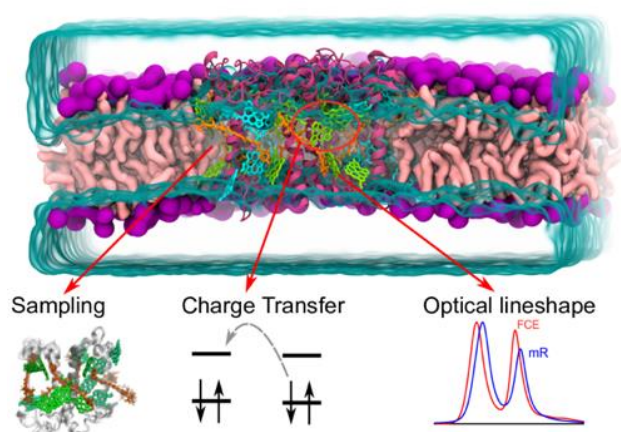
- [1] Stein, C. J., Reiher, M., *J. Comput. Chem.* 40 (2019), 2216-2226.
- [2] Stein, C. J., Reiher, M., *J. Chem. Theory Comput.* 12 (2016), 1760-1771.
- [3] Stein, C. J., von Burg V., Reiher, M., *J. Chem. Theory Comput.* 12 (2'16), 3764-3773.
- [4] Stein, C. J., Reiher M., *Chimia* 71 (2017), 170-176.
- [5] Unsleberet, J. et al., *J. Chem. Phys.* 158 (2022), 084803.
- [6] Bensberg, M., Reiher, M., *J. Phys. Chem. Lett.* 14 (2023), 2112-2118.
- [7] Kinoshita, T., Hino, O., Bartlett, R. J., *J. Chem. Phys.* 123 (2005), 074106.
- [8] Veis, L. et al., *J. Phys. Chem. Lett.* 7 (2016), 4072-4078.
- [9] Mörchen, M., Freitag, L., Reiher, M., *J. Chem. Phys.* 153 (2020), 24413.
- [10] Freitag, L. et al., *J. Chem. Theory Comput.* 13 (2017), 451-459.

# Multiscale Quantum Mechanical Modeling of Light-Harvesting Complexes

Lorenzo Cupellini

Università di Pisa, Italy

Multichromophoric systems represent a challenge for traditional multiscale quantum chemical (QM) methods, as they owe their photophysical properties both to the coupling among chromophores and to the interaction with the surrounding environment. A remarkable example is represented by light-harvesting complexes (LHCs), which are pigment aggregates embedded in a protein matrix. Each pigment experiences a specific protein environment, optimized by evolution towards enhancing the absorption and energy transport properties of the LHC. Strategies combining exciton models and multiscale QM calculations have significantly advanced our understanding of these systems, but major challenges still need to be faced to gain a quantitative picture of the photophysics in these systems.<sup>[1-3]</sup> Here I will focus on the main challenges for a complete description of LHCs and the strategies recently developed to tackle them. First, a faithful sampling of the complex conformational space of LHCs is needed, coupled with a statistically robust estimation of exciton parameters. To overcome this issue, we developed a machine learning strategy for predicting exciton Hamiltonians from molecular dynamics simulations.<sup>[4]</sup> Second, photophysical properties of some LHCs depend on charge-transfer (CT) excitations, which have to be included in the models.<sup>[5]</sup> Finally, a robust method is needed to predict spectral properties from the excitonic Hamiltonian computed with multiscale QM methods and obtain a fair comparison to experiments. Here, non-Markovian cumulant expansion approaches have proven effective in faithfully reproducing the optical lineshapes.<sup>[6]</sup>



[1] Cupellini, L. et al., *BBA - Bioenergetics*, 1861.4 (2020), 148049.

[2] Segatta, F. et al., *Chem. Rev.* 119 (2019), 9361–9380.

[3] Cignoni, E. et al., *J. Chem. Phys.* 156 (2022), 120901.

[4] Cignoni, E. et al., *J. Chem. Theory Comput.* 19 (2023), 965.

[5] Cupellini, L. et al. *J. Phys. Chem. Lett.* 9 (2018), 6892.

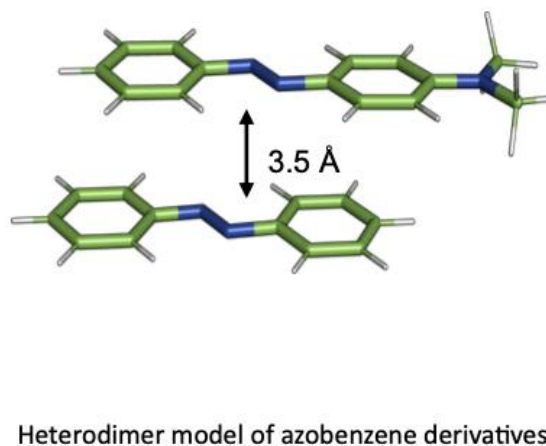
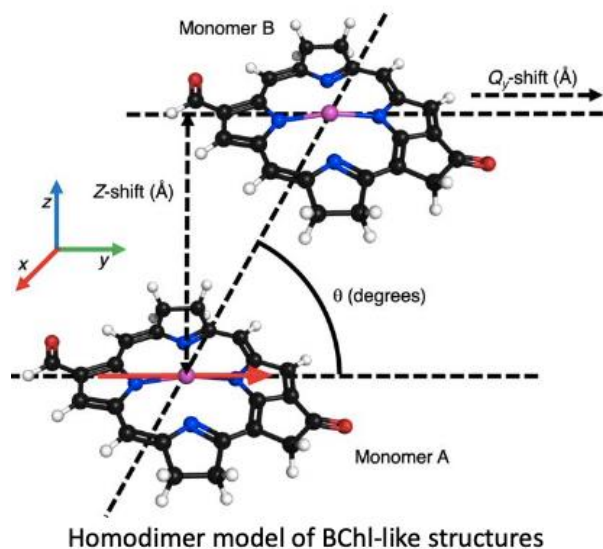
[6] Cupellini, L. et al., *J. Phys. Chem. B* 124 (2020), 8610.

## Assessing Coulomb Interactions in Molecular Aggregates: example applications of Frenkel's model

Razan E. Daoud

Università degli Studi di Siena, Italy

The accuracy of evaluating the UV-Vis absorption of noncovalently bound molecular aggregates relies on the distances between molecules. When intermolecular distances and molecular sizes are of similar magnitude, the conventional dipole-dipole approach becomes invalid, and at least Coulomb interactions have to be properly described. The Frenkel's formalism, in which the dimer is separated into two interacting monomers, has proven to be highly effective. A recent development, integrated into the OpenMolcas package,<sup>[1,2]</sup> allows for the assessment of Coulomb couplings, within Frenkel's formalism, employing multireference, multiconfigurational energetics for individual monomers, such as MS-RASPT2/SA-RASSCF. The main advantage of this method is that the computational bottleneck lies in calculating the energetics of the single interacting monomers. In this talk, I will showcase the applications of this code to dimeric aggregates of molecules with extended  $\pi$  systems, such as Bacteriochlorophyll (BChl)-like models or azobenzene derivatives. Various properties, including H- and J-aggregate formation and absorption spectra, will be discussed and compared to those of the isolated monomers.



[1] Kaiser, A. et al., *J. Chem. Theory Comput.* (2023).

[2] Li Manni, G. et al. *J. Chem. Theory Comput.* (2023).

## The shape of CASPT2 conical intersections

Ignacio Fdez. Galván<sup>1</sup>, Stefano Battaglia<sup>1</sup>

<sup>1</sup> Uppsala University, Sweden

<sup>2</sup> University of Zurich, Switzerland

Conical intersections are crucial features of the potential energy surface and play a fundamental role in the photochemistry of polyatomic molecules. The accurate computation of their shape and location is therefore of paramount importance for the simulation of photochemical processes. In this talk I will present a systematic comparison of conical intersections obtained at different levels of theory and quantitatively assess their accuracy through the use of a linear model.<sup>[1]</sup> In particular, owing to the recent implementation of analytic nuclear gradients and derivative coupling vectors for the CASPT2 approach,<sup>[2,3]</sup> the conical intersections were located for several quasi-degenerate variants of the theory<sup>[4-6]</sup> and compared to those obtained by SA-CASSCF. While in most cases the differences between the levels of theory are only quantitative, qualitative differences are observed for a few systems.

[1] Fdez. Galván, I., Delcey, M. G., Pedersen, T. B., Aquilante, F., Lindh, R., *J. Chem. Theory Comput.* 12 (2016), 3636–3653.

[2] Nishimoto, Y., *J. Chem. Phys.* 154 (2021), 194103.

[3] Nishimoto, Y., Battaglia, S., Lindh, R., *J. Chem. Theory Comput.* 18 (2022), 4269–4281.

[4] Shiozaki, T., Győrffy, W., Celani, P., Werner, H.-J., *J. Chem. Phys.* **135** (2011), 081106.

[5] Battaglia, S., Lindh, R., *J. Chem. Theory Comput.* 16 (2020), 1555–1567.

[6] Battaglia, S., Lindh, R., *J. Chem. Phys.* 154 (2021), 034102.

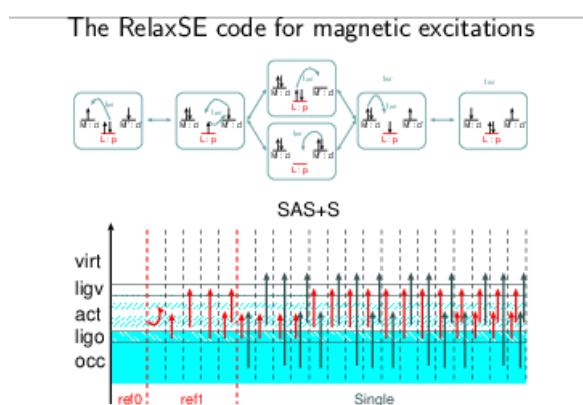
## Computing low energy excitations in strongly correlated system: RelaxSE

Marie-Bernadette Lepetit<sup>1,2</sup>, Elisa Rebolini<sup>2</sup>

<sup>1</sup> Institut Néel, CNRS Grenoble, France

<sup>2</sup> Institut Laue Langevin, Grenoble, France

Strongly correlated systems are characterized by the fact that their low energy properties are not driven by the delocalization resulting from their kinetic energy, but by the effect of Coulomb's repulsion between electrons. As a result, they cannot be described, even in a qualitative way, by a single determinant wave-function. Methods based on such a representation (HF, DFT) thus encounter difficulties to correctly describe both their ground state and their low energy excited states. Indeed, the later do often correspond to magnetic excitations, that cannot be qualitatively described as charge transfers or electronic density changes, but rather as entanglement modifications between the wave-function determinants. The accurate calculation of this type of excitation requires specific MRCI ab-initio methods. Over the years, the CAS+DDCI<sup>[1-3]</sup> method have proved its efficiency, but due to its computational cost, its use is restricted to systems with few magnetic orbitals per magnetic atom. When the number of magnetic orbitals per atoms increases, it becomes compulsory to rely on the selection with the CAS configurations such as in the SAS+S<sup>[4]</sup> method developed in our group. After an introduction on the different effects that should be taken into account for an accurate treatment of the magnetic excitations, we will present our new code RelaxSE,<sup>[5]</sup> recently developed to describe this type of excitations.



[1] Miralles, J., Daudey J. P., Caballol, R., *Chem. Phys. Lett.*, 198 (1992), 555-562.

[2] Garcia, V. M. et al., *Chem. Phys. Lett.*, 238 (195), 222-229.

[3] Garcia, V. M., Reguero, M., Caballol, R., *Theor. Chem. Acc.*, 98 (1997), 50.

[4] Gellé, A., Varignon, J., Lepetit, M.-B., *EPL* 88.3 (2009), 37003.

[5] Rebolini, E., Lepetit, M.-B., *J. Chem. Phys.*, 154 (2021), 164116.

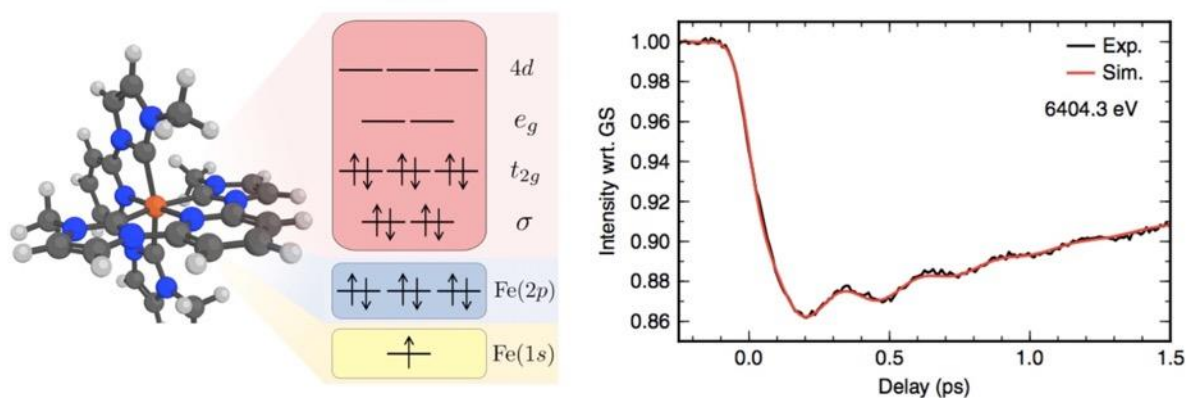


## Efficient excited-state algorithms used to simulate x-ray probes of coherent structural dynamics in iron photocatalyst

Marcus Lundberg

Uppsala University, Sweden

The outcome of photochemical reactions in transition metal complexes depends on both structural and electronic dynamics. X-rays are ideal probes of such processes as they are element specific and do not interfere with the optical pump. However, from a computational perspective the multiroot Davidson algorithm is not suitable for processes that involve hundreds of high-energy states. We show how a restricted active space wavefunction, together with a projection operator that removes low-lying electronic states (HEXS keyword), offers an efficient way to reach single and double-core-hole states when combined with an improved configuration interaction (CI) algorithm.<sup>[1]</sup> This enabled us to model the  $K\alpha$  ( $2p \rightarrow 1s$  transitions) x-ray emission signal of coherent structural dynamics ( $[\text{Fe}^{\text{II}}(\text{bmip})_2]^{2+}$  [bmip = 2,6-bis(3-methyl-imidazole-1-ylidene)-pyridine]), which is an iron photosensitizer that can donate electrons into a fuel-forming reaction with very high efficiency.<sup>[2]</sup> The sensitivity of core-to-core transitions to structural dynamics is due to a shift of the potential energy surfaces between  $1s$  and  $2p$  core-hole states.<sup>[3]</sup> Further, we show that experimental sensitivity can be optimized by tuning the energy of the emission spectrometer.<sup>[3,4]</sup> This can be used to design experiments that separate electronic and nuclear degrees of freedom in ultrafast excited state dynamics, and to interpret x-ray emission signals from highly non-equilibrium structures that are ubiquitous in photophysics and photochemistry.



[1] Delcey, M.G., Kragh Sørensen, L., Vacher, M., Couto, R.C., Lundberg, M., *J. Comput. Chem.* 40 (2019), 1789–1799.

[2] Kunnus, K. et al., *Nat. Commun.*, 11 (2020), 634.

[3] Vacher, M., Kunnus, K., Delcey, M.G., Gaffney, K., Lundberg, M., *Struct. Dyn.* 7 (2020), 044102.

[4] Rogvall, J., Singh, R., Vacher, M., Lundberg, M., *Phys. Chem. Chem. Phys.*, 25 (2023), 10447–10459.

## Performance of Multireference Wave Function and Density Functional Theories for K-Edge X-Ray Absorption Spectra of Solvated Transition Metal Ions

Soumen Ghosh

Indian Institute of Technology, Indore, India

Solvated transition metal (TM) ions in aqueous environment play an important role in many reactions occurring in chemical and biological systems as well as in industrial applications. Understanding the solvation structure of TM ions is important due to its broad impact on the kinetics, stability, and reactivity in a variety of applications in geochemistry, biochemistry, energy storage, and environmental chemistry. X-ray absorption near edge spectroscopy (XANES) is particularly useful in predicting local electronic structure and local solvation structure of an atom. A quantitative predictive tool can be useful for an easy and accurate characterization of different TM containing systems. In this work, different theoretical techniques have been used to predict XANES of TM ions solvated in water. Accuracy of different theoretical techniques have been assessed with respect to experimental XANES results measured for the TM ions with water as the common ligand that involves  $1s$  to  $3d$  electronic transitions. Among different theoretical techniques, time-dependent density functional theory (TDDFT) provided accurate results only for cases where XANES is dominated by singly excited states while multireference second order perturbative method and multiconfiguration pair-density functional theory can distinguish between singly and higher order excited states quantitatively.

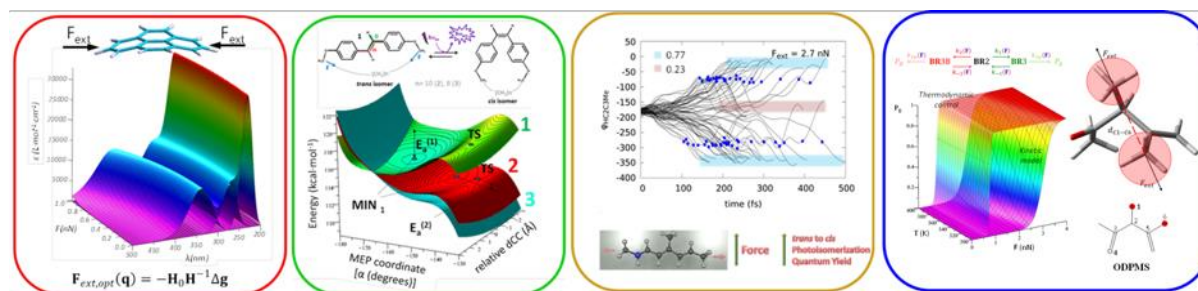
## Mechanical control of photochemical processes: computational strategies and tools

Alejandro Jodra<sup>1</sup>, Alessio Valentini<sup>2</sup>, Luis Manuel Frutos<sup>1</sup>

<sup>1</sup> Universidad de Alcalá, Spain

<sup>2</sup> Stanford University, USA

Mechano-photochemistry stands for the mechanical control of photochemical processes (*i.e.* by means of mechanical forces). In recent years it has been shown that different aspects of the photochemical reactivity can be mechanically controlled, including excitation/emission energy,<sup>[1]</sup> excited states-lifetime,<sup>[2]</sup> photoreaction quantum yield<sup>[3]</sup> or photoproducts formation<sup>[4]</sup> (see Figure 1). Different computational tools have to be implemented in order to simulate this kind of processes, some of them available in OpenMolcas, and others to be implemented.



**Figure 1.** From left to right: (a) mechanical modulation of the absorption spectrum in pyrene, (b) excited-state lifetime change induced by external forces in stilbene (c) variation of the photoisomerization quantum yield by pulling forces on retinal-type chromophore. (d) mechanical control of photoproduct formation in oxa-di-pi-methane photorearrangement.

[1] Nucci, M., Marazzi, M., Frutos, L. M., *ACS Sustainable Chem. Eng.* 7 (2019), 19496–19504.

[2] García-Iriepa, C., Sampedro, D., Mendicuti, F., Léonard, J., Frutos L. M., *J. Phys. Chem. Lett.* 10 (2019), 1063–1067.

[3] Valentini, A., Rivero, D., Zapata, F., García-Iriepa, C., Marazzi, M., Palmeiro, R., Fdez. Galván, I., Sampedro, D., Olivucci, M., Frutos L. M., *Angew. Chem. Int. Ed.* 56 (2017), 3842-3846.

[4] Jodra, A., García-Iriepa, C., Frutos, L.M., *J. Org. Chem.* 87 (2022), 12586-12595.

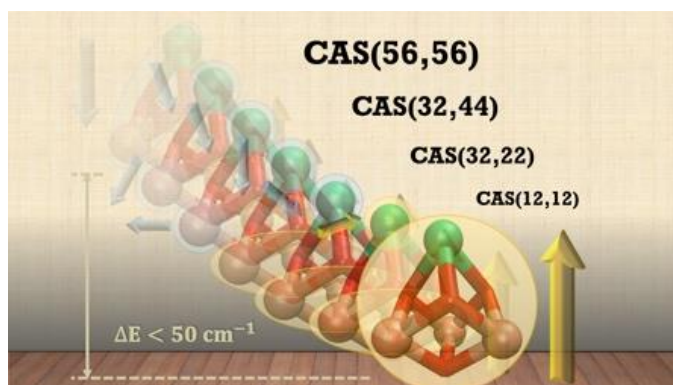
## Multi-Reference Tools in OpenMolcas to Study Poly-Nuclear Transition Metal Clusters

Giovanni Li Manni<sup>1</sup>, Sandra Luber<sup>2</sup>, Oskar Weser<sup>1</sup>, Ruocheng Han<sup>2</sup>

<sup>1</sup> University of Zurich, Switzerland

<sup>2</sup> Max Planck Institute for Solid State Research, Germany

Computer simulations of the electronic structures of poly-nuclear transition metal (PNTM) clusters, and of excited states of one-center TM complexes featuring substantial spin delocalization, represent two crucial challenges in modern quantum chemistry, due to (1) the large number of nearly-degenerate electronic states, (2) long-range spin interactions, and (3) spin-frustration effects. For these systems, multi-configurational (MC) strategies are unavoidable. In this talk we show the latest multi-reference tools, that we made available in OpenMolcas, in the form of the Stochastic-CASSCF and Stochastic-GASSCF, coupled to the post-MCSCF MCPDFT approach, to tackle both strong and dynamic correlation effects in these challenging systems. Local symmetries exist that can be revealed by a conceptual strategy, Quantum Anamorphosis, based on spin adapted bases and simple unitary orbital transformations. Quantum Anamorphosis dramatically reduces the computational costs of large active space calculations, while easing the characterization of the targeted electronic states. The foundation of Quantum Anamorphosis will be discussed. Next to the pivotal effects of Quantum Anamorphosis toward poly-nuclear transition metal clusters, we show that its applicability extends to the unique *intra-molecular singlet fission* process that leads to unexpected deexcitation paths in molecular photophysics.



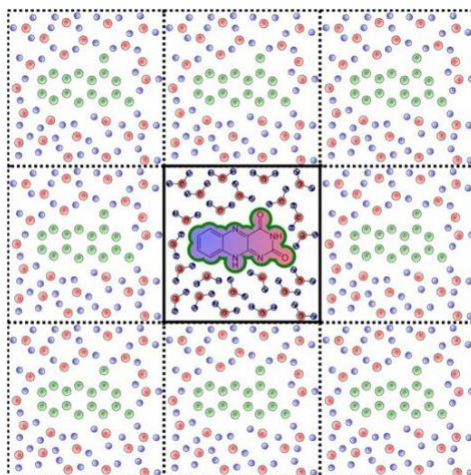
- [1] Li Manni, G., Kats, D., Liebermann, N., *J. Chem. Theory Comput.*, 19 (2023), 1218.
- [2] Han, R., Luber, S., Li Manni, G., *J. Chem. Theory Comput.* (2023).
- [3] Dobrautz, W., Katukuri, V. M., Bogdanov, N. A., Kats, D., Li Manni, G., Alavi, A., *Phys. Rev. B* 105 (2022), 195123.
- [4] Li Manni, G., *Phys. Chem. Chem. Phys.* 23 (2021), 19766.
- [5] Li Manni, G., Dobrautz, W., Bogdanov, N. A., Guthier, K., Alavi, A., *J. Phys. Chem. A* 125 (2021), 4727.
- [6] Dobrautz, W., Weser, O., Bogdanov, N. A., Alavi, A., Li Manni, G., *J. Chem. Theory Comput.* 17 (2021), 5684.
- [7] Weser, O., Guthier, K., Ghanem, K., Li Manni, G., *J. Chem. Theory Comput.* 18 (2021), 251.
- [8] Li Manni, G., Dobrautz, W., Alavi, A., *J. Chem. Theory Comput.* 16 (2020), 2202.

## Efficient *ab initio* electrostatic embedding QM/MM method in periodic boundary conditions

Miquel Huix-Rotllant

ICR, CNRS, Aix-Marseille University, France

Hybrid quantum mechanics/molecular mechanics (QM/MM) models are successful at describing the properties and reactivity of biological macromolecules. Combining *ab initio* QM/MM methods and periodic boundary conditions (PBC) is an optimal approach for modeling chemical processes in condensed phase, but frequently, these models are too time-consuming for general applicability to biological systems in a solution. In this talk, I will define a simple and efficient electrostatic embedding QM/MM model in PBC, combining the benefits of electrostatic potential fitted atomic charges and particle-mesh Ewald sums, which can efficiently treat systems of an arbitrary size at a reasonable computational cost. To illustrate this, I will show an accurate reproduction of the absorption maximum from a model for *Arabidopsis thaliana* cryptochrome 1 containing circa 93 000 atoms.



## Correlated methods for local and ultrafast processes, also involving the electronic continuum - From X-ray absorption to resonant Auger-Meitner

Sonia Coriani<sup>1</sup>, B. N. C. Tenorio<sup>1</sup>, J. Pedersen<sup>1</sup>, P. Decleva<sup>2</sup>

<sup>1</sup> Technical University of Denmark, Denmark

<sup>2</sup> University of Trieste, Italy

An overview of our most recent work targeting different types of ionization and/or excitation processes using, among others, OpenMolcas will be presented, ranging from (X)UV photoionization,<sup>[1]</sup> to double-core hole ionization,<sup>[2]</sup> X-ray absorption, XPS, and normal and resonant Auger-Meitner.<sup>[3,4,5]</sup>

[1] Tenorio, B.N.C., Ponzi, A.; Coriani, S.; Decleva, P., *Molecules* 27 (2022), 1203

[2] Tenorio, B.N.C., Decleva, P., Coriani, S., *J. Chem. Phys.* 155 (2021), 131101

[3] Tenorio, B.N.C., Møller, K. B., Decleva, P., Coriani, S., *Phys. Chem. Chem. Phys.* 24 (2022), 28150

[4] Tenorio, B.N.C., Voß, T.A., Bokarev, S.I., Decleva, P., Coriani, S., *J. Chem. Theory Comput.* 18 (2022), 4387–4407

[5] Pedersen, J., Decleva, P., Coriani S., Tenorio, B.N.C., submitted to *J. Chem. Phys.* (2023)

## Accurate CASPT2 dynamics with analytical gradients: tracking ultrafast $S_2$ deactivation in acetylacetone

Flavia Aleotti<sup>1</sup>, S. Severino<sup>2</sup>, F. Segatta<sup>1</sup>, L. Mai<sup>2</sup>, A. Corego<sup>3,4</sup>, F. Medeghini<sup>2</sup>, F. Frassetto<sup>3</sup>, L. Poletto<sup>3</sup>, M. Lucchini<sup>2,3</sup>, M. B. Reduzzi<sup>2</sup>, R. Borrego Varillas<sup>3</sup>, M. Nisoli<sup>2,3</sup>, A. Nenov<sup>1</sup>

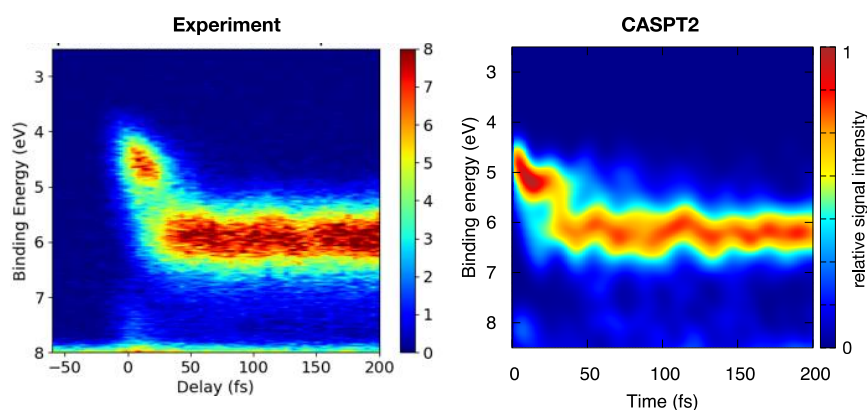
<sup>1</sup> Università di Bologna, Italy

<sup>2</sup> Politecnico di Milano, Italy

<sup>3</sup> IFN-CNR, Italy

<sup>4</sup> Universidad de Salamanca, Spain

The recent advancements in the temporal resolution of experimental spectroscopic techniques and in the accuracy of electronic structure methods have allowed to close the gap between experiment and theory and to gain a deep understanding of the coupled electronic–nuclear dynamics behind photoinduced molecular motions.<sup>[1]</sup> In the present study, we show how surface hopping nonadiabatic dynamics simulations performed with multiconfigurational wavefunction theory (CASSCF/CASPT2) for photoexcited acetylacetone are able to faithfully reproduce highly-resolved transient photoelectron spectroscopy (TRPES) experiments recently performed (by the group of Prof. Mauro Nisoli) with unprecedented temporal resolution (sub-20 fs). With over 100 nuclear trajectories, our simulations track the sub-50 fs intramolecular H-atom transfer driving the  $S_2 \rightarrow S_1$  internal conversion immediately after excitation<sup>[2]</sup> (Fig. 1) and allow to quantitatively reproduce the experimental evidence both in terms of binding energy and time-evolution of the associated signals. The protocol for TRPES simulation (along with protocols for transient UV/Vis and X-ray spectroscopies) is fully integrated in the COBRAMM package<sup>[3]</sup> and makes use of wavefunction overlap (i.e. Dyson norm) between valence and ionic excited states along the nuclear trajectories to reproduce the experimental cross-section.



**Figure 1.** experimental (gas-phase, left) and simulated (XMS-CASPT2/SA5-CASSCF(10,8)/cc-pVDZ, right) TRPES spectrum of acetylacetone in the first 200 fs after photoexcitation to the bright  $S_2$  state.

[1] Conti, I., Cerullo, G., Nenov A., Garavelli, M., *JACS* 142 (2020), 16117-16139.

[2] Poisson, L., Roubin, P., Coussan, S., Soep, B., Mestdagh, J., *JACS* 130 (2008), 2974-2983.

[3] Cobramm is Optimized in Bologna to Run Ab-initio and Molecular Mechanics (COBRAMM), available at <https://gitlab.com/cobrammgroup/cobramm/>

# POSTERS

Click for a link to the corresponding abstract

## IN PRESENCE:

- B. E. Atkinson: *"Ab initio paramagnetic NMR shifts with Hyperion"*
- T. Piteša: *"Excitonic Configuration Interaction: Going Beyond the Frenkel Exciton Model"*
- H. Ye: *"Exploiting the 'Lego brick' approach to predict accurate equilibrium structure of PA(N)Hs and biological building blocks"*
- R. Feldmann: *"Nuclear-Electronic Hartree-Fock Density Matrix Renormalization Group"*
- S. I. Bokarev: *"Spin dynamics in the basis of irreducible spherical tensors"*
- O. Weingart: *"Emission properties of the MIA chromophore in solid state environments"*
- R. K. Jingar: *"Accurate description of electric and magnetic dipole transitions in  $\text{Eu}^{3+}$  ions using selected spin-orbit quasi-degenerate perturbation theory"*
- Najat Qisse: *"Upgrading of a raw waste coffee grounds product for the treatment of Zn adsorption in wastewater effluents"*

## ONLINE:

- K. Kotsis: *"An exploration of spin states in nanoparticle structures"*
- F. Calcagno: *"Predicting the exchange coupling constant in a diiron complex"*
- R. Shepard: *"The efficient conversion between linear wavefunction expansions and nonlinear Graphically Contracted Function expansions"*
- Y. Pillco Valencia: *"Electronic properties of selenium-modified nucleic bases"*
- J. G. Vitillo: *"Heme and nonheme single-iron catalytic sites in enzymes and in reticular frameworks for methane-to-methanol oxidation"*
- I. Öztürk: *"Computational investigation of medical drugs with DNA nucleobase pairs by quantum chemical methods and QM/MM trial"*



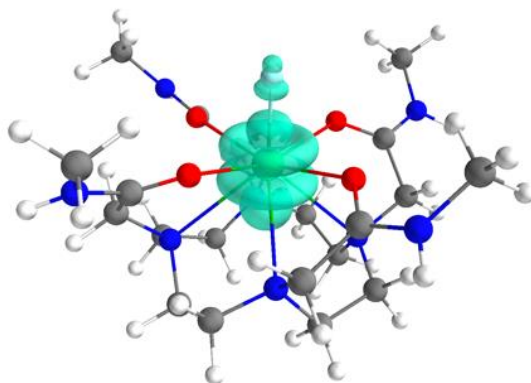


## *Ab initio* paramagnetic NMR shifts with Hyperion

Benjamin E. Atkinson, Letitia Birnoschi and Nicholas F. Chilton

The University of Manchester, UK

The paramagnetic NMR (pNMR) of open-shell f-block containing molecules offers valuable insight into their magnetic properties and bonding but can be complex and difficult to interpret, driving interest in the development of theoretical methods to predict paramagnetic chemical shifts. We have implemented the equation for the paramagnetic chemical shift derived by Van den Heuvel and Soncini, a fully *ab initio* equation derived as a partial derivative of the Helmholtz energy,<sup>[1]</sup> in Hyperion. Hyperion is a program developed in the group, capable of calculating relativistic picture-change-corrected Zeeman g-tensors and hyperfine coupling parameters from spin-orbit complete active space wavefunctions. It is open source, easy to use and interface with OpenMolcas.<sup>[2]</sup> We have profiled our implementation against a previous implementation of the Van den Heuvel and Soncini equation.<sup>[3]</sup> Additionally we have compared several systems previously studied by methods which only include the pseudo-contact part of the pNMR shift and have obtained promising improvements to the calculated shift when compared with experiment. We are also exploring the field dependence of the paramagnetic shift, which has previously been shown to be affected by the strength of the magnetic field of the spectrometer, likely due to the large number of low-lying states perturbed by the magnetic field.



**Figure 1.** The calculated spin density of the CASSCF ground state of  $[\text{Yb.DTMA.F}]^{2+}$ , a complex previously studied in the group with pseudo-contact only methods.<sup>[4]</sup>

[1] Van den Heuvel, W., Soncini, A., *J. Chem. Phys.* 138 (2013), 054113.

[2] Birnoschi, L., Chilton, N. F., *J. Chem. Theory Comput.* 18 (2022), 4719–4732, available at <https://gitlab.com/chilton-group/hyperion>

[3] Gendron, F. et al., *J. Phys. Chem.* 6 (2015), 2183–2188.

[4] Blackburn, O. A. et al., *Angew. Chem. Int. Ed.* 54 (2015), 10783 –10786.

## Excitonic Configuration Interaction: Going Beyond the Frenkel Exciton Model

Tomislav Piteša, Severin Polonius, Sebastian Mai, Leticia González

University of Vienna, Austria

Nowadays there is a versatile variety of accurate electronic-structure methods for the excited-state calculations, ranging from single-reference (TDDFT, MP/ADC, and EOM-CC etc.) to the multi-reference (CASPT2, MRCI etc.) ones. However, all of these methods scale unfavourably with the system size, and therefore are often not applicable on large molecules, such as e.g. multichromophoric systems. An alternative to the direct treatment of the full system in these cases is to employ an excitonic model. The underlying philosophy of all excitonic models is to obtain the electronic states of individual chromophores (site states), and then construct a set of their antisymmetrized products (excitonic basis). The full-system Hamiltonian is then represented in the excitonic basis and diagonalized.<sup>[1]</sup> Many of the so-far developed models rely on the famous Frenkel excitonic model, which employs an ad hoc parametrization the Hamiltonian in the basis of only local- excitation products – ones having only one site in an excited state.<sup>[2]</sup> In this work, we present the Excitonic Configuration Interaction (ECI) method – an excitonic-like approach, which (i) self-consistently constructs the excitonic basis so that it minimizes the full-system ground-state energy and (ii) can account for the contributions of both local and non-local excitations to the full-system states. The application of ECI to the strongly-correlated complexes is presented, as well as the comparison with the raw Frenkel model and with the Frenkel model coupled to the electrostatic-embedding scheme.<sup>[3]</sup>

[1] Segatta, F., Cupellini, L., Garavelli, M., Mennucci, B., *Chem. Rev.* 119 (2019), 9361.

[2] Sangiogo Gil, E., Granucci, G., Persico, M., *J. Chem. Theory Comput.* 17 (2021), 7373.

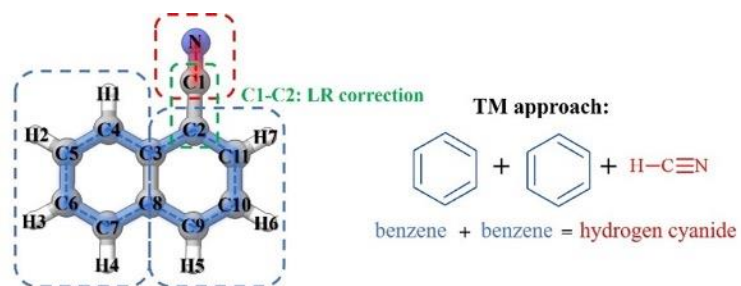
[3] Menger, M. F. S. J., Plasser, F., González, L., *J. Chem. Theory Comput.* 14 (2018), 6139.

## Exploiting the “Lego brick” approach to predict accurate equilibrium structure of PA(N)Hs and biological building blocks

Hexu Ye, Silvia Alessandrini, Mattia Melosso and Cristina Puzzarini

Università di Bologna, Italy

Currently, quantum-chemical (QC) calculations can provide highly accurate equilibrium structures only when composite schemes rooted in the coupled-cluster (CC) theory are employed. Typically, these schemes are based on CC method including single and double excitations, together with perturbative triples (CCSD(T)). This method is extrapolated to the complete basis set (CBS) limit within the frozen core approximation and it is also used to estimate the core-correlation effects.<sup>[1,2]</sup> Whenever possible higher-order terms such as the contributions of quadruple excitations or relativistic effects are included, thus greatly increasing in computational cost. Therefore, these composite schemes are rarely applicable to building blocks of biological molecules (e.g., polycyclic aromatic hydrocarbons (PAHs) and their functionalized forms, but also amino acids and dipeptides) due to their size, and one has to rely on other methodologies to obtain a good estimate of equilibrium structure. The so-called “Lego brick” approach<sup>[3,4]</sup> offers a possible way out by providing equilibrium geometries at a feasible computational cost. This approach is based on the assumption that a molecular system can be seen as formed by smaller fragments for which a very accurate equilibrium structure is available. Within this model, the “template molecule” (TM) approach<sup>[5]</sup> is employed to account for the modifications occurring in moving from the isolated fragment to the molecular system under investigation, while the “linear regression” (LR) model<sup>6</sup> is used to correct the linkage between different fragments, if present. A graphical description of the TM+LR approach is provided in Figure 1, where 1-cyanonaphthalene is used as an example and it is seen as formed by two benzene molecules and the CN group from HCN.<sup>[4]</sup> I will present and discuss how semi-experimental (SE) equilibrium structures taken from the “SE100 database”<sup>[6]</sup> can be used within the TM+LR model to retrieve the accurate equilibrium geometry of several PA(N)Hs, also addressing the accuracy of the methodology in comparison with experimental rotational constants. Indeed, these spectroscopic parameters are strongly connected to molecular structures and can be used to understand the accuracy of the TM+LR approach once the vibrational contribution to the rotational constant is considered. The latter was computed at the B3LYP/jun-cc-pVDZ level of theory. Overall, it is shown that the TM+LR and experimental rotational constants agree well within 0.1%.<sup>[4]</sup> Such a good agreement suggests that the TM+LR structures are highly accurate, which translates in errors smaller than 0.001 Å for bond lengths and 0.1° for angles.



**Figure 1.** Graphical description of the "Lego brick" TM+LR approach

- [1] Puzzarini, C., Barone, V., *Acc. Chem. Res.*, 51 (2018), 548-556.
- [2] Lupi, J., Alessandrini, S., Puzzarini, C., Barone, V., *J. Chem. Theory Comput.*, 17 (2021), 6974.
- [3] Melli, A., Tonolo, F., Barone, V., Puzzarini, C., *J. Phys. Chem. A*, 125 (2021), 9904-9916.
- [4] Ye, H. et al., *Phys. Chem. Chem. Phys.*, 24 (2022), 23254-23264.
- [5] Piccardo, M. et al., *J. Phys. Chem. A*, 119 (2015), 2058-2082.
- [6] Ceselin, G., Barone, V., Tasinato, N., *J. Chem. Theory Comput.*, 17 (2021), 7290-7311.

## An exploration of spin states in nanoparticle structures

Konstantinos Kotsis

University College Dublin, Ireland

Multireference calculations of nanoparticle structures of metals and metal oxides consider the electron spin states. The electronic ground state configuration of a metal nanoparticle, e.g. an Au or Ag nanoparticle consists of electron spin states arising off a large number of metal atoms connected to each other with covalent bonds. The spherical metal nanoparticles of 1 to 2 nm size are constructed from their crystallographic unit cells and the local symmetry is preserved in the final spherical nanoparticle structures. The electronic structure properties of nanoparticles may depend on the size and shape (Wulff, sphere) of the nanoparticle and can be examined in single reference calculations where only the lowest total spin is considered in the calculation, however, in multireference calculations we can ensure an accurate description of the electronic structure of open shell systems and strong electron correlation. A comparison between single reference and multireference calculations is shown.

## Nuclear-Electronic Hartree-Fock Density Matrix Renormalization Group

Robin Feldmann, Alberto Baiardi, and Markus Reiher

ETH Zürich, Switzerland

We introduced the Nuclear-Electronic Hartree-Fock Density Matrix Renormalization Group (NEHF-DMRG) method, designed to solve the molecular time-independent Schrödinger equation without relying on the Born-Oppenheimer approximation. By considering nuclei and electrons equally, NEHF-DMRG accurately accounts for nuclear quantum, anharmonic, and non-adiabatic effects. The convergence of NEHF is always slower than its electronic counterpart. We addressed this problem by developing a comprehensive framework for exact and approximate Newton self-consistent field (SCF) orbital optimization, utilizing concepts from differential geometry. This framework can be applied to both nuclear-electronic and electronic calculations. We have expanded the Augmented Roothaan-Hall (ARH) algorithm for unrestricted electronic and nuclear-electronic calculations, and we showed that the method offers an optimal balance between stability and computational cost for SCF problems with challenging convergence characteristics. In electronic cases, we exhibit ARH's ability to overcome slow orbital convergence in highly-correlated molecules, as illustrated by various iron-sulfur clusters. The ARH algorithm substantially improves convergence even in small molecules for nuclear-electronic calculations, as evidenced by a series of protonated water clusters.

[1] Muolo, A., Baiardi, A., Feldmann, R., Reiher, M., *J. Chem. Phys.* 152 (2020), 204103.

[2] Feldmann, R., Muolo, A., Baiardi, A., Reiher, M., *J. Chem. Theory Comput.* 18 (2022), 234-250.

[3] Feldmann, R., Baiardi, A., Reiher, M., *J. Chem. Theory Comput.* 19 (2023), 856-873.

## Spin dynamics in the basis of irreducible spherical tensors

Thies Romig<sup>1</sup>, Vladislav Kochetov<sup>1</sup>, Sergey I. Bokarev<sup>1,2</sup>

<sup>1</sup> Rostock University, Germany

<sup>2</sup> Technical University of Munich, Germany

The past decade heralds the gradual change of the ultrafast paradigm in physics and chemistry from the femtosecond to subfemtosecond and even a few tens of attoseconds domain. The fascinating growth in the number of ultrafast phenomena studies is due to the establishment of new sources such as X-ray free-electron lasers and high harmonic generation setups that give access to dynamics at electronic time scales. To keep apace with experiments, accurate and efficient theoretical methods need to be developed. In my contribution, I will present recent developments of the density-matrix-based time-dependent restricted active space configuration interaction method ( $\rho$ -TD-RASCI) to compute the ultrafast electron dynamics<sup>[1,2]</sup> which is implemented in the form of the RhoDyn module in OpenMolcas. In particular, the use of irreducible spherical tensors (state multipoles) will be demonstrated for the ultrafast spin dynamics in the core-excited transition metal complexes, and a possible reduction of the computational complexity will be discussed.<sup>[3]</sup>

[1] Kochetov, V., Bokarev, S. I., *J. Chem. Phys.* 153 (2020), 044304.

[2] Kochetov, V., Bokarev, S. I., *J. Chem. Theory Comput.* 18 (2022), 46–58.

[3] Romig, T., Kochetov, V., Bokarev, S. I., *in preparation*.

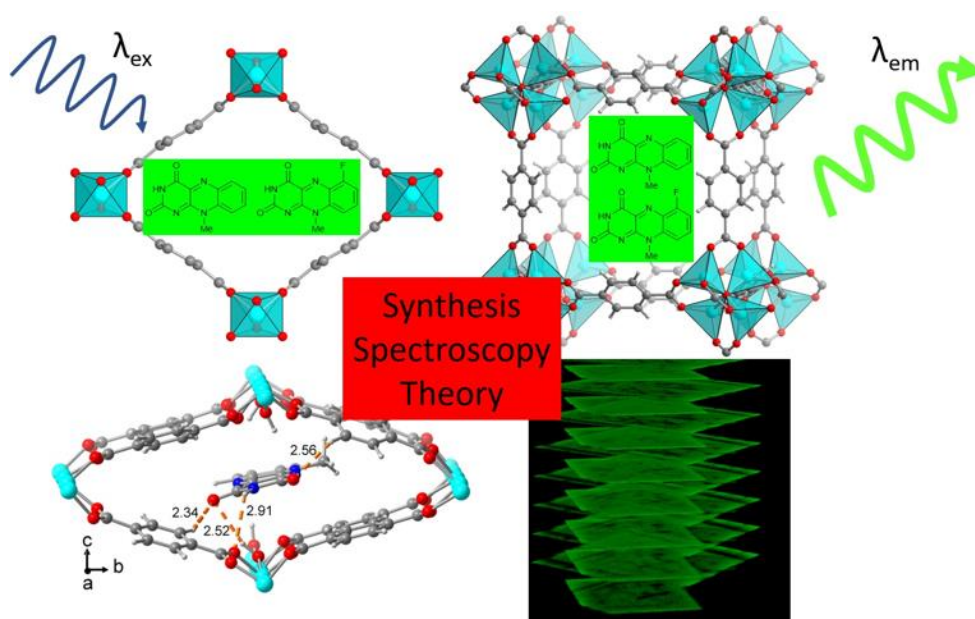


## Emission properties of the MIA chromophore in solid state environments

Simon Hédé, Oliver Weingart

Heinrich-Heine-University Düsseldorf, Germany

Flavins are luminescent chromophores that play an important role in biological photoreception.<sup>[1]</sup> Their luminescence properties strongly depend on their environment. 10-methyl-isoalloxazine (MIA) shows only weak fluorescence in the crystalline state, while it turns into a potent fluorescence emitter when embedded into various metal organic frameworks (MOFs). In this study,<sup>[2]</sup> we investigate the fluorescence emission of MIA in its crystal structure, in MIL-53(Al) and in MOF-5 with plane-wave methods<sup>[3]</sup> and with combined quantum mechanics/molecular mechanics (QM/MM) strategies.<sup>[4]</sup> Our calculations show that the mechanism of fluorescence quenching involves multiple  $\pi$ -interacting MIA molecules. The MOF can restore MIA fluorescence to its intensity in aqueous solution<sup>[5]</sup> with only little influence on absorption and emission wavelengths, thus providing a solid environment for technical applications.



- [1] Losi, A. et al., *Annu. Rev. Plant. Biol.* 63 (2012), 49.  
 [2] Püschel, D. et al., *Molecules* 28.6 (2023), 2877.  
 [3] Giannozzi, P. et al., *J. Phys. Condens. Matter.* 21.39 (2009), 395502.  
 [4] Weingart, O. et al., *J. Mol. Model.*, 24 (2018), 1-30.  
 [5] Bracker, M. et al., *Phys. Chem. Chem. Phys.* 21 (2019), 9912-9923.

## Accurate description of electric and magnetic dipole transitions in $\text{Eu}^{3+}$ ions using selected spin-orbit quasi-degenerate perturbation theory

Rahul Kumar Jingar, Sebastian Mai

University of Vienna, Austria

With certain nanophotonics techniques, it is possible to spatially separate the electric and magnetic components of electro-magnetic radiation. As a result, it becomes theoretically possible to independently measure the response of molecules to electric field–dipole and magnetic field–dipole interactions.<sup>[1]</sup> This allows for the extraction of additional spectral information about the system. However, accurately predicting the electric and magnetic dipole spectra for relevant systems—like lanthanide ions—presents a significant challenge. This challenge arises due to substantial electron correlation, highly degenerate energy levels, and the presence of strong spin–orbit coupling. In this study, our focus centers on the trivalent europium ion ( $\text{Eu}^{3+}$ ) as it exhibits well separated electric-dipole and magnetic-dipole transition.<sup>[2]</sup> To compute the electronic wavefunctions, we employ the complete active space self-consistent field (CASSCF) and the complete active space perturbation theory (CASPT2) methods. Spin–orbit couplings—to split the  $^{2S+1}L$  terms into  $^{2S+1}L^J$  sub-levels—are included by means of the spin–orbit restricted active space state interaction (SO-RASSI) technique.<sup>[3]</sup> One significant bottleneck for these calculations is performing the CASPT2 step for the required large number of states—the large spin–orbit couplings necessitate the inclusion of hundreds of spin-free states for accurate results.<sup>[4,5]</sup> Fortunately, not all spin-free states contribute equally to the spectroscopically relevant spin-orbit states. We are investigating effective computational approaches for the SO-CASPT2 treatment of  $\text{Eu}^{3+}$ , based on selecting a suitable subset of states from a CASSCF calculation encompassing a large number of states. Only the selected states are correlated with CASPT2, and the resulting states are used in the SO-RASSI step to compute the spin–orbit states. The selection of states is either based on energy thresholds with respect to a set of zero-order states, or on the ratio between the spin-orbit coupling and the energy gap involving the zero-order states. We employ this methodology to investigate various  $\text{Eu}^{3+}$  systems starting with the isolated  $\text{Eu}^{3+}$  ion,  $\text{Eu}^{3+}$  incorporated in crystals, and  $\text{Eu}^{3+}$  complexes. These systems exhibit increasing levels of complexity due to the progressive loss of symmetry, which further eliminates degeneracy in the electronic energy levels.

[1] Kasperczyk, M., Person, S., Ananias, D., Carlos, L. D., Novotny, L., *Phys. Rev. Lett.* 114 (2015).

[2] Binnemans, K., *Coord. Chem. Rev.* 295 (2015), 1–45.

[3] Malmqvist, P. Å., Roos, B. O., Schimmelpfennig, B., *Chem. Phys. Lett.* 357 (2002), 230–240.

[4] Babetto, L. et al., *Inorg. Chem.* 60 (2021), 315–324.

[5] Joos, J. J., Smet, P. F., Seijo, L., Barandiarán, Z., *Inorg. Chem. Front.* 7 (2020), 871–888.

## Predicting the exchange coupling constant in a diiron complex

Francesco Calcagno,<sup>1</sup> Francesco Montorsi,<sup>1</sup> Luca Rigamonti,<sup>2</sup> Giovanni Li Manni<sup>3</sup> and Ivan Rivalta<sup>1,4</sup>

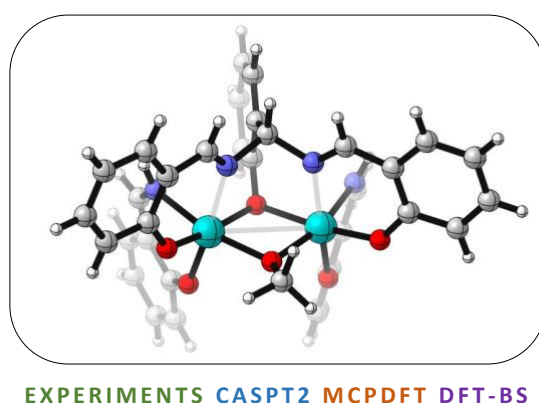
<sup>1</sup> Università di Bologna, Italy

<sup>2</sup> Università degli Studi di Modena e Reggio Emilia, Italy

<sup>3</sup> Max Planck Institute for Solid State, Germany

<sup>4</sup> ENSL, CNRS Lyon, France

In this work we investigated the electronic structure of the complex  $[\text{Fe}^{\text{III}}_2(\mu\text{-salmp})(\mu\text{-OMe})(\text{salim})_2]$  (Figure 1)<sup>[1]</sup>, a promising diiron system for catalytic oxidation reactions. We focused on the magnetic properties of this complex since the hyperfine interactions between the nuclei and electrons, which can be experimentally measured and theoretically computed, can provide fundamental structural information. Predicting relatively small magnetic exchange coupling constants ( $J$ ) is particularly challenging for quantum chemistry methods. Preliminary magnetic measurements suggested a quite small  $J$  of about  $-4 \text{ cm}^{-1}$  ( $-2J \hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2$  formalism), i.e. a weak antiferromagnetic exchange between the two iron(III) centres. We used such small  $J$  value to challenge and to compare the sensibility of different computational approaches, including wavefunction and density functional theory (DFT) methods. DFT broken symmetry (DFT-BS) formalism and the complete active space self-consistent field (CASSCF) method in conjunction with either Møller-Plesset or pair-DFT second-order corrections (i.e. CASPT2 or MC-PDFT) were compared.<sup>[2]</sup> Results show a good agreement with the experimental  $J$  for both DFT-BS and MC-PDFT with a CAS(10,10) active space, while PT2 corrections with such active space appear to overestimate the  $J$  constant. Larger active spaces were also employed to investigate the presence of super-exchange processes *via* the oxygen atoms bridging the iron centres.



**Figure 1.** Crystal structure of the complex  $[\text{Fe}(\text{III})_2(\mu\text{-salmp})(\mu\text{-OR})(\text{salim})_2]$ <sup>[1]</sup>.

[1] Rigamonti, L., Zardi, P., Carlino, S., Demartin, F., Castellano, C., Pigani, L., Ponti, A., Ferretti, A. M., Pasini, A., *Int. J. Mol. Sci.* 21.21 (2020), 7882.

[2] Li Manni, G., Fernández Galván, I., Alavi, A., Aleotti, F., Aquilante, F., Autschbach, J. et al., ChemRxiv. <https://doi.org/10.26434/chemrxiv-2023-b7f0j-v2>

## The efficient conversion between linear wavefunction expansions and nonlinear Graphically Contracted Function expansions

Ron Shepard

Argonne National Laboratory, Lemont, USA

A multifacet Graphically Contracted Function (GCF)<sup>[1]</sup> is a Matrix Product State (MPS) defined in terms of spin-adapted Configuration State Functions (CSF) using a Shavitt graph.<sup>[2]</sup> The Shavitt graph is a hierarchical directed acyclic graph (DAG), whose nodes  $k$  depend on the quantum numbers  $n_k$  (the orbital level),  $N_k$  (the number of electrons), and  $S_k$  (the  $\hat{S}^2$  quantum number). The arcs of the graph connect the nodes in adjacent levels within this graph. There are at most four lower (or upper) arcs associated with each node in the graph. Each CSF corresponds to a unique path from the tail to the head of the graph, touching a single arc between each level. A wave function may be expanded in the basis of these GCFs, and is thereby a linear combination of MPSs,  $|\Psi\rangle = \sum_P^{N_{GCF}} c_P |P\rangle$ . Each arc in the graph is associated with a rectangular matrix of arc coefficients. The coefficient of CSF  $m$  within a GCF  $P$  is given by the sequence of matrix products.

$$x_m^P = \langle m|P\rangle = \alpha_{k_0^m, k_1^m}^P \alpha_{k_1^m, k_2^m}^P \cdots \alpha_{k_{n-2}^m, k_{n-1}^m}^P \alpha_{k_{n-1}^m, k_n^m}^P$$

$\alpha_{k_{q-1}^m, k_q^m}^P$  is the matrix of arc factors associated with the arc  $(k_{q-1}^m, k_q^m)$  between node  $k_{q-1}^m$  a level  $(q-1)$  and node  $k_q^m$  at level  $q$ . When evaluated from right-to-left, this computation reduces to a sequence of matrix-vector products, and when evaluated from left-to-right, the computation is a sequence of vector-matrix products. There is one matrix for each orbital level in this product, so the effort required to compute an individual CSF is approximately  $O(n\bar{f}^2 N_{GCF})$  for  $n$  molecular orbitals and for an average of  $\bar{f}$  facets on each node. The straightforward computation of  $N_{CSF}$ , such coefficients would require  $O(n\bar{f}^2 N_{GCF} N_{CSF})$  effort. If the paths within the graph are generated with a depth-first search (DFS), then the CSF coefficients that share subsequences of arcs in the graph can reuse the shared matrix-vector products. We have found that this reuse of intermediate quantities effectively eliminates the  $O(n)$  factor, and the overall effort scales as  $O(\bar{f}^2 N_{GCF} N_{CSF})$ . In the other direction, the task is to take a list of CSF coefficients,  $|\Psi\rangle = \sum_m^{N_{CSF}} x_m |\tilde{m}\rangle$  and convert that wave function into a GCF. There are two approaches to achieve this transformation. One is a merge procedure that scales formally as  $O(n\bar{f}^3 N_{CSF})$ . The other is an iterative least-squares optimization procedure that scales as  $O(n\bar{f}^2 N_{CSF})$  each iteration. Our initial implementation shows that the  $x(\alpha)$  calculation scales as expected and is very efficient, requiring about 130ns/CSF coefficient for a sequence of full-CI wave function expansions on a laptop computer. The  $\alpha(x)$  algorithms are both problematic and require more effort than expected. These algorithms will be discussed in the poster.

[1] Shepard, R., Gidofalvi, G., Brozell, S. R., *J. Chem. Phys.* 141 (2014), 064105.

[2] Shavitt, I., *Int. J. Quantum Chem.* 12.S11 (1977), 131-148.

[3] Shepard, R., *J. Phys. Chem. A* 109 (2005), 11629-11641.

## Electronic properties of selenium-modified nucleic bases

Yeny Pillco Valencia<sup>1</sup>, Danillo Valverde<sup>2</sup>, Antonio Carlos Borin<sup>1</sup>

<sup>1</sup> University of São Paulo, Brazil

<sup>2</sup> Université de Namur, Belgium

Selenium-modified nucleic bases exhibit interesting properties, such as the formation of stable modified DNA/RNA structures, shifted absorption spectra relative to canonical nucleic bases, and efficient intersystem crossings that transfer the electron population to triplet electron states. In this work, we present some results from a systematic study carried out in our group with the aim of describing the photochemical mechanisms of relaxation of modified canonical bases, in this case containing selenium atoms, such as 8-selenoadenine (tsA). For this, we will investigate photophysical properties of the isolated compound, in aqueous medium and in DNA, through multiconfigurational quantum methods and multiscale methodologies that combine quantum mechanics and molecular mechanics (QM/MM) to treat the effects of the environment. The initial structures were generated through classical molecular dynamics simulations using the AMBER18 package. Then, QM/MM calculations were performed using the OpenMOLCAS software in conjunction with the TINKER6.3 program. The chosen QM methodology is the Extended Multi-State Complete Active Space Second-Order Perturbation Theory (XMS-CASPT2).<sup>[1,2]</sup> This method is a second-order perturbative correction using the CASSCF<sup>[3]</sup> method as a zero-order wave function. The atomic basis function used is the correlation-consistent polarized valence double- $\zeta$ -Douglas-Kroll (cc-pVDZ-DK), without the use of molecular symmetry. Initially we studied the spectrum of the canonical adenine base isolated and in the DNA strand. We observe that the energetic sequence of the electronic states of the isolated compound and on the chain is not the same. For the isolated compound, the energetically lowest electronic state is a  $n\pi^*$  state, while in DNA the lowest electronic state is a  $\pi\pi^*$  state, according to results published by Conti et al.<sup>[4]</sup> Then, we performed the same study for the tsA compound, observing a small shift in the red direction compared to that obtained for the canonical base inserted in the DNA. The same study was performed with tsA in water. Then, we started the study of the photophysical pathways of excited state deactivation. In the Frank-Condon region the lowest singlet excited states for tsA in DNA and in water are both  $^1(\pi\pi^*)$  state, located at 3.42 eV ( $f=0.012$ ) and 3.57 eV ( $f=0.08$ ) above the ground state. The excited state character  $S_2$  are both  $n\pi^*$  in nature. To monitor the deactivation, we opted for Linear Interpolation in Internal Coordinates (LIIC) due to the size of the system.

[1] Granovsky, A. A., *J. Chem. Phys.*, 134.21 (2011), 214113.

[2] Shiozaki, T., Gyórfy, W., Celani, P., Werner, H. J., *J. Chem. Phys.*, 135.8 (2011), 081106.

[3] Roos, B. O. in *Advances in Chemical Physics: Ab Initio Methods in Quantum Chemistry Part 2* 69 (1987): 399-445.

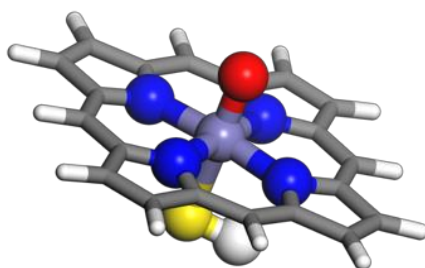
[4] Conti, I. et al., *Phys. Chem. Chem. Phys.* 12 (2010), 5016.

## Heme and nonheme single-iron catalytic sites in enzymes and in reticular frameworks for methane-to-methanol oxidation

Jenny G. Vitillo

Università degli Studi dell'Insubria, Italy

Multireference calculations are often exploited in catalysis to check the suitability of a given DFT functional for the description of open-shell systems. Here, we have used CASSCF/CASPT2 to assess the suitability of M06-L/def2-TZVP for the description of four single iron catalysts in their activated form (Fe(IV)=O): two biomimetic models (cytochrome P450 and taurine dioxygenase, TauD) and two synthetic reticular frameworks (iron-BEA zeolite and triiron oxo-centered-based metal-organic frameworks). For all the systems, the spin ladder was computed checking the convergence on the active space dimension. For nonheme systems, we were able to verify the suitability of this DFT functional for the study of these catalysts. In the heme system (P450), instead, the relative stability of the spin states showed to be strongly guess-dependent for the largest active space (13,15), spanning over 1-2 orders of magnitude, hindering de facto a reliable determination of the spin ladder. Determining the spin-state ordering in iron porphyrins is known to be challenging and in fact, they are used as a test bed for new theories and methods. Nevertheless, this difficulty is associated in the literature with their size. With this poster, we would like to point out this additional problem in handling heme systems, that if not appropriately considered, can bring a wrong assessment of different approaches.



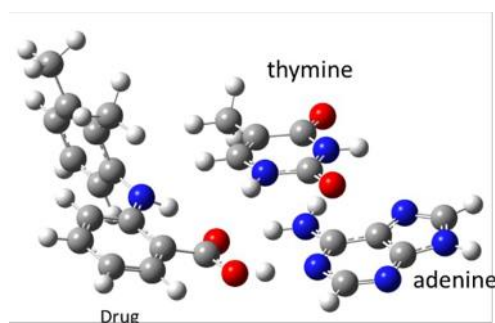
## Computational investigation of medical drugs with DNA nucleobase pairs by quantum chemical methods and QM/MM trial

Isilay Öztürk<sup>1,2</sup>, Toomas Tamm<sup>1</sup>, Armagan Kinal<sup>2</sup>

<sup>1</sup> Tallinn University of Technology, Estonia

<sup>2</sup> Ege University, Turkey

Many prescription and over-the-counter drugs exhibit DNA-altering side effects upon prolonged use. In this study, interactions between ten hypertensive (beta-blocker) and eight non-steroidal anti-inflammatory drugs (NSAIDs) with DNA nucleobases and base pairs were studied using density-functional theory. In the present study, we investigated the interactions of some nonsteroidal anti-inflammatory and anti-hypertensive drugs with nucleobase pairs with quantum chemical methods, especially with DFT ( $\omega$ B97X-D/6-31+G(d)). Knowing the strengths of these interactions will provide insight into the side effects of the drugs. When the effects of drug molecules on hydrogen bonds were examined in terms of angle and distance, mefenamic acid give the most promising results. It is a non-steroidal anti-inflammatory drug. Therefore, mefenamic acid-DNA interaction was also examined with the QM/MM method. In these simulations, mefenamic acid showed remarkable affinity with cytosine at these interaction sites in DNA. This interaction can have a breaking or disrupting influence on DNA, possibly leading to side effects upon prolonged use.



**Figure 1.** Drug interaction with DNA nucleobase pairs

[1] Toupkanloo, H. A., Rahmani, Z., *Applied Biological Chemistry* 61.2 (2018): 209-226.

[2] Kennard, O., *Pure and applied chemistry* 65.6 (1993): 1213-1222

## Upgrading of a raw waste coffee grounds product for the treatment of Zn adsorption in wastewater effluents

Najat Qisse, Mohammed Alaoui El Belghiti

Mohammed V University in Rabat, Morocco

Heavy metal pollution has become an urgent environmental problem. Removal of these metals from the environment is of considerable concern because of their effects. In this study, we used wastewater to evaluate the adsorption properties of Zn using the raw coffee grounds derivative. We performed characterization to determine the physicochemical properties of the adsorbent. As a result, the results indicated that the pseudo-second order model and all isothermal models were the most suitable to describe the Zn (II) adsorption system. The high adsorption capacity of about  $300.51\mu\text{mol/g}$  with the abatement of 92%.