

The 10th OpenMolcas Developers' Workshop



Book of Abstracts

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8-10 June 2022



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Joint Undertaking



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11:50	F. Segatta	R. Di Remigio	B. Tenorio	20'
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12:30	Lunch	Lunch	Lunch	1h30'
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14:00	A. Scemama 	P.-F. Loos & M. Boggio-Pasqua 	F. Agostini	30'
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15:30	Coffee Break	Coffee Break	Coffee Break	30'
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16:00	S. I. Bokarev	Free afternoon	L. De Vico	20'
16:20	J. Kragsskow 		S. Lehtola 	20'
16:40	P. Calio 		J. Bao 	20'
17:00	F. Montorsi		Closing	20'

Gala dinner

Invited talks

Multiconfigurational quantum chemistry from laptop to HPC

M.G. Delcey

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KTH Royal Institute of Technology, Stockholm, Sweden

Over the years, supercomputers have evolved more and more towards massively parallel architectures, and more recently, we are also seen a shift towards complicated memory access patterns, with in particular devices (e.g. GPUs) but also non-uniform memory access (NUMA) within CPU sockets. This is especially visible in the new flagship of the euroHPC project, the LUMI supercomputer in Finland. This shift has motivated our group in KTH to start the development of a new quantum chemistry software package, called Veloxchem, specifically targeting those newer architectures, as well as MultiPsi, an extension dedicated to multiconfigurational methods.

However, beyond just adapting to new hardware architectures, we opted for some of the newest software design principles, using in particular python as driver for most of our code, keeping c++ only for a few computer-intensive parts. These design principles allow us to create a programming environment which facilitates quick prototyping or implementation of a new method, easy long-term maintenance, but also provide a very easy and interactive platform for quantum chemistry education.

In this presentation, I will present Veloxchem and MultiPsi and illustrate how their design empower both teaching and development. Additionally, I will describe briefly the MCSCF implementation and show its performance on modern HPC.

The TREXIO file format and library

Anthony Scemama

8 June 2022

Within the "Targeting REal chemical accuracy at the eXascale" (TREX) European center of excellence, we are building a file format and library to help inter-operability between quantum chemistry codes, and also to help the reproducibility of calculations. This is a tedious task because the codes have different conventions such as the normalization of the basis, the ordering of atomic orbitals, the phase factors in the CI coefficients, etc. . . . We propose a file format in which these conventions are well defined, such that the users don't need to know which code produced the file to be able to use the data inside it. The access to the data in the file is made via TREXIO, a C-compatible library which has a Fortran and a Python binding. In addition to the storage of all the wave function parameters (atomic basis set, molecular orbitals, CI coefficients, . . .), the TREXIO library also allows the storage of one- and two-electron integrals as well as one- and two-body reduced density matrices.

To be defined

Daniel Opalka - European High-Performance Computing Joint Undertaking

Benchmarking multiconfigurational methods for vertical excitation energies

Martial Boggio-Pasqua¹, Pierre-François Loos¹

¹*Laboratoire de Chimie et Physique Quantiques, Université de Toulouse, CNRS, UPS, France*

In this talk, we will present some of our recent studies dedicated to the benchmarking of second- and third-order multiconfigurational methods (CASPT2, NEVPT2 and CASPT3) [1, 2] based on the highly accurate vertical excitation energies of the QUEST database [3]. More precisely, these exhaustive benchmark studies rely on 280 excited states of diverse natures (singlet, triplet, valence, Rydberg, $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$, and double excitations) computed with a large basis set (aug-cc-pVTZ) for 35 small- and medium-sized organic molecules containing from three to six non-hydrogen atoms. In particular, the effect of the disputable ionization-potential-electron-affinity (IPEA) shift on the overall accuracy of these methods will be discussed.

- [1] R. Sarkar, P. F. Loos, M. Boggio-Pasqua, and D. Jacquemin, *J. Chem. Theory Comput.* **18**, 2418 (2022).
- [2] M. Boggio-Pasqua, D. Jacquemin, and P. F. Loos, *J. Chem. Phys.* (submitted), arXiv:2204.06480.
- [3] M. Véril, A. Scemama, M. Caffarel, F. Lipparini, M. Boggio-Pasqua, D. Jacquemin, and P. F. Loos, *WIREs Comput. Mol. Sci.* **11**, e1517 (2021).

Construction of local active spaces for fragmented large systems

Max Nusspickel, Charles Scott, Basil Ibrahim, **George Booth**, Kings College London

An active space concept is at the heart of how we deal with molecular strong correlation. Fundamentally, it is a way to break up the large system into two parts (active and external), and describe the electron correlation in these subspaces quasi-self-consistently at different levels of theory. However, there are some limitations in the current constructions, particularly due to the requirement to pick an active space of ‘molecular’ orbitals from some prior mean-field, and the diversity in choices of active space for a consistent level of accuracy. This is increasingly relevant as systems get larger, or in the solid state.

In this talk, we will critically reformulate these concepts for the generation of active spaces in large and condensed phase systems, specifically leveraging the use of locality, with concepts borrowed from quantum embedding and pair natural orbitals in local correlation methods. Furthermore, we will detail a novel and fully self-consistent approach to a ‘perturb-then-diagonalize’ multi-reference perturbation theory which can be included on top of this approach, which includes infinite diagrammatic resummations in the external spaces, and avoids the requirement of any high-order density matrices.

Refs:

Systematic Improvability in Quantum Embedding for Real Materials

Max Nusspickel and George H. Booth

Phys. Rev. X **12**, 011046 (2022)

Extending density matrix embedding: A static two-particle theory

Charles J. C. Scott and George H. Booth

Phys. Rev. B **104**, 245114 (2021)

Theory and simulation of ultrafast processes in molecules with the exact factorization

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In this talk I will review the theoretical basis of the exact factorization of the electron-nuclear wavefunction [1] to describe excited-state dynamics in molecules. I will focus on two main aspects of the theory, one related to the perspective offered by the exact factorization in comparison to the usual Born-Huang representation [2,3], and one related to the development of trajectory-based algorithms for nonadiabatic dynamics. More specifically, I will apply the coupled-trajectory mixed quantum-classical (CT-MQC) algorithm [4] and its recently-proposed combination with the trajectory surface hopping idea [5] to the simulation of various ultrafast processes, such as photo- isomerization processes [6-8] or light-driven nonadiabatic dynamics [9].

References:

- [1] A. Abedi, N. T. Maitra, E. K. U. Gross, *Phys. Rev. Lett.* (2010).
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- [3] L. M. Ibele, B. F. E. Curchod, F. Agostini, *J. Phys. Chem. A*, 126, 1263-1281 (2022).
- [4] S. K. Min, F. Agostini, E. K. U. Gross, *Phys. Rev. Lett.*, 115, 073001 (2015).
- [5] C. Pieroni, F. Agostini, *J. Chem. Theory Comput.*, 17, 5969-5991 (2020).
- [6] S. K. Min, F. Agostini, I. Tavernelli, E. K. U. Gross, *J. Phys. Chem. Lett.*, 8, 3048-3055 (2017).
- [7] E. Marsili, M. Olivucci, D. Lauvergnat, F. Agostini, *J. Chem. Theory Comput.*, 10, 6032-6048 (2020).
- [8] F. Talotta, S. Morisset, N. Rougeau, D. Lauvergnat, F. Agostini, *Phys. Rev. Lett.*, 124, 033001 (2020).
- [9] M. Schirò, F. G. Eich, F. Agostini, *J. Chem. Phys.*, 154, 114101, (2021).

Contributed talks

GMM-NEA, a Machine Learning algorithm to reconstruct Nuclear Ensemble Approach absorption spectra

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The theoretical prediction of molecular electronic spectra by means of quantum mechanical (QM) computations is fundamental to gain a deep insight into many photophysical and photochemical processes. A computational strategy that is attracting significant attention is the so-called Nuclear Ensemble Approach (NEA), that relies on generating a representative ensemble of nuclear geometries around the equilibrium structure and computing the vertical excitation energies (ΔE) and oscillator strengths (f), and phenomenologically broadening each transition with a line-shape with empirical full-width δ [1]. Frequently, the choice of δ is carried out by visually finding the trade-off between artificial vibronic features (small δ) and over-smoothing of electronic signatures (large δ). Nevertheless, this approach is not satisfactory, as it relies on a subjective perception and may lead to spectral inaccuracies, overall when the number of sampled configurations is limited due to an excessive computational burden (high-level QM methods such as CASPT2, complex systems, solvent effects, ...). We have recently developed a new approach to reconstruct NEA spectra, dubbed GMM-NEA, based on the use of Gaussian Mixture Models (GMMs), a probabilistic Machine Learning algorithm, that circumvents the phenomenological broadening assumption and, in turn, the use of δ altogether [2]. In this communication I will revisit the fundamentals and philosophy behind NEA and our new methodology, I will highlight some relevant peculiarities, aspects and results of GMM-NEA, and will show how it performs against other approaches such as KDE [3] or the KREG model [4], especially for small datasets (Figure 1). Time permitting, I will show how GMM-NEA can be used in combination with MULTISPEC, our group open-source software for the calculation of electronic spectra with multiconfigurational quantum chemistry [5].

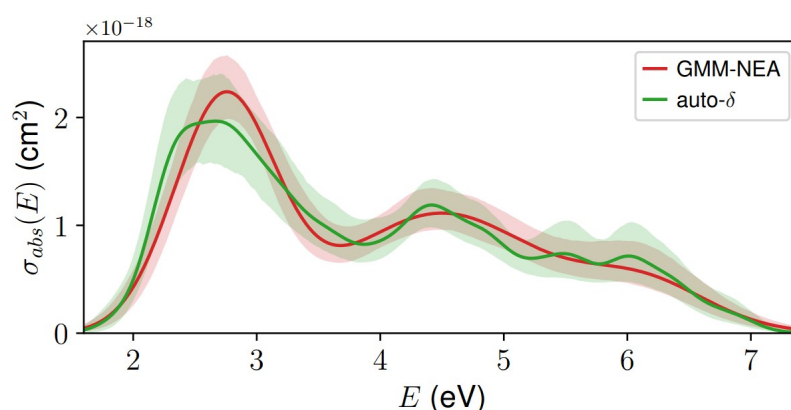


Figure 1: CASSCF/CASPT2 absorption cross section spectrum for uracil radical (U6OH) reconstructed from 100 geometries using GMM-NEA (red lines) and KDE [auto- δ] (green lines). The shaded areas represent the reconstruction 95% confidence intervals.

References

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- [3] S. Srsen and P. Slavíček, *J. Chem. Theory Comput.* 2021, 17, 6395
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- [5] <https://github.com/qcexval/multispec>

Core-level excitation and ionization with OpenMolcas: Spectrum Completeness, Quantitative Reproduction of Line Shapes, and Physical Insight

Authors: **Francesco Segatta**, F. Montorsi, A. Nenov, S. Mukamel, M. Garavelli

In this contribution, I will review some of the results we recently obtained in simulating soft X-ray spectroscopy of organic molecules (from ethylene to azobenzene) employing high quality quantum chemistry data obtained with OpenMolcas.

After a brief introduction of the protocol we developed for such spectroscopy simulations, which couples the multi-configurational restricted active space self-consistent field RASSCF/RASPT2 approach to the displaced harmonic oscillator (DHO) model (to describe the coupling between electronic transitions and molecular normal modes, or electron-phonon coupling), I will focus the discussion on the peculiarities of core-level excited / ionized states and address the following questions. How does removing a core-electron of a certain atom affect the electronic structure? How does it influence the atom's bonding with its neighbors? How does this impact the spectral line shapes? I will show that all of these questions can be answered within a unitary orbital-based framework for both core-ionization and core-excitation spectroscopies (such as X-ray photoelectron spectroscopy, or XPS, and X-ray absorption near edge structure, or XANES).

Subsequently, in the context of the aforementioned core spectroscopies, I will present some of our recent developments. In particular, I will show a *divide and conquer* approach to systematically increase the number of core-excited states while containing the computational cost, that we successfully tested on a few molecular targets (as, e.g., some fluorinated ethylene systems), and that allows to reach spectrum completeness.

Eventually, I will touch on several delicate technical aspects of the electronic structure calculations of the core-excited manifold, such as the usage of symmetry and the choice between localized or delocalized core-orbitals.

The presentation will cover some published material (F. Montorsi et al., *J. Chem. Theory Comput.* 2022, 18, 2, 1003–1016), and some recently submitted and unpublished works.

Solid State Studies with SCEPIC

Ernst Larsson - Lund University

Embedded-cluster models of crystalline solids are important to allow accurate wave function methods to be applicable to solids. The ab-initio model potential method has historically been shown to be a viable tool for describing the electronic structure in ionic solids. This method extends on a point-charge embedding by replacing the direct border between cluster and charges with ab-initio model potentials, introducing effects from exchange repulsion into the calculations.

Recently, we released a new code, SCEPIC, for generating ab-initio model potentials for any arbitrary crystal. In SCEPIC, the ab-initio model potential method is combined with a general purpose electrostatic embedding method. This method is capable of removing higher order multipole moments over the cluster. This combination allows SCEPIC to produce a reliable embedding environment for studying ionic solids in a near-automated fashion.

This talk will highlight some production results which the combination of SCEPIC and OpenMolcas can be used to achieve, showcasing examples from single-ion dopants and surface reactions.

Dispersion interactions in exciton-localised states

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We address the problem of intermolecular interaction energy calculations in molecular complexes with localized excitons. Our focus is on the correct representation of the dispersion energy. We derive an extended Casimir-Polder formula for direct computation of this contribution through second order in the intermolecular interaction operator \hat{V} . A numerical investigation is carried out for benzene, pyridine and peptide complexes with the local exciton corresponding to the lowest $\pi - \pi^*$ or $n - \pi^*$ states. The extended Casimir-Polder formula is implemented in the framework of multiconfigurational symmetry-adapted perturbation theory, SAPT(MC) [1]. A SAPT(MC) analysis shows that the creation of a localized exciton affects mostly the electrostatic component of the interaction energy of investigated complexes. Nevertheless, the changes in Pauli repulsion and dispersion energies cannot be neglected. We verify the performance of several perturbation- and adiabatic-connection-based methods. Best results are obtained with a range-separated variant of an approximate AC approach employing extended random phase approximation and CASSCF wavefunctions.

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Selected configuration interaction for transcorrelated methods

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Selected configuration interaction (SCI) methods allows to reach near full CI (FCI) energies of the standard electronic Hamiltonian $\hat{\mathbf{H}}$ by selecting the most relevant Slater-determinants in the FCI space scaling exponentially with the system size.

Being constrained by the strong computational scaling of SCI with the size of the one-electron functions set, one can improve the convergence of the wavefunction results with respect to the basis by introducing a correlation factor τ depending explicitly on the inter-electron distances. This can be accomplished effectively by incorporating the correlation factor into the Hamiltonian via a similarity transformation, and the usual Hamiltonian is then replaced by the TransCorrelated (TC) Hamiltonian defined as $\hat{\mathbf{H}}_{\text{TC}} = e^{-\hat{\tau}}\hat{\mathbf{H}}e^{\hat{\tau}}$. The TC Hamiltonian $\hat{\mathbf{H}}_{\text{TC}}$ differs from $\hat{\mathbf{H}}$ by being non-Hermitian, holding a three-electron interaction term and if the correlation factor is being properly chosen, it contains a non divergent effective two-electron interaction.

Because of these drastic changes with respect to the usual Hamiltonian, the important Slater determinants are not in general those selected in standard hermitian SCI. In this contribution, we extend the SCI algorithm for TC Hamiltonians and demonstrate its feasibility on atomic and molecular systems. After investigating the impact of different selection criteria on the convergence of the CI wavefunction, we propose a modified perturbative selection criterion which is adapted to handle the non-Hermiticity of $\hat{\mathbf{H}}_{\text{TC}}$. The obtained CI wavefunctions corresponding to the adapted importance criterion appear to be more compact and converge faster to the FCI limit. Moreover, we design a proper second-order perturbative scheme in order to further improve the convergence of the energy, as usually done in standard hermitian SCI.

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Optimization of Jastrow factors for Similarity Transformed quantum chemical methods

Pablo López Ríos, Philip Haupt, Kai Guther, Aron Cohen, and Ali Alavi

Similarity transformations allow quantum chemistry methods to combine their accurate description of static correlation with the compact representation of dynamic correlation provided by Jastrow factors from real-space variational Monte Carlo. In this talk I will discuss techniques for the optimization of Jastrow factor parameters and their use in full configuration interaction quantum Monte Carlo calculations that exploit non-hermitian nature of the similarity transformed Hamiltonian, illustrated by applications in small molecular systems.

Electron dynamics and (auto)ionization in highly-excited molecules

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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 establishing 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 experiment, accurate and efficient theoretical methods need to be developed.

In my talk, I will discuss several protocols which are incorporated or interfaced to OpenMolcas. First, I will describe efficient approaches to compute valence and core photoionization and Auger decay in molecules employing different flavors of the central-potential method and beyond it [1,2]. Second, I will present our recent developments of the density-matrix-based time-dependent restricted active space configuration interaction method (ρ -TD-RASCI) to compute the ultrafast electron dynamics [3,4]. The current implementation naturally incorporates spin-orbit coupling, population and phase relaxation due to the environment, and (auto)ionization effects. It is especially well-suited for dynamics triggered by high-frequency light, e.g., involving core-excited states. The applications of these theoretical protocols will be exemplified by the simulations of the linear X-ray spectra, high harmonic generation, ultrafast charge migration, and spin-flip dynamics in molecules and transition metal complexes.

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Ultrahard magnetism from mixed-valence dilanthanide complexes with metal-metal bonding

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We have recently reported the isolation of a series of molecules containing the first Ln-Ln bonds, consisting of a single-electron sigma bond occurring in mixed-valent homodimetallic molecules [Cp^{iPr5}LnI₃LnCp^{iPr5}] (**{Ln₂}**, Ln = Gd, Tb, Dy).^[1] The single-electron bonds consist of molecular orbitals of equal 5d_{z²}-5d_{z²} parentage from each Ln ion (Fig. 1, left), and hence each ion is formally Ln^{2.5+}. Magnetically, the sigma bonding d-orbital is orthogonal to the 4f orbitals on each ion, and hence engenders an incredibly strong ferromagnetic direct exchange between all unpaired electrons ($J = +387(4)$ cm⁻¹ for **{Gd₂}**), giving a ground state of ¹⁶S_{15/2} for **{Gd₂}**, $m_J = \pm 25/2$ from the ¹⁴I_{25/2} term for **{Tb₂}** and $m_J = \pm 31/2$ from the ¹²N_{31/2} term for **{Dy₂}**. The exchange interactions for **{Tb₂}** and **{Dy₂}** are strongly anisotropic, arising from significant orbital components including spin-other-orbit interactions and high-order, non-bilinear terms. The sigma bonding electron also provides an additional source of magnetic anisotropy, collinear to the terminal Cp^{iPr5} ligands, which serves to double the local crystal field splitting of each Ln ion. The incredibly strong magnetic exchange and the huge magnetic anisotropy combine to give large energy barriers to thermally activated magnetic relaxation, $U_{\text{eff}} = 1383(45)$ and $1631(25)$ cm⁻¹ for **{Tb₂}** and **{Dy₂}**, respectively, the latter defining the current record U_{eff} barrier for a single-molecule magnet (SMM). Magnetic hysteresis remains open for **{Tb₂}** and **{Dy₂}** up to 64 and 80 K, respectively, the latter equalling the record set for an SMM by [DyCp^{iPr5}][B(C₆F₅)₄].^[2] However, diverging from all other SMMs, **{Tb₂}** has a coercive field greater than 25 T at 50 K (Fig. 1, right): this is five times larger than industry-leading “neodymium” magnets.

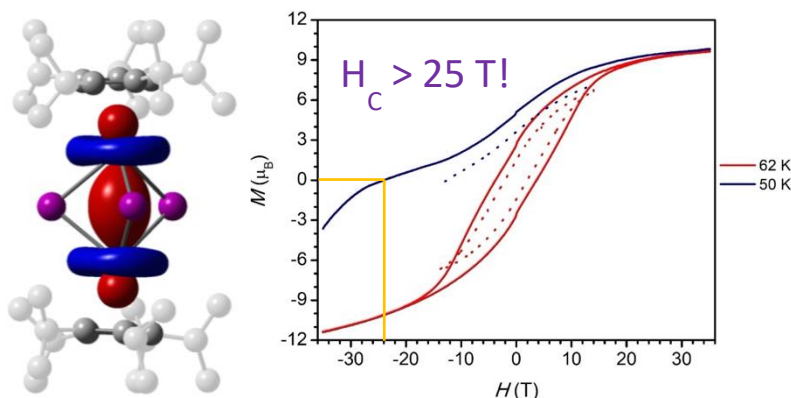


Figure 1: (left) 5d_{z²}-5d_{z²} sigma bond, (right) demagnetisation curves for **{Tb₂}**

References:

- [1] C. A. Gould, et al., Science 375, 198 (2022); [2] F.-S. Guo, et al., Science, 362, 1400 (2018)

Nonadiabatic Molecular Dynamics by Multiconfiguration Pair-Density Functional Theory

Paul B. Calio, Donald G. Truhlar, Laura Gagliardi

Multiconfiguration pair-density functional theory (MC-PDFT) is a multireference electronic structure method that in many cases has a similar accuracy (or even better accuracy) than complete active space second order perturbation theory (CASPT2) at a significantly lower computational cost. MC-PDFT analytical gradients have been developed recently, and they may be used to apply MC-PDFT to dynamical simulations of strongly correlated systems. In this presentation, I will present the first implementation of MC-PDFT *ab initio* molecular dynamics. This involves the introduction of MC-PDFT analytical gradients calculated from OpenMolcas into the *SHARC* molecular dynamics program for *ab initio*, nonadiabatic molecular dynamics simulations. I will show work that verifies our implementation by examining the intersystem crossing dynamics of thioformaldehyde, and show that we observe excellent agreement with recent CASPT2 and experimental findings, while simulating MC-PDFT with an active space that was computationally too expensive for CASPT2.

Ultrafast pump-probe spectroscopy simulations with OpenMolcas: from UV-visible to X-rays.

Authors: F. Montorsi, F. Segatta, Vishal Kumar Jaiswal, A. Nenov, M. Garavelli

Ultrafast pump-probe spectroscopy is a conceptually simple and versatile tool for resolving photoinduced dynamics in molecular systems. Due to the fast development of new experimental setups, such as synchrotron light sources and X-ray free electron lasers (XFEL), new spectral windows became accessible. On the one hand, this has enabled scientist to access faster and faster time scales and to reach unprecedented insights into dynamical properties of matter. On the other hand, the complementarity of techniques allows to study the same physical process from different points of views, integrating the advantages and overcoming the limitations of each approach. In this context, it is highly desirable to have an understanding of which type of spectroscopy captures best a certain facade of a given photo-induced process, that is, to establish a correlation between the process to be unraveled and the technique to be used.

In this contribution, I will show how computational spectroscopy, powered by OpenMolcas, can be a tool to establish such a correlation. First, I will discuss an approach, based on multiconfigurational wave function theory coupled to the displaced harmonic oscillator model (DHO), able to treat UV-visible and X-rays transient spectroscopies at equal footing. A systematic approach to the assessment of the system's response in different spectral windows will eventually be showed. Second, I will focus on a specific process, i.e. the energy transfer in the nicotinamide adenine dinucleotide dimer (NADH), and compare the results of different spectroscopic simulations: UV-VIS Transient Absorption, Transient Photoelectron, Transient Near Edge X-ray Absorption and Transient X-ray Photoelectron Spectroscopy. The comparison of the techniques will demonstrate their complementarity, eventually allowing to identify the type of spectroscopy is best suited to resolve the ultrafast energy transfer.

Analytic First-Order Derivatives of (X)MS-, XDW-, and RMS-CASPT2 Methods

Yoshio Nishimoto¹

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Analytic gradients are useful for finding minimum energy structures. However, energies of many electron correlated methods are not variationally optimized with respect to wavefunction parameters, and therefore the development of analytic derivative program for multireference methods is not straightforward.

We recently developed analytic derivatives of complete active space second-order perturbation theory (CASPT2) in OpenMolcas [1, 2]. The implementation can also be applied to the restricted active space variant (RASPT2), and the first paper demonstrated that relatively large RASs (up to (22e, 22o)) can be employed for geometry optimization. In the second study, we have made it possible to locate minimum energy conical intersections (MECIs) using various multistate CASPT2 (MS-CASPT2): namely the extended MS-CASPT2 (XMS-CASPT2) and the recent extended dynamically weighted rotated multistate CASPT2 (XDW-CASPT2 and RMS-CASPT2) [3, 4] methods.

In the talk, I will outline the derivation very quickly and demonstrate pilot geometry optimization and MECI search. In particular, we found that XMS-, XDW-, and RMS-CASPT2 methods do not exhibit irregularities in the potential energy surface around MECI regions (Figure 1) and therefore can be applied to MECI search [2].

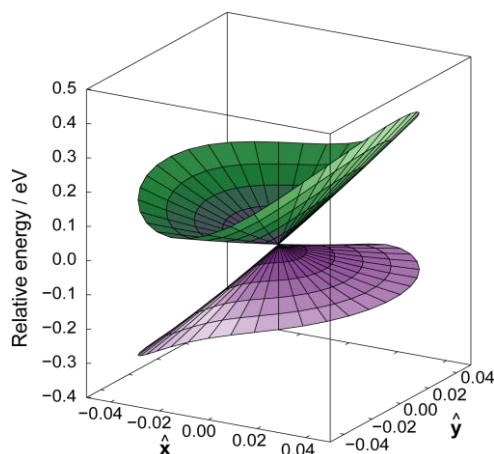


Figure 1. Potential energy surface at an MECI with RMS-CASPT2

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Exact two-component Hamiltonians for relativistic quantum chemistry: Two-electron picture-change corrections made simple

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In this talk, I will present, based on self-consistent field (SCF) atomic mean-field (amf) quantities, two simple, yet computationally efficient and numerically accurate matrix-algebraic approaches to correct both scalar-relativistic and spin-orbit two-electron picture-change effects (PCE) arising within an exact two-component (X2C) Hamiltonian framework [1]. Both approaches, dubbed amfX2C and e(xtended)amfX2C, allow us to uniquely tailor PCE corrections to mean-field models, viz. Hartree–Fock or Kohn–Sham DFT, in the latter case also avoiding the need of a point-wise calculation of exchange–correlation PCE corrections. We assess the numerical performance of these PCE correction models on spinor energies of group-18 (closed-shell) and group-16 (open-shell) diatomic molecules, achieving a consistent $\approx 10^{-5}$ Hartree accuracy compared to reference four-component data. Additional tests include SCF calculations of molecular properties such as absolute contact density and contact density shifts in copernicium fluoride compounds (CnF_n , $n=2,4,6$), as well as equation-of-motion coupled cluster calculations of X-ray core ionisation energies of $5d$ and $6d$ -containing molecules, where we observe an excellent agreement with reference data. To conclude, we are confident that our (e)amfX2C PCE correction models constitute a fundamental milestone towards a universal and reliable relativistic two-component quantum chemical approach, maintaining the accuracy of the parent four-component one at a fraction of its computational cost. Finally, I will discuss prospects for the implementation and availability of the (e)amfX2C models in OpenMolcas.

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PHOTOREACTIVITY IN NUCLEOBASES' ANCESTORS: A THEORETICAL STUDY OF OXO MODIFIED NUCLEOBASES

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Natural DNA and RNA nucleobases are characterized by their photostability against UV light continuous exposition. The internal conversion funnels, which govern the relaxation pathways of the five canonical nucleobases, facilitate the complete deactivation of the nucleic acids' monomers in an ultrafast timescale, preventing the generation of DNA photolesions¹.

Determining the structural and electronic factors behind these desirable photostable properties can help shedding light into the chemical evolution process undergone by nucleobases during the prebiotic period which converged into the current genetic alphabet. In this way, the scrutiny of the deactivation mechanism in modified nucleobases structurally related to the nucleic acids's building blocks, added to the wide knowledge on the photophysics of canonical nucleobases can help setting the key elements which control the topography of the potential energy landscape of these systems.

In this contribution we present a complete static and dynamics analysis of oxo modified pyrimidine and purine nucleobases, proposed as nucleobases' ancestors², with one of the most sophisticated multiconfigurational methods, XMS-CASPT2³. Excited state molecular dynamics simulations on the investigated systems, previously classified as photostable as they present short excited state lifetimes, comparable to the fastest DNA bases^{4,5}, reveal ring opening photodegradation along their relaxation, corroborated by experimental observations⁶. Interestingly, this unexpected photolysis seems to be a generalized phenomenon in all the considered oxo substituted pyrimidine and purine monomers, which leads us to conclude that substitution with carbonyl groups at particular positions compromises the of purine and pyrimidine derivatives.

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To be defined

Diana Wang - HLRS

ClassyQ: a new library for quantum/classical polarizable models

Roberto Di Remigio Eikås - ENCCS

Continuum models are invaluable tools in the computational modeling of solvent effects. They come in many flavors and with quite intricate implementation details. I will present our efforts in designing and implementing ClassyQ, a new library for quantum/classical polarizable models. We aim at providing a robust and reliable tool to implement QM/continuum and QM/fluctuating charges models with minimal effort. The library is the spiritual successor of PCMSolver and the two share design philosophy: a) API-based, rather than file-based host-guest communication, b) separation of concerns between QM and MM, c) usability from multiple languages. ClassyQ is intended to be a drop-in replacement for PCMSolver. I will discuss the different design choices between the two libraries, how to transition to ClassyQ, and what this means for the continuum solvation functionality in OpenMolcas.

Analytical Linear Vibronic Couplings in Single-Molecule Magnets

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Single-molecule magnets (SMM) are an interesting research subject due to their potential applications in high density data storage and spintronic devices. SMMs owe their magnetic hysteresis property to a bistable electronic ground state with distinct orientations of the magnetic moment separated by an energy barrier. Chemically controlling vibronic coupling, the cause of magnetic relaxation, i.e. equilibration of the ground state populations, has become the holy grail of SMM research. Moving past simple design criteria applied in previous discoveries, quantum chemical calculations have proven themselves to be an invaluable tool in the elucidation of relaxation pathways[1]. Spin-phonon couplings are commonly evaluated at the CASSCF-SO level and included as 1st order modulations of the crystal field potential. Previous *ab initio* studies have been relying on numerical differentiation of the crystal field parameters (CFPs)[2]. We have developed a novel method to evaluate CFP derivatives analytically by combining the linear vibronic coupling model[3] (LVC) with analytic SA-CASSCF density fitting gradients and non-adiabatic couplings available in OpenMolcas[4]. We then proceed to benchmark different electrostatic environment models and compare the performance of our analytic derivatives with conventional finite difference derivatives. Among the ghost, charge and charge+dipole representations, we find that the point charge model shows the best agreement with the reference calculation (environment described with minimal basis functions in the CASSCF step). Our analytic LVC derivatives, which closely match the numerical results, exhibit moderate computational saving when applied to isolated SMMs in the gas phase, but their full potential is realised in periodic expansions, where all environmental degrees of freedom come with no extra cost.

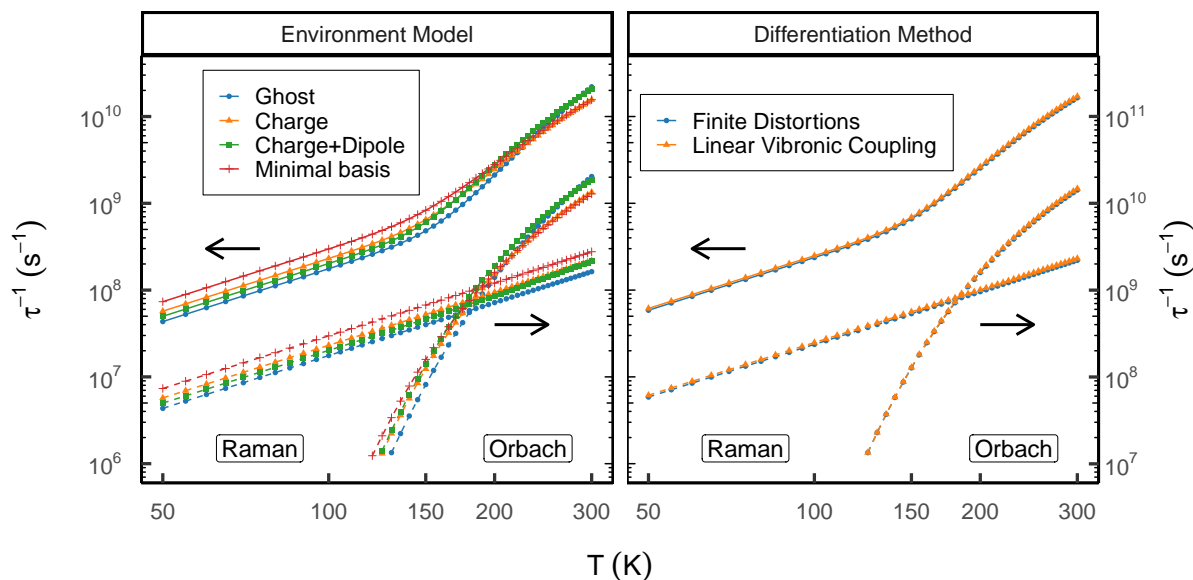


Figure 1: Temperature-dependent magnetic relaxation profiles of $\text{Dy}(\text{Cb})_2^-$ employing different environment models (left) and differentiation schemes (right). The total rates indicated by the solid lines are plotted on the primary (left) axis and the rates of the individual processes represented by the dashed lines are plotted on the secondary (right) axis.

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Uncertainty Quantification in Chemistry

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All quantum chemical methods rely on a range of approximations, the combined effect of which is usually difficult to assess. Hence, every quantum chemical result is affected by some systematic error which is unknown. However, precise knowledge of the uncertainty of a quantum chemical result is important for practical applications.

In this talk, we will summarize recent contributions of our group to the automatic uncertainty quantification of quantum chemical methods. A particular focus will be an in-depth analysis of classical benchmarking studies, which are the traditional way of evaluating the reliability of quantum chemical methods. We will show that this approach is not transferable across chemical space, and we argue that a system-focused, dynamical approach to benchmarking is more suitable for practical applications.

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Latest Stochastic MCSCF Routes for Studying Polynuclear Transition Metal Clusters

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Keywords: spin purification, magnetic susceptibility, Spin-Averaged CASSCF, Stochastic-MCSCF

As part of our continuous development of *stochastic* multiconfigurational approaches based on the FCIQMC algorithm, and its integration into Stochastic-MCSCF methods into OpenMolcas, two recent developments will be presented in my talk: (i) the spin purification scheme in Full-CI Quantum Monte Carlo via first-order penalty,^[1] and (ii) the stochastic state-averaged CASSCF across different spin (and space) symmetries.

The spin purification approach is complementary to the GUGA based spin-pure Stochastic-CASSCF.^[2] The method can efficiently be coupled to the Stochastic-GASSCF,^[3] the similarity transformed FCIQMC, the tailored-CC^[4,5] and contracted second-order perturbative correction (PT2). The method is also suitable for being coupled to anisotropic Hamiltonians and provides easy access to spin-dependent properties, such as the hyperfine-coupling constants.

The state-averaged CASSCF across multiple spin symmetries has been tested against transition metal dimers and trimers.^[6] Its comparison to the corresponding state-specific CASSCF will be discussed.

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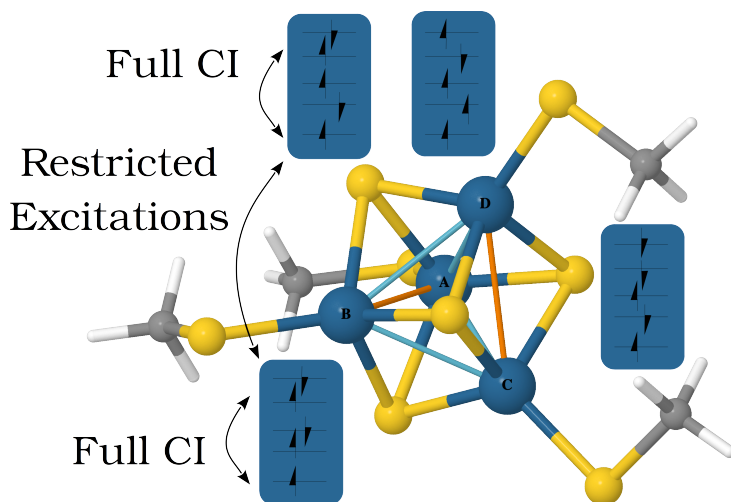
Spin pure stochastic GASSCF

The 10th OpenMolcas Developers' Workshop in Uppsala

Oskar Weser

This talk will be about the combination of Full-Configuration-Interaction-Quantum-Monte-Carlo (FCIQMC) and Generalized Active Spaces (GAS). This allows large active space (70, 70) calculations together with the flexibility of constraining excitations between different orbitals to either enhance the performance, or to probe the relevance of certain correlation effects. In the last OpenMolcas workshop we presented an extension of the Precomputed Heat-Bath (PCHB) algorithm in a Slater-determinant basis that sampled configurations with $\mathcal{O}(1)$ runtime cost while automatically adhering to GAS constraints via precalculated probability distributions. The calculation in a Slater-determinant basis left open the possibility of spin-contamination for ferromagnetically ordered systems, so a particular focus of this talk will be on the question of how to achieve spin-pure results.

We did this via two methods: The first one was a first order spin-penalty approach $\hat{H}' = \hat{H} + J \cdot \hat{S}^2$. With this we could achieve spin-purified results in a Slater-determinant basis and showed that this method works particularly well for the sparse FCIQMC algorithm. We also improved on the existing literature by providing an explanation for the best choice of the arbitrary J parameter. The second method was a formulation of Stochastic GAS in a basis of spin eigenfunctions using the Graphical Unitary Group Approach (GUGA).



Integration of New Sampling Techniques Into OpenMolcas

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Molecular dynamics (MD) is a tool which can be applied to study chemical reactions by analyzing the physical motion of molecules along reaction pathways. These simulations can help us gain better understanding of the underlying physical properties behind chemical phenomena. For MD simulations, each trajectory requires a set of initial conditions in the form of atomic positions and corresponding velocities. These initial conditions can be generated in a variety of ways using both classical and quantum mechanical sampling. Recently we have implemented three different sampling techniques into OpenMolcas^[1]: 1) normal mode sampling based on harmonic vibrational modes and a classical Boltzmann energy distribution^[2,3] 2) sampling based on a ground state Wigner distribution^[4] and 3) finite-temperature Wigner phase-space sampling^[5,6].

In this contribution, we will review the theory behind each of these newly implemented sampling procedures and provide an example of how each method can impact the trajectories themselves. Here we use formaldehyde as a simple test case to highlight the differences between each of these methods. Formaldehyde (H₂CO) can react to form either (HCO+H) or (CO+H₂) after passing through a S₁/S₀ conical intersection^[7-9]. We characterize the reaction energetics of formaldehyde at the SA-2-CASSCF(10,9)/6-31G* level of theory and run a swarm of trajectories for each new sampling procedure to highlight the differences between them.

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Modelling Luminescent Lanthanide Complexes with OpenMolcas and/or Columbus

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Luminescent lanthanide complexes can be effectively used as anion sensors in solution, e.g. for nucleotides.^[1] This contribution presents some recent work on europium complexes using the RASSCF/SO-RASSI approach in OpenMolcas. We discuss the influence of electron correlation, spin-orbit coupling (SOC), and crystal field effects on the energy levels obtained. Computed values for emission intensities are evaluated and compared to experiment. Future possibilities for characterising the states are discussed.

In a second part of the talk we review progress on the Columbus/OpenMolcas interface and its applicability to a variety of systems including lanthanides. Columbus 7.0.2 possesses a working interface to OpenMolcas allowing to evaluate gradients, nonadiabatic couplings and SOC. The source code can be obtained upon registration and an open-source release is in progress.

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Photoionization and Auger Spectra from RASPT2/DFT-Bspline Bound-Continuum Approaches

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Modeling processes involving electrons in the continuum are extremely challenging, since the asymptotic behavior of the continuum wave function is poorly described within correlated methods based on quadratically integrable finite basis sets (L^2 basis sets), commonly used for bound states. Thus, besides an accurate bound state description, which nowadays can be obtained in many ways (Coupled-Cluster, ADC, MR-CI, RASPT2 etc.) one also need an accurate description of the electron in the continuum.

A theoretical model to compute the accurate photoionization dynamical parameters (cross-sections, asymmetry parameters and orbital, or cross-section, ratios) from Dyson orbitals obtained with the multi-state complete active space perturbation theory to the second order (MS-CASPT2) method, and the electronic continuum obtained with a multicentric B-spline basis at the DFT and TD-DFT levels is presented [1].

For the Auger spectra calculation, a projection technique based on the one center approximation (OCA) is implemented within OpenMolcas [2]. One of the advantages of our approach is that by projecting the intensities on the atomic center bearing the core hole and using precalculated atomic radial two-electron integrals, the Auger decay rates can be easily obtained directly with OpenMolcas, avoiding the need to interface it with external programs to compute matrix elements with the photoelectron wave function [3].

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On the Fluorescence Enhancement of Arch Neuronal Optogenetic Reporters

Leonardo Barneschi – University of Siena

The lack of a theory capable of connecting the amino acid sequence of a light-absorbing protein with its fluorescence brightness is hampering the developments of tools for understanding neuronal communications. Here we demonstrate that a theory can be established by constructing quantum chemical models of a set of Archaeorhodopsin reporters in their electronically excited state. We found that the experimentally observed increase in fluorescence quantum yield is proportional to the computed decrease in energy difference between the fluorescent state and a nearby photoisomerization channel leading to an exotic diradical of the protein chromophore. This finding is important because, ultimately, it will make possible to develop technologies for searching novel fluorescent rhodopsin variants and unveil electrostatic changes that make light emission brighter and brighter.

New Density Matrix Renormalization Group-based Methods for Molecular Simulations

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The full configuration interaction (full CI) method represents the election algorithm for exact molecular simulations. However, its high computational cost makes it applicable only to small molecular systems. This prohibitive scaling can be tamed with tensor-based compression schemes, such as the density matrix renormalization group (DMRG).¹ To date, DMRG has been mostly applied to electronic problems. In this talk we will describe DMRG-based methods for studying three new classes of molecular simulations.¹ We will first introduce DMRG-based algorithms for simulating vibrational spectra both within²⁻⁵ and beyond^{6,7} the Born-Oppenheimer approximation. We will then introduce the time-dependent DMRG method to simulate non-equilibrium phenomena in complex molecular systems.^{8,9} Finally, we will introduce an explicitly-correlated DMRG variant that relies on the transcorrelated approach.^{10,11} We will show the reliability of all these methods, which we implemented in the `QCMAquis` module of `OpenMolcas`,¹² by comparing their accuracy with alternative state-of-the-art approaches.

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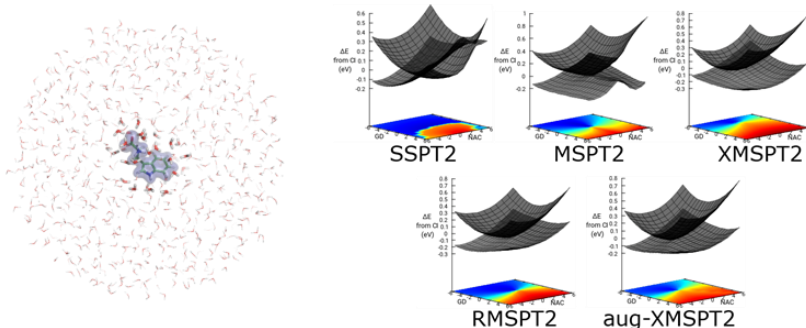
Branching Plane at different flavours of CASPT2 in solvated Tryptophan

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The ultrafast non-adiabatic dynamics of solvated tryptophan involves the interplay between the lowest two excited-states – termed L_b and L_a – driven by the topology of the relevant adiabatic surfaces around a energetically low lying conical intersection (Coln) accessible on a few femtosecond time scale. Multiconfigurational CASSCF//CASPT2 protocols are among the most accurate methods for the computation of the so called *branching plane*, i.e. the two-dimensional space around a Coln defined by the pair of gradient difference (GD) and derivative coupling (DC) vectors which lift the degeneracy and are thus best suited to study the non-adiabatic dynamics mediated by the Coln and the branching of the photoinduced reaction path.

In this presentation I will present the branching plane topology of the minimum energy Coln $_{L_a/L_b}$ in Tryptophan computed at different flavors of CASPT2 theory implemented in OpenMolcas – single- (SS) and multi-state (MS), extended (XMS) and rotated multi-state (RMS) – and will demonstrate the implications of the conceptual limitations of the various formulations. The newly published RMSPT2¹ method displays the best performance amongst the various flavors against a reference calculation performed at the XMS level with a larger active space (aug-XMS).



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Frenkel exciton protocol in OpenMolcas

Andy Kaiser – University of Rostock

Investigation of excited states and charge transfer in aggregates is a popular and important field in chemical physics. Unfortunately, MCSCF calculations of aggregates require large active spaces and thus are very time consuming. The Frenkel exciton formalism, which separates the dimer into two interacting monomers, turned out to be a very efficient tool. The initial implementation by F. Aquilante, L. de Vico et al. has been already reported [1]; here, it has been further developed for obtaining different kinds of spectra (UV-Vis, XAS, RIXS) involving the Frenkel exciton theory beyond dipole-dipole approximation. The elaborated protocol allows to do two separate RASSCF monomer calculations to obtain the wavefunctions and let them interact, obtaining all needed coupling elements to build a Frenkel exciton Hamiltonian. This Hamiltonian is then diagonalized, the resulting eigenvalues and eigenvectors are used together with the transformed transition dipole matrix to construct the spectra of the interacting monomers. In this talk, the theoretical method and its implementation will be reviewed in detail. Different properties, like H- and J-aggregate formation, and absorption spectra will be shown and discussed for different homo-molecular dimers.

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Excitonic coupling code: "cool" applications

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Abstract

Originally mentioned in the SI of "Modern quantum chemistry with [Open]Molcas" [J. Chem. Phys. 152, 2020, page 214117], a code for computing accurate excitonic couplings terms between two separate molecules has been recently extended and perfected (see the talk by Andy Kaiser, Univ. Rostock). In this talk, I will showcase a few applications of such code, geared toward interesting photochemical/photophysical systems.

Azulene crystals. Although isoelectronic with naphthalene, aromatic azulene molecules (Fig. 1) present a strong dipole moment and blue-colored crystals. Furthermore, they break the so-called Kasha's rule, by showing an $S_2 \rightarrow S_0$ fluorescence, thus representing an interesting test subject. Azulene excited states are better described through proper multireference treatment than using single-determinant methods. In this talk, I will present some preliminary results on coupling terms between azulene molecules, as found in a crystal structure, computed at the MS-CASPT2/SA-CASSCF level of theory.

Bacteriochlorophyll (BChl) molecules. BChls represent one of the major players in antenna protein/chromophore complexes. I will present the results obtained from computing excitonic coupling terms for BChl dimers (Fig. 2) extracted from two such protein complexes, LH2 and LH1. While some results were expected, others were partially surprising and will be discussed.

BChl derivatives. Finally, I will introduce some ongoing work on the extensive exploration of coupling terms modulation in BChl-derived dimers (Fig. 3). Different types of aggregates will be presented. Coupling terms for BChl and BChl-derivative dimers were computed at the MS-RASPT2/SA-RASSCF level of theory.

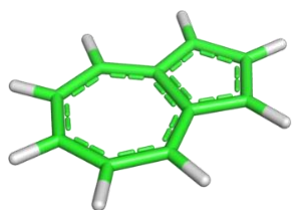


Fig. 1: Azulene aromatic molecule. Aromaticity implies a dipole moment from the 7- to the 5-membered ring

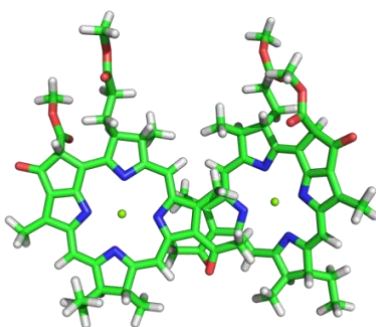


Fig. 2: A BChl dimer from LH2. Depicted are units 304 and 305, minus the saturated tail.

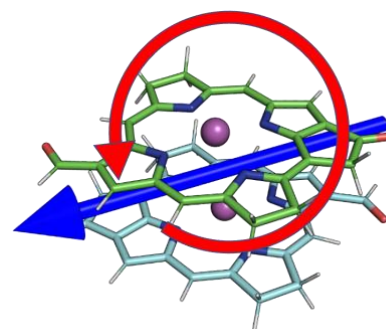


Fig. 3: Two BChl-derivatives with changing relative spatial disposition, e.g., rotating one with respect to the other (red arrow) and the computed excitonic transition dipole moment (blue arrow)

An overview of the Libxc library of density functionals and its interface in OpenMolcas

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Libxc¹ is a freely available, open-source library of density functional approximations that has been used in GPAW from early on. More recently, Libxc has become the standard implementation of density functionals across communities from the solid state to atomic and molecular physics and quantum chemistry, with numerical approaches ranging from basis set approaches (Gaussians, numerical atomic orbitals, wavelets, finite elements, plane waves) to finite-difference calculations.

In addition to the eponymous support for pure exchange (x), correlation (c) and exchange-correlation (xc) functionals, Libxc also supports kinetic (k) energy functionals and generalized Kohn-Sham schemes including global hybrids and various types of range-separated hybrids. Also double hybrids will be supported in an upcoming major release.

Although Libxc originally relied on hand-written C implementations of density functionals and their derivatives², as the approach was slow, painstaking and error-prone, the current implementation relies on automatic code generation with Maple,¹ which greatly facilitates the addition of novel functionals

and offers up to fourth derivatives for almost all functionals included in the library.

At present, Libxc contains efficient implementations of 600+ density functionals, and is written in portable C99 with Fortran and Python bindings. To the best of our knowledge, Libxc is used in over 35 electronic structure programs, including several commercial packages.

Thanks to a collaboration with Roland Lindh, OpenMolcas has been recently interfaced with Libxc. In this talk, I will discuss some aspects of the interfacing effort, and discuss what kinds of functionals are usable in the current development version of OpenMolcas.

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Compressed Multistate Pair-Density Functional Theory and its Analytic Gradients in *OpenMolcas*

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Multiconfiguration pair-density functional theory (MC-PDFT) is typically as accurate as, and sometimes even more accurate than, complete-active space second-order perturbation theory (CASPT2), but with a lower cost. However, CASPT2 and MC-PDFT should not be applied to strongly interacting states such as near conical intersections or locally avoided crossings. In such cases, one should use XMS-CASPT2 or MS-PDFT, in both of which the final step is diagonalization of a model space Hamiltonian matrix. In XMS-CASPT2 or MS-PDFT, the reference states, which are obtained from, for example, state-averaged complete active-space self-consistent field theory (SA-CASSCF), are transformed into intermediate states. In MS-PDFT, the diagonal elements of the model-space Hamiltonian matrix are the PDFT energies of the intermediate states, and the off-diagonal elements are evaluated by wave-function configuration interaction, e.g., CASCI. We have put two MS-PDFT methods in *OpenMolcas*, namely extended MS-PDFT (XMS-PDFT)[1] and compressed MS-PDFT (CMS-PDFT)[2]. The latter is more robust. In CMS-PDFT, the intermediate states are obtained by maximizing the sum-over-states of the classical Coulomb energies[3]. We derived analytic gradients for CMS-PDFT using the Lagrangian method. This talk will present the details of the implementation of CMS-PDFT and its analytic gradients in *OpenMolcas*.

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Manuscript ID: TMPH-2022-0080

Posters

Combined QM-ML Approach to Accelerate Photodynamics Simulation with High Robustness

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Trajectory surface hopping (TSH) has been applied to study various systems that include excited-state dynamics. Previously, our group has simulated 73 trajectories for the photolysis of the hydroxysulfinyl radical (HOSO) with 5 doublet states concerned[1], using MS-CASPT2 from the OpenMolcas / SHARC interface. Nevertheless, the cost of high-level QM calculation limits the number and lengths of the trajectories. Some previous works have shown the possibility to accelerate photodynamics simulation with neural networks by ~10000 times[2][3]. Despite having supreme speed, the robustness and transferability of the grey-box machine learning model remain concerns.

In this work, localized orbital locator (LOL)[4] is applied to transform the molecular coordinates into voxelized features in the 3D grid. The LOL descriptor is based on low-level DFT calculation, which is more than 100 times faster than MS-CASPT2. In addition, using the ground state energy calculated by DFT with Δ -learning provides a standard for coordinates outside the training set domain.

Combining the LOL descriptor with SchNet[5], energies and forces can be predicted accurately and show great transferability. In Figure 1, it is illustrated that the state populations of ML-predicted trajectories and QM trajectories are similar. On the other hand, the ratios of photoproducts from both methods agree well, as listed in Table 1. Moreover, the ensembled LOL and SchNet model can query underexplored geometries more efficiently in the active learning scheme, and these points can be recalculated using the OpenMolcas Interface.

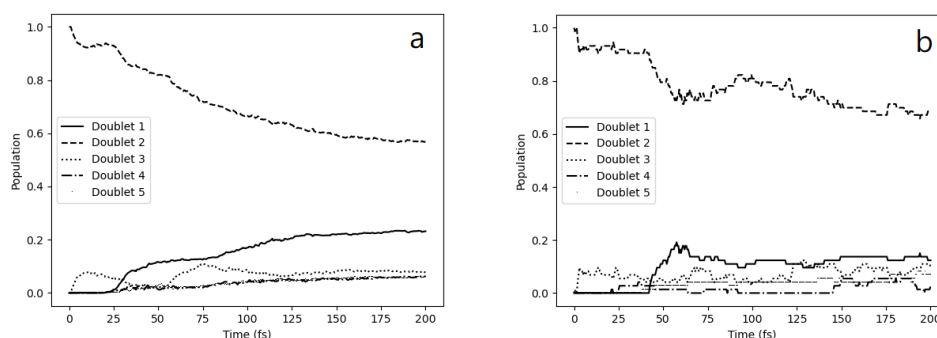


Figure 1. State population of trajectories with (a) ML+ZNSH, 1000 trajectories, (b) QM, 73 trajectories

Photoproduct	HO+SO	HOS+O	HO+SO	No photolysis
ML+ZNSH	0.561	0.002	0.010	0.427
QM	0.521	0.027	0	0.452

Table 1. Proportion of trajectories leading to different photoproducts

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Quantitative Prediction of the K-edge XANES of Hydrated Transition Metal ions

Soumen Ghosh, Niranjan Govind

Understanding the solvation structure of transition metal 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. Using water as the common ligand, we study the X-ray absorption pre-edge and near edge spectra at the K-edge of a near-complete series of hydrated first-row transition metal ions with d-orbital occupancy ranging from d^2 to d^{10} . Starting with optimized structures that were derived from an explicit solvation treatment at the density functional theory (DFT) level, we then compute the pre-edge X-ray absorption spectra at the metal ion K-edge at the time dependent density functional theory (TDDFT) and restricted active-space second-order perturbation theory (RASPT2) levels of theory. TDDFT calculations provide accurate results for spectra that are dominated by single excitations, while significant improvements were obtained with RASPT2 calculations that correctly distinguish between singly and doubly excited states, where relevant, with quantitative accuracy with respect to the experimental spectra. We analyze and assign the different pre-edge features for each metal ion in order to reveal the impact of the variations in the d orbital occupancy on the first-shell coordination environment.

ANALYSES OF FERROMAGNETIC AND ANTIFERROMAGNETIC COUPLING PATHS IN MANGANESE DIMERS

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Magnetic properties of polynuclear transition metal complexes are experimentally accessible observables. Magnetic susceptibilities are strongly correlated with the chemical composition of the complexes, in particular the nature of the bridging units. The quantum chemical interpretation of the experimental results often rests on broken symmetry density functional theory calculations. Due to their intrinsic single determinant character, it is not possible to describe every spin state on an equal footing. Instead, the J -coupling constants quantifying the strength and sign of the magnetic interaction are obtained from the energetic spacing between the ferromagnetically coupled high spin state and the so-called broken-symmetry determinant, which approximates the antiferromagnetically coupled state.^[1]

In OpenMolCAS, the QCMAQUIS module enables density matrix renormalization group (DMRG) calculations based on an *ab initio* complete active space ansatz.^[2] This allows the consideration of large active spaces and thus the characterisation of magnetic coupling in realistic examples from the experimental literature. Using orbital entanglement measures in combination with standard spin interaction models, we strive for a deeper understanding of coupling patterns.^[3]

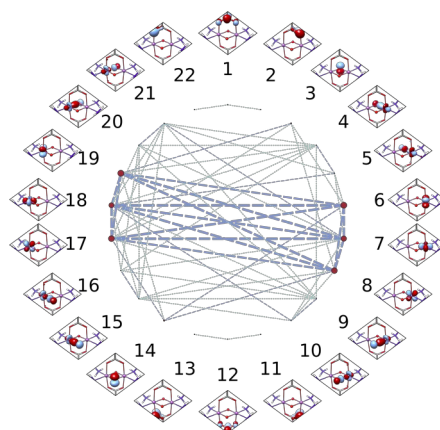


Figure 1: Entanglement diagram for a ferromagnetically coupled $(\mu\text{-O})_2\text{-}(\mu\text{-OAc})_2$ -bridged Mn^{IV} dimer obtained from a (26,22) DMRG-SCF calculation in the singlet spin state.

In this contribution, we present electronic structure analyses of ferromagnetically and antiferromagnetically coupled μ -oxo-bridged Mn^{IV} dimers in all relevant spin states. We will discuss the relative importance of static and dynamic correlation in these electronic structures, in particular with a view towards quantitative predictions of magnetic coupling magnitudes.

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Photocycloreversion mechanism of oxetane derivatives as models of (6-4) photoproduct DNA lesions

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DNA in living beings is continuously damaged by both exogenous and endogenous agents, such as UV radiation, giving rise to lesions in the DNA. The most common lesions are cyclobutene pyrimidine dimers and (6-4) photoproducts. The photoinduced (6-4) photoproducts DNA lesions can be initiated by Paternò–Büchi photocycloaddition between two adjacent pyrimidine bases, forming an oxetane ring. Then, the repair mechanism of these lesions can be characterized by the inverted mechanism of the Paternò–Büchi reaction.

In this contribution, two types of oxetanes have been studied as model compounds of the elusive oxetane intermediate present during the (6-4) photoproducts repair. The first type of oxetane arise from the reaction between two benzoquinone molecules (BQ-ox). The second type, is formed by two naphthoquinone monomers, called NQ-1. These models have been compared with previous results obtained for two stable head-to-head and head-to-tail isomers (HH-1 and HT-1, respectively) formed by reacting dimethylthymine and benzophenone[1].

CASPT2//CASSCF and DFT calculations have allowed to interpret the experimental observations. In addition, they also help us to determine the properties of relevant intermediates. It has been observed that both BQ-ox and NQ-1 will decay to the ground state, without the formation of the triplet exciplex, while HH-1 points to a favourable evolution to a triplet exciplex in a much higher extent than HT-1[1]. These findings agree with the results obtained by our experimental collaborators.

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Analysis of Excitation Patterns in Nitrogen-Splitting Complexes

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Ammonia derived from N₂ and fossil H₂ in the Haber-Bosch process represents the main source of nitrogen compounds. In order to access a more diverse range of N-containing chemicals without relying on NH₃ as an intermediate, it is of high interest to develop tailored nitrogen-activating catalysts. One way of achieving synthetic nitrogen fixation is selective light-driven N₂ cleavage. All known complexes for N₂ photoactivation have a linear core of the form M-N-N-M which undergoes geometric and electronic changes during the photochemical process. The mechanistic understanding of the underlying processes is still in its early stages and even the nature of the responsible excited state is insufficiently characterized.^[1]

For the tungsten^[2] and rhenium^[3,4] pincer complexes of Schneider and coworkers, the excitations within the M-N-N-M core are already studied in detail on the time-dependent density functional level of theory.

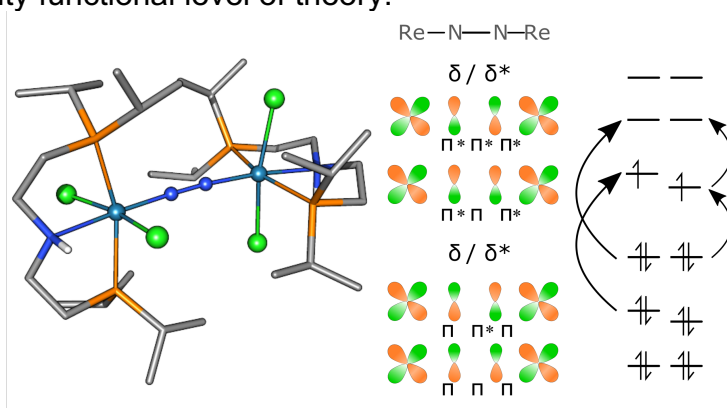


Figure 1. The rhenium pincer complex of Schneider and coworkers and exemplary excitations within the Re-N-N-Re core.

However, the complexity of the electronic structure requires the use of multiconfigurational methods. Here, we present an analysis of excitation patterns in rhenium pincer complexes based on restricted active space self-consistent field and density matrix renormalization group approaches with subsequent second-order perturbation theory calculations. This permits an appropriate treatment of spin-orbit coupling effects and captures double excitations so that their contributions to the underlying photochemical processes can be evaluated.

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Stochastic State-Averaged CASSCF for Spin-Exchange Transition Metal Clusters

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May 15, 2022

Oligonuclear Transition Metal Clusters are a common structural motif in nature, one prominent example being the Oxygen Evolving Complex of photosystem II. Understanding their catalytic activity requires accurate resolution of the low-energy spectrum. In this contribution, we investigate the magnetochemistry of one mixed-valence dinuclear¹ and two homo-valence trinuclear^{2,3} manganese model systems within the Complete Active Space framework.

To this end, a stochastic state-averaged (SA) CASSCF algorithm has been developed in OpenMolcas, which interfaces to the N-Electron CI (NECI)⁴ program to enable state-averaging across different spin sectors, as opposed to the implementation currently available that only allows same-spin SA-CASSCF. Whereas state-specific optimisation and subsequent CASPT2 on a minimal active space lead to unphysical deviation from an isotropic Heisenberg model, the new stochastic SA-CASSCF method across different spin sectors correctly reproduces the experimentally observed ordering. Since our implementation can function in both Slater determinant and CSF bases, it can be readily combined with other recent innovations such as orbital localisation and reordering⁵ inspired by the Genealogical Coupling Graph and orbital-resolved spin-spin correlation functions from stochastically sampled RDMS⁴. The latter are demonstrated to be expedient to compare CASSCF stationary points before application of perturbative corrections such as CASPT2.

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Some Comments on Different-Orbitals-for-Different-Spins Determinants

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We have recently implemented the capability to compute the spin-density matrix within the COLUMBUS Program System[1]. This is currently for MCSCF wave functions, with plans to extend it to MRCI and MR-AQCC in the future. The COLUMBUS codes are based on the graphical unitary group approach (GUGA), a spin-free formulation, so the usual simple spin-orbital expression for the spin-density matrix elements,

$$D_{qp}^{[1,0;M]} = \langle \psi; S, M | \hat{a}_{p\alpha}^\dagger \hat{a}_{q\alpha} - \hat{a}_{p\beta}^\dagger \hat{a}_{q\beta} | \psi; S, M \rangle,$$

cannot be used directly. Instead, we compute the matrix elements from linear combinations of 1-RDM and 2-RDM elements that are already available within the MCSCF procedure. In this poster, I will discuss some of the details of this formulation, and I will show some results from our initial implementation. From the spin-density matrix the spatial spin-distribution may be computed.

$$\rho^{[-;M]}(\mathbf{r}) = \sum_{p,q} \varphi_q(\mathbf{r}) D_{qp}^{[1,0;M]} \varphi_p(\mathbf{r})^*$$

While comparing our results to previous calculations, we observed that most spin-density and spin-distribution calculations are formulated with unrestricted Hartree-Fock (UHF) and unrestricted Kohn-Sham (UKS) methods which are based on different-orbitals-for-different-spins (DODS) determinants. In these approaches, the spin-polarization, which contributes to the nonzero spin-density, is intrinsically associated with spin-contamination. Our GUGA results are done entirely with spin-eigenfunctions. This led to further investigation of what exactly is computed with these spin-contaminated formulations and how do those results relate to our spin-eigenfunction formulation. A new relationship was discovered between the cosine-sine decomposition (CSD) of an orthogonal matrix and the full spin-decomposition of spin-contaminated wave functions[2]. The CSD facilitates this spin-decomposition in three ways: 1) sparsity is introduced into the spin operators \hat{S}_+ , \hat{S}_- , and \hat{S}^2 , 2) the CSD allows the identification of frozen core and frozen virtual orbitals, effectively reducing the orbital dimension, and 3) it allows the spin-eigenfunction expansion space to be truncated. The poster will include additional details of the CSD, of the spin-decomposition procedure, and of the spin-density for DODS wave functions.

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The 10th OpenMolcas Developers' Workshop

Uppsala 8th – 10th June 2022

***Ab Initio* Calculations for CO⁺ (for Radiative Association in Supernova 1987A)**

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Abstract. Potential energy curves and transition dipole-moment functions for CO⁺ are calculated at the MS-CASPT2 level, following the CASSCF calculations. Different basis sets and complete active spaces are employed, and different numbers of states are requested. The C_{2v} symmetry is employed.

The aim is to obtain reliable *ab initio* data for radiative association calculations. The special focus is on quartet states as *ab initio* data of doublet states have already been published in radiative association studies (M. Zámečníková et al. (2019, 2020)). In addition, the so-far published transition dipole-moment functions for quartet states by other authors are sparse and do not cover all transitions of our interest.

We used two versions of OpenMolcas, concretely, OpenMolcas v18.09 and OpenMolcas v20.10 suits. Both versions seem to give far better stability in convergence than other programmes. On top of that, they enabled us to calculate more electronic states.