

# NMQC 2023 Book of Abstracts



# Main Organizers



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# Program

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# Precise atomisation energies for a chemically diverse set of small molecules

Andris Gulans<sup>1</sup>

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We present a database of 832 small molecules with 65 chemical elements from rows 1–6. It accounts for chemical diversity, and each chemical element is represented in a broad range of oxidation states. For each molecule, we provide reference atomisation energies employing the PBE exchange-correlation functional and scalar-relativistic approximation. To obtain these data, we perform calculations using linearised augmented plane waves as implemented in the all-electron electronic-structure code exciting<sup>1</sup>. Using the obtained data, performance of the non-relativistic theory and the (atomic) zero-order regular approximation (ZORA)<sup>2</sup> is assessed taking the infinite-order regular approximation (IORA)<sup>3</sup> as the reference. The non-relativistic atomisation energies deviate significantly (above 1 kcal/mol) from the reference already for some molecules consisting of elements as light as those from rows 1–3. For example, these deviations are above 2 kcal/mol for PF<sub>5</sub>, HClO<sub>4</sub> and SF<sub>6</sub>. Further, we use the database for assessing our new multipole-conserving pseudopotentials (MPC) formulated within the separable dual-space Gaussian representation as well as 11 modern pseudopotential families. The MPCs reproduce the atomisation reference data well within the chemical accuracy limit of 1 kcal/mol. We use them for decomposing the total errors in atomization energies due to pseudopotentials into individual atomic contributions. Our analysis reveals that commonly state-of-the-art pseudopotential families are still not fully compliant with chemical accuracy, and the largest errors arise in molecules with atoms in high oxidation states.

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# A Quantum-compute Algorithm for Exact Laser-driven Electron Dynamics in Molecules

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In this work,<sup>1</sup> we investigate the capability of known quantum-computing algorithms for fault-tolerant quantum computing to simulate the laser-driven electron dynamics of excitation and ionization processes in small molecules such as lithium hydride which can be benchmarked against the most accurate time-dependent full configuration interaction (TD-FCI) calculations. The conventional TD-FCI wave packet propagation is reproduced using the Jordan-Wigner transformation for wave function and operators and the Trotter product formula for expressing the propagator. In addition, the time-dependent dipole moment, as an example of a time-dependent expectation value, is calculated using the Hadamard test. To include non-Hermitian operators in the ionization dynamics, a similar approach to the quantum imaginary time evolution (QITE) algorithm is employed to translate the propagator including a complex absorption potential into quantum gates. The computations are executed on a quantum-computer simulator. By construction all quantum computer algorithms except for the QITE algorithm used only for ionization but not for excitation dynamics would scale polynomially on a quantum computer with fully entangled qubits. In contrast, TD-FCI scales exponentially. Hence, quantum computation holds promises for substantial progress in the understanding of electron dynamics of excitation processes in increasingly large molecular systems as had already been witnessed in electronic structure theory.

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# The ddX-library for polarizable implicit solvation models

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In this talk, we present the ddX-library that provides efficient and accurate numerical discretizations of several polarizable implicit solvation models that rely on the domain decomposition paradigm, i.e. the ddCOSMO, ddPCM and ddLPB-method. We provide an overview of the methods, a few elements of the library and its interface with other software packages.

# Orbital Optimization using a Generalized Grid-Based Fast Multipole Method

Dage Sundholm<sup>1</sup>

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The power of massively parallel computer architectures can be utilized when the computational tasks are divided into small and independent parts that can be calculated concurrently. The main computational tasks of fully numerical electronic structure calculations are calculations of two-electron interaction potentials and optimization of the orbitals. The electrostatic and exchange potentials can be obtained by numerically integrating the Coulomb kernel. Since integration means adding, the contributions can be added in any order as long as the contributions are considered only once. The orbitals can analogously be obtained by integrating the Helmholtz kernel, which is also a six-dimensional integral that can be expanded in tensorial numerical basis functions. I shall discuss how the orbitals can be optimized by integrating the Helmholtz kernel and how long-ranged interactions can be considered by using multipole-like expansions. The generalized multipole moments of subdomains can be moved to common expansion points and combined into multipole moments of larger domains. A grid-based fast-multipole method (GB-FMM) can be obtained by using an octree approach. The computational costs scale linearly with respect to the number of subdomains, which can approach an  $N_o$  scaling when using many GPGPUs, *i.e.*, the computational wall time is independent of the grid size implying that one gets accuracy for free.

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# Fundamentals of real-space electronic structure: mean field and beyond

Edward F Valeev<sup>1</sup>

<sup>1</sup>*Department of Chemistry, Virginia Tech, USA*

In this talk I will discuss how real-space numerical representations can be used efficiently for simulation of electronic structure. The primary focus will be on the multiresolution adaptive (MRA) spectral-element representations that combine robust control of precision and ability to treat core and valence electronic energy scales on equal footing without the resort to multiple representations; the use of MRA technology will be compared/contrasted with other representations (real-space and spectral, e.g., plane-waves and atomic orbitals).

In the first part of the talk I will review the fundamentals of how real-space representations are used in the context of the mean-field (self-consistent field) methods. The second part of the talk will focus on the correlated methods with explicit description of 2-particle correlations (many-body perturbation theory, coupled-cluster); key “enablers” for such methods are the regularization of the Hamiltonian (R12/F12 style) and the tensor compression (local or global). The last part of the talk will recap recent progress in the development of robust real-space orbital solvers that can be used in conjunction with general correlated (multiconfiguration) methods.

# Towards a relativistic QED for atomic and molecular bound states

E. Mátyus<sup>1</sup>, D. Ferenc<sup>1</sup>, P. Jeszenszki<sup>1</sup>, Á. Margócsy<sup>1</sup>

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Relativistic quantum electrodynamics developments are presented with the aim of developing (the practical applicability of) the fundamental theory of molecular matter in relation with precision spectroscopy experiments. Interactions in atomic and molecular systems are dominated by electromagnetic forces and the theoretical framework must be in the quantum regime. The physical theory for the combination of quantum mechanics and electromagnetism, quantum electrodynamics has been ‘established’ by the mid-twentieth century, primarily as a scattering theory. To describe atoms and molecules, it is important to compute bound states. In the non-relativistic quantum mechanics framework, bound states can be computed to high precision using robust and general methodologies by solving *wave equations*. With the sight of the development of a computational quantum electrodynamics framework for atomic and molecular matter, the field theoretic Bethe–Salpeter wave equation expressed in space-time coordinates, its exact equal-time variant and emergence of a relativistic wave equation is reviewed. An explicitly correlated variational framework for solving this relativistic wave equation is presented, which allows to converge the energy within a (sub-)parts-per-billion (ppb) relative precision. These variational relativistic computations have extensively been tested with respect to the traditional perturbative framework, *i.e.*, expansion of the total energy about the non-relativistic reference with respect to the  $\alpha$  fine structure constant, which currently provides benchmark theoretical values for precision spectroscopy of atoms and molecules with the smallest  $Z$  nuclear charge numbers. To have results useful for precision spectroscopy from a variational relativistic approach, it is necessary to account also for pair, retardation, and radiative corrections to high precision. Ongoing work and open challenges are discussed based on the equal-time Bethe–Salpeter equation and a high-precision, variational relativistic wave function.

# Dynamics of molecules in magnetic fields

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Molecules subject to strong magnetic fields exhibit a number of novel chemical and physical phenomena. These can affect the chemical bonding and static electronic properties. Additionally, there are also velocity dependent forces that affect the dynamics and screen the Lorentz forces. These screening forces are a manifestation of the general notion of a Berry phase and have important, qualitative effects on the overall dynamics. They are also non-trivial from an implementation perspective, requiring the calculation of a Born–Oppenheimer vector potential in addition to the usual scalar Born–Oppenheimer potential as well as modifications of standard methods for integrating the equations of motion for the nuclei. In this talk, I will report recent theoretical and numerical results related to these velocity-dependent screening forces, focusing on their effect on molecular vibrations.

# Reduction of Gaussian Mixtures for Electronic Structure Calculations

Gregory Beylkin<sup>1</sup>

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We discuss a gridless approach for solving partial differential and integral equations. For our approach to work, we need

- A convergent iteration to obtain the solution.
- A family of functions (much larger than any possible basis) closed under the necessary operations
- A fast reduction algorithm to remove linear dependencies within a set of functions, i.e. for a given accuracy find “best” linear independent subset of terms to represent all functions in the set.

Assuming that all components of the problem, e.g. Green’s functions, potentials, etc. are accurately approximated within the family of chosen functions, we look for the solution as a multivariate mixture. While the number of terms in intermediate multivariate mixtures grows rapidly at each step of a convergent iteration, most of these terms are nearly linearly dependent. In order to reduce the number of terms, we use a fast algorithm to find “best” linearly independent subset of terms to approximate the initial multivariate mixture. As an example, using Gaussian mixtures, we solve the Hartree-Fock equations relying on

- A convergent iteration for solving the integral formulation of the Hartree-Fock equations.
- An efficient approximation of Green’s functions and potentials via a linear combinations of Gaussians.
- The reduction algorithm which is linear in the number of terms in the initial multivariate mixture and quadratic in the number of chosen “best” linearly independent terms.

We observe that the number of terms of the Gaussian mixture representing solution is significantly smaller than that using a multiwavelet approach. This is a joint work with Lucas Monzón and Xinshuo Yang.

# The Series Solution Method in Quantum Chemistry for Three-Body Coulomb Systems

Hazel Cox<sup>1</sup>

<sup>1</sup>*Department of Chemistry, School of Life Sciences, University of Sussex, Brighton, UK.*

As high-precision experiments become more sophisticated, and systems probed become more complex, it's important to ensure theory remains an essential tool for interpreting and predicting chemical systems and phenomena. Three-body Coulomb systems are the simplest that capture the effects of electron correlation and nuclear motion and are therefore of interest for atomic and molecular theory but also for systems containing various elementary particles such as muons and positrons.

High-accuracy, non-relativistic, quantum chemical calculations of the energy levels and wave- functions of three-body systems are calculated using a fast and efficient series solution method in a triple orthogonal Laguerre basis.<sup>1</sup> The method is adapted to calculate, in a single variational calculation, the critical mass or charge for bound state stability, and a Hartree-Fock implementation using a Laguerre basis. The correlated motion of particles is quantified using radial and angular densities.

The effects of nuclear motion,<sup>2</sup> and high-accuracy benchmark electron correlation data,<sup>3</sup> will be presented. Exploring the correlated motion of electrons at low nuclear charge just prior to electron-detachment,<sup>4</sup> and attempting to capture this behavior in future theoretical method developments, such as correlation functionals,<sup>5</sup> is an important step forward in ensuring new methods can address increasingly exotic and complex systems.

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# Incremental Treatments of the Full Configuration Interaction Problem

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The full configuration interaction (FCI) method has inevitably been transformative in helping to manifest theoretical chemistry as a scientific discipline with unquestionable interpretative and predictive powers. However, as the scope of applications for which FCI continues to prove indispensable broadens, it is important to recall the required traits in terms of robustness, efficacy, and reliability its modern approximations must satisfy<sup>1</sup>.

In this talk, I will review the recent many-body expanded FCI (MBE-FCI) method by critically assessing its advantages and drawbacks in the context of contemporary near-exact electronic-structure theory<sup>2</sup>. Besides providing a succinct summary of the short history of MBE-FCI to date within a generalized and unified theoretical setting<sup>3-6</sup>, some of its finer algorithmic details will be discussed alongside its optimized computational implementation<sup>7</sup>. A selected few of the most recent applications of MBE-FCI will be revisited before I move on to present pilot results that illustrate how to use the method as a solver in CASSCF theory as well as how to leverage exact point-group symmetries amongst spatially localized molecular orbitals to accelerate MBE-FCI simulations<sup>8</sup>.

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# Flexibilities of wavelets as a computational basis set for large-scale electronic structure calculations

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The BigDFT project was started in 2005 with the aim of testing the advantages of using a Daubechies wavelet basis set for Kohn-Sham (KS) density functional theory (DFT) with pseudopotentials. This project led to the creation of the BigDFT code, which employs a computational approach with optimal features of flexibility, performance, and precision of the results. In particular, the employed formalism has enabled the implementation of an algorithm able to tackle DFT calculations of large systems, up to many thousands of atoms, with a computational effort that scales linearly with the number of atoms. In this contribution, we recall some of the features that have been made possible by the peculiar properties of Daubechies wavelets. In particular, we focus our attention on the usage of DFT for large-scale systems. We show how the localized description of the KS problem, emerging from the features of the basis set, is helpful in providing a simplified description of large-scale electronic structure calculations. We provide some examples on how such a simplified description can be employed, and we consider, among the case-studies, biological structures of SARS-CoV-2 virus.

# Towards accurate excitation energies in supramolecular systems: combining T-CDFT and fragments in the BigDFT code

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Despite the variety of available computational approaches, state-of-the-art methods for calculating excitation energies such as time-dependent density functional theory (TDDFT), are typically computationally demanding and thus limited to moderate system sizes. Thanks to a new variation of constrained DFT (CDFT), implemented in the BigDFT code and recently published by our group, we have shown to be able to robustly model both local and charge-transfer excitation energies with a comparable precision to TDDFT for local excitations, while not exhibiting the typical limits of standard TDDFT for charge-transfer states, for a computational cost close to  $\Delta$ SCF. As T-CDFT is implemented within the linear scaling formalism it is naturally suited to be paired with the fragment approach already available in the BigDFT code. By properly combining these two infrastructures, one can use T-CDFT to impose excitations on particular fragments in supramolecular systems. In the example of local excitations on a molecule (fragment) in a given environment, where no strong coupling with the environment is expected, the constraint could be imposed between orbitals associated with the target fragment only, while still treating the full system at DFT level. In this talk, I will show how the aforementioned approach allows the exploration of explicit environment effects on excitation energies in systems such as TADF materials, paving the way for future simulations of excited states in realistic morphologies.

# Quantum Chemistry on Quantum Computers: Challenges and New Directions

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Quantum computers offer exciting possibilities for simulating electronic structure problems, but current devices still face significant challenges. These challenges include limitations in the number of qubits available, high levels of noise, and a range of technical and fundamental issues. In this talk, I will discuss how these challenges are affecting one of the most studied applications of quantum computers —quantum chemistry simulations — and present a new framework to overcome them.

As an example I will focus on three key steps, namely how to map optimally fermionic systems to qubits<sup>1</sup>, how to simulate molecules in a scalable and noise- resilient manner<sup>2,3</sup>, and how to extract information in the most efficient manner<sup>4,5</sup>.

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# Efficient response property calculations for density-functional theory

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Response calculations in density-functional theory aim at computing the change in ground-state density induced by an external perturbation. At finite temperature, these are usually performed by computing variations of orbitals, which involve the iterative solution of potentially badly conditioned linear systems, the Sternheimer equations. Since many sets of variations of orbitals yield the same variation of density matrix, this involves a choice of gauge. Taking a numerical analysis point of view, I will present the various gauge choices proposed in the literature in a common framework and discuss their stability. Beyond existing methods, I will discuss a novel approach, based on a Schur complement using extra orbitals from the self-consistent field calculations, to improve the stability and efficiency of the iterative solution of Sternheimer equations. We show the success of this strategy on nontrivial examples of practical interest, such as Heusler transition metal alloy compounds, where savings of around 40% in the number of required cost-determining Hamiltonian applications have been achieved.

This is joint work with Eric Cancès, Gaspard Kemlin, Antoine Levitt, Benjamin Stamm.

# Modern exact two-component Hamiltonians for relativistic quantum chemistry and physics: two-electron picture-change corrections made simple

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Based on atomic mean-field (amf) SCF quantities, we present two simple, yet computationally efficient and numerically accurate matrix approaches to correct scalar- relativistic and spin-orbit two-electron picture-change corrections (PCs) arising within an exact two-component (X2C) Hamiltonian framework<sup>1</sup>. Both approaches, dubbed amfX2C and eamfX2C, allow us to uniquely tailor PCs to mean-field models, viz. Hartree–Fock or Kohn–Sham DFT, in the latter case also circumventing a point-wise calculation of exchange–correlation PCs. We assess the numerical performance of these Hamiltonians on spinor energies of closed-shell and open-shell molecules, achieving a consistent  $\sim 10^{-5}$  Hartree accuracy compared to reference four-component (4c) data. Excellent agreements with reference data are also observed for molecular properties sensitive to relativistic effects such as X-ray (transient) absorption or EPR spectroscopies<sup>2–4</sup>. We believe that our (e)amfX2C Hamiltonians constitute a fundamental milestone towards a universal and reliable relativistic 2c approach for quantum chemistry and physics, maintaining the accuracy of the parent 4c one at a fraction of its computational cost.

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# Paving the way for useful computational chemistry on quantum computers with the orbital-optimised variational quantum eigensolver

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In the past years, the capability of near-term quantum computers to address the electronic structure problem for chemical systems has been successfully demonstrated for toy-model systems such as, for example, N<sub>2</sub>, H<sub>2</sub>O and hydrogen chains H<sub>n</sub> ( $n \leq 12$ ).

Hence, surpassing the limited availability, reliability and capacity of current quantum hardware still poses a major challenge to date and calls for the development of efficiently scaling (embedded) quantum algorithms to treat systems of real chemical relevance, such as for the purpose of optimising binding affinities in the lead-optimisation step of the small- molecule drug discovery pipeline.

To this end, we present in this contribution the Variational Quantum Eigensolver (VQE) combined with the self-consistent field (SCF) approach to orbital optimization<sup>1</sup>. We will discuss a classical embedding scheme based on the polarizable embedding model<sup>2</sup> to account for subtle effects of the environment on the electronic structure of the embedded quantum mechanical system in its ground and electronically excited states. Moreover, binding affinities are often governed by molecular interactions which necessitate to consider not only static but also dynamical electron-electron correlations. We address these challenges by making use of two distinct frameworks for VQE-SCF that can be classified as *diagonalise-then-perturb*<sup>3</sup> and *perturb-and-diagonalise*<sup>4</sup>, respectively.

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# Correlated Methods for Atoms and Molecules in Magnetic Fields

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Subjecting atoms or molecules into magnetic fields, either for spectroscopic applications like NMR or the generation strong-field spectra for the study of the atmospheres of magnetic White Dwarf stars typically requires reliable predictions from quantum chemical methods that are able to properly describe electron correlation effects. Additionally, in order to increase the application range in terms of system size while retaining a given accuracy, Cholesky-Decomposition methods can be employed. In this talk, challenges that are faced in terms of predictive power as well as strategies speeding up the respective calculations will be discussed for low- and high-field applications.

# Real-space density functional calculations using multi-GPUs: Preconditioning and Decomposition

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General purpose graphical processing units (GPUs) are designed to provide incredible computing power based on the single instruction multiple data scheme especially for dense matrix operations. However, the typical real-space density functional calculations involve sparse operations, which require algorithm modifications to fully utilize the hardware performance of modern GPUs. In this study, I will present two numerical methods to accelerate the diagonalization process, which is the main bottleneck of real-space density functional calculations.

The first method is the preconditioner, which is a widely adopted approach to accelerating iterative methods by linear transformations. Preconditioning can be performed without GPU-GPU communications, which is particularly important for multi-GPU computing systems. I will demonstrate the efficiency of preconditioning in real-space density functional calculations using multi-GPUs.

The second method is the Tucker decomposition of Hamiltonian matrix, which eliminates sparse operations in the diagonalization process. The DFT Hamiltonian matrix in the finite difference method can be efficiently decomposed into three small factor matrices and a core tensor. This decomposition replaces sparse matrix operations with dense tensor contractions. I will present how to implement Tucker decomposition while preserving the lowest eigenvectors during self-consistent field calculations.



# Complete basis set limit studies of the numerical behavior of density functionals

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Thanks to the improvements in algorithms and approximations accrued during several decades of development, as well as the amazing advances made in computer engineering, density functional theory (DFT) has become widely used across various disciplines to understand the structure and behavior of materials starting from first principles. Motivated by this success, many new density functional approximations (DFAs) are published every year; our Libxc library<sup>1</sup> containing over 600 DFAs at the moment. Despite this seemingly large number of available functionals, only few new DFAs get used by others than their original developers, and even fewer actually become widely used in the literature. Although the assumption is that new functionals are better than old ones, this is often not the case, as has been shown in the rich literature full of benchmarks on various functionals' accuracy on various properties of various systems, see ref.2 for a recent many-faceted review, for example. However, the numerical behavior of density functionals has been investigated to a much smaller extent. In this contribution, I will discuss our recent works related to the study into the well-behavedness of density functionals. In our definition<sup>3</sup>, a well-behaved density functional should yield total energies that converge smoothly to the complete basis set (CBS) limit by (i) affording smooth convergence to the quadrature grid limit at fixed density, (ii) a smooth convergence of the self-consistent field (SCF) procedure within a fixed basis set, as well as (iii) rapid convergence to the CBS limit in calculations with increasingly large basis sets. However, we have shown that many recent density functionals break this criterion. Already at fixed electron density, many functionals such as r<sup>2</sup>SCAN are ill-behaved in the evaluation of the total energy of atoms<sup>3</sup>. Fully numerical calculations<sup>4-7</sup> allow studying the effect of relaxing the density in self-consistent calculations, which demonstrate that most Minnesota functionals are ill-behaved already for the hydrogen atom<sup>7</sup>, producing large oscillations in the Laplacian of the density  $\nabla^2 n$ . The Li and Na atoms are also challenging for Minnesota functionals, as well as the recent B97M-V and  $\omega$ B97M-V functionals of Mardirossian and Head-Gordon<sup>8</sup>.

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# New interpretation of the two-body reduced density matrices

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In this talk I give a new interpretation of reduced density matrices based on the set of excitations of a system or Dyson orbitals. The first step is to show that these sets of excitations are isomorphic to wave functions and form a Hilbert space with a new parameterization of two-body reduced density matrices. This parametrization is based on a pair of matrices which anti-commutes following the anti-commutation relation of fermions. The interest is that the density matrices are more easily interpretable and do not appear as an array of numbers with many  $N$ -representable conditions

This new formalism allows to reduce, in a second step, the complexity of the conditions of  $N$ -representability and the calculation of the total energy by using a number of parameters of  $n^4$ . The idea is to consider these excitations as intrinsic degrees of freedom of the system, a bit like energy band diagrams. I will show where I am in the implementation, notably with SDP optimization.

# Recent developments in time-dependent coupled-cluster theory

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Highly accurate simulation of laser-driven electron dynamics is important for the prediction and interpretation of advanced spectroscopic experiments, including electronic response to sub-femtosecond laser pulses, which allow investigation and control of matter at the time scale of the electron. While multi- configurational methods have dominated the field for decades, recent years have witnessed a surge in interest in single-reference coupled-cluster methods for the simulation of electron dynamics<sup>1</sup>. Time-dependent coupled-cluster methods will be reviewed with emphasis on the major outstanding challenges for future developments.

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# Electron correlation in a relativistic perspective

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This talk addresses the definition of correlation energy within 4-component relativistic atomic and molecular calculations. In 1958 Löwdin proposed the following definition of the non-relativistic correlation energy: The correlation energy for a certain state with respect to a specified Hamiltonian is the difference between the exact eigenvalue of the Hamiltonian and its expectation value in the Hartree-Fock approximation for the state under consideration. In practice, the exact value is provided by a full Configuration Interaction (CI) calculation with some specified one-particle basis. The extension of this definition to the relativistic domain is not straightforward since the corresponding electronic Hamiltonian, the Dirac-Coulomb Hamiltonian, has no bound solutions. Present-day relativistic calculations are carried out within the no-pair approximation, where the Dirac-Coulomb Hamiltonian is embedded by projectors eliminating the troublesome negative-energy solutions. Hartree-Fock calculations are carried out with the implicit use of such projectors and only positive-energy orbitals are retained at the correlated level, meaning that the Hartree-Fock projectors are frozen at the correlated level. We argue that the projection operators should be optimized also at the correlated level and that this is possible by full Multiconfigurational Self-Consistent Field (MCSCF) calculations, that is, MCSCF calculations using a no-pair full CI expansion, but including orbital relaxation from the negative-energy orbitals. We show by variational perturbation theory that the MCSCF correlation energy is a pure MP2-like correlation expression, whereas the corresponding CI correlation energy contains an additional relaxation term. We explore numerically our theoretical analysis by carrying out variational and perturbative calculations on the two-electron rare gas atoms with specially tailored basis sets. We in particular show that the correlation energy obtained by the suggested MCSCF procedure is smaller than the no-pair full CI correlation energy, in accordance with the underlying minmax principle and our theoretical analysis.

Further reading:

Adel Almoukhalalati, Stefan Knecht, Hans J rgen Aagaard Jensen, Kenneth G. Dyall and Trond Saue, Electron correlation within the relativistic no-pair approximation, J. Chem. Phys. 145 (2016) 074104 (2016 Editors' Choice article) <http://dx.doi.org/10.1063/1.4959452>

# Fast, Accurate and Large-scale Ab-initio Calculations for Materials Modeling

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Electronic structure calculations, especially those using density functional theory (DFT), have been very useful in understanding and predicting a wide range of materials properties. The importance of DFT calculations is evident from the fact that ~20% of computational resources on some of the world's largest public supercomputers are devoted to DFT calculations. Despite the wide adoption of DFT, the state-of-the-art implementations of DFT suffer from cell-size and geometry limitations, with the widely used codes in solid state physics being limited to periodic geometries and typical simulation domains containing a few hundred atoms. This talk will present our recent advances towards the development of computational methods and numerical algorithms for conducting fast and accurate large-scale DFT calculations using adaptive finite-element discretization, which form the basis for the recently released DFT-FE open-source code (<https://github.com/dftfeDevelopers/dftfe>). Details of the implementation, including mixed precision algorithms and asynchronous computing, will be presented. The computational efficiency, scalability and performance of DFT-FE will be presented. Time permitting, extensions of this framework for TDDFT calculations will briefly be presented.

# Relativistic Methods and Large-Scale Hybrid Density Functionals for Complex Solids Using Numeric Atom-Centered Basis Sets

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This talk summarizes new developments for all-electron electronic structure theory of complex molecules and solids using numeric atom-centered basis sets in the FHI-aims code and the ELSI infrastructure. We cover three main developments: (1) Solvers in ELSI, a general purpose abstraction layer between electronic structure codes and eigenvalue and density matrix solvers, (2) large-scale all-electron hybrid density functional theory (DFT) that enables direct simulations of complex solids up to several thousand atoms (with tests ranging up to 30,000 atoms) on traditional parallel high-performance computers, and (3) incorporation of relativistic effects in energy band structures and total energy simulations, including a recent implementation of the quasi-four-component method for Dirac Kohn-Sham DFT. Using ELSI, we demonstrated a routine  $O(N^3)$  simulation (i.e., no *a priori* system type or sparsity assumptions) with 250,000 basis functions on Google's tensor processing unit (TPU) architecture. In layered lead halide perovskite semiconductors (i.e., systems for which already the basic crystallographic unit cell includes several hundred atoms), we investigate the expected energy levels and electronic doping associated with substitution of Pb with Bi and Sn impurities, using spin-orbit coupled hybrid DFT simulations and supercell sizes of several thousand atoms. Bi turns out to be a deep *n*-type donor but its doping efficiency is experimentally inferred to be limited by compensating intrinsic defects. Sn incorporation leads to weak *p*-type doping; we provide evidence that this is due to an enhanced propensity to find intrinsic *p*-doping Pb vacancies near Sn substitutional defects.

# Complexity Reduction in Density Functional Theory: Locality in Space and Energy

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Recent advances in algorithms and computational power are enabling the application of Kohn-Sham Density Functional Theory (DFT) to systems of unprecedented sizes. These developments hold significant implications for research paradigms and analysis techniques used by practitioners<sup>1</sup>. Specifically, they allow us to study the intrinsic length scales that give rise to the emergent properties of a system of interest. To extract this information, we have devised a “Complexity Reduction Framework” (QM-CR), which is able to use the results of large-scale DFT calculations to dissect systems into fragments and quantify inter-fragment interactions.

In this talk, we will discuss our recent work on enabling hybrid-DFT calculations of large systems in the Gaussian orbital-based code: NTCheM<sup>2</sup>. After briefly introducing its performance, we will showcase the insights gained by integrating it with QM-CR. In particular, we will explore the impact of Density Functional Approximation choice on locality measures, as well as the locality that exists in different energy windows. Building off this analysis, we propose two algorithms for computing the orbital energies of the Kohn-Sham Hamiltonian<sup>3</sup>. We demonstrate these algorithms can effectively be applied to systems composed of thousands of atoms and as an analysis tool that unveils the origin of spectral properties.

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# ATRIP: A Massively Parallel CCSD(T) Implementation For The Exascale Computing Age On CPUS And GPUS

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Quantum materials science (QMS) will play a key role in many technical challenges our society has to face in the next decades, including carbon capture and photovoltaics. The CCSD(T) algorithm improves the accuracy of Density Functional Theory (DFT) methods implemented by codes such as VASP and Quantum Espresso but is expensive and difficult to scale due to requiring tensor contractions on very large (>1TB) tensors. We present an algorithm for CCSD(T) that breaks the tensor contractions into many small matrix multiplications of a size that can be executed efficiently using cuBLAS on a single GPU and can achieve a sizable chunk of peak performance for non-accelerated (CPU) workflows. These matrices are distributed in such a way to minimise communication between GPUs and cached between iterations where possible. For most problem configurations, 90% of the required data can be found locally using this system, with further hiding of communication possible by overlapping data transfers between iterations, allowing scaling to hundreds of GPUs maintaining a high degree of performance.



# Future Perspective for Core-Electron Spectroscopy: Breit Hamiltonian in the Multiwavelets Framework

Christian Tantardini<sup>1,\*</sup>, Roberto Di Remigio Eikås<sup>1,2</sup>, Magnar Bjørgve<sup>1</sup>, Stig Rune Jensen<sup>1</sup>, and Luca Frediani<sup>1,\*</sup>

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New techniques in core-electron spectroscopy are necessary to solve the structures of oxides of *f*-elements and other strongly correlated materials that are present only as powders and not as single crystals. Thus, more accurate quantum chemical methods need to be developed to calculate the linear response in such materials. Here, we have presented the first development in such a direction, extending fully adaptive real-space multiwavelet basis to 4-component Dirac-Coulomb-Breit Hamiltonian. Multiwavelets were seen to be robust enough to reproduce the more traditional grid-based approach, as available in *GRASP*. Furthermore, our results confirmed that in two-electron species, the magnetic and Gauge contributions from *s*-orbitals are identical in magnitude and can account for the experimental evidence from *K* and *L* edges.

# Computing low energy excitations in strongly correlated systems

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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, as they cannot be qualitatively described as charge transfers or electronic density changes, but rather as spin state changes (spin orders between magnetic atoms) on a given charge density.

The accurate calculation of this type of excitation requires specific 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 SAS+S<sup>4</sup> method developed in our group. After a short introduction on the different effects that should be taken into account for an accurate treatment of the magnetic excitations, I will present our latest implementation RelaxSE<sup>5</sup>, developed to describe this type of excitations.

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# Importance of k-point samplings on property evaluation of periodic systems

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We investigate systematically the electronic state of low dimensional extended systems by the first-principle computation on k-space and study the impact of the sampling point number on the dispersion curve around Fermi level and consequently on the optical property for low frequency. The example for graphene shows the critical dependence of the dispersion curve that determines the final property evaluation. Further investigation of Silicon and Germanium crystal reveals the same trends of the impact which makes the evaluation of property for low frequency region with small numbers of k-point sampling little sense.

# Design and Application of Variational Quantum Circuits

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Efficient ways to prepare fermionic ground states on quantum computers are in high demand and different techniques were developed over the last years. Despite having a vast set of methods it is still not clear which method performs well for which system and concepts for the construction of quantum circuits are in high demand. Current methodologies however often lack simplicity and interpretability. Here we will encounter an interpretable guiding heuristic based on chemical graphs, that enables physical insight into each individual circuit element and allows for efficient construction, optimization, and interpretation of quantum circuits<sup>1-3</sup>.

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# Using the finite element method and numerical tensor methods to solve the Schrödinger equation for the hydrogen atom

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Tensor-product approximation provides a convenient tool for efficient numerical treatment of high dimensional problems that arise, in particular, in electronic structure calculations in  $Rd$ . It has helped to develop the tensor-structured numerical methods that have emerged as a hot topic in mathematical research as well as practical applications. In this work, we investigate solving the time independent non-relativistic Schrödinger Equation for the hydrogen atom. Our study is based on the hydrogen atom because the exact solutions are known and therefore, it is possible to make a comparison of the different numerical schemes used in this work with the exact solution. We formulate and implement the Finite Element Method via a tetrahedral mesh, the full tensor representation and the Tensor Train (TT) decomposition. One major difficulty in using the TT decomposition is the adaptive quadrature used to decompose the Coulomb operator into a canonical form. This is because it contains parameters that need to be optimised to give a good approximation of the Coulomb operator. It will be shown that, in terms of accuracy, computational cost and memory used, the Tensor Train decomposition is the best approach. These results will be used as a good benchmark for further tensor decomposition schemes.

# Polarizable embedding models in quantum and theoretical chemistry

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The accurate computational modeling of molecules embedded in complex (bio)matrices, and of their properties, requires the use of a hybrid quantum/classical description of the system. In this way, the interesting region is described through quantum mechanics (QM), while accounting for the surrounding environment in a computationally affordable way through molecular mechanics (MM)<sup>1</sup> or polarizable continuum models (PCMs)<sup>2</sup>. A possible strategy to further improve the accuracy of QM/MM methods is to endow the classical atoms with isotropic polarizabilities. In this way, the model takes into account genuine N-body interactions and important physical effects (in a similar way to PCMs). This, however, comes at the price of a more complicated theory and a higher computational cost, so it is also important to accelerate both the polarizable QM/MM and QM/PCM algorithms to make the computational cost linear scaling. Finally, both QM/MM and QM/PCM descriptions present strengths and weaknesses. Models of the first kind are particularly suited for the description of specific interactions and anisotropic environments, such as the inner region of proteins. On the other hand, models of the second kind, naturally take into account both long-range electrostatic effects and statistical sampling. So, a natural improvement is trying to capture the strengths from both by developing a multi-layered QM/MM/PCM scheme. In this contribution, we give an overview of state-of-art polarizable embedding models and how they are coupled with QM codes. First, we present how both polarizable MM and PCM models can be described using the same theoretical framework, based on an energy Lagrangian, which can be easily generalized to MM/PCM multi-layered models<sup>3</sup>. This framework can then be used to derive the coupling between a QM part and the embedding in a very general way which does not depend on the model considered. We also present state-of-art QM/MM and QM/PCM embedding models, with the first based on the advanced AMOEBA force field<sup>4</sup>, and the second based on the domain decomposition framework<sup>5-7</sup>. In particular, for continuum solvation models we present the coupling between the domain decomposition X library<sup>8</sup> and Psi4. To conclude, we present a pilot, fully coupled, QM/MM/PCM description and how it was applied to the study of green fluorescent proteins<sup>9</sup>.

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# Analytical high-dimensional operators in Canonical Polyadic Finite Basis Representation (CP-FBR)

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In the field of grid-based nuclear quantum dynamics, the Multi Configuration Time Dependent Hartree Method (MCTDH)<sup>1</sup> plays a prominent role. Indeed, MCTDH is a potentially numerically exact method. The efficiency of the method relies on all the quantities being expressed in a compact sum of products form. The main bottleneck is the potential energy surface (PES), which is often available in a form of a multidimensional function. As such, it needs to be re-expressed as a low-rank tensor format. A number of grid-based methods, which vary in the functional form used (Tucker, ML, CP, ...), are available for such purpose. The recently proposed Monte Carlo Canonical Polyadic Decomposition (MCCPD)<sup>2</sup> has been shown to be especially suitable for refitting high-dimensional surfaces. However, having a functional form which exists only on predefined grid points may pose certain challenges when the definition of the grid needs to be modified. This necessity may arise due to the fact that one does not necessarily know straightforwardly the size of the primitive grid needed to achieve numerically converged quantum dynamics calculations. Furthermore, different initial conditions might call for a different density of the primitive grid. The change of the definition of the primitive grid, in turn, would require the repetition of the refit, which can be computationally expensive for large systems. To address this problem, we introduce a simple means of obtaining an analytical (i.e. grid-free) representation stemming from a guess, non-converged, grid-based CAN-DECOMP/PARAFAC (CP) tensor decomposition. Following the SOP-FBR approach,<sup>3</sup> which yields analytical potential energy surfaces in a Tucker form, we have extended it to the CP format (CP-FBR).<sup>4</sup> The latter provides a more compact representation than Tucker, thus allowing the efficient treatment of higher-dimensional systems. In its current implementation, the workflow consists of: a) tensor decomposition of the potential on a grid much coarser than the one needed for the dynamics using either Python library Tensorly<sup>5</sup> or the MCCPD method<sup>2</sup>; b) fit of the obtained factor matrices (aka single particle potentials) using suitable polynomials (e.g. Chebyshev polynomials). The analytical CP-FBR surface yields results as accurate as MCCPD, with much less number of points, and enables further interpolation to a grid of any density without the need to repeat the decomposition. By construction, a CP-FBR form should be able to deal with any system within reach of MCCPD.

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# Development of Functional 2D Transition Metal Dichalcogenide (2DTMDs) material for energy, electronic and biomedical application

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Transition Metal Dichalcogenides (TMDs) have become an interest among researchers in recent years because of their outstanding electronic, optical, catalytic, and tribological properties. 2DTMDs are two-dimensional (2D) systems which have unique properties, a transition metal (M) atom layer is sandwiched between two chalcogenide atomic (X) layers and it is commonly assumed that the MX<sub>2</sub> slabs are stacked by vdW interactions. It is well known that the layered transition metal Dichalcogenides are strongly depending on the thickness of the materials and the properties are based on the band gap of the materials. It means that the energies of the conduction band minimum (CBM) and valence band maximum (VBM). When increasing the thickness of both CBM and VBM layers, the band gap can be tuned between the expected range, and the material become meaningful in many properties. TiS<sub>2</sub> interlayers staked between sulfides layers, when increasing the inter-layer distance, the binding energy of the system decreases due to the weaker vdW interactions between the layers. In the present project, we improve the structural, interlayer vdW binding interactions, tribological and other properties of TiSe<sub>2</sub>, TiS<sub>2</sub>, and MoS<sub>2</sub>, etc. crystals by increasing the sufficient interlayers. Moreover, the Ti has excellent biocompatibility<sup>1</sup>, but it is not strong enough for some medical applications. Since the Hf belongs to the same group as Ti, it likely possesses excellent biocompatibility. However, there are not many reports on Ti-Hf alloys. In addition to that the Ti is covalently bonded with the Se atom; the TiSe<sub>2</sub> is a 2D structure consisting of one TiSe<sub>2</sub> sheet oriented in the (0 0 1) plane. Ti<sup>4+</sup> is bonded to six equivalent Se<sup>2-</sup> atoms to form an edge-sharing TiSe<sub>6</sub> octahedral. All Ti-Se bond lengths are 2.56 Å. Se<sup>2-</sup> is bonded in a distorted T-shaped geometry to three equivalent Ti<sup>4+</sup> atoms. The layers are stacked together via Van der Waals interactions and can be exfoliated into thin 2D layers. Ti-Se belongs to the group IV transition metal Dichalcogenides. Because of the high sliding contact properties of TMDs, it is used in the manufacture of rolling-contact bearings, seals, gears, cams, tappets, piston rings, electrical brushes, and cutting and forming tools. Based on the above factors these materials can be useful in the field of energy, biomedical, and electronics.

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# Multiresolution Analysis of Frequency-Dependent Polarizabilities: Revealing Basis Set Errors and Convergence Patterns in Quantum Chemistry

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This study presents a comprehensive analysis of basis set errors in polarizabilities, employing a novel multiresolution solver to compute frequency-dependent response properties accurately. By solving the coupled response equations in an adaptive real-space framework, our method enables the calculation of response densities with guaranteed accuracy. Furthermore, with this solver, we can generate reference-quality polarizability data, which is instrumental in evaluating the accuracy of standard basis set calculations. We have investigated the frequency-dependent Hartree-Fock polarizabilities of 89 molecular systems encompassing first and second-row atoms, gauging the basis set error in Dunning-type correlation consistent basis sets. In addition, we varied the valence level, core polarization, and extent of diffuse function augmentation to examine the accuracy and convergence patterns associated with each basis set across the entire dataset. Our research reveals that convergence between first- and second-row systems differs, leading to differing basis set requirements for accurate computation. This research provides a deeper understanding of the basis set errors and underscores the potential of multiresolution analysis techniques to improve the accuracy of predictions in this field.

# A pinch of salt on MRChem: A Poisson-Boltzmann implementation in a Multiwavelet Framework

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Solvent systems are a crucial aspect in chemistry, providing an environment in which reactions and mechanism can occur. Electrolyte solutions, varying from living organisms to battery environments and plasmas, often serve as hosts for significant reactions. In our recent work, we developed a Cavity-free Polarizable Continuum Model (PCM) within the Multiwavelet Electronic Structure software MRChem. To validate its accuracy, we performed a rigorous comparison against the Integral Equation formulation of PCM, a widely accepted and well-tested variant of PCM<sup>1</sup>.

We have now incorporated the Poisson-Boltzmann (PB) equation, enabling the representation of symmetric 1:1 electrolytes in both linearized and non-linearized formulations. This integration brings additional improvements to our model.

This poster showcases the preliminary results obtained from our implementation of the PB equation, offering insights into the stability and convergence of our implementation. These findings contribute to the validation and advancement of our solvent representation model within the Multiwavelet Electronic Structure software, fostering more reliable simulations of chemical systems in diverse solvent environments.

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# Tiled Monte Carlo linear solver for many-body problems.

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For huge linear algebra problems, a Monte Carlo linear solver can be one of the only practical tools. However, the applicability of the Monte Carlo algorithm is highly restricted with only a small class of matrices guaranteed to have a convergent transition probability. We introduce a tiled Monte Carlo linear solver that samples a tile of the matrix instead of individual elements. The tiled algorithm changes the convergence problem into one of computational practicality. We apply the tiled algorithm to problems from chemistry and physics.

# Scalar-relativistic radial Kohn-Sham solver via integral-equation approach

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We present a highly precise numerical tool<sup>1</sup> for solving the Kohn-Sham problem for spherically symmetric atoms. The solver is interfaced with the libxc library, and it supports local and hybrid exchange-correlation functionals including screened and long-range corrected hybrids. The tool employs either the non-relativistic or scalar-relativistic approximation. Relativistic effects are particularly important to account for near nuclei, but this is where they cause numerical issues. *s*-orbitals diverge at the nuclear site, making the Kohn-Sham equation difficult to solve. To overcome this problem, we use a smeared nucleus model, which assumes a Gaussian nuclear charge distribution instead of the commonly used point-like nuclei.

The tool solves the Kohn-Sham problem using the integral-equation approach which allows us to obtain extremely precise total energies. In particular, the obtained Hartree-Fock energies coincide with benchmark values<sup>2</sup> within 14 decimal places. We use the solver as a verification tool for other DFT codes as well as a library for core orbital calculation in the full-potential all-electron code exciting that employs linearized augmented plane waves.

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# Band structures of 2D transition-metal dichalcogenides films from relativistic four-component Dirac--Kohn--Sham theory using all-electron Gaussian-type orbitals

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Two-dimensional (2D) transition-metal dichalcogenides (TMDs) films are currently drawing intense interest from the materials community because they exhibit a wide range of remarkable properties, many of which are driven by strong spin--orbit coupling (SOC) effects that arise from the presence of heavy elements in the most promising TMDs. Using Gaussian-type orbitals (GTOs) for treating electronic structures of the TMDs can open avenues for the application of a range of methods common in quantum chemistry to allow a handle on the interaction of nuclear spins with electrons and accurate modeling of electron correlation effects. However, calculations with full variational account of the SOC in an all-electron setting and moderately large GTO basis sets are nonexistent.

Here, we discuss a methodology for efficient and stable convergence of the electronic band structures of various phases of 2D TMDs using the four-component Dirac-Coulomb Hamiltonian with all-electron triple-zeta GTO basis sets without requiring the removal of any diffuse functions. We investigate large spin-orbit-induced splittings and the quantum spin-Hall effect found in TMDs and compare the corresponding results obtained using plane waves. Work supported by the US Department of Energy and the Research Council of Norway.

# Scalar relativistic effects with Multiwavelets: Implementation and benchmark

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Relativistic methods are steadily gaining momentum in the quantum chemistry community, because their importance for accurate modeling of heavier elements (5th row and below) is nowadays widely recognized. However, relativistic calculations also pose a challenge to traditional basis sets. The core region, where relativistic effects manifest, are difficult to model due to the nuclear cusp. Multiwavelets overcome this challenge, due to a foundation in multiresolution analysis that leads to robust error control and adaptive algorithms that automatically refine the basis set description until the desired precision is reached. In this work we present a ZORA implementation in the multiwavelet code MRChem, and we provide a small benchmark of total energies for the 5th row elements.

# The Contributions of Diffuse Atomic Orbitals in Correlated Calculations

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Accurate treatment of electron correlation energies in molecules requires basis set extrapolation or explicitly correlated wavefunctions to address electron cusps in the wavefunction<sup>1</sup>. Practical, robust F12 methods require the use of basis sets including diffuse AOs, even for neutral species<sup>2</sup>. However, the inclusion of these diffuse AOs hinders the applicability of such methods to large molecular systems due to poor numerical conditioning. Here, we explore the contributions of these diffuse AOs in CCSD and CCSD-F12 calculations in order to understand why they are necessary. We implement a dual-basis formulation of the CCSD and CCSD-F12 methods<sup>3</sup> in which the occupied and virtual orbitals are expanded in different AO basis sets. We conclude that diffuse AOs are in fact quite important in conventional (non-F12) CCSD calculations, and their apparently greater importance in CCSD-F12 calculations are due to the substantial reduction of basis set incompleteness error such that the absence of diffuse AOs in the orbital basis produces errors comparable to the residual basis set error. We suggest that dual-basis CC-F12 calculations are a promising candidate for accurate F12 reduced-scaling many-body electronic structure treatment of molecules.

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# PyOpenRSP, the CEO of analytic response properties

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We present here an open-ended response theory program, PyOpenRSP. It enables the analytic calculation of high-order molecular properties at the Hartree-Fock and DFT levels and thus can be used to calculate properties for advanced spectroscopic simulation.

Being a new Python implementation of the OpenRSP methodology<sup>1-3</sup>, PyOpenRSP offers an easy way to interface with modern electronic structure codes for the necessary contributions which PyOpenRSP, the CEO, will assemble into the properties. Here, we demonstrate it with interface callbacks to the VeloxChem program<sup>4</sup> and with calculations of selected molecular properties.

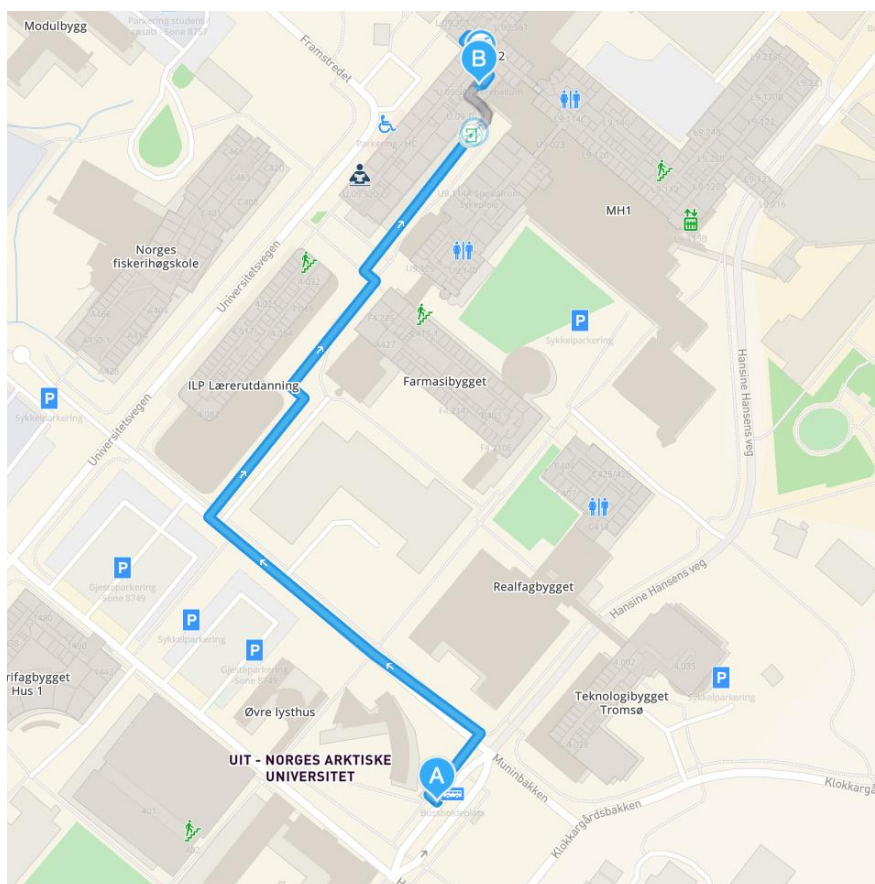
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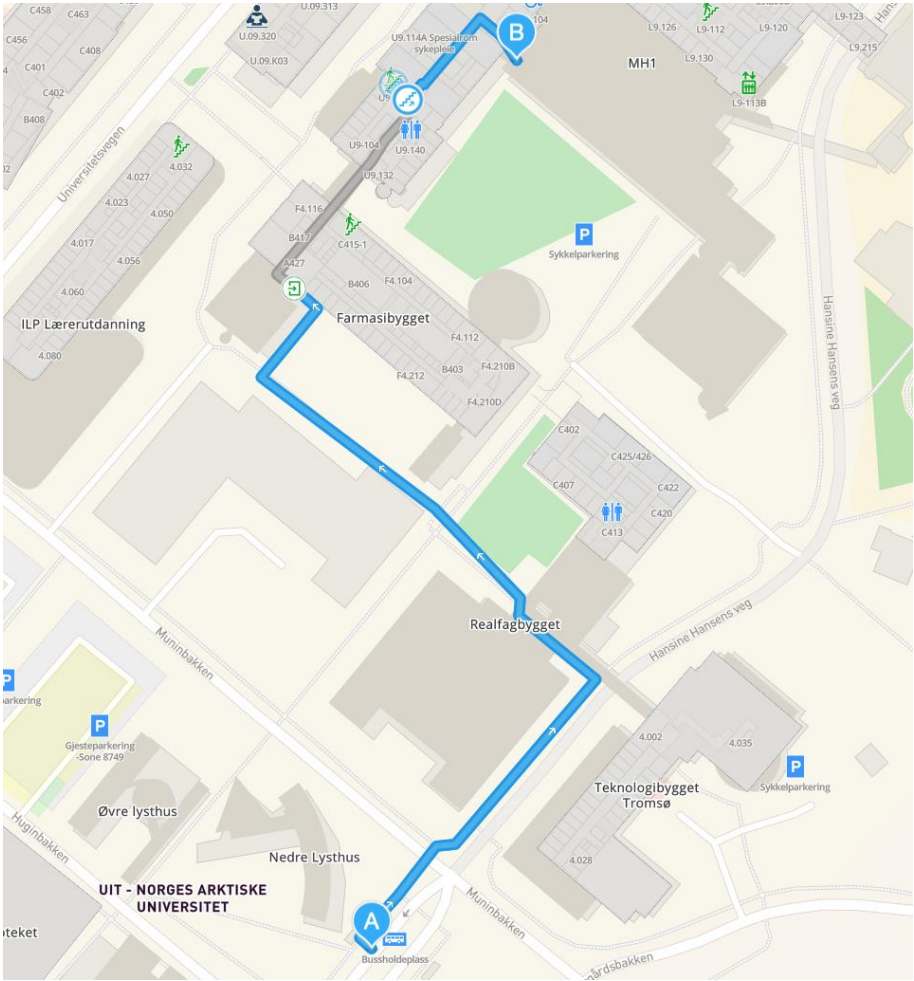


# Maps

Monday all day. While the other days only till 15.00



## Tuesday-Poster Session



### Wednesday and Thursday tutorials in the afternoon

