

BOOK OF ABSTRACTS



Numerical Methods in Quantum Chemistry 2025

18-20 June 2025

Berlin



Funded by
The Research
Council of Norway



Hidden Sources of Error in Numerical Electronic Structure Calculations

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Numerical electronic structure calculations are frequently considered as some sort of *best-possible* solution to the problem of electronic structure in atoms, molecules and periodic systems (polymer chains, slabs, crystals). In this context, it must not be forgotten that any numerical mathematical method has some method-dependent intrinsic error(s), which affect(s) any calculated result(s) to some extent. Errors (or uncertainties) in calculated results, caused by errors of the numerical approach, may go unnoticed. But intrinsic numerical errors, if unrecognized, may also even cause failure in getting or finding a desired result, e. g. failure of convergence in self-consistent field (SCF) iterations. For illustration, several case studies will be shown.

The multichannel Dyson equation: coupling many-body Green's functions

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I will present the multichannel Dyson equation that combines two or more many-body Green's functions to describe the electronic structure of materials. I will show how the coupling of the one-body Green's function with the three-body Green's function can be used to model photoemission spectra [1,2]. I will demonstrate that, unlike methods using only the one-body Green's function, our approach puts the description of quasiparticles and satellites on equal footing.

Moreover, we propose a multichannel self-energy that is static and only contains the bare Coulomb interaction, making frequency convolutions and self-consistency unnecessary. Despite its simplicity, I will show that important many-body effects, such as screening are included in our approach. I will also present a numerical framework based on an effective Hamiltonian that can be solved for any many-body system using standard numerical tools. Our approach yields exact results for the Hubbard dimer [1].

Similary, the two-body Green's function can be coupled to the four-body Green's function to simulate absorption spectra. I will show how our approach can correctly describe double excitations [3].

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Full minimal coupling Maxwell-TDDFT for ab initio beyond-dipole spectroscopy

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We present an ab initio, nonrelativistic quantum electrodynamics (QED) framework for simulating light-matter interactions beyond the electric dipole approximation, avoiding multipolar truncations [1]. This method extends the Maxwell-Pauli-Kohn-Sham approach to a full minimal coupling Hamiltonian, enabling a self-consistent treatment of the time- and space-dependent electromagnetic vector potential coupled to the quantum matter system. The electromagnetic back reaction is included via the full electronic current density, allowing for accurate modeling of radiation effects. Implemented in the open-source Octopus code [2], the framework supports large-scale, multiscale simulations using real-space grids for the electromagnetic and matter subsystems. We demonstrate its capabilities through applications to spectroscopic phenomena, including magneto-optical responses in non-chiral molecules, frequency shifts due to radiation reaction, and nonlinear spectra under twisted light carrying orbital angular momentum [3]. This approach provides a predictive, first-principles tool for exploring and interpreting complex spectroscopic signatures in molecular and nanoscale systems, especially under structured or strong light fields.

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The Basis Set Truncation Error Revisited: Comparison of Multi-wavelet and Gaussian Basis Sets for Computing Properties from First Principles

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A set of 225 molecules and 5726 reactions are used to examine errors present in linear-combination of atomic orbital (LCAO) calculations using standard atom-centered Gaussian basis sets at the Hartree-Fock and density functional theory levels of theory. We advance beyond previous studies by extending the test set to include heavier atoms, by probing the origin and nature of errors in LCAO calculations including transferability of basis sets between HF and different DFT functionals, by reporting computational times for the multiwavelet calculations and by examining errors in reaction energies, where errors are computed by comparing LCAO results to numerically converged solutions in the MW basis. Calculations in uncontracted basis sets quantify the different errors arising from contraction and incompleteness in the primitive Gaussian basis. Analysis indicates significantly larger errors associated with atoms in the third or lower rows of the periodic table.

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Meta Generalized Gradient Approximation Made Magnetic

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The Jacob's ladder of density functional theory (DFT) proposes the compelling view that by extending the form of successful approximations—being guided by exact conditions and selected (least empirical) norms—upper rungs will do better than the lower, thus allowing to balance accuracy and computational effort. Meta-generalized gradient approximations (MGGAs) belong to the last rung of the semilocal approximations before hybridization with nonlocal wave function theories. Among the MGGAs, the strongly constrained and appropriately normed approximation (SCAN) greatly improves upon GGAs from the lower rung [1]. But the over magnetized solutions of SCAN make GGAs more reliable for magnetism [2]. Here [3], we provide a solution that satisfies the most pressing desiderata for a density functional approximations for ferromagnetic, antiferromagnetic and noncollinear states. The approach is available in an implementation in the crystal electronic structure package [4].

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MULTI-CONFIGURATIONAL OPTIMIZATION FOR TWO-ELECTRON SYSTEMS

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The multiconfiguration self-consistent-field (MCSCF) method is revisited with the specific focus on the two electron systems for simplicity. A wave function is represented as a linear combination of Slater determinants. Both orbitals and coefficients of this configuration interaction expansion are optimized following the variational principle making use of the Newton optimization technique. It reduces the MCSCF problem to solving a particular differential Newton system, which can be discretized with multiwavelets and solved iteratively.

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Exploring the phase diagram of α -Sn using self-consistent GW

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We present a comprehensive investigation of semi-metallic and topological phases in α -Sn using *ab initio* relativistic self-consistent GW (scGW) theory, through the lens of numerical method development. Conventional density functional theory (DFT) predictions vary widely, from negative band-gap semimetals to zero-gap semiconductors, and fail to capture the strong dependence of topological properties on lattice distortions observed in experiments. By incorporating a high-level description of electron correlation through scGW, along with relativistic effects using exact two-component theory, we systematically study the electronic structure of α -Sn. Furthermore, using the newest numerical advances in handling analytical continuation, we present a novel analysis of the zeros of the ab-initio Green's function to characterize topological properties, with which we identify the emergence of a topologically insulating phase. We further determine a Dirac semimetal phase under anisotropic lattice strain by studying the band structure. Additionally, we find that the GW bands exhibit a visible temperature dependence, underpinning the high sensitivity of α -Sn's electronic structure—an effect not captured by ground-state theories. These findings provide critical insights into the interplay of correlation, relativistic effects, and structural deformations in the topological properties of a-Sn as well as into the development of numerical methods necessary to describe topological materials.

Fast and scalable real-space methods for ground-state and time-dependent density functional theory using finite-element discretization

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This talk will present our recent advances towards the development of computational methods and numerical algorithms for conducting fast and accurate large-scale DFT [1,2] and TDDFT calculations [3,4] using adaptive higher-order finite-element discretization, which form the basis for or leverage the open-source code DFT-FE (<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. A few application problems tackled using DFT-FE will be presented.

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State-Specific Optimization for Strongly Correlated Electronic Excited States

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Molecular excited states of photochemical processes often involve wave function characteristics that go beyond the simplifying assumptions of mean field and single-reference theories, such as the appropriate treatment of strong electron correlation and orbital relaxations. We discuss a fully excited-state-specific approach to CASSCF where, similar to ground state theories that shape the wave function to minimize the energy, our methodology seeks to minimize an objective function whose minima are exact excited states. Despite the additional numerical difficulties of optimizing a more involved objective function, using a property-guided generalized variational principle (GVP) built around the square energy gradient norm reliably provides state-specific orbital descriptions and robust convergence in the face of challenges such as root flipping and avoided crossings that often cause traditional formulations to fail [1,2]. Extending these state-targeting strategies to much larger systems where high-level methods become intractable, we explore their application in quantum embedding methods. Bootstrap wave function-in-wave function embedding (BE) with overlapping fragments has been shown to reliably recover the ground state electron correlation energy at a fraction of the computational cost [3]. Applying an excited state fragment solver and exploring GVP-style state-targeting, we look toward reconstructing excited-state-specific energetics using the BE framework to access larger and often more realistically sized photochemical models.

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Coherent Potential Approximation with Bloch Gaussian Orbitals: Probing the Interplay of Disorder and Electronic Correlation

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Doping and disorder have become powerful tools for manipulating material properties, such as in semiconductors, as well as for inducing emergent behavior beyond the sum of its constituent effects, e.g., in high-entropy alloys. Simulating the electronic structure of disordered systems typically demands large supercells, which is computationally expensive. The coherent potential approximation (CPA) offers an efficient alternative by introducing an effective medium that averages the effect of a disordered environment around a given atomic site. Existing *ab initio* CPA methods are largely constrained by the atomic sphere and single-site approximations, which express the nonlinear exchange-correlation potential as a sum of site-specific contributions. These approximations often oversimplify electronic interactions, limiting CPA's applicability beyond mean-field theories. Here, we present a novel implementation of CPA within first-principles density functional theory to study disorder effects in extended materials. By leveraging a modified approach based on Bloch Gaussian orbitals, we systematically improve the treatment of electron correlation. Our implementation represents a significant theoretical advancement, broadening the applicability of CPA to disorder-driven material design.

Hyperpolarizabilities at the Basis Set Limit using MADNESS

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Multiresolution analysis (MRA) using a multiwavelet basis has proven effective for computing reference-quality molecular energies and properties at the basis set limit [1], [2]. This work features a newly developed molecular response solver in MADNESS [3] for the computation of higher-order frequency-dependent Hartree-Fock and DFT response properties. First, we present results for HF hyperpolarizabilities, evaluating basis set errors in Dunning correlation-consistent basis sets across various small atoms and molecules. We follow by examining basis set errors in a set of push-pull π -conjugated α, ω -nitroaminopolyenes of increasing length.

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Iterative subspace solvers in relativistic linear response TDDFT

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Linear response TDDFT can be formulated in two ways: i) as a system of equations $\mathbf{Ax} = \mathbf{b}$, where matrix \mathbf{A} characterizes the molecular system, vector \mathbf{b} represents the interaction with an external field, and the unknown vector \mathbf{x} describes the system's response; or ii) as a generalized eigenvalue problem $\mathbf{Ax}_n = \omega_n \mathbf{Sx}_n$, where the eigenvalue ω_n is the n -th excitation energy of the molecular system, \mathbf{S} is a metric, and the eigenvector \mathbf{x}_n describes the transition density of the excited state. In both formulations, the matrix \mathbf{A} can be large enough that direct inversion or elimination methods become impractical for many systems of chemical interest. Instead, the equations must be solved iteratively. This is typically achieved using subspace projection-based solvers, where the solution vector is approximated as a linear combination of so-called trial vectors that are generated in the course of the iterations. We present iterative subspace solvers for *relativistic* linear response TDDFT applicable to both formulations [1,2] and to both closed- and open-shell systems, as implemented in the relativistic spectroscopy program ReSpect. [3,4] These solvers divide the equations by hermicity and time reversal symmetry, and use tailored trial vectors to ensure robust convergence. In addition, we will also present how such a solver can be adapted for the case when the molecular system is strongly coupled to photon modes of an optical cavity. [5]

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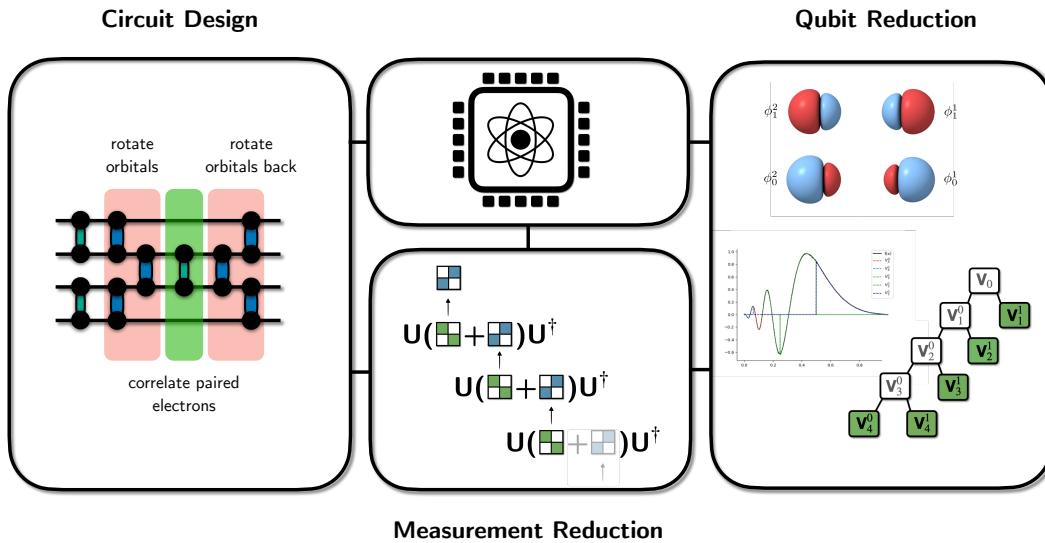
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Bridging Quantum and Classical Algorithmics

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One of the key applications of quantum computation remains the simulation of nature itself. An important domain is the electronic structure problem from quantum chemistry, which aims to compute electronic eigenstates and their associated properties. Finding an electronic ground state is already considered an intractable task, and efficient (classical and quantum) algorithms for general instances of the problems are not expected to exist. Heuristics are, therefore, essential for the development of applicable computational methods. Moreover, the successful computation of molecular properties requires multiple computations, starting from the discretization of the original problem and ending with the evaluation of expectation values on determined approximations of the discretized eigenstates. To progress to scalable and applicable approaches, three major algorithmic problems need to be addressed: Circuit design, qubit reduction and measurement reduction.



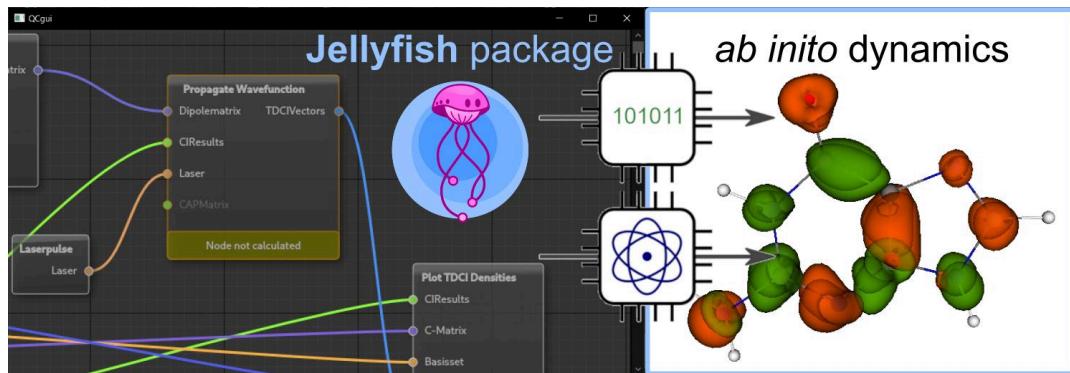
Accurate solutions to the electronic structure problem require holistic approaches that consider all of these individual aspects. I will highlight some recent efforts from the quantum algorithmics group to tackle these challenges.

Jellyfish: Ab Initio Electron Dynamics by Traditional and Quantum Algorithms

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Light-induced dynamics in many-electron systems is notoriously difficult to comprehend. In this endeavor, the illustration of electron-hole pair formation in the time domain provides mechanistic insights into such ultrafast processes.^[1,2] With Jellyfish, a novel analysis toolbox is presented that enables the entire workflow of an electron dynamics simulation and its analysis, to be carried out in a single package.^[3,4]



This program package not only allows the simulation of correlated electron dynamics driven by light, but also the visualization of the resulting time-dependent wavefunction. Various analysis tools are implemented to monitor the electronic processes on their natural atto- and femtosecond timescale. This tool box is used by chemistry students in lectures and theses as it comes with an intuitive graphical user interface (GUI). Is published under Open-Source license and its developer-friendly plugin system facilitates the expansion without requiring in-depth knowledge of the program.

Besides the classical wave packet propagations, Jellyfish also has the capability to compute the dynamics through quantum algorithms.^[5] By using the Jordan-Wigner transformation for wave functions, the Trotter product formula for expressing the propagator, or the Hadamard test to compute the time-dependent expectation values, quantum algorithms can be simulated and developed within the Jellyfish package.

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Moreau–Yosida Kohn–Sham inversion

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Kohn–Sham density-functional theory calculations aim at obtaining the ground-state particle density of a system by employing an approximate exchange-correlation functional. A successful output can then be both an approximate ground-state density and an approximate exchange-correlation potential. The inverse Kohn–Sham approach determines the exchange-correlation potential from an “exact” ground-state density, which does not need the involvement of an approximate exchange-correlation functional. Accurate determination of potentials from the inverse Kohn–Sham method can be used as constraints for approximate functionals. Moreau–Yosida regularisation offers a strict mathematical framework to obtain the exchange-correlation potential using the proximal point of a ground-state density. The proximal point is determined through a minimisation involving just a “Kohn–Sham” non-interacting functional. This talk will give an overview of Moreau–Yosida Kohn–Sham inversion including numerical aspects.

The advent of fully variational quantum eigensolvers using a hybrid multiresolution approach

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Quantum computers have the potential to revolutionize quantum chemistry by providing accurate electronic structure calculations for complex molecules. However, existing quantum algorithms often rely on rigid basis sets and struggle with scalability. In this work, we present a fully variational quantum eigensolver (VQE) approach that dynamically optimizes both the quantum circuit and the underlying electronic orbital representation using a multiresolution wavelet framework. This approach enables higher accuracy and adaptability compared to standard fixed-basis methods.

To demonstrate the power of our method, we applied it to molecules ranging from small test cases (H_2 , LiH , BeH_2)[1] to larger systems, including benzene with an active space of 30 electrons in 30 spatial orbitals. For benzene, our method significantly outperforms similarly large standard basis sets, highlighting its potential for complex molecular simulations. In addition, at Algorithmiq we are developing a fermionic quantum simulator that surpasses alternative simulators such as matrix product state (MPS) simulators in efficiency and allows circuit optimizations and expectation value estimations beyond 50 qubits. This capability is crucial for optimizing classically quantum circuits for ensuing experiments on real quantum hardware at utility scale and beyond.

Together with a proprietary post-processing technique, we present an end-to-end procedure - from defining a molecular structure to computing its corrected ground-state energy using real quantum hardware. This marks a significant step toward practical, hardware-compatible quantum chemistry simulations.

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Variational Gaussian wave packets and magnetic Schrödinger dynamics

Caroline Lasser

The talk considers the time-dependent magnetic Schrödinger equation, which describes the dynamics of charged particles under the influence of an electromagnetic field. We analyse the accuracy of Gaussian wave packet approximation obtained via the time-dependent Dirac-Frenkel variational principle, emphasizing observable accuracy. We address the numerical time integration of the equations of motion by an extension of the classical Boris algorithm. This is joint work with M. Hochbruck, M. Scheifinger and K. Busch.

Real-time TDDFT as a versatile tool to simulate spectroscopic (linear) response

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April 30, 2025

Since almost 30 years [1] RT-TDDFT has been used as a technique to simulate response properties of molecular systems. It complements the most common perturbation theory based approaches to (linear) response by working well for high density of states, showing a favorable scaling and ease of implementation, as well as being inherently non-perturbative allowing to apply the electro-magnetic perturbation explicitly.

In this contribution these advantages of integrating the time-dependent Kohn-Sham equations in the time domain are highlighted with special emphasis on the choice of gauge in practical calculations allowing to move to larger and periodic simulation cells. The choice of gauge becomes especially important for periodic simulations cells, if pseudo potentials are used to describe the core electrons or if magnetic response properties are of concern. In these cases certain choices of gauge perform better than others, in particular the velocity gauge is required for periodic simulation cells. To illustrate this, applications are shown for electronic response such as UV-VIS [2] and electric circular dichroism (ECD)[3, 4] spectra. Additionally, mixed electronic and vibrational degrees of freedom are considered in the Born–Oppenheimer approximation for non-resonance and resonance Raman[2, 5] and Raman optical activity spectra [6].

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Development of relativistic damped response TDDFT solvers for predicting X-ray absorption spectra of open-shell systems

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The damped response time-dependent DFT method (DR-TDDFT), or also known as the complex polarization propagator approach is a perturbational method used as an alternative to standard eigenvalue TDDFT. The method provides better applicability in systems with high density of states or in high-frequency domains. The size of the systems commonly computed are too large for direct calculations to be viable, which only leaves iterative approaches as a practical solution. The present iterative subspace solver considers hermiticity and time reversal symmetry [1,2], and is applicable only to closed-shell singlet configuration systems. Methods for treatment of open-shell systems require the separation of time-symmetric general terms into symmetric and antisymmetric parts, which provides a new layer of complexity. The goal of this project is to extend the scope of the DR-TDDFT methodology by developing the formalism that allows the inclusion of open-shell systems, include it in the ReSpect software package, and assess the performance by comparing the results with experimental data.

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Enhanced Krylov methods for molecular Hamiltonians via tensor hypercontraction

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Tensor network methods, particularly the matrix product state (MPS) representation of an electronic wave function, are a powerful computational tool to simulate strongly correlated chemical systems. In this talk, we show how a molecular Hamiltonian's tensor hypercontraction (THC) representation can be used for a highly parallel and memory-efficient application to an MPS. In detail, the THC form leads to a sum of products of simple matrix product operators, which can be applied to an MPS and summed up in parallel with interleaved compression steps. The methodology is useful as a matrix-vector multiplication step in Krylov methods. As application examples, we compute eigenstates and simulate the time dynamics for the water molecule, hydrogen chains, and ammonia. We supplement this framework by devising an improved Lanczos algorithm using restarts with multiple states to find several low-lying eigenstates with high accuracy. Based on [arXiv:2409.12708](#) and [arXiv:2504.21786](#).

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Efficient Computation of Electron Repulsion Integrals on the Novel AI Engine Architecture

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The evaluation of four-center electron repulsion integrals (ERIs) using Gaussian-type orbitals as basis functions is a fundamental building block of quantum chemistry codes using hybrid exchange-correlation functionals [1-3]. Accordingly, many algorithms have been developed to reduce the computational complexity of the ERI computation [4-6], resulting in several software libraries that implement these algorithms on modern hardware [7-9]. However, the current software libraries only target CPU and GPU platforms, while in the current *new golden age of computer architecture* [10], many novel computing devices are available. These devices often provide high computational throughput at low power consumption, and while most are marketed for AI workloads, their architecture is often more general. AMD's AI Engines (AIEs) [11] are one such example, and in our poster we will present our implementation of the Rys quadrature algorithm [4] for computing ERIs on them.

Our implementation can compute ERIs up to angular momentum $L = 5$, i.e. quartet classes $(ss|ss) - (hh|hh)$, for which we had to implement a flexible design using 1-12 AIEs depending on the size of the quartet class. Furthermore, we developed a novel vectorization scheme specific to the AIE architecture, but with concepts that may be transferable to CPU implementations. Finally, we show that our implementation is more energy efficient than CPU [7,9] and GPU [8] implementations and is competitive in terms of performance. Here, the high energy efficiency is of particular interest to research efforts such as *GreenHPC* [12], which aims to reduce the environmental footprint of high performance computing.

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Adaptive control of numerical error in all-electron simulation of periodic solids

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The dominant numerical representations for the electronic structure simulation of periodic solids, namely, plane waves augmented with pseudopotentials and the atomic orbitals, are inadequate for confident control of numerical error, especially for all-electron simulation. To address their shortcomings we extended the adaptive multiwavelet numerical technology to the treatment of periodic solids using the mean-field methods (Hartree–Fock and semilocal and generalized Kohn-Sham density functional theory). To address the unphysical periodicity of reduced density matrices due to the finite quadrature over the first Brillouin zone it is mandatory to use a modified Poisson kernel that smoothly restricts its range in a manner similar to the approach used for the optimal plane-wave evaluation of the exact exchange operator.¹ The use of the modified kernel yields the exponential convergence to the thermodynamic limit for mean-field models of non-metals while enjoying the optimal rate of convergence of the numerical error; this approach also eliminates the well-known divergence of the exact exchange energy.² The current implementation is Γ -point only, but the efficiency will be soon improved further by explicit utilization of translational (k -point) symmetry. The periodic extension of the MW technology has been incorporated into the universal correlated orbital solver,³ positioning it for the use with correlated electronic structure simulation of periodic solids.

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Optimal Real-Space Orbitals for Relativistic Multiconfiguration Electronic Structure

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Atomic orbital representations, dominant in molecular electronic structure, are increasingly ill-conditioned and incompatible with fast algorithms when pushed to higher-precision computation. In heavy element applications, these challenges are further exacerbated by the increased dynamical range introduced by primitive bases and the possibility of variational collapse. Adaptive multiwavelet (MW) representations offer a compelling alternative that allow fast convergence to the numerical 1-particle limit for mean-field models, inherently bypassing many of the weaknesses of the atomic orbital representations. By building on the initial demonstrations of the Dirac-Coulomb mean-field MW approach [1] and the MW multiconfiguration orbital solver [2], we will demonstrate the first Dirac-Coulomb multiconfiguration MW solver applicable to general molecules. Among notable features of the solver is the lack of the explicit treatment of negative energy states, thereby avoiding concomitant issues such as the Brown-Ravenhall disease and the need for kinetic balance. Initial benchmarks against the state-of-the-art atomic solver (GRASP) and the Gaussian AO molecular solvers will be presented.

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Real-Time Methods for Attosecond Spectroscopies – Chirality and Relativistic Effects

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We present advancements in real-time time-dependent density functional theory (RT-TDDFT) for simulating attosecond electron dynamics, emphasizing the role of relativistic effects and electronic chirality. [1-3] In order to characterize the physical mechanism underlying the ultrafast process, we investigate charge and current density migration triggered by the external laser field.

We demonstrate the need of a relativistic treatment through simulations of L-edge X-ray transient absorption spectroscopy, where both scalar and spin-orbit coupling plays a crucial role. To balance accuracy and computational efficiency, we employ the modern atomic mean-field exact two-component Hamiltonian, making our approach viable for large-scale applications. [2,4]

Furthermore, we introduce a novel physical mechanism that enables inducing electronic chirality in oriented achiral molecules by a circularly polarized laser pulse. This chiral character is due to the underlying chiral induced current density, which oscillates in time with frequencies corresponding to the higher order harmonics of the laser pulse. The chiral wavepacket is long-lived and can be probed experimentally via transient absorption circular-dichroism.

To deepen our understand of non-equilibrium dynamics induced by a pump pulse, we derive a generalized form of non-equilibrium response function for transient absorption and circular dichroism spectroscopies. [2,3]

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Wavefunction optimization at the complete basis set limit with Mutliwavelets and DMRG

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The density matrix renormalization group (DMRG) is a powerful numerical technique to solve strongly correlated quantum systems [1]: it deals well with systems which are not dominated by a single configuration (unlike coupled cluster (CC)) and it converges rapidly to the full configuration interaction (FCI) limit (unlike truncated configuration interaction (CI) expansions). In this work, we develop an algorithm integrating DMRG within the multiwavelet-based multiresolution analysis (MRA) [2]. Unlike fixed basis sets, multiwavelets offer an adaptive and hierarchical representation of functions, approaching the complete basis set limit to a specified precision. As a result, this combined technique leverages the multireference capability of DMRG and the complete basis set limit of MRA and multiwavelets. More specifically, we adopt a pre-existing Lagrangian optimization algorithm for orbitals represented in the MRA domain [3] and improve its computational efficiency by replacing the original CI calculations with DMRG [4]. Additionally, we substitute the reduced density matrices computation with the direct extraction of energy gradients from the DMRG tensors. We apply our method to small systems such H₂, He, HeH₂, BeH₂ and N₂. The results demonstrate that our approach reduces the final energy while keeping the number of orbitals low compared to FCI calculations on an atomic orbital basis set.

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Helium-like ions: the Lagrange Mesh approach

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In this talk, the problem of the two-electron sequence of the helium atomic type ($Z; e, e$) is studied by using the Lagrange Mesh Method (LMM). The method (LMM), which allows to reach 13-14 figures in energies for any Z for low-lying states, is a procedure for solving the Schrödinger equation by placing it into a non-uniform lattice defined by zeroes of classical orthogonal polynomials and using a basis of Lagrange functions, and the associated Gauss quadratures. The obtained energies are smooth functions of Z that can be easily interpolated by a simple, but non-trivial function. In addition, the first three significant digits of the sum of (known) mass, relativistic, QED corrections to the ground state energies are easily described by a 4th order polynomial in Z across the sequence.

If time permits the Born-Oppenheimer rovibrational spectrum of diatomic molecules in LMM will be mentioned by taking CS as an example.

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Fixing issues with numerical inaccuracy of DFT derivatives with multiwavelets

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Density Functional Theory (DFT) has become a cornerstone in quantum chemistry and materials science for computing electronic structure properties, due to its efficient cost per accuracy. The main challenge with DFT is the approximation of the exchange-correlation energy. In contrast to wave function based methods, DFT requires a numerical integration of the exchange-correlation term, which introduces an error. This error is not very big when considering the total energy of a system, however, it has shown to be significant for properties depending on the energy derivatives [1], such as vibration frequencies, polarizability and dipole moments, to name a few. When using Gaussian type basis functions, Sitkiewicz et al. [1] has suggested that increasing the integration grid, can help reduce this error to some extent, but that it still poses as a general issue with modern DFT methods.

MRChem [2] is a multiresolution quantum chemistry software, utilizing multiwavelets as the basis representation. As the potentials are functions of the density in real space, they are calculated numerically on an adaptive grid, resulting in a trivial solution to the numerical integration of the exchange-correlation term. As the grid alters depending on the wanted accuracy of the calculation, using multiwavelets methods to calculate energy derivative dependent properties, should result in less spurious errors. This work explores the numerical errors associated with higher order derivatives of molecular potential energy surfaces using multiwavelets.

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Electronic Transitions in Isolated Molecules and Supramolecular Aggregates

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Electronic transitions in molecular systems can proceed either radiatively — through the absorption or emission of light — or non-radiatively, upon the breakdown of the Born-Oppenheimer approximation, which enables energy transfer between electronic and nuclear motion.

In my presentation I will describe the mixed quantum-classical approach to the simulation and assignment of static electronic spectra of isolated molecules. [1] Further, I will present the framework for simulation of ultrafast non-adiabatic dynamics following an electronic excitation, as well as of corresponding ultrafast pump-probe signals, such as time-resolved photoelectron spectra. [2,3]

Finally, I will present the excitonic configuration interaction (ECI) method [4,5] — an exciton-like framework for efficient calculations of the dense spectra of extended multichromophoric systems, such as supramolecular aggregates. I will also discuss prospects for extending ECI to the simulation of ultrafast energy-transfer processes in multichromophoric systems, such as Förster resonance energy transfer, Dexter energy transfer, singlet fission, and charge transfer.

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Two-Component relativistic methods in multiwavelets, approximate and numerically exact

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We present a prototype implementation of the two-component ZORA method to solve the Dirac-Hartree-Fock equation using multiwavelets as basis set, serving as a first step for spinorial methods in multiwavelet bases. Furthermore, we also present a method to obtain the exact decoupling operator, up to desired precision when projected onto multiwavelets. This latter method shows attractive properties for , such as energy gauge invariance, with minimal overhead compared to the ZORA method for self-consistent solvers.

In both methods, the Hamiltonian can be cast in the form

$$H = V + (\sigma \cdot p)\kappa(\sigma \cdot p), \quad (1)$$

where κ is an operator only dependent on the potential.

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Simulating X-ray Photoelectron Spectroscopy using Multiwavelets

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Core level X-ray photoelectron spectroscopy (XPS) is a widely used technique for characterising molecules and materials. However, its interpretation typically relies on comparison to reference spectra, which is challenging, if not impossible, in the case of large molecules or complex solids containing many different local chemical environments. The computation of core binding energies (BEs) is therefore invaluable for interpreting core XPS. One approach, based on density functional theory (DFT), which has shown great promise for core BE calculations is DeltaSCF. However, its use in Gaussian basis codes is complicated by the need to use either very large or specifically constructed basis sets which are adapted for core-excited calculations. At the same time, such codes may also suffer from problems such as core-hole hopping, which can lead to poor convergence or inaccurate results. In this talk we will describe how an adaptive multi-wavelet basis can be used to overcome these problems, by either combining all electron and pseudopotential-based approaches, or by using the (initial) maximum overlap method. We will show how these approaches prove to be robust even for large molecules, offering new opportunities for interpreting core XPS of large molecules.

Excited State Properties using Equation Of Motion Coupled-Cluster Theory: Implementation using ORCA equation and code generator

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The implementation of EOM-CCSD (Equation of Motion Couple-Cluster Singles and Doubles) method [1] using the ORCA-AGE (ORCA-Automated Generator Environment) tool set [4,5] is being explored. Using the mentioned ORCA equation and code generator, the implementation of EOMCCSD analytic gradients of excited state energy [2,3] and transition moments between ground state and excited states[1,3] are being presented as well.

Within the ORCA-AGE framework, the equations are derived using commutator technique for second-quantized operators and the equations are further optimized by introduction of various types of intermediates. And finally, the code corresponding to those optimized equations are generated with computational efficiency in mind. Thus, the final generated code can be as efficient as hand-written code. The above-mentioned implementations are applied to polyene chain and the generated code's performance is being analysed.

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Molecular Dynamics with Hybrid Functionals on Materials: Theory and Numerics

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In the framework of Density Functional Theory (DFT), semilocal density functionals approximations can often be insufficient to achieve a good description of the electronic properties associated to the potential energy surface. This problem can be partially mitigated by introducing hybrid density functionals, which incorporates a fraction of nonlocal exact exchange, but at the expense of a higher computational cost. Among the quantum-mechanical ab initio programs for the simulation of condensed matter systems, the CRYSTAL code has been heralded for its high efficiency in evaluating the exact exchange series,[1] thanks to the use of atom-centered basis functions within a linear combination of atomic orbitals to describe the crystalline wavefunction. The corresponding efficiency of the code has driven to the implementation of a rich variety of hybrid density functional approximations at a low computational cost, thus allowing to study electronic, magnetic, mechanical, spintronic and lattice-dynamical properties of materials using hybrid functionals.[1] In this work, the capabilities of the CRYSTAL code have been extended to include a computational package for the study of structural and electronic properties at a finite temperature, based on the Born-Oppenheimer ab initio molecular dynamics (AIMD) technique applied to the microcanonical and canonical ensembles,[2,3,4] as well as for the calculation and the characterization of transition states, using the Nudged Elastic Band (NEB) method.[5] Moreover, the possibility to perform structural optimizations based on AIMD concepts, using the Fast Inertial Relaxation Engine scheme,[6] has been introduced,[7] paving the way to the possibility of analyzing equilibrium crystalline structures at finite temperature. A full and detailed description of the theoretical methodologies and of the algorithmic implementations, followed by a critical evaluation of the accuracy and performance of this approach on multiprocessor architectures, will be given. Taking the periodic liquid water (H_2O)₃₂ and different phases of solid nitrogen as reference systems, the post-processing analysis of the AIMD trajectories leads to a detailed characterization of the structural and dynamical properties of these systems at different temperatures, which is capable of giving insights and shedding lights on their atomic scale features, that have been debated for a long time in literature.[8,9]

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Tensor-Decomposed Iterative Distinguishable Cluster Triples

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Obtaining high-accuracy data for extended molecular systems is one of the big challenges in quantum chemistry. We present a technique that allows one to reach a very high methodological level - distinguishable cluster with singles, doubles and iterative triples [1] - at a substantially reduced computational cost. This is achieved by tensor decomposing the triples amplitudes [2]. We refer to this method as SVD-DC-CCSDT [3].

The tensor decomposition leads to a drastic compression of the amplitude space and reduction of both the scaling and prefactor without compromising the accuracy. The reaction energies calculated with the presented technique are on average within around 0.1 kcal/mol from the CCSDT(Q) results and converge quickly with respect to the decomposition tightness.

Furthermore, the new method is applied to non covalent interactions included in the A24 dataset [4], for which SVD-DC-CCSDT outperforms CCSD(T) when benchmarked to CCSDT(Q), demonstrating the importance of full iterative triples.[5]

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Ab initio quantum electrodynamics: from microscopic details to thermodynamics

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In this talk I will highlight how the microscopic details of an ab-initio quantum-electrodynamical description of matter [1] can lead to changes in the thermodynamics. To elucidate this connection I will use different representative models from polaritonic chemistry and cavity materials engineering.

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First-Principles Electron Dynamics Simulations of Attosecond Phenomena in Solids

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Recent advancements in optical science and technology have enabled the observation of electron dynamics in solids with attosecond temporal resolution through ultrafast spectroscopic experiments. However, inferring the underlying microscopic physical processes from the macroscopic observables obtained in such measurements remains a challenge.

To uncover the origins of these complex nonequilibrium phenomena, we have been developing and applying first-principles calculations to describe microscopic electron dynamics based on time-dependent density functional theory (TDDFT) [1].

In this presentation, we first introduce real-time electron dynamics simulations based on TDDFT, revisiting linear response calculations for the optical properties of solids. We then extend the real-time linear response framework to pump-probe setups to investigate nonequilibrium systems under strong light fields [2,3].

Next, we present recent applications of first-principles calculations to attosecond transient absorption spectroscopy. As an initial application, we discuss the transient absorption of transition metals, explaining the many-body effects and their ab initio analysis using electron dynamics calculations [4,5]. We find that light induces electron localization in transition metals.

As a second application, we analyze the transient absorption of magnetic systems, using bulk cobalt as an example, to explore light-induced dynamics of the spin degree of freedom in metals [6]. Based on microscopic analysis, we found that, in addition to the light-induced electron localizations discussed above, a light-induced spatial spin transfer occurs on the attosecond timescale. This result indicates the possibility of observing light-induced spin dynamics through transient optical measurements by linking transient optical properties with transient magnetic properties. Furthermore, this knowledge could open up possibilities for manipulating the spin and magnetization degrees of freedom using light.

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Unconventional Approaches to Wavefunction-Based First-Principles Simulations: From TDCIS to Quantum-Inspired Methods

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Recent advances in wavefunction-based electronic structure methods have opened new avenues for simulating strongly correlated and time-dependent quantum systems. In this talk, I will present a series of unconventional, yet practically promising, computational strategies for time-dependent and time-independent first-principles simulations of many-electron systems.

We begin with the time-dependent configuration interaction singles (TDCIS) approach [1–3], reformulated to avoid the explicit use of virtual orbitals by introducing channel orbitals. This reformulation enables grid-based simulations of highly excited and ionizing processes, particularly when combined with absorbing boundary conditions. I will discuss recent developments including gauge-invariant formulations [4–5], multireference extensions, and size-extensive generalizations of TDCIS.

Next, I will introduce a time-dependent coupled-cluster method employing quasi-variational time-dependent orbitals [4,5]. Special attention will be paid to a novel asymmetric truncation scheme [5] for the left and right cluster operators:

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \cdots, \quad \hat{\Lambda} = \hat{\Lambda}_2 + \hat{\Lambda}_3 + \cdots,$$

which circumvents limitations of the original symmetric \hat{T}_1 -missing ansatz [4] in reaching exact solutions even with untruncated operators.

If time permits, I will also present a variational method for strongly correlated systems, based on a classically simulatable yet quantum-circuit-compatible ansatz. This framework may offer an effective solution to the optimization bottleneck in variational quantum eigensolvers (VQEs) [6].

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Molecular QED

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An ideal situation for accurate calculations is a molecule alone in space at 0K. However, is the vacuum really empty ? It has been shown that placing a molecule in an otherwise empty cavity will change its reactivity [1]. This is explained by the coupling of the molecule to the zero-point vibrations of the quantized electromagnetic field.



European Research Council
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The project HAMP-vQED [Highly Accurate Molecular Properties using variational Quantum Electrodynamics] investigates the possible role of quantum electrodynamics (QED) in chemistry. It will provide a protocol for highly accurate calculations of molecular properties, with particular attention to properties that probe the electron density in the close vicinity of atomic nuclei, where the QED-effects associated with the Lamb shift are created. A first line of attack is the introduction of effective QED potentials in molecular calculations [2,3]. Here we report progress on a second line of attack which is a variational formulation of QED adapted to the usual framework of molecular calculations, notably the use of finite basis sets [4].

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Ab initio Simulation of Electronic Structure in Quantum Dots

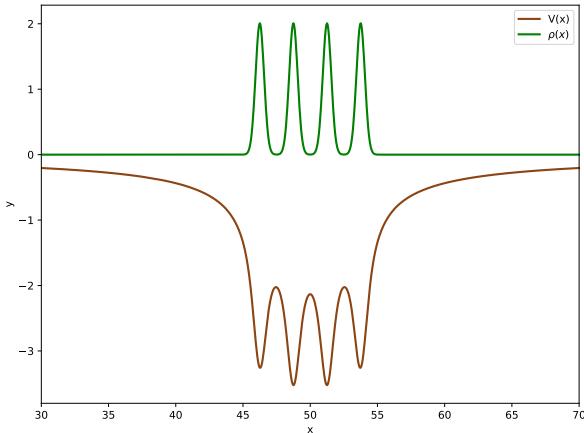
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As quantum dots have become a popular research topic in the field of quantum computing, interest in their electronic structure has increased significantly. A deeper understanding of this structure is essential to explore their potential in quantum technologies.

In this work, we adapt the variational quantum eigensolver method, employing a multiresolution analysis (MRA) ansatz that allows a fully variational approach to solve the electronic structure problem for quantum dot potentials. This fully variational approach is implemented within the MADNESS framework, building upon existing methods to allow for accurate and efficient computation of the electronic structure.



Quantum Dot Potential with four Wells

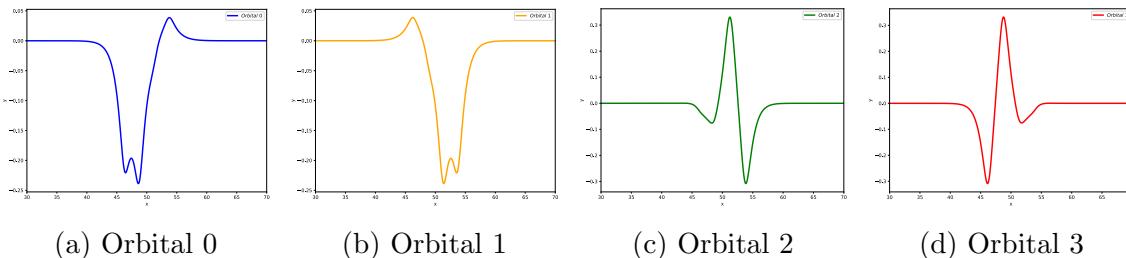


Figure 1: Visualization of a quantum dot potential with four wells and the charge density and the corresponding orbitals of the first four eigenstates

Importance of k-point sampling on the property evaluation in periodic and quasi-periodic systems

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Abstract

There are choices in the boundary condition of the wavefunction in extended systems. Though energy dispersion and density of the state can be numerically reproduced with relatively small number of k-points, response property evaluations require many k-points sampling. We investigate the influence of k-point sampling in response properties in extended systems and many k-points are necessary to reproduce the correct behavior of the frequency dependence in the low frequency region around Dirac points. This reflects the importance of phase change in the intermediate state wavefunctions upon the response. We further investigate the influence of k-point sampling in the topological property evaluation of the periodic and/or quasi-periodic systems so as to establish the reliable k-point samplings in the numerical method for topological materials.

Localization and reduced virtual space in Hartree-Fock approach

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We have shown an alternative way to obtain the Slater determinant ground state solution within an independent-particle approximation using the exponential ansatz for the wave function (Thouless theorem)[1] and exact treatment in terms of variational coupled cluster singles(VCCS) [2,3]. The non-terminating expansions of the wave function within the VCCS can be exactly treated by summing up the one-particle density matrix elements in the occupied block using simple recurrence relation. At the same time, this leads to an extremely simple diagonalization-free algorithm for the solution of the Hartree-Fock equations.

We apply this approach with a starting determinant using localized orbitals, i.e. we present a localized Hartree-Fock method[4]. The initial guess was obtained from diagonalising the Fock matrix constructed from the superposition of atomic densities. Starting molecular orbitals were localized using Pipek-Mezey procedure, or incomplete Cholesky decomposition of density matrix. Next, we were running VCCS iterations in local molecular orbitals. Convergence behavior and number of nonzero elements of T_1 amplitudes and density matrix were examined for series of medium sized molecules.

Furthermore we present unique algorithm[5] which reducing the virtual orbital space in VCCS approach and it significantly speed up the calculations.

Acknowledgement

This work has been supported by the Slovak Research and Development Agency (APVV-21-0497). JS acknowledges support from the EU NextGenerationEU through the Recovery and Resilience Plan for Slovakia under project No. 09I03-03-V04-00117.

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Coupled-cluster theory for molecules in extreme environments

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In this talk, the environments that strongly change the molecular electronic structure like strong magnetic fields and the (electronic) strong coupling regime and their accurate treatment using coupled cluster theory will be explored. Magnetic fields of up to 100000 Tesla are found on magnetic white dwarf stars. Within the strong-field regime, their spectra change in complex and often non-intuitive manners, hampering their assignment. As corresponding experiments cannot be performed, highly accurate predictions from theory are essential. [1-6]

Another extreme condition is encountered in the context of polaritonic chemistry, where molecules are placed in a cavity forming light-matter states. If the coupling is sufficiently strong, polaritonic states form that may, for example, influence reaction rates, barriers and photophysical properties.[7-9] We investigate the changes of the electronic structure induced by symmetry changes and the interplay of the different handles on the electronic structure.

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Quantum Monte Carlo calculation on the effect of molecular vibrations for the positron-binding to polyatomic molecules

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The positron, the anti-particle of the electron, is now widely used in both scientific and technological areas. However, the detailed mechanism of such processes is still unclear at the molecular level. A positron affinity (PA) value, which is the binding energy of a positron to an atom or molecule, has now been experimentally measured by Surko and co-workers for many molecular species, such as acetaldehyde, acetone, and acetonitrile molecules [1], based on the vibrational Feshbach resonance by incident low-energy positrons. Thus, to elucidate the mechanism of the positron binding to molecules, the theoretical analysis including the effect of molecular vibrations is indispensable. In this study, we will show the effect of molecular vibrations on PA values, based on *ab initio* multi-component quantum Monte Carlo (QMC) [2] and molecular orbital (MCMO) [3] methods for the electronic and positronic wave functions simultaneously, and the anharmonic vibrational quantum Monte Carlo (QMC) method [4].

In order to analyze the PA value including the effect of molecular vibrations, we introduced vibrational averaged PA (PA_v) defined by the following equation:

$$\text{PA}_v \equiv \frac{\int \text{PA}^{[X]}(\mathbf{Q}) |\Psi_v(\mathbf{Q})|^2 d\mathbf{Q}}{\int |\Psi_v(\mathbf{Q})|^2 d\mathbf{Q}},$$

where \mathbf{Q} is a set of vibrational coordinates and Ψ_v is the vibrational wave function of the v -th vibrational excited state. The $\text{PA}^{[X]}(\mathbf{Q})$ is the vertical PA value at the molecular geometry \mathbf{Q} , defined by the total energy difference of the parent molecule (X) and its positron attached system ($[X; e^+]$) as $\text{PA}^{[X]}(\mathbf{Q}) \equiv E^{[X]}(\mathbf{Q}) - E^{[X; e^+])(\mathbf{Q})$. In this study, $E^{[X; e^+])(\mathbf{Q})$ and $\Psi_v(\mathbf{Q})$ were calculated with configuration interaction level of MCMO theory [3] and vibrational QMC method [4], respectively.

In the case of the formaldehyde (CH_2O) molecule, the vertical PA value at the equilibrium position is predicted as +25(3) meV with QMC calculation. Applying the anharmonic vibrational analysis, the vibrational excitation of the C=O stretching mode enhances the PA value, whereas the excitation of the CH_2 rocking mode deenhances it. We confirmed that such PA variations arise from the change in both permanent dipole moment and dipole-polarizability at each vibrational excited state. We will show some results of other larger molecules.

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Adaptive Control of Numerical Error in All-Electron Simulation of Periodic Solids

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To address the shortcomings of mainstream numerical representations used for electronic structure simulations – namely, the unsystematic convergence and poor conditioning of atomic orbitals (AOs), and the lack of dynamic range for explicit simulation of core electrons with plane waves (PW) – we are exploring how to use the multiresolution framework established by Harrison, Beylkin, and others for a wider range of electronic structure simulations. We recently introduced first multiconfiguration self-consistent field approach applicable to general molecules with multiwavelet representation of orbitals[1]. Here we report the extension of such multiwavelet numerical technology to infinite solids treated under Born-van-Karman (BvK) periodic boundary conditions [2]. For robust convergence to the thermodynamic limit of one-body methods with exact exchange (Hartree-Fock, generalized Kohn-Sham) and many-body methods it is essential to use the Poisson kernel smoothly restricted to the Wigner-Seitz supercell. Efficient evaluation of the resulting matrix elements is possible with relatively minor modifications of the standard nonperiodic formalism. Initial applications to mean-field simulation of paradigmatic solids in up to 3 dimensions will illustrate the potential of the multiwavelet representation for all-electron simulation of solids.

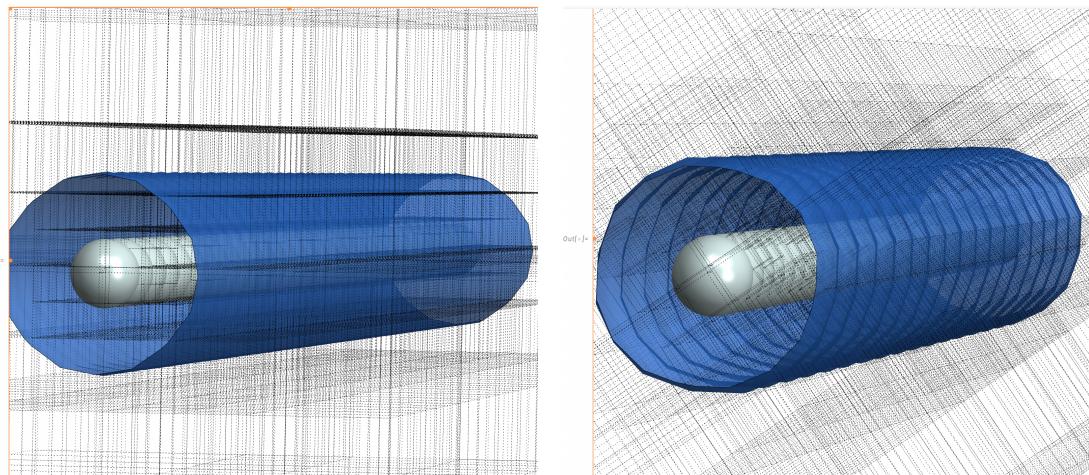


Figure 1: Electron density of regular and symmetry-broken Hartree-Fock solutions of the infinite hydrogen chain ($R_{\text{H-H}} = 1.8a_0$) evaluated in MW basis.

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Real-space, real-time approach to quantum-electrodynamical time-dependent density functional theory

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We have developed a QED-DFT and Quantum-Electrodynamical Time-Dependent Density Functional Theory (QED-TDDFT) approach, using a coupled electron–photon wave function. In this approach the wave function is defined as a tensor product of a real-space grid for the electrons and Fock state representation for photons. Unlike other QED-DFT approaches, the photons are not treated by a mean field approximations. The non-relativistic Pauli-Fierz Hamiltonian is used to describe the interaction of matter and light [2-3]. Applications for molecules in cavities show the accuracy of the approach. Examples include the coupling strength and light frequency dependence of the energies, wave functions, optical absorption spectra, and Rabi splitting magnitudes in cavities, as well as a description of high harmonic generation in cavities. We have also developed an approach that calculates the wave functions and energies of small atoms and molecules coupled to quantum field modes in cavity QED numerically exactly [3]. This method can help to test the accuracy of the QED-DFT calculations for test systems.

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Non-Covalent Interaction in the Hydroboration of CO₂ Revealed by Symmetry-Adapted Perturbation Theory

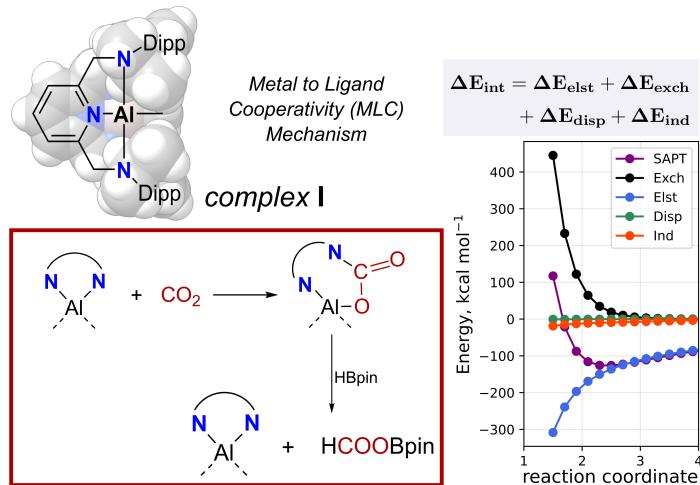
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The reactivity of an unusual square-planar aluminium amide complex (**I**) toward carbon dioxide has been explored, unveiling both distinctive structural behavior and promising catalytic activity. The reaction proceeds via a metal–ligand cooperativity mechanism, enabling the activation of CO₂ and allowing for subsequent hydroboration at various reduction levels. This system represents a rare example of aluminium-based catalysis using a single-component complex under mild conditions.

Ongoing mechanistic investigations, including symmetry-adapted perturbation theory (SAPT) analyses, aim to elucidate the noncovalent interactions that govern this transformation. A comprehensive understanding of these processes will contribute to the rational design of next-generation main-group catalysts for small molecule activation, particularly in the context of sustainable carbon management.



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Progress in Bootstrap Embedding and Fast Interpolation of Reaction Paths

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This talk covers two main topics: (a) recent advancements in the Van Voorhis group's bootstrap embedding (BE) method and (b) efficient interpolation of chemically meaningful reaction paths.

Bootstrap Embedding (BE) is a fragment-based embedding approach derived from Density Matrix Embedding Theory (DMET) that enables linear-scaling for many quantum chemistry methods. When coupled with methods such as coupled-cluster (CC), BE achieves linear scaling, favourably comparing with specialized linear-scaling CC methods such as DLPNO-CC. BE's major advantage lies in its versatility — it can be paired with various electronic structure methods, applied to periodic systems, and can transform a single large Hamiltonian into several smaller ones that are amenable for applications in quantum computing. The method is now mature enough that we released an open-source library, making it available to the scientific community.

However, challenges remain as system size increases. For large systems, the computational bottleneck shifts from higher-order electronic structure methods to the integral transformation step, which folds the surrounding environment into the fragments. I will present strategies to mitigate these bottlenecks and achieve true linear scaling for large systems, pushing computational limits.

Another recent development of the group is partially updated BE, where only fragments with changing internal coordinates are recalculated along a reaction path. This naturally carries over to the second part of the talk. Here I present an efficient, black-box algorithm for the chemically meaningful interpolation of reaction paths using redundant internal coordinates. These paths can be directly used to estimate activation barriers or serve as initial guesses for nudged elastic band (NEB) calculations. The method significantly reduces the number of steps needed to achieve convergence in NEB compared to state-of-the-art techniques, such as independent pair potentials (IDPP), Z-matrix interpolation, or geodesic interpolation, while also being generally faster in terms of wall clock time. The approach is computationally efficient, with the most expensive step being either a matrix pseudoinversion or a least-squares fit per path image, and leads to starting guesses remarkably close to the final converged path.

High-Performance and Energy-Efficient Computation of Electron Repulsion Integrals on Field-Programmable Gate Arrays

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The computation of Electron Repulsion Integrals (ERIs) over Gaussian-type orbitals is a major performance bottleneck in quantum chemistry calculations [1]. While advanced algorithms and parallelization techniques enable large-scale *ab initio* molecular dynamics simulations in High-Performance Computing (HPC), power consumption has become a critical constraint, with top HPC systems exceeding 30 megawatts. Thus, high-performance and energy-efficient acceleration for the computation of ERIs is essential in HPC for sustainable large-scale quantum chemistry calculations.

Field-Programmable Gate Arrays (FPGAs) are reconfigurable integrated circuits that enable custom hardware implementation with high flexibility, offering superior parallelism and energy efficiency in many application domains. As a result, FPGAs are increasingly being deployed as high-performance accelerators in HPC systems [2], providing a power-efficient alternative to traditional CPUs and GPUs.

In this contributed talk, we will present our recent work on using FPGAs as high-performance and energy-efficient accelerator for the ERI computations in quantum chemistry [3-6]. Performance evaluation demonstrates that the FPGA kernels achieve superior performance and energy efficiency compared to the state-of-the-art **libint** on AMD EPYC 7713 CPU (64-core) and **libintx** on NVIDIA A40 GPU.

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Homotopy continuation method for solving Dyson equation fully self-consistently
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Solution of the Dyson equation for the small-gap systems can be plagued by large non-converging iterations. In addition to the convergence issues, due to a high non-linearity, the Dyson equation may have multiple solutions. We apply the homotopy continuation approach to control the behavior of iterations. We used the homotopy continuation to locate multiple fully self-consistent GW solutions for NdNiO₂ solid and to establish the corresponding Hartree-Fock limits. Some of the solutions found are qualitatively new and help to understand the nature of electron correlation in this material.

We show that there are multiple low-energy charge-transfer solutions leading to a formation of charge-density waves. Our results qualitatively agree with the experimental conductivity measurements. To rationalize the structure of solutions, we compare the k-point occupations and generalize the concept of natural difference orbitals for correlated periodic solids.