UNIVERSITY
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University
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in Katowice

Virtual WARSAW MOLECULAR ELECTRONIC STRUCTURE CONFERENCE

WMES 2020

Warsaw, Poland
September 1-4, 2020

Programme & Book of Abstracts

Edited by Monika Musiał and Krzysztof Pachucki

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ABOUT

The International Conference on Molecular Electronic Structure organized by the Faculty of Physics, University of Warsaw will be held in September 1-4, 2020. The conference will have a virtual character, all lectures will be broadcasted online via Google Meet. The current meeting follows the conferences and series of workshops on Molecular Electronic Structure which were held in: Metz, France (2018), Buenos Aires, Argentina (2016), Amasya, Turkey (2014) and Cannakale, Turkey (2012). Conference sessions cover various aspects of molecular electronic structure and related areas, as well as the supporting mathematics.

CONFERENCE PROGRAMME

WARSAW MOLECULAR ELECTRONIC STRUCTURE CONFERENCE (WMES 2020)

Warsaw Time CEST=UTC +2

Tuesday **1.09**	**Wednesday** **2.09**	**Thursday** **3.09**	**Friday** **4.09**
9:50-10:00 AM Opening			
Session 1 Chair: Krzysztof Pachucki	**Session 4** Chair: Monika Musiał	**Session 7** Chair: Artur Michalak	**Session 10** Chair: Philip Hoggan
10:00-10:30 AM L-1 Michał Lesiuk	**10:00-10:30 AM** L-9 Leszek Meissner	**10:00-10:30 AM** L-18 Sonia Coriani	**10:00-10:30 AM** L-26 Maria Belen Ruiz
10:30-11:00 AM L-2 Mariusz Puchalski	**10:30-11:00 AM** L-10 Ugur Bozkaya	**10:30-11:00 AM** L-19 Roland Lindh	**10:30-11:00 AM** L-27 Artur Michalak
11:00-11:30 AM L-3 Michał Tomza	**11:00-11:30 AM** L-11 Philip Hoggan	**11:00-11:30 AM** L-20 Marcin Czapla	**11:00-11:30 AM** L-28 Thibaud Etienne
11:30-12:00 PM L-4 Anastasia Borschevsky	**11:30-12:00 PM** L-12 Jiri Pittner	**11:30-12:00 PM** L-21 Alessandro Genoni	**11:30-12:00 PM** L-29 Shirin Faraji
12:00-2:00 PM Break	**12:00-2:00 PM** Break	**12:00-2:00 PM** Break	**12:00-12:15 PM** O-8 Tadeusz Pluta
Session 2 Chair: Jacek Komasa	**Session 5** Chair: Jiri Pittner	**Session 8** Chair: Roland Lindh	**12:15-12:25 PM** Concluding remarks - End of conference
2:00-2:30 PM L-5 Piotr Żuchowski	**2:00-2:30 PM** L-13 Thomas Jagau	**2:00-2:30 PM** L-22 Simen Kvaal	
2:30-3:00 PM L-6 Stella Stopkowicz	**2:30-3:00 PM** L-14 Ireneusz Grabowski	**2:30-3:00 PM** L-23 David Tew	
3:00-3:30 PM L-7 Ksenia Bravaya	**3:00-3:30 PM** L-15 Viktor Staroverov	**3:00-3:30 PM** L-24 Avram Sidi	
3:30-4:00 PM L-8 So Hirata	**3:30-4:00 PM** L-16 Artur Izmaylov	**3:30-4:00 PM** L-25 Stefan Vuckovic	
4:00-4:30 PM Break	**4:00-4:30 PM** Break	**4:00-4:30 PM** Break	
Session 3 Chair: Mariusz Puchalski	**Session 6** Chair: Ireneusz Grabowski	**Session 9** Chair: Ugo Ancarani	
4:30-4:45 PM O-1 Michał Przybytek	**4:30-5:00 PM** L-17 Dario Mitnik	**4:30-4:45 PM** O-5 Huseyin Aksu	
4:45-5:00 PM O-2 Paweł Czachorowski		**4:45-5:00 PM** O-6 Abdallah Ammar	
5:00-5:15 PM O-3 Michał Siłkowski	**5:00-5:15 PM** O-4 Katarzyna Jakubowska	**5:00-5:15 PM** O-7 Tymon Kilich	

Lectures - 30 min. including discussion (25+5)
Oral presentations - 15 min. including discussion (12+3)

INVITED SPEAKERS

- Anastasia Borschevsky (University of Groningen, Netherlands)
- Ugur Bozkaya (Hacettepe University, Turkey)
- Ksenia Bravaya (Boston University, USA)
- Sonia Coriani (Technical University of Denmark, Denmark)
- Pawel Czachorowski (University of Warsaw, Poland)
- Marcin Czapla (University of Gdansk, Poland)
- Thibaud Etienne (University of Montpellier, France)
- Alessandro Genoni (Universite de Lorraine, France)
- Ireneusz Grabowski (Nicolaus Copernicus University, Poland)
- Shirin Faraji (University of Groningen, Netherlands)
- So Hirata (University of Illinois, USA)
- Philip Hoggan (University Clermont-Auvergne, France)
- Artur Izmaylov (University of Toronto, Canada)
- Thomas Jagau (Catholic University of Leuven, Belgium)
- Simen Kvaal (University of Oslo, Norway)
- Michał Lesiuk (University of Warsaw, Poland)
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- Mariusz Puchalski (Adam Mickiewicz University, Poland)
- Maria Belen Ruiz (Friedrich Alexander University Erlangen-Nurnberg, Germany)
- Avram Sidi (Israel Institute of Technology, Israel)
- Viktor Staroverov (University of Western Ontario London, Canada)
- Stella Stopkowicz (Johannes Gutenberg-Universitat Mainz, Germany)
- David Tew (University of Oxford, UK)
- Michał Tomza (University of Warsaw, Poland)
- Stefan Vuckovic (University of California Irvine, USA)
- Piotr Żuchowski (Nicolaus Copernicus University, Poland)

Timetable

Tuesday 1.09

9:50-10:00 AM
Opening

Session 1
Chair: **Krzysztof Pachucki**

10:00-10:30 AM L-1 Michał Lesiuk	Implementation of the full CCSDT electronic structure model with tensor decompositions
10:30-11:00 AM L-2 Mariusz Puchalski	Quantum Electrodynamics of the hydrogen molecule
11:00-11:30 AM L-3 Michał Tomza	Relativistic and QED effects in many-electron diatomic NaLi and AlF molecules
11:30-12:00 PM L-4 Anastasia Borschevsky	High accuracy investigations of atomic properties of heavy elements

12:00-2:00 PM
Break

Session 2
Chair: **Jacek Komasa**

2:00-2:30 PM L-5 Piotr Żuchowski	Dispersion energy from the time-independent coupled-clusters polarization propagator
2:30-3:00 PM L-6 Stella Stopkowicz	Electronic structure of atoms and molecules in strong magnetic fields and implications for their detection on stars
3:00-3:30 PM L-7 Ksenia Bravaya	Extending bound state quantum chemistry methods to resonances
3:30-4:00 PM L-8 So Hirata	Low-temperature catastrophe of many-body perturbation theory for thermodynamics

4:00-4:30 PM
Break

Timetable

Session 3
Chair: **Mariusz Puchalski**

4:30-4:45 PM O-1 Michał Przybytek	Theoretical determination of polarizability and magnetic susceptibility of neon
4:45-5:00 PM O-2 Paweł Czachorowski	Second virial coefficient for helium from relativistic interaction potential
5:00-5:15 PM O-3 Michał Siłkowski	High-accuracy Born-Oppenheimer potentials of excited states of hydrogen molecule

Timetable

Wednesday 2.09

Session 4
Chair: **Monika Musiał**

10:00-10:30 AM L-9 Leszek Meissner	Extension of the Fock-space coupled-cluster method with singles and doubles to the three-valence sector
10:30-11:00 AM L-10 Ugur Bozkaya	Linear Scaling Coupled Cluster Methods with Molecular Fragmentation Approaches
11:00-11:30 AM L-11 Philip Hoggan	Quantum Monte Carlo methods for metal catalysis: some examples
11:30-12:00 PM L-12 Jiri Pittner	Recent progress on the DMRG-tailored coupled clusters method

12:00-2:00 PM
Break

Session 5
Chair: **Jiri Pittner**

2:00-2:30 PM L-13 Thomas Jagau	Recent advances in quantum chemistry of electronic resonances: Towards larger molecules
2:30-3:00 PM L-14 Ireneusz Grabowski	Accurate ionization potentials obtained from the spin-resolved second-order approaches. From simple molecules to nanotubes
3:00-3:30 PM L-15 Victor Staroverov	Average Local Ionization Energy in Finite Basis Sets
3:30-4:00 PM L-16 Artur Izmaylov	Quantum computing approaches to the electronic structure problem

4:00-4:30 PM
Break

Timetable

Session 6
Chair: **Ireneusz Grabowski**

4:30-5:00 PM L-17 Dario Mitnik	Generalized Sturmian Functions in Prolate Spheroidal Coordinates
5:00-5:15 PM O-4 Katarzyna Jakubowska	NMR Spin–Spin Coupling Constants Derived from Relativistic Four-Component DFT Theory - Analysis and Visualization

Timetable

Thursday 3.09

Session 7
Chair: **Artur Michalak**

10:00-10:30 AM L-18 Sonia Coriani	Coupled cluster methods for spectroscopic effects in the XUV and X-ray regimes
10:30-11:00 AM L-19 Roland Lindh	Restricted-Variance Molecular Geometry Optimization Based on Gradient-Enhanced Kriging
11:00-11:30 AM L-20 Marcin Czapla	Silicon instead of Carbon – Silicon Amino Acids
11:30-12:00 PM L-21 Alessandro Genoni	QM/ELMO Method: a Fully Quantum Mechanical Embedding Scheme Based on Extremely Localized Molecular Orbitals

12:00-2:00 PM
Break

Session 8
Chair: **Roland Lindh**

2:00-2:30 PM L-22 Simen Kvaal	A state-specific multireference coupled-cluster method based on the bivariational principle
2:30-3:00 PM L-23 David Tew	Triple natural orbital theory for three-body electron correlation
3:00-3:30 PM L-24 Avram Sidi	Vector extrapolation/convergence acceleration methods for solution of large systems of equations
3:30-4:00 PM L-25 Stefan Vuckovic	An MP2 correction for accurate description of non-covalent interactions

4:00-4:30 PM
Break

Timetable

Session 9
Chair: **Ugo Ancarani**

4:30-4:45 PM O-5 Huseyin Aksu	Understanding of the Quantum Nature of Electron Transfer and Explaining Spectral Asymmetries in Photosynthetic Bacteria Reaction Center: Screened Range-Separated Hybrid Functionals
4:45-5:00 PM O-6 Abdallah Ammar	Representation of continuum wavefunctions by complex Gaussians: application to photoionization processes
5:00-5:15 PM O-7 Tymon Kilich	Singly linked Hylleraas method for four electron atom

Timetable

Friday 4.09

Session 10
Chair: **Philip Hoggan**

10:00-10:30 AM L-26 Maria Belen Ruiz	Exponentially Correlated Hylleraas-configuration interaction non-relativistic energy of the ^1S ground state of the helium atom
10:30-11:00 AM L-27 Artur Michalak	Theoretical modeling of catalytic activity of complex processes catalyzed by transition-metal complexes
11:00-11:30 AM L-28 Thibaud Etienne	Matrix (in)equalities in the context of molecular excited-state quantum-chemical calculations
11:30-12:00 PM L-29 Shirin Faraji	PySurf: a framework for database accelerated excited-state direct dynamics
12:00-12:15 PM O-8 Tadeusz Pluta	Estimation of Dipole Polarizability for Excited States

12:15-12:25 PM
Concluding remarks - End of conference

Lectures

Implementation of the full CCSDT electronic structure model with tensor decompositions

Michał Lesiuk[1,2]

[1]*ETH Zürich, Laboratory of Physical Chemistry, Vladimir-Prelog-Weg 2, 8093 Zürich, Switzerland*
[2]*Faculty of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland*

We report a complete implementation of the coupled-cluster method with single, double, and triple excitations (CCSDT) [1, 2] where tensor decompositions are used to reduce its scaling and overall computational costs. For the decomposition of the electron repulsion integrals the standard density fitting format is used [3]. The coupled-cluster single and double amplitudes are treated conventionally, and for the triple amplitudes tensor we employ the Tucker-3 compression formula [4], $t_{ijk}^{abc} = t_{XYZ}\, U_{ai}^{X}\, U_{bj}^{Y}\, U_{ck}^{Z}$. The auxiliary quantities U_{ai}^{X} come from singular value decomposition (SVD) of an approximate triple amplitudes tensor based on perturbation theory. The efficiency of the proposed method relies on an observation that the dimension of the "compressed" tensor t_{XYZ} sufficient to deliver a constant relative accuracy of the correlation energy grows only linearly with the size of the system, N. This fact, combined with proper factorization of the coupled-cluster equations, leads to practically N^6 scaling of the computational costs of the proposed method, as illustrated numerically for linear alkanes with increasing chain length. This constitutes a considerable improvement over the N^8 scaling of the conventional (uncompressed) CCSDT theory. The accuracy of the proposed method is verified by benchmark calculations of total and relative energies for several small molecular systems and comparison the exact CCSDT method. The accuracy levels of 1 kJ/mol are easily achievable with reasonable SVD subspace size, and even more demanding levels of accuracy can be reached with a considerable reduction of the computational costs. Extensions of the proposed method to include higher excitations are briefly discussed, along with possible strategies of reducing other residual errors.

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Lectures L2

Quantum Electrodynamics of the hydrogen molecule

Mariusz Puchalski[1], Jacek Komasa[1], Anna Spyszkiewicz[1],
Paweł Czachorowski[2], Grzegorz Łach[2], and Krzysztof Pachucki[2]

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[2] *Faculty of Chemistry, Adam Mickiewicz University, Poland*

Theoretical studies of hydrogen molecule is the cornerstone of the molecular quantum mechanics. Due to its simplicity, the achieved precision for rovibrational transitions is the highest among all molecules and still has a potential of significant enhancement. This high precision of theoretical predictions for hydrogen molecules leads to improved tests of quantum electrodynamics (QED), and may be the source of fundamental constants and bounds on hypothetical interactions. We search for discrepancies between highly accurate spectroscopic measurements for the hydrogen molecules and theoretical predictions based on QED, in order to discover new effects or even new interactions which might result in the developement of Standard Model of fundamental interactions [1, 2]. We will also present the latest advances in the calculation of the leading hyperfine interactions for molecular levels in the HD molecule within the Born-Oppenheimer (BO) approximation and in the fully nonadiabatic approach [3, 4].

References

[1] Nonadiabatic QED Correction to the Dissociation Energy of the Hydrogen Molecule Mariusz Puchalski, Jacek Komasa, Anna Spyszkiewicz, Paweł Czachorowski, and Krzysztof Pachucki, Phys. Rev. Lett. 122, 103003 (2019); Phys. Rev. A 100, 020503(R) (2019)

[2] Jacek Komasa, Mariusz Puchalski, Paweł Czachorowski, Grzegorz Łach, and Krzysztof Pachucki, Phys. Rev. A 100, 032519 (2019)

[3] Jacek Komasa, Mariusz Puchalski, and Krzysztof Pachucki Phys. Rev. A 102, 012814 (2020)

[4] Mariusz Puchalski, Jacek Komasa, and Krzysztof Pachucki, *in preparation*

Relativistic and QED effects in many-electron diatomic NaLi and AlF molecules

M. Gronowski[2], A. Koza[1], Sangami G. S.[1], and M. Tomza[1]

[1] *Faculty of Physics, University of Warsaw, Pasteura 5, 02-093 Warsaw Poland*

Ultracold polar and magnetic NaLi molecules in the rovibrational ground state of the lowest triplet $a^3\Sigma^+$ electronic state have been recently produced. Experimental studies of laser coolable AlF molecules in the $X^1\Sigma^+$ and $a^3\Sigma^+$ electronic states have also been started. NaLi in the $a^3\Sigma^+$ state forms a weakly bound van der Waals type complex, while AlF in both electronic states is deeply bound. Here, in a comparative study, we calculate accurate Born-Oppenheimer potential energy curves for these two many-electron diatomic molecules using state-of-the-art *ab initio* methods of quantum chemistry and investigate the importance of higher-level-excitation, core-electron correlation, relativistic, QED, and adiabatic corrections in these systems. We employ the hierarchy of the coupled-cluster wave functions and large Gaussian basis sets extrapolated to the complete basis set limit.

We calculate the electronic and rovibrational structure of the 14-electron ^{23}Na^{6}Li molecule in the triplet $a^3\Sigma^+$ state with spectroscopic accuracy ($< 0.5\,\mathrm{cm}^{-1}$) [1]. We show that the inclusion of higher-level excitations, core-electron correlation, relativistic, QED, and adiabatic corrections is necessary to reproduce accurately scattering and spectroscopic properties of alkali-metal systems. We obtain the well depth, $D_e = 229.9(5)\,\mathrm{cm}^{-1}$, the dissociation energy, $D_0 = 208.2(5)\,\mathrm{cm}^{-1}$, and the scattering length, $a_s = -84^{+25}_{-41}$ bohr, in good agreement with recent experimental measurements. These values are obtained without any adjustment to experimental data, showing that quantum chemistry methods are capable of predicting scattering properties of many-electron systems, provided relatively weak interaction and small reduced mass of the system.

For 24-electron AlF molecule, despite of two orders of magnitude deeper potential energy curves, we obtain a similar relative accuracy of the dissociation energies and spectroscopic parameters.

References

[1] M. Gronowski, A. M. Koza, M. Tomza, arxiv:2003.12051 (2020)

High accuracy investigations of atomic properties of heavy elements.

Anastasia Borschevsky[1]

[1] *Van Swinderen Institute for Particle Physics and Gravity (VSI), University of Groningen, Nijenborgh 4, 9747AG Groningen, The Netherlands*

Theory can provide important support at all the stages of spectroscopic experiments, from planning the measurements, through extracting the properties of interest from the data, and to the interpretation of the results and their comparison to predicted values. This support is especially important for experiments on heavy and unstable elements, which are challenging due to the short lifetimes and the low quantities of the investigated species. To provide useful predictions, highly accurate calculations of atomic properties are needed. In order to be reliable, such calculations must include both relativistic effects and electron correlation on the highest possible level. Relativistic coupled cluster is considered one of the most powerful methods for accurate treatment of these effects and for calculations of properties of heavy elements. One of the advantages of this approach is that it allows us to set an uncertainty on the calculated results, facilitating their use in experimental research.

A brief introduction to the relativistic coupled cluster method (in particular the multireference Fock space coupled cluster variant) will be provided in the talk, including the recently developed scheme for uncertainty evaluation. In the rest of the presentation I will focus on the recent successful applications of the coupled cluster approach to spectra, hyperfine structure, and other properties of heavy elements.

References

[1] D. Leimbach, J. Karls, Y. Guo, *et al,* Nature Comm. **11**, 3824 (2020)

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Dispersion energy from the time-independent coupled-clusters polarization propagator.

Piotr S. Żuchowski[1], Robert Moszyński[2]

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University in Torun, Grudziadzka 5/7, 87-100 Torun
[2]Quantum Chemistry Laboratory, Departament of Chemistry, University of Warsaw,
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We present a new method of calculation of the dispersion energy in the second-order symmetry adapted perturbation theory. Using the time-independent coupled-cluster response function theory of Moszynski et al. (2005) [1], and Casimir-Polder-like integral, we introduce the equations for the so-called dispersion amplitudes, which can be obtained by solving the linear equations. These are used to express the dispersion energy in terms of dispersion- and cluster amplitudes. Apart from general formulation of theory we introduce non-perturbative approximation valid up to the fourth-order of MBPT, which we subsequently compare to existing methods [2-5].

Acknowledgments: Piotr Żuchowski acknowledges NCN grant Sonata Bis (UMO-2019/34/E/ST4/00407), while R. Moszynski is grateful to the NCN grant number 2016/21/B/ST4/03877

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Electronic structure of atoms and molecules in strong magnetic fields and implications for their detection on stars

Stella Stopkowicz[1], Florian Hampe[1,2], and Marios-Petros Kitsaras[1]

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For a sufficiently strong magnetic field, the electronic structure of molecules and even atoms changes in intricate and complex ways. For example, molecules that are unbound in the field-free case can become bound by unfamiliar bonding mechanisms. [1] Indeed, potential energy surfaces are full of both level crossings and avoided crossings, which, as we demonstrate, has a profound impact on the intensity of electronic transitions. [2]

Such strong fields exist for example on magnetic White Dwarf stars. Even though such field strengths are not directly accessible in the lab, strong field-effects can be encountered on Earth in cases where the Coulomb interaction is damped as for example in Rydberg states or semiconductors.[3]

In this contribution, the implications on the electronic spectra of candidate atoms and molecules for White Dwarf stars will be assessed. In particular, we discuss the influence of a strong magnetic field on energies, transition wave-lengths and intensities with an emphasis on the excited states of atoms and molecules determined using highly-accurate electronic structure methods such as finite-field equation-of-motion coupled-cluster theory.[4]

Acknowledgments: The Deutsche Forschungsgemeinschaft (DFG) is acknowledged for the financial support through grant STO 1239/1-1 .

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Extending bound state quantum chemistry methods to resonances

James Gayvert[1] and Ksenia Bravaya[1]

[1] *Boston University, 590 Commonwealth ave., 02215, Boston, USA*

In this talk I will discuss the recent developments in description of electronic structure of metastable electronic states. In particular, I will introduce OpenCAP, the software we developed to extend the capability of conventional quantum chemistry methods and software packages to description of resonances. OpenCAP allows one to combine complex absorbing potential (CAP) methodology with bound state methods implemented in external quantum chemistry packages. OpenCAP extracts the relevant information (such as state energies, density matrices and transition density matrices) from a bound state calculation performed in advance, calculates CAP matrix in the corresponding atomic orbital basis, and uses the data to perform a projected CAP calculation. OpenCAP has been interfaced with a developer version of Q-Chem, OpenMolcas, and pyscf packages. The benchmark calculations on a series of model systems will be presented.

Low-temperature catastrophe of many-body perturbation theory for thermodynamics

So Hirata[1], Punit K. Jha[1]

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(1) Low-order perturbation corrections to the electronic grand potential, internal energy, chemical potential, and entropy in the grand canonical ensemble are determined numerically as the λ-derivatives of the respective quantity calculated exactly with a perturbation-scaled Hamiltonian, $H_0+\lambda V$. On this basis, we show that the finite-temperature many-body perturbation theory in many textbooks is incorrect and does not converge at the exact limit [1].

(2) The correct analytical first- [2] and second-order [3] correction formulas for the grand potential, internal energy, and chemical potential are derived in the sum-over-state and reduced analytical expressions algebraically. The time-independent, non-diagrammatic derivation is based on straightforward analytical differentiation of thermal full configuration interaction using the sum rules of the Hirschfelder–Certain degenerate perturbation energy corrections and several identities of Boltzmann sums introduced by us.

(3) Benchmark data are presented for the zeroth- through third-order many-body perturbation corrections to the electronic Helmholtz energy, internal energy, and entropy in the canonical ensemble in a wide range of temperature. Sum-over-states analytical formulas for up to the third-order corrections to these properties are also derived as analytical λ-derivatives [4].

(4) On the basis of (1)–(3), we show both analytically and numerically that the finite-temperature many-body perturbation theory in the grand canonical ensemble has zero radius of convergence at zero temperature when the energy ordering or the degree of degeneracy of the ground state changes with the perturbation strength. Contrary to the earlier suggestions of renormalizability by the chemical potential, this nonconvergence, first suspected by W. Kohn and J. M. Luttinger, is caused by the nonanalytic nature of the Boltzmann factor at $T=0$, also plaguing the canonical ensemble. The finding reveals a severe flaw in quantum field theory for thermodynamics, rooted in the mathematical limitation of the power-series expansion [5].

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Extension of the Fock-space coupled-cluster method with singles and doubles to the three-valence sector

Leszek Meissner[1] and Monika Musiał[2]

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The single-reference coupled-cluster (CC) method has proven very effective in the *ab initio* description of atomic and molecular systems but its successful application is limited to states dominated by a single Slater determinant which is used as the reference [1]. In cases where several determinants are important in the wave function expansion, i.e., we have to deal with nondynamic correlation effects, a multi-reference version of the coupled-cluster method is required. The multi-reference coupled-cluster approaches are based on the effective Hamiltonian formulation providing a two-step procedure in which dynamic correlation effects can be efficiently evaluated by the wave operator while nondynamic correlation contributions are given by diagonalization of the effective Hamiltonian in the final step [2]. There are two fundamental multi-reference coupled-cluster formulations, the Fock-space CC method [3] and the Hilbert-space one [4]. We focus on the Fock-space approach in its basic version with one- and two-particle operators in the exponent. Computational schemes using this truncation scheme for the cluster operator have been successfully applied in calculations in one- and two-valence sectors of the Fock space. We show that the approach can be easily extended and effectively employed in the three-valence sector calculations. That can done by supplementing the zero-, one- and two-body contributions to the effective Hamiltonian that are present in the two-valence sector calculations, with the lowest-order evaluation of the three-body term. That allows us to apply the method in the three-valence sector of the Fock-space. Our preliminary calculations for some atomic and molecular systems show that such a simple evaluation of the three-body effects in the effective Hamiltonian seems sufficient to obtain good quality results.

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Linear Scaling Coupled Cluster Methods with Molecular Fragmentation Approaches

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The coupled-cluster (CC) singles and doubles with perturbative triples [CCSD(T)] method is frequently referred to as the "gold standard" of modern computational chemistry. However, the high computational cost of CCSD(T) [$O(N^7)$], where N is the number of basis functions, limits its applications to small-sized chemical systems. To address this problem, efficient implementations of linear-scaling coupled-cluster methods, which employ the systematic molecular fragmentation (SMF) approach, are reported. In this study: (1) to achieve exact linear-scaling and to obtain a pure *ab inito* approach, we revise the handling of nonbonded interactions in the SMF approach (2) a new fragmentation algorithm, which yields smaller sized fragments; hence, better fits high-level CC methods is introduced (3) the new SMF approach is integrated with the high-level CC methods, denoted by LSSMF-CC, for the first time. Performances of the LSSMF-CC approaches, such as LSSMF-CCSD(T), are compared with their canonical versions for a set of alkane molecules, C_nH_{2n+2} (n=6–10), which includes 142 molecules. Our results demonstrate that the LSSMF approach introduces negligible errors compared with the canonical methods, mean absolute errors (MAEs) are between 0.20–0.59 kcal mol^{-1} for LSSMF-CCSD(T). To further assess the accuracy of the LSSMF-CCSD(T) approach, we also consider several polyethylene (PE) models. For the PE set, the error of LSSMF-CCSD(T)/cc-pVDZ with respect to the experimental polymerization energies per unit are between 0.08–0.63 kcal mol^{-1}. To illustrate the efficiency and applicability of the LSSMF-CCSD(T) approach, we consider an alkane molecule with 10004 atoms. For this molecule, the LSSMF-CCSD(T)/cc-pVTZ energy computation on a Linux cluster with 100 nodes, 4 cores and 5 GB of memory are provided to each node, is performed just in $\sim$ 24 hours. As far as we know, this computation is an application of the CCSD(T) method on the largest chemical system to date. Overall, we conclude that (1) the LSSMF-CCSD(T) method can be reliably used for large scale chemical systems, where the canonical methods are not computationally affordable (2) the LSSMF-CCSD(T) method is very promising for accurate computation of energies in macromolecular systems (3) we believe that our study is a significant milestone in developing CC methods for large-scale chemical systems.

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Quantum Monte Carlo methods for metal catalysis: some examples.

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Over 90 % of all chemical manufacture uses a solid catalyst. Related work thus responds to major societal demand.

Many chemical reactions involve bond-dissociation. This process is often the key to rate-limiting reaction steps at solid surfaces. Since bond-breaking is poorly described by Hartree-Fock and DFT methods, this work demonstrates a novel Quantum Monte Carlo (QMC) methodology.

Heterogeneous catalysis applications will be presented using the embedded active site approach so that a Full CI wave-function may be used for the 'molecular' part of the reactng system.

The whole active-site-substrate system is then expanded in periodic functions for use with features of the CASINO software [1] (of which PEH is a developer) such as the generic Jastrow factor. This has been developed and tested for carbon monoxide, adsorbed at metal surfaces e.g. copper, platinum other noble metals. The presentation describes some industrial reactions based on these systems.

Carbon-monoxide (CO)on platinum reacts with water to produce hydrogen (water-gas shift). This work uses Quantum Monte Carlo methods to investigate the early steps of this catalysed reaction at close-packed Pt(111) [2].

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We are also grateful for access to Finland's National Computer resources csc.fi (CSC – IT Center for Science) for some computational capacity (all Molpro runs).

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Recent progress on the DMRG-tailored coupled clusters method

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We present a new implementation of density matrix renormalization group based tailored coupled clusters method (TCCSD), which employs the domain-based local pair natural orbital approach (DLPNO). Compared to the previous local pair natural orbital (LPNO) version of the method, the new implementation is more accurate, offers more favorable scaling and provides more consistent behavior across the variety of systems. On top of the singles and doubles, we include the perturbative triples correction (T), which is able to retrieve even more dynamic correlation. The methods were tested on three systems: tetramethyleneethane, oxo-Mn(Salen) and Iron(II)-porphyrin model. The first two were revisited to assess the performance with respect to LPNO-TCCSD. For oxo-Mn(Salen), we retrieved between 99.8–99.9% of the total canonical correlation energy which is the improvement of 0.2% over the LPNO version in less than 63% of the total LPNO runtime. Similar results were obtained for Iron(II)-porphyrin. When the perturbative triples correction was employed, irrespective of the active space size or system, the obtained energy differences between two spin states were within the chemical accuracy of 1 kcal/mol using the default DLPNO settings.

We present also extension of the DMRG-tailored CC method to the relativistic domain. There are three essential problems in computational relativistic chemistry: electrons moving at relativistic speeds, close lying states and dynamical correlation. Currently available quantum-chemical methods are capable of solving systems with one or two of these issues. However, there is a significant class of molecules, in which all the three effects are present. These are the heavier transition metal compounds, lanthanides and actinides with open d or f shells. For such systems, sufficiently accurate numerical methods are not available, which hinders the application of theoretical chemistry in this field. Here we combine the relativistic versions of coupled cluster methods and density matrix renormalization group methods in order to address this challenging class of molecules. On the example of TlH, AsH and SbH we demonstrate that the DMRG-TCC method brings a significant reduction of computational cost compared to DMRG-only calculation, which becomes prohibitive in a large active space. Recently, we have extended the implementation of the method to polyatomic molecules with no spatial symmetry ("quaternion double groups").

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Recent advances in quantum chemistry of electronic resonances: Towards larger molecules

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In many settings involving plasma, X rays, or strong laser fields, electrons are no longer bound to the nuclei. The interaction of such unbound electrons with matter can be described in terms of autoionizing resonances, that is, electronic states with complex energy.[1, 2]

Resonances are, however, difficult to describe with electronic structure methods designed for bound states. An elegant solution to this problem consists in techniques from non-Hermitian quantum mechanics [1, 2] (for example, complex scaling, complex basis functions and complex-absorbing potentials). However, the focus of most developments in this regard lay on atoms and small molecules, whereas methods for larger systems remained scarce.

In this presentation, I will focus on our recent efforts to devise electronic structure methods suitable for the treatment of electronic resonances in larger molecules. In particular, we have introduced a resolution-of-the-identity (RI) approximation [3, 4] and an integral screening procedure [5] for complex-scaled basis functions. In conjunction with MP2 and CC2 theories, these developments enable the characterization of electronic resonances in molecules with up to ca. 50 atoms. I will discuss the relevance of molecules in this size range in the context of autoionization and strong-field ionization and illustrate the performance of our recently developed complex-variable RI-MP2 methods.

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Accurate ionization potentials obtained from the spin-resolved second-order approaches. From simple molecules to nanotubes

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A practical, accurate, cost- and implementation-free method (**ΔMP2-SCS(IP)**) for the calculation of vertical ionization potentials is proposed [1]. The method is based on a single step, diagonal, frequency-independent approximation to the second-order self-energy expression, combined with the spin-component-scaled technique. A new optimal parametrization for the spin-resolved ΔMP2 methods is proposed to accurately predict IPs. As we have shown, the IPs calculated using our new methods are of almost Δ-CCSD(T) or IP-EOM-CCSD quality. Moreover, the ΔMP2-SCS(IP) and ΔMP2-SOS(IP) require only single step post HF calculation which scales like $O(N^3)$.

We present the calculations of vertical ionization potentials for systems of various sizes, ranging from simple molecules, DNA/RNA bases, donor and acceptor organic molecular systems as well as nanotubes[2]. We show that a combination of the ΔMP2-SCS methods with the resolution of identity technique is effective and reliable alternative to the semi-empirical density functional theory methods and Green's function-based calculations of IPs for large molecular systems such as silicon-based or organic-based solar cells, for which the IP-EOM-CCSD calculations are too expensive for routine calculations.

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Average Local Ionization Energy in Finite Basis Sets

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The average local ionization energy (ALIE) is an important concept arising in diverse contexts of electronic structure theory. In principle, the ALIE should asymptotically approach the first ionization energy of the system, but finite-basis-set representations of the ALIE often exhibit seemingly random and sometimes dramatic deviations from the expected behavior. We analyze various scenarios of what can happen to the ALIE in finite basis sets and explain the puzzling observations. The findings have implications for finite-basis-set *ab initio* and density-functional methods, extended Koopmans theorem, and development of property-optimized basis sets.

Quantum computing approaches to the electronic structure problem

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Quantum computers are an emerging technology intended to address computational problems that are exponentially hard for classical computers. The electronic structure problem is one of such problems. One of the most practical approaches to engaging currently available universal-gate quantum computers to this problem is the variational quantum eigensolver (VQE) method. In this talk, I will discuss three recent improvements of the VQE method: 1) introducing symmetry constraints [1], 2) devising efficient low-depth quantum circuits [2, 3], and 3) improving projective measurement process [4, 5, 6].

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Generalized Sturmian Functions in prolate spheroidal coordinates

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The molecular ion H_2^+, as well as the isotopic forms such as HD^+ or D_2^+, and other one–electron diatomics such as HHe^{+2} or HLi^{+3}, are the simplest molecular quantum three–body problem with Coulomb interactions. H_2^+, in particular, has been largely studied since the early days of quantum mechanics, and serves as benchmark to test any new molecular approach and numerical method.

In the last decade, a spectral method named GSF has been developed and implemented to study successfully a variety of bound and scattering problems on atoms [1, 2], and to a much lesser extent to "one–centre" molecules [3]. However, for diatomic molecules, nothing has yet been proposed. We have recently developed a spectral method which makes use of GSF in prolate spheroidal coordinates (ξ, η, ψ). To start with, we obtained accurate ground and excited states of one–electron diatomic molecules [4]. This first step opens up the possibility to extend the use of GSF for diatomic molecules, and in particular to investigate their continuum states which is a very challenging task. The application to the ground and excited states of one–electron diatomics (H_2^+, HHe^{+2}, HLi^{+3}) puts our proposal on solid grounds and, at the same time, illustrates its computational efficiency and superiority with respect to other methods. The advantages of the GSF approach is based on the intrinsic good property that all GSF basis elements are constructed as to obey appropriate physical boundary conditions. An illustration is given by the Figure 1 in which the radial part of nine GSF basis elements are shown to exponentially decay in the same manner as a function of the coordinate $\xi = (r_1+r_2)/R$, where r_1 and r_2 stand for the electron–nuclei distances and R the internuclear distance. The present GSF implementation in prolate spheroidal coordinates for bound states is a necessary benchmark step, paving the way for the study of the more difficult task of studying continuum states involved in ionization of one or two–electron diatomic targets.

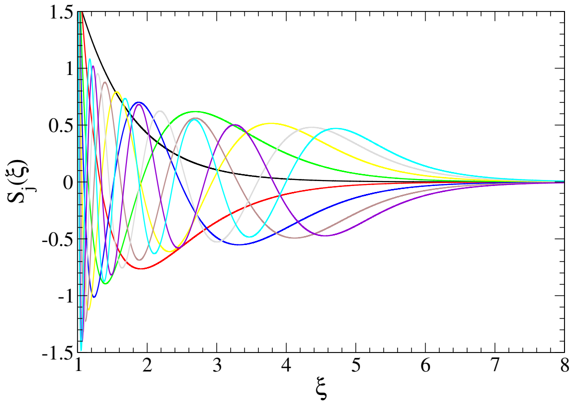

Figure 1: First 9 radial basis elements $\mathcal{S}_j(\xi)$ for $m = 0$.

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Coupled cluster methods for spectroscopic effects in the XUV and X-ray regimes

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Massive investments in light source facilities working in the XUV and X-ray frequency ranges has increased spectroscopic techniques exploiting these types of radiation to probe molecular systems. At the same time, it has stimulated the development of quantum-chemical theory and computational tools to simulate and elucidate such spectra. Theory and simulation tools are essential components to unambiguously relate experimental measurements to both structural and dynamical properties of the probed system.

Photoelectron spectroscopy (PES) is a prototypical technique in XUV, offering detailed information about the electronic structure of the target molecule and the properties ofthe ejected electrons. Photoionization has recently become important as an ultrafast probe in time-resolved experiments, in the femto- and attosecond domains, as well as in the description of many strong-field phenomena. However, the interpretation of such spectroscopic signatures requires that relaxation and correlation effects in the description of bound and continuum states are taken into account. The accurate description of the core excited states involved in the X-ray spectroscopy also presents specific challenges, that have for a long time prevented the application of electronic structure methods, like the coupled cluster ones, generally considered among the most reliable and accurate to describe excited states.

A key focus area of our research during the last decade has been the development of approaches, rooted on the coupled cluster ansatz, to address X-ray spectroscopic techniques like X-ray absorption (XAS) [1-11], emission (XES) [11-14], circular dichroism (XCD) [13], resonant inelastic x-ray scattering (RIXS) [12-14], photoelectron (XPS) [7,11,15], that are applied to probe both the electronic ground state and electronic excited states in a pump-probe [5,8,10,15] set up, and at different absorption edges. More recently, we have addressed the accurate determination of photoionization dynamic properties from the combined used of CC Dyson orbitals and B-spline DFT continuum [16].

An overview of the performance and capabilities of our methods will be presented.

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Restricted-Variance Molecular Geometry Optimization Based on Gradient-Enhanced Kriging

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Machine learning techniques, specifically Gradient-Enhanced Kriging (GEK), has been implemented for molecular geometry optimization. GEK has many advantages as compared to conventional -- step-restricted second-order truncated – molecular optimization methods. In particular, the surrogate model associated with GEK can have multiple stationary points, will smoothly converge to the exact model as the size of the data set increases, and contains an explicit expression for the expected average error of the model function at an arbitrary point in space. In this respect GEK can be of interest for methods used in molecular geometry optimizations. GEK is usually, however, associated with abundance of data, contrary to the situation desired for efficient geometry optimizations. In this presentation we will demonstrate how the GEK procedure can be utilized in a fashion such that in the presence of few data points, the surrogate surface will in a robust way guide the optimization to a minimum of a molecular structure. Thus the GEK procedure will be used to mimic the behavior of a conventional second-order scheme, but retaining the flexibility of the superior machine learning approach -- GEK is an exact interpolator. Moreover, the expected variance will be used in the optimization to facilitate restricted-variance rational function optimizations(RV-RFO). A procedure which relates the eigenvalues of the Hessian-model-function Hessian with the individual characteristic lengths, used in the GEK, reduce the number of empirical parameters to two – the value of trend function and the threshold for the variance. These parameters are determined using the extended Baker (e-Baker) test suite, at the HF level of approximation, and a single reaction of the Baker transition-state (Baker-TS) test suite as a training set. The so-created optimization procedure – RV-RFO-GEK – is tested using the e-Baker, the full Baker-TS, and the S22 test suites, at the DFT level for the two Baker test suites and at the second order Møller-Plesset level of approximation for the S22 test suite, respectively. The tests show that the new method is generally on par with state of the art conventional method, while for tricky cases exhibits a definite advantage.

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Silicon instead of Carbon – Silicon Amino Acids

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Silicon-containing amino acids represent a very interesting class of non-proteinogenic amino acids due to their unique properties. Silicon substitution results in resistance to degradation, increased lipophilicity, greater steric size and changes in electron density of such modified amino acids as well as peptides containing these improved residues [1].

One of the hypothetical areas of chemistry is silicon biochemistry related to the possible usage of silicon atoms as the basis of alternative biochemical structures. In general, silicon properties are similar to those of a carbon atom, hence, it is possible that this element could be used instead of carbon to form biological molecules on the other planets in the Universe where carbon does not appear. In our work we postulate the existence of the silicon analogues (i.e., silicon glycine, silicon alanine, and silicon valine) of three natural amino acids (i.e., glycine, L-alanine, and L-valine) which we suggest to term "SiAA" (Silicon Amino Acids).

The existence and gas phase stability of silicon glycine, silicon alanine and silicon valine were investigated theoretically on the basis of ab initio QCISD and MP2 calculations. All the molecules studied are structurally comparable to their proteinogenic counterparts and capable of forming several conformers as such. The IR spectra of the Si-Gly, Si-Ala, and Si-Val global minima were also simulated theoretically and discussed [2].

Taking into account that the predicted properties of the SiAA seem to be similar to those of their corresponding natural amino acids, we hope that the structures of these compounds, their interactions with other species and possible applications will be the subject of experimental investigations in the future.

Acknowledgments: The calculations have been carried out using resources provided by Wroclaw Centre for Networking and Supercomputing (http://wcss.pl) Grant No. 350.

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QM/ELMO Method: a Fully Quantum Mechanical Embedding Scheme Based on Extremely Localized Molecular Orbitals

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Embedding methods are computational strategies that undoubtedly allow to obtain the best compromise between accuracy and computational cost, especially when they are applied to large molecular systems. In this context, different techniques have been devised over the years and prominent places are occupied by the well known quantum mechanics/molecular mechanics (QM/MM) techniques [1] and the more recent density matrix and density functional embedding strategies [2].

In this context, we present the new quantum mechanics/extremely localized molecular orbital (QM/ELMO) approach [3, 4], namely a recently proposed multi-scale embedding technique in which the chemically active region of the investigated systems is treated at fully quantum mechanical level, while the remaining part is described through frozen extremely localized molecular orbitals [5] previously transferred from proper libraries [6] or tailor-made model molecules. Although the QM region could be initially treated only at Hartree-Fock (HF) level [3], the method has been afterwards extended to a large variety of quantum chemical approaches [4], ranging from density functional theory (DFT) to post-HF techniques (e.g., MP2 or Coupled Cluster). Extensions to methods for the treatment of excited states are also currently underway.

In this presentation, other than providing the theoretical details at the basis of the QM/ELMO embedding strategy, we will also show and discuss the results of preliminary test-bed calculations, which have been performed to assess the performances of the new method when it is applied to investigate chemical reactions, bond dissociations and intermolecular interactions. The obtained results have shown that, in practically all the cases taken into account, the new embedding approach enables to reproduce the results of the corresponding fully quantum mechanical computations within chemical accuracy, but with a significantly reduced computational cost, especially when correlated post-HF techniques are used to describe the quantum mechanical subsystem [4].

In light of this, we already plan to exploit the new QM/ELMO method (especially in its post-HF versions) to the study of more challenging problems, such as the modeling of enzyme catalysis, the study of excited states of biomolecules, and the refinement of macromolecular X-ray crystal structures.

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A state-specific multireference coupled-cluster method based on the bivariational principle

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One of the greatest challenges in electronic-structure theory is the *multireference* or *static/strong correlation* problem. For the single-reference situation (or dynamically correlated situation), the *de facto* standard approach is the conventional coupled-cluster (CC) method. The reason is that the CC hierarchy of methods is *polynomially scaling* and *size-consistent* under mild conditions. However, no unique and truly successful multireference coupled-cluster (MRCC) method exists. Indeed, one can say that the hunt for such a method is also a great challenge of quantum chemistry.

In this talk, we will present a novel MRCC approach, the bivar-MRCC method [1], based on the bivariational principle (BIVP), a formal generalization of the usual Rayleigh–Ritz variational principle to operators that are not necessarily self-adjoint (i.e., non-Hermitian in the finite-dimensional case) [2]. Our method is based on single-reference theory, and is therefore easy to learn, as opposed to most established MRCC methods. It uses a standard complete-active space approach, is size-consistent under mild conditions, scales polynomially, and can be efficiently implemented. While the theory contains a formal reference determinant, any artificial bias can to a large extent be eliminated by bivariational optimization, a powerful feature of the BIVP.

The BIVP is an elegant platform for development of CC type methods, as the bra and ket are independently parameterized using cluster operators, forming a unique non-Hermitian approximation to the state. While unconventional, the use of the bivariational principle has the important benefit that convergence and quadratic energy errors can en proven in the form of *a priori* error estimates [3]. The BIVP also allows transparent derivation of excited-state theory, properties of any order, and explicitly time-dependent electron dynamics.

After presenting the general theory, we show benchmark results for the insertion of Be into H_2, a small yet challenging problem for multireference methods due to the transition from single-reference to multireference and back, with a dramatic change in the dominant determinant along the reaction path. Comparing with established MRCC methods in the literature [4] such as internally-contracted MRCC (ic-MRCC), Mukherjee's state-specific MRCC (Mk-MRCC), and Adamowicz and coworkers' CASCC, we conclude that the bivar-MRCC method is of comparable accuracy and always within chemical accuracy for the tested systems. The moderate cost of bivar-MRCC method indicates that it has the potential to become a useful tool for the general quantum chemist.

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Triple natural orbital theory for three-body electron correlation

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Low-rank approximations that exploit the locality of electron correlation can reduce the cost of coupled-cluster calculations from N^7 for CCSD(T) to N for system size N. In pair natural orbital theory the principal way spatial locality is exploited is by truncating the space of doubles amplitudes on the basis of low-cost estimates of the first-order wavefunction. In this talk I will discuss the formal extension of pair natural orbital theory to three-body correlation and how this differs from earlier low-scaling triples approximations. I will then present a linear-scaling approach to computing the (T) energy that combines triple natural orbitals, triples principal domains of projected atomic orbitals and the Laplace transform approximation.

Vector extrapolation/convergence acceleration methods for solution of large systems of equations

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An important problem that arises in different areas of science and engineering is that of computing limits of sequences of vectors $\{\boldsymbol{x}_n\}$, where $\boldsymbol{x}_n \in \mathbb{C}^N$ with N very large. Such sequences arise, for example, in the solution of systems of linear or nonlinear equations by fixed-point iterative methods, and their limits are simply the required solutions of these systems. In most cases of interest, however, these sequences converge to their limits extremely slowly. One practical way to make these sequences converge more quickly is to apply to them *vector extrapolation methods*. In this lecture, we review three polynomial-type vector extrapolation methods that have proved to be very efficient convergence accelerators; namely, the *minimal polynomial extrapolation* (MPE) [1] and the *reduced rank extrapolation* (RRE) [2], [3], and *SVD-based minimal polynomial extrapolation* (SVD-MPE) [4]. We discuss their derivation, describe the most accurate and stable algorithms for their computer implementation along with the effective modes of usage, and present their convergence and stability theory. We also discuss their close connection with well known *Krylov subspace methods* for linear systems. Finally, we consider some applications of these methods, to the numerical solution of systems of nonlinear equations, summation of vector-valued power series, and computation of the PageRank of the Google Web matrix. For a detailed study of all aspects of vector extrapolation methods and their various applications, see the recent book by the author [5].

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An MP2 correction for accurate description of non-covalent interactions

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In this talk, I will present our recent advances in the description of non-covalent interactions by using the models for the adiabatic connection that has as weak-interaction expansion the Møller-Plesset (MP) perturbation theory. The resulting models provide a correction to MP2 correlation energy that comes at no additional computational cost. These models require no empirical dispersion correction, and for specific systems they are by an order of magnitude more accurate than MP2 (e.g. stacking and large complexes for which the MP series may even converge [1]). The resulting models have also enabled us to construct MP2 accuracy predictor (MAP) for weak interactions [2].

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Exponentially Correlated Hylleraas-configuration interaction non-relativistic energy of the ^1S ground state of the helium atom

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A generalization of the Hylleraas-configuration-interaction method (Hy-CI) [1] first proposed by Wang et al. [2], the Exponentially Correlated Hylleraas-configuration-interaction method (E-Hy-CI) in which the single r_{ij} of an Hy-CI wave function is generalized to a form of the generic type $r_{ij}^{\nu_{ij}} e^{-\omega_{ij} r_{ij}}$, i..e., an exponentially correlated Slater type orbital (STO), is explored. This type of correlation, suggested by Hirshfelder in 1960, has the right behavior both in the vicinity of the r_{12} cusp and as r_{12} goes to infinity, but until now there have been no calculations to prove whether wave functions containing both linear and exponential r_{ij} factors converge more rapidly than either one alone.

In this work are discussed the first E-Hy-CI calculations to date, which are on the ^1S ground state of the helium atom. The requisite two-electron repulsion and kinetic energy integrals have been evaluated analytically in a very stable and efficient way by relating them to the Gamma function of Harris [3] and solving them using recursion relations. The kinetic energy integral evaluation was also facilitated by a derivation using an exponentially correlated form of the Kolos and Roothan transformation and a parametric differentiation [4].

The parallelized calculations with quad-double with exponent (QDE) precision in a basis of s-, p-, d-, ... i-orbitals (l = 0,6) and optimization of the ω parameter lead to an energy result of more than 21 significant digits accuracy.

The convergence of the E-Hy-CI wave function expansion is compared with that of the Hy-CI wave function [5, 6] without the exponential factors, demonstrating both convergence acceleration and an improvement in the accuracy for the same basis. This fact makes the application of the E-Hy-CI method to systems with $N > 4$, for which this formalism with at most a single $r_{ij} e^{-\omega_{ij} r_{ij}}$ factor per term leads to solvable integrals, very promising.

Acknowledgments: The authors would like to dedicate this work to the memory of our great teacher and friend Stanley Hagstrom, the inspiration behind Hy-CI.

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Theoretical modeling of catalytic activity of complex processes catalyzed by transition-metal complexes

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Predicting the activity of the catalyst based on results computational studies is often challenging, since there exist many factors affecting the experimental measures of catalytic activity. Also, in the case of complex processes involving many alternative isomeric complexes at each stage of the process, not only the reaction barriers for the minimum energy pathways have to be taken into account, but as well the population of those alternative isomers that determine probability of the alternative pathways.

In this account, the results of theoretical (DFT) studies will be used to rationalize structure-activity relationship and to model the catalyst activity in the ethylene polymerization processes catalyzed by the half-metalocene complexes of titanium(IV) [1] and the CO_2/epoxide copolymerization with salen-based cobalt(III) catalysts. [2] In these processes, a large number of alternative isomers / huge conformational space result in a presence of many alternative polymer-propagation pathways, that must be taken into account in the modeling of catalytic activity.

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Matrix (in)equalities in the context of molecular excited-state quantum-chemical calculations

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During the past few years we focused our efforts on building and using models that provide improvements in the understanding of the behaviour of the electronic system of a molecule interacting with light. The tools we used in this context involve reduced density matrices and the natural orbitals representation of one-body reduced density (and transition density) operators. Depending on whether the eigendecomposition of the one-body difference density matrix or singular value decomposition of the one-body transition density matrix is concerned, two types of natural orbitals arise: the so-called natural difference orbitals (NDOs) and natural transition orbitals (NTOs), respectively. The two natural orbitals decompositions are then used to build two separate pairs of one-body charge density functions: detachment/attachment (D/A) densities from the NDOs; hole/electron densities from the NTOs. In this talk we will discuss how knowing the difference in essence between these two pairs of objects (and their origins) allows a disambiguation in the representation of an electronic transition in the case of the unrelaxed time-dependent density-functional theory (TDDFT) method. Without such a disambiguation, and considering the possibility to imply auxiliary many-body wavefunctions (three types will be introduced in the presentation), the representation of an unrelaxed TDDFT electronic transition would be either incomplete, arbitrary, or equivocal.

Besides, we will provide more matrix inequalities in the case where orbital relaxation is accounted for through the addition of the so-called Z-vector to the unrelaxed TDDFT one-body reduced difference density matrix, and few matrix equalities in the case where the D/A machinery is applied to unrelaxed/relaxed difference density matrix instead of ground/excited-state difference density matrix to measure and visualize the global effects of orbital relaxation on the electronic-structure reorganization occurring during the electronic transition.

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[1] More info and relevant references at thibaudetienne.wordpress.com

PySurf: a framework for database accelerated excited-state direct dynamics

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Photo-induced ultrafast processes often proceed on multiple electronic states and are controlled by nonadiabatic couplings between electronic and nuclear degrees of freedom. Theoretical strategies introduced for this purpose rely on two complementary approaches. Namely, quantum wave-packet propagation and full-dimensional semiclassical molecular dynamics. In both approaches potential energy surfaces are needed for the propagation, either by pre-computing and fitting them, which becomes infeasible for large systems, or by computing them on-the-fly, which is computationally demanding.

Herein, PySurf will be introduced as an innovative Python based code framework [1]. It is specifically designed for rapid prototyping and development tasks for data science applications in computational chemistry. It comes with a powerful Plugin and Workflow engine, which allows an intuitive customization for individual tasks. Data is automatically stored within the database framework, which enables interpolation of properties in previously evaluated regions of the conformational space. To illustrate the potential of the framework, a code for nonadiabatic surface-hopping simulations based on the Landau-Zener algorithm will be presented here, that allows full-dimensional nonadiabatic surface-hopping simulations using only adiabatic energies, leading to the so-called energy-only simulations. Simulations of pyrazine models and ab initio-based calculations of the SO_2 molecule show that energy-only calculations with PySurf are able to correctly predict the nonadiabatic dynamics of these prototype systems. The results reveal the degree of sophistication, which can be achieved by the data-based accelerated energy-only surface-hopping being competitive to fully quantum dynamical or commonly used semi-classical approaches.

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Oral presentations

Theoretical determination of polarizability and magnetic susceptibility of neon

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We report theoretical determination of the dipole polarizability of the neon atom, including its frequency dependence. Corrections for the relativistic, quantum electrodynamics, finite nuclear mass, and finite nuclear size effects are taken into account. We obtain the value $\alpha_0 = 2.66080(36)$ for the static polarizability, and $\alpha_2 = 2.850(7)$ and $\alpha_4 = 4.932(14)$ for the first two polarizability dispersion coefficients (Cauchy moments); all values are in atomic units (a.u.). In the case of static polarizability, our result agrees with the best experimental determination [1], but our estimated uncertainty is significantly larger. For the dispersion coefficients, the results obtained in this work appear to be the most accurate to date overall compared to published theoretical and experimental data. We also calculated the static magnetic susceptibility of the neon atom, needed to obtain the refractive index of gaseous neon. Our result, $\chi_0 = -8.484(19) \cdot 10^{-5}$ a.u., is about 9% larger in absolute value than the recommended experimental value [2].

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Second virial coefficient for helium from relativistic interaction potential

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Science relies on systems which can be both measured and described theoretically with good accuracy. Helium is a good example of such an entity. Knowledge of its properties, most notably the virial coefficients, is crucial to fundamental metrology [1, 2]. It can also be utilized in development of new pressure standards [3].

Helium atoms iteract very weakly – e.g. there is only one bound rovibrational state for a pair of helium-4 atoms and none for helium-3. Due to that, the virial coefficients can be mostly described in terms of the pair interaction potential, three- and more-body effects being important at larger pressures only. Because of simplicity of the system, the pair interaction potential can be calculated relatively accurately, and not only at the Born-Oppenheimer nonrelativistic level of theory, but also the adiabatic, nonadiabatic, relativistic and quantum-electrodynamic contributions can be included. We constructed such a potential and used it to calculate the second virial coefficient and the second acoustic virial coefficient for helium-4 and helium-3 for a range of temperatures (1K–1000K) [4].

The computed virial coefficients represent at least five-fold improvement in accuracy compared to the previous work [5]. They agree well with the most accurate recent measurements but have smaller uncertainty. The results will be presented during the presentation, together with a discussion of the methods we employed.

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High-accuracy Born-Oppenheimer potentials of excited states of hydrogen molecule

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We present high-accuracy Born-Oppenheimer potentials for variety of bound states of H_2 calculated with the upgraded version of H2SOLV [1]. This numerical package is capable of high-precision variational calculations of Born-Oppenheimer energy of almost any bound state (Σ, Π, Δ and Φ) of diatomic molecule. Based on efficient computational method [2] with explicitly correlated exponential functions, it allows for multithreaded, large-scale computations limited only by the computer resources available and can produce results of relative accuracy better than 10^{-12}.

Employing explicitly correlated functions has proven essential to obtain highly accurate results required to numerically resolve long-standing controversy of long-range asymptotics of exchange energy [3]. Excited states calculations performed with improved H2SOLV provide valuable input to Multichannel Quantum Defect Theory (MQDT) applied to Rydberg states and find direct applications to frequency-dependent polarizability calculations and more.

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NMR Spin–Spin Coupling Constants Derived from Relativistic Four-Component DFT Theory - Analysis and Visualization

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An unambiguous assignment of coupling pathways plays an important role in the description and rationalization of NMR indirect spin–spin coupling constants (SSCCs). Unfortunately, the SSCC analysis and visualization tools currently available to quantum chemists are restricted to non-relativistic theory. Here we present the theoretical foundation for novel relativistic SSCC visualization techniques based on analysis of the SSCC densities and the first-order current densities induced by the nuclear magnetic dipole moments. Details of the implementation of these techniques in the ReSpect program package are discussed. Numerical assessments are performed on through-space SSCCs, choosing as our examples the heavy-atom Se-Se, Se-Te and Te-Te coupling constants in three similar molecules for which experimental data are available. SSCCs were calculated at the nonrelativistic, scalar relativistic and four-component relativistic density functional levels of theory. Furthermore, with the aid of different visualization methods we discuss the interpretation of the relativistic effects, which are sizable for Se-Se, very significant for Se-Te, and cannot be neglected for Te-Te couplings. A substantial improvement of the theoretical SSCC values is obtained by also considering the molecular properties of a second conformation.

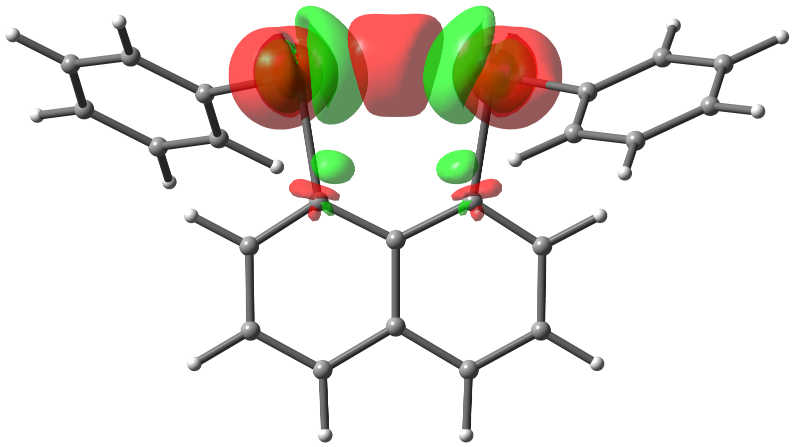

Figure 1: Te-Te scalar relativistic through-space SSCC pathway

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Understanding of the Quantum Nature of Electron Transfer and Explaining Spectral Asymmetries in Photosynthetic Bacteria Reaction Center: Screened Range-Separated Hybrid Functionals

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Spectral peaks of the special pair (P) and adjacent pigments in the bacterial reaction center (BRC) are investigated computationally. We employ a novel computational framework based on a polarization-consistent treatment of the dielectric environment, combining the polarizable continuum model (PCM) with time-dependent screened range-separated hybrid density functional theory (TD-SRSH-DFT). Our calculations quantitatively reproduce the recently measured spectral peak splits between P states, and spectral asymmetries within pairs of the adjacent bacteriochlorophyll a (BChl) and bacteriopheophytin a (BPhe) pigments. Measured spectral trends are correctly reproduced [1] based on X-Ray resolved structures (1PCR and 2J8C), and where the effect of neighboring pigments on the electronic structure is addressed through an effective dielectric environment.

We have calculated the charge transfer rates within the pair and investigate the rectification ratio. We identify the roles of stereo structural asymmetry between the two BChl units and of the dielectric environment in stabilizing and discriminating between the CT processes. We also identify the specific structural mode that breaks the symmetry between the two units leading to the rectified CT behavior [2]. Excitation energies, oscillator strengths, electronic couplings are obtained by the use of TDDFT employing a recently developed framework based on SRSH within a polarized continuum model (PCM).

We also analyze the inherited charge rectification, $P_A{+}P_B{}^-$, of special pair and CT to active branch A, $(P_A{+}P_B)B_A{}^-$, with and without [His-M202][Tyr-M210][H2O] bridge groups between P_B and B_A. For special pair, we found unique two lower CT states, one is blue shifted, both characterized as $P_A{+}P_B{}^-$, at $\epsilon = 3.5$ at which also there occurs highest rate of CT to the active branch, characterized as $(P_A{+}P_B)B_A{}^-$. We attributed this dominated charge separation to the strong symmetry breaking between two possible intrapair CT processes due to bridge groups. We realized the effect of the functional groups of special pair on the CT process [3].

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Representation of continuum wavefunctions by complex Gaussians: application to photoionization processes

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Real Gaussians (r-Gs) are widely used in computational chemistry and molecular physics because they make easy a number of integration, in particular the *Gaussian product theorem* allows the evaluation of multicenter integrals in closed form (see, for instance, [1] and references therein). While r-Gs are able to deal with low-lying bound states, their use to represent highly oscillating continuum states is a priori not appropriate and results to be numerically very challenging if large radial domains are to be considered. On the other hand, complex Gaussians (c-Gs), that it to say Gaussians with complex exponents, possess an intrinsically oscillatory behavior. For this reason, they offer an alternative and possibly more suitable way of representing continuum states.

In a recent investigation [2], we presented and implemented a computational method that optimizes a set of Gaussians and we highlighted the advantage of c-Gs over r-Gs when dealing with non-vanishing continuum states. The efficiency of c-Gs has been successfully illustrated by considering the hydrogen ionization by both electron and photon impact. The corresponding cross sections are obtained from matrix elements $\langle \psi_f^- | \widehat{O} | \psi_i \rangle$, where the operator $\widehat{O}$ describes the transition between initial ψ_i and final ψ_f^- states. Adopting an all-Gaussian approach in which both the initial and final states are expanded in Gaussians, the resulting radial integrals are all very simple and analytically performed. Closed form expressions for the cross sections allowed us to benchmark our numerical method.

More recently, we have extended our study to molecular photoionization in the single-active-electron approximation, and considered the CH_4, NH_3 and H_2O molecules. Their initial states is taken as one-center expansions over Slater-type orbitals [3, 4, 5]. The ejected electron is described by a pure Coulomb wave (with unit charge) or a distorted wave issued from a model central potential: in either case the radial functions are fitted by c-Gs. In this molecular application the radial integrals were performed both analytically and numerically. Our cross section calculations confirm the reliability of optimized sets of c-Gs to represent continuum states over sufficiently large radial distances.

Work is ongoing to extend our proposal to study ionization processes with molecular targets where ψ_i is given by multicenter expansions on Gaussians, and thus to deal with multicenter integrals.

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Singly linked Hylleraas method for four electron atom

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Hylleraas method is routinely used to yield extremely accurate results for two and three electron systems, such as helium [1] and lithium [2] atoms. For few electron systems with four [3] and more [4] electrons most accurate results are obtained using explicitly correlated Gaussian functions, due to the lack of efficient methods of computation of matrix elements with Hylleraas type basis functions.

Using recent developments for three [5] and four [6] electron integrals we perform variational computations based on the Hylleraas method. In order to make such calculations feasible, we restrict basis set to the singly-linked form

$$\Psi = \sum_k c_k r_{a,b}^n \prod_i^N \phi_k(i), \quad 0 < a < b < N, \tag{1}$$

where N-electron product of Slater type orbitals (ϕ_k) and single correlation factor in monomial form ($r_{a,b}^n$) is taken for each term of linear combination.

Working program for systems up to four electrons is developed and used to study convergence of the method for lithium and beryllium atoms and compare it against existing results. In this communication we present results of these computations and perspectives for future extensions.

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Estimation of Dipole Polarizability for Excited States

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Accurate determination of the ground state dipole polarizability tensor α is now almost a routine calculation. For the electronic excited states both experimental and computational studies are relatively rare. In this study we want to assess the performance of a simple approach based on the combination of the well-known TDDFT method and the numerical Finite Field (FF) technique. This approach was successfully used to determine dipole polarizability of the low-lying states of uracil [1]. Recently, two advanced approaches have been developed and implemented. The first one is based on the EOM-CCSD-EE formalism [2], and the second uses algebraic-diagrammatic construction for the polarization propagator (ADC) method [3]. Both methods were tested on a series of small organic molecules.

We use widely used CAM-B3LYP, and M062X and ωB97X functionals, Pol basis sets designed for the efficient evaluation of molecular electric properties, and geometries of the studied organic molecules from [2]. Generally, our TDDFT/FF results agree very well with the results from [2] and [3]. The case of the excited states of *para*-nitroaniline of a charge-transfer character proved challenging, but even here our results are reasonably close to the elaborated EOM-CCSD-EE results of Krylov [2].

We also studied B_1 and A_2 Rydberg states of H_2O. We compare our TDDFT results with the CASSCF data [4] and here, as expected, we can only claim a modest success. Using the complex polarization propagator formalism, *e.g.* [5], within the framework of the CASSCF method for the excited states allows us to study components of the dynamic polarizability tensor $\alpha(\omega)$ for a wide range of frequencies. As a final test of the accuracy of our approach we determined C_6 dispersion coefficients for the ground and excited states of water.

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