ICQC 2023

Satellite Meeting on Strong Correlation in Molecules

20 - 23th June
Znojmo, Czech Republic

J. Heyrovský Institute of Physical Chemistry

WIGNER

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About

17th International Congress of Quantum Chemistry

The International Congress of Quantum Chemistry (ICQC) is held triennially under the patronage of the International Academy of Quantum Molecular Science. It is a unique opportunity for scientists working in the field of theoretical and computational chemistry to present and discuss the latest developments and research advances. The first ICQC took place in Menton, France, in 1973, where it also returned 45 years later for its 16th iteration. The 15th congress, in 2015, took place in Beijing, China.

The 17th ICQC scientific program will be composed of invited plenary lectures, selected invited contributions and presentations, and discussions in two poster sessions. Invited contributions will be selected by the Local Organizing Committee and the International Advisory Committee. Priority will be given to recent interesting new ideas and presentations by young scientists.

Satellite Meeting on Strong Correlation in Molecules

Satellite Meeting on Strong Correlation in Molecules is organized by J. Heyrovský Institute of Physical Chemistry CAS, Czech Republic and Wigner Research Centre for Physics, Hungary. Satellite meeting will be held in the Moravian town of Znojmo, Czech Republic on June 20-23, 2023. In addition to the Invited Lectures, the scientific programme offers tentatively 18 slots for shorter Contributed Talks. Student participants will be enrolled in a competition for outstanding posters and the best poster prize will be awarded on thursday evening.

Organizing committee

Jiří Pittner   Örs Legeza

Technical support

Jakub Martinka

Timetable

C : Contributed Talk, I : Invited talk.

Tuesday, 20 of June

13:00–15:00	**Registration**		
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Chair:	**Jiří Pittner**		
15:10–15:45	I1	**Simen Kvaal**	Development of multireference coupled-cluster methods from singlestate and multistate bivariational principles
15:45–16:20	I2	**Karol Kowalski**	Sub-system self-consistency in coupled-cluster theory
16:20–16:40	C1	**Jan Brandejs**	Generating coupled cluster code for modern distributed memory tensor software
16:40–17:10	**Coffe Break**		
Chair:	**Henrik Larsson**		
17:10–17:45	I3	**Christian Schilling**	The Electron Correlation Problem from a Quantum Information Perspective
17:45–18:05	C2	**Mihály Máté**	Compressing multireference character of wave functions via fermionic mode optimization
18:05–18:25	C3	**Lexin Ding**	Quantum Information-Assisted Complete Active Space Optimization (QICAS)
18:25–18:45	C4	**Gabriel Rodrigues**	Multiconfigurational Pair-Density Functional Theory is More Complex Than You May Think
18:45–20:00	**Dinner**		

Wednesday, 21 of June

Chair:	**Karol Kowalski**		
8:25–9:00	I4	**Ágnes Szabados**	Spin-violating geminal wave functions and their correction by peturbation theory
9:00–9:35	I5	**Gustavo Scuseria**	Strong-weak dualities for spin systems
9:35–9:55	C5	**Matej Veis**	Many-body Perturbation Theory formulated in terms of physically motivated parameters for 1D atomic chains
9:55–10:15	C6	**Peter Surjan**	To which extent can strong correlation be treated by single reference perturbati on theory?
10:15–10:45	**Coffe Break**		
Chair:	**Christian Schilling**		
10:45–11:20	I6	**Artur Izmaylov**	Quantum computing approaches to strongly correlated systems
11:20–11:55	I7	**Henrik Larsson**	Tensor network states for computing vibrational and electronic states
11:55–12:15	C7	**Hugh Burton**	Unitary product states: A quantum-compatible approach for strong correlation
12:15–13:45	**Lunch**		
Chair:	**Örs Legeza**		
13:45–14:20	I8	**Markus Reiher**	Tensor Train Methods for Stationary and Dynamical General Many-Particle Problems
14:20–14:55	I9	**Nicholas Mayhall**	New tensor product state approximations for strongly correlated molecules
14:55–15:15	C8	**Mikuláš Matoušek**	Adding dynamic correlation to DMRG via adiabatic connection
15:15–15:35	C9	**Szymon Śmiga**	The Kohn-Sham calculations with Adiabatic Connection Models with Improved Treatment of the Strong-Interaction Limit
15:35–16:05	**Coffe Break**		

Chair:	**Peter Surjan**		
16:05–16:40	I10	**Gero Friesecke**	Recent theoretical results on the QC-DMRG method
16:40–17:00	C10	**James Shee**	Capturing both weak and strong correlations in transition metal chemistry using classical and quantum methods
17:00–17:20	C11	**Paul Johnson**	Strong Electronic Correlation with Richardson-Gaudin States
17:20–17:40	C12	**Jiří Klimeš**	Understanding the accuracy of random phase approximation for binding energies
17:40–18:00	C13	**Johann Pototschnig**	Relativistic effects and orbital contributions to the electric field gradient
18:00–19:30	**Dinner**		
19:30–22:00	**Poster session**		

Thursday, 22 of June

Chair:	**Mihály Kállay**		
8:25–9:00	I11	**Masaaki Saitow**	Reduced-Scaling Multireference Perturbation Theories using Orthonormal Localized Virtual Orbitals
9:00–9:35	I12	**Daniel Kats**	Ten years of the Distinguishable Cluster: Past, Present and Future
9:35-9:55	C14	**Hiroshi Nakatsuji**	Quantum chemistry with accurate solutions of the Schrödinger equation
9:55-10:15	C15	**Jaroslav Hofierka**	Many-body theory of positron interactions with polyatomic molecules
10:15–10:45	**Coffe Break**		
Chair:	**Ágnes Szabados**		
10:45–11:20	I13	**Mihály Kállay**	Explicitly correlated coupled-cluster methods including triple and quadruple excitations

11:20–11:55	I14	**Alex Thom**	Holomorphic Hartree-Fock Theory: A basis for multireference electronic structure
11:55-12:15	C16	**Éva Zsuzsanna Mihálka**	Exploring amplitude functions in the coupled-cluster framework - an alternative approach to convergence improvement
12:15–13:45	**Lunch**		
13:45–19:00	**Free afternoon/Excursion**		
19:00–24:00	**Conference Dinner**		

Friday, 23 of June

Chair:	**Gustavo Scuseria**		
9:00–9:20	C17	**Maarten van Damme**	
9:20–9:40	C18	**Jeremy Coe**	Analytic Gradients for Selected Configuration Interaction: Development and Applications
9:40-10:15	I15	**Dominika Zgid**	GW in Gaussian Bloch Orbitals for solids relativistic effects, pseudopotentials, and impact of different self-consistency cycles
10:15–10:45	**Break**		
Chair:	**Miroslav Urban**		
10:45–10:55			Personal reminiscences of Joe Paldus
10:55–11:40	I16	**Piotr Piecuch**	Externally Corrected Coupled-Cluster Methods: Review and Recent Progress
11:40-12:25	I17	**Rodney Bartlett**	Alternative Single Reference Coupled-cluster approaches for multi-reference problems: pCCD+TCCSD for Excited States
12:25–12:30	**Closing**		
12:30–14:00	**Lunch**		

List of Abstracts – Talks

Tuesday, 20 of June

Development of multireference coupled-cluster methods from singlestate and multistate bivariational principles

Simen Kvaal[1,*], **Reinhold Schneider**[2] , **Tilmann Bodenstein**[1], **Andre Laestadius**[3,1]
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I1

The bivariational principle due to Arponen and Löwdin [1,2] is a useful reformulation of the Schrödinger equation and a natural foundation for single-reference coupled-cluster theory and state-specific multireference theory [3]. It also provides a framework for mathematical a priori error analysis [4], and is a natural starting point for introducing internal corrections to externally corrected coupled-cluster methods such as tailored coupled-cluster theory using tensor-network states [5, 6]. After discussing the singlestate case, I describe a novel multistate bivariational principle which could be a natural foundation for multistate (state-universal) multireference coupled-cluster methods. I discuss some multireference coupled-cluster approaches that are under investigation inour team.

[1] J. S. Arponen, Ann. Phys., **151** (1983), 311–382.
[2] P. O. Löwdin, J. Math. Phys., **24** (1983), 70–87.
[3] T. Bodenstein, S. Kvaal, J. Chem. Phys., **153** (2020), 024106.
[4] A. Laestadius, S. Kvaal, SIAM J. Numer. Anal., **56** (2018), 660–683.
[5] L. Veis, A. Antalik, J. Brabec, F. Neese, Ö. Legeza, J. Pittner, J. Phys. Chem. Lett., **7** (2016), 4072–4078.
[6] S. Kvaal, arXiv:2205.08792v1
[7] S. Kvaal, *et al.*, in preparation.

Sub-system self-consistency in coupled-cluster theory

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I2

The double unitary coupled cluster (DUCC) ansatz [1], an extension of the subsystem embedding sub-algebras coupled cluster (SES-CC) formalism [2], allows one to include dynamical (outside the active space) correlation effects in a complete active space effective Hamiltonian. In contrast to the standard single-reference SES-CC theory, the unitary CC approach results in a Hermitian form of the effective Hamiltonian, which has been promising for quantum computing applications, among others. We will review the DUCC theory in this presentation and discuss its time-dependent extension [3] and the recent high-performance implementation. We will discuss the effect of the commutator expansion in approximations [4] and demonstrate the applicability of the DUCC approach through several ground- and excited-state applications.

[1] N. P. Bauman, E. J. Bylaska, S. Krishnamoorthy, G. H. Low, N. Wiebe, C. E. Granade, M. Roetteler, M. Troyer, K. Kowalski, J. Chem. Phys., **151** (2019), 014107.
[2] K. Kowalski, J. Chem. Phys., **148** (2018), 094104.
[3] K. Kowalski, N. P. Bauman, J. Chem. Phys., **152** (2020), 244127.
[4] N. P. Bauman, K. Kowalski, J. Chem. Phys., **156** (2022), 094106.

Generating coupled cluster code for modern distributed memory tensor software

Jan Brandejs[1], **Johann Pototschnig**[1], **André Gomes**[2], **Trond Saue**[1]
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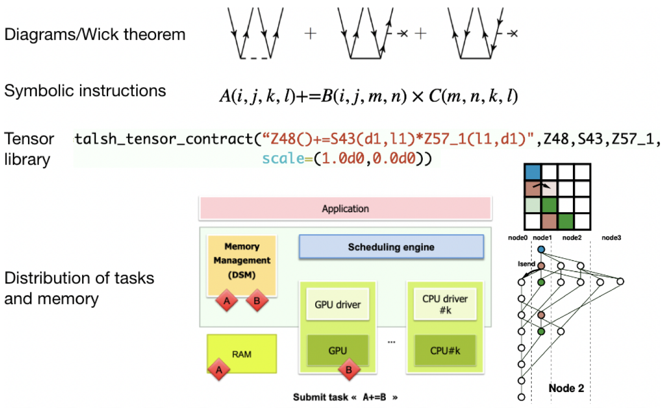
[2] Laboratoire de Physique des Lasers, Atomes et Molécules, CNRS, Lille, France

C1

The goal of this project is to design a set of software tools for elegant development of relativistic coupled clusters methods.



```
talsh_tensor_contract("Z48()+=S43(d1,l1)*Z57_1(l1,d1)",Z48,S43,Z57_1,
                      scale=(1.0d0,0.0d0))
```

Figure 1: The workflow scheme of the **tenpi** toolchain includes a code generator, intermediate optimizer and a unified interface towards tensor libraries. Fig. from [1]

Modern computer architectures are composed of heterogeneous processing and memory hierarchies. Data movement cost often dominates the cost of computation and only a fraction of peak CPU/GPU power is used. Despite this, most software still uses programming systems lacking any reasoning about the placement and movement of data.

Unlike BLAS for matrix operations, there is no unified tensor interface/library used by the community. Available distributed memory libraries used for chemical applications are not adapted to heterogeneous architectures. The **tenpi** toolchain addresses this problem.

Motto: *"Separate science from the computational platform."*

The first application of the **tenpi** toolchain is on molecular properties as part of the HAMP-vQED project [2]. Studies so far indicate that QED-effects (electron self-energy and vacuum polarization) reduce relativistic effects by about 1%. However, such investigations have been limited to valence properties, since there are currently no reliable tools for general molecules to study the core region, where QED-effects are generated [3].

[1] https://starpu.gitlabpages.inria.fr, visited 2. 6. 2023.
[2] A. Sunaga, M. Salman, T. Saue, J. Chem. Phys., **157** (2022), 164101.
[3] P. Pyykkö, J. F. Stanton, Chem. Rev., **112** (2012), 1.

The Electron Correlation Problem from a Quantum Information Perspective

Christian Schilling[1]

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I3

Describing strongly interacting electrons is one of the crucial challenges of modern quantum physics. A comprehensive solution to this electron correlation problem would simultaneously exploit *both* the pairwise interaction and its spatial decay. By taking a quantum information perspective, we explain how this structure of realistic Hamiltonians gives rise to two conceptually different notions of correlation and entanglement. The first one describes correlations between *orbitals* while the second one refers more to the *particle* picture. We illustrate those two concepts of orbital and particle correlation and present measures thereof. Our results for different molecular systems reveal that the total correlation between molecular orbitals is mainly classical, raising questions about the general significance of entanglement in chemical bonding. Finally, we also speculate on a promising relation between orbital and particle correlation and explain why this may replace the obscure but widely used concept of static and dynamic correlation.

Compressing multireference character of wave functions via fermionic mode optimization

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C2

The aim of the localization of orbitals in quantum chemistry is twofold. On the one hand, localization leads to chemically intuitive orbitals for rationalizing electronic structure of molecular systems. On the other hand, localized molecular orbitals has proven to be useful in making the high-level correlated quantum chemical methods more tractable computationally. These methods usually involve the optimization of the expectation value of specific physical quantities (e.g., radial extent or charge of the orbitals).

A brief overview of the orbital optimization is presented within the framework of tensor network state (TNS) methods, and demonstrate that it has the potential to compress the multireference character of the wave functions after finding optimal molecular orbitals (modes), based on entanglement minimization. This is the quantum chemical application of the more general fermionic mode transformation [1], which is a joint optimization approach that optimizes both the tensors and the modes simultaneously. This strategy is expected to lead to a routine application of TNS methods for strongly correlated multireference problems.

Numerical simulations have been performed for the nitrogen dimer in the cc-pVDZ orbital set for the equilibrium and for stretched geometries [2].

[1] C. Krumnow, L. Veis, Ö. Legeza, J. Eisert., Phys. Rev. Lett., **117** (2016), 210402.
[2] M. Máté, K. Petrov, S. Szalay, Ö. Legeza, J. Math. Chem., **61** (2022), 362–375.

Quantum Information-Assisted Complete Active Space Optimization (QICAS)

L. Ding[1,2], **S. Knecht**[3,4], **C. Schilling**[1,2]
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[2] Munich Centre for Quantum Science and Technology, Germany
[3] Algorithmiq, Helsinki, Finnland
[4] ETH Zürich, Switzerland

C3

Automated active space selection is arguably one of the most challenging and essential aspects of multiconfigurational methods. If accomplished, it would elevate active space methods such as CASSCF to complete black-box machineries. As it turns out, this may be systematically achieved, by using precise quantum information tools for electronic structure analysis [1-5]. In particular, based on a preceding low-cost calculation, suitable active orbitals can be selected in an *ab initio* manner based on their unique high entanglement profile [4].

In this work we take these promising ideas to the next level by proposing a quantum information-assisted complete active space optimization method (QICAS) [6]. Instead of just selecting active orbitals as the most entangled Hartree-Fock orbitals, we *transform* the active space by minimizing the entanglement of the complementary inactive orbitals, which results in remarkably accurate optimal active orbitals. For instance, for C_2, the energy of a post-QICAS CASCI calculation matches nearly exactly with the CASSCF one.

Accordingly, our study reveals and validates for the first time a profound empirical statement: the optimal inactive space contains the least entanglement. This in turns inspires an energy-free orbital optimization method which places most of the correlation within the optimal active space. For challenging systems, QICAS offers an ideal starting point, from which the number of expensive CASSCF iterations needed for chemical accuracy is greatly reduced.

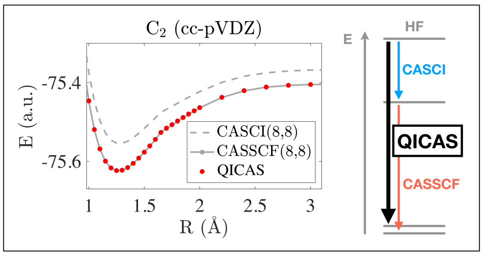

Figure 1: i-CAS energy compared to CASCI and CASSCF energies for C_2 in cc-pVDZ basis.

[1] L. Ding, S. Mardazad, S. Das, S. Szalay, U. Schollwöck, Z. Zimborás, C. Schilling, J. Chem. Theory Comput., **17** (2021), 79-95.
[2] L. Ding. S. Knecht, C. Schilling, Quantum Sci. Technol., **8** (2023), 015015.
[3] C. Krumnow, L. Veis, Ö. Legeza, J. Eisert, Phys. Rev. Lett., **117** (2016), 210402.
[4] C. J. Stein, M. Reiher, J. Chem. Theory Comput., **12** (2016), 1760-1771.
[5] M. Bensberg, M. Reiher, J. Phys. Chem. Lett., **14** (2023), 2112-2118.
[6] L. Ding, S. Knecht, C. Schilling, forthcoming.

Multiconfigurational Pair-Density Functional Theory is More Complex Than You May Think

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C4

Among different methods that have been proposed for combining DFT with MCSCF, the multiconfigurational pair-density functional theory (MC-PDFT) [1] approach is one of the most popular. In MC-PDFT, instead of taking spin-densities as our functional arguments as in standard spin-density DFT (SDFT), we define it in terms of the total density ρ and the on-top pair density Π. This idea is a generalization of KS-DFT and it was already suggested in 1995 by Becke, Savin and Stoll [2], upon realizing that SDFT can lead to unphysical results, *e.g.* failing to describe the degeneracy of the three triplet components.

The standard SDFT functionals can be translated to PDFT functionals so that they give identical results for a single determinant by using the relations between ρ, Π and the usual spin-densities: $\rho(r) = \rho_\alpha(r) + \rho_\beta(r)$ and $\Pi(r) = 2\rho_\alpha(r)\rho_\beta(r)$, resulting in a pair of solutions that correspond to α and β densities:

$$\rho_{\alpha/\beta} = \frac{\rho \pm \sqrt{\rho^2 - 2\Pi}}{2} \tag{1}$$

Observing Eq. 1, the value in square root can be negative in some conditions, making our densities complex with non-zero imaginary component. This problem was already noticed in the 1995 article where the authors showed that this would happen in a spin-adapted open-shell singlet. Despite the fact that this configuration is relatively common, the wide popular implementation of Li Manni [3] neglected theses cases by setting the square root to zero (absence of spin-polarization) or resorting to an *ad-hoc* modification of the translation formula to smooth its behavior around 0.

In this work we present a new implementation of MC-PDFT that is not only variationally optimized, but considers the complex nature of Eq. 1 and extends the translation to cases where $\phi^2 - 2\Pi$ is negative. The implementation was done in the very efficient massively parallel MultiPsi code and it is noteworthy that the resulting algorithm is more efficient than standard MCSCF, at roughly the cost of regular DFT for small to medium active spaces.

Finally, we showcase both the performance of variational MC-PDFT and the importance of the new translation by benchmarking on several examples, including a number of singlet-triplet gaps and open-shell singlets from low-lying excited states. Our results show that our new translated formulas improved the accuracy of MC-PDFT for PDFT versions of SLDA and PBE, and it is the way to go when translating spin-density functionals to on-top pair density ones.

[1] G. Li Manni, R. K. Carlson, S. Luo, D. Ma, J. Olsen, D. G. Truhlar, L. Gagliardi, J. Chem. Theory Comput., **10** (2014), 3669-3680.
[2] A. D. Becke, A. Savin, H. Stoll, Theor. Chim. Acta, **91** (1995), 147-156.
[3] R. K. Carlson, D. G. Truhlar, L. Gagliardi, J. Chem. Theory Compu., **11** (2015), 4077-4085.

Wednesday, 21 of June

Spin-violating geminal wave functions and their correction by peturbation theory

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I4

We review our work on strongly orthogonal two-electron functions (geminals) for capturing static correlation. Violation of geminal spin is admitted in order to overcome the shortcomings of the perfect pairing approximation in this framework. Performance of the geminal reference based correction step for describing dynamic correlation is a sensitive function of the extent of spin contamination. Breakdown of perturbation theory (PT) may be observed, analogously to the case of unrestricted Hartree-Fock based Moller-Plesset treatment.

We get around the problem by restoring the spin of the geminal product via full projection and half-projection (HP) with subsequent variation[1,2]. A necessary drawback of spin purification by projection, size-inconsistency is assessed in numerical terms. A further facet of projective schemes is the reference becoming a linear combination of geminal products, interfering with a geminal Hamiltonian based construction of the zero-order operator of PT. For this reason a dynamic correlation treatment, not assuming any special structure of the zero-order function, termed multi-configuration PT is investigated[3]. We also explore adopting the formalism of symmetry adapted PT (SAPT)[4], with HP playing the role of the symmetry operator involved[5]. Numerical tests on singlet-triplet gaps of biradicaloids illustrate the performance of the PT schemes.

[1] P. Jeszenszki, P. R. Surján, Á. Szabados, J. Chem. Theory Comput., **11** (2015), 3096.
[2] Zs. É. Mihálka, P. R. Surján, Á. Szabados, J. Chem. Theory Comput., **16** (2020), 892.
[3] Zs. É. Mihálka, Á. Szabados, P. R. Surján, J. Chem. Phys., **154** (2021), 234110.
[4] B. Jeziorski, R. Moszynski, K. Szalewicz, Chem. Rev., **94** (1994), 1887.
[5] Zs. É. Mihálka, P. R. Surján, Á. Szabados, J. Chem. Theory Comput., **17** (2021), 4122.

Strong-weak dualities for spin systems

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I5

The Jordan–Wigner (JW) transformation establishes a duality between su(2) and fermionic algebras. This means that full CI is identical in both frames, but approximations are not. I will present qualitative arguments and numerical evidence showing that when mapping spins to fermions, the transformation makes strong correlation weaker [1]. The presence of many-body JW strings operators has been traditionally viewed as a fundamental obstacle for the implementation of many-body methods on the transformed fermionic Hamiltonian. However, strings are Thouless rotations, and can be dealt with at low computational cost. Our proof of principle results for the Heisenberg XXZ and J1-J2 Hamiltonians (in 1D and 2D) demonstrate that the fermionic frame provides a better starting point for addressing challenging spin problems.

[1] T. M. Henderson, G. P. Chen, G. E. Scuseria, J. Chem. Phys., **157** (2022), 194114.

Many-body Perturbation Theory formulated in terms of physically motivated parameters for 1D atomic chains

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C5

Contributions to the correlation energy at MP2 level are examined for a finite chain of hydrogen atoms. We demonstrate that restricting oneself to a subset of MP2 terms, such as pair-states, either doesn't involve a scaling reduction or vanishes at the thermodynamic limit†. Similarities between the terms do appear, and allow for them to be classified by three effective parameters, i.e. momentum transfer, depth and asymmetry of the corresponding diagram. Formulating the perturbative series with respect to these physically motivated parameters not only gives an insight regarding the magnitude of terms, but also allows for their separation into similar groups. Integrating over such groups leads to a size extensive scheme, with bounds on error, that does involve a scaling reduction. As a proof of concept the method was benchmarked against full MP2 and CCSD with STO-6G and cc-pVDZ.

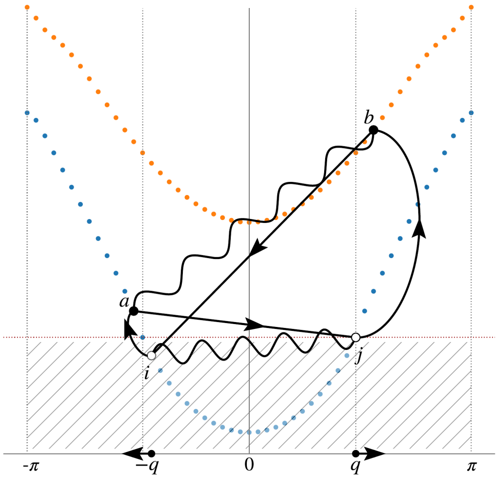

Figure 1: Exchange diagram of a two band H_{50} chain at quarter filling. Conservation of momenta restricts the momentum transfers $\mathbf{q}_{i\to a}$ and $\mathbf{q}_{j\to b}$ to be of same magnitude and opposite direction. Number of diagrams with given $\mathbf{q}$ is porportional to $\mathbf{q}^2$ and the magnitude is observed to sharply decay with increasing $\mathbf{q}$. Implications associated to dimensionality, the multi-band nature, and the role of the other two effective parameters are discussed.

[1] S. Kedžuch, J. Šimunek, M. Veis, J. Noga, J. Chem. Theory Comput., **16** (2020), 7372-7380.

[2] M. Veis, PhD. Thesis, Perturbative and coupled cluster methods utilizing the concept of electronic pair states, and the study of electronic, Comenius University Bratislava 2023.

†: This statement remains valid, for 1D chains at half-filling, regardless of the choice of the subset. Note that the scaling reduction associated with the translational symmetry is already acounted for.

To which extent can strong correlation be treated by single reference perturbation theory?

András Gombás[1], **Zsuzsanna É. Mihálka**[1], **Ágnes Szabados**[1], **Péter Burlacu**[1], **Péter R. Surján**[1]

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C6

Single-reference many-body perturbation theory, performed in the basis of either canonical or some localized orbitals, is a standard tool for the estimation of the electronic correlation energy in molecular systems. However, it usually fails when applied in the strong correlation regime. This failure can be manifested in improper low-order contributions as well as in the divergence of the perturbation series. Multi-reference perturbation theory is an obvious remedy, but it requires a complicated formalism, may get expensive for large reference spaces, and sometimes violates the extensivity requirement.

Therefore, interest remains in investigating less-standard formulations and techniques of single reference perturbation theories which may treat strongly correlated electronic systems to some extent. We shall consider two different possibilities:

1. Replacing the standard Fockian of Møller-Plesset partitioning by an alternative one-body zero-order Hamiltonian

2. Applying some kind of resummation techniques in divergent cases.

As to 1, we shall discuss the so-called *Dyson partitioning*[1] in which the canonical orbital energies in the denominators are replaced by correlated ionization potentials emerging from, e.g., the Dyson equation, and the *Knowles partitioning*[2], in which special equations are solved for obtaining a better one-electron zero order Hamiltonian prior to computing the perturbation corrections. As to 2, we shortly discuss analytic continuation methods including extrapolation[3,4] with quadratic Padé approximants and the so-called inverse boundary problem[5] technique.

[1] P. R. Surján, Á. Szabados. Int. J. Quantum Chem., **69** (1998), 713.
[2] P. J. Knowles. J. Chem. Phys., **156** (2022), 011101.
[3] Zs. É. Mihálka, P. R. Surján. Phys. Rev. A, **96**, (2017), 062106.
[4] Zs. É. Mihálka, Á. Szabados, P. R. Surján. J. Chem. Phys., **150** (2019), 031101.
[5] Zs. É. Mihálka, P. R. Surján, Á. Szabados, Theor. Chem. Acc., **137** (2018), 149.

Quantum computing approaches to strongly correlated systems

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I6

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

Tensor network states for computing vibrational and electronic states

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I7

Mostly independently from each other, the fields of electronic structure and vibrational quantum dynamics developed powerful methods in order to accurately solve the Schrödinger equation. In particular, methods that decompose the high-dimensional wavefunction as a complicated contraction over smaller dimensional functions have attracted much attention. They have led to impressive applications for challenging quantum systems in both fields. While the underlying wavefunction representations, tensor network states, are very similar, the algorithms used to solve the Schrödinger equation for electronic and vibrational motions are very different. A systematic comparison of the strengths and weaknesses of the different approaches is missing but would allow for a better understanding and useful cross-fertilization of ideas. Here, first attempts in this direction are made.

In the first part of my talk, I will show how to use a method from electronic structure theory, the density matrix renormalization group (DMRG), for vibrational simulations[1]. I will compare the DMRG to an algorithm used for vibrational dynamics, the multi-layer multi-configuration time-dependent Hartree (ML-MCTDH) method. I will apply these algorithms to the vibrational spectra simulation the Zundel ion, $H_5O_2^+$, where a proton is sandwiched between two water units, a challenging system exhibiting large amplitude motion and Fermi resonances. For this system, I will show how the DMRG method can compute eigenstates at least an order of magnitude faster than the ML-MCTDH method. By computing 1000 eigenstates to high accuracy, I will show how subtle energetic effects will lead to a vastly different infrared spectrum of the Zundel ion[2].

In the second part of my talk, I will show how a technique widely used for MCTDH can allow for faster electronic structure DMRG calculations whenever many virtual orbitals with few electronic excitations are involved[3]. With a combination of this and existing methods, I will then show how to compute a very accurate potential energy curve (PEC) of the chromium dimer, a grand challenge problem of small molecule spectroscopy, where theory and experiment have been at odds for decades. The computed PEC allows for a new analysis of the existing experimental data and hints at a new assignment of the vibrational levels of the chromium dimer[4].

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Unitary product states: A quantum-compatible approach for strong correlation

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C7

The preparation of systematically improvable electronic wave functions for treating strong electron correlation is a key challenge for quantum chemistry applications using emerging quantum computers. For near-term devices, these wave functions must achieve high-accuracy with shallow quantum circuits and simple numerical optimisation. It has been shown theoretically that an arbitrary wave function can be constructed using a product of unitary one- and two-body fermionic operators. However, because this product depends on the choice and ordering of fermionic operators, we do not know how to construct these wave functions in practice. In this presentation, I will explore the systematic construction of near-exact quantum-compatible wave functions using the minimum number of quantum operators. I will show how we can build and optimise a product of unitary operators taken from a minimal pool containing only one-body and paired two-body fermionic operators. Using discrete optimisation techniques, I show how the selection and ordering of these operators can be systematically improved to identify the most accurate and compact fermionic wave function. This approach obtains highly-accurate energies for strongly correlated systems using significantly fewer quantum operators than current state-of-the-art techniques, and provides a new route to numerically investigate the properties of future quantum-compatible wave function approximations.

Tensor Train Methods for Stationary and Dynamical General Many-Particle Problems

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I8

In my talk, I will discuss some of the latest developments in my group on matrix product states in theoretical chemistry. These developments address rather diverse targets, which extend the general applicability of this type of tensor network states [1]:

We introduced transcorrelated DMRG (tcDMRG) [2] to address the nagging dynamic correlation problem. tcDMRG optimizes the right eigenvectors of non-Hermitian Hamiltonians with the imaginary-time TD-DMRG algorithm [7]. We found that tcDMRG applied to the two-dimensional Fermi-Hubbard Hamiltonian enhances convergence of DMRG with respect to the bond dimension [2]. The first implementation of tcDMRG for molecular systems has also been presented with density fitting to leverage the calculation of the two- and three-body integrals [3].

Furthermore, we introduced DMRG[FEAST] [4] which exploits the FEAST algorithm for the calculation of excited-state MPS wave functions. Although the demonstration of DMRG[FEAST] was in the context of vibrational DMRG (vDMRG) [5,6], it can be straightforwardly extended to electronic structure theory.

In the first implementation of tangent-space time-dependent DMRG for molecular simulations [7] we focused on vibronic and excitonic dynamics. Tangent-space TD-DMRG was then also employed in electronic structure theory to calculate absorption spectra with the correlation function formalism, dynamical response properties beyond the linear-response approximation, and ionization dynamics [8].

Moreover, we introduced the nuclear-electronic all-particle DMRG method [9] with stochastic optimization of all wave function parameters to obtain ground and excited state energies and electron-nuclear orbital entanglement [10].

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New tensor product state approximations for strongly correlated molecules

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I9

Developing accurate and robust ab initio methods capable of describing strong electron correlation remains a critical outstanding challenge for theoretical chemistry. Part of the difficulty in modeling strongly correlated systems arise from the fact that most of the approximation methods developed rely on a delocalized Hartree-Fock reference state, which becomes qualitatively incorrect as the strong interactions between electrons drives the system to a more localized structure. In this talk, I will discuss some of our group's recent work on developing new ab initio methods that are realized directly in a basis of tensor products of locally correlated many-body states. For systems that retain identifiable local character (excitonic excited states in molecular materials, low-energy levels in organometallic compounds, etc.), correlated tensor product states increase compactness of the wavefunction, allowing larger active spaces to be modelled. To illustrate the practical usefulness of theseapproaches, I will show recent numerical examples of biexcitonic excited states in singlet fission chromophores as well as low-energy states of organometallic complexes.

Adding dynamic correlation to DMRG via adiabatic connection

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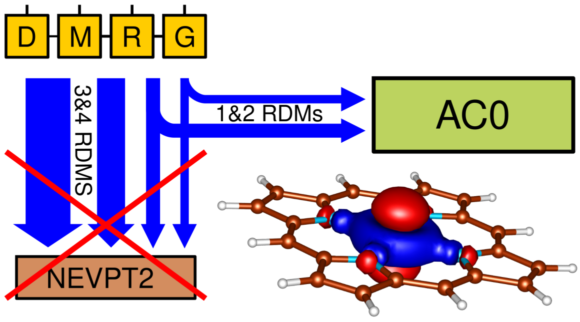
C8



For multireference calculations, CASSCF is the method of choice. Due to exponential scaling, CASSCF is limited to around 20 strongly correlated orbitals in the active space. With the DMRG method, we can push this limit to more than 50 orbitals without losing much accuracy. However, the orbitals outside of the active space are not correlated and to make accurate predictions, we also need to capture the weaker dynamic correlation outside of the active space. Most state-of-the-art methods for multireference dynamic correlation treatment (NEVPT2 for example) use up to 4 particle reduced density matrices (RDMs) from the active space, which leads to an unfavorable scaling with the active space size. While this is not an issue with canonical CASSCF, as the imposed limit is close to the limits of CASSCF itself, it completely prohibits the use of these methods with the large active spaces typical for DMRG-CASSCF.

In this talk we present the new Adiabatic Connection (AC) method of Kasia Pernal, which needs only 1&2 RDMs from the active space, which in combination with DMRG-CASSCF allows us to perform accurate multireference calculations with huge active spaces. We illustrate the usefulness of this approach on several challenging systems.

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The Kohn-Sham calculations with Adiabatic Connection Models with Improved Treatment of the Strong-Interaction Limit

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C9

Adiabatic connection models (ACMs), which interpolate between the limits of weak and strong interaction, are powerful tools to build accurate exchange-correlation functionals within Kohn-Sham Density Functional Theory (KS-DFT)[1]. If the exact weak-interaction expansion from second order perturbation theory is included, a self-consistent implementation of these functionals is challenging and still absent in the literature. In this work [2] we fill this gap by presenting a fully self-consistent-field (SCF) implementation of some popular ACM functionals. While using second order perturbation theory at weak interactions, we have also introduced new generalised gradient approximations (GGA's), beyond the usual point charge-plus-continuum model, for the first two leading terms at strong interactions, which are crucial to ensure robustness and reliability.

We then assess the SCF-ACM functionals for molecular systems and for prototypical strong-correlation problems (Hooke's atom, dissociation of H_2). We find that they perform well for both the total energy and the electronic density and that the impact of SCF orbitals is directly connected to the accuracy of the ACM functional form.

For the H_2 dissociation the SCF-ACM functionals yield significant improvements with respect to standard functionals, also thanks to the use of the new GGA's for the strong-coupling functionals.

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Recent theoretical results on the QC-DMRG method

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I10

I will present some recent theoretical results on the QC-DMRG method, including

- the fact that with bond dimension 3 and optimized orbitals it is exact for two-electron wavefunctions [1]

- the exact formulation of the infinite basis limit by a half-infinite chain of MPS matrices of increasing size [2]

- a power law scaling of errors for the restricted active space density matrix renormalization group (DMRG-RAS) method [3].

These results are illustrated by numerical calculations for diatomic molecules and - in case of [3] - the FeMoco complex.

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Capturing both weak and strong correlations in transition metal chemistry using classical and quantum methods

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C10

Reliable computational modeling of transition metal compounds requires electronic structure theories that can accurately describe both weak and strong correlations in a scalable manner. Weak (dynamical) correlations include dispersion and screening effects, which are crucial in many types of organometallic bonding. Strong (static) correlations can arise due to the presence of nearly-degenerate electronic states, leading to low-spin states of open-shell character encountered, e.g., in polynuclear transition metal complexes. I will introduce two *ab initio* methods which capture these essential features in a systematically improvable way - phaseless auxiliary-field quantum Monte Carlo, and variational cluster Jastrow wavefunctions inspired by Hubbard physics. These approaches can yield near-exact ground-state energies with tractable computational costs, and can be implemented on both classical and quantum computers.

Strong Electronic Correlation with Richardson-Gaudin States

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C11

Weakly-correlated electronic systems are well-described as individual electrons: the wavefunction is a Slater determinant of the occupied orbitals with small corrections from single- and double-excitations. This is not the case for strongly-correlated systems. The wavefunction is very complicated in terms of Slater determinants and thus the correct physical picture is not independent electrons.

For strongly-correlated molecular systems, we have shown that the eigenvectors of reduced Bardeen-Cooper-Schrieffer Hamiltonians, so-called Richardson-Gaudin (RG) states, are a much better starting point. They describe weakly-correlated pairs of electrons. They are tractable variationally and form a basis for the Hilbert space allowing for systematic improvement.

We will show for the isomers of H_{10} that a single RG state is a very good approximation to the wavefunction. Corrections for the remaining weak electronic correlation are obtainable with an approximate functional, or with a short CI expansion in RG states. Thus, the present development is an analogue of both Kohn-Sham DFT and correlated wavefunction theories based on Slater determinant references.

Understanding the accuracy of random phase approximation for binding energies

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C12

The random phase approximation (RPA) with singles corrections (RSE or *GW* SE) was shown to give binding energies of molecular solids within only a few percent of the reference values [1]. However, comparison to a single number can be misleading as the good performance can be result of a favourable cancellation of errors. To understand the binding energies of RPA in detail we employed many-body expansion (MBE) in which the binding is divided into contributions of molecular dimers and corrections from higher-body terms. We performed MBE for binding energy of methane in water clathrate [2] and for crystals of short hydrocarbons [3]. Apart from PBE input states, used in [1], we also used SCAN and the hybrid variants of both functionals.

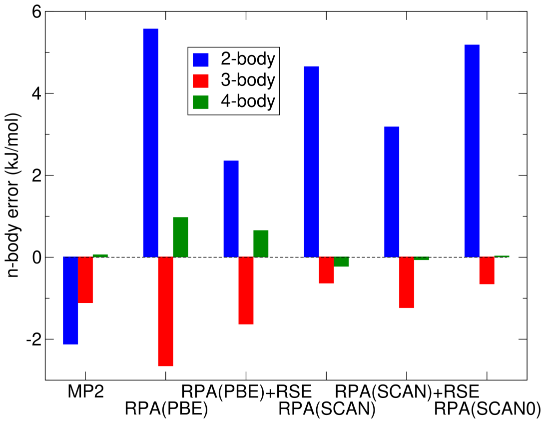

Figure 1: Errors of many-body energies of different methods for ethylene crystal.

We find that PBE- and SCAN-based RPA often lead to similar binding energies, the difference is less than 0.1 kJ/mol for ethylene and around 0.5 kJ/mol when RSE are included. However, their many-body errors substantially differ, as shown in the figure. Specifically, the 3- and 4-body errors are larger in magnitude for PBE- and PBE0-based RPA than when SCAN or SCAN0 input is used. As a result, there is substantially more error cancellation between the different MBE orders for PBE-based RPA than there is for RPA(SCAN). The larger 3- and 4-body errors of RPA(PBE) are a consequence of larger many-body errors of the PBE functional. Compared to MP2, RPA leads to more consistent errors across the different systems. However, MP2 has usually very small 4-body errors which we ascribe to the use of Hartree-Fock input states.

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Relativistic effects and orbital contributions to the electric field gradient

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C13

The electric field gradient (EFG) is important for experimental studies, such as nuclear quadrupole resonance measurements and Mössbauer spectroscopy. It couples to the nu- clear quadrupole moment resulting in observable energy levels. The EFG has an inverse cubic distance dependence, i. e. it probes the region close to the nuclei. Relativistic ef- fects are also most pronounced in this region and so it is expected that they are important for an accurate computation of EFGs.

In the current work the EFGs of several molecules were studied using different relativistic and non-relativistic Hamiltonians. Furthermore projection analysis[1] was applied to identify the contributions of different atomic orbitals to the EFG. This will be compared to a simple model devised by by Dailey and Townes [2], which allows to relate the EFG to the ionic character and hybridization of the bond for centers with partially filled valence p-shells. An extension of this model to a relativistic framework was already presented by Pyykkö and Seth [3] and we will compare it to our approach.

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Thursday, 22 of June

Reduced-Scaling Multireference Perturbation Theories using Orthonormal Localized Virtual Orbitals

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I11

In this talk, we present our recent works on the development and application of the reduced-scaling implementations of the second-order multireference perturbation theories (MRPT2) on the basis of localized orbital basis.[1,2] The MRPT2 schemes such as CASPT2 or NEVPT2 methods are capable of providing accurate results for molecules with complicated electronic structures, recovering dynamic electron correlation effect on top of the CASSCF reference functions. A major drawback of such methods is that floating point operations (FPOs) for generating the electron repulsion integrals scales by $O(N^5)$. Moreover, storage of the perturbative amplitude scales by $O(N^4)$. Therefore, application of the MRPT2 methods to systems involving more than 50 atoms is often quite demanding.

To remove such bottlenecks, Neese[3] and Werner[4] independently developed the reduced-scaling version of the MRPT2 methods (DLPNO-NEVPT2 and PNO-CASPT2 schemes) using the concept of the so-called pair-natural orbitals (PNOs). In both approaches, the projected atomic orbitals (PAOs) are used as an intermediate basis in the virtual space. The PAOs are a set of linearly-dependent and over complete functions. Therefore, in such approaches, the orthonormalization should be performed for each surviving orbital pairs.

To remove such redundancy in the PNO-based schemes, we introduce the localized virtual orbitals (LVOs), which are orthonormal set of functions, instead of PAOs. Previous studies,[5,6] however, claim that (1) to achieve a certain accuracy, more LVOs are needed in an orbital domain than PAOs and (2) standard orbital localization algorithms such as Jacobi rotations often fails for virtual orbitals. To overcome such difficulties associated with use of LVOs, we introduce a new domain construction scheme for LVOs using the so-called differential overlap integrals (DOIs). For an efficient orbital localization, we use augmented Hessian-based localizer for LVOs.

Our LVO-based PNO-CASPT2 and NEVPT2 schemes are shown applicable to systems involving hundreds of atoms. With the DOI-based domain construction scheme, performance of LVOs is shown comparable to that of PAOs in the framework of local correlation schemes. In addition to the state-specific formalisms, we show a multistate extension of the LVO-based methods.

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Ten years of the Distinguishable Cluster: Past, Present and Future

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I12

Modified coupled cluster (MCC) methods motivated by higher efficiency or superior accuracy have been developed from early days of coupled cluster theory. Already in the first publication on coupled cluster methods in quantum chemistry, [1] the linearized version has been introduced, and the connection between the ring-coupled-cluster with doubles method and the random-phase approximation has been recognized. A non-complete list of MCC methods [2] include CEPA, [3] ACP-D45,[4] ACCD,[5] ACPQ,[6] ACP-D14,[7] nCC,[8] pCCSD[9]. In 2013, we have developed a new addition to this list called the distinguishable cluster (DC) approach[10].

As many other MCC methods, DC is exact for two electrons, size extensive and invariant with respect to subspace-orbital rotations. Numerous benchmark studies over the past ten years have demonstrated higher accuracy of DC with singles and doubles (DCSD) compared to standard CCSD for description of weakly correlated systems. But the most striking aspect of DC is the qualitatively correct description of even very strongly correlated systems.

In my talk I will review the progress on DC methods, combinations of DC with other approaches and discuss potential future developments.

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Quantum chemistry with accurate solutions of the Schrödinger equation

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C14

The theory that solves the Schrödinger equation exactly is a goal and a starting point of the quantum chemistry. The free complete-element function (FC) theory is such a theory born in 2004. The theory has been extended since then and its accuracy, reliability, and high performance have been confirmed. It predicts the energies and properties of atoms and molecules in high accuracy that is comparable to or even better than the experimental values. To develop this theory for general use in quantum chemistry is our current subject.

The equation that gives the solution of the Schrödinger equation with the variational method is the scaled Schrödinger equation $g(H-E)\Psi = 0$[1], where $g(r)$ is the scaling function that is always positive and its correct function behaves as $g = r + O(r^2)$ near $r = 0$ and $g \to 1$ when $r \to \infty$. As such correct function, the following five are known[2].

$$1-\exp(-\gamma r),\ Ei(-\gamma_1 r-\gamma_2)-Ei(-\gamma_2),\ r/(r+1/a),\ \arctan(\gamma r),\ \tanh(\gamma r) \tag{1}$$

The function r, frequently used, does not satisfy the above correct behaviors. Actually,[2] the correct functions give usually better results than the function r that has been used frequently. For general molecules, the integrals for g_{ij} is difficult. So, the variational parameters are optimized by the sampling method that uses the Schrödinger equation itself as a deterministic equation[3]. It is called local Schrödinger equation (LSE) method[3]. As sampling method, the Metropolis method is popular, but because it is a stochastic method, it usually includes the error caused by the randomness. So, we introduced the inverse transformation (direct) method using the integrable initial functions of the FC theory[4]. With this method, we could obtain highly accurate potential energy curves for the lower nine valence states of the Li_2 molecule[5]. They agreed in the absolute energy to the experimental RKR potentials within the difference of 0.058 kcal/mol from the experimental values. The chemical reaction dynamics of the ground and excited states of this molecule is governed by these potential curves, and therefore, the FC theory is able to describe the reaction dynamics of this molecule almost completely. We are also developing the FC theory for the BO treatment.

Since the FC theory is an exact theory, it can predict not only the energies, but also the properties observed by many different experiments highly accurately. For example, for the ^2S and ^2P states of the Li atom, we calculated the spin densities at the nucleus that are widely observed by the ESR experiments, electron-nuclear and electron-electron cusp values, etc. For example, for the spin densities of the ^2S and ^2P states, the experimentally observed values were 0.2313 and -0.01693, respectively, while the calculated values with the FC theory were 0.2311 and -0.01693, respectively, while the calculated values with the FC theory were 0.2311 and -0.01704, respectively, which are almost complete agreement with the experimental values.

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Many-body theory of positron interactions with polyatomic molecules

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C15

Positrons are unique probes of matter, with applications in materials science (ultra-sensitive diagnostic studies of surfaces, defects and porosity), medical imaging (PET), astrophysics, molecular spectroscopy [1], and fundamental physics. Positron interactions with matter are characterised by strong many-body correlations. They significantly modify scattering, and enhance annihilation rates by orders of magnitudes (see [2] for a review). They also make the theoretical study of positron-matter interactions very challenging.

We have developed a diagrammatic many-body description of positron-molecule interactions that takes ab initio account of the correlations, implemented in the state-of-the-art code `EXCITON+` [3]. We solve the Dyson equation for the positron quasiparticle wavefunction in a Gaussian basis, constructing the positron-molecule self-energy including the *GW* diagram (at RPA/TDHF/BSE levels of theory), describing polarisation, screening and electron-hole attraction interactions, the ladder series of positron-electron interactions that describes virtual positronium formation, and the ladder series of positron-hole interactions. We have used it to calculate binding energies for a range of polar and non-polar molecules, focusing chiefly on the molecules for which both theory and experiment exist [3,4], but also making predictions (e.g. of positron binding to DNA nucleobases [3], and of the effect of fluorination vs chlorination in hydrocarbons [4]). Delineating the effects of the correlations, we show, in particular, that virtual-positronium formation significantly enhances binding in polar molecules, and moreover, that it can be essential to support binding in non-polar molecules. Overall, we find the best agreement with experiment to date (to within a few percent in cases). We have recently developed and extended the method to the calculation of the positron scattering [5] and annihilation gamma spectra in molecules [6] providing insight that should support the development of fundamental experiments and the myriad of antimatter-based technologies and applications. Moreover, the positron-molecule problem provides a testbed for the development of methods to tackle the quantum many-body problem, for which our results can serve as benchmarks.

*This work is funded by DGG's ERC grant 804383 "ANTI-ATOM".

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Explicitly correlated coupled-cluster methods including triple and quadruple excitations

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I13

Recently, we have proposed a new approach to reduce the basis set incompleteness error of the triple excitation correction in explicitly correlated coupled-cluster (CC) singles and doubles with perturbative triples [CCSD(T)] calculations [1]. The approach, which is based on the orbital-specific scaling of the contributions of the perturbative triples correction, is size-consistent and significantly speeds up the basis set convergence of the triples correction. Here, we discuss its extension to the CC singles, doubles, triples (CCSDT) with perturbative quadruples [CCSDT(Q)] method. While the adaptation of the approach to the (Q) correction is straightforward, its extension to CCSDT is less trivial. We discuss several possibilities and assess their performance for total energies and energy differences. In addition, we also propose the extension of the more rigorous extended SP triple excitation ansatz of Köhn [2, 3] to CCSDT. We demonstrate that this approach results in a much more involved and expensive but more accurate explicitly correlated CCSDT method. It is also shown that the method can be considerably sped up with reasonable approximations.

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Holomorphic Hartree-Fock Theory: A basis for multireference electronic structure

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I14

A particular challenge in electronic structure theory is that of bond-breaking, where single reference electronic structure methods often break down producing qualitatively incorrect binding curves. Associated with the onset of the multi-reference character of these wavefunctions is the existence of multiple, often symmetry-broken, solutions to the Hartree-Fock (HF) equations which can be challenging to find with conventional methods[1]. In more complicated systems the the lowest energy Hartree-Fock state may even change discontinuously between such solutions, and theories built upon a single HF state often perform very poorly.

An potentially effective approach to remedy this is that of Non-Orthogonal Configuration Interaction (NOCI), where the Hamiltonian is expressed in the basis of these different HF solutions, and the resulting energies and wavefunctions (for both ground and excited states) can smoothly vary between the optimal HF solutions at each geometry[2] and require little computational effort to calculate.

This approach is hampered by the coalescence and disappearance of HF solutions, as typified by the Coulson-Fischer point in the dissociating hydrogen molecule, and all but renders NOCI built upon conventional HF solutions useless as disappearing HF solutions lead to discontinuities in the potential energy surface.

We have developed an alternative analytic continuation of HF theory, holomorphic Hartree-Fock (hHF) theory[3], which proves identical to conventional HF where real-valued solutions exist, and produces smoothly varying analytic continuations of these into the complex plane when solutions would conventionally coalesce. These hHF solutions are a smooth and continuous basis for NOCI calculations, and provide a compact representation of multireference wavefunctions[4], upon which foundation perturbation theory methods may be used to give good correlation energies[5].

This talk will showcase some examples of multiple Hartree–Fock solutions and their holomorphic extensions and their use in creating smooth potential energy surfaces for diatomics and transition metal complexes.

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Exploring amplitude functions in the coupled-cluster framework – an alternative approach to convergence improvement

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C16

The single reference (SR) coupled-cluster (CC) formalism is a well established method in electronic structure theory and its variants are routinely applied to the correlation problem. The corresponding nonlinear equations are usually solved in an iterative fashion. However, in certain cases (e.g., bond dissociation), the conventional iterative process which starts from the first order Møller–Plesset (MP) amplitudes converges slowly or not at all. Several remedies — extrapolation techniques, a different iteration route – have been proposed, one of the best known examples is the direct inversion in the iterative subspace (DIIS) [1, 2] method.

We present an alternative approach, which is a result of a broader investigation: if the perturbational parameter λ formally appearing in many-body perturbation theory (MBPT) and relatedly, the CC framework, is included explicitly in the Hamiltonian and the CC formalism, all quantities involved (correlation energy, amplitudes) become functions of λ. Employing the MP partitioning, properties of the resulting λ-dependent amplitude functions are discussed.

Based on known values of the CC amplitudes $\mathbf{T}(\lambda)$ at different $|\lambda| < 1$ points (which are easier to obtain), we take advantage of the discussed properties of $\mathbf{T}(\lambda)$ to estimate the CC amplitudes without solving the relevant equations at $\lambda = 1$ (corresponding to the original, physical problem), an idea which has been tested successfully in the context of MBPT [3]. While we explore this idea only in the SR case, it can also be generalized to other CC schemes designed to treat systems where strong correlation plays an important role.

We limit ourselves to CC truncated at the level of singles and doubles (CCSD), and investigate the adequacy of the approximate amplitudes provided by this procedure. Aiming at improving the convergence pattern of the solution process, this set of amplitudes can also be used as the starting point for the CCSD iterations, and combined with DIIS it can resolve the divergence issues of the conventional sequence [4].

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Friday, 23 of June

Maarten van Damme[1]

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C17

Analytic Gradients for Selected Configuration Interaction: Development and Applications

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C18

Selected configuration interaction (CI) approaches iteratively build up a compact wave-function by repeatedly adding and removing configurations based on certain criteria. They are increasingly of interest partly due to their ability to cope with multireference problems without requiring an active space to be chosen.

To efficiently use these methods for geometry optimization then analytic energy gradients are crucial. However, unlike CASSCF or CISD, all pairs of orbitals in principle need to be considered when implementing analytic gradients for selected CI. This may be expected to lead to numerical problems when there are (near) degenerate orbitals, due to $(\epsilon_i - \epsilon_j)^{-1}$ terms arising from the coupled perturbed Hartree-Fock equations. I will present how this can be overcome and demonstrate that selected CI can give highly accurate analytic gradients using just a small fraction of the full configuration interaction (FCI) space [1]. Fig. 1 shows that selected CI analytic gradients for trigonal planar ammonia are practically indistinguishable to FCI despite only using around 8000 determinants compared with the FCI space of about a quarter of a million determinants. I will also discuss progress building on this work to calculate non-adiabatic couplings and optimize geometries.

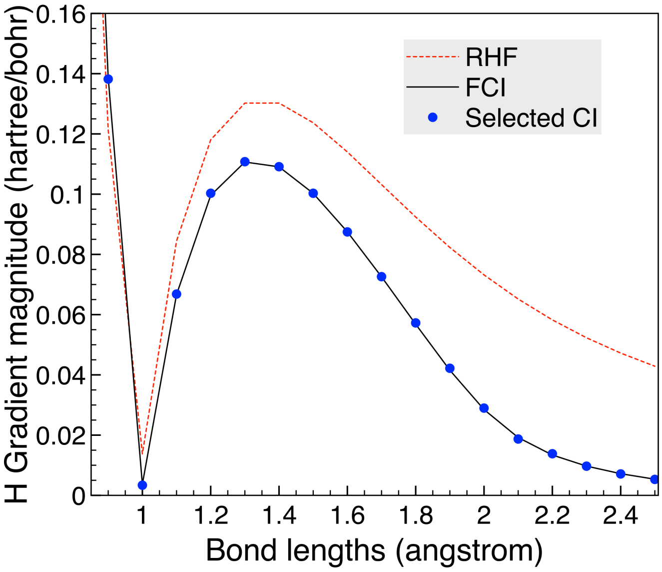

Figure 1: Magnitude of the analytic gradient vector for an H atom in trigonal planar ammonia using 6-31G.

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GW in Gaussian Bloch Orbitals for Solids - relativistic effects, pseudopotentials, and impacts of different self-consistency cycles

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I15

I will present recent developments in GW with Gaussian Bloch Orbitals for Solids that happened in my group. First, I will present a formulation of relativistic self-consistent GW for solids based on the exact two-component formalism with one-electron approximation (X2C1e) and non-relativistic Coulomb interactions. Our theory allows us to study scalar relativistic effects, spin-orbit coupling, and the interplay of relativistic effects with electron correlation without adjustable parameters. The simplicity of X2C1e enables the construction of higher order theories, such as embedding theories, on top of perturbative calculations.

Next, I will analyze different variants of self-consistency that can be performed in GW exclusively on the imaginary axis. To access the real axis quantities, we are using Nevanlinna analytic continuation. Within this framework, I will analyze G0W0, GW0, quasiparticle self-consistent GW scheme of Schilfgaarde, Kotani, and Faleev and QP-II scheme introduced by Kutepov, Haule, Savrasov, and Gabriel Kotliar.

Finally, I will discuss the impact of using pseudopotentials on GW calculations.

Externally Corrected Coupled-Cluster Methods: Review and Recent Progress

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I16

In the first part of this talk, we will embark on a journey to honor the life and work of the late Professor Josef Paldus. With Professor Paldus‘ passing earlier this year, our community has lost an extraordinary person and legendary scientist, whose seminal work on exploiting dynamical symmetries, resulting in the unitary group approach, and the introduction (with Professor Jiří Čížek) of the coupled-cluster (CC) theory to molecular electronic structure have revolutionized quantum chemistry. Many of us, including the presenter of this lecture, have lost a cherished friend, collaborator, and mentor. This talk is our humble tribute to Professor Paldus‘ exceptional life and contributions and his enduring impact on the work of a great many, including the presenter.

One of the topics that the presenter of this talk pursued with Professor Paldus between 1988 and 1996 is the externally corrected CC (ec-CC) methodology, which represents one of the most promising ways of improving the results of single-reference CC calculations in multi-reference and strongly correlated situations [1]. The ec-CC approaches are based on the observation that by solving the CC amplitude equations projected on the singly and doubly excited determinants for the one- and two-body clusters, T_1 and T_2, respectively, in the presence of their exact three-body (T_3) and four-body (T_4) counterparts extracted from full configuration interaction (FCI), one obtains the exact T_1 and T_2 and, thus, the exact energy. This suggests that by using external, non-CC, wave functions capable of generating an accurate representation of T_3 and T_4 clusters, and subsequently solving for T_1 and T_2, one should not only produce energies that are much better than those obtained with CCSD, but also substantially improve the results of the calculations providing T_3 and T_4. We will examine the validity of the latter premise and, with the help of suitable theorems and numerical analysis [2], demonstrate that the truncated CI wave functions that are best suited for the ec-CC computations are those that efficiently sample the many-electron Hilbert space, without saturating the lower-rank excitation manifolds too rapidly, while adjusting the singly through quadruply excited CI amplitudes to the dominant higher–than–quadruply excited contributions, such as those obtained with the selected CI model abbreviated as CIPSI and FCI Quantum Monte Carlo (FCIQMC) propagations. We will then discuss our CIPSI-driven [2] and FCIQMC-driven [3] eFormer member of the Piecuch group (defended his Ph.D. in 2021). Currently at Emory University.c-CC models and their performance in applications involving chemical bond dissociations [2,3(a)], molecules beyond the reach of FCI [3(b)], and strongly correlated systems that emerge in modeling metal–insulator transitions [3(c)], where the traditional CCSD, CCSDT, CCSDTQ, etc. hierarchy breaks down. We also hope to touch upon our recent results in the area of the approximate coupled-pair methods, which belong to the oldest category of the ec-CC approaches using T_4 clusters extracted from the projected unrestricted Hartree–Fock wave function, capable of describing strongly correlated systems by retaining and/or scaling selected $(T_2)^2$ diagrams in the CCSD equations [4].

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[†] Former member of the Piecuch group (defended his Ph.D. in 2020). Currently at Emptor, New York.

Alternative Single Reference Coupled-cluster approaches for multi-reference problems: pCCD+TCCSD for Excited States

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I17

To Joe Paldus: A mentor to all of us

In the competition between single reference CC/EOM-CC and multi-reference methods, SR-CC/EOM usually provides better results at far less effort. The reason is that CC/EOM gets to the full CI very quickly, and the full CI does not suffer from any MR aspect. The argument for MR methods is that choosing 'active' orbitals to define a MR starting point should be superior, since it offers a better zeroth-order starting point that is worth all the additional MR overhead required. But is that true? The objective of predictive quantum chemistry is a basis set converged full CI, but when one introduces a selection of 'active' orbitals that necessitates a MR description, the calculation must also converge for the particular active orbital choice. And there will be different choices for different states or situations. Contrast this with the fact that CCSD is virtually insensitive to orbital choice, rapidly approaching the invariance of the full CI. But SR-CC can also readily use UHF, Brueckner, Natural, KS, ROHF, QRHF, orbital optimized, and our COT orbital choices as easily as HF ones, if orbital choice offers anything important to a calculation.

What about 'strong correlation'. I think that strong correlation should mean that there is no subset of 'active' orbitals that can describe the situation. requiring that all be included: an obvious impossibility. In between this strong correlation limit and real-world problems lie cases where a couple of active orbitals would be a natural choice in a MR-CC method like GVB -PP for single bond breaking. We presented TD-CCSD some years ago as the simplest state universal, Hilbert space method for open-shell singlets and GVB examples. But even this simple method retains its two determinant reference form, making adding things like EOM on top of it different than in the normal SR case.

When SR-CC fails, it is usually because the single reference determinant prohibits correct separation, commonly like RHF references for closed shell molecules separating into open shell fragments. UHF fixes the incorrect separation, but likely by breaking symmetry. Some would say a better solution for this would be a GVB reference that can retain spin symmetry. But what is useful is a *single reference form* of the GVB solution that can be improved by adding higher orders of CC theory. This is where the pair coupled-cluster doubles method becomes useful. John Cullen recognized that if one modified a CCD program to only retain the pair double excitations like T2 (Aα, Aβ; Iα, Iβ) (only NocNvirt in number) followed with an orbital optimization, then one would essentially have a GVB wavefunction in CC form. As GVB PP can correctly break a single bond, it manifests non-dynamic correlation. Consequently, adding dynamic correlation via higher-order CC to such a fixed starting point offers a more quantitative description. We call this ‘tailoring’, where the essential dynamic correlation is described by additional terms in the CC like the rest of the T2’s plus singles. This method is termed pCCD+TCCSD. Any such ‘tailored’ CC wavefunction can be used almost exactly like its untailored counterpart, to treat excited states with EOM, analytical gradients, density matrices, properties, etc.

In this talk we will discuss pCCD +TCCSD for excited states, looking at singly excited, doubly excited, and singlet-triplet separations for multi-reference biradical problems, and as a function of selected orbital choices, as pCCD is not orbitally invariant to even occ-occ or virt-virt rotations. pCCD+TCCSD benefits from tailoring with pCCD, though the other examples do not. We will show that only the last has important MR effects, enabling tailoring with pCCD to pay dividends, particularly with GVB orbitals.

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Time-dependent Vibrational Electronic Coupled Cluster (VECC) theory for non-adiabatic dynamics

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Non-adiabatic dynamics is associated with many photo-electron chemical processes where the nuclear wavefunction is strongly coupled with the electronic wavefunction near the conical intersection of the potential energy surface (PES). In this work we present the Vibrational Electronic Coupled Cluster (VECC) method which provides a compact time-dependent representation of the wavefunction for non-adiabatic vibronic models. The wave function is parameterized using a second quantized representation for the vibrational degrees of freedom, and diabatic electronic labels. This representation can be used to calculate time-correlation functions and hence vibronic spectra. A similar representation is used in a thermofield representation of quantum statistical mechanics, and this allows the calculation of thermal properties for vibronic models in an analogous fashion. This work builds on the general formulation of the Thermal Normal Ordered Exponential (TNOE) ansatz [1]. By introducing this compact representation, the time-dependent and thermal properties can be determined by solving a set of coupled cluster equation of motions (CC-EOMs). The computational complexity to solve the CC-EOMs has a polynomial scaling as the number of the normal mode of the vibronic models. In this way, our approach is more efficient comparing to the conventional basis set based approaches that have an exponential scaling.

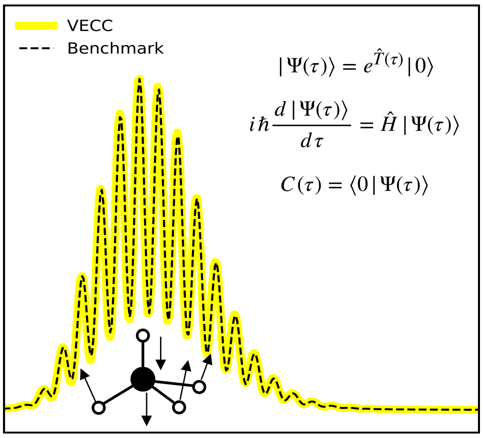

Figure 1: Illustration of the VECC method

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Spectroscopy of Copper-Superoxo Complexes: a Revival Based on Correlated Methods

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Copper-dioxygen complexes play a crucial role in numerous (bio)-chemical processes, including oxygen activation in several enzymes, such as copper-containing monooxygenases. Many efforts have been devoted to studying bioinspired cupric-superoxide end-on complexes for their capacity to perform oxidation reactions: [1,2] understanding the electronic structure of these species is essential for elucidating their reactivity and catalytic mechanisms.

Copper-dioxygen complexes represent challenging systems for DFT based methods due to the presence of the d^9 copper center and, possibly, π-conjugated ligands. As UV-vis spectroscopy is routinely employed to characterise these often short-lived, unstablespecies, a comprehensive investigation of the low-lying excited states of some $[\mathrm{LCu(O_2)}]^+$ complexes is highly desirable from a theoretical point of view. We performed state-of-the-art multireference calculations using MS-RASPT2, DMRG and ICE-CI to probe the electronic structure of some challenging systems. The energies of the different states are extremely sensitive to charge-transfer mechanisms between the ligand and metal center, which are notably difficult to model, even with wavefunction based methods.[3,4,5] This work offers the opportunity to discuss the methodological implications of combining these approaches to provide new insights on the electronic structure of this class of strongly correlated systems. Our aim is to provide a solid reference for future theory-experience studies and assess the tools at our disposable to diagnose the possible shortcomings of the more widely applicable DFT.

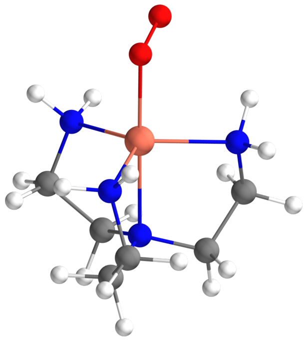

Figure 1: $[\mathrm{LCu(O_2)}]^+$ studied in this work

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Hilbert space multireference coupled clusters tailored by matrix product states: study of tetramethyleneethane

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In the last decade, the quantum chemical version of the density matrix renormalization group (DMRG) method[1] has established itself as the method of choice for calculations of strongly correlated molecular systems. However, despite its favorable scaling, it is in practice not suitable for computations of dynamic correlation. Several approaches to include that in post-DMRG methods exist; in our group we focused on the tailored-CC (TCC) approach [2, 3], which employs T_1 and T_2 amplitudes from the DMRG active space to externally correct the single-reference CC method. This method works well in many situations, however, in exactly degenerate cases (with two or more determinants of equal weight), it exhibits a bias towards the reference determinant representing the Fermi vacuum. Although in some cases it is possible to use a compensation scheme to avoid this bias for energy differences, as we did in a previous work on the singlet-triplet gap in the tetramethylenethane (TME) molecule, it is certainly a drawback.

In order to overcome the single-reference bias of the TCC method, we have developed a Hilbert-space multireference version of tailored CC, which can treat several determinants on an equal footing. We have employed a multireference analysis of the DMRG wave function in the matrix product state form to get the active amplitudes for each reference determinant and their constant contribution to the effective Hamiltonian. We have implemented and compared the performance of three Hilbert-space MRCC variants - the state universal one, and the Brillouin-Wigner and Mukherjee’s state specific ones.

We assess these approaches on the tetramethylenethane (TME) molecules, which is a diradical with exactly degenerate determinants at a certain geometry. Two DMRG active spaces have been selected based on orbital entropies, while the MRCC active space comprised the HOMO and LUMO orbitals needed for description of the diradical. We have also investigated the sensitivity of the results on orbital rotation of the HOMO-LUMO pair, as it is well known that Hilbert-space MRCC methods are not invariant to such transformations.

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Nuclear-Electronic Hartree–Fock Density Matrix Renormalization Group

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

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A DMRG-based framework for large-scale anharmonic vibrational calculations

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As countless chemical processes are influenced by molecular vibrations, methods that provide an accurate description of the correlated nuclear wave function are sought-after for a reliable characterization of strongly anharmonic molecules. Towards this end, we present a versatile framework based on the density matrix renormalization group (DMRG) algorithm for anharmonic *ab initio* vibrational calculations [1,2]. Our framework builds upon modal basis functions which are optimized with the vibrational self-consistent field (VSCF) method in conjunction with an on-the-fly calculated potential energy surface (PES) in the *n*-mode format. The obtained anharmonic modals form a compact basis set for vibrational configuration interaction (VCI)-type methods. As systems with more than 15 correlated vibrational degrees of freedom are extremely challenging for conventional VCI algorithms, we introduce a new VSCF-based formulation of the vibrational DMRG (vDMRG) theory applicable to general *n*-mode PES [3]. By expressing the VCI wave function as a matrix product state, *n*-mode vDMRG can target systems with up to 30 coupled vibrational modes. Hence, the combined VSCF/vDMRG approach allows for large-scale vibrational calculations of strongly anharmonic molecules through the proper inclusion of vibrational correlation effects.

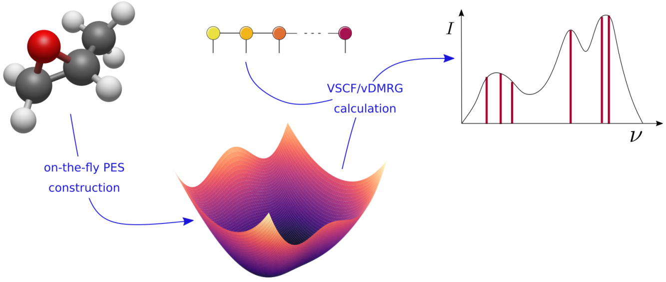

Figure 1: Illustration of the computational workflow of a VSCF/vDMRG calculation

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Spin-Adapted Coupled Cluster for Arbitrary Open-Shell States

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Coupled cluster has emerged as the method of choice for treating dynamic correlation in molecules, with the desirable properties of size consistency and high accuracy relative to other methods of comparable cost. However, the problem of spin contamination arises when treating molecules with open shell character, and systems with strong static correlation have required a multireference treatment, introducing intruder states and problems of multiple parentage that have not yet been satisfactorily resolved. Using a normal-ordered *ansatz*, We generate spin-free coupled cluster equations for open shell reference states using a new implementation of a fermionic operator algebra and tensor contraction engine. The spin-adapted reference states are configuration state functions constructed from Hartree–Fock orbitals to incorporate the strong correlation due to spin coupling. We have generated equations for reference wavefunctions of one and two open-shell electrons, both in the triplet and singlet configurations, and in principle equations can be generated for arbitrary states of high or low spin. Initially, we focus on the normal-ordered *ansatz* with double excitations, restricted to linear terms (NO-LCCD), but with no contractions between amplitudes, higher order terms can be readily incorporated. These automatically generated equations represent a step towards a method that would ultimately leverage the benefits of coupled cluster for dynamic correlation onto states for which the treatment of strong static correlation is already included.

Basis Set Limit CCSD(T) Energies for Extended Molecules via a Reduced-Cost Explicitly Correlated Approach

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Several approximations are introduced and tested to reduce the computational expenses of the explicitly correlated coupled-cluster singles and doubles with perturbative triples [CCSD(T)] method for both closed and open-shell species. First, the well-established frozen natural orbital (FNO) technique is adapted to explicitly correlated CC approaches. Second, our natural auxiliary function (NAF) scheme is employed to reduce the size of the auxiliary basis required for the density fitting approximation regularly used in explicitly correlated calculations. Third, a new approach, termed the natural auxiliary basis (NAB) approximation, is proposed to decrease the size of the auxiliary basis needed for the expansion of the explicitly correlated geminals. The performance of the above approximations and that of the combined FNO-NAF-NAB approach are tested for atomization and reaction energies. Our results show that overall speedups of 7-, 5-, and 3-times can be achieved with double-, triple-, and quadruple-ζ basis sets, respectively, without any loss in accuracy. The new method can provide, e.g., reaction energies and barrier heights well within chemical accuracy for molecules with more than 40 atoms within a few days using a few dozen processor cores, and calculations with 50+ atoms are still feasible. These routinely affordable computations considerably extend the reach of explicitly correlated CCSD(T).

A Second-Order Optimisation Approach to Configurational State Functions

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Bond breaking is a ubiquitous occurrence in chemistry, yet it remains a challenging process to describe by computational methods. A prototypical example would be the failure of Restricted Hartree—Fock theory to describe bond breaking as it cannot describe open-shell configurations.

We have demonstrated in a recent work that a small number of valence states is sufficient to describe bond breaking. These valence states have open-shell configurations and Configuration State Functions (CSFs) are natural representations for them. CSFs are constructed from an underlying set of molecular orbitals, and the quality of these CSFs depend on these orbitals. Throughout the process of bond breaking, different orbitals (and hence CSFs) would be required to describe the process. However, figuring out the orbitals required is not trivial.

In this work, we explore the possibility of using a second-order optimisation scheme to optimise the orbitals used. We demonstrate that this method can produce CSFs which gives a good qualitative description of bond breaking and can serve as good reference functions for other sophisticated electronic structure approaches.

Photodissociation of vinylbromide: a non-adiabatic molecular dynamics and machine learning study

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This work presents our efforts in utilizing machine learning (ML) techniques to accelerate non-adiabatic molecular dynamics (NAMD) simulations. NAMD plays a crucial role in the computational modeling of various photo-induced processes, such as photosynthesis, DNA damage/stability, phototherapy, and photovoltaics. Recent advancements in ML have shown great promise in the field of computational (quantum) chemistry, offering the potential for significantly faster calculations compared to traditional methods while maintaining comparable accuracy[1].

In this study, we explore the applicability of a kernel ridge regression technique, implemented in MLatom[2], as a potential tool for accelerating NAMD simulations involving non-adiabatic and spin-orbital couplings. We investigated the dynamics of vinyl bromide, a small molecule with a heavy bromine atom, which serves as an appropriate test system for NAMD simulations incorporating these couplings using Newton-X[3]. Figure 1a displays scatter plots comparing the ML predictions with reference values, demonstrating the performance of the ML models. Our analysis indicates that active learning should be employed in specific regions, as can be seen from Figure 1b, which shows the difference between two ML models and reference values.

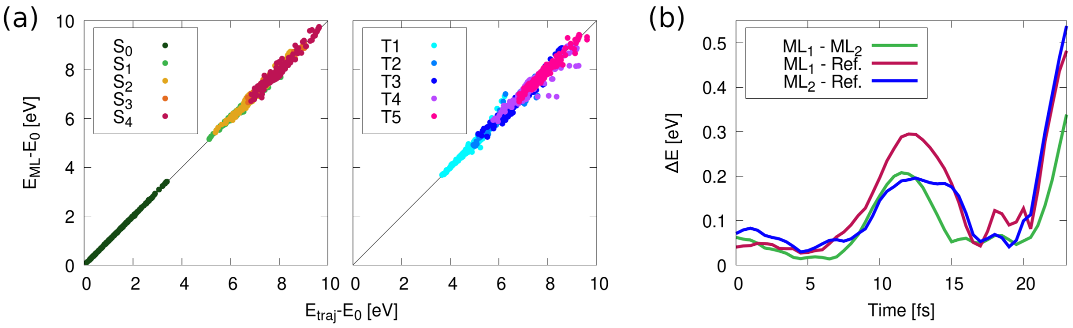

Figure 2: (a) Scatter plots comparing ML predictions to reference values can be used to analyze the accuracy of ML models. (b) Difference between ML predictions and references indicating the extrapolation regime.

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Autonomous Active Space Calculations through AutoCAS

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In order to describe strongly correlated systems correctly, the choice of an active space imposes one of the greatest problems in multi-configurational quantum chemistry. In the AutoCAS algorithm, concepts from quantum information theory are exploited in order to automatically and consistently select orbitals for an active space. We present our `Python`-based AutoCAS [1, 2, 3, 4] module, which can be customized and employed in existing workflows to streamline multi-configurational calculations in a black-box manner. Due to the black-box-like selection of active spaces, post-active space methods like Tailored Coupled Cluster [5, 6, 7] or second order perturbation theory [8] can be routinely applied to recover dynamic correlation. Furthermore, in the AutoRXN workflow [9], a workflow for the exploration of chemical reaction networks, we automatically validated CCSD(T) energies with potential multi-reference character through AutoCAS.

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Transcorrelated Coupled Cluster Methods and the xTC Approach

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Methods for calculating electronic correlation are often plagued by the necessity to use large basis-sets, which severely limits their applicability. In recent years transcorrelation has shown to be a promising alternative to more established methods to improve basis-set convergence, like F12-methods. In the transcorrelation approach the Hamiltonian is similarity-transformed by a Jastrow factor. In our work we use sophisticated Jastrow factors optimized system-specific by variational Monte Carlo. [5] This approach does not only accelerate basis-set convergence, but also compress the wave function and by doing so can ease the strong electron correlation problem.

The similarity transformation with a Jastrow factor introduces numerous three-electron integrals, which for a long time rendered the approach unattractive. Our work on transcorrelated coupled cluster [1, 2, 3] has shown that a majority of the correlation stemming from the three-electron integrals can be conveniently incorporated into the one and two-electron integrals without significant accuracy loses. Building on these findings we developed the transcorrelation method via exclusion of explicit three body correlation (xTC). [4]

The xC approach makes use of the concept of generalized normal-ordering pioneered by Kutzelnigg and Mukherjee in order to contract intermediates incorporating three-electron correlation with density matrices, resulting in a non-Hermitian Hamiltonian with no more than two-body integrals. The eigenvalues of the xTC transformed Hamiltonian can be obtained with any quantum chemistry method, which can accommodate non-Hermitian two-electron integrals, including coupled cluster methods with arbitrarily high excitations.

We will present the theory of transcorrelated coupled cluster with singles and doubles (TC-CCSD) and the xTC approach, followed by benchmark calculations justifying thexTC approximation with a comparison of the full transcorrelated TC-CCSD with approximate TC-CCSD, neglecting the three-electron integrals normal-ordered with respect to the HF determinant for atoms and molecules on the HEAT set. [2, 3] Calculations with xTC-CCSD, which can be used with a normal-ordering with respect to a non-HF reference function, are presented as well. [4] Additionally, we explore the benefits of using the distinguishable cluster approximation in transcorrelated coupled cluster methods, showing further improvements over traditional coupled cluster methods.

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Using local molecular orbitals in diagonalization-free Hartree-Fock calculations.

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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[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. This treatment corresponds to a non-unitary transformation of orbitals, however, preserving the idempotency of the density matrix.

We apply this approach with a starting determinant using localized orbitals, i.e. we present a localized Hartree-Fock method. 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 T1 amplitudes and density matrix were examined for series of medium sized molecules.

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Separation of electron correlation energy based on the FNDMC energy with the node from the Hartree-Fock Slater determinant

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Distinguishing between dynamic and non-dynamic electron correlation energy is a fundamental concept in quantum chemistry. It can be challenging to make a clear distinction between the two types of correlation energy or to determine their actual contributions in specific cases using wave-function theory (WFT). This is because both single-reference and multi-reference WFT methods cover both types of correlation energy to some extent. Fixed-node diffusion quantum Monte Carlo (FNDQMC) accurately covers dynamic correlations, but it is limited in overall accuracy by the node of the trial wave function. We propose a method for separating electron correlation energy into dynamic and non-dynamic components by using FNDQMC and a restricted Hartree-Fock Slater determinant to fix the node. This approach provides an unambiguous and useful procedure for separating electron correlation energy, as demonstrated on multiple systems, including the He atom, bond breaking of H_2, BH, HF, and the H_2-H_2 system.

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Applications of FNDMC based separation of electron correlation energy

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Separation of dynamic and non-dynamic electron correlation energy is a useful concept in quantum chemistry. However, it may be difficult to make unambiguous distinction between these, or, evaluate their actual contributions in specific scenarios. Most often, non-dynamic correlation energy is obtained by taking the difference between the full-valence complete active space self-consistent field (CASSCF) calculation and HF reference. As we will show, CASSCF naturally includes some a priori unknown portion of dynamic correlation energy, making the separation somewhat unpredictable. Fixed-node diffusion quantum Monte Carlo (FNDQMC) method covers dynamic correlations exactly, and, its accuracy is limited by the node of the supplied trial wave function. Here we show that a combination of WFT and FNDQMC method using Hartree-Fock Slater determinant to fix the node within FNDQMC, enables an unambiguous and useful procedure for separation of electron correlation energy into dynamic and non-dynamic contributions. Moreover, such separation allows for quantifying the amount of dynamic correlation contained in CASSCF correlation energy. This is illustrated on multiple systems including bond breaking of HF, BH and CO molecules, and parametric H4 system. The proposed separation procedure provides useful insights for our understanding of electron correlation effects in complex systems.

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[3] E. Ramos-Cordoba, P. Salvador, E. Matito, Phys. Rev. E, **18** (2016), 24015.

List of Invited Speakers

- **Rodney J. Bartlett**, *University of Florida, USA*
- **Gero Friesecke**, *Technical University of Munich, Germany*
- **Artur F. Izmaylov**, *University of Toronto, Canada*
- **Mihály Kállay**, *Budapest University of Technology and Economics, Hungary*
- **Daniel Kats**, *Max Planck Institute for Solid State Research, Germany*
- **Karol Kowalski**, *Pacific Northwest National Laboratory, USA*
- **Simen Kvaal**, *University of Oslo, Norway*
- **Henrik R. Larsson**, *University of California, USA*
- **Nicholas Mayhall**, *Virginia Polytechnic Institute and State University, USA*
- **Piotr Piecuch**, *Michigan State University, USA*
- **Markus Reiher**, *ETH Zürich, Switzerland*
- **Masaaki Saitow**, *Nagoya University, Japan*
- **Christian Schilling**, *Ludwig Maximilian University, Germany*
- **Gustavo E. Scuseria**, *Rice University, USA*
- **Ágnes Szabados**, *Eötvös Loránd University, Hungary*
- **Alex Thom**, *University of Cambridge, England*
- **Dominika Zgid**, *University of Michigan, USA*

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Hugh Burton	University of Oxford, UK
Leo Chaussy	Aix-Marseille University CNRS, France
Jeremy Coe	Heriot-Watt University, UK
Ondrej Demel	J. Heyrovský Institute of Physical Chemistry, CAS, Czech Repulic
Lexin Ding	Ludwig Maximilian University of Munich, Germany
Robin Feldmann	ETH Zurich, Switzerland
Gero Friesecke	Technical University of Munich, Germany
Martin Ganahl	SandboxAQ, USA
Nina Glaser	ETH Zürich, Switzerland
Alexander Gunasekera	University of Oxford, UK
Jaroslav Hofierka	Queen's University Belfast, UK
Réka Anna Horváth	Budapest University of Technology and Economics, Hungary
Artur Izmaylov	University of Toronto Scarborough, Canada
Paul Johnson	Université Laval, Canada
Mihály Kállay	Budapest University of Technology and Economics, Hungary
Daniel Kats	Max Planck Institute for Solid State Research, Germany
Jiří Klimeš	Charles University, Czech Republic
Karol Kowalski	Pacific Northwest National Laboratory, USA
Simen Kvaal	University of Oslo, Norway
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Matej Veis	Comenius University / Faculty of Natural Sciences, Slovakia
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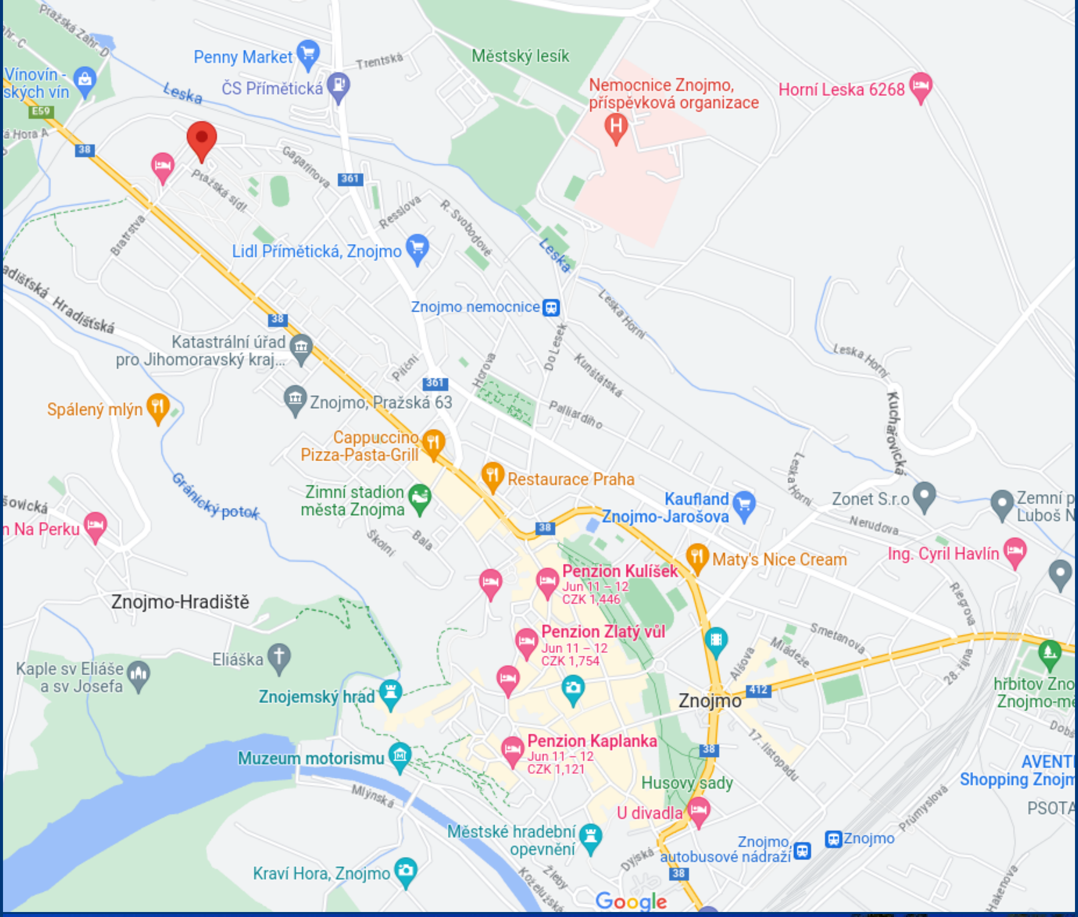
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Katastrální úřad pro Jihomoravský kraj...
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Cappuccino Pizza-Pasta-Grill
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Maty's Nice Cream
Ing. Cyril Havlín
Penzion Kulíšek
Jun 11 – 12
CZK 1,446
Znojmo-Hradiště
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