Project closing report: K100908

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1 Summary of the project according to the main goals

1.1 Background

Our modern society, without the possibilities provided by the information technology, is nearly unimaginable, and the industrial developments are based entirely on computer simulations. Nowadays, expensive models are not built only for the selection of the most suitable one from those, this is done based on simulations done by professional scientific softwares. The situation is not so simple in the case of smaller and smaller sizes, (e.g., the information technological devices of the future), where the familiar laws of classical physics cannot be applied, but the methods of quantum physics are needed. It would be a huge gain to simulate these systems by the use of computers only, sparing the huge expenses of experiments. Unfortunately, the situation is not so simple, we have to use approximative methods because of the complexity of the description of quantum mechanical systems. These methods do not often give sufficient description of the phenomena, or just give contradictory results. Because of this, experiments, theoretical calculations, and computer simulations are held together inseparably. The theoretical research, carried out during the four-year time period, is focusing on the development of new mathematical algorithms based on the laws of quantum mechanics, which altogether makes possible the simulation of quantum systems more complex than ever, and the prediction of their behavior or the designing of their properties.

1.2 Our main goals

We present our period closing report according to the project proposal submitted in 2012. That time we have defined our main goals as: “to study new exotic states and phase transitions in strongly correlated systems by taking advantage of analytic and numerical methods and to further develop the DMRG-like methods for correlated systems in which the interactions are long-ranged. The proposed work is a continuation of our previous research on the field financed by the OTKA grants K68340 and K73455 and it is part of various international collaborations. All of this activity is fundamental research. The results will be published in refereed scientific journals and in conference proceedings. During the full period about 20 scientific papers are expected.

Our study of strongly correlated systems and elements of information theory will be based on the non-local version of the DMRG method. Almost all physical models described by two-particle scattering processes can be described by a Hamiltonian of the form

$$\mathcal{H} = \sum_{ij\sigma} T_{ij} c^{\dagger}_{i\sigma} c_{j\sigma} + \sum_{ijkl\sigma\sigma'} V_{ijkl} c^{\dagger}_{i\sigma} c^{\dagger}_{j\sigma'} c_{k\sigma'} c_{l\sigma}, \tag{1}$$

where operators such as $c_{i\sigma}$ act on the Hilbert space formed from one-particle basis states. The indices i, j, k, l label quantum sites, which can be lattice sites in real-space representation, band and momentum indices in momentum space representation, or molecular orbitals in quantum chemical applications. The operators $c^{\dagger}_{i\sigma}$ or $c_{i\sigma}$ usually denote spin ladder or fermion creation and destruction operators, but other definitions are also possible. The matrix elements of the one-particle Hamiltonian are denoted with T_{ij}, while the matrix elements of two-particle interaction operator are given by V_{ijkl}. We plan to apply the non-local DMRG to models described in real and momentum space and to quantum chemical systems. Recent developments in the time-dependent DMRG and in matrix-product state expansion and tensor network techniques will also be integrated into our non-local DMRG code. Since the non-local DMRG can be viewed as an interdisciplinary method, it is expected to form a bridge between various fields of science, e.g., condensed matter physics, quantum chemistry, quantum information theory, nuclear physics, and quantum optics."

1.3 Our main results

We have developed scientific softwares (**Budapest QC-DMRG program package**), which have been used with great success in numerous research institutes and universities around the world, for, e.g., simulating material properties of solid state systems or molecular quantum chemistry, or for the quantum simulation of the information technology itself. The more and more complex applications demanded the continuous development of our methods. Various applications were carried out within numerous international collaborations (Czech Republic, Germany, Switzerland, Austria, Canada, USA, Spain and France). Among others, we have examined the strongly correlated electrons in magnetic materials in several quantum phases, exotic quantum phases in ultra cold atomic systems, and determined the correlation and entanglement patterns in molecules playing important role in chemical reactions.

Publications: According to the research plan we have studied various strongly correlated magnetic and electronic systems using analytical methods and numerical approaches. Our results are highly interdisciplinary and they cover the fields of Anderson and Kondo systems, ultra-cold atomic systems, quantum chemistry, relativistic quantum chemistry, nuclear structure theory, computer science, material science, quantum information theory and mathematical aspects of various numerical algorithms. Our results have been presented in international conferences and published in high quality journals. We have accomplished the tasks outlined in the proposal. Some partial tasks were not treated as new research areas emerged that we found to be more important. **Altogether we have published some 44 scientific papers, 5 dissertations, 4 on-line accessible lecture notes.**

Code developments:

- We have further developed the quantum chemistry version of the DMRG method and the tree-TNS algorithm.
- We have developed a four-component method (4c-DMRG) to deal with relativistic problems.
- We have presented an efficient implementation of the DMRG algorithm to treat nuclear shell models by utilizing various concepts of quantum information theory.
- We have presented a smart hybrid CPU-GPU implementation of the DMRG, which exploits the power of both CPU and GPU and tolerates problems exceeding the GPU memory size
- In a collaboration with the group of Prof. Noack we have applied an efficient, optimized version of the momentum-space DMRG to the Hubbard model in one and two dimensions. Two new codes were developed: one sequential code based on a strongly modified version of the open-source ITensor library, and one parallelized code based on a self-written tensor library.

Workshops: We have also organized an international focus workshop, which took place at the MPIPKS, Dresden in 2012. It provided a forum to bring together quantum chemists with their expertise on molecular properties, orbital sets, and current quantum chemical methods based on low-rank tensor factorizations on the one hand and condensed matter physicists and mathematicians that are developing more general tensor network methods based on quantum information insights, on the other hand. We have organized another international workshop on the topic of new wavefunction methods and entanglement based optimization methods in Mariapfarr, Austria in 2014. Also, on the national level, we have jointly organized two workshops on quantum entanglement, which took place in Budapest, in 2014 and 2015. This series is going to be continued.

Below we present our results in detail according to the research plan.

2 Applications and results in detail according to the research plan

2.1 Ultra-cold atoms

1. G. Barcza, E. Szirmai, Ö. Legeza, J. Sólyom: *Emergence of Quintet Superfluidity in the Chain of Partially Polarized Spin-3/2 Ultracold Atoms,* Phys. Rev. A Rapid Comm **86**, 061602 (2012).

   The system of ultracold atoms with hyperfine spin F=3/2 might be unstable against the formation of quintet pairs if the interaction is attractive in the quintet channel. We have investigated the behavior of correlation functions in a model including only s-wave interactions at quarter filling by large-scale density-matrix renormalization-group simulations. We show that the correlations of quintet pairs become quasi-long-ranged when the system is partially polarized, leading to the emergence of various mixed superfluid phases in which BCS-like pairs carrying different magnetic moment coexist.

2. E. Szirmai: *Two-orbital physics of high spin fermionic alkaline earth atoms confined in a one-dimensional chain,* Phys. Rev. B *88*, 195432 (2013).

   We study the effect of the coupling between the electronic ground state of high spin alkaline-earth fermionic atoms and their metastable optically excited state, when the system is confined in a one-dimensional chain, and show that the system provides a possible realization of a finite momentum pairing (Fulde-Ferrell-Larkin-Ovchinnikov-like) state without spin- or bare mass imbalance. We determine the β-functions of the renormalization group trajectories for general spin and analyze the structure of the possible gapped and gapless states in the hydrodynamic limit. Due to the SU(N) symmetry in the spin space, complete mode separation can not be observed even in the fully gapless 2N-component Luttinger liquid state. Contrary, 4 velocities characterize the system. We solve the renormalization group equations for spin-9/2 strontium-87 isotope and analyze in detail its phase diagram. The fully gapless Luttinger liquid state does not stabilize in the two-orbital system of the ^{87}Sr atoms, instead, different gapped non-Gaussian fixed points are identified either with dominant density or superconducting fluctuations. The superconducting states are stable in a nontrivial shaped region in the parameter space as a consequence of the coupling between the two electronic states.

3. P. Sinkovicz, A. Zamora, E. Szirmai, M. Lewenstein, G. Szirmai: *Spin liquid phases of alkaline-earth-metal atoms at finite temperature,* Phys. Rev. A **88**, 043619 (2013).

   We study spin liquid phases of spin-5/2 alkaline-earth-metal atoms on a honeycomb lattice at finite temperatures. Our analysis is based on a Gutzwiller projection variational approach recast to a path-integral formalism. In the framework of a saddle-point approximation we determine spin liquid phases with lowest free energy and study their temperature dependence. We identify a critical temperature, where all the spin liquid phases melt and the system goes to the paramagnetic phase. We also study the stability of the saddle-point solutions and show that a time-reversal symmetry breaking state, a so-called chiral spin liquid phase, is realized even at finite temperatures. We also determine the spin structure factor, which, in principle, is an experimentally measurable quantity and is the basic tool to map the spectrum of elementary excitations of the system.

4. G. Barcza, E. Szirmai, J. Sólyom, Ö. Legeza: *Phase Separation of Superfluids in the Chain of Four-Component Ultracold Atoms,* Eur. Phys. J. ST **224**: 533-538 (2015).

   We investigate the competition of various exotic superfluid states in a chain of spin-polarized ultracold fermionic atoms with hyperfine spin F=3/2 and s-wave contact interactions. We show that the ground state is an exotic inhomogeneous mixture in which two distinct superfluid phases — spin-carrying pairs and singlet quartets — form alternating domains in an extended region of the parameter space.

5. D. Jakab, E. Szirmai, M. Lewenstein, G. Szirmai: *Competing valence bond and symmetry breaking Mott states of spin-3/2 fermions on a honeycomb lattice,* arXiv:1509.07362, submitted to Phys Rev B (2015).

The two-dimensional generalization of the so called Affleck-Kennedy-Lieb-Tasaki (AKLT) state can play a central role in the progress of quantum information theory, however, its experimental realization is still an open problem. In this paper we have shown that the ground state of the spin-3/2 ultracold atomic system in a honeycomb lattice is such a resonatig valence bond (RVB) state which can be considered as an SU(4) symmetric, two-dimensional generalization of the AKLT state. We have also shown that this state is stable against perturbations which violate the SU(4) symmetry. The competing phases emerged for strong perturbations are also analyzed.

6. E. Szirmai, G. Barcza, J. Sólyom, Ö. Legeza: *Interplay between exotic superfluidity and magnetism in a chain of four-component ultracold atoms,* arXiv:1512.06669, submitted to Phys Rev Lett (2015).

   We investigate the spin-polarized chain of ultracold fermionic atoms with spin-3/2 described by the fermionic Hubbard model with SU(4) symmetric attractive interaction. The competition of bound pairs, trions, quartets and unbound atoms is studied analytically and by density matrix renormalization group simulations. We find several distinct states where bound particles coexist with the ferromagnetic state of unpaired fermions. In particular, an exotic inhomogeneous Fulde-Ferrell-Larkin-Ovchinnikov (FFLO)-type superfluid of quartets in a magnetic background of uncorrelated atoms is found for weaker interactions. We show that the system can be driven from this quartet-FFLO state to a molecular state of localized quartets which is also reflected in the static structure factor. For strong enough coupling, spatial segregation between molecular crystals and ferromagnetic liquids emerges due to the large effective mass of the composite particles.

2.2 Kondo and Anderson systems

7. I. Hagymási, K. Itai, J. Sólyom: *Periodic Anderson model with correlated conduction electrons: Variational and exact diagonalization study,* Phys. Rev. B **85**, 235116 (2012).

   We investigate an extended version of the periodic Anderson model (the so-called periodic Anderson-Hubbard model) with the aim to understand the role of interaction between conduction electrons in the formation of the heavy-fermion and mixed-valence states. Two methods are used: (i) variational calculation with the Gutzwiller wave function optimizing numerically the ground-state energy and (ii) exact diagonalization of the Hamiltonian for short chains. The f-level occupancy and the renormalization factor of the quasiparticles are calculated as a function of the energy of the f orbital for a wide range of the interaction parameters. The results obtained by the two methods are in reasonably good agreement for the periodic Anderson model. The agreement is maintained even when the interaction between band electrons, U_d, is taken into account, except for the half-filled case. This discrepancy can be explained by the difference between the physics of the one- and higher-dimensional models. We find that this interaction shifts and widens the energy range of the bare f level, where heavy-fermion behavior can be observed. For large-enough U_d this range may lie even above the bare conduction band. The Gutzwiller method indicates a robust transition from Kondo insulator to Mott insulator in the half-filled model, while U_d enhances the quasiparticle mass when the filling is close to half filling.

8. I. Hagymási, K. Itai, J. Sólyom: *Periodic Anderson model with d-f interaction,* Proceedings of the European Conference Physics of Magnetism 2011, Poznan, Acta Physica Polonica (2012).

   We investigate an extended version of the periodic Anderson model where an interaction is switched on between the doubly occupied d- and f-sites. We perform variational calculations using the Gutzwiller trial wave function. We calculate the f-level occupancy as a function of the f-level energy with different interaction strengths. It is shown that the region of valence transition is sharpened due to the new interaction.

9. I. Hagymási, K. Itai, J. Sólyom: *Quantum criticality and first-order transitions in the extended periodic Anderson model,* Phys. Rev. B **87**, 125146 (2013).

   We investigate the behavior of the periodic Anderson model in the presence of d-f Coulomb interaction (U_{df}) using mean-field theory, variational calculation, and exact diagonalization of finite chains. The variational approach based on the Gutzwiller trial wave function gives a critical value of U_{df} and two quantum critical points (QCPs), where the valence susceptibility diverges. We derive the critical exponent for the valence susceptibility and investigate how the position of the QCP depends on the other parameters of the Hamiltonian. For larger values of U_{df}, the Kondo regime is bounded by two first-order transitions. These first-order transitions merge into a triple point at a certain value of U_{df}.

For even larger U_{df} valence skipping occurs. Although the other methods do not give a critical point, they support this scenario.

10. I. Hagymási, K. Itai, J. Sólyom: *Hubbard physics in the symmetric half-filled periodic anderson-hubbard model,* JOURNAL OF THE KOREAN PHYSICAL SOCIETY **62**:(10) pp. 1423 (2013).

    Two very different methods – exact diagonalization on finite chains and a variational method – are used to study the possibility of a metal-insulator transition in the symmetric half-filled periodic Anderson-Hubbard model. With this aim we calculate the density of doubly occupied d sites as a function of various parameters. In the absence of on-site Coulomb interaction (U_f) between f electrons, the two methods yield similar results. The double occupancy of d levels remains always finite just as in the one-dimensional Hubbard model. Exact diagonalization on finite chains gives the same result for finite U_f, while the Gutzwiller method leads to a Brinkman-Rice transition at a critical value (U_d^c), which depends on U_f and V.

11. I. Hagymási, J. Sólyom, Ö. Legeza: *Interorbital interaction in the one-dimensional periodic Anderson model: A density-matrix renormalization-group study,* Phys. Rev. B **90**, 125137 (2014).

    We investigate the effect of the Coulomb interaction, U_{cf}, between the conduction and f electrons in the periodic Anderson model using the density matrix renormalization group algorithm. We calculate the excitation spectrum of the half-filled symmetric model with an emphasis on the spin and charge excitations. In the one-dimensional version of the model, it is found that the spin gap is smaller than the charge gap below a certain value of U_{cf} and the reversed inequality is valid for stronger U_{cf}. This behavior is also verified by the behavior of the spin and density correlation functions. We also perform a quantum information analysis of the model and determine the entanglement map of the f and conduction electrons. It is revealed that for a certain U_{cf} the ground state is dominated by the configuration in which the conduction and f electrons are strongly entangled, and the ground state is almost a product state. For larger U_{cf}, the sites are occupied alternatingly dominantly by two f electrons or by two conduction electrons.

12. I. Hagymási: *Nehézfermionos és vegyes valenciájú viselkedés kiterjesztett periodikus Anderson-modellekben,* PhD Thesis, ELTE (2014).

13. I. Hagymási, J. Sólyom, Ö. Legeza: *Competition between Hund's coupling and Kondo effect in a one-dimensional extended periodic Anderson model,* Phys. Rev. B **92**, 035108 (2015).

    We study the ground-state properties of an extended periodic Anderson model to understand the role of Hund's coupling between localized and itinerant electrons using the density-matrix renormalization group algorithm. By calculating the von Neumann entropies we show that two phase transitions occur and two new phases appear as the hybridization is increased in the symmetric half-filled case due to the competition between Kondo effect and Hund's coupling. In the intermediate phase, which is bounded by two critical points, we found a dimerized ground state, while in the other spatially homogeneous phases the ground state is Haldane-like and Kondo-singlet-like, respectively. We also determine the entanglement spectrum and the entanglement diagram of the system by calculating the mutual information thereby clarifying the structure of each phase.

14. I. Hagymási, J. Sólyom, Ö. Legeza: *Momentum distribution functions in a one-dimensional extended periodic Anderson model,* Adv. in Cond. Mat. Phys. **2015**, 614017 (2015).

    We study the momentum distribution of the electrons in an extended periodic Anderson model, where the interaction, U_{cf}, between itinerant and localized electrons is taken into account. In the symmetric half-filled model, due to the increase of the interorbital interaction, the f electrons become more and more delocalized, while the itinerancy of conduction electrons decreases. Above a certain value of U_{cf} the f electrons become again localized together with the conduction electrons. In the less than half-filled case, we observe that U_{cf} causes strong correlations between the f electrons in the mixed valence regime.

2.3 Other spin and fermion models

15. G. Barcza, Ö. Legeza, R. M. Noack, J. Sólyom: *On the dimerized phase in the cross-coupled antiferromagnetic spin ladder,* Phys. Rev. B **86**, 075133 (2012).

We revisit the phase diagram of the frustrated s=1/2 spin ladder with antiferromagnetic rung and diagonal couplings. In particular, we reexamine the evidence for the columnar dimer phase, which has been predicted from analytic treatment of the model and has been claimed to be found in numerical calculations. By performing density-matrix renormalization-group (DMRG) calculations on long ladders, keeping a large number of states within the DMRG, and carrying out careful scaling in number of states kept and system size, we calculate the behavior of the dimer order parameter as a function of frustration strength. We find no positive numerical evidence for a finite dimer order parameter in the thermodynamic limit anywhere in the parameter regime in which the columnar dimer phase is expected to appear. Conservative error estimates in the scaling of our data place stringent limits on the maximum possible value of the dimer order parameter and the maximum possible extent of the parameter regime in which a sufficiently weak dimer phase could still exist.

16. W. Brzezicki, I. Hagymási, J. Dziarmaga, Ö. Legeza: *Second-order Peierls transition in the spin-orbital Kumar-Heisenberg model,* Phys. Rev. B **91**, 205137 (2015).

    We add a Heisenberg interaction term $\propto \lambda$ in the one-dimensional SU(2)$\otimes$XY spin-orbital model introduced by B. Kumar. At $\lambda = 0$ the spin and orbital degrees of freedom can be separated by a unitary transformation leading to an exact solution of the model. We show that a finite $\lambda > 0$ leads to spontaneous dimerization of the system which in the thermodynamic limit becomes a smooth phase transition at $\lambda \to 0$, whereas it remains discontinuous within the first order perturbation approach. We present the behavior of the entanglement entropy, energy gap and dimerization order parameter in the limit of $\lambda \to 0$ confirming the critical behavior. Finally, we show the evidence of another phase transition in the Heisenberg limit, $\lambda \to \infty$, and give a qualitative analytical explanation of the observed dimerized states both in the limit of small and large λ.

17. G. Barcza, R. M. Noack, and J. Sólyom, Ö Legeza: *Entanglement patterns and generalized correlation functions in quantum many body systems,* Phys. Rev. B **92**, 125140 (2015).

    We introduce transition operators that in a given basis of the single-site states of a many-body system have a single nonvanishing matrix element and introduce their correlation functions. We show that they fall into groups that decay with the same rate. The mutual information defined in terms of the von Neumann entropy between two sites is given in terms of these so-called generalized correlation functions. We confirm numerically that the long-distance decay of the mutual information follows the square of that of the most slowly decaying generalized correlation function. The main advantage of our procedure is that, in order to identify the most relevant physical processes, there is no need to know a priori the nature of the ordering in the system, i.e., no need to explicitly construct particular physical correlation functions. We explore the behavior of the mutual information and the generalized correlation functions for comformally invariant models and for the SU(n) Hubbard model with $n = 2, 3, 4$, and 5, which are, in general, not conformally invariant. In this latter case, we show that for filling $f = 1/q$ and $q < n$, the ground state consists of highly entangled q-site units that are further entangled by single bonds. In addition, we extend the picture of the two-site mutual information and the corresponding generalized correlation functions to the n-site case.

18. E. Szirmai, H. Nonne: *Competing valence bond states of spin-3/2 fermions on strongly coupled ladder,* Phys. Rev. B **90**, 245135 (2014).

    We study the possible ground state configurations of two strongly coupled chains of charge neutral spin-3/2 fermionic atoms interacting via short range van der Waals interaction. The coupling between the two chains is realized by relatively large hopping amplitude. Exploiting that such a ladder configuration can be mapped to an effective one-band model we analyze the emerging ground states of the system. We show that various spatially inhomogeneous states, valence bond states, plaquette states compete depending on the filling and the ratio of the interaction strengths in the singlet and quintet scattering channel. We find that a Luttinger liquid state is the ground state of the strongly coupled ladder in an extended region of the parameter space, and we also show that a topologically nontrivial charge Haldane state can emerge in the strongly coupled ladder at quarter and three-quarter fillings.

2.4 Polydiacetylenes

19. G. Barcza, W. Barford, F. Gebhard, Ö. Legeza: *Excited states in polydiacetylene chains: A density matrix renormalization group study,* Phys. Rev. B **87**, 245116 (2013).

We study theoretically poly-diacetylene chains diluted in their monomer matrix. We employ the density-matrix renormalization group method (DMRG) on finite chains to calculate the ground state and low-lying excitations of the corresponding Peierls–Hubbard-Ohno Hamiltonian which is characterized by the electron transfer amplitude t_0 between nearest neighbors, by the electron-phonon coupling constant α, by the Hubbard interaction U, and by the long-range interaction V. We treat the lattice relaxation in the adiabatic limit, i.e., we calculate the polaronic lattice distortions for each excited state. Using chains with up to 102 lattice sites, we can safely perform the extrapolation to the thermodynamic limit for the ground-state energy and conformation, the single-particle gap, and the energies of the singlet exciton, the triplet ground state, and the optical excitation of the triplet ground state. The corresponding gaps are known with high precision from experiment. We determine a coherent parameter set $(t_0^* = 2.4\,\mathrm{eV}, \alpha^* = 3.4\,\mathrm{eV/Å}, U^* = 6\,\mathrm{eV}, V^* = 3\,\mathrm{eV})$ from a fit of the experimental gap energies to the theoretical values which we obtain for 81 parameter points in the four dimensional search space (t_0, α, U, V). We identify dark in-gap states in the singlet and triplet sectors as seen in experiment. Using a fairly stiff spring constant, the length of our unit cell is about one percent larger than its experimental value.

20. G. Barcza, F. Gebhard, Ö. Legeza: *Rigorous treatment of strong electronic correlations in polydiacetylene chains,* Mol. Phys. **111**, 2506 (2013).

    We study theoretically polydiacetylene chains diluted in their monomer matrix. We employ the density-matrix renormalisation group method (DMRG) on finite chains to calculate the ground state and low-lying excitations of the corresponding Peierls–Hubbard-Ohno Hamiltonian that is characterised by the electron transfer amplitude t_0 between nearest-neighbours, by electron–phonon coupling constant α, by Hubbard interaction U, and by long-range interaction V. We treat lattice relaxation in the adiabatic limit, i.e., we calculate the polaronic lattice distortions for each excited state. We present accurate DMRG results for the single-particle gap, the singlet exciton, the triplet ground state and its optical excitation, and find a good agreement with experimental data for PDA–3BCMU chains.

21. Timár M.: *Erősen korrelált rendszerek vizsgálata renormálási módszerekkel,* BsC Thesis, BME (2013).

22. M. Timár: *Investigation of low energy optical properties of a π-conjugated polymer,* OTDK Thesis (2015, first prize).

23. M. Timár: *Investigation of low energy optical properties of a π-conjugated polymer,* MSc thesis, BME (2015).

24. M. Timár, G. Barcza, F. Gebhard, L. Veis, Ö. Legeza: *Hückel–Hubbard-Ohno modeling of π-bonds in ethene and ethyne with application to trans-polyacetylene,* arXiv:1512.03229, submitted to Phys. Chem. Chem. Phys. (2015).

    Quantum chemistry calculations provide the potential energy between two carbon atoms in ethane ($H_3C{-}CH_3$), ethene ($H_2C{=}CH_2$), and ethyne ($HC{\equiv}CH$) as a function of the atomic distance. Based on the energy function for the σ-bond in ethane, $V_\sigma(r)$, we use the Hückel model with Hubbard–Ohno interaction for the π electrons to describe the energies $V_{\sigma\pi}(r)$ and $V_{\sigma\pi\pi}(r)$ for the $\sigma\pi$ double bond in ethene and the $\sigma\pi\pi$ triple bond in ethyne, respectively. The fit of the force functions shows that the Peierls coupling can be estimated with some precision whereas the Hubbard-Ohno parameters are insignificant at the distances under consideration. We apply the Hückel-Hubbard-Ohno model to describe the bond lengths and the energies of elementary electronic excitations of trans-polyacetylene, $(CH)_n$, and adjust the σ-bond potential for conjugated polymers.

2.5 Quantum chemistry

25. K. Boguslawski, K. H. Marti, Ö. Legeza, M. Reiher: *Accurate ab initio spin densities,* J. Chem. Theory Comput. **2012**, 8, 1970 (2012).

    We present an approach for the calculation of spin density distributions for molecules that require very large active spaces for a qualitatively correct description of their electronic structure. Our approach is based on the density-matrix renormalization group (DMRG) algorithm to calculate the spin density matrix elements as a basic quantity for the spatially resolved spin density distribution. The spin density matrix elements are directly determined from the second-quantized elementary operators optimized by the DMRG algorithm. As an analytic convergence criterion for the spin density distribution, we employ our recently developed sampling-reconstruction scheme [J. Chem. Phys.2011, 134, 224101] to build an accurate complete-active-space configuration-interaction (CASCI) wave function from the optimized matrix product states. The spin density matrix elements can then also be determined as an expectation value employing the reconstructed wave function expansion. Furthermore, the explicit reconstruction of a CASCI-type wave function provides insight into chemically interesting features of the molecule under study such as the distribution of α and β electrons in terms of Slater determinants, CI coefficients, and natural orbitals. The methodology is applied to an iron nitrosyl complex which we have identified as a challenging system for standard approaches [J. Chem. Theory Comput.2011, 7, 2740].

26. K. Boguslawski, P. Tecmer, Ö. Legeza, M. Reiher: *Entanglement Measures for Single- and Multi-Reference Correlation Effects,* J. Phys. Chem. Lett., **2012**, 3 (21), 3129 (2012).

    Electron correlation effects are essential for an accurate ab initio description of molecules. A quantitative a priori knowledge of the single- or multireference nature of electronic structures as well as of the dominant contributions to the correlation energy can facilitate the decision regarding the optimum quantum chemical method of choice. We propose concepts from quantum information theory as orbital entanglement measures that allow us to evaluate the single- and multireference character of any molecular structure in a given orbital basis set. By studying these measures we can detect possible artifacts of small active spaces.

27. Ö. Legeza, M. Reiher, B. Paulus, R. Schneider: *Entanglement based approaches in quantum chemsitry* (EBAQC), MPI-PKS, Dresden (2012).

28. K. Boguslawski, P. Tecmer, G. Barcza, Ö. Legeza, M. Reiher: *Orbital entanglement in bond-formation processes,* J. Chem. Theory Comput. **9**, 2959, (2013).

    The accurate calculation of the (differential) correlation energy is central to the quantum chemical description of bond-formation and bond-dissociation processes. In order to estimate the quality of single- and multireference approaches for this purpose, various diagnostic tools have been developed. In this work, we elaborate on our previous observation [J. Phys. Chem. Lett.2012, 3, 3129] that one- and two-orbital-based entanglement measures provide quantitative means for the assessment and classification of electron correlation effects among molecular orbitals. The dissociation behavior of some prototypical diatomic molecules features all types of correlation effects relevant for chemical bonding. We demonstrate that our entanglement analysis is convenient to dissect these electron correlation effects and to provide a conceptual understanding of bond-forming and bond-breaking processes from the point of view of quantum information theory.

29. E. Fertitta, B. Paulus, G. Barcza, Ö. Legeza: *Investigation of metal-insulator-like transition through the ab initio density matrix renormalization group approach,* Phys. Rev. B **90**, 245129 (2014).

    We have studied the metal–insulator-like transition in pseudo-one-dimensional systems, i.e., lithium and beryllium rings, through the ab initio density matrix renormalization group (DMRG) method. Performing accurate calculations for different interatomic distances and using quantum information theory, we investigated the changes occurring in the wave function between a metallic-like state and an insulating state built from free atoms. We also discuss entanglement and relevant excitations among the molecular orbitals in the Li and Be rings and show that the transition bond length can be detected using orbital entropy functions. Also, the effect of different orbital bases on the effectiveness of the DMRG procedure is analyzed comparing the convergence behavior.

30. M. Mottet, P. Tecmer, K. Boguslawski, Ö. Legeza, M. Reiher: *Quantum entanglement in carbon-carbon, carbon-phosphorus and silicon-silicon bonds,* Phys. Chem. Chem. Phys. **16**, 8872 (2014).

    The chemical bond is an important local concept to understand chemical compounds and processes. Unfortunately, like most local concepts, the chemical bond and the bond order do not correspond to any physical observable and thus cannot be determined as an expectation value of a quantum chemical operator. We recently demonstrated [Boguslawski et al., J. Chem. Theory Comput., 2013, 9, 2959–2973] that one- and two-orbital-based entanglement measures can be applied to interpret electronic wave functions in terms of orbital correlation. Orbital entanglement emerged as a powerful tool to provide a qualitative understanding of bond-forming and bond-breaking processes, and allowed for an estimation of bond orders of simple diatomic molecules beyond the classical bonding models. In this article we demonstrate that the orbital entanglement analysis can be extended to polyatomic molecules to understand chemical bonding.

31. Ö. Legeza: *New wavefucntion methods and entanglement optimizations in quantum chemistry,* `http://tagung-theoretische-chemie.uni-graz.at/en/past-workshops/workshop-2014/`, lecture notes (2014).

32. P. Tecmer, K. Boguslawski, Ö. Legeza, M. Reiher: *Unravelling the quantum-entanglement effect of noble gas coordination on the spin ground state of CUO,* Phys. Chem. Chem. Phys. **16**, 719 (2014).

    The accurate description of the complexation of the CUO molecule by Ne and Ar noble gas matrices represents a challenging task for present-day quantum chemistry. Especially, the accurate prediction of the spin ground state of different CUO–noble-gas complexes remains elusive. In this work, the interaction of the CUO unit with the surrounding noble gas matrices is investigated in terms of complexation energies and dissected into its molecular orbital quantum entanglement patterns. Our analysis elucidates the anticipated singlet–triplet ground-state reversal of the CUO molecule diluted in different noble gas matrices and demonstrates that the strongest uranium–noble gas interaction is found for CUOAr4 in its triplet configuration.

33. C. Duperrouzel, P. Tecmer, K. Boguslawski, G. Barcza, Ö. Legeza, P. W. Ayers: *A quantum informational approach for dissecting chemical reactions,* Chem. Phys. Lett. **621**, 160 (2015).

    We present a conceptionally different approach to dissect bond-formation processes in metal-driven catalysis using concepts from quantum information theory. Our method uses the entanglement and correlation among molecular orbitals to analyze changes in electronic structure that accompany chemical processes. As a proof-of-principle example, the evolution of nickel-ethene bond-formation is dissected, which allows us to monitor the interplay of back-bonding and π-donation along the reaction coordinate. Furthermore, the reaction pathway of nickel-ethene complexation is analyzed using quantum chemistry methods, revealing the presence of a transition state. Our study supports the crucial role of metal-to-ligand back-donation in the bond-forming process of nickel–ethene.

34. E. Fertitta, B. Paulus, G. Barcza, Ö. Legeza: *On the calculation of complete dissociation curves of closed-shell pseudo-onedimensional systems through the multireference method of increments,* J. Chem. Phys. **143**, 114108 (2015).

    The Method of Increments (MoI) has been employed using a multireference approach to calculate the dissociation curve of beryllium ring-shaped clusters Ben of different sizes. Benchmarks obtained through different single and multireference methods including the ab initio Density Matrix Renormalization Group (DMRG) were used to verify the validity of the MoI truncation which showed a reliable behavior for the whole dissociation curve. Moreover we investigated the size dependence of the correlation energy at different distances in order to extrapolate the values for the periodic chain and to discuss the transition from a metal-like to a insulating-like behavior of the wave function through quantum chemical considerations.

35. Y. Zhao, K. Boguslawski, P. Tecmer, C. Duperrouzel, G. Barcza, Ö. Legeza, P. W Ayers: *Dissecting the Bond Formation Process of d^{10}-Metal-Ethene Complexes with Multireference Approaches,* Theor. Chem. Acc. 2015, 134:120 (2015).

    The bonding mechanism of ethene to a nickel or palladium center is studied by the density matrix renormalization group algorithm, the complete active space self consistent field method, coupled cluster theory, and density functional theory. Specifically, we focus on the interaction between the metal atom and bis-ethene ligands in perpendicular and parallel orientations. The bonding situation in these structural isomers is further scrutinized using energy decomposition analysis and quantum information theory. Our study highlights the fact that when two ethene ligands are oriented perpendicular to each other, the complex is stabilized by the metal-to-ligand double-back-bonding mechanism. Moreover, we demonstrate that nickel-ethene complexes feature a stronger and more covalent interaction between the ligands and the metal center than palladium-ethene compounds with similar coordination spheres.

36. T. Szilvási, G. Barcza, Ö. Legeza: *Concept of chemical bond and aromaticity based on quantum information theory,* arXiv:1509.04241, submitted to J. Am. Chem. Soc. (2015).

    Quantum information theory (QIT) emerged in physics as standard technique to extract relevant information from quantum systems. It has already contributed to the development of novel fields like quantum computing, quantum cryptography, and quantum complexity. This arises the question what information is stored according to QIT in molecules which are inherently quantum systems as well. Rigorous analysis of the central quantities of QIT on systematic series of molecules offered the introduction of the concept of chemical bond and aromaticity directly from physical principles and notions. We identify covalent bond, donor-acceptor dative bond, multiple bond, charge-shift bond, and aromaticity indicating unified picture of fundamental chemical models from ab initio.

2.6 Relativistic Quantum Chemistry

37. S. Knecht, Ö. Legeza, M. Reiher: *Four-Component Density Matrix Renormalization Group,* J. Chem. Phys. **140**, 041101 (2014).

    We present the first implementation of the relativistic quantum chemical two- and four-component density matrix renormalization group algorithm that includes a variational description of scalar-relativistic effects and spin–orbit coupling. Numerical results based on the four-component Dirac–Coulomb Hamiltonian are presented for the standard reference molecule for correlated relativistic benchmarks: thallium hydride.

38. L. Veis and O. Legeza, *Effect of various tensor representations on the 4c-DMRG method,* unpublished manuscript

2.7 Tensor network states

39. R. Schneider, T. Rohwedder, Ö. Legeza: *Numerical approaches for high-dimensional PDE's for quantum chemistry,* Encyclopedia of Applied and Computational Mathematics, Springer (2013).

    The treatment of high-dimensional problems such as the Schrödinger equation can be approached by concepts of tensor product approximation. We have presented general techniques that can be used for the treatment of high-dimensional optimization tasks and time-dependent equations, and connect them to concepts already used in many-body quantum physics.

40. Ö. Legeza, Th. Rohwedder, R. Schneider, Sz. Szalay: *Tensor Product Approximation (DMRG) and Coupled Cluster method in Quantum Chemistry,* book chapter in V. Bach, L. Delle Site: Many-Electron Approaches in Physics, Chemistry and Mathematics, Heidelberg (2014). pp 53-76 ISBN:978-3-319-06378-2 (arXiv:1310.2736).

    We present the Coupled Cluster (CC) method and the Density matrix Renormalization Group (DMRG) method in a unified way, from the perspective of recent developments in tensor product approximation. We present an introduction into recently developed hierarchical tensor representations, in particular tensor trains which are matrix product states in physics language. The discrete equations of full CI approximation applied to the electronic Schrödinger equation is casted into a tensorial framework in form of the second quantization. A further approximation is performed afterwards by tensor approximation within a hierarchical format or equivalently a tree tensor network. We establish the (differential) geometry of low rank hierarchical tensors and apply the Driac Frenkel principle to reduce the original high-dimensional problem to low dimensions. The DMRG algorithm is established as an optimization method in this format with alternating directional search. We briefly introduce the CC method and refer to our theoretical results. We compare this approach in the present discrete formulation with the CC method and its underlying exponential parametrization.

41. V. Murg, F. Verstraete, R. Schneider, P. R. Nagy, O. Legeza: *Tree tensor network state study of the ionic-neutral curve crossing of LiF,* J. Chem. Theory Comput. **11**, 1027 (2015).

    We study the tree-tensor-network-state (TTNS) method with variable tensor orders for quantum chemistry. TTNS is a variational method to efficiently approximate complete active space (CAS) configuration interaction (CI) wave functions in a tensor product form. TTNS can be considered as a higher order generalization of the matrix product state (MPS) method. The MPS wave function is formulated as products of matrices in a multiparticle basis spanning a truncated Hilbert space of the original CAS-CI problem. These matrices belong to active orbitals organized in a one-dimensional array, while tensors in TTNS are defined upon a tree-like arrangement of the same orbitals. The tree-structure is advantageous since the distance between two arbitrary orbitals in the tree scales only logarithmically with the number of orbitals N, whereas the scaling is linear in the MPS array. It is found to be beneficial from the computational costs point of view to keep strongly correlated orbitals in close vicinity in both arrangements; therefore, the TTNS ansatz is better suited for multireference problems with numerous highly correlated orbitals. To exploit the advantages of TTNS a novel algorithm is designed to optimize the tree tensor network topology based on quantum information theory and entanglement. The superior performance of the TTNS method is illustrated on the ionic-neutral avoided crossing of LiF. It is also shown that the avoided crossing of LiF can be localized using only ground state properties, namely one-orbital entanglement.

42. Ö. Legeza: *Generalized tensor methods and entanglement measurements for strongly correlated systems,* `http://ldqs.iyte.edu.tr/wp-content/uploads/2014/08/Legeza_izmir_2014_v01.pdf`, lecture notes (2014).

43. Sz. Szalay, M. Pfeffer, V. Murg, G. Barcza, F. Verstraete, R. Schneider, Ö. Legeza: *Tensor product methods and entanglement optimization for ab initio quantum chemistry,* Int. J. Quant. Chem. **115**, 1342 (2015).

    The treatment of high-dimensional problems such as the Schrödinger equation can be approached by concepts of tensor product approximation. We present general techniques that can be used for the treatment of high-dimensional optimization tasks and time-dependent equations, and connect them to concepts already used in many-body quantum physics. Based on achievements from the past decade, entanglement-based methods—developed from different perspectives for different purposes in distinct communities already matured to provide a variety of tools – can be combined to attack highly challenging problems in quantum chemistry. The aim of the present paper is to give a pedagogical introduction to the theoretical background of this novel field and demonstrate the underlying benefits through numerical applications on a text book example. Among the various optimization tasks, we will discuss only those which are connected to a controlled manipulation of the entanglement which is in fact the key ingredient of the methods considered in the paper. The selected topics will be covered according to a series of lectures given on the topic "New wavefunction methods and entanglement optimizations in quantum chemistry" at the Workshop on Theoretical Chemistry, February 18–21, 2014, Mariapfarr, Austria.

2.8 Basis optimizations

44. Ch. Krumnow, Ö. Legeza, J. Eisert: *Fermionic orbital optimisation in tensor network states,* arXiv:1504.00042, submitted to Phys. Rev. Lett (2015).

    Tensor network states and specifically matrix-product states have proven to be a powerful tool for simulating ground states of strongly correlated spin models. Recently, they have also been applied to interacting fermionic problems, specifically in the context of quantum chemistry. A new freedom arising in such non-local fermionic systems is the choice of orbitals, it being far from clear what choice of fermionic orbitals to make. In this work, we propose a way to overcome this challenge. We suggest a method intertwining the optimisation over matrix product states with suitable fermionic Gaussian mode transformations, hence bringing the advantages of both approaches together. The described algorithm generalises basis changes in the spirit of the Hartree-Fock methods to matrix-product states, and provides a black box tool for basis optimisation in tensor network methods.

2.9 Development of non-local DMRG

45. G. Ehlers, J. Sólyom, Ö. Legeza, R. M. Noack: *Entanglement structure of the Hubbard model in momentum space,* Phys. Rev. B **92**, 235116 (2015).

    We study the properties of the ground states of the one- and two-dimensional Hubbard models at half-filling and moderate doping using entanglement-based measures, which we calculate numerically using the momentum-space density matrix renormalization group (DMRG). In particular, we investigate quantities such as the single-site entropy and two-site mutual information of single-particle momentum states as well as the behavior of the bipartite subsystem entropy for partitions in momentum space. The distribution of these quantities in momentum space gives insight into the fundamental nature of the ground state, insight that can be used to make contact with weak-coupling-based analytic approaches and to optimize numerical methods, the momentum-space DMRG in particular. We study the site and subsystem entropies as a function of interaction strength U and system size. In both the one- and two-dimensional cases, we find that the subsystem entropy scales proportionally to U^2 for weak U and proportionally to volume. Nevertheless, the optimized momentum-space DMRG can provide variationally accurate results for the two-dimensional Hubbard model at weak coupling for moderate system sizes.

46. G. Barcza: *Nonlocal density matrix renormalization group applied to strongly correlated systems,* PhD thesis, ELTE (2015).

2.10 New research area not included in the research plan: Multipartite entanglement and correlation theory

47. Sz. Szalay: *Quantum entanglement in finite-dimensional Hilbert spaces,* arXiv:1302.4654, PhD thesis, BME (2013).

    In the past decades, quantum entanglement has been recognized to be the basic resource in quantum information theory. A fundamental need is then the understanding its qualification and its quantification: Is the quantum state entangled, and if it is, then how much entanglement is carried by that? These questions introduce the topics of separability criteria and entanglement measures, both of which are based on the issue of classification of multipartite entanglement. In this dissertation, after reviewing these three fundamental topics for finite dimensional Hilbert spaces, we present our contribution to knowledge. Our main result is the elaboration of the partial separability classification of mixed states of quantum systems composed of arbitrary number of subsystems of Hilbert spaces of arbitrary dimensions. This problem is simple for pure states, however, for mixed states it has not been considered in full detail yet. We give not only the classification but also necessary and sufficient criteria for the classes, which make it possible to determine to which class a mixed state belongs. Moreover, these criteria are given by the vanishing of quantities measuring entanglement. Apart from these, we present some side results related to the entanglement of mixed states. These results give some illustrations and examples.

48. Sz. Szalay: *Entanglement and correlations: an introduction,* slides of lectures (Entanglement Day, 2014, see `https://indico.kfki.hu/event/206/`)

49. Sz. Szalay: *Multipartite entanglement: the curious case of three qubits,* slides of a lecture (Entanglement Day, 2015, see `https://indico.kfki.hu/event/315/`)

50. Sz. Szalay: *Multipartite entanglement measures,* Phys. Rev. A **92**, 042329 (2015).

    The main concern of this paper is how to define proper measures of multipartite entanglement for mixed quantum states. Since the structure of partial separability and multipartite entanglement is getting complicated if the number of subsystems exceeds two, one can not expect the existence of an ultimate scalar entanglement measure, which grasps even a small part of the rich hierarchical structure of multipartite entanglement, and some higher order structure characterizing that is needed. In this paper we make some steps towards this direction. First, we reveal the lattice-theoretic structure of the partial separability classification, introduced earlier [Sz. Szalay and Z. Kokenyesi, Phys. Rev. A 86, 032341 (2012)]. It turns out that, mathematically, the structure of the entanglement classes is the up-set lattice of the structure of the different kinds of partial separability, which is the down-set lattice of the lattice of the partitions of the subsystems. It turns also out that, physically, this structure is related to the LOCC convertibility: If a state from a class can be mapped into another one, then that class can be found higher in the hierarchy. Second, we introduce the notion of multipartite monotonicity, expressing that a given set of entanglement monotones, while measuring the different kinds of entanglement, shows also the same hierarchical structure as the entanglement classes. Then we construct such hierarchies of entanglement measures, and propose a physically well-motivated one, being the direct multipartite generalization of the entanglement of formation based on the entanglement entropy, motivated by the notion of statistical distinguishability. The multipartite monotonicity shown by this set of measures motivates us to consider the measures to be the different manifestations of some "unified" notion of entanglement.

2.11 New research area not included in the research plan: Graphene

51. G. Zs. Magda, X. Y. Jin, I. Hagymási, P. Vancsó, Z. Osváth, P. Nemes-Incze, C. Y. Hwang, L. P. Biro, L. Tapasztó: *Room-temperature magnetic order on zigzag edges of narrow graphene nanoribbons,* Nature **514**, 608 (2014).

Magnetic order emerging in otherwise non-magnetic materials as carbon is a paradigmatic example of a novel type of s-p electron magnetism predicted to be of exceptional high-temperature stability. It has been demonstrated that atomic scale structural defects of graphene can host unpaired spins. However, it is still unclear under which conditions long-range magnetic order can emerge from such defect-bound magnetic moments. Here we propose that in contrast to random defect distributions, atomic scale engineering of graphene edges with specific crystallographic orientation, comprising edge atoms only from one sub-lattice of the bipartite graphene lattice, can give rise to a robust magnetic order. We employ a nanofabrication technique based on Scanning Tunneling Microscopy to define graphene nanoribbons with nanometer precision and well-defined crystallographic edge orientations. While armchair ribbons display quantum confinement gap, zigzag ribbons narrower than 7 nm reveal a bandgap of about 0.2 - 0.3 eV, which can be identified as a signature of interaction induced spin ordering along their edges. Moreover, a semiconductor to metal transition is revealed upon increasing the ribbon width, indicating the switching of the magnetic coupling between opposite ribbon edges from antiferromagnetic to ferromagnetic configuration. We found that the magnetic order on graphene edges of controlled zigzag orientation can be stable even at room temperature, raising hope for graphene-based spintronic devices operating under ambient conditions.

2.12 New research area not included in the research plan: Nuclear structure theory

52. Ö. Legeza, L. Veis, A. Poves, J. Dukelsky: *Advanced density matrix renormalization group method for nuclear structure calculations,* Phys. Rev. C **92**, 051303 (2015).

    We present an efficient implementation of the Density Matrix Renormalization Group (DMRG) algorithm that includes an optimal ordering of the proton and neutron orbitals and an efficient expansion of the active space utilizing various concepts of quantum information theory. We first show how this new DMRG methodology could solve a previous 400 KeV discrepancy in the ground state energy of ^{56}Ni. We then report the first DMRG results in the $pf + g9/2$ shell model space for the ground 0^+ and first 2^+ states of ^{64}Ge which are benchmarked with reference data obtained from Monte Carlo shell model. The corresponding correlation structure among the proton and neutron orbitals is determined in terms of the two-orbital mutual information. Based on such correlation graphs we propose several further algorithmic improvement possibilities that can be utilized in a new generation of tensor network based algorithms.

2.13 New research area not included in the research plan: Hybrid CPU/GPU parallelization

53. Cs. Nemes, G. Barcza, Z. Nagy, Ö. Legeza, P. Szolgay: *Implementation trade-offs of the density matrix renormalization group algorithm on kilo-processor architectures,* in proceeding of the 21st European Conference on Circuit Theory and Design, DOI:10.1109/ECCTD.2013.6662251 (2013).

    Numerical analysis of strongly correlated quantum lattice models has a great importance in quantum physics. The exponentially growing size of the Hilbert space makes these computations difficult, however sophisticated algorithms have been developed to balance the size of the effective Hilbert space and the accuracy of the simulation. One of these methods is the density matrix renormalization group (DMRG) algorithm which has become the leading numerical tool in the study of low dimensional lattice problems of current interest. In the algorithm a high computational problem can be translated to a list of dense matrix operations, which makes it an ideal application to fully utilize the computing power residing in both current multi-core processors and novel kilo-processor architectures.

54. Cs. Nemes, G. Barcza, Z. Nagy, Ö. Legeza, P. Szolgay: *The density matrix renormalization group algorithm on kilo-processor architectures: implementation and trade-offs,* arXiv:1309.5571; Comp. Phys. Commun. **185** 1570 (2014).

    In the numerical analysis of strongly correlated quantum lattice models one of the leading algorithms developed to balance the size of the effective Hilbert space and the accuracy of the simulation is the density matrix renormalization group (DMRG) algorithm, in which the run-time is dominated by the iterative diagonalization of the Hamilton operator. As the most time-dominant step of the diagonalization can be expressed as a list of dense matrix operations, the DMRG is an appealing candidate to fully utilize the computing power residing in novel kilo-processor architectures. In the paper a smart hybrid CPU–GPU implementation is presented, which exploits the power of both CPU and GPU and tolerates problems exceeding the GPU memory size. Furthermore, a new CUDA kernel has been designed for asymmetric matrix–vector multiplication to accelerate the rest of the diagonalization. Besides the evaluation of the GPU implementation, the practical limits of an FPGA implementation are also discussed.