2023

In this year we have continued our research on various strongly correlated systems using the Density Matrix Renormalization Group (DMRG) and Matrix Product State (MPS). We have wide range international collaborations with more than twenty institutes around the world, resulting in twelve research articles in high rank international journals, and five preprints. We have given some twenty talks on different conferences and seminars, and we have presented six posters. We have applied our scientific software (Budapest QC-DMRG program package) to various spin and electron systems, 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 molecules, or for the quantum simulation of the information technology itself. As will be presented below, among many others, we have examined strongly correlated electrons in magnetic materials in several quantum phases, identified exotic quantum phases of matter, investigated time dependent phenomena, studied entanglement in nucleon systems, and identified classical and quantum correlations in molecules, playing important role in chemical compounds. We have also presented detailed mathematical analysis of various concepts in quantum entanglement theory of qubits and fermions, and dynamics of open quantum systems. Here we summarize only selected results due to length restrictions.

Condensed matter and statistical physics:
We determined the ground-state phase diagram for the 1/r-Hubbard model with repulsive nearest-neighbor interaction at half band-filling using the density-matrix renormalization group (DMRG) method. Due to the absence of Umklapp scattering, the phase diagram displays finite regions for the three generic phases, namely, a Luttinger liquid metal for weak interactions, a Mott-Hubbard insulator for dominant Hubbard interactions, and a charge-density-wave insulator for dominant nearest-neighbor interactions. Up to moderate interactions strengths, the quantum phase transitions between the metallic and insulating phases are continuous, i.e., the gap opens continuously as a function of the interaction strength. We concluded that generic short-range interactions do not change the nature of the Mott transition qualitatively. [1]

We showed that dynamical hadron formation can be spectroscopically detected in an ultracold atomic setting within the most paradigmatic and simplest model of condensed matter physics, the repulsive SU(N) Hubbard model. We found that by starting from an appropriately engineered high-energy initial state of the strongly interacting SU(3) Hubbard model, doublons (mesons) and trions (barions) naturally emerged during time evolution and thermalized to a negative temperature quantum gas, as demonstrated by extensive one-dimensional simulations and exact diagonalization calculations. For strong interactions, trions become heavy and attract each other strongly. Their residual interaction with doublons generates doublon diffusion, that we captured by the evolution of the equal time density correlation function. Although our numerical calculations are performed on one-dimensional chains, many of our conclusions extend to a large variety of initial conditions and hold for other spatial dimensions and all SU($N > 2$) Hubbard models. [2]

The collective tunneling of a Wigner necklace – a crystalline state of a small number of strongly interacting electrons confined to a suspended nanotube and subject to a double well potential – was theoretically analyzed and compared with experiments in [Shapir et al., Science 364, 870 (2019)]. Density Matrix Renormalization Group computations, exact diagonalization, and instanton theoryprovided a consistent description of this very strongly interacting system, and showed good agreement with experiments. Experimentally extracted and theoretically computed tunneling amplitudes exhibited a scaling collapse. We found that collective quantum fluctuations renormalized the tunneling, and substantially enhanced it as the number of electrons increased. [3]

We investigated the quantum quench dynamics of the interacting Hatano-Nelson model with open boundary conditions using both Abelian bosonization and numerical methods. Specifically, we followed the evolution of the particle density and current profile in real space over time by turning the imaginary vector potential on or off in the presence of weak interactions. Our results revealed spatiotemporal Friedel oscillations in the system with light cones propagating ballistically from the open ends, accompanied by local currents of equal magnitude for both switch-off and -on protocols. Remarkably, the bosonization method accurately accounted for the density and current patterns with a single overall fitting parameter. The continuity equation was satisfied by the long-wavelength part of the density and current, despite the nonunitary time evolution when the Hatano-Nelson term was switched on. [4]

Recent experiments demonstrated that single-particle quantum walks can reveal the topological properties of single-particle states. Here, we generalized this picture to the many-body realm by focusing on multiparticle quantum walks of strongly interacting fermions. After injecting N particles with multiple flavors in the interacting SU(N) Su-Schrieffer-Heeger chain, their multiparticle continuous-time quantum walk was monitored by a variety of methods. We found that the many-body Berry phase in the N-body part of the spectrum signaled a topological transition upon varying the dimerization, similarly to the single-particle case. This topological transition was captured by the single- and many-body mean chiral displacement during the quantum walk and remains present

for strong interaction as well as for moderate disorder. Our predictions were well within experimental reach for cold atomic gases and can be used to detect the topological properties of many-body excitations through dynamical probes. [5]

We explored the Kardar-Parisi-Zhang (KPZ) scaling in the one-dimensional Hubbard model, which exhibits global $SU_c(2)xSU_s(2)$ symmetry at half filling, for the pseudocharge and the total spin. We analyzed dynamical scaling properties of high-temperature charge and spin correlations and transport. At half filling, we observed a clear KPZ scaling in both charge and spin sectors. Away from half filling, the $SU_c(2)$ charge symmetry is reduced to $U_c(1)$, while the $SU_s(2)$ symmetry for the total spin is retained. Consequently, transport in the charge sector becomes ballistic, while KPZ scaling is preserved in the spin sector. These findings confirmed the link between non-Abelian symmetries and KPZ scaling in the presence of integrability. We studied two settings of the model: one involving a quench from a bipartitioned state asymptotically close to the T to infinity equilibrium state of the system, and another where the system is coupled to two Markovian reservoirs at the two edges of the chain. [6]

Parafermions are anyons with the potential for realizing non-local qubits that are resilient to local perturbations. Compared to Majorana zero modes, braiding of parafermions implements an extended set of topologically protected quantum gates. This, however, comes at the price that parafermionic zero modes can not be realized in the absence of strong interactions whose theoretical description is challenging. We constructed a simple lattice model for interacting spinful electrons with parafermionic zero energy modes. The explicit microscopic nature of the considered model highlights new realization avenues for these exotic excitations in recently fabricated quantum dot arrays. By density matrix renormalization group calculations, we identified a broad range of parameters, with well-localized zero modes, whose parafermionic nature is substantiated by their unique 8π periodic Josephson spectrum. [7]

Quantum chemistry:

We theoretically derived and validated with large scale simulations a remarkably accurate power law scaling of errors for the restricted active space density matrix renormalization group (DMRG-RAS) method [J. Phys. Chem. A 126, 9709] in electronic structure calculations. This yields a new extrapolation method, DMRG-RAS-X, which reaches chemical accuracy for strongly correlated systems such as the chromium dimer, dicarbon up to a large cc-pVQZ basis and even a large chemical complex such as the FeMoco with significantly lower computational demands than those of previous methods. The method is free of empirical parameters, performed robustly and reliably in all examples we tested, and has the potential to become a vital alternative method for electronic structure calculations in quantum chemistry and more generally for the computation of strong correlations in nuclear and condensed matter physics. [8]
Tailored-CC (TCC) approach 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. In order to overcome the single-reference bias of the TCC method, we developed a Hilbert-space multireference version of tailored CC, which can treat several determinants on an equal footing. We 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 have assessed these approaches on the cyclobutadiene and tetramethylenethane (TME) molecules, which are both diradicals with exactly degenerate determinants at a certain geometry. [9]

We also presented a brief overview of the fermionic mode optimization within the framework of tensor network state methods (Krumnow et al. in Phys Rev Lett 117:210402, 2016), and demonstrated that it has the potential to compress the multireference character of the wave functions after finding optimal molecular orbitals (modes), based on entanglement minimization. Numerical simulations were performed for the nitrogen dimer in the cc-pVDZ basis for the equilibrium and for stretched geometries. [10]

We have presented a tutorial paper to bring novel concepts on orbital optimization protocols employed in the DMRG procedure closer to the quantum chemistry community. While a more rigorous mathematical approach has been presented previously, here we focused on technical aspects to obtain natural orbital (NO) and Rényi entropy based orbital (REMO) optimization in practice via low-cost DMRG calculations. We also showed how large scale DMRG calculations can be brought closer to the FCI limit at the negligible additional computational cost of NO- or REMO-generation. [11]

Material science:

We studied the symmetric carbon tetramer clusters in hexagonal boron nitride and proposed them as spin qubits for sensing. We utilized periodic-DFT and quantum chemistry approaches to reliably and accurately predict the

electronic, optical, and spin properties of the studied defect. We showed that the nitrogen-centered symmetric carbon tetramer gives rise to spin state-dependent optical signals with strain-sensitive intersystem crossing rates. Furthermore, the weak hyperfine coupling of the defect to their spin environments results in a reduced electron spin resonance linewidth that can enhance sensitivity. [12]

We proposed the negatively charged nitrogen split interstitial defect in hBN as a plausible microscopic model for the blue emitter. We carefully analyzed the accuracy of first principles methods and showed that the commonly used HSE hybrid exchange-correlation functional fails to describe the electronic structure of this defect. Using the generalized Koopman's theorem, we fine tuned the functional and obtained a zero-phonon photoluminescence (ZPL) energy in the blue spectral range. We showed that the defect exhibits high emission rate in the ZPL line and features a characteristic phonon side band that resembles the blue emitter's spectrum. We also studied the electric field dependence of the ZPL and numerically showed that the defect exhibits a quadratic Stark shift for perpendicular to plane electric fields, making the emitter insensitive to electric field fluctuations in first order. [13]

Nuclear physics:

We proposed a novel many-body framework combining the density matrix renormalization group (DMRG) with the valence-space (VS) formulation of the in-medium similarity renormalization group. This hybrid scheme admitted for favorable computational scaling in large-space calculations compared to direct diagonalization. The capacity of the VS-DMRG approach was highlighted in ab initio calculations of neutron-rich nickel isotopes based on chiral two- and three-nucleon interactions, and allowed us to perform converged ab initio computations of ground and excited state energies. We also studied orbital entanglement in the VS-DMRG, and investigated nuclear correlation effects in oxygen, neon, and magnesium isotopes. The explored entanglement measures revealed nuclear shell closures as well as pairing correlations. [14]

Algorithmic aspects:

The interplay of quantum and classical simulation and the delicate divide between them is in the focus of massively parallelized tensor network state (TNS) algorithms designed for high performance computing (HPC). We presented novel algorithmic solutions together with implementation details to extend current limits of TNS algorithms on HPC infrastructure building on state-of-the-art hardware and software technologies. Benchmark results obtained via large-scale density matrix renormalization group (DMRG) simulations are presented for selected strongly correlated molecular systems addressing problems on Hilbert space dimensions up to 2.88×10^{36}. [15]

We also presented novel algorithmic solutions together with implementation details utilizing non-Abelian symmetries via hybrid CPU-multiGPU solution where scheduling is decentralized, threads are autonomous and inter-thread communications are solely limited to interactions with globally visible lock-free constructs. Benchmark tests demonstrated the utilization of NVIDIA's highly specialized tensor cores, leading to performance around 110 TFLOPS on a single node supplied with eight NVIDIA A100 devices. In comparison to U(1) implementations with matching accuracy, our solution had an estimated effective performance of 250-500 TFLOPS. [16]

We presented a hybrid numerical approach to simulate quantum many body problems on two spatial dimensional quantum lattice models via the non-Abelian ab initio version of the density matrix renormalization group method on state-of-the-art high performance computing infrastructures. We demonstrated for the two dimensional spinless fermion model and for the Hubbard model on torus geometry that altogether several orders of magnitude in computational time can be saved by performing calculations on an optimized basis and by utilizing hybrid CPU-multiGPU parallelization. At least an order of magnitude reduction in computational complexity resulted from mode optimization, while a further order of reduction in wall time is achieved by massive parallelization. Our results were measured directly in FLOP and seconds. A detailed scaling analysis of the obtained performance as a function of matrix ranks and as a function of system size up to 12x12 lattice topology was discussed. [17]

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2020

In this year we have continued our research on various strongly correlated systems using the *Density Matrix Renormalization Group (DMRG)*, *Matrix Product State (MPS)* and *Tree Tensor Network State (TTNS)* methods. We have wide range international collaborations with more than twenty institutes around the world, resulting in twelve research articles in high rank international journals, and six preprints. Due to the pandemic, we gave only some ten talks on different conferences and seminars, and we have presented a poster (half of these were online). We have further developed our scientific software **(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 molecules, or for the quantum simulation of the information technology itself. Further algorithmic developments have also been carried out concerning *the 4-component relativistic quantum chemistry DMRG, post-DFT DMRG calculations (DFT-CAS-DMRG) for boron vacancy qubit in hexagonal boron nitride*, and we have carried out the most large-scale calculations available in the literature for various molecules. We have also improved parallelization in several parts of the code (Budapest QC-DMRG, MOLMPS) as part of scientific collaboration with Pacific Northwest National Laboratory (Prof. Karol Kowalski, PNNL, Richland, Washington State, USA). In collaboration with researchers from the groups of Budapest University of Technology, Ludwig Maximilian Universität München, Freie Universität Berlin, Technische Universität Berlin, University of Oslo, Philipps Universität Marburg, and Nicolaus Copernicus University Torun, we have been working on new algorithmic solutions together with applications. As will be presented below, among many others, we have examined strongly correlated electrons in magnetic materials in several quantum phases, Bose-Einstein condensation in confined systems in a Mexican hat like potential, identified exotic quantum phases of matter, investigated time dependent phenomena, studied entanglement in two-nucleon systems, and identified classical and quantum correlations in molecules, playing important role in chemical compounds. We have also presented detailed mathematical analysis of various concepts in quantum entanglement theory of qubits and fermions, and dynamics of open quantum systems.

Strongly correlated fermionic and bosonic systems
Frustrated three dimensional quantum magnets are notoriously impervious to theoretical analysis. We used a

combination of three computational methods to investigate the three dimensional pyrochlore S=1/2 quantum antiferromagnet, an archetypical frustrated magnet, at finite temperature T: canonical typicality for a finite cluster of 2x2x2 unit cells (32 sites), a finite-T matrix product state method on a larger cluster with 48 sites, and the numerical linked cluster expansion (NLCE) using clusters up to 25 lattice sites, which include non-trivial hexagonal and octagonal loops. We focused on thermodynamic properties (energy, specific heat capacity, entropy, susceptibility, magnetisation) besides the static structure factor. We found a pronounced maximum in the specific heat at T = 0.57 J, which is stable across finite size clusters, and converged in the series expansion. This is well-separated from a residual amount of spectral weight of 0.47 k_B ln(2) per spin, which has not been released even at approximately T = 0.25 J, the limit of convergence of our results. This is a large value compared to a number of highly frustrated models and materials, such as spin ice or the Kagome S=1/2 Heisenberg antiferromagnet. We also found a non-monotonic dependence on T of the magnetisation at low magnetic fields, reflecting the dominantly non-magnetic character of the low-energy spectral weight.

We analyzed the numerical aspects of the inherently multi-reference DMRG calculations on top of the periodic Kohn-Sham density functional theory (DFT), using the complete active space (CAS) approach. We illustrated the potential of the framework by studying the vertical many-body energy spectrum of hexagonal boron nitride (hBN) nano-flakes embedding a single boron vacancy point defect with prominent multi-reference character. Results obtained from standard quantum chemical atom-centered basis calculations and plane-wave based counterparts showed excellent agreement. We also discussed the spectrum of the periodic sheet, which is in good agreement with extrapolated data of finite clusters. These results paved the way toward applying DMRG method in extended correlated solid state systems, such as point qubit in wide band gap semiconductors.

We proposed and studied a model for N hard-core bosons, which allows for the interpolation between one- and high-dimensional behavior by variation of just a single external control parameter t/s. It consisted of a ring-lattice of d sites with a hopping rate t and an extra site at its center. Increasing the hopping rate s between the central site and the ring sites induces a transition from the regime of a quasi-condensed number to complete condensation. An excitation gap makes the condensate robust against thermal fluctuations at low temperatures. These findings are supported and extended to the full parameter regime by large scale DMRG computations. We show that ultracold bosonic atoms in a Mexican-hat-like potential represent an experimental realization allowing to observe the transition from quasi to complete condensation by creating a well at the hat's center.

For most chiralities, semiconducting nanotubes display topologically protected end states of multiple degeneracies. We demonstrated using density matrix renormalization group based quantum chemistry tools that the presence of Coulomb interactions induced the formation of robust end spins. These are the close analogs of ferromagnetic edge states emerging in graphene nanoribbons. The interaction between the two ends is sensitive to the length of the nanotube, its dielectric constant, and the size of the end spins: for S=1/2 end spins, their interaction is antiferromagnetic, while for S>1/2, it changes from antiferromagnetic to ferromagnetic as the nanotube length increases. The interaction between end spins can be controlled by changing the dielectric constant of the environment, thereby providing a possible platform for two-spin quantum manipulations.
We introduced the notion of non-Abelian tensors and used them to construct a general non-Abelian time evolving block decimation (NA-TEBD) scheme that uses an arbitrary number of Abelian and non-Abelian symmetries. Our approach increases the speed and memory storage efficiency of matrix product state based computations by several orders of magnitude and makes large bond dimensions accessible even on simple desktop architectures. We used it to study post-quench dynamics in the repulsive SU(3) Hubbard model and to determine the time evolution of various local operators and correlation functions efficiently. Interactions turn algebraic charge relaxation into exponential and suppress coherent quantum oscillations rapidly.

Strongly correlated molecular clusters
There are three essential problems in computational relativistic chemistry: electrons moving at relativistic speeds, close lying states, and dynamical correlation. Currently available quantum-chemical methods are capable of solving systems with one or two of these issues. However, there is a significant class of molecules in which all the three effects are present. These are the heavier transition metal compounds, lanthanides and actinides with open d or f shells. For such systems, sufficiently accurate numerical methods are not available, which hinders the application of theoretical chemistry in this field. We combined two numerical methods in order to address this challenging class of molecules. These are the relativistic versions of coupled cluster methods and DMRG method. We presented the first relativistic implementation of the coupled cluster method externally corrected by DMRG. The method brings a significant reduction of computational costs, as we demonstrated on the system of TlH, AsH and SbH.

Fe(II)-porphyrins (FeP) play an important role in many reactions relevant to material science and biological processes, due to their closely lying spin states. Although the prevalent opinion is that these systems posses the triplet ground state, the recent experiment on Fe(II)-phthalocyanine under conditions matching those of an isolated molecule points toward the quintet ground state. We examined the importance of geometrical

parameters, the Fe-N distances in particular, and conclude that the system possesses the quintet ground state, which is in our calculations well-separated from the triplet state.

We provided a refined discussion of quantum information theoretical concepts by introducing the physical correlation and its separation into classical and quantum parts as distinctive quantifiers of electronic structure. In particular, we succeeded in quantifying the entanglement. Intriguingly, our results for different molecules revealed that the total correlation between orbitals is mainly classical, raising questions about the general significance of entanglement in chemical bonding. Our work also showed that implementing the fundamental particle number superselection rule, so far not accounted for in quantum chemistry, removes a major part of correlation and entanglement seen previously. In that respect, realizing quantum information processing tasks with molecular systems might be more challenging than anticipated.

Nuclear Physics
We examined the mode entanglement and correlation of two fermionic particles. We studied the one- and two-mode entropy and a global characteristic, the one-body entanglement entropy. We considered not only angular momentum coupled states with single configuration but use the configuration interaction method. With the help of the Slater decomposition, we derived analytical expressions for the entanglement measures. We showed that when the total angular momentum is zero, specific single configurations describe maximally entangled states. It turned out that for a finite number of associated modes, the one- and two-mode entropies have identical values. In the shell model framework, we numerically studied two valence neutrons in the sd shell. The one-body entanglement entropy of the ground state is close to the maximal value and the associated modes have the largest mutual information.

Mathematical physics
We investigated a case of the Hu-Paz-Zhang master equation of the Caldeira-Leggett model without Lindblad form obtained in the weak-coupling limit up to the second-order perturbation. In our study, we used Gaussian initial states to be able to employ a sufficient and necessary condition, which can expose positivity violations of the density operator during the time evolution. We demonstrated that the evolution of the non-Markovian master equation has problems when the stationary solution is not a positive operator, i.e., does not have physical interpretation. We also showed that solutions always remain physical for small times of evolution. Moreover, we identifed a strong anomalous behavior, when the trace of the solution is diverging. We also provided results for the corresponding Markovian master equation.
The operator algebra of fermionic modes is isomorphic to that of qubits, the difference between them is twofold: the embedding of subalgebras corresponding to mode subsets and multiqubit subsystems on the one hand, and the parity superselection in the fermionic case on the other. We discussed these two fundamental differences extensively, and illustrate these through the Jordan--Wigner representation in a coherent, self-contained, pedagogical way, from the point of view of quantum information theory. By analogy, we constructed useful tools for the treatment of fermionic systems, such as the fermionic (quasi-)tensor product, fermionic canonical embedding, fermionic partial trace, fermionic products of maps and fermionic embeddings of maps. We formulated these by direct, easily applicable formulas, without mode permutations, for arbitrary partitionings of the modes. It was also shown that fermionic reduced states can be calculated by the fermionic partial trace, containing the proper phase factors. We also considered variants of the notions of fermionic mode correlation and entanglement, which can be endowed with the usual, local operation based motivation, if the fermion number parity superselection rule is imposed.

We found three qubit Greenberger–Horne–Zeilinger diagonal states which tell us that the partial separability of three qubit states violates the distributive rules with respect to the two operations of convex sum and intersection. The gaps between the convex sets involving the distributive rules are of nonzero volume.

Algorithmic and code developments
We presented the first attempt to exploit the supercomputer platform for quantum chemical DMRG calculations. In case of the largest calculation, which is the nitrogenase FeMo cofactor cluster with the active space comprising 113 electrons in 76 orbitals and bond dimension equal to 6000, our parallel approach scaled up to approximately 2000 CPU cores.

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2019

In this year we have continued our research on various strongly correlated systems using the *Density Matrix Renormalization Group* (DMRG), *Matrix Product State* (MPS) and *Tree Tensor Network State* (TTNS) methods. We have published twelve research articles in high rank international journals, one in a Hungarian journal, and seven preprints. We have also given close to twenty talks on different conferences and seminars, and we have presented some ten posters. We have further developed our scientific software (**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 molecules, or for the quantum simulation of the information technology itself. Further algorithmic developments have also been carried out concerning the quantum chemistry DMRG and Coupled-Cluster (CC) algorithms, in light of Local-Pair-Natural-Orbital (LPNO) and Domain-Local-Pair-Natural-Orbital (DLPNO) approximations, and we have carried out the most large-scale calculations available in the literature for various molecules. We have also improved parallelization in several parts of the code as part of scientific collaboration with Pacific Northwest National Laboratory (Prof. Karol Kowalski, PNNL, Richland, WA, USA). In collaboration with researchers from the groups of Budapest University of Technology, Ludwig Maximilian Universität München, Freie Universität Berlin, Technische Universität Berlin, University of Oslo, Philipps Universität Marburg, and Nicolaus Copernicus University Torun, we have been working on new algorithmic solutions together with applications. As will be presented below, among many others, we have examined strongly correlated electrons in magnetic materials in several quantum phases, identified exotic quantum phases of matter, investigated time dependent phenomena, and determined multi-orbital correlation and entanglement patterns in molecules, playing important role in chemical compounds.

Imaging the Wigner crystal of electrons in one dimension. — The quantum crystal of electrons, predicted more than eighty years ago by Eugene Wigner, is still one of the most elusive states of matter. Recently, it has become possible to design experiments that observe the one-dimensional Wigner crystal directly, by imaging its charge density in real space. The obtained images, of few electrons confined in one-dimension, match those of strongly interacting crystals, with electrons ordered like pearls on a necklace. In order to further support the existence of such a state, we have performed large-scale DMRG calculations on the given system. Comparison to theoretical modeling demonstrates the dominance of Coulomb interactions over kinetic energy and the weakness of exchange interactions. The experiments together with our numerical simulations has provided direct evidence for this long-sought electronic state, and open the way for studying other fragile interacting states by imaging their many-body density in real-space. The results were published in Science.

Dynamical topological quantum phase transitions in nonintegrable models. — We have considered sudden quenches across quantum phase transitions in the S=1 XXZ model starting from the Haldane phase. We have demonstrated that dynamical phase transitions may occur during these quenches that are identified by nonanalyticities in the rate function for the return probability. In addition, we have shown that the temporal behavior of the string order parameter is intimately related to the subsequent dynamical phase transitions. Furthermore, we have found that the dynamical quantum phase transitions can be accompanied by enhanced two-site entanglement. The results were published in Physical Review Letters.

Interaction quench and thermalization in a one-dimensional topological Kondo insulator. — We have studied the nonequilibrium dynamics of a one-dimensional topological Kondo insulator, modelled by a *p*-wave Anderson lattice model, following a quantum quench of the on-site interaction strength. Our goal was to examine how the quench influences the topological properties of the system, and therefore our main focus was the time evolution of the string order parameter, entanglement spectrum, and the topologically protected edge states. We have pointed out that postquench local observables can be well captured by a thermal ensemble up to a certain interaction strength. Our results have demonstrated that the topological properties after the interaction quench are preserved. Though the absolute value of the string order parameter decays in time, the analysis of the entanglement spectrum, Loschmidt echo and the edge states have indicated the robustness of the topological properties in the time-evolved state. These predictions could be directly tested in state-of-the-art cold-atom experiments. The results were published in Physical Review B.

Stability of edge magnetism against disorder in zigzag MoS_2 nanoribbons. — Molybdenum disulfide nanoribbons with zigzag edges show ferromagnetic and metallic properties based on previous ab initio calculations. The investigation of the role of disorder on the magnetic properties is, however, still lacking due to the computational costs of these methods. We have filled this gap by studying the magnetic and electronic properties of several-nanometer-long MoS_2 zigzag nanoribbons using tight-binding and Hubbard Hamiltonians. Our results have revealed that proper tight-binding parameters for the edge atoms are crucial to obtain quantitatively the metallic states and the magnetic properties of MoS_2 nanoribbons. With the help of the fine-tuned parameters, we have performed large-scale calculations and predict the spin domain-wall energy along the edges, which has been found to be significantly lower compared to that of the zigzag graphene nanoribbons. The tight-binding approach has allowed us to address the effect of edge disorder on the magnetic properties. Our results have opened the way for investigating electron-electron effects in realistic-size nanoribbon devices in MoS2 and also provided valuable information for spintronic applications. The results were published in Physical Review Materials.

Ground-state properties of the symmetric single-impurity Anderson model on a ring from DMRG, Hartree-Fock, and Gutzwiller theory. — We have analyzed the ground-state energy, magnetization, magnetic susceptibility, and Kondo screening cloud of the symmetric single-impurity Anderson model (SIAM) that is characterized by the bandwidth W, the impurity interaction strength U, and the local hybridization V. We have compared Gutzwiller variational and magnetic Hartree-Fock results in the thermodynamic limit with numerically

exact data from the DMRG method on large rings. To improve the DMRG performance, we have used a canonical transformation to map the SIAM onto a chain with half the system size and open boundary conditions. We have compared to Bethe ansatz results for the ground-state energy, magnetization, and spin susceptibility that become exact in the wide-band limit. Our detailed comparison has shown that the field-theoretical description is applicable to the SIAM on a ring for a broad parameter range. Hartree-Fock theory gives an excellent ground-state energy and local moment for intermediate and strong interactions. However, it lacks spin fluctuations and thus cannot screen the impurity spin. The Gutzwiller variational energy bound becomes very poor for large interactions because it does not describe properly the charge fluctuations. Nevertheless, the Gutzwiller approach provides a qualitatively correct description of the zero-field susceptibility and the Kondo screening cloud. The DMRG provides excellent data for the ground-state energy and the magnetization for finite external fields. At strong interactions, finite-size effects make it extremely difficult to recover the exponentially large zero-field susceptibility and the mesoscopically large Kondo screening cloud. The results were published in Physical Review B.

Spin fluctuations after quantum quenches in the S=1 Haldane chain: numerical validation of the semi-semiclassical theory. — We have studied quantum quenches in the S=1 Heisenberg spin chain and show that the dynamics can be described by the recently developed semi-semiclassical method based on particles propagating along classical trajectories but scattering quantum mechanically. We have analyzed the non-equilibrium time evolution of the distribution of the total spin in half of the system and compare the predictions of the semi-semiclassical theory with those of a non-Abelian time evolving block decimation (TEBD) algorithm which exploits the SU(2) symmetry. We have shown that while the standard semiclassical approach using the universal low energy scattering matrix cannot describe the dynamics, the hybrid semiclassical method based on the full scattering matrix gives excellent agreement with the first principles TEBD simulation. The results were published in Physical Review B.

Quantum information-based analysis of electron-deficient bonds. — Recently we developed the correlation theory of the chemical bond, which applies concepts of quantum information theory for the characterization of chemical bonds, based on the multiorbital correlations within the molecule. We have applied this mathematical toolbox for the first time for the description of electron-deficient bonds. We have started by verifying the theory on the textbook example of a molecule with three-center two-electron bonds, namely the diborane(6). Then we have shown that the correlation theory of the chemical bond is able to properly describe bonding situation in more exotic molecules, which have been synthetized and characterized only recently, in particular the diborane molecule with four hydrogen atoms [diborane(4)] and neutral zerovalent s-block beryllium complex, whose surprising stability was attributed to a strong three-center two-electron π bond stretching across the C-Be-C core. Our approach is of a high importance especially in the light of a constant chase after novel compounds with extraordinary properties where the bonding is expected to be unusual. The results were published in Journal of Chemical Physics.

Towards the Efficient Local Tailored Coupled Cluster Approximation and the Peculiar Case of Oxo-Mn(Salen). — We have introduced a new implementation of the coupled cluster method tailored by matrix product states wave functions (DMRG-TCCSD), which employs the local pair natural orbital approach (LPNO). By exploiting locality in the coupled cluster stage of the calculation, we have been able to remove some of the limitations that hindered the application of the canonical version of the method to larger systems and/or with larger basis sets. We have assessed the accuracy of the approximation using two systems: tetramethyleneethane (TME) and oxo-Mn(Salen). Using the default cut-off parameters, we were able to recover over 99.7% and 99.8% of canonical correlation energy for the triplet and singlet state of TME respectively. In case of oxo-Mn(Salen), we have found out that the amount of retrieved canonical correlation energy depends on the size of the active space (CAS) - we have retrieved over 99.6% for the larger 27 orbital CAS and over 99.8% for the smaller 22 orbital CAS. The use of LPNO-TCCSD has allowed us to perform these calculations up to quadruple-ζ basis set amounting to 1178 basis functions. Moreover, we have examined dependance of the ground state of oxo-Mn(Salen) on CAS composition. We have found out that the inclusion of 4dxy orbital plays an important role in stabilizing the singlet state at the DMRG-CASSCF level via double-shell effect. However, by including dynamic correlation the ground state has been found to be triplet regardless of the size of the basis set or composition of CAS, which is in agreement with previous findings by canonical DMRG-TCCSD in smaller basis. The results were published in Journal of Chemical Physics.

Elucidating cation-cation interactions in neptunyl dications using multireference ab initio theory. — Understanding the binding mechanism in neptunyl clusters formed due to cation-cation interactions is of crucial importance in nuclear waste reprocessing and related areas of research. Since experimental manipulations with such species are often rather limited, we have to rely on quantum-chemical predictions of their electronic structures and spectroscopic parameters. We have presented a state-of-the-art quantum chemical study of the T-shaped and diamond-shaped neptunyl(V) and neptunyl(VI) dimers. Specifically, we have scrutinized their molecular structures, (implicit and explicit) solvation effects, the interplay of static and dynamical correlation, and the influence of spin-orbit coupling on the ground state and lowest-lying excited states for different total spin

states and total charges of the neptunyl dications. Furthermore, we have used the picture of interacting orbitals (quantum entanglement and correlation analysis) to identify strongly correlated orbitals in the cation-cation complexes that should be included in complete active space calculations. Most importantly, our study has highlighted the complex interplay of correlation effects and relativistic corrections in the description of the ground and lowest-lying excited states of neptunyl dications. The results were published in Physical Chemistry Chemical Physics.

k-stretchability of entanglement, and the duality of k-separability and k-producibility. — The notions of k-separability and k-producibility are useful and expressive tools for the characterization of entanglement in multipartite quantum systems, when a more detailed analysis would be infeasible or simply needless. We have revealed a partial duality between them, which is valid also for their correlation counterparts. This duality can be seen from a much wider perspective, when we consider the entanglement and correlation properties which are invariant under the permutations of the subsystems. These properties are labeled by Young diagrams, which we have endowed with a refinement-like partial order, to build up their classification scheme. This general treatment has revealed a new property, which we call k-stretchability, being sensitive in a balanced way to both the maximal size of correlated (or entangled) subsystems and the minimal number of subsystems uncorrelated with (or separable from) one another. The results were published in Quantum.

Numerical and Theoretical Aspects of the DMRG-TCC Method Exemplified by the Nitrogen Dimer. — We have investigated the numerical and theoretical aspects of the coupled-cluster method tailored by matrix-product states. We have investigated formal properties of the used method, such as energy size consistency and the equivalence of linked and unlinked formulation. The existing mathematical analysis has been here elaborated in a quantum chemical framework. In particular, we have highlighted the use of what we have defined as a complete active space-external space gap describing the basis splitting between the complete active space and the external part generalizing the concept of a HOMO–LUMO gap. Furthermore, the behavior of the energy error for an optimal basis splitting, i.e., an active space choice minimizing the DMRG-TCCSD error, has been discussed. We have shown numerical investigations on the robustness with respect to the bond dimensions of the single orbital entropy and the mutual information, which are quantities that are used to choose a complete active space. Moreover, the dependence of the ground-state energy error on the complete active space has been analyzed numerically in order to find an optimal split between the complete active space and external space by minimizing the DMRG-TCC error. The results were published in Journal of Chemical Theory and Computation.

Analysis of The Tailored Coupled-Cluster Method in Quantum Chemistry. — In quantum chemistry, one of the most important challenges is the static correlation problem when solving the electronic Schrödinger equation for molecules in the Born-Oppenheimer approximation. We have analyzed the TCC, one particular and promising method for treating molecular electronic-structure problems with static correlation. The TCC method combines the single-reference coupled-cluster (CC) approach with an approximate reference calculation in a subspace [complete active space (CAS)] of the considered Hilbert space that covers the static correlation. A one-particle spectral gap assumption is introduced, separating the CAS from the remaining Hilbert space. This replaces the nonexisting or nearly nonexisting gap between the highest occupied molecular orbital and the lowest unoccupied molecular orbital usually encountered in standard single-reference quantum chemistry. The analysis covers, in particular, CC methods tailored by tensor-network states (TNS-TCC methods). The problem has been formulated in a nonlinear functional analysis framework, and, under certain conditions, such as the aforementioned gap, local uniqueness and existence are proved using Zarantonello's lemma. From the Aubin-Nitsche-duality method, a quadratic error bound valid for TNS-TCC methods is derived, e.g., for linear-tensor-network TCC schemes using the DMRG method. The results were published in SIAM Journal of Numerical Analysis.

Symmetric single-impurity Kondo model on a tight-binding chain, a comparison of analytical and numerical ground-state approaches. — We have analyzed the ground-state energy, local spin correlation, impurity spin polarization, impurity-induced magnetization, and corresponding zero-field susceptibilities of the symmetric single-impurity Kondo model on a tight-binding chain with bandwidth W=2D and coupling strength JK. We have compared perturbative results and variational upper bounds from Yosida, Gutzwiller, and first-order Lánczos wave functions to the numerically exact data obtained from the DMRG and from the NRG methods. The Gutzwiller variational approach has become exact in the strong-coupling limit and reproduces the ground-state properties from DMRG and NRG for large couplings. We calculate the impurity spin polarization and its susceptibility in the presence of magnetic fields that are applied globally/locally to the impurity spin. The Yosida wave function has provided qualitatively correct results in the weak-coupling limit. In DMRG, chains with about 103 sites are large enough to describe the susceptibilities down to $J_K/D \approx 0.5$. For smaller Kondo couplings, only the NRG has provided reliable results for a general host-electron density of states $\rho_0(\epsilon)$. To compare with results from Bethe Ansatz, we have studied the impurity-induced magnetization and zero-field susceptibility. For small Kondo couplings, the zero-field susceptibilities at zero temperature has approached $\chi_0(J_K \ll D)/(g\mu_B)^2 \approx \exp[1/(\rho_0(0)J_K)]/(2CD(\pi e \rho_0(0)J_K)^{1/2})$, where ln(C) is the regularized first inverse moment of the density of states. Using NRG, we have determined the universal sub-leading corrections up to second order in ρ0(0)JK. The results were published on arXiv (published in Physical Review B in 2020).

Partial separability/entanglement violates distributive rules. — We have found three qubit Greenberger-Horne-Zeilinger diagonal states which tells us that the partial separability of three qubit states violates the distributive rules with respect to the two operations of convex sum and intersection. The gaps between the convex sets involving the distributive rules are of nonzero volume. The results were published on arXiv (accepted in Quantum Information Processing, 2020).

Dimension reduction with mode transformations - **Simulating two-dimensional fermionic condensed matter systems.** — We have advocated the paradigm that for two-dimensional fermionic models, matrix-product states are still applicable to significantly higher accuracy levels than direct embeddings into one-dimensional systems allow for. To do so, we have exploited schemes of fermionic mode transformations and have overcome the prejudice that one-dimensional embeddings need to be local. This approach takes the insight seriously that the suitable exploitation of both the manifold of matrix-product states and the unitary manifold of mode transformations can more accurately capture the natural correlation structure. By demonstrating the residual low levels of entanglement in emerging modes, we have shown that matrix-product states can describe ground states strikingly well. The power of the approach has been exemplified by investigating a phase transition of spin-less fermions for lattice sizes up to 10x10. The results were published on arXiv (two positive referee reports).

Towards overcoming the entanglement barrier when simulating long-time evolution. — Quantum many-body systems out of equilibrium pose some of the most intriguing questions in physics. Unfortunately, numerically keeping track of time evolution of states under Hamiltonian dynamics constitutes a severe challenge for all known methods. Prominently, tensor network methods are marred by an entanglement blowup, which allows to simulate systems following global quenches only to constant time. We have presented a scheme that allows to significantly extend the simulation time for interacting fermionic or equivalent spin systems. In the past when keeping track of evolution in one-dimensional real space, the subspace parametrized by real-space matrix product states satisfying area laws - often dubbed the "physical corner" of Hilbert space - was chosen as variational set. In contrast, if the manifold containing both tensor network states and fermionic mode transformations is chosen, significantly longer times can be achieved. We have argued and our results have suggested that in many cases it is genuine correlations between modes that is the actual limiting factor: The system at hand is for intermediate times contained in the "physical corner", but a different one than what is commonly assumed. The results were published on arXiv.

Topologically protected, correlated end spin formation in carbon nanotubes. — For most chiralities, semiconducting nanotubes display topologically protected end states of multiple degeneracies. Using DMRG based quantum chemistry tools, we have demonstrated that the presence of Coulomb interactions induces the formation of massive end spins. These are the close analogues of ferromagnetic edge states emerging in graphene nanoribbon. The interaction between the two ends is sensitive to the length of the nanotube, its dielectric constant, as well as the size of the end spins: for S=1/2 end spins their interaction is antiferromagnetic, while for S>1/2 it changes from antiferromagnetic to ferromagnetic with increasing nanotube length. The interaction between end spins can be controlled by changing the dielectric constant of the environment, thereby providing a possible platform for two-spin quantum manipulations. The results were published on arXiv.

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

Ab initio theory of negatively charged boron vacancy qubit in hBN. — We have identified highly correlated orbitals coupled with phonons in two-dimension for paramagnetic and optically active boron vacancy in hexagonal boron nitride by first principles methods which are responsible for recently observed optically detected magnetic resonance signal. We have done ab initio analysis of the correlated electronic structure of this center by DMRG and Kohn-Sham DFT methods. By establishing the nature of the bright and dark states as well as the position of the energy levels, we have provided a complete description of the magneto-optical properties and corresponding radiative and non-radiative routes which are responsible for the optical spin polarization and spin dependent luminescence of the defect. Our findings have paved the way toward advancing the identification and

characterization of room temperature quantum bits in two-dimensional solids. The results were published on arXiv.

2018

Tensor factorization in high dimensional problems and applications to strongly correlated systems in condensed matter physics and quantum chemistry.

In this year we have continued our research on various strongly correlated systems using the Density Matrix Renormalization Group (DMRG), Matrix Product State (MPS) and Tree Tensor Network State (TTNS) methods. We have also given close to twenty talks on different conferences and seminars, and we have presented some ten posters. In addition, we have further developed our 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 molecules, or for the quantum simulation of the information technology itself. Further algorithmic developments have also been carried out concerning the quantum chemistry DMRG and Coupled-Cluster (CC) algorithms. In addition, in collaboration with Prof. Karol Kowalski, PNNL, Richland, Washington State, USA we have worked on the migration of the DMRG algorithm into the NWChem (commercial) program package, which ensures the possibility of massive parallelization. In collaboration with guest researchers from the groups of Uni Ghent and Uni Marburg, we have been working on new algorithmic solutions on the tree-TNS algorithm. As will be presented below, among many others, we have examined strongly correlated electrons in magnetic materials in several quantum phases, exotic quantum phases in ultracold atomic systems, and we have determined multi-orbital correlation and entanglement patterns in molecules, playing important role in chemical compounds.

Numerical and Theoretical Aspects of the DMRG-TCC Method Exemplified by the Nitrogen Dimer – We have investigated the numerical and theoretical aspects of the coupled-cluster method tailored by matrix-product states. We have investigated chemical properties of the used method, such as energy size extensivity and the equivalence of linked and unlinked formulation. The existing mathematical analysis was elaborated in a quantum chemical framework. In particular, we highlighted the use of a so-called CAS-ext gap describing the basis splitting between the complete active space and the external part. Moreover, the behavior of the energy error as a function of the optimal basis splitting were discussed. We have shown numerical investigations on the robustness with respect to the bond dimensions of the single orbital entropy and the mutual information, which are quantities that are used to choose the complete active space. Furthermore, we have extended the mathematical analysis with a numerical study on the complete active space dependence of the error.

Ground-state properties of the symmetric single-impurity Anderson model on a ring from Density-Matrix Renormalization Group, Hartree-Fock, and Gutzwiller theory - We have analyzed the ground-state energy, magnetization, magnetic susceptibility, and Kondo screening cloud of the symmetric single-impurity Anderson model (SIAM) that is characterized by the band width, the impurity interaction strength, and the local hybridization. We have compared Gutzwiller variational and magnetic Hartree-Fock results in the thermodynamic limit with numerically exact data from the DMRG method on large rings. To improve the DMRG performance, we have used a canonical transformation to map the SIAM onto a chain with half the system size and open boundary conditions. We have compared to Bethe-Ansatz results for the ground-state energy, magnetization, and spin susceptibility that become exact in the wide-band limit. Our detailed comparison have shown that the field-theoretical description is applicable to the SIAM on a ring for a broad parameter range. Hartree-Fock theory gives an excellent ground-state energy and local moment for intermediate and strong interactions. However, it lacks spin fluctuations and thus cannot screen the impurity spin. The Gutzwiller variational energy bound becomes very poor for large interactions because it does not describe properly the charge fluctuations. Nevertheless, the Gutzwiller approach provides a qualitatively correct description of the zero-field susceptibility and the Kondo screening cloud. The DMRG provides excellent data for the ground-state energy and the magnetization for finite external fields. At strong interactions, finite-size effects make it extremely difficult to recover the exponentially large zero-field susceptibility and the mesoscopically large Kondo screening cloud.

Elucidating cation--cation interactions in neptunyl dications using multireference ab initio theory - Understanding the binding mechanism in neptunyl clusters formed due to cation-cation interactions is of crucial importance in nuclear waste reprocessing and related areas of research. Since experimental manipulations with such species are often rather limited, we have to rely on quantum-chemical predictions of their electronic structures and spectroscopic parameters. We have presented a state-of-the-art quantum chemical study of the T-shaped and diamond-shaped neptunyl(V) and neptunyl(VI) dimers. Specifically, we have scrutinized their molecular structures, solvation effects, the interplay of static and dynamical correlation, and the influence of spin-orbit coupling on the ground state and lowest-lying excited states for different total spin states and total charges of the neptunyl dications. Furthermore, we have used the picture of interacting orbitals (quantum entanglement

and correlation analysis) to identify strongly correlated orbitals in the cation-cation complexes that should be included in complete active space calculations. Most importantly, we have highlighted the complex interplay of correlation effects and relativistic corrections in the description of the ground and lowest-lying excited states of neptunyl dications.

Imaging the Wigner Crystal of Electrons in One Dimension - The quantum crystal of electrons, predicted more than eighty years ago by Eugene Wigner, is still one of the most elusive states of matter. Recently it became possible to design experiments that observe the one-dimensional Wigner crystal directly, by imaging its charge density in real-space. The obtained images, of few electrons confined in one-dimension, match those of strongly interacting crystals, with electrons ordered like pearls on a necklace. In order to further support the existence of such state, we have performed large scale DMRG calculations on the given sysetm. Comparison to theoretical modeling demonstrates the dominance of Coulomb interactions over kinetic energy and the weakness of exchange interactions. Our experiments together with numerical simulations provide direct evidence for this long-sought electronic state, and open the way for studying other fragile interacting states by imaging their many-body density in real-space.

Analysis of The Coupled-Cluster Method Tailored by Tensor-Network States in Quantum Chemistry - We have analyzed the tailored coupled-cluster (TCC) method, which is a multi-reference formalism that combines the single-reference coupled-cluster (CC) approach with a full configuration interaction (FCI) solution covering the static correlation. This covers in particular the high efficiency coupled-cluster method tailored by tensor-network states (TNS-TCC). For statically correlated systems, we have introduced the conceptually new CAS-ext-gap assumption for multi-reference problems which replaces the unreasonable HOMO-LUMO gap. We have characterized the TCC function and have shown local strong monotonicity and Lipschitz continuity such that Zarantonello's Theorem yields locally unique solutions fulfilling a quasi-optimal error bound for the TCC method. We have performed an energy error analysis revealing the mathematical complexity of the TCC-method. Due to the basis-splitting nature of the TCC formalism, the error decomposes into several parts. Using the Aubin-Nitsche-duality method we have derived a quadratic (Newton type) error bound valid for the linear-tensor-network TCC scheme DMRG-TCC and other TNS-TCC methods.

Three-Legged Tree Tensor Network States - We have presented a new variational tree tensor network state (TTNS) ansatz, the three-legged tree tensor network state (T3NS). Physical tensors have been interspersed with branching tensors. Physical tensors have one physical index and at most two virtual indices, as in the matrix product state (MPS) ansatz of the DMRG ansatz. Branching tensors have no physical index, but up to three virtual indices. In this way, advantages of DMRG, in particular a low computational cost and a simple implementation of symmetries, have been combined with advantages of TTNS, namely incorporating more entanglement. Our code has been capable of simulating quantum chemical Hamiltonians, and we have presented several proof-of-principle calculations on LiF, N_2, and the bis(μ-oxo) and μ–η^2:η^2 peroxo isomers of $[Cu_2O2]^{2+}$.

Full Configuration Interaction Quantum Monte Carlo Benchmark and Multireference Coupled Cluster Studies for Tetramethyleneethane - We have performed a full configuration interaction (FCI) quality benchmark calculation for the tetramethyleneethane molecule in the cc-pVTZ basis set employing a subset of complete active space second order perturbation theory, CASPT2(6,6), natural orbitals for the FCI quantum Monte Carlo calculation. The results have been in an excellent agreement with the previous large scale diffusion Monte Carlo calculations by Pozun et al. and available experimental results. Our computations have verified that there is a maximum on the potential energy surface (PES) of the ground singlet state (^{1}A) 45° torsional angle, and the corresponding vertical singlet–triplet energy gap is 0.01 eV. We have employed this benchmark for the assessment of the accuracy of Mukherjee's coupled clusters with up to triple excitations (MkCCSDT) and CCSD tailored by the DMRG method. Multireference MkCCSDT with CAS(2,2) model space, though giving good values for the singlet–triplet energy gap, has not been able to properly describe the shape of the multireference singlet PES. Similarly, DMRG(24,25) has not been able to correctly capture the shape of the singlet surface, due to the missing dynamic correlation. On the other hand, the DMRG-tailored CCSD method has described the shape of the ground singlet state with excellent accuracy but for the correct ordering requires computation of the zero-spin-projection component of the triplet state ($^3B_1$).

Analysis of electron-correlation effects in strongly correlated systems (N_2 and N_2^+) by applying the DMRG method and quantum information theory - The dissociation of N_2 and N^{2+} has been studied by using the ab initio density-matrix renormalization-group (DMRG) method. Accurate potential energy surfaces (PESs) have been obtained for the electronic ground states of N_2 ($X_1\Sigma_g^+$) and N_2^+ ($X_2\Sigma_g^+$) as well as for the N_2^+ excited state $B_2\Sigma_u^+$. Inherent to the DMRG approach, the eigenvalues of the reduced density matrix and their correlation functions have been at hand. Thus we could apply quantum information theory directly and we have investigated how the wave function changes along the PES and depicted differences between the different states. Moreover, by characterizing quantum entanglement between different pairs of orbitals and analyzing the reduced density matrix, we have achieved a better understanding of the multireference character featured by these systems.

Towards a multiconfigurational method of increments - The method of increments (MoI) allows one to

successfully calculate cohesive energies of bulk materials with high accuracy, but it encounters difficulties when calculating dissociation curves. The reason is that its standard formalism is based on a single Hartree–Fock (HF) configuration whose orbitals are localized and used for the many-body expansion. In situations where HF does not allow a size-consistent description of the dissociation, the MoI cannot be guaranteed to yield proper results either. We have addressed the problem by employing a size-consistent multiconfigurational reference for the MoI formalism. This has led to a matrix equation where a coupling derived by the reference itself is employed. In principle, such an approach allows one to evaluate approximate values for the ground as well as excited states energies. While the latter are accurate close to the avoided crossing only, the ground state results are very promising for the whole dissociation curve, as has been shown by the comparison with DMRG benchmarks. We have tested this two-state constant-coupling MoI on beryllium rings of different sizes and studied the error introduced by the constant coupling.

The classification of multipartite quantum correlation - In multipartite entanglement theory, the partial separability properties have an elegant, yet complicated structure, which becomes simpler in the case when multipartite correlations are considered. We have elaborate this, by giving necessary and sufficient conditions for the existence and uniqueness of the class of a given class-label, by the use of which we have worked out the structure of the classification for some important particular cases, namely, for the finest classification, for the classification based on k-partitionability and k-producibility, and for the classification based on the atoms of the correlation properties.

An entropy production based method for determining the position diffusion's coefficient of a quantum Brownian motion - Quantum Brownian motion of a harmonic oscillator in the Markovian approximation has been described by the respective Caldeira–Leggett master equation. This master equation can be brought into Lindblad form by adding a position diffusion term to it. The coefficient of this term is either customarily taken to be the lower bound dictated by the Dekker inequality or determined by more detailed derivations on the linearly damped quantum harmonic oscillator. We have explored the theoretical possibilities of determining the position diffusion term's coefficient by analyzing the entropy production of the master equation.

An Isolated Molecule of Iron(II) Phthalocyanin Exhibits Quintet Ground-State: A Nexus between Theory and Experiment - Iron(II) phthalocyanine (FePc) is an important member of the phthalocyanines family with potential applications in the fields of electrocatalysis, magnetic switching, electrochemical sensing, and phototheranostics. Despite the importance of electronic properties of FePc in these applications, a reliable determination of its ground-state is still challenging. We have presented combined state of the art computational methods and experimental approaches, that is, Mössbauer spectroscopy and Superconducting Quantum Interference Device magnetic measurements to identify the ground state of FePc. While the nature of the ground state obtained with density functional theory depends on the functional, giving mostly the triplet state, multi-reference complete active space second-order perturbation theory and DMRG methods assign quintet as the FePc ground-state in gas-phase. This has been confirmed by the hyperfine parameters obtained from 57Fe Mössbauer spectroscopy performed in frozen monochlorobenzene. The use of monochlorobenzene guarantees an isolated nature of the FePc as indicated by a zero Weiss temperature. The results open doors for exploring the ground state of other metal porphyrin molecules and their controlled spin transitions via external stimuli.

Interaction quench and thermalization in a one-dimensional topological Kondo insulator – We have studied the nonequilibrium dynamics of a one-dimensional topological Kondo insulator, modelled by a p-wave Anderson lattice model, following a quantum quench of the on-site interaction strength. Our goal was to examine how the quench influences the topological properties of the system, therefore our main focus was the time evolution of the string order parameter, entanglement spectrum and the topologically-protected edge states. We have pointed out that postquench local observables can be well captured by a thermal ensemble up to a certain interaction strength. Our results have demonstrated that the topological properties after the interaction quench are preserved at finite times; however, the absolute value of the string order parameter decays in time. These predictions could be directly tested in state-of-the-art cold-atom experiments.

2017

Tensor factorization in high dimensional problems and applications to strongly correlated systems in condensed matter physics and quantum chemistry. — In this year we have continued our research on various strongly correlated systems using the Density Matrix Renormalization Group (DMRG), Matrix Product

State (MPS) and Tree Tensor Network State (TTNS) methods. In addition, we have further developed our 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 molecules, or for the quantum simulation of the information technology itself. Further algorithmic developments have also been carried out concerning the quantum chemistry DMRG and Coupled-Cluster (CC) algorithms, and we have carried out the most large-scale calculations available in the literature for tetramethyleneethane molecule. We have also implemented parallelization in several parts of the code, and worked on further MPI, open-MP and GPU based developments. In addition, during a two-week visit at PNNL (Prof. Karol Kowalski, PNNL, Richland, Washington State, USA) we started the migration of the DMRG algorithm into the NWChem (commercial) program package, which ensures the possibility of massive parallelization. In collaboration with guest researchers from the groups of Uni Ghent and Uni Marburg, we have been working on new algorithmic solutions on the tree-TNS algorithm. As will be presented below, among many others, we have examined strongly correlated electrons in magnetic materials in several quantum phases, exotic quantum phases in ultracold atomic systems, and we have determined multi-orbital correlation and entanglement patterns in molecules, playing important role in chemical compounds.

Interaction effects in a chaotic graphene quantum billiard. — We have investigated the local electronic structure of a Sinai-like, quadrilateral graphene quantum billiard with zigzag and armchair edges using scanning tunneling microscopy (STM) at room temperature in collaboration with the Research Institute for Materials Science, Centre for Energy Research, HAS. We have revealed that besides the $(\sqrt{3}\times\sqrt{3})R30^\circ$ superstructure, which is caused by the intervalley scattering, its overtones also appear in the STM measurements, which are attributed to the Umklapp processes. We have pointed out that these results can be well understood by taking into account the Coulomb interaction in the quantum billiard, accounting for both the measured density of state values and the experimentally observed topography patterns. The analysis of the level-spacing distribution substantiates the experimental findings as well. We have also revealed the magnetic properties of our system which should be relevant in future graphene based electronic and spintronic applications.

A magnetic phase-transition graphene transistor with tunable spin polarization. — Graphene nanoribbons have been proposed as potential building blocks for field effect transistor (FET) devices due to their quantum confinement bandgap. We have proposed a novel graphene nanoribbon device concept, enabling the control of both charge and spin signals, integrated within the simplest three-terminal device configuration. In a conventional FET device, a gate electrode is employed to tune the Fermi level of the system in and out of a static bandgap. By contrast, in the switching mechanism we proposed, the applied gate voltage can dynamically open and close an interaction gap, with only a minor shift of the Fermi level. Furthermore, the strong interplay of the band structure and edge spin configuration in zigzag ribbons enables such transistors to carry spin polarized current without employing an external magnetic field or ferromagnetic contacts. Using an experimentally validated theoretical model, we have shown that such transistors can switch at low voltages and high speed, and the spin polarization of the current can be tuned from 0% to 50% by using the same back gate electrode. Furthermore, such devices are expected to be robust against edge irregularities and can operate at room temperature. Controlling both charge and spin signal within the simplest FET device configuration could open up new routes in data processing with graphene based devices.

Entanglement and magnetism in high-spin graphene nanodisks. — We have investigated the ground-state properties of triangular graphene nanoflakes with zigzag edge configurations. The description of zero-dimensional nanostructures requires accurate many-body techniques since the widely used density-functional theory with local density approximation or Hartree-Fock methods cannot handle the strong quantum fluctuations. Applying the unbiased density-matrix renormalization group algorithm, we have calculated the magnetization and entanglement patterns with high accuracy for different interaction strengths and compared them to the mean-field results. With the help of quantum information analysis and subsystem density matrices, we have revealed that the edges are strongly entangled with each other. We have also addressed the effect of electron and hole doping and demonstrated that the magnetic properties of triangular nanoflakes can be controlled by electric field, which reveals features of flat-band ferromagnetism. This may open up new avenues in graphene based spintronics.

Optical phonons for Peierls chains with long-range Coulomb interactions. — We have considered a chain of atoms that are bound together by a harmonic force. Spin-1/2 electrons that move between neighboring chain sites (Hückel model) induce a lattice dimerization at half band filling (Peierls effect). We have supplemented the Hückel model with a local Hubbard interaction and a long-range Ohno potential, and calculated the average bond-length, dimerization, and optical phonon frequencies for finite straight and zigzag chains using the DMRG method. We have tested our numerical approach against analytic results for the Hückel model. The Hubbard interaction mildly affects the average bond length but substantially enhances the dimerization and increases the optical phonon frequencies whereas, for moderate Coulomb parameters, the long-range Ohno interaction plays no role.

Interplay between exotic superfluidity and magnetism in a chain of four-component ultracold atoms. — We have investigated the spin-polarized chain of ultracold alkaline-earth-metal 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 has been studied analytically and by DMRG. We have found 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 has been found for weaker interactions. We have shown that the system can be driven from this quartet-FFLO state to a molecular state of localized quartets where spatial segregation between molecular crystals and ferromagnetic liquids emerges, and this transition is reflected in the static structure factor.

Role of the pair potential for the saturation of generalized Pauli constraints. — The dependence of the (quasi-)saturation of the generalized Pauli constraints on the pair potential is studied for ground states of few-fermion systems. For this, we have considered spinless fermions in one dimension which are harmonically confined and interact by pair potentials of the form $|x_i-x_j|^s$ with $-1\leq s\leq 5$. Using the DMRG approach and large orbital basis sets ensures the convergence on more than ten digits of both the variational energy and the natural occupation numbers. Our results confirm that the conflict between energy minimization and fermionic exchange symmetry results in a quasi-saturation of the generalized Pauli constraints (quasipinning), implying structural simplifications of the fermionic ground state. However, a self-consistent perturbation theory reveals that most of that relevance has to be assigned to Pauli's original exclusion principle, except for the harmonic case, i.e., $s=2$. This emphasizes the unique nature of the strong, non-trivial quasipinning found recently for the Harmonium model.

An entropy production based method for determining the position diffusion's coefficient of a quantum Brownian motion. — Quantum Brownian motion of a harmonic oscillator in the Markovian approximation is described by the respective Caldeira-Leggett master equation. This master equation can be brought into Lindblad form by adding a position diffusion term to it. The coefficient of this term is either customarily taken to be the lower bound dictated by the Dekker inequality or determined by more detailed derivations on the linearly damped quantum harmonic oscillator. We have explored the theoretical possibilities of determining the position diffusion term's coefficient by analyzing the entropy production of the master equation. We have shown that the obtained value has a linear dependence on the temperature, which is in marked contrast to previous studies.

The correlation theory of the chemical bond. — The quantum mechanical description of the chemical bond is generally given in terms of delocalized bonding orbitals, or, alternatively, in terms of correlations of occupations of localized orbitals. However, in the latter case, multiorbital correlations were treated only in terms of two-orbital correlations, although the structure of multiorbital correlations is far richer; and, in the case of bonds established by more than two electrons, multiorbital correlations represent a more natural point of view. For the first time, we have introduced the true multiorbital correlation theory, consisting of a framework for handling the structure of multiorbital correlations, a toolbox of true multiorbital correlation measures, and the formulation of the multiorbital correlation clustering, together with an algorithm for obtaining that. These make it possible to characterize quantitatively how well a bonding picture describes the chemical system. As a proof of concept, we have applied the theory for the investigation of the bond structures of several molecules. We have shown that the non-existence of well-defined multiorbital correlation clustering provides a reason for debated bonding picture.

Correlation analysis of electron-deficit bonds. — We have extended the use of quantum information theory to classify chemical bonds based on multiorbital correlations within the molecule to electron deficient bonds, employing the adequate multireference method of DMRG. First, we have analyzed the bonding structure of the standard diborane(6) molecule and the newly discovered prototype, diborane(4), and we have confirmed that this theory is capable of correct description of bonding in electron deficient bonds, like diborans. Subsequently, we have studied neutral zerovalent s-block beryllium complex, a substance first synthesized in 2016, whose surprising stability was attributed to a strong three-center two-electron π-bond stretching over the C-Be-C core. Our calculations have provided quantitatively adequate images of correlations within the beryllium complex and confirmed the theoretical suggestions on the molecule’s stability.

On the multi-reference nature of plutonium oxides PuO_2^{2+}, PuO_2, PuO_3 and $PuO_2(OH)_2$. — Actinide-containing complexes present formidable challenges for electronic structure methods due to the large number of degenerate or quasi-degenerate electronic states arising from partially occupied 5f and 6d shells. Conventional multi-reference methods can treat active spaces that are often at the upper limit of what is required for a proper treatment of species with complex electronic structures, leaving no room for verifying their suitability. We have addressed the issue of properly defining the active spaces in such calculations, and introduced a protocol to determine optimal active spaces based on the use of the DMRG algorithm and concepts of quantum information theory. We have applied the protocol to elucidate the electronic structure and bonding mechanism of volatile plutonium oxides (PuO_3 and $PuO_2(OH)_2$), species associated with nuclear safety issues for which little is known about the electronic structure and energetics. We have shown how, within a scalar relativistic framework, orbital-pair correlations can be used to guide the definition of optimal active spaces which provides an accurate

description of static/non-dynamic electron correlation, as well as to analyze the chemical bonding beyond a simple orbital model. From this bonding analysis, we have been able to show that the addition of oxo- or hydroxo-groups to the plutonium dioxide species considerably changes the π-bonding mechanism with respect to the bare triatomics, resulting in bent structures with a considerable multi-reference character.

Full configuration interaction quantum Monte Carlo benchmark and multireference coupled cluster studies of tetramethyleneethane diradical. — We have performed an FCI-quality benchmark calculation for the tetramethyleneethane molecule in cc-pVTZ basis set employing a subset of CASPT2(6,6) natural orbitals for the FCIQMC calculation. The results are in an excellent agreement with the previous large scale diffusion Monte Carlo calculations by Pozun et al. and available experimental results. Our computations have verified that there is a maximum on potential energy surface of the ground singlet state (1A) 45◦ torsional angle and the corresponding vertical singlet-triplet energy gap is 0.01 eV. We have employed this benchmark for the assessment of the accuracy of MkCCSDT and DMRG-tailored CCSD (TCCSD) methods. Multireference MkCCSDT with CAS(2,2) model space, though giving good values for the singlet-triplet energy gap, is not able to properly describe the shape of the multireference singlet potential energy surface. Similarly, DMRG(24,25) is not able to correctly capture the shape of the singlet surface, due to the missing dynamic correlation. On the other hand, the DMRG-tailored CCSD method describes the shape of the ground singlet state with an excellent accuracy, but for the correct ordering, computation of the zero-spin-projection component of the triplet state (3B1) is required.