Project closing report: K120569

Strong correlations and entanglement in nuclei, through molecules to ultra cold atom and condensed matter systems

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Background and general overview: One of the main achievements of the physics of the previous century was the development of systematic perturbative approaches, which assume that the interactions are weak in the sense that one can treat them as perturbations around some simple, well-understood Hamiltonian. Many systems that occur in nature, however, lie out of the reach of these conventional perturbative methods. These so-called ‘strongly correlated’ systems, like various heavy fermion compounds, manganites, high-temperature superconductors, and molecular magnets, exhibit very rich physical properties, which depend strongly on the interaction parameters. Unfortunately, strongly correlated materials are typically rather difficult to treat theoretically. They have a complicated band structure, and it is quite difficult to determine which minimal model describes their essential physical properties correctly. It is, therefore, evident that understanding and investigating strongly correlated systems is a major challenge in modern condensed matter, atomic physics and in transition metal chemistry.

Numerical simulations: Simulating quantum systems on classical computers is a major challenge in theoretical physics, a challenge that has been addressed by a number of recent algorithmic developments. Such simulation is particularly difficult when strong correlations, as reflected in a high level of entanglement, are present. For one-dimensional systems, the matrix-product-state-(MPS) based density matrix renormalization group (DMRG) method is the most effective tool to calculate the properties of the ground and selected excited states. In higher dimensions, the DMRG is less efficient at representing the entanglement structure of states, due to its one-dimensional topology. Developments in the past decade have led to several alternative methods that potentially overcome the limitations of the DMRG. These include the multi-scale entanglement renormalization ansatz (MERA), the projected entangled pair states (PEPS), the tree-tensor network state (TTNS), quantum Monte Carlo (QMC), and the density matrix embedding theory (DMET). All these methods have advantages and disadvantages; each one of them has competitive performance in particular circumstances. However, there is no single method yet, that can be applied efficiently as a black-box tool to a general quantum lattice problem. Therefore, despite substantial efforts over many years, DMRG is still a very robust alternative method to carry out large scale calculations in general. The DMRG method can thus effectively be used for the study of transitional metal clusters, delocalized electron systems, ultracold atomic systems, or nuclear physics. Such systems are approximated with effective models, containing finite number of parameters on the one hand, or treated directly by the use of ab initio calculations on the other. In the latter case, there exists only a few methods for the treatment of dynamic correlations on top of DMRG.

Major goals: The OKTA-Project K120569 focuses on two major goals. On the one hand, we aimed to carry out major algorithmic developments to treat dynamic correlations efficiently, thus extending the capability of the DMRG method to treat more complex systems. On the other hand, we aimed to determine the properties of exotic phases (topological and phase separated) and phase transitions in strongly correlated quantum many body systems in which the interactions are long-ranged, by taking advantage of several concepts of quantum information theory. Therefore, one of the aims of the project was to develop a multireference coupled cluster (CC) method, which has been augmented by information coming from a DMRG calculation and became able to compute the remaining dynamic correlations, absent in DMRG itself. For example, such methods are the ones based on the tailored CC approach, the (N,M)-CCSD approach, and the universal state selective approach. Besides these, using exact mathematical approach of correlations, we investigated the entanglement of the states of tripartite and multipartite subsystems, and their realization in nature in ultracold atomic systems and molecular systems, and in nuclear physics. The new methods made possible the investigation of, e.g., the effect of the boundary topology in graphene nanoribbons, or the properties of mixed phases in four-component ultracold atomic systems. Beyond the fundamental new knowledge gained about quantum systems, a main result of the project is a computer code (Budapest QC-DMRG), which was interfaced with standard softwares (Orca, NWChem) and provides a broad range of possibilities in applications for the scientific community.

Main results and achievement despite the COVID-19 pandemic: Unfortunately, the COVID-19 pandemic had a major negative effect on our research program, even the PI was in immediate danger of death, and treated on intense care for more than a month. His full recovery took more than two years. In addition, due to the lock-downs worldwide, cancellation of conferences and travel restrictions, we had to reschedule our budget two times. Therefore, the originally planned 4-year budget was extended to a 6-year research period. **Nevertheless, our research has resulted in close to 80 publications in high quality scientific journals, 90% of which belong to category D1.** Our research projects have been part of intense international collaborations (*Austria, Canada, Belgium, Czech Republic, Germany, Switzerland, Spain, Poland, United Kingdom, United States*). As recognition of the high impact results, the PI was granted with the Humboldt Research Award from the Alexander Humboldt Foundation in 2018, with the Hans Fischer Senior Award and Fellowship from the Institute for Advanced Studies of the Technical University of Munich in 2021 and the Academy Prize of the Hungarian Academy of Sciences in 2021. Two senior researches received the Bolyai and Bolyai+ Award and Research Scholarship from the Hungarian Academy of Sciences.

Workshops and scientific visits: We organized an international workshop at the Max Planck Institute, Dresden (MPIPKS) “Tensor Product Methods for Strongly Correlated Molecular Systems, Entanglement based approaches in quantum chemistry (TPMSCS-2020)”, (finally shifted to 2021), an international workshop “Entanglement Days”, Budapest in 2018, the “ELFT Vándorgyűlés”, Sopron and Veszprém (organizing sections) in 2019 and 2022, and “Quantum Mechanics” summer school, Répáshuta in 2022. We also organized several scientific visits annually, and collaborating partners also spent several days or weeks in our institute. We also gave several talks on international conferences, public talks in elementary and high-schools and in public events.

Algorithmic and code developments: We made major algorithmic developments related to the DMRG algorithm by utilizing various concepts of quantum information theory, analysis based on rigorous mathematics, and solution taken from conventional methods. All these serve a systematic reduction of entanglement when quantum many body systems are represented by tensor network topologies. These include tensor topology together with basis optimization, utilization of Abelian and non-Abelian symmetries, and various post-DMRG solutions to capture dynamic correlations more efficiently. Here the restricted active space DMRG (DMRG-RAS) has in fact the potential to became one of the most powerful method for multireference/strongly correlated problems. We also achieved significant results for dynamic systems, i.e., the combination of the time dependent variational principle (TDVP) together with fermionic mode transformation. Various applications to quenched and dissipative systems were also considered. In addition, we designed and implemented new algorithmic solutions for massive parallelization via message passing interface (MPI) and novel solutions to further boost our code on graphical processing units (GPU).

Interaction and collaboration with experimental groups: Although, the main focus of our research is on the fundamental aspects of the nature of correlations from theoretical point of view, we also interacted strongly with experimental groups, leading to fruitful collaborations and joint publications. Here we just mention a few among many others: the realization of qubit systems, formation of Wigner crystals, and verifying exotic states of matter. The very novel research direction related to nuclear structure DMRG, in fact, has the potential to push current limits of simulations to a much higher level and provide direct computational/theoretical verification of recent experimental results in the near future.

Scientific results from the past year: Here we provide a more detailed description of our research activity, focusing on five main areas: *applied mathematics, quantum information theory, condensed matter systems, quantum chemistry and nuclear structure theory*. These resulted in 12-16 publications. There are another 3 preprints in near final stage before submission.

Applied mathematics and algorithmic developments: We presented the exact representation of a fully correlated electronic wavefunction as the single-particle basis approaches completeness. It consists of a half-infinite chain of matrices of exponentially increasing size. The complete basis limit was illustrated numerically using the density matrix renormalization group (DMRG) method by computing the core-valence entanglement in the C_2 ground state in increasing subsets of cc-pVTZ and pVQZ bases until convergence is reached. *PhysRevB.105.165144*

We presented a theoretical analysis and a new theory-based extrapolation method for the recently introduced restricted active space DMRG (DMRG-RAS) method [arXiv:2111.06665] in electronic structure calculations. Large-scale numerical simulations showed that our approach, DMRG-RAS-X, reached chemical accuracy for challenging strongly correlated systems such as the chromium dimer or dicarbon up to a large cc-pVQZ basis with moderate computational demands. 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. *arXiv:2209.14190*

Condensed matter theory: In crystalline solids the interactions of charge and spin can result in a variety of emergent quantum ground states, especially in partially filled, topological flat bands, such as Landau levels or in 'magic-angle' bilayer graphene. Much less explored is rhombohedral graphite (RG), perhaps the simplest and structurally most perfect condensed matter system to host a flat band protected by symmetry. By scanning tunneling microscopy we mapped the flat band charge density of 8, 10 and 17 layers and identified a domain structure emerging from a competition between a sublattice antiferromagnetic insulator and a gapless correlated paramagnet. Our DMRG calculations explained the observed features and demonstrated that the correlations are fundamentally different from graphene based magnetism identified until then, forming the ground state of a quantum magnet. We established RG as a new platform to study many-body interactions beyond the mean-field approach, where quantum fluctuations and entanglement dominate. *Science Advances 8, eabo6879 (2022)*

We investigated the ground-state properties of the nearest-neighbor S=1 pyrochlore Heisenberg antiferromagnet using two complementary numerical methods, DMRG and pseudofermion functional renormalization group (PFFRG). Within DMRG, we were able to reliably study clusters with up to 48 spins by keeping 20 000 SU(2) states. The investigated 32-site and 48-site clusters both show indications of a robust C_3 rotation symmetry breaking of the ground-state spin correlations and the 48-site cluster additionally features inversion symmetry breaking. Our PFFRG analysis of various symmetry-breaking perturbations corroborated the findings of either C_3 or a combined C_3/inversion symmetry breaking. Moreover, in both methods the symmetry-breaking tendencies appeared to be more pronounced than in the S=1/2 system. *arXiv:2207.01642*

We investigated the charge-density wave (CDW) transition for one-dimensional spinless fermions at half band-filling with nearest-neighbor electron transfer amplitude t and interaction V.The model is equivalent to the anisotropic XXZ Heisenberg model for which the Bethe Ansatz provides an exact solution. For $V>V_c=2t$, the CDW order parameter and the single-particle gap are finite but exponentially small, as is characteristic for a Kosterlitz-Thouless transition. It is notoriously difficult to locate such infinite-order phase transitions in the phase diagram using approximate analytical and numerical approaches. Second-order Hartree-Fock theory is qualitatively applicable for all interaction strengths, and predicts the CDW transition to occur at $V_{c,2}^{(2)}\approx 1.5t$. Second-order Hartree-Fock theory is almost variational because the density of quasi-particle excitations is small. We applied the DMRG for periodic boundary conditions for system sizes up to 514 sites which permits a reliable extrapolation of all physical quantities to the thermodynamic limit, apart from the critical region. We investigated the ground-state energy, the gap, the order parameter, the momentum distribution, the quasi-particle density, and the density-density correlation function to locate V_c from the DMRG data. Tracing the breakdown of the Luttinger liquid and the peak in the quasi-particle density at the band edge permitted us to reproduce V_c with an accuracy of one percent. *arXiv:2208.07620*

Particle formation represents a central theme in various branches of physics, often associated to confinement. 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. By starting from an appropriately engineered initial state of the SU(3) Hubbard model, not only mesons (doublons) but also baryons (trions) are naturally generated during the time evolution. In the strongly interacting limit, baryons become heavy and attract each other strongly, and their residual interaction with mesons generates meson diffusion, as captured by the evolution of the equal time density correlation function. Hadrons remain present in the long time limit, while the system thermalizes to a negative temperature state. Our conclusions extend to a large variety of initial conditions, all spatial dimensions, and for SU($N>2$) Hubbard models. *arXiv.2207.00994*

We developped a non-Abelian time evolving block decimation (NA-TEBD) approach to study of open systems governed by Lindbladian time evolution, while exploiting an arbitrary number of Abelian or non-Abelian symmetries. We illustrated this method in a one-dimensional fermionic SU(2) Hubbard model on a semi-infinite lattice with localized particle loss at one end. We observed a ballistic front propagation with strongly renormalized front velocity, and a hydrodynamic current density profile. For large loss rates, a suppression of the particle current was observed, as a result of the quantum Zeno effect. Operator entanglement was found to propagate faster than the depletion profile, preceding the latter. *Phys. Rev. B 105, 195144 (2022)*

Quantum Chemistry and material science: We presented a brief overview of the fermionic mode optimization within the framework of tensor network state methods, 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. *Journal of Mathematical Chemistry (2022) https://doi.org/10.1007/s10910-022-01379-y*

Point defect qubits in semiconductors have demonstrated their outstanding high spatial resolution sensing capabilities of broad multidisciplinary interest. Two-dimensional (2D) semiconductors hosting such sensors have recently opened up new horizons for sensing in the subnanometer scales in 2D heterostructures. However, controlled creation of quantum sensor in a single layer 2D materials with high sensitivity has been elusive so far. We reported on a novel 2D quantum sensor, the VB2 centre in hexagonal boron nitride (hBN), with superior sensing capabilities. The centre's inherently low symmetry configuration gives rise to unique electronic and spin properties that implement a qubit in a 2D material with unprecedented sensitivity. The qubit was found to be decoupled from its dense spin environment at low magnetic fields that gives rise to the reduction of the spin resonance linewidth and elongation of the coherence time. The VB2 centre is also equipped with a classical memory that can be utilized in storing population information. Using scanning transmission electron microscopy imaging, we confirmed the presence of the point defect structure in free standing monolayer hBN created by electron beam irradiation. Our results provide a new material solution towards atomic-scale sensing in low dimensions. *arXiv:2111.09589*

We presented an alternative, memory-efficient, Schmidt decomposition-based extension of the inherently bipartite restricted active space scheme, which can be implemented effortlessly within the DMRG method via the dynamically extended active space procedure. Demonstrative calculations were benchmarked against state-of-the-art results of C_2, which is notorious for its multi-reference character. Besides the uncontracted solution, internal contraction could also be naturally realized in the formalism by keeping only the most relevant Schmidt states. *arXiv:2111.06665*

We investigated the convergence properties of DMRG calculations for vertical electronic excitations performed on three bimolecular complexes motivated by Szalay's recent benchmark results [JCTC. 2020;16:7]. Besides the high-level coupled-cluster reference spectrum, the extrapolated truncation-free DMRG results were compared against several alternative solutions based on multireference configuration interaction and coupled-cluster theories. By taking advantage of the error cancellation effects, which are inherent in the state-averaged computational scheme, we demonstrated that the extrapolated solution based on only low bond-dimensional DMRG data could already provide quantitative predictions even for large active spaces. We also showed that orbital optimisation improves further the accuracy of the DMRG results which systematically approach the excitation energies of coupled cluster single-double-triple at similar computational costs. *Molecular Physics, e2130834*

<u>*Nuclear structure theory:*</u> We studied mode-entanglement in the seniority model, derived analytic formulas for the one-body reduced density matrix of states with seniority $\nu=0,1,2$, and $\nu=3$, and also determined the particle number dependence of the one-body reduced density matrix for arbitrary seniority. We carried out numerical calculations for the lightest calcium isotopes and for ^{94}Ru nucleus, and investigated the structure of their ground and low energy yrast states. We investigated the fulfillment of several predictions of the seniority model regarding the behavior of one-mode entropies, which we compared with the results of configuration interaction (CI) and DMRG computations. For ^{94}Ru, the seniority model accounts for the $0_{g9/2}$ mode entropies, but seniority mixing is important for certain yrast states. Interaction induced quantum fluctuations decrease the occupation of the $0_{f5/2}$, $1_{p3/2}$ and $1_{p1/2}$ shells, and amount in finite mode entropies on these shells, too, clearly outside the scope of the simple $(0_{g9/2})^4$ seniority model. The $0_{f7/2}$ shell based seniority model is more accurate for the light Ca isotopes, but seniority mixing is substantial for some ^{44}Ca yrast states, too. *https://doi.org/10.48550/arXiv.2112.15513*

We proposed a novel many-body framework combining the DMRG with the valence-space (VS) formulation of the in-medium similarity renormalization group. This hybrid scheme admits 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. *arXiv:2207.01438*

Selected scientific results from the previous five-year time period: Below we organize our main results to main categories, however, due to the high number of publications only a selected set will be presented.

1. Condensed matter systems:

We investigated the low-lying excitation spectrum and ground-state properties of narrow graphene nanoribbons with zigzag edge configurations. Nanoribbons of comparable widths have been synthesized very recently [P. Ruffieux et al., Nature (London) 531, 489 (2016)], and their descriptions require more sophisticated methods since in this regime conventional methods, like mean-field or density-functional theory with local-density approximation, fail to capture the enhanced quantum fluctuations. Using the unbiased DMRG algorithm, we calculated the charge gaps with high accuracy for different widths and interaction strengths and compare them with mean-field results. Applying the elements of quantum information theory, we also revealed the entanglement structure inside a ribbon and examined the spectrum of subsystem density matrices to understand the origin of entanglement. We examined the possibility of magnetic ordering and the effect of magnetic field. Our findings are relevant for understanding the gap values in different recent experiments and the deviations between them.

We also 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 DMRG algorithm, we calculated the magnetization and entanglement patterns with high accuracy for different interaction strengths and compare them to the mean-field results. With the help of quantum information analysis and subsystem density matrices, we revealed that the edges are strongly entangled with each other. We also addressed the effect of electron and hole doping and demonstrate 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.

Graphene nanoribbons have been proposed as potential building blocks for field effect transistor (FET) devices due to their quantum confinement bandgap. We 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 showed 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.

We 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. It has been revealed that besides the $\left(\sqrt{3}\times\sqrt{3}\right)R30^\circ$ superstructure, which is caused by the intervalley scattering, its overtones also appear in the STM measurements, which are attributed to the Umklapp processes. We 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 also revealed the magnetic properties of our system which should be relevant in future graphene based electronic and spintronic applications.

The quantum crystal of electrons, predicted more than eighty years ago by Eugene Wigner, is still one of the most elusive states of matter. We performed DMRG calculations in collaboration with Prof. G. Zaránd to provide theoretical description of images obtained by experiments, i.e., when a few electrons confined in one-dimension. These match those of strongly interacting crystals, with electrons ordered like pearls on a necklace. Comparison to theoretical modelling demonstrated the dominance of Coulomb interactions over kinetic energy and the weakness of exchange interactions. Our results 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.

We 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 W, the impurity interaction strength U, and the local hybridization V. We compare 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 used a canonical transformation to map the SIAM onto a chain with half the system size and open boundary conditions. We 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 showed that the field-theoretical description is applicable to the SIAM on a ring for a broad parameter range. Advantageous properties and drawback of each method was discussed in detail.

We 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 J_K. We 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 Numerical Renormalization Group (NRG) methods.

The dependence of the (quasi-)saturation of the generalized Pauli constraints on the pair potential was studied for ground states of few-fermion systems. We considered spinless fermions in one dimension which are harmonically confined and interact by pair potentials of the form $|x_i-x_j|^s$ with $-1\leq s\leq 5$. Our results confirmed that the conflict between energy minimization and fermionic exchange symmetry results in a universal and non-trivial quasi-saturation of the generalized Pauli constraints (quasipinning), implying tremendous structural simplifications of the fermionic ground state for all s.

We considered sudden quenches across quantum phase transitions in the S=1 XXZ model starting from the Haldane phase. We 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 showed that the temporal behavior of the string order parameter is intimately related to the subsequent dynamical phase transitions. We furthermore found that the dynamical quantum phase transitions can be accompanied by enhanced two-site entanglement.

We also studied quantum quenches in the S=1 Heisenberg spin chain in collaboration with group of G. Zaránd, and showed 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 analyzed the non-equilibrium time evolution of the distribution of the total spin in half of the system and compared 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 showed 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.

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 is not 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 addressed the ground-state properties of the long-standing and much-studied three-dimensional quantum spin liquid candidate, the S=1/2 pyrochlore Heisenberg antiferromagnet. By using SU(2) DMRG, we were able to access cluster sizes of up to 128 spins. Our most striking finding was a robust spontaneous inversion symmetry breaking, reflected in an energy density difference between the two sublattices of tetrahedra, familiar as a starting point of earlier perturbative treatments. We also determined the ground-state energy, $E_0/N_{\text{sites}} = -0.490(6)J$, by combining extrapolations of DMRG with those of a numerical linked cluster expansion. These findings suggested a scenario in which a finite-temperature spin liquid regime gives way to a symmetry-broken state at low temperatures.

We also studied the S=1/2 pyrochlore Heisenberg antiferromagnet in a magnetic field. Using large scale DMRG calculations for clusters up to 128 spins, we found indications for a finite triplet gap, causing a threshold field to nonzero magnetization in the magnetization curve. We obtained a robust saturation field consistent with a magnon crystal, although the corresponding 5/6 magnetization plateau is very slim and possibly unstable. Most remarkably, there is a pronounced and apparently robust 12 magnetization plateau where the groundstate breaks (real-space) rotational symmetry, exhibiting oppositely polarized spins on alternating kagome and triangular planes. Reminiscent of the kagome ice plateau of the pyrochlore Ising magnet known as spin ice, it arises via a much more subtle “quantum order by disorder” mechanism.

We applied the DMRG method to a one-dimensional Hubbard model that lacks Umklapp scattering and thus provides an ideal case to study the Mott-Hubbard transition analytically and numerically. The model has a linear dispersion and displays a metal-to-insulator transition when the Hubbard interaction~U equals the band width, $U_c=W$, where the single-particle gap opens linearly, $\Delta(U\geq W)=U-W$. The simple nature of the elementary excitations permitted to determine numerically with high accuracy the critical interaction strength and the gap function in the thermodynamic limit. The jump discontinuity of the momentum distribution n_k at the Fermi wave number k_F=0 could not be used to locate accurately U_c from finite-size systems. However, the slope of n_k at the band edges, $k_B=\pm\pi$, revealed the formation of a single-particle bound state which can be used to determine U_c reliably from n_k using accurate finite-size data.

2. Quantum chemistry and quantum information theory

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. We, for the first time, 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 proof of concept, we applied the theory for the investigation of the bond structures of several molecules. We showed that the non-existence of well-defined multiorbital correlation clustering provides a reason for debated bonding picture.

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.

Recently, we developed 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 extended the use of this mathematical toolbox for the description of electron-deficient bonds. We verified the theory on the textbook example of a molecule with three-center two-electron bonds, namely the diborane(6). We showed 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 dissociation of N_2 and N_2^+ was studied by using the DMRG method. Accurate potential energy surfaces (PES) were 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 $B^2\Sigma_u^+$. Inherently to the DMRG approach, the eigenvalues of the reduced density matrix and their correlation functions were at hand. Thus we applied quantum information theory directly, and investigated how the wave function changes along the PES and depict differences between the different states. Moreover by characterizing quantum entanglement between different pairs of orbitals and analyzing the reduced density matrix, we achieved a better understanding of the multi-reference character featured by these systems.

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. We 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 elucidated 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 showed how, within a scalar relativistic framework, orbital-pair correlations can be used to guide the definition of optimal active spaces which provide 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 were 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 considerable multi-reference character.

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 presented a state-of-the-art quantum chemical study of the T-shaped and diamond-shaped neptunyl(V) and neptunyl(VI) dimers. Specifically, we scrutinized their molecular structures, solvation effects, the interplay of static and dynamic 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 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 highlighted the complex interplay of correlation effects and relativistic corrections in the description of the ground and lowest-lying excited states of neptunyl dications.

We 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 were 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 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 found out that the amount of retrieved canonical correlation energy depends on the size of the active space (CAS) - we retrieved over 99.6% for the larger 27 orbital CAS and over 99.8% for the smaller 22 orbital CAS.

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.

Coupled cluster calculations are traditionally performed over Hartree-Fock reference orbitals (HF-CC methodology). However, it has been repeatedly argued in the literature that the use of a Kohn-Sham reference (KS-CC methodology) might result in improved performance relative to HF-CC at the same computational cost. We re-examined the relation of HF-CC and KS-CC methods by comparing the results of widely applied truncated CC calculations (CCSD, CCSD(T), CCSDT) to the limit of full configuration interaction (FCI), which – in contrast to wave-function diagnostics with vague physical meaning or experimental data with considerable uncertainty – serves as an undebatable reference point of accuracy. We selected different sets of reference orbitals and different basis sets (STO-3G, 6-31G, cc-pVDZ, cc-pVTZ) to perform calculations on various small molecules with increasing multi-reference character. Convergence rate, errors were analyzed in detail.

Tailored coupled cluster theory represents a computationally inexpensive way to describe static and dynamical electron correlation effects. We scrutinized the performance of various tailored coupled cluster methods externally corrected by electronic wave functions of polynomial cost. Specifically, we focused on frozen-pair coupled-cluster (fpCC) methods, which are externally corrected by pair-coupled cluster doubles (pCCD), and coupled cluster theory tailored by matrix product state wave functions optimized by the DMRG algorithm. As test system, we selected a set of various small- and medium-sized molecules for which conventional single-reference coupled cluster singles and doubles (CCSD) is not able to produce accurate results for spectroscopic constants, potential energy surfaces, and barrier heights. Most importantly, DMRG-tailored and pCCD-tailored approaches yield similar errors in spectroscopic constants and potential energy surfaces compared to multireference and/or experimental reference data and generally outrank the conventional single-reference CCSD approach.

3. Algorithmic developments

In the last decade, the quantum chemical version of the DMRG method has established itself as the method of choice for calculations of strongly correlated molecular systems. Despite its favourable scaling, it is in practice not suitable for computations of dynamic correlation. We presented a novel method for accurate "post-DMRG" treatment of dynamic correlation based on the tailored coupled cluster (CC) theory in which the DMRG method is responsible for the proper description of non-dynamic correlation, whereas dynamic correlation is incorporated through the framework of the CC theory. We illustrated the potential of this method on prominent multireference systems, in particular N_2, Cr_2 molecules and also oxo-Mn(Salen) for which we performed the first "post-DMRG" computations in order to shed light on the energy ordering of the lowest spin states.

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 is far from clear which choice of fermionic orbitals to make. We proposed a way to overcome this challenge. We suggested a method intertwining the optimization over matrix product states with suitable fermionic Gaussian mode transformations. The described algorithm generalizes basis changes in the spirit of the Hartree-Fock method to matrix-product states, and provides a black box tool for basis optimization in tensor network methods.

We presented a new variational tree tensor network state (TTNS) ansatz, the three-legged tree tensor network state (T3NS). Physical tensors are 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. 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) were combined with advantages of TTNS (namely, incorporating more entanglement). Our code is capable of simulating quantum chemical Hamiltonians, and we presented several proof-of-principle calculations on LiF, N_2 and the bis(μ-oxo) and $\mu-\eta^2:\eta^2$ peroxo isomers of $[Cu_2O_2]^{2+}$.

We performed a 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 verified that there is a maximum on PES of the ground singlet state (^1A) 45° torsional angle and the corresponding vertical singlet-triplet energy gap is 0.01 eV. We employed this benchmark for assessment of the accuracy of MkCCSDT and DMRG-tailored CCSD (TCCSD) methods. MR 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 PES. Similarly, DMRG(24,25) was 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 described the shape of the ground singlet state with an excellent accuracy, but the correct ordering requires computation of the zero-spin-projection component of the triplet state ($^3B_1$).

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 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 parametrised 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 argued and our results suggest 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.

Tensor network methods have progressed from variational techniques based on matrix-product states able to compute properties of one-dimensional condensed-matter lattice models into methods rooted in more elaborate states such as projected entangled pair states aimed at simulating the physics of two-dimensional models. We 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 exploited schemes of fermionic mode transformations and 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 showed that matrix-product states can describe ground states strikingly well. The power of the approach is exemplified by investigating a phase transition of spin-less fermions for lattice sizes up to 10x10

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. We further optimized several parts of our code, focusing on especially in massive parallelization and non-Abelian symmetries. Communication overhead for MPI parallelization was significantly reduced.

4. Conjugated polimers

We considered a chain of atoms that are bound together by a harmonic force. Spin-1/2 electrons that move between neighbouring chain sites (Hückel model) induce a lattice dimerization at half band filling (Peierls effect). We 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 zig-zag chains using the DMRG method. We 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.

5. Ultracold atomic systems

We 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 is studied analytically and by DMRG simulations. We 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 is found for weaker interactions. We showed 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.

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.

6. Mathematical analysis:

We proposed a comprehensive mathematical framework for Coupled-Cluster-type methods. These aimed at accurately solving the many-body Schrödinger equation. We established existence results and qualitative information about the solutions of these equations that also shed light on some of the numerically observed behavior. For the truncated Coupled-Cluster method, we derived an energy error bound for approximate eigenstates of the Schrödinger equation.

We also 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 CC method tailored by tensor-network states (TNS-TCC). For statically correlated systems, we introduced the conceptually new CAS-ext-gap assumption for multi-reference problems which replaces the unreasonable HOMO-LUMO gap. We characterized the TCC function and show 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 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 derived a quadratic (Newton type) error bound valid for the linear-tensor-network TCC scheme DMRG-TCC and other TNS-TCC methods.

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 identified 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.

7. Carbon based systems:

For most chiralities, semiconducting nanotubes display topologically protected end states of multiple degeneracies. We demonstrated using DMRG based quantum chemistry tools 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.

Highly correlated orbitals coupled with phonons in two-dimension are identified 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 reported ab initio analysis of the correlated electronic structure of this center by DMRG and Kohn-Sham density functional theory methods. By establishing the nature of the bright and dark states as well as the position of the energy levels, we 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 paved the way toward advancing the identification and characterization of room temperature quantum bits in two-dimensional solids.

8. Nuclear structure theory:

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.

9. Quantum information theory:

A recent development in quantum chemistry has established the quantum mutual information between orbitals as a major descriptor of electronic structure. This has already facilitated remarkable improvements in numerical methods and may lead to a more comprehensive foundation for chemical bonding theory. Building on this promising development, our work 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.

10. Quantum impurities and defect quantum bits

We analyzed the numerical aspects of the inherent multireference DMRG calculations on top of the periodic Kohn–Sham density functional theory using the complete active space approach. The potential of the framework was illustrated by studying hexagonal boron nitride nanoflakes embedding a charged single boron vacancy point defect by revealing a vertical energy spectrum with a prominent multireference character. We investigated the consistency of the DMRG energy spectrum from the perspective of sample size, basis size, and active space selection protocol. Results obtained from standard quantum chemical atom-centered basis calculations and plane-wave based counterparts showed excellent agreement. Furthermore, 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 the DMRG method in extended correlated solid-state systems, such as point defect qubit in wide band gap semiconductors.

Defect quantum bits (qubits) constitute an important emerging technology. However, it is necessary to explore new types of defects to enable large-scale applications. We examined the potential of magnesium-vacancy (MgV) in diamond to operate as a qubit by computing the key electronic- and spin properties with robust theoretical methods. We found that the electronic structure of MgV permits the coexistence of two loosely separated spin-states, where both can emerge as a ground state and be interconverted depending on the temperature and external strain. These results demonstrated a route to control the magneto-optical response of a qubit by modulating the operational conditions.