Studying strongly correlated systems with tensor network state methods and quantum information theory

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Preliminaries

Elementary particles in physics are indistinguishable in principle, and they have either *fermionic* or *bosonic* nature. They arrange to different structures according to the environment. In this work special problems are studied in the field of the quantum chemistry and ultracold physics. Although, their characteristic energies are of different order of magnitude moreover, in the former case we deal with interacting electrons in the external potential of the nuclei, and the latter case we study interacting trapped bosons, they require similar treatment because of the emerging strong correlations in the systems.

Composite systems, for example, system of identical particles, are described by tensor product structure. The *tensor network state* (TNS) methods [Hac12, Cir21], are based on the subsequent optimization of the tensor factors corresponding to the local factor spaces. There are three main approaches of simulating physical systems by tensor networks: tree tensor network state (TTNS), tensor networks with loops, especially projected entangled pair states and the multiscale entanglement renormalization ansatz. Although the *density matrix renormalization group* (DMRG) method [Whi92] was developed to simulate low dimensional strongly correlated systems appearing in the field of solid-state physics, it shows its potential in strongly correlated many-body problems. This algorithm inherently provides the *matrix product state* (MPS) representation of the wave function [Ö95, Rom97, Sch11], which is a simple case of the TNSs. Also, MPS is a tree tensor network state, so, by the Schmidt decomposition (or, in a numerical point of view, singular value decomposition), we have access to the entanglement in the system for the given bipartition. In the past two decades TNS methods have become vital alternative approaches to treat strongly correlated, that is, multireference problems in quantum chemistry [Whi99, Leg08, Cha08, Leg14, Sza15]. Here we investigate systems in quantum chemistry and ultracold physics that are treated by DMRG or methods that are supported by DMRG.

Concerning quantum chemistry, from the exact solution of the hydrogen atom, one may infer to the properties of the hydrogen-like atoms and ions, since they can be approximated by a simple system, that is, the problem of the valence electron and the positive core. From the analytic solution of the hydrogen molecule ion, H_2^+, that is, the problem of two fixed proton and a single electron, the notion of the covalent bond can be grasped. The two analytic solutions give us deeper insight to the characteristics of molecular systems, however, the many-body problem of the interacting electrons are intractable both analytically and numerically. Both in theoretical and experimental chemistry, it is of central importance to explore the shape of the potential energy surface, since this shows the fundamental properties of a molecule, such as the equilibrium geometry and the corresponding energy, spectroscopic constants and dissociation energy. For this, numerous approximation techniques are developed to find the ground-state energy of the electronic system within chemical accuracy for a fixed nucleus configurations [Hel00]. However, there is no universal method applicable to quantum chemistry systems being superior both in numerical cost and accuracy. Moreover, it is often observed that the correlation in the system changes when going through a path in the potential energy surface. For example, describing the bond breaking of a molecule requires careful treatment, since the system is dominated by dynamical correlation at equilibrium geometry and static correlation close to dissociation. The coupled cluster (CC) method performs well in the first case but fails in the latter [Kow00, Lya12]. In quantum chemistry, a kind of standard computational method is the CC up to single and double excitations with perturbative triples, which performs well in many cases of small and medium sized molecules [Rag89, Bar07]. Since this method relies on a single-reference Slater determinant, it may work if the system can be approximated well with a single Slater determinant and fail otherwise, hence we say for these two cases that the system is of *single-reference character* and *multireference character*, respectively. Also, we say that the system is

dynamically correlated and *statically correlated* (or it is *strongly correlated*, with terminology in physics), respectively. Moreover, the CC approach also fail if the energy gap between the highest occupied molecular orbital and the lowest unoccupied molecular orbital (*HOMO-LUMO gap*) becomes small. On the other hand, the DMRG is a powerful method in statically correlated system [Whi99], however, setting an the computational demands are governed by the bond dimension. From this, two remarks can be drawn that we elaborate. First, the hybrid numerical approaches may be developed to capture both dynamic and static correlation in the system. Second, since the correlation in the system is basis dependent, the optimization of the underlying basis may yield a favourable problem setting for the numerical methods. The corresponding methods, investigated and discussed in this work, are the *DMRG tailored CC* (DMRG-TCC) and the *mode transformation and -optimization*, respectively.

Concerning ultracold gases, the Bose–Einstein condensation (BEC) is one of the most striking quantum phenomena in nature [Gri95, Pit16]. While its theoretical prediction dates back almost one hundred years ago, it has more recently seen a revival of interest due to its realization in trapped gases [And95, Dav95]. The accurate study of BEC by theoretical and computational approaches particularly for systems with strong quantum correlations is rather challenging. This has been the reason why most studies of BEC so far were concerned with weakly interacting bosons (corresponding to the experimental situation for ultracold gases) or even ideal Bose gases, eventually allowing for feasible mean-field approaches. Prime examples are the Bogoliubov theory for uniform systems, Gross–Pitaevskii theory for general inhomogeneous systems, and perturbation theoretical approaches. Although these widely used approaches have led to a deeper understanding of BEC, their range of validity is limited.

Objectives

In the present dissertation, first, we recall the description of quantum systems, the tensor network methods (particularly the two-site DMRG), the formalism of identical particles and the conventional single-reference approaches in computational chemistry (particularly the CC method). Then the following objectives are set and investigated.

1. In quantum chemistry, one of the possibilities to effectively simulate strongly correlated systems is using externally corrected CC. That is, splitting of the full space into active space and external space to resolve the static and dynamical correlation, respectively. Computational advantages can be gained by the density matrix renormalization group tailored coupled cluster (DMRG-TCC) method restricted to single and double excitations, which was demonstrated on large and statically correlated systems [Vei16, Vei18]. However, the systematic analysis was still lacking. The key point investigated in this work is the strong dependence on the basis splitting of the DMRG-TCC solution, which was neglected in the performed mathematical analysis [Fau19a] since the explicit consideration of this dependence carries many mathematical challenges.
2. The choice of orbital set and the localization of orbitals are crucial in quantum chemistry. On the one hand, localization leads to chemically intuitive orbitals for rationalizing electronic structure of molecular systems. On the other hand, localization has proven to be useful in making the high-level correlated quantum chemical methods more tractable computationally [Pip89]. Optimal modes can lead to localization of the correlation and entanglement in the system [Fer14], so here we present an orbital optimization that is based on the entanglement localization. Also there are situations, for example, strongly open-shell systems, where the choice of a reference determinant becomes ambiguous, therefore, methods based on single-reference formulation (CC, DMRG-TCC) could potentially run into problems, and the choice of the reference is a bias in the method. Qualitatively we say that a many-body system is of multireference character if the single-reference methods fail. In this work we investigate *quantitatively* the multireference character via the tomography of the state, and the numerical details of the joint optimization discussed in the two-site DMRG framework. Although only the quantum chemistry application is studied here, this optimisation scheme is more general [Kru16, Kru21] and can be applicable also in solid-state and nuclear physics.
3. In general, the occurrence of the BEC also depends on the temperature and on the possible inhomogeneities or disorder, for example, due to the presence of an external field [Sac11], but in this work we restrict our discussion to the *interaction strength* and the *spatial dimensionality* affecting the presence of the BEC. At zero-temperature an interacting Bose gas exhibits two qualitatively different phases, a quasi-condensate in one dimension and a true Bose–Einstein condensate in three or higher dimensions. Therefore, it is of interest to search for a model which exhibits a transition (or a crossover) between these two phases, and in particular allows to check whether this special transition has common properties with general quantum phase transitions. We propose the *Hubbard wheel* lattice model of *hard-core bosons*, which exhibits a crossover between quasi-condensation and complete Bose–Einstein condensation. The model is studied both analytically and numerically, then a potential experimental realization is proposed.

New scientific results

1. We investigated the *coupled cluster tailored by tensor network state method* theoretically and numerically exemplified by the nitrogen dimer for different geometries. We perform a systematic study on the error of the method, in particular when the system become strongly correlated. We showed the strong dependence of the DMRG-TCC solution on the basis splitting. In order to minimize the energy error and carry out large-scale DMRG-TCCSD calculations, we developed a rigorous routine procedure to determine the optimal basis splitting. We show the robustness of the entropic quantities, which are the guides in determining the optimal basis splitting, with respect to the bond dimension.
   The publication belonging to this thesis statement is [1].

2. *Orbital optimization based on entanglement minimization* within the framework of tensor network state methods was studied and numerically exemplified by the nitrogen dimer for different geometries. The analysis, based on the tomography of the state, occupation numbers and entropic quantities, shows that the developed joint optimization procedure has the potential to compress the multireference character of the wave function. The orbital optimization provide significantly more optimal MOs for TNS methods.
   The publication belonging to this thesis statement is [3].

3. The *Hubbard wheel* lattice model of *hard-core bosons* was proposed and investigated theoretically and numerically. The tuning of just a single control parameter allows a crossover from one- to "infinite"-dimensionality, which also drives a transition from quasi-condensation to complete Bose–Einstein condensation. We showed that the mutual information possesses the qualitatively similar dependence on the control parameter as the number of the condensed bosons. We showed the existence of an excitation gap, which is usually highly demanding, and a possible experimental realization was also proposed.
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The publications are listed in chronological order.

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Further publications

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