Ph.D. thesis points

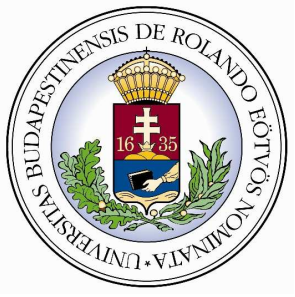
Nonlocal density matrix renormalization group applied to strongly correlated systems

Gergely Barcza

Adviser:
Örs Legeza
scientific adviser, D.Sc.

Eötvös University, Budapest
Physics Doctoral School
Material Science and Solid State Physics Program

Doctoral school leader: Prof. László Palla, D.Sc.
Program leader: Prof. János Lendvai, D.Sc.



Wigner Research Centre for Physics
Institute for Solid State Physics and Optics
Budapest
2014

Introduction

Interacting particles in condensed matter and molecular physics are described in terms of quantum mechanical equations. However, due to the exponential scaling of the problem with the system size, solving the Schrödinger equation for many particles is a major challenge in modern condensed matter physics. Any method to find the wave function of a quantum system will have to compromise between the demanded accuracy on the one hand and the computational complexity of the problem on the other. One of the main achievements of the previous century was the development of systematic perturbative approaches which gained overwhelming success to describe weakly interacting many-body systems. These methods have in common that the interactions between the particles are assumed to be weak so that the interactions can be treated as an averaged perturbative field and the system is effectively reduced to an ensemble of non-interacting entities. Nevertheless, there are numerous physical systems which lie out of the reach of this mean-field description and in which correlation effects cannot be neglected. These so-called 'strongly correlated' materials, including various transition metals, heavy fermion-compounds, colossal magnetoresistant manganites, and high temperature superconductors, prototypically exhibit open d- or f-electron shells with narrow energy bands and show versatile physical properties. Strong correlation effects are also decisive in strongly anisotropic materials and low dimensional interacting systems. In such systems, the constrained motion of the particles and the reduced screening results in significant effective interaction strength and increased quantum fluctuations due to the diminished Fermi surface. In these systems each particle influences significantly the behavior of its neighbors and their effect cannot be considered as an effective mean potential [Sóly09].

Entanglement is a fundamental property of multi-component quantum systems, corresponding to the quantum correlation between particles or collections of particles forming larger subsystems. This forms the basis of the successful density matrix renormalization group method [Whi92] (DMRG), which is nowadays the standard numerical approach suited to describe effectively low-dimensional interacting quantum systems of finite size with high precision. The thermodynamic properties of the physical system can be extrapolated performing careful finite-size scaling, while the error of the approximation is controlled by applying the dynamic block state selection method [Leg].

Investigated physical systems and applied methods

In the past decades a number of new types of materials have been synthesized in which atoms form a quasi-one-dimensional structure. As a consequence of their special geometry, they exhibit fascinating physical properties and promising potential as building blocks for electronics, spintronics, as well as optoelectronics. In fact, weakly interacting two-leg ladder type geometry is observed in various metal oxide materials, $La_4Sr_{10}Cu_{24}O_{41}$ and $CaCu_2O_3$. Several corner-sharing spin chain oxide materials, such as $SrCuO_2$ and Sr_2CuO_3, can be characterized by additional cross couplings. The competing interactions prevent magnetic order and these spin systems become frustrated and exhibit a plethora of interesting behavior. Moreover, a similar arrangement of bonds is observed in high-T_c cuprates possessing a two-dimensional square lattice formed of corner-sharing chains. Thus, such materials give not only experimental insights in to the fundamental physical phenomena specific to low-dimensional systems, i.e., Luttinger liquid behavior, spin-charge separation, Peierls instabilities, and one-dimension Mott insulating, but they can also help to understand the spectacular electronic properties of high-T_c superconductors drawing both theoretical and experimental attention [LCF06].

In my thesis, I investigated the spin-1/2 ladder system with rung and diagonal couplings which exhibits various topologically ordered insulating phases, such as the rung-singlet state, the columnar dimerized state and the Haldane state. My results are summarized in thesis points 1. and 2.

A special field where the theoretical predictions of quantum physics for strongly correlated electrons can be tested is polydiacetylene (PDA) which is an experimentally excellently characterized polymer. The strongly anisotropic organic PDAs exhibit a simple linear microstucture of monomers (C_4R_2) comprised of four carbon atoms and R is hydrogen or an alkyl group. There are a number of reasons why a computational and theoretical study of the electronic states of PDAs is both interesting and instructive. First, in common with all one-dimensional conjugated polymers, polydiacetylene exhibits a wealth of different kinds of excitations including polarons, bound polarons, and excitons. As the relative energetic ordering of these excitations determines the optical properties of the polymer, understanding the actual ordering can be an important predictive tool [Sch06]. Another important aspect of polydiacetylenes is that they can be related to nanotechnology. PDAs are promising candidates for universal nanometric transducers as they are known, for well-chosen side groups, to undergo drastic optical absorption and fluorescence changes under applied mechanical stress, light or heat exposure, pH change, or upon exposure to specific biochemicals making these polymers also attractive for bio- and chemosensing [WS12].

In the thesis, I studied the low-lying spectrum of poly-diacetylene chains by

DMRG simulations in order to reproduce available experimental data. These insulating materials can be understood by the behavior of the mobile π electrons. The effective long-range Coulomb interaction is described by the Hubbard-Ohno potential and the lattice distortion is treated in the adiabatic limit by the Peierls potential. The resulting model is characterized by the electron transfer amplitude t_0, the electron-phonon coupling constant α, the local Hubbard repulsion U, and the long-range interaction V. My results are discussed in thesis point 3.

The computation of the electronic structure is of utmost importance for molecular engineering in modern chemistry and material science. In this context, the accurate computation of the electron correlation is a fundamental and extremely difficult problem. Even though single-reference methods became dominant in the field of electronic structure calculations, there are some special areas where their accuracy is not satisfactory owing to their failure to describe electron correlation quantitatively. Such quantum chemical systems include open d and f shell molecules with a large number of unpaired electrons, as they occur in multiple transition metal complexes or in molecular magnets. Unfortunately, the applicability of highly accurate multi-reference calculations for such problems is limited to relatively small systems due to their high computational cost. Therefore, computationally less demanding new methods offering ways to accurately compute the electronic correlation are of high importance. In this respect, the DMRG combines a number of favorable features that suggest it might represent a novel, flexible approach in quantum chemistry: The more general concept of data-sparsity inherent in the DMRG representation allows for the efficient representation of a much bigger class of wave functions than accessible by state-of-the-art methods.

In the thesis, I analyzed the electronic structure of distinct isomers of $[Cu_2O_2]^{2+}$, e.g. the bis-oxygen-bridged cluster with broken O–O bond and the dioxygen binding peroxo isomer in terms of quantum information theory. In order to obtain the relative energy of the isomers efficiently, I employed various entropy based approaches in the DMRG calculations. The related results are detailed in thesis point 4.

The single but key feature shared by each studied interacting quantum system is that they fall into the category of strongly correlated systems. Therefore, one needs efficient numerical methods, like the DMRG, to simulate them with high accuracy. All DMRG computations were performed applying the BUDAPEST DMRG program [Leg] which is primarily developed and maintained by Örs Legeza. Nevertheless, I extended its applicability and functionality by developing several features for the code. All presented numerical results which are based on DMRG computations and the evaluation of the raw simulation data were performed by myself.

New scientific results and theses

In the following thesis points, I summarize my contribution to the distinct issues discussed in the previous section. The publications related to the thesis statements are enlisted in the following section.

1. I analyzed the numerical evidences for the possible existence of the columnar dimer phase proposed in several previous analytical and numerical studies for antiferromagnetic intraleg couplings. By keeping several thousand block states and studying significantly longer ladders compared to previous DMRG based studies, I demonstrated that the open problem is particularly sensitive to the numerical accuracy of DMRG calculations due to the criticality of the frustrated system. I showed that the numerical evidence, discussed in the literature [HS10], for the appearance of the dimerization was not unequivocal in light of my detailed analysis. Even though the possible appearance of a dimerized phase in the antiferromagnetic cross-coupled ladder cannot be completely ruled out, I set upper bound for the dimer order parameter that was significantly smaller compared to the results of the previous numerical studies [BLNS12].

2. I developed numerical tools to determine the mutual information for arbitrary quantum system where the distinct matrix elements of the two-site density matrix can be computed in an efficient parallel manner [BLNS14]. In particular, I applied the procedure to study the mutual information in the different phases of the frustrated spin-1/2 ladder system. Based on my computations, I observed a general tendency that the mutual information, combined of the one- and two-site entropy functions, decays twice as fast as the slowest decaying correlation function used to compose the two-site density matrix. I argued by analytical calculations that this property could be understood in terms of the logarithmic averaging applied in the definition of the two-site entropy, I also showed that this observation holds generally for arbitrary lattice models.

3. I investigated the low-lying spectrum of poly-diacetylene chains theoretically in order to reproduce available experimental data. Studying the Peierls–Hubbard-Ohno Hamiltonian using DMRG, I performed an optimization search over a broad regime of the four dimensional parameter space of (t_0, α, U, V) and determined the parameter set $(t_0^* = 2.4\,\mathrm{eV}, \alpha^* = 3.4\,\mathrm{eV/\AA}, U^* = 6\,\mathrm{eV}, V^* = 3\,\mathrm{eV})$ which reproduces the experimentally measured band gap, the energy of the singlet exciton, the triplet ground state, as well the optical excitation of the triplet ground state consistently. Moreover, I identified optically dark in-gap states in the singlet and triplet sectors and obtained the length of relaxed unit cell in agreement with experiments. My results are discussed in papers [BLGN10, BBGL13, BGL13].

4. Studying the electronic structure of dicopper complexes in terms of DMRG, my results indicate that the application of entropy based orbital ordering and initial configuration selection provides the possibility to perform DMRG calculations in a black-box manner and improves significantly the convergence of the DMRG calculations for quantum chemical problems. Besides investigating the relative energy of the isomers, I studied various entropy measures including the mutual information to identify highly entangled molecular orbitals. The determined entanglement profiles also helped us to understand the consequences for chemical bonding and for the structural transition of the isomers [BLMR11, BTBLR13].

Publications referred to in the PhD thesis

[BLGN10] G. Barcza, Ö. Legeza, F. Gebhard and R. M. Noack, *Density-matrix renormalization group study of excitons in poly-diacetylene chains*, Phys. Rev. B **81**, 045103 (2010) [arXiv:0908.4160]

[BLMR11] G. Barcza, Ö. Legeza, K. H. Marti and M. Reiher, *Quantum information analysis of electronic states at different molecular structures*, Phys. Rev. A **83**, 012508 (2011) [arXiv:1008.4607]

[BLNS12] G. Barcza, Ö. Legeza, R. M. Noack, and J. Sólyom, *The dimerized phase in the cross-coupled antiferromagnetic spin ladder*, Phys. Rev. B **86**, 075133 (2012) [arXiv:1104.3990]

[BBGL13] G. Barcza, W. Barford, F. Gebhard, and Ö. Legeza, *Singlet and triplet excited states in poly-diacetylene chains: A density-matrix renormalization group study*, Phys. Rev. B **87**, 245116 (2013) [arXiv:1303.2492]

[BGL13] G. Barcza, F. Gebhard, and Ö. Legeza, *Rigorous treatment of strong electronic correlations in poly-diacetylene chains*, Mol. Phys. **111** 16-17 (2013)

[BLNS14] G. Barcza, Ö. Legeza, R. M. Noack, and J. Sólyom, *Generalized correlation functions and entanglement patterns* (to be submitted)

[BTBLR13] K. Boguslawski, K. Tecmer, G. Barcza, Ö. Legeza, and M. Reiher, *Orbital entanglement in bond-formation processes*, J. Chem. Theor. Comp. **9**, 7 (2013) [arXiv:1303.7207]

Publications not related to the PhD thesis

[BSzLS12] G. Barcza, E. Szirmai, Ö. Legeza, and J. Sólyom, *Emergence of quintet superconductivity in the chain of partially polarized spin-3/2 ultracold atoms* Phys. Rev. A **86**, 061602(R) (2012) [arXiv:1201.3837]

[NBNLSz13] Cs. Nemes, G. Barcza, Z. Nagy, Ö. Legeza, and P. Szolgay, *Implementation trade-offs of the density matrix renormalization group algorithm on kilo-processor architectures*, ECCTD2013 proceedings (2013)

[NBNLSz13] Cs. Nemes, G. Barcza, Z. Nagy, Ö. Legeza, and P. Szolgay, *The density matrix renormalization group algorithm on kilo-processor architectures: implementation and trade-offs*, Computer Physics Communications **185**, 6 (2014) [arXiv:1309.5571]

Further references

[Sóly09] J. Sólyom, *Fundamentals of the Physics of Solids* I-III., Springer (2009).

[Whi92] S. R. White, Phys. Rev. Lett. **69**, 2863 (1992).

[LCF06] J. G. Lu, P. Chang, Z. Fan, Materials Science and Engineering (R) **52** 1-3 (2006).

[HS10] T. Hikihara and O. A. Starykh, Phys. Rev. B. **81**, 064432 (2010).

[Sch06] M. Schott, *Photophysics of molecular materials: from single molecules to single crystals*, ed. by G. Lanzani (Wiley-VCH, Weinheim, 2006).

[WS12] S. H. Won, and S. J. Sim, Analyst **137**, 5 (2012)

[Leg] Ö. Legeza, QC-DMRG-Budapest, A Program for Quantum Chemical DMRG Calculations. Copyright 2000–2013, HAS RISSPO Budapest