Final report on the European Research Area Chemistry
(Budapest-Vienna-Berlin-network)
administrated under grant number NN110360 in the OTKA system.

General overview: The main objective of the research was the development of the *generalized tensor network state method for quantum chemical systems* and further development of the *density matrix renormalization group method* (DMRG) using concepts of *quantum information theory* (QIT). Therefore, one of our aims was to develop the very first tree-tensor network state (TTNS) algorithm with variable order, and to apply it to quantum chemical systems (QC-TTNS). In order to achieve such final aim, the project has been decomposed into several partial tasks, distributed among the three nodes of the research network. These included among others the development of the mathematical framework of the TTNS method, implementation of the algorithmic solutions, and performing numerical simulations. Since the TTNS inherits various algorithmic solutions developed in the DMRG framework, first we have developed and tested these using our existing DMRG code. In addition, as a byproduct of our developments, several features could have been generalized and applied not only in quantum chemistry but also in *strongly correlated condensed matter* and *ultra cold atomic systems*, and in *nuclear structure theory*. As a short remark on the novelty of our pilot project, we would like mention that, at the time when our proposal was submitted in 2012, there existed only one publication in the field of QCTTNS (Murg, Verstraete, Legeza, Noack, Phys. Rev. B 82, 2010), and even at present there are only four works out of which three are devoted to our attempts. The latter two has received more than 14 and 40 citations within two years and these numbers have increased drastically this year. In addition, our paper on nuclear shell model DMRG provides state-of-the-art solution for the largest systems that can be studied by Monte Carlo shell models, and it is expected to outperform standard methods based on the favorable polynomial scaling of the method.

The original project plan was designed for three years, but we have asked for one year of extension in order to use the available budget more efficiently, and to finance additional subprojects. Fortunately, many groups expressed their interest to collaborate with us on the national and also on the international level. This has stimulated new collaborations and submission of new research proposals in Germany, Poland, Czech Republic and Canada. At present, our codes are used by some fifteen research groups worldwide, and within the four-year time period we have had 32 publications, presented more than 15 invited talks at international conferences, and developed three code structures. Even though the funding period is over, we are continuously working on the project, and as an example new PhD students of Prof. Verstraete and Prof. van Neck (Vienna, Ghent) and students of Prof. Noack (Marburg) have spent a month in September in Budapest, further developing the TTNS algorithm. As a recent result, the speed of the new code has been increased by a factor of ten. Within the scope of the ERA-Chemistry, Dr. Libor Veis from Prague has spent eight months at our group, and the whole group of Prof. Pittner (Prague) has joined the DMRG and TTNS developments bringing a new impetus to the TNS developments by cross fertilization of DMRG/TTNS with *tailored coupled cluster method*. Our novel method, the DMRG-CCSDT is currently one of the most efficient method to treat strongly correlated molecular systems. Such new approach has a great interest within the mathematical community as well and currently together with Prof. Schneider (Berlin) a rigorous mathematical analysis of the DMRG-TCCSD is under progress. Based on our achievements, the TNS (DMRG) is planned to be migrated into the NWChem professional program package built on its massively parallelized tensor library, therefore, the PI (Legeza) has been invited to the Pacific Northwest National Laboratory (PNNL, WA, USA) to work out a long term collaboration for such development tasks.

Unfortunately, after the second year of the funding period, Dr. Valentin Murg has left science and found a job in the industry due to family related and financial reasons. Since major code developments were done by Dr. Murg in the QC-TTNS code, we had to find a replacement of him, which took us more than a year. Although the PI (Legeza) had a thorough knowledge of the QC-TTNS code structure, as developments were carried out by both of them, new students and postdocs had to learn the details of the theory and implementations. Currently, Klaas Gunst PhD student from Ghent, Markus Scheb PhD student from Marburg, and Mihály Máté PhD student from Budapest are working on the project. Our former PhD student (Máté Timár) working on the project has also left science due to financial reasons, and found a job as a programmer at an IT-company. On the other hand, Dr. Libor Veis has submitted a grant proposal on the field on the national level in the Czech Republic, and a five node grant application (Berlin, Budapest, Ghent, Marburg, Prague) has already been prepared.

In the research proposal, subtasks assigned to the Budapest group has been indicated as “BUD”. In what follows, we will briefly summarize our main achievements presented in a chronological order in order to show how the research has been carried out. We focus on code developments and results of the 40 publications are not discussed, in order to provide a coherent report. (Vienna and Berlin groups are indicated by “VIE” and “BER”.)

Workshops and scientific visits: We have organized an international workshop in the Max Planck Institute, Dresden (MPIPKS) “*Entanglement based approaches in quantum chemistry* (EBAQC-2012)”, an international winter school “*New wave function methods and entanglement optimizations in quantum chemistry*”, at Mariapfarr Austria (2014), two mini workshops in Budapest in the spring of 2014 and 2015. Among the three nodes of the ERA network, we organized some three-four scientific visits annually, and new collaborating partners have also spent several weeks in our institute.

Book chapters and review articles: We have written two book chapters (BUD,BER) on the field (Legeza, Rohwedder, Schneider, Szalay, *Tensor Product Approximation (DMRG) and Coupled Cluster Method in Quantum Chemistry* In: Bach, Delle Site (Eds.), Many-Electron Approaches in Physics, Chemistry and Mathematics, Heidelberg: Springer International Publishing, 2014. pp. 53-76; Legeza, Rohwedder, Schneider, *Numerical approaches for high-dimensional PDE's for quantum chemistry* In: Engquist, Chan, Cook, Hairer, Hastad, Iserles, Langtangen, Le Bris, Lions, Lubich, Majda, McLaughlin, Nieminen, Oden, Souganidis, Tveito (Eds.) Encyclopedia of Applied and Computational Mathematics, Berlin: Springer Verlag, 2013. ISBN:978-3-540-70530-7). We have also written a 110 pages tutorial review (BUD,VIE,BER), which is the most comprehensive work on the field at present, including the detailed discussion of the mathematical framework of tensor product factorization, description of the QC-TTNS and QC-DMRG methods, and practical guides on the various optimization methods to be performed in order to carry out numerical simulations efficiently (Szalay, Pfeffer, Murg, Barcza, Verstraete, Schneider, Legeza, *Tensor product methods and entanglement optimization for ab initio quantum chemistry*, International Journal of Quantum Chemistry 115:(19) pp. 1342-1391 (2015)).

Code developments: We have developed a tree-TNS code for ab initio quantum chemistry (QC-TTNS) with variable tensor order. This means that tensors assigned to each molecular orbital can have arbitrary number of legs (arbitrary order), thus the network structure can be optimized according to the entanglement/correlation pattern of the given chemical complex. This work included several subtasks to be solved. First, similarly to the DMRG method, we had to develop an efficient factorization of the operators distributed among the various tensor spaces (subsystems). In the research plan this was indicated as “partial summation of operators” (BUD,VIE). In case of fermions, the proper treatment of the phase factors due to the anticommutation of fermionic operators had to be worked out as there is no such natural ordering of tensors in case of TTNS as in case of DMRG (BUD,VIE). Several features of our highly optimized DMRG code has been transferred to the QC-TTNS code step-by-step, making it more efficient (BUD,VIE). Unfortunately, the highly general TTNS requires a lot of further optimization tasks, thus it is still slower than our DMRG code, however, its scaling behavior could have already been tested, as shown in: Murg, Verstraete, Schneider, Nagy, Legeza, *Tree tensor network state with variable tensor order: An efficient multireference method for strongly correlated systems,* Journal of Chemical Theory and Computation 11:(3) pp. 1027-1036 (2015).

The QC-TTNS code has been developed in a similar structure as the QC-DMRG code, i.e., it contains a model dependent initialization part to define the given Hamiltonian of the problem, and a model-independent algorithmic part to carry out the numerical solution of the eigenvalue problem. Therefore, the QC-TTNS could be used not only in quantum chemistry but also in other fields building on recent DMRG developments as given below.

We were the first to develop the relativistic version of the DMRG code, named as 4c-DMRG, and demonstrated its power on the TlH molecule (BUD): Knecht, Legeza, Reiher, J. Chem. Phys. 140 041101 (2014). Currently, the group of Dr. Pawel Tecmer and Dr. Katharina Boguslawski in Poland are carrying out their research using our code developments. In addition, together with Prof. Pittner, a combination of the 4c-DMRG with CC is is under progress, in order to develop the relativistic version of the DMRG-TCCSD method.

We were the first to develop the quantum information based nuclear structure version of the DMRG code. We have reported the first DMRG results in the *pf*+*g*9/2 shell model space for the ground 0+ and first 2+ states of 64Ge, which were benchmarked with reference data obtained from Monte Carlo shell model. Our work is the state-of-the art DMRG in the field, reaching the capability of the Monte Carlo calculations: Legeza, Veis, Poves, Dukelsky, Phys. Rev. C 92, 051303 (2015). We have also found that in these problems the proton and neutron orbitals are highly entangled and many orbitals have maximum entropy. Therefore, a more general network would be very favorable, thus similar developments in the framework of the QC-TTNS is part of our current research.

We have developed an unrestricted version of the DMRG (UHF-QCDMRG)by generalizing the Hamiltonian and the related factorization of the various interaction terms. Application of the method is under progress, and similar generalization of the QC-TTNS is straightforward.

Network optimization by quantum information theory: We have further developed our optimization protocols based on quantum information theory (QIT). The structure of the tensor network significantly influences the efficiency and accuracy of the calculations, therefore, optimization of the network is a crucial task. We have developed an iterative procedure (BUD,VIE) to optimize the TTNS network. First we start calculations from an energetic ordering of orbitals using the DMRG framework (z=2 TTNS) with low bond dimension. Next we determine optimized ordering using quantum information entropies and we repeat this procedure a couple of times systematically increasing the bond dimension. Once a reasonable convergence is reached, we determine the two-orbital mutual information and design our TTNS network according to such correlation pattern by placing the highly correlated clusters in the center of the network. The success of this protocol we have demonstrated in JCTC 11:(3) 1027 (2015).

Optimization of the sweeping in QC-TTNS: TNS methods are local optimization methods, thus one has to sweep through the network several times. In case of DMRG such sweeping path is trivial due to the one-dimensional topology. Contrast to this, in QC-TTNS there is a freedom how to sweep through the network. We have tried various schemes (VIE,BUD), and based on our network structure optimization (see above) we have found a general rule that provides quasi-optimal solution: we start from the center and sweep through the network until the edge is reached. Next we go back to the closest branching point and sweep again toward the edge. By this way orbitals lying closer to the center are traversed several times in a full sweep, so their contribution is taken into account more rigorously: JCTC 11:(3) 1027 (2015).

Optimization of basis: Tensor network states and specifically matrix-product states have proven to be a powerful tool for simulating ground states of strongly correlated spin models. A new freedom arising in non-local fermionic systems (quantum chemistry) is the choice of orbitals, it being far from clear what choice of fermionic orbitals to make. We have proposed a way to overcome this challenge. We have 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: Krumnow, Veis, Legeza, Eisert, Phys. Rev. Lett. 117, 210402 (2016).

Parallelizations: In the numerical analysis of strongly correlated quantum lattice models and in quantum chemistry, one of the leading algorithms developed to balance the size of the effective Hilbert space and the accuracy of the simulation is the TNS algorithm. In these methods, the run-time is dominated by the iterative diagonalization of the Hamilton operator. As the most time-dominant step of the diagonalization can be expressed as a list of dense matrix operations, the TTNS/DMRG is an appealing candidate to fully utilize the computing power residing in novel kilo-processor architectures. We have developed a smart hybrid CPU-GPU implementation, which exploits the power of both CPU and GPU, and tolerates problems exceeding the GPU memory size. Furthermore, a new CUDA kernel has been designed for asymmetric matrix-vector multiplication to accelerate the rest of the diagonalization. Besides the evaluation of the GPU implementation, the practical limits of an FPGA implementation are also discussed. In such pilot project power of our parallelization has been presented for Heisenberg and Hubbard-like Hamiltonians, and migration of the related C++ kernel into the QC-DMRG and QC-TTNS is still in progress. As an intermediate step, using shared memory parallelization features of BLAS and LAPACK we have developed a slightly modified C++ CPU based kernel which is already part of the QC-DMRG code and will be migrated into the QC-TTNS code as well. Extension of such parallelization strategies building on the massively parallelized tensor library structure of the NWChem software is under progress.

TTNO framework: Our QC-TTNS code has been developed in the framework of precontracted (renormalized) operators but an alternative solution based on tensor network operator framework has also been considered and outlined in our review. Similar developments are under progress in a collaboration with the group of Prof. Noack (Marburg).

Symmetries: We have further developed the treatment of symmetries and included non-Abelian symmetries in the QC-DMRG framework as well (BUD). Extension of this task in the case of TTNS is far more complicated and it is part of our current collaboration with Prof. Verstraete (Ghent) and Prof. Zaránd (Budapest).

Post DMRG/TNS methods: TNS methods are very efficient to pick up the so-called static correlations but they require the treatment of the full orbital space with large number of sweepings to recover the dynamic correlations. Standard methods like CC, on the other hand, are very efficient to recover dynamic correlations. Therefore, an ideal strategy is to combine the two methods. In collaboration, with Prof. Pittner, we have interfaced our DMRG code with the ORCA code (Prof. Neese) and developed the novel DMRG-TCCSD method. The main idea is that orbital space is split into two parts by using quantum information entropy measures, and the smaller active space which included highly correlated orbitals are solved by the DMRG method. From the MPS wave function given by the DMRG method, the coefficients of the single and double excitations are determined, and the CC amplitudes are calculated and given as an input to the CC code to solve the original full orbital space. As a result, the dynamic correlations lost by the DMRG are recovered, and very accurate calculations can be carried out in a fraction of computational time and resources: Veis, Antalik, Neese, Legeza, Pittner, *Coupled cluster method with single and double excitations tailored by matrix product state wave functions*, Journal of Physical Chemistry Letters, 7 (20) 4072-4078 (2016). This allows us to increase the capability of the DMRG tremendously, and the procedure can directly be migrated into the QC-TTNS method building on the TTNS wave function.

Graphical user interface: TNS methods are still in development stage, and to perform efficient calculations requires a lot of knowledge. In order to make these methods useful on the daily basis, much of the technical settings/details must be hidden, so that users could use the methods without going into too much technical details. Therefore, we have collected general rules and strategies to set parameters of TNS and also provided a graphical user interface (GUI). Our GUI is written in a general framework, so it can be extended easily. At present, DMRG and TTNS, and QIT-based utilities are accessible, but other codes can be migrated as well. Thus users can click-and-run, and set the required inputs in integrated user interface.

Application of quantum information theory: Our code developments and novel protocols based on QIT have been applied to various chemical complexes, strongly correlated condensed matter and ultracold atomic systems, and in nuclear structure theory. In the QC framework we aimed to determine how the information/correlation is distributed, according to QIT in molecules. Rigorous analysis of the fundamental quantities of QIT on systematic series of molecules offered the introduction of the concept of chemical bond and aromaticity directly from physical principles and notions. We have identified covalent bond, donor-acceptor dative bond, multiple bond, charge-shift bond, and aromaticity indicating unified picture of fundamental chemical models from ab initio. In addition, for 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 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: Szalay, Barcza, Szilvási, Veis, Legeza, *The correlation theory of the chemical bond*, Scientific Reports 7, 2237 (2017).