New electron correlation theories and haptic exploration of molecular systems

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New Electron Correlation
Theories and Haptic Exploration
of Molecular Systems

A dissertation submitted to

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DOCTOR OF SCIENCES

presented by
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I. Abstract

In transition metal catalysis, the precise characterization of the relative energies is of paramount importance. In particular, it is still a challenging task to predict energy differences between states of different spin accurately using a wide variety of modern standard quantum chemical methods. For the calculation of relevant transition metal catalysts one is limited to the application of broken-symmetry DFT since other methods are hardly feasible. However, broken-symmetry DFT often exhibits deficiencies in accuracy — apart from conceptual difficulties. In multi-configuration methods, on the other hand, one usually needs a large (often prohibitively large) active space for a qualitatively correct description of the electronic structure. This is highlighted especially in binuclear or polynuclear transition metal compounds. The density matrix renormalization group (DMRG) algorithm allows for the treatment of a large active space which is by far not reachable using standard \textit{ab initio} quantum chemical methods. We investigate the DMRG algorithm as a substitute for CASSCF in cases where CASSCF fails to produce a qualitatively correct electronic structure, i.e., where the required active space is larger than 18 electrons in 18 spatial orbitals.

The encouraging results of the DMRG algorithm for complicated molecular electronic structure theory stimulated further research in this direction. We describe how the concept of quantum information entropy can efficiently be exploited and cast into an algorithm which aims to improve the convergence of the DMRG optimization. The entropy-based DMRG algorithm takes an important step towards DMRG calculations in a black-box fashion. Moreover, the DMRG algorithm implicitly constructs a matrix product state (MPS) which is the simplest one-dimensional tensor network state. The efficiency of the DMRG algorithm primarily lies in the nature of its underlying wave function which does not depend on an explicit expansion in terms of Slater determinants.

Based on the numerical evidence compiled in our DMRG studies, tensor network states have the potential to largely improve the standard methods of quantum chemistry by circumventing the factorial scaling bottleneck of current multi-reference approaches. The idea is to develop a tensor network state that captures electron correlation naturally by its design. We propose a new fermionic tensor network ansatz for molecular systems: The complete-graph tensor network (CGTN) states. We discuss its variational optimization by means of a Monte Carlo scheme using replica exchanges to prevent convergence to local minima. The CGTN states are employed to describe spin splitting in methylene and ozone, as well as the high-spin ground state of a transition metal compound.
The CGTN and MPS ansätze provide the theoretical framework to describe spin states of molecular systems and especially of transition metal containing compounds qualitatively and quantitatively correct which allows for the construction of accurate potential energy surfaces within the Born–Oppenheimer approximation. For the construction of the high-dimensional hypersurfaces the interpolation-moving least-squares (IMLS) method has been utilized and extended to an efficient and automated procedures for sampling the relevant and chemically interesting region of the energy surface. We also show how a minimum-energy path can be computed and how a structure optimization can be performed on an IMLS constructed surface. Furthermore, the localization of minimum-energy crossing points between two hypersurfaces of quantum states of different spin multiplicity has been implemented and discussed for the phenylcation. Finally, we present a new way of analyzing potential energy surfaces of chemical reaction mechanisms by means of a haptic exploration. The haptic methodology is shown to allow chemists to physically experience the quantum mechanical forces acting on reactants, to actively influence the chemical reaction, and to probe different reaction channels which are not accessible by conventional molecular dynamics simulations without employing additional methods like local elevation. The haptic machinery is demonstrated at the example of the protonation of a water molecule.
II. Zusammenfassung


beschreiben.


III. Acknowledgements

To survive a war, you gotta become war.
That why they pick you? Because you like to fight?
Nah... I’m expendable.
Expendable... What mean expendable?
It’s like... someone... invites you to a party, and you
don’t show up; it doesn’t really matter.

Co Bao and John Rambo

I am very grateful to Prof. Dr. Markus Reiher for supervising my PhD. He always showed enormous interest in my ideas, suggestions, and projects and supported me in every possible aspect with his extensive knowledge. He taught me that persistence, endurance, and creativity in scientific projects ensures success in the end. Especially when I had thousands of thrilling but digressing ideas, he helped me to focus on the important and relevant part of my work. He was not just a caring and thoughtful supervisor and mentor but also a true friend.

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The initial seed to the tensor network state project was planted by Prof. Dr. Frank Verstraete during the workshop of numerical approaches to quantum many-body problems at UCLA whom I owe many thanks for sharing his ideas with me. The discussions with physicist have been a great source of knowledge and experience and have helped me gain a deeper understanding of the concept behind tensor network states. I am thus deeply indebted to Bela Bauer with whom I implemented the variational optimization algorithm for the CGTN states.

The work on combining DMRG and quantum information theory would have never been possible without the initiative and know-how of Prof. Dr. ¨Ors Legeza and Gergeley Barcza whom I am also very thankful for the invitation to Marburg.

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Of most importance to me was the constant support by Jasmin, my three sisters Andrea, Bettina, and Marie-Louise and by my parents throughout my thesis.
1. **Relevance of electronic structure theory to chemistry**

Molecular electronic structure theory has gained momentum and influence in all branches of chemistry over the last decades [1, 2]. Physical chemists apply quantum mechanics for example to calculate thermodynamic properties, to assign vibrational bands in complicated spectra, or to estimate rate constants of chemical reactions by locating transition states. Organic chemists can gain insight into what happens in their flasks on a molecular level by estimating the relative stability of educts and products, calculating properties of intermediate species, investigating reaction mechanisms, and analyzing NMR spectra. Analytical chemists benefit from the ability of quantum mechanics to predict the frequencies and intensities of lines in spectra, which is most helpful for the interpretation of them. Inorganic chemists can now study and design catalytic processes *in silico*. This list is by far not complete. The importance of electronic structure theory will further grow as a consequence of developments that enlarge the realm of applicability of highly sophisticated and accurate quantum chemical methods to large molecules such as biomolecules, transition metal containing catalysts, and molecular magnets.

1.1 **Computational challenges in transition metal chemistry**

Quantum chemistry meets one of its greatest challenges in the field of transition-metal compounds [3]. The description of the electronic structure of transition metal complexes and clusters on the basis of the first principles of quantum mechanics is still an involved and difficult task in theoretical chemistry [4]. Such quantum chemical calculations without resorting to empirical data are the basis of any truly predictive theoretical attempt to predict molecular structures, molecular properties, as well as reactions mediated by transition metal complexes. The starting point of such an endeavor is the accurate solution of the electronic Schrödinger equation for a given molecular structure to obtain the electronic wave function [5, 6]. It was soon realized that this was and still is a very difficult task, and semi-quantitative descriptions based on ligand-field-like or semi-empirical theories have never faded away but are alive and kicking [7–14].
At the beginning of the 1990s, the situation seemed to change with the advent of gradient-corrected density functionals that became readily available in standard quantum chemistry packages like GAUSSIAN [15]. The reason for this is the fact that — based on sound density functional theory (DFT) — density functional calculations are usually implemented in the framework invented by Kohn and Sham which is very similar to Hartree–Fock theory [16]. Approximate density functionals had put computational chemists into a position to routinely carry out structure optimizations for complexes [17] whose structure had not to be compromised by simplification of ligands for feasibility reasons. Also, the total electronic energies obtained turned out to be quite accurate for the calculation of reaction energies, although the total electronic DFT energy calculated with an approximate density functional can deviate significantly from the exact total electronic energy because of empirical parameters in the functional approximation.

After the first gold rush of DFT-based studies in coordination chemistry [18–24], which even enabled experimentalists to study the complexes synthesized in the laboratory on a routine basis, deficiencies of approximate gradient-corrected density functionals became evident. One such example is the calculation of the energy splitting of states of different spin, e.g., the energy difference between low- and high-spin complexes [25]. At about the same time, Reiher et al. found [26, 27] that this energy splitting depends linearly on the admixture of Hartree–Fock-type exchange, so-called exact exchange, in hybrid density functionals, an invention of Becke in 1993 [28, 29]. It was this linear dependence that turned out to make the major difference in spin splitting calculations with at that time existing density functional approximations, so general that these authors conducted a systematic investigation [30], which confirmed the general validity and led to the ℠-terminology with 5%-reduced exact exchange admixture (e.g., B3LYP™). Variants have then been studied in detail by Harvey [31], and this insight found also its way into some of the most recent density functional parametrizations like the M06-L functional [32].

Although insights into terms of the functional are of decisive importance for the accuracy of calculated observables, the available density functional approximations still carry uncertainties. Only statistical knowledge is available on the performance of functionals for a certain test set of molecular data. Often, the accuracy is remarkable, but uncertainties of calculated DFT results on molecules outside such test sets remain. If there are indications, e.g., from experiment, that DFT results are not sufficiently accurate, we have no means to improve on them in a systematic manner. It would be helpful if reliable reference data could be generated for at least one specimen of a class of molecules. It is not even possible to assess the error of a particular calculation on some observable. For this reason, systematically improvable, but feasible ab initio methods are still sought.

In general, coupled-cluster (CC) methods have turned out to be very reliable [33]. However, the standard coupled-cluster approach is built upon a closed-shell ref-
1.2 Overview

This work is organized as follows: In chapter 2, the fundamentals of quantum mechanics with an emphasis on the important concepts in quantum chemistry are introduced. After the theoretical basis has been laid, we proceed to discuss the basic ingredients of the density matrix renormalization group (DMRG) algorithm with its underlying analytic wave function which is composed of two MPS in chapter 3. We present its advantages and disadvantages in the application to molecular systems, and provide illustrative results accentuating the potential of DMRG to treat large active spaces that are far from the capabilities of traditional CASSCF approaches. In chapter 4, we elaborate on tensor network states. We also highlight the benefit of taking results from quantum information theory into account for the design of new classes of variational states which are tailored to capture the entanglement present in molecular systems. Based on these findings, we propose a particular type of tensor network states, the complete-graph tensor network states, in chapter 5. For a sound analysis of these states, we also show how the entanglement is localized during the variational
optimization in terms of multiple quantum channels. The numerical results of this new ansatz on the spin splitting of two different electronic states with a different spin multiplicity then lead to the development of a hybrid approach where the principles of configuration interaction theory and the idea of tensor networks states are combined. In chapter 6, we review the concept of multi-state reactivity and point out its primary obstacle which is the quest of obtaining accurate relative energies either between two structures on the same potential energy surface or between two spin states. We demonstrate that the DMRG method and especially the tensor network approaches such as the matrix product and the complete-graph tensor network states provide accurate relative energies for molecular systems where DFT and CASSCF fail. We have then implemented algorithms that allow for the exploration of the potential energy surface. The potential energy surface is represented as a set of discrete points which need to be connected by interpolation to provide a continuous surface. For this endeavor, we select the IMLS method which implicitly contains an error facility that enables us to improve regions of the surface that are not yet accurately represented. Moreover, the potential energy surface can also be explored directly by means of the haptic technology for quantum chemistry developed in chapter 7. We present a first haptic quantum chemical study on the protonation of water where a chemist can direct the protonation reaction guided by her/his perception of the forces acting on the approaching proton.
2. Quantum chemistry — A quantum theory for molecules

In the late seventeenth century, Isaac Newton formulated the laws of motion of macroscopic objects which we know as classical mechanics. In the early twentieth century, however, physicists realized that many phenomena arising from the interaction of light and matter cannot be accurately described or explained with classical mechanics. The correct behavior and description of very small particles such as the electrons and nuclei of atoms and molecules can be predicted by quantum mechanics. In Schrödinger quantum mechanics, the observables are represented by operators that are constructed by the correspondence principle from classical mechanics. The application of quantum mechanics to problems in chemistry is known as quantum chemistry.

2.1 Electronic problem in quantum chemistry: A small step for electrons, a giant leap for theoretical chemists

The electronic problem refers to the mathematical difficulty in describing the motion of electrons interacting through the Coulomb force in the field of fixed nuclear point charges. The electron–electron repulsion term introduces correlations among all electrons.

The full non-relativistic time-independent Schrödinger equation for an N-electron system of M nuclei in the electronic state $A$ is written as

$$\hat{H} |\Phi_{A}^{(N)}(r,R)\rangle = E_{A} |\Phi_{A}^{(N)}(r,R)\rangle$$

(2.1)

and the Hamiltonian operator in Hartree atomic units (\(\hbar = m_{e} = e = 4\pi\varepsilon_{0} = 1\)) is given in first quantization as

$$\hat{H} = -\sum_{i=1}^{N} \frac{1}{2} \nabla_{i}^{2} - \sum_{A=1}^{M} \frac{1}{2M_{A}} \nabla_{A}^{2} - \sum_{i=1}^{N} Z_{A} \frac{1}{r_{iA}} + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{r_{ij}} + \sum_{A=1}^{M} \sum_{B>A}^{M} \frac{Z_{A}Z_{B}}{R_{AB}}$$

(2.2)

in a molecular coordinate system where the indices $i$ and $j$ are running over the set of $N$ electrons and $A$ and $B$ over the set of $M$ nuclei [64]. The distances $r_{iA}$, $r_{ij}$, and $R_{AB}$ are the absolute values of the difference vector between either the position of the electrons or nuclei in the frame of the chosen molecular coordinate system. The Laplacian operators $\nabla_{i}^{2}$ and $\nabla_{A}^{2}$ differentiate the coordinates of the $i$th electron and the $A$th nucleus, respectively. The wave function $\Phi_{A}^{(N)}$
is an eigenstate of the Hamiltonian operator and describes a specific quantum mechanical state \( A \) of the molecular system as a function of \( N \)-electronic and \( M \)-nuclear coordinates, abbreviated as \( r \) and \( R \).

Since the Hamiltonian operator in Eq. (2.2) is constructed from the correspondence principle, each of its terms has a classical counterpart. The first term describes the kinetic energy of the electrons; the second, the kinetic energy of the nuclei. The third term stands for the Coulomb attraction between the negatively charged electrons and the positively charged nuclei, whereas the last two terms represent the Coulombic repulsion between pairs of electrons and between pairs of nuclei, respectively.

When analyzing the numerical values of the terms in the full non-relativistic time-independent Hamiltonian operator (Eq. (2.2)), one realizes that the kinetic energy of the electrons is much larger than the kinetic energy of the nuclei due to the mass difference. In the case of the hydrogen atom, the rest mass for the nucleus is about 1836 times heavier than the rest mass of the electron. In an approximate picture, the electrons adiabatically follow the nuclear displacements of the molecule; thus they can be seen as moving in the field of fixed nuclei. Hence we can separate the kinetic energy operator of the nuclei in the full Hamiltonian operator, and the nuclear repulsion terms can be considered constant. This adiabatic approximation for the separation of the nuclear and electronic degrees of freedom yields the Born–Oppenheimer approximation. The Born–Oppenheimer approximation states that the total wave function can be written as product of a function of the nuclear coordinates and a function of the electronic coordinates where the nuclear coordinates enter as parameters.

Within this approximation, we define the electronic Hamiltonian as,

\[
\hat{H}_{\text{elec}} = -\sum_{i=1}^{N} \frac{1}{2} \nabla_i^2 - \sum_{i=1}^{N} \sum_{A=1}^{M} \frac{Z_A}{r_{iA}} + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{r_{ij}} + \sum_{A=1}^{M} \sum_{B>A}^{M} \frac{Z_A Z_B}{R_{AB}}.
\]  

(2.3)

The solution of the electronic Schrödinger equation,

\[
\hat{H}_{\text{elec}} |\Psi_{A}^{(N)}\rangle = E_{\text{elec}} |\Psi_{A}^{(N)}\rangle,
\]  

(2.4)

employing the electronic Hamiltonian is the electronic wave function,

\[
|\Psi_{A}^{(N)}\rangle = |\Psi_{A}^{(N)}(\{r\}; \{R\})\rangle
\]  

(2.5)

which depends parametrically on the nuclear coordinates. This parametric dependence of the electronic wave function affects the electronic energy which is expressed as a function of the nuclear coordinates:

\[
E_{\text{corr}}^{A} = E_{\text{corr}}^{A}(\{R\}).
\]  

(2.6)

As a consequence, the Born–Oppenheimer approximation introduces the notion of potential energy surfaces, as functions of nuclear coordinates for a given
2.1. Electronic problem in quantum chemistry

Electronic state \( A \). In Figure 2.1, an example of a projection of a potential energy surface onto two of its degrees of freedom is shown.

Figure 2.1: A pictorial representation of the singlet potential energy surface (PES) for the substitution reaction of \( \text{NH}_2\text{Cl} + \text{Cl}^- \). The substitution mechanism is schematically shown for one point on the reaction surface in panel (a). A projection of the electronic ground-state PES as a function of the two bond distances in Å between the nitrogen atom and the chloride atoms, Cl1 and Cl2, is given in (b). The Cl1-N-Cl2 angle of 131.4 degrees and the nitrogen–hydrogen bonds of 1.02779 Å were kept fix. The ammonium chloride structure was previously optimized with BP86/def-TZVP using TURBOMOLE [65].

![Figure 2.1: A pictorial representation of the singlet potential energy surface (PES) for the substitution reaction of \( \text{NH}_2\text{Cl} + \text{Cl}^- \).](image)

The nuclear Schrödinger equation describes how the nuclei move on the potential energy surface obtained by previously solving the electronic problem. This statement is a qualitative interpretation of the Born–Oppenheimer approximation. A mathematically more rigorous discussion of this topic can be found, e.g., in the work of Sutcliffe [66].

From a mathematical point of view, the calculation of the electronic structure corresponds to solving the full non-relativistic time-independent Schrödinger equation defined in Eq. (2.4). The solution of this seemingly intractable model of correlated electrons is one of the central issues in quantum chemistry and the most important concern of this work. Note that the structure of the Hamiltonian is completely known [67]. The many-electron wave function, on the other hand, provides ample room for approximations to the Schrödinger equation. The form of the wave function and its variational optimization have been and still are the key quantities for the development of efficient electronic-structure methods.
2.2 Exact and approximate many-electron wave functions

The essential technique employed by all quantum chemical methods to calculate a many-electron wave function is the expansion into a suitable set of basis functions. Of course, two different basis sets are required. The quantum mechanical \( N \)-electron state is expanded into a set of \( N \)-electron basis functions (e.g., Slater determinants or configuration state functions). However, these \( N \)-electron basis functions need to be constructed themselves. They can be set up from a Hartree product of one-electron functions antisymmetrized with respect to pair permutations of any two electronic coordinates in order to fulfill the Pauli exclusion principle [68, 69]. The distribution of \( N \) electrons over a given number of one-electron states scales factorially. In electronic-structure theory, this factorial scaling in the dimension of the Hilbert space with system size poses the biggest challenge in the exact description of strongly correlated systems of electrons.

2.2.1 Constructing Slater determinants from spin or spatial orbitals

**Pauli exclusion principle**

Using the fine structure of atomic spectra, Uhlenbeck and Goudsmit [70, 71] showed in 1926 that electrons possess an intrinsic angular momentum called spin which has no classical counterpart. The electronic Hamiltonian as defined in Eq. (2.3) only depends on the spatial coordinates of the electrons. Hence the spin must be additionally specified. Note that this requirement comes from the deficiencies of Schrödinger’s quantum mechanics. In Dirac’s relativistic quantum theory of the electron, the spin naturally arises by means of the Pauli spin matrices [67]. Hence, to completely describe an electron in the context of the non-relativistic quantum theory we introduce two spin functions, \( \alpha(\omega) \) and \( \beta(\omega) \), which represent a spin-up and spin-down state, respectively, where \( \omega \) stands for a spin coordinate [64]. We further assume that the set of these functions are complete and that they are orthonormal. The state of an electron is now completely characterized by its spatial position \( \mathbf{r} \) and its spin coordinate \( \omega \). These four coordinate are collectively denoted by \( \mathbf{x} \),

\[
\mathbf{x} = \{\mathbf{r}, \omega\}. \tag{2.7}
\]

A wave function \( \Psi \) of an \( N \)-electron system is thus a function of the \( x_1, x_2, \ldots, x_N \) coordinates written as \( \Psi^{(N)}(x_1, x_2, \ldots, x_N) \). The exact \( N \)-electron wave function is not only an eigenstate of the electronic Hamiltonian, but also fulfills the antisymmetry requirement, a manifestation of the Pauli exclusion principle. This antisymmetry requirement applies to wave functions describing fermionic systems and is one of the fundamental theorems of quantum mechanics. It states that a many-electron wave function must be antisymmetric under the interchange of the coordinate \( \mathbf{x} \) of any two electrons,

\[
\Psi^{(N)}(x_1, \ldots, x_i, \ldots, x_j, \ldots, x_N) = -\Psi^{(N)}(x_1, \ldots, x_j, \ldots, x_i, \ldots, x_N). \tag{2.8}
\]
Orbitals in quantum chemistry

An orbital is a one-electron function which can either be a spatial orbital, \( \psi_i(r) \), or a spin orbital, \( \chi_i(x) \). The spin orbitals are defined as a one-electron function of the spatial and spin coordinates \( x \). Two spin orbitals can be formed by multiplying a spatial orbital with the two spin functions, \( \alpha(\omega) \) and \( \beta(\omega) \), respectively.

The spatial orbitals are also known as molecular orbitals since we are concerned with the study of the electronic structure of molecular systems. They are functions of the spatial position of an electron and cannot be observed or measured by experiments. The squared amplitude of a spatial orbital, \( |\psi_i(r)|^2 d^3r \), gives the probability of finding an electron in the small volume element \( d^3r \) surrounding \( r \).

In principle, the set of spatial orbitals \( \{\psi_i\} \) must be complete to provide the exact solution, but in practice we will never have a complete set available and must restrict the set of spatial orbitals to a finite number \( k \), \( \{\psi_i|i = 1, 2, \ldots, k\} \). These \( k \) orbitals span a certain region of the complete space with a hopefully large overlap of the space needed to represent the exact solution. However, within this finite one-particle basis set, we can calculate the ”exact” solution within the subspace of the \( k \) orbitals.

The Slater determinant

In the previous section, we have discussed the functions describing a single electron, we now proceed to construct a wave function for a collection of electrons. The set of one-electron functions constitutes our one-particle basis which is employed to construct the many-particle basis for the expansion of the electronic wave function. We start with a simple wave function ansatz, the Hartree product, which is just a product of one-electron functions. The Hartree product is an uncorrelated wave function and corresponds to an eigenfunction of a system of non-interacting electrons. It does not, however, obey the antisymmetry requirement for fermionic systems.

We thus need to antisymmetrize the Hartree product and achieve this by transforming it into a suitable mathematical object, a determinant, which inherently satisfies the antisymmetry principle. By interchanging the coordinates, or in the mathematical language of determinants, by interchanging the columns, the overall sign changes in accordance with the Pauli exclusion principle. A single Slater determinant forms the exact, antisymmetrized wave function of a system of non-interacting electrons. For a system consisting of \( N \) electrons, the Slater determinant in terms of spin orbitals reads

\[
\Phi^{(N)}(x_1, x_2, \ldots, x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix}
\chi_1(x_1) & \chi_2(x_1) & \cdots & \chi_N(x_1) \\
\chi_1(x_2) & \chi_2(x_2) & \cdots & \chi_N(x_2) \\
\vdots & \vdots & \ddots & \vdots \\
\chi_1(x_N) & \chi_2(x_N) & \cdots & \chi_N(x_N)
\end{vmatrix}. \quad (2.9)
\]
In second quantization \[67\], one usually works with occupation number vectors where the antisymmetry requirement is built into the algebra of the elementary creation and annihilation operators \[33\].

### 2.2.2 The exact wave function in a given one-electron basis

We have discussed how a Slater determinant can be constructed from spatial orbitals and that such a single determinant exactly describes a system of \(N\) non-interacting electrons. This is, however, not a very satisfactory solution for molecular systems where the electrons are in a spatially confined volume and strongly interacting with each other by means of the Coulomb potential generated by all other electrons.

To describe the physics of the interacting electrons correctly, we need to take all Slater determinants into account that can be generated by distributing the \(N\) electrons among the \(2k\) spin orbitals. If we had employed a complete set of one-electron functions, the set of Slater determinants would be infinite as well. For practical purposes, we restricted the size of the one-particle functions as mentioned already above. The consequences are that the size of the many-particle basis is finite as well. Nevertheless, as combinatorics teaches us, the number of Slater determinants that can be generated by distributing \(N\) electrons among the \(2k\) spin orbitals scales factorially,

\[
\binom{2k}{N} = \frac{(2k)!}{N!(2k-N)!}. \tag{2.10}
\]

The diagonalization of the finite electronic Hamiltonian matrix provides a solution that is exact within the subspace spanned by the \(2k\) spin orbitals and within the \(N\)-electron many-particle space spanned by the set of \(\binom{2k}{N}\) determinants.

The exact wave function in a given one-particle basis is known as the full-configuration-interaction (FCI) ansatz and takes the form of

\[
|\Psi_{\text{FCI}}^{(N)}\rangle = c_0 |\Phi_0\rangle + \sum_{ar} c_r^a |\Phi_r^a\rangle + \sum_{a<b,r<s} c_{rs}^{ab} |\Phi_{rs}^{ab}\rangle + \sum_{a<b<c,r<s<t} c_{rst}^{abc} |\Phi_{rst}^{abc}\rangle + \ldots \tag{2.11}
\]

where the expansion is constructed by exciting electrons from occupied orbitals \(a,b,c,\ldots\) of a reference state, the Hartree–Fock determinant \(\Phi_0\), into virtual orbitals \(r,s,t,\ldots\). The restrictions on the summation indices ensure that a given excited determinant is not included several times.

### 2.2.3 Electron correlation

The motions of the electrons are correlated which is not properly reflected in the single-determinant model. The energy due to the electron correlation is quantified by taking the difference between the mean-field (Hartree–Fock)
energy where one electron is exposed to the average mean-field of all the other electrons and the exact non-relativistic energy in a given one-particle basis. The correlated motion of electrons can be split into two parts, the Fermi and the Coulomb correlation. The Fermi correlation arises from the antisymmetry requirements of the wave function for fermionic systems. It is thus very unlikely — even in the Hartree–Fock case — to find two electrons with the same spin in the same region of space, which is denoted as the Fermi hole.

The Coulomb correlation can be further divided in dynamical and static correlation. Although they both originate from the same physical effect, namely the Coulomb repulsion, these terms are helpful in discussing the performance of different quantum chemical methods since their distinction is connected to the machinery we employ to treat them [72]. In the wave function approach, the description of electron correlation is improved by a superposition of orbital configurations which is the topic of the next section.

### 2.2.4 Truncated configuration-interaction wave function

The explicit expansion of the FCI wave function in terms of Slater determinants which would then span the entire \( N \)-particle Hilbert space is not feasible for most molecular systems due to the factorial complexity in the construction of the many-particle basis. Most standard CI-type quantum chemical methods thus restrict the FCI expansion in Eq. (2.11) to determinants with a certain excitation pattern only and one thus hopes that the approximate wave function in the subspace spanned by the selected determinants overlaps with the exact solution of the full \( N \)-particle Hilbert space. These methods differ in the way the restricted set of Slater determinants is selected. A most efficient one is the coupled-cluster expansion [33].

The construction of the many-particle basis of approximate wave functions shall be explained for the truncated configuration interaction (CI) method. A clear understanding of how this wave function is built up allows us to fully appreciate the advantages of tensor network states in terms of the required variational parameters which will be explained in detail in chapters 4 and 5.

Part of the “art” of the CI method is choosing those Slater determinants that will make the greatest contribution to the electronic wave function [2]. The truncated CI approach neglects determinants that differ by more than a certain number of spin orbitals (two for the CISD method) from the Hartree–Fock reference determinant. The CISD wave function thus contains only the Hartree–Fock state and singly and doubly excited determinants,

\[
|\Psi^{(N)}_{\text{CISD}}\rangle = c_0 |\Phi_0\rangle + \sum_{ar} c_a^r |\Phi_a^r\rangle + \sum_{a<b,r<s} c_{ab}^{rs} |\Phi_{ab}^{rs}\rangle,
\]

which is assumed to give the major fraction of the correlation energy. The reason for neglecting all other excited determinants lies in the fact that the Hartree–Fock state is for most molecules the most important determinant with
the largest weight. Since the electronic Hamiltonian couples at most four spin orbitals, the high-dimensional integrals between the Hartree–Fock determinant and a triply or higher excited determinant over the electronic Hamiltonian are zero. However, if we consider molecular systems with a strong multi-reference character, i.e., when more than one determinant has a large weight, the CISD method turns out to be a rather weak approximation of the electronic structure since it heavily relies on the Hartree–Fock reference state. Actually, all single-reference methods face the same problem. In coupled cluster theory, however, a clever approach for selecting the determinantal subspace leads to a size-consistent wave function which must be corrected for in the CISD wave function as this approximation is not size-consistent [33].

2.3 The intrinsic property of fermions: The electron spin in quantum chemistry

The electronic Hamiltonian operator commutes with the total spin and projected spin operators since it does not depend on the spin coordinates. The exact, non-relativistic wave function thus constitutes an eigenfunction of the total spin and the projected spin operators but the Slater determinants which form the expansion of the electronic wave function are only eigenfunctions of the projected spin operator but not of the total spin operator. However, it is often advantageous to transform the basis of Slater determinants into a set of configuration state functions (CSF) which are constructed to be spin-adapted eigenfunctions of the Hamiltonian and total spin operator. This transformation is achieved by taking linear combinations of determinants. The procedure will be discussed below.

The total spin operator $S^2$ is defined as the sum of the squared spin operators $S_x$, $S_y$ and $S_z$,

$$S^2 = S_x^2 + S_y^2 + S_z^2. \quad (2.13)$$

where, e.g., $S_z$ is the operator for the $z$ component of the spin angular momentum. In analogy to the orbital angular-momentum operators, we can write the commutators of the $S_x$, $S_y$, and $S_z$ operators as

$$[S_x, S_y] = i\hbar S_z, \quad [S_y, S_z] = i\hbar S_x, \quad [S_z, S_x] = i\hbar S_y. \quad (2.14)$$

Each of the spin angular-momentum operators commutes with the $S^2$ operator

$$[S^2, S_x] = [S^2, S_y] = [S^2, S_z] = 0. \quad (2.15)$$

Because of the commutation relation of the spin angular-momentum operators with each other as given in Eq. (2.14), it is helpful to reformulate the $S^2$ operator in terms of ladder operators. The ladder operators $S_-$ and $S_+$ then take the form of

$$S_- = S_x - iS_y, \quad S_+ = S_x + iS_y. \quad (2.16)$$
Employing these spin ladder operators, we can conveniently express the total spin operator $S^2$ as

$$S^2 = S_- S_+ + S_z (S_z + 1).$$  \hfill (2.17)

In second quantization, the $S_-, S_+, S_z$ operators read

$$S_- = \sum_i c_{i,\beta}^\dagger c_{i,\alpha},$$  \hfill (2.18)

$$S_+ = \sum_i c_{i,\alpha}^\dagger c_{i,0},$$  \hfill (2.19)

$$S_z = \frac{1}{2} \sum_i (c_{i,\alpha}^\dagger c_{i,\alpha} - c_{i,\beta}^\dagger c_{i,\beta}),$$  \hfill (2.20)

where the summation runs over all spin orbitals and the creation and annihilation operators, $c_{i,\sigma}^\dagger$ and $c_{i,\sigma}$, respectively, either occupy orbital $i$ with an electron of projected spin $\sigma$ or delete it. The elementary operators in second quantization are acting on occupation number vectors which can be depicted as a simple vector of binary numbers representing occupied or unoccupied spin orbitals. A detailed theoretical discussion of second quantization can be found in Refs. [33] and [64].

For the CSF construction, we employ a genealogical coupling scheme. This coupling scheme can be visualized by means of a branching diagram as shown in Figure 2.2. A closed-shell Slater determinant where all orbitals are doubly occupied is an eigenstate of the total spin operator and hence we need only focus on the unpaired electrons. A CSF of $N$ unpaired electrons is thus generated in a sequence of $N$ steps. At each step, the next unpaired electron is taken into account and coupled to the already included ones. This entire procedure builds up intermediate CSFs that are represented by the beads in Figure 2.2. The number within the bead represents the number of combinations that can be formed using previously constructed CSFs with a smaller number of unpaired electrons. One starts with a single orbital occupied with an unpaired electron which thus represents a doublet spin eigenfunction. In the subsequent step, a second electron is introduced situated in another orbital which couples the doublet spin state to either a singlet or triplet spin eigenfunction. This steps is repeated until all unpaired electrons have been considered.

In the actual implementation of the CSF construction scheme, one selects the node on the graph with the correct spin and number of unpaired electrons. All paths to the starting state of one unpaired electron in a doublet state can be built and thus one can then determine the coefficients of the Slater determinants for the CSF that is sought for. Each of those paths represents an individual CSF for the corresponding orbital configuration.
Figure 2.2: The genealogical coupling scheme is depicted as a branching diagram for up to 7 unpaired electrons \( N \) [33]. The total spin \( S \) is given on the ordinate. The lines between the nodes represent all genealogical spin functions and the number of distinct spin couplings for each value of \( N \) and \( S \) is also shown in the circles.

Employing the notation used in Ref. [33], the expansion coefficients for the Slater determinants in a given CSF are given in terms of Clebsch–Gordan coefficients \( C_{t_n, p_n}^{T_n} \) as

\[
d(p|t)^c = \prod_{n=1}^{N} C_{t_n, p_n}^{T_n},
\]

(2.21)

where the superscripts \( d \) and \( c \) differentiate between the determinant with index \( p \) and the CSF with index \( t \), respectively, and \( T_n \) represents the total spin resulting from the spin coupling of the first \( n \) electrons, \( P_n \) gives the total projected spin of the first \( n \) orbitals, the \( t_n \) and \( p_n \) determine the difference in the total spin and projected spin from the previous CSF. Note that for a given orbital configuration, all necessary Slater determinants can easily be constructed. Each of those determinants are then used in the linear combinations forming the set of CSFs. The Clebsch–Gordan coefficients are evaluated according to

\[
C_{1/2,\sigma}^{S,M} = \sqrt{\frac{S + 2\sigma M}{2S}}
\]

(2.22)

\[
C_{-1/2,\sigma}^{S,M} = -2\sigma \sqrt{\frac{S + 1 - 2\sigma M}{2(S + 1)}}
\]

(2.23)

where \( S \) is the total spin, \( M \) the spin projection, and \( \sigma \) corresponds to the difference in the project spin to the previous step.
3. A new paradigm for quantum chemistry: The DMRG algorithm

3.1 Numerical renormalization group

The factorial scaling in the dimension of the Hilbert space poses the biggest challenge in the exact description of strongly correlated condensed matter and molecular systems. One way of preventing an factorial growth of the number of basis states spanning the Hilbert space of interest is to integrate out degrees of freedom which are not necessary to represent energetically low-lying states. This was indeed found by Wilson [51] studying the Kondo problem. He realized that contributions of the energy levels can be averaged out when they are far from the Kondo resonance since they decay exponentially. Qualitatively speaking, physical properties are mostly dominated by low-energy scales and fluctuations on shorter length scales can be integrated out and summed up into quantitative modifications of the low-energy behavior [58]. This understanding of the scale separation led to the development of the numerical renormalization group (NRG) [51, 52].

The numerical renormalization group algorithm is based on the assumption that one can divide the total system into smaller parts for which the Hamiltonian can be solved exactly. So, instead of letting the Hilbert space grow exponentially with system size, we define a subspace on which we project the original Hamiltonian. The eigenstates of the subspace Hamiltonian corresponding to the biggest eigenvalues form a new improved basis for the description of the enlarged system. The high-energy part of the problem, the Hamiltonian on the subsystem, is solved first and the eigenstates of the Hamiltonian are then used to build a new effective Hamiltonian which omits the highest energy states. This step is repeated until the basis consists of low-energy states only. This procedures assumes that the ground state of the system is composed of the energetically low-lying states.

The success of NRG lies in the decimation procedure which restricts the size of the Hilbert space. NRG provides excellent results for quantum impurity problems applying either the Kondo or Anderson Hamiltonians [73, 74]. However, due to the way the new basis states are defined, the method was not able to describe the ground-state properties of other many-body Hamiltonians such as the Hubbard or Heisenberg models where a clear energy scale separation is not present.

In 1992, the breakdown of the numerical renormalization group could be demon-
strated by White and Noack [54] for the particle-in-a-box problem. They pointed out that the eigenstates of a Hamiltonian defined on a particular subsystem are not optimal basis states for the description of an enlarged system. In other words, the ground-state wave function for the particle-in-a-box problem cannot be approximated by the low-energy eigenstates of smaller boxes which is schematically represented in Figure 3.1.

Figure 3.1: A single particle in a box in the continuum limit. The lowest eigenstates of the left and right subblocks (illustrated as dashed lines) are schematically drawn [58]. In the numerical renormalization group algorithm, the eigenstates of one of the subblock span the new basis of the compound block and produce an artificial kink at the position where the ground state (magenta) of the compound block has actually its maximum amplitude. As a result, the striking failure of the numerical renormalization group for some systems can even be demonstrated for the simple particle-in-the-box model [54].

The reason why the eigenstates of smaller blocks are not appropriate to describe larger blocks lies in the boundary conditions. For any state in a smaller block, the amplitude is zero at the boundaries which produces kinks in the approximate state of a larger system. To remove these kinks, one would need to keep many more states which would lead again to an exponential increase of the Hilbert space. White and Noack then realized that the correct boundary conditions can be obtained by embedding the system in an environment from the viewpoint of statistical mechanics.
The new basis states are the eigenstates of the reduced density matrix where the environment states are traced out. These states feature now the correct boundary conditions to describe a larger block of the problem correctly.

### 3.2 Historical perspectives and recent developments

The past ten to twenty years have seen the rise of a new correlation method in quantum chemistry [49]. This is the density matrix renormalization group (DMRG) approach introduced by White in solid state physics in 1992 [53] and based on Wilson’s renormalization idea. In this approach, a reduced number of many-particle basis states is determined which approximate the total quantum mechanical state most efficiently. By contrast to Wilson’s renormalization approach, White noted that the selection of states for renormalization should not be the lowest energy eigenstates of the Hamiltonian but the eigenstates of the reduced density matrix. The reduction of basis states is then achieved by a contraction of Slater determinants with weights given by \( m \) eigenvectors of the reduced density matrix with largest eigenvalues. In principle, DMRG allows one to systematically approach the full configuration interaction (FCI) solution in a given active space of one-electron functions.

The application of DMRG in quantum chemistry then started with the work of Shuai et al. [75], Yaron et al. [76], and Fano et al. [77] who performed DMRG calculations on molecular systems using the semi-empirical Pariser–Parr–Pople Hamiltonian. Shortly afterwards, White and collaborators [78,79] used the full many-electron Hamiltonian. They also introduced the use of complementary operators which are products of elementary creation and annihilation operators. The complementary operators are able to reduce the scaling of the algorithm and emerged from the work of Xiang [80] who used these kinds of operators for Hubbard-type model Hamiltonians in the momentum-space DMRG algorithm. Several other groups investigated DMRG as well and these developments have been reviewed in Refs. [48, 49, 58].

Daul et al. [79] performed DMRG calculations for methane, which reached FCI accuracy in the chosen one-electron basis. In 2003, Legeza et al. [81] calculated the ionic–neutral curve crossing of LiF. They showed that the avoided crossing of the two singlet states is correctly described by the DMRG algorithm. Chan and Head-Gordon performed DMRG calculations on the water molecule with 41 active orbitals [82]. In a follow-up article Chan described the parallelization of their DMRG code [83]. Chan also compared DMRG and coupled-cluster results for the potential energy curve of \( \text{N}_2 \) [84]. DMRG total energies were found in between the CCSDTQ and CCSDTQPH coupled-cluster results close to the equilibrium geometry but were significantly better at longer bond distances. Already in 2001, Mitrushenkov et al. [85] compared DMRG and FCI results for the equilibrium structure and dissociation energies of several diatomic molecules, such as \( \text{Be}_2 \), \( \text{HF} \), and \( \text{N}_2 \). The results for \( \text{Be}_2 \) and \( \text{HF} \) agreed very well with the FCI results. For the \( \text{N}_2 \) molecule, they could improve their result by...
incorporating excited states into the reduced density matrix. They employed natural orbitals from a preceding CASSCF or MRCI calculations to obtain the one-electron and two-electron integrals.

In 2006, Hachmann et al. [86] implemented a quadratic scaling DMRG algorithm for long, one-dimensional molecules. These one-dimensional molecules resemble closely the one-dimensional lattices studied by the condensed-matter community, for which DMRG was originally developed. Quadratic scaling could be achieved by prescreening the two-electron integrals and neglecting those which lie below a certain threshold.

**Orbitals and convergence**

Daul et al. [79] investigated the effect of different orbital bases on DMRG calculations. They employed canonical Hartree–Fock orbitals, localized Hartree–Fock orbitals, and Kohn-Sham orbitals. Quite contrary to the authors’ expectation, the localization procedure did not significantly change or improve the convergence behavior or the converged energy as was originally anticipated from the experience of the condensed-matter community. This misconception has probably originated from DMRG studies on spin lattices where the DMRG method was originally applied on.

Furthermore, Daul et al. studied the HHeH system as a magnetic toy problem with an active space consisting of 18 orbitals. The spin splitting between the singlet and the triplet spin state could be predicted up to FCI accuracy with 64 DMRG states.

In a systematic study, the influence of various types of orbitals and different orbital orderings in a DMRG calculation was examined by Mitrushenkov et al. [87]. Canonical CASSCF orbitals delivered significantly better results than the localized orbitals. Nevertheless, the localized orbitals appear to be particularly effective in the weak interaction region. They also tried to improve the orbital ordering by selecting those orbitals with the biggest interactions and placing them near each other. The interaction between two orbitals \( \phi_i \) and \( \phi_j \) was related to the squared Coulomb two-electron integral \( V_{ijji} \) and divided by the difference in orbital energies, \( V_{ijji}^2 / (E_i - E_j) \).

DMRG calculations on the nitrogen molecule using their orbital localization protocol and the orbital ordering produced slightly worse results compared to a standard DMRG calculations employing natural orbitals obtained from a MRCI calculation and an orbital ordering according to the occupation numbers. The advantage of the former is that there is no need for an expensive MRCI calculation.

In the spirit of the orbital interaction scheme proposed by Mitrushenkov et al. [87], Legeza and Sólyom applied the von Neumann entropy to quantify the importance of a subsystem configuration [88]. In quantum information theory, the von Neumann entropy measures the entanglement of a bipartite system, i.e., between the active subsystem and the complementary subsystem. Legeza
and Sólyom determined the entropies for subsystems of one single orbital in the Hubbard Hamiltonian and placed the orbitals with largest entropies in the middle of the orbital chain. The same ansatz was also proposed for the DMRG application in quantum chemistry where the molecular orbitals with the highest entropy correspond to the frontier orbitals. But in a follow-up article, the authors could demonstrate that their ansatz for the orbital ordering does not necessarily optimize the convergence behavior of the DMRG algorithm [89].

A similar approach based on the von Neumann entropy was also chosen by Rissler et al. [90] to improve the orbital ordering. The authors devised a scheme to compute the entanglement between any two orbitals using the von Neumann entropy. The idea is to place strongly interacting orbitals next to each other in order to reduce the entanglement of the entire system. They tested their orbital ordering scheme to CO, N$_2$, and F$_2$. The DMRG calculations were performed for 28 active orbitals in a cc-pVDZ basis set with up to 600 DMRG states. Their optimized orbital sequences gave in all cases lower converged energies than the reference ordering where the orbitals are ordered by Hartree–Fock energies. The disadvantage of this method is, of course, that preceding DMRG calculations have to be performed in order to devise the optimized orbital ordering.

In spin lattices, the local spins on each site are spatially separated and therefore a localization of the orbitals in the quantum chemical DMRG algorithm makes sense to reduce electron correlation which in turn reduces the complexity of the corresponding electronic wave function. It is, however, not necessary from an algorithmic point of view to employ localized orbitals at all. In quantum chemistry, the spin lattices can be best compared to conjugated polymers, e.g., linear polyenes, where the elongated structure maps almost exactly to a one-dimensional lattice. The localization of the orbitals in such cases, reduces the number of two-electron integrals with a significant contribution and thus facilitates the implementation of a quadratic-scaling algorithm [86]. By a localization procedure, the complex electron correlation problem can be reduced to a good degree to nearest-neighbor-like interactions in elongated molecules. In molecules with a low entanglement between system and environment, the number of DMRG states can then be chosen rather small while still accurate results are obtained [86].

Mitrushenkov et al. [87] suggested to reformulate the DMRG algorithm in a non-orthonormal basis in order to improve the orbital localization which should then lead to a better convergence. Chan and Van Voorhis [91] adapted their DMRG code to support non-orthogonal molecular orbitals. They implemented a biorthogonal basis where several modifications were necessary to deal with non-Hermitian operators.

In 2002, Chan and Head-Gordon [92] provided one of the most comprehensive overview of the DMRG algorithm for quantum chemistry. They examined the DMRG algorithm in terms of computational cost, memory usage, and disk storage. They also realized the slow convergence of DMRG when applied to quantum chemical systems. To solve the convergence issue, an optimized ordering was
proposed by reordering the orbitals to block-diagonalize the one-electron integral matrix using the reverse Cuthill–McKee algorithm [93,94]. Another important aspect of their work was the application of white noise to avoid convergence to local energy minima. Local minima may occur when the initial guess of the basis of the environment is insufficient. This means that the truncated basis might not contain important states to represent the total state accurately. Due to the nature of the DMRG algorithm, such states will never be picked up in the wave function since they have no support in the reduced density matrix and are thus never picked up by the algorithm, consequently. The proposed addition of white noise on the truncation matrix [92] tries to collect these basis states by mixing randomly states during the initialization procedure. Another strategy to prevent local minima on a more sound theoretical basis is the perturbative correction suggested by White [95]. The perturbative correction tries to construct the initial guess of environment in such a way that all states on the system have a counterpart. Both methods do not guarantee to converge to the global minimum.

Our group has investigated convergence of the plain DMRG algorithm without any such precautions to guarantee the pick-up of relevant many-electron states in the environment. Then, convergence to local minima can be observed, but does not always occur. In particular, it depends on the ordering of orbitals, i.e., on the sequence of orbitals to be picked up sequentially by the increasing active subsystem. For this comparison Moritz and Reiher [96] prepared optimized orbital orderings via a genetic optimization procedure. While noise affects the environment states in a random manner, Moritz et al [97] studied the feasibility of explicit environment guesses as well as of systematically increased environment states. A decomposition of the DMRG basis functions in terms of Slater determinants has been carried out in Ref. [98], in order to study and eventually better understand energy convergence during DMRG iterations.

**Orbital optimization**

DMRG-SCF implementations have been proposed by Zgid and Nooijen [99] and by Ghosh et al. [100]. The DMRG-SCF algorithm optimizes the orbitals in the active space similar to the CASSCF method [46]. In the two implementations a similarity-transformed Hamiltonian was constructed as in coupled-cluster theory. The orbital-rotation amplitudes are obtained from a coupled-cluster type exponential parameterization $e^A$ where $A$ is obtained from the single excitations,

$$A = \sum_{ij} A_{ij} a_i^\dagger a_j$$

(3.1)

with $A_{ij} = -A_{ji}^*$. The similarity-transformed Hamiltonian has the same form as the original second quantized Hamiltonian but the one-electron and two-electron integrals must be adjusted for the orbital rotation. The transformed Hamiltonian is given by

$$H^T = e^{-A} H e^A$$

(3.2)
and the energy after the orbital rotation can be written as

\[ E^T = \langle \Psi | H^T | \Psi \rangle \]

\[ = \sum_{ij} h^T_{ij} \gamma_{ij} + \frac{1}{2} \sum_{ijkl} V^T_{ijkl} \gamma_{ijkl} \]

where \( | \Psi \rangle \) approximates the target eigenstates of the Hamiltonian matrix \( H \) and the \( \gamma_{ij} \) and \( \gamma_{ijrs} \) represent the one-particle and two-particle density matrices, respectively. The procedure is now iterated until convergence in the wave function is reached.

To evaluate the resulting energy expression, the one-particle and two-particle density matrices are required. Zgid and Nooijen as well as Ghosh et al. presented two approaches that differ only slightly on how to assemble the two-particle density matrices [100, 101]. Note that the one-particle density matrices can be calculated at any position of the sweep without additional memory cost. The approach taken by Zgid and Nooijen is slightly more efficient than the one by Ghosh et al. since the computational scaling can be reduced by forming simple intermediates.

Zgid and Nooijen combined the two-site DMRG algorithm to converge the DMRG wave function to the variational optimum and switch then to the one-site algorithm where the two-particle density matrix can be easily constructed. In the one-site algorithm, the energy converges monotonically and the wave function stays the same at every step in the sweep which avoids a possible \( N \)-representability problem. Since the wave function stays the same in the one-site DMRG algorithm, the two-particle density matrix can be assembled piece by piece over an entire sweep. Zgid and Nooijen also pointed out that the one-site DMRG method might get easily stuck in a local minimum even though a perturbative correction as suggested by White [95] is applied.

Zgid and Nooijen presented preliminary result on the \( \text{Cr}_2\text{Mn}_2 \) metal cluster with their DMRG-SCF implementation. They employed an active space of 24 orbitals and 22 electrons with 150 DMRG states. Their result are still quite far from the FCI limit but their goal was to show that DMRG calculations with a small number of DMRG basis states can be used to perform an initial orbital optimization. They also noted that low \( m \) DMRG calculations provide the qualitative correct features.

Ghosh et al. presented state-averaged DMRG-SCF calculations for \( \beta \)-carotene using the full \( \pi \)-valence active space consisting of 22 projected atomic orbitals and 22 electrons. They obtained the correct state ordering as in experiment but the excitation energies were generally overestimated which might be most likely due to the lack of the \( \sigma - \pi \) dynamic correlation.

The DMRG-SCF implementation can also be cast into an acceleration algorithm to improve the convergence in large-scale CASSCF calculations as described in a recent work by Yanai et al. [102]. In this method, the DMRG algorithm replaces the CI calculation step in a two-step CASSCF calculation to reduce
the number of iterations and therefore of expensive exact diagonalization steps. The one-step CASSCF calculation as implemented in the Molpro program package [103], where the optimization of the molecular orbitals and CI coefficients are performed simultaneously, still converges faster for the same small active space.

### Variational nature of the DMRG ansatz

A variational electronic structure theory is of great benefit since the energy represents always an upper bound to the exact energy. The quality of the trial wave function can then be related to the energy and one can systematically improve the result. The nature of the DMRG algorithm is variational because the algorithm restricts the Hilbert space in which the Hamiltonian is solved at each iteration step [58,92]. Nevertheless, one cannot guarantee that the energy is successively lowered since there exists no simple relationship between the Hilbert spaces spanned by states of two subsequent iterations due to the basis truncation. As a result, one observes small deviations in the energy during a sweep which is caused by local fluctuations originating from an increase in the flexibility of the many-particle basis.

### Excitation structure

The strength of DMRG lies in the way it adaptively improves its \( N \)-particle basis. It may pick any state in the entire Hilbert space. This can be seen in the DMRG wave function which will be discussed in depth in section 3.5. In the DMRG ansatz, the sum over the Slater determinants spanning the full \( N \)-particle Hilbert space is not restricted to any preselected expansion scheme as in CISD or CCSD (see section 2.2 for the CISD wave function). Most traditional quantum chemistry methods rely on an expansion of the approximate wave function as a single or a set of Slater determinants as a reference which favors some determinants of a certain excitation level over others. The very flexible DMRG ansatz automatically constructs any possible Slater determinant that can be generated in the orbital space of the total system during in the renormalization procedure. The flexibility also provides no bias towards single- or multireference problems and can describe equally well dynamical and static correlations in complex electronic structures. The construction of the basis states of the total system as tensor products of the system and environment basis states guarantees that the most significant electronic configurations can be picked up, even highly excited determinants which would have never been considered in most standard quantum chemical methods. This renders the DMRG algorithm as a very useful method to describe any part of the potential energy surface if accurate relative energies are needed and thus individual calculations with fixed error bounds are sought for. In previous work, it was shown that DMRG reproduces potential energy curves for nitrogen [84] and cesium hydride [104] with spectroscopic accuracy. In addition, DMRG can also cope with delicate
problems where a proper balance between static and dynamic electron correlation plays an significant role along the potential energy surface [105].

**Excited states and DMRG response theory**

In 2007, Dorando et al. [106] investigated the state-averaged harmonic Davidson algorithm to describe excited states. The harmonic Davidson approach is an iterative technique that works with shifted and inverted operators which allow one to specifically target excited states within the DMRG algorithm. The advantage over the traditional state-averaged Davidson approach is that it is not necessary to calculate and represent all states between the ground state and excited state of interest. The authors calculated several low-lying excited states of acenes ranging from naphthalene to pentacene. The ground states of the acenes were previously studied by the same group [107]. They found that the harmonic Davidson approach delivers a better accuracy in the energies than the state-averaged harmonic Davidson approach. The state-averaged harmonic Davidson algorithm, however, shows a stable convergence without root flipping if nearby competing states are included in the average.

An analytic response theory was also implemented into the DMRG algorithm by Dorando et al. [108]. The basis of the analytic response DMRG method was the reformulation of the DMRG method in terms of a Lagrangian formalism [109]. The optimal DMRG wave function was obtained in a variational sense by minimizing these Lagrangians. Static and frequency-dependent response properties were implemented, where the response properties correspond to analytic derivatives of DMRG observables with respect to the applied perturbations. The analytic response implementation changes the computational scaling of the DMRG algorithm by a constant factor only. The authors calculated static and frequency-dependent longitudinal polarizabilities of a chain of up to six oligodiacylenes. The analytic DMRG response theory results were consistent with semiempirical calculations but the authors noted that larger basis sets and calculations on longer chain lengths are necessary to draw a final conclusion about the saturation of the polarizability as a function of the chain length.

**Spin and symmetry adaptation of DMRG**

Zgid and Nooijen [110] implemented a fully spin-adapted DMRG algorithm which allows one to target spin and spatial symmetry states of interest. The implementation does not alter the computational scaling at all. Spin adaptation in the DMRG method has already been introduced before by McCulloch and Gulácsi for the Kondo lattice model [111–113]. Their implementation is based on the Clebsch–Gordan transformation and the elimination of quantum numbers by the use of the Wigner–Eckart theorem. Zgid and Nooijen decided to sacrifice computational efficiency in order to avoid the Clebsch–Gordan transformation and to obtain a simpler implementation of the spin adaptation. They made
sure that always complete sets of multiplets are included in the DMRG wave function expansion. A second important condition is the adaptation of the eigenvectors of the modified reduced density matrix to be eigenfunctions of the total spin operator of either the system or environment.

Another scheme to target spin states was used in the DMRG study of Moritz et al. [104] on the calculation of the potential energy curve of CsH where spin contamination became a problem at large nuclear distances, since near-degeneracies in the Davidson diagonalization procedure might lead to a mixing of excited states with a different total spin resulting in spin contamination. The spin contamination was eliminated by modifying the Hamiltonian matrix in such a way that states with a wrong total spin are shifted up in energy. The shifted Hamiltonian can be written as

$$H_{\text{shift}} = H + \alpha (S^2 - S_z^2 - S_z)$$

where the parameter $\alpha$ is a positive constant.

**Relativistic DMRG algorithm**

In 2005, the first scalar relativistic DMRG calculations were performed by Moritz et al. [104] for the potential energy curve of the ground state and $^1\Sigma^+$ first excited state of cesium hydride. For the cesium atom, relativistic effects cannot be neglected. The scalar relativistic effects were incorporated by means of the generalized arbitrary-order Douglas–Kroll–Hess protocol up to tenth order [114–116]. The basic idea of the generalized Douglas–Kroll–Hess transformation is to decouple the relativistic Dirac Hamiltonian in order to reduce the computational cost and to get rid of the unphysical negative-energy states. The decoupling procedure leads to a block diagonalization of the Dirac Hamiltonian which can be obtained by a sequence of suitably chosen unitary transformations [117–121]. The DMRG calculations were performed in an active space of 46 molecular orbitals correlating 10 electrons. For a comparison of the DMRG energies, MRCISD calculations in a smaller active space of 10 orbitals and 10 electrons were performed. For 400 DMRG basis states, the DMRG energies were consistently lower than the MRCISD energies. Near the avoided crossing of the ionic–neutral potential energy curves, some MRCI calculations were slightly lower which indicated that more DMRG basis states would have been necessary to obtain energies of same accuracy. At small internuclear distances — near the equilibrium structure — CCSD(T) energies were lower by $4mE_h$. The energy difference can be attributed to the fact that DMRG does not account for the virtual orbitals at all. The spectroscopic constants of the DMRG potential energy curve agree with the values obtained for MRCI and CCSD(T) around the equilibrium structure. Nevertheless, the spectroscopic constants deviate from the experimental values. The authors suggested to extend the basis set to include polarization functions with higher angular momentum quantum numbers to reproduce the experimental reference data.
Figure 3.2: Graphical representation of a Cayley tree tensor network with a coordination number of 3 for 22 molecular orbitals. Each circle represents a rank-4 tensor where \( k \) labels the physical site-index which is omitted here for the sake of brevity.

**Generalized DMRG algorithm with tree tensor network state**

In principle, a DMRG-like optimization method can be applied to any general quantum state in which local sites are coupled to more than two neighboring auxiliary sites. Qualitatively speaking, for any state that allows a bipartition of the entire system. Murg et al. [122] expanded the spatial topology of the one-dimensional MPS to tree tensor network states (TTNS). An example of a TTNS with coordination number 3 is the Cayley tree (also known as a Bethe lattice) which is shown in Figure 3.2. The advantage of a tree-like DMRG approach over the conventional, one-dimensional DMRG algorithm is evident. For the tree-like ansatz, the long-range correlation deviates from the mean-field value polynomially with the distance, in contrast to the one-dimensional MPS where the long-range correlation decays only exponentially. Since this tree tensor network is bipartite, one can adapt the DMRG algorithms to tensor product states on the tree network. This is possible by a generalized DMRG algorithm with \( z \) blocks instead of two for a tree tensor network with the coordination number \( z \). Murg et al. [122] have applied the TTNS to the Heisenberg model, one-dimensional and two-dimensional spinless fermions, and the Beryllium atom. The orbital ordering problem, however, cannot be solved by the TTNS ansatz since there are still many different possible topologies of the alignment of the highly entangled orbitals. The successful application of the TTNS largely depends on the question if one can directly map the information of the two-orbital entanglement topology to a tree tensor network or not.
3.3 A quick tour through the DMRG algorithm

The DMRG algorithm is an iterative procedure which optimizes the adaptive many-particle basis that defines matrix representations of creation and annihilation operators in the second-quantized Hamiltonian given in Eq. (3.6). The full Hilbert space is approximated by the renormalized DMRG system basis states yielding \(16m^2\) total basis states, where \(m\) is a parameter set prior to the calculation. The electronic Hamiltonian in second quantization reads in Hartree atomic units ('\(\hbar = m_e = e = 4\pi\epsilon_0 = 1\ a.u.\')

\[
\hat{H}_{el} = \sum_{i,j} h_{ij} a_i^{\dagger} a_j + \frac{1}{2} \sum_{i,j,k,l} V_{ijkl} a_i^{\dagger} a_j^{\dagger} a_k a_l, \tag{3.6}
\]

which contains one-electron integrals \(h_{ij}\) over spatial orbitals \(\psi_i(\mathbf{r})\) given in non-relativistic theory by [67]

\[
h_{ij} = \frac{1}{2} \nabla^2 - \frac{Z_I}{r_I} \psi_j(\mathbf{r}) d^3r, \tag{3.7}
\]

with nuclear charge number \(Z_I\) of atomic nucleus \(I\) and electron–nucleus-\(I\) distance \(r_I = |\mathbf{r} - \mathbf{R}_I|\). The nucleus–nucleus repulsion term is suppressed for the sake of brevity. The two-electron integrals \(V_{ijkl}\) are defined as

\[
V_{ijkl} = \iint \frac{\psi_i^*(\mathbf{r}_1)\psi_j^*(\mathbf{r}_2)\psi_k(\mathbf{r}_2)\psi_l(\mathbf{r}_1)}{r_{12}} d^3r_1 d^3r_2, \tag{3.8}
\]

The Hamiltonian and its ingredients may also be written in terms of spin orbitals \(\chi_i(\mathbf{x}) = \psi_i(\mathbf{r})\sigma\), where \(\sigma\) is a spin-up or spin-down spin eigenfunction. Coordinate \(\mathbf{x}\) then denotes both spatial and spin variables.

By definition, the total system is composed of the molecular orbitals defined in a particular active space and is divided into the *active subsystem* (AS), where the many-particle basis is renormalized, two explicitly represented sites, and the *complementary subsystem* (CS) [98]. In solid state physics, the AS is usually referred to as the *system* and the CS as the *environment*.

A *sweep* is a series of microiterations starting from left to right on the one-dimensional lattice on which the orbital are aligned. If the sweep reaches the end of the orbital sequence, the direction is reversed and thus the CS block becomes the new AS block and AS the new CS, respectively. The next sweep commences now in the reverse direction.

Each of the four blocks contains a many-particle space which is spanned by the orbitals in the corresponding block. The many-particle space spanning an individual block is a subspace of the Fock space of the orbitals within the block. Matrix representations of the elementary operators can be explicitly calculated for the explicitly represented orbital. The Fock subspaces of the AS and CS are spanned by \(m\) many-particle basis states or the DMRG block states.
the first sweep, the size of AS is chosen such that one can explicitly create all necessary auxiliary operators. The DMRG algorithm sweeps then forth and back until the energy is converged.

In a qualitative picture of the DMRG algorithm, a microiteration can be divided into three steps [91]. First, the AS and CS are enlarged by calculating the tensor product of the many-particle basis of the corresponding blocks with the explicitly represented orbitals which are located in-between the AS and CS block on the one-dimensional orbital alignment. The tensor product of the enlarged many-particle spaces of the AS and CS then forms the superblock many-particle basis in which the second-quantized Hamiltonian is calculated. The dimension of the spaces of AS and the single molecular orbital are \( m \) and 4 (for spatial orbitals), respectively. The superblock then contains \( 4m \) many-particle states. Second, the superblock Hamiltonian matrix in the product space of the enlarged AS and CS blocks can be diagonalized which provides an approximation to the exact state. The product space is of dimension \( 16m^2 \) for molecular orbitals and \( 8m^2 \) for spin orbitals and is restricted to basis states of the correct number of particles and projected spin. Third, the approximate wave function of the superblock Hamiltonian can be used to construct the many-particle reduced density matrix of the AS system which provides the improved set of many-particle state for the AS block. The enlarged AS block of dimension \( 4m \) is then renormalized to the new many-particle basis states of dimension \( m \). The decimated system block is used as a starting point for the next microiteration, starting with blocking the next two molecular orbitals.

In the next section, the renormalization step is examined in more detail.

### 3.4 The heart of the DMRG algorithm: The reduced many-particle density matrix

The systematic way of choosing the new many-particle basis for an improved description of the active subsystem lies at the heart of the DMRG algorithm [123]. The new many-particle basis states are selected by diagonalizing the reduced density matrix and keeping only the dominant eigenvectors which correspond to the highest eigenvalues and represent the optimal basis to expand our target state [53–55] (see also below).

For later convenience, we shall briefly review how the eigenvectors of the reduced density matrix of the active subsystem are optimal basis states in a least-squares sense for the total-system states [53–55]. We assume to have an orthonormal many-particle basis on the AS \( \{i| i = 1, ..., M_{AS}\} \) and one on the CS \( \{j| j = 1, ..., M_{CS}\} \) where \( M_{AS} \) and \( M_{CS} \) are the dimensions of the Fock spaces defined on the active and on the complementary subsystems, respectively. Any total-system state can be expressed as

\[
|\Psi\rangle = \sum_{ij} W_{ij} |i\rangle \otimes |j\rangle
\]  

(3.9)
where the expansion coefficients $W_{ij}$ are chosen to be real. We now construct a new orthonormal basis on the active subsystem \{\ket{u^\lambda}_\lambda = 1, \ldots, m\} with $m < M_{\text{AS}}$. In this truncated basis we can write an approximation $|\tilde{\Psi}\rangle$ to the wave function $|\Psi\rangle$ as
\begin{equation}
|\tilde{\Psi}\rangle = \sum_{\lambda j} c_{\lambda j}|u^\lambda\rangle \otimes |j\rangle.
\end{equation}

To find the new basis states we minimize the quadratic norm $S$ between $|\Psi\rangle$ and $|\tilde{\Psi}\rangle$
\begin{equation}
S = |||\Psi\rangle - |\tilde{\Psi}\rangle||^2
\end{equation}
derived from the constraint $\langle u^\lambda|u^\mu\rangle = \delta_{\lambda\mu}$ for $\lambda, \mu = 1, \ldots, m$. It is convenient to write $|\tilde{\Psi}\rangle$ in the Schmidt decomposition form
\begin{equation}
|\tilde{\Psi}\rangle = \sum_{\lambda} c_\lambda|u^\lambda\rangle \otimes |v^\lambda\rangle
\end{equation}
where we have introduced a new basis $|v^\lambda\rangle$ on the complementary subsystem which satisfies $\langle j|v^\lambda\rangle = N_\lambda c_{\lambda j}$ and $N_\lambda^2 \sum_j |c_{\lambda j}|^2 = 1$. The quadratic norm of the approximation error in Eq. (3.11) can be cast into a least-squares problem by calculating the scalar product of $|u^\lambda\rangle$ and $|v^\lambda\rangle$ with respect to the basis \{\ket{i}\} and basis \{\ket{j}\}. This gives
\begin{equation}
S = ||W_{ij} - \sum_{\lambda} c_\lambda u^\lambda_i v^\lambda_j||^2
\end{equation}
with $u^\lambda_i = \langle i|u^\lambda\rangle$ and $v^\lambda_j = \langle j|v^\lambda\rangle$. The coefficients $c_\lambda$ and the set of states \{\ket{u^\lambda}\} can then simply be calculated by setting the partial derivative of the quadratic norm in Eq. (3.13) with respect to $c_\lambda$ to zero and solve the normal equations by a singular value decomposition as follows
\begin{equation}
W = (W_{ij}) = \sum_{ij} \sum_{\lambda} c_\lambda u^\lambda_i v^\lambda_j = UDV^T.
\end{equation}
The matrix $D$ contains the $M_{\text{AS}}$ singular values of the matrix $W$, whereas $U$ and $V$ are orthogonal and of dimension $(M_{\text{AS}} \times M_{\text{AS}})$ and $(M_{\text{CS}} \times M_{\text{AS}})$, respectively. The optimal set of coefficients $c_\lambda$ are now given by the $m$ largest singular values. The optimal set of states for the reduced basis on the system \{\ket{u^\lambda}\} is given by the column vectors of $U$ corresponding to the largest singular values.
Furthermore, there exists a very interesting relationship between the reduced density matrix of the active subsystem $\rho_{\text{AS}}$ and the column vectors of matrix $U$ obtained from the singular value decomposition. Let us start by defining a many-particle density matrix operator $\hat{\rho}$ for a pure total-system state as defined in Eq. (3.9)
\begin{equation}
\hat{\rho} = |\Psi\rangle\langle\Psi| = \sum_{i'j'} W_{ij} W_{i'j'} |i\rangle\langle i'| \otimes |j\rangle\langle j'|.
\end{equation}
3.4. The role of the reduced many-particle density matrix

The active-subsystem reduced density matrix operator $\hat{\rho}_{AS}$ can be constructed from $\hat{\rho}$ by integrating out the states on the complementary subsystem which is equivalent to taking the trace over $\{|j\rangle\}$

\[
\hat{\rho}_{AS} = \text{tr}_{CS}\hat{\rho} = \sum_{j''} \sum_{i'j'} W_{ij} W_{i'j'} |i\rangle \langle i'| \otimes |j''\rangle \langle j'| |j''\rangle
\]

\[
= \sum_{i'j} W_{ij} W_{i'j'} |i\rangle \langle i'|.
\]  \hspace{1cm} (3.16)

Since the reduced density matrix can be expressed in terms of a matrix, an element of $\rho_{AS}$ is given by \((W)_{ii'} = \Sigma_j W_{ij} W_{i'j} \). We can use Eq. (3.14) to reformulate Eq. (3.16) to arrive at

\[
\rho_{AS} = WW^T = UDV^T VDU^T = U D^2 U^T \]  \hspace{1cm} (3.17)

where we have used the orthonormality of $V$. In Eq. (3.17) we could show that the optimal set of new basis states \(|u^\lambda\rangle\} diagonalizes the reduced density matrix $\rho_{AS}$ and are therefore eigenstates of $\hat{\rho}_{AS}$. In addition, the eigenvalues $w_\lambda$ of $\hat{\rho}_{AS}$ are given by $w_\lambda = c_\lambda^2$. Based on these findings, one can say that the optimal basis states can be found by diagonalizing the reduced density matrix of the active subsystem. The eigenvalues $w_\lambda$ can be interpreted as a selection criterion for choosing the new eigenstates, since the ground state of the system is optimal described by retaining those states with the largest weight $w_\lambda$ in a least-squares sense.

This can easily be shown by calculating the expectation value of a bounded Hermitian operator $\hat{A}$ acting on the active subsystem [124]. The expectation value is given by

\[
\langle \hat{A} \rangle = \frac{\langle \hat{A} \rangle}{\langle \Psi | \Psi \rangle} = \text{tr}_{AS}\hat{\rho}\hat{A}.
\]  \hspace{1cm} (3.18)

We can now express Eq. (3.18) in the eigenbasis of the density-matrix operator $\hat{\rho}$, yielding

\[
\langle \hat{A} \rangle = \sum_{\lambda=1}^{M_{AS}} w_\lambda \langle w_\lambda | \hat{A} | w_\lambda \rangle.
\]  \hspace{1cm} (3.19)

If the AS basis is now projected onto the $m$ basis states $|w_\lambda\rangle$ with largest eigenvalues $w_\lambda$, the approximated expectation value in the truncated basis reads

\[
\langle \hat{A} \rangle_{\text{approx}} = \sum_{\lambda=1}^{m} w_\lambda \langle w_\lambda | \hat{A} | w_\lambda \rangle.
\]  \hspace{1cm} (3.20)

Hence, the expectation value of a bounded operator is optimally described (in a least-squares sense) by a reduced basis that spans the AS subspace with those eigenstates of the reduced system density matrix corresponding to the largest eigenvalues.
The truncation procedure can also be explained as a variational principle for the wave function. The total-system state $|\Psi\rangle$ and the approximation to it, $|\tilde{\Psi}\rangle$, can be written in the Schmidt decomposition form,

$$|\Psi\rangle = \sum_{\lambda}^{M_{AS}} \sqrt{w_\lambda} |u^\lambda\rangle \otimes |v^\lambda\rangle$$  \hspace{1cm} (3.21)

and

$$|\tilde{\Psi}\rangle = \sum_{\lambda}^{m} \sqrt{w_\lambda} |u^\lambda\rangle \otimes |v^\lambda\rangle,$$  \hspace{1cm} (3.22)

respectively. Eqs. (3.21) and (3.22) are then used to calculate the quadratic norm $S$ as defined in Eq. (3.11) which defines the truncation error $\epsilon$,

$$|| |\Psi\rangle - |\tilde{\Psi}\rangle ||^2 = 1 - \sum_{\lambda=1}^{m} w_\lambda \equiv \epsilon$$  \hspace{1cm} (3.23)

with $\sum_{\lambda=1}^{M_{AS}} w_\lambda = 1$ since the density matrix in Eq. (3.15) was constructed from a pure state. The truncation error $\epsilon$ measures the sum of eigenvalues which are discarded by the truncation procedures and is therefore a key estimate for the accuracy of a DMRG calculation. Obviously, the performance of the truncation relies on a fast decay of the density-matrix eigenvalues $w_\lambda$. The total error of a DMRG calculation does not solely depend on the truncation error but also on the environment error as will be discussed below.

### 3.5 On the construction of an analytic DMRG wave function

In order to understand how DMRG [49] constructs the electronic wave function $\Psi_{A,el}^{(N)}$ for $N$ electrons in total electronic state $A$, we start from the full configuration-interaction (FCI) ansatz,

$$\Psi_{A,el}^{(N)} = \Phi_{A,FCI}^{(N)} = \sum_{I}^{M} C_{I}^{(A)} \Phi_{I}^{(N)} (\psi_{I_1}, \psi_{I_2}, \ldots, \psi_{I_N})$$  \hspace{1cm} (3.24)

(with $M = \infty$) which is an exact representation of an $N$-electron wave function if all Slater determinants $\Phi_{I}^{(N)}$ that can be constructed from a complete one-electron basis set $\{\psi_i\}$ — i.e., from the spin orbitals — are included in the superposition of configurations in Eq. (3.24). Note that then the one-electron basis set must be complete (implying an infinite number of elements), and hence the total number of configurations will be infinite.

In the basis of these $N$-electron functions $\Phi_{I}^{(N)}$, the electronic Hamiltonian $\hat{H}_{el}$ becomes a matrix $H = \{H_{KL}\}$, which requires the evaluation of $3N$-dimensional
3.5. Construction of the DMRG wave function

integrals $H_{KL} = \langle \Phi^{(N)}_K | \hat{H}_{el} | \Phi^{(N)}_L \rangle$. Such a high-dimensional integration is most conveniently carried out in second quantization which is in this context a clever book-keeping scheme for the implementation of the Slater–Condon rules for particle number conserving operator expectation values [67]. In addition, second quantization allows one to work in the Fock space where a simple tensor product structure ansatz for the wave function is possible and the antisymmetry requirement is elegantly built into the algebra of the elementary operators.

It is important to note here that for all such configuration-expansion methods — like FCI or the truncated CI methods — the $N$-electron basis set is explicitly constructed, and hence the Hamiltonian matrix elements can be explicitly calculated for these $N$-electron basis functions. However, it is only feasible if the one-electron basis set is finite so that the $N$-electron basis set is also finite though still extremely large. Since this large number of configurations can at most be handled up to about one billion [125], the standard approach in quantum chemistry is to reduce the number of configurations by imposing additional restrictions on the sum in Eq. (3.24), which can be a simple truncated CI expansion $\Psi^{(N)}_{A,el} \approx \Phi^{(N)}_{A,CI}$ with $M$ being finite, i.e., with a limited number of configurations $M$.

For large $M$, configurations can no longer be picked manually and an automatic scheme is to be defined though this may compromise the accuracy of the approximation. One scheme is the systematic substitution of one-electron functions in a reference $N$-electron basis function (e.g., substitution of molecular spin orbitals in the Hartree–Fock Slater determinant), which is usually denoted ‘excitation’ (it must not be confused with true electronic excitation as these occur between states $A$ expressed by different sets of CI expansion coefficients $\{C^{(A)}_I\}$, but expanded in the same set of $N$-electron functions).

Names for the CI substitution hierarchy are well-known: singles excitations, doubles excitations, triples excitations etc. as well as combinations of them. To improve on the expansion one may even start ‘excitations’ from a couple of pre-selected configurations (multi-reference CI). However, the most efficient scheme to select configurations is the coupled-cluster ansatz, which features excitation operators for singles, doubles, etc. in an exponential whose series expansion contains product excitations. If applied to an actual vacuum the excitation rank gets truncated at the number of total electrons. [33].

Of course, also the choice of the one-electron basis functions employed for the construction of configurations can determine the number $M$ of relevant configurations. One choice are natural orbitals, which diagonalize the one-electron density matrix and show a better convergence of the CI expansion than canonical Hartree–Fock orbitals [126]. In principle, any type of one-electron functions can be chosen for the construction of the determinants. Even atom-centered Gaussian basis functions, which are, in general, non-orthogonal, can be employed. For such non-orthogonal one-electron basis sets, the second-quantized electronic Hamiltonian involves then creation and annihilation operators that fulfill anticommutation relations involving elements of the (one-electron) overlap
3.5.1 Expansion of the DMRG wave function into Slater determinants

The DMRG wave function is constructed in a completely different way when compared to the CI excitation hierarchy as we shall see now. Since the limiting factor of all large CI or coupled-cluster calculations is the factorial growth of the number of \(N\)-electron basis functions with the excitation (substitution) grade and with the number of one-electron basis functions, we need to find a solution to the dilemma of including all possible configurations — because we cannot know in advance for any arbitrary molecular structure with a given number of electrons which Slater determinants will be most important — but without explicitly representing them. Hence, we must give up the explicit knowledge of the composition of our \(N\)-electron basis functions, but want to assure at the same time that any important configuration can be picked up. How can this be achieved?

It is clear that the expansion of the total DMRG state \(\Phi_{\text{A,DMRG}}^{(N)}\) must be in terms of \(N\)-electron basis functions, which are themselves CI-type (or even FCI-type) basis functions \(\Omega_{K}^{(N)}\),

\[
\Psi_{A,\text{el}}^{(N)} = \Phi_{A,\text{DMRG}}^{(N)} = \sum_{K} M' B_{K}^{(A)} \Omega_{K}^{(N)} \left( \{ \Phi_{I}^{(N)} \} \right) \tag{3.25}
\]

in order to span the same space. However, the explicit constitution of DMRG basis functions in terms of configurations \(\Phi_{L}^{(N)}\),

\[
\Omega_{K}^{(N)} = \sum_{L} D_{L}^{(K)} \Phi_{L}^{(N)} (\psi_{L1}, \psi_{L2}, \ldots, \psi_{LN}) \tag{3.26}
\]

can only be known in those cases for which a FCI or CASSCF reference calculation is still possible [98].

Some expansion coefficients \(D_{L}^{(K)}\) may be very close to zero, but they will still define a fixed ratio between all configurations considered. Thus, in order to have full flexibility of the individually contributing configurations \(\Phi_{I}^{(N)}\), the required number of DMRG states \(M'\) must not be too small and depends, of course, on the electronic structure to be studied. The number of DMRG basis functions \(M'\) can only be equal to one in the case for which \(\Omega_{1}^{(N)}\) is the FCI solution.

Now, assume that we are able to represent the electronic Hamiltonian in the basis of DMRG states \(\Omega_{K}^{(N)}\). Then the \(B_{K}^{(A)}\) are obtained simply by diagonalization of this Hamiltonian matrix (we do not discuss how the construction of the Hamiltonian is actually achieved, but may refer, for instance, to Ref. [98] for more details; for the diagonalization, a standard Davidson subspace iteration scheme can be used [127, 128]). The remaining (and most difficult) task to tackle is how to obtain the \(N\)-electron contraction coefficients \(D_{L}^{(K)} = \{ D_{L}^{(K)} \}\) for the configurations in Eq. (3.26) without ever knowing all configurations.
explicitly (as otherwise the advantage of DMRG fades away). In order to avoid the exponentially growing number of $N$-electron basis functions this has to be handled stepwise. i.e., the $N$-electron basis has to be successively constructed and then contracted. The contraction of the determinants must be done in such a way that the total electronic state $A$ can be represented best. Hence, we have to answer the question of how a contracted $N$-electron basis can represent the uncontracted FCI basis optimally. White showed in his early papers [53–55] that an optimum representation can be found by exploiting features of the reduced many-particle density matrix. The reduced many-particle density matrix in the context of the DMRG algorithm is not related to the one-particle or two-particle density matrix often encountered in quantum chemistry. It is the density matrix of a pure state where basis states in the Fock space spanned by some orbitals are integrated out. The eigenstates of the reduced density matrix with the largest eigenvalues minimize the quadratic norm between the uncontracted and contracted basis to obtain maximal overlap with the exact state.

In order to construct the DMRG basis functions $\Omega^{(N)}_K$, we proceed stepwise. First, we choose an active space of orbitals from which all configurations $\Phi^{(N)}_I$ could be constructed in principle. Their actual number, however, is too large to be manageable. Hence, we must construct the $\Omega^{(N)}_K$ functions by first considering only a few spin orbitals (the procedure can be easily generalized to spatial orbitals). Taking the first spin orbital from the active space, we can represent two states in this one-electron basis: occupied and unoccupied. Then we consider the next spin orbital from the active space which contributes two possible states (again: occupied and unoccupied) from which $2^2 = 4$ total states can be constructed. All these states defined on the first two spin orbitals can still be explicitly represented (also, note the different particle numbers of these states in Fock space). Considering the next four spin orbitals (yielding in total six spin orbitals), we have already $2^6 = 64$ total basis states with occupation numbers ranging from zero to six electrons. Now, this is already quite large (in the case of spatial orbitals we would have $4^6 = 4096$ many-electron states already) and we shall find a way to reduce the number of states defined on this subsystem of orbitals, which we shall call the active subsystem as it is constructed systematically.

As pointed out above, the eigenstates of the reduced density matrix are the means to accomplish the reduction (decimation). But then, we need to calculate the total electronic state first from the total Hamiltonian. Since we have considered only one part of the active space of orbitals, namely those orbitals that define the active subsystem, we are lacking any information about the remaining orbitals in the active space, which we call the complementary subsystem [98] and which functions as an environment to the active subsystem.

In general, we will not be able to construct the many-electron states on the large complementary subsystem of orbitals for the very same reason that we could not solve this task for the total active space of orbitals in the first place. There is thus only one option: we need to guess these states and hope that
we can find a way to make sure that the algorithm is able to pick up all relevant configurations defined on the complementary subsystem, a feature that will crucially determine DMRG convergence.

So, we express the electronic Hamiltonian in terms of a basis constructed as a tensor product from states \( \Omega_{AS,I}^{(N')} \) defined on the active subsystem and from (guessed) states \( \Omega_{CS,J}^{(N'')} \) defined on the complementary subsystem

\[
\Psi_{A,el}^{(N)} = \Phi_{A,DMRG}^{(N)} = \sum_{IJ} W_{IJ}^{(A)} \left[ \Omega_{AS,I}^{(N')} \otimes \Omega_{CS,J}^{(N'')} \right]
\]  

(3.27)

where we have as a natural boundary conditions for the electrons represented by these states \( N' + N'' = N \). This equation also explains why we have to take into account all states of different particle number defined on the two subsystems, \( N', N'' \leq N \).

Diagonalizing the total Hamiltonian in the basis of all \( \Omega_{K}^{(N)} \rightarrow \Omega_{AS,I}^{(N')} \otimes \Omega_{CS,J}^{(N'')} \) contracted functions yields the CI-type coefficients \( W_{IJ}^{(A)} \), which are, of course, related to the \( B_{K}^{(A)} \) coefficients of Eq. (3.25). Although these coefficients are obtained as a vector, they feature two indices, \( I \) and \( J \), in order to denote that they are defined with respect to a product basis. From the construction of the total electronic state \( A \) in terms of a tensor product basis of two determinants defined for the two subsystems that build up the complete electronic system it can be shown that DMRG iteratively refines a matrix product state [48,56,57,61,86,90,129–137].

In a computer program, all \( W_{IJ}^{(A)} \) form a single eigenvector for the electronic state \( A \), but since it is clear from the construction of the total Hamiltonian matrix what \( N' \)-electron active-subsystem state \( I \) has been combined (multiplied) with what \( N'' \)-electron complementary-subsystem state \( J \), the composite index \( IJ \) of each entry in the eigenvector is known. From this eigenvector, we now compute the reduced density matrix by summation over all complementary-subsystem states for a given state \( I \) of the active subsystem. The active-subsystem reduced density matrix operator is given in Eq. (3.16).

Next, we include into our systematic construction procedure also all one-electron states defined on the next orbital to be incorporated into our explicitly constructed (i.e., ‘active’) subsystem. This enlarges the dimension of all many-electron states that can be represented on the enlarged active subsystem from \( m \) to \( 2m \) in the case of spin orbitals (and to \( 4m \) in the case of spatial orbitals).

We can then use the same procedure to again reduce (i.e., to ‘renormalize’) the size of the basis back to only \( m \) contracted many-electron states by (1) setting up the total Hamiltonian, (2) diagonalizing it, (3) constructing the active-subsystem reduced density matrix, (4) selecting those \( m \) eigenvectors with largest eigenvalue to set up the renormalization matrix, and (5) to renormalize the many-electron states defined on the active subsystem with this matrix.

Hence, in each DMRG iteration step, we have a modified basis representation for the many-electron states composed from the states defined on \( AS \) and on
Construction of the DMRG wave function

\[ \Omega_{AS,i}^{(N',i)} = \sum_{L} R_{AS,L}^{(i)} \Phi_{L}^{(N')} \]  
(3.28)

\[ \Omega_{CS,J}^{(N'',i)} = \sum_{L} R_{CS,L}^{(j)} \Phi_{L}^{(N'')} \]  
(3.29)

with weights \( R_{AS,L}^{(i)} \) and \( R_{CS,L}^{(i)} \) changing in each DMRG iteration step \( i \). Note that \( M' \) in Eq. (3.25) refers to the number of DMRG states before decimation and is therefore given by \( M' = (2m) \times (2m) = 4m^2 \) (or \( M' = (4m) \times (4m) = 16m^2 \) in the case of spatial orbitals). The changes of the weights are, of course, determined by the eigenvectors of the reduced density matrix [98]. The procedure described terminates when the last orbital is picked from the set defined by the active space. Then, the active subsystem comprises all orbitals and no environment (complementary subsystem) is left over. Once this is achieved, a so-called sweep has been completed, which we occasionally also call a completed macroiteration step. Consequently, we have then obtained a first approximation to the electronic state by sequential renormalization steps. From the description of the algorithm given so far, it is clear that the quality of the renormalized basis \( \{ \Omega_{K}^{(N)} \} \) will depend on how good our guess was for the states defined on the complementary subsystem, which had been used to construct the total Hamiltonian matrix affecting thus its eigenstates and hence also the reduced density matrix.

Therefore, the algorithm must be supplemented by a means to improve the complementary (environment) states. This can be done by a rather ingenious trick: The sequence of orbitals picked up step-by-step by the algorithm defines the orbital ordering (a purely technical term of the DMRG algorithm). After having completed the first sweep, the orbital ordering has been fixed. Now, we reverse this ordering and start with the orbital included in the last step to proceed with the algorithm. We take the second last orbital to explicitly construct many-electron states on this new active subsystem. For the construction of the total Hamiltonian we require renormalized states defined on the new complementary subsystem, i.e., on the active space without the two orbitals that define the new active subsystem. But these complementary states we can take from the second last step in our first sweep if stored in this first sweep. In such a way, the active subsystem constructed stepwise in the previous sweep is now taken as the complementary subsystem. And if we iterate this process, i.e., sweeping with change of direction along the orbital ordering, we can sequentially improve the states defined on the complementary subsystem (the active-subsystem states are always constructed systematically as described above).

Once these macroiterations are converged, the final DMRG basis functions \( \{ \Omega_{K}^{(N)} \} \) have been found. Since their structure in terms of determinants cannot be known for active spaces larger than about 18 electrons in 18 active spatial orbitals, the DMRG algorithm produces renormalized operator representations.
in this basis instead (rather than the renormalized basis itself). Since all observables, and especially the energy, can be expressed in second quantization employing annihilation and creation operators defined for the orbitals of the active space, all what needs to be done is to renormalize the matrix representation of these creation and annihilation operators. All observables can then be constructed from these matrices. Having said this, it is obvious how to construct the matrix representation of the total Hamiltonian constructed from active and complementary subsystem states. Since creation and annihilation operators for the orbitals have been defined with respect to the active and complementary subsystems’ bases, they can simply be used to set up the electronic Hamiltonian for the complete active space via direct products and matrix additions.

Now we know how to systematically construct a pre-contracted $N$-electron basis that can eventually pick up all relevant configurations, if the environment guess in the first step allows for this. The basis itself is (in general) never explicitly constructed and instead we have access only to operators expressed in second quantization in terms of this basis.

### 3.6 Controlling the accuracy of the DMRG algorithm using an automated Richardson-type extrapolation

Despite its very short history, for electronic structures featuring pronounced static electron correlation effects DMRG has already become a true competitor to standard quantum chemical methods like coupled-cluster or multi-configuration self-consistent field approaches. DMRG requires in the first macroiteration (sweep) a guess for the so-called environment states (see below for further explanations). The quality of this guess crucially determines the convergence behavior of the subsequent iteration steps — especially if no convergence acceleration is invoked or if $m$ is chosen to be small as we shall discuss later in this work. Hence, DMRG calculations involve steps which may lead to numerical instability and which make the development of rigorous and automatic convergence control procedures difficult.

Though results from DMRG calculations are currently simply denoted by this single abbreviation 'DMRG', it should be understood that DMRG results are obtained for a chosen number $m$ of renormalized DMRG system states and their accuracy thus depends on this number. On the one hand, if $m$ is chosen sufficiently large — as is possible in the highly efficient and parallel implementation by Chan et al. [82–84] and Kurashige and Yanai [138] — one may always expect to reach the FCI result in the chosen active space, although these calculations will be prohibitively expensive in terms of computing time. On the other hand, a small $m$ would increase the DMRG applicability range to large molecules, but it may also introduce a non-negligible error in the electronic energy. Moreover, a minimal value $m$ required for sufficient accuracy will always depend on the size of the active space and on the molecular structure under investigation.
For this reason, Chan et al. [86,91] argued that the standard DMRG algorithm works best for molecular structures that resemble a spatially extended structure like the spin chains in solid state physics for which it was originally developed. To overcome this, the concept of tensor network states [132,134,136,137,139,140] might be useful which allows for a more flexible (non-linear) construction of approximate basis states for a better representation of the total electronic state. Such new concepts may be very helpful for the extension of the algorithm to the regime of spatially compact structures or structures for which localized orbitals are not easily available as we will elaborate on in the later chapters 4 and 5.

In the past years, we have studied the DMRG algorithm from a different perspective. Since molecular orbitals are generically non-local and the spatial locality idea of solid state physics is therefore not directly applicable, we investigated the 'generic' DMRG algorithm. For this, we looked at the significance of the orbital ordering [96] and at the construction of the first guess for the environment states [97]. It soon turned out that one may easily converge to local minima as already summarized by White in 2005 [95] for the one-site DMRG algorithm. Nevertheless, while the pioneering papers by Chan and collaborators did touch this issue only briefly, we considered it worthwhile to provide more details on these failures. The reasons why Chan et al. did not elaborate more on these issues are probably two-fold. Firstly, if the number of \( m \) DMRG states is sufficiently large, convergence to a local energy minimum is not likely to occur. Secondly, these authors always applied a sort of convergence acceleration absent in our first studies of the generic algorithm.

A simple but efficient convergence acceleration is the addition of white noise to the transformation matrix at the initialization procedure in the first macroiteration of the DMRG procedure as this will randomly mix in environmental states that otherwise might never have been picked up. At first sight, the addition of white noise seems to be a shaky recipe in quantum chemical calculations, but it is very efficient. Moreover, White [95] has introduced a perturbative correction which allows one to pick up missing states in the environment through a more deterministic scheme. How the addition of noise can be most efficiently done has been investigated by Chan and Head-Gordon [92] and Kurashige and Yanai [138].

In this section we elaborate on ideas by Mitrushenkov et al. [87], Chan and Head-Gordon [92] as well as by Legeza et al. [141] and aim at a routine extrapolation scheme that may allow the automatic termination of DMRG calculations as well as a reduction to a minimal number of \( m \) renormalized DMRG system states supplemented by a reliable error estimate on the electronic energy obtained. Especially the latter is decisive for routine calculations of potential energy surfaces requiring an overall constant error in the electronic energy (for smooth surfaces) at the cost of a number of DMRG system states \( m \) that depends on the molecular structure \( R, m = m(R) \).

We present an automated DMRG error protocol which maps the electronic energies of DMRG calculations with different numbers \( m \) of renormalized DMRG
system states to a rational function which can then be used to extrapolate to an estimate for the fully converged electronic energy. This automated DMRG control scheme is based on Richardson’s deferred approach to the limit [142,143]. The error estimates function as a tool to assure the accuracy of the extrapolated energy and allow us to compare different DMRG energies without referring to the number of renormalized states \( m \). As a consequence, we can assure that the energies along a potential energy surface are equally accurate. Our general goals here are to investigate whether the DMRG energies can be systematically improved and whether the extrapolation procedure can be applied to different molecular systems.

The truncation error \( \epsilon \) can be used as a measure of the accuracy of the DMRG calculation [141,144]. If the eigenvalue spectrum decays fast, the truncation error is small and therefore we can truncate the basis without losing any accuracy in the description of the system.

In numerical studies it is found that the truncation error \( \epsilon \) decreases by increasing the number of \( m \) DMRG states [82,141]. In principle, the DMRG calculations can be fully converged as is evident if the increase in \( m \) does not change the energy anymore. This case corresponds to a truncation error of zero since all important electronic contributions are picked up. One can therefore assume to obtain energies of FCI accuracy by extrapolating the truncation error to zero.

In quantum chemistry, however, we do not need to account for all basis states of the Hilbert space if chemical accuracy of roughly 1 kcal mol\(^{-1}\) in relative energies is required. Therefore the number of DMRG states can, in principle, be set to a much smaller value which results in calculations that are feasible for large chemical systems such as transition metal clusters where a large active space is mandatory [105].

The two sources of error in the DMRG algorithm are the truncation of the basis and the initial guess of the basis states on the complementary system (environment). The truncation error shall be reduced by the automated error protocol to be devised here. The environmental error manifests itself in convergence to a local minimum of the electronic energy. Local minima can be encountered if certain important states are not initially represented in the basis of the environment. If these states are lacking in the guessed initial environment, they will never show up in the reduced density matrix and in the wave function. In such cases, we shall aim at a convergence control protocol that is able to detect the local minima.

The convergence behavior of the DMRG algorithm relies heavily on the way the initial environment basis is built up [96]. We suggested [97] the use of a nested DMRG start-up procedure where one starts with a small number of DMRG states and increases \( m \) subsequently to the desired value. To capture the essential environment states in the case of the first small \( m \) values, the addition of white noise to the reduced density matrix [92] or the perturbative correction [95] is recommended. However, these schemes do also not guarantee convergence to the global energy minimum. Despite these numerical difficulties we still shall
aim for an analytic convergence control protocol even if this might occasionally fail to rigorously extrapolate the low-\(m\) approximations to the electronic energy, which is tolerable as long as the scheme is capable to 'interpolate' the collected data points with then limited extrapolation capacity.

A major advantage of such an automated convergence control scheme will be evident when considering relative energies. So far, relative energies were computed between DMRG calculations with the same number of renormalized DMRG basis states \(m\) neglecting the fact that some total states might then be better described than others (see, e.g., the curve crossing in CsH [104]). If one can define an error estimate for a total energy, the number of states \(m\) may be chosen such as to produce the same error estimate for all energies that are to be compared. In this way, the calculation of relative energies becomes somewhat independent of the chosen \(m\), and hence \(m\) can be adjusted as needed.

### 3.6.1 Review of extrapolation approaches

It has already been realized since the introduction of the DMRG algorithm in quantum chemistry that extrapolation is feasible to approach the FCI energy [144]. Chan and Head-Gordon [92] developed an empirical expression for the relative error \(\Delta E(m)\) as a function of the \(m\) DMRG states obtained from calculations on the Ne atom and the water molecule,

\[
\ln |\Delta E(m)| = -k (\ln m)^2 \tag{3.30}
\]

where \(k\) is a system-specific parameter determined by a linear regression analysis. Eq. (3.30) was then validated for a chain of hydrogen molecules, dinitrogen for which 25 orbitals were used in the active space, and water in a DZP basis with 28 active orbitals.

Mitrushenkov et al. [87] improved on the extrapolation scheme suggested by Chan and Head-Gordon [92] by increasing the flexibility of Eq. (3.30). The extrapolation is performed in terms of the incremental energies \(\Delta E_m = E_m - E_{m-1}\) to the asymptotic value within the appropriate range of \(m\) by the following formula,

\[
\lim_{m \to \bar{m}} \Delta E_m = \lim_{m \to \bar{m}} \frac{c + dE_m}{f_m} = 0 \tag{3.31}
\]

with

\[
f_m \sim \sqrt{m^2 n^4 + 2m^3 n^2} \tag{3.32}
\]

where \(n\) is the number of orbitals and \(m\) the number of DMRG states. In Eq. (3.31), the parameters \(c\) and \(d\) are determined by a fit to the calculated DMRG data.

Since the truncation error \(\epsilon\) measures the missing contribution of the neglected eigenvectors to the trace of the reduced density matrix, Legeza et al. [141] proposed a dynamic block state selection protocol to attain a certain accuracy in the DMRG energy. The underlying idea is that the number of DMRG states
may vary in each iteration step in such a way that the truncation error in
the renormalization step can be kept constant. The authors showed for the $F_2$
molecule that the spectrum of eigenvalues of the reduced density matrix decays
exponentially upon convergence. For methylene with 13 active orbitals, a linear
relationship was found between the truncation error $\epsilon$ and the absolute error
in the energy which led to an extrapolation formula of the form
\[
\ln \frac{E_{\text{DMRG}} - E_{\text{FCI}}}{E_{\text{FCI}}} = a \ln \epsilon + b \tag{3.33}
\]
where $E_{\text{FCI}}$, $a$, and $b$ are obtained from a fit to the numerical data.
It is clear that any extrapolation and hence also the one based on the truncation
error $\epsilon$ in Eq. (3.33) will be difficult if numerical instabilities occur. Then
the quantity to be extrapolated does not smoothly depend on the parameters
of the calculation. As an example, we refer to the kinks in energy versus
truncation error plots of Ref. [112] obtained for spin model Hamiltonians (see
also Ref. [87]). Such kinks also occur in quantum chemical DMRG calculations
if the environment guess in the first sweep was not appropriate and convergence
to a local energy minimum occurs as we shall discuss in more detail later.

### 3.6.2 Automated DMRG error protocol

A drawback of all extrapolation schemes discussed so far is that they represent
a posteriori extrapolations rather than extrapolations on the fly which could
be exploited for convergence control. We shall now present an extrapolation
protocol of this latter type.

The core of our automated DMRG error protocol is Richardson’s deferred ap-
proach to the limit [142, 143]. The idea is that the result of a numerical
calculation is an analytical function of an adjustable parameter $h$. This analyt-
ical function is probed at various values of $h$ until sufficient knowledge about
the behavior of the function has been accumulated. None of these calculations
needs to be of the accuracy desired. The next step is to fit the obtained data
to the analytic function and then evaluate it at $h = 0$ which is expected to be
the exact result. In case of our implementation, the parameter $h$ corresponds
to the number of many-particle DMRG states $m$ which then determines the
truncation error $\epsilon$.

Of course, one has to choose the proper form of the fitting function to apply this
extrapolation. In a Richardson-type algorithm, the extrapolation is performed
using rational functions which overcomes the constraint of the power series
and its limited radius of convergence [143]. The rational functions used in our
approach can be written as
\[
E^{(\nu \nu)}(\epsilon) = \frac{P_\mu(\epsilon)}{Q_\nu(\epsilon)} = \frac{p_0 + p_1 \epsilon + \cdots + p_\mu \epsilon^\mu}{q_0 + q_1 \epsilon + \cdots + q_\nu \epsilon^\nu} \tag{3.34}
\]
where $\mu$ and $\nu$ are the orders of the polynomials in the denominator and in
the numerator, respectively, and are determined by the number of data points.
This ansatz has the advantage of enlarged flexibility to overcome the rigidness of fixed analytical expressions used in previous extrapolation schemes as discussed in the last section. In particular, one can expect that the flexibility is sufficient to deal with kinks in the raw-data dependence of $E^{(\mu\nu)}$ on $\epsilon$. Note in particular that the degree of the polynomials, $\mu$ and $\nu$, increases with the number of data points. All data points are exactly represented by the rational function.

For the rational function extrapolation, the Bulirsch–Stoer algorithm was used which is based on a recurrence relation similar to the Neville extrapolation algorithm for polynomials [143]. In the Neville algorithm, a tableau is constructed column by column where the entries are subsequently build up starting with unique polynomials of degree zero passing through each of the data points. The tableau is then filled from left to right by values corresponding to polynomials of higher orders leading to a single value at the extreme right. Now for the Bulirsch–Stoer extrapolation algorithm with rational functions, a tableau is also constructed producing a result and an error estimate. The orders of the polynomials in the denominator and numerator in Eq. (3.34) are equal if the number of data points is even. If, however, the number of data points is odd the degree of the denominator is increased by one. For the derivation of this standard algorithm we refer the reader to Ref. [145].

The automated DMRG procedure spawns a DMRG calculation at a predefined number of renormalized states $m$. The number of DMRG system basis states $m$ is then subsequently increased by a constant factor. At each value of $m$ a DMRG calculation is converged. The last sweep after convergence is used to identify the microiteration where a maximal truncation error $\epsilon$ occurred. The truncation error and the corresponding energy value are stored for the extrapolation step. After the first three DMRG calculations, an extrapolation of the energies to a truncation error of zero with rational functions is performed and delivers an error estimate. The error protocol algorithm decides if another DMRG calculation with an increased number of DMRG basis states $m$ is required or if the error estimate is within a previously defined threshold, which would stop the automated DMRG extrapolation. This scheme allows us to obtain DMRG results with a controllable constant accuracy in the energy. In Figure 3.3, a flowchart describing the protocol is presented.

We have already mentioned that we expect the rational-function ansatz to be flexible enough in order to deal with discontinuities in the numerical raw data. Recall that kinks may show up if the guess for the environment states in the first sweep turns out to be not sufficient. In such cases the set of data points is still exactly represented by the rational function. However, the extrapolated energy might then be somewhat higher than the best energy in the data set. This is a clear indication of a numerical instability (kink) and can be automatically detected by the convergence protocol. Then, additional DMRG steps with increased $m$ values are carried out until this deficiency is cured (if the deviation is small and the accuracy sufficient, the DMRG iterations may equally well be stopped).
3. A new paradigm for quantum chemistry: DMRG

Figure 3.3: Flowchart of the automated DMRG control facility using the Richardson-type rational function extrapolation procedure as described in the text. The initial calculations are necessary for a first extrapolation guess. Three initial DMRG calculations are usually sufficient to start with. In the next step, the DMRG calculations are analyzed and the required information to perform the extrapolation are extracted from the DMRG output. A Richardson-type extrapolation to a truncation error of zero using rational function is then applied which delivers an error estimate. Based on this error estimate, the algorithm decides if a new DMRG calculation with more DMRG basis states should be started or if the DMRG energy is converged to a certain accuracy.

It is important to understand that our algorithm detects any such kinks in the data set and points the user to those $m$ values that led to a local energy minimum. Once such a kink has been found and an extrapolated optimal minimum $m$ value has been obtained from extrapolation, one may always run one or a few additional DMRG calculations with slightly larger $m$ value than
3.6. Accuracy control using extrapolation techniques

the recommended one in order to probe the extrapolated result. This is still more efficient than to use a brute force scheme choosing \( m \) as large as possible (computationally feasible). We shall now see how this works in numerical case studies.

3.6.3 Assessment of the DMRG control on the relative energies on the ground-state potential energy surface of H\(_2\)O

Since a single example is not sufficient for a proof-of-principle study, we are advised to investigate relative energies for another test system that features a different type of electron correlation. In this section, the behavior of the automated DMRG error protocol is examined for the relative energy of two water structures — one with stretched bond lengths — with the threshold for the error estimate set to \( 10^{-5} \) \( E_h \).

We report DMRG calculations at the equilibrium geometry 1 and at another geometry 2 where the OH bond lengths are stretched by 1.5 times its equilibrium bond length of 1.843 45 Bohr. Both structures are considered in \( C_{2v} \) symmetry where the HOH angle is fixed to 110.6 degrees. The selected geometries are consistent with the ones previously reported in FCI studies on water by Saxe et al. [146] and Olsen et al. [147]. We have used the DZ basis of Dunning [148] neglecting polarization functions. All ten electrons have been correlated which produces in total 1'002'708 determinants in \( A_1 \) symmetry. The one-electron and two-electron integrals were calculated for canonical Hartree–Fock orbitals.

Table 3.1: Extrapolation of the energy of two H\(_2\)O structures 1 and 2 on the ground-state potential energy surface using the automated DMRG error protocol. All calculations are performed in a DZ basis. The threshold of the convergence criteria for the error estimate is set to \( 10^{-5} \) \( E_h \).

<table>
<thead>
<tr>
<th>( M )</th>
<th>( E_1/E_h )</th>
<th>( E_2/E_h )</th>
<th>( \Delta E/E_h )</th>
<th>( \Delta E/\text{kJmol}^{-1} )</th>
</tr>
</thead>
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<tr>
<td>32</td>
<td>−76.155 224 32</td>
<td>−76.009 421 30</td>
<td>−0.145 803</td>
<td>−382.81</td>
</tr>
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<td>−76.010 221 19</td>
<td>−0.145 785</td>
<td>−382.76</td>
</tr>
<tr>
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<td>−76.011 057 95</td>
<td>−0.145 072</td>
<td>−380.89</td>
</tr>
<tr>
<td>54</td>
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<td>−76.011 961 08</td>
<td>−0.144 739</td>
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</tr>
<tr>
<td>64</td>
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<td>−76.012 549 62</td>
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<td>−379.14</td>
</tr>
<tr>
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<td></td>
</tr>
<tr>
<td>91</td>
<td>−76.157 430 97</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>109</td>
<td>−76.157 481 77</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Extrapolated
| Extrapolated | −76.157 506 91 | −76.014 542 47 | −0.142 964 | −375.35 |

Error estimate
| 2.7\( \times 10^{-5} \) | 4.1\( \times 10^{-5} \) |

FCI
| −76.157 865 95 | −76.014 476 58 | −0.143 389 | −376.47 |
In Table 3.1, the results of the automated DMRG error protocol are shown. The DMRG calculations are started at \( m = 32 \), a value which was then increased steadily by a factor of 1.2 as in the case of CoH. The extrapolated number of DMRG basis states for structure 1 is \( m = 112 \) and for structure 2 \( m = 101 \). This indicates that the convergence of the DMRG algorithm for structure 2 is somewhat smoother compared to structure 1 and an extrapolation can be already applied at \( m = 64 \) to get accurate extrapolated energies. Note again that the DMRG algorithm is capable of describing relative energies qualitatively correct even for a very small number \( m \) of DMRG basis states.

The automated DMRG error protocol stops the DMRG calculation before the DMRG energies are converged to the exact FCI energies as a consequence of the chosen threshold. The extrapolated DMRG energies, however, recover a major part of the missing electron correlation. In this case, the extrapolation procedure is not only able to approach the FCI reference energy but also to significantly improve the relative energy between the two structures. We also see that the error estimate of an Richardson-type extrapolation can be used to describe relative energies accurately, to monitor the convergence of DMRG calculations, and to produce DMRG energies of the desired accuracy.

Finally, we shall investigate the kink problem for DMRG convergence in both H\(_2\)O structures. Since the threshold has not been set as tight as in the CoH case, we may expect a less smooth structure of DMRG energies depending on the truncation error \( \epsilon \). For both structures we find kinks (for structure 1 even two). These are detected by our automatic extrapolation facility. In view of DMRG convergence for H\(_2\)O in its equilibrium structure 1 the question arises whether extrapolation for only the last three points after the kink might be more efficient than employing all data points. If only these last three data points are used, we arrive at an extrapolated energy of \(-76.15748705\) a.u. with an error estimate of \(1.89 \times 10^{-6}\). This energy is very similar to (even slightly higher than) the result of the unmodified algorithm in Table 3.1, \(-76.15750691\) a.u., and thus does not point to a modification of the standard protocol. Recall, however, that an extrapolation within a reduced set of data points also reduces the flexibility of the rational function and has to be considered with care despite the fact that the numerical instability (and the prior data points leading to this kink) has been excluded from the reduced data set.

As a final remark, we shall note that we also carried out all these calculations with white noise applied to the environment in the first sweep to investigate whether the kinks remain or whether they are numerical artifacts of the generic DMRG optimization. The energies used for the extrapolation are then slightly below those reported here (on average by \(5 \times 10^{-5}\) a.u., the effect is larger for the equilibrium structure 1 than for 2 as one would have expected in view of the convergence reported in Table 3.1), but still feature the kinks and hence all discussion of the extrapolation protocol so far also holds for these calculations including the application of noise.
3.7 Illustrative results

3.7.1 Remark on the convergence of total DMRG energies

The convergence of total energies with the DMRG algorithm is not trivial [3]. One may converge to local energy minima — especially in the one-site DMRG variant [95] but also for two-site DMRG calculations [96,97] — if not measures against it are taken like white noise [92], perturbative correction [138], entropy-based orbital ordering, dynamic block state selection (DBSS) and configuration-interaction dynamically extended active space (CI-DEAS) procedures [81,88,89,141]. The converged DMRG energy may depend on various parameters that are not clearly visible if only the attribute 'DMRG' is given in order to characterize it. There exists currently no established notation for DMRG calculations. They differ in the number of AS states \( m \), in the number of active electrons and active orbitals, in the type of orbitals used to generate the one- and two-electron integrals. The orbitals can be relaxed or kept frozen. And finally, DMRG iterations have not a well defined end point as the total electronic energy may converge in jumps. Especially the fact that the orbitals can be relaxed makes DMRG total energies difficult to compare in cases where orbital relaxation was not carried out. Of course, within a series of calculations the relative energies are meaningful and can be compared with those from a series with differing set up.

3.7.2 Performance on spatially non-extended molecular systems

The DMRG algorithm is known to reach the FCI accuracy for molecular systems [79,82–85]. In a pioneering study, we investigated DMRG for the prediction of relative energies of transition metal complexes and clusters of different spin and molecular structure [105], namely on cobalt hydride and the binuclear oxo-bridged copper clusters. In the first case, we examine if DMRG provided accurate spin-splitting between the singlet and triplet state of CoH. In the latter study, we evaluate the DMRG algorithm for the accurate description of the relative energies between two isomers on the same potential energy surface. We should emphasize that even though DMRG/MPS can be systematically improved to reach FCI accuracy by increasing the number of DMRG states \( m \), it is for many interesting chemical problems not at all required to do so. To understand reaction mechanisms in chemistry, accurate relative energies between two isomers or spin states are decisive. In 2008, we found [105] that an MPS parametrization lead to qualitatively correct relative energies between two spin states although the absolute energies for each of the states were not fully converged.

Table 3.2 lists the relative energies of the DMRG calculations on the singlet and triplet state of CoH (the size of the active space is 10 electrons in 14 molecular orbitals). Note that already for 100 DMRG states the relative energy has converged within chemical accuracy. However, this cannot be expected in
A new paradigm for quantum chemistry: DMRG

In particular, the calculation of the relative energies between two spin states for a fixed number \( m \) of renormalized states is not ideal since for a given number of DMRG block states either the singlet or the triplet state might be better represented. Our recently improved version of the DMRG algorithm incorporating principles from quantum information theory allows us to obtain a desired error bound in the DMRG energies using the above-mentioned DBSS and CI-DEAS procedures [149]. The DBSS method monitors the quantum information loss during the renormalization step and thus assures the selection of an appropriate number of DMRG states for a desired accuracy in the energies for both spin states. We also considered the problem of varying block state numbers \( m \) for different states or structures by application of an extrapolation protocol demonstrated at the CoH example [123].

Table 3.2: Results of CASSCF and CASPT2 reference and DMRG calculation for the singlet and triplet states of CoH for 10 electrons distributed over 14 active spatial orbitals in Hartree atomic units. Relative energies are given in kJ mol\(^{-1}\).

<table>
<thead>
<tr>
<th>method</th>
<th>( E_{\text{singlet}}/E_h )</th>
<th>( E_{\text{triplet}}/E_h )</th>
<th>( \Delta E/\text{kJ mol}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMRG((m=64))</td>
<td>-1381.977 619</td>
<td>-1382.020 168</td>
<td>111.7</td>
</tr>
<tr>
<td>DMRG((m=100))</td>
<td>-1381.979 697</td>
<td>-1382.020 507</td>
<td>107.2</td>
</tr>
<tr>
<td>DMRG((m=400))</td>
<td>-1381.981 062</td>
<td>-1382.020 808</td>
<td>104.4</td>
</tr>
<tr>
<td>DMRG((m=600))</td>
<td>-1381.981 090</td>
<td>-1382.020 812</td>
<td>104.3</td>
</tr>
<tr>
<td>CASSCF((10,14))</td>
<td>-1381.981 097</td>
<td>-1382.020 814</td>
<td>104.3</td>
</tr>
<tr>
<td>CASPT2((10,14))</td>
<td>-1382.192 371</td>
<td>-1382.242 103</td>
<td>130.6</td>
</tr>
<tr>
<td>DFT/BP86</td>
<td>-1383.504 019</td>
<td>-1383.585 212</td>
<td>213.1</td>
</tr>
<tr>
<td>DFT/B3LYP</td>
<td>-1383.202 267</td>
<td>-1383.279 574</td>
<td>203.0</td>
</tr>
</tbody>
</table>

Accurate energies for the spin splitting of the singlet and triplet state of cobalt hydride were obtained. We demonstrated that the DMRG algorithm is capable of solving the spin state problem in quantum chemistry for mononuclear transition metal complexes [26, 27, 150, 151].

Based on our numerical DMRG studies of the mononuclear complexes, we made the interesting observation that the relative energy appears to converge faster than the total absolute energy when increasing the number of DMRG states [105]. We note that no white noise or perturbative correction was applied. Nevertheless, a smooth convergence to the reference energy by increasing successively the DMRG basis states could be achieved.

After the successful application of the DMRG algorithm to the spin state problem, we tackle the question whether a reliable calculation of relative energies on a given potential energy surface of the same total spin is possible. Note that DMRG is also well suited for complex electronic structures that require
large active spaces already for a qualitatively correct description of the ground state wave function. As an example, we investigate oxygen-bridged dicopper transition metal clusters previously studied by Cramer et al. [152, 153].

Table 3.3: Relative energies of $\mu$-η$^2$:η$^2$ peroxo and bis(μ-oxo) $[\text{Cu}_2\text{O}_2]^2^+$ isomers with $D_{2h}$ symmetry in an active space of 44 orbitals with 26 electrons. The superscript ($wn$) denotes DMRG calculations where white noise has been applied as described in Ref. [92] and bs stands for a broken-symmetry solution. The DMRG results by Kurashige and Yanai [138] were obtained for a larger active space of 32 electrons in 62 orbitals and with White’s perturbative correction. While total electronic energies are given in Hartree ($E_h$), the relative energies $\Delta E$ are given in kJ/mol.

<table>
<thead>
<tr>
<th>method</th>
<th>$E_{\text{bisoxo}}/E_h$</th>
<th>$E_{\text{peroxo}}/E_h$</th>
<th>$\Delta E$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CASSCF(8,8) [105]</td>
<td>-541.431 345</td>
<td>-541.425 641</td>
<td>-15.0</td>
</tr>
<tr>
<td>CASPT2(8,8) [105]</td>
<td>-541.505 663</td>
<td>-541.510 178</td>
<td>11.9</td>
</tr>
<tr>
<td>CASSCF(16,14) [152]</td>
<td>-541.503 07</td>
<td>-541.503 45</td>
<td>1.0</td>
</tr>
<tr>
<td>CASPT2(16,14) [152]</td>
<td>-542.062 08</td>
<td>-542.064 35</td>
<td>6.0</td>
</tr>
<tr>
<td>bs-B3LYP [152]</td>
<td>-544.194 19</td>
<td>-544.278 44</td>
<td>221.2</td>
</tr>
<tr>
<td>RASPT2(24,28) [154]</td>
<td></td>
<td></td>
<td>119.7</td>
</tr>
</tbody>
</table>

DMRG energies from Ref. [105]

| DMRG ($m$=64) | -541.456 375 | -541.479 969 | 61.9 |
| DMRG ($m$=100) | -541.463 697 | -541.494 473 | 80.8 |
| DMRG ($m$=200) | -541.466 781 | -541.496 680 | 78.5 |
| DMRG ($m$=400) | -541.467 527 | -541.497 171 | 77.8 |
| DMRG ($m$=600) | -541.467 721 | -541.497 274 | 77.6 |
| DMRG ($m$=800) | -541.467 794 | -541.497 314 | 77.5 |

DMRG energies ($\text{new code [155]}$)

| DMRG ($m$=32) | -541.440 272 | -541.478 196 | 99.6 |
| DMRG ($m$=44) | -541.446 006 | -541.483 405 | 98.2 |
| DMRG ($m$=64) | -541.458 021 | -541.497 468 | 103.6 |
| DMRG ($m$=128) | -541.473 082 | -541.514 702 | 109.3 |

| DMRG ($wn$) ($m$=128) | -541.476 645 | -541.515 621 | 102.3 |
| DMRG ($m$=2400) [138] | -541.968 391 | -542.025 139 | 149.0 |

From a qualitative picture of the electronic structure of binuclear transition metal clusters, we concluded in Ref. [105] that the one-particle active space must be doubled compared to the mononuclear transition metal complexes in order to retain a qualitative correct description of the wave function. At present, the only multireference method able to deal with such large active spaces is the DMRG algorithm. In Table 3.3, we compare the DMRG energies from
our original work in Ref. [105] with new results obtained with our new DMRG code [155] where the environment basis is built up as described in Ref. [97]. For these DMRG calculations, the same active space, basis set and effective core potential as in Ref. [105] was used. For the Cu we employed the Stuttgart pseudopotential and associated basis functions (ECP10MDF) [156] and for O a [14s9p4d|4s3p2d] contracted ANO basis set [157]. From Table 3.3 it is clear that the guess of the environment has a large effect on the DMRG energies. We now achieve lower DMRG energies at smaller $m$ values even without the application of noise or a perturbative correction. If we apply noise for $m = 128$ DMRG states, however, the absolute DMRG energies are lower but the relative energy lies in the same region.

Kurashige and Yanai [138] provided the best reference data available so far for the binuclear copper cluster. Their best results are incorporated in Table 3.3. Note the larger active space and the one order of magnitude larger number of renormalized states $m$. Their expensive reference DMRG calculations clearly support our findings made previously in Ref. [105] that the DMRG algorithm is ideally suited to provide a qualitatively correct description of the relative energies in transition metal chemistry of open-shell complexes and clusters. However, it is also clear that a low number $m$ of DMRG basis states is desirable for feasibility reasons, though $m = 128$ is apparently not yet sufficient for quantitative agreement. Nevertheless, our small-$m$ DMRG results are already in good agreement with RASPT2 results and significantly better than the DFT and CASSCF results given in Table 3.3.

### 3.8 Summary and perspective

The application of DMRG in quantum chemistry during the past decade has seen tremendous progress as demonstrated here. While previous presentations of the DMRG algorithm often focused on the original derivation based on the tensor-product nature of $N$-electron states, the relation to standard quantum chemical approaches like configuration interaction was not that obvious, which is the reason why we presented a derivation of the DMRG algorithm in terms of interactions of electronic configurations in this chapter. The derivation of the DMRG wave function in terms of MPS will be discussed in section 4.2.

The algorithm is now very well elaborated and for specific classes of molecules DMRG has already been established as the best method available. Not only extended $\pi$-systems of organic chemistry, which feature a large amount of static electron correlation, belong to these classes, DMRG is also very suitable for rather compact molecules like transition metal complexes and clusters, in which the correlated motion of electrons is spatially very much confined.

The DMRG extrapolation scheme is a step towards a black-box scheme for DMRG studies in which the convergence of the individual DMRG calculations can be monitored in order to detect when to stop the DMRG iterations. The stop criterion is met when the desired accuracy of the energy has been reached.
by means of error estimates obtained from an extrapolation scheme. An error control facility enables one to perform feasible DMRG calculations at a low number $m$ of DMRG basis states for larger systems without the need of having fully converged absolute energies. Our approach can be used to obtain total electronic energies of comparable accuracy and decouples the dependence of the DMRG energies from the number of renormalized DMRG basis states. We can then obtain relative energies from extrapolated DMRG total electronic energies using an automated Richardson-type extrapolation algorithm with the intrinsic error control facility. This procedure is tailored to provide low-$m$ DMRG results for molecular systems in order to increase the applicability range of the method.

Clearly, DMRG is a truly numerical method in the sense that the guess for the environment states in the first sweep may significantly affect the convergence behavior of the DMRG energy and hence also of the Richardson-type extrapolation scheme. Still, if numerical instabilities occur (e.g., local energy minima for some values of $m$), the algorithm allows one to detect the local minima. If the data points contain numerical instabilities that lead to an extrapolated value higher than the best energy from the data set, additional DMRG steps are carried out with increased $m$ values. However, the number of data points may already be that large that the rational function smoothes the instability. Then the Richardson extrapolation is reliable if all data points are included. Also the extrapolated value can always be probed by considering one or a few additional DMRG calculations with $m$ values slightly larger than the extrapolated minimal value for $m$ required for a pre-defined accuracy.

A fine-tuning of the automated DMRG error protocol requires more DMRG calculations on larger active spaces, a larger set of test molecules, a detailed analysis of the environment states in terms of our determinant decomposition [98] and the consideration of white noise applied in the first sweep of these calculations.
3. A new paradigm for quantum chemistry: DMRG
4. Novel representations of quantum states

In quantum chemistry, the full-configuration-interaction (FCI) expansion of the total electronic wave function in terms of spin-adapted configuration state functions exactly solves the non-relativistic time-independent Schrödinger equation in a given one-particle basis of orbitals. The FCI wave function can be understood as a linear combination of occupation number vectors in the direct-product basis of the one-particle Hilbert spaces. Occupation number vectors are generated by distributing \( N \) electrons among the \( k \) orbitals. The FCI wave function of total electronic state \( A \) then reads

\[
|\Psi_{A,\text{FCI}}^{(N)}\rangle = \sum_{n_1n_2\ldots n_k}^q C_{n_1n_2\ldots n_k}^{(A)} |n_1n_2\ldots n_k\rangle
\]  

(4.1)

where \( C_{n_1n_2\ldots n_k}^{(A)} \) are the (F)CI expansion coefficients of state \( A \) and \( |n_1n_2\ldots n_k\rangle \) denotes an occupation number vector. Note that we restrict the sum in Eq. (4.1) to those vectors that represent \( N \) electrons and thus span the \( N \)-particle Hilbert space. The sum runs over the dimension \( q \) of the local Hilbert spaces of the set of orbitals \( \{1,2,\ldots,k\} \). For spin orbitals holds \( q = 2 \), the occupied and unoccupied one-electron state \( \{|1\rangle,|0\rangle\} \). In the case of spatial orbitals, the basis of the local Hilbert space \( \{|n_i\rangle\} \) consists of four states, \( \{|\rangle,|\uparrow\rangle,|\downarrow\rangle,|\uparrow\downarrow\rangle\} \). Each occupation number vector \( |n\rangle \equiv |n_1n_2\ldots n_k\rangle \) is constructed as a sequence of direct products of the states of the local Hilbert spaces

\[
|n\rangle \equiv |n_1n_2\ldots n_k\rangle = |n_1\rangle \otimes |n_2\rangle \otimes \ldots \otimes |n_k\rangle.
\]  

(4.2)

The number of variational CI parameters required to describe an electronic state (or a quantum state in general) grows factorially with system size, which is a direct consequence of the underlying tensor-product structure of the Hilbert space.

The exponentially growing number of parameters in the FCI ansatz renders it unfeasible for molecules containing more than a few atoms. Nevertheless, because of the nature of the interactions we may hope that there exists an efficient parametrization of a class of variational wave functions such that the low-energy sector of the electronic Hamiltonian is described with sufficient accuracy [137,158–161]. In addition, the huge body of numerical evidence compiled during the past forty to fifty years in quantum chemistry demonstrates that various truncated configuration-interaction expansions are efficient and reliable to approximate an electronic state [33]. This latter observation indicates that
provided we find an efficient parametrization of all CI coefficients in the FCI expansion, we do not need to sample all occupation number vectors but only the most important ones for the total electronic energy. Otherwise, the procedure would be as unfeasible for large molecules as the FCI approach itself.

A way of finding an efficient parametrization of states is to approximate the high-dimensional coefficient tensor $C_{n_1 n_2 \ldots n_k}$ by a tensor network. Tensor network states build a new class of variational wave functions. The high-dimensional coefficient tensor is broken down into low-rank tensors which are arranged on an arbitrary network [62,63,132,134,136,137,162,163]. The primary advantage of tensor network states compared to the standard FCI expansion is the reduced number of variational parameters which approximately scales as $O(k \chi^p)$ where $k$ is the number of orbitals, $\chi$ the bond dimension and $p$ is the rank of the tensor. Tensor network states can be designed in a way to directly map the entanglement of the underlying system [139,140].

The work of Affleck, Kennedy, Lieb and Tasaki [60] on finitely correlated states provided the foundations of tensor network states. The basic idea of tensor network states is to approximate ground-state wave functions of strongly correlated systems by spanning only the relevant part of the Hilbert space of the system of interest [137]. In the case of a limited amount of entanglement in the system, only a subspace of the full Hilbert space needs to be considered. This low-entanglement subspace can then be efficiently approximated by tensor network states tailored to represent the entanglement structure of the system.

The MPS constructed by the DMRG algorithm are the simplest example of tensor network states for one-dimensional systems [133,134,163]. An MPS with open-boundary conditions is defined as

$$|\Psi^{(N)}_{\text{MPS}}\rangle = \sum_{n_1 n_2 \ldots n_k} A_1[n_1] A_2[n_2] \cdots A_k[n_k] |n_1 n_2 \ldots n_k\rangle$$ (4.3)

where the rank-3 tensors $A_i$ are written as $m \times m$ matrices $A_i[n_i]$ for a specific local state $n_i$ [61,129–131]. Note that $A_1[n_1]$ and $A_k[n_k]$ are vectors because open-boundary conditions are applied and that we have dropped here and in the following the state index $A$ for the sake of brevity. The DMRG algorithm optimizes the tensors by keeping the eigenvectors of the reduced density matrix corresponding to the dominant eigenvalues (see also McCulloch [135] and Verstraete et al. [137] who discussed the additional flexibility when using both wave function and Hamiltonian in an MPS representation).

Other variational families of states have been proposed for strongly correlated systems which can be efficiently contracted for Variational Monte Carlo calculations. These include string-bond states (SBS) [164] and subsequently Entangled-Plaquette States (EPS) [165] and Correlator Product States (CPS) [166].
4.1 Tensor network states in quantum chemistry

The exact wave function of an $N$-electron system is often given as a multi-determinantal expansion where the Slater determinants are composed of one-electron functions (see chapter 2). The introduction of a one-electron basis set reduces the exact, infinite $N$-particle Hilbert space to a finite $N$-particle Hilbert space that is spanned by all Slater determinants.

In molecular systems, usually only a few basis states of the Hilbert space contribute with a large CI coefficient to the electronic wave function and are therefore important for an accurate description of the electronic structure of chemical systems [105]. Hence, it should be possible to devise a smart parametrization of the electronic wave function that covers the physical states in the Hilbert space, e.g., the electronic ground states [137,158] without the need of a factorially large number of parameters.

The concept of tensor network states (TNS) [60, 62, 139, 167–169] provides the framework to define new classes of states with a tailored and efficient parametrization. TNS is actually not a new concept. Such states have already been applied a long time ago in the condensed-matter community in a different context [60,129] but only recently to study molecular systems in quantum chemistry [50,122,164–166].

4.2 Understanding the DMRG wave function in terms of matrix product states

In 1995, Östlund and Rommer [56,57] realized that the density-matrix renormalization group (DMRG) algorithm implicitly generates a position-dependent MPS in the thermodynamic limit which is shown in Eq. (4.3) where the rank-3 tensors $A_i$ are written as $m \times m$ matrices $A_i[n_i]$ for a specific local state $n_i$ [61,129–131]. An analytic wave function ansatz is highly desirable for a better understanding of the advantages and possible pitfalls of the DMRG algorithm [48]. In addition, the connection of matrix product states and quantum information theory provided additional insights on the DMRG algorithm from a new perspective [88–90,133,134,149,163,170].

For a better understanding of the general tensor-network approach, we will now provide the principles of the construction of MPS within the context of the DMRG algorithm and summarize previous work on this subject [48,58,59,86,135,171].

An MPS is generated by retaining $m$ DMRG system states (also called block states) through a reduced basis transformation. Let us assume that the Hilbert space of an active subsystem (AS) is spanned by $m$ DMRG states $\{|AS_i^{(p)}\rangle| i = 1,..,m\}$ where $p$ indicates the number of orbitals already included in the AS basis. If we increase the AS by a single orbital, the basis of the enlarged active subsystem (eAS) $\{|eAS_i^{(p+1)}\rangle| i = 1,..,q \cdot m\}$ can be constructed by
means of a direct product of \( \{|\text{AS}_i^{(p)}\}\) times the basis of the single orbital \( \{|n_i^{(p+1)}\}_i = 1,\ldots ,q\) leading to the \( q \cdot m \) enlarged active subsystem basis states

\[
\{|eAS_i^{(p+1)}\}\rangle = \{|\text{AS}_i^{(p)}\}\rangle \otimes \{|n_i^{(p+1)}\}\rangle
\]  

(4.4)

where \( q \) is the dimension of the local Hilbert space describing orbital \( p + 1 \) in the chain.

The next step is to truncate the enlarged basis with dimension \( q \cdot M \) back to a basis with the optimal \( m \) states which we denote \( \{|\text{AS}_i^{(p+1)}\rangle \}_i = 1,\ldots ,m\). The index \( p + 1 \) indicates the orbital set already included in the basis of the active subsystem.

The truncation matrices \( A_i[n_i] \) in Eq. (4.3) can be defined as scalar products between the enlarged basis and the truncated basis

\[
\langle eAS_i^{(p+1)} | AS_j^{(p+1)} \rangle = \langle AS_j^{(p)} n^{(p+1)} | AS_j^{(p+1)} \rangle = (A^{(p+1)})_{AS_j^{(p+1)}; AS_j^{(p)} n^{(p+1)}}
\]  

(4.5)

This equation holds since the \( A_i[n_i] \) matrices can also be interpreted as rank-3 tensors. Note that we have dropped the position-index superscript for the sake of brevity.

From the definition of the transformation matrices \( A_i[n_i] \) in Eq. (4.7), it is clear that the orthonormality condition

\[
\sum_i A_i[n_i] A^\dagger_i[n_i] = 1
\]  

(4.8)

is fulfilled [58]. This ensures that the new truncated basis is orthonormal under the assumption that the \( \{|\text{AS}_i^{(p)}\}\) are orthonormal as well.

The \( m \) optimal basis states on the active subsystem spanning a space composed of \( (p + 1) \) orbitals can be expressed with Eq. (4.7) as

\[
|\text{AS}_i^{(p+1)}\rangle = \sum_j \sum_{n^{(p+1)}} (A_{n^{(p+1)}})_{AS_j^{(p+1)}; AS_j^{(p)}} |AS_j^{(p)}\rangle \otimes |n^{(p+1)}\rangle
\]  

(4.9)

where \( |AS_j^{(p)}\rangle \) form the renormalized basis of the space spanned by \( p \) orbitals.

We can now apply a recursive procedure to build up the renormalized basis spanning the entire orbital space [56]. This recursion procedure leads to an iterative cycle that expands the basis by a single orbital and subsequently renormalizes back to \( m \) basis states describing the enlarged system. The recursion is terminated if the number of orbitals \( \lambda \) in the active subsystem span \( m \) states exactly.

The renormalized basis can therefore be written as

\[
|\text{AS}_i^{(p+1)}\rangle = \sum_j \sum_{n^{(p+1)}} (A_{n^{(p+1)}})_{AS_j^{(p+1)}; AS_j^{(p)}} |AS_j^{(p)}\rangle \otimes |n^{(p+1)}\rangle
\]  

(4.10)
4.2. Understanding the DMRG wave function in terms of matrix product states

We can further simplify Eq. (4.10) by replacing the set of \{\mid \text{AS}_j^{(\lambda-1)} \rangle \mid j = 1, .., m \} states by the tensor product of the states in the space containing \lambda orbitals since this space is not being truncated.

The \( m \) renormalized basis states approximating an orbital space composed of \((p+1)\) orbitals can be written in a FCI fashion by replacing the high-dimensional coefficient tensor of Eq. (4.1) by a chain of \( m \times m \) truncation matrices where the sum runs over all possible occupation vectors in the Fock space of the \( k \) orbitals

\[
\mid \text{AS}_i^{(p+1)} \rangle = \sum_{n^{(1)},..,n^{(p+1)}} (A \mid n^{(\lambda)} \rangle \cdots A \mid n^{(p+1)} \rangle)_{n^{(1)},..,n^{(p+1);AS_i}} \mid n^{(1)} \cdots n^{(\lambda)} \cdots n^{(p+1)} \rangle.
\]

(4.11)

The renormalized basis state in Eq. (4.11) is called a \textit{matrix product state}.

Analogously to the definition of the \( A[n^{(\lambda)}] \) matrices in Eq. (4.7) that truncate the active subsystem basis states, truncation matrices can be defined for the complementary subsystem (CS), the environment,

\[
\langle \text{CS}_j^{(p)} | e\text{CS}_i^{(p)} \rangle = \langle \text{CS}_j^{(p)} | \text{CS}_i^{(p+1)} n^{(p)} \rangle \equiv (A \mid n^{(p)} \rangle)_{CS_i^{(p);CS_j^{(p+1)} n^{(p)}}} \]

(4.12)

where \( e\text{CS} \) stands for the enlarged complementary subsystem in the two-site DMRG algorithm and the renormalized basis states on the complementary subsystem are obtained in the same way as for the active subsystem, consequently.

The total-system wave function is constructed by a direct product of the enlarged active and the enlarged complementary subsystem,

\[
\mid \Psi_{\text{DMRG}}^{(N)} \rangle = \sum_{i,j} c_{e\text{AS}_i^{(p)} e\text{CS}_j^{(p+1)}} | e\text{AS}_i^{(p)} \rangle \otimes | e\text{CS}_j^{(p+1)} \rangle \]

(4.13)

where \( N \) is the number of electrons and \( p \) indicates the number of orbitals in the enlarged active subsystem and orbitals from \((p+1)\) to \( k \) in the enlarged complementary subsystem. Note that the sum over basis states of the enlarged active and enlarged complementary subsystem is restricted to states with the correct number of electrons, projected spin, and point-group symmetry. In the two-site DMRG approach, both enlarged subsystems can be written as a direct product of the subsystem part times a single orbital,

\[
\mid \Psi_{\text{DMRG}}^{(N)} \rangle = \sum_{i,j} \sum_{n^{(p)} n^{(p+1)}} c_{AS_i^{(p-1)} n^{(p)} n^{(p+1);CS_j^{(p+2)}}} | AS_i^{(p-1)} \rangle \otimes | n^{(p)} \rangle \otimes | n^{(p+1)} \rangle \otimes | CS_j^{(p+2)} \rangle.
\]

(4.14)

As we can see in Eq. (4.14), the two-site DMRG algorithm treats two orbitals, \( | n^{(p)} \rangle \) and \( | n^{(p+1)} \rangle \), exactly whereas in the one-site algorithm, only the active subsystem is enlarged by one orbital. At this stage we can substitute the renormalized basis states derived in Eq. (4.11) into Eq. (4.14) to express the DMRG wave function in terms of two matrix product states for the active and
complementary renormalized basis plus two exactly represented orbitals,

\[ |\Psi^{(N)}_{\text{DMRG}}\rangle = \sum_{ij} c_{AS_i}^{(p-1)} n_p n_{p+1} c_{CS_j}^{(p+2)} \left(A \left[n^{(\lambda)}\right] \cdots A \left[n^{(p-1)}\right]\right)_{n^{(1)}, \ldots, n^{(p-1)}; AS_i} \times \left(A \left[n^{(p+2)}\right] \cdots A \left[n^{(k-\lambda)}\right]\right)_{CS_j, n^{(p+2)}, \ldots, n^{(k-\lambda)}} |n^{(1)} \ldots n^{(k)}\rangle. \quad (4.15) \]

The coefficients in Eq. (4.15) are rank-3 tensors which can be reformulated into a set of \( q^2 \) matrices with dimension \( m \times m \). This so-called center matrix formulation [48] can be used to rephrase the DMRG ansatz consistently as a chain of \( m \times m \) matrix products,

\[ |\Psi^{(N)}_{\text{DMRG}}\rangle = \sum_{ij} \left(A \left[n^{(\lambda)}\right] \cdots A \left[n^{(p-1)}\right]\right)_{n^{(1)}, \ldots, n^{(p-1)}; AS_i} C \left[n^{(p)} n^{(p+1)}\right]_{AS_i}^{(p-1)} c_{CS_j}^{(p+2)} \times \left(A \left[n^{(p+2)}\right] \cdots A \left[n^{(k-\lambda)}\right]\right)_{CS_j, n^{(p+2)}, \ldots, n^{(k-\lambda)}} |n^{(1)} \ldots n^{(k)}\rangle. \quad (4.16) \]

The form of the ansatz in Eq. (4.16) clearly illustrates that the optimization of the DMRG ansatz is performed variationally as a sequence of local optimization steps of the wave function [48, 58]. Note that locality refers to the variational parameter space and not necessarily to the underlying orbitals. The variational coefficients \( c_{AS_i}^{(p-1)} n_p n_{p+1} c_{CS_j}^{(p+2)} \) are optimized and lead to an improved ansatz since these variational coefficients are used to construct a new reduced basis transformation. Therefore, the DMRG algorithm acts as a self-consistent method improving the truncation matrices \( A \) iteratively.

### 4.3 Benefit of concepts from quantum information theory

The most important property of multi-component quantum systems is entanglement which corresponds to quantum correlations between particles or a collection of particles forming a larger subsystem [172]. The degree of entanglement is decisive for the behavior of all multi-component quantum systems and for the numerical algorithms developed to simulate such systems [50, 53, 54, 122, 166, 173–177]. The concepts of quantum information theory (QIT) have been introduced to the density matrix renormalization group (DMRG) method [53, 54] and created a fresh impetus to the development of new methods that focus on entanglement optimization [88, 159]. Quantum information entropy can function as a direct measure of the behavior of quantum systems. Thus, the development of methods and techniques to obtain as much information as possible from entropy analysis is a logical step [60, 88–90, 178, 179].

A key ingredient of the DMRG method related to its multi-component subsystem wave function representation is entanglement. A controlled manipulation of it is expected to extend capabilities of DMRG to treat larger systems in a more efficient way. The development of entanglement reduction algorithms (ERA) is thus very appealing. Matrix product states (MPS) [56] that are inherently produced by the DMRG algorithm can be used to localize the entanglement
by reordering sites [88,90,92,96,141] or by optimization of the basis [99,100,110,122,178,180–183]. Considering the entanglement between arbitrarily chosen pairs of sites [50,90], a network topology can be determined for tensor-network-state (TNS) algorithms [122]. Further gain in speed of convergence can be achieved by an optimization of the initialization procedure [88,97] in which highly entangled states are taken into account from the very beginning.

By contrast to traditional approaches in quantum chemistry like configuration interaction or coupled cluster, the new tensor-network-based approaches to the electronic wave function construct CI-like coefficients from assumptions on how a total state is best represented in terms of correlations between the underlying one-particle states. It is therefore crucial to develop means that highlight the one-particle state correlations to facilitate a tailored construction of the many-particle basis. In the above-mentioned standard approaches, various recipes have evolved on how to selectively include or reject certain virtual orbitals in the excitation hierarchy. In the early days of CI-type approaches the manual selection was mandatory for the sake of feasibility, while in modern algorithms it can be automated, see Ref. [39] for an example. One such approach relies on the localization of orbitals and the definition of self-consistent electron pairs [184–186].

The question now is how these one-particle state correlations can be defined in an automated manner for the set-up of DMRG or TNS calculations. Here, Legeza and co-workers [81,88,89,141] introduced concepts from quantum information theory that turned out to be very useful for the quantitative description of such correlations. Of course, the applicability of these tools depends on the ease with which they can be evaluated. If their evaluation is very demanding in terms of computer resources, this will limit their applicability.

In the DMRG algorithm, the molecular orbitals must be lined up as an artificial one-dimensional lattice. Since the molecular orbitals are usually not spatially confined, the optimal solution of the orbital ordering problem is not trivial [96]. The aligned orbitals are then divided into an active subsystem and a complementary subsystem. On both subsystems, approximate representations of the elementary creation and annihilation operators in terms of matrices can be constructed which are employed to calculate the second-quantized Hamiltonian for the total (superblock) system. By diagonalizing the superbloc Hamiltonian, an approximate wave function for the entire system can be obtained which is needed for the calculation of the reduced density matrix of the active subsystem. The reduced density matrix allows us to select a new set of basis states for an improved description of the elementary operators [123].

For each molecular orbital, one-site entropies can be calculated from the eigenvalues of the reduced density matrix of that particular orbital. These one-site entropies can be used to modify the DMRG block entropy by reordering the molecular orbitals on the lattice [88]. The block entropy is defined as the von Neumann entropy of the reduced density matrix of the active subsystem. For optimal convergence and efficient use of computational resources, the molecular
orbitals should be ordered in such a way that the DMRG blocks are highly entangled only for a few iterations. An entanglement localization is sought since a larger number of DMRG states needs to be taken into account for a given error bound if the entanglement between two DMRG blocks is large and this will be discussed in section 4.3.2.

The selection of DMRG states in each renormalization step can be controlled by the dynamic block state selection (DBSS) protocol [141] (section 4.3.1) which monitors the quantum information loss — that is the difference in entropy of the complete reduced density matrix and the entropy of the states kept for the renormalization — by neglecting some DMRG superblock states and thus truncating the $N$-particle Hilbert space.

The configuration-interaction based dynamically extended active space (CI-DEAS) procedure [88, 187, 188], which is discussed in section 4.3.5, constructs optimal environment blocks at each iteration from the one-particle basis of the molecular orbitals with the largest one-site entropies. It also reduces the effective system size by identifying double-occupied or empty orbitals in the environment block.

Based on these procedures, we have recently formulated an entropy-based optimization scheme including the (CI-)DEAS and the dynamic block state selection (DBSS) procedures that are vital ingredient to obtain highly accurate results with tremendous savings in computation resources and time. In addition, it is a smart way of reducing the Hilbert space which allows us to study large active spaces with a modest number of renormalized states in contrast to inefficient and expensive brute-force DMRG calculations at a fixed number of renormalized states.

For the description of these procedures, we focus on the $\mu - \eta^2 : \eta^2$ peroxo isomer of $[\text{Cu}_2\text{O}_2]^{2+}$ [149] with the same set up as we have already employed in our earlier studies [49, 105] (see also section 3.7). The final results for both isomers, the bis($\mu$-oxo) and $\mu - \eta^2 : \eta^2$ peroxo, of the binuclear oxo-bridged copper cluster are, however, later discussed in section 6.2.

4.3.1 Dynamic block state selection

A fundamental concept related to the inseparability and non-locality of quantum mechanics is entanglement. Since the DMRG algorithm approximates a composite system with long-range interactions, the results of quantum information theory can be used to understand the criteria of its convergence.

The two-site variant of the DMRG method has originally been employed with a fixed number of block states while the degree of entanglement between the DMRG blocks for a given superblock configuration is related to the Schmidt number $r_{\text{Schmidt}} \leq \min(M_{\text{eAS}}, M_{\text{eCS}})$. For a pure target state $|\Psi_{TS}\rangle \in \Lambda = \Lambda_{\text{eAS}} \otimes \Lambda_{\text{eCS}}$, with $\dim \Lambda_{\text{eAS}} = M_{\text{eAS}}$, $\dim \Lambda_{\text{eCS}} = M_{\text{eCS}}$, the Schmidt decomposition
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states that

\[ |\Psi_{TS}\rangle = \sum_{\lambda=1}^{r_{\text{Schmidt}}} c_\lambda |u^\lambda\rangle \otimes |v^\lambda\rangle \]  

(4.17)

where \( |u^\lambda\rangle \otimes |v^\lambda\rangle \) form a bi-orthogonal basis \( \langle u^\lambda |u^{\mu}\rangle = \langle v^\lambda |v^{\mu}\rangle = \delta_{\lambda\mu} \), and \( 0 \leq c_\lambda \leq 1 \) with the condition \( \sum_{\lambda} c_\lambda^2 = 1 \). If \( r_{\text{Schmidt}} > 1 \) then according to Ref. [189] \( |\Psi_{TS}\rangle \) is inseparable and the two blocks are entangled.

Since possible measures of entanglement for fermionic systems are the von Neumann and Rényi entropies, it is more efficient to control the truncation error [141] or the quantum information loss \( \chi \) [89] at each renormalization step. In the DMRG procedure, during the renormalization step the block \( |eAS(p+1)\rangle \) is formed of the subblock \( |AS(p)\rangle \) and the site \( n^{(p+1)} \). Denoting by \( s_{AS}(p) \) the entropy of the active subsystem of length \( p \) and by \( s_{p+1} \) the entropy of the \( p+1 \)th site, the change of the block entropy by forming a larger block, \( |eAS(p+1)\rangle \), is given as

\[ s_{AS}(p) + s(1)_{p+1} + I_{AS}(p) = s_{eAS}(p+1) \]  

(4.18)

where the von Neumann entropy of a block with \( p \) orbitals is given as

\[ s_{AS}(p) = - \sum_\alpha \omega_\alpha \ln \omega_\alpha = - \sum_{\lambda} c_\lambda^2 \ln c_\lambda^2 \]  

(4.19)

where \( \omega_\alpha \) stands for the eigenvalues of the reduced density matrix of the block \( |AS(p)\rangle \) and \( c_\lambda \) are the Schmidt coefficients. The so-called mutual information \( I_{AS}(p) \leq 0 \) quantifies the correlation between the subsystem and a single site. The mutual information is zero if and only if the two blocks are uncorrelated.

In order to control the quantum information loss, \( M_{eAS} \) (or \( M_{eCS} \)) is increased systematically at each renormalization step until the following condition holds

\[ s_{AS}(p+1) - s_{AS}^{\text{Trunc}}(p+1) < \chi \]  

(4.20)

where \( \chi \) is an \textit{a priori} defined error margin. For \( s_{AS}(p+1) \), i.e., before the truncation, \( \alpha = 1 \ldots M_{AS} \times q_{p+1} \) while for \( s_{AS}^{\text{Trunc}}(p+1) \) according to Eq. (4.20) \( M_{AS}^{\text{Trunc}} < M_{AS} \times q_{p+1} \) is used. This approach guarantees that the number of block states are adjusted according to the entanglement between the DMRG blocks and the \textit{a priori} defined accuracy can be reached [89]. In addition, an entropy sum rule can be used as an alternative test of convergence [89]. Therefore, we set the minimum number of block states to \( M_{\text{min}} \) and \( \chi \). By setting \( M_{\text{min}} \sim q^3 \) or \( q^4 \), convergence to local minima can be avoided. In our implementation, we have \( q = 4 \) and the basis states correspond to the \( |0\rangle, |\downarrow\rangle, |\uparrow\rangle \) and \( |\downarrow\uparrow\rangle \) states. The maximum number of block states selected dynamically during the course of iterations will be denoted by \( M_{\text{max}} \). This approach, however, does not work for the one-site variant of the DMRG algorithm since the Schmidt number of a one-site superblock configuration \( M_{eAS} = M_{AS} \times q_{p+1} \) cannot be larger than \( M_{CS} \). This prevents \( M_{AS} \) to increase above \( M_{CS} \) based on Eq. (4.17).
4. Novel representations of quantum states

Figure 4.1: Single-orbital entropy function obtained for the $\mu - \eta^2 : \eta^2$ peroxo isomer of $[\text{Cu}_2\text{O}_2]^{2+}$ by setting the quantum information loss $\chi = 10^{-5}$. The symbols indicate corresponding point-group symmetries of the energetically ordered orbitals.

4.3.2 Entanglement and interaction localization

The von Neumann and Rényi entropies have been studied for quantum chemical systems as well and it was shown that orbitals lying closer to and further away from the Fermi surface possess larger and smaller orbital entropy, respectively [88]. The orbital entropy is related to the mixture of a local state and it is expressed by the eigenvalues of the reduced density matrix for a given orbital, namely

$$s(1)_i = - \sum_{\alpha} \omega_{\alpha,i} \ln \omega_{\alpha,i}, \quad (4.21)$$

where $i = 1 \ldots N$ labels the orbital index while $\omega_{\alpha,i}$ stands for $\alpha = 1 \ldots q_i$ the eigenvalues of the reduced density matrix of orbital $i$. In Figure 4.1, the single-orbital entropy is shown for the $\mu - \eta^2 : \eta^2$ peroxo isomer of $[\text{Cu}_2\text{O}_2]^{2+}$ calculated by setting the quantum information loss $\chi = 10^{-5}$. Orbitals with a large entropy significantly contribute to the correlation energy whereas other little entangled orbitals do not. Since the orbitals possess different single-orbital entropies, the ordering of orbitals along the one-dimensional chain of orbitals in the DMRG algorithm has a major impact on the block entropy $s(p)$, so that the block entropy profile can be changed based on the ordering of the orbitals [88]. The block entropy also determines the required computational resources to reach a given accuracy [88, 89]. If an optimized ordering is used, DMRG results can be obtained using a considerably smaller number of block states for a given error bound.
Figure 4.2: Pictorial representation of the magnitude of components $T_{ij}$ of the one-electron operator for the $\mu-\eta^2 : \eta^2$ peroxo isomer of $[\text{Cu}_2\text{O}_2]^{2+}$. For better visibility the one-dimensional orbital chain is plotted on a circle with modulated radius in a clockwise direction. Orbitals belonging to different irreducible representations are shown by different symbols. Numbers next to the symbols label molecular orbitals.

An optimal orbital alignment by means of speed of convergence can be obtained by reordering the orbitals, so that the DMRG blocks are entangled only for a few iterations. This can be achieved by placing highly entangled orbitals at one of the ends or close to the center of the chain.

Unfortunately, this is not true in general, since the independent interaction terms, like $t_{ij}$ and the local direct, pair-hopping, and spin-flip terms of $V_{ijkl}$ which occur in the second-quantized, electronic Hamiltonian (Eq. (3.6)) act as independent quantum channels; they all generate different amounts of entanglement [178]. Hence, localizing entanglement generated by one channel, e.g., the one-electron term, might lead to delocalized entanglement in another channel. As an example, the one-electron operators are analyzed for the $\mu-\eta^2 : \eta^2$ peroxo isomer of $[\text{Cu}_2\text{O}_2]^{2+}$ shown in Figure 4.2. In this case they do not couple orbitals among different irreducible representations of the $D_{2h}$ point group while the two-electron Coulomb repulsion operator does. A proper cost function to take care of interaction and entanglement localization can be expressed based on the two-orbital mutual information,

$$I_{i,j} = s(2)_{i,j} - s(1)i - s(1)j,$$

(4.22)

where $s(2)_{i,j}$ is the two-orbital entropy between a pair of sites which was introduced by Rissler et al. [90]. If the electron–electron interactions are neglected,
the two-orbital mutual information has a similar structure as shown in Figure 4.2, where only the orbitals of the same irreducible representations are entangled. The resulting single-orbital entropy, block-entropy, and the mutual information are shown in Figure 4.3 obtained by the DMRG method after the seventh sweep. The block entropy oscillates and is exactly zero when all orbitals of the same irreducible representations belong to the left or to the right DMRG block. Therefore, the total wave function can be expressed as a product state of the wave functions of the subblocks of irreducible representations. When the two-electron integrals are also considered, orbitals among different irreducible representations are also entangled as shown by the components of the two-orbital mutual information in Figure 4.4 for the $\mu - \eta^2 : \eta^2$ peroxo isomer of $[\text{Cu}_2\text{O}_2]^{2+}$. Since the one-electron integrals are usually an order of magnitude larger in chemical systems, an optimal ordering can be found by reordering the orbitals within the same irreducible representation and reordering the blocks of
Figure 4.4: Components of the two-orbital mutual information which are larger than $10^{-4}$ for the $\mu - \eta^2 : \eta^2$ peroxo isomer of $[\text{Cu}_2\text{O}_2]^{2+}$ obtained with $\chi = 10^{-5}$ and for the energetical ordering. The role of symbols and numbers is the same as in Figure 4.2.

The reordering concept can be put in a more rigorous form by minimizing the entanglement distance, which can be expressed as a cost function,

$$\hat{I}_{\text{dist}} = \sum_{i,j} I_{i,j} \times |i - j|^{\eta},$$

(4.23)

where the entanglement between pair of sites is weighted by the distance in the chain between the orbitals. In Ref. [90], the effect of the parameter $\eta = -2$ has been analyzed using simulated annealing. Additional parameters to weight the off-diagonal elements of $I$ have been studied as well. In our approach, we use both $\eta = 1$ and 2. The latter choice also has the advantage that it can be related to the spectral algorithms of seriation problems [190].

The main aim is to sequence a set of $N$ objects, i.e., to bijectively map the elements to the integers $1, \ldots, N$ based on a real valued correlation function $f(i, j) = f(j, i)$ which reflects the desire for items $i$ and $j$ to be near each other in the sequence. The two-orbital mutual information is such a function which can also be seen as a weighted graph. In general, the problem of finding all ways to sequence the elements, so that the correlations are consistent, becomes NP-complete [191] in the presence of inconsistencies. In such a case, there may be no consistent solution and one needs to find the best approximation. If a consistent ordering is
possible, the problem is \textit{well posed}. Most of the combinatorial algorithms for well-posed problems break down when the data is inconsistent, limiting their value for many problems. In our approach, the minimization is performed iteratively with the constraint that orbitals of the same irreducible representations are kept together, thus reordering of orbitals is allowed within irreducible representations and reordering the blocks of orbitals of the irreducible representation is also allowed. As a result, a highly optimized ordering can be obtained as is shown in Figure 4.5. The value for the energetical ordering $I_{\text{dist}} = 821.4$ is reduced to 134.1 using $\eta = 2$. A smaller value of 63 could be reached by excluding the constraint discussed above. However, the DMRG calculations perform considerably worse for that ordering.

The cost function can also be discussed in terms of spectral algorithms. Since the minimization of the cost function $g(\pi) = \sum_{ij} f(i,j)(\pi_i - \pi_j)^2$ is hard in terms of permutations $\pi$, it can be approximated by a cost function like $I_{\text{dist}}$ of continuous variables $x_i$ that maintains its structure. From spectral graph theory it follows that the so called Fiedler vector $x = (x_1, \ldots, x_N)$ is the solution that minimizes $F(x) = x^\dagger L x = \sum_{ij} I_{i,j}(x_i - x_j)^2$ subject to the following constraints that $\sum_i x_i = 0$ and $\sum_i x_i^2 = 1$, where the graph Laplacian is $L = D - I$ with $D_{i,i} = \sum_j I_{i,j}$. The second eigenvector of the Laplacian is the Fiedler vector \cite{192,193} which defines a (1-dimensional) embedding of the graph on a line that tries to respect the highest entries of $I_{i,j}$ and the edge length of the graph. Ordering the entries of the Fiedler vector by non-decreasing or non-increasing way provides us a possible ordering. A naive application of optimization methods based on the Fiedler vector yielded a worse ordering than the one shown in Figure 4.5.

\subsection*{4.3.3 Definition of the single-orbital entropy}

The single-orbital entropy can be calculated for each renormalization step of a full sweep, thus $s(1)_i$ can be obtained for $i = 1 \ldots N$. The single-orbital entropy profile for a given ordering of molecular orbitals can be determined as a function of the DMRG sweeps \cite{88,187}. Once the wave function has converged by means of the entropy sum rule \cite{89}, the single-orbital entropy profile for the given target state can be obtained. This well known procedure of collecting data points from subsequent renormalization steps of a full sweep was also used by Ghosh \textit{et al.} \cite{100} to efficiently calculate four-point correlation functions. The one-orbital entropy, on the other hand, can also be expressed in terms of the occupation-number representation \cite{90}. The calculation of $s(1)_i$ is also possible once the required operators are determined for the given superblock configuration. A direct comparison of data points obtained by the two approaches provides a reliable error estimate.
4.3. Benefit of concepts from quantum information theory

Figure 4.5: Components of the two-orbital mutual information which are larger than $10^{-4}$ for the bis($\mu$-oxo) isomer of $[\text{Cu}_2\text{O}_2]^{2+}$ obtained with $\chi = 10^{-5}$ and for the reordered orbitals.

4.3.4 On the calculation of the two-orbital entropy function

The two-orbital entropy function can be expressed in terms of the occupation-number representation [90]. Unfortunately, it requires the calculation of 23 independent two-point correlation functions. Since all two-point correlation functions have to be renormalized and stored in memory or on disk due to the truncation of the superblock Hilbert space, the efficient calculation of these operators is crucial for feasible calculations with respect to wall time and computational resources.

In the DMRG algorithm, the correlation functions are usually calculated for the symmetric superblock configuration, i.e., when the size of the left and right blocks are equal. This configuration provides the most accurate result for a fixed number of block states since the block entropy reaches its maximum value, so that the highest level of entanglement can be reached [89]. In fact, the largest error in a measurable quantity is related to the largest truncation error within a full DMRG sweep [144]. In contrast to this, using the DBSS method, the error can be kept below an a priori defined threshold, and hence an accurate calculation of the correlation functions is possible for the non-symmetric superblock configurations as well. In addition, if two non-interacting orbitals are attached to both ends of the chain the reduced block density matrix at the turning points of a sweep, where all orbitals belong to the left or the right block, has only one non-zero eigenvalue according to the Schmidt decomposition. Renormalized operators required for the two-orbital entropy function reduce to
Figure 4.6: Number of entanglement bonds emerging from the orbitals based on Figure 4.4. The meaning of the symbols is the same as in Figure 4.1.

![Graph showing number of bonds vs orbital index.](image)

single numbers \(M_{AS} = M_{CS} = 1\) [89,187], consequently. Even without this trick, an efficient calculation of the correlation function at the turning points is possible because the environment block contains \(q\) basis states and the system block only \(M_{\text{min}}\) states when the DBSS procedure is used. This is crucial in the quantum information analysis since the construction of the mutual entropy is very costly. In our approach, all the required operators are generated only for the superblock configuration at the turning points for which the correlation functions are calculated. This is achieved by subsequent renormalization of the operators based on the \textit{a priori} determined transformation matrices [56].

### 4.3.5 Configuration interaction based dynamically extended active space

The non-local version of the DMRG method is very sensitive to the initialization procedure. If a poorly approximated starting configuration is used, the convergence can be very slow and the DMRG can even be trapped in local minima [97]. This can, however, be avoided by including highly entangled orbitals from the very beginning and expanding the active space dynamically [88]. This approach has also been extended to include protocols based on the configuration interaction (CI) procedure [187,188].

Taking a look at Figure 4.4, some orbitals are highly entangled with several other orbitals while others are entangled with a few orbitals only. The number of entanglement bonds emerging from the orbitals based on Figure 4.4 is shown in Figure 4.6.
4.3. Benefit of concepts from quantum information theory

In order to guarantee fast convergence the highly entangled orbitals — those with several entanglement bonds — should be included from the very beginning of the calculations. In the DEAS procedure, we introduce a complete-active-space (CAS) vector that selects the highly entangled orbitals. The CAS vector (CASV) is formed by ordering orbitals with decreasing entropy values.

Since the DMRG algorithm itself is a basis-state transformation protocol, that transforms single-particle basis states to multi-particle basis states, the environment block in the DEAS procedure is formed for each DMRG iteration step from the one-particle basis states of those orbitals which posses the largest single-orbital entropies. In the first iteration step, the active subsystem (system block) contains one orbital represented by $q$ states while the complementary subsystem (environment block) contains $k - l - 2$ orbitals for a total of $k$ orbitals. Since the exact representation of the environment block within the two-site DMRG algorithm would require $q^{k-1-2}$ states which is too large for most molecular systems, only a subset of orbitals has been considered in the active space. At each DMRG iteration step of the warm up procedure, i.e., for iterations $1 \ldots k - 3$ the $M_{CS}$ states are formed from those components of the CAS vector which belong to the environment block and possess largest entropies. The starting value of $M_{CS}$ ($M_{start}$) is set prior of the calculation but during the iteration procedure $M_{CS}$ is adjusted as $M_{CS} = \max(M_{AS}, M_{start})$ in order to construct at least as many environment states as the system block has in order to satisfy the constraints set by the Schmidt decomposition. Identifying orbitals of the right block as doubly filled, empty or active orbitals the effective size of the environment block can be reduced significantly. The empty orbitals can be neglected, while a partial summation over the doubly filled orbitals results in a constant shift in the energy. If DMRG auxiliary operators [80] are formed by partial summations on the active subsystem, the effective system size of the problem is determined by the active orbitals only [88, 187, 188]. Therefore, in the warm up procedure the effective size of the system is reduced to 5 to 7 orbitals which allows one to use larger $M_{start}$ without a significant increase in computational time.

In order to construct even better environment states, we also utilize CI expansion procedures. In standard CI techniques, the trial wave function is written as a linear combination of determinants with expansion coefficients determined by requiring that the energy should be minimized [5]. The molecular orbitals used for building the excited Slater determinants are taken from a CASSCF calculation and kept fix. The exact wave function in a given one-particle basis is the full-CI wave function which we have previously encountered and discussed in Eq. (2.11). Since the segment of the Hartree–Fock orbitals belonging to the complementary subsystem is known, the restricted subspace of the environment block can be formed for a given CI-level in the DEAS procedure. The environment block thus contains states for a given excitation level while the total wave function can contain even higher excitations as well due to the correlation between the two blocks. The environment block states are constructed at each
iteration step, so that the environment block is always optimized for the renormalized system block. This procedure guarantees that several highly entangled orbitals are correlated from the very beginning and both static and dynamic correlations are taken into account. The reduced density matrix is well defined, thus block states can be selected efficiently based on the entropy considerations and convergence to local minima can be avoided. Since a significant part of the correlation energy can be obtained in this way, usually at the end of the initialization procedure, i.e., after one-half sweep, chemical accuracy is often reached. The initial CAS vector can be determined based on the chemical character of the molecule or in a self-consistent fashion. In the latter approach, the CAS vector is set first as \( \text{CASV} = [k, k - 1, \ldots, 1] \) to include long range interactions between the system block and the rightmost sites of the chain and a calculation using small values of \( M_{\text{min}} \) and \( M_{\text{start}} \) is performed. After a full sweep, the entropy functions are calculated and the ordering as well as the CAS vector are determined. Even though the DMRG wave function has not yet converged, most relevant information of the system can already be extracted. In addition, the DMRG results can be systematically improved using the optimized ordering and the CAS vector as a starting point for new DMRG calculations. The CI-DEAS method allows a simple and fast calculation of all physical quantities at the end of the first sweep.
5. Chemistry with complete-graph tensor network states

Over the last two decades, we have witnessed the rise of the Density Matrix Renormalization Group (DMRG) algorithm [53–55], which had a tremendous impact on the fields of condensed matter physics [58] and quantum chemistry [48,49] (see also chapter 3). In 1995, Rommer and Östlund [56,57] showed that the DMRG wave function can be described by a Matrix Product State (MPS) [61,194] which is — qualitatively speaking — a one-dimensional chain of rank-3 tensors and was covered in chapter 4. The understanding of the structure of the DMRG wave function stimulated further developments to efficiently represent ground states of strongly correlated systems. In this chapter, a class of tensor network states specifically designed to capture the electron correlation within a molecule of arbitrary structure is introduced. An obvious advantage of tensor network methods is that they are not biased towards any reference configuration in contrast to many standard quantum chemical methods. We will show that this feature is just one of many reasons why tensor network states are in particular useful and allow to obtain accurate relative energies between electronic states which is central to molecular physics and chemistry.

5.1 An efficient parametrization of the electronic wave function

We study a new class of approximations, which we denote Complete-Graph Tensor Network (CGTN) states [50], to represent electronic wave functions of molecular systems described by a complete pair-entanglement network of one-particle states (spin orbitals). A CGTN state provides an efficient and compact description in terms of variational parameters because the $2^k$ expansion parameters for the many-electron states that can be constructed from $k$ spin orbitals are approximated by the entries of a matrix symmetric in the orbital indices, i.e., only $[(k^2 - k)/2 + k] \times q^2 = k(k+1)/2 \times q^2$ parameters are needed in our CGTN approach (where $q$ is the dimension of the one-particle Hilbert space, i.e., $q=2$ for spin orbitals). Of course, a detailed numerical analysis of the accuracy to approximate a total electronic state is required for this reduced parameter set. Note that an artificial one-dimensional ordering of the molecular orbitals for the construction of the total basis states, which can create convergence problems to local energy minima as in the quantum chemical DMRG algorithm [81,96,97], is explicitly circumvented.
We will build upon an extension of the previously mentioned families of states to treat the full electronic Hamiltonian for molecular systems. Our extension is twofold: (i) SBS [164], EPS [165] and CPS [166] have only been applied to local spin Hamiltonians so far, while we aim at the full electronic Hamiltonian as given in Eq. (3.6) and (ii) we include all pair correlations of the one-electron basis states and do not impose any restriction on these pairs.

In the case of an MPS parametrization of a wave function, sites — or orbitals in a quantum chemical context — have to be mapped on a suitably chosen lattice. Then, correlations are transmitted over the one-dimensional lattice by the size of the matrices occurring in the matrix product state. Naturally, this ansatz is more suitable for molecular systems with an inherent linear structure rather than for those with long-range correlations. Orbital ordering on this lattice is then crucial for the convergence of the variational optimization technique employed, e.g., for the DMRG algorithm [96,97]. Molecular orbitals are mostly delocalized and therefore contain no spatial information that would dictate a unique orbital ordering – in contrast to a clear spatial structure of spin models that can be easily mapped onto a one-dimensional lattice. Furthermore, a localization procedure cannot be efficiently applied for most compact molecules under the constraint of keeping the orthogonality of the orbitals. Hence, an MPS state might be difficult to optimize for a general molecule of arbitrary structure. By contrast, in the CGTN approach to be introduced now non-local correlations are directly embedded into the non-linear tensor network ansatz. The complete-graph tensor network replaces the high-dimensional coefficient tensor in the FCI ansatz of Eq. (4.1) by a network of tensors that connects all orbitals with each other,

$$\Psi_{\text{CGTN}}^{(N)} = \sum_{n_1n_2\ldots n_k} \prod_{\alpha \beta} f^{n_\alpha n_\beta}_{\alpha \beta} |n_1n_2\ldots n_k\rangle \quad (5.1)$$

where \(f = \{f^{n_\alpha n_\beta}\} \) represents a rank-\([k(k+1)/2]\) tensor which depends on the orbitals \(\alpha, \beta \in \{1, 2, \ldots, k\}\). The local states of the spin orbitals \(n_\alpha, n_\beta\) can either be occupied or unoccupied \(|\uparrow\rangle, |\downarrow\rangle\) (i.e., for spin orbitals \(q=2\)). The sum runs over all possible occupation number vectors \(|\rangle\) in the \(N\)-electron Hilbert space (in principle, in the full Fock space) with the correct number of electrons, projected spin, and point-group symmetry.

The above ansatz is built on the key idea that every orbital is “connected” with every other orbital. Hence all CI coefficients are constructed from such pair correlations optimized for all orbitals. The number of variational parameters in our ansatz depends on the number of spin orbitals \(k\) and on the bond dimension \(d\) and is given as \(\frac{1}{2}k(k+1)d^2\) where \(d = 2\). Comparing this to the number of parameters in the FCI ansatz which scales as \(O(2^k)\) for spin orbitals, it is clear that CGTN states are much more efficient in terms of the number of variational parameters. It is important to emphasize that we do not need to specify any reference configuration like in most post-Hartree–Fock methods. Our ansatz
comprises naturally all basis states which can be generated in the Hilbert space of interest. Thus, although the CI coefficients are approximated by the reduced set of CGTN parameters, we can expect that CGTN calculations are (at least approximately) size-consistent.

Compared to the tensor networks suggested so far for local (spin) Hamiltonians, CGTN states form a subspace of the very general CPS parametrization, which is so general that it basically covers any non-hierarchical tensor network approximation of a wave function. In particular, they correspond to two-site CPS including all long-range correlation effects. A similar parametrization of a simple variational wave function was also chosen by Huse and Else to describe ground states of frustrated quantum spin systems [167]. However, the question arises how accurate this parametrization is for the non-local electronic Hamiltonian of Eq. (3.6), which shall be investigated in this work. Although undesirable from the point of view of feasibility, inaccuracies may be cured by also including three-orbital, four-orbital, ... correlations as is possible with the general CPS ansatz. Thus, we may easily increase the flexibility of CGTN states by including higher-order correlators (summing over three or more indices instead of two) or by increasing the bond dimension of the tensors from scalar values to matrices. In this work, the number of pair-correlation parameters is determined by the definition of an active orbital space, which is a standard procedure in quantum chemistry [33]. The next step is to variationally optimize the non-linear tensor network ansatz.

5.2 Variational optimization of tensor network states

We apply a variational Monte Carlo scheme to optimize the CGTN state. In the context of tensor-network states, this was demonstrated by Schuch et al. [164] and by Sandvik and Vidal [169] for local Hamiltonians. We augment the optimization with a parallel tempering scheme. The energy of the system is written as an expectation value of the electronic Hamiltonian operator over an \( N \)-electron wave function \( |\Psi^{(N)}_{\text{CGTN}}\rangle \)

\[
E_{\text{FCI}} = \frac{\langle \Psi^{(N)}_{\text{FCI}} | \hat{H}_d | \Psi^{(N)}_{\text{FCI}} \rangle}{\langle \Psi^{(N)}_{\text{FCI}} | \Psi^{(N)}_{\text{FCI}} \rangle} \leq \frac{\langle \Psi^{(N)}_{\text{CGTN}} | \hat{H}_d | \Psi^{(N)}_{\text{CGTN}} \rangle}{\langle \Psi^{(N)}_{\text{CGTN}} | \Psi^{(N)}_{\text{CGTN}} \rangle} \tag{5.2}
\]

which delivers an upper bound to the exact FCI energy in a given one-particle basis.

For the sake of brevity, the tensor product in front of the occupation number vector in our CGTN ansatz is abbreviated by a scalar function \( C_I \)

\[
C_I = \langle I | \Psi^{(N)}_{\text{CGTN}} \rangle = \prod_{\alpha} \prod_{\beta \leq \alpha} f^{I_\alpha I_\beta}_{\alpha \beta} \tag{5.3}
\]

which corresponds to a (unnormalized) CI-like coefficient for a given occupation.
number vector $|I\rangle$ in configuration-interaction theory,

$$|\Psi_{\text{CGTN}}^{(N)}\rangle = \sum_I C_I |I\rangle$$  \hspace{1cm} (5.4)

Inserting Eq. (5.4) into the normalization integral in the denominator of (5.2) yields the well-known CI-like normalization condition

$$\langle \Psi_{\text{CGTN}}^{(N)} | \Psi_{\text{CGTN}}^{(N)} \rangle = \sum_{IK} C^*_I C_K \langle I | K \rangle = \sum_I C^*_I C_I \delta_{IK} = \sum_I C^2_I$$  \hspace{1cm} (5.5)

where the sum takes the square of the weights over all possible basis states in the Hilbert space with correct symmetry.

We now insert Eq. (5.5) into Eq. (5.2) to get an approximation to the energy expectation value of the electronic Hamiltonian for our wave function ansatz and then substitute the ket in the denominator by Eq. (5.4),

$$E_{\text{approx}} = \frac{\sum_I C_I \langle \Psi_{\text{CGTN}}^{(N)} | \hat{H}_{\text{el}} | I \rangle}{\sum_I C^2_I}.$$  \hspace{1cm} (5.6)

After rewriting this sum to become

$$E_{\text{approx}} = \frac{\sum_I C^2_I \langle \Psi_{\text{CGTN}}^{(N)} | \hat{H}_{\text{el}} | I \rangle}{\sum_I C^2_I}$$  \hspace{1cm} (5.7)

we can perform Monte Carlo sampling with strictly non-negative probabilities $C^2_I$. We define an energy estimator $E(I)$ as a function of the occupation number vector $|I\rangle$ that reads

$$E(I) \equiv \frac{\langle \Psi_{\text{CGTN}}^{(N)} | \hat{H}_{\text{el}} | I \rangle}{C_I} = \sum_J \frac{C_J}{C_I} \langle J | \hat{H}_{\text{el}} | I \rangle.$$  \hspace{1cm} (5.8)

For a given $|I\rangle$, the number of basis states $\langle J |$ contributing to this sum is bounded by the number of terms in the Hamiltonian. Since the occupation number vector $|I\rangle$ is not an eigenstate of the Hamiltonian, $\langle I | \hat{H}_{\text{el}} | I \rangle$ produces a linear combination of occupation number vectors with coefficients constructed from the one-electron and two-electron integrals occurring in the Hamiltonian. For a molecule, the sum over $J$ can therefore be performed exactly. The Monte Carlo expectation value of an operator is calculated using the ALPS code [195]. The calculation of the energy estimator $E(I)$ scales as $O(k^4)$ where $k$ is the number of spin orbitals. The quotient of the two weights $C_J/C_I$ scales as $O(1)$ since it only depends on the difference between them. The evaluation of the high-dimensional integral of the electronic Hamiltonian between $J$ and $I$, however, scales as $O(k^4)$ due to the electron–electron repulsion operator.
A variational optimization is in general not guaranteed to converge to a global minimum — instead, it may be trapped in local minima and yield incorrect results. In our ansatz, the highly non-linear structure and the complex energy landscape of molecules make such trapping quite likely. In particular, the approach of Sandvik and Vidal [169] which applies gradient information to propose a new set of variational parameters turns out to be unreliable in our case. We therefore use a stochastic optimization procedure that works entirely without gradient information. To each choice of variational parameters $f = \{ f_n^{a_n^\alpha \beta} \}$, we can assign an electronic energy $E(f)$. After introducing an artificial temperature $T$ (actually, a parameter with the dimension of an energy; here measured in Hartree units, $E_h$), we can sample the continuous variables $f$ following a canonical ensemble with the weight of a configuration given by $\exp(-E(f)/T)$. The limit $T \rightarrow 0$ $E_h$ will yield the desired ground state of the molecule. It should be emphasized that this ensemble does not correspond to a physical ensemble at any finite temperature.

The advantage of this approach is that we can easily control the optimization procedure by tuning the parameter $T$. While an accurate simulation of the ground state is only possible for $T \rightarrow 0$ $E_h$ that may get stuck in local minima, a simulation at larger $T$ may easily surmount high energy barriers between local minima. We therefore use a parallel tempering/replica exchange scheme [196] where simulations are run at several temperatures simultaneously. After a certain number of updates, replica $i$ and replica $i+1$ at neighboring temperatures are exchanged with a probability

$$p(((T_i, E_i) \leftrightarrow (T_{i+1}, E_{i+1})) = \min\{1, \exp(-\Delta E/\Delta T)\} \quad (5.9)$$

with $\Delta E = E_{i+1} - E_i$ and $\Delta T = T_{i+1} T_i / (T_i - T_{i+1})$. The set of temperatures has to be chosen in such a way that the lowest temperatures are close to $T=0$ $E_h$ to yield information about the ground state and the highest temperatures are sufficient to overcome energy barriers. Hence, the choice depends very much on the specific problem at hand. It might be desirable to dynamically optimize the temperatures for some specific applications [197], but for the purpose of this work, we restrict ourselves to a static choice of the temperatures. For a temperature set of $M$ temperatures in the range $[T_1, T_M]$, we choose for the remaining $M - 2$ temperatures $T_l$ with $T_1 < T_l < T_M$:

$$T_l = T_1 \left( \exp \frac{\ln T_M - \ln T_1}{M - 1} \right)^{l-1}, \quad l = 1 \ldots M. \quad (5.10)$$

It is, of course, possible to finally take the state obtained from the above procedure as an input state for a direct optimization using gradient information, which may yield better accuracy close to the minimum.
5.3 Multiple quantum channels for the entanglement localization in CGTN states

As we have mentioned above, TNS approaches aim at breaking down the high-dimensional coefficient tensor into a tensor network that only depends on a small number of parameters. The $4^k$ coefficients of a quantum state consisting of $k$ (spatial) molecular orbitals are thus constructed from a reduced set of parameters.

All our findings with the CGTN states can be generalized to any CPS with an arbitrary order in the site correlators, i.e. three-site, four-site, etc. correlators.

We now introduce a decomposition scheme for CPS-type wave functions [3] to gain additional insight into the entanglement structure of molecular quantum states. In this section, we show that the entanglement can be quantified by considering only a subset of two-site correlators of the complete graph, namely those having indices on both subsystems. Moreover, the variational optimization of the CGTN states minimizes the entanglement between the two subsystems through multiple quantum channels starting from a maximally-entangled, random state.

The emerging CGTN state approximates the high-dimensional coefficient tensor of the exact wave function by a product of two-site correlators $\mathbf{f} \equiv \{ f_{\alpha\beta}^{n\alpha n\beta} \}$ as described in Eq. (5.1). The sum in Eq. (5.1) runs over all basis states in the $N$-particle Hilbert space with the correct quantum numbers (e.g., correct number of electrons, projected spin, and point-group symmetry). An advantage of the CGTN state is that it does not rely on an artificial orbital ordering which is necessary for MPS in the DMRG algorithm for quantum chemistry [50].

The set of one-electron functions, used to construct the many-electron basis functions of the $N$-particle Hilbert space, is bipartitioned into two subsystems, which shall be denoted as $\mathcal{A}$ and $\mathcal{B}$. The exact wave function can be written, according to the bipartitioning $\mathcal{A}$ and $\mathcal{B}$, as

$$|\Psi_{\text{exact}}^{(\mathcal{A};\mathcal{B})}\rangle = \sum_{l}^{d_{\mathcal{A}}} \sum_{r}^{d_{\mathcal{B}}} C_{lr}^{(\text{exact})} |\mathcal{A}_l\rangle \otimes |\mathcal{B}_r\rangle$$

(5.11)

where the sums over $l$ and $r$ run over all basis states of the Fock space spanned by the molecular orbitals in $\mathcal{A}$ and in $\mathcal{B}$, respectively. Note that only combinations of $l$ and $r$ appear in $|\Psi_{\text{exact}}^{(\mathcal{A};\mathcal{B})}\rangle$ that describe a state $|\mathcal{A}_l\rangle \otimes |\mathcal{B}_r\rangle$ contained in the $N$-particle Hilbert space. The exact coefficients $C_{lr}^{(\text{exact})}$ are approximated by the CGTN coefficients as

$$C_{lr}^{(\text{CGTN})} \approx C_{lr}^{(\text{CGTN})} = C_l^\mathcal{A} \cdot C_{lr}^{\mathcal{A}\cap\mathcal{B}} \cdot C_r^\mathcal{B}$$

(5.12)
5.3. Multiple quantum channels in CGTN states

where

\[ C_t^A = \prod_{\alpha} \prod_{\beta \leq \alpha} f^{l_{\alpha \beta}} \]  \hspace{1cm} (5.13)  
\[ C_{lr}^{A \cap B} = \prod_{\alpha} \prod_{\beta \leq \alpha} f^{l_{\alpha \beta}} \]  \hspace{1cm} (5.14)  
\[ C_r^B = \prod_{\alpha} \prod_{\beta \leq \alpha} f^{r_{\alpha \beta}} \]  \hspace{1cm} (5.15)

\( C_t^A \) and \( C_r^B \) only depend on the states of the corresponding subsystem. The decomposition of the CGTN coefficients according to Eq. (5.12) is graphically shown for an example of four spin orbitals in Figure 5.1.

Figure 5.1: Pictorial representation of the decomposition of the CGTN coefficients. The bipartitioning defines two subsystems \( \mathcal{A} \) and \( \mathcal{B} \) each consisting of one molecular orbital, \( |n_1\rangle \otimes |n_2\rangle \) and \( |n_3\rangle \otimes |n_4\rangle \), respectively, where \( \{n_i| i = 1, \ldots , 4\} \) are spin orbitals. The correlations between \( \mathcal{A} \) and \( \mathcal{B} \) are solely described by the inter-two-site correlators \( C_{lr}^{A \cap B} \) (dashed pink lines). The two-site correlators \( C_t^A \) in \( \mathcal{A} \) (green) and \( C_r^B \) in \( \mathcal{B} \) (red) would form a product state if the inter-two-site correlators were neglected, and therefore they have no direct influence on the entanglement of that particular bipartitioning.

We can express the CGTN state for the two subsystems as

\[
|\Psi_{\text{CGTN}}^{(A:B)}\rangle = \sum_{l} \sum_{r}^{d_A} \sum_{l}^{d_B} C_{lr}^{A \cap B} |A_{\psi_l}\rangle \otimes |B_{\psi_r}\rangle
\]  \hspace{1cm} (5.16)

\[
= \sum_{l} \sum_{r}^{d_A} C_{lr}^{A \cap B} |A_{\psi_l}\rangle \otimes |B_{\psi_r}\rangle
\]  \hspace{1cm} (5.17)
by introducing scaled bases \(|\mathcal{A}_{\psi_l}\rangle |l = 1, \ldots, d_A\rangle\) for \(\mathcal{A}\) and \(|\mathcal{B}_{\psi_r}\rangle |r = 1, \ldots, d_B\rangle\) for \(\mathcal{B}\). These sets of states, however, need not be normalized.

If we assume that we can write a spectral decomposition of the matrix \(M\) of scalar products of the states in \(\mathcal{A}\),

\[
M_{ll'} \equiv \langle \mathcal{A}_\psi | \mathcal{A}_{\psi'} \rangle = C_A^l \cdot C_A^{l'} \delta_{ll'}
\]

with \(M = XDX^\dagger\) and \(D_{ll'} = \delta_{ll'} d_l\) and \(XX^\dagger = X^\dagger X = I\), then an orthonormalized set for the states in \(\mathcal{A}\) can then be obtained by the following basis transformation,

\[
|\tilde{\mathcal{A}}_\psi \rangle = \frac{1}{\sqrt{d_l}} \sum_k \langle X^\dagger \rangle_{lk} |\mathcal{A}_\psi \rangle.
\]

The same procedure can be applied to generate an orthonormal set \(|\tilde{\mathcal{B}}_\psi \rangle\) for \(\mathcal{B}\).

The CGTN state for the bipartition now reads

\[
|\Psi_{\text{CGTN}}^{(A:B)}\rangle = \sum_{l}^{d_A} \sum_{r}^{d_B} C_{lr}^{A\cap B} |\tilde{\mathcal{A}}_\psi \rangle \otimes |\tilde{\mathcal{B}}_\psi \rangle.
\]

The Schmidt form of \(|\Psi_{\text{CGTN}}^{(A:B)}\rangle\) is constructed by a singular value decomposition of the coefficients \(C_{lr}^{A\cap B}\) as

\[
C_{lr}^{A\cap B} \equiv (C^{A\cap B})_{lr} = \sum_{\alpha} (U)_{ld} (D)_{\alpha\alpha} (V^\dagger)_{\alpha r}
\]

with \(U^\dagger U = VV^\dagger = I\) and \(D\) is a diagonal matrix with the Schmidt coefficients \(\lambda_\alpha = (D)_{\alpha\alpha}\). The Schmidt bases are then given by the unitary matrices \(U\) and \(V\) according to

\[
|\Phi^A_\alpha \rangle = \sum_l (U^\dagger)_{\alpha l} |\tilde{\mathcal{A}}_\psi \rangle
\]

\[
|\Phi^B_\alpha \rangle = \sum_r (V)_{\alpha r} |\tilde{\mathcal{B}}_\psi \rangle
\]

leading to the Schmidt decomposition of the CGTN state,

\[
|\Psi_{\text{CGTN}}^{(A:B)}\rangle = \sum_{\alpha}^{\min\{d_A,d_B\}} \lambda_\alpha |\Phi^A_\alpha \rangle \otimes |\Phi^B_\alpha \rangle.
\]

The reduced density matrix of \(\mathcal{A}\) is calculated by performing the partial trace over \(\mathcal{B}\),

\[
\hat{\rho}_A = \text{Tr}_B \left( |\Psi_{\text{CGTN}}^{(A:B)}\rangle \langle \Psi_{\text{CGTN}}^{(A:B)}| \right) = \sum_{\alpha} \lambda_\alpha^2 |\Phi^A_\alpha \rangle \langle \Phi^A_\alpha|\]

which determines the von Neumann entropy,

\[
S(\rho_A) = -\text{Tr}(\rho_A \ln \rho_A) = -\sum_{\alpha} \lambda_\alpha^2 \ln \lambda_\alpha^2.
\]
In quantum information theory, the von Neumann entropy characterizes the entanglement between two subsystems. By taking advantage of the structure of the CPS, we just demonstrated that the entanglement between two groups of orbitals described by a CGTN state is parametrized by the set of inter-two-site correlators. In a qualitative sense, this subnetwork of correlators provides multiple quantum channels for the entanglement localization.

5.4 Analysis of the accuracy of CGTN states

Our primary goals in this section are: (i) to analyze the CGTN ansatz for the description of electronic energies and CI coefficients of molecules and (ii) to show that we can optimize the CGTN ansatz by means of a variational parallel-tempering Monte Carlo algorithm.

Our test molecules are ozone and the cobalt(II)-tetraqua complex. For the variational optimization of these test molecules, we did not apply the sampling of many-particle basis since the selected active spaces still allow the sum in Eq. (5.6) to be carried out explicitly. Hence we use the above-described sampling scheme to sample the coefficients only. As a consequence, we avoid the sampling error of the occupation number vectors and thus obtain a reliable picture of the quality of our CGTN ansatz.

5.4.1 A strongly correlated molecular system: Ozone

We begin our numerical study with a most difficult case selected to probe the capabilities of the CGTN ansatz: The electronic structure of ozone at the transition state structure of the O$_2$ + O chemical reaction is a complex multireference problem [198]. We performed CAS(8,9)-CI reference calculations for the singlet and triplet states of ozone at the transition structure reported in Ref. [198]. For this calculation, we select Dunning’s cc-pVTZ basis set [199,200] and an active space consisting of the 9$-14a'$ 1$-3a''$ molecular orbitals. The Hilbert space of the singlet state is then spanned by 7'956 and the one for the triplet state by 5'268 occupation number vectors. The CGTN state contains only 684 variational parameters which is an efficient reduction by 91% compared to the singlet CASSCF wave function. The singlet energies of the ozone molecule at a transition state structure are given in Table 5.1 and show the highly multireference nature of the electronic structure when compared to the Hartree–Fock energy.
Table 5.1: Electronic energy of the singlet state of transition-state ozone in Hartree. The correlation energy ($E_{corr}$) denotes the energy difference between the Hartree–Fock energy and the energy obtained by a correlation method. All calculations were performed with an active space of 9 molecular orbitals comprising 8 electrons. The DMRG calculations were taken from Ref. [155] for comparison and $m$ represents the number of many-particle DMRG system basis states. The CGTN energy for the singlet state is evaluated in a spin-adapted configuration state function (CSF) basis.

<table>
<thead>
<tr>
<th>Method</th>
<th>$E_{S=0}/E_h$</th>
<th>$E_{S=1}/E_h$</th>
<th>$E_{corr}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>-224.282 841</td>
<td>-224.357 167</td>
<td>46.640</td>
</tr>
<tr>
<td>CASCI</td>
<td>-224.384 301</td>
<td>-224.416 172</td>
<td>19.999</td>
</tr>
<tr>
<td>DMRG($m=48$)</td>
<td>-224.384 252</td>
<td>-224.412 775</td>
<td>19.532</td>
</tr>
<tr>
<td>DMRG($m=156$)</td>
<td>-224.384 301</td>
<td>-224.412 775</td>
<td>19.532</td>
</tr>
<tr>
<td>CGTN</td>
<td>-224.381 648</td>
<td>-224.412 775</td>
<td>19.532</td>
</tr>
</tbody>
</table>

The vertical spin splitting between the first excited singlet and ground-state triplet state is reported in Table 5.2. For the first excited state of singlet symmetry a CSF basis has been constructed to obtain a spin pure state without spin contamination (see also section 2.3). For the triplet ground state, we have tested the levelshift approach as well as no spin constrains at all and found that levelshift calculations are prone to get stuck in a local minimum. This can be circumvented if no spin constraints are applied. Then, however, spin contamination might become a problem. For the levelshift calculation, $\epsilon = 1$ was used.

Table 5.2: Vertical spin-splitting energy differences between the singlet and triplet state of ozone at the transition geometry. All calculations were in an active space of 9 molecular orbitals comprising 8 electrons. For the singlet CGTN energy, a CSF basis was employed whereas no spin constraints were imposed on the triplet state calculation.

<table>
<thead>
<tr>
<th></th>
<th>$E_{S=0}/E_h$</th>
<th>$E_{S=1}/E_h$</th>
<th>$\Delta E$/kcalmol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>-224.282 841</td>
<td>-224.357 167</td>
<td>46.640</td>
</tr>
<tr>
<td>CASCI</td>
<td>-224.384 301</td>
<td>-224.416 172</td>
<td>19.999</td>
</tr>
<tr>
<td>CGTN</td>
<td>-224.381 648</td>
<td>-224.412 775</td>
<td>19.532</td>
</tr>
</tbody>
</table>

The relative energies between the singlet and triplet states converge much faster than the total electronic energies — even for this highly multireference system. For the parallel-tempering Monte Carlo simulation, we use eight replicas at different temperatures in the range $[1 \times 10^{-8} E_h, 0.001 E_h]$. 

In Figure 5.2, the convergence behavior for the triplet ground state calculation is shown. It can be seen that convergence difficulties arise when the levelshift operator is applied. In the algorithm, the $\hat{S}_-\hat{S}_+$ operator translates into a high-order polynomial which features many roots and therefore many local minima.

Figure 5.2: The convergence of the energy for the replica with $T = 1.0 \times 10^{-8} \text{E}_h$ of the triplet CGTN state of ozone in an active space of 9 molecular orbitals and 8 electrons is shown. The inner panel shows a zoom of the first thousands Monte Carlo iterations with the Hartree–Fock and CASCI energies. It is evident that the calculation employing the levelshift operator got stuck in a local minimum. The other CGTN calculation has no spin restriction. However, since the ground state is a triplet spin state, no spin contamination is expected. This is also seen in the expectation value of the converged triplet CGTN state of $\langle \hat{S}^2 \rangle = 1.99$.

Qualitatively speaking, the CGTN states “carved” the important occupation number vectors out of the entire $N$-electron Hilbert space that characterizes the electronic structure of the underlying molecular system. Therefore, a qualitatively correct description of the electronic structure is provided by the CGTN wave function.

### 5.4.2 Assessment of the CGTN states for transition metal complexes

In order to investigate the suitability of the CGTN parametrization for transition-metal containing molecules, we performed CGTN calculations on the high-spin ground-state of the cobalt(II)-tetraqua complex, $[\text{Co(II)(H}_2\text{O)}_4]^{2+}$ in $C_1$
point-group symmetry. The structure was optimized with DFT using the BP86 exchange-correlation functional [201,202] as implemented in the TURBOMOLE V5.10 [65] program package. For the DFT calculations, the resolution-of-the-identity (RI) technique [203–205] with the def-TZVP one-particle basis [206] and the corresponding auxiliary basis set [207] were used. In preparatory calculations, we calculated the one-electron and two-electron integrals as well as CASSCF reference energies with the Molpro program package [103]. The molecular orbitals have been expanded in the cc-pVTZ one-particle basis set [199, 200, 208]. We employ an active space consisting of 9 electrons and 9 molecular orbitals. For the parallel-tempering Monte Carlo simulation, we use 8 replicas at different temperatures in the range $[1 \times 10^{-8} E_h, 0.001 E_h]$. 

Figure 5.3: The BP86/RI/def-TZVP optimized structure of $[\text{Co}^{\text{II}}(\text{H}_2\text{O})_4]^{2+}$ for the quartet spin state.

In Table 5.3, the ability of the CGTN states to represent the electronic structure of $[\text{Co}^{\text{II}}(\text{H}_2\text{O})_4]^{2+}$ is assessed by comparing the tensor-network coefficients to the CI coefficients of the reference CAS(9,9)-SCF calculation. The BP86/RI/def-TZVP optimized structure of the compound is shown in Figure 5.3. The accurate representation of the seven largest CI coefficients in Table 5.3 is evident. Nevertheless, a systematic discrepancy between the coefficients exists. The squared CGTN coefficients are slightly larger than the corresponding squared CASSCF coefficients which can be understood by taking a closer look at the highly non-linear CGTN ansatz. Since the CGTN coefficients are constructed as a product of two-site correlators, they are best suited to describe highly multi-reference cases where the CI-coefficient profile shows a flat distribution rather than just one large coefficient with many small ones. In other words, the description of
the electronic structure by the CGTN state is not as efficient for single-reference as for multi-reference cases due to the nature of this particular ansatz.

Table 5.3: The squared CASSCF and CGTN coefficients of the seven largest occupation number vectors (ONV) for the quartet spin state of \([\text{Co(II)(H}_2\text{O)}_4]^{2+}\) are compared with each other.

| ONV \(_i\) | \(|C_{i}|^2\) \(_\text{CASSCF}\) | \(|C_{i}|^2\) \(_\text{CGTN}\) |
|-----------|----------------|----------------|
| 2 2 2 + + + 0 0 0 | 0.988835 | 0.991055 |
| 2 2 0 + + + 2 0 0 | 0.001522 | 0.001697 |
| 2 0 2 + + + 0 2 0 | 0.001500 | 0.001672 |
| 2 + + + + + + 0 + | 0.000813 | 0.000969 |
| 2 − − + + + + − 0 | 0.000812 | 0.000969 |
| 2 2 + + + 0 − 0 + | 0.000572 | 0.000691 |
| 2 + 2 + + + 0 0 − + | 0.000568 | 0.000685 |

Nevertheless, the tensor network approximates the largest CI coefficients very accurately, but the steady decay of the small CI coefficients is difficult to model. In section 5.5, we present a hybrid approach \([209]\) for molecular systems where some large CI coefficients, e.g., of the Hartree–Fock state, are expressed by a single parameter. The TNS then approximates the large number of small CI coefficients.

Table 5.4: The absolute energies of the quartet spin state of \([\text{Co(II)(H}_2\text{O)}_4]^{2+}\) for the CGTN and CASSCF calculations are shown in Hartree atomic units. The number of variational parameters are also given. The CGTN parametrization provides an efficient and compact representation of the electronic wave function requiring only a tenth of the total number of parameters compared to the dimension of the Hilbert space of the CASSCF calculation.

<table>
<thead>
<tr>
<th>Hartree–Fock</th>
<th>CAS(9,9)-SCF</th>
<th>CGTN</th>
</tr>
</thead>
<tbody>
<tr>
<td>E / Hartree</td>
<td>−1685.235 055</td>
<td>−1685.293 744</td>
</tr>
<tr>
<td>Parameters</td>
<td>7056</td>
<td>684</td>
</tr>
</tbody>
</table>
Figure 5.4: Snapshots of the CGTN parameters during the variational optimization of the ground state of \( [\text{Co(II)}(\text{H}_2\text{O})_4]^{2+} \). The images show the two-site correlators for the (a) 1st, (b) 54000th, (c) 108000th, and (d) 164000th Monte-Carlo iteration with an absolute value larger than 0.1. All correlators have been scaled by the reciprocal value of the largest one for comparison reason. The magnitude of the two-site correlators is color-coded. The smallest correlators are drawn in dark-blue whereas the largest are magenta. The ground-state energy for the corresponding set of CGTN parameters is given in Hartree atomic units (\( E_h \)).

In Figure 5.4, the evolution of the CGTN state during the variational optimization of the parallel-tempering Monte Carlo procedure is illustrated. At the beginning, all two-site correlators have the same magnitude. During the optimization, most correlators fall below the arbitrarily chosen 0.1-threshold value and disappear, consequently. Here, we observe the localization of entanglement.
We have demonstrated in section 5.3 that the entanglement between two groups of orbitals only depends on the two-site correlators connecting them. Already without full convergence of the energy, one can define two groups of orbitals with minimal entanglement.

5.5 Unifying configuration interaction and tensor network theories: A hybrid approach

Our numerical study on the $[\text{Co(H}_2\text{O)}_4]^{2+}$ electronic ground state in section 5.4.2 has demonstrated that CGTN states are suited to describe transition metal systems. The tensor network ansatz detects the most important occupation number vectors of the factorially large $N$-particle Hilbert space and approximates these large coefficients accurately. The challenge, however, is the correct description of the large number of small coefficients which usually suffers from the crude approximations inherently made in a CGTN state. This highly-non linear ansatz thus seems to be most efficient in the description of a flat-distribution profile of the CI coefficients where most occupation number vectors have a similar coefficient.

We thus propose a modification of the CGTN ansatz to incorporate principles from configuration-interaction theory. In the hybrid tensor-network/configuration-interaction approach, the dominant occupation number vectors are explicitly represented by individual CI coefficients whereas the tensor network is used to approximate the small CI coefficients of the factorially large rest of determinants. The hybrid CGTN (Hy-CGTN) wave function reads

$$|\Psi_{\text{Hy-CGTN}}\rangle = \sum_{I}^{N_{\text{CI}}} C_I |I\rangle + \sum_{n_1,n_2,\ldots,n_k}^{q} \prod_{\alpha}^{k} \prod_{\beta \leq \alpha} \int_{n_{\alpha} n_{\beta}}^{n_{n_{\alpha} n_{\beta}}} \prod_{\alpha \beta}^{n_{n_{\alpha} n_{\beta}}} |n_1, n_2, \ldots, n_k\rangle$$ (5.27)

where $k$ is the number of spin orbitals and $N_{\text{CI}}$ the number of explicitly represented Slater determinants. This hybrid ansatz tries to uncouple the large and small CI coefficients, enabling the tensor network to describe the rather flat distributed small CI coefficients.

The number of variational parameters increases only marginally, linearly in the number of explicitly treated determinants, that is by $O(N_{\text{CI}})$ to an overall scaling of $O(N_{\text{CI}} + k(k + 1)d^2)$ with $d$ as the dimension of the local Hilbert space basis.

Our first preliminary hybrid CGTN results on the high-spin cobalt(II)-tetraqua complex are very encouraging. With only one additional parameter, treating the Hartree–Fock state explicitly, the convergence of the energy can be substantially improved as shown in Table 5.5 for the energies and in Table 5.6 for the CI coefficients.
Table 5.5: The Hy-CGTN energy of the quartet spin state of [Co(II)(H₂O)₄]²⁺ is compared to the results for the CGTN and CASSCF calculations listed in Table 5.4. Note that all energy values are given in Hartree atomic units. The Hy-CGTN approach has only one additional parameter compared to the CGTN approach but provides a better energy in a variational sense.

<table>
<thead>
<tr>
<th></th>
<th>CAS(9,9)-SCF</th>
<th>CGTN</th>
<th>Hy-CGTN</th>
</tr>
</thead>
<tbody>
<tr>
<td>E / Hartree</td>
<td>−1685.293 744</td>
<td>−1685.279 408</td>
<td>−1685.290 398</td>
</tr>
<tr>
<td># of parameters</td>
<td>7056</td>
<td>684</td>
<td>685</td>
</tr>
</tbody>
</table>

Table 5.6: The squared CASSCF, CGTN, and Hy-CGTN coefficients of the seven largest occupation number vectors (ONV) of the quartet spin state of [Co(II)(H₂O)₄]²⁺ are compared with each other.

| ONVᵢ           | |Cᵢ|² | |Cᵢ|² | |Cᵢ|² |
|----------------|--------------|------|------|------|
| 2 2 2 ++ + 0 0 0 | 0.988835     | 0.991055 | 0.989864 |
| 2 2 0 ++ + 2 0 0 | 0.001522     | 0.001697 | 0.001487 |
| 2 0 2 ++ + 0 2 0 | 0.001500     | 0.001672 | 0.001440 |
| 2 + + + + + + 0 | 0.000813     | 0.000969 | 0.000775 |
| 2 + + + + + + 0 | 0.000812     | 0.000969 | 0.000760 |
| 2 2 ++ + 0 0 + 0 | 0.000572     | 0.000691 | 0.000543 |
| 2 + 2 ++ + 0 + 0 | 0.000568     | 0.000685 | 0.000538 |

In Figure 5.5, the correlators of the converged CGTN and Hy-CGTN calculations are compared. The same color-coding scheme has been applied to represent the magnitudes of the two-site correlators as in Figure 5.4. By removing the largest CI coefficient, the Hartree–Fock state in this case, the tensor network in the Hy-CGTN approach can focus entirely on the description of a rather flat complementary coefficient profile and does not have to worry about the large difference in magnitude between invididual CI values. Currently, the explicitly treated occupation number vectors are heuristically selected but they can easily be identified by a regular run of a CGTN calculations. These exploratory CGTN calculations, however, need not be fully converged. The compiled numerical evidence of the previous section suggests that already after a few replica-exchanges the most significant occupation number vectors have been selected, and the rest of the optimization is just about fiddling with the representation of the small CI coefficients. For further studies on molecular systems, we thus recommend to perform first an exploratory CGTN calculation to find the dominant determinants that can be treated explicitly afterwards in a Hy-CGTN calculation.
Figure 5.5: (a) The two-site correlators for the converged CGTN calculation of the high-spin state of the cobalt(II)-tetraqua complex. (b) The two-site correlators for the converged Hy-CGTN calculations. Note that the tensor network describes in the hybrid approach coefficients of all occupation number vectors except the Hartree–Fock one. We see a difference in magnitude of the correlators in the two networks. In (a), there are more correlators with a large value compared to (b). Since there are many large correlators in (a), it is very difficult for the tensor network to approximate the small CI coefficients accurately. The magnitude of the correlators are color-indicated as in Figure 5.4.

5.6 Summary and perspective

We have demonstrated that tensor network states have a significant potential for routine quantum chemical calculations. They are an important concept in quantum chemistry for the design of novel parametrizations of the electronic wave functions.

We introduced a general class of tensor network states, which we denoted complete-graph tensor network states, to approximate the electronic wave function of a molecular system. This ansatz assumes pair correlations of one-electron states (orbitals) to construct all CI expansion coefficients of a total electronic state. Hence, instead of $2^k$ — or $4^k$ in the case of spatial orbitals — variational parameters, we employ only $k(k+1)/2 \times q^2$. CGTN states are a subclass of the most general CPS form of tensor network approximations to the FCI state. The accuracy of the CGTN approximation of total electronic states of molecules has been numerically studied for ozone and the cobalt(II)-tetraqua complex. We should note that this is the first application of a tensor network parametrization for molecular wave functions employing the full non-local electronic many-particle Hamiltonian. For this purpose, the $k(k+1)/2 \times q^2$ CGTN
parameters have been optimized with a variational Monte Carlo protocol that we have augmented by parallel tempering in order to prevent convergence to local minima of the electronic energy hypersurface in this parameter space.

In molecular physics and chemistry, we are primarily interested in obtaining accurate relative energies between two spin states or between two configurations on the same potential energy surface to describe the thermodynamics and kinetics of chemical reactions. The accurate calculation of relative energies is therefore mandatory. CGTN states provide the flexibility to describe electronic structures without relying on an a priori chosen reference configuration such as the Hartree–Fock state. The CGTN ansatz is therefore not biased to any particular Slater determinant and capable of finding the most important occupation number vectors in the Hilbert space of the molecular system.

In particular, the calculation of the electronic structure of transition metal clusters faces diverse challenges due to many of near-degenerate electronic states resulting in the failure of most standard quantum chemical methods. We expect the efficient parametrization of the CGTN states to be a very promising approach to deal with the multi-reference nature and the large active spaces mandatory for an accurate description of transition metal clusters. Moreover, we found that the connection of the tensor network approach with configuration-interaction principles leads to a better convergence of the variational optimization and should thus be preferred in the application to molecular systems.

Very encouraging perspectives on the application of the CGTN parametrization are strongly correlated systems such as hydrogen clusters at certain interatomic distances. These clusters exhibit interesting features in their electronic wave function where most occupation number vectors have a similar weight, and hence all basis states need to be taken into account for a qualitatively correct description of the electronic structure. The CGTN states may be well suited to describe electronic wave functions with a flat distribution of the coefficients over the Hilbert space basis.

So far, we have only studied the small-CAS Co complex with CGTN states. However, TNS-type approaches will certainly be investigated in detail in the near future. Due to the particular structure of the CGTN ansatz, there might exist a relation between the two-site correlators and the magnetic couplings in transition metal clusters as described in an effective spin Hamiltonian such as the Heisenberg model. It is, however, not yet established in theory whether one can directly extract this information from the two-site correlators.

In addition, the CGTN parametrization does not rely on a particular orbital ordering and thus treats all molecular orbitals on an equal footing. The magnitude of the two-site correlators might provide a tool to systematically devise an optimized orbital ordering for an MPS with an improved convergence behavior during the DMRG optimization. The CGTN states might provide relevant information to improve the convergence of DMRG calculations employing the MPS or TTNS ansatz.
6. Towards accurate potential energy surfaces of molecular systems

An accurate representation of the potential energy surface (PES) is of decisive importance to quantum chemistry since it forms the basis for understanding the kinetic behavior of molecules and chemical reaction dynamics. The PES represents the potential energy of a given system as a high-dimensional function of all atomic or internal coordinates. Nature prefers low-energy structures and hence local minima on the PES are of great interest in the study of reaction mechanisms, and thus most optimization methods deal with the issue of efficiently finding these minima. The relative energies between two local minima and the volumes of configuration space associated with them provide insight into the equilibrium thermodynamic properties [210]. The dynamical behavior, on the other hand, depends on how these minima are connected and the height of the energetical barrier the system has to surmount. The present chapter elaborates on the performance of our new electronic structure methods to accurately calculate the relative energies between two PES of different spin or two structures on the same PES. In addition, the construction of approximate PES using interpolation techniques is discussed.

6.1 Multi-state reactivity

The accurate quantum chemical calculation of electronic states of different spin multiplicity is of great importance to chemistry; in particular, for chemical reactions in which a spin-crossing event occurs [26, 27, 30, 150, 151, 211–214]. The electronic structure of transition metal compounds often features many dense-lying electronic states with a different spin which is one reason for their importance as catalysts. For such a set-up, the Born–Oppenheimer approximation might break down due to non-negligible couplings of the electronic spin and the orbital angular momentum that can induce a spin conversion — a jump from one spin state to another [67]. The likeliness of such a spin flip depends on the energetical difference of two spin states and thus the minimum-energy crossing point (MECP) between two surfaces is a decisive quantity. At the MECP, one assumes that a spin flip is more probable to occur than at other configurations [215, 216]. Hence if a MECP exists for a certain chemical reaction involving transition metals, a spin-crossing event might occur. A general discussion of the importance of different spin states in transition metal catalysis can be found in the work of Minaev and Ågren [217] who also coined the term
The concept of multi-state reactivity is a generalization of the two-state reactivity scheme which goes back to the pioneering work of Schröder, Shaik, and Schwarz [213,214,218]. The importance of the two-state reactivity (TSR) concept can not be stressed enough, especially since it opens up a new class of reaction mechanisms, in which activation barriers of chemical reactions are lowered by switching to an electronic state of different spin multiplicity [31,150,219–225]. The detailed theoretical description of TSR faces many challenges, especially in the realm of Schrödinger’s quantum mechanics where the spin–orbit coupling operator needs to be included artificially if insight is sought for spin conversion processes. In Dirac’s quantum theory, on the other hand, the spin and the spin–orbit operator arises naturally, but 4-component or even 2-component relativistic calculations are challenging for transition metal systems [67]. However, a detailed quantum chemical picture of the spin flip is often not required; it just matters whether one can keep track of the energetical levels of the two electronic states involved [105]. The applicability and usefulness of the TSR concept thus heavily depends on the ability of quantum chemical methods to provide accurate relative energies of electronic states of different spin multiplicities.

### 6.1.1 Singlet and triplet CGTN states of polyatomic radicals: The methylene example

For spin-crossing events, it is of decisive importance to obtain accurate relative energies between two spin states and thus describe the two potential energy surfaces qualitatively and quantitatively correct. There is, however, no way to tell the variational CGTN optimization algorithm described in section 5.2 how to converge directly to the desired spin state. The optimization algorithm might get easily trapped in local minima corresponding to a spin-contaminated total state. One possible solution would be to sample over the basis of spin-adapted configuration state functions (CSF) which can easily be constructed as linear combinations of occupation number representations using Clebsch–Gordan coefficients producing a SU(2) eigenstate of the Hamiltonian with well-defined total spin (see section 2.3). In that case, however, the complete occupation number vector basis must be constructed.

Another solution, which we need to employ in our second example below, is the application of a level-shift operator as used, for instance, for the DMRG algorithm in [105]. The concept of the level-shift operator can be easily implemented in the current optimization scheme. The idea is to substitute the original Hamiltonian by an effective shifted Hamiltonian where the unwanted states with a higher multiplicity are shifted up in energy. The lowest energy state of the total system is then a spin-pure state with the correct total spin. The shifted Hamiltonian is gives as in Eq. (3.5) where we added the product of the spin ladder operator to the original Hamiltonian. This prevents the occurrence of states which possess the same projected spin but have a different...
We choose methylene as our test molecule, for which we determine the vertical spin splitting of the singlet and triplet states. Methylene is the smallest polyatomic radical featuring a triplet ground state and several low-lying singlet states where strong correlations effects are present [226]. We are particularly interested in the energies of the triplet ground state and the lowest-lying singlet state with point-group symmetries $B_1$ and $A_1$, respectively.

In preparatory calculations, we calculated the one-electron and two-electron integrals as well as complete-active-space (CAS) self-consistent-field (SCF) reference energies with the Molpro program package [227]. The orbitals have been expanded in Dunning’s cc-pVTZ basis set [199, 200]. The electronic energies of the singlet and triplet state of CH$_2$ were studied at a C–H bond distance of 1.0753 Å and an H–C–H angle of 133.82 degrees in $C_1$ symmetry as reported in [226]. The integrals for the CGTN calculations are calculated over the natural orbitals of the corresponding CASSCF calculation. Within this theoretical setup, the CGTN calculations can be seen as CASCI-equivalent calculations, where the CI weights are iteratively improved rather than obtained from an expensive diagonalization step. For the parallel-tempering Monte Carlo simulation (see section 5.2, we use eight replicas at different temperatures in the range $[1 \times 10^{-8} E_h, 0.001 E_h]$. We investigate three active spaces that are successively enlarged, starting with a CAS(4,4) of four spatial orbitals comprising four electrons that is increased in each step by an occupied and a virtual orbital around the Fermi level yielding in total CAS(4,4), CAS(6,6), and CAS(8,8). The CAS is specified in parentheses as $(n,m)$ where $n$ is the number of electrons in $m$ molecular orbitals. The number of variational parameters in the CGTN states does not depend on the dimension of the $N$-particle Hilbert space but on the number of orbitals in the corresponding active space. The selected active spaces provide insight into the convergence behavior of the CGTN parametrization. For the CAS(4,4), the number of variational parameters is around three times larger than the size of the Hilbert space of CH$_2$ (resulting in an over-parametrization), whereas for CAS(6,6) it is of comparable size. For the CAS(8,8), however, there are about nine times more many-electron basis states (i.e., occupation number vectors) than variational parameters in the CGTN ansatz. While the first two smaller active spaces allow us to demonstrate that the CGTN ansatz is able to reproduce the CASSCF reference, the third CAS probes the efficiency of the reduced-parameter CGTN ansatz. In order to prevent spin-contamination in the CGTN state, the energy evaluation is performed in the basis of spin-adapted configuration state functions (CSF) for the singlet and triplet calculation. The weight for the CSF is calculated as a linear combination of the weights for the occupation number vector.

In Figure 6.1 and Table 6.1, CASSCF energy splittings between singlet and triplet spin states are compared to those obtained in the CGTN calculations. The number of variational parameters are given for each calculation as well.
Figure 6.1: Graphical representation of the vertical spin splitting of the singlet and triplet states of methylene with increasing size of the active space. For the singlet (×) and triplet (□) CGTN calculations, a spin-adapted configuration state function (CSF) basis was employed. The singlet and triplet CASSCF calculations are shown as (+) and (∗), respectively.

Table 6.1: Difference of triplet ground state and lowest-lying singlet state energies of methylene (CH$_2$) as obtained from CASSCF reference and CGTN calculations. The number of variational parameters in the CASSCF wave function corresponds to the number of occupation number vectors with the correct particle number and projected spin in the given active space: $\dim \mathcal{H}^{S=0}_{\text{CASSCF}}$ and $\dim \mathcal{H}^{S=1}_{\text{CASSCF}}$ parameters. The singlet and triplet states approximated by the CGTN ansatz comprise an equal number of variational parameters (#CGTN) in the wave functions. In the last column, the difference between CASSCF and CGTN spin-splitting energies $\Delta \Delta E$ are given in kcal mol$^{-1}$.

<table>
<thead>
<tr>
<th>CAS</th>
<th>$\Delta E_{\text{CASSCF}}/E_h$</th>
<th>$\dim \mathcal{H}<em>{S=0}^{S=0}/\dim \mathcal{H}</em>{S=1}^{S=1}$</th>
<th>$\Delta E_{\text{CGTN}}/E_h$</th>
<th>#CGTN</th>
<th>$\Delta \Delta E$/kcal mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(4,4)</td>
<td>0.0466</td>
<td>36/16</td>
<td>0.0466</td>
<td>144</td>
<td>0.0</td>
</tr>
<tr>
<td>(6,6)</td>
<td>0.0435</td>
<td>400/225</td>
<td>0.0441</td>
<td>312</td>
<td>−0.38</td>
</tr>
<tr>
<td>(8,8)</td>
<td>0.0378</td>
<td>4900/3136</td>
<td>0.0381</td>
<td>544</td>
<td>−0.18</td>
</tr>
</tbody>
</table>

The total absolute energies cannot be quantitatively reproduced by the CGTN states but they provide a qualitatively correct description of the energy difference.
between different spin states for a set of active spaces. For the CAS(4,4), the CGTN calculation exactly reproduce the CASSCF reference calculations and verify that the ansatz optimized with the parallel-tempering Monte Carlo optimization can indeed find the correct ground-state wave function. The next question to answer is whether the CGTN ansatz can also extract the essential features of the electronic structure for larger active spaces because even if total electronic energies are not well reproduced, it would be sufficient to reliably produce relative energies of chemical accuracy (of about 1 kcal mol$^{-1}$).

Figure 6.2: The squared CI coefficients of the most important occupation number vectors are shown for the singlet (+) and triplet (♦) CASSCF and the singlet (×) and triplet (□) CGTN calculations for methylene in a CAS(8,8). Even though the CGTN state has about 90% less parameters than the CASSCF wave function, it finds the most important occupation number vectors and provides highly accurate CI coefficients.

We already found [105] that MPS as optimized by the DMRG algorithm can reproduce the energetical spin splitting in transition metal complexes and clusters although the one-dimensional MPS parametrization is not very suited for this problem. The energy difference between two states can converge much faster than the total electronic energies of the individual states. Considering that during a chemical process (reaction, spin flip) only a small number of orbitals is needed to qualitatively describe the changes in electronic structure, it can be understood that the parametrization of the total electronic states requires
a balanced representation of all occupation number vectors that involve these orbitals. We may expect that this balanced description is possible with a CGTN ansatz. This is exactly what we observe in the CAS(6,6)- and CAS(8,8)-CGTN calculations. The relative energies appear to be better reproduced than the absolute energies for the different spin states. Even though the parametrization in terms of the CGTN states consists of only a small fraction of parameters compared to the dimension of the Hilbert space in the CAS(8,8) case, the vertical spin splitting is accurately reproduced.

The accuracy of the CGTN to represent the electronic structure can also be assessed by performing an analysis of the CI coefficients of the CASSCF and the CGTN calculations. In Figure 6.2 and Table 6.2, the CI coefficients of the ten most important occupation number vectors for the singlet and triplet CGTN and CASSCF calculations are compared. According to the spectrum of the CI coefficients, the relative energy between the two spin states is accurately described even though the CGTN energies are slightly higher than the CASSCF reference energies. The CGTN parametrization of the total electronic states approximates the dominant occupation number vectors with high accuracy. However, it lacks a proper description of most of the very small coefficients of a large set of occupation number vectors that significantly affects the total energy but has basically no influence on the energy difference. The reason of this deficiency lies in the few parameters used for the construction of the CGTN ansatz and might be systematically improvable by using higher-order correlators, a strategy already described by Chan et al. [166].

Table 6.2: The CI coefficients of the CASSCF and the CGTN wave functions of singlet and triplet spin symmetry are shown for the ten most important occupation number vectors. The CGTN coefficients qualitatively and even quantitatively agree with the CASSCF reference which is the exact solution for the CAS(8,8) in the given one-particle basis.

<table>
<thead>
<tr>
<th>ONV</th>
<th>$C_{\text{CASSCF}}^{(S=0)}$</th>
<th>$C_{\text{CGTN}}^{(S=0)}$</th>
<th>$C_{\text{CASSCF}}^{(S=1)}$</th>
<th>$C_{\text{CGTN}}^{(S=1)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.9623</td>
<td>0.9624</td>
<td>0.9945</td>
<td>0.9950</td>
</tr>
<tr>
<td>2</td>
<td>-0.2436</td>
<td>-0.2452</td>
<td>-0.0375</td>
<td>-0.0380</td>
</tr>
<tr>
<td>3</td>
<td>-0.0607</td>
<td>-0.0613</td>
<td>-0.0320</td>
<td>-0.0316</td>
</tr>
<tr>
<td>4</td>
<td>-0.0352</td>
<td>-0.0369</td>
<td>-0.0271</td>
<td>-0.0269</td>
</tr>
<tr>
<td>5</td>
<td>-0.0297</td>
<td>-0.0299</td>
<td>0.0249</td>
<td>0.0206</td>
</tr>
<tr>
<td>6</td>
<td>-0.0277</td>
<td>-0.0282</td>
<td>0.0236</td>
<td>0.0240</td>
</tr>
<tr>
<td>7</td>
<td>-0.0277</td>
<td>-0.0282</td>
<td>0.0232</td>
<td>0.0234</td>
</tr>
<tr>
<td>8</td>
<td>0.0269</td>
<td>0.0261</td>
<td>-0.0225</td>
<td>-0.0220</td>
</tr>
<tr>
<td>9</td>
<td>0.0269</td>
<td>0.0261</td>
<td>-0.0205</td>
<td>-0.0205</td>
</tr>
<tr>
<td>10</td>
<td>-0.0262</td>
<td>-0.0272</td>
<td>0.0205</td>
<td>0.0213</td>
</tr>
</tbody>
</table>
6.1.2 Spin splitting of the transition metal model compound CoH

Cobalt hydride is a small molecule particularly suited as a toy model to assess the performance of the automated DMRG extrapolation methodology described in section 3.6.2 to provide accurate PES.

The methodology applied for the CoH molecule corresponds to the one that we reported in Ref. [105]. In Ref. [105], the DMRG calculations were performed on the triplet ground state and on the higher-lying singlet state. Relative energies were obtained from calculations with the same number of basis states $m$. We already noted in Ref. [105] that more basis states are required in the calculation for the singlet state than for triplet state. Hence the DMRG energies for the triplet state already converged at a smaller number of DMRG basis states indicating that the accuracy in the singlet and triplet energy may be different for a fixed number of renormalized states $m$. For accurate relative energies, it is crucial to compare energies with the same accuracy. The automated DMRG extrapolation procedure provides now a way to determine the necessary number of renormalized states $m$ to obtain reliable relative energies by means of the error estimates.

At this point, we should emphasize that the primary objective of the automated DMRG extrapolation is not necessarily obtaining total electronic energies with FCI accuracy but rather to provide an error control facility to monitor the convergence of a DMRG calculation. This allows us to determine the number of renormalized states $m$ required for each total state to obtain accurate relative energies.

All preparatory calculations for the one-electron and two-electron integrals, $h_{ij}$ and $V_{ijkl}$, were carried out with the Molpro program package [103]. All DMRG calculations were performed with the Qc-Dmrg-ETH program developed in our group [98]. The singlet and triplet energies of CoH were calculated at a bond distance of 156.271 pm, which was obtained from a structure optimization in $C_2v$ symmetry using CCSD(T) and a Dunning cc-pVTZ basis set [199, 200].

The DMRG calculations were performed in an active space consisting of 10 molecular orbitals and 10 electrons. The active space was chosen according to Table I in Ref. [105]. The same active space has also been applied for the CASSCF reference calculations. For the singlet state DMRG calculations, a level shift operator was applied to obtain a wave function of pure spin. The energies presented in this work for the singlet state of CoH were obtained by diagonalization of the shifted Hamiltonian. The one-electron and two-electron integrals were calculated from the natural orbitals of the CASSCF reference calculation. The DMRG calculations should therefore converge to the CASSCF reference energy.

In Table 6.3, the vertical energy splitting of the singlet and triplet states of cobalt hydride is listed for DMRG energies with increasing number of states $m$. For the automated DMRG extrapolation, we started the calculation at $m = 32$ and increased this value by a factor of 1.2. The threshold for the error estimate
was set to $10^{-8} \text{E}_h$.

Table 6.3: Extrapolation of the singlet and triplet energy of CoH using the automated DMRG extrapolation scheme. The threshold of the convergence criteria for the error estimate is set to $10^{-8} \text{E}_h$. The singlet state requires a larger number of DMRG basis states in order to reproduce the CASSCF reference energy than the triplet state. This means that at $m = 91$, e.g., the triplet energy is better described than the singlet energy. Therefore, we need a scheme to determine energies for both states with the same accuracy in order to obtain accurate relative energies.

<table>
<thead>
<tr>
<th>$M$</th>
<th>$E(S = 0)/\text{E}_h$</th>
<th>$E(S = 1)/\text{E}_h$</th>
<th>$\Delta E/\text{E}_h$</th>
<th>$\Delta E/\text{kJmol}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>32</td>
<td>$-1381.951 \ 525 \ 98$</td>
<td>$-1381.995 \ 036 \ 50$</td>
<td>0.043 510</td>
<td>114.24</td>
</tr>
<tr>
<td>38</td>
<td>$-1381.951 \ 804 \ 85$</td>
<td>$-1381.995 \ 069 \ 19$</td>
<td>0.043 264</td>
<td>113.59</td>
</tr>
<tr>
<td>45</td>
<td>$-1381.951 \ 973 \ 54$</td>
<td>$-1381.995 \ 091 \ 48$</td>
<td>0.043 117</td>
<td>113.21</td>
</tr>
<tr>
<td>54</td>
<td>$-1381.952 \ 033 \ 11$</td>
<td>$-1381.995 \ 102 \ 10$</td>
<td>0.043 068</td>
<td>113.08</td>
</tr>
<tr>
<td>64</td>
<td>$-1381.952 \ 053 \ 94$</td>
<td>$-1381.995 \ 106 \ 68$</td>
<td>0.043 052</td>
<td>113.03</td>
</tr>
<tr>
<td>76</td>
<td>$-1381.952 \ 063 \ 57$</td>
<td>$-1381.995 \ 109 \ 01$</td>
<td>0.043 045</td>
<td>113.02</td>
</tr>
<tr>
<td>91</td>
<td>$-1381.952 \ 070 \ 29$</td>
<td>$-1381.995 \ 110 \ 03$</td>
<td>0.043 039</td>
<td>113.00</td>
</tr>
<tr>
<td>109</td>
<td>$-1381.952 \ 072 \ 69$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>130</td>
<td>$-1381.952 \ 073 \ 73$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>156</td>
<td>$-1381.952 \ 073 \ 86$</td>
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<td></td>
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</tbody>
</table>

Extrapolated $-1381.952 \ 073 \ 65$ $-1381.995 \ 110 \ 63$ 0.043 037 112.99

Error estimate 3.0 × $10^{-9}$ 6.3 × $10^{-9}$

CASSCF(10,10) $-1381.952 \ 073 \ 95$ $-1381.995 \ 110 \ 45$ 0.043 037 112.99

In Table 6.3, it is clearly shown that a larger number of DMRG basis states is needed to describe the singlet state compared to the triplet state in order to reach the reference energy. Also, the effective number of DMRG states can be chosen much smaller if we apply the automated DMRG extrapolation. Our approach can dynamically identify the maximal number of DMRG states required for a certain accuracy in the energy. By contrast, a brute-force scheme would employ a very large $m$ for both states so that the energies can be considered converged which is neither desirable nor feasible for larger molecules.

In addition, we have tested Legeza’s extrapolation approach as defined in Eq. (3.33). The extrapolation parameters $a$, $b$, and $E_{\text{FCI}}$ are presented in Table 6.4. For Legeza’s approach only the last three DMRG calculations have been used. That is for the CoH singlet state DMRG calculations with $m = 109, 130, 156$ and for the CoH triplet state DMRG calculations with $m = 64, 76, 91$. We find that the extrapolated energies are in very good agreement with the CASSCF reference calculations.
Furthermore, we have performed all DMRG calculations on the singlet and triplet state of CoH by applying white noise during the initialization of the matrix representations on the complementary system and then gradually turned it off in the course of the first ten macroiterations. Then, however, only the DMRG calculations with a low number of DMRG system states \((m = 32, 38, 45)\) show a slight improvement in the final energy and after \(m = 54\) there was no effect at all in the converged energy. Since the effect of white noise is minimal, these data are not presented here. But note that the electronic energies converge fast in the case of CoH and thus no general conclusion regarding the application of noise should be drawn from this example.

Table 6.4: Parameters for Legeza’s extrapolation scheme as described in Eq. (3.33) are listed for the singlet and triplet spin state of cobalt hydride. The extrapolated FCI energies are in good agreement with the CASSCF reference energies for the singlet and triplet state of CoH.

<table>
<thead>
<tr>
<th>Spin State</th>
<th>(a)</th>
<th>(b)</th>
<th>(E_{\text{FCI}}/E_h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(S = 0)</td>
<td>3.464 230 20</td>
<td>1.804 660e14</td>
<td>-1381.952 073 87</td>
</tr>
<tr>
<td>(S = 1)</td>
<td>1.293 303 18</td>
<td>369.848 301</td>
<td>-1381.995 110 48</td>
</tr>
</tbody>
</table>

In Figure 6.3, the results of Table 6.3 are shown with the extrapolated energy and the extrapolated number of DMRG states. The extrapolated number of DMRG system states points to the maximal number required to approach a truncation error of zero. Hence the CoH example is a successful application of the automated DMRG error protocol. In particular, we note that the automated extrapolation scheme stopped the DMRG iterations at the appropriate number of DMRG basis states. However, the DMRG calculations on CoH for small \(m\) values converge for both spin states comparatively fast to the CASSCF reference results. This is the reason why we had to employ a very tight convergence criterion in order to be able to study the extrapolation protocol. A close inspection of the extrapolated result for the singlet \(S=0\) state shows that this energy is slightly higher than the DMRG energy obtained for \(m=156\) and thus also slightly farther away from the CASSCF reference. By contrast, the extrapolated energy of the triplet \(S=1\) state is found slightly below the FCI reference. For both states, these differences occur at the 7th and 8th figure behind the decimal point. Note, however, that the relative energy remains unaffected by these findings, which is most important in view of practical applications of DMRG. Nevertheless, we shall have a closer look into what is going at the 7th and 8th figure behind the decimal point. These findings are best understood by investigating the dependence of the DMRG energies on the truncation error \(\epsilon\), which is determined by the chosen number of renormalized system states \(m\), in Figure 6.3. We see in the top panel that a
kink occurs for $m=54$ for the singlet state, while a weaker kink is present for the triplet state at $m=38$. These kinks prohibit a very accurate extrapolation.

Figure 6.3: Graphical representation of the data in Table 6.3. Top: extrapolated energy ($E = -1381.95207365\, E_h$) and extrapolated number of DMRG states ($m = 173$) for CoH in the singlet state. Bottom: extrapolated energy ($E = -1381.95511063\, E_h$) and extrapolated number of DMRG states ($m = 112$) for CoH in the triplet state. (The energies of the DMRG calculations are marked by stars, “∗”, whereas the number of DMRG basis states is indicated by “+”.)

Depending on the size of the instability (kink) the extrapolated energy carries
an error, which shows up after the 7th digit in our present test case. If this error starts to increase the extrapolated energy above the best energy in the data set, then this points to a nonnegligible effect of the kink to be removed by an additional DMRG run with increased value of \( m \) to be started automatically by our automated convergence control protocol.

6.2 Quantum information analysis of electronic states at different molecular structures: The Cu\(_2\)O\(_2\) example

In this section, we demonstrate how quantum information entropies assist DMRG calculations in providing efficient and accurate electronic energies for the construction of potential energy surfaces of very complicated chemical systems such as transition metal clusters [149].

In 2006, Cramer et al. investigated several theoretical models on the [Cu\(_2\)O\(_2\)]\(^{2+}\) torture track and found incisive discrepancies between them [152]. The CASSCF calculations even yield a qualitatively wrong interpretation of the energy difference between the two isomers. The reason for this striking failure lies in the inability of the CASSCF method to include all relevant molecular orbitals into the one-particle active space that would be necessary to obtain a qualitatively correct description of the electronic structure. Already the qualitative picture of an extended Hückel calculation indicated the requirement of more than doubling the active space for binuclear transition metal clusters compared to the mononuclear analog [105]. An additional support for the fact that a very large active space is needed for a correct description of the electronic structure of transition metals is the finding of Pierloot et al. to include a second \( d \) shell to obtain accurate results [228]. As we showed in our previous work [105], the DMRG algorithm is an ideal candidate to tackle the description of challenging electronic structures that require large active spaces occurring in transition metal chemistry.

The very challenging binuclear oxo-bridged copper clusters identified in Ref. [152] as a very difficult case for complete-active-space-like calculations pose an ideal test for the DMRG algorithm. In a pioneering study, some of us investigated the DMRG algorithm for the prediction of relative energies of transition metal clusters of different molecular structures, the bis(\( \mu \)-oxo) and \( \mu - \eta^2 : \eta^2 \) peroxy isomers of [Cu\(_2\)O\(_2\)]\(^{2+}\) [105]. Based on these results, we drew the conclusion that the DMRG algorithm is suited to study transition metal complexes and clusters. Kurashige and Yanai have picked up that same problem as well and performed massively parallel DMRG calculations employing 2400 renormalized basis states but on a larger active space with a smaller one-particle basis [138]. In their study, a new aspect was the inclusion of a perturbative correction introduced originally by White [95] for the one-site DMRG algorithm to prevent convergence to local minima during the optimization process. Here, we show that no convergence acceleration technique such as white noise [92] or perturbative correction [138]
Towards accurate potential energy surfaces

is needed if an entropy-based optimization scheme is employed. We reinvestigate the dicopper clusters with an improved methodology transforming the DMRG approach eventually into a black-box method with significantly reduced computational requirements. For our DMRG calculations, the same active space, one-particle basis set and effective core potential as in Ref. [105] was used.

6.2.1 Electronic ground state of $[\text{Cu}_2\text{O}_2]^{2+}$

We started with a short DMRG calculation using a limited set of block states in order to obtain the most important characteristics of the entropy functions and to determine the low-lying energy spectrum. In order to use DMRG in an automated manner as a black-box method, we did not use any specific ordering or CAS vector related to the chemical characteristics of the problem.

In order to determine the multiplicity of the converged target state, we have also calculated the expectation value of the second-quantized $S^2$ operator given in Eq. (2.17). The expectation value is equal to $S(S + 1)$ in Hartree atomic units, i.e., zero for a singlet state and two for a triplet state.

We have performed a calculation with fixed $M = 64$ states, using the energetical ordering, and the CAS vector was simply set to CASV $\equiv [N, N-1, \ldots, 1]$. This latter choice guarantees that during the initialization procedure long range interaction between the system block (left-block) and the rightmost sites of the chain is taken into account. In this calculation, we have restricted the CI-DEAS procedure to include determinants with at most triple excitations from the Hartree–Fock state. The convergence of the ground state energy in the $A_g$ irreducible representation of the point group $D_{2h}$ is shown in Figure 6.4(a) as the square symbols. Although the convergence is rather slow, the results obtained in our previous work with $M = 800$ block states [105] — shown by the dashed line — can be reached after eight sweeps. The convergence to the singlet state has been confirmed by the expectation value of the total-spin operator $\langle S^2 \rangle = 10^{-3}$.

The block entropy profile converges very slowly as shown in Figure 6.5(b). In fact, the entropy profile corresponding to the CI-DEAS procedure represented by the red circle symbol is almost zero for most of the superblock configurations which indicates the lack of entanglement between the DMRG blocks. As a consequence, the DMRG algorithm selected inappropriate states for the description of the environment blocks.

A detailed analysis of the entropy functions revealed an improved convergence behavior of the DMRG energy. The obtained single-orbital and block entropies as a function of DMRG sweeps are shown in Figure 6.5. By comparing Figures 6.5(a) and 4.1, we see that orbitals with large entropies can already be identified and a reasonable CAS vector can thus be constructed. In Figure 6.5(b), one also recognizes that once the third orbital is pushed in the left block, i.e., for $l \geq 3$ the block entropy increases significantly. This is because the third
Figure 6.4: (a) Convergence of the ground state energy in Hartree for various parameters for the $\mu - \eta^2 : \eta^2$ peroxo isomer. The dashed line gives the ground state energy obtained in Ref. [105] using $M = 800$ block states. (b) Number of block states as a function of iteration steps for $\chi = 10^{-4}$ corresponding to Figure 6.6.
Figure 6.5: (a) Single-orbital entropy, (b) block entropy and (c) mutual information profile for the $\mu - \eta^2 : \eta^2$ peroxo isomer of $[\text{Cu}_2\text{O}_2]^{2+}$ using energetical ordering, without optimized CAS vector for the singlet ground state of $A_g$ symmetry with fixed $M = 64$ block states. The convergence of the ground state energy in Hartree is shown in Figure 6.4(a) by the square symbol.
Figure 6.6: (a) Single-orbital entropy, (b) block-entropy, and (c) mutual information obtained for the \( \mu - \eta^2 : \eta^2 \) peroxo isomer of \([\text{Cu}_2\text{O}_2]^{2+}\) as a function of DMRG sweeps with optimized ordering, CAS vector, and by setting the quantum information loss \( \chi = 10^{-4} \). The CI-DEAS initialization procedure corresponds to symbols with red circle. The optimized ordering and CAS vector is given in Table 6.5.

Orbital index is highly entangled with orbitals 14 and 25 as can be seen in Figure 4.4. The largest values of the block entropy is reached for \( 13 < l < 35 \) when the highly entangled orbitals 13 and 35 belong to the two different blocks. In order to localize entanglement, ordering optimization based on the two-orbital mutual information can also be carried out according to the procedure described in Sec. II and a block entropy profile shown in Figure 6.6(b) is obtained. By comparing Figures 6.5(b) and 6.6(b) it is clear that in the latter case the block entropy is highly localized, i.e., it takes large values only for a few superblock configurations. Repeating the calculation with fixed \( M = 64 \) block states again but using an optimized ordering and CAS vector yields a ground state energy estimate of \( E_{\text{peroxo}} = -541.55533 \) Hartree. The fast convergence is shown in Figure 6.4 by the diamond symbol. In fact, the ground state energy after the first half sweep, i.e., at the end of the CI-DEAS procedure is already far below
Table 6.5: Optimized ordering and CAS vector for the $\mu - \eta^2 : \eta^2$ peroxo isomer of $[\text{Cu}_2\text{O}_2]^{2+}$.

<table>
<thead>
<tr>
<th>ORD=</th>
<th>44 41 42 43 40 31 30 33 32 29 11 10 9 8 7</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20 21 19 18 22 1 2 5 6 4 3 14 12 17 16</td>
</tr>
<tr>
<td></td>
<td>15 13 35 34 36 38 37 39 25 26 24 27 28 23</td>
</tr>
<tr>
<td></td>
<td>CASV=[35 13 14 34 3 25 26 18 4 36 7 15 12 10 2</td>
</tr>
<tr>
<td></td>
<td>19 40 20 8 33 29 42 21 32 24 16 11 43 1 41</td>
</tr>
<tr>
<td></td>
<td>17 44 31 30 9 22 6 39 38 5 27 23 37 28]</td>
</tr>
</tbody>
</table>

Table 6.6: Optimized ordering and CAS vector for the bis($\mu$-oxo) isomer of $[\text{Cu}_2\text{O}_2]^{2+}$.

<table>
<thead>
<tr>
<th>ORD=</th>
<th>44 41 43 40 42 31 30 33 32 29 11 10 9 8 7</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>20 21 19 18 22 1 2 5 6 4 3 12 17 16 15</td>
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<tr>
<td></td>
<td>14 13 35 34 36 38 37 39 25 26 24 27 28 23</td>
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<tr>
<td></td>
<td>CASV=[35 13 14 34 3 25 26 18 7 4 8 36 22 15 12</td>
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<tr>
<td></td>
<td>2 9 10 19 40 5 42 1 11 29 24 43 44 33 41</td>
</tr>
<tr>
<td></td>
<td>32 30 6 21 17 31 27 20 28 38 23 29 16 37]</td>
</tr>
</tbody>
</table>

the one given by Ref. [105] and the block entropy profile has the same structure as the one obtained after eight sweeps. This can be attributed to the CI-DEAS procedure for selecting the appropriate environment block states at each iteration step by taking care of the renormalized system block and the inclusion of the highly entangled orbitals from the beginning.

There is no need to use additional methods to guarantee convergence like white noise [92] or perturbative correction [138] which is an interesting observation in view of the results of Kurashige and Yanai. The optimized ordering and CAS vectors used in the calculation are summarized in Table 6.5. Carrying out the same procedure for the bis($\mu$-oxo) isomer of $[\text{Cu}_2\text{O}_2]^{2+}$, the convergence of the ground state energy with fixed $M = 64$ states without optimized ordering and CAS vector is shown in Figure 6.7(a) by the square symbol. We also observe for the bis($\mu$-oxo) isomer, that our DMRG energies reproduce the results given in Ref. [105] with a fraction of the computational resources. It is clear that the convergence of the energy is very slow to the value given in Ref. [105], however, after the entropy-based optimization procedures, a much faster convergence to a much lower value can be reached. As a result, the optimized CAS vector based on the single-orbital entropy shown in Figure 6.8 is given in Table 6.6. The highly localized two-dimensional entanglement matrix for the optimized ordering is understood from the comparison of Figures 6.9 and 6.10. The optimized ordering vector utilized in the calculation is given in Table 6.6. The entanglement distance $\hat{I}_{\text{dist}} = 1043$ for the energetical ordering is reduced to $\hat{I}_{\text{dist}} = 102.5$ for the optimized ordering. The resulting entropy profiles as a
Figure 6.7: (a) Convergence of the ground state energy in Hartree for various parameters for the bis(µ-oxo) isomer. The dashed line gives the ground state energy obtained in Ref. [105] using $M = 800$ block states. (b) Number of block states as a function of iteration steps for $\chi = 10^{-4}$. 

\[ \text{Energy} \]

\[ \text{Iteration step} \]

\[ \text{Block states} \]
Figure 6.8: Single-orbital entropy function obtained for the bis(µ-oxo) isomer of [Cu₂O₂]²⁺ by setting the quantum information loss $\chi = 10^{-5}$. The symbols indicate corresponding point-group symmetries of the energetically ordered orbitals.

Figure 6.9: Components of the two-orbital mutual information which are larger than $10^{-4}$ for the bis(µ-oxo) isomer of [Cu₂O₂]²⁺ obtained with $\chi = 10^{-5}$ and for the energetical ordering.
Figure 6.10: Components of the two-orbital mutual information which are larger than $10^{-4}$ for the bis($\mu$-oxo) isomer of $[\text{Cu}_2\text{O}_2]^{2+}$ obtained with $\chi = 10^{-5}$ and for the optimized ordering.

function of sweeps are shown in Figure 6.11. Again the block entropy takes large values only for a few iteration steps within a full sweep.

Since a very important observable related to transition metal clusters is the energy difference between the two isomers, the ground state energies should be calculated for the same error margin. This cannot be guaranteed with a fixed number of block states but it can be achieved by the DBSS procedure (or an automated Richardson-type error protocol [123]). We have thus calculated the ground state energies of the two isomers using the same parameter set, namely for $M_{\min} = 64$, $\chi = 10^{-4}$, $M_{\text{start}} = 256$. The convergence of the ground state energy is plotted in Figure 6.4(a) by the triangle symbol, while the number of block states selected dynamically in Figure 6.4(b). Since the block entropy is highly localized for the optimized ordering for most of the superblock configurations the number of block states were determined by $M_{\min}$ as can be seen in Figure 6.4(b) and Figure 6.7(b). We found $E_{\text{peroxo}} = -541.55628$ Hartree and $E_{\text{bisoxo}} = -541.54116$ Hartree yielding an energy differences of 0.04212 Hartree, i.e., 110 kJ/mol. For both isomers we have obtained $\langle S^2 \rangle = 10^{-4}$ for the ground state as expected from the given error margin.

The convergence of the ground state energy for the bis($\mu$-oxo) isomer is shown in Figure 6.7(a) by the triangle symbol. The fast convergence is again evident. The effective size of the environment block during the first $N$ iteration steps, i.e., for the CI-DEAS procedure, was found to be less than five orbitals. Therefore, using a larger number of block states for the environment block ($M_{\text{start}}$) increases
Figure 6.11: (a) Single-orbital, (b) block-entropy, and (c) mutual information obtained for bis(µ-oxo) isomer of [Cu₂O₂]^{2+} as a function of DMRG sweeps with optimized ordering and CAS vector and for setting the quantum information loss to £χ = 10^{-4}. The CI-DEAS initialization procedure corresponds to symbols with red circle. The optimized ordering and CAS vector is given in the text.
the computational time insignificantly. This result indicates that the application of DBSS and CI-DEAS procedures in the entropy-based optimization guarantees that the DMRG algorithm can be used in a black-box fashion, and that chemical accuracy can be reached using very limited computational resources. In fact, the reduced effective system size in the CI-DEAS procedure allows one to obtain the most relevant characteristics of the entropy functions within a few minutes.

To ensure that during the CI-DEAS procedure an even better represented environment blocks are constructed, we have repeated the calculations using \( M_{\text{min}} = 256 \) and \( M_{\text{start}} = 1024 \). After eight sweeps, we obtained the following \( E_{\text{peroxo}} = -541.57900 \) Hartree and \( E_{\text{bisoxo}} = -541.53599 \) Hartree with a gap of 113 kJ/mol. In addition, we have performed more accurate calculations for \( \chi = 10^{-5} \), \( M_{\text{min}} = 256 \), and \( M_{\text{start}} = 512 \). The maximum number of block states selected dynamically was around 1000 for the peroxo isomer, while for the bis(\( \mu \)-oxo) isomer we found that slightly more states were required to reach the same accuracy, so that \( M_{\text{max}} \) was in the range of 1200. In both calculations, we obtained \( \langle S^2 \rangle = 10^{-5} \) as expected for a singlet state. For the given error margin, we found \( E_{\text{peroxo}} = -541.58114 \) Hartree, \( E_{\text{bisoxo}} = -541.53853 \) Hartree, thus the difference is 0.04261 Hartree that is 112 kJ/mol.

In Table 6.7, all relevant DMRG calculations for the bis(\( \mu \)-oxo) and \( \mu - \eta^2 : \eta^2 \) peroxo isomers of the binuclear copper cluster are listed. Total electronic energies of the two isomers reported by Malmqvist et al. [154] and Kurashige and Yanai [138] were calculated in a different active space. The latter authors then carried out new DMRG calculations [182], where they reduced their active space, but applied the canonical-transformation (CT) approach [181] and optimized the orbitals. A comparison of absolute energies is therefore not very meaningful as the total energy depends on the size of the CAS and the type of orbitals chosen. Instead we shall focus on the relative energy which is central to the chemistry of such systems. Our entropy-based DMRG calculations agree quantitatively with the RASPT2(24,28) and DMRG-SCF/CT calculations, even though no procedure — such as canonical transformation — has been employed to account for dynamical correlation in our studies. However, this is not surprising because Yanai et al. found [182] that the effect of CT is only about 4 kJ/mol in the given one-particle basis set. In the first study [105] on this problem we already found the relative DMRG energies converge faster than the absolute energies of each isomer. This finding has been confirmed by Yanai et al. [182]. It is evident from Table 6.7 that already our first DMRG estimate [105] for this relative energy was much closer than the CASSCF result to the correct splitting, which we may expect between 110 and 160 kJ/mol based on the RASPT2 calculation and the Kurashige–Yanai DMRG result for a much larger active space. Our improved result for the splitting [49], which we obtained for the original active space but with a reduced number of block states \( M_l = 128 \) is with 109 kJ/mol already very close to the DMRG-SCF/CT and RASPT2 results of 113 and 120 kJ/mol, respectively.
Table 6.7: The relative energies for the bis(µ-oxo) and µ-η² : η² peroxo [Cu₂O₂]²⁺ isomers obtained in this work and from previously published studies are listed in kJ/mol. All total energies are given in Hartree. The CAS is denoted in parentheses as ‘(electrons,orbitals)’ while the information on DMRG block states $M$ is given in brackets. Note that total energies for different CAS and different types of orbitals cannot be directly compared. All results from this work employ entropy-based optimization applying the DBSS and CI-DEAS procedures. The ‘∗’ denotes keeping slightly more DMRG environment states during the initialization than necessary for a given quantum information loss $\chi$. The square brackets $[M_{\text{min}}/M_{\text{start}}/\chi]$ state that the DMRG calculation starts with $M_{\text{start}}$ block states, and the minimal number of block states is set to $M_{\text{min}}$, respectively.

<table>
<thead>
<tr>
<th>Ref., method</th>
<th>$E_{\text{bisoxo}}$</th>
<th>$E_{\text{peroxo}}$</th>
<th>$\Delta E$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference energies</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>[152], CASSCF(16,14)</td>
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<td>−541.50345</td>
<td>1</td>
</tr>
<tr>
<td>[152], CASPT2(16,14)</td>
<td>−542.06208</td>
<td>−542.06435</td>
<td>6</td>
</tr>
<tr>
<td>[152], bs-B3LYP</td>
<td>−544.19419</td>
<td>−544.27844</td>
<td>221</td>
</tr>
<tr>
<td>[154], RASPT2(24,28)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Previously published DMRG energies</td>
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</tr>
<tr>
<td>[105], DMRG(26,44)[800]</td>
<td>−541.46779</td>
<td>−541.49731</td>
<td>78</td>
</tr>
<tr>
<td>[49], DMRG(26,44)[128]</td>
<td>−541.47308</td>
<td>−541.51470</td>
<td>109</td>
</tr>
<tr>
<td>[138], DMRG(32,62)[2400]</td>
<td>−541.96839</td>
<td>−542.02514</td>
<td>149</td>
</tr>
<tr>
<td>[182], DMRG(28,32)[2048]-SCF</td>
<td>−541.76659</td>
<td>−541.80719</td>
<td>107</td>
</tr>
<tr>
<td>[182], DMRG(28,32)[2048]-SCF/CT</td>
<td></td>
<td></td>
<td>113</td>
</tr>
<tr>
<td>DMRG energies from this work</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DMRG(26,44)[64/256/10⁻⁴]</td>
<td>−541.51416</td>
<td>−541.55628</td>
<td>111</td>
</tr>
<tr>
<td>DMRG∗(26,44)[256/512/10⁻⁴]</td>
<td>−541.53499</td>
<td>−541.57896</td>
<td>115</td>
</tr>
<tr>
<td>DMRG∗(26,44)[256/1024/10⁻⁴]</td>
<td>−541.53599</td>
<td>−541.57900</td>
<td>113</td>
</tr>
<tr>
<td>DMRG(26,44)[256/512/10⁻⁵]</td>
<td>−541.53737</td>
<td>−541.58057</td>
<td>113</td>
</tr>
<tr>
<td>DMRG(26,44)[256/1024/10⁻⁵]</td>
<td>−541.53853</td>
<td>−541.58114</td>
<td>112</td>
</tr>
</tbody>
</table>

Even the total energies turned out to be improved and in the case of the peroxo copper cluster below the small-CAS CASSCF result as it should be. In view of the fact that a discrepancy in relative energy of about 5 to 10 kJ/mol is acceptable for chemical accuracy, we emphasize that all DMRG results tend to converge and that hence already the small DMRG calculation is a feasible means to yield such relative energies.
6.2.2 Entropic analysis of the two [Cu₂O₂]²⁺ isomers

Besides the relative energies of the two isomers, one might deduce more information from the entropy functions related to the chemical properties of the binuclear copper cores. By comparing Figures 4.1 and 6.8, it is clear that the importance of the orbitals is different for the two isomers as shown by the different distribution of the single-orbital entropy. In general, almost all orbitals possess some 10-20% larger entropy for the bis(µ-oxo) isomer but some of the orbitals have 2.5 – 3 times larger entropy than those of the peroxo isomer. For example, orbitals 3, 14, 34 produce much larger contributions to the total entanglement in case of the bis(µ-oxo) isomer. The total quantum correlation encoded in the ground state, $I_{\text{Tot}} = \sum_{i=1}^{N} s(1)_i$, is 3.49 and 5.39 for the µ – η² : η² peroxo and bis(µ-oxo) isomers, respectively. Thus, the bis(µ-oxo) isomer is more entangled which is also reflected by the larger maximum value of the block entropy for the bis(µ-oxo) isomer as can be seen by comparing Figures 6.6 and 6.11.

Figure 6.12: Molecular orbital pictures of the highly entangled orbitals for the bis(µ-oxo) isomer. The orbitals were selected with respect to their one-site entropy as shown in Figure 6.8. The number below each orbital corresponds to the orbital index and the occupation number is written in the parentheses.

The highly entangled molecular orbitals for the µ – η² : η² peroxo and bis(µ-oxo) isomers are shown in Figures 6.12 and 6.13. The molecular orbital analysis shows that the highly entangled orbitals have an occupation number that strongly deviates from either being doubly occupied or empty. The entropy-based optimization scheme accurately determines those orbitals and thus allows one to perform efficient DMRG calculations with the smallest possible active space for a desired accuracy in the DMRG energy. The selected orbitals are close to the Fermi surface and would be included in a standard CASSCF calcu-
lation if one could employ these large active spaces as in DMRG calculations. For example, orbitals 3, 14, 34 produce much larger contributions to the total entanglement in case of the bis(μ-oxo) isomer. The total quantum correlation encoded in the ground state, \( I_{\text{Tot}} = \sum_{i=1}^{N} s_i(1) \), is 3.49 and 5.39 for the \( \mu - \eta^2 : \eta^2 \) peroxo and bis(μ-oxo) isomers, respectively. Thus, the bis(μ-oxo) isomer is more entangled which is also reflected by the larger maximum value of the block entropy for the bis(μ-oxo) isomer as can be seen by comparing Figures 6.6 and 6.11.

Figure 6.13: Molecular orbital pictures of the highly entangled orbitals for the peroxo isomer. The orbitals were selected with respect to their one-site entropy as shown in Figure 4.1. The number below each orbital corresponds to the orbital index and the occupation number is written in the parentheses.

6.3 Walking along the crossing seam of two different electronic spin surfaces

The MPS and CGTN ansätze are two multireference approaches to accurate relative energies between two electronic states of different spin multiplicities. In the future, they will allow us to examine radiationless spin crossover compounds and non-adiabatic spin-forbidden chemical reactions by means of an efficient computation of the minimum-energy crossing point (MECP). In section 6.1, we mentioned the importance of accurate energy surfaces and highlighted their role in understanding the mechanisms and dynamics of many non-adiabatic chemical and biochemical processes. The MECP is the point where two surfaces intersect with minimum energy and thus mark the point in the configuration space where a transition likely occurs based on kinetic arguments [229, 230].

There exist several sophisticated methods and strategies to locate the MECP [229–233]. All of them have in common that they define two gradients; one points
directly to the crossing seam between the two surfaces and is given by

\[ f = (E_1(q) - E_2(q)) \left[ \left( \frac{\partial E_1(q)}{\partial q} \right) - \left( \frac{\partial E_2(q)}{\partial q} \right) \right] = (E_1(q) - E_2(q)) \ x_1 \quad (6.1) \]

where \( E_1(q) \) and \( E_2(q) \) denote the potential energies of the two different spin states at the molecular structure \( q \). On the other hand, the second gradient is chosen to be perpendicular to the crossing seam. A Gram–Schmidt orthogonalization projects the gradient of \( E_2 \) onto the \((n-2)\)-dimensional orthogonal complement space [231]. Therefore the second gradient \( g \) points along the seam to the minimum energy point and reads

\[ g = \left( \frac{\partial E_1(q)}{\partial q} \right) - \frac{x_1}{|x_1|} \left[ \left( \frac{\partial E_1(q)}{\partial q} \right) \cdot \frac{x_1}{|x_1|} \right] \quad (6.2) \]

The MECP can be located by minimizing along the negative direction of the sum of the two gradients \( f + g \). The line search algorithm along that direction minimizes the following objective function

\[ L(q) = \frac{E_1(q) + E_2(q)}{2} + \epsilon \ (E_1(q) - E_2(q))^2 \quad (6.3) \]

where \( \epsilon \) is a positive constant that controls the desired accuracy in the energy difference between the two spin surfaces \( E_1 \) and \( E_2 \).

Chachiyo and Rodriguez [230] employed a Hessian-based optimization scheme and applied it to the phenyl cation and to a spin-crossover complex, \([\text{Fe(ptz)}_6]^-(\text{BF}_4)_2\), where ptz stands for 1-propyltetrazole. This iron compound exhibits interesting properties such as light-induced excited spin state trapping (LIESST) [234, 235] and potential applications in molecular memory storage and display technologies [235].

We have developed and implemented a conjugate-gradient minimization procedure to locate the MECP using the template programming C++ language to interface standard quantum chemical software packages. Currently, interfaces for MOLPRO [103] and TURBOMOLE V5.10 [65] exist. Hence, the same minimization algorithm to find the MECP can be employed for any desired electronic structure method implemented in one of the two program packages. We have tested our implementation by locating the MECP of the phenyl cation, \([\text{C}_6\text{H}_5]^+\), using CASSCF and B3LYP calculations of the singlet and triplet surfaces. The CASSCF calculations were performed with the MOLPRO program package [103] employing an active space of 6 electrons in 10 active orbitals in the cc-pVDZ basis set [199,200] within the \( C_1 \) point-group symmetry. For the unrestricted B3LYP calculations, the Coulomb-fitting approximation in the cc-pVDZ basis with the corresponding auxiliary basis set [206,207] have been used. The equilibrium structure on the \( ^1A_1 \) surface has been previously obtained using the unrestricted RI-BP86/def-TZVP method as implemented in TURBOMOLE V5.10 [65]. The maximally allowed step size for the line search algorithm was
set to 0.01 Å and ϵ to 1000 $E_h^{-1}$. We thus expect converged energies of the singlet and triplet state agreeing up to the fourth digit in a first run. The convergence criterion can then be tightened until the desired accuracy has been reached, say $\epsilon = 10^6 \, E_h^{-1}$, if the energies shall agree up to the 6th digit. Note that the first line search is performed along gradient $f$ only. The convergence to the MECP is shown in Figure 6.14.

Figure 6.14: The location of the MECP for the CAS(6,10)SCF method in a cc-pVDZ one-particle basis is shown. The initial step of the optimization minimized the energies between the singlet and triplet states and determined a structure close to the crossing seam. The subsequent optimization steps then walked along the seam to the minimum energy structure. For the converged structure, the energies for the singlet and triplet state are $-229.8477 \, E_h$ and $-229.8476 \, E_h$, respectively, for $\epsilon = 1000 \, E_h^{-1}$.

The fully converged energies for the CAS(6,10)SCF optimized MECP are $-229.847659 \, E_h$ for the singlet and triplet states with $\epsilon = 10^6 \, E_h^{-1}$. In Table 6.8, the converged MECP structures of the CASSCF and B3LYP methods are compared to each other and to those from the literature [230,233]. The parameters listed in Table 6.8 are indicated in the $^1A_1$ in the RI-UBP86/def-TZVP optimized structure shown in Figure 6.15. The MECP obtained by the DFT methods are quite similar except the one reported by Harvey et al. [233] which slightly differs. This discrepancy might be an effect of the poor quality of the one-particle basis. However, it is interesting to note that the predicted CASSCF MECP structure deviates significantly from the DFT structures. Additional data is needed to investigate this issue in more detail. The reason might be either
6.3. Walking along the crossing seam of two surfaces

caused by the small or poorly selected active space of the CASSCF calculations or a manifestation of the spin state problem in DFT. The MECP structure is very sensitive to an energetical shift in the PES of the two spin states.

Table 6.8: The geometric parameters and energies of \([C_6H_5]^+\) for the \(^1A_1\) state and the MECP are list for comparison. The reference entry “tw” stands for this work. The parameters \(R_1\), \(R_2\), and \(\alpha_1\) are explained in Figure 6.15. \(R_1\) and \(R_2\) are given in Å units and \(\alpha_1\) in degrees. The parentheses for the CASSCF calculations denotes the employed active space where the first number represents the number of electrons and the second the number of molecular orbitals. It is interesting to see that the DFT calculations predict approximately the same MECP structure whereas the CASSCF method converges to a slightly different one.

<table>
<thead>
<tr>
<th>Ref., method</th>
<th>basis set</th>
<th>(R_1)</th>
<th>(R_2)</th>
<th>(\alpha_1)</th>
<th>(E_h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^1A_1) minimum</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>tw,CAS(6,10)SCF</td>
<td>cc-pVDZ</td>
<td>1.324</td>
<td>1.424</td>
<td>147.9</td>
<td>−229.867 620</td>
</tr>
<tr>
<td>tw,CF-UB3LYP</td>
<td>cc-pVTZ</td>
<td>1.318</td>
<td>1.431</td>
<td>147.7</td>
<td>−231.193 606</td>
</tr>
<tr>
<td>tw,RI-UBP86</td>
<td>def-TZVP</td>
<td>1.324</td>
<td>1.441</td>
<td>147.1</td>
<td>−231.340 762</td>
</tr>
<tr>
<td>[230],UB3LYP</td>
<td>cc-pVTZ</td>
<td>1.318</td>
<td>1.431</td>
<td>147.7</td>
<td>−231.341</td>
</tr>
<tr>
<td>[233],B3LYP</td>
<td>DZ</td>
<td>1.339</td>
<td>1.447</td>
<td>144.5</td>
<td>−231.023 226</td>
</tr>
<tr>
<td>MECP</td>
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<td></td>
<td></td>
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</tr>
<tr>
<td>tw,CAS(6,10)SCF</td>
<td>cc-pVDZ</td>
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<td>1.385</td>
<td>132.8</td>
<td>−229.847 382</td>
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<tr>
<td>tw,CF-UB3LYP</td>
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<td>1.373</td>
<td>129.0</td>
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<tr>
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<td>1.415</td>
<td>1.392</td>
<td>128.9</td>
<td>−230.997 122</td>
</tr>
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</table>

Figure 6.15: The schematic figure of the RI-UBP86/def-TZVP optimized equilibrium structure on the \(^1A_1\) surface is shown. The indicated parameters are compared in Table 6.8 as descriptors of the effect on the MECP by employing different electronic structure methods.
6.4 Constructing potential energy surfaces: Interpolating moving least-squares

In principle, we have the tools at hand to construct a PES with high accuracy through electronic structure calculations. With regard to the complexity of the PES for very large molecules, it is by no means computationally feasible to sample the whole PES with high-level electronic structure calculations. These expensive calculations can be elegantly circumvented by applying a general interpolation scheme for constructing a reliable PES from a small set of \textit{ab initio} data points. These electronic energy data points can then either be pre-calculated for a grid of points or obtained on the fly. There exists a variety of general interpolation schemes based on splines [236], reproducing Kernel Hilbert space interpolation [237,238], modified Shepard [239], neural networks [240], and interpolating moving least-squares (IMLS) [241–247].

We apply the IMLS procedure for constructing the PES based on a set of \textit{ab initio} data points. The other methods often lack robustness and scalability. Another advantage of the IMLS interpolation scheme is that it does not require first- or second-order derivatives of the PES as, e.g., the modified Shepard method. It is therefore possible to obtain a PES from electronic structure calculations where it is not feasible to calculate gradient or Hessian information. However, if gradient or Hessian data is available, they can be incorporated in the IMLS method to reduce the number of data points necessary for a certain accuracy of the fit [248]. In the IMLS scheme, it is straightforward to systematically improve the fitted PES by adding new \textit{ab initio} single-point calculations. This step can also be automated resulting in a "black box" method for constructing a PES with the desired accuracy (see section 6.4.2).

The cost of a general interpolation method consists of two parts. First, the effort of the electronic structure calculation plays an important role but due to the efficient use of \textit{ab initio} data in the IMLS scheme, IMLS bears an advantage over other interpolation schemes. And second, the evaluation cost is usually larger for IMLS than for other interpolation procedures since it solves the weighted least-square problem at every evaluation point. The weights in the solution give the method a nonlinear flexibility which is not present in other interpolation schemes [249]. However, it has been shown that the IMLS evaluation cost can be minimized by using numerical procedures which restrict the number of required data points [247]. In addition, only the most important basis functions should be included in the fitting basis set [245]. There exists also a variant of the IMLS method which does not require to solve the least-squares equations for every evaluation point via local approximants [250]. The local interpolation moving least-squares method (L-IMLS) requires to calculate at every \textit{ab initio} data point the set of coefficients \(
\{a_i\}\) which results in an \(N \times m\) matrix. At every evaluation point, it is then simply necessary to calculate a weighted average over the coefficients of the data points near the evaluation point. The L-IMLS method is presented in section 7.3.1 as an optimization technique for speeding
6.4. Constructing potential energy surfaces

Up to the gradient calculation.

The aim of the present work is concerned with obtaining accurate energies and gradients for creating a precise and representative PES. This can be easily achieved using IMLS since it fits the coefficients of a polynomial with any desired order at the evaluation point. We therefore have an analytic expression of the gradient at any position of the PES after an IMLS evaluation.

In addition, we are able to construct a PES solely based on energy values obtained from quantum chemical electronic structure calculations. The number and position of the \textit{ab initio} data points can be chosen until the desired accuracy is reached. With such a reliable PES we can calculate gradients at any position by performing an IMLS evaluation. Of course, the interpolation can always be refined on the fly and the obtained PES may also be stored for later use at any time.

6.4.1 IMLS method and extensions

There are several excellent descriptions of the IMLS method in the literature [241–250]. Therefore, we only briefly recall its basic ingredients. We assume that we can approximate the PES at a given nuclear configuration \( q \) by a set of linearly independent basis functions \( \{ b_i(q) \} \) with

\[
V_{\text{fit}}(q) = \sum_{i=1}^{m} a_i(q) b_i(q),
\]

(6.4)

where \( m \) is the number of basis functions. Our goal is to determine the optimal set of coefficients \( \{ a_i(q) \} \) at the configuration \( q \) for Eq. (6.4). This is achieved by using a weighted least-squares error functional

\[
E[V_{\text{fit}}(q)] = \sum_{i=1}^{N} w_i(|q - q^{(i)}|) \left[ \sum_{j=1}^{m} a_j(q) b_j(q^{(i)}) - V(q^{(i)}) \right]^2
\]

(6.5)

under the minimization condition \( \partial E/\partial a_i = 0 \) where \( V(q^{(i)}) \) is the \textit{ab initio} energy of data point \( q^{(i)} \) and \( w_i(|q - q^{(i)}|) \) is a weight function depending on the distance between the configuration \( q^{(i)} \) and the evaluation point \( q \). It is more convenient to express the minimization condition in a matrix–vector notation which yields the following equations

\[
B^T W B a = B^T W v
\]

(6.6)

where \( a \) and \( v \) are \( N \times 1 \) column vectors, \( W \) is a \( N \times N \) diagonal matrix, and \( B \) contains \( m \) basis-function values at \( N \) data points,

\[
B = \begin{pmatrix}
b_1(q^{(1)}) & b_2(q^{(1)}) & \cdots & b_m(q^{(1)}) \\
b_1(q^{(2)}) & b_2(q^{(2)}) & \cdots & b_m(q^{(2)}) \\
\vdots & \vdots & \ddots & \vdots \\
b_1(q^{(N)}) & b_2(q^{(N)}) & \cdots & b_m(q^{(N)})
\end{pmatrix}
\]

(6.7)
In IMLS calculations, the inverse of $B^T W B$ is required to solve the normal equations for the set of coefficients $\{a_i(q)\}$. This might lead to an ill-conditioned numerical problem for high-order polynomials and thus singular value decomposition (SVD) is applied to solve Eq. (6.6). The SVD technique also provides further advantages such as an improved numerical conditioning and that it can handle rank-deficient cases. We choose the weight function as

$$w_i(q) = \frac{1}{|q - q^{(i)}|^p + \epsilon}$$

(6.8)

where the parameters $p$ and $\epsilon$ were set to $p = 6$ and $\epsilon = 1.0 \cdot 10^{-7}$. $\epsilon$ was chosen to be a small positive value ensuring that the weight function has a finite value at $q = q^{(i)}$ to avoid singularity and numerical failure. The purpose of the weight function is to increase the influence of data points in the vicinity of the evaluation point and thus makes the interpolation scheme local.

**Basis set**

Figure 6.16: We present a construction scheme for the monomials spanning the basis functions of a polynomial with an arbitrary order. A monomial is described by the upper (blue) box. In the lower box, the remaining degree of freedom are shown. The construction scheme starts with a value of one, then we subsequently multiply this value by every degree of freedom forming a new box in which the degrees of freedom are reduced by one element from the previous list of degree of freedoms. In this scheme, the construction plan for a second-order polynomial is shown.

The basis functions are constructed as polynomials of $q^{(i)}$ up to any order. Our code uses a tree-based scheme to determine all monomials for any $(m - 1)$-order polynomial with any number of degrees of freedom $d$. We found that good fitting results are obtained by using polynomials with an order of at least the number of degrees of freedom $d$. In Figure 6.16, we show the construction of a second-order polynomial with three degrees of freedom corresponding to the Cartesian coordinates $\{x, y, z\}$. First, we create a recipe for the basis of
a polynomial containing all degrees of freedom up to the desired order. The construction scheme for the plan is schematically shown in Figure 6.16. The matrix $B$ in Eq. (6.7) is then calculated using this protocol. It is straightforward to generate $d$ recipes for the derivatives with respect to any of the degrees of freedom based on the polynomial construction plan.

**High-dimensional model representation basis set**

For high-dimensional PES, the fitting basis set can be substantially improved by employing the concepts of the high-dimensional model representation (HDMR) [251–256]. The HDMR technique dramatically reduces the sampling effort for simulating the input–output behavior of high-dimensional systems. Electronic structure methods define a map of relationships between the high-dimensional input, the nuclear coordinates $x = \{x_1, x_2, \ldots, x_n\}$, and the output, the potential energy $V(x)$. The output function can be expressed as a hierarchical correlated function expansion in terms of the cooperative and/or independent input variables,

$$
V(x) = V_0 + \sum_{i=1}^{n} V_i(x_i) + \sum_{1 \leq i < j \leq n} V_{ij}(x_i, x_j) + \sum_{1 \leq i < j < k \leq n} V_{ijk}(x_i, x_j, x_k) + \ldots \tag{6.9}
$$

where $V_0$ corresponds to the mean value over the entire domain of $x$. The set of one-coordinate functions $V_i(x_i)$ represents the effect of the input variable $x_i$ acting independently on the output $V(x)$ and the set of two-coordinate functions $V_{ij}(x_i, x_j)$ describes the cooperative effects of the input variables $x_i$ and $x_j$. The same scheme applies for higher-order functions.

The basic assumption underlying the HDMR technique is that in actual problems it is very unlikely to encounter high-order cooperativity between the input variables and thus the output function can be well approximated by truncating the exact function expansion in Eq. (6.9) after the two-coordinate functions,

$$
V(x) \approx V_0 + \sum_{i=1}^{n} V_i(x_i) + \sum_{1 \leq i < j \leq n} V_{ij}(x_i, x_j), \tag{6.10}
$$

which should provide a satisfactory description of high-dimensional systems.

In the IMLS algorithm, the HDMR concept translates to a reduction of the size of the fitting basis set [257]. A HDMR-type fitting basis set is usually denoted as HDMR(12,9) which means that the one-coordinate functions are truncated after the 12th order and the two-coordinate functions after the 9th order. For very accurate PES, one can easily include the functions for three cooperative variables as well.

Note that the advantage of the HDMR technique becomes evident for high-dimensional, complicated PES representations but can be neglected for simple, two- or three-dimensional surfaces.
6.4.2 Automated growth by simulated annealing

In order to keep the dimension of the matrices in Eq. (6.6) small the PES should be generated with the fewest number of data points necessary to achieve a certain accuracy. In 2008, Dawes et al. [257] presented a way for an efficient placement of new data points in the automated growth of a PES fit. That region of the PES which is poorly fitted and which thus requires new data points, is determined by performing two IMLS fits using successive orders of the basis set. The points are then chosen by applying a conjugate gradient minimization on the negative squared difference surface generated from the two fits. This step can be iteratively used to construct accurate PES to the desired accuracy.

We choose a different way to determine the global minimum of the negative squared difference surface by applying simulated annealing. Simulated annealing is nature’s own minimization algorithm and an efficient technique for optimization problems of large scale, especially in cases where the PES is highly frustrated and the global minimum is hidden among many local minima [258, 259]. Other minimization methods, such as conjugate gradient, are greedily converging to a local minimum. Our implementation of the simulated annealing method uses the Metropolis algorithm to choose a random step in the configuration space. The objective function $E$ which is to be minimized is the negative squared difference surface that can be evaluated for every structure by performing two IMLS fits with different polynomial orders. The control parameters are $k$ and $T$ which are defined in a Boltzmann probability function as

$$p = \exp\left\{-\frac{[E_2(q^{(i)}) - E_1(q^{(j)})]}{kT}\right\}$$

(6.11)

where $E_1$ and $E_2$ are values of the negative squared difference function at two different configurations $q^{(i)}$ and $q^{(j)}$. These parameters often need physical insight or trial-and-error experiments.

In Ref. [257], the automatic growth procedure is activated after a certain number of seed points have been calculated which requires initial guidance by the user or a very rough sampling of all degrees of freedom of the PES. The reason for this was the argument that the IMLS procedure provides only reliable data if it can “interpolate” between data points. In our approach, however, we choose to start with just one point and let the IMLS algorithm determine where new points should be placed. Of course, the first few iterations are performed on a rather inaccurate surface which does not yet represent all features of the PES appropriately. Despite this apparent deficiency, the IMLS growth facility converges quickly to a reasonable approximation of the PES. We observe that the algorithm places points first near the boundaries of the constraint configuration space which is selected in advance by the user. This prevents the IMLS algorithm from improving regions of the PES that are often completely irrelevant to describe rare events or MEP studied on the approximate surface.

We have tested our modification of the IMLS growth procedure on an analytic function, the Müller model potential [260], which takes the following form in
arbitrary units (a.u.)

\[ U_{\text{Müller}}(x,y) = -200 \, e^{-(x-1)^2-10y^2} - 100 \, e^{-x^2-10(y-0.5)^2} \]
\[ -170 \, e^{-6.5(x+0.5)^2+11x+0.5(y-1.5)-6.5(y-1.5)^2} \]
\[ + 15 \, e^{0.7(x+1)^2+0.6(x+1)(y-1)+0.7(y-1)^2}. \] (6.12)

For the simulated-annealing procedure, we choose the temperature to be \( T = 500 \, \text{K} \) and the factor \( k = 0.001 \, (\text{a.u.})^2/\text{K} \), respectively. We started the runs on the negative squared difference surface at the origin and constrain the search to a rectangular box which was centered at \((0.125, 1.0)\) with side length of 3.25 and 3.0. A 7th and 8th order polynomial fitting basis has been applied in the calculation of the negative squared difference surface. We also tested this same procedure with an energy constraint in order to sample only the low-energy part of the problem which contains chemically interesting features of the PES. In real chemical problems, the energy range can be reliably guessed by taking the energy of the equilibrium structure which is usually available and then roughly estimates the relevant energy scale for the theoretical study. In our second run, the energy range on the Müller potential was set to \(-150\) a.u. up to 300 a.u. for the 8th order polynomial.

The effect of the energy constraint has a tremendous impact on the computational effort and on the number of points required to describe the basic PES features as shown in Figure 6.17. In the first case, the IMLS growth procedure mostly places new point in the high-energy part after the low-energy region has been well approximated. The high-energy part, however, provides no chemical insight and can thus be safely neglected and needs not to be optimized.

In Figure 6.17(b), the energy constraint on the 8th order polynomial properly restricts the IMLS growth procedure to the interesting region of the PES which can be seen by the density of points in the low-energy part. During the warm-up phase, some configurations were selected in the high-energy region. The reason lies in the quality of the 8th order IMLS fit which is used to evaluate the energy at the corresponding point. Apparently, the IMLS interpolation had not yet gathered enough data points to accurately approximate that region and thus the fitted energy value lies within the energy boundaries. As soon as those points have been incorporated, the curvature of the high-energy part is well described and the sampling of new points can now solely focus on the other region of the configurational space.
Figure 6.17: The points on the configuration space selected by the IMLS growth procedure for the Müller potential are plotted on the analytical function density with (a) the configuration space constraint only and (b) the configuration space and energy constraints. During the IMLS surface construction, the energy constraint is critical for an efficient convergence of a certain region of the PES in terms of the number of required grid points and thus of the computational effort.
In the previous application of the IMLS growth procedure [257], the authors claimed that it is necessary to provide some initial seed points. They argue that the IMLS fit is based on a least-square approximation of the polynomial coefficients and thus relies on sufficient data points. Despite the logical argumentation the generation of the seed points requires either to sample of most of the configuration space or to use chemical intuition to determine the region of interest. Both are not desirable techniques. In our studies, we have realized that the IMLS interpolation already provides for a very small number of data points a crude, but qualitatively correct approximation of most features which can then easily be refined by additional points.

The essential part, however, was to change the weighting function in the IMLS equations as applied in Eq. (6.6) which was decisive for the surface generation procedure. The weighting function employed here takes the form of

$$w(r) = \frac{\exp(-r^2)}{r^4 + 10^{-2}}$$

(6.13)

where $r$ is the Euclidean metric between one of the grid structures of the interpolation basis and the current configuration divided by its unit. A high order in the distance between points is necessary for an very accurate representation of the PES at the evaluation point. For our purpose, however, the location of new points can be improved by taking more surrounding data points into account. Since the point density at the beginning of the surface refinement is very low, the weighting function should basically gather as much information as possible.

The fast convergence of the IMLS growth method starting from just one point can be seen by monitoring the root mean square (RMS) for each added data point as demonstrated in Figure 6.18. The RMS is calculated between the 8th order IMLS interpolated value and the analytical function evaluation on the Müller potential at the corresponding configuration. It is evident that the energy constraint results in a much faster convergence of the RMS. In the first run, many of the new points are placed in the undesired high-energy part.
Figure 6.18: The RMS as a function of the number of data points on the analytical surface. The first 50 data points are shown in green and the rest was drawn in black.
6.4.3 Minimum energy paths on IMLS surfaces

The identification of a minimum energy path (MEP) on a potential energy surface provides valuable insights into the mechanism of chemical reactions. A minimum energy path connects two stable structure by a transition state with a sequence of ordered intermediate structures, the so-called images. The intermediate structure corresponding to the highest energy gives an approximation to the real transition state of that specific chemical reaction channel which is modeled by the MEP. However, the description of chemical reactions by a MEP is nevertheless limited to only one potential energy surface in the framework of the Born–Oppenheimer approximation but this is usually a valid approximation for many chemical reactions.

We now present the MEP-IMLS method to elegantly locate a minimum energy path (MEP) on an IMLS fitted PES which is constructed using the automatic point generation scheme described in section 6.4.2. The idea behind finding the minimum energy path consists of spanning a virtual string between the two configurations $q^{(A)}$ and $q^{(B)}$. The string $d$ is defined as the difference vector between these two structures,

$$d = q^{(B)} - q^{(A)}. \quad (6.14)$$

We then place a certain number of images on the string and relax them under a constraint on the fitted PES. The constraint only allows the images to move perpendicular to the string direction $d$ as defined in Eq. (6.14). For every images the energy is calculated by the IMLS procedure according to Eq. (6.4). For every IMLS evaluation, the gradient can be calculated without additional effort since it corresponds to the analytical derivative of the fitted polynomial and thus the gradient $x$ is easily accessible as well. We cannot blindly follow the direction of the gradient $x$ since it is not necessarily perpendicular to the direction of the string. Therefore, we are applying the first step of a Gram–Schmidt orthogonalization scheme to compute the component $c$ of the gradient $x$ which is satisfying the constraint condition. This corresponds to subtracting the projection of the gradient $x$ onto the string direction $d$ from $x$ according to

$$c = x - \hat{P}(d, x), \quad (6.15)$$

where the projection operator $\hat{P}$ is defined as

$$\hat{P}(d, x) = \frac{d \cdot x}{||d|| \cdot ||d||} \quad (6.16)$$

The magnitude of the vector $d$ is written as $||d||$. The image is then relaxed in a steepest-descent fashion following the direction of $c$ until the energy is converged and is not significantly changing anymore. This is iteratively performed for every image until the change in energy is below a certain threshold. This naive scheme for the MEP localization can be applied because the user of a haptic device
(see next chapter) can gain additional knowledge of the PES due to the force feedback information and to efficiently place the starting point \( q^{(A)} \) and ending point \( q^{(B)} \) in the configuration space. The haptic device will be introduced in chapter 7.

**Extension to the MEP-IMLS algorithm**

The MEP-IMLS procedure is comparable to the nudged elastic band (NEB) [261–265], string [266], MaxFlux [267] methods. All these methods optimize a continuous reaction pathway connecting two states to the MEP. However, they elementarily differ in the underlying surface used for locating the MEP and how the images on the string are kept equally spaced along the pathway. In NEB, a spring force is defined between two adjacent images which constrain them to a certain distance. In the string method, the images are repositioned equally spaced along the path after each iteration.

We employ the principles of the NEB method to the IMLS-constructed surfaces. The images are thus kept equally spaced along the MEP by simple harmonic oscillators. They are then relaxed by the component of the gradient which is perpendicular to the tangential direction of the MEP.

Each of the images — except the first and the last one, denoted as \( q^{(A)} \) and \( q^{(B)} \) — is connected with two harmonic oscillators with force constants \( k_{j+1} \) and \( k_j \), respectively. The force of the springs is given as the external force \( F^\text{ext}_j \) acting on the \( j \)th image,

\[
F^\text{ext}_j = k_{j+1}(q_{j+1} - q_j) + k_j(q_{j-1} - q_j). \tag{6.17}
\]

In addition, the image feels the internal force \( F^\text{int}_j \) of the PES which is described by the negative gradient at the corresponding position,

\[
F^\text{int}_j = -g_j. \tag{6.18}
\]

To prevent the convergence of all of the images to the nearest stationary point, we apply the constraint that the external force of the harmonic oscillators on image \( j \) is acting along the tangent \( \hat{t}_j \) of the path while the internal force acts perpendicular to it. The definition of a tangent vector at any point of the path is, however, not trivial since position information only is available and not an explicit representation of the path. The tangent of the path can be approximated by simply choosing the normalized difference vector between the two neighboring images,

\[
\hat{t}_j = \frac{q_{j+1} - q_{j-1}}{|q_{j+1} - q_{j-1}|}. \tag{6.19}
\]

as the tangent of the path. This definition of the tangent to the path, however, might produce kinks during the optimization of the MEP. In addition, corner-cutting might cause problems for some molecular systems [265]. Trygubenko and Wales [265] suggested to use a different variant of the tangent where just
one neighboring image is used. Since there exist two neighboring images for each image (except the ones at the end), the bead with the higher energy is selected. The image to be optimized can thus be seen as hanging on the image with the larger energy and then wobble to the MEP. The choice for the higher-energy image is obvious since it is easier to follow the steepest-descent path downhill than uphill. The improved tangent to the path is defined by

\[ \hat{t}_{\text{Wales},j} = \frac{(i - j)q_i - q_j}{|q_i - q_j|} \] (6.20)

where \( j \) and \( i \) are two adjacent images and \( E_j < E_i \).

The total force \( F_j \) on image \( j \) consists of the parallel and the perpendicular force components, \( F_j = F_j^\parallel + F_j^\perp \), with respect to the tangential direction given as

\[ F_j^\parallel = (F_j^{\text{ext}} \cdot \hat{t}_j) \hat{t}_j \] (6.21)
\[ F_j^\perp = F_j^{\text{int}} - (F_j^{\text{int}} \cdot \hat{t}_j) \hat{t}_j. \] (6.22)

The MEP is calculated by relaxing the images using a conjugate-gradient minimization scheme and a one-dimensional line-search [143].

In Figure 6.19, we compare the two different tangent formulations as defined Eqs. (6.19) and (6.20). Note that the spacing of the images can be controlled by the force constant of the harmonic springs between two images. For our test runs, we have set all force constants to \( k = 1 \). In the MEP optimized with the regular tangent, we indeed see kinks in the converged path, especially around the equilibrium structure where many points are near each other. In this region of the configurational space, the MEP employing the Wales tangent provide a better description. Overall, both paths accurately find the correct MEP and the barrier heights are well reproduced as it is clear from Figure 6.20. For the location of the MEP, an IMLS fitted surface employing a polynomial of 13th order has been used.
Figure 6.19: The MEP were calculated on the Müller potential for 41 images starting from previously located minima for a comparison of the two presented definitions of the gradient along the path. The regular tangent is defined in Eq. (6.19) and the Wales tangent in Eq. (6.20). (a) The optimized MEPs are shown on the Müller potential surface with the regular tangent (orange) and the Wales tangent (green). (b) The same information as in (a) is also plotted as a density map for a better visibility of the converged positions of the individual images.
6.5 Molecular structure optimization using IMLS

Figure 6.20: The energy profile of the MEPs for both tangent formulations are compared. The barrier height are very well approximated by both MEPs.

We should emphasize that the surface on which the MEPs were located was previously constructed with the IMLS grow procedure presented in the previous section in a very efficient manner that required only 223 energy and gradient evaluation. This is very encouraging for further application to real molecular systems.

6.5 Molecular structure optimization using IMLS

The IMLS fitting error estimation facility provides the functionality to determine regions of the configuration space that are not accurately described in terms of the negative squared difference surface between two IMLS interpolations employing a different order in the fitting basis set. In section 6.4.2, we have reviewed the automatic PES growth scheme which tries to find the global minimum on this negative squared difference surface with a simulated annealing algorithm.

This feature of the IMLS interpolation can be further employed to obtain the equilibrium structure of molecular systems, i.e., to find stationary points on the IMLS-constructed PES. For this endeavor, we incorporate the gradient information at each point in the error functional that defines the normal equations to be solved in a least-square sense for a more accurate representation of the PES. The reasons for adding the gradient information are twofold. First we want to make sure that we get the best possible representation of the fitted
surface with the available data and fewest number of points, and second, we also need very accurate gradients for the minimization on the IMLS surface. The IMLS structure optimization is an iterative procedure. We construct a function of two IMLS surfaces of successive degree of the fitting basis set that hopefully guides us to the exact minimum under the constraint of minimizing the energetical difference between the two interpolated energy values. The larger the difference between two IMLS interpolations, the worse is the IMLS approximation to the exact surface. We then try to locate the global minimum on the fitted surface using a one-dimensional line-search algorithm along the conjugate-gradient direction [143]. The objective function \( L(q) \) is defined as

\[
L(q) = E_{\text{high}}^{(\text{IMLS})} + \alpha \left( E_{\text{high}}^{(\text{IMLS})} - E_{\text{low}}^{(\text{IMLS})} \right)^2
\]

(6.23)

where \( q \) denotes a structure in the given configuration space, \( \alpha \) is tunable parameter to adjust the weight of the penalty function, and the terms high and low represent the two IMLS surface with a high-order and a low-order fitting polynomial. A high-order IMLS surface usually provides a more accurate representation than a low-order interpolation. The interpolated energy of the high-order IMLS surface forms the basis of Eq. (6.23). The first derivative of the objective function \( L(q) \) with respect to the structure \( q \) can simply be written as

\[
\frac{d}{dq} L(q) = \nabla_{\text{high}}^{(\text{IMLS})} + 2\alpha \left( \nabla_{\text{high}}^{(\text{IMLS})} - \nabla_{\text{low}}^{(\text{IMLS})} \right) \left( \nabla_{\text{high}}^{(\text{IMLS})} - \nabla_{\text{low}}^{(\text{IMLS})} \right).
\]

(6.24)

The objective function and its gradient are calculated solely from quantities of the IMLS surface. After the equilibrium structure has been found on the approximate surface, the energy and gradient information is evaluated on the exact surface using quantum chemical methods and incorporated into the next IMLS microiteration. This two-step procedure is repeated until the convergence criterion is satisfied and the "true" minimum structure has been located. The convergence criterion is fulfilled if the norm of the IMLS gradient falls below a certain threshold value of \( 10^{-10} \) or the absolute difference between two consecutive energy evaluations is smaller than \( 10^{-12} \). Note that the expensive part constitutes the first-principles calculations of the electronic energy and gradients and not the conjugate-gradient minimization on the IMLS surface.

As a proof of principle, we have selected a one-dimensional Morse potential \( V_{\text{Morse}}(x) \) as a test system which is defined in arbitrary units as

\[
V_{\text{Morse}}(x) = \left[ 1 - \exp \left( -0.5 (x - 1.4) \right) \right]^2.
\]

(6.25)

We started the IMLS optimization with two previously calculated structures at \( x_0 = 6.0 \) and \( x_1 = 4.0 \) with a second order and a first order IMLS polynomial. The order of the IMLS polynomial is increased by two each iteration step until the sixth and fifth orders have been reached. The parameter \( \alpha \) occurring in Eq. (6.23) was set to 1.0, and the maximal step size for the line-search
algorithm to 0.5. In each IMLS iteration, the starting point corresponds to the previously found configuration. Note that the weighting function used in the IMLS interpolation for the structure optimization takes the same form as the one used for the IMLS growth procedure defined in Eq. (6.13).

The convergence of the IMLS structure optimization for the Morse potential is shown in Figure 6.21. A very good approximation of the exact minimum is found within just four energy and gradient evaluations on the exact surface.

Figure 6.21: The convergence of the approximate IMLS surface to the exact Morse potential that is defined in Eq. (6.25) is illustrated. The exact Morse potential is drawn as a red, dashed line. The other three lines represent the objective functions depending on the two IMLS surfaces of different polynomial orders given in the parentheses. The first IMLS step selects step1 = 0.0299 as a first approximation to the exact minimum. The IMLS structure optimization has bracketed the minimum and thus converges now steadily to the exact one at $x_e = 1.4000$. The successively obtained structures are step2 = 1.5657, step3 = 1.3914, and the final step4 = 1.4000 (Note that step4 is not shown in the picture).

The IMLS structure optimization has been implemented in the Molcas program package [268] and is currently extensively studied and tuned for a set of test molecules. The second derivative which is easily obtained in a straightforward manner in the IMLS framework can also be incorporated into the interpolation for a more sophisticated minimum search on the IMLS surface and for improving the convergence of the optimization.
6.6 Summary on electronic energy surfaces

The accuracy of the CGTN approximation of total electronic states of different spin multiplicity has been numerically studied for methylene. The spin splitting between the singlet and triplet state could be accurately calculated using only a tenth of the number of variational parameters used in the CASSCF reference calculation.

In particular, the calculation of the electronic structure of transition metal clusters faces diverse challenges due to many of near-degenerate electronic states resulting in the failure of most standard quantum chemical methods. We expect the efficient parametrization of the CGTN states to be a very promising approach to deal with the multi-reference nature and the large active spaces mandatory for an accurate description of transition metal clusters.

Moreover, we have studied a transition metal cluster from a quantum information theory perspective using the DMRG method. By calculating various entropy functions and the two-orbital mutual information we have proposed recipes to perform DMRG calculations in a black-box fashion on complex chemical compounds. Our results confirm the importance of taking entanglement among molecular orbitals into account and the usefulness of graph theory for carrying out efficient calculations. Chemical characteristics of the two isomers of Cu$_2$O$_2$ have also been analyzed and interpreted in terms of the entropy functions. From the one- and two-orbital entropies we can deduce information on the physical nature of the clusters. It was possible to clearly identify the highly entangled orbitals in our model oxide–copper. These orbitals do neither belong to the essentially doubly occupied ‘closed-shell’ molecular orbitals nor to those that have vanishing natural occupation numbers. Interestingly, from Figures 6.12 and 6.13 it is clear that in both cluster structures the highly entangled orbitals are very similar as can be understood in terms of the nodal surfaces of each molecular orbital. We note that the orbitals that feature large one-orbital entropies lead to particularly large two-orbital entropies. However, while orbital pairs 3–14 and 13–35 are highly entangled in the peroxo structure, this is the case for all five orbitals 3, 13, 14, 34, and 35 in the quadrangular bis(µ-oxo) structure. In the former case, we note that the entropy is large for corresponding bonding and anti-bonding orbitals, while in the latter case we see a uniformly distributed entanglement which both reflect the different molecular structures of the two clusters: The O–O bond is intact in the peroxo structure, we find four equivalent Cu–O bonds in the bisoxo structure. Moreover, most of the highly entangled orbitals possess nodal planes between the two oxygen atoms which is an indication of the O–O bond breaking process that is described by the transition from the peroxo to the bisoxo isomer. For the description of static correlation the highly entangled orbitals are indispensable as is clear from the entropy analysis. Their proper treatment in the DMRG algorithm guarantees that the approximate DMRG wave function has all qualitatively correct features which eventually makes the calculations quantitatively predictive.
These results indicate that even small-$M$ DMRG calculations provide a qualitatively correct description of transition metal clusters as demonstrated in section 3.7 and Refs. [49, 105]. It also indicates that highly entangled orbitals form subgroups. Therefore, a coarse-graining approach might be possible which could be efficiently implemented by the multiscale-entanglement-renormalization ansatz (MERA) [177].

The tensor network states, in particular MPS, are ideally suited to describe potential energy surfaces quantitatively and qualitatively correctly for isomers on the same surfaces or the relative difference between states of different spin multiplicity.

Furthermore, we provided an extensive overview of the IMLS interpolation scheme with its fitting error facility that allows the automated construction of potential energy surfaces. We gave an instructive example of the capabilities of the IMLS growth procedure for the Müller potential. The incorporation of a specific energy constraint to limit the PES to the chemically interesting regions are decisive for a fast convergence of the automated growth procedure. The approximated PES surface can be used afterwards for the study of the its features like efficiently computing the MEP.

We also extended the current application range of the IMLS procedure to structure optimizations. Thus, the interpolation of just a few points has been used to “extrapolate” in the near vicinity of the accurately fitted surface. This could be achieved by means of the IMLS error facility. We have demonstrated the IMLS structure optimization for a simple Morse oscillator.

In summary, we have developed and implemented a theoretical framework and algorithmic toolbox to generate accurate PES that describe chemical reactions on a single surface or on surfaces of different spin.
6. Towards accurate potential energy surfaces
7. Haptic quantum chemistry

In this chapter, an implementation designed to physically experience quantum mechanical forces between reactants in chemical reactions is presented [269]. This allows one to screen the profile of potential energy surfaces for the study of reaction mechanisms. For this, we have developed an interface between the user and a virtual laboratory by means of a force-feedback haptic device. Potential energy surfaces of chemical reactions can be explored efficiently by rendering in the haptic device the gradients calculated with first-principles methods. The underlying potential energy surface is accurately fitted on the fly by the interpolating moving least-squares (IMLS) scheme to a grid of quantum chemical electronic energies (and geometric gradients).

7.1 Rare events in complex chemical systems

Theoretical studies of molecular reactivity are governed by two major approaches: The static quantum chemical approach aims at the search for stationary points on the potential energy surface that can be identified as minima representing stable educts, intermediates, or products as well as transition states [5, 6], while molecular dynamics extracts mechanistic and even kinetic information from the analysis of trajectories [270]. Both of these approaches have one aspect in common and that is the fact that all implementations try to provide this information with as little guiding as possible. Of course, transition state searches in quantum chemistry benefit from educational guesses of transition structures and molecular dynamics simulations may be controlled via constraints and restraints [271]. One very successful approach to improve the searching properties in molecular dynamics simulation was the introduction of the concept of memory by means of the local elevation procedure [272] or its variants like metadynamics [273]. The local elevation method tries to guide the molecular systems into new areas of configurational space rather than sampling the low-energy regions over and over again. However, all of these approaches are designed to produce insight into chemical reactions with as little human interference as possible. Still, chemists would like to play with molecules in order to figure out what the reactivity might be. For this, hardly any method is available that allows the exploration of chemical reactivity with sufficient rigor, namely on the first-principles basis of quantum mechanics.

Here, we propose to use what we call Haptic Quantum Chemistry meaning the ability to manually explore the potential reactivity of molecules with a haptic
device, i.e., a hardware extension which not only allows to manipulate a reactive system *in silico*, but which is also capable of transmitting the system’s response to the user (see Fig. 7.1 for the device employed in this work). Of course, the traditional approaches can then still be used once the user has gained a good overview on potential reaction paths. The explored paths may be directly used for further refinement in quantum chemical or molecular dynamics approaches.

Figure 7.1: The PHANTOM OMNI device from SensAble Technologies, Inc. is depicted in its resting state where the stylus is placed in the ink well. This device supports six degrees of freedom to move the haptic pointer in the virtual space of the haptic frame, corresponding to the left/right, up/down, in/out, rotating, twisting, and tilting motion. These degrees of freedom are also indicated in the figure.

The idea is thus to employ external hardware periphery in order to allow the user to let reactants approach in many different fashion in real-time. In order to experience the likeliness of a potential reaction channel, the hardware extension, i.e., the haptic device, must provide a response to the user. For instance, if the chosen channel is repulsive, the user must be able to feel this repulsiveness. A force-feedback haptic device can produce such information. It is most important, of course, that this information is provided in real-time in order to be a valuable tool in chemical research. This is a particular challenge if forces that act between molecules are calculated quantum chemically rather than via a classical force field, which could be evaluated fast. However, we clearly need to benefit from the *first-principles* nature of quantum mechanical forces that do not need any parameterization for specific chemical situations.

We should mention that this is not the first work to report on the usefulness of external hardware for the study of chemical processes *in silico*. However, all previous approaches employed *classical* force fields of simple analytical form. Satoh *et al.* have described an apparatus called SPIDAR [274–277] that allows
one to draw and push a ball on wires with the option to produce a feedback through the wires in accordance with the position of the ball in a one-dimensional Lennard-Jones-type potential well (primarily designed for chemical education purposes) [278]. Much more elaborate than this toy model is the interactive molecular dynamics method developed by Schulten and co-workers [279] who employ a hardware extension to grab a molecule and move it in a supramolecular assembly (e.g., to grab a water molecule and drag it through an aquaporin channel [280]). Still, the interaction mediated through the external hardware to the scientist are classical forces from standard biomolecular force fields. However, there is a very interesting theoretical catch to the Schulten approach and this is the option to calculate the equilibrium reaction free energy for this process from the non-equilibrium work of the steered molecular dynamics through Jarzynski’s identity [281]. We should also mention early work by Levine et al. [282] on molecular docking processes studied by an interactive system in a virtual reality environment but without the force-feedback option.

In this work, we present the first attempt on a haptic quantum chemical research platform. For this endeavor it is clear that apart from the technical realization of the haptic hardware, for which we employ a commercially available peripheral add-on (see the appendix for technical references), many implementation-specific problems need to be solved. Therefore, we describe here, how a modular object-oriented haptic quantum chemistry software can be designed that controls the haptic device and allows user actions as well as responses to be transferred back to the user. Then, a couple of computational difficulties must be efficiently solved because, in the end, the first-principles force between molecules needs to be evaluated in real-time and must be transmitted to the haptic device. Already with present-day desktop hardware we are able to show that this can be accomplished for first model reactive systems. The ongoing hardware development of computational capabilities by emerging multi-core multi-socket central processing units is, of course, a side effect that will make haptic approaches more and more feasible for much more elaborate reactive ensembles.

7.2 Technical section: Design and algorithmic structure of the implementation

The basic functionality of our program is to provide a tool which allows the specification of a rigid and a mobile molecular part of a reactive system. The coordinates of the atoms specified in the rigid molecular part enter the potential energy surface as parameters and are not considered to change during the haptic exploration. Usually the mobile part represents a ligand, but it can also stand for any other molecular fragment depending on the chemical system under study. Of course, future developments will aim at the total flexibility of the molecular ensemble in our virtual laboratory box. For instance, we envisage that the user may define parts of the molecular structure that are kept frozen first and that
Haptic quantum chemistry may be sequentially thawed in the process of a haptic simulation. Through the haptic device, the chemist can move the fragment on the potential energy surface of the entire molecular system feeling the forces which are acting on the mobile part. This provides the possibility to feel and touch through the landscapes of the — usually very rough — potential energy surface and thus exploring minimum energy paths of chemical reactions. Compared to the two standard approaches mentioned in the section 7.1, the advantage is that (i) one has not to wait for a certain event to occur as in regular molecular dynamic simulations and (ii) one does not need to make an educated guess for a transition state structure to be eventually found by a sophisticated search algorithm which scales badly with increasing molecular size. On the contrary, one can immediately try several approaches based on chemical intuition.

We employ the PHANTOM OMNI device developed by SensAble Technologies, Inc. which is simply referred to as the haptic device. The PHANTOM OMNI device comes together with a library providing the application programming interface for communicating with the device in a similar fashion as with the OpenGL Application Programming Interface (API) library. The communication with the haptic device drivers is performed through different abstraction layers provided by SensAble’s OPENHAPTICS Toolkit components. The OPENHAPTICS Toolkit consists of the Haptic Library API (HLAPI) and the Haptic Device API (HDAPI). The HDAPI provides low-level access to the haptic device, enables programmers to render forces directly, offers control over configuring the runtime behavior of the drivers, and provides convenient utility features and debugging aids. The HLAPI, on the other hand, provides high-level haptic rendering and is designed to be familiar to OpenGL API programmers. Our code was developed on a Dell Latitude D820 running Debian GNU/Linux Lenny with kernel version 2.6.18 with an Intel Core™ 2 CPU.

The design of our software aimed at code reuse, scalability, compatibility to future projects, and data abstraction. These requirements can be perfectly realized using the C++ programming language. It allows for a very efficient modular programming style where classes represent different concepts or modules. The advantage of this approach is that the modules can be developed independently of other modules. They do not rely on each other which provides the necessary flexibility for improving or adjusting the code for any future needs. We start by introducing the scene manager class which is our control structure.

The scene manager provides a minimal interface for the communication of the different modules. It controls the flow of information and takes care of all user-related interactions. Its main purpose is to display the molecular system under study and to provide a way for the user to communicate and work with it. It is also responsible for the communication with the underlying OpenGL API (version 2.0) used for the graphics display and thus manages the camera and light positions. The scene manager can be considered as the head office of the code and administrates the graphics module, the force module, and the haptic device interface.
The graphics module can be considered as the storage of all graphics related information. It parses a control file and collects the molecular structure as well as all other relevant parameters such as atom connectivity, initial camera and light position, the dimension of the view frustum and the path to the relevant files for the force module. The control file allows the user to influence the execution of the code without recompilation.

The force module takes care of the calculation of the gradient which is then rendered by the haptic device. It reads the potential energy surface in terms of positions of the atoms and the corresponding energy which is specified in an input file. This input file has to be previously generated by any desired quantum-chemical program package. The path is then retrieved by the parsing routine of the graphics module. In addition, gradients for every atom can also be read in, which is then used for drawing the forces. The gradient information is optional. Based on this information, an interpolation algorithm performs a fitting at the evaluation point. The evaluation point is determined through different transformations from the haptic device coordinates to the Cartesian coordinates, and to the frame in which the molecular structure is specified.

The haptic device interface represents the physical haptic device as a resource which is encapsulated into a class to easily control and manage it. The constructor of the class initializes the haptic device and the destructor is responsible to shut it down properly. The main task is to retrieve the haptic coordinates, then transform them to the Cartesian coordinates, and finally proceed to the force calculation.

Managing transformations between different sets of coordinates using frames

Frames are introduced to simplify the transformations between different sets of coordinates. Frames are just virtual constructs which group similar objects together. It bears several advantages to have all transformation matrices pivotally stored, e.g., preventing race conditions through simple spin locks in a multi-threaded design approach for shared-memory architectures. In software engineering, a spin lock is a synchronization technique which prevents the execution of critical code by more than one thread simultaneously (see also below).

As shown in Figure 7.2, the program consists of three frames. Each frame contains a coordinate system which best fits the need to express a particular problem. The haptic frame manages the coordinates of the haptic device which refer to the haptic workspace. The world frame handles the Cartesian coordinates which define the molecular structure and are used to represent the fitted potential energy surface (PES). The graphics frame, on the other hand, simply contains the information to draw the Cartesian coordinates from the world frame. The definition of the graphics frame allows one to rotate, scale, and manipulate the molecular system in any way one desires and provides the best insight into the problem under study while letting the original coordinates
of the molecule untouched. Figure 7.2 also provides a comprehensive overview of the flow of data and the transformations between all the frames. The haptic device coordinates are transformed to the Cartesian coordinate system in which the molecule is defined. The haptic device coordinates can also be transformed to the graphics frame for drawing the mobile part of the system.

Figure 7.2: Frame overview. The flow of information and transformations used between different frames are schematically shown in the figure. Refer to the text for more information.

Based on the transformed coordinates of the mobile part in the world frame, the force acting on the mobile part is calculated as the gradient at the particular position on the fitted PES. The calculated gradient is then returned to the haptic frame where it is rendered onto the haptic device. The rigid part of the molecule and the calculated gradient in the world frame can trivially be transformed to the graphics frame and then drawn as well. To summarize, the introduction of the frames is a helpful way of keeping track of all different transformations without accidently mixing different coordinates.

7.3 Optimization techniques to improve performance

In real-time applications, performance is of utmost importance. The bottleneck is the evaluation of the least-squares equations of the IMLS algorithm at every point where gradient information is needed. The IMLS interpolation scheme for the construction of the PES has been described in section 6.4. In order to avoid the perception of force discontinuities, the haptic device needs to refresh the forces at a rate of 1000 Hz [283]. A calculation of the gradient using a first-principles approach at this rate is clearly not feasible with present-day hardware and software. In comparison to the force rendering, the graphics display will
refresh the framebuffer approximately at 50-60 Hz. Therefore, the focus is on
the optimization of this least-squares evaluation applying four different schemes.
First, the IMLS algorithm can be slightly modified to use local approximants.
Second, the code is tuned with respect to level 1 data cache use. The data
structures in our code are optimized in order to improve cache hits and to
reduce cache misses to the largest extent. Third, we maintain a cache register
where we store all data points which were evaluated by the IMLS method. An
evaluation is only started when the haptic device moves away a certain distance
in space from the proximity of an evaluation point. Fourth, the entire function
dealing with the evaluation of the IMLS method is moved into a separate thread
of execution.

7.3.1 IMLS using local approximants

The L-IMLS procedure requires an initial calculation of all coefficients for every
data point. Guo et al. introduced the local approximants for improving the
efficiency of the IMLS method [250]. A local approximant approximates the
potential energy surface $V(q)$ around a configuration $q^{(i)}$ by using the coefficients
$\{a_j(q^{(i)})\}$ for $j = 1, \ldots, m$ obtained from the initial least-squares solution at that
particular configuration and is defined as

$$L_{q^{(i)}} V(q) = \sum_{j=1}^{m} a_j(q^{(i)}) b_j(q). \quad (7.1)$$

For every $ab\ initio$ data point we evaluate the local approximant and generate $N$
local approximants $L_{q^{(i)}}$ which are then used in a weighted sum to approximate
the fitted PES $V_{\text{fit}}(q)$ as

$$V_{\text{fit}}(q) = \sum_{i=1}^{N} w_i(|q - q^{(i)}|) L_{q^{(i)}} (q) = \sum_{i=1}^{N} w_i(|q - q^{(i)}|) \sum_{j=1}^{m} a_j(q^{(i)}) b_j(q) \quad (7.2)$$

where $w_i(|q - q^{(i)}|)$ is again the weighting function already defined in Eq. (6.8).
We use a slightly adapted version of the L-IMLS protocol proposed by Guo et al.
in which the energy values are not stored but rather the entire set of coefficients
$\{a_j(q^{(i)})\}$. This generates a $N \times m$ matrix $A$ where the rows represent the set of coefficients for every data point. Again, it is very convenient to write Eq. (7.2)
in terms of a matrix–vector notation yielding

$$V_{\text{fit}}(q) = w^T(q) A b(q) \quad (7.3)$$

where $w(q)$ is a $N \times 1$ column vector, $A$ is a $N \times m$ matrix containing the coefficients from the local approximants, and $b$ is a $m \times 1$ column vector containing the basis functions at the configuration $q$. The set of coefficients for configuration $q$ is described by the matrix–vector multiplication $a^T = w^T(q)A$
and can be used to calculate the gradient according to the plan described in section 6.4.1. The advantage is obvious compared to the regular IMLS method. It requires only the solution of the least-squares equations for \( N \) data points. For any evaluation point, the cost is then simply reduced to the multiplication of \( \mathbf{w}^T(q) \mathbf{A} \) to get the gradient. However, this procedure heavily relies on the requirement that \( \text{ab initio} \) data points are close to the evaluation points of interest for a satisfactory accuracy.

### 7.3.2 CPU cache tuning

Cache memory is a small, expensive, but extremely fast memory buffer which is located between the CPU and the physical memory. Whenever data is read from memory, an entire cache line is loaded into the cache. A cache consists of a collection of cache lines. Each line consists of two parts: a data section and a tag specifying the memory addresses. When the CPU tries to access a memory address it first looks through the tags of the cache lines if the corresponding data is already present in the cache. The cache line with the matching memory tag pretends to be that memory address range in main memory and the CPU can load the data from the cache line considerably faster. This is called a cache hit. A cache miss, on the other hand, means that the CPU is looking for an address which first must be retrieved from the slower main memory. As an impression for the reader of the costs associated with cache hits and misses the time for accessing different types of memories in terms of CPU cycles is less than 1 cycle for registers, \( \sim 3 \) cycles for level 1 cache, and \( \sim 240 \) cycles for main memory accesses [284].

Memory access is the performance determining step. If one aims at improving the performance of a code, it is advisable to focus on changes affecting the level 1 data cache since those will likely yield the best results. The guideline for programming cache efficient programs is to improve spatial and temporal locality of the data.

In our case, we restrict cache tuning only to the part of the code where the calculation of the least-squares solution is performed. The data structure of the underlying matrices appearing in Eq. (6.6) were modified in order to improve cache hits and to reduce cache misses as much as possible. Apart from the changes to the data structure, we also arranged nested loops in a way that the most inner loop runs over a part of sequential memory. This leads to an increased spatial locality of the data and consequently reduces cache misses. Most loop reorderings are corrected by sophisticated compilers nowadays.

In Table 7.1, the level 1 cache miss sum is listed for each optimization step. For the evaluation of the level 1 cache hits and misses we use the valgrind --tool=cachegrind program [285] and have disabled multi-threading for the benchmark measurements. In the first optimization step the multiplications of the matrices and vectors in the IMLS algorithm were slightly rearranged for
an improved temporal locality. The second optimization step was focusing on the matrices and the underlying memory model. For matrix multiplications where the right operand is in a column-major memory layout spatial locality is improved. Therefore we achieve more cache hits compared to the regular row-major memory layout. In the second optimization step, we rearranged the nested loops in order to iterate over sequential memory areas as much as possible. This loop rearrangement could not be optimized by the compiler since it depends on the data structure used in our code.

Table 7.1: Cache tuning increases performance by reducing the number of cache misses. A cache miss means that more time is needed to access a memory address on the main memory instead of the faster level 1 cache. The CPU cycles for various optimization steps are compared for three IMLS evaluations. It is evident that a properly cache aligned data structure and cache aware loops improve performance significantly. Level 1 cache miss sums are measured on Intel\textsuperscript{(R)} Core\textsuperscript{TM} 2 CPU and the elapsed time is measured in seconds.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>L1 Cache Miss Sum</td>
<td>15\textsuperscript{7}212\textsuperscript{8}56</td>
<td>3\textsuperscript{3}395\textsuperscript{0}90</td>
<td>638\textsuperscript{2}66</td>
</tr>
<tr>
<td>Relative</td>
<td>100%</td>
<td>21.6%</td>
<td>4.1%</td>
</tr>
<tr>
<td>Elapsed time</td>
<td>0.12</td>
<td>0.05</td>
<td>0.03</td>
</tr>
</tbody>
</table>

7.3.3 Cache register and proxy positioning

The cache register is a simple data structure implemented as a list containing all calculated gradients. This approach is advantageous for performance reasons due to the fact that one is usually not interested in experiencing the entire PES but rather in a spatially confined space where one might often visit the same configuration again and again. Instead of evaluating the same least-squares equation several times for a certain configuration, the cache register is browsed through to inspect if a gradient was already stored within a certain area around this configuration. We used a threshold radius of 0.05 Å to determine if a gradient is stored in the cache register or not. The proxy positioning is based on a similar principle as the cache register. One assumes that the gradient is not changing over a very small distance in space. This distance is usually dependent on the curvature of the electronic structure but can be reasonably well approximated. This prevents the request for a new calculation of the gradient or the searching through the cache register if one only moves the haptic device pencil insignificantly. We found that the best value for the proxy positioning is 0.1 Å.

The cache register and the proxy positioning help to reduce the number of expensive least-squares solutions and therefore boost the overall performance of
our program.

7.3.4 Multithreading

Computer systems with multi-core processors have become now ubiquitously available in recent years. Shared memory architecture made parallel programming mandatory for performance-sensitive applications. However, it is not straightforward at first sight how to decompose a program into several threads of execution. Problems may arise due to the presence of concurrency in parallel programs such as race conditions. Race conditions can be cured by implementing locks. Locks are a synchronization technique and are working by preventing the execution of a critical part of the code by more than one thread simultaneously. Our software is a real-time program where a quick response to the user input is essential; and the most time consuming part is the gradient calculation by the IMLS method. We therefore moved the bottleneck of the code into a separate thread, independent from the user-interface and the haptic device. This ensures a smooth behavior of the haptic device at every time. The second thread consists solely of the interpolation kernel and is only dedicated to number crunching. It is fed by the main thread with data for which the solution of the least-squares equations is calculated without slowing down any other part of the program. Our program does not rely on threading libraries. We implemented threads by directly invoking the \texttt{clone} system call provided by the Linux kernel. Spin locks were used for synchronization and were written in assembler language.

7.4 Experiencing the quantum mechanical forces at reactants: The H$_2$O + H$^+$ toy model

To validate our software, we were looking for a small toy system and found the protonation of a water molecule ideally suited for this purpose. The PES is easily accessible for studying the accuracy of the IMLS interpolation scheme and the procedure for locating minimum-energy paths. In addition, the haptic pointer position corresponds to the proton and thus the desired PES surface can be described by three variables, the Cartesian coordinates of that proton. The water molecule is held fixed at all times and the proton is used to probe the “best” way to protonate the oxygen atom. In Figure 7.3, we present five scenes showing the approach of the haptic device pointer to the oxygen atom of the water molecule.

For the sake of simplicity, we pre-computed certain portions of the PES on a grid of points. More specifically, we constructed the PES of the protonation reaction by dividing the configuration space around the center of the molecule in two equidistant grids with different point densities. The inner grid is composed of 2500 \textit{ab initio} points spanning a rectangular region (4 Å×4 Å×5 Å) and the outer grid of 13960 \textit{ab initio} points spanning a cube (10 Å×10 Å×10 Å) centered the origin. Note that the number of grid points is mostly determined...
by the size of our virtual laboratory box, which embraces the reactants, rather than by the reactive system under study. Also note that such large numbers of grid points can be handled even for large molecular assemblies as the efficient methods of first-principles molecular dynamics have demonstrated [286], where some thousands of electronic energies need to be calculated for a sufficiently long trajectory.

At every grid point, we evaluated the *ab initio* single-point energy and gradient using BP86 as implemented in the Molpro program package [227] (employing a TZVPP basis set for the O atom and the H atoms [287]).

Figure 7.3: In this slide-show the haptic device pointer is approaching the water molecule showing the calculated force vector illustrated by the red dot. The oxygen atom is represented by the big red sphere and the hydrogen atoms by the white ones. One visually and physically experiences the attractive character of the gradient in the first three slides which then changes to a repulsive one when moving along this path.

For the calculation of the energies and gradients, the algorithm fully exploits the point-group symmetry of the water molecule. At this stage of the code, the gradient information is optional. It is not used in the IMLS algorithm and only serves for drawing the force vector at the grid points. We assessed the accuracy of our PES by calculating the root mean square deviation (RMSD) of the fitted energies from the IMLS and the L-IMLS procedure to the *ab initio* data points along the $z$ axis ranging from $-5 \text{ Å}$ to $5 \text{ Å}$. In Figure 7.4, the *ab initio* data and all IMLS and L-IMLS interpolations with different orders are shown and in Table 7.2 all RMSD values are presented.
Figure 7.4: This figure shows the \textit{ab initio} energies as well as the fitted second-order IMLS and L-IMLS energies along the $z$ axis (which corresponds to the C$_2$ rotation axis of the water molecule) ranging from $-5$ Å to $5$ Å. The \textit{ab initio} energies which are calculated at the same points as the fitted energies are drawn as red stars. The other \textit{ab initio} energies are in green filled squares and they correspond to the points of the PES along the C$_2$ axis which are used for the interpolation. The second-order IMLS (blue filled circles) and L-IMLS (magenta filled triangles) data are also shown.

Table 7.2: The RMSD values are given for any combination of \textit{ab initio} and fitted energy values from the IMLS and L-IMLS procedures applying second-order and third-order polynomials. The RMSD values are given in Hartree.

<table>
<thead>
<tr>
<th>RMSD</th>
<th>\textit{ab initio}</th>
<th>2nd-IMLS</th>
<th>3rd-IMLS</th>
<th>2nd-L-IMLS</th>
<th>3rd-L-IMLS</th>
</tr>
</thead>
<tbody>
<tr>
<td>\textit{ab initio}</td>
<td>0.000 000</td>
<td>3.518 324</td>
<td>3.512 681</td>
<td>3.471 453</td>
<td>3.441 968</td>
</tr>
<tr>
<td>2nd-IMLS</td>
<td>0.000 000</td>
<td>0.093 336</td>
<td>0.198 979</td>
<td>0.197 491</td>
<td></td>
</tr>
<tr>
<td>3rd-IMLS</td>
<td>0.000 000</td>
<td>0.278 134</td>
<td>0.256 944</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2nd-L-IMLS</td>
<td>0.000 000</td>
<td>0.074 983</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3rd-L-IMLS</td>
<td>0.000 000</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

From Figure 7.4, one sees that the region very close to the oxygen atom is not well represented in our constructed PES which causes the comparatively
high RMSD values for all interpolation schemes. This can be attributed to the limited resolution of our grid. However, the RMSD values between the fitted data is rather small and leads to the conclusion that both methods, the IMLS and L-IMLS procedure, are capable of providing accurate and reliable PESs. We also notice that the order of the polynomials has a larger effects on the L-IMLS data compared to the IMLS procedure which is rather insensitive to different polynomial orders. In our studies, we use the IMLS approach with third-order polynomials.

After the construction of the PES, 500 additional points were determined by the simulated annealing scheme as demanded by the automatic error control facilities in the IMLS scheme described in section 6.4.2 starting from the position of the oxygen atom to improve the accuracy of the PES in the chemically interesting configuration space. The initial values of the parameters were set to $T = 300 \text{ K}$ and $k = 0.001 \text{ Hartree}^2 \text{ K}^{-1}$ where the unit K has been introduced for the sake of convenience, while \text{Hartree}^2 is determined by the negative squared difference surface of the fitted energies in Eq. (6.11). Our annealing schedule reduces $T$ by a factor of 0.9 either after 90 accepted steps or after 1000 steps.

Figure 7.5: In this figure, the calculated gradients are shown as cones at every grid point to illustrate the data which was used for the interpolation.
at every grid point. A harmonic potential correction is applied to all forces for a smooth transition to the desired force to circumvent high-frequency force buzzing artefact. This is achieved by calculating the difference vector between the currently rendered force and the calculated one. The calculated force is not directly rendered, but rather an approximate force which is determined by adding the scaled difference vector to the currently rendered force. The multiplicative scaling factor is chosen to be 0.1 in our work. If it is set to 1.0, the newly calculated force is rendered directly and no correction is applied. This approximate force is approaching the calculated force with the frequency of the refresh rate of the haptic device which is 1000 Hz. This is an ad-hoc correction to prevent the haptic device of rendering forces which differ largely and lead therefore to feeling discontinuities.

The configurations required by the MEP-IMLS method were obtained by combining chemical intuition and the knowledge gained by the exploration of the PES. This allows us to efficiently locate the two global minima on the PES under study. The global minima found by applying our MEP-IMLS method correspond exactly to the fully optimized structure of $\text{H}_3\text{O}^+$. We have calculated several minimum-energy paths using MEP-IMLS which are shown in Figure 7.6.

Figure 7.6: The MEP-IMLS scheme delivers various minimum-energy paths depending on the starting and ending configurations. All these paths finally allow one to locate the electronic energy minimum, i.e., the stable configuration on the PES, which is the point in the configuration space where most of the minimum-energy paths cross.

Already this simple example allows to physically experience the attractive and repulsive forces acting on the proton while being moved around the water
molecule by the user of the haptic device. Keeping track of the paths, we obtain a guess for the stable bound structure, which is then verified to be the local $\text{H}_3\text{O}^+$ minimum structure.

### 7.5 Summary and perspective

In this chapter, we presented a haptic quantum chemical approach for the study of chemical reactivity. We have demonstrated how a haptic device can be utilized efficiently to explore potential reaction paths of a chemical system in real-time. Once the user has gained a certain experience with a reactive system set up \textit{in silico} in our virtual laboratory, the haptic device allows to record the potential reaction path for further refinement in standard stationary quantum chemical or trajectory-based molecular mechanics approaches.

We have achieved to design and to build an efficient, modular, object-oriented program which interfaces our virtual laboratory with the user through a haptic device. We have demonstrated that our software provides accurate forces to explore a three dimensional PES of a toy model in real-time. The accuracy of the forces can also be verified by the newly introduced MEP-IMLS scheme. There, they were used to calculate minimum-energy paths leading to true global minima.

While our first steps into this direction have already been successful, new developments are at the horizon and are currently explored in our laboratory. In particular, we are working on (1) more efficient and adaptive interpolation methods for the representation of the potential energy surface from which the forces are calculated, on (2) a formalism, which allows us to assess the minimum accuracy of quantum chemical geometry gradient calculations that is determined by the force resolution of the haptic device as well as by the specific real-time situation of the haptic experiment, on (3) tests with a simple force field driver to study the general capabilities and pitfalls for haptic quantum chemistry when applied to much larger molecules (typically those for supramolecular host–guest interaction), and on (4) transition metal catalysis with diatomic ligands, which requires an extension of the present case to accommodate six instead of three parameters for the haptic pointer position. In the end, a haptic tool box will emerge that will eventually complement everyday quantum chemical studies of synthetic chemists.
8. Conclusions and Outlook

The central problem in electronic structure theory is the factorial complexity of the underlying many-particle Hilbert space for large molecular systems that prevents the application of most standard CI-type quantum chemical methods. The factorial complexity arises due to the expansion of the electronic wave function in terms of Slater determinants. This brute-force approach, however, can be circumvented by designing new classes of variational states that are able to capture the relevant quantum correlations and thus mimic the entanglement of the molecular system under study.

In this work, we took a first step into this direction by breaking down the complexity of the high-dimensional coefficient tensor of an exact wave function into a suitable network of small-ranked tensors. So, instead of restricting the basis of Slater determinants to some excitation pattern, the complete many-particle Hilbert space is taken into account. The approximation to the electronic wave function lies in the reduced parameter set used to construct the coefficients of each individual Slater determinant. Hence, the clever design of such networks of tensors is essential, but can be guided by principles from quantum information theory. Quantum information theory provides the theoretical framework to quantify quantum correlations by means of the entanglement between two subsystems. The description of the fundamental physics in molecular systems thus depends on how accurately this entanglement is approximated and embedded in the electronic wave function.

The efficient decimation of the entire Hilbert space is key in developing a competitive electronic structure method that scales polynomially instead of factorially. In order to finally achieve this goal, we employed the principles of quantum information theory to formulate a DMRG protocol that surmounts current algorithmic limitations. The entanglement entropies of single orbitals in a given electronic state are employed to devise an optimized orbital ordering. The concept of entanglement localization sets the physical basis for selecting the number of DMRG basis states dynamically according to the underlying electronic structure and the desired error bound. With these new recipes, we have developed an entropy-based DMRG algorithm and tested it for the prediction of energy differences between the two isomers of a very challenging binuclear copper cluster that we introduced as the benchmark molecule for DMRG calculations [105]. We found that the incorporation of the principles of quantum information theory in the DMRG algorithm substantially improve the convergence behavior and limits the computer resources required for a given accuracy.
of the calculated energy. The one-orbital entropies allow for an optimized orbital ordering by manipulating the block entropy profile. It is very instructive to compare the relative energies between the two copper isomers obtained from the standard DMRG algorithm and the sophisticated entropy-based DMRG protocol. Even though the relative energies of both calculations are similar, the total absolute energies for the standard DMRG algorithm employing a small number of DMRG states are not fully converged. This finding is important with respect to chemistry since accurate energetics are of utmost importance in understanding chemical reactions and can be attributed to the underlying DMRG wave function. Therefore, we have also discussed the construction of the DMRG wave function in detail which is composed of two MPS that span in principle the entire Hilbert space. Understanding the construction of the DMRG wave function provides an explanation for the accuracy of results obtained with a small number of DMRG states. DMRG is capable of selecting the most important basis state of the wave function spanning the full Hilbert space. Determining the most important basis states is of course crucial for accurate and qualitatively correct relative energies.

In addition, we augmented the standard DMRG algorithm with an extrapolation scheme that provides an automated accuracy control facility to calculate DMRG energies that are independent of the number of DMRG states. This procedure is based on the observation that two different electronic or spin states require a different number of DMRG states for a certain error bound of the energy, i.e., a high-spin state might require less basis states for the same accuracy of the energy as for a low-spin state. We have applied this extrapolation procedure to accurately predict the vertical energy splitting between the singlet and triplet states of cobalt hydride — another test molecule that we established for DMRG calculations [105]. This example showed that a smaller number of DMRG states was necessary for the triplet state for accurate relative energies.

In continuation of our work on DMRG, we have designed a new class of variational states based on the tensor network approach which we denote complete-graph tensor network states. The complete-graph tensor network states form a subclass of the very general correlator product state formulations. In our approach, all two-site correlators that can be defined within a given active space are used to construct the electronic wave function. The structure of correlator product states can be exploited to gain additional information about the entanglement structure by a rigorous mathematical analysis of the decomposition of the set of correlators into a bipartite system. As a result, we have shown that quantum correlations in a particular molecular system are approximated by the inter-block correlators and hence the variational optimization corresponds to an entanglement localization which has already been discussed previously in the context of DMRG. For the complete-graph tensor network states, we have implemented an efficient variational optimization algorithm based on a parallel-tempering Monte Carlo scheme.

The application of the complete-graph tensor network states to the spin splitting
of methylene and ozone provided excellent results with a dramatically reduced set of parameters compared to the exact ansatz. Nevertheless, the quality of the tensor network wave function suffers from the large difference in magnitude of the individual CI coefficients, especially for electronic structure that are well represented by a single determinant. This problem emerges due to the structure of the highly non-linear tensor network ansatz proposed. To improve this ansatz for molecular systems, we have introduced a hybrid approach relying on configuration interaction and on tensor network theories. The determinants with a very large weight are explicitly represented by single coefficients as in the CI method while the vast majority of determinants with a small coefficient are collectively approximated by the tensor network. The magnitude scale separation present in the CI coefficients of the full many-particle Hilbert space can thus be turned into an advantage. With a marginal increase in the number of variational parameters, we have obtained substantially improved total electronic energies as well as more accurate coefficients of the Slater determinants.

A major conclusion from this work is that the tensor network states constitute very promising classes of states that shine light on a new way out of the factorial complexity trap in which most wave function based methods are captured. If the variational optimization of the tensor network states can be significantly improved — as in the case of MPS with the DMRG algorithm — tensor network states will form a new and encouraging branch of research in quantum chemistry, especially in the applications on transition metal containing molecular systems. Our pioneering developments in the efficient parametrization of the electronic wave function clear the track to the application of the multi-state reactivity concept which crucially depends on accurate relative energies between two surfaces to predict and understand reaction mechanisms as well as rate constants of catalytic reactions. In catalysis, transition metals often play a decisive role but require an electronic structure method that provides a qualitatively correct wave function. The catalysts are often rather large in molecular size and one usually resorts to DFT since no other methods are feasible anymore. DFT, however, suffers from the spin state problem that manifests itself in a functional-dependent description of the energetical difference between two spin states. Our studies showed that DMRG as a variational method within the class of MPS is ideally suited for such kind of problems. The theoretical study of many fascinating and challenging problems involving transition metal compounds is now within reach.

Within the Born–Oppenheimer approximation, chemical reactions can be understood as trajectories on a potential energy surface of a given electronic state. The multi-state reactivity concept now suggests that a spin flip might occur at a specific point in the configuration space where the energies of two spin states are the same and the energy on the crossing seam is minimal. This so-called minimum-energy crossing point has been calculated for a model system, the phenyl cation, using DFT and CASSCF. Our DFT-MECP structure corresponds the the ones reported in the literature. The CASSCF-MECP structure,
however, significantly differs from the DFT-MECP one. Hence the success or failure to locate the MECP lies not primarily in the shape of the underlying PESs, but only in the accuracy of their relative energies. Unfortunately, most electronic structure methods are still too expensive in terms of computational resources to calculate a continuous surface. One rather defines a set of discrete points covering the chemically relevant part of the configuration space and relies on an interpolation scheme to construct an approximate, continuous surface. We have implemented a framework based on the interpolating moving least-squares method that allows us to construct potential energy surfaces to the desired accuracy. On these fitted surfaces, we can study chemical reaction mechanisms by means of minimum-energy paths. The optimization of such a minimum-energy path has been tested on the Müller potential which has been constructed previously with the IMLS growth procedure. Two variants of the tangent along the path that keep the images equally spaced have been investigated. We found that Wales’s tangent formulation eliminates artificial kinks and corner-cutting effects which is in accordance with the literature. Moreover, we developed a prototype of a new structure optimization algorithm which is based on an approximate surface. The interpolative structure optimization has been successfully tested on a simple Morse potential example. The ultimate anthropogenic exploration of the potential energy surface, however, has been realized in this work by the newly developed haptic technology for quantum chemistry. Haptic quantum chemistry allows a chemist to physically experience the forces acting on the reactants in chemical reactions and to participate and guide actively the reactions in a virtual laboratory. We have developed a state-of-the-art software package and employed it in the study of the protonation of a water molecule. Haptic quantum chemistry has the potential to become an invaluable tool for chemists who design new catalysts or ligands which are tailored at tuning chemical properties of specific reaction channels for some substrates. With our haptic quantum chemical technology one can immediately and individually probe the desired reaction channel \textit{in silico}.

8.1 Outlook

The DMRG algorithm provides the theoretical framework to truncate the Hilbert space in a very efficient manner and to approximate the low-energy physics of molecular systems. The many-particle basis transformation in DMRG, however, can also be applied to other challenging problems in quantum chemistry where a factorial scaling in the dimension of the underlying basis states exists. The solution of the nuclear Schrödinger equations for vibrational spectroscopy constitutes one of the promising examples where DMRG can substantially improve on current methods. In addition, there is a very interesting theoretical catch to the vibrational DMRG calculations. The key is to come up with an exact mapping of a bosonic site $i$ (say a vibrational mode) containing $2^{n_i}$ states in total, where $n_i$ denotes the number of basis functions used to expand mode
As demonstrated in this work, the DMRG algorithm also provides systematically improvable electronic energies that can be employed for the accurate calculation of relative energies between two electronic states of different total electron spin. It is thus of fundamental interest to benchmark other standard quantum chemical methods such as DFT in the localization of MECP compared to DMRG results. These results are especially important for transition-metal mediated reactions where DFT is the only feasible method and therefore the only choice for a theoretical investigation.

Moreover, the novel CGTN parametrization should be further investigated whether the two-site correlators carry a physical meaning in connection with the underlying electronic structure or whether they are just a very cleverly chosen set of variational parameters. From the converged correlators, for example, one might be able to extract approximate spin–spin interaction coefficients as employed in spin Hamiltonians, such as the Heisenberg model, to qualitatively understand the spin couplings in transition metal magnets and clusters.

The next step in the haptic exploration of molecular systems is to extend the single-atom mobile part to diatomics, such as dioxygen or dinitrogen, and to incorporate additional degrees of freedom in the frozen rest of the molecular system. These additional degrees of freedom then allow the system to relax and respond to the interactions of the haptically guided mobile fragment. For this endeavor, however, we must simultaneously develop sophisticated strategies to define sets of relevant coordinates that efficiently describe the PES, also with hindsight to the required efficiency in the computational part of the interpolation. The definition and implementation of an appropriate method for the relaxation of the rigid part is not trivial or straightforward at all since the entire chemical reaction should ideally be reversible and still computationally feasible for on-the-fly calculations of electronic energies.
9. List of Publications and Invited Talks

Publications

A full circle, •, in the following list of publications denotes the papers that evolved from this work.

- K. H. Marti, I. Malkin Ondík, G. Moritz, and M. Reiher,
  Density matrix renormalization group calculations on relative energies of transition metal complexes and clusters,

- D. P. Geerke, K. H. Marti, S. Luber, and W. F. van Gunsteren,
  On the calculation of the free energy of quantization for molecular systems in the condensed phase,

- K. H. Marti and M. Reiher,
  Haptic quantum chemistry,

- K. H. Marti and M. Reiher,
  The density matrix renormalization group algorithm in quantum chemistry,

- K. H. Marti and M. Reiher,
  DMRG control using an automated Richardson-type error protocol,

- K. H. Marti, M. Reiher, B. Bauer, M. Troyer, F. Verstraete,
  Complete-graph tensor network states: New fermionic wave function ansatz for molecules,

- K. H. Marti and M. Reiher,
  New electron correlation theories for transition metal complexes,

- G. Barcza, Ö. Legeza, K. H. Marti, M. Reiher,
  Quantum information analysis of electronic states at different structures,
Invited Talks


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Personal

Born on February 18, 1984.
Citizen of Switzerland.
Place of Origin Engi, GL.
German (native language), English, French, basic Latin knowledge.
Interests in rock climbing, mountaineering, programming, value investing and entrepreneurship.
Member of Sigma Xi, The Scientific Research Society.
Member of the Swiss Alpine Club, Section Tödi.

Education

PhD in Theoretical Chemistry, ETH Zurich, 2008 – present.
MSc Chemistry, ETH Zurich, 2006 – 2008.
Electives: Computer Simulation in Chemistry, Biology and Physics, Advanced Quantum Chemistry.
Electives: Synthesis of Natural Products, Algorithms and Programming in C++, Quantum Chemistry.
Evergreen State College, Olympia, WA, USA.
Core Subjects: Applied Mathematics and Physics.
Elective: Chemistry.
Professional Experience

Design and implementation of a C/C++ code library for the analysis of seismographic data; programming of a graphical interface to manage and control the acquired data with a particular emphasis on spectral data analysis in the low-frequency regime.

The density matrix renormalization group algorithm for the spin state problem in quantum chemistry.

Calculation of the free energy difference between a classical and a quantum system using Feynman’s path integral formulation by molecular dynamics simulations of liquid neon at 32 K with the GROMOS force field.

Iridium-catalyzed enantioselective synthesis of allylic alcohols using silanolates as hydroxide equivalents for a novel entry to chiral phthalide building blocks.

Kalkfabrik Netstal AG, Netstal, June – October 2003.
Supervision and management of processes in the production and dispatching departments.

Military Service Gren RS 14/03, Isone, February – May 2003.
Basic training as Grenadier in the Swiss military forces.

Awards


Poster Prize Winner of the World Association of Theoretically Oriented Chemists (WATOC), Sydney, 2008.