Doctoral Thesis

Efficient Algorithms for the Matrix Product Operator Based Density Matrix Renormalization Group in Quantum Chemistry

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Efficient Algorithms for the Matrix Product Operator Based Density Matrix Renormalization Group in Quantum Chemistry

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The Density Matrix Renormalization Group (DMRG) algorithm invented by White in the year 1992 has been a rising star for the accurate \textit{ab initio} exploration of Born-Oppenheimer potential energy surfaces in theoretical chemistry.

Existing implementations of DMRG for quantum chemistry have been based on the traditional formulation of the method, which was developed from the point of view of Hilbert space decimation. Recently, a new formulation emerged in which a special class of ansatz states known as matrix product states (MPS) are variationally optimized and operators are correspondingly represented as matrix product operators (MPO). This new formulation provides for increased flexibility through a decoupling of wavefunctions, operators and contraction routines. In this way, MPOs for different symmetries – abelian and non-abelian – and different relativistic and non-relativistic models may then be solved in a unified program framework. While the new matrix product based formalism was quickly adopted by the solid state physics community, early quantum chemical matrix product based DMRG was hampered by inefficiency and sub-optimal computational scaling. In this thesis, we describe how to efficiently construct the quantum chemical Hamiltonian operator in matrix product form and present its implementation as a DMRG algorithm for quantum chemical applications. The MPO construction scheme presented here eliminates the previous performance disadvantages while retaining the additional flexibility provided by a matrix product approach. Additionally, we employ the Wigner-Eckart theorem to arrive at a fully $SU(2)$-invariant description of wave function and operator, conserving the total spin quantum number.

In the new program, called QCMAQUIS, $SU(2)$-invariant MPSs and MPOs have been implemented. It has been made available as a stand-alone program or integrated into the MOLCAS program-package. QCMAQUIS is based on the ALPS MPS code developed in the group of Matthias Troyer at ETH Zürich. The new program allows one to solve larger active spaces than previously accessible by standard complete active space self consistent field (CASSCF) implementations, but the DMRG algorithm depends on additional input parameters whose influence on accuracy is discussed.

Finally, QCMAQUIS has been applied in several chemical applications, some of which are reviewed at the end of this thesis.
Zusammenfassung


Im Rahmen dieser Arbeit wurde das Programm QCMAQUIS entwickelt, in dem SU(2)-invariante MPSs und MPOs implementiert wurden. Es ist sowohl als eigenständiges Programm, als auch als Modul für das MOLCAS-Programmpaket erhältlich. QCMAQUIS basiert auf dem ALPS MPS Programm, welcher in der Gruppe von Matthias Troyer und der ETH Zürich entwickelt wurde. Das neue Programm kann grössere aktive Räume behandeln im Vergleich zur Complete-Active-Space Self-Consistent-Field (CASSCF) Methode, jedoch erfordert der DMRG Algorithmus zusätzliche Inputparameter, deren Einfluss...
auf die Genauigkeit hier besprochen wird.

QCMAQUIS wurde in verschiedenen theoretischen Studien angewandt, von denen einige hier zusammenfassend dargestellt werden.
The Born-Oppenheimer approximation provides two central ingredients for quantum chemistry: one is the concept of molecular structure [1] and the other one is the electronic energy, which acts as a potential energy that determines the motion of the atomic nuclei (in this approximation the ‘potential in which the nuclei move’) and from which thermodynamic as well as kinetic insights can be extracted. The electronic energy is thus central for theoretical chemistry and calculated as the eigenvalue of the electronic Schrödinger equation. However, the accurate solution of this equation is a delicate problem. Two major directions emerged, namely wave-function theory (WFT) and density-functional theory (DFT). While DFT is doubtlessly the most frequently applied approach in quantum chemistry, it lacks the option of a systematic improvement on results obtained with some setting (i.e., with some choice for an approximate functional). For this reason, wave-function methods are under continuous development, although they are usually prohibitively expensive in terms of computer time for large molecules of, say, 100 or more atoms.

The standard ansatz in these latter methods is the pre-definition of a many-electron basis set. From a chemist’s perspective, this may be viewed as a generalization of the textbook LCAO concept for orbitals to the total electronic wave function, which is the eigenfunction in the electronic Schrödinger equation. The standard many-electron basis set comprises (linear combinations of) Slater determinants containing the molecular orbitals. The linear expansion parameters in front of the determinants can be determined either variationally (e.g., in configuration interaction (CI) methods) or by projection (as performed in standard coupled-cluster (CC) approaches). Although the expansion in terms of Slater determinants assumes a single-particle picture (as it rests on the orbital approximation), it can be made exact, if the determinant basis is complete. Then, any electronic state of a molecule can be expanded exactly in such a complete many-electron basis set, which is called ‘Full-CI’ in chemistry and ‘exact diagonalization’ in physics. Unfortunately, the albeit simple construction of this complete basis set comes with the
1.1. Overview of the DMRG algorithm

flaw that the basis-set size grows factorially, which makes its construction by a computer program unfeasible.

Naturally, approximations have been devised which contributed popular and accurate methods such as multi-reference CI or singles and doubles plus perturbatively treated triples coupled-cluster, CCSD(T), to the tools of trade of computational chemistry. Although the success of CC models is remarkable and although highly efficient implementations have been devised [2], their extension to the general multi-configurational case turned out to be cumbersome so that no clear-cut, efficient solution of this problem appears to be in sight. However, from a different field, namely the physics of spin chains, a totally new ansatz emerged: the Density Matrix Renormalization Group (DMRG). The DMRG algorithm was designed for correlated quantum problems in Condensed Matter Physics [3–5], which usually assume a local, nearest-neighbors-only interaction operator. Despite the fact that the full Coulomb interaction of the electrons in a molecule does, in general, not sustain any of the locality assumptions made for the development of DMRG, it was shown that DMRG can be applied to challenging quantum-chemical problems [6–10]. A formal analysis of the electronic state optimized by DMRG leads to a so-called ‘matrix product state’ (MPS) [11]. The MPS concept can be generalized to a more general framework, which has been called ‘tensor network state’ [12] and has also found application for the full quantum chemical interaction operator [7, 13–15].

1.1. Overview of the DMRG algorithm

For a given (finite) set of molecular orbitals, DMRG can systematically approach the finite-basis Full-CI result in this active orbital space. DMRG is variational and also capable of describing multi-reference states occurring in complicated electronic situations as found, for instance, in transition metal complex and cluster chemistry [16].

Similar to a CI wavefunction ansatz, in DMRG, the ansatz for the electronic wavefunction in L orbitals can be respresented as a linear combination of Slater determinants

\[ |\Psi\rangle = \sum_{\sigma} M^{\sigma_1} M^{\sigma_2} \cdots M^{\sigma_L} |\sigma_1, \sigma_2, \ldots, \sigma_L\rangle, \]  

in which the coefficients are encoded as a product of matrices \( M \). Therefore, states in this particular format are called matrix product states. The bold index \( \sigma \) is an abbreviation for the occupation number vector \( \sigma_1, \ldots, \sigma_L \) which runs over all possible orbital occupations and thus labels the orthonormal basis states of the L-orbital system that are the Slater determinants. For each orbital, there is a set of four matrices corresponding to the four possible orbital occupations, \( |\uparrow\downarrow\rangle, |\uparrow\rangle, |\downarrow\rangle, |0\rangle \), labeled by the upper index \( \sigma_i \). Choosing an occupation for each orbital determines the Slater determinant as well as one matrix per orbital, in DMRG jargon called site. The contraction of the selected
Chapter 1. Introduction

Figure 1.1.: Partition of a chosen active molecular orbital space into left, active and right subsystems on which DMRG many-electron basis states are constructed. If the sweep is processed from left to right, then the left subsystem is the active subsystem, on which many-electron states are systematically constructed, while the right (complementary) subsystem carries the many-particle states optimized in the previous sweep processed in the opposite direction, i.e. from right to left. In a DMRG iteration step, the left subsystem is now enlarged to incorporate the left active site and the leftmost site of the right subsystem becomes active.

matrices via ordinary matrix-matrix multiplication yields the CI coefficient of the according determinant. Since these coefficients are scalar, the matrices for the first and last orbitals are required to be row and column vectors, respectively.

The DMRG algorithm then consists of an iterative protocol, in which the site matrices are variationally optimized with respect to the energy in sequential order. The basic ingredient of these local optimization problems is the diagonalization of the matching local part of the electronic Hamiltonian operator, which can be achieved by employing a sparse diagonalizer such as the Jacobi-Davidson algorithm. The sites that are undergoing optimization constitute the active subsystem, as shown in Fig. 1.1. As a result of the optimization, the entries of the site matrices are replaced by a new, optimized set of entries which correspond to the eigenvector of the local Hamiltonian operator with the lowest eigenvalue. Combining the local optimizations, the electronic ground-state energy is calculated iteratively by passing through all sites from left to right and vice versa, referred to as sweeping, until the energy is converged. The rate at which this happens strongly depends on whether a single site is optimized at a time (single-site DMRG) or two sites simultaneously (two-site DMRG). While the former variant performs well for local interaction operators, such as different versions of the Hubbard model in solid state physics, in quantum chemistry, this single-site DMRG gets trapped in local energy minima for even the simplest systems. Two-site DMRG turns out to have much more robust convergence properties, albeit at a higher numerical cost.

A central feature of the ansatz in Eq. (1.1) is that its accuracy can be controlled by adjusting the maximum dimension $m$ that each matrix is allowed to assume. If $m$ is allowed to grow exponentially according to the Hilbert space dimension of a system,
1.1. Overview of the DMRG algorithm

DMRG becomes essentially the Full-CI method. What allows DMRG in many cases to perform much better in terms of the scaling behavior than standard Full-CI, however, is that the maximum matrix dimension $m$ need only make up a tiny fraction of an exponentially large Hilbert space to achieve the same result as Full-CI within numerical precision. In one dimensional systems with finite range interactions, $m$ can even be held constant with increasing system size and without loss of precision. The physical basis for this phenomenon, the so-called area laws of entanglement, has been rigorously studied by the condensed matter physics and quantum information theory community [17, 18]. The amount of entanglement between the two parts of any system bipartition, measured by the van Neumann entropy, is either constant or a logarithmic function of the system size [19]. Because the maximum amount of entanglement that a state in the form of Eq. (1.1) can encode is determined by $m$, this parameter is thus a central quantity of the DMRG algorithm. It is called the number of ‘renormalized basis states’ or the number of ‘block states’ as it is also equal to the number of left and also to the number of right subsystem basis states if one divides the total system into two parts. It is important to note that the number of many-electron DMRG basis states, each of which can be understood as complicated linear combinations of Slater determinants, is actually $m \times 4 \times 4 \times m = 16m^2$ for the two-site DMRG algorithm. Hence, the number of variational parameters, which are CI-type expansion coefficients in front of the DMRG basis states, is also $16m^2$. Another appealing feature of DMRG is that, at least in the two-site variant of the algorithm, the error introduced by limiting $m$ can be tracked in a systematic way which will become clear in a moment.

Extending the left and the right subsystem of orbitals by the adjacent active site on its right and on its left, respectively, yields the total system now bipartitioned into two subsystems represented by $4m$ many-electron basis states. The eigenvalue problem for the combination of both enlarged subsystems is thus of dimension $16m^2$. After diagonalizing the Hamiltonian of this total system – sometimes called the superblock Hamiltonian – a reduced density matrix can be constructed from the Hamiltonian eigenvector by tracing out all states on the complementary subsystem. Diagonalizing this reduced density matrix for the active subsystem yields $m$ eigenvectors with highest eigenvalue that form a rectangular renormalization matrix needed for the dimension reduction of all creation and annihilation operators in the Hamiltonian from $4m$ back to $m$. The truncated weight of the $m$ states, defined as the sum of their eigenvalues, is a useful measure for the accuracy of the approximate wave function as it tends to zero if $m$ is increased towards the dimension of the complete Hilbert space. The selection of $m$ highest-eigenvalue eigenvectors for the dimension reduction of all operators (called ‘decimation’) can be understood as a least-squares fit to reduced-dimensional many-electron basis sets defined for the two subsystems.

What makes DMRG a successful method in quantum chemistry is that, if the active space is smaller than 100 orbitals, between $10^3$ and $10^4$ subsystem states $m$ are usually
Chapter 1. Introduction

sufficient to reduce the truncated weight enough to calculate ground state energies with sub-nHartree precision.

1.2. Variants of DMRG

The original formulation of the DMRG algorithm did not employ the MPS in Eq. (1.1). After White’s first work on DMRG [3, 4] in 1992, it took three years until the inception of MPS [11] and ten more years before the connection between the DMRG wavefunction and MPS was discovered [20]. Originally, the DMRG wavefunction was expressed in terms of a bipartition of the total system of size $L$ at site $s$ into $\mathcal{L}^s$ (spanning sites $1, \ldots, s$) and $\mathcal{R}^s$ (spanning sites $s + 1, \ldots, L$), such that the total state can be expressed as

$$|\Psi\rangle = \sum_{ij} \psi_{ij}^s |a_i\rangle_{\mathcal{L}^s} \otimes |a_j\rangle_{\mathcal{R}^s},$$

(1.2)

where $\mathcal{L}^s$ and $\mathcal{R}^s$ are represented maximally by $m$ many-body states $|a_i\rangle_{\mathcal{L}^s}$ and $|a_j\rangle_{\mathcal{R}^s}$. The diagonalization of Hamiltonian operator in this basis yields the coefficient matrix $\psi_{ij}^s$ and consequently a new set of states $|a_i\rangle_{\mathcal{L}^{s+1}}$ and $|a_j\rangle_{\mathcal{R}^{s+1}}$ selected according to largest weight in the reduced density matrix is constructed for the bipartition shifted by one site, allowing the Hamiltonian operator to be represented in an optimized basis. The transition from $s$ to $s + 1$ requires the transformation of $\psi_{ij}^s$ to $\psi_{ij}^{s+1}$ as well as the transformation of all matrix elements of the operator terms occurring in the Hamiltonian operator to the new basis $|a_i\rangle_{\mathcal{L}^{s+1}}$ and $|a_j\rangle_{\mathcal{R}^{s+1}}$. Repeating this process back and forth across all sites, referred to as sweeping, finally yields an optimal approximation to the ground state for a given basis size $m$.

As an alternative to the original formulation, which we refer to as traditional DMRG, the variational optimization of the ansatz state in Eq. (1.1) yields an equivalent algorithm, which we refer to as second-generation DMRG. The connection between DMRG and the MPS optimization provided the necessary formalism for a theoretical understanding of why DMRG works well for one-dimensional systems but becomes inefficient in higher dimensions [21–23]. Moreover, it allowed for very flexible implementations in which wave functions and operators can be combined arbitrarily in operations such as overlap and expectation value calculations as well as operator-wave function action and operator-operator action. In quantum chemical MPS-DMRG in conjunction with a Hamiltonian expressed as a matrix product operator (MPO), the main challenge is the construction of the MPO, because the performance of the method depends critically on it and naïve schemes lead to a wrong scaling of the method. How the electronic Schrödinger Hamiltonian can be constructed as an MPO is one of the novel contributions from this work. The basic construction is described in chapter 2 and symmetry aspects are covered in chapter 3.
1.3. Matrix product formalism

By employing our Hamiltonian MPO construction, we have been able to implement quantum chemical DMRG in the program QCMaquis, which was the first second-generation quantum chemical DMRG implementation with the proper scaling. Compared to traditional DMRG, second-generation DMRG is more versatile in that the decisive quantities, namely wave functions and operators, can be handled independently of each other. As a consequence, we have been able to implement for example relativistic Hamiltonians simply by exchanging the MPO while reusing all the contraction routines handling the application of the MPO to the MPS. Another example is the incorporation of non-abelian spin symmetry along with conventional abelian symmetries such as $S_z$ and particle number.

1.3. Matrix product formalism

1.3.1. Matrix product states and operators

Any state $|\psi\rangle$ in a Hilbert space spanned by $L$ spatial orbitals can be expressed in terms of its configuration interaction (CI) coefficients $c_{\sigma}$ with respect to occupation number vectors $|\sigma\rangle$.

$$|\psi\rangle = \sum_{\sigma} c_{\sigma} |\sigma\rangle,$$

with $|\sigma\rangle = |\sigma_1, \ldots, \sigma_L\rangle$ and $\sigma_l = |\uparrow\rangle, |\downarrow\rangle, |0\rangle$. For MPSs, the CI coefficients $c_{\sigma}$ are encoded as the product of $L$ matrices $M^{\sigma_l}$, explicitly written as

$$c_{\sigma} = \sum_{a_1,\ldots,a_{L-1}} M^{\sigma_1}_{a_1} M^{\sigma_2}_{a_1a_2} \cdots M^{\sigma_L}_{a_{L-1}},$$

so that the quantum state reads

$$|\psi\rangle = \sum_{\sigma} \sum_{a_1,\ldots,a_{L-1}} M^{\sigma_1}_{a_1} M^{\sigma_2}_{a_1a_2} \cdots M^{\sigma_L}_{a_{L-1}} |\sigma\rangle.$$

Collapsing the explicit summation over the $a_i$ indices in the previous equation as matrix-matrix multiplications, we obtain in compact form

$$|\psi\rangle = \sum_{\sigma} M^{\sigma_1} M^{\sigma_2} \cdots M^{\sigma_L} |\sigma\rangle,$$

where $M^{\sigma_1}, M^{\sigma_l}$ and $M^{\sigma_L}$ ($l < 1 < L$) are required to have matrix dimensions $1 \times m_1$, $m_{l-1} \times m_l$, and $m_{L-1} \times 1$, respectively, as the above product of matrices must yield the scalar coefficient $c_{\sigma}$.

The reason why Eq. (1.6) is not simply a more complicated way of writing the CI expansion in Eq. (1.3) is that the dimension of the matrices $M^{\sigma_l}$ may be limited to some maximum dimension $m_l$, referred to as the number of renormalized block states.
This restriction is the key idea that reduces the exponential growth of the original Full-CI expansion to a polynomially scaling wave-function ansatz. While the evaluation of all CI coefficients $c_\sigma$ is still exponentially expensive, the ansatz in Eq. (1.6) allows one to compute scalar products $\langle \psi | \psi \rangle$ and expectation values $\langle \psi | \hat{O} | \psi \rangle$ of an operator $\hat{O}$ in polynomial time as shown in Sec. 1.4.1. At the example of the norm,

$$\langle \psi | \psi \rangle = \sum_\sigma c_\sigma^* c_\sigma = \sum_\sigma M^{\sigma_L \dagger} \cdots M^{\sigma_1 \dagger} M^{\sigma_1} \cdots M^{\sigma_L}, \quad (1.7)$$

we observe that the operational complexity will only reduce from exponential to polynomial, if we group the summations as

$$\langle \psi | \psi \rangle = \sum_{\sigma_L} M^{\sigma_L \dagger} \cdots \sum_{\sigma_1} (M^{\sigma_1 \dagger} M^{\sigma_1}) \cdots M^{\sigma_L}, \quad (1.8)$$

in addition to limiting the matrix dimensions.

The price to pay, however, is that such an omission of degrees of freedom leads to the introduction of interdependencies among the coefficients. Fortunately, in molecular systems, even MPSs with a drastically limited number of renormalized block states $m$ accurately approximate ground and low-lying excited state energies (see Refs. [16, 24, 25] for examples). Moreover, MPSs are systematically improvable towards the FCI limit by increasing $m$. Extrapolation techniques are available to estimate the distance to this limit for a calculation with finite $m$.

Despite the interesting properties of MPSs, Eq. (1.6) might still not seem useful, as we have not discussed how the $M^{\sigma_i}$ matrices can be constructed for some state in the form of Eq. (1.3). Although the transformation from CI coefficients to the MPS format is possible [5], it is of no practical relevance, because the resulting state would only be numerically manageable for small systems, where FCI would be feasible as well [26]. DMRG calculations may, for instance, be started from a random guess [27] or from one based on criteria from quantum information theory [28–30]. The lack of an efficient conversion to and from a CI expansion is therefore not a disadvantage of the MPS ansatz. We also note that given an MPS state, the most important CI coefficients can be reconstructed even for huge $\{|\sigma\rangle\}$ spaces [31].

MPSs that describe eigenstates of some given Hamiltonian operator inherit the symmetries of the latter and the constituent MPS tensors $M^{\sigma_i}$ therefore feature a block diagonal structure. Refs. [32] and [33] contain examples of how block diagonal tensors induced by abelian symmetries can be exploited in numerical computations and chapter 3 covers the details of non-abelian $SU(2)$ symmetry applied to matrix product tensors.

With the same reasoning as for the MPS case, we can factorize the coefficients $w_{\sigma \sigma'}$ of a general operator

$$\tilde{W} = \sum_{\sigma, \sigma'} w_{\sigma \sigma'} |\sigma\rangle \langle \sigma'| \quad (1.9)$$
1.3. Matrix product formalism

\[ M = U S V^\dagger = U S V^\dagger \]

Figure 1.2.: Possible matrix shapes occurring in the SVD for \( m < n \) (left) and \( m > n \) (right). The diagonality of \( S \) is denoted with a diagonal line.

into a product of matrices such that the operator \( \hat{W} \) reads

\[ \hat{W} = \sum_{\sigma\sigma'} \sum_{b_1,\ldots,b_{L-1}} W_{\sigma b_1}^{\sigma_1 \sigma_i' \ldots} W_{b_{i-1} b_i}^{\sigma_i' \sigma_l'} \cdots W_{b_{L-1} b_L}^{\sigma_L \sigma_l'} |\sigma\rangle \langle \sigma'|. \]  

(1.10)

While in the MPS case, the content of the matrices is determined through variational optimization, here we are interested in constructing the MPO for a given operator \( \hat{W} \), normally a Hamiltonian operator and related observables. How this construction can be achieved efficiently is described in chapter 2.

1.3.2. Singular value decomposition

The singular value decomposition (SVD) of an \( m \times n \) matrix \( M \) with real (or complex) numbers affords a decomposition

\[ M = U S V^\dagger, \]  

(1.11)

with matrices \( U, m \times \min(m,n) \) orthogonal (unitary), \( S, \min(m,n) \times \min(m,n) \) diagonal with real positive numbers and \( V, \min(m,n) \times n \) orthogonal (unitary), corresponding to the matrix shapes shown in Fig. 1.2.

Of the many properties of the SVD, most relevant for MPS is its characteristic of providing the best low-rank approximation \( M' \) with rank \( r < \min(m,n) \) to \( M \) in the sense that \( ||M - M'|| \) becomes minimal for

\[ M' = U S' V^\dagger, \quad \text{with} \quad S'_{ii} = \begin{cases} S_{ii} & i \leq r \\ 0 & i > r \end{cases}. \]  

(1.12)

As previously mentioned, the matrices \( M^\sigma_i \) will generally require truncation to a maximum rank \( m \) corresponding to the number of block states. This task is achieved through Eq. (1.12). Furthermore, the orthogonal properties of \( U \) and \( V^\dagger \) are useful to construct MPS matrices \( M^\sigma_i \) with additional properties described in Sec. 1.3.3.

1.3.3. Left- and right-normalized MPS

The definition in Eq. (1.6) is not unique, i.e. a given state \( |\psi\rangle \) may be equivalently represented with different matrices \( M^\sigma_i \). The non-uniqueness stems from the existence
of a gauge degree of freedom [5] in which two adjacent sets of matrices \( M^{\sigma_i} \) and \( M^{\sigma_{i+1}} \) are transformed as
\[
M^{\sigma_i} \rightarrow M^{\sigma_i} X, \forall \sigma_i \quad M^{\sigma_{i+1}} \rightarrow X^{-1} M^{\sigma_{i+1}}, \forall \sigma_{i+1},
\]
where \( X \) is an invertible matrix.

Two special cases among the possible variants can be constructed by employing a series of successive SVDs: Starting from
\[
c^{\sigma} = \sum_{\sigma_1, \ldots, \sigma_L} M^{\sigma_1} M^{\sigma_2} \ldots M^{\sigma_L}.
\]
we explicitly write all indices of the \( M^{\sigma_1} \) matrices and group the lower indices together, such that we obtain an intermediate matrix \( M_{(\sigma_1, a_1)} \) in which the original set of matrices \( M^{\sigma_1} \) has been stacked on top of each other. An SVD of \( M \) yields
\[
M = ASV^\dagger \quad (U \text{ from Eq. (1.11)) will become a left-normalized MPS tensor, which conventionally is called } A).
\]
Substitution of the decomposed expression into Eq. (1.14) yields
\[
c^{\sigma} = \sum_{\sigma_1, \ldots, \sigma_L} A_{(\sigma_1, a_1), s_1} S_{s_1, s_1} V_{s_1, a_1}^\dagger M^{\sigma_2}_{a_1, a_2} \ldots M^{\sigma_L}_{a_L, a_L}. 
\]
If we reshape \( A_{(\sigma_1, a_1), s_1} \) back into \( A^{\sigma_1} \), due to \( A^\dagger A = I \), we find that
\[
\sum_{\sigma_1} A^{\sigma_1} = I.
\]
Note, that this reshape is equivalent to the pairing arrangement described in Sec. 4.2.1. An MPS tensor which fulfills Eq. (1.16) is called left-normalized.

We may now multiply the remainders of the SVD, \( S_{s_1, s_1} \) and \( V_{s_1, a_1}^\dagger \) into \( M^{\sigma_2}_{a_1, a_2} \) and obtain
\[
c^{\sigma} = \sum_{\sigma_1, \ldots, \sigma_L} A^{\sigma_1}_{1, s_1} \sum_{a_1} (S_{s_1, s_1} V_{s_1, a_1}^\dagger M^{\sigma_2}_{a_1, a_2}) \ldots M^{\sigma_L}_{a_L, a_L}.
\]
By iterative continuation of the steps above, on obtains left-normalized MPS tensors on each site, until the coefficient \( c^{\sigma} \) reads
\[
c^{\sigma} = \sum_{\sigma_1, \ldots, \sigma_L} A^{\sigma_1}_{1, s_1} \ldots A^{\sigma_L}_{s_L, 1}.
\]
If an MPS consists only of left-normalized matrices as in Eq. 1.19, it is called left-canonical. By construction such an MPS is guaranteed to be normalized and furthermore, for any lattice bipartition at site \( l \), the states
\[
|a_l\rangle_L = \sum_{\sigma_1, \ldots, \sigma_l} (A^{\sigma_1} \ldots A^{\sigma_l})_{1, a_1} |\sigma_1, \ldots, \sigma_l\rangle
\]
spanning the left subsystem on sites 1 to \(l\) form an orthonormal basis.

Of course it is also possible to start normalizing an MPS through successive SVDs from the right hand side. In this case, the physical \(\sigma\) index must be grouped with the column index and for the SVD we write \(M = USB\), such that \(BB^\dagger = I\) holds. In a first step one obtains

\[
c_\sigma = \sum_{\sigma_1, \ldots, \sigma_L} M_{a_1, \sigma_1}^{\sigma_1} \cdots M_{a_{L-2}, \sigma_{L-2}}^{\sigma_{L-2}} M_{a_{L-1}, \sigma_{L-1}}^{\sigma_{L-1}} M_{a_{L}, \sigma_L}^{\sigma_L} (1.21)
\]

\[
= \sum_{\sigma_1, \ldots, \sigma_L} M_{a_1, \sigma_1}^{\sigma_1} \cdots M_{a_{L-2}, \sigma_{L-2}}^{\sigma_{L-2}} \sum_{s_{L-1}} \left( U_{a_{L-1}, s_{L-1}} S_{s_{L-1}, s_{L-1}} B_{s_{L-2}, s_{L-1}}^{\sigma_{L-2}, \sigma_{L-1}} \right) (1.22)
\]

\[
= \sum_{\sigma_1, \ldots, \sigma_L} \sum_{a_1} M_{a_1, \sigma_1}^{\sigma_1} \cdots \tilde{M}_{a_{L-2}, s_{L-1}}^{\sigma_{L-2}} B_{s_{L-1}, s_{L-1}}^{\sigma_{L-2}, \sigma_{L-1}} (1.23)
\]

\[
\tilde{M}_{a_{L-2}, s_{L-1}}^{\sigma_{L-2}, \sigma_{L-1}} = \sum_{s_{L-1}} U_{a_{L-1}, s_{L-1}} S_{s_{L-1}, s_{L-1}} B_{s_{L-2}, s_{L-1}}^{\sigma_{L-2}, \sigma_{L-1}} (1.24)
\]

which can be extended by further SVDs to

\[
c_\sigma = \sum_{\sigma_1, \ldots, \sigma_L} \sum_{s_1, \ldots, s_{L-1}} B_{s_1, s_1}^{\sigma_1} \cdots B_{s_{L-2}, s_{L-1}}^{\sigma_{L-2}, \sigma_{L-1}} B_{s_{L-1}, s_{L-1}}^{\sigma_{L-1}, \sigma_L} (1.25)
\]

where all \(B^\sigma\) matrices fulfill the right-normalization constraint. The resulting tensor with coefficients encoded according to Eq. (1.25) is referred to as right-canonical. We find again, that the \(B_{\sigma_{l+1}, \ldots, \sigma_L}^{\sigma_{l+1}, \ldots, \sigma_L}\) matrices encode an orthogonal basis for subsystems on sites \(l + 1, \ldots, L\). It is given by

\[
|a_l\rangle_R = \sum_{\sigma_{l+1}, \ldots, \sigma_L} (B_{\sigma_{l+1}, \ldots, \sigma_L}^{\sigma_{l+1}, \ldots, \sigma_L})_{a_1, \sigma_{l+1}, \ldots, \sigma_L} |\sigma_{l+1}, \ldots, \sigma_L\rangle. (1.26)
\]

1.3.4. Schmidt decomposition

The Schmid decomposition of a pure state \(|\psi\rangle\) into a general bipartition of the total Hilbertspace into subsystems \(L|R\) reads

\[
|\psi\rangle = \sum_a s_a |a\rangle_L |a\rangle_R, (1.27)
\]

where \(|a\rangle_L\) and \(|a\rangle_R\) are orthonormal bases of \(L\) and \(R\), respectively.

Due to the choice of notation, we immediately recognize that the Schmidt decompo-
sition at site \( l \) of an MPS can be realized with a mixed-canonical representation

\[
|\psi\rangle = \sum_{\sigma_1, \ldots, \sigma_L} S_{a_1, a_1} \cdots S_{a_l, a_l} B_{a_{l+1}, a_{l+1}} \cdots B_{a_L, a_L} |\sigma_1, \ldots, \sigma_L\rangle
\]  

(1.28)

in which site tensors 1 to \( l \) and \( l+1 \) to \( L \) have been left- and right-normalized, respectively. A relevant application for DMRG of the Schmidt decomposition is the optimal approximation of

\[
|\psi\rangle \quad \text{with a lower dimensional} \quad |\psi'\rangle = \sum_{a_l=1}^r S_{a_l, a_l} |a_l\rangle_\mathcal{L} |a_l\rangle_\mathcal{R},
\]  

(1.31)

where \( r < \text{dim}(|\psi\rangle) \), such that \(|||\psi\rangle - |\psi'\rangle|| \) is minimized for given \( r \).

### 1.3.5. Reduced density operators and entanglement

Considering again some general pure state \( |\psi\rangle \) defined on a Hilbert space partitioned into \( \mathcal{L} \) and \( \mathcal{R} \), the corresponding reduced density operators are defined as

\[
\hat{\rho}_\mathcal{L} = \text{Tr}_\mathcal{R} |\psi\rangle \langle \psi|, \quad \hat{\rho}_\mathcal{R} = \text{Tr}_\mathcal{L} |\psi\rangle \langle \psi|.
\]  

(1.32)

By employing the Schmidt decomposition from Eq. (1.27) for \( |\psi\rangle \), we can immediately evaluate the partial traces and obtain

\[
\hat{\rho}_\mathcal{L} = \sum_a s_a^2 |a\rangle_\mathcal{L} \langle a|, \quad \hat{\rho}_\mathcal{R} = \sum_a s_a^2 |a\rangle_\mathcal{R} \langle a|,
\]  

(1.33)

revealing that \( \hat{\rho}_\mathcal{L} \) and \( \hat{\rho}_\mathcal{R} \) possess the same eigenvalue spectrum consisting of the squares of the singular values \( s_a \). Consequently, the Schmidt decomposition of an MPS for a certain bipartition \( \mathcal{L}|\mathcal{R} \) allows us to calculate the van Neumann entropy of entanglement defined as

\[
S_{\mathcal{L}|\mathcal{R}} = -\text{Tr} \hat{\rho}_\mathcal{L} \log_2 \hat{\rho}_\mathcal{L} = -\sum_a s_a^2 \log_2 s_a^2.
\]  

(1.34)
1.4. The DMRG ground-state algorithm

Now that we have described the representation of many-electron states in the MPS format and established the MPO structure of arbitrary operators (for the actual MPO content see chapter 2), we would like to calculate ground states of given Hamiltonians and subsequently compute expectation values of physical observables on these states.

1.4.1. Expectation Values

Based on the definitions in Eqs. (1.6) and (2.5), we can immediately write down an expression for the transition operator matrix elements by introducing a second state

\[ |\phi\rangle = \sum_{\sigma, a_1, \ldots, a_{L-1}} N_{a_1 a_2}^{\sigma_1} \cdots N_{a_{L-1} a_1}^{\sigma_L} |\sigma\rangle, \]

(1.35)

or for expectation values:

\[ \langle \phi | W | \psi \rangle = \sum_{\sigma, \sigma'} \left( (N_{a_{L-1} a_1}^{\sigma} \cdots N_{a_{L-1} a_1}^{\sigma_L})^* \sum_{b_1 \ldots b_{L-1}} W_{b_1 a_1}^{\sigma_1} \cdots W_{b_{L-1} a_1}^{\sigma_L} \right) \cdot (M_{a_1 a_1'}^{\sigma_L'} \cdots M_{a_{L-1} a_{L-1}'}^{\sigma_L'}), \]

(1.36)

assuming \( \langle \sigma | \sigma' \rangle = \delta_{\sigma \sigma'} \). This expression is exponentially expensive to evaluate, but suitable regrouping reduces the operation count to \( O(L^4 m^3) \):

\[ \langle \phi | W | \psi \rangle = \sum_{\sigma, \sigma'} \left( \sum_{a_{L-1} a_1} (N_{a_{L-1} a_1}^{\sigma_L} W_{b_{L-1} a_1}^{\sigma_L}) \cdots \sum_{a_{L-1} a_1} (N_{a_{L-1} a_1}^{\sigma_2} W_{b_1 a_1}^{\sigma_2}) \right) \cdot \left( \sum_{a_{L-1} a_1} (M_{a_1 a_1'}^{\sigma_L}) M_{a_1 a_1'}^{\sigma_L'} \cdots M_{a_{L-1} a_{L-1}'}^{\sigma_L'} \right). \]

(1.37)

The iterative character of the previous expression is already apparent from the fact that, proceeding from the innermost bracket outwards, at each step the tensor objects of the respective site are added to the contracted expression in the center. By introducing the initial value \( L_{a_0 a_0}^{b_0} = 1 \), \( a_0, a_0', b_0 = 1 \) we may therefore translate Eq. (1.37) into an iterative equation:

\[ L_{a_1 a_1'}^{b_1} = \sum_{a_{L-1} a_1, b_1} N_{a_{L-1} a_1}^{\sigma_L} W_{b_1 a_1}^{\sigma_L} L_{a_{L-1} a_{L-1}'}^{b_1} M_{a_{L-1} a_{L-1}'}^{\sigma_L'}. \]

(1.38)

Since \( N_{a_{L-1} a_1}^{\sigma_L} \) and \( M_{a_{L-1} a_{L-1}'}^{\sigma_L'} \) each only have one column and one row (and \( W_{b_1 a_1}^{\sigma_L} \) being a scalar), the dimensions of matrix multiplications match at all steps. We refer to the objects \( L_{a_1 a_1'}^{b_1} \).
generated in this fashion as left boundaries, whose structure may be understood as a matrix-valued vector indexed by $b_l$. From Eqs. (1.38) and (1.5) we can further infer that its elements are square matrices with indices $(a_l, a'_l)$. The last boundary $L^b_{a_l a'_l}$ is a scalar as well as the first one, and, according to Eq. (1.37), equal to the desired expectation value $\langle \phi | \hat{W} | \psi \rangle$.

In Fig. 1.3, we illustrate the detailed operations contained in Eq. (1.38). The schematic representation in the upper part depicts MPS tensors $M^\sigma_{a_l a'_l}$ as circles and MPO tensors $W^\sigma \sigma'_l$ as squares. Note that the $b$ indices are independent from the MPS tensor indices $a$. A change in the number of renormalized states modifies the size of $a$ but leaves $b$ unaffected. This can also be understood graphically in Fig. 1.3: The column on the left in this figure contains blocks. The number of these blocks yields the size of the $b$ index, while each block now has a dimension determined by the $a$ index.

In Fig. 1.3, both diagrams feature a leg for each tensor index sticking out and legs are connected to indicate a contraction over the two corresponding indices. In detail, the boundary propagation starts with the contraction of $L^b_{a_l a'_l} M^\sigma_{a_l a'_l}$ by matrix-matrix multiplication (Fig. 1.3, step 1), after which the resulting products are multiplied by the MPO coefficient and have their quantum number mapped from $\sigma'_l$ to $\sigma_l$ in step 2. As the final product with $N^\sigma_{a_l a'_l}$ does not involve $b_{l-1}$, the summation over $b_{l-1}$ into the temporary objects

$$T^b_{a_l a'_l} = \sum_{\sigma_l, a'_l} W^\sigma_{a_{l-1} a'_l} L^b_{a_{l-1} a'_l} M^\sigma_{a_{l-1} a'_l}$$

is most efficiently performed at this stage (step 3) and finally followed by multiplication with the bra MPS tensor $N^\sigma_{a_l a_{l-1}}$ (step 4), yielding $L^b_{a_l a'_l}$.

At this point, we note that we could have started to contract the tensors from the right-hand side as well, which leads us to define right boundaries as

$$R^b_{a_{l-1} a'_l} = \sum_{\sigma_l, a'_l} M^\sigma_{a'_l a'_l} W^\sigma_{a_{l-1} a'_l} R^b_{a_{l-1} a'_l} N^\sigma_{a_l a_{l-1}}.$$  

(1.40)

From Eq. (1.37) we deduce that they can be assembled to yield the desired expectation value with a matching left boundary as

$$\langle \phi | \hat{W} | \psi \rangle = \sum_{a_l a'_l} L^b_{a_l a'_l} R^b_{a_l a'_l}.$$  

(1.41)

While these variants may seem redundant at this point, they will later allow us to maximize the reuse of contracted objects during the sweeping procedure of the ground-state search.
1.4. The DMRG ground-state algorithm

Figure 1.3.: Operations involved in enlarging the contracted left network $L_{b_{l-1}a_{l-1}a_{l-1}}$ by one site to $L_{b_{l}a_{l}a_{l}}$. Step 1: Contraction of $L_{b_{l-1}a_{l-1}a_{l-1}}$ with the MPS tensor $M^{\sigma}_{a_{l-1}a_{l-1}}$ (depicted as a set of four matrices, one for each value of $\sigma_l$) by matrix-matrix multiplication. Step 2: Summation over the local operator input $\sigma'_l$ of $W^l_{b_{l-1}b_{l}}$. Step 3: Summation over $b_{l-1}$. Step 4: Multiplication of $N^{\sigma_l}_{a_{l}a_{l}}$ with the temporary $T^{b_{l}}_{a_{l-1}a_{l}}$ and summation over $\sigma_l$ yields $L_{b_{l}a_{l}a_{l}}$. 

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1.4.2. Ground-state search

While in traditional DMRG, ground states are determined by repeatedly diagonalizing a superblock Hamiltonian formed at shifting lattice bipartitions, in second-generation DMRG discussed here, the energy is minimized through a variational search with the MPS tensor entries as parameters. According to standard MPS-DMRG theory \cite{5, 11}, both approaches eventually result in the diagonalization of the same local Hamiltonian matrices, which is tackled by large sparse eigensolver techniques, such as Jacobi-Davidson. To clarify how both formulations are related, we first reconstruct the left and right block basis states as well as the superblock Hamiltonian from traditional DMRG in an MPS-MPO framework. Subsequently, we derive the same eigenvalue equation for the local site optimization from a variational point of view.

For a bipartition into $L$ and $R$ at site $l$, the left and right block basis states are given by

$$|a_{l-1}\rangle_L = \sum_{\sigma_1, \ldots, \sigma_{l-1}} (M^{\sigma_1} \cdots M^{\sigma_{l-1}})_{1,a_{l-1}} |\sigma_1, \ldots, \sigma_{l-1}\rangle \quad (1.42)$$

$$|a_l\rangle_R = \sum_{\sigma_{l+1}, \ldots, \sigma_L} (M^{\sigma_{l+1}} \cdots M^{\sigma_L})_{a_l,1}|\sigma_{l+1}, \ldots, \sigma_L\rangle \quad (1.43)$$

such that we can write the total state as

$$|\psi\rangle = \sum_{a_{l-1}, a_l} M^a_{a_{l-1}, a_l} |a_{l-1}\rangle_L |\sigma_l\rangle |a_l\rangle_R \quad (1.44)$$

The matrix elements of the superblock Hamiltonian $\langle a_{l-1} \sigma_l a_l | \hat{H} | a'_{l-1} \sigma'_{l} a'_{l} \rangle$ can then be calculated by substituting $|a_{l-1}\rangle_L, |a_l\rangle_R$ and $\hat{H}$ with the corresponding MPO expressions, which leads to the eigenvalue problem

$$\varepsilon M^a_{a_{l-1}, a_l} = \sum_{a'_{l-1}, \sigma'_{l} a_{l}} \langle a_{l-1} \sigma_l a_l | \hat{H} | a'_{l-1} \sigma'_{l} a'_{l} \rangle M^a_{a_{l-1}, a_l} \quad (1.45)$$

Alternatively, we can minimize the energy $\langle \psi | \hat{H} | \psi \rangle$ with respect to the entries of one MPS tensor $M^a_{\sigma_l}$ under the constraint that $\langle \psi | \psi \rangle = 1$ and arrive at the same eigenvalue equation \cite{5, 11}. Starting from Eq. (1.41), we first expose the coefficients $M^a_{a_{l-1}, a_l}$ in

$$\langle \psi | \hat{H} | \psi \rangle = \sum_{a_l a_l' b_l} M^a_{a_l a_l'} L_{b_l a_l a_l'} R^b_{a_l a_l'} \quad (1.46)$$

$$= \sum_{\sigma_{l-1}, \sigma_l, a_l a_l'} W_{a_{l-1} b_l}^{\sigma_{l-1}} L_{b_l a_{l-1} a_l} M^a_{a_{l-1}, a_l} R^b_{a_l a_l'} \quad (1.47)$$
1.4. The DMRG ground-state algorithm

Figure 1.4.: Schematic representation of the matrix-vector operation computing the Hamiltonian-wavefunction product $\mathcal{H}\psi$.

such that we can minimize the energy with respect to $M_{a_{l-1}a_l}$ by introducing a Lagrangian multiplier $\lambda$: $\delta[\langle \psi | \hat{H} | \psi \rangle - \lambda (\langle \psi | \psi \rangle - 1)] = 0$. Under the assumption that $L^b_l$ and $R^b_l$ were formed from left- and right-normalized MPS tensors respectively, the derivative of $\langle \psi | \psi \rangle$ with respect to $M_{a_{l-1}a_l}$ is simply $M_{a_{l-1}a_l}$ and we arrive at the standard eigenvalue problem

$$
\sum_{a_{l-1}^{'},a_l^{'}} W^{\sigma_l \sigma_l^{'}}_{b_{l-1} b_l} L_{a_{l-1}^{'},a_l^{'}} M^{\sigma_l^{'}}_{a_{l-1}^{'},a_l^{'}} R^{b_l}_{a_{l-1},a_l} = \lambda M_{a_{l-1}a_l}. \tag{1.48}
$$

The computationally relevant operation is the matrix-vector multiplication on the left-hand side of the equation above as it is the key operation in sparse matrix eigensolvers (see the pictorial representation in Fig 1.4). Investigating this operation in detail, we find that it is very similar to the boundary iteration in Eq. (1.38): steps 1–3 from Fig. 1.3 are identical, but instead of multiplying the intermediary quantities $T^{b_l}_{a_{l-1}a_l}$ by the MPS conjugate tensor, a scalar product with $R^{b_l}_{a_{l-1},a_l}$ is formed. With the implementation of Eqs. (1.38), (1.40), and (1.48) we have thus all operations at hand to calculate ground states of Hamiltonian MPOs. Moreover, in case of the quantum chemical Hamiltonian of Eq. (2.8), the compression technique described in chapter 2 ensures the optimal execution time scaling of $O(m^3L^3) + O(m^2L^4)$. The complete algorithm now sweeps through the lattice sequentially as indicated in Fig. 1.5, optimizing each of the tensors until convergence is reached.

In addition to the eigenvalue problem in Eq. (1.48) for a single site, the procedure described in Ref. [34] improves convergence by introducing a tiny ad-hoc noise term which helps to avoid local minima by reshuffling the renormalized states.
1.4.3. Single-site and two-site DMRG

In the previous section, we described the optimization of a single site, which in practice has a high probability to become trapped in a local energy minimum. Although the convergence behaviour may be improved by introducing a tiny ad-hoc noise term [34], for chemical applications, the so-called two-site DMRG algorithm, in which two sites are optimized at the same time, achieves faster convergence and is much less likely to get stuck in local minima. In the MPS-MPO formalism, we can optimize two sites at once by introducing the two-site MPS tensor

$$P_{\sigma_l \sigma_{l+1}} = \sum_{a_l} M_{\sigma_l a_l} M_{\sigma_{l+1} a_l}$$

and the two-site MPO tensor

$$\hat{V}_{\sigma_l \sigma_{l+1}} = \sum_{b_l} \hat{W}_{\sigma_l b_l} \hat{W}_{\sigma_{l+1} b_l}.$$ 

The latter case corresponds to a matrix-matrix multiplication of the operator valued $\hat{W}$-matrices, whose entries are multiplied by forming the tensor product of the local site operators. If $\sigma_l \sigma_{l+1} = \sigma_l \otimes \sigma_{l+1}$ is treated as a single 16-dimensional local space $\tau_{l,l+1}$, we can extend Eq. (1.48) from the previous section to two-site DMRG by exchanging $M$ with $P$ and $W$ with $V$ and obtain

$$\sum_{\tau_{l,l+1}, \sigma_l, \sigma_{l+1}} V_{\tau_{l,l+1}} \hat{W}_{\sigma_l \sigma_{l+1}} P_{\sigma_l \sigma_{l+1}} = \lambda P_{\sigma_l \sigma_{l+1}}.$$ 

The different steps in evaluating the expression above are essentially the same as for the single-site case so that the same program routines can be used for both optimization schemes after the generation of the two-site tensors.
1.4.4. Two-site truncation

Upon the construction of the two-site tensor $P_{\sigma_l \sigma_{l+1} a_{l-1} a_{l+1}}$ through matrix-matrix multiplication of $M_{\sigma_l a_{l-1}}$ and $M_{\sigma_{l+1} a_{l+1}}$, the number of degrees of freedom increases from $4m^2$ per single-site tensor to $16m^2$ for the two-site tensor due to the unrestricted combination of the local $\sigma_l$ and $\sigma_{l+1}$ degrees of freedom. After $P_{\sigma_l \sigma_{l+1} a_{l-1} a_{l+1}}$ has been variationally optimized, we thus have to find a way to transform the two-site tensor back to $M_{\sigma_l a_{l-1}}$ and $M_{\sigma_{l+1} a_{l+1}}$ with minimal loss of accuracy. As discussed in Sec. 1.3.2, this can be achieved by performing a singular value decomposition of $P_{\sigma_l \sigma_{l+1} a_{l-1} a_{l+1}}$,

$$P_{\sigma_l \sigma_{l+1} a_{l-1} a_{l+1}} = P_{(\sigma_l a_{l-1}) (a_{l+1} \sigma_{l+1})} = U_{(\sigma_l a_{l-1})} S_{(a_{l+1} \sigma_{l+1})} V_{(a_{l+1} \sigma_{l+1})}, \quad (1.52)$$

and subsequently discarding the smallest $3m$ singular values in $S_{(a_{l+1} \sigma_{l+1})}$, obtaining $S_{a_{l} a_{l+1}}$. Correspondingly, we discard the last $3m$ columns of $U$ and the last $3m$ rows of $V$, such that we may set

$$M_{\sigma_l a_{l-1}} = U_{(\sigma_l a_{l-1})}, \quad (1.53)$$

$$M_{\sigma_{l+1} a_{l+1}} = \frac{1}{1 - \sum_{s_l=m+1}^{4m} S_{s_l}, s_l} S_{a_{l} a_{l+1}} V_{a_{l+1} \sigma_{l+1}}. \quad (1.54)$$

In the process of truncation, we have to retain normalization by rescaling $M_{\sigma_{l+1} a_{l+1}}$ with the retained weight $1 - \sum_{s_l=m+1}^{4m} S_{s_l}, s_l$. The magnitude of the discarded weight, $\sum_{s_l=m+1}^{4m} S_{s_l}, s_l$, is an indication of the wavefunction quality. For very large matrix sizes $m$, it tends to zero, and is therefore a valuable tool to assess wavefunction convergence with respect to $m$. Moreover, the calculated energy of a ground or excited state as a function of the discarded weight, usually called truncation error

$$\varepsilon = \sum_{s_l=m+1}^{4m} S_{s_l}, s_l = ||\psi_{16m^2} - \psi_{4m^2}|| \quad (1.55)$$

can be employed to obtain an energy error estimate through extrapolation as described in Sec. 5.1.7.

1.4.5. Excited states

The MPS-based state-specific algorithm to calculate excited states [35] repeatedly orthogonalizes the excited state against a supplied list of orthogonal states at every microiteration during the Jacobi-Davidson diagonalization step. Let $|\phi_n\rangle$ denote the $n$-th supplied orthogonal state and $|\psi\rangle$ the target wave function. We can then define the partial overlaps

$$C_n = \sum_{\sigma_l} M_{\sigma_l} \cdots \left( \sum_{\sigma_l} M_{\sigma_l} N_{n}^{\sigma_l} \right) \cdots N_{n}^{\sigma_l} \quad (1.56)$$
and
\[ D_n^{l-1} = \sum_{\sigma_l} N_{n_l}^{\sigma_l} \cdots \left( \sum_{\sigma_L} N_{n_L}^{\sigma_L} M_{n_L}^{\sigma_L \dagger} \right) \cdots M_{n_1}^{\sigma_1 \dagger}, \tag{1.57} \]

where \(|\phi_n\rangle\) and \(|\psi\rangle\) are defined according to Eqs. (1.6) and (1.35), yielding \(\langle \psi | \phi_n \rangle = \text{tr}(C_n^l D_n^l)\) for the overlap.

At every site \(l\), the orthogonal vectors \(V_n\), which the Jacobi-Davidson eigensolver takes as input parameters, can now be calculated as
\[ V_n = \sum_{\sigma_l} C_n^{l-1} N_{n_l}^{\sigma_l} D_n^l. \tag{1.58} \]

We note that \(V_n\) has the property \(\text{tr}(M_{\sigma_l}^{\sigma_l \dagger} V_n) = \langle \psi | \phi_n \rangle\). After diagonalization, \(C_n^l\) and \(D_n^{l-1}\) are updated with the optimized \(M_{\sigma_l}^{\sigma_l}\) tensor during a left and right sweep, respectively. Finally, the converged \(|\psi\rangle\) will be orthogonal to all \(|\phi_n\rangle\).
Efficient matrix product operator representation

The original DMRG algorithm formulated by White is a variant of other renormalization group methods, relying on Hilbert space decimation and reduced basis transformations. Instead of truncating the eigenstates of the Hamiltonian according to their energy, the selection of eigenstates based on their weight in reduced density matrices dramatically improved the performance for one-dimensional systems studied in condensed matter physics.

An important contribution towards the present understanding of the algorithm was made by Östlund and Rommer [11], who showed that the block states in DMRG can be represented as MPSs. They permitted predictions [21–23] for the decay of the spectra of reduced density matrices via area laws [17, 36] for the entanglement entropy. Verstraete et al. [20] derived the DMRG algorithm from a variational principle.

At first, MPS were mainly a formal tool to study the properties of DMRG; an application for numerical purposes was only considered for special cases, such as calculations under periodic boundary conditions [20]. The usefulness of the matrix-product formalism for general applications was demonstrated by McCulloch [35] and by Crosswhite et al. [37] who employed the concept of MPOs to represent Hamiltonian operators. MPOs were previously introduced in Ref. [38] to calculate finite-temperature density matrices.

The main advantage of MPS is that they encode wave functions as stand-alone objects that can directly be manipulated arithmetically as a whole. In traditional DMRG by contrast, a series of reduced basis transformations entails a sequential dependency dictating when a certain part of the stored information becomes accessible. An MPS-based algorithm may therefore process the information from independently computed wave functions. McCulloch [35] exploited this fact to calculate excited states by orthogonalizing the solution of each local DMRG update against previously calculated lower-lying states. This state-specific procedure converges excited states fast and avoids
the performance penalty incurred by a state-average approach, where all states must be represented in one common and consequently larger basis. We are not aware of any excited-state algorithm based on projecting out lower-lying states in the context of traditional DMRG, but note that Wouters et al. [39] employed such an algorithm in the CheMPS2 DMRG program, which represents the wave function as an MPS, but invokes a traditional operator format. We may refer to these traditional DMRG programs in quantum chemistry as first-generation programs and denote a truly MPO-based implementation of the DMRG algorithm a second-generation DMRG algorithm in quantum chemistry.

Such a second-generation formulation allows for more flexibility in finding the optimal state and allows for a wider range of applications. The possibility to store the wave function in the MPS form allows us to perform (complex) measurements at a later time without the need to perform a full sweep through the system for the measurement.

In the MPO formalism, we can perform operator arithmetic, such as additions and multiplications. An example where this is useful is the calculation of the variance \( \Delta E = \langle H^2 \rangle - \langle H \rangle^2 \), requiring the expectation value of the squared Hamiltonian. Since the variance vanishes for an exact eigenstate, it is a valuable measure to assess the quality of DMRG wave functions, albeit of limited relevance for quantum chemistry, because quantum chemical DMRG calculations are limited by the size of the Hamiltonian MPO, whose square is too expensive to evaluate for large systems. But apart from the possibility of operator arithmetic, the adoption of MPOs for quantum chemical DMRG has additional advantages. The MPO structure inherently decouples the operator from core program routines performing operations on MPS and MPOs. The increased flexibility for Hamiltonian operators, on the one hand, permitted us to implement both abelian and non-abelian symmetries with only one set of common contraction routines. We note that the relativistic Dirac-Coulomb Hamiltonian [40] can also be solved by the same set of program routines. An example is shown in Sec. 3.7 and we will further describe relativistic DMRG in a future work [41]. Measuring observables, on the other hand, requires no additional effort; only the locations of the elementary creation and annihilation operators need to be specified for a machinery capable of calculating expectation values of arbitrary MPSs and MPOs. The 26 different correlation functions required to calculate single- and two-site entropies [30, 42], for example, can thus be specified as a program input.

The algorithm that we develop in this chapter is implemented based on the ALPS MPS program [33], which is a state-of-the-art MPO-based computer program applied in the condensed matter physics community. To its quantum chemical version presented in this work we refer to as QCMAQUIS.

This chapter is organized as follows. In Sec. 2.1 we first review the basic concepts of MPOs followed by two explicit MPO construction algorithms. The inclusion of fermionic anticommutation is discussed in Sec. 2.2. Finally, we apply our implementation to the
problem of correlated electrons in graphene fragments in Sec. 2.3.

## 2.1. Matrix Product Operators

Formally, the MPS concept can be generalized to MPOs. The coefficients $w_{\sigma,\sigma'}$ of a general operator

$$\hat{W} = \sum_{\sigma,\sigma'} w_{\sigma,\sigma'} |\sigma\rangle \langle \sigma'|,$$  \hspace{1cm} (2.1)

may be encoded in matrix-product form as

$$w_{\sigma,\sigma'} = \sum_{b_1,\ldots,b_{L-1}} W_{b_1}^{\sigma_1\sigma'_1} \cdots W_{b_{L-1}}^{\sigma_{L-1}\sigma'_{L-1}}.$$  \hspace{1cm} (2.2)

Since we are mainly interested in operators corresponding to scalar observables, the two indices $b_0$ and $b_L$ are restricted to 1 such that we may later express the contraction over the $b_i$ indices again as matrix-matrix multiplications yielding a scalar sum of operator terms.

Combining Eqs. (2.1) and (2.2), the operator $\hat{W}$ reads

$$\hat{W} = \sum_{\sigma,\sigma'} \sum_{b_1,\ldots,b_{L-1}} W_{b_1}^{\sigma_1\sigma'_1} \cdots W_{b_{L-1}}^{\sigma_{L-1}\sigma'_{L-1}} |\sigma\rangle \langle \sigma'|.$$  \hspace{1cm} (2.3)

In contrast to the MPS tensors $M^{\sigma_l}$ in Eq. (1.6), the $W_{b_{l-1}b_l}^{\sigma_l\sigma'_l}$ tensors in Eq. (2.3) each have an additional site index as superscript originating from the bra-ket notation in Eq. (2.1). To simplify Eq. (2.3), we perform a contraction over the local site indices $\sigma_l, \sigma'_l$ by defining

$$\hat{W}_{b_{l-1}b_l}^{\sigma_l\sigma'_l} = \sum_{\sigma_l,\sigma'_l} W_{b_{l-1}b_l}^{\sigma_l\sigma'_l} |\sigma_l\rangle \langle \sigma'_l|,$$  \hspace{1cm} (2.4)

so that Eq. (2.3) reads

$$\hat{W} = \sum_{b_1,\ldots,b_{L-1}} \hat{W}_{b_1}^{1} \cdots \hat{W}_{b_{L-1}}^{L}.$$  \hspace{1cm} (2.5)

The motivation for this change in notation is that the entries of the resulting $\hat{W}_{b_{l-1}b_l}^{l}$ matrices are the elementary operators acting on a single site, such as the creation and annihilation operators $\hat{c}^\dagger_{l\sigma}$ and $\hat{c}_{l\sigma}$. To see this, note that we may write, for instance,

$$\hat{c}^\dagger_{l+1} = |\downarrow\rangle \langle \downarrow| + |\uparrow\rangle \langle 0|,$$  \hspace{1cm} (2.6)

which, in practice, can be represented as a $4 \times 4$ matrix with two non-zero entries equal to 1. Hence, $\hat{W}_{b_{l-1}b_l}^{l}$ essentially collects all operators acting on site $l$ in matrix form. If
2.1. Matrix Product Operators

we again recognize the summation over pairwise matching indices \( b_i \) as matrix-matrix multiplications, we may drop them and rewrite Eq. (2.5) as

\[
\hat{W} = \hat{W}^1 \ldots \hat{W}^L.
\]  

(2.7)

In practical applications one needs to find compact representations of operators corresponding to physical observables. For our purposes, the full electronic Hamiltonian,

\[
\hat{H} = \sum_{ij \sigma} t_{ij} \hat{c}_i^{\dagger} \hat{c}_j + \frac{1}{2} \sum_{ijkl \sigma \sigma'} V_{ijkl} \hat{c}_i^{\dagger} \hat{c}_{k \sigma} \hat{c}_{l \sigma'} \hat{c}_j,
\]  

(2.8)

is particularly important. The MPO formulation now allows us to arrange the creation and annihilation operators in Eq. (2.8) into the operator valued matrices \( \hat{W} \) from Eq. (2.7). In the following, we present two ways to find such an arrangement. First, a very simple scheme is discussed to explain the basic concepts at a simple example. Then, to obtain the same operational count as DMRG in its traditional formulation, we describe in a second step how the \( \hat{W} \) matrices can be constructed in an efficient implementation.

2.1.1. Na"ive construction

We start by encoding the simplest term appearing in the electronic Hamiltonian of Eq. (2.8), \( t_{ij} \hat{c}_i^{\dagger} \hat{c}_j \), as an MPO \( \hat{T}(i, j) \). With the identity operator \( \hat{I} \) on sites \( l \neq i, j \), we may write

\[
\hat{T}(i, j) = t_{ij} \hat{I} \otimes \cdots \otimes \hat{c}_i^{\dagger} \hat{I}_{i+1} \otimes \cdots \otimes \hat{c}_j \hat{I}_L.
\]  

(2.9)

For simplicity, we neglected the inclusion of fermionic anticommutation, which will be discussed in section 2.2. To express this operator as an MPO, we need to find operator-valued matrices \( \hat{T}_l \) such that \( \hat{T}(i, j) = \hat{T}_1 \cdots \hat{T}_L \). In this case, there is only one elementary operator per site available. The only possible choice is therefore

\[
\hat{T}_l = \hat{I}, \ l \neq i, j, \quad \hat{T}_{i1} = t_{ij} \hat{c}_i^{\dagger}, \quad \hat{T}_{j1} = \hat{c}_j \hat{I}_L.
\]  

(2.10)

which recovers \( \hat{T}(i, j) \) after multiplication. Note that the coefficient \( t_{ij} \) could have been multiplied into any site and its indices are therefore not inherited to the \( \hat{T}_l \) notation. By substituting the identity operators in Eq. (2.9) with elementary creation or annihilation operators at two additional sites, we can express two-electron terms as an MPO. Whereas this changes the content of the \( \hat{T} \) matrices at those sites sites, their shape is left invariant.

Turning to the MPO representation of the Hamiltonian in Eq. (2.8), we enumerate its terms in arbitrary order such that we may write

\[
\hat{H} = \sum_n \hat{U}_n.
\]  

(2.11)
where \( \hat{U}_n \) is the \( n \)-th term of the Hamiltonian in the format of Eq. (2.9). By introducing the site index \( i \), we can refer to the elementary operator on site \( i \) of term \( n \) as \( \hat{U}_n^i \) and generalize Eq. (2.10) to

\[
\hat{H}_1 = \hat{U}_1^n, \quad \hat{H}_n = \hat{U}_n^i, \quad i \neq 1, L, \quad \hat{H}_L = \hat{U}_L^n.
\]

The formulae above state how a sum of an arbitrary number of terms can be encoded in matrix-product form. Since all matrices are diagonal, except \( \hat{H}_1 \) and \( \hat{H}_L \) which are row and column vectors respectively, the validity of

\[
\hat{H} = \hat{H}_1 \cdots \hat{H}_L
\]

is easy to verify. The resulting operator placement is shown in Fig. 2.1.

As the number of terms in the Hamiltonian operator is equal to the number of non-zero elements of each \( \hat{W}^i \), the cost of applying the MPO on a single site scales as \( O(L^4) \) with respect to the number of sites, and hence the total operation of \( \hat{H}|\psi\rangle \) possesses a complexity of \( O(L^5) \). This simple scheme of constructing the Hamiltonian operator in matrix-product form thus leads to an increase in operational complexity by a factor of \( L \) compared to the traditional formulation of the DMRG algorithm for the quantum chemical Hamiltonian of Eq. (2.8) [43].

### 2.1.2. Compact construction

It is possible to optimize the Hamiltonian MPO construction and reduce the operational count by a factor of \( L \). We elaborate on the ideas presented in Refs. [44] and [33], where identical subsequences among operators of the form in Eq. (2.9) are exploited. If one considers tensor products as graphical connections between two sites, we can abstract the term in Eq. (2.9) to a single string running through all sites. Because of the nature of matrix-matrix multiplications, each element in column \( b \) of \( \hat{W}^i \) will be multiplied by
2.1. Matrix Product Operators

each element in row \( b \) of \( \hat{W}^{i+1} \) in the product \( \hat{W}^i \cdot \hat{W}^{i+1} \). In the naïve representation in Eq. (2.12) of the Hamiltonian in Eq. (2.8), operators were only placed on the diagonal such that each matrix entry on site \( i \) is multiplied by exactly one entry on site \( i + 1 \). In a connectivity diagram, the construction discussed in the previous section therefore results in parallel strings, one per term, with no interconnections between them.

The naïve scheme may be improved in two different ways. First, if two or more strings are identical on sites 1 through \( k \), they can be collapsed into one single substring up to site \( k \), which is then forked into new strings on site \( k + 1 \), splitting the common left part into the unique right remainders. This graphical analogy translates into placing local operators on site \( k + 1 \) on the same row of the MPO matrix \( \hat{W}^{k+1} \). Because each operator on the site of the fork will be multiplied by the shared left part upon matrix-matrix multiplication, the same operator terms are obtained. The second option is to merge strings that match on sites \( l \) through \( L \) into a common right substring, which will be realized if local operators on site \( l - 1 \) of the strings to merge are placed on the same column in \( \hat{W}^{l-1} \). If the Hamiltonian operator in Eq. (2.8) is constructed in this fashion, there will also be strings with identical subsections in the middle of the lattice of sites. If we wanted to collapse, for instance, two of these shared substrings, we would first have to merge strings at the start of the matching subsection and subsequently fork on the right end. In general, however, it is not possible to collapse shared substrings in this manner, because each of the two strings to the left of the merge site will be multiplied by both forked strings to the right. Four terms are thus obtained where there were initially only two. As an example, the MPO manipulation techniques discussed in this paragraph are illustrated in Fig. 2.2. We encode the two terms \( c_1^{\dagger} c_2^{\dagger} c_5 c_7 \) and \( c_1^{\dagger} c_3^{\dagger} c_6 c_7 \) in an MPO according to the naïve construction and subsequently apply fork and merge optimizations.

To compact the \( \hat{W} \) matrices, we collapse strings from both sides of the orbital-chain lattice simultaneously. Starting from the naïve construction of the Hamiltonian operator, each string is divided into substrings between the sites, which we call MPO bonds.

Next, we assign to each MPO bond a symbolic label which will later indicate, where we may perform merges and forks. The decisive information, that such a symbolic label carries, is a list of (operator, position)-pairs which either have already been applied to the left, implying forking behavior, or which will be applied to the right, leading to merging behavior.

More specifically, if we assign an MPO bond between sites \( k \) and \( k + 1 \) with one of the labels

\[
\text{fork: } \hat{c}_i^{\dagger}, i; \hat{c}_j^{\dagger}, j \quad \text{and} \quad \text{merge: } \hat{c}_i^{\dagger}, l; \hat{c}_p^{\dagger}, p ,
\]

we will denote in the first case that, on the current string, operators \( \hat{c}_i^{\dagger} \) and \( \hat{c}_j^{\dagger} \) were applied on sites \( i \) and \( j \) to the left and \( i, j \leq k \). We refer to this type of label as a fork label, because we defined forking as the process of collapsing substrings to the left. For
Figure 2.2.: The terms $c_1^\dagger c_2^\dagger c_5 c_7$ and $c_1^\dagger c_3^\dagger c_6 c_7$ are encoded in one MPO, whose matrices are depicted in the figure for the seven sites. The naïve construction leads to the matrices shown in panel A. A fork optimization was carried out in panel B to exploit the common operator on site 1. The combination of both fork and merge optimizations yields panel C. Finally, the attempt to exploit the common identity operator on site 4 in panel D by introducing an additional fork and merge optimization fails as unwanted cross terms are generated. We note that C will only be possible if both terms have the same matrix elements (1 in this example).
2.1. Matrix Product Operators

Figure 2.3.: The series of operators terms $V_{ijkl} \hat{c}_{i,\sigma}^\dagger \hat{c}_{k,\sigma'}^\dagger \hat{c}_{l,\sigma} \hat{c}_{j,\sigma'}$, $l = k + 1 \ldots j - 1$, $i < k < l < j$, with combined common subsequences. Open squares correspond to operators, filled squares to operators multiplied by the matrix element $V_{ijkl}$.

this reason the label must serve as an identifier for the left part of the current string. In the second case, operators $\hat{c}_{i,\sigma}^\dagger$ and $\hat{c}_{l,\sigma}^\dagger$ will be applied on sites $l$ and $p$, respectively, to the right, $l, p \geq k + 1$, which serves as an identifier for the right substring from site $k + 1$ onwards.

For both types of labels we imply the presence of identity operators on sites not mentioned in the label. Between each pair of sites, all MPO bonds with identical labels may now be collapsed into a single bond to obtain a compact representation of the Hamiltonian operator. Duplicate common substrings between different terms are avoided in this way, because the row and column labels will be identical within shared sections. In a final stage, at each MPO bond, we enumerate the symbolic labels in arbitrary order, which yields the $b_{l-1}$ and $b_l$ matrix indices of $\hat{W}_{b_{l-1}b_l}$.

This leads to the question of when to apply which type of label. The general idea is to start with fork labels from the left and with merge labels from the right. Considering, for instance, a term $V_{ijkl} \hat{c}_{i,\sigma}^\dagger \hat{c}_{k,\sigma'}^\dagger \hat{c}_{l,\sigma} \hat{c}_{j,\sigma'}$, $i < k < l < j$, the four non-trivial operators divide the string running over all sites into the five substrings $1-i$, $i-k$, $k-l$, $l-j$ and $j-L$ with different symbolic labels. Since we start with fork from the left and merge from the right, we need to concern ourselves with the three substrings in the center. Regarding the connectivity types of the labels for these substrings, the combinations fork-fork-merge or fork-merge-merge lead to particularly compact MPO representations. The former combination is shown in Fig. 2.3: all terms in the series $V_{ijkl} \hat{c}_{i,\sigma}^\dagger \hat{c}_{k,\sigma'}^\dagger \hat{c}_{l,\sigma} \hat{c}_{j,\sigma'}$, $l = k + 1 \ldots j - 1, i < k < l < j$ share the operators at sites $i, k$ and $j$ such that the matrix element $V_{ijkl}$ has to be multiplied by the operator at site $l$, coinciding with the position at which the label type changes from fork to merge.

We now focus on one site $s$ only and describe the shape of $\hat{W}_{b_{s-1}b_s}$ for an MPO containing the terms $\sum_{i \neq j \neq k \neq l} V_{ijkl} \hat{c}_{i,\sigma}^\dagger \hat{c}_{k,\sigma'}^\dagger \hat{c}_{l,\sigma} \hat{c}_{j,\sigma'}$. This simplification will retain the dominant structural features of the MPO for the Hamiltonian in Eq. (2.8), because there are still
$O(L^4)$ terms in this set. Assigning to all terms the described labels and subsequent numbering on each MPO bond yields $\hat{W}^s$, $s = 1, \ldots, L$. Fig. 2.4 shows the result with labels sorted such that distinct subblocks can be recognized. From their labels we can infer the following properties:

**A**: One non-trivial operator ($\hat{c}^\dagger$ or $\hat{c}$) was applied to the left.

**B**: Continuation of terms with two non-trivial operators to the left (by means of identity operators).

**C**: The application of the second non-trivial operator (if $k = s$) takes the same input as A but forks into labels with two operators, which will thus be part of the input to block $B$ and $D$ on the next site.

**D**: If $l = s$, the third non-trivial operator is multiplied by $V_{ijkl}$ and placed in block $D$. There exists a term for every possible combination of operator pairs on sites $i, k$ to the left and the operator on site $j$. Thus $D$ is dense.

**E**: Terms with three non-trivial operators on the left are extended by $\hat{F}$ operators to site $s + 1$ to eventually connect to the last non-trivial operator on site $j$.

Both rows and columns contain labels with at most two positions, implying that the matrix size scales as $O(L^2) \times O(L^2)$. The cost of contracting the operator with the MPS on one site is proportional to the number of non-zero elements in the MPO matrix. As block $D$ has $O(L^2)$ rows and $O(L)$ columns, the algorithm will scale as $O(L^4)$, because it performs $L$ iterations with a complexity of $O(L^3)$ in one sweep.

Note that the first and last operator (i.e., $s = i$ and $s = j$) of each term is missing in Fig. 2.4; their inclusion only adds a constant number of rows and columns to $\hat{W}^s$ (one for each of $\hat{c}^\dagger_i, \hat{c}^\dagger_j, \hat{c}_i, \hat{c}_j$). Terms omitted from the previous discussion may easily be accommodated in Fig. 2.4. The middle operator of two-electron terms with one matching pair of indices, for instance, will enter the square above block $D$.

As an additional remark, we note that our construction scheme for the $b$ indices implies that it is not possible to reduce their size to introduce systematic approximations to the complete operator, because terms in the sum of Eq. (2.8) would be arbitrarily omitted. This is in contrast to the MPS tensor indices $a$ which are sorted according to decreasing weight in the singular value decomposition. Truncating the $a$ indices can therefore guarantee an optimal approximation to the original tensor for a given matrix rank.
2.1. Matrix Product Operators

Figure 2.4.: MPO tensor $\hat{W}_{s}^{b_{s-1}b_{s}}$ on some site $s$. $A$, $B$, $C$ and $E$ are diagonal blocks which extend incoming operator terms to the next site, while $D$ is dense and contains creation or annihilation operators multiplied by $V_{ijks}$. The first and last operator of each term, corresponding to $s = i$ and $s = j$, were omitted.
2.2. Fermionic anticommutation

In the operator construction scheme that we described in the previous section we omitted the description of fermionic anticommutation,

\[ \{ \hat{c}_{i\sigma}^\dagger, \hat{c}_{j\sigma'} \} = \delta_{ij} \delta_{\sigma\sigma'}, \]
\[ \{ \hat{c}_{i\sigma}^\dagger, \hat{c}_{j\sigma'}^\dagger \} = \{ \hat{c}_{i\sigma}, \hat{c}_{j\sigma'} \} = 0. \quad (2.14) \]

We can include it by performing a Jordan-Wigner transformation \[45\] on the elementary creation and annihilation operators. Introducing the auxiliary operator

\[ \hat{F} = \begin{pmatrix} |\uparrow, \uparrow\rangle & |\uparrow, \downarrow\rangle & |\downarrow, \uparrow\rangle & |\downarrow, \downarrow\rangle \\ |\uparrow\downarrow\rangle & 1 & 0 & 0 \\ |\uparrow\rangle & 0 & -1 & 0 \\ |\downarrow\rangle & 0 & 0 & 1 \end{pmatrix}, \quad (2.15) \]

we transform each elementary creation or annihilation operator \( \hat{\gamma} \) (\( \hat{\gamma} = \hat{c}_{\sigma}^\dagger, \hat{c}_{\sigma} \)) as

\[ \hat{\gamma}_i \mapsto \left( \prod_{s<i} \hat{F}_s \right) \hat{\gamma}_i = \hat{\gamma}^{\text{JW}}_i, \quad (2.16) \]

such that Eqs. (2.14) are fulfilled by the transformed operators. Since \( \hat{F}_s^2 = \mathbb{I} \) and \( [\hat{F}_s, \hat{\gamma}_i] = 0 \) if \( s \neq j \), we can simplify

\[ \hat{\gamma}^{\text{JW}}_i \hat{\gamma}^{\text{JW}}_j = \mathbb{I}_1 \otimes \ldots \otimes \mathbb{I}_i \hat{F}_i \otimes \hat{F}_{i+1} \otimes \ldots \otimes \hat{F}_{j-1} \otimes \mathbb{I}_j \otimes \ldots \otimes \mathbb{I}_L. \quad (2.17) \]

and find that in terms with an even number of fermionic operators, the sign operators only have to be applied in sections with an odd number of fermions to the left.

The described transformation ensures that fermions on different sites anticommute, but since the two kinds of electrons, \( \uparrow \) and \( \downarrow \), can coexist on the same site, we have to modify Eq. (2.16) in order to obtain the correct behavior: the operator \( \hat{c}_{\downarrow}^\dagger \) has to be multiplied by \( \hat{F} \), yielding \( \hat{c}_{\downarrow}^\dagger \hat{F} \) prior to the transformation in Eq. (2.16) (\( \hat{c}_{\downarrow} \mapsto \hat{F} \hat{c}_{\downarrow} \) by hermitian conjugation). The additional sign operator keeps track of the phase factor originating from the anticommutation of electrons on the same site with opposite spin.

2.3. Example

The efficiency of an MPO-DMRG implementation critically depends on the representation of the MPO. As we have shown, both a compact construction and the exploitation of sparsity are necessary to achieve optimal scaling.
To demonstrate its capabilities, we calculated ground- and excited-state energies of the graphene fragments G2 and G3 shown in Fig. 2.5. The double-bond conjugation in both molecules creates long-range correlations in two dimensions. These molecules are therefore difficult to treat with DMRG, which performs best for one-dimensional and quasi one-dimensional systems. In other systems with less delocalization and mixed active spaces, containing both $\sigma$- and $\pi$-type molecular orbitals and possibly exhibiting spatial point group symmetry, often a significant fraction of the two-electron integrals have negligible magnitude, leading to smaller MPOs such that even larger active spaces become affordable.

We chose the $\pi$-orbitals for the active space, represented by a minimal STO-3G basis set [46]. While this choice of basis precludes obtaining accurate energies, it does not simplify the correlation problem within the active space, which we are interested to solve with DMRG. A set of different condensed polyaromatic systems has recently been calculated by Olivares-Amaya et al. [47], employing the same basis set. In accordance with their work, we found that performing Pipek-Mezey localization [48], first within the active occupied orbitals, followed by a second Pipek-Mezey localization of the active virtual orbitals, provided the molecular orbital basis exhibiting best DMRG convergence. The efficiency gain compared to Hartree-Fock orbitals more than compensated the loss of spatial point group symmetry.

In order to obtain accurate energies, we exploit non-abelian spin symmetry whose implementation with the quantum chemical DMRG Hamiltonian is described in chapter 3. Furthermore, the type of orbitals and the orbital ordering have to be carefully chosen to improve performance. By computing the Fiedler vector [13, 49, 50] based on the mutual information [30, 51], we determined an efficient orbital ordering. In Fig. 2.6, it is shown for the G2 fragment together with the mutual information drawn as lines with
Figure 2.6.: Orbital ordering for the fragment G2. The mutual information between pairs of orbitals is drawn with bold black lines for magnitudes $> 0.1$, dashed gray lines ($0.01 - 0.1$) and dotted green lines ($0.001 - 0.1$).

Figure 2.7.: Energy per carbon atom in G2 and G3, extrapolated towards truncation error $\varepsilon \to 0$. First panel: ground state of G3 with $m = 2000$, 1500 and 1000. Second panel: lowest singlet excited state of G2 with $m = 1000$, 950, 900, 850. Third panel: lowest triplet excited state of G2 with $m = 1000$, 950, 900, 850. Fourth panel: ground state of G2 with $m = 350$, 300, 250, 200 and a reference calculation with $m = 3000$.
2.3. Example

varying thickness according to entanglement strength. We observe that, based on this entanglement measure, the Fiedler ordering reliably grouped strongly entangled bonding and anti-bonding orbitals pairs next to each other and arranged orbitals according to their spatial position such that the hexagonal fragment is traversed through the longest possible pathway across two adjacent corners. The application of the Fiedler ordering to G3 resulted in a similar type of orbital arrangement.

With this configuration, we performed ground- and excited-state calculations with QCMAQUIS. The obtained energies per carbon atom are shown in Fig. 2.7. For the G2 ground-state calculation, the number of renormalized block states $m$ was chosen such that we obtained truncation errors in the same range as for the G3 ground-state calculation. This choice affords wave functions of similar quality in both cases and accordingly similar distances in the extrapolated energy, with the advantage that for the smaller G2 fragment we can verify the extrapolation error by an accurate reference calculation with $m = 3000$. From the extrapolation, we estimate an error per carbon atom of $\pm 0.05 \text{ mH}$ for G2 and $\pm 0.1 \text{ mH}$ for G3, respectively.
Spin-adapted matrix product states and operators

The incorporation of non-abelian symmetries into the DMRG algorithm enhances both accuracy and computational efficiency. In the context of DMRG, total electronic spin symmetry, which is a non-abelian symmetry induced by the special unitary group $SU(2)$, was first exploited in the interaction round a face model by Sierra and Nishino [52] for quantum spin chains. McCulloch and Gulácsi [53–55] later presented a spin symmetric description in a more versatile way based on a quasi density matrix and studied a broad range of models, including the Fermi–Hubbard model. Their approach was subsequently adopted by Zgid and Nooijen [56] and by Sharma and Chan [25] to formulate a spin-adapted DMRG method for the quantum chemical Hamiltonian. Non-abelian symmetries beyond $SU(2)$ were discussed, for instance, in Refs. [57] and [58]. Note, however, that these more general approaches preclude the application of sum rules for Clebsch–Gordan coefficients only available for $SU(2)$. These sum rules involve the Wigner-6$j$ and Wigner-9$j$ symbols and result in increased numerical efficiency.

Since the emergence of matrix product based DMRG [11, 20, 35, 37], $SU(2)$ invariant MPSs and MPOs for the Hamiltonian operators of the above mentioned condensed matter models were also described [35]. These systems feature simple Hamiltonian operators with few terms compared to the quantum chemical Hamiltonian [59]. The spin-adaptation of the latter is a non-trivial task because all terms must first be expressed with local operators transforming according to some irreducible representation of $SU(2)$ and subsequently be incorporated into a matrix product structure, requiring additional coupling coefficients.

Here, we present the spin-adaptation of the efficient matrix product operator based formulation of the DMRG algorithm for quantum chemistry discussed in the previous chapter.

In Sec. 3.1, we briefly introduce the relevant formulae from quantum mechanical an-
The role of symmetries

The matrix product state ansatz for a state $|\psi\rangle$ in a Hilbert space spanned by $L$ spatial orbitals reads

$$|\psi\rangle = \sum_{\sigma} \sum_{a_1, \ldots, a_{L-1}} M_{\sigma a_1}^{a_2} \cdots M_{\sigma a_{L-1}}^{a_1} |\sigma\rangle,$$

(3.1)

with $|\sigma\rangle = |\sigma_1, \ldots, \sigma_L\rangle$, and $\sigma_l = |\uparrow\downarrow\rangle, |\uparrow\rangle, |\downarrow\rangle, |0\rangle$, which can be interpreted as a configuration interaction (CI) expansion where the CI coefficients are encoded as a product of matrices.

If a Hamiltonian operator possesses global symmetries, we can label its eigenstates with quantum numbers that are the irreducible representations of the global symmetry groups. These labels also apply to the MPS tensors $M_{\sigma i a_{i-1} a_i}^{a_i}$ in Eq. (3.1) and induce a block-diagonal structure. For the special case of total spin symmetry, the Wigner–Eckart theorem applies, which allows us to label the irreducible representations according to total spin (rather than to the spin projection quantum number $S_z$) and populate the symmetry blocks with reduced matrix elements.

The effect of spin symmetry adaptation is therefore two-fold. Firstly, MPS tensors $M_{\sigma i a_{i-1} a_i}^{a_i}$ assume a block-diagonal structure labeled by quantum numbers. Secondly, these symmetry blocks consist of reduced matrix elements obtained through the Wigner–Eckart theorem.

3.1.1. Quantum numbers

We are interested in diagonalizing the non-relativistic electronic Coulomb Hamiltonian

$$\hat{H} = \sum_{ij\sigma} t_{ij} \hat{c}_{i\sigma}^{\dagger} \hat{c}_{j\sigma} + \frac{1}{2} \sum_{ijkl\sigma\sigma'} V_{ijkl} \hat{c}_{i\sigma}^{\dagger} \hat{c}_{k\sigma'} \hat{c}_{l\sigma'} \hat{c}_{j\sigma},$$

(3.2)

defined on $L$ orbitals, referred to as sites. Apart from the total spin, it conserves the particle number and point group symmetry. We can therefore label the eigenstates with the quantum numbers $(S, N, I)$, corresponding to total spin $S$, number of electrons $N$, and the irreducible representation $I$ of the point group of a molecule. According to the Clebsch–Gordan expansion, we find that a composite system consisting of the two
representations $D(S_1, N_1, I_1)$ and $D(S_2, N_2, I_2)$ decomposes according to
\[
D(S_1, N_1, I_1) \otimes D(S_2, N_2, I_2) = \bigoplus_{S=|S_1-S_2|} D(S, N_1+N_2, I_1 \otimes I_2),
\]
(3.3)
where $I_1 \otimes I_2$ denotes the application of the point group multiplication table. By employing Eq. (3.3), we will later be able to determine the symmetry dependent block structure of the MPS tensors.

### 3.1.2. Reduced matrix elements

For later reference, we introduce the required formulae for the handling of reduced matrix elements and follow the standard treatment as presented, for example, in the book by Biedenharn and Louck [60].

Due to the fact that MPSs as well as MPOs behave like rank-$k$ tensor operators, the Wigner–Eckart theorem is the fundamental equation to exploit spin symmetry. It states that the matrix element of the $M$-th component $T_M^{[k]}$ of a rank-$k$ tensor operator $T^{[k]}$ is generated from a reduced matrix element multiplied by the Clebsch–Gordan coefficient $C_{m M m'}^{j k j'}$,
\[
\langle j'm'||T^{[k]}||j m\rangle = \langle j'||T^{[k]}||j\rangle C_{m M m'}^{j k j'}.
\]
(3.4)
The double vertical line denotes Condon and Shortley’s notation for a reduced matrix element, which is independent of any projection quantum number. We further distinguish the reduced matrix elements with bold symbols from their conventional counterparts, a convention that we will follow throughout this work. In the equation above, $j$ and $j'$ refer to a spin quantum number (an irreducible $SU(2)$ representation), $m$, $m'$ and $M$ are projection quantum numbers such as the $z$-component of the spin if the $z$-axis is chosen as the axis of quantization. As the multiplet $M = -k, \ldots, k$ is determined by a single reduced matrix element, the Wigner–Eckart theorem entails information compression allowing operators to be stored more efficiently.

For setting up the DMRG algorithm with irreducible tensor operators, it will be necessary to calculate the matrix elements of products of tensor operators. If $S_{\mu_1}^{[k_1]}$ and $T_{\mu_2}^{[k_2]}$ are rank-$k_1$ and rank-$k_2$ tensor operators respectively, their product will be given by
\[
[S_{\mu_1}^{[k_1]} \times T_{\mu_2}^{[k_2]}]_{\mu}^{[k]} = \sum_{\mu_1, \mu_2} C_{m M m'}^{j k j'} S_{\mu_1}^{[k_1]} T_{\mu_2}^{[k_2]}.
\]
(3.5)
To benefit from information compression, we are interested in expressing the reduced matrix element of the above product by reduced matrix elements of the individual factors. By applying the Wigner–Eckart theorem to the product as a whole as well as to
the individual elements of $S^{[k_1]}$ and $T^{[k_2]}$, one obtains (for a detailed derivation see Ref. [60])

$$
\langle j'\| [S^{[k_1]} \times T^{[k_2]}]^{[k]}\| j \rangle = (-1)^{j + j' + k_1 + k_2} \times \sum_{j''} \sqrt{(2j'' + 1)(2k + 1)} \left\{ \begin{array}{ccc}
    j' & k_1 & j'' \\
    k_2 & j & k
\end{array} \right\} \times \langle j'\| S^{[k_1]}\| j'' \rangle \langle j''\| T^{[k_2]}\| j \rangle,
$$

(3.6)

where the quantity in curly brackets is a Wigner-6$j$ symbol.

If $S^{[k_1]}$ and $T^{[k_2]}$ act on different spaces, i.e.

$$
S^{[k_1]} = S^{[k_1]}(1) \otimes I(2),
$$

(3.7)

$$
T^{[k_2]} = I(1) \otimes T^{[k_2]}(2),
$$

(3.8)

the summation over the intermediate states $j''$ in the coupling law of Eq. (3.6) can be eliminated to yield

$$
\langle j'(j'_1j'_2)\| [S^{[k_1]}(1) \otimes T^{[k_2]}(2)]^{[k]}\| j(j_1j_2) \rangle = \begin{bmatrix}
    j_1 & j_2 & j \\
    k_1 & k_2 & k \\
    j'_1 & j'_2 & j'
\end{bmatrix} \langle j'_1\| S^{[k_1]}(1)\| j_1 \rangle \langle j'_2\| T^{[k_2]}(2)\| j_2 \rangle,
$$

(3.9)

where $j(j_1j_2)$ means that $j_1$ and $j_2$ couple according to Eq. (3.3) to yield $j$ and the term in brackets is defined as the product of a Wigner-9$j$ symbol and a normalization factor,

$$
\begin{bmatrix}
    j_1 & j_2 & j \\
    k_1 & k_2 & k \\
    j'_1 & j'_2 & j'
\end{bmatrix} \equiv [(2j'_1 + 1)(2j'_2 + 1)(2j + 1)(2k + 1)]^{1/2}
\times \left\{ \begin{array}{ccc}
    j_1 & j_2 & j \\
    k_1 & k_2 & k \\
    j'_1 & j'_2 & j'
\end{array} \right\}.
$$

(3.10)

In the subsequent sections, examples will be provided of how Eq. (3.6) and Eq. (3.9) are exploited.

### 3.2. Symmetry-adapted MPS

To understand the symmetry properties of the MPS tensors in Eq. (3.1), it is important to note that the states

$$
|a_{l-1}\rangle = \sum_{\sigma_1, \ldots, \sigma_{l-1}} (M_{\sigma_1}^{a_1} \cdots M_{\sigma_{l-2}}^{a_{l-2}})_{1,a_{l-1}} |\sigma_1, \ldots, \sigma_{l-1}\rangle
$$

(3.11)
defined on the sublattice spanned by \( l - 1 \) sites (spatial orbitals) are mapped by \( M_{a_{l-1}a_1}^{\sigma_l} \) to the states
\[
|a_i\rangle = \sum_{\sigma_{l-1}} M_{a_{l-1}a_1}^{\sigma_l}|a_{l-1}\rangle \otimes |\sigma_l\rangle
\] (3.12)
on \( l \) sites. For each value of \( \sigma_l \), the MPS tensor \( M_{a_{l-1}a_1}^{\sigma_l} \) therefore behaves like an operator that maps input states to a system enlarged by one site (spatial orbital), where \( \sigma_l \) labels the local site basis states \( \{|\uparrow\downarrow\rangle, |\uparrow\rangle, |\downarrow\rangle, |0\rangle\} \), characterized by the quantum numbers
\[
|S, S_z, N, I\rangle = \{|0, 0, 2, A_g\rangle, |1, 1, 1, I\rangle, |0, 0, 0, A_g\rangle\}.
\]
The operators \( M^{(\uparrow\downarrow)} \) and \( M^{(0)} \) behave like rank-0 tensor operators, while \( M^{(\uparrow)} \) and \( M^{(\downarrow)} \) are the two \( S_z \) components of a rank-\( \frac{1}{2} \) tensor operator. According to the Wigner–Eckart theorem, we can therefore calculate the elements of both components from one reduced operator labeled by total spin only, such that the spin-adapted local basis reads
\[
|S, N, I\rangle = \{|0, 2, A_g\rangle, |1, 1, 1, I\rangle, |0, 0, 0, A_g\rangle\}.
\]

We now proceed as follows: from the nature of the local basis, we infer the structure of the symmetry blocks for the complete MPS in the following section and apply the Wigner–Eckart theorem to the reduced matrix elements contained in those blocks in Sec. 3.2.2.

### 3.2.1. Symmetry blocks

We observe that if a subsystem consisting of sites 1 to \( l - 1 \) is represented by states with quantum numbers \( q_{l-1} \), the system extended to \( l \) sites will be represented by states with quantum numbers \( q_{l-1} \otimes \sigma_l \), where the tensor product for the corresponding representations is defined in Eq. (3.3) and \( \sigma_l \) labels a local basis state. If we now associate each MPS tensor \( a \)-index from Eq. (3.1) with a quantum number
\[
q_l = (S_l, N_l, I_l),
\] (3.13)
each MPS tensor \( M_{q_{l-1}q_{l-1}}^{a_{l-1}a_l} \) will then be characterized by the symmetry constraint
\[
q_l \in q_{l-1} \otimes \sigma_l,
\] (3.14)
which partitions the MPS tensor into symmetry blocks, indicated by the extended index \( q_{l-1}a_{l-1}; q_la_l \) supplemented with the quantum numbers \( q_{l-1} \) and \( q_l \) and separated by a semicolon for better readability. Since they contain an \( SU(2) \) irreducible representation, the corresponding MPS tensor consists of reduced matrix elements, which we denote by a
3.2. Symmetry-adapted MPS

bold symbol. Note that for an abelian symmetry, e.g., particle number, Eq. (3.14) simply requires that for each block $q_{l-1} q_l$ in $M_{q_{l-1}q_l}^{\sigma_l}$, $N_l = N_{l-1} + N(\sigma_l)$ holds, where $N(\sigma_l)$ equals the number of particles in $\sigma_l$. We deduce that the MPS tensor $M_{q_{l-1}q_l}^{\sigma_l}$ on site $l$ is in fact an operator that maps states from the subsystem spanning sites 1 to $l - 1$ to the subsystem enlarged to site $l$. We therefore refer to $q_{l-1}, q_l$, and $\sigma_l$ as input, output, and operator quantum numbers, respectively.

The sequence of MPS tensors as they appear in Eq. (3.1) builds up the target state site by site from the vacuum state. Consequently, the quantum numbers appearing in the MPS tensors on opposite ends are the vacuum state and the target state. By choice, we start with the vacuum state on the left hand side and finish with the target state on the right hand side of Eq. (3.1). The application of the symmetry constraint in Eq. (3.14) now determines which blocks will appear in the MPS tensors. For $M_{q_0q_1a_1a_2}^{\sigma_1}$, we have one block of size 1 denoted by $q_0 : a_0 = \{(0,0,A_g) : 1\}$ and

\[
q_1 : a_1 = \{(0,2,A_g) : 1, (\frac{1}{2},1,I_1) : 1, (0,0,A_g) : 1\},
\]

(3.15)

meaning that $M_{q_0q_1a_1a_2}^{\sigma_1}$ consists of three $1 \times 1$ blocks. The MPS tensor on site 2 shares $q_1 : a_1$ with $M_{q_0q_2a_1a_2}^{\sigma_1}$ and the output quantum numbers are

\[
q_2 : a_2 = \{(0,4,A_g) : 1, (\frac{1}{2},3,I_1) : 1, (\frac{1}{2},3,I_2) : 1,
\]

\[
(1,2,I_1 \otimes I_2) : 1, (0,2,I_1 \otimes I_2) : 1, (0,2,A_g) : 2,
\]

\[
(\frac{1}{2},1,I_1) : 1, (\frac{1}{2},1,I_2) : 1, (0,0,A_g) : 1\}.
\]

(3.16)

Note that the output quantum number $q_2 = (0, 2, A_g)$ appears twice in the combination of the input quantum numbers with the local site basis, namely $q_1 \otimes \sigma_2 = (0, 0, A_g) \otimes (0, 2, A_g)$ and $(0, 2, A_g) \otimes (0, 0, A_g)$. The two blocks $q_1 \times q_2 = (0, 0, A_g) \times (0, 2, A_g)$ and $(0, 2, A_g) \times (0, 2, A_g)$ therefore have a $1 \times 2$ shape, reflecting the fact that there are two different $(0, 2, A_g)$ states defined on sites 1 and 2. The continuation of this scheme towards the right leads to exponentially growing block sizes, which must be limited (with the requirement that the output block sizes on site $l$ match with the input blocks sizes on site $l + 1$).

We further note that in this way blocks are obtained which do not appear in the set of possible blocks of the reverse process that starts from the right hand side of the MPS by deducing the local basis states from the target quantum number. The correct block structure is therefore obtained from the common subset of the build-up procedure from the left and the decomposition from the right.

3.2.2. Reduced matrix elements

In the previous section, we established that the MPS tensor $M_{q_{l-1}q_l}^{\sigma_l}$ behaves like a set of two rank-0 and one rank-$\frac{1}{2}$ irreducible tensor operator. The application of the
Wigner–Eckart theorem to the reduced matrix elements yields

\[
M_{N_{l-1}S_{z,l-1}(k_{l-1}+a_{l-1});N_lS_{z,l}(k_l+a_l)}^{\sigma_l} = M_{q_{l-1}a_{l-1};qa_l}^{\sigma_l} C_{S_{z,l-1}mS_{z,l}}^{S_{l-1}S_{\sigma_l}S_l},
\]

(3.17)

where the blocks of the abelian MPS tensor on the left hand side of Eq. (3.17) are labeled by pairs of the particle number \( N \) and the spin projection \( S_z \). The latter may assume the values

\[
S_{z,l-1} = -S_{l-1}, \ldots, S_{l-1},
\]

\[
S_{z,l} = -S_{l}, \ldots, S_{l},
\]

\[
m = S_{z,l} - S_{z,l-1}.
\]

If \( S_{\sigma_l} \), the spin of the local basis state \( \sigma_l \), is zero, the corresponding Clebsch–Gordan coefficient will be equal to 1. Note that the \( a \) indices are identical on both sides of Eq. (3.17), meaning that the reduced blocks are transferred as a whole and multiplied by a single Clebsch–Gordan coefficient. In general, there is more than one reduced block on the right hand side of Eq. (3.17) that transforms into a given block \( (N_{l-1}S_{z,l-1}, N_lS_{z,l}) \) on the left hand side, such that one has to introduce pairs of row and column offsets \( (k_{l-1}, k_l) \) to arrange the reduced blocks in a block-diagonal fashion within the larger \( S_z \) blocks.

Eq. (3.17) would apply if a spin-adapted MPS with reduced matrix elements had to be transformed to the full matrix elements with abelian particle number and \( S_z \) symmetry (see Fig. 3.1), but not to ground state calculations, where the reduced MPS matrix elements are directly determined by variational optimization.
3.3. Symmetry-adapted MPO

We denote the generalization of the MPS concept to MPOs as [5, 61]

\[ \hat{W} = \sum_{\sigma \sigma'} W_{b_1 b_1}^{\sigma \sigma'} \cdots W_{b_{L-1} b_{L-1}}^{\sigma \sigma'} |\sigma \rangle \langle \sigma'|. \]  

(3.18)

A contraction over the local site indices \( \sigma_l, \sigma'_l \) in \( \sigma, \sigma' \) leads us to define the quantities

\[ \hat{W}_{b_l - 1 b_l} = \sum_{\sigma_l, \sigma'_l} W_{b_l b_l}^{\sigma \sigma'} |\sigma_l \rangle \langle \sigma'_l|, \]  

(3.19)

which are operator-valued matrices; the entries of the \( \hat{W}_{b_l b_l} \) matrices are the elementary operators acting on a single site such as the creation and annihilation operators \( \hat{c}_l^\dagger \) and \( \hat{c}_l \).

3.3.1. Elementary site operators

Elementary site operators are represented by \( 4 \times 4 \) matrices with respect to a basis of \( \{|\uparrow\downarrow\rangle, |\uparrow\rangle, |\downarrow\rangle, |0\rangle\} \), e.g.,

\[ \hat{c}_l^\dagger = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}, \quad \hat{c}_l = \begin{pmatrix} 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \end{pmatrix}, \]

and

\[ \hat{F} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}, \]

where \( \hat{F} \) represents the fermionic auxiliary operator to describe fermionic anticommutation (see Ref. [61]). Note that the definition of \( \hat{c}_l^\dagger \) contains a minus sign so that \( \hat{c}_l^\dagger |\uparrow\rangle = -|\uparrow\downarrow\rangle \), corresponding to our choice of ordering the \( \uparrow \)-electron before the \( \downarrow \)-electron on a single site.

To those site operators that transform according to an irreducible \( SU(2) \) representation, we may again apply the Wigner–Eckart theorem in Eq. (3.4). The pairs \( \hat{c}_l^\dagger, \hat{c}_l^\dagger \) and \( \hat{c}_l, \hat{c}_l \), for instance, each form the two components of a rank-\( \frac{1}{2} \) tensor operator with reduced matrix elements

\[ \hat{c}^\dagger = \begin{pmatrix} 0 & -\sqrt{2} & 0 \\ 0 & 0 & 1 \\ 0 & 0 & 0 \end{pmatrix}, \quad \hat{c} = \begin{pmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \\ 0 & \sqrt{2} & 0 \end{pmatrix}, \]  

(3.20)

with respect to the basis \( \{|0, 2, A_g\rangle, |1, \frac{1}{2}, I\rangle, |0, 0, A_g\rangle\} \). The application of Eq. (3.4) to \( \hat{c}^\dagger \) and \( \hat{c} \) yields \( \{\hat{c}_l^\dagger, \hat{c}_l^\dagger\} \) and \( \{\hat{c}_l, -\hat{c}_l\} \), respectively.
3.3.2. Operator terms

We now turn to the description of the operator terms appearing in the Hamiltonian in Eq. (3.2). In analogy to the MPS case where an index with associated quantum number \( q_{l-1}, a_{l-1} \) is mapped to \( q_{l}, a_{l} \) by calculating the tensor product with the local site occupation \( \sigma_{l} \), the MPO \( b \) indices of Eq. (3.19) may be labeled with quantum numbers as well, where the transition from \( b_{l-1} \) to \( b_{l} \) is mediated through the action of the local site operator located at \( \hat{W}_{b_{l-1}b_{l}} \). Introducing the quantum numbers \( p_{l-1} \) and \( p_{l} \), defined according to Eq. (3.13), we extend the notation to \( \hat{W}_{p_{l-1}b_{l-1};p_{l}b_{l}} \), which associates a (non-abelian) quantum number with each \( b \) index and \( k \) corresponds to the rank of the elementary site operator at the location \( p_{l-1}b_{l-1};p_{l}b_{l} \). The term

\[
t_{ij}c_{i\sigma}^{\dagger}c_{j\sigma} = t_{ij}\hat{I}_{1} \otimes \cdots \otimes \hat{c}_{i\sigma}^{\dagger}\hat{F} \otimes \hat{F}_{i+1} \cdots \otimes \hat{c}_{j\sigma} \otimes \hat{I}_{j+1} \cdots
\]

emerges from the repeated action of the \( \hat{W}_{k}^{[k]} \) tensors on each site, where the total operator quantum number is encoded in the final \( p_{L} \) index. We deduce that the \( \hat{W}_{p_{l-1}b_{l-1};p_{l}b_{l}} \) tensors behave like rank-\( k \) tensor operators, where \( k \) equals the rank of the elementary site operator at position \( b_{l-1}, b_{l} \). The Wigner–Eckart theorem applies twice, first (in analogy to the MPS case) to the elements of \( \hat{W}^{\sigma_{l}\sigma_{l}'}_{[k]} \). Since the elements in this case are irreducible tensor operators themselves, the Wigner–Eckart theorem applies a second time and yields another Clebsch–Gordan coefficient that transforms the reduced elementary site operator to full matrix elements. In summary one obtains

\[
\hat{W}^{\sigma_{l}\sigma_{l}'}_{N_{l-1}S_{z,l-1}I_{l-1}b_{l-1};N_{l}S_{z,l}I_{l}b_{l}} = \hat{W}^{\sigma_{l}\sigma_{l}'}_{p_{l-1}b_{l-1};p_{l}b_{l}} C^{S_{p_{l-1}b_{l-1}}kS_{p_{l}}} C^{S_{l}S_{l}'}_{S_{z,l}S_{z,l}},
\]

again with the local quantum numbers

\[
S_{z,l-1} = -S_{p_{l-1}}, \ldots, S_{p_{l-1}};
S_{z,l} = -S_{p_{l}}, \ldots, S_{p_{l}};
\]
\[
m = S_{z,l} - S_{z,l-1},
\]
\[
S_{z,\sigma'} = -S_{\sigma'}, \ldots, S_{\sigma'};
S_{z,\sigma} = -S_{\sigma}, \ldots, S_{\sigma};
\]
\[
\mu = S_{\sigma} - S_{\sigma'},
\]

as before. Note that the symmetry constraint \( p_{l} \in p_{l-1} \otimes k \) applies and, as the Hamiltonian operator is a spin-0 operator, we find that \( S_{p_{L}} = 0 \) for each term in Eq. (3.2).

We are now in a position to express the term in Eq. (3.21) with reduced matrix elements. For this we need \( \hat{c}^{\dagger}\hat{F} \) in reduced form,

\[
\hat{c}^{\dagger}\hat{F} = \begin{pmatrix}
0 & \sqrt{2} & 0 \\
0 & 0 & 1 \\
0 & 0 & 0
\end{pmatrix},
\]

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3.4. MPS-MPO operations

and the coefficients for the reduced elements of the $\hat{W}^k_{p_{l-1}^b b_{l-1}}$ tensors. The corresponding Clebsch–Gordan coefficients in Eq. (3.22) are all equal to 1, except on site $j$ where we find

$$ C_{\frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2}} = \frac{1}{\sqrt{2}}, \quad C_{\frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2}} = -\frac{1}{\sqrt{2}}. \quad (3.24) $$

Consequently, the reduced term

$$ \tau_{ij}^{\frac{1}{2} \frac{1}{2}} = t_{ij} \sqrt{2} \hat{c}_i \hat{c}_j \quad (3.25) $$

expands to the terms $t_{ij} \hat{c}_i^\dagger \hat{c}_j^\dagger$ and $t_{ij} \hat{c}_i^\dagger \hat{c}_j$. For the $\downarrow$-case, the minus sign from the expansion of $\hat{c}$ to $-\hat{c}_i$ is balanced by the Clebsch–Gordan coefficient from Eq. (3.24).

Note that since $\hat{W}^k_{p_{l-1}^b b_{l-1}}$ in general contains elementary site operators of different ranks, it does not transform irreducibly as a whole. We may only apply the Wigner–Eckart theorem to its elements $b_{l-1}, b_l$ individually. Further examples of reduced terms appearing in the sum of Eq. (3.2) are given in the appendix.

3.4. MPS-MPO operations

3.4.1. Calculations with reduced matrix elements

We can now describe the Hamiltonian in Eq. (3.2) and its eigenstates with MPOs and MPSs containing reduced matrix elements. Additionally, we have established, that the latter may be transformed with Eq. (3.4) to the MPSs and MPOs that we are familiar with from DMRG with abelian symmetries. The representation based on reduced matrix elements is more efficient compared to full matrix elements, because there are less elements to store. In order to exploit that fact in a DMRG algorithm, however, we need to be able to directly optimize the reduced elements in an MPS without any intermediate steps involving the full matrix elements.

The decisive equations of a second-generation DMRG implementation [61] are the propagation of the boundaries $L_{b_l}$ defined by the starting value $L_{b_1} = 1$ and the recursive relation

$$ L_{a_{l-1}^b a_{l-1}} = \sum_{a_{l-1}^b a_{l-1}^b} N_{a_{l-1}^b}^\sigma W_{b_{l-1}^a}^\sigma a_{l-1}^b \sum_{a_{l-1}^b} M_{a_{l-1}^b}^\sigma a_{l-1}^b, \quad (3.26) $$

where the matrices $N_{a_{l-1}^b}^\sigma$ describe a second state

$$ |\phi\rangle = \sum_{\sigma, a_{l-1}^b} N_{a_{l-1}^b}^\sigma \cdots N_{a_{l-1}^b}^\sigma \cdots N_{a_{l-1}^b}^\sigma |\sigma\rangle, \quad (3.27) $$

and the matrix vector multiplication

$$ M_{a_{l-1}^b}^\sigma a_{l-1}^b = \sum_{a_{l-1}^b} W_{b_{l-1}^a}^\sigma a_{l-1}^b a_{l-1}^b M_{a_{l-1}^b}^\sigma a_{l-1}^b a_{l-1}^b, \quad (3.28) $$

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with the right boundary $\mathbb{R}^{b_i}$ defined in analogy to Eq. (3.26). Both equations are introduced in our earlier work on second-generation DMRG [61]. It is our goal to calculate the reduced matrix elements of the quantities on the left hand side from the reduced matrix elements of the quantities on the right hand side. Incidentally, the boundary propagation and the matrix-vector multiplication possess the same symmetry properties, i.e., they contain the same number of tensor operators, because $\mathcal{N}_{a| a'_{i-1}}^{a_i}$ and $\mathbb{R}^{a'_i| a_i}$ both behave like a tensor operator whose elements obey Eq. (3.4). Therefore, we only have to derive one formula for the reduced matrix elements. In Eq. (3.26), we apply the Wigner–Eckart theorem by substituting each object with the right hand side of Eq. (3.4), which yields

$$L_{q|a_1|:a'|q'|}^{p|b_1} C_{m|m'}^{S_{q|} S_{a_1|} S_{q'|} S_{a'|}} = \sum_{\sigma_i} \sum_{m'_{i-1} m_{i-1}} \sqrt{(2S_{q|1} + 1)(2S_{q'|1} + 1)}$$

$$\times N_{q|a_1|:a'|q'|}^{\sigma_i} C_{m|m'}^{S_{q|} S_{a_1|} S_{q'|} S_{a'|}} W_{p|b_1|:b'}^{\sigma_i} C_{m|m'}^{S_{p|} S_{b_1|} S_{p'|} S_{b'|}}$$

$$\times L_{p|b_1}^{p|b_1} C_{m|m'}^{S_{q|} S_{a_1|} S_{q'|} S_{a'|}} M_{q'|a'|}^{p|b_1}.$$

Our choice of the normalization factor with the square root ensures that Eq. (3.29) remains valid for the generation of $\mathbb{R}^{b_i}$ from $\mathbb{R}^{b_{i+1}}$.

Fortunately, we may simplify the previous equation by employing the relation [60]

$$\sum_{m'_{i-1} m_{i-1}} \left[C_{m|m'}^{S_{q|} S_{a_1|} S_{q'|} S_{a'|}} S_{p|} S_{b_1|} S_{p'|} S_{b'|}\right]$$

$$= \left[S_{q|} S_{a_1|} S_{q'|} S_{a'|}\right] C_{m|m'}^{S_{q|} S_{a_1|} S_{q'|} S_{a'|}},$$

and obtain

$$L_{q|a_1|:a'|q'|}^{p|b_1} C_{m|m'}^{S_{q|} S_{a_1|} S_{q'|} S_{a'|}} = \sum_{\sigma_i} \sum_{m'_{i-1} m_{i-1}} \sqrt{(2S_{q|1} + 1)(2S_{q'|1} + 1)}$$

$$\times N_{q|a_1|:a'|q'|}^{\sigma_i} C_{m|m'}^{S_{q|} S_{a_1|} S_{q'|} S_{a'|}} W_{p|b_1|:b'}^{\sigma_i} C_{m|m'}^{S_{p|} S_{b_1|} S_{p'|} S_{b'|}}$$

$$\times L_{p|b_1}^{p|b_1} C_{m|m'}^{S_{q|} S_{a_1|} S_{q'|} S_{a'|}} M_{q'|a'|}^{p|b_1}.$$
where the coefficient $C_{S_{m}S_{m'}}^{S_{l}}$ cancels out. Eq. (3.31) differs from the original version with full matrix elements [Eq. (3.26)] only by the modified Wigner-9j coupling coefficient from Eq. (3.10). It is important to note that the Wigner-9j symbol includes the summation over all possible $S_z$ projections of all tensor operators in Eq. (3.31). As a consequence, the evaluation of the expectation value $\langle \psi | \sqrt{2} t_{ij} \hat{c}_{i} \hat{c}_{j} | \psi \rangle$ according to Eq. (3.31) yields

$$\langle \psi | \sqrt{2} t_{ij} \hat{c}_{i} \hat{c}_{j} | \psi \rangle = \langle \psi | t_{ij} \hat{c}_{i} \hat{c}_{j} | \psi \rangle + \langle \psi | t_{ij} \hat{c}_{i} \hat{c}_{j} | \psi \rangle.$$  \hspace{1cm} (3.32)

If we exchange in Eq. (3.31) $N_{\sigma}^{\alpha \dagger}$ by $R^k$, the right hand side becomes $M_{\sigma}^{\alpha \dagger}$, the reduced elements of the MPS tensor at site $l$ multiplied by the Hamiltonian, which is calculated by Krylov subspace based eigensolvers such as the Jacobi–Davidson algorithm.

### 3.4.2. The spin-adapted Hamiltonian

In the previous section, we saw that the two expansion products of the term in Eq. (3.24) are both contained in the Hamiltonian in Eq. (3.2). However, this is not always the case. The group of terms

$$\sum_{\sigma \sigma'} V_{ijij} \hat{c}_{i \sigma}^{\dagger} \hat{c}_{j \sigma}', \hat{c}_{i \sigma'} \hat{c}_{j \sigma} = -V_{ijij} (\hat{n}_{\uparrow} \hat{n}_{\downarrow} + \hat{n}_{\downarrow} \hat{n}_{\uparrow} + \hat{c}_{i \uparrow} \hat{c}_{j \downarrow} \hat{c}_{j \uparrow} + \hat{c}_{i \downarrow} \hat{c}_{j \uparrow} \hat{c}_{j \downarrow}),$$  \hspace{1cm} (3.33)

for example, contains nontrivial site operators like $\hat{c}_{i \uparrow} \hat{c}_{i \downarrow}$ and $\hat{c}_{j \uparrow} \hat{c}_{j \downarrow}$, which are the $S_z = 1$ and $S_z = -1$ components of a rank-1 irreducible tensor operator. In reduced form, the matrix elements of these site operators are

$$\hat{c}_{i}^{\dagger} \hat{c}^{[1]} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & \sqrt{3/2} & 0 \\ 0 & 0 & 0 \end{pmatrix},$$  \hspace{1cm} (3.34)

as the expansion to the full matrix elements [Eq. (3.4)] confirms, because the operators $\{-\hat{c}_{i \uparrow} \hat{c}_{i \downarrow}, \frac{1}{\sqrt{2}} (\hat{n}_{\uparrow} - \hat{n}_{\downarrow}), \hat{c}_{i \uparrow} \hat{c}_{i \downarrow} \}$ are obtained. If we now attempt to generate the terms in Eq. (3.33) from

$$\tau_{ij}^{[1,1]} = V_{ijij} \sqrt{3} \hat{c}_{i}^{\dagger} \hat{c}^{[1]} \hat{c}_{j}^{[1]} \hat{c}_{j}^{[1]},$$  \hspace{1cm} (3.35)

where the factor of $\sqrt{3}$ balances the magnitudes of the Clebsch–Gordan coefficients at site $j$ from Eq. (3.22), e.g. $C_{1-10}^{10}$, we will find that there are several different possibilities of expanding the term in Eq. (3.35) to full matrix elements. The sum of all possibilities with a total spin of 0 is

$$\sum_{\sigma \sigma' \sigma' \sigma} C_{m_{1}^{\prime} \sigma_{1} \sigma m_{1}^{\prime} \sigma_{1} \sigma}^{S_{a}^{1} 1 1} C_{m_{2} \sigma_{2} \sigma_{2} m_{2}^{\prime} \sigma_{2} \sigma}^{S_{a}^{1} 1 1} = -V_{ijij} \times (\hat{c}_{i \uparrow} \hat{c}_{i \downarrow} \hat{c}_{j \uparrow} + \hat{c}_{i \downarrow} \hat{c}_{i \uparrow} \hat{c}_{j \downarrow} + \frac{1}{2} (\hat{n}_{\uparrow} - \hat{n}_{\downarrow})_{i} (\hat{n}_{\uparrow} - \hat{n}_{\downarrow})_{j}),$$  \hspace{1cm} (3.36)
which does not match Eq. (3.33). For this reason, we must add a correction of \(-\frac{1}{2}\hat{n}_i\hat{n}_j\) to the term in Eq. (3.35) so that Eq. (3.33) is reproduced.

We have performed the analysis above for all the terms of the Hamiltonian in Eq. (3.2), a detailed list is provided in Sec. 3.6.

### 3.4.3. Reduced two-site MPS tensors

The variational optimization of two MPS sites at the same time involves the formation of the two-site MPS tensor

\[
P_{q_i-1}^{\sigma_i\sigma_{i+1}} = \sum_{a_i} M_{q_i-1a_i}^{\sigma_i} M_{q_i a_{i+1}}^{\sigma_{i+1}}.
\]  

(3.37)

To obtain the reduced elements of \(P\), we follow the description by Wouters et al. [39] and employ the formula in Eq. (3.6), which couples two tensor operators and reads

\[
P_{q_i-1}^{\sigma_i\sigma_{i+1},[k]} = (-1)^{S_{q_i-1} + S_{q_i + 1} + S_{q_i + 1} + S_{e_i}}
\times \sum_{S_{q_i}} \sqrt{(S_{q_i} + 1)(2k + 1)} \begin{bmatrix} S_{q_i+1} & S_{\sigma_i} \\ S_{\sigma_{i+1}} & S_{q_i-1} \end{bmatrix} 
\times M_{q_i-1}^{\sigma_i} M_{q_i a_{i+1}}^{\sigma_{i+1}},
\]  

(3.38)

where \(k\) runs over the expansion products of \(\sigma_i \otimes \sigma_{i+1}\). To split the two-site tensor \(P_{q_i}^{\sigma_i\sigma_{i+1}}\) by singular value decomposition into \(M^{\sigma_i}\) and \(M^{\sigma_{i+1}}\), we first need to back-transform \(P_{q_i}^{\sigma_i\sigma_{i+1}}\) into

\[
\tilde{P}_{q_i-1}^{\sigma_i\sigma_{i+1},[k]} = M_{q_i-1}^{\sigma_i} M_{q_i a_{i+1}}^{\sigma_{i+1}},
\]  

(3.39)

corresponding to the bare matrix-matrix product of \(M^{\sigma_i}\) and \(M^{\sigma_{i+1}}\). It is given by

\[
\tilde{P}_{q_i-1}^{\sigma_i\sigma_{i+1}} = (-1)^{S_{q_i-1} + S_{q_i + 1} + S_{q_i + 1} + S_{e_i}}
\times \sum_{k} \sqrt{(S_{q_i} + 1)(2k + 1)} \begin{bmatrix} S_{q_i+1} & S_{\sigma_i} \\ S_{\sigma_{i+1}} & S_{q_i-1} \end{bmatrix} 
\times M_{q_i-1}^{\sigma_i} M_{q_i a_{i+1}}^{\sigma_{i+1}},
\]  

(3.40)

A singular value decomposition yields

\[
\tilde{P}_{q_i-1}^{\sigma_i\sigma_{i+1}} = \sum_{a_i} U_{q_i-1}^{\sigma_i} S_{q_i a_i} V_{q_i a_i}^{\sigma_{i+1}},
\]

(3.41)

after which we can set \(M^{\sigma_i} = U\), \(M^{\sigma_{i+1}} = S \cdot V\) when sweeping towards the right and \(M^{\sigma_{i+1}} = S \cdot V\), \(M^{\sigma_i} = U\) during a left sweep. Note that, compared to Ref. [39], we do not apply any normalization factor in Eq. (3.41).
3.4.4. Reduced two-site MPO tensors

The calculation of the reduced matrix elements of the two-site MPO tensor

$$\tilde{V}_{b_{t-1}b_{t+1}}^{\sigma_{l}\sigma_{l}+1\sigma_{l}'} = \sum_{b_{t}} \tilde{W}_{b_{t-1}b_{t}}^{\sigma_{l}\sigma_{l}'} \tilde{W}_{b_{t}b_{t+1}}^{\sigma_{l}+1\sigma_{l}'}$$ \hspace{1cm} (3.42)

requires the application of Eq. (3.6) in analogy to the two-site MPS tensor case to couple the matrix $b$ indices and Eq. (3.9) to form the tensor product of two elementary site operators acting on separate spaces. In summary, we obtain

$$V_{p_{t-1}b_{t-1}p_{t+1}b_{t+1}}^{\sigma_{l}\sigma_{l}+1\sigma_{l}'} = (-1)^{S_{p_{t-1}}+S_{p_{t+1}}+k_{1}+k_{2}}$$

$$\times \sum_{S_{p_{t}}} \sqrt{(S_{p_{t}}+1)(2k+1)} \left\{ S_{p_{t+1}} \begin{array}{c} k_{1} \\ k_{2} \end{array} \right\} \left( S_{l} \begin{array}{c} S_{l}+1 \sigma_{l} \sigma_{l}+1 \sigma_{l}^{'} \end{array} \right) \left( W_{p_{t-1}b_{t-1}p_{t}b_{t}}^{\sigma_{l}\sigma_{l}'} W_{p_{t}b_{t}p_{t+1}b_{t+1}}^{\sigma_{l}+1\sigma_{l}'} \right).$$ \hspace{1cm} (3.43)

We emphasize, that Eq. (3.31) remains valid after an exchange of $M$ with $P$ and $W$ with $V$.

3.5. Example

For illustration purposes, we compare our spin- and non-spin-adapted implementations in QCMAQUIS [61] at the example of the dioxygen molecule and calculated the lowest-lying singlet state $^1\Delta_g$, which is the first excited state above the triplet ground state $^3\Sigma_g$. For our calculations, we employed the cc-pVTZ basis set [62], which was also used in the coupled-cluster calculation, and correlated all 16 electrons in all 60 orbitals (full configuration-interaction).

The non-spin-adapted total electronic energies for the singlet state in Table 3.1 with $S_z = 0$, but without point group symmetry converged to the triplet state, such that the singlet state is inaccessible with the non-spin-adapted algorithm if point group symmetry is not enforced. In the $D_{2h}$ subgroup of $D_{\infty h}$, the two singlet delta components reduce to $A_g$ and $B_{1g}$ symmetry so that considering point group symmetry allows us to select which state to calculate (the $z$ axis is along the internuclear axis). With the spin-adapted algorithm we may set the total spin $S$ equal to zero and describe the singlet state correctly, even if point group symmetry is not enforced. For comparison with coupled-cluster results, we extrapolated a series of DMRG calculations with a varying number of renormalized block states $m$ comprising $m = 1000 - 4000$ to calculate the singlet energy. A conservative estimate of the accuracy is 0.5 mHartree, the difference
Table 3.1.: O$_2$ total electronic energies for the $^1\Delta_g$ and $^3\Sigma_g$ states in Hartree, $E_H$ (in a Dunning cc-pVTZ basis set). 'FULL' denotes that all electrons including the 1s electrons were correlated. Internuclear distances are 1.22217 Å and 1.20700 Å for the singlet and triplet states, respectively.

<table>
<thead>
<tr>
<th>Method</th>
<th>$E_{el}(^1\Delta_g) / E_H$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMRG(16,60), $S_z = 0, m = 1000$</td>
<td>-150.147 369</td>
</tr>
<tr>
<td>DMRG(16,60), $S = 0, m = 1000$</td>
<td>-150.114 826</td>
</tr>
<tr>
<td>DMRG(16,60), $S = 0, m = 2000$</td>
<td>-150.116 789</td>
</tr>
<tr>
<td>DMRG(16,60), $S = 0, m = 4000$</td>
<td>-150.117 657</td>
</tr>
<tr>
<td>DMRG(16,60), $S = 0, m = 1000$-4000, $D_{2h}$, extrapolated</td>
<td>-150.118 164</td>
</tr>
<tr>
<td>CCSD(T)=FULL [63]</td>
<td>-150.105 829</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Method</th>
<th>$E_{el}(^3\Sigma_g) / E_H$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMRG(16,60), $S = 1, m = 1000$</td>
<td>-150.151 163</td>
</tr>
<tr>
<td>DMRG(16,60), $S = 1, m = 2000$</td>
<td>-150.153 533</td>
</tr>
<tr>
<td>DMRG(16,60), $S = 1, m = 4000$</td>
<td>-150.154 643</td>
</tr>
<tr>
<td>DMRG(16,60), $S = 1, m = 1000$-4000, $D_{2h}$, extrapolated</td>
<td>-150.155 142</td>
</tr>
<tr>
<td>CCSD(T)=FULL [63]</td>
<td>-150.153 620</td>
</tr>
</tbody>
</table>
between the extrapolated value and the best variational result with $m = 4000$. In Table 3.1, we also include results from the triplet ground state calculation for comparison.

Table 3.1 clearly shows that the non-spin-adapted ($S_z = 0$) result is too low in energy, whereas the correct, spin-adapted electronic energy of the singlet state is higher by about 0.033 Hartree. The former actually converged towards the triplet state, but the energy for this state is not fully converged as a comparison with the converged triplet ground state DMRG(16,60)[4000] energy in Table 3.1 shows. Note also that the CCSD(T) result is higher in energy than the DMRG results because this coupled-cluster model restricts the excitation operators to double substitutions with perturbatively corrected triples.

The (adiabatic) singlet-triplet gap is 125.5 kJ/mol with CCSD(T) and 97.1 kJ/mol with DMRG(16,60) $\text{extr}$. The experimental result for this gap is in the range of 94 to 95 kJ/mol [64] and therefore in very good agreement with the DMRG result.

### 3.6. Reduced operators for the quantum-chemical Hamiltonian

For reference purposes, we provide the complete list of reduced matrix elements implemented in QCMAQUIS to represent the Hamiltonian in Eq. (3.2).

#### 3.6.1. Reduced elementary site operators

Local basis: $\{|0,2,A_g\}, |1,\frac{1}{2}, I\rangle, |0,0,A_g\}$.

\[
\hat{c}^\dagger = \begin{pmatrix} 0 & -\sqrt{2} & 0 \\ 0 & 0 & 1 \\ 0 & 0 & 0 \end{pmatrix} \quad \hat{c} = \begin{pmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \\ 0 & \sqrt{2} & 0 \end{pmatrix}
\]

(3.44)

\[
\hat{n} = \begin{pmatrix} 2 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad \hat{c}^\dagger \hat{c}^{[II]} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & \sqrt{3/2} & 0 \\ 0 & 0 & 0 \end{pmatrix}
\]

(3.45)

\[
\hat{c}^\dagger \hat{n} = \begin{pmatrix} 0 & -\sqrt{2} & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad \hat{n} \hat{c} = \begin{pmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}
\]

(3.46)
\[ \hat{p}^\dagger = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad \hat{p} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix} \] 

(3.47)

3.6.2. Reduced Hamiltonian terms

The definition of the two-electron integrals according to the notation in Ref. [65] reads

\[ V_{ijkl} = \int d^3r d^3r' \phi_i^*(r) \phi_k^*(r') V(|r - r'|) \phi_j(r) \phi_l(r'), \] 

(3.48)

and exhibits the permutation symmetries

\[ V_{ijkl} = V_{klij} = V_{jilk}^* = V_{lkji}^*, \] 

(3.49)

which give rise to equivalence classes of index permutations that share the same two-electron integral. We partition the Hamiltonian in Eq. (3.2) according to these equivalence classes described in Table 3.2. The format for the one- and two-electron integrals described in Ref. [65] only lists unique integral values. Therefore, the second column of Table 3.2 contains the terms for all permutations given in the first column. Note, that in the first column of Table 3.2 only half of the possible two-electron index permutations are listed in order to cancel the factor 1/2 in Eq. (3.2).
Table 3.2.: Terms of the Hamiltonian partitioned into one- and two-electron equivalence classes.

<table>
<thead>
<tr>
<th>integral</th>
<th>terms</th>
<th>reduced</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t_{ii}$</td>
<td>$\sum_{\sigma} \hat{c}<em>{\sigma i}^\dagger \hat{c}</em>{\sigma i}$</td>
<td>$\hat{n}$</td>
</tr>
<tr>
<td>$t_{ij} = t_{ji}$</td>
<td>$\sum_{\sigma} \hat{c}<em>{\sigma i}^\dagger \hat{c}</em>{\sigma j}$</td>
<td>$\sqrt{2}[\hat{c}<em>{\uparrow i}^\dagger \hat{c}</em>{\uparrow j} - \hat{c}<em>{\downarrow i} \hat{c}</em>{\downarrow j}]$</td>
</tr>
<tr>
<td>$V_{iiii}$</td>
<td>$\hat{n}<em>{\uparrow i} \hat{n}</em>{\downarrow i}$</td>
<td>$\hat{d}_{i}$</td>
</tr>
<tr>
<td>$V_{jjjj} = V_{jjji}$</td>
<td>$\sum_{\sigma \neq \sigma'} \hat{c}<em>{\sigma i}^\dagger \hat{c}</em>{\sigma j} \hat{n}_{\sigma' j}$</td>
<td>$\sqrt{2}[\hat{c}<em>{\uparrow i}^\dagger \hat{n} \hat{c}</em>{\downarrow j} - \hat{n} \hat{c}<em>{\downarrow i} \hat{c}</em>{\downarrow j}]$</td>
</tr>
<tr>
<td>$V_{ijij} = V_{jiji}$</td>
<td>$(\hat{n}<em>{\uparrow i} + \hat{n}</em>{\downarrow i})(\hat{n}<em>{\uparrow j} + \hat{n}</em>{\downarrow j})$</td>
<td>$\hat{n}<em>{\uparrow} \hat{n}</em>{\downarrow}$</td>
</tr>
<tr>
<td>$V_{iilk} = V_{iklt} = V_{klii}$</td>
<td>$\sum_{\sigma \sigma''} \hat{n}<em>{\sigma i} \hat{c}</em>{\sigma' k}^\dagger \hat{c}_{\sigma'' l}$</td>
<td>$\sqrt{2}\hat{c}<em>{\downarrow i}^\dagger \hat{n} \hat{c}</em>{\uparrow l}^\dagger \hat{c}_{\uparrow l}$</td>
</tr>
<tr>
<td>$V_{lki} = V_{kili}$</td>
<td>$-\sum_{\sigma \sigma''} \hat{n}<em>{\sigma i} \hat{c}</em>{\sigma' k}^\dagger \hat{c}_{\sigma'' l}$</td>
<td>$-\sqrt{2}\hat{c}<em>{\downarrow i}^\dagger \hat{n} \hat{c}</em>{\uparrow l}^\dagger \hat{c}_{\uparrow l}$</td>
</tr>
<tr>
<td>$V_{ijjl} = V_{ljji}$</td>
<td>$\sum_{\sigma \sigma'} \hat{c}<em>{\sigma i}^\dagger \hat{c}</em>{\sigma' j} \hat{c}<em>{\sigma' l}^\dagger \hat{c}</em>{\sigma l}$</td>
<td>$\sqrt{2}\hat{p}<em>{\downarrow i} \hat{c}</em>{\uparrow j}^\dagger \hat{c}<em>{\uparrow l}^\dagger \hat{c}</em>{\uparrow l}$</td>
</tr>
<tr>
<td>$V_{jill} = V_{ljii}$</td>
<td>$\sum_{\sigma \sigma' \sigma''} \hat{c}<em>{\sigma i} \hat{c}</em>{\sigma' j} \hat{c}<em>{\sigma'' l}^\dagger \hat{c}</em>{\sigma l}$</td>
<td>$\sqrt{2}\hat{p}<em>{\downarrow i} \hat{c}</em>{\uparrow j}^\dagger \hat{c}<em>{\uparrow l}^\dagger \hat{c}</em>{\uparrow l}$</td>
</tr>
<tr>
<td>$V_{ijkl} = V_{ijlk}$</td>
<td>$\sum_{\sigma \sigma' \sigma''} \hat{c}<em>{\sigma i}^\dagger \hat{c}</em>{\sigma' j} \hat{c}<em>{\sigma'' k} \hat{c}</em>{\sigma'' l}$</td>
<td>$\sqrt{2}\hat{n} \hat{c}<em>{\uparrow i}^\dagger \hat{c}</em>{\uparrow l}^\dagger + \sqrt{2}\hat{n} \hat{c}<em>{\uparrow i}^\dagger \hat{c}</em>{\uparrow l}^\dagger$</td>
</tr>
<tr>
<td>$V_{jikl} = V_{jlki}$</td>
<td>$\sum_{\sigma \sigma' \sigma''} \hat{c}<em>{\sigma i}^\dagger \hat{c}</em>{\sigma' j} \hat{c}<em>{\sigma'' k} \hat{c}</em>{\sigma'' l}$</td>
<td>$\sqrt{2}\hat{n} \hat{c}<em>{\uparrow i}^\dagger \hat{c}</em>{\uparrow l}^\dagger + \sqrt{2}\hat{n} \hat{c}<em>{\uparrow i}^\dagger \hat{c}</em>{\uparrow l}^\dagger$</td>
</tr>
<tr>
<td>$V_{ijkl} = V_{ijlk}$</td>
<td>$\sum_{\sigma \sigma' \sigma''} \hat{c}<em>{\sigma i}^\dagger \hat{c}</em>{\sigma' j} \hat{c}<em>{\sigma'' k} \hat{c}</em>{\sigma'' l}$</td>
<td>see Table 3.3</td>
</tr>
</tbody>
</table>

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Table 3.3: continued from Table 3.2, lower right. Reduced Hamiltonian terms for the case $i \neq j \neq k \neq l$.

<table>
<thead>
<tr>
<th>$k &gt; l$, $l &gt; j$</th>
<th>$\alpha = -\sqrt{3}$, $\beta = 1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k &gt; j$, $j &gt; l$</td>
<td>$\alpha = -\sqrt{3}$, $\beta = 1$</td>
</tr>
<tr>
<td>$j &gt; k$, $k &gt; l$</td>
<td>$\alpha = 0$, $\beta = 2$</td>
</tr>
</tbody>
</table>
3.7. Relativistic DMRG

<table>
<thead>
<tr>
<th>Double Group</th>
<th>Algebra</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{\infty v}$,$C_{2v}$,$D_{2h}^*$</td>
<td>Real</td>
</tr>
<tr>
<td>$C_{2h}$,$C_{s}$,$C_{s}^*$</td>
<td>Complex</td>
</tr>
<tr>
<td>$C_{1}$,$C_{1}^*$</td>
<td>Complex</td>
</tr>
</tbody>
</table>

Table 3.4.: Available double groups in QCMAQUIS.

3.7. Relativistic DMRG

Since we are able to treat any second-quantized Hamiltonian of the form in Eq. (3.2) with a wide selection of symmetries either with complex or real integrals, a realization of a relativistic model within the presented framework could be readily obtained and was carried out by Stefano Battaglia during his master thesis in our group [41]. Most generally, we may write a fully relativistic Hamiltonian operator as

$$\hat{H} = \sum_i \hat{h}_D(i) + \frac{1}{2} \sum_{i \neq j} \hat{g}(i,j) + V_{NN},$$  \hspace{1cm} (3.50)

where $\hat{h}_D(i)$ corresponds to the one-electron Dirac Hamiltonian, $\hat{g}(i,j)$ to the two-electron interaction and $V_{NN}$ to the nucleus-nucleus repulsion, giving rise to modified one-electron integrals

$$t_{ij} = \int \phi_i^*(r_1) \hat{h}_D(r_1) \phi_j(r_1) dr_1$$  \hspace{1cm} (3.51)

to be supplied to Eq. (3.2).

To the DMRG formalism as we introduced it, only the one- and two-electron integrals $t_{ij}$ and $V_{ijkl}$ as generated for instance by the Dirac program package [66] together with a definition of the elementary creation and annihilation operators and corresponding symmetry properties matter. The relativistic model implemented in QCMAQUIS is therefore compatible with various relativistic Hamiltonian operators featuring either a 2- or 4-component description. Specifically, our implementation assumes a $U(1) \otimes DG$ symmetry, a combination of the abelian $U(1)$ symmetry induced by particle number conservation and the abelian double group DG symmetry induced by spacial and time-inversion symmetry. Possible choices for $DG$ are given in Table 3.4. Quantum numbers are therefore specified as $|N,g\rangle$, a tuple of particle number $N$ and an irreducible representation $g$. The elementary operators on a certain site belonging to the irreducible representation $g_l$ are then defined as

$$c_i^\dagger = |1,g_l\rangle\langle 0,0|, \quad c_l = |0,0\rangle\langle 1,g_l|. \hspace{1cm} (3.52)$$

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Table 3.5.: Total electronic energy differences (in mH) at five different internuclear distances. The outcomes of the different methods are all compared to the reference 4c-CCSDTQ calculation. Data taken from Ref. [41].

<table>
<thead>
<tr>
<th>Method</th>
<th>$\Delta E_{1.7720}$</th>
<th>$\Delta E_{1.8220}$</th>
<th>$\Delta E_{1.8720}$</th>
<th>$\Delta E_{1.9220}$</th>
<th>$\Delta E_{1.9720}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4c-CISD</td>
<td>41.09</td>
<td>41.31</td>
<td>41.55</td>
<td>41.80</td>
<td>42.07</td>
</tr>
<tr>
<td>4c-CISDT</td>
<td>-</td>
<td>-</td>
<td>32.80</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4c-CISDTQ</td>
<td>2.57</td>
<td>2.60</td>
<td>2.63</td>
<td>2.66</td>
<td>2.70</td>
</tr>
<tr>
<td>4c-CCSDT</td>
<td>0.32</td>
<td>0.33</td>
<td>0.33</td>
<td>0.33</td>
<td>0.33</td>
</tr>
<tr>
<td>4c-CCSDT(Q)</td>
<td>-0.07</td>
<td>-0.06</td>
<td>-0.07</td>
<td>-0.07</td>
<td>-0.06</td>
</tr>
<tr>
<td>4c-QCDMRG[$M = 4500]$</td>
<td>-</td>
<td>-</td>
<td>2.57</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4c-QCDMRG[$M \to \infty$]</td>
<td>-</td>
<td>-</td>
<td>0.7</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4c-MAQUIS[$M = 500$]</td>
<td>-</td>
<td>-</td>
<td>28.16</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4c-MAQUIS[$M = 1000$]</td>
<td>-</td>
<td>-</td>
<td>18.35</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4c-MAQUIS[$M = 2000$]</td>
<td>-</td>
<td>-</td>
<td>8.44</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4c-MAQUIS[$M = 4000$]</td>
<td>3.18</td>
<td>3.17</td>
<td>3.16</td>
<td>-</td>
<td>3.15</td>
</tr>
<tr>
<td>4c-MAQUIS[$M = 5000$]</td>
<td>2.53</td>
<td>-</td>
<td>2.51</td>
<td>2.45</td>
<td>2.51</td>
</tr>
<tr>
<td>4c-MAQUIS[$M \to \infty$]</td>
<td>-</td>
<td>-</td>
<td>0.1</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

3.7.1. A benchmark application: TlH

The thallium hydride (TlH) molecule shows large relativistic effects and is thus well suited to test relativistic quantum mechanical simulations. Employing QCMAQUIS, we calculated the ground state energy of TlH at five different bond lengths and compared our results with those shown in an earlier work by Knecht and Legeza [67] who employed the relativistic version of the Budapest DMRG program [68]. For the integral generation we used the Dirac program package, computing the Hartree-Fock ground state of the four-component Dirac-Coulomb Hamiltonian in a Kramers-restricted triple-$\zeta$ (cv3z) [69, 70] basis for Tl and a cc-pVTZ [62] basis for H. In the active space of the subsequent DMRG calculation, all natural spinors with an occupation number between 1.98 and 0.001, as determined with MP2, were included, yielding 94 spinors in which 14 electrons are correlated. The resulting ground state energies in mHartree relative to a 4-component CCSDTQ reference calculation are shown in Table 3.5. In summary, QCMAQUIS performs well, yielding a lower energy than the best alternative variational result (4c-CISDTQ) and lower than the Budapest DMRG program (4c-QCDMRG). An extrapolation towards zero truncation error results in an energy 0.1 mHartree higher compared to the coupled cluster reference. Since TlH is dominated by dynamical correlation effects, which are well described by single reference methods, this is a reasonable result.
4

Implementational aspects

4.1. Artificial local basis states

For abelian symmetries, two quantum numbers always combine to a unique third quantum number. In the case of non-abelian symmetries, this is no longer true. Instead, the product of two irreducible representations belonging to $SU(2)$ for instance, decomposes according to the Clebsch-Gordan expansion (Eq. (3.3)) into several other irreducible representations.

A symmetry framework may be designed to handle general non-abelian symmetries, thereby allowing for a vectorial result of quantum number multiplication, but this would result in computational overhead for abelian symmetries, where a product only yields a single value. If a description of spin-$1/2$ particles is deemed sufficient, however, there is another possibility of integrating both abelian and non-abelian $SU(2)$ symmetries in a common framework; spin-$1/2$ irreducible representations can only combine in two ways with another irreducible representation. The result is either a product spin increase or decrease of $1/2$. We can employ this fact to mimic the result of the Clebsch-Gordan expansion if we introduce an additional auxiliary state and subsequently couple all quantum numbers according to a simple abelian group operation. We define the local $SU(2)$-invariant site basis $B$ with quantum numbers in the format $(S, N)$ with $S =$ spin and $N =$ particle number as

$$B = \{(0, 2), (1, \frac{1}{2}), (1, -\frac{1}{2}), (0, 0)\} \quad (4.1)$$

and define the abelian group operation as

$$\left(S_1, N_1\right) \oplus^a \left(S_2, N_2\right) = \begin{cases} (S_1 + S_2, N_1 + N_2) & S_1 + S_1 \geq 0 \\ (S_1 + S_2, N_1 + N_2^2) & S_1 + S_2 < 0 \end{cases} \quad (4.2)$$
4.2. Performance critical aspects of the DMRG algorithm

The product $Q \otimes a B = \{ q \otimes a b \mid q \in Q, b \in B \}$ with an arbitrary collection of quantum numbers $Q$ now contains the exact same coupling products compared to $Q \otimes^{CG} B' = \{ q \oplus^{CG} b \mid q \in Q, b \in B' \}$, where $\oplus^{CG}$ denotes the Clebsch-Gordan expansion and $B'$ corresponds to the true local site basis without the state $(1, -\frac{1}{2})$.

In QCMAQUIS, various Hamiltonian operators with abelian symmetries are implemented alongside $SU(2)$-invariant Hamiltonians for spin-1/2 electrons in a common framework through the introduction of the auxiliary state $(1, -\frac{1}{2})$ into $SU(2)$-invariant local site bases.

4.2. Performance critical aspects of the DMRG algorithm

When the first version of QCMAQUIS with a working implementation of the full Coulomb Hamiltonian suitable for quantum chemical calculations was completed in the year 2013, the framework was already in a very mature state after several years of development for applications in solid state physics. Still, this first version was around five orders of magnitude slower, already for small systems with less than 10 active orbitals, compared to the most recent version at the time of writing this thesis. Compared to typical solid state physics models, which are about as sparsely populated with terms as Siberian tundra, the Coulomb Hamiltonian is as packed as the Tokyo metro at rush-hour, requiring radically different kinds of optimizations. Doubtlessly, the most significant speed-ups were achieved through the algorithmic improvements described in chapters 2 and 3. Technical tricks also played a major role for attaining reasonable performance, some of which merely reflect established practices for fast numerical code. Other tricks, however, are based on physical concepts; they deserve to be mentioned here.

4.2.1. Pairing

Conceptually, an MPS tensors $M_{q_{i-1}q_ia_i}$ consists of a block matrix for each of the local basis states $\sigma_i$. For efficiency reasons, these block matrices are collected in a single block matrix. There are two ways to achieve this; either by stacking blocks on top of each other or next to each other. In the former case, blocks are grouped together if the right hand quantum numbers belonging to $q_i$ match and if

$$p \oplus l = r \quad \text{for} \quad p \in \sigma_i, \quad l \in q_{i-1} \quad \text{and} \quad r \in q_i$$

(4.3)

holds. As a consequence, the resulting block matrix is indexed by the quantum numbers in $q_i$ on both sides. For the right paired case, we group blocks, such that

$$l = r \oplus -p \quad \text{for} \quad p \in \sigma_i, \quad l \in q_{i-1} \quad \text{and} \quad r \in q_i.$$  

(4.4)
Figure 4.1.: Left- and right-paired tensors. By left-pairing, the physical index is fused with the left index, by right-pairing, the inverse of the physical index is fused with the right index.

The right paired block matrix will then be indexed by $q_{l-1}$ on both sides. Schematically, we can think of the physical index $\sigma_i$ being paired with either the left or right indices $q_{i-1}$ and $q_i$ as depicted in Fig. 4.1. An example for the two possible arrangements of an MPS tensor is shown in Fig. 4.2. Identical matrix elements are depicted with the same color in both variants. The left-paired version of the shown tensor corresponds to a site 2 tensor with abelian quantum numbers $(n^\uparrow, n^\downarrow)$

$$q_2 = \{(2, 2) : 1, (2, 1) : 2, (2, 0) : 1, (1, 2) : 2, (1, 1) : 4, (1, 0) : 2, (0, 2) : 1, (0, 1) : 2, (0, 0) : 1\},$$

while the right-paired version is indexed by

$$q^I_l = \{(1, 1) : 1, (1, 0) : 1, (0, 1) : 1, (0, 0) : 1\}$$

and

$$q^R_l = \{(1, 1) : 9, (1, 0) : 9, (0, 1) : 9, (0, 0) : 9\}$$

on the left and right sides.

We may now employ paired tensors in the contraction formulae of chapter 2. The example of the norm calculation $\langle \psi | \psi \rangle$ in Eq. (1.7) can be illustrated as shown in Fig. 4.3. In the figure, the object $i-1 = \sum_{\sigma_1, \ldots, \sigma_{i-1}} M^{\sigma_{i-1}} \cdots M^{\sigma_1} M^{\sigma_1} \cdots M^{\sigma_{i-1}}$ is contracted with the right-paired MPS tensor $\sigma_i$. After a reshape of the resulting product to the left-paired representation followed by contraction with the adjoint of the left-paired $M^{\sigma_i}$ we have grown the contracted network by one site.

Concerning performance, in the paired version of Eq. (1.7), $n_{\text{dim}}(\sigma_i)$ times less matrix multiplications are performed on matrices that are $n_{\text{dim}}(\sigma_i)$ times bigger. Additionally, the summation over $\sigma_1, \ldots, \sigma_i$ is implicitly covered in the last step of Fig. 4.3. While the total number of floating point operations stays the same, matrix-matrix multiplications only reach peak performance on current architectures, if the matrix dimensions exceed a certain minimum. The matrix sizes typically encountered in quantum chemical DMRG are below this minimum, such that the matrix size increase through pairing improves performance.
4.2. Performance critical aspects of the DMRG algorithm

Figure 4.2.: Left- and right-paired versions of an MPS tensor. The positions of the individual matrix elements in both shapes is resolved through the color code.

Figure 4.3.: Operations involved in calculating the norm $\langle \psi | \psi \rangle$ according to Eq. (1.7) with paired tensors.
4.2.2. Hermitian boundaries

By construction, the left and right boundary objects $L_{bl}a_l,a_l'$ and $R_{bl-1}a_{l-1},a_{l-1}'$, as defined in Eq. (1.38) and Eq. (1.40), contain expectation values of the form $\langle a_l,(L,R)|\hat{o}|a_l',(L,R)\rangle$ for each of the MPO-$b_l$ indices, where $\hat{o}$ stands for a partial hamiltonian term consisting of one to four elementary site operators whose expectation values are stored with respect to the orthonormal subsystem states $|a_l,(L,R)\rangle$ defined in Eq. 1.20 and Eq. 1.26. If two operators $\hat{o}_1$ and $\hat{o}_2$ are the hermitian conjugate of each other, the resulting expectation values stored in the boundary will also be related through hermitian conjugation. As an example, we have

$$\langle a_l,L|\hat{c}_i^\dagger \hat{c}_j|a_l',L\rangle = \langle a_l',L|\hat{c}_j^\dagger \hat{c}_i|a_l,L\rangle. \quad \text{(4.9)}$$

This means that for each value of $b_l$ in $L_{bl}a_l,a_l'$, if the evaluated partial operator contained in $b_l$ is not self-adjoint, there is a second index $b_l'$, such that

$$L_{bl}a_l,a_l' = L_{b_l'}a_{l'},a_l. \quad \text{(4.10)}$$

As discussed in chapter 2, if $L$ is the total number of sites, $b_l$ comprises $O(L^2)$ terms with two elementary operators acting on two different sites, but only $O(L)$ terms contain an elementary operator acting on just one site, some of which are self-adjoint (e.g. $\hat{n}_i$). For most $b_l$, we can therefore find an index $b_l'$ which contains the hermitian conjugate matrix, such that the storage requirements of $L_{bl}a_l,a_l'$ and $R_{bl-1}a_{l-1},a_{l-1}'$ can essentially be halved. While the execution time for the boundary propagation $L_{bl} \mapsto L_{b_l+1}$ (Eq. (1.38)) is also halved, this does unfortunately not hold for the time-critical matrix-vector multiplication $|\psi\rangle \mapsto \hat{H}|\psi\rangle$, in which the MPS tensor $M_{al+1}^{\sigma_{l+1}}$ is multiplied with $L_{bl}b_l$ corresponding to a matrix-matrix multiplication for each value of $b_l$; it is not possible to express $L_{b_l'}a_{l'},a_l M_{al+1}^{\sigma_{l+1}}$ through $L_{b_l}a_l,a_l'M_{al+1}^{\sigma_{l+1}}$.

4.2.3. Boundaries on disk

During the optimization of a certain active site $a$, only the adjacent boundaries to the immediate left and right hand side are required to compute the matrix-vector product corresponding to the application of the Hamiltonian operator to the wavefunction. Other boundaries, at sites depicted with blank circles in Fig. 4.4 should be stored on disk, reducing the memory storage requirements from $O(L^3)$ to $O(L^2)$ for a system with $L$ sites.

4.2.4. Sorted indices

As the number of possible symmetry sectors labeled by quantum number grows exponentially with the system size, the lookup of a certain sector in an index (list of quantum
4.2. Performance critical aspects of the DMRG algorithm

Figure 4.4.: Storage layout for boundary objects. During the optimization of the active site labeled \( a \), only the adjacent boundaries \( \mathbb{L} \) and \( \mathbb{R} \) are needed in memory. Boundary objects at sites represented with a blank circle may reside on disk. To prevent delays due to limited disk I/O-speed, the boundary on the right hand side of \( \mathbb{R} \) is loaded into memory during the optimization at site \( a \), while the boundary to the left of \( \mathbb{L} \) is being stored to disk during a sweep towards the right (and vice versa for a left-sweep).

numbers) becomes increasingly expensive. For this reason, quantum numbers in QCMAQUIS feature a comparison operation that sequentially compares each constituent symmetry. Indices can then be maintained sorted, allowing a certain quantum number to be located in logarithmic time through a binary search.

4.2.5. Grouping of quantum numbers for improved memory locality

In present day computing architectures, the memory bandwidths to sustain the ever faster CPUs with data have not been able to keep up with the increasing processing capabilities. Fast caches are able to keep the processors busy, but their limited size requires a careful analysis of memory access patterns by the programmer in order to be of any use. For this reason, computer code that reuses data in the caches once fetched from memory will run faster.

The most compute intensive part in QCMAQUIS is the contraction of a boundary with the MPS and MPO tensors as depicted in Fig. 1.3. In steps 2 and 3 in the figure, each of the symmetry blocks (depicted with a gray box) in \( \mathbb{L}_{b_{l-1}a_{l-1}} \) is fetched exactly once from memory, multiplied with a scale factor from \( \hat{W}_{b_{l-1}b_{l}} \) and finally added to a symmetry block in \( \mathbb{T}_{a_{l-1}a_{l}'}^b \). Blocks from the entire range of \( b_{l-1} \) are thereby added to only one block-matrix in \( \mathbb{T}_{a_{l-1}a_{l}'}^b \) with a fixed value of \( b_{l} \). Therefore, there is data reusage in the elements of \( \mathbb{T} \), while elements from \( \mathbb{L} \) are used only once. Consequently, the blocks in \( \mathbb{L} \) should be accessed in groups with fixed destination block in \( \mathbb{T} \).

4.2.6. The minimum number of Hamiltonian terms

Obviously, in the full electronic Coulomb Hamiltonian as denoted in Eq. (4.11),

\[
\hat{\mathcal{H}} = \sum_{ij} t_{ij} \hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma} + \frac{1}{2} \sum_{ijkl} V_{ijkl} \hat{c}_{i\sigma}^\dagger \hat{c}_{k\sigma'}^\dagger \hat{c}_{l\sigma'} \hat{c}_{j\sigma},
\]

(4.11)
each term appears exactly twice in the sum running over the four indices $i, j, k, l$, can-
celling the factor $\frac{1}{2}$. But the number of terms can be further reduced in two ways. First, for each term with $\sigma = \sigma'$ in the two-electron sum, there exists a second term with an identical operator/index combination but a different coefficient. By adding the coefficients, we can further reduce the total number of terms by 25%. Secondly, the one-electron terms with coefficients $t_{ij}$ can be incorporated into the two-electron terms with the following formula

$$V'_{ijkl} = V_{ijkl} + \frac{1}{N-1} \left( t_{ik}\delta_{jl} + t_{jl}\delta_{ik} \right),$$

(4.12)

where $N$ stands for the number of electrons.
MPO DMRG for Chemistry

5.1. Determining Factors for the Accuracy of DMRG in Chemistry [71]

5.1.1. Performance of the method

As with other active-space methods, the decisive parameter determining the cost of a calculation is the number of correlated electrons in the number of active orbitals. While traditional methods such as CASSCF are exponentially expensive with respect to the size of the active space, DMRG formally exhibits a scaling of $O(m^2 L^4) + O(m^3 L^4)$. One must keep in mind, however, that this behavior breaks down if the amount of entanglement measured by the van Neumann entropy between the two parts of any bipartition of the system increases with the system size [29]. If this is the case, the number of renormalized basis states $m$ needed to attain a certain accuracy may increase dramatically. In the worst case, exponential scaling is recovered. Fortunately, many molecules with a complicated electronic structure still exhibit some degree of locality, such that the amount of entanglement does not increase linearly with the system size. Besides the fundamental limitations of active space size and entanglement, other, more technical aspects also have a strong influence on DMRG convergence and thus on efficiency.

5.1.2. Assessing convergence and accuracy

Here, we attempt to provide a complete list of determining factors that affect DMRG accuracy and are thus essential factors to report if results from DMRG calculations are exploited in chemical research. The example data provided in this section were computed with QCMAQUIS [61] and with the Budapest quantum-chemical DMRG program developed by ¨O. Legeza since the year 2000 [68].
5.1. Determining Factors for the Accuracy of DMRG in Chemistry

5.1.3. Size of the active space

Despite the substantially higher computational efficiency that DMRG achieves compared to Full-CI, the exact treatment of the electron correlation problem in the full orbital basis remains out of reach on today’s computers. For this reason, the concept of a complete active space, which emerged during the development of traditional electron correlation methods, is important in DMRG calculations as well. This concept selects a limited part of the full orbital basis, in which the electronic correlation is treated exactly and which is chosen, such that it presumably contains the relevant contributions of the differential electron correlation decisive for chemical purposes. Physically, this subspace referred to as the 'Complete Active Space' can be selected in a meaningful way, because the strongest correlation effects occur within the orbitals that lie close to the Fermi Level. The remainders of the full orbital basis below and above the active space are referred to as 'core' and 'virtual' orbitals and they are assumed to be fully occupied and empty, respectively. The larger number of determinants involving virtual orbitals neglected from the active space tend to have smaller weights. Their contributions to the electronic wavefunction is referred to as dynamic correlation. The advantage of such a subdivision of the total orbital basis is that dynamic correlation effects can be accounted for less resource intensively with perturbation-theory or other methods [24, 72]. Often, the choice of a subdivision is made based on empirical criteria. As an aid in choosing an active space and assessing its reliability, we have developed a set of criteria based on entanglement measures [42, 73].

5.1.4. Choice of the molecular orbitals

The introduction of an active space entails that only a part of the orbital basis is contained within the model. These molecular orbitals are therefore well suited for a calculation if they allow one to express a large share of the total static correlation within an active space of a computationally feasible size. Hence, the electronic energies depend on the orbital choice. In cases, where a smaller active space than used with DMRG can be meaningfully selected for CASSCF, the resulting preoptimized molecular orbitals are better suited for the subsequent DMRG treatment than plain Hartree-Fock molecular orbitals. Employing localized molecular orbitals can have an effect on the performance of DMRG. If long-ranged 'interactions' among localized orbitals become weak enough, it might be possible to eliminate some of the terms in the electronic Hamiltonian by a screening of the two electron integrals without affecting accuracy. If localized molecular orbitals in addition help to reduce the amount of entanglement in the system, a smaller number of renormalized basis states will be required to attain a certain accuracy, such that the performance is further enhanced. The orbital-dependence of DMRG energies may be conveniently resolved by combining the DMRG optimization with an orbital re-
Warm-up guess  Hartree-Fock  CI-DEAS

Sweep 1  \(-198.886421\)  \(-198.962112\)

Sweep 20 (converged)  \(-198.970559\)  \(-198.970711\)

Table 5.1.: Total DMRG electronic energy of F\(_2\) with a CAS(14,32) converged starting from a Hartree-Fock (middle column) and a CI-DEAS initial state (right column) All calculations were carried out with \(m = 1024\) and an internuclear distance of 141 pm. Preoptimized orbitals from a CASSCF(14,8) calculation were employed and the orbital orderings are Hartree-Fock and mutual information optimized [30]. Note that for the moderate choice of \(m = 1024\), converged energies depend on the initial guess.

DMRG is an iterative method. The speed at which a converged solution is obtained strongly depends on the initial guess, i.e. the initial content of the \(M\) matrices in Eq. (1.6). In practice this guess requires the explicit construction of many-electron states in the complementary subsystem in the first (warm-up) sweep [76]. The simplest option is to encode the Hartree-Fock determinant and to add white noise to the reduced density matrix in order to avoid losing important basis states in the warm-up sweep [77]. Instead of white noise, one may apply a perturbative correction [34]. However, a more involved alternative, the CI dynamically extended active space (CI-DEAS) protocol [28] usually achieves the fastest convergence, i.e. requires the smallest number of sweeps, in our experience. In the warm-up sweep, the \(m\) most important determinants of the complementary subsystem, called the environment, which lies ahead of the current active sites, are selected such that the entanglement between it and the rest of the system is maximized. Table 5.1 shows how two different initial guesses affect the convergence rate in ground-state calculations of the F\(_2\) molecule with 14 electrons in 32 active orbitals and \(m = 1024\).
5.1. Determining Factors for the Accuracy of DMRG in Chemistry

5.1.6. Ordering of the orbitals

The ordering of the one-dimensional chain of orbitals can also have a strong impact on the convergence characteristics of a DMRG calculation [77, 78]. Unfortunately, there exists no obvious or simple relation between the ordering, which determines which explicitly treated site is considered next in a sweep, and the convergence properties of the iterations. Moreover, the choices of an optimal ordering and initial guess are intertwined. While a Hartree-Fock initial state performs well with a Hartree-Fock energetically orbital ordering, the entropy based CI-DEAS initial guess develops its full potential in combination with an ordering that tends to group pairs of orbitals with large mutual interaction close to each other, as described by Rissler [29, 30].

5.1.7. Choice of the number of renormalized subsystem states $m$

The magnitude of the error introduced in DMRG by limiting the number of renormalized basis states to some fixed number $m$ may limit the accuracy of a converged total electronic energy. However, $m$ is chosen by feasibility constraints as the computational effort depends on $m$. Whether a chosen value for $m$ might introduce errors into the converged energy can be assessed by inspecting the eigenvalue spectrum of the reduced density matrix as this determines the optimum number $m$ of eigenvectors to be selected for the decimation step. In practice, the convergence can be checked with calculations for different values of $m$. Clearly, results from different DMRG calculations can be extrapolated [7, 28, 77], for example with the formula

$$
\ln \left( \frac{E_{\text{DMRG}} - E_{\text{FCI}}}{E_{\text{FCI}}} \right) = a \ln \varepsilon + b.
$$

Because the truncation error $\varepsilon$ tends to zero if $m$ is increased, the precision of the obtained energies can be estimated by extrapolating them towards a truncation error of zero, which corresponds to an unlimited resource of $m$. A possible fit function, Eq. 5.1, which works well if $m$ is varied over an order of magnitude or more, was given by Legeza [28]. In Fig. 5.1, an extrapolation employing this fit function was performed for different ground state calculations of the F$_2$ molecule. From the figure, the estimated error is less than 10 $\mu$Hartree.

Besides extrapolation, the energy fluctuations that occur in two-site DMRG when the wave function is almost converged also indicate whether the number of renormalized basis states was chosen sufficiently large. With increasing $m$, the difference between the minimum and maximum energy obtained within a sweep tends to zero. The reason for these fluctuations is that the two explicitly treated sites in between the two subsystems can combine to produce different amounts of entanglement, depending on their position in the orbital chain. If $m$ was not limited, no loss of entanglement would occur and...
thus no fluctuations either. The error in the energy is therefore at least as large as the fluctuations.

5.2. Active space selection according to natural occupation numbers [79]

In spite of tremendous advances in the computer simulation of molecular electronic structure, the accurate description of systems with strong (non-dynamical or static) correlation is still far from being satisfactorily solved. Static correlation can be conveniently defined by the occupation numbers of the charge natural orbitals of the first order reduced density matrix, although this is an a posteriori definition, and can be applied only if a good approximation to the exact wavefunction is available. In closed-shell systems, orbitals with occupation numbers between $x$ and $1 - x$, with $x \approx 0.02$, correspond to the intuitive notion of static correlation and are called active orbitals. Although the transition between static and dynamical correlations is gradual, the two types of correlation differ qualitatively. Dynamical correlation arises from a large number of small contributions, and, although important for energy differences, it does not cause major local changes in potential energy surfaces. Nondynamical (static) correlation involves a modest number of orbitals with larger weights and often changes the nature of the wave-
function and the potential energy surface qualitatively. Dynamical correlation is well localized while the orbitals participating in static correlation are more delocalized. The importance of static correlation is that it is present in the transition states of chemical reactions which involve breaking or forming bonds, and also in most excited states. Systems with small HOMO-LUMO bandgap, such as compounds of electronegative first-row elements, conjugated and aromatic systems, and transition metal compounds, exhibit static correlation also in their equilibrium ground state.

As with any other active space method, the application of the DMRG algorithm to quantum chemical problems requires the choice of an active orbital space, which prior to a calculation may be selected based on empirical criteria or determined a posteriori according to natural orbital occupation numbers. A systematic procedure for active space selection has been proposed by Pulay in the 1980s with the Unrestricted Natural Orbital-CAS (UNO-CAS) method \[80, 81\]. It postulates that the charge natural orbitals of an unrestricted \[82, 83\] wavefunction with significant fractional occupancy (roughly between 0.02 and 1.98) should constitute the active space for nondynamical correlation. For a non-orthogonal finite basis set, they are given as

$$S(D_\alpha + D_\beta)SC = SCN,$$  \hspace{1cm} (5.2) 

where $S$ is the overlap matrix, $D_\alpha$ and $D_\beta$ are the reduced first order density matrices for the $\alpha$ and $\beta$ spins, respectively, the columns of $C$ contain the coefficients of the natural orbitals, and the diagonal matrix $n$ holds the occupation numbers.

A comprehensive evaluation of the adequacy of the UNO criterion, however, was impossible in the 1980s because of the lack of appropriate theoretical methods and computer resources. This evaluation requires comparison to CAS-type calculations with large active spaces (FCI or large active space CASSCF), to make sure that all orbitals with significant fractional occupancy have been identified. The exponential scaling and high cost of CAS calculations with large active spaces prevented this in the past. With the availability of fast quantum chemical DMRG implementations and increased computer resources, however, we were able to evaluate the UNO criterion in a collaboration with Pulay. We have compared UNO-CAS and CASSCF occupation numbers with DMRG results to assess the suitability of UNO-CAS for automatic active space generation \[79\]. The investigated systems included compounds of highly electronegative first-row elements (F$_2$ at several internuclear distances, ozone, and NO$_2$), conjugated (hexatriene, octatetraene, and decapentaene) and aromatic (naphthalene, azulene, anthracene, and nitrobenzene) molecules, aromatic radicals (benzyl, and phenoxo) and diradicals (o-, m-, and p-benzyne), and transition metal compounds (nickel-acetylene and Cr$_2$).

The analysis revealed, that UNO-CAS performs very well for most organic molecules. These systems usually have a single dominant correlating orbital associated with each strongly correlated occupied orbital. It is less successful for systems in which a strongly occupied orbital has several dominant correlation partners. In such cases, there are
Table 5.2.: Ground state energies of anthracene for different active spaces. Calculations performed in $D_{2h}$ symmetry.

usually multiple unrestricted Hartree-Fock (UHF) solutions which are often difficult to find because the UHF energy is a complicated function of orbital mixing angles, with several minima. The average UHF density usually gives the most important active orbitals. However, borderline orbitals with occupancies near the dynamical/static correlation threshold, say 0.02–0.05 and 1.95–1.98 may be missing.

As an example, we show the data for anthracene, one of the molecules studied. In this case, all methods determined the electronic $\pi$-system as the appropriate active space.

5.2.1. Example: ground state energies and natural orbital occupation numbers for anthracene

DMRG calculations in Table 5.2 are labeled as $\text{DMRG}(n_e, n_{\text{orb}})[m_{\text{min}}, m_{\text{max}}, \chi]$, where $n_e$, $n_{\text{orb}}$ are the number of correlated electrons and orbitals, $m_{\text{min}}$, $m_{\text{max}}$ the minimum and maximum number of renormalized basis states and $\chi$ the quantum information loss. If additionally $\text{DMRG}(x,y)[m_{\text{start}}, m_{\text{min}}, m_{\text{max}}, \chi]$ is specified, $m_{\text{start}}$ was used as minimal number of active-system states in the initialization procedure. Starting orbitals were generated with the MOLPRO program package [84].

Natural orbital isosurfaces

Orbitals labeled with $\text{C}$ are contained within the CASSCF active space. Orbitals marked with $\text{D1}$ are contained within the DMRG active space of 28 orbitals. If in addition $\text{D2}$ is specified, the orbital is also contained within the DMRG active space of 53 orbitals. The isovalues of the surfaces are $\pm 0.02$. 

<table>
<thead>
<tr>
<th>Method</th>
<th>$E$/Hartree</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAS(14,14)SCF</td>
<td>$-536.334$309</td>
</tr>
<tr>
<td>DMRG(14,28)[128,1024,10^{-5}]</td>
<td>$-536.355$217</td>
</tr>
<tr>
<td>DMRG(14,28)[256,1024,10^{-5}]</td>
<td>$-536.355$269</td>
</tr>
<tr>
<td>DMRG(26,53)[128,1024,10^{-5}]</td>
<td>$-536.363$438</td>
</tr>
<tr>
<td>DMRG(26,53)[256,1024,10^{-5}]</td>
<td>$-536.367$250</td>
</tr>
<tr>
<td>DMRG(26,53)[512,1024,10^{-5}]</td>
<td>$-536.367$331</td>
</tr>
</tbody>
</table>
5.2. Active space selection according to natural occupation numbers

<table>
<thead>
<tr>
<th>Orbital</th>
<th>UHF</th>
<th>UNO-CAS (14,14)</th>
<th>CAS-SCF (14,14)</th>
<th>DMRG(14,28) [256, 1024, 10^{-5}]</th>
<th>DMRG(26,53) [512, 1024, 10^{-5}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1b_{3u}</td>
<td>1.97433</td>
<td>1.96586</td>
<td>1.96551</td>
<td>1.96512</td>
<td>1.96520</td>
</tr>
<tr>
<td>1b_{1g}</td>
<td>1.96175</td>
<td>1.95457</td>
<td>1.95373</td>
<td>1.95432</td>
<td>1.95458</td>
</tr>
<tr>
<td>2b_{3u}</td>
<td>1.91847</td>
<td>1.93123</td>
<td>1.93196</td>
<td>1.93406</td>
<td>1.93494</td>
</tr>
<tr>
<td>1b_{2g}</td>
<td>1.91150</td>
<td>1.92650</td>
<td>1.92712</td>
<td>1.92843</td>
<td>1.92952</td>
</tr>
<tr>
<td>1a_{u}</td>
<td>1.84925</td>
<td>1.89743</td>
<td>1.90177</td>
<td>1.90472</td>
<td>1.90679</td>
</tr>
<tr>
<td>2b_{1g}</td>
<td>1.81315</td>
<td>1.88439</td>
<td>1.88932</td>
<td>1.89425</td>
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</tr>
<tr>
<td>2b_{2g}</td>
<td>1.55822</td>
<td>1.82102</td>
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<td>1.84439</td>
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<tr>
<td>3b_{3u}</td>
<td>0.44178</td>
<td>0.18444</td>
<td>0.17586</td>
<td>0.16289</td>
<td>0.15842</td>
</tr>
<tr>
<td>2a_{u}</td>
<td>0.18685</td>
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<td>0.11412</td>
<td>0.10379</td>
<td>0.10123</td>
</tr>
<tr>
<td>3b_{1g}</td>
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<td>0.10257</td>
<td>0.09841</td>
<td>0.09166</td>
<td>0.08946</td>
</tr>
<tr>
<td>4b_{3u}</td>
<td>0.08850</td>
<td>0.07271</td>
<td>0.07147</td>
<td>0.06638</td>
<td>0.06490</td>
</tr>
<tr>
<td>3b_{2g}</td>
<td>0.08153</td>
<td>0.06860</td>
<td>0.06759</td>
<td>0.06219</td>
<td>0.06086</td>
</tr>
<tr>
<td>3a_{u}</td>
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<td>0.04237</td>
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<td>0.03805</td>
</tr>
<tr>
<td>4b_{2g}</td>
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<td>0.02980</td>
<td>0.02980</td>
<td>0.02719</td>
<td>0.02664</td>
</tr>
</tbody>
</table>

Table 5.3.: Natural occupation numbers for anthracene.
Chapter 5. MPO DMRG for Chemistry

Figure 5.2.: Orbitals $11a_g - 14a_g$

(a) $11a_g$
(b) $12a_g$
(c) $13a_g$
(d) $14a_g$

$D2$

Figure 5.3.: Orbitals $15a_g - 17a_g$

(a) $15a_g$
(b) $16a_g$
(c) $17a_g$

$D2$

Figure 5.4.: Orbitals $9b_{2_u} - 12b_{2_u}$

(a) $9b_{2_u}$
(b) $10b_{2_u}$
(c) $11b_{2_u}$
(d) $12b_{2_u}$

$D2$

Figure 5.5.: Orbitals $13b_{2_u} - 15b_{2_u}$

(a) $13b_{2_u}$
(b) $14b_{2_u}$
(c) $15b_{2_u}$

$D2$

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5.2. Active space selection according to natural occupation numbers

Figure 5.6.: Orbitals $10b_{1u} - 13b_{1u}$

Figure 5.7.: Orbitals $14b_{1u} - 15b_{1u}$

Figure 5.8.: Orbitals $8b_{3g} - 11b_{3g}$

Figure 5.9.: Orbital $12b_{3g}$
Chapter 5. MPO DMRG for Chemistry

Figure 5.10.: Orbitals $1b_{3u}$ – $4b_{3u}$

Figure 5.11.: Orbitals $5b_{3u}$ – $8b_{3u}$

Figure 5.12.: Orbitals $1b_{1g}$ – $4b_{1g}$

Figure 5.13.: Orbitals $5b_{1g}$ – $6b_{1g}$
5.2. Active space selection according to natural occupation numbers

![Orbitals 1b₂g – 4b₂g](image1)

(a) $1b₂g$

$C, D₁, D₂$

(b) $2b₂g$

$C, D₁, D₂$

(c) $3b₂g$

$C, D₁, D₂$

(d) $4b₂g$

$C, D₁, D₂$

Figure 5.14.: Orbitals $1b₂g – 4b₂g$

![Orbitals 5b₂g – 8b₂g](image2)

(a) $5b₂g$

$D₁, D₂$

(b) $6b₂g$

$D₁, D₂$

(c) $7b₂g$

$D₁, D₂$

(d) $8b₂g$

$D₁, D₂$

Figure 5.15.: Orbitals $5b₂g – 8b₂g$

![Orbitals 1aₜ – 4aₜ](image3)

(a) $1aₜ$

$C, D₁, D₂$

(b) $2aₜ$

$C, D₁, D₂$

(c) $3aₜ$

$C, D₁, D₂$

(d) $4aₜ$

$D₁, D₂$

Figure 5.16.: Orbitals $1aₜ – 4aₜ$

![Orbitals 5aₜ – 6aₜ](image4)

(a) $5aₜ$

$D₁, D₂$

(b) $6aₜ$

$D₁, D₂$

Figure 5.17.: Orbitals $5aₜ – 6aₜ$
Using the DMRG algorithm, $n$-orbital reduced density matrices are easily obtained from the full density matrix by tracing out contributions from all orbitals in the complementary set of orbitals in the active space. As a consequence, entanglement measures such as the single-orbital entropy [86] and mutual information [30, 87] calculated from the one-orbital and two-orbital reduced density matrix, respectively, are easily accessible. These orbital-based entanglement measures can be applied to examine the multireference character of the electronic wave function. In particular, they can be correlated with the amount of static and dynamic electron correlation in an electronic wavefunction [73] or exploited to study chemical bonding in molecule formation and dissociation processes [42, 88]. Thus, they complement the traditional orbital-based correlation measures such as the natural orbital and geminal analysis [80].

From the CI-type expansion coefficients of the DMRG wavefunction, a density matrix is constructed, in which environment states can be traced out. These states are defined on orbitals of the active space that are not considered part of a selected subsystem of orbitals. In the single-orbital case, the selected subsystem consists of only one spatial orbital with four possible states (empty, spin-up, spin-down and doubly-occupied) quantum-mechanically embedded into all other orbitals of the active space. States defined on these complementary orbitals are the environment states traced out in the (then) reduced density matrix. The four eigenvalues of this reduced density matrix, $\omega_{\alpha,i}$, enter a von Neumann entropy expression, which yields the single-orbital entropy, $s(1)_i$, for a given orbital $i$, which can be understood as a measure of the interaction of one orbital with all other orbitals:

$$s(1)_i = -\sum_{\alpha} \omega_{\alpha,i} \ln \omega_{\alpha,i}. \quad (5.3)$$

In the same way, a two-orbital entropy, $s(2)_{i,j}$, can be calculated from the sixteen eigenvalues of the reduced density matrix that is valid for the subsystem consisting of the two selected orbitals $i, j$:

$$s(2)_{i,j} = -\sum_{\alpha} \omega_{\alpha,i,j} \ln \omega_{\alpha,i,j}. \quad (5.4)$$

As this two-orbital entropy still contains single-orbital-entropy contributions, the two single-orbital entropies may be subtracted, which yields the mutual information, $I_{i,j}$, for orbitals $i$ and $j$:

$$I_{i,j} = \frac{1}{2} \left( s(2)_{i,j} - s(1)_i - s(1)_j \right)(1 - \delta_{i,j}). \quad (5.5)$$

The central aspect of these measures is that the quantum entanglement of the states defined on one and two orbitals, respectively, has been properly encoded through the eigenvalues of the reduced density matrices.
5.4. Considering a structural chemical environment

These entanglement measures are implemented in QCMAQUIS and have been used to investigate the electronic structure of the ruthenium coordination sphere in the trans-[RuCl₄(NO)(1H-indazole)]-complex [85], which is closely related to the anti-cancer drug KP1019 [89]. Fig. 5.18 shows the entanglement between localized orbitals in the DMRG(18,18)[100] S₀ wavefunction with m as indicated within the brackets. From the plot, orbitals 4, 5, 7, 9, 10, 11 can be distinguished from the other orbitals as strongly interacting, participating in static correlation. Furthermore, the weak entanglement of orbitals 14 to 18 indicate, that the inclusion of these double d-shell orbitals in the active space does not significantly affect the entanglement in the Ru-NO bond. A population analysis of the S₀ wavefunction expressed in terms of configuration state functions (CSFs) transformed to the localized orbitals shown in Fig. 5.18 reveals, that RuIII(d⁶) and RuII(d⁶) configurations are equally important [85], yielding a formal oxidation state of 2.5 for the ruthenium atom.

5.4. Considering a structural chemical environment [90]

Chemical reactions are local phenomena, in which usually only one or two bonds are formed or broken at a time. For this reason, the cluster approach was established in computational chemistry, in which the atomistic rearrangements under study are embedded in a structural model that is as large as necessary to comprise all electronic effects on the reactive subsystem (see, for instance, the extensive work on such cluster models for active sites of metalloproteins by Siegbahn, Himo, and co-workers [91]). In general, long-range electrostatic interactions may not be neglected and schemes have been devised to incorporate them (most prominent are quantum-mechanical/molecular-mechanical embedding [92, 93] and polarizable continuum models [94]).

Clearly, the embedding of a quantum system of interest into a more or less electronically noninnocent environment is the realm of open-system quantum theory [95]. The central quantity of this well-known theory is the reduced density matrix of a subsystem rather than the wavefunction of a stationary state. This formalism has recently been adapted for an embedding framework [96, 97]. However, it is not straightforward to employ (for instance, the environment had to be approximated in a mean-field fashion). Practical suggestions for the applicability to large chemical systems have been made [98].

Considering the success of density functional theory (DFT) for routine applications in computational chemistry, a feasible approach that is able to describe chemically complex and structured environments should also be based on DFT. In the frozen density embedding [99] (FDE) scheme, which is based on subsystem DFT [100, 101], a subsystem is calculated in a Kohn–Sham (KS) approach by adding an effective potential to the KS potential of the isolated subsystem. It takes into account all interactions with the
Figure 5.18.: Single-orbital entropy, $s_i(1)$, and mutual information, $I_{i,j}$, in the DMRG(18,18)[1000] $S_0$ wavefunction of RuHIndNO. The size of the red circles next to the orbitals correlates with the magnitude of the corresponding single-orbital entropy. The lines connecting the dots represent the mutual information: solid lines indicate strong entanglement ($I_{i,j} > 0.1$), dashed grey lines stand for middle entanglement ($0.01 > I_{i,j} > 0.1$) and dotted green lines indicate weak entanglement ($0.001 > I_{i,j} > 0.01$). The line width is also proportional to the absolute value of $I_{i,j}$. This figure was reprinted from the original publication [85].
environment, assuming a constant (frozen) environmental electron density. In FDE not only the exchange–correlation energy contribution, but also the non-interacting kinetic energy term is calculated from an approximate explicit density functional. No knowledge of orbitals of the supersystem is needed for an FDE/subsystem DFT calculation, nor do the orbitals of the active subsystem need to be orthogonal to those of the environmental subsystems. In this way, large environments can be considered, but due to the limited accuracy of kinetic energy functionals for chemical systems, FDE cannot be directly applied to subsystems which are connected via bonds with covalent character [102].

In FDE, the total electron density is represented by a sum of subsystem densities, here denoted as an active ($\rho_{\text{act}}$) and environmental ($\rho_{\text{env}}$) density,

$$\rho_{\text{tot}}(\mathbf{r}) = \rho_{\text{act}}(\mathbf{r}) + \rho_{\text{env}}(\mathbf{r}).$$

A goal of FDE is determining $\rho_{\text{act}}(\mathbf{r})$, given a certain $\rho_{\text{env}}(\mathbf{r})$. The active subsystem density is found by variationally optimizing the energy of the total system w.r.t. the density $\rho_{\text{act}}(\mathbf{r})$. Through an iterative exchange of the role of active and environmental densities known as 'freeze-and-thaw' (f&t) [103], FDE becomes equivalent to subsystem DFT[104]. The computational steps for embedding an active subsystem represented by and MPS into an environment described by DFT are then as follows:

1. Calculate initial DFT densities $\rho_{\text{env}}^{(0)}$ and $\rho_{\text{act}}^{(0)}$ (as well as DFT density gradients, DFT Hessians, and electrostatic potentials) for the isolated subsystems; set iteration counter $i = 1$.

2. Calculate an embedding potential for the environmental subsystem,

$$v_{\text{emb}}^{\text{env}}(\rho_{\text{env}}^{(i-1)}; \rho_{\text{act}}^{(i-1)})(\mathbf{r}).$$

3. Perform an embedded DFT calculation on the environmental subsystem with $v_{\text{emb}}^{\text{env}}(\rho_{\text{env}}^{(i-1)}; \rho_{\text{act}}^{(i-1)})$ and then calculate $\rho_{\text{env}}^{(i)}$ (as well as its gradient, Hessian, and the electrostatic potential).

4. Calculate an embedding potential for the active subsystem, $v_{\text{emb}}^{\text{act}}(\rho_{\text{act}}^{(i)}; \rho_{\text{env}}^{(i)})(\mathbf{r})$.

5. Carry out the 4-index transformation to obtain the two-electron integrals in the molecular orbital basis of the active subsystem; the basis-functions to molecular-orbitals transformation of the one-electron integrals yields the WFT part that carries the embedding information.

6. Perform an embedded DMRG calculation on the active subsystem using $v_{\text{emb}}^{\text{act}}(\rho_{\text{act}}^{(i)}; \rho_{\text{env}}^{(i)})$ and then calculate $\rho_{\text{act}}^{(i)}$ (as well as its gradient, Hessian, and the electrostatic potential) from the DMRG wavefunction.

7. Increase iteration counter $i$ by 1. Repeat steps 2 to 6 until convergence is achieved.
<table>
<thead>
<tr>
<th>Method</th>
<th>Active fragment(s)</th>
<th>Env.</th>
<th>$\mu$ (per HCN)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Monomer</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DMRG(10,9)[4096]-SCF</td>
<td>A</td>
<td>...</td>
<td>3.09</td>
</tr>
<tr>
<td>DFT</td>
<td>A</td>
<td>...</td>
<td>2.96</td>
</tr>
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<td>DMRG(10,9)[4096]-SCF</td>
<td>A</td>
<td>DFT</td>
<td>3.54</td>
</tr>
<tr>
<td>DFT</td>
<td>A</td>
<td>DFT</td>
<td>2.42</td>
</tr>
<tr>
<td>DMRG(10,9)[4096]-SCF</td>
<td>B</td>
<td>DFT</td>
<td>3.43</td>
</tr>
<tr>
<td>DFT</td>
<td>B</td>
<td>DFT</td>
<td>2.32</td>
</tr>
<tr>
<td><strong>Dimer</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DMRG(20,18)-SCF[4096]</td>
<td>A+B</td>
<td>...</td>
<td>3.44</td>
</tr>
<tr>
<td>DMRG(20,18)-SCF[4096]</td>
<td>A+B</td>
<td>DFT</td>
<td>3.91</td>
</tr>
<tr>
<td>DFT</td>
<td>A+B</td>
<td>DFT</td>
<td>3.93</td>
</tr>
<tr>
<td><strong>Tetramer</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DMRG(40,36)-SCF[2048]</td>
<td>all</td>
<td>...</td>
<td>3.81</td>
</tr>
</tbody>
</table>

Table 5.4.: Dipole moment $\mu$ in debye per HCN molecule in the presence and absence of other HCN molecules as depicted in Fig. 5.19. Isolated HCN (central) dimer and tetramer calculations are compared to the corresponding ones for the embedded monomer and dimer, respectively, in which the environment "Env." is represented by a DFT density. Data taken from Ref. [105].

At the example of a HCN tetramer shown in Fig. 5.19 the dipole moment per molecule was investigated [90] with the described embedding strategy. HCN chains exhibit cooperative behaviour which increases the dipole moment per molecule in the chain compared to isolated HCN. Table 5.4 comprises the calculated dipole moments obtained using either a supermolecular or the DMRG/DFT-in-DFT approach. The reference DMRG-SCF calculation on the (central) supermolecular dimer comprised an active space of 20 electrons in 18 orbitals (twice the valence complete active space for one HCN molecule, which is a CAS(10,9)). We observe only small differences in the dipole moments between the DFT and the DMRG calculations. A qualitatively correct polarization of the embedded HCN molecule compared to its isolated counterpart can be observed. An advantage of the subsystem approach is the possibility to investigate the properties of only one subsystem in the presence of other subsystems. To demonstrate this feature, we collected the different dipole moments for the two different HCN molecules A and B in Table 5.4.
5.4. Considering a structural chemical environment

Figure 5.19.: Structure of the (HCN)$_4$ benchmark system. Internuclear distances, which specify the linear HCN chain, are given in Å. The shaded regions denote the two HCN molecules that serve as an environment for the dimer (HCN)$_2$ (i.e., A + B) in the DMRG-in-DFT embedding calculation. This figure was reprinted from the original publication [90].
Conclusions & Outlook

In this work, we provided a prescription for the efficient construction of the quantum chemical Hamiltonian in Eq. (2.8) as an MPO. Our construction scheme ensures the same computational scaling as traditional DMRG, compared to which a similar performance is achieved. In order to be efficient, traditional first-generation quantum chemical DMRG programs require to define many auxiliary operators which consider contractions of sequences of creation and annihilation operators in the Hamiltonian that are defined on the same part of the lattice (e.g., on the environment). Especially the four elementary operators in each term of the full electron-electron Coulomb interaction then generate most of these auxiliary operators. The algorithm presented here does not require to predefined such auxiliary operators, but instead, this formal structure — i.e., assignment of elementary operators to the corresponding parts of the lattice and subsequent contraction — is taken care of implicitly by the algorithmic structure of the program. This feature makes an efficient implementation of any observable easy and elegant in our MPO-based implementation. Whereas a naive construction of the Hamiltonian MPO would lead to a computational scaling of $O(m^3L^5)$, our algorithm presented here yields the same scaling as traditional DMRG, $O(m^3L^3) + O(m^2L^4)$. When it comes to convergence characteristics, we note that our MPO-based quantum chemical DMRG algorithm will behave as a traditional one. Therefore, we have implemented all established means for the warm-up sweep that help accelerating convergence to the correct electronic energy. The advantages of a full matrix product formulation of all wave functions and operators involved in the DMRG algorithm are the efficient calculation of low-lying excited states, straightforward implementation of new observables, and additional flexibility that allows us to accommodate different models and symmetries in a single source code.

Additionally, we developed a formalism for the incorporation of non-abelian spin symmetry into second-generation DMRG, which is a purely MPO-based formulation of the DMRG algorithm for quantum chemistry. The MPO concept allows one to clearly separate the operator from the contraction formula in which the operator is applied to a wave
function. We can therefore achieve spin adaptation for all the building blocks consisting of elementary site-operators, the matrix product basis, and the contraction formula in Eq. (3.31) individually. This modularity facilitates a flexible implementation, which was then applied to dioxygen as a numerical example.

Concerning applications, different parameters of the DMRG algorithm determine the accuracy and performance DMRG calculations. As with other active space methods, the selection of the orbital basis and the active space has a strong effect on the quality of results obtained. However, by contrast to standard approaches such as CASSCF, DMRG involves another decisive parameter and that is the number of renormalized states kept on the active subsystem during the iterations. In addition, the factors that control DMRG convergence are the initial guess and the orbital ordering. Finally, the accuracy of results can be verified by performing an extrapolation. All these parameters need to be reported and kept in mind when DMRG results are discussed. Hence, the favorable polynomial scaling of DMRG, which makes it a true competitor to standard methods, affords a set of parameters that need to be well controlled in order to guarantee results exploitable in the study of spectroscopy and chemical reactivity.

While the addition of DMRG to the toolset of theoretical chemistry redefined the limits of active space calculations, especially for systems that exhibit static correlation, DMRG remains too expensive to describe dynamical correlation in the total orbital space. Instead, perturbative approaches, especially NEVPT2 (second-order N-electron valence state perturbation theory) [106–108], provide a promising route for the inclusion of dynamical correlation on top of a DMRG reference wavefunction [109–112]. The link between DMRG and perturbation theory is mediated through higher order (up to 4th order in the case of NEVPT2) reduced density matrices, the efficient calculation of which will provide new challenges in future work.
QCMaquis program structure

Matrix-product tensor subunit

The matrix-product tensor subunit contains the MPS and MPO classes and related classes that build up the MPS and MPO through composition.

Symmetry groups

Various symmetry group classes abstract the action of symmetry through a common interface; each group provides a fuse function that performs quantum number addition. The symmetry group is a system-wide C++ template, such that all tensor objects are agnostic of any symmetry detail.

Quantum numbers (charges)

Each symmetry group provides its class of quantum number, referred to as charge in the code. They are (small) arrays of integers that participate in the fuse group action defined in the symmetry group. The elementary charges defining the basis states on a single site are defined once in the constructor of each model class.

Indices

Indices are sorted vectors of (charge, integer) pairs and as such a) label the matrix blocks in the block_matrix class with a quantum number and a size and b) describe how many states with a given quantum number occur in a subsystem spanning sites 1...s or s...L, s = 1...L. Due to the sorted property, quantum numbers can be retrieved in logarithmic time with respect to the index size. Indices support a multiplication operation. The product index

\[ I_C = I_A \ast I_B; \]  

(A.1)
contains all the possible combinations of quantum numbers in $I_A$ and $I_B$, corresponding to a tensor product of the two bases.

**Dense matrices**

QCMAQUIS employs the dense matrix class from the ALPS libraries to represent the blocks of the block matrix class. ALPS dense matrices feature automatic dispatch of BLAS operations (addition, scalar-matrix multiplication, matrix-matrix multiplication) to fast BLAS libraries such as MKL.

**Block matrices**

The block matrix class represents a collection of dense matrix blocks corresponding to certain symmetry sectors labeled by quantum numbers. It is composed of two indices to describe the blocks and of the dense matrix blocks themselves. A wide range of manipulation functions (such as block insertion, removal) and arithmetic operations (such as addition, multiplication, singular value decomposition) are implemented.

**MPS tensors**

To describe the three sets of quantum numbers $\sigma_i, q_{i-1}$ and $q_i$ of an MPS tensor $M_{\sigma_i q_{i-1} q_i a_{i-1} a_i}$, the MPS tensor class consists of three index objects. For efficiency reasons (see Sec. 4.2.1), the block matrices corresponding to the local basis states $\sigma_i$ are collected in a single block matrix data, which is either in a left- or right-paired state. The MPS tensor class also contains the necessary routines for converting between both representations and functions for left- and right-normalization through singular value decomposition.

**MPO tensors**

MPO tensors are matrix-valued matrices, which is directly reflected in the implementation. The outer matrix is represented with a sparse matrix class from the boost library. The entries of this sparse matrix correspond to elementary site operators represented with block matrices; in the implementation, only a scale factor and an offset into a table containing a list of site operators is stored in the sparse matrix. In this way, the unique site operators, of which there are but a few, need only be stored once.
Figure A.1.: UML diagram of the matrix-product tensor subunit
Simulation/model subunit

Simulation

The `sim` class is the control center of the QCMAQUIS program. It stores the MPS and the MPO and keeps pointers to a lattice and model instance. The derived classes `dmrg_sim` and `measure_sim` start optimization or measuring tasks.

Model

The various model classes gather model specific properties and information and implement different Hamiltonians. Constituting steps are the definition of a local basis for each site and corresponding elementary site operators. All terms occurring in the desired Hamiltonian are then generated by combining the site operators with one- and two-electron integrals.

Lattice

Lattice specific properties are the number connectivity of the sites, presence or absence of point group symmetry and barred- or unbarred-labeling of spinors in the case of relativistic calculations.

Contraction engines subunit

In the contraction engines subunit, MPS and MPO object are combined in expectation value computations and the matrix-vector multiplication employed by sparse eigenvalue solvers such as the Jacobi-Davidson algorithm.

Engines

The ablian and SU2 engines correspond to an interface class, implementing a common interface with the rest of the code for accessing contraction routines. But due to the design of QCMAQUIS, the specific type of contraction engine used is hidden to client code through template specialization rather than virtual functions. The main operations provided through the engine interface are the boundary propagation towards the left and the right (Eq. (1.38) and Eq. (1.40)) as well as the matrix-vector multiply operation `site_hamil`. 
Figure A.2.: UML diagram of the simulation/model subunit
**Generic contractions**

Some of the contraction routines can be formulated in a general fashion independent of symmetry, where the symmetry dependent part is encapsulated in numeric routines called kernels. In the engine interface class, the correct templates are supplied to the functions listed here, allowing code reuse for all symmetry groups.

**Kernels**

These functions perform tasks 2 and 3 in Fig. 1.3, i.e. they take the product of a boundary with and \texttt{MPSTensor} and apply and \texttt{MPOTensor} row- or column-wise. Most of the execution time is spent in these numeric kernels.

**Boundaries**

Boundaries are vectors of \texttt{block matrices} and store partially contracted tensor networks, typically a left or right subsystem. In these partial contractions, local site indices $\sigma_i$ have been summed over, which is why \texttt{block matrices} rather than MPSTensors are employed. Another noteworthy feature of boundaries is the disk-I/O handling. For economical memory usage, boundaries may be asked to write themselves to disk for later usage. This is done in an asynchronous thread and therefore not impacting runtime performance. Moreover, there is no latency penalty through slow disk access if the boundary is asked early enough prior to usage to transfer itself to memory again.
Appendix A. QCMAQUIS program structure

**SU2 Engine**
- `+site_hamil(ket_tensor:MPSTensor, left:Boundary, right:Boundary, mpo:MPOTensor): MPSTensor`

**Abelian Engine**
- `+site_hamil(ket_tensor:MPSTensor, left:Boundary, right:Boundary, mpo:MPOTensor): MPSTensor`

**Generic contractions**

**SU2 kernels**
- `+rbtm_kernel(right_mult_mps:Boundary, mpo:MPOTensor): block_matrix`
- `+lbtm_kernel(left_mult_mps:Boundary, mpo:MPOTensor): block_matrix`
- `+gemm(A:block_matrix, B:block_matrix): block_matrix`

**SU2 Engine**
- `+site_hamil(ket_tensor:MPSTensor, left:Boundary, right:Boundary, mpo:MPOTensor): MPSTensor`

**Abelian site_hamil**
- `+site_hamil(ket_tensor:MPSTensor, left:Boundary, right:Boundary, mpo:MPOTensor): MPSTensor`

**SU2 site_hamil**
- `+site_hamil(ket_tensor:MPSTensor, left:Boundary, right:Boundary, mpo:MPOTensor): MPSTensor`

Figure A.3.: UML diagram of the contraction engine subunit
Keywords and Options for QCMaquis

Dr. S. Knecht is gratefully acknowledged for compiling the following list of keywords and tools.

In the following we describe (i) compulsory keywords (Section B), (ii) optional keywords (Section B) for QCMaquis DMRG calculations as well as (iii) keywords for property calculations (Section B). Most of the QCMaquis keywords have default settings that guarantee convergence in the general case and are inserted automatically by the host program (MOLCAS [113] in this case). A reasonable choice of default values for optional keywords is given in our example QCMaquis input file in Section B.

Caution! QCMaquis has many features beyond quantum chemistry, e.g. related to solid state physics. Some keywords listed in the example file in Section B are therefore not explained in the following and are not to be changed if a quantum chemical calculation is desired.

Compulsory keywords

The keywords in Table B.1 have to be set for every DMRG calculation since they may crucially affect the accuracy of the final result. Their choice depends for example on the molecule under consideration (do you expect strong static electron correlation and/or dynamical correlation to play a major role), the nature of the reference orbitals (Hartree-Fock orbitals, natural orbitals of some kind, . . . ), the size of the active space, and many other aspects. We refer the reader to Ref. [71] which gives a detailed introduction to DMRG calculations in quantum chemistry. Further examples starting from different computational setups are discussed for example in Refs. [85, 90, 112, 114, 115].
Some of the compulsory keywords listed in Table B.1 are indeed automatically set if you run a QCMAQUIS DMRG calculation through the QCMAQUIS host program driver which is the case for MOLCAS-QCMAQUIS DMRG calculations. In this case skip the upper part of Table B.1 and proceed immediately to the lower part marked by “Keywords NOT set by the host program MOLCAS”.

Table B.1.: Compulsory keywords to be set in all QCMAQUIS DMRG calculations.

<table>
<thead>
<tr>
<th>keyword</th>
<th>description</th>
</tr>
</thead>
<tbody>
<tr>
<td>nelec</td>
<td>Total number of electrons.</td>
</tr>
<tr>
<td>irrep</td>
<td>Irreducible representation of the point group symmetry of the target state. <strong>Note:</strong> Counting starts with 0 which has to be the totally symmetric representation.</td>
</tr>
<tr>
<td>spin</td>
<td>Total spin ((2 \times S)) of the target state, for example: (\text{spin}=0) (singlet), (\text{spin}=1) (doublet), (\text{spin}=2) (triplet), …</td>
</tr>
<tr>
<td>L</td>
<td>Length of lattice = number of orbitals in the active space.</td>
</tr>
<tr>
<td>integral_file</td>
<td>Path and filename of the integral file, for example  (\text{integral_file} = /path/to/file/FCIDUMP)</td>
</tr>
<tr>
<td>chkpfile</td>
<td>Path and name of the folder in which the MPS is stored.</td>
</tr>
</tbody>
</table>
Table B.1 – continued from previous page

<table>
<thead>
<tr>
<th>keyword</th>
<th>description</th>
</tr>
</thead>
<tbody>
<tr>
<td>resultfile</td>
<td>Path and filename of the result file.</td>
</tr>
<tr>
<td></td>
<td>If an excited state calculation is desired, the number of states the current wave function is to be orthogonalized against shall be specified here.</td>
</tr>
<tr>
<td>n_ortho_states</td>
<td>Path(s) and filename(s) of the MPS checkpoint file(s) that store the lower lying states to which the current MPS shall be orthogonal to.</td>
</tr>
<tr>
<td>ortho_states</td>
<td>Possible options are default, thin and hf. The default and thin initializations fill the initial MPS with random numbers, the difference being that a singular value decomposition reduces the bond dimension to init_bond_dimension in the case of thin. Usage of hf generates an MPS consisting of only the determinant defined on the hf_occ card. Note that the CI-DEAS procedure [86, 114] (as invoked by dmrginit.py, see Section B) behaves like a restart from the newly generated CI-DEAS MPS.</td>
</tr>
<tr>
<td>init_state</td>
<td>default in Molcas: init_state = &quot;default&quot;</td>
</tr>
</tbody>
</table>
Table B.1 – continued from previous page

<table>
<thead>
<tr>
<th>keyword</th>
<th>description</th>
</tr>
</thead>
<tbody>
<tr>
<td>max_bond_dimension</td>
<td>Maximum number of renormalized states (commonly referred to as $m$-value or virtual bond dimension) kept during each microiteration step of a forward- or backward sweep.</td>
</tr>
<tr>
<td>nsweeps</td>
<td>Maximum number of DMRG sweeps. Please be aware that $\text{nsweeps}$ sets the number of combined forward and backward sweeps. Thus, the actual number of sweeps is $2 \times \text{nsweeps}$.</td>
</tr>
<tr>
<td>conv_thresh</td>
<td>Sets the energy convergence threshold (in Hartree). If the lowest energy from the previous sweep differs from the lowest energy of the current sweep by less than the value set here, the calculation is stopped.</td>
</tr>
</tbody>
</table>

**Optional keywords**

The keywords summarized in Table B.2 may be exploited by the more experienced user but can be safely ignored by those who just want to get started. They may affect the convergence and accuracy of the final result, though. For the inexperienced user however, we advise to not change these settings and accept the default values provided by QCMAQUIS.
<table>
<thead>
<tr>
<th>keyword</th>
<th>description</th>
</tr>
</thead>
<tbody>
<tr>
<td>orbital_order</td>
<td>Manual ordering of the orbitals along the one dimensional lattice. The order has to be entered as a string of comma separated orbital numbers. We recommend the Fiedler ordering based on the mutual information [13, 114] which can be obtained by means of the python script fiedler.py (see Section B). default: orbital_order = &quot;1,2,3,4,5,6,...&quot;</td>
</tr>
<tr>
<td>init_bond_dimension</td>
<td>Adjusts the maximal bond dimension of the MPS produced by the CI-DEAS procedure [86, 114].</td>
</tr>
<tr>
<td>ietl_jcd_tol</td>
<td>Convergence threshold for the Jacobi-Davidson diagonalization.</td>
</tr>
<tr>
<td>ietl_jcd_maxiter</td>
<td>Maximum number of iterations in the Jacobi-Davidson diagonalization.</td>
</tr>
<tr>
<td>truncation_initial</td>
<td>If during the ngrowsweeps, the sum of the discarded singular values for m retained states is lower than the value defined here, more block states will be discarded until the discarded sum increases to truncation_initial</td>
</tr>
<tr>
<td>truncation_final</td>
<td>If during the nmainsweeps, the sum of the discarded singular values for m retained states is lower than the value defined here, more block states will be discarded until the discarded sum increases to truncation_final</td>
</tr>
<tr>
<td>keyword</td>
<td>description</td>
</tr>
<tr>
<td>---------------------</td>
<td>-----------------------------------------------------------------------------</td>
</tr>
<tr>
<td>nmainsweeps</td>
<td>Number of sweeps in which truncation_final is used in the singular value decomposition.</td>
</tr>
<tr>
<td>ngrowsweeps</td>
<td>Number of sweeps in which truncation_initial is used in the singular value decomposition.</td>
</tr>
<tr>
<td>measure_each</td>
<td>Tells the program to compute the expectation values every $2 \times \text{measure_each}$ sweeps.</td>
</tr>
<tr>
<td>symmetry</td>
<td>Defines the total symmetry group. Default is the combined spin (SU2) and point symmetry group (PG) su2u1pg, where the pg-suffix should be omitted for better performance if the molecule is C1-symmetric. For test purposes, it is possible to switch off spin-adaptation, again with or without point group symmetry: 2u1(pg). In the latter case the keywords spin and nelec (see Section B) have no meaning. Instead u1_total_charge1 and u1_total_charge2 corresponding to the number of up and down electrons have to be specified.</td>
</tr>
</tbody>
</table>
Table B.2 – continued from previous page

<table>
<thead>
<tr>
<th>keyword</th>
<th>description</th>
</tr>
</thead>
<tbody>
<tr>
<td>chkp_each</td>
<td>Tells the program to update the checkpoint file every (2 \times \text{chkp_each}) sweeps.</td>
</tr>
</tbody>
</table>

Occupation of the starting orbitals (e.g. Hartree-Fock occupation) to be entered as a comma separated string of occupation aliases. The aliases are defined as follows: 4 = full, 3 = up, 2 = down, 1 = empty. This information has to be entered in case of hf as init\_state and for the CI-DEAS procedure \cite{86, 114} as invoked by dmrginit.py.

example: hf\_occ = "4,4,4,2,2,1" for a CAS(8,6) triplet state setup where the unpaired electrons are “located” in orbital # 4 and # 5.

---

**Keywords for expectation value calculations**

QCMAQUIS can (in principle) compute expectation values for any one- or two-particle operator that can be formulated in second quantization. Table B.3 comprises a list of the available property keywords in the release version of QCMAQUIS. For further updates/other properties please contact dmr@phys.chem.ethz.ch. The one-particle reduced density matrix as well as the one-particle spin-density matrix are implicitly computed from the expectation values of some of the operators contained in MEASURE[ChemEntropy].
Table B.3.: Expectation value calculations available in the release version of QC-Maquis.

<table>
<thead>
<tr>
<th>expectation value</th>
<th>description</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEASURE[ChemEntropy]</td>
<td>All expectation values over the operators required to calculate the mutual information (as specified in Ref. [73]) will be computed. Please note that this is available only for SU2 symmetry.</td>
</tr>
<tr>
<td>MEASURE[1rdm]</td>
<td>Computes the one-particle reduced density matrix, without the additional correlators contained in the ChemEntropy measurement.</td>
</tr>
<tr>
<td>MEASURE[2rdm]</td>
<td>Computes the two-particle reduced density matrix.</td>
</tr>
</tbody>
</table>
| MEASURE_LOCAL[name] = "op" | Computes \( \langle \psi | op_i | \psi \rangle \), \( i = 1 \ldots L \). \( \text{Nup, Ndown} \) and \( \text{Nup*Ndown} \) are meaningful choices for \( \text{op} \). Available for \( 2u1(pg) \) only.  
*Note: name defines the name under which the expectation values are stored on the resultfile.* |
| MEASURE_HALF_CORRELATIONS[name] = "op_1:op_2" | Computes \( \langle \psi | op_{i_1} op_{j_2} | \psi \rangle \), \( i = 1 \ldots L, j = i + 1 \ldots L \). \( \text{Nup, Ndown, Nup*Ndown, cdag_up, cdag_down, c_up, c_down, cdag_up*Ndown, c_up*Ndown, cdag_down*Nup, c_down*Nup, cdag_up*cdag_down, c_up*c_down, cdag_up*c_down, and cdag_down*c_up, as \( op_1 \) and \( op_2 \) are recognized by the program. Available for \( 2u1(pg) \) only.  
*Note: name defines the name under which the expectation values are stored on the resultfile.* |
QCMaquis tools

QCMaquis comes with several tools that allow for example further manipulation of the MPS or to acquire additional wave function analysis information. The tools `det2mps"symmetry", mps2ci` and `mps_transform(\"pg\")` will be briefly described in the following. These tools are provided in the `my-Molcas-build/qcmaquis/bin` folder.

<table>
<thead>
<tr>
<th>tool</th>
<th>description</th>
</tr>
</thead>
<tbody>
<tr>
<td><code>det2mps_symmetry</code></td>
<td>This tool generates determinants based on the CI-DEAS procedure [86] and inserts them in an MPS from which a new DMRG calculation can be started. Starting from such an MPS is likely to improve convergence behaviour and is less prone to get stuck in local minima. The current implementation is described in Ref. [114]. The number of determinants will be chosen such that the maximal bond order at any site does not exceed the value set in <code>init_bond_dimension</code>. The new MPS will be stored in the checkpoint folder specified in <code>chkpfile</code>.</td>
</tr>
</tbody>
</table>

Command line:
`det2mps"symmetry" dmrg-input`

Note: "symmetry" must equal the total symmetry specified in the input file `dmrg-input`. |
<table>
<thead>
<tr>
<th>tool</th>
<th>description</th>
</tr>
</thead>
<tbody>
<tr>
<td>mps_transform(_pg)</td>
<td>This tool allows for a transformation of an su2u1(pg) MPS wave function to 2u1(pg) symmetry.</td>
</tr>
<tr>
<td></td>
<td><strong>Command line:</strong> mps_transform(_pg) chkpfile</td>
</tr>
<tr>
<td></td>
<td><strong>Note:</strong> for an su2u1(pg) MPS with $S &gt; 0$ 2u1(pg) MPSs for all $S_z$ components are generated.</td>
</tr>
<tr>
<td>mps2ci_2u1(pg)</td>
<td>Given a text file determinant_list.txt containing a list of determinant strings, this tool calculates the CI-coefficients of the respective determinants [26]. The determinant strings have to encode the occupation of the orbitals as described for the hf_occ keyword (4 = full, 3 = up, 2 = down, 1 = empty).</td>
</tr>
<tr>
<td></td>
<td><strong>Command line:</strong> mps2ci_2u1(pg) chkpfile determinant_list.txt</td>
</tr>
<tr>
<td></td>
<td><strong>Note:</strong> with the conversion tool mps_transform(_pg) this analysis becomes possible also for MPS of the full symmetry su2u1(pg).</td>
</tr>
<tr>
<td>mps_overlap_symmetry(_pg)</td>
<td>This tool calculates the overlap between two MPS $\Theta_1$ and $\Theta_2$, respectively, according to $\langle \Theta_1</td>
</tr>
<tr>
<td></td>
<td><strong>Command line:</strong> mps_overlap_&quot;symmetry&quot;(_pg) chkpfile_1 chkpfile_2</td>
</tr>
<tr>
<td></td>
<td><strong>Note:</strong> &quot;symmetry&quot; must equal the full symmetry specified in the input file dmr - input.</td>
</tr>
</tbody>
</table>
QCMaquis PYTHON scripts for wave function analysis and visualization

The python scripts of QCMaquis are helpful to analyze and visualize the results of a DMRG calculation. Their usage should be evident from the documentation strings in the PYTHON files. However, those that are most frequently used will be briefly explained here. All scripts except dmrginit.py take the QCMaquis output file resultfile as input. They are located in the folder my-Molcas-build/qcmaquis/lib/python/pyeval.

Table B.5.: Overview of QCMaquis PYTHON analysis and visualization scripts.

<table>
<thead>
<tr>
<th>Script</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>dmrginit.py</td>
<td>Starts a QCMaquis DMRG calculation with max_bond_dimension = 200 and nsweeps = 2, measures the entropy information [30, 73] from this unconverged calculation and based on this, generates a new MPS with the CI-DEAS procedure according to all settings specified in the input file dmrg-input. We recommend to use this script for the preparation of calculations for active spaces that are larger than those that can be handled with traditional CAS methods. Command line: dmrginit.py dmrg-input</td>
</tr>
<tr>
<td>sweeps.py</td>
<td>Plots the energy for each microiteration. Command line: sweeps.py resultfile Note: use this tool to check the convergence wrt the number of sweeps.</td>
</tr>
</tbody>
</table>
### Table B.5 – continued from previous page

<table>
<thead>
<tr>
<th>script</th>
<th>description</th>
</tr>
</thead>
</table>
| **fiedler.py** | Optimizes the ordering based on entropy information as proposed in Ref. [13]. The current implementation is described in Ref. [114]. The ordering ensures that highly entangled orbitals are close to each other in the one dimensional lattice. The first ordering in the output ignores the point group symmetry of the orbitals, while the second version orders the orbitals within each irreducible representation and then reorders these symmetry blocks.  
  
  **Command line:**  
  ``` 
  fiedler.py resultfile 
  ```  
  **Note:** we recommend to use the second option.  
  This script recovers the complete QCMaquis input file `dmrg-input` from a given `resultfile`.  
  **Command line:**  
  ``` 
  input.py resultfile 
  ```  

| **input.py**   | Produces mutual information plots [73] given that an expectation value calculation for `MEASURE[ChemEntropy]` has been performed.  
  
  **Command line:**  
  ``` 
  mutinf.py resultfile 
  ```  
  **Note:** if orbital images (in .png format) named 1.png, 2.png, ..., L.png (with L being the number of active orbitals) are present in the same folder where `mutinf.py` is executed, they can be added to the mutual information plot by providing the optional argument `-i` to `mutinf.py`.  

---

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Example file for QCMaquis – DMRG-CASCI(8,8)

//active-space dependent parameters
L = 8
nelec = 8
// target symmetry (spin and spatial) of the wave function:
// 2*spin = 0 (singlet) + totally symmetric point group irrep
spin = 0
irrep = 0
//parameter to control the actual DMRG calculation
nsweeps = 8
max_bond_dimension = 256
conv_thresh = 1e-6
// initialization procedure
init_state = "default"
// technical parameters
symmetry = "su2u1pg"
integral_cutoff = 1e-40
truncation_initial = 1e-50
truncation_final = 1e-7
chkpfile = "chkp.h5"
resultfile = "result.h5"
integral_file = "FCIDUMP"
storagedir = "/scratch/$USER/boundaries"
LATTICE = "orbitals"
lattice_library = "coded"
MODEL = "quantum_chemistry"
model_library = "coded"
//all expectation value calculations required for entropy measures
MEASURE[ChemEntropy]


Bibliography


[81] J. M. Bofill and P. Pulay. “The unrestricted natural orbital-complete active space (UNO-CAS) method: An inexpensive alternative to the complete active space self-


The following publications are reproduced in this thesis:

- S. Keller, M. Reiher,  
  *Spin-adapted Matrix Product States and Operators*,  

- S. Keller, M. Dolfi, M. Troyer and M. Reiher,  
  *An efficient matrix product operator representation of the quantum chemical Hamiltonian*,  

- S. Keller and M. Reiher,  
  *Determining Factors for the Accuracy of DMRG in Chemistry*,  
  Chimia, 68, 200 (2014)

Selected parts of the following publications are reproduced in this thesis:

- S. Knecht, E. D. Hedegård, S. Keller, A. Kovyrshin, Y. Ma, A. Muolo, C. J. Stein, M. Reiher,  
  *New Approaches for ab initio Calculations of Molecules with Strong Electron Correlation*,  
  Chimia, 70, 244 (2016)

- L. Freitag, S. Knecht, S. Keller, M. G. Delcey, F. Aquilante, T. B. Pedersen, R. Lindh, M. Reiher, and L. Gonzalez,  
  *Orbital entanglement and CASSCF analysis of the Ru–NO bond in a Ruthenium nitrosyl complex*,  

- S. Keller, K. Boguslawski, T. Janowski, M. Reiher and P. Pulay,  
  *Selection of active spaces for multiconfigurational wavefunctions*,  
• T. Dresselhaus, J. Neugebauer, S. Knecht, S. Keller, Y. Ma and M. Reiher, 
  *Self-Consistent Embedding of Density-Matrix Renormalization Group Wave Functions in a Density Functional Environment*,

Additional publications not considered for this thesis:

• M. Dolfi, B. Bauer, S. Keller and M. Troyer,
  *Pair correlations in doped Hubbard ladders*,

• M. Dolfi, B. Bauer, S. Keller, A. Kosenkov, T. Ewart, A. Kantian, T. Giamarchi and M. Troyer,
  *Matrix product state applications for the ALPS project*,

• M-E. Moret, S. Keller, J. C. Slootweg and P. Chen,
  *Mononuclear Platinum(II) Complexes Incorporating k2-Carboxylate Ligands: Synthesis, Structure, and Reactivity*,
# Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMRG</td>
<td>density matrix renormalization group</td>
</tr>
<tr>
<td>MPS</td>
<td>matrix product state</td>
</tr>
<tr>
<td>MPO</td>
<td>matrix product operator</td>
</tr>
<tr>
<td>SVD</td>
<td>singular value decomposition</td>
</tr>
<tr>
<td>SU(2)</td>
<td>special unitary group of degree 2</td>
</tr>
<tr>
<td>LCAO</td>
<td>linear combination of atomic orbitals</td>
</tr>
<tr>
<td>CAS</td>
<td>complete active space</td>
</tr>
<tr>
<td>CASSCF</td>
<td>CAS self-consistent field method</td>
</tr>
<tr>
<td>CI</td>
<td>configuration interaction</td>
</tr>
<tr>
<td>FCI</td>
<td>Full-CI</td>
</tr>
<tr>
<td>UNO-CAS</td>
<td>unrestricted natural orbital CAS</td>
</tr>
<tr>
<td>UHF</td>
<td>unrestricted Hartree-Fock</td>
</tr>
<tr>
<td>CCSD(T)</td>
<td>coupled cluster doubles and singles with perturbative triples</td>
</tr>
<tr>
<td>CISDTQ</td>
<td>CI singles doubles triples quadruples</td>
</tr>
<tr>
<td>DFT</td>
<td>density functional theory</td>
</tr>
<tr>
<td>CI-DEAS</td>
<td>CI dynamically extended active space</td>
</tr>
<tr>
<td>HOMO</td>
<td>highest occupied molecular orbital</td>
</tr>
<tr>
<td>LUMO</td>
<td>lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>CSF</td>
<td>configuration state function</td>
</tr>
<tr>
<td>FDE</td>
<td>frozen density embedding</td>
</tr>
<tr>
<td>NEVPT2</td>
<td>second order N-electron valence state perturbation theory</td>
</tr>
</tbody>
</table>