Controlling the accuracy of the density matrix renormalization group method: The Dynamical Block State Selection approach

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We have applied the momentum space version of the Density Matrix Renormalization Group method (k-DMRG) in quantum chemistry in order to study the accuracy of the algorithm in the new context. We have shown numerically that it is possible to determine the desired accuracy of the method in advance of the calculations by dynamically controlling the truncation error and the number of block states using a novel protocol which we dubbed Dynamical Block State Selection (DBSS). The relationship between the real error and truncation error has been studied as a function of the number of orbitals and the fraction of filled orbitals. We have calculated the ground state of the molecules CH₂, H₂O, and F₂ as well as the first excited state of CH₂. Our largest calculations were carried out with 57 orbitals, the largest number of block states was 1500–2000, and the largest dimensions of the Hilbert space of the superblock configuration was 800,000–1,200,000.

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I. INTRODUCTION

Since its first appearance in 1992, the Density Matrix Renormalization Group method has witnessed great developments and it soon became one of the most widely applied numerical methods in one-dimensional solid state physics. Within a short period of time, the real space renormalization method had been further extended and the momentum space version of the method \((k\text{-DMRG})\) was introduced by Xiang in 1996. Unfortunately, test calculations on the Hubbard model indicated relatively poor performance compared to the real space version which hindered further application of the method for several years.

Quite recently, DMRG was used to study models of cyclic polyenes and models of polyacetylenes. S. R. White has successfully applied \(k\text{-DMRG}\) in quantum chemistry to calculate the ground state energy of molecules represented in the framework of the usual Linear Combination of Atomic Orbitals (LCAO) approximation, using small basis sets. His results seemed challenging and attracted considerable attention which stimulated various groups to start to work on the new field.

Among all the various models studied by DMRG during the past decade the accuracy of the algorithm has always been a problem which is still not satisfactorily solved. The recent application of DMRG in quantum chemistry gives further grounds for benchmark investigations of this question within the new framework. In all attempts so far, the accuracy of the method was analyzed a posteriori by means of comparison with the corresponding full CI (FCI) benchmark results. For instance, recently, Chan et al. reexamined the scaling behavior of the real error, developing an extrapolation approach as a function of the number of block states \((M)\).

In this paper we show that in contrast to previous approaches, the desired accuracy of a DMRG calculation can be established in advance if we take into account the dynamic change of the reduced density matrix of the subsystem. Within our approach, described in the next section, we will be able to show that if the number of block states is adjusted dynamically, a linear relationship obtains between the logarithm of the real error and the truncation error, which, in turn, can be used to derive a novel method to extrapolate to the full CI result.

Our main goal in this paper is to determine the accuracy of \(k\text{-DMRG}\) in quantum chemistry and show that the algorithm converges to the accuracy that was set up in advance of the calculation. We have, therefore, carried out a detailed DMRG study of \(\text{CH}_2\), \(\text{H}_2\text{O}\) and \(\text{F}_2\) molecules with various number of orbitals each representing different test cases. We have also addressed problems related to the initial block-state configuration that arise within the framework of \(k\text{-DMRG}\). Since the focus of the paper is on the dynamic scaling of the density matrix and parameters of DMRG, we recall only those main definitions and formulas in this paper that are relevant to the question and not well known in quantum chemistry. Therefore, details of our numerical procedure and developments will be published elsewhere. Although we have analyzed the general trend of the numerical error of \(k\text{-DMRG}\) through quantum-chemical calculations, our results can be generally applied to other quantum system as well.

The setup of the paper is as follows. In Sec. II we briefly describe the main steps of DMRG and recall the main sources of the numerical error. Sec. III is devoted to the details of the numerical procedure used to determine the dynamic scaling behavior of the density matrix and to the problems that appear in the context of quantum chemistry. Sec. IV contains the numerical results and analysis of the observed trends of the numerical error. The summary of our conclusions and a few general comments about the algorithm is presented in Sec. V.

II. BACKGROUND OF THE NUMERICAL ERROR

Detailed description of the DMRG algorithm can be found in the original papers and its application in the context of quantum chemistry is summarized in two recently published papers. Therefore, we present only the most important formulas and definitions that are relevant to the question of accuracy.

The main purpose of DMRG is to treat the electron–electron correlation in a rigorous way which allows the minimization of the energy and calculation of measurable quantities. Since DMRG is a variational procedure, it always provides an upper bound for all the calculated quantities. In the context of quantum chemistry a one dimensional chain that is studied by DMRG is built up from the molecular orbitals that were obtained, e.g., in a Hartree–Fock calculation. The electron–electron correlation is taken into account by an iterative procedure that minimizes the Rayleigh quotient corresponding to the Hamiltonian describing the electronic structure of the molecule, given by

$$
\mathcal{H} = \sum_{ij} T_{ij} c^\dagger_{i\sigma} c_{j\sigma} + \sum_{ijkl} V_{ijkl} c^\dagger_{i\sigma} c_{j\sigma} c_{k\sigma'} c_{l\sigma'} \quad (1)
$$

and thus determines the full CI wavefunction. In Eq. \((1)\) \(T_{ij}\) denotes the matrix elements of the one-particle Hamiltonian comprising kinetic energy and the external electric field of the nuclei, and \(V_{ijkl}\) stands for the matrix elements of the electron repulsion operator. In order to show what are the key concepts and parameters of the numerical renormalization procedure and what are those drawbacks which hinder the analytical study of the method we have included a brief overview of the renormalization group methods.
A. Block renormalization group method (BRG)

In order to determine the eigenvalue spectrum of the Hamiltonian corresponding to an infinite long quantum chain (in the context of quantum chemistry this means infinitely many orbitals) built up from quantum sites represented by $q$ basis states, blocks were formed from each of two adjacent sites, and the Hamiltonian was determined on the new configuration as is shown on Fig. 1. First the Hamiltonian of the model is diagonalized for two sites and then the $q$ lowest energy states are selected out of the $q^2$ states whereby the so called block site will represent the two-sites problem in the subsequent iteration step. Operators defined on the selected $q$ basis states are obtained from the original site operators according to a renormalization procedure given by the equation

$$A_{\text{ren}} = O A O^\dagger,$$  \hspace{1cm} (2)

where operator $O$ is constructed from the selected $q$ eigenfunctions of the two-sites problem. In order to retain the original structure of the Hamiltonian operator, on-site (in the figure labeled by $h$) and inter-site (denoted by $\lambda$) coupling constants are renormalized as well, shown as $h'$ and $\lambda'$. In the subsequent step the $q^2$-dimensional Hamiltonian operator is diagonalized for two adjacent block sites, and again $q$ states with lowest energy are selected out for the block site that will represent four sites in the following iteration step. Since the structure of the original Hamiltonian operator is retained and the number of coupling constants is unchanged, changes of the coupling constants (flow equations) can be studied analytically. When subsequent iteration of the renormalization steps leaves the coupling constants unchanged, the algorithm has reached a fix point which represents the infinite length (thermodynamic) limit of the model.

B. Wilson’s renormalization group method

Besides a few analytically solvable models it turned out that the BRG method can be used only numerically and its systematically increasing inaccuracy hindered the application of the method. In 1975 Wilson introduced another procedure for the numerical renormalization method, in which a quantum chain with finite length $L$ is built up systematically from quantum sites represented by $q$ basis states by keeping the size of the Hilbert space fixed as is shown on Fig. 1.

The main idea of the method was again to solve the Hamiltonian of the model for two sites and selecting $q'$ lowest energy states out of the $q^2$ states where $q'$ was increased systematically up to a maximum value during the first few iteration steps based on the energy spectrum and kept constant afterwards. Operators were renormalized according to Eq. (2). The key difference of Wilson’s method compared to BRG is that he did not retain the original structure of the Hamiltonian operator, but he analyzed the scaling behavior of the energy as a function of the chain length. Systematical application of the renormalization procedure introduces new terms and coupling constants. However, many of them become irrelevant for longer chains and the method also drives the system into the fixpoint. The major drawback of the method is that since the structure of the Hamiltonian changes with increasing chain lengths, flow equations can not be defined and the method can not be studied analytically.

C. Density matrix renormalization group method (DMRG)

In spite of the powerful properties of Wilson’s procedure, the numerical error of the method grew systematically with increasing chain length, which drawback has led to the fact that longer chains could not be studied numerically. Besides the truncation of the Hilbert space through the renormalization procedure, the numerical error had another main source. When an additional unrenormalized site was added to the block site, the coupling was taken into account only between the block site...
and this new site. In each iteration step the problem was, therefore, reduced to an isolated two-sites problem with open boundary conditions. These observations has led S. R. White to construct a larger auxiliary system (superblock configuration) which contains an environment in addition to the original block site problem to take care of the boundary effects in a more reliable way, as is shown on Fig. 3. According to the figure the structure of the superblock configuration is defined as \( B_L \bullet \bullet B_R \) where \( B_L \) represents the block site, \( \bullet \) the new site under consideration, the additional \( \bullet B_R \) configuration the environment and \( M_L \) and \( M_R \) denotes the number of block states, respectively. In order to minimize the error introduced in the representation of the block state in the truncation process, S. R. White has constructed the \( O \) matrix using the eigenfunctions of the reduced density matrix of the subsystem \( B_L \bullet \). It has been recognized in different context \( 12 \) that the reduced subsystem density matrix describes the interactions of two subsystems in a particularly efficient way. Using these two key ingredients, a DMRG iteration step first includes the diagonalization of the Hamiltonian constructed on the superblock configuration to obtain the target state. The target state is chosen from the eigenvalue spectrum of the Hamiltonian that we want to calculate. It can also be a linear combination or even an incoherent superposition of more eigenstates as well. If \( |I\rangle \) and \( |J\rangle \) denote basis states for \( B_L \bullet \) and \( \bullet B_R \), respectively, then the target state is written as

\[
\Psi_{\text{Target}} = \sum_{I,J} \psi_{I,J} |I,J\rangle,
\]

where \( \psi_{I,J} \) is determined by diagonalization of the superblock Hamiltonian. After the target state is obtained, the reduced density matrix of the \( B_L \bullet \) subsystem

\[
\rho_{I,I'} = \sum_{J} \psi_{I,J}\psi_{I',J}^\dagger
\]

is diagonalized and the \( M \) eigenstates with largest eigenvalues (\( \omega_n \)) are selected to build up the \( O \) matrix. The site operators are renormalized according to Eq. 3. The error of the truncation procedure in the DMRG method can be measured by means of the deviation of the total weight of the selected states from unity which is defined as

\[
TRE = 1 - \sum_{\alpha=1}^{M_L} \omega_\alpha.
\]

The initial \( B_L \) and \( B_R \) configuration contain one site per block each, thus the superblock Hamiltonian is determined on \( q^4 \) basis states restricted to the conserved quantum numbers like the total spin or the number of electrons. In each iteration step the size of the chain is increased by two sites until the desired chain length is reached as is shown on Fig. 3. This procedure is the so called infinite lattice algorithm. In order to average out long-wavelength fluctuations, the superblock configuration is asymmetrised by increasing the size of \( B_L \) and decreasing the size of \( B_R \) until the left block contains \( L - 3 \) sites and the right block one site. The same procedure is then carried out in the reverse way and when the configuration is symmetric again, the first sweep of the so called finite lattice algorithm ends. This procedure can be repeated infinitely many times and is usually stopped when the energy does not change within two subsequent sweeps. There is again a major difference between BRG and DMRG which makes the analytical study of the scaling behavior of the latter method very complicated: In the DMRG method the number of selected block states (\( M \)) is larger then \( q \) and the original structure of the Hamiltonian is not retained, thus flow equations of the coupling constants can not be determined.

According to the two key ingredients of the method, the numerical error of the DMRG algorithm has basically two independent components which are the truncation error and the environmental error. The first one is generated during the renormalization step due to the truncation of Hilbert space, while the environmental error appears because the chain is built up from blocks and the long range interactions are cut off. As it was shown in Ref. 13 using the finite lattice method, the environmental error can be averaged out and finally there remains a linear relationship on a log–log scale between the real error and truncation error.

The truncation error, on the other hand, strongly depends on the shape of the eigenvalue spectrum of the reduced subsystem density matrix and on the number of block states kept for the subsequent iteration step. It has also long been known that the structure of the density matrix depends on the criticality of the model. For systems with finite energy gap and coherence length the density matrix eigenvalue spectra decays exponentially, while for critical models with infinite coherence length it has a power-law tail. Besides these, in case of analytically solvable models the structure of the eigenvalue spectra of the density matrix determines the energy spectrum of the model as it was shown in Ref. 14.

In addition to all the points discussed above, the decay of the eigenvalue spectrum also changes as the target state gets closer to the exact solution. It is, therefore, evident that selecting out the \( M \) most probable states with highest eigenvalues will be an insufficient condition to control the accuracy of the DMRG method. Instead, one has to take care of the dynamic changes of the spectrum of the density matrix and keep the truncation error below a given threshold. Since the structure of the density matrix represents the whole system as well, it naturally arises that the number of block states should be selected out in a way that the truncation error satisfies an initial condition that was introduced in advance of the calculation.
D. QC-DMRG method

In the context of quantum chemistry, a one dimensional chain containing $L$ molecular orbitals is generated by ordering the orbitals employed to build up the multi-particle states with increasing energy or by other rules, analogous to $k$ points in $k$-DMRG. These molecular orbitals are calculated by standard numerical methods of quantum chemistry.

It worth to note that the optimal ordering of the orbitals in the chain is still an open field of research. Note that the initial chain length of the QC-DMRG is $L$ from the very beginning and the block operators for the left and right blocks are generated by a “warm up” procedure instead of the infinite lattice algorithm. The effect of the electron–electron correlation is taken into account by the systematic sweeps in the framework of the finite lattice algorithm. Since the overall performance of the QC-DMRG method differs from the real-space version, it is also expected that new problems arise due to the inaccuracy of the starting wave function. This will be also investigated in detail in the next section.

The most straightforward procedure to represent the unrenormalized site operators is to define them on spin-orbital basis states, in which case $q$ is equal to two. The phase operator is then taken care of automatically by the standard definition of fermion creating and annihilating operators. On the other hand, if orbitals from, e.g., a restricted Hartree–Fock (RHF) calculations are employed, it is possible to define a super site built up from the ordered tensor product of spin-down and spin-up basis states, in which case $q$ is 4 and the phase factor must be explicitly taken care of. This method offers considerable efficiency gains because in this way the chain is only half the size compared to an unrestricted HF (UHF) type formulation, using spin orbitals for each site. Thus the number of multiplications using quadratic auxiliary operators during the superblock Hamiltonian diagonalization procedure is roughly reduced by a factor of 4 compared to the spin-orbital formulation. In our implementation we have built up the chain from super sites.

III. CONTROLLING THE ABSOLUTE ERROR OF DMRG

A. Dynamic adjustment of the number of block states

In order to control the accuracy of the DMRG procedure, the selection of the multi-particle states of the superblock Hamiltonian which are used for renormalization is obviously the decisive issue. Keeping all states featuring eigenvalues of the subsystem reduced density matrix larger than a fixed parameter which we called $DM_{cut}$ during the renormalization procedure, the truncation error can be as small as $DM_{cut}$, but it can be larger if the integrated contribution of the neglected states is still significant. To avoid such problem we propose to adjust $DM_{cut}$ dynamically, thus the number of selected states is increased as long as the integrated weight of neglected states is larger then a maximum value $TRE_{max}$, which can be fixed at the beginning of the calculation. This enables us to set up the desired accuracy of the DMRG algorithm at the beginning of the calculation. The number of states will be adjusted by this protocol in a dynamical fashion, depending on the structure of the density matrix spectrum.

Since the truncation error is not immediately connected to the error in energy, one can control only the relative error in this way. In order to control the absolute error in energy, $TRE_{max}$ should be scaled by the Hartree–Fock energy or by the energy value calculated by the DMRG method which usually has the same order of magnitude as the exact value even after the first few iterations. We then expect the relative error of the energy to converge to this scaled threshold within a few sweeps of the DMRG procedure.

From technical point of view, dynamic selection of block states has another important advantage. In the standard DMRG calculation the number of block states is fixed. Using our dynamical adjustment, the largest number of block states required to guarantee a given truncation error develops, however, only close to the symmetric configuration during the sweep. For most of the remaining steps the threshold $TRE_{max}$ is reached with considerably smaller number of block states, leading to substantial gains in efficiency in the renormalization step and the construction of the next superblock Hamiltonian, when dynamic block state selection is used.

Within the framework of our procedure, it is also evident why previously developed extrapolation methods based on functions of the number of block states failed to estimate the scaling behavior of the error in a rigorous way. The value of $M$ is only one of the factors that determines the largest value of the truncation error during a full sweep. Using it exclusively, changes of the density matrix are not taken care of. Thus it is almost impossible to derive a reliable formula to estimate the real error as a function of the number of block states for the general case.

B. Initial condition for the number of block states

The straightforward application of dynamical control of $DM_{cut}$ during the first few sweeps is complicated by the fact that there is a major difference between the wave function of a given chain length generated by the infinite lattice algorithm of the real space version and that of generated by ordering the orbitals in the case of $k$-DMRG. In the first method, the wave function of the target state is always very close to the one which is obtained after several sweeps of the finite lattice method; however this is
not true in general for the momentum space version when
the wave function strongly depends on the ordering of the
orbitals. For example, it typically happens that during
the first few steps the density matrix eigenvalue spectra
will have very few states with large eigenvalues and many
states with almost zero weight. In this case, the number
of selected states will be cut drastically, which will limit
seriously the size of the Hilbert space in the subsequent
iterations, causing the algorithm being trapped in a local
minimum. This situation happens in other optimization
methods as well, and for example in the case of simulated
annealing the so called adiabatic heating is used to move
the algorithm out from the attractor of a local minimum.
In the context of DMRG the introduction of virtual states
is required in this situation, which means that we keep
also those states that had almost zero eigenvalue up to
a fixed number that we called $M_{\text{min}}$ during the first two
sweeps. Usually after the first sweep the decay of the
density matrix spectrum becomes smooth and it changes
dynamically as the target state gets closer to the exact
one.

C. New criteria for convergence and extrapolation of
the FCI energy

Up to now the condition for the number of sweeps
was determined in an empirical way, using the condition
that the algorithm is stopped when the energy value
obtained by two subsequent sweep does not change any
more. Within the framework of DBSS we have a new
criterion for the convergence. We have found that after
convergence not only the energy value remains stable,
but also the eigenvalue spectrum of the density matrix
and thus the block states selected out by the algorithm
for a given $B_L \bullet \bullet B_R$ configuration are the same during
all subsequent sweeps. Although all subsequent sweeps
leave the density matrix unchanged, still a fix point is
not obtained since the structure of the density matrix
and thus the truncation error and the relative error af-
ter convergence can slightly change (but within the same
order of magnitude) depending on the initial condition,
for example on different $M_{\text{min}}$. On the other hand, we
can treat the energy values obtained for various $TRE_{\text{max}}$
values as points on a flow equation that converge to the
fix point at the end, which is the FCI energy. Based on
our previous results and those presented in the next
section we can extrapolate to the FCI energy using the
equation

$$\log\frac{E - E_{\text{FCI}}}{E_{\text{FCI}}} = a \cdot \log(TRE) + b,$$

(6)

where $a$, $b$, $E_{\text{FCI}}$ are parameters determined from the fit
of the numerical result. As discussed below, our numeri-
cal results show that the value of $a$ is close to one.

D. Error of the excited states due to the inaccuracy
of starting block states

Besides the problem of the initial structure of the den-
sity matrix there is another difficulty which stems from
the inaccuracy of the starting block wave functions. By
contrast to the infinite lattice method when the tar-
gestate always remains in the same spin symmetry
or changes sign periodically as a function of the chain
length, the symmetry of the target state depends on
the initial ordering in the case of $k$-DMRG. This can
lead to a major error, because the DMRG algorithm can
lose the target state if its symmetry changes during the
first few sweeps. It can happen that for example target-
ing the second level the coefficients of the wave function
of the ground state and excited states will mix and the
spin symmetry of the target state changes randomly, and
thus the energetically lowest level will be lost and the
third level will become the target state.

E. Introduction of local symmetry operators

In order to avoid the random change of the spin sym-
metry we have introduced partial spin adaption making
sure that the permutational symmetry of the spins is
odd for even $S$ and even for odd $S$, which implements
the spin reversal operator that flips the spins along the
$z$-directions as it was shown in Ref. [11]. In case of $k$-
DMRG the starting block wave function is constructed
in a way that it contains basis states with $N_{\text{up}}$ and $N_{\text{down}}$
quantum numbers, thus fixing $m_s$, and their symmetric
components (i. e. , states with $-m_s$) as well. During the
renormalization procedure a state and its partner belong
to same eigenvalue of the density matrix, thus the dy-
namic selection rule automatically ensures that both of
them are kept. It worth to note, that this is not the full
adaptation of $S^2$ symmetry, which would be clearly be
desirable, but more complicated to achieve in the frame-
work of DMRG. Thus, components of the singlet and
quintets levels can still mix, but it is not a problem since
they are usually well separated. Application the corre-
sponding spin reversal operator effectively ensures that
the target state will remain in the spin symmetry sector
that was fixed at the beginning of the calculation.

From technical point of view, this has the additional
advantage that one needs to target only the first level in
both spin symmetry sectors, which always requires less
block states to achieve a given accuracy. In addition, the
number of auxiliary operators needed during the diagno-
salization of the superblock Hamiltonian is decreased by
a factor of two which doubles the speed of the algorithm.
For the half-filled case the particle–hole symmetry oper-
ator can be introduced in the same way. Details of the
numerical procedure will be published elsewhere.
F. Error of the expectation value of one- and two particle operators

The expectation value of the one- and two electron operators can be calculated from the one particle density matrix according to

$$\langle A \rangle = TR(\rho A). \quad (7)$$

where $A$ is a $L \times L$ matrix of operator for a first-order property (e.g., dipole moment) in the same representation as the original $T_{ij}$ and $V_{ijkl}$. So with $A = T_{ij}$ Eq. (8) provides the kinetic energy of the FCI wave function. Once the target state was obtained, the one particle reduced density matrix can be formed for any $BL\cdot$ configuration as

$$\rho_{ij} = \langle \Psi_{Target} | \sum_\sigma c^\dagger_{i\sigma} c_{j\sigma} | \Psi_{Target} \rangle \quad (8)$$

where $i$, $j$ denote sites in the left block. The one-particle density matrix for the right block is determined in a similar way. If $i$ is in the left block and $j$ in the right block, then $\rho_{ij}$ is constructed from the one-particle operators of the two blocks. The latter case was used to calculate two-point correlation functions in real space DMRG and was shown that the error of the one- and two-point correlation function is larger by one or two orders of magnitude compared to the error of the ground state energy. Since the dynamic block state selection rule controls the accuracy of the ground state, it also ensures the same scaling behavior of the correlation functions as well. Besides that, the fluctuation of the error shown in Ref. 13 because of the fluctuation of the truncation error within a full sweep caused by to the constant value of $M$ also diminishes.

The two-particle reduced density matrix can be obtained in a similar way

$$\Gamma_{ijkl} = \langle \Psi_{Target} | \sum_{\sigma\sigma'} c^\dagger_{i\sigma} c^\dagger_{j\sigma'} c_{k\sigma'} c_{l\sigma} | \Psi_{Target} \rangle, \quad (9)$$

where the four-operator term is decomposed into four independent terms depending on the distribution of the $i, j, k, l$ indices along the chain making use of the usual partially contracted operators of $k$-DMRG.

IV. NUMERICAL RESULTS

In order to study the performance of $k$-DMRG in quantum chemistry, we followed a route similar to the one used to study the accuracy of the real-space DMRG. We performed calculations on molecules with different properties for which DMRG is expected to possess different scaling behavior. Thus we have carried out a detailed DMRG study of the absolute error of the energy as a function of the number of orbitals and the fraction of filled orbitals on molecules CH$_2$, H$_2$O, and F$_2$. The Hartree–Fock orbitals in a given basis of Gaussian orbitals were calculated, and the $T_{ij}$ and $V_{ijkl}$ matrix elements were transformed to the Hartree–Fock basis using the MOLPRO program package, which was also used for the calculation of the benchmark full-CI energies.

We used various basis sets and geometries for the molecules which we selected for benchmark calculations. The geometries, references to the basis sets employed, and results obtained in SCF calculations as well as full CI energies are detailed in Table I. The models employed for the water molecule have also been used in White’s study. We include these cases here in order to enable a direct comparison with previous work. A more interesting test case was to study the CH$_2$ molecule, for which we report energies for the triplet ground state as well as for the first excited (singlet) state. Hartree–Fock orbitals of the closed-shell singlet configuration were employed in all calculations on CH$_2$. Calculations of the FCI energy of the triplet state were carried out in both the $m_s = 0$ and $m_s = \pm 1$ spin sectors. In order to show that the relative error scales to $TRE_{max}$ independently of the fraction of filled orbitals we have studied the half-filled chains by calculating the ground state of F$_2$ with 14 electrons and 14 orbitals (freezing the fluorine 1s orbitals and discarding the two highest virtual orbitals) and with 18 electrons and 18 orbitals. The latter calculation provides evidence that QC-DMRG is capable to provide cutting-edge CASSCF calculations with the potential to push their limits to active spaces well beyond a size which is feasible nowadays by standard methods.

A. Dynamic selection of Block states

QC-DMRG calculations on the water molecule demonstrate the dynamic selection of block states. In the first two panels of Fig. 2 we have plotted the number of block states which were selected in a calculation correlating 10 electrons in 14 orbitals by means of QC-DMRG, starting with different values of $M_{min}$.
In the third panel of Fig. 2 we give the relative error as a function of iteration obtained with \( M_{\text{min}} = 16, 64, 164 \). In all cases the 10 electrons of the \( \text{H}_2\text{O} \) molecule were correlated in the double-zeta water model with 14 orbitals, and \( \text{TRE}_{\text{max}} = 10^{-10} \) was set in advance of the calculations.

The number of block states for the left and right blocks is denoted by \( M_L \) and \( M_R \), respectively. In the third panel of Fig. 2 we give the relative error \((|E_{\text{DMRG}} - E_{\text{FCI}}|)/E_{\text{FCI}}\) of the calculation as a function of \( M_{\text{min}} \) and the the iteration step. The value of \( \text{TRE}_{\text{max}} \) was set to \( 10^{-10} \) in advance of the calculations. It is evident from the figure that the maximum number of block states does not depend on the prescribed minimum value \( M_{\text{min}} \), although it is reached faster for larger \( M_{\text{min}} \). In order to show that the converged value of the accuracy does not depend on the threshold value (once a large enough value was taken) we have also included the result obtained with \( M_{\text{min}} = 164 \). It can be seen in the figure that the relative error converges to \( \text{TRE}_{\text{max}} \) in all cases, but the speed of convergence strongly depends on \( M_{\text{min}} \). In order to show that the QC-DMRG algorithm is trapped in a local minimum if \( M_{\text{min}} \) is chosen too small, we carried out calculations with \( M_{\text{min}} = 4, 8 \) and found that the number of block states is hindered to grow up. Similar test calculations on longer chains indicated that a larger value of \( M_{\text{min}} = 64–100 \) is needed, thus we suggest that in order to to avoid problems related to local attractors and to obtain a faster performance a value of \( M_{\text{min}} \) no less than 150–200 should be taken for longer chains.

Investigating the scaling of the relative error shown in the third panel of Fig. 2 one can find long plateaus where the accuracy of the method is not improved. In the usual DMRG calculations going through such plateaus costs almost the same amount of time as calculating the region where the error drops significantly. By contrast, it can be seen on the figure that the minimum value of \( M \) occurs in the region of the plateaus resulting in a very fast traversal of these regions. In addition, the maximum values of \( M_L \) and \( M_R \) occur at different iteration steps, thus for a given superblock configuration we find that even if one of them is very large, the other is usually much smaller. These two facts, finally, optimize the computational time and memory resources within a full sweep of the method.

In order to show the dynamic change of the structure of the reduced subsystem density matrix, we have plotted in Fig. 3 the eigenvalues of the reduced subsystem density matrix obtained at the symmetric configuration (left and right blocks contained 6 orbitals) from a calculation of the \( \text{F}_2 \) molecule represented by 14 electrons and 14 orbitals.

There are several conclusions that one can draw from the figure. First of all, the density matrix spectrum decays very rapidly during the first few sweeps \((S=0)\) is part of the “warm up” procedure) which clearly implies the requirement of introduction of virtual states. On the other hand, as the target state gets closer to the FCI limit, the fraction of eigenvalues larger than \( 10^{-15} \) increases significantly. It can be seen from the figure that the decay of the spectrum can be fitted by a linear line on a semilogarithmic scale for the largest eigenvalues, thus the density matrix spectrum decays exponentially, where the slope is related to the finite coherence length of the model. On the other hand, the slope of the line changes as a function of sweeps until the algorithm converges. Once the relative error converged to \( \text{TRE}_{\text{max}} \) (which means for \( S > 7 \) in the case at hand) the slope of the decay remains the same, and this is the reason why the number of selected block states are the same for the subsequent sweeps. It worth to note that since the decay of the density matrix can be fitted by a straight line in
this model, the truncation error can be estimated as a function of the block states. However, in order to obtain a rigorous scaling behavior of the error as a function of block states one has to include the change of the slope as well, which in general strongly depends on the static and dynamic correlations of the models.

B. Relationship between the relative error and $TRE_{\text{max}}$

In order to test that the relative error converges to a given value of $TRE_{\text{max}}$ we have ran independent calculations for all the test molecules by adjusting $TRE_{\text{max}}$ from $10^{-3}$ up to $10^{-11}$. The relative error of the first excited state obtained for the CH$_2$ molecule with 6 electrons and 13 orbitals using $M_{\text{min}} = 32$ as a function of the iteration step and $TRE_{\text{max}}$ is shown on Figure 4. It can be seen on Fig. 4b, that the relative error of the first excited state also

![Figure 4a](image-url)  
**FIG. 4.** Calculations for CH$_2$ with $L = 13$ sites shows the relationship between relative error and $TRE_{\text{max}}$. The straight line is the result of the fit. GS denotes the triplet ground state, and 1XS denotes the first excited (singlet) ground state.

converges to the values of $TRE_{\text{max}}$ set up in advance of the calculations. The converged value of the relative error as function of $TRE_{\text{max}}$ for the first excited as well as for the ground state is plotted on Fig. 4b. It is clear from the figure that there is a linear relationship between the converged value of the relative error and the truncation error, the fitted slope being 0.98. Fitting our results obtained for various length cases also with different $M_{\text{min}}$ values, we have found that the slope was always around 0.95 and 1.1. Calculations in the $m_s = \pm 1$ spin sectors provided a faster convergence for the ground state, as expected. The residual splitting of the $m_s = 0, 1, -1$ components of the triplet level was as low as $10^{-12}$ a.u.

Calculations performed on the other test molecules with different number of basis states and for various values of $M_{\text{min}}$ showed that the relative error scales to $TRE_{\text{max}}$ independently of the number of orbitals, fraction of filled orbitals and the threshold level of the number of block states. Of course, the convergence gets slower for longer chain lengths and we usually needed 6-8 sweeps to gain an absolute accuracy of $10^{-4}$ a.u. in the case of the CH$_2$ molecule calculated with 57 orbitals.

From the technical point of view, one can start a DMRG calculation by setting $TRE_{\text{max}}$ to $10^{-3}$ and when the algorithm has converged (the energy is unchanged, the number of block states are unchanged, the slope of the density matrix remains the same ) $TRE_{\text{max}}$ can be adjusted by an order of magnitude until the desired maximum value of the accuracy is reached. Using the calculated energy values and the truncation error obtained for various values of $TRE_{\text{max}}$ (which is slightly below $TRE_{\text{max}}$) the FCI energy can be estimated by Eq. 11. This equation contains three free parameters ($E_{\text{FCI}}, a, b$) to determine from the fit. However, based on our results we can set the parameter $a$ to one. We have found that one can gain one to three orders of magnitude improvements in the error of the correlation energy by the extrapolation method and that fixing the parameter $a$ to one always provides an upper bound. In order to obtain a more accurate fit one needs more data points, thus $TRE_{\text{max}}$ should be adjusted in even smaller steps, especially, if the calculations are carried out only up to a relative accuracy of $10^{-5}$, but we have not done such analysis yet.

In case of solid state physics, chains with various lengths are calculated and the thermodynamic limit is extrapolated by the so-called finite-size scaling method. Using our procedure one can improve the energy values obtained for a given length $L$ by two to three orders of magnitude, thus the overall performance of finite-size scaling procedure can be improved significantly.

C. Scaling of the number of block states

As we have shown, the number of block states depends on the structure of the reduced density matrix spectrum. Thus it is not possible to determine the scaling behavior of the maximum number of block states as a function of the number of orbitals and the fraction of filled orbitals in a rigorous way. On the other hand, in order to present a rough indication of computational resources used during our calculations we have we have collected the values of the maximum number of block states selected dynamically by our the method in Table II.

D. Other factors that affects the accuracy

It is important to note that our scaling results are obtained only for a proper ordering of the orbitals in the initial chain. We have found that for some cases the
accuracy can be improved significantly if the HF levels were ordered with increasing energy (labeled by \( \text{Ord}_2 \) on Fig. 5) while for other cases we had to "mirror" the chains and placed orbitals occupied in the HF configuration to the center of the chain (labeled by \( \text{Ord}_1 \)). A non-optimal ordering can in fact lead the method to be trapped by a local minimum. This situation is shown explicitly in Fig. 5, indicated by \( \text{Ord}_1 \). Even if \( \text{M}_{\text{min}} \) was almost tripled, the relative error converged to the same local minimum, which, on the other hand, also supports our previous statements that \( \text{M}_{\text{min}} \) does not affect the final convergence significantly. Changing the ordering, we have found for \( \text{Ord}_2 \) that the algorithm has always converged to the value of \( \text{TRE}_{\text{max}} \). Studying the optimal ordering can be a major field of research. Chan et al. already suggested a procedure to optimize the ordering in a recently published paper. We have not analyzed their solution yet.

Another field of study can be the optimization of the superblock configuration. In our largest calculations for the half-filled case (18 electron in 18 orbitals) the number of selected block states grew up to 1500–1800 with sizes of the Hilbert space of the superblock configuration increasing beyond 1,000,000. In order to decrease the size of the Hilbert space we have derived an alternate protocol, modifying the superblock configuration as \( B_L \bullet B_R \) in a similar way as was done by Xiang. We found a considerably worse performance for these calculations. We believe that in the future it can worthwhile analyzing the speed of convergence for various superblock configurations.

\[ \begin{align*}
\text{ML} & \quad \text{CH}_2 \ L=23 \\
\text{MR} & \quad \text{CH}_2 \ L=23
\end{align*} \]

\[ \begin{align*}
\text{M}_{\text{max}}=164, \text{Ord}_2, \text{TRE}_{\text{max}}=1e^{-8} \\
\text{M}_{\text{max}}=164, \text{Ord}_1, \text{TRE}_{\text{max}}=1e^{-8} \\
\text{M}_{\text{max}}=164, \text{Ord}_1, \text{TRE}_{\text{max}}=1e^{-10}
\end{align*} \]

\[ \begin{align*}
\text{M}_{\text{max}}=164, \text{Ord}_2, \text{TRE}_{\text{max}}=1e^{-10} \\
\text{M}_{\text{max}}=164, \text{Ord}_1, \text{TRE}_{\text{max}}=1e^{-10} \\
\text{M}_{\text{max}}=164, \text{Ord}_1, \text{TRE}_{\text{max}}=1e^{-10}
\end{align*} \]

\[ \begin{align*}
\text{M}_{\text{max}}=164, \text{Ord}_2, \text{TRE}_{\text{max}}=1e^{-10} \\
\text{M}_{\text{max}}=164, \text{Ord}_1, \text{TRE}_{\text{max}}=1e^{-10} \\
\text{M}_{\text{max}}=164, \text{Ord}_1, \text{TRE}_{\text{max}}=1e^{-10}
\end{align*} \]

FIG. 5. The figure shows that an incorrect ordering can drive DMRG to a local minimum.

\[ \begin{align*}
\text{M}_{\text{max}} & = \text{Ord}_2 \\
\text{TRE}_{\text{max}} & = \text{Ord}_1
\end{align*} \]

V. SUMMARY

We have applied the momentum-space version of DMRG in quantum chemistry in order to study the accuracy of the method. Analyzing the eigenvalue spectrum of the reduced density matrix and based on our previous results obtained for real space DMRG, we have shown that it is possible to set up the accuracy of the method in advance of the calculation by dynamically controlling the truncation error and the number of block states. We have carried out a detailed QC-DMRG study of the molecules H\(_2\)O, CH\(_2\), and F\(_2\) obtained with various basis sets in order to show that the relative error scales to the maximum threshold value of the truncation error that was fixed in advance of the calculation. We found that the linear relationship between the logarithm of the relative error and the logarithm of the maximum value of the truncation error is independent of the number of orbitals and the fraction of filled orbitals for the cases considered. Based on these results we have presented a novel approach to extrapolate the FCI energy, a method which could also improve the accuracy of the finite-size scaling method when \( k \)-DMRG is applied in solid state physics. We have addressed new problems related to the inaccuracy of starting block state configuration and presented solutions to achieve faster convergence and better stability of the target state.

The maximum number of block states that the algorithm selected out in the dynamic fashion was in the range of 1500–2000, the largest size of the Hilbert space related to the superblock Hamiltonian was 800,000–1,200,000, and the longest chains that we have studied contained 57 sites.

Although momentum is not a good quantum number if \( k \)-DMRG is applied in quantum chemistry, there are still a few remarks which might indicate why QC-DMRG method can work well in the field:

1. In most of the cases the calculations are carried out in the small \( U \) limit known to converge fast.
2. The number of electrons is fixed for a given molecule. Therefore, doubling the length of the system will not imply in general keeping the fraction of filled orbitals fixed. Thus calculating a molecule with more basis states would mean longer chains but with lower filling value which usually has a better convergence.
3. The practical use of DMRG in quantum chemistry can open a route to active spaces well beyond today's limits, yielding complete active space self-consistent field (CASSCF) solutions with a relative error of the correlation energy of the order of \( 10^{-4} \) to \( 10^{-5} \). This can be realized by a few thousand block states, which also expected to hold for longer chains as well. Therefore, we believe that 3000–4000 block state will provide satisfactory results for all the chain lengths and fillings which are of interest in the immediate future.
4. Although the structure of the Hamiltonian is very complicated, it is decomposed into several parts. This
means that during the diagonalization step each component of the Hamiltonian can be applied on the wavefunction independently, therefore, the method is an excellent candidate for parallel computers.

Our source code was written in the the framework of the Matlab programming environment and the C++ code as well as the standalone code was produced by the Matlab compiler. Most of our numerical calculations were carried out on Athlon XP 1800+ processors under Linux and in some cases on a SGI 3000 machine of the local computer center. For the largest calculations comprising $M=1700–2000$ block states (F$_2$ 18/18) the program required 200–500 MB of RAM, running about 50–60 hours on Athlon XP 1800+ processor to achieve $10^{-4}$–$10^{-5}$ a.u. absolute accuracy. The scaling of computational time with the number of orbitals still cannot be determined with sufficient accuracy. The present stage of our code limited the number of block states around 2000, however, solving a few technical points we expect that the feasible $M$ can be increased significantly in the future.

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| basis set reference | bond distance (a.u.) | bond angle (degrees) | electrons | orbitals |
|---------------------|----------------------|----------------------|----------|---------|
| H$_2$O Double-Zeta | 1.84345              | 110.565              | 10       | 14      |
| H$_2$O DZ          | 1.80973              | 104.500              | 8        | 25 (24) |
| CH$_2$ $^1$A$_1$ DZ | 2.02230              | 129.4667             | 6        | 14 (13) |
| CH$_2$ $^1$B$_1$   | 2.02230              | 129.4667             | 6        | 24 (23) |
| CH$_2$ $^2$A$_1$ cc-pVDZ | 2.02230       | 129.4667             | 6        | 24 (23) |
| CH$_2$ $^2$B$_1$   | 2.02230              | 129.4667             | 6        | 58 (57) |
| F$_2$ DZ           | 2.63473              | 129.4667             | 14       | 20 (14) |
| F$_2$ split valence| 2.68797              | 129.4667             | 18       | 18      |

TABLE I. Geometries and benchmark energy values for the calculated molecules. The number of correlated orbitals is given in parentheses, unless it agrees with the total number of orbitals.
|       | CH₂ | H₂O | F₂ | CH₂ | H₂O | F₂ | CH₂ |
|-------|-----|-----|----|-----|-----|----|-----|
| L     | 6/13| 10/14| 14/14| 6/23 | 8/24 | 18/18| 6/57 |
| Filling | 0.230 | 0.357 | 0.500 | 0.130 | 0.166 | 0.500 | 0.052 |

| ΔE_{Abs} | M_{max} | M_{max} | M_{max} | M_{max} | M_{max} | M_{max} |
|-----------|---------|---------|---------|---------|---------|---------|
| 10^{-2}   | 25      | 40      | 280     | 150     | 130     | 170     | 300    |
| 10^{-3}   | 40      | 60      | 350     | 280     | 320     | 520     | 480    |
| 10^{-4}   | 100     | 140     | 800     | 370     | 440     | 1100    | 620    |
| 10^{-5}   | 160     | 300     | 1450    | 580     | 650     | 1800    |        |
| 10^{-6}   | 230     | 420     | 670     | 820     |         |         |        |
| 10^{-7}   | 300     | 530     | 720     |         |         |         |        |
| 10^{-8}   | 360     | 650     | 880     |         |         |         |        |
| 10^{-9}   | 420     | 780     |         |         |         |         |        |

**TABLE II.** The maximum number of the block states selected out dynamically by DMRG to reach a given value of absolute accuracy. The second row contains the number of electrons and orbitals of each test calculations and below the fraction of filled orbitals is listed.