

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 this 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 that we dubbed dynamical block state selection protocol. 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 CH_2 , H_2O , and F_2 as well as the first excited state of CH_2 . 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 (DMRG) method^{1,2} 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 -DMRG) was introduced by Xiang³ 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 polyenes⁴ and models of polyacetylene.⁵ S. R. White and co-workers have successfully applied k -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.^{6,7} His results seemed challenging and attracted considerable attention, which stimulated various groups^{8,9} to start to work on the new field.

Among all the various models studied with the DMRG method during the past decade the accuracy of the algorithm has always been a problem that 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 configuration-interaction (FCI) benchmark results. For instance, recently, Chan and Head-Gordon⁹ 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 sub-

system. 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 is obtained 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 the k -DMRG method in quantum chemistry and show that the algorithm converges to the error margin that was set up in advance of the calculation. We have therefore carried out a detailed DMRG study of CH_2 , H_2O , and F_2 molecules with various numbers 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 the k -DMRG method. Since the focus of the paper is on the dynamic scaling of the density matrix and parameters of the DMRG method, 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 the k -DMRG method 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 the DMRG method and recall the main sources of the numerical error. Section 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. Section 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 are presented in Sec. V.

II. BACKGROUND OF THE NUMERICAL ERROR

A detailed description of the DMRG algorithm can be found in the original papers, Refs. 1–3, and 10 and its application in the context of quantum chemistry is summarized in

two recently published papers Refs. 8 and 9. Therefore, we present only the most important formulas and definitions that are relevant to the question of accuracy.

The main purpose of the DMRG method is to treat the electron-electron correlation in a rigorous way that allows the minimization of the energy and calculation of measurable quantities. Since the DMRG method 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 the DMRG procedure 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

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

and thus determines the full CI wave function. In Eq. (1) T_{ij} denotes the matrix elements of the one-particle Hamiltonian comprising the 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 the key concepts and parameters of the numerical renormalization procedure and the drawbacks that hinder the analytical study of the method, we have included a brief overview of the renormalization-group methods.

A. Block renormalization-group method

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 from 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-site 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

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

where operator O is constructed from the selected q eigenfunctions of the two-site problem. In order to retain the original structure of the Hamiltonian operator, on-site (in the figure labeled by h) and intersite (denoted by λ) coupling constants are renormalized as well, shown as h' and λ' . 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 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

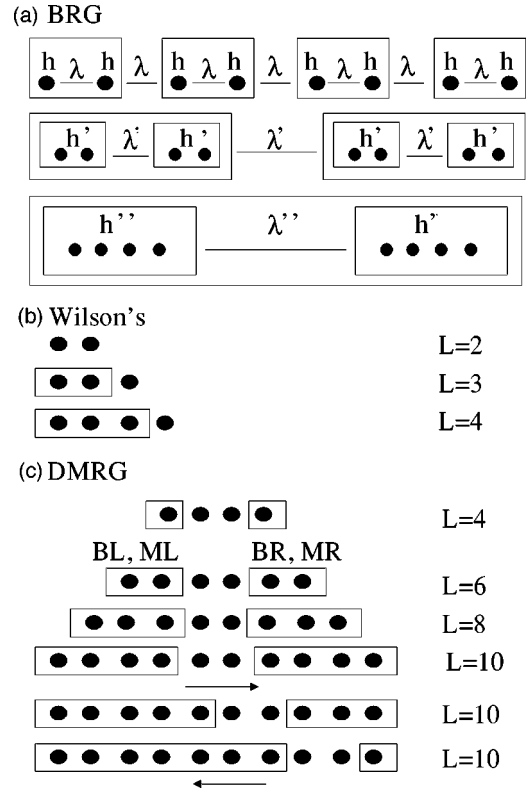


FIG. 1. Schematic plot of the spin couplings in the BRG, Wilson's and DMRG renormalization methods.

analytically. When subsequent iteration of the renormalization steps leaves the coupling constants unchanged, the algorithm has reached a fix point that 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 block renormalization-group (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^{11,12} 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 to select 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 the BRG method is that Wilson did not retain the original structure of the Hamiltonian operator but 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 fixed point.

The major drawback of the method is that since the structure of the Hamiltonian changes with increasing chain lengths, flow equations cannot be defined and the method cannot be studied analytically.

C. Density-matrix renormalization-group method

In spite of the powerful properties of Wilson's procedure, the numerical error of the method grew systematically with increasing chain length, a drawback that 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-site problem with open boundary conditions. These observations has led White to construct a larger auxiliary system (superblock configuration) that contains an environment in addition to the original block site problem to take care of the boundary effects in a more reliable way, as shown in Fig. 1. 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 represents the new site under consideration, the additional $\bullet B_R$ configuration represents the environment, and M_L and M_R denote the number of block states, respectively. In order to minimize the error introduced in the representation of the block state in the truncation process, 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 a different context¹³ that the reduced subsystem density matrix describes the interactions of two subsystems in a particularly efficient way. Using these two key ingredients, the 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

$$\Psi_{\text{target}} = \sum_{I,J}^{M_L q, M_R q} \psi_{I,J} |IJ\rangle, \quad (3)$$

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

$$\rho_{I,I'} = \sum_J \psi_{I,J} \psi_{I',J} \quad (4)$$

is diagonalized and the M eigenstates with largest eigenvalues (ω_α) are selected to build up the O matrix. The site operators are renormalized according to Eq. (2). 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

$$\text{TRE} = 1 - \sum_{\alpha=1}^{M_L} \omega_\alpha. \quad (5)$$

The initial B_L and B_R configurations contain one site per block each; thus the superblock Hamiltonian is determined on q^4 basis states restricted to the conserved quantum numbers such as 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. 1. This procedure is the so-called *infinite lattice* algorithm. In order to average out long-wavelength fluctuations, the superblock configuration is asymmetricized 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 the BRG and DMRG methods that 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 than q and the original structure of the Hamiltonian is not retained, thus flow equations of the coupling constants cannot 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 error 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. 14 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 the case of analytically solvable models, the structure of the eigenvalue spectra of the density matrix determines the energy spectrum of the model as was shown in Ref. 15.

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 such a way that the truncation error satisfies an initial condition that was introduced in advance of the calculation.

D. Quantum-chemical DMRG method

In the context of quantum chemistry (QC), a one-dimensional chain containing L molecular orbitals is generated by ordering the orbitals employed to build up the multiparticle states with increasing energy or by other rules, analogous to k points in the k -DMRG method.³ These molecular orbitals are calculated by standard numerical methods of quantum chemistry.

It worth noting 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 method is L from the very beginning and the block operators for the left and right blocks are generated by a “warm up” procedure³ 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. These 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 creation and annihilation operators. On the other hand, if orbitals from, e.g., a restricted Hartree-Fock (RHF) calculation are employed, it is possible to define a supersite 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 procedure⁶ is roughly reduced by a factor of 4 compared to the spin-orbital formulation. In our implementation we have built up the chain from supersites.

III. CONTROLLING THE ABSOLUTE ERROR OF THE DMRG METHOD

A. Dynamic adjustment of the number of block states

In order to control the accuracy of the DMRG procedure, the selection of the multiparticle states of the superblock Hamiltonian that are used for renormalization is obviously the decisive issue. With all states featuring eigenvalues of the subsystem reduced density matrix kept larger than a fixed parameter that 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 a 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 than 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 a 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. With use of 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 a 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. By 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 generated by ordering the orbitals in the case of the k -DMRG procedure. In the first method, the wave function of the target state is always very close to the wave function that 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 the DMRG method the introduction of virtual states is required in this situation, which means that we also keep those states that had almost zero eigenvalue up to a fixed number that we called M_{\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 better stability for 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 sweeps no longer changes. Within the framework of the dynamical block state selection 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 fixed point is not obtained since the structure of the density matrix and thus the truncation error and the relative error after convergence can slightly change (but within the same order of magnitude), depending on the initial condition, for example, on different M_{\min} . On the other hand, we can treat the energy values obtained for various TRE_{\max} values as points on a flow equation that converge to the fixed point at the end, which is the FCI energy. Based on previous results^{1,14,16-18} and those presented in the next section, we can extrapolate to the FCI energy using the equation

$$\ln \frac{E - E_{\text{FCI}}}{E_{\text{FCI}}} = a \ln(\text{TRE}) + b, \quad (6)$$

where a , b , and E_{FCI} are parameters determined from the fit of the numerical result. As discussed below, our numerical results show that the value of a is close to 1.

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

Besides the problem of the initial structure of the density matrix there is another difficulty that stems from the inaccuracy of the starting block wave functions. In contrast to the *infinite lattice* method, when the target state always remains in the same spin symmetry or changes sign periodically as a function of the chain length,¹⁹ the symmetry of the target state depends on the initial ordering in the case of the k -DMRG method. 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 is possible, for example, that with targeting the second level, the coefficients of the wave function of the ground state and excited states may mix and the spin symmetry of the target state will change randomly. 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 symmetry, 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 was shown in Ref.19. In case of the k -DMRG method the starting block wave function is constructed in such a way that it contains basis states with N_{up} and N_{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 dynamic selection rule automatically ensures that both of them are kept. It worth noting that this is not the full adaption of S^2 symmetry, which would be clearly be desirable but more complicated to achieve in the framework of the DMRG method. Thus, components of the singlet and quintet levels can still mix, but this would not be a problem since they are usually well separated. Application of the corresponding 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 a 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 diagonalization of the superblock Hamiltonian is decreased by a factor of 2, which doubles the speed of the algorithm. For the half-filled case the particle-hole symmetry operator 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

$$\langle A \rangle = \text{Tr}(\rho A). \quad (7)$$

where A is a L by 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} were. So with $A = T_{ij}$ Eq. (7) provides the kinetic energy of the FCI wave function. Once the target state is obtained, the one-particle reduced density matrix can be formed for any $B_L \bullet$ configuration as

$$\rho_{ij} = \langle \Psi_{\text{target}} | \sum_{\sigma} c_{i\sigma}^{\dagger} c_{j\sigma} | \Psi_{\text{target}} \rangle, \quad (8)$$

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.

	Basis set	Bond distance (a.u.)	Bond angle (deg)	Electrons	Orbitals	HF energy (a.u.)	FCI energy (a.u.)
H ₂ O	Double- ζ (DZ) ^a	1.843 45	110.565	10	14	-76.009 838	-76.157 866
H ₂ O	DZP ^b	1.889 73	104.500	8	25 (24)	-76.040 551	-76.25 6634
CH ₂ ¹ A ₁	DZ ^{c,d}	2.022 30	129.4667	6	14 (13)	-38.909 437	-38.932 107
CH ₂ ³ B ₁				6	14 (13)		-38.979 393
CH ₂ ¹ A ₁	cc-pVDZ ^e	2.043 240	129.112 075	6	24 (23)	-38.865 895	-39.006 652
CH ₂ ³ B ₁				6	24 (23)	-38.921 824	-39.041 774
CH ₂ ¹ A ₁	cc-pVTZ ^e	2.022 30	129.4667	6	58 (57)	-38.932 575	-39.087 006
F ₂	DZ ^{c,d}	2.643 73		14	20 (14)	-198.707 822	-198.915 252
F ₂	Split valence ^f	2.687 97		18	18	-198.484 167	-198.761 551

^aReference 23.^bReference 24. DZP denotes a double-zeta basis set with polarization functions.^cReference 25.^dReference 26.^eReference 27. cc-pVDZ denotes the correlation-consistent polarized valence double-zeta basis set, cc-pVTZ denotes the correlation-consistent polarized valence triple-zeta basis set.^fReference 28.

where i and 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 ρ_{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 showed 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. 14 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,

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

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 -DMRG³.

IV. NUMERICAL RESULTS

In order to study the performance of the k -DMRG method in quantum chemistry, we followed a route similar to the one we used to study the accuracy of the real-space DMRG method.¹⁴ We performed calculations on molecules with different properties for which the DMRG method 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 CH₂, H₂O, and F₂. 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,²⁰ which was also used for the calculation of the benchmark (FCI) energies.^{21,22}

We used various basis sets and geometries for the molecules that we selected for benchmark calculations. The geometries, references to the basis sets employed, and results obtained in self-consistent field (SCF) calculations as well as FCI energies are detailed in Table I. The models employed for the water molecule have also been used in the White-Martin study.⁶ We include these cases here in order to enable a direct comparison with previous work. A more interesting test case was to study the CH₂ 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 CH₂. 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 F₂ 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 method is capable of providing cutting-edge complete active space SCF (CASSCF) calculations with the potential to push their limits to active spaces well beyond a size that 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

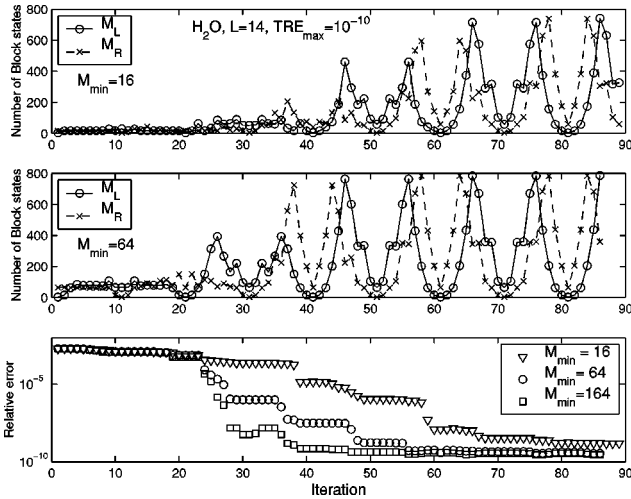


FIG. 2. Dynamically selected number of left and right block states B_L and B_R , respectively, for two values of the minimum threshold value $M_{min}=16,64$ and the relative error as a function of iteration obtained with $M_{min}=16,64,164$. In all cases the 10 electrons of the H_2O molecule were correlated in the double ζ water model with 14 orbitals, and $TRE_{max}=10^{-10}$ was set in advance of the calculations.

panels of Fig. 2 we have plotted the number of block states that were selected in a calculation correlating 10 electrons in 14 orbitals by means of the QC-DMRG method, starting with different values of M_{min} .

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 $[(E_{DMRG}-E_{FCI})/E_{FCI}]$ of the calculation as a function of M_{min} and the iteration step. The value of TRE_{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_{min}), although it is reached faster for larger M_{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 $M_{min}=164$. It can be seen in the figure that the relative error converges to the error margin determined by TRE_{max} in all cases, but the speed of convergence strongly depends on M_{min} . In order to show that the QC-DMRG algorithm is trapped in a local minimum if M_{min} is chosen too small, we carried out calculations with $M_{min}=4,8$ and found indeed the number of block states being hindered to increase. Similar test calculations on longer chains indicated that a larger value of $M_{min}=64-100$ is needed. Thus we suggest that in order to avoid problems related to local attractors and to obtain a faster performance, a value of M_{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 in the

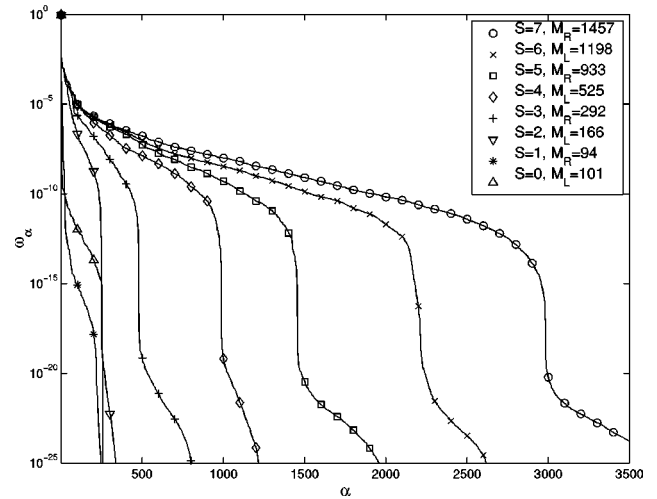


FIG. 3. Eigenvalue spectrum of the reduced subsystem density matrix obtained for the F_2 molecule after the end of the sweeps (S) of the *finite lattice* method. In the legend we have also included the number of selected block states (M_L, M_R) as a function of sweeps.

figure that the minimum value of M occurs in the region of the plateaus, resulting in a very fast transverse 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 F_2 molecule represented by 14 electrons and 14 orbitals. There are several conclusions that one can draw from the figure. First, 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 the 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 the error margin determined by TRE_{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 is worth noting 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

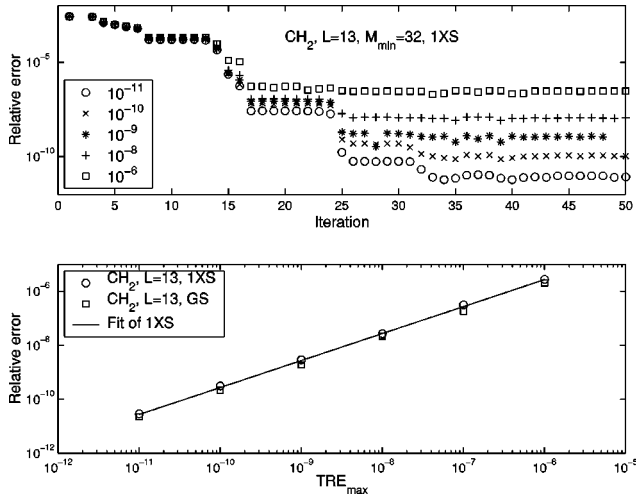


FIG. 4. Calculations for CH_2 with $L=13$ sites shows the relationship between relative error and TRE_{\max} . The straight line is the result of the fit. GS denotes the triplet ground state, and 1XS denotes the first excited (singlet) ground state.

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_{\max}

In order to test that the relative error converges to a given value of the error margin determined by TRE_{\max} we have run independent calculations for all the test molecules by adjusting TRE_{\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 $M_{\min}=32$ as a function of the iteration step and TRE_{\max} is shown in Fig. 4. It can be seen in Fig. 4(a), that the relative error of the first excited state also converges to the values of the error margin determined by TRE_{\max} set up in advance of the calculations. The converged value of the relative error as a function of TRE_{\max} for the first excited as well as for the ground state is plotted in Fig. 4(b). 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 the various tests cases also with different M_{\min} values, we have found that the slope was always between 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_{\min} showed that the relative error scales to TRE_{\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 a technical point of view, one can start a DMRG calculation by setting TRE_{\max} to 10^{-3} and when the algo-

rithm has converged (the energy is unchanged, and the number of block states are unchanged, the slope of the density matrix remains the same) TRE_{\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_{\max} (which is slightly below TRE_{\max}) the FCI energy can be estimated by Eq. (6). This equation contains three free parameters (E_{FCI}, a, b) to determine from the fit. However, based on our results we can set the parameter a to 1. We have found that one can gain 1–3 orders of magnitude improvements in the error of the correlation energy by the extrapolation method and that fixing the parameter a to 1 always provides an upper bound. In order to obtain a more accurate fit one needs more data points. Thus TRE_{\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 an analysis yet.

In the 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 2–3 orders of magnitude. Thus the overall performance of the 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 collected the values of the maximum number of block states selected dynamically by our method in Table II.

D. Other factors that affect 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 Ord_2 in 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 Ord_1). A nonoptimal ordering can in fact lead the method to be trapped by a local minimum. This situation is shown explicitly in Fig. 5 indicated by Ord_1 . Even if M_{\min} was almost tripled, the relative error converged to the same local minimum, which, on the other hand, also supports our previous statements that M_{\min} does not affect the final convergence significantly. Changing the ordering, we have found for Ord_2 that the algorithm has always converged to the value of the error margin determined by TRE_{\max} . Studying the optimal ordering can be a major field of research. Chan and Head-Gordon⁹ has already suggested a procedure

TABLE II. The maximum number of the block states selected dynamically by the DMRG method 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.

	CH ₂	H ₂ O	F ₂	CH ₂	H ₂ O	F ₂	CH ₂
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}	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					

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 superbloc configuration. In our largest calculations for the half-filled case (18 electrons in 18 orbitals), the number of selected block states increased to 1500–1800 with sizes of the Hilbert space of the superbloc configuration increasing beyond 1 000 000. In order to decrease the size of the Hilbert space we have derived an alternate protocol, modifying the superbloc 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 superbloc configurations.

V. SUMMARY

We have applied the momentum-space version of the DMRG procedure 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 the real-space DMRG procedure, 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 H₂O, CH₂, and F₂ obtained with various basis sets in order to show that the relative error scales with 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 an alternative approach to extrapolate the FCI energy, a method that could also improve the accuracy of the finite-size scaling method when the k -DMRG procedure is applied in solid state physics. We have addressed new problems related to the inaccuracy of starting block state configuration and presented solutions for achieving faster convergence and better stability of the target state.

The maximum number of block states that the algorithm selected in the dynamic mode was in the range of 1500–2000, the largest size of the Hilbert space related to the superbloc 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 the k -DMRG method is applied in quantum chemistry, there are still a few remarks which might indicate why the QC-DMRG method can work well in the field:

(1) In most of the cases the calculations carried out in the small U limit are 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 a lower filling value that usually has a better convergence.

(3) The practical use of the DMRG method in quantum chemistry can open a route to active spaces well beyond today's limits, yielding CASSCF solutions with a relative

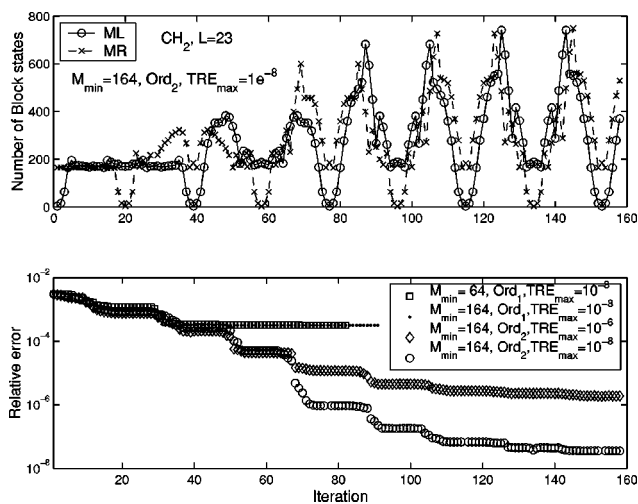


FIG. 5. Incorrect ordering can drive the DMRG procedure to a local minimum.

error of the correlation energy on the order of 10^{-4} – 10^{-5} . This can be realized by a few thousand block states, which is also expected to hold for longer chains as well. Therefore, we believe that 3000–4000 block states will provide satisfactory results for all the chain lengths and fillings that 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 wave function 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 stand alone 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 electrons and 18 orbitals) the

program required 200–500 Mbytes of RAM, running about 50–60 h on an 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 because of the development stage of our code, but as a rough indication it took some 15 h for the eight-electron, 24-orbital chain and more than a week for the six-electron, 57-orbital case. 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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¹S. R. White, Phys. Rev. Lett. **69**, 2863 (1992).

²S. R. White, Phys. Rev. B **48**, 10 345 (1993).

³T. Xiang, Phys. Rev. B **53**, 10 445 (1996).

⁴G. Fano, F. Ortolani, and L. Ziosi, J. Chem. Phys. **108**, 9246 (1998).

⁵L. Bendazzoli, S. Evangelisti, G. Fano, F. Ortolani, and L. Ziosi, J. Chem. Phys. **110**, 1277 (1999).

⁶S. R. White and R. L. Martin, J. Chem. Phys. **110**, 4127 (1998).

⁷S. Daul, I. Ciofini, C. Daul, and S. R. White, Int. J. Quantum Chem. **79**, 331 (2000).

⁸A. O. Mitrushenkov, G. Fano, F. Ortolani, R. Linguerri, and P. Palmieri, J. Chem. Phys. **115**, 6815 (2001).

⁹G. K.-L. Chan and M. Head-Gordon, J. Chem. Phys. **116**, 4462 (2002).

¹⁰S. Nishimoto, E. Jeckelmann, F. Gebhard, and R. M. Noack, Phys. Rev. B **65**, 165114 (2002).

¹¹K. G. Wilson, Rev. Mod. Phys. **47**, 773 (1975).

¹²K. G. Wilson, Rev. Mod. Phys. **55**, 583 (1983).

¹³W. Kutzelnigg and F. Maeder, Chem. Phys. **32**, 451 (1978).

¹⁴Ö. Legeza and G. Fáth, Phys. Rev. B **53**, 14 349 (1996).

¹⁵I. Peschel, M. Kaulke, and Ö. Legeza, Ann. Phys. (Leipzig) **8**, 1533 (1999).

¹⁶E. Jeckelmann and S. White, Phys. Rev. B **57**, 6376 (1998).

¹⁷J. Bonca, J. E. Gubernatis, M. Guerrero, E. Jeckelmann, and S. R. White, Phys. Rev. B **61**, 3251 (2000).

¹⁸T. Xiang, J. Lou, and Z. Su, Phys. Rev. B **64**, 104414 (2001).

¹⁹Ö. Legeza and J. Sólyom, Phys. Rev. B **56**, 14 449 (1997).

²⁰R. D. Amos, A. Bernhardsson, A. Berning, P. Celani, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, C. Hampel, G. Hetzer, P. J. Knowles, T. Korona, R. Lindh, A. W. Lloyd, S. J. McNicholas, F. R. Manby, W. Meyer, M. E. Mura, A. Nicklass, P. Palmieri, R. Pitzer, G. Rauhut, M. Schütz, U. Schumann, H. Stoll, A. J. Stone, R. Tarroni, T. Thorsteinnsson, and H.-J. Werner. MOLPRO, a package of *ab initio* programs designed by H.-J. Werner and P. J. Knowles, version 2002.1, 2002.

²¹P. J. Knowles and N. C. Handy, Chem. Phys. Lett. **111**, 315 (1984).

²²P. J. Knowles and N. C. Handy, Comput. Phys. Commun. **54**, 75 (1989).

²³P. Saxe, H. F. Schaefer, III, and N. C. Handy, Chem. Phys. Lett. **79**, 202 (1981).

²⁴C. W. Bauschlicher, Jr. and P. R. Taylor, J. Chem. Phys. **85**, 2779 (1986).

²⁵S. Huzinaga, J. Chem. Phys. **42**, 1293 (1965).

²⁶T. H. Dunning, Jr., J. Chem. Phys. **53**, 2823 (1970).

²⁷T. H. Dunning, Jr., J. Chem. Phys. **100**, 2975 (1994).

²⁸A. Schäfer, H. Horn, and R. Ahlrichs, J. Chem. Phys. **97**, 2571 (1992).