We describe how density-matrix renormalization group (DMRG) can be used to solve the full-CI problem in quantum chemistry. As an illustration of the potential of this method, we apply it to a paramagnetic molecule. In particular, we show the effect of various basis set, the scaling as the fourth power of the size of the problem, and compare the DMRG with other methods.

I. INTRODUCTION

First-principle quantum chemistry is employed successfully to obtain thermochemical data; molecular structures; force fields and frequencies; assignments of NMR-, photoelectron-, E.S.R-, and UV-spectra; transition state structures as well as activation barriers; dipole moments and other one- or two-electron properties. Two routes of calculation are available: (i) ab initio Hartree-Fock (HF) and post-HF methods; and (ii) density functional theory (DFT). Though both approaches are rigorous, the former one necessitates lengthy configuration interaction (CI) treatment to account for electron correlation; whereas the latter one crucially depends upon the quest for accurate exchange and correlation functionals. The recently acquired popularity of DFT stems in large measure from its computational efficiency, allowing it to treat medium to large size molecules at a fraction of the time required for HF or post-HF calculations. More importantly, expectation values derived from DFT are, in most cases, better in line with experiment than results obtained from HF calculations. This is particularly the case for systems involving transition metals. Nevertheless, if one wants to achieve experimental accuracy for small polyatomic molecules, the method reaches its limits. On the other hand, post-HF overcomes these limits and goes even beyond experimental accuracy, e.g. in case of H$_2$. The drawback is of course its very high cost in computational power. However these very accurate calculations of small systems may provide the best route to obtaining more accurate exchange-correlation potentials using the constrained search algorithm of Levy [1].

Keeping the discussion to ab initio (HF and post-HF) quantum chemistry, let us now consider the state of the art in this topic. We now know how to do very large calculations, using the direct methodology [2]. We can also manage to work with good basis sets for such calculations, although it is considered that 6-31G* are not good enough, and probably something nearer to TZ2P is required for definitive SCF calculations. Beyond SCF there are major difficulties, all associated with trying to more accurately represent the electron-electron cusp. We know from the work of Kutzelnigg [3], that the convergence of this problem is very slow, something like $(\ell + \frac{1}{2})^{-4}$, with $\ell$ the orbital angular momentum quantum number. This means that very large basis sets are required for correlated calculations. We know that it is more important to include $d$ and $f$ basis functions than to improve the methodology (e.g. 6-31G* basis are not appropriate for correlated studies). We also know that the raw cost of the main correlated methods, MP2, MP3, MP4, CISD, QCISD, and QCISD(T) increase with powers of the size of the problem as 5, 6, 7, 6, 6, 7, respectively. We recognize that QCISD(T), with large basis sets, can make predictions for small molecules which are of “chemical accuracy” (e.g. the G2 quantum chemistry of J. Pople at al.). Considering “coupled cluster” technology, although this method is very promising, we have to realize that it is not yet possible to contemplate calculations with 1000 basis functions. The rapid progress that computer companies have made in the development of their hardware, such as more memory, vectorization compilers, and parallel machines will not cure these basis set problems.

Recently, one of us (S.W.) and R. L. Martin have shown that with the density matrix renormalization group (DMRG), one can calculate “exactly” (full CI) the electronic structure of N interacting electrons in a field of M nuclei [4]. By “exactly” we mean that the correctness of the treatment of correlations increases very rapidly and systematically with the calculational effort, so that one is essentially only
limited by the accuracy of representing the Hamiltonian in a finite basis set. Moreover, these authors showed that the method theoretically scales as $\mathcal{O}(N^4)$ and hence the calculation of much larger molecules will be feasible. More precisely, this $N^4$ dependence originates from the summation over four indices in the second quantized form of our Hamiltonian (Eq. 13). Hence, it will be possible to exploit the short sightedness of interatomic interactions in the future e.g. in using localized basis function (cf. vide infra). Thus we expect to achieve linear scaling, $\mathcal{O}(N)$, for large linear molecules when teraflop CPU’s and peta bytes storage media will become routinely available to us. Moreover, we would like to point out that the method at hand is well suited for CAS calculations. Indeed, since the basis functions used will usually be Hartree-Fock or Kohn-Sham eigenfunctions, we can easily use the corresponding eigenvalues to setup an active space by discarding inner shell orbitals (in keeping their occupation frozen) or in eliminating those with very large energies.

This paper is organized as follows. In Sec. II, we recall the physical principles of the DMRG. Then we reformulated, in a more chemical language, the basic algorithm for molecules in Sec. III. Finally, in Sec. IV we apply the technique on a paramagnetic molecule and discuss the performance of the method as a function of the basis set used.

II. PRINCIPLES OF THE DENSITY MATRIX RENORMALIZATION GROUP (DMRG)

A. The Renormalization Group

The idea of the Renormalization Group (RG) is to apply a transformation to the Hamiltonian which eliminates degrees of freedom that are unimportant for the description of the states in the energy range we are interested in. For example, if we are interested in the low energy states of a system with an energy cutoff $\Lambda$, one integrates out modes with energy

$$\Lambda - \delta \Lambda \leq \omega \leq \Lambda$$

where $\delta \Lambda$ is a small energy interval. Then we rescale the parameters of the new system so that it reproduces the previous one. In other words, given a Hamiltonian $H$ of a system with $N$ variables, a renormalization transformation $R_b$ is a mapping in the Hamiltonian space which maps $H$ to $H'$,

$$H' = R_b(H).$$

This new Hamiltonian describes a system with $N' = N/b \leq N$ variables. The RG transformation must be unitary, i.e. it has to preserve the partition function ($Z = \text{Tr} \, e^{-H/kT}$),

$$Z_{N'} [H'] = Z_N [H].$$

This set of transformations is called a group because the transformations must be associative:

$$R_{U'} (R_b(H)) = R_{U'b}(H).$$

An exact transformation is usually not possible. For example, Wilson and Fisher worked in Fourier space and used a perturbative scheme in order to analytically solve this problem. Another approach is to consider the Hamiltonian on a lattice and to work in real space. A RG transformation could be the elimination of every second site and then the redefinition of the Hamiltonian parameters in order to reproduce the original problem.

A numerical implementation for a quantum mechanical problem was given by Wilson who succeeded in constructing a non-perturbative RG transformation for the Kondo model. The same transformation has since then been applied to a wide range of similar quantum impurity models with equal success. On the other hand, it has proven to be more difficult to develop similar RG transformation for quantum lattice models. These difficulties with RG approaches in real space provided the motivation for the development of DMRG.
Let $H$ be a one-dimensional Hamiltonian describing an interacting system of electrons on a lattice with $L$ sites labeled $i$. Each site has one (Wannier) orbital which can be in 4 different states: $|0\rangle$, $|\uparrow\rangle$, $|\downarrow\rangle$ and $|\uparrow\downarrow\rangle$. The dimension of the Hilbert space for $N_\uparrow$ up-spin electrons and $N_\downarrow$ down-spin electrons is thus

$$\dim \mathcal{H} = \binom{L}{N_\uparrow} \binom{L}{N_\downarrow}.$$  

(5)

Which is, for $L = 100$ and $N_\uparrow = N_\downarrow = 50$, $\dim \mathcal{H} = 10^{58}$. This is of course intractable numerically. The idea is to obtain the low energy eigenstates of that system by keeping only a small number of states, e.g. 1000.

For the sake of clarity we will first directly apply Wilson’s scheme to quantum lattice systems and then show why it does not work with a simple example. We will describe next a RG step.

**FIG. 1. Wilson’s blocking scheme for real-space renormalization group.**

Let $B_\ell$ be a block describing the first $\ell$ sites for which we only keep $m$ states to describe the Hamiltonian of that part of the system. The internal Hamiltonian $H_\ell$ is then represented by an $m \times m$ matrix. One adds to this block (see Fig. 1) another block $B_{\ell'}$ describing $\ell'$ sites with internal Hamiltonian $H_{\ell'}$. The Hamiltonian of the new block $B_{\ell+\ell'}$ has dimension $mm'$ and can be written as

$$H_{\ell+\ell'} = H_\ell \otimes 1 + 1 \otimes H_{\ell'} + \sum_\alpha c_\alpha A^\alpha \otimes B^\alpha.$$  

(6)

Here, the last term represents the interactions between $B_\ell$ and $B_{\ell'}$, where the $A^\alpha$ are operators in $B_\ell$ and the $B^\alpha$ are in $B_{\ell'}$ (See Section III.C.) The RG idea is then to reduce the size of this many body basis from $mm'$ to $m$. For this purpose, in Wilson’s original formulation, one diagonalizes $H_{\ell+\ell'}$ and keeps only the $m$ states with the lowest energy eigenvalues, since we seek the low energy states.

This method has been directly applied to quantum lattice systems [8] but the spectra become inaccurate after a few iterations. The problem originates from the treatment of the boundary conditions. To illustrate this, we will consider the problem of a free particle on a lattice of size $L$ with open boundary conditions or, in other words, the discretized version of a free particle in a box. The eigenstates of this system are

$$\chi_n(x) \sim \sin \left( \frac{n\pi x}{L} \right)$$  

(7)

where $n$ is a positive integer. We now consider the addition of two blocks of size $L$. In the RG procedure, the lowest few eigenstates of system of length $L$ are combined to form the low-lying eigenstates of the system of length $2L$. The lowest eigenstates of two systems of length $L$ and of a single system of length $2L$ are shown in Fig. 2. One sees clearly that a combination of the ground states of the two small systems (size $L$) cannot reproduce the ground state of the large system (size $2L$). The kink in the superposition of the two ground states of the small systems can only be removed if one keeps almost all the eigenstates of the smaller systems.
This example shows that the treatment of the boundaries of the block is crucial. White and Noack formulated two types of RG procedures which solve this problem. Both are based on choosing a new basis for $H_{2L}$ which is not the set of eigenstates of $H_L$. In their first procedure, the combination of boundary conditions method, the new basis is obtained from the low-lying eigenstates of several different block with different boundary conditions at the edge of the block. In the second type of procedure they proposed, the superblock method, the new basis for $H_{2L}$ exploits the idea that it will eventually be used to make up parts of a larger system. These two methods were applied to the free particle in a box and both yielded accurate results. While the first method is not so well suited for many particle problems, the second one necessitates an optimal projection from the superblock. This gave rise to the DMRG scheme which is described in the next section.

C. Density-Matrix approach

The fundamental difficulty in the standard approach lies in the choice of the lowest energy eigenstates of $H_{\ell+\ell'}$ as the new truncated basis. Since $H_{\ell+\ell'}$ contains no connections to the rest of the lattice, its eigenstates exhibit inappropriate features at the block boundaries. One way of avoiding this problem is to diagonalize a larger system (a “superblock”) which contains the new block $B_{\ell+\ell'}$. The idea is that fluctuations in the rest of the superblock (the “environment”) lead to a more appropriate treatment of the boundary of $B_{\ell+\ell'}$. The wave function for the superblock is projected onto $B_{\ell+\ell'}$ producing a set of states of $B_{\ell+\ell'}$ which are then retained.

Let $\{|i\rangle\}$ be a complete set of states of $B_{\ell+\ell'}$ and $\{|j\rangle\}$ be the states of the rest of the superblock. We can then write

$$|\psi\rangle = \sum_{i,j} \psi_{ij} |i\rangle |j\rangle.$$  

In Ref. [10] one of us (S.W) shows that the optimal states to be kept are the eigenvectors of the reduced density matrix of the superblock,

$$\rho_{ij} = \sum_{k} \psi_{ik} \psi_{jk}.$$  

Let us denote by $\omega_\nu$ the eigenvalues of $\rho$ in decreasing order. The $m$ optimal states we seek, $u^{\nu}$, are the eigenstates of $\rho$ with the largest eigenvalues. Each $\omega_\nu$ represents the probability of the system being in the state $u^{\nu}$, hence $\sum_\nu \omega_\nu = 1$. The deviation of

$$P_m = \sum_{\nu=1}^{m} \omega_\nu,$$

from unity measures the accuracy of the truncation of the $m$ states (typically, $1 - P_m \leq 10^{-6}$).
1. Density-Matrix algorithm

In practice we take one block to be just a single site. Fig. 3 shows the superblock configuration that we use. We adopt the notation $B_\ell \bullet B_{\ell'}$ for this configuration, where $B_\ell$ represents a block composed of $\ell$ sites, $B_{\ell'}$ is a block of length $\ell'$, $\bullet$ represents a single site, and the length of the superblock is therefore $L = \ell + \ell' + 2$. Hence, the new block $B_{\ell+1}$ is formed by the left block plus a single site.

![FIG. 3. The configuration of blocks used for the density matrix calculations.](image)

In general, DMRG algorithms can be divided into two classes according to how the environment block $B_{\ell'}$ is chosen. In the infinite system algorithm, $B_{\ell'}$ is chosen to be $B_R^\ell$, the reflection of $B_\ell$. Therefore the superblock grows as $B_\ell$ is built up. For the finite system algorithm, $B_{\ell'}$ is usually chosen so that the length of the superblock is $L$. It begins with the use of the infinite system algorithm (see Fig. 4) for $\frac{L}{2} - 1$ steps, such that the final superblock obtained is of size $L$.

![FIG. 4. Schematic infinite system algorithm.](image)

That is, we start with a four site chain $B_1 \bullet \bullet B_R^1$. Then we calculate the density matrix and construct an effective Hamiltonian for $B_2$. In the second step, we diagonalize $B_2 \bullet \bullet B_R^2$ where we have formed $B_R^2$ by reflecting $B_2$. We continue in this manner, diagonalizing the configuration $B_\ell \bullet \bullet B_R^\ell$, setting $B_{\ell+1}'$ equal to $B_\bullet$, and then using $B_{\ell+1}$ and its reflection in the next step. Once the system $B_{\frac{L}{2} - 1} \bullet \bullet B_R^{\frac{L}{2} - 1}$ is used to form $B_{\frac{L}{2}}$, the next step is to form $B_{\frac{L}{2} + 1}$. This system and all the other superblocks to follow will involve exactly $L$ sites. We continue to form the other blocks up to size $L - 3$ using the superblock $B_\ell \bullet \bullet B_R^{L-\ell-2}$ to build $B_{\ell+1}$. This sequence of steps corresponds to the first iteration of the finite system algorithm.

![FIG. 5. Schematic finite system algorithm](image)
The second and subsequent iterations use superblocks of fixed length $L$ (see Fig. 3). We start by diagonalizing $B_1 \bullet B_{L-3}^R$ forming $B_2$ up to $B_{L-3} \bullet B_L^R$ where we use the blocks obtained from the previous iteration to build the reflected blocks $B_L^R$. On the very last iteration we stop after diagonalizing $B_{L-1}^R \bullet B_{L-1}^R$ and then use the wave function of the $L$ sites system to measure ground-state properties, e.g. correlation functions. At each sweep (left-to-right and right-to-left iteration) we increase the number of states $m$ used to represent the Hamiltonian and other operators inside the block.

Since we truncate the basis, the algorithm is variational and in practice the calculated value for the ground-state energy obeys the empirical law

$$E(m) = E_0 + \Delta e^{-m/m^*}$$  \hspace{1cm} (11)

where $E_0$ is the targeted energy; $\Delta$ and $m^*$ are adjustable parameters.

An important improvement in efficiency can be made by keeping track of the wave function in the process of adding a site \cite{11}. We can then construct a better initial wave function for the Davidson diagonalization of the superblock, thus reducing the number of steps needed to obtain convergence.

### III. QUANTUM CHEMISTRY WITH THE DMRG

#### A. The non-relativistic time-independent Schrödinger equation

We will now show how the DMRG can be applied to ab initio quantum chemistry \cite{4}. Essentially the DMRG will yield both the energy and the wave function of the ground state and of some excited states. More precisely, we consider a molecule with $N$ interacting electrons moving in the field of $M$ fixed nuclei. The Hamiltonian describing this system is

$$H = -\frac{1}{2} \sum_{i=1}^{N} \Delta_i - \sum_{i=1}^{N} \sum_{k=1}^{M} \frac{Z_k e^2}{|r_i - r_k|} + \frac{1}{2} \sum_{i,j} \frac{e^2}{|r_i - r_j|}$$  \hspace{1cm} (12)

and we will use atomic units throughout this paper.

#### B. Second quantized form of the Hamiltonian

To perform calculations, this Hamiltonian is represented in a finite basis of $K$ functions. One chooses usually atomic orbitals $\chi_i$ with $i = 1, \ldots, K$ which are described, for example, by the product of a few Gaussians and spherical harmonics. This set expands a smaller (finite size) Hilbert space and is not orthogonal. The first step is to orthogonalize these functions to be able to represent the Hamiltonian (12) in second quantization. In practice one can perform a Hartree-Fock calculation in order to generate a set of basis functions. In doing so, we have a good (low energy) starting point for the calculation of the correlation energy.

Consider a set of $K$ molecular orbitals (MO), $\{\varphi_i\}, i = 1, \ldots, K$, which we reorder with increasing energy. We mainly used Hartree-Fock molecular orbitals, but we do not have to restrict ourselves to them, and we have also used Kohn-Sham orbitals (see discussion in IV B). In case of closed shell systems, an approximate ground state would be when the first $N/2$ orbitals are occupied by 2 electrons and the remainders (virtual orbitals) are empty. These MO can be obtained from the atomic orbitals by the well-known Linear Combination of Atomic Orbitals - Self Consistent Field (LCAO-SCF) scheme \cite{12}. One uses then the second quantization formalism to reexpress the Hamiltonian (12). An introduction to that technique can be found, e.g., in Ref. \cite{13}. The creation (annihilation) operator $c_{i\sigma}^\dagger \ (c_{i\sigma})$ creates (annihilates) an electron with spin $\sigma$ in the MO $\varphi_i$. The Hamiltonian we shall use from now on reads then

$$H = \sum_{i,j} \sum_{\sigma} H_{i,j} c_{i\sigma}^\dagger c_{j\sigma} + \frac{1}{2} \sum_{i,j,k,l} G_{ijkl} \sum_{\sigma,\sigma'} c_{i\sigma}^\dagger c_{j\sigma}^\dagger c_{k\sigma'} c_{l\sigma}.$$  \hspace{1cm} (13)

The sum is over all orbitals and spin $\sigma$. The integrals

\[\text{...}\]
\[
H_{ij} = \int dr \phi_i^* (r) \left[ -\frac{1}{2} \Delta - \sum_{k=1}^{M} \frac{Z_k e^2}{|r - r_k|} \right] \phi_j (r) \tag{14}
\]
represent the elements of the core Hamiltonian (kinetic energy and nuclear attraction), while
\[
G_{ijkl} = \int \int d\mathbf{r} d\mathbf{r}' \phi_i^* (\mathbf{r}) \phi_j^* (\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \phi_k (\mathbf{r}') \phi_l (\mathbf{r}) \tag{15}
\]
are the interelectronic repulsion integrals. Using the occupation number formalism, a Slater determinant \( \psi \) of \( N \) electrons can be written as
\[
\psi = c_{i_1 \sigma_1}^\dagger c_{i_2 \sigma_2}^\dagger \cdots |0\rangle \tag{16}
\]
where \( |0\rangle \) is the vacuum state. As an example, the singlet Hartree-Fock eigenstate for a closed shell system is
\[
\psi_{\text{HF}}^{0} = c_{1\uparrow}^\dagger c_{1\downarrow}^\dagger c_{2\uparrow}^\dagger c_{2\downarrow}^\dagger \cdots c_{N/2\uparrow}^\dagger c_{N/2\downarrow}^\dagger |0\rangle. \tag{17}
\]

A full-CI calculation is then the exact diagonalization of (13) in this occupation number representation of the Hilbert space basis. Since the size of the matrix of (13) is \( O(N!) \), e.g. 10 spin-up electrons and 10 spin-down electrons with 40 orbitals has a dimension of approximately \( 10^{18} \), one cannot use the Lanczos \([14]\) or Davidson \([15]\) algorithm to solve this problem. Instead we use the DMRG to obtain the ground state and some excited states of the Hamiltonian (13) for small to medium sized polyatomic molecules.

Since the DMRG was initially developed for one-dimensional quantum lattices, a molecular wave function (such as the Hartree-Fock MO) becomes a site which can be empty, singly occupied with an up or down-spin electron or doubly occupied. Hence a molecule described by \( K \) orbitals becomes a lattice with \( L = K \) sites and the Hamiltonian given in Eq. (13). As input for the DMRG we need the matrix elements \( H_{ij} \) and \( G_{ijkl} \). Since our Hamiltonian conserves the total number of particles and the total spin, we also specify the number of electrons \( N \) and the projection of the total spin on a quantization axis \( S_z \) in order to reduce the dimension of the Hilbert space.

### C. One DMRG step

We want to describe here explicitly the major part of the DMRG applied to quantum chemistry, a renormalization step with the density matrix. We use the finite-size algorithm of the DMRG and target only the ground state. In a warmup procedure, we construct an approximated ground state (e.g. Hartree-Fock). Then we start the algorithm following the description in Ref. \([16]\). Let us consider in detail the addition of an arbitrary orbital (site). We already have built a subspace \( S_\ell \) which describes partially the electronic structure of the molecule using the first \( \ell \) MOs. In the original DMRG formalism this subspace spanned by \( \ell \) basis functions, which were Wannier functions located on each site, was called a block. To avoid possible confusion with quantum lattice concepts, we prefer here to use the word “subspace”. For the description of that subspace we keep only \( m \) states. These states are used to represent i) the part of the ground state in that subspace; ii) the internal part of the Hamiltonian, i.e. terms that only involve indices which belong to the subspace \( (i, j, k, l \leq \ell) \); and iii) terms that will be used in constructing the interactions between the subspaces, such as \( [c_{i\sigma}^\dagger, [c_{i\sigma}, [c_{j\sigma}^\dagger, c_{j\sigma}^\dagger] \cdots \).

We add then the \((\ell + 1)\)th orbital (site) to the current subspace (see Fig. 6) and construct the internal Hamiltonian for the new subspace \( S_{\ell+1} \) and for all other operators needed as well.

---

**FIG. 6.** Schematic view of the left subspace with one orbital added.
The Hamiltonian reads

\[ H_{\ell+1} = H_\ell \otimes 1 + 1 \otimes H_1 + \sum_{i \leq \ell} \sum_{\sigma} H_{i,\ell+1} \left[ c_{i\sigma}^\dagger \right]_\ell \otimes \left[ c_{\ell+1,\sigma} \right]_1 + \ldots \]  
\[ \quad + \sum_{i,j \leq \ell+1, \sigma, \sigma'} G_{ij,\ell+1,\ell+1} \left[ c_{i\sigma}^\dagger c_{j\sigma'}^\dagger \right]_\ell \otimes \left[ c_{\ell+1,\sigma'} c_{\ell+1,\sigma} \right]_1 + \ldots \]  

where \([A]_\ell\) denotes the matrix of the operator \(A\) represented in the basis of the \(m\) most significant states of the subspace \(S_\ell\) and \([A]_1\) denotes the matrix of the operator \(A\) represented in the Hilbert space of one orbital. For example, if the order of the basis set is \(\{|0\rangle, \uparrow, \downarrow, \uparrow\downarrow\}\), where \(\uparrow\downarrow\) is defined as \(c_\uparrow^\dagger c_\downarrow^\dagger |0\rangle\), the matrix for the creation operator of an up-spin electron for the MO \(\ell + 1\) is

\[ \left[ c_{\ell+1,\uparrow}^\dagger \right]_1 = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}. \]

The new subspace is now described by \(4m\) states. We will illustrate now how to reduce this number to \(m\). To this purpose we need to construct the environment which involves all the residual orbitals. In case of a molecule, we can not reflect the current subspace (block) as in case of a quantum lattice system since there is, in general, no equivalent reflection symmetry. We apply the same procedure for the right subspace \(S_{L-\ell-2}\). In Fig. 7 we show the construction of the left and right subspaces.

At the end we will have two subspaces \(S_{\ell+1}\) and \(S_{L-\ell-1}\): the first describing partially the electronic structure of the molecule within the first \(\ell + 1\) orbitals and the second one, the rest of the molecule with the remaining \(L - \ell - 1\) orbitals. In order to retain only the \(m\) states of \(S_{\ell+1}\) which best represents the whole molecule, we construct the full molecule by adding the two subspaces together. We build a representation of the full Hilbert space by adding the two subspaces together, which means taking the direct product of the two subspaces. We then compute the ground state of the whole molecule using the Davidson algorithm. We then construct the projected density matrix. The full Hamiltonian could be constructed in the same way as when adding two blocks together, Eq. (19), but to be more efficient, we use the following procedure. In the Davidson algorithm, the time consuming part is the \(H|\Psi\rangle\) multiplication. The matrix of the molecular Hamiltonian can be written in the general form as

\[ \left[ H_{\text{molecule}} \right]_{ij;i'j'} = \sum_{\alpha} A_{ii'}^\alpha B_{jj'}^\alpha \]  

where the index \(i\) and \(i'\) stands for states in the left subspace and \(j, j'\) for the right subspace. The sum on \(\alpha\) is over all terms of the Hamiltonian. Then the product \(H_{\text{molecule}}|\Psi\rangle\) can be written as

\[ \sum_{i',j'} \left[ H_{\text{molecule}} \right]_{ij;i'j'} \Psi_{ij} = \sum_{\alpha} \left[ \sum_{i'i'} A_{ii'}^\alpha \left( \sum_{jj'} B_{jj'}^\alpha \Psi_{ij'} \right) \right] \]  

The last sum is performed first as a matrix multiplication of \(B^\alpha\) with \(\Psi^T\), to form a temporary matrix \(C_{ij'}.\) Then a matrix multiplication of \(A^\alpha\) by \([C^\alpha]^T\) yields a partial term, which is added into the resulting vector, giving a sum on \(\alpha\). Using the Davidson algorithm one obtains the ground state \(\Psi_0\) and some excited states, if desired.
Then we construct the reduced density matrix tracing out the environment components
\[ \rho_{ii'} = \sum_j \Psi_{ij}^* \Psi_{i'j}. \]  
(23)

One diagonalizes \( \rho \), obtaining \( 4m \) eigenvectors \( \phi^{\nu} \) and the corresponding eigenvalues \( \omega^{\nu} \). Each \( \omega^{\nu} \) represents the probability of the system being in the state \( \phi^{\nu} \), with
\[ \sum_{\nu=1}^{4m} \omega^{\nu} = 1. \]  
(24)

One chooses the \( m \) states with the highest \( \omega^{\nu} \) value. The discarded weight
\[ 1 - \sum_{\nu=1}^{m} \omega^{\nu}, \]  
(25)
measures the accuracy of the truncation to \( m \) states.

The reader may notice a similarity between this procedure and the construction of natural orbitals. However, a crucial difference is that the density matrix here is a many particle density matrix, with an exponentially large dimension, not a single particle density matrix. The resulting basis is a many particle basis, with each state representing a complicated sum over large numbers of configurations.

When the new basis is formed \((m \text{ elements})\), the operators must be updated. The eigenstates \( \phi^{\nu} \) can be written in the form
\[ \phi^{\nu}_{ij}, \]  
(26)
where \( i \) denotes a state in the subspace \( S_\ell \) and state \( j \) corresponding to the \((\ell + 1)\)th orbital. We store them in a \( m \times 4m \) matrix \( \mathcal{O} \). Thus each operator \( A \) that is needed is replaced by
\[ \tilde{A} = \mathcal{O} A \mathcal{O}^T. \]  
(27)

Adding the \((\ell + 1)\)th orbital to the subspace \( S_\ell \) corresponds to one DMRG step. There are a total \((K - 2)\) DMRG steps to zip through all \( K \) orbitals, and another \((K - 2)\) DMRG steps to zip back to the beginning, with the roles of the left and right subspaces switched. This is a complete DMRG sweep, keeping always \( m \) states per RG step. After one iteration we increase the number of significant states \( m \), e.g. by doubling it, and start again using the preceding result for \( S_{\ell - \ell - 2} \) to describe environment (i.e. the complementary space). Since we truncate the basis of the full Hilbert space but calculate the Hamiltonian exactly within this basis, this algorithm is variational. In the limit where we keep enough states \( m \) to solve the full-CI problem, this algorithm is also clearly size consistent.

At the end, we obtain the energy and a representation of the ground state from which we can compute the density, the natural orbitals, the two-electron density matrix, etc.

D. Illustration

In order to illustrate the DMRG procedure, let us consider a simple example, the methane molecule with \( T_d \) symmetry (\( \text{CH}_4 \)). We follow the procedure outlined above:

1. Choose a minimal basis : STO-3G (9 orbitals).
2. Perform a Hartree-Fock calculation obtaining 9 MO and the Hartree-Fock electronic energy \( E = -53.248968 \ldots \).
3. Represent the Hamiltonian in this basis, i.e. calculate all \( H_{ij} \) and \( G_{ijkl} \).
4. Apply the DMRG to obtain the ground state of the molecule (see Appendix for some technical points).
In Fig. 8 we show the ground-state energy $E$ as a function of the number of significant states $m$ retained in each DMRG iteration. We also show results obtained by the CAS method. In CAS($\nu,\mu$) we consider the complete active space configuration interaction of $\mu$ electrons for $\nu$ orbitals. We see that DMRG is variational and converges to the CAS(10,9) result which is full CI.

![Ground-state energy of CH$_4$](image)

**FIG. 8.** Ground-state energy $E$ of CH$_4$ as a function of the number of states retained $m$ at each DMRG iteration. The lines are the Hartree-Fock and CAS results.

In Table I we also show the occupation numbers $\langle n_i \rangle = \langle c_{i\uparrow}^\dagger c_{i\uparrow} \rangle + \langle c_{i\downarrow}^\dagger c_{i\downarrow} \rangle$ (28)
of the MO as a function of the progress of calculation. For instance it can be seen that the occupation of symmetry equivalent orbitals ($t_2$) becomes equal at the last iteration. DMRG achieves the accuracy of CAS(8,8) (occupation of 1$a_1$ orbital frozen) when $m > 32$. The analysis of the occupation numbers shows the importance of the higher energy states in the description of the ground state of this typical closed-shell system. A significant occupation of the orbitals usually unoccupied in the HF procedure is observed.

| Irreducible representation | Hartree Fock eigenvalue | $\langle n_{i_1} \rangle$ after warmup | $\langle n_{i_1} \rangle$ after first iteration | ... | $\langle n_{i_1} \rangle$ after last iteration |
|---------------------------|------------------------|----------------------------------------|---------------------------------------------|----|----------------------------------------|
| $1a_1$                    | -11.02969              | 2.000000                               | 1.999997                                   | ...| 1.999965                               |
| $2a_1$                    | -0.91210               | 2.000000                               | 1.998077                                   | ...| 1.985416                               |
| $1t_2$                    | -0.52050               | 2.000000                               | 1.996863                                   | ...| 1.976450                               |
| $1t_2^*$                  | -0.52050               | 2.000000                               | 1.992911                                   | ...| 1.976450                               |
| $1t_2$                    | -0.52050               | 2.000000                               | 1.988980                                   | ...| 1.976450                               |
| $1t_2$                    | -0.52050               | 2.000000                               | 1.988980                                   | ...| 1.976450                               |
| $2t_2$                    | 0.71922                | 0.000000                               | 0.021086                                   | ...| 0.021952                               |
| $2t_2$                    | 0.71922                | 0.000000                               | 0.005932                                   | ...| 0.021952                               |
| $2t_2$                    | 0.71922                | 0.000000                               | 0.010275                                   | ...| 0.021951                               |
| $3a_1$                    | 0.76106                | 0.000000                               | 0.009580                                   | ...| 0.019412                               |

**TABLE I.** Occupation numbers $\langle n_{i_1} \rangle$ of the MO as a function of the progress of the calculation.
IV. RESULTS AND DISCUSSION

In order to demonstrate the performance of the DMRG when applied to quantum chemical problems, we have chosen a simple magnetic system which has already been the subject of extensive post-HF and DFT studies. In fact, computing the energy difference between multiplets of different spins is a difficult task for standard computational approaches. This is due to the very high accuracy required for the calculation of the ground- and excited-state energies and the intrinsic need of taking into account the mixing with states of higher energy (configuration interaction). For this reason, we believe that this calculation can be a useful benchmark to test the performance of DMRG in quantum chemistry. The crucial features of any new quantum chemical method are scaling and convergence. In the following we address this point, both when starting from localized and non-localized Hartree-Fock MO as well as from Kohn-Sham orbitals.

A. HHeH

The linear HHeH molecule (Fig. 9) was chosen as a typical example for a model magnetic system. In this simple case the two paramagnetic centers, carrying each an unpaired spin, are the hydrogen atoms. They are linked via a diamagnetic bridge constituted by the He atom. The spins of the two paramagnetic electrons can be parallel or antiparallel yielding two different spin states, namely a singlet ($S = 0$) and a triplet ($S = 1$). The difference in energy between these two spin states as a function of the H-He distance, has been subject of both post-HF and DFT calculations [17,18], and shows the importance of electron correlation.

In Table II the results found in literature [17] are compared to the exact results obtained with both full-CI approach and DMRG using the same basis set (6-311G** [21]). This basis set contains a total of 18 orbitals. The following notation is used: CAS($\nu, \mu$) = complete active space configuration interaction considering $\nu$ electrons and $\mu$ orbitals; QCISD(T) = quadratic CI including single and double excitations and also triple excitations perturbatively; BS = broken symmetry [20]; SD = single determinant [19]; LDA = local density approximation for exchange correlation functional in the Vosko-Wilk-Nusair parameterization [28]; BP = generalized gradient approximation for exchange and correlation functional using the Becke parameterization [29]. The data obtained with post-HF methods show that a large part of electron correlation is already included at a modest CAS level. Both DF based techniques, the single determinant method [19] (SD) and the broken symmetry approach [20] (BS), which are less expensive in terms of computational resources, are just adequate to yield qualitative results.

| Method       | Distance=1.25 Å |
|--------------|-----------------|
| CAS(2,2)     | 4204            |
| CAS(4,3)     | 4294            |
| QCISD(T)     | 4298            |
| BS-LDA       | 12432           |
| BS-BP        | 10529           |
| SD-LDA       | 9050            |
| SD-BP        | 7799            |
| Full-CI      | 4860            |
| DMRG         | 4859            |

TABLE II. HHeH Singlet-triplet energy gap (in cm$^{-1}$) as a function of the H-He distance for various methods.
In Fig. 10 the singlet-triplet energy gap as a function of \( m \) is reported for a H-He distance of 1.25 Å. For \( m > 64 \) the DMRG procedure has converged to the exact result (full CI). Results superior to those obtained with DFT are observed already when \( m \approx 32 \). The same level of accuracy as with CAS(4,3) is also reached for this \( m \) value.

![Graph showing singlet-triplet energy gap](image)

**FIG. 10.** Singlet-triplet energy gap of HHeH as a function of \( m \) for a H-He distance of 1.25 Å

**B. Choice of the basis**

The results obtained with DMRG when applied to quantum lattice systems [22] suggests that the use of localized basis sets, which reduce the interactions between far distant neighbors, will enhance convergence. Therefore we attempted to localize the starting MO basis set using standard localization techniques. Amongst the classical quantum chemical localization techniques [23–25], we have chosen to apply the procedure of Mezey and Pipek [26] due to the fact that just overlap integrals are needed to perform the localization. This procedure is based on the minimization of a mean localization measure of the occupied molecular orbitals \( D \) defined as

\[
D^{-1} = N^{-1} \sum_{i=1}^{N} d_{i}^{-1}
\]

with

\[
d_{i}^{-1} = \sum_{k=1}^{M} (Q_{ik}^{L})^{2}
\]

and where \( k \) are the different nuclei of the molecule, \( i \) the molecular orbitals, and \( Q_{ik}^{L} \) are the gross atomic Mulliken population of the orbital \( i \). Rather than localizing all the MO, we only localized the subset of the virtual MO (not occupied at a HF level). The two subsets, formed by the occupied non-localized MO and the virtual localized MO, are still orthonormal. In fact, the localization of the whole set of MO would yield a substantial increase of the starting energy of the DMRG procedure, while localizing the virtual orbitals only does not. Recalling the empirical dependence of the electronic energy upon \( m \) (Eq. 11), we show in Fig. [11] \( E(m) - E_0 \) versus \( m \) to illustrate the convergence of the DMRG procedure using localized and non-localized Hartree-Fock MO. Unfortunately, we observe that the localization procedure does not yield a faster convergence. In fact, it should be stressed that this system is not the most adequate to test the impact of localization. Indeed, there are only a few electrons involved and the spatial extent of the molecule is rather small. Nevertheless, we expect that this localization procedure should improve the convergence of the DMRG for larger systems, e.g. linear chain like molecules for which most of the \( V_{ijkl} \) terms will vanish or become negligible when using localized basis functions.
Another feature we investigated was the possibility to use Kohn-Sham orbitals as basis functions. We performed DMRG calculation starting from Hartree-Fock orbitals as well as from Kohn-Sham orbitals obtained using both LDA and GGA functionals. The results obtained for the singlet state with a H-He distance of 1.25 Å are shown in Fig. 12. We see that all three basis functions have essentially the same convergence rate.

C. Scaling of the method

In order to test the numerical effort spent with DMRG we performed several tests on the HHeH singlet state at a distance of 1.25 Å, either using different basis sets (varying K at constant m) or keeping the basis set (varying m at constant K). The aim of these calculations was twofold. First, to test the scaling of DMRG and second, to demonstrate its superiority with respect to standard post-HF approaches (full CI, QCISD or QCISD(T)). The main disadvantage of post-HF solutions (apart from their scaling) is the lack of at least one of the main feature of DMRG: size consistency and variational character. The only theoretical approach which fulfills all these requirements is presently full CI. For example, CID or QCISD methods are variational but not size consistent. On the other hand, all perturbative techniques (MPn), whose scaling are comparable with the one of DMRG, are not variational and practically feasible only up to n = 4 (inclusion of quadruple excitations).
The theoretical scaling of DMRG (neglecting the cost of the preliminary Hartree-Fock procedure) is $O(K^4m^2)$. In our case $K$ is relatively small ($K_{\text{max}} = 30$), while $m$ can be an order of magnitude bigger than $K$ ($m_{\text{max}} = 264$). In Fig. 13 the plots of the CPU time versus $K$ at fixed $m$ and versus $m$ at fixed $K$ are shown. The slope, obtained by linear regression, observed in part a) is in agreement with the theoretical predictions, i.e. $O(K^4)$. While the slope in part b) is lower than predicted since we use highly optimized BLAS to perform the matrix operations (cf Appendix). Thus the scaling of DMRG appears to be competitive even with QCISD, which scales as $O(K^7)$, while yielding much better results.

![Graph a) and b)](image)

FIG. 13. a) CPU time as a function of $K$ on a log-log scale; b) CPU time as a function of $m$ on a log-log scale. Both plots are for HHeH.

V. ACKNOWLEDGMENTS

IC, CD and SD acknowledge support from the Swiss National Science Foundation, SD also acknowledges support from the ITP under NSF grant #PHY94-07194 and SRW acknowledges support from the NSF under grant #DMR98-70930.

APPENDIX A: IMPLEMENTATION OF THE METHOD

The program we use is written in C++, an object-oriented language. We have to keep track of all sorts of matrices connecting different subspaces with different quantum numbers, which is conveniently done using classes and overloading operators. In addition, the program uses a matrix library, developed by S. White and R. Noack, which links the matrix-matrix and matrix-vector multiplication to corresponding BLAS to be more efficient. In order to save memory, only the information for the specific blocks in use are loaded, while the rest is stored on disk. For the moment we cannot exceed a number of basis function of $K = 40$ (which uses about 2 Gb of memory). And right now we are working on rewriting the program in order to be able to handle 100 basis functions.

The program runs under Unix and has mainly been used on workstations such as Linux PC, Dec Alpha, HP, SGI and Cray. A tutorial program for a particle in a box and the matrix library can be found at [http://hedrock.ps.uci.edu/](http://hedrock.ps.uci.edu/).

[1] M. Levy, Proc. Nat. Acad. Sci. USA 60, 62 (1976); Phys. Rev A 26, 1200 (1982).
[2] J. Almlof, K. Faegri, K. Korsell, J. Comput. Chem. 3, 385 (1982).
[3] W. Kutzelnigg, W. Klopper, J. Chem. Phys. 96, 2020 (1991).
[4] S. R. White, R. L. Martin, J. Chem. Phys. 110, 4127 (1999).
[5] See for example the review article by K. G. Wilson and J. Kogut, Phys. Rep. C 12, 75 (1974).
[6] K. G. Wilson, Rev. Mod. Phys. 43, 773 (1975).
[7] H. B. Krishnamurthy, J. W. Wilkins and K. G. Wilson, Phys. Rev. B 21, 1044 (1980).
[8] S. T. Chui and J. W. Bray, Phys. Rev. 18, 2426 (1978); J. W. Bray and S.-T. Chui, Phys. Rev. 19, 4876 (1979).
[9] S. R. White and R. M. Noack, Phys. Rev. Lett. 68, 3487 (1992).
[10] S. R. White, Phys. Rev. Lett. 69, 2863 (1992); Phys. Rev. B 48, 10345 (1993).
[11] S. R. White, Phys. Rev. Lett. 77, 3633 (1996).
[12] LCAO-SCF ref.
[13] A. Szabo and N. S. Ostlund, “Modern Quantum Chemistry”, MacMillan Publishing Co., Inc., New York (1982).
[14] C. Lanczos, Proc. Nat. Acad. Sci 20, 529 (1934).
[15] E. R. Davidson, J. Computational Phys. 17, 87 (1975).
[16] R. M. Noack and S. R. White, “Density-Matrix Renormalization”, Workshop proceedings, Dresden, Germany (1998), edited by Peschel et al., Springer (1999).
[17] A. Bencini, F. Totti, V. Barone, F. Fantucci, K. Doclo, C. A. Daul, Inorg Chem. 36, 5022 (1997).
[18] J. R. Hart, A. K. Rappé, S. M. Gorun, T. H. Upton, J. Phys. Chem. 96 6264, (1992).
[19] C. A. Daul, Int. J. Quant. Chem. 52 867, (1994).
[20] L. Noodleman, J. G. Norman, J. Phys. Chem. 70 4903, (1979).
[21] R. Krishnan, J.S. Binkley, R. Seeger, J.A. Pople, J. Chem. Phys. 72, 650 (1980).
[22] Density-Matrix Renormalization edited by I. Peschel, X. Wang, M. Kauke and K. Hallberg, 197 (1998), Lectures Notes in Physics, Springer.
[23] S. F. Boys, Rev. Mod. Phys. 32, 296 (1960)
[24] C. Edmiston, K. Ruedenberg, rev. Mod. Phys. 35, 457 (1963).
[25] W. von Niessen, J. Chem. Phys. 56, 4290 (1972).
[26] J. Pipek, P. G. Mezey, J. Chem. Phys. 90, 4916 (1989).
[27] J. P. Perdew, K. Burke, Y. Wang, Phys. Rev. B 54, 16533 (1996)
[28] S. H. Vosko, L. Wilk, M. Nusairur, Can. J. Phys. 58, 1200 (1980).
[29] A. D. Becke, Phys. Rev. A 38, 3098 (1988); J. P. Perdew Phys. Rev. B 33, 8822, (1986).