The Density Matrix Renormalization Group in Quantum Chemistry

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Abstract

The density matrix renormalization group is a method that is useful for describing molecules that have strongly correlated electrons. Here we provide a pedagogical overview of the basic challenges of strong correlation, how the density matrix renormalization group works, a survey of its existing applications to molecular problems, and some thoughts on the future of the method.

1. STRONG CORRELATION IN CHEMISTRY

1.1. The Problem of Exponential Complexity

Strong correlation: in electronic structure, characterizes systems that are poorly described by Hartree-Fock theory

Multireference: a wave function that is a superposition of many significant determinants

Quantum chemical methods are now widely applied to understand all kinds of chemical phenomena. Many theories exist to compute approximate solutions of the Schrödinger equation, ranging from density functional methods to sophisticated wave-function theories, such as the coupled-cluster hierarchy. In the traditional quantum chemical picture, we write the wave function as

$$|\Psi\rangle = |\Psi_{\mathrm{HF}}\rangle + |\Psi_{corr}\rangle, \tag{1}$$

$$\langle\Psi_{\mathrm{HF}}|\Psi\rangle = 1, \tag{2}$$

where $|\Psi_{\mathrm{HF}}\rangle$ is the mean-field or Hartree-Fock wave function, and $|\Psi_{corr}\rangle$ is the correlation part. In most quantum chemical methods, it is assumed that $|\Psi_{corr}\rangle$ is in some sense small—the electronic structure is well described by a single configuration of the electrons in the orbitals—and thus the electron correlation is weak. In systems in which this assumption is true, and with recent computational advances, it is now possible to obtain physical observables with very high accuracy, e.g., vibrational spectra to better than 1 cm^{-1} (1), and for very large systems, such as calculations on thousands of atoms (2).

Challenges arise, however, when the traditional weak correlation assumption breaks down. In such strongly correlated states, the coefficients in the determinant expansion of $|\Psi_{corr}\rangle$ are large, i.e., on the order of unity (or greater). (In this article we take strong correlation to be synonymous with the term multireference.) Strongly correlated states most commonly arise when there is near degeneracy in the underlying orbitals. As a familiar example, the hydrogen molecule at equilibrium (in a minimal basis) possesses energetically well-separated bonding σ_g and antibonding σ_u orbitals, and $|\Psi\rangle$ is well approximated by the single configuration σ_g^2. However, as the bond is stretched, σ_g and σ_u become near degenerate, and $|\Psi\rangle$ evolves into a strongly correlated superposition of configurations with different occupancies across the two orbitals.

Although the correlation between the valence electrons in stretched H_2 is strong, it can of course be exactly described by many traditional methods. This is because $|\Psi_{corr}\rangle$ contains only one determinant with large weight, σ_u^2. In larger systems, however, the number of significant determinants in $|\Psi_{corr}\rangle$ can rise very rapidly. For example, let us consider a set of hydrogen atoms arranged in a lattice (**Figure 1**). As we expand the lattice constant (i.e., stretch the bonds), we recover a large degeneracy in the underlying orbitals, and $|\Psi_{corr}\rangle$ consists of a superposition of

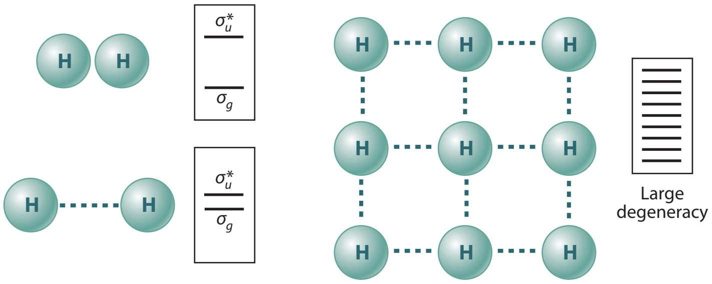


Figure 1

When a hydrogen bond is stretched, the bonding electrons become strongly correlated as the orbitals become nearly degenerate. In a hydrogen lattice, if we stretch all the bonds, there is a very large degeneracy in the one-particle levels, and the resulting ground-state wave function is a superposition of a very large number of configurations.

many configurations distributed across all the orbitals. The strongly correlated superposition of such a large set of configurations can now no longer be described by traditional theories, such as the coupled-cluster hierarchy. Of course, a hydrogen lattice problem is artificial from a chemistry standpoint, but one can readily find realistic examples of large-scale strongly correlated electronic structure. Any molecule with multiple transition metals contains many near-degenerate d (and possibly f) orbitals, which experience only limited overlap with neighboring orbitals, much like the atomic orbitals in the expanded hydrogen lattice.

From a theoretical perspective, the primary challenge of strong correlation is the very large number of determinants, which contribute significantly to the wave function. As the number of strongly correlated orbitals increases, the number of important determinants increases exponentially, and the strong correlation problem thus appears intractable.

DMRG: density matrix renormalization group

Tensor network: a generalization of the matrix product state to efficiently encode locality in arbitrary dimensions

1.2. The Principle of Locality

A little thought, however, shows that the apparent exponential complexity of strong correlation cannot really hold. Although quantum mechanics admits many unusual states—such as Schrödinger cat states—most of quantum phase space is not explored by physical ground states. Indeed, nature imposes many constraints on the structure of quantum states. One of the most important is the locality principle. Regardless of the complexity of a physical system, be it a complicated transition metal molecule at a stretched region of the potential energy surface or a complex phase of a high-temperature superconducting material, the response of the system to an external perturbation always remains local. In more chemical terms, reactions on one side of the material do not cause changes a macroscopic distance away.

As a consequence of locality, although the wave function in a strongly correlated state may consist of an exponentially large number of determinants, the coefficients of the expansion must be highly structured to reflect locality. In fact, they should be parameterizable by an amount of information that is proportional to the size of the system. The challenge of strongly correlated electronic structure may therefore be translated into a simple mathematical problem—how do we encode locality in a wave function that involves an expansion, in principle, across all possible determinants?

In recent years, work in the area of the density matrix renormalization group (DMRG), and its modern development into tensor networks, has provided a conceptual and in some cases practical solution to this question. This article focuses primarily on the DMRG, which has now matured to the extent that it can be routinely applied to difficult quantum chemical problems. We focus first on the basic theory and structure of the DMRG. Then, because our understanding of the DMRG in quantum chemistry comes to a great extent from its application to specific problems, we survey the behavior of the method in a variety of chemical problems.

2. THE DENSITY MATRIX RENORMALIZATION GROUP WAVE FUNCTION

The DMRG was first conceived by White (3, 4) as a way to tackle strongly correlated quantum lattices. In the current context we view the DMRG as a special wave-function ansatz (5, 6), and we do not discuss much of the renormalization group structure, which is described in other articles (3, 4, 7–10).

To understand the wave-function structure of the DMRG, we establish some basic notation. Let us consider an N-electron wave function expanded in a complete basis of determinants, through the full configuration interaction (FCI) expansion,

$$|\Psi\rangle = \sum_{\{n\}} \Psi^{n_1 n_2 n_3 \ldots n_k} |n_1 n_2 n_3 \ldots n_k\rangle, \tag{3}$$

$$\{n\} = \{|\text{vac}\rangle, |\uparrow\rangle, |\downarrow\rangle, |\uparrow\downarrow\rangle\}, \tag{4}$$

$$\sum_i \{n\} = N. \tag{5}$$

FCI: full configuration interaction

Matrix product state: the mathematical structure of the DMRG wave function that efficiently encodes locality in one dimension

Here $|n_1 \ldots n_k\rangle$ is the occupation-number representation of the determinant, where n_i is the occupation of orbital i. The total number of orbitals is k, and N is the total number of electrons.

The dimension of the coefficient tensor Ψ in the above expansion is 4^k, which is intractable for values of k much larger than 10. In a strongly correlated problem, we expect a large fraction of these coefficient to be nonzero, and thus we cannot impose a sparsity pattern on Ψ as is normally done in configuration interaction. Instead we need to find an ansatz in which Ψ is expressed more compactly and sparsity is not assumed. In general, we would want such an ansatz to require only a polynomial amount of information as a function of the number of orbitals in the system, k.

A simple ansatz would be to approximate the high-dimensional coefficient tensor Ψ by a tensor product of vectors. In elemental form, this would be

$$\Psi^{n_1 n_2 n_3 \ldots n_k} \approx \psi^{n_1} \psi^{n_2} \psi^{n_3} \ldots \psi^{n_k}. \tag{6}$$

We note that the vector ψ^n is not an orbital vector, but rather is an occupancy vector of length 4 that reflects the different occupancies of a given orbital. Also, ψ^{n_1} and ψ^{n_2} are taken to represent elements of different vectors. The above product ansatz contains only $4k$ parameters and is certainly tractable. However, it is also not, in general, very accurate!

To improve the ansatz, we need to increase the flexibility of the vectors ψ^n. We can introduce additional auxiliary indices, making each vector into a tensor, i.e.,

$$\psi^n \rightarrow \psi^n_{ii'}. \tag{7}$$

The new indices i and i' are auxiliary in the sense that they do not appear in the final coefficient tensor Ψ and must be contracted over in some fashion. The simplest arrangement is to contract the indices sequentially from one ψ^n tensor to the next. We then have

$$\Psi^{n_1 n_2 n_3 \ldots n_k} \approx \sum_{i_1 i_2 i_3 \ldots i_{k-1}} \psi^{n_1}_{i_1} \psi^{n_2}_{i_1 i_2} \psi^{n_3}_{i_2 i_3} \ldots \psi^{n_k}_{i_{k-1}}. \tag{8}$$

More compactly, we can use matrix notation,

$$\Psi^{n_1 n_2 n_3 \ldots n_k} \approx \psi^{n_1} \psi^{n_2} \psi^{n_3} \ldots \psi^{n_k}, \tag{9}$$

where we understand, e.g., $\psi^{n_2}\psi^{n_3}$ to denote the matrix product between the two involving the auxiliary indices. For simplicity, we assume that the dimensions of all auxiliary indices are the same, and we call this dimension M. Then the tensors ψ^n are of dimension $4 \times M \times M$ (except for the first and the last), and the total number of parameters in the wave-function ansatz is $O(4M^2k)$.

This approximation given in Equation 9 is the DMRG wave function. It is commonly referred to as the DMRG wave function with M states. In calculations it is typically used in a variational fashion, in which the components $\psi^n_{ii'}$ are the coefficients to be varied (see Section 6). By increasing the dimension M, we make the ansatz arbitrarily flexible, and eventually exact. Because the wave-function coefficients are obtained as a series of matrix products, the ansatz is also referred to in the literature as the matrix product state (7, 11, 12). Combining the above ansatz for the coefficient tensor explicitly with the Slater determinants yields the full DMRG wave function,

$$|\Psi_{\mathrm{DMRG}}\rangle = \sum_{\{n\}} \psi^{n_1}\psi^{n_2}\psi^{n_3}\ldots\psi^{n_k}|n_1 n_2 n_3 \ldots n_k\rangle. \tag{10}$$

2.1. The Canonical Form

The DMRG wave function in Equation 10 is invariant to a number of transformations. (This is analogous to the invariance of the Hartree-Fock determinant to rotations of occupied orbitals.) In particular, we can insert between any two consecutive components (such as ψ^{n_2} and ψ^{n_3}) the identity XX^{-1}, where X is an arbitrary invertible matrix, and leave the overall wave function unchanged (13). In practical DMRG calculations, one exploits this arbitrariness to choose a canonical form of the DMRG wave function, which brings certain orthogonality properties. In canonical form, the DMRG wave function is written as

$$|\Psi\rangle = \sum_{\{n\}} \mathbf{L}^{n_1}\ldots\mathbf{L}^{n_{p-1}}\mathbf{C}^{n_p}\mathbf{R}^{n_{p+1}}\ldots\mathbf{R}^{n_k}|n_1\ldots n_k\rangle, \tag{11}$$

where $\mathbf{L}^n$ and $\mathbf{R}^n$ satisfy orthogonality conditions

$$\sum_n \mathbf{L}^{n\dagger}\mathbf{L}^n = 1, \tag{12}$$

$$\sum_n \mathbf{R}^n\mathbf{R}^{n\dagger} = 1. \tag{13}$$

Formally, the string of $\mathbf{L}^n$ and $\mathbf{R}^n$ defines sets of renormalized many-particle basis states $\{l\}$, $\{r\}$, respectively,

$$|l_i\rangle = \sum_{\{n\}} [\mathbf{L}^{n_1}\mathbf{L}^{n_2}\ldots\mathbf{L}^{n_{p-1}}]_i|n_1 n_2\ldots n_{p-1}\rangle, \tag{14}$$

$$|r_i\rangle = \sum_{\{n\}} [\mathbf{R}^{n_{p+1}}\mathbf{R}^{n_{p+1}}\ldots\mathbf{R}^{n_k}]_i|\, n_{p+1}n_{p+2}\ldots n_k\rangle, \tag{15}$$

and $\mathbf{C}^{n_p}$ gives the coefficients of the wave function in the product basis $\{l\}\otimes\{n_p\}\otimes\{r\}$. Thus the determinant expansion given in Equation 11 is equivalent to an expansion in the smaller orthonormal renormalized basis

$$|\Psi\rangle = \sum_{lnr} C^{n_p}_{lr}|l n_p r\rangle. \tag{16}$$

This is closely tied to the renormalization group structure of the DMRG. Although the renormalization group interpretation of the DMRG is quite powerful, we do not explore it more here and instead refer the reader to other references (e.g., 3, 4, 7, 8).

2.2. Locality in the Density Matrix Renormalization Group

As argued above, the key to efficiently describing strongly correlated problems is to incorporate locality. The DMRG encodes locality in strong correlated quasi-one-dimensional problems. How is this achieved?

Let us consider, for simplicity, a set of orbitals arranged in a line, as shown in **Figure 2**. (Concretely, we may imagine a one-dimensional hydrogen chain in a minimal, orthonormalized basis.) The DMRG encodes locality through the special structure of contractions of auxiliary indices. From Equation 8, we see the first auxiliary index i_1 is associated with occupancies n_1 and n_2, and the first two components $\psi^{n_1}_{i_1}$ and $\psi^{n_1}_{i_1 i_2}$. If i_1 were not present, the wave function would

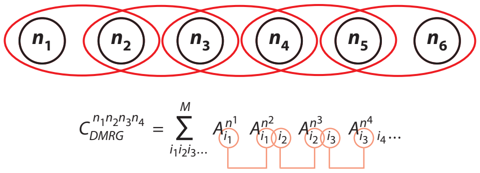


Figure 2

The sequence of contractions of the auxiliary indices in the density matrix renormalization group (DMRG) wave function induces local correlations.

factorize between the n_1 occupancy and the other occupancies in the system. Consequently, i_1 and its subsequent contraction give rise to correlations between occupancies n_1 and n_2. Similarly, auxiliary index i_2 is associated with occupancies n_2 and n_3, and the subsequent contraction of i_2 introduces correlations between occupancies n_2 and n_3 (**Figure 2**). This pattern is repeated for the other auxiliary indices in the wave function. Although there is no direct coupling between non-neighboring occupancies (such as n_1 and n_3) via auxiliary indices, there is correlation between them by virtue of the correlation between n_1, n_2, and n_2, n_3.

We see that the DMRG encodes a sequential structure to the correlation. If the orbitals considered are local and the underlying topology is quasi-one dimensional, then this is exactly the structure of correlation produced by locality. In fact, in one-dimensional orbital topologies, the DMRG can be considered a perfect encoding of locality, and this optimality can be proved in a rigorous manner, in which it is related to the area law in quantum information (14, 15). Thus we can formally regard the DMRG as solving the problem of strong correlation in one dimension.

The sequential encoding of correlation in the DMRG is both a strength and a weakness. On the one hand, it is the correct structure for one-dimensional topologies, and the structure leads to highly efficient algorithms to evaluate expectation values such as the energy. On the other hand, for systems that are not topologically one dimensional, the DMRG no longer provides an optimal encoding of locality. Whereas the complexity of strongly correlated states formally appears to scale exponentially with all three dimensions of the problem, the DMRG wave function removes the exponential scaling associated with only one of the dimensions. A complete reduction to polynomial complexity for general orbital topologies requires more flexible wave-function structures. This is what is promised by the recent development of tensor networks (15). Nonetheless, even in its current form, the DMRG wave function is still a powerful wave function for strongly correlated states in arbitrary dimensions, and a perfect wave function for strong correlation in quasi-one-dimensional problems, and this is what is observed in its practical application to quantum chemistry.

3. DENSITY MATRIX RENORMALIZATION GROUP ALGORITHMS

3.1. Expectation Values and Energy Evaluation

Given the DMRG wave function, how do we use it for quantum chemical calculations? The advantage of the matrix product form given in Equation 9 is that the computation of expectation values is efficient. This means that the DMRG can be used in a variational calculation of the energy. To see why the computation of expectation values is easy, let us consider the overlap between two DMRG wave functions. For general states, Ψ, Φ, the overlap is

$$\langle\Psi|\Phi\rangle = \sum_{\{n\}} \Psi^{n_1n_2n_3\ldots n_k}\Phi^{n_1n_2n_3\ldots n_k}. \tag{17}$$

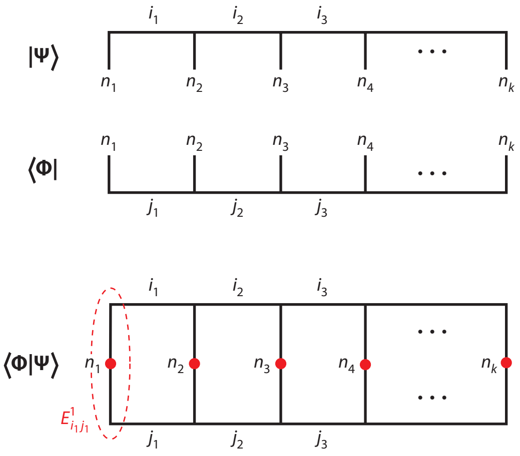


Figure 3

(*Top panel*) Pictorial representations of density matrix renormalization group wave functions (matrix product states). Open lines represent free indices, and lines with no open ends represent indices that are summed over. (*Bottom panel*) The overlap. Note that we are joining the occupancy lines ($\{n\}$), which are summed over in the overlap expression given in Equation 18. Each rung of the ladder is an E tensor.

Now if the states are DMRG wave functions, i.e., if they are of matrix product form, Equation 17 becomes

$$\langle\Psi|\Phi\rangle = \sum_{\{n\},\{i\},\{j\}} \left(\psi^{n_1}_{i_1}\phi^{n_1}_{j_1}\right)\left(\psi^{n_2}_{i_1 i_2}\phi^{n_2}_{j_1 j_2}\right)\dots\left(\psi^{n_k}_{i_{k-1}}\phi^{n_k}_{j_{k-1}}\right) = \sum_{\{ij\}} E^1_{i_1 j_1} E^2_{i_1 j_1 i_2 j_2}\dots E^2_{i_{k-1} j_{k-1}}; \qquad (18)$$

i.e., the overlap itself can be computed as a matrix product of E overlaps associated with each site, in $O(M^3k)$ time. It is sometimes useful to visualize the computation of expectation values graphically, as shown in **Figure 3**.

The calculation of more general expectation values, such as the energy, proceeds in a similar way. The Hamiltonian written in second quantization is a sum of operators,

$$H = \sum_i h_i o_i. \qquad (19)$$

Each individual operator o_i (e.g., $a_2^\dagger a_3$) acting on a DMRG wave function produces a new DMRG wave function, and the expectation value $\langle\Psi|H|\Psi\rangle$ is then simply a sum of overlap computations of the form given in Equation 18. In the case of quantum chemical Hamiltonians, there are $O(k^4)$ terms in the sum given in Equation 19, and this suggests that the total time for the calculation of the energy is $O(M^3k^5)$. However, with the formulation of efficient intermediates, the scaling can be reduced to $O(M^3k^3) + O(M^2k^4)$ (10).

Because the DMRG energy expectation value can be computed efficiently, it can also be variationally optimized with respect to the individual components ψ^n. This is usually done one component at a time, giving rise to the so-called sweep algorithm, although in principle direct minimization of all components via a Newton-Raphson scheme is also possible. The component-wise optimization resembles Hartree's self-consistent algorithm for Hartree-Fock theory in which one orbital is updated at a time. Finally, we mention that, because the DMRG energy can be obtained variationally, analytic derivatives and response properties can also be computed, as described in References 16 and 17.

3.2. Orbital Ordering and Orbital Optimization

CASSCF: complete active-space self-consistent field

Active space: a set of orbitals, typically the valence shells, in which important correlations that establish the qualitative electronic structure take place

Dynamic correlation: correlations involving orbitals outside of the valence space; does not qualitatively change the electronic structure but is important for quantitative prediction

Because the matrices (each associated with an orbital occupancy) in the DMRG wave function do not generally commute, a DMRG calculation requires not only a choice of the particular orbitals to correlate, but also a specification of their ordering in the calculation. In the one-dimensional quantum lattice problems, there is a natural ordering along the lattice. In molecular problems, however, the choice is not so simple. With respect to the ordering, it is important to choose one that minimizes the correlation length along the lattice. Determining the optimal ordering is an NP (nonpolynomial)-hard problem, and the heuristic construction of good orderings has been studied in a number of works (8, 18, 19). In general, we find that one only needs to find an ordering that is reasonable, rather than the truly optimal one. As a rule of thumb, when using delocalized Hartree-Fock orbitals, it is often advantageous to order bonding and antibonding orbitals near each other (20, 21).

The shape of the DMRG orbitals can be optimized by minimizing the energy with respect to orbital rotations, similar to the procedures used in any active-space calculations (22, 23). Orbital optimization in the DMRG was introduced in References 24–27 and leads to the DMRG-SCF or DMRG-CASSCF methods. In each case orbital optimization is based on calculating the DMRG active-space one- and two-body density matrices. Unlike more sophisticated orbital optimization algorithms used in some modern active-space theories, current DMRG orbital optimization implementations decouple the optimization of the orbital parameters and the wave-function coefficients in Equation 11. Acceleration of this two-step procedure can be achieved through direct inversion in the iterative subspace techniques (24, 26).

4. QUANTUM CHEMICAL PROPERTIES OF THE DENSITY MATRIX RENORMALIZATION GROUP

Variational calculations using the DMRG exhibit many formal properties that are considered important for quantum chemical applications. Some of these are noted below.

4.1. Multireference

In the DMRG wave function, there is no division into occupied and virtual orbitals; all orbitals appear on an equal footing in the ansatz (10). In particular, the Hartree-Fock reference has no special significance here. For this reason, we expect (and observe) the ansatz to be well-balanced for describing nondynamic correlation in multireference problems (e.g., see 28–30). Conversely, the ansatz is inefficient in describing dynamic correlation, as in treating dynamic correlation one would benefit from the knowledge of which orbitals are in the occupied and virtual spaces. We return to this topic in Section 5.3.

4.2. Size Consistency

The DMRG ansatz is consistent in size when using a localized basis. To illustrate this in an informal way, let us assume that we have two DMRG wave functions $|\Psi_A\rangle$ and $|\Psi_B\rangle$ for subsystems A and B separately. Both Ψ_A and Ψ_B have a matrix product structure, i.e.,

$$|\Psi_A\rangle = \sum_{\{n_a\}} \psi^{n_{a1}} \ldots \psi^{n_{ak}} |n_{a1} \ldots n_{ak}\rangle, \tag{20}$$

$$|\Psi_B\rangle = \sum_{\{n_b\}} \psi^{n_{b1}} \ldots \psi^{n_{bk}} |n_{b1} \ldots n_{bk}\rangle. \tag{21}$$

Their product is also a DMRG wave function with a matrix product structure. This then describes the combined system AB in a size-consistent way, i.e.,

$$|\Psi_{AB}\rangle = |\Psi_A\rangle|\Psi_B\rangle = \sum_{\{n_a\}\{n_b\}} \psi^{n_{a1}} \ldots \psi^{n_{ak}} \psi^{n_{b1}} \ldots \psi^{n_{bk}} |n_{a1} \ldots n_{ak} n_{b1} \ldots n_{bk}\rangle. \tag{22}$$

5. APPLICATIONS OF THE DENSITY MATRIX RENORMALIZATION GROUP

5.1. Small Molecules

Over the past decade, the DMRG has been applied to many different molecular problems in the context of ab initio quantum chemistry. Early applications, such as the pioneering work of White & Martin (10), focused on reproducing benchmark FCI results. These studies were limited to small molecules and modest basis sets. Nonetheless, they were important to understand both how to efficiently formulate the DMRG algorithm and to discover the strengths and weaknesses of the method for quantum chemistry. Some notable examples include small basis studies of the water molecule, the singlet-triplet gap in HHeH (31), the N_2 curve (8, 32), ethylene twisting (8), singlet-triplet gaps in methylene (33), and the ionic-covalent curve crossing in LiF (34).

With the development of an efficient parallel implementation of the DMRG, the possibility of using the DMRG for a brute-force near-exact solution of the Schrödinger equation (beyond the capabilities of standard FCI) began to be explored (21, 28, 33, 35, 36). One example was a study of the water molecule in a triple-zeta, double-polarization basis (20), in which the FCI space contains 5.6×10^{11} determinants. **Table 1** shows the results of this calculation. We see that the electronic energy smoothly converges with the number of DMRG states M, and in fact, it is easy to extrapolate to the $M = \infty$ FCI result (20). However, although the DMRG can be used in this brute-force way, it is now clear that this is not a good use of the method. Correlation in the water molecule (especially near equilibrium) is essentially dynamic in character, and the wave function is heavily weighted toward the Hartree-Fock reference. Because the DMRG does not distinguish between occupied and unoccupied orbitals, it provides an inefficient treatment of dynamic correlation. This is reflected by the fact that when moving from a double-zeta to a triple-zeta basis in the water molecule, the number of states in the DMRG calculation had to be increased by an order of magnitude (8, 20).

Table 1 Electronic energy of the water molecule in a triple-zeta, double-polarization basis

DMRG states (M)	Energy/E_h
800	−76.3143
1,200	−76.3145
2,400	−76.31464
3,200	−76.31468
5,400	−76.31471
∞	−76.314715

With a Hilbert space dimension of 5.6×10^{11}, this system is too large to be treated by conventional full configuration interaction (FCI) approach. As M is increased, the electronic energy converges smoothly, and we can extrapolate to the exact (FCI) result. DMRG, density matrix renormalization group. Table taken from Reference 20.

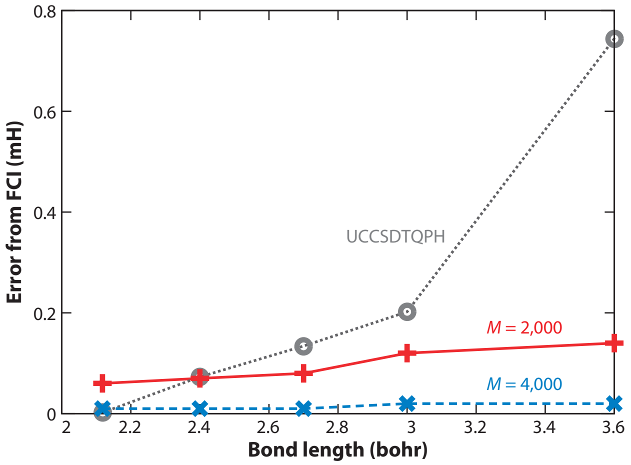


Figure 4

Errors from frozen-core full configuration interaction (FCI) for the nitrogen binding curve. The large $M = 4{,}000$ density matrix renormalization group (DMRG) calculation is nearly exact. However, even when we halve the number of states, the $M = 2{,}000$ DMRG calculation remains parallel to the exact result, demonstrating the balanced treatment of strong correlation in the method. By contrast, the unrestricted coupled cluster with hextuple excitations (UCCSDTQPH) theory gives excellent results near equilibrium, but the error grows very rapidly as the bond is stretched. Figure adapted from Reference 28.

The more promising domain of application of the DMRG method in molecules is to solve active-space strong correlation or multireference problems, which do not benefit from a bias toward the Hartree-Fock reference, particularly in cases in which the spaces are too large for an FCI treatment. One study that demonstrated this possibility was a calculation of the nitrogen binding curve (28) (**Figure 4**). As seen in the figure, the DMRG curves exhibit errors that are reasonably parallel, indicating that they achieve a balanced description of the correlation across the potential energy curve. By contrast, unrestricted coupled cluster with hextuple excitations theory, although extremely accurate at the equilibrium geometry, shows a very rapid increase in error as the bond is stretched.

Given the strength of the DMRG for large multireference electronic problems, a clear domain of application is complicated transition metal problems. A number of preliminary studies have been carried out in this area on molecules with one or two metal atoms, particularly by the group of Reiher (18, 37–40) and recently by Kurashige & Yanai (21). One common finding, as pointed out in studies of Cu_2O_2 models of the tyrosinase core (21, 40), is that, although the valence active spaces involved in many transition metal problems may be very large—e.g., 50 orbitals or more—in many cases one can exploit the balance of the DMRG method to obtain converged energy differences at much smaller M than is required to converge the total energy. (The Cu_2O_2 problem is described further in the next section.) Recently, the DMRG was used to obtain a near-exact solution of the active-space electronic structure in the Cr_2 molecule, with a 24-electron, 30-orbital active space (21). These results are shown in **Table 2**. They show the importance of high-body correlations in this molecule: CCSDTQ theory is still off by 14 mE_h. This study illustrates the potential applicability of the DMRG for quite large active spaces even in the absence of a true one-dimensional topological structure to the correlations.

Table 2 Electronic energy of the Cr_2 molecule in a 24-electron, 30-orbital active space

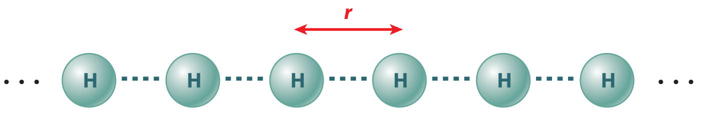
DMRG states (M)	Energy/E_h	Error/E_h
CCSDT	−2,086.380485	0.040671
CCSDTQ	−2,086.406695	0.014461
800	−2,086.413450	0.007706
1,600	−2,086.417287	0.003869
3,200	−2,086.419221	0.001935
6,400	−2,086.420196	0.000960
10,000	−2,086.420525	0.000631
∞	−2,086.421156	

Errors measured relative to the $M = \infty$ extrapolated result. Because of the strong correlation of the electrons, even the CCSDTQ energy is in error by 14 mE_h. The large density matrix renormalization group (DMRG) calculations can be extrapolated to better than chemical accuracy. Table taken from Reference 21.

5.2. Larger Molecules

Given that the DMRG provides an efficient encoding of locality in one of the spatial dimensions, it is natural to consider the DMRG as a local multireference method for molecules with largely one-dimensional connectivity. Indeed, if the orbital connectivity is topologically one dimensional (such as in a chain of atoms), then the size of the system treated by the DMRG can be very large. For example, Reference 41 demonstrates how the DMRG essentially exactly describes the simultaneous bond-breaking of 49 bonds in a hydrogen chain, a problem nominally requiring a 50-electron, 50-orbital active space (see **Table 3**). Although the Hilbert space appears infeasibly large (10^{28} determinants), it is locality that makes such a calculation feasible—there is strong correlation between an electron pair in one dissociating bond, but such a pair is only weakly correlated with electron pairs far away. We see that with only a small number of $M = 500$ states, the DMRG is able to obtain the correlation energy to essentially μE_h accuracy.

Table 3 Correlation energy of H_{50} under simultaneous stretching of all bonds



r/r_e	CCSD	$M = 100$	$M = 250$	$M = 500$
1.0	−0.40729	−0.41727	−0.41914	−0.41919
1.2	−0.47011	−0.48521	−0.48635	−0.48638
1.6	−0.63118	−0.65674	−0.65718	−0.65719
2.0	−0.88329	−0.91776	−40.91789	−0.91789
2.4	n.c.	−1.32477	−1.32481	−1.32481
3.2	n.c.	−2.67195	−2.67195	−2.67195

The full Hilbert space dimension is 10^{28}. Note the very rapid convergence of the correlation energy with M, due to the ideal one-dimensional topology of the correlations; at $M = 500$ we have reached μE_h accuracy. CCSD breaks down for longer bond distances with no solutions to the amplitude equations. n.c. stands for not converged. Table taken from Reference 41.

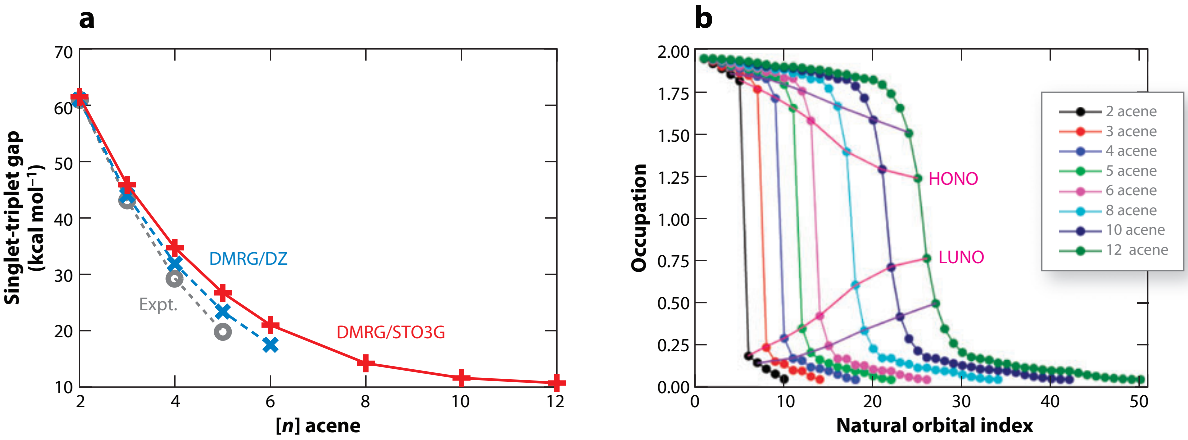


Figure 5

(*a*) Extrapolation of the experimental singlet-triplet gap suggests that longer acenes are triplets, but density matrix renormalization group (DMRG) calculations in the full π-valence space show that the singlet remains in the ground state for all lengths. (*b*) As the acene length increases, there are greater amounts of single occupancy near the highest occupied natural orbitals (HONOs) and lowest unoccupied natural orbitals (LUNOs.) This suggests that longer acenes increasingly acquire a polyradical character. Figure adapted from Reference 41.

We have used the DMRG in a number of problems of this kind, both for molecules that are topologically one dimensional and otherwise. These calculations include studies of the radical character in the acene series (41), magnetism in oligo-phenylcarbenes (26), dark states in light-harvesting pigments (25), polarizabilities of oligo-poly-di-acetylenes (16), and excitations in oligo-phenylvinylenes (42). Here we highlight briefly results of our calculations on the acenes in **Figure 5**, which illustrate the possibility of capturing unusual correlations with the DMRG. Although the extrapolation of experimental singlet-triplet gaps leads to the erroneous conclusion that the ground state of long acenes is a triplet, the DMRG calculations show that the singlet remains in the ground state in the longer acenes. However, the singlet begins to develop an unusual polyradical character, as illustrated by the natural occupancies in the DMRG. Ultimately, this unusual electronic structure stems from the one-dimensional nature of the system in which the metallic state is unstable with respect to the formation of a Luttinger liquid.

5.3. Combination with Dynamic Correlation Methods

As described above, a major deficiency in the DMRG methodology is the inefficient description of dynamic correlation. Viewing the DMRG as an active-space methodology, we can incorporate dynamic correlation in different ways, such as through perturbation theory, configuration interaction, or a cluster operator. Currently, the best approach remains an active topic of investigation. We mention here canonical transformation (CT) theory, which we have used to treat dynamic correlation in conjunction with the DMRG. Given the one- and two-particle density matrices obtained by the DMRG in an active space (43), CT theory introduces dynamic correlation through an exponential operator. It may be considered a kind of multireference coupled-cluster theory, but with simplifications arising from the use of cumulants and operator decompositions such that the final energy and amplitude expressions require only the one- and two-particle density matrices of the reference wave function (44, 45). The theory is described in detail in Reference 46.

CT: canonical transformation

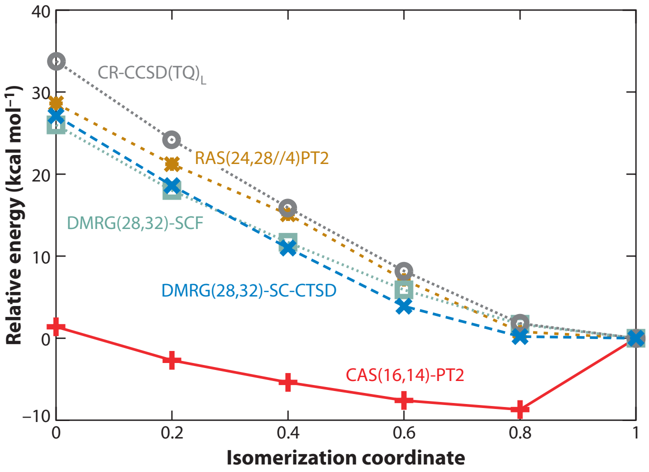


Figure 6

Energies along an isomerization coordinate of Cu_2O_2. We see that CASPT2 yields an unphysical minimum along the profile, due to an insufficiently large active space. The density matrix renormalization group (DMRG) calculation in the 32-orbital active space [DMRG(28,32)-SCF] yields a reaction curve without the minimum. Adding dynamic correlation [DMRG(28,32)-SC-CTSD] modifies the curve only slightly, presumably due to the balanced treatment of correlation in the large 32-orbital active space, which captures most of the differential correlation effects. The DMRG-SC-CTSD results are comparable with those of the recent restricted active-space perturbation theory (RASPT2) calculation by Malmqvist et al. (49). Figure adapted from Reference 47.

We recently reported some applications of the joint CT and DMRG theory in the copper-oxo dimer isomerization problem, as well as in the study of excited states in porphins. **Figure 6** displays our calculation of the potential energy curve along an isomerization coordinate of the Cu_2O_2 molecule, a model for the isomerization process in the tyrosinase active site. This system has risen to prominence in recent years due to the disagreement between several theoretical methods, in particular coupled-cluster and density functional calculations, and CASPT2 (complete active-space second-order perturbation theory). The latter predicts a minimum along the isomerization profile that is not expected on experimental grounds. The failure of the CASPT2 calculations can be attributed to the insufficient active space, which is limited to at most 16 orbitals in conventional treatments. With the DMRG, we can treat much larger active spaces, and furthermore, we can incorporate the remaining orbital correlations through CT theory. We illustrate the results of this procedure in **Figure 6**. The use of a 32-orbital active space (including the Cu 3d/4d and the O 2p/3p orbitals) at the DMRG-SCF level yields a curve with no minimum. The incorporation of dynamic correlation through CT theory (in a large basis) shifts the curve slightly. In fact, here we see that the dynamic correlation has a relatively small effect on the overall shape of the curve, a testament to the sufficiency of the active-space DMRG treatment (47). These kinds of calculations illustrate the emerging conclusion that in arbitrary molecules, the DMRG enables the treatment of active spaces with up to approximately 30 orbitals, and that CT theory will allow us to accurately fold in the description of dynamic correlation in large basis sets.

6. CONCLUSIONS

There is no universally efficient parameterization for every quantum state. Consequently, the DMRG is not a method that is suited to all quantum chemical problems. However, it is a powerful method to describe systems with a large number of strongly correlated electrons, a problem that has traditionally been quite difficult for quantum chemistry. It is especially ideal for strong correlation in long molecules, in which active spaces of more than 100 orbitals can be handled, but even in compact molecules it can be used to extend limits of complete active-space methodologies to 30 orbital active spaces or more. In this context, we consider applications to polymetallic transition metal systems to be especially promising.

The DMRG is powerful because it provides an efficient encoding of locality in one of the spatial dimensions. However, if we are to eventually treat even more complex strongly correlated molecules or bulk problems, work remains to find practical ways to encode locality in two and three dimensions. The past few years have seen great activity in the area of tensor networks, which include such wave functions as projected entangled pair states, string-bond states, correlator product states, and entangled plaquette states (48). These represent different but related approaches to the problem of encoding locality in two and three dimensions. In addition, although CT theory has been successfully used to incorporate the structure of dynamic correlation into the DMRG, much room remains for further investigation in this area also.

SUMMARY POINTS

1. The DMRG is a method to treat molecules with strongly correlated electrons. Strong correlation often arises because of near-orbital degeneracies. This is common in transition metal problems.
2. The DMRG supplies a variational wave function that reduces the exponential complexity of strong correlation by efficiently encoding locality in one of the spatial dimensions.
3. Energies, expectation values, and response properties can be obtained.
4. The DMRG is best applied within a complete active-space formulation. In compact molecules, active spaces with approximately 30 active orbitals can be accurately described, whereas in long molecules more than 100 active orbitals can be treated.
5. Investigators have applied the DMRG to a variety of systems, ranging from organic chromophores to transition metals.
6. Dynamic correlation can be incorporated via CT theory.

FUTURE ISSUES

1. Although the DMRG can be used in arbitrary systems, it only efficiently describes locality in one spatial dimension. The extension to wave functions that properly encode locality in two and three dimensions will be essential to treat strongly correlated electrons in bulk systems, or extremely large molecules. Tensor networks appear promising in this regard.
2. Other methods to include dynamic correlation in conjunction with the DMRG need to be explored.

DISCLOSURE STATEMENT

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