Optimizing Hartree-Fock Orbitals by the Density Matrix Renormalization Group

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Also see poster session
Fundamental issue in quantum chemistry calculation

How to solve the Schrodinger equation of molecules accurately and efficiently?

The Schrodinger Equation:

$$i\hbar \frac{\partial}{\partial t} \psi (r, R) = \left[ -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 + V(r, R) \right] \psi (r, R)$$

$$V(r, R) = -\sum_{il} \frac{Z_l e^2}{|r_i - R_l|} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|}$$
The basic difficulty to solve the equation is the exponential wall problem.

For example, for a water molecule, which has 10 electrons, if $N$ molecule orbitals are used, the total number of basis states is

$$C_N^5 C_N^5 \sim N^{10}$$

The total degree of freedom increases exponentially with the number of electrons!
In practical calculation, some truncation approximations are made, as show in the cartoon.

Due to the limit resources, for a given one-electron basis set, one only can obtain a finite many-body states, an approximation solution.
If one increases the many-body states, the one-electron basis set has to be reduced.

Exact solution
If one increases the one-electron basis, the many-body states have to be decreased.
Aim of our work:
using less optimized one-electron basis and many-body states to obtain much accurate result

Exact solution
How to apply DMRG to quantum chemistry

The starting point is to represent the Hamiltonian in the second quantized form by using a set of HF orbitals:

\[
H = \sum_{i j \sigma}^N t_{i j} c_{i \sigma}^+ c_{j \sigma} + \frac{1}{2} \sum_{i j r t, \sigma \sigma'}^N V_{i j r t} c_{i \sigma}^+ c_{j \sigma}^+ c_{t \sigma} c_{r \sigma}
\]

One-electron integral

One-electron integral:

\[
t_{i j} = \int dr \varphi_i^*(r) \left[ -\frac{1}{2} \Delta - \sum_{k=1}^{N} \frac{Z_k e^2}{|r - r_k|} \right] \varphi_j(r)
\]

Two-electron integral

Two-electron integral:

\[
V_{i j r t} = \int \int dr dr' \varphi_i^*(r) \varphi_j^*(r') \left[ \frac{e^2}{|r_i - r_j|} \right] \varphi_t(r') \varphi_r(r)
\]

Molecular orbital: HF single particle basis
But, the interaction includes $N^4$ terms, thus the compute time and storage cost expensive, $> O(N^5)$

$$\hat{H} = \sum_{ij}^{N} t_{ij} c_i^+ c_j + \frac{1}{2} \sum_{ijkl}^{N} V_{ijkl} c_i^+ c_j c_k^+ c_l$$

$N^4$ terms!

Only a small number of Hartree-Fock orbitals can be used, thus it is impractical in quantum chemistry calculation!
The way to solve this problem is regrouping operators introduced by T. Xiang in 1996, namely, if some orbitals in the same block, the summation can be performed in advance, as a result some complementary operators are introduced.

\[
O = \sum_{ijkl \in \text{Sys}} V_{ijkl} c_i^+ c_j^+ c_k^+ c_l^+ \quad \rightarrow \quad O(N^4) \rightarrow O(1)
\]

\[
O_i = \sum_{jrt \in \text{Sys}} V_{ijrt} c_j^+ c_t^+ c_r^+ 
\quad \rightarrow \quad O(N^4) \rightarrow O(N)
\]

\[
O_{ij} = \sum_{rt \in \text{Sys}} V_{ijrt} c_t^+ c_r^+ 
\quad \rightarrow \quad O(N^4) \rightarrow O(N^2)
\]

\(O(N^4)\) terms \(\rightarrow O(N^2)\) terms

\[
\hat{H} = \sum_{ij} N t_{ij} c_i^+ c_j + \frac{1}{2} \sum_{ijkl} V_{ijkl} c_i^+ c_j^+ c_k^+ c_l^+ 
\]

\(N^4\) terms!
In 1999, White and Martin performed for the first time the \textit{ab initio} DMRG calculation of the ground state energy of a water molecule, in the case of about 300 many-body states kept, the result is almost exact one, \textit{which gives us confidence to apply the DMRG to quantum chemistry calculation}.

![Graph of ground state energy of H\textsubscript{2}O](image)

\textbf{Use 25 H\textsubscript{2}O molecular orbitals}

\textbf{DMRG: 1s\textsuperscript{2} of oxygen is frozen}

Exact solution (within a triple-zeta, double polarization basis set) of the electronic Schrodinger equation for water

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Martin Head-Gordon  
*Department of Chemistry, University of California, Berkeley, California 94070*

✓ In 2003, Chan and Head-Gordon gave a benchmark calculation of the ground state energy of water molecule. This large scale calculation obtained near-exact result for 41 Hartree-Fock orbitals.

<table>
<thead>
<tr>
<th>Orbital #: N</th>
<th>Unrestricted Hartree-Fock</th>
<th>Coupled Cluster (SDT)</th>
<th>DMRG(^1) (\text{(M=6000)})</th>
<th>Quantum Monte Carlo(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>41</td>
<td>-85.254555</td>
<td>-85.511075</td>
<td>-85.511649 (\text{(M=6000)})</td>
<td>-85.5132(6)</td>
</tr>
<tr>
<td>92</td>
<td>-85.257519</td>
<td>-85.564462</td>
<td></td>
<td>-85.567(1)</td>
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</table>

Our goal:
One can handle large basis set, for example, 200, even more.

Basis idea:
Optimizing the HF orbitals by the DMRG

See poster session
New result for ground state energy of water molecule (unpublished)

\[ E_{gs} = -85.575 \text{(a.u.)} \]

\( (N_{tot} = 172 \text{ orbitals, } N = 60 \text{ orbitals, } M = 128, M_{\text{max}} = 512) \)

This is the best result obtained by DMRG for 172 Hartree-Fock orbitals.

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Animation to display the optimizing process of the HF orbitals

![Graph showing orbital index against energy change and step of DMRG optimization.]
Electronic density distribution

Ground State Energy

Step of DMRG Optimization
Thank you for your attentions!