DMRG in Quantum Chemistry: From its relation to traditional methods to $n$-orbital density matrices and beyond

Markus Reiher

Laboratorium für Physikalische Chemie, ETH Zürich, Switzerland

http://www.reiher.ethz.ch

April 2016
Dear Markus,

How are you?

We have booked some accommodation for you for 11-15 April in the Lincoln college:

http://www.lincoln.ox.ac.uk/

Concerning your talk (65min + 10 min for questions) we would be happy if you could provide an overview presentation on the application of DMRG in Quantum Chemistry. Ideally, this would include:

1) Brief historic discussion of numerical methods in QChem: HF, MCSCF/CASSCF, FCI, Coupled Cluster, DFT, RDMFT, ....
   How successful are those methods (and in which regimes: number of electrons, strength of physical correlation, ground state versus excited states, ...)
2) Why does one use DMRG in Quantum Chemistry?
3) Where is the 1-dim. local structure (as required for DMRG(?))? 
4) Concept of orbital entanglement and correlations
5) Details on how to implement DMRG for atoms/ How does it work?
6) benchmark calculations and comparison to results obtained by resorting to different methods
7) comments on scaling behavior (w.r.t. number of electrons and dimension of truncated 1-particle Hilbert space)/CPU time
8) Open problems
Non-Relativistic Many-Electron Hamiltonian

- many-electron Hamiltonian in position space (Hartree atomic units)

\[
H_{el} = \sum_{i}^{N} \left( -\frac{1}{2} \nabla_{i}^{2} - \sum_{I} \frac{Z_{I}}{r_{iI}} \right) + \sum_{i<j}^{N} \frac{1}{r_{ij}} \tag{1}
\]

with \( r_{ij} = |r_{i} - r_{j}| \) and \( N \) being the number of electrons.

- eigenvalue equation: electronic Schrödinger equation

\[
H_{el} \Psi_{el}^{\{R_{I}\}}(\{r_{i}\}) = E_{el}(\{R_{I}\}) \Psi_{el}^{\{R_{I}\}}(\{r_{i}\}) \tag{2}
\]

- central in electronic structure theory: how to approximate \( \Psi_{el} \)?
Standard Procedure: Construction of Many-Electron Basis

- Construct many-electron (determinantal) basis set \( \{ \Phi_I \} \) from a given (finite) one-electron (orbital) basis set \( \phi_i \).
- From the solution of the Roothaan–Hall equations, one obtains \( n \) orbitals from \( n \) one-electron basis functions.
- From the \( N \) orbitals with the lowest energy, the Hartree–Fock (HF) Slater determinant is constructed.
- The other determinants (configurations) are obtained by subsequent substitution of orbitals in the HF Slater determinant \( \Phi_0 \):
  \[
  \Phi_0 \rightarrow \{ \Phi^a_i \} \rightarrow \{ \Phi^a_{ij} \} \rightarrow \{ \Phi^a_{ijk} \} \rightarrow \ldots
  \]  
  (3)
- Determinants are classified by number of ’excitations’ (= substitutions in HF reference determinant).
Standard Full Configuration Interaction (FCI)

- Including all possible excited Slater determinants for a finite or infinite one-electron basis set leads to the so-called **full CI** approach.

- Number of Slater determinants $n_{SD}$ for $N$ spin orbitals chosen from a set of $L$ spin orbitals (colloquial: $N$ electrons in $L$ spin orbitals):

  $$n_{SD} = \binom{L}{N} = \frac{L!}{N!(L-N)!}$$  \hspace{1cm} (4)

  **Example:** There are $\approx 10^{12}$ different possibilities to distribute 21 electrons in 43 spin orbitals.

  CI calculations employing a complete set of Slater determinants are only feasible for small basis sets.
Truncated CI Wave Functions

Standard recipe to avoid the factorial scaling of the many-electron basis-set size: **truncate basis!** *Note: basis is pre-defined!*

**Assumption:** Substitution hierarchy is a useful measure to generate a systematically improvable basis set.

CIS: all singly-(S)-excited determinants are included:

\[
\Psi_{el}^{\text{CIS}} = C_0 \Phi_0 + \sum_{(ai)} C_{(ai)} \Phi_i^a
\]  

(5)

CISD: all singly- and doubly-(D)-excited determinants are included:

\[
\Psi_{el}^{\text{CISD}} = C_0 \Phi_0 + \sum_{(ai)} C_{(ai)} \Phi_i^a + \sum_{(ai)(bj)} C_{(ai,bj)} \Phi_{ij}^{ab}
\]  

(6)

\[C_0, C_{(ai)}, C_{(ai,bj)} \in \{CI\}\]  

(7)
Determination of the CI Expansion Coefficients $C_I$

\[
E_{el}^{CI} = \frac{\langle \Psi_{el}^{CI} | H_{el} | \Psi_{el}^{CI} \rangle}{\langle \Psi_{el}^{CI} | \Psi_{el}^{CI} \rangle} = \frac{\sum_{I,J} C_I^* C_J \langle \Phi_I | H_{el} | \Phi_J \rangle}{\sum_{I,J} C_I^* C_J \langle \Phi_I | \Phi_J \rangle}
\] (8)

$C_I$ determined from variational principle:
Calculate all derivatives $\partial E_{el}^{CI} / \partial C_K^*$ and set them equal to zero, which yields the CI eigenvalue problem:

\[
H \cdot C = E_{el} \cdot C
\] (9)

Essential: $H$ is constructed from matrix elements $\langle \Phi_I | H_{el} | \Phi_J \rangle$ in pre-defined determinantal basis $\{\Phi_I\}$
Standard 'Technical’ Trick: Second Quantization

Operators and wave functions are expressed in terms of creation and annihilation operators to implement the Slater–Condon rules for the evaluation of matrix elements $\langle \Phi_I | H_{el} | \Phi_J \rangle$ directly into the formalism.

$H_{el}$ in second quantization ($i, j, k, l$ are spin orbital indices):

$$
\Rightarrow \quad H_{el} = \sum_{ij} \langle \phi_i | h(i) | \phi_j \rangle c_i^\dagger c_j \\
+ \frac{1}{2} \sum_{ijkl} \langle \phi_i(1) | \phi_k(2) | g(1, 2) | \phi_l(2) \rangle \phi_j(1) \rangle c_i^\dagger c_j^\dagger c_k c_l
$$

CI wave function in second quantization:

$$
\Psi_{el}^{\text{FCI}} = C_0 \Phi_0 + \sum_{(ai)} C_{(ai)} c_i^\dagger c_i \Phi_0 + \sum_{(ai)(bj)} C_{(ai,bj)} c_b^\dagger c_j c_a^\dagger c_i \Phi_0 \cdots
$$
CI Energy in Second Quantization

\[ E_{el}^{CI} = \langle \Psi_{el}^{CI} | H_{el} | \Psi_{el}^{CI} \rangle \]  \hspace{1cm} (12)

\[ = \sum_{ij}^{L} \sum_{IJ}^{n_{SD}} C_I^* C_J t_{ij}^{IJ} \langle \phi_i(1) | h(1) | \phi_j(1) \rangle \]

\[ \equiv h_{ij} \]

\[ + \sum_{ijkl}^{L} \sum_{IJ}^{n_{SD}} C_I^* C_J T_{ijkl}^{IJ} \langle \phi_i(1) \langle \phi_k(2) | g(1,2) | \phi_l(2) \rangle \phi_j(1) \rangle \]

\[ \equiv g_{ijkl} \]

\[ = \sum_{ij}^{L} \gamma_{ij} h_{ij} + \sum_{ijkl}^{L} \Gamma_{ijkl} g_{ijkl} \]  \hspace{1cm} (14)

\( t_{ij}^{IJ} \) or \( T_{ijkl}^{IJ} \) are matrix elements of determinantal basis functions over pairs or quadruples of elementary operators \( c^\dagger \) and \( c \).

\( \gamma_{ij} \) are \( \Gamma_{ijkl} \) are density matrix elements (compare: RDMFT and 2RDM methods).
Is there a better way to construct the finite-dimensional determinantal basis set in order to avoid the factorial scaling?
Coupled-Cluster — An Advanced CI-type Wave Function Ansatz:

\[ \Psi_{el}^{CC} = \exp(T) \Phi_0 \]  

(15)

Excitation operator:

\[ T = T_1 + T_2 + T_3 + \cdots \]  

(16)

where

\[ T_\alpha = \sum_{ab \cdots i j \cdots} t_{ij}^{ab \cdots} \underbrace{c_b^{\dagger} c_j \cdots c_a^{\dagger} c_i}_{\alpha \text{ pairs } c^\dagger c} \Rightarrow T_1 = \sum_{ai} t_a^{i} c_a^{\dagger} c_i \]  

(17)

Notation:

CCS \ (T = T_1), \ CCSD \ (T = T_1 + T_2), \ CCSDT \ (T = T_1 + T_2 + T_3), \cdots

Coupled-cluster improves on truncated CI, because certain (disconnected) higher excited configurations (e.g., \( t_i^a c_a^{\dagger} c_i t_{jk}^{bc} c_c^{\dagger} c_k c_b^{\dagger} c_j \)) are included.
However, all of this is too expensive and often too limited (MRCC would be nice, but requires 5e-RDMs ...)

**DFT is the workhorse in transition metal chemistry**

(structures(!), energies, spectroscopic signatures)

in critical cases, its accuracy is difficult to assess

... illustrated by an example
The Spin State Problem in Quantum Chemistry

- To predict the correct energy gaps between states of different spin $S$ is crucial in chemistry (e.g., two-state reactivity); in kJ/mol
- Present-day DFT has difficulties to cope with this problem
- E.g., the results strongly depend on exact exchange admixture $c_3$
- Example: the thermal spin-crossover complex $[\text{Fe(phen)}_2(\text{NCS})_2]$
Ab initio Methods for benchmarks needed

Well-established for open-shell transition metal complexes:
CASSCF/CASPT2 and MRCI
(incl. RASSCF/RASPT2)
Orbital subspaces in CAS approaches

- Virtual orbitals: ~ $10^2 - 10^3$
- Active orbitals:
  - CASSCF: up to 18
  - DMRG-SCF: up to 100
- Inactive orbitals:
  - ~ 50 - 100

- Orbitals are subdivided in doubly occupied \textit{inactive} orbitals, \textit{active} orbitals and unoccupied \textit{virtual} orbitals.

- Huge virtual orbital subspace is not considered in CAS approaches (but should be (dynamic correlation)!

- Exponential scaling of many-particle basis set size permits exact diagonalization up to only CAS(18,18)
Ab initio Methods for benchmarks needed

Well-established for open-shell transition metal complexes: CASSCF/CASPT2 and MRCI (incl. RASSCF/RASPT2)

... but what if active orbital space is too large?

Promising new approaches?
Parameterization of the Wave Function

\[ |\Psi\rangle = \sum_{i_1i_2 \cdots i_N} C_{i_1i_2 \cdots i_N} |i_1\rangle \otimes |i_2\rangle \otimes \cdots \otimes |i_N\rangle \]

- Restricted sum over basis states with a certain excitation pattern
  → yields a pre-defined (!) many-particle basis set
- Configuration Interaction ansatz

\[ |\text{CI}\rangle = \left( 1 + \sum_{\mu} C_{\mu} \hat{\tau}_\mu \right) |\text{HF}\rangle \]

- Coupled Cluster ansatz

\[ |\text{CC}\rangle = \left( \prod_{\mu} [1 + t_{\mu} \hat{\tau}_{\mu}] \right) |\text{HF}\rangle \]

- numerous specialized selection/restriction protocols
Instead of standard CI-type calculations by diagonalization/projection

\[ |\Psi\rangle = \sum_{i_1 i_2 \cdots i_N} C_{i_1 i_2 \cdots i_N} |i_1\rangle \otimes |i_2\rangle \otimes \cdots \otimes |i_N\rangle \]

construct CI coefficients from correlations among orbitals

\[ |\Psi\rangle = \sum_{i_1 i_2 \cdots i_N} C_{i_1 i_2 \cdots i_N} |i_1\rangle \otimes |i_2\rangle \otimes \cdots \otimes |i_N\rangle \]
Density Matrix Renormalization Group: Principles

- New wavefunction parametrization:

\[ |\psi\rangle = \sum_{\sigma} c_\sigma |\sigma\rangle \quad \rightarrow \quad |\psi\rangle = \sum_{\sigma} M^{\sigma_1} M^{\sigma_2} \cdots M^{\sigma_L} |\sigma\rangle \]

- complete active space (CAS) partitioning and iterative sweeping:

  In essence: dimension reduction by least-squares fitting
Reviews on DMRG in Quantum Chemistry


DMRG Parameters

Active space selection, as in MCSCF, but need additional parameters:

- Number of renormalized basis states \( m \)
- Orbital ordering
- Choice of initial environment guess

These parameters do depend on each other.

Two variants of DMRG:

Traditional DMRG

\[ |\psi\rangle = \sum_{LR} C_{LR} |\sigma_L\rangle \otimes |\sigma_R\rangle \]

- coefficients valid for one bipartition into L and R (need basis transformations)
- Excited states only with state averaging
- faster for ground states?

MPS DMRG (2nd generation)

\[ |\psi\rangle = \sum_{\sigma} M^{\sigma_1} M^{\sigma_2} \cdots M^{\sigma_L} |\sigma\rangle \]

- coefficients valid for the whole system
- Easy and efficient implementation of
  - \[ \langle \phi | \psi \rangle \]
  - \[ \langle \psi | a_i \dagger \hat{H} a_j | \psi \rangle \]
  - 3- and 4-body RDMs
  - excited states
Matrix product states (MPS) and Matrix product operators (MPO)

\[ |\psi\rangle = \sum_{\sigma} c_{\sigma} |\sigma\rangle \quad \rightarrow \quad |\psi\rangle = \sum_{\sigma} \sum_{a_1, \ldots, a_{L-1}} M^{\sigma_1}_{a_1} M^{\sigma_2}_{a_1 a_2} \cdots M^{\sigma_L}_{a_{L-1}} |\sigma\rangle \]

\[ \hat{W} = \sum_{\sigma, \sigma'} w_{\sigma \sigma'} |\sigma\rangle \langle \sigma'| \quad \rightarrow \quad \hat{W} = \sum_{\sigma \sigma'} \sum_{b_1, \ldots, b_{L-1}} W^{\sigma_1 \sigma'_1}_{b_1} \cdots W^{\sigma_l \sigma'_l}_{b_{l-1} b_l} \cdots W^{\sigma_L \sigma'_L}_{b_{L-1} b_L} |\sigma\rangle \langle \sigma'| \]

Matrix product operators (MPO)

\[ \hat{\mathcal{H}} = \sum_{ij\sigma} t_{ij} \hat{c}_{i\sigma} \hat{c}_{j\sigma} + \frac{1}{2} \sum_{ijkl\sigma\sigma'} V_{ijkl} \hat{c}_{i\sigma} \hat{c}^\dagger_{k\sigma'} \hat{c}_{l\sigma'} \hat{c}_{j\sigma}, \]

\[ t_{ij} \hat{c}_{i\uparrow} \hat{c}_{j\uparrow} = t_{ij} \cdot \hat{I}_1 \otimes \cdots \otimes \hat{c}_{i\uparrow} \otimes \hat{I}_{i+1} \otimes \cdots \otimes \hat{c}_{j\uparrow} \otimes \cdots \otimes \hat{I}_L \]
MPO compression

Consider the terms $c_1^\dagger c_2^\dagger c_5 c_7 + c_1^\dagger c_3^\dagger c_6 c_7$

<table>
<thead>
<tr>
<th></th>
<th>$c_1^\dagger$</th>
<th>$c_1^\dagger$</th>
<th>$c_2^\dagger$</th>
<th>$c_2^\dagger$</th>
<th>$I_2$</th>
<th>$I_3$</th>
<th>$I_4$</th>
<th>$c_3^\dagger$</th>
<th>$I_5$</th>
<th>$I_6$</th>
<th>$c_6$</th>
<th>$c_7$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>$c_1$</th>
<th>$c_2$</th>
<th>$I_2$</th>
<th>$I_3$</th>
<th>$I_4$</th>
<th>$c_5$</th>
<th>$I_6$</th>
<th>$c_6$</th>
<th>$c_7$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>$c_1^\dagger$</th>
<th>$c_2^\dagger$</th>
<th>$I_2$</th>
<th>$I_3$</th>
<th>$I_4$</th>
<th>$I_5$</th>
<th>$c_5$</th>
<th>$I_6$</th>
<th>$c_6$</th>
<th>$c_7$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>$c_1^\dagger$</th>
<th>$c_2^\dagger$</th>
<th>$I_2$</th>
<th>$I_3$</th>
<th>$I_4$</th>
<th>$I_5$</th>
<th>$c_6$</th>
<th>$I_6$</th>
<th>$c_7$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

DMRG in Quantum Chemistry

Markus Reiher
MPS-MPO operations: expectation values

\[ \langle \phi | \hat{\mathcal{W}} | \psi \rangle = \sum_{a_{L-1} a'_{L-1} b_{L-1}} N_{1a_{L-1} \sigma_L \sigma'_{L}} W_{b_{L-1} 1 \sigma'_L} \left( \cdots \sum_{a_1 a'_1 b_1 \sigma_2 \sigma'_2} N_{a_2 a_1 \sigma_2 \sigma'_2} W_{b_1 b_2 \sigma'_2} \right) \]

\[
\cdot \left( \sum_{\sigma_1 \sigma'_1} N_{a_1 1 \sigma_1 \sigma'_1} W_{1 b_1 \sigma'_1} M_{1 \sigma'_1 a_1} \right) M_{a_1 a_2'} \cdots M_{a'_{L-1} 1} \]

\[ N^{1\dagger} \]

\[ W^{1} \]

\[ M^{1} \]
Spin symmetry adaptation: MPS and MPO put together

\[ F_{i'j'}^{[a']} (l + 1) = \sum_{aijkss'} \text{Wigner-9j} [jsj'] M_{i'i}^{[s']} \text{W}_{aa'} [k]^{ss'} F_{ij}^{[a]} (l) M_{j'j}^{[s]} \]

The QCMaquis DMRG program

Input: $t_{ij}$ and $V_{ijkl}$ integrals, target state quantum numbers

The system (atom, molecule, ...) is encoded in $t_{ij}$

Co-developed with the ALPS MPS project (Troyer).

Integrated into the Molcas program package.

Source code available from www.reiher.ethz.ch/software

- Parallelized by MPI and threading
- C++ / C++11, 60k lines core program + 50k lines associated libs + standard libs (boost, etc.)

chains rectangles honeycomb etc.

non-relativistic relativistic
Heisenberg spin chains Fermi/Boson Hubbard etc.

\[
U1 \otimes U1(\otimes PG) \\
SU2 \otimes U1(\otimes PG) \\
DG \otimes U1(\otimes PG)
\]

\[
\begin{pmatrix}
|\psi\rangle \\
|\psi^*\rangle \\
\Gamma_{ijkl}
\end{pmatrix}
\]

\textbf{Lattice} \leftrightarrow \textbf{Model} \leftrightarrow \textbf{SymmGroup}

\textbf{L-boundary} \textbf{MPO} \textbf{R-boundary}

\textbf{MPS}

\textbf{ContractionEngine}
A well working example: FCI for N2 (14e, 28o)

\[ \text{extrapolation: } -109.282173 \]
A well working example: FCI for N2 (14e, 28o)
Does DMRG Work for Compact Molecules?

- Original 'opinion' in the DMRG community: 
  *Works only for pseudo-one-dimensional, non-compact systems!*

- Test for a mononuclear transition metal system CAS(10,10): CoH

<table>
<thead>
<tr>
<th>m</th>
<th>$E_{\text{singlet}}/E_h$</th>
<th>$E_{\text{triplet}}/E_h$</th>
<th>$\Delta E$/kJmol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>64</td>
<td>(-1381.952,054)</td>
<td>(-1381.995,106)</td>
<td>(113.03)</td>
</tr>
<tr>
<td>76</td>
<td>(-1381.952,063)</td>
<td>(-1381.995,109)</td>
<td>(113.02)</td>
</tr>
<tr>
<td>91</td>
<td>(-1381.952,070)</td>
<td>(-1381.995,110)</td>
<td>(113.00)</td>
</tr>
<tr>
<td>109</td>
<td>(-1381.952,073)</td>
<td>(-1381.995,110)</td>
<td>(112.99)</td>
</tr>
<tr>
<td>CAS(10,10)</td>
<td>(-1381.952,074)</td>
<td>(-1381.995,110)</td>
<td>(112.99)</td>
</tr>
<tr>
<td>CASPT2(10,10)</td>
<td>(-1382.189,527)</td>
<td>(-1382.241,333)</td>
<td>(130.57)</td>
</tr>
<tr>
<td>DFT/BP86</td>
<td>(-1383.504,019)</td>
<td>(-1383.585,212)</td>
<td>(213.1)</td>
</tr>
<tr>
<td>DFT/B3LYP</td>
<td>(-1383.202,267)</td>
<td>(-1383.279,574)</td>
<td>(203.0)</td>
</tr>
</tbody>
</table>

Example: Analysis of Spin Density Distributions with DMRG
Noninnocent Iron Nitrosyl Complexes

- Transition metal nitrosyl complexes have a complicated electronic structure.
- Qualitatively different spin densities reported by Conradie & Ghosh. 
  
  \begin{center}
  \end{center}

- Systematic comparison of DFT spin densities with CASSCF:
  
  \begin{center}
  \end{center}

  see also work by K. Pierloot *et al.*
DFT Spin Densities: A Case Study

Only for high-spin complexes similar spin densities are obtained

$\Rightarrow [\text{Fe(NO)}]^ {2+}$ moiety determines the spin density
The Model System for Accurate Reference Calculations

Structure:

- Four point charges of $-0.5 \, \text{e}$ model a square-planar ligand field ($d_{dp} = 1.131 \, \AA$)

$\Rightarrow$ Similar differences in DFT spin densities as present for larger iron nitrosyl complexes

Advantage of the small system size:

- Standard correlation methods (CASSCF, ...) can be efficiently employed
- Study convergence of the spin density w.r.t. the size of the active orbital space

DFT Spin Densities

Spin density isosurface plots

Spin density difference plots w.r.t. OLYP

⇒ Similar differences as found for the large iron nitrosyl complexes
Reference Spin Densities
from Standard Electron Correlation Methods
Reference Spin Densities from CASSCF Calculations

Defining the active orbital space:

- Minimal active space: Fe 3d- and both NO $\pi^*$-orbitals $\Rightarrow$ \textbf{CAS(7,7)}

- Consider also both NO $\pi$-orbitals $\Rightarrow$ \textbf{CAS(11,9)}

- Additional shell of Fe $d$-orbitals (double-shell orbitals) is gradually included $\Rightarrow$ \textbf{CAS(11,11)} to \textbf{CAS(11,14)}

- Include one ligand $\sigma$-orbital and the antibonding $\sigma^*$-orbital upon the \textbf{CAS(11,11)} $\Rightarrow$ \textbf{CAS(13,13)}

$\Rightarrow$ Analyze convergence of spin density w.r.t. the dimension of the active orbital space
CASSCF Results: Oscillating Spin Densities

- CAS(11,14): spin density; all others: spin density differences
- stable CAS with all important orbitals is difficult to obtain

⇒ Reference spin densities for very large CAS required
DMRG Spin Densities — Measures of Convergence

- **Qualitative** convergence measure: spin density difference plots
- **Quantitative** convergence measure:

\[ \Delta_{\text{abs}} = \int |\rho_1^s(r) - \rho_2^s(r)|\,dr < 0.005 \]  \hspace{1cm} (18)

\[ \Delta_{\text{sq}} = \sqrt{\int |\rho_1^s(r) - \rho_2^s(r)|^2\,dr} < 0.001 \]  \hspace{1cm} (19)

- **Quantitative** convergence measure: quantum fidelity \( F_{m_1,m_2} \)

\[ F_{m_1,m_2} = |\langle \Psi^{(m_1)} | \Psi^{(m_2)} \rangle|^2 \]  \hspace{1cm} (20)

\( \Rightarrow \) Reconstructed CI expansion of DMRG wave function can be used!

DMRG Spin Densities for Large Active Spaces

$\Delta_{\text{abs}}$ and $\Delta_{\text{sq}}$ for DMRG(13,$y$)[$m$] calculations w.r.t. DMRG(13,29)[2048] reference

<table>
<thead>
<tr>
<th>Method</th>
<th>$\Delta_{\text{abs}}$</th>
<th>$\Delta_{\text{sq}}$</th>
<th>Method</th>
<th>$\Delta_{\text{abs}}$</th>
<th>$\Delta_{\text{sq}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMRG(13,20)[128]</td>
<td>0.030642</td>
<td>0.008660</td>
<td>DMRG(13,29)[128]</td>
<td>0.032171</td>
<td>0.010677</td>
</tr>
<tr>
<td>DMRG(13,20)[256]</td>
<td>0.020088</td>
<td>0.004930</td>
<td>DMRG(13,29)[256]</td>
<td>0.026005</td>
<td>0.006790</td>
</tr>
<tr>
<td>DMRG(13,20)[512]</td>
<td>0.016415</td>
<td>0.003564</td>
<td>DMRG(13,29)[512]</td>
<td>0.010826</td>
<td>0.003406</td>
</tr>
<tr>
<td>DMRG(13,20)[1024]</td>
<td>0.015028</td>
<td>0.003162</td>
<td>DMRG(13,29)[1024]</td>
<td>0.003381</td>
<td>0.000975</td>
</tr>
<tr>
<td>DMRG(13,20)[2048]</td>
<td>0.014528</td>
<td>0.003028</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

DMRG in Quantum Chemistry

Markus Reiher 42 / 77
Importance of Empty Ligand Orbitals

**Table:** Some important Slater determinants with large CI weights from DMRG(13,29)[m]

Upper part: Slater determinants containing an occupied $d_{x^2−y^2}$-double-shell orbital (marked in bold face). Bottom part: Configurations with occupied ligand orbitals (marked in bold face). 2: doubly occupied; a: $\alpha$-electron; b: $\beta$-electron; 0: empty.

<table>
<thead>
<tr>
<th>Slater determinant</th>
<th>CI weight $m = 128$</th>
<th>CI weight $m = 1024$</th>
</tr>
</thead>
<tbody>
<tr>
<td>b2b222a0a00000000</td>
<td>0.003 252</td>
<td>0.003 991</td>
</tr>
<tr>
<td>bb2222aa00000000</td>
<td>−0.003 226</td>
<td>−0.003 611</td>
</tr>
<tr>
<td>222220ab00000000</td>
<td>−0.002 762</td>
<td>−0.003 328</td>
</tr>
<tr>
<td>ba2222ab00000000</td>
<td>0.002 573</td>
<td>0.003 022</td>
</tr>
<tr>
<td>b2a222a0b00000000</td>
<td>−0.002 487</td>
<td>−0.003 017</td>
</tr>
<tr>
<td>202222ab00000000</td>
<td>0.002 405</td>
<td>0.002 716</td>
</tr>
<tr>
<td>b222a2a0b00000000</td>
<td>0.010 360</td>
<td>0.011 558</td>
</tr>
<tr>
<td>22b2a2a0a00000000</td>
<td>0.009 849</td>
<td>0.011 366</td>
</tr>
<tr>
<td>22b2a2a0b00000000</td>
<td>−0.009 532</td>
<td>−0.011 457</td>
</tr>
<tr>
<td>b2222aab00000000</td>
<td>−0.009 490</td>
<td>−0.010 991</td>
</tr>
<tr>
<td>a2222baa00000000</td>
<td>−0.009 014</td>
<td>−0.010 017</td>
</tr>
<tr>
<td>b2b222a0a00000000</td>
<td>0.008 820</td>
<td>0.010 327</td>
</tr>
</tbody>
</table>
Assessment of CASSCF Spin Densities (Differences)

⇒ CASSCF spin densities oscillate around DMRG reference distribution
DFT–DMRG Spin Densities Differences

Analyzing DMRG and correlated wave functions with concepts from quantum information theory
Entanglement Measures for Embedded Subsystems

- See pioneering work by Ö. Legeza within QC-DMRG
- Consider one or two orbitals embedded in a CAS
- Measure for entanglement of states on orbital $i$ with those defined on environment:


**von-Neumann-type single-orbital entropy**

$$ s(1)_i = - \sum_{\alpha=1}^{4} \omega_{\alpha,i} \ln \omega_{\alpha,i} \quad (21) $$

$$ (\omega_{\alpha,i} \text{ is an eigenvalue of the 1o-RDM of spatial orbital } i \text{ — states defined on all other orbitals of the CAS have been traced out}) $$
Entanglement Measures for Embedded Subsystems

- Measure for entanglement of states living on orbital $i$ and orbital $j$ with those in the environment:

**von-Neumann-type two-orbital entropy**

\[
s(2)_{ij} = - \sum_{\alpha=1}^{16} \omega_{\alpha,ij} \ln \omega_{\alpha,ij} \tag{22}
\]

($\omega_{\alpha,ij}$ is an eigenvalue of the 2o-RDM of two spatial orbitals $i$ and $j$ — states defined on all other orbitals of the CAS have been traced out)

- Note the difference between $ne$-RDMs and $no$-RDMs!
Entanglement Measures for Embedded Subsystems

- \( s(2)_{ij} \) contains also the ’on-site’ entropies for the two orbitals

\[ \Rightarrow \text{Subtract these contributions to obtain the ’inter-orbital entropy’}: \]


Mutual information

\[ I_{ij} \propto s(2)_{ij} - s(1)_i - s(1)_j \quad (23) \]

- Successfully applied to optimize orbital ordering and to enhance DMRG convergence by Ö. Legeza
How To Read the (New) Mutual Information Plots

The value of mutual information is encoded in lines connecting orbital symbols:

- Solid line: $10^{-1}$
- Dashed line: $10^{-2}$
- Dotted line: $10^{-3}$

Definition of the entropy measures:

$$s(1)_i = - \sum_\alpha w_{\alpha,i} \ln w_{\alpha,i}$$

$$s(2)_i = - \sum_\alpha w_{\alpha;i,j} \ln w_{\alpha;i,j}$$

$$I_{i,j} = s(2)_{i,j} - s(1)_i - s(1)_j$$

- $w_{\alpha,i}$: eigenvalues of one-orbital reduced density matrix
- $w_{\alpha;i,j}$: eigenvalues of two-orbital reduced density matrix
Entanglement and Orbitals — Single Orbital Entropy

- Three groups of orbitals
  ⇒ large single orbital entropy
  ⇒ medium single orbital entropy
  ⇒ tiny single orbital entropy

- Configurations belonging to the third block have small $C_I$ ⇒ important for dynamic correlation

- Note: more structure than in spectrum of 1e-RDM

K. Boguslawski, P. Tecmer, Ö. Legeza, M. Reiher,


- 4 point charges in $xy$-plane at $d_{pc} = 1.133$ Å
- Natural orbital basis: CAS(11,14)SCF/cc-pVTZ
- DMRG(13,29) with DBSS ($m_{\text{min}} = 128, m_{\text{max}} = 1024$)
Three groups of orbitals
⇒ high entanglement
⇒ medium entanglement
⇒ weak entanglement

Strong entanglement for pairs:

\((d, \pi^*) \leftrightarrow (d, \pi^*)^*\)

\(\pi \leftrightarrow \pi^*\)

\(\sigma_{\text{Metal}} \leftrightarrow \sigma_{\text{Ligand}}\)

⇒ Important for static correlation (chemical intuition of constructing a CAS)

4 point charges in \(xy\)-plane at \(d_{pc} = 1.133\ \text{Å}\)

Natural orbital basis: CAS(11,14)SCF/cc-pVTZ

DMRG(13,29) with DBSS \((m_{\text{min}} = 128, m_{\text{max}} = 1024)\)

K. Boguslawski, P. Tecmer, Ö. Legeza, M. Reiher,

Entanglement Measures can Monitor Bond Breaking/Formation Processes: Dinitrogen

\[ I_{i,j} = \frac{1}{2}(s(2)_{i,j} - s(1)_i - s(1)_j)(1 - \delta_{ij}) \]

Part of entanglement is already encoded in molecular orbitals changing with the structure!

Atomic-like non-orthogonal basis fcts. exhibit large entanglement measures among each other.
Bond Breaking in Dinitrogen at 1.69 Ångström

Part of entanglement is already encoded in molecular orbitals changing with the structure!

Atomic-like non-orthogonal basis fcts. exhibit large entanglement measures among each other.

(b) $d_{NN} = 1.69Å$
Bond Breaking in Dinitrogen at 2.22 Ångström

Part of entanglement is already encoded in molecular orbitals changing with the structure! Atomic-like non-orthogonal basis fcts. exhibit large entanglement measures among each other.

$\text{(d) } d_{NN} = 2.22\text{Å}$
Bond Breaking in Dinitrogen at 3.18 Ångström

Part of entanglement is already encoded in molecular orbitals changing with the structure!

Atomic-like non-orthogonal basis fcts. exhibit large entanglement measures among each other.

\[
(f) \; d_{NN} = 3.175 \text{Å}
\]
Artifacts of Small Active Space Calculations

Comparison of DMRG(11,9)[220] and DMRG(11,11)[790] to DMRG(13,29)[128,1024,10^{-5}] for [Fe(NO)]^{2+}

- $I_{ij}$ (and $s(1)_i$) overestimated for small active spaces
- Entanglement of orbitals too large
- Missing dynamic correlation is captured in an artificial way
How to choose an active space?
How to choose an active space? — Opinions

- “… the choice of the active space actually used in more complex systems is highly subjective and can lead to serious problems.”
  

- ”CAS-based methods are another alternative, although the selection of the active space is a tremendous challenge.”
  

- “Choosing the “correct” active space for a specific application is by no means trivial; often the practitioner must “experiment” with different choices in order to assess adequacy and convergence behavior. While every chemical system poses its own challenges, certain rules of thumb apply.”
  
How to choose an active space? — Recipes

- B. O. Roos (1989)
The Complete Active Space Self-Consistent Field Method and Its Applications in Electronic Structure Calculations; in *Ab Initio Methods in Quantum Chemistry*, K.P. Lawley (Ed.), John Wiley & Sons Ltd., 399–446.

- most active orbitals should appear paired (one highly occupied and one corresponding almost empty orbital)
- conjugated and aromatic bonds should be included in the CAS
- both the bonding and antibonding orbitals of a bond that is broken have to be included
- orbitals describing C-H bonds are not to be included in active space
How to choose an active space? — Recipes

- unrestricted Hartree-Fock natural orbitals (UNOs) are used as starting orbitals for CASSCF calculations
- orbitals with occupation numbers between 0.02 and 1.98 are selected for the active space

- the idea has been explored further by comparison to DMRG results:
  
Can one choose the CAS in an automated way?
Exploit Two Advantages of DMRG for the CAS choice

- DMRG results obtained after (micro)iterations, qualitative structure of wave function converges quickly
- The CAS is not limited by exponentially scaling basis size (the scaling depends on the no. of orbitals, not on the no. of electrons; 100 orbitals are about the limit)
Example: Transition Structure of Ozone


(see this reference also for a 'first-generation' DMRG flow chart)
Example: Transition Structure of Ozone

\[ \text{O}_3 \text{ transition state energy} \]

\[ \text{O}_3 \text{ transition state CI coefficients} \]


(see this reference also for a 'first-generation' DMRG flow chart)
Example: Transition Structure of Ozone

![Transition State Chart]


(see this reference also for a 'first-generation' DMRG flow chart)
Exploit Two Advantages of DMRG for the CAS choice

- DMRG is iterative
- DMRG can handle large CAS sizes

⇒ ... towards an automated CAS determination
Partially converged entanglement information is sufficient

 HF orbitals, \( m = 200 \)
4 sweeps
HF guess

\( E = -1449.266845 \text{ E}_H \)

 HF orbitals, \( m = 500 \)
8 sweeps
CI-DEAS guess

\( E = -1449.290301 \text{ E}_H \)

 HF orbitals, \( m = 2000 \)
16 sweeps
CI-DEAS guess

\( E = -1449.302426 \text{ E}_H \)

 HF orbitals, \( m = 200 \)
4 sweeps
HF guess

\( E = -2658.144420 \text{ E}_H \)

 HF orbitals, \( m = 500 \)
8 sweeps
CI-DEAS guess

\( E = -2665.877397 \text{ E}_H \)

 HF orbitals, \( m = 2000 \)
16 sweeps
CI-DEAS guess

\( E = -2665.878045 \text{ E}_H \)

- sufficiently accurate entanglement information can be obtained from partially converged calculations

Complete Automation of CAS Selection

**Generate Initial Orbitals**
- **Recommended**: CASSCF with small CAS or DMRG-SCF

**Initial DMRG Calculation**
- With a large CAS around the Fermi level
- **Recommended Settings**: CI-DEAS guess, \( m = 500 \), 8 sweeps

**Calculate Entanglement Measures**

**Consistency Test**
- Do entanglement measures of the final calculation agree qualitatively with those of the initial calculation?
- **Yes**
- **No**

**Generate Threshold Diagrams**

**Can Orbitals be Excluded?**
- Can orbitals with \( s_i(1) < 1-2\% \) max. \( s_i(1) \)
  - **Yes**
  - Include orbitals kept in the first, clearly identifiable plateau at low thresholds
  - **No**

**Is it Feasible to Converge a Calculation with this CAS Size?**
- **Yes**
  - Converge calculation with CASSCF or DMRG-SCF
- **No**
  - **Stop**: Unfeasible for DMRG

**Single-Configuration Case**
- Select CAS anyway

**Consistency Test**
- Increase initial CAS
- **Yes**
- **No**

---

Same CAS selection for different types of orbitals

- the same CAS is automatically selected for all orbital bases considered

Subtile correlation effects are automatically captured

- correlation effects attributed to the covalency of the bonds are automatically accounted for

The Cu$_2$O$_2^{2+}$ torture track

Automated approach gives qualitatively correct wave function

Regularizing effect of short-range DFT: Water

**DMRG–srDFT for the WCCR10 test set**

![Chemical structure](image)

Calculated dissociation energies in kJ/mol

<table>
<thead>
<tr>
<th>Method</th>
<th>$D_e$ (kJ/mol)</th>
<th>$D_0$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMRG<a href="30,22">2000</a></td>
<td>173.5</td>
<td>165.1</td>
</tr>
<tr>
<td>DMRG<a href="20,18">2000</a></td>
<td>169.9</td>
<td>161.5</td>
</tr>
<tr>
<td>DMRG<a href="10,10">2000</a></td>
<td>132.8</td>
<td>124.3</td>
</tr>
<tr>
<td>DMRG<a href="30,22">2000</a>-srPBE</td>
<td>225.1</td>
<td>216.6</td>
</tr>
<tr>
<td>DMRG<a href="20,18">2000</a>-srPBE</td>
<td>227.9</td>
<td>219.4</td>
</tr>
<tr>
<td>DMRG<a href="10,10">2000</a>-srPBE</td>
<td>216.5</td>
<td>208.0</td>
</tr>
<tr>
<td>PBE</td>
<td>240.2</td>
<td>231.8</td>
</tr>
<tr>
<td>PBE (full complex/def2-TZVP)</td>
<td>257.5</td>
<td>249.0</td>
</tr>
<tr>
<td>PBE (full complex/def2-QZVPP from WCCR10)</td>
<td>247.5</td>
<td>239.0</td>
</tr>
<tr>
<td>Exp. (from WCCR10)</td>
<td>226.7</td>
<td>218.2</td>
</tr>
</tbody>
</table>

Conclusion

- new and efficient second-generation DMRG program for full Schrödinger–Coulomb (Dirac–Gaunt/Breit) Hamiltonian available: QCMaquis
- HF-, split-localized- and CASSCF-orbitals allow to select an active space that is in line with the literature suggestions
- the whole CAS evaluation procedure is fast
  ... and can be automatized
- dynamic correlation introduced through short-range DFT regularizes the CAS
Acknowledgments

Christopher Stein, Sebastian Keller
Stefan Knecht, Arseny Kovyrshin
Yingjin Ma, Erik Hedegård
Andrea Muolo, Pawel Tecmer
Katharina Boguslawski
… as well as the rest of the group →