Towards Large-Scale Quantum Chemistry with Second-Generation Density Matrix Renormalization Group - QCMaquis

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Review of our QCMAquis toolbox based on the density matrix renormalization group approach

New Approaches for ab initio Calculations of Molecules with Strong Electron Correlation

Stefan Knecht, Erik Donovan Hedegård, Sebastian Keller, Arseny Kovyryshin, Yingjin Ma, Andrea Muolo, Christopher J. Stein, Markus Reiher

(Submitted on 31 Dec 2015)

Reliable quantum chemical methods for the description of molecules with dense-lying frontier orbitals are needed in the context of many chemical compounds and reactions. Here, we review developments that led to our newcomputational toolbox which implements the quantum chemical density matrix renormalization group in a second-generation algorithm. We present an overview of the different components of this toolbox.

Chimia, 70, 244-251 (2016)
http://arxiv.org/abs/1512.09267
Library requirements for QCMaquis

- Entirely written in C++, hosted on Gitlab
- OpenMP parallelization available
- Ambient library ([http://ambientcxx.org](http://ambientcxx.org)) developed at ETH/CSCS for MPI parallelization (in progress)
- Boost
- ALPS library ([A](A)lgorithms and [L](Libraries) for [P](Physics) [S](Simulations), [http://alps.comp-phys.org](http://alps.comp-phys.org))
- Linear algebra libraries: dgemm, daxpy, SVD, …
Acknowledgment

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Motivation: Large-Scale Quantum Chemistry in terms of molecular size

- Understanding the spectroscopy and small-molecule activation (CO, CO$_2$, N$_2$, ...) by U-complexes
- Rationalizing the magnetic properties of f-element complexes


S. C. Bart et al., JACS, 130, 12356 (2008)
General remarks

- Relativity (spin-orbit coupling [SOC]) and electron correlation → to be treated on equal footing
- SOC in general not a perturbation for $f$-elements
- Large number of near-degenerate electronic shells require → multi-configurational methods
  → large active orbital spaces
- Wave function methods preferential (solution of the electronic Schrödinger equation

\[ H_{el} \Psi_{el}^{\{R_I\}} (\{r_i\}) = E_{el} (\{R_I\}) \Psi_{el}^{R_I} (\{r_i\}) \]
How to approximate $\Psi_{el}$?

- 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 as $n$ orbitals from $n$ one-electron basis functions:

$$\text{FC} = \text{SC} \epsilon$$

- From the $N$ orbitals with the lowest energy, the Hartree–Fock (HF) Slater determinant $\Phi_0$ is constructed.

- The other determinants (many-particle basis states) are obtained by subsequent substitution of orbitals in the HF Slater determinant $\Phi_0$:

$$\{\Phi_I\} \rightarrow \Phi^a_i, \Phi^b_j, \ldots \rightarrow \Phi^{ab}_{ij}, \Phi^{ac}_{ik}, \ldots \rightarrow \Phi^{abc}_{ijk}, \Phi^{abd}_{ijl}, \ldots$$
From traditional to new wave function parameterizations

- Instead of standard CI-type calculations by diagonalization/projection …

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

- … construct CI coefficients from correlations among orbitals

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

→ tensor construction of expansion coefficients: DMRG
QCMaquis
First 2nd generation quantum-chemical DMRG code

- MPS/MPO formalism
- Convergence acceleration techniques
- Works with 1-, 2-, 4-component Hamiltonians
- Parallelized: OMP/(MPI)
- Interfaces: Molcas, Dalton, Dirac, Bagel

QCMaquis
S. Keller et al., JCP, 143, 244118 (2015)
S. Keller and M. Reiher, JCP, 144, 134101 (2016)
www.reiher.ethz.ch/software/maquis.html

- Analytic gradients for DMRG
- Spin-orbit coupling/relativity
- DMRG + dynamical correlation
- DMRG + environment effects
- State-interaction: SOC, NACE, …
- DMRG-SCF: orbital optimization

**State-average:** Y. Ma, S. Knecht, S. Keller, R. Lindh, M. Reiher, in preparation

**State-specific:** Y. Ma, S. Knecht, M. Reiher, in preparation

**DMRG-srDFT**
E. Hedegård et al., JCP, 142, 224108 (2015)

**CASPT2:** S. Knecht, S. F. Keller, T. Shiozaki, M. Reiher, in progress

**NEVPT2:** S. Knecht, S. Keller, C. Angeli, M. Reiher, in progress

**2nd order:** Y. Ma, S. Knecht, S. Keller, M. Reiher, in preparation

**FDE-DMRG**
T. Dresselhaus et al., JCP, 142, 044111 (2015)

**DMRG:**
T. Dresselhaus et al., JCP, 142, 044111 (2015)
Properties of DMRG

DMRG
- Variational
- Size consistent
- (approximate) FCI for a CAS
- Polynomial scaling (~$L^4 m^3$)
- MPS wave function
- For large $m$ (number of renormalized states) invariant wrt orbital rotations
- Up to 100 active orbitals possible: CAS(x,100)

CASCI
- Variational
- Size consistent
- FCI for a CAS
- Exponential scaling
- Linearly parametrized wave function
- Invariant wrt orbital rotations
- Computational limit: CAS(18,18)
## Properties of DMRG

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### Related References

- G. K.-L. Chan, WIREs, 2, 907 (2012)
- S. Szalay et al., Int. J. Quant. Chem. 115, 1342 (2015)
Matrix product states (MPS) representation: Singular value decomposition of the FCI tensor

\[ M^{(m \times n)} = U^{(m \times m)} S^{(m \times n)} V^{(n \times n)^*} \]

- Matrix
- Matrix product
- Rank-3 tensor
- Physical index: \( \sigma_i/n_i \)
- Virtual index: \( a_{i-1}/a_i \)

FCI tensor representation

MPS representation
Matrix product states (MPS) representation: Singular value decomposition of the FCI tensor

FCI tensor representation

$$|\Psi_{\text{FCI}}\rangle = \sum_{\{n_k\}} C^{n_1 n_2 \ldots n_L} |n_1 n_2 \ldots n_L\rangle$$

Singular value decomposition

$$M^{(m \times n)} = U^{(m \times m)} S^{(m \times n)} V^{(n \times n)^*}$$

MPS representation

$$|\Psi_{\text{FCI}}\rangle = \sum_{\{n_k\}\{a_j\}} A^{n_1}_{1,a_1} A^{n_2}_{a_1,a_2} \ldots A^{n_{L-1}}_{a_{L-2},a_{L-1}} A^{n_L}_{a_{L-1},1} |n_1 n_2 \ldots n_L\rangle$$

→ optimization and reduction of dimensionality to of $A$ matrices
MPS Structure of Operators: MPOs

- Quantum chemical Hamiltonian in second quantization
  \[ \mathcal{H}_{\text{full}} = \sum_{ij \sigma} t_{ij} \hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma} + \frac{1}{2} \sum_{ijkl \sigma \sigma'} V_{ijkl} \hat{c}_{i\sigma}^\dagger \hat{c}_{k\sigma'}^\dagger \hat{c}_{l\sigma'} \hat{c}_{j\sigma} \]

- Consider occupation-number-vector basis states \( |\sigma\rangle \) and \( |\sigma'\rangle \)

- The coefficients \( \mathcal{W}_{\sigma\sigma'} \) of a general operator

  \[ \hat{\mathcal{W}} = \sum_{\sigma, \sigma'} w_{\sigma\sigma'} |\sigma\rangle \langle \sigma'| \]

  ... may be encoded in matrix-product form

  \[ w_{\sigma, \sigma'} = \sum_{b_1, \ldots, b_{L-1}} W_{1b_1}^{\sigma_1 \sigma_1'} \cdots W_{b_{L-1}b_L}^{\sigma_L \sigma_L'} \]

  ... combining both, the operator \( \hat{\mathcal{W}} \) reads

  \[ \hat{\mathcal{W}} = \sum_{\sigma, \sigma'} \sum_{b_1, \ldots, b_{L-1}} W_{1b_1}^{\sigma_1 \sigma_1'} \cdots W_{b_{L-1}b_L}^{\sigma_L \sigma_L'} |\sigma\rangle \langle \sigma'| \]
Simplify by contraction over the local site indices \( \sigma_l, \sigma'_l \)

\[
\hat{W}^l_{b_{l-1}b_l} = \sum_{\sigma_l, \sigma'_l} W^{\sigma_l \sigma'_l}_{b_{l-1}b_l} |\sigma_l\rangle \langle \sigma'_l|
\]

... which then yields

\[
\hat{W} = \sum_{b_1, \ldots, b_{L-1}} \hat{W}^1_{b_1} \cdots \hat{W}^l_{b_{l-1}b_l} \cdots \hat{W}^L_{b_{L-1}b_L}
\]

Motivation for this: Entries of the resulting \( \hat{W}^l_{b_{l-1}b_l} \) matrices are the elementary creation and annihilation operators acting on a single site (=orbital)! \( \hat{c}^\dagger = |\uparrow\downarrow\rangle \langle \downarrow\uparrow| + |\uparrow\rangle \langle 0| \rightarrow 4 \times 4 \) matrix

MPS concept has been transferred to operators (MPOs)

\( \rightarrow \) First 2\textsuperscript{nd} generation QC-DMRG:
Compact MPO construction

Quantum chemical Hamiltonian in second quantization

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

Represent Hamiltonian terms in a tree-like data structure by forking them from a trivial branch of identity operators. In- and outgoing branches on site \(i\) translate into tensor indices \(b_{i-1}\) and \(b_i\).

Uncompressed MPO network

Compressed MPO network

L^5 scaling

L^4 scaling

MPS optimization: DMRG

- Search for $|\Psi\rangle$ which minimizes
  \[ E = \frac{\langle \Psi | \mathcal{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \]

- Introduce Lagrangian multiplier $\lambda$ and solve
  \[ \mathcal{L} = \langle \Psi | \mathcal{H} | \Psi \rangle - \lambda \langle \Psi | \Psi \rangle \]

- by optimizing the entries of $A_{a_{l-1},a_{l+1}}^{n_l,n_{l+1}}$ (two sites combined) at a time while keeping all others fixed
MPS optimization: DMRG

- To minimize $\mathcal{L}$ we take

$$\frac{\partial}{\partial A_{a_{l-1},a_{l+1}}^{n_l,n_{l+1}}}(\langle \Psi | H | \Psi \rangle - \lambda \langle \Psi | \Psi \rangle) = 0$$

- Find lowest EV+ EVC of the effective $H$ (dimension: 16 $m^2$)

$$\sum \sum \sum L_{b_{l-1}}^{a_{l-1},a_{l-1}'} W_{b_{l-1}}^{n_l,n_{l+1}} R_{b_{l+1}}^{a_{l+1},a_{l+1}'} A_{a_{l-1},a_{l+1}}^{n_l,n_{l+1}} \Psi_{a_{l-1},a_{l-1}'} A_{a_{l-1},a_{l+1}'}^{n_l,n_{l+1}} \Psi_{a_{l+1},a_{l+1}'} = 0$$

which can be written as

$$H \nu - \lambda N \nu = 0,$$
MPS optimization: DMRG

- Perform SVD of \( \nu \) reshaped into
  \[ A_{n_l, n_{l+1}}^{a_{l-1}, a_{l+1}} = U S V^+ \]
- Truncate sum of singular values to the largest \( m \) values (\( \leftrightarrow \) eigenvalues of reduced density matrix)
- Reshape \( U \) into \( A_{n_l}^{a_{l-1}, a_l} \)
- Multiply \( S \) with \( V^+ \) and reshape into \( A_{n_l+1}^{a_{l+1}, a_{l+1}} \)
- Move on to sites \( l+1 \) and \( l+2 \) until end of lattice is reached; then inverse direction
MPS optimization: DMRG - summary

S. Keller and M. Reiher, Chimia, 68, 200-203 (2014)

- DMRG algorithm: protocol for the iterative improvement of the A matrices
- Scaling determined by the number of renormalized basis states $m$: current limits around $m=10\,000$
- Orbital ordering is crucial but can be optimized
- Sum of discarded singular values can be used as a quality measure and/or for extrapolation of energies
- Start guess for environment is important, recipes:
  
  Y. Ma, S. Keller, C. Stein, S. Knecht, R. Lindh, M. Reiher, in preparation
QC-DMRG at work..

Going beyond DMRG(-SCF): dynamical electron correlation
DMRG(-SCF) + dynamical correlation

- DMRG(-SCF) is an efficient approach to take into account static correlation effects
- Dynamical correlation is missing to a large extent
- Requires excitations from the inactive/active to the active/secondary orbital space
Going beyond DMRG-SCF: dynamical electron correlation

- DMRG can in principle be combined with any post-HF approach ("diagonalize-the-perturb" ansatz):
  - (Internally-contracted) multi-reference CI
  - Multi-reference CC
  - Multi-reference perturbation theory to 2nd order (MRPT2): CASPT2, NEVPT2, …
  - CASSCF/CASPT2 is one of the most successful and versatile approaches in quantum chemistry (landmark CASPT2 paper has more than 1200 citations!)

- Conceptually different approach: short-range DFT-long-range DMRG

Dynamical correlation through MRPT2: CASPT2 or NEVPT2?

**CASPT2**
- $H^{(0)}$: Fock-type zeroth-order Hamiltonian
- *(Nearly)* Size-extensive
- Multi-state formulation possible
- Prone to intruder states
- Requires 3-particle (and partial 4-particle) reduced density matrix within the active orbital space of size $L$ ($\sim L^{2n}$ elements with $n=3,4$)

**NEVPT2**
- $H^{(0)}$: Dyall Hamiltonian (full $H^{\text{CAS-CI}}$ for active orbitals, Fock-type for core/secondary orbitals)
- Size-extensive
- No intruder-state problem
- Multi-state formulation possible
- Requires 4-particle reduced density matrix within the active orbital space of size $L$ ($\sim L^{2n}$ elements with $n=4$)
Higher-order n-particle reduced density matrices

- 3-particle (transition) and 4-particle reduced density matrices (RDMs) need to be calculated accurately
- Compressed MPS wave function for RDM calculation

- Cumulant approximation of higher–order n-RDMs → loss of N-representability of the n-RDM (possible)!

Outlook: Towards Large-Scale Quantum Chemistry in an HPC sense

- CAAR::DIRAC project (OLCF):
  - Optimized MPI implementation of QC-DMRG algorithm based on the Ambient library ([http://ambientcxx.org](http://ambientcxx.org)) developed at ETH/CSCS
  - GPU-accelerated calculation of higher-order n-particle reduced density matrix elements (for n=4, ca. $L^8$ elements are needed)

$$
\langle \Psi | C_i^\dagger C_j^\dagger \ldots C_m^\dagger C_n^\dagger \ldots | \Phi \rangle
$$

→ Requires optimized re-usage of pre-contracted matrix-matrix products in order to minimize data exchange between CPU and GPU
Thank you for your kind attention