Efficiency and accuracy of the Density Matrix Renormalization Group Method for Multiconfigurational systems

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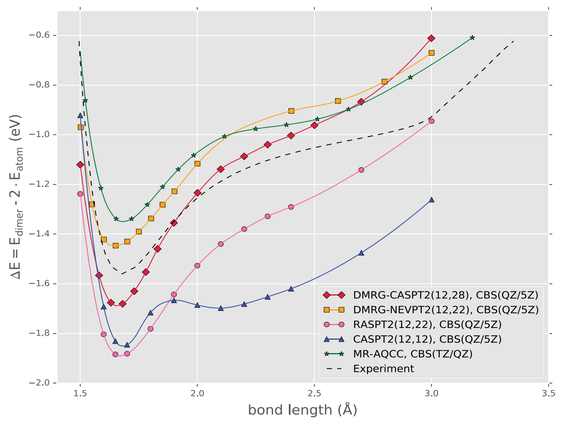
Limitations of CAS

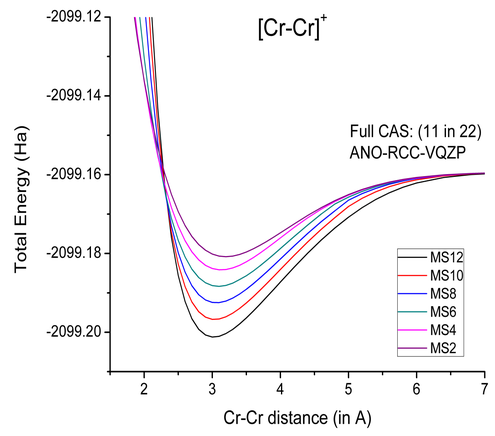
Chemical species that display multiconfigurational character are some of the most difficult to treat theoretically, and different methods have over the years been devised to address this issue. One of the most successful approaches includes all possible configurations within a complete active space (CAS). However, the computational effort increases dramatically with the size of active space, which is a large hindrance for the use of CAS methods, which is in practice is limited by 16 active orbitals.

Examples of state-of-the-art calculations on CASSCF/ RASSCF level

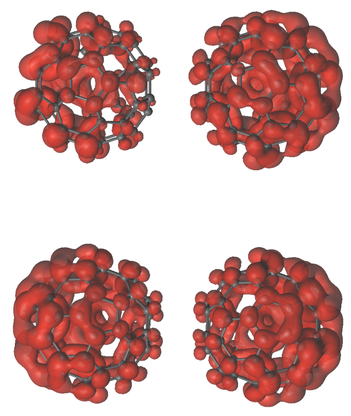
Cr_2 PES



Cr_2^+



$(C60)_2^{-n}$

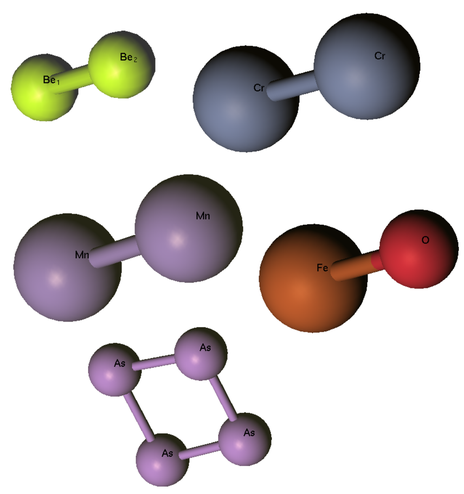


DMRG

The Density Matrix Renormalization Group (DMRG) method is a very efficient approximation to a CAS, making it possible to reach larger active spaces. DMRG is still under development, and is defined in different formalisms in a number of different programs. In all formalisms, both the efficiency and accuracy of the approximation relies on a few technical parameters (e.g. the number of renormalized states). We have here benchmarked the convergence of DMRG-SCF ground-state energies with respect to these technical parameters for three different implementations of DMRG (QCMaquis[1], cheMPS2[2] and Block[3]), integrated into the MOLCAS [4] code.

Test suite for DMRG

* Set of molecules:
* Small-medium-large active space
* Different flavours of DMRG
* Dependence on *m*
* Energy accuracy
* Convergence
* Faulty minima
* Speed
* Other limitations



CI ansatz:

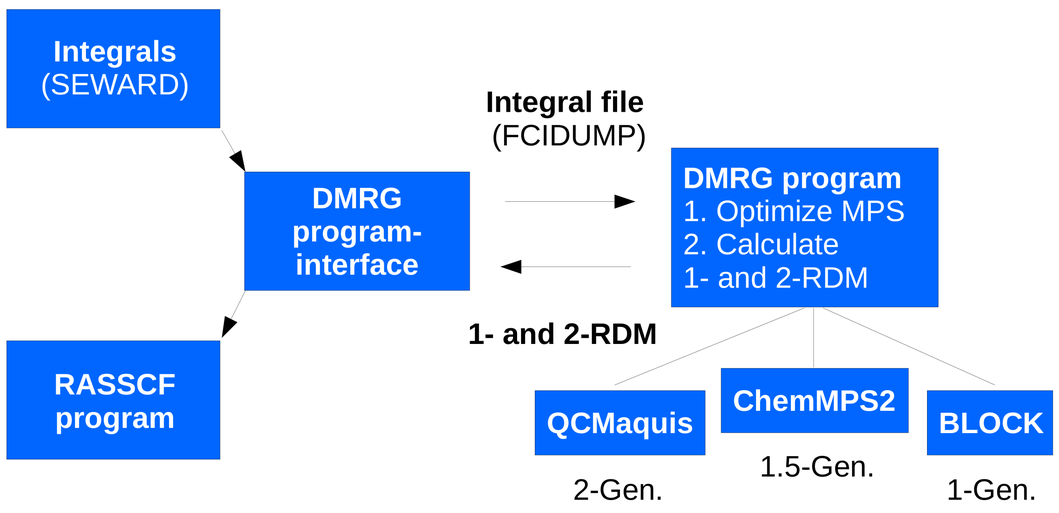
$$|\Psi\rangle = \sum_{\sigma} c_{\sigma}|\sigma\rangle = \sum_{\sigma_1 \cdots \sigma_L} c_{\sigma_1 \cdots \sigma_L}|\sigma_1 \cdots \sigma_L\rangle$$

DMRG ansatz:

$$|\Psi\rangle = \sum_{\sigma_1 \cdots \sigma_L} \sum_{a_1 \cdots a_{L-1}} M^{\sigma_1}_{1 a_1} M^{\sigma_2}_{a_1 a_2} \cdots M^{\sigma_L}_{a_{L-1} 1} =$$

$$= \sum_{\sigma} M^{\sigma_1} M^{\sigma_2} \cdots M^{\sigma_L}|\sigma\rangle$$

Implementations of DMRG codes in MOLCAS



Notes on installation:

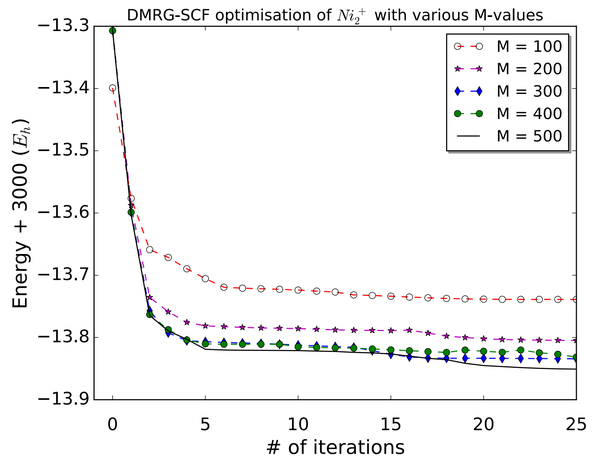
- Depend on math libraries
- Molcas 8.2+
- QCMaquis will be open soon
- Non trivial installation
- Not easy to install in parallel

Timing as a function of *m*: Ni_2^+, basis set:86, active space 19/28

M	# iter	Time per iter, sec	Total time
100	39	923	10h 36’
200	94	1378	1d 12h
300	54	2133	1d 8h
400	87	2234	2d 6h
500	40	3240	1d 12h

Results

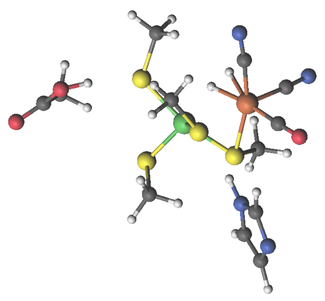
* For small molecules - DMRG (all types) gives the same result as CASSCF.
* Cr_2 is *really* bad case - DMRG converges to a wrong minimum
* Strong dependence on *m* value
* Perturbation theory is still needed
* Work is still in progress....



Real life applications:

DMRG-CASPT2 calculations for [NiFe]-hydrogenase

22 electrons in 22 orbitals *m*=1000 [5]



References:

[1] S. Keller, M. Dolfi, M. Troyer, M. Reiher, *J. Chem. Phys.*, 143, 244118 (2015)
[2] S. Wouters, W. Poelmans, P. W. Ayers, D. Van Neck, *Computer Phys. Comm.*, 185, 1501 (2014)
[3] K.-L. Chan, M. Head-Gordon, *J. Chem. Phys.*, 116, 4462 (2002)
[4] http://www.molcas.org
[5] G. Dong, Q.M. Phung, S.D. Hallaert, K. Pierloot, U. Ryde, *PCCP*, 19(16), 10590 (2017)