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CHEMPS2: Improved DMRG-SCF routine and correlation functions

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ABSTRACT

CHEMPS2, our spin-adapted implementation of the density matrix renormalization group (DMRG) for ab initio quantum chemistry (Wouters et al., 2014), has several new features. A speed-up of the augmented Hessian Newton–Raphson DMRG self-consistent field (DMRG-SCF) routine is achieved with the direct inversion of the iterative subspace (DIIS). For extended molecules, the active space orbitals can be localized by maximizing the Edmiston–Ruedenberg cost function. These localized orbitals can be ordered according to the topology of the molecule by approximately minimizing the bandwidth of the exchange matrix with the Fiedler vector. The electronic structure can be analyzed by means of the two-orbital mutual information, spin, spin-flip, density, and singlet diradical correlation functions.

New version program summary

Manuscript Title: CHEMPS2: improved DMRG-SCF routine and correlation functions

Authors: Sebastian Wouters, Ward Poelmans, Stijn De Baerdemacker, Paul W. Ayers and Dimitri Van Neck

Program Title: CHEMPS2

Catalogue identifier: AESE_v2_0

Program Summary URL: http://cpc.cs.qub.ac.uk/summaries/AESE_v2_0.html

Program obtainable from: CPC Program Library, Queen's University, Belfast, N. Ireland

Licensing provisions: GNU General Public License, version 2

No. of lines in distributed program, including test data etc.: 221647

No. of bytes in distributed program, including test data etc.: 3028042

Distribution format: tar.gz

Programming language: C++

Computer: x86-64

Operating system: Linux

RAM: 10 MB–512 GB

Number of processors used: 1–48 (shared memory multiprocessing with OpenMP)

Keywords: SU(2) spin-adapted DMRG, ab initio quantum chemistry, DIIS, Edmiston–Ruedenberg orbital localization, Fiedler vector, two-orbital mutual information

Classification: 16.1 Molecular Physics and Physical Chemistry: Structure and Properties

External routines/libraries: Basic Linear Algebra Subprograms (BLAS), Linear Algebra Package (LAPACK), GNU Scientific Library (GSL), Hierarchical Data Format Release 5 (HDF5), and Open Multi-Processing (OpenMP)

Catalogue identifier of previous version: AESE_v1_0

Journal reference of previous version: Computer Physics Communications 185 (6), 1501–1514 (2014)

Does the new version supersede the previous version?: Yes

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Nature of problem:

The many-body Hilbert space grows exponentially with the number of single-particle states. Exact diagonalization solvers can therefore only handle small active spaces, of up to 16 electrons in 16 orbitals. Interesting active spaces are often significantly larger.

Solution method:

The density matrix renormalization group allows to extend the size of active spaces, for which numerically exact solutions can be found, significantly. In addition, it provides a rigorous variational upper bound to energies, as it has an underlying wavefunction ansatz, the matrix product state.

Reasons for the new version:

The DMRG routine is 20% faster in the new version. Several features were added to the augmented Hessian Newton–Raphson DMRG-SCF routine. In addition, five correlation functions were implemented to study the electronic structure in a comprehensible way. A python interface to the library is provided.

Summary of revisions:

1. The DMRG routine is 20% faster compared to the previous version [1]. The active space of N_2 in the cc-pVDZ basis consists of 14 electrons in 28 orbitals. We have calculated the $X^1\Sigma_g^+$ ground state near equilibrium. Canonical orbitals are used (D_{2h} symmetry), grouped in irrep blocks, and sorted to place bonding and antibonding blocks adjacent [1]. The average wall time per sweep on a dual Intel Xeon Sandy Bridge E5-2670 (total of 16 cores at 2.6 GHz) is shown in Table 1 for the new and previous program versions, for several values of the reduced virtual dimension $D_{SU(2)}$.

Table 1
The average wall time per sweep on a dual Intel Xeon Sandy Bridge E5-2670 (total of 16 cores at 2.6 GHz) for the $X^1\Sigma_g^+$ ground state of N_2 near equilibrium in the cc-pVDZ basis. Canonical orbitals are used, grouped in irrep blocks, and sorted to place bonding and antibonding blocks adjacent. The new version is 20% faster than the previous version.

$D_{SU(2)}$	t_{new} (s)	$t_{previous}$ (s)	$t_{new}/t_{previous}$
1000	117	152	0.77
1500	279	356	0.78
2000	529	668	0.79
3000	1339	1647	0.81

2. Several features have been added to the augmented Hessian Newton–Raphson DMRG-SCF routine. An instance of the `DMRGSCFoptions` class has to be passed to `CASSCF::doCASSCFnewtonraphson`, which allows to overwrite the default options:
   - `DMRGSCFoptions::setDoDIIS(bool value)`: If value is true, a speed-up of the augmented Hessian Newton–Raphson DMRG-SCF routine is achieved with the direct inversion of the iterative subspace (DIIS) [2]. Examples can be found in `test6`, `test8`, and `test9`.
   - `DMRGSCFoptions::setWhichActiveSpace(int value)`: If value is 0, no rotations are performed in addition to the DMRG-SCF occupied-active, active-virtual, and occupied-virtual rotations. If value is 1, natural orbitals are used in the active space, sorted within each irrep according to their occupation number. If value is 2, localized and ordered orbitals are used in the active space. The localization is performed by maximizing the Edmiston–Ruedenberg cost function [3]. Thereto we have implemented a Newton–Raphson maximization algorithm, with exact Hessian of the cost function. The ordering is determined by approximately minimizing the bandwidth of the exchange matrix with the Fiedler vector [4]. Examples can be found in `test6`, `test8` and `test9`.
   - `DMRGSCFoptions::setStateAveraging(bool value)`: When an excited state is targeted with DMRG-SCF and value is true, the DMRG-SCF gradient and Hessian are calculated based on an equally weighted average of the 2-RDMs of the targeted state and all lower-lying states. An example can be found in `test6`.
3. The electronic structure can be analyzed by means of the two-orbital mutual information [5,6]

$$I(i,j) = \frac{1}{2}\left(S_1(i) + S_1(j) - S_2(i,j)\right)\left(1 - \delta_{ij}\right) \geq 0, \tag{1}$$

   where $S_1(i)$ is the single-orbital entropy of orbital i and $S_2(i,j)$ the two-orbital entropy of orbitals i and j. Additional information is contained in the following correlation functions:
   - The spin correlation function $C_{spin}(i,j) = 4\langle \hat{S}_i^z \hat{S}_j^z \rangle - 4\langle \hat{S}_i^z \rangle \langle \hat{S}_j^z \rangle$.
   - The spin-flip correlation function $C_{spinflip}(i,j) = \langle \hat{S}_i^+ \hat{S}_j^- \rangle + \langle \hat{S}_i^- \hat{S}_j^+ \rangle$
   - The density correlation function $C_{dens}(i,j) = \langle \hat{n}_i \hat{n}_j \rangle - \langle \hat{n}_i \rangle \langle \hat{n}_j \rangle$
   - The singlet diradical correlation function [7] $C_{dirad}(i,j) = \langle \hat{d}_{i\uparrow} \hat{d}_{j\downarrow} \rangle + \langle \hat{d}_{i\downarrow} \hat{d}_{j\uparrow} \rangle - \langle \hat{d}_{i\uparrow} \rangle \langle \hat{d}_{j\downarrow} \rangle - \langle \hat{d}_{i\downarrow} \rangle \langle \hat{d}_{j\uparrow} \rangle$, where $\hat{d}_{i\sigma} = \hat{n}_{i\sigma}(1 - \hat{n}_{i\,-\sigma})$

   After a DMRG calculation, these five correlation functions can be printed by calling `DMRG::calc2DMandCorrelations()` and subsequently `DMRG::getCorrelations()->Print()`. An example can be found in `test4`. During DMRG-SCF calculations, they can be printed by setting `DMRGSCFoptions::setDumpCorrelations(true)`. An example can be found in `test8`.

Restrictions:
Our implementation of the density matrix renormalization group is spin-adapted. This means that targeted eigenstates in the active space are exact eigenstates of the total electronic spin operator. Hamiltonians which break this symmetry cannot be handled by our code.

Unusual features:
The nature of the matrix product state ansatz allows for exact spin coupling. In CheMPS2, the total electronic spin is imposed (not just the spin projection), in addition to the particle-number and abelian point-group symmetries.

Additional comments:
A more elaborate overview of the new features can be found in the `CASSCF`, `Correlations`, `DMRGSCFunitary`, and `EdmistonRuedenberg` class references in the doxygen documentation, either generated by the instructions in `README.md` or online [8]. Updated versions of CheMPS2 will be provided at its public git repository [9].

Running time:
Examples are given in Table 1. It should be mentioned that the running time depends strongly on the size of the targeted active space, the density of states, the orbital choice and ordering, and the reduced virtual dimension $D_{SU(2)}$.

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Acknowledgments

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