Quantum Package 2.0

An Open-Source Determinant-Driven Suite of Programs

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Configuration Interaction

Full Configuration Interaction (FCI)

- Exact solution of $\hat{H}\Psi = E\Psi$ in a complete basis of Slater determinants
- The determinant basis is derived from the one-electron basis set
- Only approximation : one-electron basis-set incompleteness
- Intractable : $\mathcal{O}(N!)$ scaling
- All the post-Hartree-Fock methods are approximations of the FCI within the same basis set

Configuration Interaction

Configuration Interaction (CI)

- CISD, CISDTQ, etc : Truncate the determinant space based on the degree of excitation with respect to the Hartree-Fock determinant
- CAS-SCF : FCI within a restricted set of MOs, improved with orbital optimization
- MR-CI : Truncate the determinant space based on the degree of excitation with respect to the CAS

Selected Configuration Interaction

THE JOURNAL OF CHEMICAL PHYSICS **147**, 184111 (2017)

Pushing configuration-interaction to the limit: Towards massively parallel MCSCF calculations

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A new large-scale parallel multiconfigurational self-consistent field (MCSCF) implementation in the open-source NWChem computational chemistry code is presented. The generalized active space approach is used to partition large configuration interaction (CI) vectors and generate a sufficient number of batches that can be distributed to the available cores. Massively parallel CI calculations with large active spaces can be performed. The new parallel MCSCF implementation is tested for the chromium trimer and for an active space of 20 electrons in 20 orbitals, which can now routinely be performed. Unprecedented CI calculations with an active space of 22 electrons in 22 orbitals for the pentacene systems were performed and a single CI iteration calculation with an active space of 24 electrons in 24 orbitals for the chromium tetramer was possible. The chromium tetramer corresponds to a CI expansion of one trillion Slater determinants (914 058 513 424) and is the largest conventional CI calculation attempted up to date. *Published by AIP Publishing.*
https://doi.org/10.1063/1.4989858

Full Configuration Interaction

FCI has seen a breakthrough in 2007

- DMRG[1]
- FCI-QMC : Stochastic solution of FCI equations.[2]
- First row diatomics cc-pV5Z.[3]
- Selected Configuration Interaction
- Scaling is still $\mathcal{O}(N!)$, but pre-factor is killed.
- Much larger active spaces are possible today

[1] G. K.-L. Chan *et al* , arXiv:0711.1398 (2007)
[2] G.H. Booth *et al* , J. of Chem. Phys. 131, 054106 (2009).
[3] D. Cleland *et al* , J. Chem. Theory Comput. 8, 4138 (2012)

Selected Configuration Interaction

OpenMolcas: From Source Code to Insight

Preprint submitted on 06.06.2019, 09:41 and posted on 06.06.2019, 18:08 by Ignacio Fdez. Galván, Morgane Vacher, Ali Alavi, Celestino Angeli, Jochen Autschbach, Jie J. Bao, Sergey I. Bokarev, Nikolay A. Bogdanov, Rebecca K. Carlson, Liviu F. Chibotaru, Joel Creutzberg, Nike Dattani, Mickaël G. Delcey, Sijia Dong, Andreas Dreuw, Leon Freitag, Luis Manuel Frutos, Laura Gagliardi, Frédéric Gendron, Angelo Giussani, Leticia Gonzalez, Gilbert Grell, Meiyuan Guo, Chad E. Hoyer, Marcus Johansson, Sebastian Keller, Stefan knecht, Goran Kovačević, Erik Källman, Giovanni Li Manni, Marcus Lundberg, Yingjin Ma, Sebastian Mai, João Pedro Malhado, Per Åke Malmqvist, Philipp Marquetand, Stefanie A. Mewes, Jesper Norell, Massimo Olivucci, Markus Oppel, Quan Manh Phung, Kristine Pierloot, Felix Plasser, Markus Reiher, Andrew M. Sand, Igor Schapiro, Prachi Sharma, Christopher J. Stein, Lasse Kragh Sørensen, Donald G. Truhlar, Mihkel Ugandi, Liviu Ungur, Alessio Valentini, Steven Vancoillie, Valera Veryazov, Oskar Weser, Per-Olof Widmark, Sebastian Wouters, J. Patrick Zobel, Roland Lindh

In this article we describe the OpenMolcas environment and invite the computational chemistry community to collaborate. The open-source project already includes a large number of new developments realized during the transition from the commercial MOLCAS product to the open-source platform. The paper initially describes the technical details of the new software development platform. This is followed by brief presentations of many new methods, implementations, and features of the OpenMolcas program suite. These developments include novel wave function methods such as stochastic complete active space self-consistent field, density matrix renormalization group (DMRG) methods, and hybrid multiconfigurational wave function and density functional theory models. Some of these implementations include an array of additional options and functionalities. The paper proceeds and describes developments related to explorations of potential energy surfaces. Here we present methods for the optimization of conical intersections, the simulation of adiabatic and nonadiabatic molecular dynamics and interfaces to tools for semiclassical and quantum mechanical nuclear dynamics.

CATEGORIES

- Computational Chemistry and Modeling
- Theory - Computational
- Chemoinformatics - Computational Chemistry
- Spectroscopy (Physical Chem.)
- Physical and Chemical Properties

KEYWORD(S)

Multiconfigurational methods · Molecular dynamics · Wave function analysis · Spectroscopy · Basis sets

Selected Configuration Interaction

JCTC Journal of Chemical Theory and Computation

Article

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Cheap and Near Exact CASSCF with Large Active Spaces

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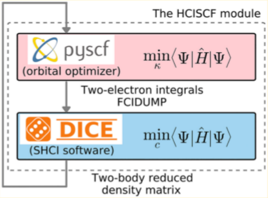

ABSTRACT: We use the recently developed Heat-bath Configuration Interaction (HCI) algorithm as an efficient active space solver to perform multiconfiguration self-consistent field calculations (HCISCF) with large active spaces. We give a detailed derivation of the theory and show that difficulties associated with non-variationality of the HCI procedure can be overcome by making use of the Lagrangian formulation to calculate the HCI relaxed two-body reduced density matrix. HCISCF is then used to study the electronic structure of butadiene, pentacene, and Fe−porphyrin. One of the most striking results of our work is that the converged active space orbitals obtained from HCISCF are relatively insensitive to the accuracy of the HCI calculation. This allows us to obtain nearly converged CASSCF energies with an estimated error of less than 1 mHa using the orbitals obtained from the HCISCF procedure in which the integral transformation is the dominant cost. For example, an HCISCF calculation on the Fe−porphyrin model complex with an active space of (44e, 44o) took only 412 s per iteration on a single node containing 28 cores, out of which 185 s was spent in the HCI calculation and the remaining 227 s was used mainly for integral transformation. Finally, we also show that active space orbitals can be optimized using HCISCF to substantially speed up the convergence of the HCI energy to the Full CI limit because HCI is not invariant to unitary transformations within the active space.

Selected Configuration Interaction (sCI)

- Select determinants on-the-fly
- with perturbation theory (CIPSI[4]) or based only on the matrix elements of $\hat{H}$ (SHCI[5])
- Target spaces : Full-CI, MR-CISD, large CAS
- Use PT2 to estimate the missing part

[4] B. Huron *et al* , J. Chem. Phys. 58, 5745 (1973).
[5] A.A. Holmes *et al* , J. Chem. Phys. 147, 164111 (2017)

Algorithm

CIPSI Algorithm

Start with $\mathcal{D}_0 = \{|\mathrm{HF}\rangle\}$ and $|\Psi_0\rangle = |\mathrm{HF}\rangle$.

Algorithm

CIPSI Algorithm

Start with $\mathcal{D}_0 = \{|\mathrm{HF}\rangle\}$ and $|\Psi_0\rangle = |\mathrm{HF}\rangle$.

1. $\forall\, |i\rangle \in \{\, \hat{T}_{\mathrm{SD}} |\Psi_n\rangle\} \setminus \{\mathcal{D}_n\}$, compute $e_i = \frac{\langle i|\mathcal{H}|\Psi_n\rangle^2}{E(\Psi_n) - \langle i|\mathcal{H}|i\rangle}$

Algorithm

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2. if $|e_i| > \epsilon_n$, select $|i\rangle$

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2. if $|e_i| > \epsilon_n$, select $|i\rangle$
3. Estimated energy : $E(\Psi_n) + E_{\mathrm{PT2}}(\Psi_n) = E(\Psi_n) + \sum_i e_i$

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4. $\mathcal{D}_{n+1} = \mathcal{D}_n \cup \{\cup_{i(\mathrm{selected})}|i\rangle\}$

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5. Minimize $E(\Psi_{n+1})$ (Davidson),
   $\Psi_{n+1} = \Psi_n + \sum_{i(\mathrm{selected})} c_i|i\rangle$

CIPSI Algorithm

Start with $\mathcal{D}_0 = \{|\mathrm{HF}\rangle\}$ and $|\Psi_0\rangle = |\mathrm{HF}\rangle$.

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6. Choose $\epsilon_{n+1} < \epsilon_n$

Algorithm

CIPSI Algorithm

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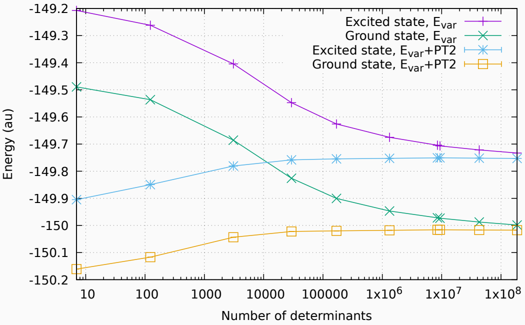
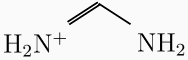
   $\Psi_{n+1} = \Psi_n + \sum_{i(\mathrm{selected})} c_i|i\rangle$
6. Choose $\epsilon_{n+1} < \epsilon_n$
7. Iterate

Selected CI



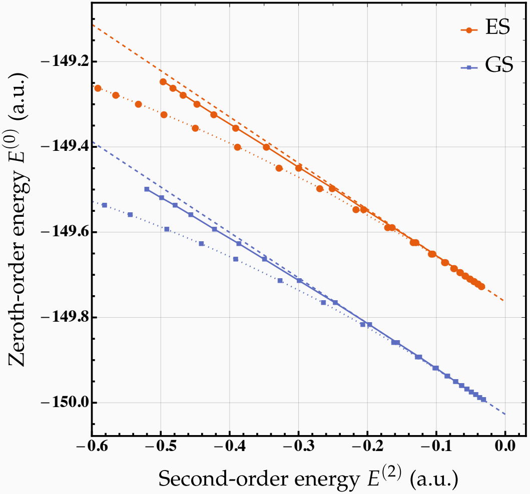


aug-cc-pVDZ

- When $N_{\text{det}} = N_{\text{FCI}}$, $E_{\text{PT2}} = 0$, CI is solved *exactly*.
- Every CI problem can be solved by iterative perturbative selection

Selected CI

- exFCI : Extrapolate $E = f(E_{\mathrm{PT2}})$ at $E_{\mathrm{PT2}} = 0$, estimates the complete CI solution.



FCI wave function can't be computed or even stored:

$$N_{\mathrm{FCI}} = 2.5 \times 10^{25} = 42.4 \text{ moles}$$

About Quantum Package

https://quantumpackage.github.io/qp2

- Open-source programming environment for quantum chemistry
- Uses determinant-driven algorithms : can solve CI problems with arbitrary CI spaces
- Efficient CIPSI and stochastic PT2 computational kernels
- Designed first for for programmers, but easy to use
- Users are encouraged to develop their own plugins, which they can redistribute autonomously

About Quantum Package

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Article
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Quantum Package 2.0: An Open-Source Determinant-Driven Suite of Programs

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ABSTRACT: Quantum chemistry is a discipline which relies heavily on very expensive numerical computations. The scaling of correlated wave function methods lies, in their standard implementation, between $O(N^5)$ and $O(e^N)$, where N is proportional to the system size. Therefore, performing accurate calculations on chemically meaningful systems requires (i) approximations that can lower the computational scaling and (ii) efficient implementations that take advantage

About Quantum Package

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About Quantum Package

Quantum Package @LCPQ

- post-Hartree-Fock methods (MR-CCSD, MR-CISD, DDCI, . . .)
- Excited states
- Stochastic perturbation theory
- Coupling with Quantum Monte Carlo (post-FCI methods)
- Efficient algorithms and implementation

About Quantum Package

Quantum Package @LCT

- Development of DFT functionals
- sCI combined with range-separated DFT
- Density-Based Basis-Set Correction
- Implementation of selected CAS-SCF

About Quantum Package

Quantum Package @Argonne

- Development of sCI for perdiodic systems
- Interface with QMCPack
- Compilation scripts and tools

Some applications

CI-related applications

- Shifted-B_k : Dress the Hamiltonian with the PT2 and iterate[6]
- MR-CCSD : Express the MR-CCSD problem as a MR-CISD with a dressed Hamiltonian[7]
- Orthogonal Valence Bond Hamiltonians incorporating dynamical correlation effects [8]
- Benchmarks for Excited states[9] [10]
- FCI for molecules with Slater-type orbitals[11]

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[6] Y. Garniron, *et al* (2018), J. Chem. Phys., 149:6(064103)
[7] Y. Garniron *et al* (2017), J. Chem. Phys., 146:15(154107).
[8] E. Giner *et al* (2017), Comput. Theor. Chem., 1116(134-140)
[9] P.-F. Loos *et al* (2018), J. Chem. Theory Comput., 14, 8, 4360-4379
[10] P.-F. Loos *et al* (2019), J. Chem. Theory and Comput., 15, 3, 1939-1956
[11] M. Caffarel, *work in progress*

Some applications

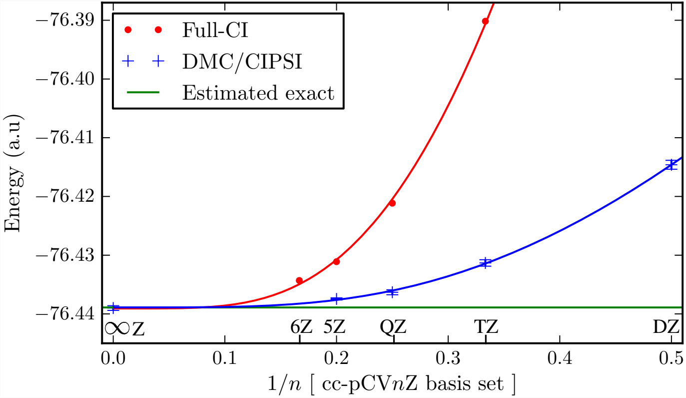
DFT-related applications

- A Density-Based Basis-Set Correction for Wave Function Theory[12]
- Range-separated multideterminant DFT [13]
- Range-separated multideterminant DFT with QMC[14]

[12] P.-F. Loos *et al* , (2019), J. Phys. Chem. Lett., 10:11(2931–2937)
[13] Ferté *et al* , (2019), J. Chem. Phys. 150, 084103.
[14] A. Benali, A. Scemama, P.-F. Loos, E. Giner, *work in progress*

Post-FCI Quantum Monte Carlo

Use large CIPSI expansions as trial wave functions.



Water

[14] M. Caffarel, T. Applencourt, E. Giner and A. Scemama (2016), J. Chem. Phys., 144:15(151103)

Some applications

QMC-related applications

- Post-FCI Quantum Monte Carlo[15]
- Excited states[16]
- Geometry optimization[17]
- Geometry optimization for excited states[18]
- Thermo. limit of Diamond with perdiodic CIPSI/QMC.[19]

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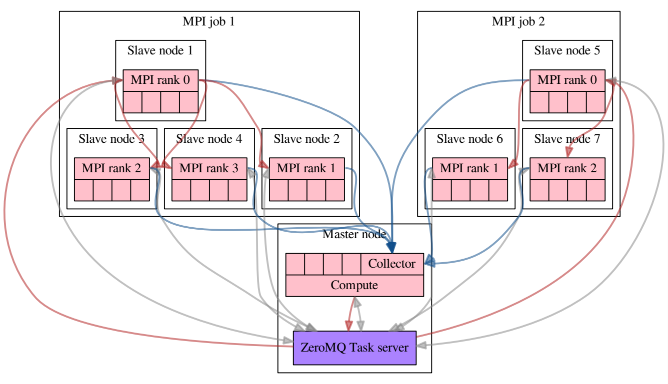
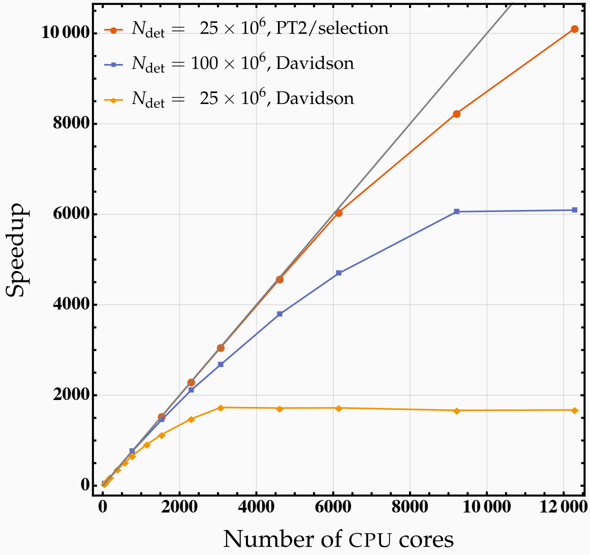
[15] M. Caffarel *et al* (2016) ACS Pub., Recent Progress in QMC, 1234, ch2, 46.
[16] A. Scemama *et al* (2018), J. Chem. Phys., 149(034108)
[17] M. Dash *et al* (2018), J. Chem. Theor. Comput., 14:8(4176–4182)
[18] M. Dash *et al* (2019) arXiv:1905.06737
[19] K. Gasperich, T. Applencourt, Y. Luo, L. Shulenburger, P. Kent, J. Krogel, K. Jordan, P.-F. Loos, A. Scemama, M. Caffarel, and A. Benali, *work in progress*

Parallelism



Ongoing project : one calculation delocalized in CALMIP (Occitanie) and CRIANN (Normandie)

Parallelism



Benchmark made on Irene (TGCC/GENCI)

Conclusion

- Web site: `https://quantumpackage.github.io/qp2/`
- Video tutorials
- Try in the browser
- Source code: `https://github.com/QuantumPackage/qp2`
- Documentation:
  `https://quantum-package.readthedocs.io`