

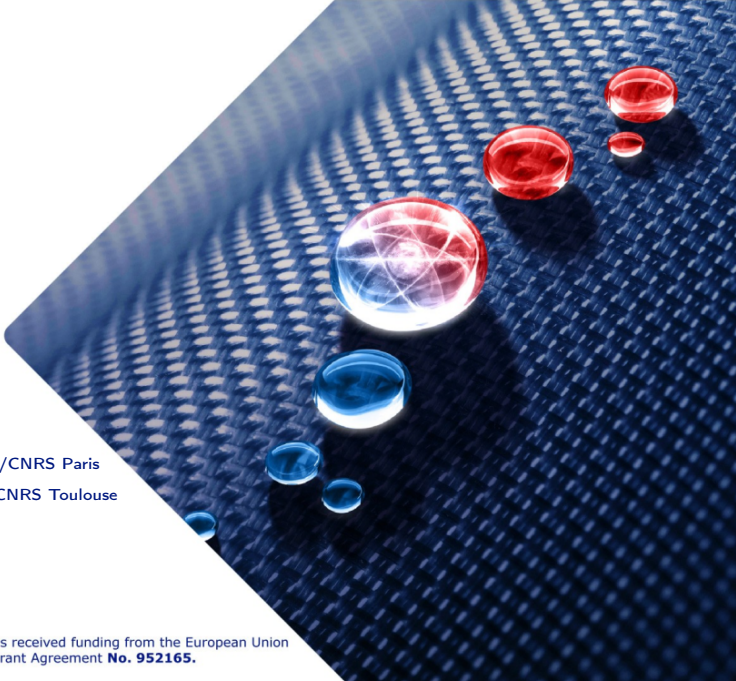
Quantum Package

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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

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>

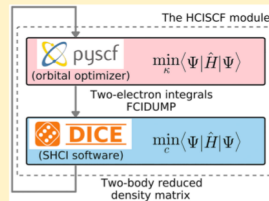
Cheap and Near Exact CASSCF with Large Active Spaces

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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.

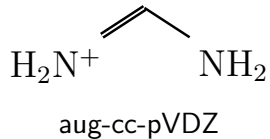
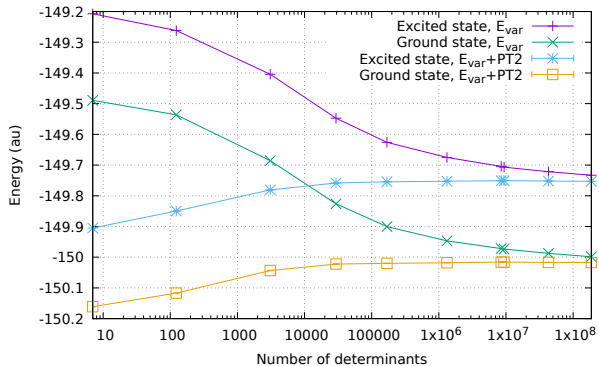


CIPSI Algorithm¹

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

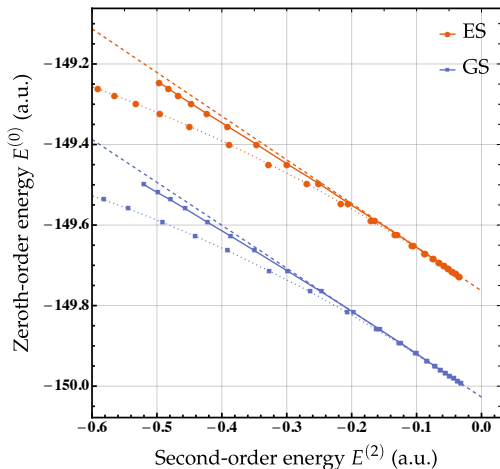
- 1 $\forall |i\rangle \in \{\hat{T}_{\text{SD}}|\Psi_n\rangle\} \setminus \{\mathcal{D}_n\}$, compute $e_i = \frac{\langle i|\mathcal{H}|\Psi_n\rangle^2}{E(\Psi_n) - \langle i|\mathcal{H}|i\rangle}$
- 2 if $|e_i| > \epsilon_n$, select $|i\rangle$
- 3 Estimated energy : $E(\Psi_n) + E_{\text{PT2}}(\Psi_n) = E(\Psi_n) + \sum_i e_i$
- 4 $\mathcal{D}_{n+1} = \mathcal{D}_n \cup \{\cup_{i(\text{selected})} |i\rangle\}$
- 5 Minimize $E(\Psi_{n+1})$ (Davidson),
 $\Psi_{n+1} = \Psi_n + \sum_{i(\text{selected})} c_i |i\rangle$
- 6 Choose $\epsilon_{n+1} < \epsilon_n$
- 7 Iterate

¹B. Huron, J.P. Malrieu, and P. Rancurel, *J. Chem. Phys.* **58**, 5745 (1973).



- 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

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

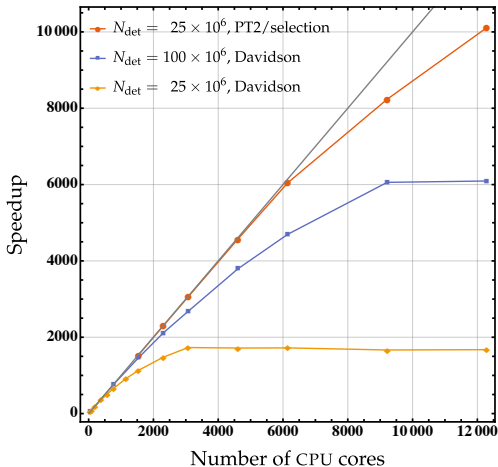


FCI wave function can't be computed or even stored:

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

$$= 42.4 \text{ moles}$$

- OpenMP / MPI / ZeroMQ
- HPC environments
- Cloud environments
- Resources can be increased dynamically



The Quest for Highly Accurate Excitation Energies: A Computational Perspective

Pierre-François Loos*, Anthony Scemama, and Denis Jacquemin*



Cite This: *J. Phys. Chem. Lett.* 2020, 11, 2374–2383



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ABSTRACT: We provide an overview of the successive steps that made it possible to obtain increasingly accurate excitation energies with computational chemistry tools, eventually leading to chemically accurate vertical transition energies for small- and medium-size molecules. First, we describe the evolution of *ab initio* methods employed to define benchmark values, with the original Roos CASPT2 method, then the CC3 method as in the renowned Thiel set, and more recently the resurgence of selected configuration interaction methods. The latter method has been able to deliver consistently, for both single and double excitations, highly accurate excitation energies for small molecules, as well as medium-size molecules with compact basis sets. Second, we describe how these high-level methods and the creation of representative benchmark sets of excitation energies have allowed the fair and accurate assessment of the performance of computationally lighter methods. We conclude by discussing possible future theoretical and technological developments in the field.



QUESTDB: A database of highly accurate excitation energies for the electronic structure community

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Abstract

We describe our efforts of the past few years to create a large set of more than 500 highly accurate vertical excitation energies of various natures ($\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$, double excitation, Rydberg, singlet, doublet, triplet, etc.) in small- and medium-sized molecules. These values have been obtained using an incremental strategy which consists in combining high-order coupled cluster and selected configuration interaction calculations using increasingly large diffuse basis sets in order to reach high accuracy. One of the key aspects of the so-called QUEST database of vertical excitations is that it does not rely on any experimental values, avoiding potential biases inherently linked to experiments and facilitating theoretical cross comparisons. Following this composite protocol, we have been able to produce theoretical best estimates (TBEs) with the aug-cc-pVTZ basis set for each of these transitions, as well as basis set corrected TBEs (i.e., near the complete basis set limit) for some of them. The TBEs/aug-cc-pVTZ have been employed to benchmark a large number of (lower-order) wave function methods such as CIS(D), ADC(2), CC2, STEOM-CCSD, CCSD, CCSDR(3), CCSDT-3, ADC(3), CC3, NEVPT2, and so on (including spin-scaled variants). In order to gather the huge amount of data produced during the QUEST project, we have created a website (https://lcpq.github.io/QUESTDB_website) where one can easily test and compare the accuracy of a given method with respect to various variables such as the molecule size or its family, the nature of the excited states, the type of basis set, and so on. We hope that the present review will provide a useful summary of our effort so far and foster new developments around excited-state methods.

This article is categorized under:

Electronic Structure Theory > Ab Initio Electronic Structure Methods

KEYWORDS

benchmark, coupled cluster theory, database, excitation energies, excited states, full configuration interaction

Accurate full configuration interaction correlation energy estimates for five- and six-membered rings

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ABSTRACT

Following our recent work on the benzene molecule [P.-F. Loos, Y. Damour, and A. Scemama, J. Chem. Phys. 153, 176101 (2020)], motivated by the blind challenge of Eriksen et al. [J. Phys. Chem. Lett. 11, 8922 (2020)] on the same system, we report accurate full configuration interaction (FCI) frozen-core correlation energy estimates for 12 five- and six-membered ring molecules (cyclopentadiene, furan, imidazole, pyrrole, thiophene, benzene, pyrazine, pyridazine, pyridine, pyrimidine, s-tetrazine, and s-triazine) in the standard correlation-consistent double- ζ Dunning basis set (cc-pVDZ). Our FCI correlation energy estimates, with an estimated error smaller than 1 millihartree, are based on energetically optimized-orbital selected configuration interaction calculations performed with the configuration interaction using a perturbative selection made iteratively algorithm. Having at our disposal these accurate reference energies, the respective performance and convergence properties of several popular and widely used families of single-reference quantum chemistry methods are investigated. In particular, we study the convergence properties of (i) the Møller-Plesset perturbation series up to fifth-order (MP2, MP3, MP4, and MP5), (ii) the iterative approximate coupled-cluster series CC2, CC3, and CC4, and (iii) the coupled-cluster series CCSD, CCSDT, and CCSDTQ. The performance of the ground-state gold standard CCSD(T) as well as the completely renormalized CC model, CR-CC(2,3), is also investigated. We show that MP4 provides an interesting accuracy/cost ratio, while MP5 systematically worsens the correlation energy estimates. In addition, CC3 outperforms CCSD(T) and CR-CC(2,3), as well as its more expensive parent CCSDT. A similar trend is observed for the methods including quadruple excitations, where the CC4 model is shown to be slightly more accurate than CCSDTQ, both methods providing correlation energies within 2 millihartree of the FCI limit.

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Ground- and Excited-State Dipole Moments and Oscillator Strengths of Full Configuration Interaction Quality

Yann Damour,* Raúl Quintero-Monsebaiz, Michel Caffarel, Denis Jacquemin, Fábris Kossoski, Anthony Scemama, and Pierre-François Loos*



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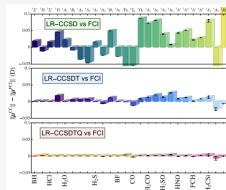
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ABSTRACT: We report ground- and excited-state dipole moments and oscillator strengths (computed in different “gauges” or representations) of full configuration interaction (FCI) quality using the selected configuration interaction method known as *Configuration Interaction using a Perturbative Selection made Iteratively* (CIPSI). Thanks to a set encompassing 35 ground- and excited-state properties computed in 11 small molecules, the present near-FCI estimates allow us to assess the accuracy of high-order coupled-cluster (CC) calculations including up to quadruple excitations. In particular, we show that incrementing the excitation degree of the CC expansion (from CC with singles and doubles (CCSD) to CC with singles, doubles, and triples (CCSDT) or from CCSDT to CC with singles, doubles, triples, and quadruples (CCSDTQ)) reduces the average error with respect to the near-FCI reference values by approximately 1 order of magnitude.





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