EXTREME ACCURACY FOR BENCHMARK SYSTEMS

A. Scemama, P.-F. Loos, M. Caffarel

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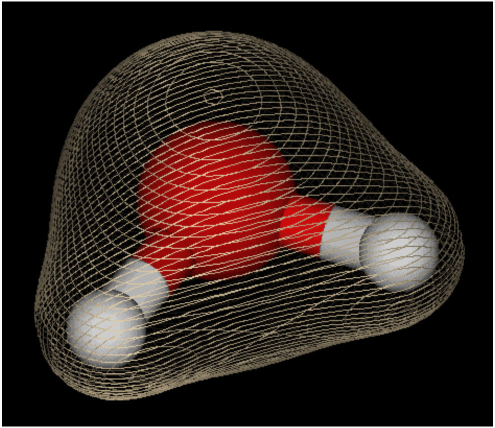
Lab. Chimie et Physique Quantiques, IRSAMC, UPS/CNRS, Toulouse

QUANTUM CHEMISTRY

- Description of the electron cloud
- Nuclei are considered as fixed point charges (Born-Oppenheimer approximation).



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Schrödinger's equation for electrons

$$\hat{H}\Psi(\mathrm{r}_1, \ldots, \mathrm{r}_N) = E\,\Psi(\mathrm{r}_1, \ldots, \mathrm{r}_N) \tag{1}$$

- E: Energy of the system
- Hamiltonian operator:

$$\hat{H} = \hat{T} + \hat{V} = -\frac{1}{2}\nabla^2 + V_{NN} + V_{eN} + V_{ee} \tag{2}$$

- $\Psi(\mathrm{r}_1, \ldots, \mathrm{r}_N)$: electronic wavefunction.
- $[\Psi(\mathrm{r}_1, \ldots, \mathrm{r}_N)]^2$: $3N$-dimensional probability density

What does $\hat{H}\Psi = E\Psi$ mean?

- Ψ is an eigenfunction of $\hat{H}$
- E is the associated eigenvalue

$$E_{\text{local}}(\mathbf{r}_1, \dots, \mathbf{r}_N) = \frac{\hat{H}\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)}{\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)} = \text{constant} \tag{3}$$

Whatever the positions of the electrons, the total energy must be constant : conservation of energy !

Plot of E_{local} in BeH_2

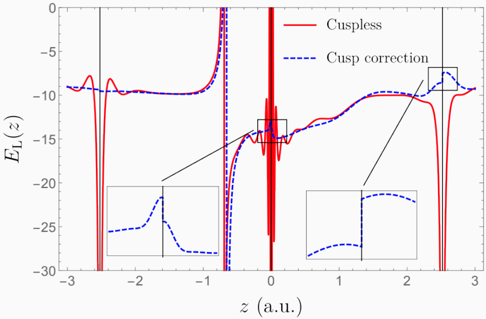
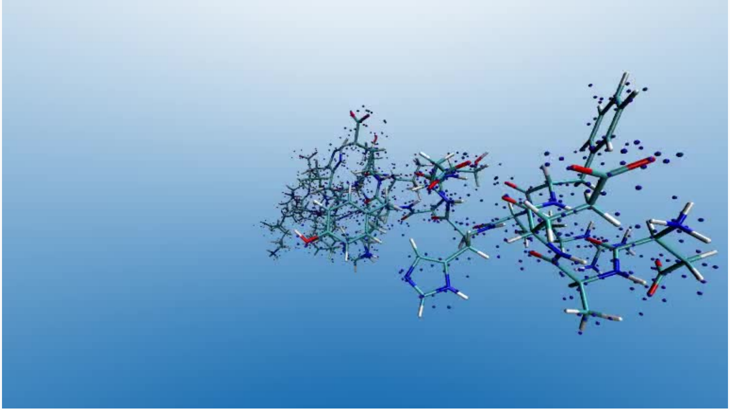


Figure 5: Local energy $E_L(r)$ of the cuspless and cusp-corrected HF wave functions as an electron is moved through the nuclei (marked with thin black lines) of the BeH_2 molecule at experimental geometry. The other electrons have been positioned randomly. The Gaussian basis set is Pople's 6-31G basis and the Slater exponents have been obtained via Eq. (22).

Difficulties of quantum chemistry

- Each electron ”sees” the $N - 1$ other electrons
- Electron correlation : electrons are not independent
- Correlation is $< 0.5\%$ of the electronic energy
- Without correlation, F_2 is not bound!
- Schrödinger’s equation is a differential equation in $3N$ dimensions
- Can be solved exactly only for small models, but not ”real” molecules $\Longrightarrow$ we look for approximate solutions

QUANTUM MONTE CARLO SIMULATION OF AMYLOID-β PEPTIDE



QUANTUM CHEMISTRY METHODS IN 1 SLIDE

$3N$-dimensional PDE

- FCI : considered unreachable
- Post-Hartree-Fock methods : Approximations of FCI

3-dimensional PDE

- Hartree-Fock : No ↑↓ electron correlation
- DFT : Electron correlation treated as an effective potential. Best ratio accuracy/cost.

QUANTUM CHEMISTRY

Absolute energies are dramatically bad with conventional methods:

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- If a method is *uniformly bad*, energy differences are good!

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Why does it work?

- Chemistry is all about *energy differences*
- If a method is *uniformly bad*, energy differences are good!
- Cancellation of errors is the key

Hierarchy of approximations

1. Hylleraas-type methods

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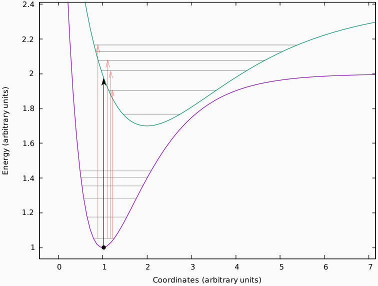
5. Multi-Reference methods (MR-CI, CAS-PT2, DMRG,...)
6. Single reference QMC ($\sim 100 atoms$)
7. Post-HF Single-reference methods (CCSD, MP2, ...)
8. Density Functional Theory (DFT) ($\sim$ 1000 atoms)
9. Tight-Binding DFT (DFTB) ($\sim$ 10 000 atoms)
10. Semi-empirical methods (MNDO, AM1, PM3, PM6, ...). Parameterized on experimental data.

BENCHMARKS

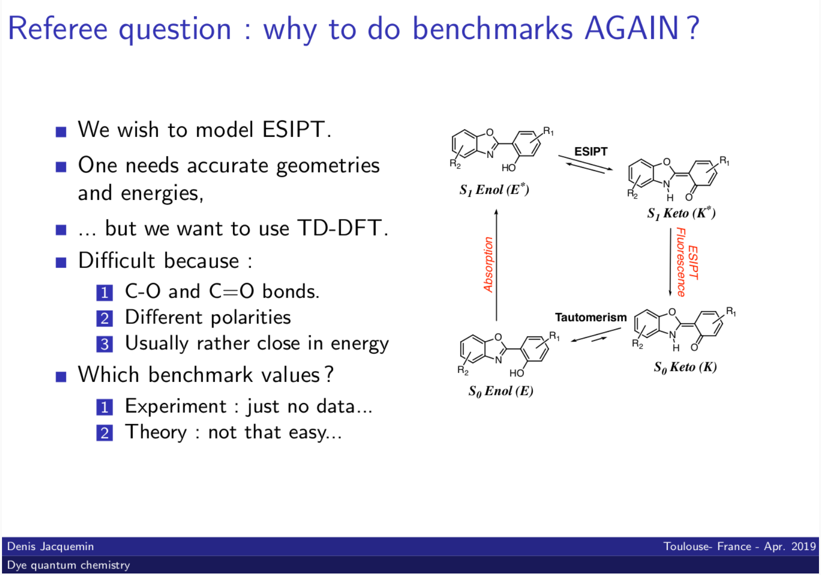
Why benchmarks?

- Improving approximate models requires accurate references
- All post-Hartree-Fock methods are approximations of FCI
- Some quantities we calculate are not accessible experimentally



- Experiment : Vibrational states
- Computation : Points of the potential energy surfaces

BENCHMARKS



Referee question : why to do benchmarks AGAIN ?

- We wish to model ESIPT.
- One needs accurate geometries and energies,
- ... but we want to use TD-DFT.
- Difficult because :
  1. C-O and C=O bonds.
  2. Different polarities
  3. Usually rather close in energy
- Which benchmark values ?
  1. Experiment : just no data...
  2. Theory : not that easy...

Denis Jacquemin
Dye quantum chemistry
Toulouse- France - Apr. 2019

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[1] Slide taken from a seminar given by Denis Jacquemin

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FULL-CI

Full Configuration Interaction (FCI)

All possible ways to put $N_\uparrow$ electrons in M orbitals *and* $N_\downarrow$ electrons in M orbitals:

$$\Psi = c_1 \begin{pmatrix} -- \\ -- \\ \upharpoonleft\downharpoonright \end{pmatrix} + c_2 \begin{pmatrix} -- \\ \upharpoonleft- \\ -\downharpoonright \end{pmatrix} + c_3 \begin{pmatrix} \upharpoonleft- \\ -- \\ -\downharpoonright \end{pmatrix} + c_4 \begin{pmatrix} -- \\ -\downharpoonright \\ \upharpoonleft- \end{pmatrix} + c_5 \begin{pmatrix} -- \\ \upharpoonleft\downharpoonright \\ -- \end{pmatrix} + c_6 \begin{pmatrix} \upharpoonleft- \\ -\downharpoonright \\ -- \end{pmatrix} + c_7 \begin{pmatrix} -\downharpoonright \\ -- \\ \upharpoonleft- \end{pmatrix} + c_8 \begin{pmatrix} -\downharpoonright \\ \upharpoonleft- \\ -- \end{pmatrix} + c_9 \begin{pmatrix} \upharpoonleft\downharpoonright \\ -- \\ -- \end{pmatrix}$$

$$N_{\text{det}} = \left(\frac{M!}{N_\uparrow!(M-N_\uparrow)!}\right) \times \left(\frac{M!}{N_\downarrow!(M-N_\downarrow)!}\right)$$

FULL-CI

Full Configuration Interaction (FCI)

- Exact when $M \to \infty$ (Complete Basis Set, CBS)
- Only approximation : one-electron basis set (orbitals)
- Can be computed exactly for small systems
- Breakthrough in 2009[1]: Can be computed numerically with FCI-QMC for larger systems
- Can be approached with selected-CI methods (CIPSI, SHCI, etc) + perturbation theory and extrapolation
- Involves only a few groups in the world

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[1] G. H. Booth, A. W. Thom, A. Alavi, *J. Chem. Phys.* **131**, 054106 (2009).

SELECTED CI

Algorithm

1. Start with a single determinant : $\Psi_n = \begin{pmatrix} -- \\ -- \\ \upharpoonleft\downharpoonright \end{pmatrix}$

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2. Among other determinants, estimate which one will be the most important, and add it to the vector space
3. Minimize the energy E and obtain a new wave function and energy: $\Psi_{n+1} = c_1 \begin{pmatrix} -- \\ -- \\ \uparrow\downarrow \end{pmatrix} + c_2 \begin{pmatrix} -- \\ \uparrow\downarrow \\ -- \end{pmatrix}$

SELECTED CI

Algorithm

1. Start with a single determinant : $\Psi_n = \begin{pmatrix} -\,- \\ -\,- \\ \upharpoonleft\downharpoonright \end{pmatrix}$
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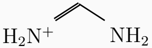
4. Estimate with perturbation theory (PT2) the energy of all the excluded determinants : $E_{\mathrm{FCI}} \approx E + E_{\mathrm{PT2}}$
5. Go back to step 2

SELECTED CI

Ground state and 1$^{\text{st}}$ excited state of



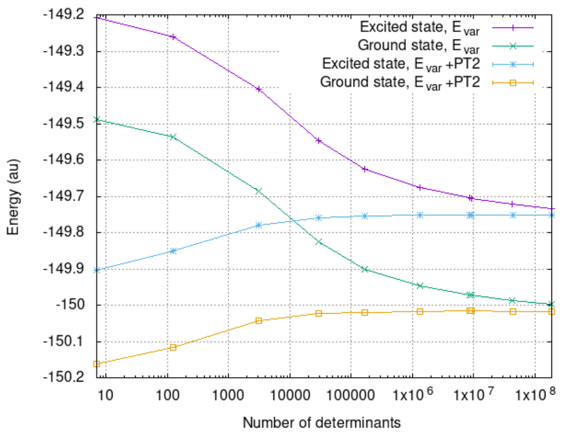
aug-cc-pVDZ

18 electrons in

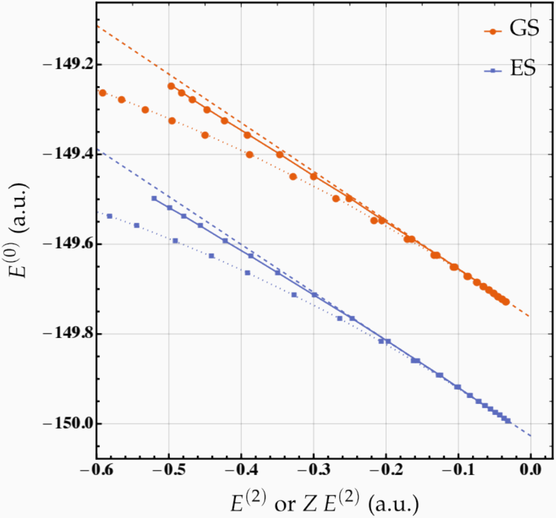
111 orbitals

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

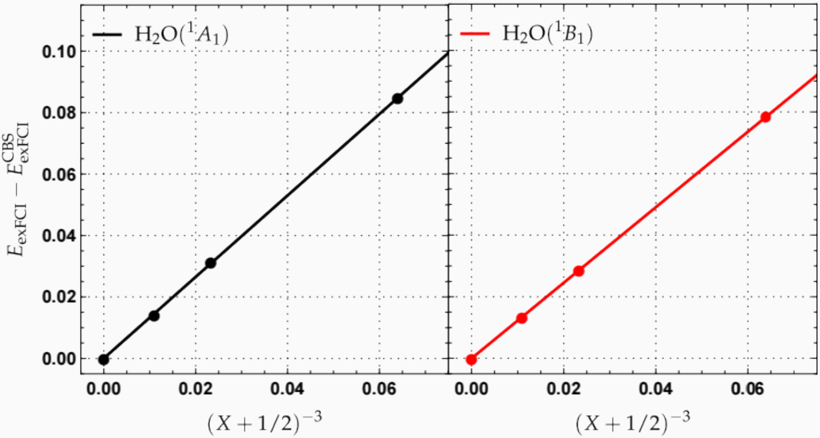
(42.4 moles)



Extrapolation to FCI limit (exFCI)



Extrapolation of exFCI to Complete Basis Set limit (CBS)



APPLICATION 1

- 110 transitions
- 18 molecules (H_2O, H_2S, NH_3, HCl, N_2, CO, C_2H_2, C_2H_4, CH_2O, CH_2S, formamide, ketene, methanimine, nitrosomethane, streptocyanine, acetaldehyde, cyclopropene, diazomethane)
- Extrapolate selected-CI to FCI (exFCI)
- Extrapolate exFCI to complete basis set (CBS)
- Test 12 excited-states methods

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[1] Loos et al, *J. Chem. Theory Comput.* **14**, 8, 4360-4379, (2018)

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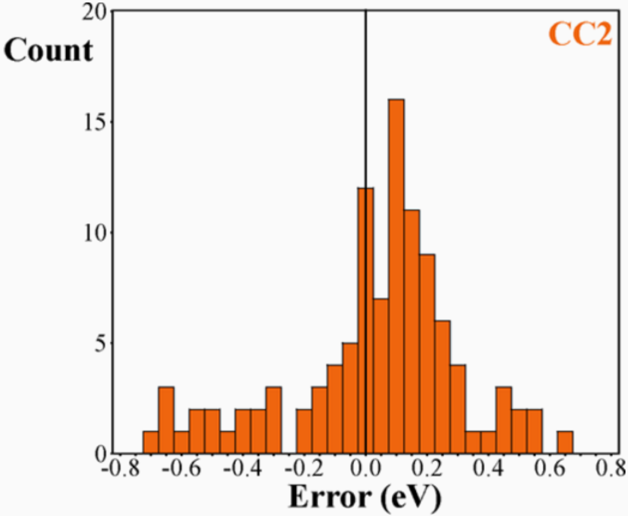

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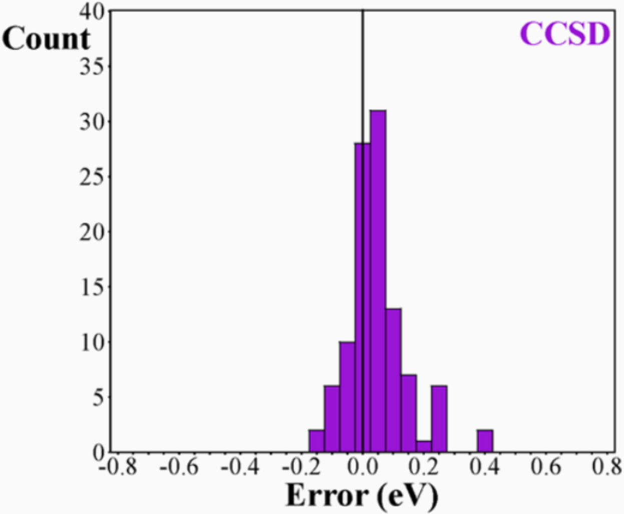

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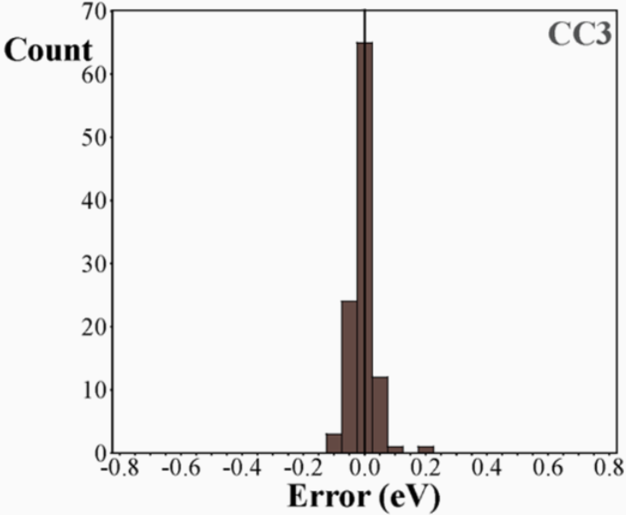

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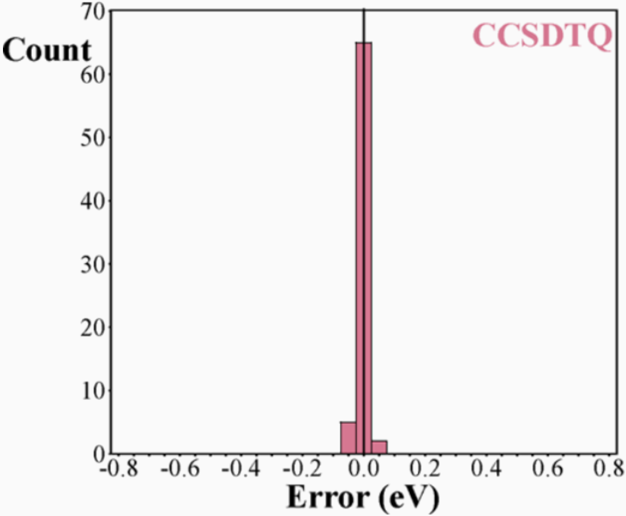

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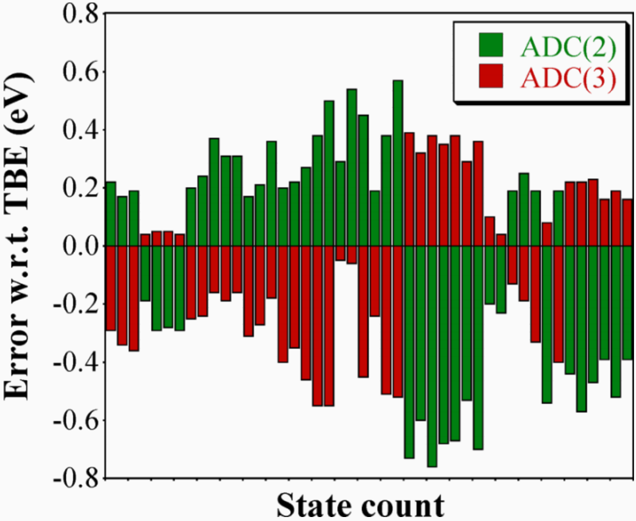

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[1] Loos et al, *J. Chem. Theory Comput.* **14**, 8, 4360-4379, (2018)

APPLICATION 2

- Doubly excited states
- Experimentally dark
- Can’t be described by conventional methods (TD-DFT)
- 20 vertical transitions
- 14 molecules
- Extrapolate selected-CI to FCI (exFCI)
- Extrapolate exFCI to complete basis set (CBS)

---

[1] Loos et al, *J. Chem. Theory Comput.* 15, 3, 1939-1956, (2019)

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APPLICATION 2

- Doubly excited states
- Extremely difficult with conventional methods (TD-DFT)
- 20 vertical transitions
- 14 molecules
- Extrapolate selected-CI to FCI (exFCI)
- Extrapolate exFCI to complete basis set (CBS)
- Conclusion: CC3 is excellent for single excitations, but still not sufficient for doubles, where multi-configurational methods are required

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[1] Loos et al, *J. Chem. Theory Comput.* **15**, 3, 1939-1956, (2019)

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BEYOND FCI

- Water molecule
- Quantum Monte Carlo on top of selected-CI
- The most accurate energy obtained today (lowest upper-bound)
- Lowest excited states

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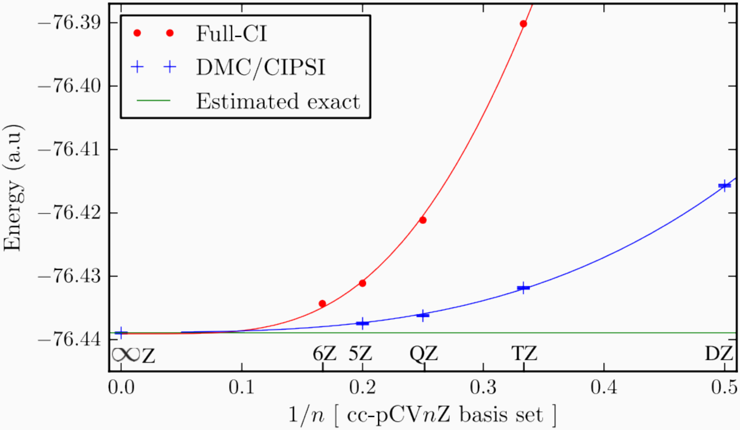
[1] Caffarel et al, *J. Chem. Phys.* **144**, 151103 (2016).

[2] Scemama et al, *J. Chem. Phys.* **149**, 034108 (2018).

BEYOND FCI



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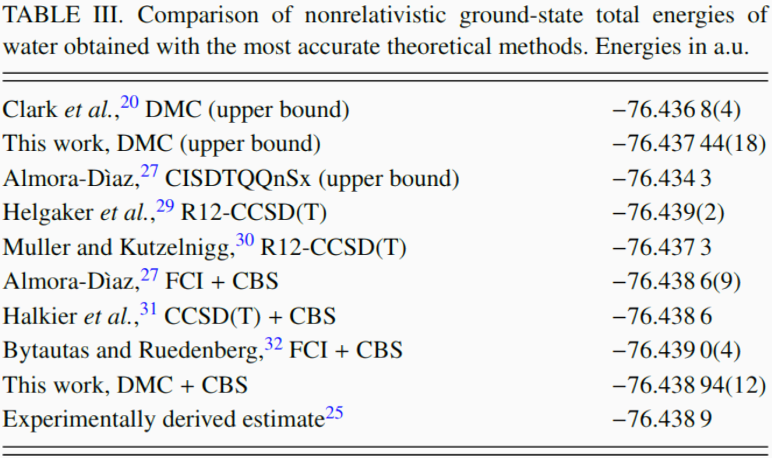

TABLE III. Comparison of nonrelativistic ground-state total energies of water obtained with the most accurate theoretical methods. Energies in a.u.

Clark *et al.*,[20] DMC (upper bound)	−76.436 8(4)
This work, DMC (upper bound)	−76.437 44(18)
Almora-Dìaz,[27] CISDTQQnSx (upper bound)	−76.434 3
Helgaker *et al.*,[29] R12-CCSD(T)	−76.439(2)
Muller and Kutzelnigg,[30] R12-CCSD(T)	−76.437 3
Almora-Dìaz,[27] FCI + CBS	−76.438 6(9)
Halkier *et al.*,[31] CCSD(T) + CBS	−76.438 6
Bytautas and Ruedenberg,[32] FCI + CBS	−76.439 0(4)
This work, DMC + CBS	−76.438 94(12)
Experimentally derived estimate[25]	−76.438 9

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[1] Caffarel et al, *J. Chem. Phys.* **144**, 151103 (2016).

BEYOND FCI

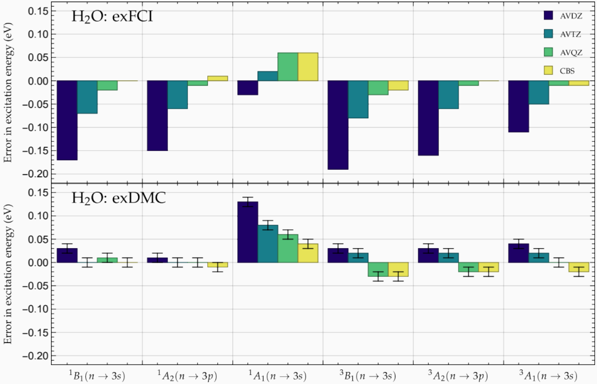

FIG. 2. Error (in eV) compared to the TBE of Ref. 78 for the three lowest singlet and three lowest triplet exFCI (top) and exDMC (bottom) vertical excitation energies of the water molecule computed with various basis sets. The CBS values (in yellow) are also reported. The error bar corresponds to one standard error.

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[1] Scemama et al, *J. Chem. Phys.* **149**, 034108 (2018).

PERSPECTIVES

Improve the convergence to CBS limit

1. F12-Full Configuration Interaction
2. Combine DFT with FCI to cure basis set incompleteness (E. Giner and J. Toulouse, LCT)
3. Post-F12-FCI Quantum Monte Carlo
4. Use Slater-type atomic orbitals (M. Caffarel)

COMPUTATIONAL DETAILS

- Quantum Monte Carlo calculations with QMC=Chem developed in our group
- New methods and algorithms developed in *Quantum Package*

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Quantum Package

- Open-source software developed by LCPQ (Toulouse), LCT (Paris)
- Massively parallel : benchmarks with up to 12 000 cores on Irene (TGCC)
- `https://quantumpackage.github.io/qp2/`
- ArXiv : 1902.08154
- Fork for periodic systems with A. Benali's group at Argonne National Labs