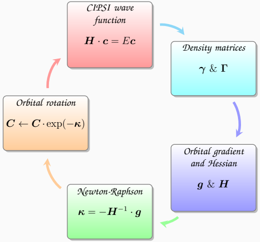
Accurate trial wave functions from selected CI for ground and excited states

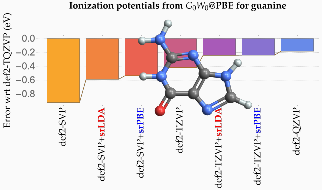
Anthony Scemama, Michel Caffarel & Pierre-François (Titou) Loos

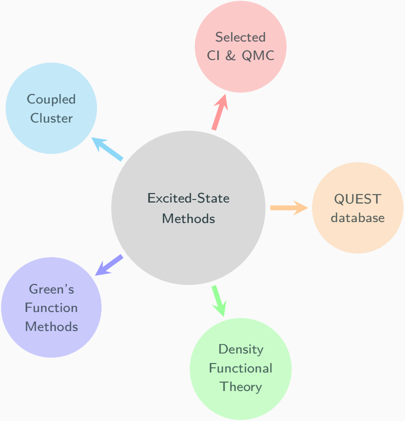
Laboratoire de Chimie et Physique Quantiques, IRSAMC, UPS/CNRS, Toulouse
https://lcpq.github.io/pterosor

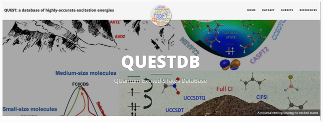
17th Dec 2025

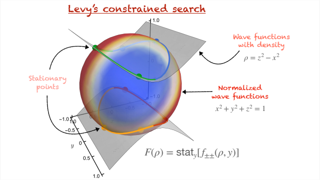
General Overview of our Research Group





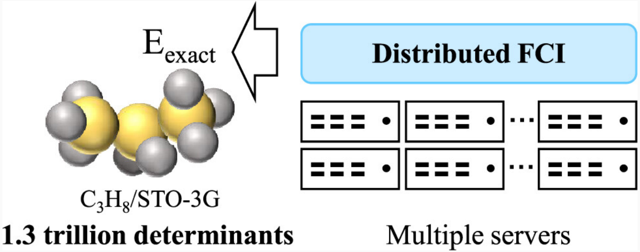






https://lcpq.github.io/PTEROSOR

FCI Calculation on Propane



- 🥴 FCI energy of propane (C_3H_8) in STO-3G
- 😖 Active space of 26 electrons in 23 orbitals $\Rightarrow 1.3 \times 10^{12}$ determinants!
- 😱 512 processes on 256 nodes (40 cores each) for a total wall time of 113.6 hours $\Rightarrow \approx 10^6$ CPU hours $\Rightarrow \approx 10\,\mathrm{MW\,h} \Rightarrow \approx$ 2 household years
- 🤯 19 TB of memory required!

Gao et al. JCTC 20 (2024) 1185

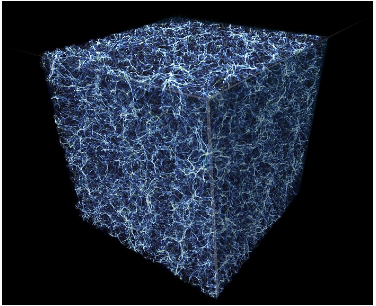
Schrödinger’s Tree

$$\frac{1}{\sqrt{2}}\left|\text{🍃}\right\rangle + \frac{1}{\sqrt{2}}\left|\text{🍂}\right\rangle$$

Selected Configuration Interaction (SCI)

What do we know?

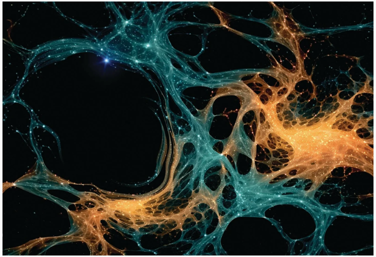
- Size of Hilbert space increases exponentially fast with system size
- FCI matrix is (very) large but full of zeros!
- Only a tiny fraction of the determinants significantly contributes to the energy
- SCI performs a sparse exploration of the FCI space



Selected Configuration Interaction (SCI)

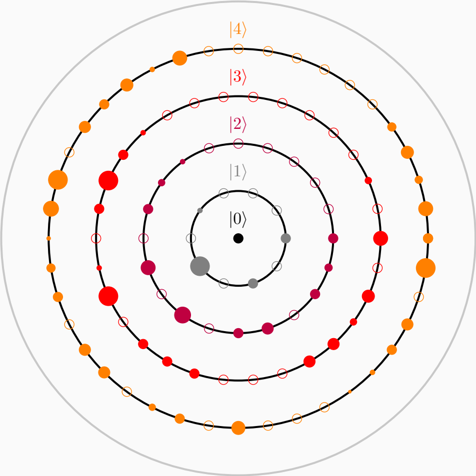
What do we know?

- Size of Hilbert space increases exponentially fast with system size
- FCI matrix is (very) large but full of zeros!
- Only a tiny fraction of the determinants significantly contributes to the energy
- SCI performs a sparse exploration of the FCI space

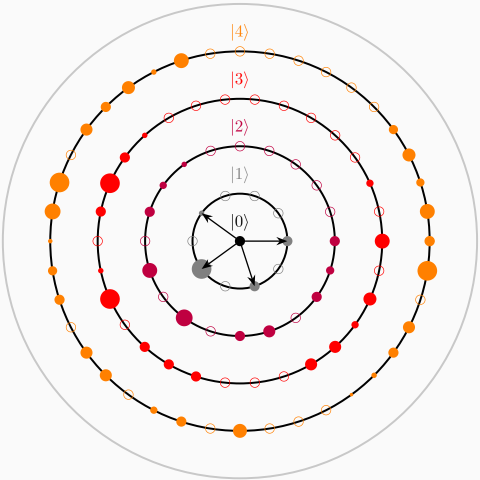


Lemonick, *"Cosmic Nothing"*, Scientific American, 330 (2024) 20

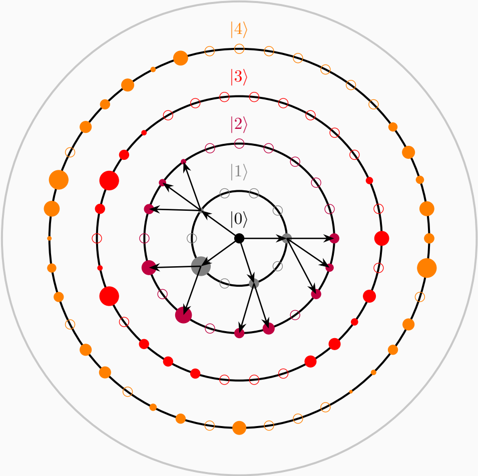
Hilbert Space "Onion"



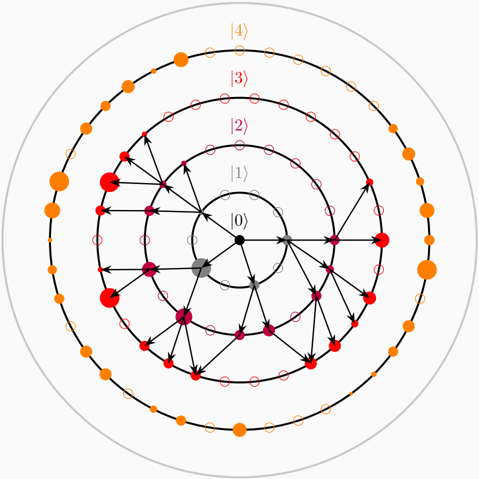
Hilbert Space "Onion"



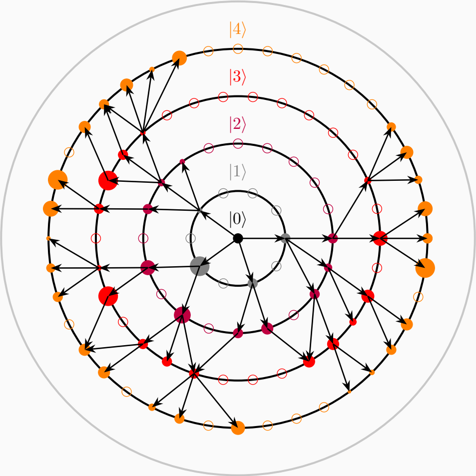
Hilbert Space “Onion”



Hilbert Space “Onion”

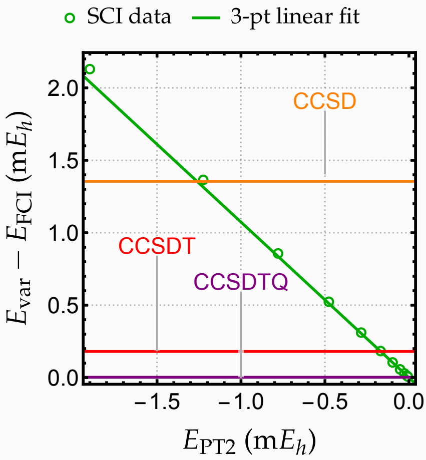


Hilbert Space "Onion"



Energy of C_3H_8 in STO-3G basis

Method	Energy (E_h)	Error wrt FCI
FCI[1]	$-117.100\,122\,681\,461$	
CCSD	$-117.098\,767$	$1.355\,\mathrm{m}E_\mathrm{h}$
CCSD(T)	$-117.099\,708$	$0.414\,\mathrm{m}E_\mathrm{h}$
CCSDT	$-117.099\,942\,158$	$0.181\,\mathrm{m}E_\mathrm{h}$
CCSDTQ	$-117.100\,120\,230$	$2.451\,\mu E_\mathrm{h}$
SCI[2]	$-117.100\,093\,52$	$0.029\,\mathrm{m}E_\mathrm{h}$
SCI+PT2[3]	$-117.100\,120\,66$	$2.021\,\mu E_\mathrm{h}$
exFCI[4]	$-117.100\,122\,89(6)$	$-0.21(6)\,\mu E_\mathrm{h}$



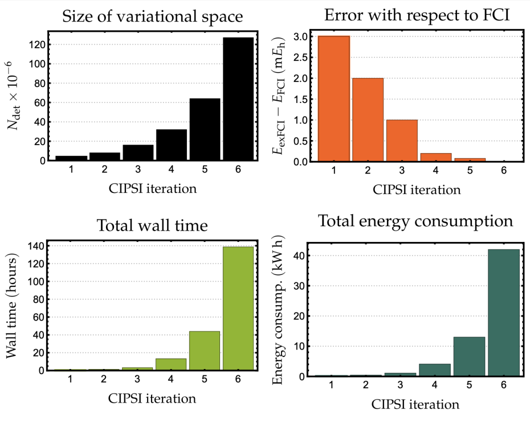
[1] Gao et al. JCTC 20 (2024) 1185

[2] Variational energy obtained with $N_\mathrm{det} = 32 \times 10^6$

[3] Perturbatively-corrected variational energy obtained with $N_\mathrm{det} = 32 \times 10^6$

[4] Extrapolated FCI value obtained via a 3-point linear fit using $N_\mathrm{det} = 32 \times 10^6$ as the largest variational space

Memory, CPU & Energy Consumptions

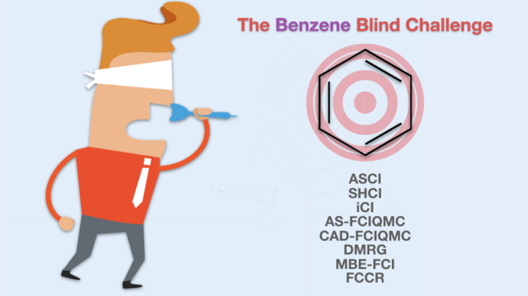


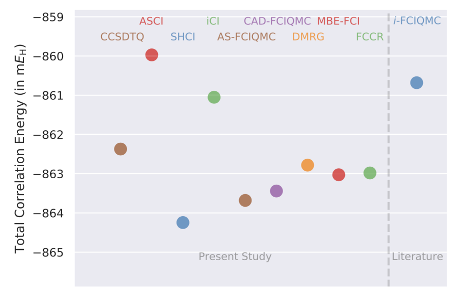
N_{det}	Wall time (hh:mm)	Memory consump.	Energy consump.	Error wrt FCI
2×10^6	00:14	5.3 GB	74 W h	3 μE_{h}
4×10^6	00:33	8.1 GB	176 W h	3 μE_{h}
8×10^6	01:19	15 GB	438 W h	2 μE_{h}
16×10^6	03:12	25 GB	1.1 kW h	1 μE_{h}
32×10^6	13:16	47 GB	4.1 kW h	0.2 μE_{h}
64×10^6	43:54	83 GB	13 kW h	0.08 μE_{h}
127×10^6	138:44	138 GB	42 kW h	0.01 μE_{h}

Burton & Loos JCP 160 (2024) 104102; Loos et al, arXiv:2402.13111[1]

[1] Single-node calculation (dual-socket Intel Skylake 6140 CPU@2.3 Ghz with 192 GB of memory and 36 physical CPU cores)

The Benzene Blind Challenge: Frozen-Core Correlation Energy (cc-pVDZ)

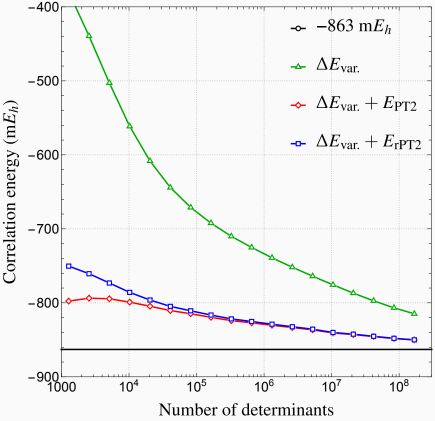


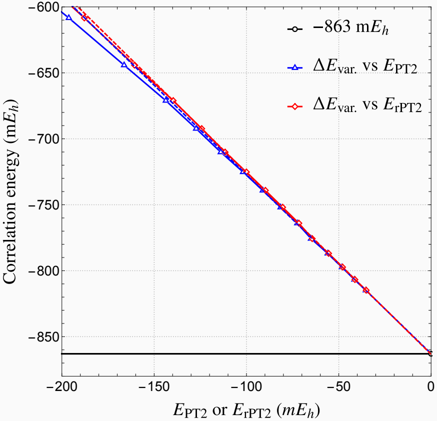


$$\text{CAS}(30{,}108) \quad \Rightarrow \quad 10^{35} \text{ determinants!}$$

Eriksen et al. JPCL 11 (2020) 8922

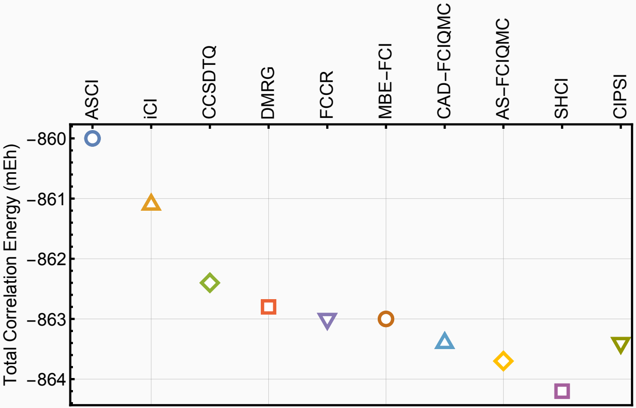
Performance of CIPSI for C_6H_6/cc-pVDZ (1)





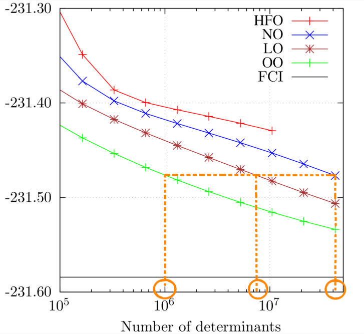
Loos, Damour & Scemama, JCP 153 (2020) 176101

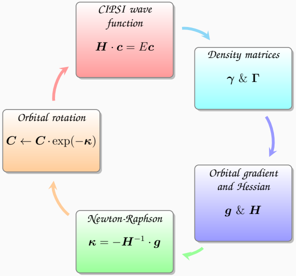
Performance of CIPSI for C_6H_6/cc-pVDZ (2)



Loos, Damour & Scemama, JCP 153 (2020) 176101

Orbital-Optimized CIPSI for C_6H_6/cc-pVDZ (and many others)





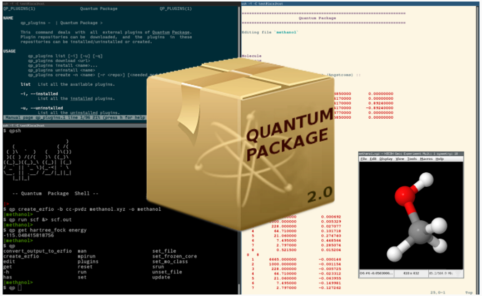
- Orbital optimization largely accelerates the convergence of selected CI
- Trust-region Newton-Raphson algorithm

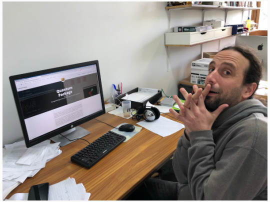
Yann Damour (PhD)

Damour, Véril, Kossoski, Caffarel, Jacquemin, Scemama & Loos, JCP 155 (2020) 176101

Quantum Package 2.0

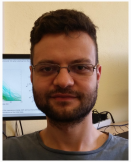
"SCI+PT2 methods provide near full CI (FCI) quality quantities with only a small fraction of the determinants of the FCI space"





Anthony Scemama

"Quantum Package 2.0: An Open-Source Determinant-Driven Suite of Programs",
Garniron et al., JCTC 15 (2019) 3591



Fábris Kossoski
(Toulouse)

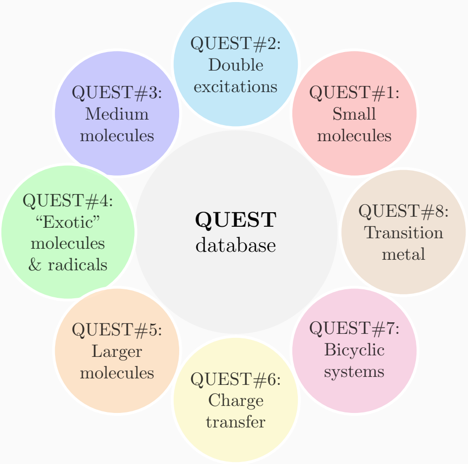
Filippo Lipparini
(Pisa)

Martial Boggio-Pasqua
(Toulouse)

Denis Jacquemin
(Nantes)

Highly-Accurate Excitation Energies: The QUEST database

"The QUEST project aims to provide to the community a large set of highly-accurate excitation energies for various types of excited states"

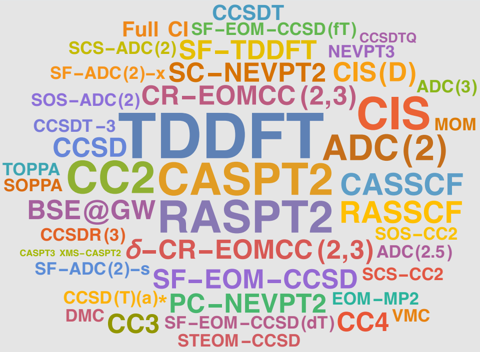


- #1: JCTC 14 (2018) 4360
- #2: JCTC 15 (2019) 1939; JCTC 20 (2024) 5655
- #3: JCTC 16 (2020) 1711
- #4: JCTC 16 (2020) 3720
- #5: WIREs 11 (2021) e1517
- #6: JCTC 17 (2021) 3666
- #7: JPCA 125 (2021) 10174
- #8: JCTC 19 (2023) 8782

Zoo of functionals...

"Although benchmarking is one of the most boring topics in quantum chemistry, it is also one of the most important ones." — Reviewer #3

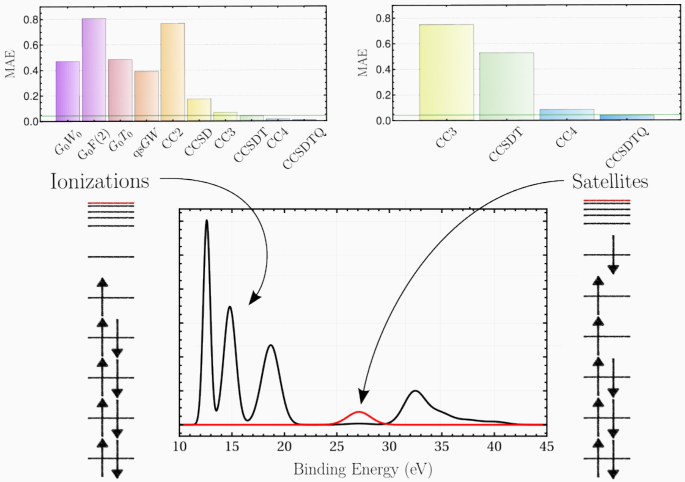
And this is just for excited states...



Other Research Groups Using QUEST

- **Head-Gordon's group:** orbital-optimized DFT for double excitations [JCTC 16 (2020) 1699; JPCL 12 (2021) 4517] and TD-DFT benchmark [JCTC 18 (2022) 3460]
- **Kaupp's group:** assessment of hybrid functionals [JCP 155 (2021) 124108]
- **Kallay's and Goerigk's groups:** double hybrids [JCTC 15 (2019) 4735; JCTC 17 (2021) 927; JCTC 17 (2021) 5165; JCTC 17 (2021) 4211]
- **Truhlar/Gagliardi's group:** pair DFT [JCTC 18 (2022) 6065; JCTC 19 (2023) 7983; JCTC 19 (2023) 8118]
- **Bartlett's group:** Variants of EOM-CC for doubly-excited states [JCP 156 (2022) 201102; JPCA 127 (2023) 828; JCP 159 (2023) 094101]
- **Gould's group:** ensemble DFT [JPCL 13 (2022) 2452; PRL 134 (2025) 228001]
- **Neuscamman's group:** QMC for doubly-excited states [JCP 153 (2022) 234105]
- **Filippi's group + Scemama's group:** QMC for excited states [JCTC 15 (2019) 4896; JCTC 17 (2021) 3426; JCTC 18 (2022) 1089; JCTC 18 (2022) 6722; JCP 163 (2025) 024119]

Extension to Charged Excitations

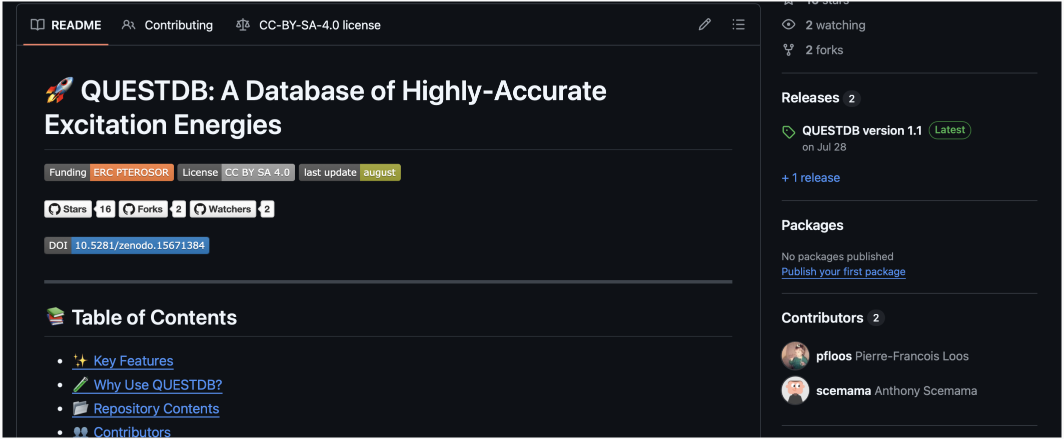


Antoine Marie (PhD)

(core ionizations coming soon!)

Marie & Loos JCTC 20 (2024) 4751

GitHub Repository



https://github.com/pfloos/QUESTDB

Loos et al., JCTC 21 (2025) 8010

CIPSI Trial Wave Functions for Excited States

THE JOURNAL OF CHEMICAL PHYSICS **149**, 034108 (2018)

Excitation energies from diffusion Monte Carlo using selected configuration interaction nodes

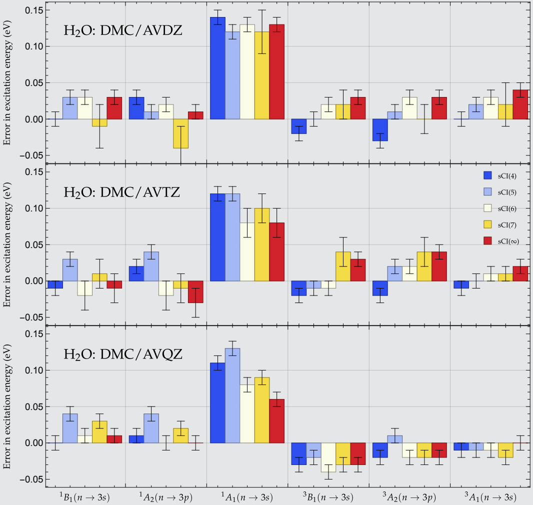
Anthony Scemama,[1] Anouar Benali,[2] Denis Jacquemin,[3] Michel Caffarel,[1] and Pierre-François Loos[1,a)]
[1]*Laboratoire de Chimie et Physique Quantiques, Université de Toulouse, CNRS, UPS, Toulouse, France*
[2]*Computational Science Division, Argonne National Laboratory, Argonne, Illinois 60439, USA*
[3]*Laboratoire CEISAM—UMR CNRS 6230, Université de Nantes, 2 Rue de la Houssinière, BP 92208, 44322 Nantes Cedex 3, France*

(Received 24 May 2018; accepted 5 July 2018; published online 20 July 2018)

See also Scemama et al. JCTC 14 (2018) 1395; Res. Chem. 1, 100002 (2019)

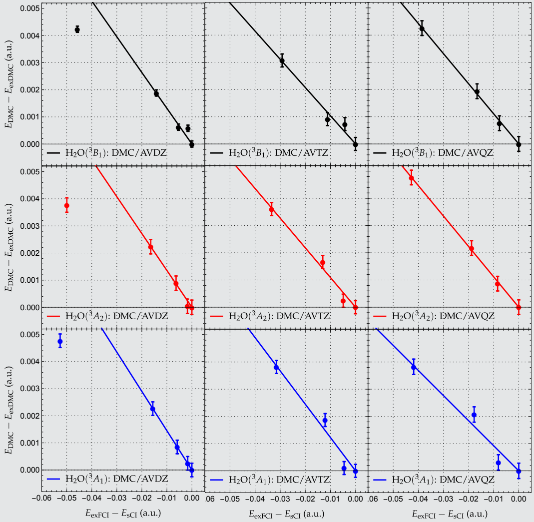
Fixed-node error in excited states: water

Water: (all-electron) DMC@CIPSI



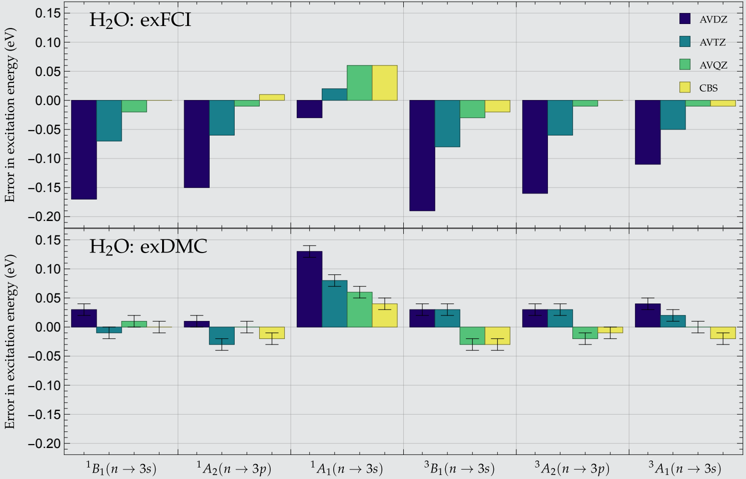
Fixed-node error in excited states: water

Water: Extrapolated DMC results (exDMC) for triplets



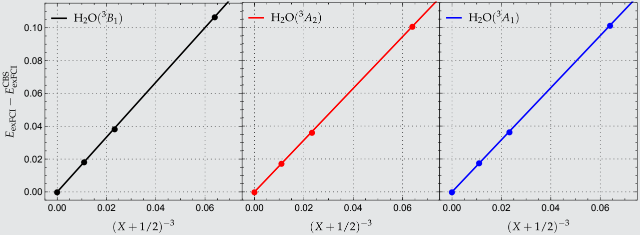
Fixed-node error in excited states: water

Water: exFCI vs exDMC

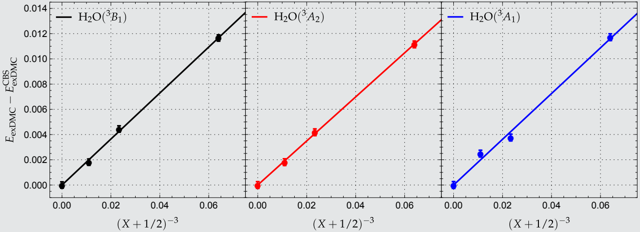


Complete Basis Set (CBS) Extrapolation

Triplet states of water: exFCI (AVDZ, AVTZ, AVQZ and CBS)



Triplet states of water: exDMC (AVDZ, AVTZ, AVQZ and CBS)



CIPSI Trial Wave Functions for Periodic Solids

Toward a systematic improvement of the fixed-node approximation in diffusion Monte Carlo for solids—A case study in diamond

Cite as: J. Chem. Phys. **153**, 184111 (2020); https://doi.org/10.1063/5.0021036
Submitted: 06 July 2020 . Accepted: 12 October 2020 . Published Online: 11 November 2020

Anouar Benali, Kevin Gasperich, Kenneth D. Jordan, Thomas Applencourt, Ye Luo, M. Chandler Bennett, Jaron T. Krogel, Luke Shulenburger, Paul R. C. Kent, Pierre-François Loos, Anthony Scemama, and Michel Caffarel

Michel Caffarel
(Toulouse)

See also Scemama et al. JCP 153 (2021) 174107 for a range-separated approach in molecules

Recent Extensions

- Complex absorbing potential + SCI for electronic resonances
  Damour et al. JPCL 15 (2024) 8296
- Transcorrelated SCI: compactification of the determinant expansion
  Ammar et al, JCP 161 (2024) 084104
- Interface between CIPSI and AFQMC (ipie)
  JCP 161 (2024) 162502
- TREXIO: A file format and library for quantum chemistry
  JCP 158 (2023) 174801
- QMCkl: Quantum Monte Carlo Kernel Library
  https://github.com/TREX-CoE/qmckl

TREX Targeting Real chemical accuracy at the EXascale

Acknowledgements & Funding

- **Anthony Scemama & Michel Caffarel**
- Denis Jacquemin, Martial Boggio-Pasqua, Filippo Lipparini & Fábris Kossoski
- Antoine Marie, Enzo Monino, Roberto Orlando & Yann Damour
- Abdallah Ammar, Sara Giarrusso & Raúl Quintero-Monsebaiz

European Research Council
Established by the European Commission

https://pfloos.github.io/WEB_LOOS
https://lcpq.github.io/PTEROSOR