Highly Accurate Excited-State Energies and Properties: The QUEST database

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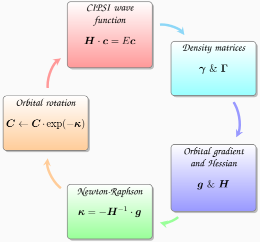
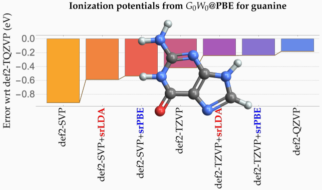
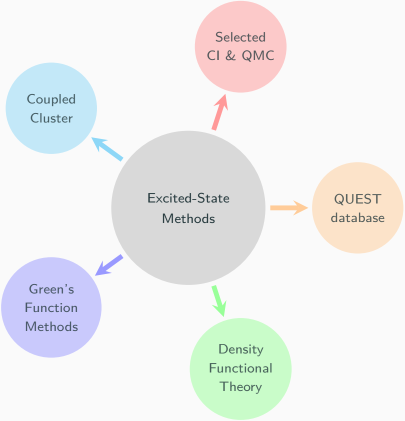
https://pfloos.github.io/WEB_LOOS

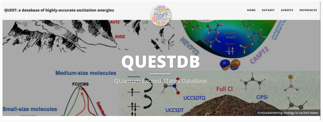
4th May 2026

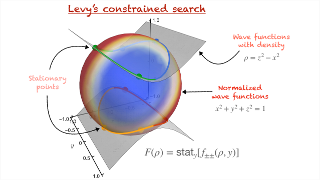
General Overview of our Research Group





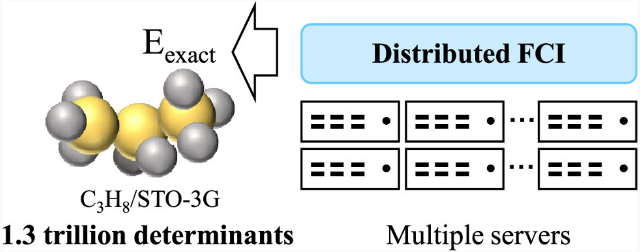






https://pfloos.github.io/WEB_LOOS

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

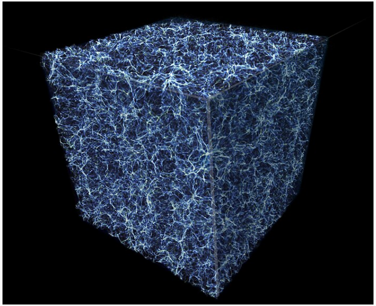
Schrödinger's Tree

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

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



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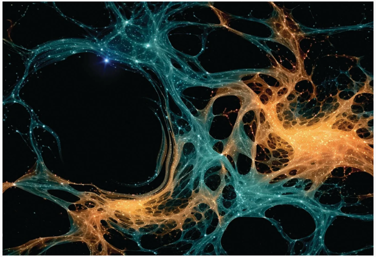
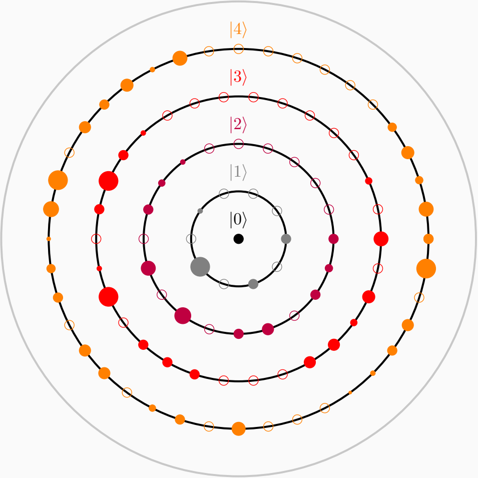


Lemonick, *"Cosmic Nothing"*, Scientific American, 330 (2024) 20

Hilbert Space "Onion"



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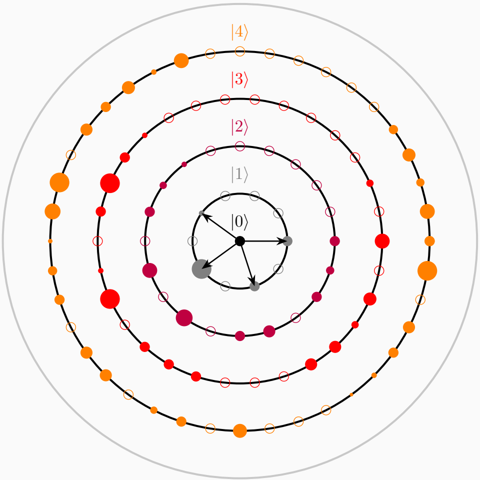

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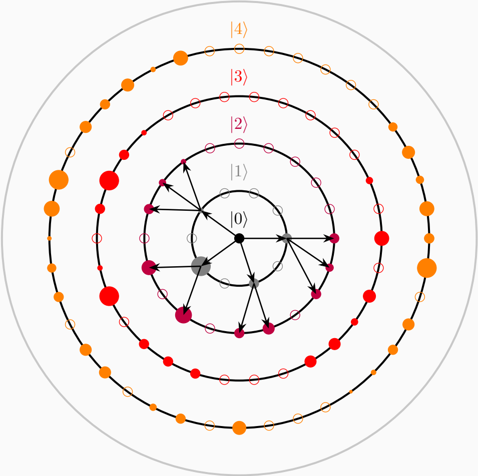

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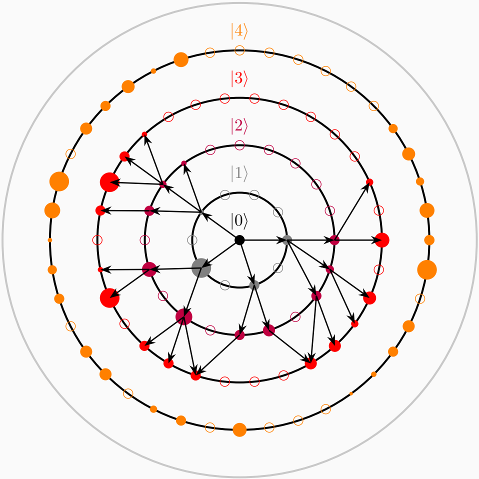

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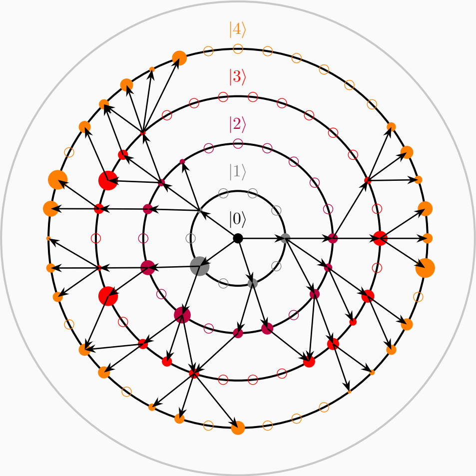
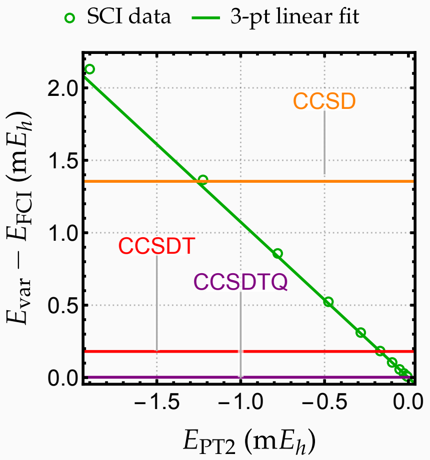


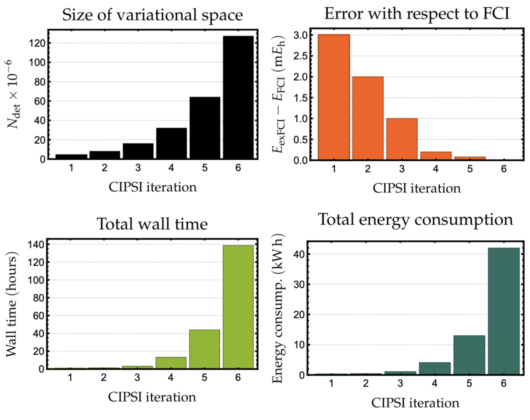
Energy of C_3H_8 in STO-3G basis

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

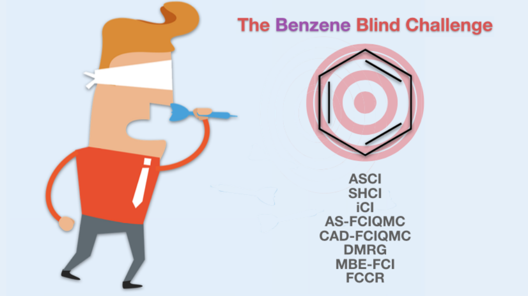


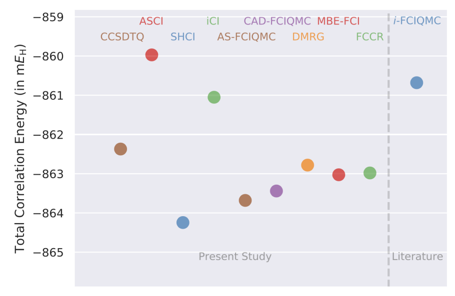
N_{det}	Wall time (hh:mm)	Memory consump.	Energy consump.	Error wrt FCI
2×10^6	00:14	5.3 GB	74 W h	3 μE_h
4×10^6	00:33	8.1 GB	176 W h	3 μE_h
8×10^6	01:19	15 GB	438 W h	2 μE_h
16×10^6	03:12	25 GB	1.1 kW h	1 μE_h
32×10^6	13:16	47 GB	4.1 kW h	0.2 μE_h
64×10^6	43:54	83 GB	13 kW h	0.08 μE_h
127×10^6	138:44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

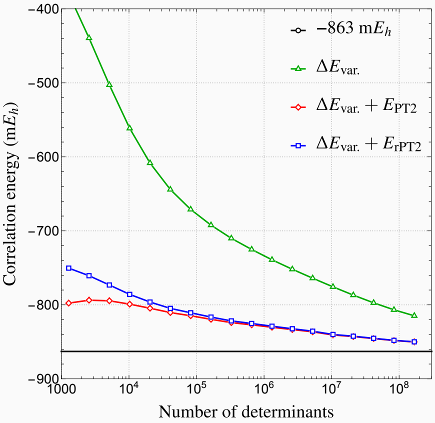


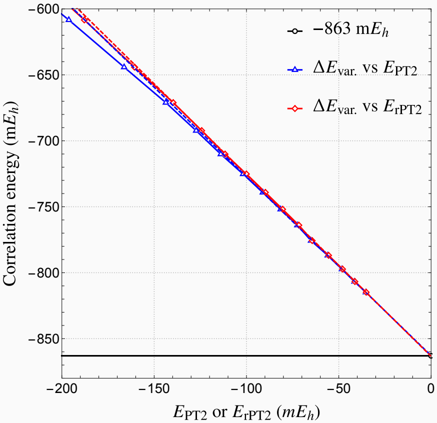


CAS(30,108) $\Rightarrow$ 10^{35} determinants!

Eriksen et al. JPCL 11 (2020) 8922

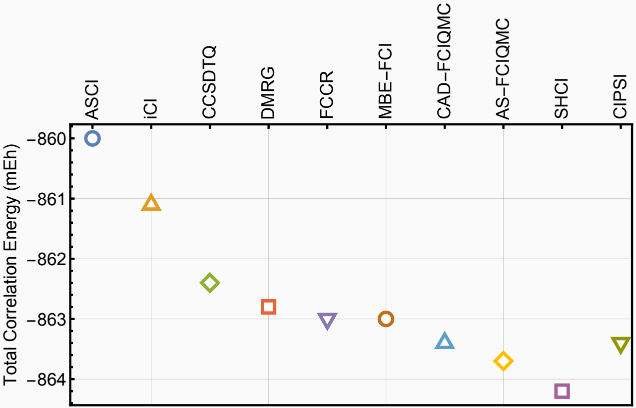
Performance of CIPSI for C_6H_6/cc-pVDZ (1)





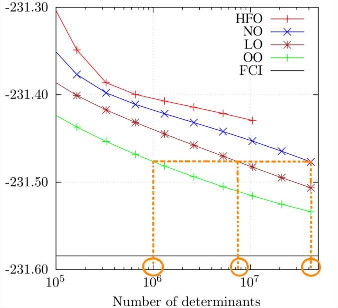
Loos, Damour & Scemama, JCP 153 (2020) 176101

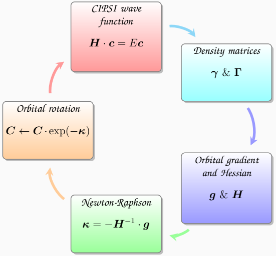
Performance of CIPSI for C_6H_6/cc-pVDZ (2)



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

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



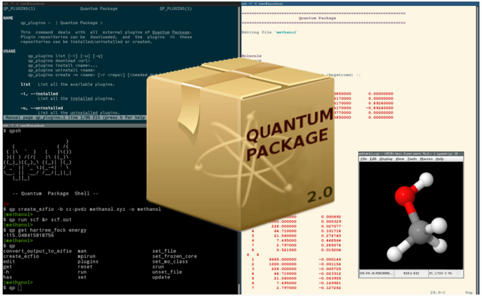


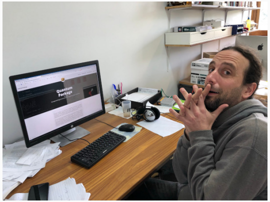
- Orbital optimization largely accelerates the convergence of selected CI
- Trust-region Newton-Raphson algorithm

Yann Damour (PhD)

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

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

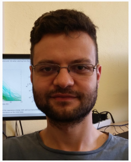




Anthony Scemama

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

Extension to Excited States: The QUEST Database



Fábris Kossoski
(Toulouse)

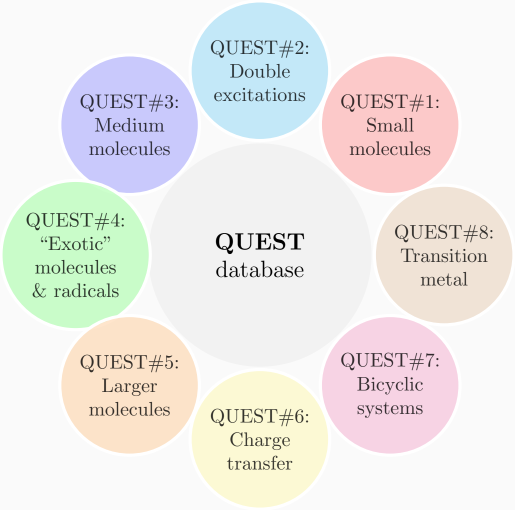
Filippo Lipparini
(Pisa)

Martial Boggio-Pasqua
(Toulouse)

Denis Jacquemin
(Nantes)

Highly-Accurate Excitation Energies: The QUEST Database

"The QUEST project provides the community with an extensive set of highly accurate excitation energies covering a wide range of excited states."



- #1: JCTC 14 (2018) 4360
- #2: JCTC 15 (2019) 1939; 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

Density-Based Nightmare...

Zoo of functionals...

Wavefunction-Based Nightmare...

"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...

Highly Accurate Excitation Energies: The QUEST Database

Why use QUESTDB?

- You are looking for a specific excitation and would rather not recompute it yourself
- You have a brand new excited-state method that works *remarkably well* (on selected examples)
- You need a trustworthy reference to confirm that your code is indeed wrong
- You would like to quantify the accuracy of a method beyond a few carefully chosen cases
- You want to calibrate or train data-driven models (e.g., ML approaches)
- You want to perform a fair and reproducible comparison between methods
- You suspect your favorite method has systematic failures and would like to know where

Loos, Boggio-Pasqua, Blondel, Lipparini & Jacquemin, JCTC 21 (2025) 8010

What Can You Find in the QUEST Database?

Current Status

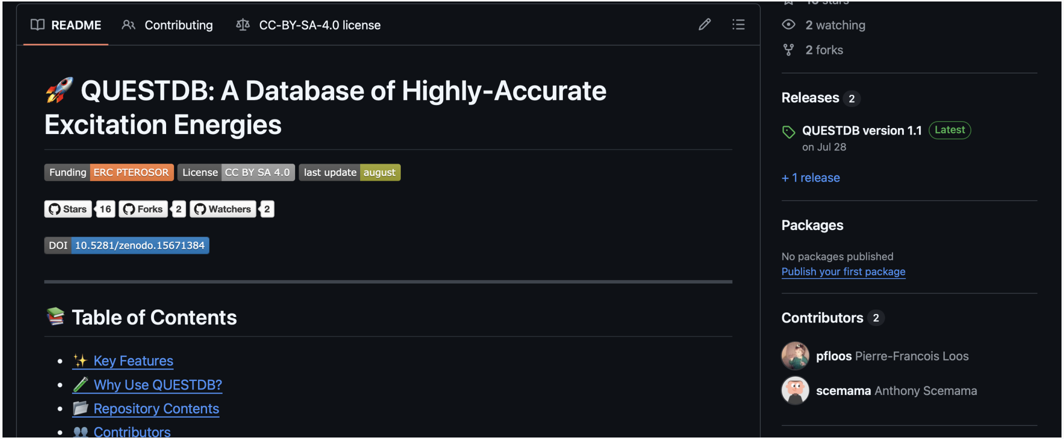
- 184 molecules (up to 16 non-hydrogen atoms)
- 1489 transitions, including 1294 chemically accurate values (error < 0.05 eV)
- Spatial and spin symmetries, as well as the nature of each transition, are provided
- Available properties: oscillator strengths and excited-state dipole moments
  JCTC 17 (2021) 416; JCTC 17 (2021) 1106; JCTC 19 (2023) 221
- Detailed description of the active space for each system and transition
  JCTC 18 (2022) 2418; JCP 157 (2022) 014103
- Availability of reduced "diet" subsets
- Nearly large enough for ML purposes...

Loos, Boggio-Pasqua, Blondel, Lipparini & Jacquemin, JCTC 21 (2025) 8010

Other Research Groups Using QUEST

- **Head-Gordon group:** orbital-optimized DFT for double excitations and TD-DFT benchmarks [JCTC 16 (2020) 1699; JPCL 12 (2021) 4517; JCTC 18 (2022) 3460]
- **Kaupp group:** assessment of hybrid functionals [JCP 155 (2021) 124108]
- **Kállay and Goerigk groups:** development and assessment of double-hybrid functionals [JCTC 15 (2019) 4735; JCTC 17 (2021) 927; JCTC 17 (2021) 4211; JCTC 17 (2021) 5165]
- **Truhlar and Gagliardi groups:** pair-density functional theory (PDFT) [JCTC 18 (2022) 6065; JCTC 19 (2023) 7983; JCTC 19 (2023) 8118]
- **Bartlett group:** variants of EOM-CC for doubly excited states [JCP 156 (2022) 201102; JPCA 127 (2023) 828; JCP 159 (2023) 094101]
- **Gould group:** ensemble DFT [JPCL 13 (2022) 2452; PRL 134 (2025) 228001]
- **Neuscamman group:** QMC and state-specific CC approaches for singly and doubly excited states [JCP 153 (2022) 234105; JCTC 20 (2024) 2761; arXiv:2601.20089]
- **Filippi and Scemama groups:** QMC methods for excited states [JCTC 15 (2019) 4896; JCTC 17 (2021) 3426; JCTC 18 (2022) 1089; JCTC 18 (2022) 6722; JCP 163 (2025) 024119]

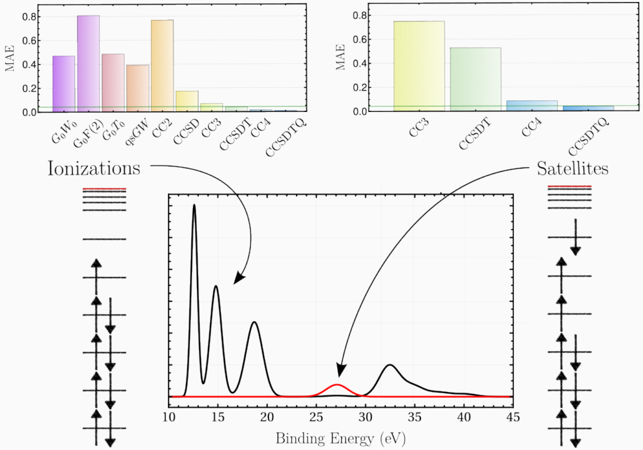
GitHub Repository



https://github.com/pfloos/QUESTDB

Loos, Boggio-Pasqua, Blondel, Lipparini & Jacquemin, JCTC 21 (2025) 8010

Extension to Charged Excitations: Inner- and Outer-Valence Ionizations



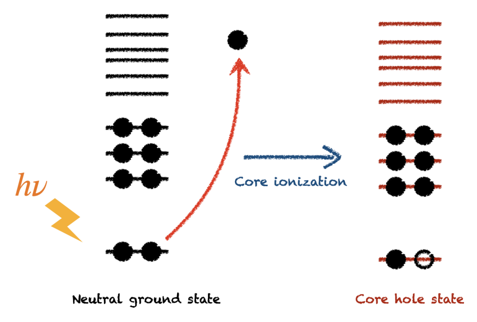
Marie & Loos, JCTC 20 (2024) 4751

Antoine Marie (PhD)

Benchmark Set

- 58 valence IPs
- 42 satellite transition energies
- FCI values up to aug-cc-pVQZ (at least aug-cc-pVTZ)

Extension to Charged Excitations: Core Ionizations



Marie, Burth & Loos, arXiv:2604.05920

Double core holes: Marie et al. JCP 162 (2025) 134105
See Ferté et al. JPCL 11 (2020) 4359

Features of Core IPs

- Element- and site-specific
- Electron correlation crucial
- Strong orbital relaxation
- Relativistic effects are not negligible
- Basis set sensitive

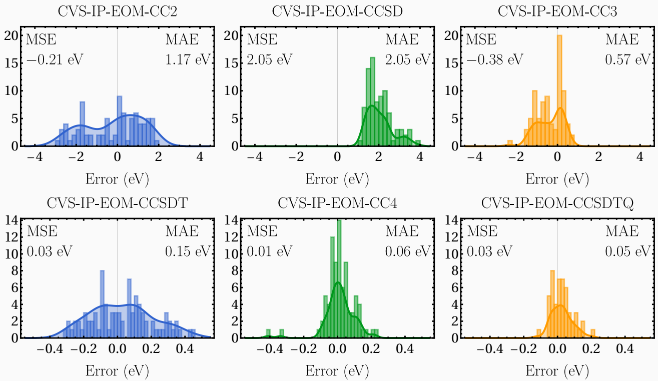
Theoretical Challenges

- Core-valence separation (CVS) approximation
- Linear-response vs state-specific methods

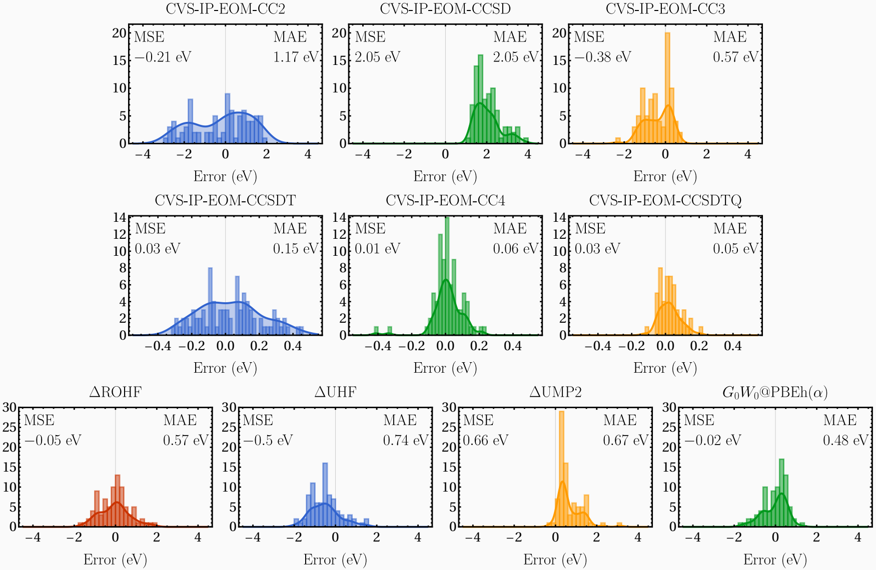
Benchmark Set

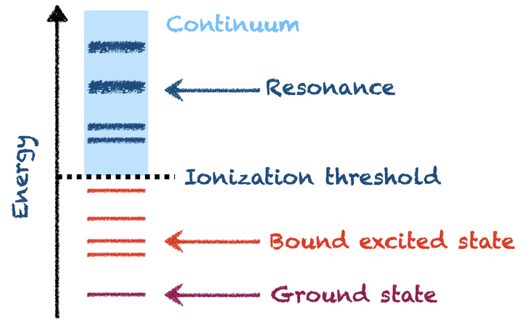
- 84 non-relativistic CVS-FCI values (73 second-row & 11 third-row IPs)
- aug-cc-pCVXZ (with core and diffuse functions)

Benchmark for Core IPs

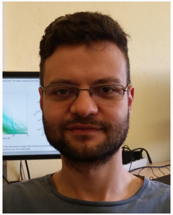


Benchmark for Core IPs





Jagau, Chem. Comm. 58 (2022) 5205

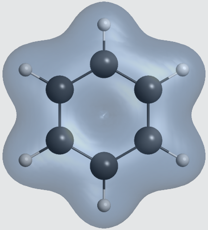


Yann Damour (PhD) Fábris Kossoski (Postdoc)

Damour, Kossoski & Loos, JPCL 15 (2024) 8296
Burth, Kossoski & Loos, JCTC 21 (2025) 11463

Photochemistry

$$h\nu + AB \rightarrow \boldsymbol{AB^*} \rightarrow A + B$$

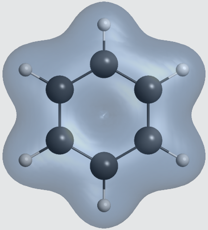


Bound state

Chemistry With Electrons Instead of Photons

Photochemistry

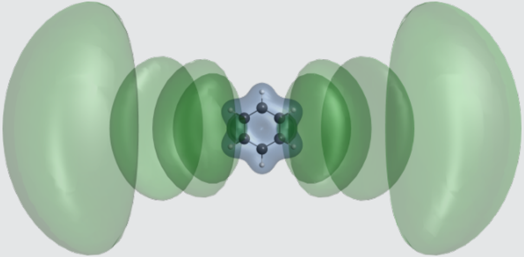
$$h\nu + AB \rightarrow \boldsymbol{AB^*} \rightarrow A + B$$



Bound state

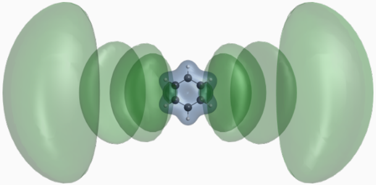
Low-energy electron-induced chemistry

$$e^- + AB \rightarrow \boldsymbol{AB^-} \rightarrow A^- + B$$
$$\rightarrow e^- + AB^*$$



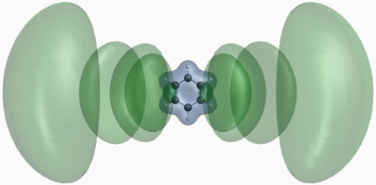
Resonance

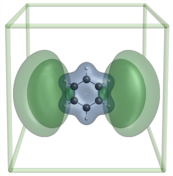
Complex Absorbing Potential (CAP)



Riss & Meyer, JPB 26 (1993) 4503

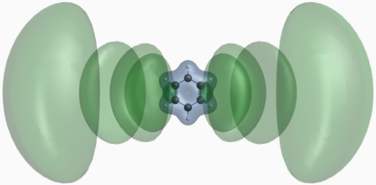
Complex Absorbing Potential (CAP)

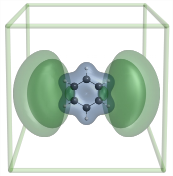




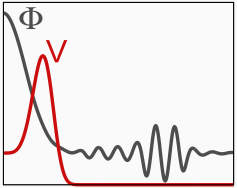
Riss & Meyer, JPB 26 (1993) 4503

Complex Absorbing Potential (CAP)





$$H = T + V$$



Riss & Meyer, JPB 26 (1993) 4503

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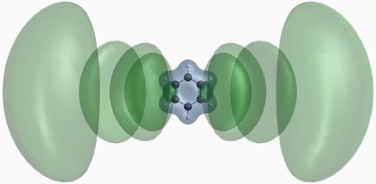
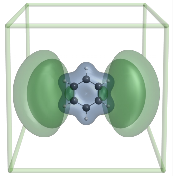
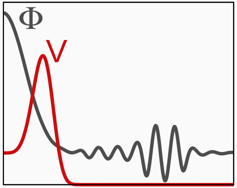
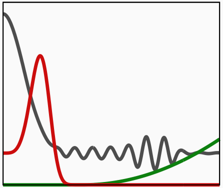




$H = T + V$

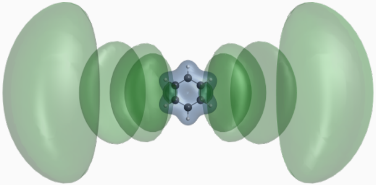
$H(\eta) = T + V - i\eta W$

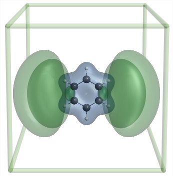




Riss & Meyer, JPB 26 (1993) 4503

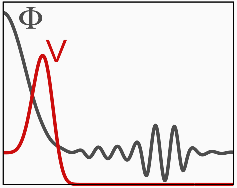
Complex Absorbing Potential (CAP)

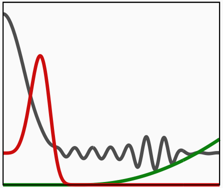


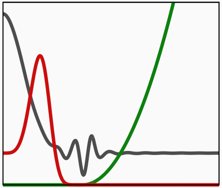


$H = T + V$

$H(\eta) = T + V - i\eta W$







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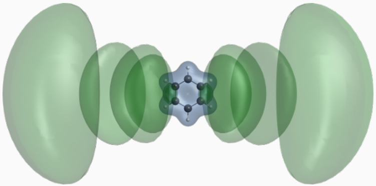
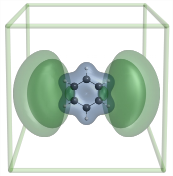
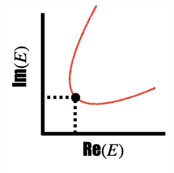
Complex Absorbing Potential (CAP)







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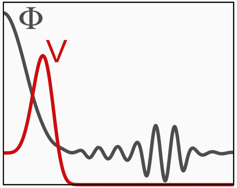

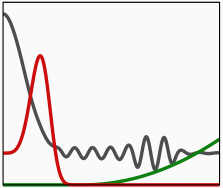

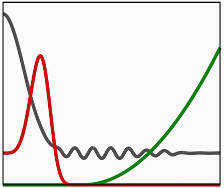

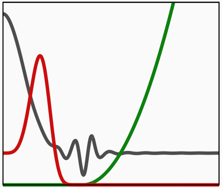

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Complex-valued energy

CAP Hamiltonian → $\hat{H}(\eta)$; Absorbing potential → $\hat{W}$

$$\hat{H}(\eta) = \hat{T} + \hat{V} - i\eta \hat{W} \quad (\eta > 0)$$

Energy → E; Resonance position → E_R; Resonance width → Γ

$$E = E_R - i\,\Gamma/2$$

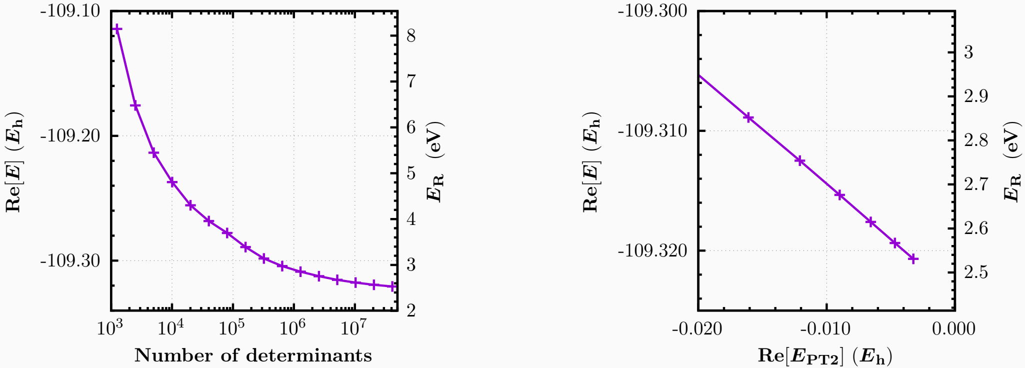
NB: $1/\Gamma$ is proportional to the resonance lifetime

N_2^-/aug-cc-pVTZ+3s3p3d

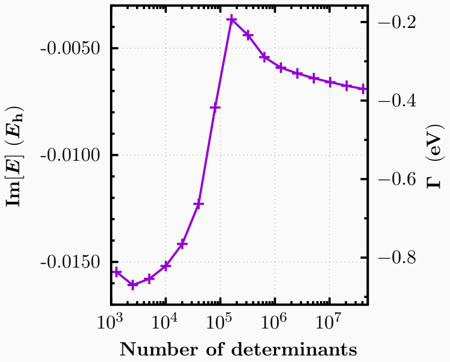
Method	E_R (eV)	Γ (eV)
Experiment[1]	2.316	0.414
CAP-EA-EOM-CCSD[2]	2.487	0.417
CAP-CIPSI	2.449(1)	0.391(3)

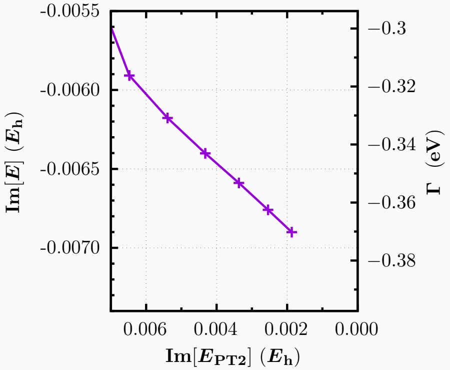
[1] Berman et al. PRA 28 (1983) 1363
[2] Zuev et al. JCP 141 (2014) 024102

Resonance Position



Resonance Width



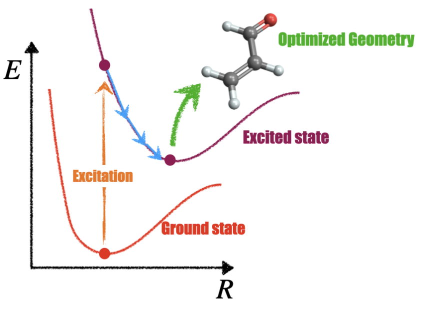


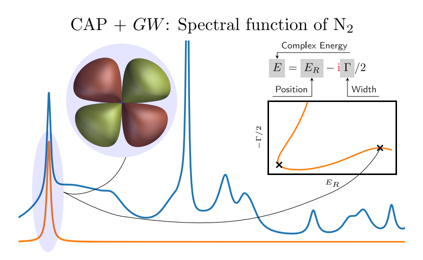
The *GW* Approximation and Beyond

- BSE@*GW* analytic derivatives for geometry optimization (and more)
  Tölle, JPCL 16 (2025) 3672; Tölle, Kitsaras & Loos, JPCL 16 (2025) 11134; Kitsaras, Tölle & Loos, JCP 164 (2026) 044122

- CAP-*GW* for transient anions
  Burth, Kossoski & Loos, JCTC 21 (2025) 11463

- Beyond *GW*
  - Parquet theory
    Marie & Loos, JCP 163 (2025) 194115
  - Connection between (extended) coupled-cluster theory and *GW*
    Tölle, Kitsaras, Irmler, Grüneis & Loos, arXiv:2602.10887
  - Algebraic-diagrammatic construction of $G3W2$
    Marie, Tölle & Loos, in preparation





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- Collaborators: Johannes Tölle, Hugh Burton, Pina Romaniello & Xavier Blase

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