Selected CI for Excited States

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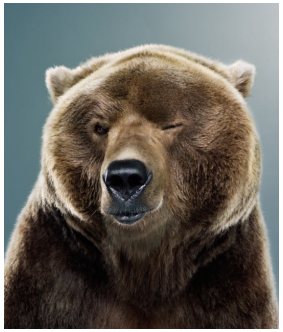
4th September 2019

Anthony Scemama



Yann Garniron

Michel Caffarel

Manu Giner

Martial Boggio-Pasqua

Mika Véril

Denis Jacquemin

Julien Toulouse

Section 2

Selected CI: Theory

CIPSI = CI using a Perturbative Selection made Iteratively

- Based on old idea by Bender and Davidson, and Whitten and Hackmeyer
  Bender & Davidson, Phys. Rev. 183 (1969) 23
  Whitten & Hackmeyer, JCP 51 (1969) 5584

- Further developments in Toulouse many years ago
  Huron, Malrieu & Rancurel, JCP 58 (1973) 5745

- CIPSI $\approx$ deterministic version of FCIQMC
  Caffarel et al., Recent Progress in Quantum Monte Carlo (2016) Chap. 2, 15-46.

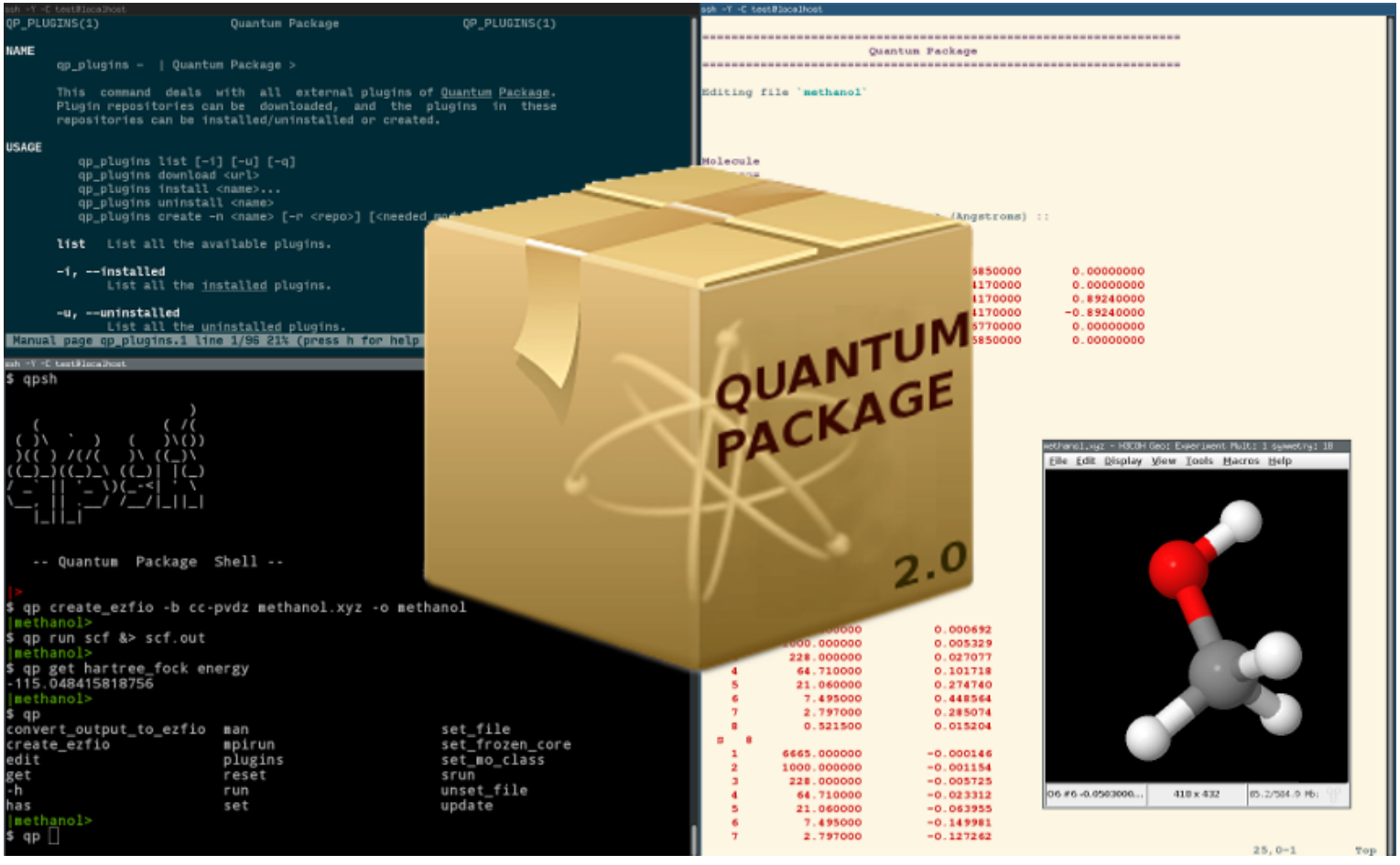
- CIPSI is a good candidate for massively parallel wave function calculations
  Giner, Scemama & Caffarel, JCP 142 (2015) 044115
  Caffarel et al., JCP 144 (2016) 151103

Flavours of

"sCI methods provide near full CI (FCI) quality energies with only a small fraction of the determinants of the FCI space"

- CIPSI (Malrieu, Evangelisti, Angeli, Spiegelman, Caffarel, Scemama, etc)
- Heat-bath CI (Sharma & Umrigar)
- Adaptive sampling CI (Evangelista & Tubman)
- Incremental CI (Zimmerman)
- Iterative CI (Liu & Hoffmann)
- FCIQMC (Alavi & Booth)
- ...

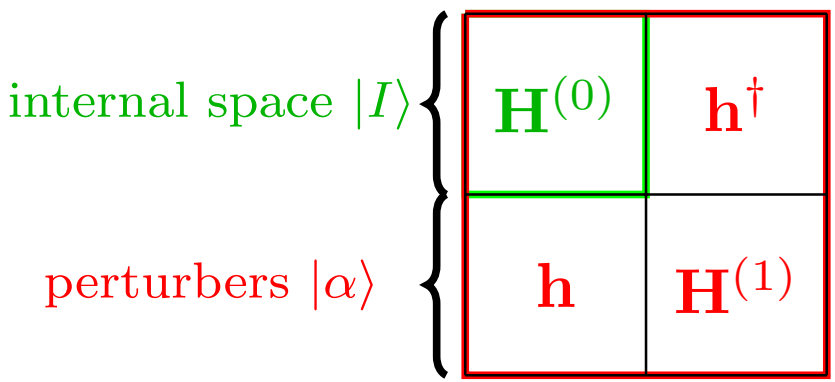
Quantum Package 2.0: the greatest thing since sliced baguette



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

Internal vs External

- **Green:** reference/variational/internal wave function (zeroth-order or model space)
- **Red:** perturbers or external wave function (first-order or perturbative space)



CIPSI algorithm

1. Define a (zeroth-order) *reference* wave function:

$$|\Psi^{(0)}\rangle = \sum_{I \in \mathcal{D}} c_I |I\rangle \qquad E^{(0)} = \frac{\langle \Psi^{(0)}|\hat{H}|\Psi^{(0)}\rangle}{\langle \Psi^{(0)}|\Psi^{(0)}\rangle}$$

2. Generate external determinants:

$$\mathcal{A} = \left\{ (\forall I \in \mathcal{D}) \left(\forall \hat{T} \in \mathcal{T}_1 \cup \mathcal{T}_2 \right) : |\alpha\rangle = \hat{T}\,|I\rangle \right\}$$

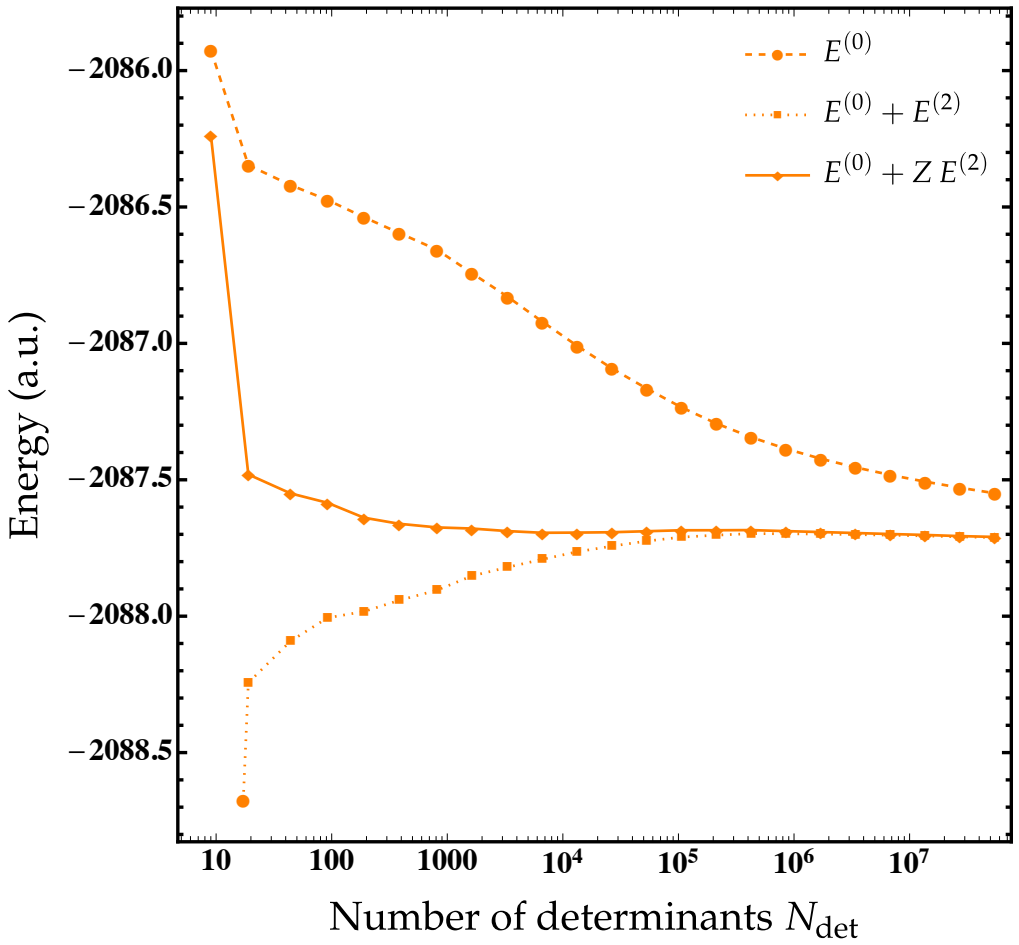
3. Second-order perturbative contribution of each $|\alpha\rangle$:

$$\delta E(\alpha) = \frac{|\langle \Psi^{(0)}|\hat{H}|\alpha\rangle|^2}{E^{(0)} - \langle \alpha|\hat{H}|\alpha\rangle}$$

4. Select $|\alpha\rangle$ with largest $\delta E(\alpha)$ and add them to $\mathcal{D}$
5. Diagonalize $\hat{H}$ in $\mathcal{D} \Rightarrow$ update $|\Psi^{(0)}\rangle$ and $E^{(0)}$
6. Iterate

Huron, Malrieu & Rancurel, JCP 58 (1973) 5745
Giner, Scemama & Caffarel, JCP 142 (2015) 044115

Ground state of Cr_2 in cc-pVQZ: full-valence CAS(28e,198o)



Garniron et al., JCTC 15 (2019) 3591

Few remarks...

- When all $|I\rangle$ are selected, we obtain the FCI energy
- CIPSI is more an algorithm than a method
- Most of wave function methods can be performed à la CIPSI:
  CIS, CID, CISD, CISDT, CAS, CASSD, MRCI, CC, MRCC, etc.

How do we know how far we are from the FCI limit?

- Second-order Epstein-Nesbet correction:

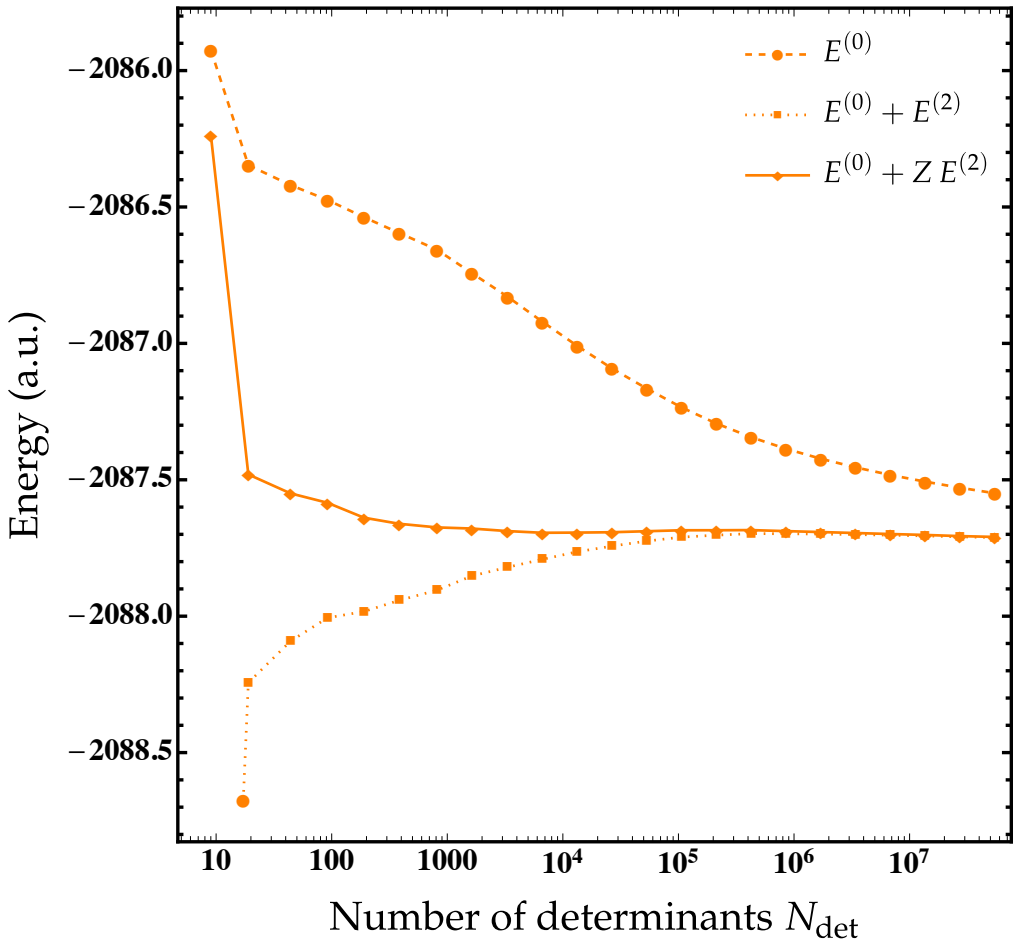
$$\boxed{E^{(2)} = \sum_{\alpha} \delta E(\alpha)}$$

- $|\alpha\rangle$'s with largest $\delta E(\alpha)$ have been added to $\Psi^{(0)}$ previously
  $\Rightarrow$ a *very* large number of *very* small contributions

- In practice, we use a semi-stochastic algorithm to compute $E^{(2)}$
  $\Rightarrow$ much faster!!
  Garniron, Scemama, Loos & Caffarel, JCP 147 (2017) 034101

- We extrapolate to $E^{(2)} = 0$ to reach the FCI limit (exFCI)

Ground state of Cr_2 in cc-pVQZ: full-valence CAS(28e,198o)

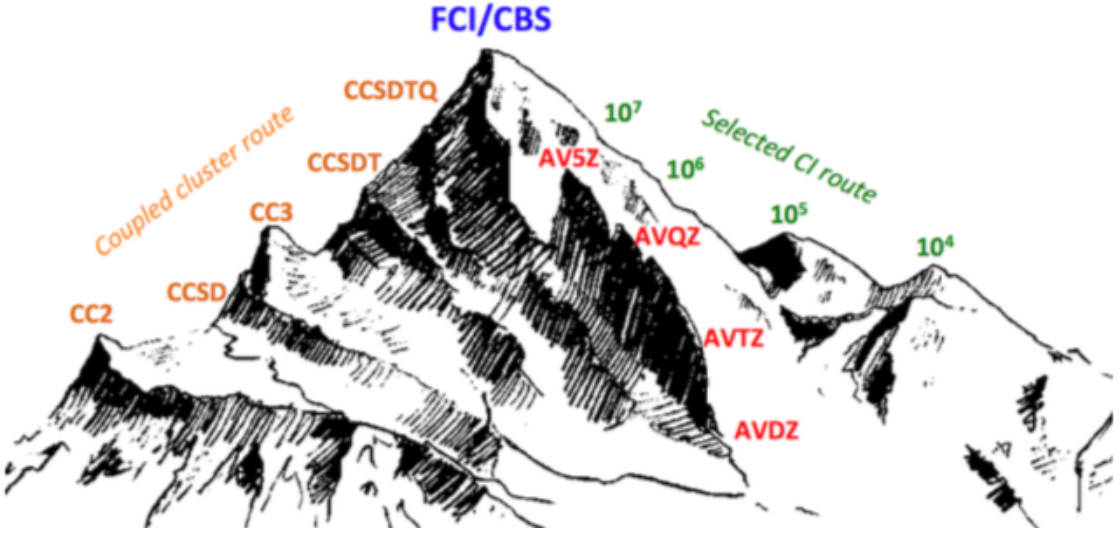


Garniron et al., JCTC 15 (2019) 3591

Section 3

Selected CI: Applications

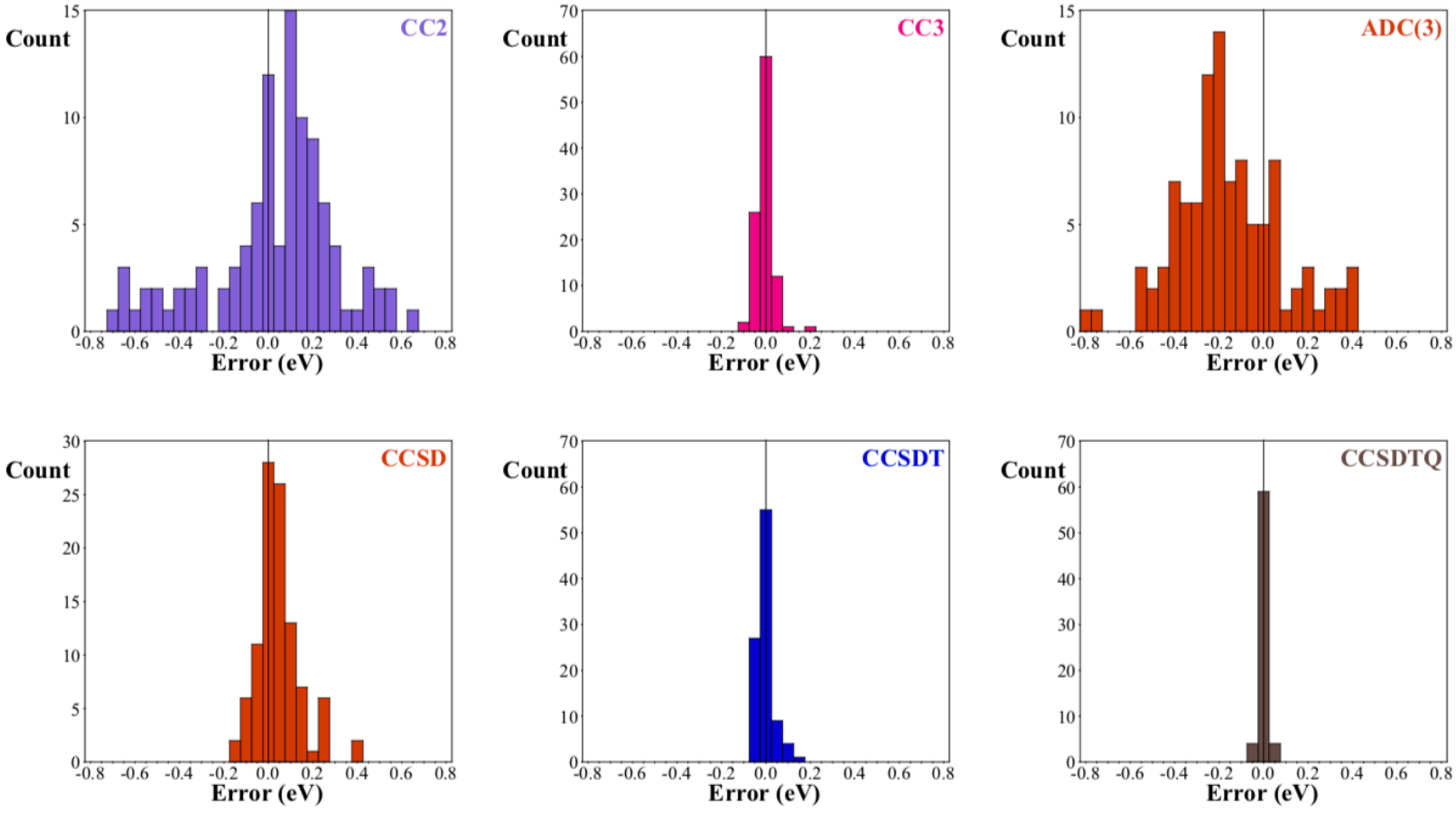
Highly-accurate reference energies for excited states



- 18 small molecules and 110 transition energies of various characters (valence, Rydberg, singlet, triplet, $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$, double excitations, etc)
- High-level CC calculations (up to CCSDTQP)
- sCI calculations (up to several millions of determinants)
- Large (diffuse) basis sets (AVXZ)

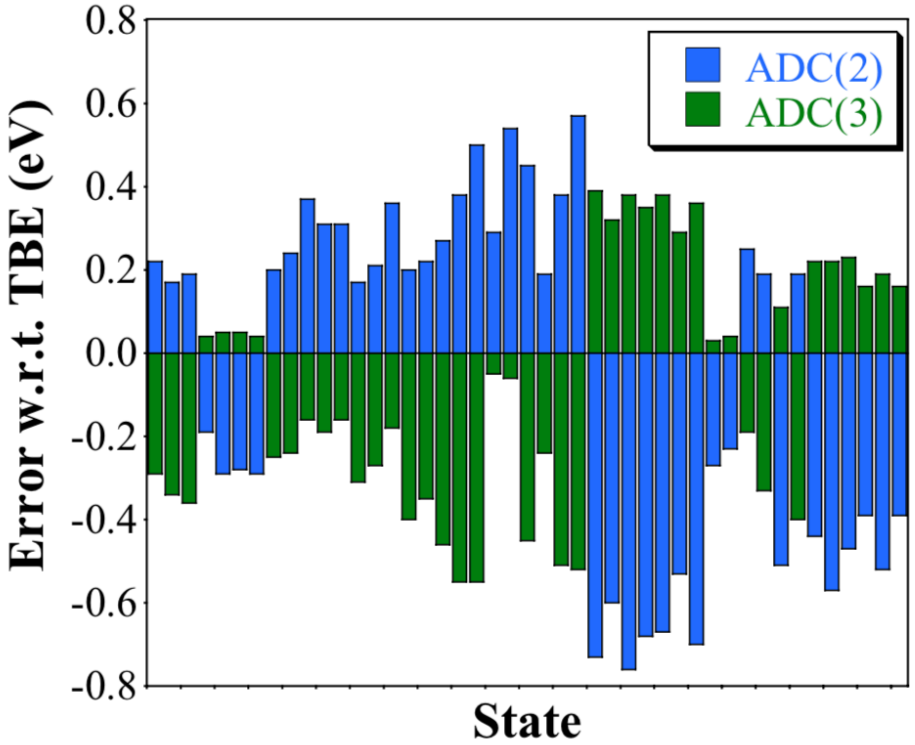
Loos, Scemama, Blondel, Garniron, Caffarel & Jacquemin JCTC 14 (2018) 4360

Benchmarking excited-state methods vs TBE/cc-pVTZ



Loos, Scemama, Blondel, Garniron, Caffarel & Jacquemin JCTC 14 (2018) 4360

Errors in ADC(2) & ADC(3) for states with large (> 0.15 eV) ADC(2) error



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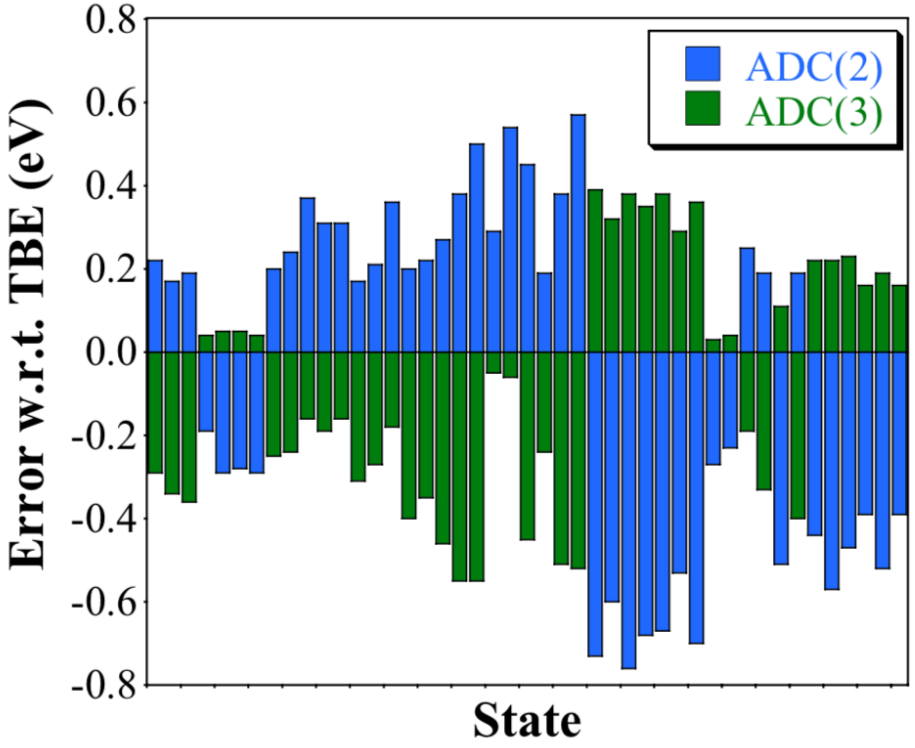
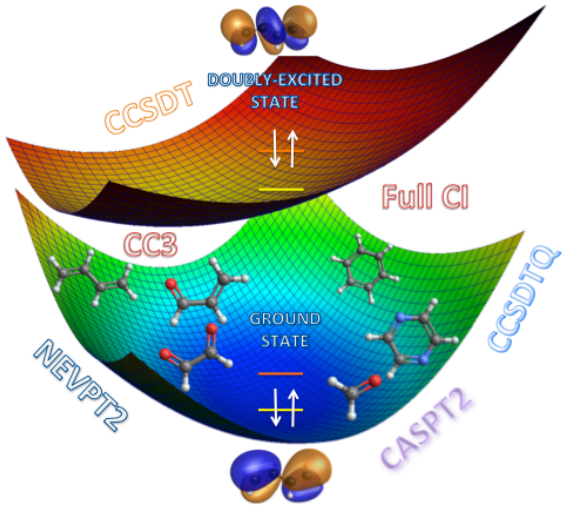
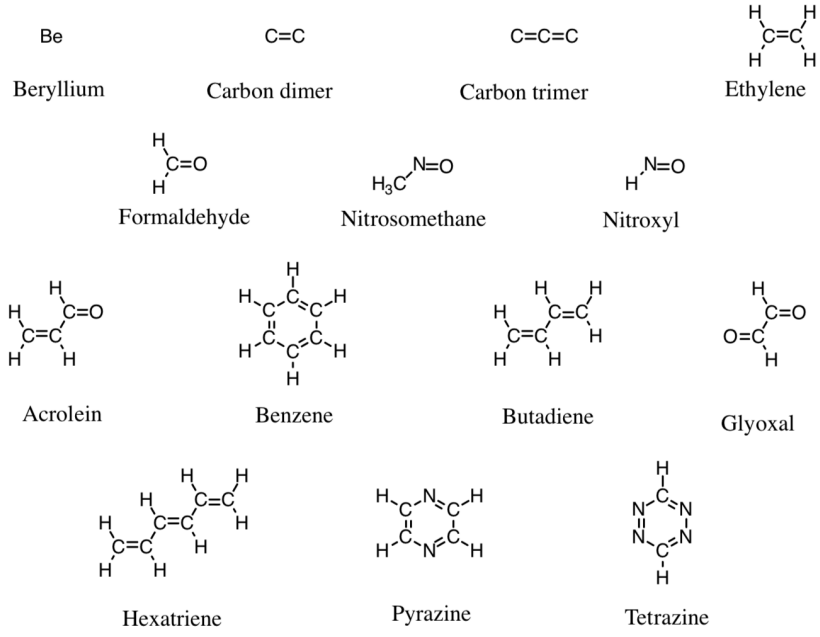


C'mon Q-Chem, we need ADC(2.5)!!

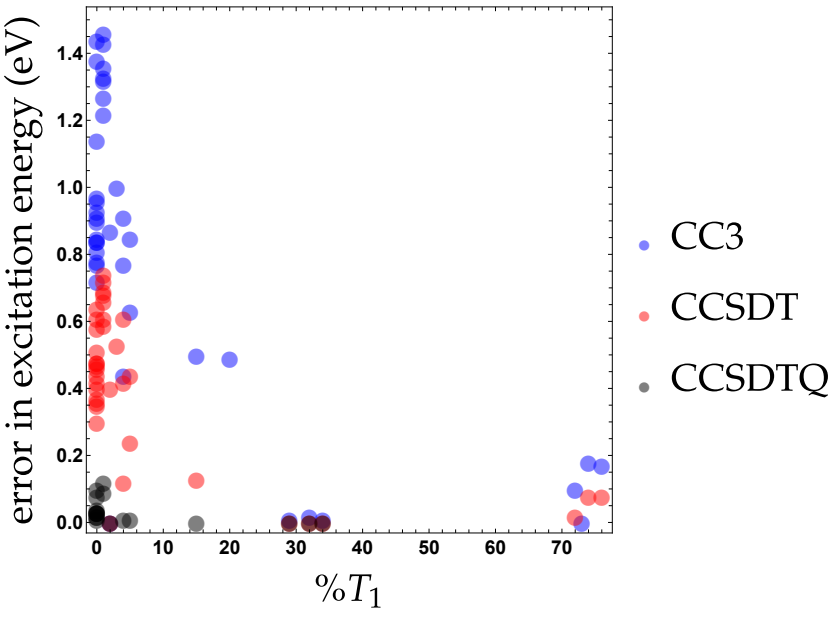
Reference energies for double excitations

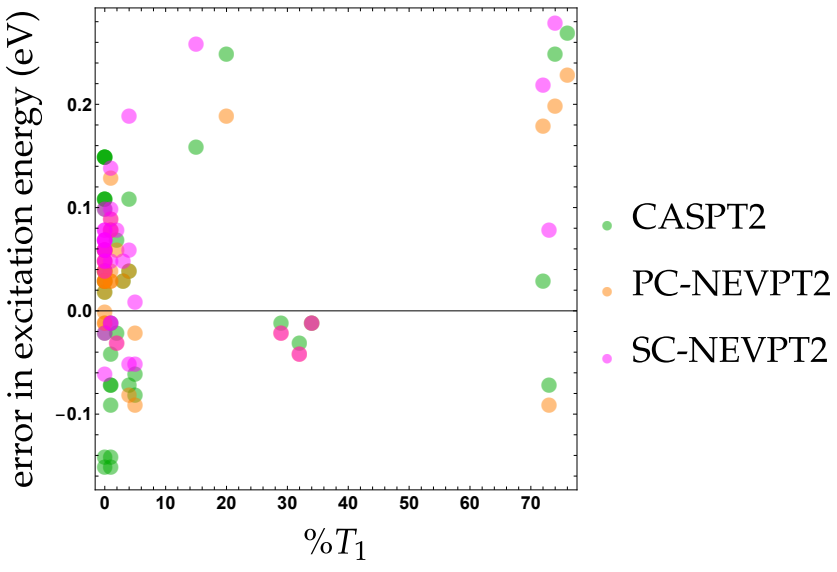




Loos, Boggio-Pasqua, Scemama, Caffarel & Jacquemin, JCTC 15 (2019) 1939

Reference energies for double excitations





Loos, Boggio-Pasqua, Scemama, Caffarel & Jacquemin, JCTC 15 (2019) 1939

Highly-Accurate Reference Excitation Energies and Benchmarks: Medium Size Molecules

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‡*Dipartimento di Chimica e Chimica Industriale, University of Pisa, Via Moruzzi 3, 56124 Pisa, Italy*

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Section 4

Selected CI: witness the incompleteness

Some applications of dressing to configuration interaction matrices

Anthony Scemama, M. Caffarel, G. David, Y. Garniron, E. Giner, P.-F. Loos, J.-P. Malrieu,

3 September 2019

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

Scemama, Caffarel, Tew & Loos (in preparation)

sCI-based trial wave function for QMC

$$\Psi_T(\boldsymbol{R}) = e^{J(\boldsymbol{R})} \sum_I c_I D_I^{\uparrow}(\boldsymbol{R}^{\uparrow}) D_I^{\downarrow}(\boldsymbol{R}^{\downarrow})$$

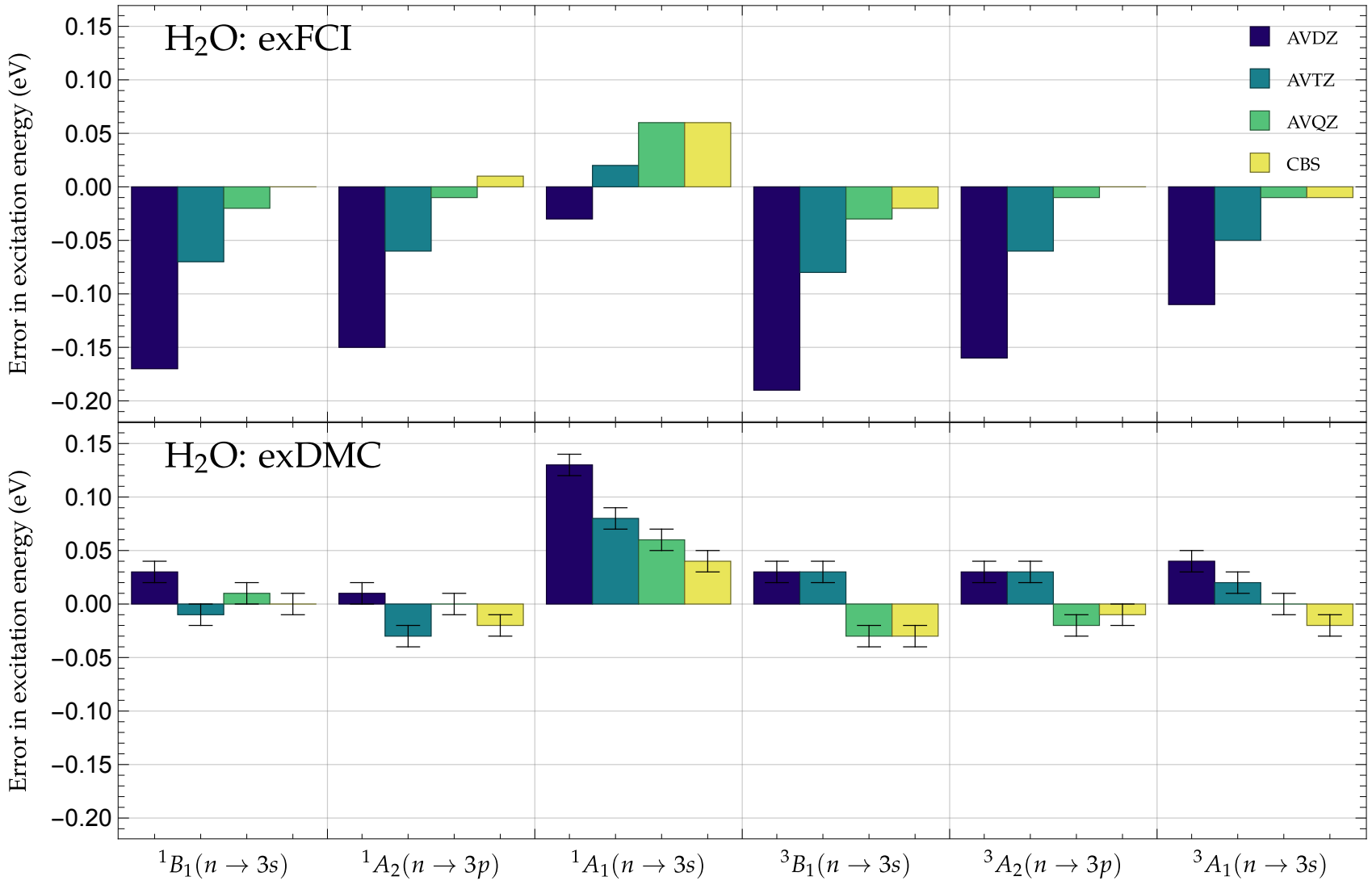
- The multideterminant part is obtained via the (selected CI) CIPSI algorithm
  Giner et al. CJC 91 (2013) 879; JCP 142 (2015) 044115
  Caffarel et al. JCP 144 (2016) 151103

- We may or may not use a "minimal" (nodeless) Jastrow $J(\boldsymbol{R})$
  $\Rightarrow$ Deterministic construction of the nodal surface
  Scemama, Garniron, Caffarel & Loos, JCTC 14 (2018) 1395

- Roughly speaking: DMC "completes" the basis...

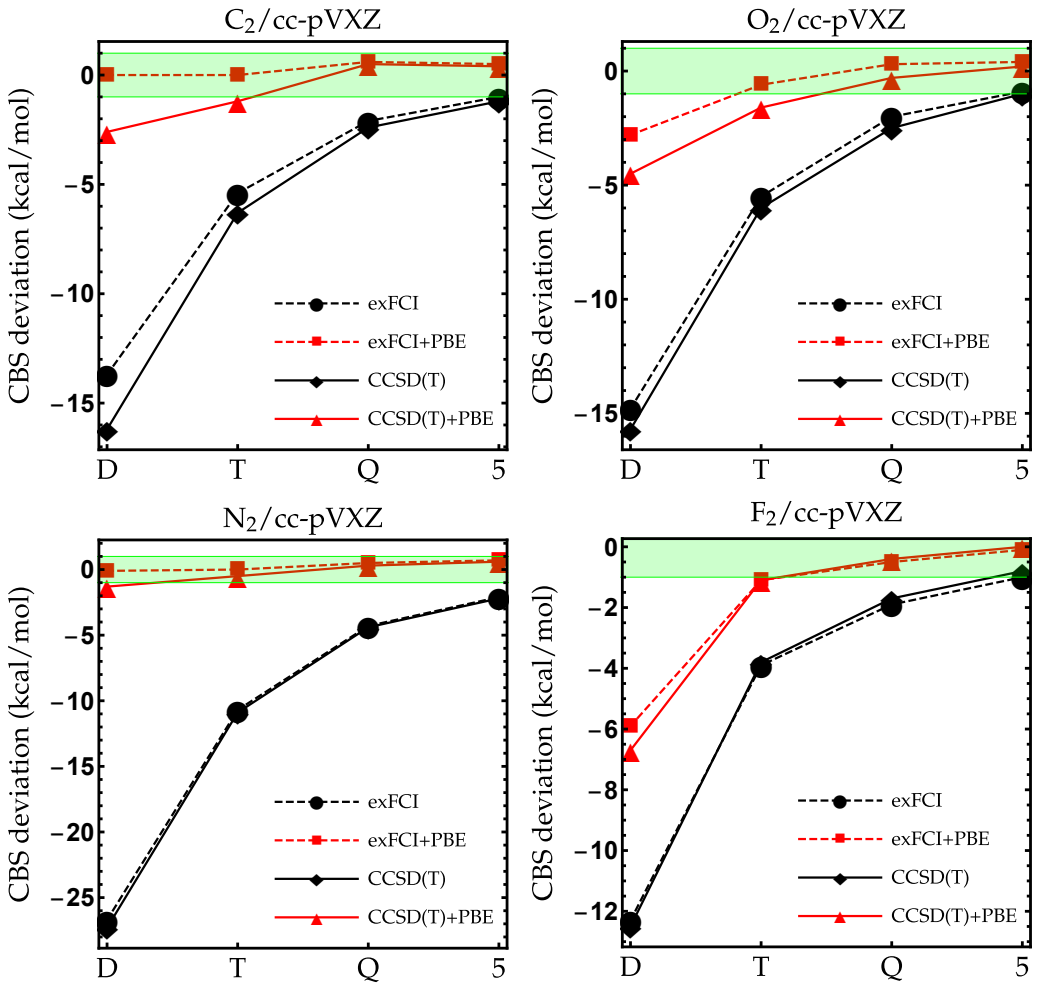
- Open-source code: QMC=CHEM (A. Scemama)
  https://github.com/scemama/qmcchem

Fixed-node error in excited states: (all-electron) water

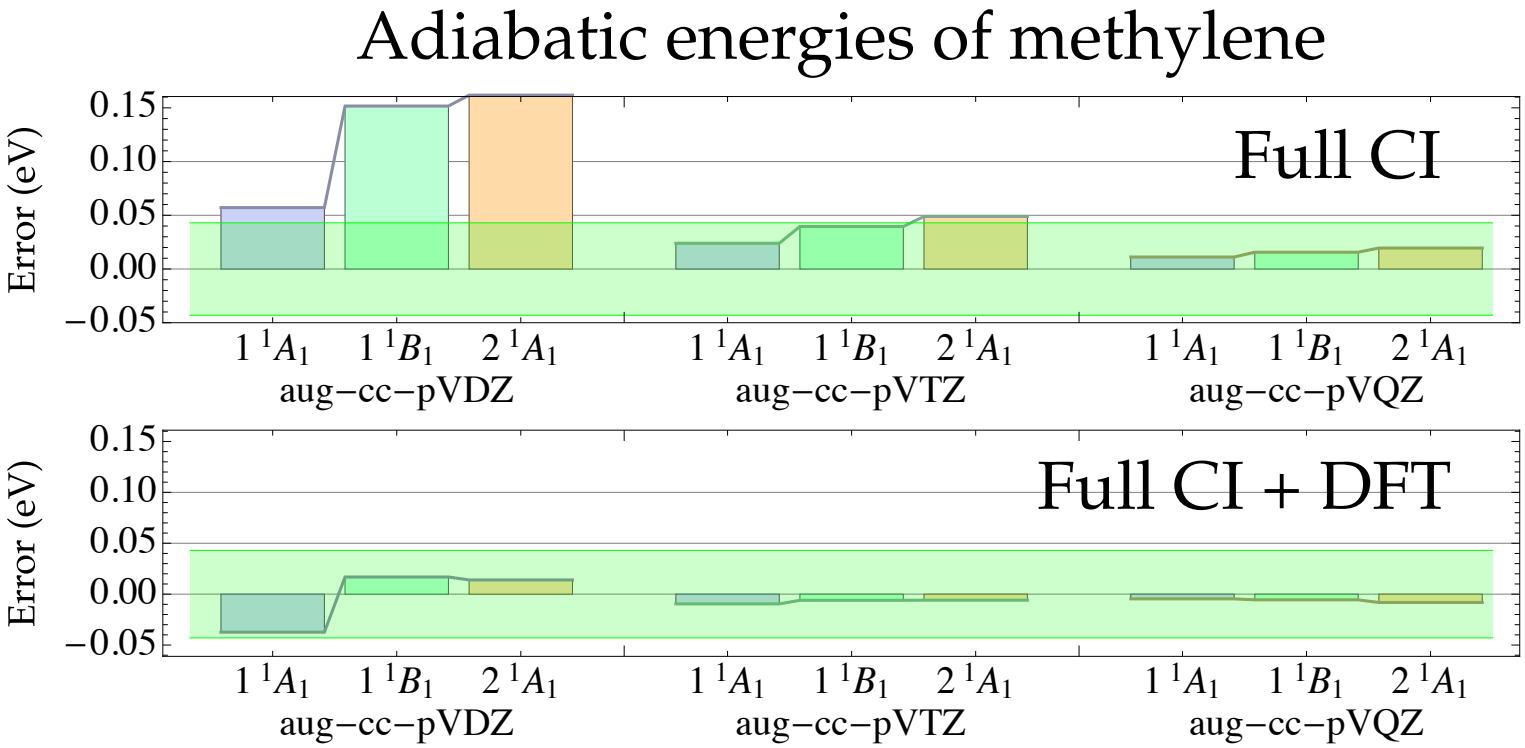


Scemama, Benali, Jacquemin, Caffarel & Loos, JCP 149 (2018) 034108

Range-separated hybrids are actually useful!!

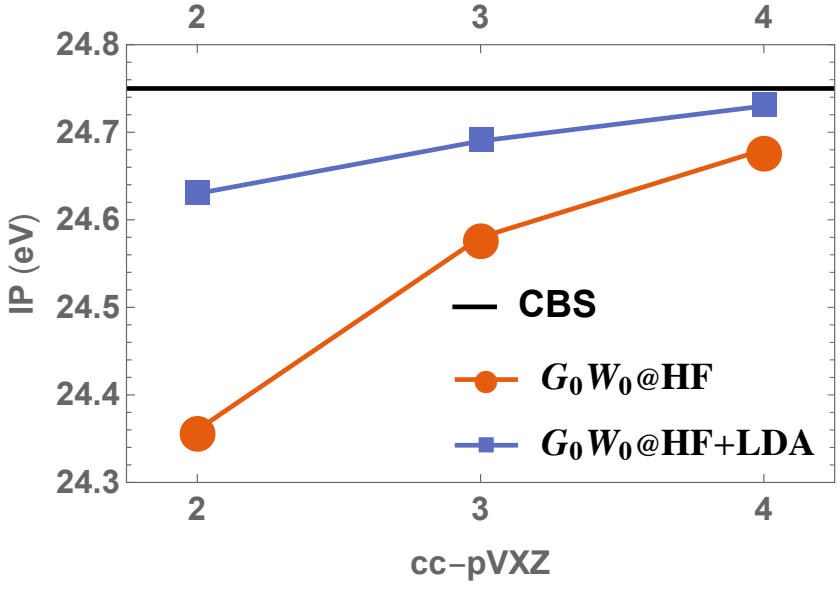


"A Density-Based Basis-Set Correction for Wave Function Theory",
Loos, Pradines, Scemama, Toulouse & Giner, JPCL 10 (2019) 2931

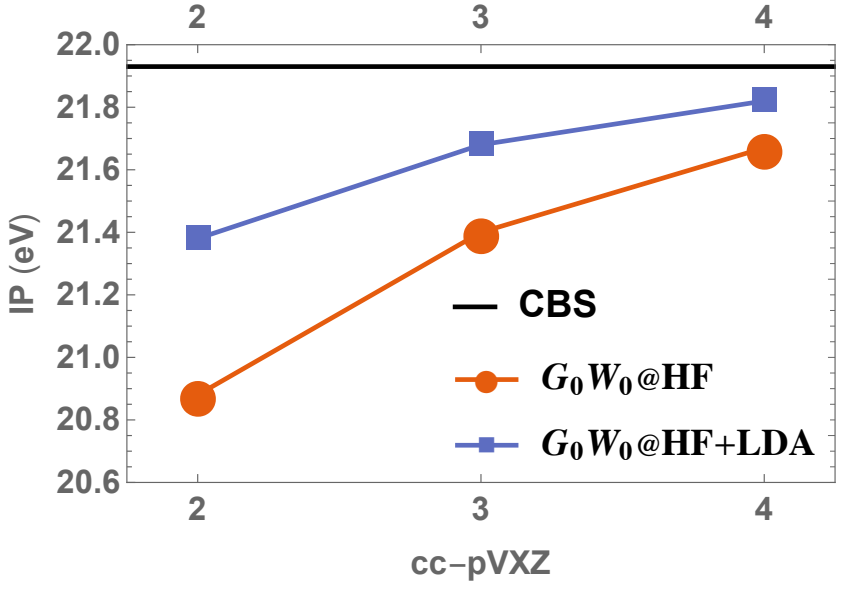


"Chemically Accurate Excitation Energies With Small Basis Sets",
Giner, Scemama, Toulouse & Loos, JCP (submitted) arXiv:1907.01245

IP of the helium atom

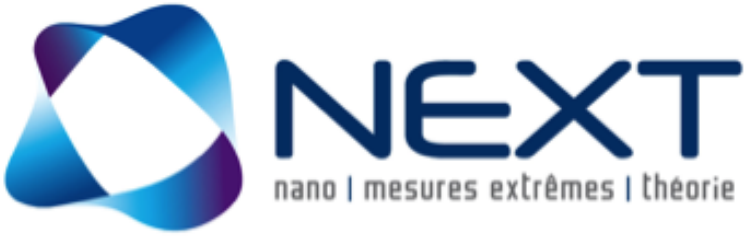


IP of the neon atom



Loos, Pradines, Scemama, Giner & Toulouse (in preparation)

Thank you!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