Selected CI and Jastrow-free QMC methods for Chemistry

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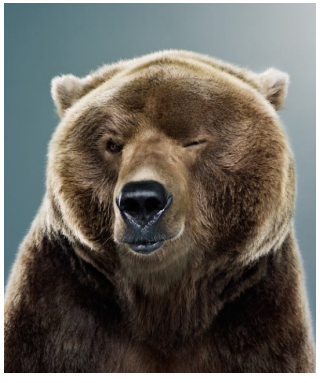
29th Aug 2018

Collaborators

Anthony Scemama



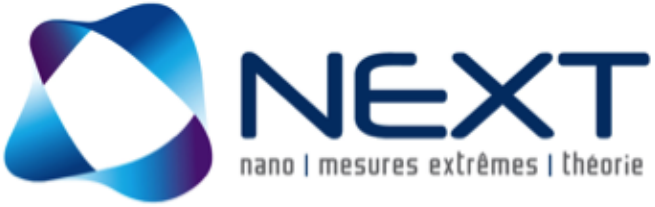
Yann Garniron

Michel Caffarel

Denis Jacquemin

Agencies I would like to thank...

Agencies I don't want to thank...



Section 2

Selected CI

Flavours of selected CI (sCI)

"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)
- ...

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

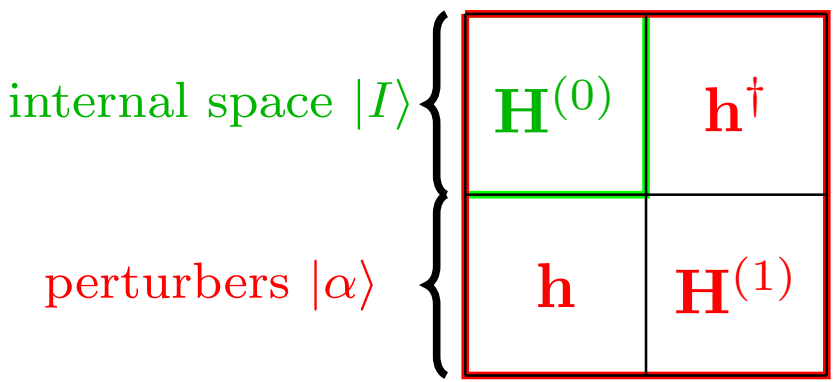
- CIPSI $\approx$ deterministic version of FCIQMC
  Caffarel et al., Recent Progress in Quantum Monte Carlo (2016) Chap. 2, 15-46.

- 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

- Open-source code: QUANTUM PACKAGE (A. Scemama)
  https://github.com/scemama/quantum_package

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:

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

2. Generate external determinants:

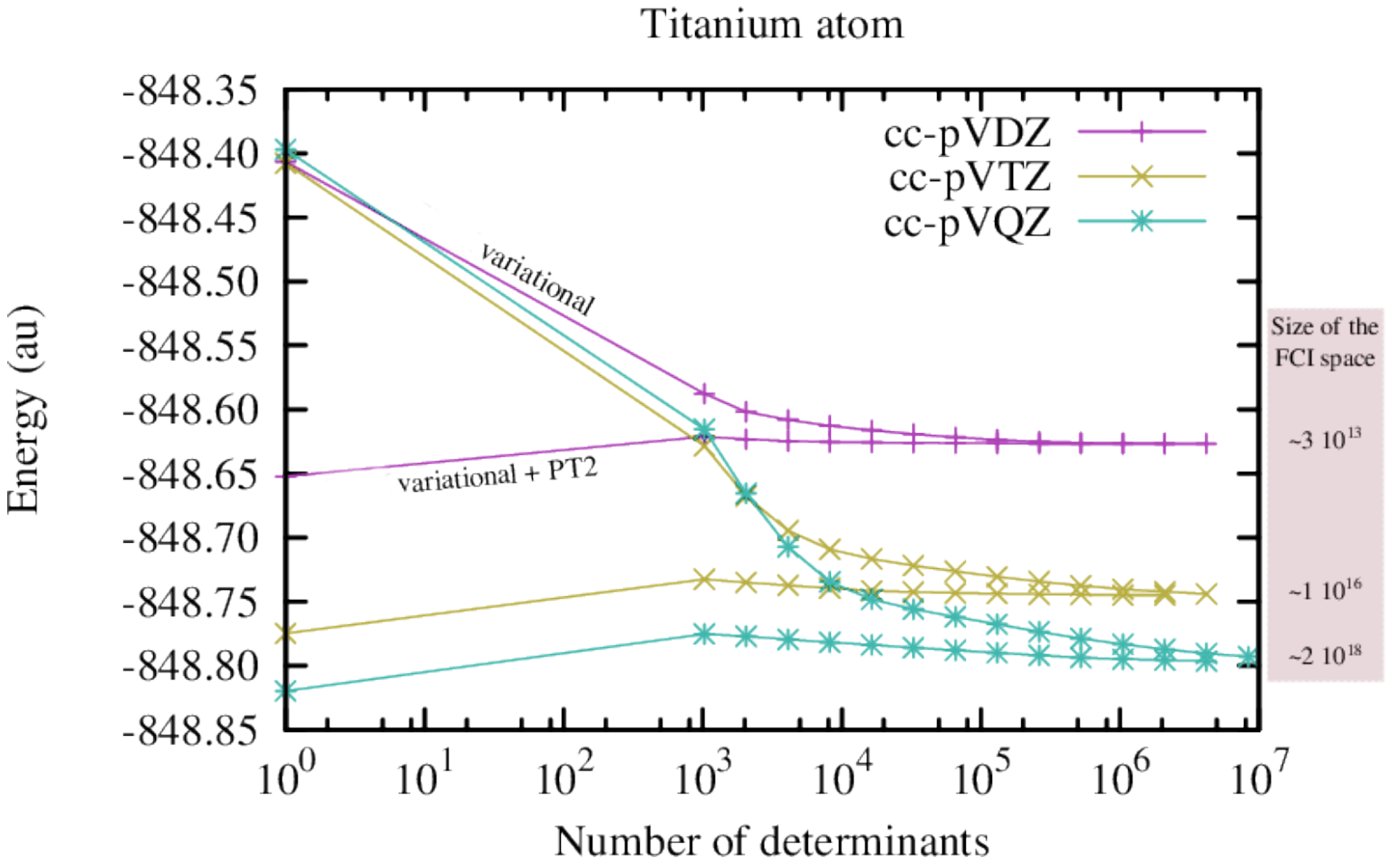
$$\mathcal{A} = \left\{ (\forall I \in \mathcal{D}) \left(\forall \hat{T} \in \mathcal{T}_1 \cup \mathcal{T}_2 \right) : |\alpha\rangle = \hat{T}\,|I\rangle \right\}$$

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


Titanium atom
Energy (au)
-848.35
-848.40
-848.45
-848.50
-848.55
-848.60
-848.65
-848.70
-848.75
-848.80
-848.85
10^0
10^1
10^2
10^3
10^4
10^5
10^6
10^7
Number of determinants
cc-pVDZ
cc-pVTZ
cc-pVQZ
variational
variational + PT2
Size of the FCI space
~3 10^{13}
~1 10^{16}
~2 10^{18}

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?

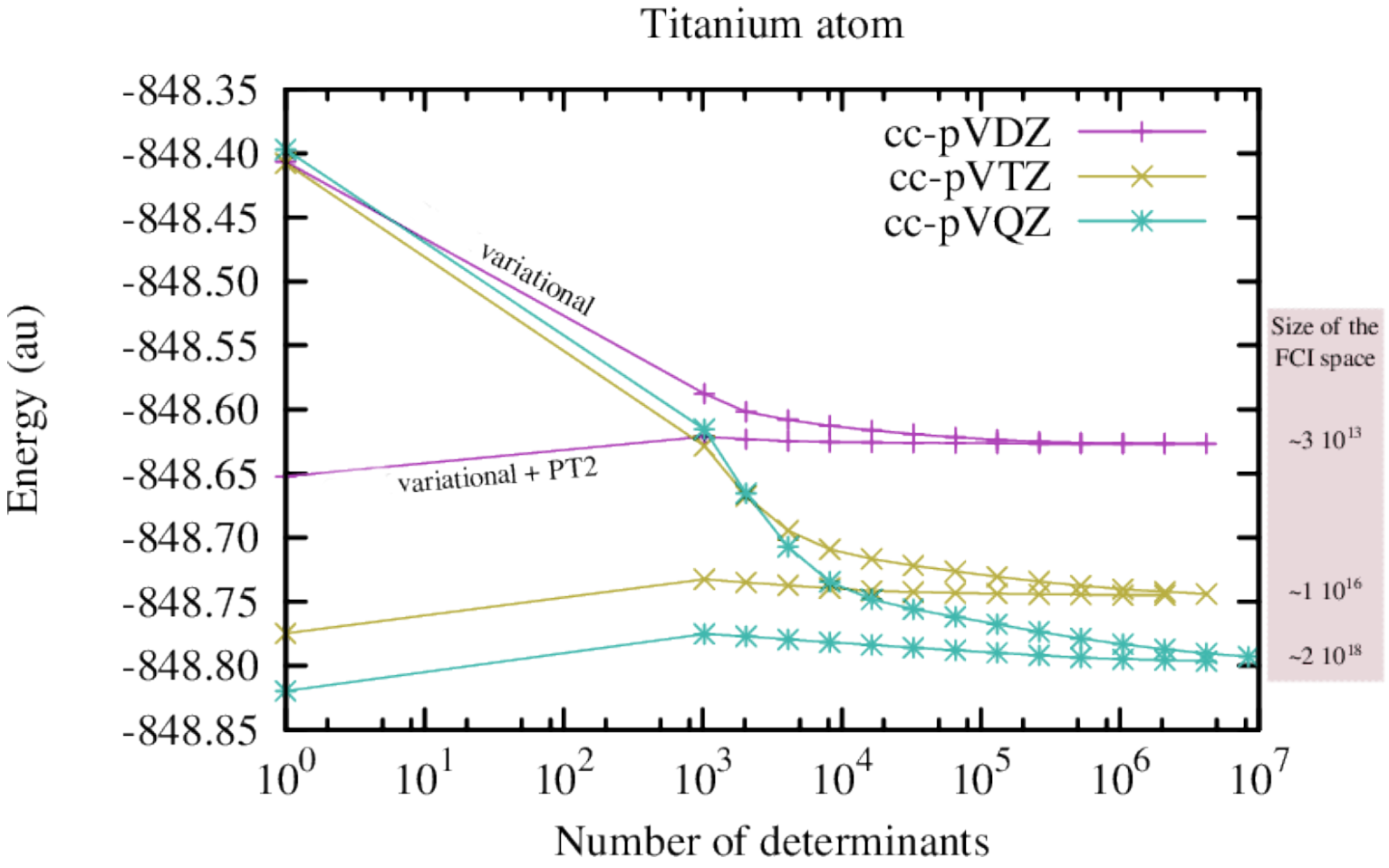
- Second-order Epstein-Nesbet correction:

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

- $|\alpha\rangle$'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)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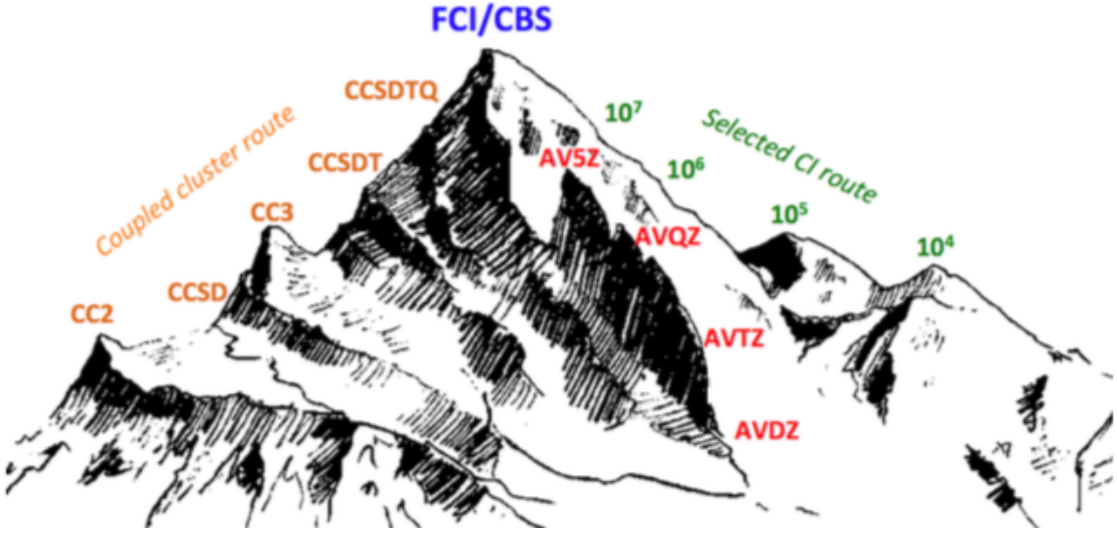
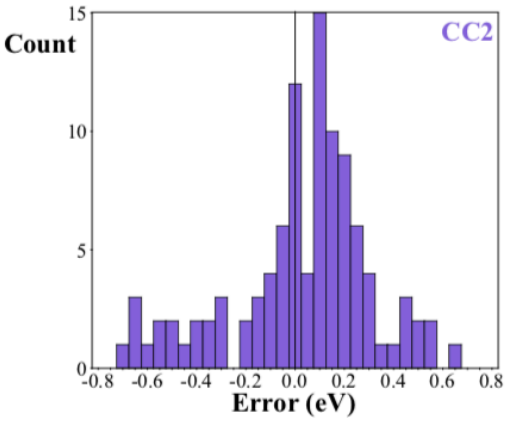
Highly-accurate reference energies for excited states

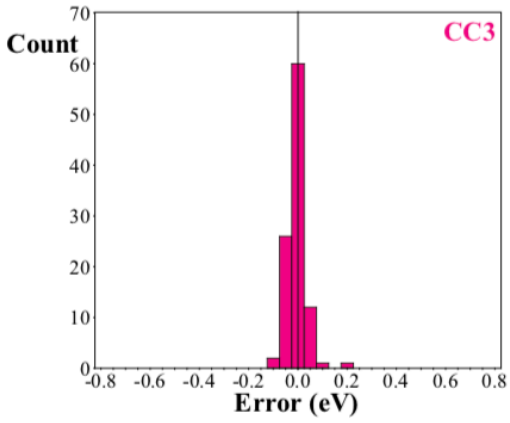


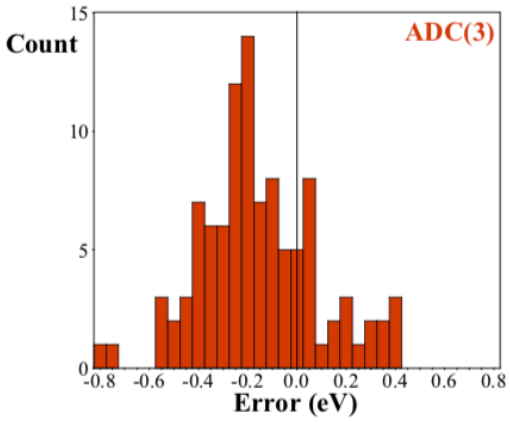
- 18 small molecules and 110 transition energies of various characters (valence, Rydberg, singlet, triplet, $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$, double excitations, etc)
- High-level CC calculations (up to CCSDTQP)
- sCI calculations (up to several millions of determinants)
- Large (diffuse)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

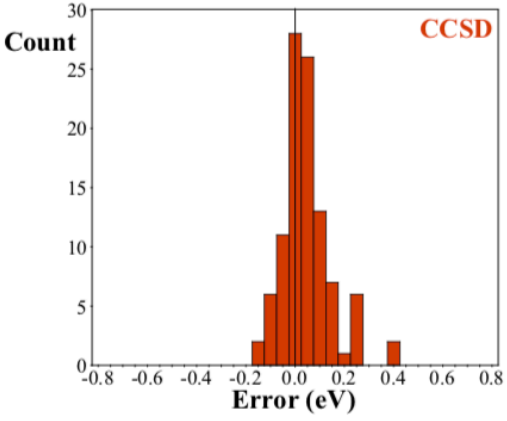
Loos, Scemama, Blondel, Garniron, Caffarel & Jacquemin JCTC 14 (2018) 4360

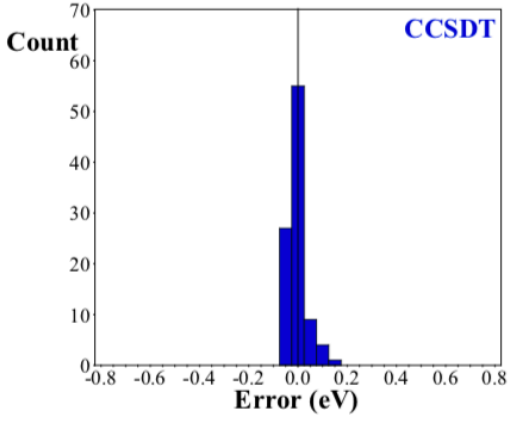
Benchmarking excited-state methods vs TBE/cc-pVTZ

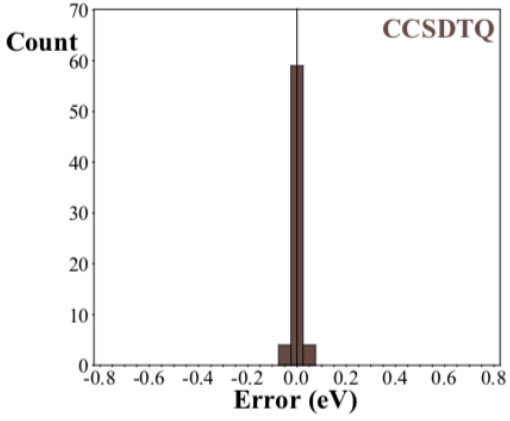












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Letter

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Theoretical 0−0 Energies with Chemical Accuracy

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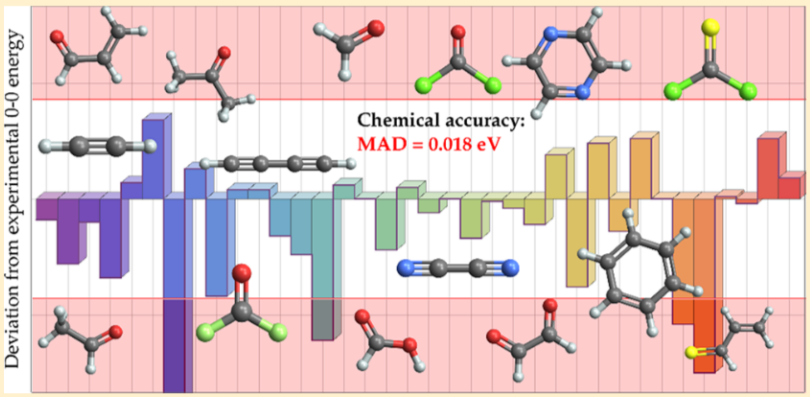
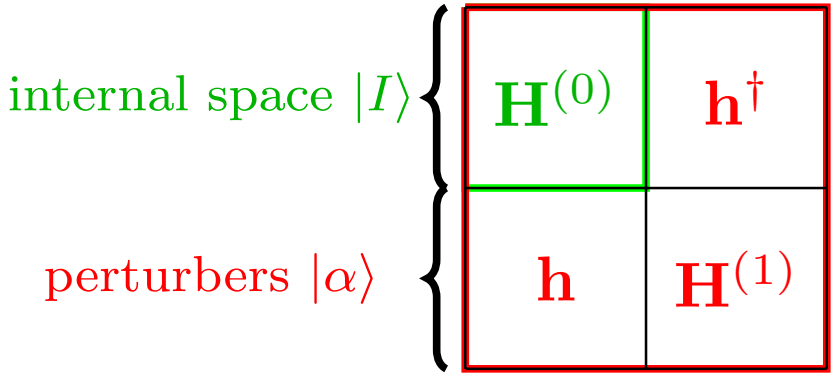
Supporting Information

ABSTRACT: Ab initio calculation of electronic excitation energies with chemical accuracy (ca. 1 kcal·mol^{-1} or 0.043 eV with respect to experiment) is a long-standing challenge in electronic structure theory. Indeed, the most advanced theories can, in practice, only be used to estimate vertical transition energies that cannot be measured experimentally, whereas the calculation of 0−0 energies requires excited-state structures and vibrations for both the ground and excited states, which drastically restrains the number of applicable methods. In this Letter, we present a composite computational protocol able to deliver chemically accurate theoretical 0−0 energies, with a mean absolute deviation of 0.018 eV for a set of 35 singlet valence states. Such accuracy, achievable for the valence states of small- and medium-sized molecules only, allows pinpointing questionable experimental assignments with very high confidence and constitutes a step toward quantitative prediction of excited-state properties.





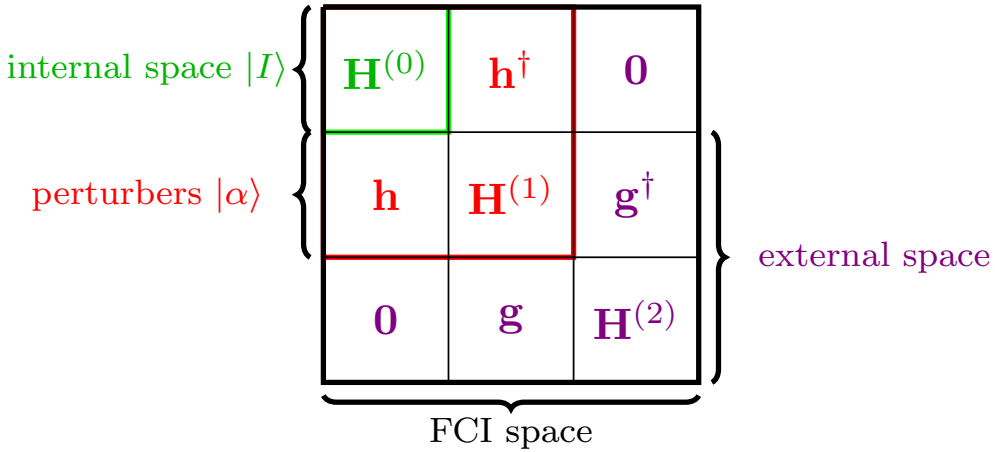
$$\mathbf{Hc} - E\mathbf{c} = \begin{pmatrix} \mathbf{H}^{(0)} & \mathbf{h}^\dagger \\ \mathbf{h} & \mathbf{H}^{(1)} \end{pmatrix} \begin{pmatrix} \mathbf{c}^{(0)} \\ \mathbf{c}^{(1)} \end{pmatrix} - E \begin{pmatrix} \mathbf{c}^{(0)} \\ \mathbf{c}^{(1)} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

$$\Rightarrow \mathbf{c}^{(1)} = -(\mathbf{H}^{(1)} - E\mathbf{I})^{-1}\mathbf{h}\,\mathbf{c}^{(0)}$$

Effective Hamiltonian: $\mathbf{H}_{\text{eff}} = \mathbf{H}^{(0)} + \mathbf{\Delta}$ Dressing term: $\mathbf{\Delta} = \mathbf{h}^\dagger \mathbf{c}^{(1)}$

Approximation #1 (Bk method): $\mathbf{\Delta}^{\text{Bk}} = \mathbf{h}^\dagger (E\mathbf{I} - \mathbf{D}^{(1)})^{-1}\mathbf{h}$

Gershgorn & Shavitt, IJQC 2 (1968) 751



$$\mathbf{Hc} - E\mathbf{c} = \begin{pmatrix} \mathbf{H}^{(0)} & \mathbf{h}^\dagger & \mathbf{0} \\ \mathbf{h} & \mathbf{H}^{(1)} & \mathbf{g}^\dagger \\ \mathbf{0} & \mathbf{g} & \mathbf{H}^{(2)} \end{pmatrix} \begin{pmatrix} \mathbf{c}^{(0)} \\ \mathbf{c}^{(1)} \\ \mathbf{c}^{(2)} \end{pmatrix} - E \begin{pmatrix} \mathbf{c}^{(0)} \\ \mathbf{c}^{(1)} \\ \mathbf{c}^{(2)} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}$$

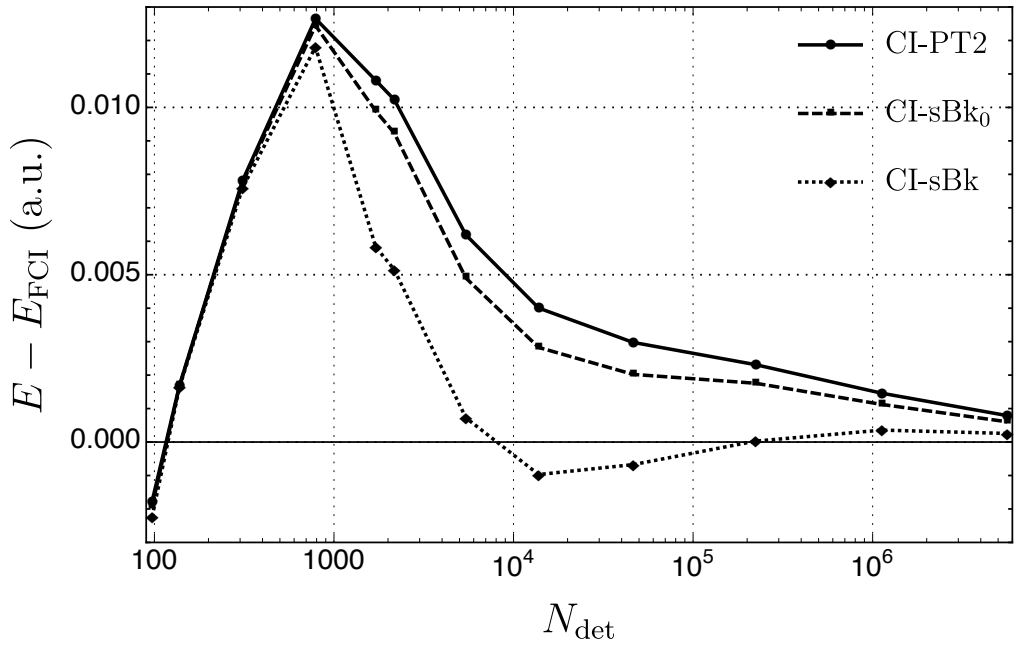
$$\Rightarrow \mathbf{c}^{(1)} = -\Big[(\mathbf{H}^{(1)} - E\mathbf{I}) - \mathbf{g}^\dagger(\mathbf{H}^{(2)} - E\mathbf{I})\mathbf{g}\Big]^{-1} \mathbf{h}\,\mathbf{c}^{(0)}$$

Effective Hamiltonian: $\mathbf{H}_{\text{eff}} = \mathbf{H}^{(0)} + \mathbf{\Delta}$ Dressing term: $\mathbf{\Delta} = \mathbf{h}^\dagger \mathbf{c}^{(1)}$

Approximation #2 (shifted-Bk method): $\mathbf{\Delta}^{\text{sBk}} = \mathbf{h}^\dagger (E^{(0)}\mathbf{I} - \mathbf{D}^{(1)})^{-1}\mathbf{h}$

Davidson, McMurchie & Day, IJQC 74 (1981) 5491

$^2\Pi_g$ ground state of the $CuCl_2$ (6-31G)



Garniron, Scemama, Giner, Caffarel & Loos, JCP 149 (2018) 064103

Comments

- Multi-state version also available
- Provides better trial wave functions for QMC

Section 3

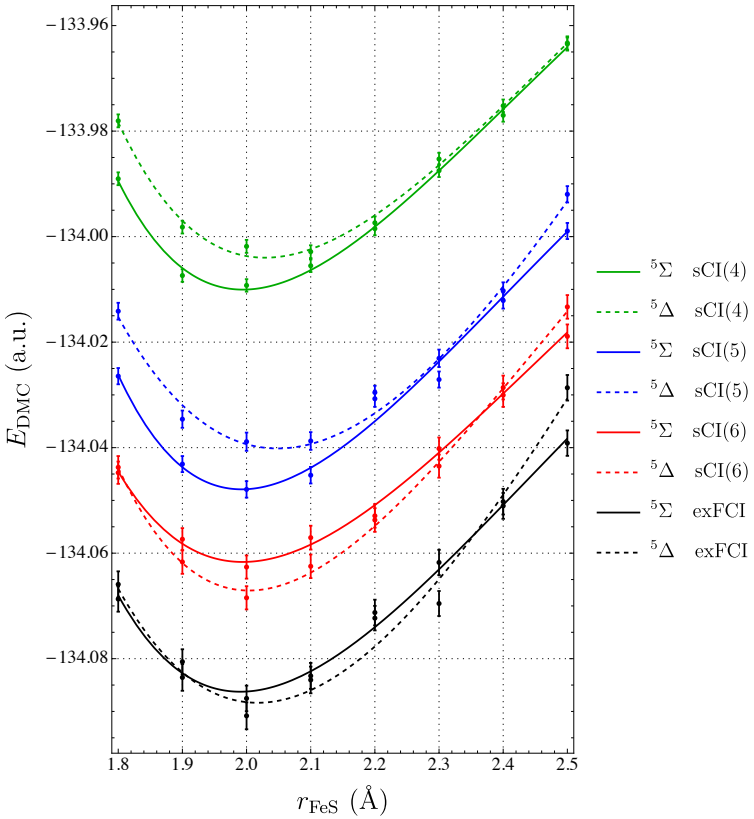
Quantum Monte Carlo

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
- Roughly speaking: DMC "complete" the basis...
- Open-source code: QMC=CHEM (A. Scemama)
  https://github.com/scemama/qmcchem
- Interface for QMCPACK also available!

Dissociation profile



Method[a]	ϵ	N_{det}	$N_{\mathrm{det}}^{\uparrow}$	$N_{\mathrm{det}}^{\downarrow}$	acronym
sCI	10^{-4}	15 723	191	188	sCI(4)
	10^{-5}	269 393	986	1 191	sCI(5)
	10^{-6}	1 127 071	3 883	4 623	sCI(6)
	0	8 388 608	364 365	308 072	sCI(∞)
exFCI	—	$\sim 10^{27}$	$\sim 10^{16}$	$\sim 10^{11}$	FCI

[a] Basis set: VTZ-ANO-BFD for Fe and VTZ-BFD for S

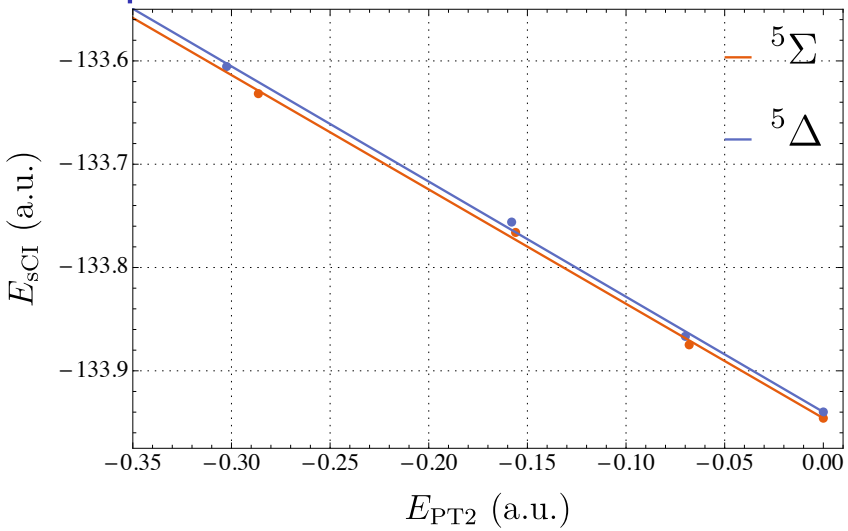
What	Who	D_0 (in eV)
Experiment	Matthew et al.	3.240 ± 0.003
CAS/Jastrow/opt	Hagagi-Mood/Luchow	3.159 ± 0.015
exFCI/DMC/extrap[a]	Scemama and co	3.271 ± 0.077

[a] DMC: Stochastic reconfiguration (fixed number of walkers)

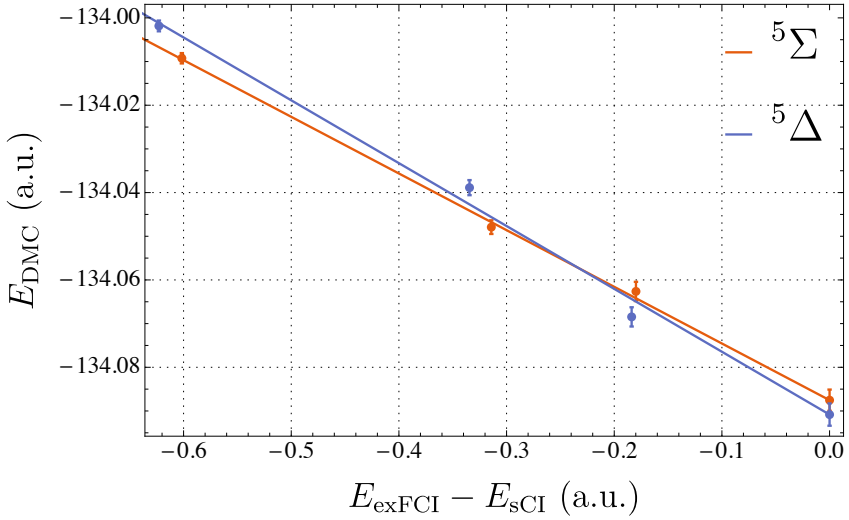
Hagagi-Mood & Luchow, JPCA 121 (2017) 6165

Scemama, Garniron, Caffarel & Loos, JCTC 14 (2018) 1395

Extrapolation to FCI **limit**

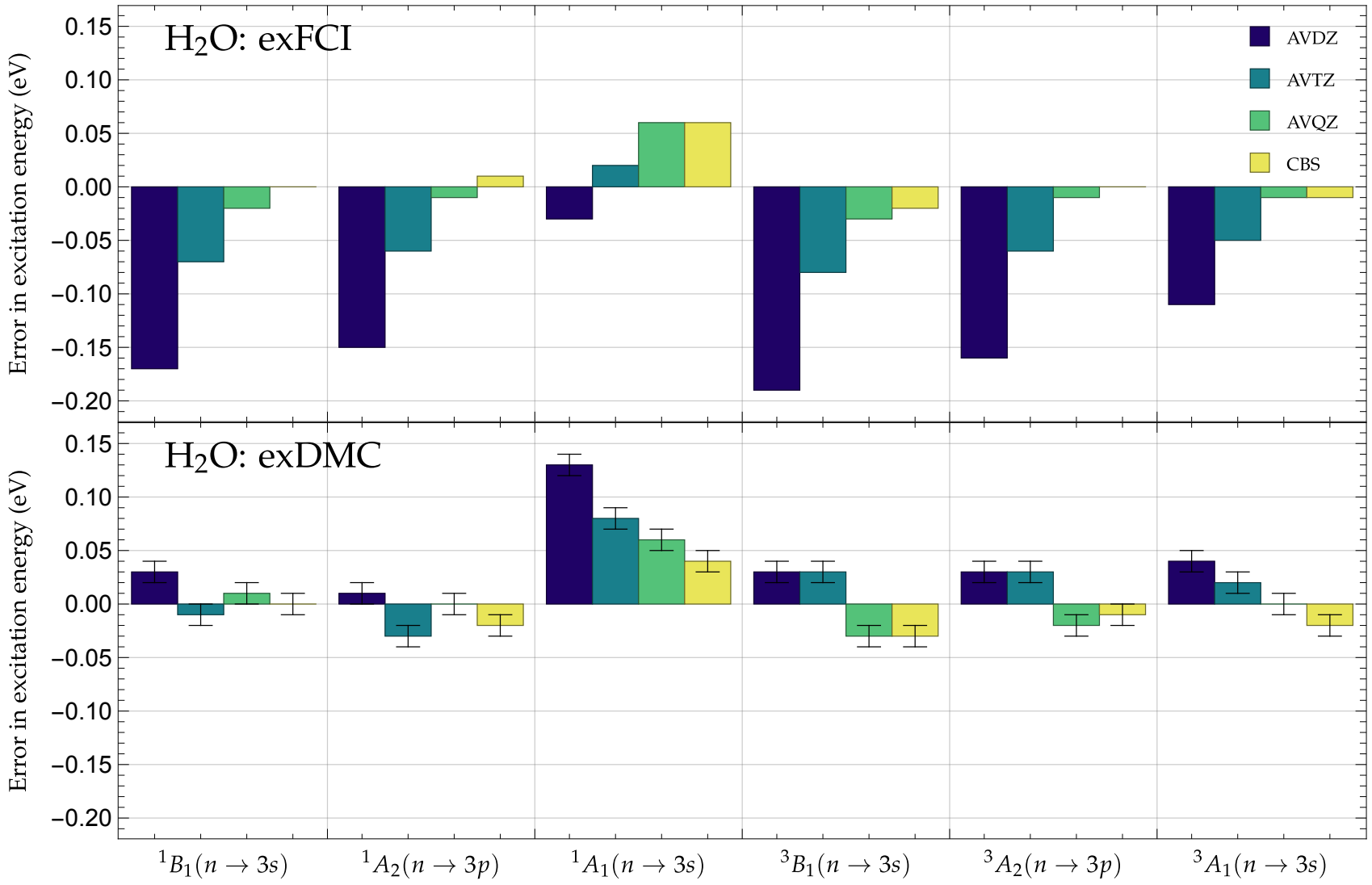


Extrapolation to FCI **nodes**



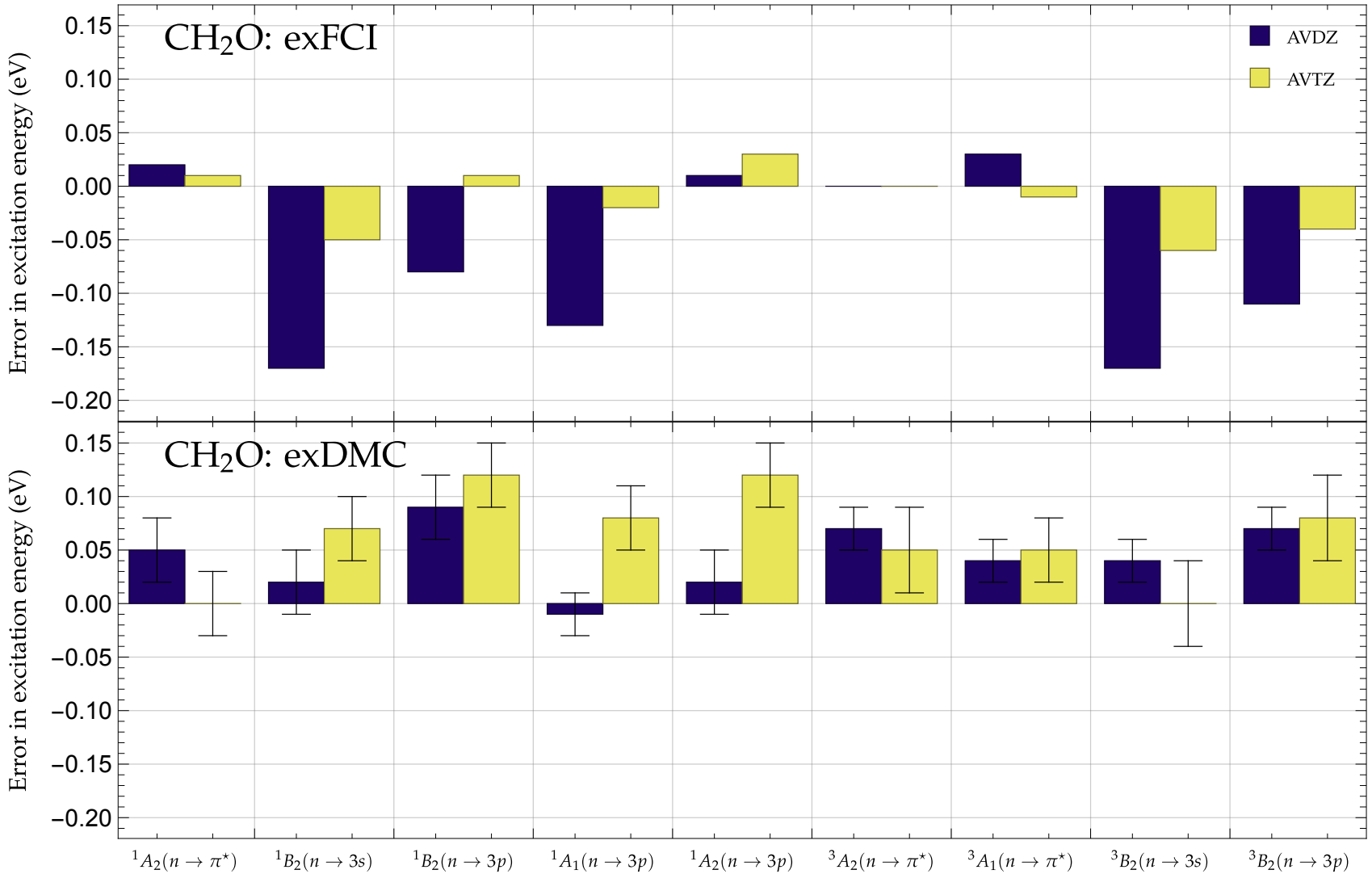
Scemama, Garniron, Caffarel & Loos, JCTC 14 (2018) 1395

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



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

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



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

Thank you!