

Selected CI and Jastrow-free QMC methods for Chemistry

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16th May 2018

Collaborators and Funding

- Selected CI and QMC



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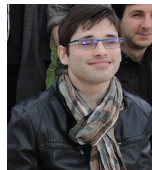
- Green function methods



Arjan
Berger

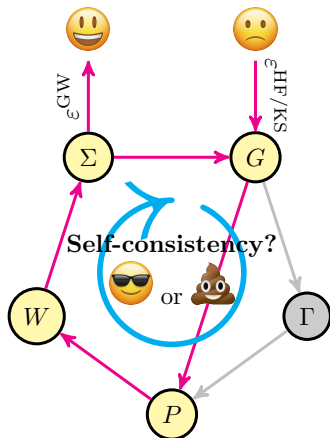


Pina
Romaniello



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Green functions and self-consistency: an unhappy marriage?



*"Green functions and self-consistency: insights from the spherium model",
Loos, Romaniello & Berger, JCTC (in press) arXiv:1803.04234*

Section 2

Selected CI

The CIPSI algorithm

CIPSI = CI using a Perturbative Selection made Iteratively

- Based on old idea by Bender and Davidson (1969)
- Further developments in Toulouse many years ago (Malrieu, Evangelisti, Daudey, Spiegelman, etc)
- CIPSI is a good candidate for **massively parallel wave function calculations** (PhD E. Giner and Y. Garniron)
- **CIPSI \approx deterministic version of FCIQMC**
Caffarel et al., Recent Progress in Quantum Monte Carlo (2016) Chap. 2, 15-46.
- Open-source code: **QUANTUM PACKAGE** (A. Scemama)
https://github.com/scemama/quantum_package

Color code

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)

$$\begin{array}{l} \text{internal space } |I\rangle \\ \text{perturbers } |\alpha\rangle \end{array} \left\{ \begin{array}{|c|c|} \hline \mathbf{H}^{(0)} & \mathbf{h}^\dagger \\ \hline \mathbf{h} & \mathbf{H}^{(1)} \\ \hline \end{array} \right.$$

CIPSI algorithm

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

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

- 2 Generate *external determinants*:

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

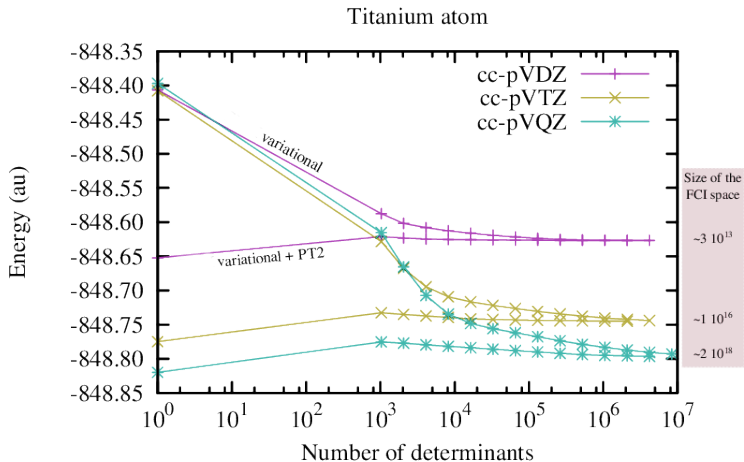
- 3 Second-order perturbative contribution of each $|\alpha\rangle$:

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

- 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

Giner, Scemama & Caffarel, JCP 142 (2015) 044115

CIPSI on the Titanium atom



Few remarks...

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

PT2 correction

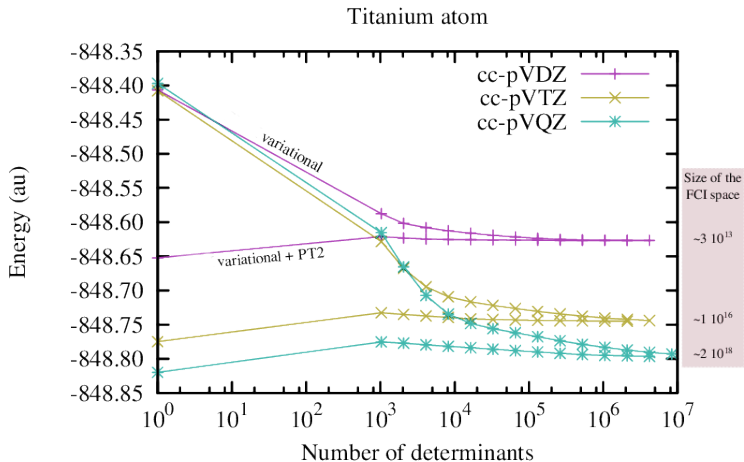
How do we know how far we are from the “true” FCI?

- Second-order Epstein-Nesbet correction:

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

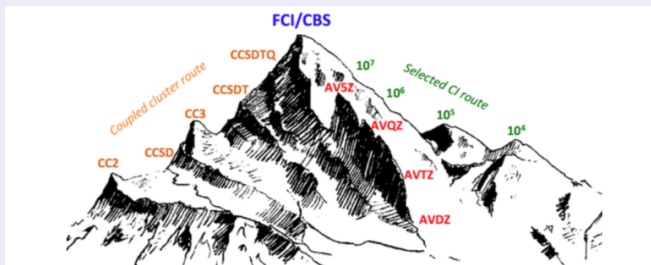
- $|\alpha\rangle$'s with largest $\delta E(\alpha)$ have been added to $\Psi^{(0)}$ previously
⇒ only small contributions remaining
- \mathcal{A} increases with \mathcal{D}
⇒ a *very large* number of *very small* contributions
- In practice, we use a semi-stochastic algorithm to compute $E^{(2)}$
⇒ *much faster!!*
Garniron, Scemama, Loos & Caffarel, JCP 147 (2017) 034101
- We linearly extrapolate to $E^{(2)} = 0$ to reach the FCI limit (exFCI)

CIPSI on the Titanium atom



A mountaineering strategy to excited states

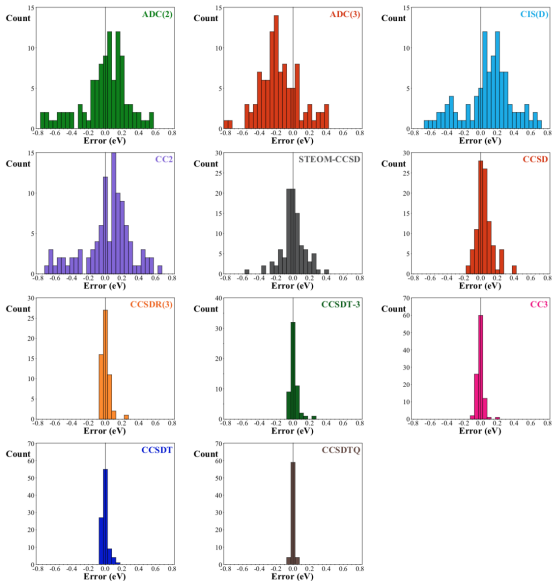
Highly-accurate reference energies for excited states

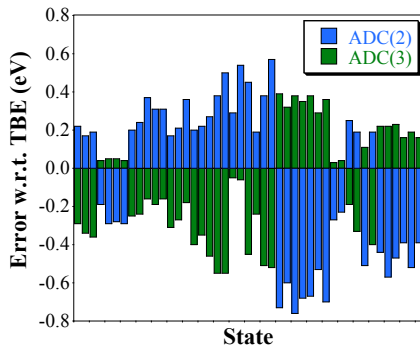


- 18 small molecules and 110 transition energies of various characters (valence, Rydberg, singlet, triplet, $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$, double excitations, etc)
- High-level CC calculations (up to CCSDTQP)
- sCI calculations (up to several millions of determinants)
- Large (diffuse)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

Loos, Scemama, Blondel, Garniron, Caffarel & Jacquemin JCTC (submitted)

Benchmarking excited-state methods vs TBE/cc-pVTZ



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

Selected shifted-Bk for very large wave functions

$$\begin{array}{l}
 \text{internal space } |I\rangle \\
 \text{perturbors } |\alpha\rangle
 \end{array}
 \left\{ \begin{array}{|c|c|}
 \hline
 \mathbf{H}^{(0)} & \mathbf{h}^\dagger \\
 \hline
 \mathbf{h} & \mathbf{H}^{(1)} \\
 \hline
 \end{array} \right.$$

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

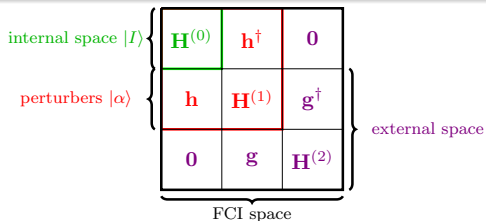
$$\Rightarrow \mathbf{c}^{(1)} = -(\mathbf{H}^{(1)} - E\mathbf{I})^{-1} \mathbf{h} \mathbf{c}^{(0)}$$

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): $\mathbf{\Delta} = \mathbf{h}^\dagger (\mathbf{E}\mathbf{I} - \mathbf{D}^{(1)})^{-1} \mathbf{h}$

Gershgorin & Shavitt, IJQC 2 (1968) 751

Selected shifted-Bk for very large wave functions



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

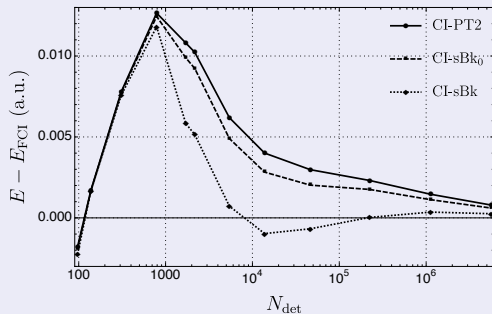
$$\Rightarrow \mathbf{c}^{(1)} = -\left[(\mathbf{H}^{(1)} - E\mathbf{I}) - \mathbf{g}^\dagger (\mathbf{H}^{(2)} - E\mathbf{I}) \mathbf{g} \right]^{-1} \mathbf{h} \mathbf{c}^{(0)}$$

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): $\mathbf{\Delta} = \mathbf{h}^\dagger (E^{(0)} - \mathbf{D}^{(1)})^{-1} \mathbf{h}$

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

Selected shifted-Bk for very large wave functions

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

Scemama, Garniron, Giner, Caffarel & Loos, (in preparation)

Comments

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

Section 3

Quantum Monte Carlo

Jastrow-free QMC protocol

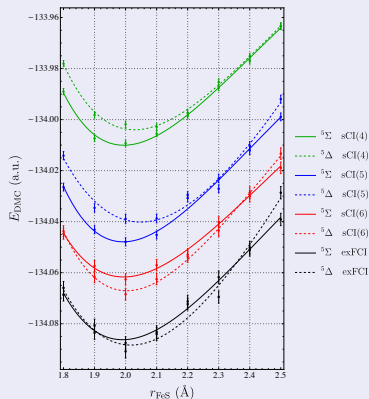
Trial wave function for QMC

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

- 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 $J(\mathbf{R})$**
⇒ **Deterministic construction of the nodal surface**
- Open-source code: **QMC=CHEM** (A. Scemama)
<https://github.com/scemama/qmcchem>
- **Interface for QMCPACK also available!**

QMC@sCI without Jastrow: dissociation of FeS

Dissociation profile



Method ^a	ϵ	N_{det}	N_{det}^{\uparrow}	N_{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

^aBasis 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

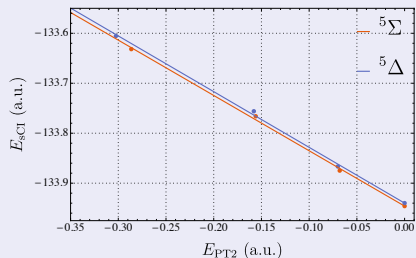
^aDMC: Stochastic reconfiguration (fixed number of walkers)

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

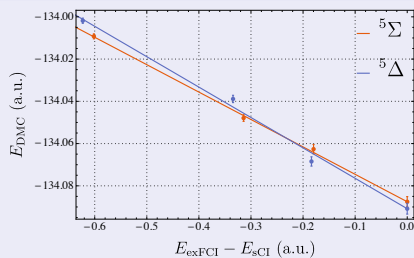
Scemama, Garniron, Caffarel & Loos, JCTC 14 (2018) 1395

The protocol: extrapolation to FCI nodes

Extrapolation to FCI limit



Extrapolation to FCI nodes



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

How do fixed-node errors compensate in excited states?

Can we get accurate excitation energies in organic molecules?

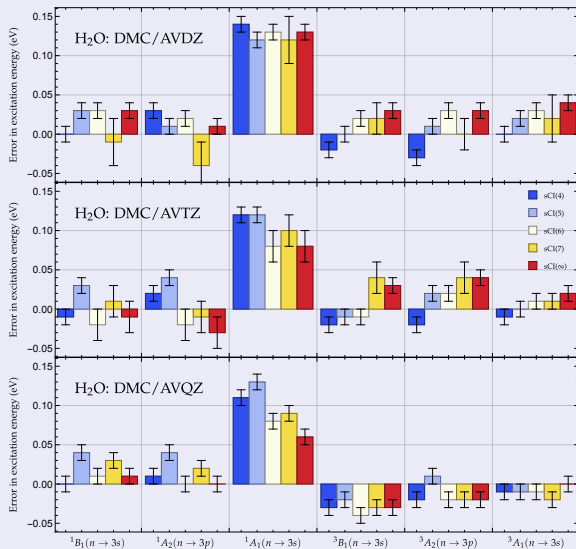
TABLE I. Number of determinants N_{det} (and their corresponding acronym) of the various sCI-based trial wave functions for the singlet and triplet spin manifolds of H_2O and CH_2O at various truncation level ϵ . The characteristics of the extrapolated FCI (exFCI) expansion are also reported.

Method	ϵ	N_{det} for singlet manifold					N_{det} for triplet manifold					acronym
		H_2O		CH_2O			H_2O		CH_2O			
		AVDZ	AVTZ	AVQZ	AVDZ	AVTZ	AVDZ	AVTZ	AVQZ	AVDZ	AVTZ	
sCI	10^{-4}	9432	9948	8576	23317	24672	5087	5760	5627	22938	23311	sCI(4)
	10^{-5}	89797	110557	74414	255802	255802	46264	58632	55637	227083	311542	sCI(5)
	10^{-6}	636324	711120	325799	770978	1584576	234862	317880	243947	1074559	1699728	sCI(6)
	10^{-7}	3119643	2256057	697703	—	—	1029683	1074337	681392	—	—	sCI(7)
exFCI	0	5869449	5589200	1139302	2043030	6773751	4566873	3760373	1833526	6637572	3172099	sCI(∞)
exFCI	—	$\sim 10^{10}$	$\sim 10^{13}$	$\sim 10^{15}$	$\sim 10^{15}$	$\sim 10^{20}$	$\sim 10^{10}$	$\sim 10^{13}$	$\sim 10^{15}$	$\sim 10^{15}$	$\sim 10^{20}$	exFCI

Scemama, Benali, Jacquemin, Caffarel & Loos (in preparation)

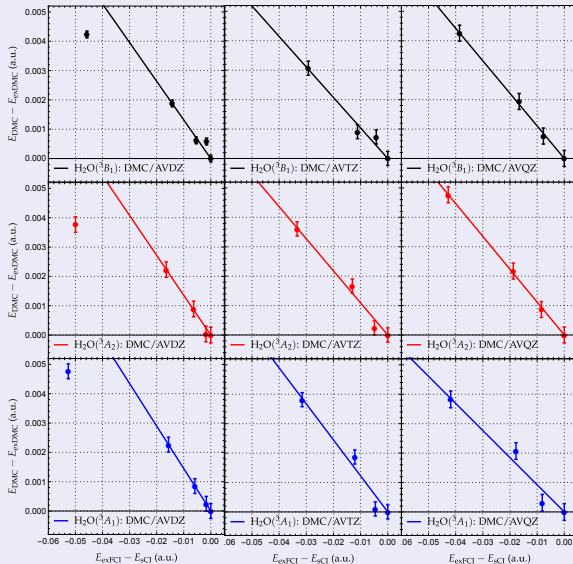
Fixed-node error in excited states: water

Water: (all-electron) DMC@CIPSI



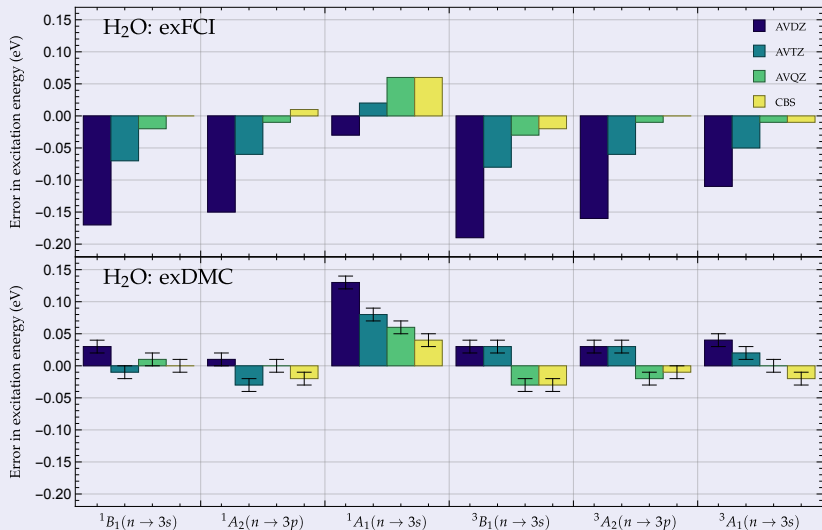
Fixed-node error in excited states: water

Water: Extrapolated DMC results (exDMC)



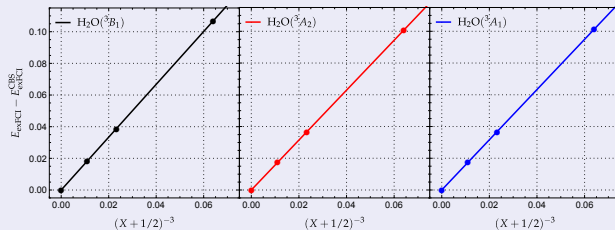
Fixed-node error in excited states: water

Water: exFCI vs exDMC

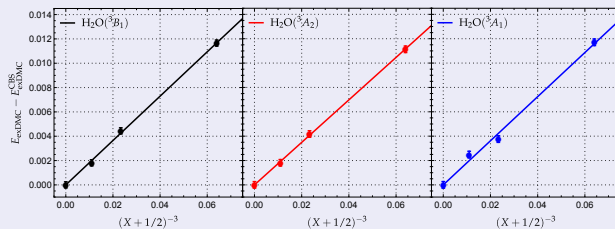


Complete basis set (CBS) extrapolation

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

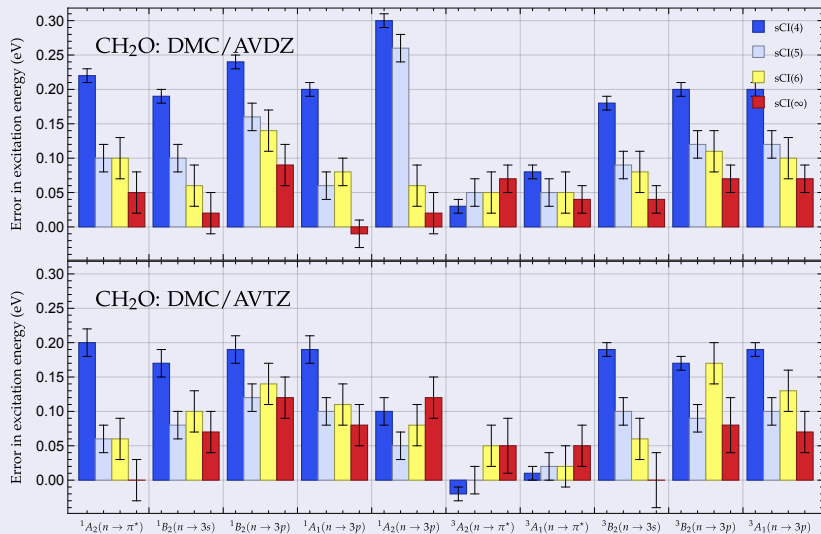


Triplet states of water: exDMC (AVDZ, AVTZ, AVQZ and CBS)



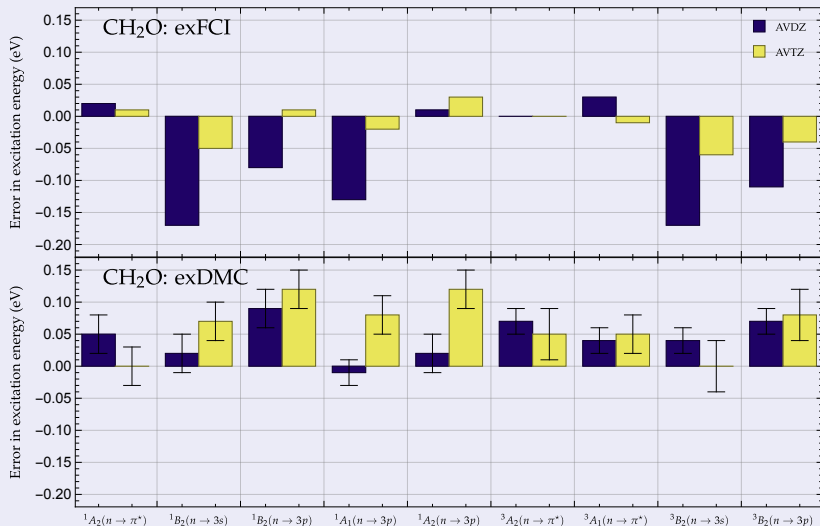
Fixed-node error in excited states: formaldehyde

Formaldehyde: (all-electron) DMC@CIPSI



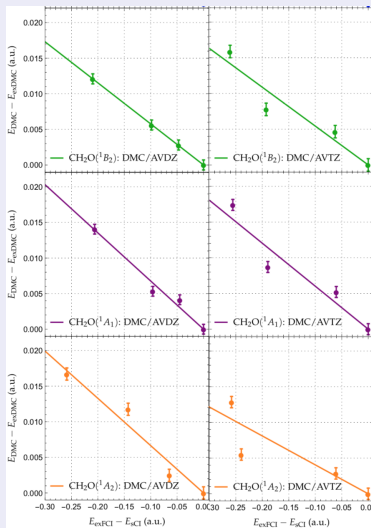
Fixed-node error in excited states: formaldehyde

Formaldehyde: exFCI vs exDMC



Fixed-node error in excited states: formaldehyde

Extrapolated DMC results: exDMC



That's the end...

Thank you!