

# Selected CI and Jastrow-free QMC methods for Chemistry

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# Collaborators and Funding

- Selected CI and QMC



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- Green function methods



Arjan  
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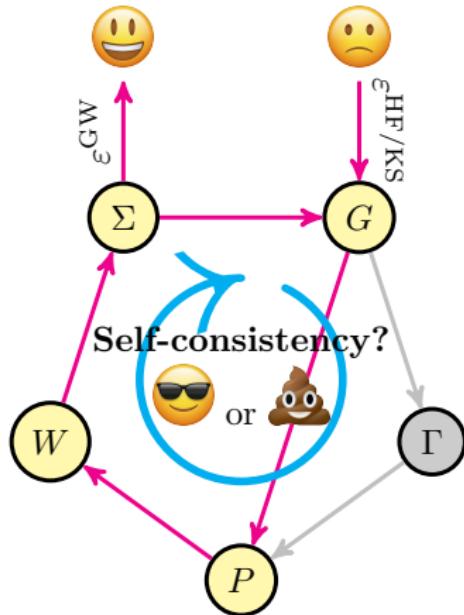


Pina  
Romaniello



Mika  
Vérité

# 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

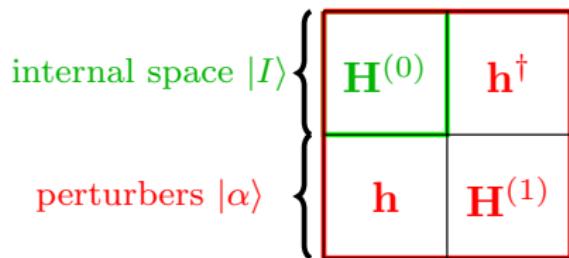
**CIPSI = CI using a Perturbative Selection made Iteratively**

- 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](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)



## 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*:

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

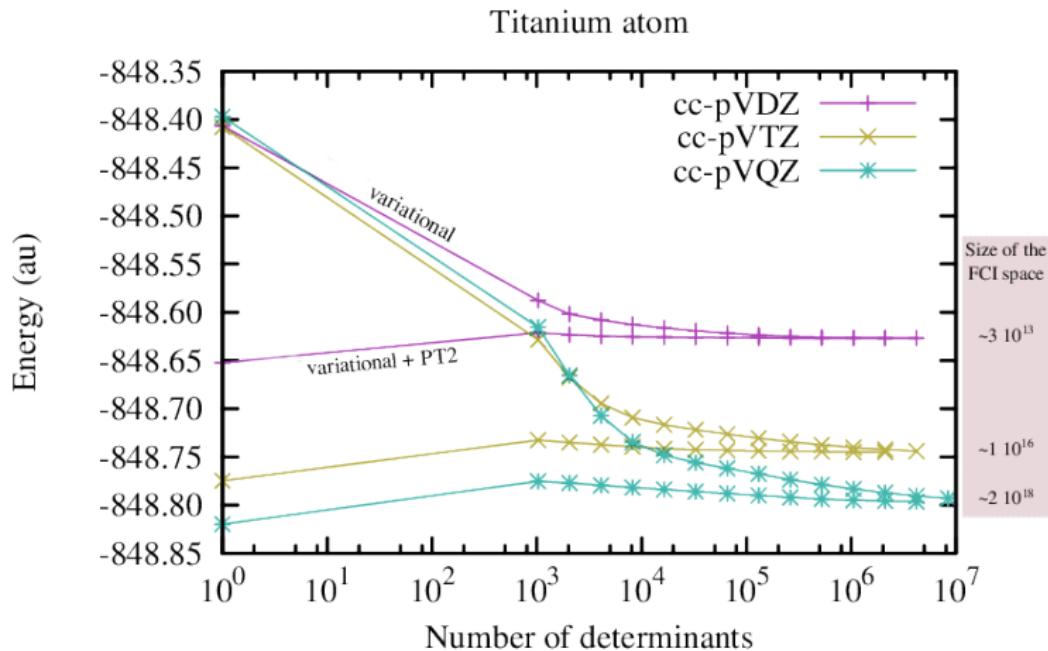
- ③ Second-order perturbative contribution of each  $|\alpha\rangle$ :

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

- 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

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

## CIPSI on the Titanium atom



## Few remarks...

- When all  $|I\rangle$  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

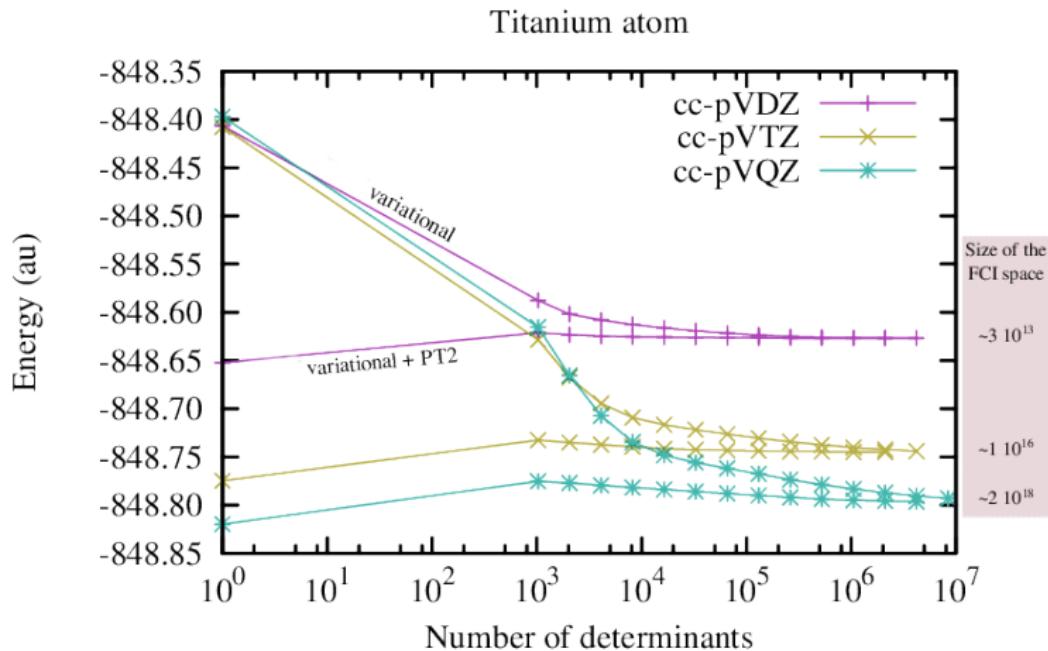
How do we know how far we are from the “true” FCI?

- Second-order Epstein-Nesbet correction:

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

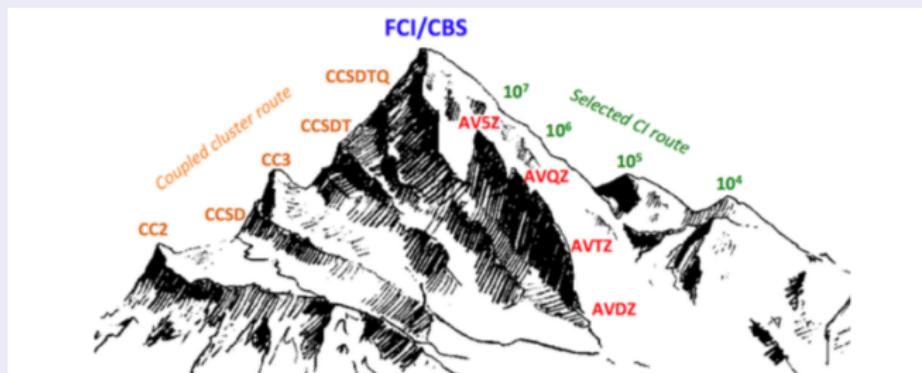
- $|\alpha\rangle$ 's with largest  $\delta E(\alpha)$  have been added to  $\Psi^{(0)}$  previously  
⇒ only small contributions remaining
- $\mathcal{A}$  increases with  $\mathcal{D}$   
⇒ a **very large** number of **very small** contributions
- In practice, we use a semi-stochastic algorithm to 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

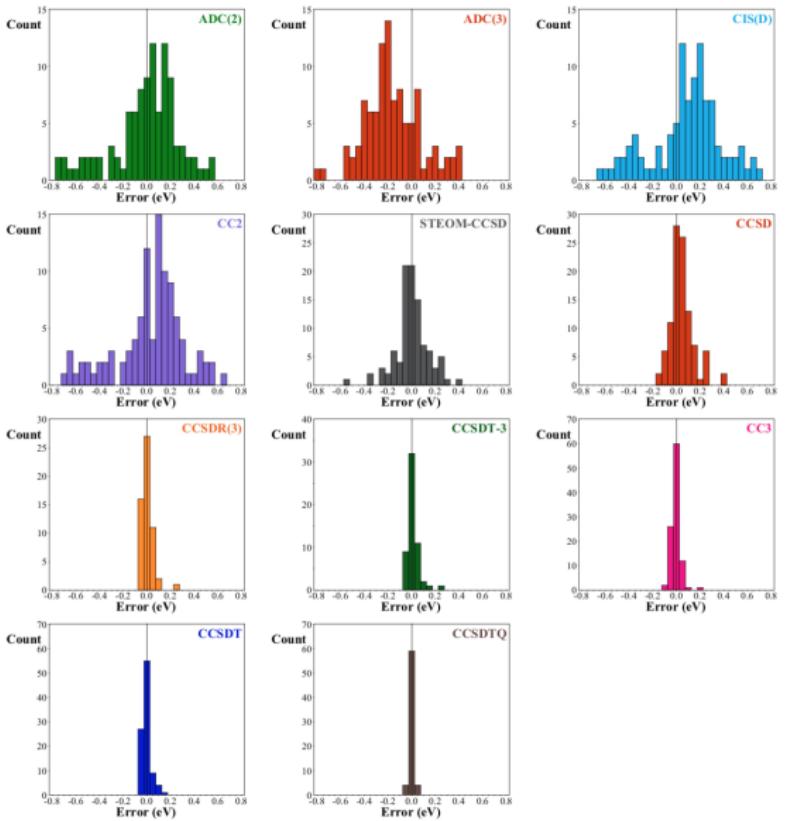
## Highly-accurate reference energies for excited states

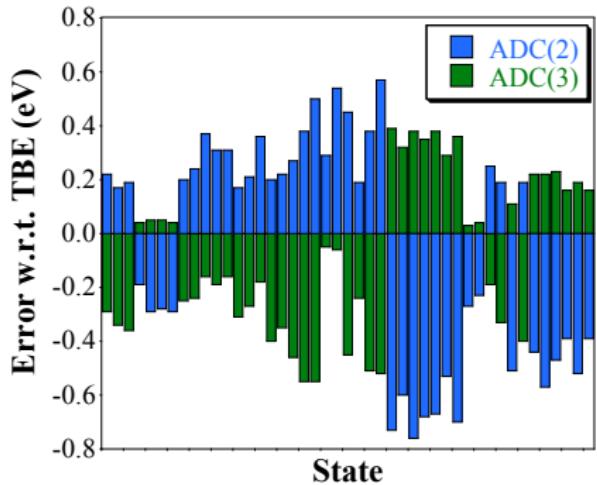


- 18 small molecules and 110 transition energies of various characters (valence, Rydberg, singlet, triplet,  $n \rightarrow \pi^*$ ,  $\pi \rightarrow \pi^*$ , double excitations, etc)
- High-level CC calculations (up to CCSDTQP)
- sCI calculations (up to several millions of determinants)
- Large (diffuse)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

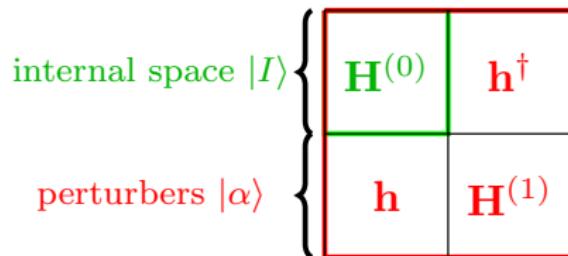
Loos, Scemama, Blondel, Garniron, Caffarel & Jacquemin JCTC (submitted)

## 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



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

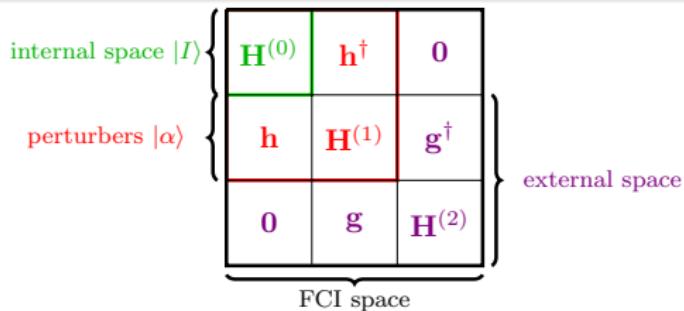
$$\Rightarrow \mathbf{c}^{(1)} = -(\mathbf{H}^{(1)} - E\mathbf{I})^{-1} \mathbf{h} \mathbf{c}^{(0)}$$

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

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

Gershgorn & Shavitt, IJQC 2 (1968) 751

## Selected shifted-Bk for very large wave functions



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

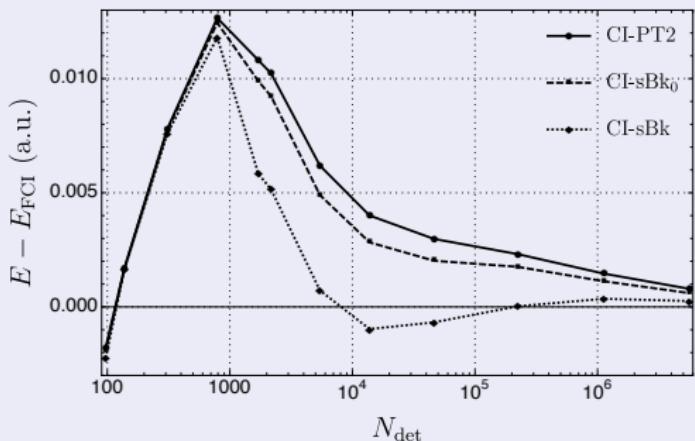
$$\Rightarrow \mathbf{c}^{(1)} = - \left[ (\mathbf{H}^{(1)} - E\mathbf{I}) - \mathbf{g}^\dagger (\mathbf{H}^{(2)} - E\mathbf{I}) \mathbf{g} \right]^{-1} \mathbf{h} \mathbf{c}^{(0)}$$

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

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

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

## Selected shifted-Bk for very large wave functions

 $^2\Pi_g$  ground state of the CuCl<sub>2</sub> (6-31G)

Scemama, Garniron, Giner, Caffarel &amp; 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

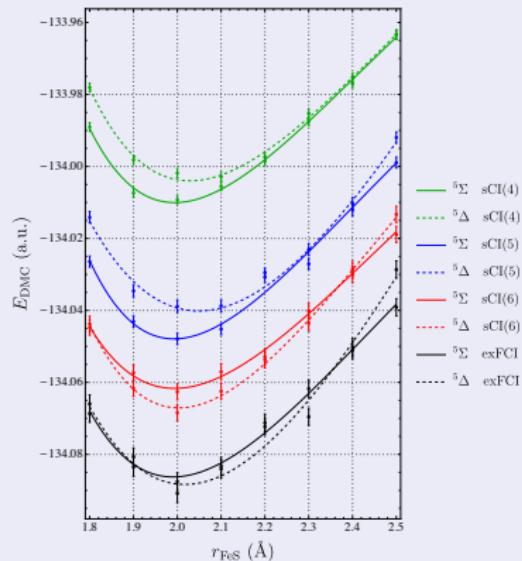
## Trial wave function for QMC

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

- 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 <sup>a</sup>	$\epsilon$	$N_{\text{det}}$	$N_{\text{det}}^{\uparrow}$	$N_{\text{det}}^{\downarrow}$	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( $\infty$ )
exFCI	—	$\sim 10^{27}$	$\sim 10^{16}$	$\sim 10^{11}$	FCI

<sup>a</sup>Basis set: VTZ-ANO-BFD for Fe and VTZ-BFD for S

What	Who	$D_0$ (in eV)
Experiment	Matthew et al.	$3.240 \pm 0.003$
CAS/Jastrow/opt	Hagagi-Mood/Luchow	$3.159 \pm 0.015$
exFCI/DMC/extrap <sup>a</sup>	Scemama and co	$3.271 \pm 0.077$

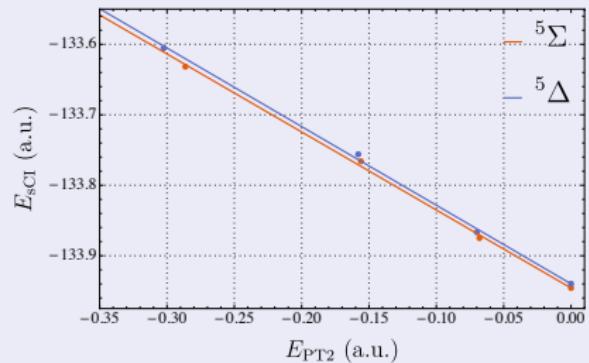
<sup>a</sup>DMC: Stochastic reconfiguration (fixed number of walkers)

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

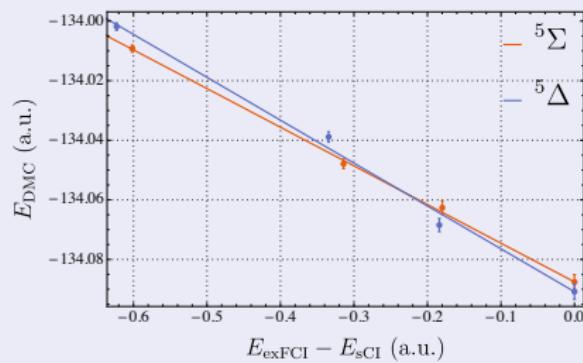
Scemama, Garniron, Caffarel & Loos, JCTC 14 (2018) 1395

# 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?

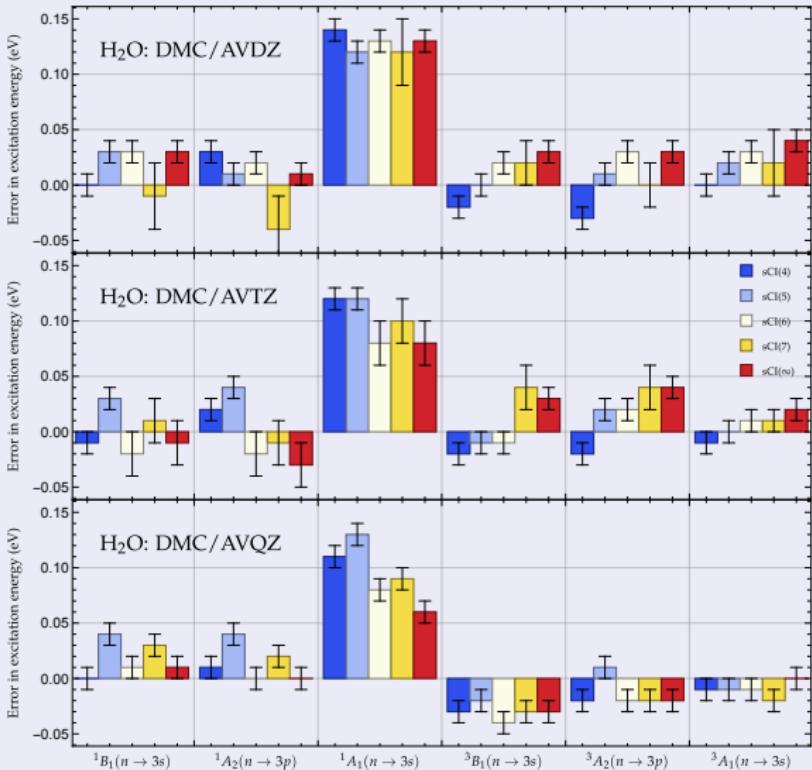
TABLE I. Number of determinants  $N_{\text{det}}$  (and their corresponding acronym) of the various sCI-based trial wave functions for the singlet and triplet spin manifolds of  $\text{H}_2\text{O}$  and  $\text{CH}_2\text{O}$  at various truncation level  $\epsilon$ . The characteristics of the extrapolated FCI (exFCI) expansion are also reported.

Method	$\epsilon$	N <sub>det</sub> for singlet manifold						N <sub>det</sub> for triplet manifold						acronym	
		H <sub>2</sub> O			CH <sub>2</sub> O			H <sub>2</sub> O			CH <sub>2</sub> O				
		AVDZ	AVTZ	AVQZ	AVDZ	AVTZ	AVDZ	AVTZ	AVQZ	AVDZ	AVTZ	AVDZ	AVTZ		
sCI	$10^{-4}$	9 432	9 948	8 576	23 317	24 672	5 087	5 760	5 627	22 938	23 311	sCI(4)			
	$10^{-5}$	89 797	110 557	74 414	255 802	255 802	46 264	58 632	55 637	227 083	311 542	sCI(5)			
	$10^{-6}$	636 324	711 120	325 799	770 978	1 584 576	234 862	317 880	243 947	1 074 559	1 699 728	sCI(6)			
	$10^{-7}$	3 119 643	2 256 057	697 703	—	—	1 029 683	1 074 337	681 392	—	—	sCI(7)			
	0	5 869 449	5 589 200	1 139 302	2 043 030	6 773 751	4 566 873	3 760 373	1 833 526	6 637 572	3 172 099	sCI( $\infty$ )			
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)

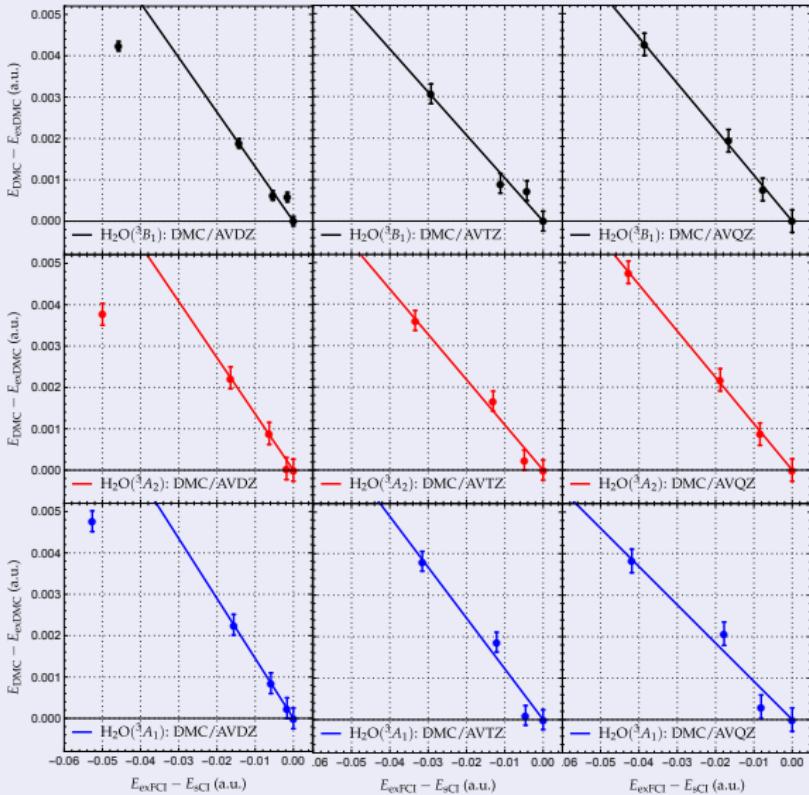
## Fixed-node error in excited states: water

## Water: (all-electron) DMC@CIPSI



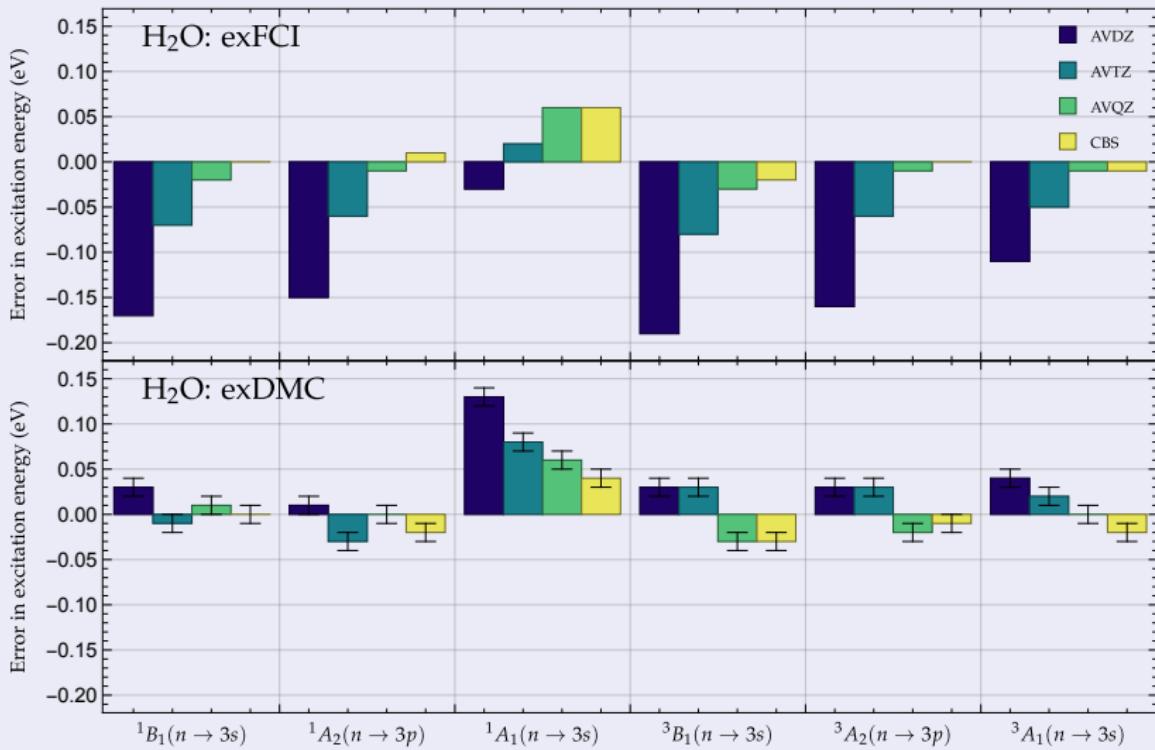
## Fixed-node error in excited states: water

## Water: Extrapolated DMC results (exDMC)



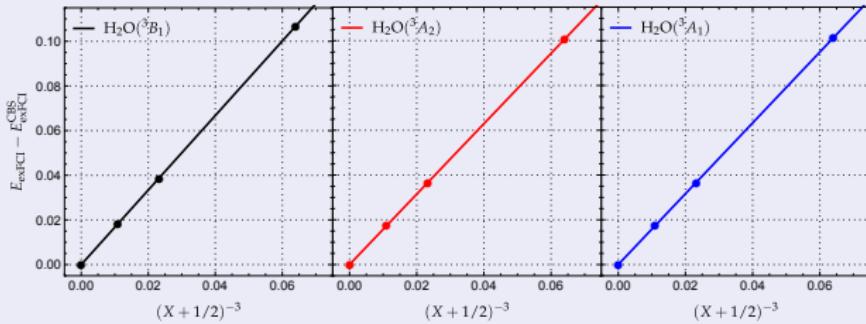
## Fixed-node error in excited states: water

## Water: exFCI vs exDMC

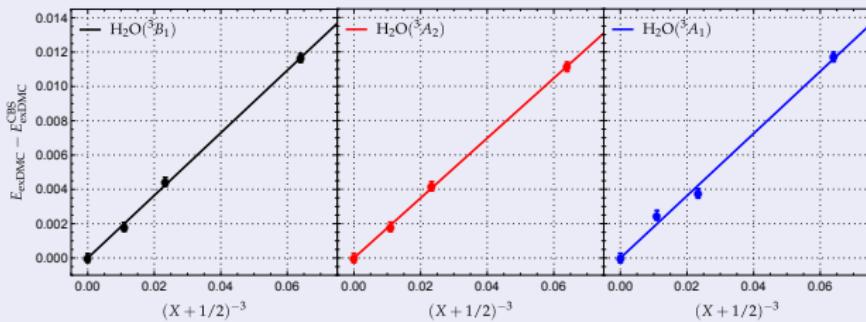


# Complete basis set (CBS) extrapolation

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

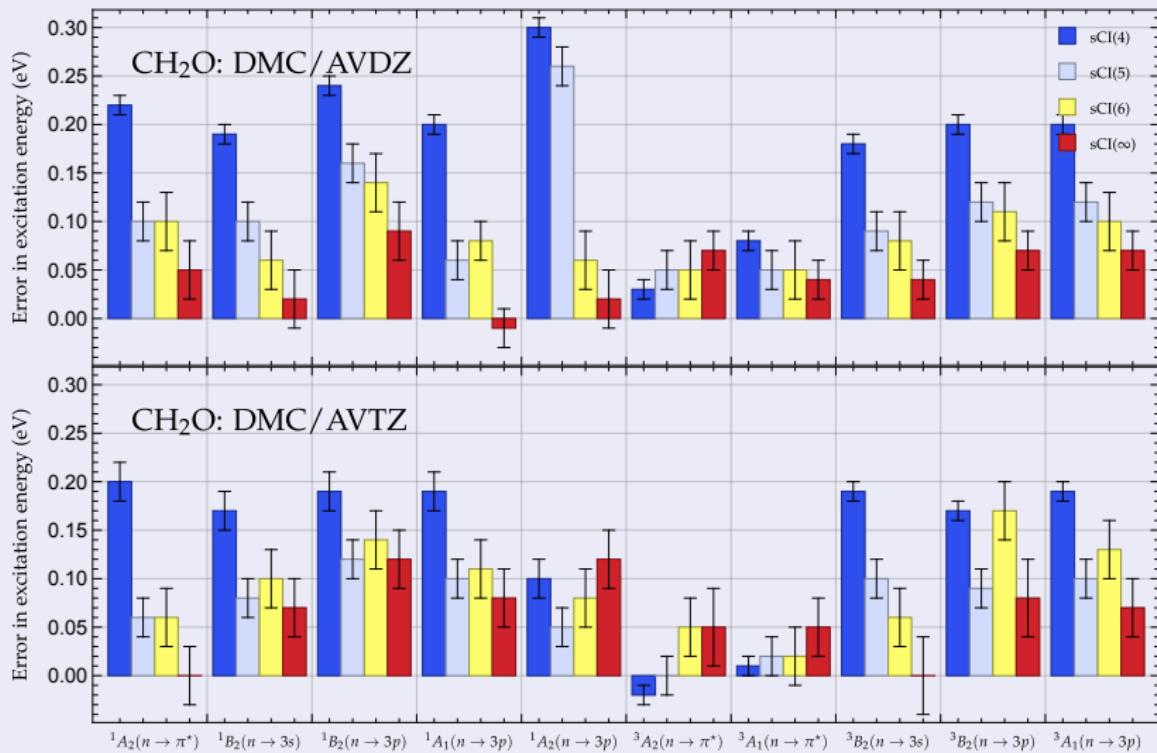


Triplet states of water: exDMC (AVDZ, AVTZ, AVQZ and CBS)



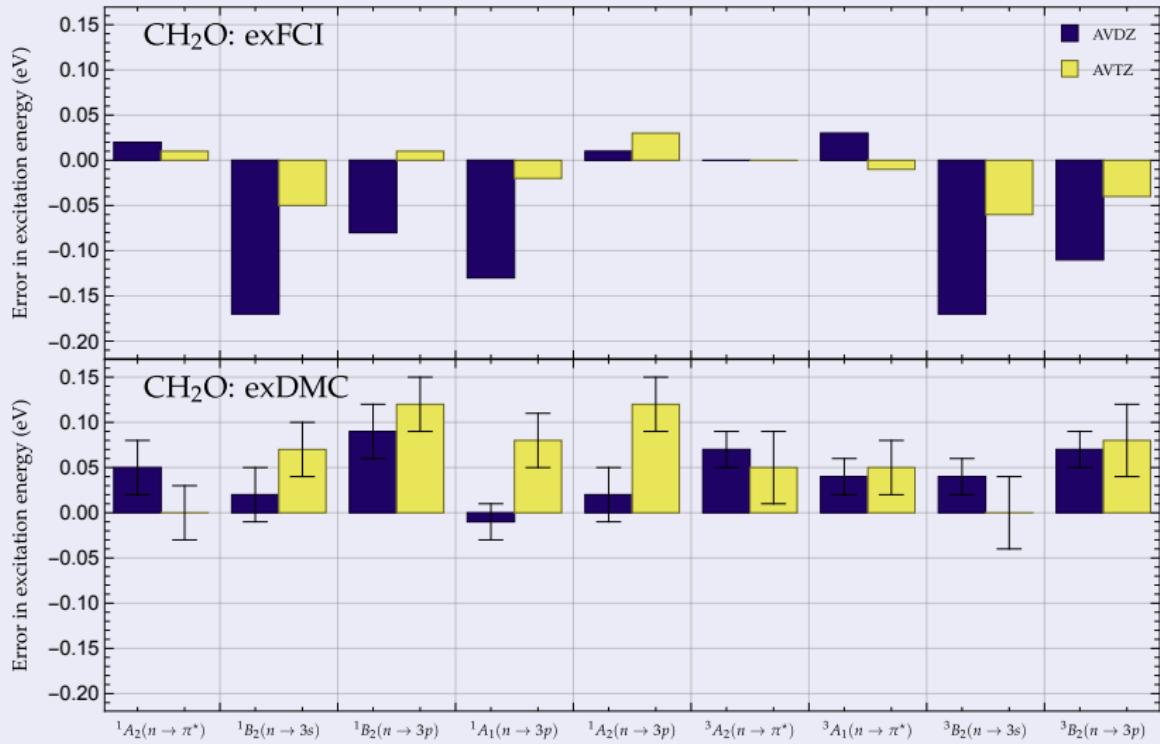
## Fixed-node error in excited states: formaldehyde

## Formaldehyde: (all-electron) DMC@CIPSI



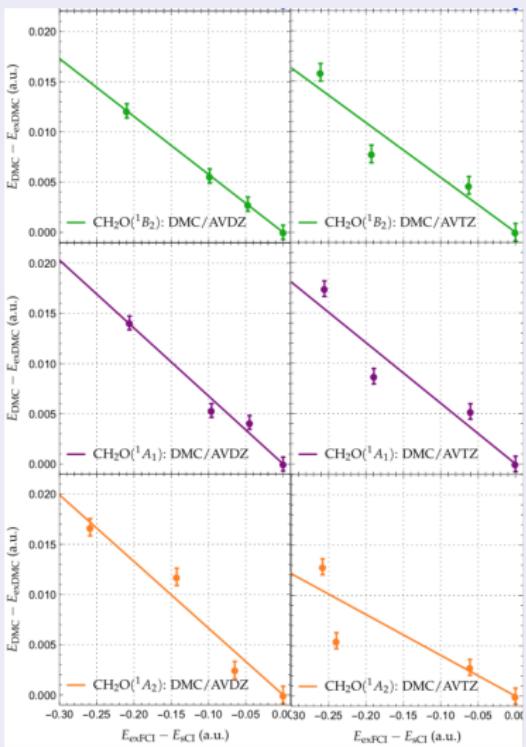
## Fixed-node error in excited states: formaldehyde

## Formaldehyde: exFCI vs exDMC



## Fixed-node error in excited states: formaldehyde

## Extrapolated DMC results: exDMC



That's the end...

*Thank you!*