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Laboratoire de Chimie et Physique Quantiques

Accurate FCI correlation energies and reduced density matrices

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https://pfloos.github.io/WEB_LOOS

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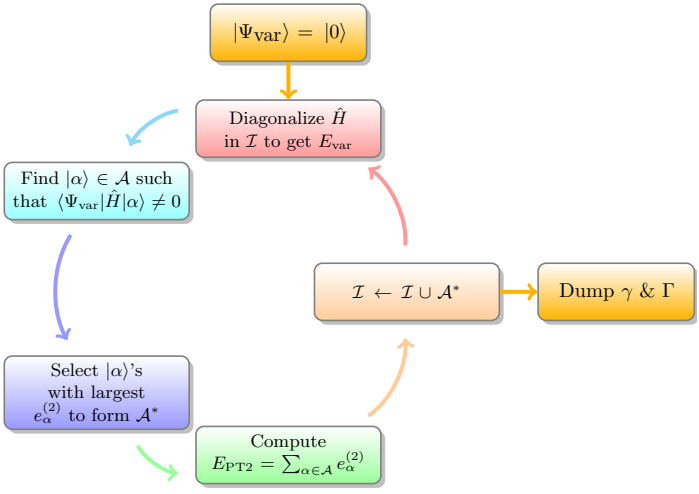
Selected Configuration Interaction (SCI): "sparse" exploration of the FCI space

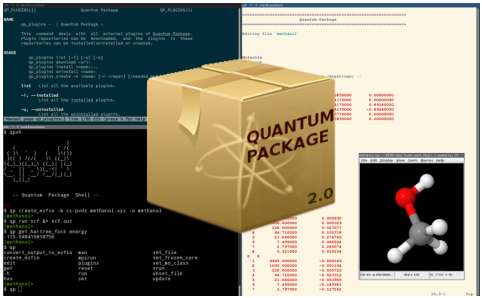
"Among the very large number of determinants contained in the FCI space, only a tiny fraction of them significantly contributes to the energy"

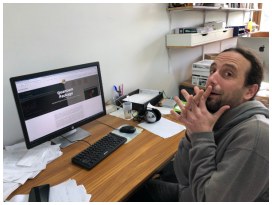
CIPSI = CI using a Perturbative Selection made Iteratively

- Developed in Toulouse many (many) years ago
  Huron, Malrieu & Rancurel, JCP 58 (1973) 5745
- 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
- CIPSI (and SCI methods in general) has been recently resurrected!
  Giner, Scemama & Caffarel, CJC 91 (2013) 879
  Giner, Scemama & Caffarel, JCP 142 (2015) 044115
- CIPSI $\approx$ heat-bath CI (Umrigar) $\approx$ adaptive sampling CI (Evangelista) $\approx$ iterative CI (Liu) $\approx$ incremental CI (Zimmerman) $\approx$ FCIQMC (Alavi)


$|\Psi_{\text{var}}\rangle = |0\rangle$
Diagonalize $\hat{H}$ in $\mathcal{I}$ to get E_{var}
Find $|\alpha\rangle \in \mathcal{A}$ such that $\langle\Psi_{\text{var}}|\hat{H}|\alpha\rangle \neq 0$
Select $|\alpha\rangle$'s with largest $e_\alpha^{(2)}$ to form $\mathcal{A}^*$
Compute $E_{\text{PT2}} = \sum_{\alpha\in\mathcal{A}} e_\alpha^{(2)}$
$\mathcal{I} \leftarrow \mathcal{I} \cup \mathcal{A}^*$
Dump γ & Γ

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

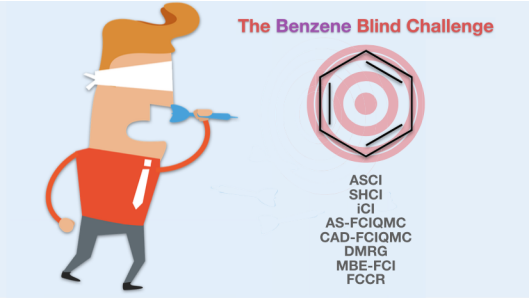


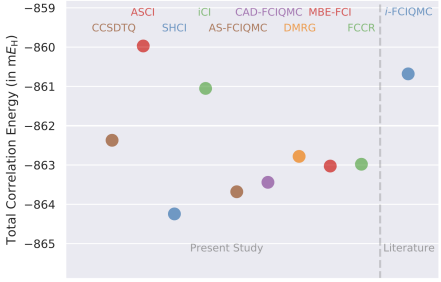


Anthony Scemama

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

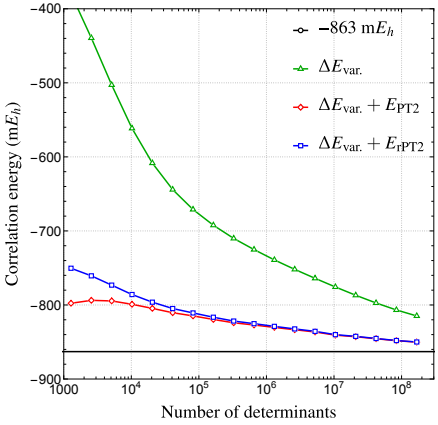
The Benzene Blind Challenge: Frozen-core correlation energy (cc-pVDZ)

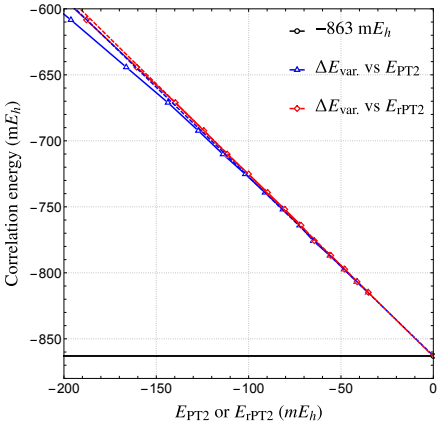




Eriksen et al. JPCL 11 (2020) 8922

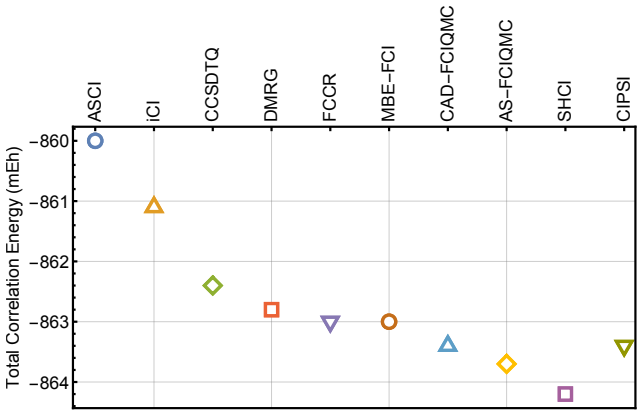
Performance of CIPSI for C_6H_6/cc-pVDZ (1)





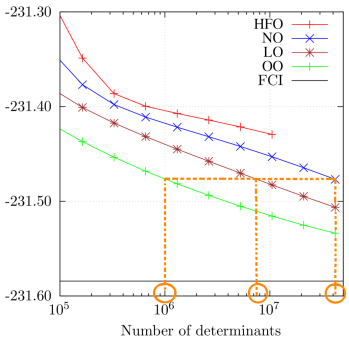
Loos, Damour & Scemama, JCP 153 (2020) 176101

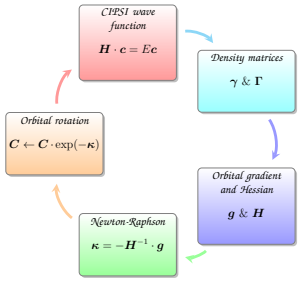
Performance of CIPSI for C_6H_6/cc-pVDZ (2)



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

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



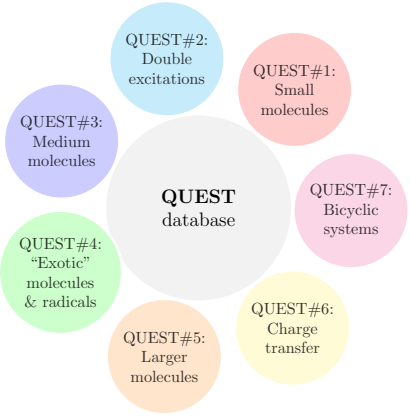


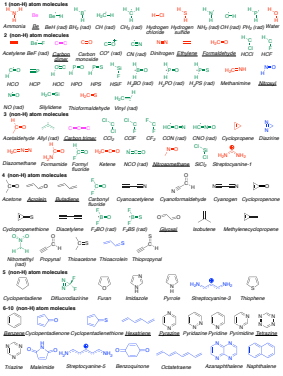
- Orbital optimization largely accelerates the convergence of selected CI
- Trust-region Newton-Raphson algorithm

Yann Damour

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

"The aim of the QUEST project is to provide to the community a large set of highly-accurate excitation energies for various types of excited states"

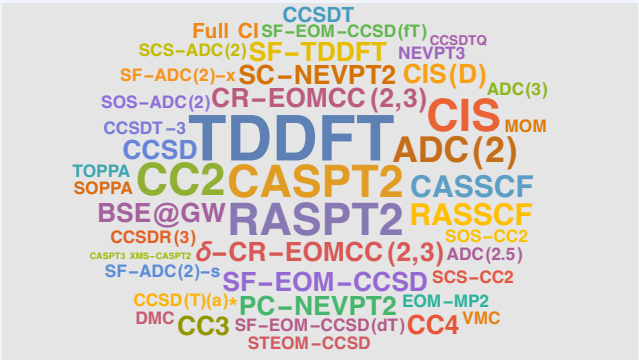




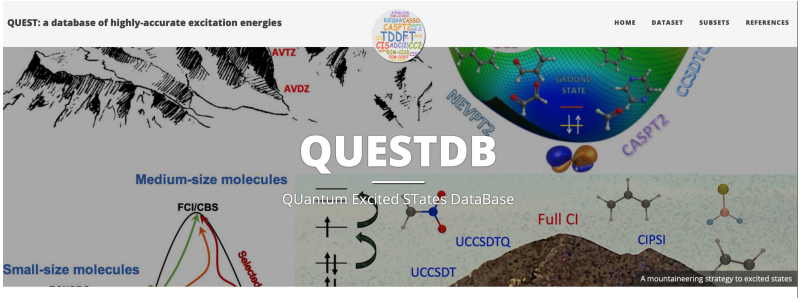
Denis Jacquemin

Zoo of functionals...

And this is just for excited states...



The QUEST website



Mika Veril

Véril et al. WIREs Comput. Mol. Sci. 11 (2021) e1517

https://lcpq.github.io/QUESTDB_website

Other research groups using QUEST

- Head-Gordon's group: orbital-optimized DFT for double excitations [JCTC 16 (2020) 1699; JPCL 12 (2021) 4517] and TD-DFT benchmark [JCTC (in press)]
- Kaupp's group: assessment of hybrid functionals [JCP 155 (2021) 124108]
- Kallay's and Goerigk's groups: double hybrids [JCTC 15 (2019) 4735; JCTC 17 (2021) 927; JCTC 17 (2021) 5165; JCTC 17 (2021) 4211]
- Neuscamman's group: QMC for doubly-excited states [JCP 153 (2022) 234105]
- Filippi's and Scemama's groups: QMC for excited states [JCTC 15 (2019) 4889; JCTC 17 (2021) 3426; JCTC 18 (2022) 1089]
- Tim Gould's group: ensemble DFT [JPCL 13 (2022) 2452]
- our group: wave function methods [JPCL 11 (2020) 974; (2020) JCTC 17 (2021) 4756; JCTC 18 (2022) 2418] and many-body perturbation theory [JCP 153 (2020) 114120; JCP 156 (2022) 164101]

Large-Scale Benchmarking of Multireference Vertical-Excitation Calculations via Automated Active-Space Selection

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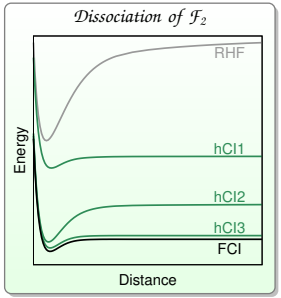
Abstract

We have calculated state-averaged complete-active-space self-consistent-field (SA-CASSCF), multiconfiguration pair-density functional theory (MC-PDFT), hybrid MC-PDFT (HMC-PDFT), and n-electron valence state second-order perturbation theory (NEVPT2) excitation energies with the approximate pair-coefficient (APC) automated active-space selection scheme for the QUESTDB benchmark database of 542 vertical excitation energies. We eliminated poor active spaces (20-30% of calculations) by ap-

Hierarchy configuration interaction (hCI)

Excitation degree e
Seniority number s
Hierarchy parameter $h = \frac{e+s/2}{2}$

e/s	0	2	4	6
0	HF			
1		hCI1		
2		hCI1.5	hCI2	
3			hCI2.5	hCI3
4				
5				
6				



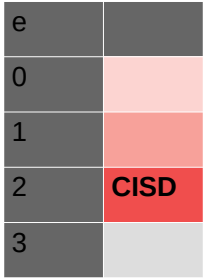
Fábris Kossoski

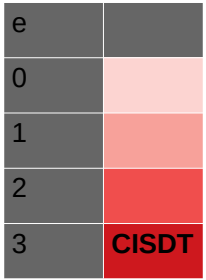
Kossoski, Damour & Loos, JPCL 13 (2022) 4342.

e	
0	
1	
2	
3	

e	
0	**HF**
1	
2	
3	

e	
0	
1	**CIS**
2	
3	

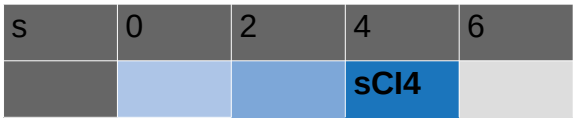

e
0
1
2
CISD
3

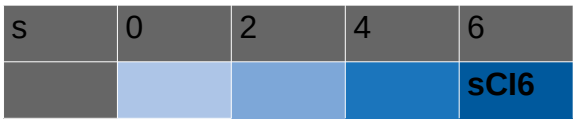

e
0
1
2
3
CISDT

s	0	2	4	6

s	0	2	4	6
	sCI0			

s	0	2	4	6
		sCI2		


s
0
2
4
6
sCI4

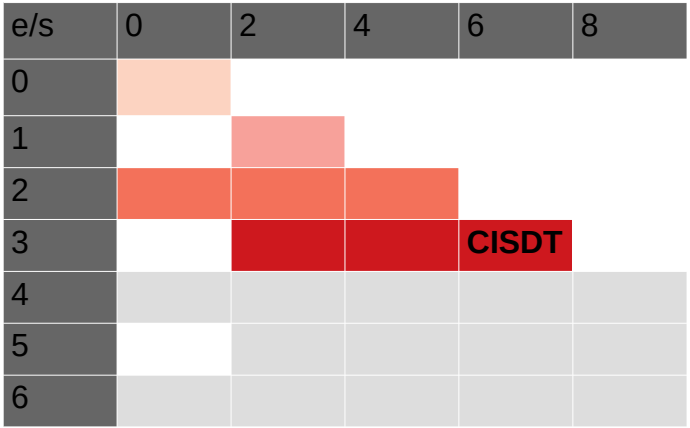

s
0
2
4
6
sCI6

e/s	0	2	4	6	8
0					
1					
2					
3					
4					
5					
6					

e/s	0	2	4	6	8
0	**HF**				
1					
2					
3					
4					
5					
6					

e/s	0	2	4	6	8
0					
1		**CIS**			
2					
3					
4					
5					
6					

e/s	0	2	4	6	8
0					
1					
2			CISD		
3					
4					
5					
6					

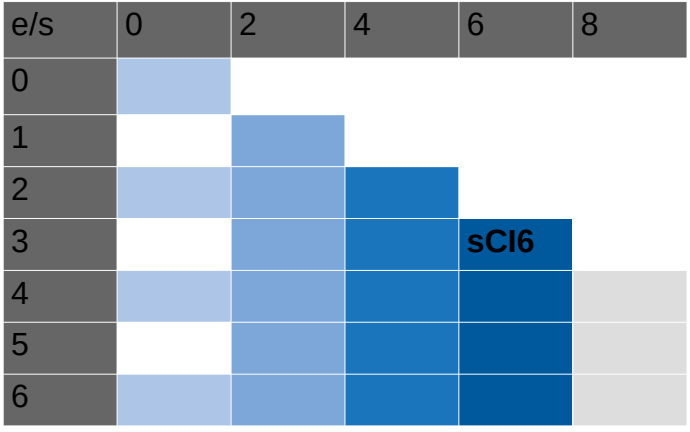

e/s
0
2
4
6
8
0
1
2
3
4
5
6
CISDT

e/s	0	2	4	6	8
0					
1					
2					
3					
4					
5					
6					

e/s	0	2	4	6	8
0	**sCI0**				
1					
2					
3					
4					
5					
6					

e/s	0	2	4	6	8
0					
1		**sCI2**			
2					
3					
4					
5					
6					

e/s	0	2	4	6	8
0					
1					
2			sCI4		
3					
4					
5					
6					


e/s
0
2
4
6
8
0
1
2
3
4
5
6
sCI6

Hierarchy CI (hCI)

$$h = \frac{e + s/2}{2}$$

- e: excitation degree
- s: seniority number
- h: hierarchy parameter

e/s	0	2	4	6	8
0					
1					
2					
3					
4					
5					
6					

e/s	0	2	4	6	8
0	**HF**				
1					
2					
3					
4					
5					
6					

e/s	0	2	4	6	8
0					
1		**hCI1**			
2					
3					
4					
5					
6					

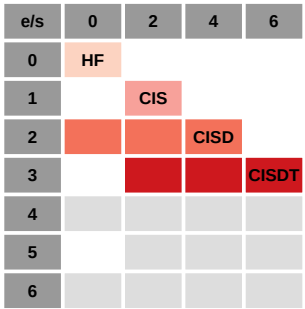
e/s	0	2	4	6	8
0					
1					
2		**hCI1.5**			
3					
4					
5					
6					

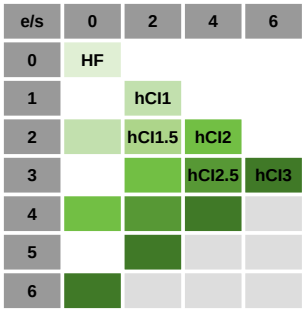
e/s	0	2	4	6	8
0					
1					
2			**hCI2**		
3					
4					
5					
6					

e/s	0	2	4	6	8
0					
1					
2					
3			**hCI2.5**		
4					
5					
6					

e/s	0	2	4	6	8
0					
1					
2					
3				hCl3	
4					
5					
6					

Excitation-based CI *vs* Hierarchy CI *vs* Seniority-based CI





Physical motivation

- Excitation-based CI quickly recovers dynamic correlation
- Seniority-based CI performs well for static correlation
- hCI aims at accounting for most of both

Empirical motivation

Any well-defined truncation scheme is valid.
Is hCI effective?

Computational motivation

- Each hierarchy level accounts for all classes of determinants whose number share the same scaling with system size

excitation-based CI	hCI	N_{det}
CIS	hCI1	$\mathcal{O}(N^2)$
-	hCI1.5	$\mathcal{O}(N^3)$
CISD	hCI2	$\mathcal{O}(N^4)$
-	hCI2.5	$\mathcal{O}(N^5)$
CISDT	hCI3	$\mathcal{O}(N^6)$

- hCI can be implemented in a selected way for additional performance

e/s	0	2	4	6	8
0	1				
1					
2					
3					
4					
5					
6					

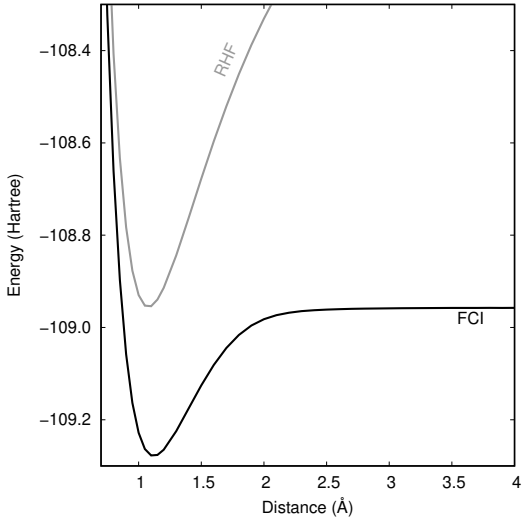
e/s	0	2	4	6	8
0	**1**				
1		**N^2**			
2	**N^2**				
3					
4					
5					
6					

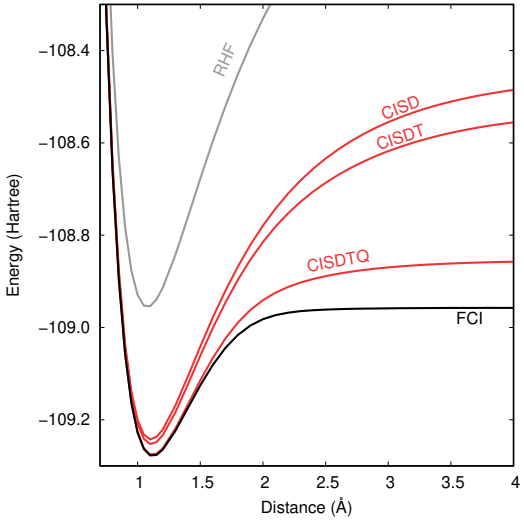
e/s	0	2	4	6	8
0	**1**				
1		**N^2**			
2	**N^2**	**N^3**			
3					
4					
5					
6					

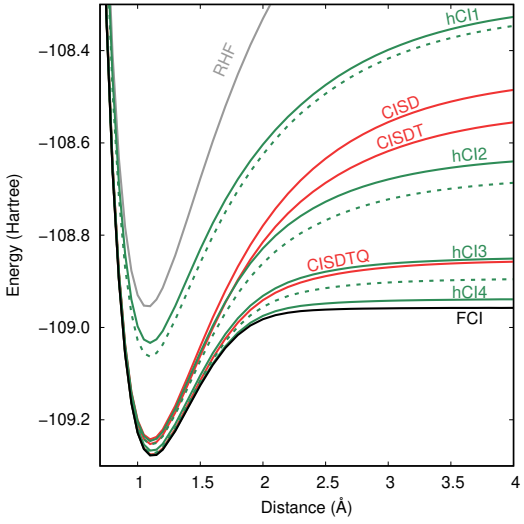
e/s	0	2	4	6	8
0	**1**				
1		N^2			
2	N^2	N^3	N^4		
3		N^4			
4	N^4				
5					
6					

e/s	0	2	4	6	8
0	**1**				
1		N^2			
2	N^2	N^3	N^4		
3		N^4	N^5		
4	N^4	N^5			
5					
6					

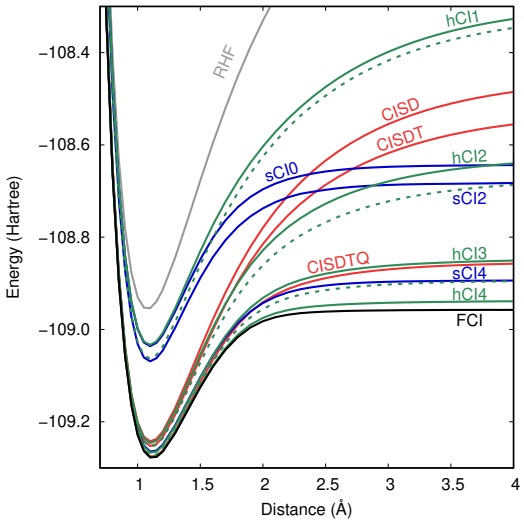
e/s	0	2	4	6	8
0	1				
1		N^2			
2	N^2	N^3	N^4		
3		N^4	N^5	N^6	
4	N^4	N^5	N^6		
5		N^6			
6	N^6				


RHF
FCI
−108.4
−108.6
−108.8
−109.0
−109.2
Energy (Hartree)
1
1.5
2
2.5
3
3.5
4
Distance (Å)

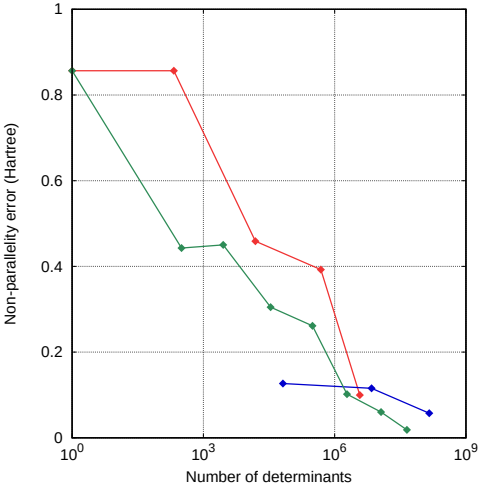

RHF
CISD
CISDT
CISDTQ
FCI
−108.4
−108.6
−108.8
−109.0
−109.2
Energy (Hartree)
1
1.5
2
2.5
3
3.5
4
Distance (Å)

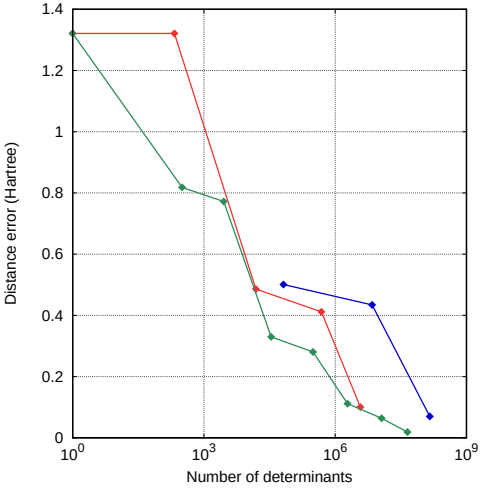

RHF
hCI1
CISD
CISDT
hCI2
CISDTQ
hCI3
hCI4
FCI
−108.4
−108.6
−108.8
−109.0
−109.2
Energy (Hartree)
1
1.5
2
2.5
3
3.5
4
Distance (Å)

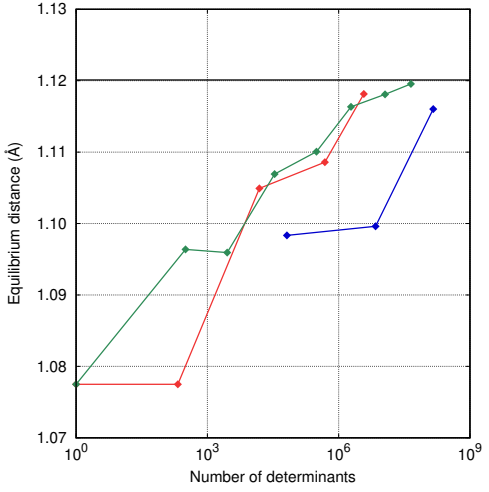
N_2/cc-pVDZ

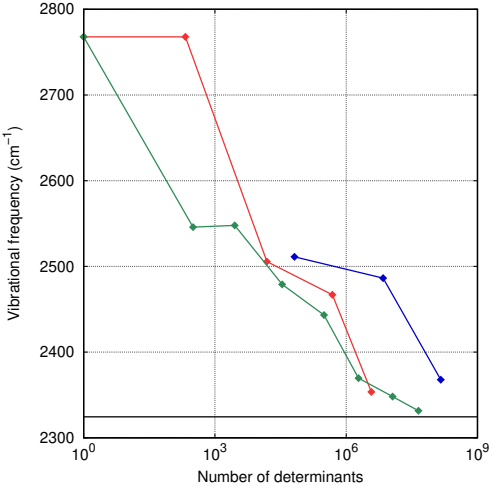

RHF
hCI1
CISD
CISDT
hCI2
sCI0
sCI2
CISDTQ
hCI3
sCI4
hCI4
FCI
−108.4
−108.6
−108.8
−109.0
−109.2
Energy (Hartree)
1
1.5
2
2.5
3
3.5
4
Distance (Å)

N_2/cc-pVDZ

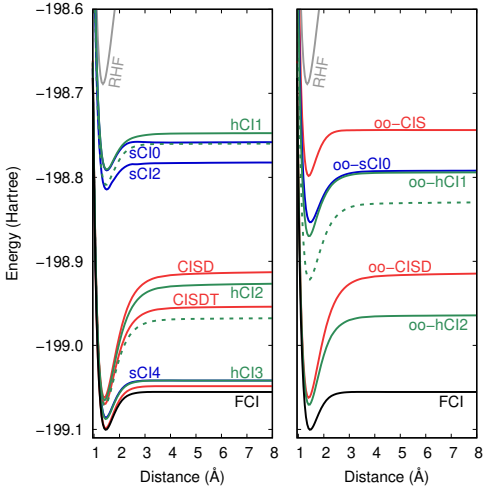

Non-parallelity error (Hartree)
1
0.8
0.6
0.4
0.2
0
10^0
10^3
10^6
10^9
Number of determinants

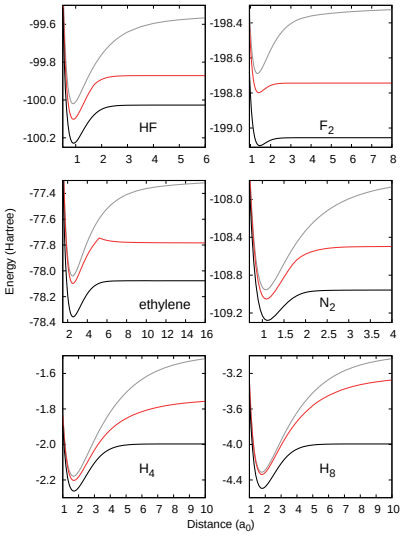

Distance error (Hartree)
1.4
1.2
1
0.8
0.6
0.4
0.2
0
10^0
10^3
10^6
10^9
Number of determinants


1.13
1.12
1.11
1.10
1.09
1.08
1.07
Equilibrium distance (Å)
10^0
10^3
10^6
10^9
Number of determinants


2800
2700
2600
2500
2400
2300
Vibrational frequency (cm^{-1})
10^0
10^3
10^6
10^9
Number of determinants

Orbital optimized CI (oo-CI): F_2/cc-pVDZ




HF
F2
ethylene
N2
H4
H8
Energy (Hartree)
Distance (a0)

Hierarchy configuration interaction (hCI)

Novel CI hierarchy, physically, computationally, and empirically inspired

Performance of hCI

Overall better than excitation-based CI, for different systems, properties, and basis sets

Orbital optimized CI (oo-CI)

Not always recommended. Stepping up the CI ladder might be a wiser choice

oo-CIS

Minimally correlated model (only single excitations), promising results

hCI

- Excited states
- Open-shell systems
- Hierarchy coupled-cluster
- Trial wave functions for Quantum Monte Carlo
- RDMFT [Senjean et al. arXiv:2204.00699]

Orbital optimization

Optimize the orbitals at a lower level of CI, then run a higher level of CI

oo-CIS

Excited states

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PTEROSOR team

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https://lcpq.github.io/PTEROSOR

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