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Laboratoire de Chimie et Physique Quantiques

Hierarchy Configuration Interaction and State-Specific Approaches for Excited States

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September 4th, 2022

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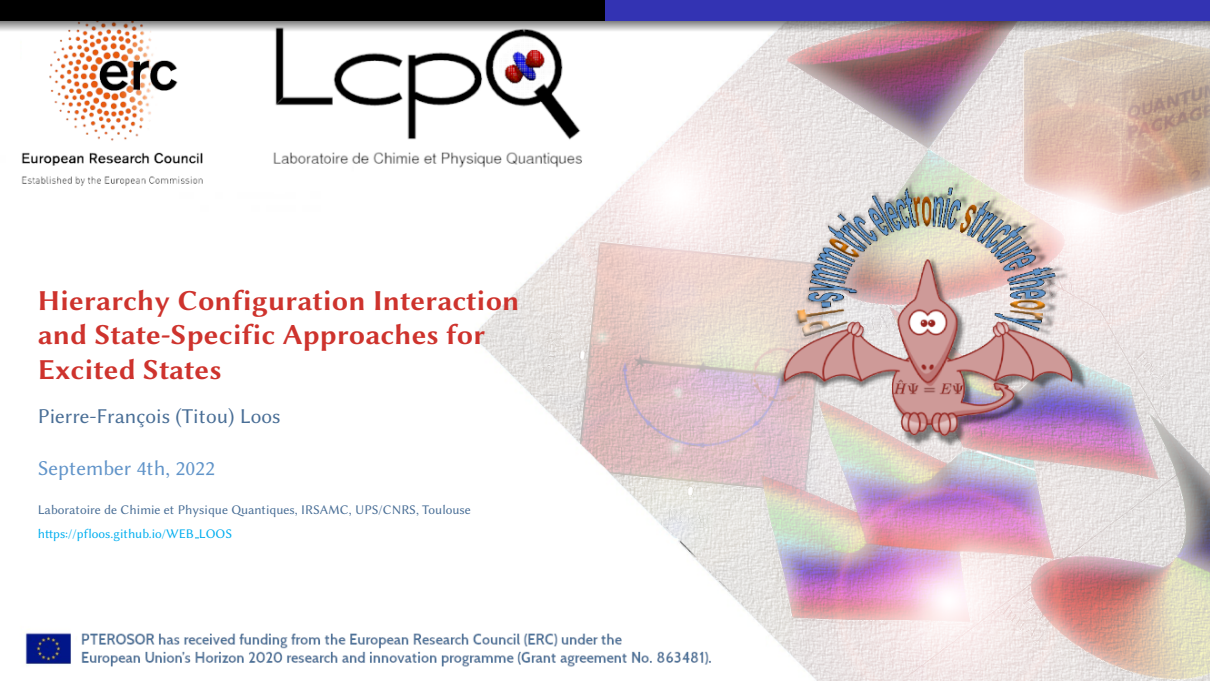
https://pfloos.github.io/WEB_LOOS

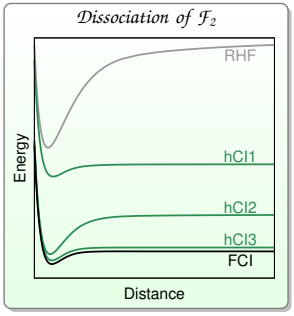


PTEROSOR has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (Grant agreement No. 863481).

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.

How to “span” the Hilbert space: Excitation-based CI

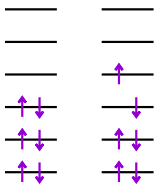
e	
0	
1	
2	
3	

How to “span” the Hilbert space: Excitation-based CI

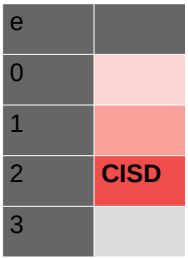
e	
0	**HF**
1	
2	
3	

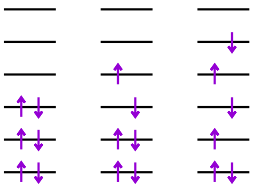
How to “span” the Hilbert space: Excitation-based CI

e	
0	
1	CIS
2	
3	



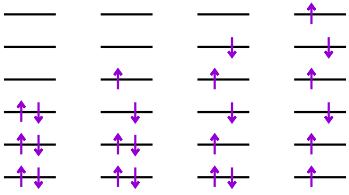
How to “span” the Hilbert space: Excitation-based CI





How to “span” the Hilbert space: Excitation-based CI

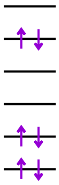
e	
0	
1	
2	
3	**CISDT**



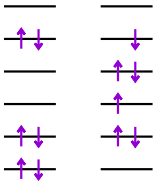
How to “span” the Hilbert space: Seniority-based CI

s	0	2	4	6

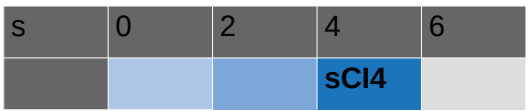
s	0	2	4	6
	sCI0			

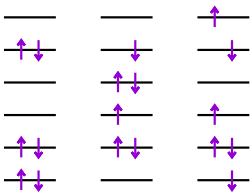


s	0	2	4	6
		sCI2		

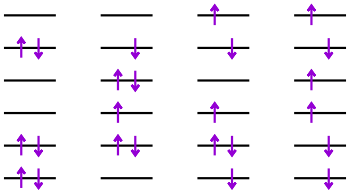


How to “span” the Hilbert space: Seniority-based CI





s	0	2	4	6
				sCI6

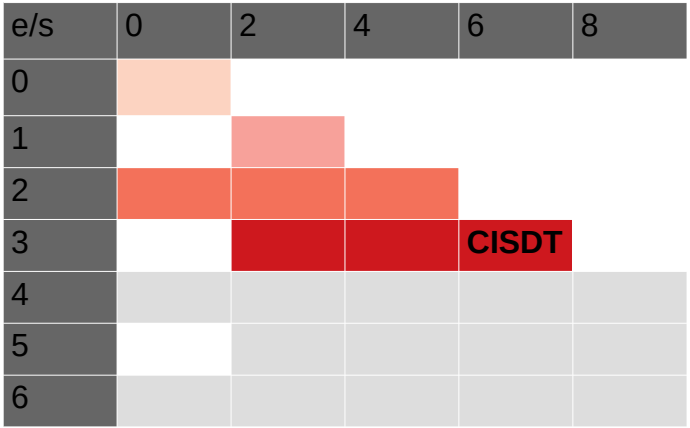


e/s	0	2	4	6	8
0					
1					
2					
3					
4					
5					
6					

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					

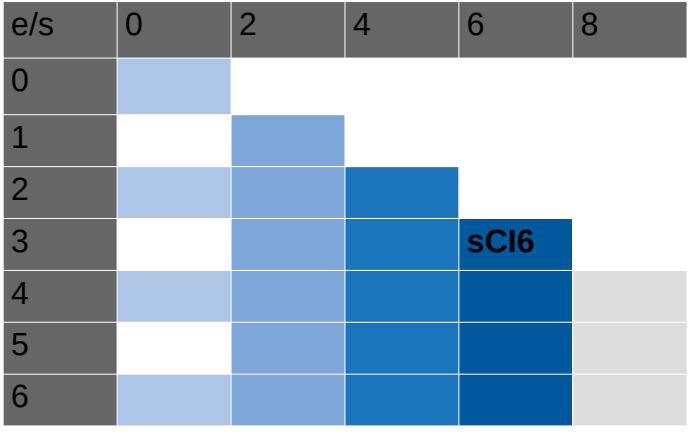

e/s
0
2
4
6
8
0
1
2
3
4
5
6
CISDT

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)

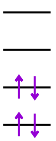
$$h = \frac{e + s/2}{2}$$

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

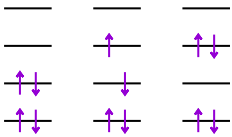
Kossoski, Damour & Loos, JPCL 13 (2022) 4342

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

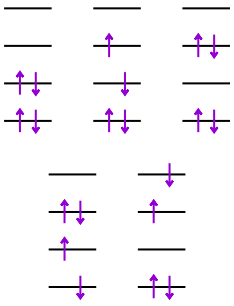
e/s	0	2	4	6	8
0	**HF**				
1					
2					
3					
4					
5					
6					



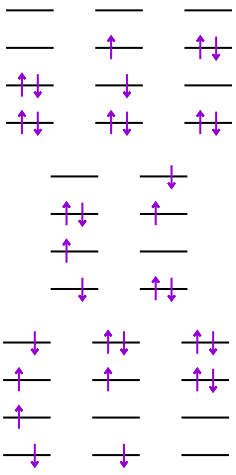
e/s	0	2	4	6	8
0					
1		**hCl1**			
2					
3					
4					
5					
6					



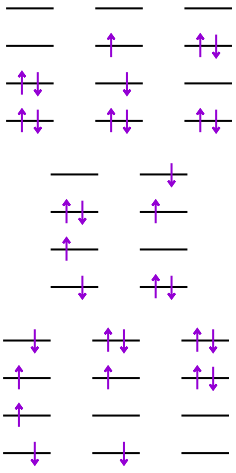
e/s	0	2	4	6	8
0					
1					
2		**hCl1.5**			
3					
4					
5					
6					



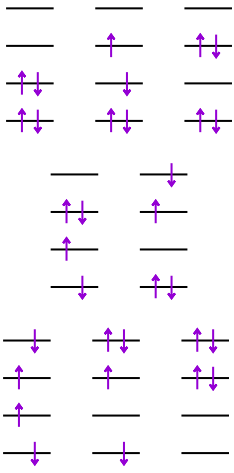
e/s	0	2	4	6	8
0					
1					
2			**hCl2**		
3					
4					
5					
6					



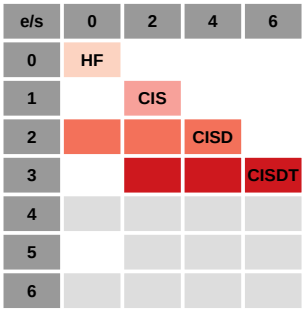
e/s	0	2	4	6	8
0					
1					
2					
3			hCl2.5		
4					
5					
6					

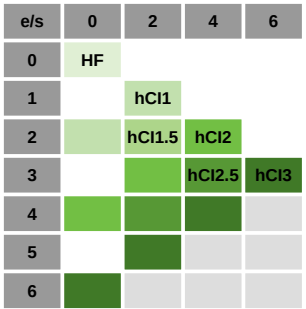


e/s	0	2	4	6	8
0					
1					
2					
3				hCl3	
4					
5					
6					



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?

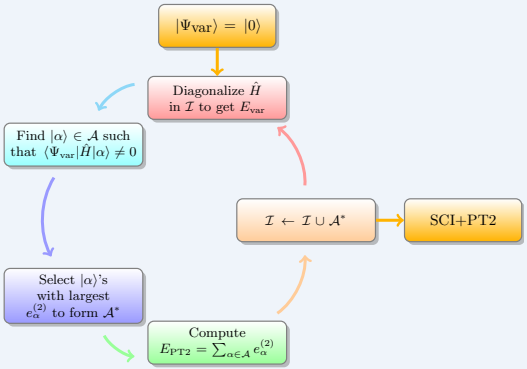
Computational motivation

- 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	$\mathcal{O}(N^6)$

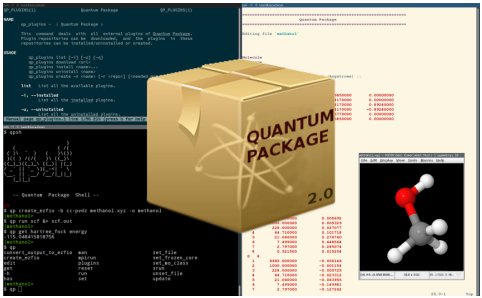
- hCI can be implemented in a selected way for additional performance

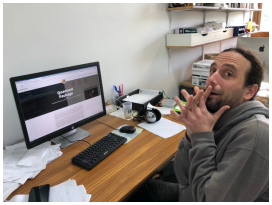
CIPSI = CI using a Perturbative Selection made Iteratively



Huron, Malrieu & Rancurel, JCP 58 (1973) 5745

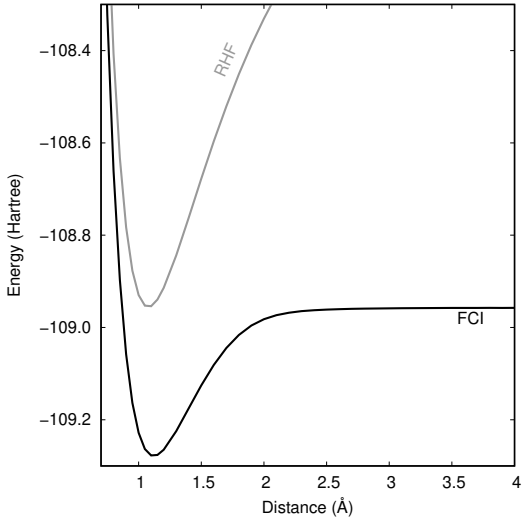
"SCI+PT2 methods provide near full CI (FCI) quality quantities with only a small fraction of the determinants of the FCI space"

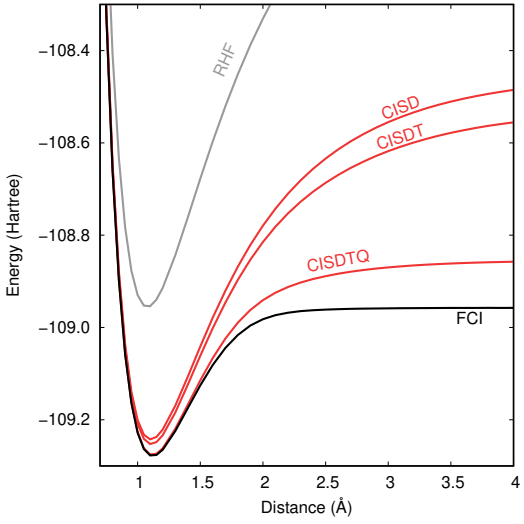


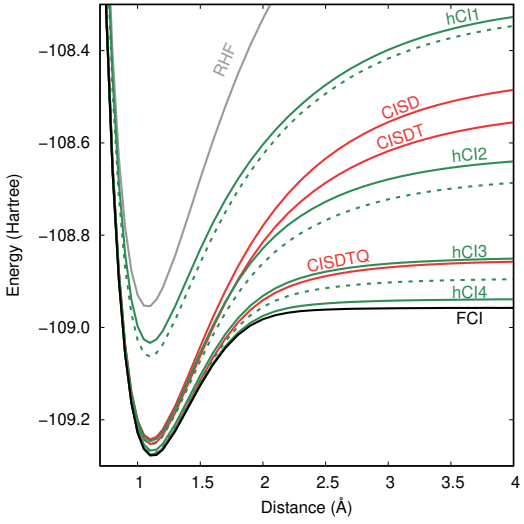


Anthony Scemama

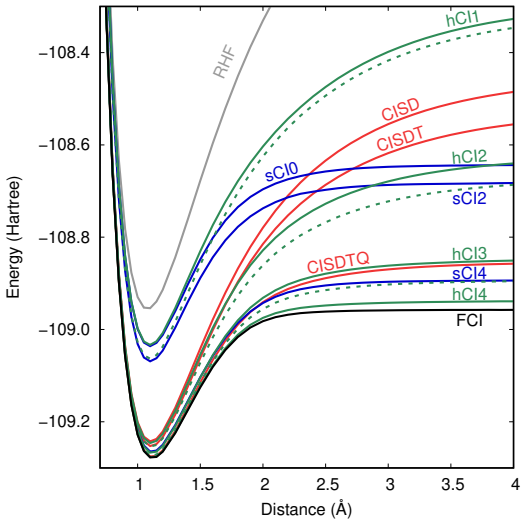
"Quantum Package 2.0: An Open-Source Determinant-Driven Suite of Programs",
Garniron et al., JCTC 15 (2019) 3591


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)

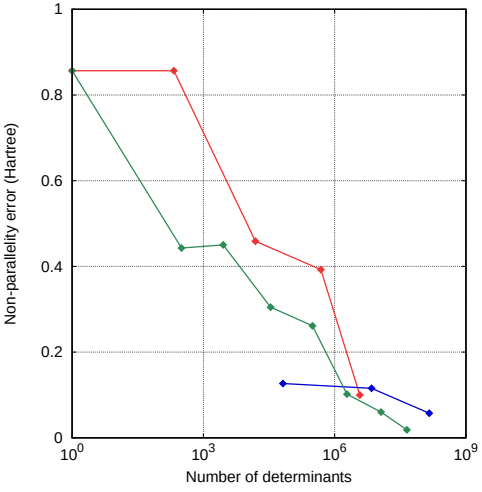

RHF
CISD
CISDT
CISDTQ
FCI
−108.4
−108.6
−108.8
−109.0
−109.2
Energy (Hartree)
1
1.5
2
2.5
3
3.5
4
Distance (Å)

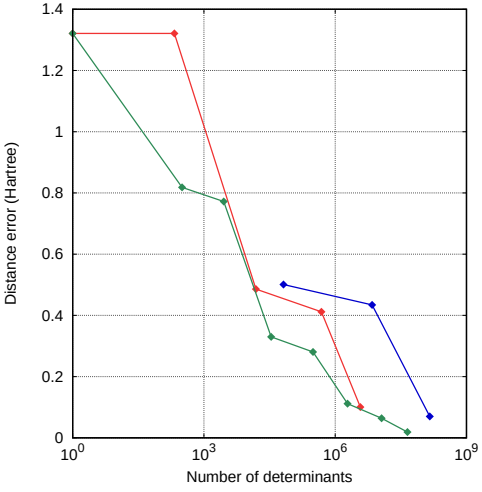

RHF
hCI1
CISD
CISDT
hCI2
CISDTQ
hCI3
hCI4
FCI
−108.4
−108.6
−108.8
−109.0
−109.2
Energy (Hartree)
1
1.5
2
2.5
3
3.5
4
Distance (Å)

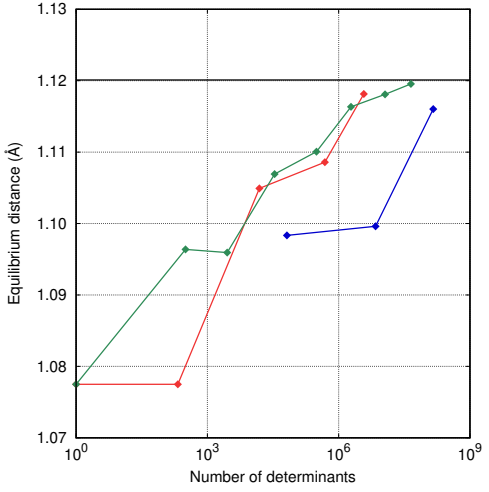
N_2/cc-pVDZ

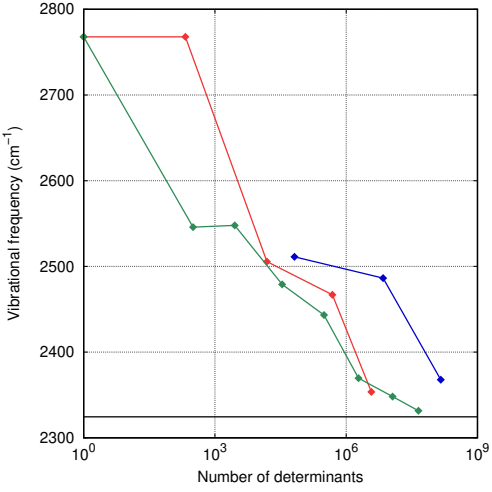

RHF
hCI1
CISD
CISDT
hCI2
sCI0
sCI2
CISDTQ
hCI3
sCI4
hCI4
FCI
−108.4
−108.6
−108.8
−109.0
−109.2
Energy (Hartree)
1
1.5
2
2.5
3
3.5
4
Distance (Å)

N_2/cc-pVDZ

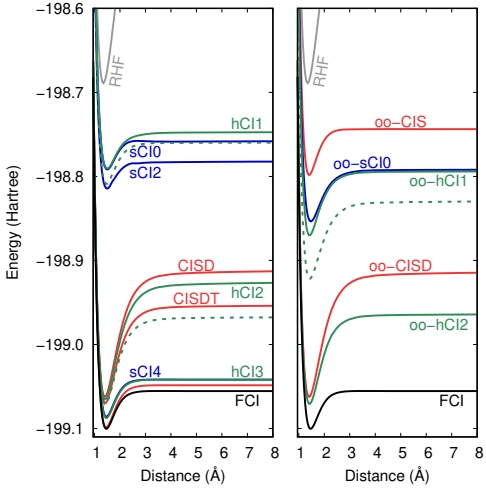

Non-parallelity error (Hartree)
1
0.8
0.6
0.4
0.2
0
10^0
10^3
10^6
10^9
Number of determinants


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

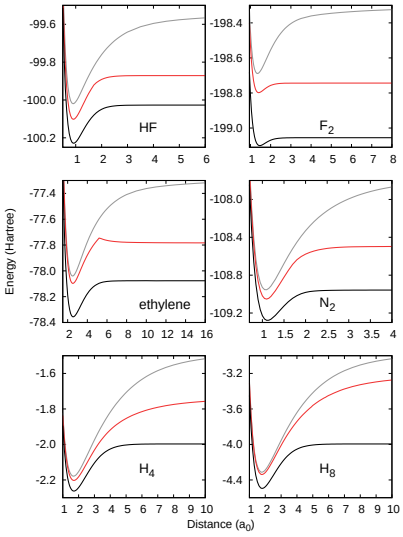

2800
2700
2600
2500
2400
2300
Vibrational frequency (cm^{-1})
10^0
10^3
10^6
10^9
Number of determinants

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



Yann Damour

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


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

State-averaged *vs* State-specific excited-state calculations

State-averaged CI

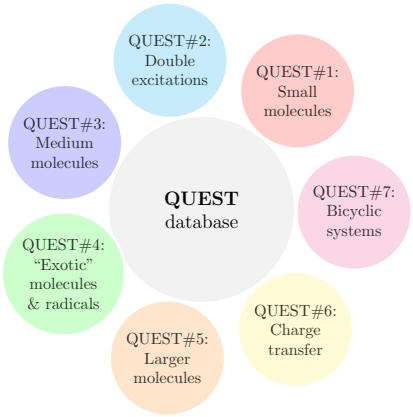
- A common set of orbitals and determinants are used to construct the ground- and excited-state wave functions
- A single calculation is required with suitable weights on the different states
- You may or may not further optimize the orbitals
- It's a half empty, half full strategy

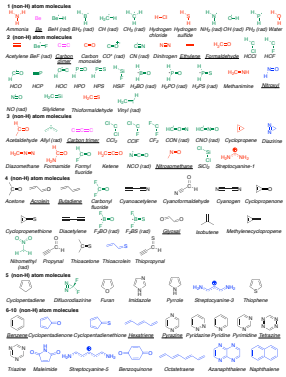
State-specific CI

- A different set of orbitals and determinants are used to construct the ground- and excited-state wave functions
- Several calculations are required, one for each state
- One must find a suitable set of orbitals for the excited states (which might not be easy)
- Further optimizing orbitals for a given specific state is hard

Kossoski et al. JCTC 17 (2021) 4756
Marie et al. JCP 155 (2021) 104105

"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"

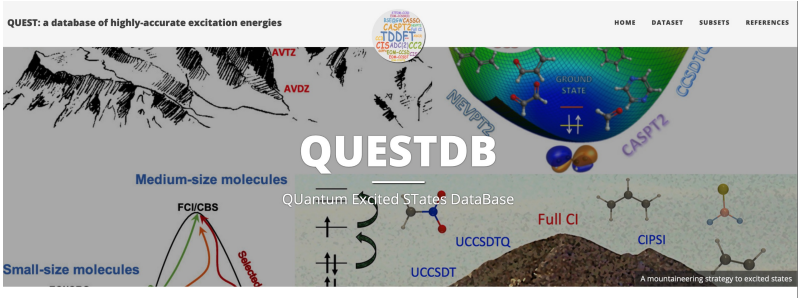




Denis Jacquemin

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

The QUEST website



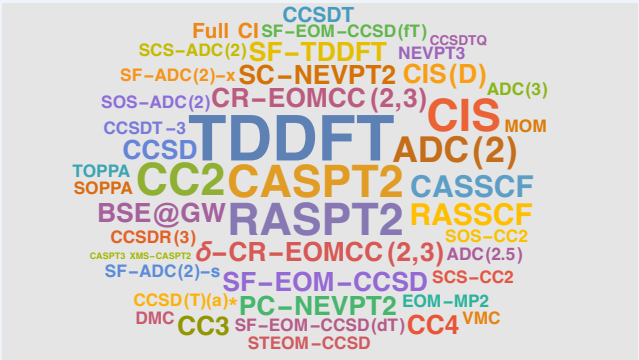
Mika Véril

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

https://lcpq.github.io/QUESTDB_website

Zoo of functionals...

And this is just for excited states...



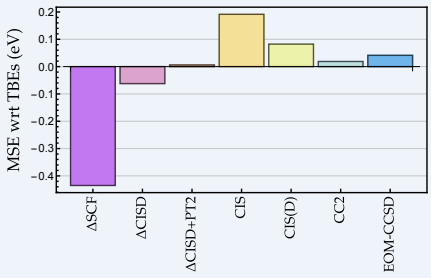
Other research groups using QUEST

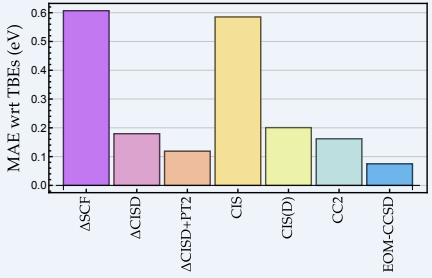
- Head-Gordon's group: orbital-optimized DFT for double excitations [JCTC 16 (2020) 1699; JPCL 12 (2021) 4517] and TD-DFT benchmark [JCTC (in press)]
- Kaupp's group: assessment of hybrid functionals [JCP 155 (2021) 124108]
- Kallay's and Goerigk's groups: double hybrids [JCTC 15 (2019) 4735; JCTC 17 (2021) 927; JCTC 17 (2021) 5165; JCTC 17 (2021) 4211]
- Truhlar/Gagliardi's group: p-DFT [10.26434/chemrxiv-2022-9g7fd]
- Bartlett's group: Variants of EOM-CC for doubly-excited states [JCP 156 (2022) 201102]
- Neuscamman's group: QMC for doubly-excited states [JCP 153 (2022) 234105]
- Filippi/Scemama's groups: QMC for excited states [JCTC 15 (2019) 4889; JCTC 17 (2021) 3426; JCTC 18 (2022) 1089]
- Gould's group: ensemble DFT [JPCL 13 (2022) 2452]
- our group: wave function methods [JPCL 11 (2020) 974; JCTC 17 (2021) 4756; JCTC 18 (2022) 2418; JCP 157 (2022) 014103] and many-body perturbation theory [JCP 153 (2020) 114120; JCP 156 (2022) 164101]

Our state-specific CI algorithm

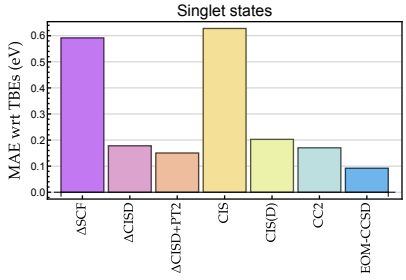
1. Determine the minimal set of orbitals involved in each state
2. Optimize this set of orbitals via energy minimization
3. Add (in a selected way) singles and doubles linked to this set $\Rightarrow$ ΔCISD
4. Add second-order Epstein-Nesbet perturbative correction $\Rightarrow$ ΔCISD+PT2

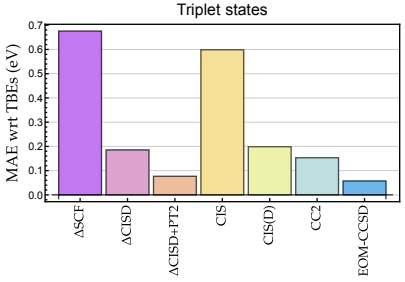
Based on more than 250 excited states of the QUEST database

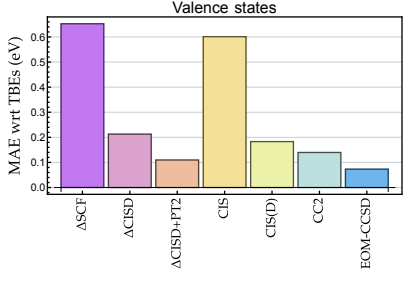


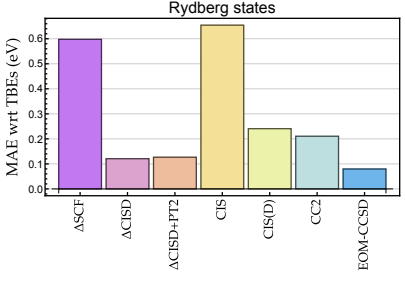


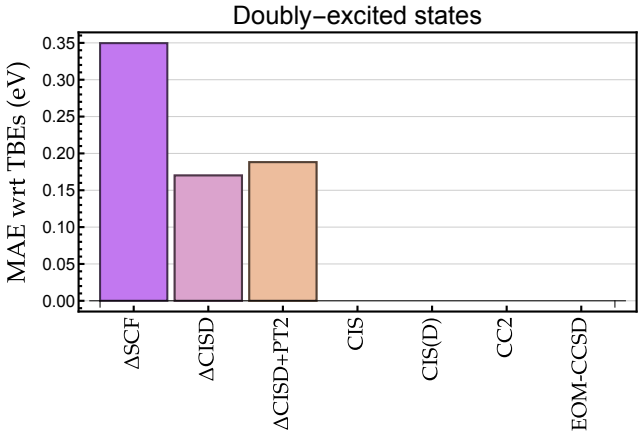
MAEs for various types of excitations



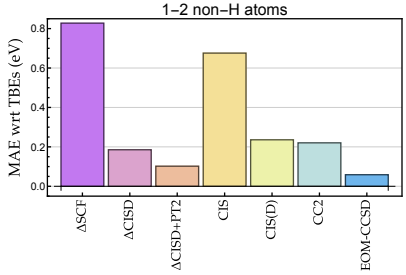


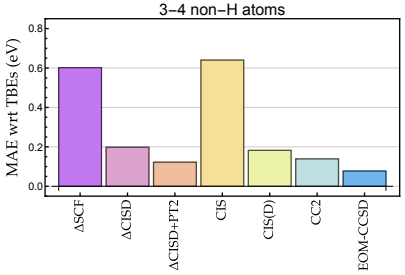


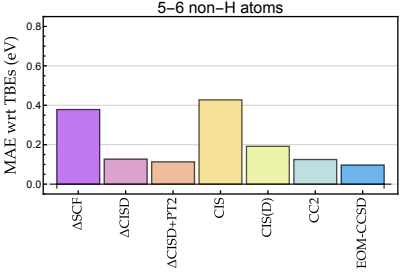



Doubly−excited states
MAE wrt TBEs (eV)
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
ΔSCF
ΔCISD
ΔCISD+PT2
CIS
CIS(D)
CC2
EOM-CCSD

MAEs wrt system size







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https://lcpq.github.io/PTEROSOR

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https://pfloos.github.io/WEB_LOOS

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