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Laboratoire de Chimie et Physique Quantiques

CIPSI: selected configuration interaction methods for ground and excited states

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19th September 2023

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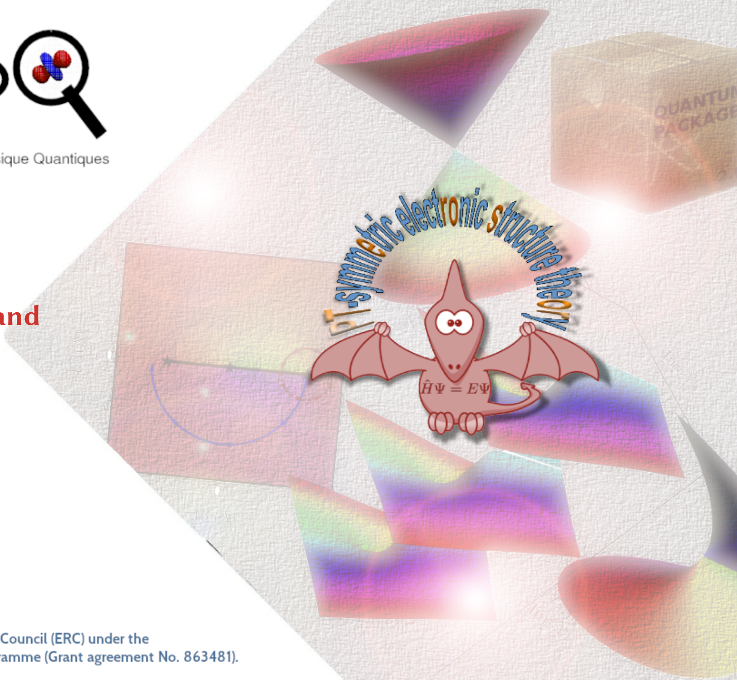
https://lcpq.github.io/pterosor



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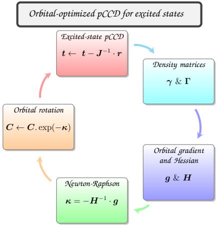
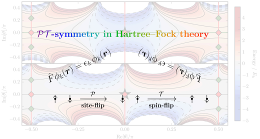
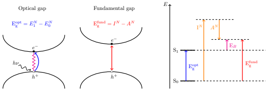
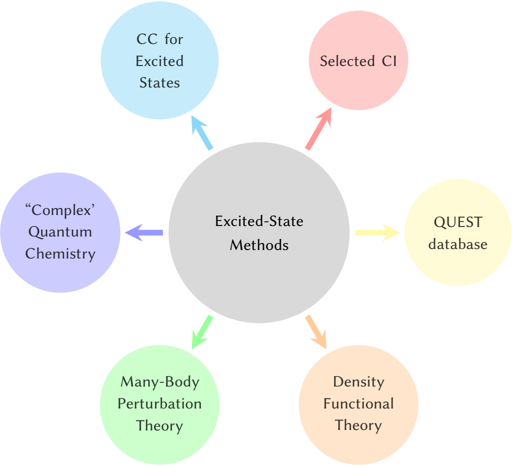
General Overview of our Research Group









Excited-State Methods

CC for Excited States

Selected CI

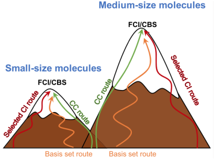
QUEST database

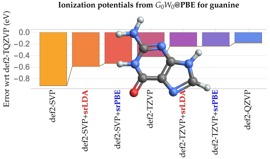
Density Functional Theory

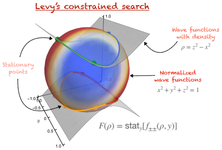
Many-Body Perturbation Theory

“Complex’ Quantum Chemistry

https://lcpq.github.io/PTEROSOR/







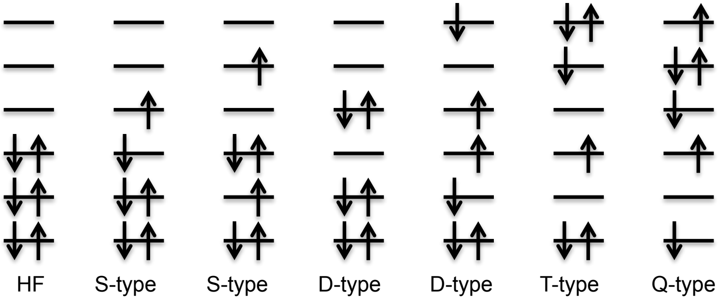
Configuration Interaction (CI)

- This is the oldest and perhaps the easiest method to understand
- The CI wave function is a linear combination of Slater determinants
- CI methods use excited determinants to "improve" the reference (usually Hartree-Fock) wave function

$$|\Phi_{\text{CI}}\rangle = \underbrace{c_0\,|\Psi_0\rangle}_{\text{reference}} + \underbrace{\sum_{\substack{i\\a}} c_i^a\,|\Psi_i^a\rangle}_{\text{singles}} + \underbrace{\sum_{\substack{i<j\\a<b}} c_{ij}^{ab}\,|\Psi_{ij}^{ab}\rangle}_{\text{doubles}} + \underbrace{\sum_{\substack{i<j<k\\a<b<c}} c_{ijk}^{abc}\,|\Psi_{ijk}^{abc}\rangle}_{\text{triples}} + \underbrace{\sum_{\substack{i<j<k<l\\a<b<c<d}} c_{ijkl}^{abcd}\,|\Psi_{ijkl}^{abcd}\rangle}_{\text{quadruples}} + \cdots$$

- CI is based on the variational principle (like the Hartree-Fock approximation)

Excited determinants



CI wave function

$$\boxed{|\Phi_{\mathrm{CI}}\rangle = c_0\,|0\rangle + c_{\mathrm{S}}\,|\mathrm{S}\rangle + c_{\mathrm{D}}\,|\mathrm{D}\rangle + c_{\mathrm{T}}\,|\mathrm{T}\rangle + c_{\mathrm{Q}}\,|\mathrm{Q}\rangle + \cdots}$$

Truncated CI

- When $|\mathrm{S}\rangle$ (singles) are taken into account: **CIS**

$$|\Phi_{\mathrm{CIS}}\rangle = c_0 |0\rangle + c_{\mathrm{S}} |\mathrm{S}\rangle$$

NB: CIS is an excited state method

- When $|\mathrm{S}\rangle$ and $|\mathrm{D}\rangle$ are taken into account: **CISD**

$$|\Phi_{\mathrm{CISD}}\rangle = c_0 |0\rangle + c_{\mathrm{S}} |\mathrm{S}\rangle + c_{\mathrm{D}} |\mathrm{D}\rangle$$

NB: CISD is the most commonly-used CI method

- When $|\mathrm{S}\rangle$, $|\mathrm{D}\rangle$ and $|\mathrm{T}\rangle$ (triples) are taken into account: **CISDT**

$$|\Phi_{\mathrm{CISDT}}\rangle = c_0 |0\rangle + c_{\mathrm{S}} |\mathrm{S}\rangle + c_{\mathrm{D}} |\mathrm{D}\rangle + c_{\mathrm{T}} |\mathrm{T}\rangle$$

- **CISDTQ**, etc.

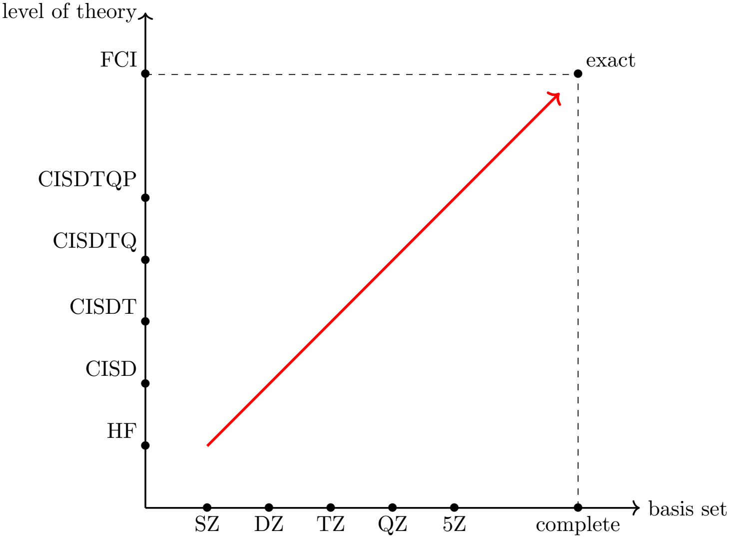
Full CI

- When all possible excitations are taken into account, this is called a Full CI calculation (**FCI**)

$$\boxed{|\Phi_{\text{FCI}}\rangle = c_0 |0\rangle + c_{\text{S}} |\text{S}\rangle + c_{\text{D}} |\text{D}\rangle + c_{\text{T}} |\text{T}\rangle + c_{\text{Q}} |\text{Q}\rangle + \ldots}$$

- FCI gives the exact solution of the Schrödinger equation within a given basis
- FCI is becoming more and more fashionable these days (e.g. FCIQMC and CIPSI methods)
- So, why do we care about other methods?
- Because FCI is super computationally expensive!

Pople diagram



Size of CI Matrix

"Assume we have 10 electrons in 38 spin MOs: 10 are occupied and 28 are empty"

- There is C_{10}^k possible ways of selecting k electrons out of the 10 occupied orbitals

$$C_n^k = \frac{n!}{k!(n-k)!}$$

- There is C_{28}^k ways of distributing them out in the 28 virtual orbitals
- For a given excitation level k, there is $C_{10}^k C_{28}^k$ excited determinants
- The total number of possible excited determinant is

$$\sum_{k=0}^{10} C_{10}^k C_{28}^k = C_{38}^{10} = 472,733,756$$

- This is a lot...

For $N = 10$ and $K = 38$:

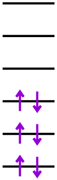
k	Num. of excitations
0	1
1	280
2	17,010
3	393,120
4	4,299,750
5	24,766,560
6	79,115,400
7	142,084,800
8	139,864,725
9	69,069,000
10	13,123,110
Tot.	472,733,756

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

e	
0	
1	
2	
3	

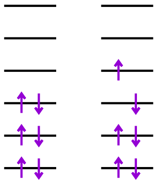
How to “span” the Hilbert space: Excitation-based CI

e	
0	**HF**
1	
2	
3	

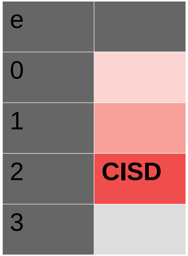


How to “span” the Hilbert space: Excitation-based CI

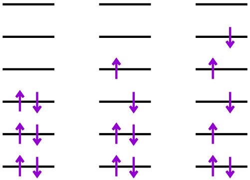
e	
0	
1	**CIS**
2	
3	



How to "span" the Hilbert space: Excitation-based CI

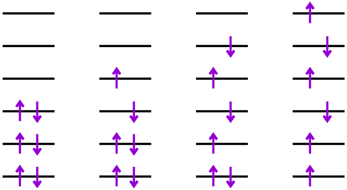


e	
0	
1	
2	**CISD**
3	



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

e	
0	
1	
2	
3	**CISDT**

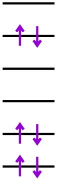


How to “span” the Hilbert space: Seniority-based CI

s	0	2	4	6

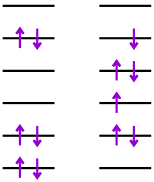
How to “span” the Hilbert space: Seniority-based CI

s	0	2	4	6
	sCI0			



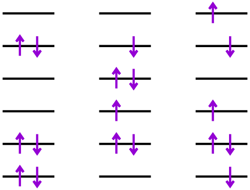
How to “span” the Hilbert space: Seniority-based CI

s	0	2	4	6
		sCI2		



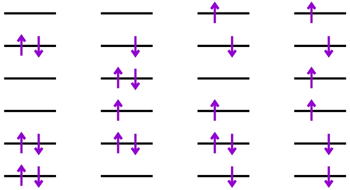
How to “span” the Hilbert space: Seniority-based CI

s	0	2	4	6
			sCI4	



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

s	0	2	4	6
				sCI6



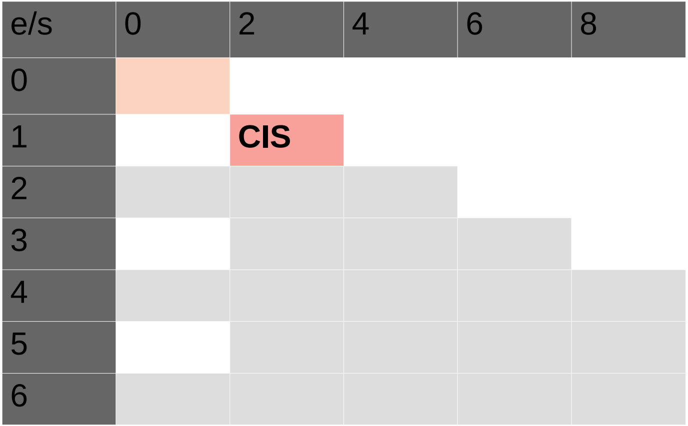
Excitation-based CI

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

Excitation-based CI

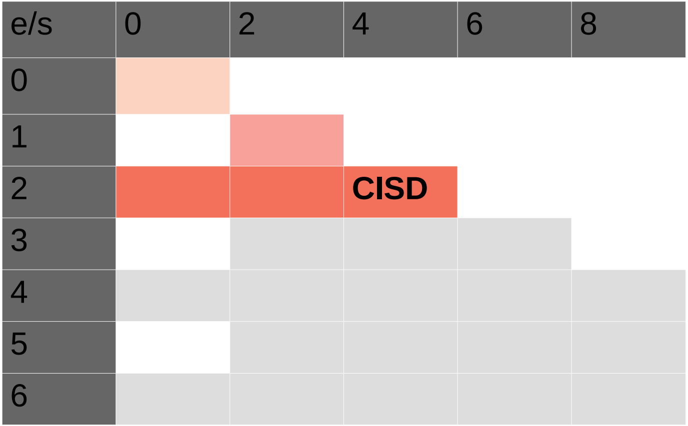
e/s	0	2	4	6	8
0	**HF**				
1		▨			
2	▨	▨	▨		
3		▨	▨	▨	
4	▨	▨	▨	▨	▨
5		▨	▨	▨	▨
6	▨	▨	▨	▨	▨

Excitation-based CI



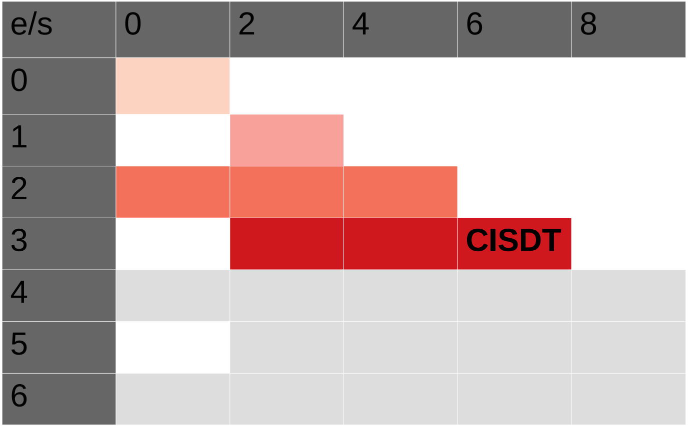
e/s	0	2	4	6	8
0	▨				
1		**CIS**			
2	▨	▨	▨		
3		▨	▨	▨	
4	▨	▨	▨	▨	▨
5		▨	▨	▨	▨
6	▨	▨	▨	▨	▨

Excitation-based CI



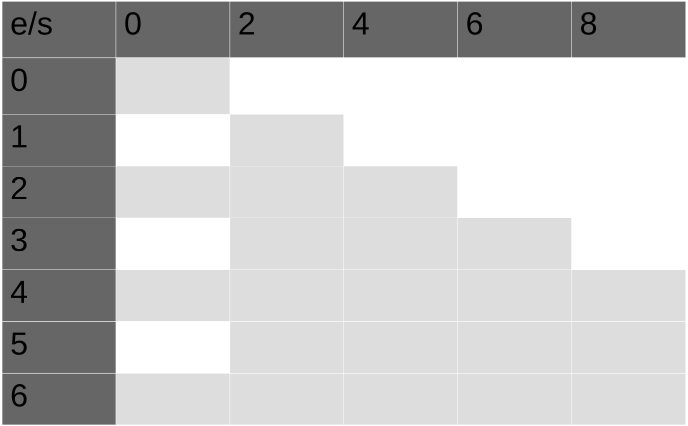
e/s	0	2	4	6	8
0	🟧				
1		🟥			
2	🟥	🟥	**CISD**		
3		▨	▨	▨	
4	▨	▨	▨	▨	▨
5		▨	▨	▨	▨
6	▨	▨	▨	▨	▨

Excitation-based CI



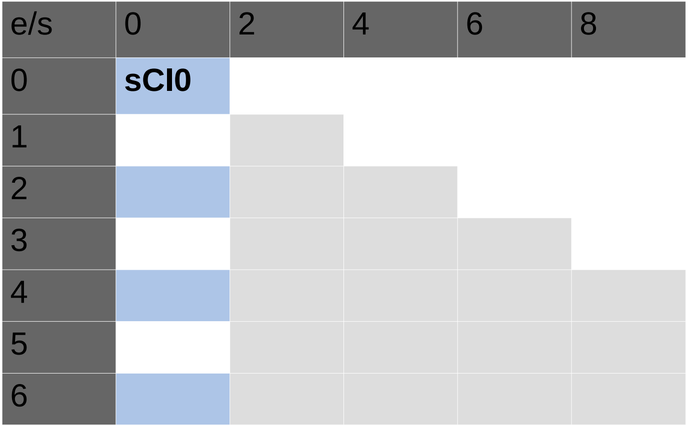
e/s	0	2	4	6	8
0	🟥				
1		🟥			
2	🟥	🟥	🟥		
3		🟥	🟥	**CISDT**	
4	▨	▨	▨	▨	▨
5		▨	▨	▨	▨
6	▨	▨	▨	▨	▨

Seniority-based CI



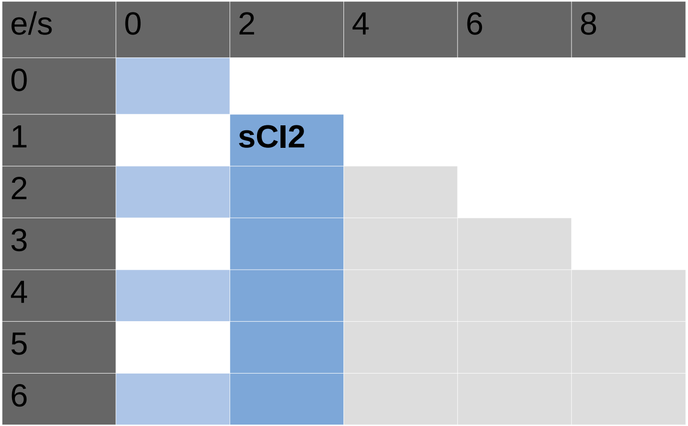
e/s	0	2	4	6	8
0	■				
1		■			
2	■	■	■		
3		■	■	■	
4	■	■	■	■	■
5		■	■	■	■
6	■	■	■	■	■

Seniority-based CI



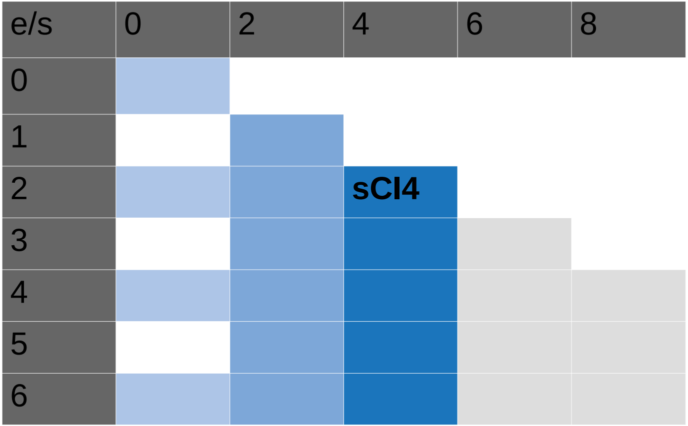
e/s	0	2	4	6	8
0	**sCI0**				
1					
2					
3					
4					
5					
6					

Seniority-based CI



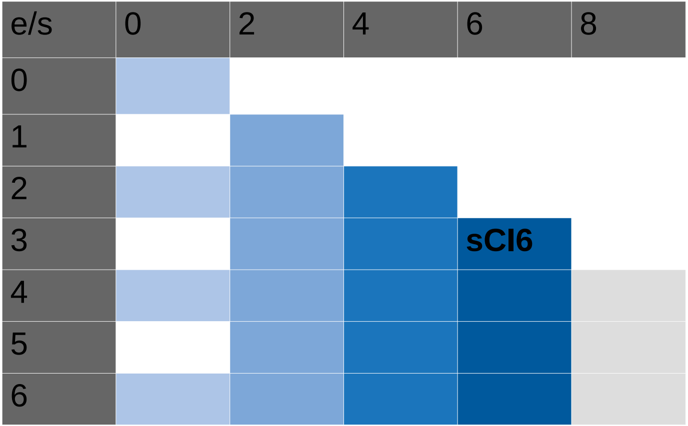
e/s	0	2	4	6	8
0					
1		**sCI2**			
2					
3					
4					
5					
6					

Seniority-based CI



e/s	0	2	4	6	8
0	░				
1		▒			
2	░	▒	▓ **sCI4**		
3		▒	▓	▩	
4	░	▒	▓	▩	▩
5		▒	▓	▩	▩
6	░	▒	▓	▩	▩

Seniority-based CI



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

Hierarchy CI (hCI)

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

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

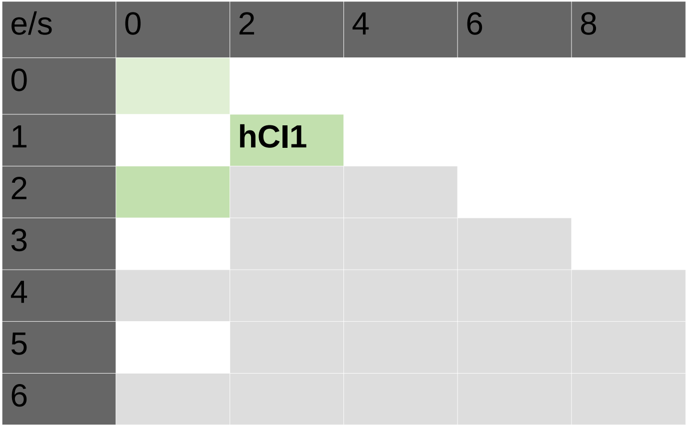
Hierarchy CI

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

Hierarchy CI

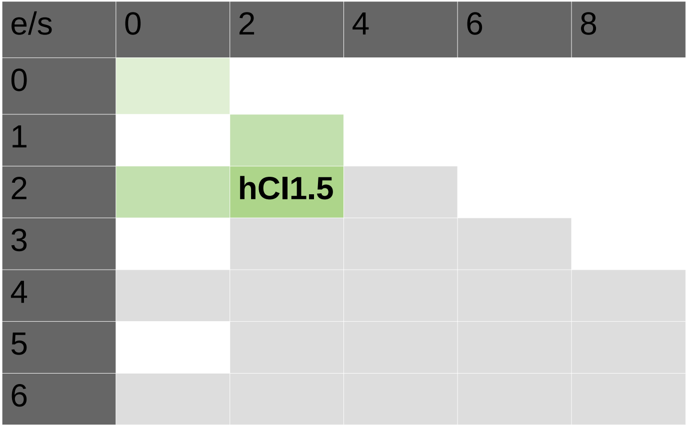
e/s	0	2	4	6	8
0	**HF**				
1		▨			
2	▨	▨	▨		
3		▨	▨	▨	
4	▨	▨	▨	▨	▨
5		▨	▨	▨	▨
6	▨	▨	▨	▨	▨

Hierarchy CI



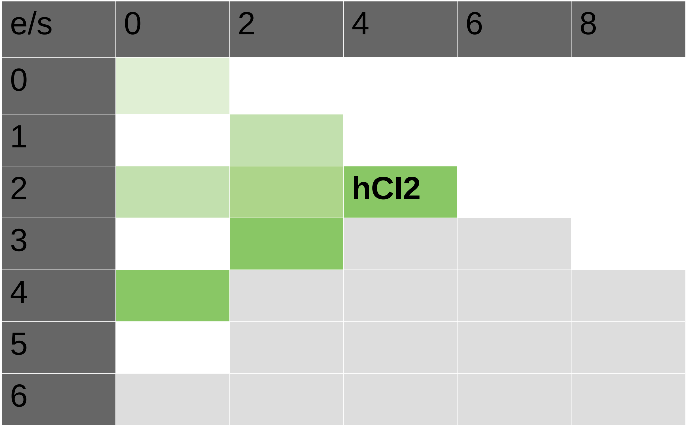
e/s	0	2	4	6	8
0	🟩				
1		hCI1			
2	🟩	▨	▨		
3		▨	▨	▨	
4	▨	▨	▨	▨	▨
5		▨	▨	▨	▨
6	▨	▨	▨	▨	▨

Hierarchy CI



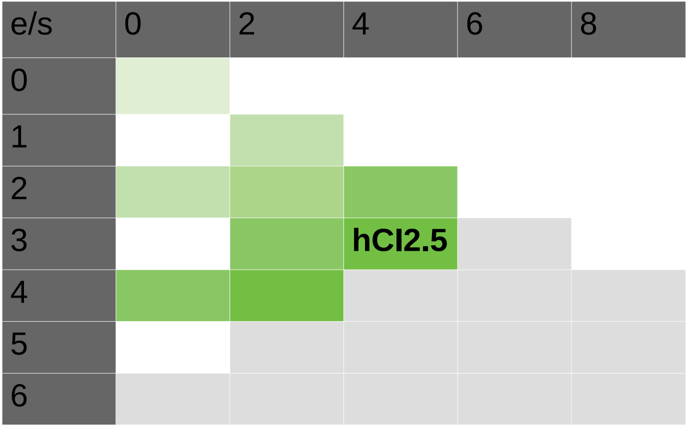
e/s	0	2	4	6	8
0					
1					
2		**hCI1.5**			
3					
4					
5					
6					

Hierarchy CI



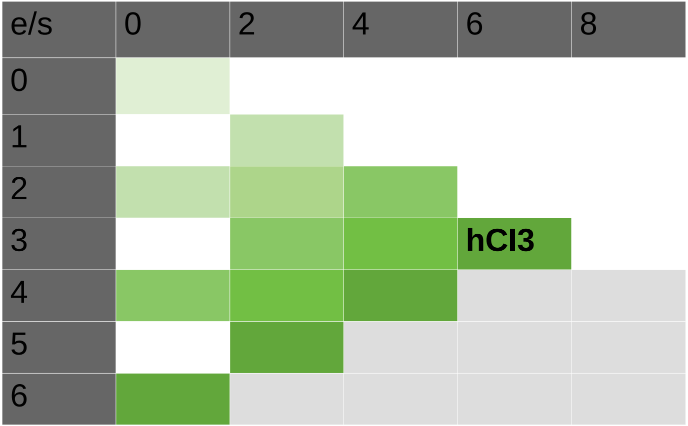
e/s	0	2	4	6	8
0					
1					
2			**hCI2**		
3					
4					
5					
6					

Hierarchy CI



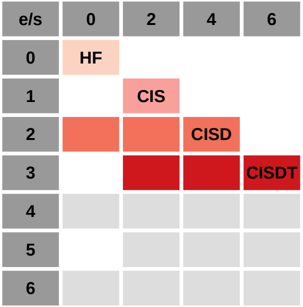
e/s	0	2	4	6	8
0					
1					
2					
3			**hCI2.5**		
4					
5					
6					

Hierarchy CI



e/s	0	2	4	6	8
0	🟩				
1		🟩			
2	🟩	🟩	🟩		
3		🟩	🟩	hCI3	
4	🟩	🟩	🟩	▨	▨
5		🟩	▨	▨	▨
6	🟩	▨	▨	▨	▨

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



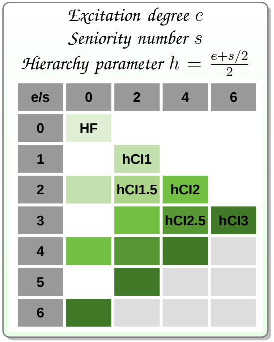
e/s	0	2	4	6
0	HF			
1		CIS		
2	🟥	🟥	CISD	
3		🟥	🟥	CISDT
4				
5				
6				

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

e/s	0	2	4	6
0	🟦			
1		🟦		
2	🟦	🟦	🟦	
3		🟦	🟦	🟦
4	🟦	🟦	🟦	🟦
5		🟦	🟦	🟦
6	sCI0	sCI2	sCI4	sCI6

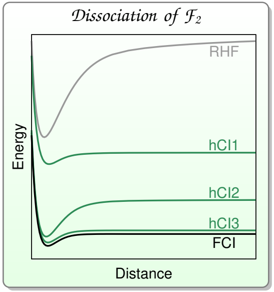
Hierarchy Configuration Interaction

Hierarchy configuration interaction (hCI)

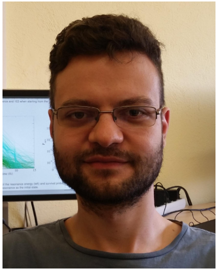


Excitation degree e
Seniority number s
Hierarchy parameter $h = \frac{e+s/2}{2}$

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



Dissociation of F_2



Fábris Kossoski

Kossoski, Damour & Loos, JPCL 13 (2022) 4342 (see also arXiv:2308.14618)

Selected Configuration Interaction: "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

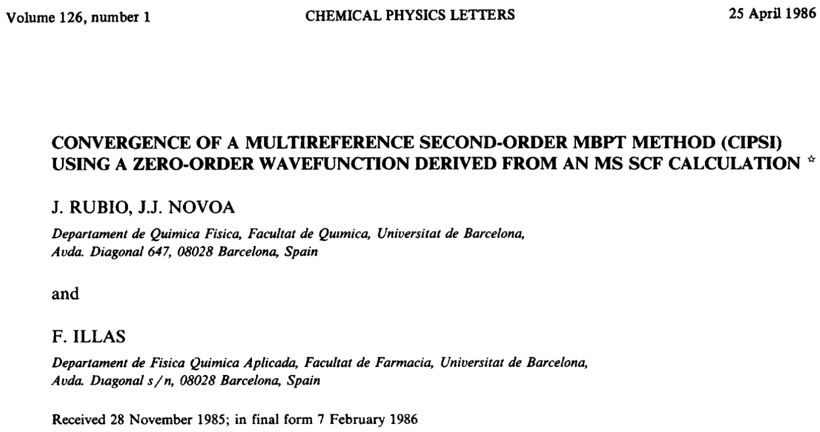
- Developed in Toulouse many (many) years ago
  Huron, Malrieu & Rancurel, JCP 58 (1973) 5745

- 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 ≈ heat-bath CI (Umrigar) ≈ adaptive sampling CI (Evangelista) ≈ iterative CI (Liu) ≈ incremental CI (Zimmerman) ≈ FCIQMC (Alavi)

CIPSI at the University of Barcelona (1)



Volume 126, number 1 CHEMICAL PHYSICS LETTERS 25 April 1986

CONVERGENCE OF A MULTIREFERENCE SECOND-ORDER MBPT METHOD (CIPSI) USING A ZERO-ORDER WAVEFUNCTION DERIVED FROM AN MS SCF CALCULATION ☆

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CIPSI at the University of Barcelona (2)

Approximate natural orbitals and the convergence of a second order multireference many-body perturbation theory (CIPSI) algorithm[a)]

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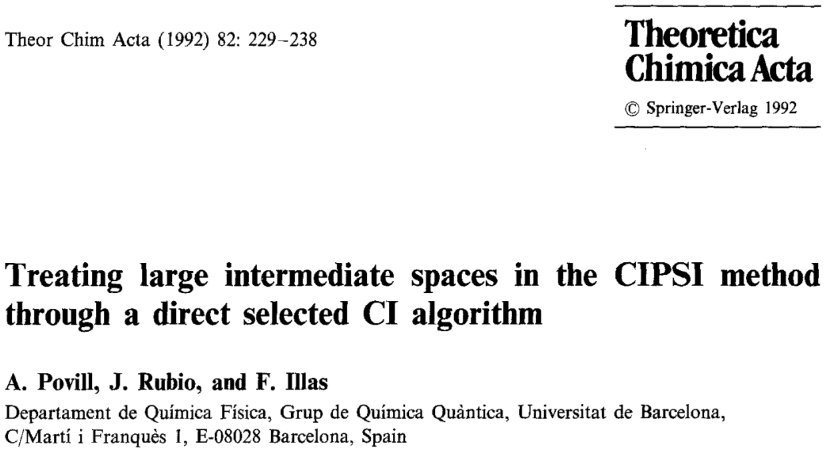
(Received 6 June 1988; accepted 9 August 1988)

CIPSI at the University of Barcelona (3)



Theor Chim Acta (1992) 82: 229–238

Theoretica Chimica Acta

Treating large intermediate spaces in the CIPSI method through a direct selected CI algorithm

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CIPSI at the University of Barcelona (3)

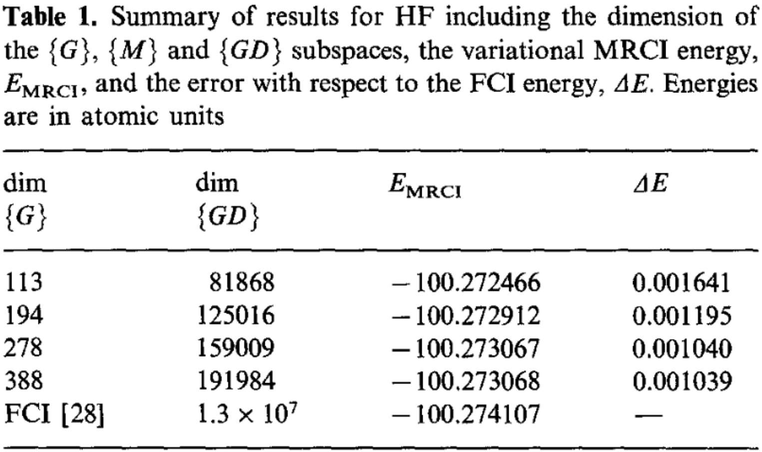
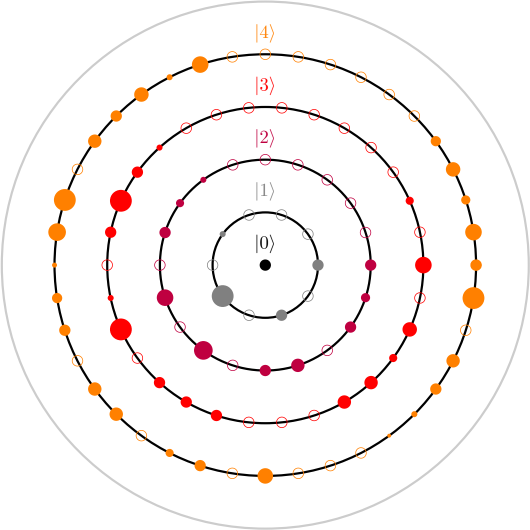


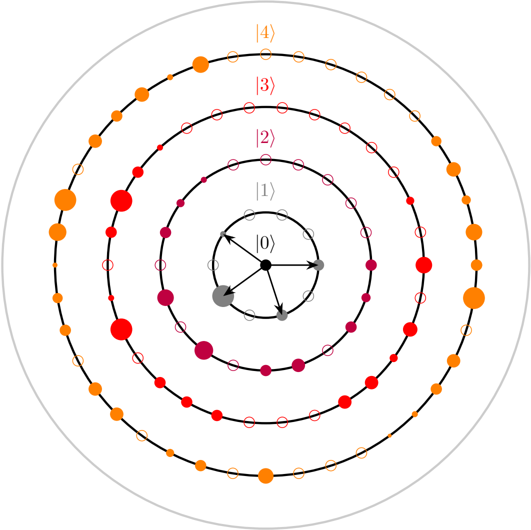
Table 1. Summary of results for HF including the dimension of the $\{G\}$, $\{M\}$ and $\{GD\}$ subspaces, the variational MRCI energy, E_{MRCI}, and the error with respect to the FCI energy, ΔE. Energies are in atomic units

dim $\{G\}$	dim $\{GD\}$	E_{MRCI}	ΔE
113	81868	−100.272466	0.001641
194	125016	−100.272912	0.001195
278	159009	−100.273067	0.001040
388	191984	−100.273068	0.001039
FCI [28]	1.3×10^7	−100.274107	—

Hilbert space “onion”



Hilbert space “onion”



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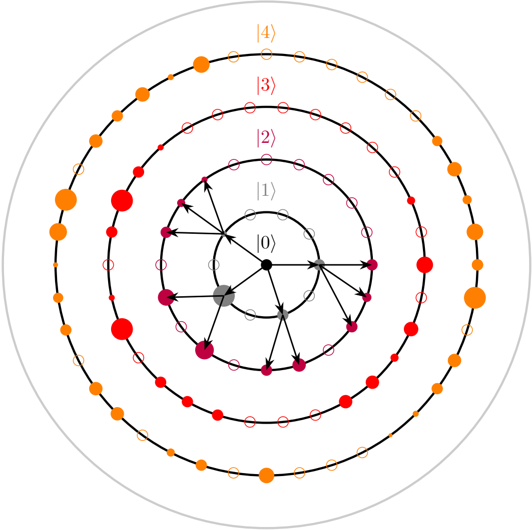

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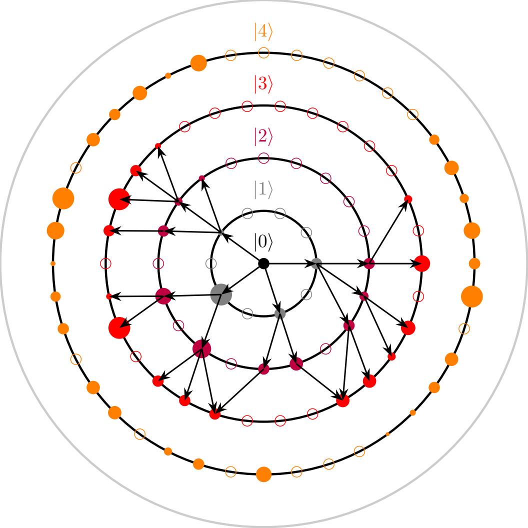
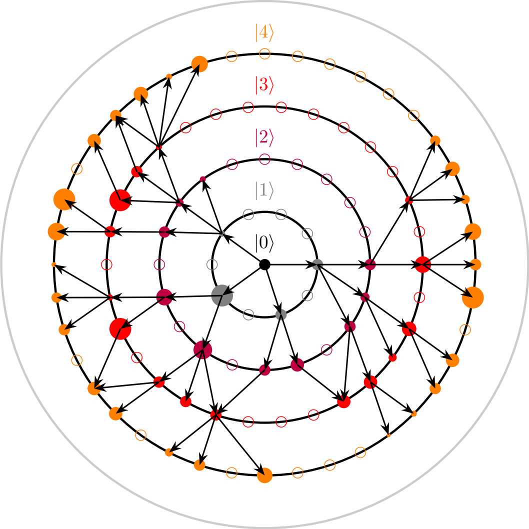
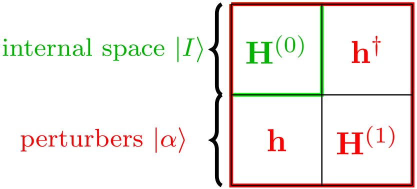


Hilbert space "onion"



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)



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

CIPSI algorithm

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

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

2. Generate external determinants:

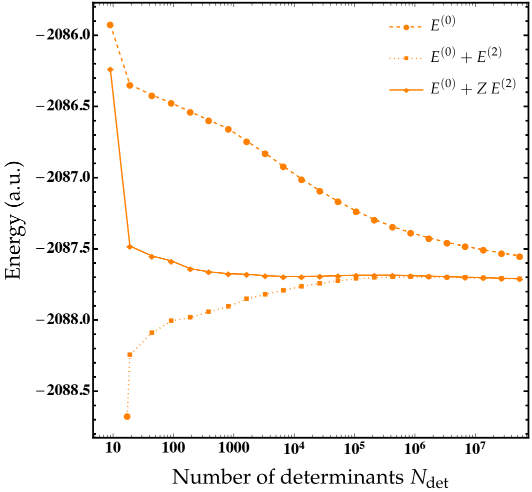
$$\mathcal{A} = \left\{(\forall I \in \mathcal{I})\left(\forall \hat{T} \in \mathcal{T}_1 \cup \mathcal{T}_2\right) : |\alpha\rangle = \hat{T}\,|I\rangle\right\}$$

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 $\mathcal{I}$
5. Diagonalize $\hat{H}$ in $\mathcal{I} \Rightarrow$ update $|\Psi^{(0)}\rangle$ and $E^{(0)}$
6. Iterate

Ground state of Cr_2 in cc-pVQZ: full-valence CAS(28e,198o)



Garniron et al., JCTC 15 (2019) 3591

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

- Second-order Epstein-Nesbet correction:

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

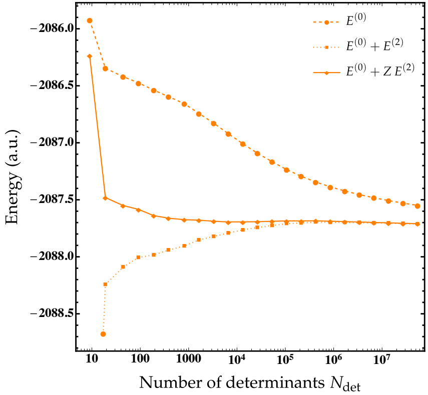
- $|\alpha\rangle$'s with largest $\delta E(\alpha)$ have been added to $\Psi^{(0)}$ previously
  $\Rightarrow$ only small contributions remaining

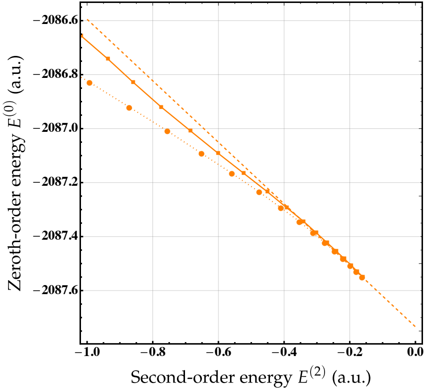
- $\mathcal{A}$ increases with $\mathcal{I}$
  $\Rightarrow$ a *very* large number of *very* small contributions

- In practice, we use a semi-stochastic algorithm to compute $E^{(2)}$
  $\Rightarrow$ much faster!!
  Garniron, Scemama, Loos & Caffarel, JCP 147 (2017) 034101

- We linearly extrapolate to $E^{(2)} = 0$ to reach the FCI limit (exFCI)

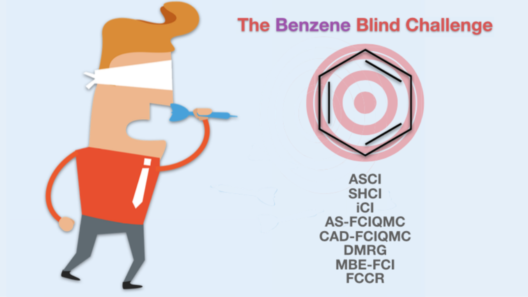
Ground state of Cr_2 in cc-pVQZ: full-valence CAS(28e,198o)





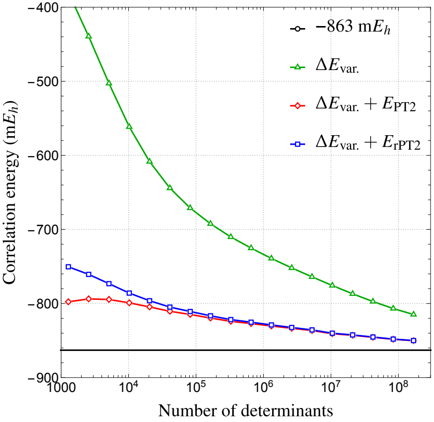
Garniron et al., JCTC 15 (2019) 3591

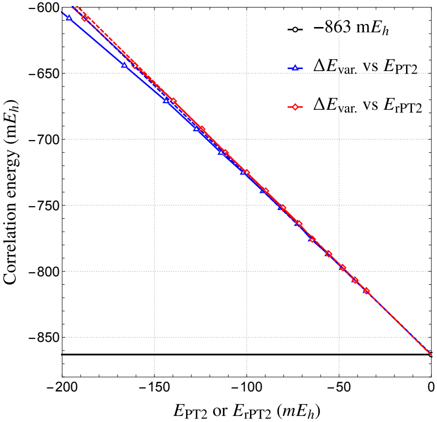
The Benzene Blind Challenge: Frozen-core correlation energy (cc-pVDZ)



Eriksen et al. JPCL 11 (2020) 8922

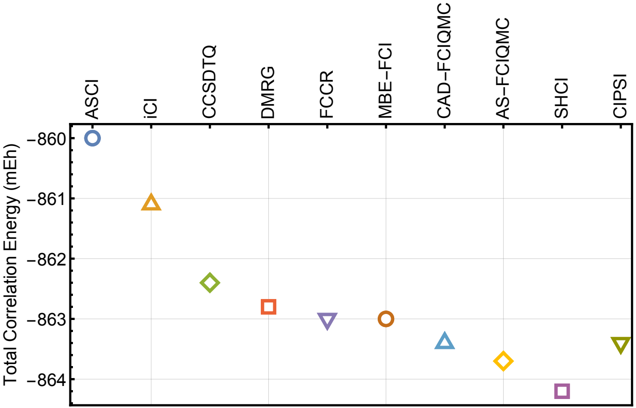
Performance of CIPSI for C_6H_6/cc-pVDZ (1)





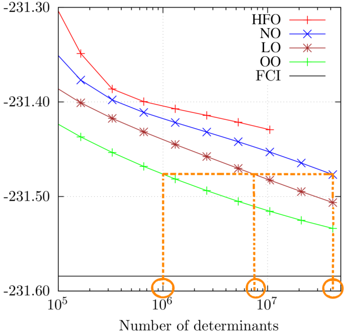
Loos, Damour & Scemama, JCP 153 (2020) 176101

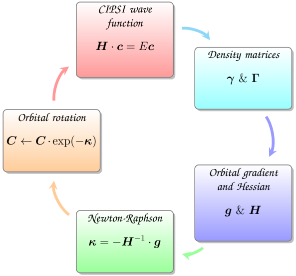
Performance of CIPSI for C_6H_6/cc-pVDZ (2)



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

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





CIPSI wave function

$\boldsymbol{H} \cdot \boldsymbol{c} = E\boldsymbol{c}$

Density matrices

$\boldsymbol{\gamma}$ & $\boldsymbol{\Gamma}$

Orbital gradient and Hessian

$\boldsymbol{g}$ & $\boldsymbol{H}$

Newton-Raphson

$\boldsymbol{\kappa} = -\boldsymbol{H}^{-1} \cdot \boldsymbol{g}$

Orbital rotation

$\boldsymbol{C} \leftarrow \boldsymbol{C} \cdot \exp(-\boldsymbol{\kappa})$

- 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

Toward a systematic improvement of the fixed-node approximation in diffusion Monte Carlo for solids—A case study in diamond

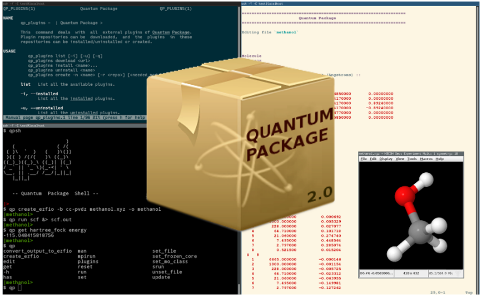
Cite as: J. Chem. Phys. **153**, 184111 (2020); https://doi.org/10.1063/5.0021036
Submitted: 06 July 2020 . Accepted: 12 October 2020 . Published Online: 11 November 2020

Anouar Benali, Kevin Gasperich, Kenneth D. Jordan, Thomas Applencourt, Ye Luo, M. Chandler Bennett, Jaron T. Krogel, Luke Shulenburger, Paul R. C. Kent, Pierre-François Loos, Anthony Scemama, and Michel Caffarel

Michel Caffarel

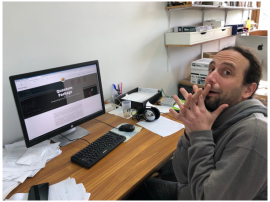
Quantum Package 2.0

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



```
QP_PLUGINS(1)                  Quantum Package                  QP_PLUGINS(1)

NAME
       qp_plugins -  | Quantum Package >

       This  command  deals  with  all  external plugins of Quantum Package.
       Plugin repositories can be  downloaded,  and  the  plugins  in  these
       repositories can be installed/uninstalled or created.

USAGE
          qp_plugins list [-i] [-u] [-q]
          qp_plugins download <url>
          qp_plugins install <name>...
          qp_plugins uninstall <name>
          qp_plugins create -n <name> [-r <repo>] [<needed

       list   List all the available plugins.

       -i, --installed
              List all the installed plugins.

       -u, --uninstalled
              List all the uninstalled plugins.
 Manual page qp_plugins.1 line 1/96 21% (press h for help
```

```
$ qpsh

   -- Quantum  Package  Shell --

|>
$ qp create_ezfio -b cc-pvdz methanol.xyz -o methanol
|methanol>
$ qp run scf &> scf.out
|methanol>
$ qp get hartree_fock energy
-115.048415818756
|methanol>
$ qp
convert_output_to_ezfio  man                      set_file
create_ezfio             mpirun                   set_frozen_core
edit                     plugins                  set_mo_class
get                      reset                    srun
-h                       run                      unset_file
has                      set                      update
|methanol>
$ qp
```



Anthony Scemama

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

Highly-accurate excitation energies: The QUEST project

“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”

QUEST database

QUEST#1: Small molecules

QUEST#2: Double excitations

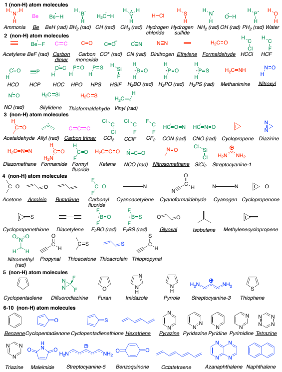
QUEST#3: Medium molecules

QUEST#4: “Exotic” molecules & radicals

QUEST#5: Larger molecules

QUEST#6: Charge transfer

QUEST#7: Bicyclic systems



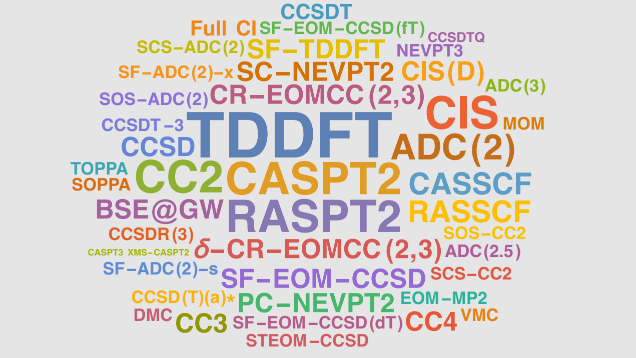
Denis Jacquemin

Density-based nightmare...

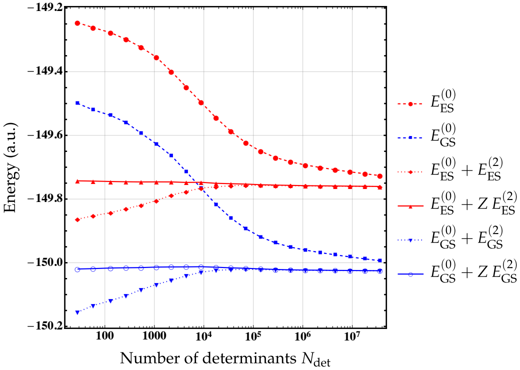
Zoo of functionals...

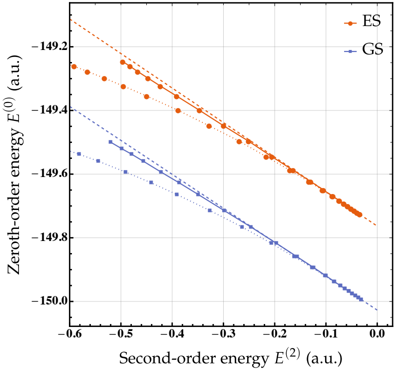
Wavefunction-based nightmare…

And this is just for excited states…



Cyanine $H_2N-CH=NH_2^+$/aug-cc-pVDZ: CAS(24,114)





Garniron et al., JCTC 15 (2019) 3591

Cyanine $H_2N-CH=NH_2^+$/aug-cc-pVDZ: CAS(24,114)

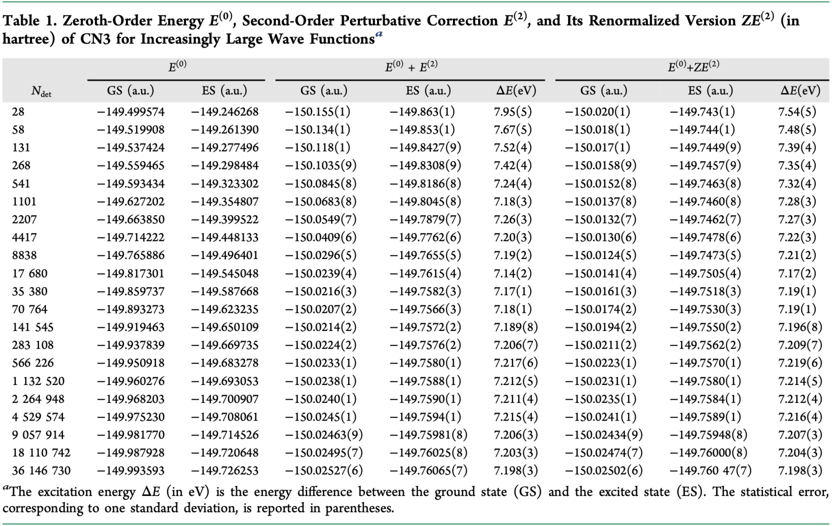


Table 1. Zeroth-Order Energy $E^{(0)}$, Second-Order Perturbative Correction $E^{(2)}$, and Its Renormalized Version $ZE^{(2)}$ (in hartree) of CN3 for Increasingly Large Wave Functions[a]

	$E^{(0)}$		$E^{(0)} + E^{(2)}$			$E^{(0)}+ZE^{(2)}$		
N_{det}	GS (a.u.)	ES (a.u.)	GS (a.u.)	ES (a.u.)	ΔE(eV)	GS (a.u.)	ES (a.u.)	ΔE(eV)
28	−149.499574	−149.246268	−150.155(1)	−149.863(1)	7.95(5)	−150.020(1)	−149.743(1)	7.54(5)
58	−149.519908	−149.261390	−150.134(1)	−149.853(1)	7.67(5)	−150.018(1)	−149.744(1)	7.48(5)
131	−149.537424	−149.277496	−150.118(1)	−149.8427(9)	7.52(4)	−150.017(1)	−149.7449(9)	7.39(4)
268	−149.559465	−149.298484	−150.1035(9)	−149.8308(9)	7.42(4)	−150.0158(9)	−149.7457(9)	7.35(4)
541	−149.593434	−149.323302	−150.0845(8)	−149.8186(8)	7.24(4)	−150.0152(8)	−149.7463(8)	7.32(4)
1101	−149.627202	−149.354807	−150.0683(8)	−149.8045(8)	7.18(3)	−150.0137(8)	−149.7460(8)	7.28(3)
2207	−149.663850	−149.399522	−150.0549(7)	−149.7879(7)	7.26(3)	−150.0132(7)	−149.7462(7)	7.27(3)
4417	−149.714222	−149.448133	−150.0409(6)	−149.7762(6)	7.20(3)	−150.0130(6)	−149.7478(6)	7.22(3)
8838	−149.765886	−149.496401	−150.0296(5)	−149.7655(5)	7.19(2)	−150.0124(5)	−149.7473(5)	7.21(2)
17 680	−149.817301	−149.545048	−150.0239(4)	−149.7615(4)	7.14(2)	−150.0141(4)	−149.7505(4)	7.17(2)
35 380	−149.859737	−149.587668	−150.0216(3)	−149.7582(3)	7.17(1)	−150.0161(3)	−149.7518(3)	7.19(1)
70 764	−149.893273	−149.623235	−150.0207(2)	−149.7566(3)	7.18(1)	−150.0174(2)	−149.7530(3)	7.19(1)
141 545	−149.919463	−149.650109	−150.0214(2)	−149.7572(2)	7.189(8)	−150.0194(2)	−149.7550(2)	7.196(8)
283 108	−149.937839	−149.669735	−150.0224(2)	−149.7576(2)	7.206(7)	−150.0211(2)	−149.7562(2)	7.209(7)
566 226	−149.950918	−149.683278	−150.0233(1)	−149.7580(1)	7.217(6)	−150.0223(1)	−149.7570(1)	7.219(6)
1 132 520	−149.960276	−149.693053	−150.0238(1)	−149.7588(1)	7.212(5)	−150.0231(1)	−149.7580(1)	7.214(5)
2 264 948	−149.968203	−149.700907	−150.0240(1)	−149.7590(1)	7.211(4)	−150.0235(1)	−149.7584(1)	7.212(4)
4 529 574	−149.975230	−149.708061	−150.0245(1)	−149.7594(1)	7.215(4)	−150.0241(1)	−149.7589(1)	7.216(4)
9 057 914	−149.981770	−149.714526	−150.02463(9)	−149.75981(8)	7.206(3)	−150.02434(9)	−149.75948(8)	7.207(3)
18 110 742	−149.987928	−149.720648	−150.02495(7)	−149.76025(8)	7.203(3)	−150.02474(7)	−149.76000(8)	7.204(3)
36 146 730	−149.993593	−149.726253	−150.02527(6)	−149.76065(7)	7.198(3)	−150.02502(6)	−149.760 47(7)	7.198(3)

[a] The excitation energy ΔE (in eV) is the energy difference between the ground state (GS) and the excited state (ES). The statistical error, corresponding to one standard deviation, is reported in parentheses.

QUEST #1 — small molecules —

JCTC Journal of Chemical Theory and Computation **Article**

Cite This: *J. Chem. Theory Comput.* 2018, 14, 4360–4379 pubs.acs.org/JCTC

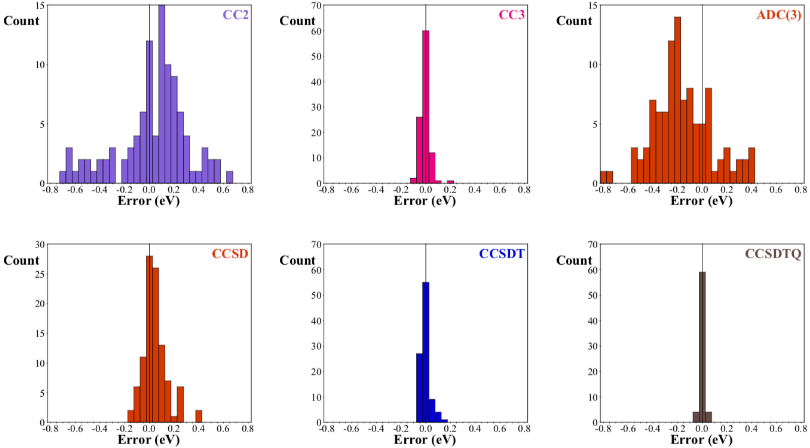
A Mountaineering Strategy to Excited States: Highly Accurate Reference Energies and Benchmarks

Pierre-François Loos,*,† Anthony Scemama,† Aymeric Blondel,‡ Yann Garniron,† Michel Caffarel,† and Denis Jacquemin*,‡

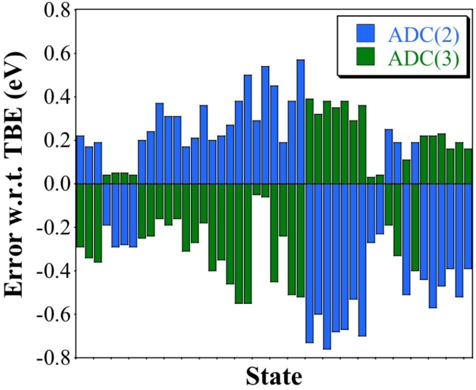
†Laboratoire de Chimie et Physique Quantiques, Université de Toulouse, CNRS, UPS, 31013 Toulouse Cedex 6, France
‡Laboratoire CEISAM - UMR CNRS 6230, Université de Nantes, 2 Rue de la Houssinière, BP 92208, 44322 Nantes Cedex 3, France

- 110 vertical excitation energies (VTEs) and oscillator strengths
- 18 small molecules from 1 to 3 non-H atoms
- CC3/aug-cc-pVTZ geometries
- mostly singly-excited states and very few doubly-excited states
- rely on FCI to define “theoretical best estimates” (TBEs)
- aug-cc-pVTZ and CBS vertical energies
- benchmark popular excited-state methods accounting for double and triple excitations

Benchmarking excited-state methods vs TBE/aug-cc-pVTZ

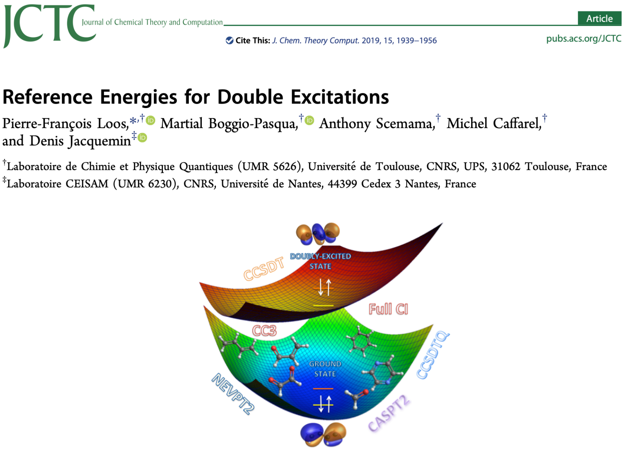


Errors in ADC(2) & ADC(3) for states with large (> 0.15 eV) ADC(2) error



See also Loos & Jacquemin, JPCL 11 (2020) 974

QUEST #2 — double excitations —



JCTC Journal of Chemical Theory and Computation **Article**

Cite This: *J. Chem. Theory Comput.* 2019, 15, 1939−1956 pubs.acs.org/JCTC

Reference Energies for Double Excitations

Pierre-François Loos,[*,†] Martial Boggio-Pasqua,[†] Anthony Scemama,[†] Michel Caffarel,[†]
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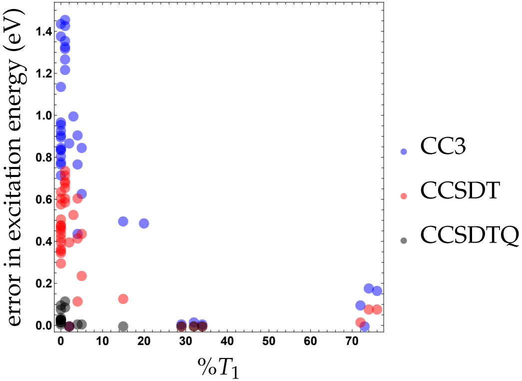
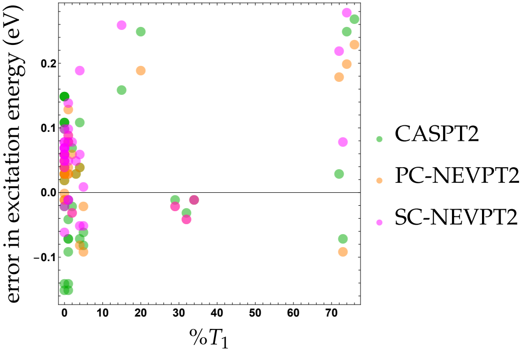
[‡] Laboratoire CEISAM (UMR 6230), CNRS, Université de Nantes, 44399 Cedex 3 Nantes, France

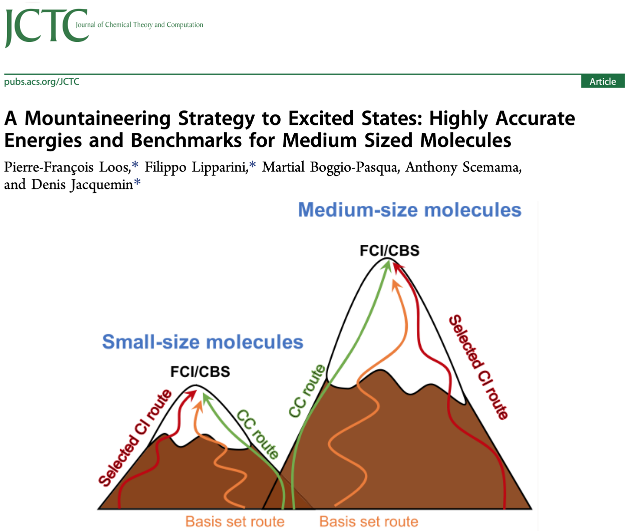
- 20 VTEs for doubly-excited states
- 14 small- and medium-sized molecules
- mostly rely on FCI to define TBEs (except for the largest molecules)
- aug-cc-pVTZ and CBS vertical energies
- benchmark excited-state methods including at least triple excitations
- additional benchmarks of multi-configurational methods

Reference energies for double excitations





QUEST #3 — medium-sized molecules —



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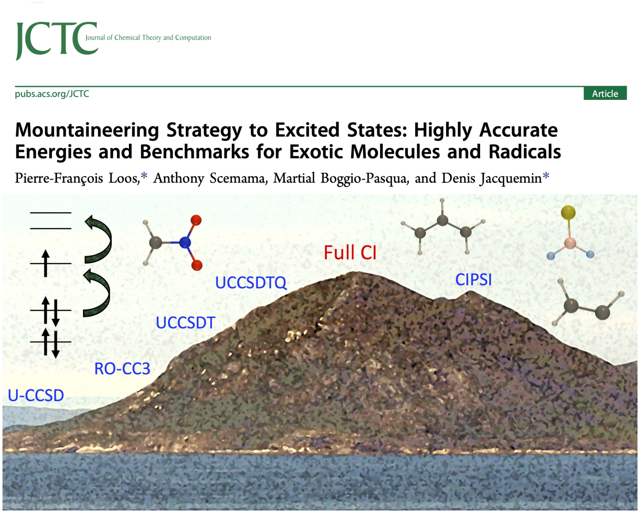
A Mountaineering Strategy to Excited States: Highly Accurate Energies and Benchmarks for Medium Sized Molecules

Pierre-François Loos,* Filippo Lipparini,* Martial Boggio-Pasqua, Anthony Scemama, and Denis Jacquemin*

- 238 VTEs (and oscillator strengths) with mostly singly-excited states and aug-cc-pVTZ basis
- 27 small- and medium-sized molecules with 4 to 6 non-H atoms
- rely mostly on CCSDT or CCSDTQ to define TBEs
- benchmark popular excited-state methods accounting for double and triple excitations
- recently improved TBEs with CC4 and CCSDTQ [JCP 154 (2021) 221103; JCTC 18 (2022) 4418]

QUEST #4 — “exotic” molecules and radicals —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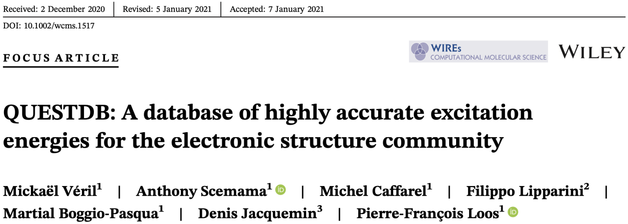
Mountaineering Strategy to Excited States: Highly Accurate Energies and Benchmarks for Exotic Molecules and Radicals

Pierre-François Loos,* Anthony Scemama, Martial Boggio-Pasqua, and Denis Jacquemin*

- two subsets of excitations and oscillator strengths
- an “exotic” subset of 30 VTEs for closed-shell molecules containing F, Cl, P, and Si
- a “radical” subset of 51 doublet-doublet transitions in 24 small radicals
- total of 81 TBEs mostly obtained at the FCI/aug-cc-pVTZ level
- benchmark popular excited-state methods (U vs RO)

QUEST #5 — larger molecules —



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FOCUS ARTICLE

WIREs COMPUTATIONAL MOLECULAR SCIENCE
WILEY

QUESTDB: A database of highly accurate excitation energies for the electronic structure community

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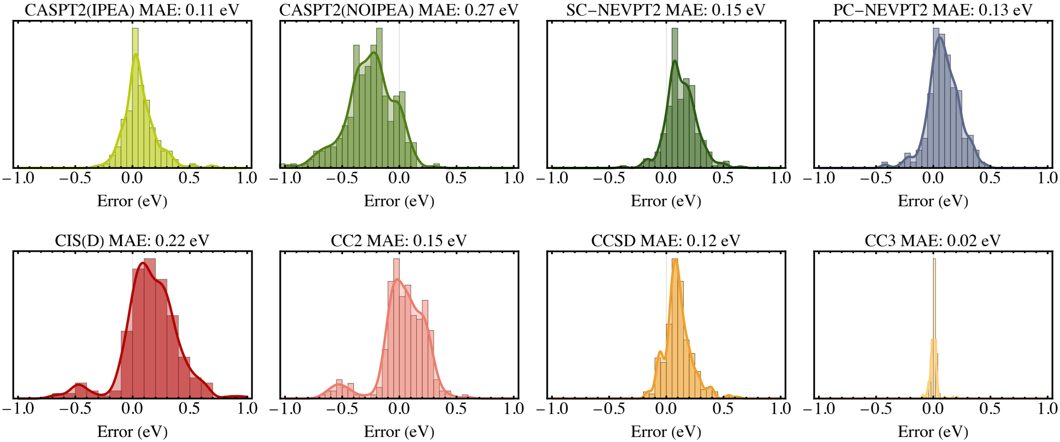
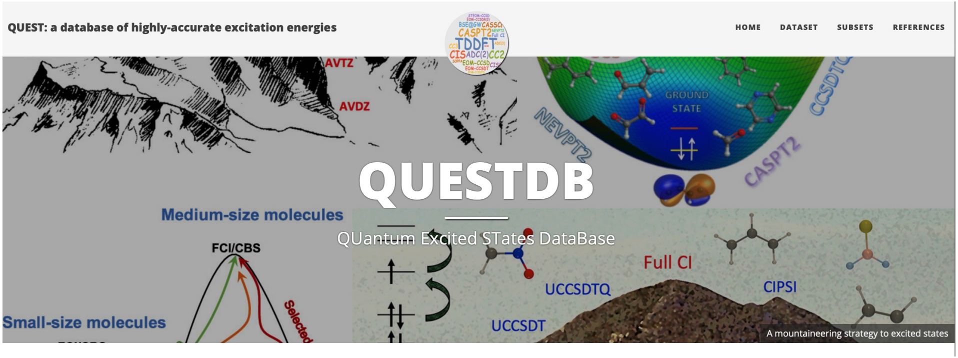
- 13 new systems composed by small molecules as well as larger molecules
- 80 new transitions the vast majority being of CCSDT quality
- benchmark popular excited-state methods over the entire database

Single- vs Multi-reference methods



JCTC 18 (2022) 2418; JCP 157 (2022) 014103

The QUEST website



QUEST: a database of highly-accurate excitation energies

HOME DATASET SUBSETS REFERENCES

QUESTDB

QUantum Excited STates DataBase

A mountaineering strategy to excited states

Mika Véril

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 18 (2022) 3460]
- 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 [JCTC 18 (2022) 6065]
- Bartlett's group: Variants of EOM-CC for doubly-excited states [JCP 156 (2022) 201102; JPCA 127 (2023) 828; JCP 159 (2023) 094101]
- 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; JCTC 18 (2022) 6722]
- Gould's group: ensemble DFT [JPCL 13 (2022) 2452]

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https://pfloos.github.io/WEB_LOOS

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