Targeting Real chemical accuracy at the EXascale

CIPSI: selected configuration interaction methods for ground and excited states

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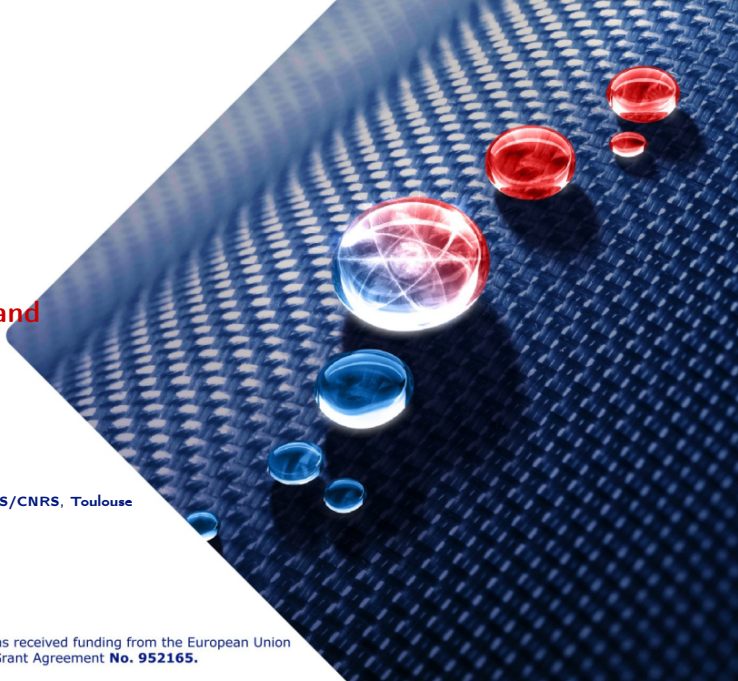
https://lcpq.github.io/pterosor



Targeting Real Chemical Accuracy at the Exascale project has received funding from the European Union Horizoon 2020 research and innovation programme under Grant Agreement **No. 952165.**

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"

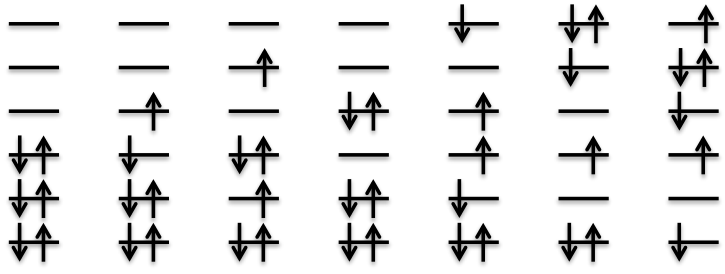
CIPSI = CI using a Perturbative Selection made Iteratively

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

- This is the oldest and perhaps the easiest method to understand
- CI is based on the variational principle [like the Hartree-Fock (HF) approximation]
- The CI wave function is a linear combination of determinants
- CI methods use excited determinants to "improve" the reference (usually HF) wave function

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

Excited determinants



CI wave function

$$|\Phi_{CI}\rangle = c_0 |0\rangle + c_S |S\rangle + c_D |D\rangle + c_T |T\rangle + c_Q |Q\rangle + \cdots$$

- 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.

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

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

- 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!

"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

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

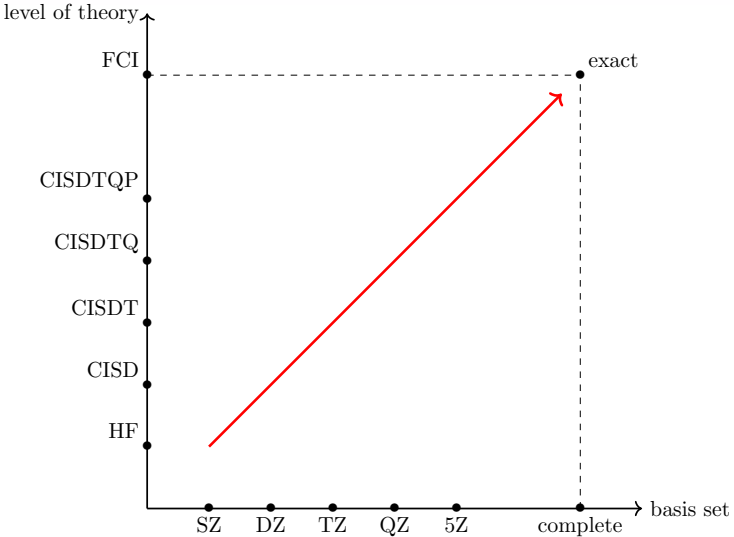
- There is C_{28}^k ways of distributing them out in the 28 virtual orbitals
- For a given excitation level k, there is $C_{10}^k C_{28}^k$ excited determinants
- The total number of possible excited determinant is

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

- This is a lot...

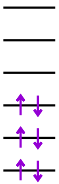
For $n = 10$ and $N = 38$:

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

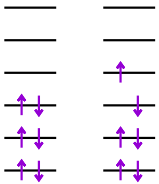

level of theory
FCI
exact
CISDTQP
CISDTQ
CISDT
CISD
HF
SZ
DZ
TZ
QZ
5Z
complete
basis set

e	
0	
1	
2	
3	

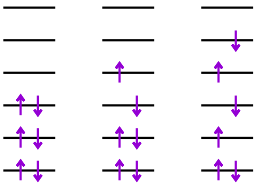
e	
0	**HF**
1	
2	
3	



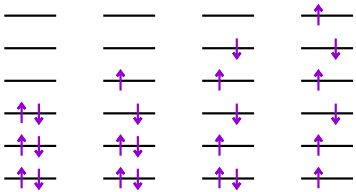
e	
0	
1	**CIS**
2	
3	



e	
0	
1	
2	**CISD**
3	

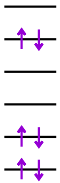


e	
0	
1	
2	
3	**CISDT**

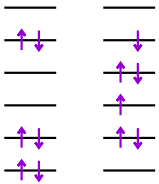


s	0	2	4	6

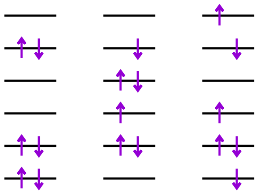
s	0	2	4	6
	sCI0			



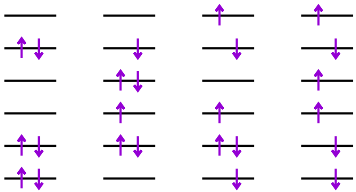
s	0	2	4	6
		sCI2		



s	0	2	4	6
			sCI4	



s	0	2	4	6
				sCI6

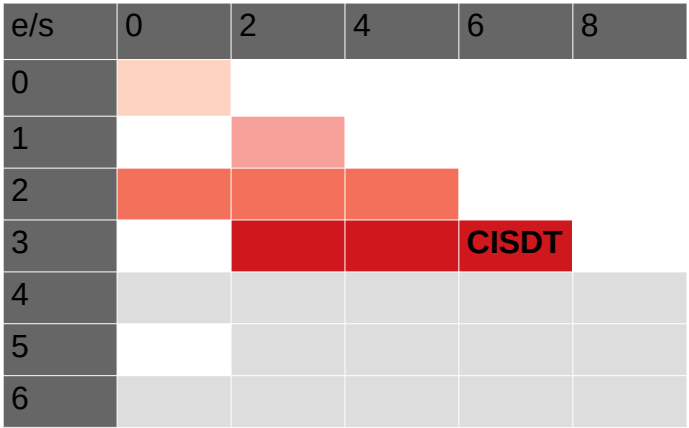


e/s	0	2	4	6	8
0					
1					
2					
3					
4					
5					
6					

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					

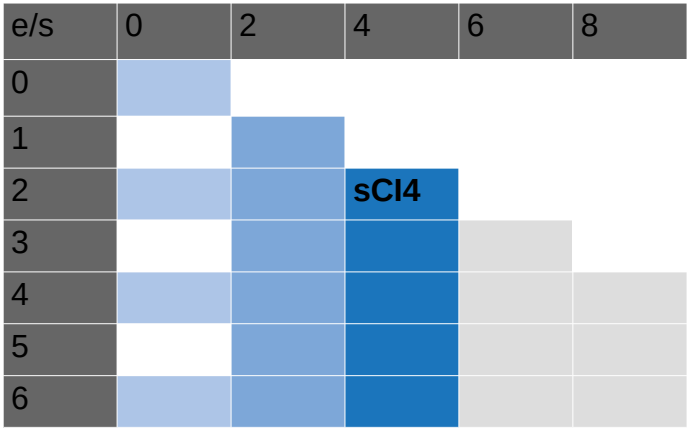
e/s	0	2	4	6	8
0					
1					
2			CISD		
3					
4					
5					
6					

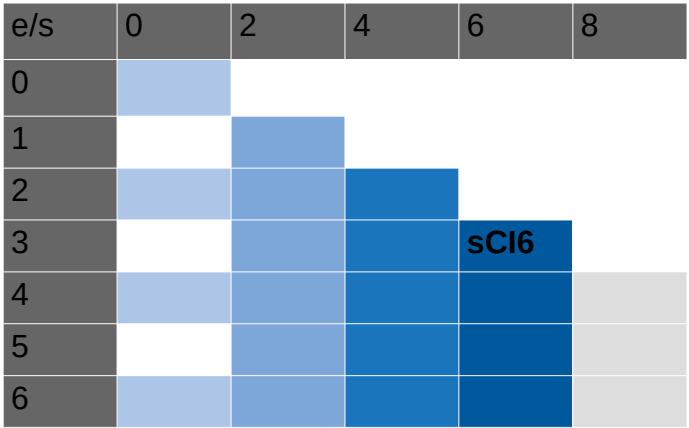

e/s
0
2
4
6
8
0
1
2
3
4
5
6
CISDT

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					

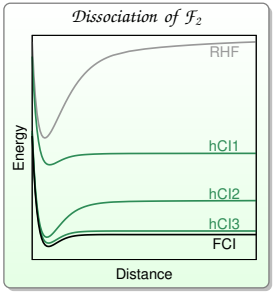

e/s
0
2
4
6
8
0
1
2
3
4
5
6
sCI4


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

Hierarchy configuration interaction (hCI)

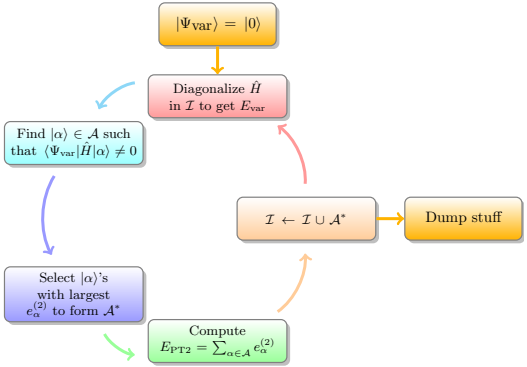
Excitation degree e
Seniority number s
Hierarchy parameter $h = \frac{e+s/2}{2}$

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

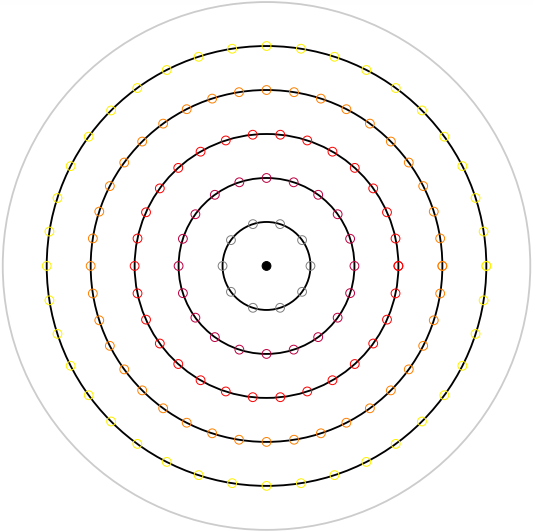


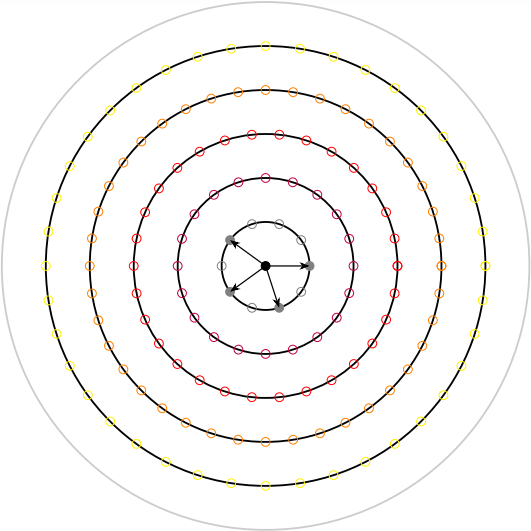
Fábris Kossoski

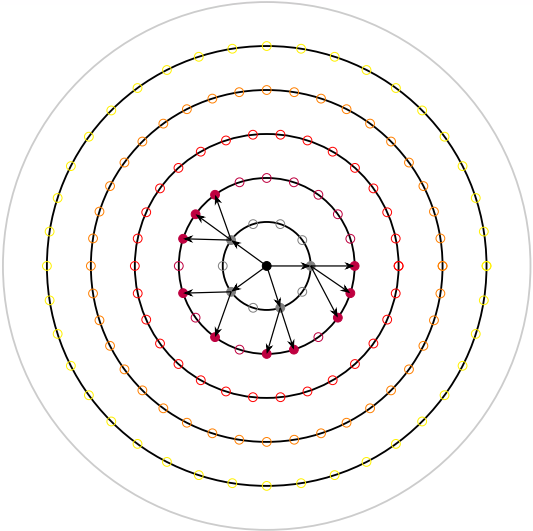
Kossoski, Damour & Loos, JPCL 13 (2022) 4342

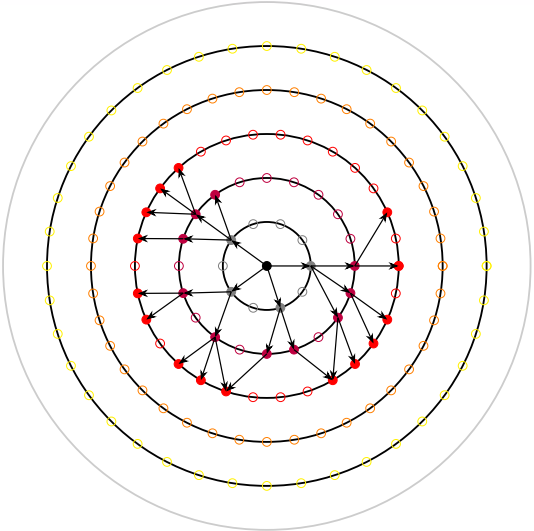


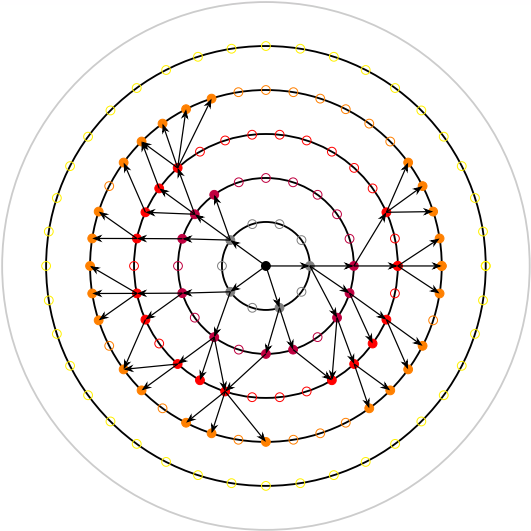
CIPSI is an algorithm, not a method...

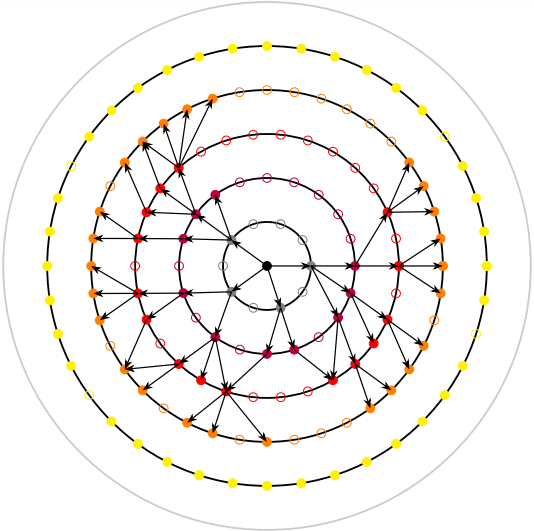




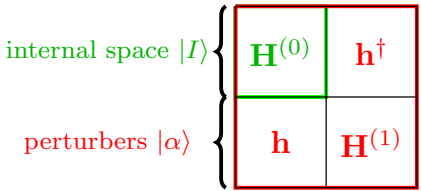








- **Green:** reference/variational/internal wave function (zeroth-order or model space)
- **Red:** perturbers or external wave function (first-order or perturbative space)



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

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

2. Generate external determinants:

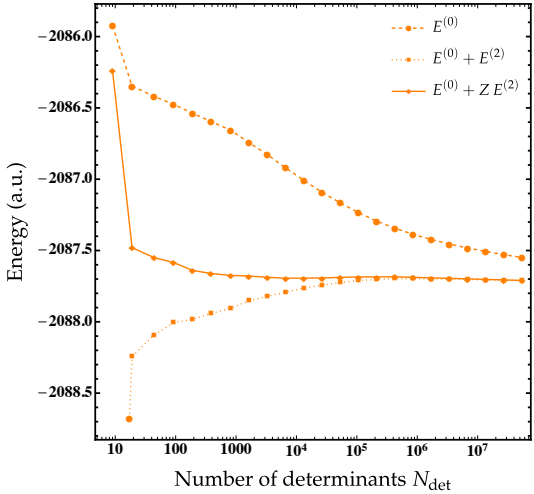
$$\mathcal{A} = \left\{ (\forall I \in \mathcal{D}) \left(\forall \hat{T} \in \mathcal{T}_1 \cup \mathcal{T}_2 \right) : |\alpha\rangle = \hat{T} |I\rangle \right\}$$

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

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



Garniron et al., JCTC 15 (2019) 3591

- Second-order Epstein-Nesbet correction:

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

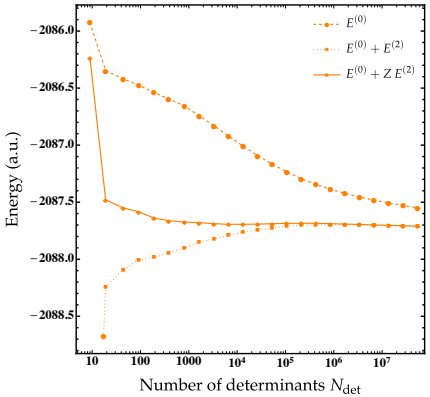
- $|\alpha\rangle$'s with largest $\delta E(\alpha)$ have been added to $\Psi^{(0)}$ previously
  $\Rightarrow$ only small contributions remaining

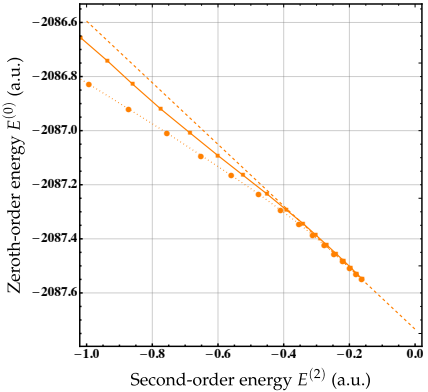
- $\mathcal{A}$ increases with $\mathcal{D}$
  $\Rightarrow$ a *very* large number of *very* small contributions

- 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

At a given CIPSI iteration, the SCI+PT2 energy is given by

$$E = E^{(0)} + E^{(2)}$$

Let us introduce the following energy-dependent second-order self-energy

$$\Sigma^{(2)}[E] = \sum_{\alpha} \frac{\langle \alpha | \hat{H} | \Psi^{(0)} \rangle^2}{E - \langle \alpha | \hat{H} | \alpha \rangle} \quad \text{with} \quad \Sigma^{(2)}[E^{(0)}] = E^{(2)}$$

Brillouin-Wigner perturbation theory tells us

$$E = E^{(0)} + \Sigma^{(2)}[E]$$

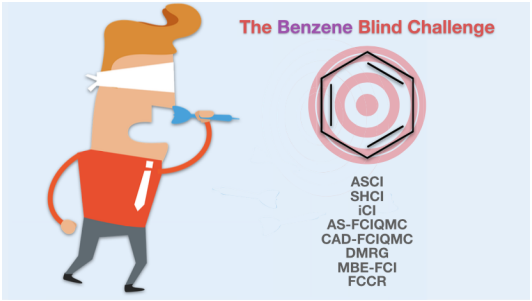
Assuming that $\Sigma^{(2)}[E]$ behaves linearly for $E \approx E^{(0)}$

$$\Sigma^{(2)}[E] \approx \Sigma^{(2)}[E^{(0)}] + (E - E^{(0)}) \left. \frac{\partial \Sigma^{(2)}[E]}{\partial E} \right|_{E=E^{(0)}}$$

This yields

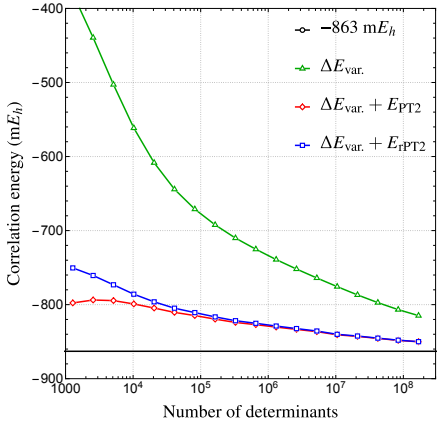
$$E = E^{(0)} + \Sigma^{(2)}[E^{(0)}] + (E - E^{(0)}) \left. \frac{\partial \Sigma^{(2)}[E]}{\partial E} \right|_{E=E^{(0)}} = E^{(0)} + Z\, E^{(2)} \quad \text{with} \quad Z = \left[1 - \left. \frac{\partial \Sigma^{(2)}[E]}{\partial E} \right|_{E=E^{(0)}} \right]^{-1}$$

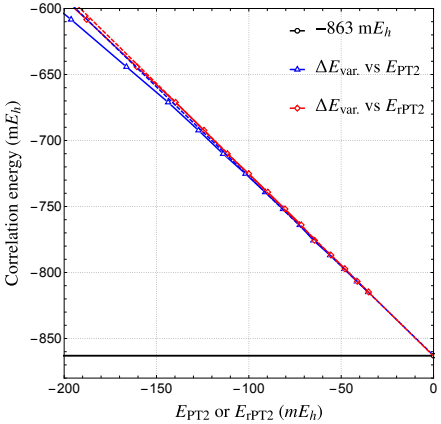
The Benzene Blind Challenge: Frozen-core correlation energy (cc-pVDZ)



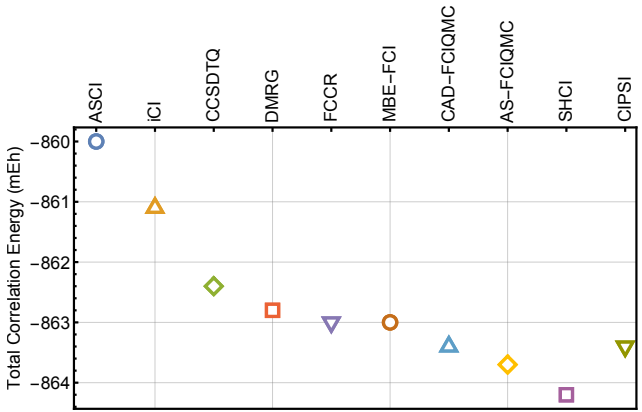
Eriksen et al. JPCL 11 (2020) 8922

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



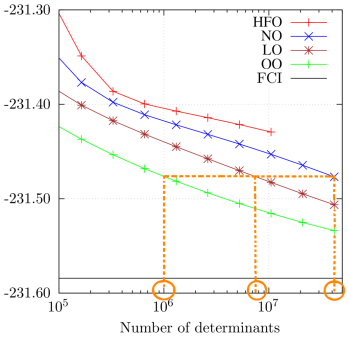


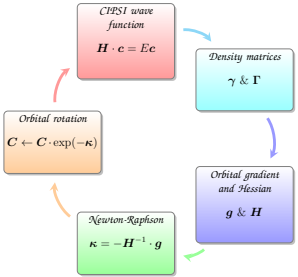
Loos, Damour & Scemama, JCP 153 (2020) 176101



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

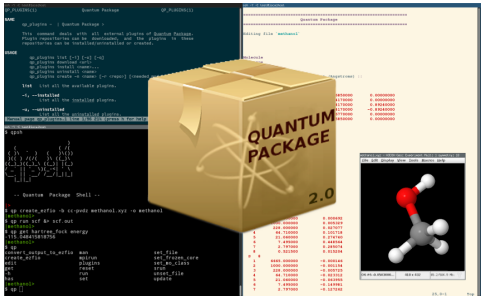
Toward a systematic improvement of the fixed-node approximation in diffusion Monte Carlo for solids—A case study in diamond

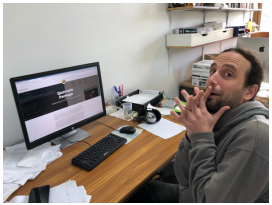
Cite as: J. Chem. Phys. **153**, 184111 (2020); https://doi.org/10.1063/5.0021036
Submitted: 06 July 2020 . Accepted: 12 October 2020 . Published Online: 11 November 2020

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

See also Scemama et al. JCP 153 (2021) 174107 for a range-separated approach in molecules

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

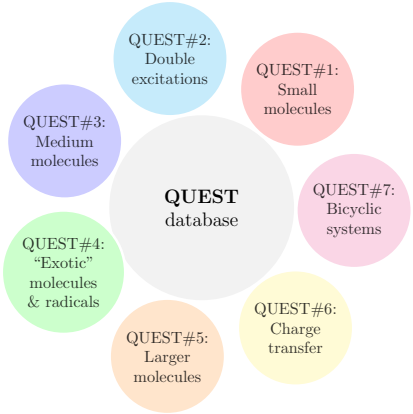


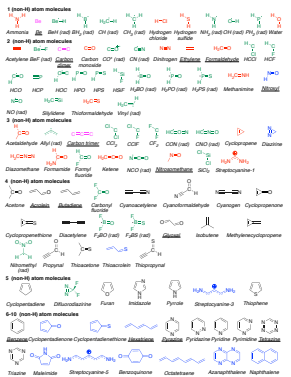


Anthony Scemama

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

"The 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"

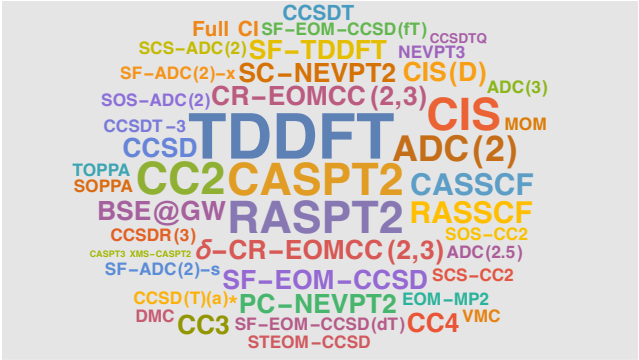




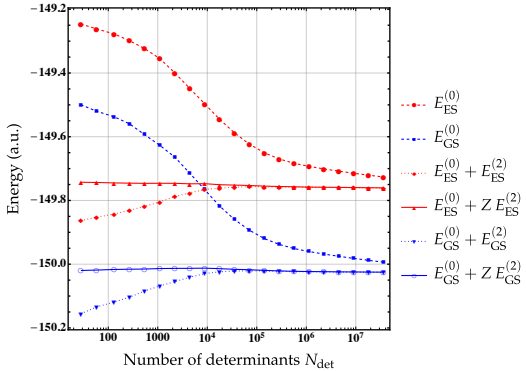
Denis Jacquemin

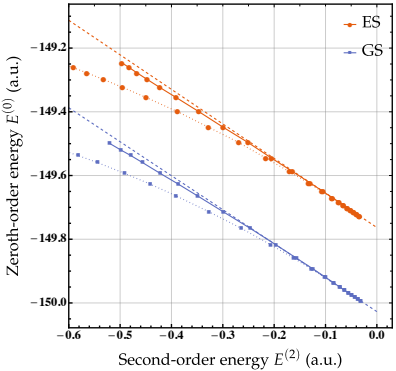
Zoo of functionals...

And this is just for excited states...



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





Garniron et al., JCTC 15 (2019) 3591

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)

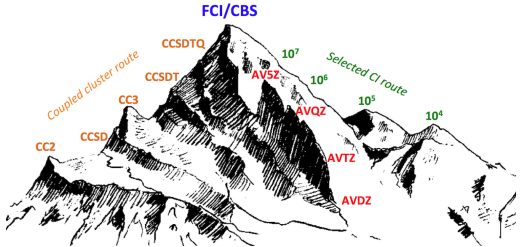
[a]The excitation energy ΔE (in eV) is the energy difference between the ground state (GS) and the excited state (ES). The statistical error, corresponding to one standard deviation, is reported in parentheses.

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

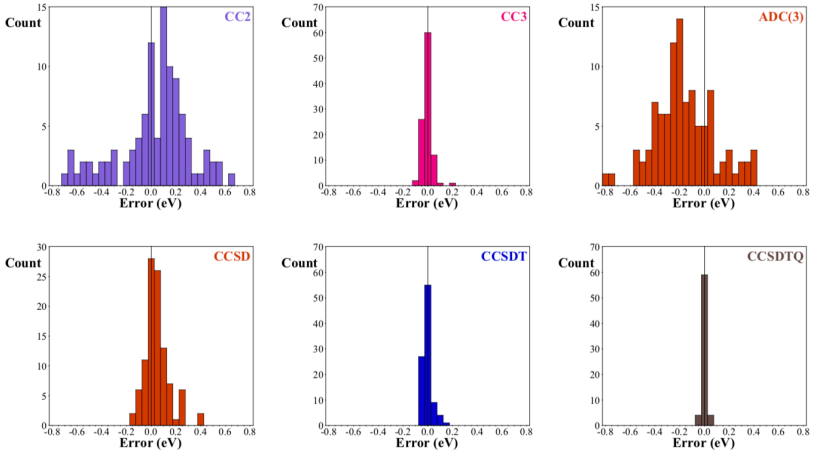
Pierre-François Loos,*[†] Anthony Scemama,[†] Aymeric Blondel,[‡] Yann Garniron,[†] Michel Caffarel,[†] and Denis Jacquemin*[,‡]

[†]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

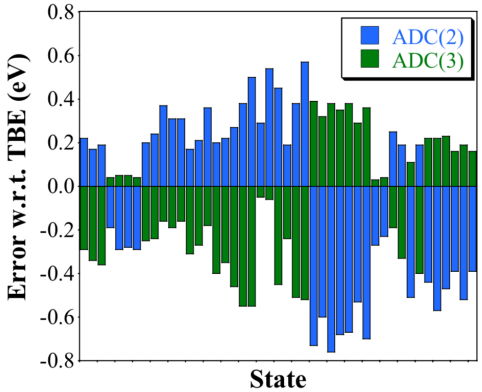


- 110 vertical excitation energies (VTEs) and oscillator strengths
- 18 small molecules with 1 to 3 non-H atoms
- CC3/aug-cc-pVTZ geometries
- mostly singly-excited states and very few doubly-excited states
- rely on FCI to define "theoretical best estimates" (TBEs)
- aug-cc-pVTZ and CBS vertical energies
- 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

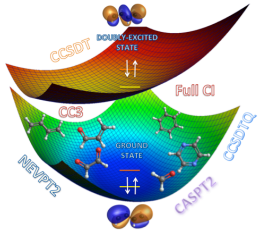


JCTC Journal of Chemical Theory and Computation
Article
Cite This: J. Chem. Theory Comput. 2019, 15, 1939−1956
pubs.acs.org/JCTC

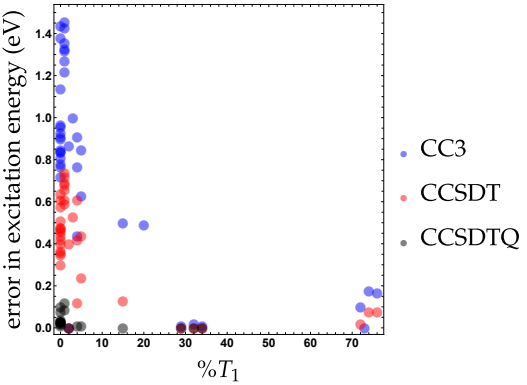
Reference Energies for Double Excitations

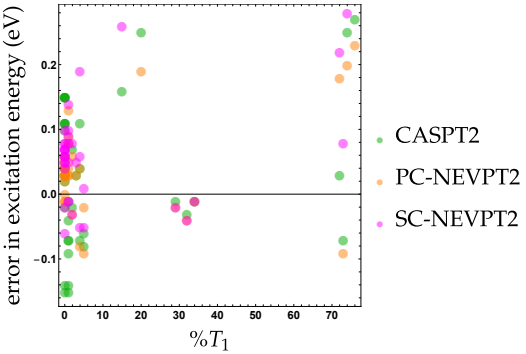
Pierre-François Loos,*[†] Martial Boggio-Pasqua,[†] Anthony Scemama,[†] Michel Caffarel,[†] and Denis Jacquemin[‡]

[†]Laboratoire de Chimie et Physique Quantiques (UMR 5626), Université de Toulouse, CNRS, UPS, 31062 Toulouse, France
[‡]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


error in excitation energy (eV)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
10
20
30
40
50
60
70
%T_1
CC3
CCSDT
CCSDTQ


error in excitation energy (eV)
0.2
0.1
0.0
−0.1
0
10
20
30
40
50
60
70
%T_1
CASPT2
PC-NEVPT2
SC-NEVPT2

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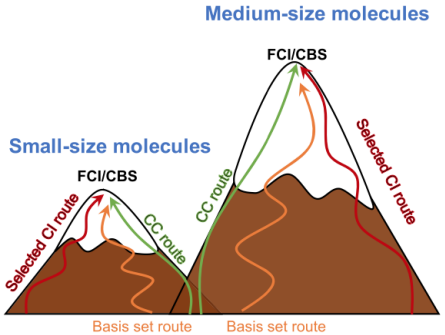
A Mountaineering Strategy to Excited States: Highly Accurate Energies and Benchmarks for Medium Sized Molecules

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



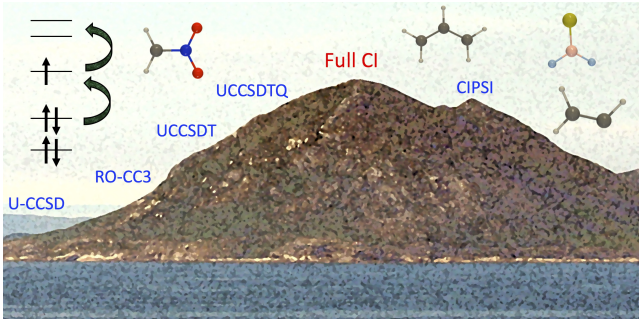
- 238 VTEs (and oscillator strengths) with mostly singly-excited states and aug-cc-pVTZ basis
- 27 small- and medium-sized molecules with 4 to 6 non-H atoms
- rely mostly on CCSDT or CCSDTQ to define TBEs
- benchmark popular excited-state methods accounting for double and triple excitations
- recently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

JCTC Journal of Chemical Theory and Computation

pubs.acs.org/JCTC Article

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)

Received: 2 December 2020 | Revised: 5 January 2021 | Accepted: 7 January 2021
DOI: 10.1002/wcms.1517

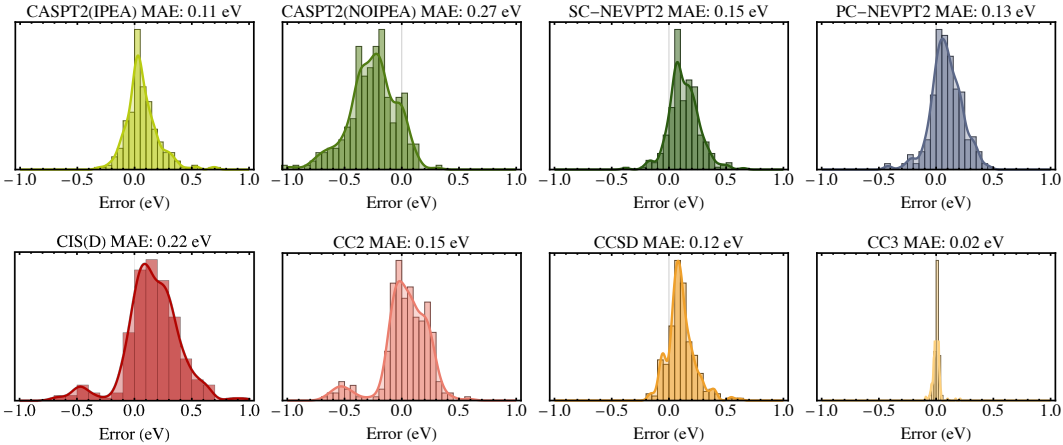
FOCUS ARTICLE

WIREs COMPUTATIONAL MOLECULAR SCIENCE WILEY

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

Mickaël Véril[1] | Anthony Scemama[1] | Michel Caffarel[1] | Filippo Lipparini[2] | Martial Boggio-Pasqua[1] | Denis Jacquemin[3] | Pierre-François Loos[1]

- 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



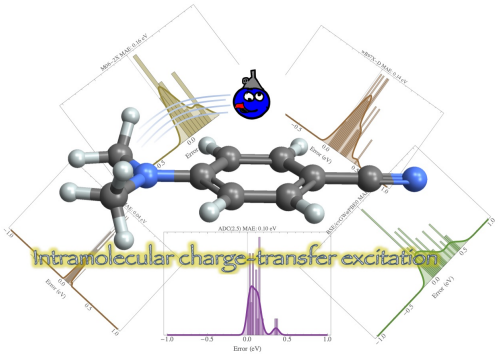
JCTC 18 (2022) 2418; JCP 157 (2022) 014103

JCTC Journal of Chemical Theory and Computation

pubs.acs.org/JCTC Article

Reference Energies for Intramolecular Charge-Transfer Excitations

Pierre-François Loos,* Massimiliano Comin, Xavier Blase,* and Denis Jacquemin*



- intramolecular charge-transfer transitions in π-conjugated molecules
- 30 transitions of CCSDT quality in 17 systems with cc-pVTZ
- Basis-set correction up to aug-cc-pVQZ computed with CCSD and CC2
- benchmark popular excited-state methods
- additional benchmarks of BSE@*GW* and TD-DFT (hybrids and range-separated hybrids)

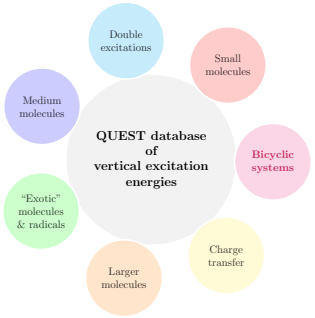
THE JOURNAL OF PHYSICAL CHEMISTRY A
A JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

pubs.acs.org/JPCA Article

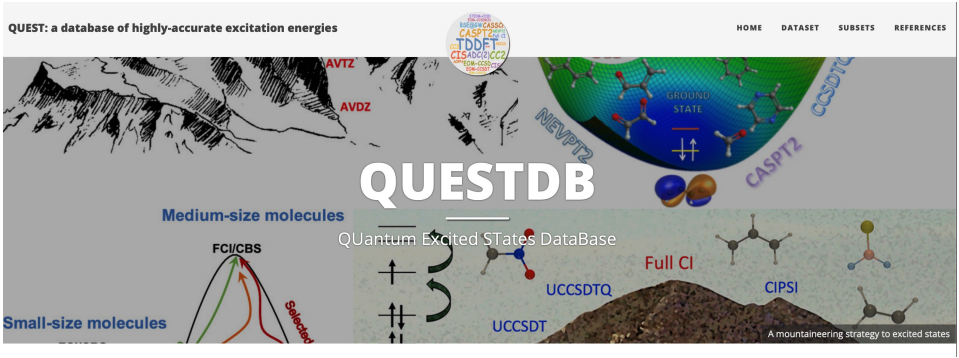
A Mountaineering Strategy to Excited States: Highly Accurate Energies and Benchmarks for Bicyclic Systems

Published as part of The Journal of Physical Chemistry virtual special issue "Vincenzo Barone Festschrift".

Pierre-François Loos* and Denis Jacquemin*



- VTEs for 10 bicyclic molecules
- 91 new transitions of CCSDT quality for larger systems
- benchmark popular excited-state methods accounting for double and triple excitations



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]
- 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]

✗ Forget about large systems/basis sets:
JCTC 16 (2020) 1711
- 1-3 non-H atoms with triple- or quadruple-ζ basis
- 4-6 non-H atoms with double-ζ basis

✓ Open-shell systems are "easy" (no spin contamination and independent of starting orbitals)
JCTC 16 (2020) 3720

✓ Double excitations are easily accessible (especially if they have the same symmetry as the ground state)
JCTC 15 (2020) 1939

✓ You can post-process CIPSI wave functions!
- one- and two-body density matrices
- QMC trial wave functions