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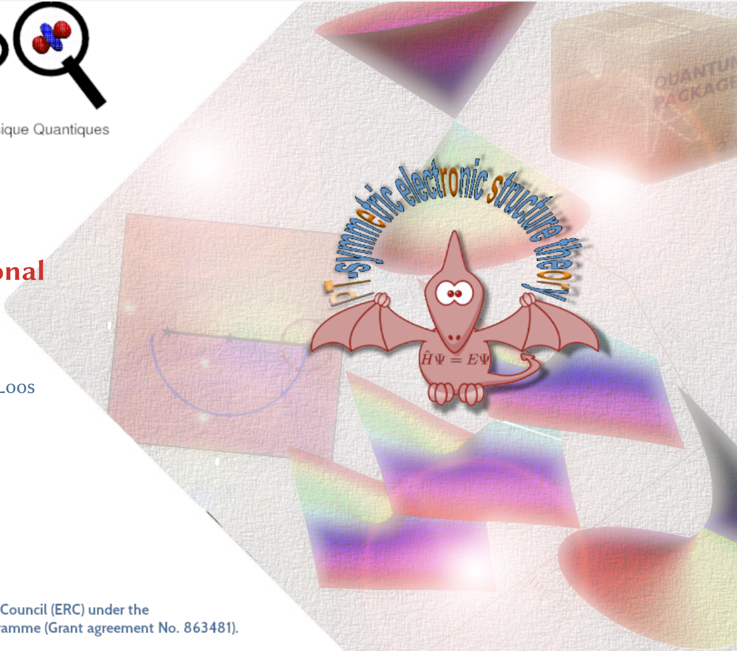
Benchmarking multiconfigurational methods for vertical excitation energies

Martial Boggio-Pasqua & Pierre-François (Titou) Loos

10th OpenMolcas Developers' Workshop

Laboratoire de Chimie et Physique Quantiques (UMR 5626),
Université de Toulouse, CNRS, UPS, Toulouse, France.



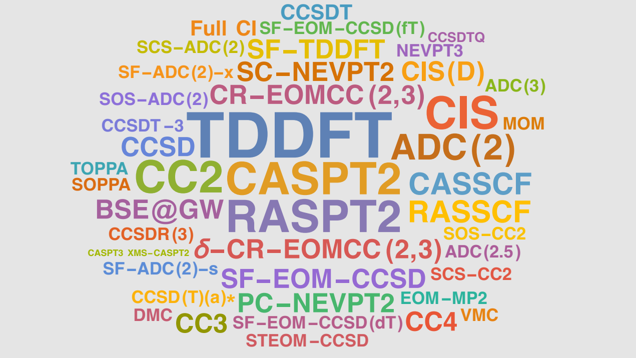
PTEROSOR has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (Grant agreement No. 863481).

Density-based nightmare...

Zoo of functionals...

Wavefunction-based nightmare...

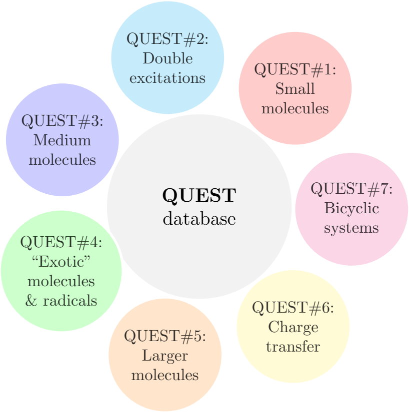
And this is just for excited states...



TD-DFT vs CC/ADC [JCTC 15 (2019) 4581; JCTC 17 (2021) 1106]

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

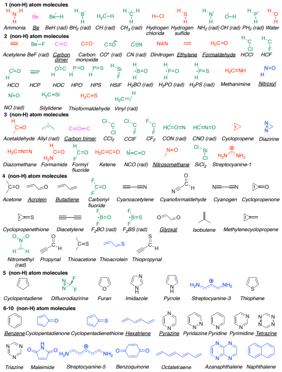
QUEST#3: Medium molecules

QUEST#4: "Exotic" molecules & radicals

QUEST#5: Larger molecules

QUEST#6: Charge transfer

QUEST#7: Bicyclic systems



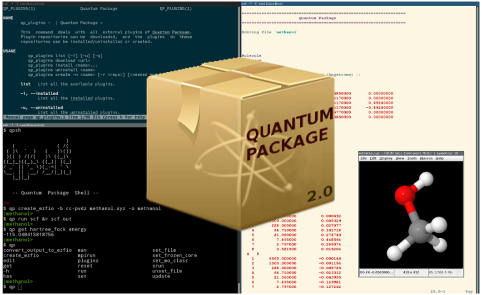
Mika Véril

Martial Boggio-Pasqua

Denis Jacquemin

Selected CI methods

“SCI+PT2 methods provide near full CI (FCI) quality energies 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

                     )
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   -- 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 
```
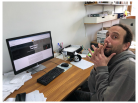

```
================================================================
                       Quantum Package
================================================================

Editing file `methanol`



Molecule

      4      64.710000      0.101718
      5      21.060000      0.274740
      6       7.495000      0.448564
      7       2.797000      0.285074
      8       0.521500      0.015204
   p   8
      1    6665.000000     -0.000146
      2    1000.000000     -0.001154
      3     228.000000     -0.005725
      4      64.710000     -0.023312
      5      21.060000     -0.063955
      6       7.495000     -0.149981
      7       2.797000     -0.127262
                                                       25,0-1        Top
```

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



Anthony Scemama

Emmanuel Giner

Michel Caffarel

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

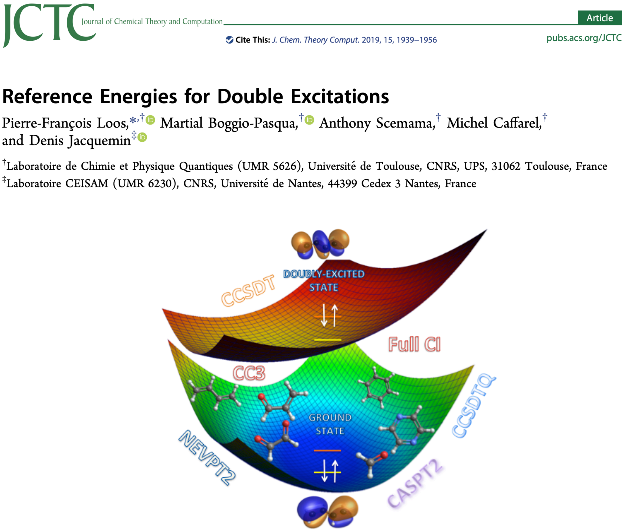
Pierre-François Loos,*[,†] Anthony Scemama,[†] Aymeric Blondel,[‡] Yann Garniron,[†] Michel Caffarel,[†] and Denis Jacquemin*[,‡]

[†]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 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

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,[†]
and Denis Jacquemin[‡]

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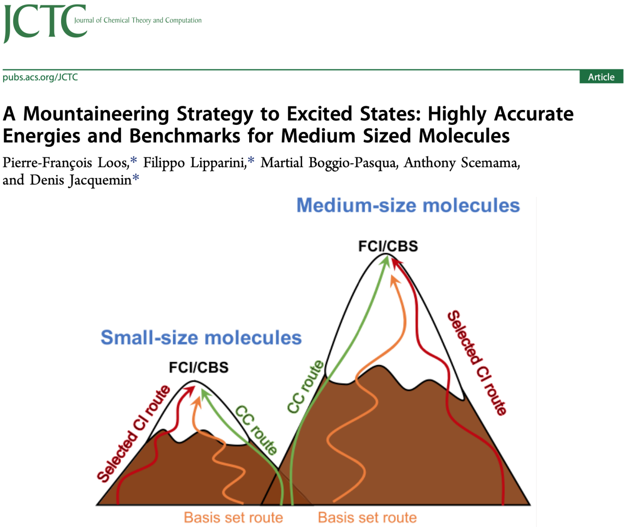
[‡]Laboratoire CEISAM (UMR 6230), CNRS, Université de Nantes, 44399 Cedex 3 Nantes, France

- 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

QUEST #3 — medium-sized molecules —



JCTC Journal of Chemical Theory and Computation

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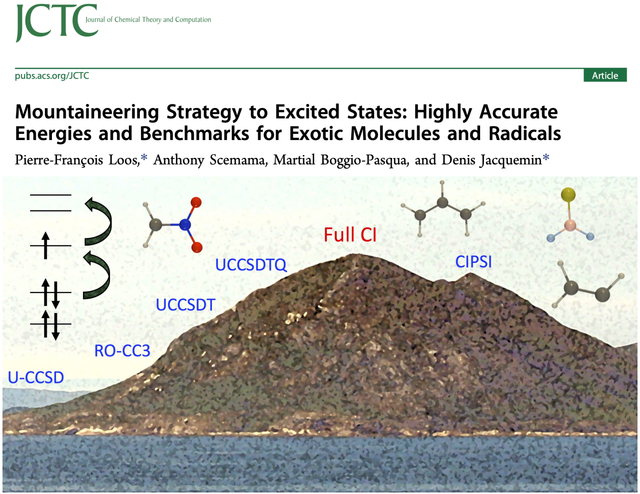
A Mountaineering Strategy to Excited States: Highly Accurate Energies and Benchmarks for Medium Sized Molecules

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; arXiv:2204.11658]

QUEST #4 — “exotic” molecules and radicals —



JCTC Journal of Chemical Theory and Computation

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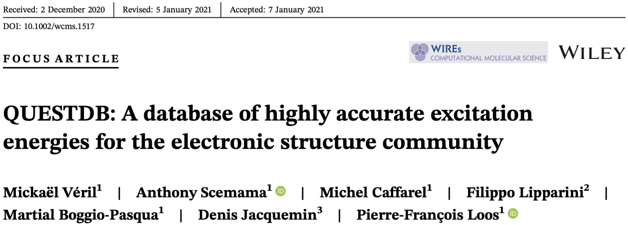
Article

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)

QUEST #5 — larger molecules —



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

FOCUS ARTICLE

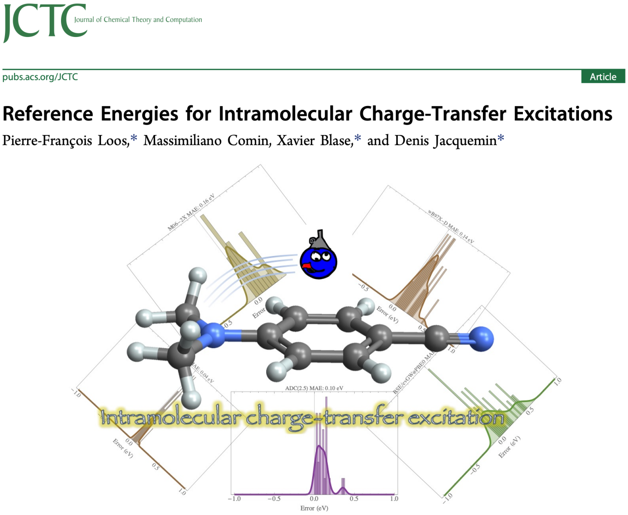
WIREs COMPUTATIONAL MOLECULAR SCIENCE WILEY

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

QUEST #6 — charge-transfer states —



JCTC Journal of Chemical Theory and Computation

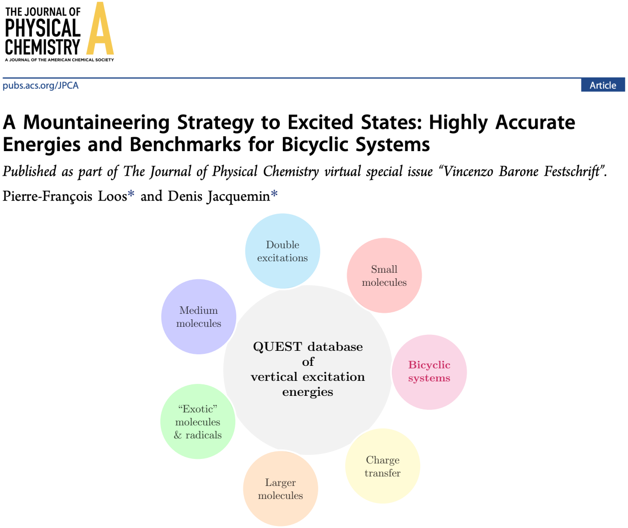
pubs.acs.org/JCTC Article

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)

QUEST #7 — bicyclic molecules —



pubs.acs.org/JPCA

Article

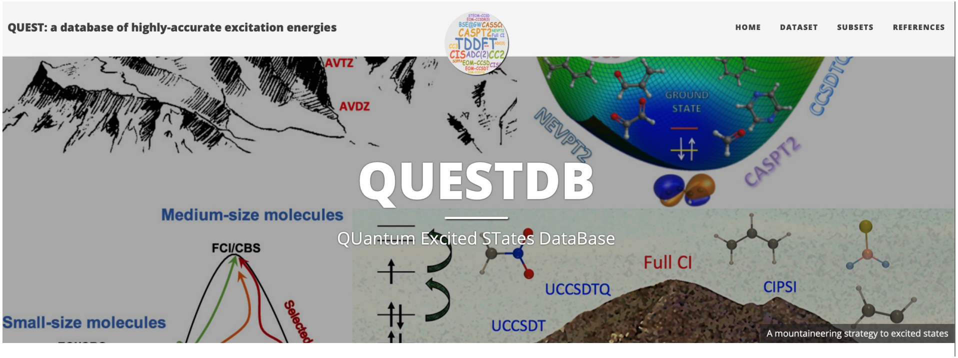
A Mountaineering Strategy to Excited States: Highly Accurate Energies and Benchmarks for Bicyclic Systems

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

The QUEST website



QUEST: a database of highly-accurate excitation energies

Mika Véril

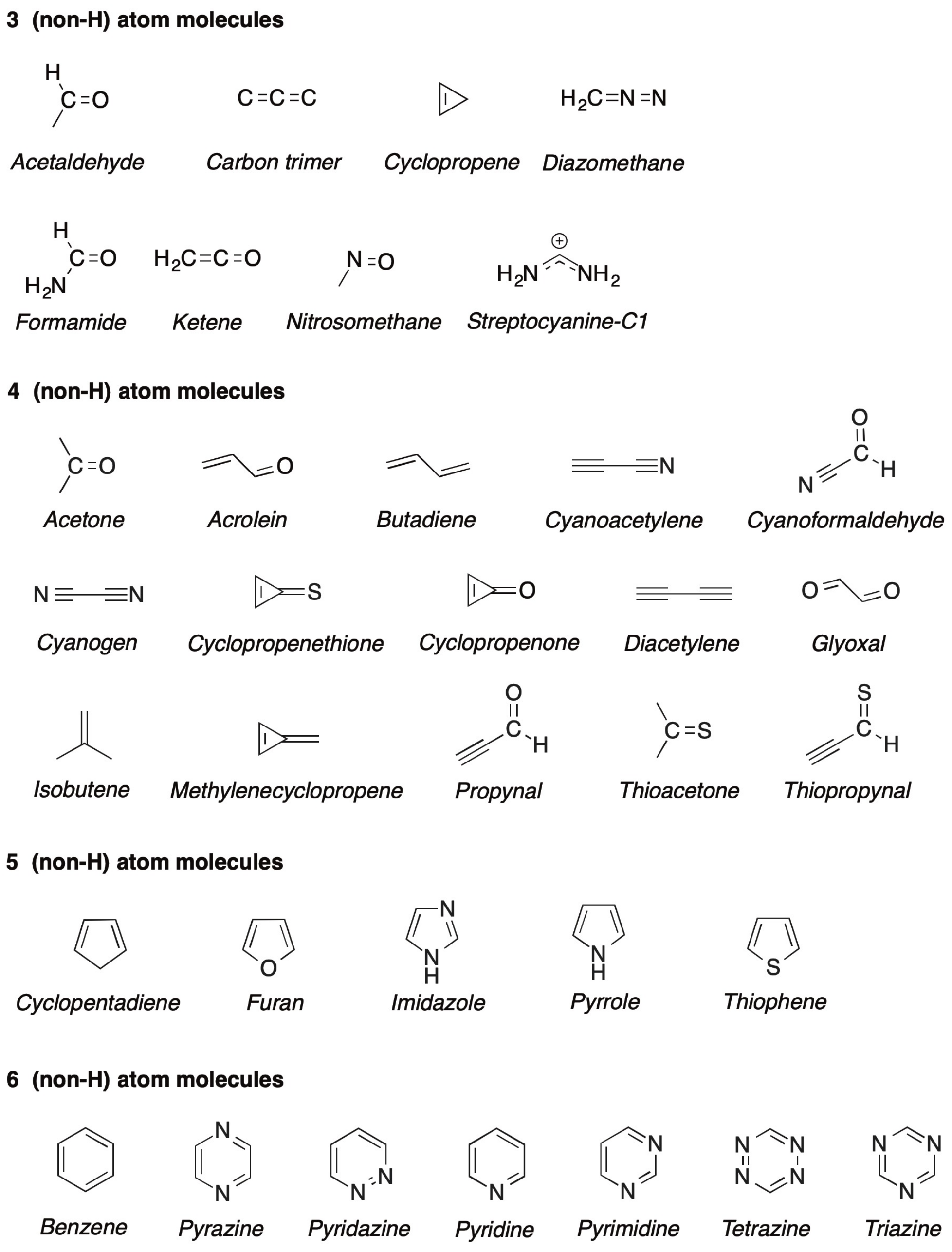
Véril et al. WIREs Comput. Mol. Sci. 11 (2021) e1517

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 (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] and many-body perturbation theory [JCP 153 (2020) 114120; JCP 156 (2022) 164101]

Benchmarking MR-PT2 & -PT3 methods for vertical transition energies



- 284 VTEs at CC3/aug-cc-pVTZ geom.:
  - 174 singlet
  - 110 triplet
  - 206 valence →
    - 78 n→π*
    - 119 π→π*
    - 9 double excitations
  - 78 Rydberg

- NEVPT2
  - aug-cc-pVTZ
  - frozen core
  - SC and PC versions
  - state-specific calculations

- CASPT2 / CASPT3
  - aug-cc-pVTZ
  - frozen core
  - IPEA = 0.25 E_h or = 0 (no IPEA)
  - Level shift = 0.3 E_h
  - state-specific calculations

- Performed in Molpro

R. Sarkar et al., *J. Chem. Theory Comput.* **2022**, *18*, 2418–2436.
M. Boggio-Pasqua et al., **2022**, arXiv:2204.06480.

Reference CASSCF calculations

Choice of active space and state-averaging in the reference CASSCF wavefunction:

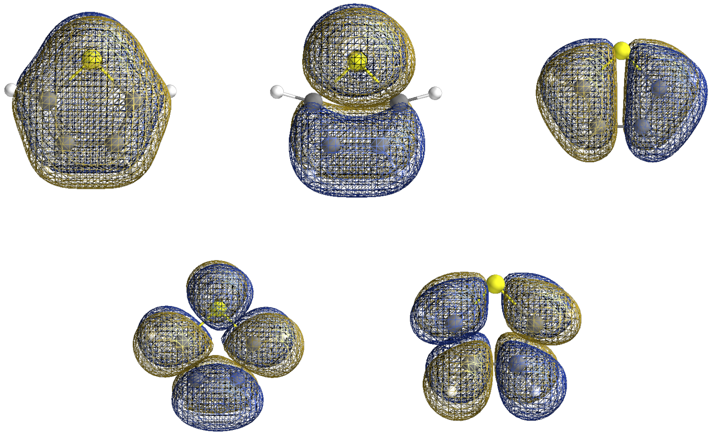
- state-average between ground state and the excited state(s) of interest
  -> minimize bias between GS and ESs

- state-average between states of different electronic symmetries
  -> allows to preserve degeneracy in doubly-degenerate irreducible representations (E, Π, Δ) of non-Abelian point groups (D_{3h}, D_{6h}, $C_{\infty v}$, $D_{\infty h}$)

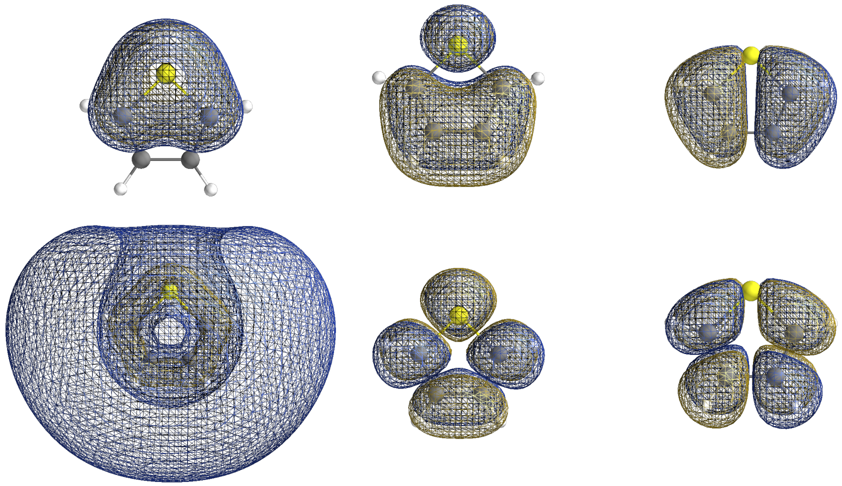
- active space chosen as “intuitive” as possible but for difficult cases

Thiophene example

$^1A_1(\pi,\pi^*)$ excited states
SA3-CASSCF(6,5)



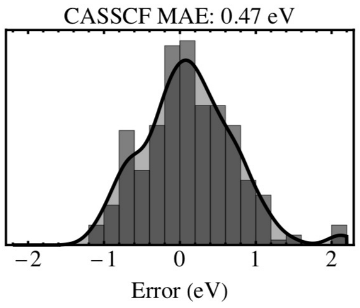
$^1A_2(\pi,3s)$ excited state
SA2-CASSCF(6,6)

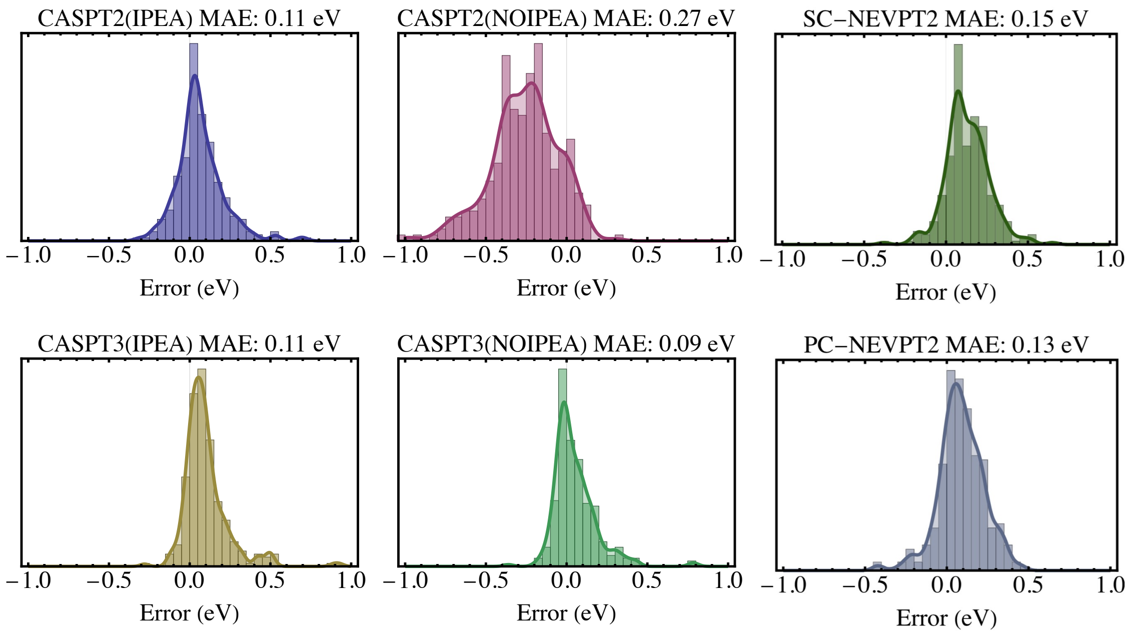


Results: Global trends

Errors (in eV) taking the TBEs as reference.

Method	MSE	MAE	RMSE	SDE	max(+)	max(–)
SA-CASSCF	**0.12**	**0.47**	0.61	0.58	2.15	–1.18
SC-NEVPT2	**0.13**	**0.15**	0.19	0.14	0.65	–0.38
PC-NEVPT2	**0.09**	**0.13**	0.17	0.14	0.46	–0.57
CASPT2(IPEA)	**0.06**	**0.11**	0.16	0.14	0.71	–0.32
CASPT2(NOIPEA)	**–0.26**	**0.27**	0.33	0.21	0.30	–1.02
CASPT3(IPEA)	**0.10**	**0.11**	0.17	0.14	0.93	–0.28
CASPT3(NOIPEA)	**0.05**	**0.09**	0.14	0.13	0.79	–0.36

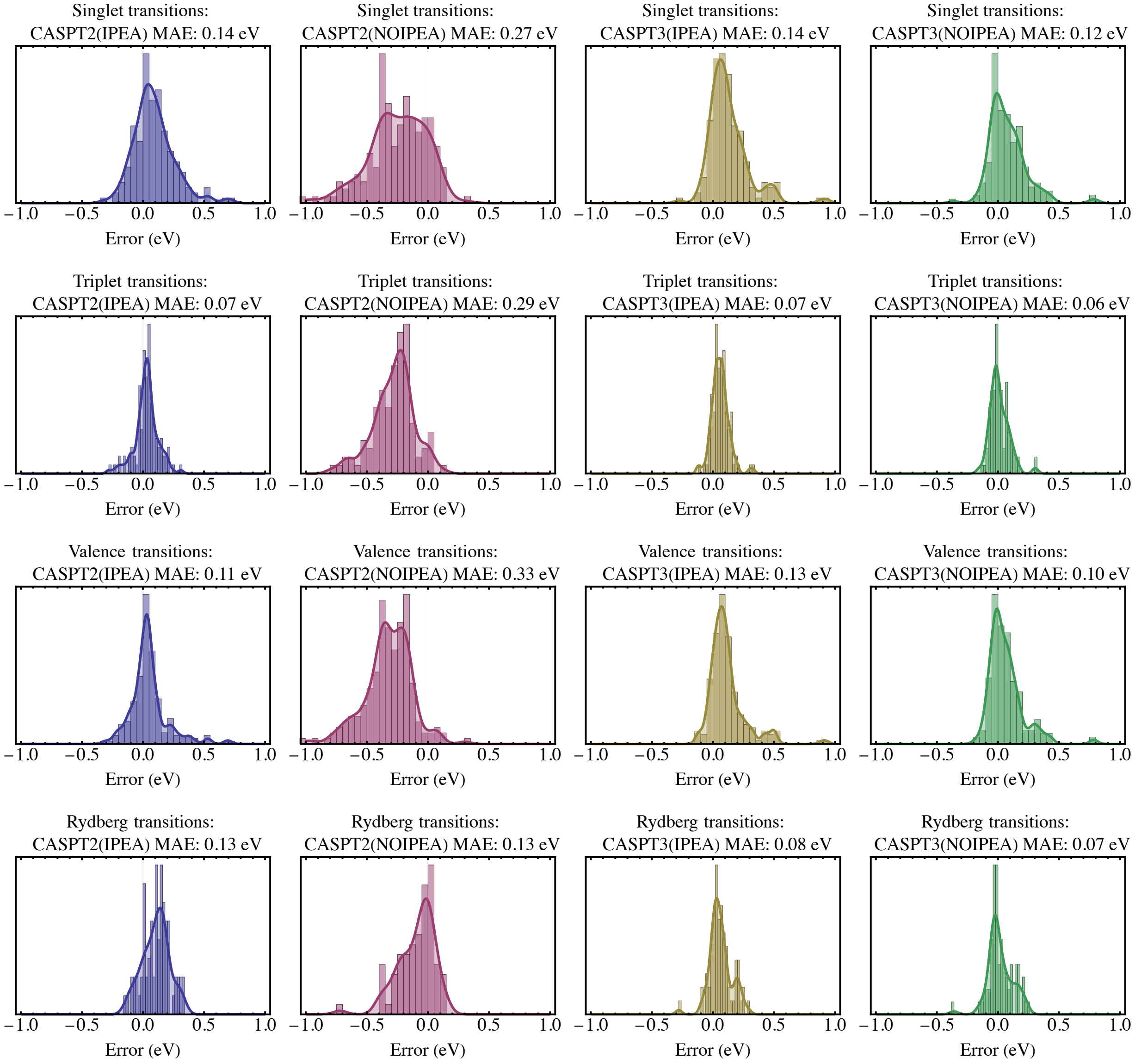


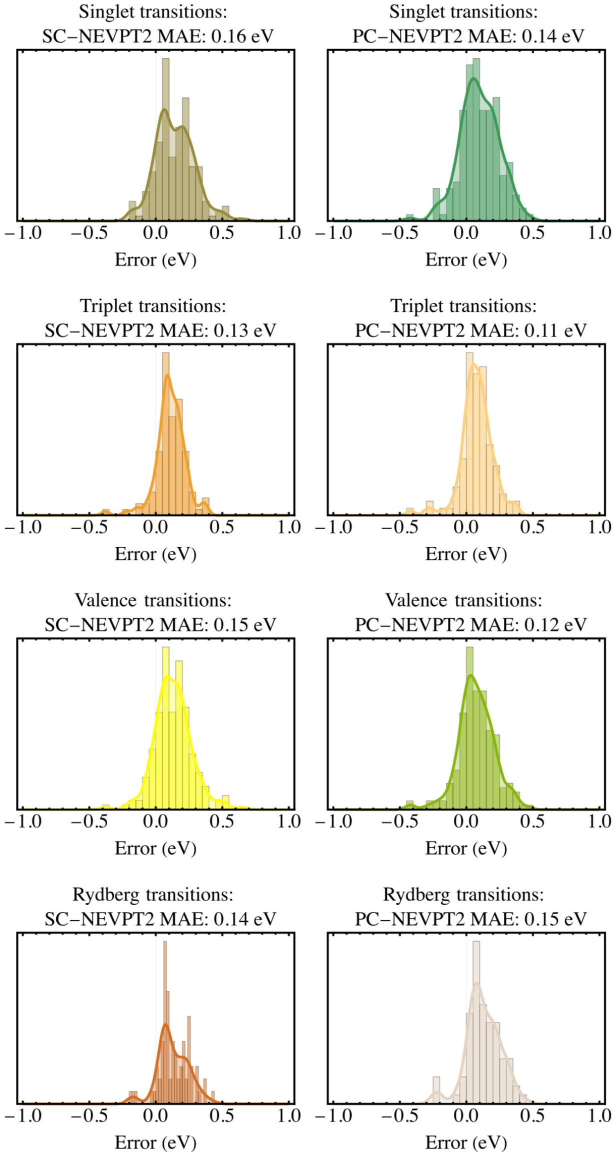


Some conclusions:

- CASSCF: small MSE, large MAE and max(+/–)
- CASPT2(NOIPEA): poor MSE & MAE
- CASPT2(IPEA): good MSE & MAE
- PC-NEVPT2 competitive with CASPT2(NOIPEA)
- SC-NEVPT2 slightly inferior
- CASPT3(NOIPEA) only slightly better than CASPT2(IPEA)

Results: Global trends with type of transition

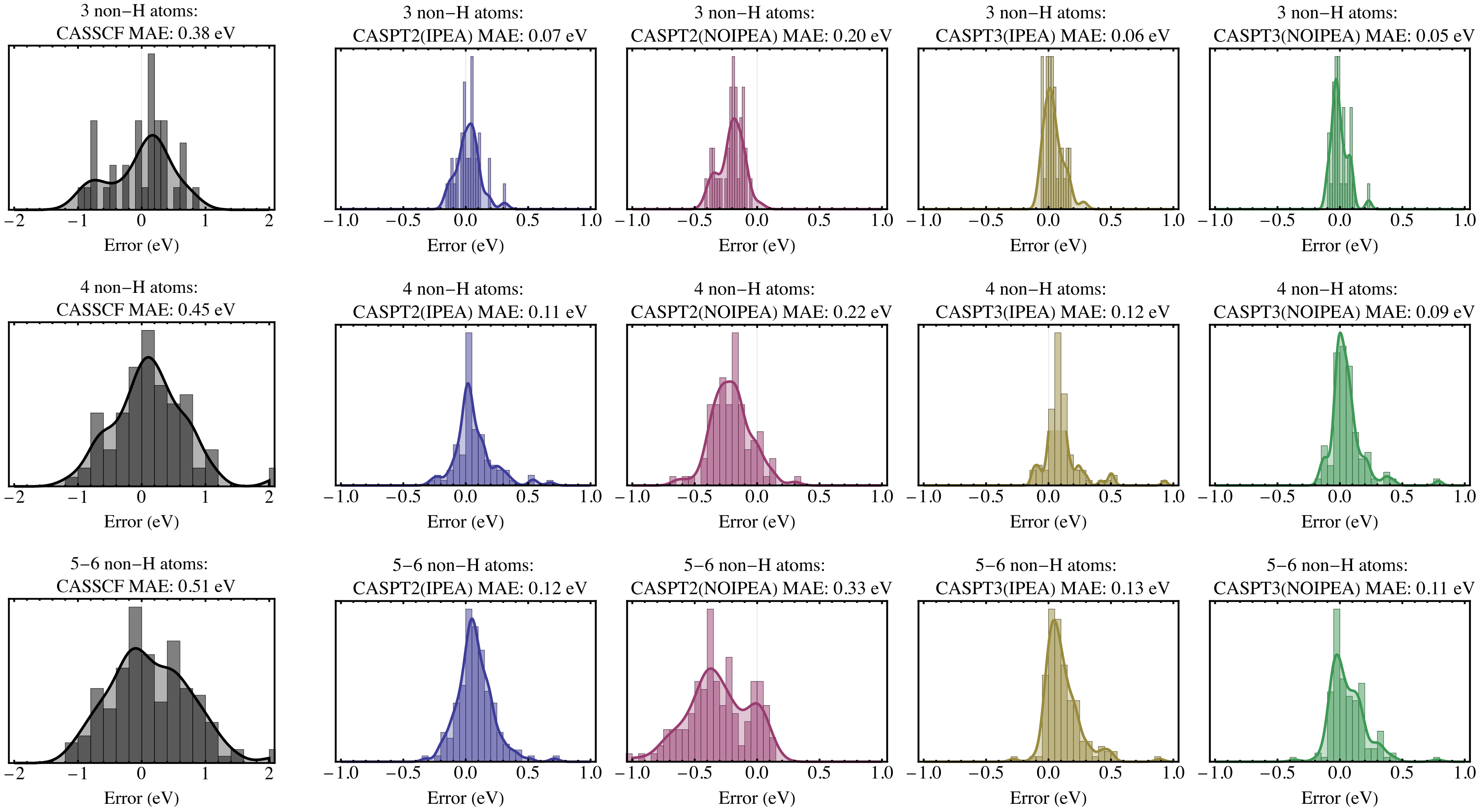




Some conclusions:

- VTEs to triplet states more accurate than those to singlet states
- Similar accuracy for valence and Rydberg transitions
- CASPT2(NOIPEA) reasonable only for Rydberg transitions

Results: Global trends with system size



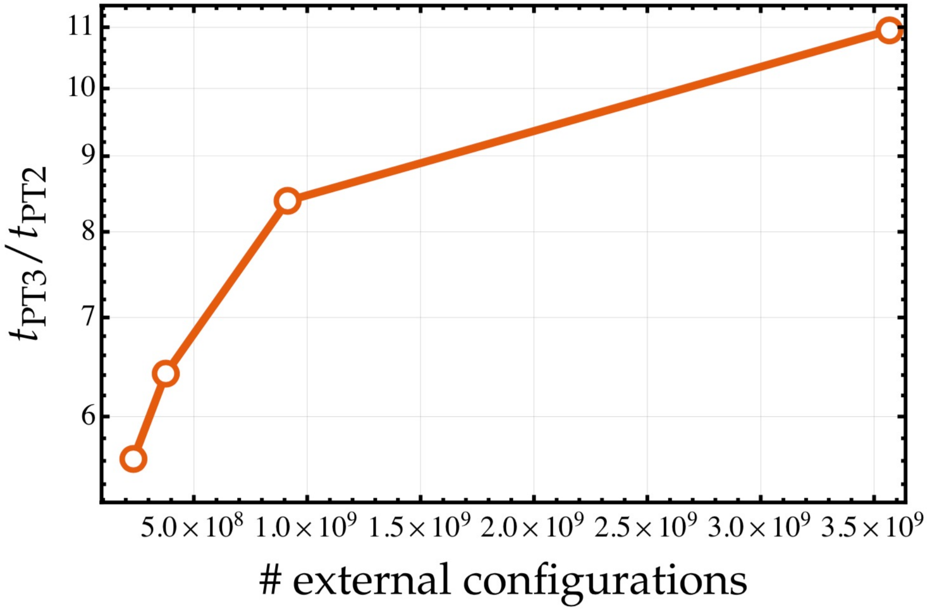
Some conclusions:

- Accuracy gets slightly worse as system size increases
- CASPT3(NOIPEA) does not improve on CASPT2(IPEA) for larger systems

Results: CASPT3 vs CASPT2 timings

Timings (in sec) for CASPT2 and CASPT3 energies of benzene.

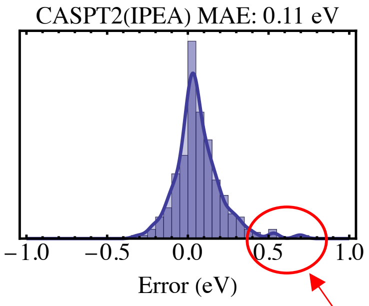
Active space	# CAS det.	# contracted config.	# uncontracted config.	t_{PT2}	t_{PT3}
(6e,6o)	104	4.50×10^6	2.29×10^8	11	60
(6e,7o)	165	7.27×10^6	3.69×10^8	39	249
(6e,8o)	412	1.59×10^7	8.98×10^8	159	1333
(6e,9o)	1800	3.96×10^7	3.53×10^9	578	6332

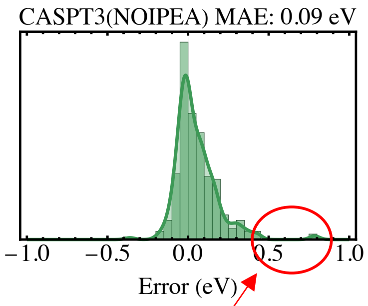


Some conclusions:

- CASPT3 probably not worth the extra computational effort (at least for large systems)…

Results: Handling difficult cases





max(+) > 0.4 eV

Challenging cases:

$^1B_u(\pi,\pi^*)$ in butadiene
$^1B_2(\pi,\pi^*)$ in cyclopentadiene
$^1A_1(\pi,\pi^*)$ in cyclopropenone
$2^1B_{1u}(\pi,\pi^*)$ in pyrazine
$^1E'(\pi,\pi^*)$ in triazine

Too small AS

⇩

Need to include σ-π
correlation for ionic states
(dynamic σ polarization)

Example of $2^1B_{1u}(\pi,\pi^*)$ state in pyrazine:

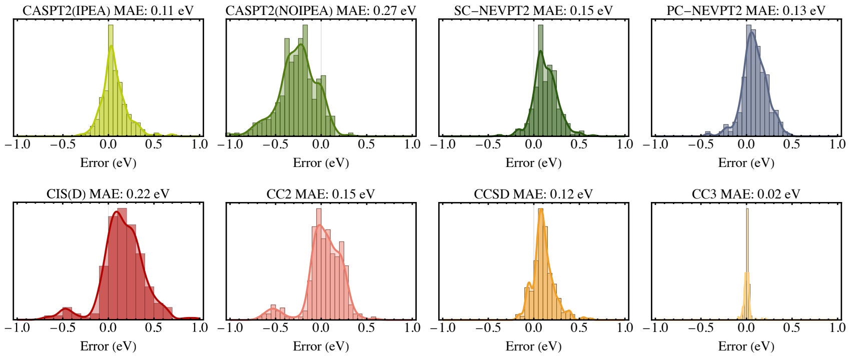
SA4-CASSCF(6,9)	9.65 eV	(valence π + three $3p_x$ for radial correlation : artificial valence/Rydberg mixing)
CASPT2(IPEA)	8.59 eV	
CASPT3(NOIPEA)	8.57 eV	
TBE	**7.98 eV**	

SA3-RASSCF(6,6+6+6)[1,1]	9.16 eV	(valence π in RAS2 + σ_{CC}/σ_{CN} in RAS1 + $\sigma^*_{CC}/\sigma^*_{CN}$ in RAS3 to remove valence/Rydberg mixing)
CASPT2(IPEA)	7.92 eV	
CASPT3(NOIPEA)	8.10 eV	

Conclusions & Perspectives

General conclusions based on the present data set (small organic systems):

- IPEA important for CASPT2/aug-cc-pVTZ but not necessary for CASPT3/aug-cc-pVTZ
- CASPT2(IPEA) good accuracy (ca. 0.1 eV)
- PC-NEVPT2 competitive with CASPT2(IPEA) (with no need for shifts & 1.5 to 3 times faster)
- SC-NEVPT2 slightly inferior to PC-NEVPT2
- CASPT3(NOIPEA) only slightly better than CASPT2(IPEA)
- CASPT2(IPEA) similar accuracy as ADC(2), CC2, CCSD but describes double excitations



Perspectives:

- multi-state CASPT2
- larger systems (CT excitations in π conjugated systems, bicyclic systems, …)
- benchmark away from GS geometry (e.g., along photochemical paths)