A selected configuration interaction study of ground- and excited-state electric dipole moments

Yann Damour[1]

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PTEROSOR Team

Usefulness of electric dipole moments

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- ■ Experimental chemistry
  - Spectroscopy
  - Identification of the structure/isomer of a molecule
- ■ Computational chemistry
  - "Theoretical" spectroscopy
  - Descriptor of the quality of the electronic density
    (Hait et al. Phys. Chem. Chem. Phys. 20, 19800 (2018))

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Expectation value

$$\boldsymbol{\mu} = -\sum_{i}^{N\text{elec}} \langle \Psi | \boldsymbol{r}_i | \Psi \rangle + \sum_{A}^{N\text{nucl}} Z_A \boldsymbol{R}_A \qquad (2)$$

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■ Oscillator strengths $\propto$ transition intensities.

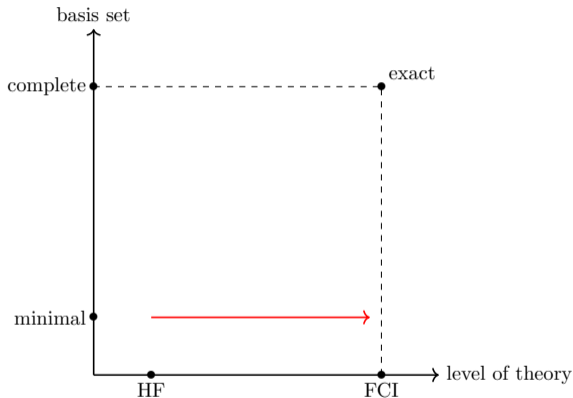# Aiming for the exact solution (0/2)
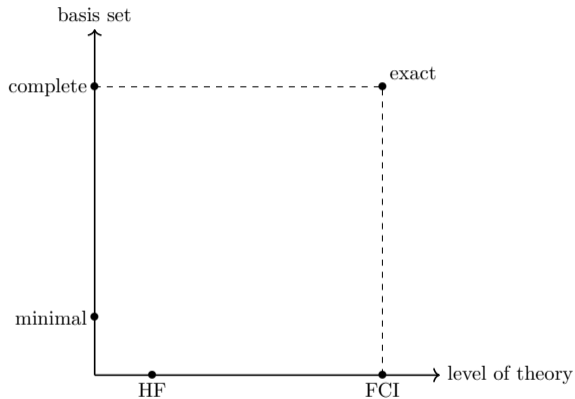
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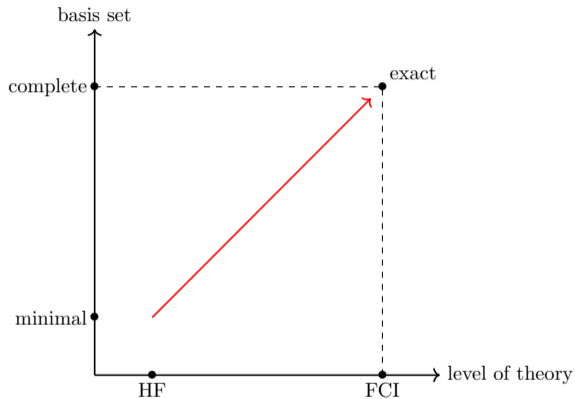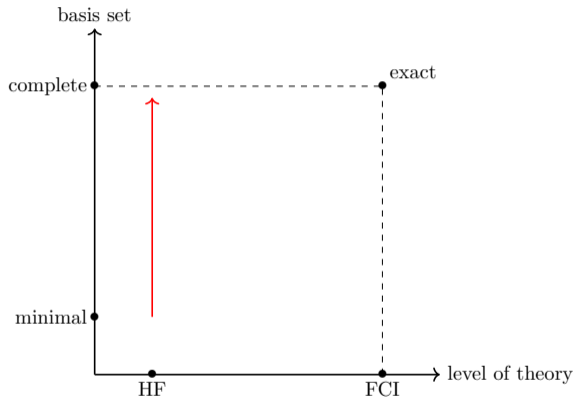
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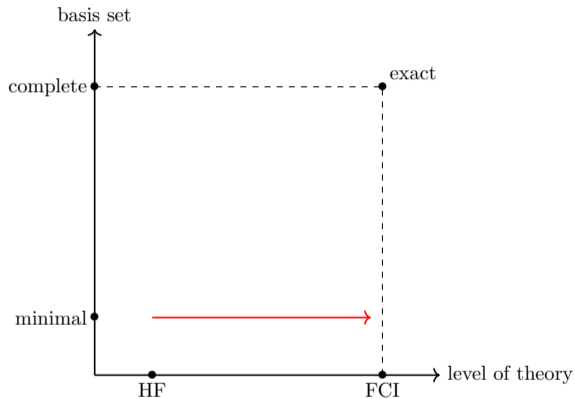
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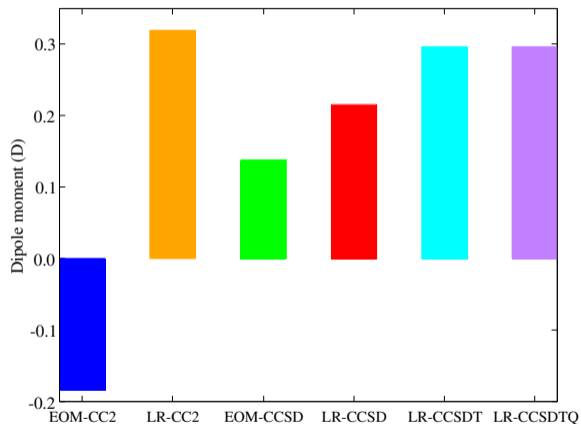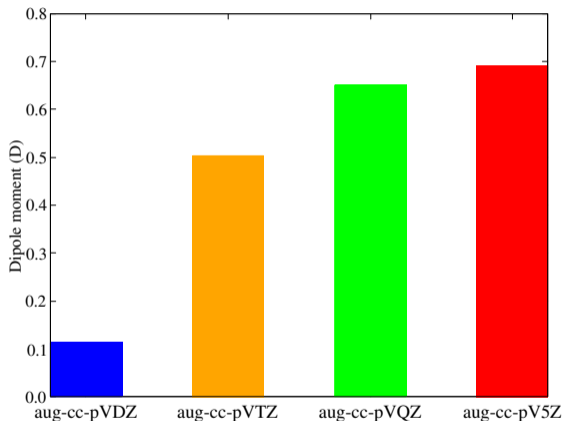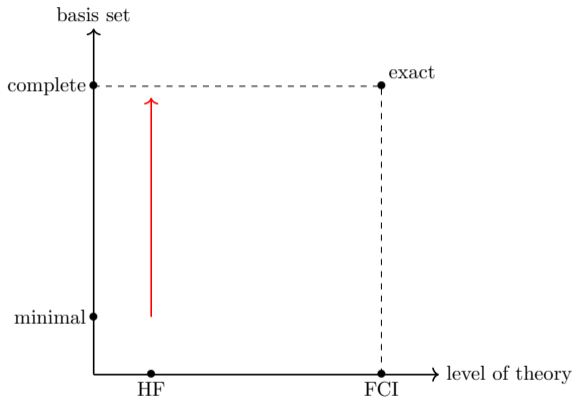

BF, first excited state in aug-cc-pVTZ.

[1]R. Sarkar et al. J. Chem. Theory Comput. 2021, 17.2, 1117–1132.

Aiming for the exact solution (2/2)

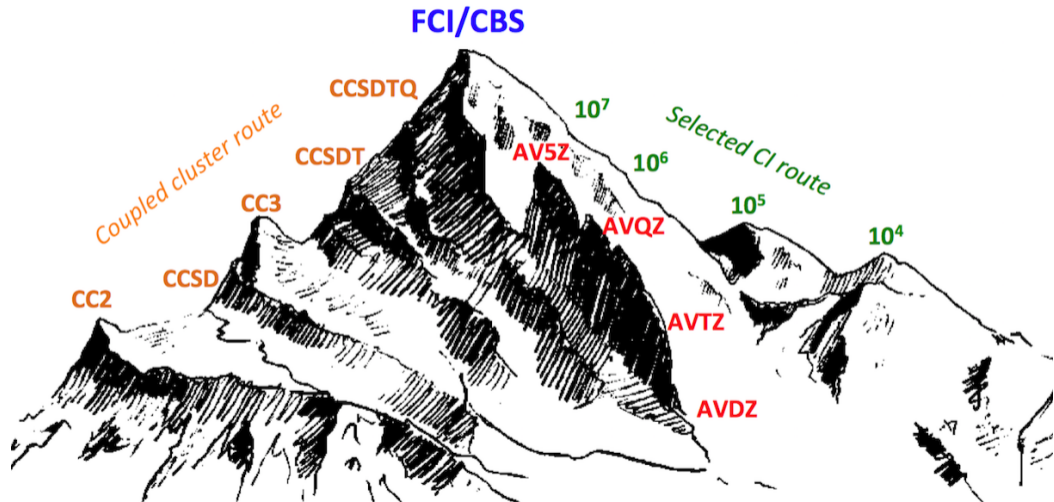[2]A. Chrayteh et al. J. Chem. Theory Comput. 2021, 17.1, 416–438.

Aiming for the exact solution (2/2)

H$_2$S, first excited state with LR-CCSD.[2]

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[2]A. Chrayteh et al. J. Chem. Theory Comput. 2021, 17.1, 416–438.

Another road to FCI ?

FCI/CBS

CCSDTQ

Coupled cluster route

CCSDT

CC3

CCSD

CC2

10^7

AV5Z

Selected CI route

10^6

AVQZ

10^5

10^4

AVTZ

AVDZ

[3]P.-F.Loos et al. J. Chem. Theory Comput. 2018, 14, 4360–4379.

CIPSI

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- Configuration Interaction using a Perturbative Selection made Iteratively[4]
- Selection of the "important" electronic configurations (Slater determinants)

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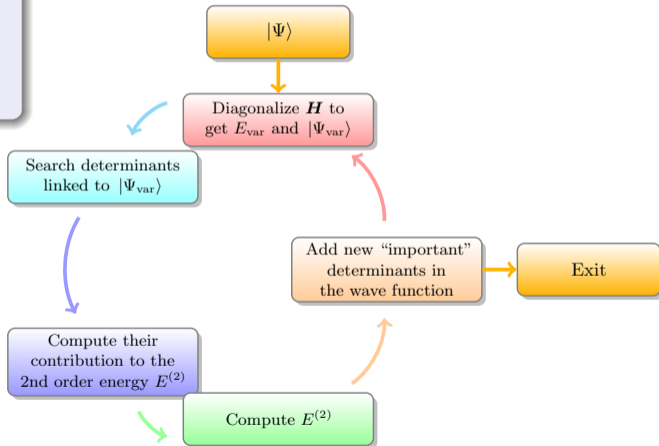
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Targeting FCI

Benzene / cc-pVDZ[5]

- FCI $\rightarrow$ (30e/108o) $= 8 \times 10^{35}$ determinants

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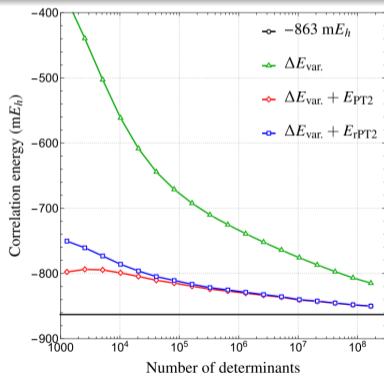[5]P.-F. Loos et al. J. Chem. Phys. 153 (2020), 176101

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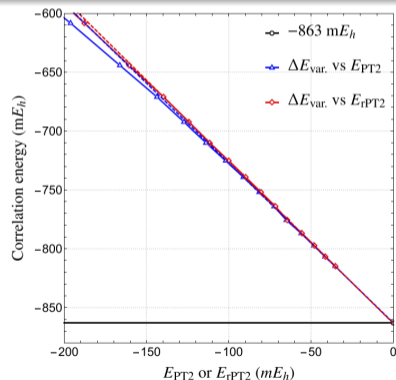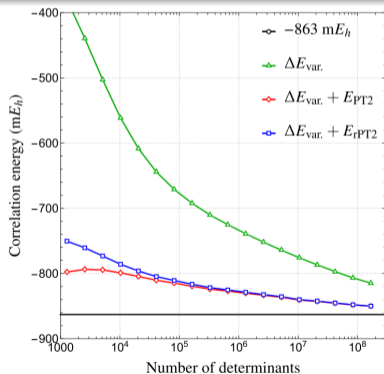
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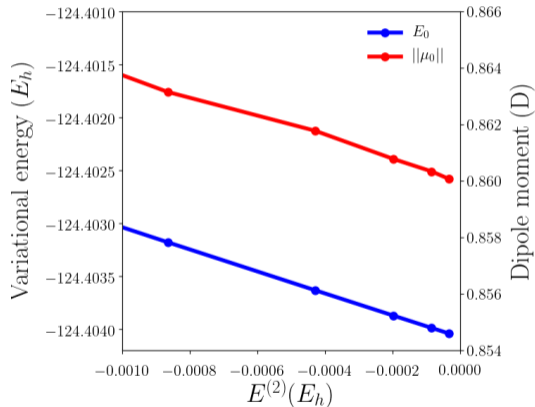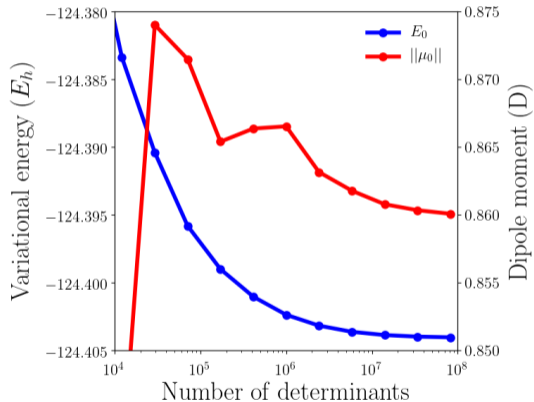

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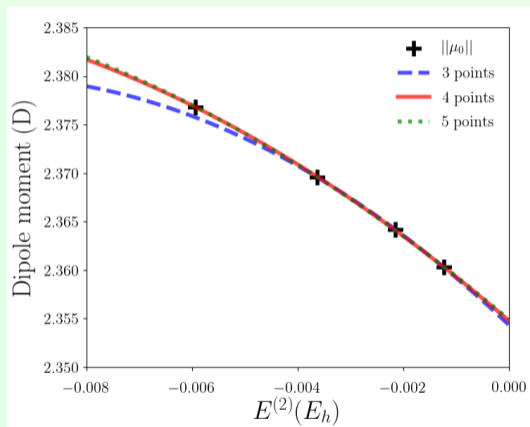# What about dipole moments? ground state of BF/aug-cc-pVDZ
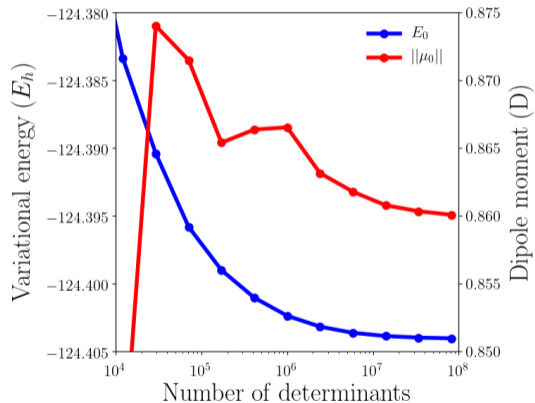
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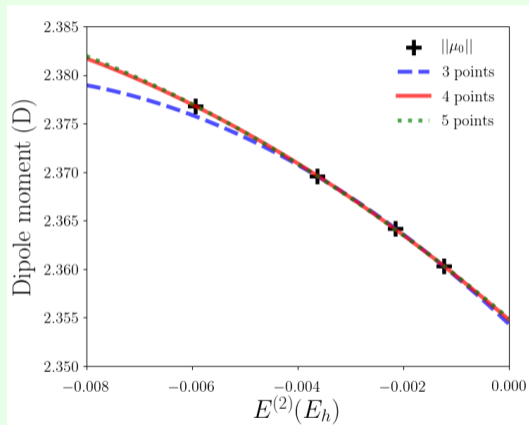
Extrapolation

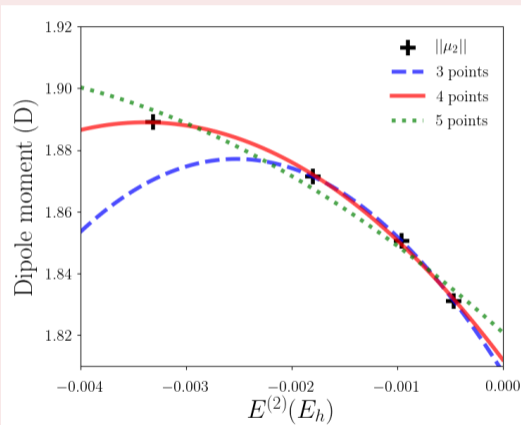## Good case...

H_2CO / aug-cc-pVDZ, ground state.

Extrapolation

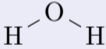## Good case...

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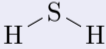
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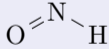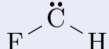H$_2$S / aug-cc-pVQZ, 2nd excited state.

Study

CC3/aug-cc-pVTZ geometries[3]

Boron monohydride	$B-H$	$^1\Sigma^+$, $^1\Pi$	Carbon dioxide	$C=O$	$^1\Sigma^+$, $^1\Pi$
Hydrochloric acid	$Cl-H$	$^1\Sigma^+$, $^1\Pi$	Formaldehyde	$H_2C=O$	$^1A_1$, $^1A_2$
Water	$H-O-H$	$^1A_1$, $^1B_1$, $^1A_2$, $^1A_1$	Thioformaldehyde	$H_2C=S$	$^1A_1$, $^1A_2$
Hydrogen sulfide	$H-S-H$	$^1A_1$, $^1A_2$, $^1B_1$	Nitroxyl	$O=N-H$	$^1A'$, $^1A''$
Boron monofluoride	$B-F$	$^1A_1$, $^1\Pi$	Fluorocarbene	$F-\ddot{C}-H$	$^1A'$, $^1A''$

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[3]A. Chrayteh et al. J. Chem. Theory Comput. 17 (2021), 416-438

Results

Few numbers

- H_2S
  - aug-cc-pVDZ (8e,40o): few hours < 1 mD
  - aug-cc-pVQZ (8e,171o): few weeks ~ 10 mD
- H_2CS
  - aug-cc-pVDZ (12e,62o): one week ~ 1 mD
  - aug-cc-pVTZ (12e,136o): few weeks $\sim$ few mD

- Configuration (Hilbert) space
  - (24e,24o) $\sim 7 \times 10^{12}$
  - (8e,171o) $\sim 1 \times 10^{15}$
  - (12e,136o) $\sim 6 \times 10^{19}$

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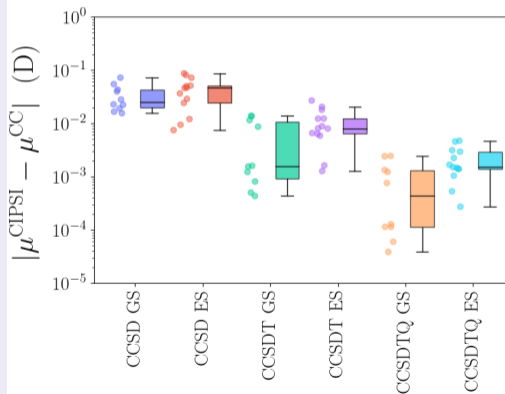 - aug-cc-pVDZ (12e,62o): one week ~ 1 mD
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CC & CIPSI / aug-cc-pVDZ

Acknowledgments

Pierre-François Loos

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Raúl Quintero-Monsebaiz

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