The WFA module in MOLCAS
Turning numbers into chemical insight

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Introduction

New developments in MOLCAS

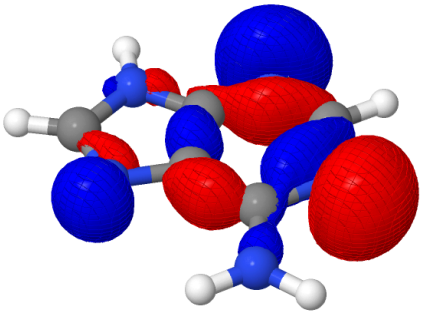
☺ *Quantum chemical methods*
DMRG, RASPT2, MC-PDFT

☺ *Algorithmic efforts*
Parallelization, RI-CD, stochastic MCSCF, heat-bath CI

☺ *Fancy stuff*
Second-order SOC, Auger spectra, X-ray spectra

? How do we analyze these computations

☹ **Look at the HOMO and LUMO**



Introduction

- Detailed **analysis of electronic wavefunctions**
- Photophysical and photochemical processes

→ **Chemical insight**

→ **Understand** and **benchmark** the computations

- Tasks
- **Visualization**
- **Quantitative analysis**

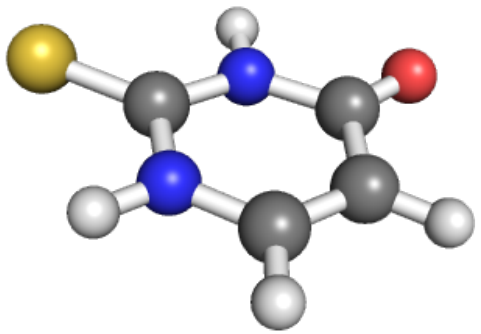
→ The `WFA` module in MOLCAS[1]

[1] FP, S. Mewes, A. Dreuw, L. González *JCTC* **2017**, 13,5343.

2-Thiouracil

- 2-Thiouracil
- MS-CASPT2(14,10)

? What are the state characters



State	ΔE	f	μ
S_1	3.81	0.000	5.1
S_2	4.32	0.421	5.4
S_3	4.64	0.000	2.2
T_1	3.34		3.8
T_2	3.85		3.3
T_3	3.85		4.6

[1] S. Mai, FP, M. Pabst, F. Neese, A. Köhn, L. González *J. Chem. Phys.* **2017**, 147, 184109.

Natural transition orbitals

1-Electron transition density matrix (1TDM)

$$D^{0I}_{\mu\nu} = \langle \Psi_0 | \hat{a}^\dagger_\mu \hat{a}_\nu | \Psi_I \rangle$$

→ Produced by `RASSI`

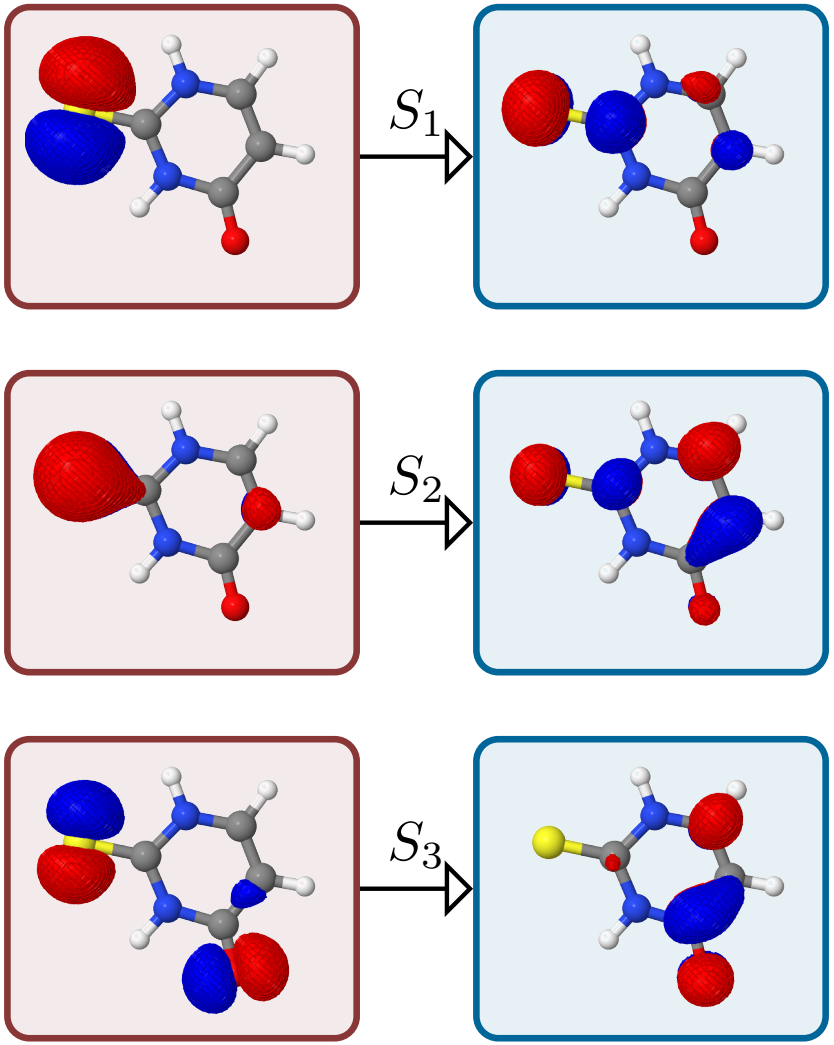
Natural transition orbitals

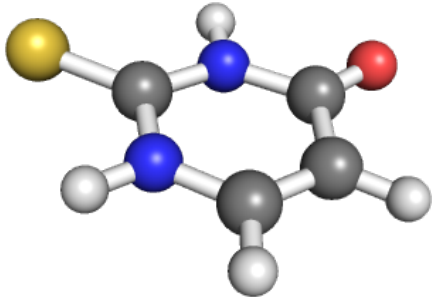
$$\mathbf{D}^{0I} = \mathbf{U} \times \mathrm{diag}\left(\sqrt{\lambda_1}, \sqrt{\lambda_2}, \ldots\right) \times \mathbf{V}^{\mathrm{T}}$$

- $\mathbf{U}$ **Hole** orbital coefficients
- λ_i Transition amplitudes
- $\mathbf{V}$ **Electron** orbital coefficients

[1] R. L. Martin *J. Chem. Phys.* **2003**, 11, 4775.

2-Thiouracil





State	ΔE	f	μ
$S_1(^1n_S\pi^*)$	3.81	0.000	5.1
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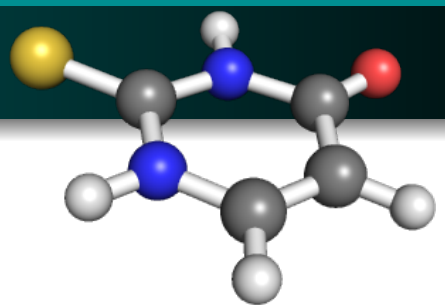
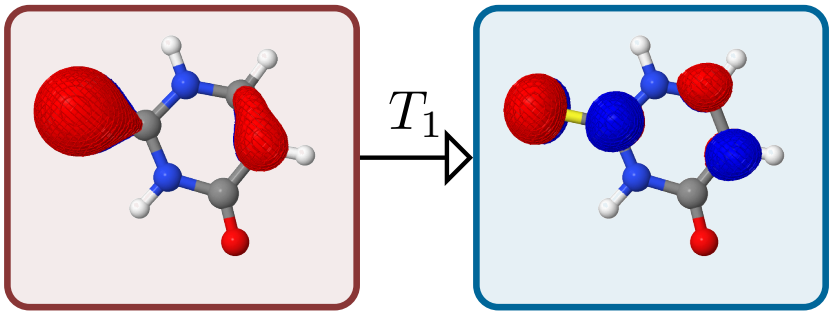
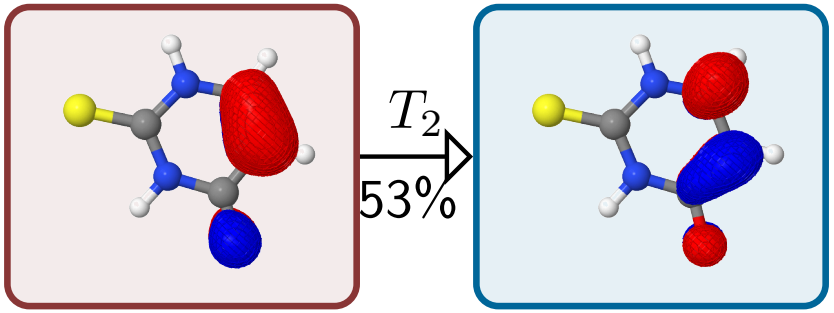
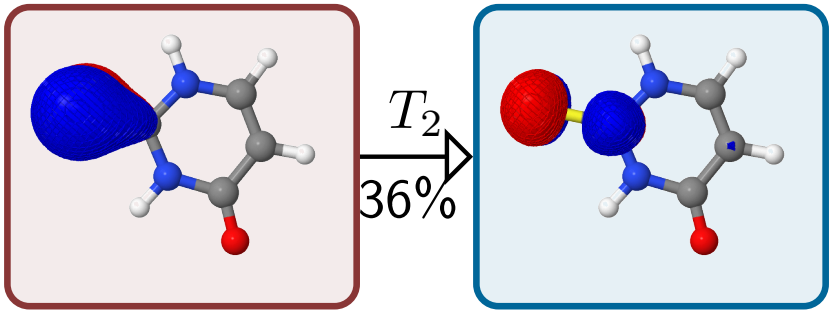
2-Thiouracil









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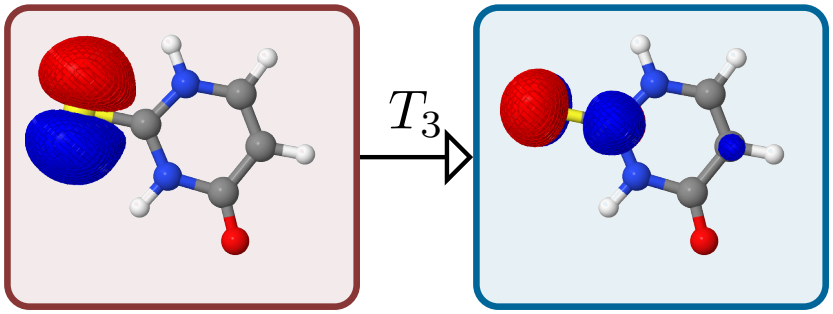
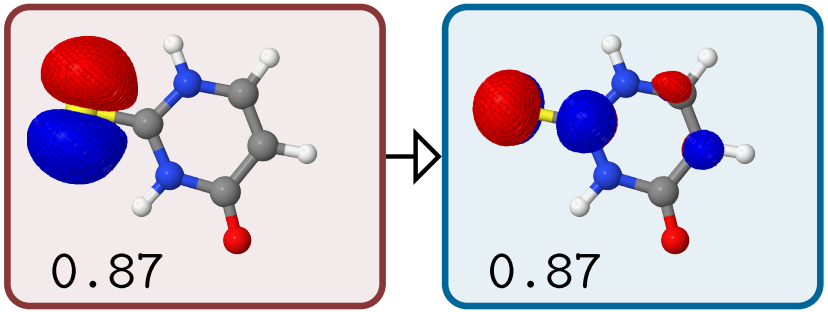
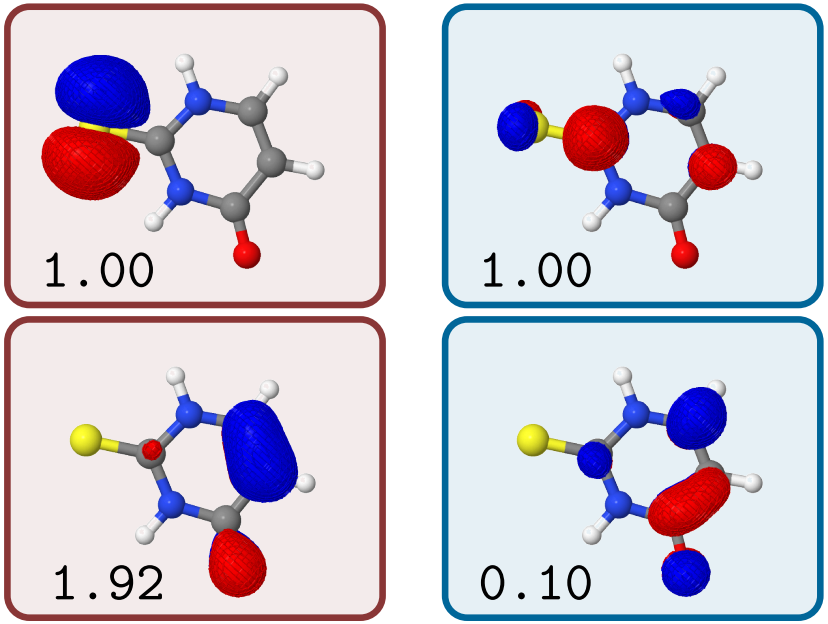


- S_1 state

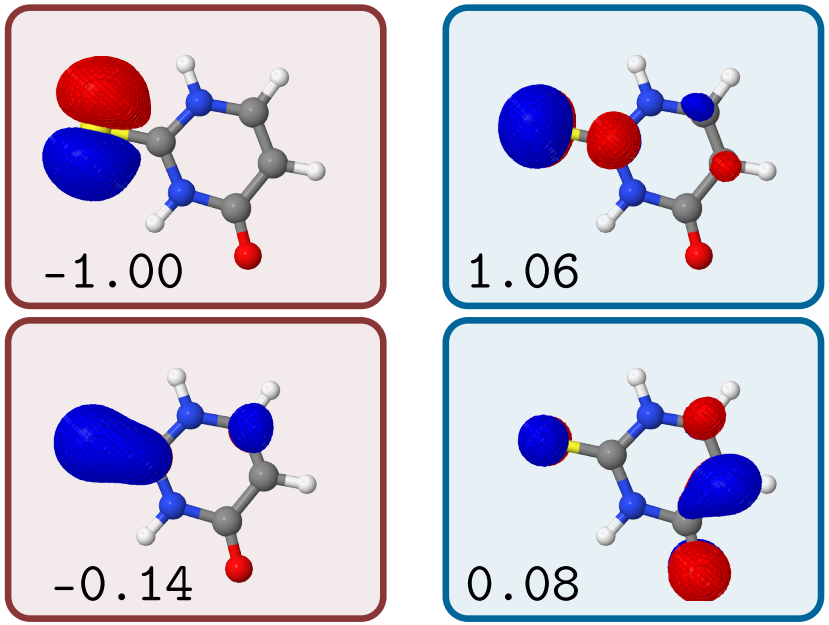
→ Natural **transition** orbitals



→ **Natural** orbitals (state-specific)

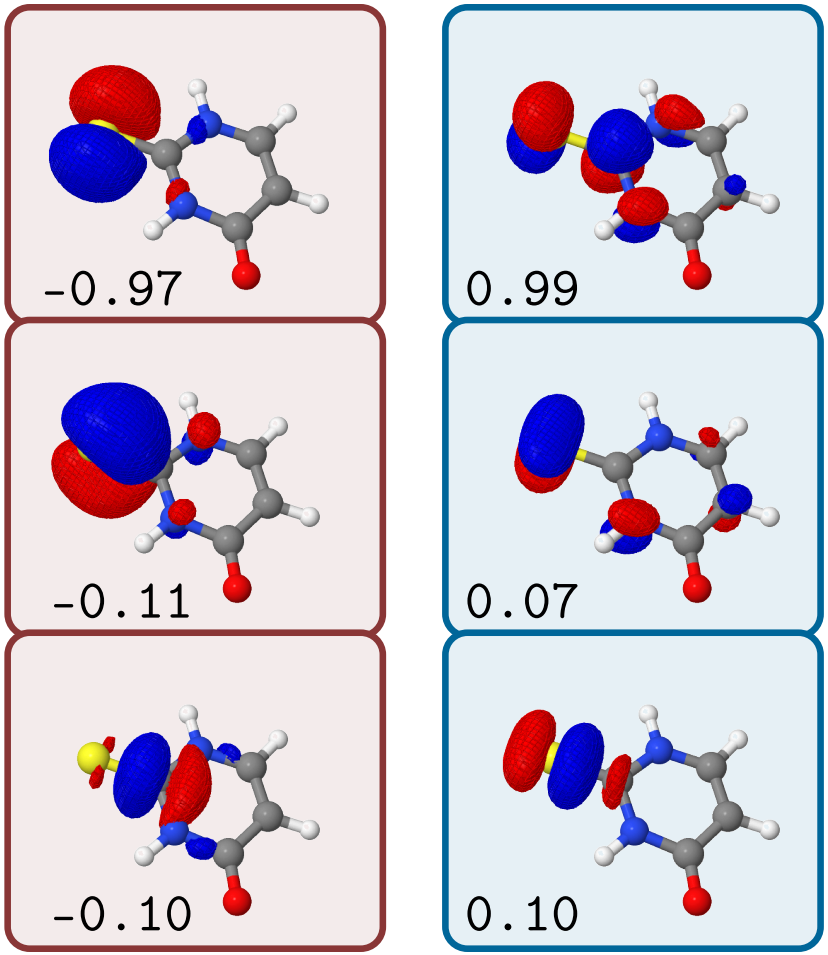


→ Natural **difference** orbitals

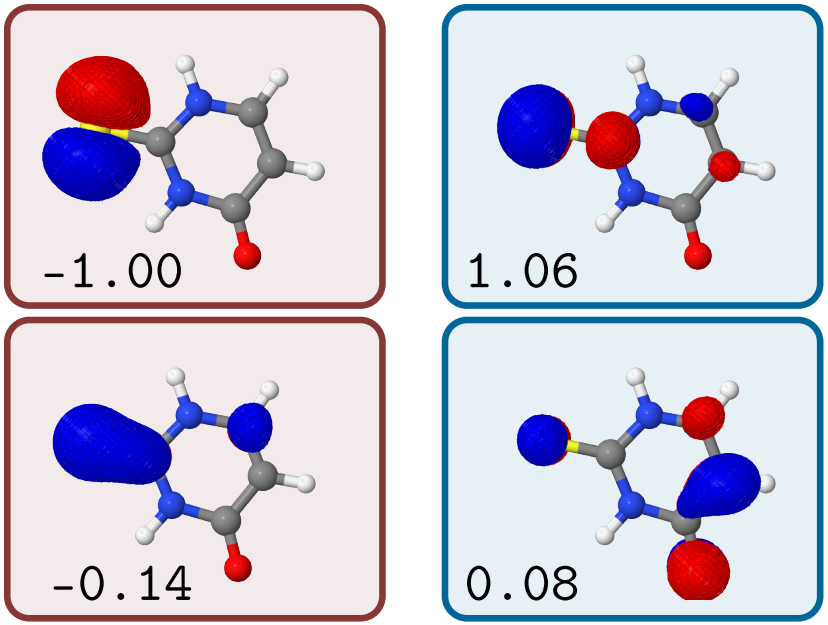


Natural difference orbitals[1]

ADC(3)/aug-cc-pVTZ (Q-Chem)

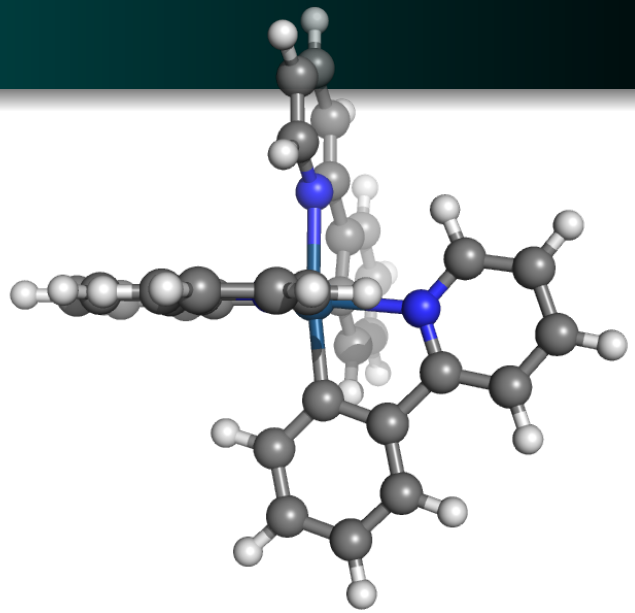


MS-CASPT2(CASSCF)/SVP



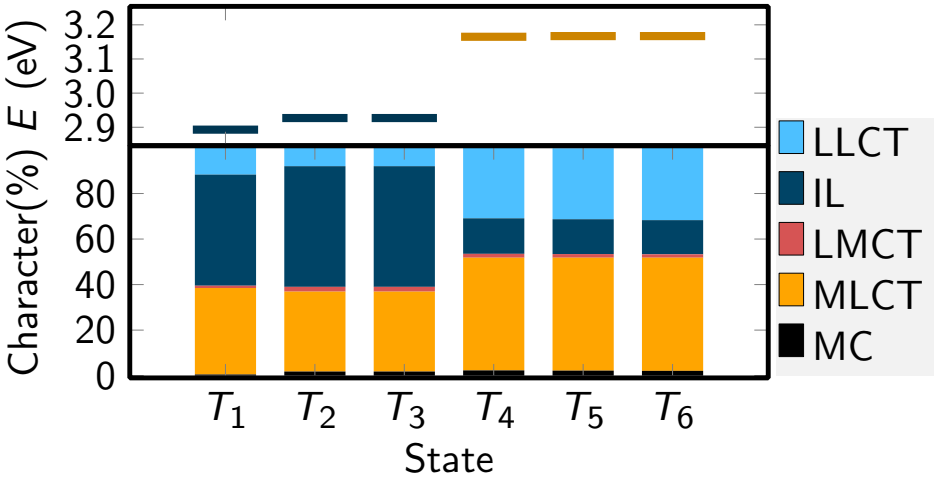
[1] FP, S. A. Bäppler, M. Wormit, A. Dreuw *JCP* **2014**, 141, 024107.

Transition metal complexes



- Excited-state classification in **transition metal complexes**
  - 2-dim. population analysis of the 1TDM

→ Metal-to-ligand CT (**MLCT**)
→ Intraligand (**IL**)
→ Ligand-to-ligand CT (**LLCT**)



[1] FP, A. Dreuw *JPCA* **2015**, 119,1023.
[2] S. Mai, FP, J. Dorn, M. Fumanal, C. Daniel, L. González *CCR* **2018**, 361, 74.

Case studies

Other recent applications

- Quantification of excited-state delocalization in **DNA**[1] (TDDFT)
- Excitons in **conjugated polymers**[2] (ADC)
- Charge transfer in **push-pull molecules**[3] (ADC,TDDFT)

[1] J. J. Nogueira, FP, L. González *Chem. Sci.* **2017**, 8, 5682.
[2] S. A. Mewes, J.-M. Mewes, A. Dreuw, FP *PCCP* **2016**, 18,2548.
[3] P. Kautny, F. Glöcklhofer, T. Kader, et al. FP *PCCP* **2017**, 19, 18055.

The WFA module

- New `WFA` **module** in MOLCAS[1]
- Analysis of
  - SCF
  - RASSCF
  - MS-CASPT2 via RASSI
  - SO-RASSCF/RASPT2 via RASSI (?)
- Communication via HDF5 files

[1] FP, S. Mewes, A. Dreuw, L. González *JCTC* **2017**, 13,5343.

Usage

Input file

```
&SCF

&WFA
H5file = $Project.scf.h5

&RASSCF

&WFA
H5file = $Project.rasscf.h5

&RASSI
TRD1

&WFA
H5file  $Project.rassi.h5
```

Orbital/density visualization

- Orbitals are written to the HDF5 file
- Export to Molden format via `molpy`[1]

```
penny MOLCAS.rassi.h5 --wfaorbs molden
```

- Automatic rendering Jmol

→ `jmol_MOs.py`

- Creation of grid files for densities

- `ORBKIT`[2]

- Automatic rendering in VMD

→ `vmd_plots.py`

[1] https://github.com/steabert/molpy
[2] http://orbkit.github.io

Post-processing - TheDORE

TheoDORE - **Theo**retical **D**ensity, **O**rbital **R**elaxation and **E**xciton analysis[1]

- Analysis of **charge transfer** and excited-state **delocalization**[2]
- Classification of excited states in **transition-metal complexes**[3,4]

- Copy back the `*ctnum_atomic.om` files

- **TODO**: Make more flexible

→ Do everything with TheoDORE

→ Do everything in the `MOLCAS` workflow (?)

→ Do everything with `molpy` (?)

[1] `http://theodore-qc.sourceforge.net`
[2] FP, H. Lischka *JCTC* **2012**, 8, 2777.
[3] FP, A. Dreuw *JPCA* **2015**, 119,1023.
[4] S. Mai, FP, J. Dorn, M. Fumanal, C. Daniel, L. González *CCR* **2018**, 361,74.

Installation

- `libwfa` - An open-source wavefunction analysis tool library[1]
  - Included as submodule in `External`
- Additional libraries
  - Armadillo: C++ linear algebra library
  - HDF5 libraries for C++

Installation

```
cmake -DLINALG=MKL -DWFA=ON -D ARMADILLO_INC=armadillo-x.y/include ..
```

- Same functionality available in **Q-Chem**
  - ADC, EOM-CC, TDDFT

[1] https://github.com/libwfa/libwfa

Distribution

- Sometimes difficult to compile

? Distribution of statically linked executables

- For WFA and for MOLCAS in general
- Problems with licences?

→ Distribute binaries + source

- Other problems?

? Columbus + MOLCAS

Conclusion

- New `WFA` **module** in MOLCAS[1]
  - Analysis of excited-state wavefunctions
  - Visualization and quantiative analysis

☺ Useful
☺ User friendly
☺ Fun

[1] FP, S. Mewes, A. Dreuw, L. González *JCTC* **2017**, 13,5343.

Acknowledgements

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