Meanwhile in Lund: from development to applications

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Part I. Development...

No revolutionary things, but necessary improvements.

- Binatural orbitals
- Cluster Embedding
- Understanding the size of CI
- Core-hole RASSCF
- Small relativistic basis set
- New basis set
- Symmetrization of orbitals

Binatural orbitals: problem

OpenMolcas paper, *Molecular Physics, 110, 2455, 2012*

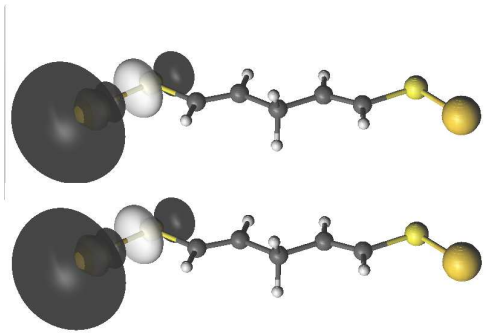
Molcas was paying very little attention to properties, in particular to transition between different states.

$A_{IJ} = \langle \Psi_I | A | \Psi_J \rangle$

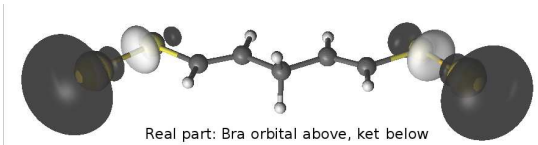
Binatural orbitals

More convenient interface for RASSI

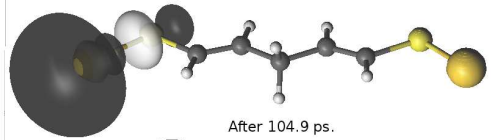
Time dependent transition:



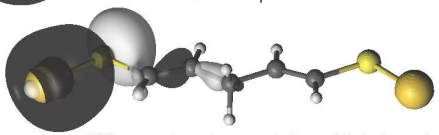
After 0 ps: Ket and bra orbitals are identical



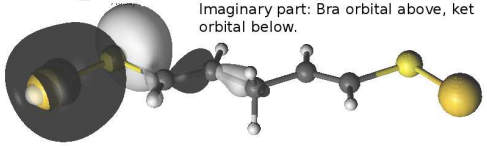
Real part: Bra orbital above, ket below

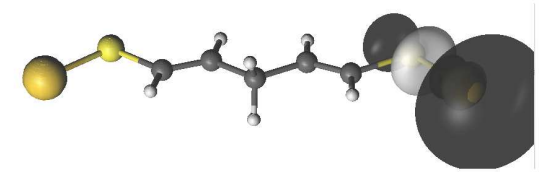


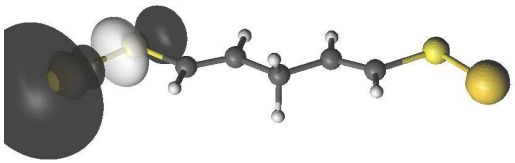
After 104.9 ps.



Imaginary part: Bra orbital above, ket orbital below.







After 209.9 ps, electron transfer completed.
Bra orbital above, ket orbital below.

Multiconfigurational description of solids

(work in progress)

Possibilities of Molcas did increased, but still the solids are beyond the reach: periodic models are limited by MP2 level of theory, cluster models requires embedding (usually a hand made), etc..

Cluster embedding

- 1) automatic procedure to construct AIMP (ab initio model potential) (based on EMBQ)
- 2) self consistent procedure for presenting the electronic density as a charge cloud.
- 3) density from a periodic calculation is used to embed a cluster

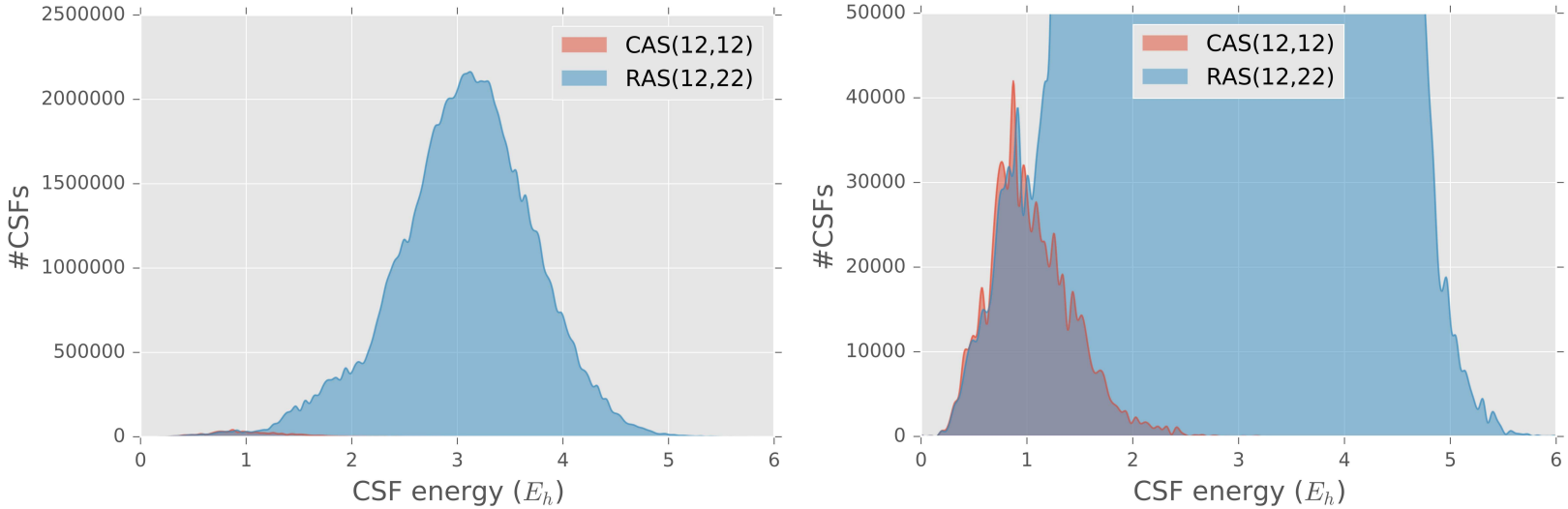
on a way to Full CI :)

 (Work in progress)

- Our multiconfigurational calculations are too expensive..
- DMRG is a brute force solution, which makes calculations even heavier. But looking forward to see it working :)
- Stochastic CAS, Local CAS, etc..
- Analyse the contributions and discard (optionally move to PT2 step) some e.g. non local excitations.

Understanding the size of CI

Step 1: analyse the contributions



Step 2: try to find patterns (e.g. using deep learning) but on the level of excitations, not orbitals!

Core-hole RASSCF


(OpenMolcas paper)

In order to describe spectroscopy which includes core-hole excitations one need to modify RASSCF (fun part†) and make special basis sets (routine part‡)..

† - done

Basis sets for core-hole RASSCF

Table: Preliminary calculation for C, N, O, and F 1s cores, only, shows that standard contracted bases cannot represent the 1s and $1s^2$ states with acceptable accuracy, but a small optimized basis (8s,5p) is accurate. Oxygen results: Energies (au) and errors.

Basis	$1s^1$	$1s^1$ error	$1s^2$	$1s^2$ error
ANO-L-VQZP	-31.9754	0.0246 (0.670 eV)	-59.1159	0.0407 (1.108 eV)
Optim. 8s5p	-31.9996	0.00039 (0.011 eV)	-59.1469	0.0097 (0.263 eV)
Exact	-32.0000	—-	-59.15659512	—-

Small relativistic basis set

JCP, 149, 194102, 2018

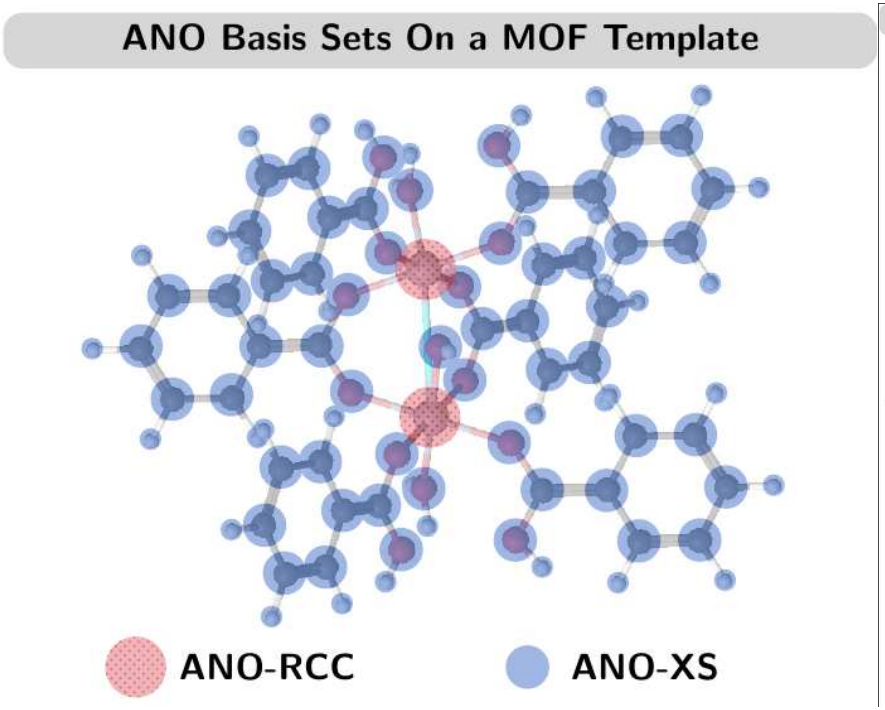
Most typical usage of ANO-RCC is: one heavy metal and a lot of ligands..

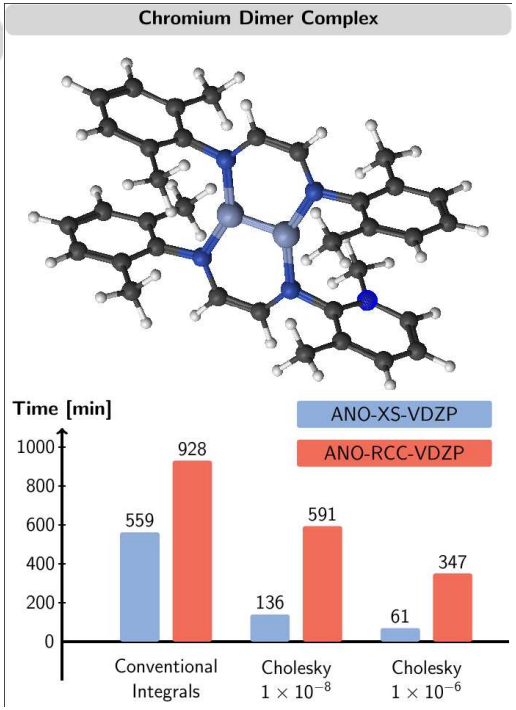
```
&GATEWAY
EXPERT
BASIS=Fe.ANO-RCC-VQZP,C.6-31G*
```

or,

```
&GATEWAY
BASIS=Fe.ANO-RCC-VQZP,C.ANO-RCC-MB
```

Extra small relativistic basis set - primitive functions





Replacement for ANO-RCC

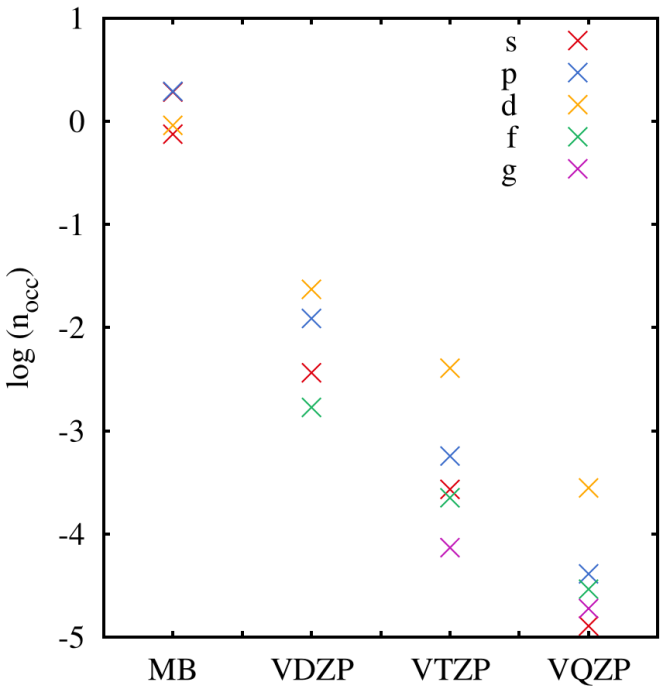

(manuscript in preparation)

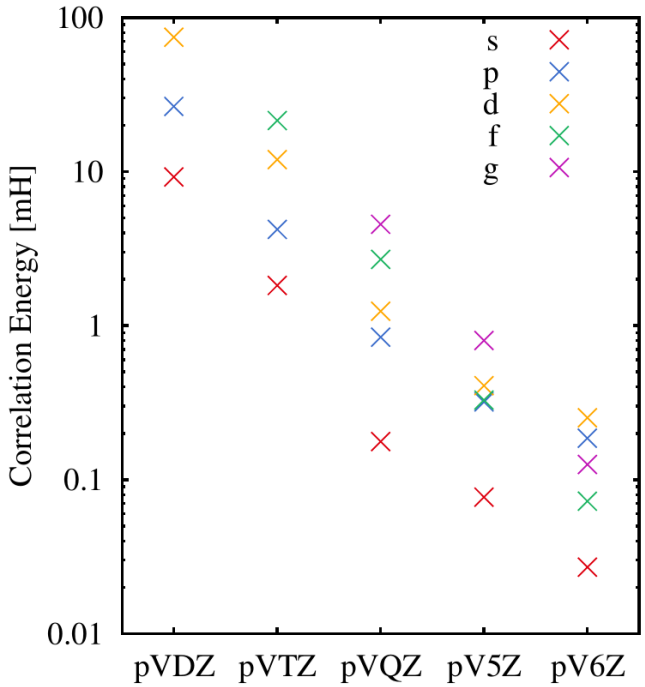
Existing ANO-RCC basis set has so many issues...

- the top of hall of shame: 'C' cut–and–paste error
- heavy elements with too similar exponents
- creation of new basis sets is 'Lund know-how'

Inconsistency in current basis sets

- classification (VDZ etc..), which is not consistent for all elements and it is not regular
- And this is not only 'our' problem

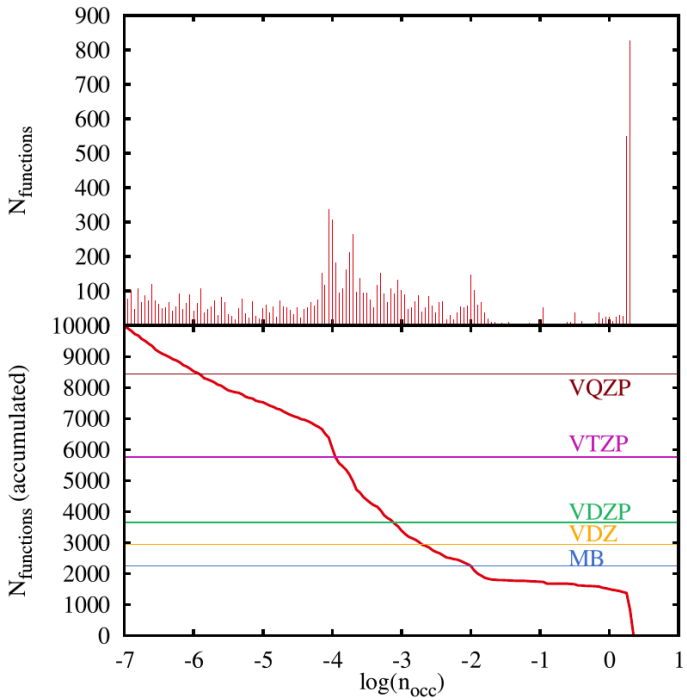




New basis set: ANO-R

- completely revised set of exponents
- customized and 'generic' set of contraction coefficients

Elements H-Rn: Natural Orbital Occupation Numbers (compare with ANO-RCC)



Symmetry in Molcas

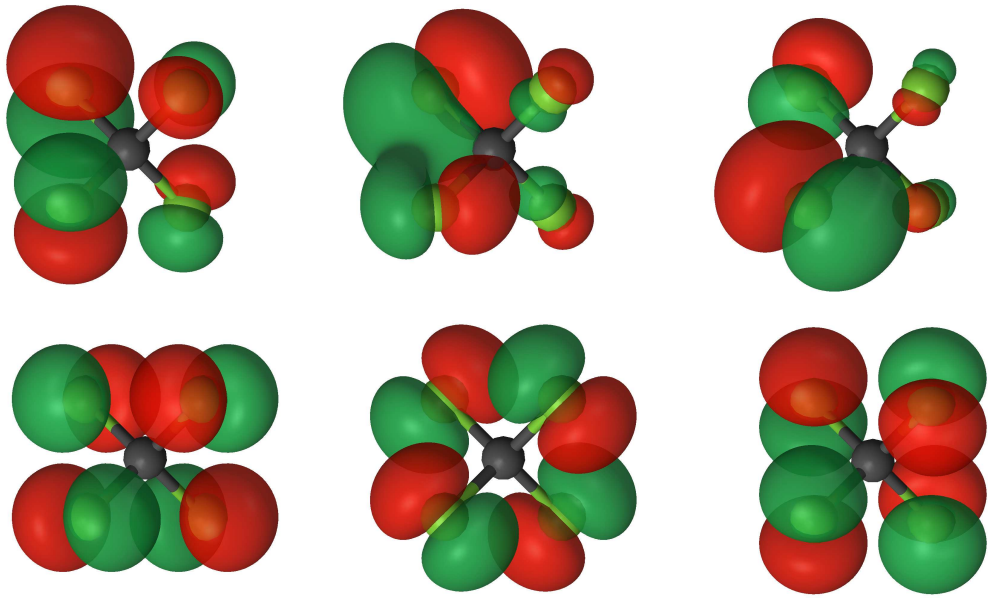


Journal of cheminformatics 9 (1), 8, 2017

- D_{2h} is the best we can do
- using full symmetry is a demanded feature,
  but it is very hard to implement
- most of the new codes in Molcas ignore symmetry!

libmsym: post factum symmetrization

Post factum symmetrization of an Orbital file (before: top line and after: bottom line).



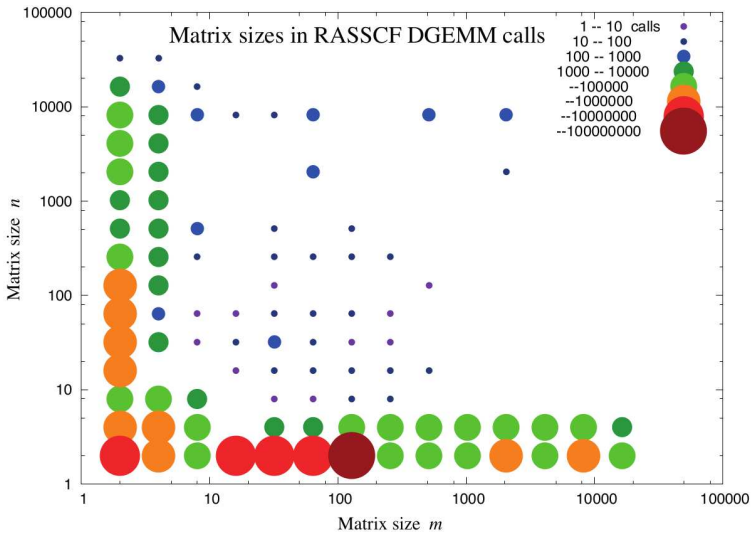
An implementation problem: for small distortions it should be used only once. So, can be run separately. For large distortions - the code/algorithm should be revised.
Implementation into each computational code is under development..

Part II. Extras...

- Performance in serial
- Parallel performance
- EMIL
- SAGIT
- LUSCUS

Performance improvements

- Know your code
- BLAS: tiny-large-huge
- I/O



Performance improvements: benchmark suite

Test 987

Test 984: small molecule, huge active space

Test 981: large molecule, tiny active space

Test 988: large molecule, huge active space

Test 985: large molecule, large active space

Test 982: large molecule, small active space

Test 986: large molecule, huge active space

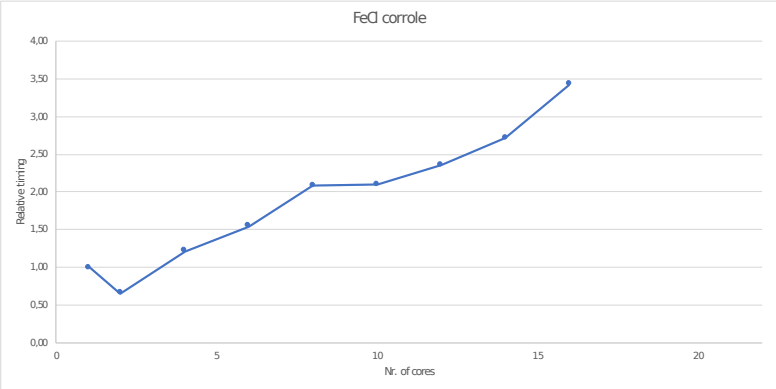
Test 983: tiny molecule, large active space

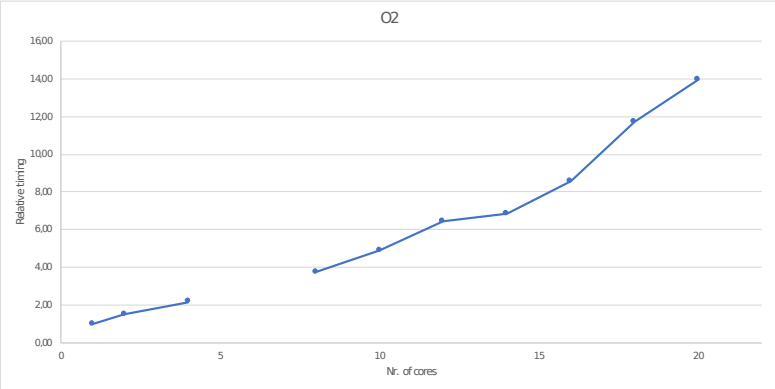
Parallelization in Molcas

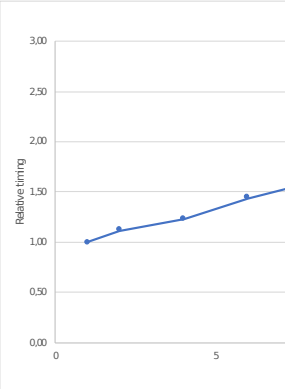
- GA or DGA based
- parallel model (replica based)
- performance (inside one node/CPU and across the nodes).
- There are new software tools for parallel benchmark

Parallelization benchmark

RASSCF (not perfect but reasonable scaling):







CASPT2:

- NPROCS is limited by memory
- one sleeping process
- poor performance across the nodes
- needs a second look..

Molcas Input Language

- implemented before the development of parallel environment
- shared filesystem vs classical linux cluster
- multiple file copies
- not friendly with different location/treatment of files, e.g. FiM
- security issues

EMIL updates

- New concept of directories naming
- Sand-box for file locations
- customization of prgm files
- integration with parnell
- integration with external parcing (json based)
- Work in progress

Visualization of orbitals

- Grid files are too large
- Grid files are produced by Molcas
- *GRID_IT* depends on Seward
- An issue with the license model
- General problem: what should I save after a (thousands) calculation(s) ?

SAGIT

- An attempt to create a consistent file, to be used to restart a calculation.
- InpOrb version 2.3: new sections - COORD and BASIS
- Ugly implementation of RunFile dump.
- Sagit - StandAlone Grid IT.
- Usage: sagit InpOrb
  sagit InpOrb [-f file] [-k "keys"]
- Can be called from GUI on demand

GUI for Molcas

Journal of cheminformatics 7 (1), 16, 2015

- GV is back! (but still very unfriendly)
- MolGUI (LU-BNU project), not supported..
- LUSCUS: new generation of GV.
- What kills all GUI: from Windows to Avogadro..
- How to stay light and be maintained?

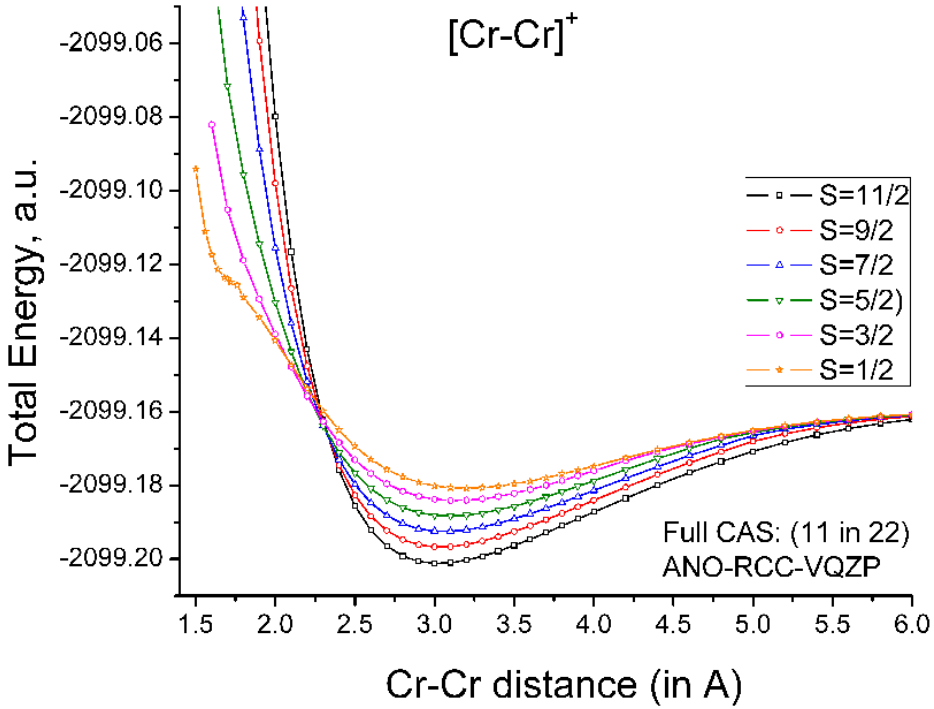
LUSCUS development

- v. 0.8.6
- automatic plugin .xyz -¿.lus
  - use extension to find the plugin
  - run plugin to re-create lus file
  - visualize lus file
- customized plugin
  - requires a screen or a tab, so it must be invoked by user
  - graphical elements are written in a plugin def file
  - GUI display the screen and generates a command line for the plugin
  - plugin executes
- Examples:
  - run sagit
  - run symmetrization library
  - run MING (GUI for Molcas Input Generation)
  - run Molcas

Part III. Applications...

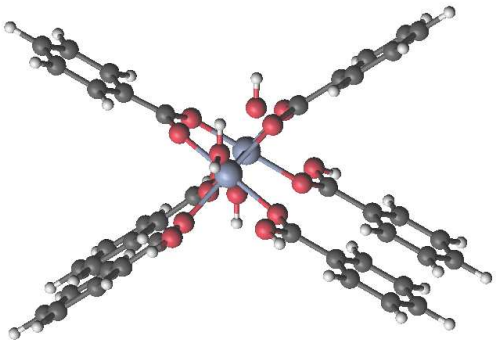
- Cr_2^+
- MOFs
- Exciplexes
- Concrete

- Symmetric or asymmetric?
- Nasty low spin curve..



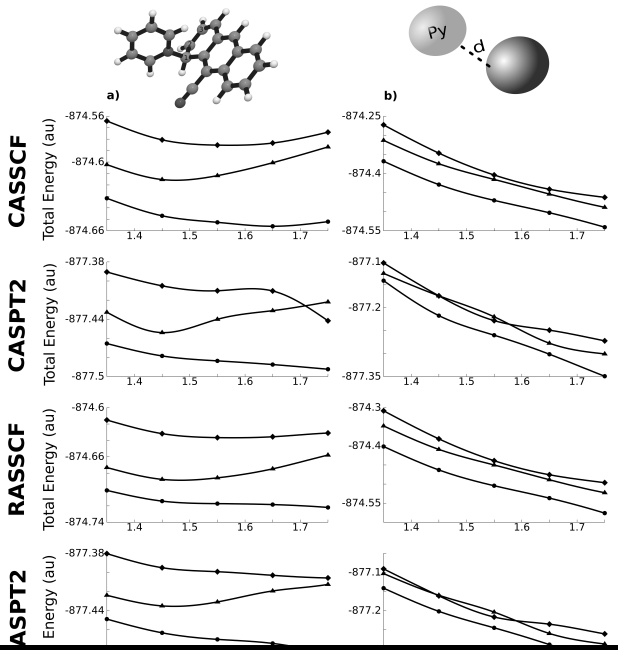
MOFs

- Bending properties
- Playground for embedding models
- Playground for large active space problems



Exciplexes

- Binding but only in excited states
- Nice example where TDDFT fails
- Project has been initiated by BOR long time ago..

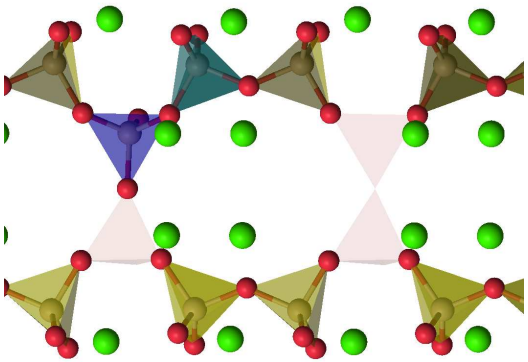


Concrete structure



AIP Conference Proceedings 2040 (1), 020007, 2018

- C-S-H structure
- from FF to PM6 to DFT to hybrid-DFT
- Cluster models



and finally...

- OpenMolcas: freedom of development
- Molcas: stable, user oriented build
- Molcas84 (released this month)
- separation between LGPL and extra codes
- Orville: fork of OpenMolcas
- it works...
-
- The future: more focus on developers' camps and more focus on education..

Thanks!