The Centre for Theoretical and Computational Chemistry

Density Functional Theory at the Basis Set Limit with Multiwavelets

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Outline

Multiwavelets

SCF and Response

Orbital Free DFT

The MRChem program

Results

Acknowledgments

- Current group members
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  - Stig-Rune Jensen
  - Peter Wind
- Previous group members
  - Antoine Durdek
  - Eirik Fossgaard
  - Jonas Juselius
- Support
  - Norwegian Research Council ($$)
  - NOTUR (High Performance Computing)

Main motivations

- Mainstream basis sets have reached a limit
- Very accurate calculations of energy and properties are extremely challenging
- A real-space basis set is better posed to harvest modern computational resources
- It's fun to do something completely different

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Remove this

remove this

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Languages

- Python scripting for configuration and input parsing
- C++ as the main working language
- CMAKE for compilation
- Git repository with Redmine interface
- Doxygen for documentation

Libraries

- Eigen3 for vector and matrix manipulation
- Several boost libraries (serialization, iterators...)
- XCFun for density functionals[a]
- MPI and OpenMP for parallelization

[a] U. Ekström, L. Visscher, R. Bast, A. J. Thorvaldsen, and K. Ruud, *J Chem Theory Comput* **6**, 1971 (2010)

Structure of the code

- Function library (projections, algebraic operations)
- Operator library (application of operators)
- Chemistry overlay

Current capabilities

- Parallel, linear scaling application of Poisson/Helmholtz operators
- Solution of HF and KS equations
- Extensive library of functionals (XCFun)
- Static and dynamic linear response

Planned developments:

- Geometric gradients
- Quadratic minimization (HF/DFT)
- Higher order response (open-ended)
- Periodic boundary condition
- Four components relativistic treatment
- Time-development

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Accurate DFT energies, (PBE, a.u.)

ϵ	H (D)	C (T)	C_2H_6 (S)
10^{-6}	-0.499 990 657 5	-37.798 756 012	-79.739 938 330
10^{-7}	-0.499 990 573 5	-37.798 755 587	-79.739 935 054
10^{-8}	-0.499 990 554 0	-37.798 755 547	-79.739 934 708
10^{-9}	-0.499 990 553 5	-37.798 755 551	
ϵ	O (T)	H_2CO (S)	CH_3OH (S)
10^{-6}	-74.908 932 164	-114.429 271 744	-115.642 211 851
10^{-7}	-74.908 930 679	-114.429 269 873	-115.642 208 530
10^{-8}	-74.908 930 544	-114.429 269 608	-115.642 208 152
10^{-9}	-74.908 930 532	-114.429 269 573	
ϵ	F (D)	Cl (D)	FCl (S)
10^{-6}	-99.676 140 835	-459.974 686 431	-559.766 352 774
10^{-7}	-99.676 138 874	-459.974 673 116	-559.766 341 825
10^{-8}	-99.676 138 663	-459.974 672 043	-559.766 340 099
10^{-9}	-99.676 138 640		-559.766 340 136

NMR Shieldings: a difficult case for GTOs

k	ϵ	$\Delta\phi$	RHF		B3LYP	
			$\sigma(Mg)$	$\sigma(O)$	$\sigma(Mg)$	$\sigma(O)$
5	10^{-3}	10^{-2}	1041.20	-6738.21	964.09	-2051.05
6	10^{-4}	10^{-3}	1538.92	-16726.34	1002.59	-2454.58
7	10^{-5}	10^{-4}	1584.11	-17466.48	1006.22	-2484.34
8	10^{-6}	10^{-5}	1578.73	-17358.68	1007.08	-2492.02
9	10^{-7}	10^{-6}	1579.46	-17375.42	1007.15	-2491.87
	pcS-0	(19)	448.69	4880.30	8890.43	-63570.32
	pcS-1	(33)	94.45	11293.43	1513.58	-6292.74
	pcS-2	(61)	-19388.24	386900.50	1047.52	-2799.52
	pcS-3	(121)	1757.72	-20822.54	1013.94	-2536.79
	pcS-4	(199)	1617.50	-18143.84	1007.66	-2498.74

Outlook

- Potential: simplicity and robustness
- Technical Challenge: memory requirements
- Fundamental challenge: curse of dimensionality

Thank you!

All photos are from Francesco Verugi
(https://www.flickr.com/photos/francesco_verugi/)