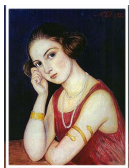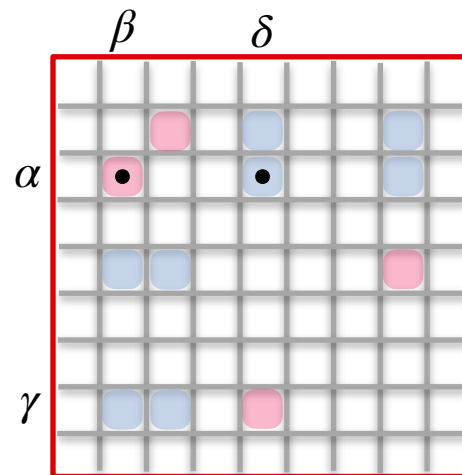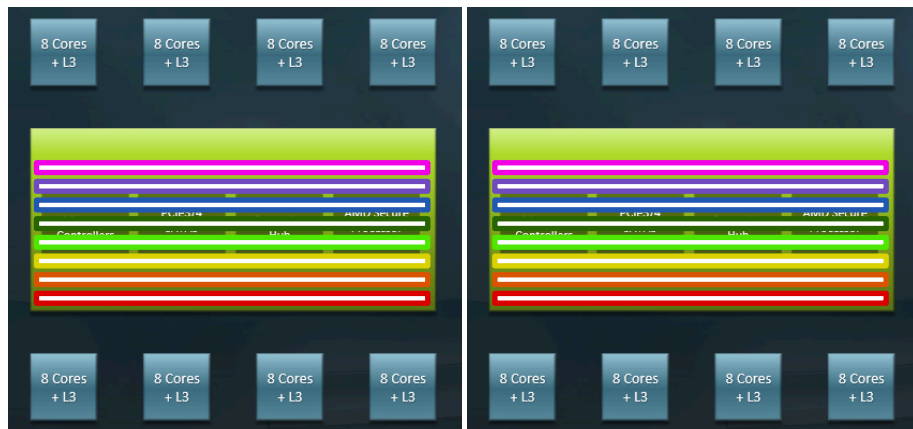# Fock matrix construction

$$(\alpha\beta\,|\,\gamma\delta) = \iint \frac{\phi_\alpha(\mathbf{r}_1)\phi_\beta(\mathbf{r}_1)\phi_\gamma(\mathbf{r}_2)\phi_\delta(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}d^3\mathbf{r}_1 d^3\mathbf{r}_2$$

$$E[n(\mathbf{r})] = T_s[n(\mathbf{r})] + \int v^{\text{ext}}(\mathbf{r})\,n(\mathbf{r})\,d^3\mathbf{r} + J[n(\mathbf{r})] + E_{\text{xc}}[n(\mathbf{r})]$$

DFT energy

$$F_{\alpha\beta} = h_{\alpha\beta} + D_{\gamma\delta}\left[(\alpha\beta\,|\,\gamma\delta) - c_{\text{HF}}(\alpha\delta\,|\,\gamma\beta)\right] + F_{\alpha\beta}^{\text{xc}}$$

Formally scales as ~N⁴
with screening ~N²·⁵

Fock matrix construction: Complete property/spectrum calculations

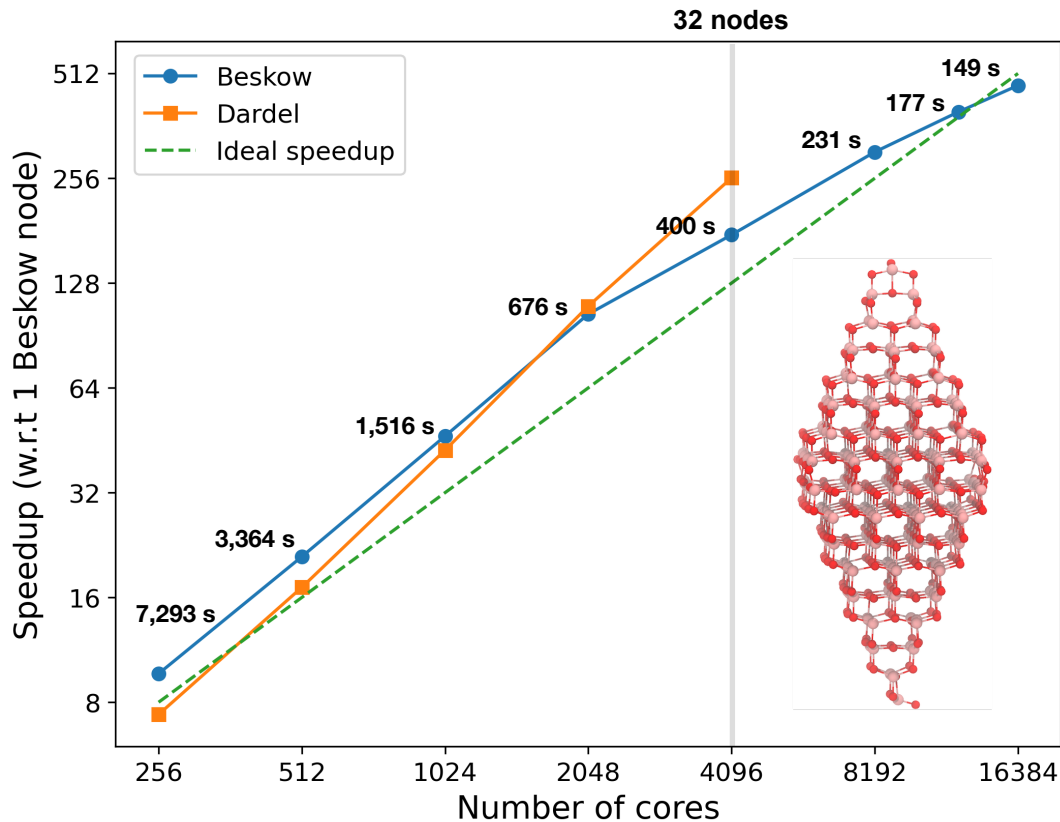| Job type (molecule)	Method (#basis functions)	Per-core speedup (w.r.t. Beskow)	Per-node speedup (w.r.t. Beskow)
Polarizability (C60 fullerene)	B3LYP/def2-SVPD (1200)	1.07x	4.3x
C6 dispersion (C60 fullerene)	B3LYP/def2-SVPD (1200)	1.15x	4.6x
Two-photon absorption (full) (BPVB)	HF/def2-SVPD (1314)	1.23x	4.9x
Two-photon absorption (reduced) (BPVB)	HF/def2-SVPD (1314)	1.26x	5.0x
UV/vis absorption (RPA) (noradrenaline)	HF/aug-cc-pVDZ (375)	1.36x	5.4x
Circular dichroism (CPP) (noradrenaline)	HF/aug-cc-pVDZ (375)	1.55x	6.2x

VELOXCHEM

Fock matrix construction: Titanium oxide nanoparticle $Ti_{165}O_{330}$

Basis: DEF2-SVP

	Contr. GTOs	Prim. GTOs
Ti	(5S,3P,2D,1F)	(14S,9P,5D,1F)
O	(3S,2P,1D)	(7S,4P,1D)

Number Contracted: **8,580**
Number Primitive: **18,810**

ELOXCHEM

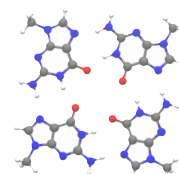# Model Chesmistries

Density-Functional Theory

XC functional ladder:
- range-separated
- hybrid GGA
- meta-GGA
- GGA
- LDA

Exact result

s-aug d-aug t-aug

DZ TZ QZ **Basis set**

Wave-Function Theory

Method

- FCI
- CC3
- CCSD(T)
- MP4
- CASPT2
- CCSD/ADC3
- MCSCF
- MP3
- CI
- CC2/ADC2
- MP2
- HF

Exact result

s-aug d-aug t-aug

DZ TZ QZ **Basis set**
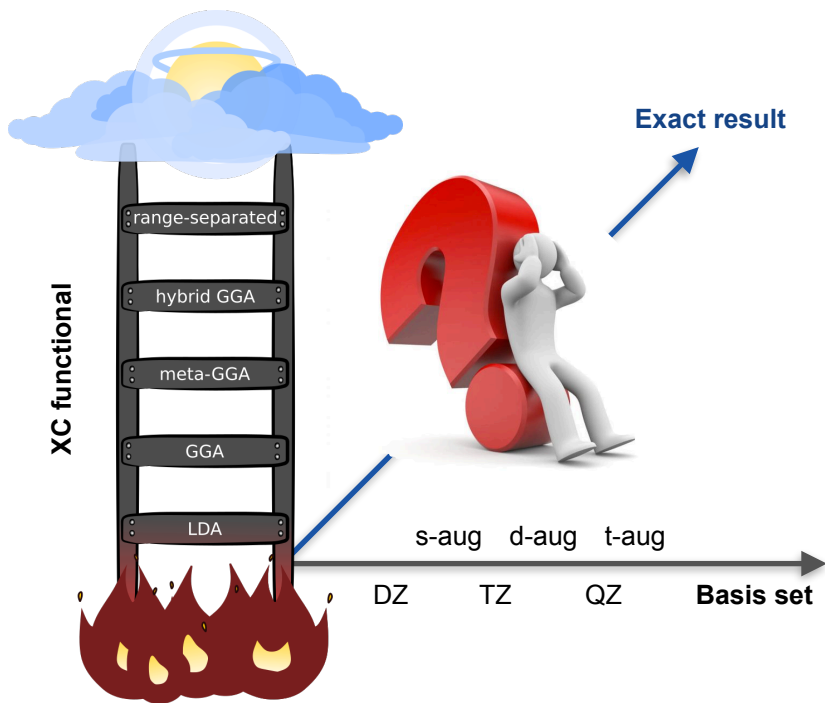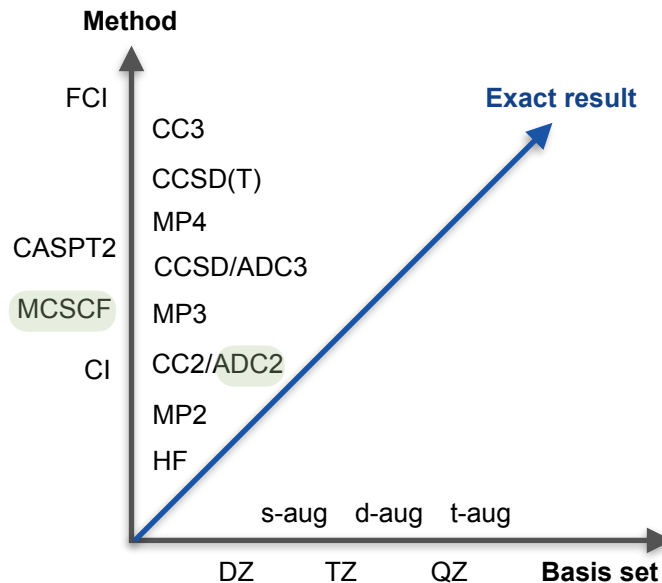
ADC(2)

Chem. Eur. J. **2018**, *24*, 15577

Plot legend:
- Oscillator strengths, $O(N^{6.05})$
- MO integrals, $O(N^{4.80})$
- Nonlinear eigensolver, $O(N^{3.39})$

Gator

Y-axis: Core-hours (100, 1000, 10000, 100000)
X-axis: Number of contracted basis functions (2×10^2, 3×10^2, 4×10^2, 6×10^2, 1000)

Annotations:
- 27 min
- 2 h 9 min
- 5 h 7 min
- 13 h 27 min
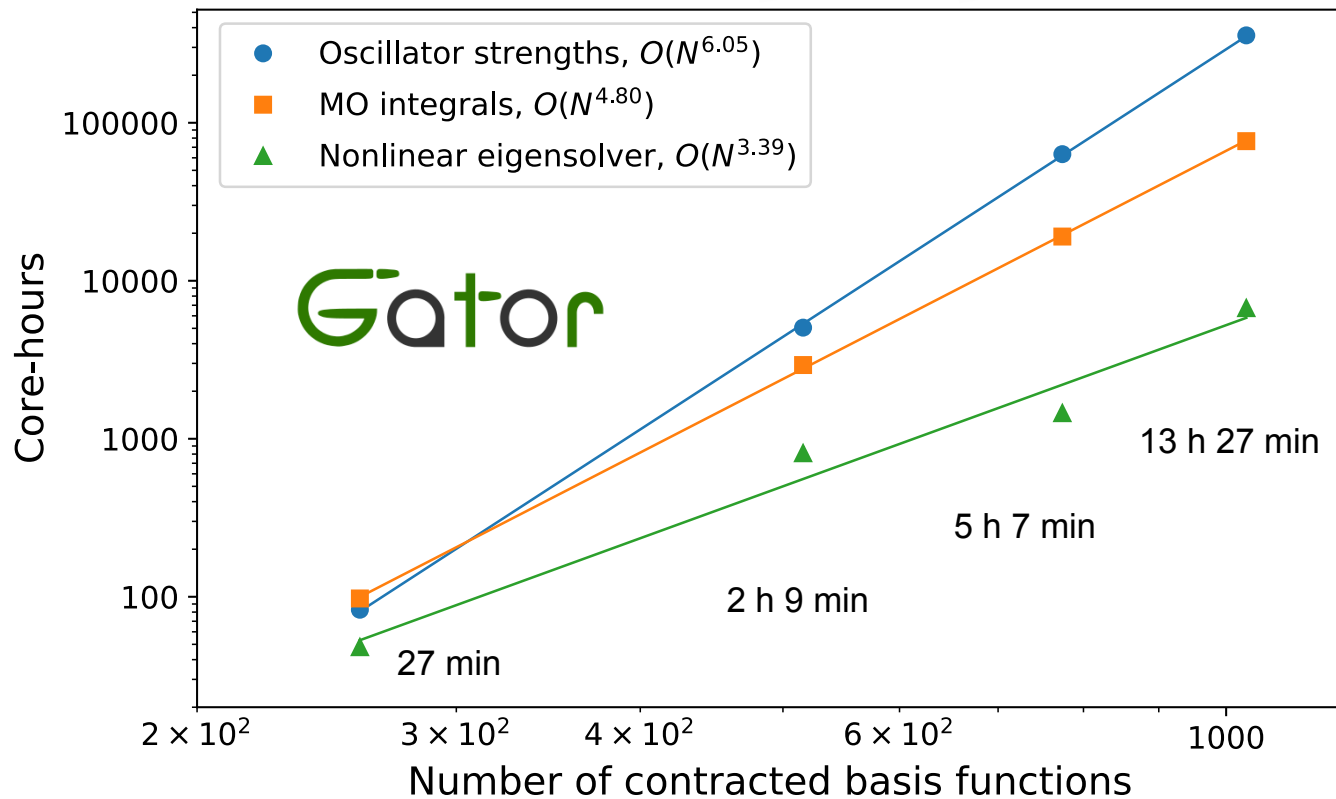
MCSCF: Strong electron correlation

MultiPsi

- VeloxChem based multi-reference module
- Python/C++
- OpenMP/MPI
- Node-distributed memory
- NUMA aware

OpenMP multithreading performance
OMP PRT CSIND spread

OpenMP

Scaling   Ideal

Ideal

Scaling

Number of cores

MPI parallelization performance

Total time   **MPI**   Ideal

Ideal

Total time

Number of nodes
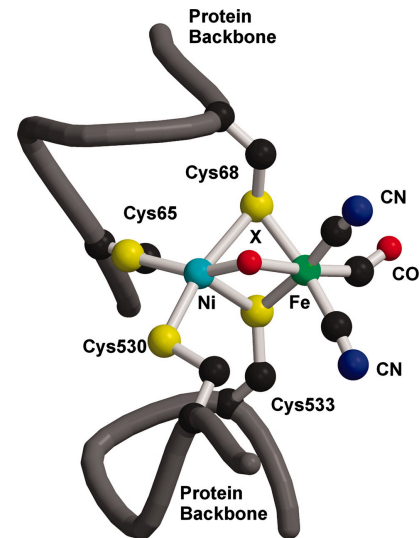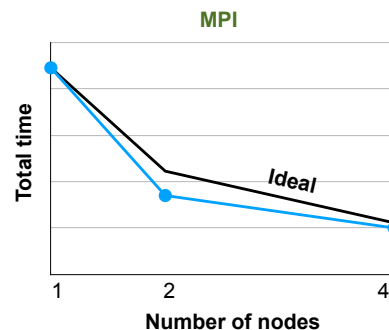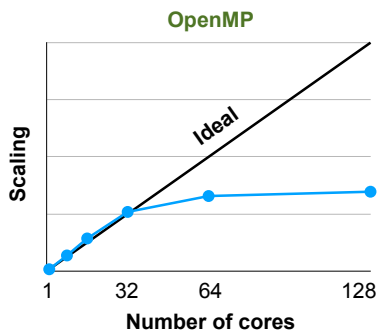
Large-scale CAS calculations

- 418 billion determinants
- CI optimization
  - 22 iterations
  - 48 h
- Spin state
  - singlet by *ca* 5 kcal/mol

[NiFe]hydrogenase
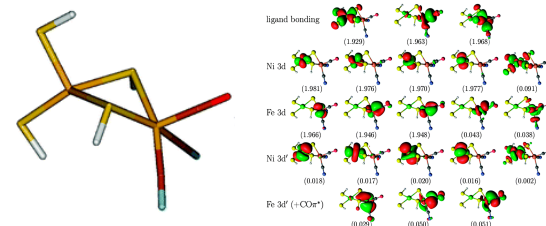
NiFe model system

Delcey *et al.*, PCCP **2014**, *16*, 7927

Summary and conclusions

- Dardel will serve chemistry well

- VeloxChem efficiently
  - implements DFT-based energy and spectroscopy calculations
  - serves Gator for single-reference methods
  - serves MultiPsi for multi-reference methods

So was I wrong?

Already a fading memory…

The fundamental methods necessary for the computational treatment of the whole of **chemistry** are thus completely known, and the difficulty lies only in the fact that application of these methods is made prohibitively hard on the all too complex hardware of today.

…stay tuned for Dardel Phase II!