molsturm:
Modular electronic structure theory framework

A tale inspired by Coulomb-Sturmians

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Oberwolfach workshop
Mathematical Methods for Quantum Chemistry

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An ideal basis

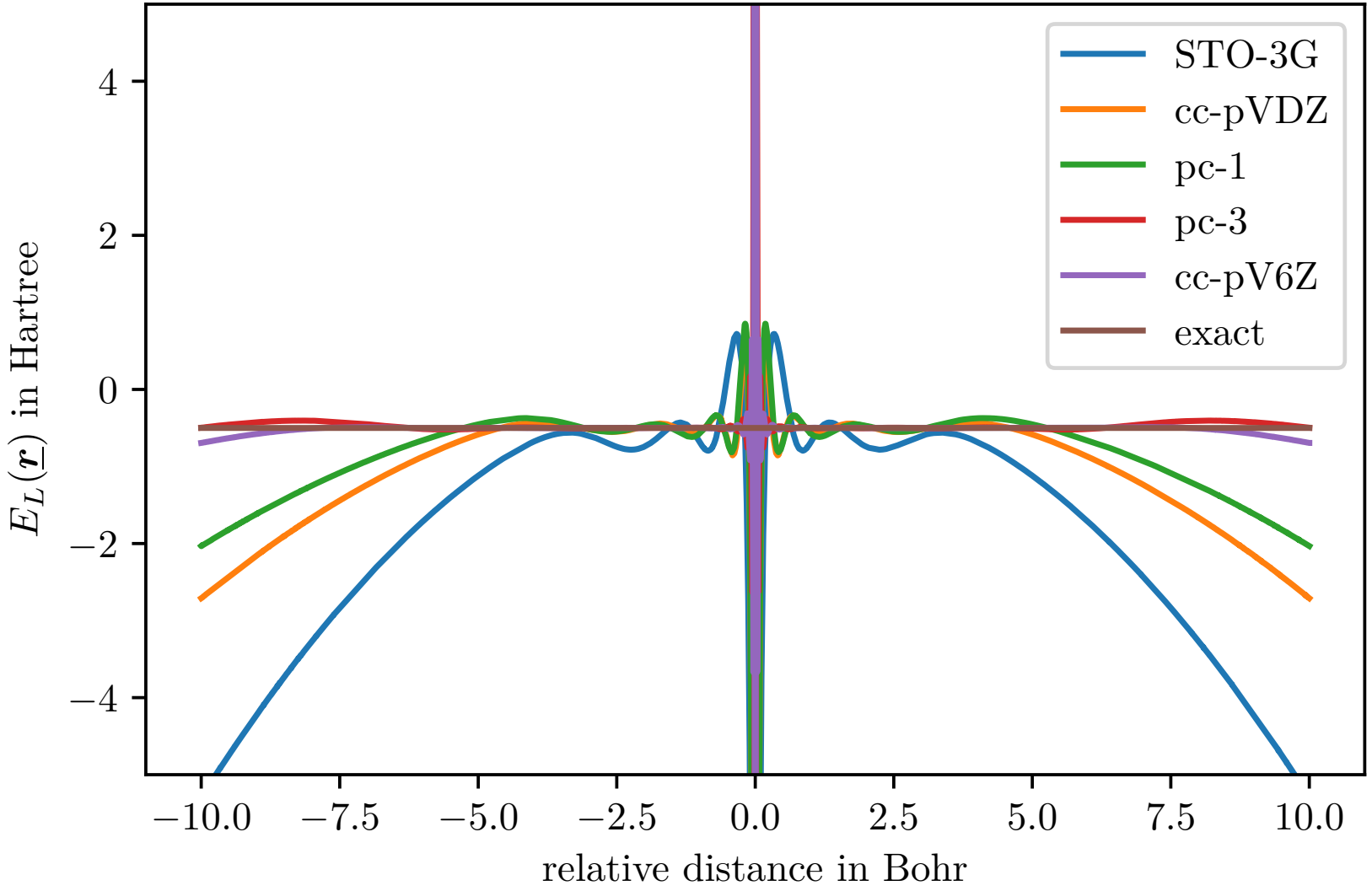
- Represents physical system well
- Results reliable
  - Error margin known
  - Systematic improvement possible
- Prior knowledge
  - Little required
  - If available: Can be incorporated
- Integrals and eigenproblem are feasible

$\Rightarrow$ In reality need a good compromise

Basis function types

- Gaussian-type orbitals
- Geminals
- Slater-type orbitals
- Wavelets
- Finite elements
- Plane wave
- Augmented plane waves
- ...

Discretising hydrogen



Coulomb-Sturmians

- Iso-energetic solutions φ_{nlm} to hydrogen-like equation[1]

$$\left(-\frac{1}{2}\Delta - \beta_n \frac{Z}{r}\right)\varphi_{nlm}(\underline{\boldsymbol{r}}) = E\varphi_{nlm}(\underline{\boldsymbol{r}})$$

- Scaling factor β_n chosen to uniform energy:

$$\beta_n = \frac{kn}{Z} \quad \Rightarrow \quad E = -\frac{k^2}{2}$$

- φ_{nlm} look like hydrogenic orbitals with $\frac{Z}{n}$ replaced by k
- Radial part R_{nl} satisfies

$$\left(-\frac{1}{2r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{l(l+1)}{2r^2} - \frac{nk_{\text{exp}}}{r} - E\right)R_{nl}(r) = 0.$$

$\Rightarrow$ Sturm-Liouville equation[2]

[1] Shull and Löwdin 1959
[2] Rotenberg 1962, Rotenberg 1970

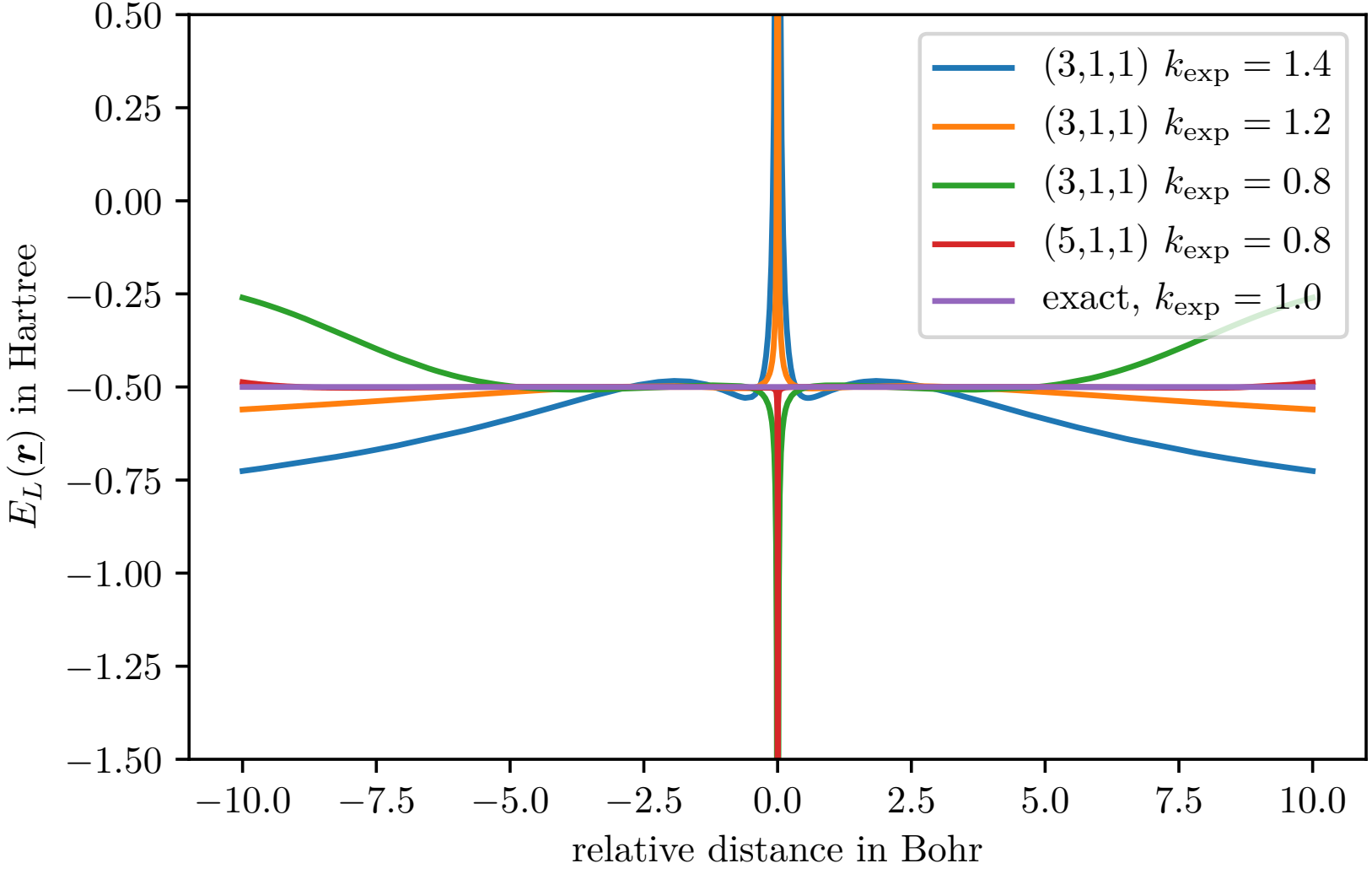
Coulomb-Sturmians properties

- Only atoms: Different Sturmians for molecules required
- Complete basis for $H^1(\mathbb{R}^3)$[1]
- Correctly represent nuclear cusp
- Proper exponential decay for large r
- All functions have the same k_{exp}

- One-to-one onto hyperspherical harmonics
- One-electron integrals sparse and analytic
- Two-electron integrals sparse tensor contraction

[1] Klahn and Bingel 1977

Discretising hydrogen



Fock matrix structures

- Main concern: Hartree-Fock
- After discretisation:

$$\mathbf{F}[\mathbf{C}]\,\mathbf{C} = \mathrm{diag}(\varepsilon_1, \ldots, \varepsilon_n)\,\mathbf{S}\,\mathbf{C}$$

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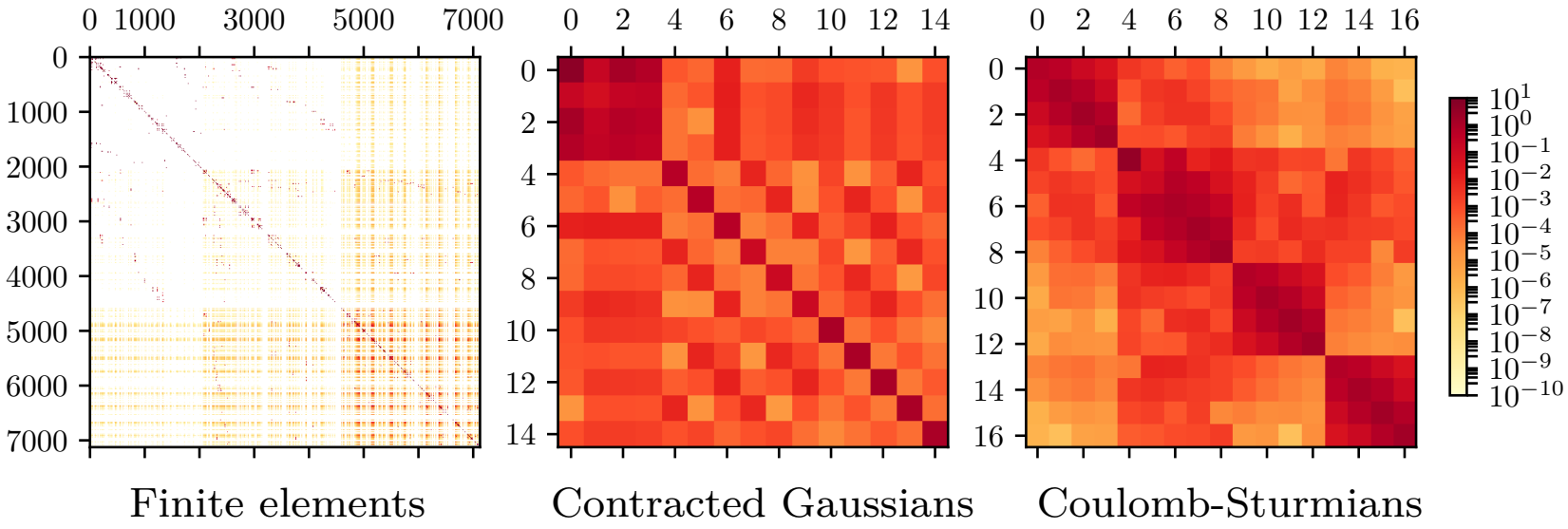

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SCF scheme

Start with guess $\mathbf{F}^{(0)}$ and iterate for $n = 1, 2, 3, \ldots$

- Diagonalise

$$\tilde{\mathbf{F}}^{(n-1)}\mathbf{C}_F^{(n)}\mathrm{diag}(\varepsilon_1, \ldots, \varepsilon_N) = \mathbf{S}\mathbf{C}_F^{(n)}\mathbf{E}^{(n)}$$

  under the condition

$$\left(\mathbf{C}_F^{(n)}\right)^\dagger \mathbf{S}\mathbf{C}_F^{(n)} = \mathbf{I}_N.$$

- Construct the occupied matrix $\mathbf{C}^{(n)}$ from the full matrix $\mathbf{C}_F^{(n)}$ by the Aufbau principle.
- Build the Fock matrix $\mathbf{F}\left[\mathbf{C}^{(n)}\right]$ and check for convergence.
- Build a trial Fock matrix $\tilde{\mathbf{F}}^{(n)}$ somehow using $\mathbf{F}^{(n)}$ and all insight into the problem gathered so far.

Contraction-based SCF scheme

- Iterative solvers only need matrix-vector products

⇒ Contraction-based or matrix-free[1] algorithm:

  - Never build Fock matrix in storage
  - Use matrix-vector contraction expressions

- Avoid full density matrix
  - Employ SCF iterating orbital coefficients $\mathbf{C}$

[1] Kronbichler and Kormann 2012

Characteristics of contraction-based algorithms

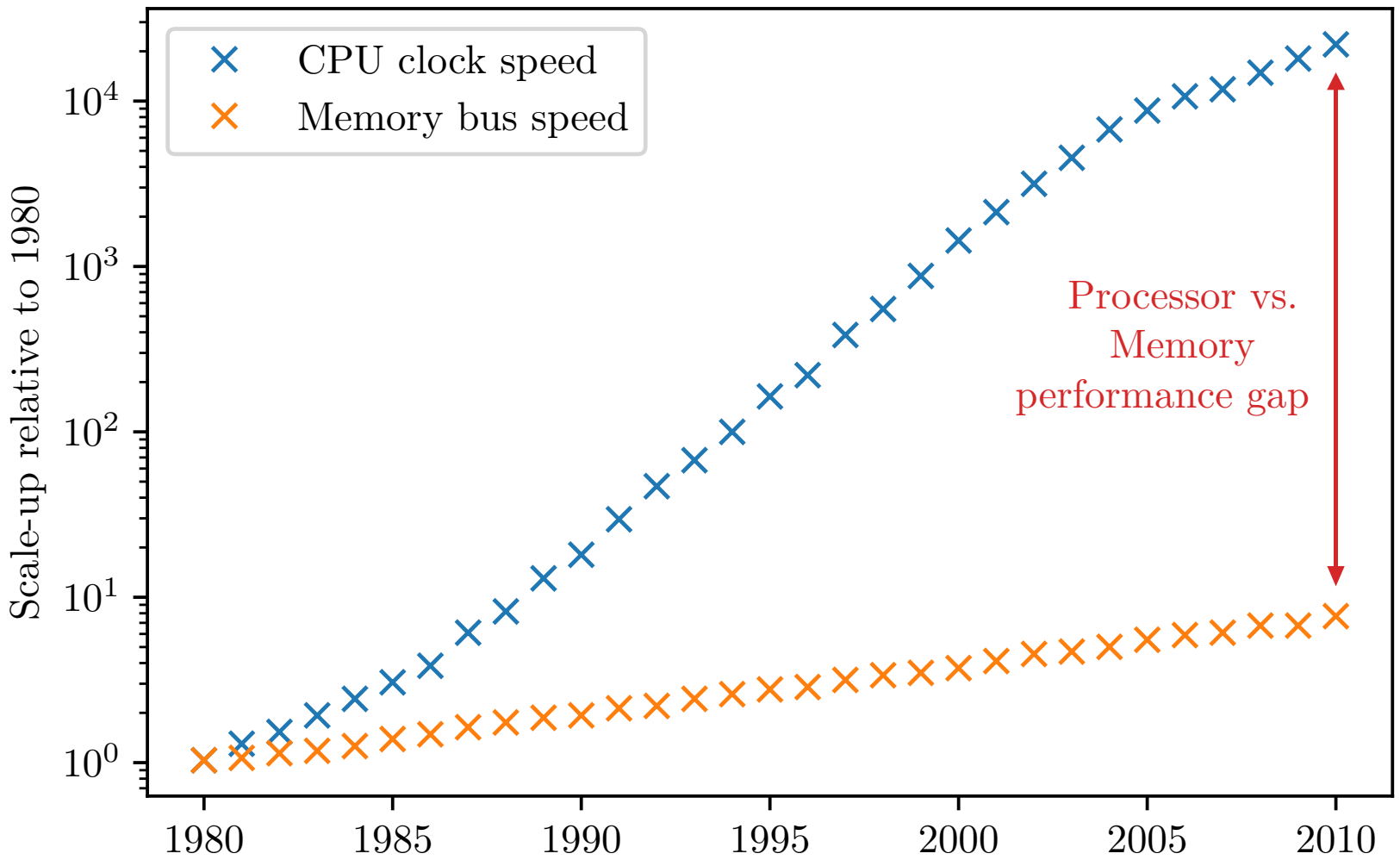
Advantages

- Scaling (storage and time) reduced
- Parallelisation easier
  - ⇒ Less data management
  - ⇒ Easier modularisation
- Hardware trends are in favour

Disadvantages

- Matrices more intuitive than contraction-functions
- More computations
  - ⇒ Need efficient contraction schemes for the contraction
  - ⇒ Algorithms more complex

Characteristics of contraction-based algorithms



Data from `https://dave.cheney.net/2014/06/07/five-things-that-make-go-fast`

Characteristics of contraction-based algorithms

Storage layer	Latency /ns	FLOPs
L1 cache	0.5	13
L2 cache	7	180
Main memory	100	2600
SSD read	$1.5 \cdot 10^4$	$4 \cdot 10^5$
HDD read	$1 \cdot 10^7$	$3 \cdot 10^8$

Data from
`https://people.eecs.berkeley.edu/~rcs/research/interactive_latency.html`
FLOPs for a Sandy Bridge 3.2GHz CPU with perfect pipelining

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Lazy matrices

- Stored matrix: All elements reside in memory
- Lazy matrix:
  - Generalisation of matrices
    - Elements may be expressions
    - May represent non-linear operators
    - State

  $\Rightarrow$ Obtaining elements expensive
  - Evaluation of internal expression: Delayed until contraction
  - For convenience: Offer matrix-like interface

Using lazy matrices

- Program as usual

$$\mathbf{D} = \mathbf{A} + \mathbf{B}$$

- Build expression tree internally

$$\boxed{\mathbf{D}} = \boxed{\mathbf{A}} + \boxed{\mathbf{B}}$$

- On application:

$$\mathbf{D}\underline{x} = (\mathbf{A}\underline{x}) + (\mathbf{B}\underline{x})$$

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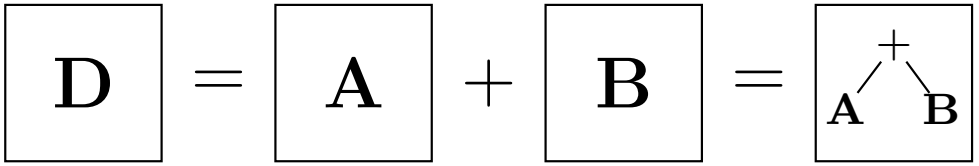

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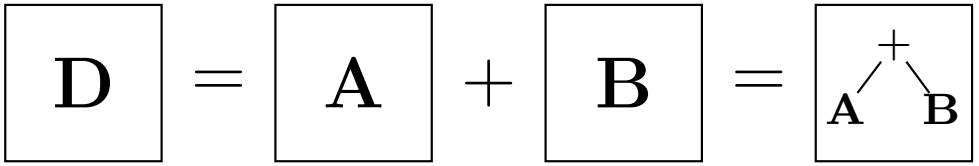


- On application:

$$\mathbf{D}\underline{\boldsymbol{x}} = (\mathbf{A}\underline{\boldsymbol{x}}) + (\mathbf{B}\underline{\boldsymbol{x}})$$

Observations

- Lazy matrices allow layered responsibility for computation, e.g. $(\mathbf{A} + \mathbf{B})\underline{\boldsymbol{x}}$
  - $\mathbf{A}\underline{\boldsymbol{x}}$ and $\mathbf{B}\underline{\boldsymbol{x}}$ decided by implementation of $\mathbf{A}$ and $\mathbf{B}$
  - $(\mathbf{A}\underline{\boldsymbol{x}}) + (\mathbf{B}\underline{\boldsymbol{x}})$ done in linear algebra backend

$\Rightarrow$ Proper modularisation between

- Higher-level algorithms
- Lazy matrix implementations
- LA backends

Lazy matrices for Hartree-Fock codes

- Contraction-based algorithms

⇒ Lower memory footprint, scaling improvements

- Abstraction between integrals and SCF algorithms

⇒ Plug and play integral libraries

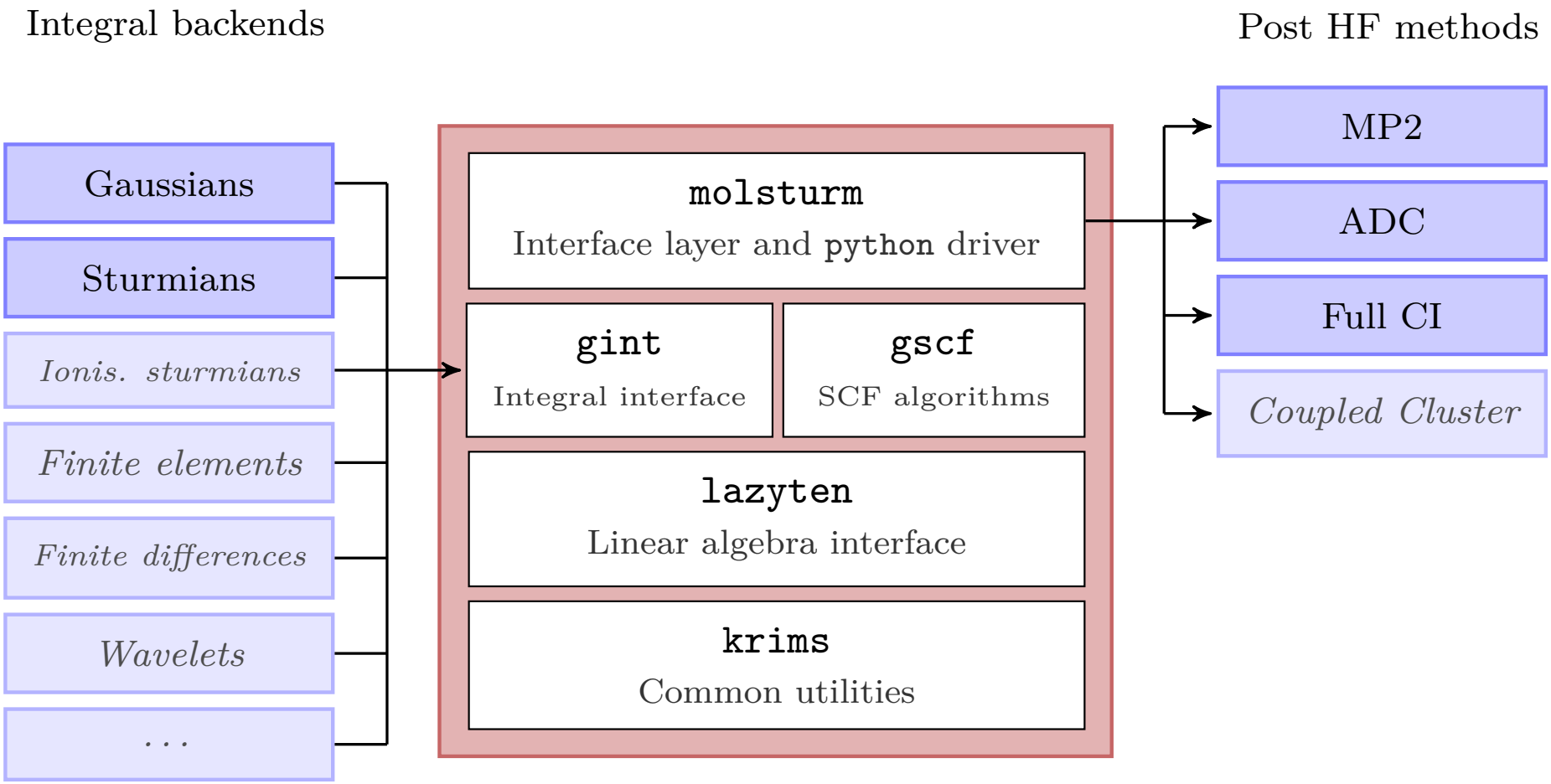
⇒ Swap LA backends

⇒ Basis-type independent SCF

- Integral back end stays in control of contraction

⇒ Decides order of data production and consumption

molsturm structure



- *Italic*: planned

molsturm design

- Lightweight connection between integrals and Post-HF
- Flexiblity as primary goal
- Behaviour controlled via `python`
  - Keywords to change basis type or solver
  - All computed data available in `numpy` format
  - No input file, just a `python` script
- `python` utilities
  - Import / export results
  - Post-HF calculations
- Integration with `python` ecosystem

molsturm interface: CCD residual (parts)

$$
\begin{aligned}
r_{ij}^{ab} = &-\frac{1}{2}\sum_{mnef}\langle mn||ef\rangle\, t_{mn}^{af}\, t_{ij}^{eb} + \frac{1}{2}\sum_{mnef}\langle mn||ef\rangle\, t_{mn}^{bf}\, t_{ij}^{ea} - \frac{1}{2}\sum_{mnef}\langle mn||ef\rangle\, t_{in}^{ef}\, t_{mj}^{ab} \\
&+\frac{1}{2}\sum_{mnef}\langle mn||ef\rangle\, t_{jn}^{ef}\, t_{mi}^{ab} + \frac{1}{4}\sum_{mnef}\langle mn||ef\rangle\, t_{mn}^{ab}\, t_{ij}^{ef} + \frac{1}{2}\sum_{mnef}\langle mn||ef\rangle\, t_{im}^{ae}\, t_{jn}^{bf} \\
&-\frac{1}{2}\sum_{mnef}\langle mn||ef\rangle\, t_{jm}^{ae}\, t_{in}^{bf} - \frac{1}{2}\sum_{mnef}\langle mn||ef\rangle\, t_{im}^{be}\, t_{jn}^{af} + \frac{1}{2}\sum_{mnef}\langle mn||ef\rangle\, t_{jm}^{be}\, t_{in}^{af}
\end{aligned}
$$

```
eri_phys = state.eri.transpose((0, 2, 1, 3))
eri = eri_phys - eri_phys.transpose((1, 0, 2, 3))
res = \
    - 0.5  * einsum("mnef,manf,iejb->iajb", eri.block("oovv"), t2, t2) \
    + 0.5  * einsum("mnef,mbnf,ieja->iajb", eri.block("oovv"), t2, t2) \
    - 0.5  * einsum("mnef,ienf,majb->iajb", eri.block("oovv"), t2, t2) \
    + 0.5  * einsum("mnef,jenf,maib->iajb", eri.block("oovv"), t2, t2) \
    + 0.25 * einsum("mnef,manb,iejf->iajb", eri.block("oovv"), t2, t2) \
    + 0.5  * einsum("mnef,iame,jbnf->iajb", eri.block("oovv"), t2, t2) \
    - 0.5  * einsum("mnef,jame,ibnf->iajb", eri.block("oovv"), t2, t2) \
    - 0.5  * einsum("mnef,ibme,janf->iajb", eri.block("oovv"), t2, t2) \
    + 0.5  * einsum("mnef,jbme,ianf->iajb", eri.block("oovv"), t2, t2)
```

Contents

Outlook

- Exploring further basis functions
  - Molecular Sturmians
  - Ionising Sturmians
  - k_{exp}-free Hartree-Fock
- `pammap`
  - Hierachical interface
  - Data transfer between high and low level
  - Easy parameter adjustment from `python`, `julia`, ...
- Fuzzing of integral back ends
- Lazy matrix expression optimisation

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- Dr. James Avery
- Prof. Andreas Dreuw
- Prof. Guido Kanschat
- HGS Mathcomp

Questions?

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- Projects: `https://lazyten.org` and `https://molsturm.org`