Coulomb Sturmian basis functions in electronic structure theory

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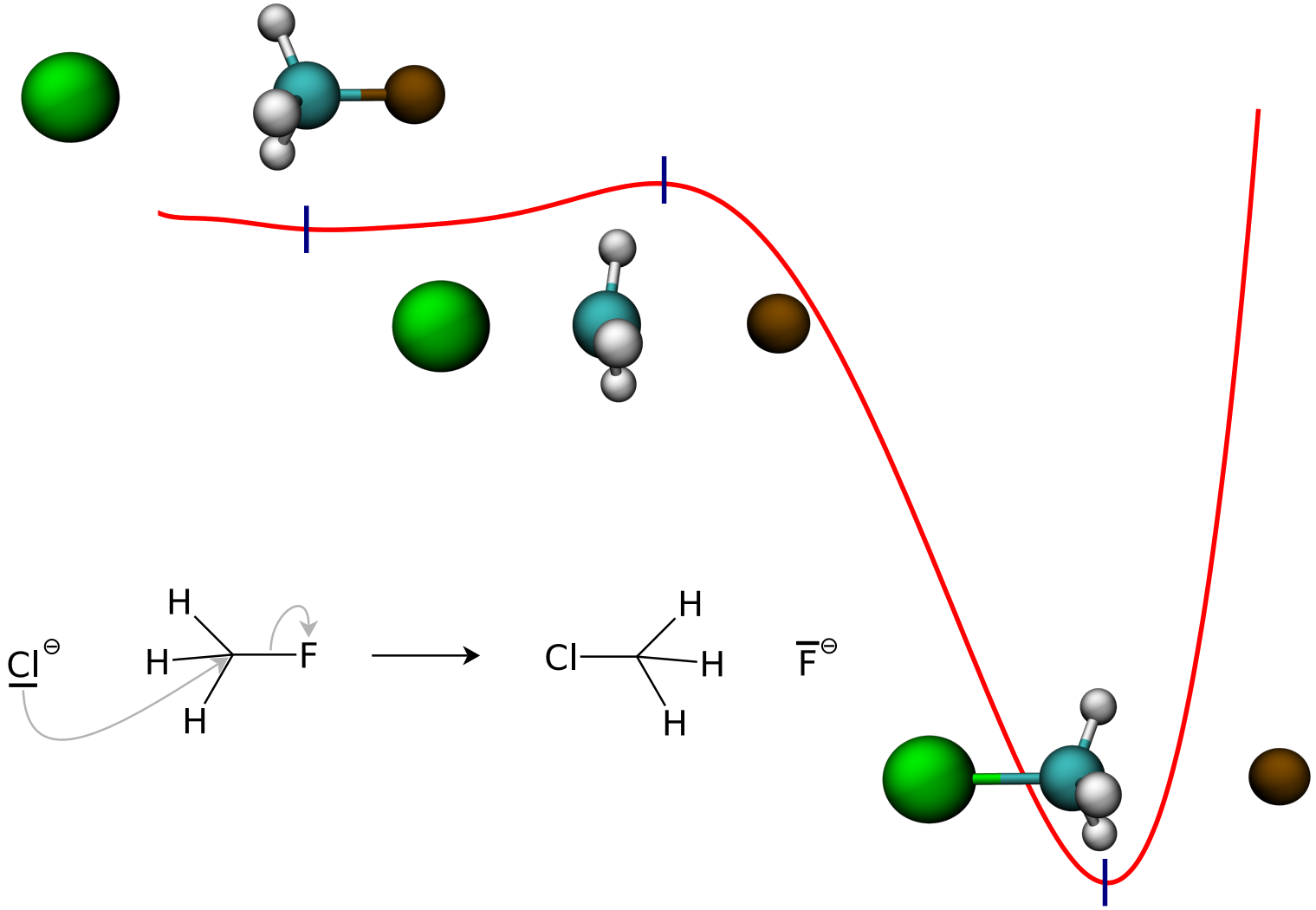
https://michael-herbst.com/talks/2019.05.03_coulomb_sturmians_metz.pdf

Contents

Describing chemistry



Electronic structure theory

- Goal: Describing chemical reactivity / properties
- Electronic Schrödinger equation:

$$\hat{\mathcal{H}}\Psi_i = E_i\Psi_i$$

- Operator $\hat{\mathcal{H}}$: Physical description of molecular system
- Most important: Ground state, i.e. E_0 and Ψ_0

Solving the Schrödinger equation: How hard can it be?

- Main ingredient: Min-max principle

$$E_0 \leq \min_{\Psi \in S} \mathcal{E}(\Psi) = \min_{\Psi \in S} \frac{\left\langle \Psi \middle| \hat{\mathcal{H}} \Psi \right\rangle}{\langle \Psi | \Psi \rangle}$$

where $S \subset H^1(\mathbb{R}^{3N}, \mathbb{C})$ and $L^2(\mathbb{R}^{3N}, \mathbb{C})$ inner product $\langle \cdot | \cdot \rangle$

- Discretisation: Curse of dimensionality:
  - $\langle \cdot | \cdot \rangle$ involves integral over $3N$-dim. space
  - Assume 2 quadrature points only
  - Chloromethane: $N = 26 \Rightarrow 2^{78} \approx 3 \cdot 10^{23}$ quadrature points

$\Rightarrow$ Finished in 1 year: ≈ 100 attoseconds per quadrature point

Now what?

- Need a suitable inexact model
- Plenty have been developed
- Our focus: Hartree-Fock approximation
  - Single-particle functions: $\psi_i \in H^1(\mathbb{R}^3, \mathbb{R})$
  - Slater-determinant:

$$\Phi = \frac{1}{\sqrt{N}} \det \begin{pmatrix} \psi_1(\underline{\boldsymbol{r}}_1) & \psi_2(\underline{\boldsymbol{r}}_1) & \cdots & \psi_N(\underline{\boldsymbol{r}}_1) \\ \psi_1(\underline{\boldsymbol{r}}_2) & \psi_2(\underline{\boldsymbol{r}}_2) & \cdots & \psi_N(\underline{\boldsymbol{r}}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(\underline{\boldsymbol{r}}_N) & \psi_2(\underline{\boldsymbol{r}}_N) & \cdots & \psi_N(\underline{\boldsymbol{r}}_N) \end{pmatrix}$$

  - Subspace S: Choose the best single-determinant subspace

Hartree-Fock approximation

- For trial determinant $\tilde{\Phi}$ made up of $\{\tilde{\psi}_i\}_i$:

$$E_0 \leq E_0^{\mathsf{HF}} \leq \mathcal{E}^{\mathsf{HF}}\left(\tilde{\Phi}\right)$$

$\Rightarrow$ Minimisation problem for $\{\tilde{\psi}_i\}_i$

- Unique minimising set $\Theta^0 = \{\psi_i^0\}_i$ exists!
- Euler-Lagrange equations:

$$\hat{\mathcal{F}}_{\Theta^0}\psi_i^0 = \varepsilon_i\psi_i^0 \qquad\qquad \left\langle \psi_i^0 \middle| \psi_j^0 \right\rangle = \delta_{ij}$$

- Fock operator $\hat{\mathcal{F}}_{\Theta^0}$ depends on solution

$\Rightarrow$ Self-consistent field problem

The standard approach

- Note: HF is in single-particle space, i.e. 3D
- Discretise $\hat{\mathcal{F}}_{\Theta^0}$ in a basis $\{\varphi_\mu\}_\mu$

$\Rightarrow$ Problem now: Find the lowest-energy $\{\psi_i^0\}_i$, built from $\{\varphi_\mu\}_\mu$

- Self-consistent field procedure:
  1. Guess trial coefficients $\mathbf{C}^{(0)}$
  2. Build trial Fock matrix $\mathbf{F}^{(0)}$
  3. Solve Euler-Lagrange equations $\Rightarrow$ New $\mathbf{C}^{(1)}$
  4. Build next Fock matrix $\mathbf{F}^{(1)}$
  5. Repeat

Contents

Electron-repulsion integrals

- Electron-repulsion integrals (ERI)

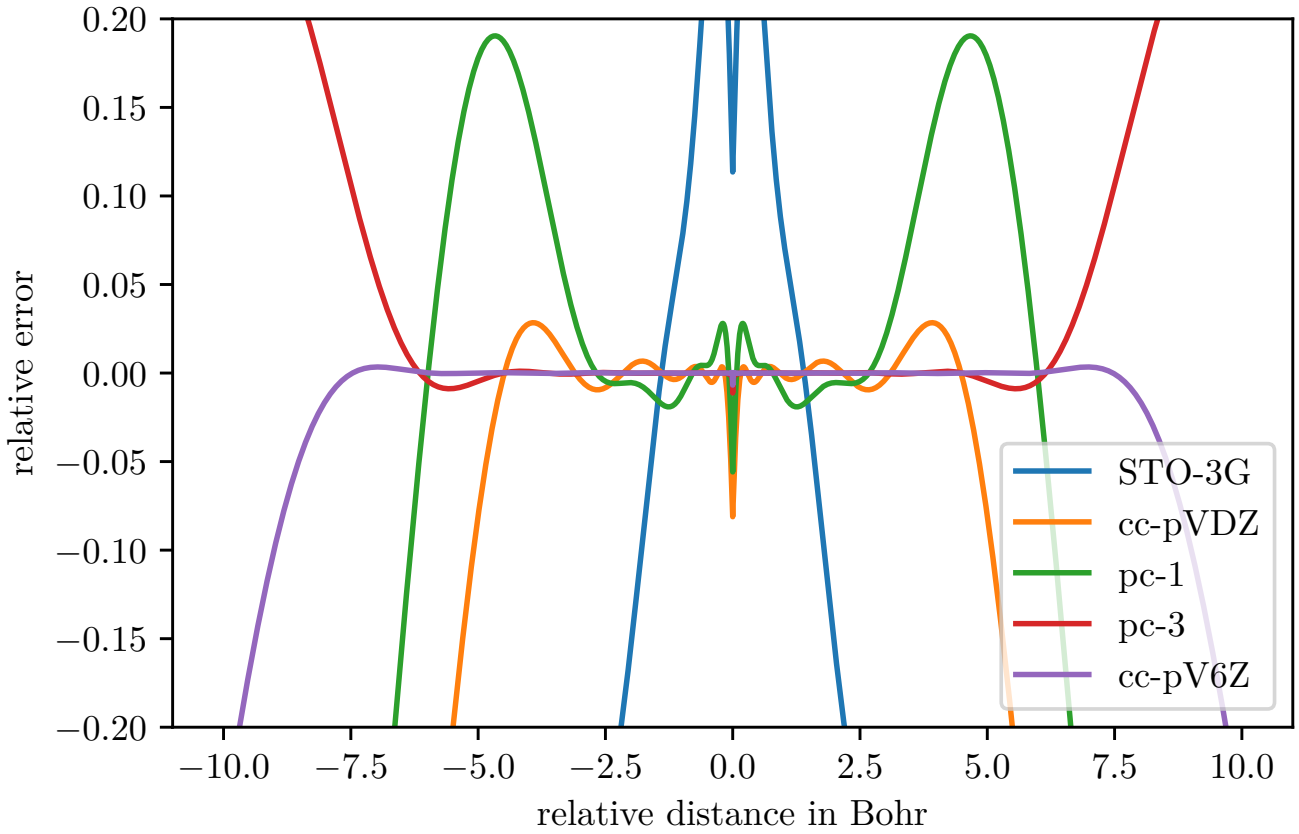
$$\int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\varphi_\mu^*(\underline{\boldsymbol{r}}_1)\varphi_\nu(\underline{\boldsymbol{r}}_1)\ \varphi_\lambda^*(\underline{\boldsymbol{r}}_2)\varphi_\kappa(\underline{\boldsymbol{r}}_2)}{\|\underline{\boldsymbol{r}}_1 - \underline{\boldsymbol{r}}_2\|} \,\mathrm{d}\underline{\boldsymbol{r}}_1\,\mathrm{d}\underline{\boldsymbol{r}}_2$$

- Occur in computation of Fock matrix
- Most expensive step (in a naive SCF)
- Depending on the basis: Easier or harder

$\Rightarrow$ Especially easy: Gaussians

The standard basis: Gaussian-type basis sets

$$\varphi_\mu^{\mathsf{GTO}}(\underline{\boldsymbol{r}}) = r^{l_\mu} \sum_i^{N_{\mathsf{contr}}} c_{\mu,i} \exp(-\alpha_{\mu,i} r^2) \cdot Y_{l_\mu}^{m_\mu}(\hat{\underline{\boldsymbol{r}}})$$



Beyond Gaussian-type orbitals

- Issues of cGTOs:
  - Representing the core region?
  - Representing the exponential decay?
  - Error estimates?
  - Black box modelling?
  - Distributed memory parallelisation?

$\Rightarrow$ Playing field to try other basis function types

Basis function types

- Gaussian-type orbitals
- Geminals

- Slater-type orbitals
- Sturmian-type orbitals

- ...

- Plane waves
- Augmented plane waves

- Wavelets
- Finite elements

- ...

The potential of Coulomb Sturmians

- Prospect of CS:
  - Exponential-type basis functions
  - ✓ Represent the core region
  - ✓ Represent exponential decay
  - ? Error estimates
  - ? Black box modelling
  - ?? Distributed memory parallelisation

⇒ (Atomic) implementation inside `molsturm`[1] and `sturmint`

[1] M. F. Herbst, A. Dreuw and J. E. Avery. J. Chem. Phys., **149**, 84106 (2018)

Contents

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

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

$\Rightarrow$ Sturm-Liouville equation[2]

[1] H. Shull and P.-O. Löwdin. J. Chem. Phys., **30**, 617 (1959)

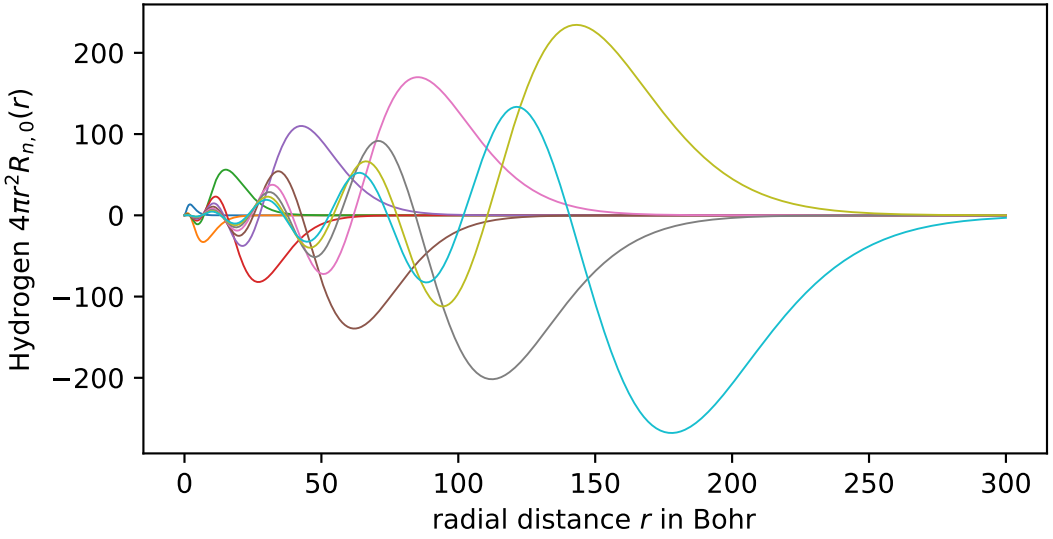
[2] M. Rotenberg. Ann. Phys., **19**, 262 (1962)

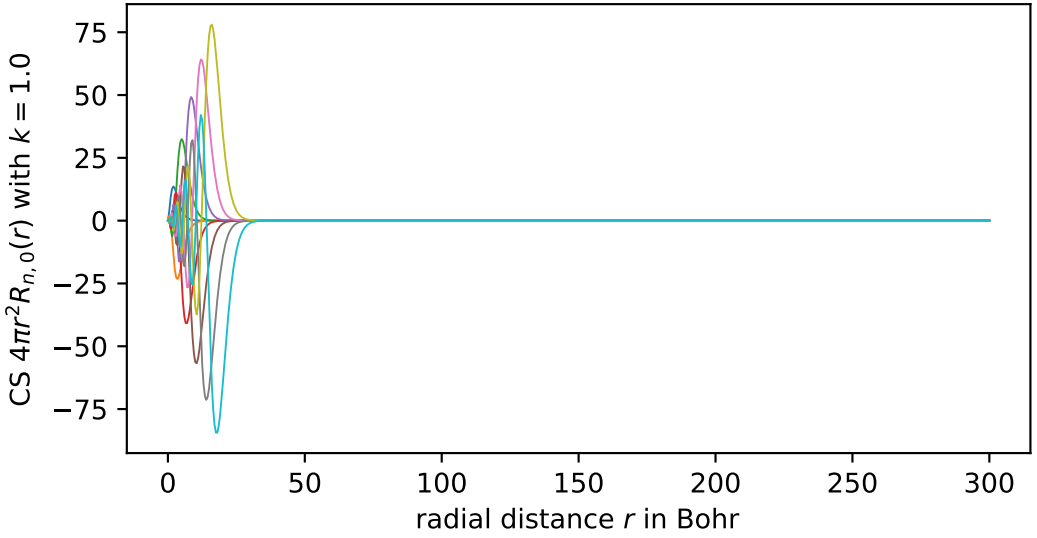
Examples of the Coulomb Sturmian radial parts

$$\varphi_\mu(\underline{\boldsymbol{r}}) \equiv \varphi_{nlm}(\underline{\boldsymbol{r}}) = R_{nl}(r) Y_l^m(\hat{\underline{\boldsymbol{r}}})$$

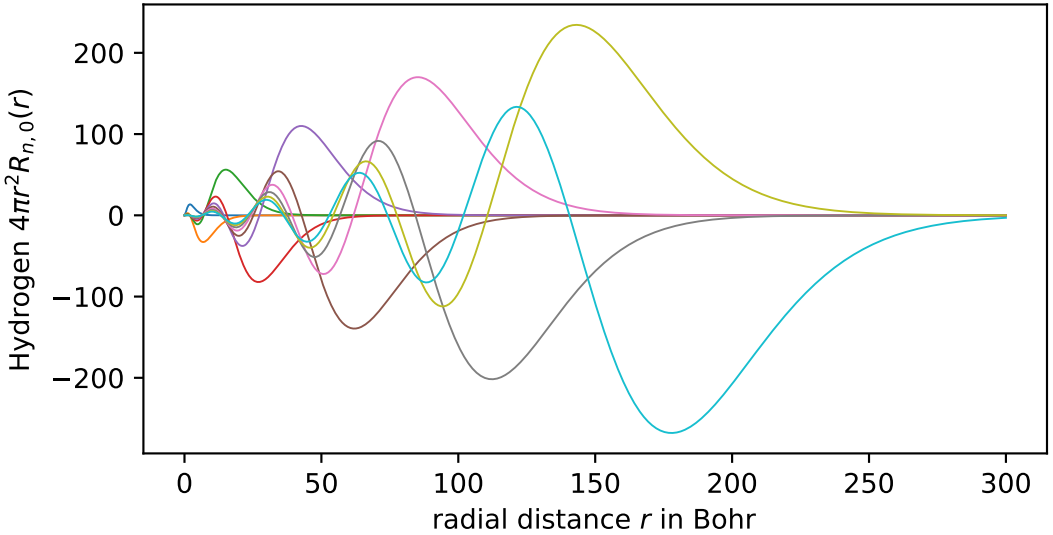
	n	l	$R_{nl}(r)$		
$1s$	1	0	$2k^{3/2}$		$\exp(-kr)$
$2s$	2	0	$2k^{3/2}$	$(1-kr)$	$\exp(-kr)$
$2p$	2	1	$2k^{3/2}$	kr	$\exp(-kr)$
$3s$	3	0	$2k^{3/2}$	$\left(1-2kr+\frac{2}{3}(kr)^2\right)$	$\exp(-kr)$
$3p$	3	1	$2k^{3/2}$	$\frac{2\sqrt{2}}{3}kr\left(1-\frac{kr}{2}\right)$	$\exp(-kr)$
$3d$	3	2	$2k^{3/2}$	$\frac{\sqrt{2}}{3\sqrt{5}}(kr)^2$	$\exp(-kr)$
general			$2k^{3/2}$	$P_{nl}(kr)$	$\exp(-kr)$

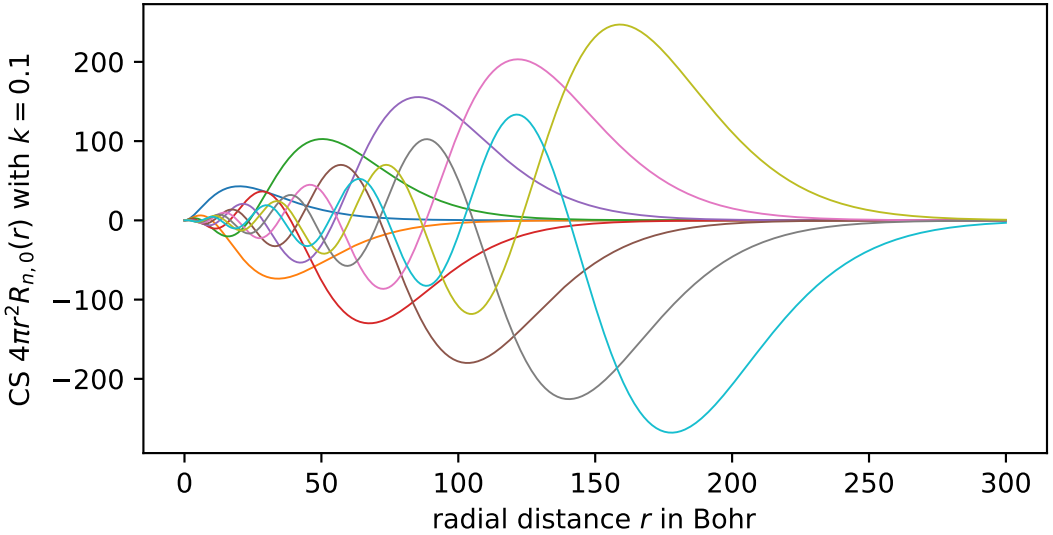
Hydrogen vs. CS radial distribution functions ($k = 1.0$)





Hydrogen vs. CS radial distribution functions ($k = 0.1$)





Classical turning point and concentration

- Classical turning point: Zero kinetic energy
- Hydrogen-like functions:

$$-\frac{1}{n^2} = -\frac{Z}{r_T} \Leftrightarrow r_T = Zn^2$$

- Coulomb Sturmians:

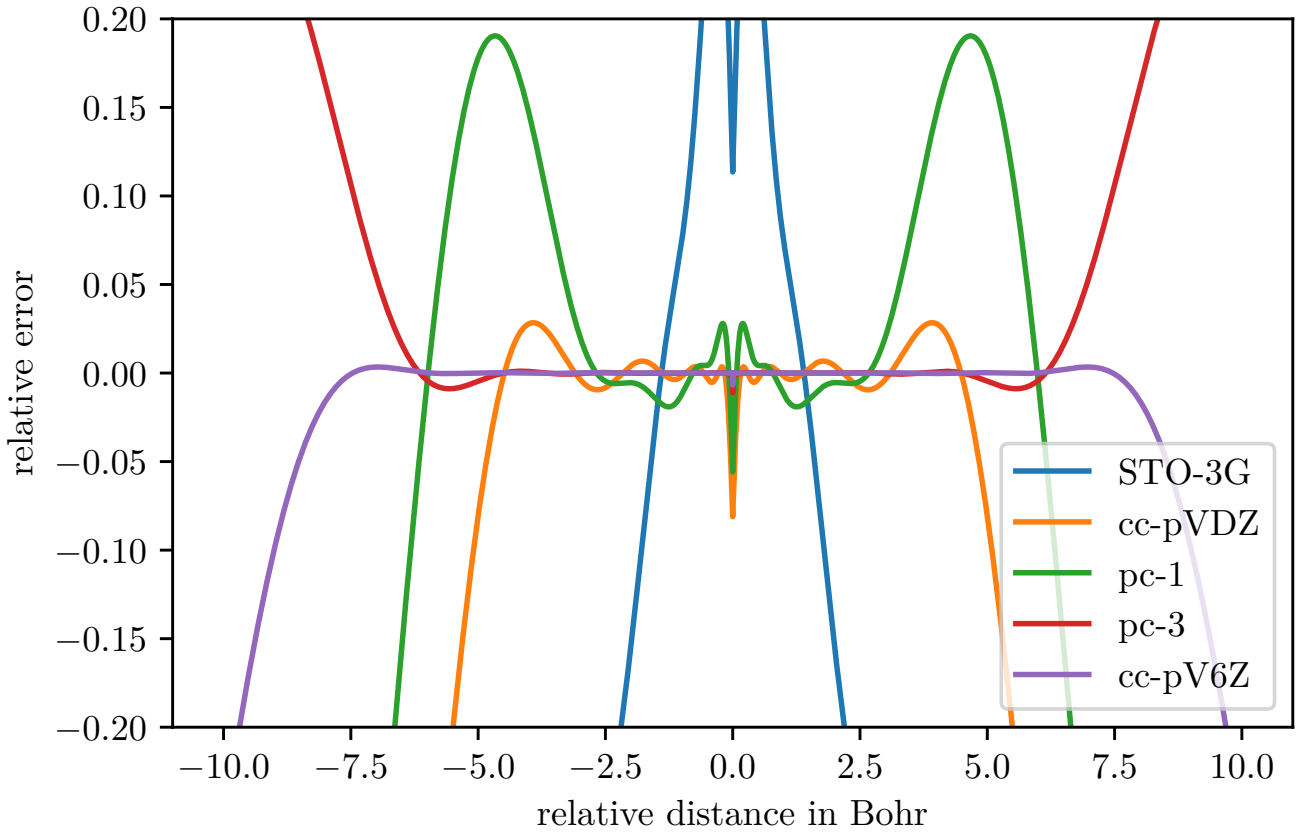
$$-\frac{k^2}{2} = -\beta_n \frac{Z}{r_T} \Leftrightarrow r_T = \frac{2Z\beta_n}{k^2} = \frac{2n}{k}$$

$\Rightarrow$ Hydrogen-like functions escape too fast into continuum

$\Rightarrow$ Exponent k allows to tune concentration of CS

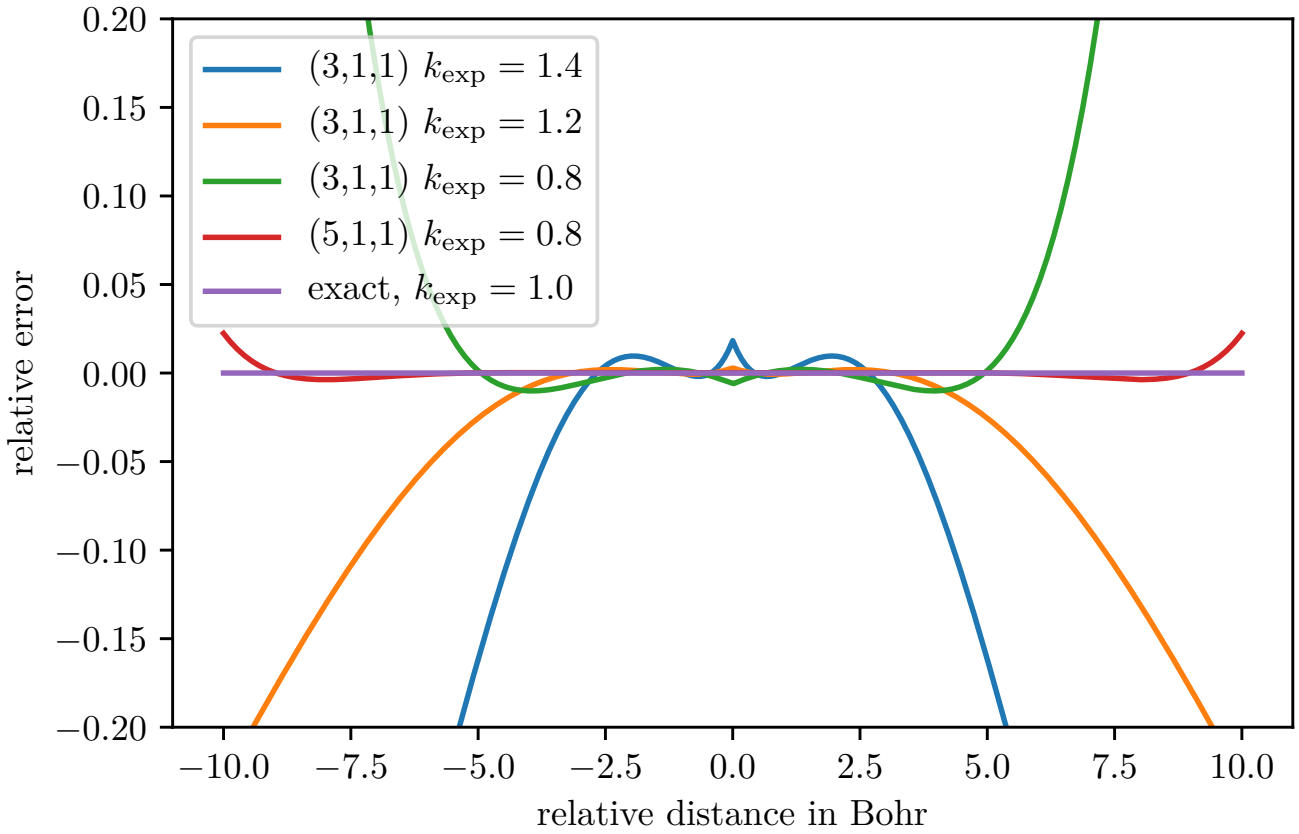
Coulomb-Sturmians vs Gaussians (for hydrogen)

$$\varphi_\mu^{\mathsf{GTO}}(\underline{\boldsymbol{r}}) = r^{l_\mu} \sum_i^{N_{\mathsf{contr}}} c_{\mu,i} \exp(-\alpha_{\mu,i} r^2) \cdot Y_{l_\mu}^{m_\mu}(\hat{\underline{\boldsymbol{r}}})$$



Coulomb-Sturmians vs Gaussians (for hydrogen)

$$\varphi_\mu^{\mathsf{CS}}(\underline{\boldsymbol{r}}) = 2k^{3/2} P_{nl}(2kr)\exp(-kr)\cdot Y_l^m(\hat{\underline{\boldsymbol{r}}})$$



(Atomic) Coulomb-Sturmians properties overview

- Complete (Schauder) basis[1,2]
- More physical: Nuclear cusp and exponential decay
- CS exponent k:
  - Identical for each basis function
  - Controls concentration of basis functions
- One-electron integrals sparse and analytic
- Two-electron integrals sparse tensor contraction
- Generalisation to molecules possible[3]

[1] B. Klahn and W. A. Bingel. Theoretica chimica acta, **44**, 9 (1977)

[2] B. Klahn and W. A. Bingel. Theoretica chimica acta, **44**, 27 (1977)

[3] J. E. Avery and J. S. Avery. vol. 70 of *Advances in Quantum Chemistry*, 265 – 324. Academic Press (2015)

Contents

Construction of CS basis sets

- All CS basis functions share common exponent k
- Index restrictions by CS equations:

$$n > 0 \qquad 0 \leq l < n \qquad -l \leq m \leq l$$

- Basis set construction:[1] Additional restrictions

$$n \leq n_{\text{max}} \qquad l \leq l_{\text{max}} \qquad m \leq m_{\text{max}}$$

- Restriction by m_{max}, sometimes l_{max} neglected

$\Rightarrow$ Physically motivated

[1] M. F. Herbst, J. E. Avery and A. Dreuw. Physical Review A, **99**, 012512 (2019)

The parameters n_{max}, l_{max} and m_{max}

- Sturm-Liouville form of radial part (for each l):

$$\forall 0 \leq l < n : \quad R_{nl} \in \operatorname{span}\{R_{n',0}\}_{n' \leq n}$$

  $\Rightarrow$ n_{max} controls radial discretisation

  $\Rightarrow$ l_{max} and m_{max} control angular discretisation

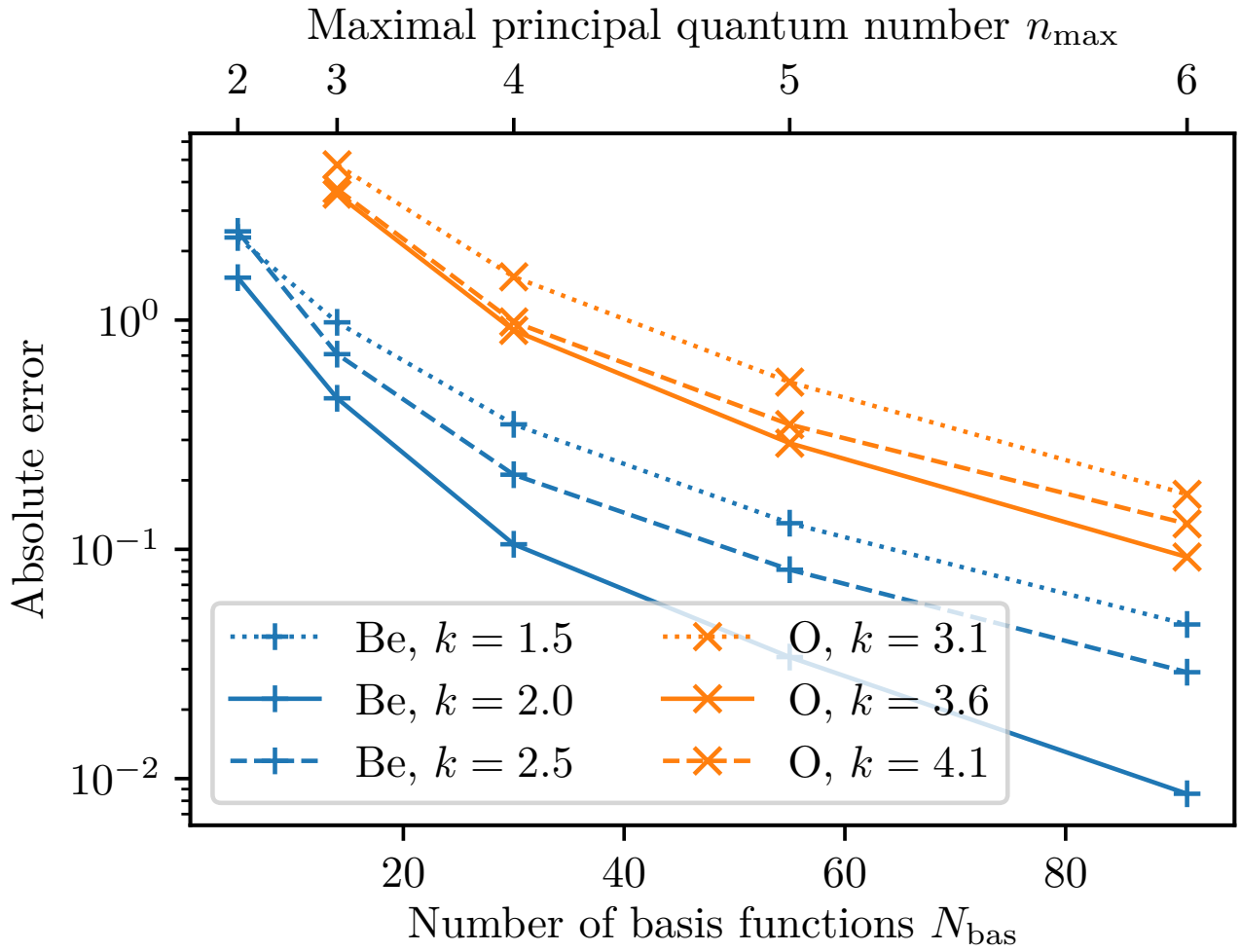
- Scaling of basis size if only restricted by n_{max}:

$$N_{\text{bas}}(n_{\text{max}}) = \frac{(2n_{\text{max}}+1)(n_{\text{max}}+1)n_{\text{max}}}{6} \in \mathcal{O}(n_{\text{max}}^3)$$

- Scaling of basis size if restricted by n_{max} and l_{max}:

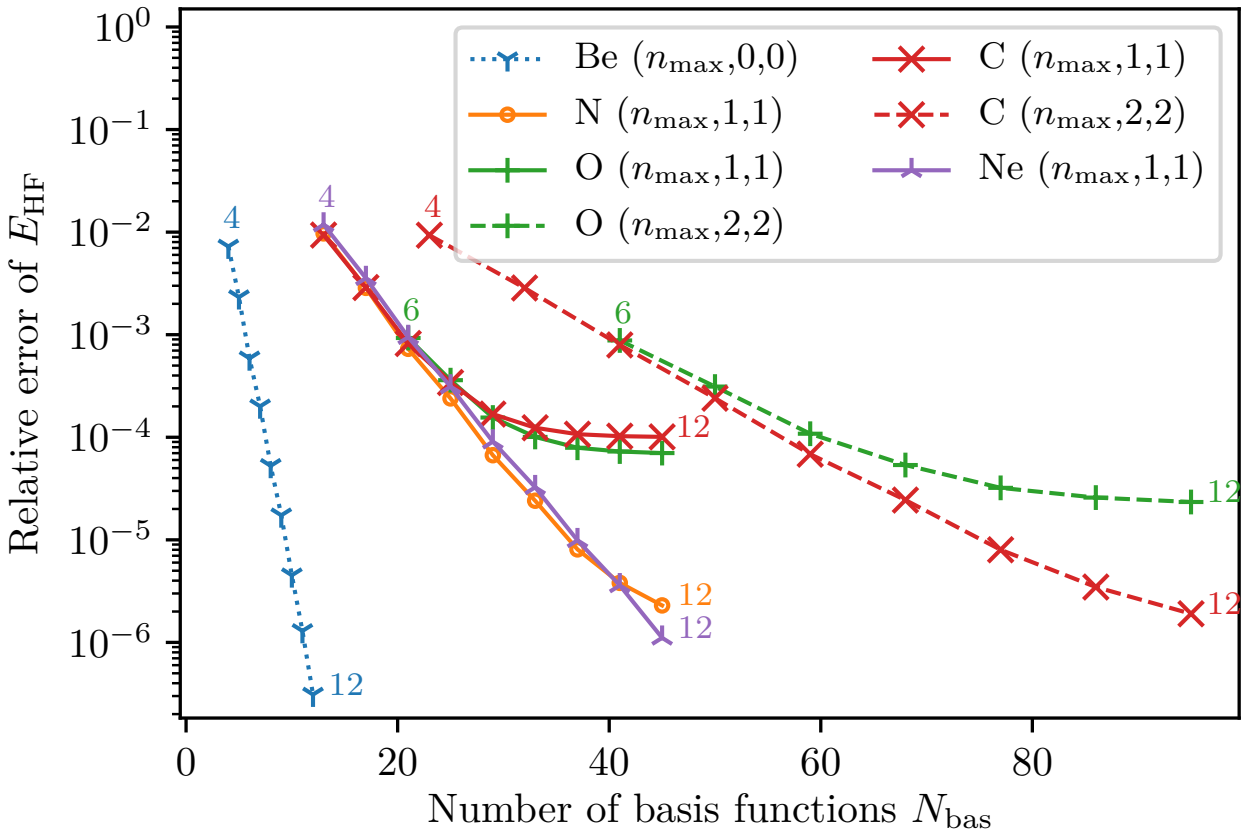
$$N_{\text{bas}}(n_{\text{max}}) = (n_{\text{max}}-1)(l_{\text{max}}+1)^2 \in \mathcal{O}(n_{\text{max}} l_{\text{max}}^2)$$

Energy convergence[1]



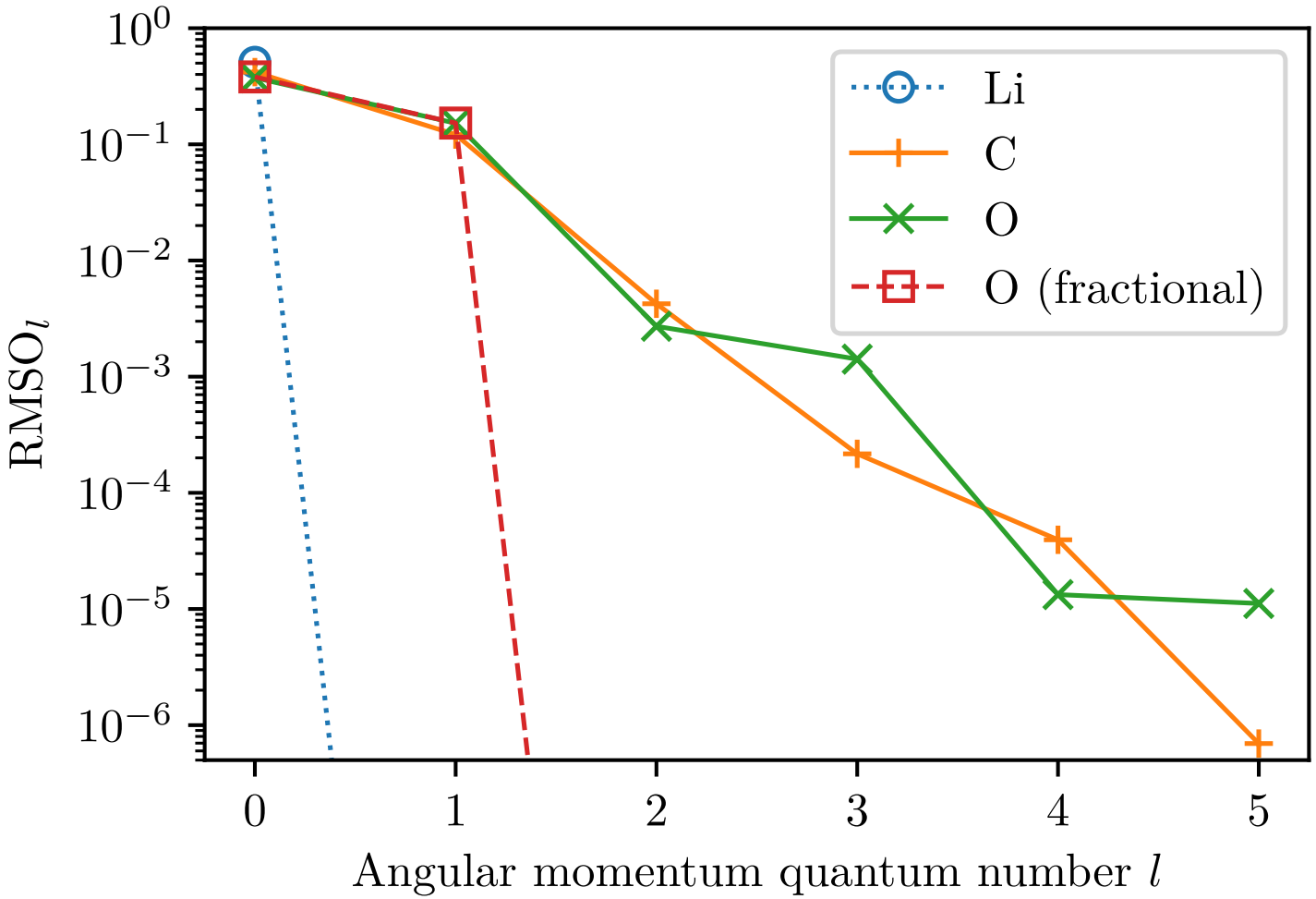
[1] M. F. Herbst, J. E. Avery and A. Dreuw. Physical Review A, **99**, 012512 (2019)

Basis progressions: Energy versus basis size[1]



[1] M. F. Herbst, J. E. Avery and A. Dreuw. Physical Review A, **99**, 012512 (2019)

Energy convergence: Deviating behaviour of elements[1]



[1] M. F. Herbst, J. E. Avery and A. Dreuw. Physical Review A, **99**, 012512 (2019)

Root mean square coefficient value per l

- Root mean square occupied coefficient par AM l:

$$\mathrm{RMSO}_l = \sqrt{\sum_{\mu} \sum_{i} \sum_{\sigma \in \{\alpha,\beta\}} \frac{1}{N^{\sigma}_{\mathrm{elec}} \; N_{\mathrm{bas},l}} \left(C^{\sigma}_{\mu,i} \, f^{\sigma}_{ii} \right)^2}$$

where i runs over orbitals, μ over basis functions and

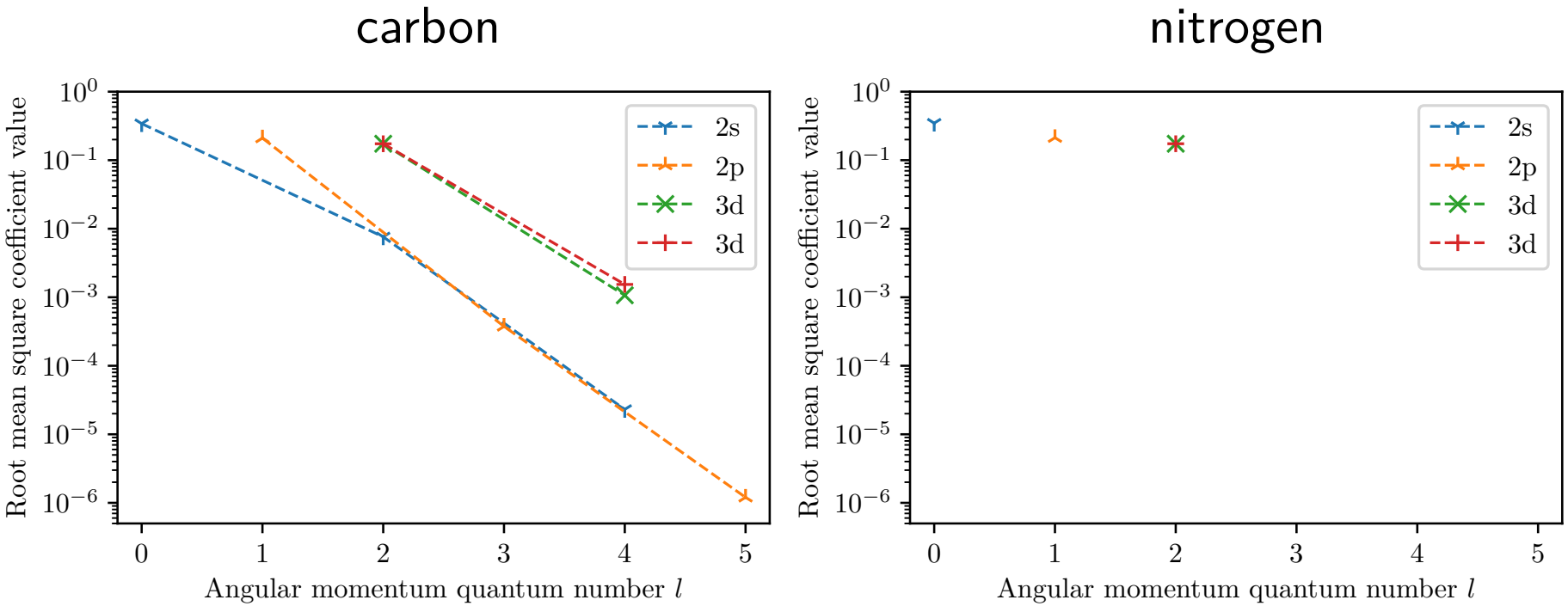
$N^{\sigma}_{\mathrm{elec}}$ Number of electrons with spin σ

f^{σ}_{ii} Occupation number

$N_{\mathrm{bas},l}$ Number of basis functions of AM l

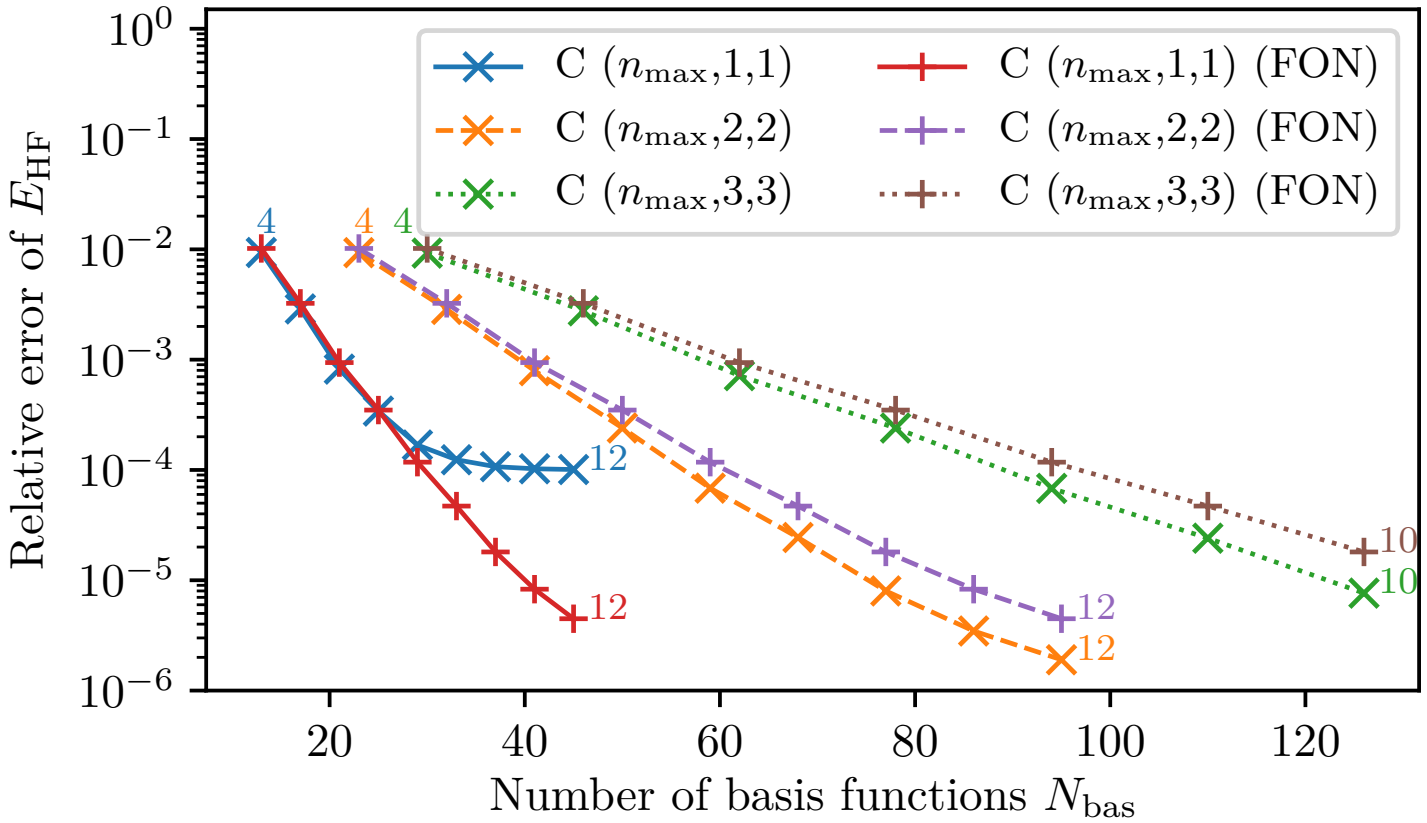
- Measure for importance of l in HF wave function

RMSO$_l$ plots[1]



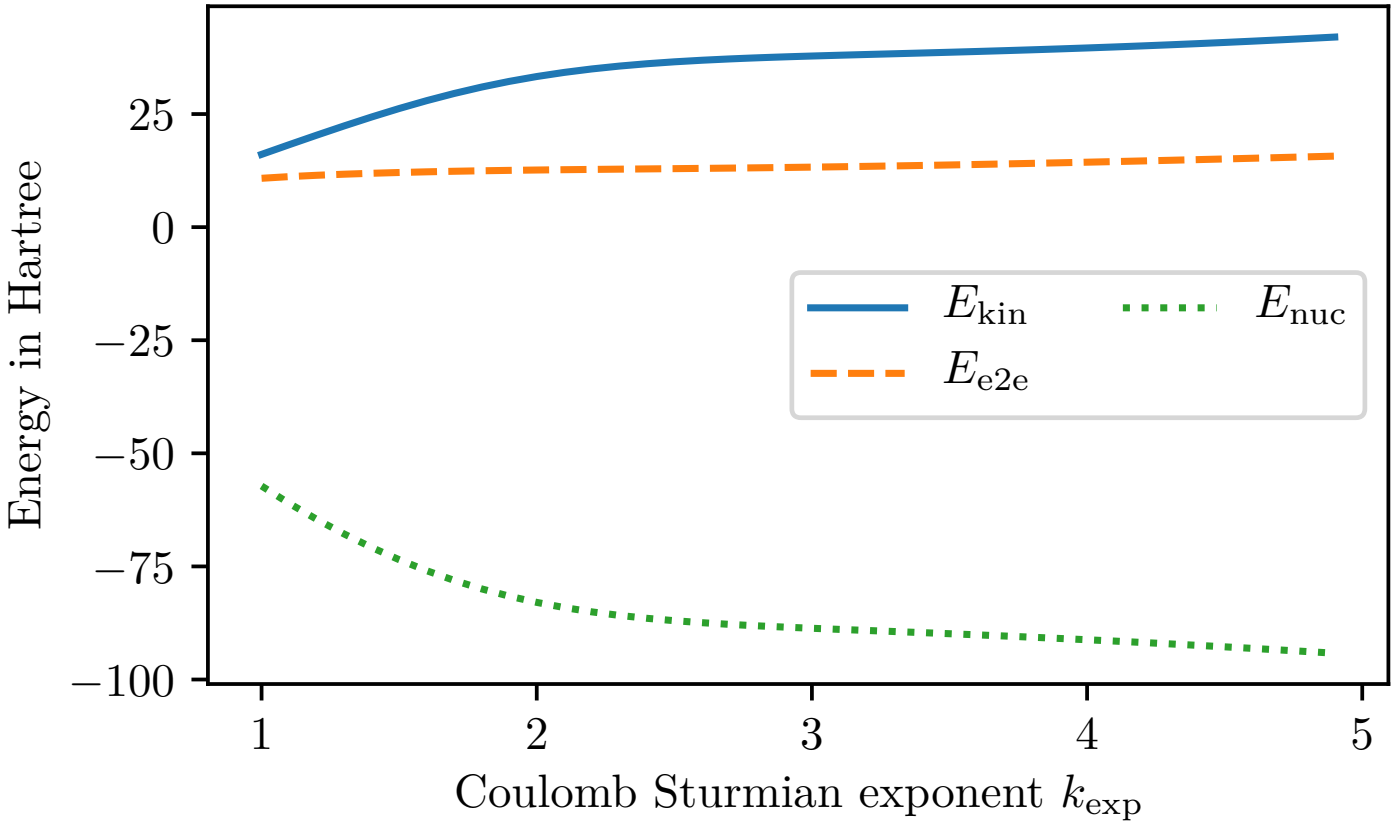
[1] M. F. Herbst, J. E. Avery and A. Dreuw. Physical Review A, **99**, 012512 (2019)

Basis progressions: Carbon[1]



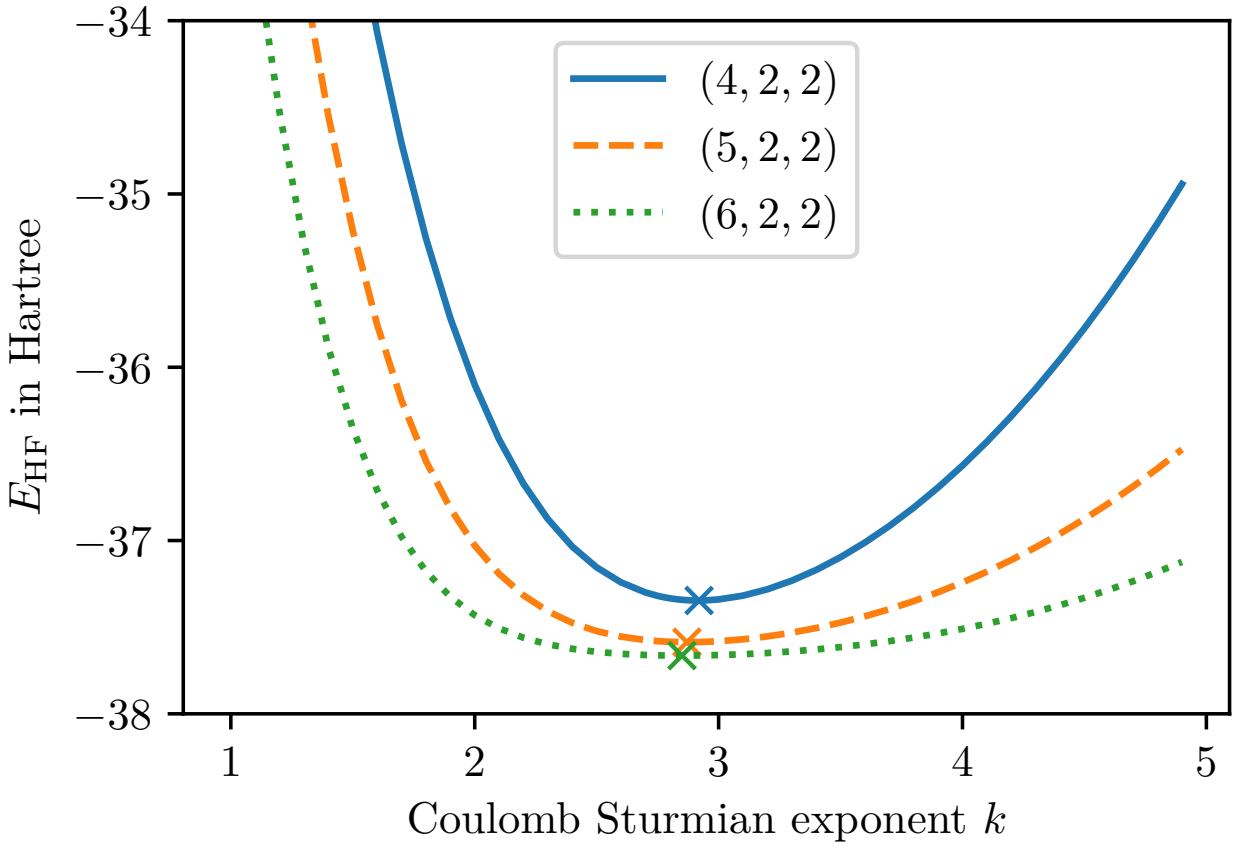
[1] M. F. Herbst, J. E. Avery and A. Dreuw. Physical Review A, **99**, 012512 (2019)

k-dependence terms carbon[1]



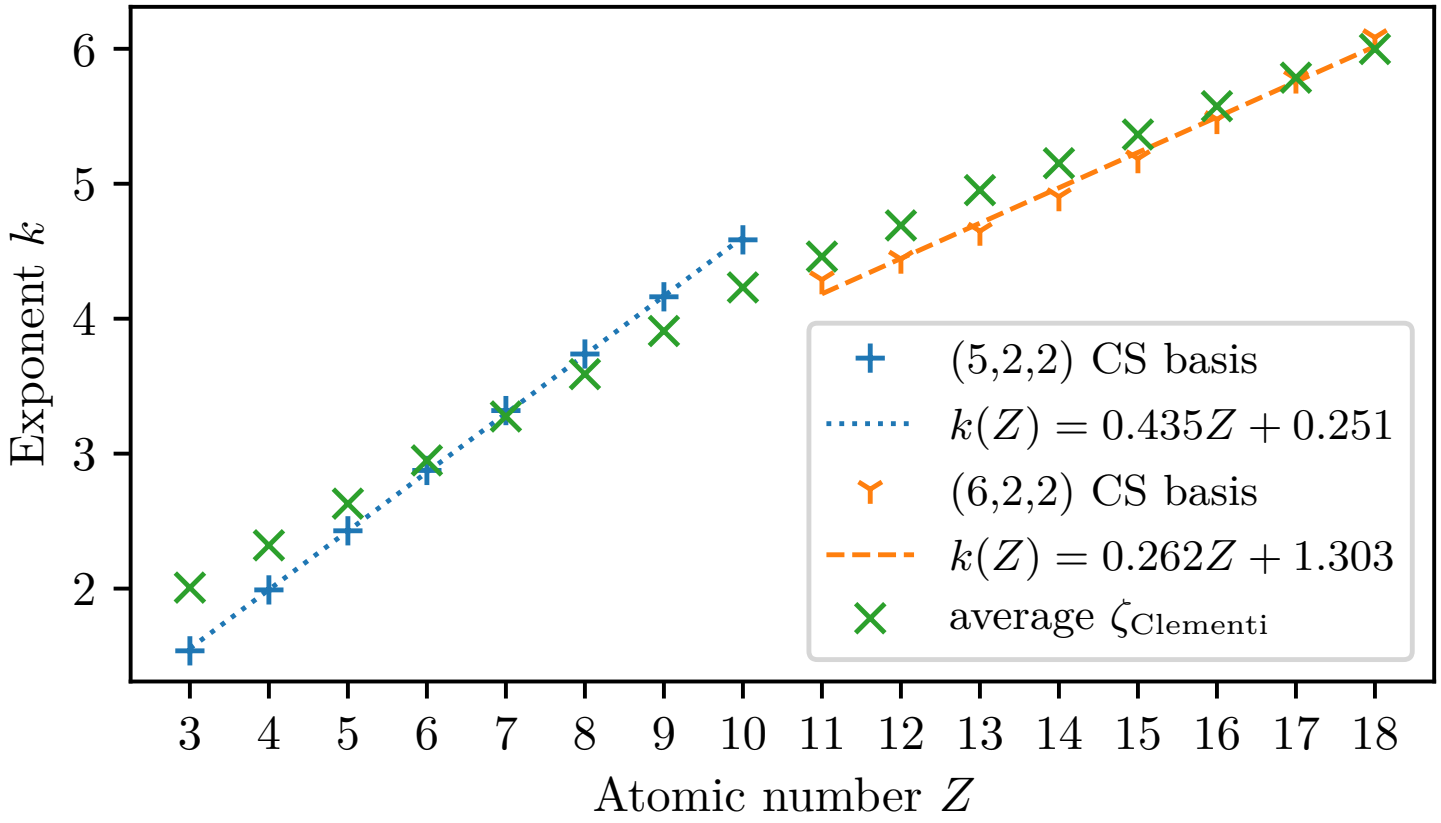
[1] M. F. Herbst, J. E. Avery and A. Dreuw. Physical Review A, **99**, 012512 (2019)

k-dependence total Hartree-Fock energy[1]



[1] M. F. Herbst, J. E. Avery and A. Dreuw. Physical Review A, **99**, 012512 (2019)

Optimal exponent versus Clementi exponents[1]

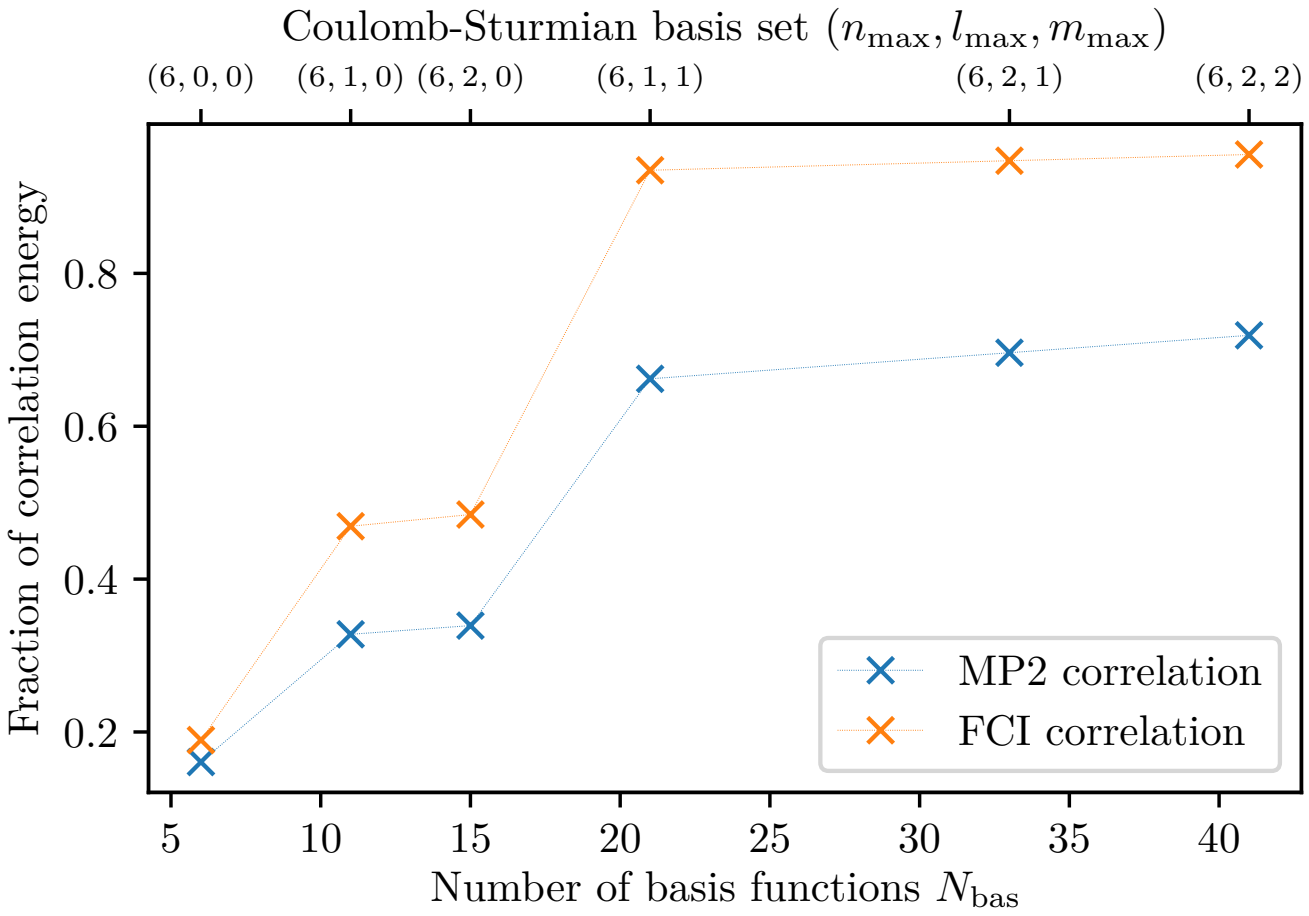


[1] M. F. Herbst, J. E. Avery and A. Dreuw. Physical Review A, **99**, 012512 (2019)

Contents

MP(2) and FCI (basis size)[1]

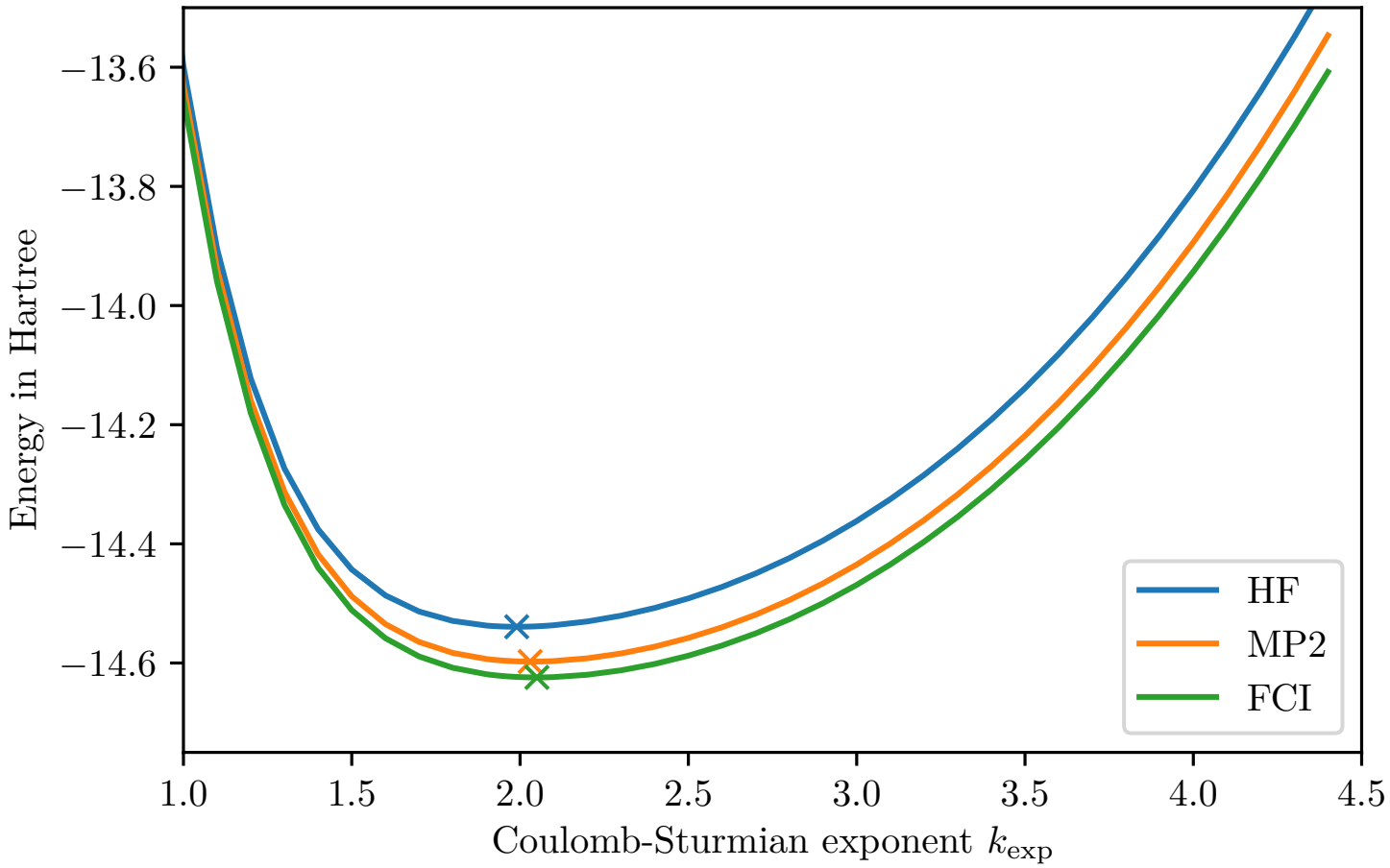
- Beryllium, $k = 2.1$, correlation energy relative to FCI $(10, 2, 2)$



[1] M. F. Herbst. Ph.D. thesis, Ruprecht-Karls-Universität Heidelberg (2018)

MP(2) and FCI (k dependence)[1]

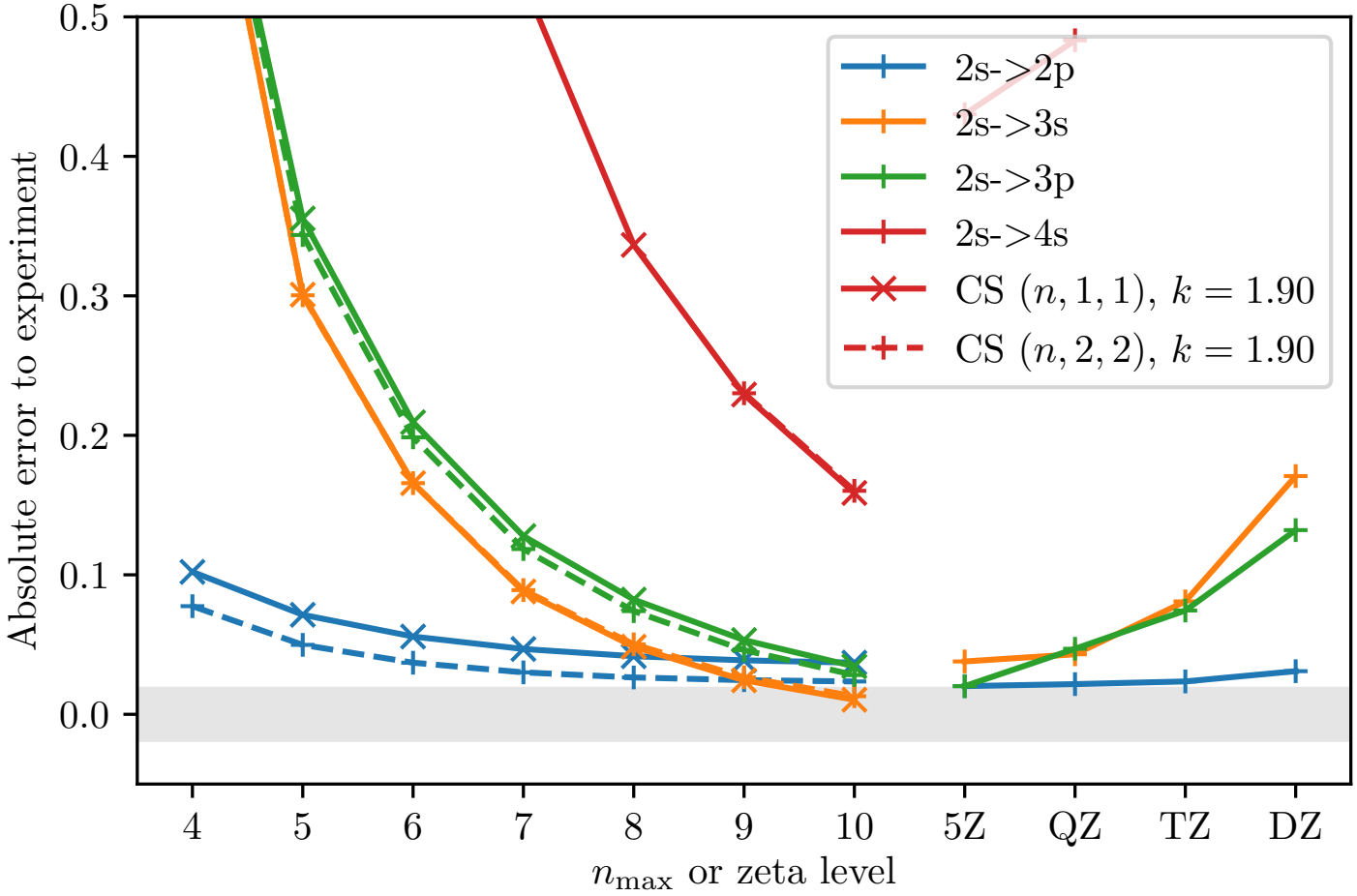
- Beryllium, $(5, 1, 1)$ CS basis



[1] M. F. Herbst. Ph.D. thesis, Ruprecht-Karls-Universität Heidelberg (2018)

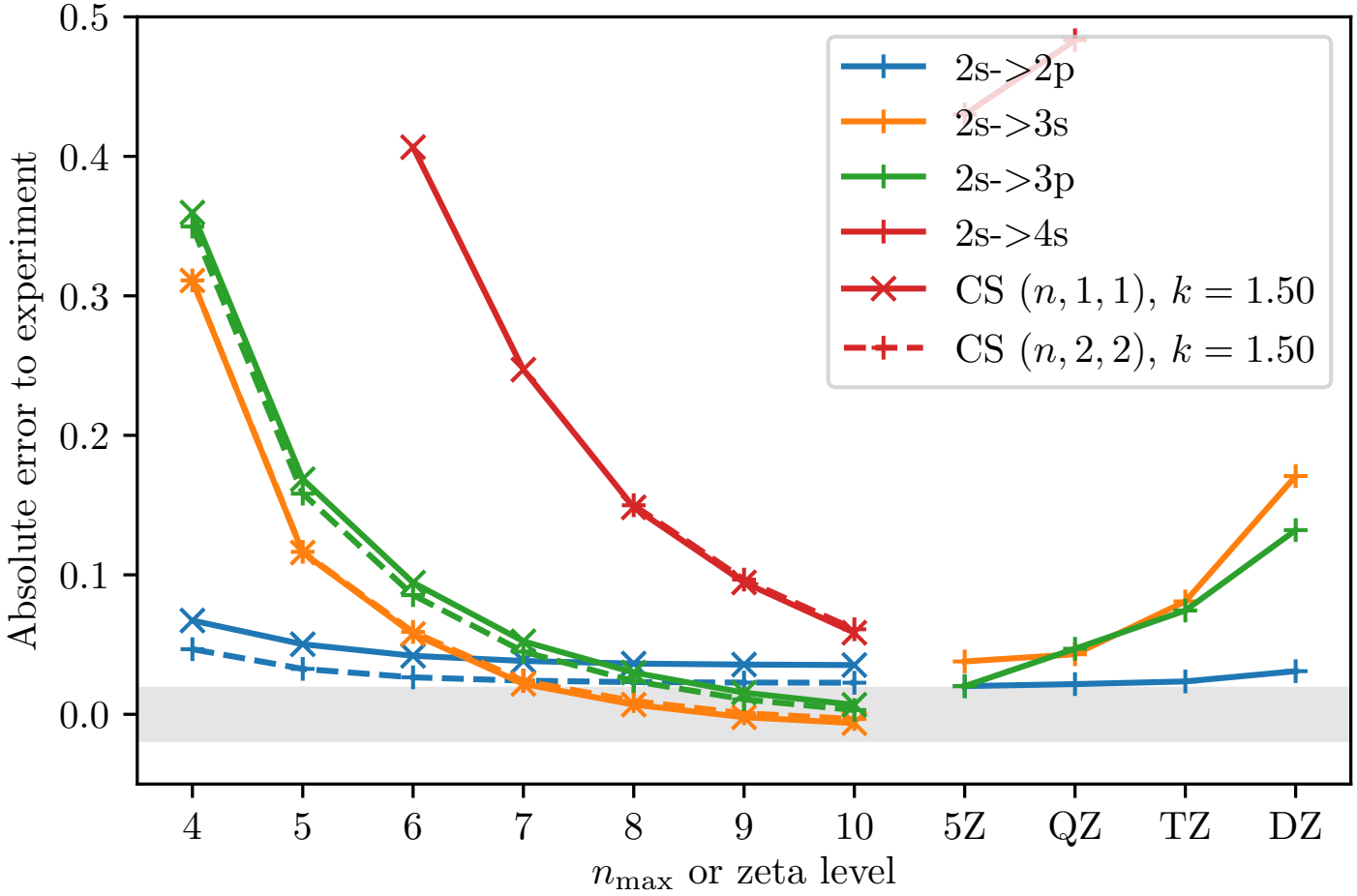
ADC(2) absolute error

- Beryllium CS progressions vs. Gaussians



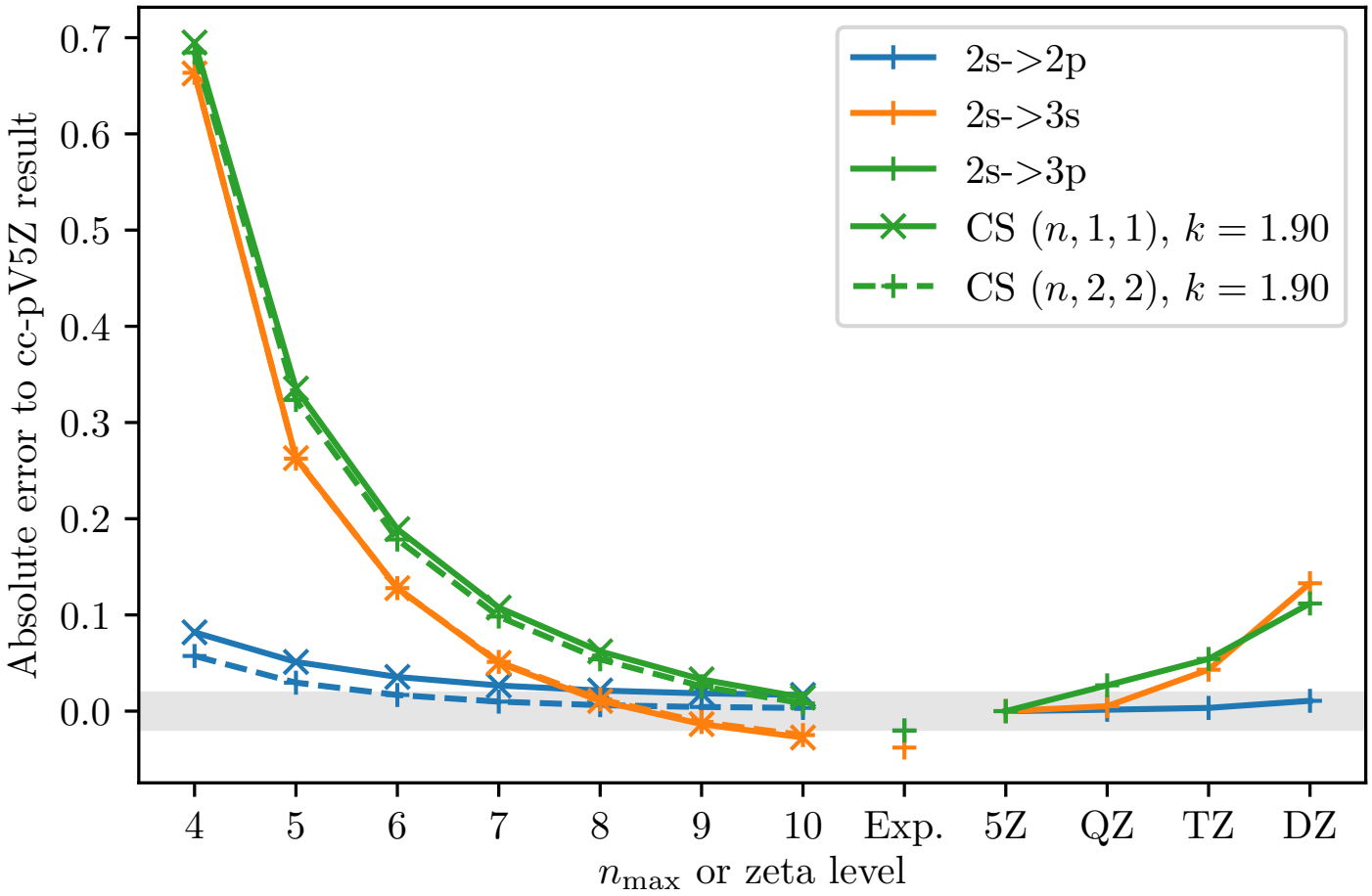
ADC(2) absolute error

- Beryllium CS progressions vs. Gaussians



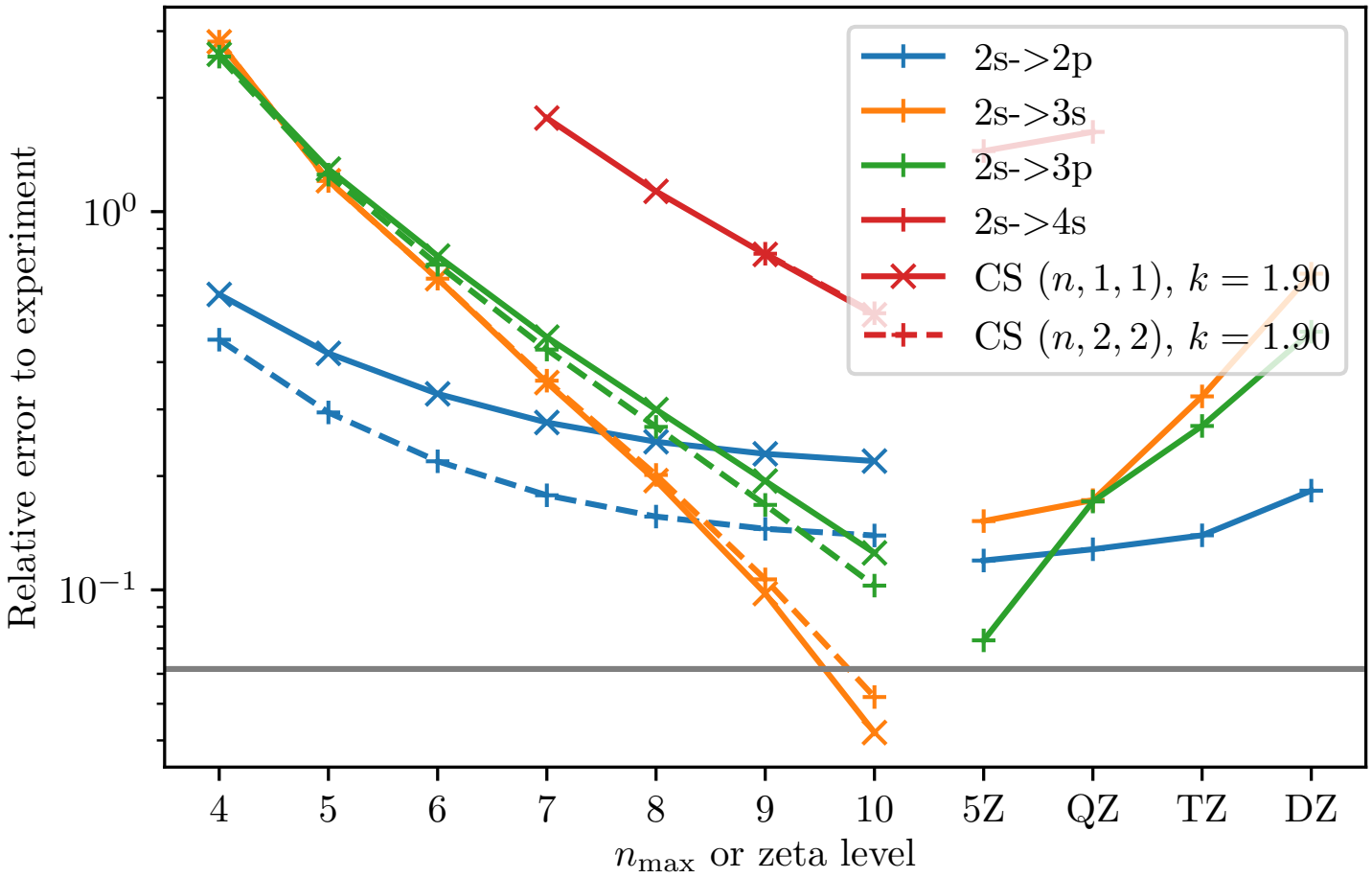
ADC(2) Gaussians error

- Beryllium CS progressions vs. Gaussians



ADC(2) relative error

- Beryllium CS progressions vs. Gaussians



Coulomb-Sturmians for correlated methods

- Convergence behaviour?
- Systematic basis set construction?
- Contracted Coulomb-Sturmian basis sets?
- Basis sets with multiple ks?
- Molecular Coulomb Sturmians?

`adcc`: `python`-driven ADC for SCF codes

- Joint project with M. Scheurer, T. Fransson, D. R. Rehn, A. L. Dempwolff (Dreuw group, Heidelberg University)
- Algebraic-diagrammatic construction (ADC) approach to electronic excitations
- `python` layer:
  - Connection to SCF drivers (4 codes so far)
  - Numerical algorithms (eigensolver / linear response)
  - Controls computational workflow
- `libtensor`[1] `C++` library: Heavy tensor-contractions
- Part of Gator framework for computational spectroscopy[2]

[1] E. Epifanovsky, M. Wormit, T. Kuś et al. J. Comput. Chem., **34**, 2293 (2013)

[2] D. R. Rehn, Z. Rinkevicius, M. F. Herbst, et. al. *Gator: A python-driven wave-function correlated program for spectroscopy calculations.* In preparation.

`DFTK.jl`: density-functional theory toolkit

- Joint project with Antoine Levitt and Eric Cancès (Matherials)
- Plane-wave-based density-functional theory
- `julia`-framework
- Just started, aim:
  - Accessible to mathematicians, physicists, computer scientists
  - Numerical experiments to accompany proof
  - Algorithmic developments

  $\Rightarrow$ Support both toy problems and full-scale applications
- Code: `https://github.com/mfherbst/DFTK.jl`

Coulomb Sturmians in essence

- Complete, exponential-type basis
  - ⇒ May capture cusp and decay behaviour
  - ⇒ Parameter k to tune concentration
- Basis set construction for HF problems:[1]
  - Physical rationale for arising parameters
  - Convergence explained by physical arguments
  - Implementation for atoms: `sturmint` and `molsturm`[2]
- Extension to molecular integrals feasible
- Basis sets for correlated methods required

[1] M. F. Herbst, J. E. Avery and A. Dreuw. Physical Review A, **99**, 012512 (2019)

[2] M. F. Herbst, A. Dreuw and J. E. Avery. J. Chem. Phys., **149**, 84106 (2018)

Acknowledgements

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SORBONNE UNIVERSITÉ

UNIVERSITÄT HEIDELBERG ZUKUNFT SEIT 1386

IWR Interdisciplinary Center for Scientific Computing

HGS MathComp

Questions?

Papers: M. F. Herbst, A. Dreuw and J. E. Avery. J. Chem. Phys., **149**, 84106 (2018)

M. F. Herbst, J. E. Avery and A. Dreuw. Physical Review A, **99**, 012512 (2019)

Thesis: `https://michael-herbst.com/phd-thesis.html`

Email: `michael.herbst@enpc.fr`

Blog: `https://michael-herbst.com/blog`

Achievements of molsturm

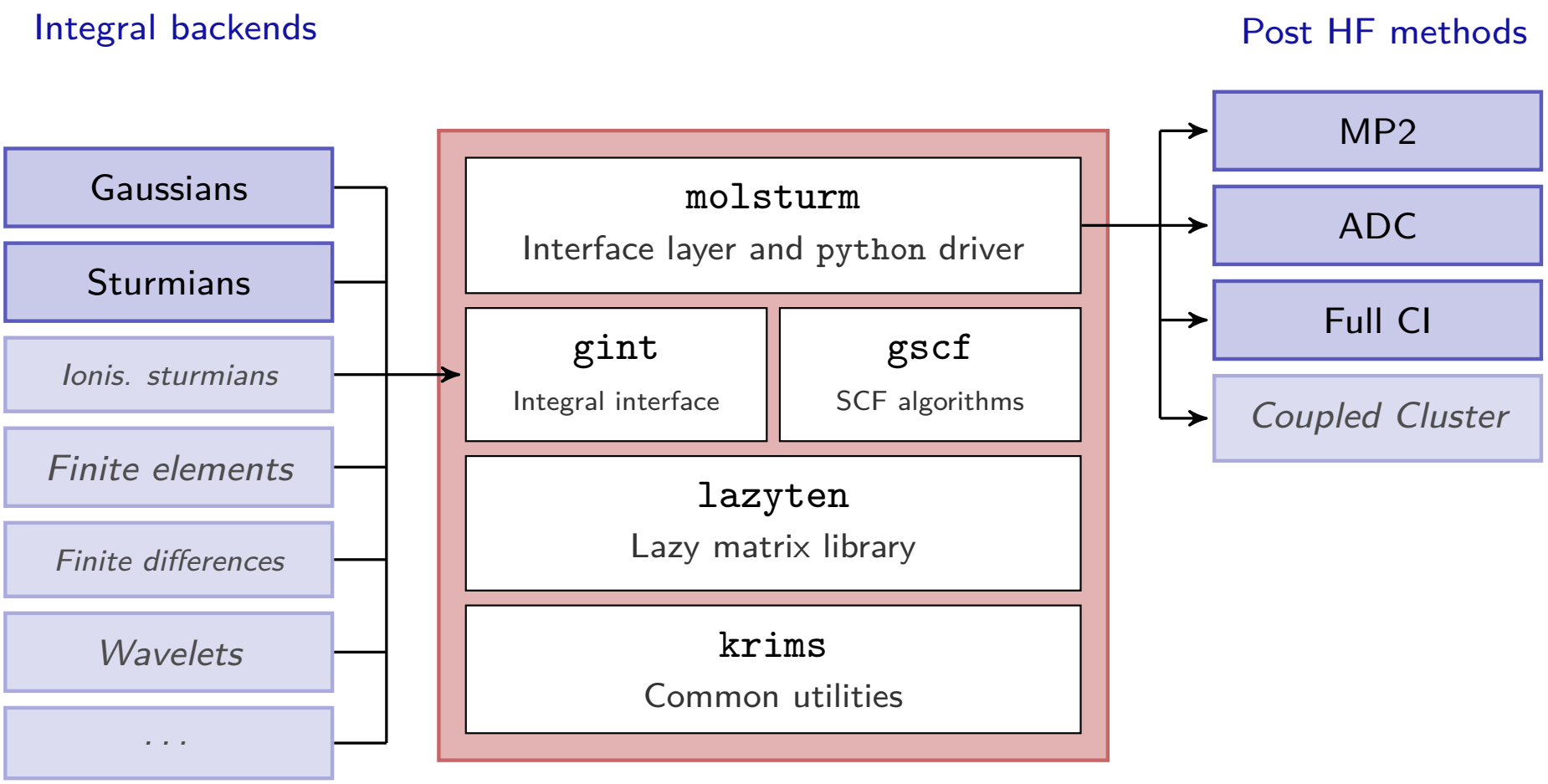
- Basis-function independent design
  - Plug and play new discretisations
  - Basis-type agnostic SCF procedure
- Easy-to-use interfaces
  - Integrate with existing code (e.g. Post-HF)
  - Avoid reinventing the wheel
  - Rapid prototyping, testing and analysis

⇒ Explore methods across basis function types[1,2]

[1] M. F. Herbst, A. Dreuw and J. E. Avery. J. Chem. Phys., **149**, 84106 (2018)

[2] M. F. Herbst. Ph.D. thesis, Ruprecht-Karls-Universität Heidelberg (2018)

molsturm structure



Principle ingredient: Contraction-based methods

- Contraction-based methods
  - Avoid storing matrices
  - Employ iterative, subspace-based algorithms
  - Contraction expressions (e.g. matrix-vector products)
  - Common in Post-HF: *Working equations*

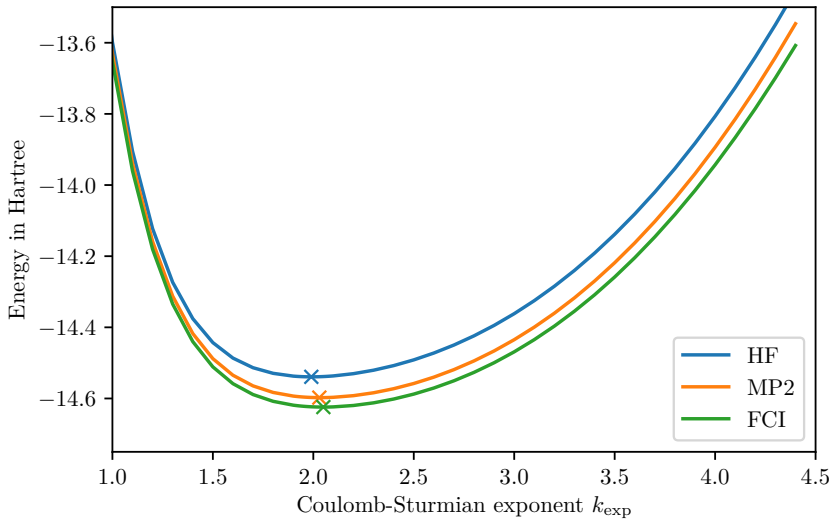
$\Rightarrow$ SCF code only needs Fock contraction

$\Rightarrow$ Hide discretisation details inside Fock object

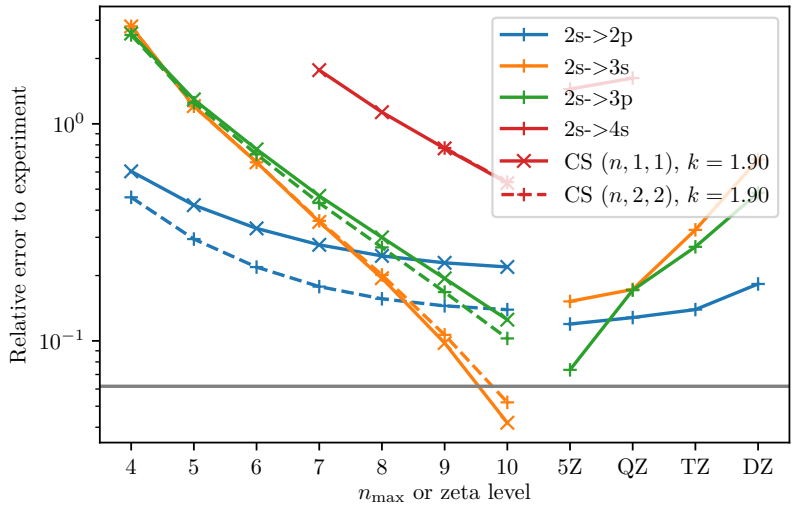
$\Rightarrow$ Flexible to exploit discretisation-specific properties

molsturm interface: Linked codes

Coulomb-Sturmian based MP2 and FCI



Coulomb-Sturmian and Gaussian based ADC(2)



- FCI from `pyscf`[1]
- Coulomb Sturmians from `sturmint`[2]

- ADC(2) from `adcman`[3]
- Gaussians from `libint`[4] or `libcint`[5]

[1] Q. Sun et al. WIREs Comput Mol Sci, **8**, e1340 (2017).

[2] J. E. Avery and M. F. Herbst. `https://molsturm.org/sturmint` (2018)

[3] M. Wormit et al. Mol. Phys., **112**, 774 (2014).

[4] E. Valeyev et al. *evaleev/libint: 2.3.1* (2017).

[5] Q. Sun. J. Comput. Chem., **36**, 1664 (2015)

Evaluating integrals: Useful relations

- Potential-weighted orthonormality relation:

$$\int_{\mathbb{R}^3} \varphi^*_{\mu'}(\underline{\boldsymbol{r}}) \frac{n}{kr} \varphi_\mu(\underline{\boldsymbol{r}}) \, \mathrm{d}\underline{\boldsymbol{r}} = \delta_{\mu\mu'}$$

- Fourier-transform of Coulomb Sturmians:

$$\begin{aligned}\hat{\varphi}_\mu(\underline{\boldsymbol{p}}) &= \frac{1}{(2\pi)^{3/2}} \int_{\mathbb{R}^3} \varphi_\mu(\underline{\boldsymbol{r}}) e^{-\imath \underline{\boldsymbol{p}} \cdot \underline{\boldsymbol{x}}} \, \mathrm{d}\underline{\boldsymbol{r}} \\ &= \frac{4k^{5/2}}{(k^2+p^2)^2} Y_{\lambda,l,m}(\underline{\hat{\boldsymbol{u}}})\end{aligned}$$

with $\underline{\boldsymbol{p}} \equiv (p_1, p_2, p_3)^T$, $\lambda \equiv n-1$ and

$$\underline{\hat{\boldsymbol{u}}} \equiv \left(\frac{2kp_1}{k^2+p^2}, \frac{1kp_2}{k^2+p^2}, \frac{2kp_3}{k^2+p^2}, \frac{k^2-p^2}{k^2+p^2} \right)^T$$

- Fock transformation to hyperspherical harmonics $Y_{\lambda,l,m}(\underline{\boldsymbol{u}})$[1]

[1] V. Fock. Zeitschrift für Physik, **98**, 145 (1935)

One-electron integrals

- Overlap:

$$S_{\mu',\mu} = \delta_{m',m}\delta_{l',l} \begin{cases} n = n' & 1 \\ |n - n'| = 1 & s^{(l)}_{n,n+1} \in \mathbb{R} \\ \text{else} & 0 \end{cases}$$

where

$$s^{(l)}_{n,n+1} = -\frac{1}{2}\sqrt{\frac{(n-l)(n+l+1)}{n(n+1)}}$$

- Nuclear attraction:

$$V_{\mu',\mu} = -\delta_{\mu',\mu}\frac{kZ}{n}$$

- Kinetic:

$$T_{\mu',\mu} = k^2(\delta_{\mu',\mu} - S_{\mu',\mu})$$

Two-electron integrals

- ERI tensor from kernel $I_{\mu\nu}$

$$(\varphi_{\mu_1}\varphi_{\mu_2}|\varphi_{\mu_3}\varphi_{\mu_4}) = \sum_{\mu\nu} \mathcal{C}^{\mu}_{\mu_2\mu_1} I_{\mu\nu} \mathcal{C}^{\nu}_{\mu_3\mu_4}$$

  where

$$I_{\mu\mu'} = \delta_{ll'}\delta_{mm'} I^{(l)}_{nn'},$$

  thus sparse and storable (30 kB for $n = 20$).

- The $\mathcal{C}^{\mu}_{\mu_1\mu_2}$ are the coefficients in

$$\varphi^*_{\mu_1}(\underline{\boldsymbol{r}})\varphi_{\mu_2}(\underline{\boldsymbol{r}}) = \sum_{\mu} \mathcal{C}^{\mu}_{\mu_1\mu_2} \varphi_{\mu}(2k, \underline{\boldsymbol{r}}),$$

  again sparse (220 MB for $n = 20$).

$\Rightarrow$ Like *exact* density fitting

Evaluating molecular CS 1e integrals[1]

- Let $\tau \equiv (A, n, l, m)$ and $\varphi_\tau(\underline{\boldsymbol{r}}) \equiv \varphi_\mu(\underline{\boldsymbol{r}} - \underline{\boldsymbol{R}}_A)$
- Key quantity: Shibuya-Wulfman integrals

$$\begin{aligned}\mathfrak{S}_{\tau\tau'} &= \int_{\mathbb{R}^3} \varphi_\tau^*(\underline{\boldsymbol{r}}) \left(\frac{-\Delta + k^2}{2k^2}\right) \varphi_{\tau'}(\underline{\boldsymbol{r}}) \, \mathrm{d}\underline{\boldsymbol{r}} \\ &= (2\pi)^{3/2} \sum_{\mu''} f_{n'',l''}(S) \, Y_{l''}^{m''}(\hat{\underline{\boldsymbol{S}}}) \, c_{\mu'';\mu,\mu'}\end{aligned}$$

with $\underline{\boldsymbol{S}} = k(\underline{\boldsymbol{R}}_A - \underline{\boldsymbol{R}}_{A'})$, $c_{\mu'';\mu,\mu'}$ sparse and pre-computable

- $f_{nl}(S)$: analytic in S, related to CS radial part $R_{nl}(S)$

[1] J. E. Avery and J. S. Avery. vol. 70 of *Advances in Quantum Chemistry*, 265 – 324. Academic Press (2015)

Evaluating molecular CS ERI integrals[1]

- Following a similar idea as before

$$(\varphi_{\tau_1}\varphi_{\tau_2}|\varphi_{\tau_3}\varphi_{\tau_4}) \simeq \sum_{\mu\nu} \mathcal{C}^{\tau}_{\tau_2\tau_1} I_{\tau\tau'} \mathcal{C}^{\tau'}_{\tau_3\tau_4}$$

where

$$\varphi_{\tau_1}(\underline{\boldsymbol{r}})\varphi^*_{\tau_2}(\underline{\boldsymbol{r}}) \simeq \sum_{\tau} \mathcal{C}^{\tau}_{\tau_2\tau_1} \varphi_{\tau}(2k, \underline{\boldsymbol{r}})$$

with $\sum_\tau \equiv \sum_{A_1\mu} + \sum_{A_2\mu}$.

- For this: Solve once linear system (thus $\simeq$):

$$\sum_{\tau'} S_{\tau\tau'}(2k, \underline{\boldsymbol{S}})\, \mathcal{C}^{\tau'}_{\tau_2\tau_1} = \int_{\mathbb{R}^3} \varphi^*_{\tau}(2k, \underline{\boldsymbol{r}})\varphi_{\tau_1}(\underline{\boldsymbol{r}})\varphi^*_{\tau_2}(\underline{\boldsymbol{r}})\, \mathrm{d}\underline{\boldsymbol{r}}$$

[1] J. E. Avery and J. S. Avery. vol. 70 of *Advances in Quantum Chemistry*, 265 – 324. Academic Press (2015)