Coulomb Sturmian basis functions in electronic structure theory

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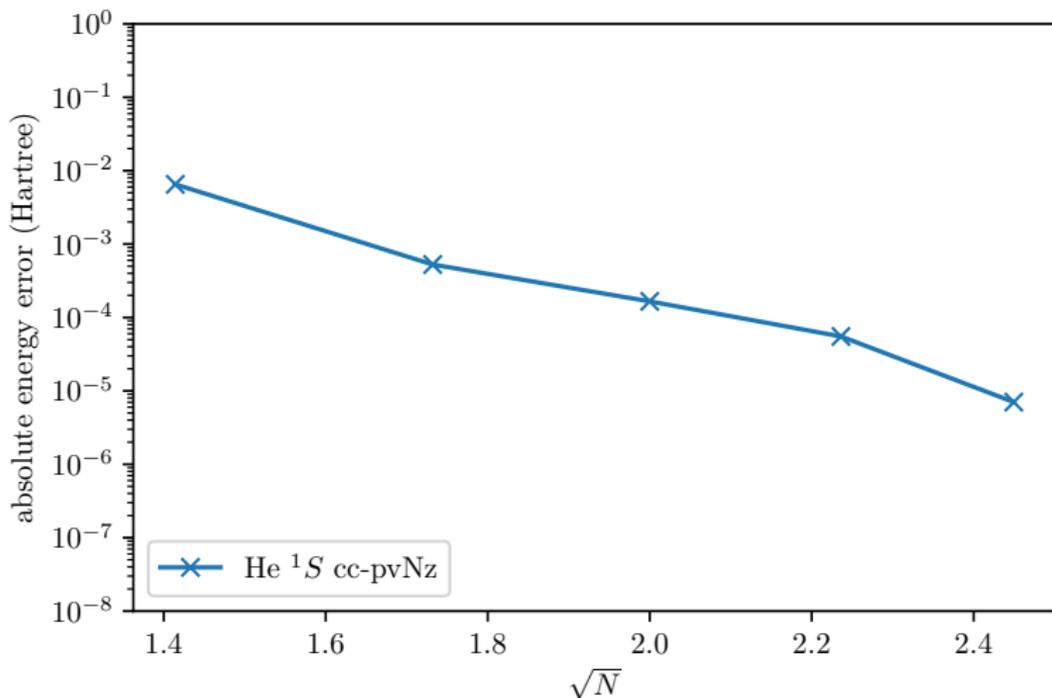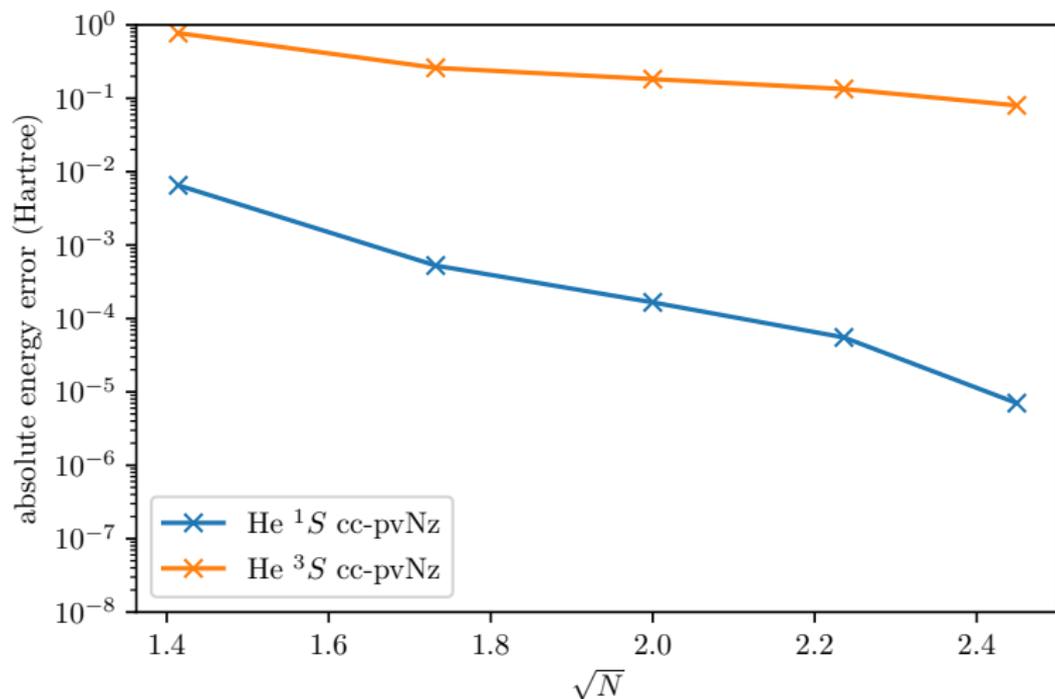
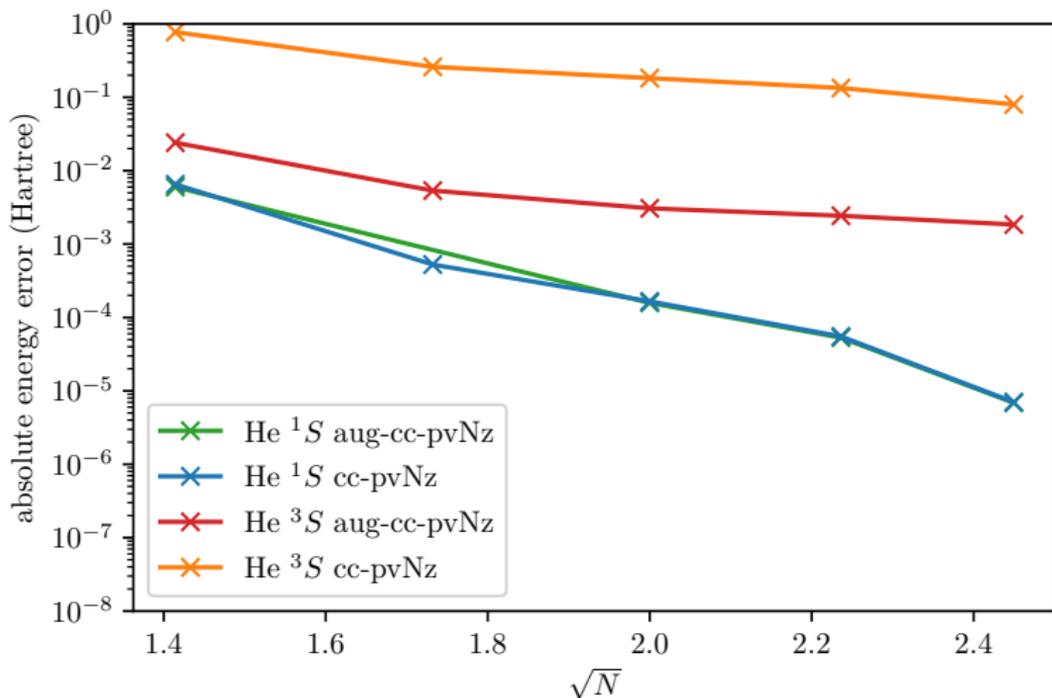# The electronic structure of Helium

- Should be easy ... right?
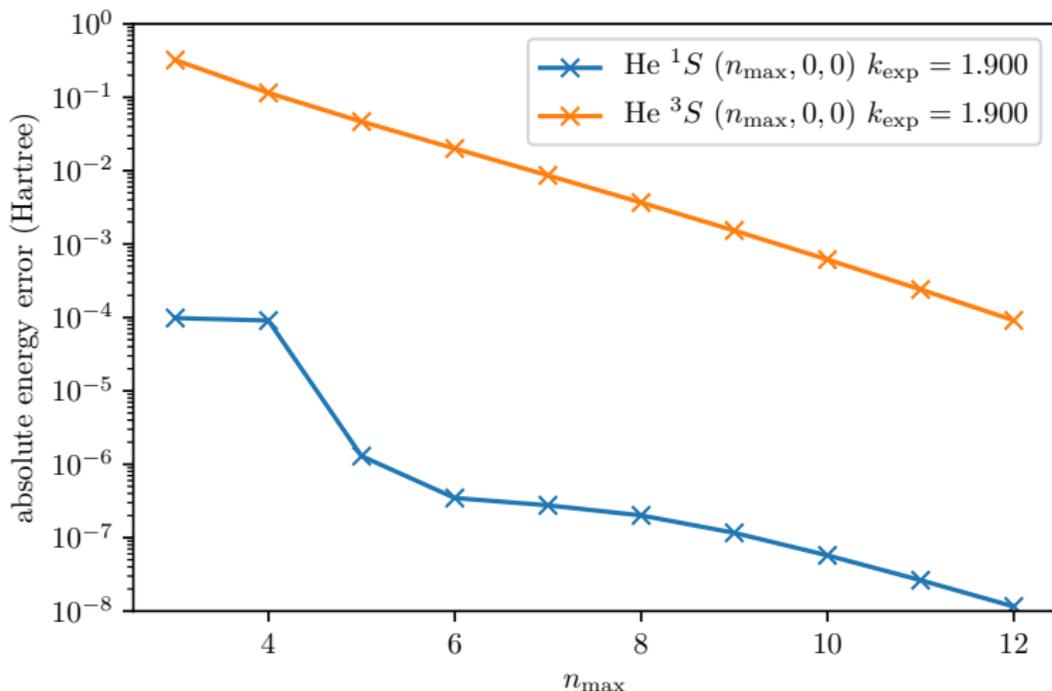
The electronic structure of Helium

- Ups . . .

The electronic structure of Helium

- Ahh ... Augmentation!

The electronic structure of Helium

- Let's try ... Coulomb Sturmians

Helium triplet . . . direct comparison

A simple example   CS properties   CS convergence studies   Ongoing work   A & Q
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The electronic structure of Helium
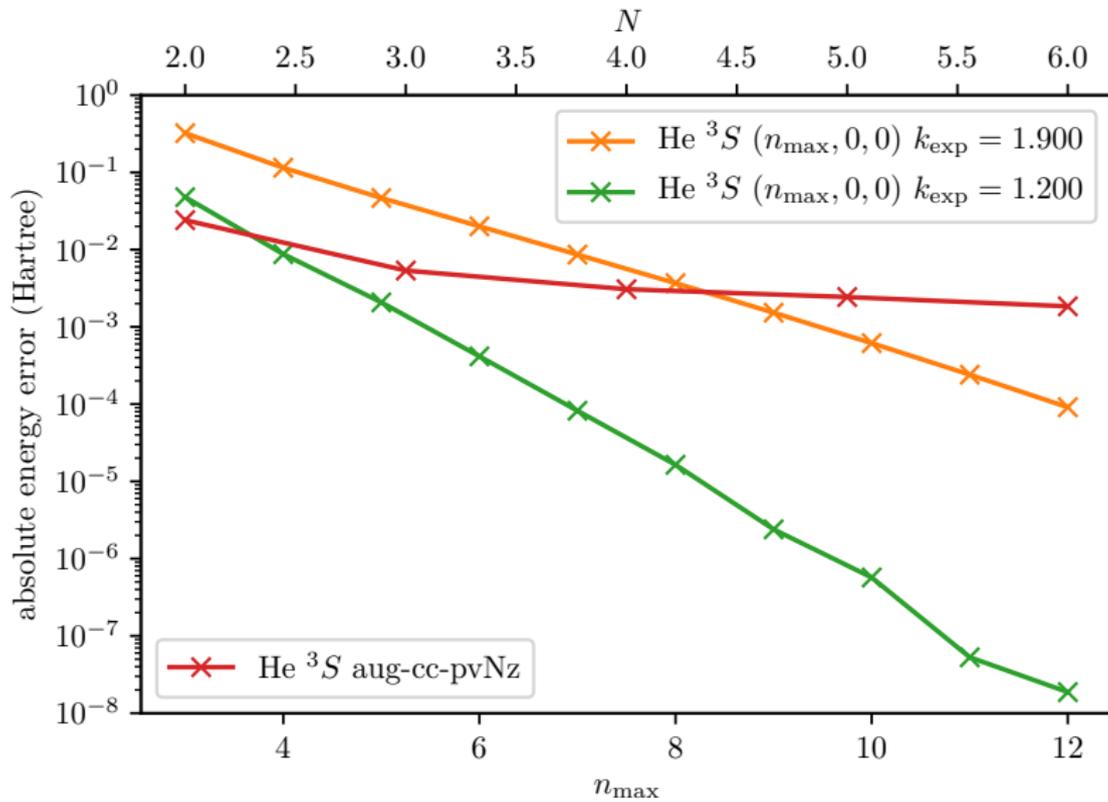
Beyond Gaussian-type orbitals

- 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

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

  ⇒ Implementation inside `molsturm`[1] and `sturmint`

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

Contents

1. Properties of Coulomb Sturmian functions

2. Coulomb-Sturmian HF convergence studies

3. Ongoing work and speculative outlook
   - Helium ^3S state
   - Correlated quantum-chemical methods
   - Modelling continuum-like states

Contents

A simple example	CS properties	CS convergence studies	Ongoing work	A & Q
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The functional form of Coulomb Sturmians

Coulomb Sturmians

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

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

- 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

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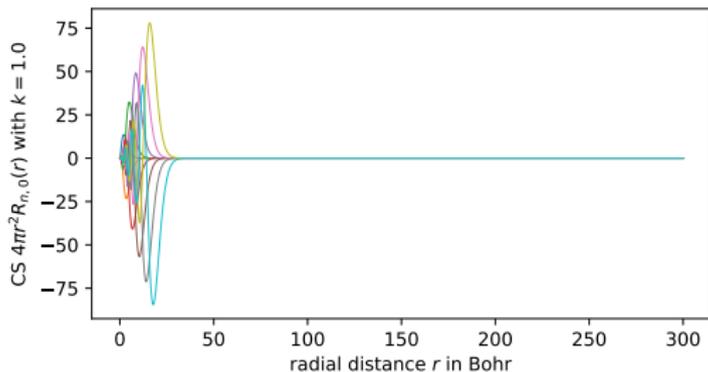
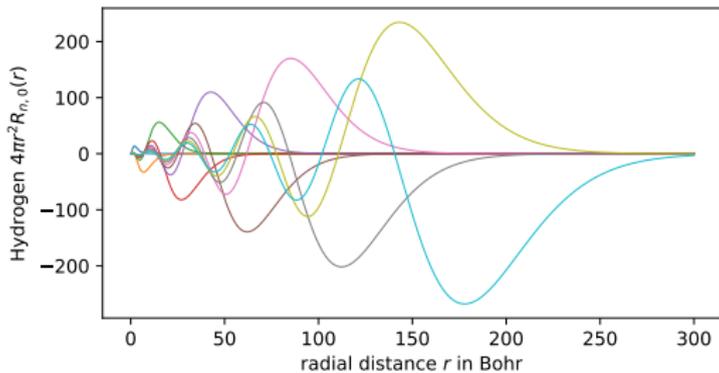$\Rightarrow$ Sturm-Liouville equation[2]

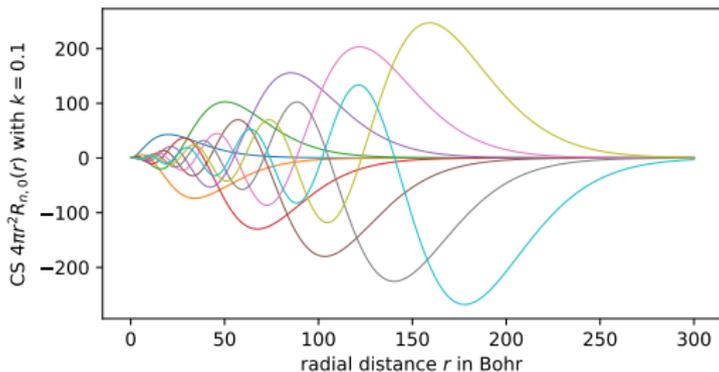[1] H. Shull and P.-O. Löwdin. J. Chem. Phys., **30**, 617 (1959)

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

A simple example	CS properties	CS convergence studies	Ongoing work	A & Q
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The functional form of Coulomb Sturmians

Examples of the Coulomb Sturmian radial parts

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

	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 ($k = 0.1$)

A simple example | CS properties | CS convergence studies | Ongoing work | A & Q
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Properties of Coulomb Sturmians
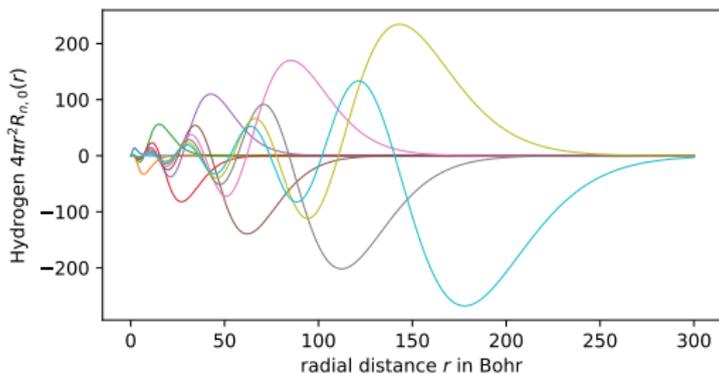
Classical turning point and concentration

- Classical turning point: Zero kinetic energy

- Hydrogen-like functions:

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

- Coulomb Sturmians:

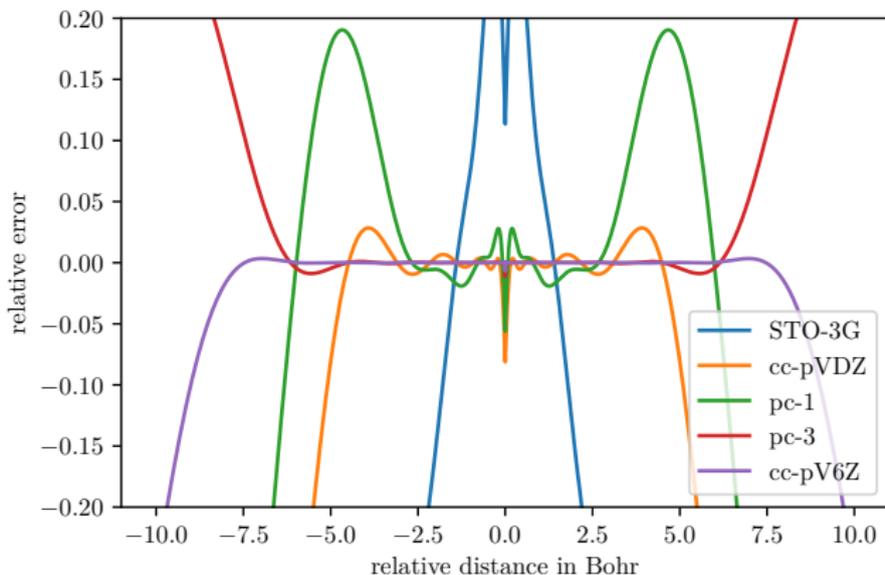$$-\frac{k^2}{2} = -\beta_n \frac{Z}{r_T} \iff r_T = \frac{2Z\beta_n}{k^2} = \frac{2n}{k}$$

$\Rightarrow$ Hydrogen-like functions escape too fast into continuum
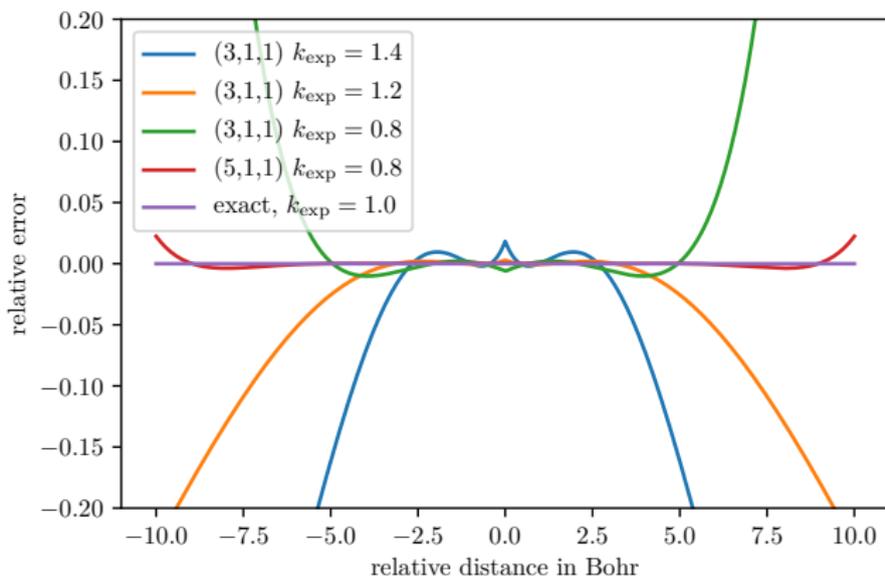
$\Rightarrow$ Exponent k allows to tune concentration of CS

Coulomb-Sturmians vs Gaussians (for hydrogen)

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

A simple example   CS properties   CS convergence studies   Ongoing work   A & Q
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Properties of Coulomb Sturmians
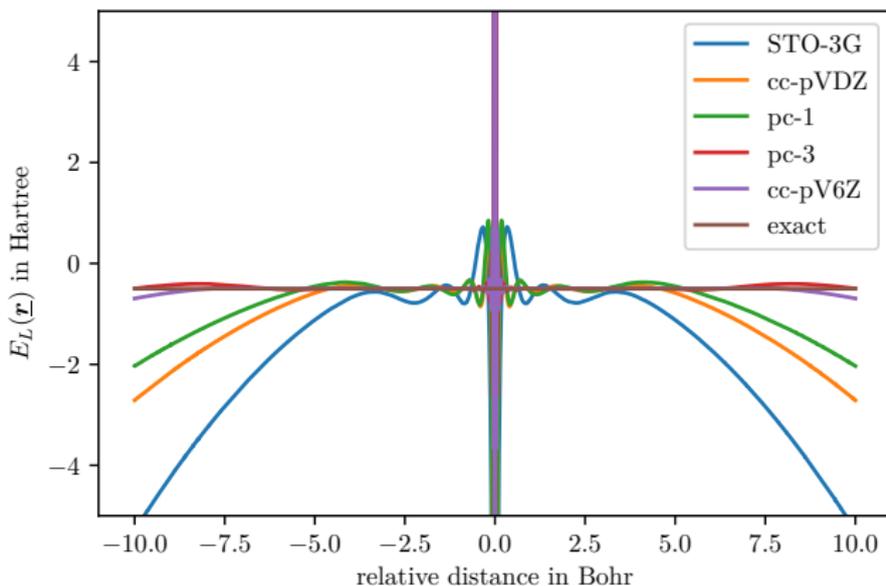
Coulomb-Sturmians vs Gaussians (for hydrogen)

$$\varphi_\mu^{\mathsf{CS}}(\underline{r}) = 2k^{3/2} P_{nl}(2kr) \exp(-kr) \cdot Y_l^m(\hat{\underline{r}})$$
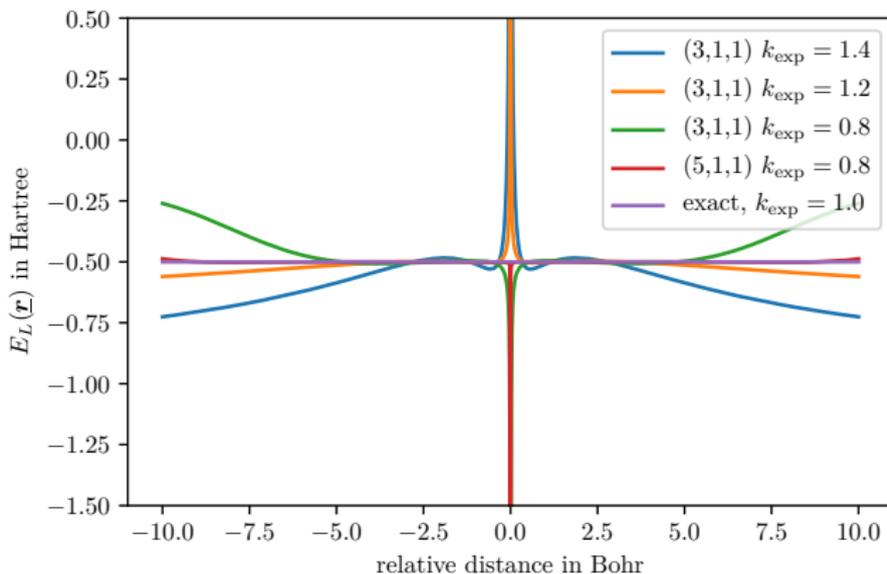
Coulomb-Sturmians vs Gaussians (for hydrogen)

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

Coulomb-Sturmians vs Gaussians (for hydrogen)

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

(Atomic) Coulomb-Sturmians properties overview

- Complete (Schauder) basis[1][2]

- Correct physics: 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]

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[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)

Evaluating integrals: Useful relations

- Potential-weighted orthonormality relation:
$$\int_{\mathbb{R}^3} \varphi_{\mu'}^*(\underline{r}) \frac{n}{kr} \varphi_\mu(\underline{r}) \, \mathrm{d}\underline{r} = \delta_{\mu\mu'}$$

- Fourier-transform of Coulomb Sturmians:
$$\hat{\varphi}_\mu(\underline{p}) = \frac{1}{(2\pi)^{3/2}} \int_{\mathbb{R}^3} \varphi_\mu(\underline{r}) e^{-\imath \underline{p} \cdot \underline{x}} \, \mathrm{d}\underline{r}$$

$$= \frac{4k^{5/2}}{(k^2 + p^2)^2} Y_{\lambda,l,m}(\hat{\underline{u}})$$

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

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

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

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

A simple example	CS properties	CS convergence studies	Ongoing work	A & Q
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Evaluating Coulomb Sturmian integrals

One-electron integrals

- Overlap:

$$S_{\mu',\mu} = \delta_{m',m}\delta_{l',l} \left\{ \begin{array}{cc} n = n' & 1 \\ |n - n'| = 1 & s_{n,n+1}^{(l)} \in \mathbb{R} \\ \text{else} & 0 \end{array} \right.$$

where

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

- 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

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

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

$\Rightarrow$ Like *exact* density fitting

A simple example | CS properties | CS convergence studies | Ongoing work | A & Q
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Hints at molecular Coulomb Sturmians

Evaluating molecular CS 1e integrals[1]

- Let $\tau \equiv (A, n, l, m)$ and $\varphi_\tau(\underline{r}) \equiv \varphi_\mu(\underline{r} - \underline{R}_A)$

- Key quantity: Shibuya-Wulfman integrals

$$\mathfrak{S}_{\tau\tau'} = \int_{\mathbb{R}^3} \varphi_\tau^*(\underline{r}) \left(\frac{-\Delta + k^2}{2k^2} \right) \varphi_{\tau'}(\underline{r}) \, \mathrm{d}\underline{r}$$

$$= (2\pi)^{3/2} \sum_{\mu''} f_{n'',l''}(S) \, Y_{l''}^{m''}(\hat{\underline{S}}) \, c_{\mu'';\mu,\mu'}$$

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

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

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[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

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

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

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

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

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[1] 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:

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

- Basis set construction:[1] Additional restrictions

$$n \le n_{\mathsf{max}} \qquad l \le l_{\mathsf{max}} \qquad m \le m_{\mathsf{max}}$$

- Restriction by m_{max}, sometimes l_{max} neglected
- ⇒ Physically motivated

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

| A simple example | CS properties | CS convergence studies | Ongoing work | A & Q |
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Coulomb-Sturmian HF convergence studies

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

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

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

  - $\Rightarrow$ $n_{\max}$ controls radial discretisation
  - $\Rightarrow$ $l_{\max}$ and $m_{\max}$ control angular discretisation

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

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

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

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

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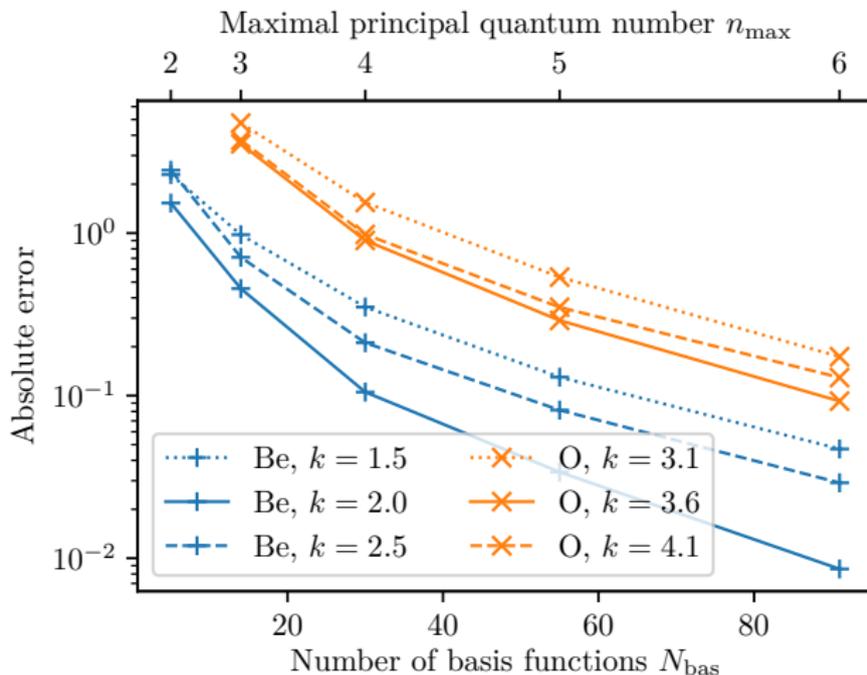
[1] M. F. Herbst, J. E. Avery and A. Dreuw. Physical Review A, **99**, 012512 (2019)

Basis progressions: Energy versus basis size[1]
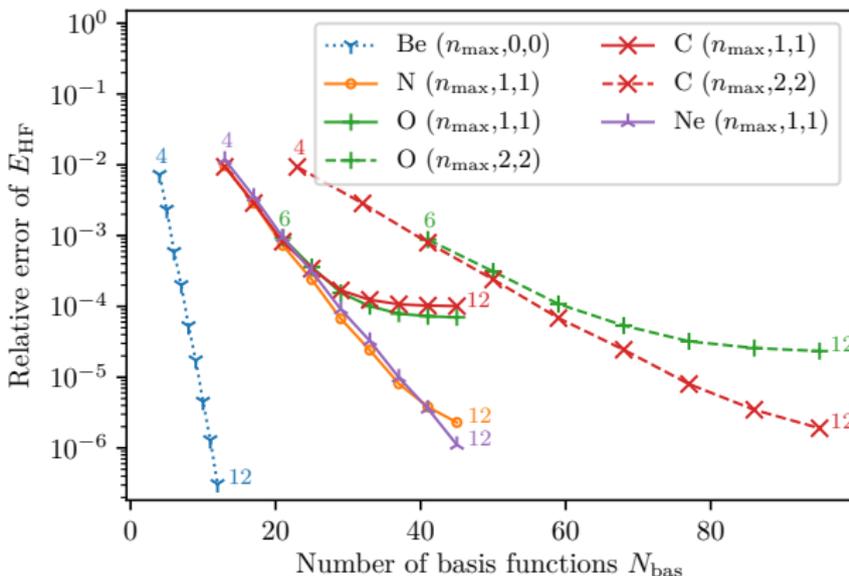
[1]M. F. Herbst, J. E. Avery and A. Dreuw. Physical Review A, **99**, 012512 (2019)

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Energy convergence: Deviating behaviour of elements[1]

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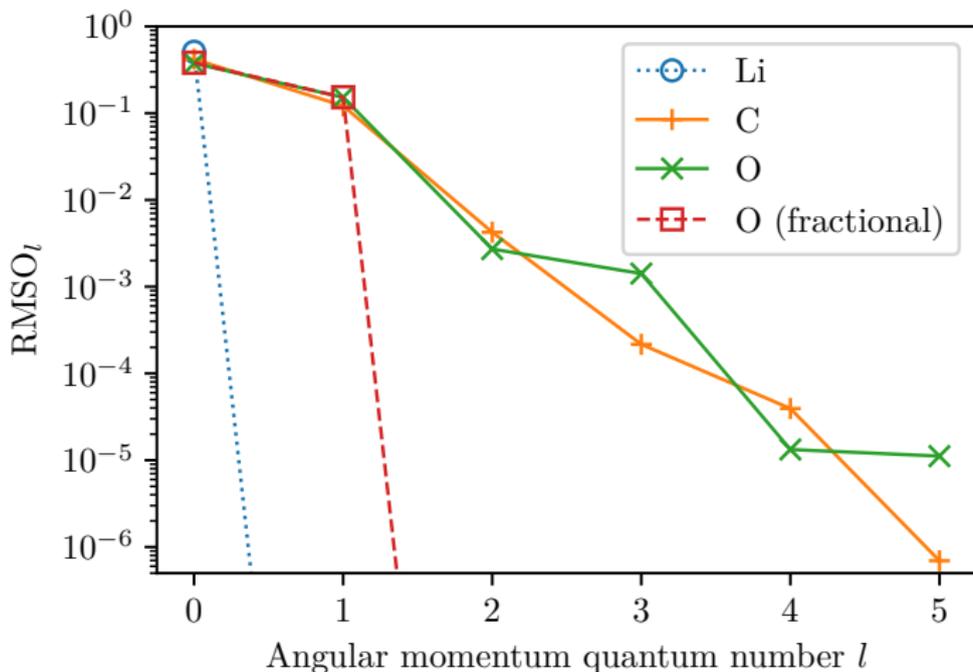
[1]M. F. Herbst, J. E. Avery and A. Dreuw. Physical Review A, **99**, 012512 (2019)

Root mean square coefficient value per l

- Root mean square occupied coefficient par AM l:

$$\text{RMSO}_l = \sqrt{\sum_\mu \sum_i \sum_{\sigma \in \{\alpha,\beta\}} \frac{1}{N_{\text{elec}}^\sigma \, N_{\text{bas},l}} \left(C_{\mu,i}^\sigma \, f_{ii}^\sigma \right)^2}$$

where i runs over orbitals, μ over basis functions and

N_{elec}^σ Number of electrons with spin σ

f_{ii}^σ Occupation number

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

- Measure for importance of l in HF wave function

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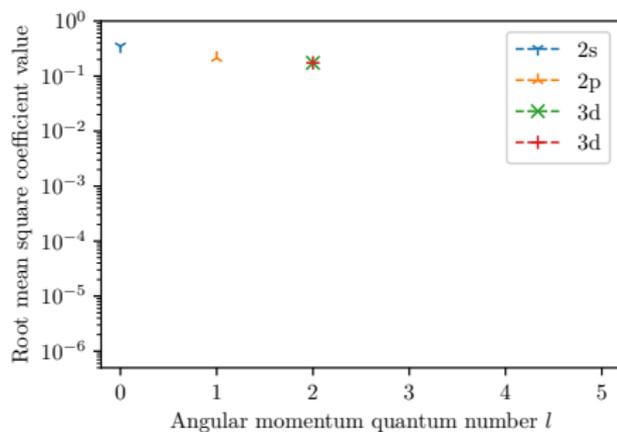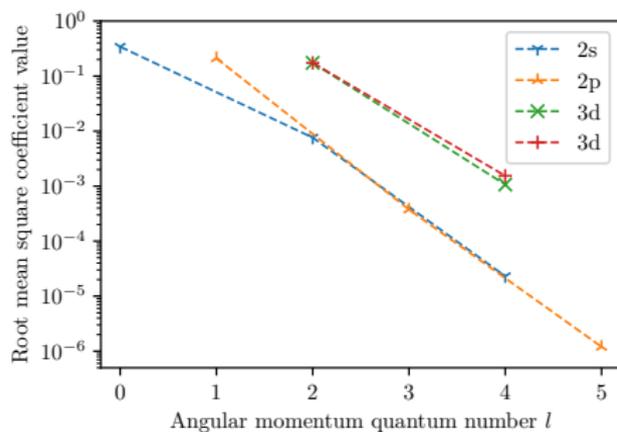
[1] M. F. Herbst, J. E. Avery and A. Dreuw. Physical Review A, **99**, 012512 (2019)

Basis progressions: Carbon[1]

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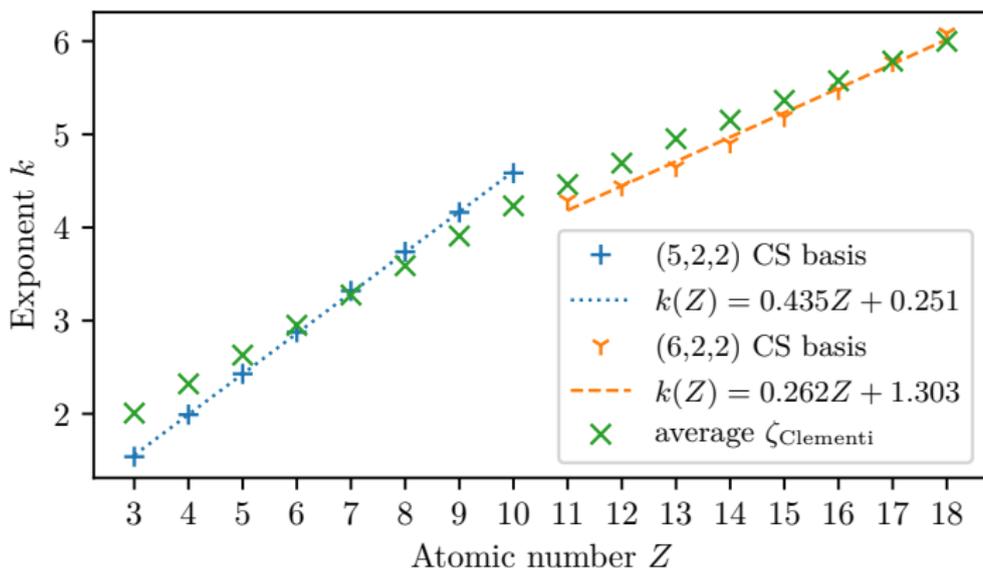
k-dependence terms carbon[1]

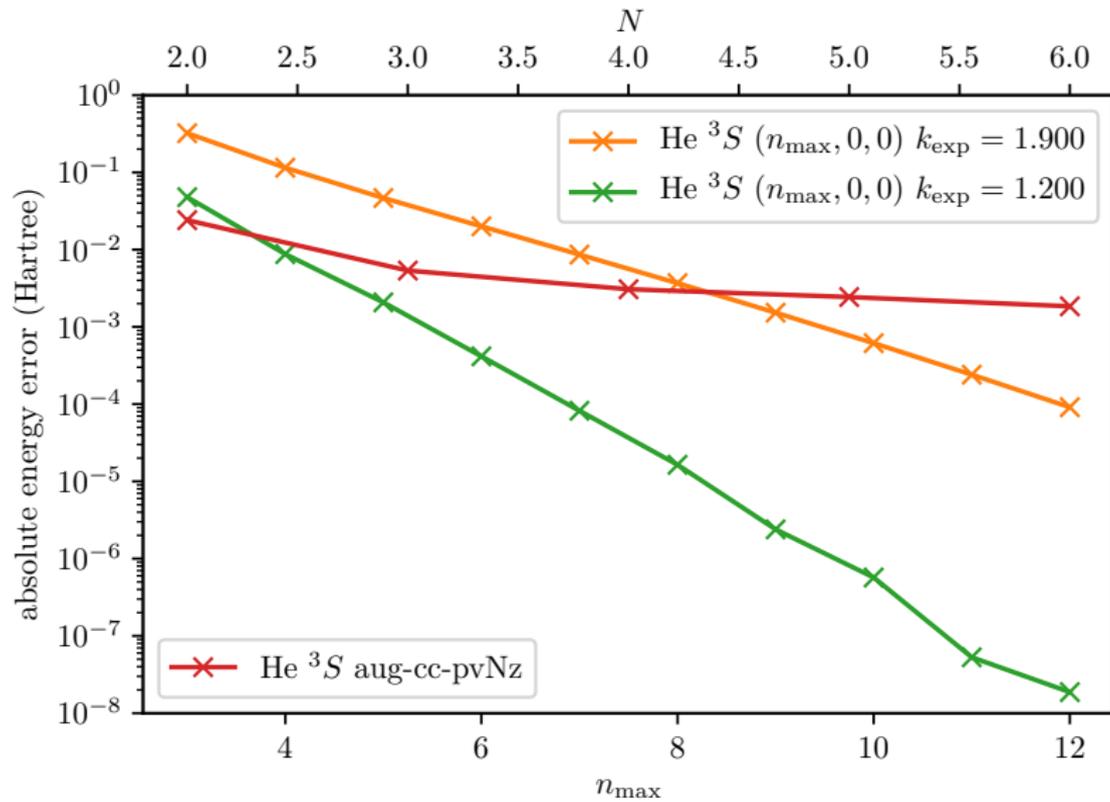[1]M. F. Herbst, J. E. Avery and A. Dreuw. Physical Review A, **99**, 012512 (2019)

k-dependence terms carbon[1]

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

Optimal exponent versus Clementi exponents[1]

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[1] M. F. Herbst, J. E. Avery and A. Dreuw. Physical Review A, **99**, 012512 (2019)
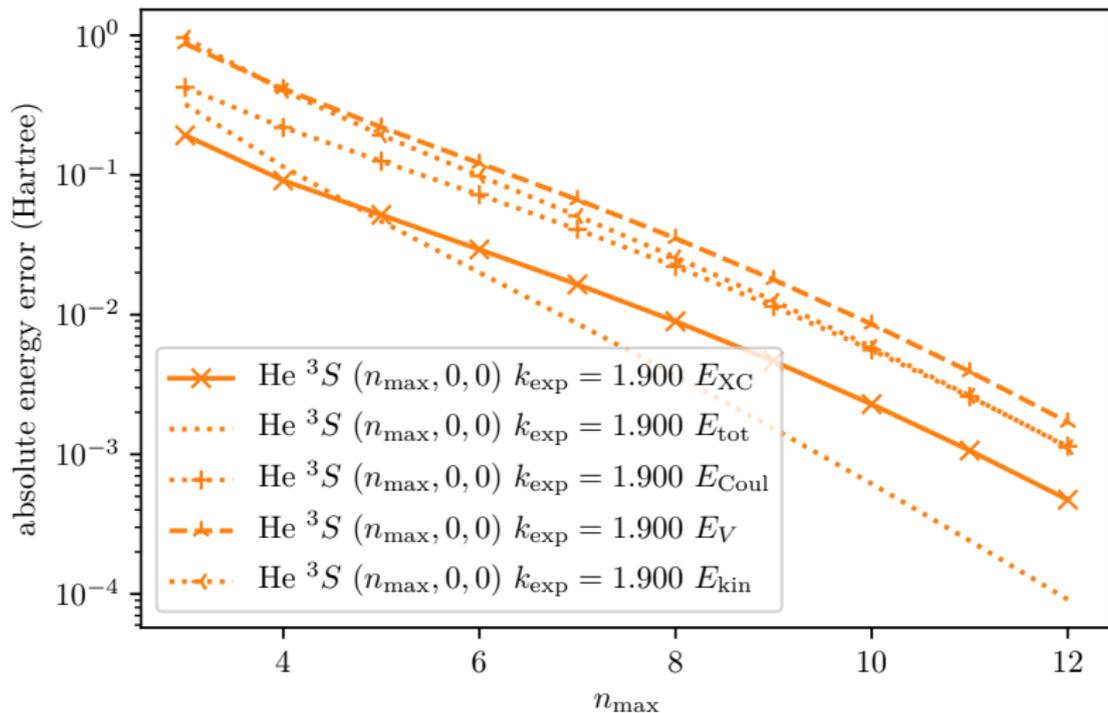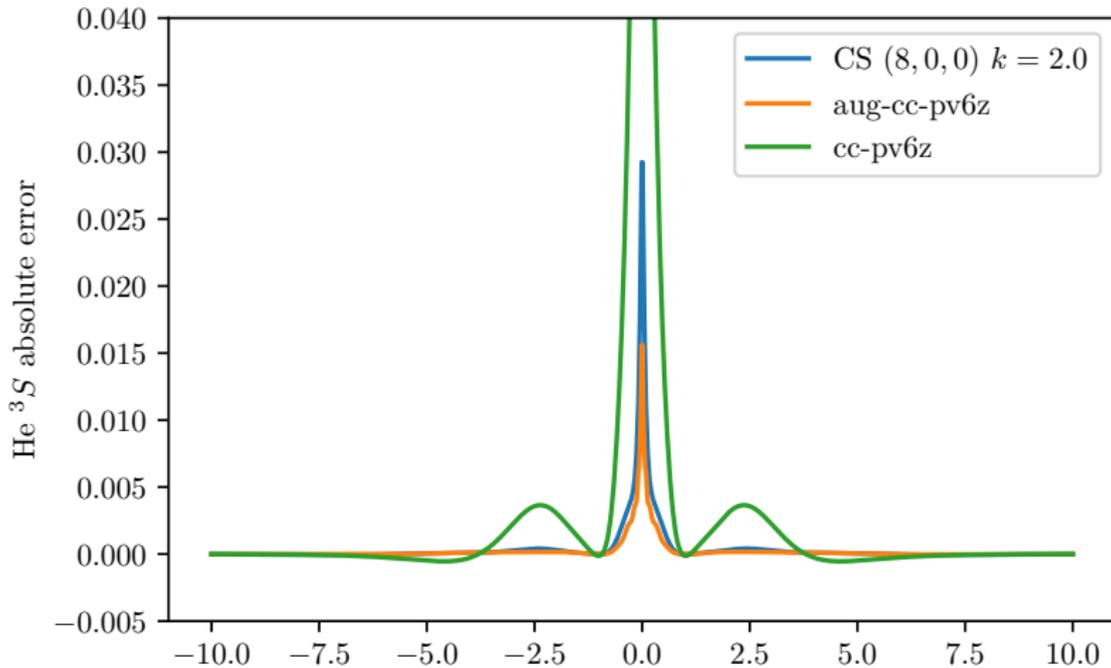
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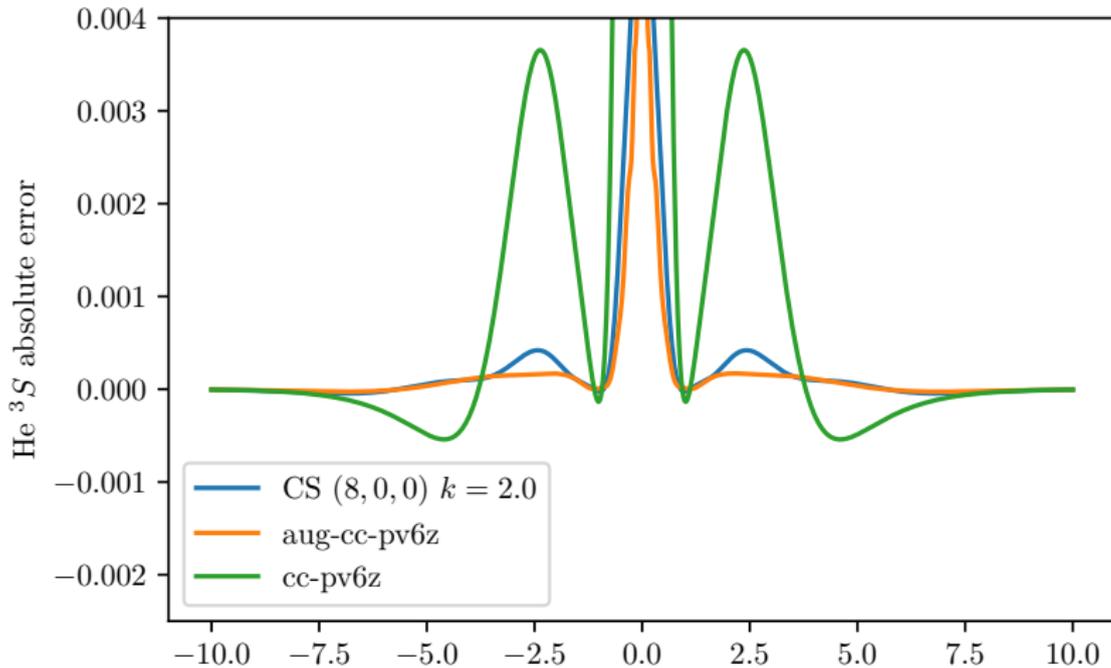# Returning to our example from before . . .

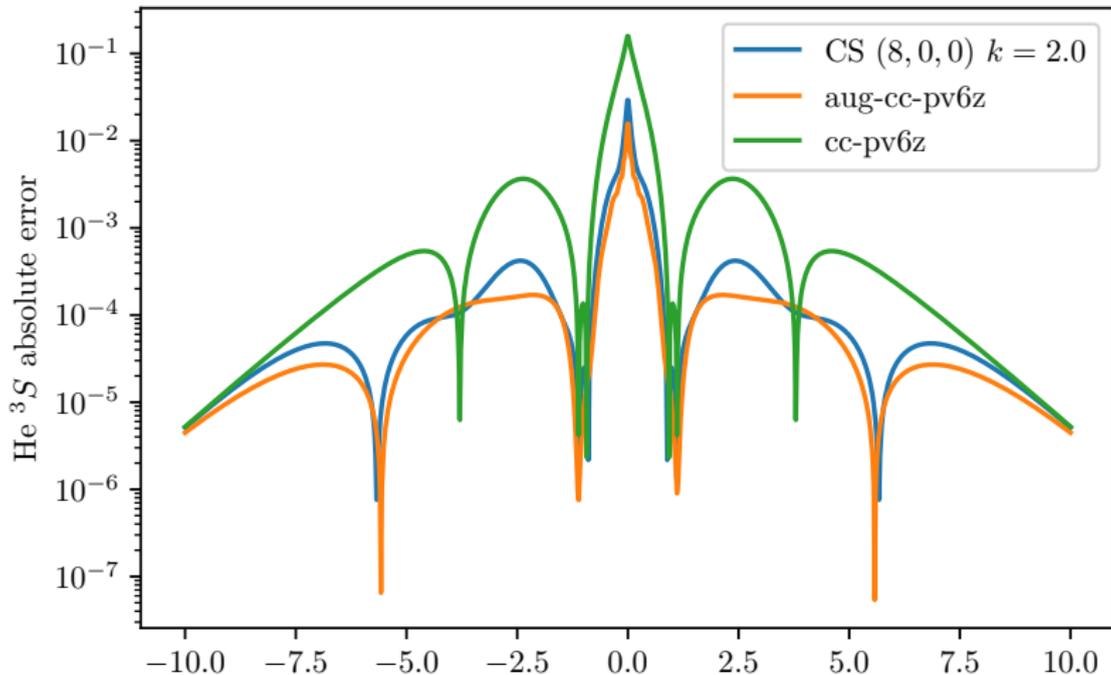# Helium ^3S term-wise convergence

Helium ^3S term-wise convergence
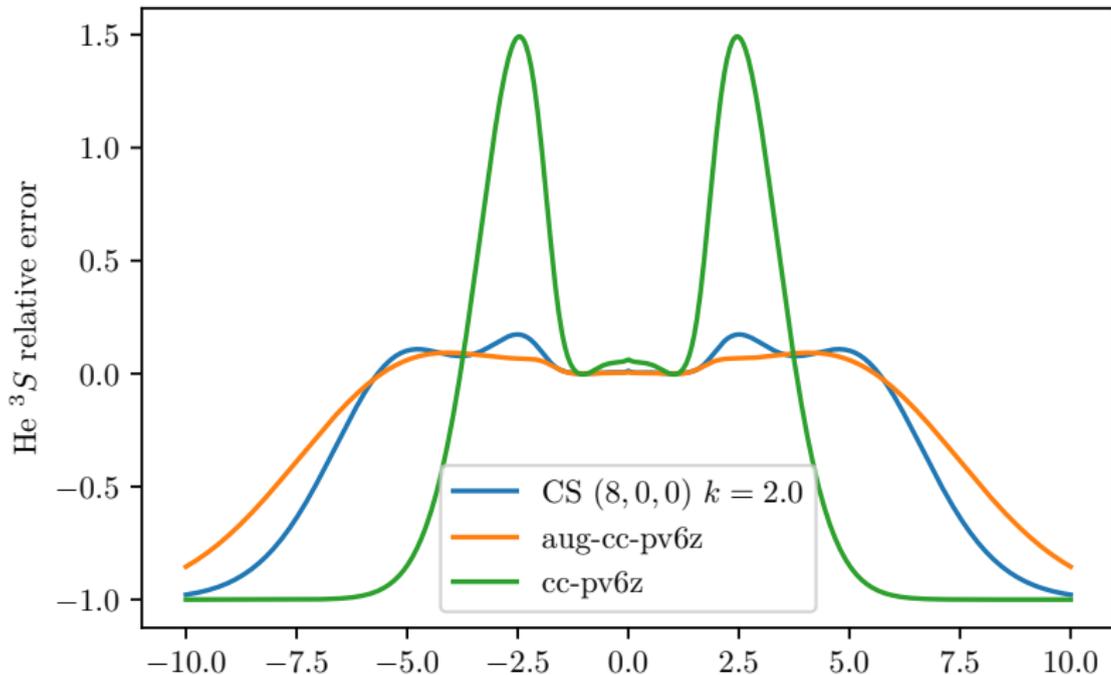
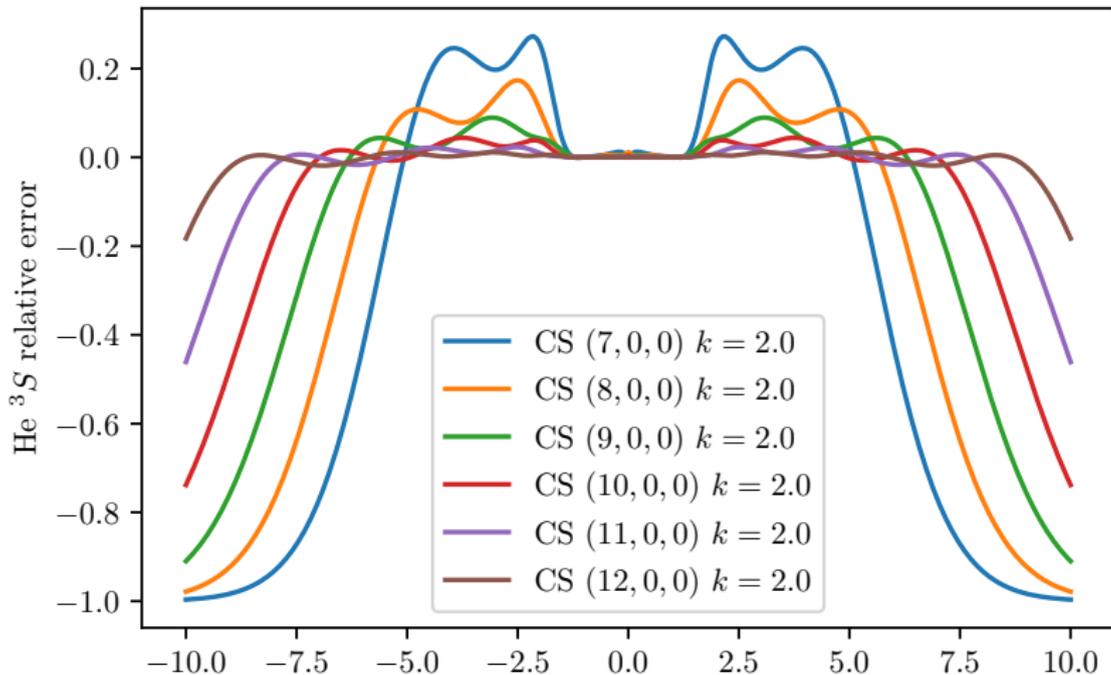# Helium ^3S density error

Helium ^3S density error

Helium ^3S density error
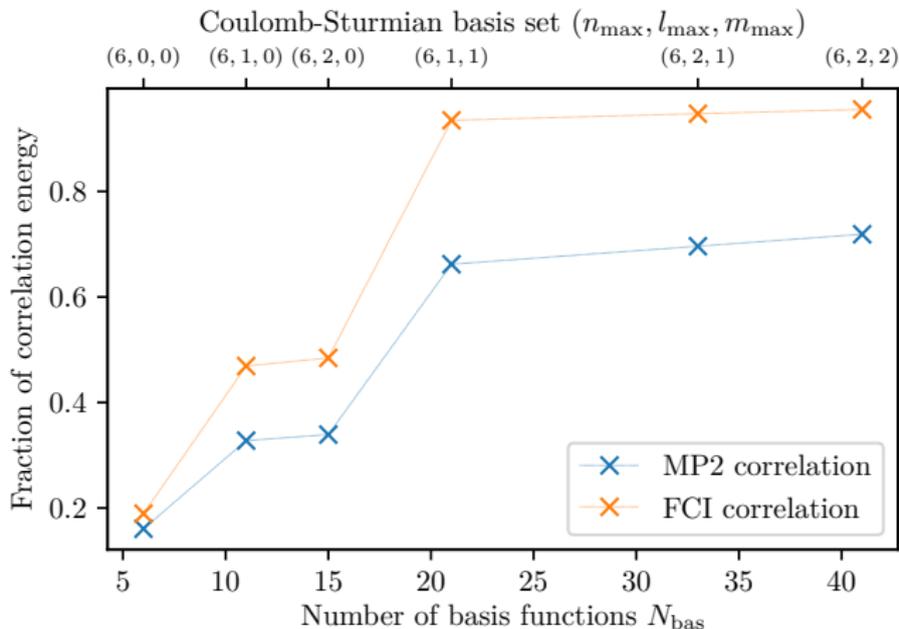
Helium ^3S density error

Helium ^3S density error

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

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

Coulomb-Sturmian basis set $(n_{\max}, l_{\max}, m_{\max})$

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

A simple example	CS properties	CS convergence studies	**Ongoing work**	A & Q
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Correlated quantum-chemical methods

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

- Beryllium, $(5, 1, 1)$ CS basis
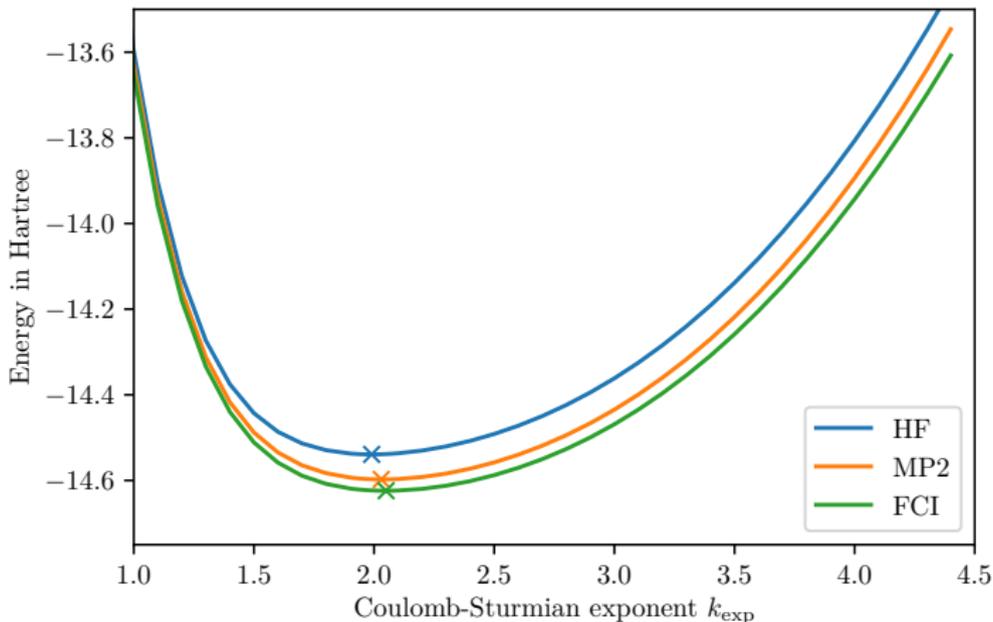
[1] M. F. Herbst. Ph.D. thesis, Ruprecht-Karls-Universität Heidelberg (2018)

| A simple example | CS properties | CS convergence studies | Ongoing work | A & Q |
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Correlated quantum-chemical methods

ADC(2) absolute error

- Beryllium CS progressions vs. Gaussians

ADC(2) absolute error

- Beryllium CS progressions vs. Gaussians

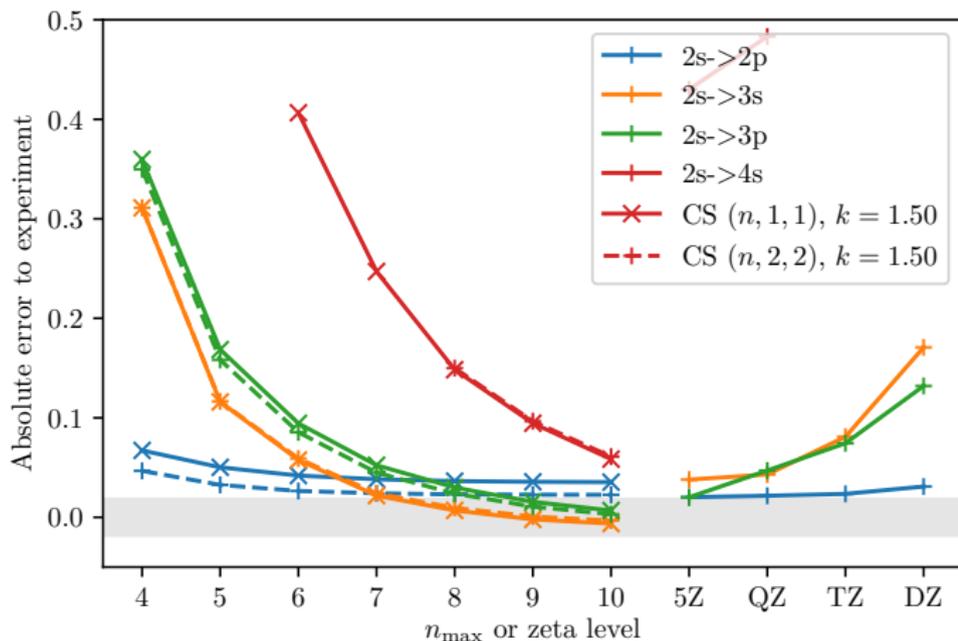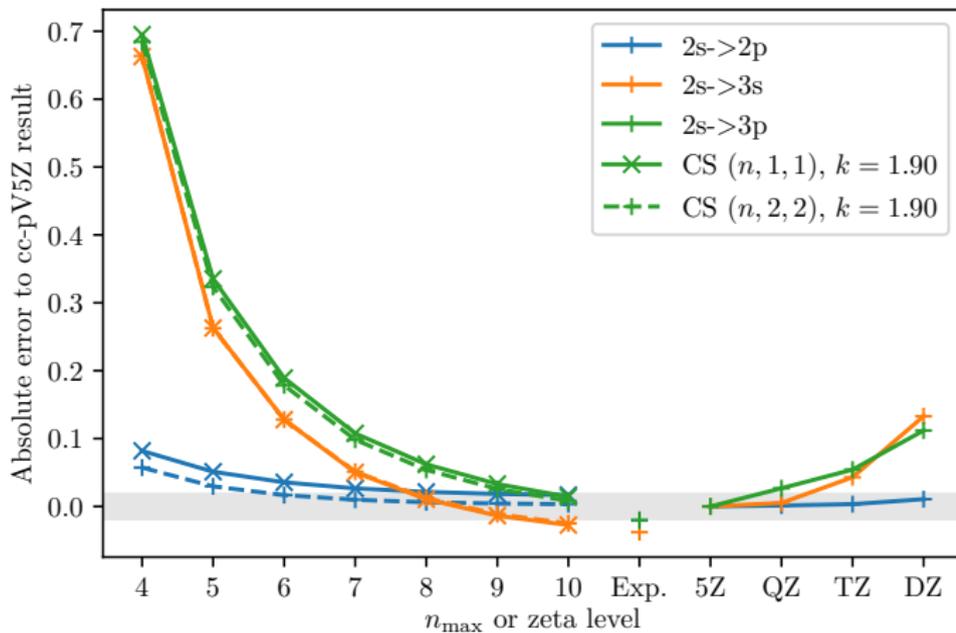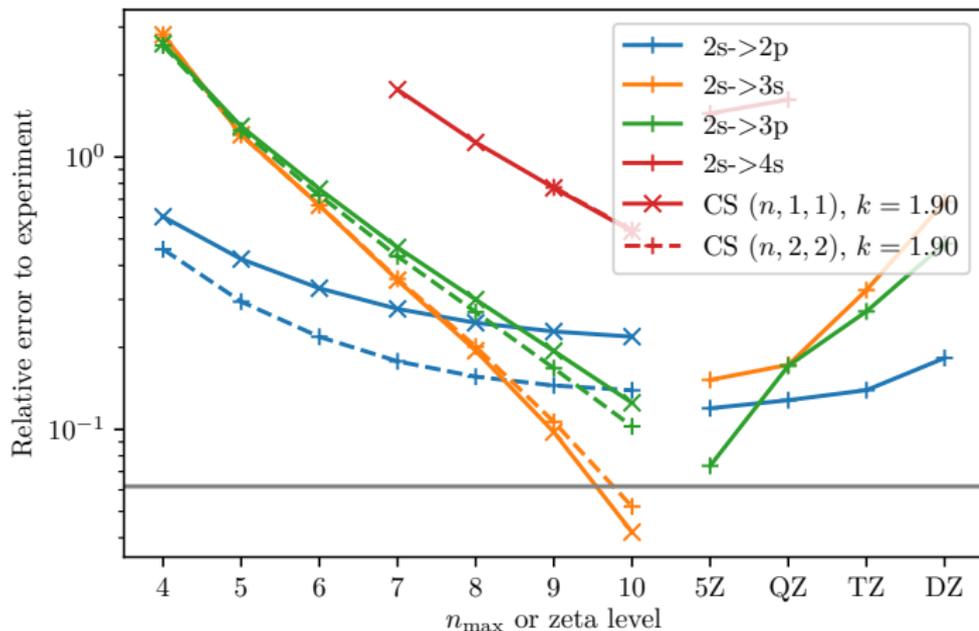| A simple example | CS properties | CS convergence studies | Ongoing work | A & Q |
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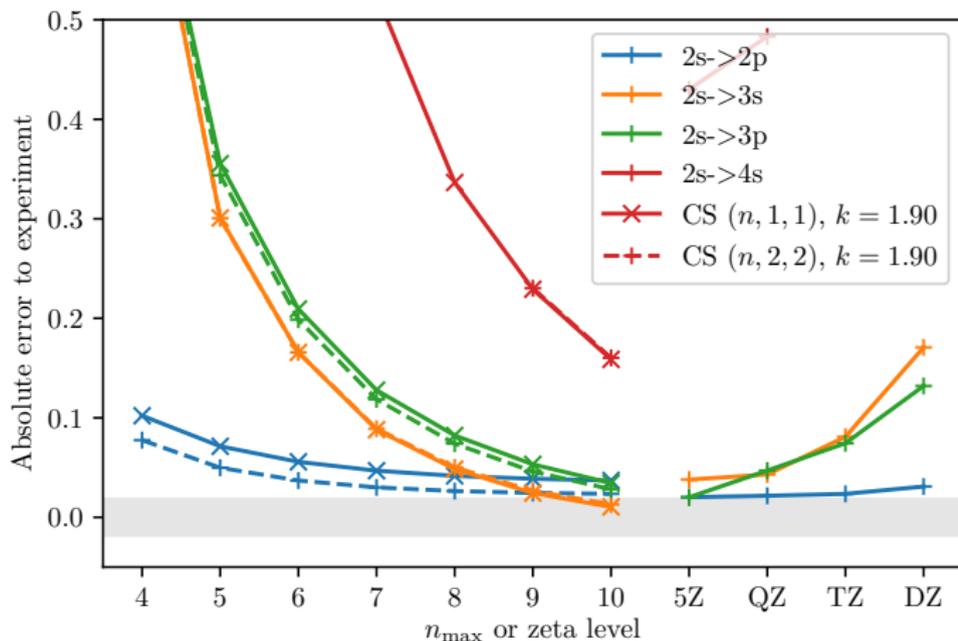
Correlated quantum-chemical methods

ADC(2) Gaussian error

- Beryllium CS progressions vs. Gaussians

ADC(2) relative error

- Beryllium CS progressions vs. Gaussians

k-targeted FCI for generalised Sturmians

- Generalised Sturmians: Atomic N-electron basis
- Relation $E = -k^2/2$ generalises to these Sturmians
- k-targeted formulation:
    - Instead of solving for E, solve directly for parameters k
- $\Rightarrow$ Each state has a different set of ks
- Similar formulation for Coulomb-Sturmian basis?
    - $\Rightarrow$ Hints how to do this in an atomic CI-like context[1]
    - Not aware of any HF / CI work on this for a CS basis

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[1] J. E. Avery and J. S. Avery. *Generalized Sturmians and Atomic Spectra.*
World Scientific (2006)

Coulomb-Sturmians for correlated methods

- Convergence behaviour?

- Systematic basis set construction?

- Contracted Coulomb-Sturmian basis sets?

- Basis sets with multiple ks?

- Molecular Coulomb Sturmians?

- k-targeted formulations for HF and configuration interaction?

- k-targeted formulations for molecular problems?

A simple example	CS properties	CS convergence studies	Ongoing work	A & Q
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Modelling continuum-like states

CS-based modelling of continuum-like states ?

- Atomic CS functions are a complete basis
- Parameters k can be tuned to capture features of interest
- k-targeted formulation could automatise this

- Sturmian-type functions successfully employed to treat photoionisation processes [1] [2] [3]

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[1] D. M. Mitnik, F. D. Colavecchia, G. Gasaneo and J. M. Randazzo. Comp. Phys. Comm., **182**, 1145 (2011)

[2] J. M. Randazzo, D. Mitnik, G. Gasaneo, L. U. Ancarani and F. D. Colavecchia. Europ. Phys. J.D, **69**, 189 (2015)

[3] C. M. Granados-Castro, L. U. Ancarani, G. Gasaneo and D. M. Mitnik. vol. 73 of *Advances in Quantum Chemistry*, 3 – 57. Academic Press (2016)

Coulomb Sturmians in essence

- Complete, exponential-type basis
  - ⇒ May capture cusp and decay behaviour
  - ⇒ Apparently less care required to converge special systems

- 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

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[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)

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James Avery   Andreas Dreuw

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)

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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
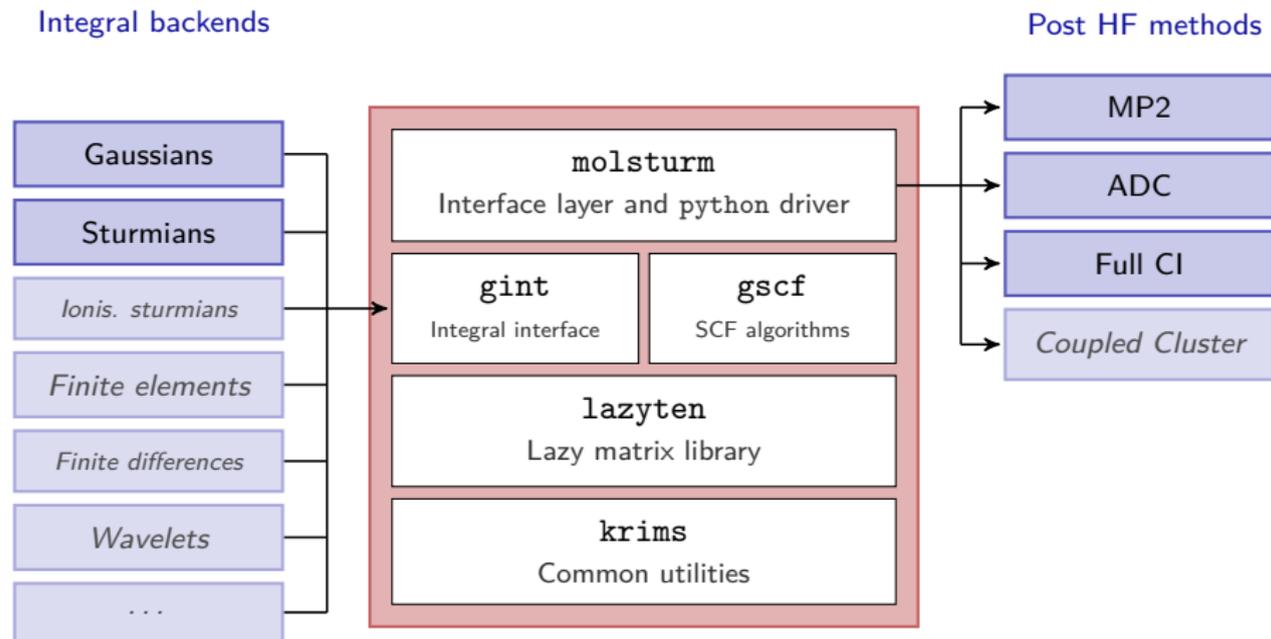 - Rapid prototyping, testing and analysis

$\Rightarrow$ Explore methods across basis function types[1,2]

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[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)
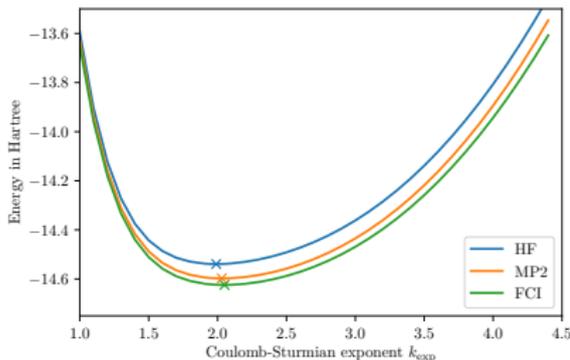 - Common in Post-HF: *Working equations*

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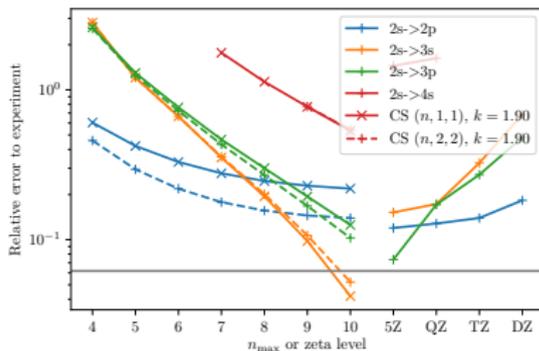
- ADC(2) from `adcman`[3]
- Gaussians from `libint`[4] or `libcint`[5]

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[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)