Coulomb Sturmians in electronic structure theory

A first look at investigating convergence properties

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Introduction

- Molecular density: Sum of atomic densities (in good approximation)

⇒ Linear combination of atomic orbitals (LCAO) ansatz
⇒ Employ atom-centred functions as discretisation basis

- Physical features ⇒ Exponential-type orbitals
- But: Contracted Gaussian-type orbitals (cGTO) less challenging integrals
- Investigated here: **Coulomb Sturmians** (CS) [1]
- Measure for discretisation error: **Local energy**

$$E_L(\underline{\boldsymbol{r}}) = \frac{\left(\hat{\mathcal{H}}\Phi\right)(\underline{\boldsymbol{r}})}{\Phi(\underline{\boldsymbol{r}})} \qquad \begin{array}{ll} \hat{\mathcal{H}}: & \text{Schrödinger operator} \\ \Phi: & \text{Trial wave function} \end{array}$$

- Fluctuation about exact energy: Local measure for error (see RHS)

Coulomb Sturmians: Mathematical properties

- Atom-centred, **exponential-type** basis function

$$\chi_{nlm}(\underline{\boldsymbol{r}}) = \chi_\mu(\underline{\boldsymbol{r}}) = P_{nl}(kr)e^{-kr}Y_{lm}(\theta,\varphi)$$

- Satisfy hydrogen-like Schrödinger equation [1]

$$\left(-\frac{1}{2}\Delta - \beta_n\frac{Z}{r} - E\right)\chi_\mu(\underline{\boldsymbol{r}}) = 0$$

with potential-scaling factor $\beta_n = \frac{kn}{Z}$ and energy $E = -\frac{k^2}{2}$.

- **Complete** basis for Sobolev space $H^1(\mathbb{R}^3)$ irrespective of k

⇒ Correctly reproduce **nuclear cusp** and **long-range decay** (see fig. 1)

- One-electron integrals are sparse and analytic
- Electron-repulsion integral tensor formed by contraction

$$(\mu_1\mu_2|\mu_3\mu_4) = \sum_{\mu\mu'}\left(\mathcal{C}^{\mu}_{\mu_1,\mu_2}\right)^* I_{\mu\mu'}\,\mathcal{C}^{\mu'}_{\mu_3,\mu_4}$$

where $\mathcal{C}$ and I are sparse, pre-computable tensors.

⇒ Ideal case for contraction-based formalism and lazy matrices [2, 3]

Convergence with basis set size

- CS basis set: Triple of maximal quantum numbers $(n_{\max}, l_{\max}, m_{\max})$
- $n_{\max}$ controls discretisation of **radial part** of wave function
- $l_{\max}$, $m_{\max}$ controls discretisation of **angular part**

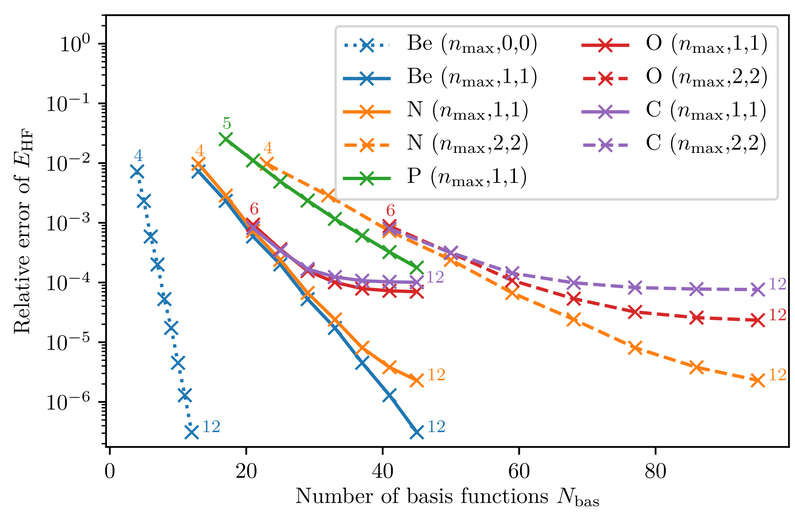

Figure 3. Relative error in Hartree-Fock energy versus the number of basis functions for selected CS basis sets of the form $(n_{\max}, l_{\max}, m_{\max})$. The lines connect progressions of increasing $n_{\max}$.

- Convergence speed in progression depends on $l_{\max}$
- Some curves bend off around $n_{\max} = 8$ ⇒ Error in **angular part dominates**
- Be only requires s-functions ($l^{\mathrm{HF}}_{\max} = 0$) at HF level
- N and P require s- and p-functions ($l^{\mathrm{HF}}_{\max} = 1$) at HF level
- O requires even higher angular momentum (f, g *and above*)

⇒ Artefact of unrestricted Hartree-Fock

- Post-HF convergence: Need at least $l^{\mathrm{HF}}_{\max} + 1$ [3]

Outlook

- More detailed investigation of Post-HF methods
- Excited states, e.g. algebraic-diagrammatic construction (ADC)
- Extension to molecular Sturmians
- Systematic comparison of Coulomb Sturmian and Gaussian basis sets

Local energies of cGTO and CS bases

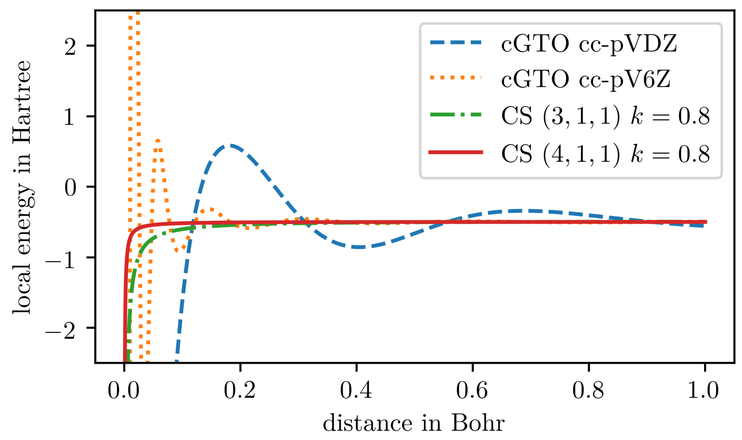

Figure 1. Local energy resulting from solving the hydrogen atom employing the indicated CS or cGTO basis sets. The deviation of this quantity from the exact ground state energy of -0.5 Hartree quantifies the discretisation error.

Implementation: molsturm [2, 4]

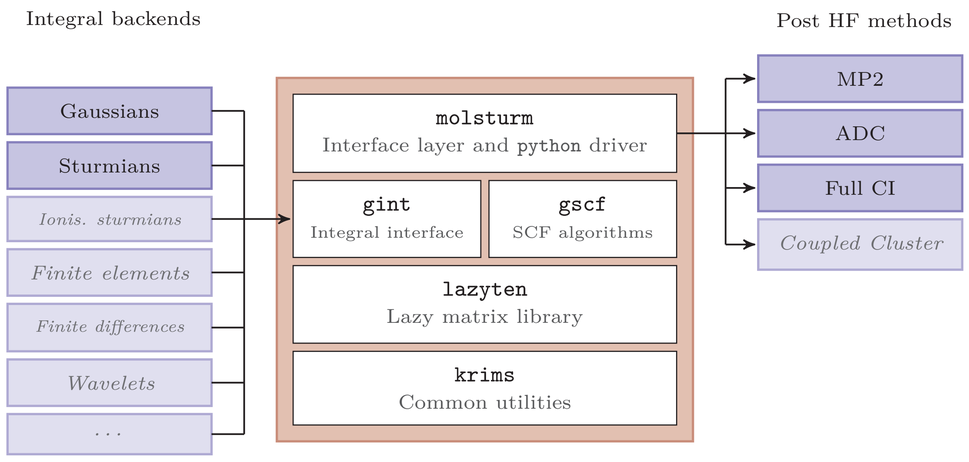

Figure 2. Structure of the molsturm modular electronic-structure theory framework [2, 3]

- Contraction-based self-consistent field (SCF) scheme
- Basis-function-independent SCF [2, 3]
- Plug-and-play integral libraries in modular framework

Convergence with exponent k

- All CS functions in basis share the same exponent k

⇒ Free parameter, but basis is complete for any choice of k

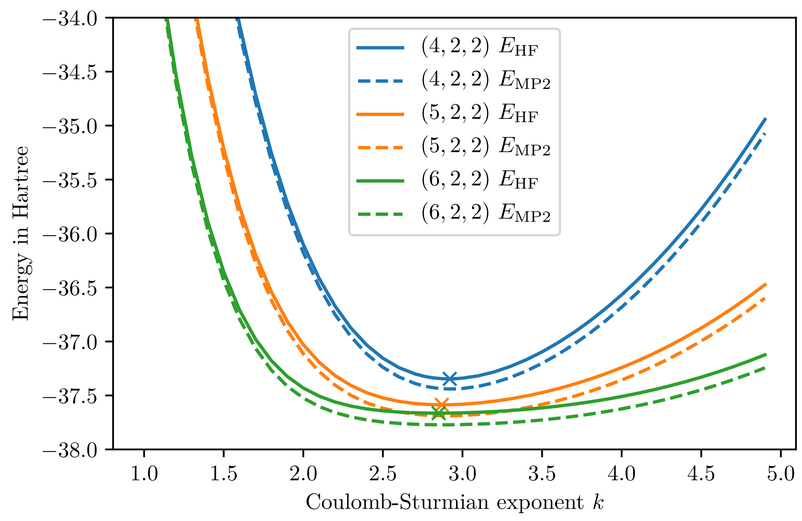

Figure 4. Unrestricted HF and unrestricted MP2 ground state energies of carbon versus CS exponent k. The optimal exponent at HF level is marked with a cross.

- **Optimal exponent** can be found [3]
- Depends on $n_{\max}$ and electronic structure method
- k influences **convergence speed** of CS discretisation
- Effect of using optimal k reduces as $n_{\max}$ increases

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References

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