New approaches towards a finite-element based Hartree-Fock method

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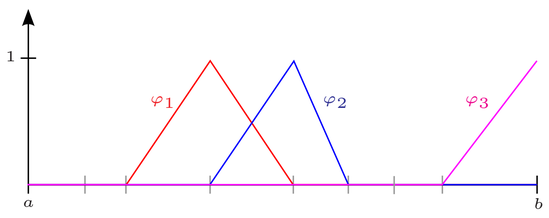
Introduction

Employing a finite-element basis in electronic structure calculations provides a novel alternative to the commonly used atom-centered (AC) basis functions [1, 2]. Expected properties:

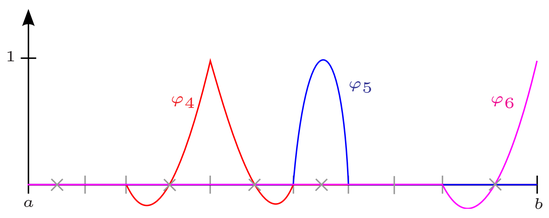
- Sparse, nearly diagonal-dominant matrices
- Easy parallelisation of code
- Adaptive refinement: Grid adapts to molecular structure automatically
- Intrinsic multiscale methods possible
- Reduction of implicit bias imposed by AC basis
- More basis functions required compared to a pure AC basis

Finite Elements (FEs)

- Piecewise polynomials $\{\varphi_j\}$ on discretised grid
- Only non-zero in a few grid cells $\Rightarrow$ strongly **localised**
- At **nodal points** $\{\underline{\boldsymbol{x}}_k\}$: $\varphi_j(\underline{\boldsymbol{x}}_k) = \delta_{jk}$
- Hence: $f(x) = \sum_j z_j \varphi_j \Rightarrow f(x_k) = z_k$



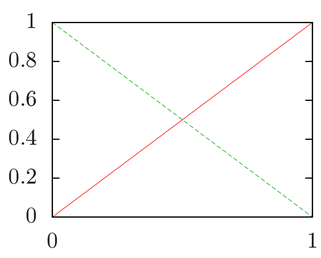
linear FEs on 1D grid



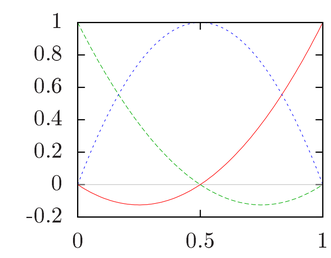
quadratic FEs on 1D grid

- **Affine map** $\mu_c : c_0 \to c$, between arbitrary cells on discretisation grid c and reference cell c_0
- Allows description of FEs by only considering a small number of **shape functions** $\{e_\alpha\}$ (Lagrange polynomials), defined on c_0:

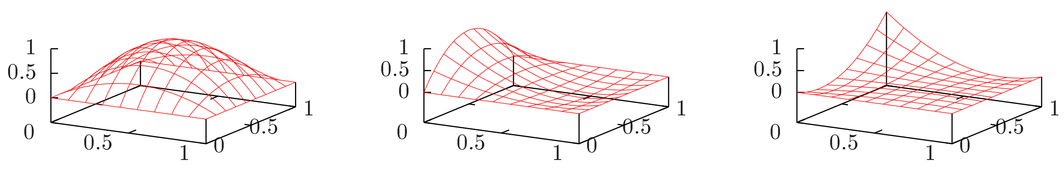
$$\varphi_k|_c(\underline{\boldsymbol{r}}) = e_\alpha\left(\mu_c^{-1}(\underline{\boldsymbol{r}})\right) \qquad \text{for some } \alpha$$



1D linear shape functions



1D quadratic shape functions



2D quadratic shape functions

- ***A posteriori* error estimation**: Estimate cell-wise error bound after calculation
- **Adaptive grid refinement**: Construct new grid, where cells with largest *a posteriori* error are refined
- **Intrinsic multiscale**: Refine grid in particular regions of space which are of special interest

Weak formulation of Hartree-Fock

- Consider orbital in FE basis: $\psi_i = \sum_j z_j^{(i)} \varphi_j$
- Define:

$$a(f,g) := \int_\Omega \frac{1}{2}\nabla f(\underline{\boldsymbol{r}}) \cdot \nabla g(\underline{\boldsymbol{r}}) + f(\underline{\boldsymbol{r}})\, V(\underline{\boldsymbol{r}})\, g(\underline{\boldsymbol{r}})\, \mathrm{d}\underline{\boldsymbol{r}} \tag{1}$$

$$V = \underbrace{V_0}_{\text{electron-nuclear interaction}} + \underbrace{V_H}_{\text{Hartree potential}} + \underbrace{V_x}_{\text{exchange potential}} \tag{2}$$

$$m(f,g) := \int_\Omega f(\underline{\boldsymbol{r}}) \cdot g(\underline{\boldsymbol{r}})\, \mathrm{d}\underline{\boldsymbol{r}} \tag{3}$$

- We solve the Hartree-Fock (HF) equation in its **weak form**

$$\begin{aligned} &\forall \varphi_j : a(\varphi_j, \psi_i) = \varepsilon_i\, m(\varphi_j, \psi_i) \\ \Rightarrow \qquad &\mathbf{A}\underline{\boldsymbol{z}}^{(i)} = \varepsilon_i \mathbf{M}\underline{\boldsymbol{z}}^{(i)} \end{aligned} \tag{4}$$

  where $A_{jk} = a(\varphi_j, \varphi_k)$ and $M_{jk} = m(\varphi_j, \varphi_k)$.
- Solving (4) in an FE basis is usually difficult due to the high dimensionality

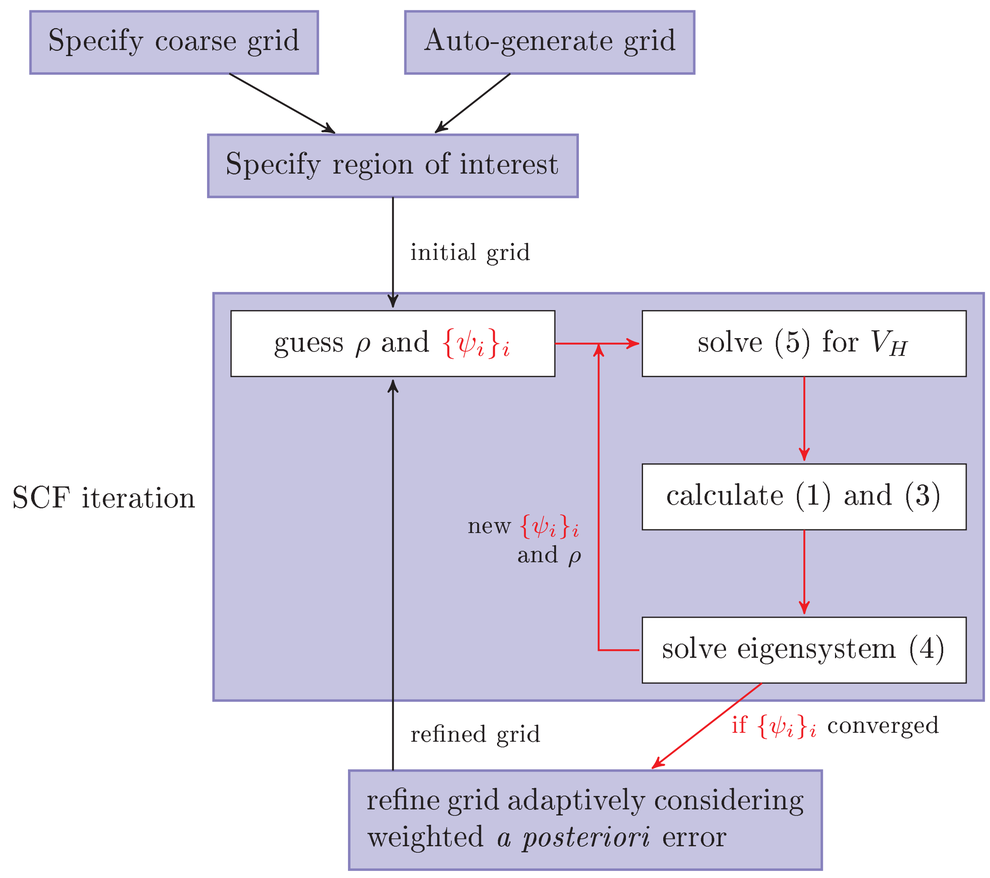
Method overview

- Based on **SIESTA** method [3, 4]
- FE basis allows calculation of Hartree potential V_H by Poisson equation

$$-\Delta V_H(\underline{\boldsymbol{r}}) = \rho(\underline{\boldsymbol{r}}) \tag{5}$$

  in **linear time**.
- To avoid dimensionality issues in the solution of (4) represent core orbitals in an AC basis
- Still treat valence orbitals in non-biased FE basis $\Rightarrow$ **reduction of bias** by AC basis
- Fit AC basis functions to FE basis functions such that core orbitals are available in both representations
- Non-local Hartree-Fock exchange potential problematic
- Back end for FE: `deal.ii` **library** [5]

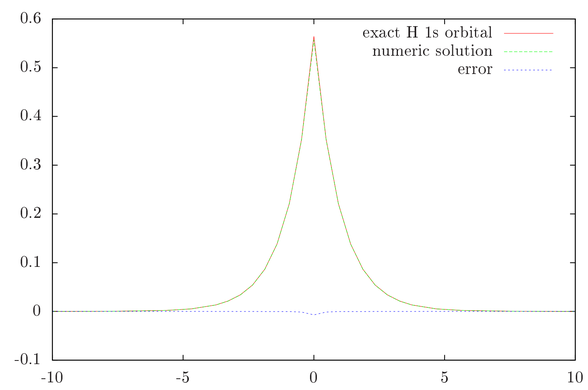
Proposed calculation scheme



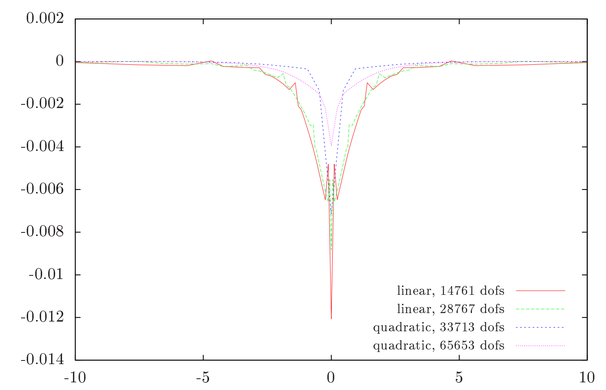
- Can also skip grid refinement and re-use grid from previous calculation

Solution for hydrogen: 1s orbital

- Comparison of analytic solution with solutions on different FE meshes plotted along the x axis



Quadratic FEs and 33713 dofs



Error for different FE meshes

- Greatest error at the discontinuity of ψ_i near the nucleus

Outlook

- Use ECPs to get rid of discontinuity at nucleus
- Develop an approximate Fock operator in the FE context to avoid using exact one each SCF iteration
- Implement automatic mesh generation and an intrinsic multiscale method

References

[1] J. E. Pask and P. A. Sterne, *Modell. Simul. Mater. Sci. Eng.*, **13** (2005), R71.
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[4] J. Avery, *New Computational Methods in the Quantum Theory of Nano-Structures*. PhD thesis, University of Copenhagen, 2011.
[5] W. Bangerth *et. al.*, The `deal.ii` library, version 8.1. `http://arxiv.org/abs/1312.2266v4`, 2013.