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

Michael F. Herbst*[1], James Avery[2], Michael Wormit[1], Guido Kanschat[1] and Andreas Dreuw[1]

[1]Interdisciplinary Center for Scientific Computing, Ruprecht-Karls Universität Heidelberg, Germany
[2]Niels Bohr Institute, Københavns Universitet, Denmark

*EMail: michael.herbst@iwr.uni-heidelberg.de — Website: http://blog.mfhs.eu

Universität Heidelberg
Zukunft. Seit 1386

IWR Interdisciplinary Center for Scientific Computing

Introduction

Employing a finite-element basis in electronic structure calculations provides an alternative to the commonly used atom-centered (AC) basis functions [1].
Potential benefits:

- Sparse, nearly diagonal-dominant matrices for local operators
- Easy parallelisation of code
- The grid (i.e. the basis) adapts to the molecular structure
- Intrinsic multiscale methods possible
- Reduction of implicit bias imposed by AC basis
- More flexible with respect to boundary conditions and potentials

Hartree-Fock in the weak formulation

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

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

$$\hat{\mathcal{V}} = \underbrace{\hat{\mathcal{V}}_0}_{\text{electron-nuclear interaction}} + \underbrace{\hat{\mathcal{V}}_H}_{\text{Hartree potential}} + \underbrace{\hat{\mathcal{V}}_x}_{\text{exchange potential}} \tag{2}$$

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

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

$$\forall \varphi_j : a(\varphi_j, \psi_i) = \varepsilon_i\, m(\varphi_j, \psi_i)$$
$$\Rightarrow \quad \mathbf{A}\underline{z}^{(i)} = \varepsilon_i \mathbf{M} \underline{z}^{(i)} \tag{4}$$

where $A_{jk} = a(\varphi_j, \varphi_k)$ and $M_{jk} = m(\varphi_j, \varphi_k)$.

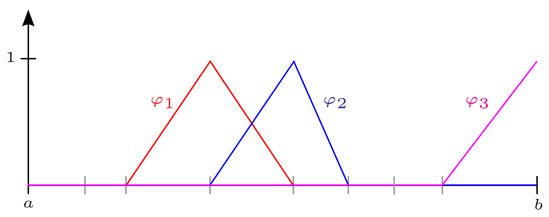
- Hartree potential $\hat{\mathcal{V}}_H$ obtained in **linear time** by solving Poisson equation

$$-\Delta \hat{\mathcal{V}}_H(\underline{r}) = \rho(\underline{r}) \tag{5}$$

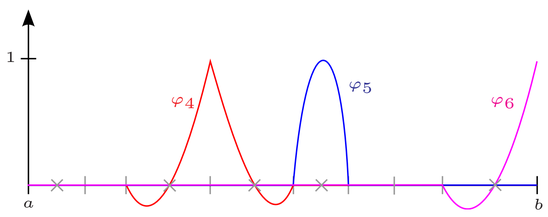
- All operators except $\hat{\mathcal{V}}_x$ are **local**, i.e. they do not correlate two points in space

Finite elements (FEs)

- Piecewise polynomials $\{\varphi_j\}$ on discretised grid
- Only non-zero in a few grid cells ⇒ strongly **localised**
- At **nodal points** $\{\underline{x}_k\}$: $\varphi_j(\underline{x}_k) = \delta_{jk}$

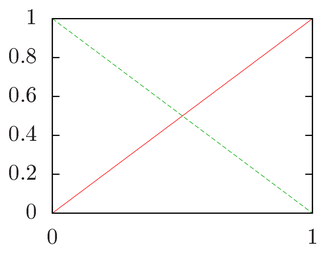


linear FEs on 1D grid

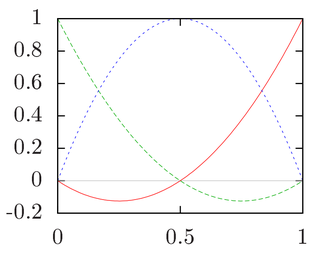


quadratic FEs on 1D grid

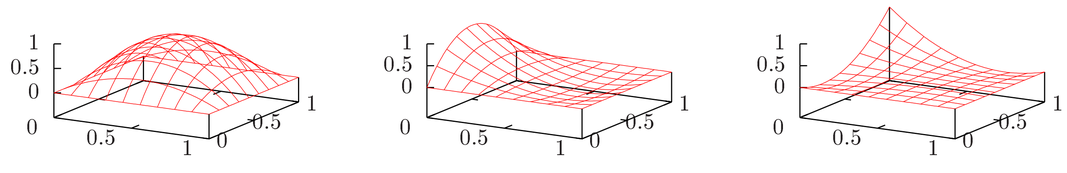
- **Affine map** between each cell on discretisation grid a reference cell, e.g. $[0,1]^{\dim}$.
- FEs can be generated by applying those affine maps to a small number of **shape functions** (Lagrange polynomials) defined on the reference cell.



1D linear shape functions



1D quadratic shape functions

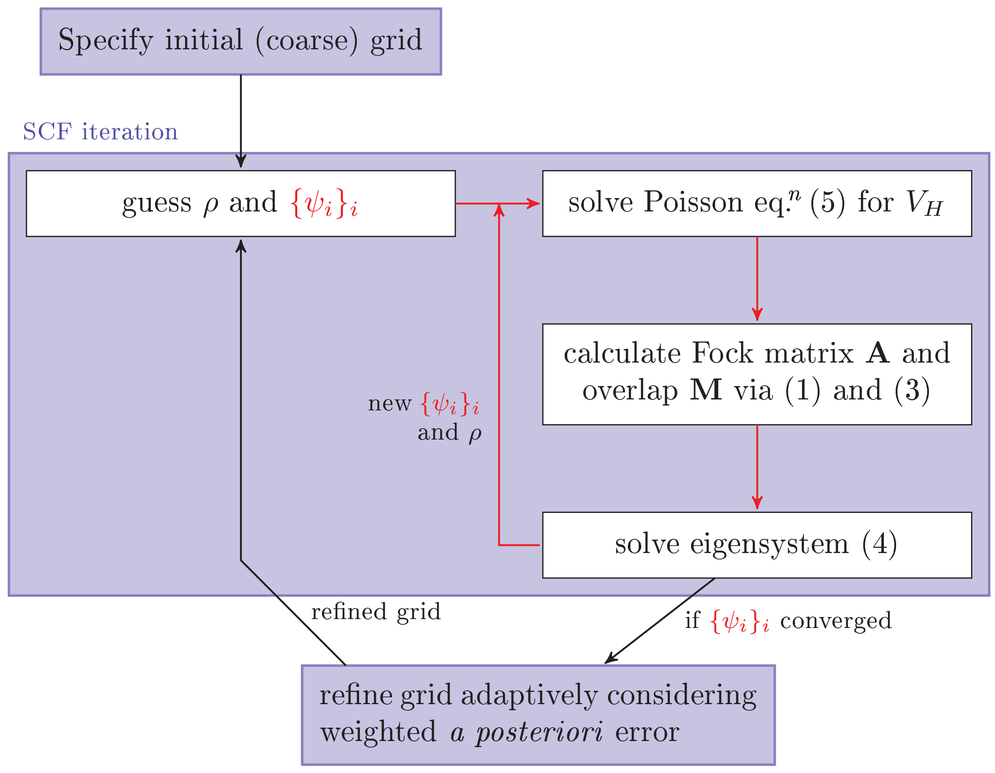


2D quadratic shape functions

- Noteworthy properties [2]:
  - ***A posteriori* error estimation**: Estimate cell-wise error bound for the solution orbitals
  - **Adaptive grid refinement**: User defined metric determines which cells are refined on the next finer grid level

  ⇒ Grid can adopt to molecule by minimising *a posteriori* error

Calculation scheme

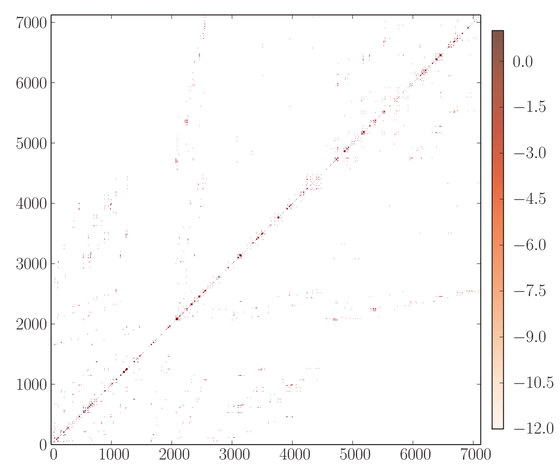


- Use approximate Fock matrix $\mathbf{A}$ until final grid found
- Autogeneration of grids and grid reuse is possible
- Back end for FE: `deal.ii` **library**

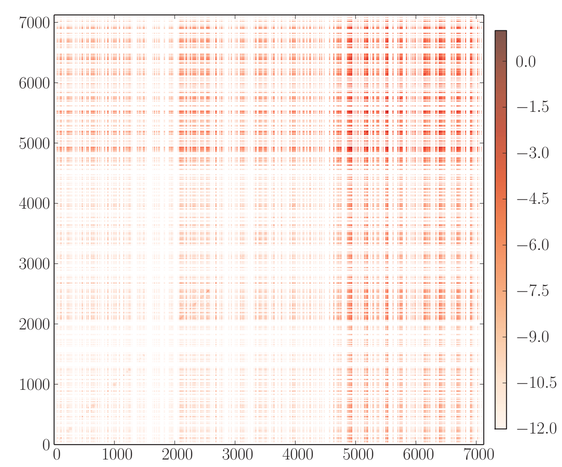
Practical challenges of finite-element HF

- Good discretisation requires large basis sets (more than 10^6 functions)
- FE theory: Discretisation matrices of local operators are sparse
- But: Hartree-Fock exchange $\hat{\mathcal{V}}_x$ is non-local
- Split up $\mathbf{A} = \mathbf{A}_{\text{local}} + \mathbf{V}_x$, where the exchange matrix is

$$(V_x)_{jk} = \int_\Omega \int_\Omega \varphi_j(\underline{r}) \frac{\sum_i \psi_i(\underline{r})\psi_i(\underline{r}')}{|\underline{r} - \underline{r}'|} \varphi_k(\underline{r}')\, \mathrm{d}\underline{r}\, \mathrm{d}\underline{r}' \tag{6}$$



Visualisation of an example for $\mathbf{A}_{\text{local}}$



Visualisation of an example for $\mathbf{V}_x$

colouring depends on the log of the entry values, $\log|(A_{\text{local}})_{jk}|$ or $\log|(V_x)_{jk}|$, respectively

⇒ Computational cost scales at least quadratically with basis set size

⇒ Memory cost scales quadratically if full Fock matrix $\mathbf{A}$ is stored

Outlook

- The computation of the exchange matrix-vector product can be written as

$$(\mathbf{V}_x \underline{z}^{(l)})_j = \int_\Omega \varphi_j(\underline{r}) \sum_i \tilde{V}_{il}(\underline{r}) \psi_i(\underline{r})\, \mathrm{d}\underline{r}$$
$$-\Delta \tilde{V}_{il}(\underline{r}) = \psi_i(\underline{r})\psi_l(\underline{r})$$

- Each application of $\mathbf{A}$ requires only N^2_{orbitals} Poisson equations to be solved

⇒ Linear scaling in memory and computational cost

- Use multigrid methods to reduce the number of diagonalisation iterations [4]
- Test non-linear diagonalisation schemes
- Develop a good approximation for the Fock operator in the FE context

References

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[4] W. Hackbusch, *Multi-Grid Methods and Applications*, Springer Berlin Heidelberg, 1985.