

The finite-element method in quantum chemistry

Michael F. Herbst

`michael.herbst@iwr.uni-heidelberg.de`

Interdisziplinäres Zentrum für wissenschaftliches Rechnen
Ruprecht-Karls-Universität Heidelberg

14 August 2014

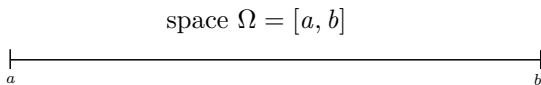
Table of Contents

- 1 Motivation
 - Finite elements from a quantum chemist's perspective
- 2 General introduction to the finite-element method (FEM)
 - The weak formulation
 - Finite Element spaces
- 3 FE based electronic structure calculations
 - The SCF iteration in detail
 - Mesh refinement in detail
- 4 Summary

Table of Contents

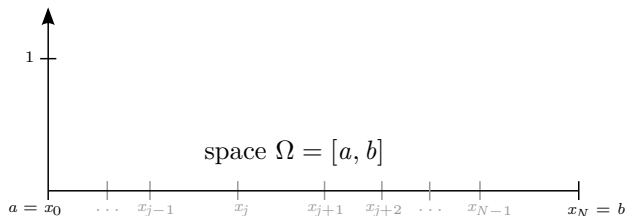
- 1 Motivation
 - Finite elements from a quantum chemist's perspective
- 2 General introduction to the finite-element method (FEM)
 - The weak formulation
 - Finite Element spaces
- 3 FE based electronic structure calculations
 - The SCF iteration in detail
 - Mesh refinement in detail
- 4 Summary

Finite elements (FEs) as basis functions



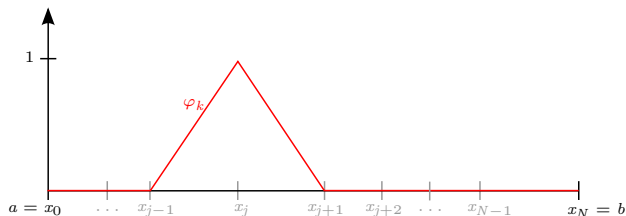
- Discretise space Ω into grid.
 - Finite elements (FEs) are piecewise polynomial functions
 - FEs are zero at large portions of space
- ⇒ Very localised
- Can be used as basis for e.g. molecular wave functions

Finite elements (FEs) as basis functions



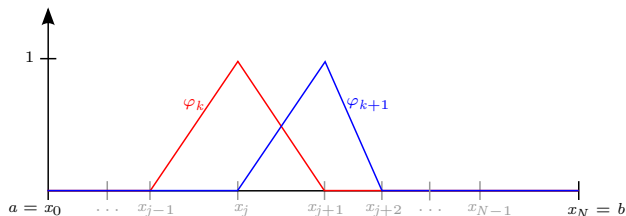
- Discretise space Ω into grid.
 - Finite elements (FEs) are piecewise polynomial functions
 - FEs are zero at large portions of space
- ⇒ Very localised
- Can be used as basis for e.g. molecular wave functions

Finite elements (FEs) as basis functions



- Discretise space Ω into grid.
 - Finite elements (FEs) are piecewise polynomial functions
 - FEs are zero at large portions of space
- ⇒ Very localised
- Can be used as basis for e.g. molecular wave functions

Finite elements (FEs) as basis functions

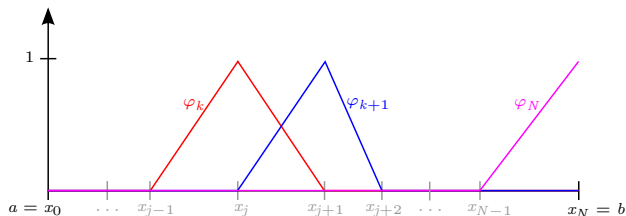


- Discretise space Ω into grid.
- Finite elements (FEs) are piecewise polynomial functions
- FEs are zero at large portions of space

⇒ Very localised

- Can be used as basis for e.g. molecular wave functions

Finite elements (FEs) as basis functions



- Discretise space Ω into grid.
 - Finite elements (FEs) are piecewise polynomial functions
 - FEs are zero at large portions of space
- ⇒ Very localised
- Can be used as basis for e.g. molecular wave functions

Potential advantages of an FE basis

- Strong locality
 - ⇒ Sparse matrices
 - ⇒ Linear scaling
 - ⇒ Easy and effective parallelisation
- Non-uniform grids are possible
 - ⇒ Intrinsic multi-scale methods
- Methods for *a posteriori* error estimation
 - ⇒ On-the-fly adaptive refinement of the grid
 - ⇒ Grid adapts to density

A true black-box method for quantum chemistry?

Possible outline of a black-box FE calculation

- 1 Specify a coarse grid (could be auto-generated)
- 2 Specify a region of interest
- 3 Run calculation
- 4 Identify regions of largest *a posteriori* error
- 5 Refine grid adaptively
- 6 Re-do steps 3-5 until desired accuracy reached

Problems and disadvantages

- Much more basis functions required (think 10^4 to 10^7)
- Non-local potential contributions problematic (e.g. Hartree-Fock exchange)

Table of Contents

- 1 Motivation
 - Finite elements from a quantum chemist's perspective
- 2 General introduction to the finite-element method (FEM)
 - The weak formulation
 - Finite Element spaces
- 3 FE based electronic structure calculations
 - The SCF iteration in detail
 - Mesh refinement in detail
- 4 Summary

The Hartree-Fock equations in strong form

- The well-known Hartree-Fock equations may be written as

$$\begin{aligned} \left(-\frac{1}{2}\Delta + V(\mathbf{r}) \right) \psi_i(\mathbf{r}) &= \varepsilon_i \psi_i(\mathbf{r}) & \mathbf{r} \in \Omega \\ \psi_i(\mathbf{r}) &= 0 & \mathbf{r} \in \partial\Omega \end{aligned}$$

where

$$V = V_0 + V_H + V_x$$

with

- the electron-nuclear interaction V_0
 - the Hartree potential V_H
 - the exchange potential V_x
- This is a differential equation and called the *strong form* of the problem

Getting the weak form (1)

- Multiply strong form by *test function* $\hat{\psi}$ and integrate

$$\left(-\frac{1}{2}\Delta + V(\underline{\mathbf{r}}) \right) \psi_i(\underline{\mathbf{r}}) = \varepsilon_i \psi_i(\underline{\mathbf{r}})$$

- Apply partial integration

$$0 = \int_{\Omega} \frac{1}{2} \nabla \hat{\psi}(\underline{\mathbf{r}}) \cdot \nabla \psi_i(\underline{\mathbf{r}}) \, d\underline{\mathbf{r}} - \int_{\partial\Omega} \frac{1}{2} \hat{\psi}(\underline{\mathbf{r}}) \nabla \psi_i(\underline{\mathbf{r}}) \cdot \hat{\mathbf{n}}_s \, ds$$

$$+ \int_{\Omega} \hat{\psi}(\underline{\mathbf{r}}) (V(\underline{\mathbf{r}}) - \varepsilon_i) \psi_i(\underline{\mathbf{r}}) \, d\underline{\mathbf{r}}$$

Getting the weak form (1)

- Multiply strong form by *test function* $\hat{\psi}$ and integrate

$$0 = -\frac{1}{2}\Delta\psi_i(\underline{\mathbf{r}}) + V(\underline{\mathbf{r}})\psi_i(\underline{\mathbf{r}}) - \varepsilon_i\psi_i(\underline{\mathbf{r}})$$

- Apply partial integration

$$0 = \int_{\Omega} \frac{1}{2} \nabla \hat{\psi}(\underline{\mathbf{r}}) \cdot \nabla \psi_i(\underline{\mathbf{r}}) \, d\underline{\mathbf{r}} - \int_{\partial\Omega} \frac{1}{2} \hat{\psi}(\underline{\mathbf{r}}) \nabla \psi_i(\underline{\mathbf{r}}) \cdot \hat{\mathbf{n}}_s \, ds \\ + \int_{\Omega} \hat{\psi}(\underline{\mathbf{r}}) (V(\underline{\mathbf{r}}) - \varepsilon_i) \psi_i(\underline{\mathbf{r}}) \, d\underline{\mathbf{r}}$$

Getting the weak form (1)

- Multiply strong form by *test function* $\hat{\psi}$ and integrate

$$0 = \int_{\Omega} \hat{\psi}(\underline{\mathbf{r}}) \left(-\frac{1}{2} \Delta \psi_i(\underline{\mathbf{r}}) + (V(\underline{\mathbf{r}}) - \varepsilon_i) \psi_i(\underline{\mathbf{r}}) \right) d\underline{\mathbf{r}}$$

- Apply partial integration

$$0 = \int_{\Omega} \frac{1}{2} \nabla \hat{\psi}(\underline{\mathbf{r}}) \cdot \nabla \psi_i(\underline{\mathbf{r}}) d\underline{\mathbf{r}} - \int_{\partial\Omega} \frac{1}{2} \hat{\psi}(\underline{\mathbf{r}}) \nabla \psi_i(\underline{\mathbf{r}}) \cdot \hat{\mathbf{n}}_s ds$$

$$+ \int_{\Omega} \hat{\psi}(\underline{\mathbf{r}}) (V(\underline{\mathbf{r}}) - \varepsilon_i) \psi_i(\underline{\mathbf{r}}) d\underline{\mathbf{r}}$$

Getting the weak form (1)

- Multiply strong form by *test function* $\hat{\psi}$ and integrate

$$0 = \int_{\Omega} \hat{\psi}(\underline{\mathbf{r}}) \left(-\frac{1}{2} \Delta \psi_i(\underline{\mathbf{r}}) + (V(\underline{\mathbf{r}}) - \varepsilon_i) \psi_i(\underline{\mathbf{r}}) \right) d\underline{\mathbf{r}}$$

- Apply partial integration

$$\begin{aligned} 0 = \int_{\Omega} \frac{1}{2} \nabla \hat{\psi}(\underline{\mathbf{r}}) \cdot \nabla \psi_i(\underline{\mathbf{r}}) d\underline{\mathbf{r}} - \int_{\partial\Omega} \frac{1}{2} \hat{\psi}(\underline{\mathbf{r}}) \nabla \psi_i(\underline{\mathbf{r}}) \cdot \hat{\mathbf{n}}_s ds \\ + \int_{\Omega} \hat{\psi}(\underline{\mathbf{r}}) (V(\underline{\mathbf{r}}) - \varepsilon_i) \psi_i(\underline{\mathbf{r}}) d\underline{\mathbf{r}} \end{aligned}$$

Getting the weak form (2)

- Physics dictates that $\psi_i(\underline{\mathbf{r}}) = 0$ on the boundary $\partial\Omega$.
- ⇒ Can also require for test function (= variation):

$$\hat{\psi}(\underline{\mathbf{r}}) = 0 \quad \text{on } \partial\Omega$$

- Boundary term in integral drops:

$$\begin{aligned} 0 &= \int_{\Omega} \frac{1}{2} \nabla \hat{\psi}(\underline{\mathbf{r}}) \cdot \nabla \psi_i(\underline{\mathbf{r}}) \, d\underline{\mathbf{r}} \\ &\quad + \int_{\Omega} \hat{\psi}(\underline{\mathbf{r}}) (V(\underline{\mathbf{r}}) - \varepsilon_i) \psi_i(\underline{\mathbf{r}}) \, d\underline{\mathbf{r}} \end{aligned}$$

Getting the weak form (3)

- Define bilinear forms

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

and

$$m(f, g) = \int_{\Omega} f(\underline{\mathbf{r}}) \cdot g(\underline{\mathbf{r}}) \, d\underline{\mathbf{r}}$$

- Rewrite integral equation to

$$0 = \int_{\Omega} \frac{1}{2} \nabla \hat{\psi}(\underline{\mathbf{r}}) \cdot \nabla \psi_i(\underline{\mathbf{r}}) \, d\underline{\mathbf{r}} + \int_{\Omega} \hat{\psi}(\underline{\mathbf{r}}) (V(\underline{\mathbf{r}}) - \varepsilon_i) \psi_i(\underline{\mathbf{r}}) \, d\underline{\mathbf{r}}$$

- The *weak formulation* of the Hartree-Fock problem is:

For all test functions $\hat{\psi}$ (2.1) holds.

Getting the weak form (3)

- Define bilinear forms

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

and

$$m(f, g) = \int_{\Omega} f(\underline{\mathbf{r}}) \cdot g(\underline{\mathbf{r}}) \, d\underline{\mathbf{r}}$$

- Rewrite integral equation to

$$0 = \int_{\Omega} \frac{1}{2} \nabla \hat{\psi}(\underline{\mathbf{r}}) \cdot \nabla \psi_i(\underline{\mathbf{r}}) \, d\underline{\mathbf{r}} + \int_{\Omega} \hat{\psi}(\underline{\mathbf{r}}) (V(\underline{\mathbf{r}}) - \varepsilon_i) \psi_i(\underline{\mathbf{r}}) \, d\underline{\mathbf{r}}$$

- The *weak formulation* of the Hartree-Fock problem is:

For all test functions $\hat{\psi}$ (2.1) holds.

Getting the weak form (3)

- Define bilinear forms

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

and

$$m(f, g) = \int_{\Omega} f(\underline{\mathbf{r}}) \cdot g(\underline{\mathbf{r}}) \, d\underline{\mathbf{r}}$$

- Rewrite integral equation to

$$0 = a(\hat{\psi}, \psi_i) - \int_{\Omega} \hat{\psi}(\underline{\mathbf{r}}) \varepsilon_i \psi_i(\underline{\mathbf{r}}) \, d\underline{\mathbf{r}}$$

- The *weak formulation* of the Hartree-Fock problem is:

For all test functions $\hat{\psi}$ (2.1) holds.

Getting the weak form (3)

- Define bilinear forms

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

and

$$m(f, g) = \int_{\Omega} f(\underline{\mathbf{r}}) \cdot g(\underline{\mathbf{r}}) \, d\underline{\mathbf{r}}$$

- Rewrite integral equation to

$$a(\hat{\psi}, \psi_i) = \varepsilon_i m(\hat{\psi}, \psi_i) \quad (2.1)$$

- The *weak formulation* of the Hartree-Fock problem is:

For all test functions $\hat{\psi}$ (2.1) holds.

Getting the weak form (3)

- Define bilinear forms

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

and

$$m(f, g) = \int_{\Omega} f(\underline{\mathbf{r}}) \cdot g(\underline{\mathbf{r}}) \, d\underline{\mathbf{r}}$$

- Rewrite integral equation to

$$a(\hat{\psi}, \psi_i) = \varepsilon_i m(\hat{\psi}, \psi_i) \quad (2.1)$$

- The *weak formulation* of the Hartree-Fock problem is:

For all test functions $\hat{\psi}$ (2.1) holds.

Introducing a basis

- It can be shown, that $\hat{\psi}$ and ψ_i are members of the same Hilbert space H_0^1 .
- Let $\Phi = \{\varphi_j\}_{j \in \mathbb{N}}$ be a basis for H_0^1 .
- Then $\psi_i(\underline{\mathbf{r}}) = \sum_j z_j^{(i)} \varphi_j$
- It holds for the weak formulation:

$$\forall \hat{\psi} \in H_0^1 : \quad a(\hat{\psi}, \psi_i) = \varepsilon_i m(\hat{\psi}, \psi_i)$$

$$\Leftrightarrow \forall \varphi_j, \varphi_k \in \Phi : \quad a\left(\varphi_j, \sum_k z_k^{(i)} \varphi_k\right) = \varepsilon_i m\left(\varphi_j, \sum_k z_k^{(i)} \varphi_k\right)$$

$$\Leftrightarrow \forall \varphi_j, \varphi_k \in \Phi : \quad \sum_k z_k^{(i)} a(\varphi_j, \varphi_k) = \varepsilon_i \sum_k z_k^{(i)} m(\varphi_j, \varphi_k)$$

Discretising the space H_0^1

- Introduce N_{FE} -dimensional subspace $V_h \subset H_0^1$
- Weak formulation becomes a generalised eigenvalue problem $\mathbf{A}\underline{\mathbf{z}}^{(i)} = \varepsilon_i \mathbf{M}\underline{\mathbf{z}}^{(i)}$.
- With *stiffness matrix*

$$A_{jk} = a(\varphi_j, \varphi_k) = \int_{\Omega} \frac{1}{2} \nabla \varphi_j(\mathbf{r}) \cdot \nabla \varphi_k(\mathbf{r}) + \varphi_j(\mathbf{r}) V(\mathbf{r}) \varphi_k(\mathbf{r}) \, d\mathbf{r}$$

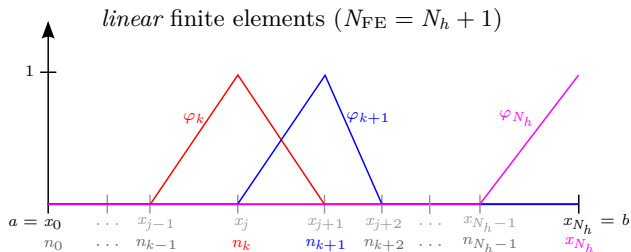
and *mass matrix*

$$M_{jk} = m(\varphi_j, \varphi_k) = \int_{\Omega} \varphi_j(\mathbf{r}) \varphi_k(\mathbf{r}) \, d\mathbf{r}$$

- Need to find a basis of V_h which gives well-conditioned \mathbf{A} and \mathbf{M} matrices and makes integration simple.

Finite elements

Properties

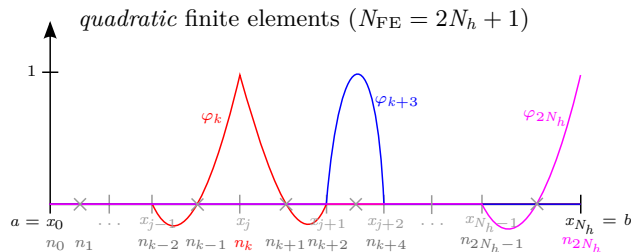


- Each FE is a polynomial when restricted to a cell
- Non-differentiable points at cell boundaries x_j
- Each FE has support only on a few neighbouring cells
- The FEs satisfy at the *nodal points*

$$\varphi_i(n_j) = \delta_{ij}$$

Finite elements

Properties

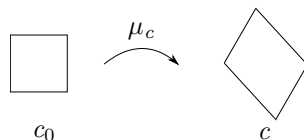


- Each FE is a polynomial when restricted to a cell
- Non-differentiable points at cell boundaries x_j
- Each FE has support only on a few neighbouring cells
- The FEs satisfy at the *nodal points*

$$\varphi_i(n_j) = \delta_{ij}$$

Finite elements

Reference cell and shape functions



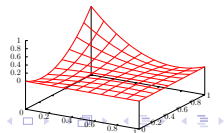
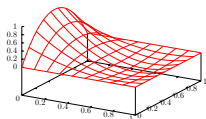
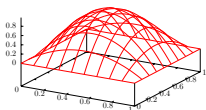
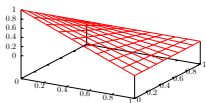
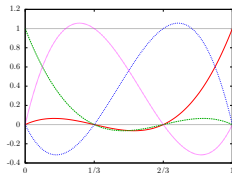
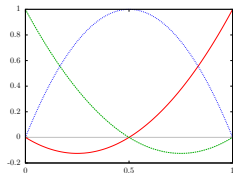
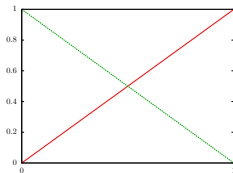
- c_0 is called the *reference cell*
- *Affine map* μ_c for each cell to construct c from c_0
- *Shape functions* $\{e_\alpha\}_{0 \leq \alpha < n_{\text{sh}}}$ form a basis for c_0
- For finite elements φ_k with support on c :

$$\varphi_k|_c(\underline{\mathbf{r}}) = e_\alpha(\mu_c^{-1}(\underline{\mathbf{r}})) \quad \text{for some } \alpha$$

- ⇒ Can transform integrals cell-by-cell onto reference cell.
- ⇒ Only need to really calculate integrals on reference cell.

Finite elements

Examples of shape functions



Integration in FE spaces (1)

Integrals as matrix-vector-products

- For each function $\hat{f} \in V_h$:

$$\hat{f} = \sum_{i=0}^{N_{\text{FE}}-1} f_i \varphi_i \quad \implies \quad f_i = \hat{f}(n_i)$$

- For all possible overlap integrals

$$\begin{aligned} \int_{\Omega} \hat{f}(\underline{\mathbf{r}}) \hat{g}(\underline{\mathbf{r}}) \, d\underline{\mathbf{r}} &= \sum_{i,j=0}^{N_{\text{FE}}-1} f_i g_j \underbrace{\int_{\Omega} \varphi_i(\underline{\mathbf{r}}) \varphi_j(\underline{\mathbf{r}}) \, d\underline{\mathbf{r}}}_{M_{ij}} \\ &= \underline{\mathbf{f}}^T \mathbf{M} \underline{\mathbf{g}} \end{aligned}$$

- Similar relations for other integrals.

Integration in FE spaces (2)

Splitting into cell contributions

- Calculate as sum of cell-wise contributions: $M_{ij} = \sum_c M_{ij}^c$

$$M_{ij}^c = \int_c \varphi_i(\underline{\mathbf{r}}) \varphi_j(\underline{\mathbf{r}}) \, d\underline{\mathbf{r}}$$

- M_{ij}^c only non-zero if φ_i and φ_j have common support on c
- Let α, β such that

$$\varphi_i|_c(\underline{\mathbf{r}}) = e_\alpha(\mu_c^{-1}(\underline{\mathbf{r}})) \quad \text{and} \quad \varphi_j|_c(\underline{\mathbf{r}}) = e_\beta(\mu_c^{-1}(\underline{\mathbf{r}}))$$

- Let $J_c(\underline{\boldsymbol{\xi}})$ be the Jacobian of the mapping $\underline{\mathbf{r}} = \mu_c(\underline{\boldsymbol{\xi}})$, i.e.

$$\left(J_c(\underline{\boldsymbol{\xi}}) \right)_{ij} = \left(\nabla_{\underline{\boldsymbol{\xi}}} \mu_c(\underline{\boldsymbol{\xi}}) \right)_{ij} = \frac{\partial \left(\mu_c(\underline{\boldsymbol{\xi}}) \right)_i}{\partial \xi_j}$$

Integration in FE spaces (3)

Transformation to unit cell and quadrature

$$M_{ij}^c = \int_c \varphi_i(\underline{\mathbf{r}}) \varphi_j(\underline{\mathbf{r}}) \, d\underline{\mathbf{r}}$$

Integration in FE spaces (3)

Transformation to unit cell and quadrature

$$M_{ij}^c = \int_c \varphi_i(\underline{\mathbf{r}}) \varphi_j(\underline{\mathbf{r}}) \, d\underline{\mathbf{r}}$$

$$\varphi_i|_c(\underline{\mathbf{r}}) = e_\alpha(\mu_c^{-1}(\underline{\mathbf{r}}))$$

Integration in FE spaces (3)

Transformation to unit cell and quadrature

$$\begin{aligned} M_{ij}^c &= \int_c \varphi_i(\underline{\mathbf{r}}) \varphi_j(\underline{\mathbf{r}}) \, d\underline{\mathbf{r}} \\ &= \int_c e_\alpha(\mu_c^{-1}(\underline{\mathbf{r}})) e_\beta(\mu_c^{-1}(\underline{\mathbf{r}})) \, d\underline{\mathbf{r}} \end{aligned}$$

$$\varphi_i|_c(\underline{\mathbf{r}}) = e_\alpha(\mu_c^{-1}(\underline{\mathbf{r}}))$$

Integration in FE spaces (3)

Transformation to unit cell and quadrature

$$\begin{aligned} M_{ij}^c &= \int_c \varphi_i(\underline{\mathbf{r}}) \varphi_j(\underline{\mathbf{r}}) \, d\underline{\mathbf{r}} \\ &= \int_c e_\alpha(\mu_c^{-1}(\underline{\mathbf{r}})) e_\beta(\mu_c^{-1}(\underline{\mathbf{r}})) \, d\underline{\mathbf{r}} \end{aligned}$$

$$\left(J_c(\underline{\boldsymbol{\xi}}) \right)_{ij} = \frac{\partial \left(\mu_c(\underline{\boldsymbol{\xi}}) \right)_i}{\partial \xi_j}$$

Integration in FE spaces (3)

Transformation to unit cell and quadrature

$$\begin{aligned} M_{ij}^c &= \int_c \varphi_i(\underline{\mathbf{r}}) \varphi_j(\underline{\mathbf{r}}) \, d\underline{\mathbf{r}} \\ &= \int_c e_\alpha(\mu_c^{-1}(\underline{\mathbf{r}})) e_\beta(\mu_c^{-1}(\underline{\mathbf{r}})) \, d\underline{\mathbf{r}} \\ &= \int_{c_0} e_\alpha(\underline{\boldsymbol{\xi}}) e_\beta(\underline{\boldsymbol{\xi}}) \det(J_c(\underline{\boldsymbol{\xi}})) \, d\underline{\boldsymbol{\xi}} \end{aligned}$$

$$(J_c(\underline{\boldsymbol{\xi}}))_{ij} = \frac{\partial (\mu_c(\underline{\boldsymbol{\xi}}))_i}{\partial \xi_j}$$

Integration in FE spaces (3)

Transformation to unit cell and quadrature

$$\begin{aligned}
 M_{ij}^c &= \int_c \varphi_i(\underline{\mathbf{r}}) \varphi_j(\underline{\mathbf{r}}) \, d\underline{\mathbf{r}} \\
 &= \int_c e_\alpha(\mu_c^{-1}(\underline{\mathbf{r}})) e_\beta(\mu_c^{-1}(\underline{\mathbf{r}})) \, d\underline{\mathbf{r}} \\
 &= \int_{c_0} e_\alpha(\underline{\boldsymbol{\xi}}) e_\beta(\underline{\boldsymbol{\xi}}) \det(J_c(\underline{\boldsymbol{\xi}})) \, d\underline{\boldsymbol{\xi}} \\
 &= \sum_{q=1}^{N_q} e_\alpha(\underline{\boldsymbol{\xi}}_q) e_\beta(\underline{\boldsymbol{\xi}}_q) \det(J_c(\underline{\boldsymbol{\xi}}_q)) w_q
 \end{aligned}$$

- Gaussian quadrature of order N_q with quad. weights w_q
- Only need to know $\det J_c$, e_α at quadrature points of c_0
- Only $\det J_c$ changes from cell to cell

Integration in FE spaces (3)

Transformation to unit cell and quadrature

$$\begin{aligned}
 M_{ij}^c &= \int_c \varphi_i(\underline{\mathbf{r}}) \varphi_j(\underline{\mathbf{r}}) \, d\underline{\mathbf{r}} \\
 &= \int_c e_\alpha(\mu_c^{-1}(\underline{\mathbf{r}})) e_\beta(\mu_c^{-1}(\underline{\mathbf{r}})) \, d\underline{\mathbf{r}} \\
 &= \int_{c_0} e_\alpha(\underline{\boldsymbol{\xi}}) e_\beta(\underline{\boldsymbol{\xi}}) \det(J_c(\underline{\boldsymbol{\xi}})) \, d\underline{\boldsymbol{\xi}} \\
 &= \sum_{q=1}^{N_q} e_\alpha(\underline{\boldsymbol{\xi}}_q) e_\beta(\underline{\boldsymbol{\xi}}_q) \det(J_c(\underline{\boldsymbol{\xi}}_q)) w_q
 \end{aligned}$$

- Gaussian quadrature of order N_q with quad. weights w_q
- Only need to know $\det J_c$, e_α at quadrature points of c_0
- Only $\det J_c$ changes from cell to cell

A *posteriori* error estimation

a posteriori error

Estimate for error of numerical solution *without knowledge* of analytical solution

- *Aim*: Understand which cells make up largest contribution
- In general: Computation difficult and expensive
- Crude guesses usually good enough
- Estimates consider:
 - Residual inside domain Ω

$$r(\underline{\mathbf{r}}) = \left(-\frac{1}{2}\Delta + V(\underline{\mathbf{r}}) - \varepsilon_i \right) \psi_i(\underline{\mathbf{r}})$$

- Discontinuities of first derivatives at cell faces.
- The size of the cells

Table of Contents

- 1 Motivation
 - Finite elements from a quantum chemist's perspective
- 2 General introduction to the finite-element method (FEM)
 - The weak formulation
 - Finite Element spaces
- 3 FE based electronic structure calculations
 - The SCF iteration in detail
 - Mesh refinement in detail
- 4 Summary

Recall from earlier:

Possible outline of a black-box FE calculation

- 1 Specify a coarse grid (could be auto-generated)
- 2 Specify a region of interest
- 3 Run calculation
- 4 Identify regions of largest *a posteriori* error
- 5 Refine grid adaptively
- 6 Re-do steps 3-5 until desired accuracy reached

Recall from earlier:

Possible outline of a black-box FE calculation

- 1 Specify a coarse grid (could be auto-generated)
- 2 Specify a region of interest
- 3 **Run calculation**
- 4 Identify regions of largest *a posteriori* error
- 5 **Refine grid adaptively**
- 6 Re-do steps 3-5 until desired accuracy reached

SCF iteration: Overview

- Once grid is set up μ_c can be constructed
- ⇒ Can map FEs $\{\varphi_j\}_{0 \leq j < N_{\text{FE}}}$ to shape functions $\{e_\alpha\}_{0 \leq \alpha < n_{\text{sh}}}$
- Calculate mass matrix \mathbf{M} and stiffness matrix \mathbf{A}
(using current $\{\psi_i\}_{0 \leq i < N_{\text{orb}}}$ and current density ρ)

$$A_{jk} = \int_{\Omega} \frac{1}{2} \nabla \varphi_j(\mathbf{r}) \cdot \nabla \varphi_k(\mathbf{r}) + \varphi_j(\mathbf{r}) \left(V_0(\mathbf{r}) + V_H(\mathbf{r}) + V_x(\mathbf{r}) \right) \varphi_k(\mathbf{r}) \, d\mathbf{r}$$

$$M_{jk} = \int_{\Omega} \varphi_j(\mathbf{r}) \varphi_k(\mathbf{r}) \, d\mathbf{r}$$

- Solve generalised eigenvalue problem:

$$\mathbf{A} \underline{\mathbf{z}}^{(i)} = \varepsilon_i \mathbf{M} \underline{\mathbf{z}}^{(i)}$$

- New set of $\{\psi_i\}_{0 \leq i < N_{\text{orb}}}$ and new ρ .

Building the stiffness matrix

$$A_{jk} = \int_{\Omega} \frac{1}{2} \nabla \varphi_j(\underline{\mathbf{r}}) \cdot \nabla \varphi_k(\underline{\mathbf{r}}) + \varphi_j(\underline{\mathbf{r}}) \left(V_0(\underline{\mathbf{r}}) + V_H(\underline{\mathbf{r}}) + V_x(\underline{\mathbf{r}}) \right) \varphi_k(\underline{\mathbf{r}}) \, d\underline{\mathbf{r}}$$

- Kinetic part and nuclear potential part can be done naively
- To get $V_H(\underline{\mathbf{r}})$ solve Poisson equation of electron density:

$$-\Delta V_H(\underline{\mathbf{r}}) = \rho(\underline{\mathbf{r}})$$

- Exchange $V_x(\underline{\mathbf{r}})$ is problematic, since non-local operator

Building the stiffness matrix

$$A_{jk} = \int_{\Omega} \frac{1}{2} \nabla \varphi_j(\underline{\mathbf{r}}) \cdot \nabla \varphi_k(\underline{\mathbf{r}}) + \varphi_j(\underline{\mathbf{r}}) \left(V_0(\underline{\mathbf{r}}) + V_H(\underline{\mathbf{r}}) + V_x(\underline{\mathbf{r}}) \right) \varphi_k(\underline{\mathbf{r}}) \, d\underline{\mathbf{r}}$$

- Kinetic part and nuclear potential part can be done naively
- To get $V_H(\underline{\mathbf{r}})$ solve Poisson equation of electron density:

$$-\Delta V_H(\underline{\mathbf{r}}) = \rho(\underline{\mathbf{r}})$$

- Exchange $V_x(\underline{\mathbf{r}})$ is problematic, since non-local operator

$$V_0(\underline{\mathbf{r}}_1) = - \sum_A \frac{Z_A}{r_{1A}}$$

Building the stiffness matrix

$$A_{jk} = \int_{\Omega} \frac{1}{2} \nabla \varphi_j(\underline{\mathbf{r}}) \cdot \nabla \varphi_k(\underline{\mathbf{r}}) + \varphi_j(\underline{\mathbf{r}}) \left(V_0(\underline{\mathbf{r}}) + V_H(\underline{\mathbf{r}}) + V_x(\underline{\mathbf{r}}) \right) \varphi_k(\underline{\mathbf{r}}) \, d\underline{\mathbf{r}}$$

- Kinetic part and nuclear potential part can be done naively
- To get $V_H(\underline{\mathbf{r}})$ solve Poisson equation of electron density:

$$-\Delta V_H(\underline{\mathbf{r}}) = \rho(\underline{\mathbf{r}})$$

- Exchange $V_x(\underline{\mathbf{r}})$ is problematic, since non-local operator

$$V_H(\underline{\mathbf{r}}_1) = \sum_j \int_{\Omega} \frac{|\psi_j(\underline{\mathbf{r}}_2)|^2}{r_{12}} \, d\underline{\mathbf{r}}_2$$

Building the stiffness matrix

$$A_{jk} = \int_{\Omega} \frac{1}{2} \nabla \varphi_j(\underline{\mathbf{r}}) \cdot \nabla \varphi_k(\underline{\mathbf{r}}) + \varphi_j(\underline{\mathbf{r}}) \left(V_0(\underline{\mathbf{r}}) + V_H(\underline{\mathbf{r}}) + V_x(\underline{\mathbf{r}}) \right) \varphi_k(\underline{\mathbf{r}}) \, d\underline{\mathbf{r}}$$

- Kinetic part and nuclear potential part can be done naively
- To get $V_H(\underline{\mathbf{r}})$ solve Poisson equation of electron density:

$$-\Delta V_H(\underline{\mathbf{r}}) = \rho(\underline{\mathbf{r}})$$

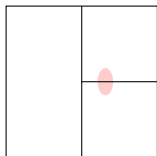
- Exchange $V_x(\underline{\mathbf{r}})$ is problematic, since non-local operator

$$V_x(\underline{\mathbf{r}}_1) \psi_i(\underline{\mathbf{r}}_1) = \sum_{j \neq i} \mathbf{V}_{ji}^x(\underline{\mathbf{r}}_1) \psi_j(\underline{\mathbf{r}}_1)$$

$$\mathbf{V}_{ji}^x(\underline{\mathbf{r}}_1) = \int_{\Omega} \frac{\psi_j^*(\underline{\mathbf{r}}_2) \psi_i(\underline{\mathbf{r}}_2)}{r_{12}} \, d\underline{\mathbf{r}}_2$$

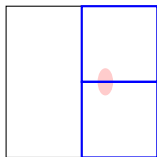
Mesh refinement in detail

- Input: *a posteriori* error for each cell
- Can scale error by importance (multi-scale methods)
- Refinement strategies:
 - Fixed number
 - Fixed fraction (preferred)
- Neighbours: Refinement level can only differ by one



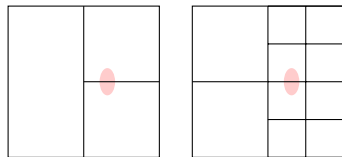
Mesh refinement in detail

- Input: *a posteriori* error for each cell
- Can scale error by importance (multi-scale methods)
- Refinement strategies:
 - Fixed number
 - Fixed fraction (preferred)
- Neighbours: Refinement level can only differ by one



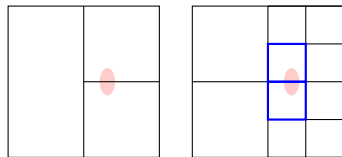
Mesh refinement in detail

- Input: *a posteriori* error for each cell
- Can scale error by importance (multi-scale methods)
- Refinement strategies:
 - Fixed number
 - Fixed fraction (preferred)
- Neighbours: Refinement level can only differ by one



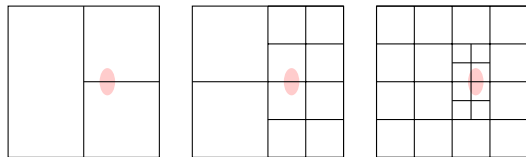
Mesh refinement in detail

- Input: *a posteriori* error for each cell
- Can scale error by importance (multi-scale methods)
- Refinement strategies:
 - Fixed number
 - Fixed fraction (preferred)
- Neighbours: Refinement level can only differ by one



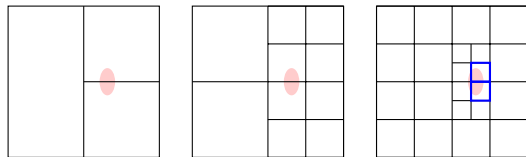
Mesh refinement in detail

- Input: *a posteriori* error for each cell
- Can scale error by importance (multi-scale methods)
- Refinement strategies:
 - Fixed number
 - Fixed fraction (preferred)
- Neighbours: Refinement level can only differ by one



Mesh refinement in detail

- Input: *a posteriori* error for each cell
- Can scale error by importance (multi-scale methods)
- Refinement strategies:
 - Fixed number
 - Fixed fraction (preferred)
- Neighbours: Refinement level can only differ by one



Mesh refinement in detail

- Input: *a posteriori* error for each cell
- Can scale error by importance (multi-scale methods)
- Refinement strategies:
 - Fixed number
 - Fixed fraction (preferred)
- Neighbours: Refinement level can only differ by one

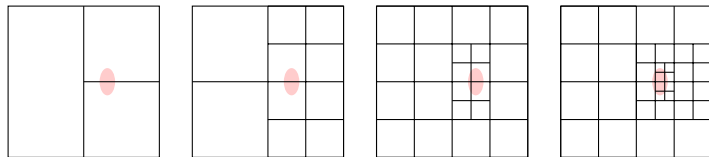


Table of Contents

- 1 Motivation
 - Finite elements from a quantum chemist's perspective
- 2 General introduction to the finite-element method (FEM)
 - The weak formulation
 - Finite Element spaces
- 3 FE based electronic structure calculations
 - The SCF iteration in detail
 - Mesh refinement in detail
- 4 Summary

Summary

- FEM very flexible wrt. chosen grid
- Adaptive refinement of grid possible
- Integration (almost always) reduces to matrix-vector multiplication
- Integration matrices can be precomputed for given grid
- Large, but sparse matrices for eigenproblem
- Linear scaling

References

- J. Avery, *New Computational Methods in the Quantum Theory of Nano-Structures*. PhD thesis, University of Copenhagen, 2011.
- P. Bastian, *Scientific Computing with Partial Differential Equations*. Lecture notes, Ruprecht-Karls-Universität Heidelberg, 2014.
- R. Alizadegan, K. J. Hsia, and T. J. Martinez, *J. Chem. Phys.*, **132** (2010), 034101.
- W. Bangerth *et. al.*, The deal.ii library, version 8.1.
<http://arxiv.org/abs/1312.2266v4>, 2013.



This work is licensed under a Creative Commons Attribution-ShareAlike 4.0 International Licence.

