Solving the Hartree-Fock equations using the finite element method

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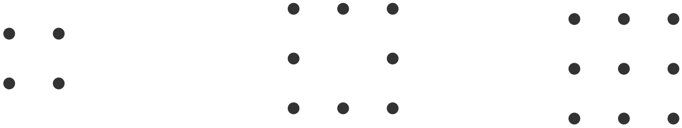
Contents

Contents

Connecting dots



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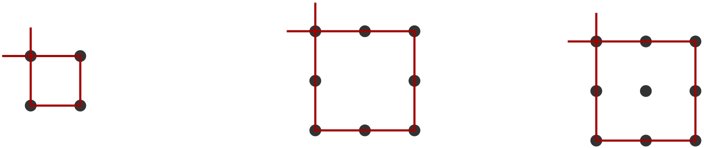

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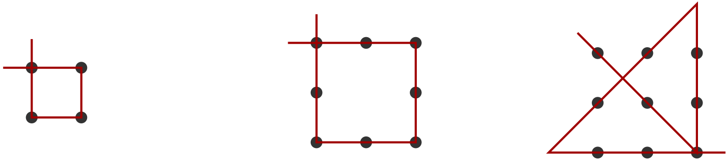

Problems with atom-centered bases

- Confined molecules
- Excited states:
  - Rydberg states
  - Resonance phenomena
- Not a free choice of boundary conditions
- Untested bias regarding electron position

Contents

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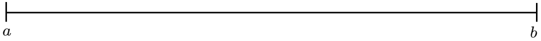
Finite elements (FEs) as basis functions

space $\Omega = [a, b]$



- Discretise open set Ω into grid of N_h cells.
- Non-differentiable only at cell boundaries x_j
- Support on just a few neighbouring cells
- At *nodal points*: $\varphi_i(n_j) = \delta_{ij}$
- N_{FE}-dim. basis for discretised Hilbert space H_0^1.

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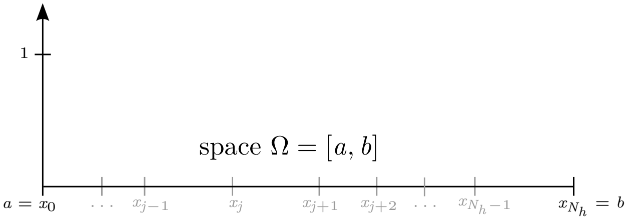

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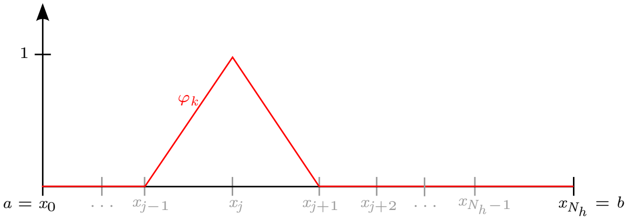

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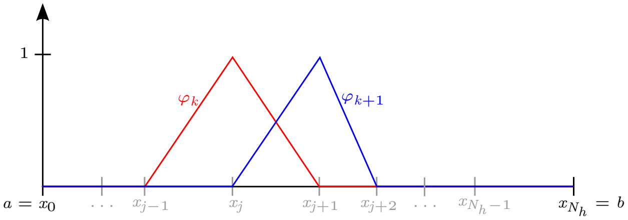

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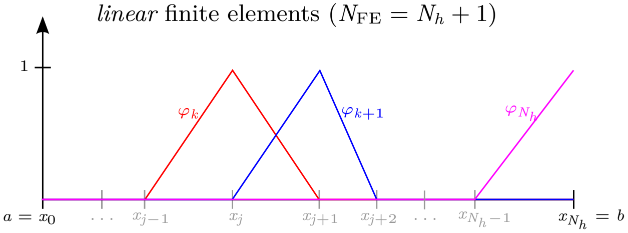

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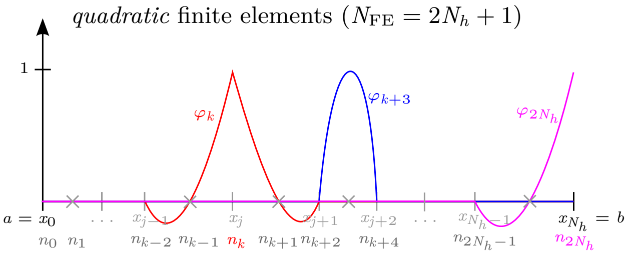

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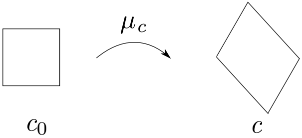
Reference cell and shape functions



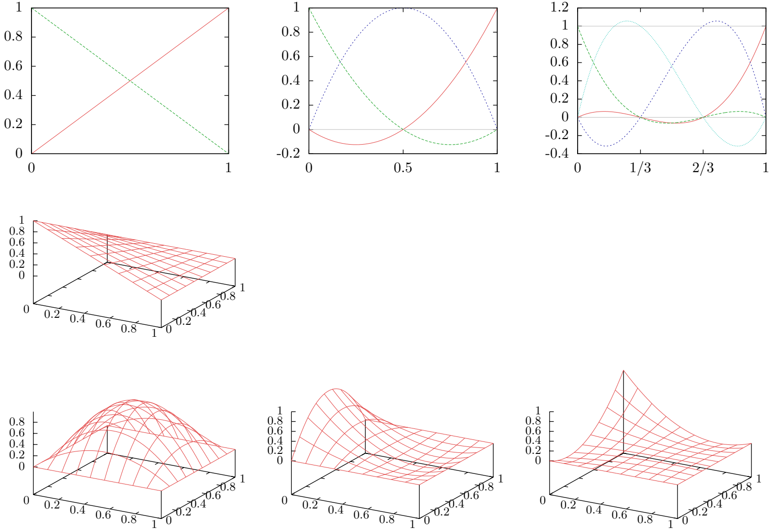
- *Reference cell* $c_0 = [0,1]^3$
- *Affine map* μ_c for each cell to construct c from c_0
- Can construct FEs φ_k from *shape functions* $\{e_\alpha\}_{0\leq\alpha<n_{\mathrm{sh}}}$:

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

$\Rightarrow$ Computation on the grid:

- Compute on reference cell once
- Transform result onto all grid cells

Examples of shape functions



The Hartree-Fock equations in strong form

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

$$\begin{aligned} \Big(-\frac{1}{2}\Delta + \hat{\mathcal{V}}(\underline{\boldsymbol{r}})\Big)\psi_i(\underline{\boldsymbol{r}}) &= \varepsilon_i\psi_i(\underline{\boldsymbol{r}}) \qquad && \underline{\boldsymbol{r}} \in \Omega \\ \psi_i(\underline{\boldsymbol{r}}) &= 0 && \underline{\boldsymbol{r}} \in \partial\Omega \end{aligned}$$

  where

$$\hat{\mathcal{V}} = \hat{\mathcal{V}}_0 + \hat{\mathcal{V}}_H + \hat{\mathcal{V}}_x$$

  with
  - the electron-nuclear interaction $\hat{\mathcal{V}}_0$
  - the Hartree potential $\hat{\mathcal{V}}_H$
  - the exchange potential $\hat{\mathcal{V}}_x$
- This is the *strong form* of the problem

Getting the weak form (1)

- Expand orbital $\psi_i(\underline{\boldsymbol{r}})$ in FE basis:

$$\psi_i(\underline{\boldsymbol{r}}) = \sum_k z_k^{(i)} \varphi_k(\underline{\boldsymbol{r}})$$

- Multiply strong form by arbitrary basis function $\varphi_j(\underline{\boldsymbol{r}})$

$$\Big(- \frac{1}{2}\Delta + \hat{\mathcal{V}}(\underline{\boldsymbol{r}})\Big)\psi_i(\underline{\boldsymbol{r}}) = \varepsilon_i \psi_i(\underline{\boldsymbol{r}})$$

- Insert basis expansion and integrate

$$\int_\Omega \varphi_j(\underline{\boldsymbol{r}})\Big(- \frac{1}{2}\Delta + \hat{\mathcal{V}}(\underline{\boldsymbol{r}})\Big)\psi_i(\underline{\boldsymbol{r}}) \,\mathrm{d}\underline{\boldsymbol{r}} = \int_\Omega \varphi_j(\underline{\boldsymbol{r}})\varepsilon_i \psi_i(\underline{\boldsymbol{r}}) \,\mathrm{d}\underline{\boldsymbol{r}}$$

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- Insert basis expansion and integrate

$$\sum_k z_k^{(i)} \int_\Omega \varphi_j(\underline{\boldsymbol{r}})\Big(-\frac{1}{2}\Delta + \hat{\mathcal{V}}(\underline{\boldsymbol{r}})\Big)\varphi_k(\underline{\boldsymbol{r}})\,\mathrm{d}\underline{\boldsymbol{r}} = \sum_k z_k^{(i)} \int_\Omega \varphi_j(\underline{\boldsymbol{r}})\varepsilon_i\varphi_k(\underline{\boldsymbol{r}})\,\mathrm{d}\underline{\boldsymbol{r}}$$

Getting the weak form (2)

- Apply partial integration

$$-\int_\Omega \varphi_j(\underline{\boldsymbol{r}})\frac{1}{2}\Delta\varphi_k(\underline{\boldsymbol{r}})\ \mathrm{d}\underline{\boldsymbol{r}} = -\int_{\partial\Omega}\frac{1}{2}\,\varphi_j(\underline{\boldsymbol{r}})\,\nabla\varphi_k(\underline{\boldsymbol{r}})\cdot\underline{\hat{\boldsymbol{n}}}_s\ \mathrm{d}s + \int_\Omega \frac{1}{2}\nabla\varphi_j(\underline{\boldsymbol{r}})\cdot\nabla\varphi_k(\underline{\boldsymbol{r}})\ \mathrm{d}\underline{\boldsymbol{r}}$$

- *Weak formulation* of the Hartree-Fock problem:
  For all basis functions φ_j it holds:

$$\sum_k z_k^{(i)}\int_\Omega \frac{1}{2}\nabla\varphi_j(\underline{\boldsymbol{r}})\cdot\nabla\varphi_k(\underline{\boldsymbol{r}}) + \varphi_j(\underline{\boldsymbol{r}})\hat{\mathcal{V}}(\underline{\boldsymbol{r}})\varphi_k(\underline{\boldsymbol{r}})\ \mathrm{d}\underline{\boldsymbol{r}} = \varepsilon_i\sum_k z_k^{(i)}\int_\Omega \varphi_j(\underline{\boldsymbol{r}})\varphi_k(\underline{\boldsymbol{r}})\ \mathrm{d}\underline{\boldsymbol{r}}$$

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$$= \varepsilon_i \sum_k z_k^{(i)} \int_\Omega \varphi_j(\underline{\boldsymbol{r}}) \varphi_k(\underline{\boldsymbol{r}}) \, \mathrm{d}\underline{\boldsymbol{r}}$$

Introducing matrices

- Mass matrix

$$M_{jk} = \int_\Omega \varphi_j(\underline{\boldsymbol{r}})\varphi_k(\underline{\boldsymbol{r}})\ \mathrm{d}\underline{\boldsymbol{r}}$$

- Stiffness matrix

$$A_{jk} = \int_\Omega \frac{1}{2}\nabla\varphi_j(\underline{\boldsymbol{r}}) \cdot \nabla\varphi_k(\underline{\boldsymbol{r}}) + \varphi_j(\underline{\boldsymbol{r}})\,\hat{\mathcal{V}}(\underline{\boldsymbol{r}})\,\varphi_k(\underline{\boldsymbol{r}})\ \mathrm{d}\underline{\boldsymbol{r}}$$

- Generalised eigenvalue problem:

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- Generalised eigenvalue problem:

$$\sum_k z_k^{(i)} A_{jk} = \varepsilon_i \sum_k z_k^{(i)} M_{jk}$$

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- Generalised eigenvalue problem:

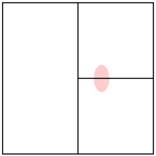
$$\mathbf{A}\underline{\boldsymbol{z}}^{(i)} = \varepsilon_i \mathbf{M}\underline{\boldsymbol{z}}^{(i)}$$

Adaptive mesh refinement

- For good results need about 10^4 to 10^7 basis functions
- Grid can be refined adaptively

$\Rightarrow$ Usually hierarchy of meshes used

- *A posteriori* error estimation
- Can scale error by importance (multi-scale methods)



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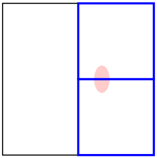

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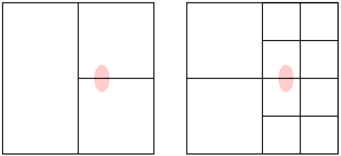

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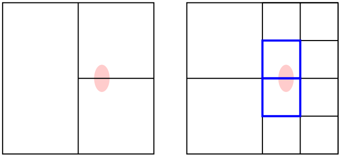

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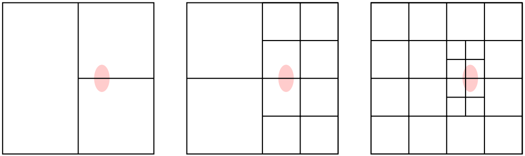

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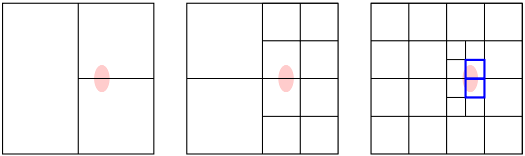

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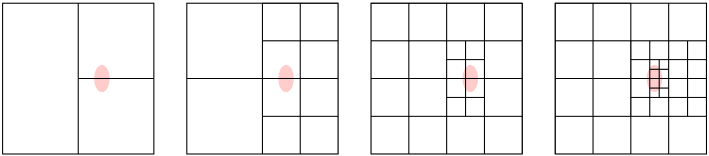

Overview of a calculation

- Need an SCF procedure: $\hat{\mathcal{V}}_H$ and $\hat{\mathcal{V}}_x$ depend on $\{\psi_i\}_i$
- Build a sufficiently good grid
  - Start from coarse grid
  - Adaptive refinement
- Run SCF calculation:
  - Calculate $\mathbf{M}$ and $\mathbf{A}$ for current $\{\psi_i\}_i$
  - Solve generalised eigenvalue problem to get new $\{\psi_i\}_i$
- Refine grid an rerun SCF

Remarks

- $\mathbf{M}$ and $\mathbf{A}$ are large, but sparse
- Expensive step is building $\mathbf{A}$, especially term containing $\hat{\mathcal{V}}_x$
- For initial grid refinement use simplified potential $\hat{\mathcal{V}}(\underline{\boldsymbol{r}})$

Contents

Splitting into cell contributions

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

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

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

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

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

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

Transformation to unit cell and quadrature

$$M_{ij}^{c} = \int_{c} \varphi_i(\underline{\boldsymbol{r}})\varphi_j(\underline{\boldsymbol{r}})\,\mathrm{d}\underline{\boldsymbol{r}}$$

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\end{aligned}
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&= \int_{c_0} e_\alpha(\underline{\boldsymbol{\xi}})\, e_\beta(\underline{\boldsymbol{\xi}}) \det\Big(J_c(\underline{\boldsymbol{\xi}})\Big) \, \mathrm{d}\underline{\boldsymbol{\xi}}
\end{aligned}
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- 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

Transformation to unit cell and quadrature

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Contributions to $\mathbf{A}$

$$A_{jk} = \int_\Omega \frac{1}{2}\nabla\varphi_j(\underline{\boldsymbol{r}}) \cdot \nabla\varphi_k(\underline{\boldsymbol{r}}) + \varphi_j(\underline{\boldsymbol{r}})\Big(\hat{\mathcal{V}}_0(\underline{\boldsymbol{r}}) + \hat{\mathcal{V}}_H(\underline{\boldsymbol{r}}) + \hat{\mathcal{V}}_x(\underline{\boldsymbol{r}})\Big)\varphi_k(\underline{\boldsymbol{r}})\,\mathrm{d}\underline{\boldsymbol{r}}$$

where

$$T^c_{jk} = \int_c \frac{1}{2}\nabla\varphi_j(\underline{\boldsymbol{r}}) \cdot \nabla\varphi_k(\underline{\boldsymbol{r}})\,\mathrm{d}\underline{\boldsymbol{r}}$$

$$\left(V_0\right)^c_{jk} = \int_c \varphi_j(\underline{\boldsymbol{r}})\,\hat{\mathcal{V}}_0(\underline{\boldsymbol{r}})\,\varphi_k(\underline{\boldsymbol{r}})\,\mathrm{d}\underline{\boldsymbol{r}}$$

$$\left(V_H\right)^c_{jk} = \int_c \varphi_j(\underline{\boldsymbol{r}})\,\hat{\mathcal{V}}_H(\underline{\boldsymbol{r}})\,\varphi_k(\underline{\boldsymbol{r}})\,\mathrm{d}\underline{\boldsymbol{r}}$$

$$\left(V_x\right)^c_{jk} = \int_c \varphi_j(\underline{\boldsymbol{r}})\,\hat{\mathcal{V}}_x(\underline{\boldsymbol{r}})\,\varphi_k(\underline{\boldsymbol{r}})\,\mathrm{d}\underline{\boldsymbol{r}}$$

Contributions to $\mathbf{A}$

$$A_{jk} = \sum_c \int_c \frac{1}{2}\nabla\varphi_j(\underline{\boldsymbol{r}}) \cdot \nabla\varphi_k(\underline{\boldsymbol{r}}) + \varphi_j(\underline{\boldsymbol{r}})\Big(\hat{\mathcal{V}}_0(\underline{\boldsymbol{r}}) + \hat{\mathcal{V}}_H(\underline{\boldsymbol{r}}) + \hat{\mathcal{V}}_x(\underline{\boldsymbol{r}})\Big)\varphi_k(\underline{\boldsymbol{r}})\,\mathrm{d}\underline{\boldsymbol{r}}$$

where

$$T^c_{jk} = \int_c \frac{1}{2}\nabla\varphi_j(\underline{\boldsymbol{r}}) \cdot \nabla\varphi_k(\underline{\boldsymbol{r}})\,\mathrm{d}\underline{\boldsymbol{r}}$$

$$\left(V_0\right)^c_{jk} = \int_c \varphi_j(\underline{\boldsymbol{r}})\,\hat{\mathcal{V}}_0(\underline{\boldsymbol{r}})\,\varphi_k(\underline{\boldsymbol{r}})\,\mathrm{d}\underline{\boldsymbol{r}}$$

$$\left(V_H\right)^c_{jk} = \int_c \varphi_j(\underline{\boldsymbol{r}})\,\hat{\mathcal{V}}_H(\underline{\boldsymbol{r}})\,\varphi_k(\underline{\boldsymbol{r}})\,\mathrm{d}\underline{\boldsymbol{r}}$$

$$\left(V_x\right)^c_{jk} = \int_c \varphi_j(\underline{\boldsymbol{r}})\,\hat{\mathcal{V}}_x(\underline{\boldsymbol{r}})\,\varphi_k(\underline{\boldsymbol{r}})\,\mathrm{d}\underline{\boldsymbol{r}}$$

Contributions to $\mathbf{A}$

$$A_{jk} = \sum_c T^c_{jk} + \left(V_0\right)^c_{jk} + \left(V_H\right)^c_{jk} + \left(V_x\right)^c_{jk}$$

where

$$T^c_{jk} = \int_c \frac{1}{2} \nabla \varphi_j(\underline{\boldsymbol{r}}) \cdot \nabla \varphi_k(\underline{\boldsymbol{r}})\, \mathrm{d}\underline{\boldsymbol{r}}$$

$$\left(V_0\right)^c_{jk} = \int_c \varphi_j(\underline{\boldsymbol{r}})\, \hat{\mathcal{V}}_0(\underline{\boldsymbol{r}})\, \varphi_k(\underline{\boldsymbol{r}})\, \mathrm{d}\underline{\boldsymbol{r}}$$

$$\left(V_H\right)^c_{jk} = \int_c \varphi_j(\underline{\boldsymbol{r}})\, \hat{\mathcal{V}}_H(\underline{\boldsymbol{r}})\, \varphi_k(\underline{\boldsymbol{r}})\, \mathrm{d}\underline{\boldsymbol{r}}$$

$$\left(V_x\right)^c_{jk} = \int_c \varphi_j(\underline{\boldsymbol{r}})\, \hat{\mathcal{V}}_x(\underline{\boldsymbol{r}})\, \varphi_k(\underline{\boldsymbol{r}})\, \mathrm{d}\underline{\boldsymbol{r}}$$

Coulomb term $\left(V_H\right)_{jk}^c$

$$\left(V_H\right)_{jk}^c = \int_c \varphi_j(\underline{\boldsymbol{r}})\,\hat{\mathcal{V}}_H(\underline{\boldsymbol{r}})\,\varphi_k(\underline{\boldsymbol{r}})\,\mathrm{d}\underline{\boldsymbol{r}}$$

$$\hat{\mathcal{V}}_H(\underline{\boldsymbol{r}}_1) = \sum_i \int_\Omega \frac{\left|\psi_i(\underline{\boldsymbol{r}}_2)\right|^2}{r_{12}}\,\mathrm{d}\underline{\boldsymbol{r}}_2$$

- $\hat{\mathcal{V}}_H(\underline{\boldsymbol{r}})$ is local potential

Coulomb term $\left(V_H\right)^c_{jk}$

$$\left(V_H\right)^c_{jk} = \int_c \varphi_j(\underline{\boldsymbol{r}})\,\hat{\mathcal{V}}_H(\underline{\boldsymbol{r}})\,\varphi_k(\underline{\boldsymbol{r}})\,\mathrm{d}\underline{\boldsymbol{r}}$$

- $\hat{\mathcal{V}}_H(\underline{\boldsymbol{r}})$ is local potential
- Obtained by solving Poisson eq.[n]:

$$\begin{aligned} -\Delta\hat{\mathcal{V}}_H(\underline{\boldsymbol{r}}) &= 4\pi\rho(\underline{\boldsymbol{r}}) && \underline{\boldsymbol{r}} \in \Omega \\ \alpha(\underline{\boldsymbol{r}})\,\hat{\mathcal{V}}_H(\underline{\boldsymbol{r}}) &= \partial_n\hat{\mathcal{V}}_H(\underline{\boldsymbol{r}}) && \underline{\boldsymbol{r}} \in \partial\Omega \end{aligned}$$

- The function $\alpha(\underline{\boldsymbol{r}})$ is determined by

$$\alpha(\underline{\boldsymbol{r}})\frac{N_{\text{elec}} - 1}{r} = \partial_n\frac{N_{\text{elec}} - 1}{r}$$

- Need a large enough grid (ca. 200 Å)

Exchange term $\left(V_x\right)_{jk}^{c}$

$$\left(V_x\right)_{jk}^{c} = \int_c \varphi_j(\underline{\boldsymbol{r}}_1)\,\hat{\mathcal{V}}_x(\underline{\boldsymbol{r}}_1)\,\varphi_k(\underline{\boldsymbol{r}}_1)\,\mathrm{d}\underline{\boldsymbol{r}}_1$$

- $\hat{\mathcal{V}}_x(\underline{\boldsymbol{r}})$ is non-local
- Quadratic scaling in N_{FE}
- Integration again by quadrature in unit cell
- Problem: r_{12}^{-1} singularity

Exchange term $\left(V_x\right)_{jk}^{c}$

$$
\begin{aligned}
\left(V_x\right)_{jk}^{c} &= \int_c \varphi_j(\underline{\boldsymbol{r}}_1)\, \hat{\mathcal{V}}_x(\underline{\boldsymbol{r}}_1)\, \varphi_k(\underline{\boldsymbol{r}}_1)\, \mathrm{d}\underline{\boldsymbol{r}}_1 \\
&= \int_c \varphi_j(\underline{\boldsymbol{r}}_1) \int_\Omega \frac{\sum_i \psi_i(\underline{\boldsymbol{r}}_1)\psi_i(\underline{\boldsymbol{r}}_2)}{r_{12}} \varphi_k(\underline{\boldsymbol{r}}_2)\, \mathrm{d}\underline{\boldsymbol{r}}_2\, \mathrm{d}\underline{\boldsymbol{r}}_1
\end{aligned}
$$

- $\hat{\mathcal{V}}_x(\underline{\boldsymbol{r}})$ is non-local
- Quadratic scaling in N_{FE}
- Integration again by quadrature in unit cell
- Problem: r_{12}^{-1} singularity

Exchange term $\left(V_x\right)^c_{jk}$

$$
\begin{aligned}
\left(V_x\right)^c_{jk} &= \int_c \varphi_j(\underline{\boldsymbol{r}}_1)\,\hat{\mathcal{V}}_x(\underline{\boldsymbol{r}}_1)\,\varphi_k(\underline{\boldsymbol{r}}_1)\,\mathrm{d}\underline{\boldsymbol{r}}_1 \\
&= \int_c \varphi_j(\underline{\boldsymbol{r}}_1) \int_\Omega \frac{\sum_i \psi_i(\underline{\boldsymbol{r}}_1)\psi_i(\underline{\boldsymbol{r}}_2)}{r_{12}} \varphi_k(\underline{\boldsymbol{r}}_2)\,\mathrm{d}\underline{\boldsymbol{r}}_2\,\mathrm{d}\underline{\boldsymbol{r}}_1 \\
&= \int_c \varphi_j(\underline{\boldsymbol{r}}_1) \int_\Omega \frac{\rho(\underline{\boldsymbol{r}}_1, \underline{\boldsymbol{r}}_2)}{r_{12}} \varphi_k(\underline{\boldsymbol{r}}_2)\,\mathrm{d}\underline{\boldsymbol{r}}_2\,\mathrm{d}\underline{\boldsymbol{r}}_1
\end{aligned}
$$

- $\hat{\mathcal{V}}_x(\underline{\boldsymbol{r}})$ is non-local
- Quadratic scaling in N_{FE}
- Integration again by quadrature in unit cell
- Problem: r_{12}^{-1} singularity

Exchange term $\left(V_x\right)_{jk}^c$

$$\begin{aligned}\left(V_x\right)_{jk}^c &= \int_c \varphi_j(\underline{\boldsymbol{r}}_1)\, \hat{\mathcal{V}}_x(\underline{\boldsymbol{r}}_1)\, \varphi_k(\underline{\boldsymbol{r}}_1)\, \mathrm{d}\underline{\boldsymbol{r}}_1 \\ &= \int_c \varphi_j(\underline{\boldsymbol{r}}_1) \int_\Omega \frac{\sum_i \psi_i(\underline{\boldsymbol{r}}_1)\psi_i(\underline{\boldsymbol{r}}_2)}{r_{12}} \varphi_k(\underline{\boldsymbol{r}}_2)\, \mathrm{d}\underline{\boldsymbol{r}}_2\, \mathrm{d}\underline{\boldsymbol{r}}_1 \\ &= \int_c \varphi_j(\underline{\boldsymbol{r}}_1) \int_\Omega \frac{\rho(\underline{\boldsymbol{r}}_1, \underline{\boldsymbol{r}}_2)}{r_{12}} \varphi_k(\underline{\boldsymbol{r}}_2)\, \mathrm{d}\underline{\boldsymbol{r}}_2\, \mathrm{d}\underline{\boldsymbol{r}}_1 \\ &= \sum_{c'} \int_c \int_{c'} \varphi_j(\underline{\boldsymbol{r}}_1) \frac{\rho(\underline{\boldsymbol{r}}_1, \underline{\boldsymbol{r}}_2)}{r_{12}} \varphi_k(\underline{\boldsymbol{r}}_2)\, \mathrm{d}\underline{\boldsymbol{r}}_2\, \mathrm{d}\underline{\boldsymbol{r}}_1\end{aligned}$$

- $\hat{\mathcal{V}}_x(\underline{\boldsymbol{r}})$ is non-local
- Quadratic scaling in N_{FE}
- Integration again by quadrature in unit cell
- Problem: r_{12}^{-1} singularity

Exchange term $\left(V_x\right)_{jk}^{c}$

$$
\begin{aligned}
\left(V_x\right)_{jk}^{c} &= \int_c \varphi_j(\underline{\boldsymbol{r}}_1)\,\hat{\mathcal{V}}_x(\underline{\boldsymbol{r}}_1)\,\varphi_k(\underline{\boldsymbol{r}}_1)\,\mathrm{d}\underline{\boldsymbol{r}}_1 \\
&= \int_c \varphi_j(\underline{\boldsymbol{r}}_1) \int_\Omega \frac{\sum_i \psi_i(\underline{\boldsymbol{r}}_1)\psi_i(\underline{\boldsymbol{r}}_2)}{r_{12}} \varphi_k(\underline{\boldsymbol{r}}_2)\,\mathrm{d}\underline{\boldsymbol{r}}_2\,\mathrm{d}\underline{\boldsymbol{r}}_1 \\
&= \int_c \varphi_j(\underline{\boldsymbol{r}}_1) \int_\Omega \frac{\rho(\underline{\boldsymbol{r}}_1, \underline{\boldsymbol{r}}_2)}{r_{12}} \varphi_k(\underline{\boldsymbol{r}}_2)\,\mathrm{d}\underline{\boldsymbol{r}}_2\,\mathrm{d}\underline{\boldsymbol{r}}_1 \\
&= \sum_{c'} \int_c \int_{c'} \varphi_j(\underline{\boldsymbol{r}}_1) \frac{\rho(\underline{\boldsymbol{r}}_1, \underline{\boldsymbol{r}}_2)}{r_{12}} \varphi_k(\underline{\boldsymbol{r}}_2)\,\mathrm{d}\underline{\boldsymbol{r}}_2\,\mathrm{d}\underline{\boldsymbol{r}}_1
\end{aligned}
$$

- $\hat{\mathcal{V}}_x(\underline{\boldsymbol{r}})$ is non-local
- Quadratic scaling in N_{FE}
- Integration again by quadrature in unit cell
- Problem: r_{12}^{-1} singularity

Ideas for approximate exchange

$$\left(V_x\right)_{jk}^{c} = \sum_{c'} \int_c \int_{c'} \varphi_j(\underline{\boldsymbol{r}}_1) \frac{\rho(\underline{\boldsymbol{r}}_1, \underline{\boldsymbol{r}}_2)}{r_{12}} \varphi_k(\underline{\boldsymbol{r}}_2)\, \mathrm{d}\underline{\boldsymbol{r}}_2\, \mathrm{d}\underline{\boldsymbol{r}}_1$$

- Use local approx.^{n} like X-α [1]
- Cell pair distance cutoff
- Only consider interior grid region

[1] R. Alizadegan, K. J. Hsia, and T. J. Martinez, *J. Chem. Phys.*, **132** (2010), 034101.

Contents

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Summary

- FEs are non-orthogonal polynomials
- Adaptive gird refinement possible
- Local potentials give automatic linear scaling
- Non-local potentials problematic
- Matrices are large, but sparse
- Flexible choice of HF boundary conditions

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