

On the adaptive finite element analysis of the Kohn-Sham equations

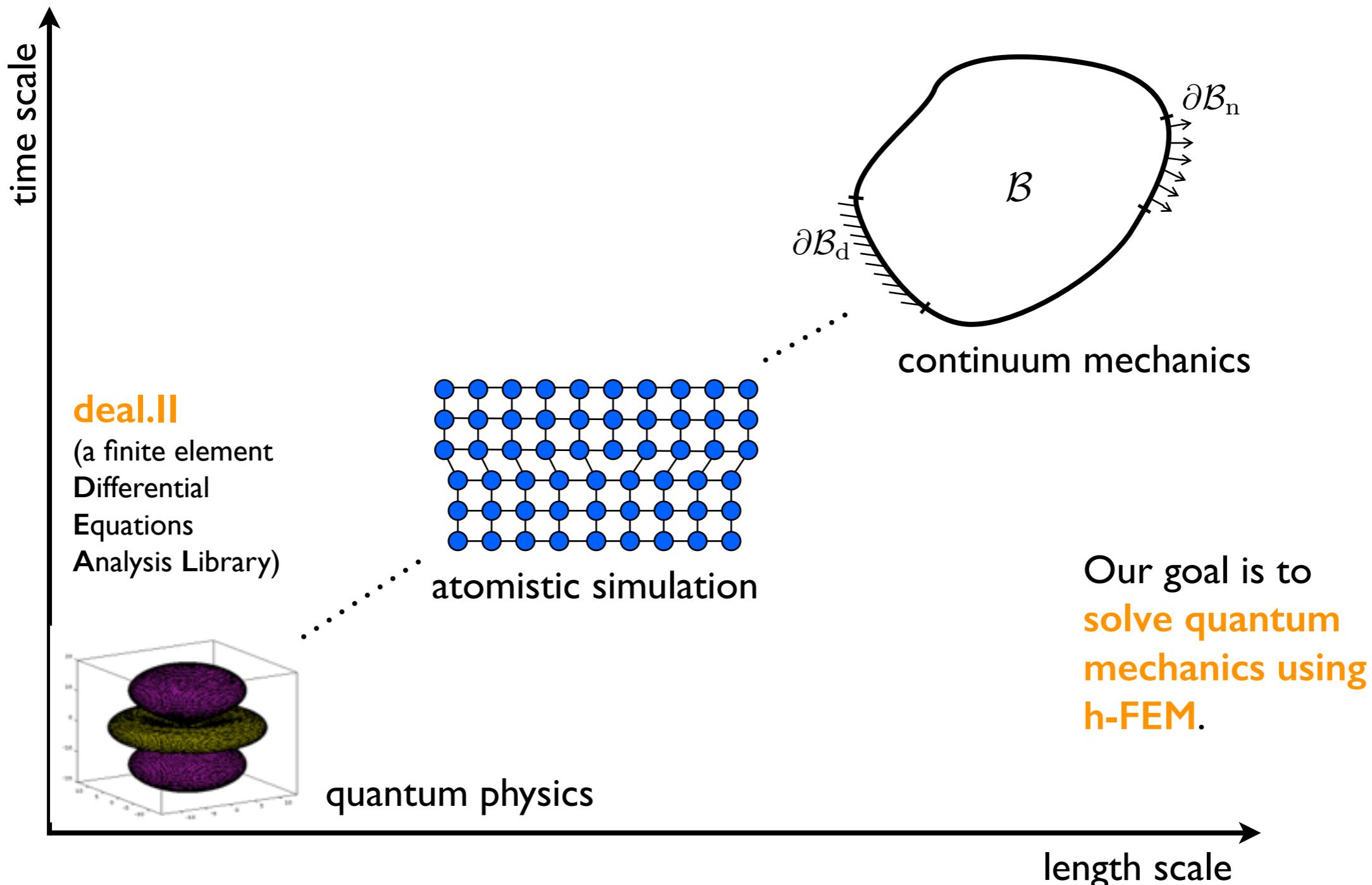
Denis Davydov, Toby Young, Paul Steinmann



Outline

1. Density Functional Theory and its discretisation with FEM
2. Mesh motion approach
3. *A posteriori* mesh refinement
4. Numerical examples and discussion
5. Conclusions and future work

Different Scales

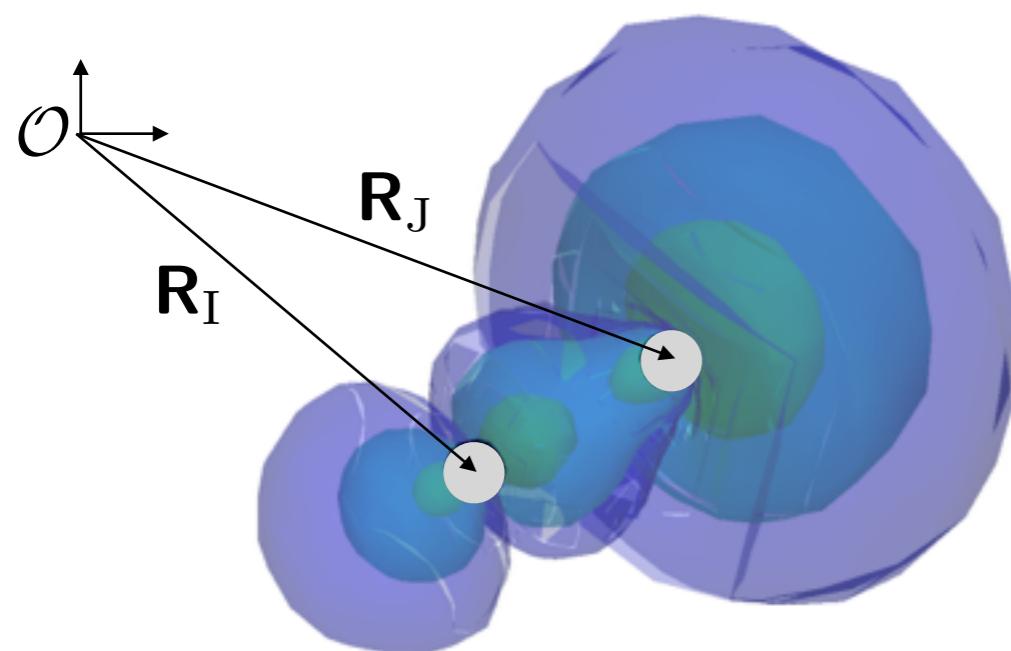


Bangerth, W., Hartmann, R., & Kanschat, G. (2007). deal.II---A general-purpose object-oriented finite element library. *ACM Transactions on Mathematical Software*, 33(4), 24–es. doi:10.1145/1268776.1268779

Kohn-Sham theorem

1. The ground state property of many-electron system is uniquely determined by an electron density $\rho(x) \quad x \in R^3$
2. There exists an energy functional of the system. In the ground state electron density minimises this functional.

Born-Oppenheimer approximation: nuclei are fixed in space, electrons are moving in a static external potential generated by nuclei.



Electronic state is described by a wavefunction $\psi(x)$

Density Functional Theory

Total energy of the system

$$E_0 = E_{\text{kin}} + E_{\text{Hartree}} + E_{\text{ion}} + E_{\text{xc}} + E_{\text{zz}}$$

The kinetic energy of non-interacting electrons:

$$E_{\text{kin}} := \sum_{\alpha} \int_{\Omega} f_{\alpha} \psi_{\alpha}^* \left[-\frac{1}{2} \nabla^2 \right] \psi_{\alpha} \, d\mathbf{x}$$

The exchange-correlation energy which represents quantum many-body interactions:

$$E_{\text{xc}} := \int_{\Omega} \rho(\mathbf{x}) \varepsilon_{\text{xc}}(\rho(\mathbf{x})) \, d\mathbf{x}$$

The Hartree energy (electrostatic interaction between electrons):

$$E_{\text{Hartree}} := \frac{1}{2} \int_{\Omega} \int_{\Omega} \frac{\rho(\mathbf{x}) \rho(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|} \, d\mathbf{x}' \, d\mathbf{x}.$$

Electrostatic interaction between electrons and the external potential of nuclei:

$$E_{\text{ion}} := \int_{\Omega} V_{\text{ion}}(\mathbf{x}) \rho(\mathbf{x}) \, d\mathbf{x} =: \int_{\Omega} \left[- \sum_I \frac{Z_I}{|\mathbf{x} - \mathbf{R}_I|} \right] \rho(\mathbf{x}) \, d\mathbf{x}$$

Repulsive nuclei-nuclei electrostatic interaction energy:

$$E_{\text{zz}} := \frac{1}{2} \sum_{I,J \neq I} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}$$

The electron density:

$$\rho(\mathbf{x}) := \sum_{\alpha} f_{\alpha} |\psi_{\alpha}(\mathbf{x})|^2$$

partial occupancy
number, such that

$$\sum_{\alpha} f_{\alpha} \equiv N_e$$

orthonormal electronic
wavefunctions

Kohn–Sham eigenvalue problem

stationary conditions

$$\left[-\frac{1}{2} \nabla^2 + V_{\text{eff}}(\mathbf{x}; \rho) \right] \psi_\alpha(\mathbf{x}) = \lambda_\alpha \psi_\alpha(\mathbf{x})$$

$$V_{\text{eff}}(\mathbf{x}) := V_{\text{ion}}(\mathbf{x}) + V_{\text{Hartree}}(\mathbf{x}) + V_{\text{xc}}(\mathbf{x}) \equiv - \sum_I \frac{Z_I}{|\mathbf{x} - \mathbf{R}_I|} + \int_{\Omega} \frac{\rho(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|} d\mathbf{x}' + \frac{\delta E_{xc}}{\delta \rho}$$

Explicit Approach: compute Hartree potential more efficiently via solving the Poisson equation

$$-\nabla^2 V_{\text{Hartree}}(\mathbf{x}) = 4\pi \rho(\mathbf{x})$$

need to evaluate V_{ion} for every quadrature point. Hence, bad scaling w.r.t. number of atoms.

Implicit Approach: recall that $1/r$ is Green's functions of the Laplace operator

$$-\nabla^2 [V_{\text{Hartree}}(\mathbf{x}) + V_{\text{ion}}(\mathbf{x})] = 4\pi \left[\rho(\mathbf{x}) - \sum_I Z_I \delta(\mathbf{x} - \mathbf{R}_I) \right]$$

solution is not in H^1 !

Kohn–Sham eigenvalue problem (cont.)

stationary conditions

$$\left[-\frac{1}{2} \nabla^2 + V_{\text{eff}}(\mathbf{x}; \rho) \right] \psi_\alpha(\mathbf{x}) = \lambda_\alpha \psi_\alpha(\mathbf{x})$$

$$V_{\text{eff}}(\mathbf{x}) := V_{\text{ion}}^S(\mathbf{x}) + [V_{\text{ion}}^L(\mathbf{x}) + V_{\text{Hartree}}(\mathbf{x})] + V_{\text{xc}}(\mathbf{x})$$

As a result evaluation of V_{ion} scales linearly w.r.t. the number of atoms.

Gaussian Approach: split Coulomb potential into fully-local short-range and smooth long-range parts

$$V_{\text{ion}}^L(\mathbf{x}) := - \sum_I Z_I \frac{\text{erf}(|\mathbf{x} - \mathbf{R}_I|/\sigma)}{|\mathbf{x} - \mathbf{R}_I|}$$

This potential corresponds to the Gaussian charge distribution, i.e.

$$-\nabla^2 V_{\text{ion}}^L(\mathbf{x}) \equiv -4\pi \sum_I \frac{Z_I}{\pi^{3/2} \sigma^3} \exp\left(-\frac{|\mathbf{x} - \mathbf{R}_I|^2}{\sigma^2}\right)$$

The remaining short-range part is used directly during assembly of the eigenvalue problem

$$V_{\text{ion}}^S(\mathbf{x}) := - \sum_I \frac{Z_I}{|\mathbf{x} - \mathbf{R}_I|} - V_{\text{ion}}^L(\mathbf{x}) = - \sum_I Z_I \frac{1 - \text{erf}(|\mathbf{x} - \mathbf{R}_I|/\sigma)}{|\mathbf{x} - \mathbf{R}_I|}$$

whereas the Hartree potential and the long-range parts are evaluated by solving the Poisson problem

$$-\nabla^2 [V_{\text{Hartree}}(\mathbf{x}) + V_{\text{ion}}^L(\mathbf{x})] = 4\pi \left[\rho(\mathbf{x}) - \sum_I \frac{Z_I}{\pi^{3/2} \sigma^3} \exp\left(-\frac{|\mathbf{x} - \mathbf{R}_I|^2}{\sigma^2}\right) \right]$$

Discretisation in space

Introduce a finite element basis for the wave-functions and the potential fields

$$\psi_\alpha(\mathbf{x}) = \sum_i \psi_{\alpha i} N_i^\psi(\mathbf{x})$$

$$\varphi(\mathbf{x}) = \sum_i \varphi_i N_i^\varphi(\mathbf{x})$$

The generalised eigenvalue problem

$$[K_{ij} + V_{ij}] \psi_{\alpha j} = \lambda_\alpha M_{ij} \psi_{\alpha j}$$

the potential matrix

$$V_{ij} := \int_{\Omega} N_i^\psi(\mathbf{x}) V_{\text{eff}}(\mathbf{x}; \varphi, \rho) N_j^\psi(\mathbf{x}) \, d\mathbf{x}$$

the mass (or overlap) matrix

$$M_{ij} := \int_{\Omega} N_i^\psi(\mathbf{x}) N_j^\psi(\mathbf{x}) \, d\mathbf{x}$$

the kinetic matrix

$$K_{ij} := \frac{1}{2} \int_{\Omega} \nabla N_i^\psi(\mathbf{x}) \cdot \nabla N_j^\psi(\mathbf{x}) \, d\mathbf{x}$$

$$\rho(\mathbf{x}) := \sum_{\alpha} f_{\alpha} |\psi_{\alpha}(\mathbf{x})|^2$$

solve iteratively until convergence i.e. split into a sequence of linear problems

The generalised Poisson problem

$$L_{ij} \varphi_j = R_j^H + R_j^V$$

contribution to the RHS from the electron density

$$R_j^H := \int_{\Omega} 4\pi N_i^\varphi(\mathbf{x}) \rho(\mathbf{x}) \, d\mathbf{x}$$

possibly non-zero contribution to the RHS from nuclei density - R_j^V

the Laplace matrix

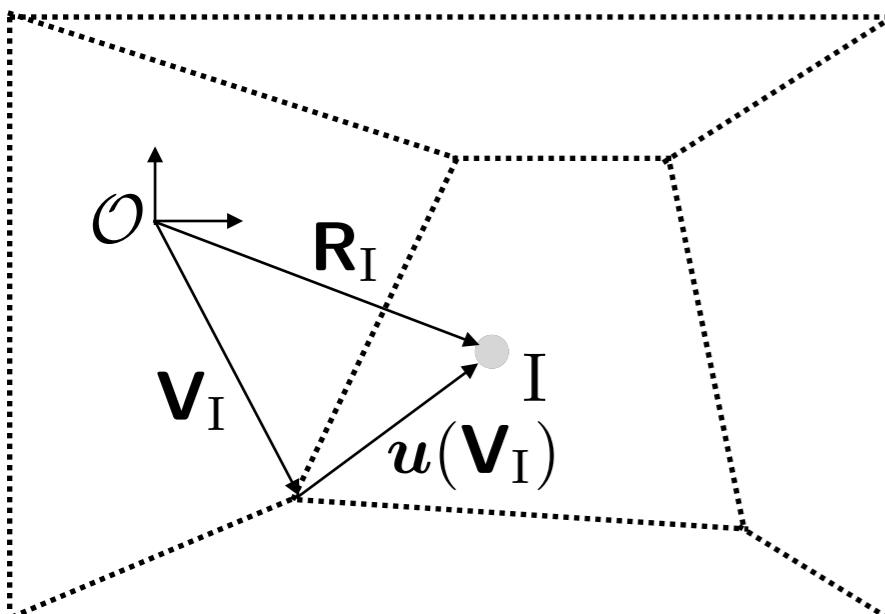
$$L_{ij} := \int_{\Omega} \nabla N_i^\varphi(\mathbf{x}) \cdot \nabla N_j^\varphi(\mathbf{x}) \, d\mathbf{x}$$

Outline

1. Density Functional Theory and its discretisation with FEM
2. Mesh motion approach
3. A *posteriori* mesh refinement
4. Numerical examples and discussion
5. Conclusions and future work

Mesh motion approach

In order to increase the accuracy of numerical solution and avoid singularities of the Coulomb potential, we need to obtain a mesh such that **ions are located at vertexes**.



- find the closest vertex
- prescribe it's motion to nucleus position
- move other nodes as to...

Hence we face a problem of determining the mesh motion field $\mathbf{u}(\mathbf{x})$ according to the specified point-wise constraints.

Approach I: Laplace equation

$$[c(\mathbf{x})\nabla \mathbf{u}(\mathbf{x})] \cdot \nabla = \mathbf{0} \quad \text{on } \Omega, \\ \mathbf{u}(\mathbf{x}) = \mathbf{0} \quad \text{on } \partial\Omega,$$

such that $\mathbf{u}(\mathbf{V}_I) = \mathbf{R}_I - \mathbf{V}_I$,

initial position
of the vertex
closest to
nuclei I.

$$c(\mathbf{x}) = \frac{1}{\min_I |\mathbf{x} - \mathbf{R}_I|}.$$

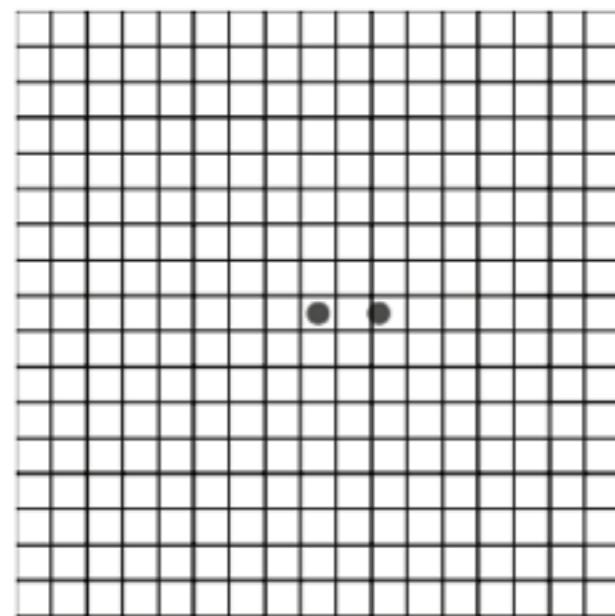
Approach II: small-strain linear elasticity

$$[c(\mathbf{x})\mathbb{C} : \nabla_{\text{sym}} \mathbf{u}(\mathbf{x})] \cdot \nabla = \mathbf{0} \quad \text{on } \Omega, \\ \mathbf{u}(\mathbf{x}) = \mathbf{0} \quad \text{on } \partial\Omega,$$

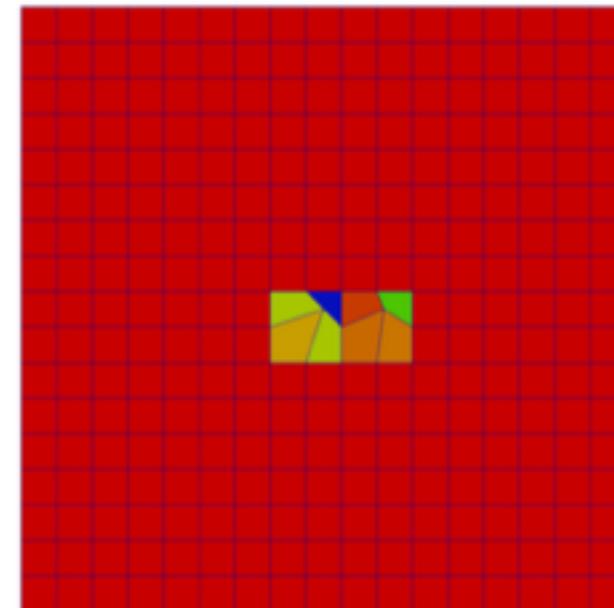
such that $\mathbf{u}(\mathbf{V}_I) = \mathbf{R}_I - \mathbf{V}_I$.

fourth order isotropic
elastic tensor with unit
bulk and shear moduli.

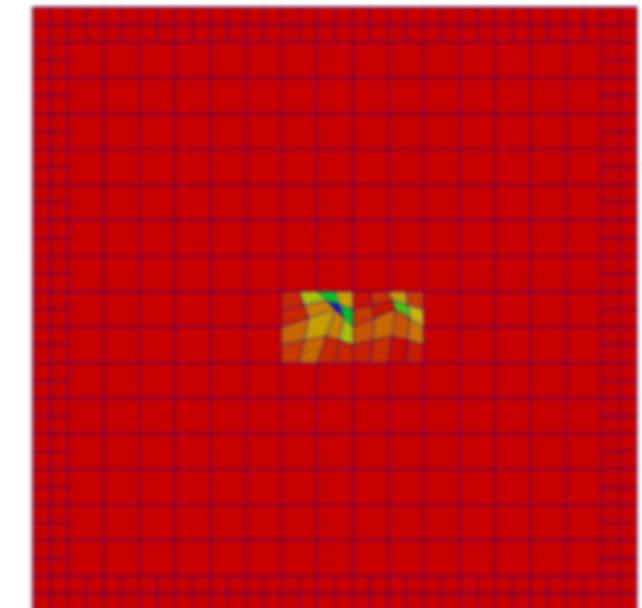
Mesh motion (scaled Jacobian element quality)



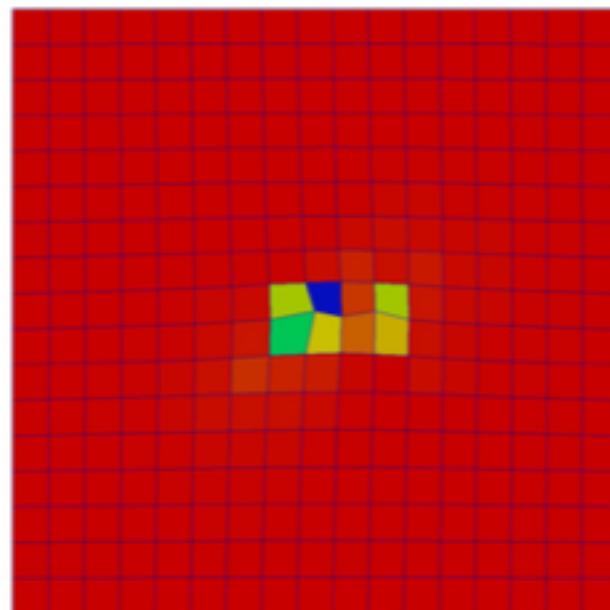
(a) Initial.



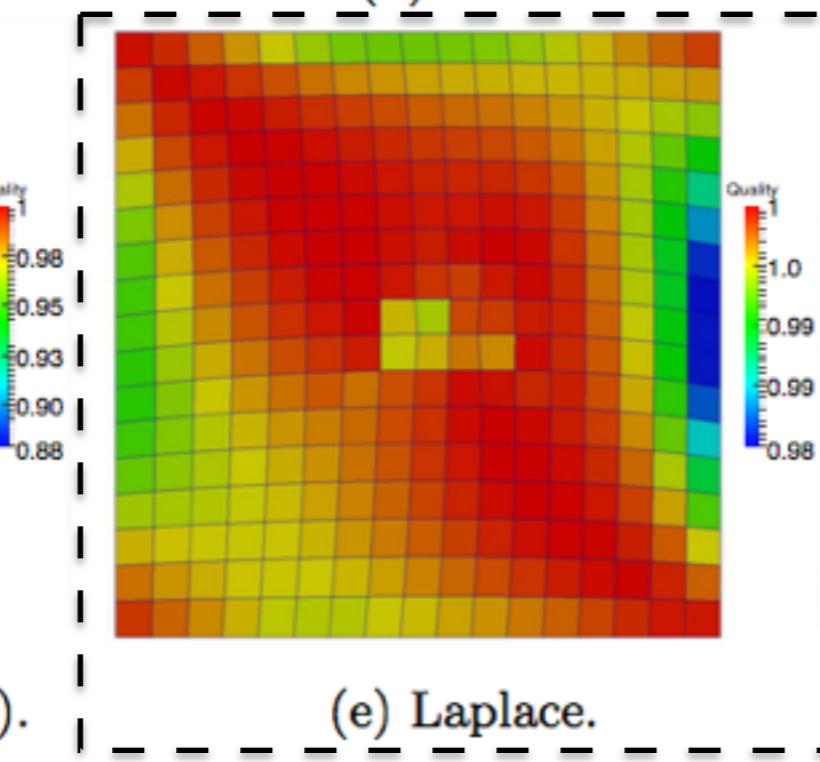
(b) Naïve.



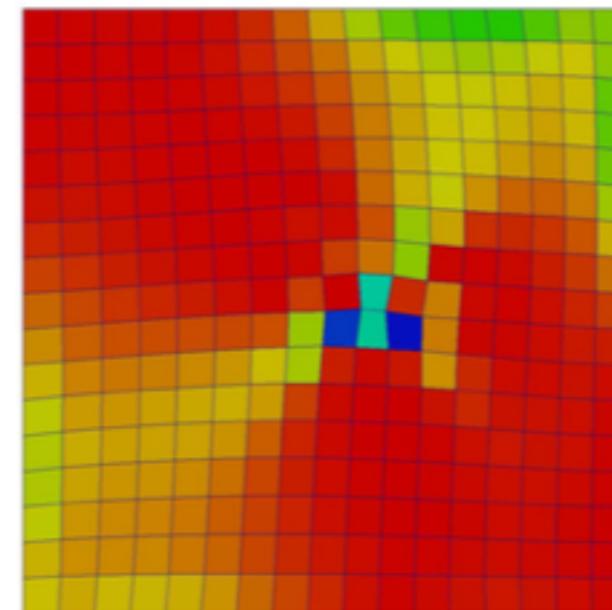
(c) Naïve (refined).



(d) Laplace (homogeneous).



(e) Laplace.



(f) Linear elastic.

- Naive displacement of the closest vertex to the position of nuclei lead to a unacceptably destroyed elements.
- Laplace approach was found to lead to a better element quality near nuclei.

Outline

1. Density Functional Theory and its discretisation with FEM
2. Mesh motion approach
3. *A posteriori* mesh refinement
4. Numerical examples and discussion
5. Conclusions and future work

A posteriori mesh refinement

Approach I: Residual based error-estimator for each eigenpair:

$$\eta_{e,\alpha}^2 := h_e^2 \int_{\Omega_e} \left(\left[-\frac{1}{2} \nabla^2 + V_{\text{eff}} - \lambda_\alpha \right] \psi_\alpha \right)^2 dx + h_e \int_{\partial\Omega_e} [\![\nabla \psi_\alpha \cdot \mathbf{n}]\!]^2 da$$

$$\eta_e^2 \equiv \sum_{\alpha} \eta_{e,\alpha}^2$$

Approach II: Kelly error estimator applied to electron density ρ or the electrostatic potential φ .

$$\eta_e^2(\bullet) := h_e \int_{\partial\Omega_e} [\![\nabla(\bullet) \cdot \mathbf{n}]\!] da$$

Marking strategy: marks a minimum subset of a triangulation $\mathcal{M} \subset \mathcal{T}$ whose squared error is more than a given fraction of the squared total error

$$\theta \left[\sum_{e \in \mathcal{T}} \eta_e^2 \right] \leq \sum_{e \in \mathcal{M}} \eta_e^2$$

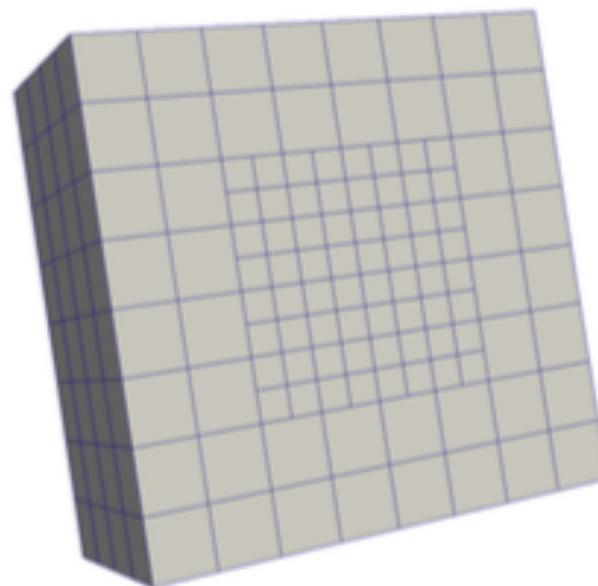
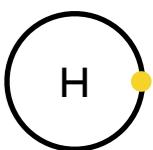
Outline

1. Density Functional Theory and its discretisation with FEM
2. Mesh motion approach
3. *A posteriori* mesh refinement
4. Numerical examples and discussion
5. Conclusions and future work

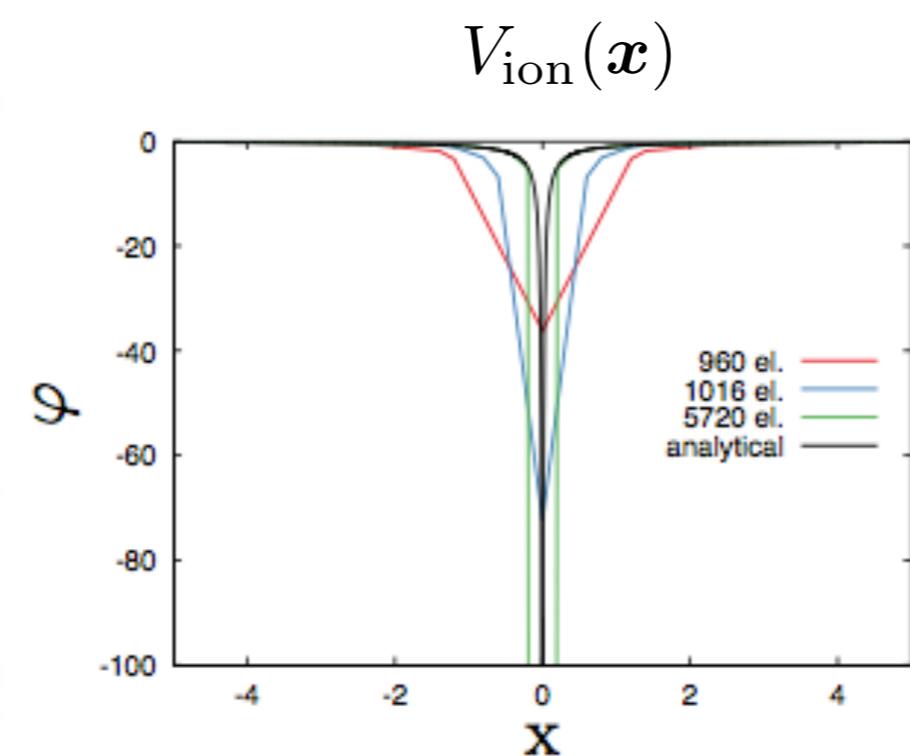
Treatment of the ionic potential

Consider hydrogen atom centered at the origin.

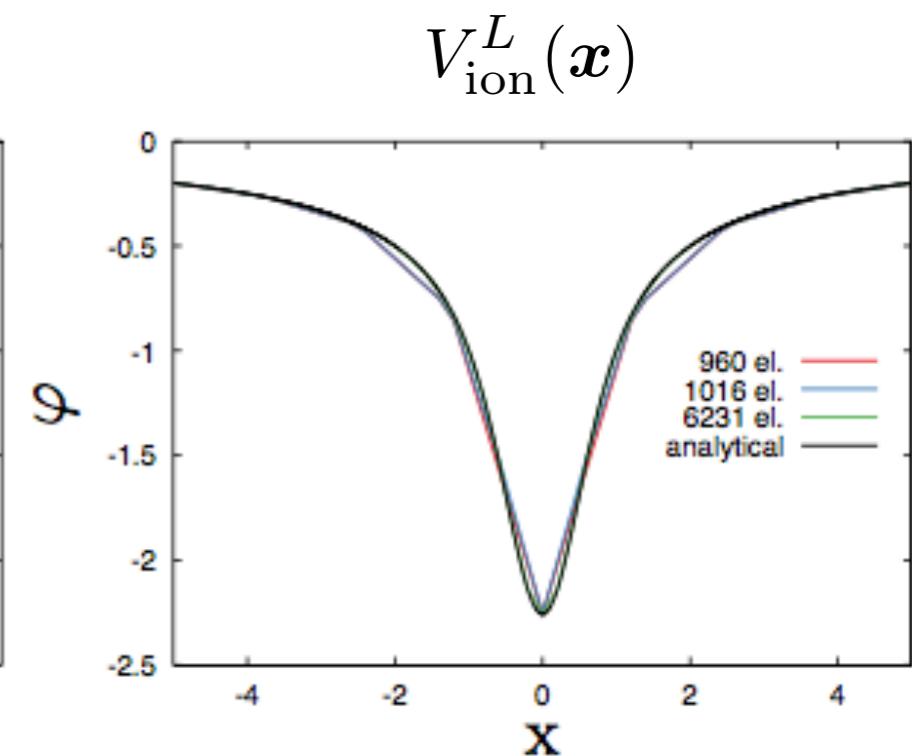
$$V_{\text{eff}} \equiv V_{\text{ion}}$$



(a) FE mesh.



(b) Implicit potential.

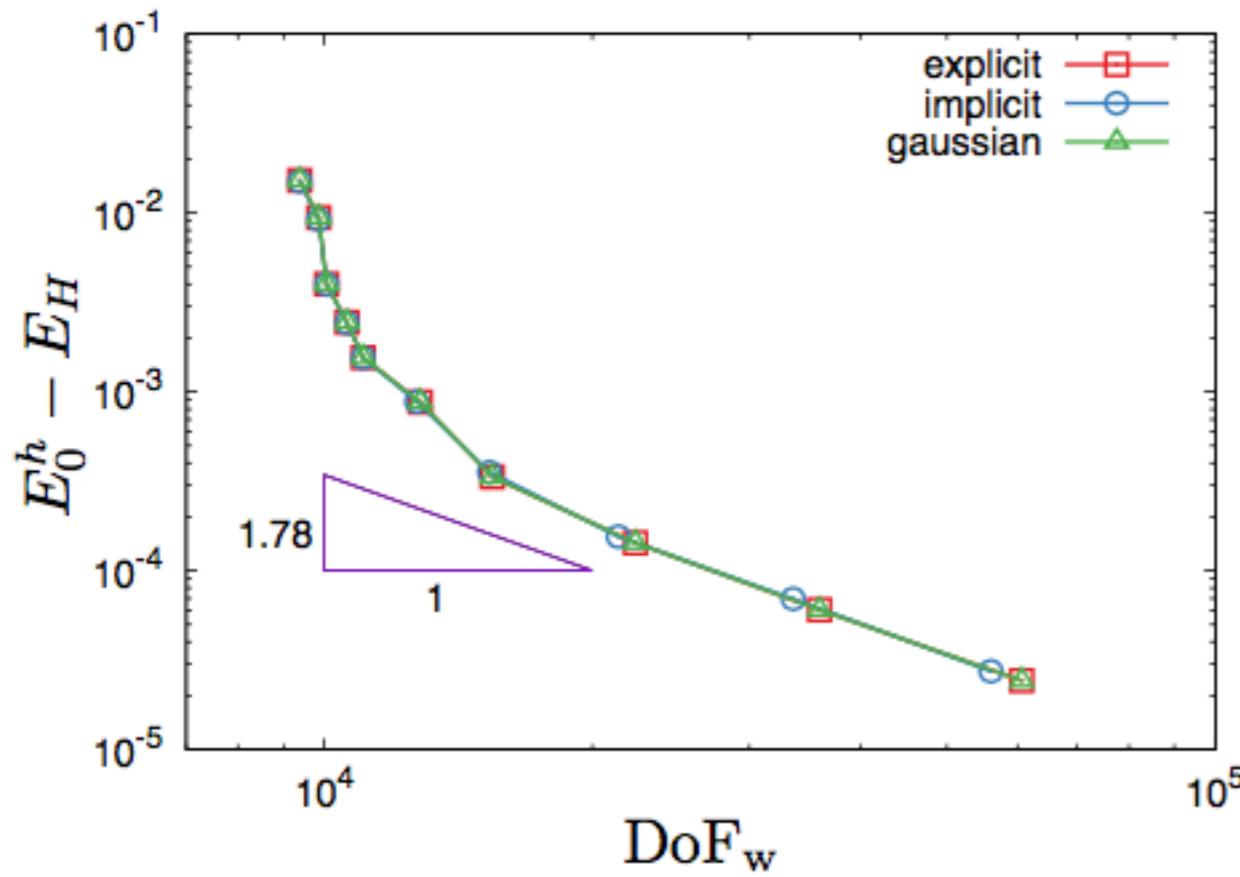
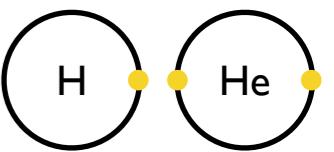


(c) Gaussian potential.

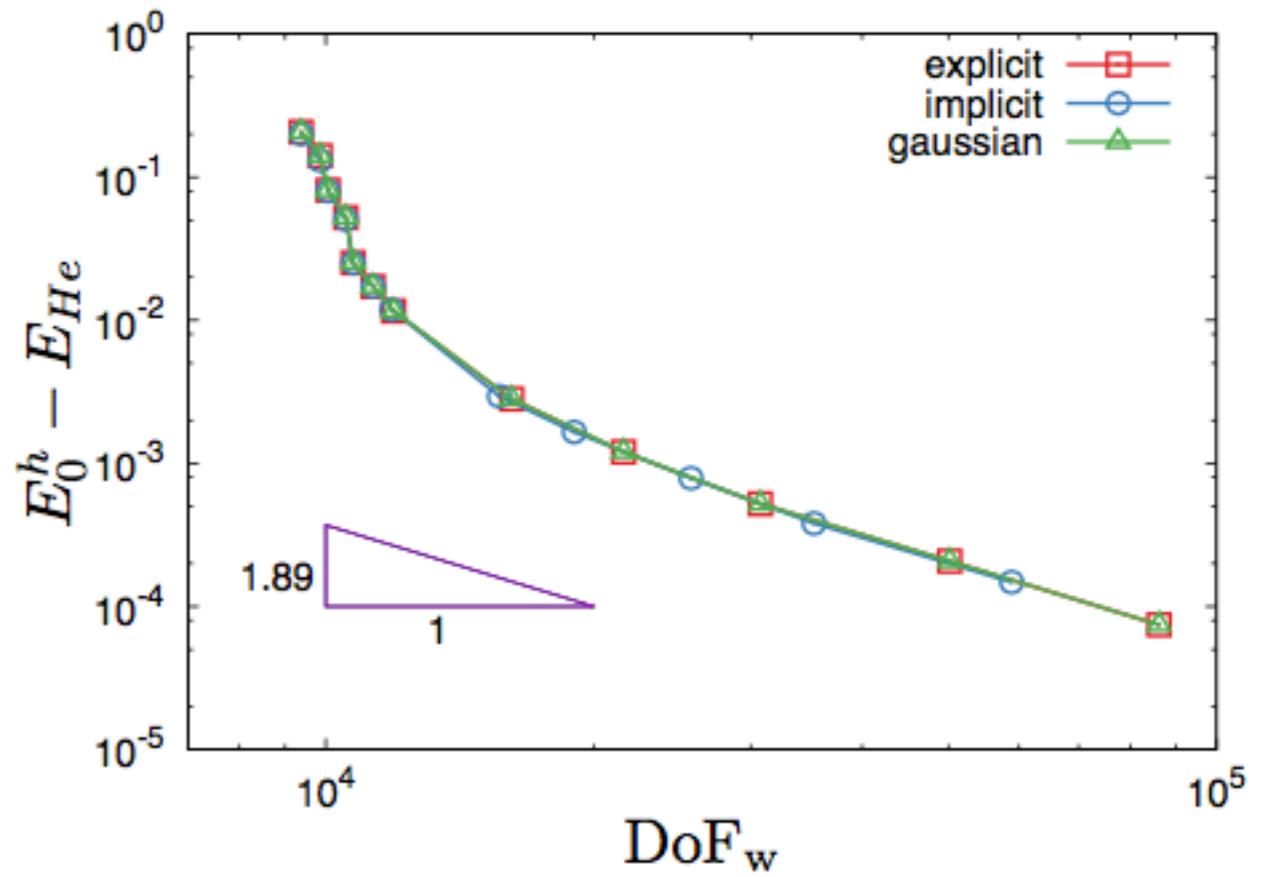
- The $1/r$ singularity can not be represented exactly by non-enhanced FE trial spaces.
- For the Gaussian charge approach a convergence to the analytical solution is evident.

Treatment of the ionic potential (cont.)

Consider hydrogen and helium atoms that are centered at the origin.



(a) Hydrogen.



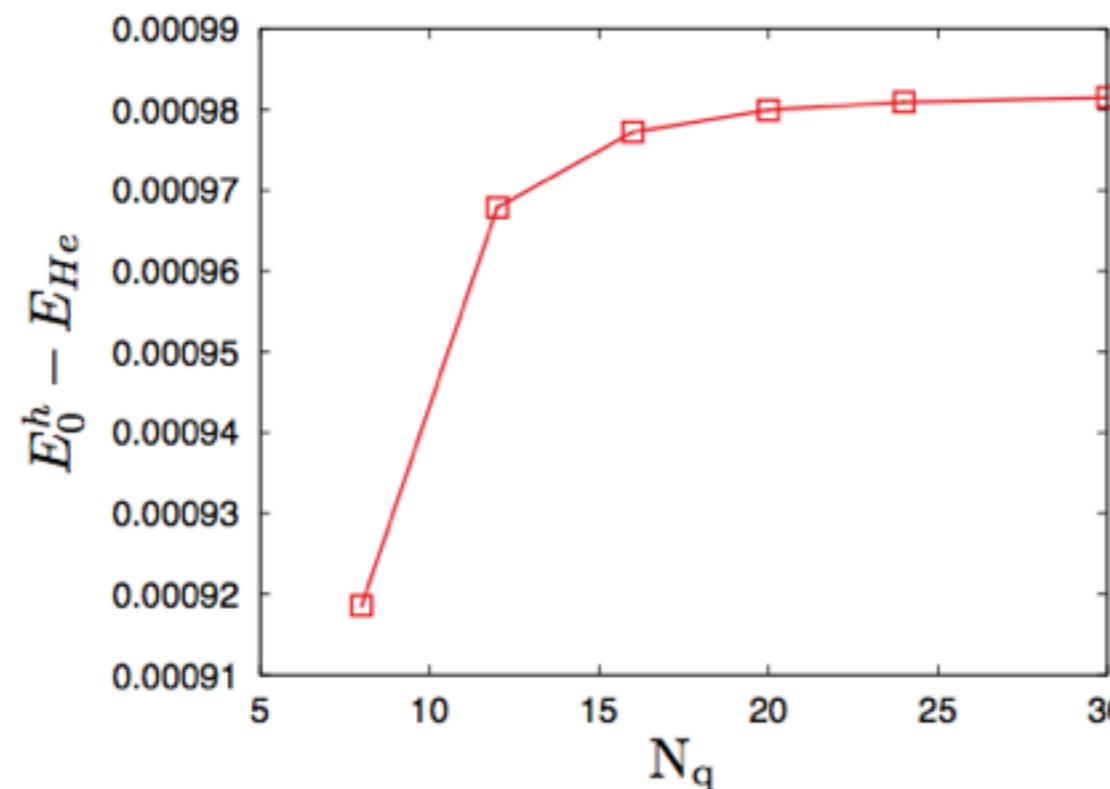
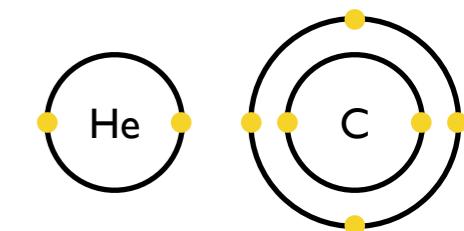
(b) Helium

- Each approach converges to the expected solution with subsequent mesh refinement.
- The split of the potential into fully local short-range and smooth long-range part is beneficial from the computational points of view. Otherwise scales badly w.r.t. the number of atoms.

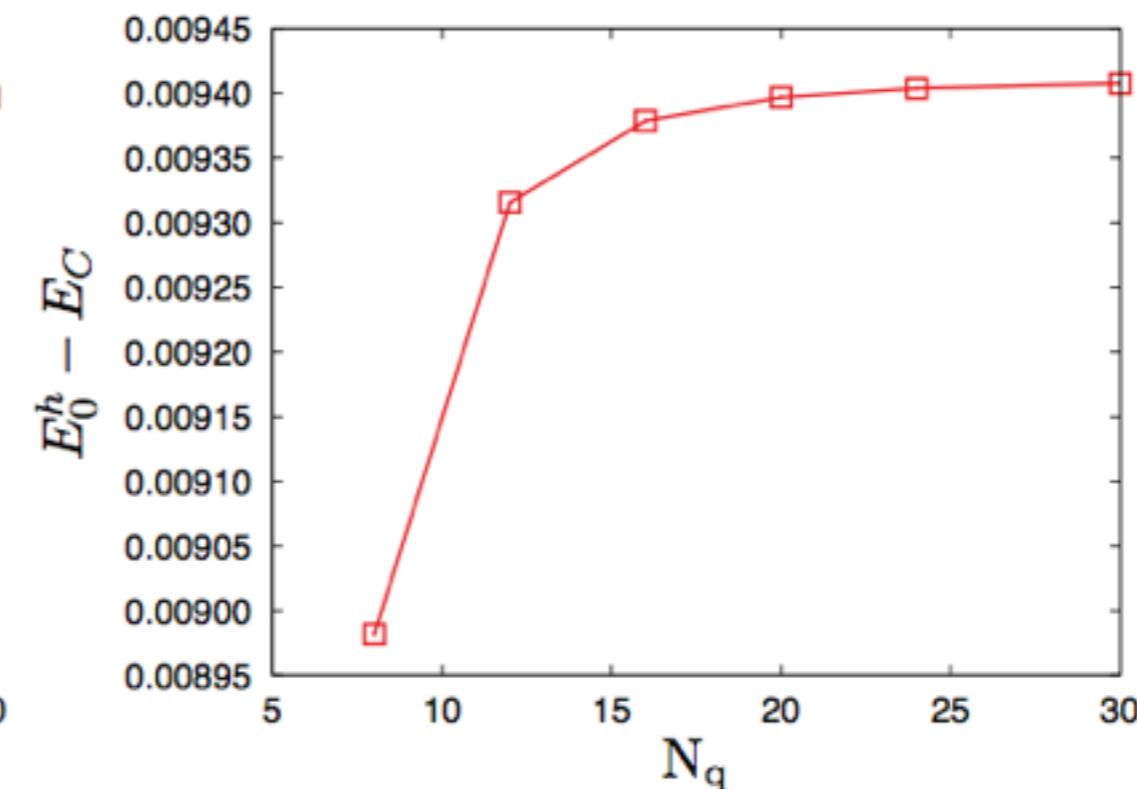
Quadrature order

For explicit treatment of ionic potential nonlinearities mainly come from the exchange-correlation potential and the Coulomb ($1/r$) potential.

Consider **helium** and **carbon** atoms with different quadrature orders used to integrate Hamiltonian matrix and RHS of the Laplace problem.



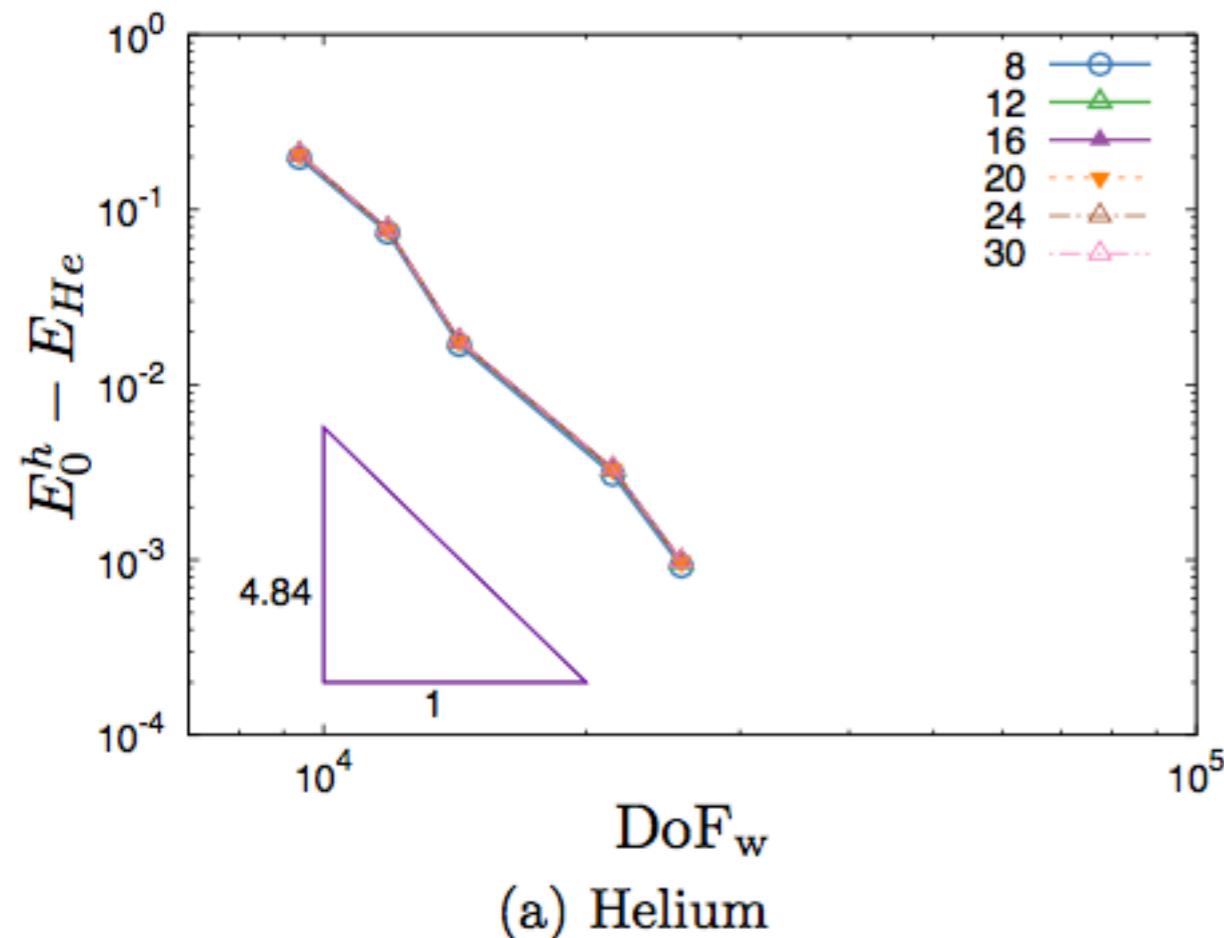
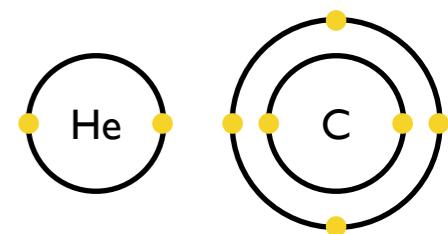
(a) Helium.



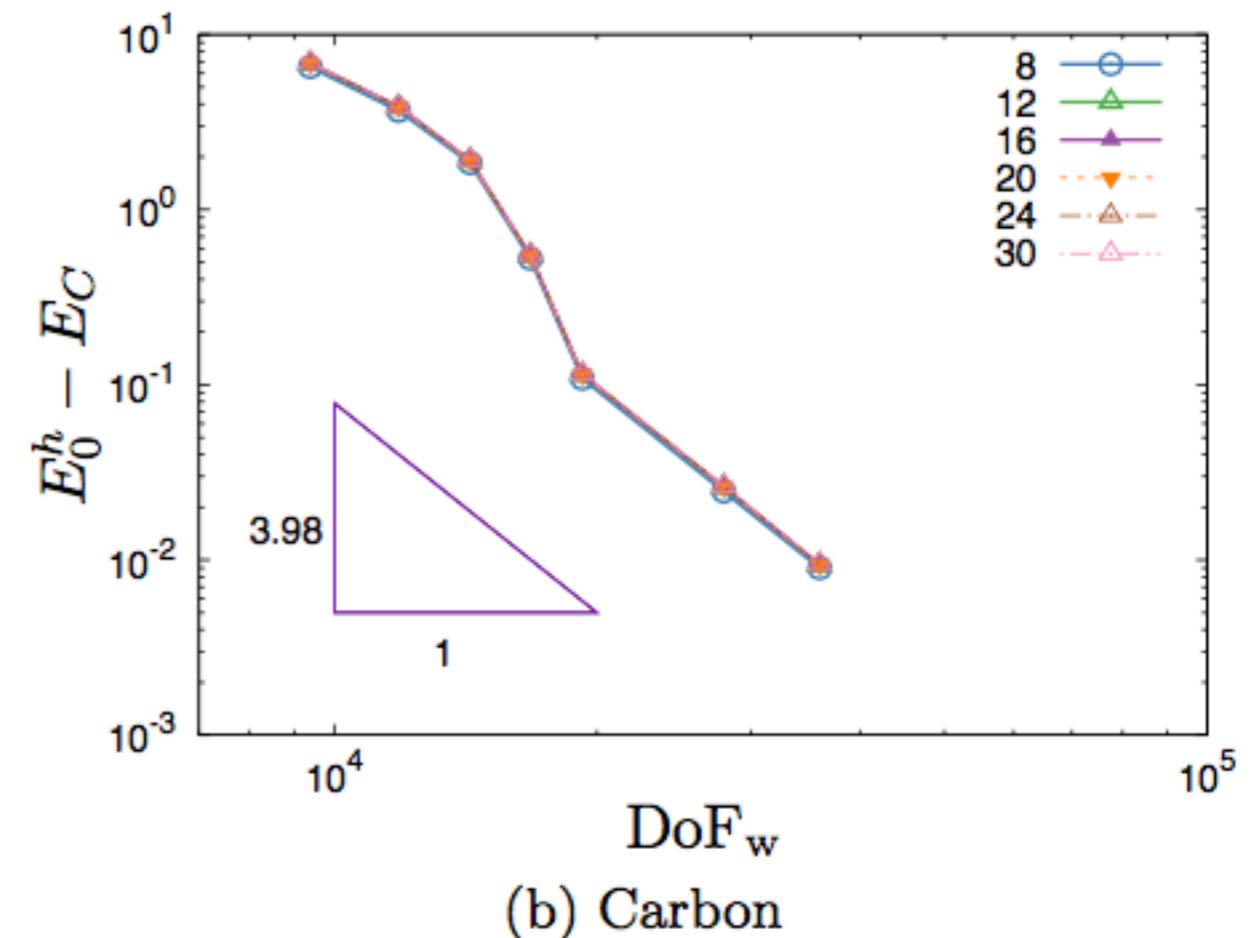
(b) Carbon.

- For both atoms energy convergence w.r.t. quadrature order is observed

Quadrature order (cont.)



(a) Helium

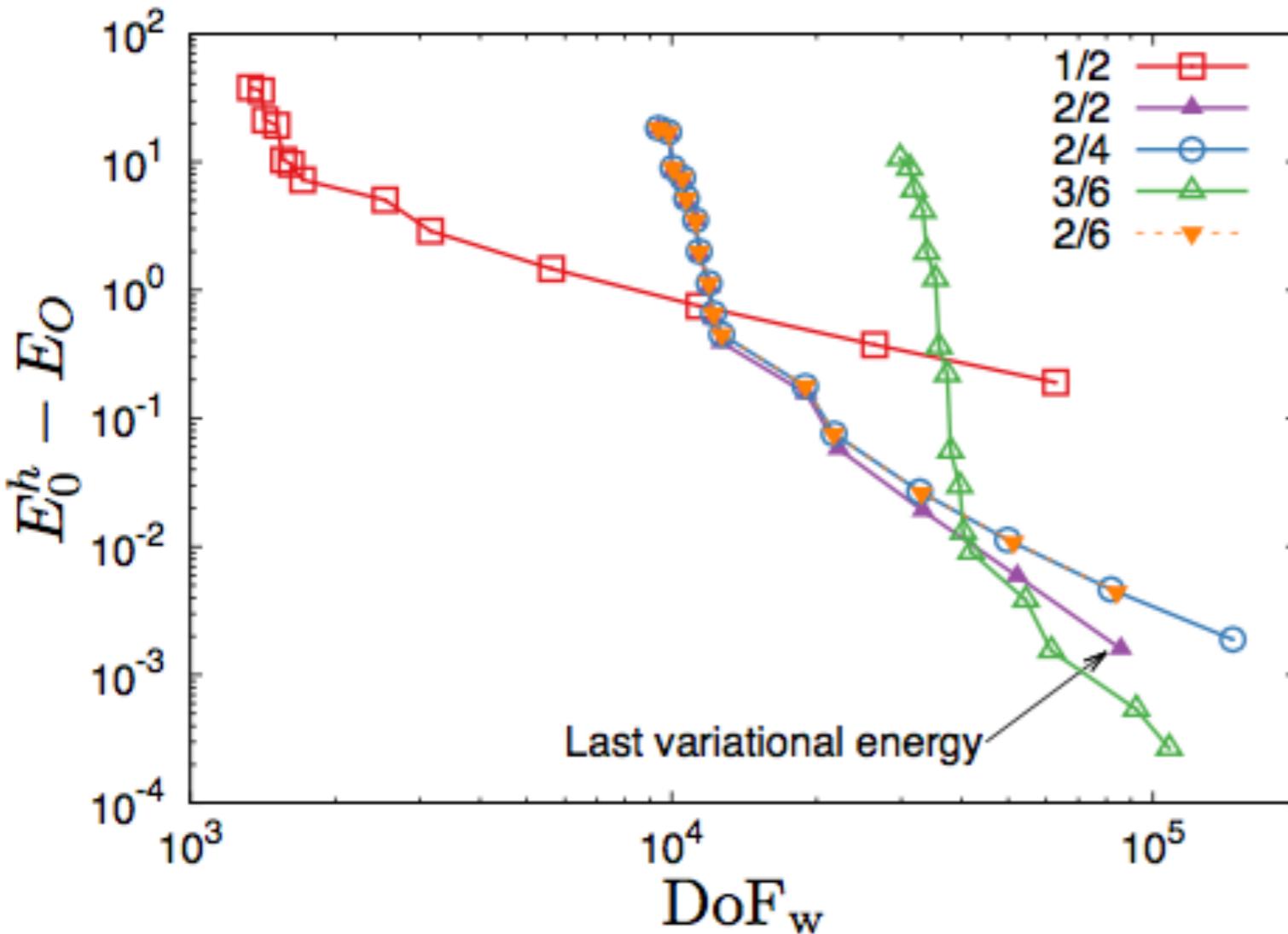
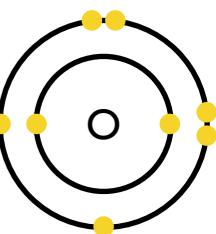


(b) Carbon

- A posteriori refinement has a bigger influence on the resulting energy in comparison to the quadrature order used in calculations.
- Insufficient quadrature rule may result in energies lower than those obtained from the radial solution (i.e. violation of the variational principle).

Choice of the polynomial degree in FE spaces

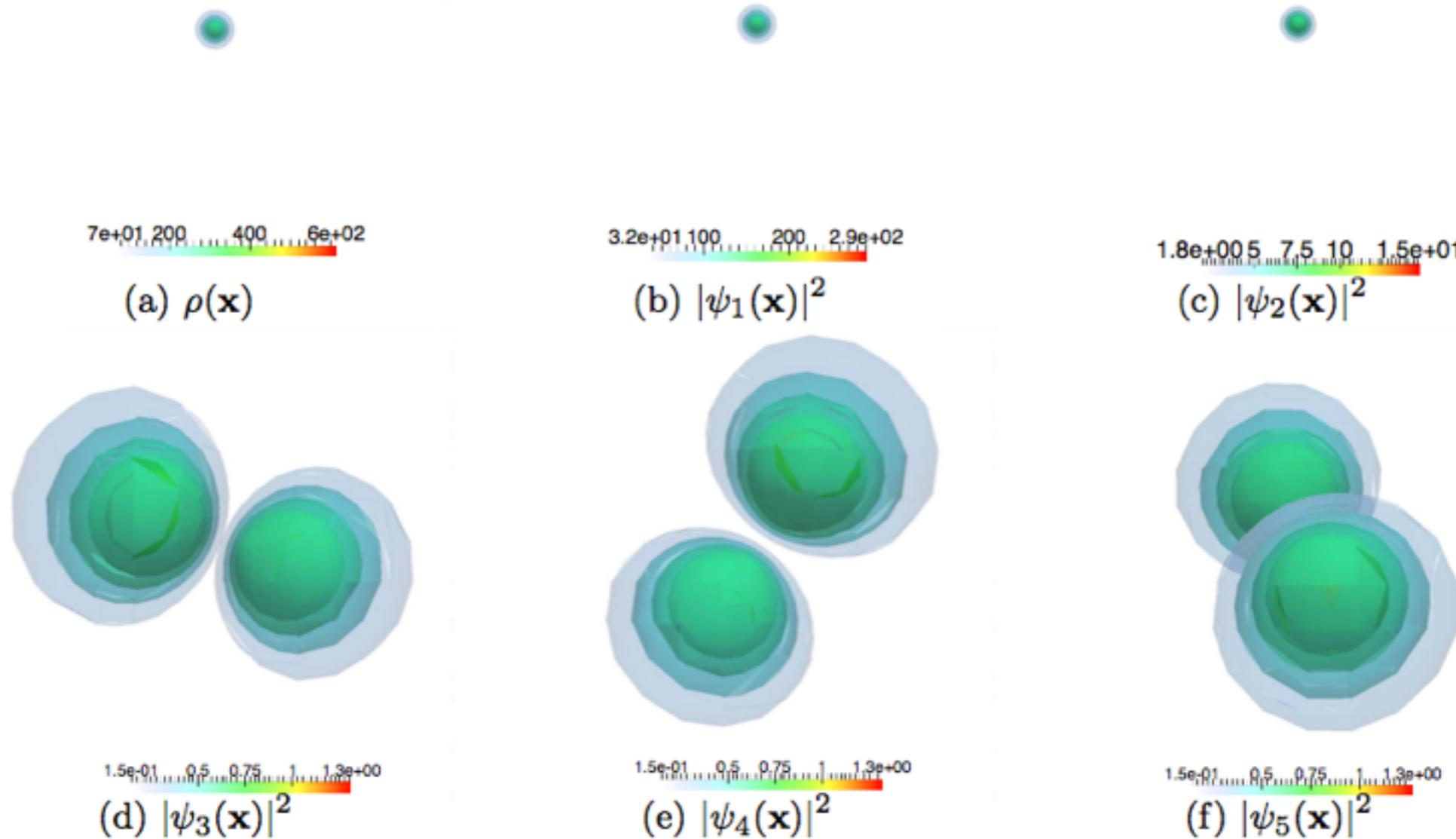
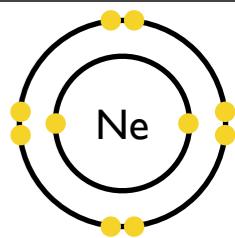
- 1) which FE basis is the “best” (DoFs per element vs interpolation properties)?
- 2) can we use the same FE basis for Poisson and eigenvalue problem?



- Linear FEs are too costly.
- The FE basis in the Poisson problem should be twice the polynomial degree of the eigenvalue problem in order to maintain variational character of the solution (the difference between energies becomes negative for 2/2 combination).
- The efficiency of the basis to reach the chemical accuracy ($1e-3$) depends on the problem.

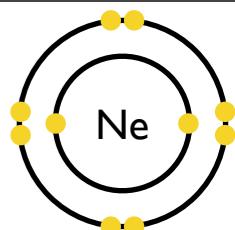
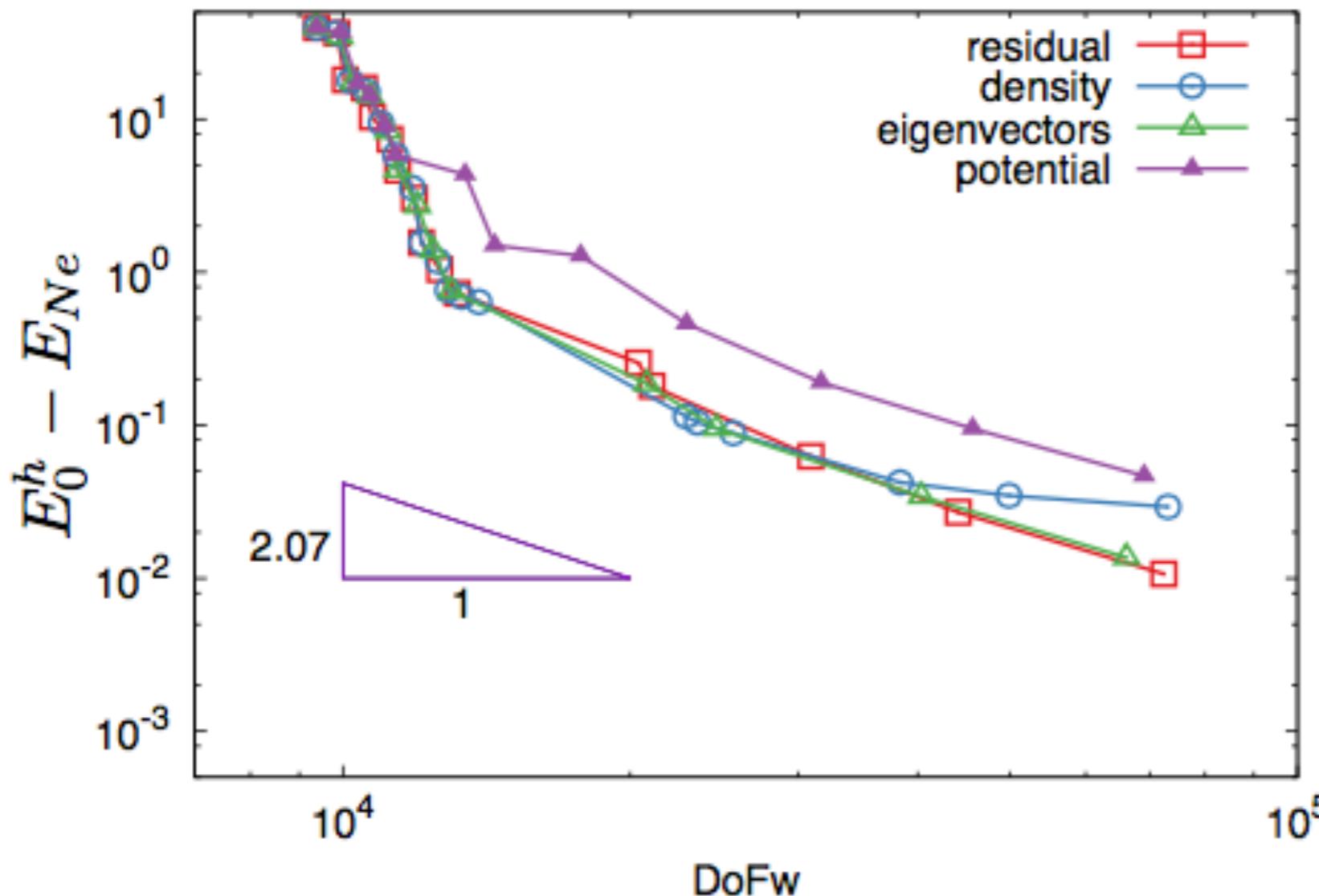
Error estimators

Consider neon (Ne) atom.



Error estimators (cont.)

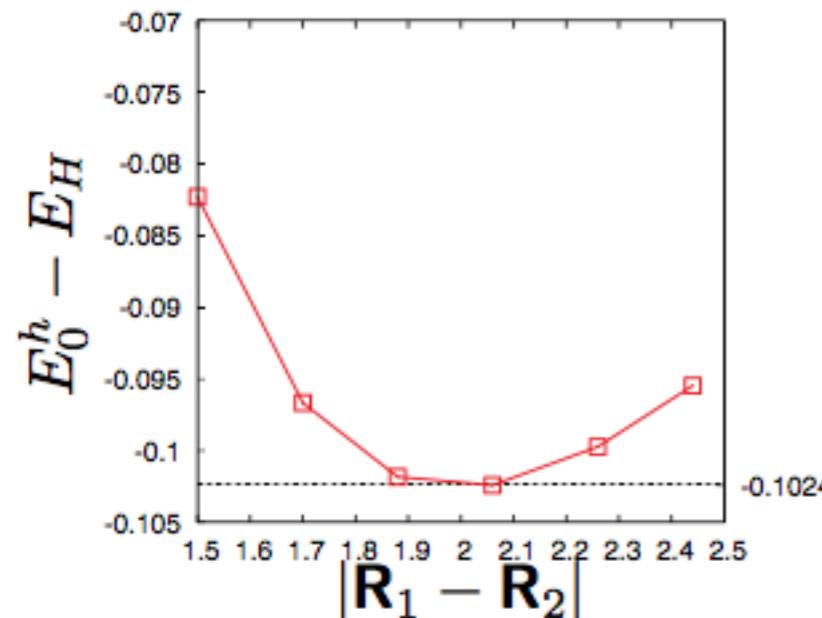
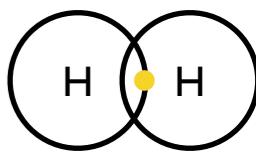
Compare different error estimators:



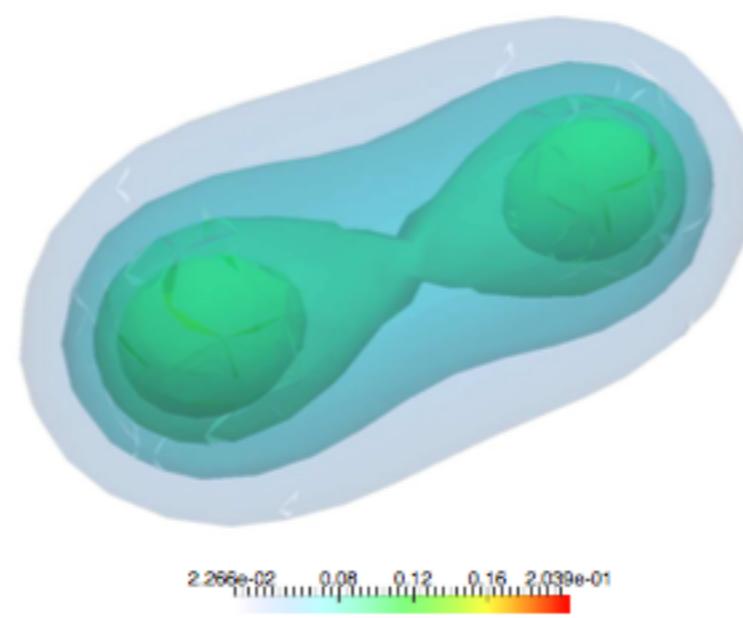
- Residual error estimator and Kelly estimator applied to eigenvectors result in a good convergence w.r.t. the expected total energy.
- The error “estimator” based on jumps in density (Kelly) does not lead to convergence.
- The Kelly estimator applied to the solution of the Poisson problem shows suboptimal convergence.

Towards optimisation of nucleus positions

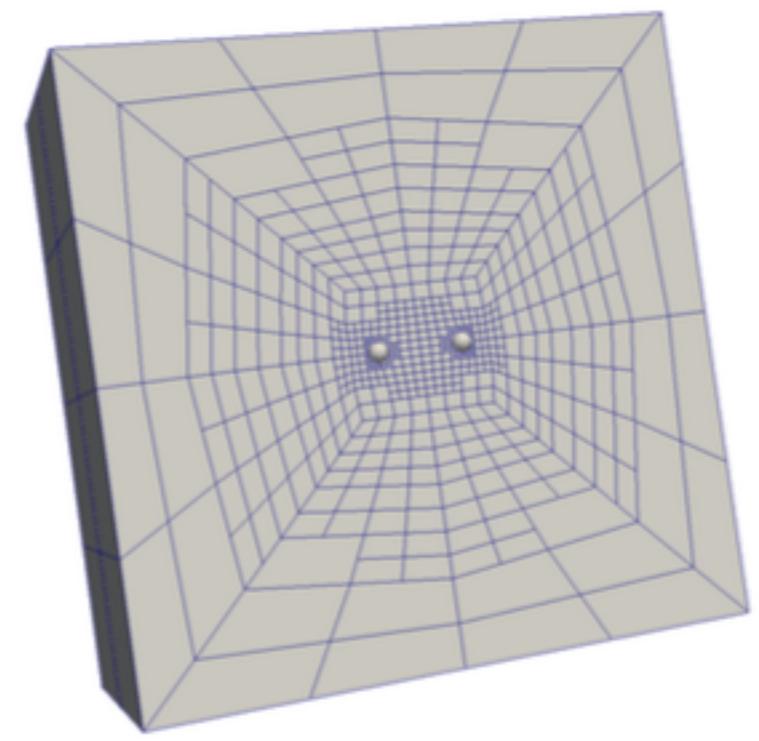
Consider a hydrogen molecule ion. Atoms are placed on the x axis symmetrically about the origin with varying interatomic distance.
The same structured mesh is used as an input.



(a) Bonding energy at the finest mesh.



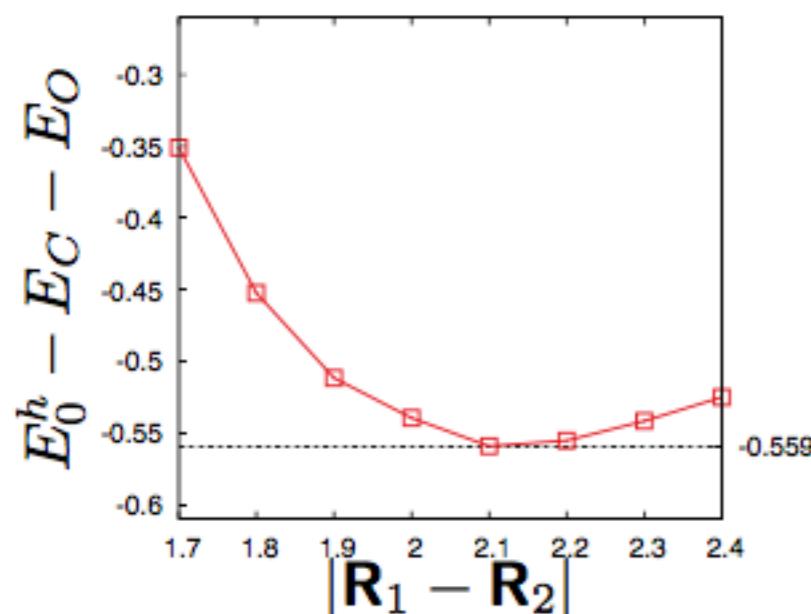
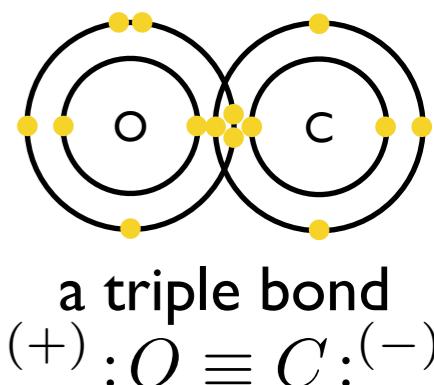
(b) $\rho(\mathbf{x})$



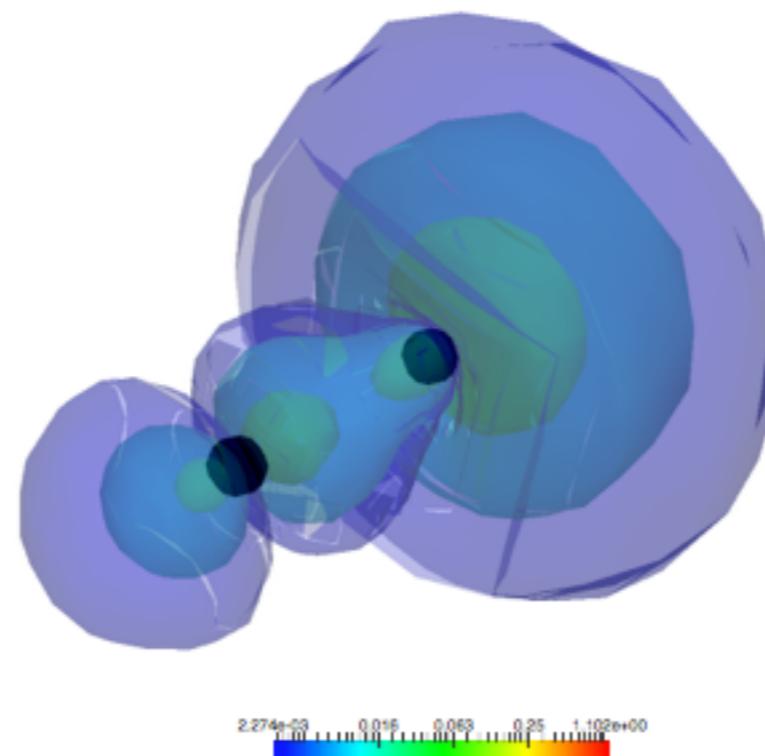
(c) Mesh.

Towards optimisation of nucleus positions

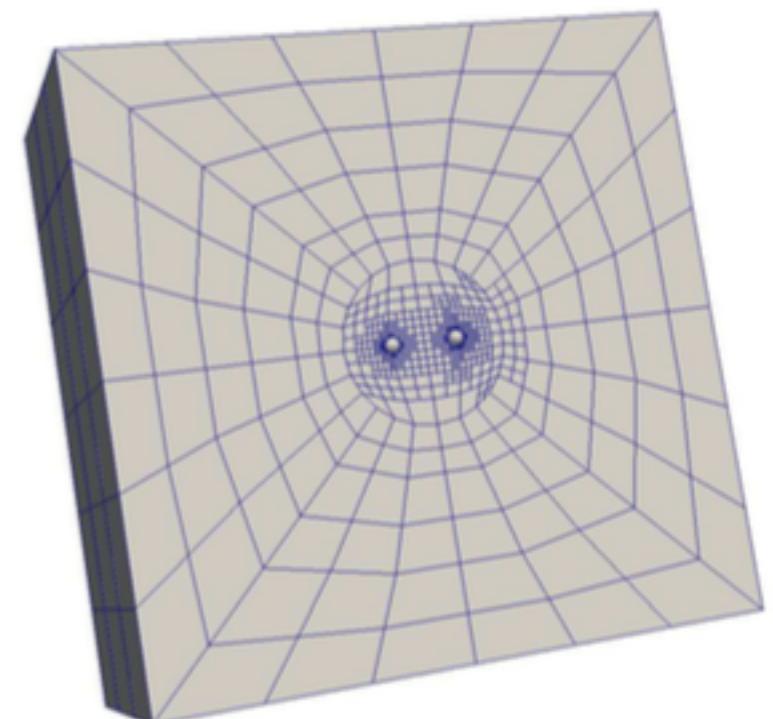
Consider carbon monoxide. Atoms are placed on the x axis symmetrically about the origin with varying interatomic distance. The same structured mesh is used as an input.



(a) Bonding energy at the finest mesh.



(b) $|\psi_7(x)|^2$



(c) Mesh.

Outline

1. Density Functional Theory and its discretisation with FEM
2. Mesh motion approach
3. *A posteriori* mesh refinement
4. Numerical examples and discussion
5. Conclusions and future work

Summary

Conclusions:

Solution of the quantum many-body problem within the context of DFT using a real-space method based on h-adaptive FE discretisation of the space has been developed.

- Different treatments of the ionic potential produce adequate results given fine enough meshes and are well behaved with respect to refinement.
- The quadrature rule is not the most influential factor so long as it is accurate enough to integrate the mass matrix.
- In order to maintain variational nature of the solution, the polynomial degree of the Poisson FE basis should be twice of that used for the eigenvalue problem.
- The effectiveness of the polynomial degree in the FE basis depends on the problem considered.
- A residual-based error estimator or Kelly-error estimator applied to eigenvectors result in adequate convergence. Error estimators based on the density should be avoided.
- The proposed mesh motion approach to move vertices in such a way that each atom has an associated vertex at its position is well suited to be applied to the structural optimisation of molecules.

Thank you for your attention

References:

Davydov, D.; Young, T. & Steinmann, P. (2015) On the adaptive finite element analysis of the Kohn-Sham equations: Methods, algorithms, and implementation. *Journal for Numerical Methods in Engineering*.



Advanced Grant MOCOPOLY

European Research Council
Established by the European Commission