Adaptive Multi-Mesh hp-FEM in Electronic Structure Calculations

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Contents

Introduction and overview:

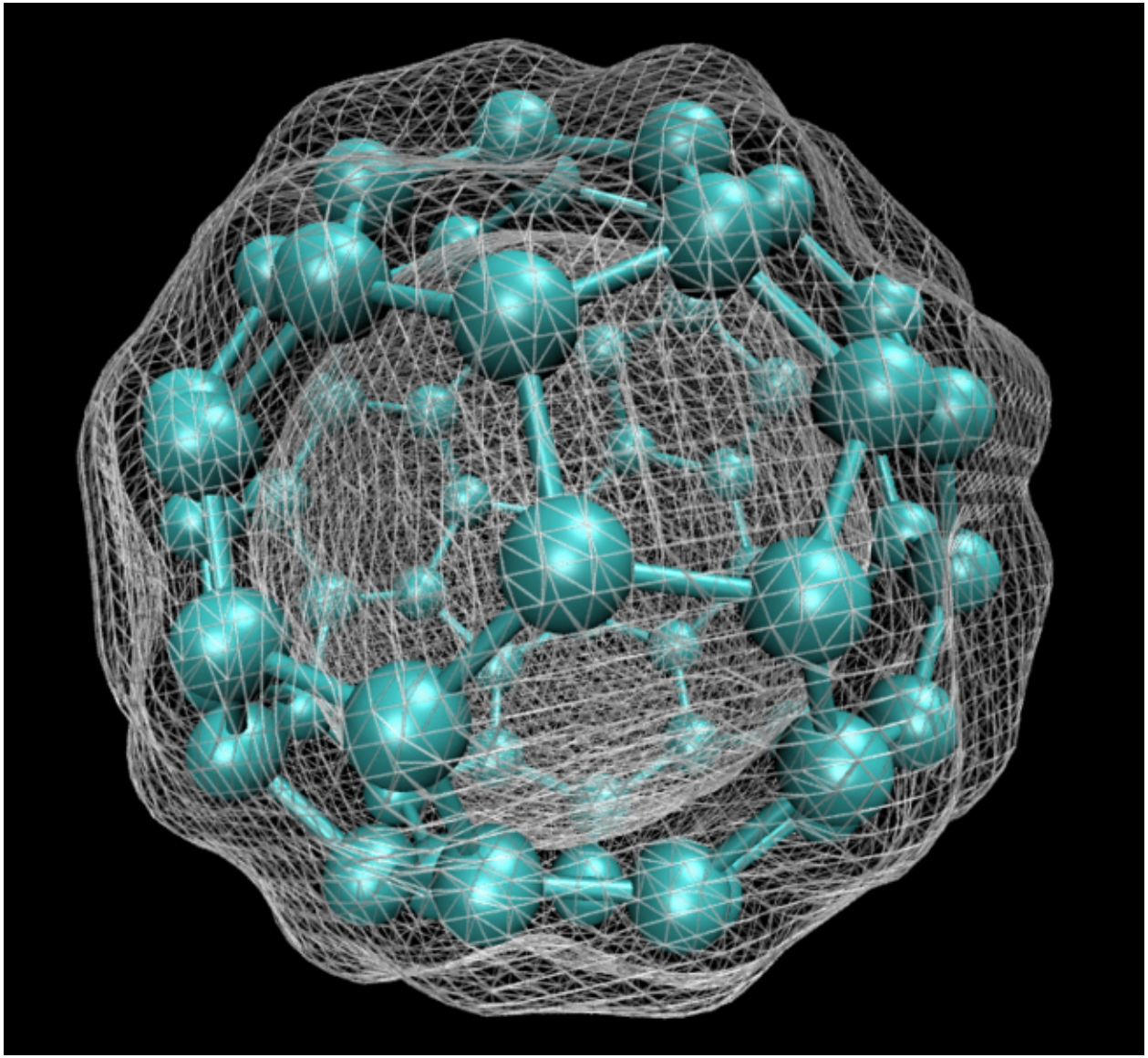
- Electronic Structure and Density Functional Theory (DFT)
- Spherically symmetric problems, examples
- Mixing schemes

Main part:

- Non-symmetric 2D and 3D problems:
  - low order Finite Element Method (FEM)
  - high order adaptive FEM

Conclusion

Why Electronic Structure?



(source: Wikipedia)

Schrödinger equation

$$\hat{H}\,|\Psi\rangle = (\hat{T} + \hat{U} + \hat{V})\,|\Psi\rangle = E\,|\Psi\rangle$$

where

$$\hat{T} = \sum_{i}^{N} -\frac{1}{2}\nabla_i^2$$

$$\hat{U} = \sum_{i<j} U(\mathbf{r_i}, \mathbf{r_j}) = \frac{1}{2}\sum_{i,j} U(\mathbf{r_i}, \mathbf{r_j})$$

$$U(\mathbf{r_i}, \mathbf{r_j}) = U(\mathbf{r_j}, \mathbf{r_i}) = \frac{1}{|\mathbf{r_i} - \mathbf{r_j}|}$$

$$\hat{V} = \sum_{i}^{N} v(\mathbf{r_i})$$

$$v(\mathbf{r_i}) = \sum_{k} -\frac{Z_k}{|\mathbf{r_i} - \mathbf{R_k}|}$$

Density Functional Theory

We solve the Kohn-Sham equations:

$$(-\tfrac{1}{2}\nabla^2 + V_H(\mathbf{r}) + V_{xc}(\mathbf{r}) + v(\mathbf{r}))\psi_i(\mathbf{r}) = \epsilon_i\psi(\mathbf{r})$$

that yield the orbitals ψ_i that reproduce the density $n(\mathbf{r})$ of the original interacting system

$$n(\mathbf{r}) = \sum_i^N |\psi_i(\mathbf{r})|^2$$

$$V_H(\mathbf{r}) = \frac{\delta E_H}{\delta n(\mathbf{r})} = \tfrac{1}{2}\int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}^3 r' \iff \nabla^2 V_H = n(\mathbf{r})$$

$$E_{xc}[n] = (T+U)[n] - E_H[n] - T_S[n]$$

$$V_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}$$

$$v(\mathbf{r}) = \sum_k -\frac{Z_k}{|\mathbf{r}-\mathbf{R_k}|}$$

Atomic wavefunctions

Spherically symmetric potential:

$$V(\mathbf{x}) = V(r)$$

$$\psi_{nlm}(\mathbf{x}) = R_{nl}(r)\, Y_{lm}\left(\frac{\mathbf{x}}{r}\right)$$

Radial Schrödinger equation:

$$R''_{nl} + \frac{2}{r} R'_{nl} + \frac{2M}{\hbar^2}(E - V)R_{nl} - \frac{l(l+1)}{r^2} R_{nl} = 0$$

Relativistic atomic wavefunctions

Dirac equation:

$$(ic\gamma^\mu D_\mu - mc^2)\psi = 0$$

$$D_\mu = \partial_\mu + ieA_\mu$$

Radial Dirac equation:

$$g_\kappa'' + \left(\frac{2}{r} + \frac{V'}{2Mc^2}\right) g_\kappa' + \left[(E - V) - \frac{\kappa(\kappa+1)}{2Mr^2} + \frac{\kappa+1}{4M^2c^2r} V'\right] 2Mg_\kappa = 0$$

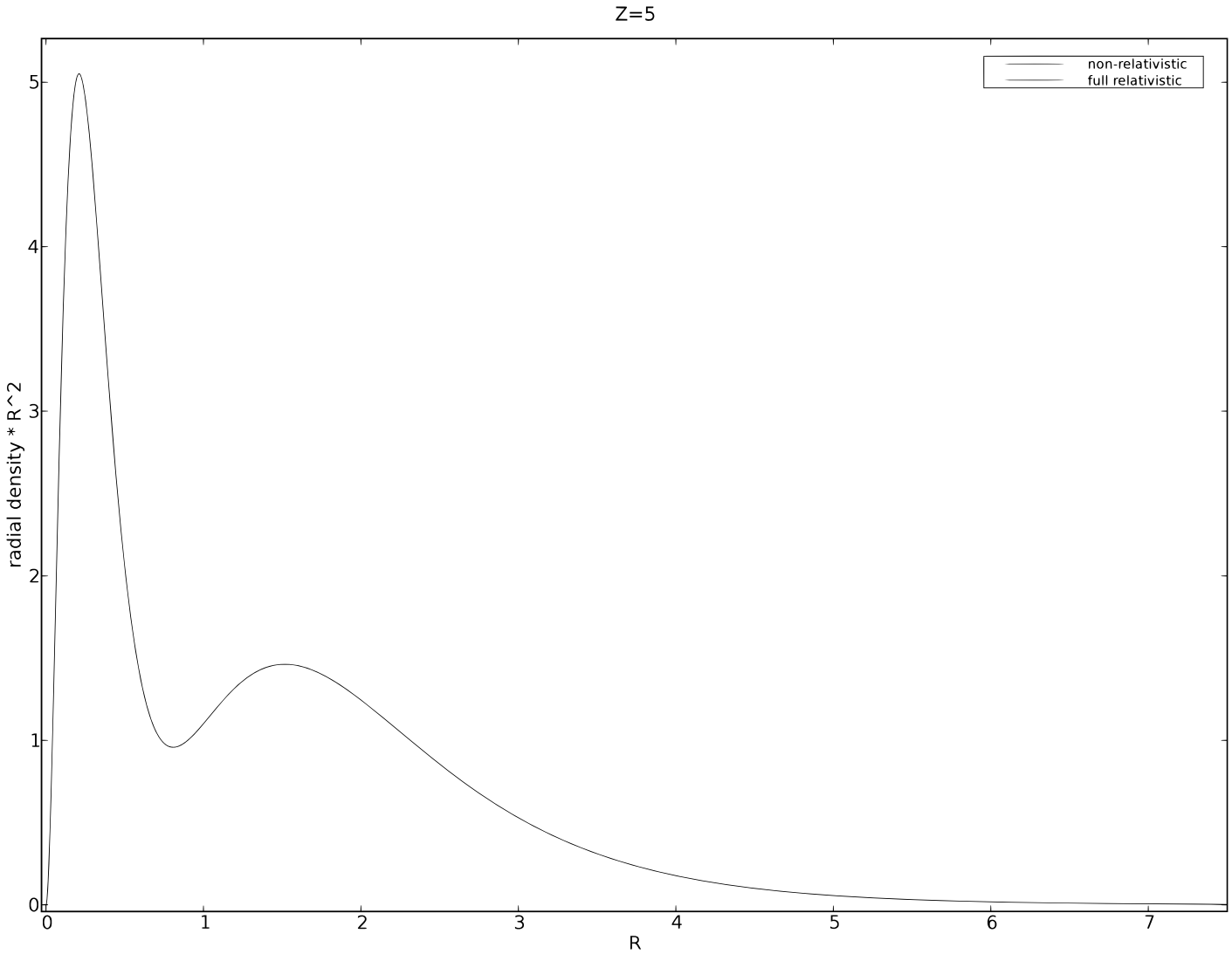
$$f_\kappa = \frac{g_\kappa'}{2Mc} + \frac{\kappa+1}{r}\frac{g_\kappa}{2Mc}$$

$$R^2 = f^2 + g^2$$

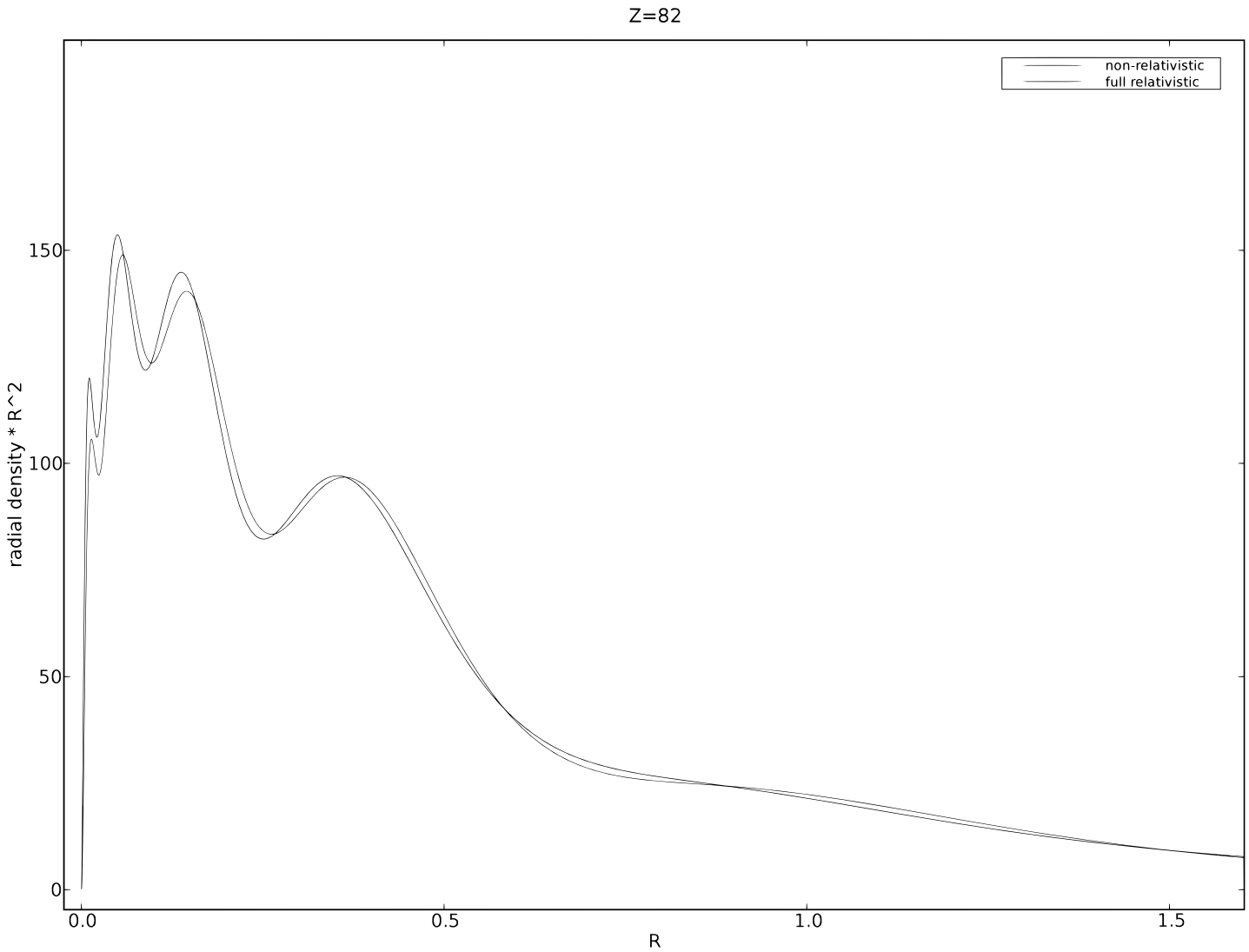
Radial Schrödinger equation:

$$R'' + \frac{2}{r}R' + \left[(E - V) - \frac{l(l+1)}{2Mr^2}\right] 2MR = 0$$

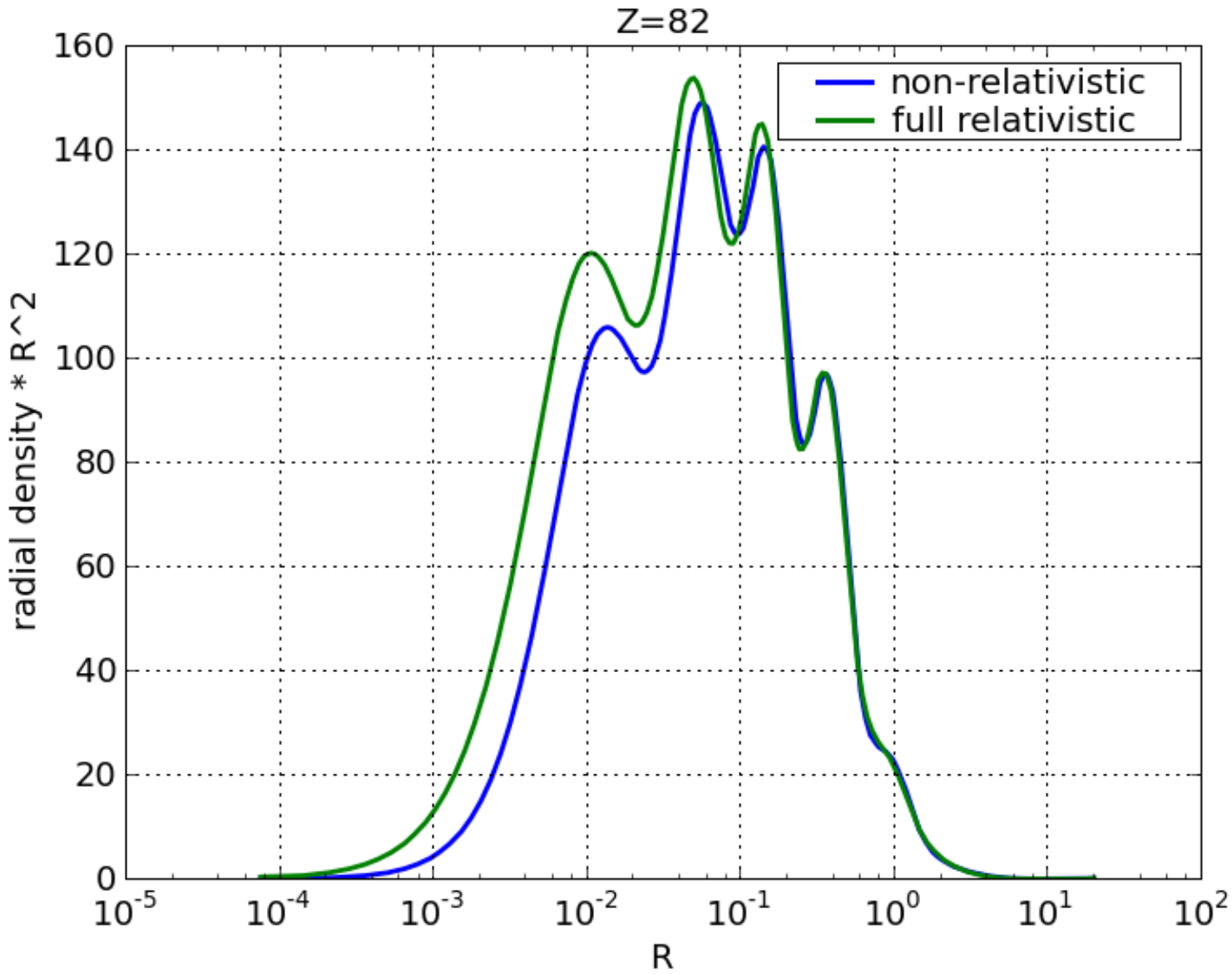
Boron


Z=5
non-relativistic
full relativistic
radial density * R^2
R
0
1
2
3
4
5
6
7

Lead


Z=82
non-relativistic
full relativistic
radial density * R^2
R
0
50
100
150
0.0
0.5
1.0
1.5

Lead


Z=82
non-relativistic
full relativistic
radial density * R^2
R
0
20
40
60
80
100
120
140
160
10^{-5}
10^{-4}
10^{-3}
10^{-2}
10^{-1}
10^{0}
10^{1}
10^{2}

Lead - nonrelativistic calculation

Iterations: 20
$|F(x)| = 0.00003516$
Agrees with NIST:
http://physics.nist.gov/

```
1s( 2): -2901.078061
2s( 2): -488.8433352
2p( 6): -470.8777849
3s( 2): -116.526852
3p( 6): -107.950391
3d(10): -91.88992429
4s( 2): -25.75333021
4p( 6): -21.99056413
4d(10): -15.03002657
4f(14): -5.592531664
5s( 2): -4.206797624
5p( 6): -2.941656967
5d(10): -0.9023926829
6s( 2): -0.3571868295
6p( 2): -0.1418313263
```

Lead - relativistic calculation

Iterations: 20
$|F(x)| = 0.00000584$

```
1s( 2) j=l+1/2: -3209.51946
2s( 2) j=l+1/2: -574.1825655
2p( 6) j=l-1/2: -551.7234408
2p( 6) j=l+1/2: -472.3716103
3s( 2) j=l+1/2: -137.8642241
3p( 6) j=l-1/2: -127.6789451
3p( 6) j=l+1/2: -109.9540395
3d(10) j=l-1/2: -93.15817605
3d(10) j=l+1/2: -89.36399096
```

```
4s( 2) j=l+1/2: -31.15015728
4p( 6) j=l-1/2: -26.73281564
4p( 6) j=l+1/2: -22.38230707
4d(10) j=l-1/2: -15.1647618
4d(10) j=l+1/2: -14.3484973
5s( 2) j=l+1/2: -5.225938506
4f(14) j=l-1/2: -4.960490099
4f(14) j=l+1/2: -4.775660273
5p( 6) j=l-1/2: -3.710458943
5p( 6) j=l+1/2: -2.889127431
5d(10) j=l-1/2: -0.8020049565
5d(10) j=l+1/2: -0.7070299184
6s( 2) j=l+1/2: -0.4209603386
6p( 2) j=l-1/2: -0.1549640727
```

Iteration to self-consistency

The problem:

$$\mathbf{F}(\mathbf{x}) = \mathbf{x}$$

equivalently

$$\mathbf{R}(\mathbf{x}) = 0$$

for $\mathbf{R}(\mathbf{x}) = \mathbf{F}(\mathbf{x}) - \mathbf{x}$. We approximate

$$\mathbf{R}(\mathbf{x}_{M+1}) - \mathbf{R}(\mathbf{x}_M) \approx \mathbf{J} \cdot (\mathbf{x}_{M+1} - \mathbf{x}_M)$$

with the Jacobian

$$J_{ij} = \frac{\partial R_i}{\partial x_j}$$

We want $\mathbf{R}(\mathbf{x}_{M+1}) = 0$:

$$\mathbf{x}_{M+1} \approx \mathbf{x}_M - \mathbf{J}^{-1} \cdot \mathbf{R}(\mathbf{x}_M)$$

$\mathbf{J}$ is approximated by a sequence of $\mathbf{J}_0$, $\mathbf{J}_1$, $\mathbf{J}_2$, ...

Linear mixing

$$\mathbf{x}_{M+1} \approx \mathbf{x}_M - \mathbf{J}_M^{-1} \cdot \mathbf{R}(\mathbf{x}_M)$$

with

$$\mathbf{J}_M^{-1} = -\alpha \mathbb{1}$$

so

$$\mathbf{x}_{M+1} = \mathbf{x}_M + \alpha \mathbf{R}(\mathbf{x}_M) = \mathbf{x}_M + \alpha(\mathbf{F}(\mathbf{x}_M) - \mathbf{x}_M)$$

SciPy

```
from scipy.optimize.nonlin import linearmixing
```

"exciting" mixing

Used in the FP-LAPW DFT code (http://exciting.sourceforge.net/)

$$\mathbf{x}_{M+1} \approx \mathbf{x}_M - \mathbf{J}_M^{-1} \cdot \mathbf{R}(\mathbf{x}_M)$$

with

$$\mathbf{J}_M^{-1} = -\mathrm{diag}(\beta_1, \beta_2, \beta_3, \dots)$$

start with $\beta_1 = \beta_2 = \beta_3 = \cdots = \alpha$ and at every iteration adjust the parameters β_i according to this very simple algorithm: if $R_i(\mathbf{x}_{M-1})R_i(\mathbf{x}_M) > 0$ then increase β_i by α otherwise set $\beta_i = \alpha$ (if $\beta_i > \alpha_{max}$, set $\beta_i = \alpha_{max}$).

SciPy

```
from scipy.optimize.nonlin import excitingmixing
```

Broyden update

The *first Broyden method*:

$$\mathbf{J}_{M+1} = \mathbf{J}_M - \frac{(\Delta\mathbf{R}(\mathbf{x}_M) + \mathbf{J}_M \cdot \Delta\mathbf{x}_M)\Delta\mathbf{x}_M^T}{|\Delta\mathbf{x}_M|^2}$$

The *second Broyden method*:

$$\mathbf{J}_{M+1}^{-1} = \mathbf{J}_M^{-1} + \frac{(\Delta\mathbf{x}_M - \mathbf{J}_M^{-1} \cdot \Delta\mathbf{R}(\mathbf{x}_M))\Delta\mathbf{R}(\mathbf{x}_M)^T}{|\Delta\mathbf{R}(\mathbf{x}_M)|^2}$$

starting with the linear mixing:

$$\mathbf{J}_0^{-1} = -\alpha\mathbb{1}$$

SciPy

```
from scipy.optimize import broyden1, broyden2
```

low memory second Broyden update

The *second Broyden method* ($\mathbf{J}_{M+1}^{-1} = \mathbf{J}_M^{-1} + \frac{(\Delta\mathbf{x}_M - \mathbf{J}_M^{-1}\cdot\Delta\mathbf{R}(\mathbf{x}_M))\Delta\mathbf{R}(\mathbf{x}_M)^T}{|\Delta\mathbf{R}(\mathbf{x}_M)|^2}$) can be written as

$$\mathbf{J}_{M+1}^{-1} = \mathbf{J}_M^{-1} + \mathbf{u}\mathbf{v}^T$$

with

$$\mathbf{u} = \Delta\mathbf{x}_M - \mathbf{J}_M^{-1}\cdot\Delta\mathbf{R}(\mathbf{x}_M)$$

$$\mathbf{v} = \frac{\Delta\mathbf{R}(\mathbf{x}_M)}{|\Delta\mathbf{R}(\mathbf{x}_M)|^2}$$

so the whole inverse Jacobian can be written as

$$\mathbf{J}_M^{-1} = -\alpha\mathbb{1} + \mathbf{u}_1\mathbf{v}_1^T + \mathbf{u}_2\mathbf{v}_2^T + \mathbf{u}_3\mathbf{v}_3^T + \cdots$$

$$\mathbf{J}_M^{-1}\cdot\mathbf{y} = -\alpha\mathbf{y} + \mathbf{u}_1(\mathbf{v}_1^T\mathbf{y}) + \mathbf{u}_2(\mathbf{v}_2^T\mathbf{y}) + \mathbf{u}_3(\mathbf{v}_3^T\mathbf{y}) + \cdots$$

SciPy

```
from scipy.optimize import broyden3
```

Other methods

The *generalized Broyden method* (modified Broyden method):

$$\sum_{p=M-k}^{M-1} (1+\omega_0^2\delta_{pn})\Delta\mathbf{R}(\mathbf{x}_n)^T\Delta\mathbf{R}(\mathbf{x}_p)\gamma_p = \Delta\mathbf{R}(\mathbf{x}_n)^T\mathbf{R}(\mathbf{x}_M)$$

$$\mathbf{x}_{M+1} = \mathbf{x}_M + \beta_M\mathbf{R}(\mathbf{x}_M) - \sum_{p=M-k}^{M-1} \gamma_p(\Delta\mathbf{x}_p + \beta_M\Delta\mathbf{R}(\mathbf{x}_p))$$

other methods: Anderson, extended Anderson

SciPy

```
from scipy.optimize import broyden_generalized,
    anderson, anderson2
```

Weak Formulation

One particle Schrödinger equation:

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)\psi = E\psi\,.$$

Truncation boundary conditions (zero Dirichlet far away).
Weak formulation

$$\int_\Omega \frac{\hbar^2}{2m}\nabla\psi\cdot\nabla v + V\psi v\,\mathrm{d}V = \int_\Omega E\psi v\,\mathrm{d}V + \underbrace{\oint_\Gamma \frac{\hbar^2}{2m}(\nabla\psi)v\cdot\mathbf{n}\,\mathrm{d}S}_{0}\,.$$

Discrete generalized eigenvalue problem

$$(K_{ij} + V_{ij})\,q_j = EM_{ij}q_j\,.$$

Finite element formulation

One particle Schrödinger equation:

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)\psi = E\psi\,.$$

FEM:

$$(K_{ij} + V_{ij})\,q_j = EM_{ij}q_j + F_i\,,$$

$$\begin{aligned} V_{ij} &= \int \phi_i V \phi_j \,\mathrm{d}V\,, \\ M_{ij} &= \int \phi_i \phi_j \,\mathrm{d}V\,, \\ K_{ij} &= \frac{\hbar^2}{2m}\int \nabla\phi_i \cdot \nabla\phi_j \,\mathrm{d}V\,, \\ F_i &= \frac{\hbar^2}{2m}\oint \frac{\mathrm{d}\psi}{\mathrm{d}n}\phi_i \,\mathrm{d}S\,. \end{aligned}$$

Usually we set $F_i = 0$.

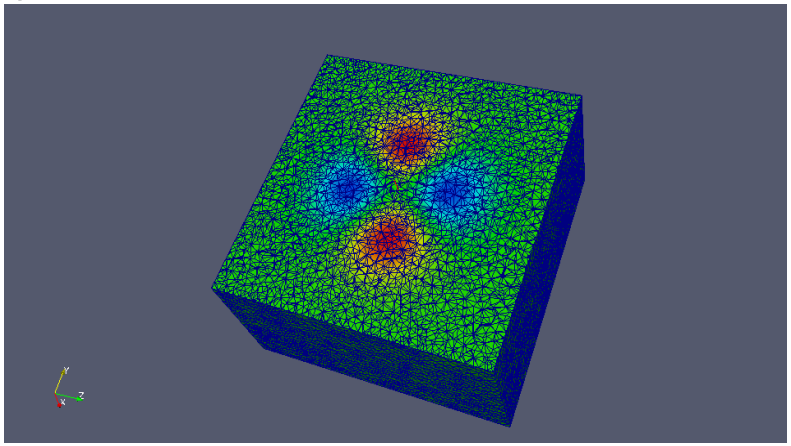
First attempt: SfePy

- SfePy = low order FEM software (non adaptive)
- BSD open-source license
- Many applications in engineering and science
- available at `http://sfepy.org`

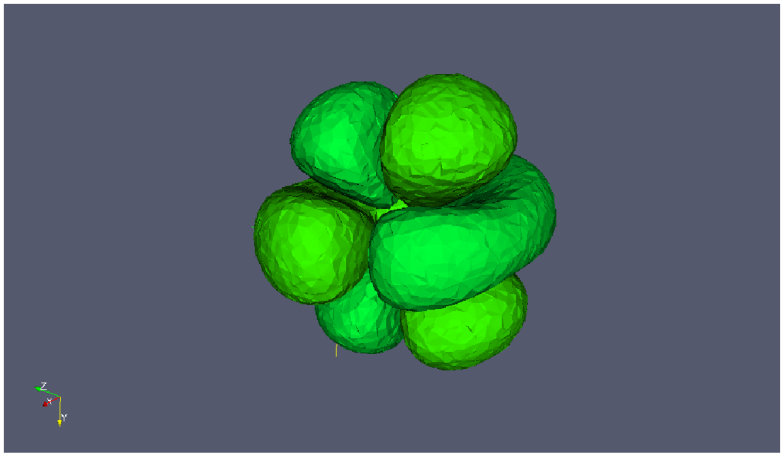
3D Harmonic oscillator

Eigenvectors:

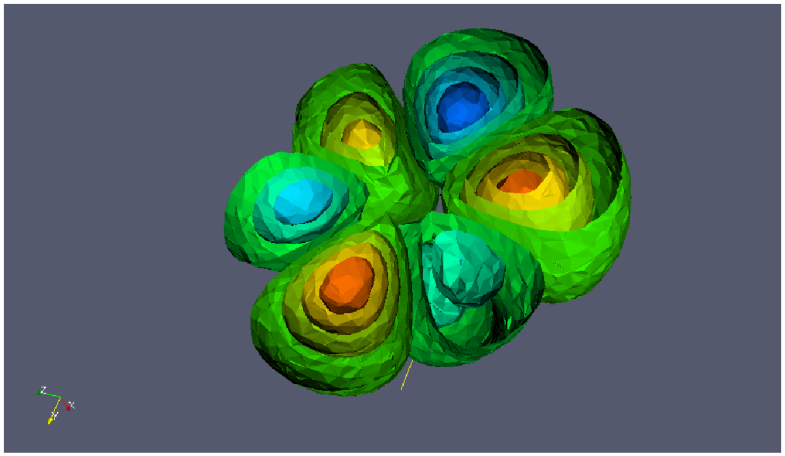
0th



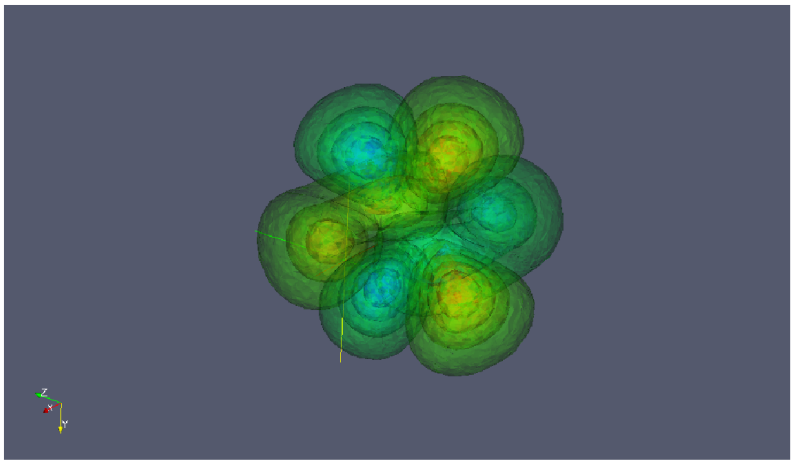
12th



10th



12th



Hydrogen atom

$$V(r) = \begin{cases} -\frac{1}{r}, & \text{inside the box} \quad a \times a \times a \\ \infty, & \text{outside} \end{cases}$$

Analytic solution in the limit $a \to \infty$:

$$E_n = -\frac{1}{2n^2}$$

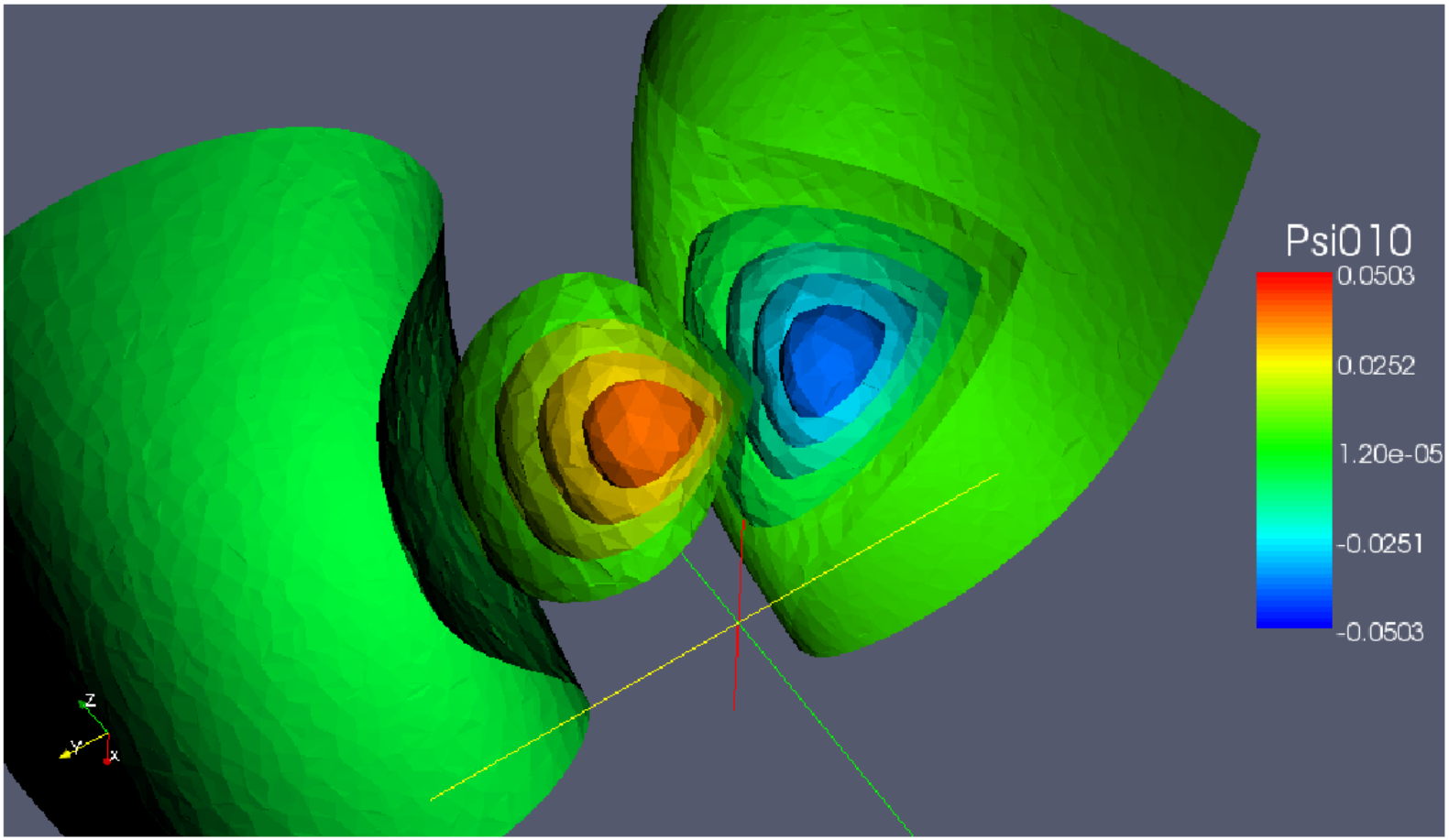
where $n = 1, 2, 3, \ldots$. Degeneracy is n^2, so: $E_1 = -\frac{1}{2} = -0.5$, $E_2 = -\frac{1}{8} = -0.125$, $E_3 = -\frac{1}{18} = -0.055$, $E_4 = -\frac{1}{32} = -0.031$.

Numerical solution ($a = 15$, 160000 nodes):

E	1	2-5	6-14	15-
theory	-0.5	-0.125	-0.055	-0.031
FEM	-0.481	-0.118	-0.006	$\cdots$

Hydrogen atom

11th eigenvalue (calculated: -0.04398532, exact: -0.056), on the mesh with 976 691 tetrahedrons and 163 666 nodes, for the hydrogen atom (V=-1/r).



We solve the Kohn-Sham equations using FEM:

$$(-\tfrac{1}{2}\nabla^2 + V_H(\mathbf{r}) + V_{xc}(\mathbf{r}) + v(\mathbf{r}))\psi_i(\mathbf{r}) = \epsilon_i\psi(\mathbf{r})$$

that yield the orbitals ψ_i that reproduce the density $n(\mathbf{r})$ of the original interacting system

$$n(\mathbf{r}) = \sum_i^N |\psi_i(\mathbf{r})|^2$$

$$\nabla^2 V_H = n(\mathbf{r})$$

$$v(\mathbf{r}) = \sum_k -\frac{Z_k}{|\mathbf{r} - \mathbf{R_k}|}$$

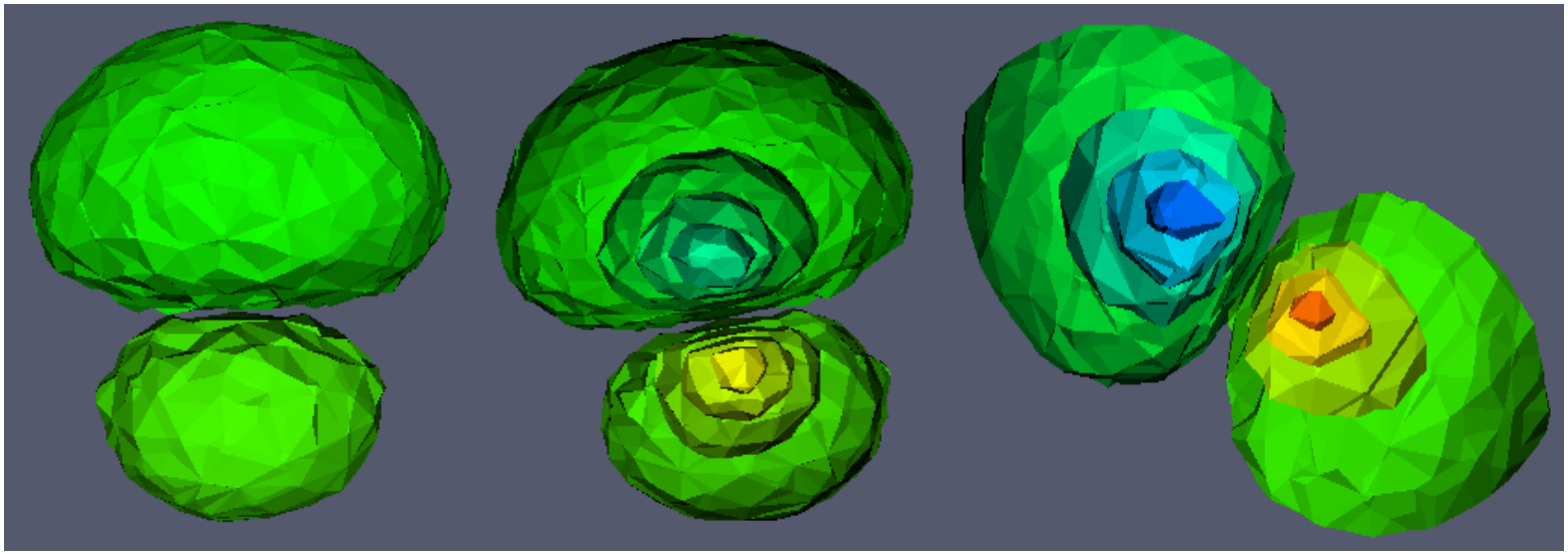
Boron (5 electrons)

Uniform tetrahedral mesh, 50 000 nodes, 5 lowest eigenvalues

radial	-6.564449519	-6.564449519	-0.3447644413	-0.3447644413	-0.1366622746
FEM	-3.18675417	-0.68091886	-0.65252624	-0.63762163	-0.58488204

- Bad convergence should greatly improve with a better mesh

2th eigenvector (contours and a slice), 3th eigenvector (slice)



Second attempt: Hermes

- Hermes = higher order adaptive FEM (hp-FEM) software
- GPL open-source license
- Many applications in engineering and science
- Developed at University of Nevada, Reno and Institute of Thermomechanics, Prague
- available at `http://hpfem.math.unr.edu`

Uniform vs Adapted Mesh

2D hydrogen atom, square box, 6 times uniformly refined:

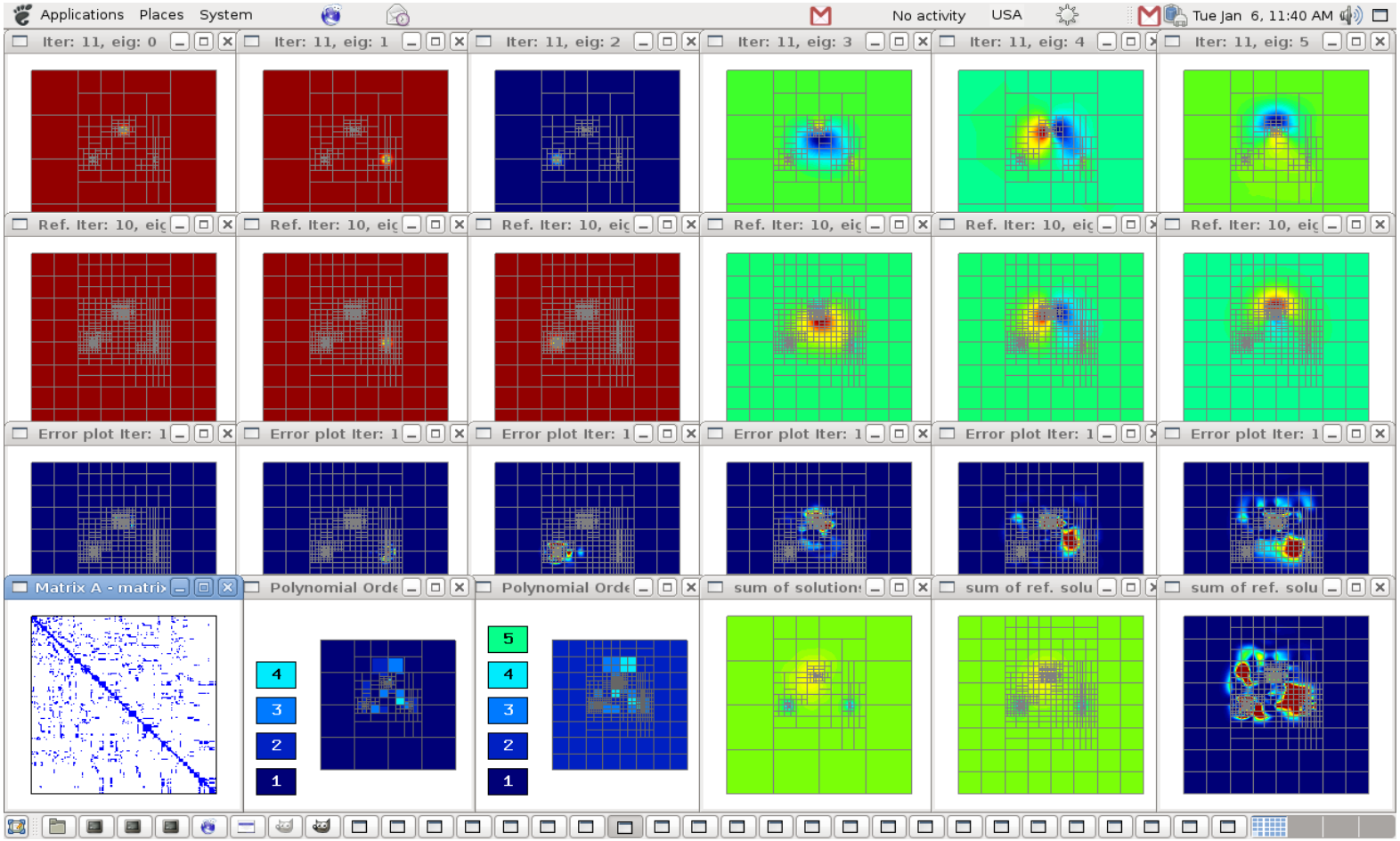
- matrix: 16129 x 16129, error: 12.6%

adaptive hp-FEM refinement:

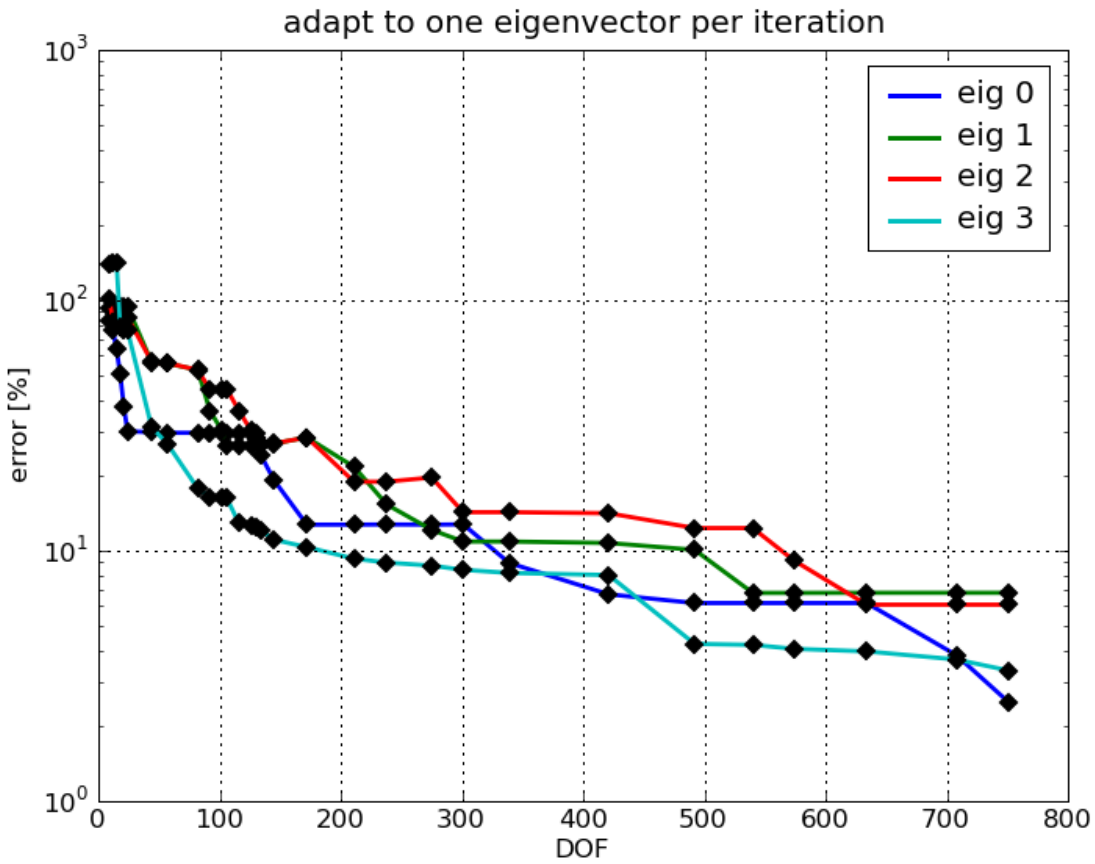
- matrix: 141 x 141, error: 7.5%

How to converge the eigenvectors?

hp-FEM on a single mesh

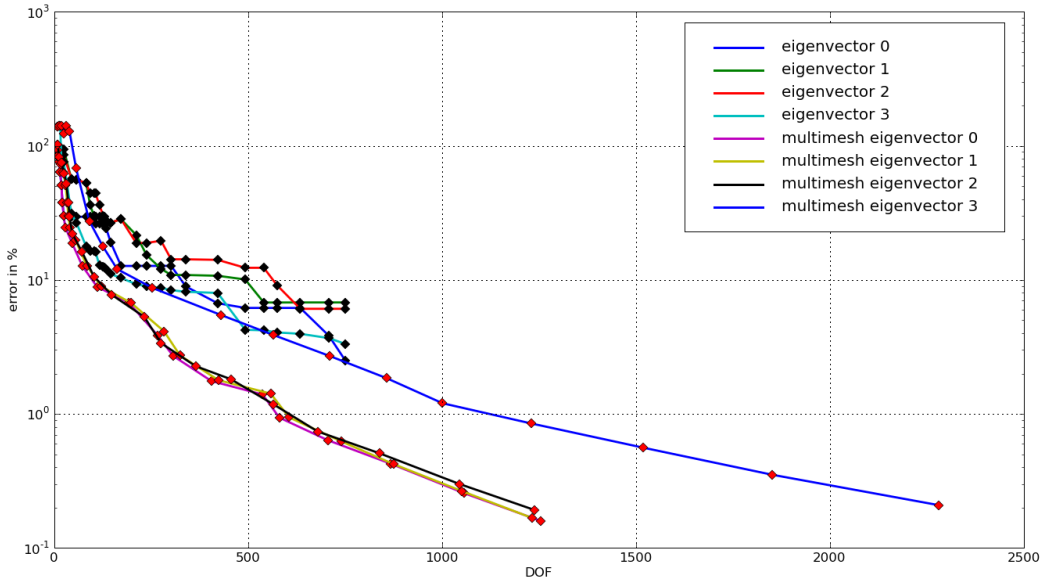


Converging one eigenvector per iteration:

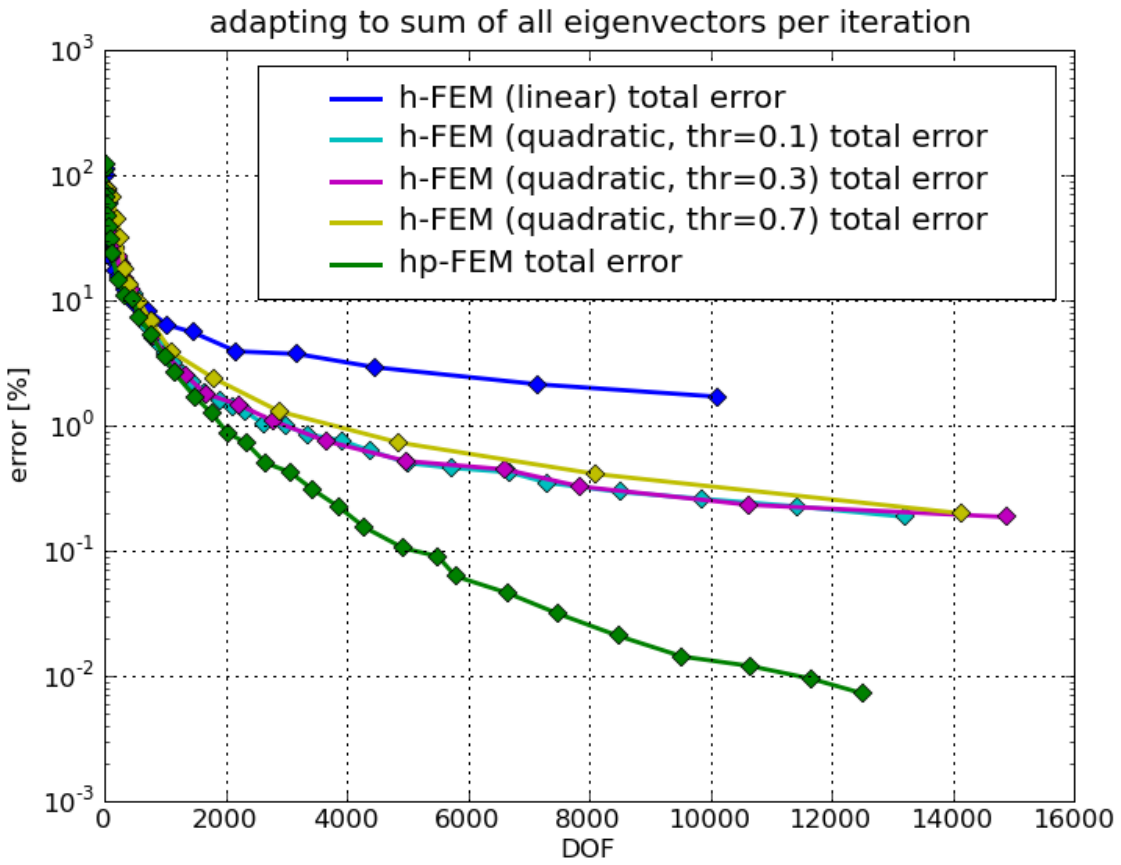


Multimesh Comparison

eigenvector 0..4: converging one eigenvector at a time
multimesh eigenvector 0..4: converging each eigenvector on its own mesh

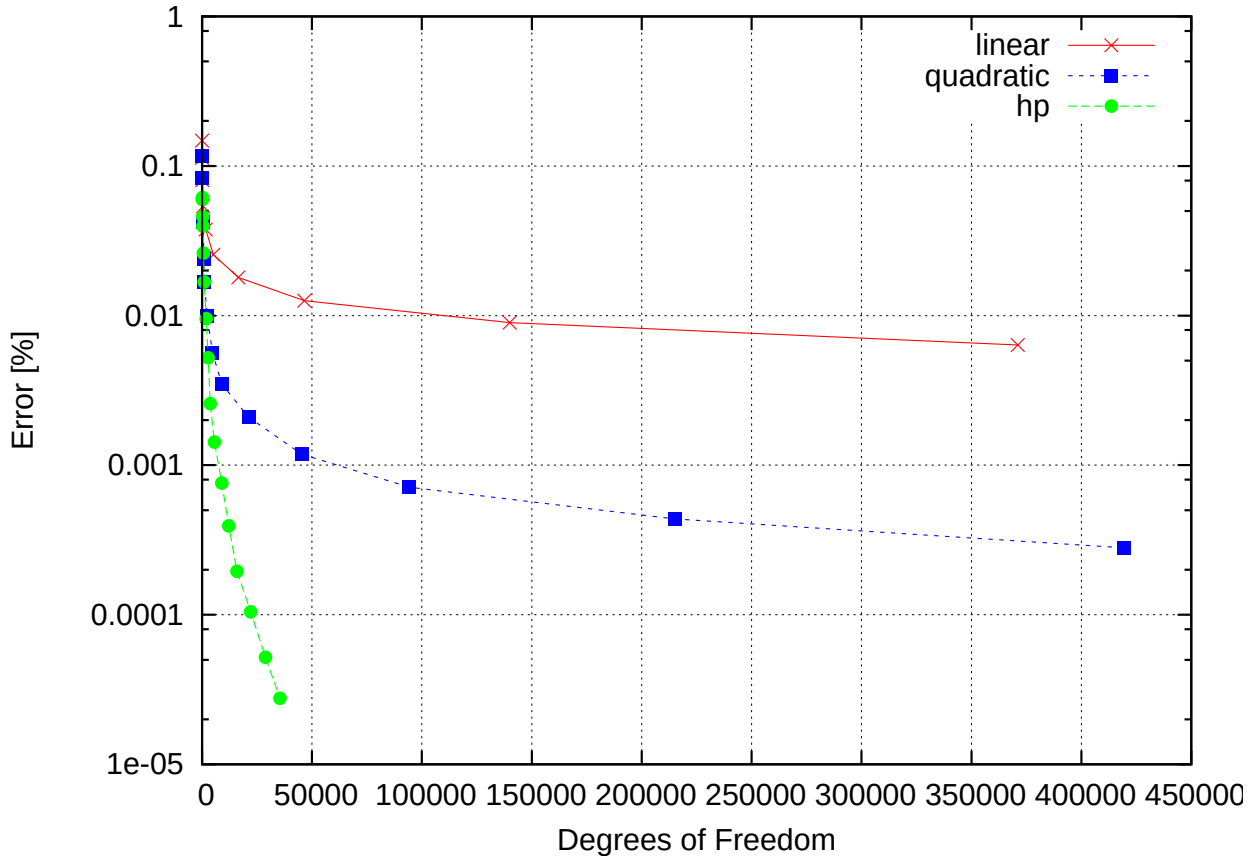


Adapting to the Sum of Eigenvectors



hp-FEM convergence in 3D

Laplace equation (note: on the y-scale, 1 means 100%):



Conclusion, Future Work

- hp-FEM treatment is necessary
- implement the DFT self-consistency cycle in 2D, then go to 3D
- use pseudopotentials (reduces the number of electrons to solve for)
- only depend on open source (free software) solutions

Acknowledgements

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