Using Python for electronic structure calculations, nonlinear solvers, FEM and symbolic manipulation

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Introduction

I'll talk about

- Density Functional Theory calculations
- SciPy nonlinear solvers
- Finite Element Method using python-petsc and libmesh
- SymPy – the symbolic manipulation package in Python

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

where

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

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

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

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

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

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

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

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

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

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

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

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:

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

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

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

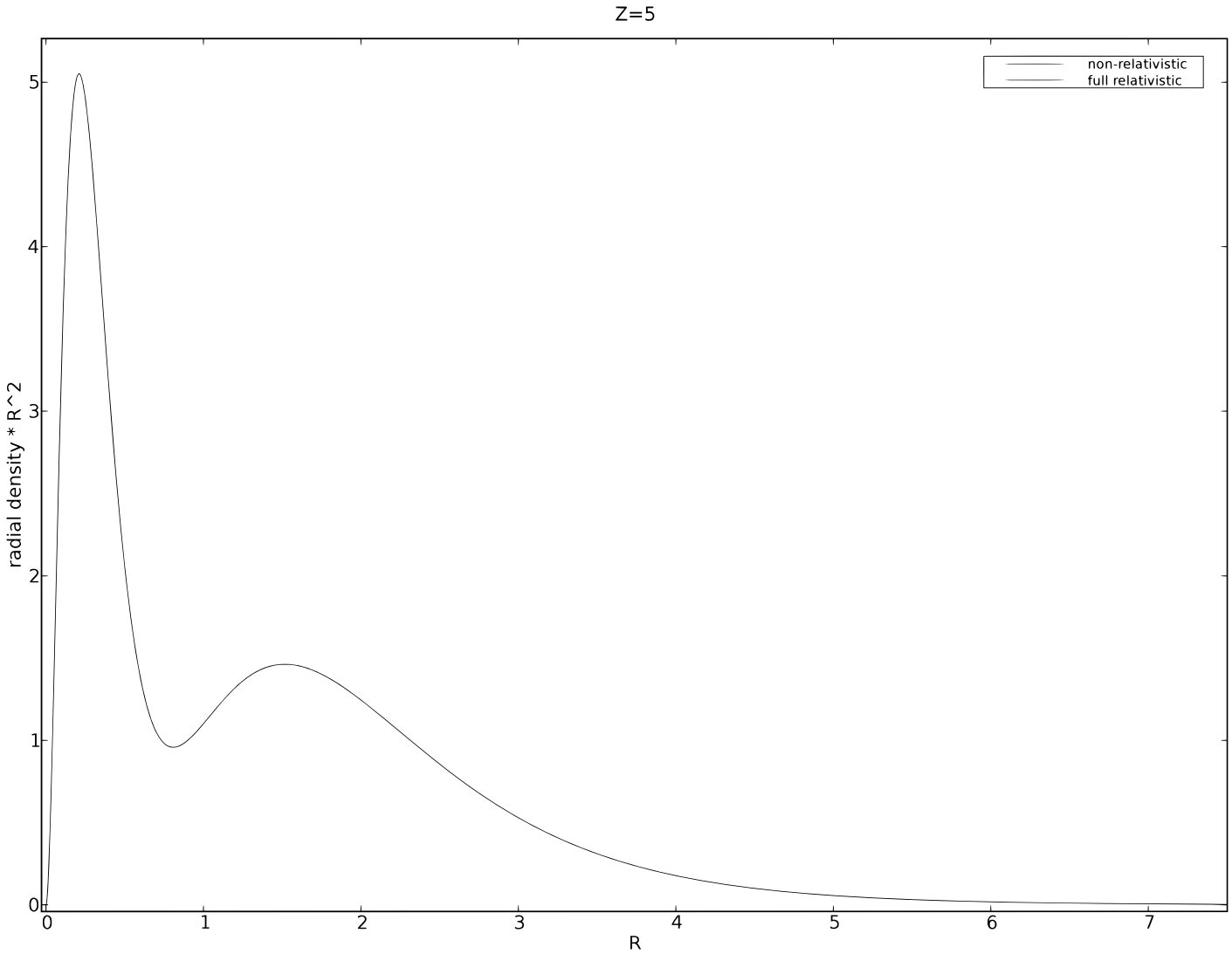
Radial Schrödinger equation:

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

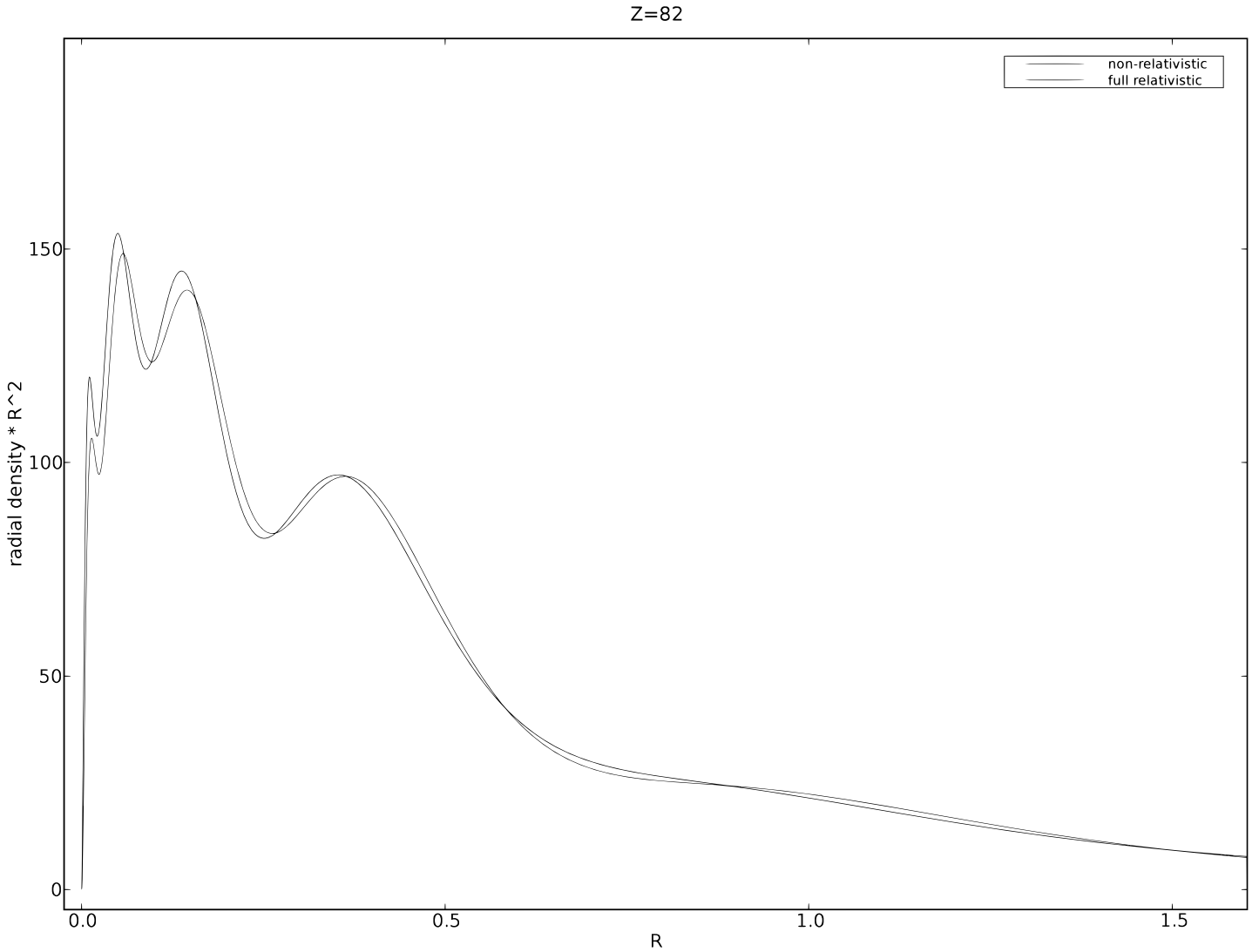
Code (300 lines in Python, 800 in Fortran)

```
from atom import atom, show
import radial
import utils
def do(Z):
    R = radial.create_log_grid(Z)
    s = atom(Z,alpha=0.3,iter=20,relat=0,grid=R)
    n5_lda = radial.KS_construct_density(s,R,Z)*R*R
    s = atom(Z,alpha=0.3,iter=20,relat=2,grid=R)
    n5_rlda = radial.KS_construct_density(s,R,Z)*R*R
    utils.makeplot(R,[
        (n5_lda,"b-","non-relativistic"),
        (n5_rlda,"g-","full relativistic"),
        ],title="Z=%d"%(Z),xleg="R",
        yleg="radial density * R^2")
do(5)
#do(82)
```

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 - 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
```

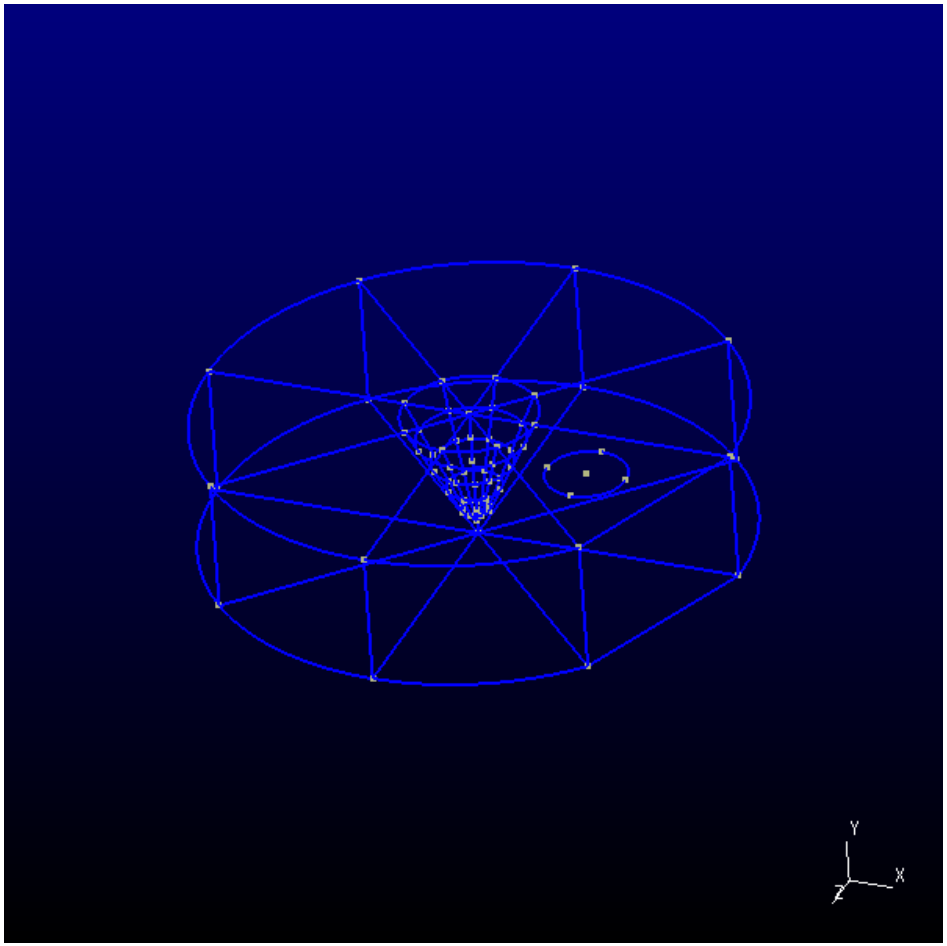
Finite element calculation

Tools I use (Debian package in parentheses):

- gmsh http://www.geuz.org/gmsh/ (gmsh)
- tetgen http://tetgen.berlios.de/ (non-free/tetgen)
- libmesh http://libmesh.sourceforge.net/ (libmesh0.6.0-pure-dev)
- petsc4py http://code.google.com/p/petsc4py/ (python-petsc)

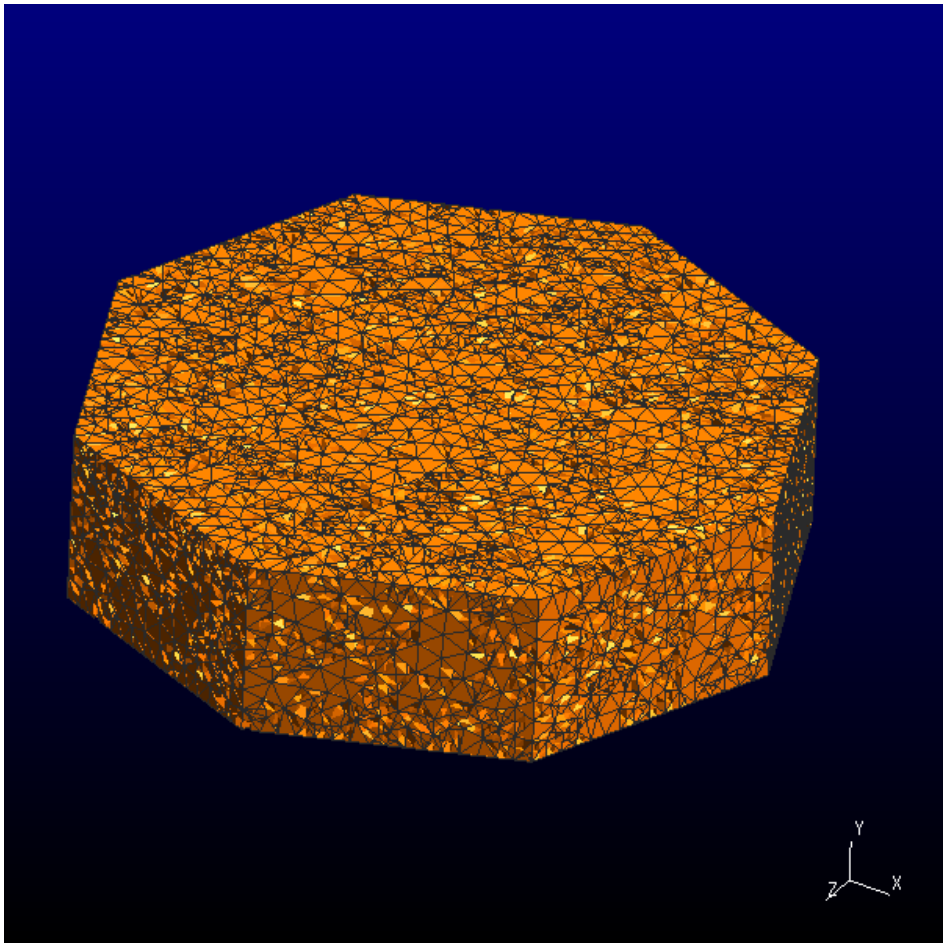
My code is at: http://code.google.com/p/grainmodel/

Geometry



Mesh

gmsh $\longrightarrow$ converter $\longrightarrow$ tetgen $\longrightarrow$ converter $\longrightarrow$ gmsh, libmesh



Formulation

Continuity equation:

$$\nabla \cdot \mathbf{j} = -\frac{\partial \rho}{\partial t}$$

and using the Ohm's law $\mathbf{j} = \sigma \mathbf{E} = -\sigma \nabla \varphi$ and setting $\frac{\partial \rho}{\partial t} = 0$ we get

$$\nabla \cdot \sigma \nabla \varphi = 0$$

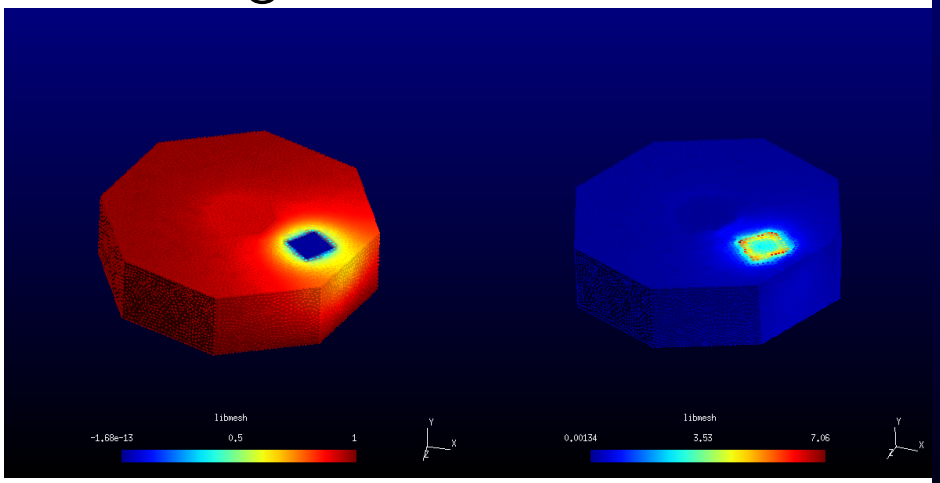
Standard FEM procedure: weak formulation, global matrix assembly, solving the large sparse problem $Ax = b$, etc.

Solver

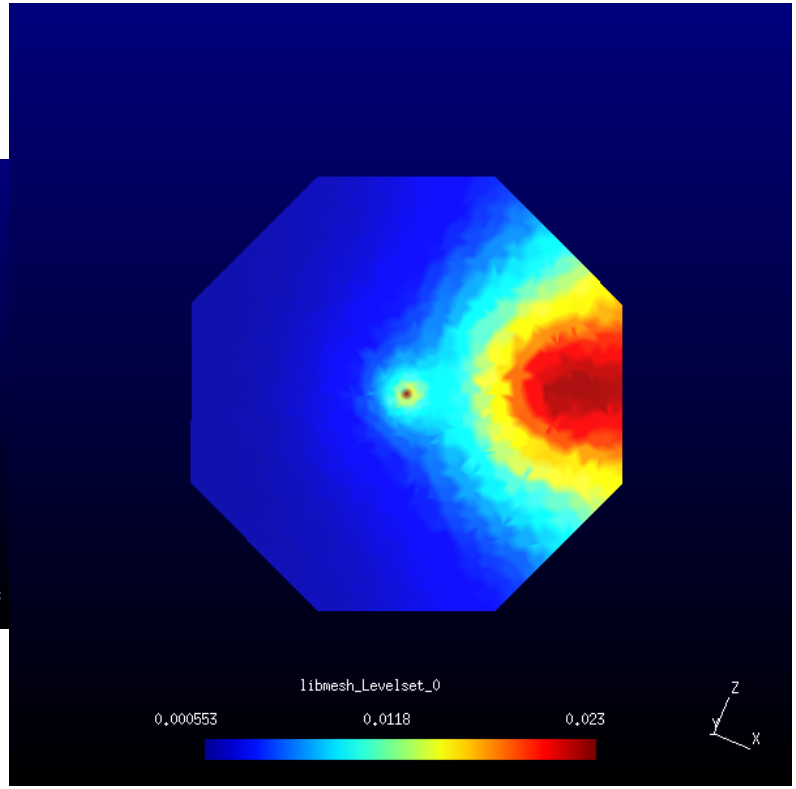
- main program in Python
- libmesh (C++), together with SWIG bindings, to assemble
- petsc (C), together with petsc4py (SWIG), to solve

Solution

solution+gradient



substrate plane



SymPy

- A Python library for symbolic mathematics
- http://code.google.com/p/sympy/

Why symbolic mathematics? The same reasons people use Maple/Mathematica, but we want to use it from Python.

```
>>> from sympy import Symbol, limit, sin, oo
>>> x=Symbol("x")
>>> limit(sin(x)/x, x, 0)
1
>>> limit((5**x+3**x)**(1/x), x, oo)
5
```

SymPy

What SymPy can do

- basics (expansion, complex numbers, differentiation, taylor (laurent) series, substitution, arbitrary precision integers, rationals and floats, pattern matching)
- noncommutative symbols
- limits and very simple integrals (so far)
- polynomials (division, gcd, square free decomposition, groebner bases, factorization)
- symbolic matrices (determinants, LU decomposition...)
- solvers (some algebraic and differential equations)
- 2D geometry module
- plotting (2D and 3D)

SymPy

In his introduction to the book A=B Donald Knuth wrote:

> Science is what we understand well enough to explain to a computer. Art is everything else we do. During the past several years an important part of mathematics has been transformed from an Art to a Science

- Being able to see the computer doing mathematics, I understand it better (symbolic limits, factorization, expansion, integration, ...)
- one example: epsilon delta gymnastics in limits

SymPy

Other symbolic manipulation software: GiNaC, Giac, Qalculate, Yacas, Eigenmath, Axiom, PARI, Maxima, SAGE, Singular, Mathomatic, Octave, ...
Problems:

- all use their own language (except GiNac, Giac and SAGE)
- GiNac and Giac still too complicated (C++), difficult to extend

What we want

- Python library and that's it (no environment, no new language, nothing)
- Rich funcionality
- Pure Python (non Python modules are only optional) – works on Linux, Windows, Mac out of the box

SAGE

- aims to glue together every useful open source mathematics software package and provide a transparent interface to all of them
- http://www.sagemath.org/

```
sage: import sympy
sage: sympy.__version__
'0.4.2'
sage: x=sympy.Symbol("x")
sage: y=sympy.Symbol("y")
sage: ((x+y)**sympy.Rational("5")).expand()
5*x**4*y+y**5+x**5+10*x**3*y**2+5*x*y**4+10*y**3*x**2
```

the Schwarzschild solution in the General Relativity

spherically symmetric metric ($diag(-e^{\nu(r)}, e^{\lambda(r)}, r^2, r^2 \sin^2\theta)$) $\rightarrow$ Christoffel symbols $\rightarrow$ Riemann tensor $\rightarrow$ Einstein equations $\rightarrow$ solver

```
ondra@pc232:~/sympy/examples$ time python relativity.py
...
[SKIP]
...
----------------------------------------
metric:
-C1 - C2/r 0 0 0
0 1/(C1 + C2/r) 0 0
0 0 r**2 0
0 0 0 r**2*sin(\theta)**2

real 0m1.092s
user 0m1.024s
sys 0m0.068s
```

How SymPy is developed

- I wrote first code 2 years ago, limits a year ago and then stopped working on it
- Fabian from Spain joined in February
- Google Summer of Code, SymPy is under the umbrella of Python Software Foundation, the Space Telescope Science Institute and Portland State University
- Now there are 8 regular contributors with svn access, other people send patches sometimes
- GSoC students wrote most of the modules, Pearu Peterson wrote a new core (10x to 100x faster than the old core), Fredrik wrote a fast floating point arithmetics in Python (faster than the Decimal module), Jurjen contributed pretty printing etc.