

Using finite elements for ab-initio calculations in material science

DFT+FEM+pseudopotential

J. Vackář

general outline:

- electronic structure & total energy calculation ... motivation for
- electronic structure & total energy calculation ... methods
- ... methods: density functional theory (DFT)
- ... methods: pseudopotentials
- DFT+FEM+pseudopotentials: about our project



INVESTMENTS IN EDUCATION DEVELOPMENT

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... is understanding the structure/material properties:

- minimizing E_{tot} as a function of atomic positions makes possible to find equilibrium atomic positions, the extent of the stability of a given structure, to compare E_{tot} of different configurations
 - — clusters
 - — adsorbed molecules, e.g. protein fractions etc.
 - — catalysis
- calculating derivatives of E_{tot} with respect to atomic positions / deformations:
 - — elastic constants
 - — cohesive strength, hardness
- spin-polarization, minimizing E_{tot} with respect to the occupation of spin-polarized states
 - — magnetic behavior of a given material
- occupation of electronic states, band structure in the case of crystalline materials
 - — x-ray spectra
 - — electrical properties (insulator, semiconductor, metallic material)
 - — superconductivity (but it's a bit more complicated)
- molecular dynamics ... etc. etc.

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We can look at sorting/systemizing the methods from *various angles*:

- by the approach to **many-particle Schrödinger equation**

$$H\Psi(e_1, e_2, \dots e_n) = E\Psi(e_1, e_2, \dots e_n)$$

... too complicated to solve ... even for 3 electrons!

- Quantum Monte Carlo
 - Hartree-Fock (wave function is approximated by a single Slater determinant)
 - ...
 - **Density Functional Theory (DFT) ($\approx 55\%$ (?))**
- by the **basis set** used for wave functions and other quantities

- the class of Bloch-function basis sets (using the Bloch-theorem, on the premise of translational symmetry)

(k-space methods, reciprocal space methods, e.g. plane waves)
Bloch theorem says: in periodic potential, the wave function can be written in the form of Bloch wave:

$$\psi_{n,\vec{k}}(\vec{x}) = e^{-i\vec{k}\vec{x}} u_{n,\vec{k}} = \dots e^{-i(\vec{k}+\vec{G})\vec{x}}$$

- real-space methods
- by the way of **treating the core** (non-valence) electrons
 - "all-electron methods"
 - pseudopotential methods
 - *ab-initio* pseudopotentials
 - *environment-reflecting* ("all-electron") pseudopotentials

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DFT+FEM+pseudopotentials: *about our project*

Real-space pseudopotential finite-element ab-initio method for non-periodic systems



outline:

- basic ingredients & motivation
- applications
- risks & problems
- what has been done so far
- next steps & outlook
- co-workers

Motivation ?

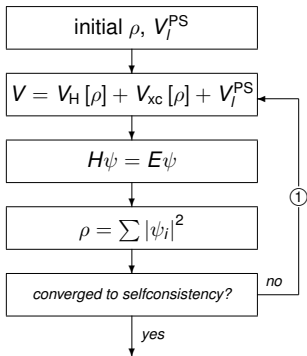
- DFT, iterative selfconsistent scheme
- Finite-element method
- Environment-reflecting (“*all-electron*”) pseudopotentials

- considerable gap among the methods focused on **non-periodic** structures (\times effort invested in the methods based on Bloch functions)
(specific ad-hoc basis sets, poor convergence control etc., problems in non-standard situations, with geometry optimization, with broken charge neutrality ...)
- several recent trial-and-error attempts with
 - finite-element / finite-difference approach
 - all-electron / pseudopotentials
 - adaptive curvilinear coordinates
- unique opportunity ... with respect to
 - long acquaintance with *ab-initio* pseudopotential-generating methods (*me*)
 - contacts to -and concern of- authors of FEM codes (*J. Plešek, P. Šolín, R. Cimrman*)
 - availability of advice/consultation in linear-algebra problems (*M. Tůma*)
 - experience with calculations of clusters, adsorbates, impurities, ... (*O. Šipr*)

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- DFT, iterative selfconsistent scheme
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Motivation ?

- DFT, iterative selfconsistent scheme ... *Why DFT?*

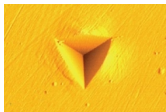


- Finite-element method
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Motivation ?

- DFT, iterative selfconsistent scheme
- Finite-element method
 - general, adaptive basis with excellent convergence control
 - applicability of (even complicated) boundary conditions
 - robust, industrially proof method in continual development, with several open-source codes available
- Environment-reflecting (“*all-electron*”) pseudopotentials
 - substantially reduces the number of electron (i.e. degrees of freedom)
 - fully relativistic core electrons are “hidden” in pseudopotential (=> no need to solve 4-component Dirac equation by FEM) possibly separate spin-up and spin-down pseudopotentials acting on valence electrons
 - eliminates high potential gradients (however, this point would be solvable also with hp-FEM or adaptive coordinates)
 - no additional approximation except for linearization

- clusters, (bio)molecules (possibly with broken charge neutrality)
 - ab-initio generation of effective potentials for modelling of
 - proteins
 - defect growth
 - ...
- with possible application of boundary condition for periodic surroundings:
 - defects, impurities
 - adsorbates
 - nanoindentation hardness →
- with possible application of 1D-translational symmetry:
 - nanowires, nanotubes
 - ...
- ...



- Kohn-Sham solver by FEM
- Poisson equation solver by FEM
- DFT selfconsistent iterative engine (in Python)
- solved some covergenece problems, debugging on 1–3 -atom molecules, without any symmetry assumptions, with (simplified) separable pseudopotential
- procedures for treating the rank-n update Hamiltonian terms
- (a bit apart) 2D full-potential models with hp-FEM (adaptive basis & mesh)

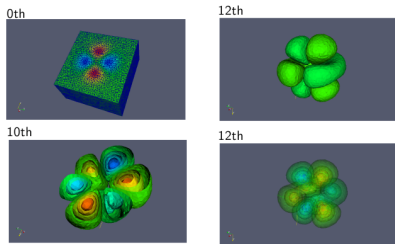


Figure: 3D-harmonic oscillator

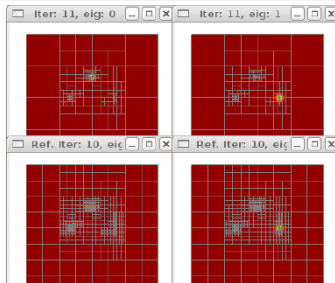


Figure: h-adaptivity in 2D (3-atom molecule, 2D full potential)

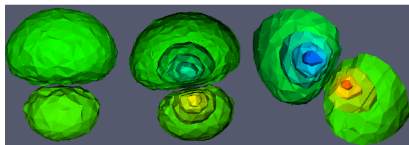


Figure: boron 2p, 3D full-potential (unrealistic, just to illustrate tetrahedron mesh)

- theoretical support & consultations:
 - O.Šipr (physics behind, fundamental problems)
 - J.Plešek (mathematical background of FEM)
 - M.Tůma (linear algebra & sparse matrices problems)
 - R.Cimrman (boundary conditions in FEM)
 - R.Podloucky and K.Kunc (occasional consultations)
- direct participation on computer code writing:
 - O.Čertík (Kohn-Sham solver, Poisson solver, 1st ver. of DFT loop, since the end of 2008 almost absorbed by his stay in University of Nevada, Reno)
 - P.Pařík (eigenvalue problem solver in PMD, interface for PMD)
 - M.Novák (treating rank-n update matrices, linear algebra routines)
 - P.Pšeno (started in summer 2009, intermitted due to health troubles)
 - R.Cimrman (SfePy, DFT iterative selfconsistency debugging, boundary conditions)
- some help with computer administration: ...