Plane wave/pseudo potential calculations in solid state — II

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Summary

1. Different basis set
    - Localised basis sets
    - Comparison: Localised basis sets vs plane waves
2. Practical calculations — What to control
3. Quantum Espresso/PWSCF

Expansion using a basis set

- For practical purposes it is necessary to expand the Kohn-Sham orbitals using a set of basis functions
- Basis set $\{\varphi_\alpha(\mathbf{r})\}_{\alpha=1}^{M}$
- Usually a linear expansion

$$\boxed{\psi_i(\mathbf{r}) = \sum_{\alpha=1}^{M} c_{\alpha i}\varphi_\alpha(\mathbf{r})}$$

Different basis sets

- Plane waves
  - quantum espresso/PWSCF, CPMD, abinit, paratec, VASP, CASTEP, . . .
- Gaussian functions
  - TurboMole, MolPro, GaussianXX, . . .
- Slater functions
  - ADF
- Numerical/δ basis
  - DMol3, numol, . . .
- Mixtures
  - CP2k, Wien2k, . . .

Atomic orbital basis sets

Philosophy

Molecules are assemblies of slightly distorted atoms

$$\varphi_\alpha(\mathbf{r}) = \varphi_\alpha(r) Y_{lm}(\Theta, \phi)$$

$$\varphi_\alpha(r) = \begin{cases} \exp[-\alpha r^2] & \text{Gaussian} \\ \exp[-\alpha r] & \text{Slater} \end{cases}$$

$\varphi_\alpha(\mathbf{r}; \mathbf{R}_I)$: basis functions are attached to nuclear positions

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Advantages / disadvantages of AO basis sets

+ according to chemical insight
+ small basis sets give already good results
– non-orthogonal
– depend on atomic position
– basis set superposition errors (BSSE)

Properties of plane waves

$$\boxed{\varphi_{\mathbf{G}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \exp[i\mathbf{G} \cdot \mathbf{r}]}$$

- Plane waves are periodic wrt. box **h**
- Plane waves are orthonormal

$$\langle \varphi_{\mathbf{G}'} | \varphi_{\mathbf{G}} \rangle = \delta_{\mathbf{G}',\mathbf{G}}$$

- Plane waves are complete

$$\psi(\mathbf{r}) = \psi(\mathbf{r} + \mathbf{L}) = \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{G}} \psi(\mathbf{G}) \exp[i\mathbf{G} \cdot \mathbf{r}]$$

Comparison to AO basis set

Plane Waves:

$$\begin{aligned} \frac{1}{2} G^2 &< E_{\text{cut}} \\ \frac{1}{2} G'^2 &< E_{\text{cut}} \\ \frac{1}{2} (G + G')^2 &< \left(\sqrt{E_{\text{cut}}} + \sqrt{E_{\text{cut}}} \right)^2 = 4E_{\text{cut}} \end{aligned}$$

Atomic orbitals: Every product results in a new function

$$\varphi_\alpha(\mathbf{r} - \mathbf{A}) \varphi_\beta(\mathbf{r} - \mathbf{B}) = \varphi_\gamma(\mathbf{r} - \mathbf{C})$$

Linear dependence for plane waves vs. quadratic dependence for AO basis sets.

Summary

How to start a new calculation

Initial considerations

- What is the best method/code available? (classical/approximate/DFT potential)
- Size of system? (computational resources available)
- Static or dynamics calculation?

Procedure for DFT calculations

- Choice of the system (number of atoms, unit cell, ...; can be modified later)
- Test for static computational parametres
    - description of nuclei (CPMD: pseudo potentials)
    - basis set (CPMD: cut-off energy only)
    - computational unit cell for isolated systems (molecules)
    - exchange-correlation functional

Choice for computational parametres: Unit cell

- In plane wave calculations one *always* has to define a computational unit cell, even for isolated objects such as atoms or molecules
  - It should be large enough so that the electronic wave functions and density vanish at the boundary of the box, or that the periodic images of the molecule do not interact with each other
  - Test simply by increasing the size of the box systematically until the main parametres of interest (energies, vibrational frequencies, Kohn-Sham eigenvalues, . . .) do not change anymore
- In naturally periodic systems like solids, liquids, slab geometries (surfaces, 2-dimensional periodicity), polymers (1-dimensional periodicity) one has to test for the convergence with respect to k point sampling

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Choice for computational parametres: XC functional

- Does the system size allow for the use of hybrid functionals?
- If not, would LDA provide better accuracy than GGA's? This is normally the case only in solids or other densely packed materials, for the bulk properties. Also used sometimes in cases where GGA's fail qualitatively (*eg* adsorbtion of molecules with phenyl ring on transition metal surfaces)
- If GGA, which one of them? BLYP (and BP86) is favoured by chemists, PBE by physicists
- Other functionals: Meta-GGA's, asymptotically corrected functionals, self-interaction corrected functionals, . . .

Choice for static computational parametres: PP

Considerations when selecting a pseudo potential

- Which valence configuration? Semi-core (= state in between “clear” core and valence states; normally $-20\ldots-50$ eV below the vacuum level) in core or valence?
- Do the core and valence electron density over-lap considerably? If yes, is NLCC necessary?
- Type of pseudo potential? Troullier-Martins, Vanderbilt, other norm-conserving one, . . .
- Kleinman-Bylander scheme or Gauß-Hermite integration?
- Which l_{max}, l_{loc}? The former is more an issue of computing time, the second crucial to avoid
- Could the core radii be larger (to reduce basis set/computing time)?

Choice for computational parametres: PP testing

- Select a (small) representative system, preferably several of them; for example of different bonding or hybridisation types (*eg* purely covalent C-C, partially ionic/polarisation C-N or C-H, ionic like H-F
- Start with a large basis set (please see next topic) in order to be sure of convergence
- Compare to all-electron or other, reliable pseudo potential calculation employing the same XC functional, if possible; comparisons with experiments have a second priority, due to the known, systematic errors in the XC functionals
- Quantities to compare: Binding energies, bond lengths, angles, vibrational frequencies, . . .
- The differences to proper all-electron calculations should be of the order of 0.01 Å or less in bond lengths, < 50 meV for binding energies, vibrational frequencies $< 20\ \mathrm{cm}^{-1}$

Choice for computational parametres: PP parametres

If you need to optimise the parametres of the pseudo potential like the core radii, NLCC radius *etc*, you have to change them and re-run these tests; again until the property of interest does not change anymore significantly (Please remember: It is always nicer to be on the safe side. . .)

Choice for computational parametres: Basis set

- With plane wave basis set only one parametre: Cut-off energy E_{cut}; units Rydberg atomic units (historical / convenience reasons: E_{cut} [Ha] = $\frac{1}{2}|\mathbf{G}_{\mathrm{max}}|^2 = \frac{1}{2}E_{\mathrm{cut}}$ [Ry] $\Rightarrow$ $|\mathbf{G}_{\mathrm{max}}|$ [1/Bohr] = $\sqrt{E_{\mathrm{cut}}\ [\mathrm{Ry}]}$)
- You can start from a low value of E_{cut} for fast convergence, increase it in steps of 5, 10 or 20 Ry until the properties of interest converge; please notice that the total energy of the system
- Typical values
  - 2*p* elements, transition metals, Troullier-Martins pp's: 50-90 Ry
  - 3*p*, 4*p* elements, alkali metals with NLCC, transition metals of the 5*p* row *etc*, Troullier-Martins pp's: 20-40 Ry
  - Vanderbilt pp's: 20-35 Ry

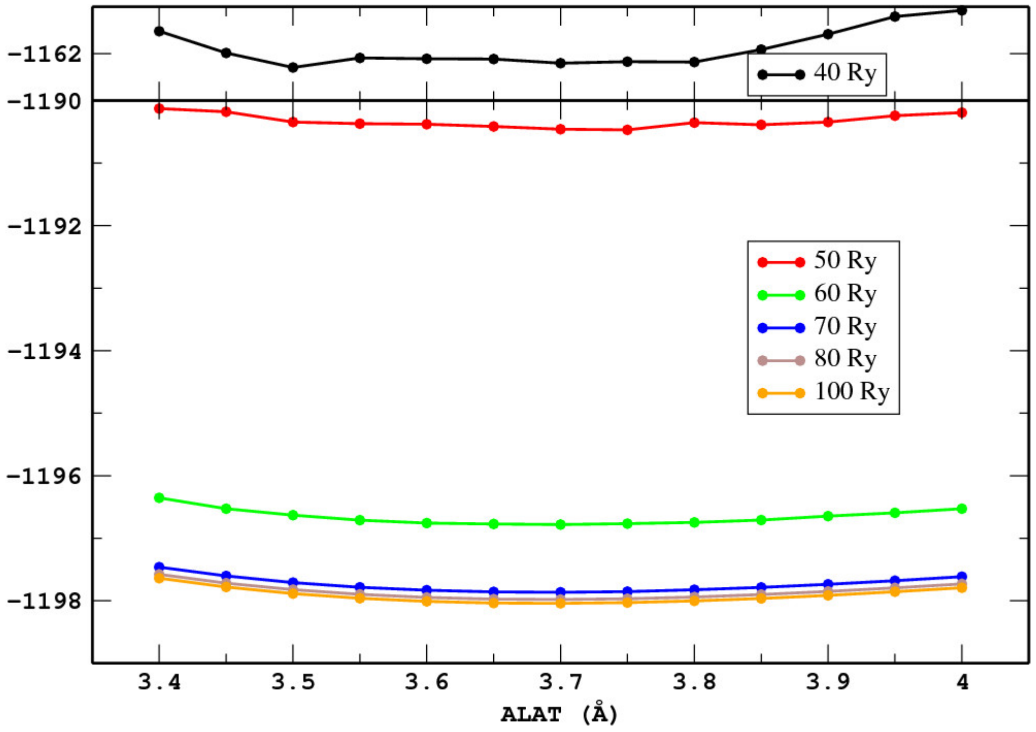
Useful tools

- `units` command: Conversion between different units:

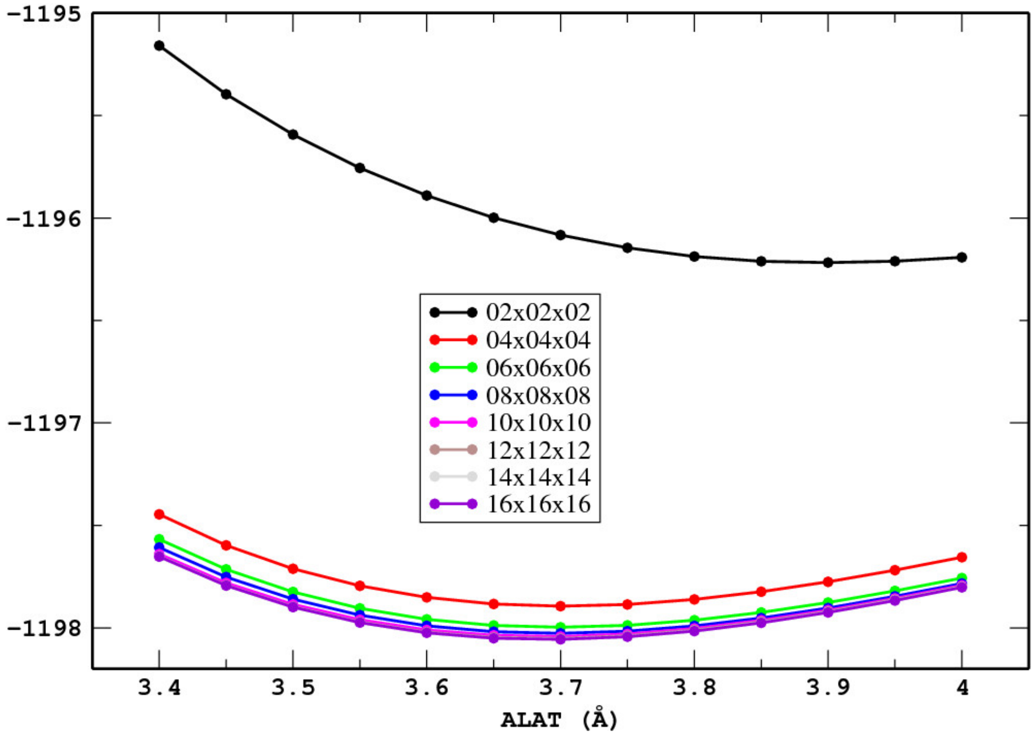
```
localhost (~) : units
2084 units, 71 prefixes, 32 nonlinear units

You have: 32*(15.9994+2*1.0067) atomicmassunit / (9.885 angstrom)^3
You want: g cm^-3
        * 0.99094647
        / 1.0091362
You have:
```

- `openbabel` converts between different graphics file formats
- `xmgrace` or `gnuplot` for 2-dimensional graphics
- `xcrysden` understand input and output of PWSCF
- graphics programs for 3-dimensional plots and atomic configurations, movies: `gOpenMol` `vmd`, `xmakemol`, . . .

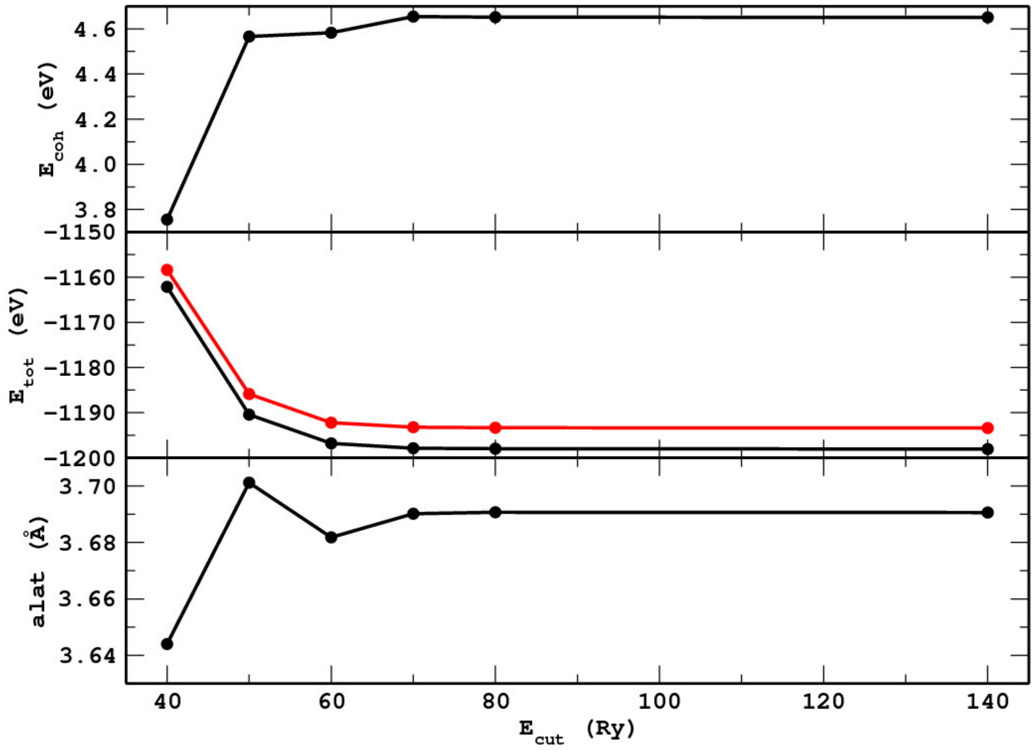
Convergence tests: Cut-off energy



Convergence tests: k point set



Convergence tests: Cut-off energy



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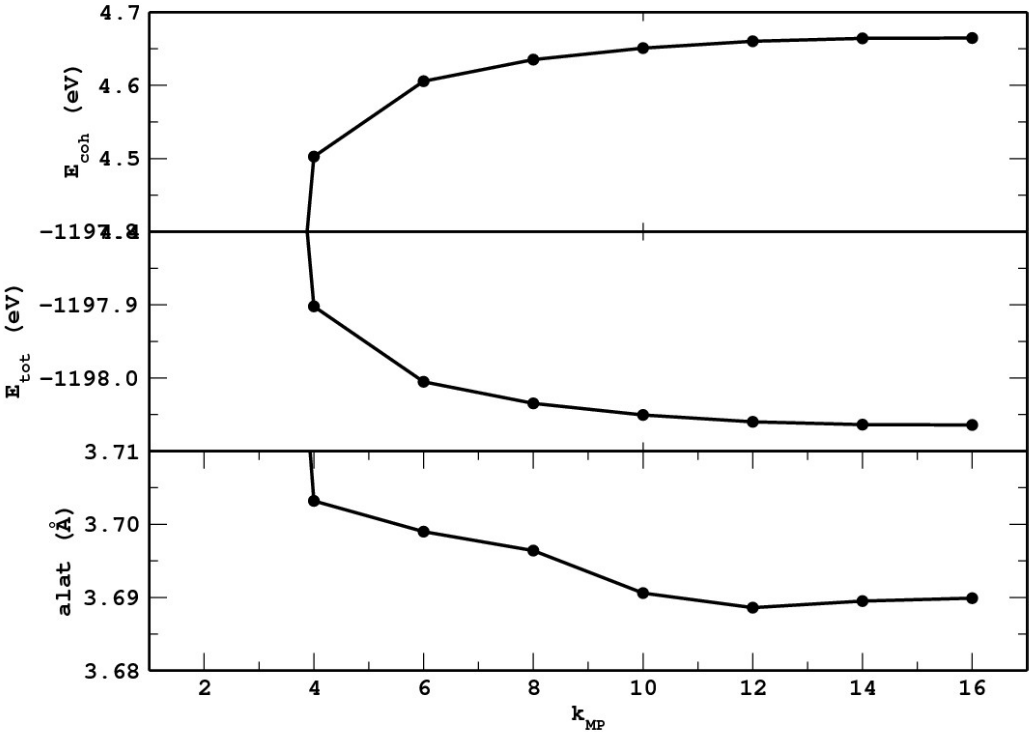

Summary

1. Different basis set
2. Practical calculations — What to control
3. Quantum Espresso/PWSCF
    - Introduction
    - Basic usage
    - Example

Quantum Espresso http://www.quantum-espresso.org/

02 October 2007
The last bugfix release of the Quantum-Espresso distribution is available for download (version 3.2.3)

27 November 2006
A new version (3.2) of the Quantum-Espresso distribution is available for download

07 July 2006
A new version (3.1.1) of the

Quantum ESPRESSO is an integrated suite of computer codes for electronic-structure calculations and materials modeling at the nanoscale. It is based on density-functional theory, plane waves, and pseudopotentials (both norm-conserving and ultrasoft).

PWSCF http://www.pwscf.org/

"The computer is a tool for clear thinking"
Freeman J. Dyson

Welcome to the PWscf Home Page!

PWscf (Plane-Wave Self-Consistent Field) is a computer code for electronic-structure calculations within Density-Functional Theory and Density-Functional Perturbation Theory, using pseudopotentials and a plane-wave basis set. PWscf is part of the Quantum ESPRESSO distribution of codes for the quantum simulation of matter at the atomic scale. PWscf is released under the GNU General Public License.

News

01 October 2007
Last bugfix release of the Quantum-Espresso distribution is available for download (version 3.2.3)

09 May 2007
New bug fixes for the 3.2 release of the Quantum-Espresso distribution are available for

NEWSLETTER
Interested users will be kept updated about PWscf through a newsletter distributed by e-mail.
The newsletter will contain information about new versions of PWscf, bug fixes, etc.
- subscribe
- archive
- search archive

USERS' FORUM
An open mailing list is also available to discuss PWscf related issues

Quantum Espresso

- Historically started from “original” Car-Parrinello code
- Joined recently from PWSCF, CPV and FPMD

Running the executable

- Machine-dependent!
- Serial run:

```
./pw.x -input my-input-file > my-output-file &
```

- Parallel run, linux

```
mpirun -np ${NSLOTS} ./pw.x -npool 4 -input my-input-file > my-output-file &
```

- Parallel run, LoadLeveler:

```
./pw.x -npool 4 -input my-input-file > my-output-file &
```

Example: fcc-Cu

```
 &control
    calculation=’scf’
    restart_mode=’from_scratch’,
    pseudo_dir = ’/home/seitsonen/usr/espresso/PP_LIBRARY/’,
    wfcdir=’/tmp/’
    prefix=’fcc-Cu’
    tstress = .true.
    tprnfor = .true.
 /
 &system
    ibrav = 2, a = 4.00, b = 4.00, c = 4.00,
    nat= 1, ntyp= 1,
    nbnd = 9
    ecutwfc = 140
!    ecutrho = 0
    occupations=’smearing’, smearing=’fermi-dirac’, degauss=.00367490107593722133
 /
 &electrons
    diagonalization=’david’
    conv_thr = 1.0e-9
    mixing_beta = 0.8
 /
ATOMIC_SPECIES
 Cu  63.5500 Cu_pbe-20071125.UPF
ATOMIC_POSITIONS angstrom
 Cu  0.0 0.0 0.0
K_POINTS (automatic)
 16 16 16 0 0 0
```

Help on input

- Input is explained in file `Doc/INPUT_*`
- One can ask for help on the Mailing list

- Different values for ’ibrav/celldm’ are explained at the end of `Doc/INPUT_PW`
- Please be aware on units for lattice vectors and coordinates: Bohr, Ångström, a_0, lattice vectors, . . .