

Quantum simulations of materials using QUANTUM ESPRESSO

P. Giannozzi

Università di Udine and CNR-IOM Democritos, Trieste, Italy

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Quantum simulation of matter at the nanoscale

Quantum, or *first-principles*, simulations: from electronic structure.

Nanoscale: phenomena on a scale of lengths up to a few tens of nm.

Basic theoretical tools:

- Density-Functional Theory (DFT) (P. Hohenberg, W. Kohn, and L. Sham, 1964-65)
- Pseudopotentials (J.C. Phillips, M.L. Cohen, M. Schlüter, D. Vanderbilt and many others, 1960-2000)
- Car-Parrinello and other iterative techniques (SISSA 1985, and many other places since)

Some authors call the above set of tools *the Standard Model* of materials simulation.

First-principles simulations

Time-dependent Schrödinger equation for electrons and nuclei:

$$i\hbar \frac{\partial \Phi(r, R; t)}{\partial t} = \left(- \sum_I \frac{\hbar^2}{2M_I} \nabla_{\vec{R}_I}^2 - \sum_i \frac{\hbar^2}{2m} \nabla_{\vec{r}_i}^2 + V(r, R) \right) \Phi(r, R; t)$$

Born-Oppenheimer approximation ($M \gg m$):

$$\left(- \frac{\hbar^2}{2m} \sum_i \nabla_{\vec{r}_i}^2 + V(r, R) \right) \Psi(r|R) = E(R) \Psi(r|R)$$

where the potential felt by electrons is

$$V(r, R) = \sum_{I \neq J} \frac{e^2}{2} \frac{Z_I Z_J}{|\vec{R}_I - \vec{R}_J|} - \sum_{i, I} \frac{Z_I e^2}{|\vec{r}_i - \vec{R}_I|} + \frac{e^2}{2} \sum_{i \neq j} \frac{1}{|\vec{r}_i - \vec{r}_j|}$$

Notation: $r \equiv (\vec{r}_1, \dots, \vec{r}_n)$ (electrons); $R \equiv (\vec{R}_1, \dots, \vec{R}_N)$ (nuclei).

Density-Functional Theory

Transforms the many-electron problem into an equivalent problem of (fictitious) non-interacting electrons, the Kohn-Sham Hamiltonian:

$$H\phi_v \equiv \left(-\frac{\hbar^2}{2m} \nabla_{\vec{r}}^2 + V_R(\vec{r}) \right) \phi_v(\vec{r}) = \epsilon_v \phi_v(\vec{r})$$

The effective potential is a *functional* of the charge density:

$$V_R(\vec{r}) = - \sum_I \frac{Z_I e^2}{|\vec{r} - \vec{R}_I|} + v[n(\vec{r})], \quad n(\vec{r}) = \sum_v |\phi_v(\vec{r})|^2$$

whose form is unknown, but for which approximate forms are known.

DFT is in principle valid for *ground-state properties* only.

Density-Functional Theory II

The total energy is also a functional of the charge density:

$$\begin{aligned} E \Rightarrow E[\phi, R] = & -\frac{\hbar^2}{2m} \sum_v \int \phi_v^*(\vec{r}) \nabla^2 \phi_v(\vec{r}) d\vec{r} + \int V_R(\vec{r}) n(\vec{r}) d\vec{r} + \\ & + \frac{e^2}{2} \int \frac{n(\vec{r}) n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}' + E_{xc}[n(\vec{r})] + \sum_{I \neq J} \frac{e^2}{2} \frac{Z_I Z_J}{|\vec{R}_I - \vec{R}_J|} \end{aligned}$$

Kohn-Sham equations from the minimization of the energy functional:

$$E(R) = \min E[\phi, R], \quad \int \phi_i^*(\vec{r}) \phi_j(\vec{r}) d\vec{r} = \delta_{ij}$$

Hellmann-Feynman theorem holds. Forces on nuclei:

$$\vec{F}_I = -\nabla_{\vec{R}_I} E(R) = - \int n(\vec{r}) \nabla_{\vec{R}_I} V_R(\vec{r}) d\vec{r}$$

Plane-Wave Pseudopotential method

- expanding the Kohn-Sham orbitals into a suitable *basis* set turns DFT into a multi-variate minimization problem, and the Kohn-Sham equations into a *non-linear matrix eigenvalue problem*
- the use of *pseudopotentials* allows one to ignore chemically inert core states and to use *plane waves*
- plane waves are *orthogonal* and easy to check for *completeness*; they allow to efficiently calculate the needed $H\phi$ products and to solve the Poisson equation using *Fast Fourier Transforms* (FFTs)
- *supercells* allow to study systems in which perfect periodicity is broken (surfaces, defects) or absent (amorphous, liquids)

Some quantities accessible to quantum simulations (that may be of interest for this community)

- Ground-state charge density, Kohn-Sham orbitals, total energy and derivatives: forces on nuclei, *pressure and stress*
- Structural optimization: *minimum-energy structures* for crystals and (using supercells) molecules, surfaces, defects (impurities, interstitials, vacancies,...); calculation of *formation energies*
- Molecular Dynamics from first principles, e.g.: *H migration*
- Reaction barriers and pathways, e.g. *vacancy and defect diffusion*
- Potential Energy Surfaces, Free Energy Surfaces
- Vibrational spectroscopy, vibrational contribution to Free Energy

Approximations: physics

We have to make a distinction between *theoretical* approximations and *numerical* limitations. Main *theoretical* approximations:

- Born-Oppenheimer (*adiabatic*) approx., *classical* ion dynamics (access to quantum dynamics possible but not simple)
- DFT is a *ground-state* theory: no easy access to excited states
- DFT **functionals**: GGA is very often good enough but it has serious limitations weakly-bonded and highly correlated systems (better than GGA functionals are now available, though)

Methodological (partly theoretical, partly numerical) approximation:

- **Pseudopotentials**: should be almost equivalent to frozen-core approximation (but sometimes they are a source of problems)

Approximations: numerical

Main *numerical* approximations / limitations:

- finite/limited supercell size – computational requirements grow up to $\mathcal{O}(N^3)$ with the **number of atoms** in the supercell
- finite basis set – computational requirements grow linearly with the no. of PWs of the basis (determined by **kinetic energy cutoff**)
- discrete Brillouin-Zone sampling (number of **k-points** in the grid)
- convergence criteria
- differentiation / integration / interpolation

The QUANTUM ESPRESSO distribution

QUANTUM ESPRESSO stands for *Quantum opEn-Source Package for Research in Electronic Structure, Simulation, and Optimization*

QUANTUM ESPRESSO is an integrated suite of software for atomistic calculations based on electronic structure, using density-functional theory, a plane-wave basis set, pseudopotentials. Freely available under the terms of the GNU General Public License

The main goals of QUANTUM ESPRESSO are

- *innovation* in methods and algorithms
- *efficiency* on modern computer architectures


A great effort is also devoted to *user friendliness* and to the formation of a *users' and developers' community*

Preview of new www.quantum-espresso.org

QUANTUMESPRESSO

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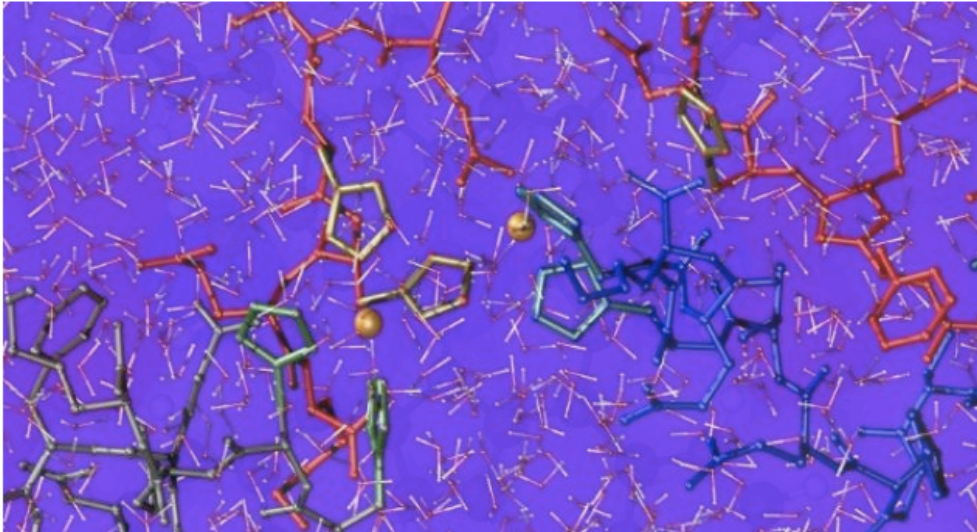
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News

16.01.2012
Quantum ESPRESSO developers meeting 24th January 2012
The annual QE developers meeting will be held the 24th January 2012 in SISSA, library red room. ...

22.11.2011
Quantum ESPRESSO 4.3.2
Version 4.3.2 of Quantum ESPRESSO is available for download. (28 July 2011)

22.11.2011
Quantum ESPRESSO for GPU
The first GPU enabled beta release of Quantum



Quantum ESPRESSO is an integrated suite of Open-Source computer codes for electronic-structure calculations and materials modeling at the nanoscale. It is based on density-functional theory, plane waves, and pseudopotentials.

What can QUANTUM ESPRESSO do?

- Structural modeling (equilibrium structures of molecules, crystals, surfaces)
- Dynamical modeling (first-principles molecular dynamics) either on the electronic ground state (Born-Oppenheimer) or with fictitious electronic kinetic energy (Car-Parrinello)
- Chemical reactivity and transition-path sampling, using Nudged Elastic Band (NEB) method
- Linear response functions (vibrational and dielectric properties), plus some non-linear ones (third-order force constants and dielectric response, non-resonant Raman)
- Computational microscopy (STM)

Advanced QUANTUM ESPRESSO capabilities

- some "beyond-DFT" methods: DFT+U, hybrid functionals
- free-energy sampling (metadynamics, with PLUMED plugin)
- computational spectroscopy
 - lattice and molecular vibrations: Raman, Infrared, Neutrons
 - magnons and spin excitations
 - photoemission (MBPT)
 - optical/UV absorption (TDDFT, MBPT soon to come)
 - NMR chemical shifts
 - X-ray spectra, core level shifts

A few examples of QUANTUM ESPRESSO usage for simulation of plasma-facing materials

- *First-principles study of neutral silicon interstitials in 3C- and 4H-SiC*
- *Energetics and metastability of the silicon vacancy in cubic SiC*
- *Evidence for a kinetic bias towards antisite formation in SiC nano-decomposition*
- *Stoichiometric Defects in Silicon Carbide*
- *Activation entropies for diffusion in cubic silicon carbide from first principles*
- *Ab initio investigation of radiation defects in tungsten: Structure of self-interstitials and specificity of di-vacancies compared to other bcc transition metals*
- *Quantum modeling (DFT) and experimental investigation of beryllium-tungsten alloy formation*

Example: formation energy of vacancies in Be

1. Find the equilibrium lattice parameters and total energy (per cell) E_b of hcp Be in the ground state
2. The chemical potential of Be is given by the energy per Be atom: $\mu_{Be} = E_b/2$ (we assume $T = 0$, $P = 0$; hcp Be has two atoms per unit cell)
3. A suitable supercell of hcp Be containing N atoms is built: its energy should be $E = N\mu_b$
4. An atom is removed, the supercell so obtained is optimized and its energy (per supercell) E_v is calculated. The formation energy is given by:

$$E_f = E_v - (N - 1)\mu_{Be}$$

In practice, there are many physical and technical aspects to be considered, and all steps must be *carefully tested and verified* for convergence

Sample (and simple) input for the pw.x code

```
&control
  calculation='scf', tprnfor=.true., tstress=.true.
  pseudo_dir='./',  outdir='./tmp'
/
&system
  ibrav= 4, celldm(1)=4.2526, celldm(3)=1.589, nat=2, ntyp= 1,
  ecutwfc = 25.0, ecutrho=200.0,
  occupations='smearing', smearing='mv', degauss=0.02
/
&electrons
  conv_thr=1.0e-8
/
ATOMIC_SPECIES
  Be  1.  Be.pbe-n-rrkjus.UPF
ATOMIC_POSITIONS crystal
  Be 0.0 0.0  0.0
  Be 1/3 2/3  1/2
K_POINTS automatic
8 8 6 1 1 1
```


Meaning of main variables

`&control .../`, `&system .../`, `&electrons .../` are fortran-90 namelists

- `calculation='scf'`, `tprnfor=.true.`, `tstress=.true.`
perform a self-consistent calculation, calculate forces and stress. We will use `calculation='relax'` and `'vc-relax'`, for fixed-cell and variable-cell optimization, with additional namelists `&ions .../`, `&cell .../`
- `ibrav= 4`, `celldm(1)=4.2526`, `celldm(3)=1.589`
specify lattice: simple hexagonal with $a = 4.2526$ a.u., $c/a = 1.589$
- `nat=2`, `ntyp=1` *there are 2 atoms of 1 type in the unit cell / supercell*
- `ecutwfc = 25.0`, `ecutrho=200.0`
kinetic energy cutoff(s) in Ry for plane waves (one for wavefunctions, one for charge density with Ultrasoft pseudopotentials)
- `occupations='smearing'`, `smearing='mv'`, `degauss=0.02`
how to deal with Fermi surface in metals: Marzari-Vanderbilt broadening

- `conv_thr=1.0e-8`
convergence threshold for self-consistency
- `Be 1. Be.pbe-n-rrkjus.UPF`
atom type, mass (not used), file containing pseudopotential; the type of DFT functional is specified in this file, PBE in this case
- `ATOMIC_POSITIONS (crystal)`
`Be 0.0 0.0 0.0`
`Be 1/3 2/3 1/2`
atomic positions (in terms of crystal lattice vectors)
- `K_POINTS automatic`
`8 8 6 1 1 1`
k-point grid: uniform grid, $8 \times 8 \times 6$, translated by half step in all directions

Many more options and input variables are available.

Sample (and simple) output

Program PWSCF v.4.99 starts on 25Jan2012 at 10:47:44

[...]

```
bravais-lattice index      =           4
lattice parameter (alat)   =       4.2526   a.u.
unit-cell volume           =       105.8323 (a.u.)^3
number of atoms/cell       =           2
number of atomic types     =           1
number of electrons        =       4.00
number of Kohn-Sham states =           6
kinetic-energy cutoff       =       25.0000   Ry
charge density cutoff      =       200.0000   Ry
convergence threshold      =       1.0E-06
mixing beta                =       0.5000
number of iterations used  =           8   plain      mixing
Exchange-correlation       =   SLA   PW   PBX   PBC ( 1 4 3 4 0)
EXX-fraction               =       0.00
```

```
celldm(1)=   4.252600   celldm(2)=   0.000000   celldm(3)=   1.589000
celldm(4)=   0.000000   celldm(5)=   0.000000   celldm(6)=   0.000000
```

```
crystal axes: (cart. coord. in units of alat)
      a(1) = (   1.000000   0.000000   0.000000 )
      a(2) = (  -0.500000   0.866025   0.000000 )
      a(3) = (   0.000000   0.000000   1.589000 )
```

```
reciprocal axes: (cart. coord. in units 2 pi/alat)
      b(1) = (   1.000000   0.577350   0.000000 )
      b(2) = (   0.000000   1.154701   0.000000 )
      b(3) = (   0.000000   0.000000   0.629327 )
```

```
PseudoPot. # 1 for Be read from file:
../Be.pbe-n-rrkjus.UPF
```

```
[...]
```

atomic species	valence	mass	pseudopotential
Be	2.00	1.00000	Be(1.00)

```
12 Sym. Ops. (no inversion) found
```

```
(note: 12 additional sym.ops. were found but ignored
their fractional transations are incommensurate with FFT grid)
```

```
[...]
```

site n.	atom	positions (alat units)
1	Be	tau(1) = (0.0000000 0.0000000 0.0000000)
2	Be	tau(2) = (0.0000000 0.5773503 0.7945000)

number of k points=40 Marzari-Vanderbilt smearing, width (Ry)=0.0200

cart. coord. in units 2pi/alat

k(1) = (0.0000000 0.0000000 0.0000000), wk = 0.0052083

[list of all k-points follows]

k(40) = (0.2500000 0.5773503 -0.3146633), wk = 0.0312500

Dense grid: 5119 G-vectors FFT dimensions: (20, 20, 32)

Smooth grid: 1785 G-vectors FFT dimensions: (15, 15, 24)

[...]

Initial potential from superposition of free atoms

[...]

Starting wfc are 8 randomized atomic wfcs

[...]

Self-consistent Calculation

iteration # 1 ecut= 25.00 Ry beta=0.50

[more iterations follow]

End of self-consistent calculation

k = 0.0000 0.0000 0.0000 (233 PWs) bands (ev):

-3.1849 3.5975 9.1242 24.2582 24.2582 26.7730

[list of k-points and of Kohn-Sham energies follows]

6.2177 6.2178 9.2427 9.2428 15.0905 15.0907

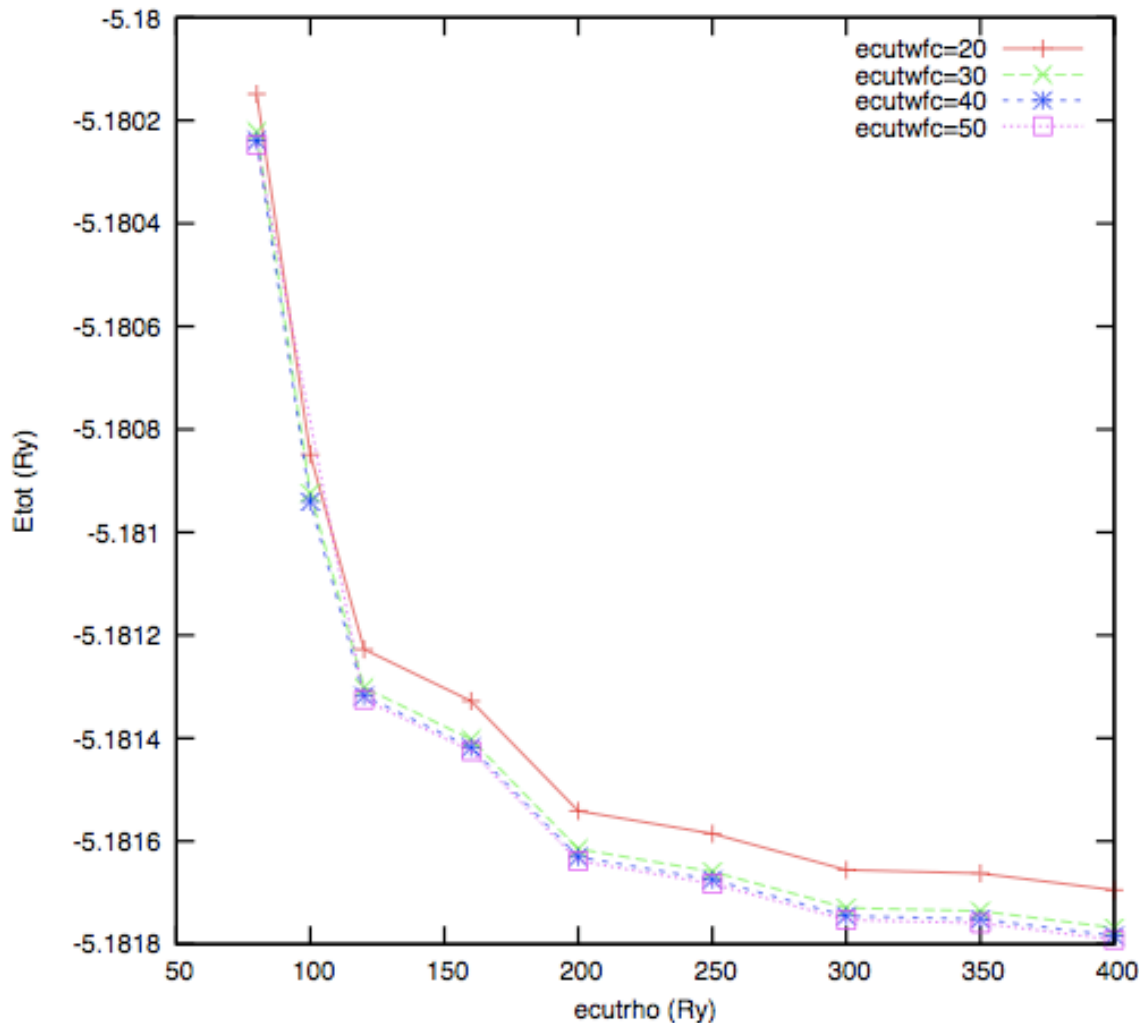
the Fermi energy is 8.8287 ev

! total energy = -5.18158944 Ry
Harris-Foulkes estimate = -5.18158897 Ry
estimated scf accuracy < 0.00000020 Ry

The total energy is the sum of the following terms:

one-electron contribution = 4.05121951 Ry
hartree contribution = 0.00508183 Ry
xc contribution = -3.08381752 Ry
ewald contribution = -6.15366201 Ry
smearing contrib. (-TS) = -0.00041124 Ry

Convergence tests: cutoff

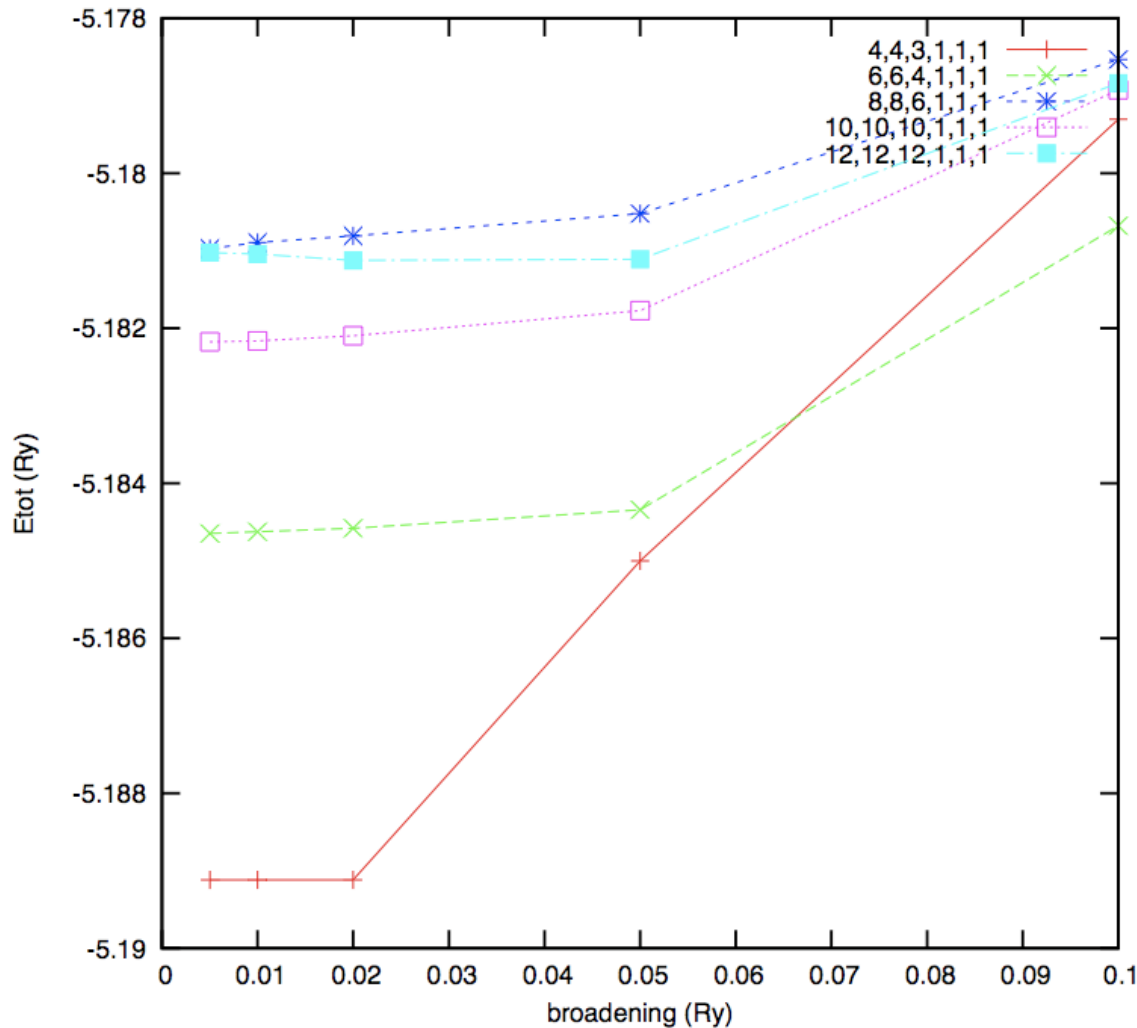


Total energy as a function of the two cutoffs `ecutwfc` and `ecutrho`. Note that

- the required cutoff depends upon the pseudopotentials, notably the *hardest* ones;
- total energy is not the best indicator of the quality of convergence: most of the error is *atomic-like* and cancels out when different structures are compared

The total energy is converged with $\sim 1\text{meV}$ for `ecutwfc=30` and `ecutrho=200`.

Convergence tests: k-points



One should look for convergence at small values of the broadening, ideally. Here a rather arbitrary but “standard” choice of uniform (Monkhorst-Pack) grids with increasing density has been done. A reasonable convergence is achieved already with a $8 \times 8 \times 6$ shifted grid (60 **k**-points: the code calculates only **k**-points in the Irreducible Brillouin Zone)

Let us try `ecutwfc=25`, `ecutrho=200`, `degauss=0.02`, `8 8 6 1 1 1` k-point grid (although likely not sufficient for a serious calculation): what do we get?

Equilibrium lattice parameter(s)

A simple way to find the equilibrium lattice parameters, a and c in this case, is to use *variable-cell optimization* (alternative way: fit to an equation of state $E(V)$)

```
&control    calculation='vc-relax' ... /  
...  
&ions       ion_dynamics='bfgs'    /  
&cell       cell_dynamics='bfgs'   /  
...
```

will produce a series of self-consistent results with different cell parameters and atomic positions, converging to the lowest-energy structure:

```
> grep ! behcp.relax.out  
!    total energy           =      -5.18080746 Ry  
!    total energy           =      -5.18100272 Ry  
!    total energy           =      -5.18105108 Ry  
!    total energy           =      -5.18105121 Ry  
!    total energy           =      -5.18104969 Ry
```

Equilibrium lattice parameter(s) II

Let us look inside the output file:

```
bfgs converged in    4 scf cycles and    3 bfgs steps  
(criteria: energy < 0.10E-03, force < 0.10E-02, cell < 0.50E+00)
```

```
End of BFGS Geometry Optimization
```

```
Final enthalpy =          -5.1810512150 Ry
```

```
Begin final coordinates
```

```
new unit-cell volume =    106.30276 a.u.^3 (    15.75244 Ang^3 )
```

```
CELL_PARAMETERS (alat= 4.25260000)
```

```
  1.007292752    0.000000000    0.000000000  
 -0.503646376    0.872341113    0.000000000  
  0.000000000    0.000000000    1.573036832
```

```
ATOMIC_POSITIONS (crystal)
```

```
Be      0.000000000    0.000000000    0.000000000  
Be      0.333333333    0.666666667    0.500000000
```

```
[...]
```

Forces acting on atoms (Ry/au):

atom	1	type	1	force =	0.00000000	0.00000000	0.00000000
atom	2	type	1	force =	0.00000000	0.00000000	0.00000000

[...]

total	stress	(Ry/bohr**3)	(kbar)	P=	0.20
0.00000126	0.00000000	0.00000000	0.19	0.00	0.00
0.00000000	0.00000126	0.00000000	0.00	0.19	0.00
0.00000000	0.00000000	0.00000151	0.00	0.00	0.22

Finally: $a = 4.284\text{a.u.} = 2.267 \text{ \AA}$; $c = 6.689\text{a.u.} = 3.54 \text{ \AA}$; $E_b = -5.18105 \text{ Ry}$.
The chemical parameter μ_{Be} has the value $\mu_{Be} = E_b/2 = -2.5905 \text{ Ry}$.

It is always a good idea to verify how much *structural parameters* (and not only total energies) depend upon the parameters of the calculation.

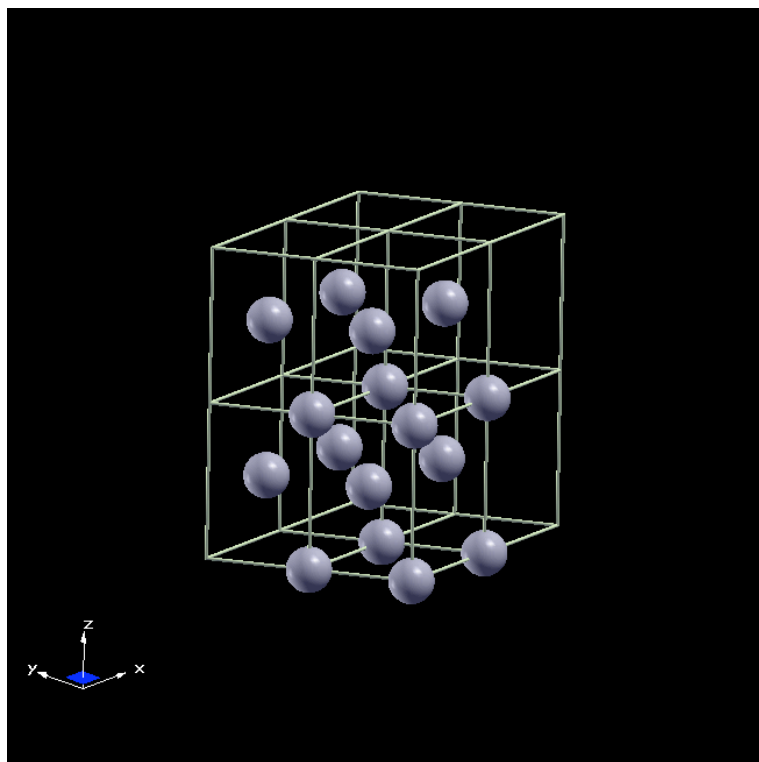
Let us try now with the 12 12 9 1 1 1 k-point grid.

We get: $a = 4.270\text{a.u.} = 2.259 \text{ \AA}$; $c = 6.724\text{a.u.} = 3.558 \text{ \AA}$; $E = -5.18120 \text{ Ry}$.

(note that the final structure may also depend a bit upon the convergence threshold for structural optimization).

A simple and small (16-atom) supercell

A small supercell of the hcp lattice can be made by multiplying all crystal axis by a factor 2 (a $2 \times 2 \times 2$ supercell). Its volume is 8 times the volume of the hcp cell, contains 16 atoms.



ATOMIC_POSITIONS crystal

```
Be 0.0 0.0 0.0
Be 1/2 0.0 0.0
Be 0.0 1/2 0.0
Be 1/2 1/2 0.0
Be 0.0 0.0 1/2
Be 1/2 0.0 1/2
Be 0.0 1/2 1/2
Be 1/2 1/2 1/2
Be 1/6+0.0 1/3+0.0 1/4+0.0
Be 1/6+1/2 1/3+0.0 1/4+0.0
Be 1/6+0.0 1/3+1/2 1/4+0.0
Be 1/6+1/2 1/3+1/2 1/4+0.0
Be 1/6+0.0 1/3+0.0 1/4+1/2
Be 1/6+1/2 1/3+0.0 1/4+1/2
Be 1/6+0.0 1/3+1/2 1/4+1/2
Be 1/6+1/2 1/3+1/2 1/4+1/2
```

The lattice vector $a = 8.568$ a.u. is twice the one for hcp. In this case, the $4 \times 4 \times 4$ $1 \times 1 \times 1$ k-point grid is exactly equivalent to the $8 \times 8 \times 8$ $1 \times 1 \times 1$ for the hcp lattice

Vacancy in 16-atom supercell

After verifying that our supercell is really what we want:

```
> grep ! be16.scf.out
```

```
be16.scf.out:!      total energy              =      -41.44839547 Ry
```

($-41.44839547\text{Ry} = 8E_b$ as expected!) with almost zero forces and stresses, we can remove one atom from the list, for instance atom 1, and set `nat=15`. Since however the vacancy causes a structural rearrangement around the site left vacant, we also need to allow structural optimization, setting `calculation='relax'`. The code will perform several steps at different atomic positions (but fixed supercell):

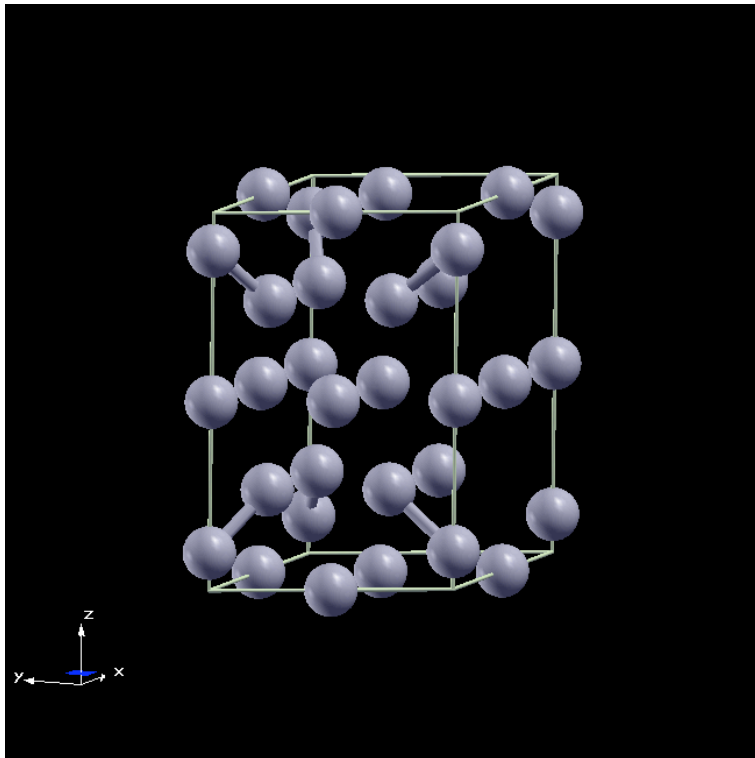
```
> grep ! be16v.relax.out
```

```
!      total energy              =      -38.75659638 Ry
!      total energy              =      -38.75726468 Ry
!      total energy              =      -38.75782185 Ry
!      total energy              =      -38.75824797 Ry
!      total energy              =      -38.75830681 Ry
!      total energy              =      -38.75832676 Ry
```

Finally we find the formation energy: $E_f = -38.75832\text{Ry} - 15\mu_{Be} = 1.35\text{ eV}$, a little bit too high (the expected range is $0.8 \div 1.0\text{ eV}$, but supercell is too small!)

Self-interstitial atoms

Another important defect is the *self-interstitial atom*, which can be simulated in the same (too small!) supercell. Here we try a “split” configuration along z (notice the position of the two first atoms in the list)



ATOMIC_POSITIONS crystal

Be 0.0 0.0 -0.1

Be 0.0 0.0 0.1

Be 1/2 0.0 0.0

Be 0.0 1/2 0.0

Be 1/2 1/2 0.0

Be 0.0 0.0 1/2

Be 1/2 0.0 1/2

Be 0.0 1/2 1/2

Be 1/2 1/2 1/2

Be 1/6+0.0 1/3+0.0 1/4+0.0

Be 1/6+1/2 1/3+0.0 1/4+0.0

Be 1/6+0.0 1/3+1/2 1/4+0.0

Be 1/6+1/2 1/3+1/2 1/4+0.0

Be 1/6+0.0 1/3+0.0 1/4+1/2

Be 1/6+1/2 1/3+0.0 1/4+1/2

Be 1/6+0.0 1/3+1/2 1/4+1/2

Be 1/6+1/2 1/3+1/2 1/4+1/2

Formation energy for a self-interstitial atom

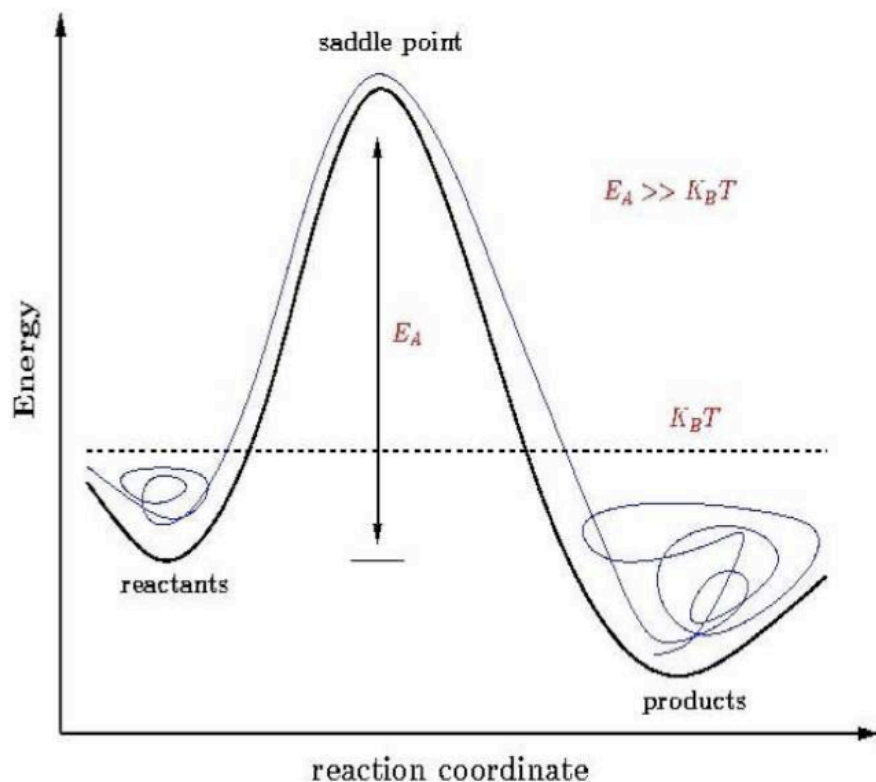
This time the structural optimization is quite large ($\delta E \sim 2.9$ eV; it was just 0.02 eV for the vacancy):

```
> grep ! be16i.relax.out
! total energy = -43.36210215 Ry
! total energy = -43.47861252 Ry
! total energy = -43.54987202 Ry
! total energy = -43.57102599 Ry
! total energy = -43.57269211 Ry
! total energy = -43.57406414 Ry
! total energy = -43.57536282 Ry
! total energy = -43.57579414 Ry
! total energy = -43.57580300 Ry
! total energy = -43.57580931 Ry
! total energy = -43.57581378 Ry
```

We find a large formation energy: $E_f = -43.57581\text{Ry} - 17\mu_{Be} \simeq 6.3$ eV, vs an expected value of ~ 4.18 eV (again, the supercell is very small and this is just *one* possible configuration!)

Reaction pathway calculation using NEB

The Nudged Elastic Band (NEB) method can be used to calculate reaction pathways and energy barriers. Basic aspects of the theory:



- The path is *discretized* into “images”, i.e. points in the configuration space.
- Fictitious “springs” connecting the images keep them apart and prevent them from falling into the same local minima.
- The minimum-energy path is located by imposing that the component of the force orthogonal to the path vanishes.

An example: diffusion of a single vacancy in Be (with our too small 16-atom cell).

We need to provide a starting and an ending image (i.e. atomic positions), such as for instance a vacancy in (0,0,0) and a vacancy in a nearby site.

A sample (and simple) NEB input

```
BEGIN
BEGIN_PATH_INPUT
  [ NEB specific options ]
END_PATH_INPUT
BEGIN_ENGINE_INPUT
  [ options for scf calculation, up to atomic positions ]
BEGIN_POSITIONS
FIRST_IMAGE
  [ atomic positions for starting image ]
LAST_IMAGE
  [ atomic positions for ending image ]
END_POSITIONS
  [ k-points and other optional cards ]
END_ENGINE_INPUT
END
```

NEB calculation is performed by a separate code `neb.x` that can in principle use any "engine" to calculate energies and forces.

A sample (and simple) NEB input

NEB-specific options:

```
&PATH
  restart_mode      = 'from_scratch'
  string_method     = 'neb',
  num_of_images     = 7,
  nstep_path        = 100,
  opt_scheme        = 'broyden'
  first_last_opt    = .true.
  CI_scheme         = "no-CI"
/
```

Beware! the path is linearly interpolated between starting and final image (unless all images are explicitly provided): atomic positions should keep the same ordering as much as possible. In the following example, the only difference between the starting and ending image is the location of the vacancy.

Starting image (vacancy in (0,0,0):

ATOMIC_POSITIONS crystal

Be 1/2 0.0 0.0

Be 0.0 1/2 0.0

Be 1/2 1/2 0.0

Be 0.0 0.0 1/2

Be 1/2 0.0 1/2

Be 0.0 1/2 1/2

Be 1/2 1/2 1/2

Be 1/6+0.0 1/3+0.0 1/4+0.0

Be 1/6+1/2 1/3+0.0 1/4+0.0

Be 1/6+0.0 1/3+1/2 1/4+0.0

Be 1/6+1/2 1/3+1/2 1/4+0.0

Be 1/6+0.0 1/3+0.0 1/4+1/2

Be 1/6+1/2 1/3+0.0 1/4+1/2

Be 1/6+0.0 1/3+1/2 1/4+1/2

Be 1/6+1/2 1/3+1/2 1/4+1/2

Ending image (vacancy in ($\frac{1}{6}, \frac{1}{3}, \frac{1}{4}$)):

ATOMIC_POSITIONS crystal

Be 1/2 0.0 0.0

Be 0.0 1/2 0.0

Be 1/2 1/2 0.0

Be 0.0 0.0 1/2

Be 1/2 0.0 1/2

Be 0.0 1/2 1/2

Be 1/2 1/2 1/2

Be 0.0 0.0 0.0

Be 1/6+1/2 1/3+0.0 1/4+0.0

Be 1/6+0.0 1/3+1/2 1/4+0.0

Be 1/6+1/2 1/3+1/2 1/4+0.0

Be 1/6+0.0 1/3+0.0 1/4+1/2

Be 1/6+1/2 1/3+0.0 1/4+1/2

Be 1/6+0.0 1/3+1/2 1/4+1/2

Be 1/6+1/2 1/3+1/2 1/4+1/2

A sample (and simple) NEB output

Program NEB v.4.99

starts on 25Jan2012 at 21:15:16

[...]

initial path length	=	4.1590 bohr
initial inter-image distance	=	0.6932 bohr
string_method	=	neb
restart_mode	=	from_scratch
opt_scheme	=	broyden
num_of_images	=	7
nstep_path	=	100
CI_scheme	=	no-CI
first_last_opt	=	T
use_freezing	=	F
ds	=	1.0000 a.u.
k_max	=	0.1000 a.u.
k_min	=	0.1000 a.u.
suggested k_max	=	0.6169 a.u.
suggested k_min	=	0.6169 a.u.
path_thr	=	0.0500 eV / A

----- iteration 1 -----

tcpu =	0.1	self-consistency for image	1
tcpu =	33.3	self-consistency for image	2
tcpu =	112.2	self-consistency for image	3
tcpu =	188.7	self-consistency for image	4
tcpu =	265.7	self-consistency for image	5
tcpu =	342.0	self-consistency for image	6
tcpu =	420.9	self-consistency for image	7

activation energy (->) = 1.109292 eV

activation energy (<-) = 1.109294 eV

image	energy (eV)	error (eV/A)	frozen
1	-527.3103098	0.382910	F
2	-526.9998863	0.480794	F
3	-526.4487600	0.808914	F
4	-526.2010173	0.830638	F
5	-526.4488256	0.809453	F
6	-526.9999361	0.480636	F
7	-527.3103110	0.382207	F

----- iteration 16 -----

[...]

activation energy (->) = 0.781966 eV

activation energy (<-) = 0.782039 eV

image	energy (eV)	error (eV/A)	frozen
1	-527.3341590	0.001658	F
2	-527.1533025	0.035645	F
3	-526.7395662	0.019141	F
4	-526.5521927	0.007748	F
5	-526.7393800	0.019049	F
6	-527.1528769	0.035554	F
7	-527.3342318	0.002877	F

path length = 4.479 bohr

inter-image distance = 0.746 bohr

Some words on computer requirements

Quantum simulations are both CPU *and* RAM-intensive.

Actual CPU time and RAM requirements depend upon:

- *size of the system under examination*: As a rule of thumb, CPU $\propto N^{2\div 3}$, RAM $\propto N^2$, where N = number of atoms
- *kind of system*: type and arrangement of atoms, influencing the number of plane waves, of electronic states, of **k**-points needed...
- *desired results*: computational effort increases from simple self-consistent (single-point) calculation to structural optimization to reaction pathways, molecular-dynamics simulations, ...

CPU time mostly spent in FFT and linear algebra.

RAM mostly needed to store Kohn-Sham orbitals.

Typical computational requirements

Basic step: self-consistent ground-state DFT electronic structure.

- Simple crystals, small molecules, up to $\sim 50 \div 100$ atoms – CPU seconds to hours, RAM up to 1-2 Gb: *may run on desktop PC*
- Surfaces, larger molecules, complex or defective crystals, up to a few hundreds atoms – CPU hours to days, RAM up to 10-20 Gb: *requires PC clusters or conventional parallel machines*
- Complex nanostructures or biological systems – CPU days to weeks or more, RAM tens to hundreds Gb: *massively parallel machines*

Main factor pushing towards parallel machines is large CPU requirements — but: when RAM requirements exceed the RAM of single machine, parallel machines are the only choice