Stress, Enthalpy and Variable Cell Shape Optimization

A solid is just a very big molecule

$$\text{equilibrium} \Longrightarrow \text{vanishing forces}$$

However: big unit cell, aperiodic, surface effects

A useful idealization is the infinite and periodic crystal

Advantages: periodicity (Bloch's theorem), small unit cell,
point group symmetry

The configuration of an infinite periodic crstal is defined by the collection of the atomic coordinates inside the unit cell (carthesian or internal) and by the size and shape of the unit cell.

$$\tau_\alpha^s = \sum_k a_\alpha^k x_k^s$$

where

τ_α^s = carthesian coordinates;
x_k^s = internal (crystal) coordinates;
a_α^k = fundamental Bravais lattice vectors, cell shape parameters

The (static) equilibrium geometry is obtained for

- vanishing forces
- vanishing stress

homogeneous deformation

$$r \quad \longrightarrow \quad r' = (1+\epsilon)r$$

stress

$$\sigma = -\frac{1}{\Omega}\frac{\partial E}{\partial \epsilon}$$

It's a first order derivative (Hellman-Feynman)

-> NO NEED to know how electrons re-adjust

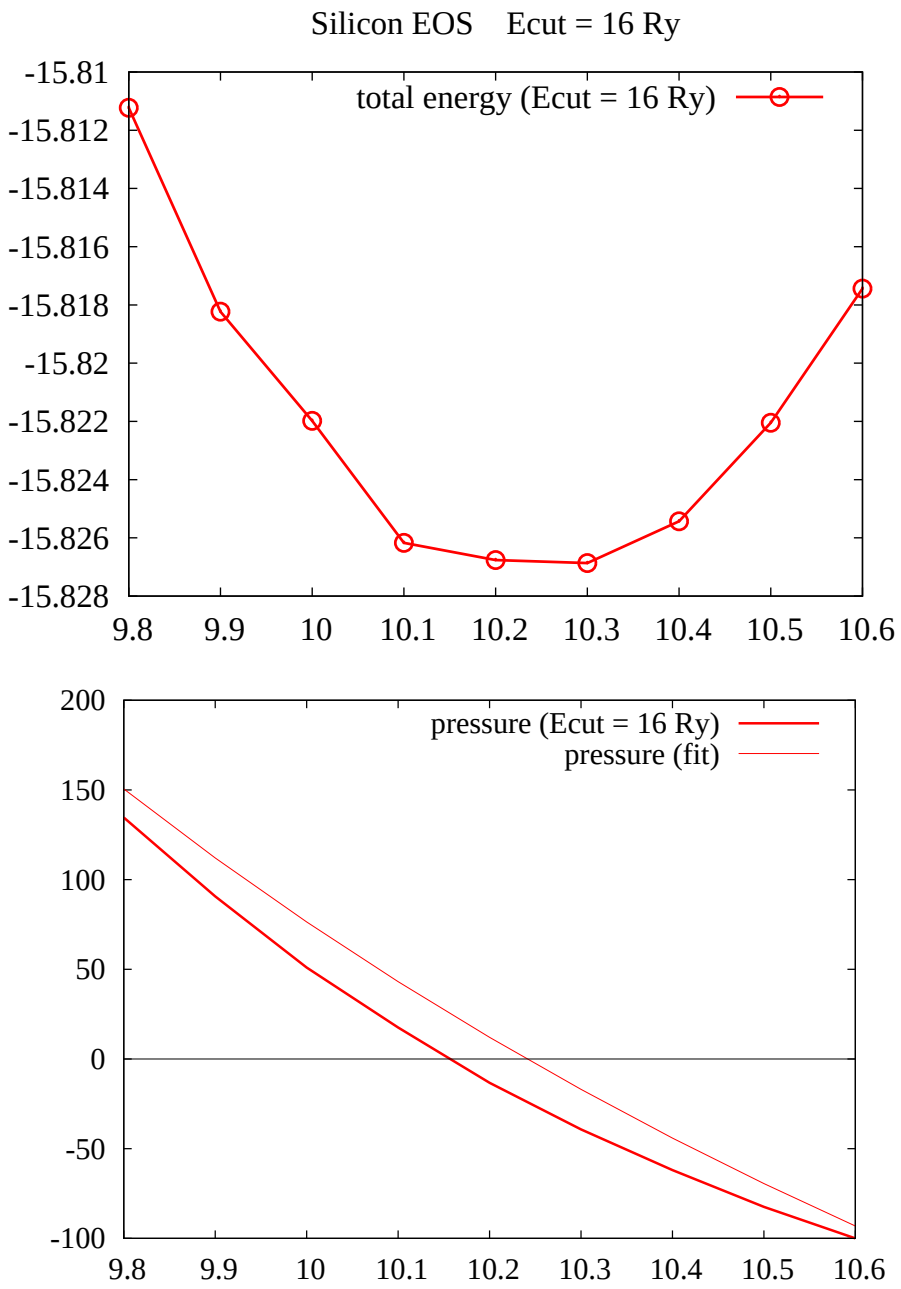
-> NO NEED to know how internal coordinates change

can be computed from the GS wavefuctions assuming homogeneous deformation

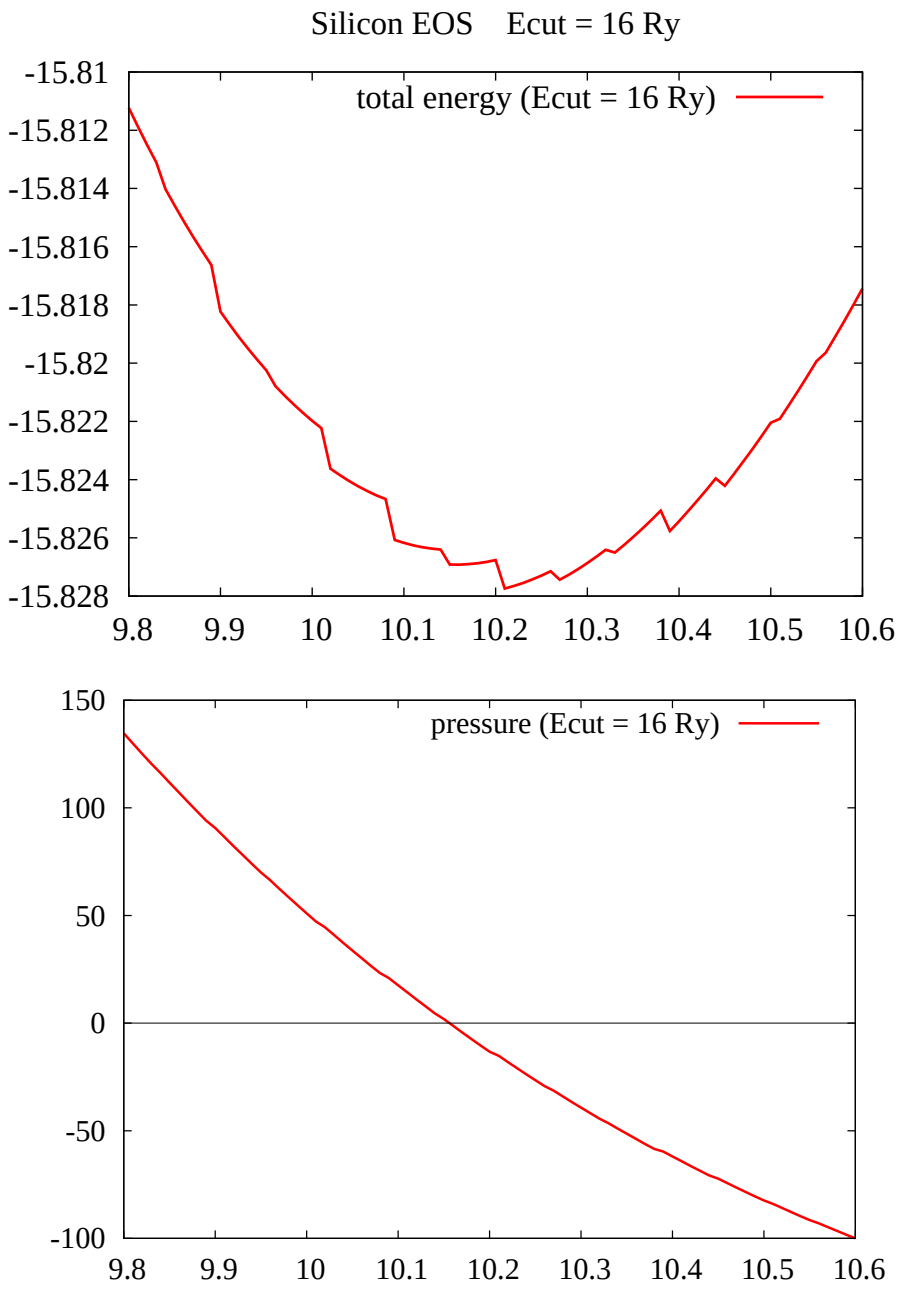
Nielsen and Martin Phys.Rev.Lett. 50, 697 (1983),
Nielsen and Martin Phys.Rev. B 32, 3780 & 3792 (1985).

```
prompt> cat Si.scf.in
 &CONTROL
    prefix='silicon',
    pseudo_dir = '/home/degironc/QE/espresso/pseudo/',
    outdir='/home/degironc/tmp/'
    tstress = .true.
 /
 &SYSTEM
    ibrav= 2, celldm(1)=10.20, nat= 2, ntyp= 1,
    ecutwfc =16,
 /
 &ELECTRONS
    conv_thr =  1.0d-8
 /
ATOMIC_SPECIES
 Si  28.086  Si.pz-vbc.UPF
ATOMIC_POSITIONS
 Si 0.00 0.00 0.00
 Si 0.25 0.25 0.25
K_POINTS
  2
  0.25 0.25 0.25 1.0
  0.25 0.25 0.75 3.0
```

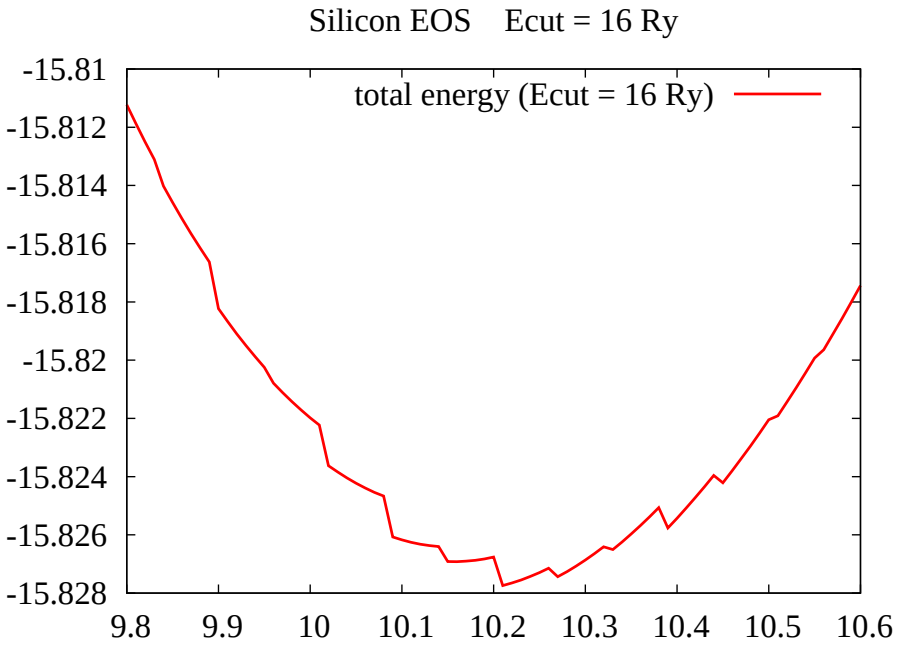
```
prompt> $QE/bin/pw.x < Si.scf.in > Si.scf.out
prompt> less Si.scf.out
... ... ...

!    total energy              =     -15.82676466 Ry
     Harris-Foulkes estimate   =     -15.82676466 Ry
     estimated scf accuracy    <          4.5E-09 Ry

     The total energy is the sum of the following terms:

     one-electron contribution =       4.80030732 Ry
     hartree contribution      =       1.09369711 Ry
     xc contribution           =      -4.82101051 Ry
     ewald contribution        =     -16.89975858 Ry

     convergence has been achieved in   6 iterations

     entering subroutine stress ...

          total   stress  (Ry/bohr**3)                   (kbar)     P=  -13.29
 -0.00009036   0.00000000   0.00000000    -13.29      0.00      0.00
  0.00000000  -0.00009036   0.00000000      0.00    -13.29      0.00
  0.00000000   0.00000000  -0.00009036      0.00      0.00    -13.29
```

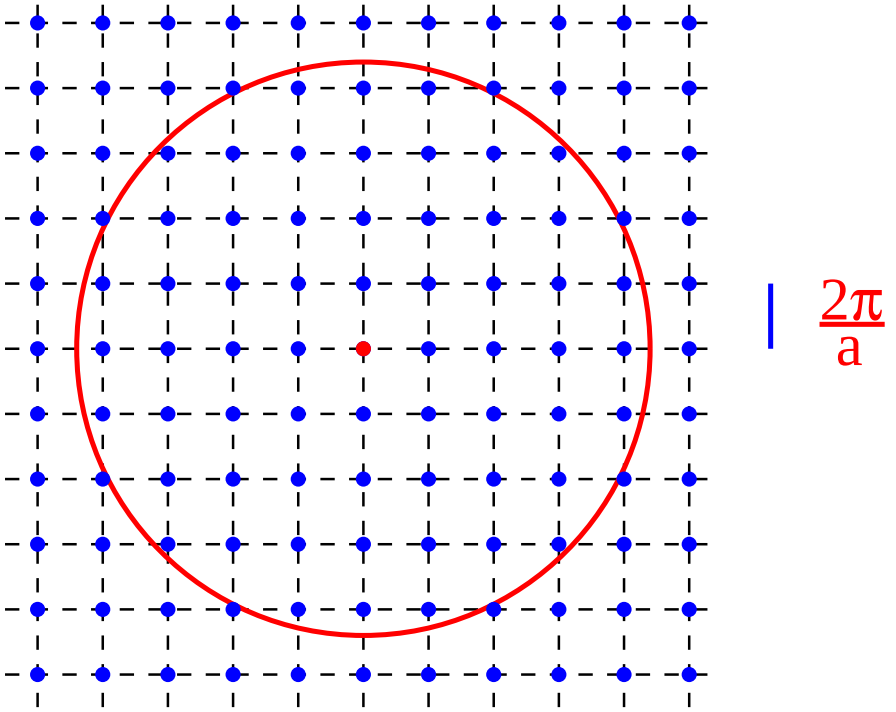


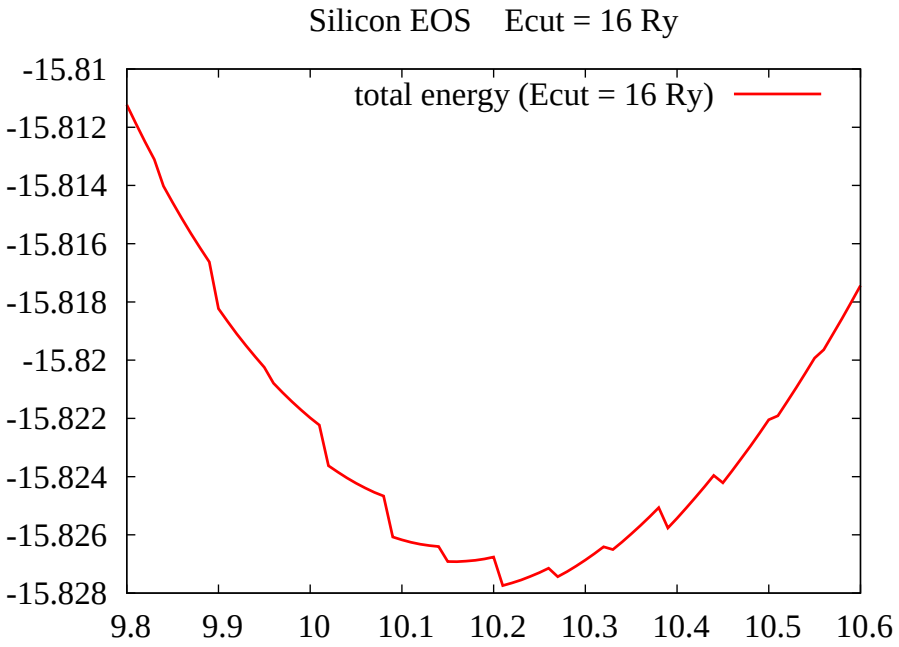
Is there something wrong ?



results for a denser grid


Silicon EOS Ecut = 16 Ry
total energy (Ecut = 16 Ry)
-15.81
-15.812
-15.814
-15.816
-15.818
-15.82
-15.822
-15.824
-15.826
-15.828
9.8
9.9
10
10.1
10.2
10.3
10.4
10.5
10.6


2π
a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-15.81
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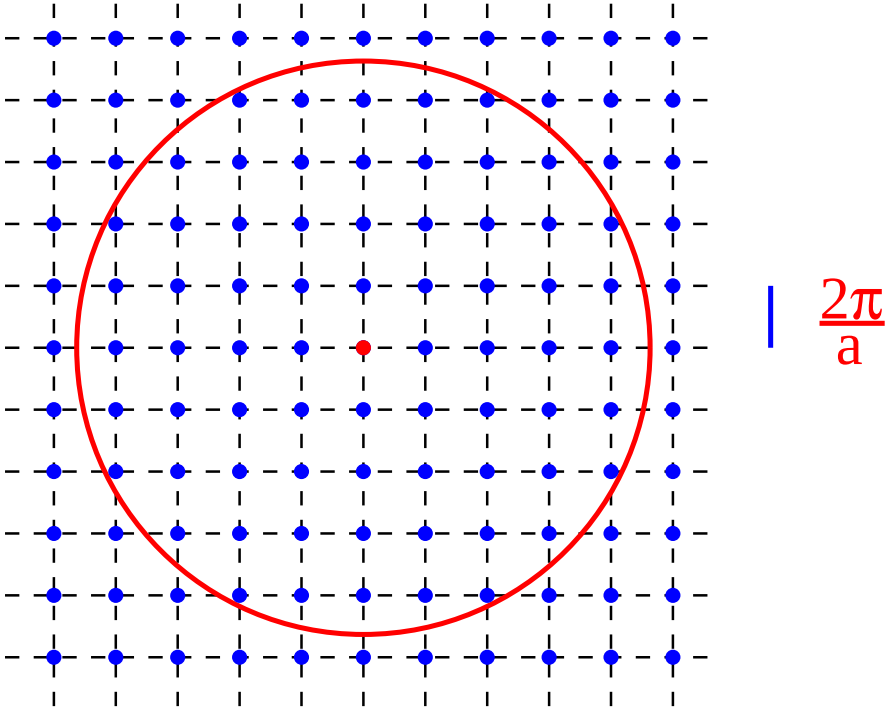
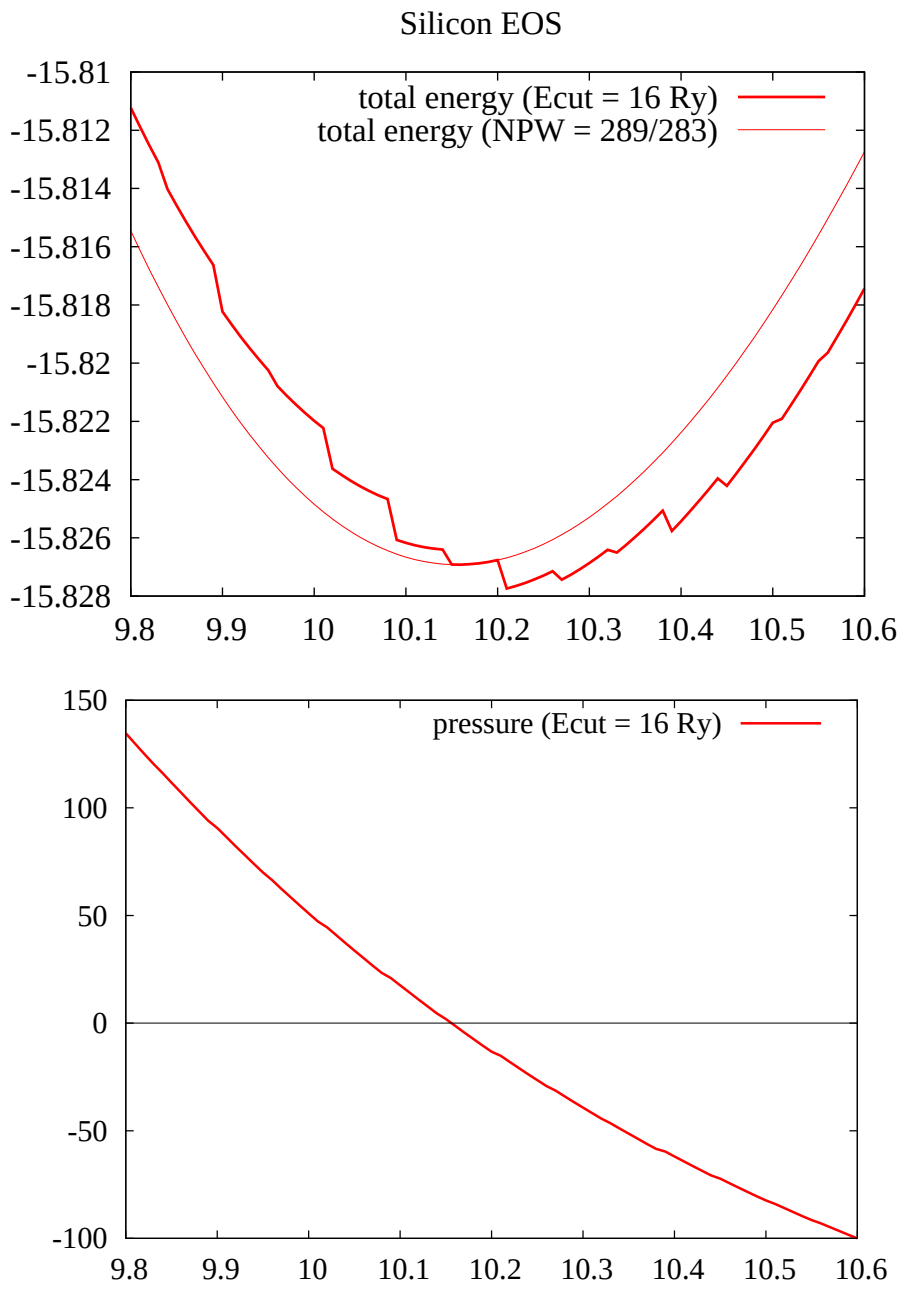
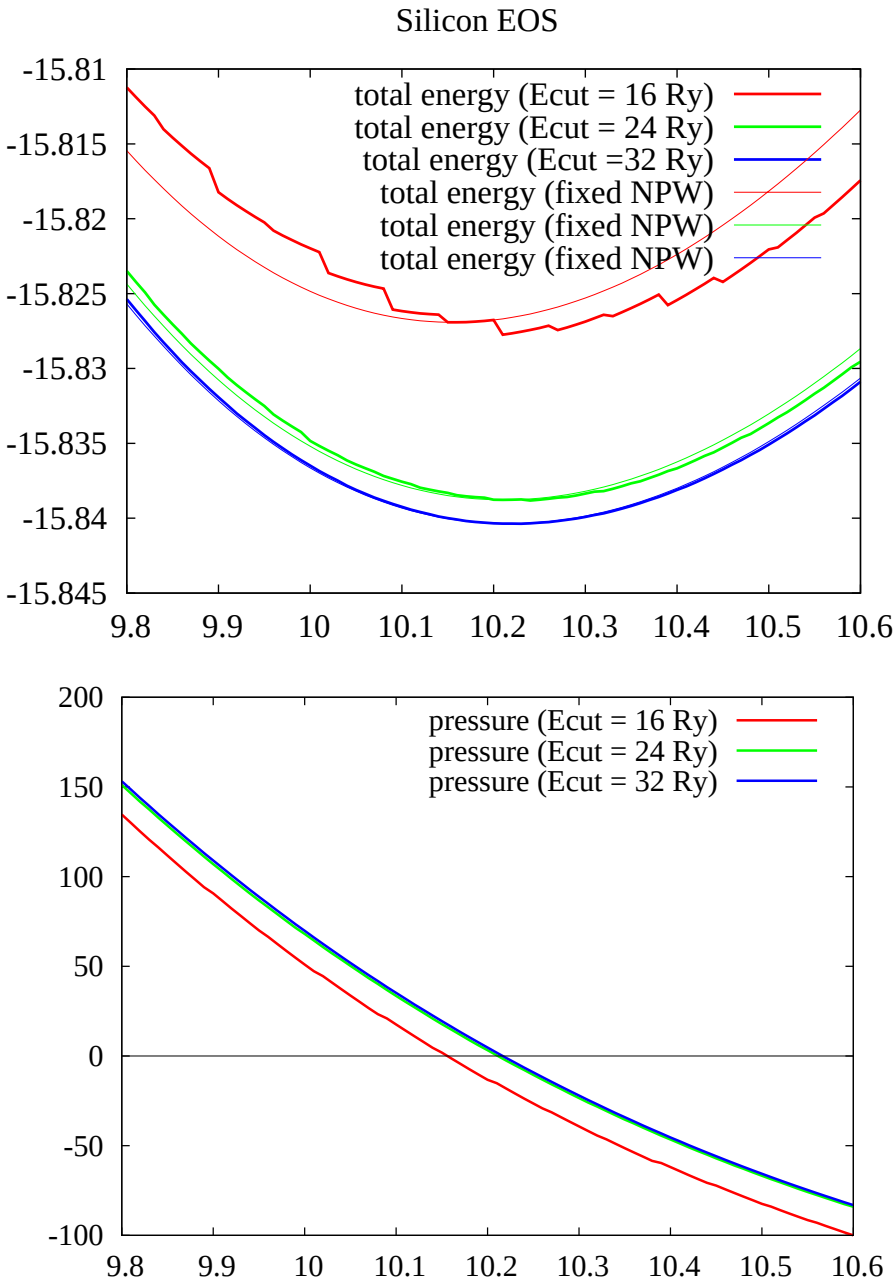
-15.822
-15.824
-15.826
-15.828
9.8
9.9
10
10.1
10.2
10.3
10.4
10.5
10.6


2π
a



fixed Cutoff *vs* fixed Number of Plane waves



fixed Cutoff *vs* fixed Number of Plane waves

Calculations at FIXED CUTOFF need some intepolation in order to extract structural parameters but converge more rapidly to the accurate structural properties than the smoothly varying calculations at FIXED NUMBER OF PW.

Complete convergence is needed for accurate calculation of stress

... or rather ...

so that the calculation of stress (that assumes a fixed number of PW) agrees with the smooth interpolated result obtained using a fixed cutoff

Sudden inclusion of more degrees of freedom is irrelevant only when they do not contribute (they are not used anyway)

Otherwise they modify the energy in a way not accounted in the stress formula.

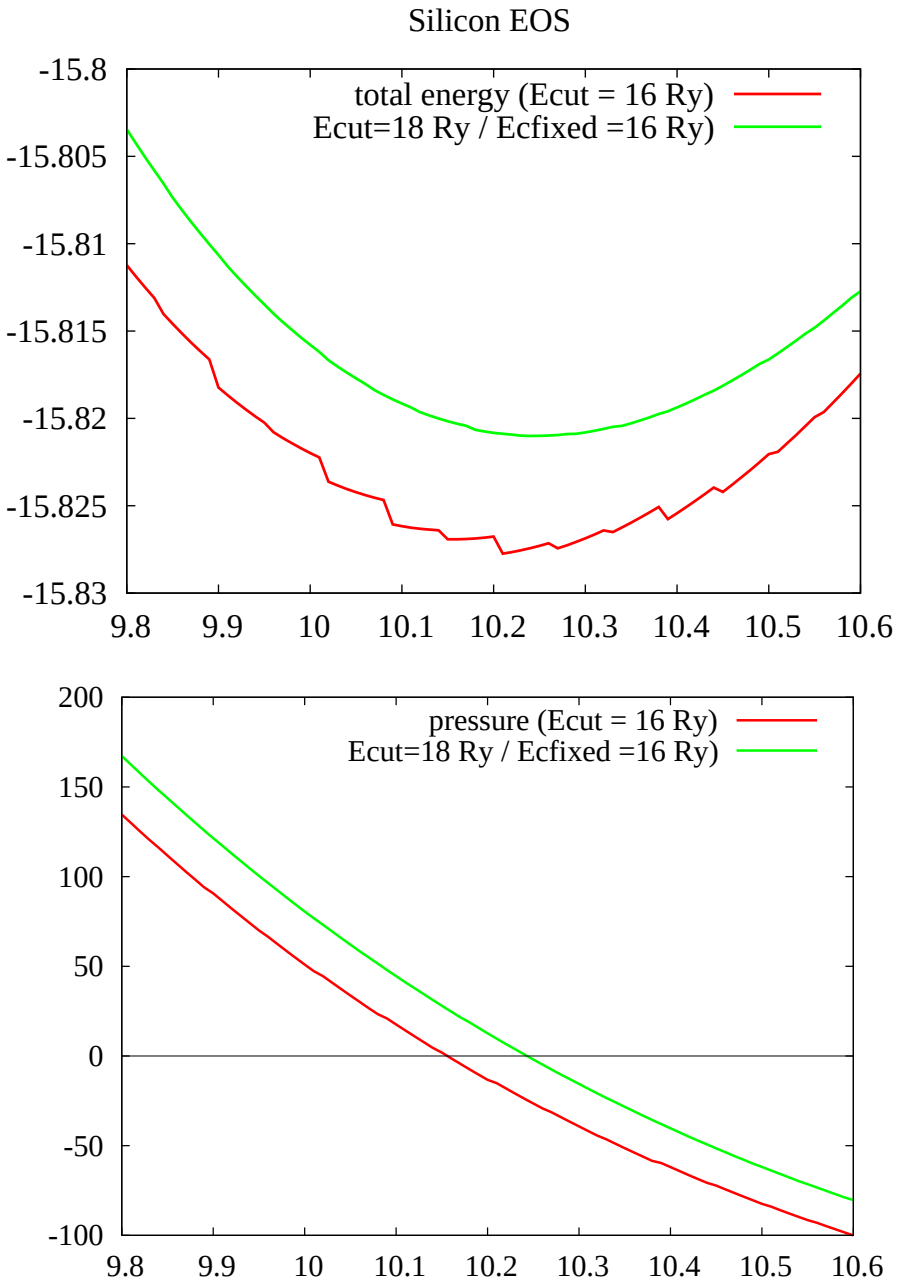
High Fourier components (around ECUT) can be artificially penalized (in a smooth way) in order to speedup convergence

$$T(G) = \frac{\hbar^2}{2m} G^2 + \texttt{QCUTZ} \left[1 + \texttt{erf} \left((\frac{\hbar^2}{2m} G^2 - \texttt{ECFIXED}) / \texttt{Q2SIGMA} \right) \right]$$

The main points are

- the plane waves around and beyond ECUT are penalized so much that they do not matter
- the smooth step function can be differentiated => it gives a well defined contribution to the stress

```
 &control
    prefix='silicon',
    pseudo_dir = '/home/degironc/QE/espresso/pseudo/',
    outdir='/home/degironc/tmp/'
    tstress = .true.
 /
 &system
    ibrav= 2, celldm(1)=10.20, nat= 2, ntyp= 1,
    ecutwfc =18, ecfixed=16.0, qcutz=30.0, q2sigma=2.0
 /
 &electrons
    conv_thr =  1.0d-8
 /
ATOMIC_SPECIES
 Si  28.086  Si.pz-vbc.UPF
ATOMIC_POSITIONS
 Si 0.00 0.00 0.00
 Si 0.25 0.25 0.25
K_POINTS
  2
  0.25 0.25 0.25 1.0
  0.25 0.25 0.75 3.0
```


Silicon EOS
total energy (Ecut = 16 Ry)
Ecut=18 Ry / Ecfixed =16 Ry)
-15.8
-15.805
-15.81
-15.815
-15.82
-15.825
-15.83
9.8
9.9
10
10.1
10.2
10.3
10.4
10.5
10.6
pressure (Ecut = 16 Ry)
Ecut=18 Ry / Ecfixed =16 Ry)
200
150
100
50
0
-50
-100
9.8
9.9
10
10.1
10.2
10.3
10.4
10.5
10.6

At finite pressure P one must optimize/sample the Enthalpy

$$H = E + PV$$

- variable Cell-Shape Relaxation

- variable Cell-Shape Molecular Dynamics

Variable Cell-Shape Relaxation

BFGS relaxation

Crystal configuration is defined by 3*NAT + 9 variables

$$\tau_\alpha^s = \sum_k a_\alpha^k x_k^s$$

x_k^s = 3*NAT internal (crystal) coordinates;

a_α^k = Bravais lattice vectors (9 variables)

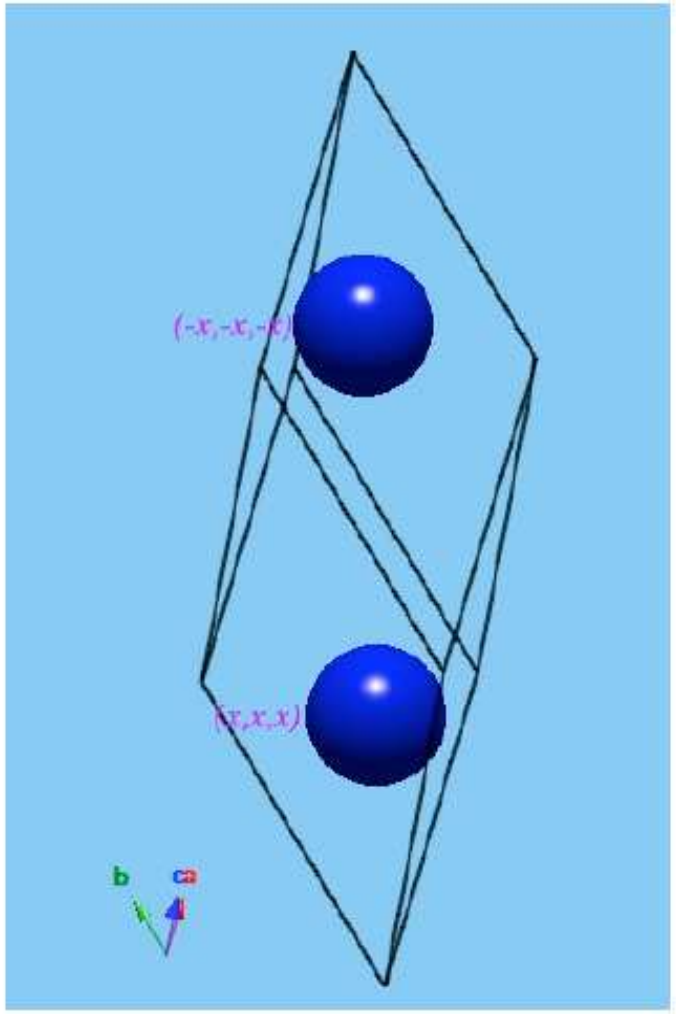
The algorithm can be applied as usual paying attention to use the appropriate generalized forces

$$-\frac{\partial H}{\partial x_k^s} = \sum_\alpha F_\alpha^s a_\alpha^k; \qquad -\frac{\partial H}{\partial a_\alpha^k} = \Omega \sum_k (a^{-1})_k^\beta \left(\sigma_{\beta\alpha} - P\delta_{\beta\alpha}\right)$$

and to start from an inverse Hessian that respects the symmetry of the crystal.

A7 to sc transition in As

- Unit Cell: (*a=b=c*, *cosAB=cosAC=cosBC*)
- Guessing *a*=3.85 Å, *x*=0.275, *cosAB*=0.49517470
- Energy Cut-Off=30 Ry.
- 2 As per unit cell
- 2As at ±(x, x, x,);
- When *x*=0.25, *cosAB*=0.5 => Simple Cubic



```
prompt> cat As0.in
 &CONTROL
   calculation = "vc-relax", outdir = './tmp/', pseudo_dir = './' ,
   etot_conv_thr = 1.0E-4, forc_conv_thr = 1.0D-3, /
 &SYSTEM
   ibrav = 0, A = 3.85, nat= 2, ntyp= 1, nbnd = 9, nelec = 10,
   occupations = 'smearing', smearing = 'mp', degauss = 0.005,
   ecutwfc = 30.0, /
 &ELECTRONS conv_thr = 1.0d-7, /
 &IONS /
 &CELL press = 0.0, /
CELL_PARAMETERS cubic
   0.58012956  0.00000000  0.81452422
  -0.29006459  0.50240689  0.81452422
  -0.29006459 -0.50240689  0.81452422
ATOMIC_SPECIES
As   74.90000  As.pz-bhs.UPF
ATOMIC_POSITIONS crystal
As    0.2750       0.2750        0.2750
As   -0.2750      -0.2750       -0.2750
K_POINTS automatic
  4 4 4   1 1 1
```

```
prompt> $QE/bin/pw.x < As0.in > As0-bfgs.out
... after a while
prompt> grep -e "enthalpy new" -e Final -e "P=" As0-bfgs.out
          total  stress  (Ry/bohr**3)                   (kbar)   P=     3.79
   enthalpy new            =     -25.5030601539 Ry
          total  stress  (Ry/bohr**3)                   (kbar)   P=   -39.98
   enthalpy new            =     -25.4864190212 Ry
          total  stress  (Ry/bohr**3)                   (kbar)   P=   -17.50
   enthalpy new            =     -25.5045246222 Ry
          total  stress  (Ry/bohr**3)                   (kbar)   P=    -5.40
   enthalpy new            =     -25.5050255319 Ry
          total  stress  (Ry/bohr**3)                   (kbar)   P=    -1.35
   enthalpy new            =     -25.5050857421 Ry
          total  stress  (Ry/bohr**3)                   (kbar)   P=     1.29
   enthalpy new            =     -25.5051054846 Ry
          total  stress  (Ry/bohr**3)                   (kbar)   P=     1.16
   enthalpy new            =     -25.5051083940 Ry
          total  stress  (Ry/bohr**3)                   (kbar)   P=     0.80
   enthalpy new            =     -25.5051113263 Ry
          total  stress  (Ry/bohr**3)                   (kbar)   P=     0.41
   Final enthalpy =    -25.5051134588 Ry
```

Variable Cell-Shape MD

Introduce the cell Bravais lattice vectors as auxiliary dynamical variables

extended lagrangian formulation

$$L = T - U, \quad T = K_{internal} + K_{cell}, \quad U = H_{el}$$

$$\frac{d}{dt}\frac{\partial L}{\partial \dot{q}_i} = -\frac{\partial L}{\partial q_i}$$

while the Kinetic Energy associated to the internal degrees of freedom is well defined (at fixed cell geometry) the KE associated to the cell has no physical meaning.
VSCMD does not provide a faithful dynamical picture but can provide accurate thermodynamical averages of NPH ensemble via ergodic theorem + equi-partition principle

Variable Cell-Shape MD

$$L = T - U, \quad T = K_{int} + K_{cell}, \quad U = H_{el} = E + PV$$

Anderson, J.Chem.Phys. 72, 2384 (1980).

$$L = V^{\frac{2}{3}} \sum_i \frac{M_i}{2} \dot{s}_i \dot{s}_i + \frac{W}{2} \dot{V}^2 - (E + PV)$$

Parrinello-Rahman, J.Appl.Phys. 52, 7182 (1981).

$$L = \sum_i \frac{M_i}{2} \dot{s}_i (h^T h) \dot{s}_i + \frac{W}{2} \dot{h}^T \dot{h} - (E + PV)$$

Wentzcovitch, Phys.Rev.B 44, 2358 (1991).

$$L = \sum_i \frac{M_i}{2} \dot{s}_i (h^T h) \dot{s}_i + \frac{W}{2} V^2 \dot{h}^T (h^T h)^{-1} \dot{h} - (E + PV)$$

Damped Variable Cell-Shape MD

VCSMD can also be used as a structural optimization tool by introducing a damping mechanism that drains kinetic energy out of the system.

quickmin: kill any generalized velocity component whose direction is opposite to the corresponding generalized force component.

pros: easy to implement if you have an MD code;
rather robust, does not assume to be close to the min

cons: you need to specify a time step (dt) and a cell mass (wmass) values which requires some experience;
it's not superlinear close to convergence as BFGS is.

```
prompt> cat As40.in
 &CONTROL
   calculation = "vc-relax", outdir = './tmp/', pseudo_dir = './' ,
   etot_conv_thr = 1.0E-4, forc_conv_thr = 1.0D-3, dt = 70 /
 &SYSTEM
   ibrav = 0, A = 3.85, nat= 2, ntyp= 1, nbnd = 9, nelec = 10,
   occupations = 'smearing', smearing = 'mp', degauss = 0.005,
   ecutwfc = 30.0, /
 &ELECTRONS conv_thr = 1.0d-7, /
 &IONS /
 &CELL press = 400.0, cell_dynamics = 'damp-w', wmass = 0.0015,/
CELL_PARAMETERS cubic
   0.58012956  0.00000000  0.81452422
  -0.29006459  0.50240689  0.81452422
  -0.29006459 -0.50240689  0.81452422
ATOMIC_SPECIES
As   74.90000  As.pz-bhs.UPF
ATOMIC_POSITIONS crystal
As    0.2750       0.2750        0.2750
As   -0.2750      -0.2750       -0.2750
K_POINTS automatic
  4 4 4   1 1 1
```

```
prompt> $QE/bin/pw.x < As40.in > As40-dampW.out
... after a while
prompt> grep -e "Etot" -e "P=" As0-dampW.out | tail -18
   Ekin =    0.00088648 Ry    T =  647.9 K  Etot =   -24.89023062
        total  stress  (Ry/bohr**3)                  (kbar)     P=  398.53
   Ekin =    0.00095682 Ry    T =  621.2 K  Etot =   -24.89024525
        total  stress  (Ry/bohr**3)                  (kbar)     P=  401.23
   Ekin =    0.00101302 Ry    T =  596.8 K  Etot =   -24.89024441
        total  stress  (Ry/bohr**3)                  (kbar)     P=  398.88
   Ekin =    0.00103502 Ry    T =  574.3 K  Etot =   -24.89024804
        total  stress  (Ry/bohr**3)                  (kbar)     P=  398.38
   Ekin =    0.00009930 Ry    T =  552.4 K  Etot =   -24.89118875
        total  stress  (Ry/bohr**3)                  (kbar)     P=  399.11
   Ekin =    0.00010526 Ry    T =  532.1 K  Etot =   -24.89118816
        total  stress  (Ry/bohr**3)                  (kbar)     P=  402.51
   Ekin =    0.00010196 Ry    T =  513.2 K  Etot =   -24.89119211
        total  stress  (Ry/bohr**3)                  (kbar)     P=  399.99
   Ekin =    0.00010141 Ry    T =  495.6 K  Etot =   -24.89119469
        total  stress  (Ry/bohr**3)                  (kbar)     P=  398.81
   Ekin =    0.00009946 Ry    T =  479.2 K  Etot =   -24.89119474
        total  stress  (Ry/bohr**3)                  (kbar)     P=  400.31
```

THE END