Forces, Stress

and

structural optimization

- Forces

* finite step methods

- Steepest Descent
- Damped Dynamics (friction,quickmin)

* Line Minimization methods:

- Conjugate Gradients
- Quasi Newton methods BFGS

* Stress, VCS relaxation and MD

Hellmann-Feynman forces

In the Born-Oppenheimer approximation the total energy $E[R_I^{3N},\rho(R_I^{3N})]$ is a function of ionic coordinates R_I^{3N} and defines a 3N-dimensional hyper-surface, called Potential Energy Surface (PES).

The forces acting on the ions are given by (minus) the gradient of the total energy. Using Hellmann-Feynman theorem:

$$\mathbf{F}_I = -\frac{\partial E(\mathbf{R})}{\partial \mathbf{R}_I} = -\left\langle \Psi(\mathbf{R}) \left| \frac{\partial H_{BO}(\mathbf{R})}{\partial \mathbf{R}_I} \right| \Psi(\mathbf{R}) \right\rangle$$

$$\mathbf{F}_I = -\int n_{\mathbf{R}}(\mathbf{r}) \frac{\partial V_{\mathbf{R}}(\mathbf{r})}{\partial \mathbf{R}_I} d\mathbf{r} - \frac{\partial E_N(\mathbf{R})}{\partial \mathbf{R}_I}$$

where the electron-nucleus interaction and the electrostatic ion-ion interaction,

$$V_{\mathbf{R}}(\mathbf{r}) = -\sum_I \frac{Z_I e^2}{|\mathbf{r} - \mathbf{R}_I|} \qquad E_N(\mathbf{R}) = \frac{e^2}{2} \sum_{I \neq J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}$$

depend only on the ionic positions

Hellmann-Feynman forces

When using plane waves no corrections are needed to the previous formula:

$$\mathbf{F}_I = -\int n_{\mathbf{R}}(\mathbf{r}) \frac{\partial V_{\mathbf{R}}(\mathbf{r})}{\partial \mathbf{R}_I} d\mathbf{r} - \frac{\partial E_N(\mathbf{R})}{\partial \mathbf{R}_I}$$

The evaluation of forces is then a cheap byproduct of the electronic structure calculation.

The quality of forces depends on the quality of the electronic structure calculation!

From the forces:

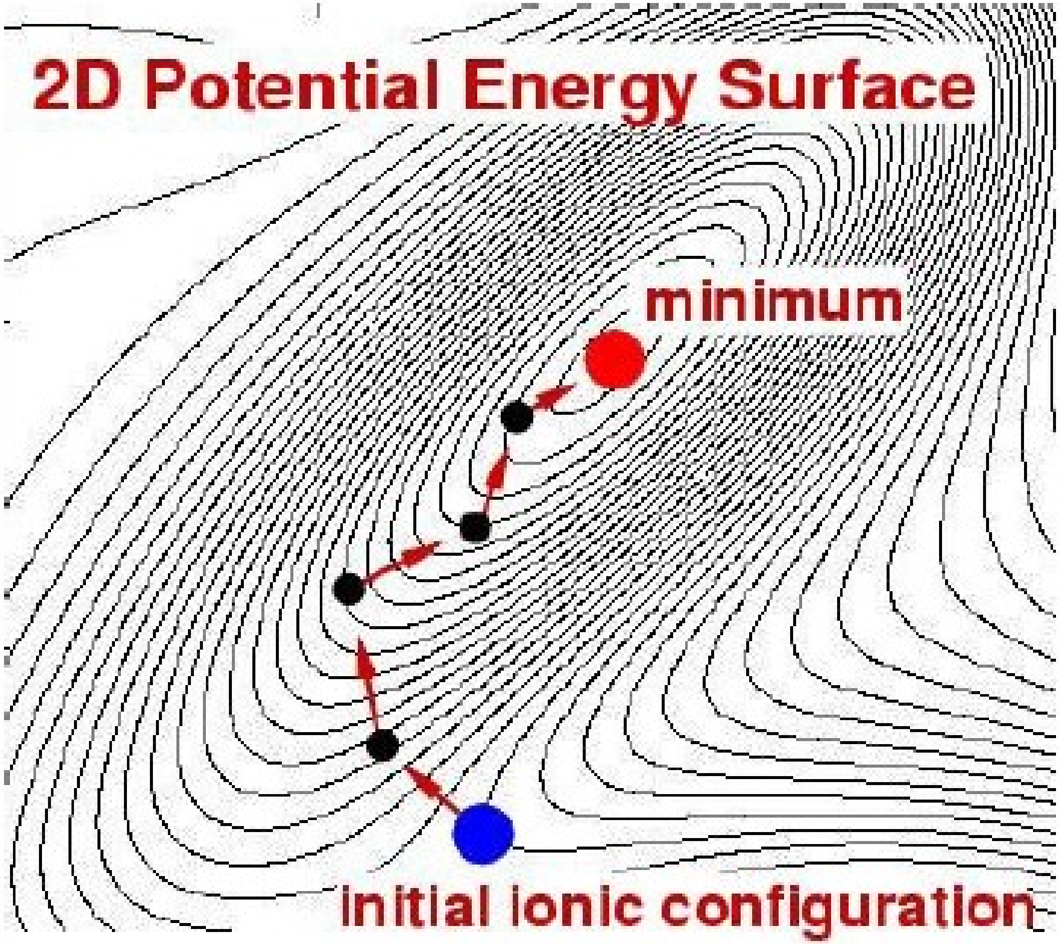
- structural optimization. Equilibrium condition given by

$$\mathbf{F}_I \equiv -\frac{\partial E(\mathbf{R})}{\partial \mathbf{R}_I} = 0$$

- molecular dynamics
- higher-order derivatives (phonons, ...)

Structural optimizations

Several algorithms for searching an equilibrium configuration, close to the initial ionic configuration (a <u>local</u> minimum of the PES). For example:



<u>S</u>teepest <u>D</u>escent optimisation

$$\dot{X}_I^{3N} \qquad F(X_I^{3N})$$

discretisation

$$X_{k+1} \qquad X_k \qquad \lambda \frac{g_k}{g_k|}$$

gradient unitary vector

VERLET DYNAMICS

$R_{new} = 2\,R - R_{old} + dt{*}dt{*}F/M$

$V = (R_{new} – R_{old}) / 2\,dt$

VELOCITY VERLET DYNAMICS

$V = V_{aux} + dt/2 * F / M$ vel @ time t

$V_{aux} = V + dt/2 * F / M$ aux vel @ time t+dt/2

$R_{new} = R + V_{aux}\,dt$ pos @ time t+dt

DAMPED VERLET DYNAMICS

As above but stop the particle whenever $<F|V> \;<\; 0$

Or rather project the velocity in the direction of the force

$$V\_new = F\ \max(0,<F|V>) / <F|F>$$

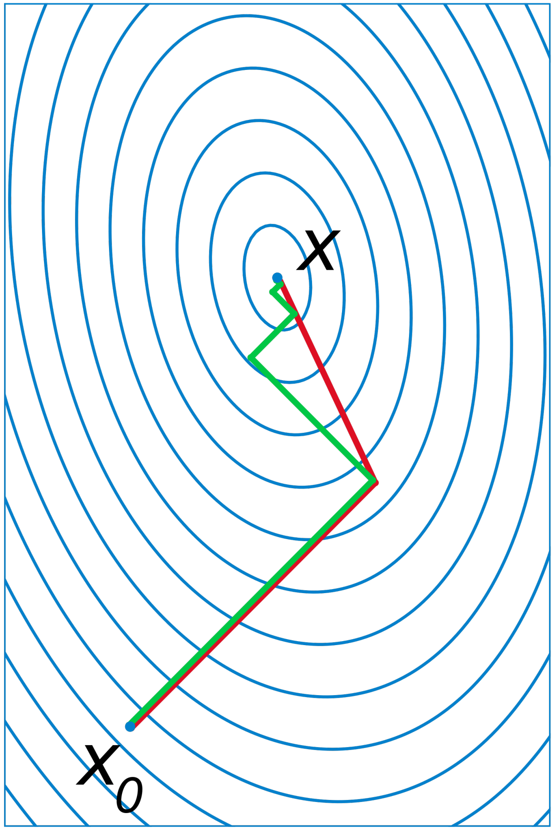
Conjugate Gradients

$E = \frac{1}{2} x A x - b x + c$

$F = -dE/dx = b - Ax = g(x)$

$X_n = X_{n-1} + \lambda h_n$

$h_i * A * h_j = 0, \quad h_i * g_j = 0 \quad \text{for } i \neq j$



small memory needs, good for quadratic functions, may need preconditioning

Quasi-Newton ionic relaxation

the Broyden Fletcher Goldfarb Shanno algorithm

Taylor expansion of the energy around a stationary point (X_{k+1}):

$s_k = X_{k+1} - X_k$

Hessian matrix

$$E(X_{k+1}) - E(X_k) = g(X_k) \cdot s_k + \frac{1}{2} s_k^T H_k s_k$$

gradient vector

Quasi-Newton ionic relaxation

the Broyden Fletcher Goldfarb Shanno algorithm

Equivalently, for the gradient vector we have:

$$g(X_{k+1}) - g(X_k) = H_k s_k$$

Stationary condition:

$$\|g(X_{k+1})\|_\infty = 0 \quad \Longrightarrow \quad s_k^{NR} = -H_k^{-1} g_k$$

Newton-Raphson step:

Quasi-Newton ionic relaxation

the Broyden Fletcher Goldfarb Shanno algorithm

trust radius

$$s_k^{NR} = -H_k^{-1} g_k$$

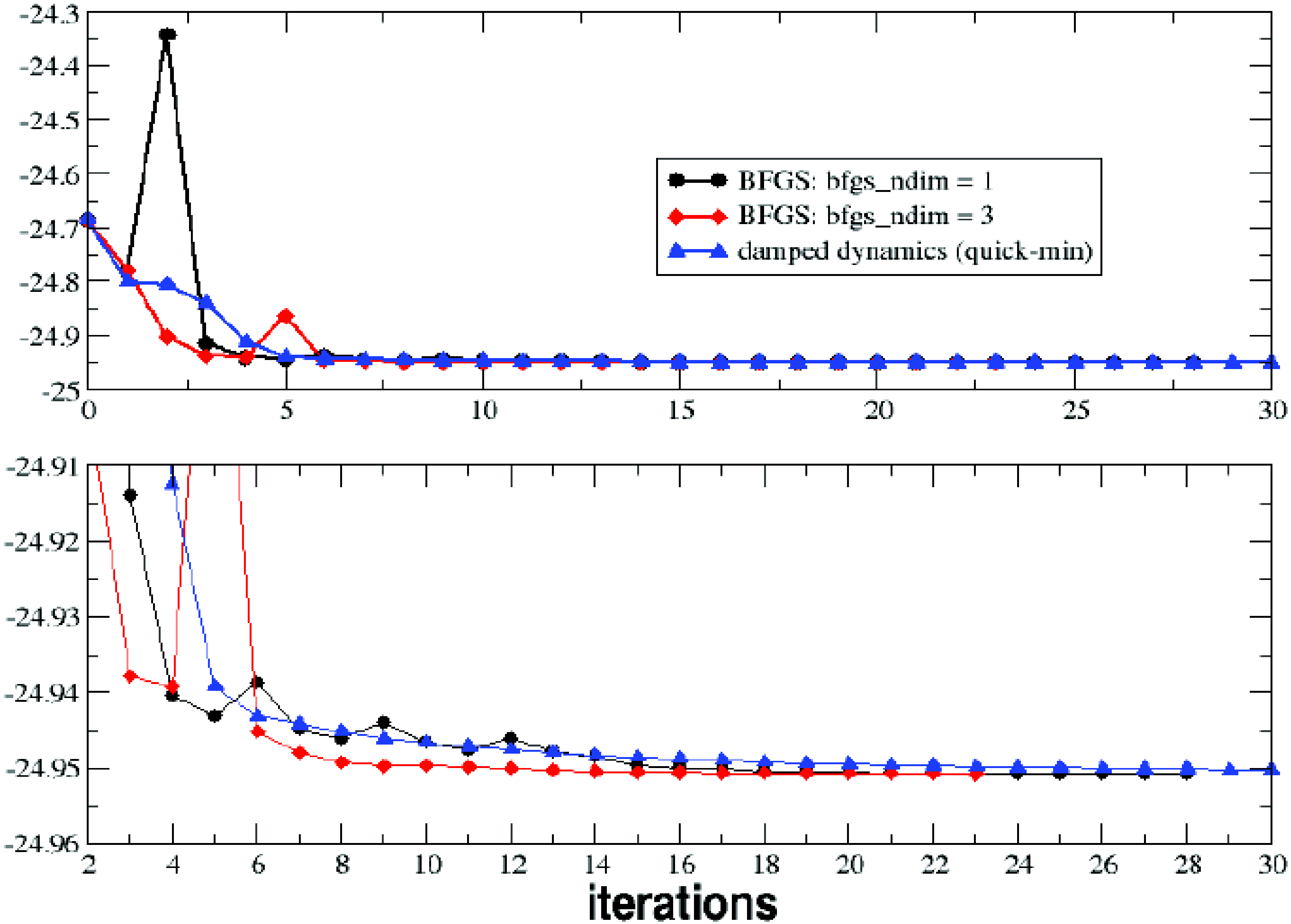
$$X_{k+1} = X_k + T_k^L \frac{s_k^{NR}}{|s_k^{NR}|}$$

The inverse Hessian matrix is updated using the BFGS scheme:

$$H_{k+1}^{-1} = H_k^{-1} + \left(1 + \frac{\gamma_k^T H_k^{-1} \gamma_k}{s_k^T \gamma_k}\right) \frac{s_k s_k^T}{s_k^T \gamma_k} - \left(\frac{s_k \gamma_k^T H_k^{-1} + H_k^{-1} \gamma_k s_k^T}{s_k^T \gamma_k}\right)$$

$$\gamma_k = g_{k+1} - g_k$$

Structural Optimization : Convergence



Stress, Enthalpy and Variable Cell Shape Optimization

A solid is just a very big molecule

equilibrium $\Longrightarrow$ 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

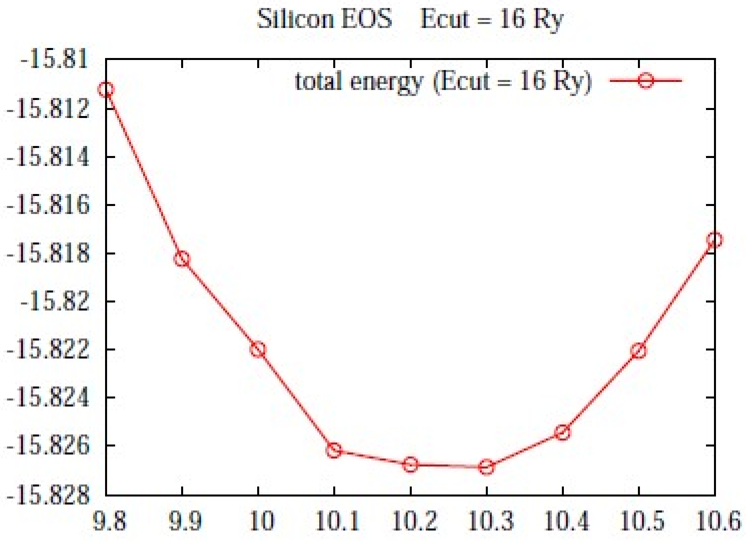
-> NO NEED to know how internal coordinates change

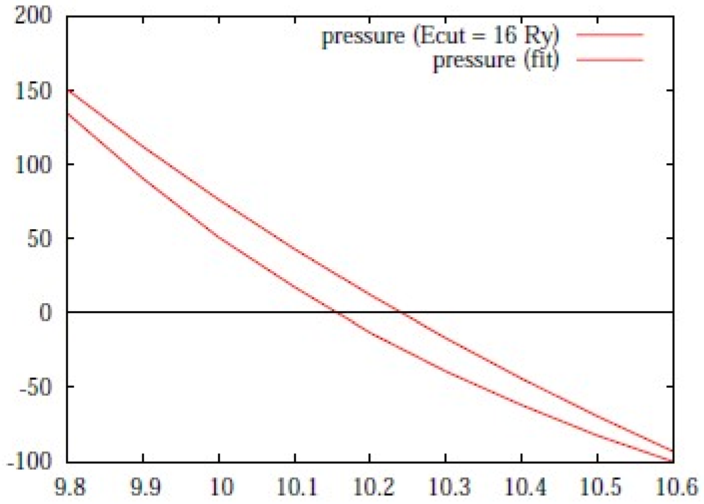
can be computed from the GS wavefuctions assuming homogeneous deformation

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

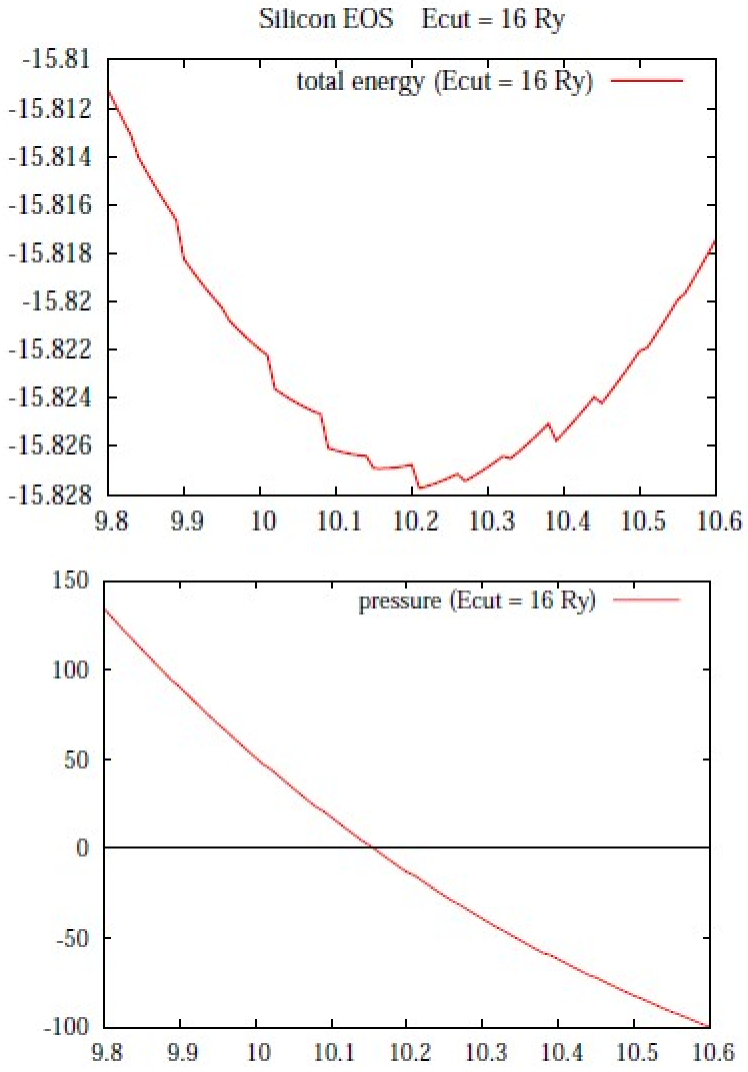
```
prompt> cat Si.scf.in
 &CONTROL
    prefix=’silicon’,
    pseudo_dir = ’/home/degironc/QE/espresso/pseudo/’,
    outdir=’/home/degironc/tmp/’
    tstress = .true.
 /
 &SYSTEM
    ibrav= 2, celldm(1)=10.20, nat= 2, ntyp= 1,
    ecutwfc =16,
 /
 &ELECTRONS
    conv_thr =  1.0d-8
 /
ATOMIC_SPECIES
 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
```

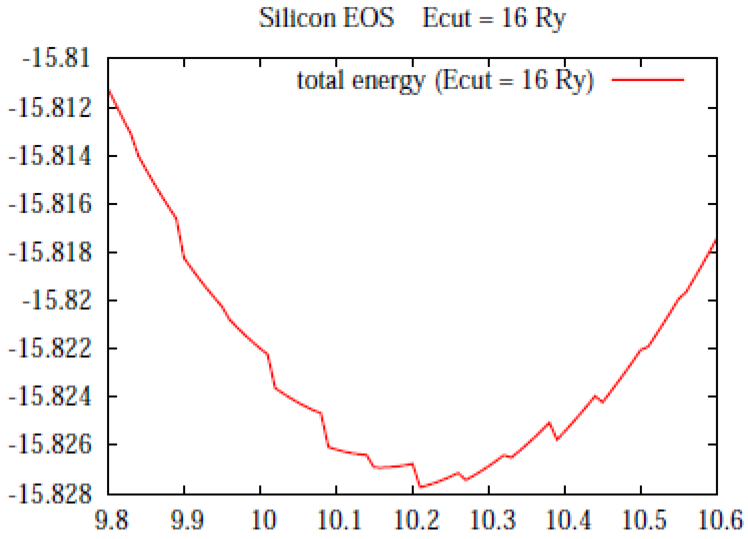


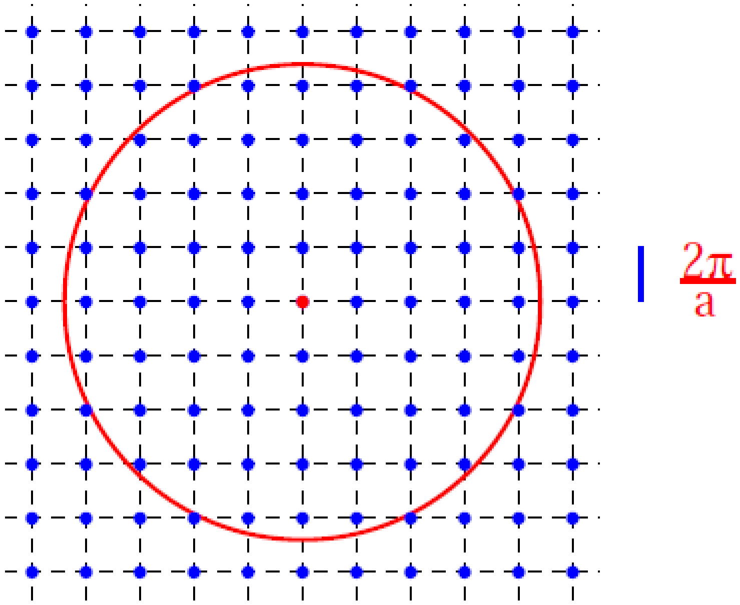


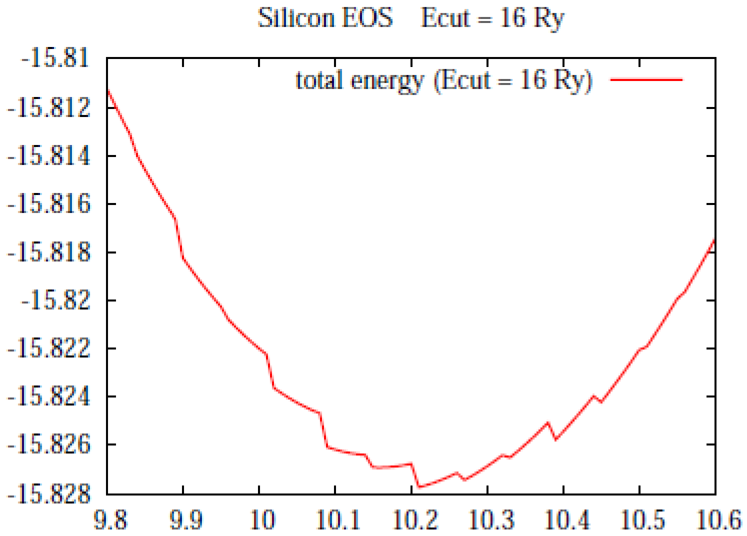
Is there something wrong ?

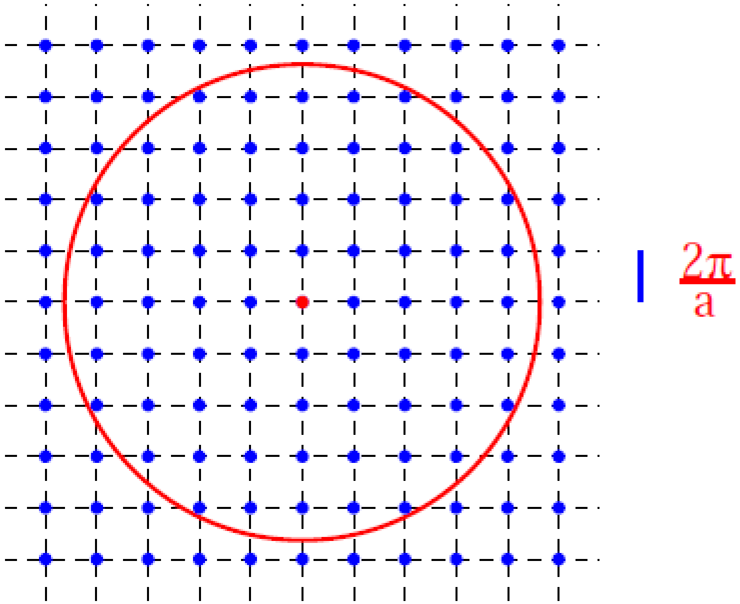


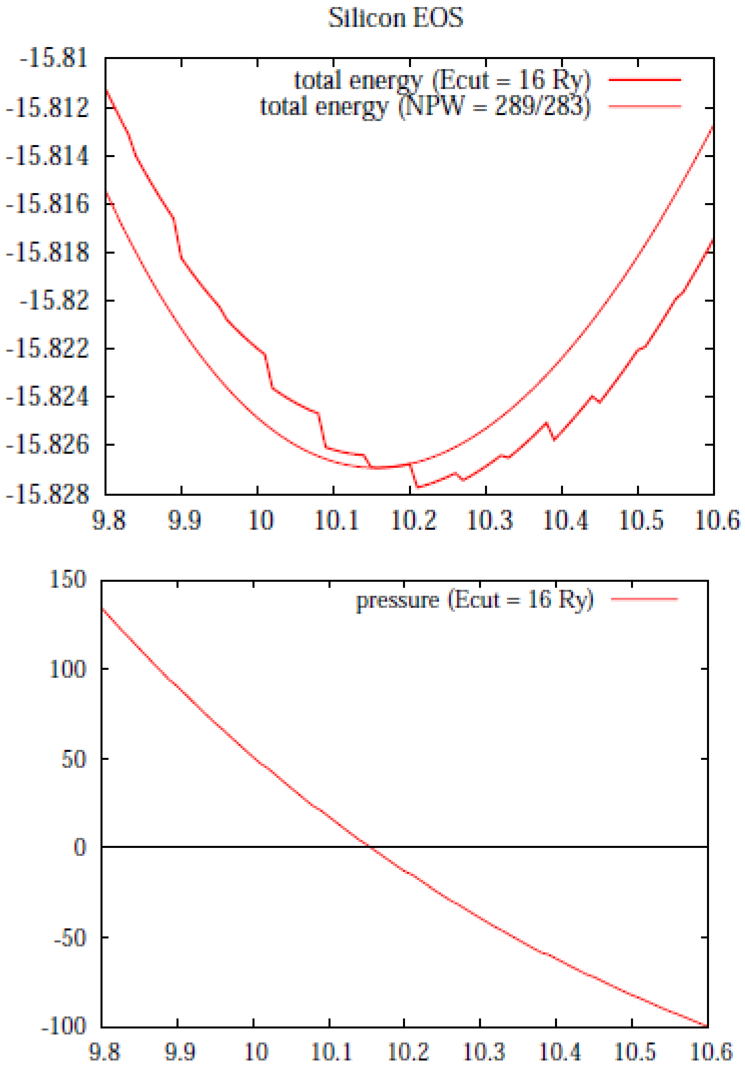
results for a denser grid


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

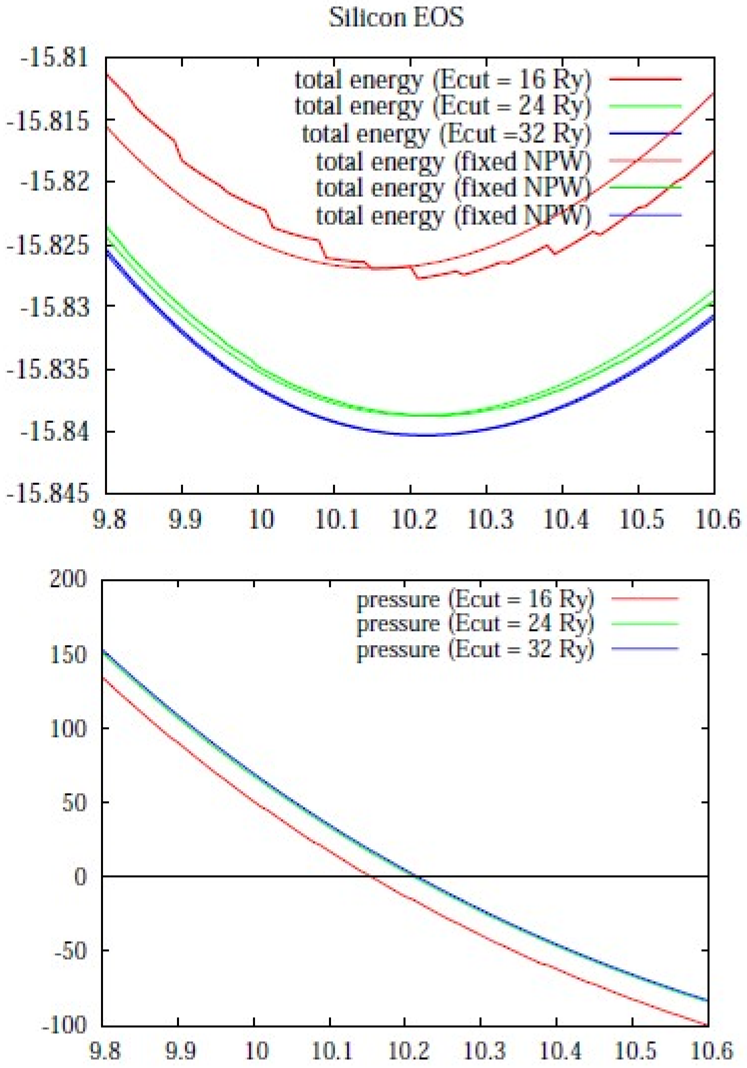

2π/a


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


$\frac{2\pi}{a}$



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.

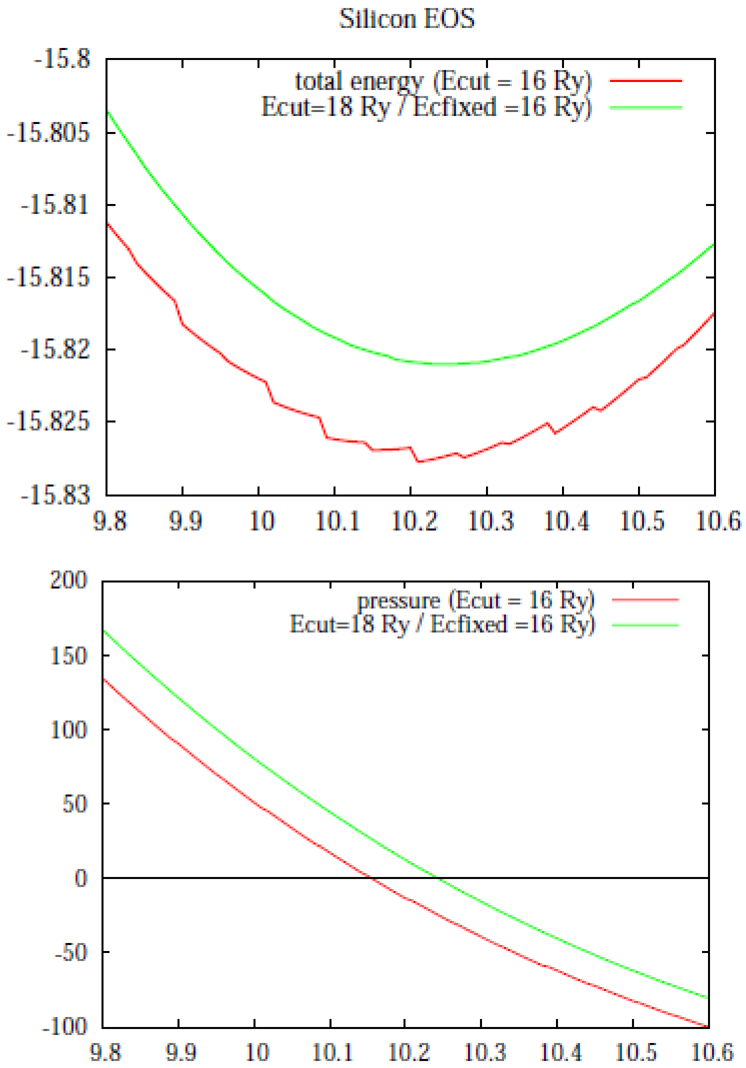
High Fourier components (around ECUT) can be artificially penalized (in a smooth way) in order to speedup convergence

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

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)

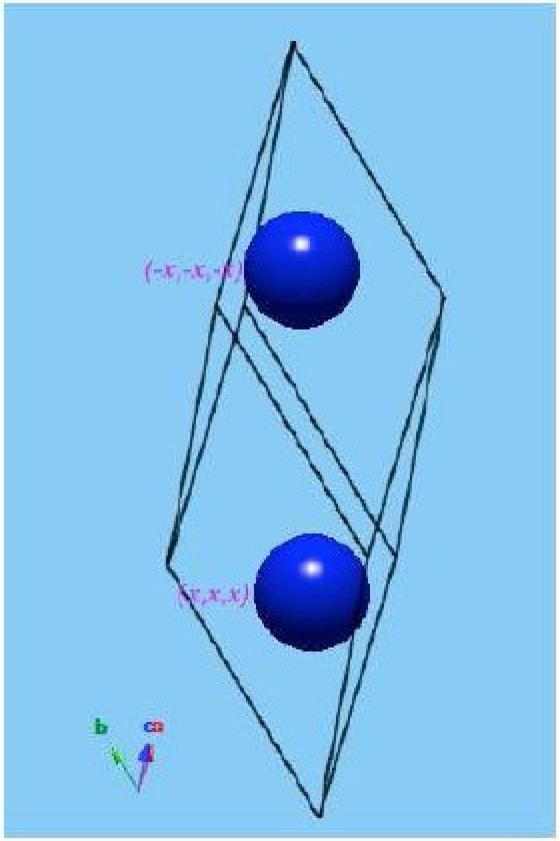
The algorithm can be applied as usual paying attention to use the appropriate generalized forces

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

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