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:

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

$$F_I = -\int n_{R}(r) \frac{\partial V_{R}(r)}{\partial R_I} dr - \frac{\partial E_{N}(R)}{\partial R_I}$$

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

$$V_{R}(r) = - \sum_{I} \frac{Z_{I}e^{2}}{|r - R_I|} \quad E_{N}(R) = \frac{e^{2}}{2} \sum_{I \neq J} \frac{Z_{I}Z_{J}}{|R_I - R_J|}$$

depend only on the ionic positions.
Hellmann-Feynman forces

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

\[ F_I = - \int n_R(r) \frac{\partial V_R(r)}{\partial R_I} \, dr - \frac{\partial E_N(R)}{\partial R_I} \]

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
  \[ F_I = - \frac{\partial E(R)}{\partial R_I} = 0 \]

- molecular dynamics

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

Structural optimizations

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

2D Potential Energy Surface

Steepest Descent optimisation

\[
\dot{X}_i^{3N} = F(X_i^{3N})
\]

discretisation

\[
X_{k+1} = X_k + \lambda \frac{g_k}{\|g_k\|}
\]

gradient unitary vector
VERLET DYNAMICS
\[ R_{\text{new}} = 2 R - R_{\text{old}} + dt \cdot dt \cdot F / M \]
\[ V = (R_{\text{new}} - R_{\text{old}}) / 2 \cdot dt \]

VELOCITY VERLET DYNAMICS
\[ V = V_{\text{aux}} + \frac{dt}{2} \cdot F / M \]
\[ V_{\text{aux}} = V + \frac{dt}{2} \cdot F / M \]
\[ R_{\text{new}} = R + V_{\text{aux}} \cdot dt \]

DAMPED VERLET DYNAMICS
As above but stop the particle whenever \[ <F|V> < 0 \]
Or rather project the velocity in the direction of the force
\[ V_{\text{new}} = F \cdot \max (0, <F|V>) / <F|F> \]
Conjugate Gradients

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

\[ F = -\frac{dE}{dx} = b - Ax = g(x) \]

\[ x_n = x_{n-1} + \lambda h_n \]

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

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 $(X_{k+1})$:

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

- $s_k = X_{k+1} - X_k$
- Hessian matrix
- 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:

\[ \| g(X_{k+1}) \|_\infty = 0 \]

Newton-Raphson step:

\[ s_k^{NR} = -H_k^{-1} g_k \]
Quasi-Newton ionic relaxation
the Broyden Fletcher Goldfarb Shanno algorithm

\[ X_{k+1} = X_k + T_k^L \frac{S_k^{NR}}{|S_k^{NR}|} \]

\[ S_k^{NR} = -H_k^{-1} g_k \]

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

\[ \text{equilibrium} \implies \text{vanishing forces} \]

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 crystal is defined by the collection of the atomic coordinates inside the unit cell (Cartesian or internal) and by the size and shape of the unit cell.

\[ \tau^s_\alpha = \sum_k a^k_\alpha x^s_k \]

where

- \( \tau^s_\alpha \) = Cartesian coordinates;
- \( x^s_k \) = internal (crystal) coordinates;
- \( a^k_\alpha \) = fundamental Bravais lattice vectors, cell shape parameters

The (static) equilibrium geometry is obtained for
- vanishing forces
- vanishing stress
homogeneous deformation

\[ r \rightarrow r' = (1 + \epsilon)r \]

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

prompt> cat Si.scf.in

&CONTROL
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    pseudo_dir = '/home/degironc/QE/espresso/pseudo/',
    outdir='/home/degironc/tmp/',
    tstress = .true.
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&SYSTEM
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    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
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 ...

<table>
<thead>
<tr>
<th>total stress (Ry/bohr**3)</th>
<th>(kbar)</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.00009036 0.00000000 0.00000000</td>
<td>-13.29 0.00 0.00</td>
<td></td>
</tr>
<tr>
<td>0.00000000 -0.00009036 0.00000000</td>
<td>0.00 -13.29 0.00</td>
<td></td>
</tr>
<tr>
<td>0.00000000 0.00000000 -0.00009036</td>
<td>0.00 0.00 -13.29</td>
<td></td>
</tr>
</tbody>
</table>
Is there something wrong?
results for a denser grid
fixed Cutoff vs fixed Number of Plane waves
fixed Cutoff vs fixed Number of Plane waves
Calculations at FIXED CUTOFF need some interpolation 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

\[ T(G') = \frac{\hbar^2}{2m} G^2 + QCUTZ \left[ 1 + \text{erf} \left( \frac{\hbar^2}{2m} \frac{G^2 - ECFIXED}{Q2SIGMA} \right) \right] \]

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
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    pseudo_dir = '/home/degironc/QE/espresso/pseudo/',
    outdir='/home/degironc/tmp/'
    tstress = .true.
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&system
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    ecutwfc =18, ecfixed=16.0, qcutz=30.0, q2sigma=2.0
/
&electrons
    conv_thr = 1.0d-8
/

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    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
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 $3\times\text{NAT} + 9$ variables

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

$x_k^s = 3\times\text{NAT}$ internal (crystal) coordinates;

$a_{\alpha}^k = \text{Bravais lattice vectors (9 variables)}$

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

$$-\frac{\partial H}{\partial x_k^s} = \sum_{\alpha} F_{\alpha}^s a_{\alpha}^k, \quad -\frac{\partial H}{\partial a_{\alpha}^k} = \Omega \sum_k (a^{-1})_{k}^\beta (\sigma_{\beta\alpha} - P\delta_{\beta\alpha})$$

and to start from an inverse Hessian that respects the symmetry of the crystal.
A7 to sc transition in As

- Unit Cell: ($a=b=c, \cos AB=\cos AC=\cos BC$)
- Guessing $a=3.85$ Å, $x=0.275$, $\cos AB=0.49517470$
- Energy Cut-Off=30 Ry.
- 2 As per unit cell
- 2As at $\pm(x, x, x)$;
- When $x=0.25$, $\cos AB=0.5$ => Simple Cubic
prompt> cat As0.in

&CONTROL
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&SYSTEM
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    occupations = 'smearing', smearing = 'mp', degauss = 0.005,
    ecutwfc = 30.0,

&ELECTRONS conv_thr = 1.0d-7,

&IONS /

&CELL press = 0.0,

CELL_PARAMETERS cubic
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    -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

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<th>stress</th>
<th>(Ry/bohr**3)</th>
<th>(kbar)</th>
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<tr>
<td>enthalpy new</td>
<td>25.5051113263 Ry</td>
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<td></td>
<td></td>
</tr>
</tbody>
</table>

Final enthalpy = -25.5051134588 Ry
Variable Cell-Shape MD

Introduce the cell Bravais lattice vectors as auxiliary dynamical variables

extended lagrangian formulation

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

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

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

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


\[ L = V^2 \sum_i \frac{M_i}{2} \dot{s}_i \ddot{s}_i + \frac{W}{2} \dddot{V}^2 - (E + PV) \]


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


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

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&ELECTRONS conv_thr = 1.0d-7, /

&IONS /

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  -0.29006459  0.50240689  0.81452422
  -0.29006459 -0.50240689  0.81452422

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As    74.90000  As.pz-bhs.UPF

ATOMIC_POSITIONS crystal
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As    -0.2750  -0.2750  -0.2750

K_POINTS automatic
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THE END