

# Quantum-ESPRESSO exercises for undergrads

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# Exercise 1: Energy minimum parabolas

a) We want to use pw.x to find the lattice parameter “a” of Sodium that minimizes the total energy of the crystal, both in fcc and bcc configurations and within LDA and GGA approximations.

INPUT Na.scf.bcc.in :

```
control
  calculation='scf'
  restart_mode='from_scratch',
  pseudo_dir = '/home/aritz/pseudo/',
  outdir='/home/aritz/tmp/',
  prefix='Na'
  tprnfor = .true.
  tstress = .true.
/
&system
  ibrav = 3,
  celldm(1) = 7.35,
  nat = 1,
  ntyp = 1,
  ecutwfc = 20.0,
  occupations = 'smearing',
  smearing = 'marzari-vanderbilt',
  degauss = 0.05
/
&electrons
  mixing_beta = 0.7
  conv_thr = 1.0d-8
/
ATOMIC_SPECIES
  Na 22.98 Na.pw-mt_fhi.UPF
ATOMIC_POSITIONS
  Na 0.00 0.00 0.00
K_POINTS automatic
15 15 15 0 0 0
```

← Type of calc.

← BCC structure. Check the lattice vector definitions.  
← a in bohr

← Pseudopotential used for the calculation. It fixes the approximation for the XC potential used, in this case LDA. The file must exist in '/home/aritz/pseudo'

The meaning of all input variables for pw.x is explained here:

[http://www.quantum-espresso.org/wp-content/uploads/Doc/INPUT\\_PW.html](http://www.quantum-espresso.org/wp-content/uploads/Doc/INPUT_PW.html)

# Exercise 1: Energy minimum parabolas

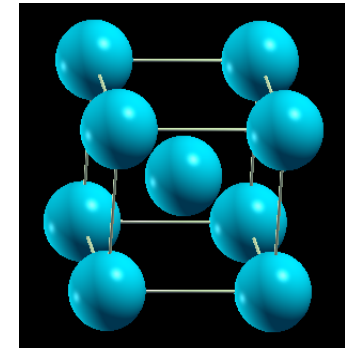
a) First, let's check whether we defined correctly our Na crystal

```
Prompt> xcrysden --pwi Na.scf.bbc.in
```

b) Run the scf calculation and check the total energy obtained at the end of the output file.

```
Prompt> pw.x < Na.scf.bbc.in > Na.scf.bcc.out
```

```
Prompt> more Na.scf.bcc.out
```



```
the Fermi energy is      0.5962 ev
```

```
!  total energy           =      -0.89730712 Ry ← Here it is!!
    Harris-Foulkes estimate =      -0.89730711 Ry
    estimated scf accuracy  <          2.6E-09 Ry
```

```
The total energy is the sum of the following terms:
```

```
one-electron contribution =      0.39134940 Ry
hartree contribution      =      0.00173840 Ry
xc contribution           =     -0.79465231 Ry
ewald contribution        =     -0.49513385 Ry
smearing contrib. (-TS)   =     -0.00060876 Ry
```

Or extract the value using the grep command

```
Prompt> grep ! Na.scf.bcc.out
```

```
!      total energy           =      -0.89730712 Ry
```

```
convergence has been achieved in    3 iterations
```

```
Forces acting on atoms (Ry/au):
```

```
atom    1 type    1    force =      0.00000000      0.00000000      0.00000000
```

```
Total force =      0.000000      Total SCF correction =      0.000000
```

```
entering subroutine stress ...
```

	total	stress (Ry/bohr**3)		(kbar)	P=
0.00010611	0.00000000	-0.00000000	15.61	0.00	-0.00
0.00000000	0.00010611	0.00000000	0.00	15.61	0.00
-0.00000000	0.00000000	0.00010611	-0.00	0.00	15.61

# Exercise 1: Energy minimum parabolas

Now that you know how to calculate Total Energies (TE), you must:

- 1) In the BCC case, calculate the TE for several values of the lattice parameter within the range  $a=[7.30,7.90]$  bohr. Plot these values versus the lattice PRIMITIVE volume.
- 2) Repeat the above procedure for the FCC case and “a” within the range  $[9.5,10.0]$

YOU SHOULD BE ABLE TO IDENTIFY THE PRECISE VALUE OF “a” THAT MINIMIZES YOUR TOTAL ENERGY.

# Exercise 2: Relaxing structures

You have just obtained manually the lattice parameter that minimizes the TE. Is there a way to automatize this procedure? The answer is YES.

Theory in a nutshell:

Equilibrium configuration

Total FORCES on ions = 0

Hellman-Feynman theorem.

(BTW this is Feynman's master thesis at the age of 21 !!!  
You could be the next)

AUGUST 15, 1939

PHYSICAL REVIEW

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## Forces in Molecules

R. P. FEYNMAN

Massachusetts Institute of Technology, Cambridge, Massachusetts

(Received June 22, 1939)

Formulas have been developed to calculate the forces in a molecular system directly, rather than indirectly through the agency of energy. This permits an independent calculation of the slope of the curves of energy vs. position of the nuclei, and may thus increase the accuracy, or decrease the labor involved in the calculation of these curves. The force on a nucleus in an atomic system is shown to be just the classical electrostatic force that would be exerted on this nucleus by other nuclei and by the electrons' charge distribution. Qualitative implications of this are discussed.



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

$$\mathbf{F}_i = - \sum_j \frac{Z_i Z_j (\mathbf{R}_i - \mathbf{R}_j)}{|\mathbf{R}_i - \mathbf{R}_j|^3} - \int n_{[\mathbf{R}]}(\mathbf{r}) \frac{\partial V_{[\mathbf{R}]}^{\text{e-I}}(\mathbf{r})}{\partial \mathbf{R}_i} d\mathbf{r} =$$

$$- \sum_j \frac{Z_i Z_j (\mathbf{R}_i - \mathbf{R}_j)}{|\mathbf{R}_i - \mathbf{R}_j|^3} - \int n_{[\mathbf{R}]}(\mathbf{r}) \frac{Z_i (\mathbf{r} - \mathbf{R}_i)}{|\mathbf{r} - \mathbf{R}_i|^3} d\mathbf{r}$$

Total STRESS of the unit cell = 0

$$\mathbf{r}_\alpha \rightarrow (\delta_{\alpha\beta} + \epsilon_{\alpha\beta}) \mathbf{r}_\beta \quad \text{strain}$$

$$\sigma_{\alpha\beta} = - \frac{1}{\Omega} \frac{\partial E}{\partial \epsilon_{\alpha\beta}} \quad \text{STRESS}$$

Stress Theorem (Nielsen & Martin, 1985) as for forces, can be calculated at a single configuration. What if the lattice vectors (specifying unit cell) are not optimal?

Forces on atoms may = 0 (e.g., an FCC crystal with wrong "a")

However **Stress** will not be zero!

< 0 → cell would like to expand.

> 0 → cell would like to contract.

We are searching for a minimum in a  $(3N_i + 3r_i)$  -dim space,

Many numerical methods: Steepest descent, BFGS, Newton-Raphson....

# Exercise 2: Relaxing structures

Now we will obtain the same value for the lattice parameter but letting QE find the minimum. The program will run a series of 'scf' calculation modifying the lattice vectors and atom positions until the energy is minimized.

```
Prompt> pw.x < Na.relax.bbc.in > Na.relax.bcc.out
```

```
Prompt> more Na.relax.bbc.in
```

```
&control  
  calculation='vc-relax' ← Variable cell relaxation: lattice + atom positions
```

```
  restart_mode='from_scratch',  
  pseudo_dir = '/home/aritz/pseudo',  
  outdir='/home/aritz/tmp',  
  prefix='Na'  
  tprnfor = .true.  
  tstress = .true.
```

Although you are relaxing the cell, by addressing `ibrav=3` you are imposing symmetry restrictions to the relaxation so that the final lattice vectors will be a multiple of the initial ones. Full relaxation is achieved by introducing by hand the cell parameters together with `ibrav=0`

```
/  
&system  
  ibrav = 3, celldm(1) = 7.2, ←  
  nat = 1, ntyp = 1, ecutwfc = 25.0,  
  occupations = 'smearing',  
  smearing = 'marzari-vanderbilt', degauss = 0.05  
/
```

```
&electrons  
  mixing_beta = 0.7  
  conv_thr=1.0d-7  
/
```

```
&ions  
/ ← Both of them must appear (&ions and &cell). Default values  
&cell  
/ are taken.
```

```
ATOMIC_SPECIES  
Na 22.98 Na.pw-mt_fhi.UPF
```

```
ATOMIC_POSITIONS
```

```
Na 0.00 0.00 0.00 0.00 0.00 ←
```

0 0 0 Fixes the ion position in x y and z, don't letting it move throughout the relaxation process.

```
K_POINTS automatic  
20 20 20 0 0 0
```

# Exercise 2: Relaxing structures

Prompt> more Na.relax.bcc.out

```
celldm(1)= 7.000000 celldm(2)= 0.000000 celldm(3)= 0.000000
celldm(4)= 0.000000 celldm(5)= 0.000000 celldm(6)= 0.000000
```

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

.....

The initial configuration is clearly under stress, note that the force on the Na atom is zero, but this is due to symmetry.

.....

Forces acting on atoms (Ry/au):

```
atom 1 type 1 force = 0.00000000 0.00000000 0.00000000
```

```
Total force = 0.000000 Total SCF correction = 0.000000
```

entering subroutine stress ...

total stress (Ry/bohr**3)			(kbar)	P=	42.73
0.00029048	0.00000000	-0.00000000	42.73	0.00	-0.00
0.00000000	0.00029048	0.00000000	0.00	42.73	0.00
-0.00000000	0.00000000	0.00029048	-0.00	0.00	42.73

At the end of the file... after 8 BFGS steps (7 scf cycles) convergence has been achieved. It is clear that the cell has expanded! Pressure and stress are zero.

```
celldm(1)= 7.000000 celldm(2)= 0.000000 celldm(3)= 0.000000
celldm(4)= 0.000000 celldm(5)= 0.000000 celldm(6)= 0.000000
```

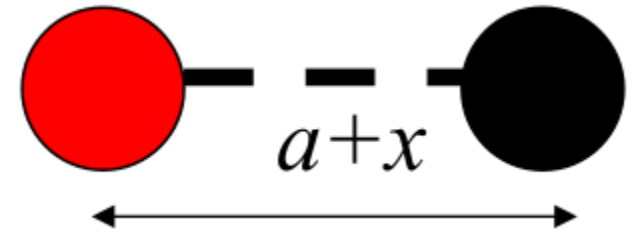
```
crystal axes: (cart. coord. in units of alat)
a(1) = ( 0.548961 0.548961 0.548961 )
a(2) = ( -0.548961 0.548961 0.548961 )
a(3) = ( -0.548961 -0.548961 0.548961 )
```

entering subroutine stress ...

total stress (Ry/bohr**3)			(kbar)	P=	0.09
0.00000060	-0.00000000	-0.00000000	0.09	-0.00	-0.00
-0.00000000	0.00000060	-0.00000000	-0.00	0.09	-0.00
-0.00000000	-0.00000000	0.00000060	-0.00	-0.00	0.09

# Exercise 3: CO molecule

The aim of this exercise is to find the equilibrium distance of the CO molecule as well as determining its vibrational frequency.



```
Prompt> more CO.relax.in
```

```
&CONTROL
  calculation = "relax",
  prefix      = "CO",
  pseudo_dir  = "/home/aritz/espresso-5.0.2/pseudo",
  outdir      = "/home/aritz/tmp",
/
```

← We only want to relax atomic positions

```
&SYSTEM
  ibrav       = 0,
  nat         = 2,
  ntyp        = 2,
  ecutwfc     = 24.D0,
  ecutrho     = 144.D0,
/
```

← No symmetry is specified and the lattice vectors must be specified below.

```
&ELECTRONS
  conv_thr    = 1.D-7,
  mixing_beta = 0.7D0,
/
```

```
&IONS
/
```

```
CELL_PARAMETERS bohr
12.0  0.0  0.0
 0.0 12.0  0.0
 0.0  0.0 12.0
```

←

We have put the molecule inside a big cubic simulation box. The code obligatory needs periodic boundary conditions so we create a supercell big enough to ensure that the interaction between adjacent molecules is negligible.

```
ATOMIC_SPECIES
O 1.00 O.pz-rrkjus.UPF
C 1.00 C.pz-rrkjus.UPF
ATOMIC_POSITIONS {bohr}
C 2.256 0.0 0.0
O 0.000 0.0 0.0 0 0 0
K_POINTS {Gamma}
```

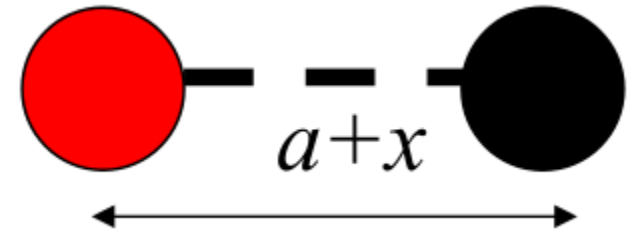
←

Atomic positions. Fix the Oxygen atom at the origin and let the Carbon atom relax. Initial distance: 2.256 bohr

← The simulation box (the supercell) is so big that its reciprocal space can be represented solely with a single point i.e. the gamma point.



# Exercise 3: CO molecule



```
Prompt> pw.x < CO.relax.in > CO.relax.out
Prompt> more CO.relax.out
```

Forces acting on atoms (Ry/au):

atom	1	type	2	force =	-0.21586732	0.00000000	0.00000000
atom	2	type	1	force =	0.21586732	0.00000000	0.00000000

Total force = 0.215867 Total SCF correction = 0.000096

.....

.....

Forces acting on atoms (Ry/au):

atom	1	type	2	force =	-0.00006319	0.00000000	0.00000000
atom	2	type	1	force =	0.00006319	0.00000000	0.00000000

Total force = 0.000063 Total SCF correction = 0.000008

SCF correction compared to forces is large: reduce conv\_thr to get better values

bfgs converged in 5 scf cycles and 3 bfgs steps  
(criteria: energy < 0.10E-03, force < 0.10E-02)

End of BFGS Geometry Optimization

a) Following classical arguments, what would be the vibrational frequency of the molecule?

b) Use xcrysden to visualize the molecule and make a movie of the relaxation

```
Prompt> xcrysden --pwo CO.relax.out
```

# Exercise 4: Band structure calculation

Coming soon ....