I. Structural optimization and Molecular Dynamics with ABINIT

I.1 Structural optimization of the O_2 molecule

Find the equilibrium distance in the O_2 molecule. Use GGA-PBE.
Examine the output file, and how the different Broyden steps are given, which information is provided. Note that O_2 is magnetic!
Input file: t_opt1.in

I.2 Structural optimization of cubic $BaTiO_3$

Find the equilibrium lattice constant of cubic $BaTiO_3$ (space group Pm-3m). Use GGA-Wu-Cohen (**ixc** 23), with PBE atomic datasets. Note that atomic forces are all zero by symmetry. Take care of convergence criteria (**tolmxf** and **tolrff**). Examine parallelization scheme.
Input file: t_opt2.in

I.3 Structural optimization of the ferroelectric phases of $BaTiO_3$

Optimize structurally (cell and atomic positions) the **tetragonal**, **orthorhombic** and **rhombohedral** ferroelectric structures of $BaTiO_3$. Use GGA-Wu-Cohen (**ixc** 23), with PBE atomic datasets. You may use the multidataset mode to do the three structures in one run (be careful with parallelization scheme if so). Take care of convergence criteria (**tolmxf** and **tolrff**).
Input file: t_opt3.in

Examine the starting geometries for the three calculations: what are the differences?
Compare the final energies of the three (relaxed) structures. Which one is the most stable? Why don't they all relax to the same final state ?

I.4 Structural optimization of iron hydride under pressure

Compute the equation of state (volume as a function of pressure), at T=0 K, of the FeH (iron monohydride) compound between 0 and ~ 30 GPa (do 6 pressures). Use GGA-

PBE. The structure is given in *t_opt4.in*. Keywords that may help: **getxred**, **getcell**. Choose yourself the parallelization scheme.

N.B.: FeH is a <u>metal</u>.

Input file: t_opt4.in

Check convergence with respect to k-point sampling (**ngkpt**) and plane-wave cut-off (**ecut**). Change the smearing (**tsmear**) to a smaller value, e.g. 0.001, and recheck convergence with respect to k-point sampling.

If you have time, you may examine the influence of magnetism by letting the system become ferromagnetic (use the keywords **nsppol** and **spinat**).

I.5 Molecular Dynamic simulation of the Zundel ion in the canonical ensemble

<u>**Molecular Dynamics**</u> simulation of the the Zundel ion (H_2O-H-OH_2)$^+$. Simulate an isolated Zundel ion at T=300 K using GGA-PBE. Use the Langevin thermostat.

Choose correctly the time step **dtion**. Plot the time evolution of temperature, internal energy (kinetic + potential). To thermalize more quickly, you may artificially increase the friction coefficient (**vis**) to a larger value than the one given (e.g. multiply by 5 or 10). Choose yourself the parallelization scheme.

Check the position of the center of mass; look at the fluctuations of the temperature and of the energy.

Input file: t_opt5.in (the starting geometry is provided, you can visualize it with xsf file zundel_geometry.xsf)

If you have time, plug the quantum effects by setting **nimage** to value larger than one, e.g. 4 or 8 (this value does not ensure converged results but should provide visible quantum effects). In order to be efficient, use the parallelization over images with **npimage**.

II. Examples of input files for structural optimizations

II.1 Structural optimization: atomic positions only

Structural optimization of the O2 molecule in a big box

cell and system
acell 20.0 20.0 20.0
natom 2 ntypat 1 typat 1 1 znucl 8.0
xangst
0.0 0.0 0.0
1.22 0.0 0.0

electronic ground state
kptopt 1
ngkpt 1 1 1 nshiftk 1 shiftk 0.0 0.0 0.0   #Gamma point here because isolated molecule
ecut 20.0 pawecutdg 30.0
nstep 50
tolrff 0.02
occopt 3 tsmear 0.0001
nband 8
nsppol 2
spinat
0 0 1
0 0 1

XC
ixc 11

structural optimization
optcell 0 ## cell fixed
ionmov 2
tolmxf 1.0d-05
ntime 50

parallelization
#paral_kgb 1 npband 1 bandpp 1 npfft 1 npkpt 1

options for printing
prtden 0 #otherwise _DEN file printed at each Broyden step
prteig 0 prtwf 0

II.2 Structural optimization: cell only

Structural optimization of cubic phase of BaTiO3

cell and system
acell 4.0 4.0 4.0 Angstrom
natom 5 ntypat 3 typat 1 2 3 3 3
znucl 56 22 8
xred
0.0 0.0 0.0
0.5 0.5 0.5
0.5 0.5 0.0
0.5 0.0 0.5
0.0 0.5 0.5

electronic ground state
kptopt 1
ngkpt 8 8 8
ecut 30.0 pawecutdg 40.0
nstep 50
tolrff 0.02
occopt 1 #occ numbers: insulator
nband 24

XC
ixc 23 ### GGA Wu-Cohen

structural optimization
optcell 2 ## cell optimized
ecutsm 0.5
dilatmx 1.1
chkdilatmx 1 #default value: set 0 if dilatmx exceeds 1.15
ionmov 2
tolmxf 1.0d-05
ntime 50

parallelization
#paral_kgb 1 npband 3 bandpp 8 npfft 1 npkpt 10

options for printing
prtden 0 #otherwise _DEN file printed at each Broyden step
prteig 0   prtwf 0

II.3 Structural optimization: atomic positions and cell

Structural optimization of the ferroelectric phases of BaTiO3

cell and system
acell 4.0 4.0 4.0 Angstrom
natom 5 ntypat 3 typat 1 2 3 3 3 znucl 56 22 8

ndtset 3
xred1
0.0 0.0 0.0
0.52 0.5 0.5
0.5 0.5 0.0
0.5 0.0 0.5
0.0 0.5 0.5

xred2
0.0 0.0 0.0
0.52 0.52 0.5
0.5 0.5 0.0
0.5 0.0 0.5
0.0 0.5 0.5

xred3
0.0 0.0 0.0
0.52 0.52 0.52
0.5 0.5 0.0
0.5 0.0 0.5
0.0 0.5 0.5

electronic ground state
kptopt 1 ngkpt 8 8 8
ecut 30.0 pawecutdg 40.0
nstep 50   tolrff 0.02
occopt 1 #occ numbers: insulator
nband 20
nline 8 diemac 5.0

XC
ixc 23 ### GGA Wu-Cohen

structural optimization
optcell 2 ## cell optimized
ecutsm 0.5   dilatmx 1.1
chkdilatmx 1 #default value: set 0 if dilatmx exceeds 1.15
ionmov 2   tolmxf 1.0d-05   ntime 50

parallelization
#paral_kgb 1 npband 3 bandpp 8 npfft 1 npkpt 10

options for printing
prtden 0 prteig 0 prtwf 0

II.4 Structural optimization: atomic positions and cell, with non-zero pressure

FeH double HCP structure

atoms and cell

natom 8   ntypat 2   znucl 26 1   typat 1 1 1 1 2 2 2 2
acell 4.74724519843949E+00   4.74724519843949E+00   1.55283696459955E+01
angdeg 90.0 90.0 120.0
xred

0.000000000000	0.000000000000	0.000000000000
0.000000000000	0.000000000000	0.500000000000
0.333333333333	0.666666666667	0.250000000000
0.666666666667	0.333333333333	0.750000000000
0.666666666667	0.333333333333	0.120642406761
0.666666666667	0.333333333333	0.379357593239
0.333333333333	0.666666666667	0.620642406761
0.333333333333	0.666666666667	0.879357593239

electronic ground state

ecut 20.0   pawecutdg 30.0
kptopt 1   ngkpt 12 12 4
nstep 100
tolrff 0.02   #also possible: toldff
occopt 7   # metallic occ numbers
tsmear 0.005
nband 44
chksymbreak 0

XC

ixc 11 # GGA-PBE

structural optimization

ntime 100
ionmov 2
optcell 2 # optimize cell
tolmxf 5.0d-5   ecutsm 0.5   dilatmx 1.15   chkdilatmx 1

ndtset 6
strtarget1 -0.001019679 -0.001019679 -0.001019679 0.0 0.0 0.0 # 30 GPa in Ha/bohr^3
strtarget2 -0.0008 -0.0008 -0.0008 0.0 0.0 0.0
strtarget3 -0.0006 -0.0006 -0.0006 0.0 0.0 0.0
strtarget4 -0.0004 -0.0004 -0.0004 0.0 0.0 0.0
strtarget5 -0.0002 -0.0002 -0.0002 0.0 0.0 0.0
strtarget6 0.0000 0.0000 0.0000 0.0 0.0 0.0

getcell -1   getxred -1

parallelization

#paral_kgb 1 npkpt 84 npband 2 bandpp 11 npfft 1

printing options

prtden 0 prtwf 0 prteig 0

II.5 Molecular Dynamics simulation using the Langevin thermostat

MD simulation of Zundel ion using Langevin thermostat

charge 1.0
pawovlp -1

cell and system
acell 20.0 20.0 20.0
natom 7 ntypat 2 typat 1 1 2 2 2 2 2
znucl 8 1
xred
   -0.010844745886   0.000000000000   0.000000000000
    0.215983400047   0.000000000000   0.000000000000
    0.102579239759   0.000000000000   0.000000000000
   -0.062054923368   0.076587460785   0.000000000000
   -0.062054923368   -0.076587460785   0.000000000000
    0.267243941657   0.076565510011   0.000000000000
    0.267243941657   -0.076565510011   0.000000000000

electronic ground state
kptopt 1
ngkpt 1 1 1 nshiftk 1 shiftk 0.0 0.0 0.0 #Gamma point only here because isolated molecule
ecut 20.0   pawecutdg 30.0
nstep 50
tolrff 0.02
occopt 1 #occ numbers: insulator
nband 8

XC
ixc 11

MD with Langevin
optcell 0 ## cell fixed
imgmov 9
ntimimage 5000
nimage 1
vis 5.0d-05
dtion 10
dynimage 1
nsym 1
mdtemp 600 300
amu 16 1   pimass 16 1
irandom 3

parallelization
#paral_kgb 1 npband 2 bandpp 4 npfft 1 npkpt 1 npimage 1

options for printing
prtden 0 #otherwise _DEN file printed at each Broyden step
prteig 0 prtwf 0