

ECE 695

Numerical Simulations

Lecture 18: Using Quantum Espresso  
for Electronic Band Structures

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# Outline

- Quantum Espresso Job File Structure
- Sample Structure: Solid Mg
- Performing 'scf' Calculations
- Converging 'scf' Energies
- Performing 'relax' Calculations

# Job File Structure

Input variables that control the amount of I/O on the hard drive and on the screen

```
&CONTROL
```

```
...
```

```
/
```

```
&SYSTEM
```

```
...
```

```
/
```

Input variables that specify the system under study.

```
&ELECTRONS
```

```
...
```

```
/
```

Name, mass, and pseudopotential used for each atomic species present in the system

```
ATOMIC_SPECIES
```

```
X Mass_X PseudoPot_X
```

```
Y Mass_Y PseudoPot_Y
```

```
Z Mass_Z PseudoPot_Z
```

Input variables that control the algorithms used to reach a self-consistent solution of the Kohn-Sham equations.

```
ATOMIC_POSITIONS { alat | bohr | crystal | angstrom }
```

```
in all cases except calculation = 'neb' or 'smd' :
```

```
X 0.0 0.0 0.0 {if_pos(1) if_pos(2) if_pos(3)}
```

```
Y 0.5 0.0 0.0
```

```
Z 0.0 0.2 0.2
```

Type and coordinates of each atom in the unit cell

```
K_POINTS { tpiba | automatic | crystal | gamma }
```

```
if (gamma)
```

```
nothing to read
```

```
if (automatic)
```

```
nk1, nk2, nk3, k1, k2, k3
```

```
if (not automatic)
```

```
nks
```

```
xk_x, xk_y, xk_z, wk
```

Coordinates and weights of the K-points used for BZ integration

# Typical input file – diamond Si

```
&control
  calculation = 'scf'
  restart_mode='from_scratch',
  pseudo_dir = '~/pseudo',
  outdir='tmp', /
&system
  ibrav = 2,
  celldm(1) = 11.0,
  nat = 2,
  ntyp = 1,
  ecutwfc = 20, /
&electrons /
ATOMIC_SPECIES
Si 1.0 Si.pbe-rrkj.UPF
ATOMIC_POSITIONS {alat}
Si 0 0 0
Si 0.25 0.25 0.25
K_POINTS {automatic}
```

# The namelist & control

- **calculation**
  - scf: single point calculation without geometric optimization
  - nscf : non-self-consistent calculation
  - relax : geometric optimization
  - md : molecular dynamics
  - vc-relax : geometric optimization with variable unit cell coordinates
- **restart\_mode**
  - from scratch : Start from an initial guess
  - restart : Start from earlier data
- **outdir**: Directory where intermediates are dumped.
- **pseudo\_dir**: Directory where the pseudopotentials live.

# The namelist & system

- nat : number of atoms
- ntyp : number of types of atoms
- nbnd : number of states to be calculated  
(unoccupied states as well)
- ecutwfc : kinetic energy cutoff (for planewaves)
- ecutrho : density cutoff (for the augmentation  
charge in USPP  $\approx 10\times$  ecutwfc)

# The namelist &system

## Lattice structure

- `ibrav` : Bravais lattice index — easy way to set up a crystal
- `celldm(1)-celldm(6)` : Various cell dimensions in B — not all six are used for most `ibrav`

0 : user-specified	<code>celldm(1) = given length</code>
1 : simple cubic	<code>celldm(1) = a</code>
2 : face-centered cubic	<code>celldm(1) = a</code>
3 : body-centered cubic	<code>celldm(1) = a</code>
4 : hexagonal	<code>celldm(1) = a</code>
	<code>celldm(3)=c/a</code>
:	:
Up to fourteen	Some <code>celldm(i)</code> length, some angle

# The namelist & system

## Occupations

- `occupations` : Occupation of Kohn-Sham states – important for metals
  - `'smearing'` : smear occupations by a some function (below)
  - `'tetrahedra'` :
  - `'fixed'` : default (for insulators)
  - `'from_input'` : read occupations from a file
- `smearing` : types of smearing
  - `'gaussian'`
  - `'methfessel-paxton'`
  - `'marzari-vanderbilt'`
  - `'fermi-dirac'`
- `degauss` : Smearing width
  - Small `degauss`  $\Rightarrow$  better accuracy
  - Large `degauss`  $\Rightarrow$  smaller number of k-points



# The namelist &system

## Magnetism

- `nspin` : spin type
  - 1 : non-polarized
  - 2 : spin-polarized (single-axis magnetization)
- `starting_magnetization (i)` : between -1 and 1. To break symmetry for the initial configuration. The index `i` runs over atom types.
- `tot_magnetization` : Fix ( $n_{maj} - n_{min}$ )
- `noncolin` : (.true./false.) Turn on noncollinear magnetism

# The namelist & electrons

## Charge mixing

- `mixing_mode` : improves convergence
  - 'plain' : Broyden mixing
  - 'TF' : simple Thomas-Fermi screening (homogeneous systems)
  - 'local-TF' : local-density-dependent TF screening (surfaces etc.)
- `mixing_beta` :  $n_{i+1} = (1 - \beta)n_i^{KS} + \beta n_i$
- `mixing_nstep` : number of iterations used in mixing scheme

## Solution of KS equations

- `diagonalization` : Minimization or iterative diagonalization
  - `david` : Davidson iterative diagonalization
  - `cg` : Minimization using the conjugate-gradients algorithm
- Various diagonalization-related keywords :
  - `diago_david_ndim`, `diago_thr_init`, `diago_cg_maxiter`

# The namelist & ions

## Ion dynamics — mostly for md

- `ion_dynamics` : Different possibilities are allowed for different calculation keywords
  - `bfgs` : for relax
  - `damp` : for relax and vc-relax
  - `verlet` : for md
- `ion_temperature` : Method of fixing the temperature during md runs
  - `'rescaling'` : rescale the velocity every given number of steps
  - `'langevin'` : use Langevin thermostat
  - `'not_controlled'` : self-evident
- NEB keywords : `opt_scheme`, `CI_scheme`, `k_min`, `k_max`

# Cards

## Related to atoms

- ATOMIC\_SPECIES

```
[ type    mass    pseudopotential ]  
  B      10.811  B.pbe-n-van.UPF  
  N      14.007  N.pbe-van_bm.UPF  
  Mn     54.938  Mn.pbe-sp-van.UPF
```

The pseudopotentials are taken from the PWSCF library or self-generated.

- ATOMIC\_POSITIONS {alat|bohr|crystal|angstrom}

```
[type      x      y      z      fix_x  fix_y  fix_z]  
  N        0.00    0.00    0.00        0      1      1  
  Mn       1.00    1.00    1.00  
  B        2.25    2.25    2.25        1      0      1
```

# Cards

## Others

- K\_POINTS { automatic }

```
[ nkx   nky   nkz   shiftx shifty shiftz ]  
      6     6     6       0       1       0
```

- K\_POINTS { tpiba | crystal | gamma }

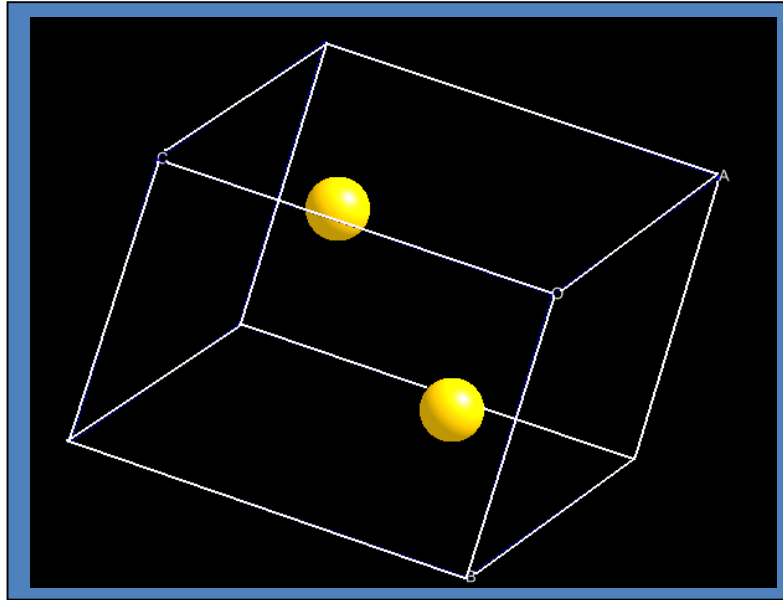
```
[ k_x      k_y      k_z      wk ]  
  0.25      0.25      0.25      0.333  
  0.75      0.25      0.00      0.666
```

- CELL\_PARAMETERS

```
a(1,1) a(2,1) a(3,1)  
a(1,2) a(2,2) a(3,2)  
a(1,3) a(2,3) a(3,3)
```

Bohr if celldm(1)=0, alat units otherwise

# Solid Mg (hcp)



- Primitive Vectors:

$$A_1 = \frac{1}{2} a X - \frac{1}{2} \sqrt{3} a Y$$

$$A_2 = \frac{1}{2} a X + \frac{1}{2} \sqrt{3} a Y$$

$$A_3 = c Z$$

- Basis Vectors:

$$B_1 = \frac{1}{3} A_1 + \frac{2}{3} A_2 + \frac{1}{4} A_3$$

$$B_2 = \frac{2}{3} A_1 + \frac{1}{3} A_2 + \frac{3}{4} A_3$$

$a = 3.21$  Angstrom

$c = 5.21$  Angstrom

Space group:  $P6_3/mmc$

## Inputting Structures into Quantum ESPRESSO

- There are multiple options in QE, for inputting structures.
- In the &SYSTEM namelist, there is a parameter called 'ibrav'
  - ibrav=4 refers to the index for an internally-specified hcp Bravais lattice.
  - ibrav=0 allows one to self-define their unit cell.

### ibrav = 4

- Internally specifies lattice vectors
- Requires the celldm() parameters to be specified [alat = celldm(1)]
- Better recognizes symmetry operations

### ibrav = 0

- Requires CELL\_PARAMETERS card for lattice vector input.
- alat = the length of the first lattice vector

## Inputting Vectors into Quantum ESPRESSO

- For the required **ATOMIC POSITIONS** card and the optional **CELL\_PARAMETERS** card, the input can be generated as follows:

```
ATOMIC_POSITIONS { alat | bohr | crystal | angstrom }  
  X v1(1) v1(2) v1(3)  
  Y v2(1) v2(2) v2(3)  
  Z v3(1) v3(2) v3(3)  
  
CELL_PARAMETERS { cubic | hexagonal }  
  v1(1) v1(2) v1(3)  
  v2(1) v2(2) v2(3)  
  v3(1) v3(2) v3(3)
```

- Note: While the three lattice vectors in the **CELL\_PARAMETERS** card can only be specified in alat-normalized Bohr units, there are four options for inputting basis vectors in **ATOMIC\_POSITIONS**:

“alat” – alat-normalized Bohr units (default)

“bohr” – Bohr units

“angstrom” – Angstrom units

“crystal” – fractional coordinates



# Performing Self-consistent Energy Calculations on Solid Mg

```
#!/bin/csh
#PBS -l size=8
#PBS -l walltime=10:00
#PBS -j oe

set echo

cd $SCRATCH

cat > mg.scf.in << !
@control
  calculation = 'scf'
  restart_mode='from_scratch',
  prefix='mg',
  tstress=.true.
  tprnfor = .true.
  pseudo_dir = '$HOME/pp',
  outdir='/scratch/swansons/tmp/'
/
@system
  ibrav = 4, celldm(1)=6.06, celldm(3)=1.62, nat = 2, ntyp= 1,
  ecutwfc = 30,
/
@electrons
  diagonalization='cg'
  mixing_mode='plain'
  mixing_beta = 0.7
  conv_thr = 1.0d-8
/
@ions
  pot_extrapolation = "second_order",
  wfc_extrapolation = "second_order",
/
ATOMIC_SPECIES
Mg 24.305 Mg.pz-bhs.UPF
ATOMIC_POSITIONS {crystal}
Mg .3333 .6667 .25
Mg .6667 .3333 .75
K_POINTS {automatic}
5 5 5 0 0 0
!
pbsyod -size $PBS_0_SIZE /usr/local/packages/espresso-4.0.4/bin/pw.x -npool 2 < mg.scf.in > mg.scf.out
grep -e ! mg.scf.out >> mg.txt
grep -e 'CPU time' mg.scf.out >> mg.txt
cp mg.txt $HOME/mg.txt
```

# SCF Output

- As intended, the 'mg.txt' file only contains the following:

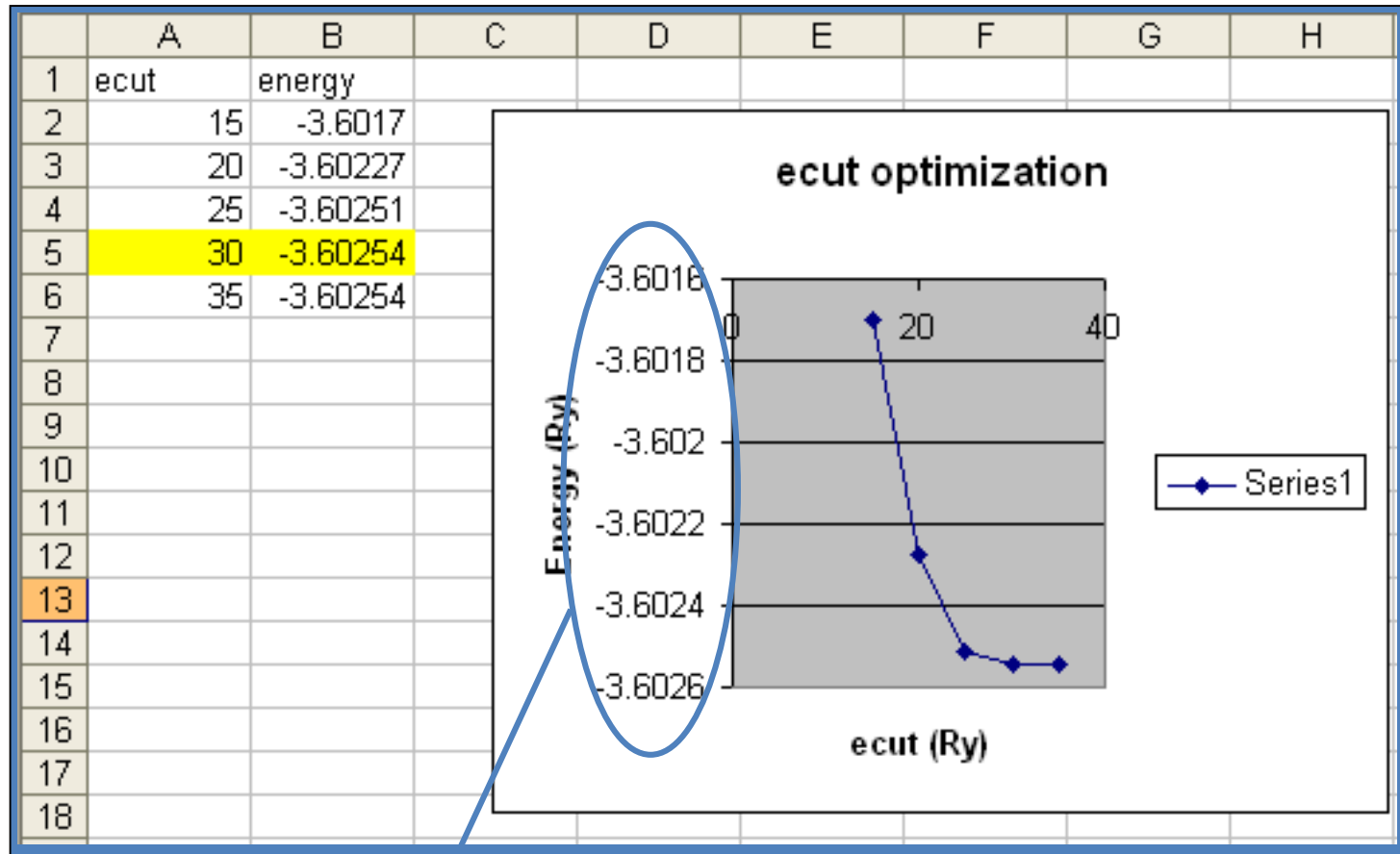
```
!      total energy          = -3.60254292 Ry  
PWSCF      : 4.90s CPU time, 4.90s wall time
```

- Reading the full 'mg.scf.out' file, however, allows us to step through the entire calculation, from initialization through each iteration. This is useful to visualize sometimes if you're unsure of your results and would like to visually inspect the convergence of your self-consistent energies.

## Ensuring $k$ and $ecut$ Lead to a Converged Energy

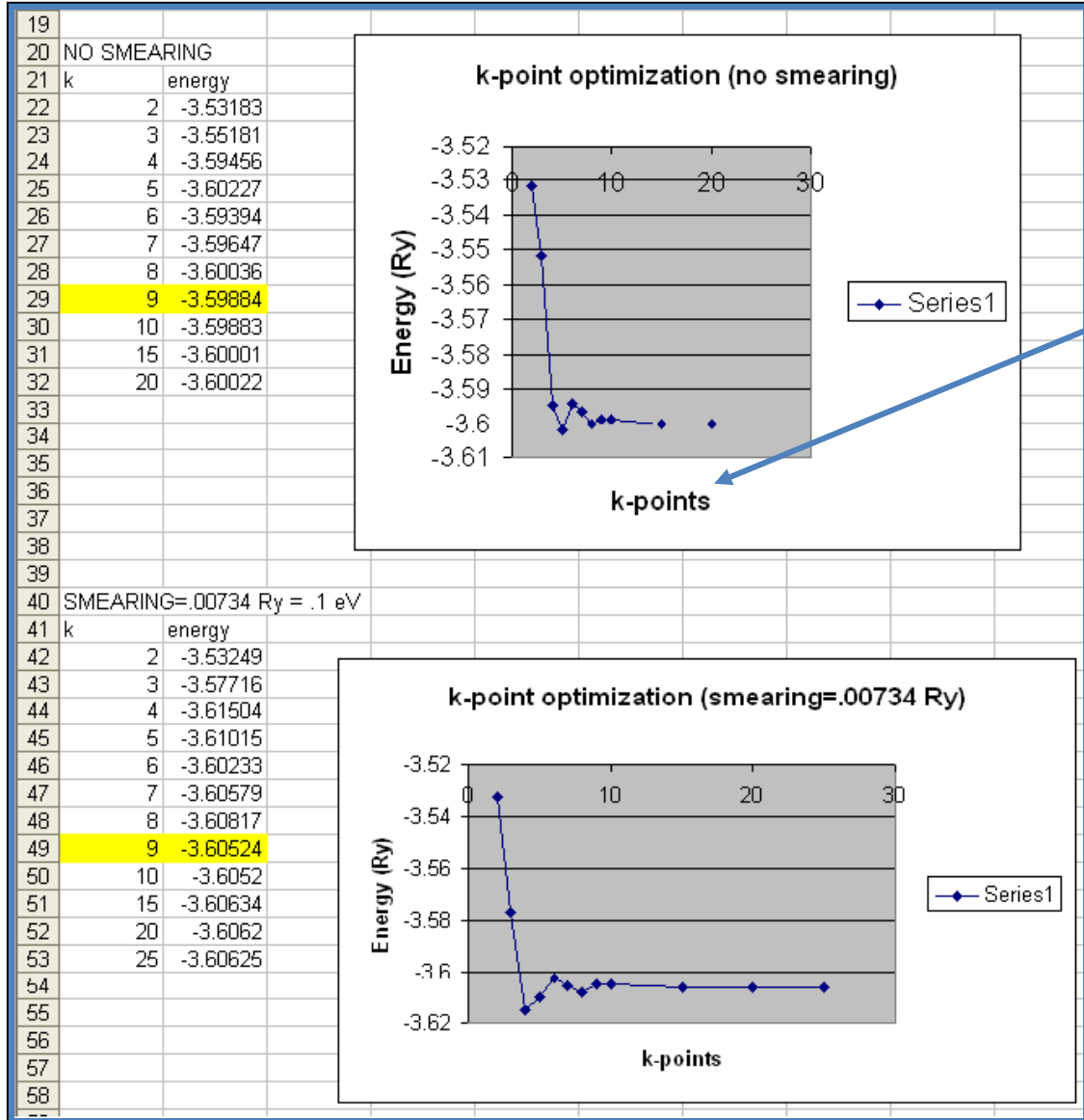
- The most important skill in performing DFT calculations is the ability to get converged energies. Since the appropriate choice of  $k$ -points and  $ecut$  vary wildly among different geometries (and even different required accuracies), it is important to be able to form the following graphs every time you perform 'scf' calculations on new geometries.
- Converged values of  $ecut$  and  $k$  should be reported any time you publish DFT results, so that someone else may reproduce your calculation and agree on the same numerical error.

# Energy Cut-off Convergence Plot



Not only should the graph look converged, but the difference in energy between the last two consecutive points should be smaller or equal to your required accuracy!

# K-point Convergence Plot



Note: In an automatic distribution of k-points, the value of k specifies how many discrete points there are equally-spaced along each lattice vector to populate the Brillouin Zone.

As we can see from the convergence plots, the presence of smearing does little to ensure convergence with fewer k-points.

# K-point Convergence Plot (cont.)

- When unit cells do not have equal-length lattice vectors, it is sometimes computationally rewarding to “geometrically-optimize” your automatic k-point distribution.
- For example, if one had a unit cell that was four times taller in one direction than its other two directions, one should specify only a quarter as many k-points along the taller direction.
  - This makes sense, because in reciprocal space, the taller distance will only be a quarter as long as the other two distances.

## Performing Geometry Relaxation Calculations on Solid Mg

```
#!/bin/csh
#PBS -l size=12
#PBS -l walltime=1:00:00
#PBS -j oe

set echo

cd $SCRATCH

cat > mgnoibrav.rx.in << !
&control
  calculation = 'vc-relax'
  prefix='mgnoibrav',
  pseudo_dir = '$HOME/pp',
  outdir='/scratch/swansons/tmp/'
  restart_mode='from_scratch'
  forc_conv_thr = 1.0d-4
  etot_conv_thr = 1.0d-5
/
&system
 ibrav = 0, celldm(1)=6.06, nat = 2, ntyp= 1,
ecutwfc = 30, occupations='smearing', smearing='f-d', degauss=0.00734
/
&electrons
  mixing_beta = 0.7
  conv_thr = 1.0d-5
/
&ions
/
&cell
  cell_dynamics='damp-w'
/
CELL_PARAMETERS hexagonal
1.0 0.0 0.0
-.5 .8660254037 0.0
0.0 0.0 1.62305
ATOMIC_SPECIES
Mg 1.0 Mg.pw91-np-van.UPF
ATOMIC_POSITIONS {crystal}
Mg .3333333333 .6666666667 .25
Mg .6666666667 .3333333333 .75
K_POINTS {automatic}
10 10 10 0 0 0
!
pbsyod -size $PBS_0_SIZE /usr/local/packages/espresso-4.0.4/bin/pw.x -npool 3 < mgnoibrav.rx.in > mgnoibrav.rx.out
cp mgnoibrav.rx.out $HOME/mgnoibrav.rx.out
```

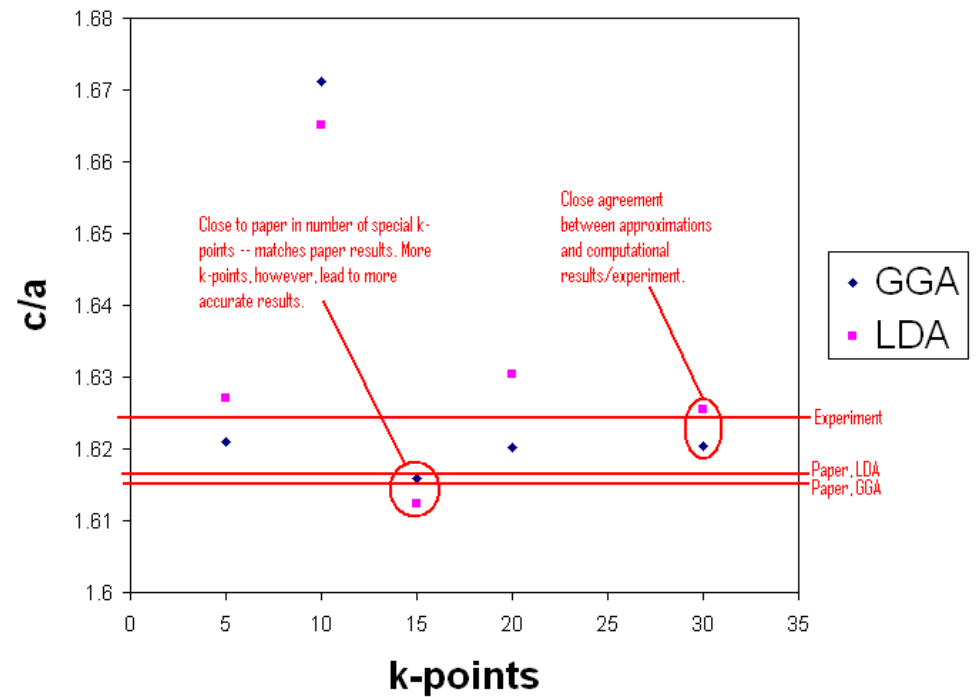
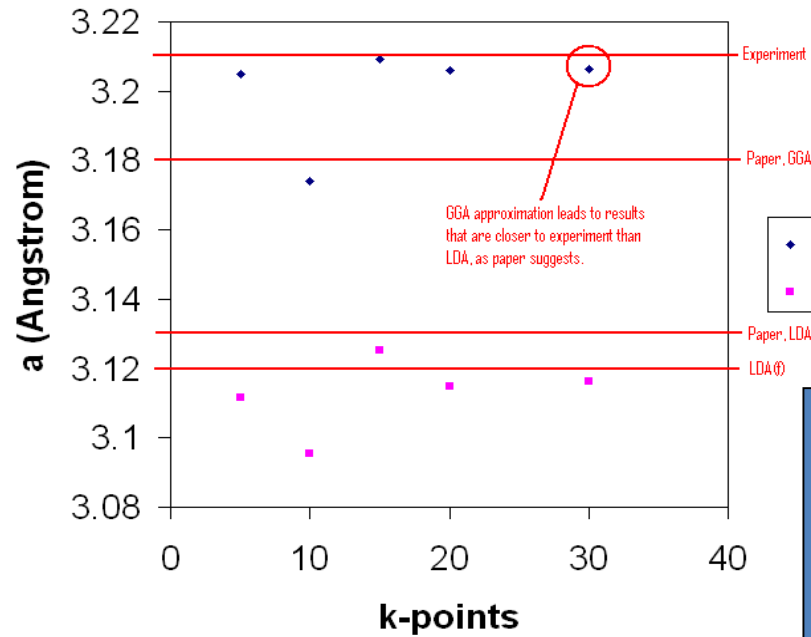
'vc-relax' differs from 'relax' only in that the cell parameters can vary during the relaxation.

# VC-RELAX Output

- Reading the full 'mg.rx.out' file allows us to step through the entire calculation, from initialization through each iteration.
- It becomes apparent that a relaxation calculation is simply a series of scf calculations with forces specified at each step and updated positions at each iteration that correspond to the strength of the forces between the atoms in the system.



# Comparing the Relaxed Structure to Literature



- On top of comparing the 'a' and 'c/a' lattice parameters to literature and to experiment, it is also useful to compare a quantity called “cohesive energy”
  - The difference between the average energy of the atoms of a crystal and that of the free atoms.
- It is important to compare cohesive energies and not specifically the self-consistent energies, because only differences in energies are physically meaningful.
  - The energy datum for an 'scf' calculation is specified by the choice of pseudopotential.

# References

- Paolo Giannozzi *et al* 2009 *J. Phys.: Condens. Matter* **21** 395502 [doi:10.1088/0953-8984/21/39/395502](https://doi.org/10.1088/0953-8984/21/39/395502)
- Ustunel, Hande 2007 Quantum-Espresso
- [www.quantum-espresso.org](http://www.quantum-espresso.org)

# Next Class

- Is Monday, Feb. 27
- Next time, we will consider transfer matrix models