



HANDS-ON WORKSHOP ON DENSITY FUNCTIONAL THEORY

Ivor Lončarić

Day 1
02/09/2021

Juraj Ovčar

QUANTUM ESPRESSO (QE)



- Suite of **open-source** computer codes for first-principles (DFT) electronic-structure calculations
- **ESPRESSO** = op**E**n-**S**ource **P**ackage for **R**esearch in **E**lectronic **S**tructure, **S**imulation and **O**ptimization
- Plane wave (PW) basis set & pseudopotentials

Journal of physics: Condensed matter, 2009, 21.39: 395502.

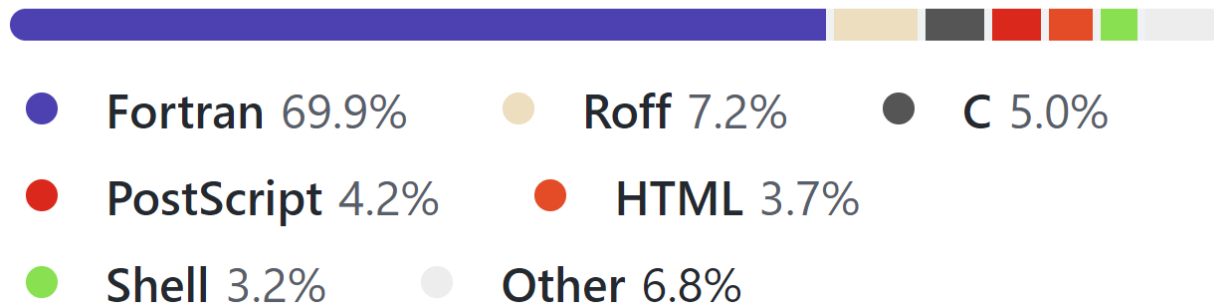
Journal of physics: Condensed matter, 2017, 29.46: 465901

<https://www.quantum-espresso.org/>

QUANTUM ESPRESSO (QE)



Languages



➤ Over 300,000 lines of code

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Journal of physics: Condensed matter, 2017, 29.46: 465901

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WHAT CAN QE DO?



1. Ground-state calculations (energies, forces, stresses, Kohn-Sham orbitals, ...)
2. Structural optimizations
3. Response properties (phonons, infrared & Raman cross-sections, ...)
4. Spectroscopic properties (X-ray, electronic excitations, ...)
5. Quantum transport
6. ...

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CORE PACKAGES



- PWscf = Plane-Wave Self-Consistent Field (pw.x)
- CP = Car-Parrinello Molecular Dynamics (cp.x)

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SPECIALIZED PACKAGES



- PostProc = Data postprocessing (pp.x)
- PHonon = Phonons with Density-Functional Perturbation Theory (ph.x)
- ...

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Journal of physics: Condensed matter, 2017, 29.46: 465901

<https://www.quantum-espresso.org/>

USEFUL RESOURCES



➤ Documentation:

<https://www.quantum-espresso.org/documentation/>

➤ Mailing list:

<https://www.mail-archive.com/users@lists.quantum-espresso.org/>

➤ Tutorials:

<https://www.quantum-espresso.org/tutorials/>

➤ QE paper on arXiv:

<https://arxiv.org/abs/0906.2569>

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XCRYSDEN



- XcrySDen is crystalline and molecular structure visualization program
- Compatible with QE input/output files
- Can be used to define k-point paths and grids in the Brillouin zone

WHERE TO FIND (CRYSTAL) STRUCTURES?

- Cambridge Crystallographic Data Centre:

<https://www.ccdc.cam.ac.uk/>

- Crystallography Open Database

<http://www.crystallography.net/cod/>

- DFT calculations database on Materials Project:

<https://materialsproject.org/>

- Papers

- If no structures are available, you have to use structure prediction algorithms

EXERCISE 1 — BASIC SCF CALCULATION

EXERCISE 1 — BASIC SCF CALCULATION

- Input data is organized as several namelists, starting with &
 - &CONTROL = general variables controlling the run (calculation type, file IO locations...)
 - &SYSTEM = structural information on the system under investigation
 - &ELECTRONS = electronic variables: self-consistency, smearing
 - &IONS (optional) = ionic variables: relaxation, dynamics
 - &CELL (optional) = variable cell relaxation, dynamics
- Namelists are followed by other fields (*cards*) introduced by keywords:
 - ATOMIC_SPECIES, ATOMIC_POSITIONS, K_POINTS, (CELL_PARAMETERS, OCCUPATIONS)

EXERCISE 1 — BASIC SCF CALCULATION

- How to choose various parameters (*ecutwfc*, *ecutrho*, k-point grid density, ...)?
- They have to be large enough so that the results (energies, forces, ...) are *converged* (don't change a lot upon further increasing of the parameters)
- Beware of computational cost vs. accuracy
- The next exercise will be on explicitly converging the results

EXERCISE 1 — BASIC SCF CALCULATION

➤ The default values of the *nbnd* variable are

1. Insulators = number of valence bands ($\# \text{electrons} / 2$)
2. Metals = number of valence bands + 20% more (minimum 4 more)

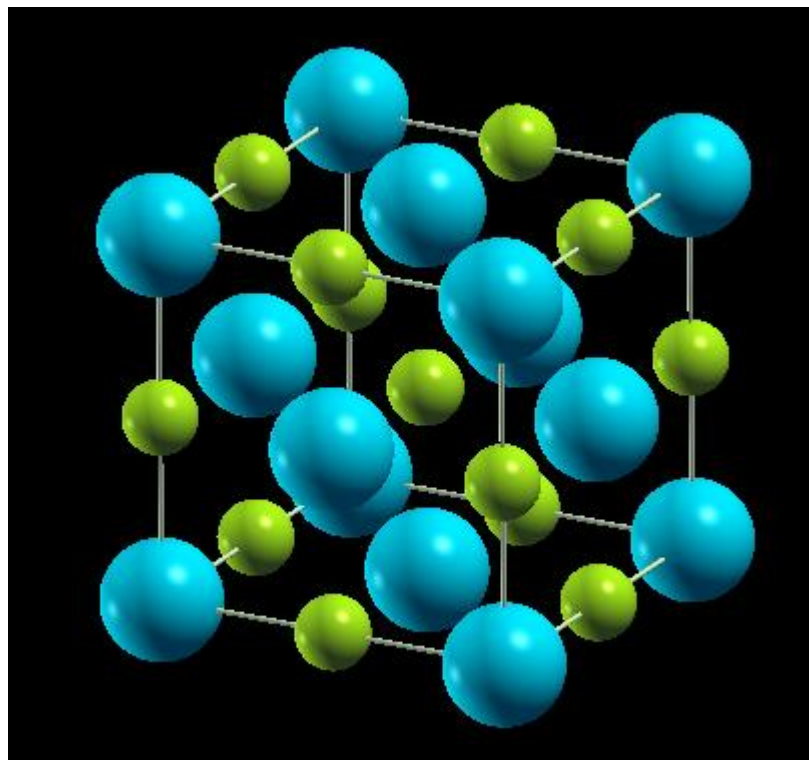
➤ The number of electrons is written in the pseudopotential files (Z valence)

➤ To view the location of the pseudopotential files, type

```
echo $ESPRESSO_PSEUDO
```

EXERCISE 1 — BASIC SCF CALCULATION

```
...  
ibrav = 2,           ! FCC  
celldm(1) = 10.571,  ! lattice constant (Bohr)  
...  
ATOMIC_POSITIONS {crystal}  
Na 0.00 0.00 0.00  
Cl 0.50 0.50 0.50
```



EXERCISE 1 — BASIC SCF CALCULATION

- After performing the pw.x calculation, we can observe the generated output files:
 - nacl.xml = information about the calculation (for multistep calculations intermediate configurations are saved)
 - nacl.save = directory containing wave functions, charge density and pseudopotentials
 - **nacl.out** = main human-readable output file

EXERCISE 1 — BASIC SCF CALCULATION

- nacl.out contents by line number:
- 13 – 35 = Parallelization information
- 39 – 683 = Information on the system, SCF parameters and symmetries
- 685 – 708 = k-points list
- 710 – 754 = Memory usage
- 756 – 1032 = SCF cycles
- 1036 – 1124 = Forces & stress contributions
- 1129 – 1197 = Timing


```

Initial potential from superposition of free atoms

starting charge      15.9937, renormalised to      16.0000

negative rho (up, down):  1.484E-02 0.000E+00
Starting wfcs are      9 randomized atomic wfcs +      1 random wfcs

total cpu time spent up to now is      1.4 secs

Self-consistent Calculation

iteration # 1      ecut=      50.00 Ry      beta= 0.70
Davidson diagonalization with overlap

ethr =  1.00E-02,  avg # of iterations =  4.7

Davidson diagonalization with overlap

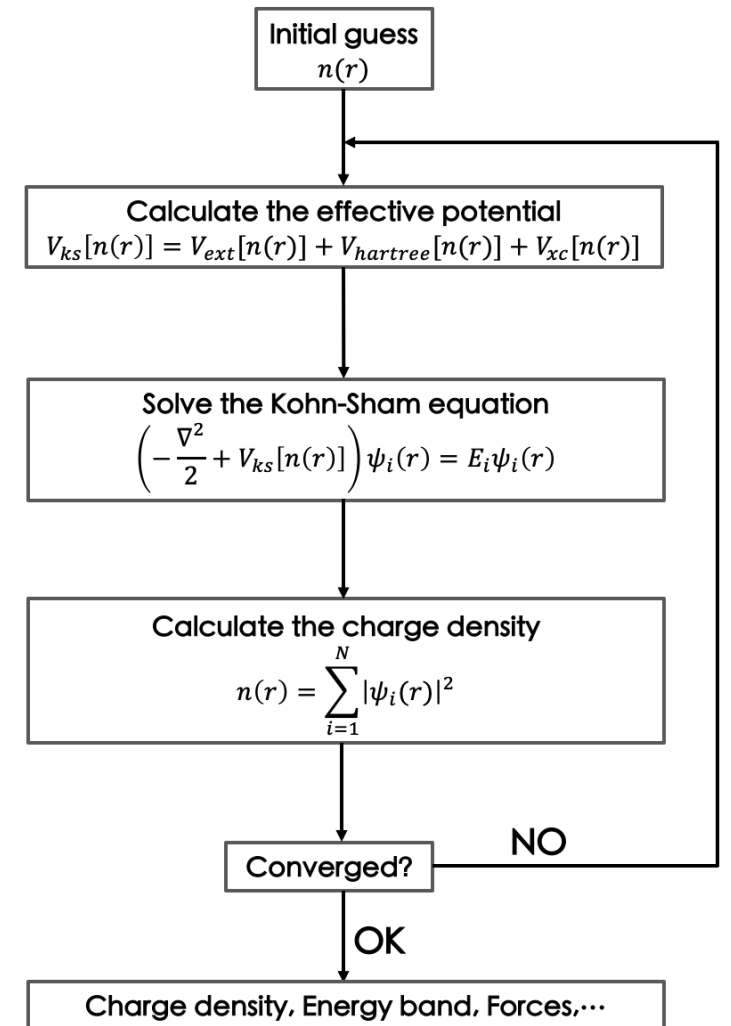
ethr =  3.33E-04,  avg # of iterations =  2.3

negative rho (up, down):  1.531E-02 0.000E+00

total cpu time spent up to now is      3.3 secs

total energy          =      -128.88647981 Ry
estimated scf accuracy <      0.05091372 Ry

```



```

total energy      = -128.88647981 Ry
estimated scf accuracy < 0.05091372 Ry
--
total energy      = -128.90106640 Ry
estimated scf accuracy < 0.01055485 Ry
--
total energy      = -128.90302693 Ry
estimated scf accuracy < 0.00022615 Ry
--
total energy      = -128.90306844 Ry
estimated scf accuracy < 0.00002059 Ry
--
total energy      = -128.90307086 Ry
estimated scf accuracy < 0.00000224 Ry
--
total energy      = -128.90307206 Ry
estimated scf accuracy < 0.00000065 Ry
--
total energy      = -128.90307218 Ry
estimated scf accuracy < 4.2E-09 Ry
--
total energy      = -128.90307218 Ry
estimated scf accuracy < 6.8E-10 Ry
--
! total energy      = -128.90307218 Ry
estimated scf accuracy < 6.6E-11 Ry

```

➤ SCF is converged when
accuracy < conv_thr

EXERCISE 2 — PARAMETER CONVERGENCE

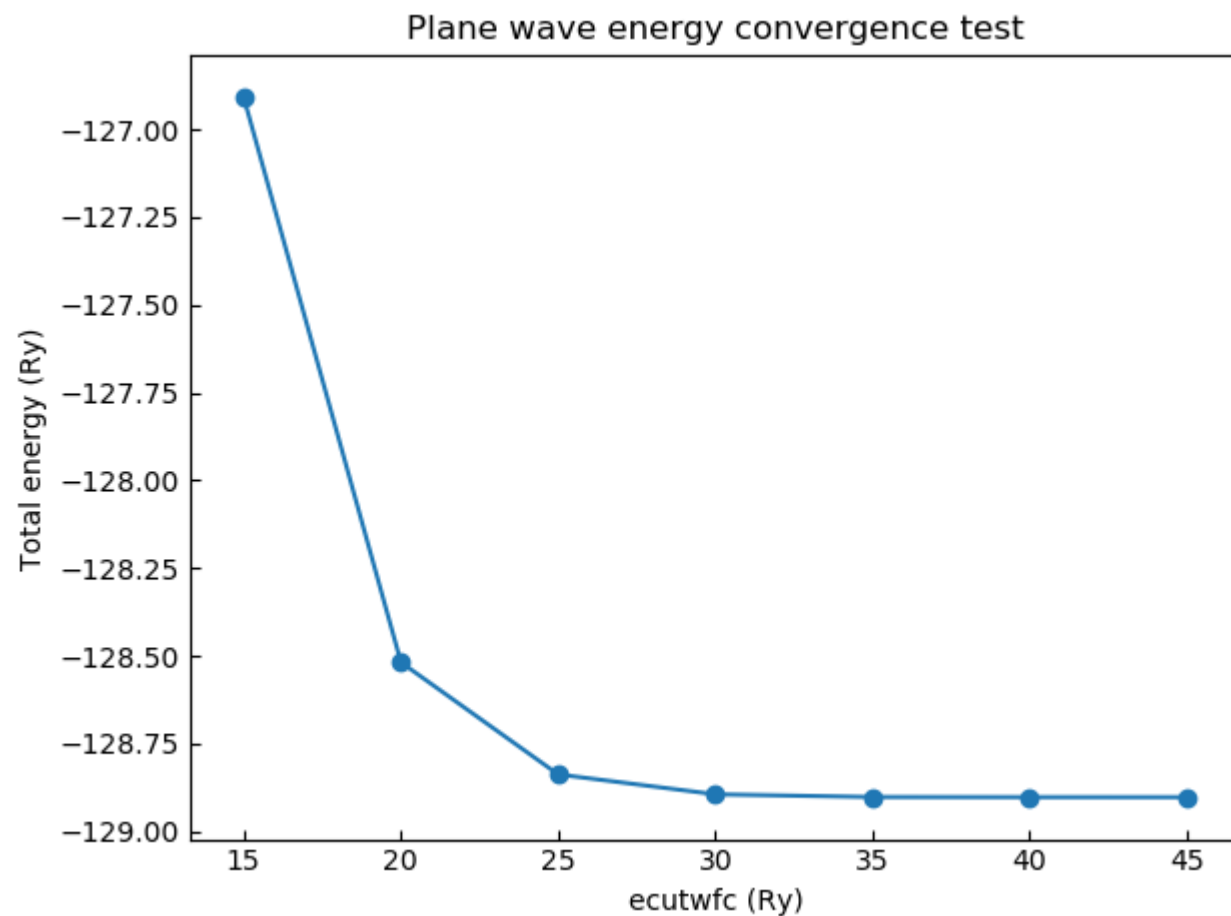
EXERCISE 2 — PARAMETER CONVERGENCE

- We must ensure that the results of a calculation do not depend on free parameters
- In this exercise, we will look at the convergence of energy with respect to:
 1. *ecutwfc*
 2. k-point grid density

EXERCISE 2 — PARAMETER CONVERGENCE

- $ecutwfc$ = plane wave (basis set) cutoff energy
- Convergence w.r.t. to $ecutwfc$ is a property of the pseudopotential(s) used
- Absolute energy typically converges slower than other properties (e.g. structure)

EXERCISE 2 — PARAMETER CONVERGENCE



EXERCISE 2 — PARAMETER CONVERGENCE

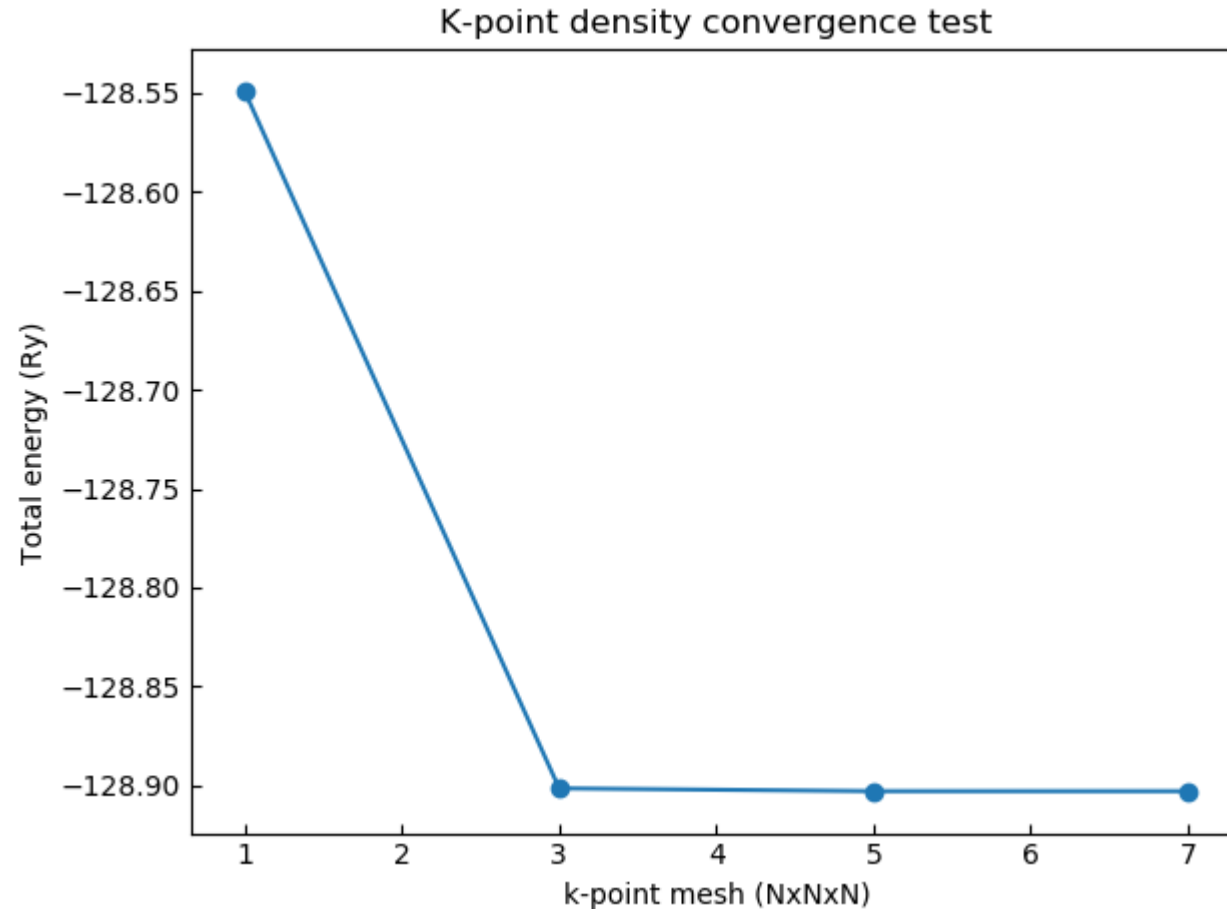
- k-points can be specified as a list of (specialized) points or a uniform grid
- If a list is chosen (usually for band structure plots): provide a list of k-points in the irreducible BZ and corresponding symmetry weights
- FAQ: where to find special k-points and their weights?
 1. Auxillary code (kpoints.x, [SeeK-Path](#))
 2. Papers
- We will also see how to explicitly select a k-point path in XcrySDen in an another exercise

EXERCISE 2 — PARAMETER CONVERGENCE

- If a uniform grid is chosen, the k-points are generated using the Monkhorst-Pack scheme
- See [pw.x documentation](#) for more info on the K_POINTS card
- Reasonably dense k-point grids can be automatically generated from structure files via

<https://www.materialscloud.org/work/tools/qeinputgenerator>

EXERCISE 2 — PARAMETER CONVERGENCE



EXERCISE 3 — CHARGE DENSITY

EXERCISE 3 — CHARGE DENSITY

- In this exercise, we will introduce the postprocessing program **pp.x**
- pp.x is used to extract information out of pw.x calculations
- pp.x input files are structured similarly to pw.x ([pp.x documentation](#))
- To show pp.x basic functionality, we will plot the ground state charge density

EXERCISE 3 — CHARGE DENSITY

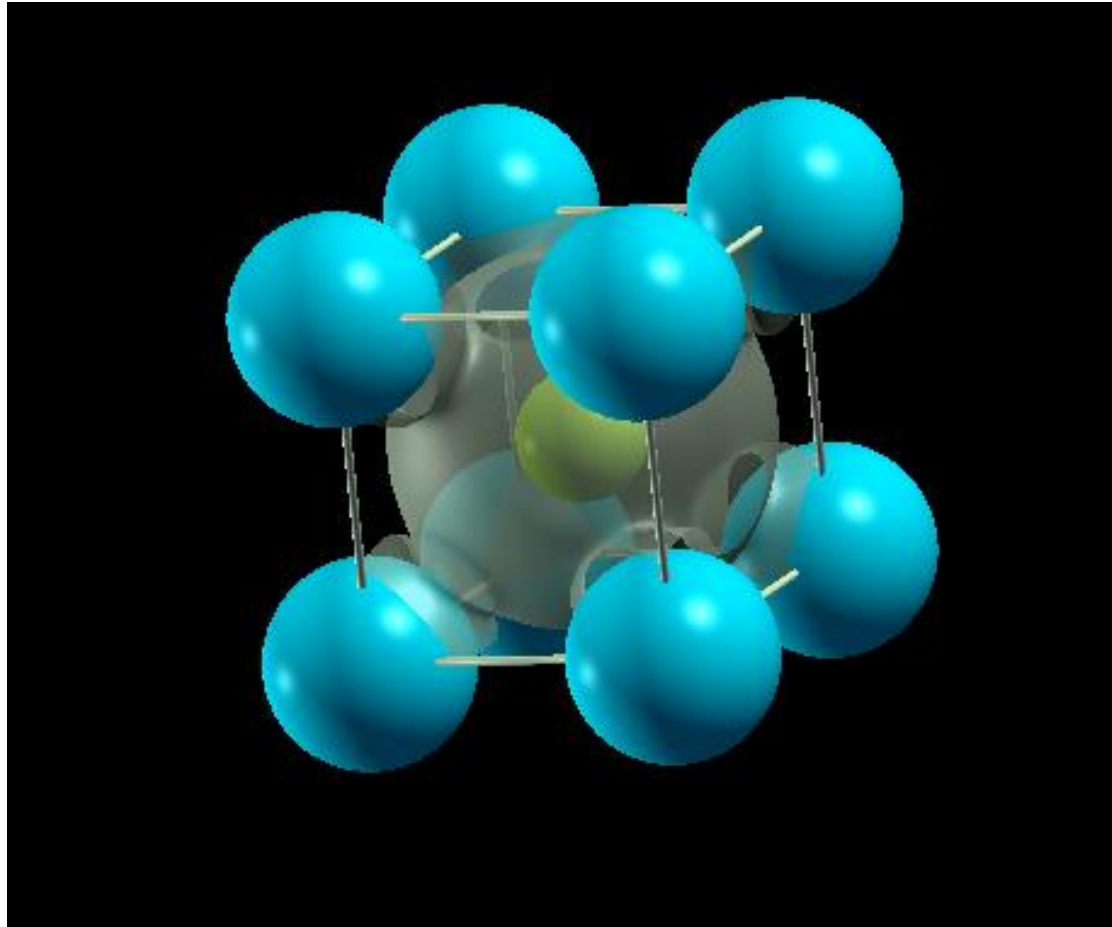
➤ pp.x has two steps

1. &INPUTPP = extract the desired data from pw.x output and write to the „filplot” file
2. &PLOT = write the extracted data to a desired format

➤ Programs for visualization of pp.x output:

1. XcrySDen
2. Vesta (**gaussian .cube** files)
3. Gnuplot
4. ...

EXERCISE 3 — CHARGE DENSITY



EXERCISE 4 — DENSITY OF STATES

EXERCISE 4 — DENSITY OF STATES

- In this exercise, we will be using a metallic system (silver) as an example
- In SCF calculations, it is necessary to perform integration over occupied states
- The step-like Fermi-Dirac distribution in metals can be a source of numerical issues
- This is avoided by replacing the FD distribution with a smoother function

EXERCISE 4 — DENSITY OF STATES

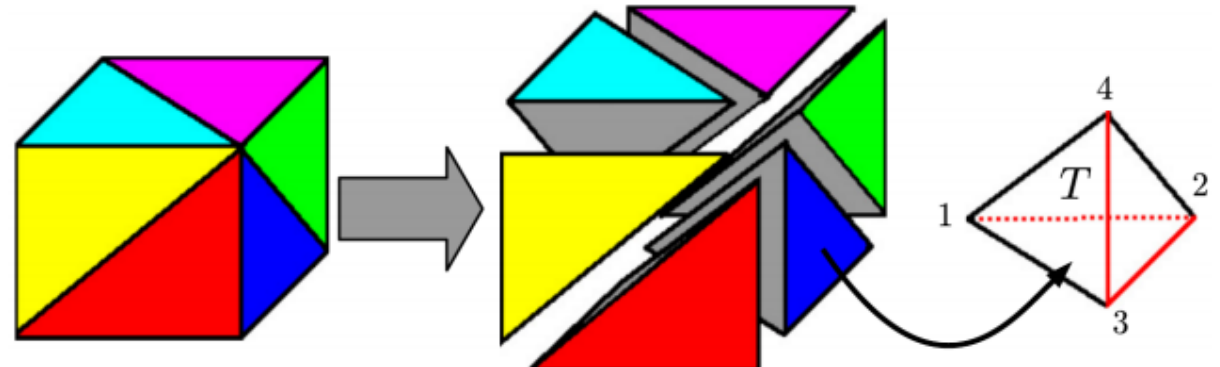
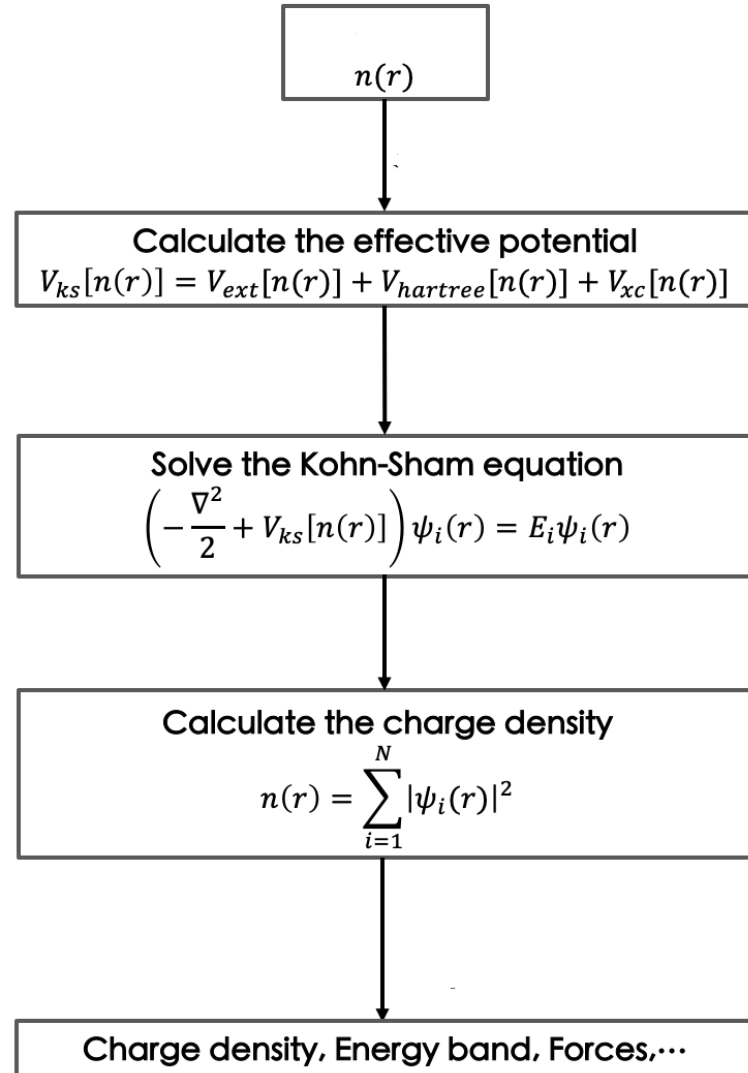
- Note the presence of three new variables in the pw.x input file:
 1. *occupations* = tell QE how to treat the occupied states (fixed, smeared, ...)
 2. *smeearing* = choose the type of smearing (Methfessel-Paxton)
 3. *degauss* = value of the gaussian spreading (Ry) for BZ integration

- Results should also be converged w.r.t. the *degauss* value

EXERCISE 4 — DENSITY OF STATES

- After running *pw.x*, notice that the Fermi energy is now calculated
- The next step is running a non-SCF *pw.x* calculation with a denser k-point mesh
- *calculation* = 'nscf', *occupations* = 'tetrahedra'

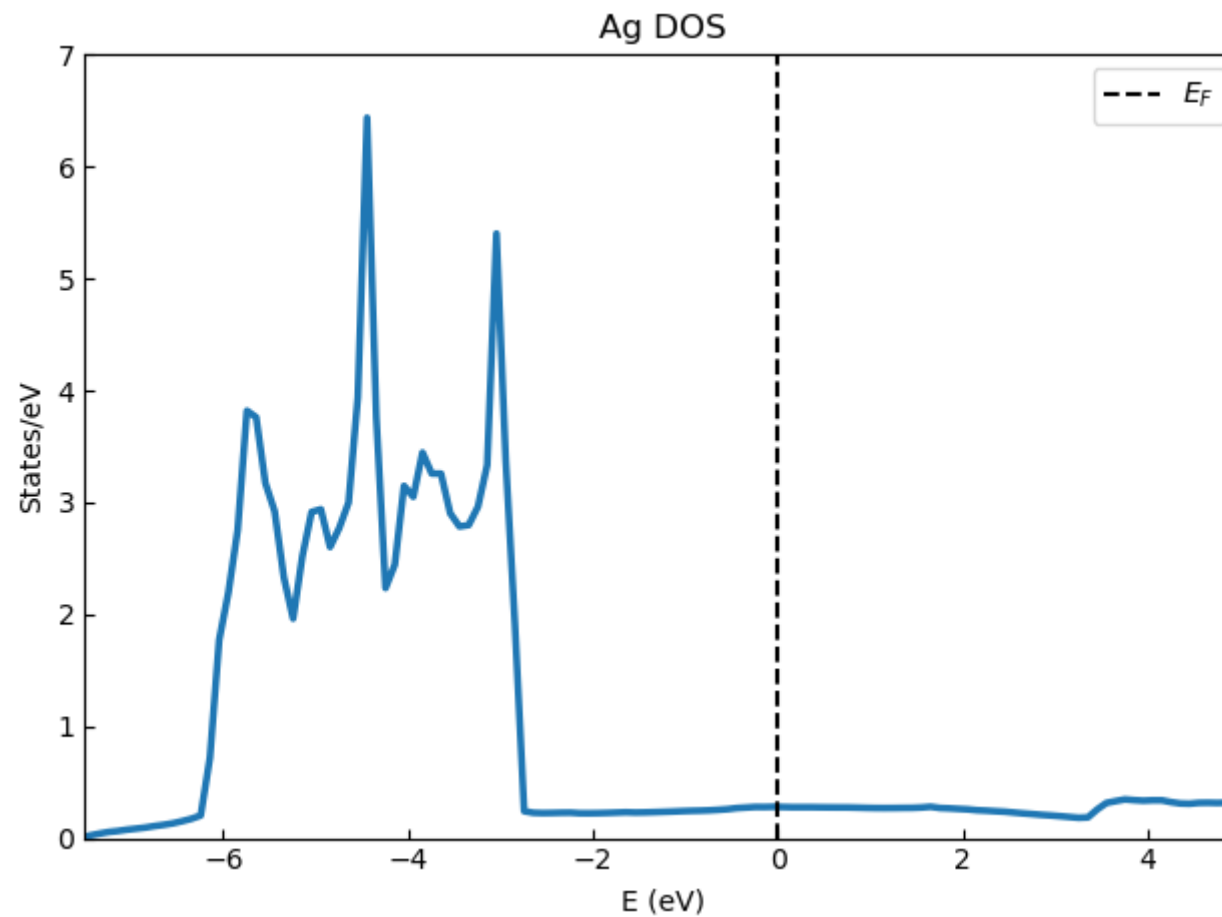
➤ *calculation* = 'nscf', *occupations* = 'tetrahedra'



EXERCISE 4 — DENSITY OF STATES

- The density of states is calculated from the NSCF output using the program `dos.x`
- Look at the [`dos.x` documentation](#)

EXERCISE 4 — DENSITY OF STATES



EXERCISE 5 — BAND STRUCTURE

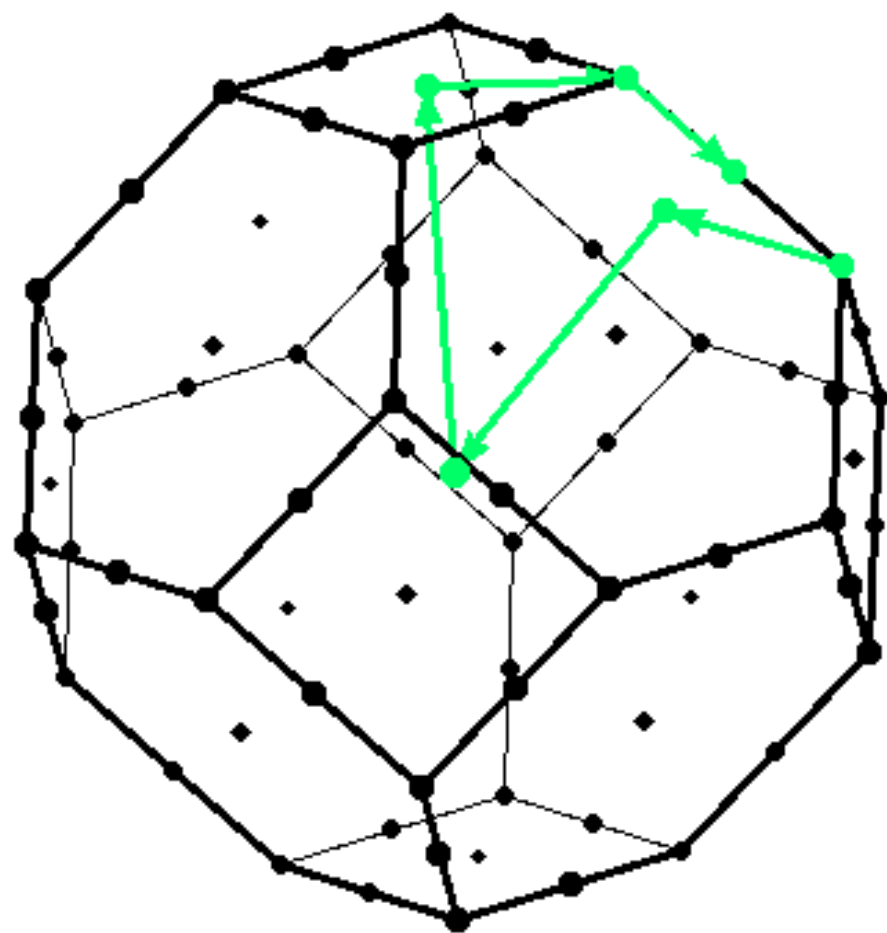
EXERCISE 5 — BAND STRUCTURE

- The usual SCF calculation is followed by an NSCF calculation along a specified path in the 1 BZ
- *calculation* = 'bands'
- Useful links for finding special points in the 1 BZ:
 1. [SeeK-path](#)
 2. [Bilbao Crystallographic Server](#)
 3. [Wikipedia BZ article](#)

EXERCISE 5 — BAND STRUCTURE

- In this exercise, we will explicitly set the k-path with XcrySDen
- There is no unique choice of the path, it is often chosen to best represent the bands of interest
- We'll use the path:

$$W - L - \Gamma - X - W - K$$



Rotation Step:

5

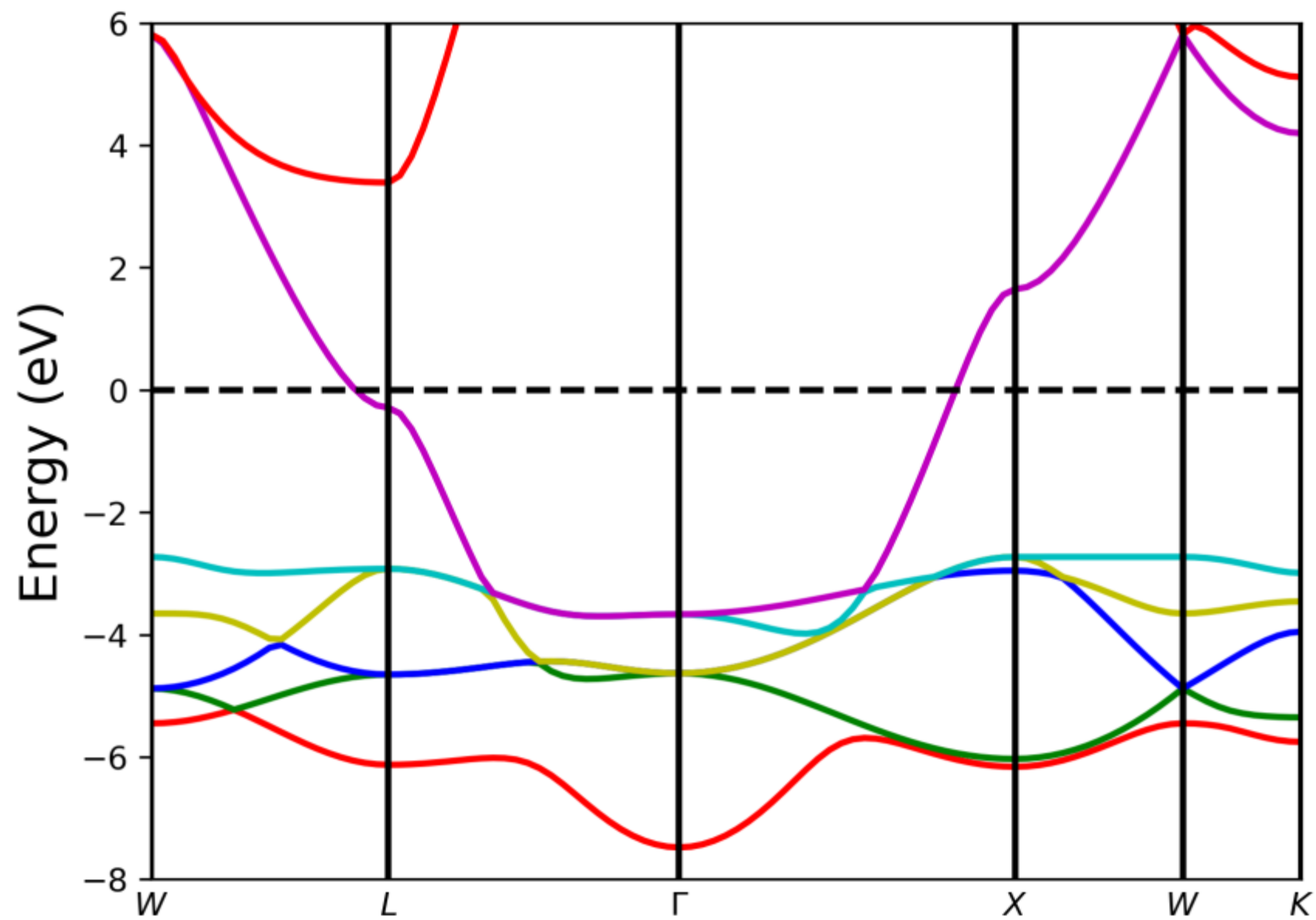
of Selected Points:

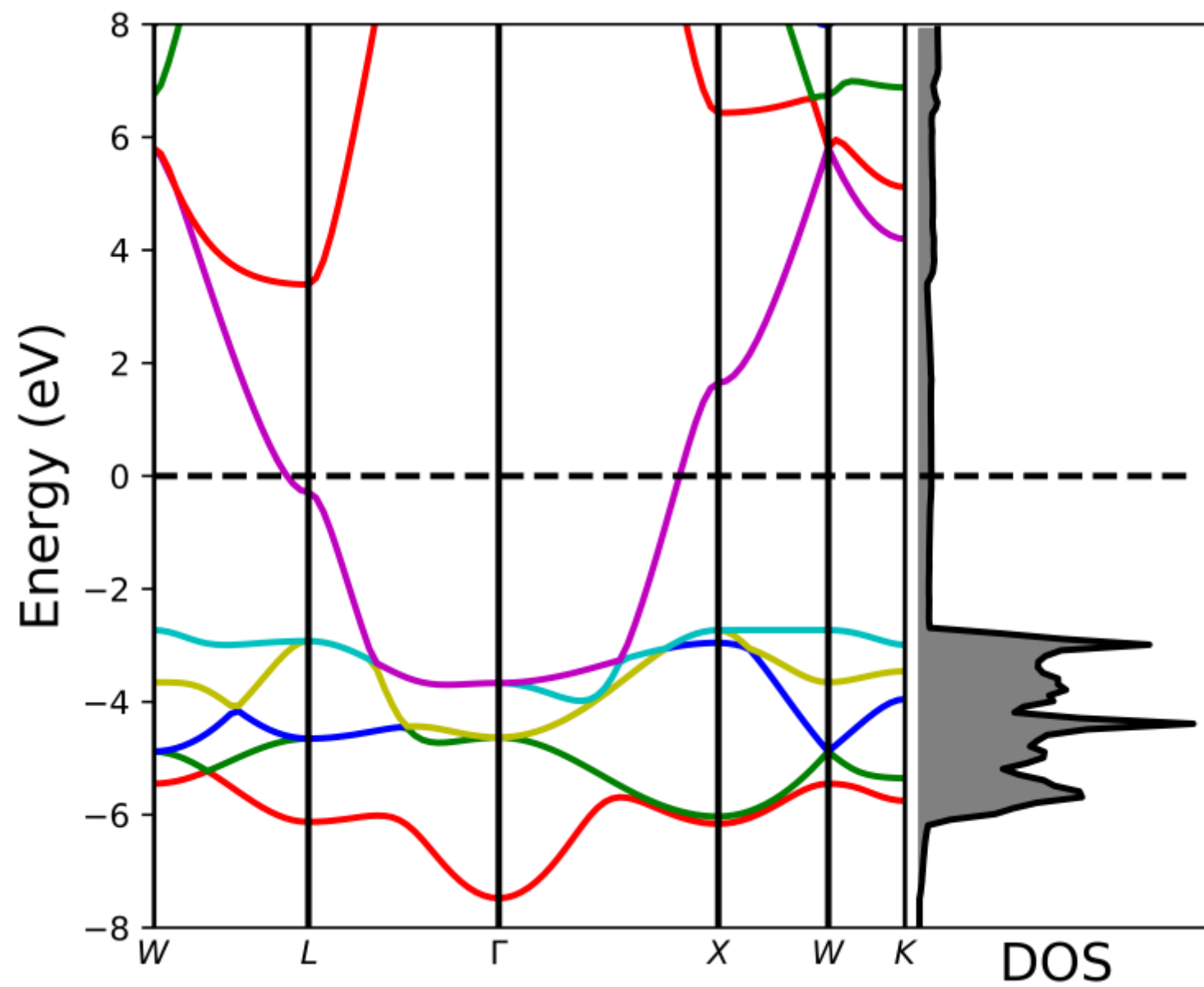
6

#	reciprocal coordinates	label
1	-0.25000 0.25000 -0.50000	W
2	0.00000 0.50000 0.00000	L
3	0.00000 0.00000 0.00000	GAMMA
4	0.50000 0.50000 0.00000	X
5	0.25000 0.50000 -0.25000	W
6	0.00000 0.37500 -0.37500	K
7		
8		
9		
10		
11		
12		
13		
14		
15		
16		

EXERCISE 5 — BAND STRUCTURE

- The band structure is extracted from the NSCF calculation using the postprocessing program *bands.x*
- [bands.x documentation](#)



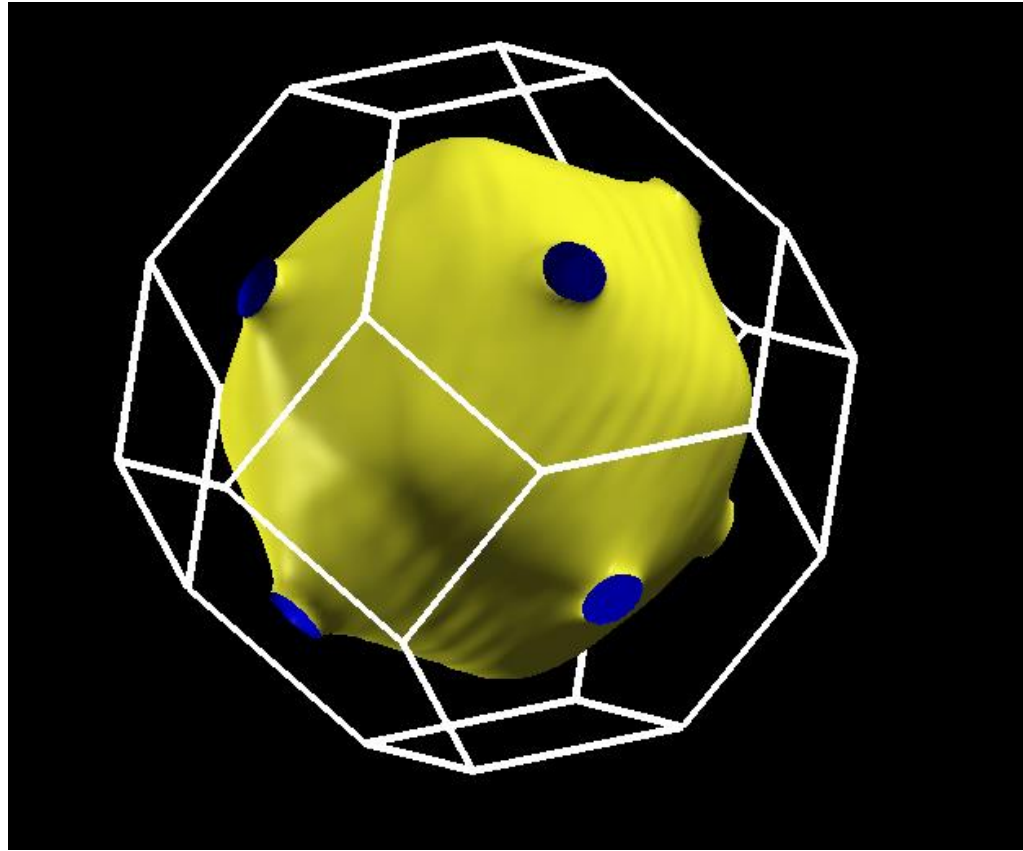


EXERCISE 6 — FERMI SURFACE

EXERCISE 6 — FERMI SURFACE

- Plotting the Fermi surface is a very simple two-step calculation
 1. SCF calculation
 2. Extracting the Fermi surface via the postprocessing program *fs.x*

EXERCISE 6 — FERMI SURFACE



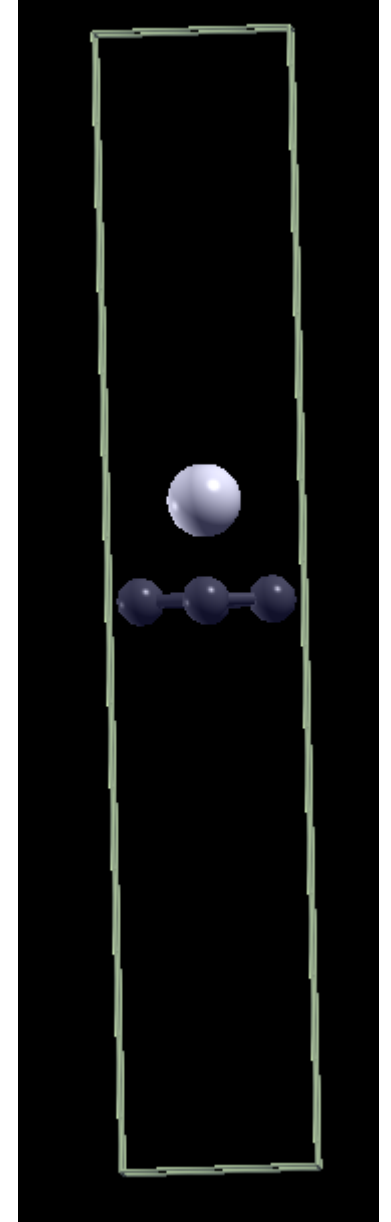
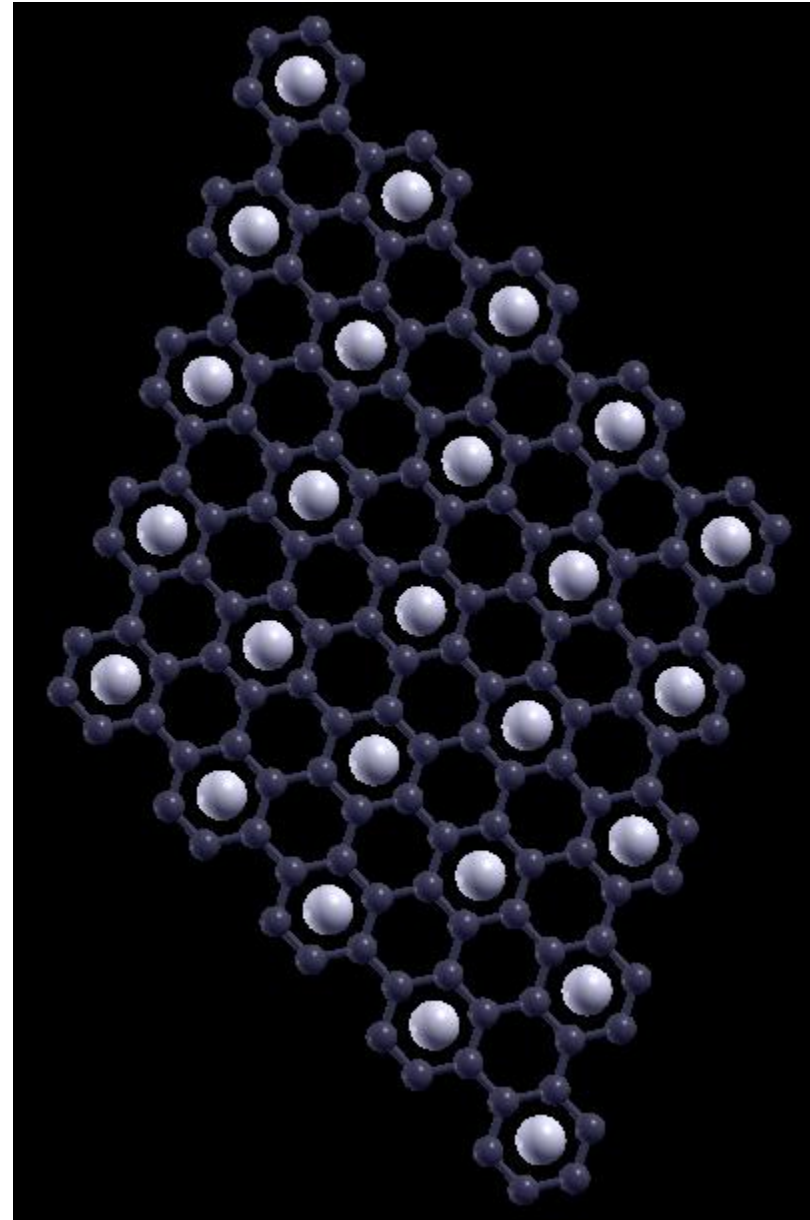
EXERCISE 7 — CHARGE TRANSFER

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➤ In this exercise, we will:

1. Calculate the formation energy of a LiC_6 two-dimensional layer
2. Observe the charge transfer due to the formation of Li-C bonds

- Note the long cell axis in the z-direction
- This is a way to treat 2D systems
- In the following exercise, we will show an alternative way to deal with non-periodic systems



EXERCISE 7 — CHARGE TRANSFER

- The formation energy is

$$E_{\text{form}} = E(\text{LiC}_6) - (E(\text{Li}) + E(\text{C}_6)) \approx -0.0207 \text{ Ry}$$

- This means that at $T = 0 \text{ K}$, adsorption of lithium on a graphene is a favourable reaction
- Note that this type of calculation doesn't give us any information on the dynamics of the process
- Molecular dynamics (MD), nudge elastic band (NEB), ...

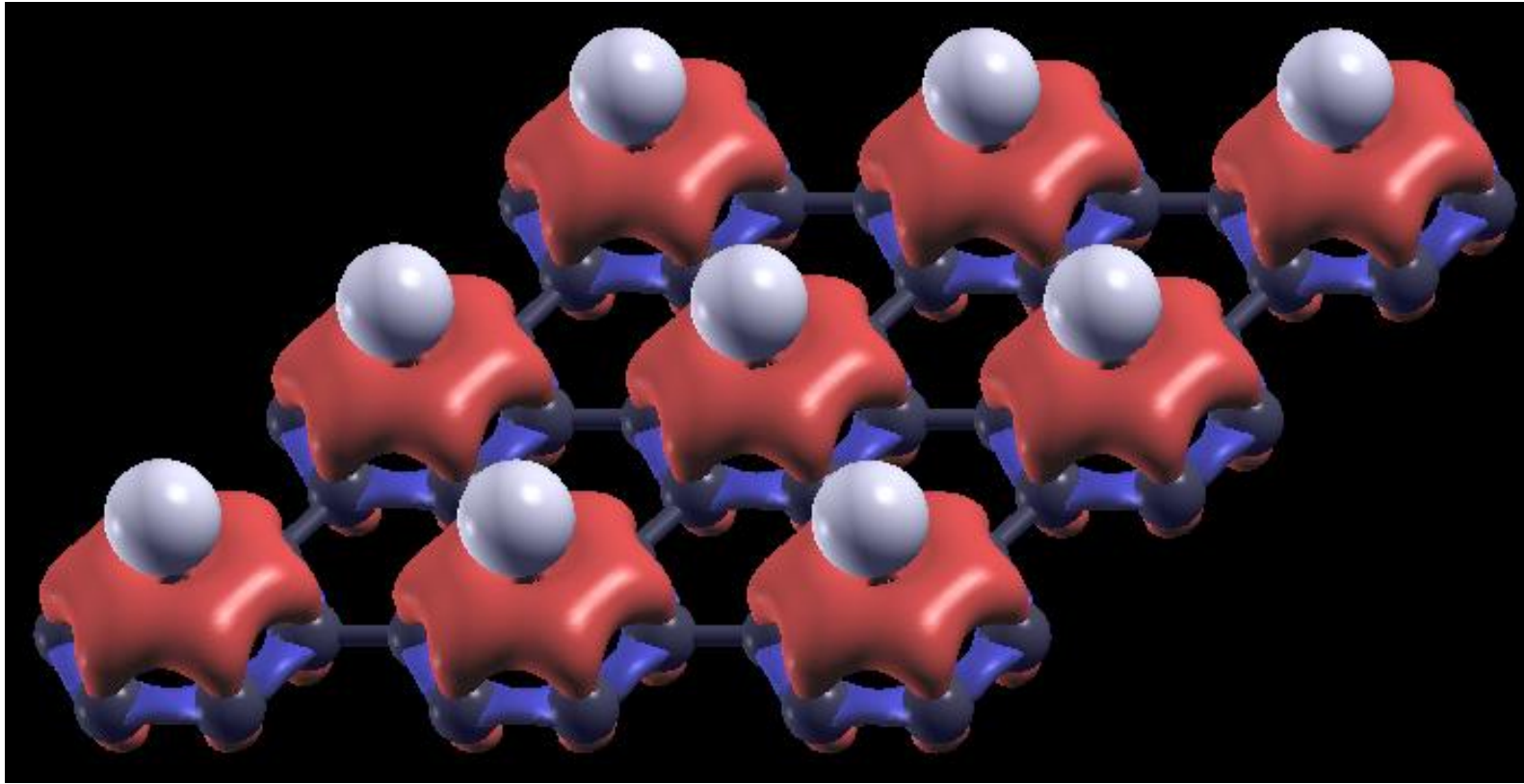
EXERCISE 7 — CHARGE TRANSFER

➤ Charge difference is similarly calculated as:

$$\rho_{\text{diff}} = \rho(\text{LiC}_6) - (\rho(\text{Li}) + \rho(\text{C}_6))$$

1. We extract the ground state density of the three systems using *pp.x* and *plot_num* = 0
2. Subtract the charges by specifying *nfile* = 3 and appropriate weights

EXERCISE 7 — CHARGE TRANSFER



➤ Surfaces of constant charge density (red = +0.0025, blue = -0.0025)

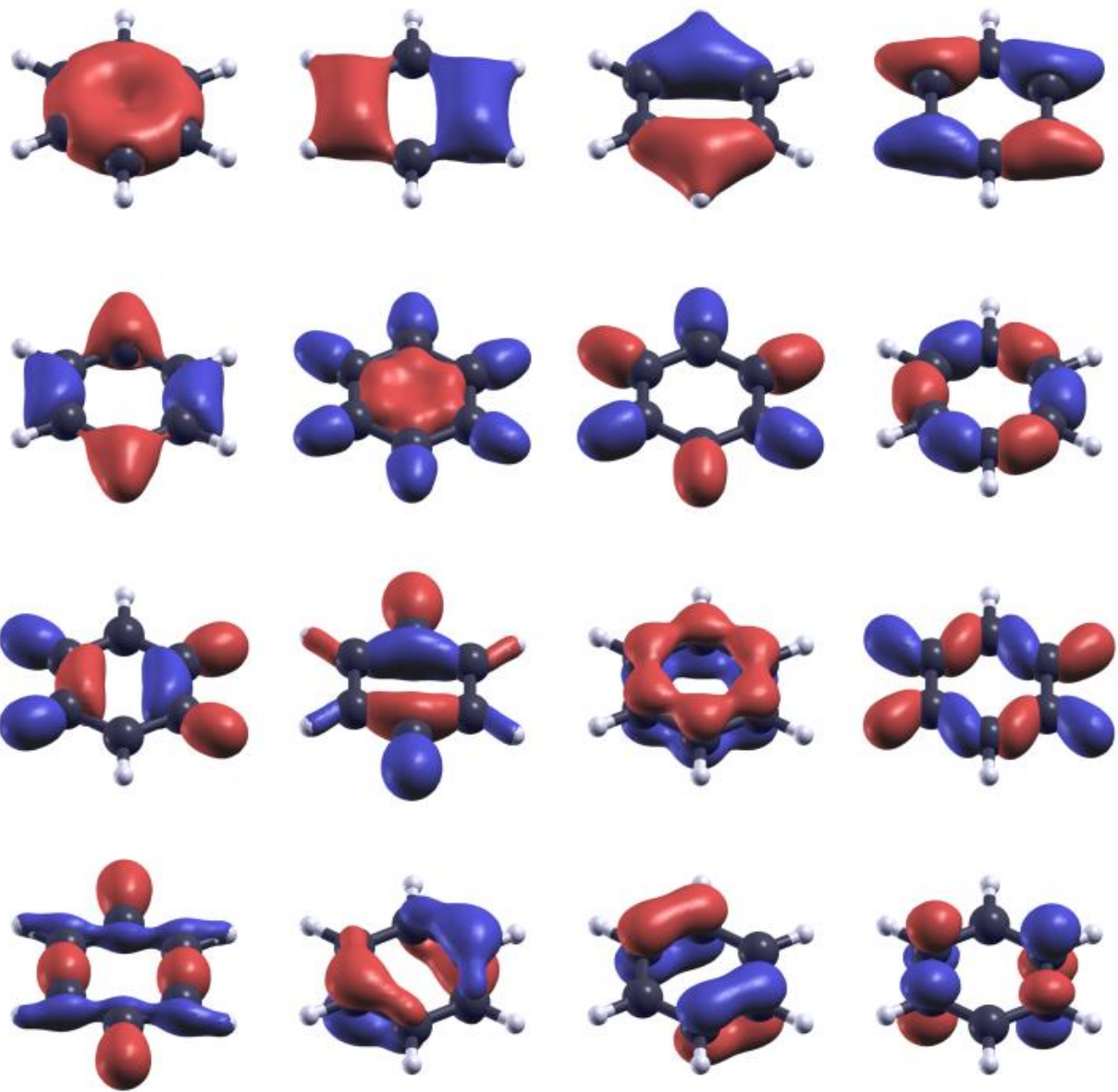
EXERCISE 8 — KOHN-SHAM ORBITALS

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- In this exercise, we will plot the Kohn-Sham orbitals of a single benzene (C_6H_6) molecule
- QE assumes periodic boundary conditions
- To simulate isolated (nonperiodic) systems we have two options
 1. Make a large cell
 2. Use one of the corrections defined under the *assume_isolated* variable in the [pw.x documentation](#)

EXERCISE 8 — KOHN-SHAM ORBITALS

- The orbitals are extracted from the SCF calculation with *pp.x* and *plot_num=7*
- LUMO is specified as *kband(2)=16* because the HOMO orbital is
- $$n_{HOMO} = \frac{N_C Z_C + N_H Z_H}{2} = \frac{6*4 + 6*1}{2} = 15$$
- The number of valence electrons Z_X of C and H atoms is specified in the pseudopotential files





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