

DFT in practice: from simple to advanced functionals

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Based on slides by Nicola Colonna³ & Iuri Timrov⁴

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⁴EPFL and NCCR-Marvel



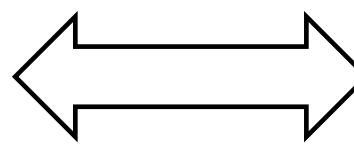
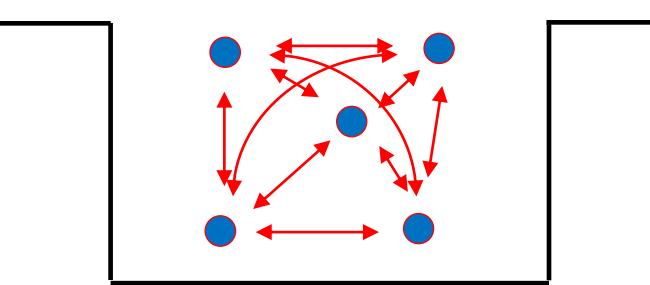
MARVEL
NATIONAL CENTRE OF COMPETENCE IN RESEARCH

QUANTUM MOBILE MAX DRIVING THE EXASCALE TRANSITION

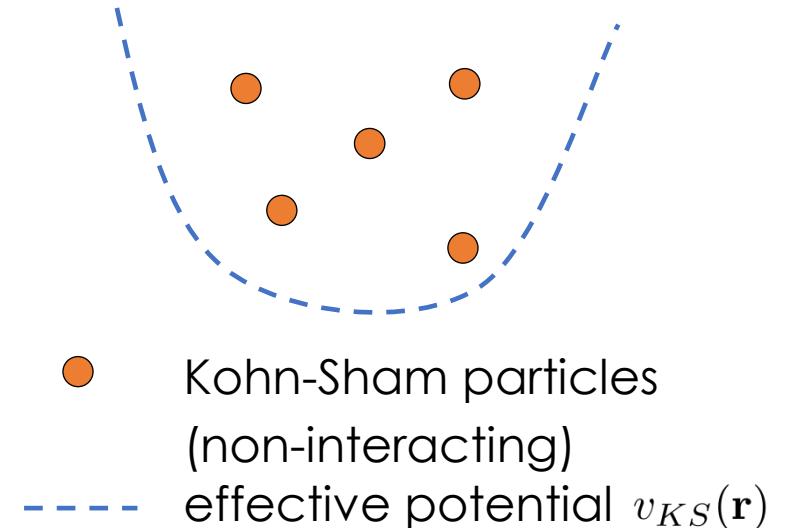
Outline

- **Brief recap on KS-DFT.** KS equations, common approximations to the xc energy functional, KS in practice
- **Exercise 0.** Standard DFT: PBE band structure of FCC Silicon
- **Exercise 1-2.** Hybrid DFT: electronic structure of FCC Silicon
- **Exercise 3-4.** Meta-GGA: electronic structure of FCC Silicon and BCC Iron using SCAN

Kohn-Sham DFT



- electrons
- ↔ interaction
- external potential $v_{ext}(\mathbf{r})$



- Kohn-Sham particles
(non-interacting)
- - - effective potential $v_{KS}(\mathbf{r})$

$$E[n] = T_s[n] + E_H[n] + E_{xc}[n] + \int d\mathbf{r} V_{ext}(\mathbf{r})n(\mathbf{r})$$

$$\left[-\frac{\hbar^2}{2m_e} \nabla^2 + v_{KS}[n](\mathbf{r}) \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

$$n(\mathbf{r}) = \sum_{i=1}^N |\phi_i(\mathbf{r})|^2$$

$$v_{KS}[n](\mathbf{r}) = V_{ext}(\mathbf{r}) + e^2 \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}$$

The exchange and correlation energy functional

- **LDA:** The xc energy density of the inhomogeneous system in \mathbf{r} is locally approximated with that of a homogeneous electron gas with density $n(\mathbf{r})$

$$E_{\text{xc}}^{\text{LDA}} = \int d\mathbf{r} n(\mathbf{r}) \varepsilon_{\text{xc}}^{\text{HEG}}(n(\mathbf{r}))$$

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- **GGA:** include the dependence on the gradient of the density

$$E_{\text{xc}}^{\text{GGA}} = \int d\mathbf{r} n(\mathbf{r}) \varepsilon_{\text{xc}}(n(\mathbf{r}), \nabla n(\mathbf{r})) = \int d\mathbf{r} n(\mathbf{r}) \varepsilon_{\text{xc}}^{\text{HEG}}(n(\mathbf{r})) F_{\text{xc}}(n(\mathbf{r}), \nabla n(\mathbf{r}))$$

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- **Meta-GGA:** include the dependency on the laplacian of the density and kinetic energy density

$$E_{\text{xc}}^{\text{mGGA}} = \int d\mathbf{r} n(\mathbf{r}) \varepsilon_{\text{xc}}(n(\mathbf{r}), \nabla n(\mathbf{r}), \nabla^2 n(\mathbf{r}), \tau) \quad \tau = \frac{1}{2} \sum_i |\nabla \psi_i(\mathbf{r})|^2$$

The exchange and correlation energy functional

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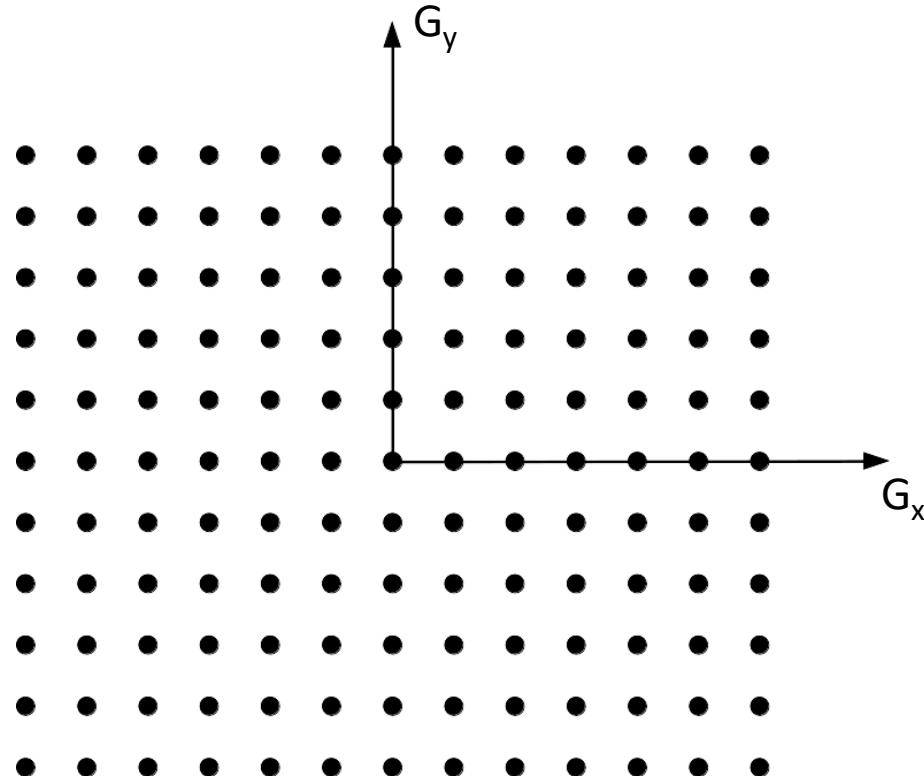
- **Hybrid functionals:** include a fraction of Fock exchange

$$E_{\text{xc}}^{\text{hyb}} = (1 - a_0) E_{\text{x}}^{\text{DFT}} + a_0 E_{\text{x}}^{\text{HF}} + E_{\text{c}}^{\text{DFT}}$$

KS-DFT in practice: PW and PP

Wavefunctions are represented in Plane Waves (PW)

$$\phi_i(\mathbf{r}) = \sum_{\mathbf{G}} c(\mathbf{G}) \exp(i\mathbf{G} \cdot \mathbf{r})$$

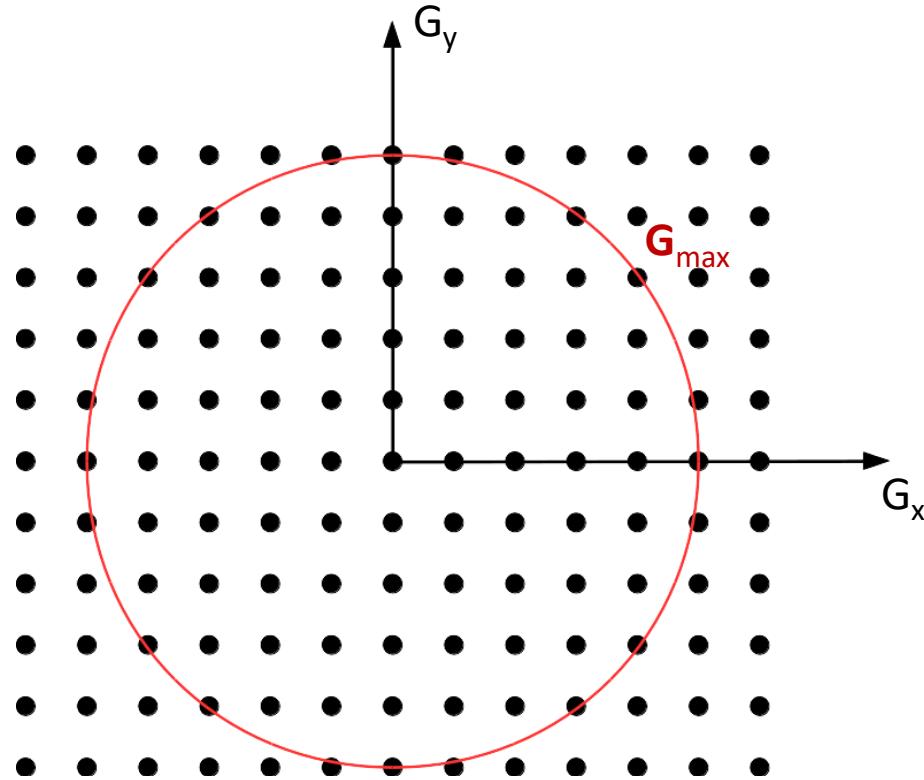


- Only Fourier components compatible with the periodicity of the lattice $\mathbf{G}=n_1\mathbf{b}_1+n_2\mathbf{b}_2$

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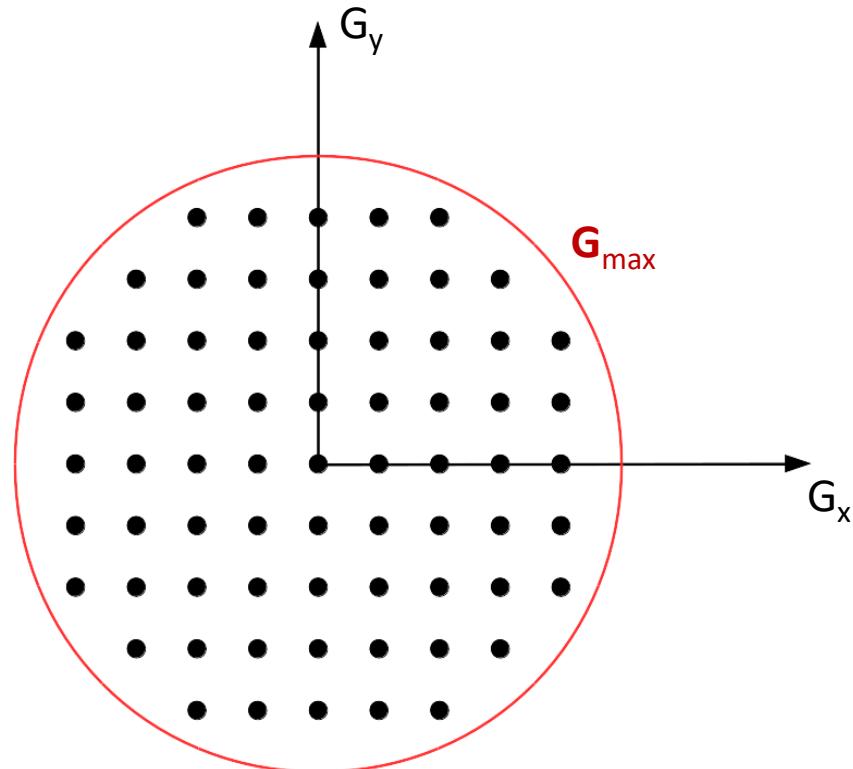


- Only Fourier components compatible with the periodicity of the lattice $\mathbf{G}=n_1\mathbf{b}_1+n_2\mathbf{b}_2$
- All \mathbf{G} vectors with norm smaller than $|\mathbf{G}|_{\max}$
- $|\mathbf{G}|_{\max}$ defined by setting a cutoff on the kinetic energy $E_{\text{cut}} = \hbar^2/2\pi |\mathbf{G}|_{\max}^2$

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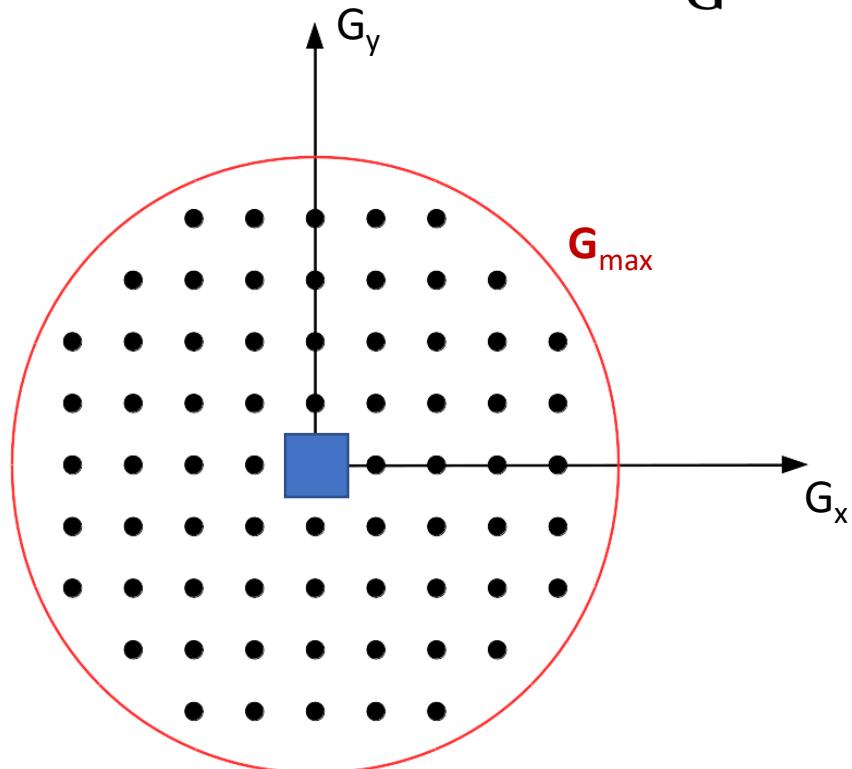


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- `ecutwfc`: QE Input parameter for E_{cut}

KS-DFT in practice: PW and PP

In a **periodic system** KS states are **Bloch functions**

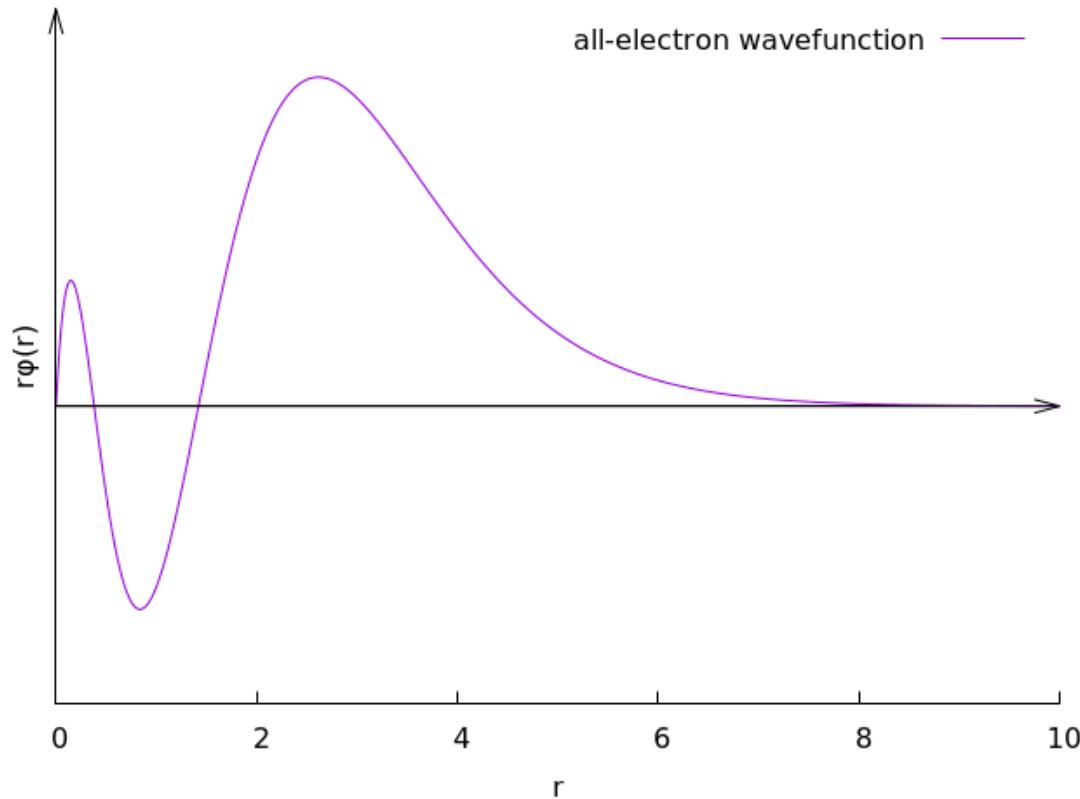
$$\psi_{\mathbf{k}n}(\mathbf{r}) = \exp[i\mathbf{k} \cdot \mathbf{r}] u_{\mathbf{k}n}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{k}n}(\mathbf{G}) \exp [i(\mathbf{G} + \mathbf{k}) \cdot \mathbf{r}]$$



- Only Fourier components compatible with the periodicity of the primitive cell $\mathbf{G} = n_1 \mathbf{b}_1 + n_2 \mathbf{b}_2$
- \mathbf{k} belong to the Brillouin zone (
- All \mathbf{G} vectors such that $\hbar^2/2\pi | \mathbf{k} + \mathbf{G} |^2 < E_{\text{cut}}$
- Many properties require integration over the \mathbf{k} -points \rightarrow BZ sampling (`K_POINTS` card)

KS-DFT in practice: PW and PP

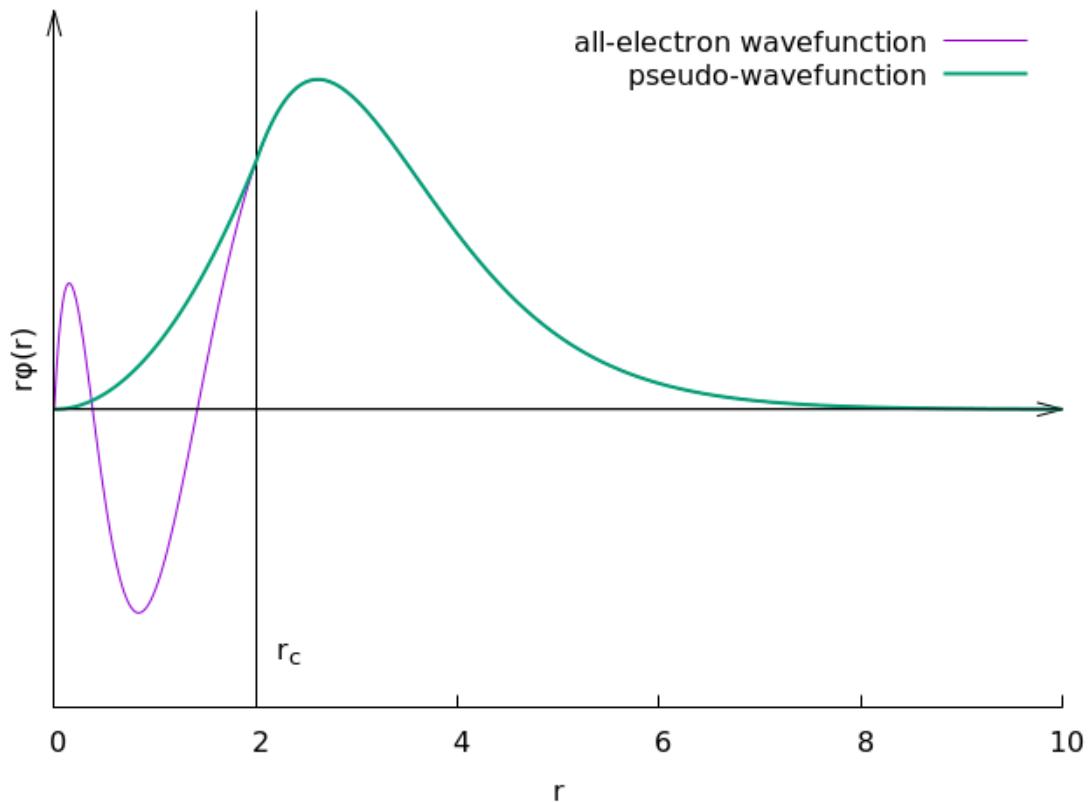
The use of pseudo-potentials allows to ignore chemically inert core electrons and make PW calculation feasible



- Strong oscillations close to the nuclei: large number of PW needed

KS-DFT in practice: PW and PP

The use of pseudo-potentials allows to ignore chemically inert core electrons and make PW calculation feasible



- Strong oscillations close to the nuclei: large number of PW needed
- Replace the coulombic potential with a pseudo-potential that produces smooth pseudo-wavefunctions
- Different recipes: Norm-conserving, Ultra-soft, Projector-augmented-wave (PAW)

Where to find PPs

Standard solid-state pseudopotentials (SSSP):

<https://www.materialscloud.org/discover/sssp/table/efficiency>

SSSP Efficiency (version 1.1.2)

$$\Delta_{\text{eff}} = 0.44 \text{ meV}$$

[Download Cutoffs table](#)

 Pseudos

[Switch to SSSP Precision](#)

Updates v1.2.0 beta



*

La 40₍₃₂₀₎ **Ce** 40₍₃₂₀₎ **Pr** 40₍₃₂₀₎ **Nd** 40₍₃₂₀₎ **Pm** 40₍₃₂₀₎ **Sm** 40₍₃₂₀₎ **Eu** 40₍₃₂₀₎ **Gd** 40₍₃₂₀₎ **Tb** 40₍₃₂₀₎ **Dy** 40₍₃₂₀₎ **Ho** 40₍₃₂₀₎ **Er** 40₍₃₂₀₎ **Tm** 40₍₃₂₀₎ **Yb** 40₍₃₂₀₎ **Lu** 45₍₃₆₀₎

Where to find PPs

Standard solid-state pseudopotentials (SSSP):

<https://www.materialscloud.org/discover/sssp/table/efficiency>

Quantum Espresso Website:

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

Optimized Norm-Conserving Vanderbilt (ONCV): SG15

http://www.quantum-simulation.org/potentials/sg15_oncv/

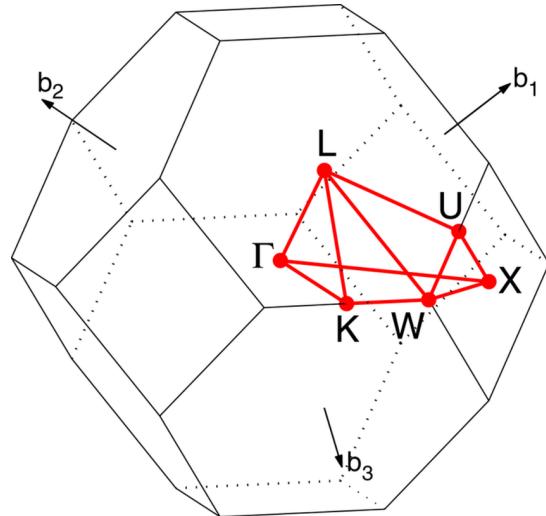
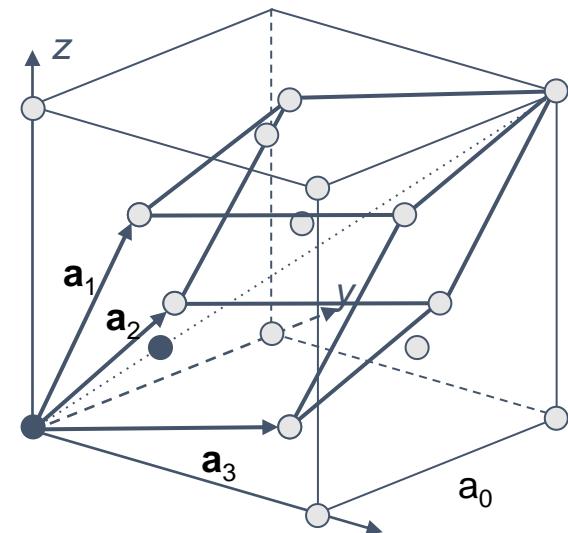
Optimized Norm-Conserving Vanderbilt (ONCV): pseudo-dojo

<http://www.pseudo-dojo.org/>

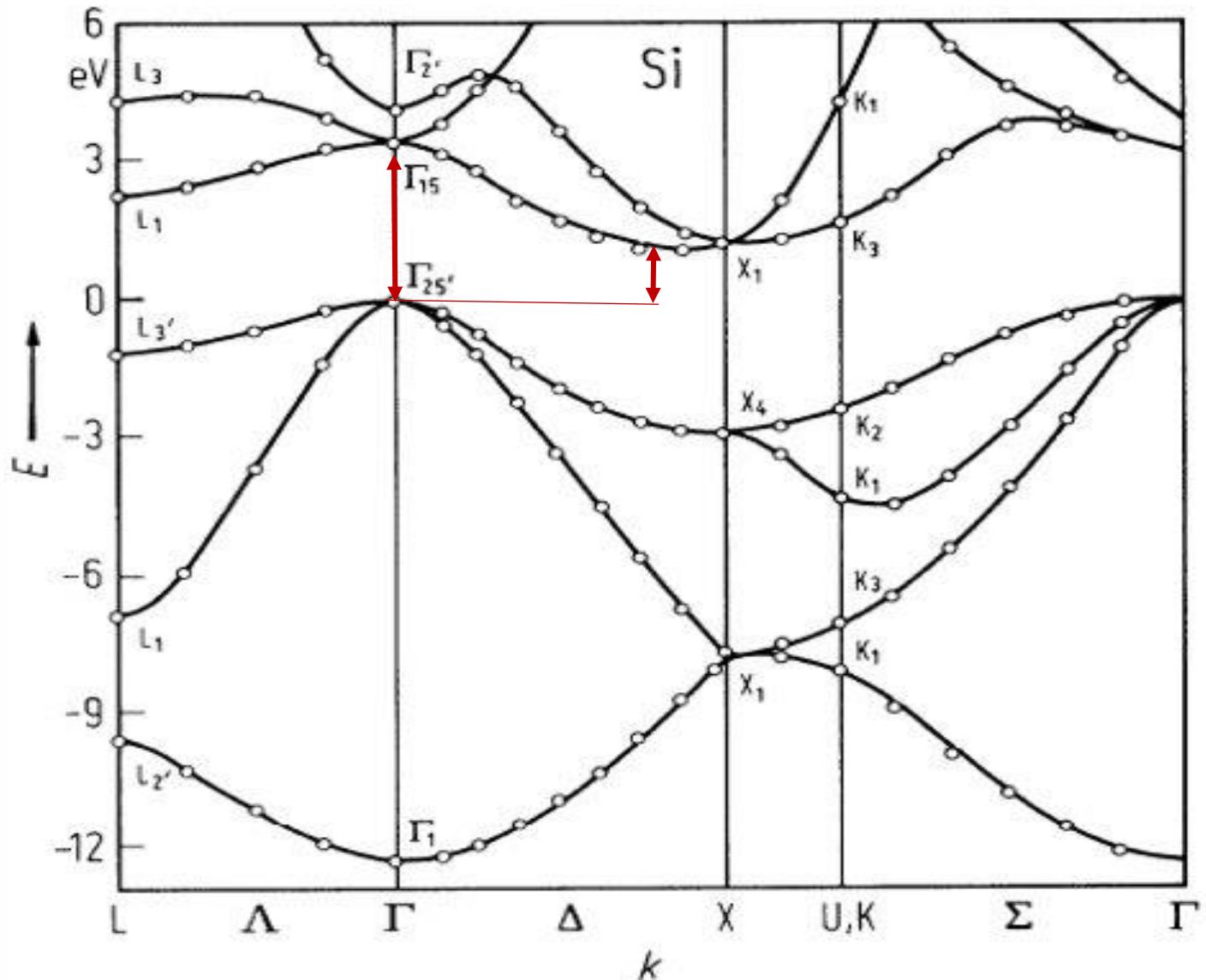
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FCC Silicon

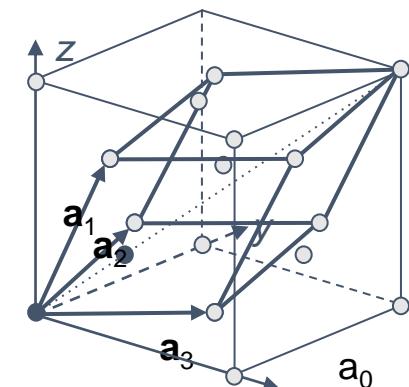


Goal of exercise0



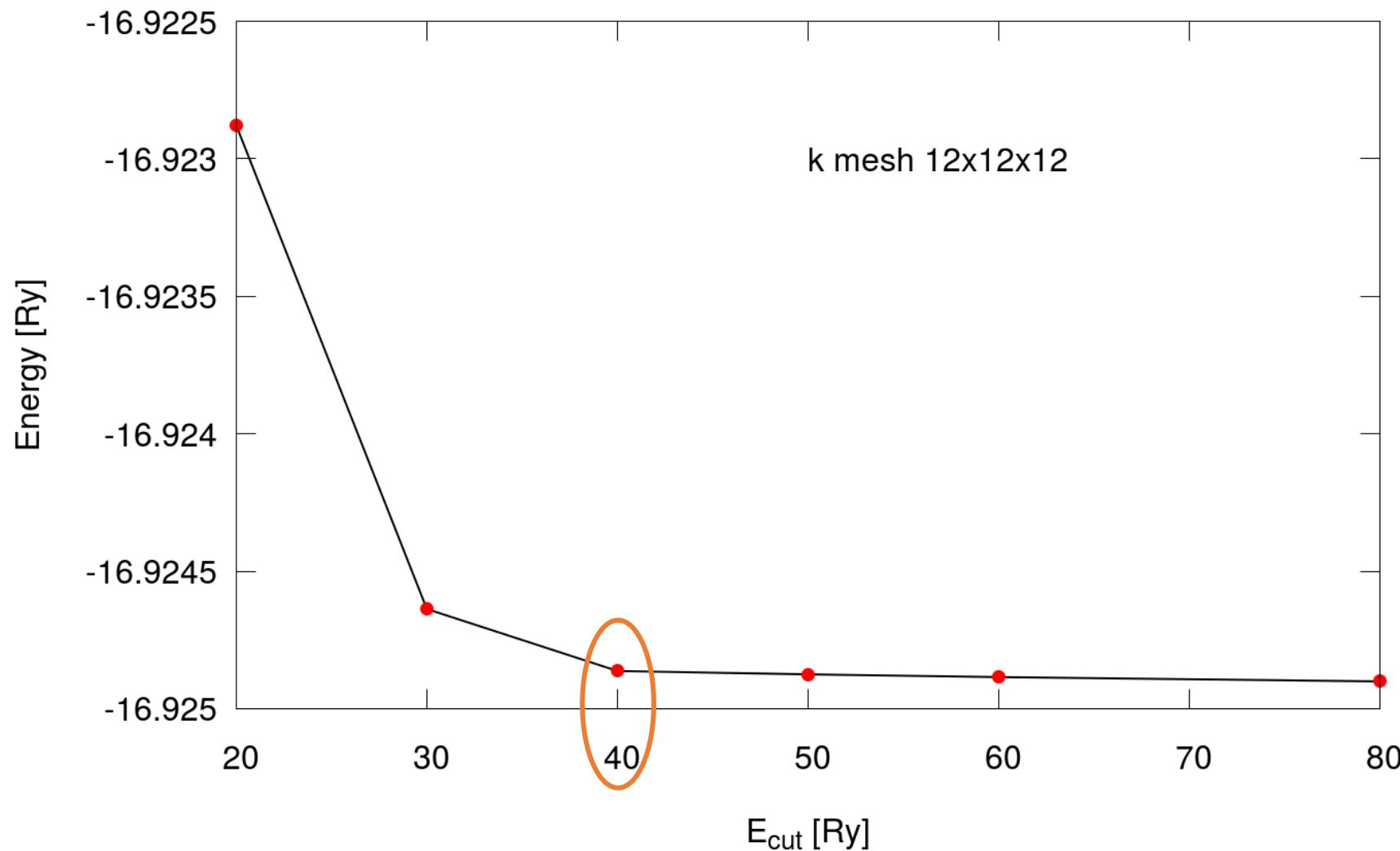
Silicon PBE electronic structure: SCF calculation

```
&control
  calculation='scf'           ← Self-consistent field calculation
  prefix='Si'
  pseudo_dir = '../files/pseudo' ← Directory containing the PPs
 outdir='./out'               ← Temporary files re stored here
/
&system
  ibrav = 2, celldm(1) = 10.262, ← Specify here the crystal structure:
  nat = 2, ntyp = 1,             FCC, alat=10.20 Bohr, 2 Si atoms
  ecutwfc = xxx,                Cutoff for the Wave-Functions
/
&electrons
  conv_thr = 1.d-8             ← Convergence threshold for the SCF problem
/
ATOMIC_SPECIES
Si 28.086 Si.pbe_PseudoDojo.UPF ← Pseudopotential file
ATOMIC_POSITIONS {alat}
Si 0.00 0.00 0.00               ← Atomic positions
Si 0.25 0.25 0.25
K_POINTS {automatic}
XXX YYY ZZZ 0 0 0             ← BZ sampling
```

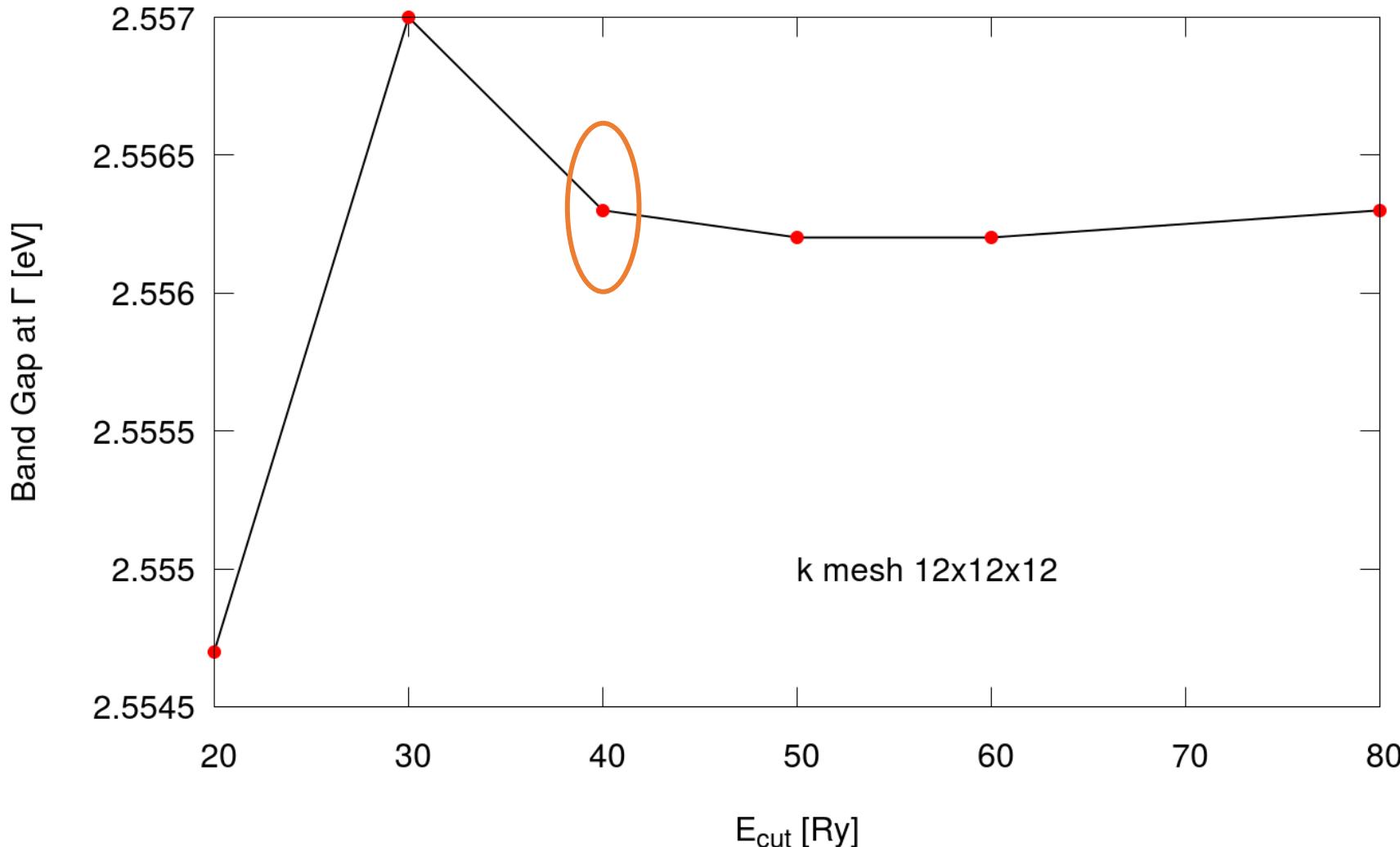


https://www.quantum-espresso.org/Doc/INPUT_PW.html

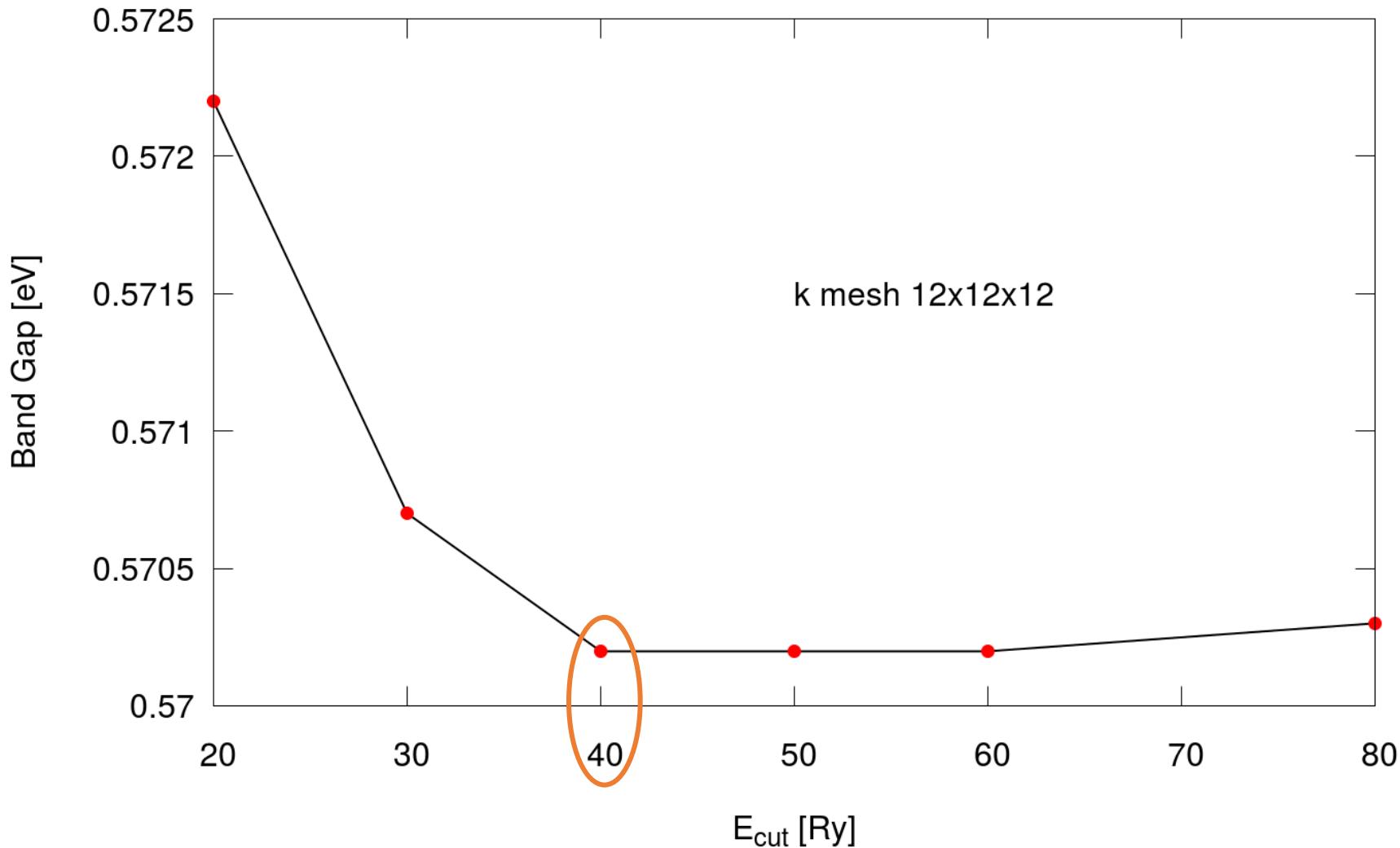
Convergence wrt ecut: total energy



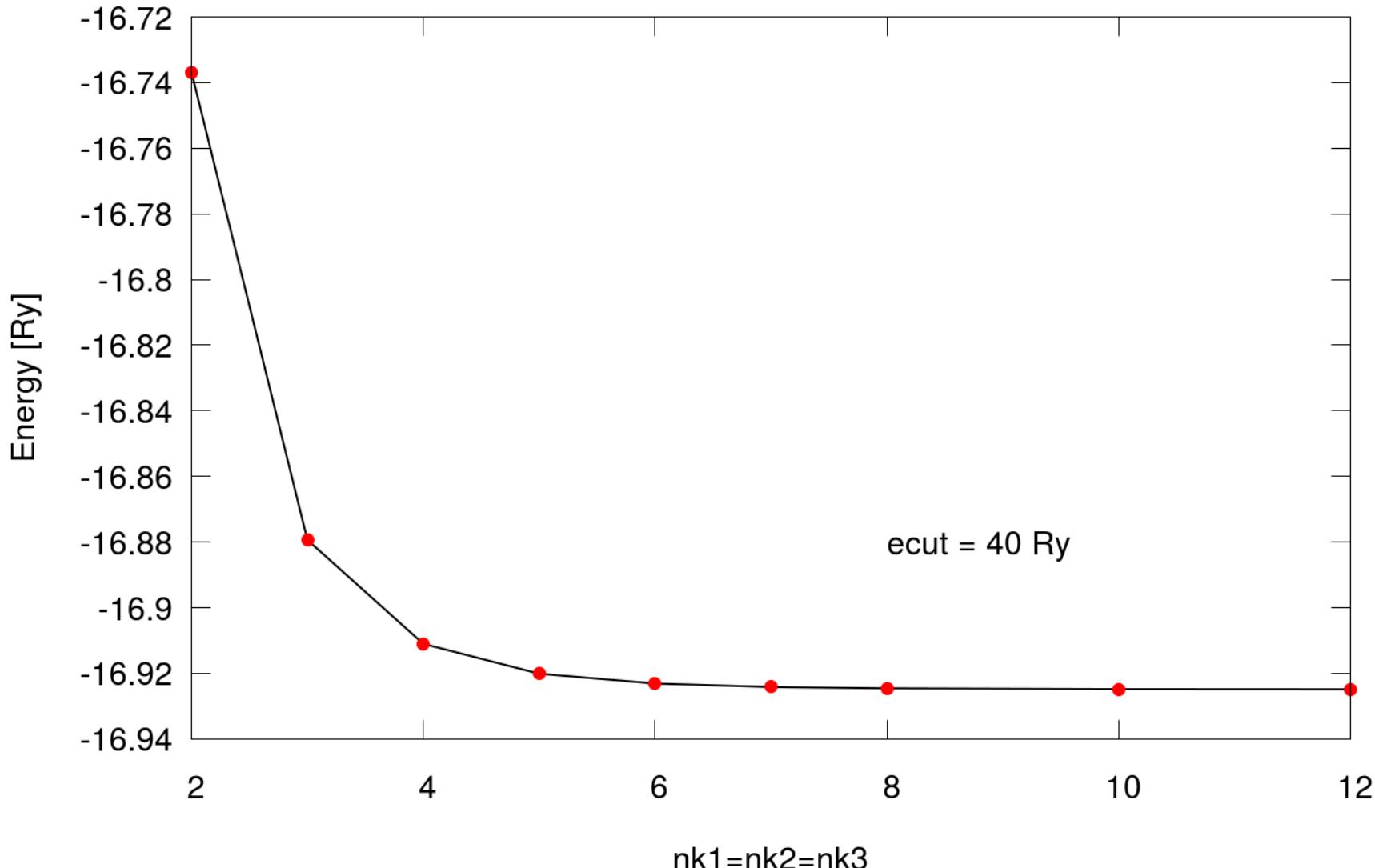
Convergence wrt E_{cut} : direct band gap



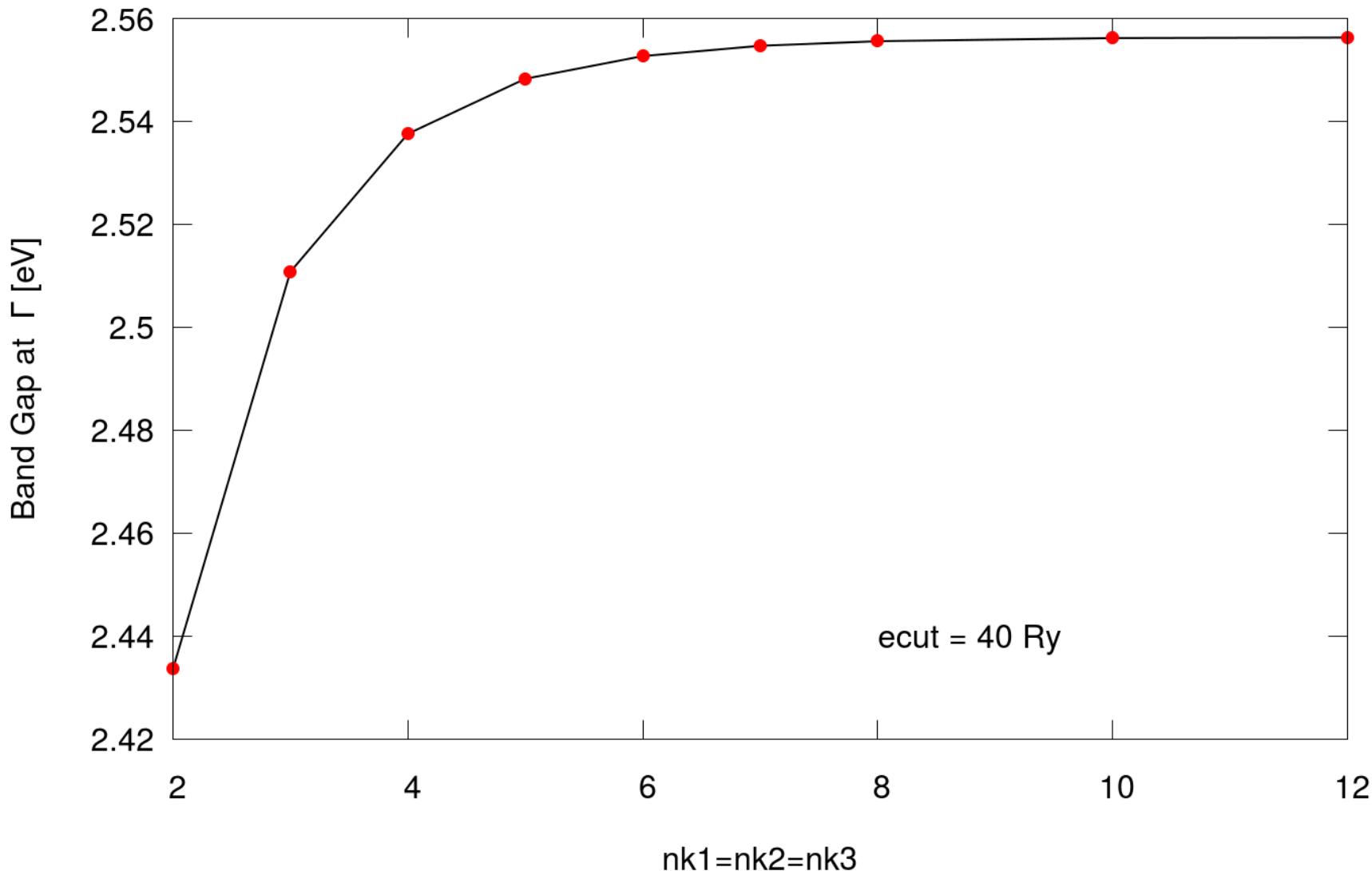
Convergence wrt E_{cut} : indirect band gap



Convergence wrt K_POINTS: total energy



Convergence wrt K_POINTS: direct band gap



Check-out the git repo

- The hands-on materials are available at github
- Clone the repository (or Download it):

```
git clone https://github.com/materialscloud-org/QuantumESPRESSO-school-2023.git
```

- Go to the exercise0 folder

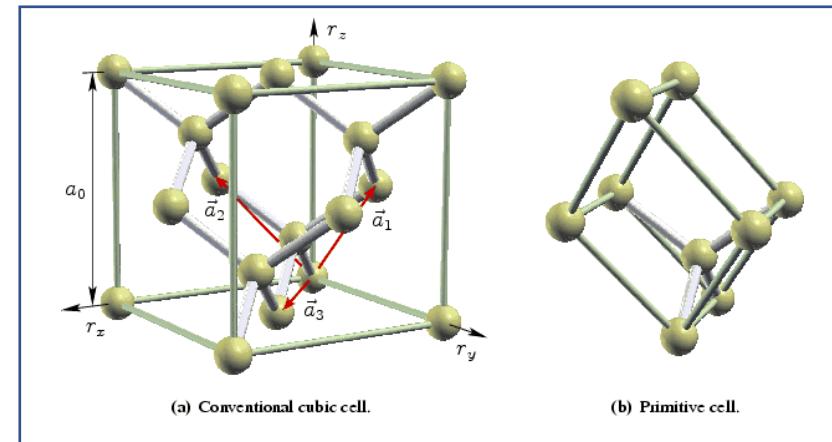
```
cd QuantumESPRESSO-school-2023/Day1/exercise0
```

Silicon PBE electronic structure: SCF calculation

```
&control
  calculation='scf'
  prefix='Si'
 outdir='./out'
/
&system
  ibrav = 2,  celldm(1) = 10.20,
  nat = 2,  ntyp = 1,
  ecutwfc = 40, ← Converged value for the Wave-Functions cutoff
/
&electrons
  conv_thr = 1.d-8
/
ATOMIC_SPECIES
Si 28.086 Si.pbe_PseudoDojo.UPF

ATOMIC_POSITIONS {alat}
Si 0.00 0.00 0.00
Si 0.25 0.25 0.25

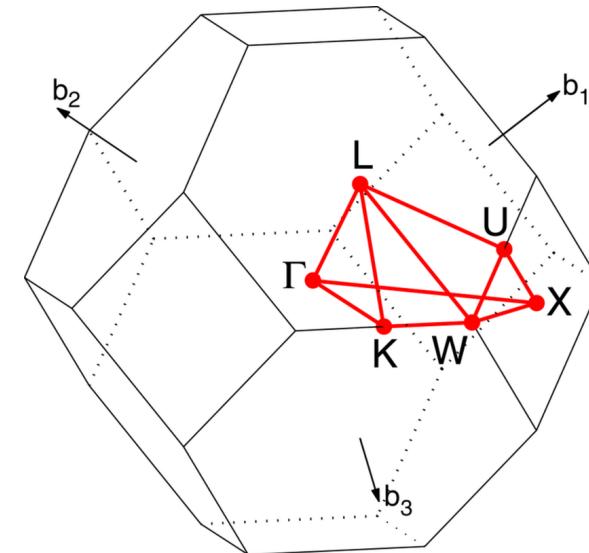
K_POINTS {automatic}
12 12 12 0 0 0 ← Converged value for the
BZ sampling
```



https://www.quantum-espresso.org/Doc/INPUT_PW.html

Silicon PBE electronic structure: BANDS calculation

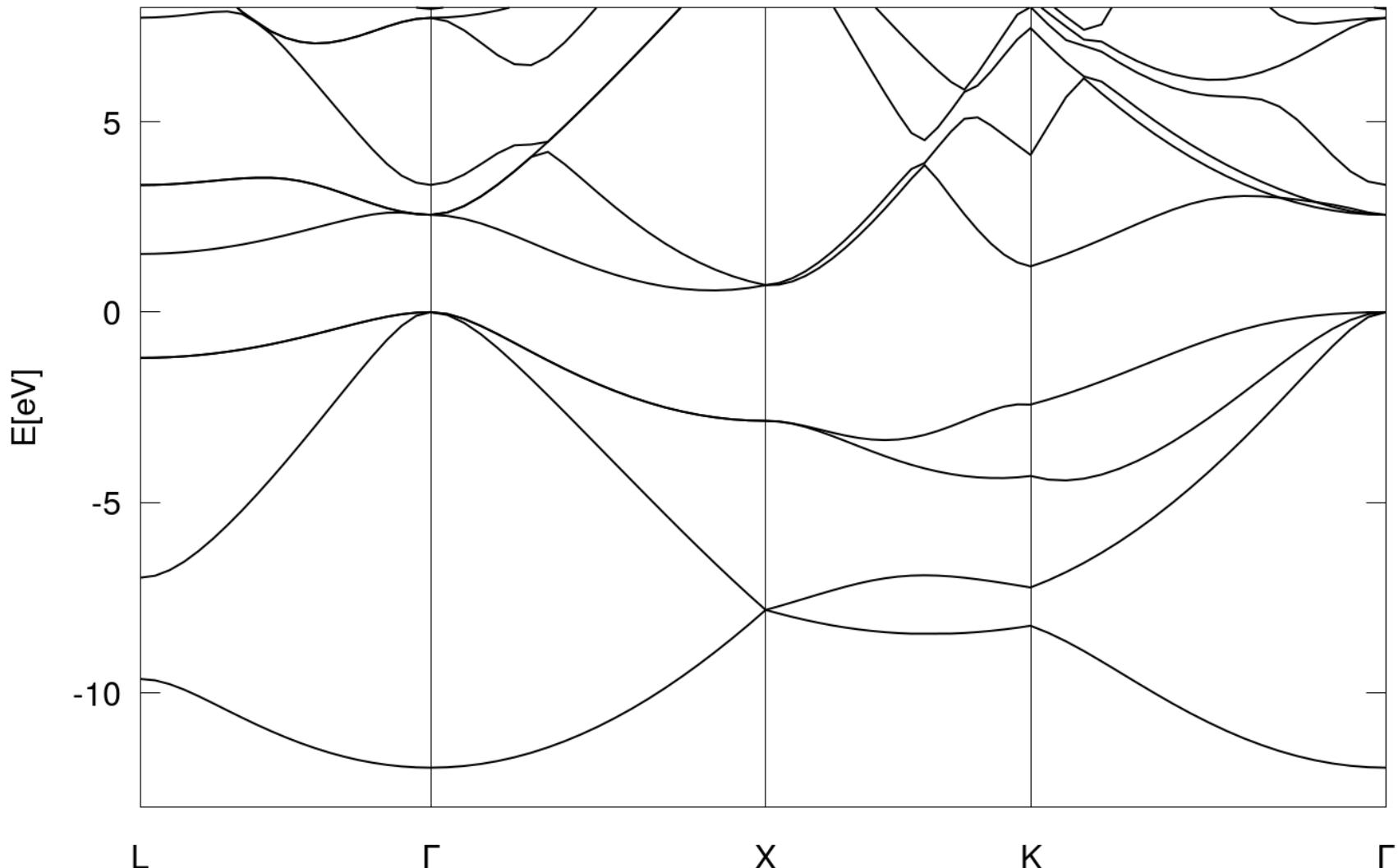
```
&control
  calculation='bands' ← "Bands" calculation
  ...
/
&system
  ...
/
&electrons
  ...
/
ATOMIC_SPECIES
...
ATOMIC_POSITIONS {alat}
...
K_POINTS {crystal_b}
5 ← Number of special k-points provided
  0.50000  0.50000  0.50000  20 ! I
  0.00000  0.00000  0.00000  20 ! G
  0.50000  0.00000  0.50000  20 ! X
  0.37500  0.37500  0.75000  20 ! K
  0.00000  0.00000  0.00000  0 ! G
```



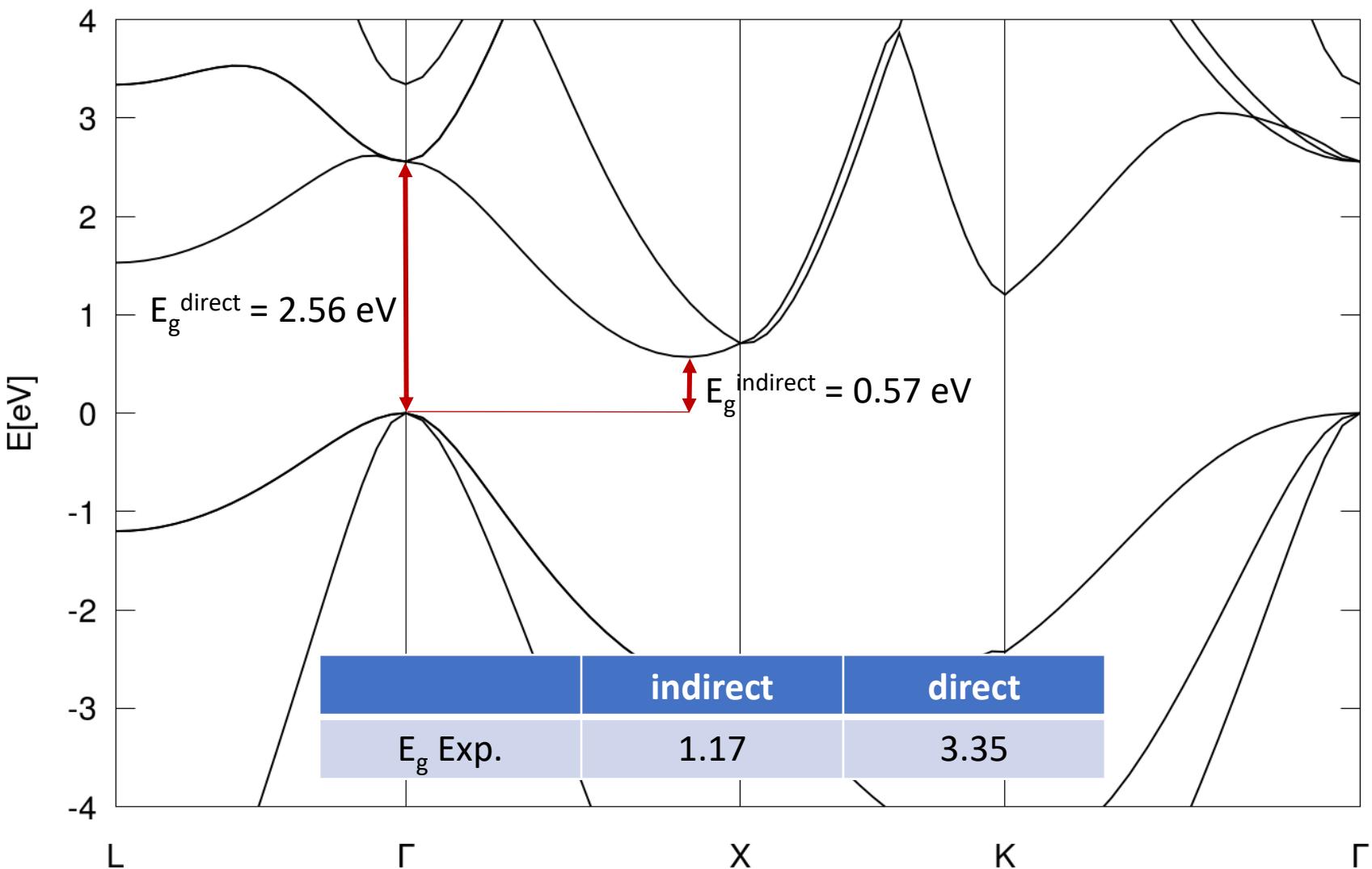
Number of special **k**-points provided

Coordinates of the special **k**-points and number of additional points QE generates between two adjacent special k-points.

PBE Silicon band structure



PBE Silicon band structure



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Hybrid functionals

Mix a fraction of exact-exchange from HF theory with semi-local exchange

- **3-parameters:** combination of x-HF, x-B88(xGGA), c-LYP(cGGA) and xc-LDA

$$E_{\text{xc}}^{\text{B3LYP}} = (1 - a_0)E_{\text{x}}^{\text{LDA}} + a_0 E_{\text{x}}^{\text{HF}} + a_x \Delta E_{\text{x}}^{\text{B88}} + a_c E_{\text{c}}^{\text{LYP}} + (1 - a_c)E_{\text{c}}^{\text{LDA}}$$

Fitted on thermochemical data: $a_0 = 0.20$, $a_x = 0.72$, $a_c = 0.81$

[Becke et al. JCP **98**, 5648 (1993), Stephens et al. J. Phys. Chem. **98**, 11623 (1994)]

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[Becke et al. JCP **98**, 5648 (1993), Stephens et al. J. Phys. Chem. **98**, 11623 (1994)]

- **Simplification:** $a_x = (1 - a_0)$, $a_c = 1$. Only 1 mixing parameter [Becke et al. JCP **104**, 1040 (1996)]

$$E_{\text{xc}}^{\text{hyb}} = (1 - a_0)E_{\text{x}}^{\text{DFT}} + a_0 E_{\text{x}}^{\text{HF}} + E_{\text{c}}^{\text{DFT}}$$

Comparison with 4° order perturbation theory: $a_0 = 1/4$: **PBE0** [Perdew et al. JCP 105, 9982 (1996)]

$$E_{\text{xc}}^{\text{PBE0}} = \frac{3}{4}E_{\text{x}}^{\text{DFT}} + \frac{1}{4}E_{\text{x}}^{\text{HF}} + E_{\text{c}}^{\text{PBE}}$$

Range-separated Hybrid functionals

Basic Idea: split the electron-electron interaction in short and long range

$$\frac{1}{r_{12}} = \underbrace{\frac{a + b \operatorname{erf}(\mu r_{12})}{r_{12}}}_{\text{Fock exchange}} + \underbrace{\frac{1 - [a + b \operatorname{erf}(\mu r_{12})]}{r_{12}}}_{\text{DFT exchange}}$$

Range-separation parameter

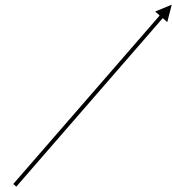
- $b = 0 \rightarrow$ Conventional hybrid functional. E.g. $\mathbf{b} = \mathbf{0}$ and $a = 0.25 \rightarrow \text{PBE0}$
 - $a = -b = 0.25$ and $\mu = 0.106 \text{ bohr}^{-1} \rightarrow \text{HSE}$
 - $a+b=1$ \rightarrow correct asymptotic ($1/r$) in **finite systems**
 - $a+b=1/\epsilon$ \rightarrow correct asymptotic ($1/\epsilon r$) in **extended systems**
 - μ can be tuned to satisfy the IP theorem (Optimal tuning)

Exact-exchange energy

$$E^{\text{HF}} = -\frac{1}{2} \sum_{\mathbf{k}, v} \sum_{\mathbf{q}, v'} \int d\mathbf{r} d\mathbf{r}' \frac{\psi_{\mathbf{k}, v}^*(\mathbf{r}) \psi_{\mathbf{k}-\mathbf{q}, v'}(\mathbf{r}) \psi_{\mathbf{k}, v}(\mathbf{r}') \psi_{\mathbf{k}-\mathbf{q}, v'}^*(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

In Reciprocal space:

$$E^{\text{HF}} = -\frac{4\pi}{2\Omega} \frac{\Omega}{(2\pi)^3} \int_{BZ} d\mathbf{q} \sum_G \frac{A(\mathbf{q} + \mathbf{G})}{|\mathbf{q} + \mathbf{G}|^2}$$



Integration over the BZ:

nqx1, nqx2, nqx3

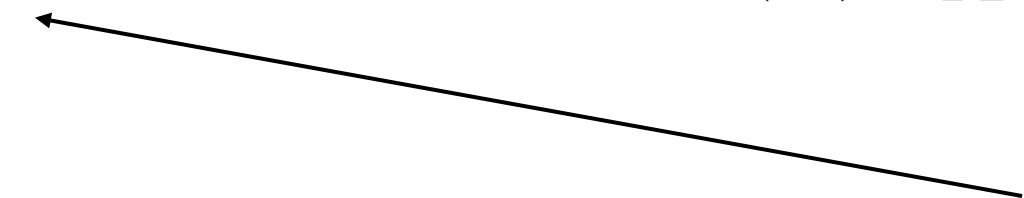
Need to be compatible
with the k mesh

PW expansion

ecutfock

Equal to ecutrho by default.
Can be reduced (but not
below ecutwfc)

$$A(\mathbf{q} + \mathbf{G}) = \frac{\Omega}{(2\pi)^3} \int_{BZ} d\mathbf{k} |\rho_{\mathbf{k}-\mathbf{q}, v'}^*(\mathbf{q} + \mathbf{G})|^2$$



Integrable divergence for $\mathbf{q} + \mathbf{G} > 0$

exxdiv_treatment='gygi-baldereschi'

x_gamma_extrapolation = .true.

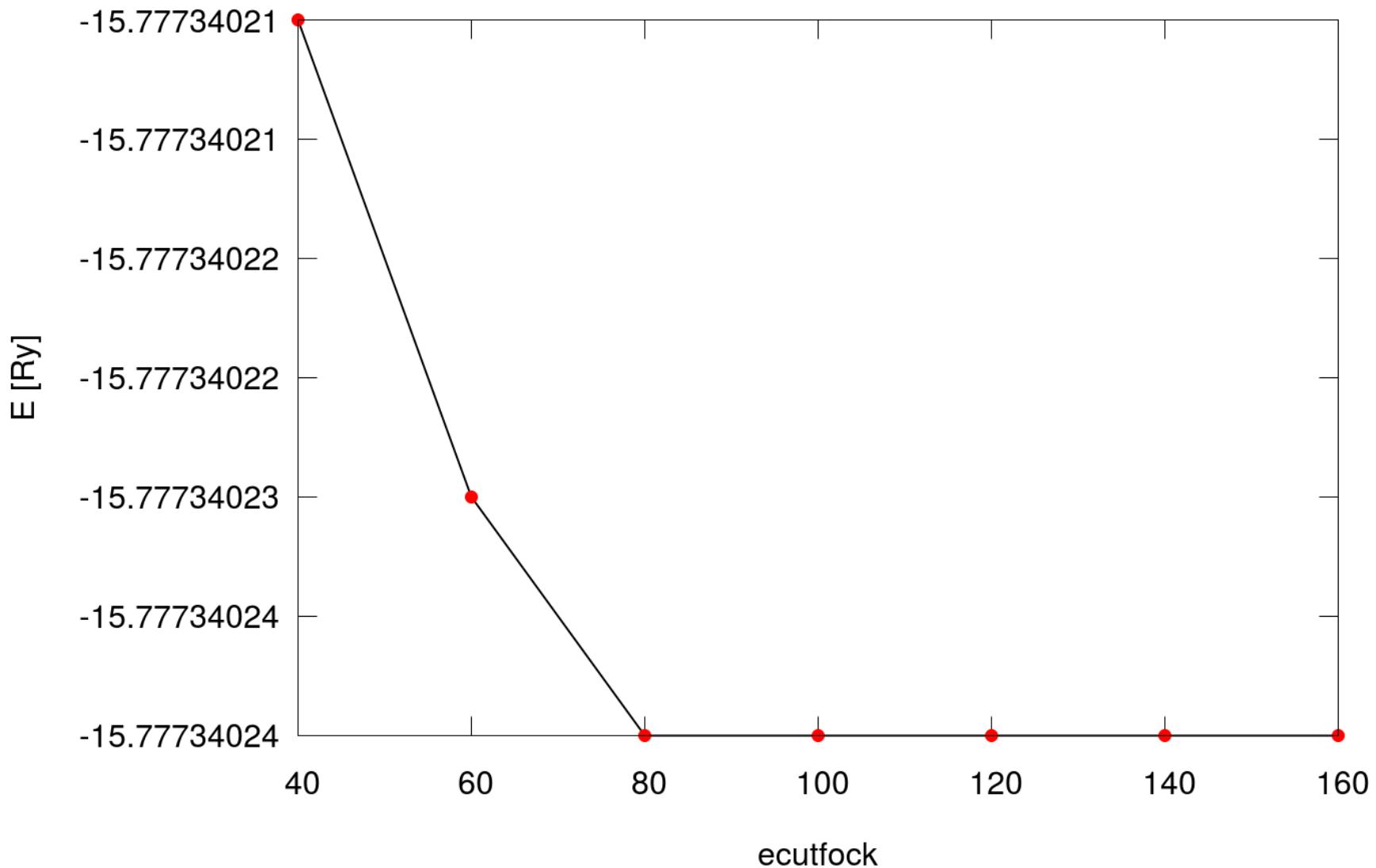
Silicon PBE0 electronic structure: SCF calculation

```
&control
  ...
/
&system
  ...
  input_dft      = "pbe0"           ← Specify which hybrid functional: PBE0/B3LYP/HSE
  nqx1 = XXX, nqx2 = XXX, nqx3 = XXX
  exxdiv_treatment = "gb"
  x_gamma_extrapolation = .true.
  ecutfock        = YYY
  exx_fraction    = ZZZ
  screening_parameter = WWW
/
&electrons
  ...
/
ATOMIC_SPECIES
...
ATOMIC_POSITIONS {alat}
...
K_POINTS {automatic}
12 12 12 0 0 0
```

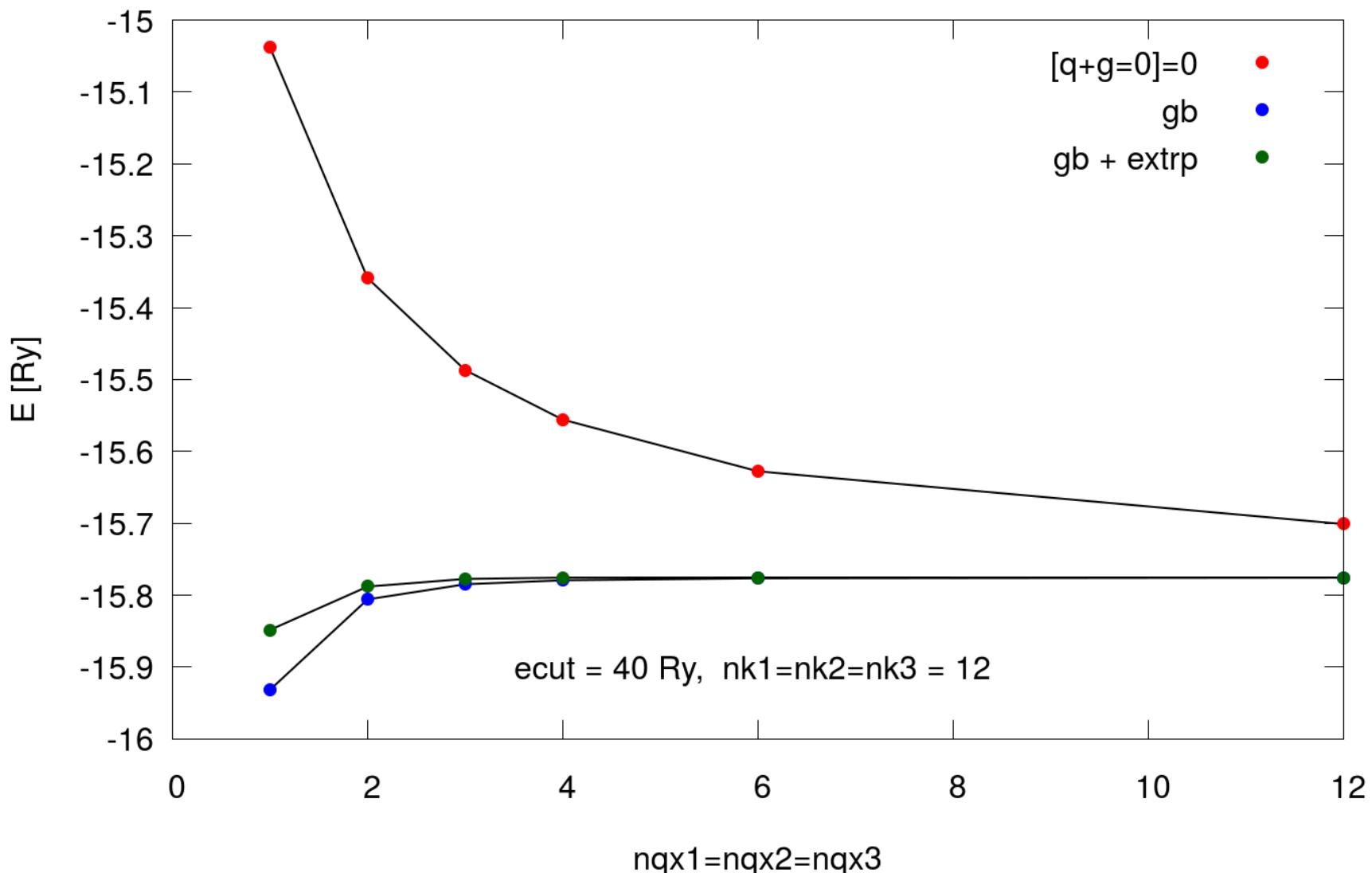
The code snippet shows a portion of a Quantum Espresso input file for a silicon system. It includes sections for control parameters, system properties, electrons, and atomic species. A specific line, 'input_dft = "pbe0"', is highlighted in cyan and has a callout arrow pointing to the right with the text 'Specify which hybrid functional: PBE0/B3LYP/HSE'. Another line, 'screening_parameter = WWW', is highlighted in yellow and has a callout arrow pointing to the right with the text 'You can change the fraction of EXX and/or the range separation parameter.'

https://www.quantum-espresso.org/Doc/INPUT_PW.html

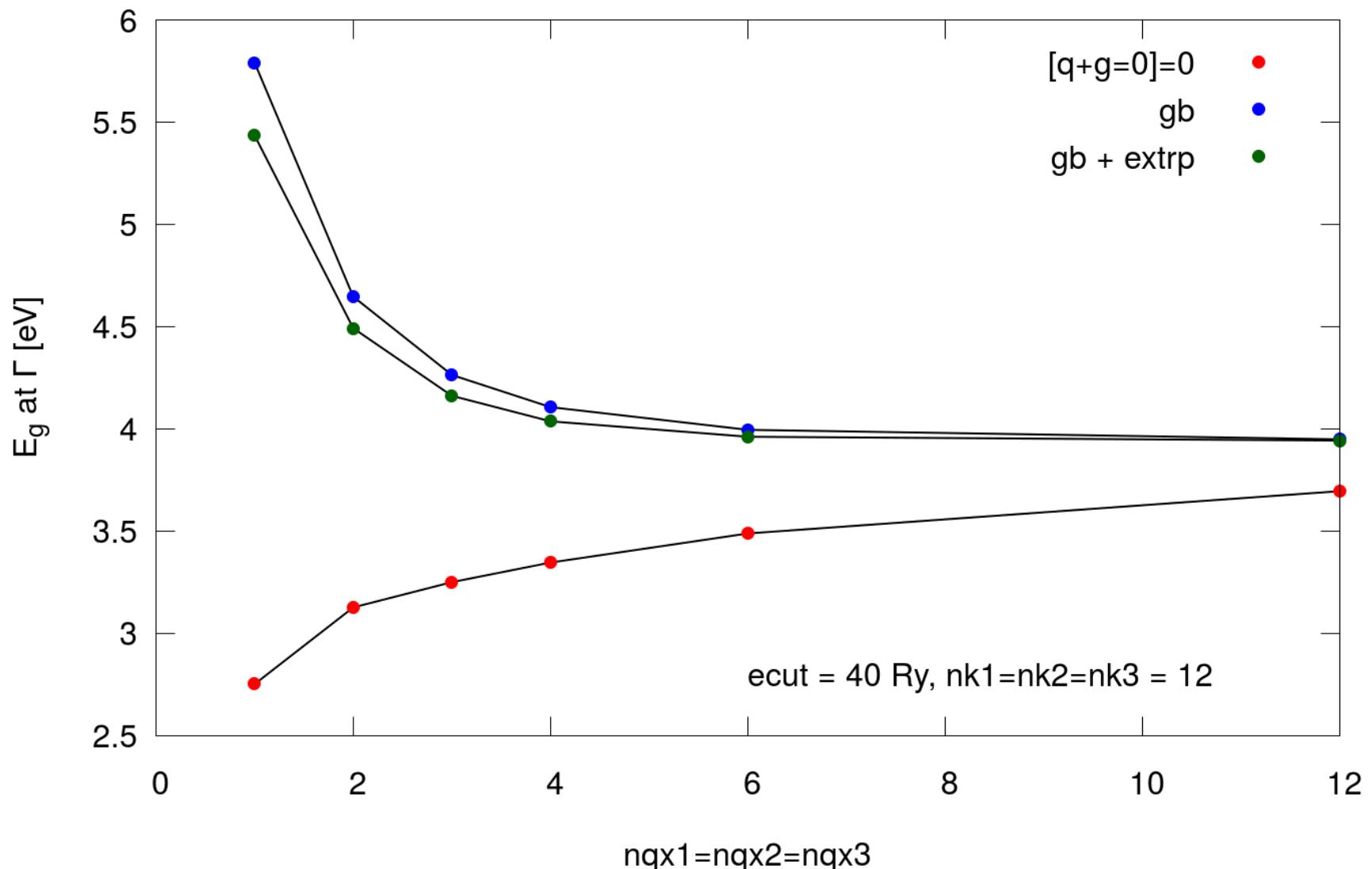
PBE0 energy convergence wrt ecutfock



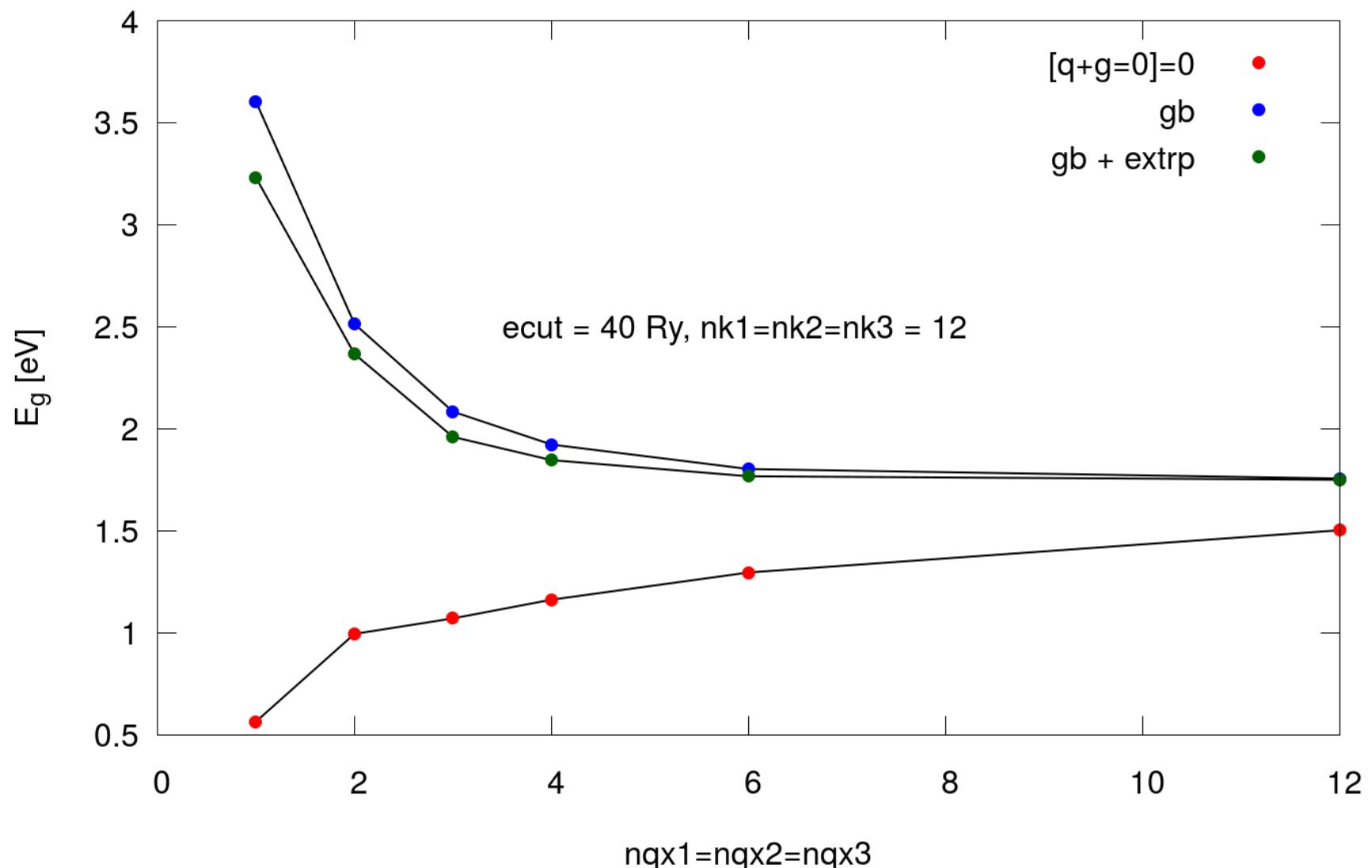
PBE0 energy convergence wrt nqx



PBEO direct band Gap convergence wrt nqx



PBE0 indirect band Gap convergence wrt nqx



Outline

- **Brief recap on KS-DFT.** KS equations, common approximations to the xc energy functional, KS in practice
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Check-out the git repo

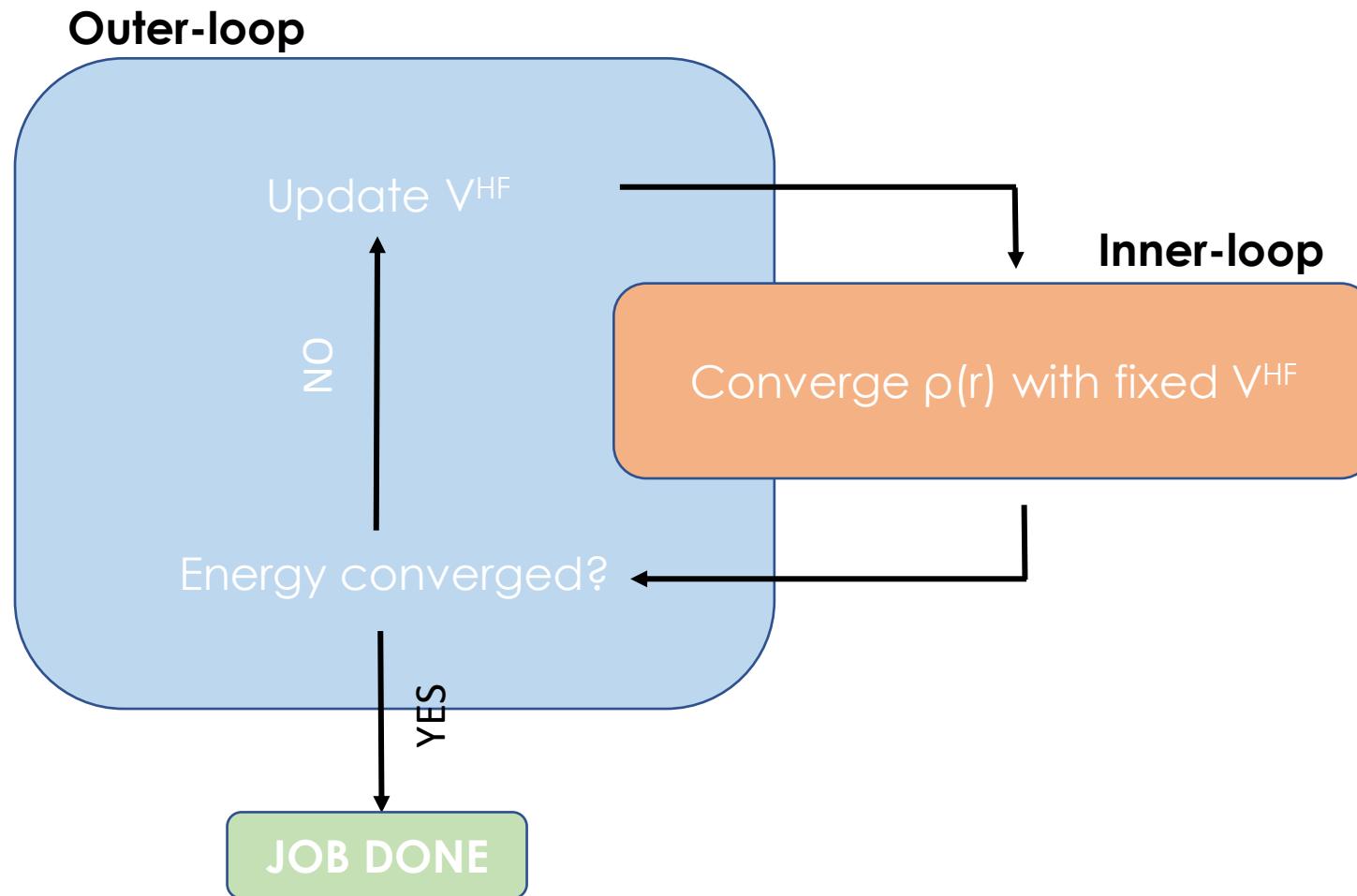
- Go to the exercise1 folder

```
cd QuantumESPRESSO-school-2023/Day1/exercise1
```

Silicon PBE0 electronic structure: SCF calculation

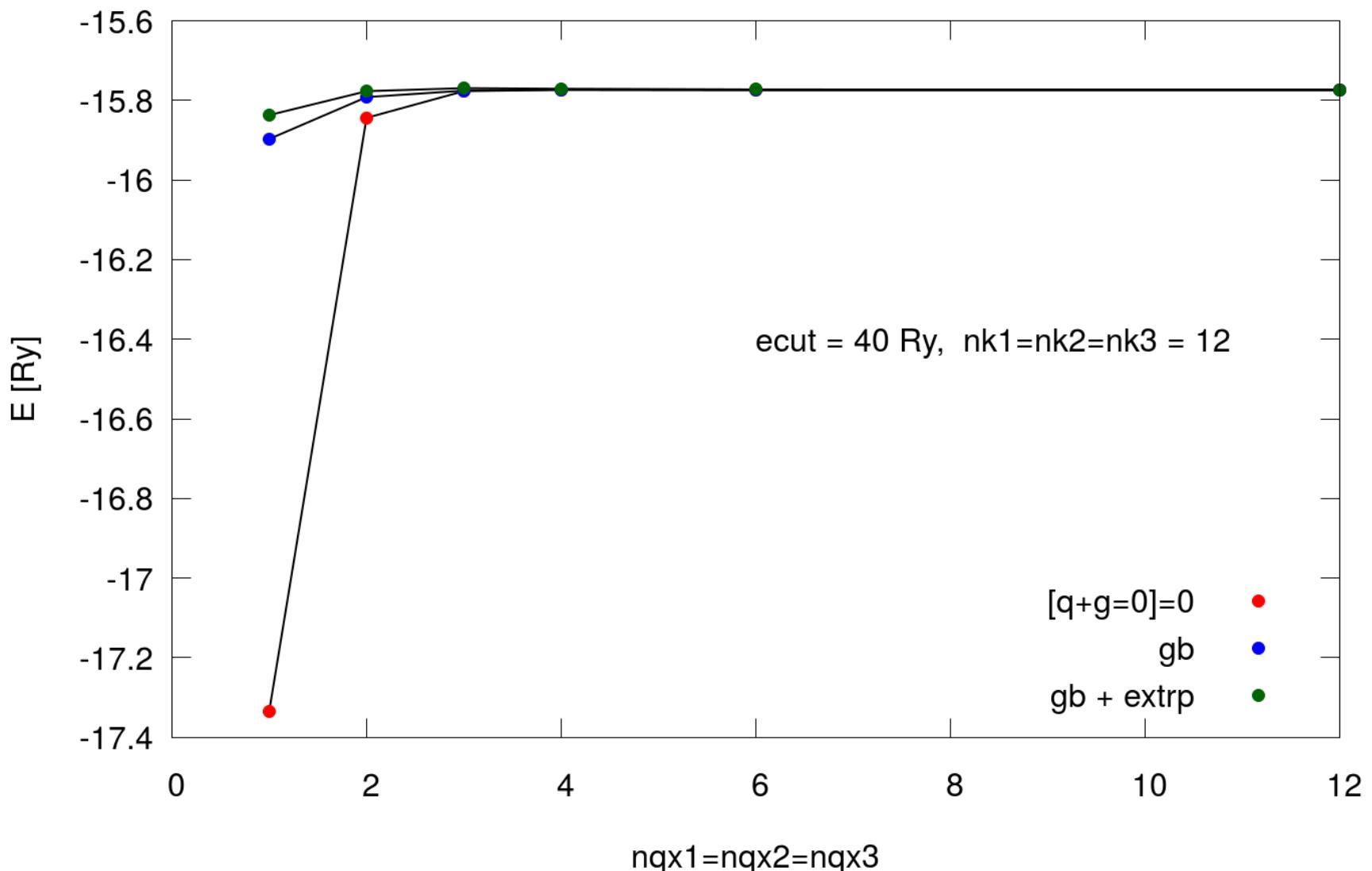
```
&control
  ...
/
&system
  ...
  input_dft      = "pbe0"
nqx1 = 4, nqx2 = 4, nqx3 = 4           ← Converged parameters for nqx
  exxdiv_treatment = "gb"
  x_gamma_extrapolation = .true.
ecutfock = 40                         ← Converged value for ecutfock
/
&electrons
  ...
/
ATOMIC_SPECIES
...
ATOMIC_POSITIONS {alat}
...
K_POINTS {automatic}
12 12 12 0 0 0
```

Nested self-consistent loop

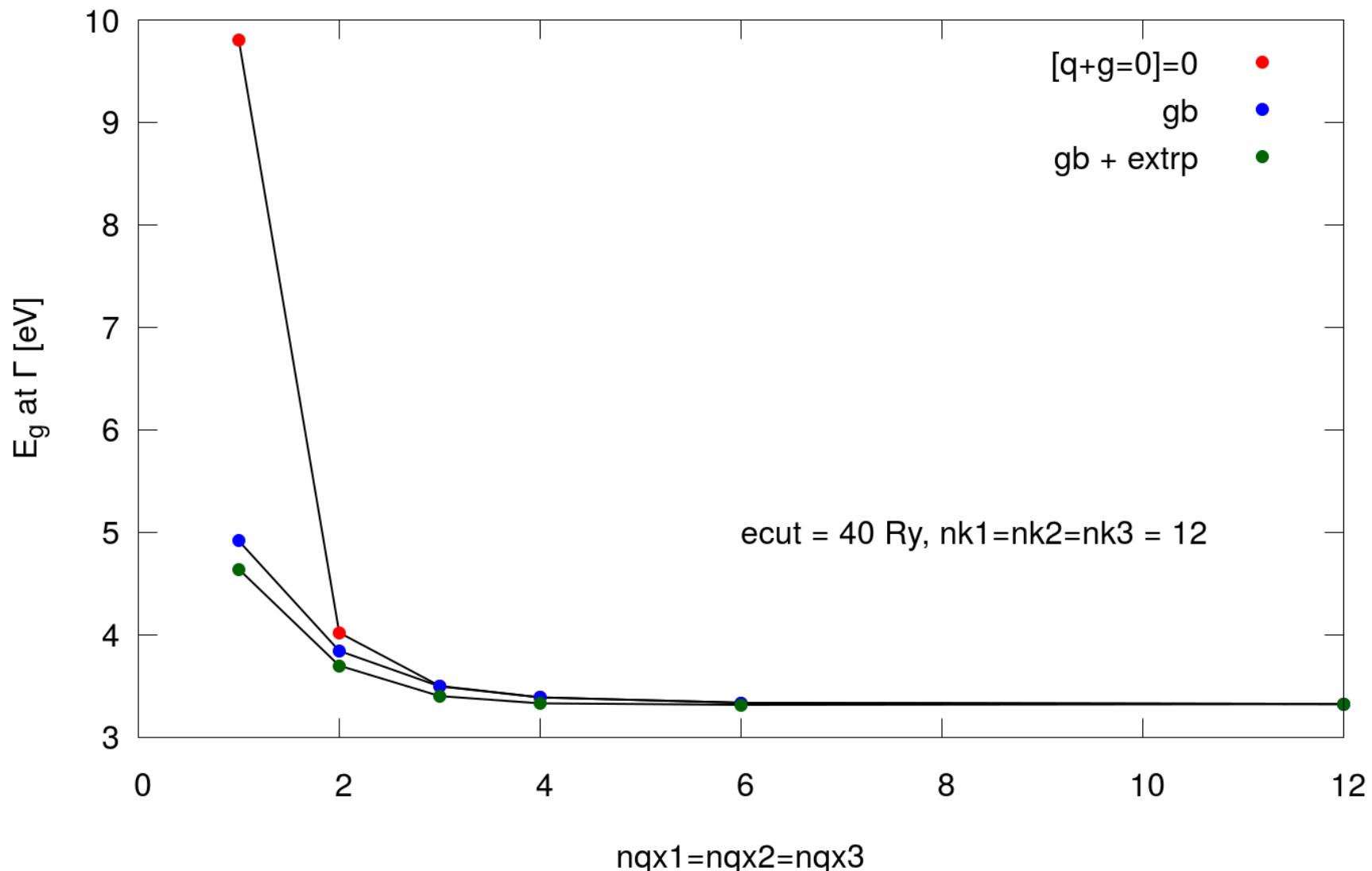


1. Normal scf (LDA or similar) is performed
2. Hybrid functional is switched. V^{HF} is calculated using the current best wfcs
3. A new scf is performed keeping V^{HF} fixed
4. Exchange error (d_{exx}) is computed
5. If $d_{exx} > \text{thr}$ the procedure is repeated from 1.

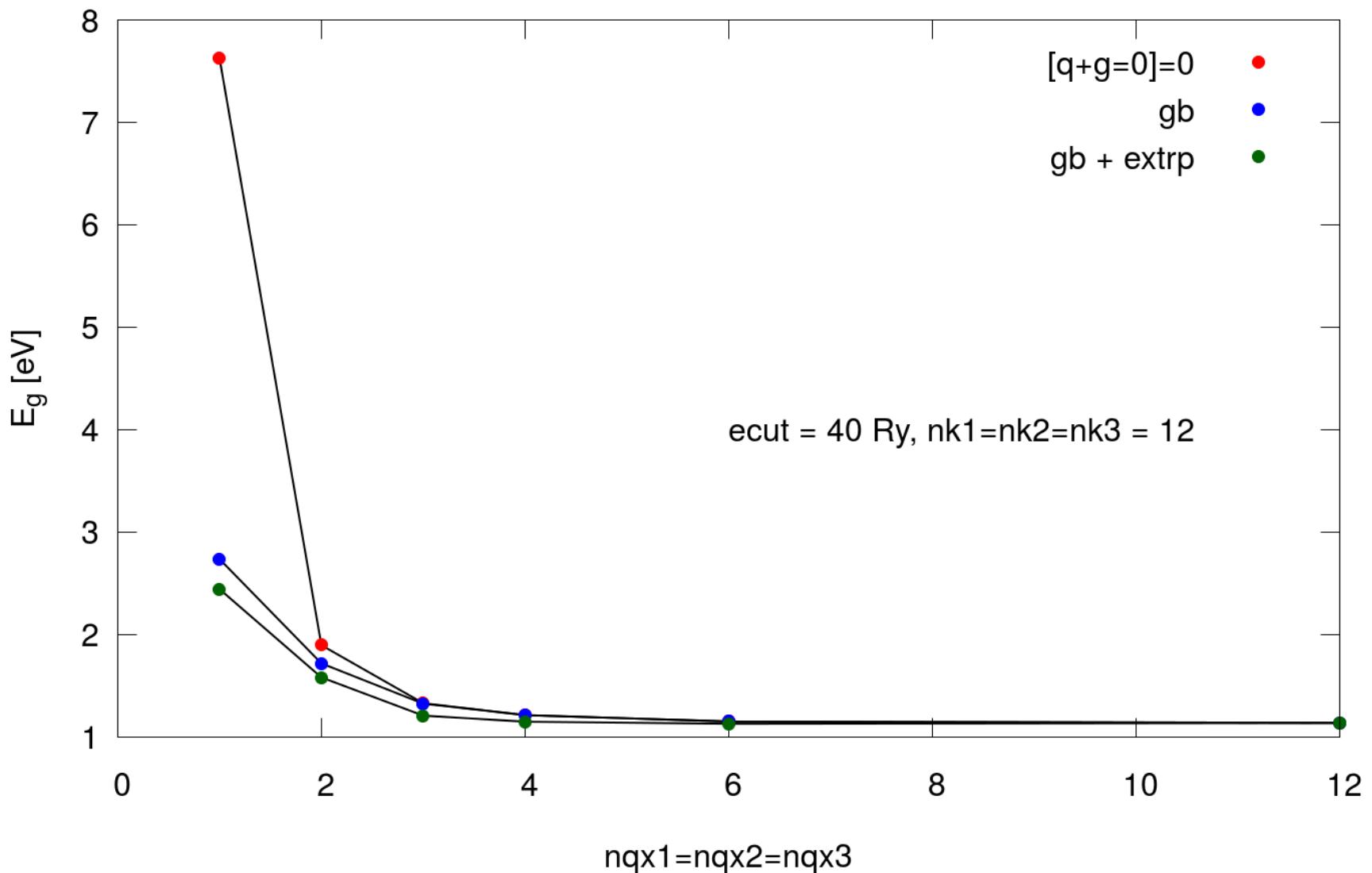
HSE energy convergence wrt nqx



HSE direct band Gap convergence wrt nqx



HSE indirect band Gap convergence wrt nqx



Silicon HSE electronic structure: SCF calculation

```
&control
  ...
/
&system
  ...
  input_dft      = "hse"
nqx1 = 4, nqx2 = 4, nqx3 = 4           ← Converged parameters for nqx
  exxdiv_treatment = "gb"
  x_gamma_extrapolation = .true.
ecutfock = 40                         ← Converged value for ecutfock
/
&electrons
  ...
/
ATOMIC_SPECIES
...
ATOMIC_POSITIONS {alat}
...
K_POINTS {automatic}
12 12 12 0 0 0
```

Silicon band Gap: summary

ecut = 40 Ry, k mesh: 12x12x12
ecutfock = 40 Ry, q mesh: 4x4x4

Functional	indirect Gap	Direct Gap	Band width
PBE	0.57	2.56	11.96
PBE0	1.85	4.04	13.32
HSE	1.15	3.33	13.26
Exp.	1.17	3.35	12.5

Hybrids: how do they perform

Atomization energies

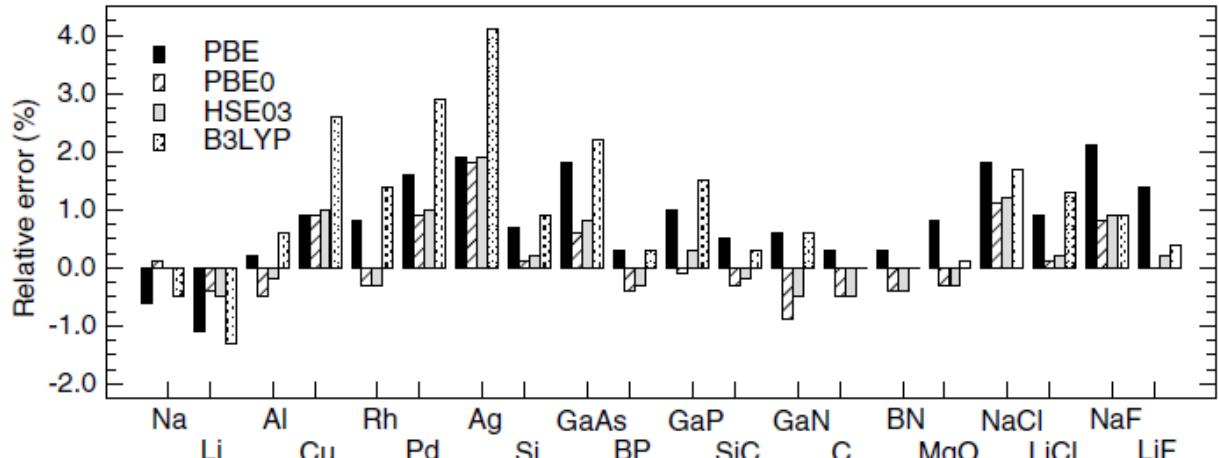
Functional	MAE(G2)	MAE(G2-1)	Max AE(G2)	Max AE(G2-1)
LDA	83.7	36.4	216	84
PBE	17.1	8.6	52	26
BLYP	7.1	4.7	28	15
B3LYP	3.1	2.4	20	10
PBE0	4.8	3.5	24	10

Mean Absolute Error (MAE) in Kcal/mol for the G2 (148 molecules) and G2-1(55 molecules) sets.

Curtiss et al. JCP 106, 1063 (1997); Scuseria et al. JCP 110, 5029 (1999)

Hybrids: how do they perform

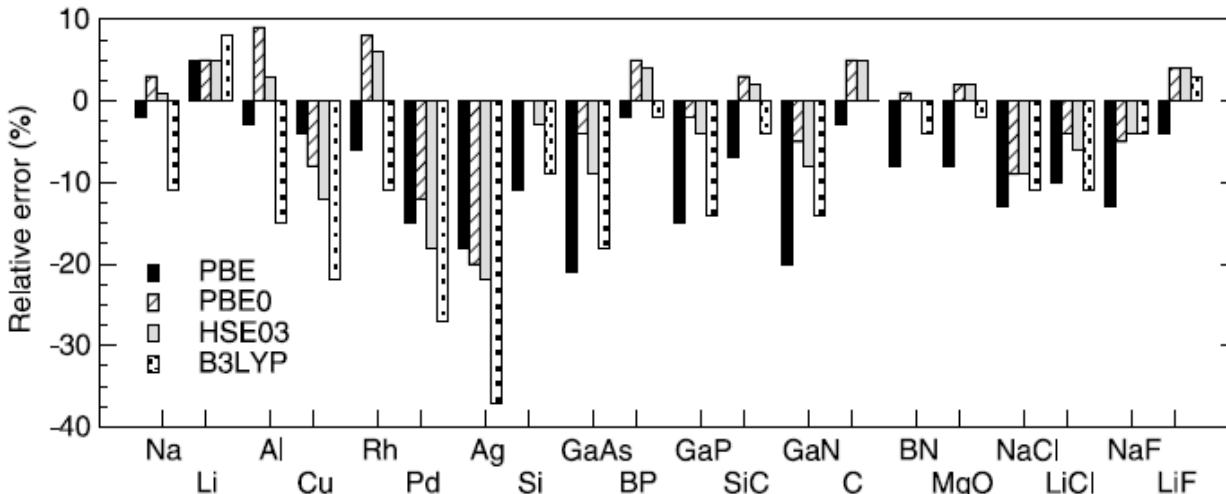
Lattice constants of solids



	PBE	PBE0	HSE	B3LYP
MRE	0.8	0.1	0.2	1.0
MARE	1.0	0.5	0.5	1.2
No-metals				
MRE	1.0	0.0	0.1	0.8
MARE	1.0	0.4	0.5	0.8

Bulk modulus of solids

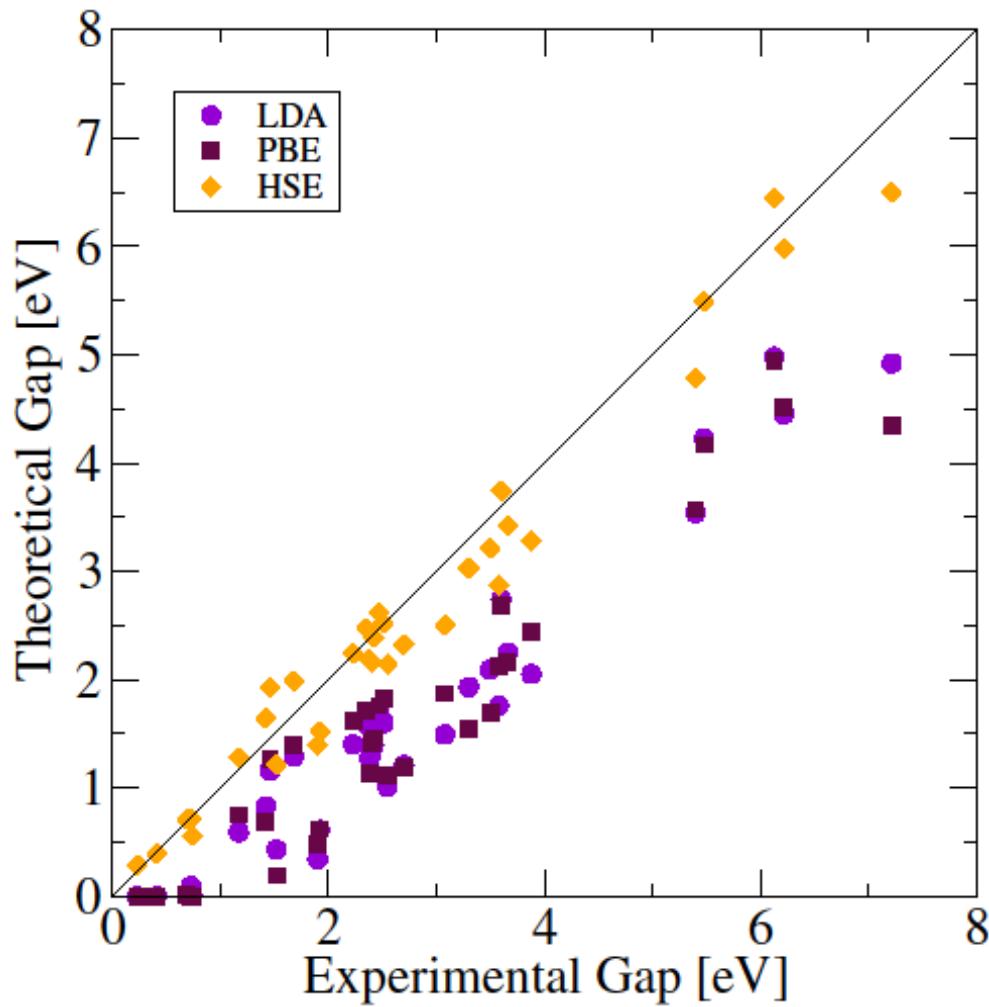
	PBE	PBE0	HSE	B3LYP
MRE	-9.8	-1.2	-3.1	-10.2
MARE	9.4	5.7	6.4	11.4
No-metals				
MRE	-10.4	-0.7	-1.8	-6.8
MARE	10.4	3.8	4.6	7.4



Marsman et al. J. Phys: Condens. Matter 20, 064201 (2008)

Hybrids: how do they perform

Band gaps



Improved band gaps for semiconducting system

HSE correctly predict semiconducting behavior in systems where LDA/GGA predicts a metal

Error (in eV) for 40 simple and binary semiconductors and insulators

	LDA	PBE	HSE
ME	-1.14	-1.13	-0.17
MAE	1.14	1.13	0.26

Caveat

1. More expensive than standard DFT (time- and memory-wise)
2. No hybrid PP. Use always a PP generated with the same local functional as the one used in the hybrid functional definition (e.g. use PBE PPs for PBE0 calculations)
3. NLCC not well defined. Avoid PPs with NLCC
4. Might need to explicitly include semi-core states electrons in the valence
5. Calculations with US and PAW PPs typically slower than those with NC PPs
6. Not all the features are implemented for US and PAW PPs
7. Wannier interpolation to get the entire band structure (see hnds-on later today)

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Meta-GGA

$$E_{\text{xc}}[n_{\uparrow}, n_{\downarrow}] = \int d^3r n(\mathbf{r}) \varepsilon_{\text{xc}}(n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r}), \nabla n_{\uparrow}(\mathbf{r}), \nabla n_{\downarrow}(\mathbf{r}), \nabla^2 n_{\uparrow}(\mathbf{r}), \nabla^2 n_{\downarrow}(\mathbf{r}), \tau_{\uparrow}(\mathbf{r}), \tau_{\downarrow}(\mathbf{r}))$$

$$n(\mathbf{r}) = \sum_{\sigma} n_{\sigma}(\mathbf{r}) \quad \text{total charge density}$$

$$n_{\sigma}(\mathbf{r}) = \sum_{v,\mathbf{k}} |\psi_{v,\mathbf{k}}^{\sigma}(\mathbf{r})|^2 \quad \text{spin-charge density} \quad \sigma = \{\uparrow, \downarrow\}$$

$$\tau_{\sigma}(\mathbf{r}) = \frac{1}{2} \sum_{v,\mathbf{k}} |\nabla \psi_{v,\mathbf{k}}^{\sigma}(\mathbf{r})|^2 \quad \text{kinetic energy density}$$

Plethora of meta-GGA functionals

BR89

r²SCAN

MVS

TPSS

rSCAN

MGGA_MS2

SCAN

TASK

revTPSS

HLE17

TM

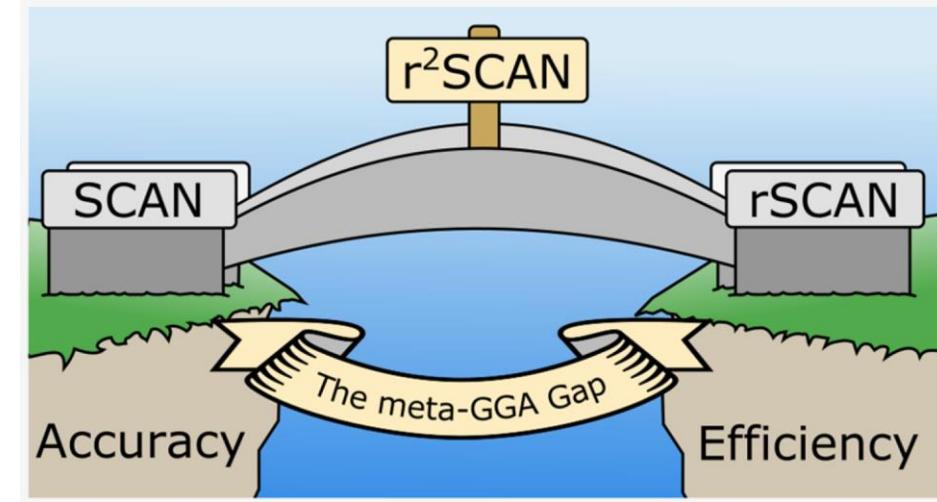
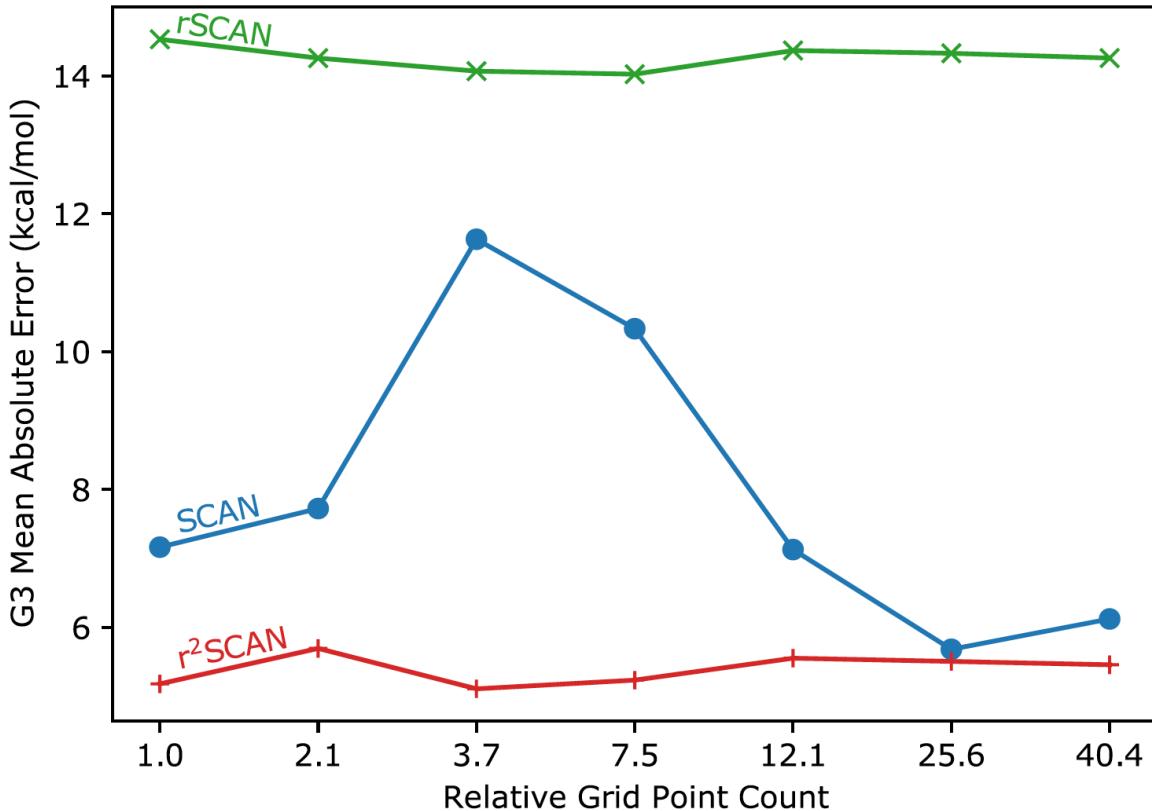
SCAN-L

SCAN, rSCAN, r²SCAN

$$E_{\text{xc}}[n_{\uparrow}, n_{\downarrow}] = \int d^3r n(\mathbf{r}) \varepsilon_{\text{xc}}(n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r}), \nabla n_{\uparrow}(\mathbf{r}), \nabla n_{\downarrow}(\mathbf{r}), \nabla^2 n_{\uparrow}(\mathbf{r}), \nabla^2 n_{\downarrow}(\mathbf{r}), \tau_{\uparrow}(\mathbf{r}), \tau_{\downarrow}(\mathbf{r}))$$

~~$\nabla^2 n_{\uparrow}(\mathbf{r})$, $\nabla^2 n_{\downarrow}(\mathbf{r})$~~

$\tau_{\uparrow}(\mathbf{r}), \tau_{\downarrow}(\mathbf{r})$



SCAN: J. Sun et al., *Phys. Rev. Lett.* **115**, 036402 (2015).

rSCAN: A. Bartok et al., *J. Chem. Phys.* **150**, 161101 (2019).

r²SCAN: J. Furness et al., *J. Phys. Chem. Lett.* **11**, 8208 (2020).

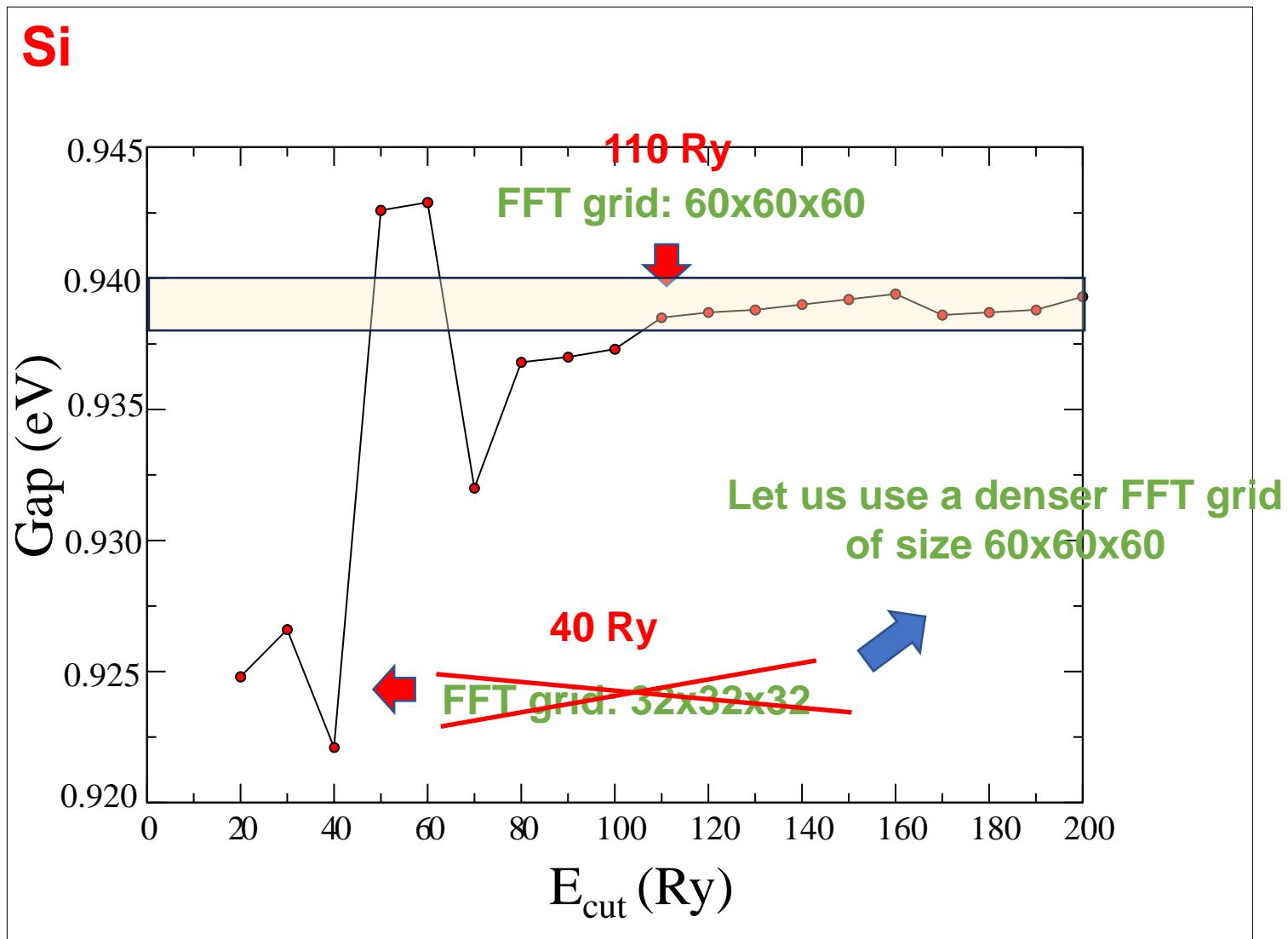
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Input file

```
&control
  calculation='scf'
  restart_mode='from_scratch',
  prefix='Si'
  pseudo_dir = '../..../files/pseudo'
 outdir='./tmp'
  verbosity='high'
/
&system
  ibrav = 2,
  celldm(1) = 10.262, ← Experimental lattice parameter
  nat = 2,
  ntyp = 1,
  ecutwfc = 40.0, ← It is necessary to perform convergence tests w.r.t ecutwfc
  input_dft = 'SCAN' ← Set up the SCAN functional from the input
  nbnd = 5
/
&electrons
  conv_thr = 1.d-10
/
ATOMIC_SPECIES
Si 28.086 Si.SCAN.UPF ← Pseudopotential generated using the SCAN functional
ATOMIC_POSITIONS {alat}
  Si 0.00 0.00 0.00
  Si 0.25 0.25 0.25
K_POINTS {automatic}
  12 12 12 0 0 0 ← It is necessary to perform convergence tests w.r.t k points mesh
```

SCAN functional & SCAN pseudopotential



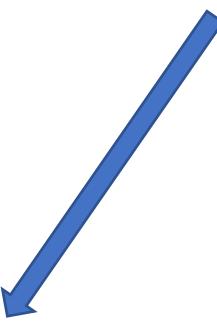
```
&control
  calculation='scf'
  restart_mode='from_scratch',
  prefix='Si'
  pseudo_dir = '../files/pseudo'
 outdir='./tmp'
  verbosity='high'
/
&system
  ibrav = 2,
  celldm(1) = 10.262,
  nat = 2,
  ntyp = 1,
  ecutwfc = 40.0,
  input_dft = 'SCAN'
  nbnd = 5
  nr1 = 60
  nr2 = 60
  nr3 = 60
/
&electrons
  conv_thr = 1.d-10
/
ATOMIC_SPECIES
Si 28.086 Si.SCAN.UPF
ATOMIC_POSITIONS {alat}
  Si 0.00 0.00 0.00
  Si 0.25 0.25 0.25
K_POINTS {automatic}
  12 12 12 0 0 0
```

FFT grid specified from the input

SCAN functional & PBE pseudopotential

```
&control
  calculation='scf'
  restart_mode='from_scratch',
  prefix='Si'
  pseudo_dir = '../files/pseudo'
 outdir='./tmp'
  verbosity='high'
/
&system
  ibrav = 2,
  celldm(1) = 10.262,
  nat = 2,
  ntyp = 1,
  ecutwfc = 110.0,
  input_dft = 'SCAN'
  nbnd = 5
/
&electrons
  conv_thr = 1.d-10
/
ATOMIC_SPECIES
Si 28.086 Si.pbe_PseudoDojo.UPF
ATOMIC_POSITIONS {alat}
Si 0.00 0.00 0.00
Si 0.25 0.25 0.25
K_POINTS {automatic}
12 12 12 0 0 0
```

Pseudo Dojo library
<http://www.pseudo-dojo.org>



```
&control
  calculation='scf'
  restart_mode='from_scratch',
  prefix='Si'
  pseudo_dir = '../files/pseudo'
 outdir='./tmp'
  verbosity='high'
/
&system
  ibrav = 2,
  celldm(1) = 10.262,
  nat = 2,
  ntyp = 1,
  ecutwfc = 110.0,
  input_dft = 'SCAN'
  nbnd = 5
/
&electrons
  conv_thr = 1.d-10
/
ATOMIC_SPECIES
Si 28.086 Si_ONCV_PBE-1.2.upf
ATOMIC_POSITIONS {alat}
Si 0.00 0.00 0.00
Si 0.25 0.25 0.25
K_POINTS {automatic}
12 12 12 0 0 0
```

SG15 library

http://www.quantum-simulation.org/potentials/sg15_oncv/

SCAN functional with different pseudopotentials

Ecut = 110 (Ry), k mesh: 12x12x12

Functional	Pseudopotential	Library	Gap (eV)
SCAN	SCAN	Yi Yao's library	0.94
SCAN	PBE	SG15 ONCV	0.83
SCAN	PBE	Pseudo Dojo	0.64

Gap_{expt} = 1.17 (eV)

SCAN functional with different pseudopotentials

Ecut = 110 (Ry), k mesh: 12x12x12

Functional	Pseudopotential	Library	Gap (eV)	
SCAN	SCAN	Yi Yao's library	0.94	NLCC=.false.
SCAN	PBE	SG15 ONCV	0.83	NLCC=.false.
SCAN	PBE	Pseudo Dojo	0.64	NLCC=.true.

WARNING →

Gap_{expt} = 1.17 (eV)

Currently, nonlinear core correction (NLCC) is not implemented for meta-GGA in Quantum ESPRESSO!

Pseudopotentials that have NLCC=.true. introduce some inconsistency for meta-GGA calculations.

SCAN functional with different pseudopotentials

Ecut = 110 (Ry), k mesh: 12x12x12

Functional	Pseudopotential	Library	Gap (eV)
SCAN	SCAN	Yi Yao's library	0.94
SCAN	PBE	SG15 ONCV	0.83
SCAN	PBE	Pseudo Dojo	0.64
PBE	PBE	SG15 ONCV	0.56
PBE	PBE	Pseudo Dojo	0.57

$$\text{Gap}_{\text{expt}} = 1.17 \text{ (eV)}$$

SCAN calculation with the SCAN pseudopotential gives the more accurate results

Y. Yao and Y. Kanai, J. Chem. Phys. 146, 224105 (2017).

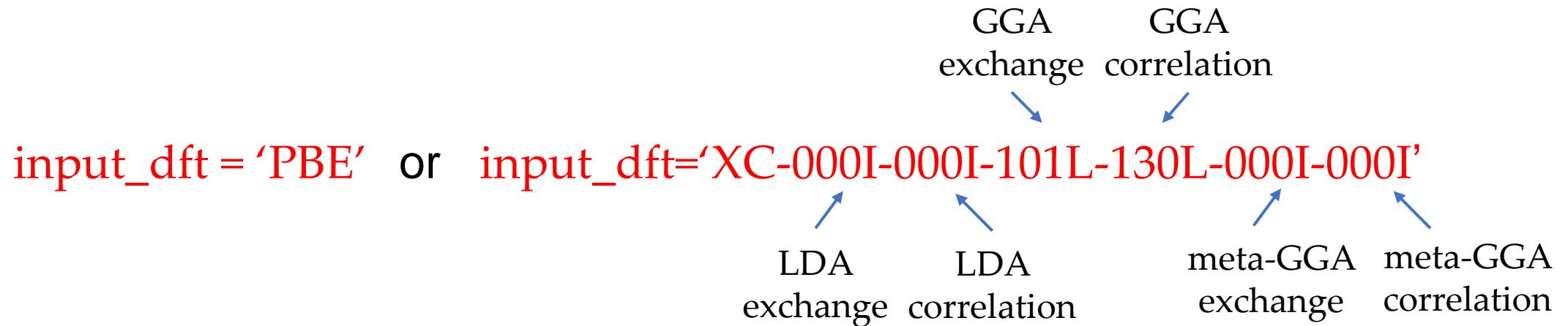
Setting up the XC functional

`input_dft = 'PBE' or input_dft='XC-000I-000I-101L-130L-000I-000I'`

Read more about this here: https://www.quantum-espresso.org/Doc/user_guide/node13.html

Libxc with IDs: <https://tddft.org/programs/libxc/functionals/libxc-6.0.0/>

Setting up the XC functional

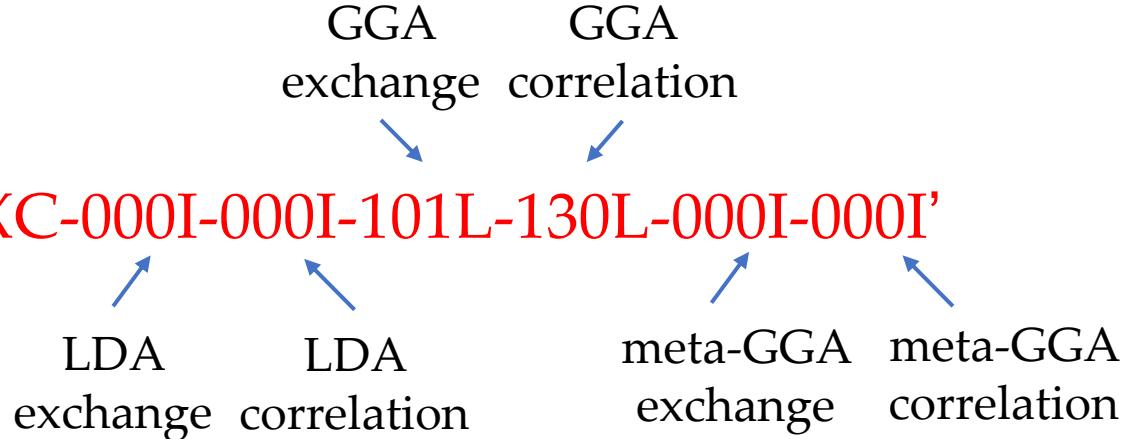


Read more about this here: https://www.quantum-espresso.org/Doc/user_guide/node13.html

Libxc with IDs: <https://tddft.org/programs/libxc/functionals/libxc-6.0.0/>

Setting up the XC functional

`input_dft = 'PBE'` or `input_dft='XC-000I-000I-101L-130L-000I-000I'`



`input_dft = 'SCAN'` or `input_dft='XC-000I-000I-000I-000I-263L-267L'`

no short
name
in QE

~~`input_dft = 'rSCAN'`~~ or `input_dft='XC-000I-000I-000I-000I-493L-494L'`

`input_dft = 'r2SCAN'` or `input_dft='XC-000I-000I-000I-000I-497L-498L'`

Read more about this here: https://www.quantum-espresso.org/Doc/user_guide/node13.html

Libxc with IDs: <https://tddft.org/programs/libxc/functionals/libxc-6.0.0/>

Different flavors of SCAN

Functional	Pseudopotential	Library	Gap (eV)
SCAN	PBE	SG15 ONCV	0.83
rSCAN	PBE	SG15 ONCV	0.71
r^2 SCAN	PBE	SG15 ONCV	0.70

$$\text{Gap}_{\text{expt}} = 1.2 \text{ (eV)}$$

SCAN is more accurate than rSCAN and r^2 SCAN for predicting the band gap of bulk Si
(at least when using the PBE pseudopotential)

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Input

```
&control
  calculation='scf'
  restart_mode='from_scratch',
  prefix='Fe'
  pseudo_dir = ' ../../files/pseudo'
 outdir='./tmp'
  verbosity='high'
/
&system
  ibrav = 3,
  celldm(1) = 5.418,                                ← Experimental lattice parameter
  nat = 1,
  ntyp = 1,
  ecutwfc = 50.0,                                     ← It is necessary to perform convergence tests w.r.t ecutwfc
  occupations = 'smearing',
  smearing ='mv',
  degauss = 0.02,
  nspin = 2,
  starting_magnetization(1) = 0.5,
  input_dft = 'SCAN'                                    ← Set up the SCAN functional from the input
/
&electrons
  conv_thr = 1.d-10
/
ATOMIC_SPECIES
Fe 55.845 Fe_ONCV_PBE-1.2.upf                  ← Pseudopotential generated using the PBE functional
ATOMIC_POSITIONS {crystal}
Fe 0.000000 0.000000 0.000000
K_POINTS {automatic}
20 20 20 0 0 0
```

Experimental lattice parameter

It is necessary to perform convergence tests w.r.t ecutwfc

Set up the SCAN functional from the input
Quantum ESPRESSO must be compiled with Libxc

Pseudopotential generated using the PBE functional
SG15 ONCV library (there is no SCAN pseudo for Fe)

It is necessary to perform convergence tests w.r.t k points mesh

SCAN functional with different pseudopotentials

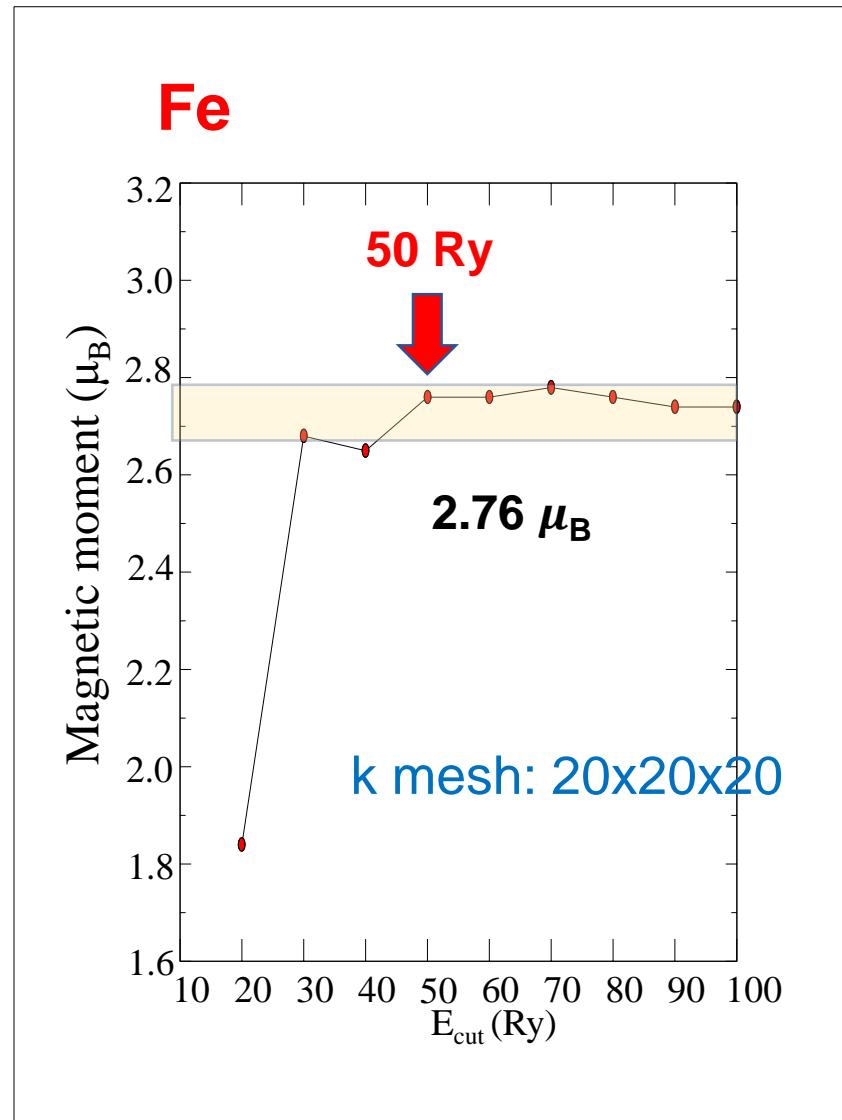
Functional	Pseudopotential	Library	$m (\mu_B)$
SCAN	PBE	SG15 ONCV	2.76
SCAN	PBE	Pseudo Dojo	2.67
PBE	PBE	SG15 ONCV	2.28
PBE	PBE	Pseudo Dojo	2.26

$$m_{\text{expt}} = 2.2 (\mu_B)$$

SCAN overestimates magnetic moments in itinerant ferromagnets

PBE is in closer agreement with experiments than SCAN for magnetic moments of itinerant ferromagnets

WARNING
NLCC=.false.
NLCC=.true.



Different flavors of SCAN

Functional	Pseudopotential	Library	$m (\mu_B)$
SCAN	PBE	SG15 ONCV	2.76
rSCAN	PBE	SG15 ONCV	2.73
r^2 SCAN	PBE	SG15 ONCV	2.73

$$m_{\text{expt}} = 2.2 (\mu_B)$$

Different flavors of SCAN give very similar magnetic moments for bulk Fe