

DFT in practice: from simple to advanced functionals

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THEOS and NCCR-Marvel

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**QUANTUM
MOBILE**

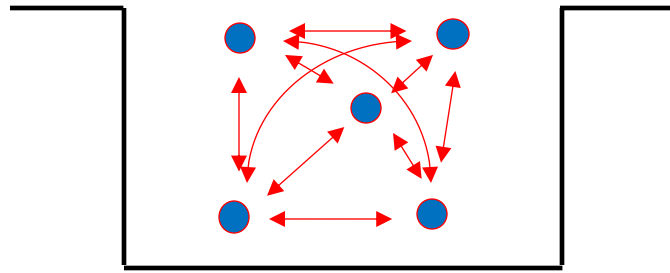


MAX DRIVING
THE EXASCALE
TRANSITION

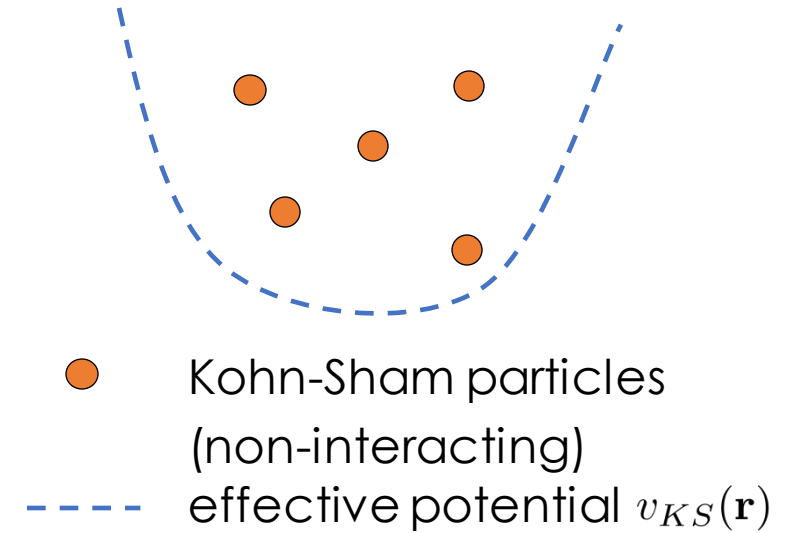
Outline

- **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



KS MAPPING



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

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

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

$$\left[-\frac{\hbar^2}{2m_e} \nabla^2 + v_{KS}[n](\mathbf{r}) \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}) \quad n(\mathbf{r}) = \sum_{i=1}^N |\phi_i(\mathbf{r})|^2$$

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

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

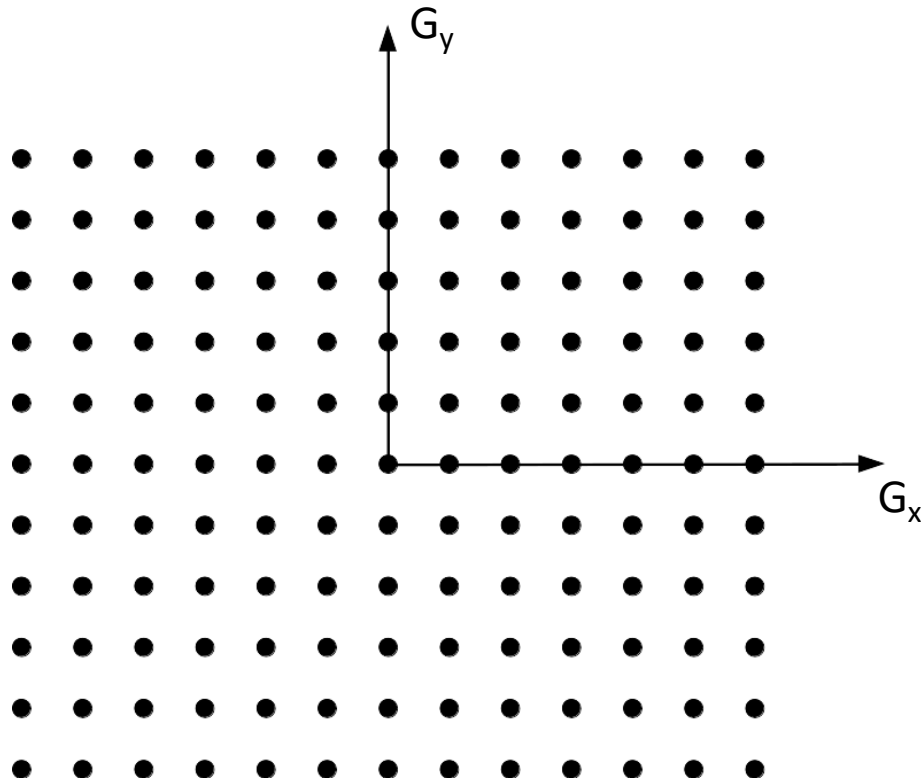
$$E_{\text{xc}}^{\text{hyb}} = (1 - a_0) E_{\text{x}}^{\text{DFT}} + a_0 E_{\text{x}}^{\text{HF}} + E_{\text{c}}^{\text{DFT}}$$

KS-DFT in practice: PW and PP

Wavefunctions are represented in Plane Waves (PW)

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

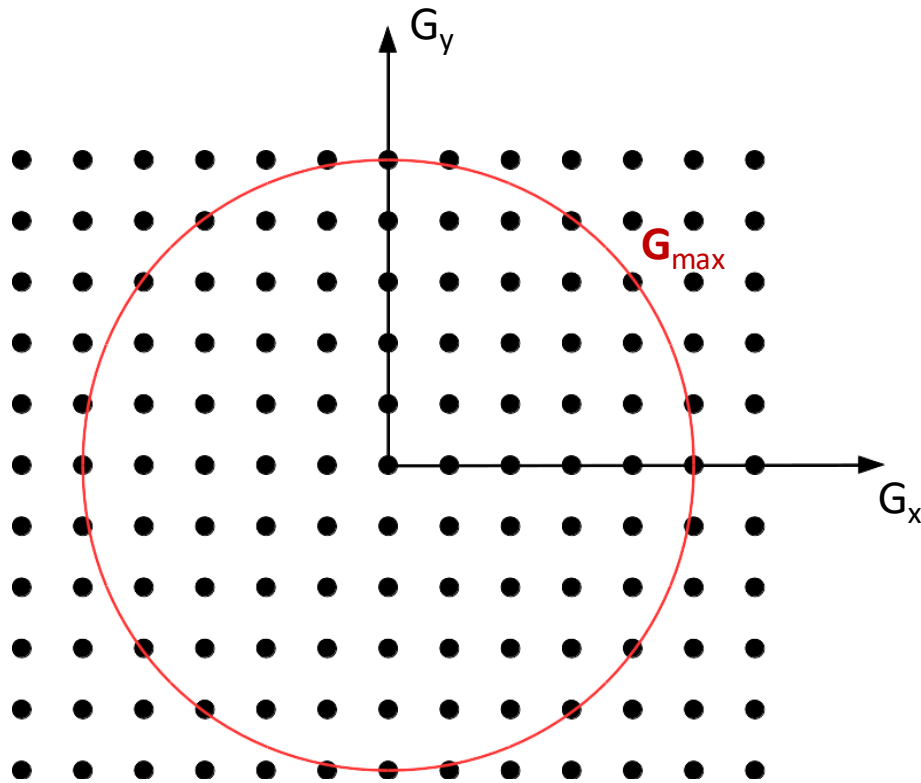
- Only Fourier components compatible with the periodicity of the lattice $\mathbf{G} = n_1 \mathbf{b}_1 + n_2 \mathbf{b}_2$



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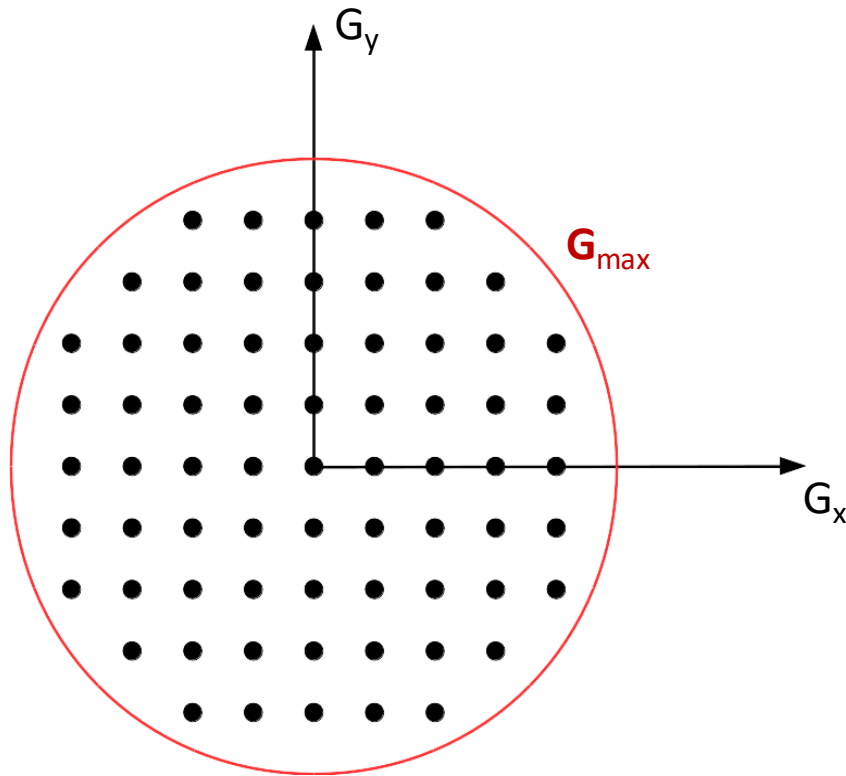


- Only Fourier components compatible with the periodicity of the lattice $\mathbf{G} = n_1 \mathbf{b}_1 + n_2 \mathbf{b}_2$
- All \mathbf{G} vectors with norm smaller than $|\mathbf{G}|_{\max}$
- $|\mathbf{G}|_{\max}$ defined by setting a cutoff on the kinetic energy $E_{\text{cut}} = \hbar^2 / 2\pi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

KS-DFT in practice: PW and PP

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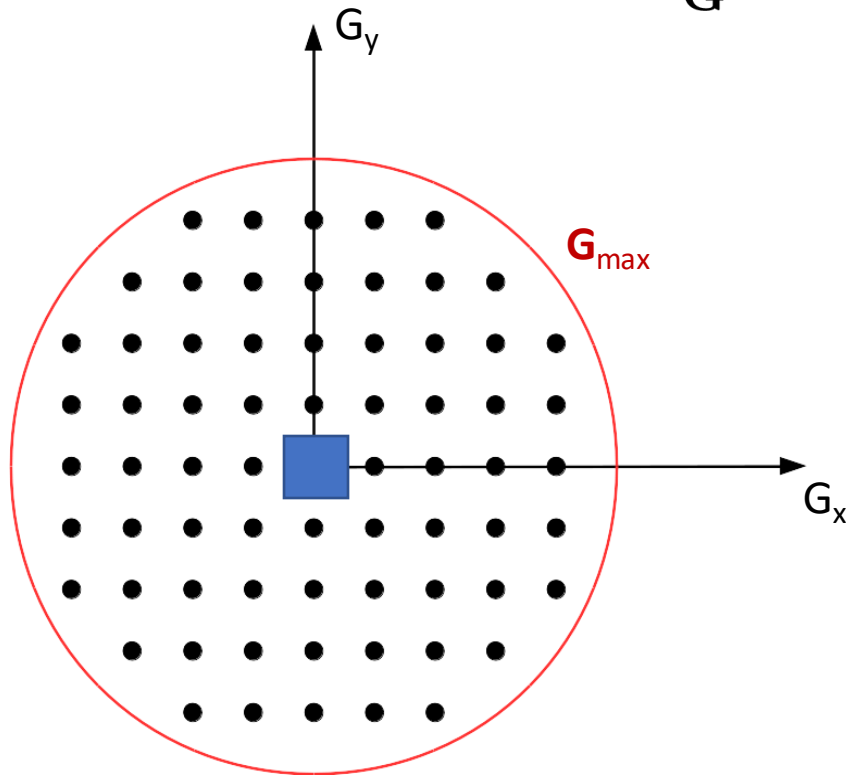


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- $|\mathbf{G}|_{\max}$ defined by setting a cutoff on the kinetic energy $E_{\text{cut}} = \hbar^2 / 2\pi |\mathbf{G}|_{\max}^2$
- `ecutwfc`: QE Input parameter for E_{cut}

KS-DFT in practice: PW and PP

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

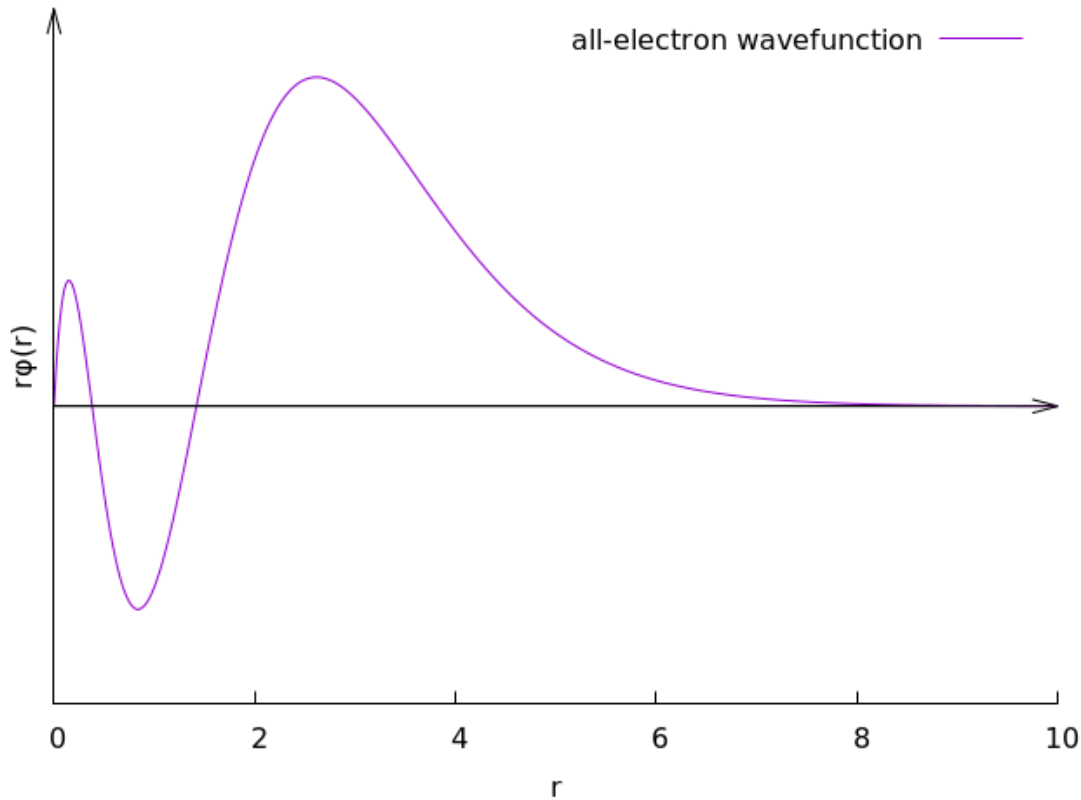
$$\psi_{\mathbf{k}n}(\mathbf{r}) = \exp[i\mathbf{k} \cdot \mathbf{r}] u_{\mathbf{k}n}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{k}n}(\mathbf{G}) \exp[i(\mathbf{G} + \mathbf{k}) \cdot \mathbf{r}]$$



- 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 requires integration over the \mathbf{k} -points \rightarrow BZ sampling (`K_POINTS` card)

KS-DFT in practice: PW and PP

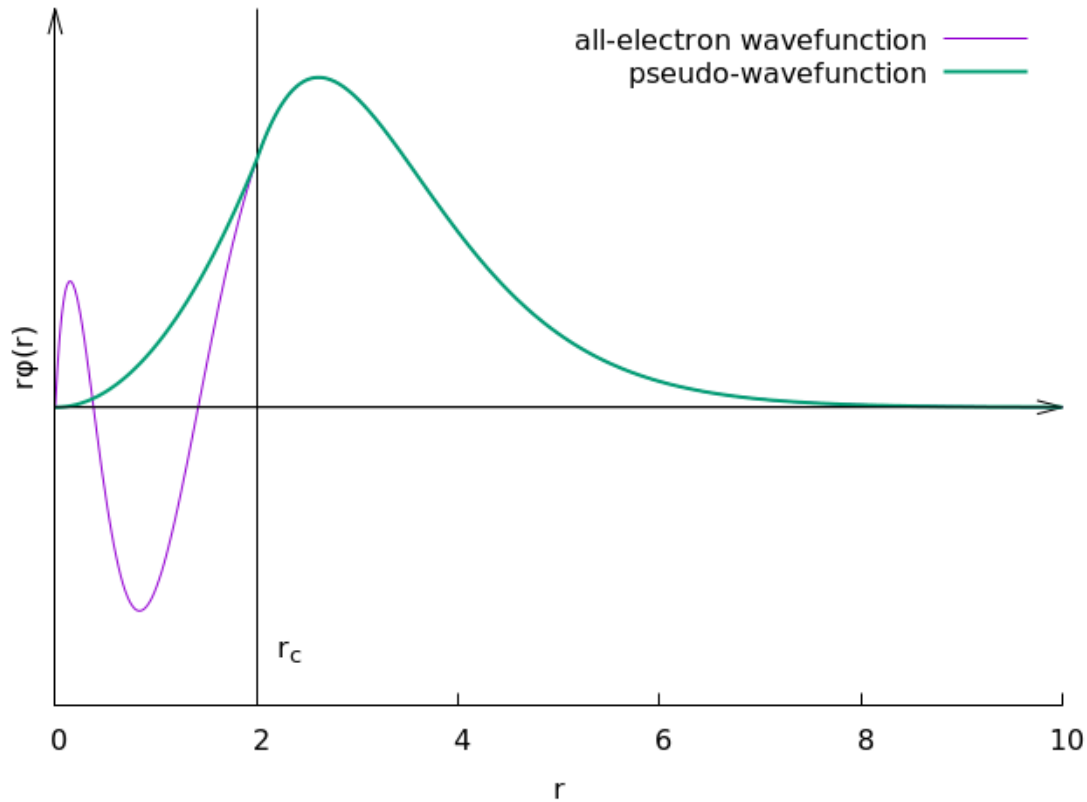
The use of pseudo-potentials allows to ignore chemically inert core electrons and make PW calculation feasible



- 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



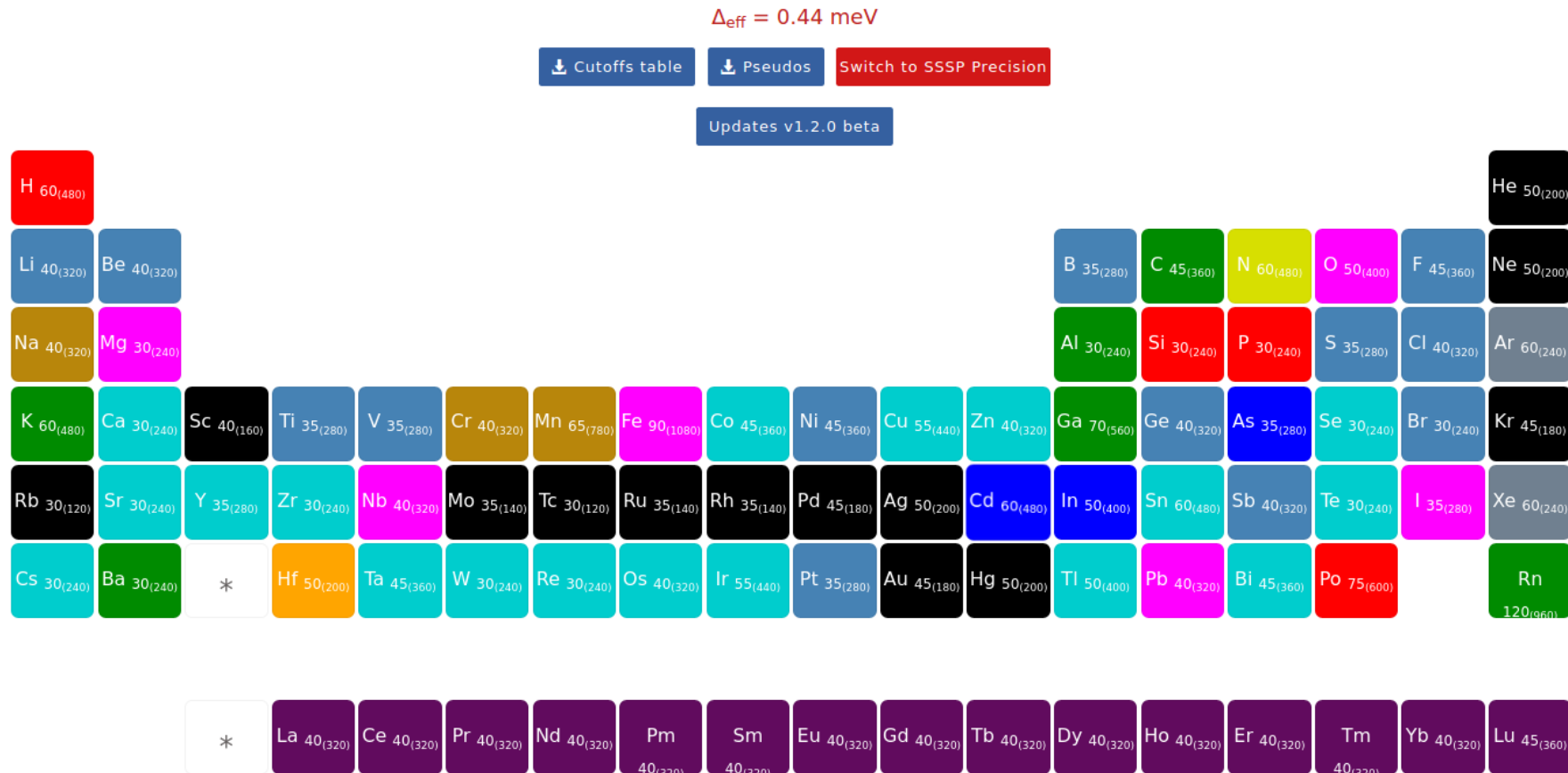
- Strong oscillations close to the nuclei: large number of PW needed
- Replace the coulombic potential with a pseudo-potential that produces smooth pseudo-wavefunctions
- Different recipes: Norm-conserving, Ultra-soft, Projector-augmented-wave (PAW)

Where to find PPs

Standard solid-state pseudopotentials (SSSP):

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

SSSP Efficiency (version 1.1.2)



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

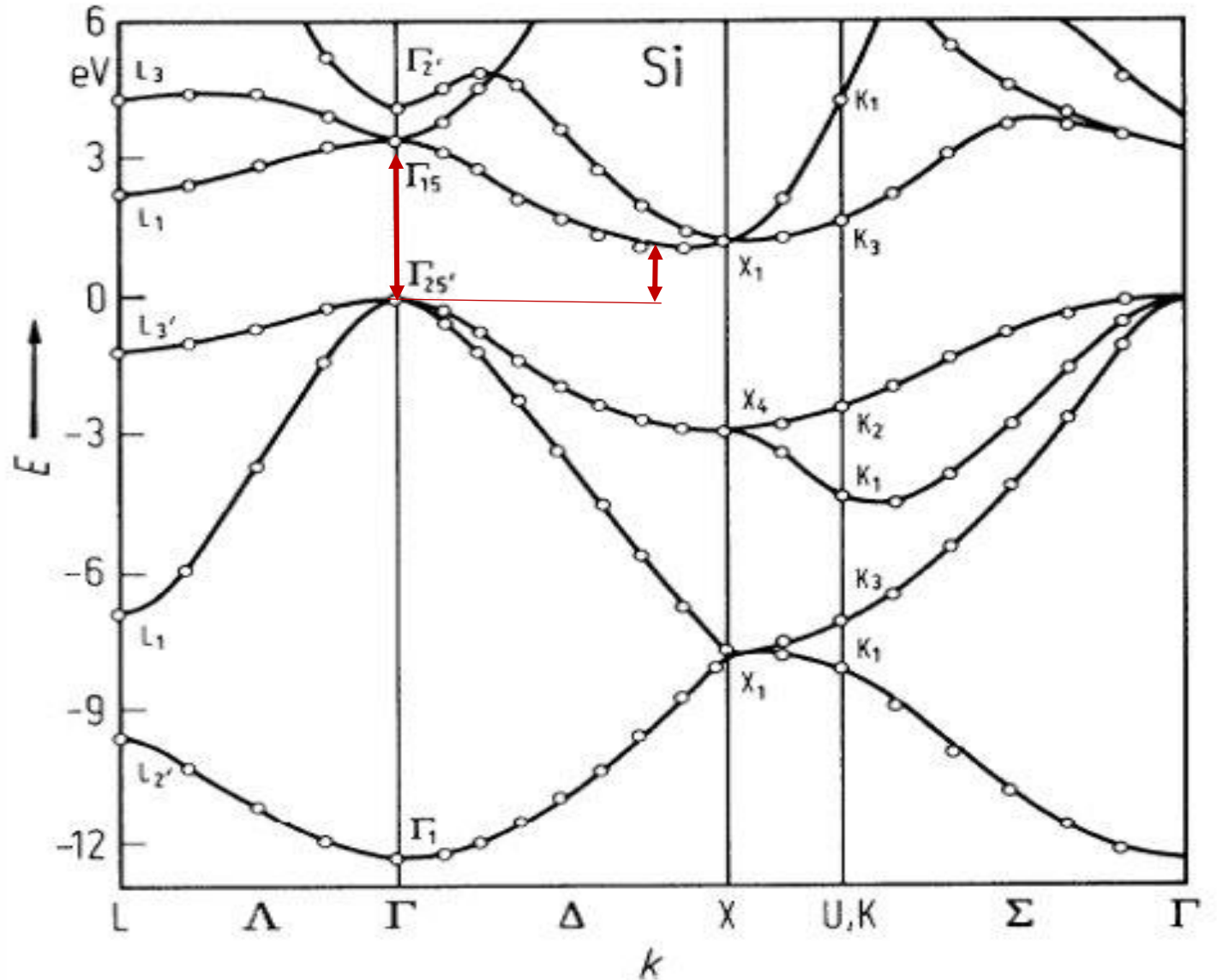
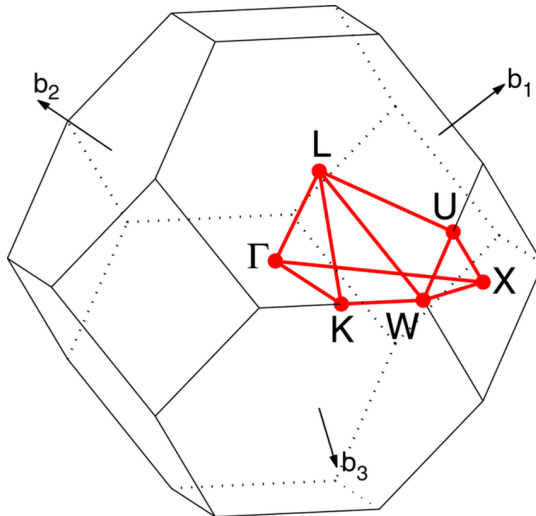
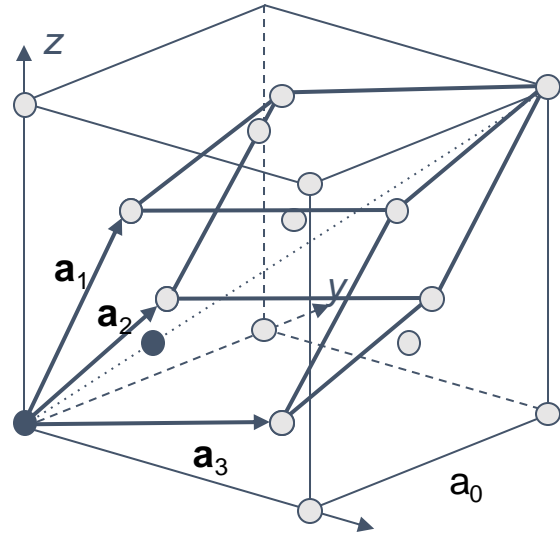
<http://www.pseudo-dojo.org/>

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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 are 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

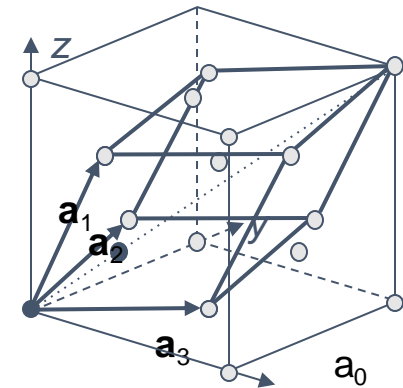
```
Si 0.25 0.25 0.25
```

```
K_POINTS {automatic}
```

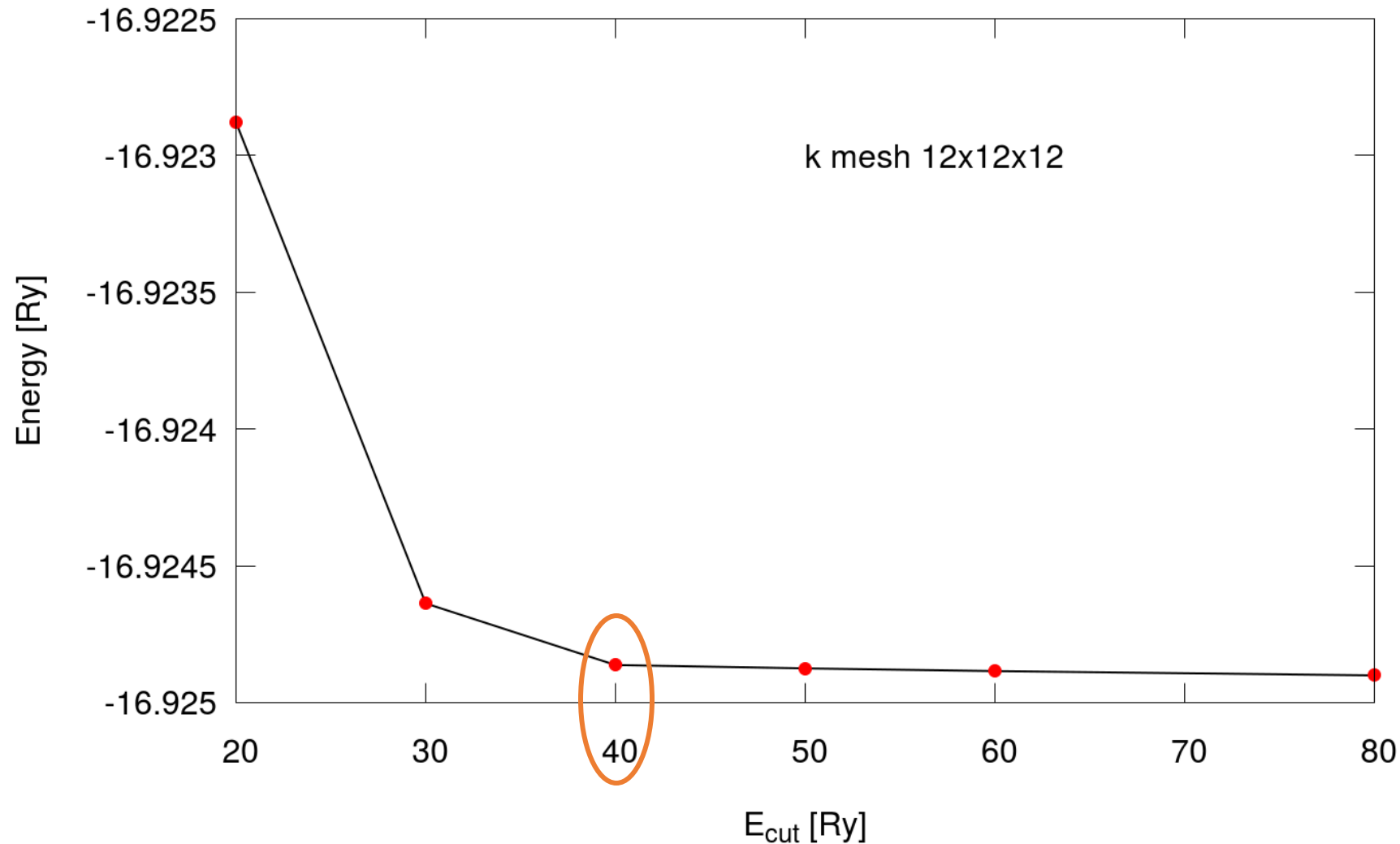
```
XXX YYY ZZZ 0 0 0
```

BZ sampling

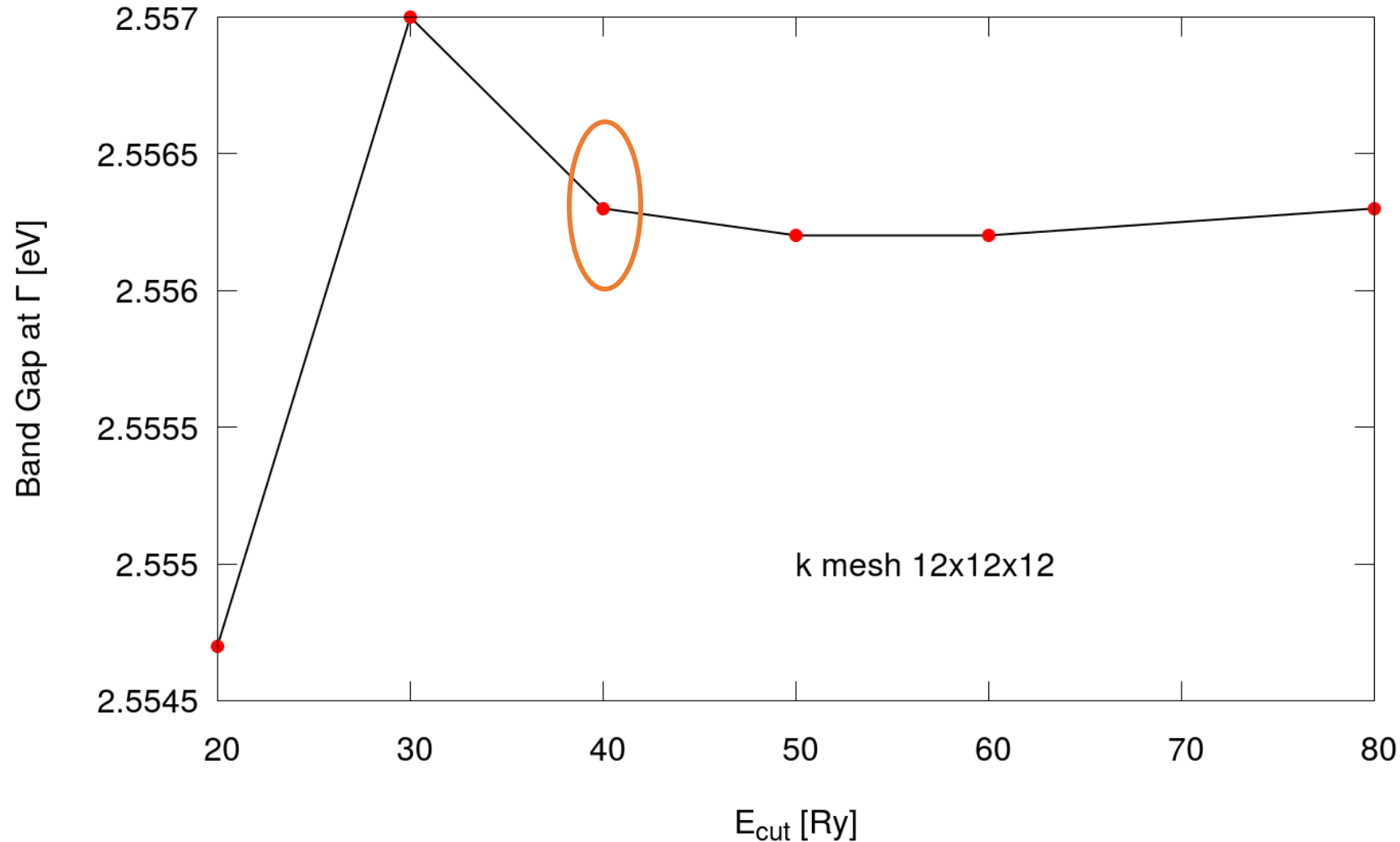
https://www.quantum-espresso.org/Doc/INPUT_PW.html



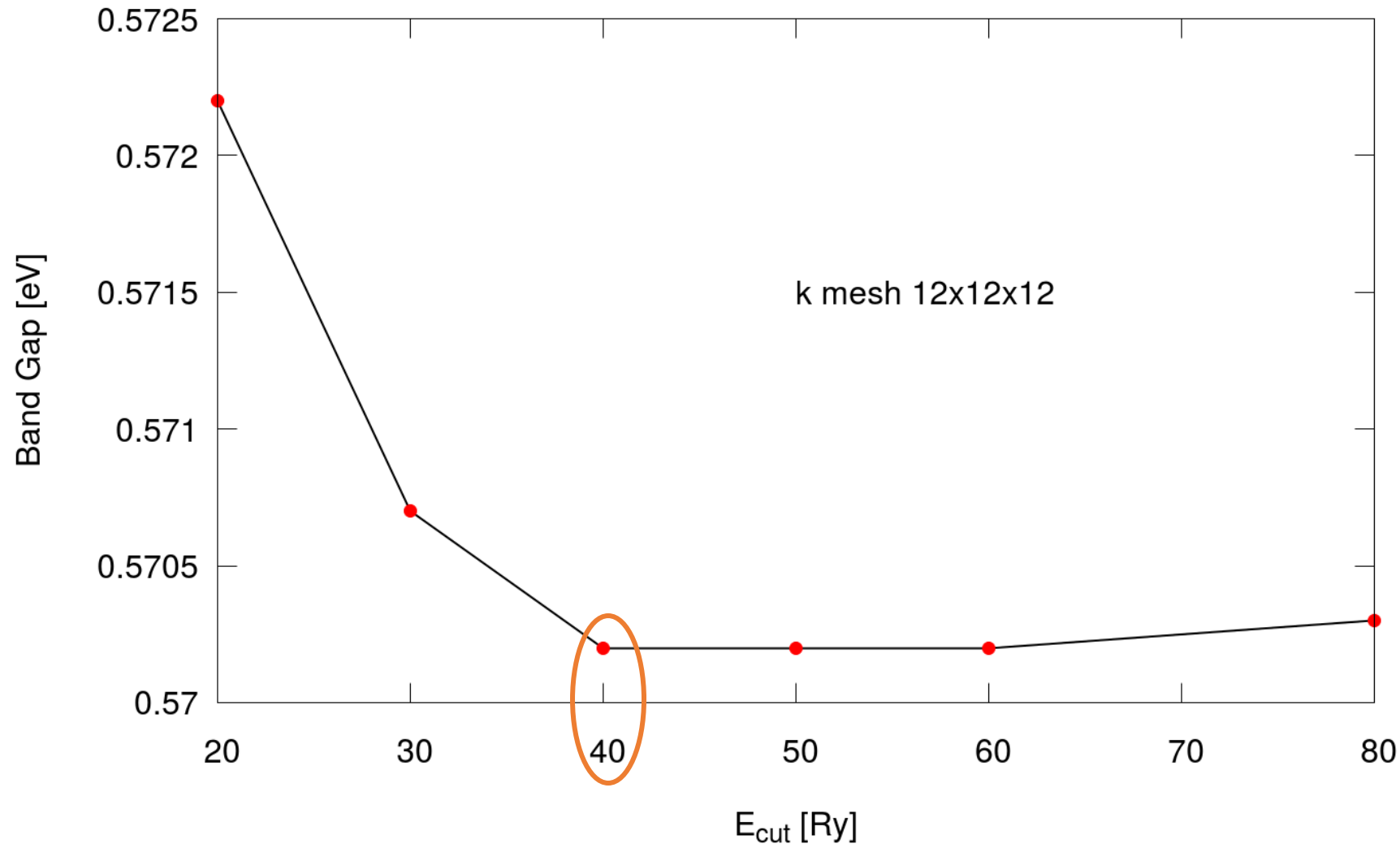
Convergence wrt E_{cut} : total energy



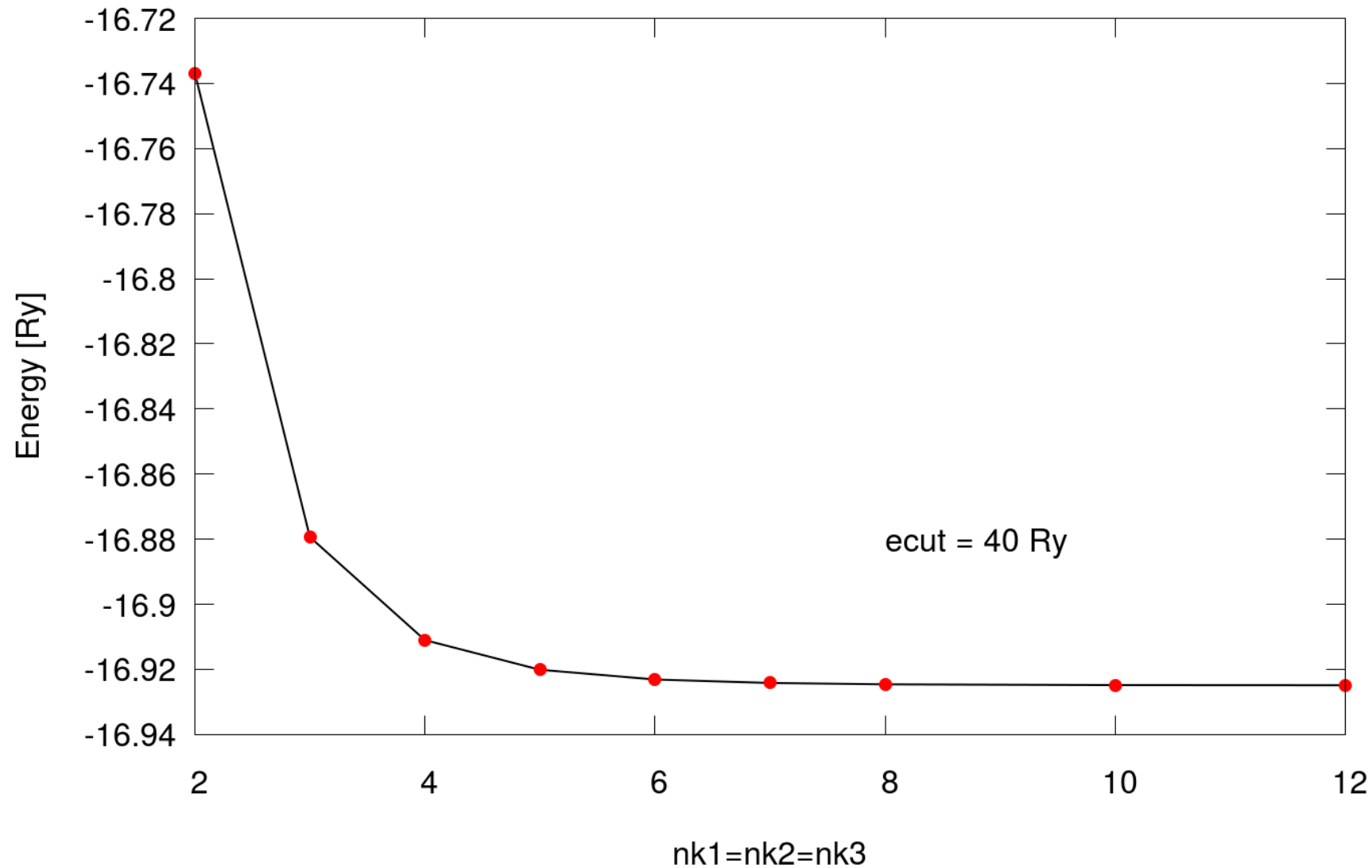
Convergence wrt E_{cut} : direct band gap



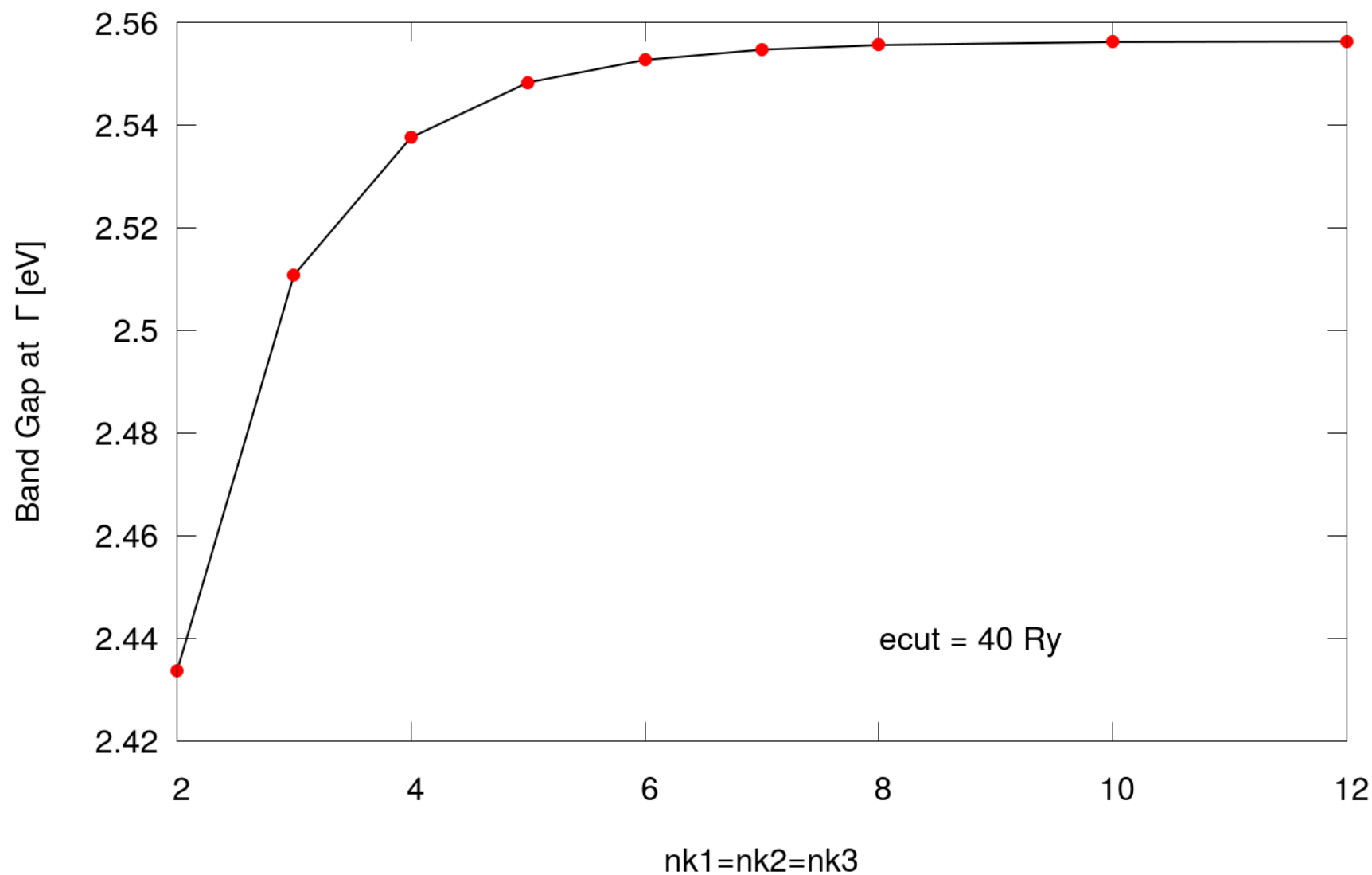
Convergence wrt E_{cut} : indirect band gap



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/hubbard-koopmans-2022
```

- Go to the exercise0 folder

```
cd hubbard-koopmans-2022/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 ,
/
&electrons
  conv_thr = 1.d-8
/
ATOMIC_SPECIES
Si 28.086  Si.pbe_PseudoDojo.UPF
```

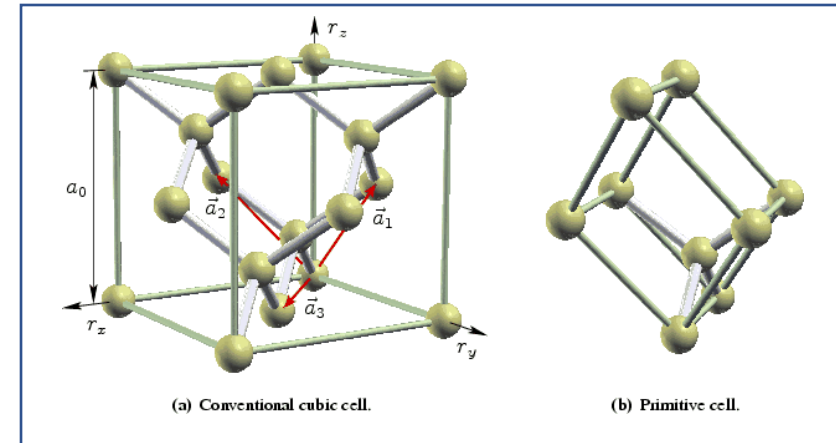
```
ATOMIC_POSITIONS {alat}
Si 0.00 0.00 0.00
Si 0.25 0.25 0.25
```

```
K_POINTS {automatic}
```

```
12 12 12 0 0 0
```

Converged value for the
BZ sampling

Converged value for the Wave-Functions cutoff



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 ! L
```

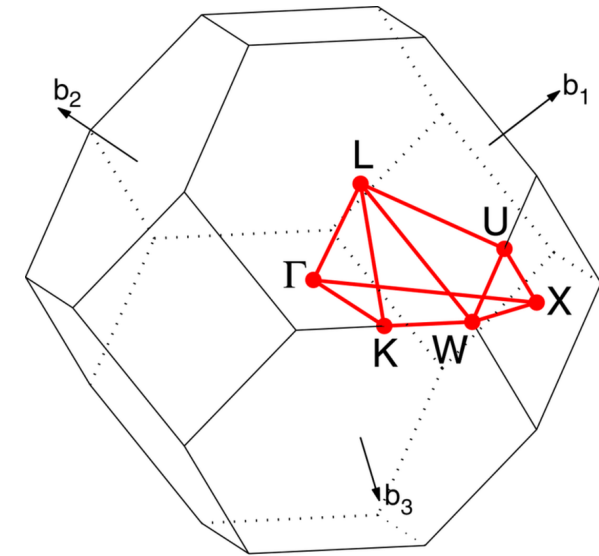
```
0.00000 0.00000 0.00000 20 ! G
```

```
0.50000 0.00000 0.50000 20 ! X
```

```
0.37500 0.37500 0.75000 20 ! K
```

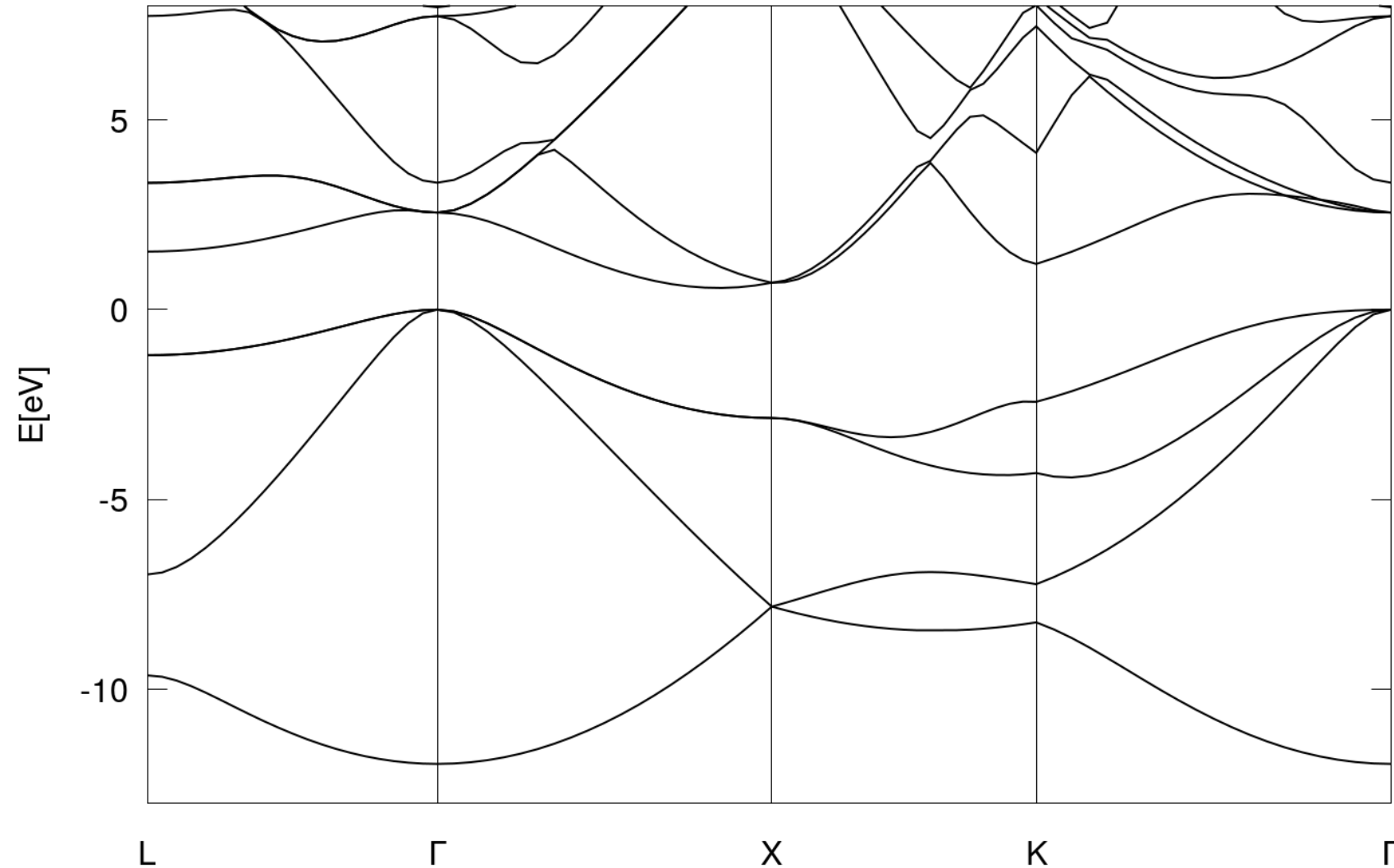
```
0.00000 0.00000 0.00000 0 ! G
```

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

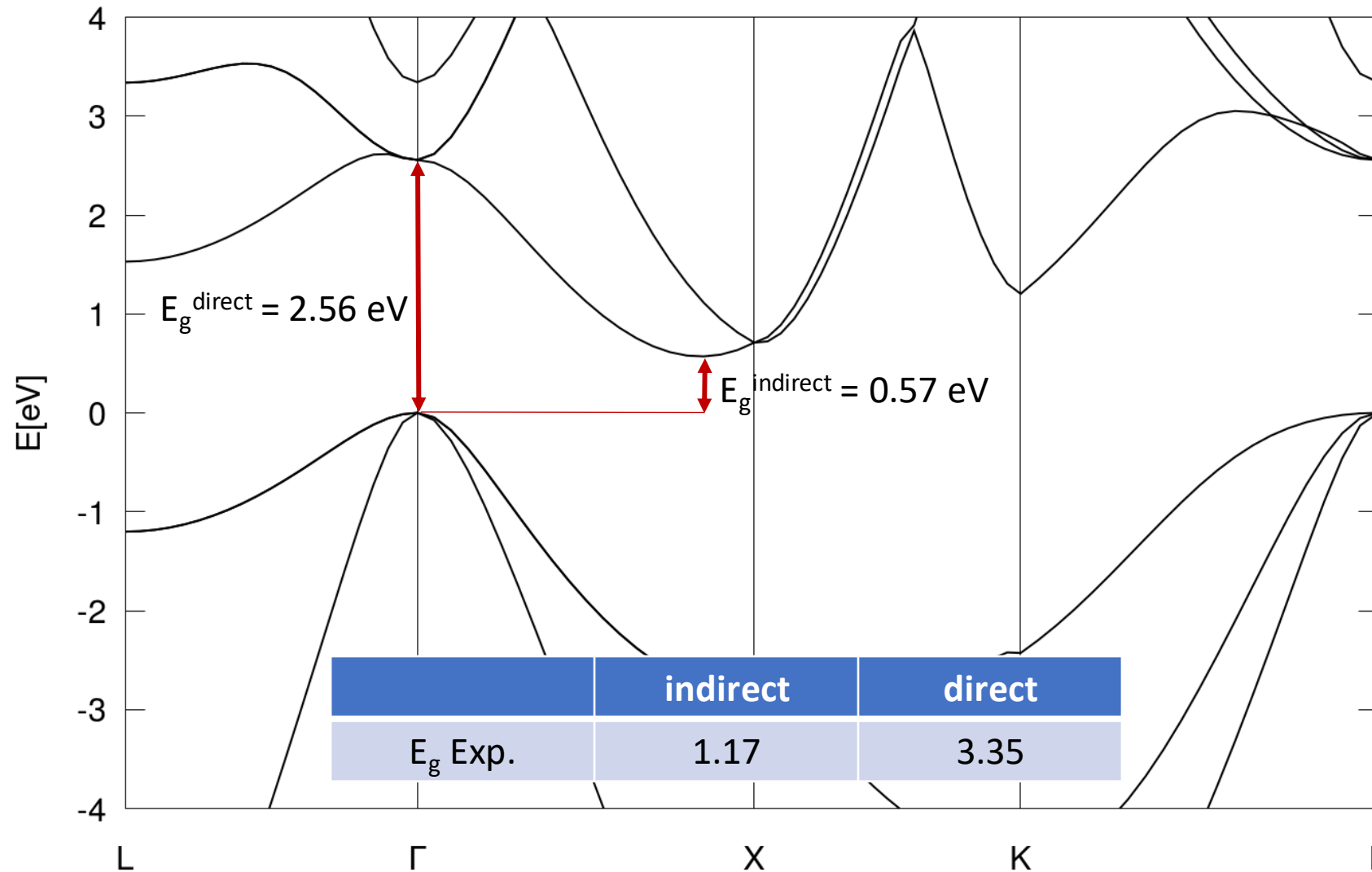


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PBE Silicon band structure



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Hybrid functionals

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

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

$$E_{xc}^{B3LYP} = (1 - a_0)E_x^{LDA} + a_0E_x^{HF} + a_x\Delta E_x^{B88} + a_cE_c^{LYP} + (1 - a_c)E_c^{LDA}$$

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)]

$$E_{xc}^{hyb} = (1 - a_0)E_x^{DFT} + a_0E_x^{HF} + E_c^{DFT}$$

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

$$E_{xc}^{PBE0} = \frac{3}{4}E_x^{DFT} + \frac{1}{4}E_x^{HF} + E_c^{PBE}$$

Range-separated Hybrid functionals

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

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

Long-Range Range-separation parameter Short-Range

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

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:

$$E^{\text{HF}} = -\frac{4\pi}{2\Omega} \frac{\Omega}{(2\pi)^3} \int_{BZ} d\mathbf{q} \sum_{\mathbf{G}} \frac{A(\mathbf{q} + \mathbf{G})}{|\mathbf{q} + \mathbf{G}|^2} \quad A(\mathbf{q} + \mathbf{G}) = \frac{\Omega}{(2\pi)^3} \int_{BZ} d\mathbf{k} |\rho_{\mathbf{k},v}^{\mathbf{k}-\mathbf{q},v'}(\mathbf{q} + \mathbf{G})|^2$$

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`)

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

`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
```

← You can change the fraction of EXX and/or the range separation parameter.

```
screening_parameter = WWW
```

```
/
```

```
&electrons
```

```
...
```

```
/
```

```
ATOMIC_SPECIES
```

```
...
```

```
ATOMIC_POSITIONS {alat}
```

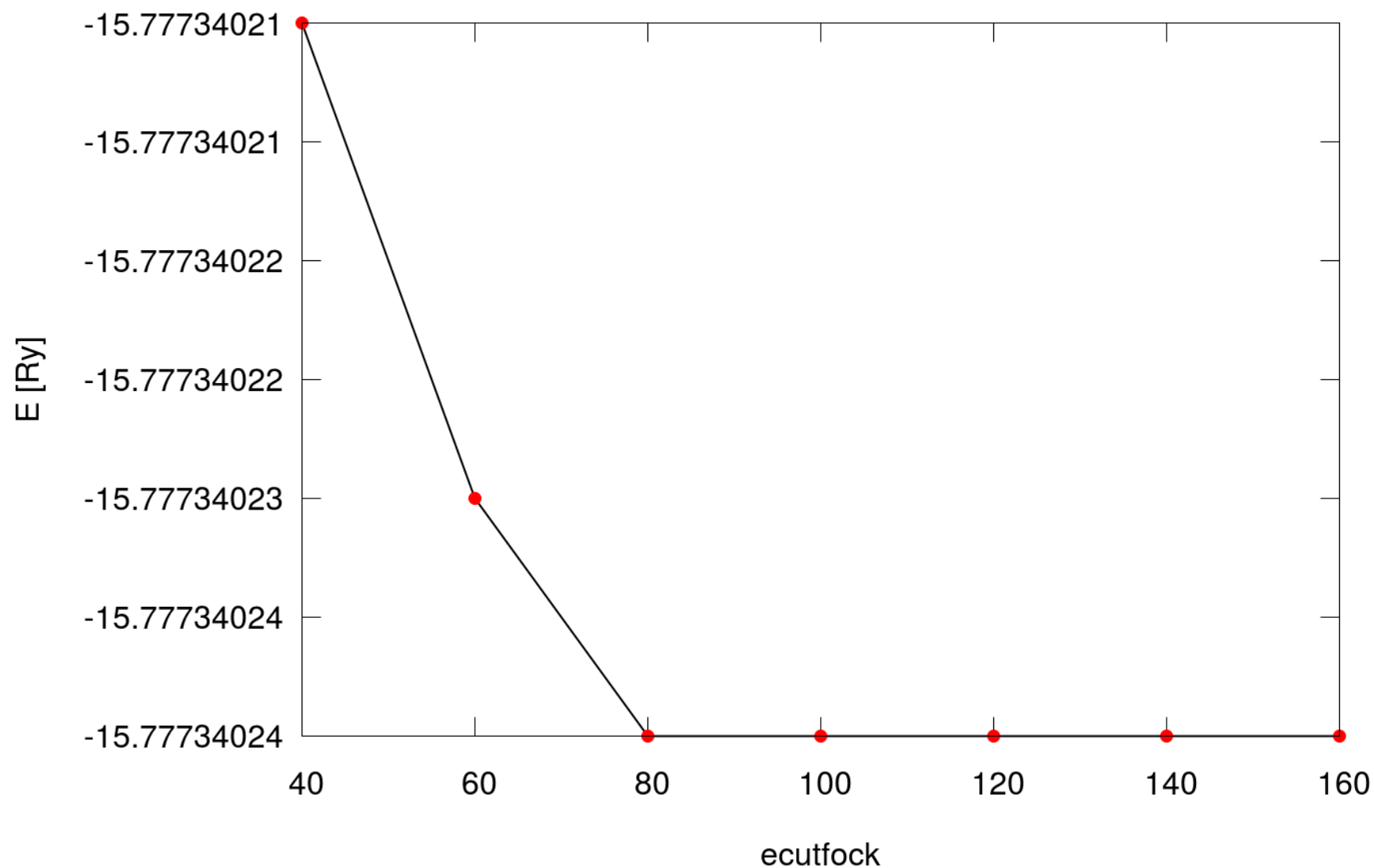
```
...
```

```
K_POINTS {automatic}
```

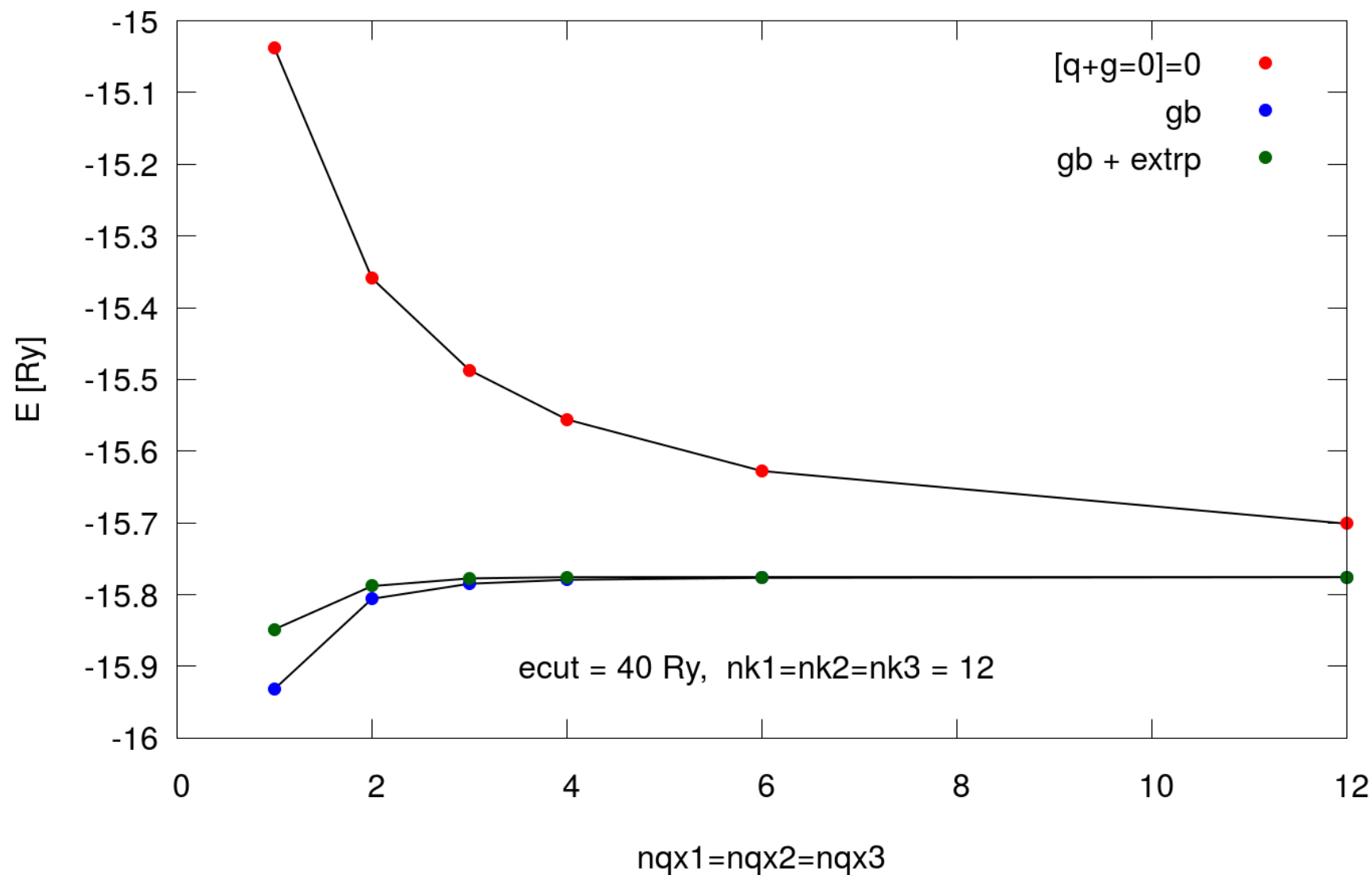
```
12 12 12 0 0 0
```

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

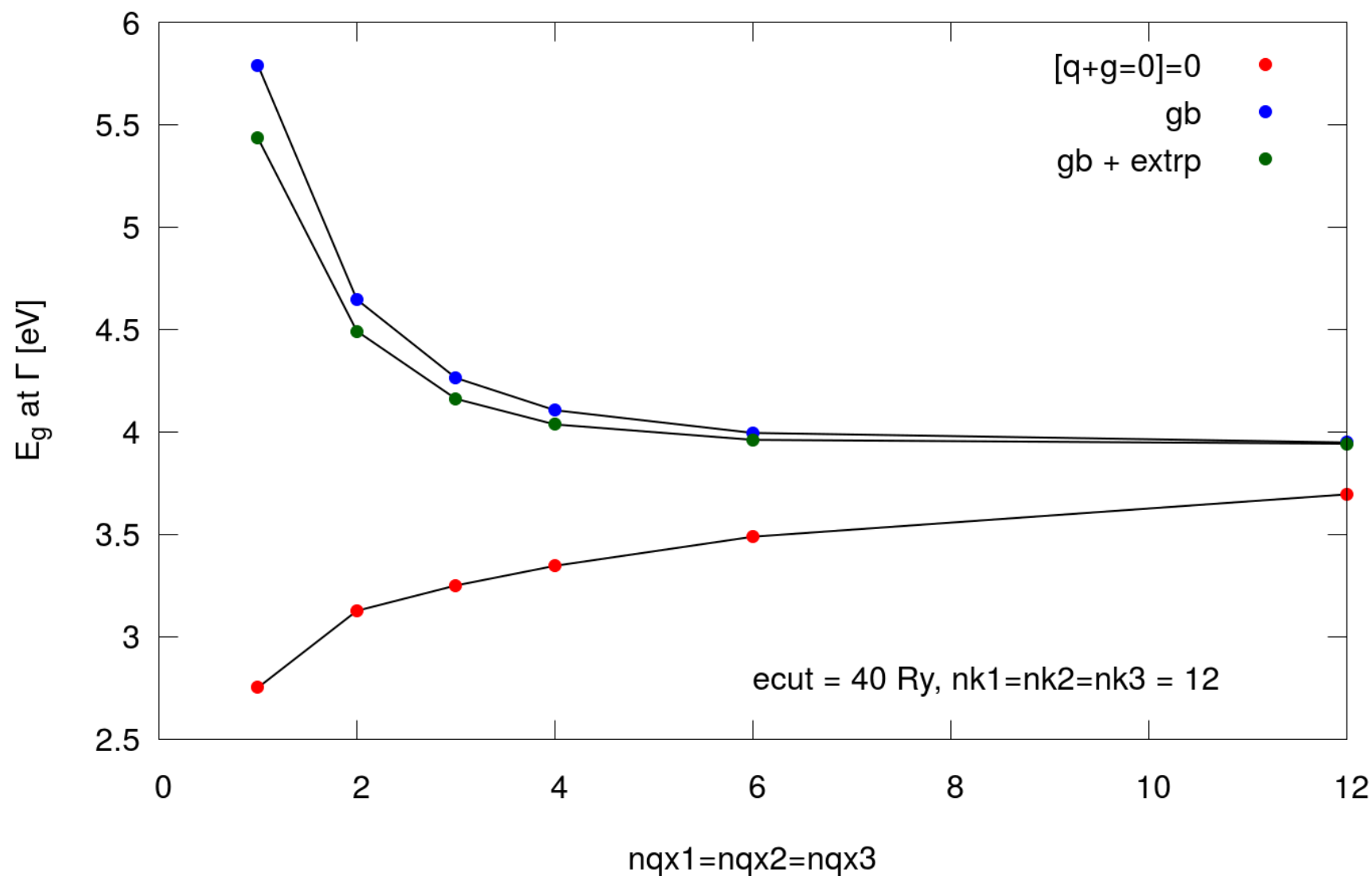
PBE0 energy convergence wrt ecutfck



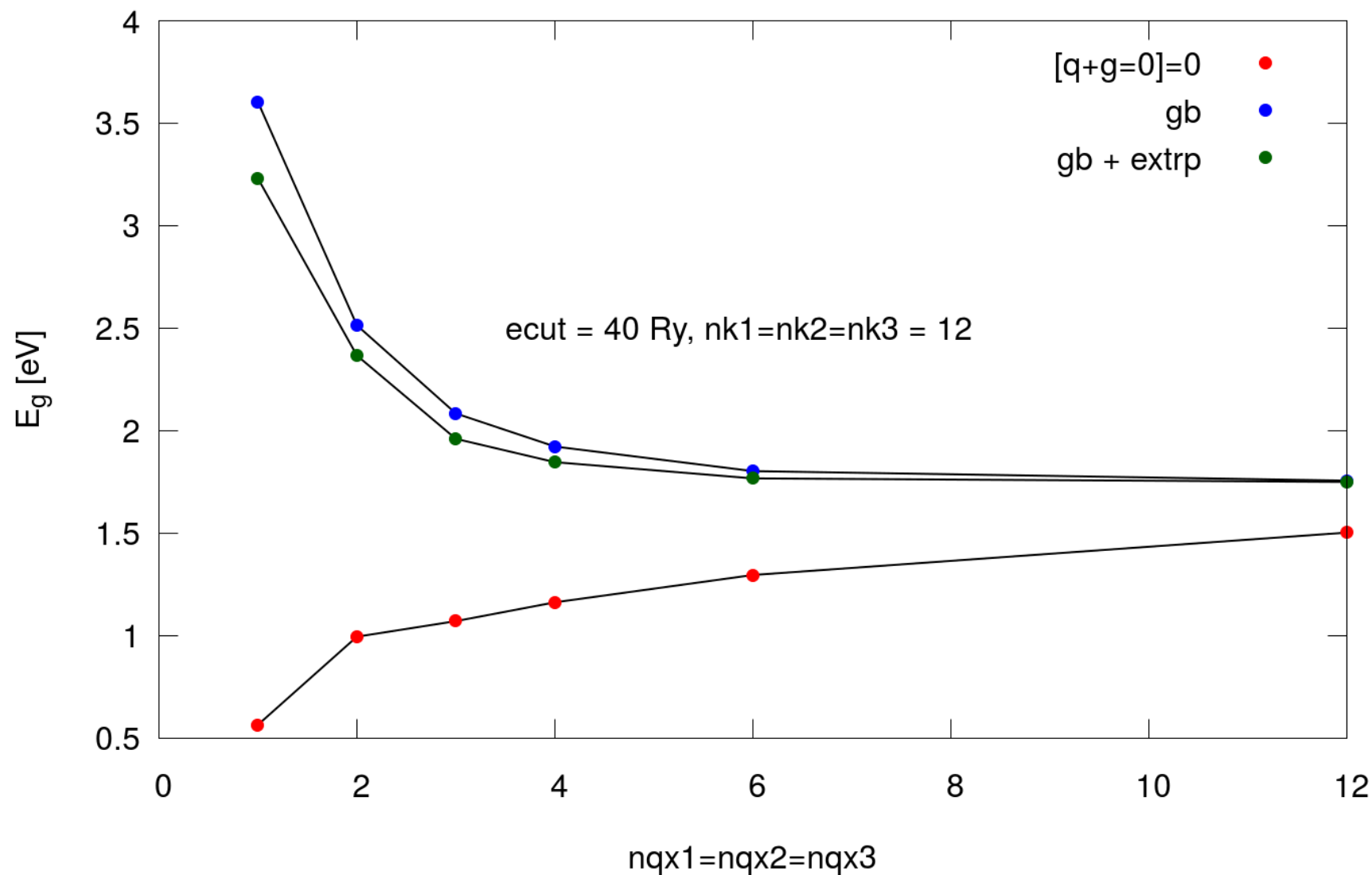
PBE0 energy convergence wrt n_{qx}



PBE0 direct band Gap convergence wrt n_{qx}



PBE0 indirect band Gap convergence wrt n_{qx}



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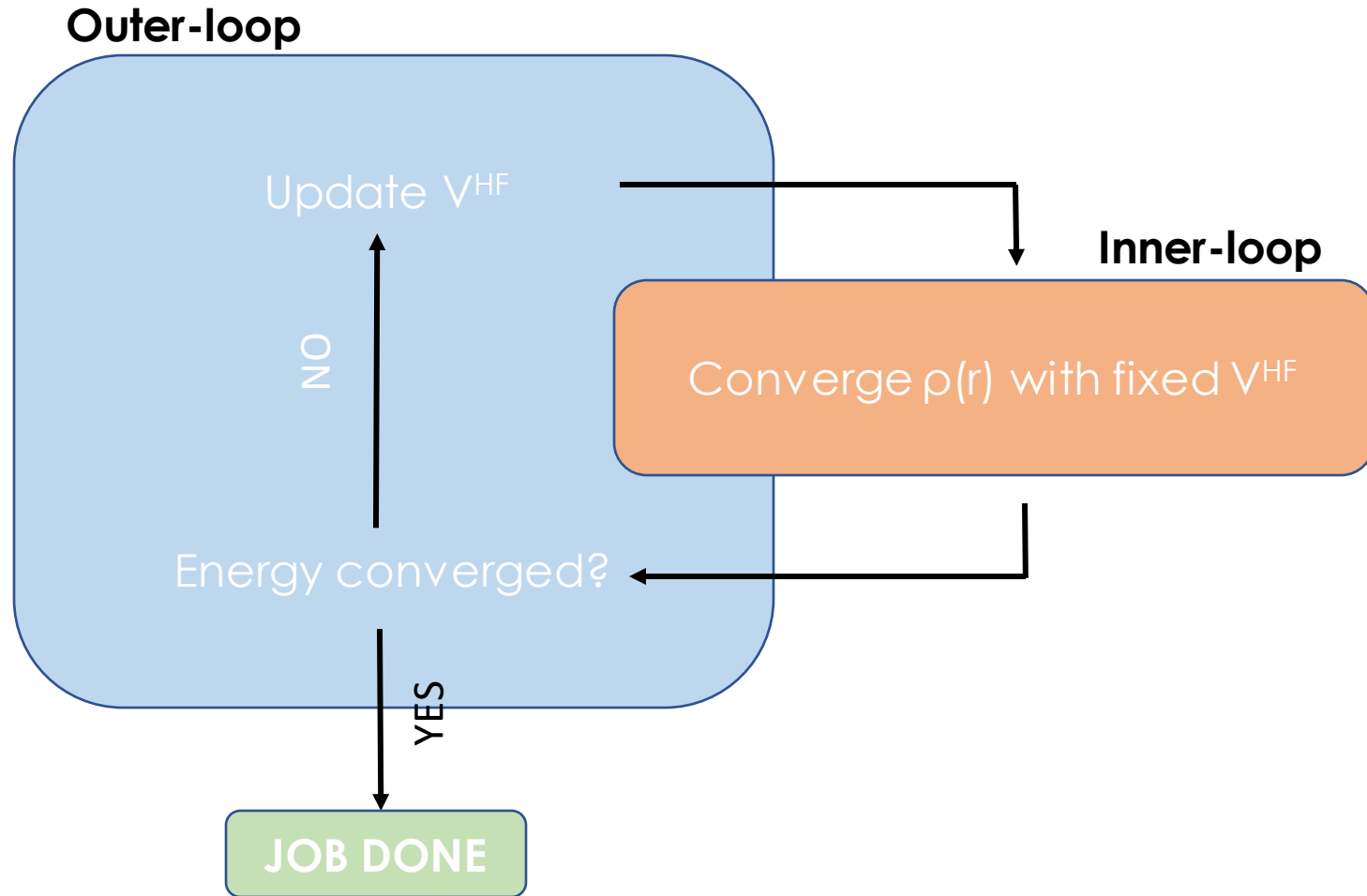
- Go to the exercise1 folder

```
cd hubbard-koopmans-2022/Day1/exercise1
```


Silicon PBE0 electronic structure: SCF calculation

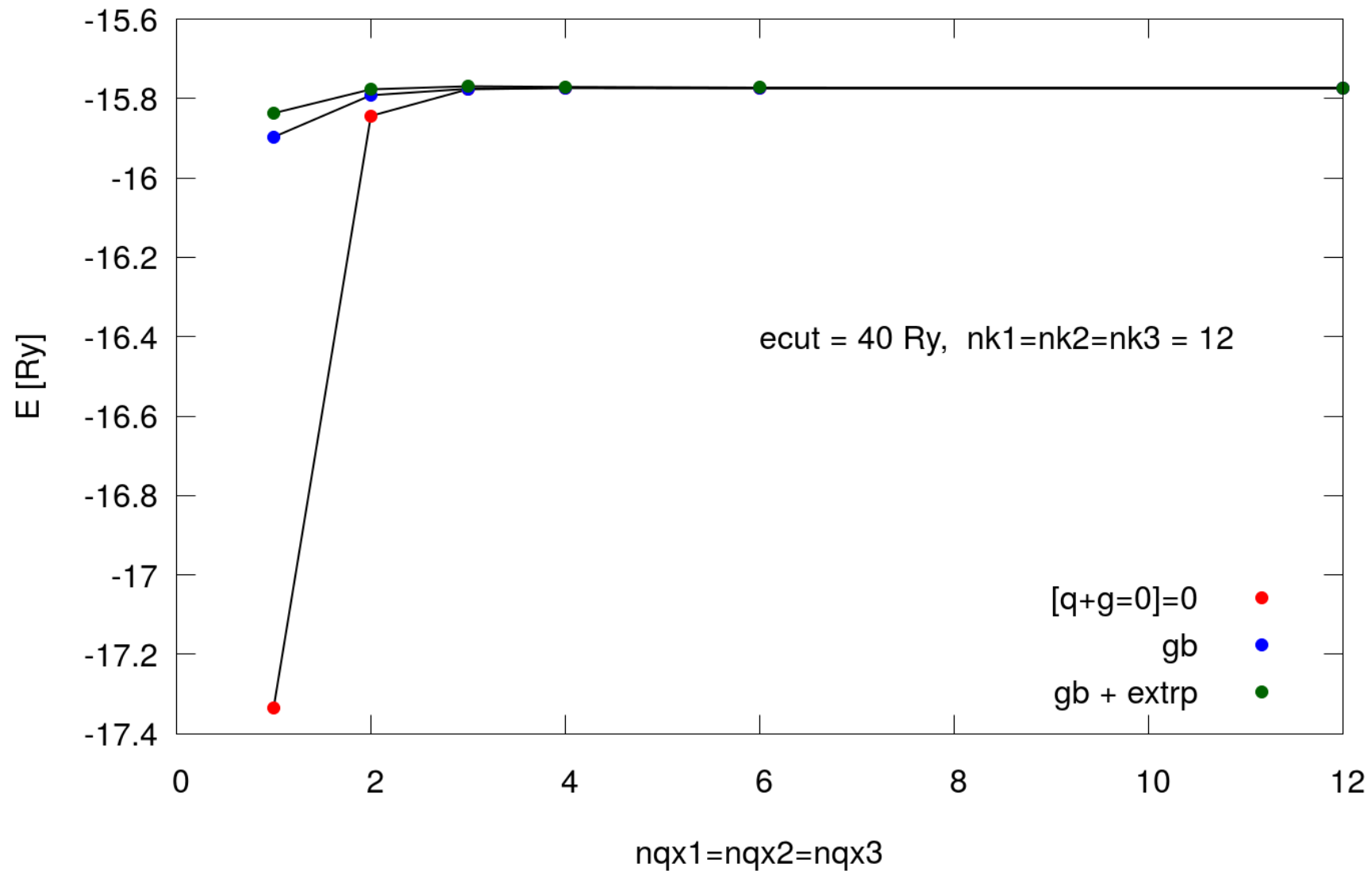
```
&control
  ...
/
&system
  ...
  input_dft          = "pbe0"
  nqx1 = 4, nqx2 = 4, nqx3 = 4 ← Converged parameters for nqx
  exxdiv_treatment = "gb"
  x_gamma_extrapolation = .true.
  ecutfock          = 40 ← Converged value for ecutfock
/
&electrons
  ...
/
ATOMIC_SPECIES
...
ATOMIC_POSITIONS {alat}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

Nested self-consistent loop

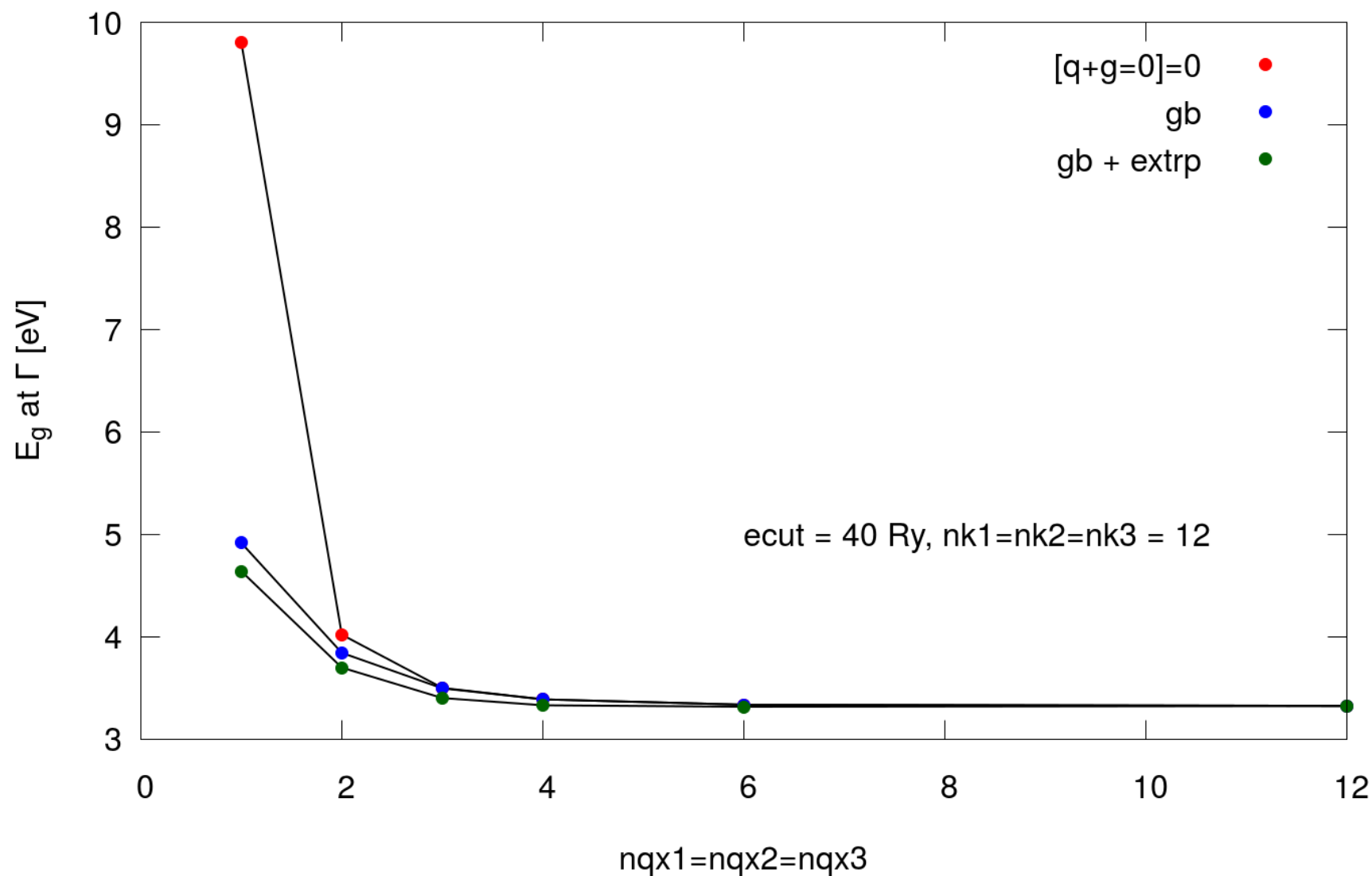


1. Normal scf (LDA or similar) is performed
2. Hybrid functional is switched. V^{HF} is calculated using the current best wfcs
3. A new scf is performed keeping V^{HF} fixed
4. Exchange error (d_{exx}) is computed
5. If $d_{\text{exx}} > \text{thr}$ the procedure is repeated from 1.

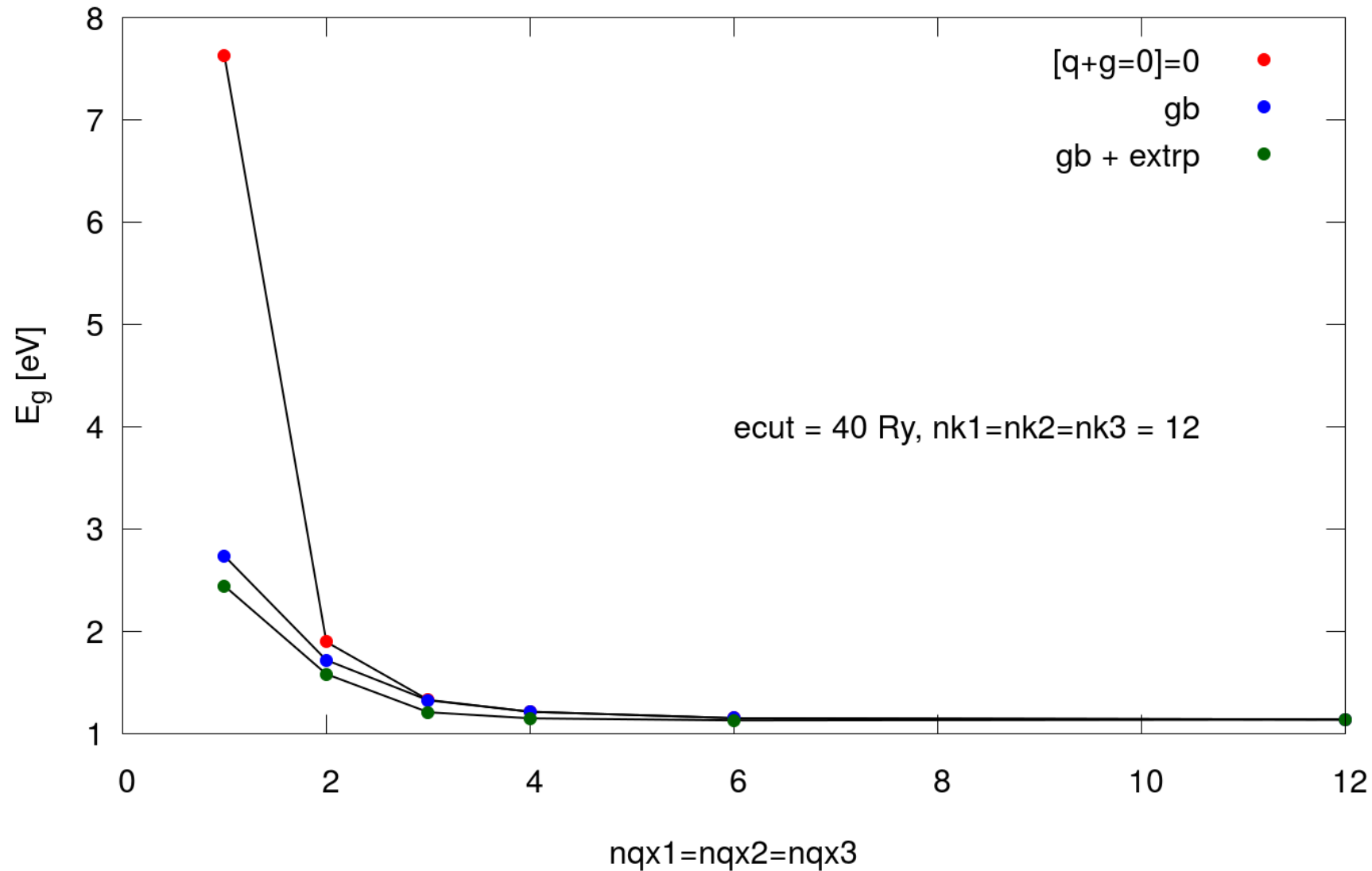
HSE energy convergence wrt n_{qx}



HSE direct band Gap convergence wrt nqx



HSE indirect band Gap convergence wrt n_{qx}



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

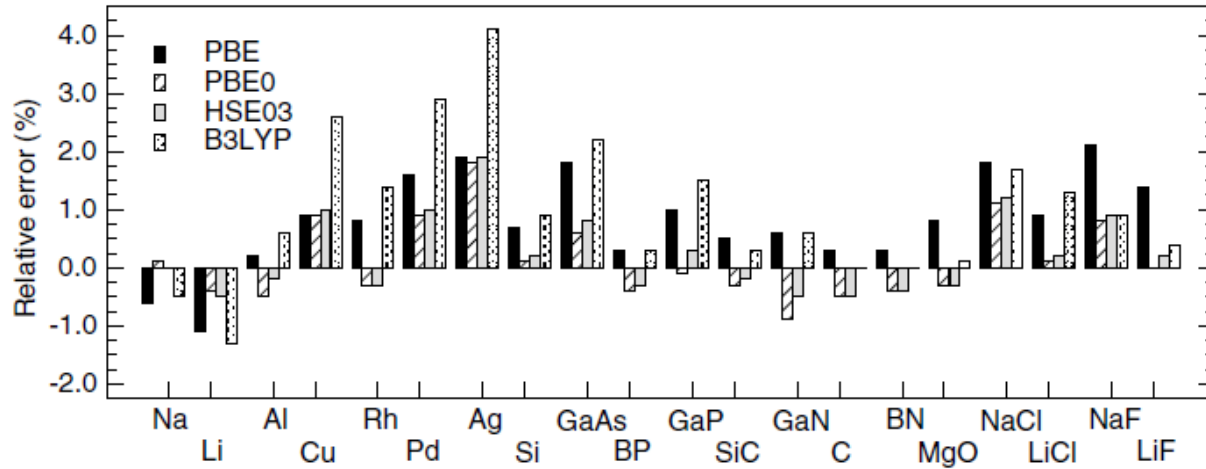
Functional	MAE(G2)	MAE(G2-1)	Max AE(G2)	Max AE(G2-1)
LDA	83.7	36.4	216	84
PBE	17.1	8.6	52	26
BLYP	7.1	4.7	28	15
B3LYP	3.1	2.4	20	10
PBE0	4.8	3.5	24	10

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

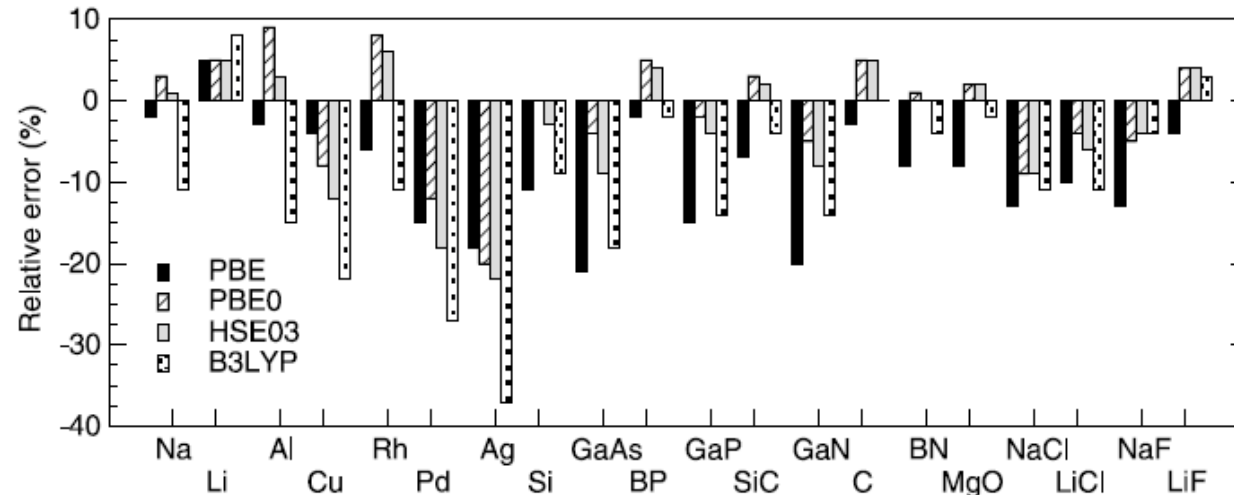
Lattice constants of solids



	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

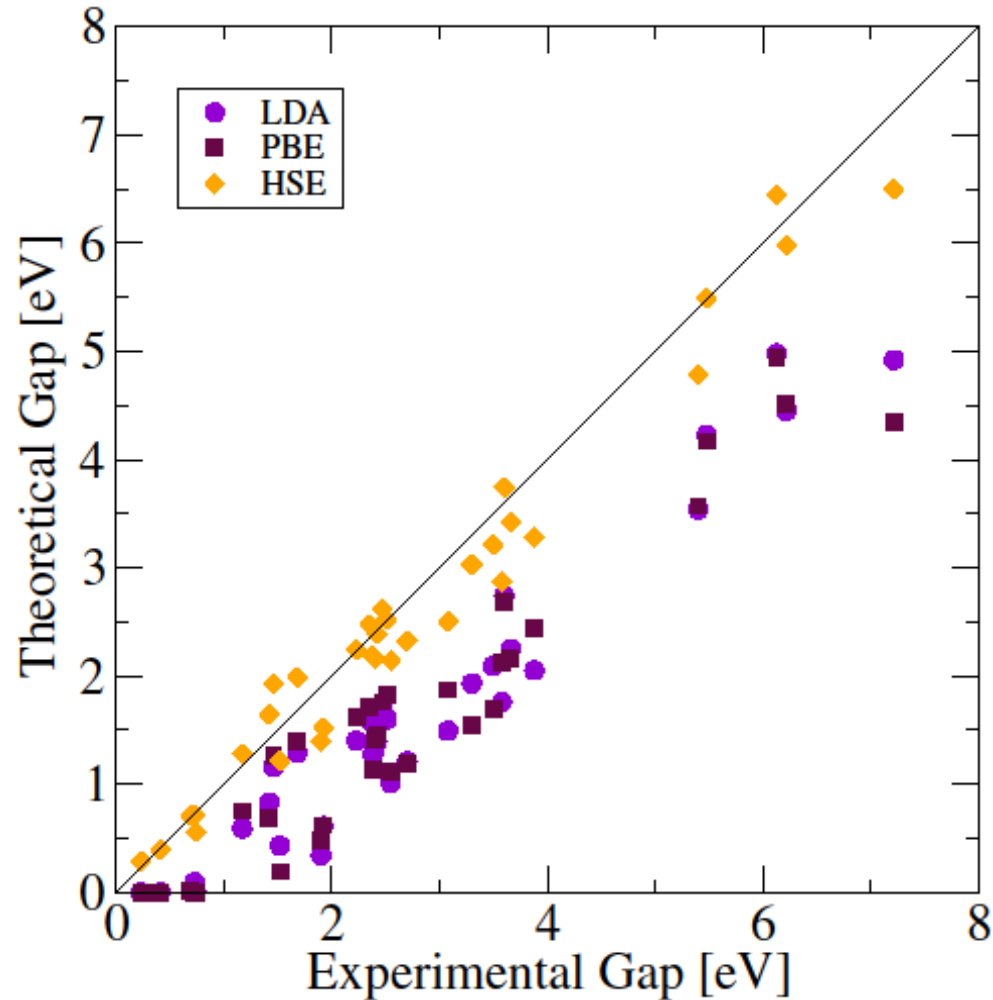
	PBE	PBE0	HSE	B3LYP
MRE	-9.8	-1.2	-3.1	-10.2
MARE	9.4	5.7	6.4	11.4
No-metals				
MRE	-10.4	-0.7	-1.8	-6.8
MARE	10.4	3.8	4.6	7.4



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

Heyd et al. JCP 123, 174101 (2005)

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 hands-on later today)