QUANTUM ESPRESSO FOUNDATION

QUANTUMESPRESSO

MaX School on Advanced Materials and Molecular Modelling
with Quantum ESPRESSO

QUANTUM ESPRESSO: overview and basic functionalities. The self-consistent cycle. PBC: supercells and k-point sampling

Ralph Gebauer

The Abdus Salam
International Centre
for Theoretical Physics

Trieste, May 17th, 2021

This school is a large-scale collaboration:

MAX

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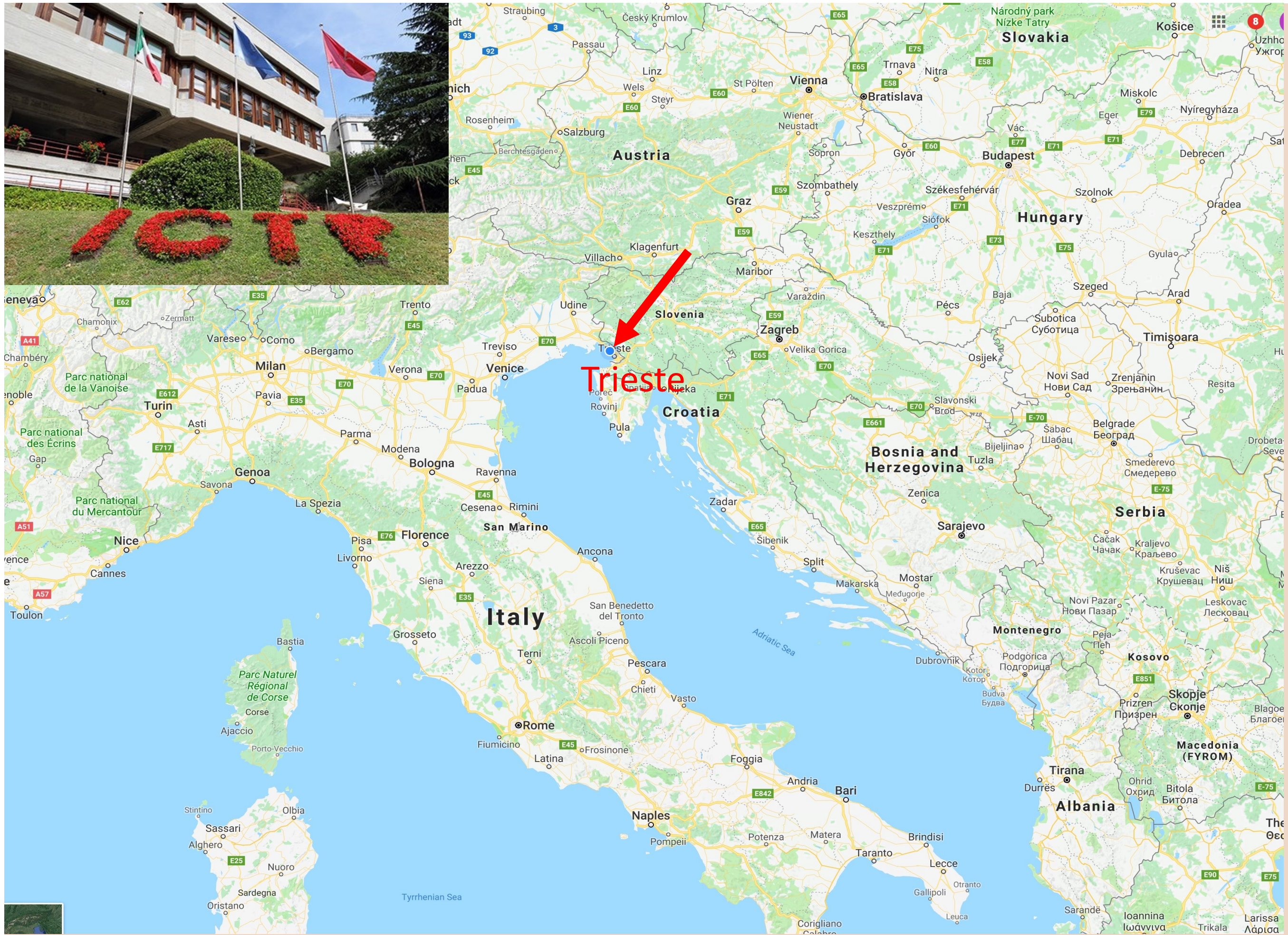
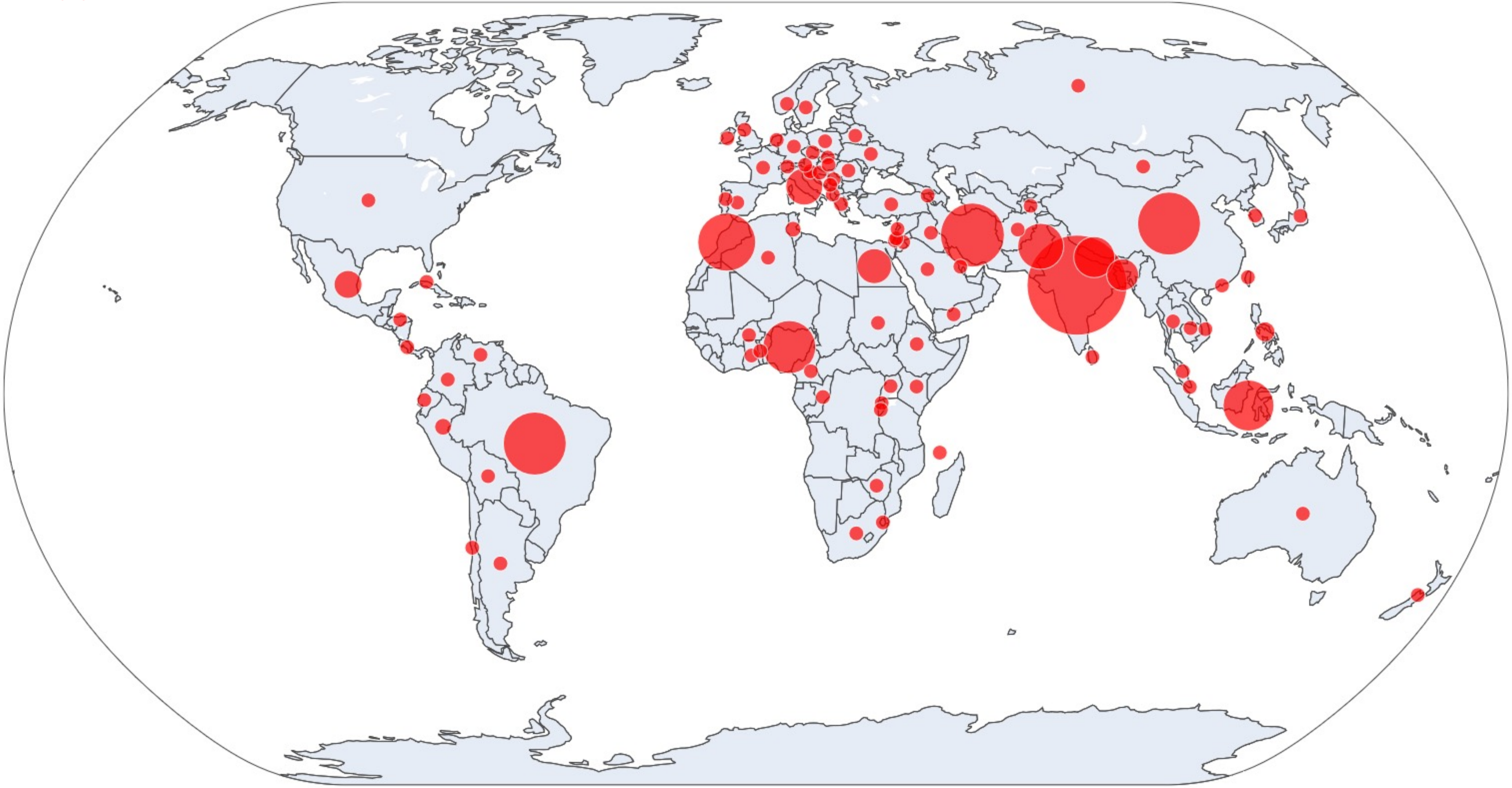
SISSA



Founded in 1964, the Abdus Salam International Centre for Theoretical Physics (ICTP) operates under the aegis of two United Nations Agencies: UNESCO and IAEA and is regularized by a seat agreement with the Government of Italy.

1292 applicants!



Special thanks to the secretaries: Monica Ancuta, Viktoriya Lvova and Adriana Pinto

The star of this school:

Quantum-ESPRESSO

Quantum ESPRESSO: Quantum opEn-Source Package for Research in Electronic Structure, Simulation, and Optimization, is a distribution (an integrated suite) of software for first-principle simulations, i.e., atomistic calculations based on electronic structure, using density-functional theory, a plane-wave basis set, pseudopotentials.

QE exists since 2002, resulting from the merge of pre-existing packages; some core components have been under development for ~ 30 years

The main goals of Quantum-ESPRESSO are:

- innovation in theoretical methods and numerical algorithms
- efficiency on modern computer architectures

The star of this school:

Quantum-ESPRESSO
License:

QE is distributed under the GNU (Gnu’s Not Unix) General Public License (GPL v.2), probably the most common free-software license.

- The source code is available.
- You can do whatever you want with the sources, but if you distribute any derived work, you have to distribute under the GPL the sources of the derived work.

Advantages:

- Everybody – including commercial entities – can contribute.
- Nobody can “steal” the code and give nothing back to the community.

The most successful example is probably the Linux Kernel.

The star of this school:

Quantum-ESPRESSO

You can get QE help, answers and general info from various sources:

the documenting papers:
J. Phys.: Condens. Matter 21, 395502 (2009) and
J. Phys.: Condens. Matter 29, 465901 (2017)

the web site: www.quantum-espresso.org

the documentation in the Doc subdirectories

the developers’ portal: github.com/QEF/q-e/releases

the mailing lists:
users@lists.quantum-espresso.org
developers@lists.quantum-espresso.org
(use first the rich ARCHIVE of these lists)

Quantum-ESPRESSO as a distribution

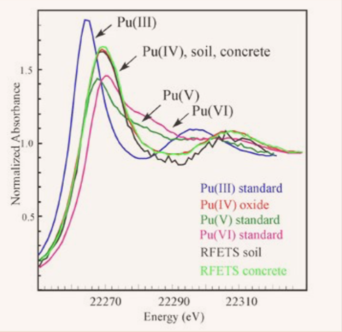
QE is not a single, executable code. It is composed of several packages:

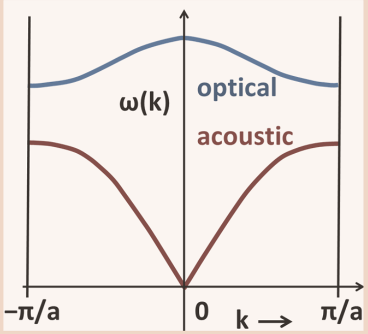
PWscf: self-consistent electronic structure, (variable-cell) structural optimization, molecular dynamics
CP: Car-Parrinello molecular dynamics, also with variable cell

They share a common installation method, input format, pseudopotential format, data output format, large parts of the basic code.

Further codes:

PHonon: linear-response calculations (phonons, dielectric properties)
PostProc: graphical and postprocessing utilities (density of states, STM, etc.)
PWneb: Nudged Elastic Band (NEB) for reaction pathways and barriers
atomic: pseudopotential generation code
PWGui: a Graphical User Interface for production of input files
PWcond: ballistic conductance
XSpectra: Calculation of X-ray near-edge adsorption spectra (XANES)
GWL: GW band structure with ultralocalized Wannier functions
TD-DFPT: Time-Dependent Density-Functional Perturbation Theory
EPW: Electron-phonon coefficients and related properties
HP: Hubbard parametes from linear response





Density Functional Theory

The ground-state energy of a system of N electrons is a functional of the electronic density n(**r**):

$$E^{DFT}[n] \qquad\qquad n(\mathbf{r}) \geq 0 \quad \int d\mathbf{r}\, n(\mathbf{r}) = N$$

The exact functional is unknown. Within the Kohn-Sham (KS) formalism, we write:

$$E^{DFT}[n] = T_s[\{\psi_i\}] + E_{ext}[n] + E_{Har}[n] + E_{xc}[n] + E_{Ions}$$

Where the KS orbitals have been introduced to approximate the kinetic energy:

$$T_s[\{\psi_i\}] = -\frac{\hbar^2}{2m}\sum_{i=1}^{N}\int d\mathbf{r}\,\psi_i^*(\mathbf{r})\nabla^2\psi_i(\mathbf{r})$$

$$\langle\psi_i|\psi_j\rangle = \delta_{i,j} \qquad i,j = 1\cdots N$$

$$n(\mathbf{r}) = \sum_{i=1}^{N}\psi_i^*(\mathbf{r})\psi_i(\mathbf{r})$$

$$\begin{aligned} E_{ext}[n] &= \int d\mathbf{r}\, n(\mathbf{r})V_{ext}(\mathbf{r}) \\ E_{Har}[n] &= \frac{e^2}{2}\int d\mathbf{r}\, d\mathbf{r}'\,\frac{n(\mathbf{r})\,n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \\ E_{Ions} &= \sum_{IJ}\frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|} \end{aligned}$$

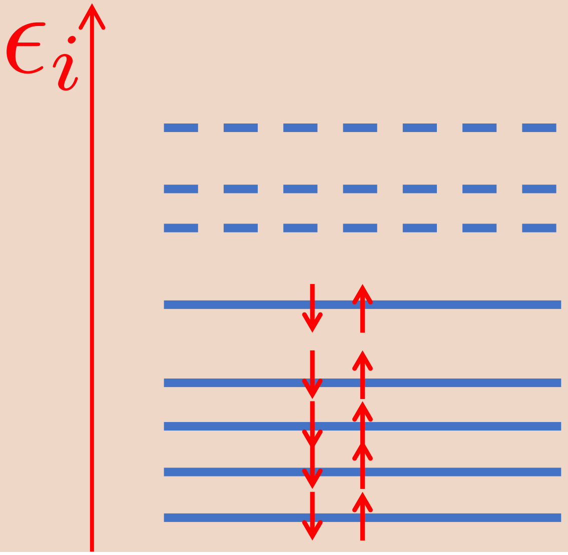
The main difficulty lies in approximating the exchange-correlation functional $E_{xc}[n]$

Density Functional Theory

Minimization of $E^{DFT}[n]$ with respect to n (actually, with respect to the KS orbitals) leads to the KS equations:

$$H^{KS}\psi_i(\mathbf{r}) = \left(-\frac{\hbar^2}{2m}\nabla^2 + V_{ext}(\mathbf{r}) + V_{Har}(\mathbf{r}) + V_{xc}(\mathbf{r})\right)\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r})$$

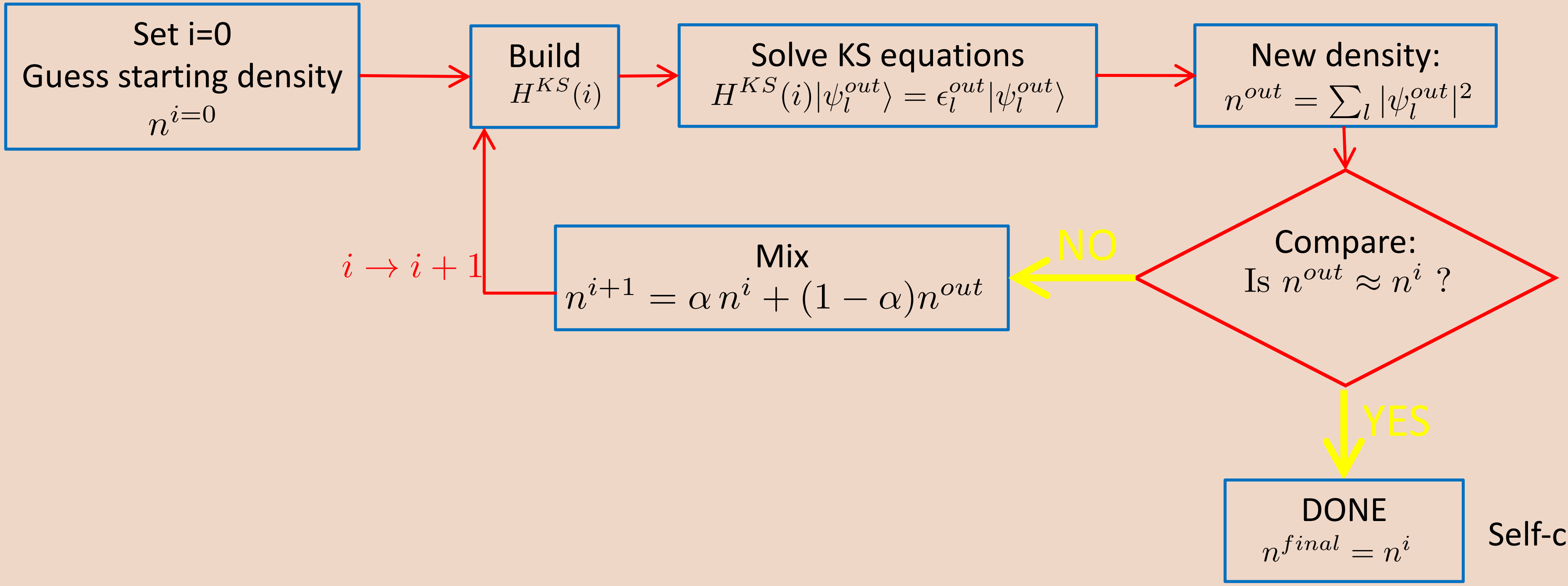
$$\begin{aligned} V_{xc}(\mathbf{r}) &= \frac{\delta E_{xc}}{\delta n(\mathbf{r})} \\ V_{Har}(\mathbf{r}) &= \frac{\delta E_{Har}}{\delta n(\mathbf{r})} = e^2 \int d\mathbf{r}' \, \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \end{aligned}$$



Problem: H^{KS} depends on the charge density ....

Density Functional Theory

The self-consistent cycle



Set i=0
Guess starting density
$n^{i=0}$

Build
$H^{KS}(i)$

Solve KS equations
$H^{KS}(i)|\psi_l^{out}\rangle = \epsilon_l^{out}|\psi_l^{out}\rangle$

New density:
$n^{out} = \sum_l |\psi_l^{out}|^2$

Compare:
Is $n^{out} \approx n^i$?

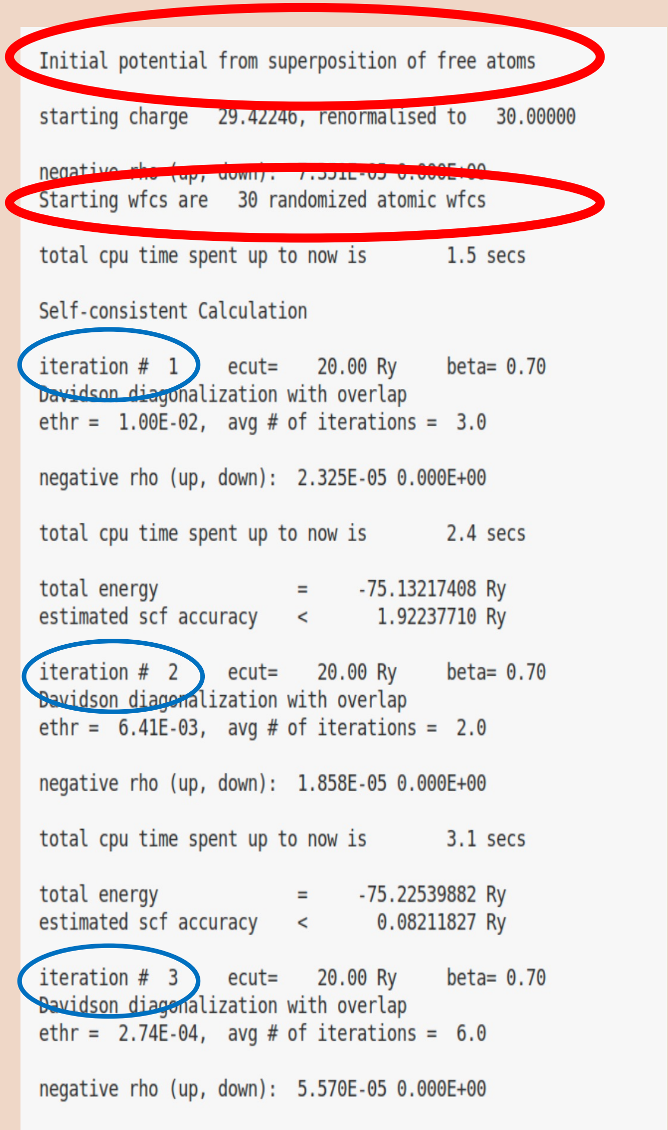
Mix
$n^{i+1} = \alpha\, n^i + (1-\alpha) n^{out}$

$i \rightarrow i+1$

DONE
$n^{final} = n^i$

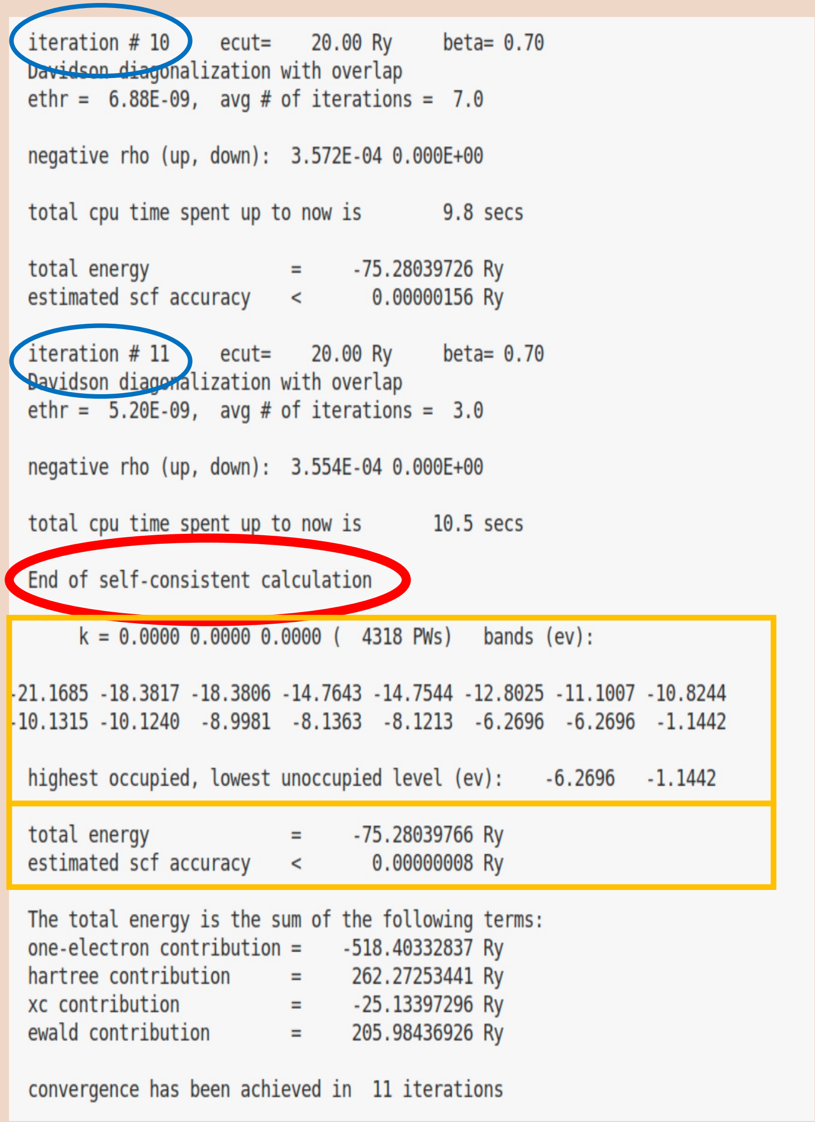
Self-consistency is reached

The self-consistent cycle



```
Initial potential from superposition of free atoms

starting charge   29.42246, renormalised to   30.00000

negative rho (up, down):  7.331E-05 0.000E+00
Starting wfcs are   30 randomized atomic wfcs

total cpu time spent up to now is        1.5 secs

Self-consistent Calculation

iteration #  1     ecut=    20.00 Ry     beta= 0.70
Davidson diagonalization with overlap
ethr =  1.00E-02,  avg # of iterations =  3.0

negative rho (up, down):  2.325E-05 0.000E+00

total cpu time spent up to now is        2.4 secs

total energy              =     -75.13217408 Ry
estimated scf accuracy    <       1.92237710 Ry

iteration #  2     ecut=    20.00 Ry     beta= 0.70
Davidson diagonalization with overlap
ethr =  6.41E-03,  avg # of iterations =  2.0

negative rho (up, down):  1.858E-05 0.000E+00

total cpu time spent up to now is        3.1 secs

total energy              =     -75.22539882 Ry
estimated scf accuracy    <       0.08211827 Ry

iteration #  3     ecut=    20.00 Ry     beta= 0.70
Davidson diagonalization with overlap
ethr =  2.74E-04,  avg # of iterations =  6.0

negative rho (up, down):  5.570E-05 0.000E+00
```

(....)



```
iteration # 10     ecut=    20.00 Ry     beta= 0.70
Davidson diagonalization with overlap
ethr =  6.88E-09,  avg # of iterations =  7.0

negative rho (up, down):  3.572E-04 0.000E+00

total cpu time spent up to now is        9.8 secs

total energy              =     -75.28039726 Ry
estimated scf accuracy    <       0.00000156 Ry

iteration # 11     ecut=    20.00 Ry     beta= 0.70
Davidson diagonalization with overlap
ethr =  5.20E-09,  avg # of iterations =  3.0

negative rho (up, down):  3.554E-04 0.000E+00

total cpu time spent up to now is       10.5 secs

End of self-consistent calculation

     k = 0.0000 0.0000 0.0000 (  4318 PWs)   bands (ev):

-21.1685 -18.3817 -18.3806 -14.7643 -14.7544 -12.8025 -11.1007 -10.8244
-10.1315 -10.1240  -8.9981  -8.1363  -8.1213  -6.2696  -6.2696  -1.1442

highest occupied, lowest unoccupied level (ev):    -6.2696   -1.1442

total energy              =     -75.28039766 Ry
estimated scf accuracy    <       0.00000008 Ry

The total energy is the sum of the following terms:
one-electron contribution =    -518.40332837 Ry
hartree contribution      =     262.27253441 Ry
xc contribution           =     -25.13397296 Ry
ewald contribution        =     205.98436926 Ry

convergence has been achieved in  11 iterations
```

Representing charge densities, KS orbitals in a computer:
Basis sets

$$f(\mathbf{r}) = \sum_{\alpha=1}^{M} c_\alpha \, b_\alpha(\mathbf{r})$$

Size of basis set

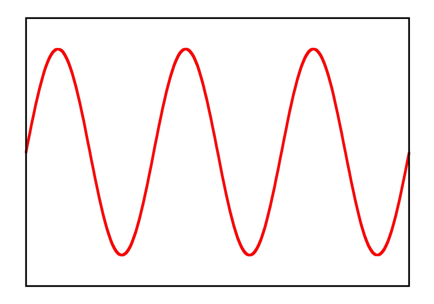
Function to be represented

Expansion coefficient

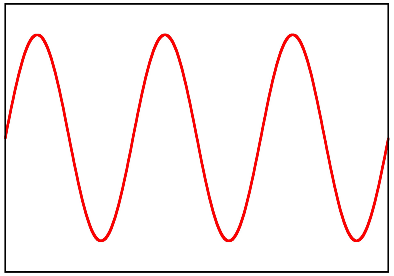
Basis function

In Quantum-ESPRESSO, plane waves are used as basis set:

$$b_\alpha(\mathbf{r}) = \frac{1}{\sqrt{V}} \exp\left(i \, \mathbf{G}_\alpha \cdot \mathbf{r}\right)$$



Advantages of plane waves as basis set



$$b_\alpha(\mathbf{r}) = \frac{1}{\sqrt{V}} \exp\left(i\,\mathbf{G}_\alpha \cdot \mathbf{r}\right)$$

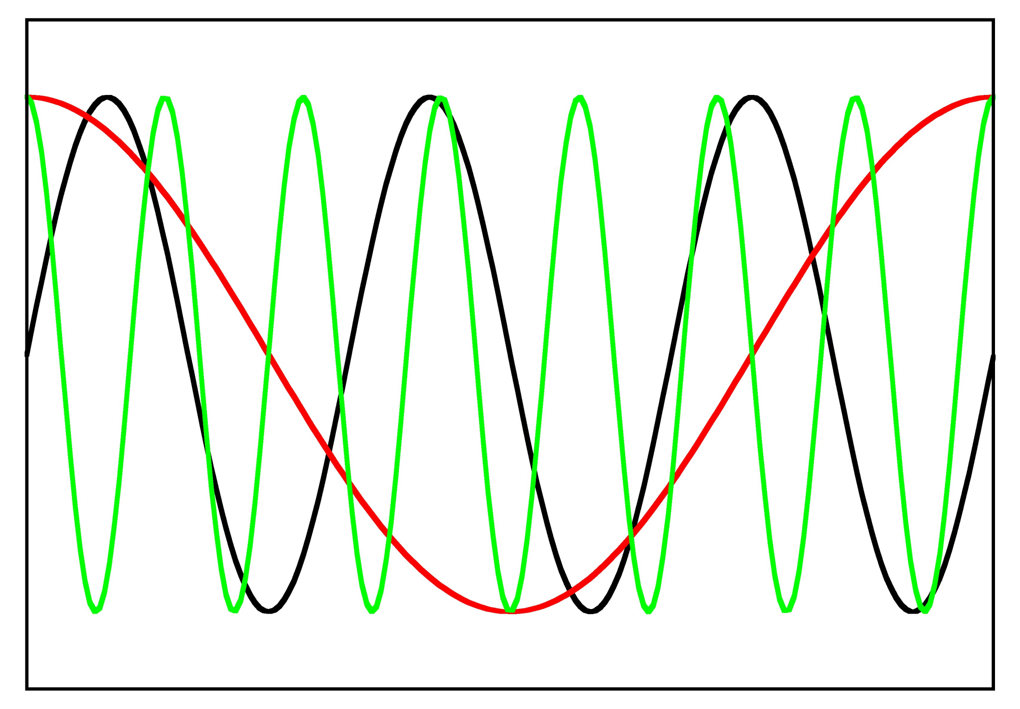
Using plane-waves as a basis set has many advantages:

- Simple analytical form: derivatives and integrals are easy to perform
- PWs are orthonormal
- Unbiased: no assumptions where charges/electrons are localized
- Independent of atomic positions: no “Pulay forces”
- Easy to control convergence of basis set size (see following slides ...)
- Straigtforward use of FFTs: easy use of R- and G-space dualities

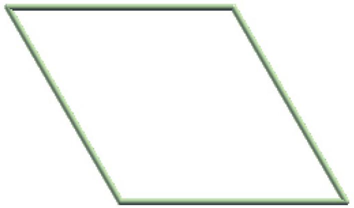
However: PW basis set are typically MUCH bigger than other sets of (localized) basis functions

Periodicity

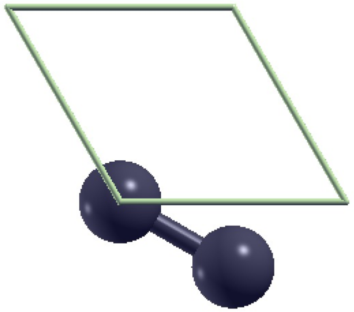
Due to the periodic nature of PWs, the use us this basis set is closely linked with the periodicity of the physical system.



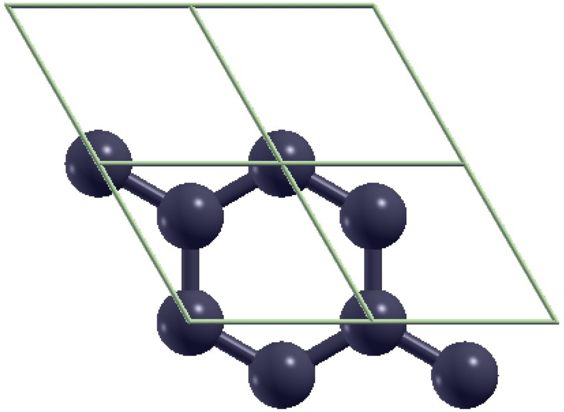
Periodicity



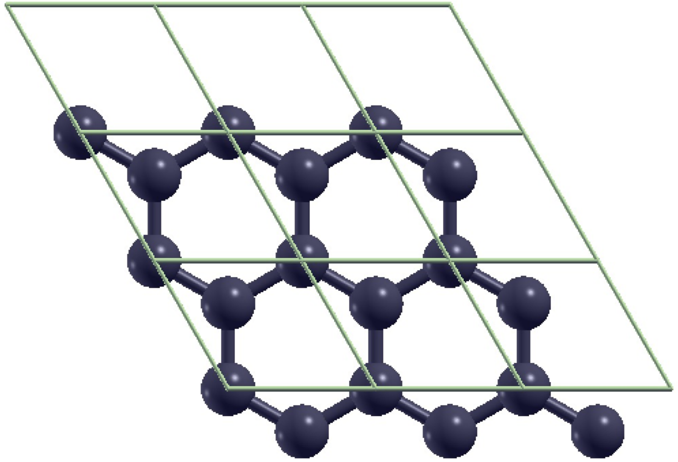
Periodicity



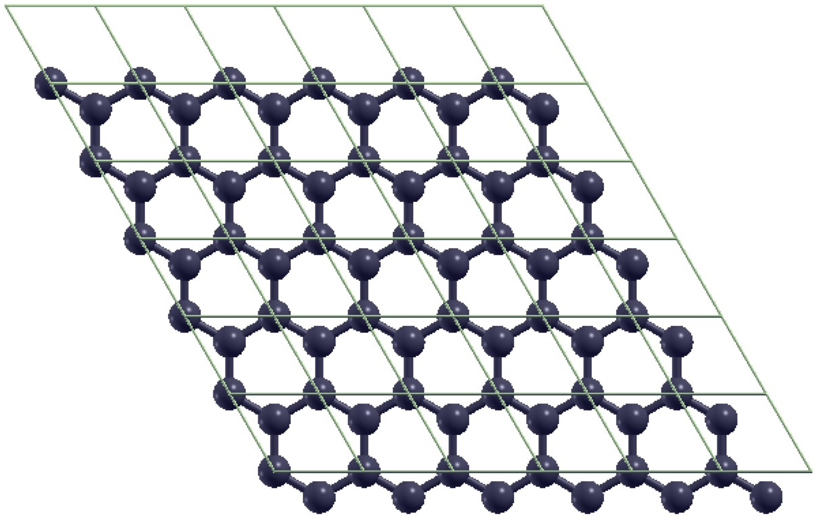
Periodicity



Periodicity



Periodicity



Periodicity

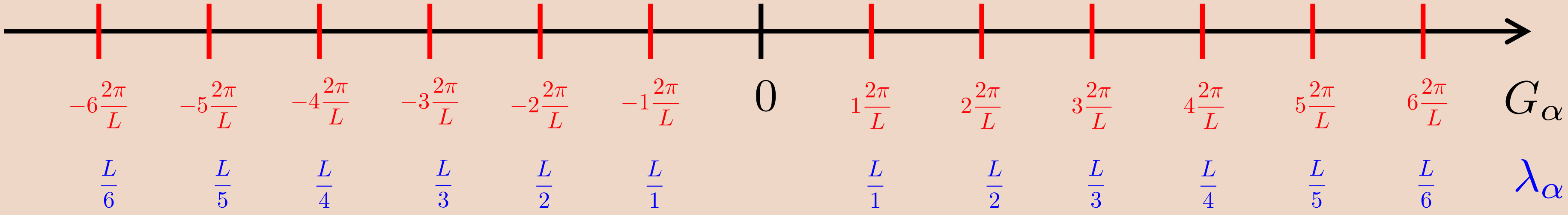
If a function is periodic in real space, its Fourier transform is non-zero only for discrete wavefectors

$$\text{In 1-D: } \exp(iG_\alpha x) \quad \rightarrow \quad G_\alpha = n \times \frac{2\pi}{L} \quad n \in \mathbb{Z}$$

$$\text{In 3-D: } \exp(i\mathbf{G}_\alpha \cdot \mathbf{r}) \quad \rightarrow \quad \mathbf{G}_\alpha = m \times \mathbf{B}_1 + n \times \mathbf{B}_2 + p \times \mathbf{B}_3 \quad m, n, p \in \mathbb{Z}$$

$$(\text{where } \mathbf{B}_{1,2,3} \text{ are reciprocal lattice vectors})$$

1-D illustration:



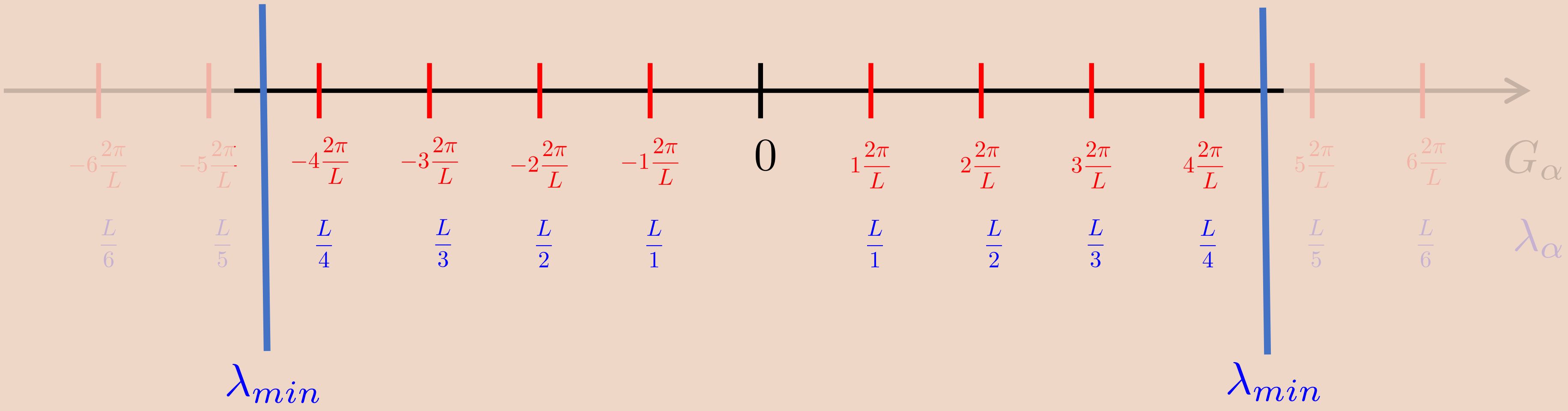
Wavelength λ_α is inversely proportional to $|\mathbf{G}_\alpha|$

Periodicity

The number of PWs compatible with a given periodicity is infinite.

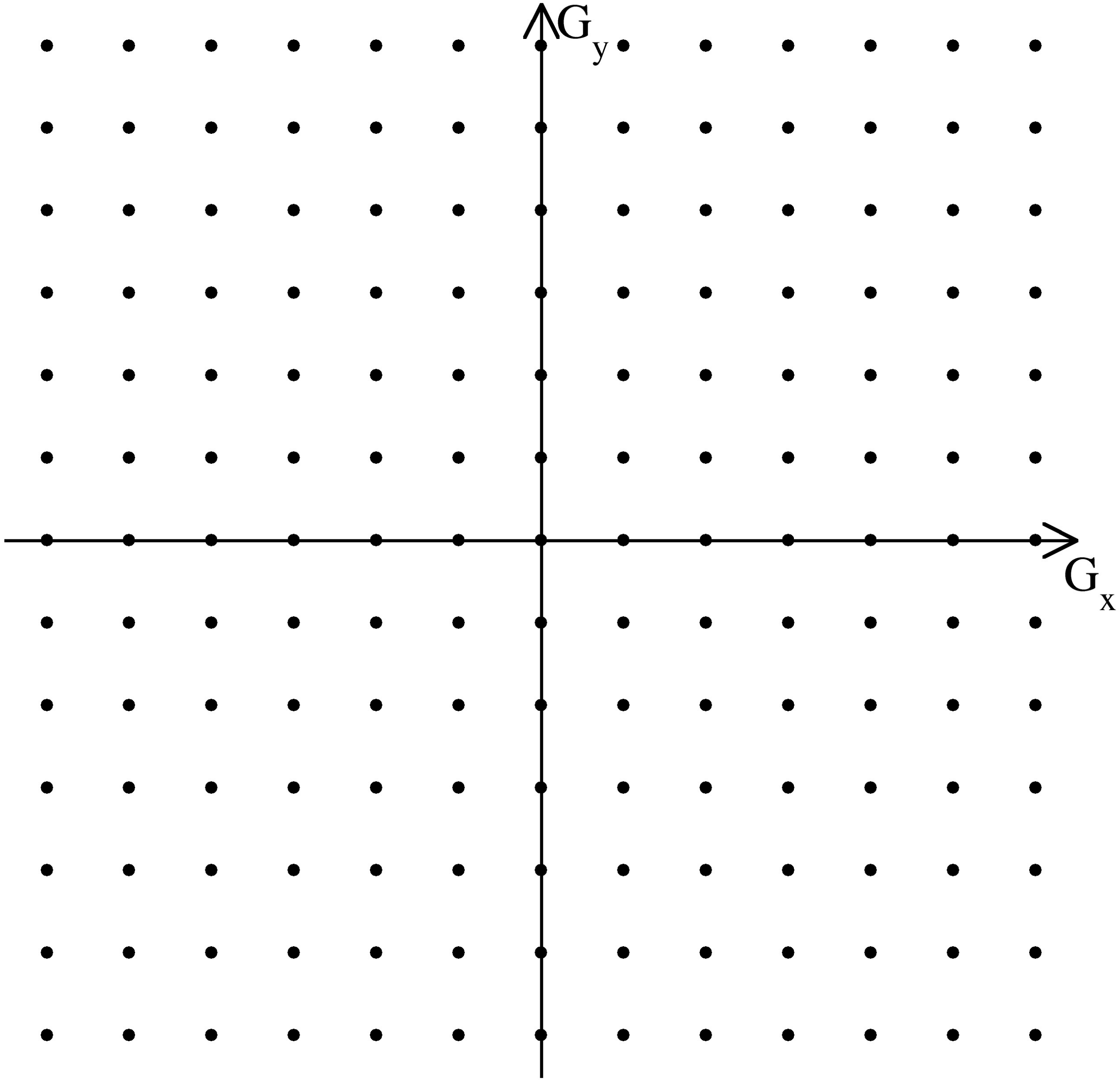
In order to obtain a finite number of basis functions, one fixes a “smallest” feature size: λ_{min}

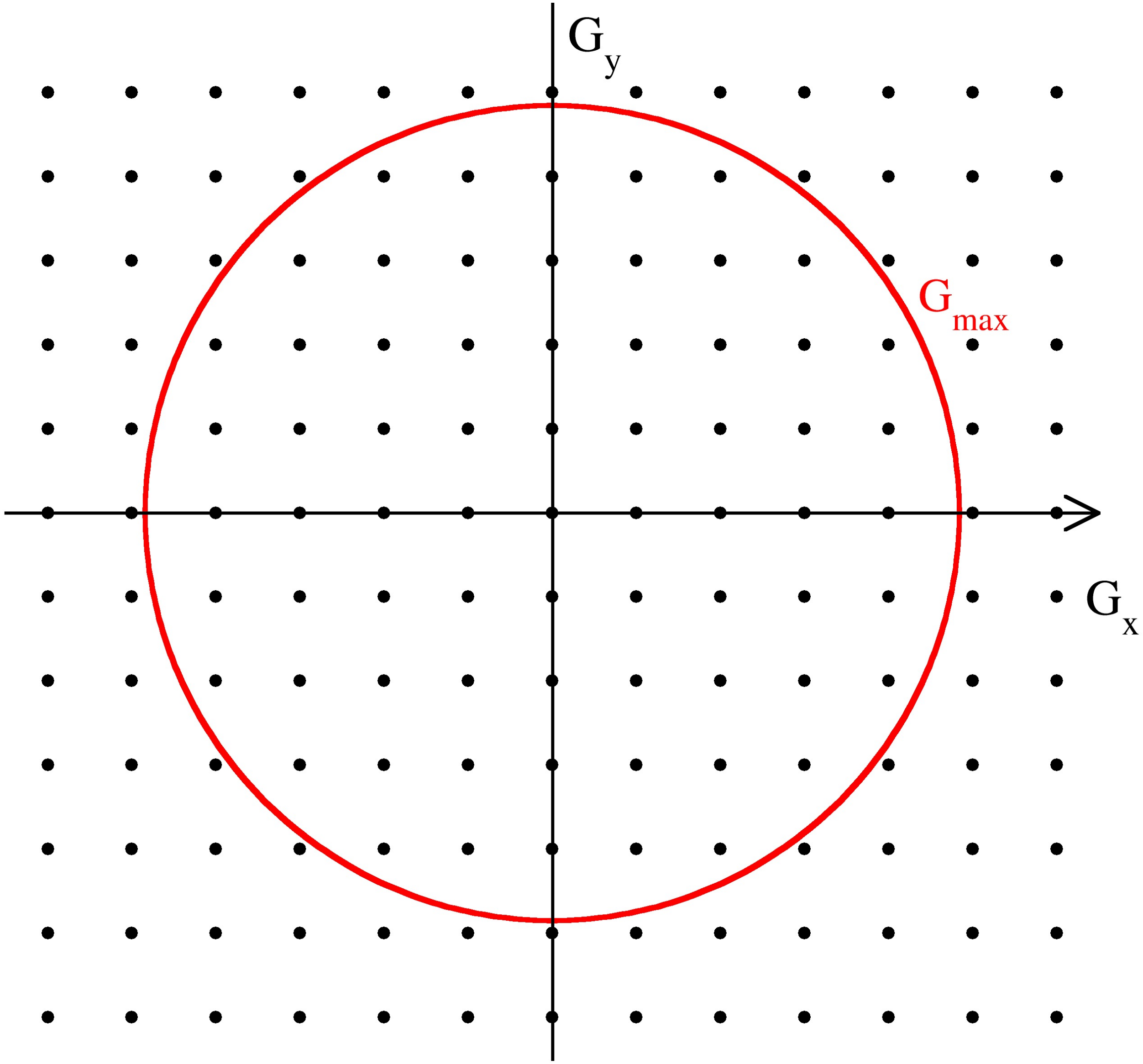
1-D illustration:

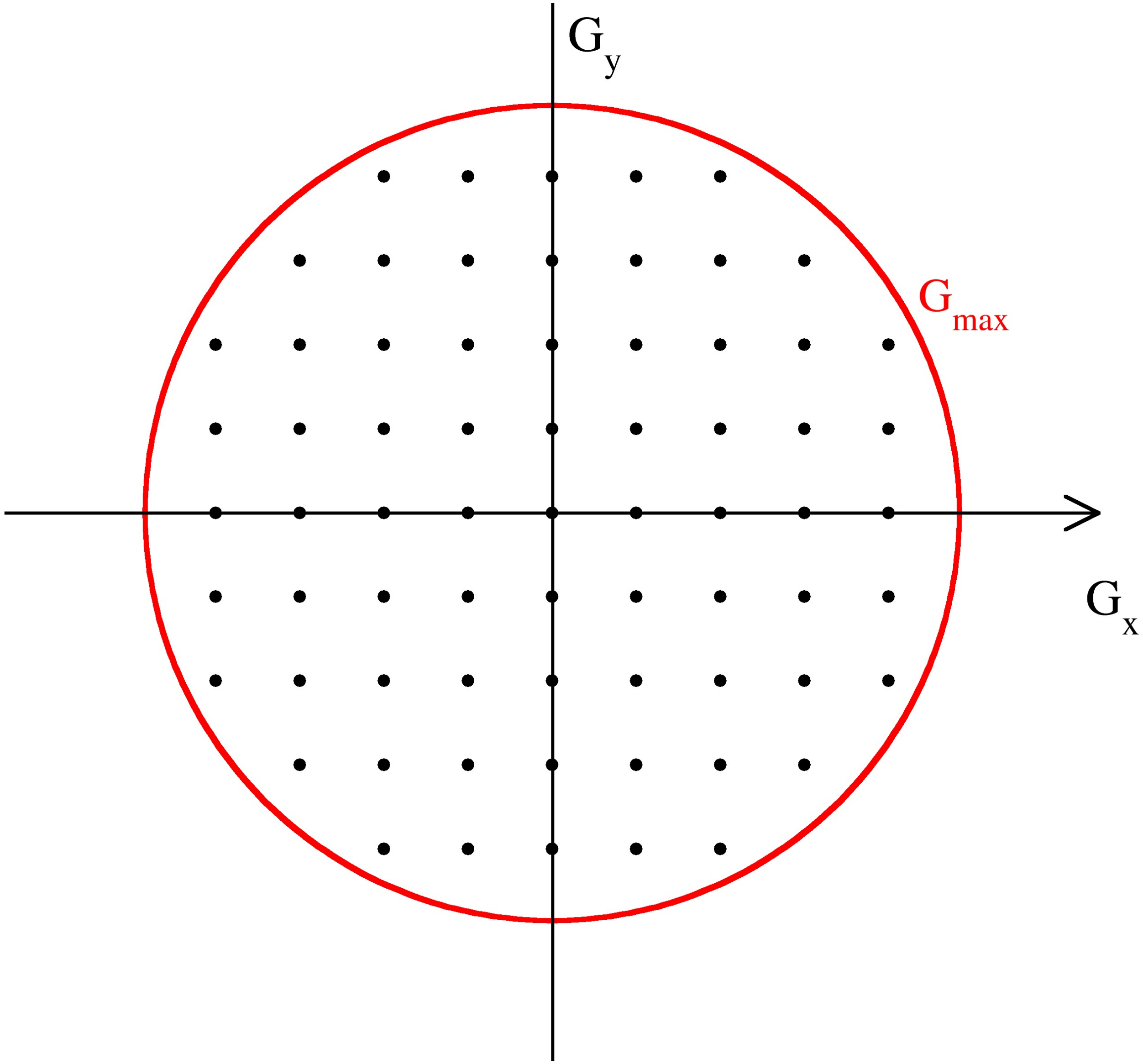


In practice, one describes a maximal norm for the wavevector: $|\mathbf{G}|_{max} = \frac{2\pi}{\lambda_{min}}$

By setting a cutoff kinetic energy for the plane-waves: $E_{cut} = \frac{\hbar^2}{2m} |\mathbf{G}|^2_{max}$


G_y
G_x


G_y
G_max
G_x


G_y
G_max
G_x

From KS orbitals to the charge density

Imagine that orbitals are represented in PWs, with a cutoff G_{max}

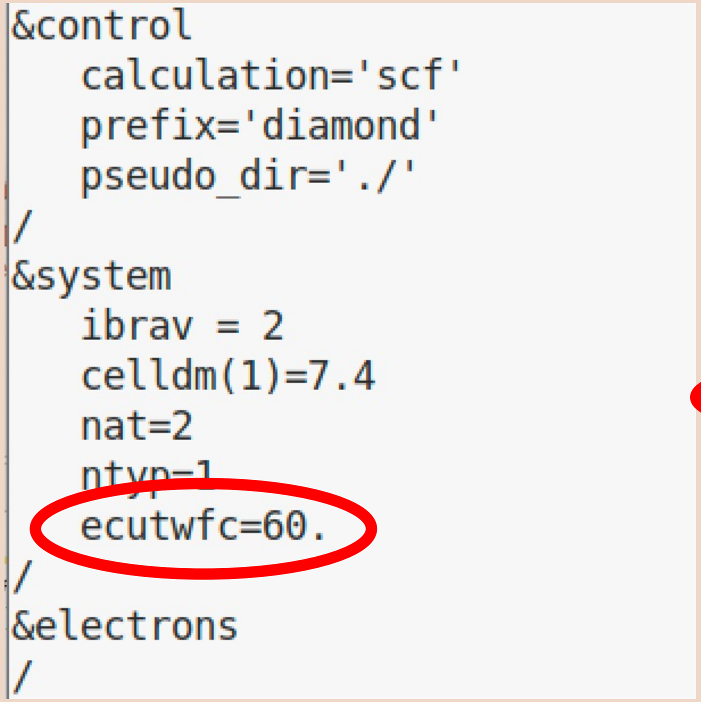
$$\psi_l(\mathbf{r}) = \sum_{|\mathbf{G}|<G_{max}} c(\mathbf{G}) \, \exp\left(i\mathbf{G}\cdot\mathbf{r}\right)$$

The charge density if given by the squared modulus of the orbitals:

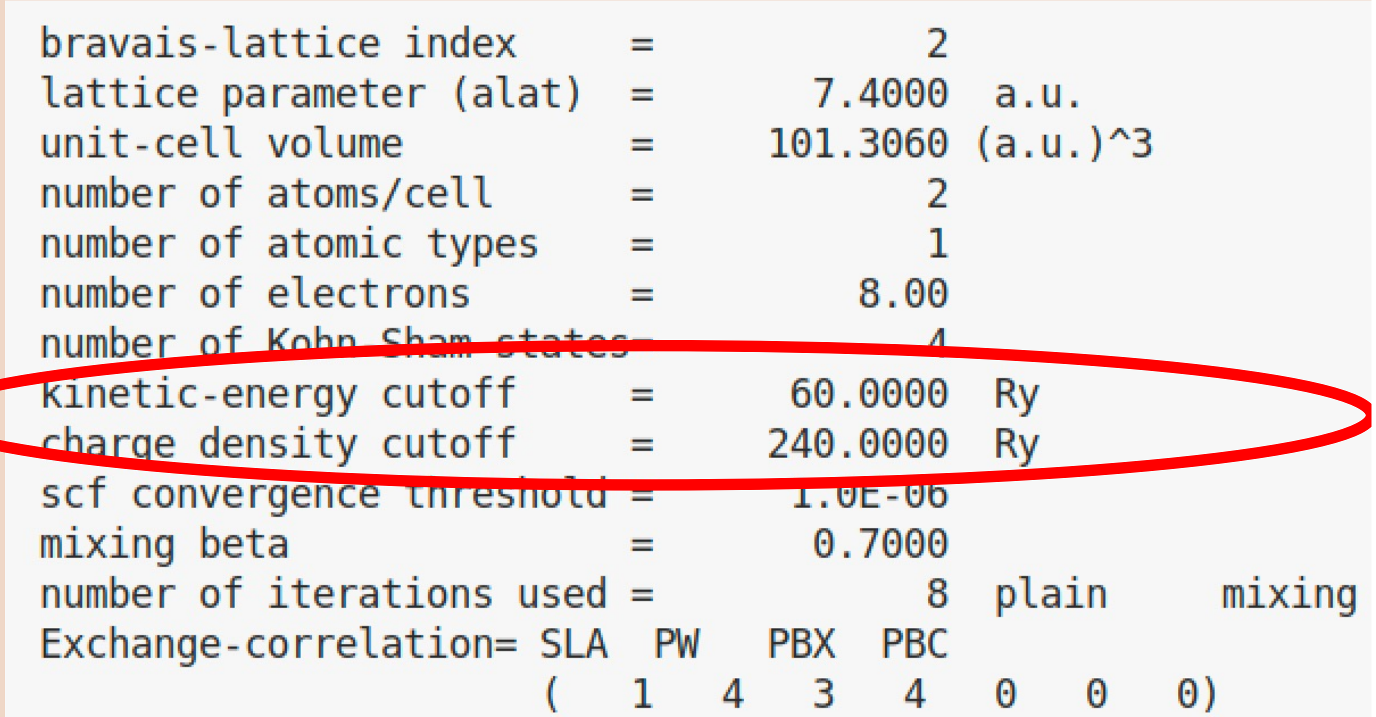
$$\begin{aligned} n(\mathbf{r}) &= \sum_l \psi_l^*(\mathbf{r})\psi_l(\mathbf{r}) \\ \tilde{n}(\mathbf{G}) &= \sum_l \sum_{|\mathbf{G}'|<G_{max}} \tilde{\psi}_l^*(\mathbf{G}')\tilde{\psi}_l(\mathbf{G}-\mathbf{G}') \end{aligned}$$

If the orbitals are represented with a cutof of G_{max}, then the charge density has non-zero Fourier components up to 2* G_{max} !!! This means: E_{cut}(rho) = 4*E_{cut}(wfc)

From KS orbitals to the charge density

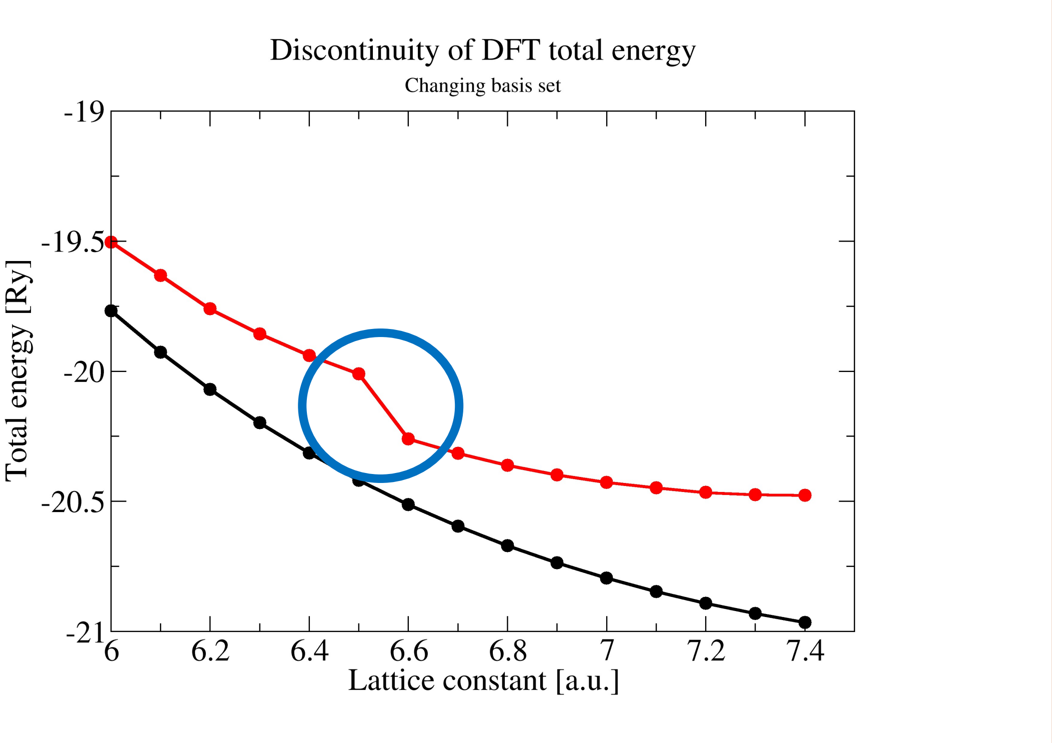


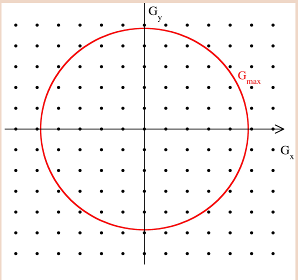
```
&control
   calculation='scf'
   prefix='diamond'
   pseudo_dir='./'
/
&system
   ibrav = 2
   celldm(1)=7.4
   nat=2
   ntyp=1
   ecutwfc=60.
/
&electrons
/
```



```
bravais-lattice index     =            2
lattice parameter (alat)  =       7.4000  a.u.
unit-cell volume          =     101.3060 (a.u.)^3
number of atoms/cell      =            2
number of atomic types    =            1
number of electrons       =         8.00
number of Kohn-Sham states=            4
kinetic-energy cutoff     =      60.0000  Ry
charge density cutoff     =     240.0000  Ry
scf convergence threshold =      1.0E-06
mixing beta               =       0.7000
number of iterations used =            8  plain     mixing
Exchange-correlation= SLA  PW   PBX  PBC
                      (   1   4   3   4   0   0   0)
```

Beware: changing the lattice constant means changing the PW basis set





Larger cell size
→ grid of G-vectors more dense
→ at fixed G_{max}, ”new” plane waves enter the calculation discontinuously
→ sudden decrease of energy when basis set is enlarged

Curing the discontinuity: Check for input variables ecfixed, qcutz, q2sigma

So have seen how periodic functions are expressed in PWs ....

BUT: orbitals in periodic systems are NOT lattice periodic!

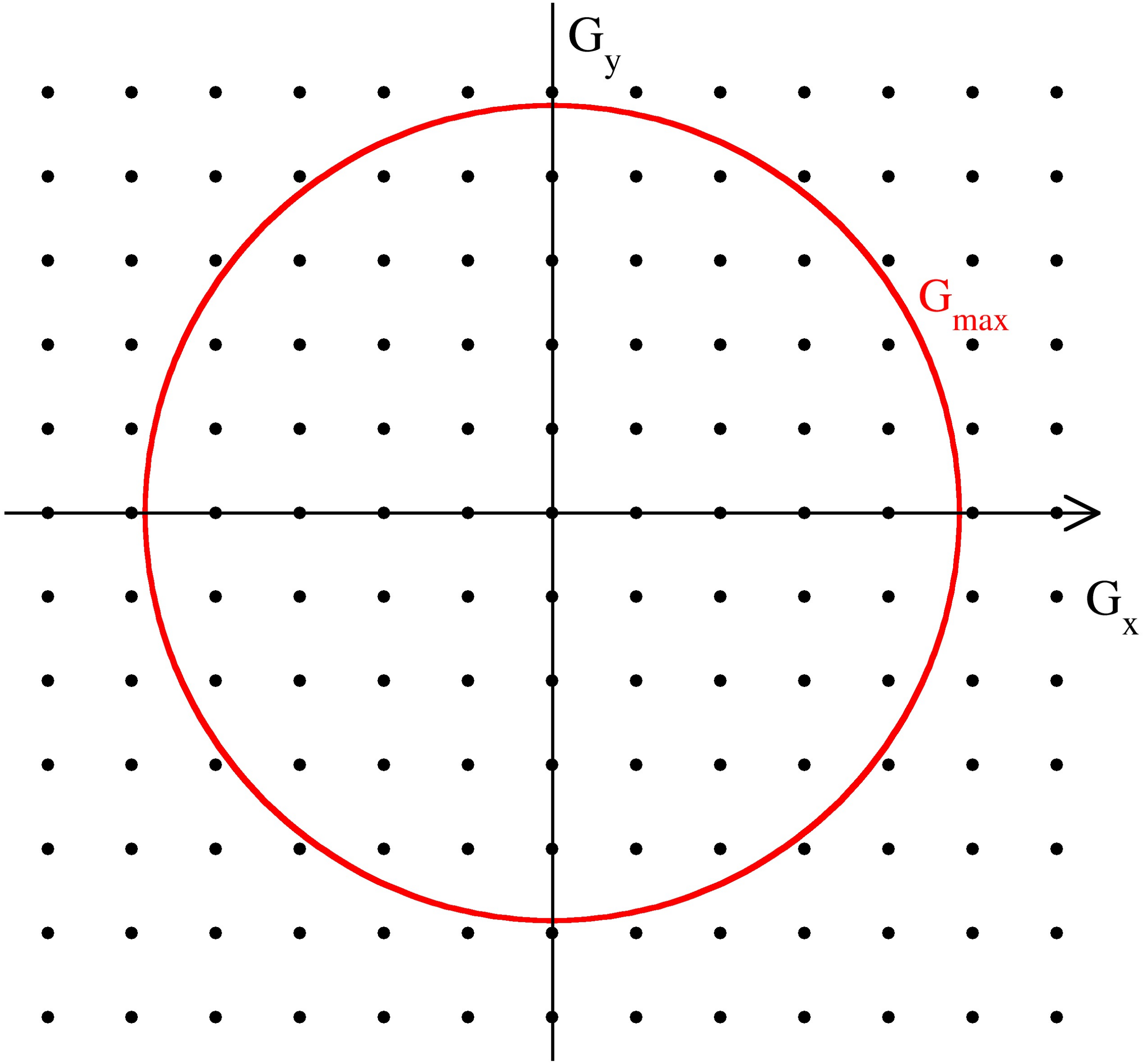
Bloch's theorem: $\psi_{\mathbf{k},l}(\mathbf{r}) = \exp\left(i\mathbf{k}\cdot\mathbf{r}\right)\, \underbrace{u_{\mathbf{k},l}(\mathbf{r})}_{\text{periodic}}$

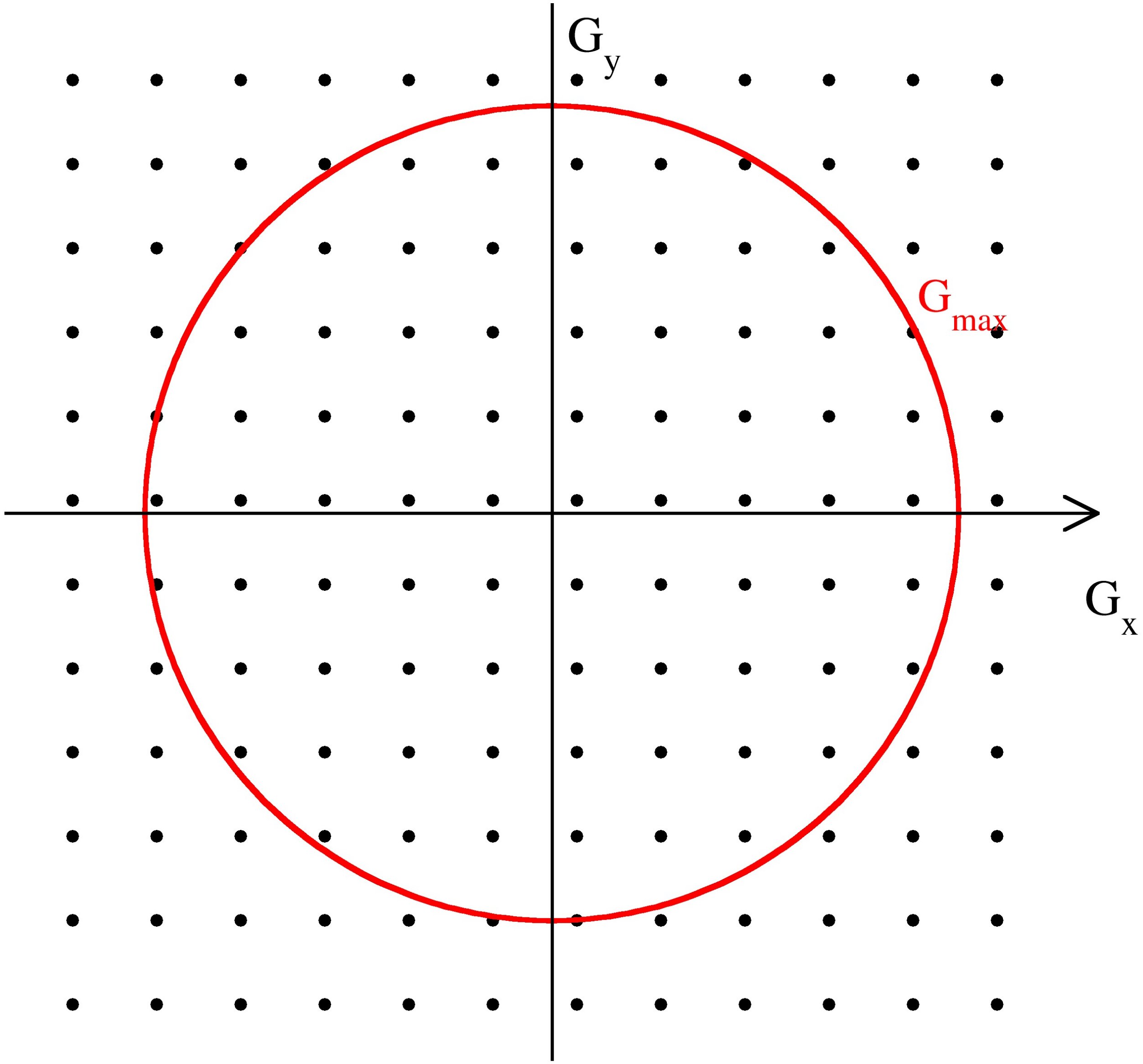
$$u_{\mathbf{k},l}(\mathbf{r}) = \sum_{|\mathbf{G}|<G_{max}} c_{\mathbf{k},l}\, \exp\left(i\mathbf{G}\cdot\mathbf{r}\right)$$

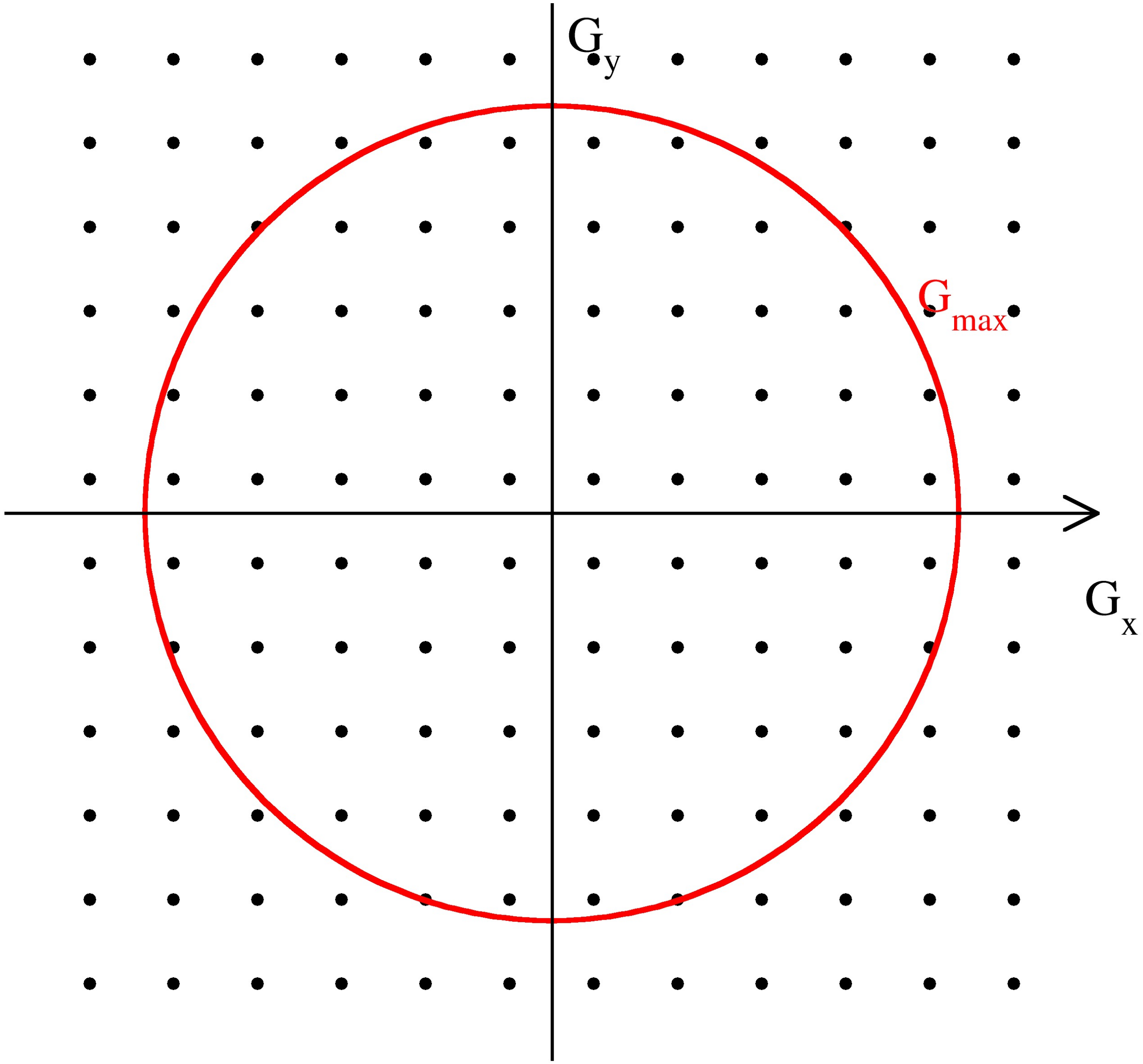
grid of G-vectors like before

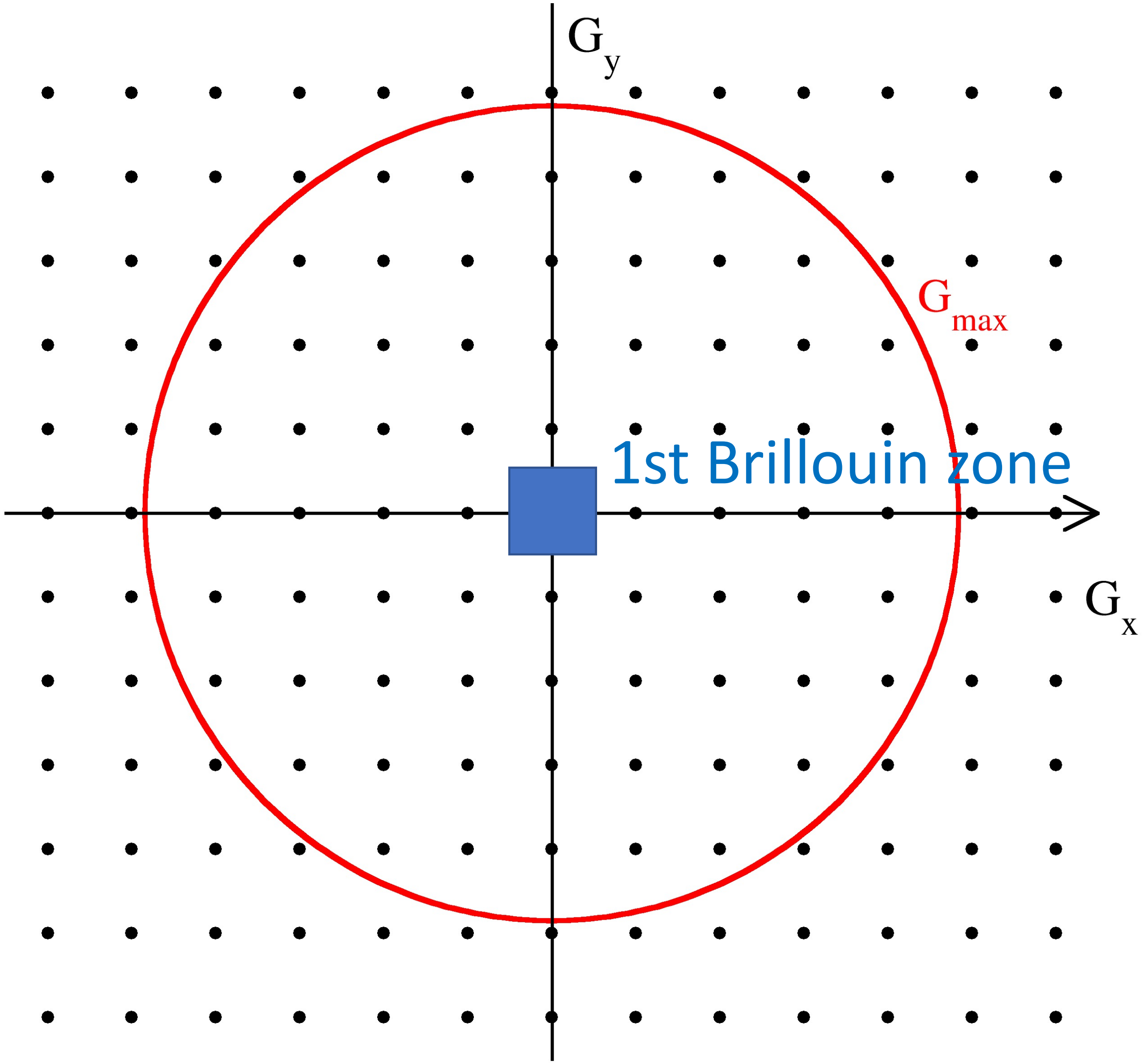
$$\psi_{\mathbf{k},l}(\mathbf{r}) = \sum_{|\mathbf{G}|<G_{max}} c_{\mathbf{k},l}\, \exp\left(i\left(\mathbf{k}+\mathbf{G}\right)\cdot\mathbf{r}\right)$$

shifted grid of (k+G)-vectors

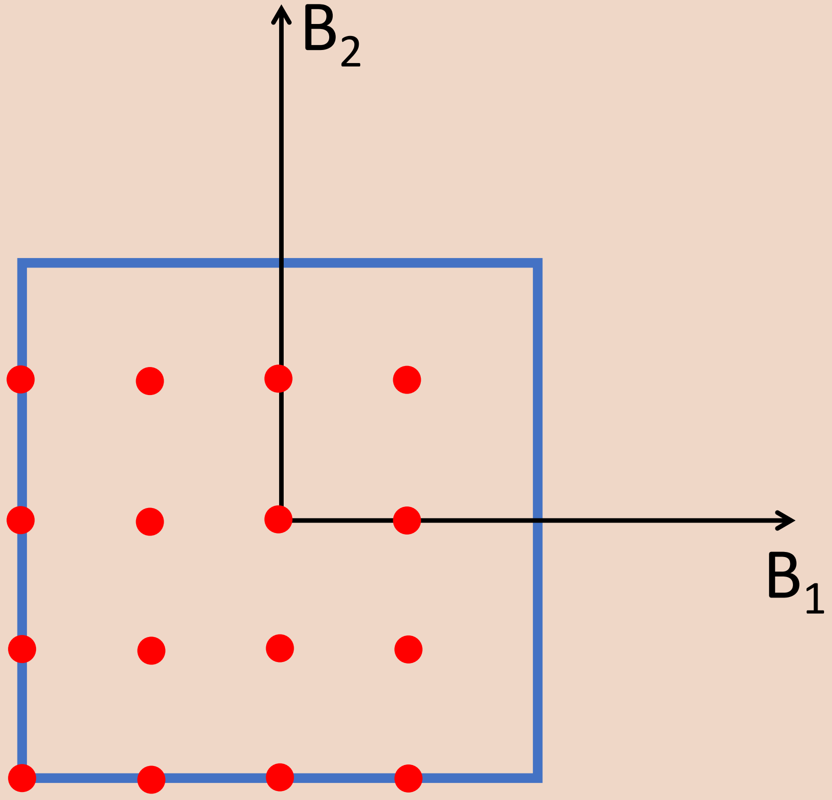

G_y
G_{max}
G_x


G_y
G_{max}
G_x


G
y
G
max
G
x

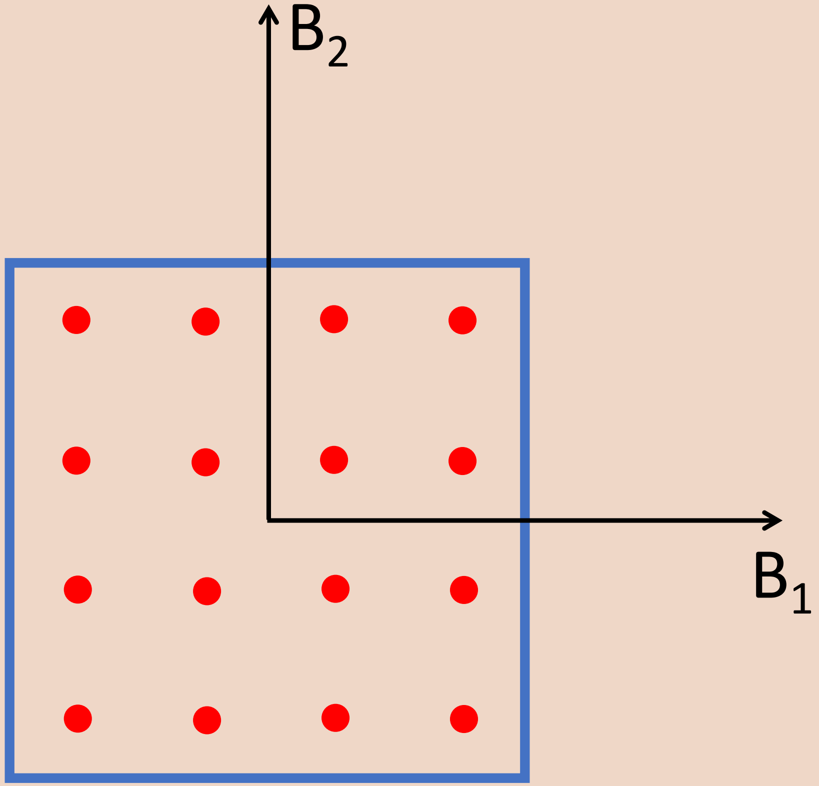

G_y
G_max
1st Brillouin zone
G_x

Sampling the Brillouin zone



BZ sampled with a 4x4 k-point grid

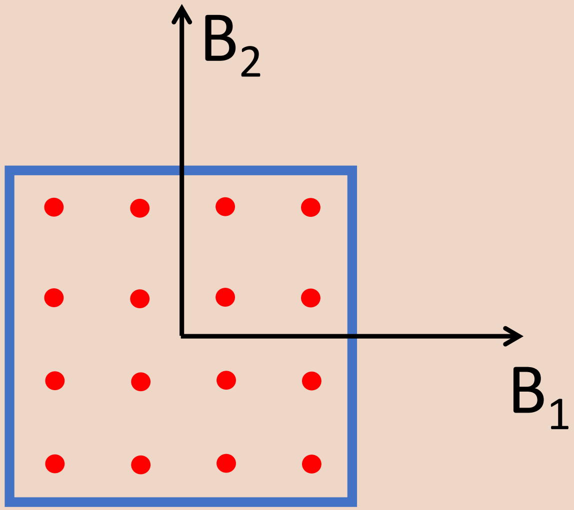
Sampling the Brillouin zone

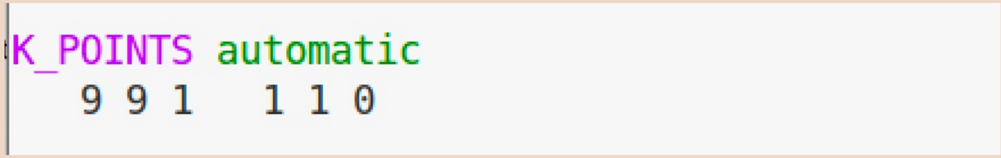


BZ sampled with a shifted 4x4 k-point grid

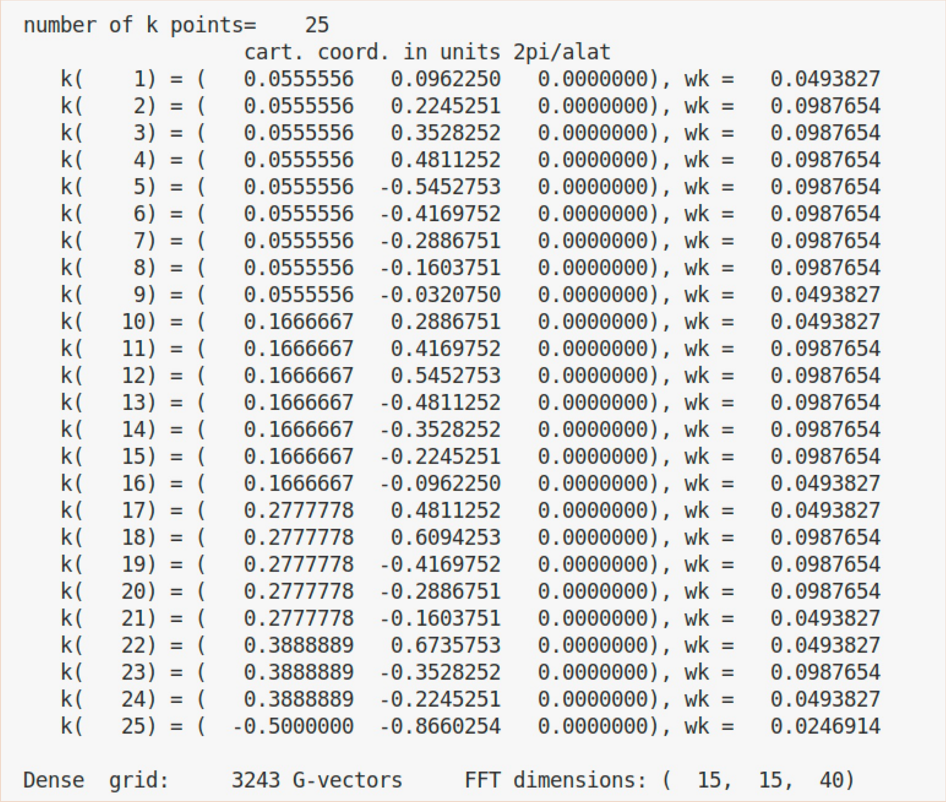
Shifted k-point grids usually converge faster (symmetry!)

Sampling the Brillouin zone





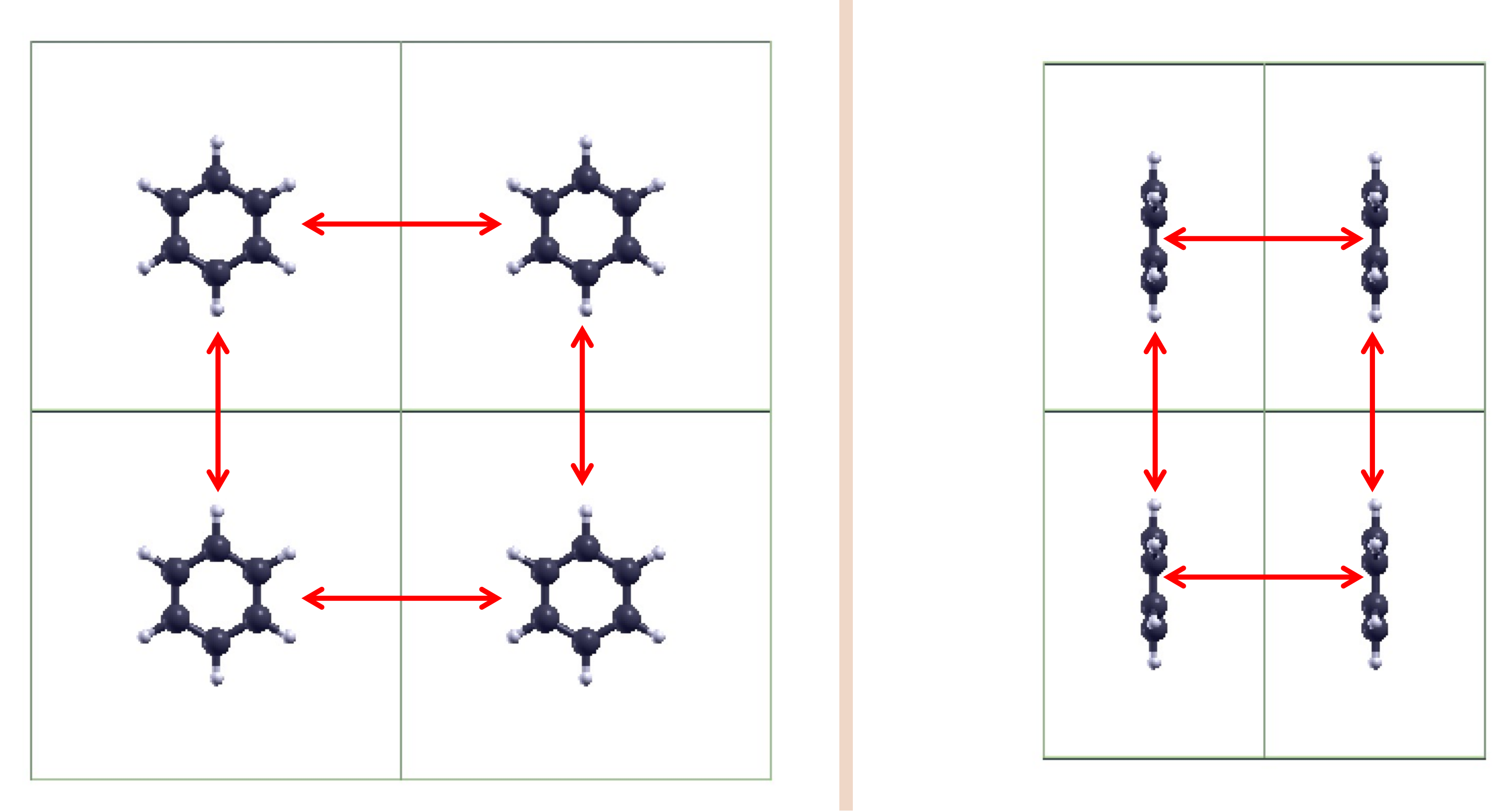
```
K_POINTS automatic
   9 9 1   1 1 0
```



```
number of k points=    25
                  cart. coord. in units 2pi/alat
   k(    1) = (   0.0555556   0.0962250   0.0000000), wk =   0.0493827
   k(    2) = (   0.0555556   0.2245251   0.0000000), wk =   0.0987654
   k(    3) = (   0.0555556   0.3528252   0.0000000), wk =   0.0987654
   k(    4) = (   0.0555556   0.4811252   0.0000000), wk =   0.0987654
   k(    5) = (   0.0555556  -0.5452753   0.0000000), wk =   0.0987654
   k(    6) = (   0.0555556  -0.4169752   0.0000000), wk =   0.0987654
   k(    7) = (   0.0555556  -0.2886751   0.0000000), wk =   0.0987654
   k(    8) = (   0.0555556  -0.1603751   0.0000000), wk =   0.0987654
   k(    9) = (   0.0555556  -0.0320750   0.0000000), wk =   0.0493827
   k(   10) = (   0.1666667   0.2886751   0.0000000), wk =   0.0493827
   k(   11) = (   0.1666667   0.4169752   0.0000000), wk =   0.0987654
   k(   12) = (   0.1666667   0.5452753   0.0000000), wk =   0.0987654
   k(   13) = (   0.1666667  -0.4811252   0.0000000), wk =   0.0987654
   k(   14) = (   0.1666667  -0.3528252   0.0000000), wk =   0.0987654
   k(   15) = (   0.1666667  -0.2245251   0.0000000), wk =   0.0987654
   k(   16) = (   0.1666667  -0.0962250   0.0000000), wk =   0.0493827
   k(   17) = (   0.2777778   0.4811252   0.0000000), wk =   0.0493827
   k(   18) = (   0.2777778   0.6094253   0.0000000), wk =   0.0987654
   k(   19) = (   0.2777778  -0.4169752   0.0000000), wk =   0.0987654
   k(   20) = (   0.2777778  -0.2886751   0.0000000), wk =   0.0987654
   k(   21) = (   0.2777778  -0.1603751   0.0000000), wk =   0.0493827
   k(   22) = (   0.3888889   0.6735753   0.0000000), wk =   0.0493827
   k(   23) = (   0.3888889  -0.3528252   0.0000000), wk =   0.0987654
   k(   24) = (   0.3888889  -0.2245251   0.0000000), wk =   0.0493827
   k(   25) = (  -0.5000000  -0.8660254   0.0000000), wk =   0.0246914

Dense  grid:     3243 G-vectors     FFT dimensions: (   15,   15,   40)
```

What if a system is NOT 3D-periodic ?

Use a supercell: introduce enough space between periodic replicas that the interaction is neglible



What if a system is NOT 3D-periodic ?

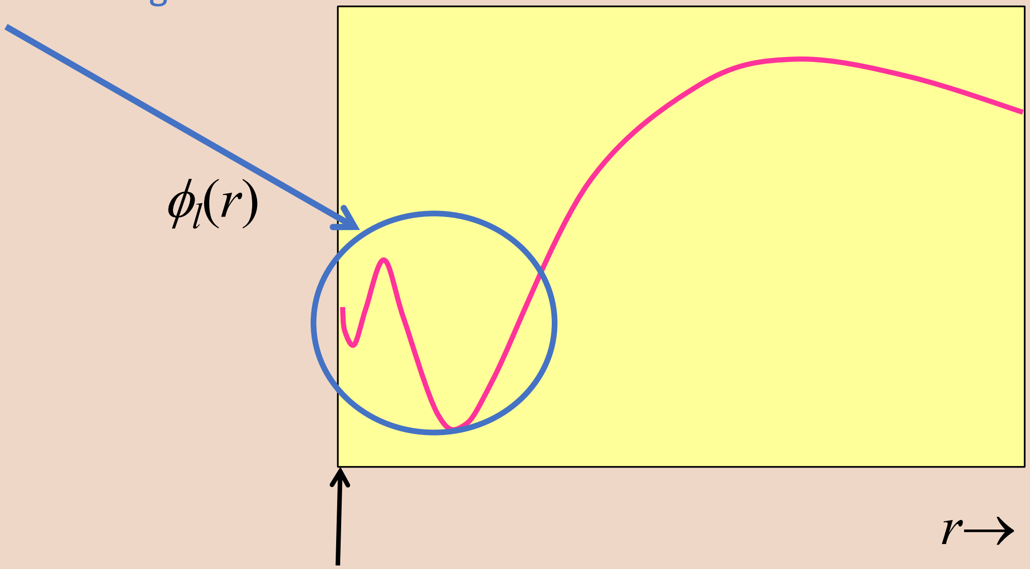
Use a supercell: introduce enough space between periodic replicas that the interaction is neglible

Can be problematic if the object is charged or has a dipole!

Solution:

- input variable assume_isolated: useful in 0-D (molecules, clusters, etc)
- introduce a dipole layer in the vacuum between surfaces (dipfield)

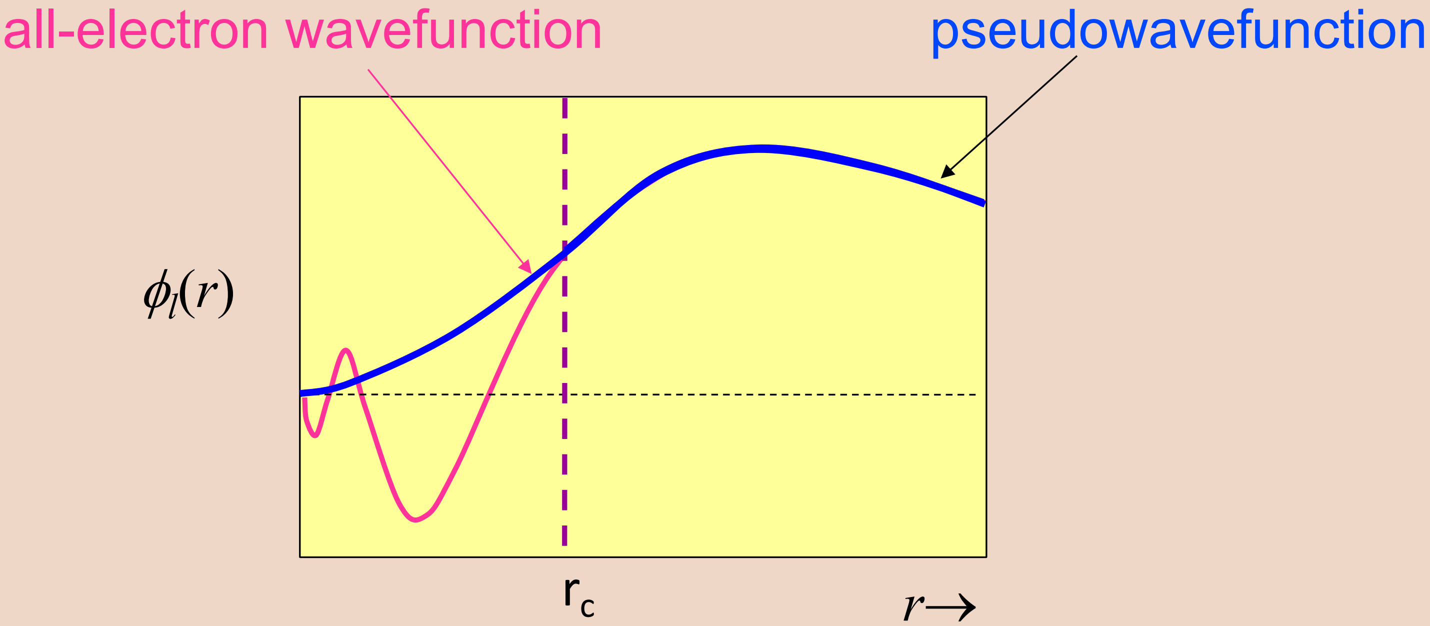
The need for pseudopotentials



rapid oscillations would need a very small wavelength basis functions

Atomic position

Pseudopotentials



all-electron wavefunction

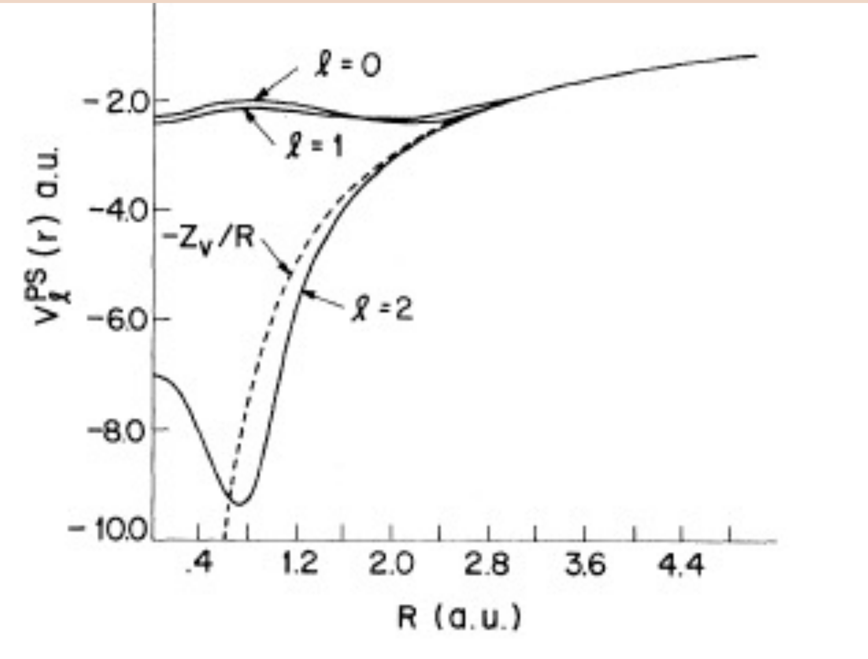
pseudowavefunction

Necessary condition for the pseudopotential to be transferable: NORM-CONSERVATION

$$\boxed{\int_0^{r_c} \phi *^{AE}(r)\phi^{AE}(r)dr = \int_0^{r_c} \phi *^{PS}(r)\phi^{PS}(r)dr}$$

What does a pseudopotential look like?

Example for Mo*:*



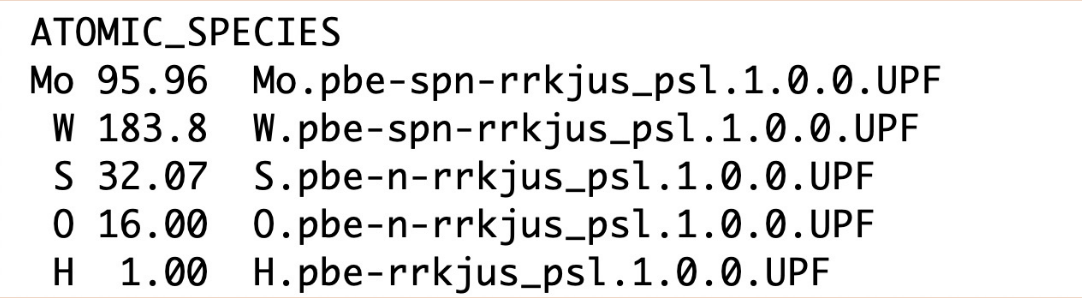
Hamann, Schluter & Chiang, 1979.

- Weaker than full Coulomb potential
- No singularity at r=0
- Different pseudopotential for each l (example of semilocal pseudopotential)
- Will be V_{ion} (replacing nuclear potential)

Pseudopotentials in quantum-ESPRESSO:

PPs in QE are provided by the user in the form of files, which contain the PP on a radial grid:

in the PW input file, the PP filenames are specified for every element in the system



```
ATOMIC_SPECIES
Mo 95.96  Mo.pbe-spn-rrkjus_psl.1.0.0.UPF
 W 183.8  W.pbe-spn-rrkjus_psl.1.0.0.UPF
 S 32.07  S.pbe-n-rrkjus_psl.1.0.0.UPF
 O 16.00  O.pbe-n-rrkjus_psl.1.0.0.UPF
 H  1.00  H.pbe-rrkjus_psl.1.0.0.UPF
```

PPs are DFT-functional specific. The code will by default apply the functional to your system with which the PP has been calculated

It is generally a bad idea to mix pseudopotentials generated with different functionals!

Beyond norm-conservation:

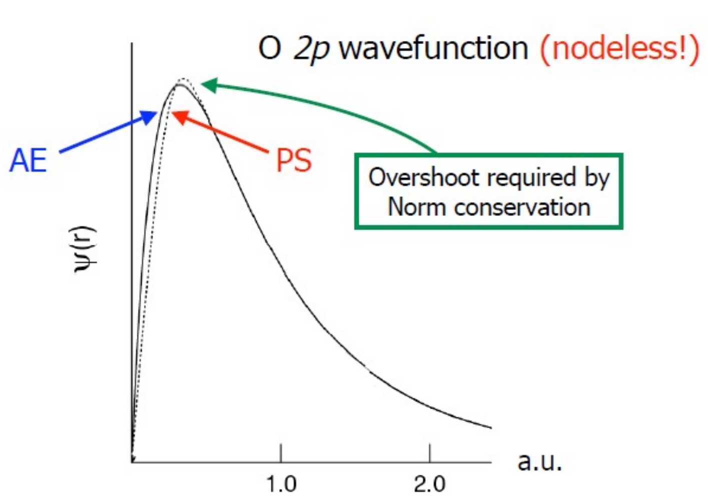
Cut-offs still higher than we would like, especially for

> first row elements (1s, 2p nodeless)

> transition metals (3d nodeless)

> rare-earths (4f nodeless)

This is because of the constraint of norm conservation...



Beyond norm-conservation:

Vanderbilt’s ultrasoft pseudopotentials:

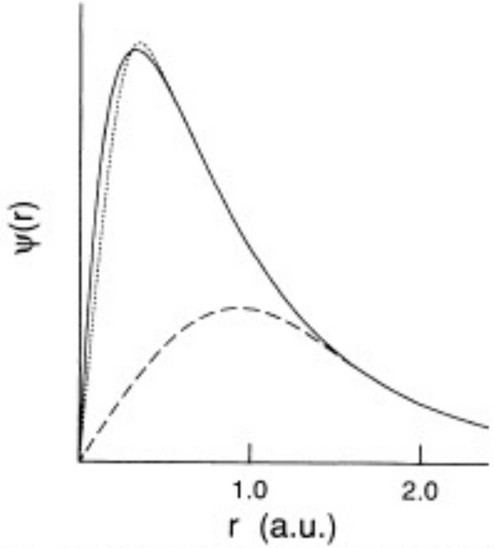


FIG. 1. Oxygen 2*p* radial wave function (solid line), and corresponding pseudo-wave-functions generated using HSC (dotted line) and current (dashed line) methods.

Remove the constraint of norm-conservation

The price to be paid: a more complicted expression for the electronic charge density:

$$n(\mathbf{r}) = \sum_{i=1}^{N} \psi_i^*(\mathbf{r})\psi_i(\mathbf{r}) + n^{aug}(\mathbf{r})$$

Augmentation charges, localized close to the nucleus
account for “missing norm”
expressed using projection functions

NB: Ultrasoft (US) and PAW pseudopotentials are (from the user’s perspective) very similar

Beyond norm-conservation:

Vanderbilt's ultrasoft pseudopotentials:

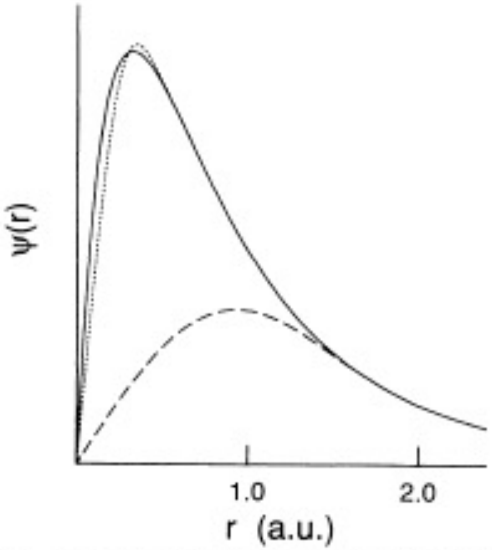


FIG. 1. Oxygen 2*p* radial wave function (solid line), and corresponding pseudo-wave-functions generated using HSC (dotted line) and current (dashed line) methods.

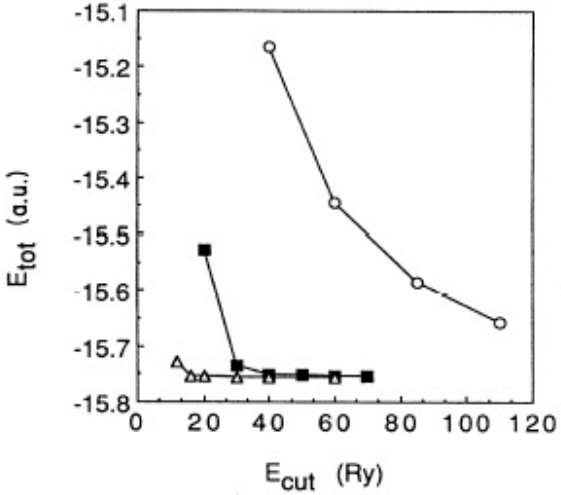
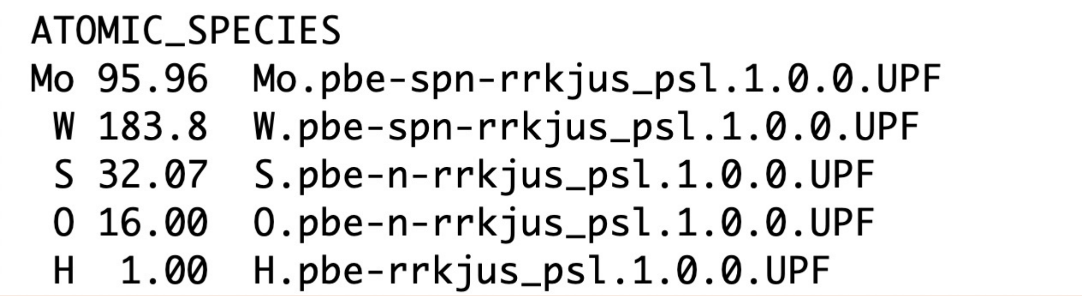


FIG. 1. Total energy of ground-state oxygen atom vs plane-wave cutoff for Bachelet-Hamann-Schlüter pseudopotential (open circles) and for Vanderbilt pseudopotential with $r_c = 1.2$ a.u. (solid squares) and $r_c = 1.8$ a.u. (open triangles).

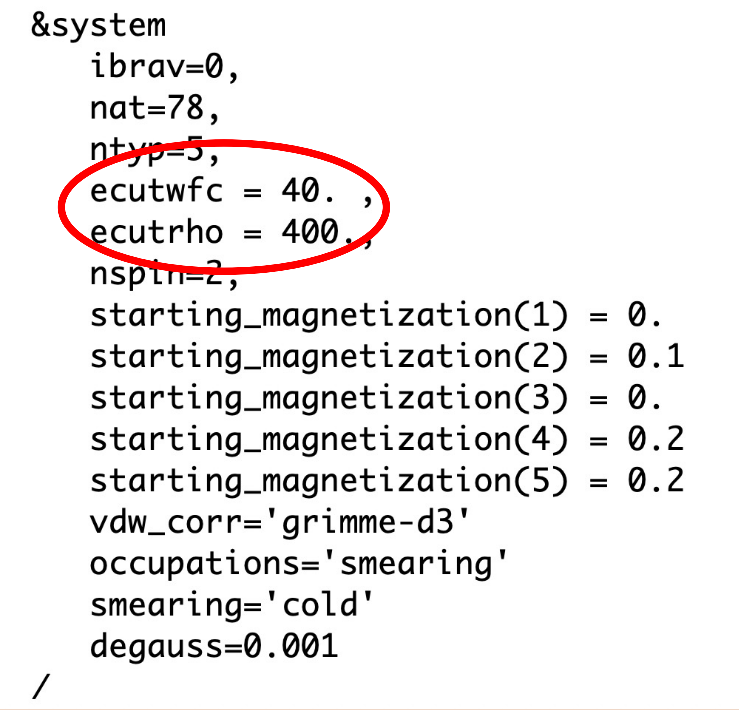
As a user: BEWARE!

Using US or PAW pseudopotentials, you need a cutoff energy E_{cut} for the cgarge density which is MORE THAN 4*E_{cut} for the orbitals



```
ATOMIC_SPECIES
Mo 95.96  Mo.pbe-spn-rrkjus_psl.1.0.0.UPF
 W 183.8  W.pbe-spn-rrkjus_psl.1.0.0.UPF
 S 32.07  S.pbe-n-rrkjus_psl.1.0.0.UPF
 O 16.00  O.pbe-n-rrkjus_psl.1.0.0.UPF
 H  1.00  H.pbe-rrkjus_psl.1.0.0.UPF
```

Employing US or PAW pseudopotentials and NOT specifying ecutrho is the most common beginner’s mistake in QE!



```
&system
   ibrav=0,
   nat=78,
   ntyp=5,
   ecutwfc = 40. ,
   ecutrho = 400.,
   nspin=2,
   starting_magnetization(1) = 0.
   starting_magnetization(2) = 0.1
   starting_magnetization(3) = 0.
   starting_magnetization(4) = 0.2
   starting_magnetization(5) = 0.2
   vdw_corr='grimme-d3'
   occupations='smearing'
   smearing='cold'
   degauss=0.001
/
```

HAPPY QE-COMPUTING!