Quantum Espresso Overview and Practical Guide
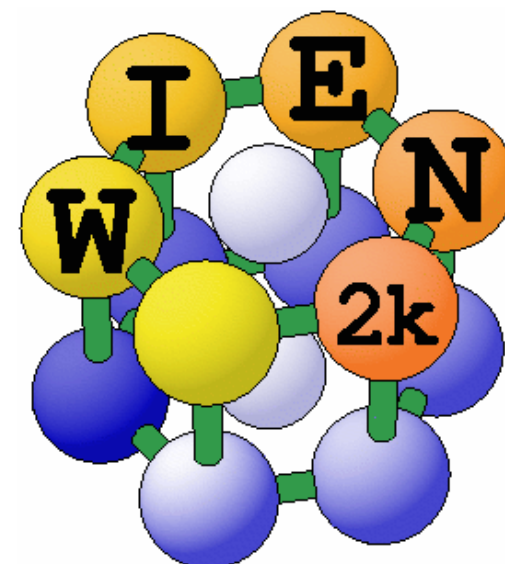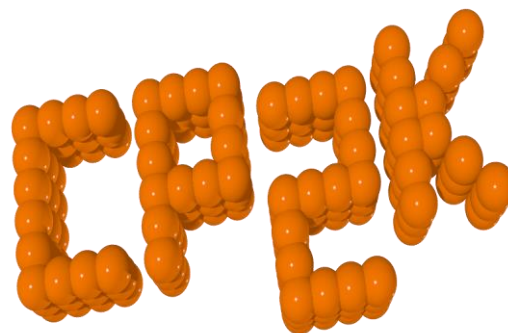
Dr. Dzade Nelson

The Pennsylvania State University

DFT codes/software

Spanish Initiative for Electronic Simulations with Thousands of Atoms

CAmbridge Serial Total Energy Package

Kohn-Sham equations

IN

RUN

OUT

Model:
unit cell
lattice vectors
basis

Physical approx:
xc-approximation
GGA, LDA, …

Numerical approx:
energy cut-off
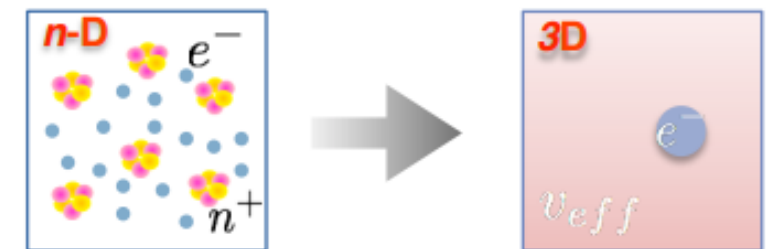k-points grid
SCF procedure

QUANTUM**ESPRESSO**

Physical quantities:
charge density
total energy
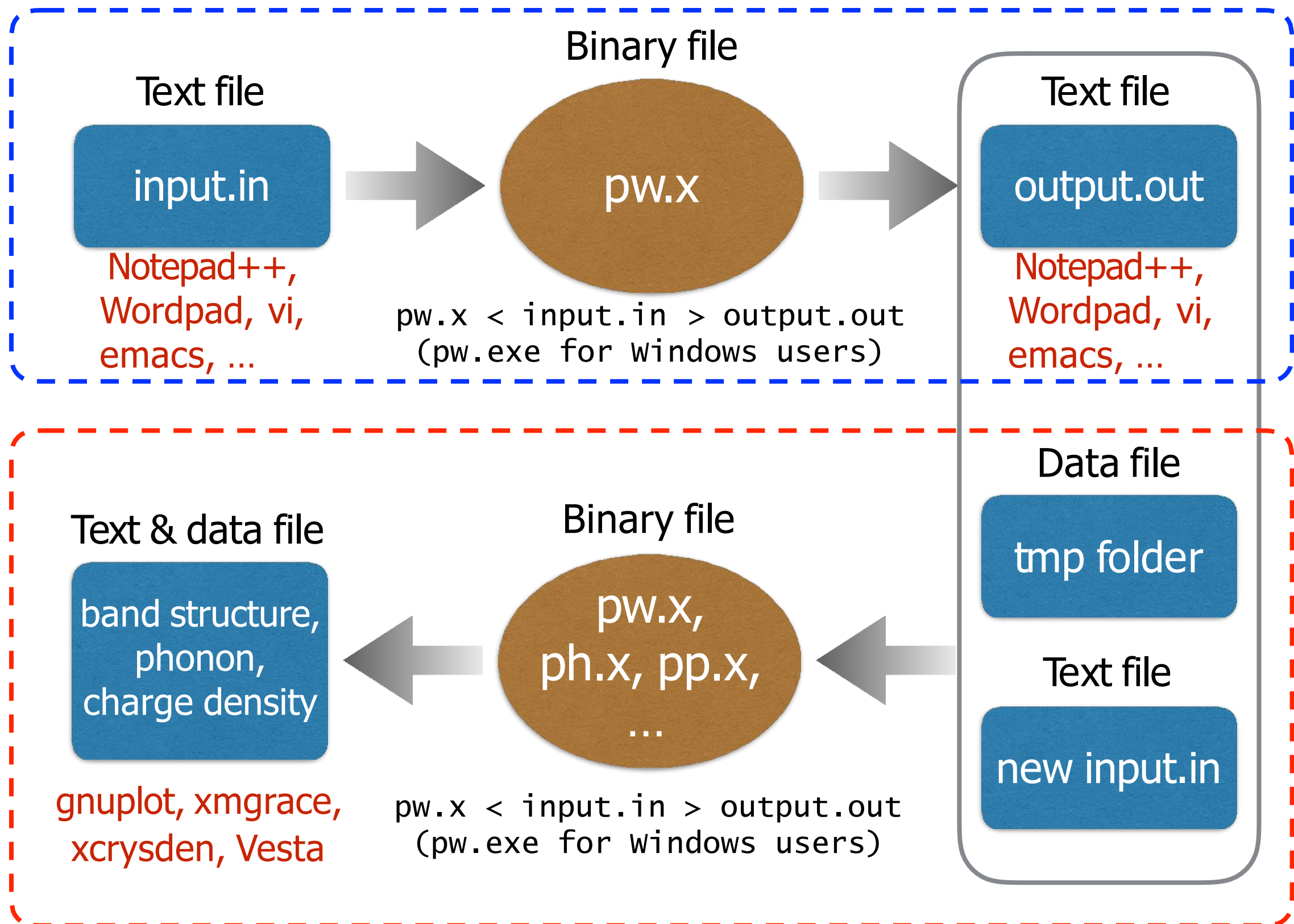KS wavefunctions
KS energies

Solve Kohn-Sham equations

$$\left[-\frac{1}{2}\nabla^2 + V_{ion}(r) + V_H[n(r)] + V_{XC}[n(r)] \right] \psi_i(r) = \varepsilon_i \psi_i(r)$$

External nuclear
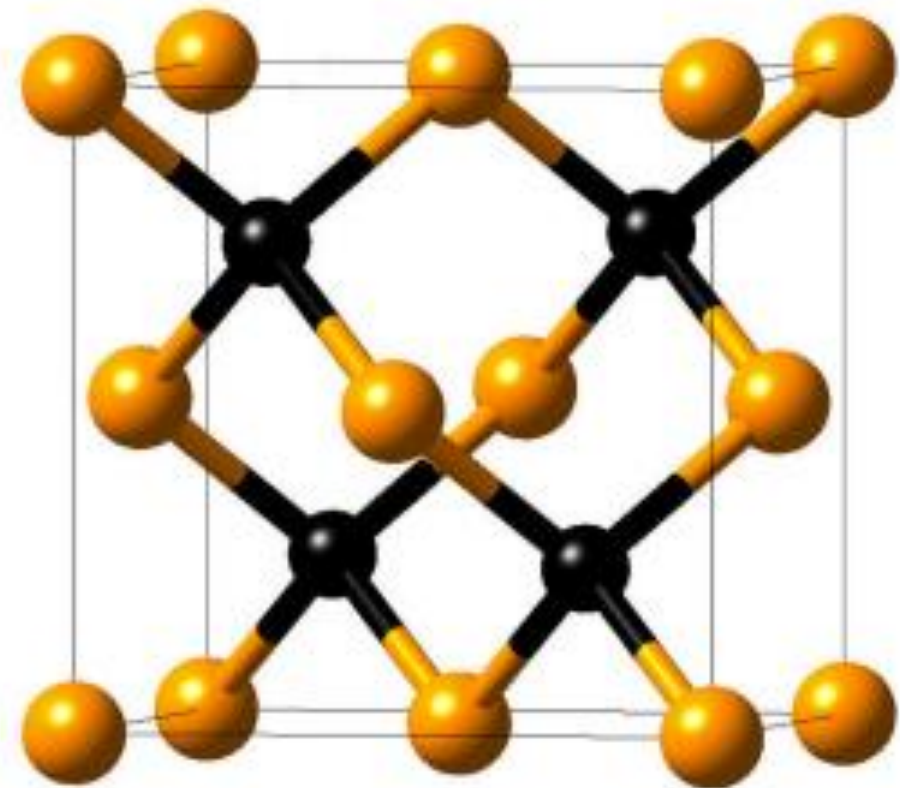potential

Hartree
potential

Exchange-correlation
potential

Structure of QE I/O file

QUANTUMESPRESSO

Binary file

Text file

input.in

Notepad++,
Wordpad, vi,
emacs, …

pw.x

pw.x < input.in > output.out
(pw.exe for Windows users)

Text file

output.out

Notepad++,
Wordpad, vi,
emacs, …

Data file

tmp folder

Text file

new input.in

Text & data file

**band structure,
phonon,
charge density**

gnuplot, xmgrace,
xcrysden, Vesta

Binary file

**pw.x,
ph.x, pp.x,
...**

pw.x < input.in > output.out
(pw.exe for Windows users)
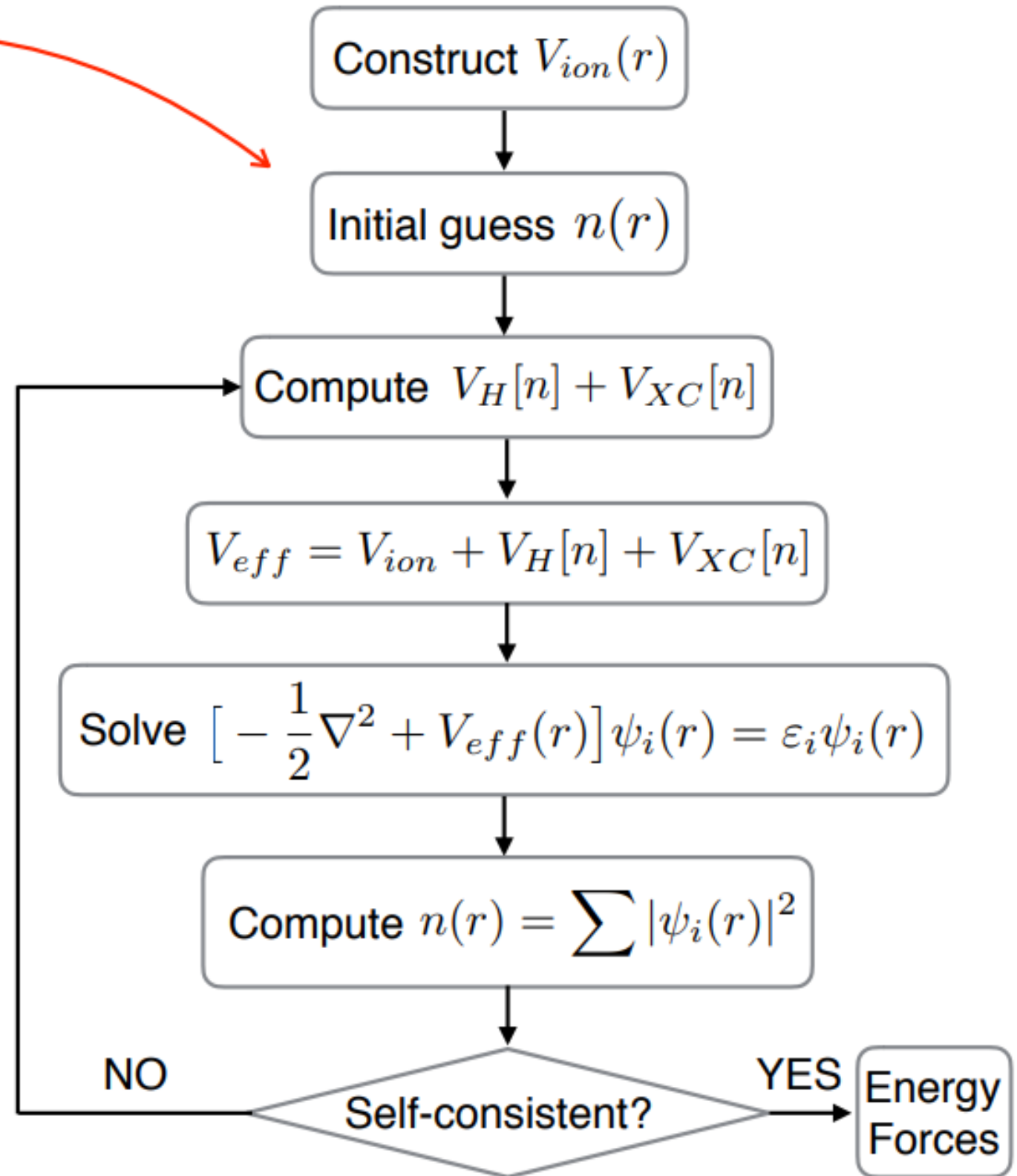
Structure of QE input file

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&ELECTRONS
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  conv_thr=1d-8,
/
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  Si 28.0855 Si.pbe-rrkj.UPF
ATOMIC_POSITIONS (alat)
Si  0.00  0.00  0.00
Si  0.25  0.25  0.25
K_POINTS automatic
4 4 4 1 1 1
```


Silicon

Structure of QE input file

```
&CONTROL
 calculation='scf',
 restart_mode='from_scratch',
 prefix='si',
 pseudo_dir='../pseudo/',
 outdir='../tmp/',
/
&SYSTEM
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/
&ELECTRONS
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 conv_thr=1d-8,
/
ATOMIC_SPECIES
 Si 28.0855 Si.pbe-rrkj.UPF
ATOMIC_POSITIONS (alat)
Si   0.00   0.00   0.00
Si   0.25   0.25   0.25
K_POINTS automatic
4 4 4 1 1 1
```

Construct $V_{ion}(r)$

Initial guess $n(r)$

Compute $V_H[n] + V_{XC}[n]$

$V_{eff} = V_{ion} + V_H[n] + V_{XC}[n]$

Solve $\left[-\frac{1}{2}\nabla^2 + V_{eff}(r) \right]\psi_i(r) = \varepsilon_i\psi_i(r)$

Compute $n(r) = \sum |\psi_i(r)|^2$

Self-consistent?

NO

YES → Energy Forces

Structure of QE input file

```
&CONTROL
  calculation='scf',
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  outdir='../tmp/',
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  nat=2,
  ntyp=1,
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  ecutrho=720.0,
/
&ELECTRONS
  mixing_beta=0.7,
  conv_thr=1d-8,
/
ATOMIC_SPECIES
  Si 28.0855 Si.pbe-rrkj.UPF
ATOMIC_POSITIONS (alat)
Si   0.00   0.00   0.00
Si   0.25   0.25   0.25
K_POINTS automatic
4 4 4 1 1 1
```

```
ibrav = 1 (SC)
ibrav = 2 (FCC)
ibrav = 4 (Hexagonal)
…
```

```
simple cubic:
v1 = a(1,0,0)
v2 = a(0,1,0)
v3 = a(0,0,1)
```
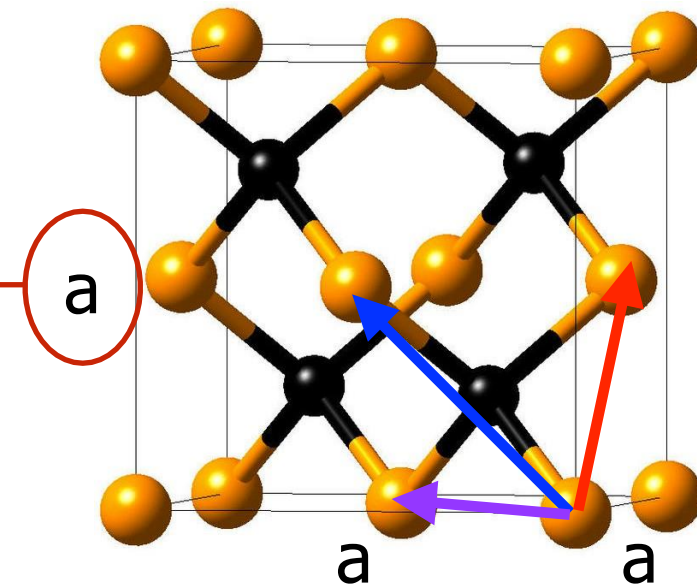
```
face centered cubic:
v1 = (a/2)(-1,0,1)
v2 = (a/2)(0,1,1)
v3 = (a/2)(-1,1,0)
```

Structure of QE input file

```
&CONTROL
  calculation='scf',
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  prefix='si',
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  outdir='../tmp/',
/
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  mixing_beta=0.7,
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ATOMIC_SPECIES
  Si 28.0855 Si.pbe-rrkj.UPF
ATOMIC_POSITIONS (alat)
Si  0.00  0.00  0.00
Si  0.25  0.25  0.25
K_POINTS automatic
4 4 4 1 1 1
```

FCC structure

unit bohr
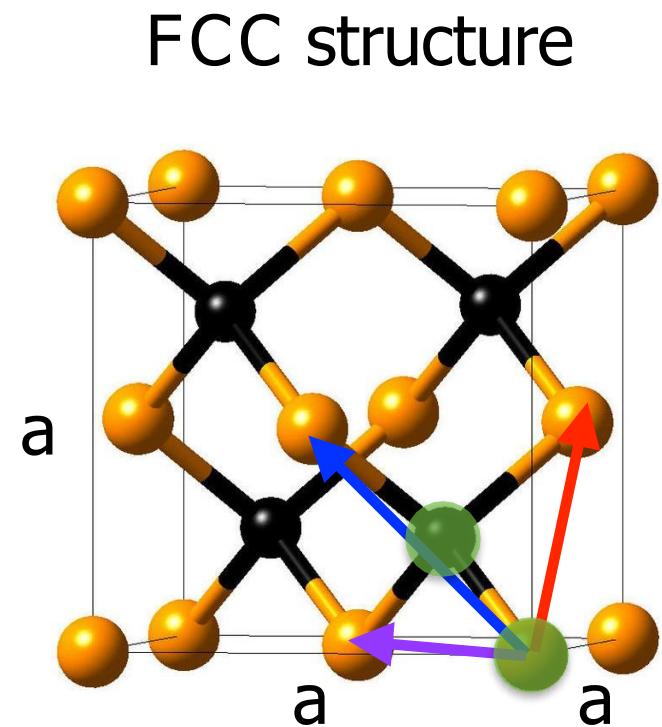
a

a   a

face centered cubic:
$v1 = (a/2)(-1,0,1)$
$v2 = (a/2)(0,1,1)$
$v3 = (a/2)(-1,1,0)$

1 bohr = 0.529177 Å

Structure of QE input file

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Si  0.25  0.25  0.25
K_POINTS automatic
4 4 4 1 1 1
```
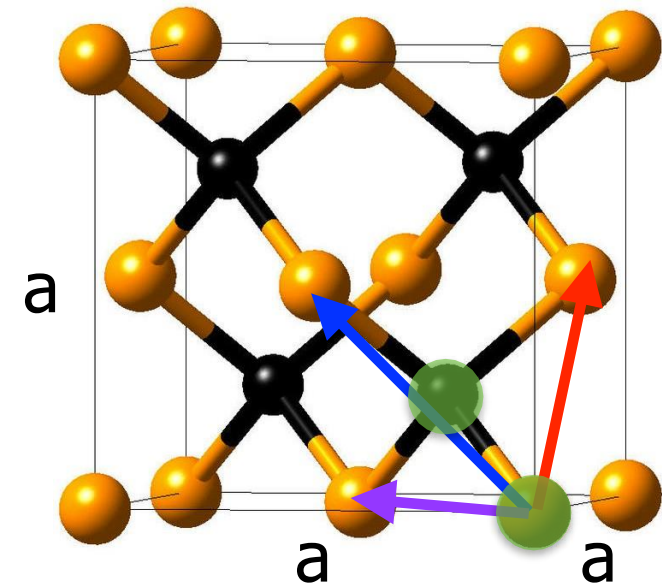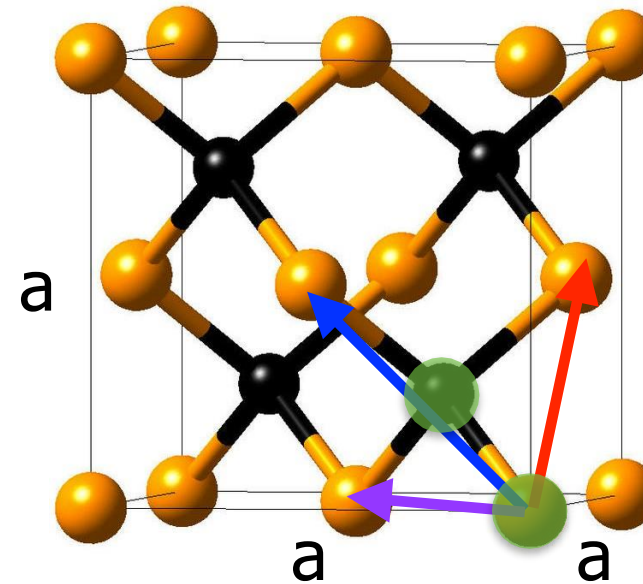

FCC structure

Structure of QE input file

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  mixing_beta=0.7,
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ATOMIC_POSITIONS (alat)
Si  0.00  0.00  0.00
Si  0.25  0.25  0.25

K_POINTS automatic
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```

Silicon

FCC structure

a

a   a

Structure of QE input file

```
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ATOMIC_POSITIONS (alat)
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Si  0.25  0.25  0.25
K_POINTS automatic
4 4 4 1 1 1
```

FCC structure

a

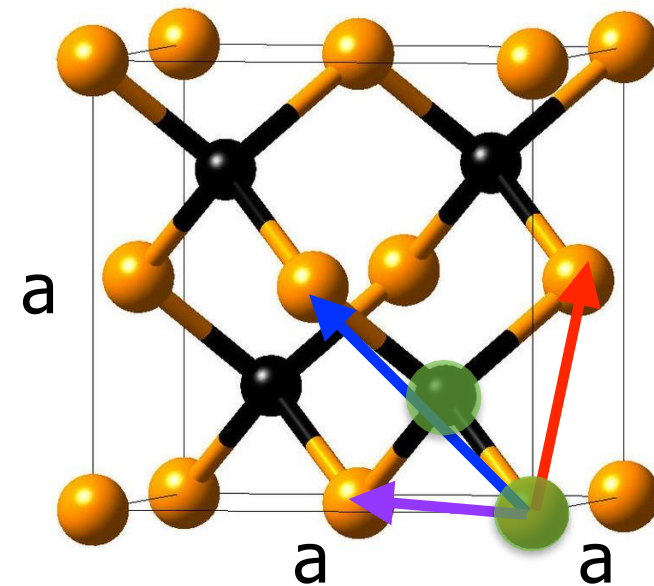a   a

Silicon

Mass of Si

Structure of QE input file

```
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ATOMIC_POSITIONS (alat)
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Si  0.25  0.25  0.25

K_POINTS automatic
4 4 4 1 1 1
```

PP file
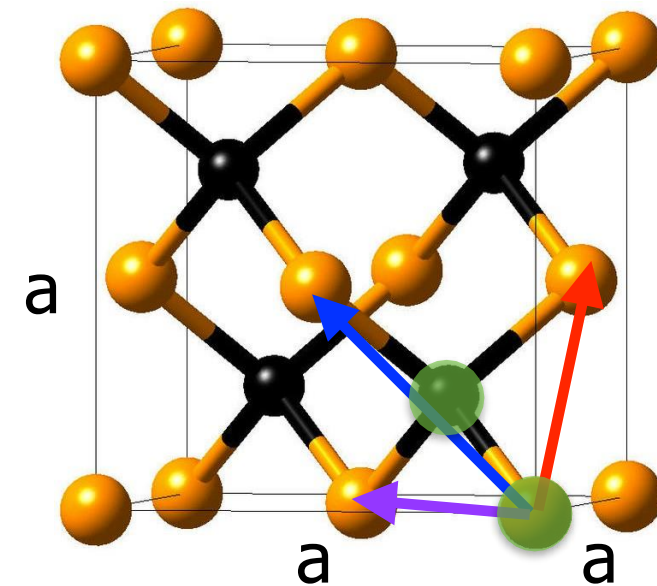
FCC structure

a

a   a

Silicon

Structure of QE input file

```
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  conv_thr=1d-8,
/
ATOMIC_SPECIES
  Si 28.0855 Si.pbe-rrkj.UPF
ATOMIC_POSITIONS (alat)
Si   0.00   0.00   0.00
Si   0.25   0.25   0.25

K_POINTS automatic
4 4 4 1 1 1
```

FCC structure

atomic positions are in cartesian coordinates, in units of the lattice parameter.

External nuclear potential
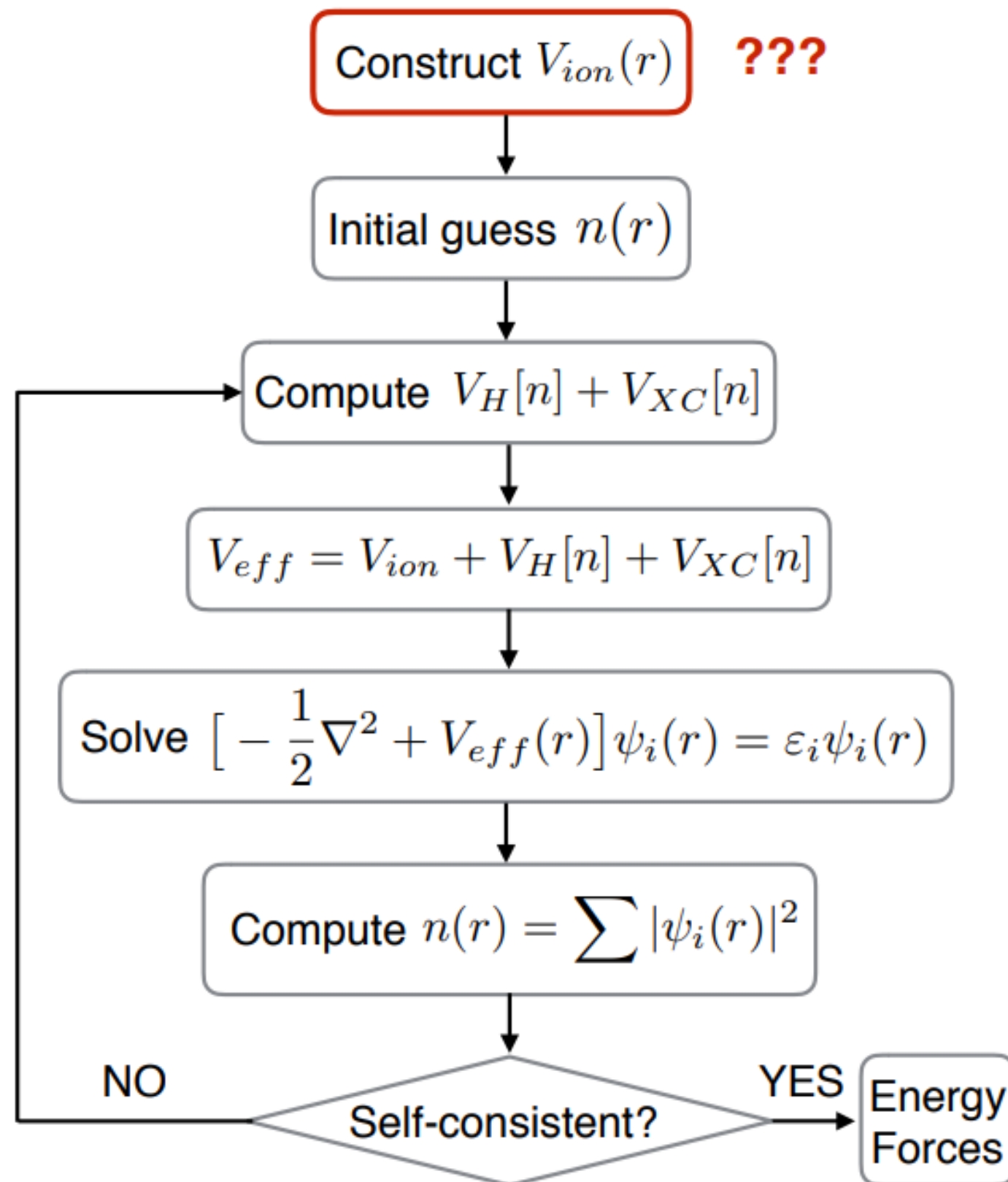
External nuclear potential

Electrons experience a Coulomb potential due to the nuclei with simple form:
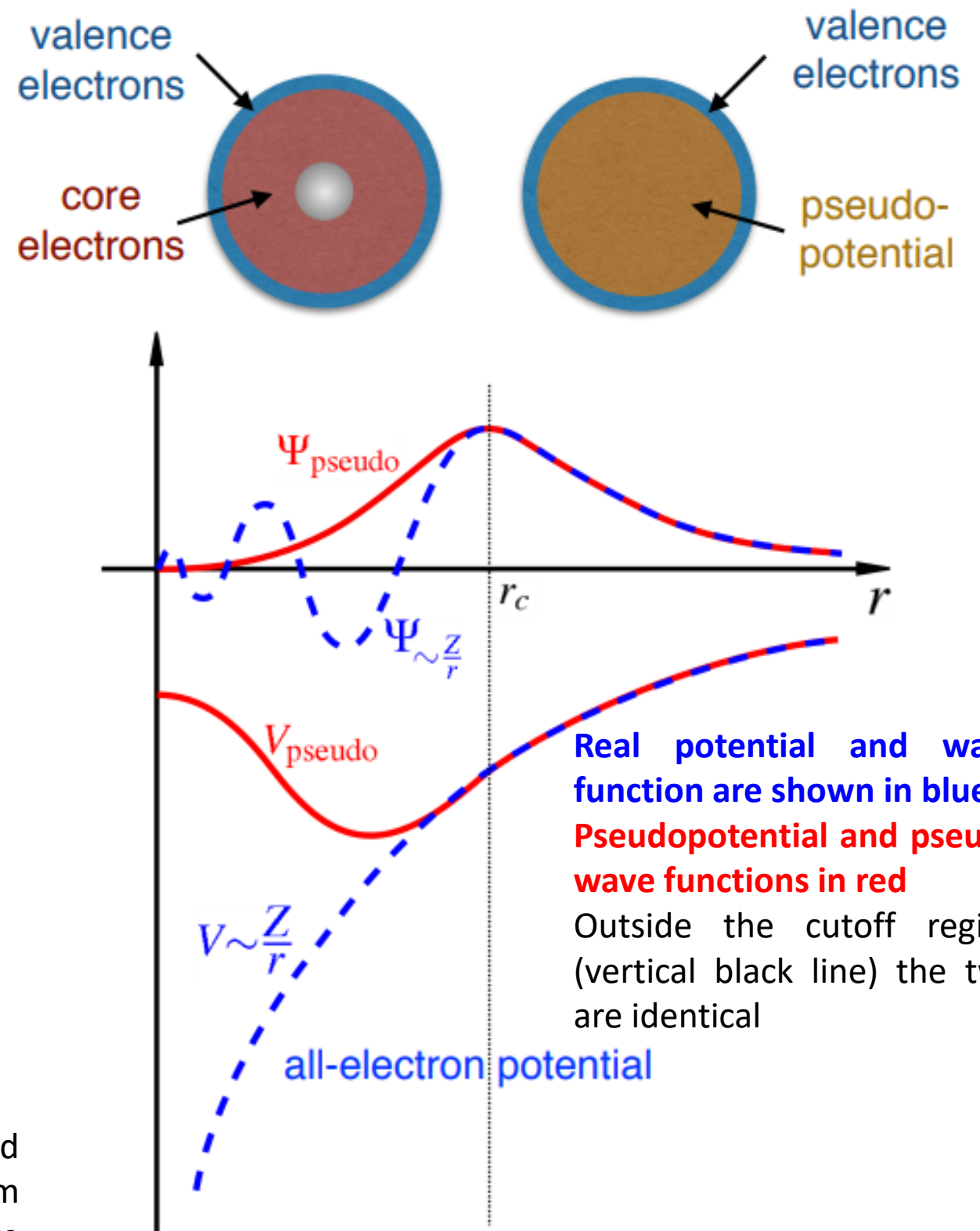
$$V_{ion} = -\frac{Z}{r}$$

But this leads to computational problems!

→ **Pseudopotential (PP):**

Replace the strong Coulomb potential of the nucleus and tightly bound core electrons by an effective ionic potential acting on the valence electrons.

The rapidly changing potential field near the atomic core is replaced by a smoother function that simulates the potential field far from the core very well. By doing so, it requires less number plane wave basis for wavefunction expansion.

valence electrons

core electrons

valence electrons

pseudo-potential

Ψ_{pseudo}

$\Psi \sim \frac{Z}{r}$

r_c

r

V_{pseudo}

$V \sim \frac{Z}{r}$

all-electron potential

Real potential and wave function are shown in blue
Pseudopotential and pseudo wave functions in red
Outside the cutoff region (vertical black line) the two are identical

Pseudopotential

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  ecutrho=720.0,
/
&ELECTRONS
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/
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ATOMIC_POSITIONS (alat)
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Si  0.25  0.25  0.25
K_POINTS automatic
4 4 4 1 1 1
```

How to get pseudopotential

http://www.quantum-espresso.org/pseudopotentials/

Si.pbe-rrkj.UPF

▷ type of exchange-correlation functional

▷ type of pseudopotential

Pseudopotential

```
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  conv_thr=1d-8,
/
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ATOMIC_POSITIONS (alat)
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Si   0.25   0.25   0.25

K_POINTS automatic
4 4 4 1 1 1
```

Si.pbe-rrkj.UPF

```
<PP_INFO>
Generated using Andrea Dal Corso code (rrkj3)
Author: Andrea Dal Corso   Generation date: unknown
Info:   Si PBE 3s2 3p2 RRKJ3
      0       The Pseudo was generated with a Non-Relativistic Calculation
  2.50000000000E+00   Local Potential cutoff radius
nl pn  l   occ              Rcut             Rcut US            E pseu
3S  1  0  2.00     2.50000000000     2.60000000000     0.00000000000
3S  1  0  0.00     2.50000000000     2.60000000000     0.00000000000
3P  2  1  2.00     2.50000000000     2.70000000000     0.00000000000
3D  3  2  0.00     2.50000000000     2.50000000000     0.00000000000
</PP_INFO>


<PP_HEADER>
      0                   Version Number
     Si                   Element
     NC                   Norm - Conserving pseudopotential
      F                   Nonlinear Core Correction
  SLA  PW   PBE   PBE     PBE  Exchange-Correlation functional
     4.00000000000        Z valence
    -7.47480832270        Total energy
  0.0000000  0.0000000   Suggested cutoff for wfc and rho
      2                   Max angular momentum component
    883                   Number of points in mesh
      2     3             Number of Wavefunctions, Number of Projectors
  Wavefunctions           nl   l   occ
                          3S   0  2.00
                          3P   1  2.00

</PP_HEADER>


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  <PP_R>
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  1.88002117930E-04  1.90843406086E-04  1.93727634813E-04  1.96655453076E-04
  1.99627519645E-04  2.02644503249E-04  2.05707082721E-04  2.08815947154E-04
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```
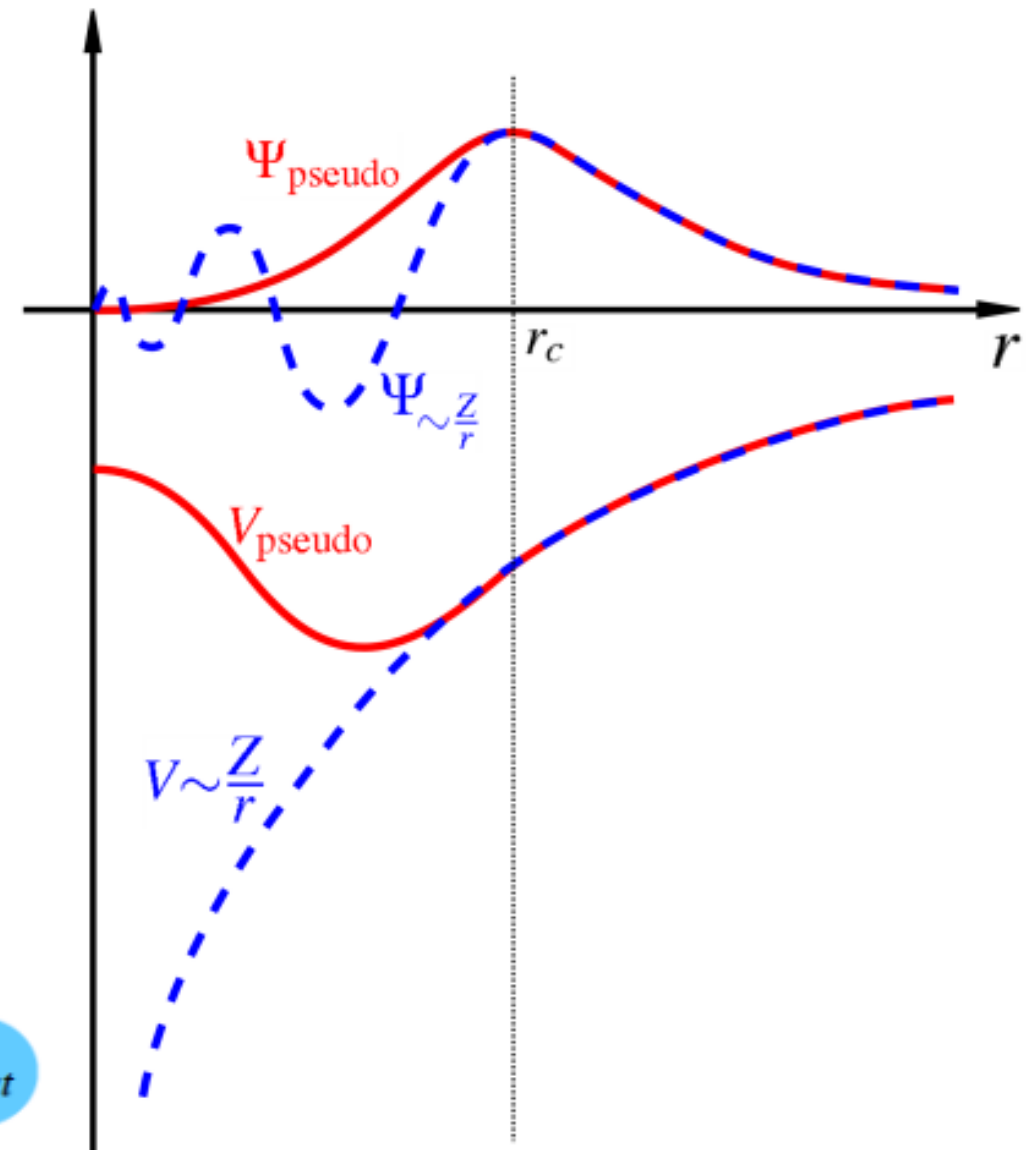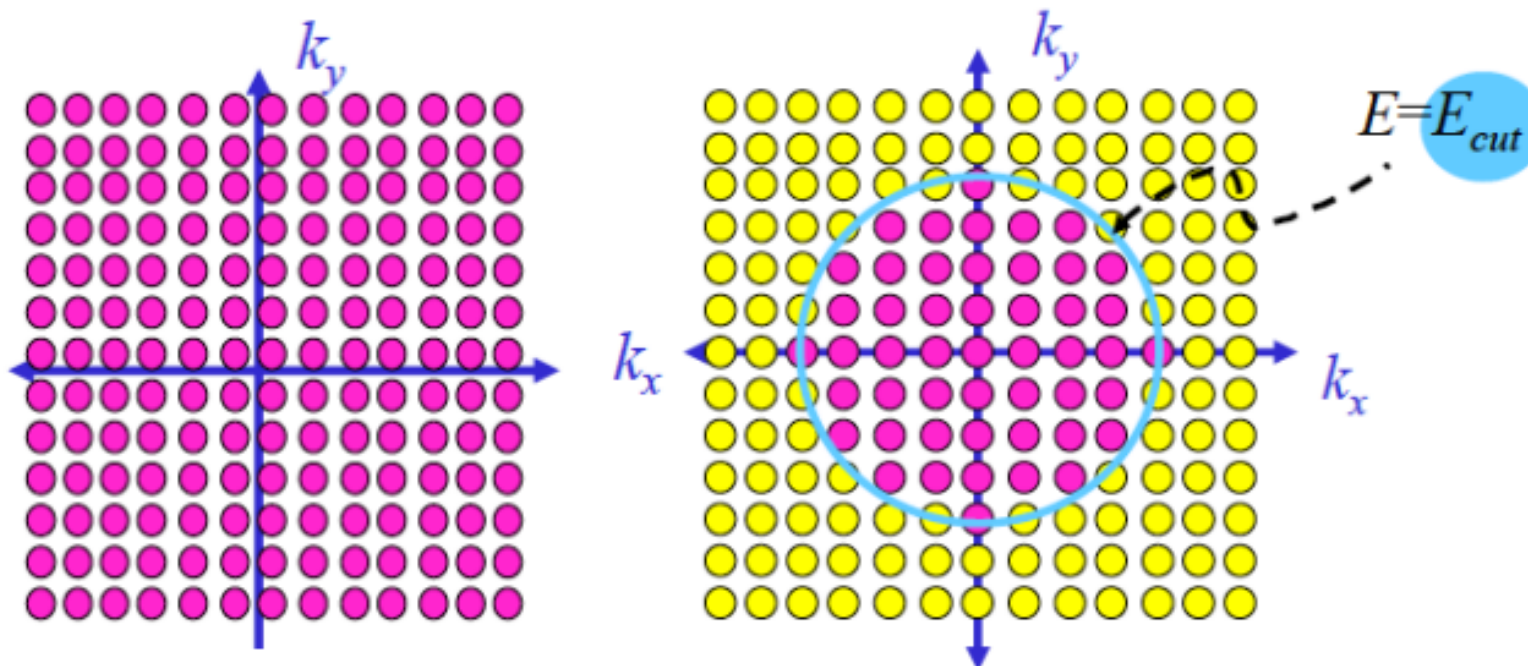
Plane wave expansion

In a periodic system we can write the KS states as a superposition of plane waves:

$$\Psi_{k,n}(r) = \frac{1}{\Omega} \sum_G c_{k,n}^G e^{i(k+G)\cdot r}$$

G are vectors in reciprocal space.
The sum, in principle infinite, can be truncated:

$$\frac{\hbar^2}{2m}|k+G|^2 \leq E_{cut}$$

Crystalline solids and plane wave DFT

A crystal: periodic arrangement atoms
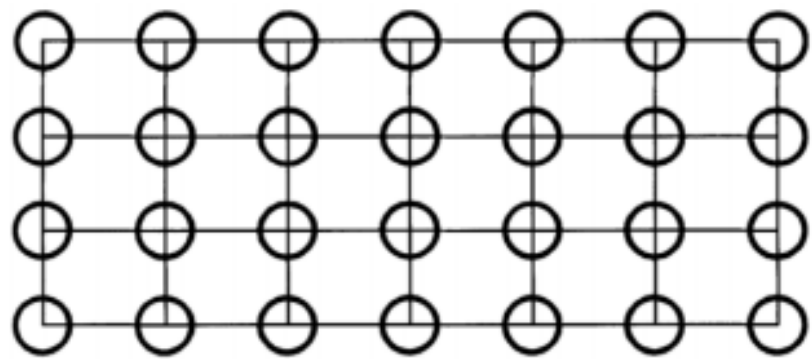
Free electrons: Plane waves:

Electrons in a periodic potential are Bloch waves:

$$\psi_{nk}(\mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{r})\, u_{nk}(\mathbf{r})$$

(Perturbed free electrons)

(a) Periodic potential, $U(\mathbf{r})$

(d) Plane wave, $e^{i\mathbf{k}\cdot\mathbf{r}}$

(b) Bloch wave, ψ_{nk}

(c) Lattice-periodic part, u_{nk}

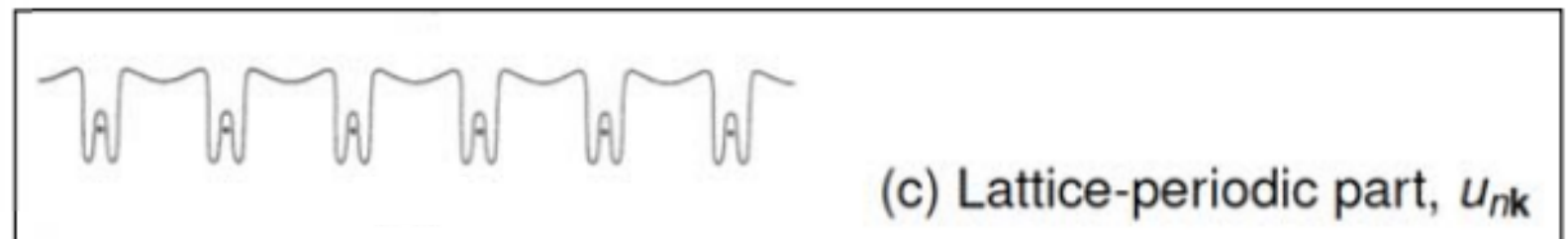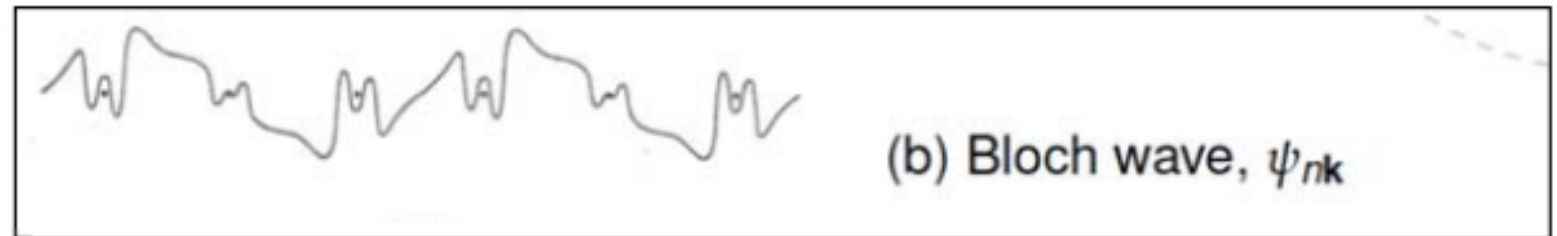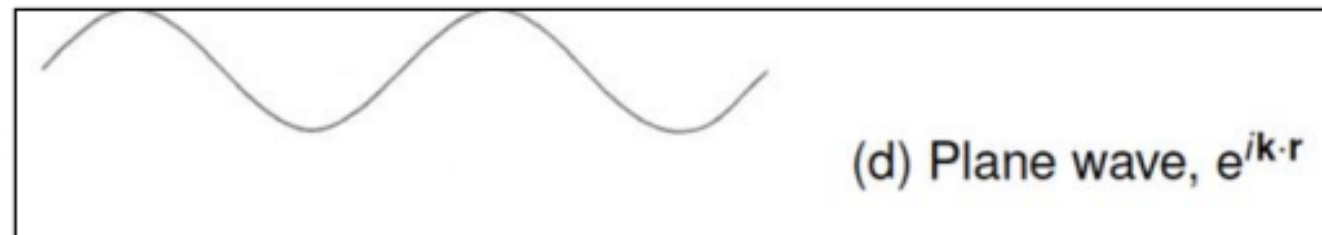# Crystalline solids and plane wave DFT -Cutoff energy

- Reciprocal space:

Real space

Reciprocal space

$$\mathcal{F}\{\quad\} = $$

G_y G_x
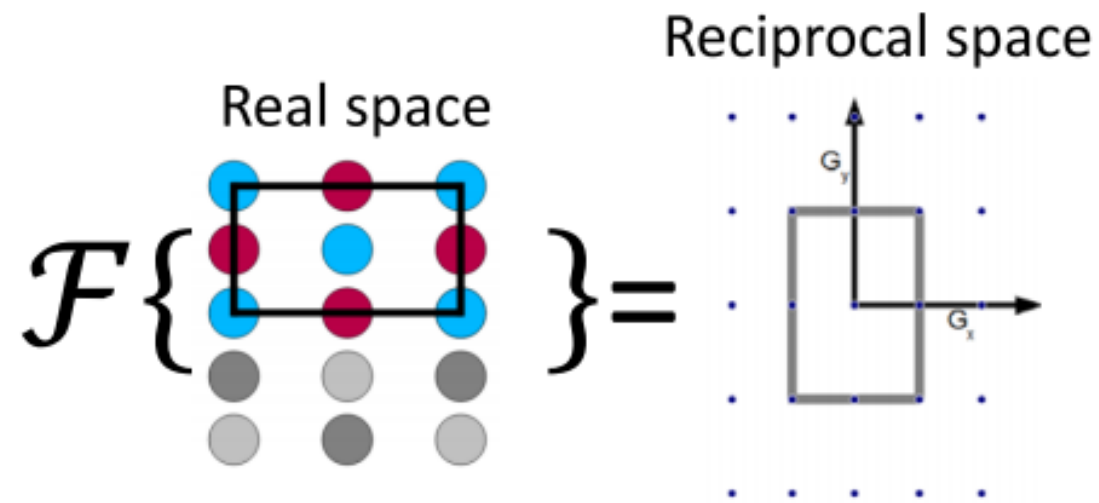
All periodic functions can be expanded by a Fourier series:

$$\psi_{n\boldsymbol{k}}(\mathbf{r}) = \exp(i\mathbf{k}\cdot\mathbf{r})\,\mathrm{u}_{n\mathbf{k}}(\mathbf{r}) = \exp(i\mathbf{k}\cdot\mathbf{r})\sum_{\boldsymbol{G}}c_{\boldsymbol{k}}\exp(i\boldsymbol{G}\cdot\boldsymbol{r})$$

(b) Bloch wave, $\psi_{n\mathbf{k}}$

= sum of plane waves

- Each plane wave in the sum have kinetic energy: $E = \dfrac{\hbar}{2m}|\mathbf{k}+\mathbf{G}|^2$
- Numerically we must define a **cutoff energy** for the expansion!
- The choice of cutoff energy must be tested with respect to energy convergence in calculations

Plane wave expansion

```
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 calculation='scf',
 restart_mode='from_scratch',
 prefix='si',
 pseudo_dir='../pseudo/',
 outdir='../tmp/',
/
&SYSTEM
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 nat=2,
 ntyp=1,
 ecutwfc=60.0,
 ecutrho=720.0,
/
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 mixing_beta=0.7,
 conv_thr=1d-8,
/
ATOMIC_SPECIES
 Si 28.0855 Si.pbe-rrkj.UPF
ATOMIC_POSITIONS (alat)
Si  0.00  0.00  0.00
Si  0.25  0.25  0.25
K_POINTS automatic
4 4 4 1 1 1
```

$$\frac{\hbar^2}{2m}|k + G|^2 \leq E_{cut}$$

Units: Ry (1 Ry = 0.5 Ha = 13.6057 eV)
For ultrasoft pseudopotentials we have also:
ecutrho = usually 8-12 × ecutwfc

Initial n(r)

Construct $V_{ion}(r)$ ✔

Initial guess $n(r)$

Compute $V_H[n] + V_{XC}[n]$

$V_{eff} = V_{ion} + V_H[n] + V_{XC}[n]$

Solve $\left[-\frac{1}{2}\nabla^2 + V_{eff}(r)\right]\psi_i(r) = \varepsilon_i\psi_i(r)$

Compute $n(r) = \sum|\psi_i(r)|^2$

NO ← Self-consistent? → YES → Energy Forces

Initial n(r)
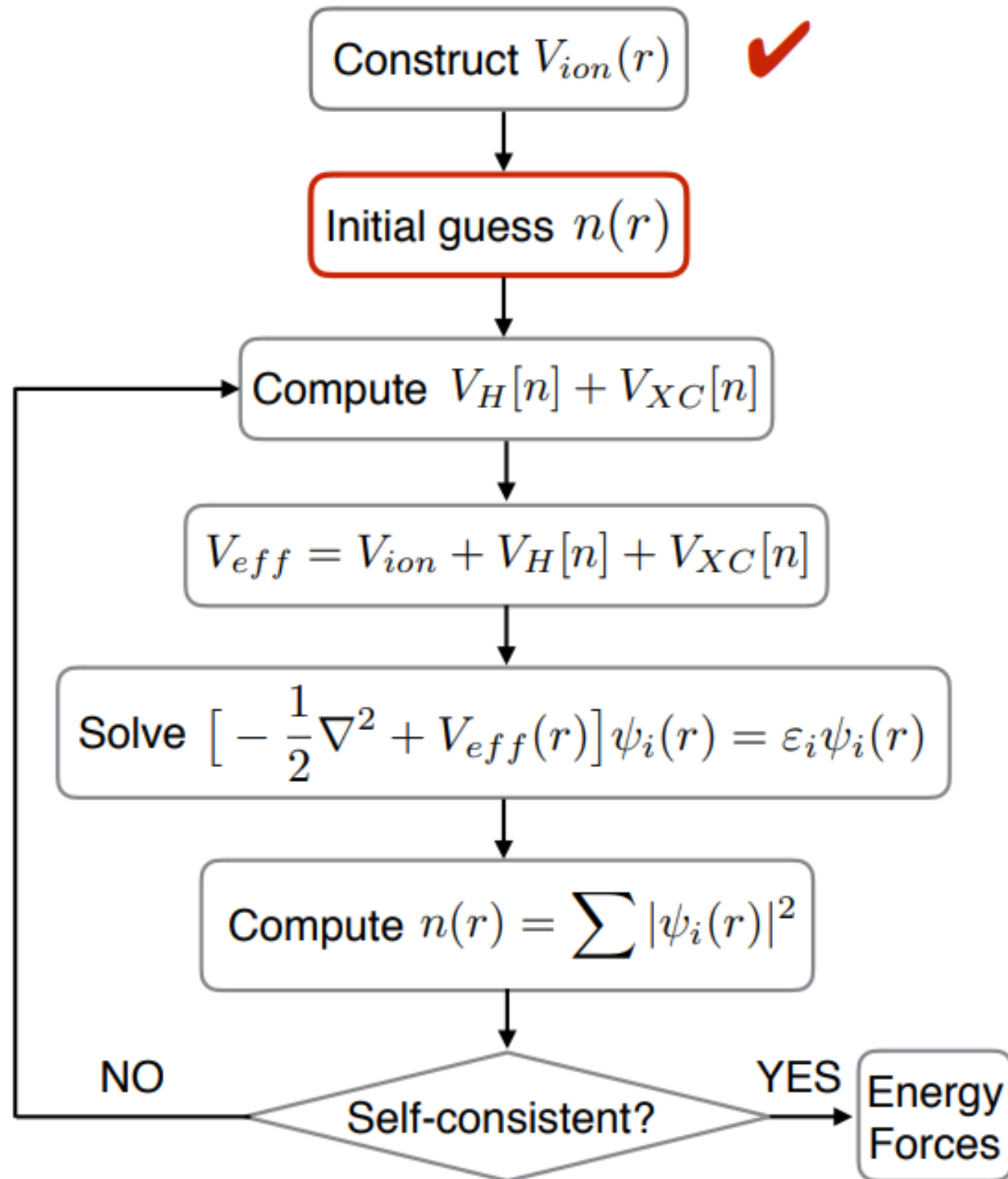
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  celldm(1)=10.2625,
  nat=2,
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  ecutrho=720.0,
/
&ELECTRONS          ←——————————    startingwfc = 'atomic'(DEFAULT)
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ATOMIC_POSITIONS (alat)
Si  0.00  0.00  0.00
Si  0.25  0.25  0.25

K_POINTS automatic
4 4 4 1 1 1
```

Sampling of the Brillouin zone

Many quantities we need to compute involve an integral over the BZ:
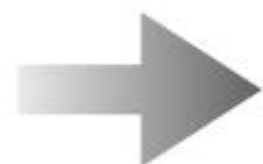
$$\bar{A} = \frac{1}{\Omega_{BZ}} \int_{BZ} A(k)d(k)$$

An example is the electronic density n(r):

$$n(r) = \frac{1}{\Omega_{BZ}} \sum_i \int_{BZ} |\Psi_{i,k}(r)|^2 f(\epsilon_{i,k} - \epsilon_F)d(k)$$

In practice the integral is discretized:

$$\frac{1}{\Omega_{BZ}} \int_{BZ} d(k) \rightarrow \sum_k \omega_k$$

How do we choose the k points to include in the sum???

Crystalline solids and plane wave DFT - k-points

Real space

Reciprocal space

- Wavevectors $k = \frac{2\pi}{\lambda} \left[\frac{1}{m}\right]$ are reciprocal space

- The primitive unit cell in reciprocal space is called the 1st **Brillouin Zone (BZ)**

$$\mathcal{F}\left\{\begin{array}{c}\end{array}\right\}=$$

- Any k-point that differ by a reciprocal lattice vector **G** are equivalent : **k`=k+G**

- Integrals need only be evaluated in the 1st BZ

1st BZ
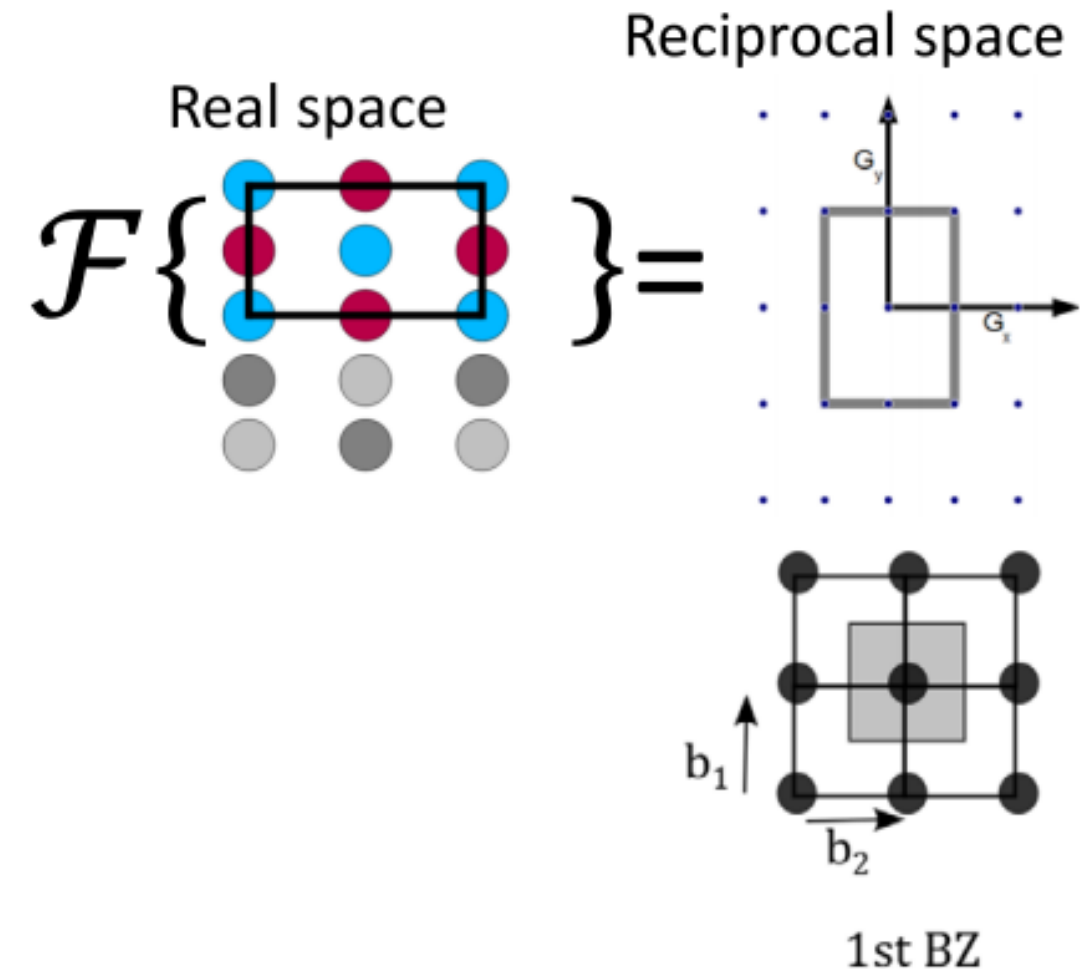
- Numerically we must chose an approprate number of k-points to sample the BZ
- The k-point sampling must be tested with respect to energy convergece

O k-point sampling

1st BZ
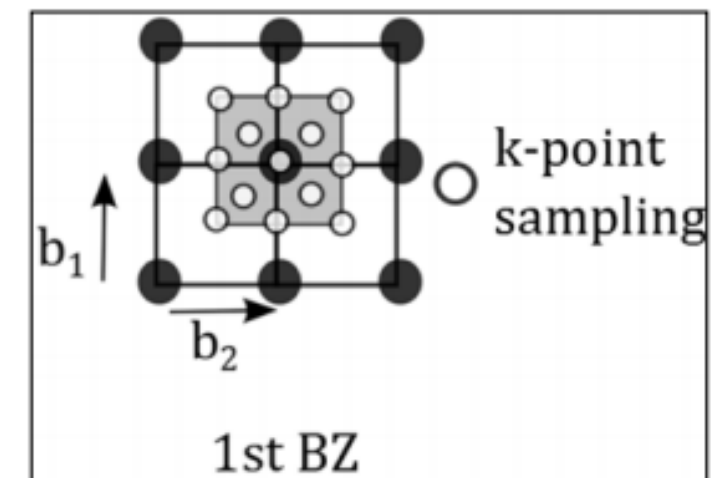
Monkhorst and Pack (1976)

Example: square 2D lattice
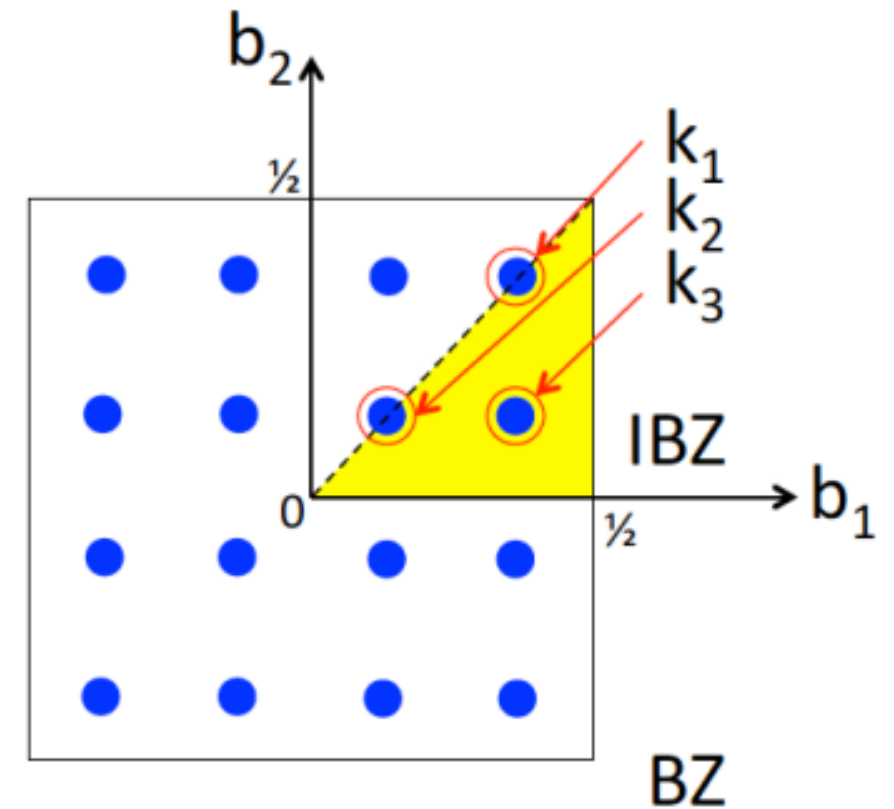
4×4 k-points grid (16 points)

3 inequivalent point (IBZ)

$$4 \times k_1 \rightarrow \omega_1 = 4/16 = 1/4$$

$$4 \times k_2 \rightarrow \omega_2 = 4/16 = 1/4$$

$$8 \times k_3 \rightarrow \omega_3 = 8/16 = 1/2$$

$$\frac{1}{\Omega_{BZ}} \int_{BZ} A(k) d(k) \simeq \frac{1}{4} A(k_1) + \frac{1}{4} A(k_2) + \frac{1}{2} A(k_3)$$

Sampling of the Brillouin zone

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  ntyp=1,
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  ecutrho=720.0,
/
&ELECTRONS
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  conv_thr=1d-8,
/
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  Si 28.0855 Si.pbe-rrkj.UPF
ATOMIC_POSITIONS (alat)
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Si  0.25  0.25  0.25
K_POINTS automatic
4 4 4 1 1 1
```
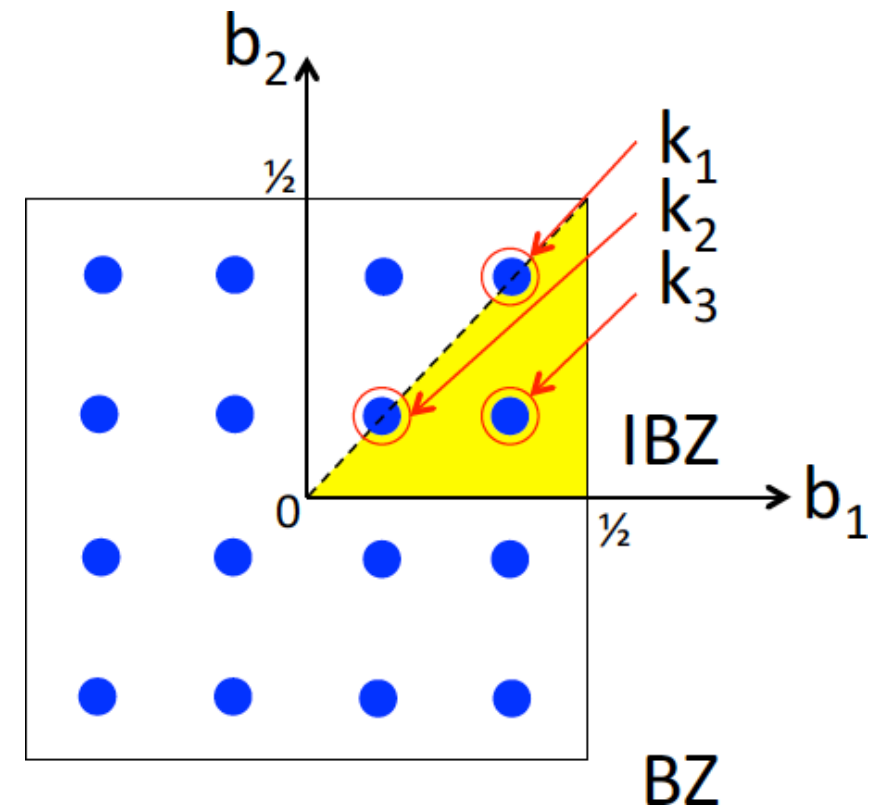


```
K_POINTS automatic
nk1, nk2, nk3, k1, k2, k3
```

nk1, nk2, nk3 as in Monkhorst-Pack
grids k1, k2, k3 must be 0 (no offset) or
1 (grid displaced by half a grid step in
the corresponding direction)

QE run
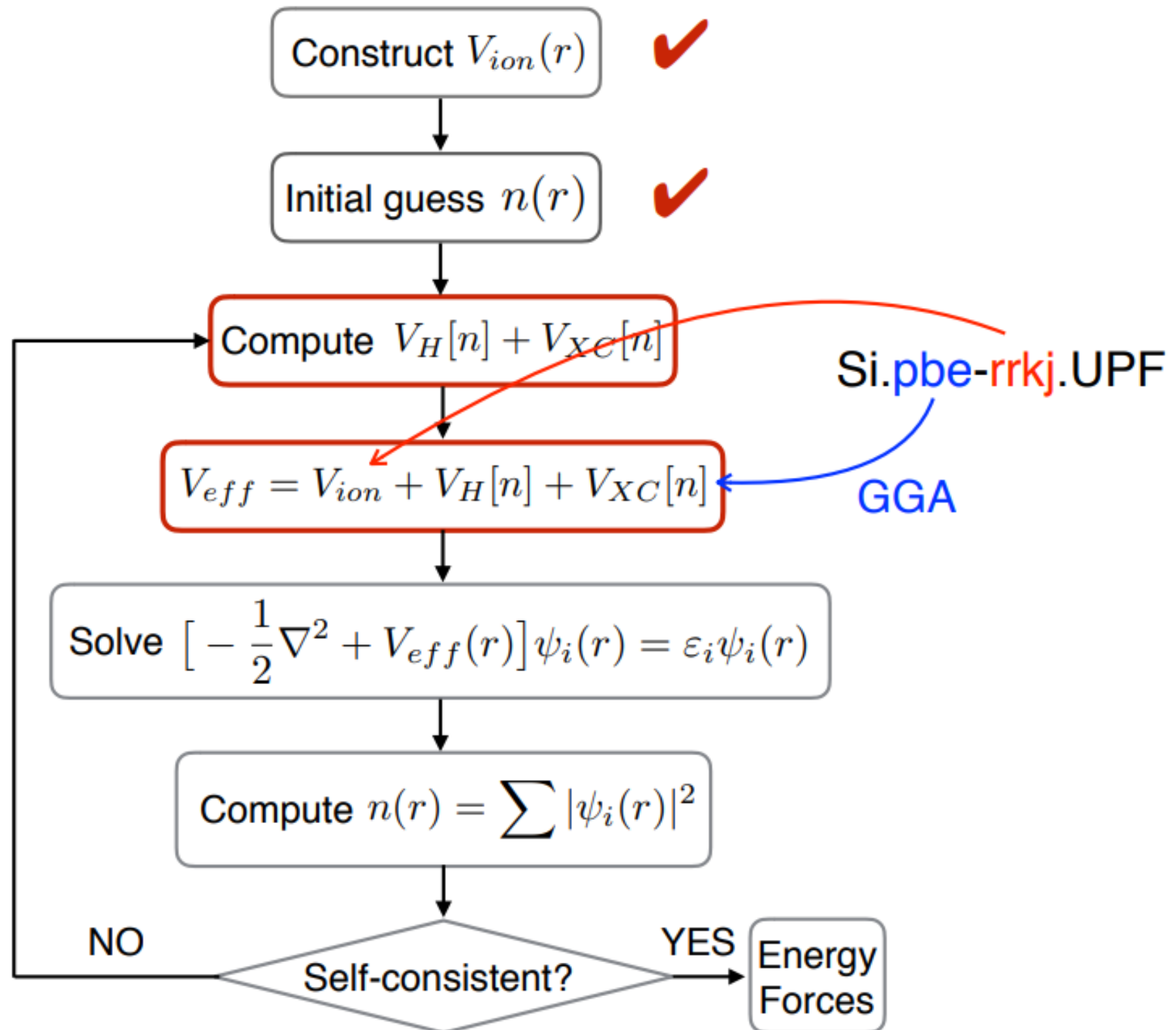
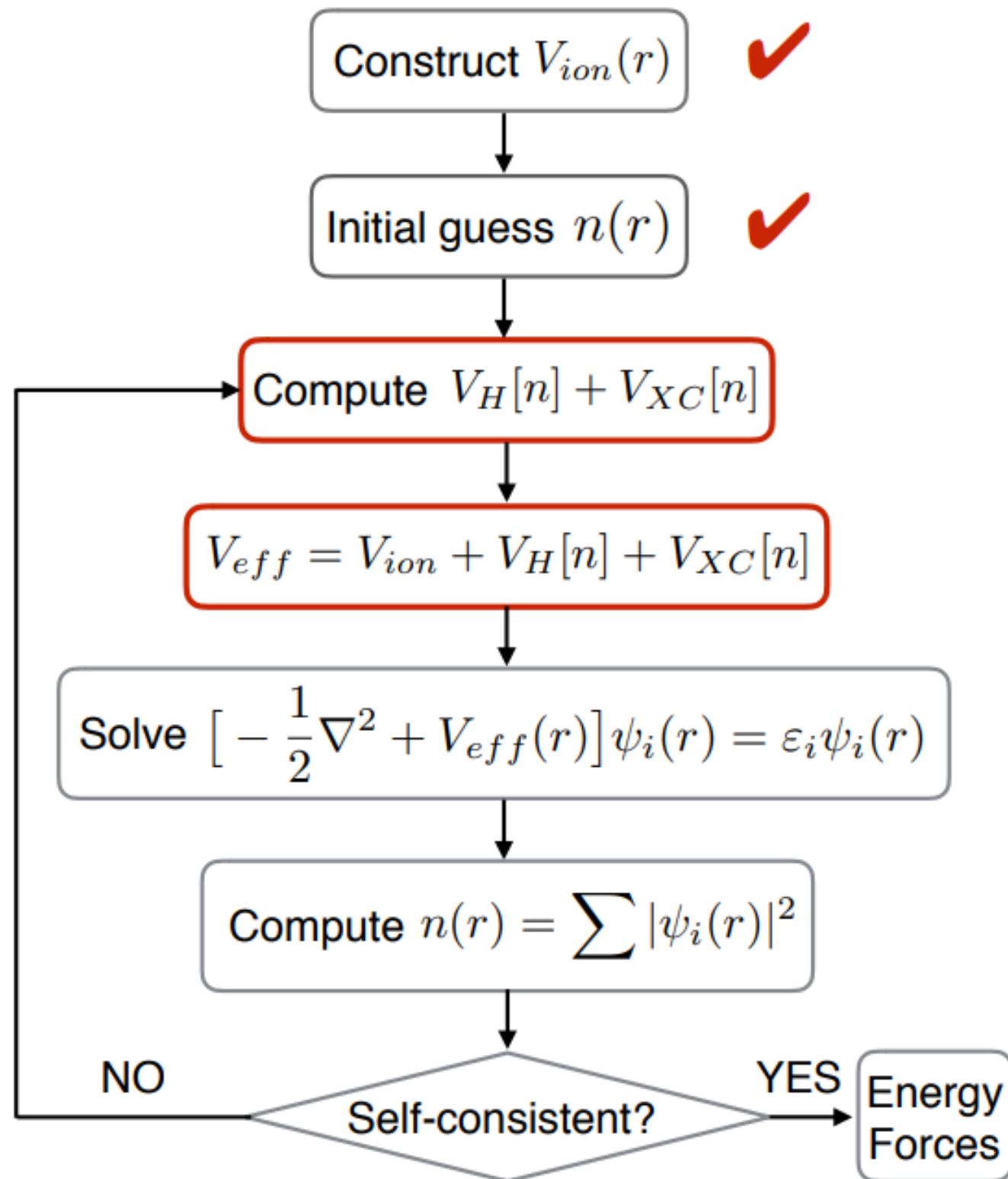# QE run
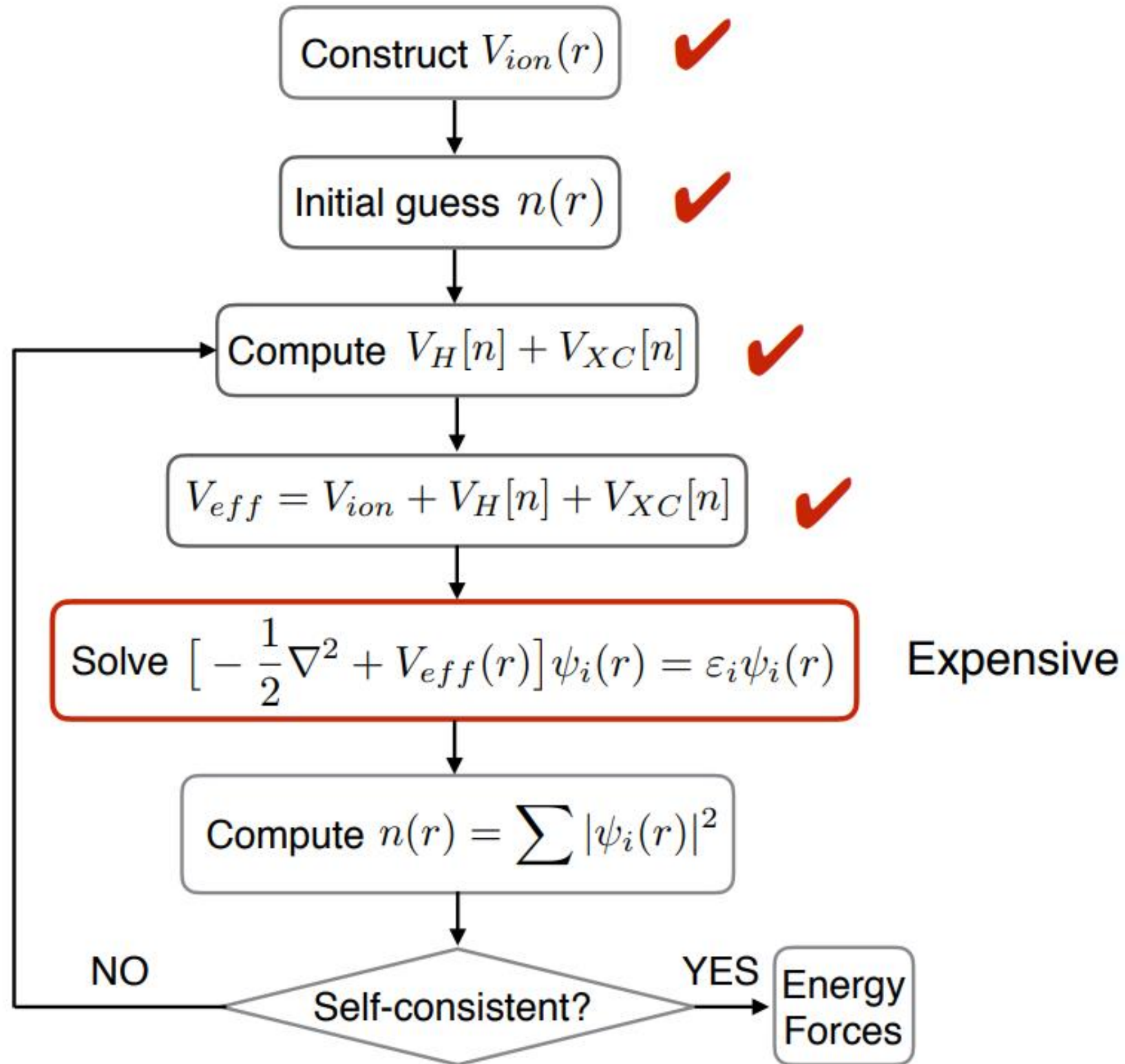
Solve wave equation

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/
&ELECTRONS
  mixing_beta=0.7,
  conv_thr=1d-8,
/
ATOMIC_SPECIES
  Si 28.0855 Si.pbe-rrkj.UPF
ATOMIC_POSITIONS (alat)
Si   0.00  0.00  0.00
Si   0.25  0.25  0.25

K_POINTS automatic
4 4 4 1 1 1
```

diagonalization = 'david' (DEFAULT)
                = 'cg'

Quantum Espresso Input File – diagonalization

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    ecutrho=720.0,
/
&ELECTRONS
    diagonalization = 'david',
    mixing_beta=0.7,
    conv_thr=1d-8,
/
ATOMIC_SPECIES
    Si 28.0855 Si.pbe-rrkj.UPF
ATOMIC_POSITIONS (alat)
Si 0.00 0.00 0.00
Si 0.25 0.25 0.25
K_POINTS automatic
4 4 4 1 1 1
```

If the Kohn-Sham equations written in the matrix form, then we have

$$\mathrm{H}[\rho]\psi_{bk} = \epsilon_{bk}\psi_{bk}$$

The corresponding energy levels of the non-interacting electrons.

Kohn-Sham orbitals (wavefunctions) for the non-interacting electrons.

Eigenenergies can be found by the diagonalization of this matrix

Davidson iterative diagonalization is the **DEFAULT** approach

```
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&SYSTEM
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    nat=2,
    ntyp=1,
    ecutwfc=60.0,
    ecutrho=720.0,
/
&ELECTRONS
    diagonalization = 'david',
    mixing_beta=0.7,
    conv_thr=1d-8,
/
ATOMIC_SPECIES
    Si 28.0855 Si.pbe-rrkj.UPF
ATOMIC_POSITIONS (alat)
Si 0.00 0.00 0.00
Si 0.25 0.25 0.25
K_POINTS automatic
4 4 4 1 1 1
```

```
Available options are:

    'david' :
        Davidson iterative diagonalization with overlap matrix
        (default). Fast, may in some rare cases fail.

    'cg' :
        Conjugate-gradient-like band-by-band diagonalization.
        MUCH slower than 'david' but uses less memory and is
        (a little bit) more robust.

    'ppcg' :
        PPCG iterative diagonalization

    'paro', 'ParO' :
        ParO iterative diagonalization

    'rmm-davidson', 'rmm-paro' :
        RMM-DIIS iterative diagonalization.
        To stabilize the SCF loop
        RMM-DIIS is alternated with calls to Davidson or
        ParO  solvers depending on the string used.
        Other variables that can be used to tune the behavior of
        RMM-DIIS are:    diago_rmm_ndim and diago_rmm_conv
```

QE run

Construct $V_{ion}(r)$ ✔

Initial guess $n(r)$ ✔

Compute $V_H[n] + V_{XC}[n]$ ✔

$V_{eff} = V_{ion} + V_H[n] + V_{XC}[n]$ ✔

Solve $\left[-\frac{1}{2}\nabla^2 + V_{eff}(r) \right]\psi_i(r) = \varepsilon_i\psi_i(r)$ ✔

Compute $n(r) = \sum |\psi_i(r)|^2$

NO

Self-consistent?

YES

Energy Forces

QE run

Construct $V_{ion}(r)$ ✔

Initial guess $n(r)$ ✔

Compute $V_H[n] + V_{XC}[n]$ ✔

$V_{eff} = V_{ion} + V_H[n] + V_{XC}[n]$ ✔

Solve $\left[-\frac{1}{2}\nabla^2 + V_{eff}(r)\right]\psi_i(r) = \varepsilon_i\psi_i(r)$ ✔

Compute $n(r) = \sum |\psi_i(r)|^2$ ✔

NO — Self-consistent? — YES — Energy Forces
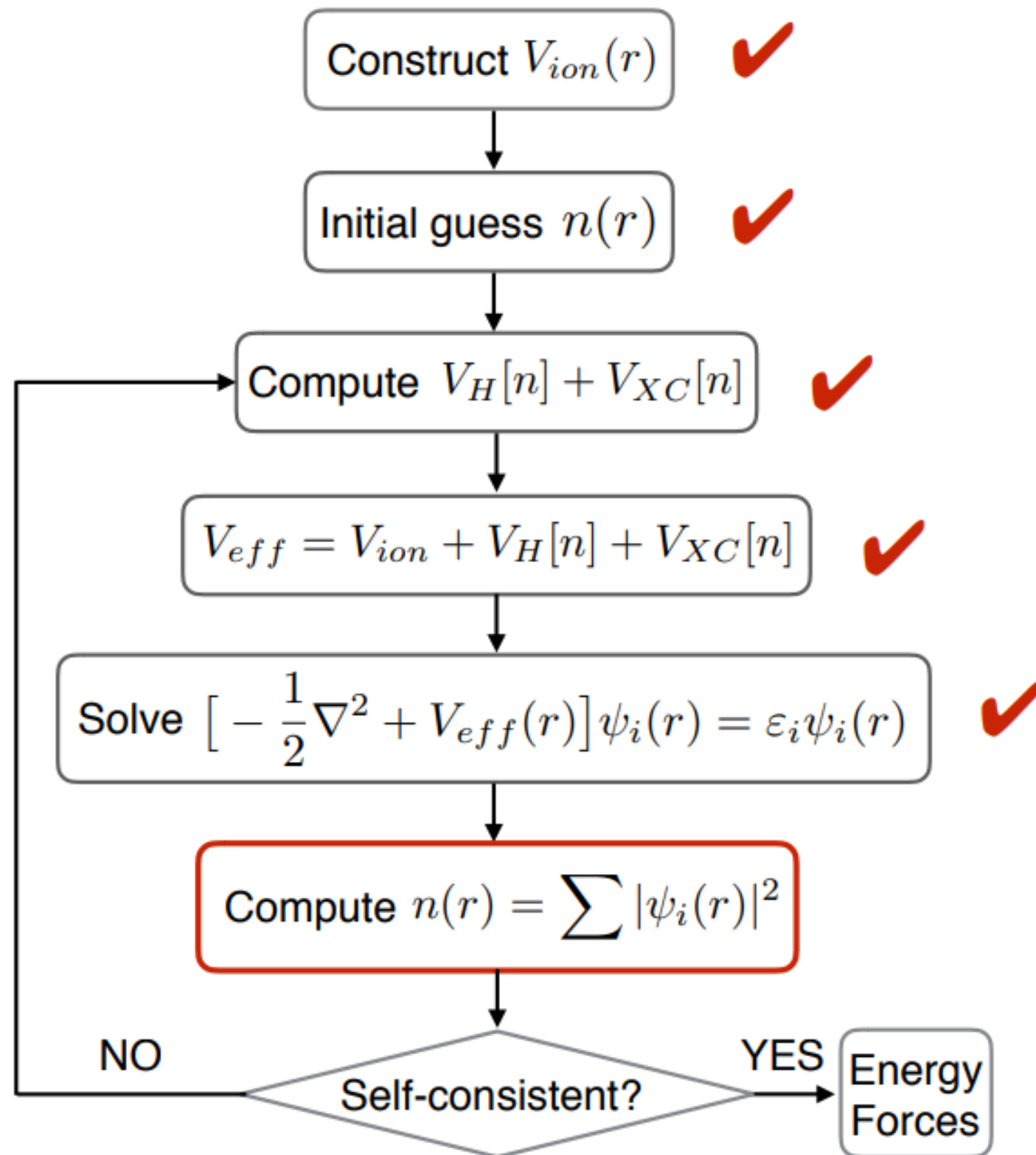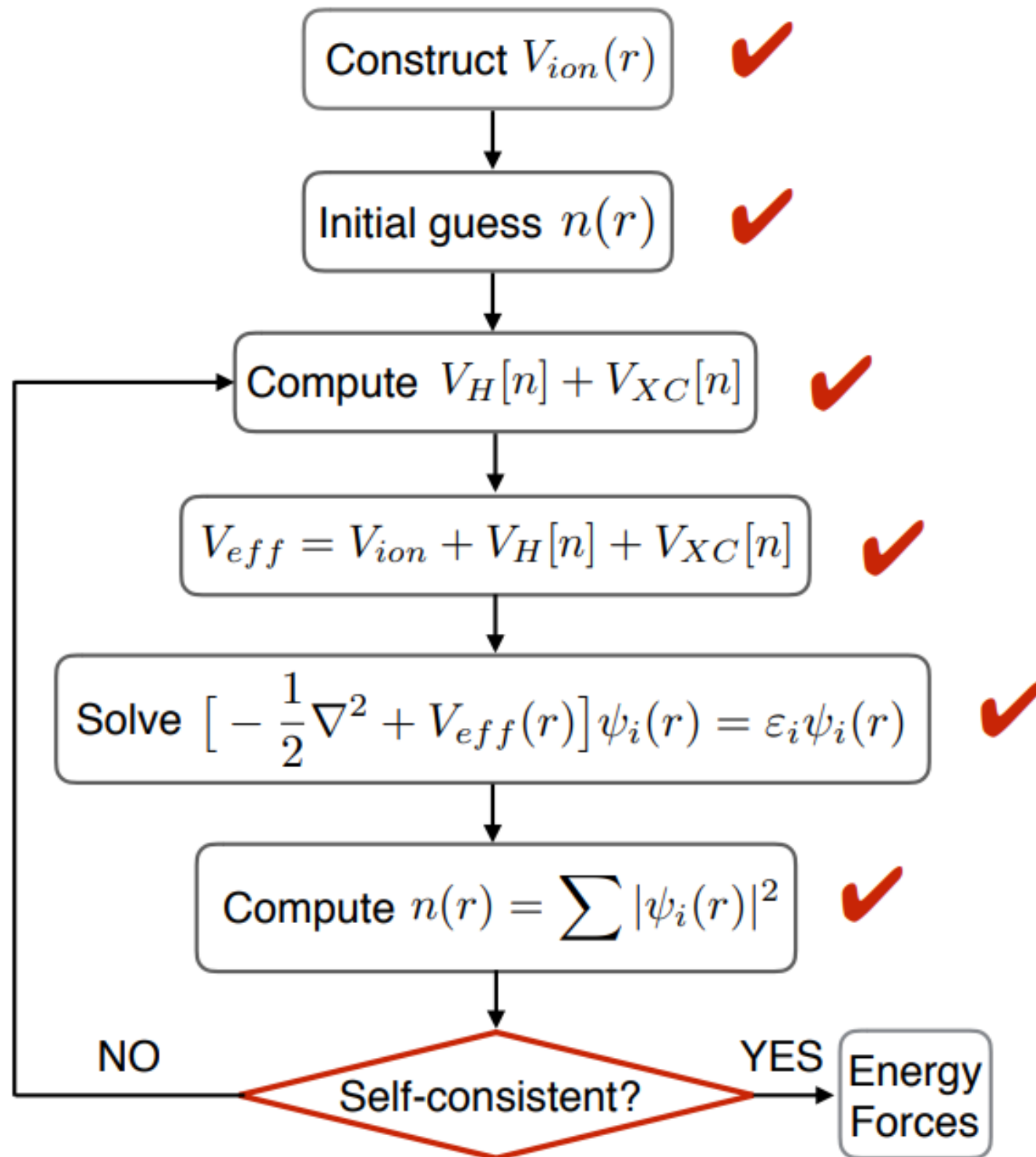
Self-consistency

```
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&SYSTEM
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  nat=2,
  ntyp=1,
  ecutwfc=60.0,
  ecutrho=720.0,
/
&ELECTRONS
  mixing_beta=0.7,
  conv_thr=1d-8,
/
ATOMIC_SPECIES
  Si 28.0855 Si.pbe-rrkj.UPF
ATOMIC_POSITIONS (alat)
Si  0.00  0.00  0.00
Si  0.25  0.25  0.25
K_POINTS automatic
4 4 4 1 1 1
```
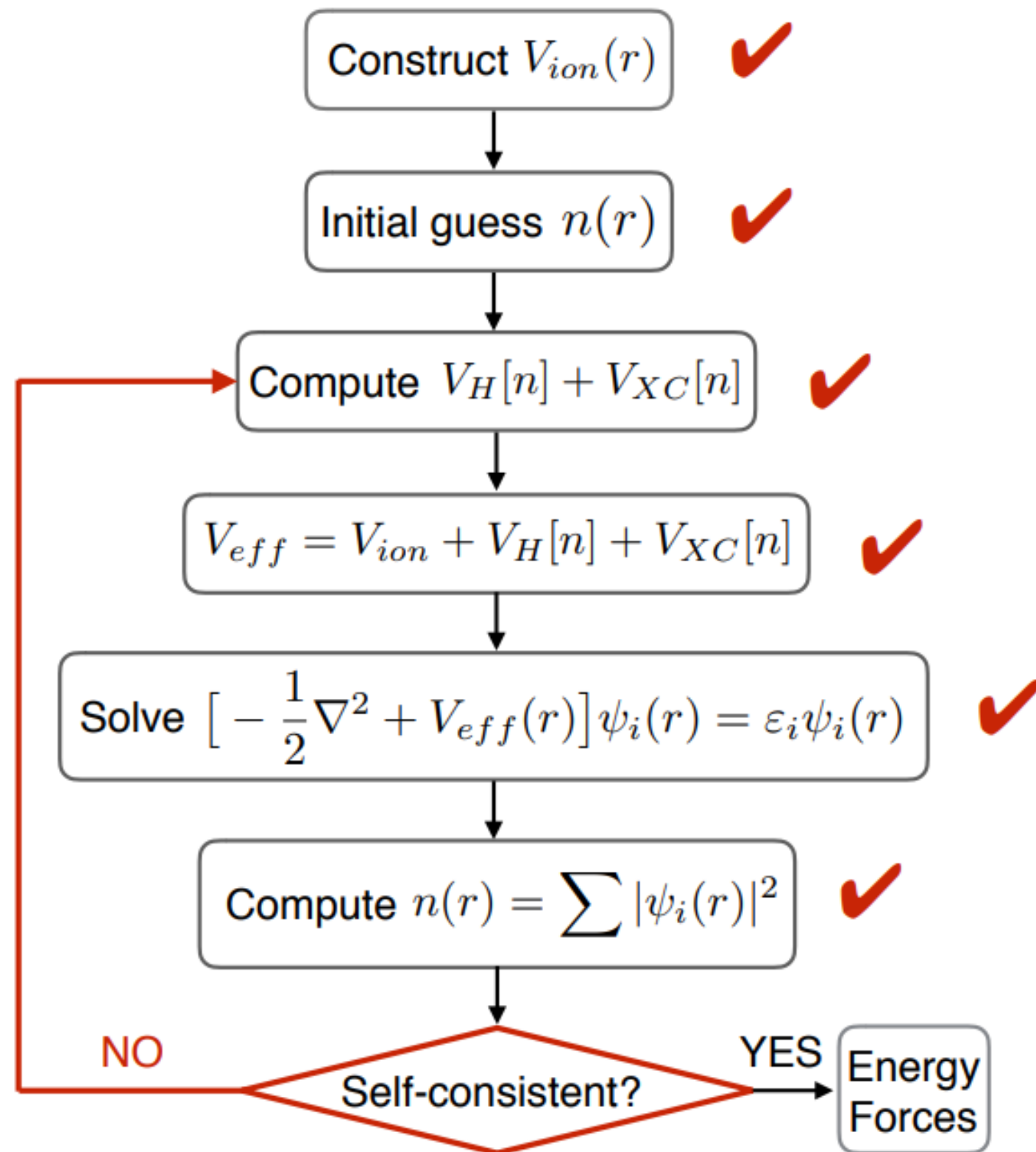
Convergence threshold for self-consistency:
estimated energy error > conv_thr (NO)
or energy error < conv_thr (YES)

QE run

Construct $V_{ion}(r)$ ✔

Initial guess $n(r)$ ✔

Compute $V_H[n] + V_{XC}[n]$ ✔

$V_{eff} = V_{ion} + V_H[n] + V_{XC}[n]$ ✔

Solve $\left[-\frac{1}{2}\nabla^2 + V_{eff}(r)\right]\psi_i(r) = \varepsilon_i\psi_i(r)$ ✔

Compute $n(r) = \sum |\psi_i(r)|^2$ ✔

NO

Self-consistent?

YES → Energy Forces

new n(r)

```
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/
&ELECTRONS
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  conv_thr=1d-8,
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ATOMIC_SPECIES
  Si 28.0855 Si.pbe-rrkj.UPF
ATOMIC_POSITIONS (alat)
Si  0.00  0.00  0.00
Si  0.25  0.25  0.25
K_POINTS automatic
4 4 4 1 1 1
```

Mix new and old density:
0.7 = 70% of the new density and
30% of old density at first step

Quantum Espresso Input File – mixing_mode

```
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    ntyp=1,
    ecutwfc=60.0,
    ecutrho=720.0,
/
&ELECTRONS
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    mixing_beta=0.7,
    conv_thr=1d-8,
/
ATOMIC_SPECIES
    Si 28.0855 Si.pbe-rrkj.UPF
ATOMIC_POSITIONS (alat)
Si 0.00 0.00 0.00
Si 0.25 0.25 0.25
K_POINTS automatic
4 4 4 1 1 1
```
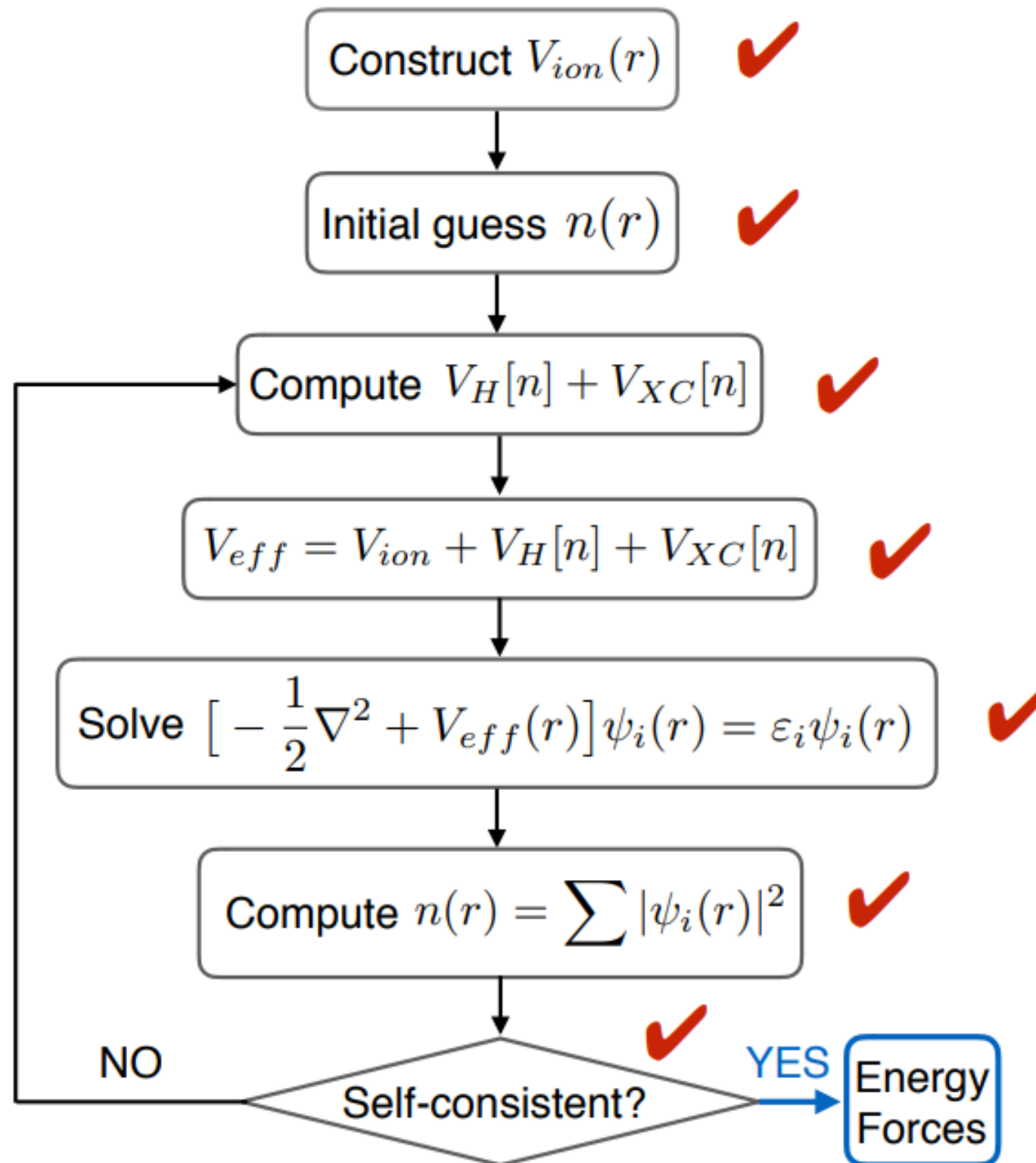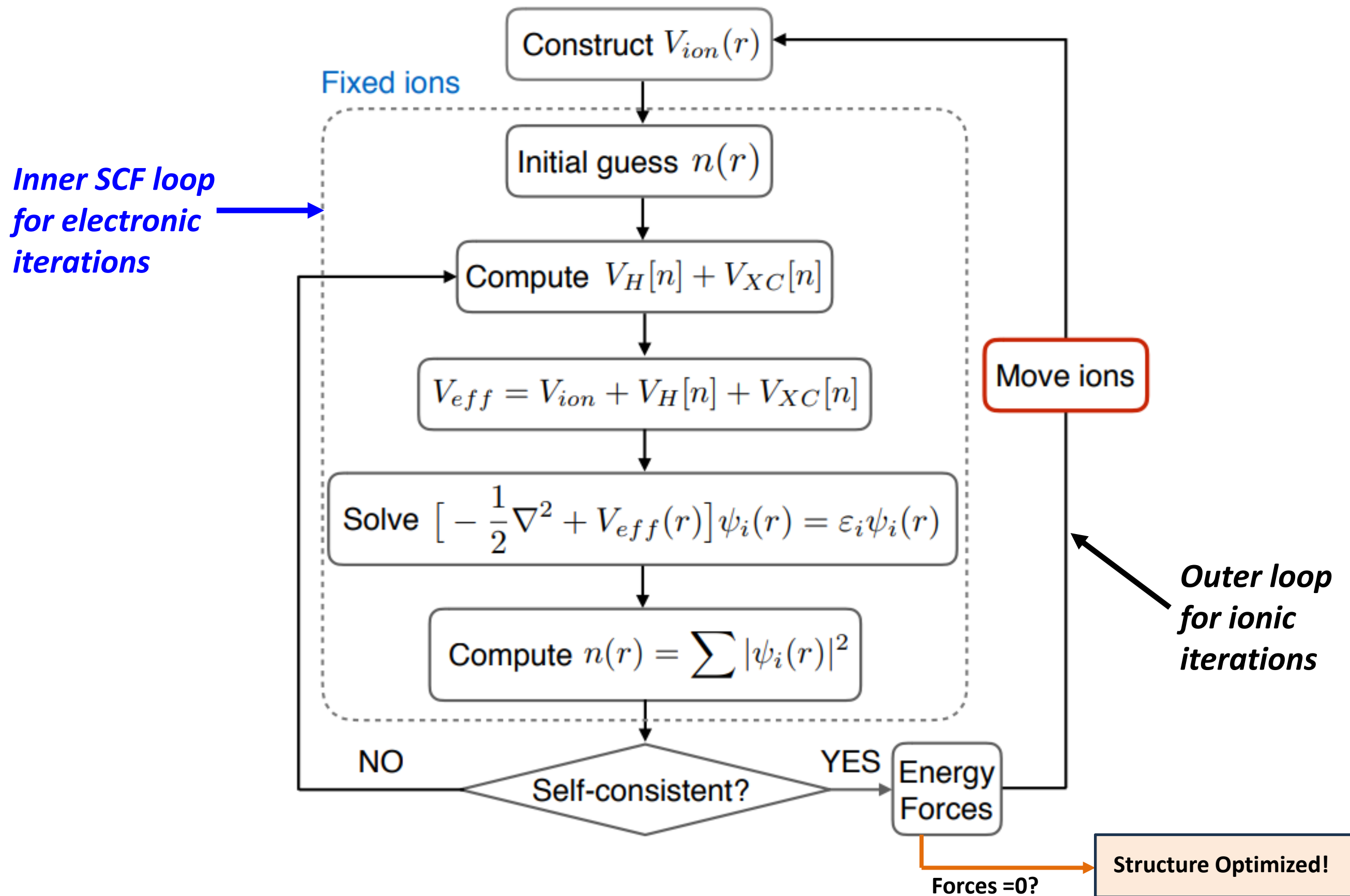
- Allows to specify the mode used for mixing electronic charge density in SCF calculations

- 'plain' : (DEFAULT)
  charge density Broyden mixing

- 'TF' :
  as above, with simple Thomas-Fermi screening
  (for highly homogeneous systems)

- 'local-TF' :
  as above, with local-density-dependent TF screening
  (for highly inhomogeneous systems)

QE run

Construct $V_{ion}(r)$ ✔

Initial guess $n(r)$ ✔

Compute $V_H[n] + V_{XC}[n]$ ✔

$V_{eff} = V_{ion} + V_H[n] + V_{XC}[n]$ ✔

Solve $\left[-\frac{1}{2}\nabla^2 + V_{eff}(r) \right] \psi_i(r) = \varepsilon_i \psi_i(r)$ ✔

Compute $n(r) = \sum |\psi_i(r)|^2$ ✔

✔

NO

Self-consistent?

YES

Energy Forces

# Forces & Geometry Optimization

QE run

# Forces on atoms easily calculated when electron ground state is obtained

$$F_I = -\frac{dE}{dr_I} = -\left\langle \psi_i \left| \frac{\partial \widehat{H}}{\partial r_I} \right| \psi_i \right\rangle$$

- By moving along the ionic forces (steepest descent) the ionic ground can be calculated

- We can displace ions from the ionic groundstate, and determine the forces on all other ions
  - Effective interatomic force constants and vibrational frequences
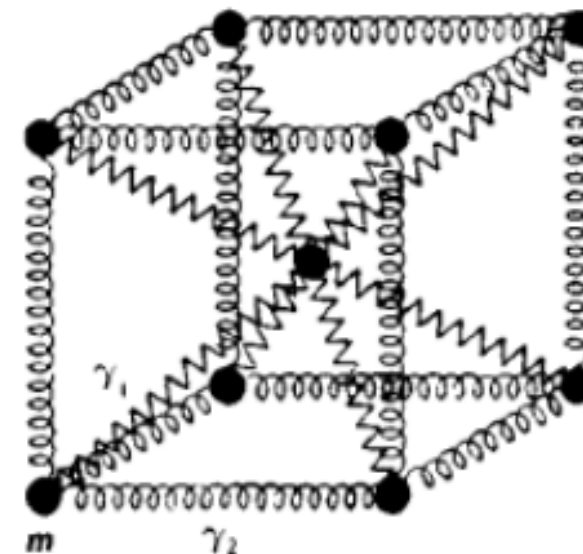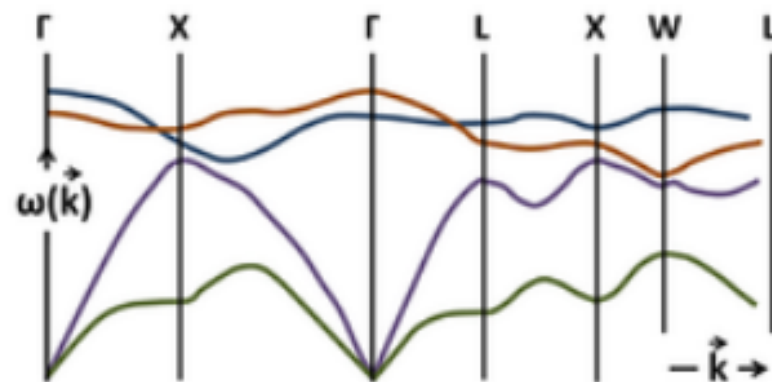
Structure optimization

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ATOMIC_SPECIES
 Si 28.0855 Si.pbe-rrkj.UPF
ATOMIC_POSITIONS (alat)
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Si  0.25  0.25  0.25
K_POINTS automatic
4 4 4 1 1 1
```
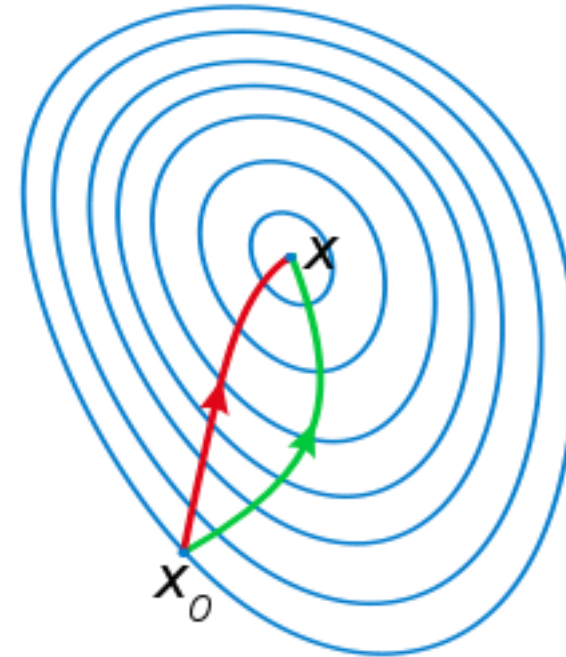

Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm is an iterative method for solving unconstrained nonlinear optimization problems.

Structure optimization

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 restart_mode='from_scratch'
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 press_conv_thr=0.5,
/
ATOMIC_SPECIES
 Si 28.0855 Si.pbe-rrkj.UPF
ATOMIC_POSITIONS (alat)
Si   0.00  0.00  0.00
Si   0.25  0.25  0.25
K_POINTS automatic
4 4 4 1 1 1
```

Cell lattice parameters and free (internal) coordinates of the atoms may be changed by relaxation

Properties Derived from the Ground State Energy

Second derivative of E_{tot} or F wrt	Physical property
d_i, d_i (atomic displacement)	Force spring const: phonons
E, E (E-field)	Dielectric constant
ε, ε (strain)	Elastic constant
E, ε	Piezo-electric constant
E, d_i	Born Dynamical charge
ε, d_i	Strain-phonon coupling
H, H (magnetic field)	Magnetic susceptibility
E, H	Magneto-electric constant
H, ε	Piezo-magnetic constant