

# Quantum Espresso: Materials Modeling with Density Functional Theory

Davide Donadio, UC Davis

Giannozzi, P.; Andreussi, O.; Brumme, T.; Bunau, O.; Buongiorno Nardelli, M.; Calandra, M.; Car, R.; Cavazzoni, C.; Ceresoli, D.; Cococcioni, M.; Colonna, N.; Carnimeo, I.; Dal Corso, A.; de Gironcoli, S.; Delugas, P.; DiStasio, R. A.; Ferretti, A.; Floris, A.; Fratesi, G.; Fugallo, G.; Gebauer, R.; Gerstmann, U.; Giustino, F.; Gorni, T.; Jia, J.; Kawamura, M.; Ko, H.-Y.; Kokalj, A.; Küçükbenli, E.; Lazzeri, M.; Marsili, M.; Marzari, N.; Mauri, F.; Nguyen, N. L.; Nguyen, H.-V.; Otero-de-la-Roza, A.; Paulatto, L.; Poncé, S.; Rocca, D.; Sabatini, R.; Santra, B.; Schlipf, M.; Seitsonen, A. P.; Smogunov, A.; Timrov, I.; Thonhauser, T.; Umari, P.; Vast, N.; Wu, X.; Baroni, S. **Advanced Capabilities for Materials Modelling with Quantum ESPRESSO**. *J. Phys.: Condens. Matter* **2017**, 29 (46), 465901. <https://doi.org/10.1088/1361-648X/aa8f79>.

Giannozzi, P.; Baroni, S.; Bonini, N.; Calandra, M.; Car, R.; Cavazzoni, C.; Ceresoli, D.; Chiarotti, G. L.; Cococcioni, M.; Dabo, I.; Dal Corso, A.; de Gironcoli, S.; Fabris, S.; Fratesi, G.; Gebauer, R.; Gerstmann, U.; Gougoussis, C.; Kokalj, A.; Lazzeri, M.; Martin-Samos, L.; Marzari, N.; Mauri, F.; Mazzarello, R.; Paolini, S.; Pasquarello, A.; Paulatto, L.; Sbraccia, C.; Scandolo, S.; Sclauzero, G.; Seitsonen, A. P.; Smogunov, A.; Umari, P.; Wentzcovitch, R. M. **QUANTUM ESPRESSO: A Modular and Open-Source Software Project for Quantum Simulations of Materials**. *J. Phys.: Condens. Matter* **2009**, 21 (39), 395502. <https://doi.org/10.1088/0953-8984/21/39/395502>.

# Materials Modeling by First Principles

## Goals:

- Compute **materials properties** using only basic physics principles and their chemical composition (+crystal structure)
- **Accuracy and predictivity**, without relying on empirical parameters (e.g. from experiments)
- **Efficiency**, without compromising scientific rigor

# Materials properties

- Ground state equilibrium properties:
  - Density, structural parameters, formation energy
- Nonequilibrium and excited state properties:
  - Mechanical response, vibrational response (phonons, IR and Raman spectra), chemical shift (NMR)
  - Transport coefficients (charge and thermal transport)
  - UV-visible and X-ray spectroscopy, photoemission

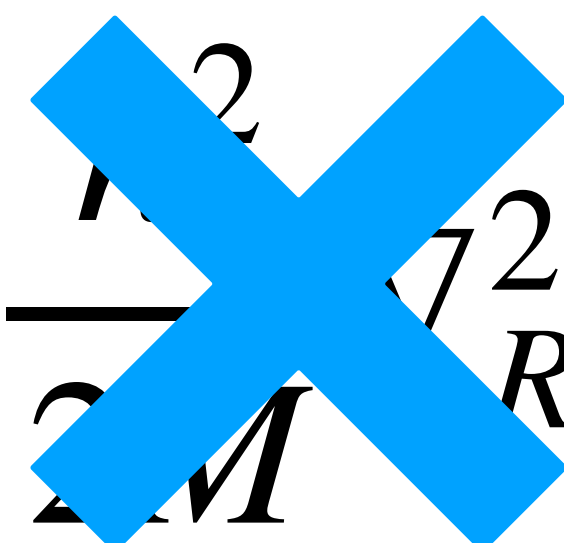
# The many-body Schrödinger equation for **electrons** and **nuclei**

$$i\hbar \frac{\partial \Psi(r, R, t)}{\partial t} = \hat{H} \Psi(R, r, t)$$

$$\hat{H} = -\frac{\hbar^2}{2M} \nabla_R^2 - \frac{\hbar^2}{2m} \nabla_r^2 + V(r, R)$$

# The many-body Schrödinger equation for **electrons** and **nuclei**

$$i\hbar \frac{\partial \Psi(r, R, t)}{\partial t} = \hat{H} \Psi(R, r, t)$$

$$\hat{H} = -\frac{\hbar^2}{2M} \nabla_R^2 - \frac{\hbar^2}{2m} \nabla_r^2 + V(r, R)$$


**Born-Oppenheimer (adiabatic) approximation:**  $m \ll M$

# The many-body Schrödinger equation for **electrons** and **nuclei**

**electrons:** 
$$\left( -\frac{\hbar^2}{2m} \nabla_r^2 + V_R(r) \right) \psi_R(r) = E(r, R) \psi_R(r)$$

**nuclei:** 
$$M \frac{d^2 R}{dt^2} = - \nabla_R E(r, R)$$

# Density functional theory

- The many-body Hamiltonian for the electrons is:

$$\hat{H} = -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 + \sum_{i>j} \frac{e^2}{|r_i - r_j|} + \sum_i V_R(r_i)$$

# Density functional theory

- The many-body Hamiltonian for the electrons is:

$$\hat{H} = -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 + \sum_{i>j} \frac{e^2}{|r_i - r_j|} + \sum_i V_R(r_i)$$

- The ground state energy (variational):

$$E[V] = \min_{\psi} \left( \langle \psi | \hat{K} + \hat{U} | \psi \rangle + \int \psi^* V_R(r) \psi dr \right) = \min_{\psi} \left( \langle \psi | \hat{K} + \hat{U} | \psi \rangle + \int \rho(r) V_R(r) dr \right)$$



# Density functional theory

- The many-body Hamiltonian for the electrons is:

$$\hat{H} = -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 + \sum_{i>j} \frac{e^2}{|r_i - r_j|} + \sum_i V_R(r_i)$$

- The ground state energy (variational):

$$E[V] = \min_{\psi} \left( \langle \psi | \hat{K} + \hat{U} | \psi \rangle + \int \psi^* V_R(r) \psi dr \right) = \min_{\psi} \left( \langle \psi | \hat{K} + \hat{U} | \psi \rangle + \int \rho(r) V_R(r) dr \right)$$

- First Hohenberg-Kohn Theorem:  $V \leftrightarrow \rho$

# Density functional theory

- The many-body Hamiltonian for the electrons is:

$$\hat{H} = -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 + \sum_{i>j} \frac{e^2}{|r_i - r_j|} + \sum_i V_R(r_i)$$

- The ground state energy (variational):

$$E[V] = \min_{\psi} \left( \langle \psi | \hat{K} + \hat{U} | \psi \rangle + \int \psi^* V_R(r) \psi dr \right) = \min_{\psi} \left( \langle \psi | \hat{K} + \hat{U} | \psi \rangle + \int \rho(r) V_R(r) dr \right)$$

- First Hohenberg-Kohn Theorem:  $V \leftrightarrow \rho$

- Second Hohenberg-Kohn Theorem:  $E[V] = \min_{\rho} \left( F[\rho] + \int \rho(r) V(r) dr \right)$

# Kohn-Sham potential

- Take the functional derivative of  $E[\rho]$  with respect to  $\rho$  :

$$F[\rho] = K[\rho] + \frac{1}{2} \int \frac{\rho(r)\rho(r')}{|r - r'|} dr dr' + E_{xc}[\rho]$$

# Kohn-Sham potential

- Take the functional derivative of  $E[\rho]$  with respect to  $\rho$  :

$$F[\rho] = K[\rho] + \frac{1}{2} \int \frac{\rho(r)\rho(r')}{|r - r'|} dr dr' + E_{xc}[\rho]$$

$$\frac{\delta E[\rho]}{\delta \rho(r)} = \frac{\delta K[\rho]}{\delta \rho(r)} + \int \frac{\rho(r')}{|r - r'|} dr' + \frac{\delta E_{xc}}{\delta \rho} + V(r)$$

# Kohn-Sham potential

- Take the functional derivative of  $E[\rho]$  with respect to  $\rho$  :

$$F[\rho] = K[\rho] + \frac{1}{2} \int \frac{\rho(r)\rho(r')}{|r - r'|} dr dr' + E_{xc}[\rho]$$

$$\frac{\delta E[\rho]}{\delta \rho(r)} = \frac{\delta K[\rho]}{\delta \rho(r)} + \underbrace{\int \frac{\rho(r')}{|r - r'|} dr' + \frac{\delta E_{xc}}{\delta \rho}}_{V_{KS}[\rho]} + V(r)$$

$V_{KS}[\rho]$  Kohn-Sham potential

# What is in $E_{xc}$ ?

- Local Density Approximation (LDA):

$$E_{xc} = \int \epsilon_{xc}(\rho(r))\rho(r)dr$$

- Generalized Gradient Approx. (GGA):

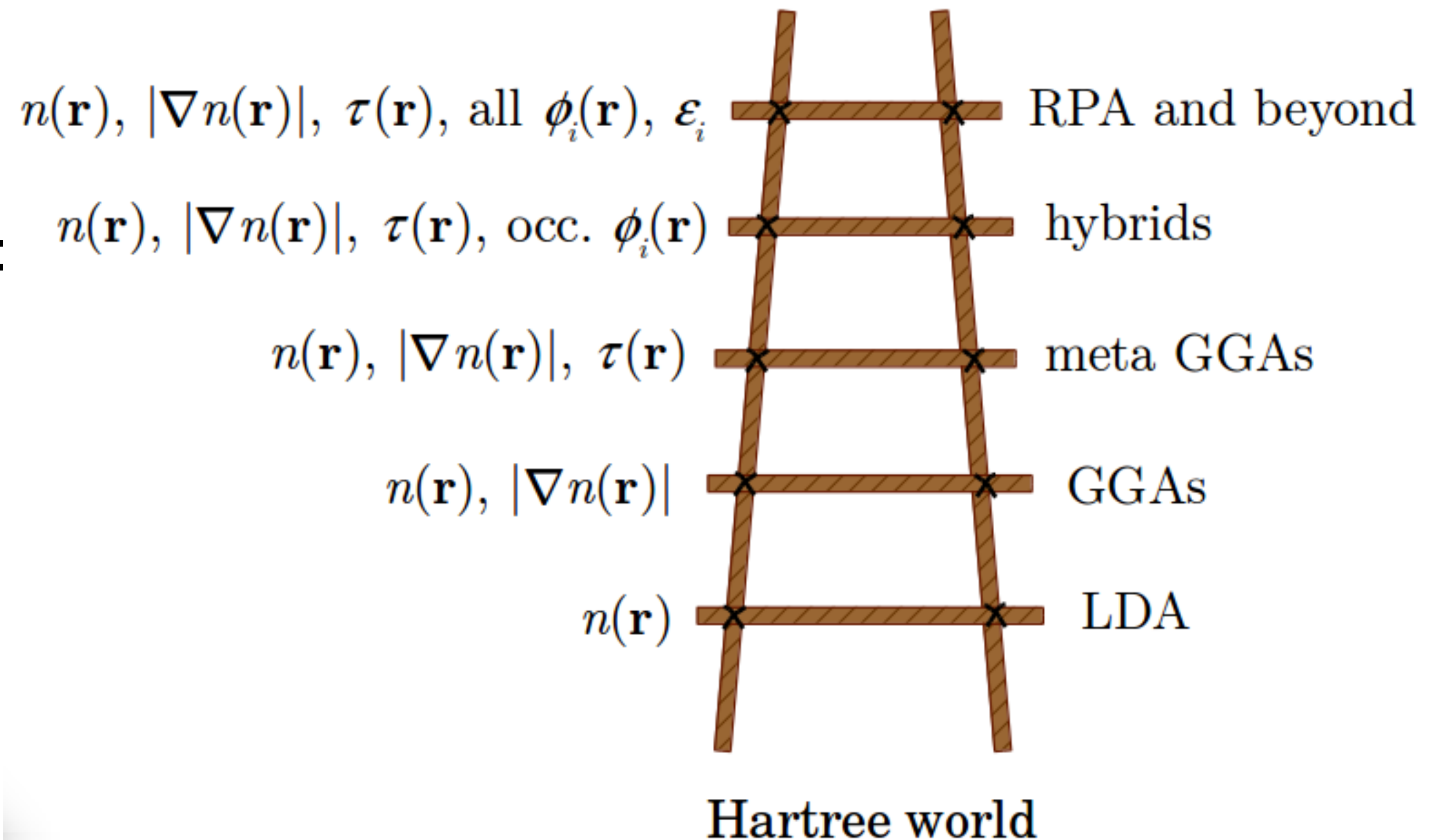
$$E_{xc} = \int \epsilon_{xc}(\rho(r), \nabla(\rho))\rho(r)dr$$

- vdW functionals:

$$E_{vdW} = \int \rho(r)\rho(r')\Phi_{vdW}(r, r')drdr'$$

- Hybrid functionals

Heaven of chemical accuracy



# Kohn-Sham equations

$$\frac{\delta E[\rho]}{\delta \rho(r)} = \frac{\delta K[\rho]}{\delta \rho(r)} + \underbrace{\int \frac{\rho(r')}{|r - r'|} dr' + \frac{\delta E_{xc}}{\delta \rho}}_{V_{KS}[\rho]} + V(r)$$

$V_{KS}[\rho]$  **Kohn-Sham potential**

$$\rho(r) = \sum_v |\psi_v(r)|^2$$

**Represent the density in terms of single-particle wavefunctions.**

**The sum runs over the occupied states.**

$$\left( -\frac{\hbar^2}{2m} \nabla^2 + V_{KS}[\rho] \right) \psi_v(r) = \epsilon_v \psi_v(r) \quad \text{Self-consistent problem.}$$

To derive the KS equations one can apply the variational principle with respect to the **noninteracting wavefunctions (Kohn-Sham):**  $\psi_v(r)$

# Plane waves basis set



# Plane waves basis set

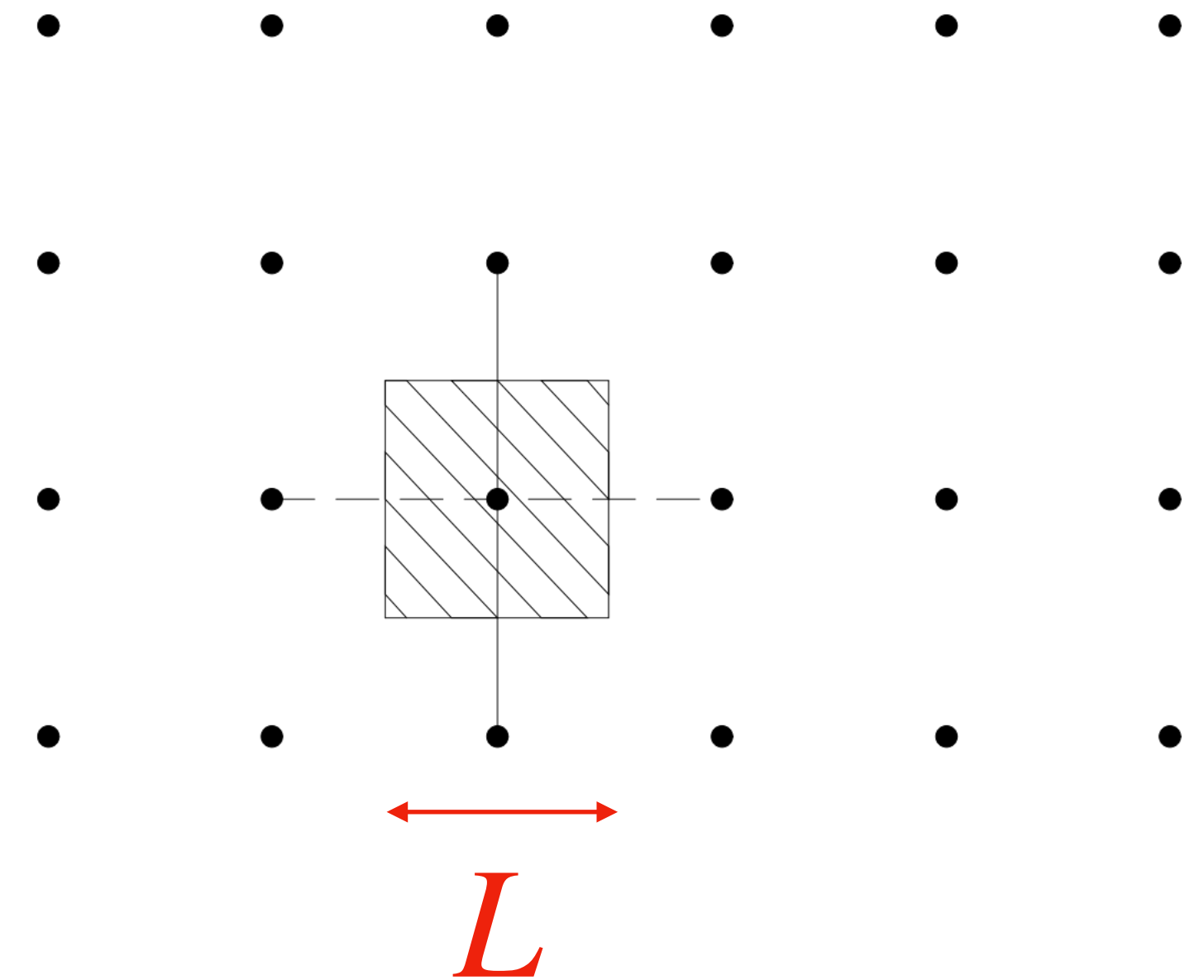
- We need to express  $\psi(r)$  on basis set:

$$\psi_v(r) = \sum_j c_{j,v} \phi_j(r)$$

# Plane waves basis set

- We need to express  $\psi(r)$  on basis set:

$$\psi_v(r) = \sum_j c_{j,v} \phi_j(r)$$



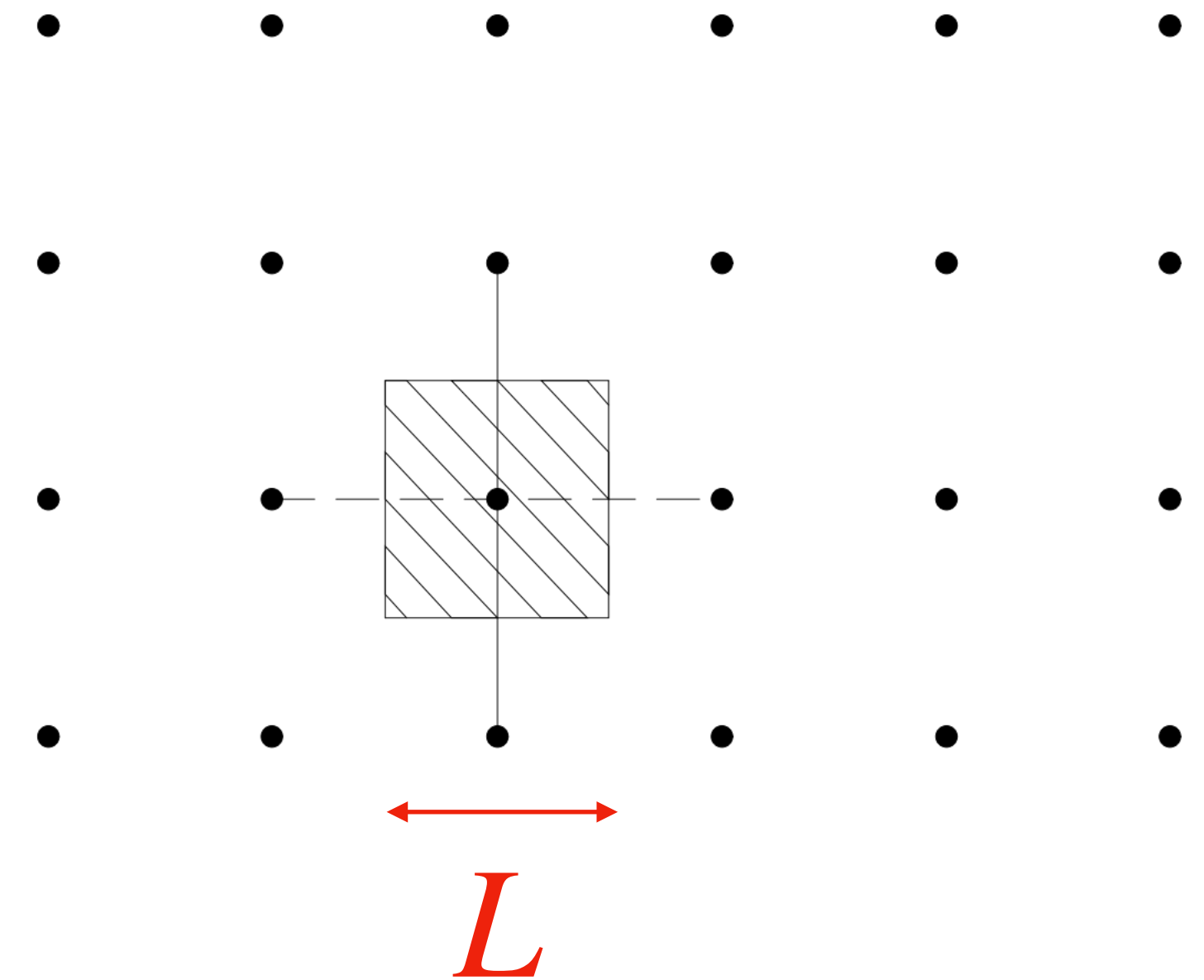
# Plane waves basis set

- We need to express  $\psi(r)$  on basis set:

$$\psi_v(r) = \sum_j c_{j,v} \phi_j(r)$$

- Plane waves naturally comply with crystal periodicity

$$\phi_j = e^{iq_j \cdot r}; \quad q_j = \frac{2\pi}{L} j \text{ with } j \in \mathbb{Z}$$



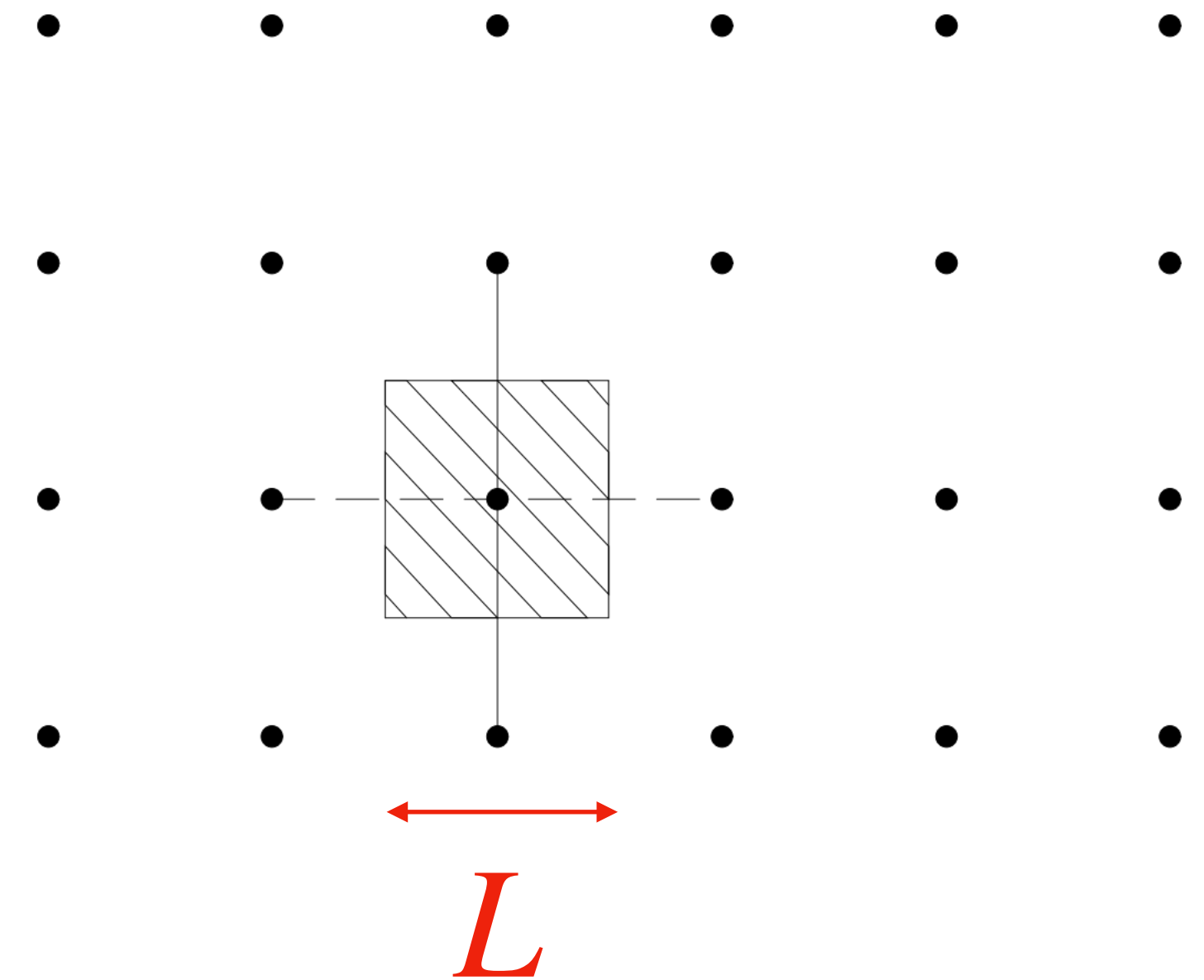
# Plane waves basis set

- We need to express  $\psi(r)$  on basis set:

$$\psi_v(r) = \sum_j c_{j,v} \phi_j(r)$$

- Plane waves naturally comply with crystal periodicity

$$\phi_j = e^{iq_j \cdot r}; \quad q_j = \frac{2\pi}{L} j \quad \text{with } j \in \mathbb{Z}$$



- How many PW shall we take?

$$\frac{\hbar^2}{2m} q_j^2 \leq E_{cut}$$

# Brillouin Zone Sampling: k-points

## Bloch Theorem

$$\psi_k(x + L) = e^{ikL}\psi_k(x)$$

$$\psi_k(x) = e^{ikx}u_k(x)$$

$$u_k(x + L) = u_k(x)$$

# Brillouin Zone Sampling: k-points

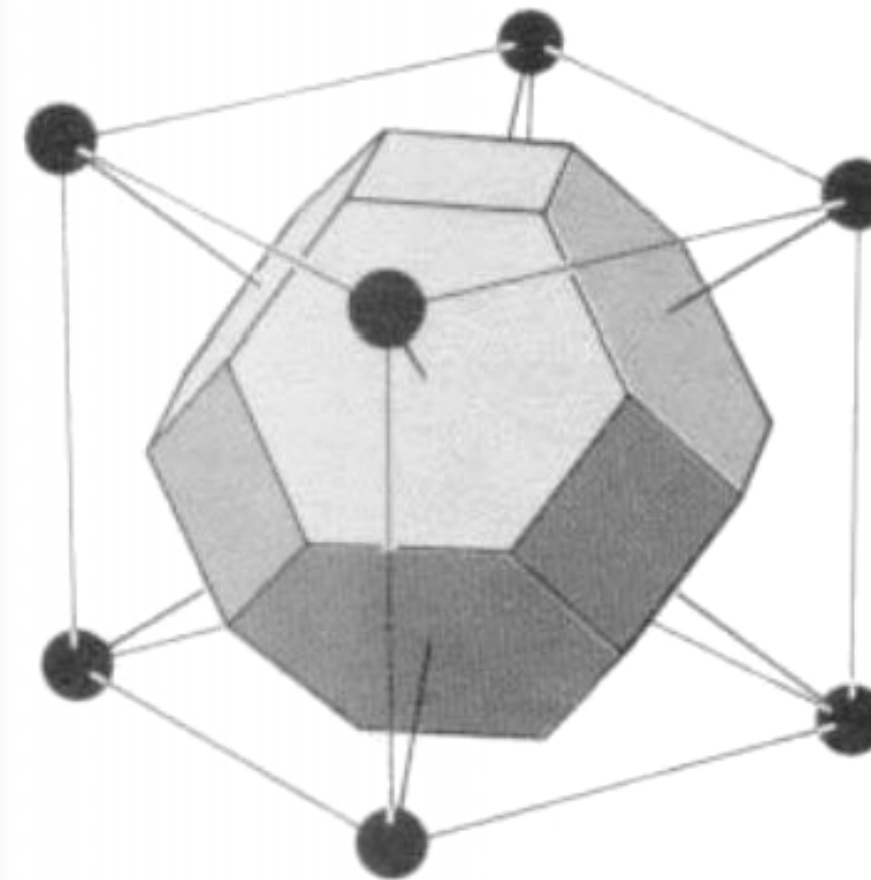
## Bloch Theorem

$$\psi_k(x + L) = e^{ikL}\psi_k(x)$$

$$\psi_k(x) = e^{ikx}u_k(x)$$

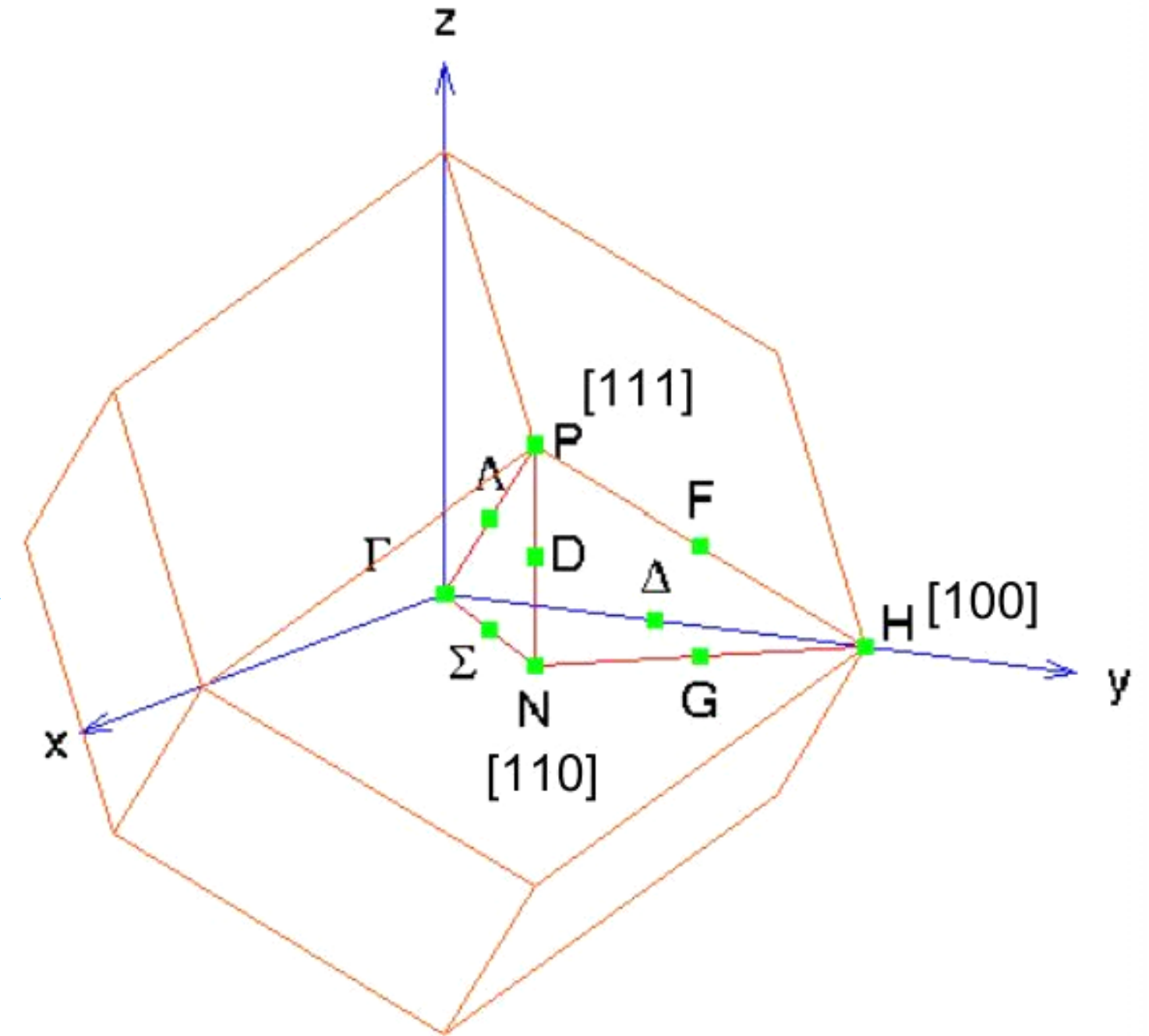
$$u_k(x + L) = u_k(x)$$

## Real Space



Wigner Seitz Cell

## Reciprocal Space



Brillouin Zone

# Brillouin Zone Sampling: k-points

## Bloch Theorem

$$\psi_k(x + L) = e^{ikL}\psi_k(x)$$

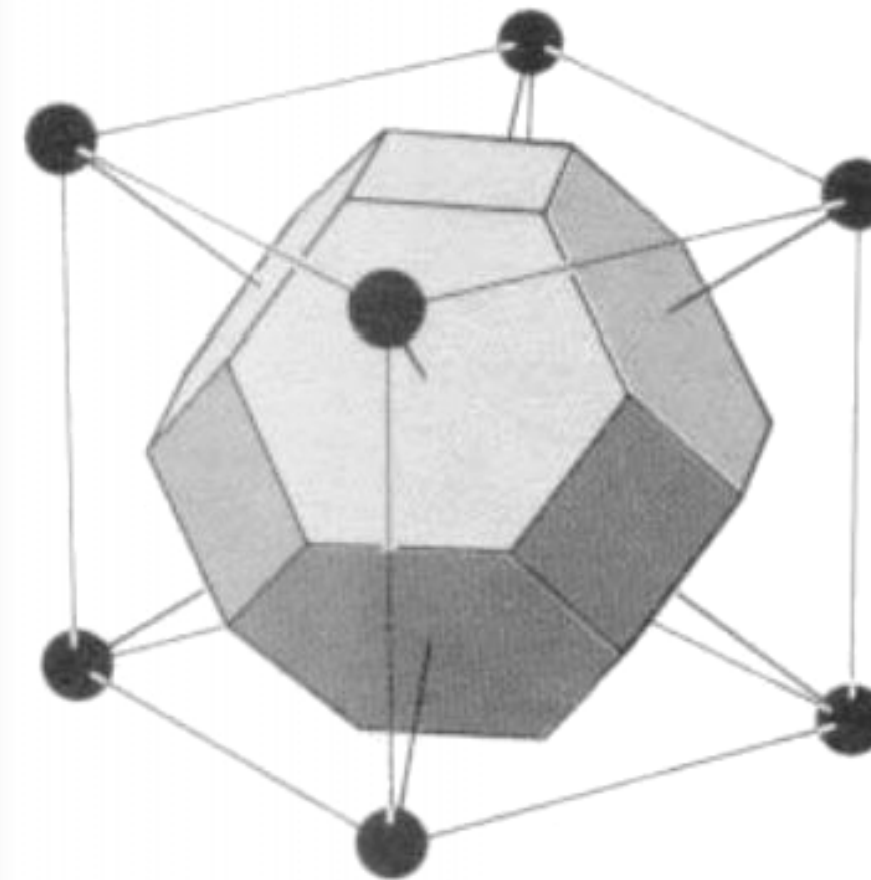
$$\psi_k(x) = e^{ikx}u_k(x)$$

$$u_k(x + L) = u_k(x)$$

Using plane waves:

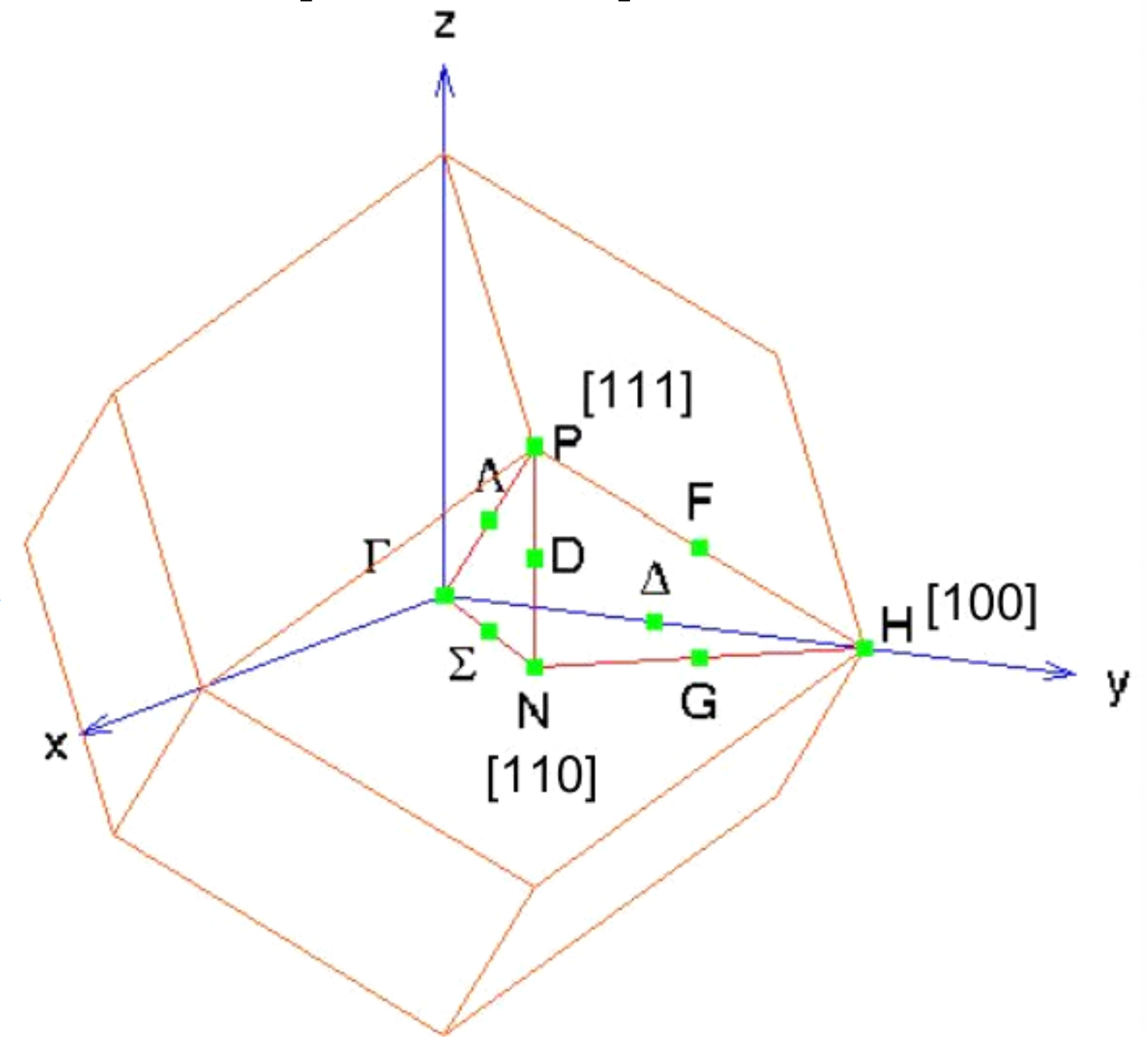
$$\psi_{v,k}(r) = e^{ik \cdot r} \sum_G c_{v,k}(G) e^{iG \cdot r}$$

## Real Space



Wigner Seitz Cell

## Reciprocal Space



Brillouin Zone

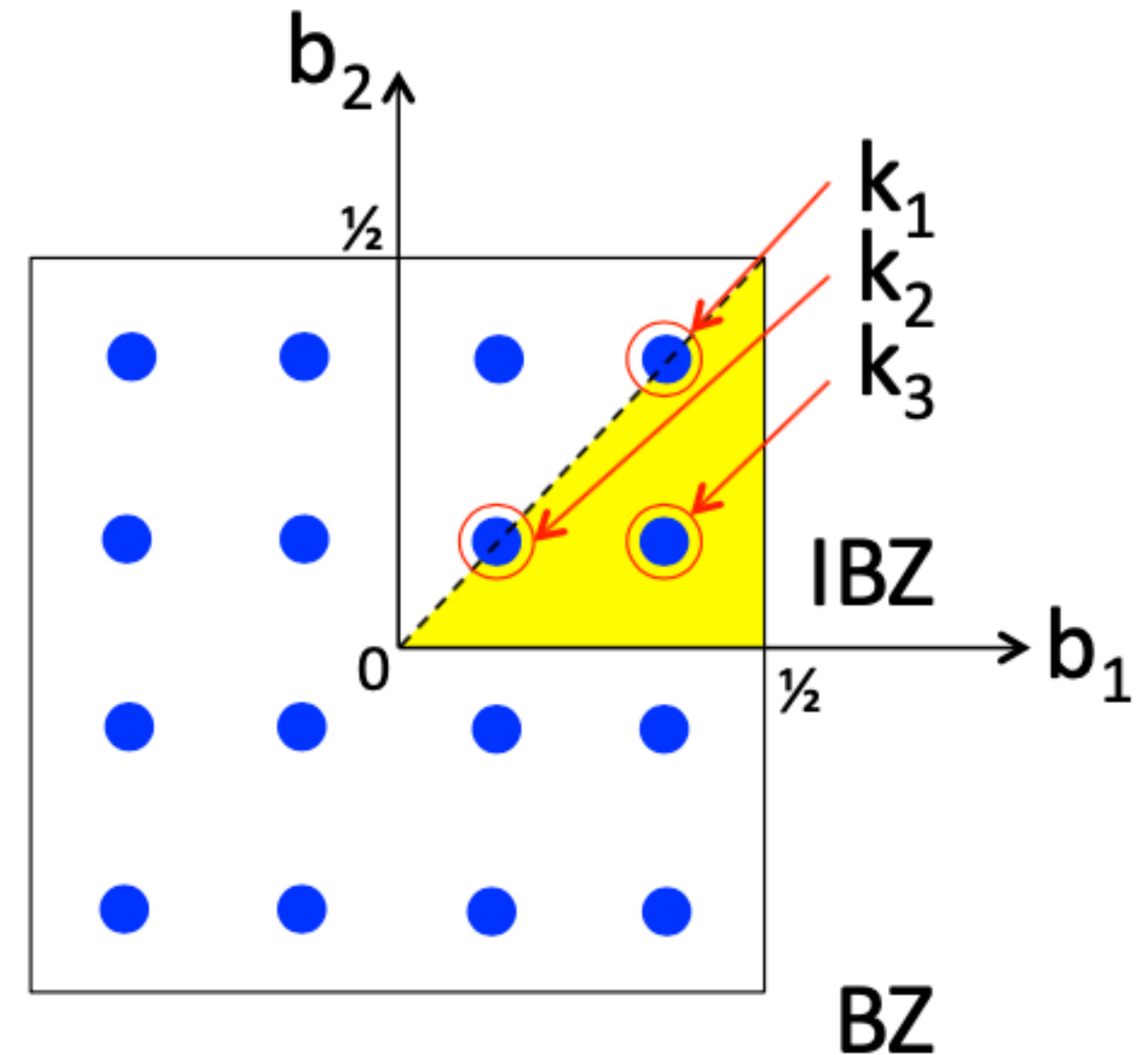
# Efficient BZ sampling

- Observables are averaged over  $k$  points

$$\langle A \rangle = \frac{1}{\Omega_{BZ}} \int_{BZ} dk A(k) = \frac{1}{N_k} \sum_i^{N_k} A(k_i)$$

- For example, the total energy is:

$$E_{tot} = \sum_i^{N_k} E_i w_i$$



It is often convenient to “shift”  
the  $k$ -point mesh



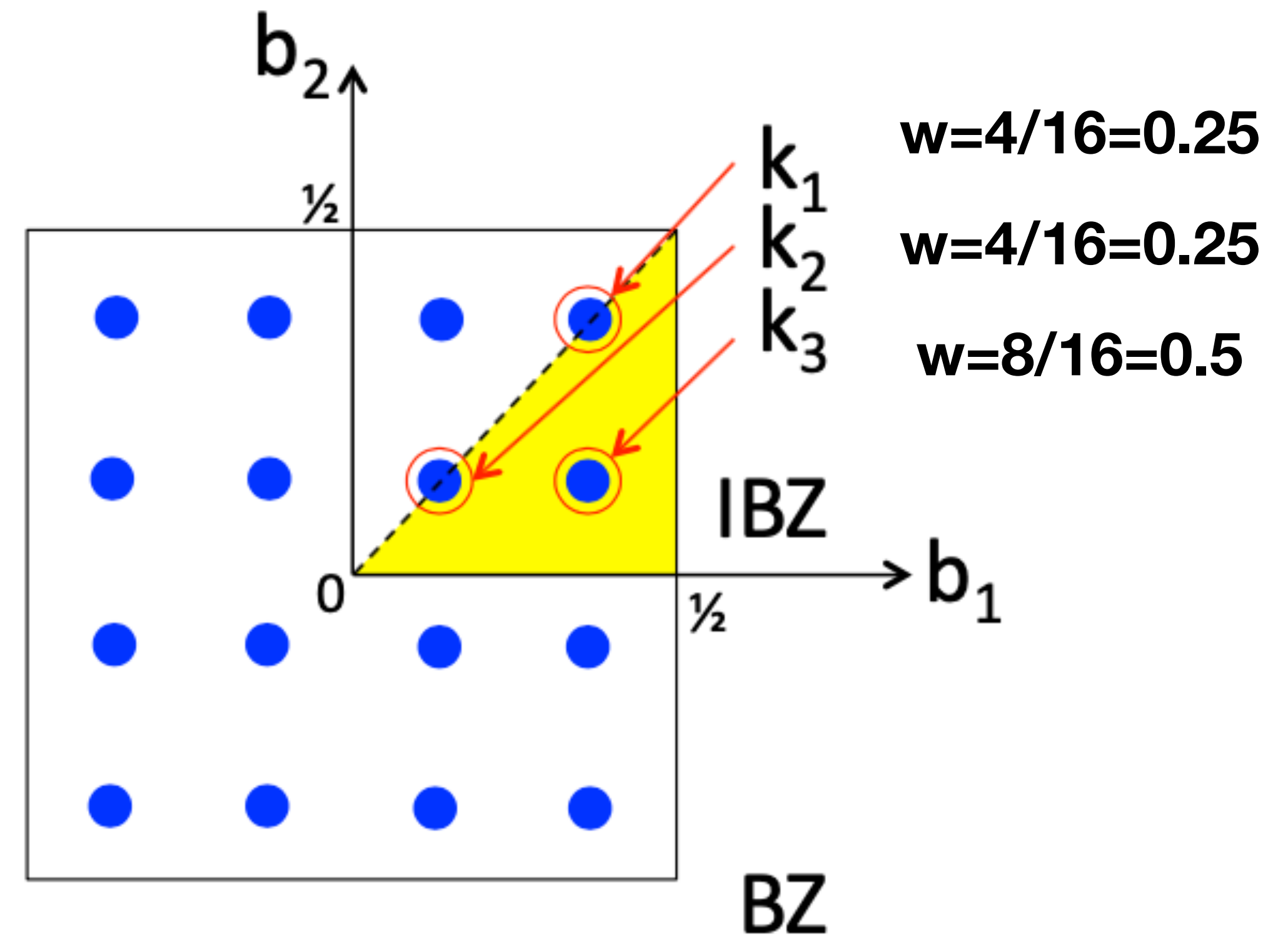
# Efficient BZ sampling

- Observables are averaged over  $k$  points

$$\langle A \rangle = \frac{1}{\Omega_{BZ}} \int_{BZ} dk A(k) = \frac{1}{N_k} \sum_i^{N_k} A(k_i)$$

- For example, the total energy is:

$$E_{tot} = \sum_i^{N_k} E_i w_i$$



It is often convenient to “shift”  
the  $k$ -point mesh

# Advantages of using plane waves

- Convergence checked by tuning only  $E_{cut}$
- Basis set independent of nuclear positions: no “Pulay forces”
- Use Fourier transform to solve Poisson equation:  $\nabla^2 V = 4\pi\rho$
- Density, Hartree, and XC potentials easily calculated
- PWs are orthonormal (normalization:  $1/\sqrt{\Omega}$ )

# Disadvantages of using plane waves

- The basis set depends on the shape/size of the cell: Pulay Stress
- One would need a huge number of PW to treat localized (core) electrons and nodes of valence electrons

# Disadvantages of using plane waves

- The basis set depends on the shape/size of the cell: Pulay Stress

**Fix: See hands on tutorial**

- One would need a huge number of PW to treat localized (core) electrons and nodes of valence electrons

# Disadvantages of using plane waves

- The basis set depends on the shape/size of the cell: Pulay Stress

**Fix: See hands on tutorial**

- One would need a huge number of PW to treat localized (core) electrons and nodes of valence electrons

**Fix: Pseudopotentials**



# Dumping core states

## “Standard” valence electrons

[illegible]

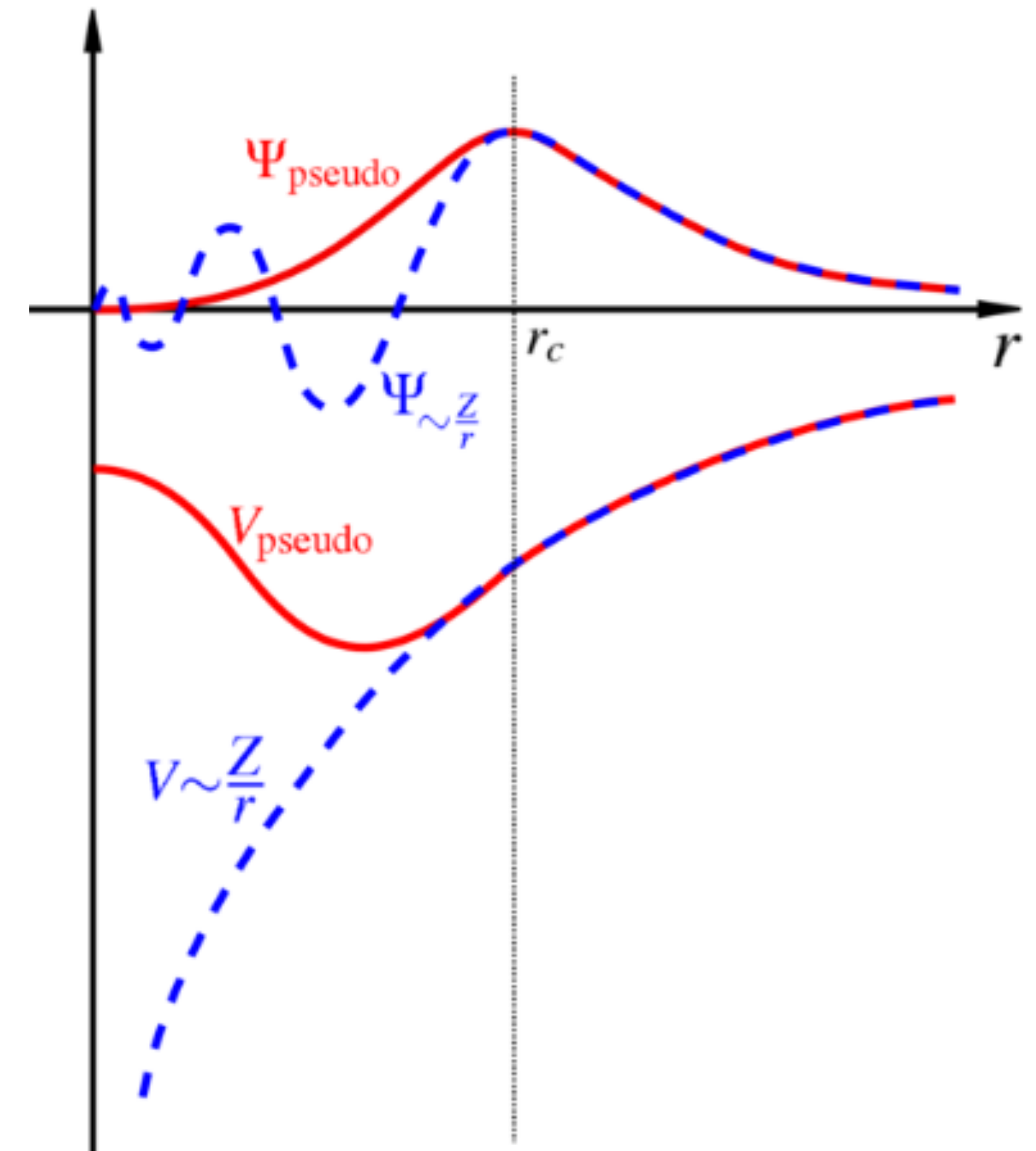
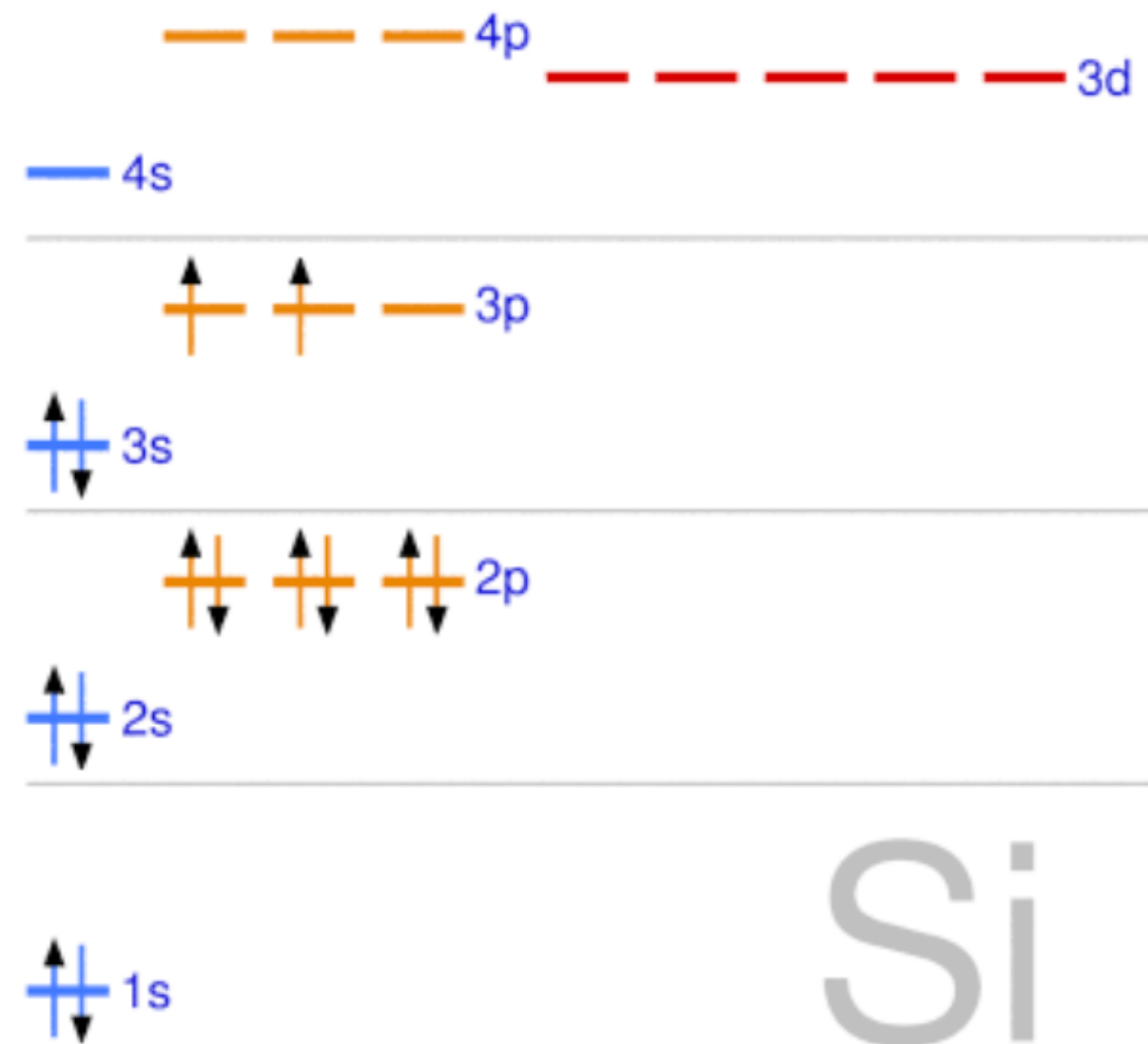
# Dumping core states

- Define a “pseudo-atom” = nucleus + core states (screened nucleus)
- Valence states are the lowest states with a given angular symmetry:

$\psi^{pp}$  is smooth and has no nodes

- The chemical behavior of the pseudo-atom has to be the same as the actual atom:
  - Same orbital energies:  $\epsilon_V^{PP} = \epsilon_V^{AE}$
  - Same wave function outside the “nuclear region”:  $\psi_V^{pp}(r) = \psi_V^{AE}(r)$  for  $r > r_C$

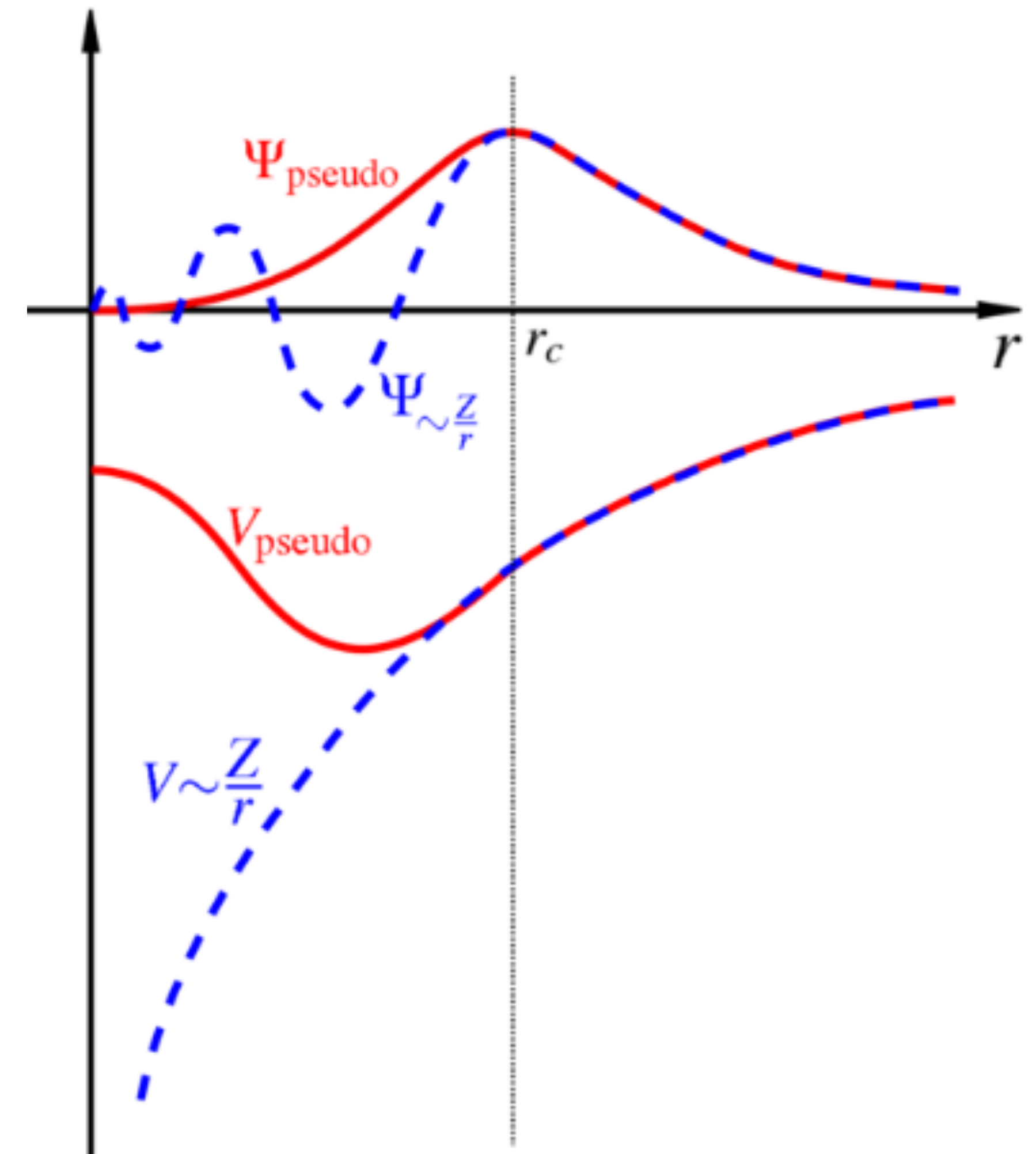
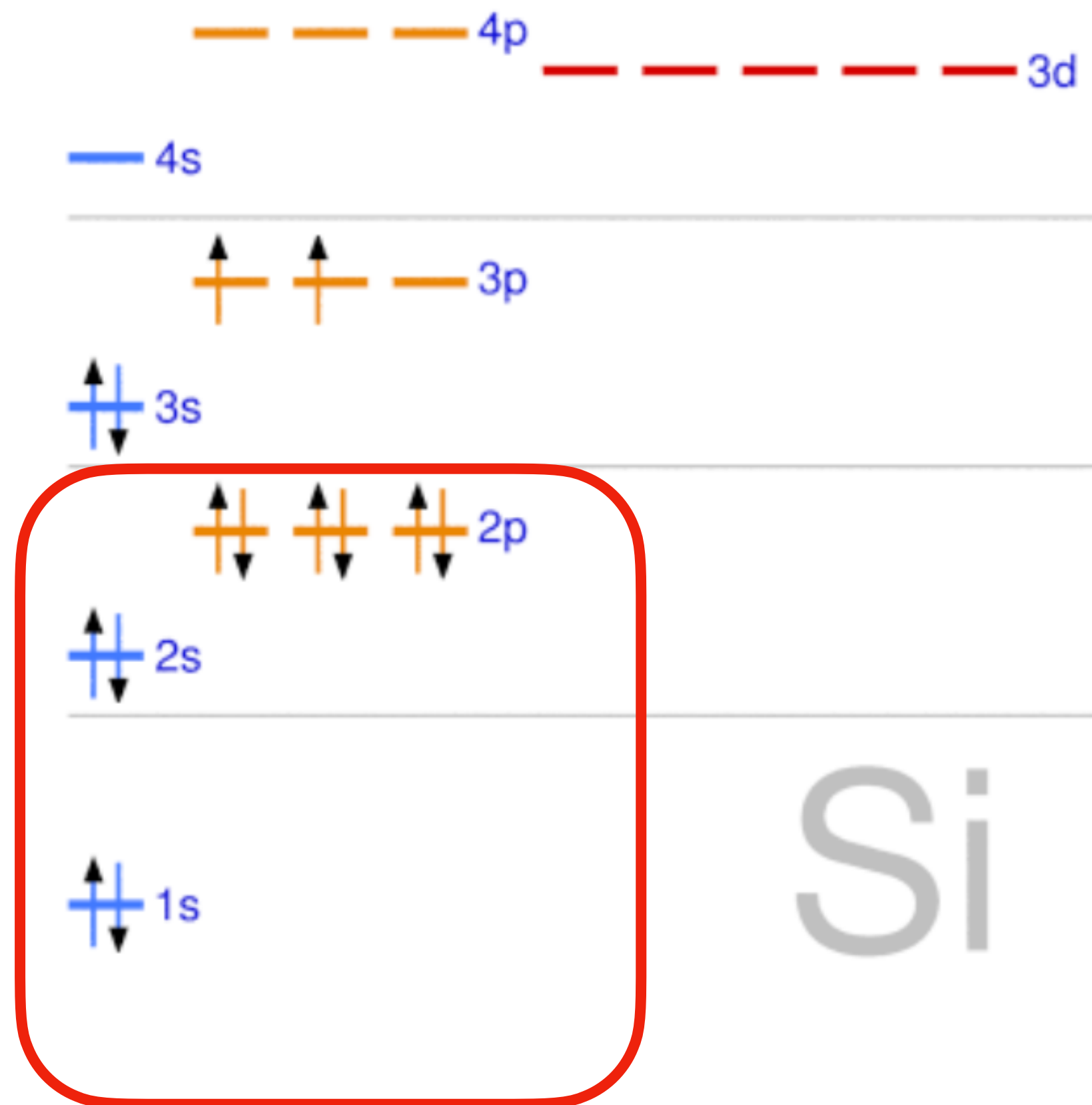
# Pseudo wavefunctions of Si



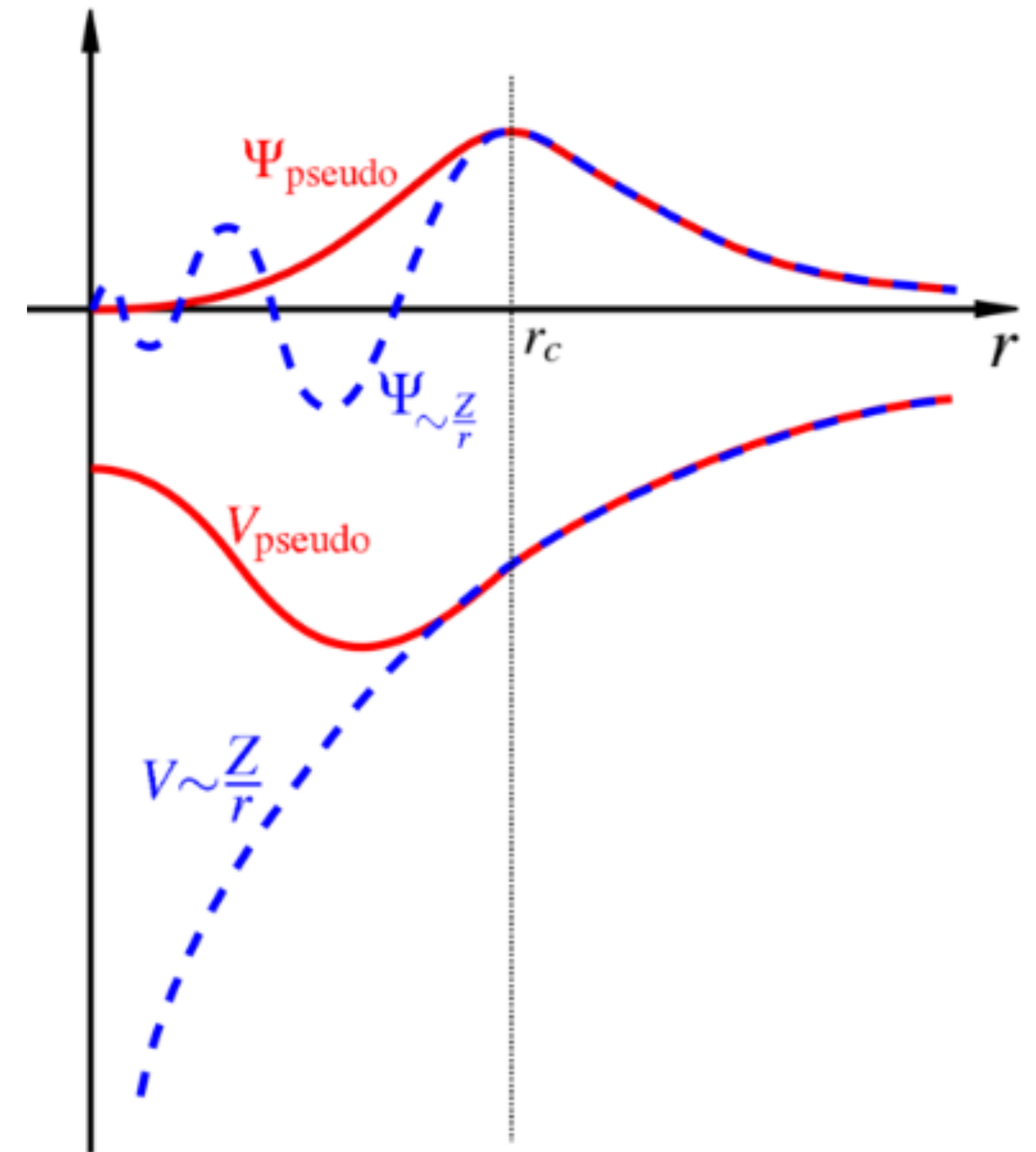
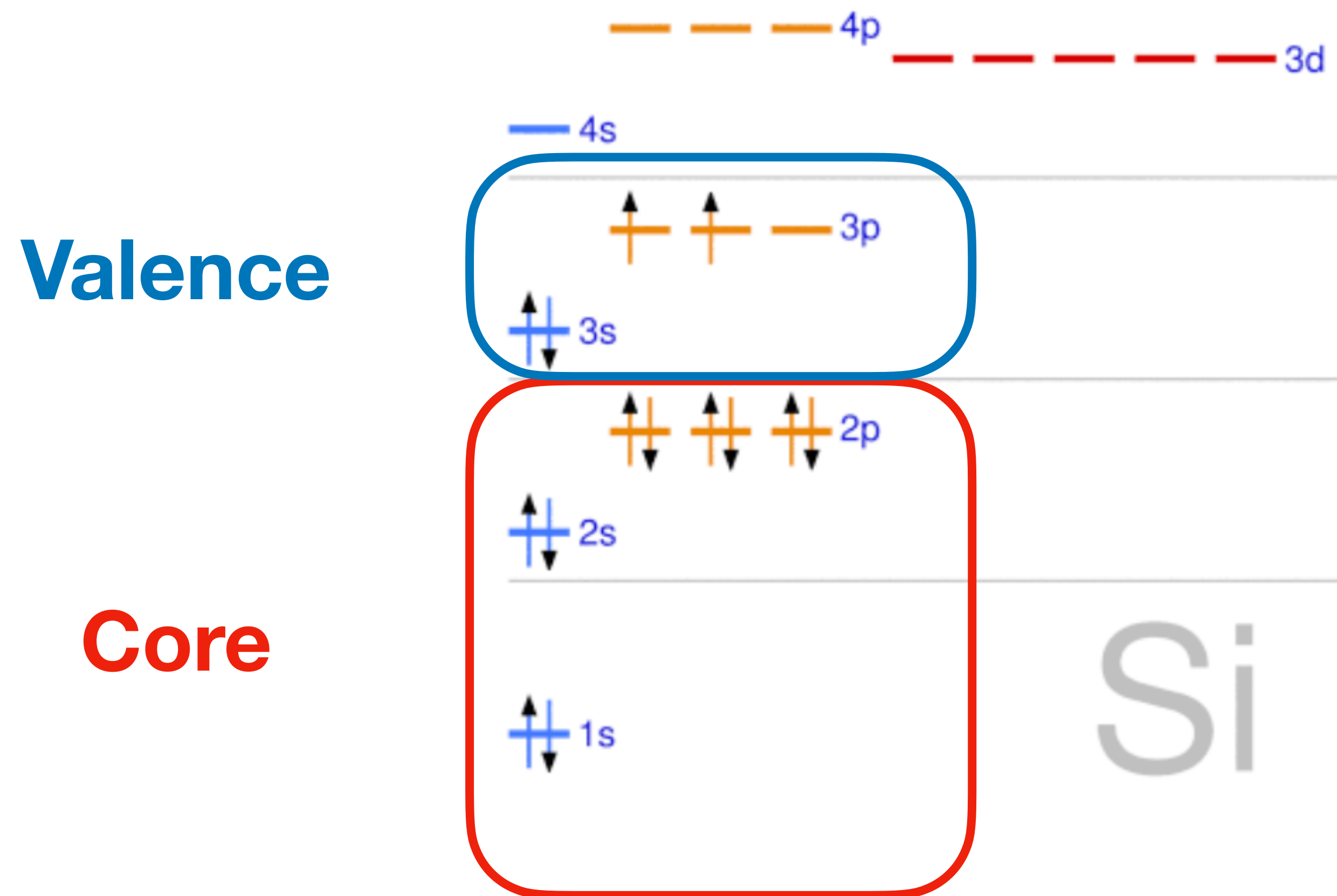


# Pseudo wavefunctions of Si

Core

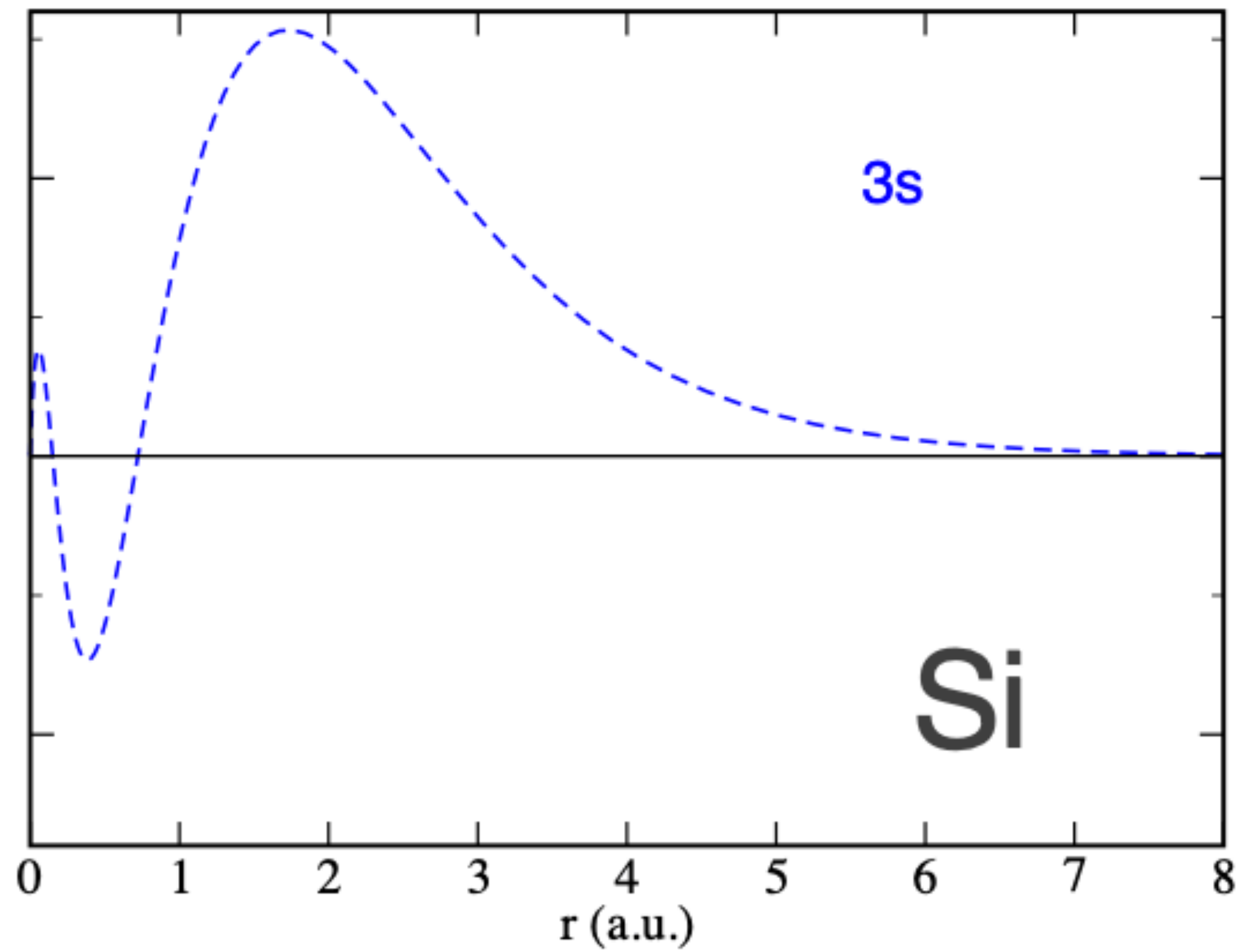


# Pseudo wavefunctions of Si



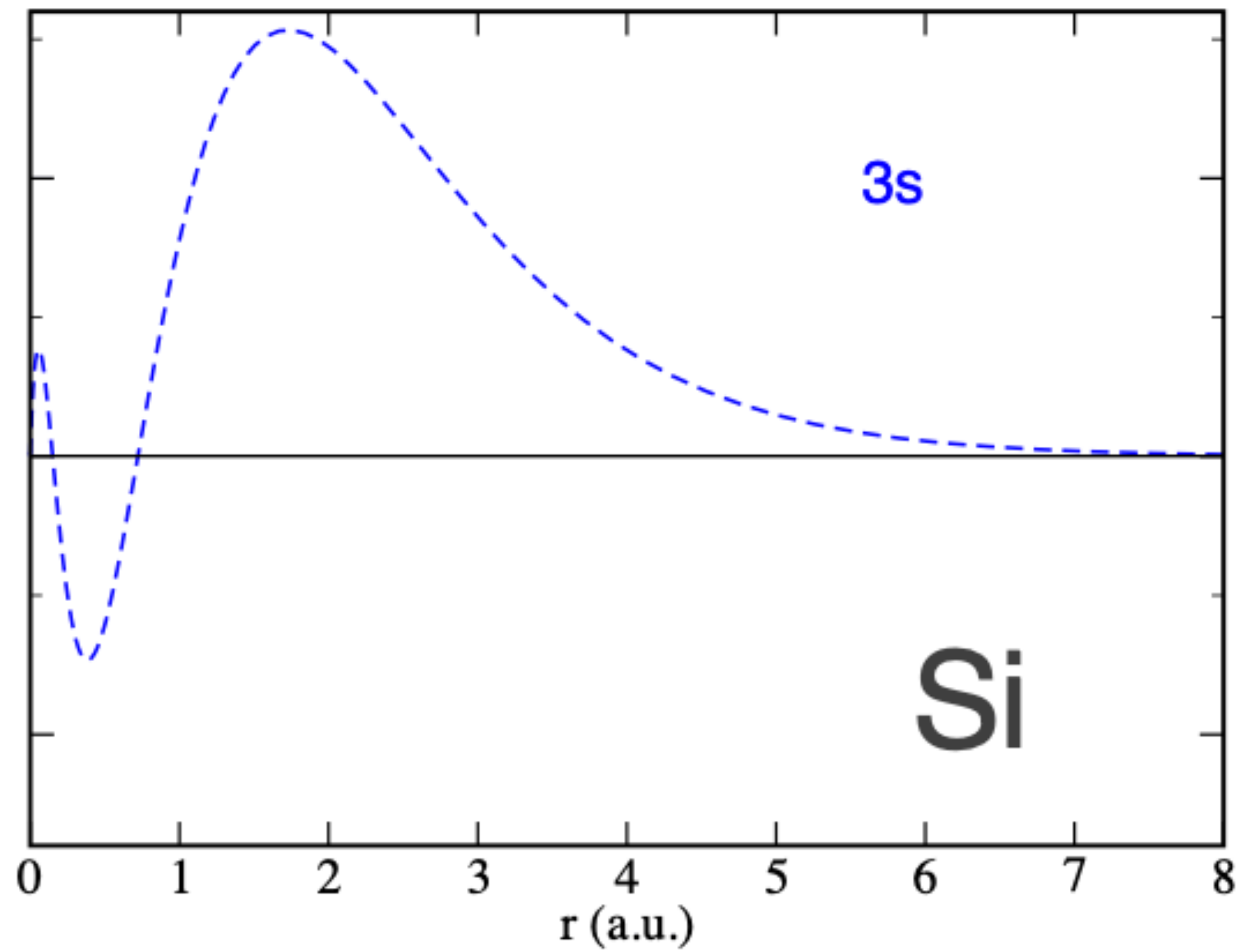
# Pseudo wavefunctions of Si

Real 3s WF

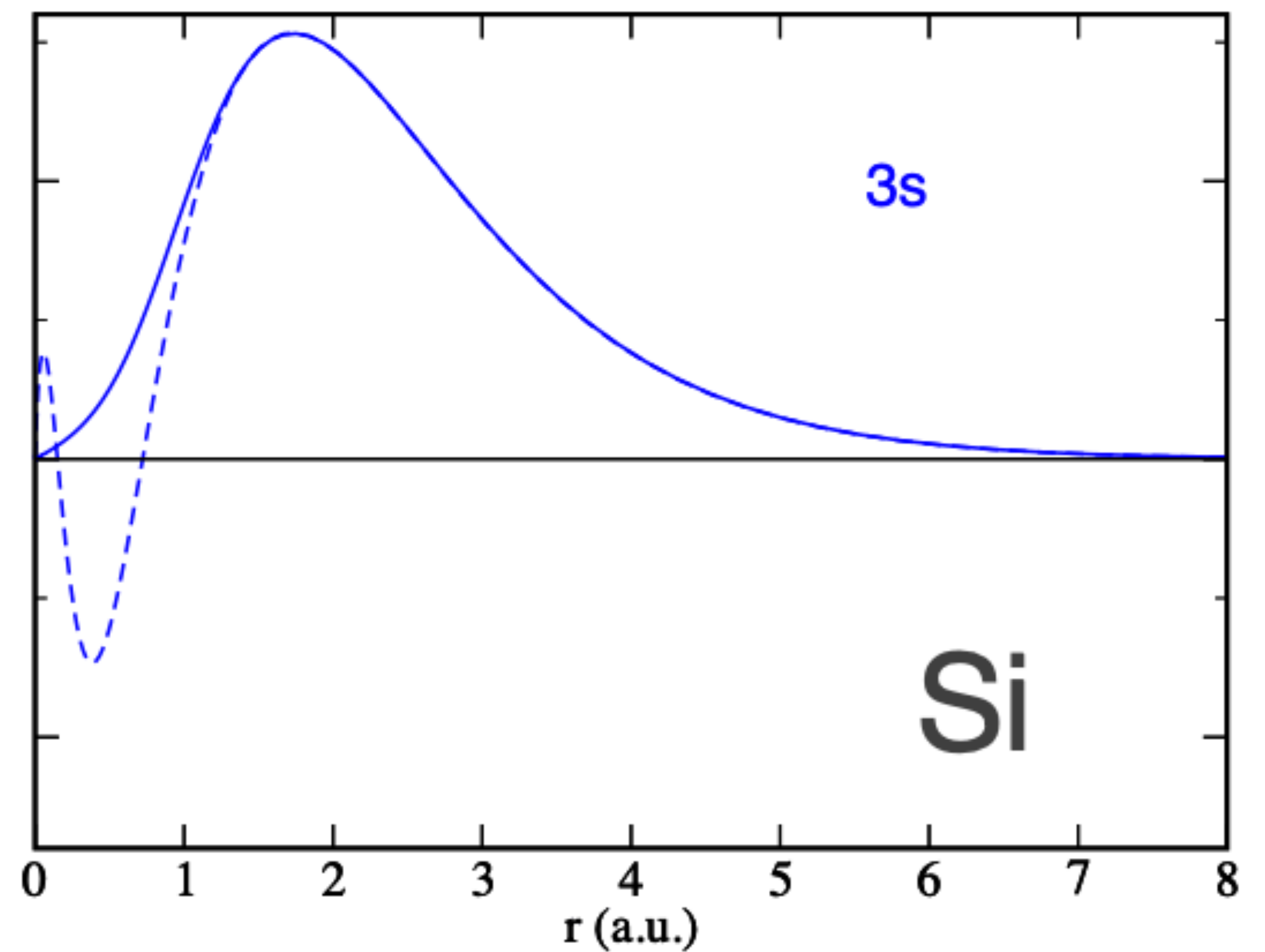


# Pseudo wavefunctions of Si

Real 3s WF



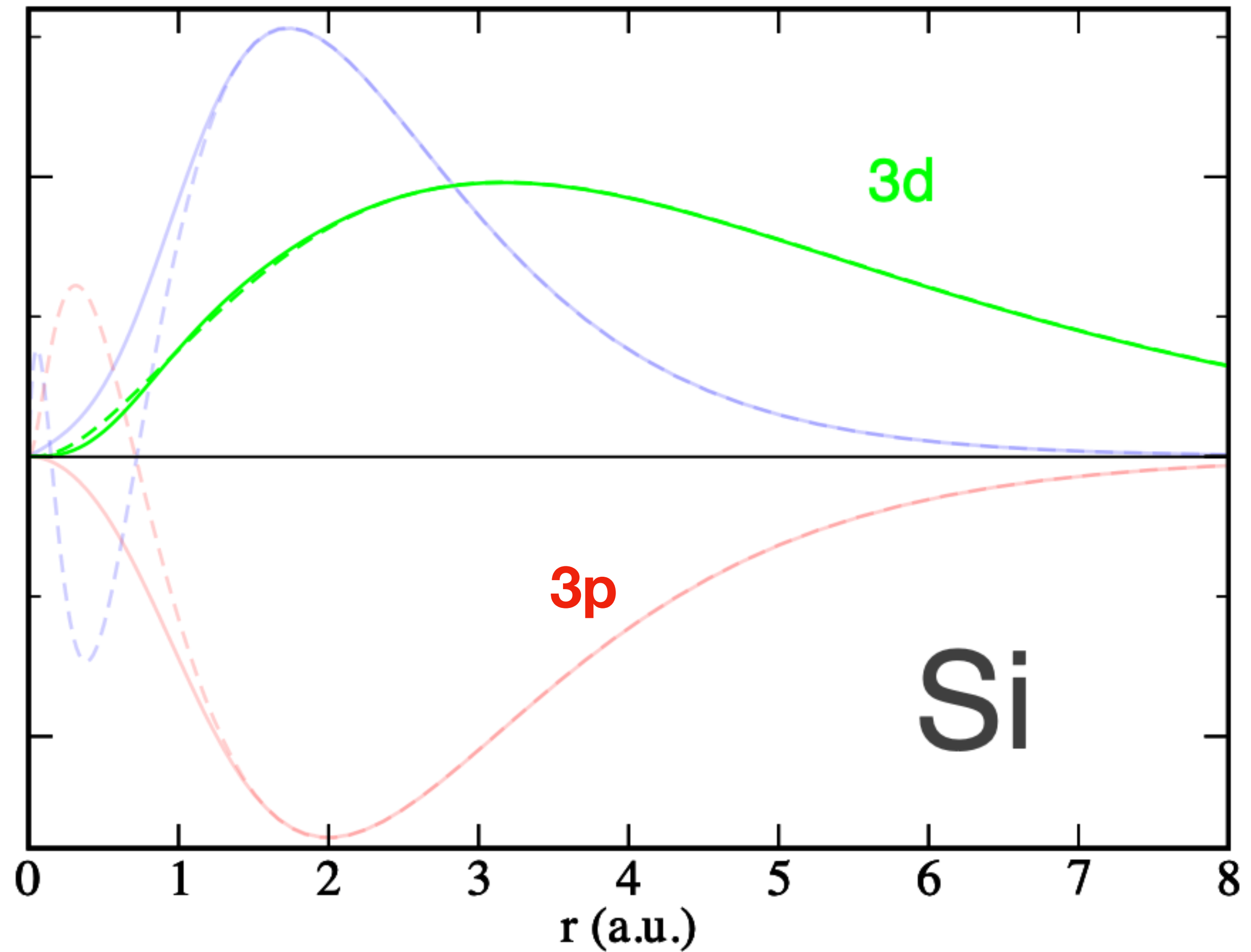
Pseudo 3s WF



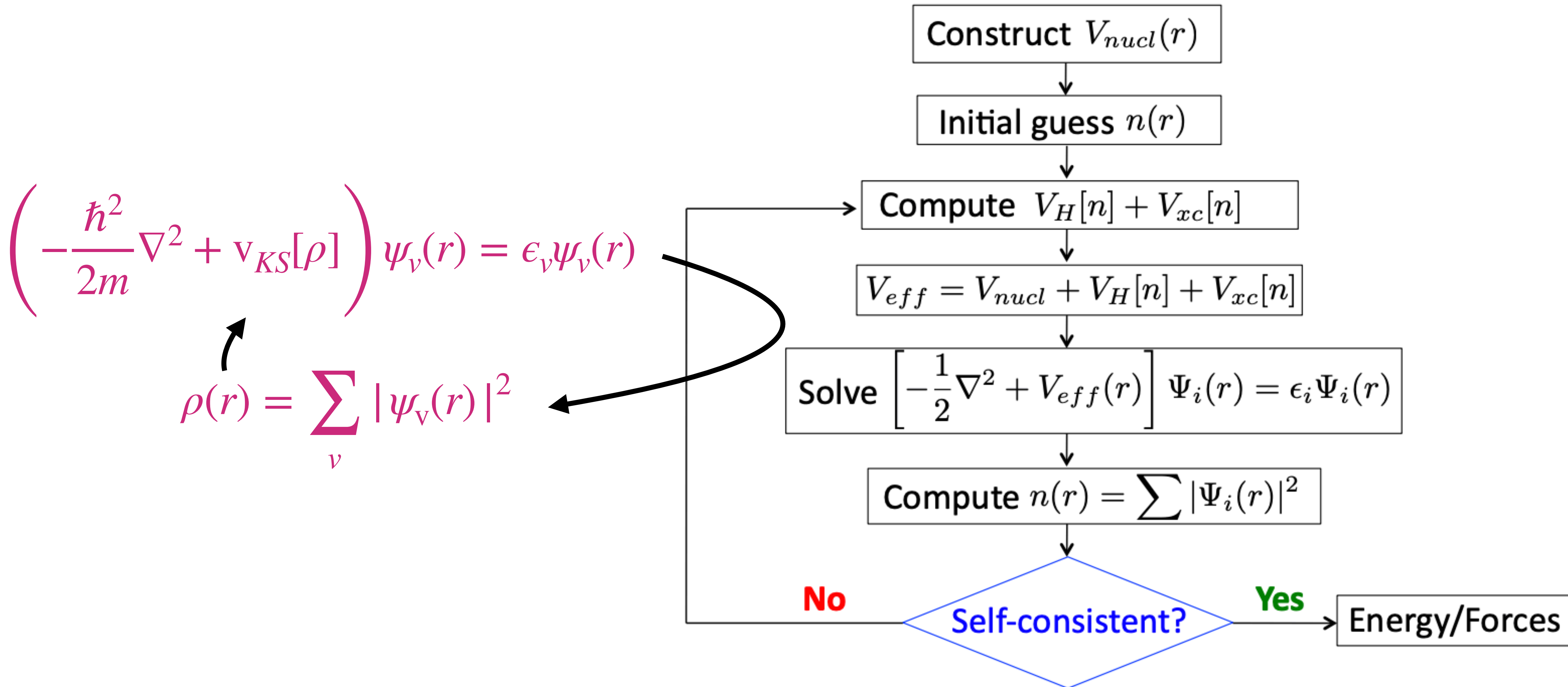
# Pseudo wavefunctions of Si

**3p and 3d\* channels**

**\* 3d is empty**



# Self consistent calculation



# Hands-on Tutorial



# Where to start

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

## PSEUDOPOTENTIALS

## More about pseudopotentials

## SSSP on Materials Cloud

## Pseudo DoJo

## ONCV Potentials

## SCAN pseudopotentials

## PSlibrary table

Original QE PP table

Hartwigesen-Goedecker-Hutter PP table

### Old FHI PP table

## PSLIBRARY

Ready-to-use pseudopotentials from **PSlibrary** (*recommended*). For other ready-to-use tables, follow the links of the menu at the left. For more info, see [here](#).

*Please cite the pseudopotentials used and give proper credit to their authors (see [this page](#) for a rather complete list of acknowledgments).*

1 H																	2 He		
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne		
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar		
19 K	20 Ca			21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr			39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57-70 *	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn	
87 Fr	88 Ra	89-102 ***	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt										

*	57	58	59	60	61	62	63	64	65	66	67	68	69	70
Lanthanoids	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
**	89	90	91	92	93	94	95	96	97	98	99	100	101	102
Actinoids	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No

- Get pseudopotentials:



# Pseudopotentials file

<UPF version="2.0.1">

<PP\_INFO>

Generated using "atomic" code by A. Dal Corso v.6.3

Author: ADC

Generation date: 6Sep2018

Pseudopotential type: PAW

Element: Ga

Functional: SLA PW PBX PBC

Suggested minimum cutoff for wavefunctions: 43. Ry

Suggested minimum cutoff for charge density: 240. Ry

The Pseudo was generated with a Scalar-Relativistic Calculation

Local Potential by smoothing AE potential with Bessel fncs, cutoff radius: 1.9000

Pseudopotential contains additional information for GIPAW reconstruction.

Valence configuration:

nl	pn	l	occ	Rcut	Rcut US	E pseu
4S	1	0	2.00	1.300	2.200	-0.657693
4P	2	1	1.00	1.300	2.200	-0.189560
3D	3	2	10.00	1.300	1.700	-1.407827

Generation configuration:

4S	1	0	2.00	1.300	2.200	-0.657691
4S	1	0	0.00	1.300	2.200	6.100000
4P	2	1	1.00	1.300	2.200	-0.189560
4P	2	1	0.00	1.300	2.200	6.300000
3D	3	2	10.00	1.300	1.700	-1.407824
3D	3	2	0.00	1.300	1.700	-1.300000

Pseudization used: troullier-martins

<PP\_INPUTFILE>

&input

title='Ga',

zed=31.,

rel=1,

config='[Ar] 4s2 4p1 3d10',

iswitch=3,

dft='PBE'

/

&inputp

lpaw = .true.,

use\_xsd=.FALSE.,

pseudotype=3,

file\_pseudopw='Ga.pbe-dn1-kjpaw\_ps1.1.0.0.UPF',

author='ADC',

lloc=-1,

rcloc=1.9,

which\_augfun='PSQ',

rmatch\_augfun\_nc=.true.,

nlcc=.true.,

new\_core\_ps=.true.,

rcore=1.1,

tm=.true.

/

6

4S 1 0 2.00 0.00 1.30 2.20 0.0

4S 1 0 0.00 6.10 1.30 2.20 0.0

4P 2 1 1.00 0.00 1.30 2.20 0.0

4P 2 1 0.00 6.30 1.30 2.20 0.0

3D 3 2 10.00 0.00 1.30 1.70 0.0

3D 3 2 0.00 -1.30 1.30 1.70 0.0

</PP\_INPUTFILE>

</PP\_INFO>

<!--

END OF HUMAN READABLE SECTION

# Input file example: GaAs

## Namelist (FORTRAN)

### Sections

```
&control  
  calculation = 'scf'  
  restart_mode='from_scratch',  
  prefix='GaSb',  
  tstress = .true.  
  tprnfor = .true.  
  pseudo_dir = '../..//Pseudo/',  
  outdir='./tmp'  
/
```

### Variables

```
&system  
  ibrav= 2,  
  celldm(1) = 10.7,  
  nat= 2,  
  ntyp= 2,  
  ecutwfc = 43.0, ! energy in Ry  
  ecutrho = 300. ! energy in Ry  
/
```

```
&electrons  
  diagonalization='david'  
  conv_thr = 1.0e-8  
  mixing_beta = 0.4  
/  
ATOMIC_SPECIES  
  Ga 69.723000d0 Ga.pbe-dnl-kjpaw_psl.1.0.0.UPF  
  As 74.921600d0 As.pbe-n-kjpaw_psl.1.0.0.UPF  
  
ATOMIC_POSITIONS crystal  
  Ga -0.125 -0.125 -0.125  
  As 0.125 0.125 0.125  
  
K_POINTS automatic  
  2 2 2 1 1 1
```

# Running pw.x

```
mpirun -np 4 pw.x -nk 2 < scf.in > scf.out
```

For bigger systems (and bigger computers)

```
mpirun -np 4096 pw.x -nk 8 -nt 4 -nd 144 < scf.in
```

↑  
**k-points**

↑  
**Tasks for 3D FFT**

↑  
**Subspace diagonalization**

```
Program PWSCF v.6.4.1 starts on  6Oct2021 at 18: 1:36
```

```
This program is part of the open-source Quantum ESPRESSO suite
for quantum simulation of materials; please cite
  "P. Giannozzi et al., J. Phys.:Condens. Matter 21 395502 (2009);
  "P. Giannozzi et al., J. Phys.:Condens. Matter 29 465901 (2017);
  URL http://www.quantum-espresso.org",
in publications or presentations arising from this work. More details at
http://www.quantum-espresso.org/quote
```

```
Parallel version (MPI), running on      1 processors
```

```
MPI processes distributed on      1 nodes
Waiting for input...
Reading input from standard input
```

```
Current dimensions of program PWSCF are:
Max number of different atomic species (ntypx) = 10
Max number of k-points (npk) = 40000
Max angular momentum in pseudopotentials (lmaxx) = 3
      file Ga.pbe-dnl-kjpaw_psl.1.1.0.0.UPF: wavefunction(s)  4S 3D renormalized
```

```
Subspace diagonalization in iterative solution of the eigenvalue problem:
a serial algorithm will be used
```

```
G-vector sticks info
```

```
-----
sticks:  dense  smooth   PW    G-vecs:  dense  smooth   PW
Sum      1177   673    199      26813   11575   1807
```

```
bravais-lattice index      =          2
lattice parameter (alat)   =    10.7000  a.u.
unit-cell volume           =    306.2607 (a.u.)^3
number of atoms/cell       =          2
number of atomic types     =          2
number of electrons        =     18.00
number of Kohn-Sham states =          9
kinetic-energy cutoff       =    43.0000  Ry
charge density cutoff      =    300.0000  Ry
convergence threshold     =    1.0E-08
mixing beta                =    0.4000
```

# Exercise 1: Electronic properties of GaAs

# Exercise 1: Electronic properties of GaAs

0 - Run your first SCF calculation for GaAs

# Exercise 1: Electronic properties of GaAs

- 0 - Run your first SCF calculation for GaAs
- 1 - Test convergence of the total energy against the k-point mesh

# Exercise 1: Electronic properties of GaAs

- 0 - Run your first SCF calculation for GaAs
- 1 - Test convergence of the total energy against the k-point mesh
- 2 - Compute the equation of state (energy vs. volume):



# Exercise 1: Electronic properties of GaAs

- 0 - Run your first SCF calculation for GaAs
- 1 - Test convergence of the total energy against the k-point mesh
- 2 - Compute the equation of state (energy vs. volume):
  - Run a sequence of SCF calculations with different lattice parameter



# Exercise 1: Electronic properties of GaAs

- 0 - Run your first SCF calculation for GaAs
- 1 - Test convergence of the total energy against the k-point mesh
- 2 - Compute the equation of state (energy vs. volume):
  - Run a sequence of SCF calculations with different lattice parameter
  - Fit to the Murnaghan equation of state (code: ev.x) and compare to experiments

# Exercise 1: Electronic properties of GaAs

- 0 - Run your first SCF calculation for GaAs
- 1 - Test convergence of the total energy against the k-point mesh
- 2 - Compute the equation of state (energy vs. volume):
  - Run a sequence of SCF calculations with different lattice parameter
  - Fit to the Murnaghan equation of state (code: ev.x) and compare to experiments
- 3 - Compute the bands and the electronic density of states.

# Exercise 1: Electronic properties of GaAs

- 0 - Run your first SCF calculation for GaAs
- 1 - Test convergence of the total energy against the k-point mesh
- 2 - Compute the equation of state (energy vs. volume):
  - Run a sequence of SCF calculations with different lattice parameter
  - Fit to the Murnaghan equation of state (code: ev.x) and compare to experiments
- 3 - Compute the bands and the electronic density of states.
  - How large is the band gap? Does it compare well to experiments?

# Exercise 1: Electronic properties of GaAs

- 0 - Run your first SCF calculation for GaAs
- 1 - Test convergence of the total energy against the k-point mesh
- 2 - Compute the equation of state (energy vs. volume):
  - Run a sequence of SCF calculations with different lattice parameter
  - Fit to the Murnaghan equation of state (code: ev.x) and compare to experiments
- 3 - Compute the bands and the electronic density of states.
  - How large is the band gap? Does it compare well to experiments?
- 4 - Repeat the band gap calculation using a hybrid functional (HSE)

# Exercise 2: Electronic properties of Al

- 1 - Modify the GaAs input file to run SCF for Aluminum: does it work?
- 2 - Use smearing to achieve SCF and test k-points convergence
- 3 - Compute the equation of state (energy)
  - Test the plane waves cutoff
  - Test the effect of the smearing
- 4 - Compute the bands and the electron

```
&system  
 ibrav      = 0,  
 nat        = 16,  
 ntyp       = 1,  
 ecutwfc    = 20.d0,  
 ecutrho    =160.0,  
 occupations='smearing',  
 degauss=0.02,  
 smearing='mp',  
/
```

# Exercise 2: Electronic properties of Al

- 1 - Modify the GaAs input file to run SCF for Aluminum: does it work?
- 2 - Use smearing to achieve SCF and test k-points convergence
- 3 - Compute the equation of state (energy vs. volume) + Murnaghan Fit
  - Test the plane waves cutoff
  - Test the effect of the smearing
- 4 - Compute the bands and the electronic density of states

# Exercise 3: Geometry of Al surface

1. Optimize the geometry of an Al (111) slab (4 layers thick)
2. Compute the band diagram and the density of states of the slab

```
&control
  calculation = 'relax'
  restart_mode='from_scratch',
  prefix='Alsurf',
  tstress = .true.
  tprnfor = .true.
  pseudo_dir = '../..//Pseudo/',
  outdir='./tmp'
  forc_conv_thr = 1.d-3
/
```

```
&ions
  ion_dynamics = 'bfgs',
  ! pot_extrapolation = 'second_order',
  ! wfc_extrapolation = 'second_order',
/
```

# Challenge:

## Compute the adsorption energy of $H_2$ on $Al(111)$

*Hints:*

Adsorption energy:

$$E_{ads} = E(Al(111) + H_2) - E(Al(111)) - E(H_2)$$

Put  $H_2$  in atop position (see example **NOT CONVERGED!!!**)

Compute  $E(H_2)$  in the same cell as  $Al(111)$

Check convergence with PW cutoff and k-points

