The Abdus Salam
International Centre
for Theoretical Physics

2522-3

Hands-on Tutorial on Electronic Structure Computations

14 - 18 January 2013

Ground State Computations with Quantum Espresso: Self-consistent field (SCF) calculations with pwscf

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Ground-State Computations with Quantum ESPRESSO

Self-consistent field (SCF) calculations

with pwscf

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The Abdus Salam
International Centre for Theoretical Physics

& *INFM-CNR Democritos National Simulation Center*

Content

Brief introduction on

- how the scf calculations are performed in pwscf
- what are the main related input parameters

Note for experienced users

For those of you who are already experienced users of pwscf

- please be patent (the fun part will come later)
- it would be nice if you could help for the hands-on part of the session (after the introduction)

From a practical point-of-view

Complete information on the input variables for pwscf

is available in the files:

`PW/Doc/INPUT_PW.txt` and **`PW/Doc/INPUT_PW.html`**

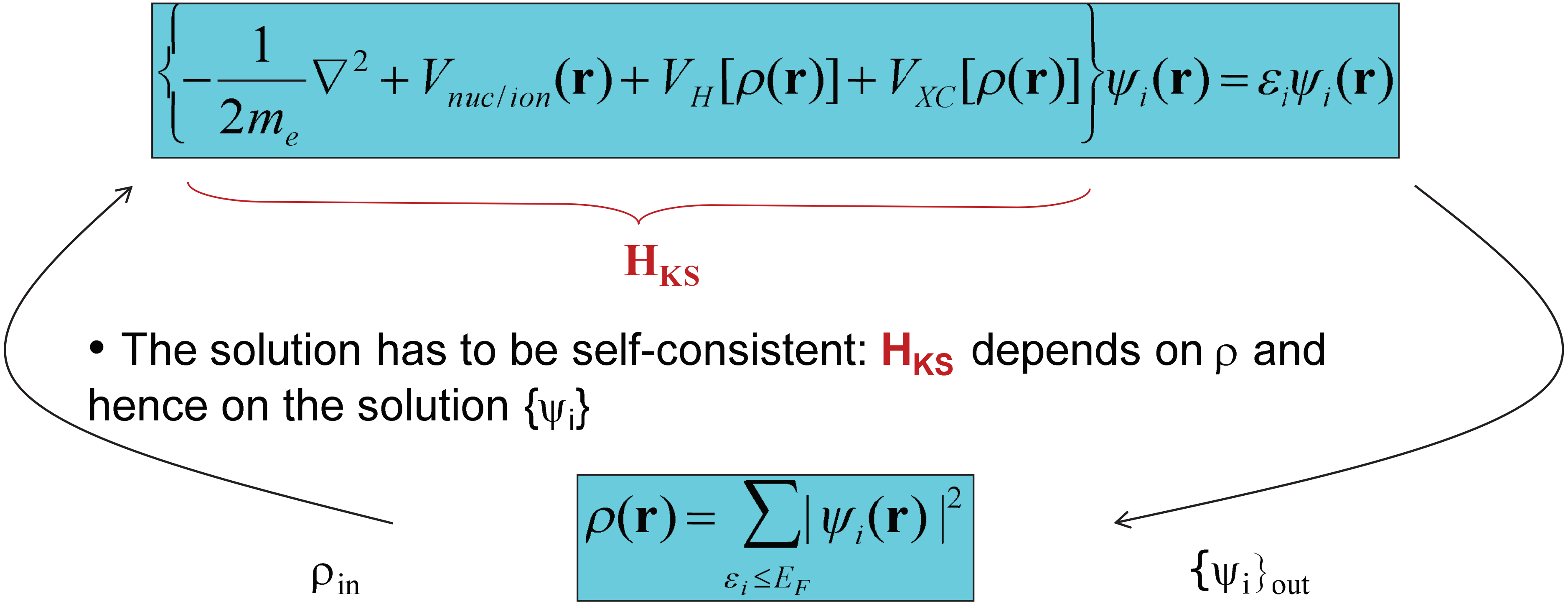
These files are the reference for input data and describe all variables

Self-consistent DFT calculations

- The goal is to solve the Kohn-Sham equations:

W. Kohn
Nobel 1998

L. J. Sham



$$\underbrace{\left\{-\frac{1}{2m_e}\nabla^2 + V_{nuc/ion}(\mathbf{r}) + V_H[\rho(\mathbf{r})] + V_{XC}[\rho(\mathbf{r})]\right\}}_{\mathbf{H}_{\mathbf{KS}}}\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r})$$

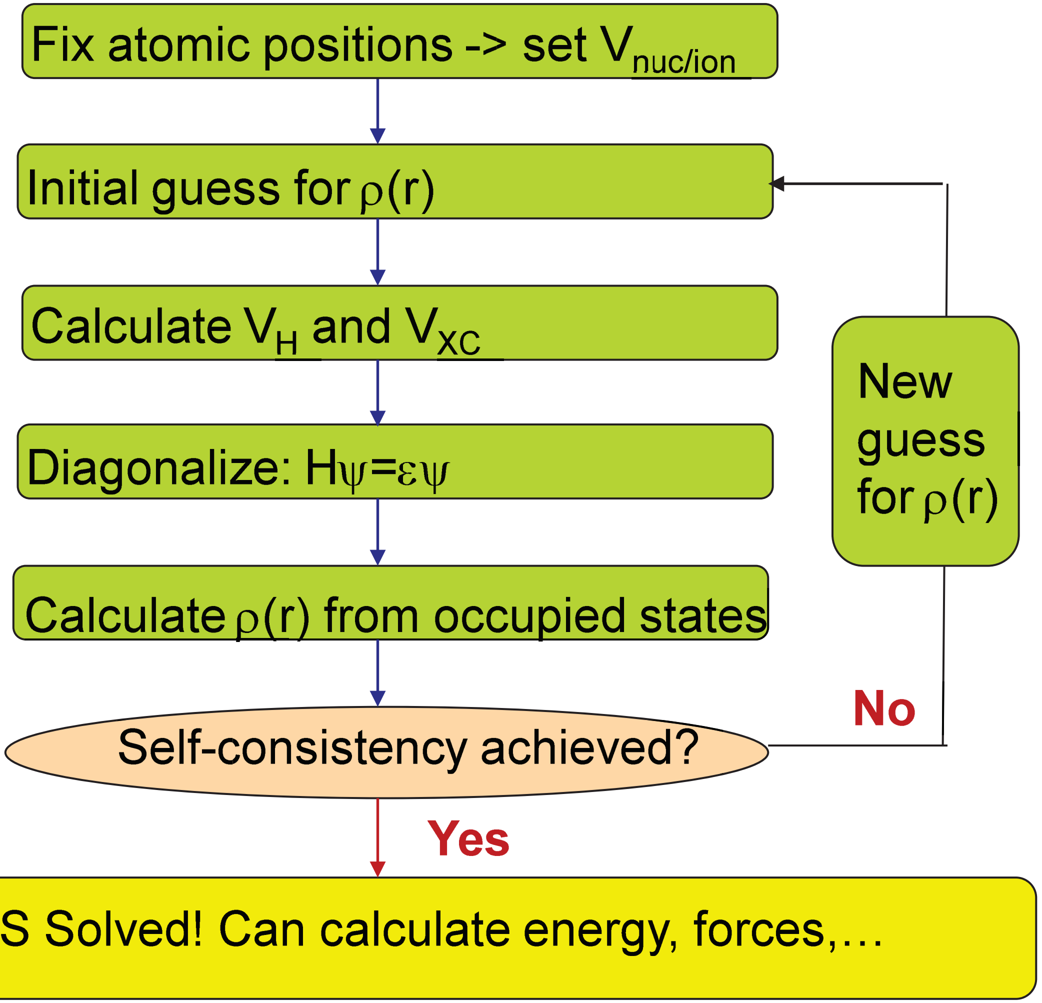
- The solution has to be self-consistent: **$\mathbf{H}_{\mathbf{KS}}$** depends on ρ and hence on the solution $\{\psi_i\}$

$$\rho(\mathbf{r}) = \sum_{\varepsilon_i \le E_F} |\psi_i(\mathbf{r})|^2$$

ρ_{in}

$\{\psi_i\}_{out}$

How to solve KS equations: general flowchart



Fix atomic positions -> set $V_{nuc/ion}$

Initial guess for $\rho(r)$

Calculate V_H and V_{XC}

Diagonalize: $H\psi=\varepsilon\psi$

Calculate $\rho(r)$ from occupied states

Self-consistency achieved?

No

New guess for $\rho(r)$

Yes

KS Solved! Can calculate energy, forces,…

Approach/ingredients for efficient computations used in pwscf

1. Plane-wave basis set and periodic systems
2. Pseudopotentials
3. Discrete k-points for numerical integrations over the Brillouin zone

1. Plane-wave basis and periodic systems

- For periodic systems:

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{k},\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G})\bullet\mathbf{r}}$$

G: reciprocal lattice vectors
K: in the Brillouin Zone (BZ)

M. Brillouin
1854–1948

- In the calculations, the plane-wave expansion is truncated, i.e., the basis includes plane waves up to a given kinetic energy cutoff (E_{cut}):

$$\frac{\hbar^2 |\mathbf{k}+\mathbf{G}|^2}{2m_e} \le E_{cut}$$

Input parameter:

`ecutwfc`

1. Plane-wave basis and periodic systems

- In practice, the contribution of high Fourier components (large |k+G|) is small when the electronic orbitals are *not* sharply peaked or have lots of wiggles near the nucleus

In general, increased wiggles/localization

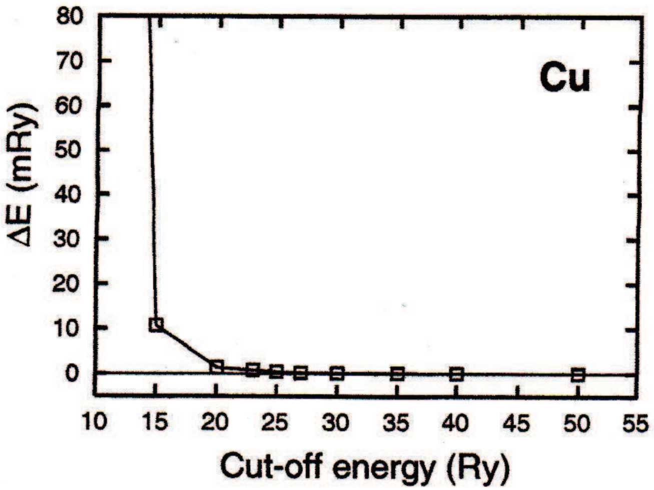
⇨ *increased Ecut*

First rule:

- One should always check the convergence with Ecut:

variational parameter

Convergence of total energy with Ecut



F. Favot, EPFL Thesis

1. Defining the periodic system

(in input file, under namelist: `SYSTEM`)

Need to specify the Bravais lattice / unit cell (⇨ pw basis: G vectors, BZ) & the atomic basis

Input parameters:


A. Bravais
1811-1863

`ibrav`	sets type of Bravais lattice (sc,bcc,hex,…)
`celldm(i)`	set lengths (and relative angles, if required) of lattice vectors $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$
`nat`	number of atoms in the unit cell
`ntyp`	number of types of atoms

Under field: `ATOMIC_POSITIONS`

positions of the nat atoms; can be chosen to be given in units of lattice vectors ("crystal") or cartesian coordinates ("bohr", "angstrom" or "alat" units)

2. Pseudopotentials

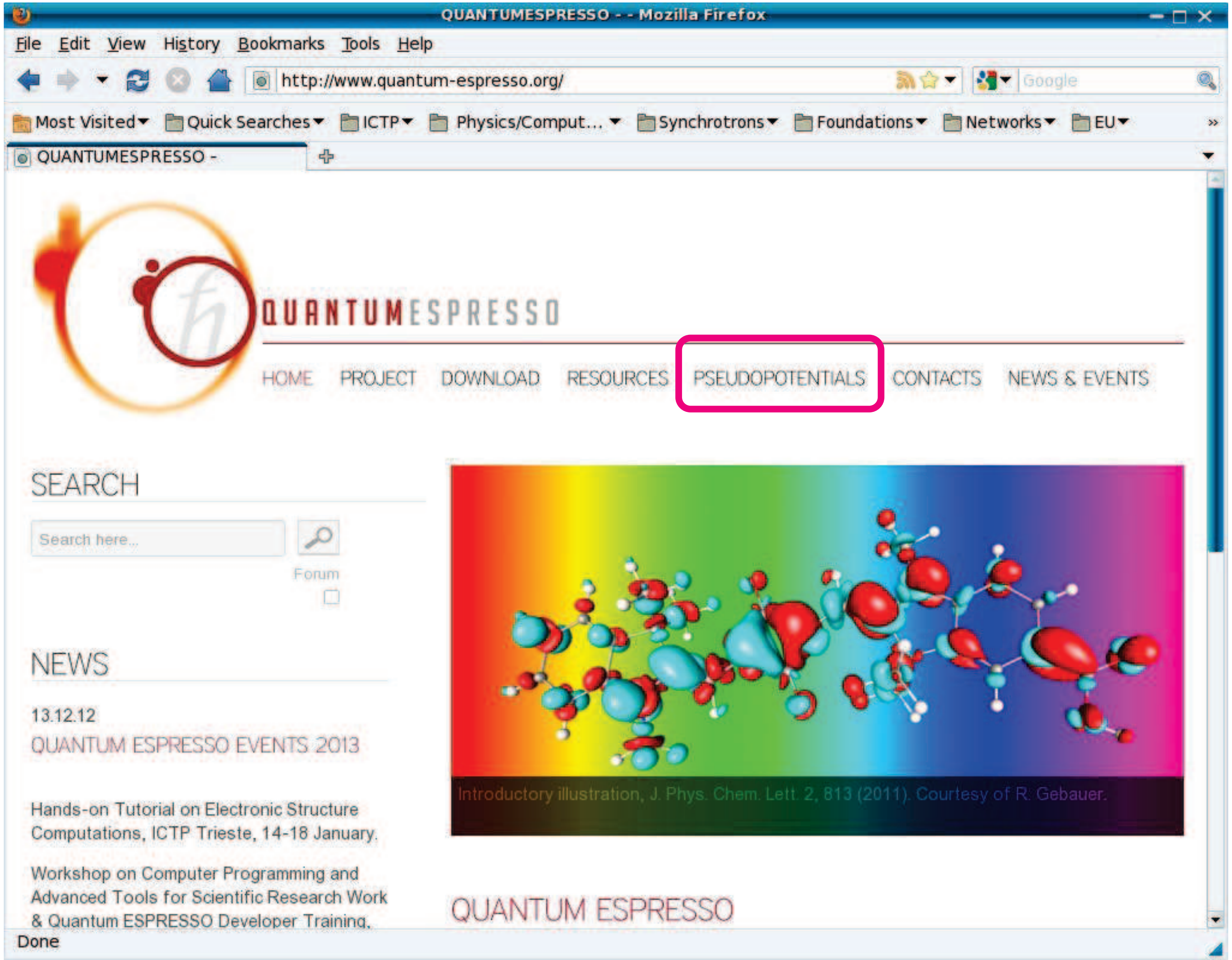
- Nuclear potential replaced by pseudopotential:

effective potential that reproduces valence-electron wave-functions outside core region (accounts for the effects of nuleus + core electrons)

  - ➢ need to solve KS only for valence electrons
  - ➢ removes wiggles/sharpness of valence wavefunctions → lowers E_{cut}

- Different types of pseudopotentials: Norm-conserving, ultrasoft,.. (which type to use depends on element)

2. Pseudopotentials at www.quantum-espresso.org



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QUANTUM ESPRESSO EVENTS 2013

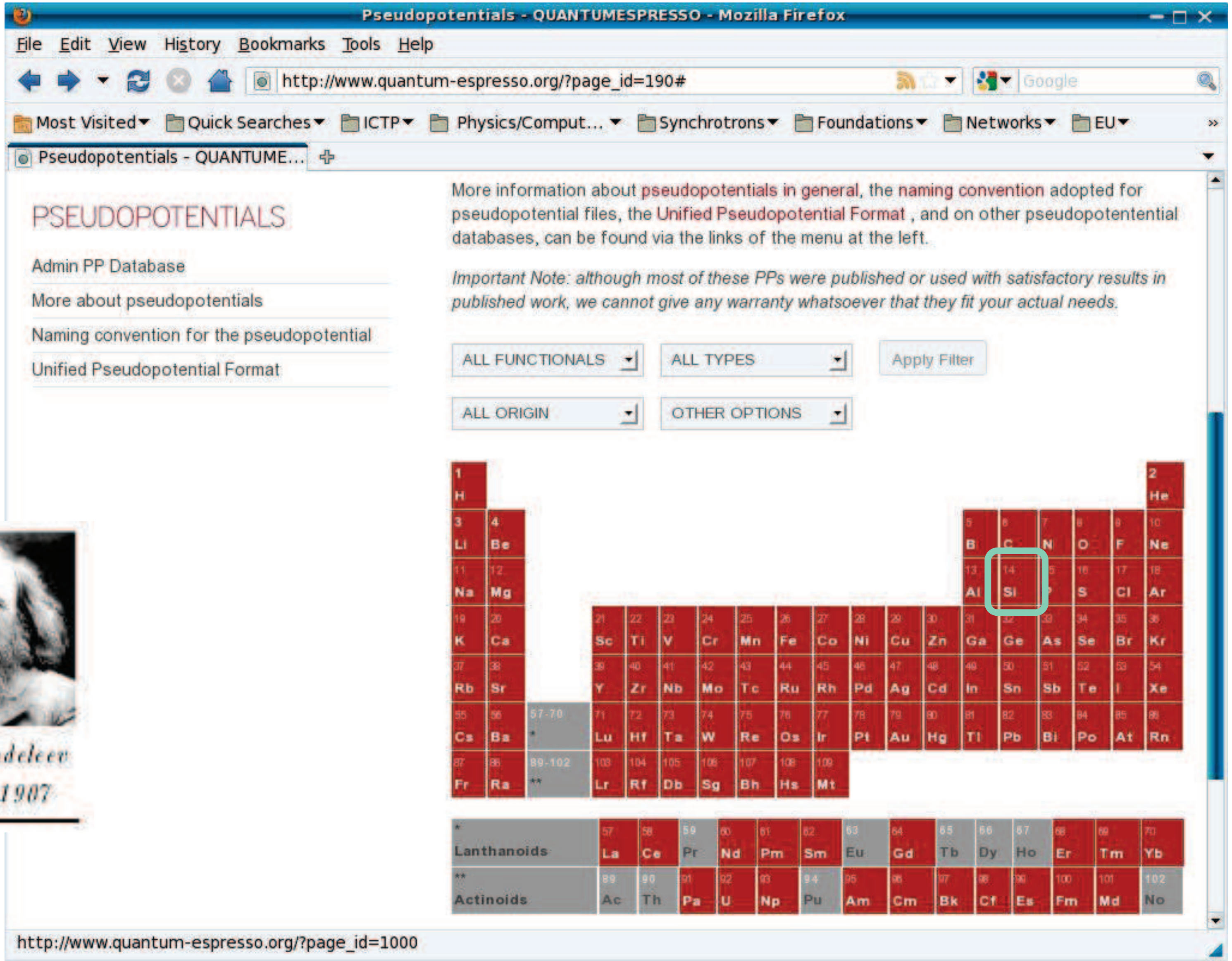
Hands-on Tutorial on Electronic Structure Computations, ICTP Trieste, 14-18 January.

Workshop on Computer Programming and Advanced Tools for Scientific Research Work & Quantum ESPRESSO Developer Training,

Introductory illustration, J. Phys. Chem. Lett. 2, 813 (2011). Courtesy of R. Gebauer.

QUANTUM ESPRESSO

2. Pseudopotentials at www.quantum-espresso.org



PSEUDOPOTENTIALS

Admin PP Database

More about pseudopotentials

Naming convention for the pseudopotential

Unified Pseudopotential Format

More information about pseudopotentials in general, the naming convention adopted for pseudopotential files, the Unified Pseudopotential Format , and on other pseudopotentential databases, can be found via the links of the menu at the left.

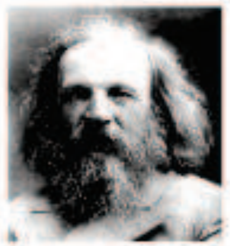
Important Note: although most of these PPs were published or used with satisfactory results in published work, we cannot give any warranty whatsoever that they fit your actual needs.

ALL FUNCTIONALS | ALL TYPES | Apply Filter

ALL ORIGIN | OTHER OPTIONS

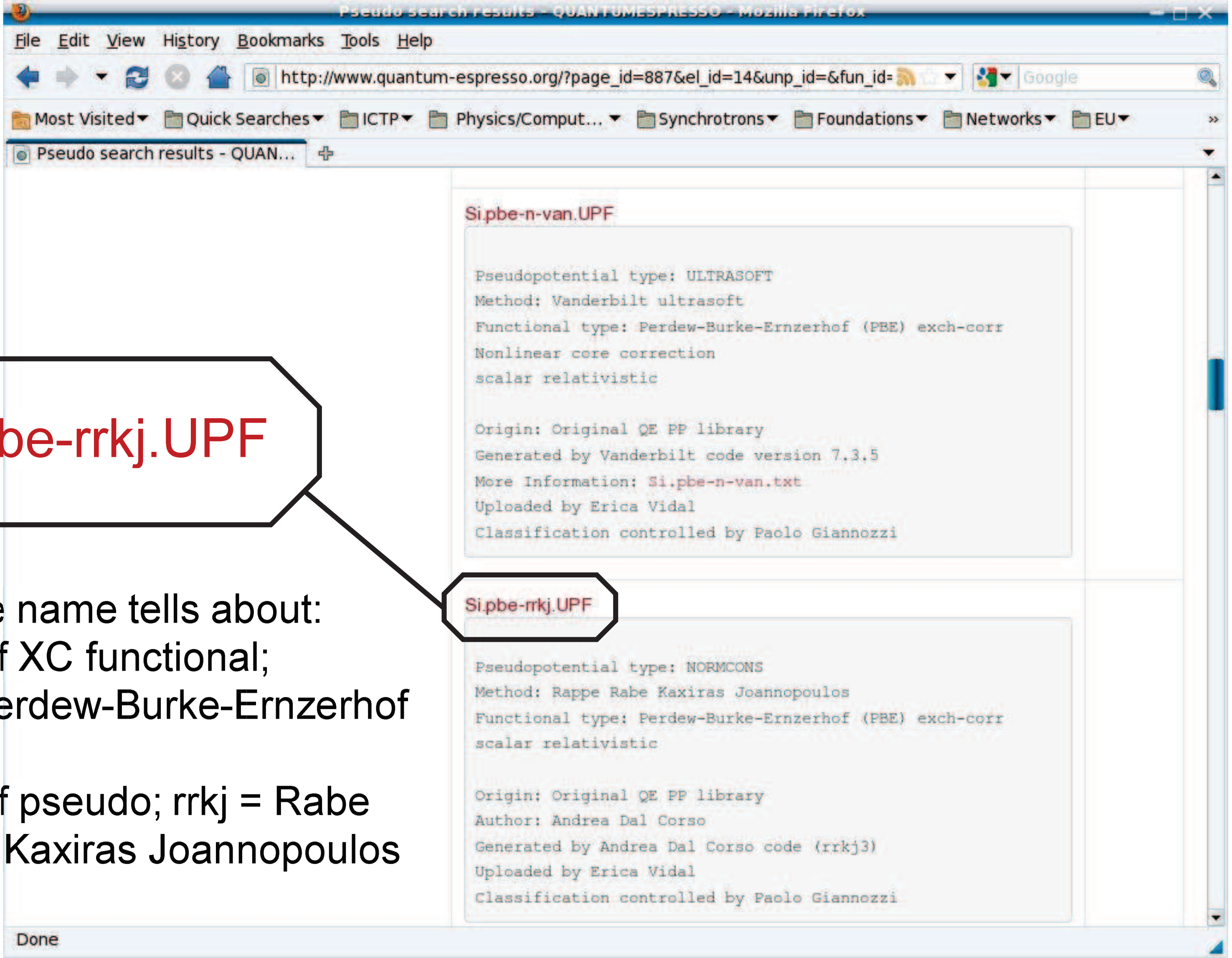
1 H																		2 He
3 Li	4 Be													5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg													13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca		21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr		39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 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									

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



D. Mendeleev
1834–1907

2. Pseudopotentials at www.quantum-espresso.org



Si.pbe-n-van.UPF

Pseudopotential type: ULTRASOFT
Method: Vanderbilt ultrasoft
Functional type: Perdew-Burke-Ernzerhof (PBE) exch-corr
Nonlinear core correction
scalar relativistic

Origin: Original QE PP library
Generated by Vanderbilt code version 7.3.5
More Information: Si.pbe-n-van.txt
Uploaded by Erica Vidal
Classification controlled by Paolo Giannozzi

Si.pbe-rrkj.UPF

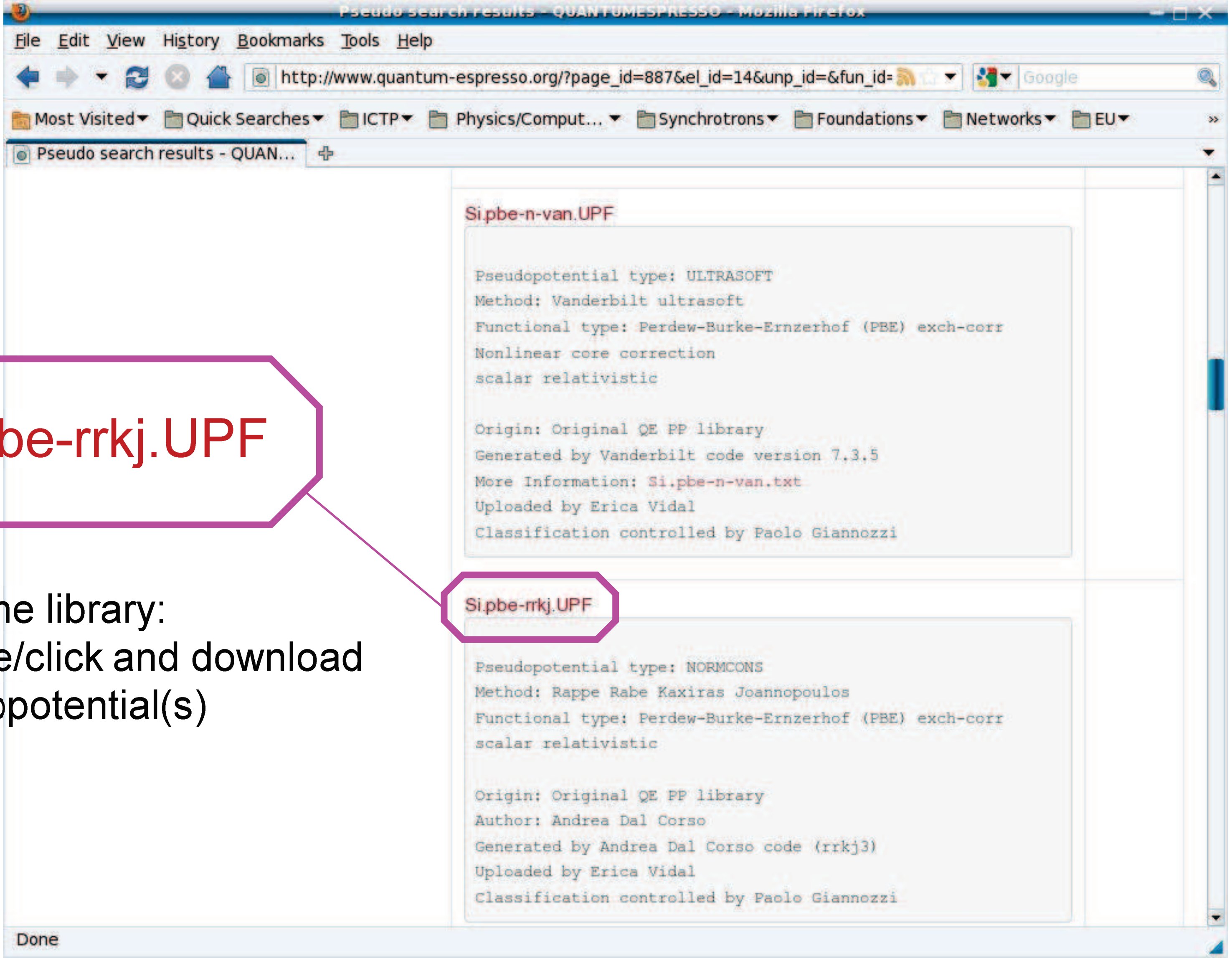
Pseudopotential type: NORMCONS
Method: Rappe Rabe Kaxiras Joannopoulos
Functional type: Perdew-Burke-Ernzerhof (PBE) exch-corr
scalar relativistic

Origin: Original QE PP library
Author: Andrea Dal Corso
Generated by Andrea Dal Corso code (rrkj3)
Uploaded by Erica Vidal
Classification controlled by Paolo Giannozzi

Si.pbe-rrkj.UPF

The file name tells about:
-type of XC functional;
pbe=Perdew-Burke-Ernzerhof (gga)
-type of pseudo; rrkj = Rabe Rappe Kaxiras Joannopoulos (soft)

2. Pseudopotentials at www.quantum-espresso.org



Si.pbe-n-van.UPF

```
Pseudopotential type: ULTRASOFT
Method: Vanderbilt ultrasoft
Functional type: Perdew-Burke-Ernzerhof (PBE) exch-corr
Nonlinear core correction
scalar relativistic

Origin: Original QE PP library
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More Information: Si.pbe-n-van.txt
Uploaded by Erica Vidal
Classification controlled by Paolo Giannozzi
```

Si.pbe-rrkj.UPF

```
Pseudopotential type: NORMCONS
Method: Rappe Rabe Kaxiras Joannopoulos
Functional type: Perdew-Burke-Ernzerhof (PBE) exch-corr
scalar relativistic

Origin: Original QE PP library
Author: Andrea Dal Corso
Generated by Andrea Dal Corso code (rrkj3)
Uploaded by Erica Vidal
Classification controlled by Paolo Giannozzi
```

Si.pbe-rrkj.UPF

From the library:
Choose/click and download pseudopotential(s)

2. Pseudopotentials & input file

- In input file, pseudopotential name under field:

```
ATOMIC_SPECIES
```

For Si, e.g.,

```
ATOMIC_SPECIES
 Si 28.086 Si.pbe-rrkj.UPF
```

Notes:

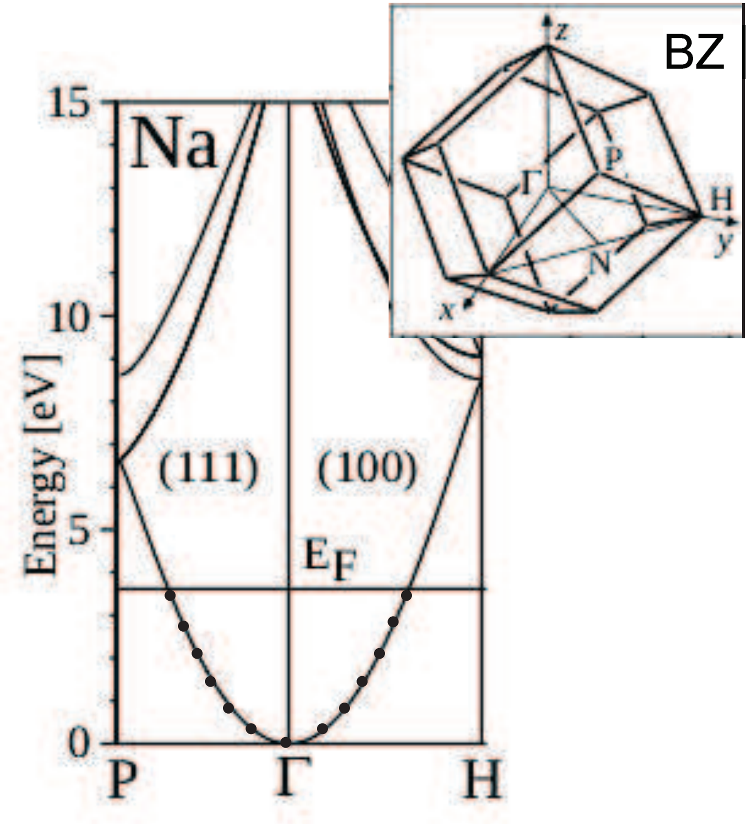
- all species in input should have pseudopotentials with the same XC functional

- if ultrasoft pseudopotentials are used, the cutoff for (augmentation) charge: `ecutrho` should be set to **`8-12 x ecutwfc`** (default 4 x ecutwfc)

3. Discrete k-points for numerial integrations over the Brillouin-Zone (BZ)

- Many needed quantities (in particular: ρ, Etot,...) require an integration over the BZ
- Done with sum over a finite nb of k-points in BZ with appropriate weights:

$$\langle Q\rangle = \sum_{\mathbf{k}\in BZ} Q(\mathbf{k})w_{\mathbf{k}}$$

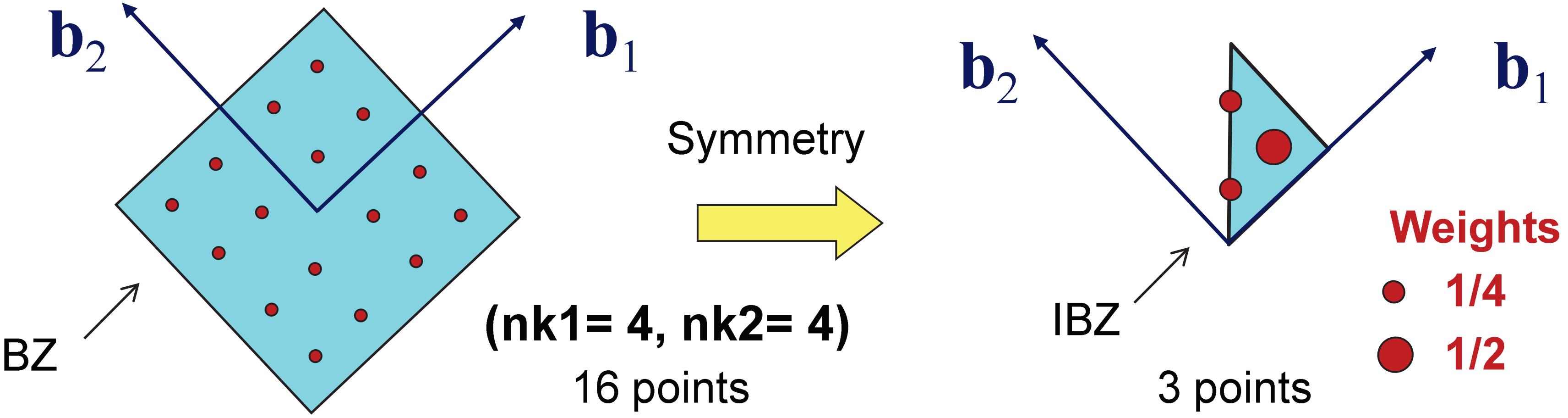


3. Discrete k-points for numerial integrations over the BZ

Type of BZ sampling points
[in chronological order]:

- **Special k-point(s):** *Baldereschi, Chadi-Cohen*
  Points derived to optimize integration with few k-points for specific classes of crystal structures

- **Monkhorst-Pack (MP) grid**:
  Grid of equally spaced points (nk1, nk2, nk3) along each of the reciprocal-lattice unit-cell vectors; may be centered at the origin or shifted



3. Brillouin-zone-sampling points

In input file, under field: `K_POINTS`

If "automatic" is specified, uses MP grid.

Ex.:

```
K_POINTS (automatic)
 4 4 4 1 1 1
```

nk1 nk2 nk3 Shift in units [$\mathbf{b}_1$/(2•nk1), $\mathbf{b}_2$/(2•nk2), $\mathbf{b}_3$/(2•nk3)]

3. For metals: one should use electronic level broadening/smearing

- Metals require lots of k-points for convergence (abrupt cut of band structure at E_F)

- Introduce smearing/broadening of the electronic levels to accelerate convergence of integrations with k-points

In input file, set

```
occupation = 'smearing'
```

and, e.g.,

```
smearing ='methfessel-paxton'
degauss = 0.02
```

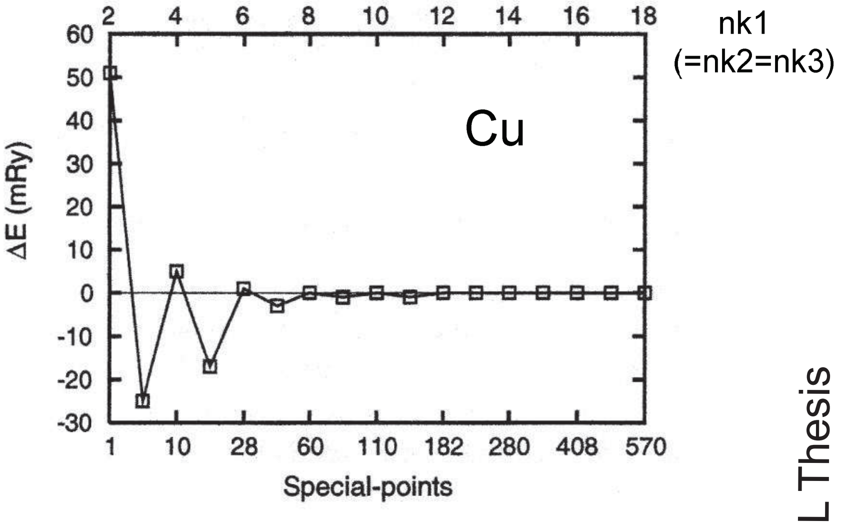
type of smearing
smearing width

- The smearing should not be too large (the larger the smearing, the faster the convergence, but also the larger the error introduced)

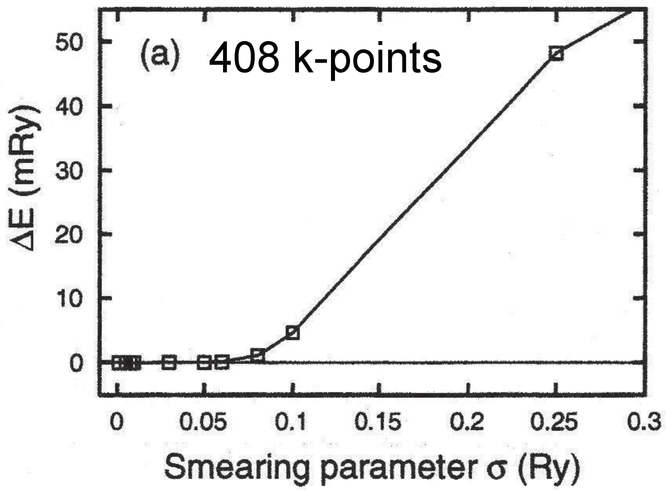
3. Checking convergence with k-points

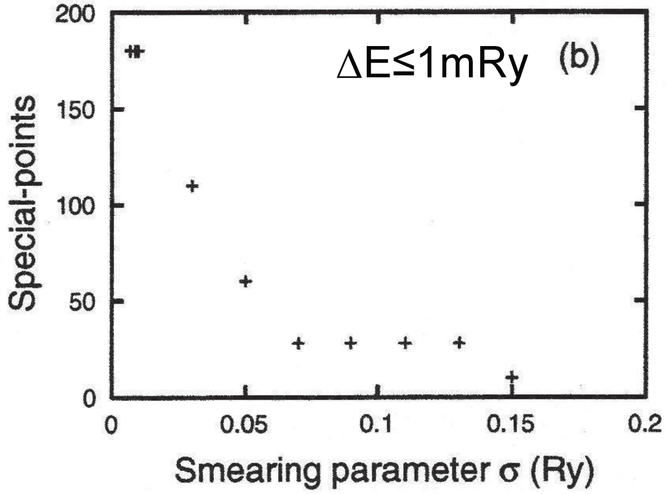
Second rule: Check convergence with k points

Convergence of total energy with nb of k points



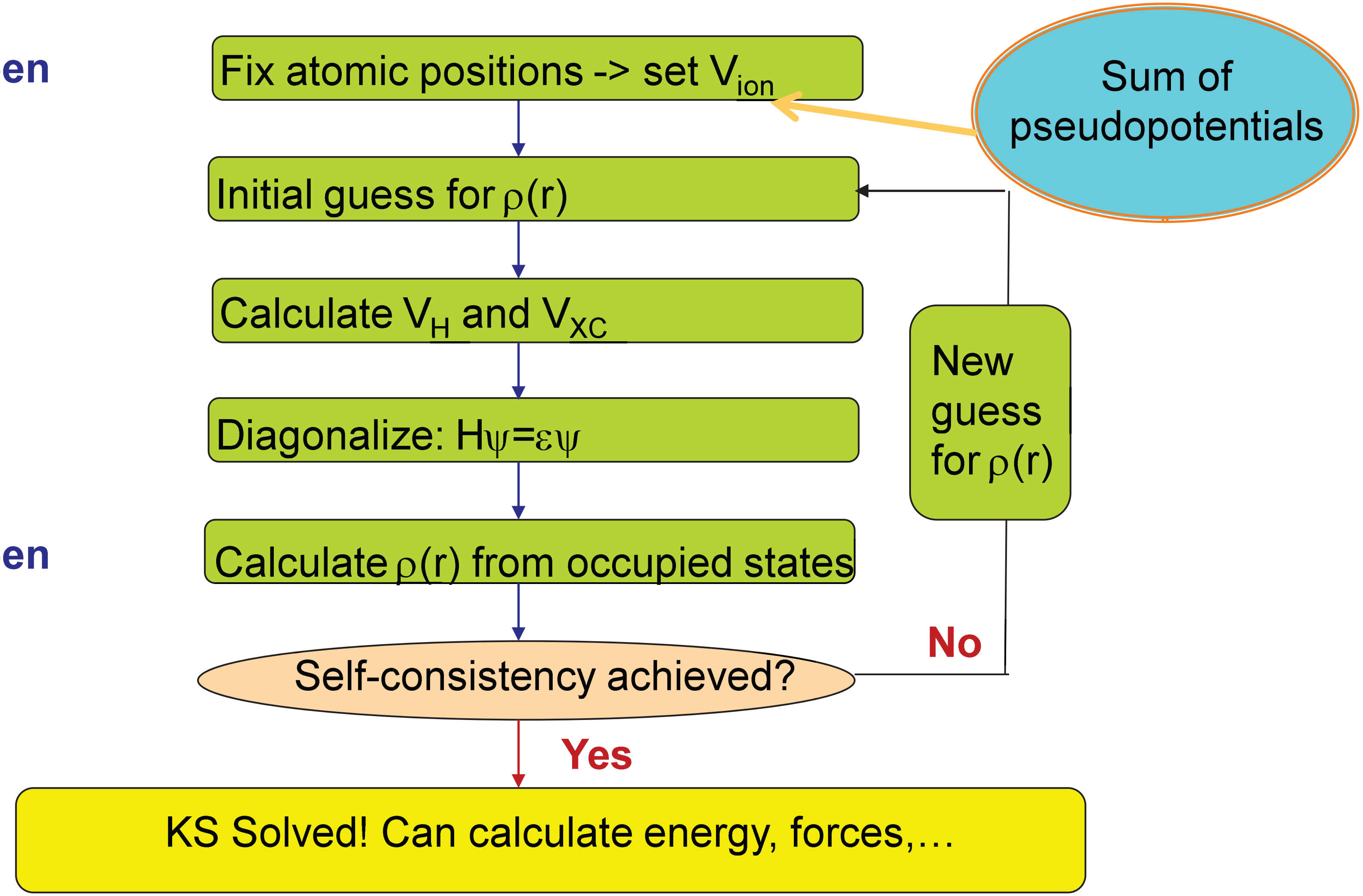
With smearing (Methfessel Paxton):





F. Favot, EPFL Thesis

Flowchart of the scf calculations



Seen

Fix atomic positions -> set V_{ion}

Sum of pseudopotentials

Initial guess for $\rho(r)$

Calculate V_H and V_{XC}

Diagonalize: $H\psi=\varepsilon\psi$

Seen

Calculate $\rho(r)$ from occupied states

Self-consistency achieved?

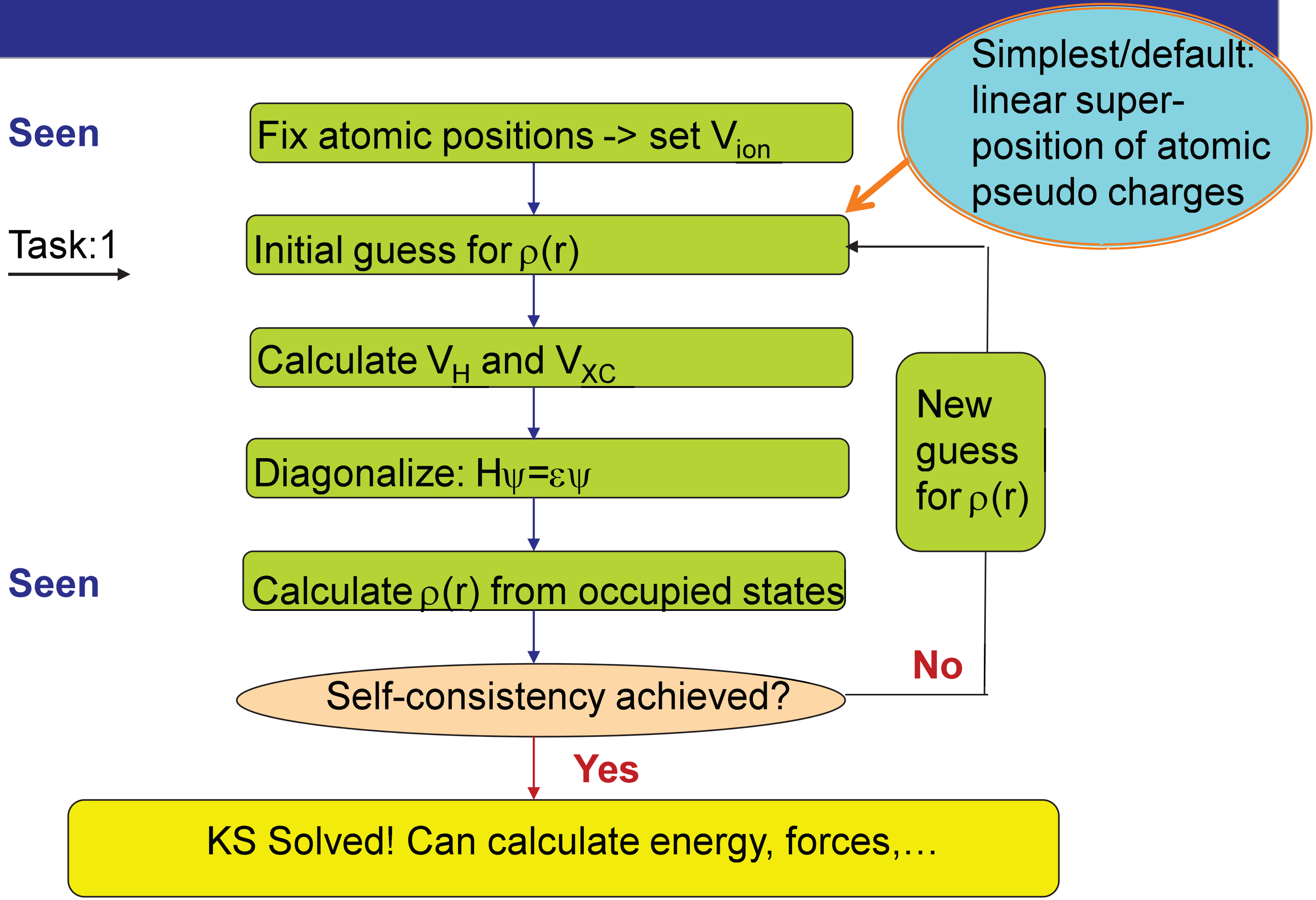
No

New guess for $\rho(r)$

Yes

KS Solved! Can calculate energy, forces,…

Other tasks in the scf calculations



Seen

Fix atomic positions -> set V_{ion}

Task:1

Initial guess for $\rho(r)$

Simplest/default: linear superposition of atomic pseudo charges

Calculate V_H and V_{XC}

Diagonalize: $H\psi=\varepsilon\psi$

Seen

Calculate $\rho(r)$ from occupied states

Self-consistency achieved?

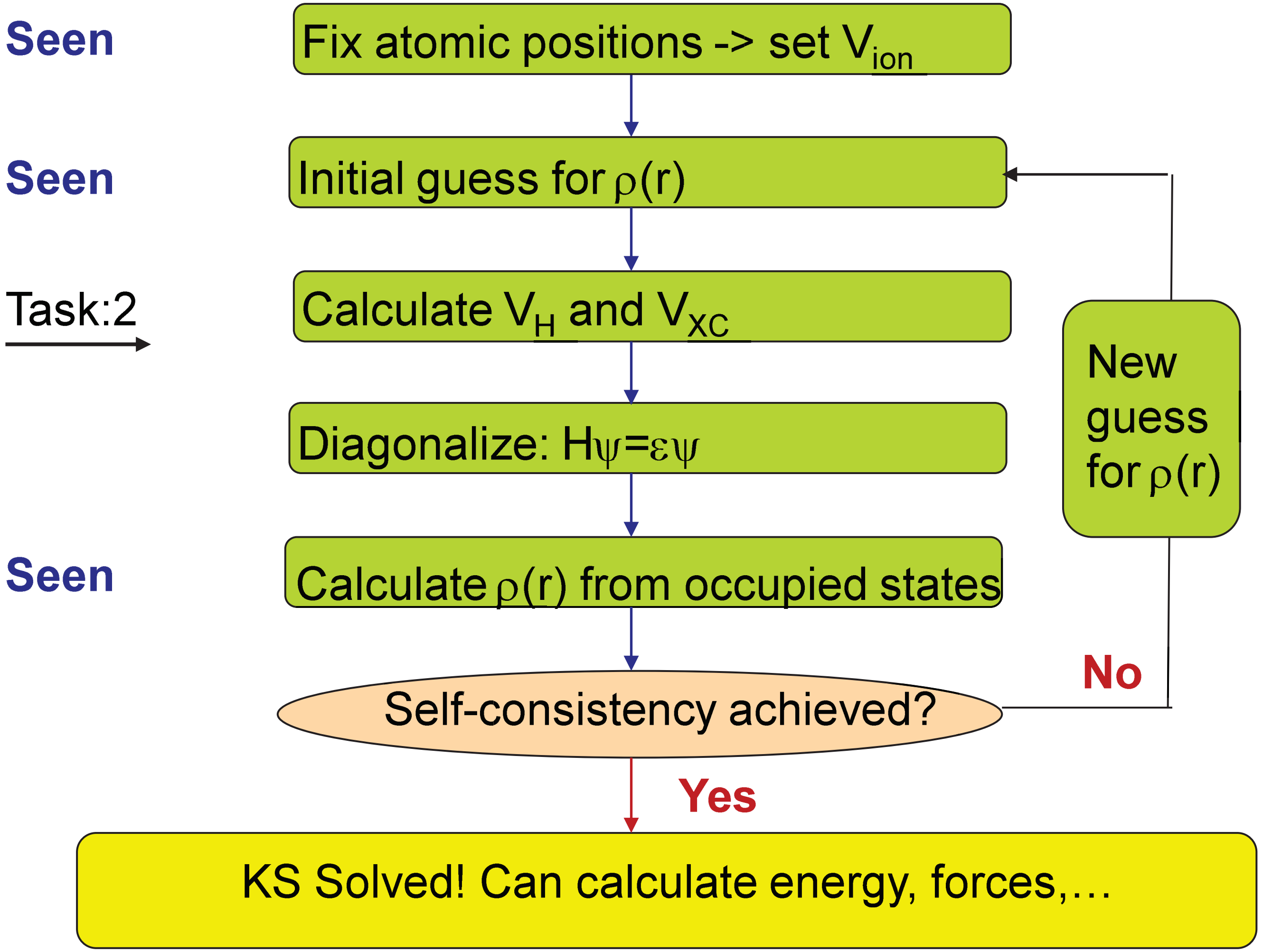
No

New guess for $\rho(r)$

Yes

KS Solved! Can calculate energy, forces,…

Other tasks in the scf calculations



Seen Fix atomic positions -> set V_{ion}

Seen Initial guess for $\rho(r)$

Task:2 → Calculate V_H and V_{XC}

Diagonalize: $H\psi=\varepsilon\psi$

Seen Calculate $\rho(r)$ from occupied states

Self-consistency achieved?

No → New guess for $\rho(r)$

Yes → KS Solved! Can calculate energy, forces,…

V_H & V_{XC} [ρ]

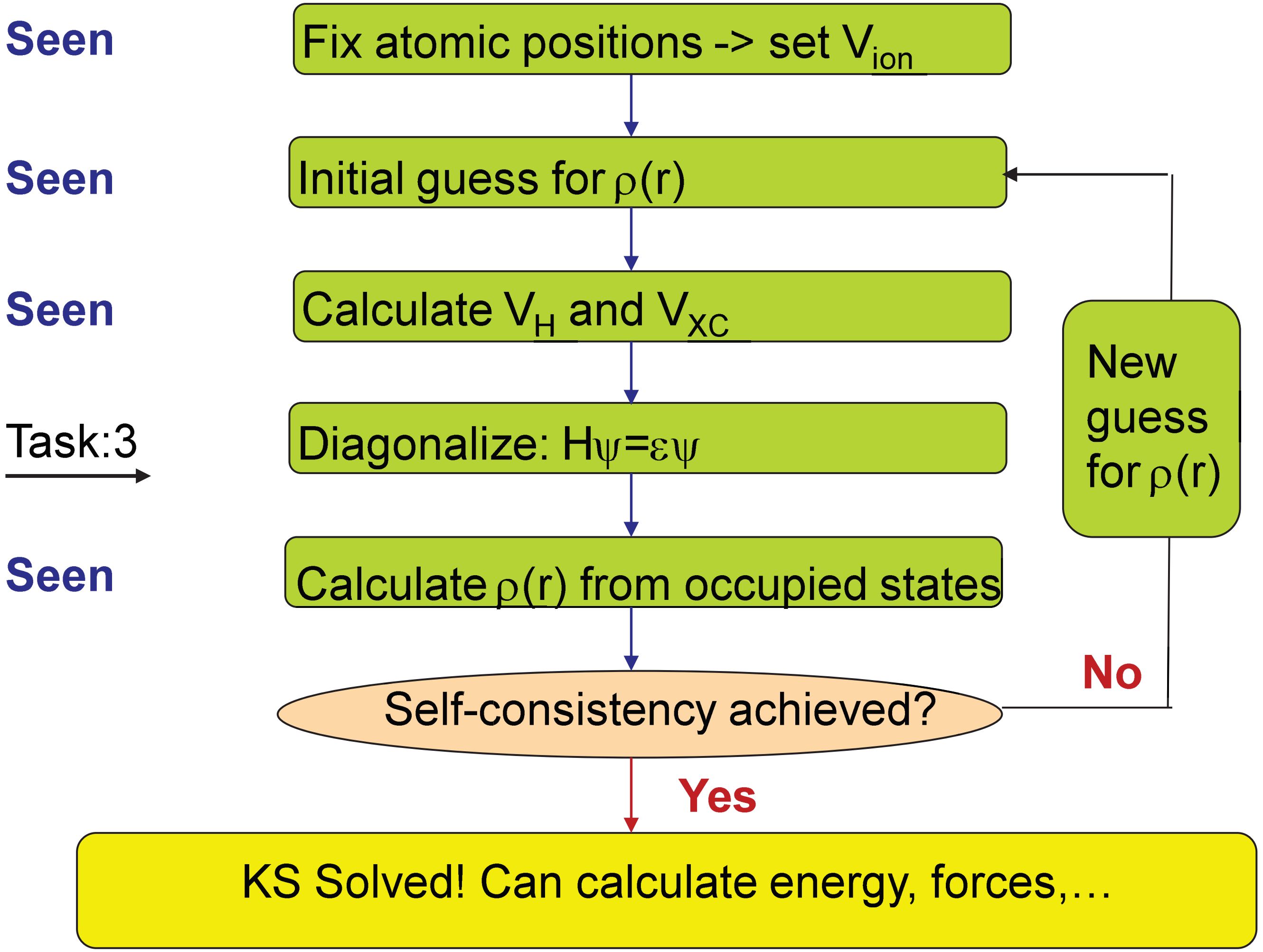
- V_H conveniently obtained in reciprocal space: $V_H(\mathbf{G}) = 4\pi\, e^2\, \rho(\mathbf{G})/G^2$ and efficient use of FFT

- V_{XC} conveniently set directly in real space: $V_{XC}[\rho(\mathbf{r}),\nabla\rho(\mathbf{r})]$

(the type of XC functional is chosen when specifying the pseudopotential)

Note: one needs then to iteratively apply H_{KS} on $\psi_{ki}^{(trial)}$: $H_{KS} e^{ikr} u_{ki}$, and the product $[V_H(r)+V_{XC}(r)]\bullet u_{ki}(r)$ is conveniently computed in real space

Other tasks in the scf calculations



Seen Fix atomic positions -> set V_{ion}

Seen Initial guess for $\rho(r)$

Seen Calculate V_H and V_{XC}

Task:3 Diagonalize: $H\psi=\varepsilon\psi$

Seen Calculate $\rho(r)$ from occupied states

Self-consistency achieved?

No New guess for $\rho(r)$

Yes KS Solved! Can calculate energy, forces,…

Iterative diagonalization

- In principle, in the plane-wave basis, the hamiltonian matrix size is $N_{PW}xN_{PW,}$ and N_{PW} is huge in general

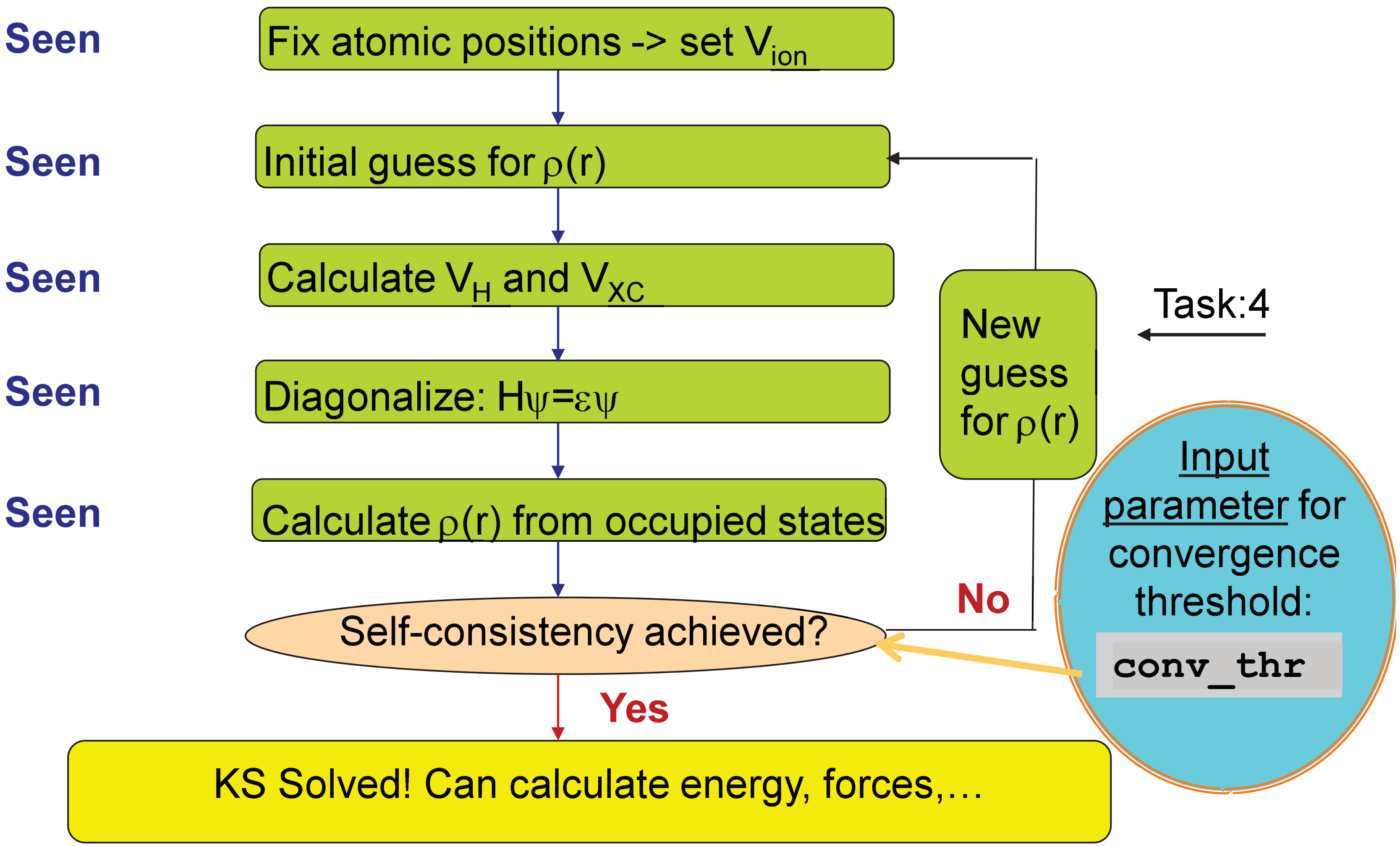
- prohibitive for exact diagonalization

- however only a small number of bands/eigenvalues are needed in general compared to N_{PW}
  -> the approach is to use iterative diagonalizations (need mainly H $\psi_i^{(trial)}$)

In input, parameters:

`diagonalization`	iterative-diagonalization algorithm: default is 'david' (Davidson), but can use also 'cg' (conjugate-gradient type)
`nbnd`	number of eigenvalues

Other main tasks in the scf calculations



Seen Fix atomic positions -> set V_{ion}

Seen Initial guess for $\rho(r)$

Seen Calculate V_H and V_{XC}

Seen Diagonalize: $H\psi=\varepsilon\psi$

Seen Calculate $\rho(r)$ from occupied states

Self-consistency achieved?

No → New guess for $\rho(r)$ ← Task:4

Yes → KS Solved! Can calculate energy, forces,…

Input parameter for convergence threshold: `conv_thr`

Mixing

- It may take many, many iterations to reach self-consistency ($\rho_{out} = \rho_{in}$)

- Using just ρ_{out}(it=i) as input charge for ρ_{in}(it=i+1) usually does not work

- It is necessary to mix, i.e., use some combinations of input and output charges (using also information from the previous iterations) to get/accelerate convergence

Input parameters:

`mixing_mode`	mixing scheme, default is 'plain' (Broyden), can be also 'TF' (plain with Thomas-Fermi-like screening)
`mixing_beta`	how much new charge is used at the 1st mixing step (typical values are 0.1 to 0.7)

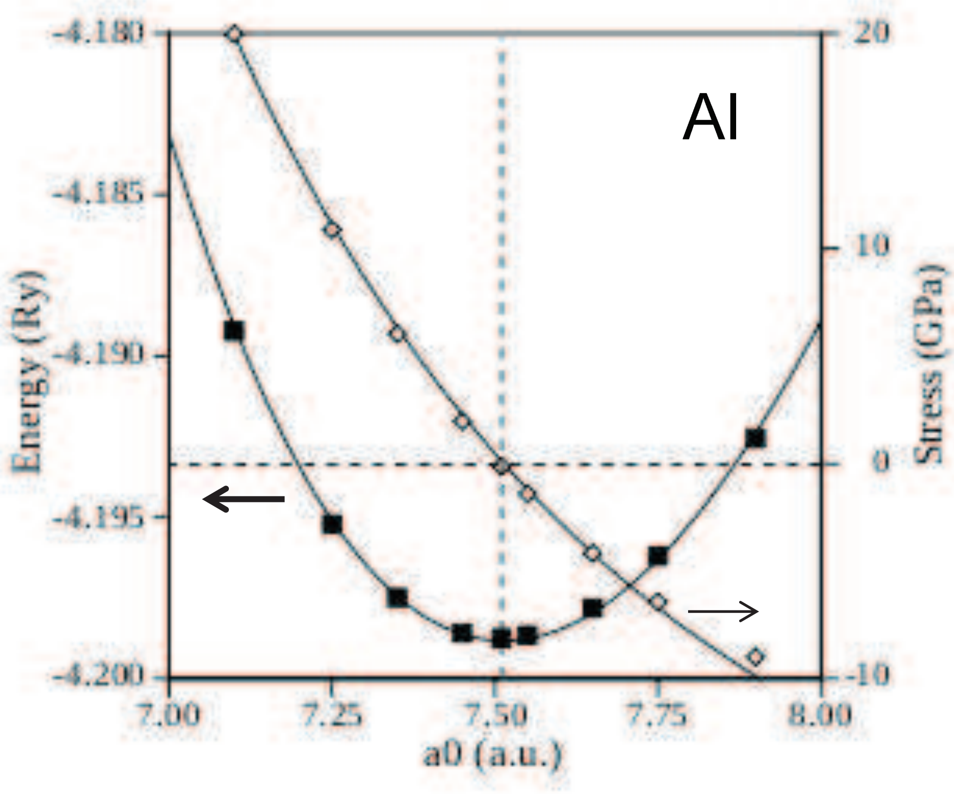
Output values: total energy, forces, stresses

- Can be used to optimize the atomic structure

e.g., lattice parameter of cubic crystal

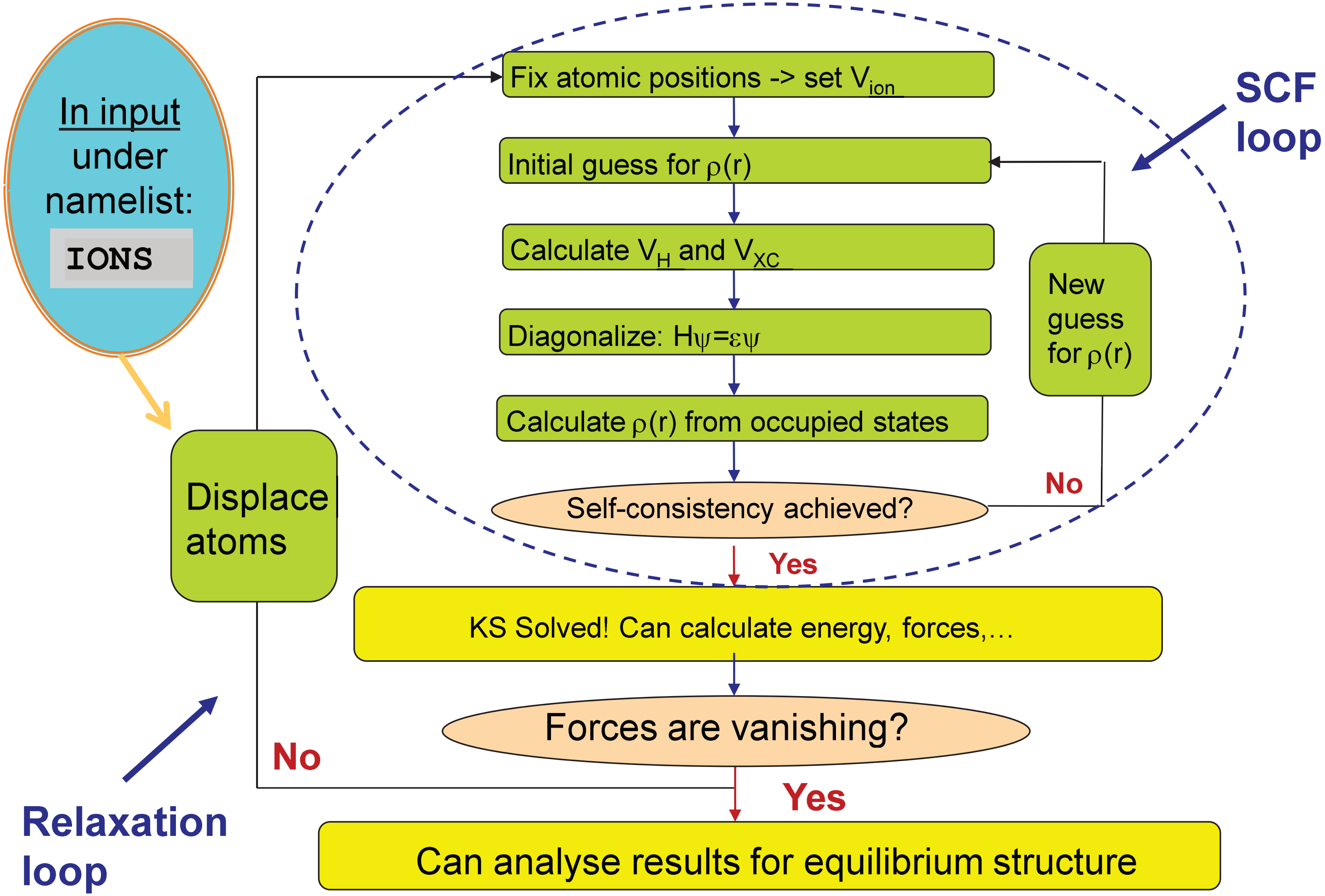
In input, to print forces and calculate stresses:

```
tprnfor = .true.
tstress = .true.
```



C. Fall EPFL Thesis

Atomic relaxation calculations



In input under namelist: `IONS`

Fix atomic positions -> set V_{ion}

Initial guess for $\rho(r)$

Calculate V_H and V_{XC}

Diagonalize: $H\psi=\varepsilon\psi$

Calculate $\rho(r)$ from occupied states

Self-consistency achieved?

No

New guess for $\rho(r)$

SCF loop

Yes

KS Solved! Can calculate energy, forces,…

Forces are vanishing?

No

Displace atoms

Yes

Can analyse results for equilibrium structure

Relaxation loop