SIESTA-PRO: SIESTA Code Ready for the Industry

The fundaments of computational simulations with SIESTA

siesta™

SIMUNE ATOMISTIC SIMULATIONS

ImagineNano - 15.03.2018

SUMMARY

- **INTRODUCTION**
  - SIMUNE and SIESTA
  - SIESTA-PRO: SIESTA code ready for the industry
- **SIESTA CODE: MAIN TECHNICAL FEATURES**
- **EXCITED STATES PROPERTIES FOR SIESTA CALCULATIONS: TDDFT and beyond**
- **HINTS TO PERFORM AN ACCURATE AND WELL-CONVERGED SIESTA CALCULATION**
  - Input file. Principal SIESTA Input Parameters
  - Pseudopotential
  - Basis set. The Delta-test
- **ANALYSIS OF THE RESULTS. POST-PROCESSING SIESTA OUTPUT**

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SIMUNE

SIMUNE is a company launched in 2014 as a joint venture of a group of scientific experts and the Nanoscience Cooperative Research Center CIC nanoGUNE (www.nanogune.eu)

Know more about us on: www.simune.eu

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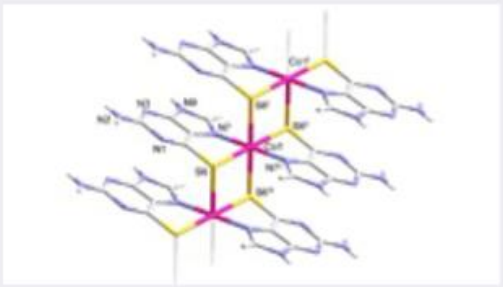
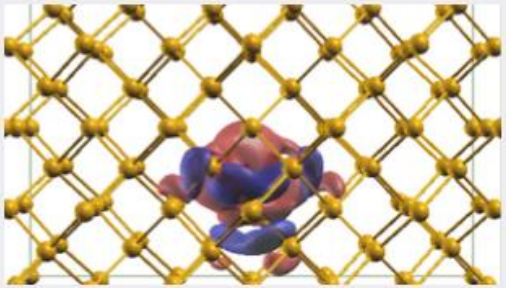
SIMUNE Services

◆ CONSULTANCY

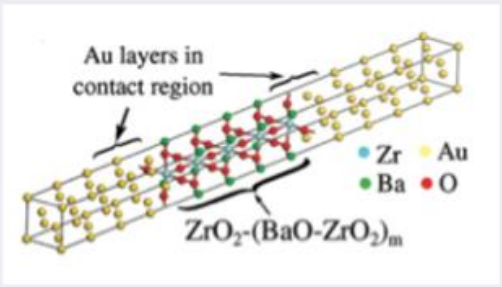
- MATERIALS DESIGN



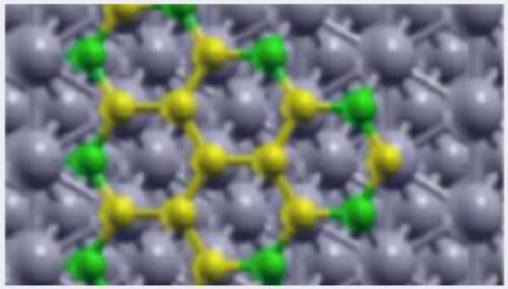
COMPLEX OXIDES



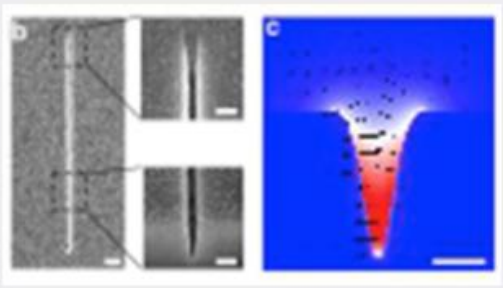
RADIATION DAMAGE



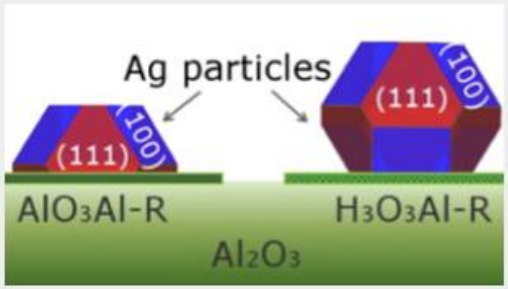
SEMICONDUCTORS



GRAPHENE



NANOPHOTONICS



CATALYSIS

SIMUNE Services

◆ **PROFESSIONAL SUPPORT** siesta™

In 2015, SIMUNE established a strategic partnership with SIESTA

- TRAINING, COURSES and STAFFING
- SIESTA-PRO: ADVANCED SOLUTIONS FOR THE PROFESSIONAL USE OF SIESTA

1 YEAR SUBSCRIPTION BASED SUPPORT: RECEIVE CUSTOMIZED AND PROFESSIONAL SUPPORT FOR YOUR MATERIALS DESIGN CHALLENGE

SIMUNE

In 2016, SIMUNE has established a collaboration agreement with the Centre for Excellence MAX (http://www.max-centre.eu) in order to offer advanced atomic-scale professional services to the European Industry.

MAX
DRIVING THE EXASCALE TRANSITION

In 2016, SIMUNE has established a collaboration agreement with JSOL in order to offer professional services for SIESTA in Japan.

株式会社JSOL

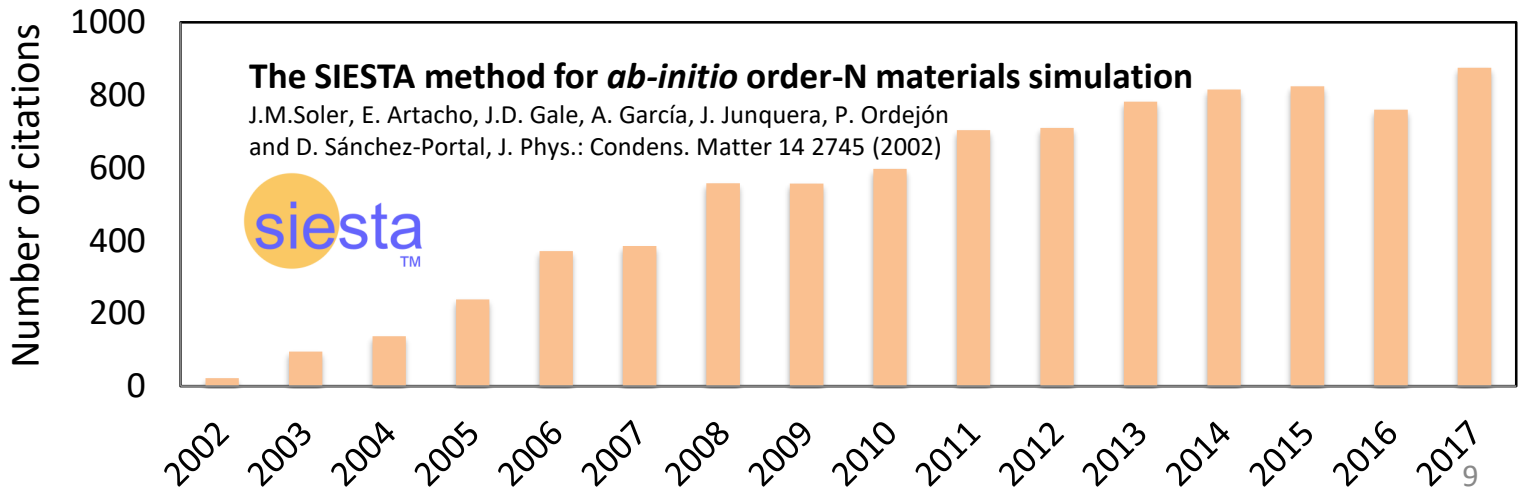
In 2017, SIMUNE has established a collaboration agreement with the MIT to beta test SIMUNE's MVP's and prototypes.

Know more about us on: www.simune.eu

SIESTA

SIESTA (Spanish Initiative for Electronic Simulations with Thousands of Atoms) is both a method and its computer program implementation, to perform efficient electronic structure calculations and *ab-initio* molecular dynamics simulations of **molecules** and **solids**

- SIESTA was born as a **collaborative project**
- SIESTA is in **continuous development** since it was implemented
- SIESTA has become very popular, being increasingly used by researchers in geosciences, biology, and engineering (apart from those in its natural habitat of materials physics and chemistry)



SIESTA-PRO: SIESTA code ready for the industry

SIMUNE has received funds to develop the project: **SIESTA-PRO** - Spanish Initiative for Electronic Simulations with Thousands of Atoms: Open Source code with professional support and warranty.

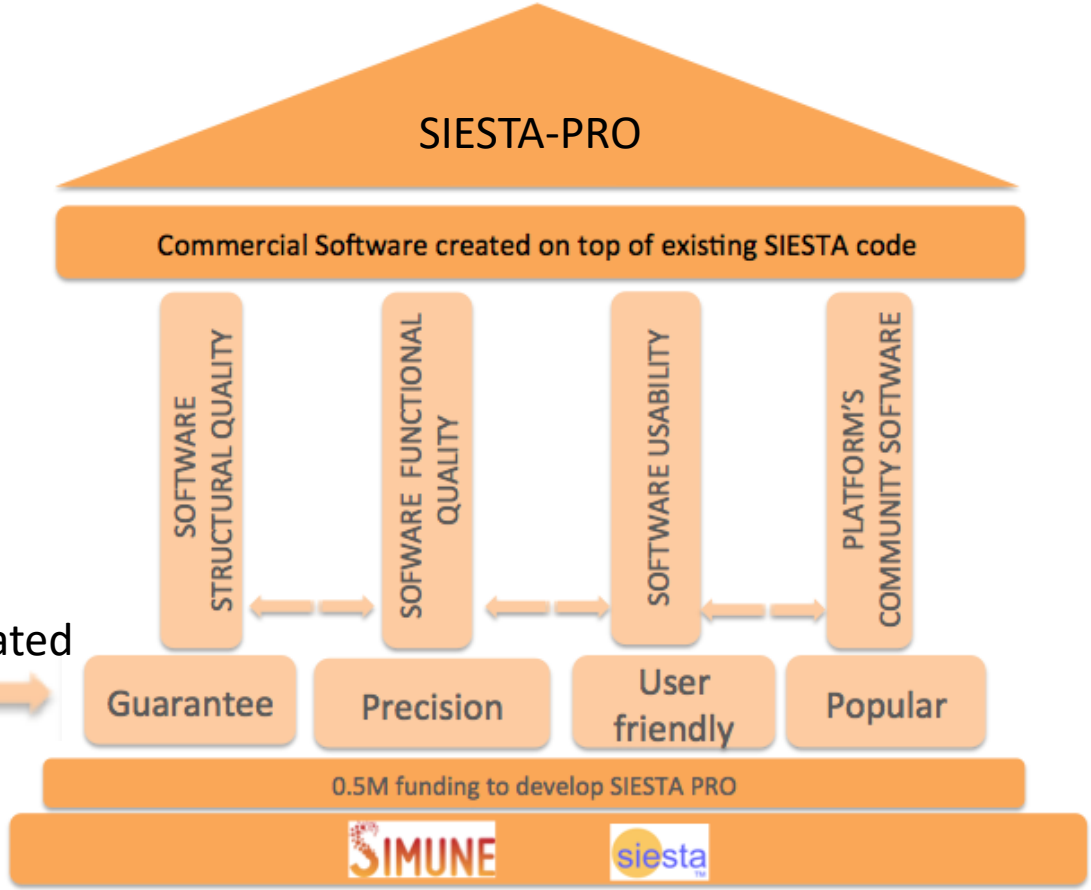
- Universidad de Cantabria (Javier Junquera)

- CFM (Daniel Sanchez Portal)

- CIC Nanogune (Emilio Artacho)

SIESTA-PRO: SIESTA code ready for the industry

SIESTA-PRO is being built on top the SIESTA code



Current developments dedicated to improving four aspects of the code

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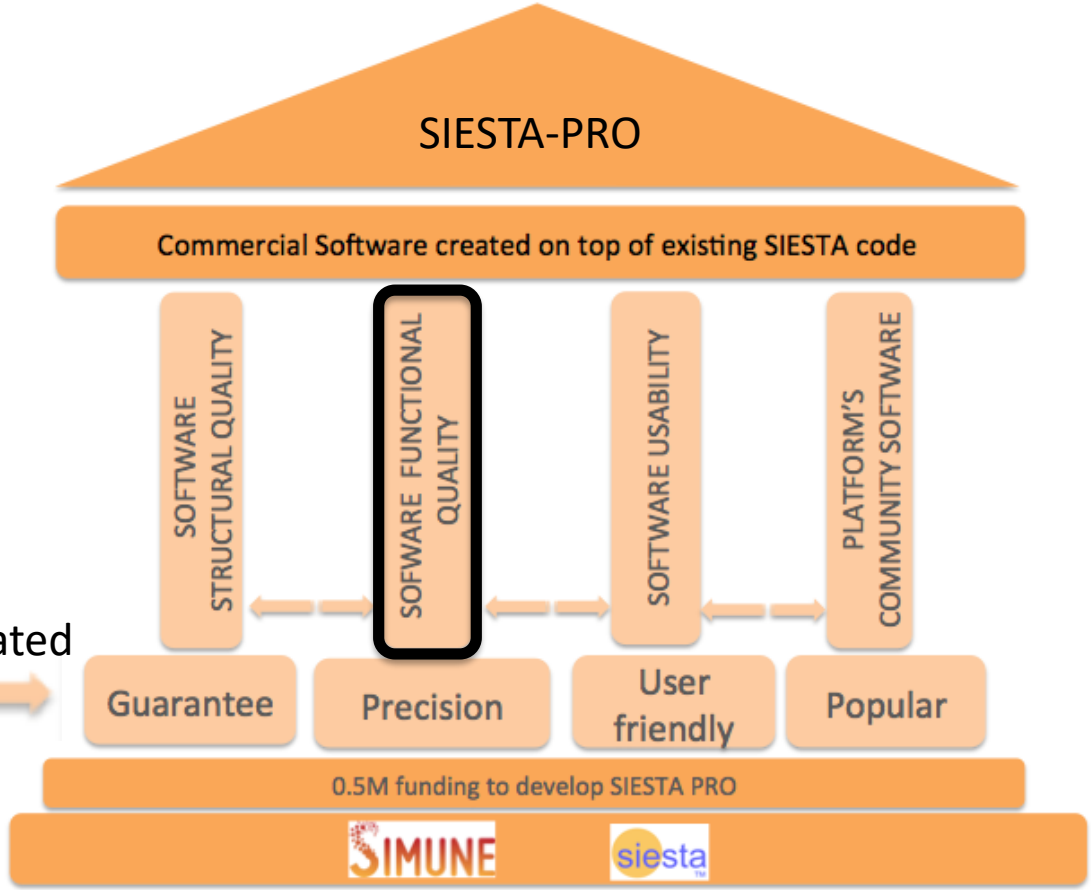

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SIESTA-PRO

SIESTA Code Capabilities

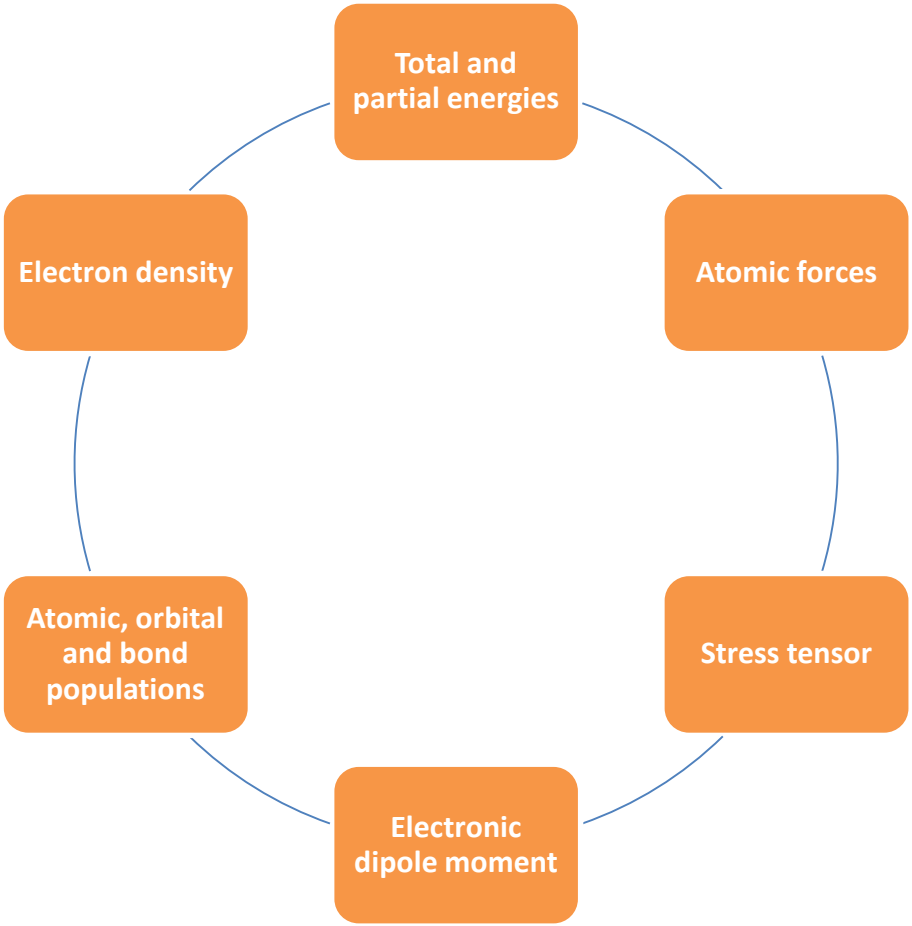
There is an effort to extend the code capabilities in the following areas:

- Material properties computed
- Implemented solutions beyond DFT
- Technical solutions enhancing the code efficiency
- Link with other codes to expand SIESTA capacity

We aim SIESTA to be the **atomistic simulation code of reference**

SIESTA-PRO: Material Properties Computed by SIESTA

SIESTA routinely provides:



SIESTA-PRO: Material Properties Computed by SIESTA

And also:

Geometry relaxation, fixed or variable cell	Constant-temperature molecular dynamics (Nose thermostat)	Variable cell dynamics (Parrinello-Rahman)
Spin polarized calculations (collinear or not)	Local and orbital-projected Density Of States (DOS)	K-sampling of the Brillouin zone
Dielectric polarization	COOP and COHP curve for chemical bonding abalysis	Band structure
Vibration (phonons)	Wannier function implementation	Ballistic electron transport (through TranSIESTA)

SIESTA-PRO: Main Solutions Implemented in SIESTA

- **Collinear and non-collinear spin polarized calculations**
  Description of magnetic systems

- Efficient implementation of **Van der Waals** functional
  Weak VdW interactions

- **Wannier function implementation:**
  Description of the chemical bonds

- **TranSIESTA/TBTrans** module (**NEW! In version 4.1**)
  Transport calculations

SIESTA-PRO: Main Solutions Implemented in SIESTA

- On-site Coulomb corrections (**LDA+U**) (**NEW! In version 4.1**)
  Description of strong localized electrons, transition metal oxides

- **Spin-orbit coupling** (**SOC**) (**NEW! In version 4.1**)
  Topological insulator, semiconductor structures, and quantum-transport calculations

- **NEB (Nudged Elastic Band):** (**NEW! In version 4.1**)
  To explore reaction paths. Important, for example, in catalysis processes.

SIESTA-PRO: SIESTA Solutions Under Development

- **GW** approximation
  Electron photoemission, photoabsorption, fotoluminiscencia, charge transfer, band gap and conduction band characteristics

- **Time Dependent DFT (TDDFT)**
  For excitation energies, photoabsoprtion spectra, induced density and time-dependent properties

- **Hybrid Functional**
  Activation energy barriers and band gap

- **Band unfolding**
  To investigate the effects of minor crystal defects

- **Poisson solver in real space**
  To improve the description of molecules and finite systems

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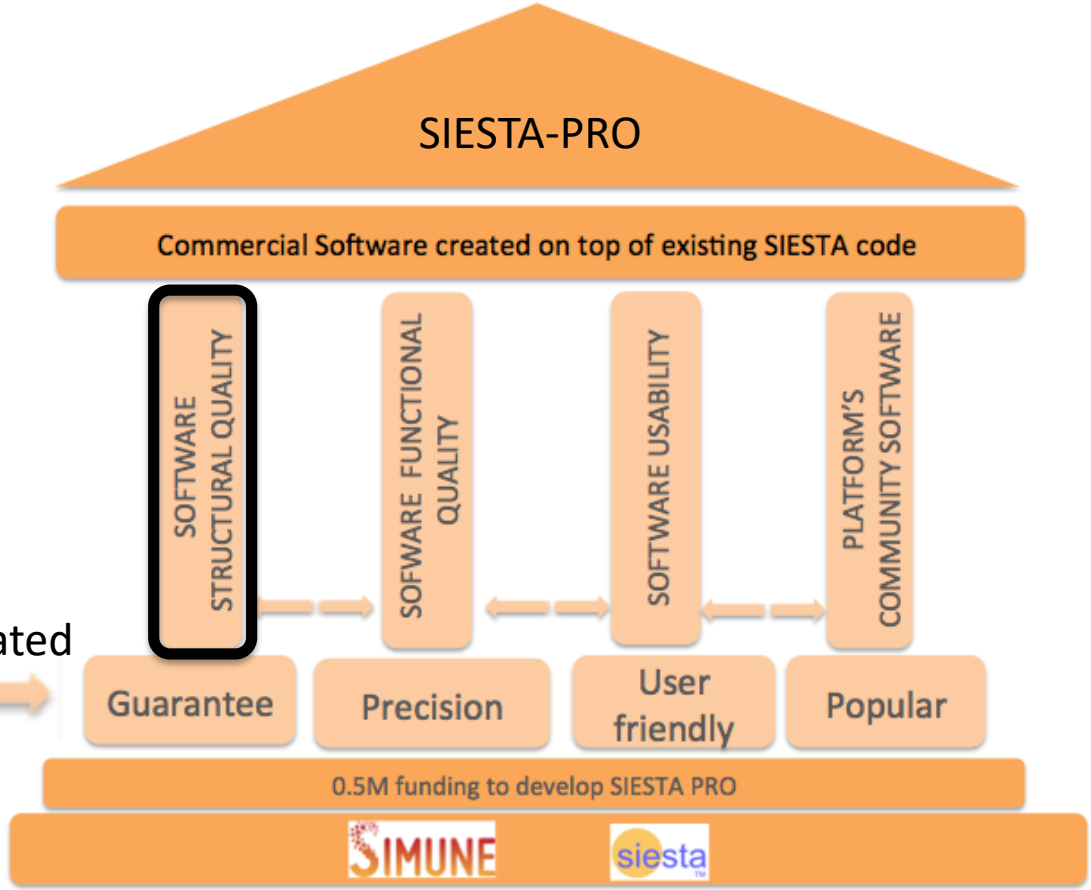
SIESTA-PRO is being built on top the SIESTA code



Current developments dedicated to improving four aspects of the code

SIESTA-PRO

SIESTA Code Quality

SIMUNE is taking the following actions to guarantee a good practice on the development of the SIESTA code:

- Extensive code documentation
- Control version system: Bazaar - Launchpad
- SIESTA code development rules
- Code testing at different level (Unit tests &Test suite)

SIESTA-PRO: SIESTA code ready for the industry

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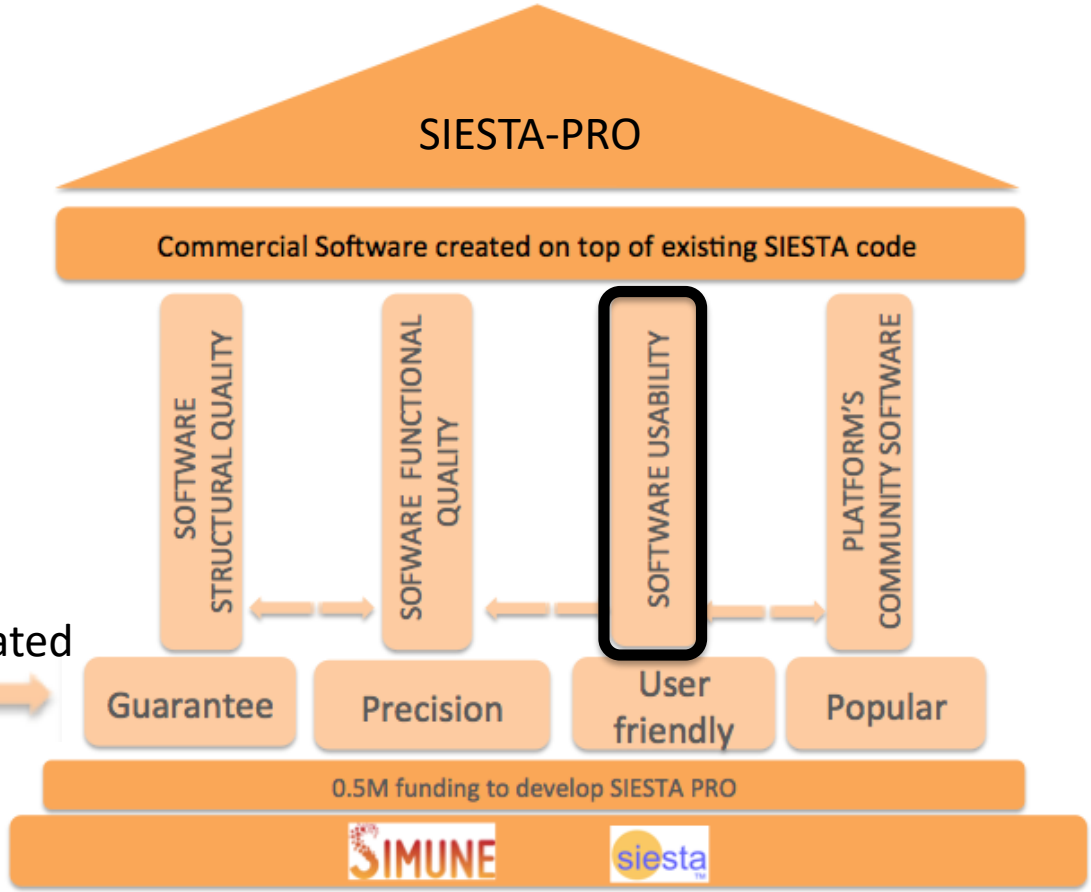
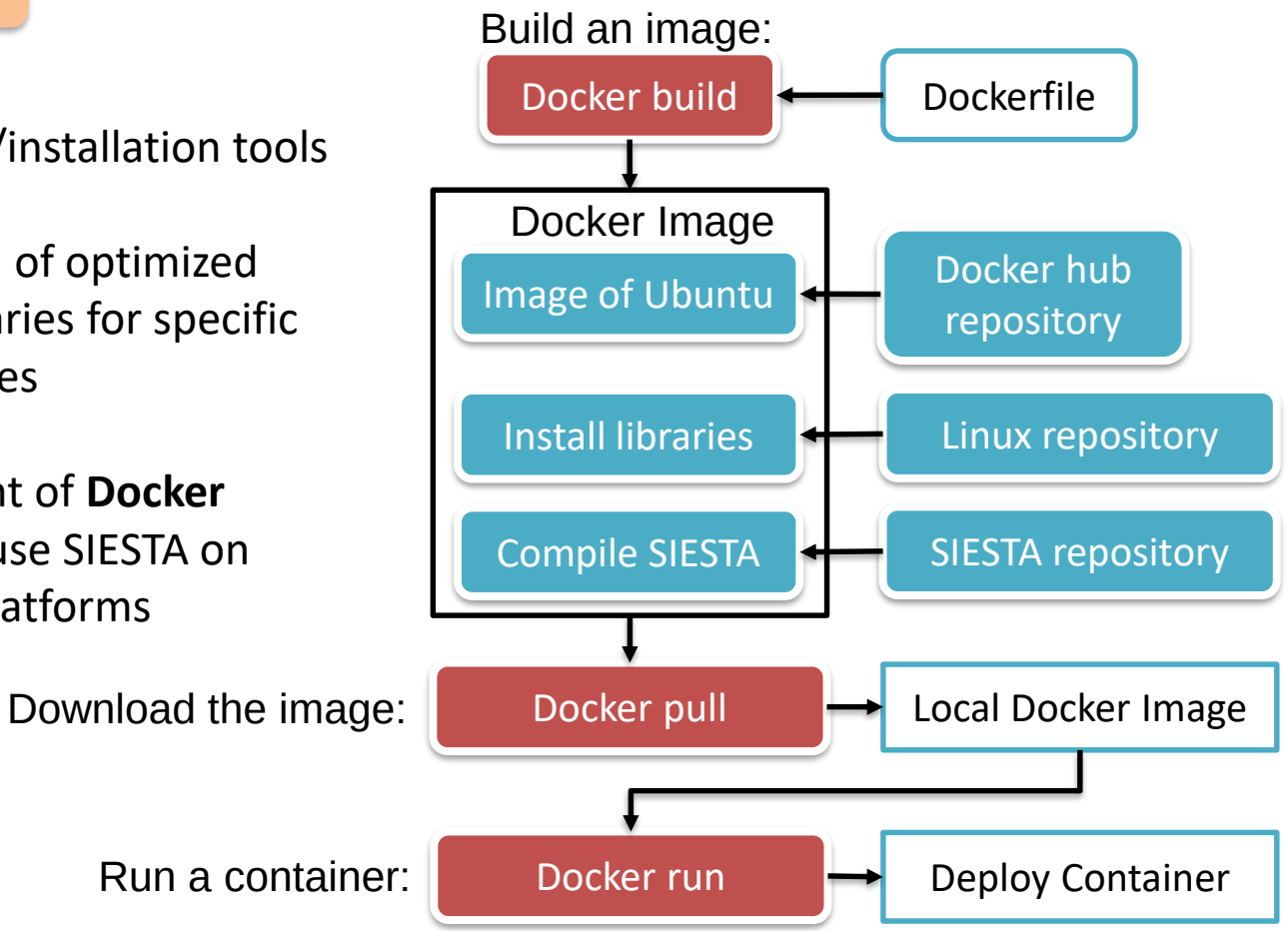


Current developments dedicated to improving four aspects of the code

SIESTA-PRO

Software Usability

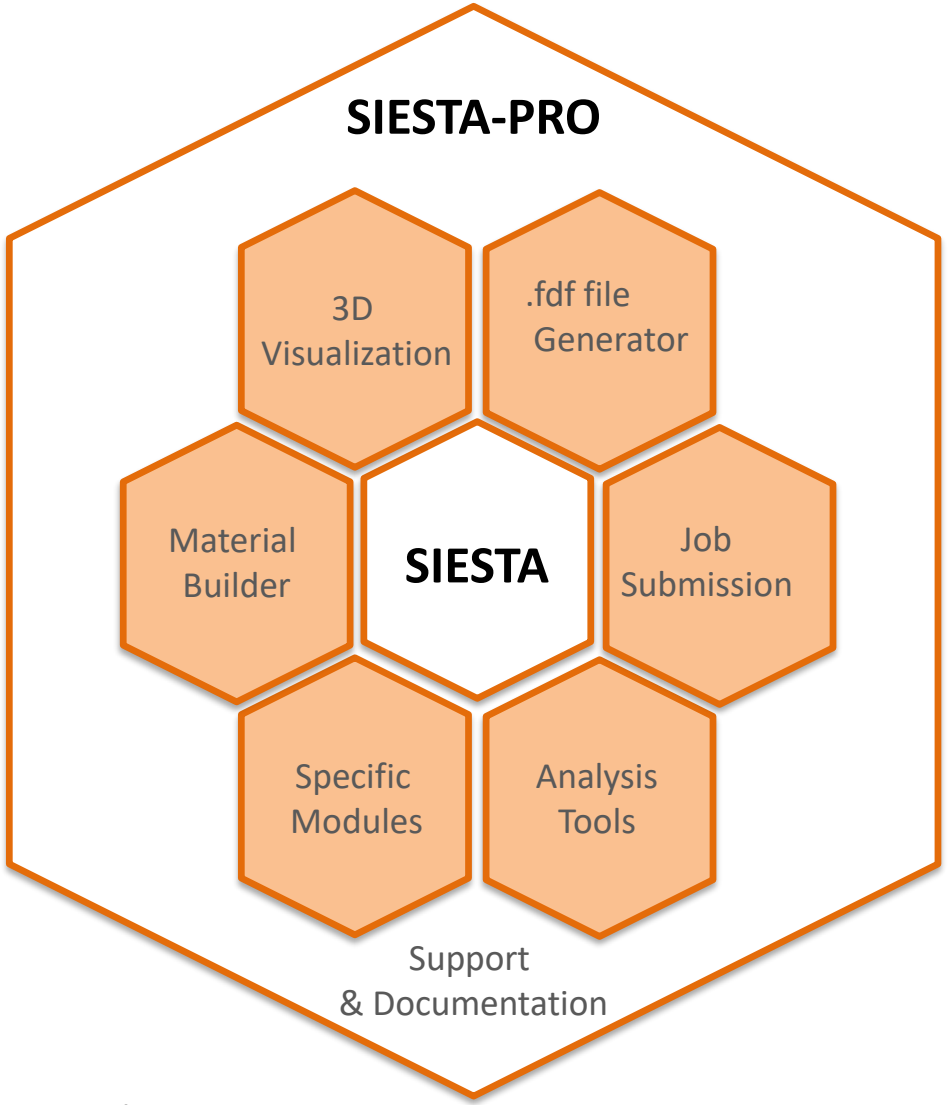
- Automatization/installation tools
  - Generation of optimized SIESTA binaries for specific architectures
  - Deployment of **Docker** images to use SIESTA on different platforms



SIESTA-PRO: GUI

Software Usability

- Graphical User Interface (GUI) for SIESTA



SIESTA-PRO

Software Usability

- Pseudopotential and basis set database
  - SIMUNE has designed an optimization protocol involving a simplex algorithm that works in conjunction with the ATOM* code to calculate highly transferable pseudopotentials
  - SIMUNE follows a well-defined standard procedure to obtain reliable highly transferable basis sets

* ATOM code is maintained by Alberto Garcia. Since 2017, the code is no longer bundled with Siesta. It can be download it from the Siesta webpage at www.icmab.es/siesta

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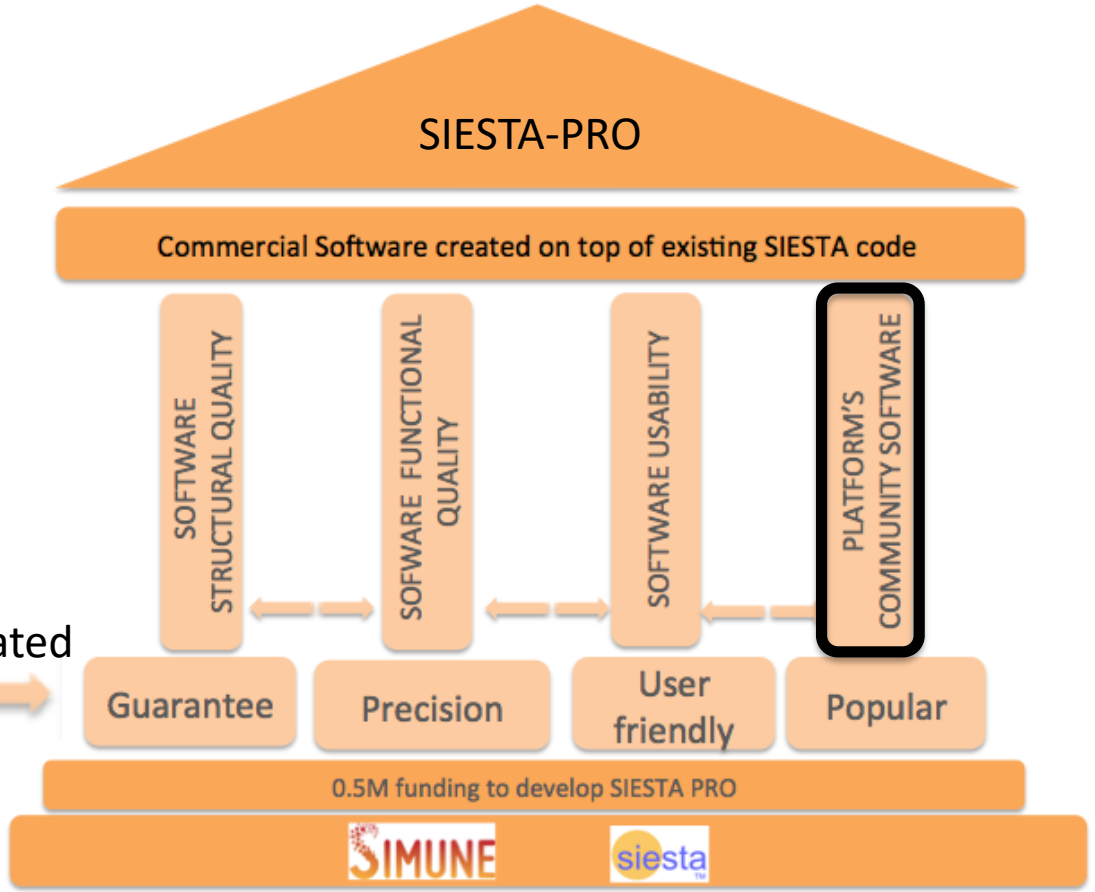


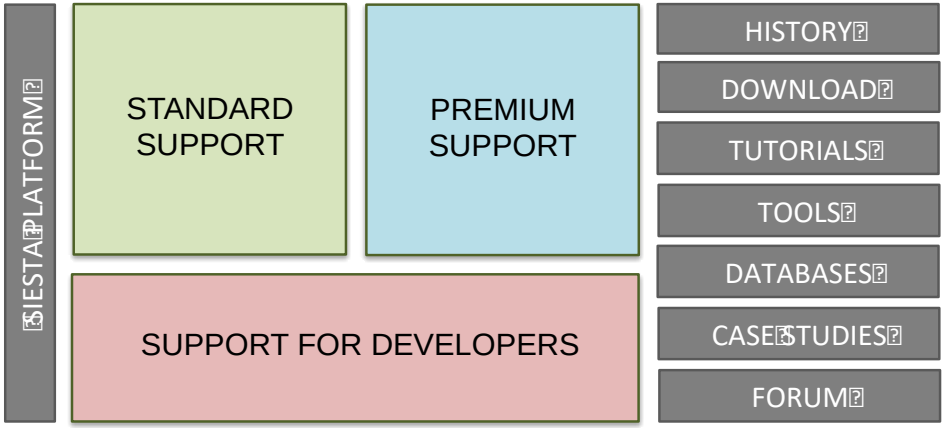
Current developments dedicated to improving four aspects of the code

SIESTA-PRO

Platform's community software

Functional and social tool around the SIESTA code

- A space to gather SIESTA community
- Platform that SIMUNE will use to provide official support to SIESTA: Forum, newsletter, bulletin, case studies…



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SIESTA Code: Main Technical Features

Characteristics Overview:

- SIESTA uses the standard Kohn-Sham self-consistent **DFT Method**
- Several **Exchange Correlation Functionals** are implemented
- Numerical evaluation of **matrix elements**
- Projection of electron wavefunctions and density onto a **real-space grid**
- It uses **norm-conserving pseudopotentials**
- It uses **atomic orbitals** as a basis set

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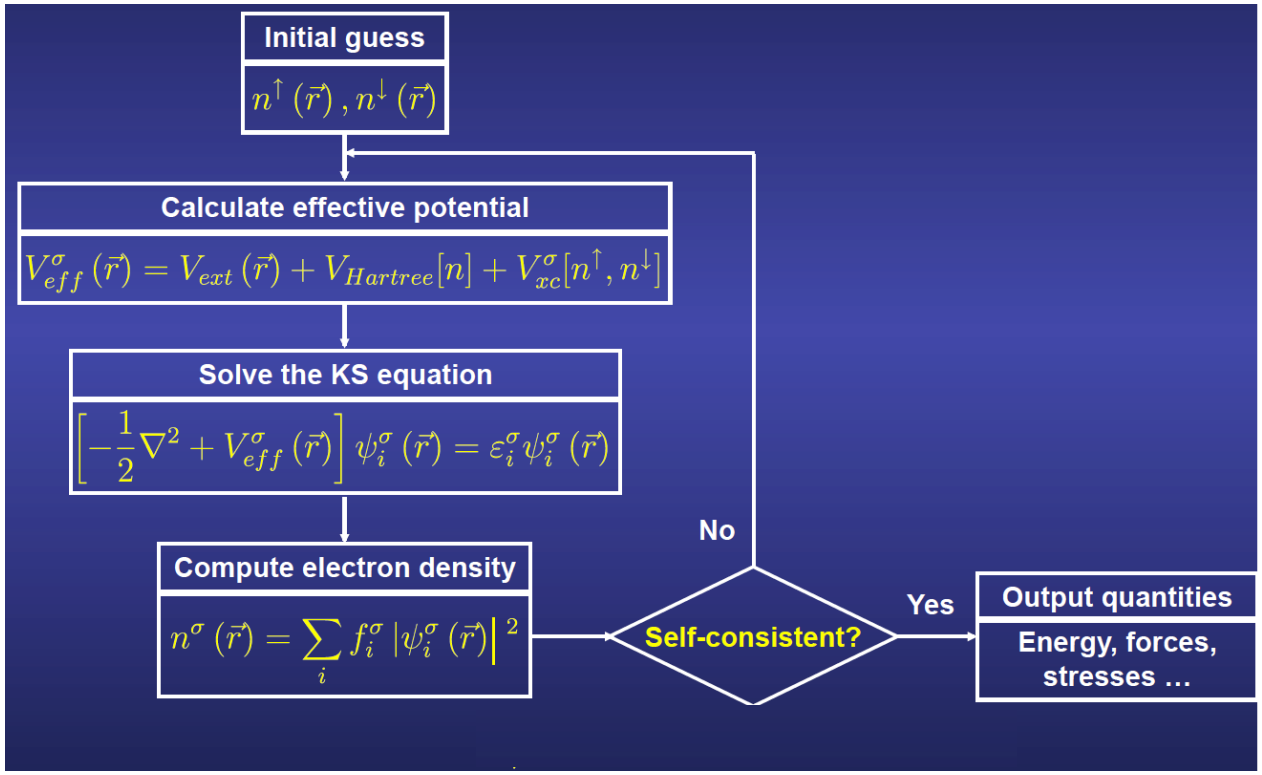
SIESTA Code: Main Technical Features

- SIESTA uses the standard Kohn-Sham self-consistent Density Functional Method (**DFT**)



The Kohn-Sham equations must be solved self-consistently
The effective potential (input) depends on the density (output)

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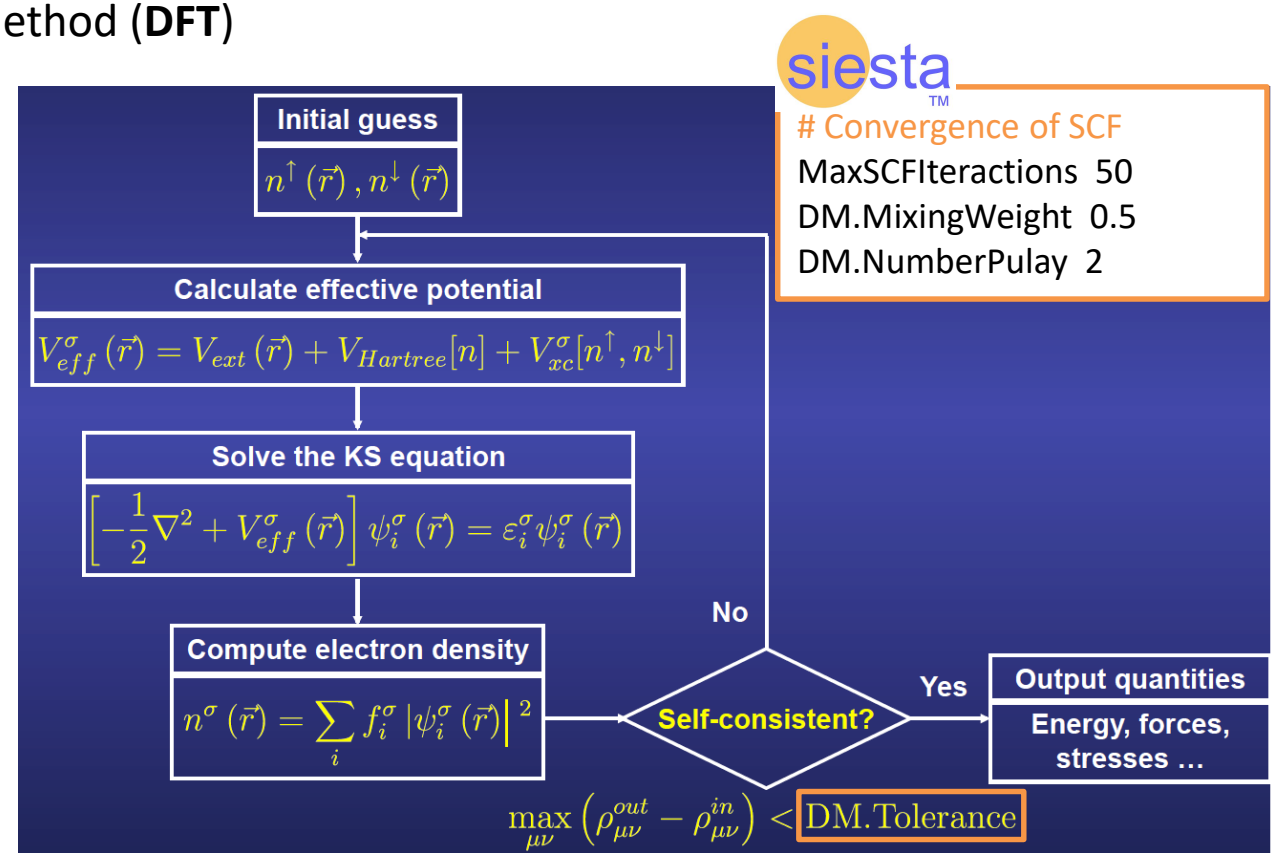

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SIESTA Code: Main Technical Features

Density functional theory hamiltonian

$$\hat{H} = \hat{T} + \sum_{\alpha} \hat{V}_{\alpha}^{PS} + V^{H}(\vec{r}) + V^{xc}(\vec{r})$$

Kinetic energy operator

Semilocal pseudopotential

Hartree potential

Exchange-correlation potential

SIESTA Code: Main Technical Features

$$\hat{H} = \hat{T} + \sum_{\alpha} \hat{V}_{\alpha}^{PS} + V^{H}(\vec{r}) + V^{xc}(\vec{r})$$

Exchange-correlation potential, *unknown*

siesta

XC.Functional	**LDA*** $V_{xc}(\rho(\mathbf{r}))$	**GGA*** $V_{xc}(\rho(\mathbf{r}), \lvert\nabla\rho(\mathbf{r})\rvert)$
XC.authors	CA / PW92	PW91 / PBE /revPBE /RPBE/WC/AM05 /PBEsol/ PBEJsJrL0/PBEJsJr HEG PBEGcGxLO PBEGcGxHEG/BLYP

*__Spin__ dependence possible: **SpinPolarized** **.true.**

$$E_{xc}\left[\rho_{\uparrow}(\mathbf{r}), \rho_{\downarrow}(\mathbf{r})\right] \Rightarrow V_{xc}^{\uparrow\downarrow}(\mathbf{r})$$

SIESTA Code: Main Technical Features

$$\hat{H} = \hat{T} + \sum_{\alpha} \hat{V}_{\alpha}^{PS} + V^{H}(\vec{r}) + V^{xc}(\vec{r})$$

Exchange-correlation potential, *unknown*

siesta

XC.Functional	**vdW** (siesta4.0) $V_{xc}(\mathbf{r}) = \int K\left(\rho(\mathbf{r}), \nabla\rho(\mathbf{r}), \rho(\mathbf{r}'), \nabla\rho(\mathbf{r}'), \lvert\mathbf{r}-\mathbf{r}'\rvert\right) d^3\mathbf{r}'$
XC.authors	DRSLL / LMKLL/ KBM / C09/ BH/ VV

- *Implementation of **Hybrid Functional** in SIESTA is under development*

SIESTA Code: Main Technical Features

Khon-Sham Equation

$$\hat{h}\psi_n(\mathbf{r}) = \epsilon_n \psi_n(\mathbf{r})$$

eigenstates eigenvalues

Generalized eigenvalue problem

$$\mathbf{H}\vec{c} = \epsilon \mathbf{S}\vec{c}$$

- **Numerical evaluation of matrix elements**

matrix elements

Hamiltonian

$$h_{nm} = \int d^3\mathbf{r}\, f_n^*(\mathbf{r})\, \hat{h} f_m(\mathbf{r})$$

Overlap

$$S_{nm} = \int d^3\mathbf{r}\, f_n^*(\mathbf{r})\, f_m(\mathbf{r})$$

Numerical integration;
Substitution of integral by a discrete sum

$$\int d\vec{r}\phi_\nu^*(\vec{r})V(\vec{r})\phi_\nu(\vec{r}) \approx \sum_i \phi_\nu^*(\vec{r})V(\vec{r})\phi_\nu(\vec{r})\Delta\vec{r}$$

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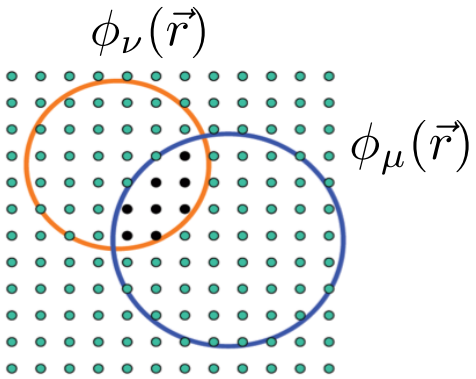
```
# Finesse of the grid
MeshCutoff   400
```

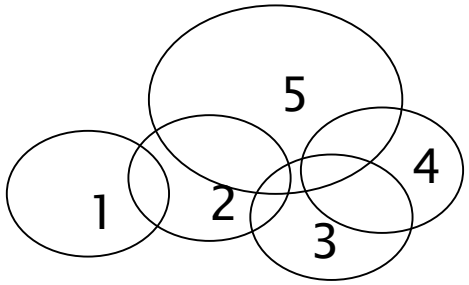
SIESTA Code: Main Technical Features

- Projects the **electron wavefunctions** and **density** onto a **real-space grid** in order to calculate the Hartree and exchange-correlation potentials and their matrix elements.

Three-dimensional real space grid



$$< \phi_\nu | V(\vec{r}) | \phi_\mu >$$



	interaction with
1	1, 2
2	1, 2, 3, 5
3	2, 3, 4, 5
4	3, 4 5
5	2, 3, 4, 5

sparsity

- Only the points falling in the overlapping region are considered
- The range of overlap of two given functions is limited. This range typically includes second / third coordination spheres around each atom, depending on the system

SIESTA Code: Main Technical Features

- **Matrix elements:** The calculation of the **H** and **S** matrix elements is always done with an **O(N)** method.

$$S_{\nu\mu} =< \phi_\nu|\phi_\mu >= \int d\vec{r}\phi^*_\nu(\vec{r})\phi_\mu(\vec{r}) \qquad H_{\nu\mu} =< \phi_\nu|\hat{H}|\phi_\mu >= \int d\vec{r}\phi^*_\nu(\vec{r})\hat{H}\phi_\mu(\vec{r})$$

- **Solution.** SIESTA can use different methods, **SolutionMethod** :

- Standard Diagonalization (**Diagon**): Cubic scaling with the size. **O(N^3)**

- Cubic scaling minimization (**OMM**). **O(N^3)** (F. Corsetti. Comput. Phys. Commun. **185**, 873 (2014))

- SIESTA-PEXSI. The actual computational cost depends on the dimensionality of the system. **1D: O(N) / 2D: O($N^{1.5}$) / 3D: O(N^2)** (metals and insulators)

- Linear scaling (**OrderN**). It only works for systems with clearly separated occupied and empty states. **O(N)** (insulators)

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◆ TranSIESTA;
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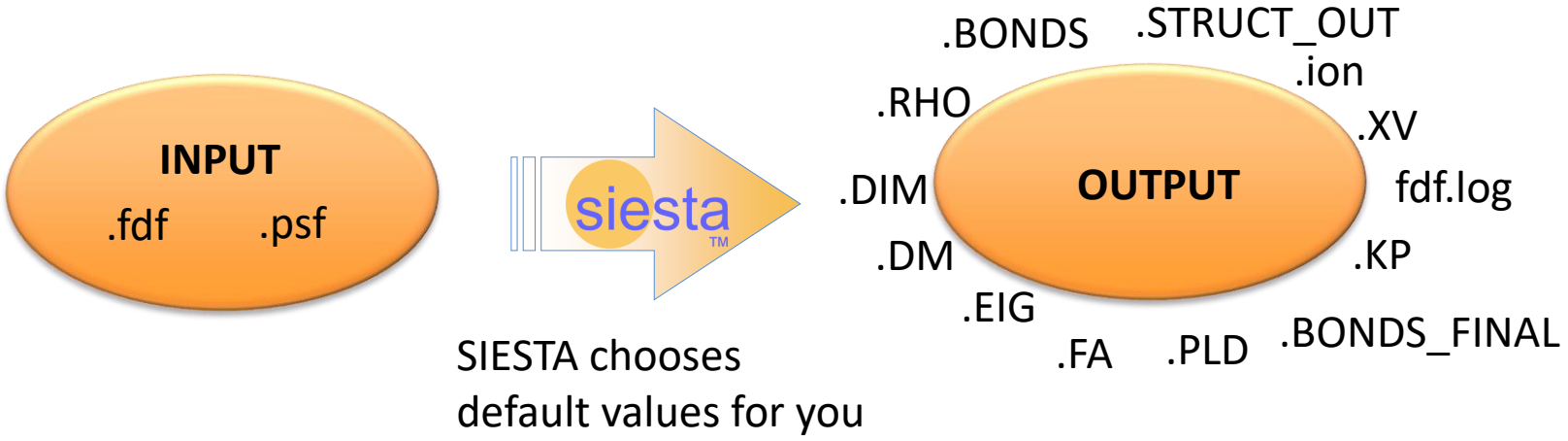
Atomistic Simulation with SIESTA



1. - An **input** file (Flexible Data Format (**.fdf**))

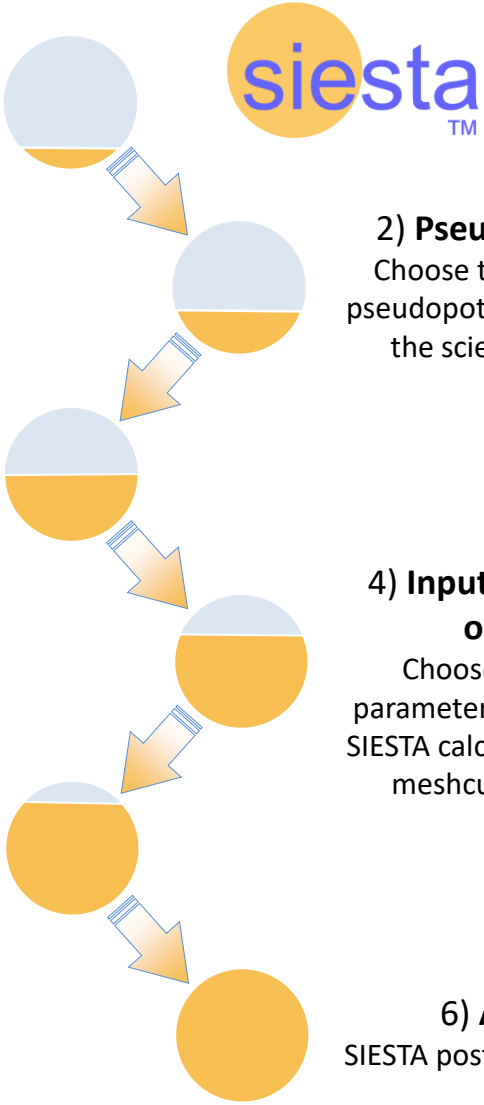
   - **Physical data** of the system

2.- A **pseudopotential** file for each kind of element in the input file (.vps, .psf or .psml)

Atomistic Simulation with SIESTA

- How to perform an accurate and well-converged SIESTA calculation

1) **Problem definition**
System model, properties , accuracy



2) **Pseudopotential**:
Choose the appropriate pseudopotential that model the science you want

3) **Basis set**:
Test the convergence of the physical properties you are interested in against the basis speed vs accuracy

4) **Input file Program options**:
Choose the specific parameters that define the SIESTA calculation (k-points, meshcutoff, XC, spin)

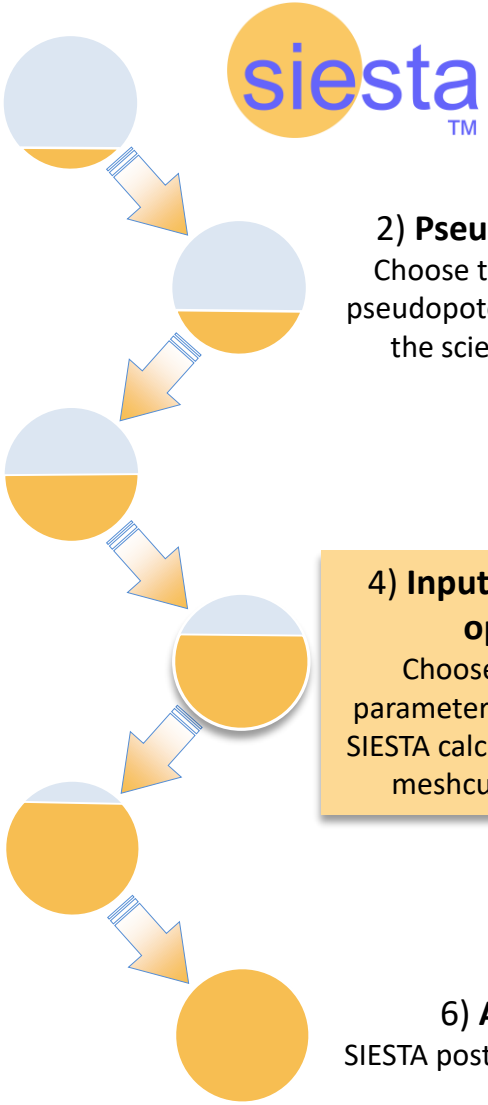
5) **Production run**

6) **Analysis**:
SIESTA post-processing tools

Atomistic Simulation with SIESTA

- How to perform an accurate and well-converged SIESTA calculation

1) **Problem definition**
System model, properties , accuracy



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Atomistic Simulation with SIESTA: Input File

Flexible Data Format (**FDF**)

- **Physical data** of the system
- Atomic Orbitals **Basis set**
- Variables to control the approximation (convergence parameters)

Atomistic Simulation with SIESTA: Input File

Flexible Data Format (**FDF**)

- **Physical data** of the system
- Atomic Orbitals **Basis set**
- Variables to control the approximation
  - Control of the Self consistent cycle (SCF)
  - Convergence parameters
    - ❖ Fineness of the grid; energy cutoff (E_{cut})
    - ❖ k-points Sampling

```
# Convergence of SCF
MaxSCFIteractions  50
DM.MixingWeight  0.5
DM.NumberPulay  2
```

```
# Fineness of the grid
MeshCutoff   400
```

```
# K-points sampling
%block kgrid_Monkhorst_Pack
3  0  0   0.5
0  3  0   0.5
0  0  3    0.5
%endblock kgrid_Monkhorst_Pack
```

Atomistic Simulation with SIESTA: Input File

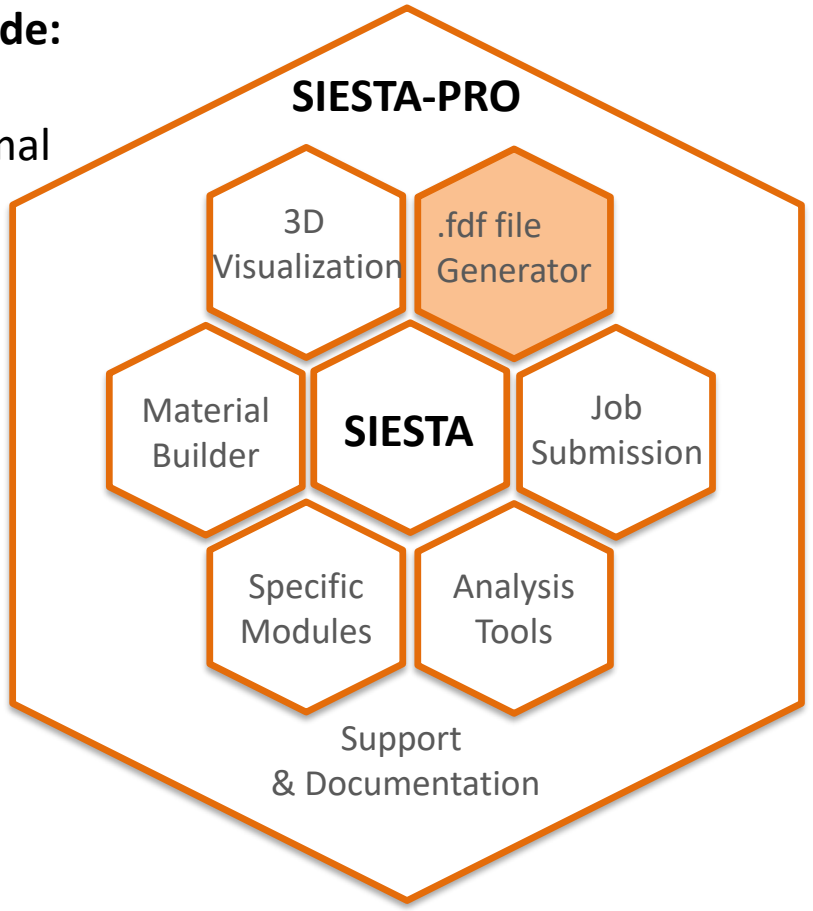
- An error-free input file (unit cell, position of atoms, parameter names) is the user responsibility. Only minimal checks are done by SIESTA (e.g. “atoms too close”)

```
# General system specifications
SystemName          CH4 molecules
SystemLabel         ch4
NumberOfAtoms       5
NumberOfSpecies     2

%block ChemicalSpeciesLabel
 1  6  C  # Species index, atomic number
 2  1  H
%endblock ChemicalSpeciesLabel

# Basis set
PAO.BasisSize  TZP


# Atomic coordinates
AtomicCoordinatedFormat Ang

%block AtomicCoordinatesAndAtomicSpecies
  0.000     0.000     0.000   1
  1.219    -0.284    -0.377   2
 -0.284     1.219    -0.377   2
%endblock AtomicCoordinatesAndAtomicSpecies
```

Atomistic Simulation with SIESTA: Input File

SIESTA-PRO GUI fdf file generator will include:

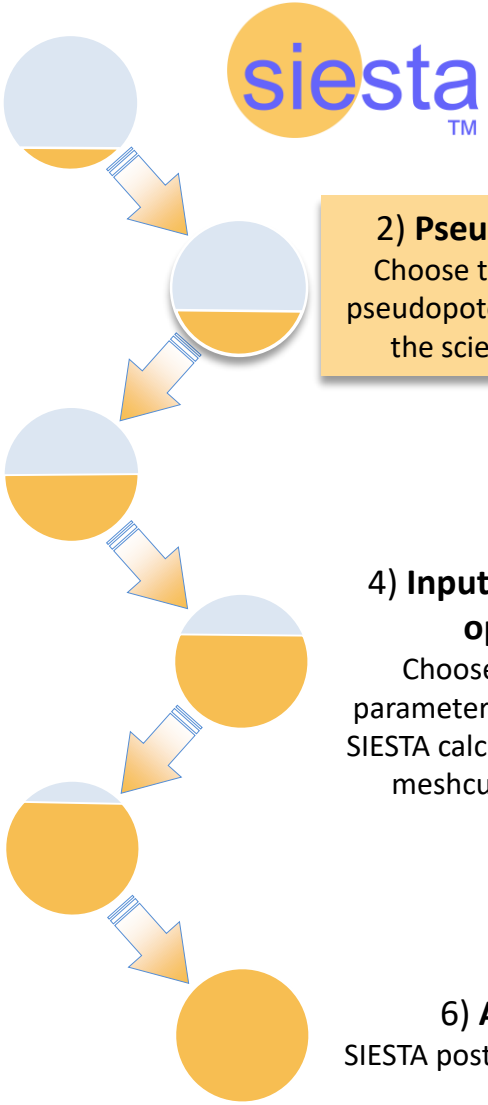
- Convergence workflow to estimate optimal calculation parameters
- Automatic pre-sets for different kind of calculations and accuracy
- a .fdf error checking



Atomistic Simulation with SIESTA

- How to perform an accurate and well-converged SIESTA calculation

1) **Problem definition**
System model, properties , accuracy



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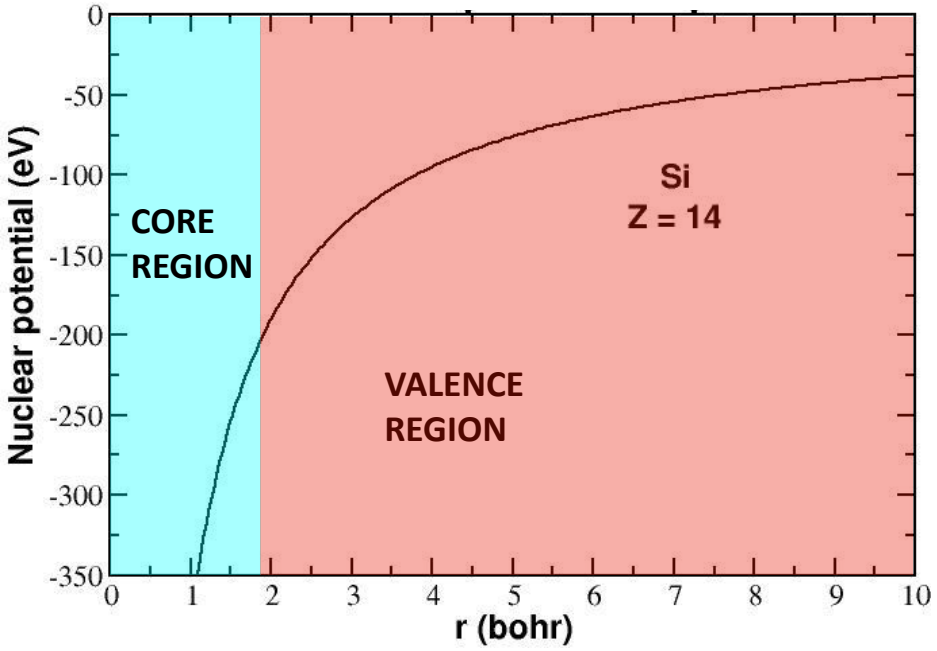
5) **Production run**

6) **Analysis**:
SIESTA post-processing tools

Atomistic Simulations with SIESTA: Pseudopotential

- **Pseudopotential idea** » Ignore the dynamics of the core electrons (freeze them) and replace their effects by an effective potential



Atomistic Simulations with SIESTA: Pseudopotential

- SIESTA uses **norm-conserving pseudopotentials** in their fully nonlocal (Kleinman-Bylander) form.

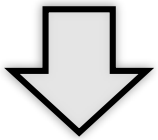
The accepted format are:

Unformatted binary (.vps)

Formatted ASCII (.psf) (more transportable and easy to look at)

Pseudpotential Markup Language (.psml) (available in the SIESTA beta version 4.1)

The SIESTA user has alternatives ways to obtain the pseudopotential file



Atomistic Simulations with SIESTA: Pseudopotential

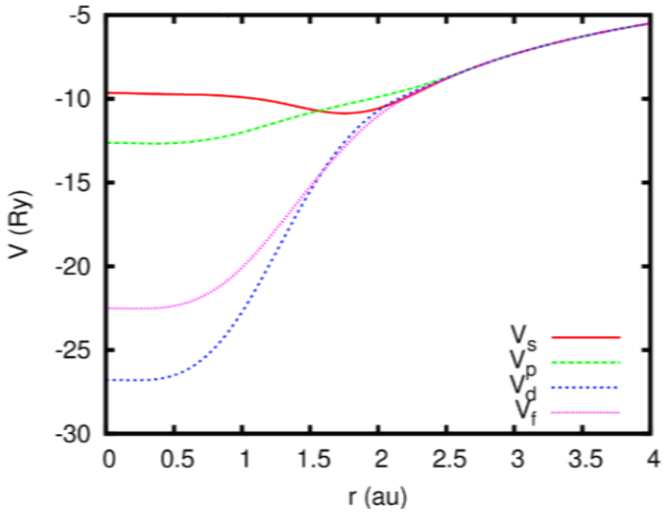
Option 1) » Visit the Virtual Vault for Pseudopotentials and use one of the pseudopotential generators listed as providing output compatible with Siesta

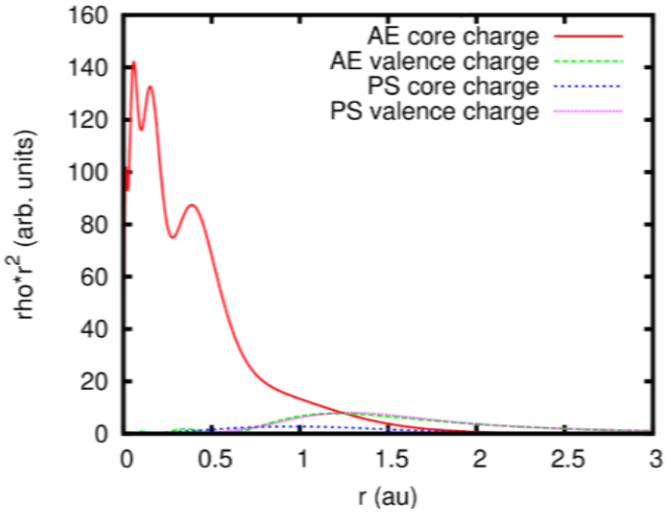
Databases of pseudopotentials should be used with care!

Au pseudo: GGA (pb), not relativistic

Input file for the ATOM program

PSF file for use in SIESTA





Atomistic Simulations with SIESTA: Pseudopotential

Option 2) » Generate and test the atomic pseudopotential using the ATOM code*

A tricky business that you must master before using Siesta responsibly

* ATOM code is maintained by Alberto Garcia. Since 2017, the code is no longer bundled with Siesta. Academic users can download it from the Siesta webpage at www.icmab.es/siesta

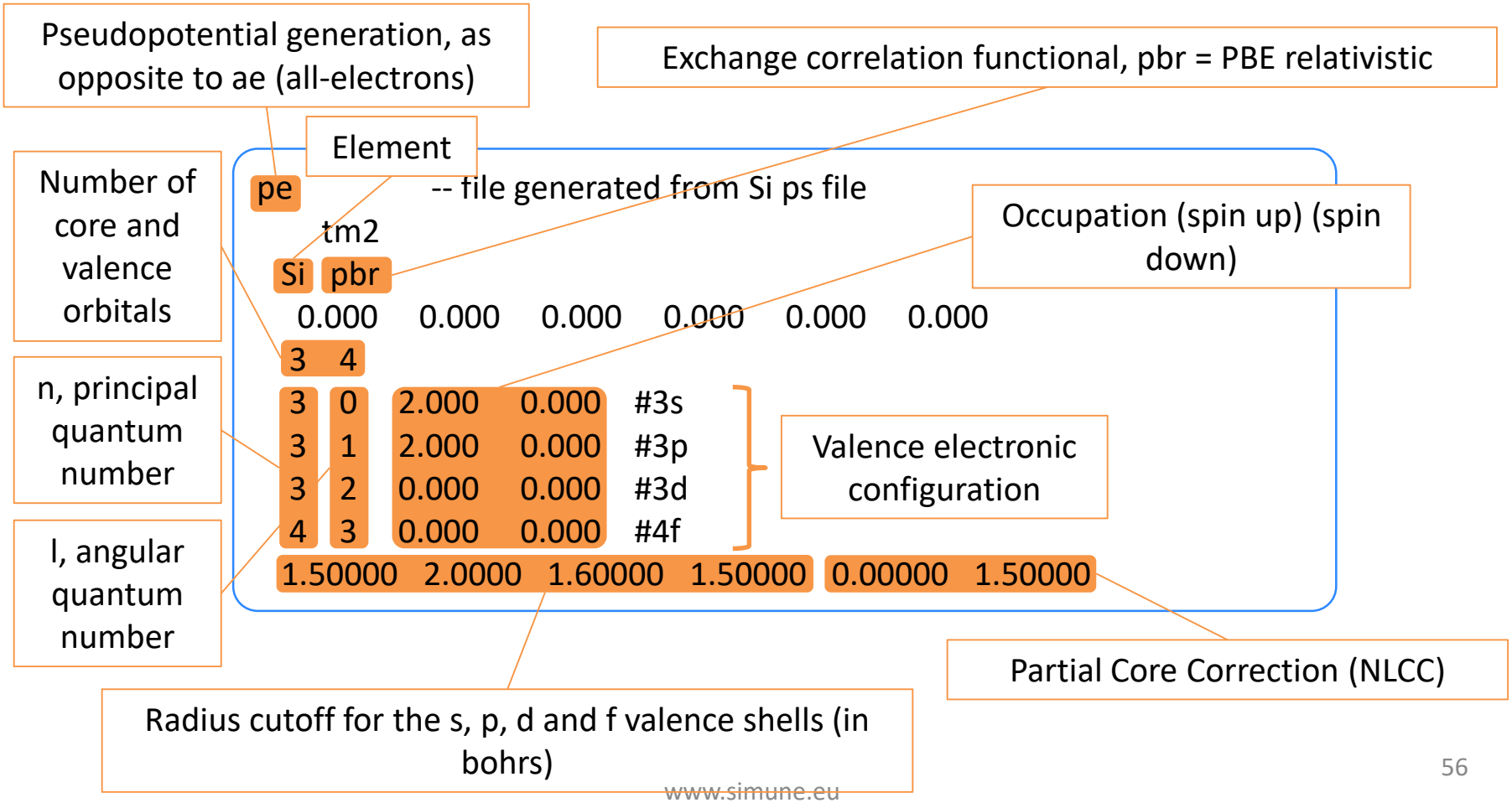
Atomistic Simulations with SIESTA: Pseudopotential

- An input file has to be properly written to generate the pseudopotential with ATOM code
  - **pg.sh**. Utility to generate the pseudopotential

```
pe              -- file generated from Si ps file
      tm2
  Si   pbr
    0.000    0.000    0.000    0.000    0.000    0.000
    3   4
    3   0    2.000    0.000    #3s
    3   1    2.000    0.000    #3p
    3   2    0.000    0.000    #3d
    4   3    0.000    0.000    #4f
  1.50000   2.0000   1.60000   1.50000   0.00000   1.50000
```

Atomistic Simulations with SIESTA: Pseudopotential

- An input file has to be properly written to generate the pseudopotential with ATOM code



Atomistic Simulations with SIESTA: Pseudopotential

- Every pseudopotential must be thoroughly checked before use (comparison of the pseudopotential energy excitations with the all-electron results)

- **pt.sh**. Utility to perform transferability tests

```
#
# All-electron calculations
#for a series of Si configurations
#
  ae Si Test -- GS 3s2 3p2 3d0 4f0
  Si   pbr
     0.0
   3    4
   3    0     2.00
   3    1     2.00
   3    2     0.00
   4    3     0.00
  ae Si Test -- 3s2 3p1 3d1 4f0
  Si   pbr
     0.0
   3    4
   3    0     2.00
   3    1     1.00
   3    2     1.00
   4    3     0.00
```

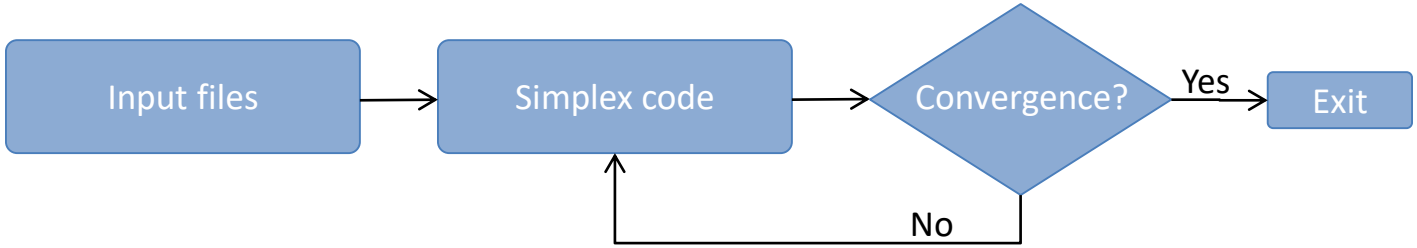
```
#
# Pseudopotential test calculations
#
#
  pt Si Test -- GS 3s2 3p2 3d0 4f0
  Si   pbr
     0.0
   3    4
   3    0     2.00
   3    1     2.00
   3    2     0.00
   4    3     0.00
  pt Si Test -- 3s2 3p1 3d1 4f0
  Si   pbr
     0.0
   3    4
   3    0     2.00
   3    1     1.00
   3    2     1.00
   4    3     0.00
```

Atomistic Simulations with SIESTA: Pseudopotential

Option 3) » Use a pseudopotential generated by SIMUNE*.

We have designed an optimization protocol involving a simplex algorithm that works in conjunction with the ATOM* code to calculate highly transferable pseudopotentials.

The protocol has been developed taking advantage of the knowledge of the SIESTA experts and makes use of properly tuned shell scripts to generate a soft-highly-transferable pseudopotentials.



* SIMUNE web page, under development

Atomistic Simulations with SIESTA: Pseudopotential

The main criteria used in the pseudopotentials generation and optimization are:

- Educated choice of the **atomic reference configuration**, i.e. a given distribution of electrons in the atomic energy levels (degree of freedom)

  (defined with the help of the SIESTA developers)

Examples:

Si $\underbrace{1s^2 2s^2 2p^6}_{\text{core}}$ $\underbrace{3s^2\ 3p^2}_{\text{valence}}$

Cu $\underbrace{1s^2 2s^2 2p^6 3s^2 3p^6}_{\text{core}}$ $\underbrace{3d^{10} 4s^1\ 4p^0 4f^0}_{\text{valence}}$

The more electrons are included in the valence region, the heavier is the SIESTA calculation with that pseudopotential

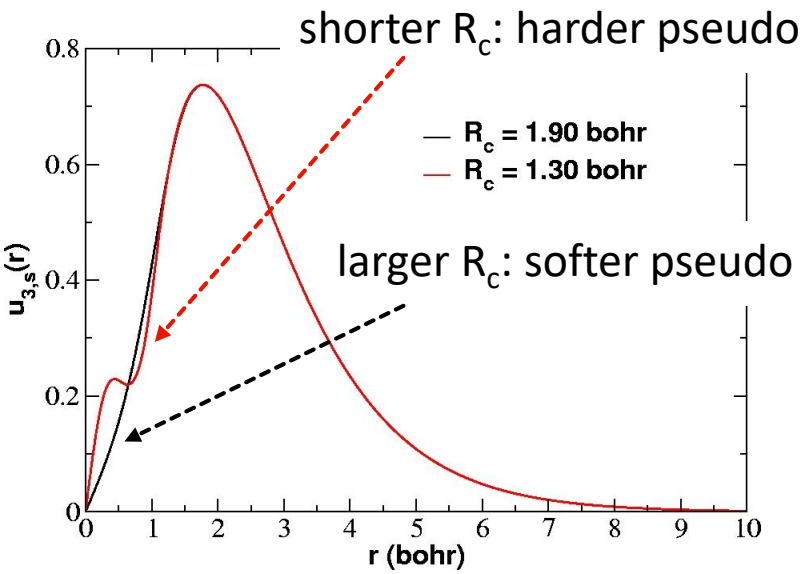
Atomistic Simulations with SIESTA: Pseudopotential

The main criteria used in the pseudopotentials generation and optimization are:

- Cutoff radii Rc(s), Rc(p), Rc(d) and Rc(f) are optimized to minimize the energy difference with all-electrons calculations (transferability)

The optimization process is designed with the aim to find a **balance** between

- **softness** (low computational cost)
- and **transferability** (accuracy in varying environments)



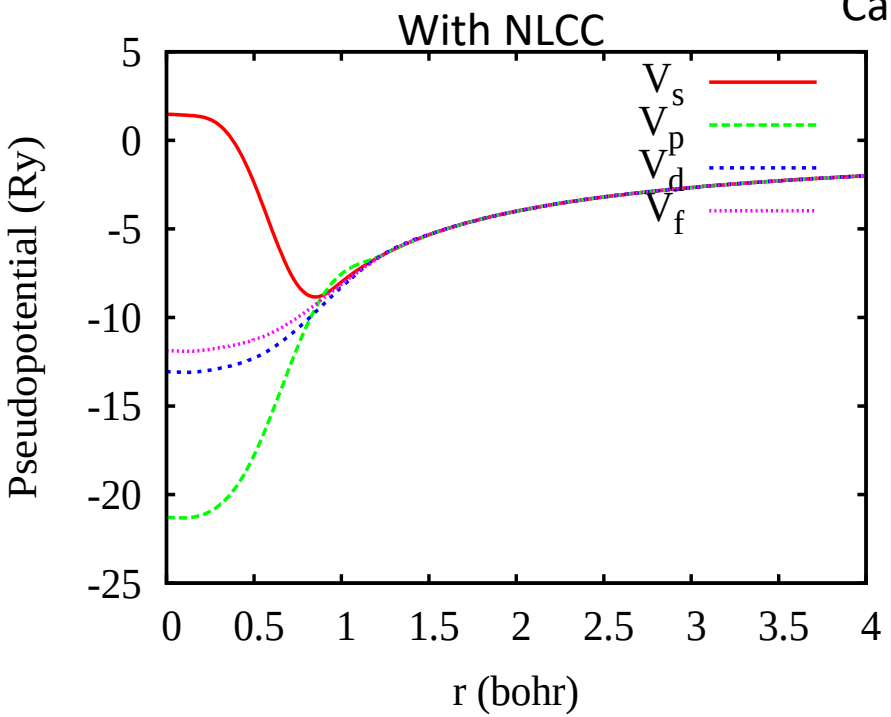
- A hard pseudo, in principle, provides a better agreement with the all-electron calculation (more transferable)
- A hard pseudo has high Fourier component and higher SIESTA meshcutoff parameter is necessary, leading to more costly calculations.

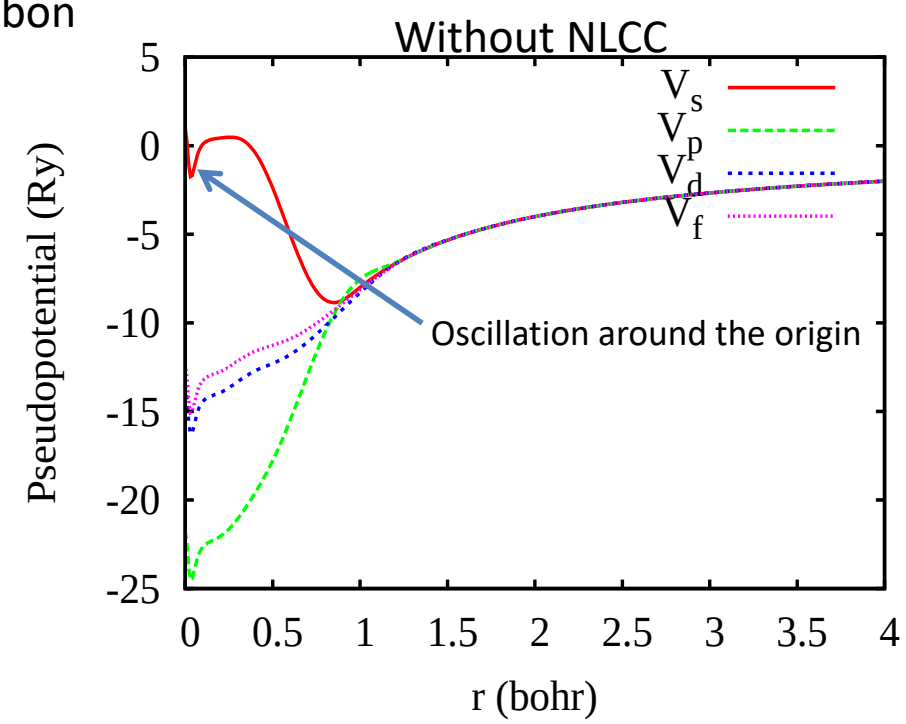
Atomistic Simulations with SIESTA: Pseudopotential

The main criteria used in the pseudopotentials generation and optimization are:

- Non-Linear Core Correction (NLCC) is optimized together with the cutoff radii

Carbon





Even when the overlap between core and valence charge density is small, a small NLCC helps to eliminate the pseudopotential wrinkles for small value of the radius.

Atomistic Simulations with SIESTA: Pseudopotential

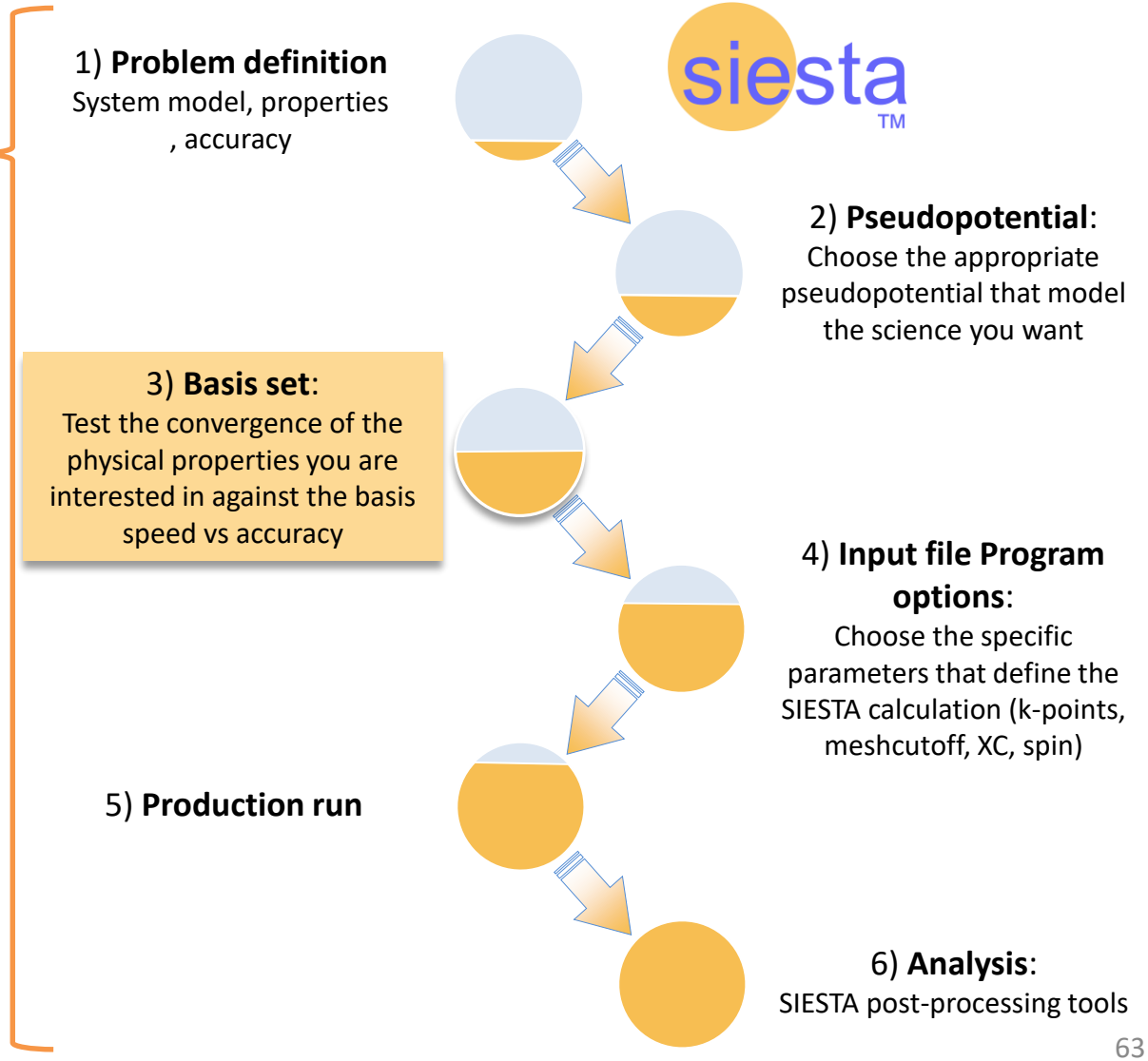
Additional criteria used in the pseudopotentials generation and optimization are:

- A penalty function is included in the minimization procedure to limit the maximum Fourier component of the pseudopotential and guarantee a soft pseudopotential

- Relativistic pseudopotentials for all elements

Atomistic Simulation with SIESTA

- How to perform an accurate and well-converged SIESTA calculation

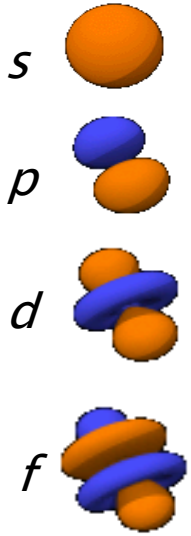


Atomistic Simulations with SIESTA: Basis Set

There are NO SIESTA basis sets !!

Atomic Orbital Basis set requirements:

1. $\phi_{Ilmn}(\vec{r}) = \underbrace{R_{Iln}(|\vec{r}_I|)}_{\text{radial component}} \underbrace{Y_{lm}(\hat{r}_I)}_{\text{angular component (spherical harmonics)}}$



2. *Finite support*

They can be:

- As many as you want (both l-channels and z's)
- Of any (radial) shape
- Of any cutoff radius
- Centred anywhere (not necessarily on atoms)

Atomistic Simulations with SIESTA: Basis Set

The SIESTA user has different options to define the basis set

Option 1) » Without specifying any basis set parameters: using the **SIESTA default** values. Good basis set in terms of accuracy versus efficiency

Not recommended for production calculations!

SIESTA default values

Basis size:	PAO.BasisSize	DZP
Range of first-zeta:	PAO.EnergyShift	0.02 Ry
Second-zeta:	PAO.BasisType	Split
Range of second-zeta:	PAO.SplitNorm	0.15

Atomistic Simulations with SIESTA: Basis Set

The SIESTA user has different options to define the basis set

Option 2) » Defining a few input variables.
More global control on the basis defining a few input variables: size and range

Basis size:

```
PAO.BasisSize      SZ    # Single zeta
PAO.BasisSize      DZ    # Double zeta
PAO.BasisSize      TZ    # Triple zeta
PAO.BasisSize      DZP   # Double zeta polarized, default value
PAO.BasisSize      TZP   # Triple zeta polarized
PAO.BasisSize      TZDP  # Triple zeta double polarized
PAO.BasisSize      TZTP  # Triple zeta triple polarized
```

Range of the first-zeta: PAO.EnergyShift

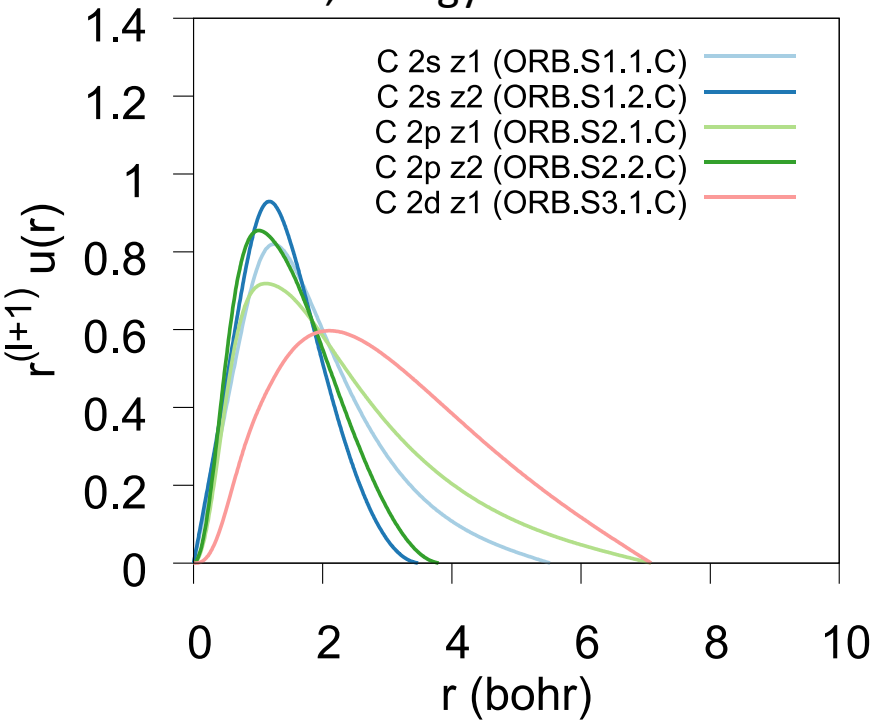
Range of the second-zeta: PAO.SplitNorm

The larger both values, the more confined the basis functions

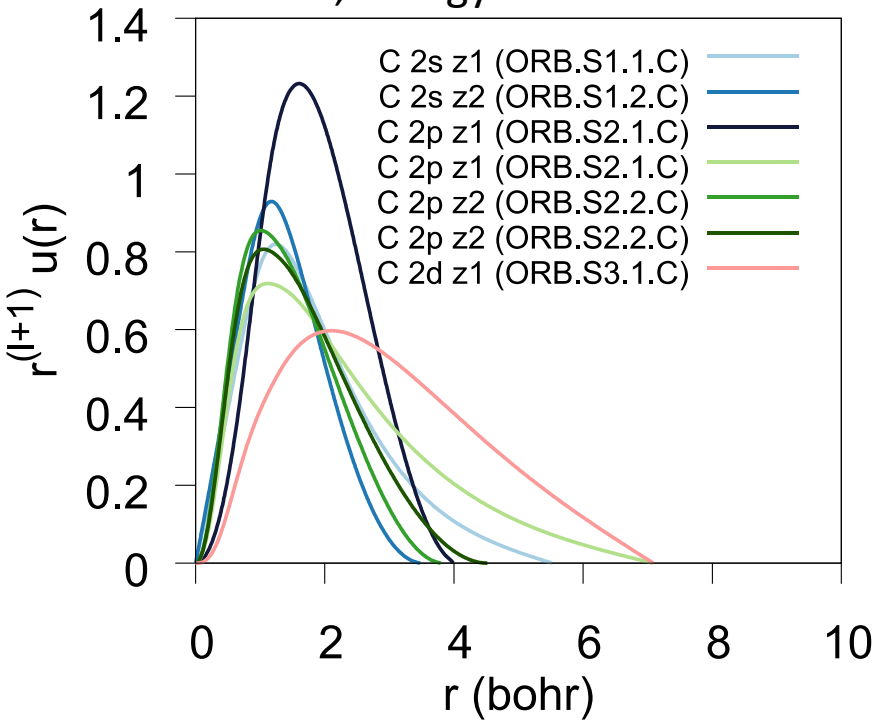
Atomistic Simulations with SIESTA: Basis Set

C $1s^2 2s^2 2p^2 2d$

Default SIESTA values:
DZP, Energyshift = 20 meV



Default SIESTA values:
TZP, Energyshift = 20 meV

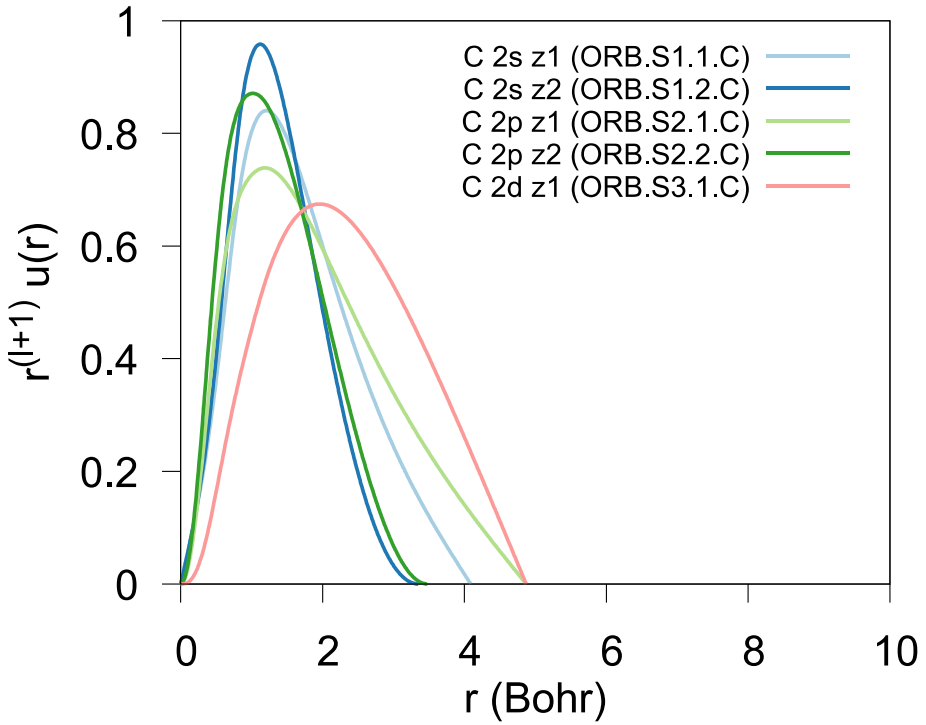


A more complete basis set provides a better description of the physical system

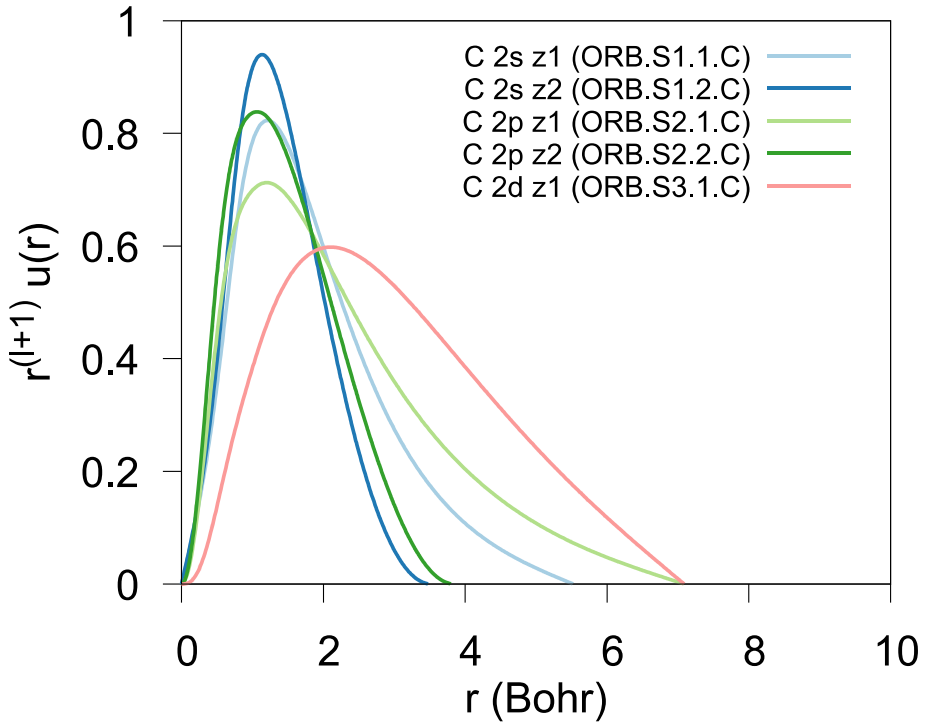
Atomistic Simulations with SIESTA: Basis Set

C $1s^2 2s^2 2p^2 2d$

Default SIESTA values
Energyshift = 272 meV



Default SIESTA values:
Energyshift = 20 meV



Atomistic Simulations with SIESTA: Basis Set

The SIESTA user has different options to define the basis set

Option 3) » Using the **PAO.Basis block**

```
%block PAO.Basis          # Define the basis set
O   2   nodes   1.0       # Label, l_shells, type (opt), ionic_charge (opt)
n=2  0  2  E 50.0 2.5     # n (opt if not using semicore levels),l,Nzeta,Softconf(opt)
   3.50  3.50             # rc(izeta=1,Nzeta)(Bohr)
   0.95  1.00             # ScaleFactor(izeta=1,Nzeta) (opt)
   1  1  P 2              # l, Nzeta, PolOrb (opt), NzetaPol (opt)
   3.50                   # rc(izeta=1,Nzeta)(Bohr)
H   2                     # Label, l_shells, type (opt), ionic_charge (opt)
   0  2  S 0.2            # l, Nzeta, Per-shell split norm parameter
   5.00  4.00  2.00       # rc(izeta=1,Nzeta)(Bohr)
   1  1 Q 3.0 0.2         # l, Nzeta, Charge conf (opt): Z and screening
   5.00                   # rc(izeta=1,Nzeta)(Bohr)
%endblock PAO.Basis
```

More specific control on the basis set

Atomistic Simulations with SIESTA: Basis Set

The SIESTA user has different options to define the basis set

Option 3) » Using the **PAO.Basis block**

First-zeta cutoff radius (bohr)

$$V(r) = V_0 \frac{e^{-\frac{r_c - r_i}{r - r_i}}}{r_c - r}$$

Soft-confinement potential, V_0 in Ry and r_i in bohr

```
%block PAO.Basis          # Define the basis set
O   2   nodes   1.0       # Label, l_shells, type (opt), ionic_charge (opt)
n=2  0  2  E 50.0 2.5     # n (opt if not using semicore levels),l,Nzeta,Softconf(opt)
   3.50  3.50             # rc(izeta=1,Nzeta)(Bohr)
   0.95  1.00             # ScaleFactor(izeta=1,Nzeta) (opt)
   1  1  P 2              # l, Nzeta, PolOrb (opt), NzetaPol (opt)
   3.50                   # rc(izeta=1,Nzeta)(Bohr)
H   2                     # Label, l_shells, type (opt), ionic_charge (opt)
   0  2  S 0.2            # l, Nzeta, Per-shell split norm parameter
   5.00  4.00  2.00       # rc(izeta=1,Nzeta)(Bohr)
   1  1 Q 3.0 0.2         # l, Nzeta, Charge conf (opt): Z and screening
   5.00                   # rc(izeta=1,Nzeta)(Bohr)
%endblock PAO.Basis
```

Second-zeta cutoff radius (bohr)

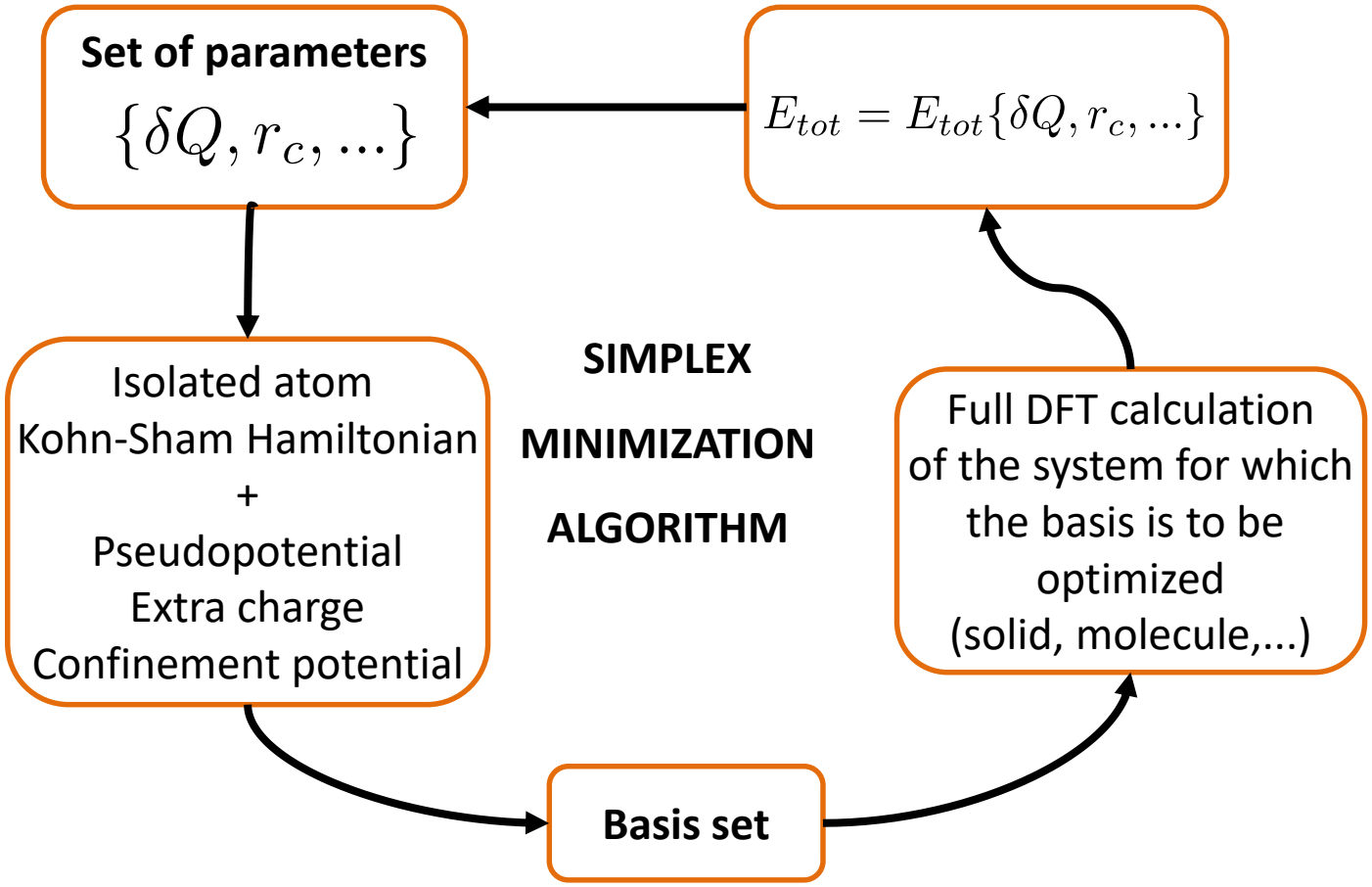
Third-zeta cutoff radius (bohr)

Yukawa potential parameter
For polarization function

$$V_Q(r) = \frac{Ze^{-\lambda r}}{\sqrt{r^2 + \delta^2}}$$

Atomistic Simulations with SIESTA: Basis Set

The parameters may be optimized for your system of interest with the Simplex minimization algorithm

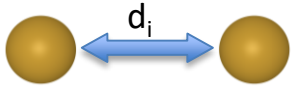


Atomistic Simulations with SIESTA: Basis Set

The SIESTA user has different options to define the basis set

Option 4) » **SIMUNE's data base** basis set optimized following a well-defined standard procedure to obtain **reliable highly transferable basis sets**

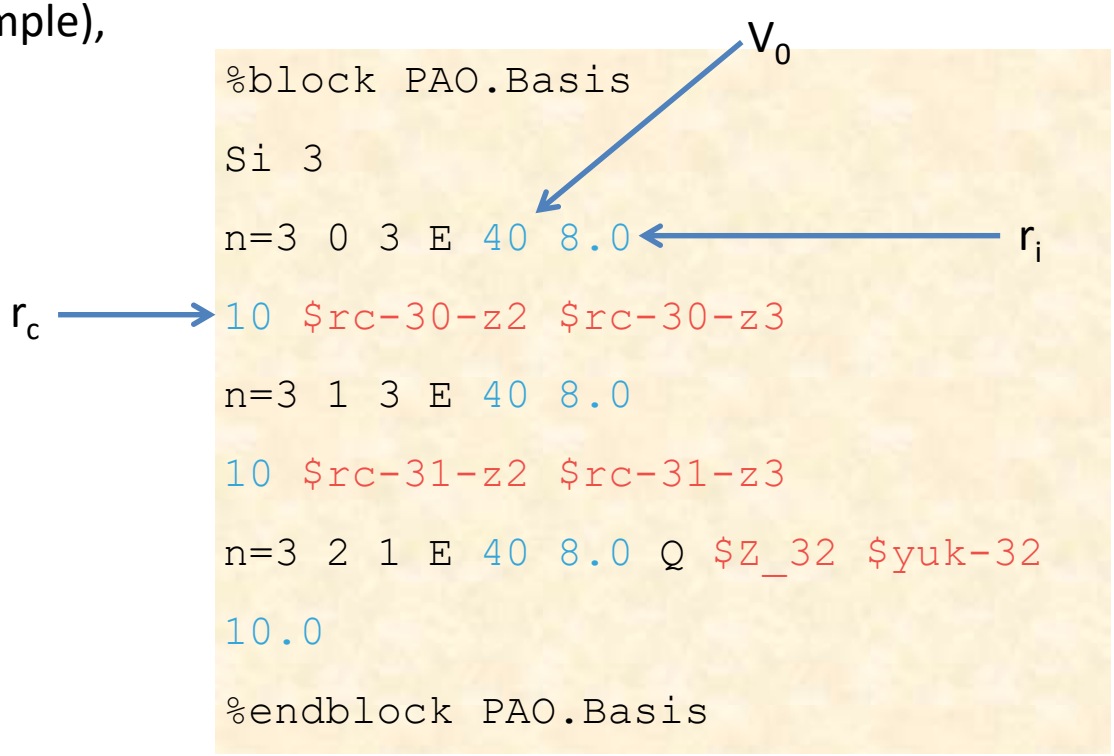
- The procedure is based on the minimization of the average free energy of the system (dimer) within a pre-determined range of distances
- The SIESTA "simplex" utility is used to find the optimal values for the basis set. The utility performs a sequence of SIESTA calculations where the free energy is minimized and the parameters of the basis set are found



- The self-consistent PBE binding energy curve obtained with a PW code is used as a starting point for the basis set optimization
- The dimer distance range, for which the basis set is minimized, is chosen based on an energy criteria

Atomistic Simulations with SIESTA: Basis Set

Example of basis set block (TZP) ready for the optimization:
Some parameters of the basis set are kept fixed for all orbitals (blue color in the example),

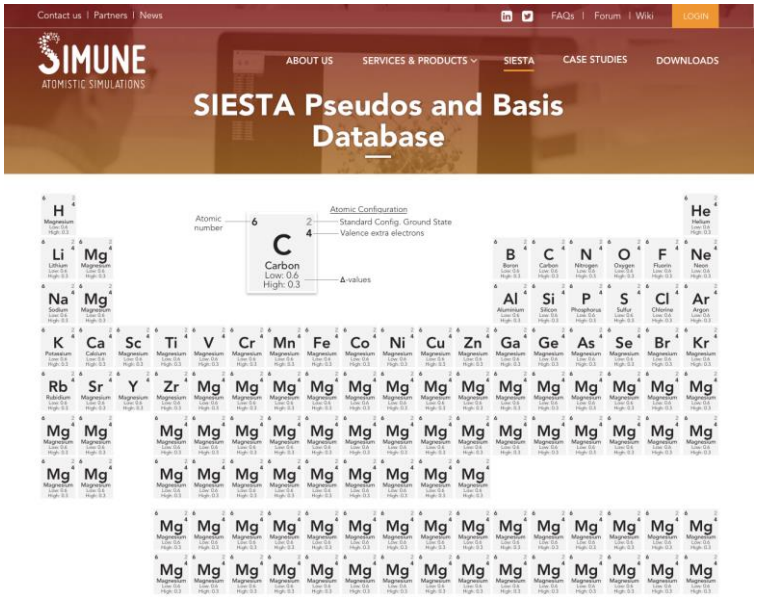


whereas the rest of the parameters are optimized (indicated by the red color in the example).

Atomistic Simulations with SIESTA: Pseudopotential

- Be aware that the quality of the pseudo as well as of the basis set can heavily affect the final results of the simulation

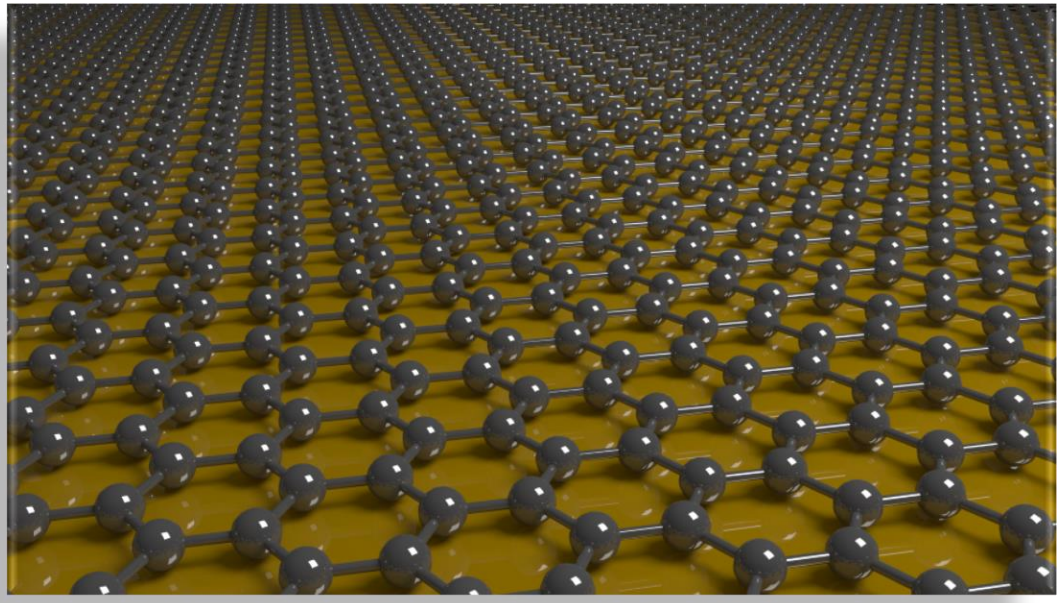
- SIMUNE is developing a repository of optimized pseudopotentials and basis sets, soon available in the SIMUNE web page (www.simune.eu)



Atomistic Simulations with SIESTA: Basis Set

The SIESTA user has different options to define the basis set

Option 5) » SIMUNE's personalized basis sets. SIMUNE's services include the optimization of basis set specifically designed for the customer target system:

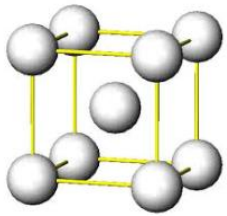


Atomistic Simulations with SIESTA: Pseudopotential and Basis Set Quality Evaluation

We make use of a benchmark test (Δ-test) to evaluate the quality and the transferability of the optimized pseudopotentials and basis sets. The all-electron code WIEN2k is used as reference.
Procedure:

- Take as model systems well-defined crystalline configurations (Δ-test structures)
- Perform series of 7 calculations with varying lattice volume with respect to the equilibrium volume V_0, (94%, …, 106%).
- Fit the obtained data with the Birch-Murnaghan empirical Equation Of State (EOS) to extract the energy analytically.[1]

$V_{0,i}$: equilibrium volume (Å^3/atom)
B_0 : bulk modulus (GPa)
B_1 : bulk modulus derivative



Atomistic Simulations with SIESTA: Pseudopotential and Basis Set Quality Evaluation

- Compute the Δ-value as:

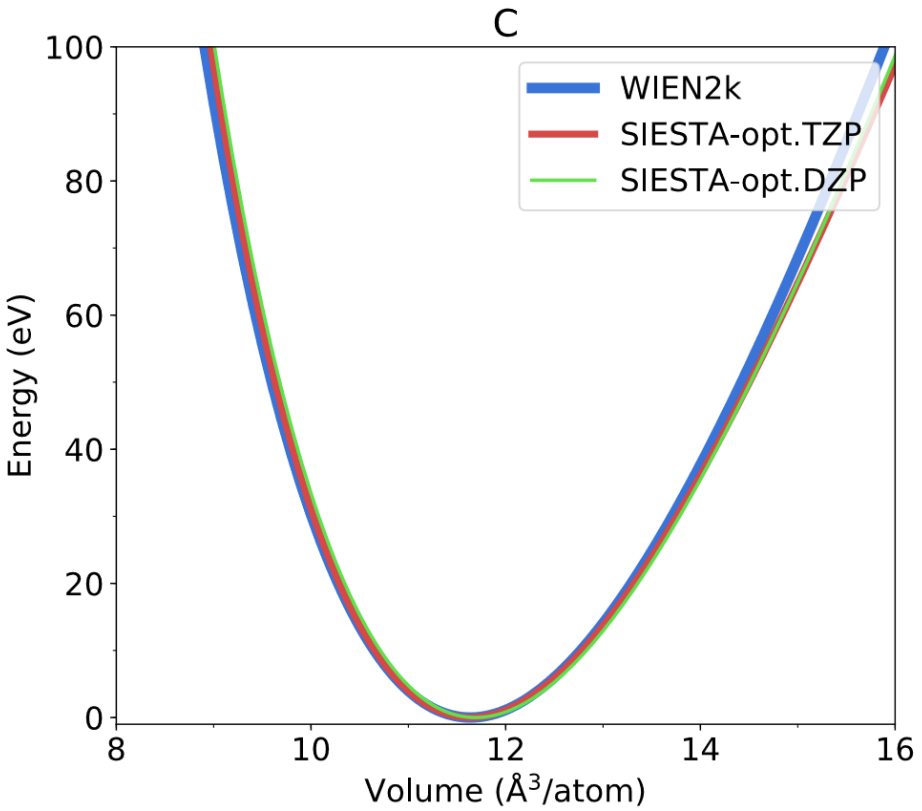
$$\Delta_i(a,b) = \sqrt{\frac{\int_{0.94V_{0,i}}^{1.06V_{0,i}} (E_{b,i}(V) - E_{a,i}(V))^2 \mathrm{d}V}{0.12V_{0,i}}}$$

$E_{a,i}(V)$: energy reference (WIEN2k)
$E_{b,i}(V)$: energy (SIESTA)
$V_{0,i}$: equilibrium volume

Extended information of the Delta-test can be found at
http://dx.doi.org/10.1080/10408436.2013.772503
http://science.sciencemag.org/content/351/6280/aad3000
https://molmod.ugent.be/deltacodesdft

Atomistic Simulations with SIESTA: Example Δ-test

Carbon Δ-value (meV/atom)	
SIESTA opt. DZP	SIESTA opt. TZP
2.59	0.09



The Δ-test by itself does not indicate the transferability of a basis set (it is only performed for a specific system). However, due to the fact that the optimized basis sets are obtained from calculations on a molecule, the Δ-value is a good indicator of the basis set transferability

Atomistic Simulations with SIESTA: Example Δ-test

Δ-test values:

	Δ-value (meV/atom)		
	SIESTA opt. DZP	SIESTA opt. TZP	OpenMX http://www.openmx-square.org/
Hydrogen	0.56	0.76	0.13
Carbon	2.59	0.09	0.88
Oxygen	9.17	7.45	4.27
Silicon	1.10	0.47	1.40

- WIEN2k (all-electron code) is always used as reference in the Δ-test
- The Δ-values for OpenMX (pseudo-atomic localized basis functions) are included for sake of comparison. The values have been extracted from https://molmod.ugent.be/deltacodesdft. The values showed for OpenMX were obtained with the goal of minimizing the Δ-value.
- In SIESTA by increasing the basis set multiplicity we expect to obtain a much better value for the Δ-test

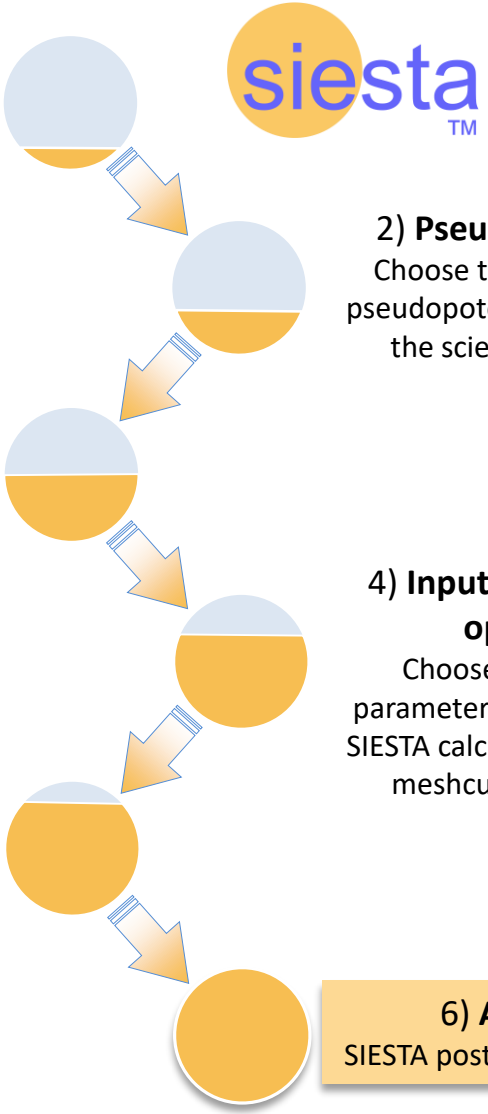
SUMMARY

- **INTRODUCTION**
  - SIMUNE and SIESTA
  - SIESTA-PRO: SIESTA code ready for the industry
- **SIESTA CODE: MAIN TECHNICAL FEATURES**
- **EXCITED STATES PROPERTIES FOR SIESTA CALCULATIONS: TDDFT and beyond**
- **HINTS TO PERFORM AN ACCURATE AND WELL-CONVERGED SIESTA CALCULATION**
  - Input file. Principal SIESTA Input Parameters
  - Pseudopotential
  - Basis set. The Delta-test
- **ANALYSIS OF THE RESULTS. POST-PROCESSING SIESTA OUTPUT**

Atomistic Simulation with SIESTA

- How to perform an accurate and well-converged SIESTA calculation

1) **Problem definition**
System model, properties , accuracy



2) **Pseudopotential**:
Choose the appropriate pseudopotential that model the science you want

3) **Basis set**:
Test the convergence of the physical properties you are interested in against the basis speed vs accuracy

4) **Input file Program options**:
Choose the specific parameters that define the SIESTA calculation (k-points, meshcutoff, XC, spin)

5) **Production run**

6) **Analysis**:
SIESTA post-processing tools

Atomistic Simulation with SIESTA: Analysis of the Results

With SIESTA, it is possible to perform a complete characterization of a material

➢ **Mechanical Properties**:
- Elastic constants
- Material robustness and strain

➢ **Structural Properties**:
- Equilibrium geometry (atomic relaxation)
- Molecular dynamics

➢ **Electronic Properties**:
- Band Structure/"fatbands"
- Density of States (DOS)
- Projected Density of States (PDOS)
- Crystal Orbital Overlap Population (COOP)
- Crystal Orbital Hamilton Population (COHP)
- Charge density & Kohn-Sham orbitals

➢ **Surface Chemistry**:
- Interaction substrate/molecule
- Absorption Energy
- Surface coverage
- Dissociation energy

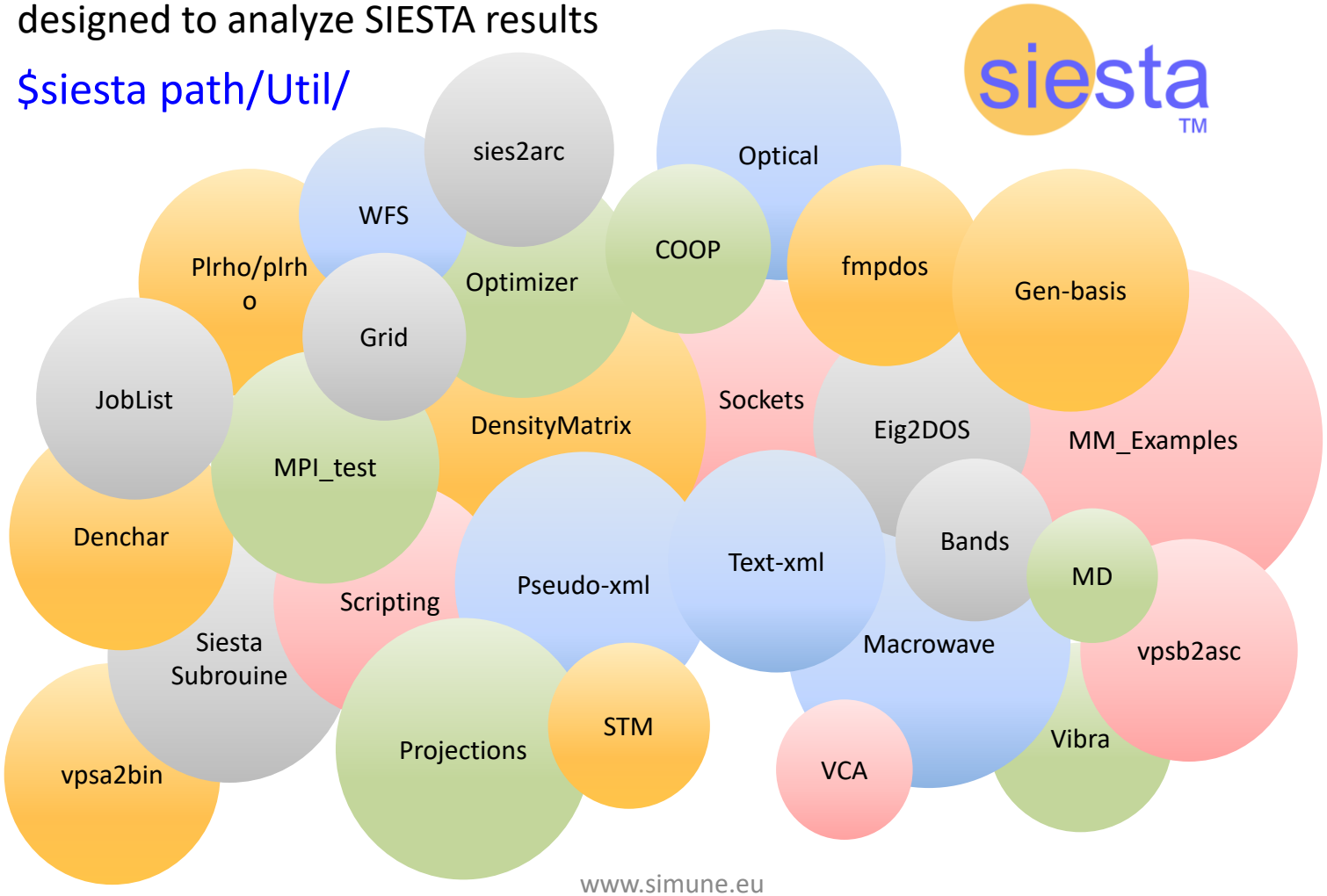
➢ **Magnetic Properties**:
- Magnetic behavior of materials

➢ **Transport Properties**
- Conductivity
- Mobility

Atomistic Simulation with SIESTA: Analysis of the Results

The SIESTA package contain a large number of POST-PROCESSING TOOLS designed to analyze SIESTA results

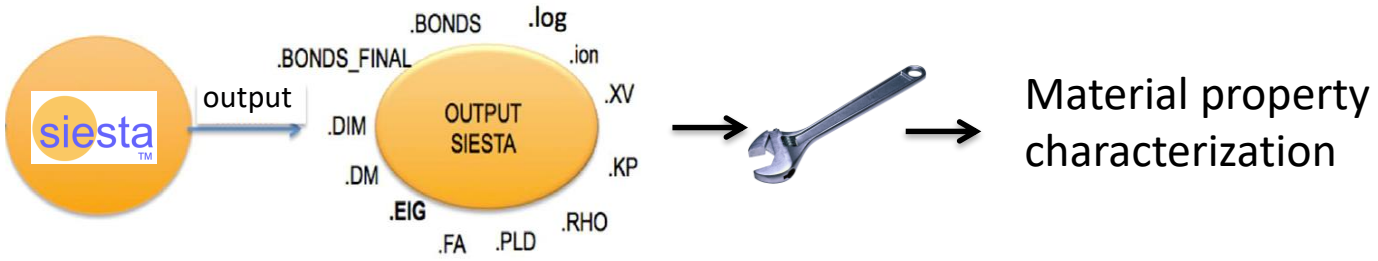
$siesta path/Util/



Atomistic Simulation with SIESTA: Analysis of the Results

The SIESTA user must follow a number of requirements before analyzing a material property

- post-processing tool compilation
- knowledge of the information stored in each SIESTA output files
- knowledge of the form of using each post-processing tool



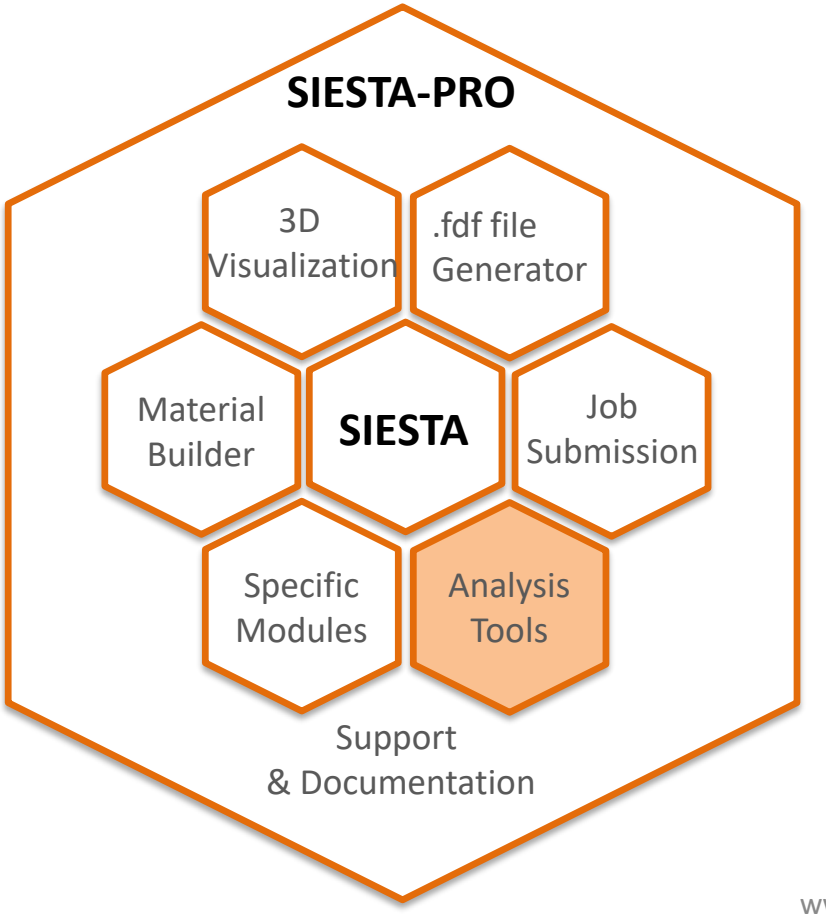
We have created specific tutorials* to help the SIESTA user in this task:

- Optimization_of_material_properties-Band_Structure
- Optimization_of_material_properties-Density_Of_States_DOS
- …

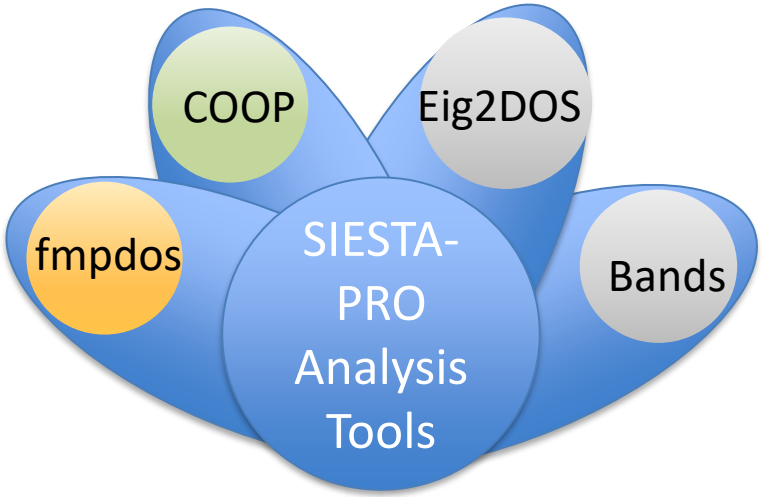
* http://simune.eu/index.php/en/siesta

Atomistic Simulation with SIESTA: Analysis of the Results

As a part of SIESTA-PRO, we have developed a GUI to facilitate the use of the SIESTA post-processing tools

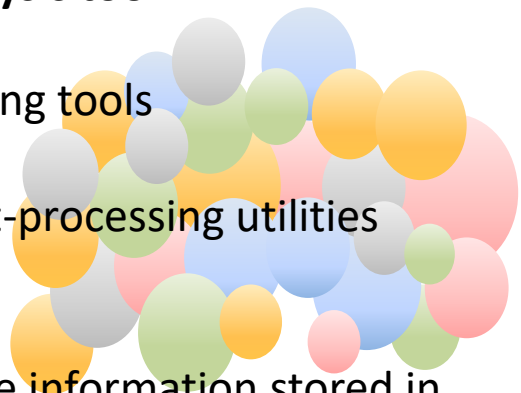


Simple, user-friendly interface approach to eliminate all the requirements that are currently needed before analyzing a material property



Atomistic Simulation with SIESTA: Analysis of the Results

Post–processing SIESTA output with SIESTA-PRO analysis tool:

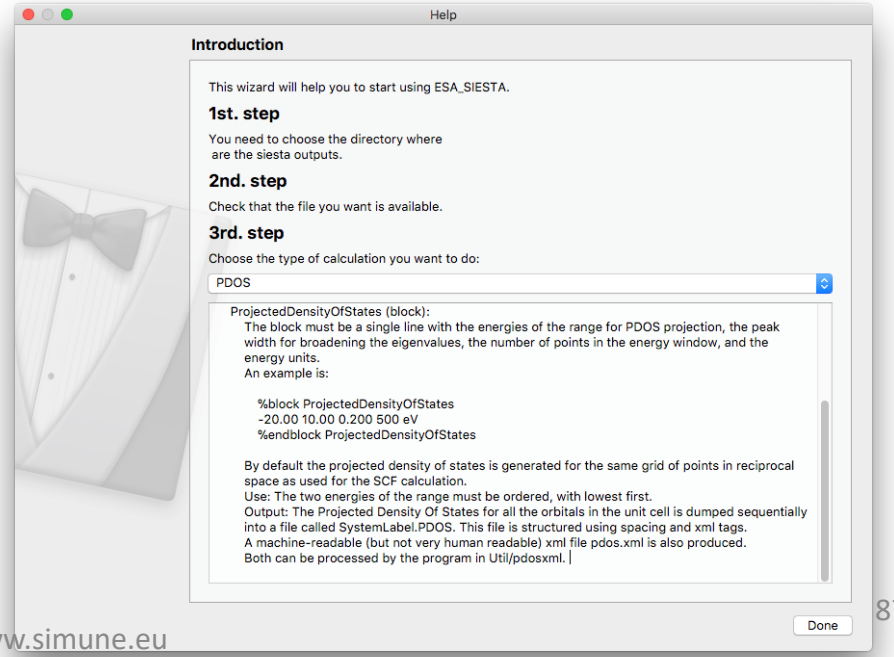


- There is no need to compile the post-processing tools
- There is no need to know how to use the post-processing utilities included in the SIESTA package
- There is no need to have the knowledge of the information stored in each of the SIESTA output files
- Gives the possibility to do post-processing analysis without the need of specific third-party software for the data interaction and visualization: the data analysis and plot visualization is encoded inside the app

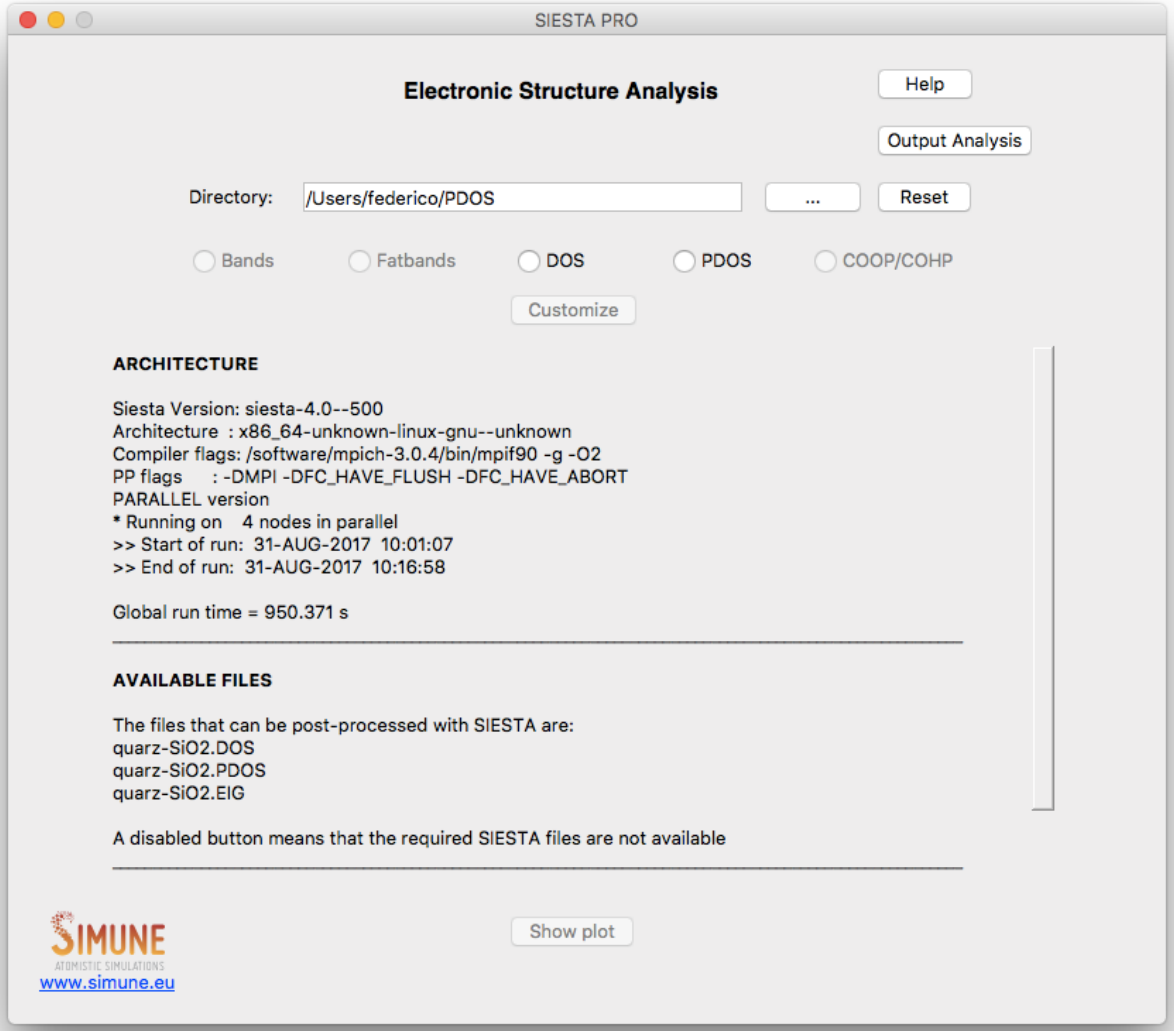
Atomistic Simulation with SIESTA: Analysis of the Results

Post–processing SIESTA output with SIESTA-PRO analysis tool:

- Avoid the use of the terminal thanks to a user-friendly graphical interface
- It is time saving: the use of a the analysis tool app speeds up your post-processing step by a factor of 10
- Contains a Help section



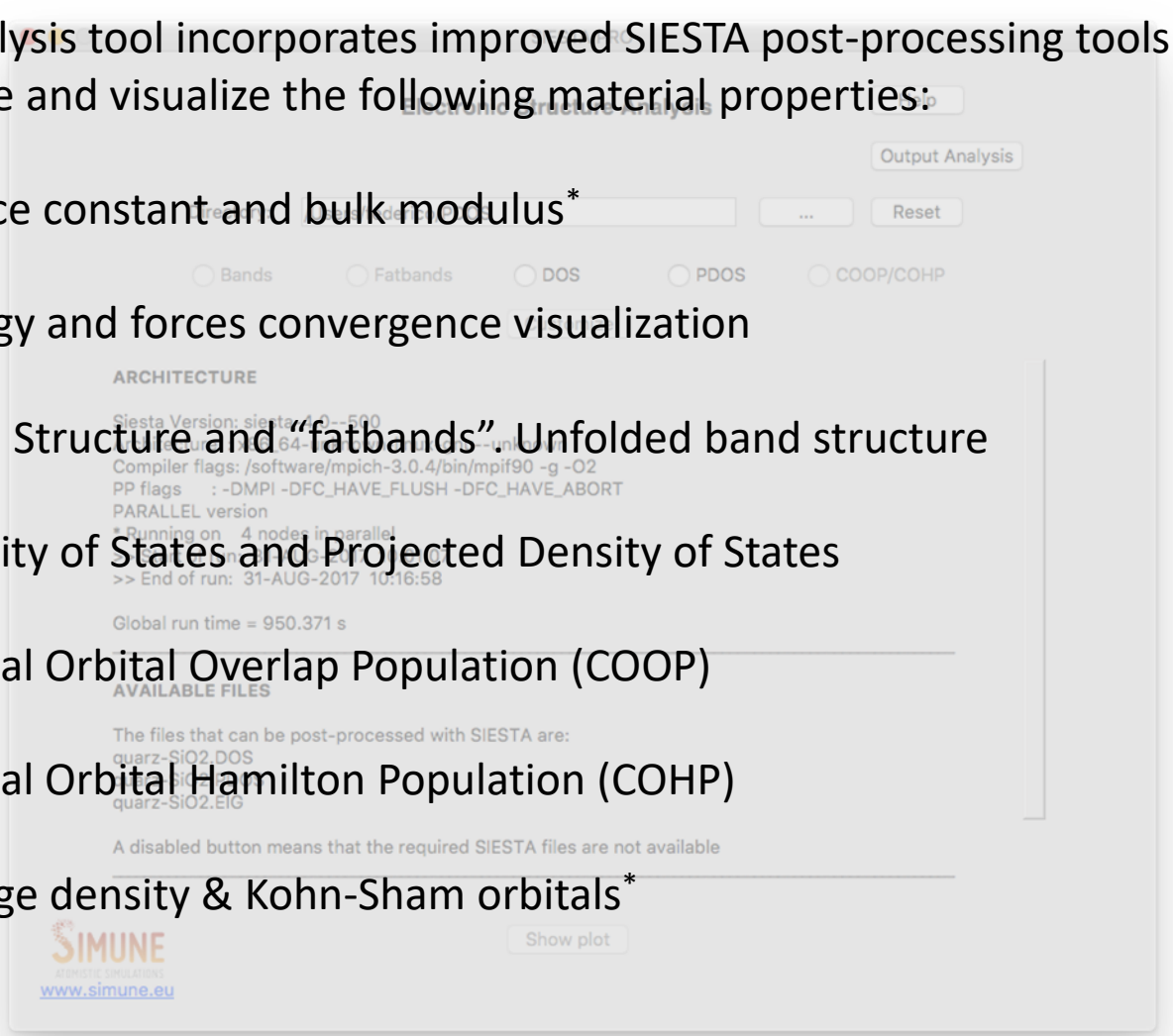
Atomistic Simulation with SIESTA: Analysis of the Results



Atomistic Simulation with SIESTA: Analysis of the Results

The analysis tool incorporates improved SIESTA post-processing tools to calculate and visualize the following material properties:

- Lattice constant and bulk modulus*
- Energy and forces convergence visualization
- Band Structure and “fatbands”. Unfolded band structure
- Density of States and Projected Density of States
- Crystal Orbital Overlap Population (COOP)
- Crystal Orbital Hamilton Population (COHP)
- Charge density & Kohn-Sham orbitals*



*solutions under development

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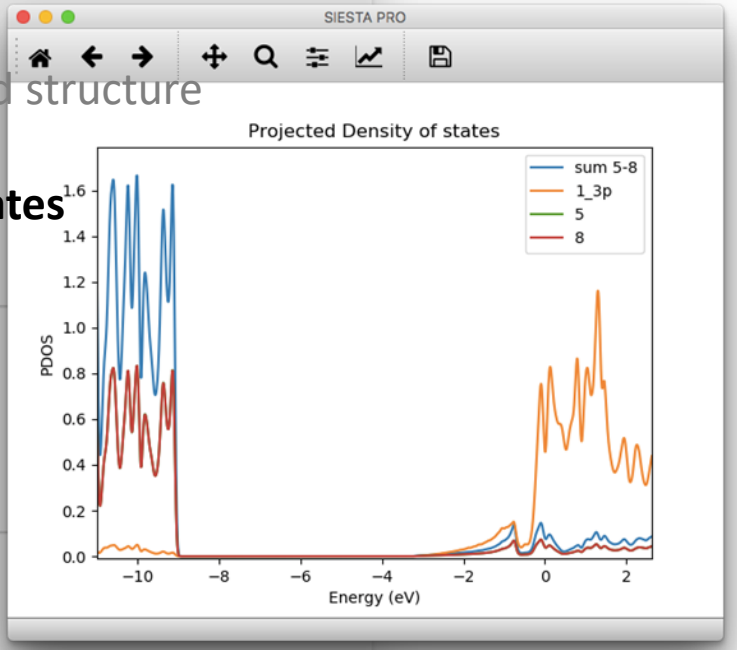

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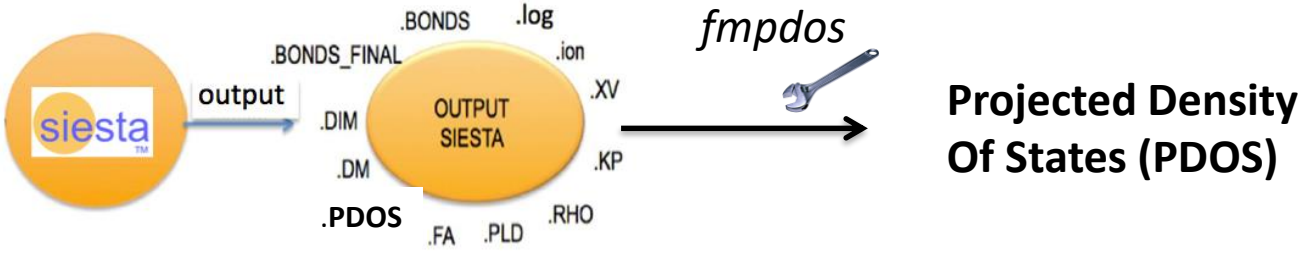
Atomistic Simulation with SIESTA: Analysis of the Results



WITHOUT SIESTA-PRO analysis tool

step-by-step procedure from command line

- Compile the *fmpdos* utility provided inside the SIESTA package
- Run the utility *fmpdos*
- Plot the results with a third-party software

Atomistic Simulation with SIESTA: Analysis of the Results

WITHOUT SIESTA-PRO analysis tool

- Running the utility fmpdos
  Define interactively:
  - The input file name
  - The output file
  - The particular orbitals you are interested to analyse in the PDOS

Data to be filled for each PDOS

```
Input file name (PDOS):
quarzt-SiO2.PDOS
Output file name :
quarzt-SiO2_pdos.out
Extract data for atom index (enter atom NUMBER, or 0 to select all),
or for all atoms of given species (enter its chemical LABEL):
0
Extract data for n= ... (0 for all n ):
2
Extract data for l= ... (-1 for all l ):
1
Extract data for m= ... (9 for all m ):
9
```

Atomistic Simulation with SIESTA: Analysis of the Results

WITHOUT SIESTA-PRO analysis tool

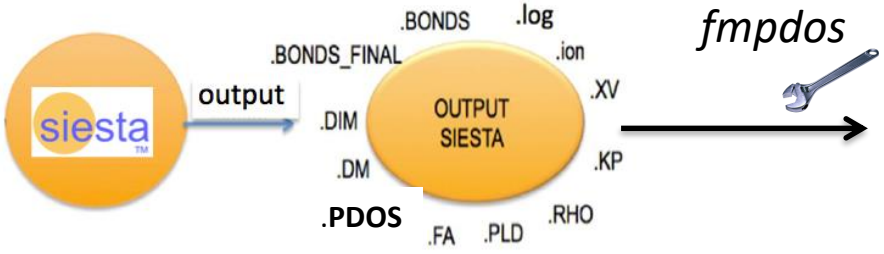
- Plot the results with a third-party software
  - Plot on the fly the output file
  - Prepare a script to automatically produce the image

```
set key Left right top width 0 samplen 1 spacing 1
set xtics 5
set terminal pdfcairo transparent enhanced font "arial,20" size 14 cm,12 cm
set xlabel "Energy (eV)"
set ylabel "PDOS"
set ytics nomirror
set xtics nomirror
set yrange[:]
set xrange[:]

set output "pdos_silica.pdf"

plot \
     'quarz-SiO2_pdos.out' u 1:2 title 'PDOS Silica' lw 2 pt 7 lc rgb "#EC4646" w l

unset output
```

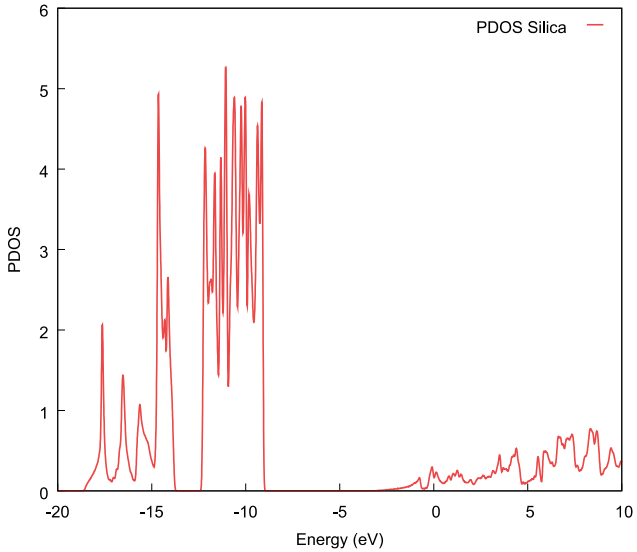
Minimal Gnuplot script to generate PDOS plot using the third-party graphic software Gnuplot

Atomistic Simulation with SIESTA: Analysis of the Results

Case Study



PDOS: Si, n=2, l=1



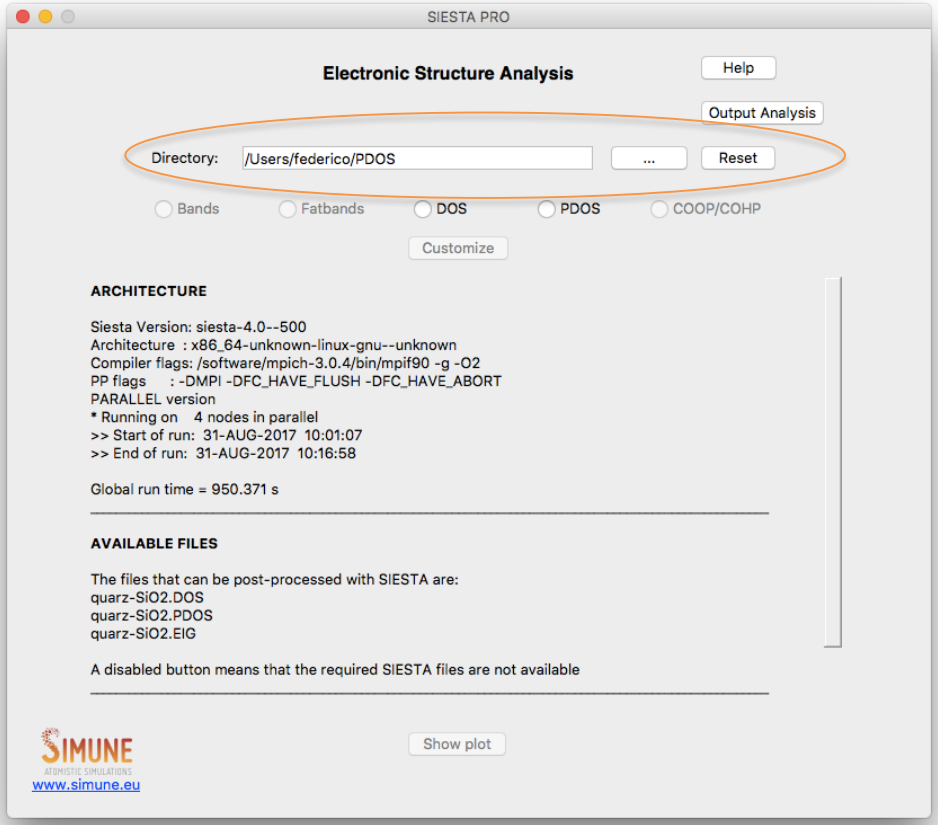
Typical PDOS analysis consists in plotting and comparing multiple PDOS files

The whole procedure should be repeated for each PDOS of interest

SIESTA-PRO: Analysis Tool

WITH SIESTA-PRO analysis tool

- Open the app and load the folder where you performed the SIESTA simulation



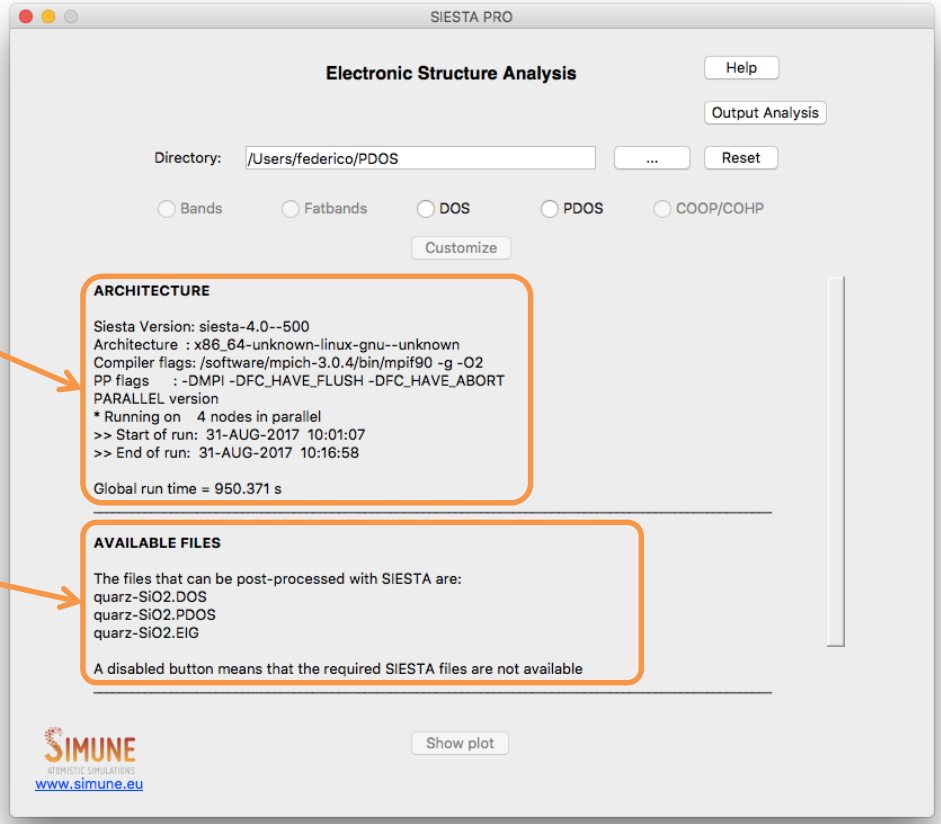
SIESTA-PRO: Analysis Tool

WITH SIESTA-PRO analysis tool

- Open the app and load the folder where you performed the SIESTA simulation

General information

Available files

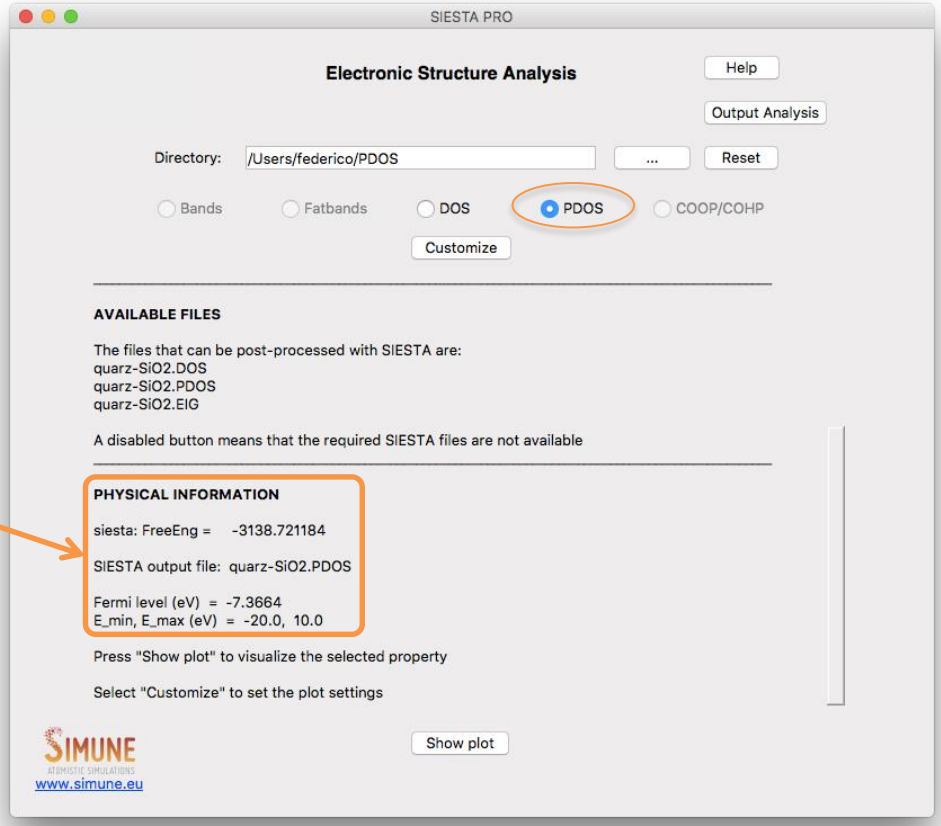


SIESTA-PRO: Analysis Tool

WITH SIESTA PRO analysis tool

- Enter in the section PDOS

Relevant information from SIESTA output

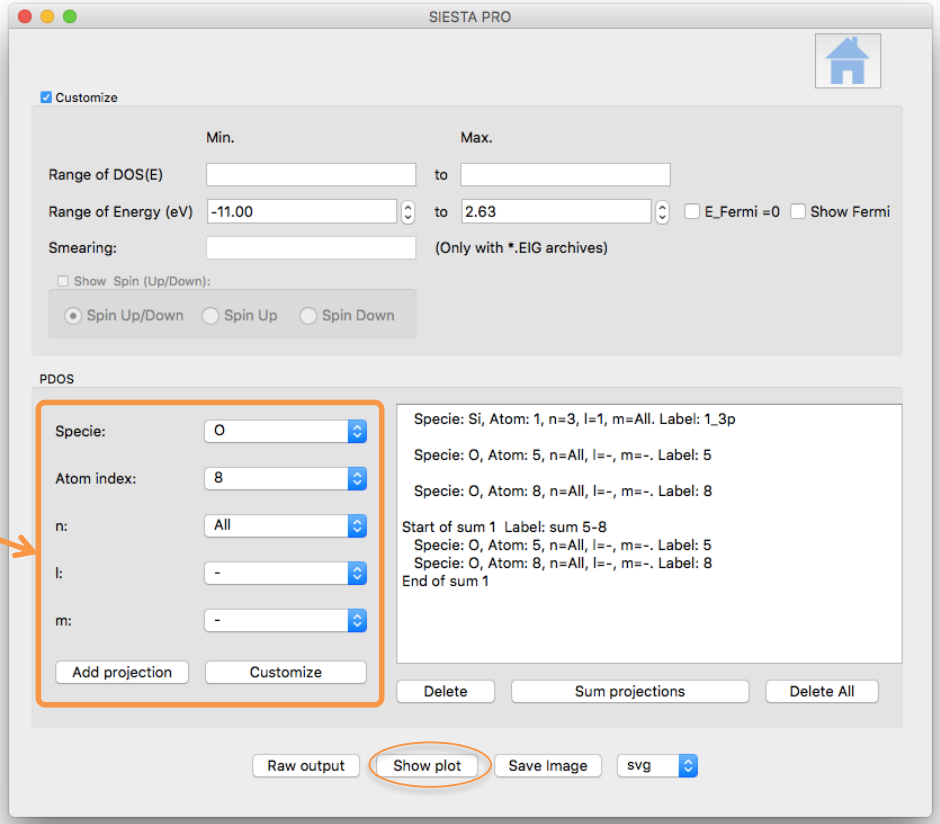


SIESTA-PRO: Analysis Tool

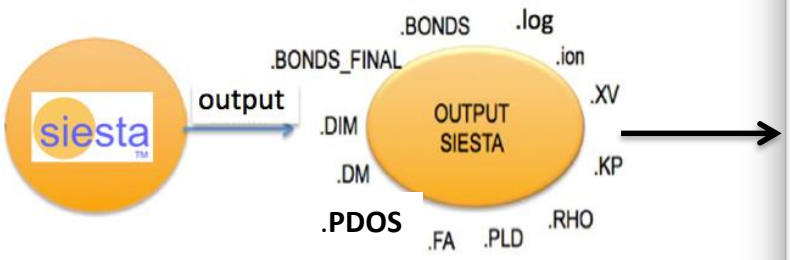
WITH SIESTA-PRO analysis tool

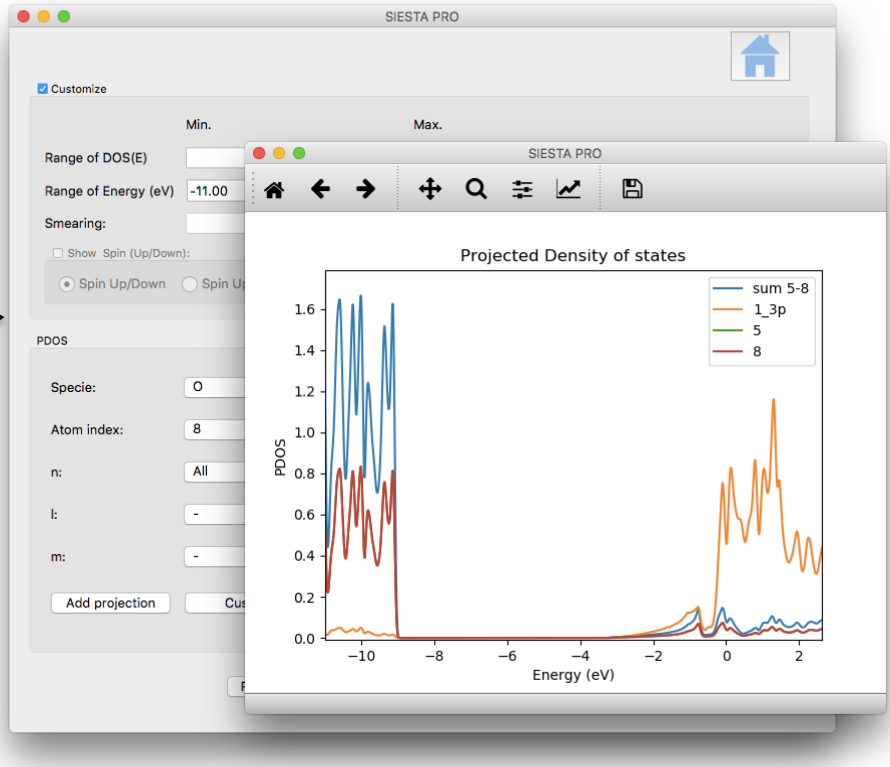
- Customize the plot
  - Indicate the projections you want to plot

Intuitive way of adding PDOS projections



Atomistic Simulation with SIESTA: Analysis of the Results





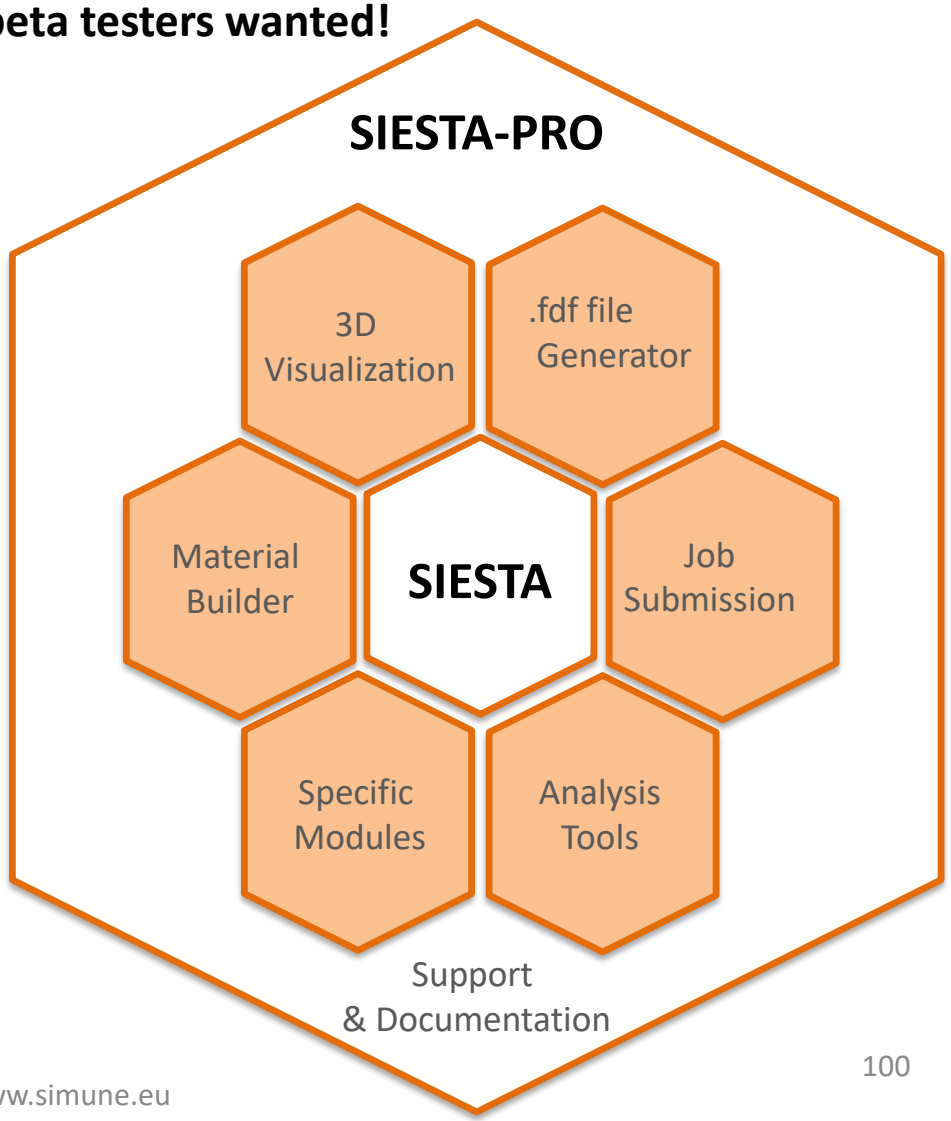
It is possible to add as many projections as you want. It is also possible to sum existing projection on the fly and re-plot the curves in matter of seconds.

SIESTA-PRO: Analysis Tool

SIESTA-PRO beta testers wanted!

SIMUNE is looking for collaborators to help us evaluating, testing and giving us feedback during SIESTA-PRO development process

Please contact us if you are interested in getting access to our powerful software before it is in the market



Thank You for Your Attention!

Acknowledgments

SIMUNE has received funds to develop the project: SIESTA -PRO - Spanish Initiative for Electronic Simulations with Thousands of Atoms: Open Source code with professional support and warranty. The project (RTC-2016-5681-7) has been funded by the Spanish Ministry of Economy, Industry and Competitiveness and has been co-financed by the European Structural and Investment Funds with the objective to promote the technological development, innovation and quality research.

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