The Abdus Salam
International Centre for Theoretical Physics

United Nations
Educational, Scientific and
Cultural Organization

IAEA
International Atomic Energy Agency

2145-4

Spring College on Computational Nanoscience

17 - 28 May 2010

Siesta Tutorial

P. ORDEJON and J.A. TORRES
CIN2 Barcelona / Univ. Madrid
Spain

SIESTA (nano)TUTORIAL

Pablo Ordejón

CSIC

ICN Institut Català de Nanotecnologia

CIN2 CENTRE D'INVESTIGACIÓ EN NANOCIÈNCIA I NANOTECNOLOGIA

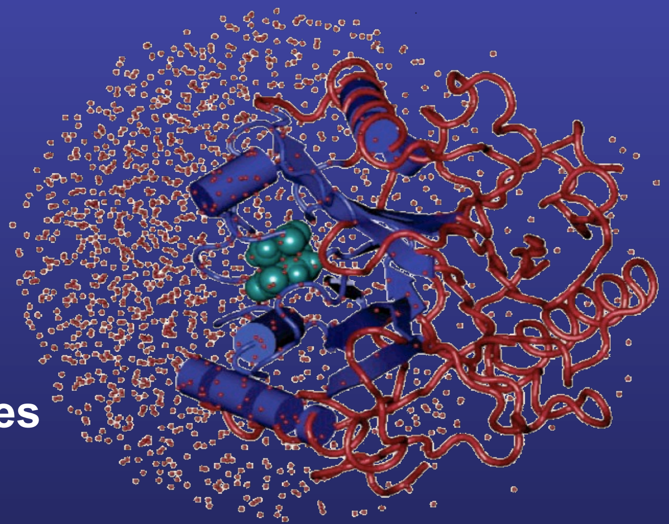
CAMPUS UAB. BELLATERRA. BARCELONA

FIRST-PRINCIPLES SIMULATIONS

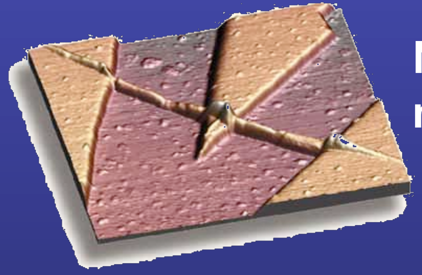
- Predictive Power
  - Fundamental laws of Physics
  - No empirical input
  - Set of “accepted” and “well tested *approximations*
  - Electrons are explicitly considered!!
- Impressive progress:
  - Quantum Chemistry (molecules)
  - Solid State Physics (solids)

Still: need to reach larger systems without a significant loose of accuracy.

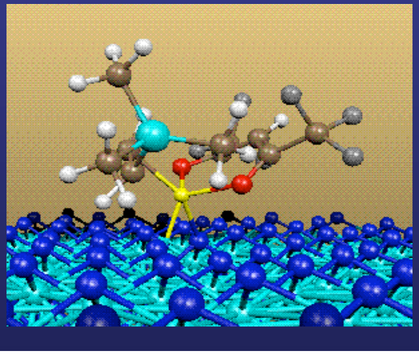
Chemistry in solution



Biomolecules



Nanoscale materials / devices



Surface physics / chemistry

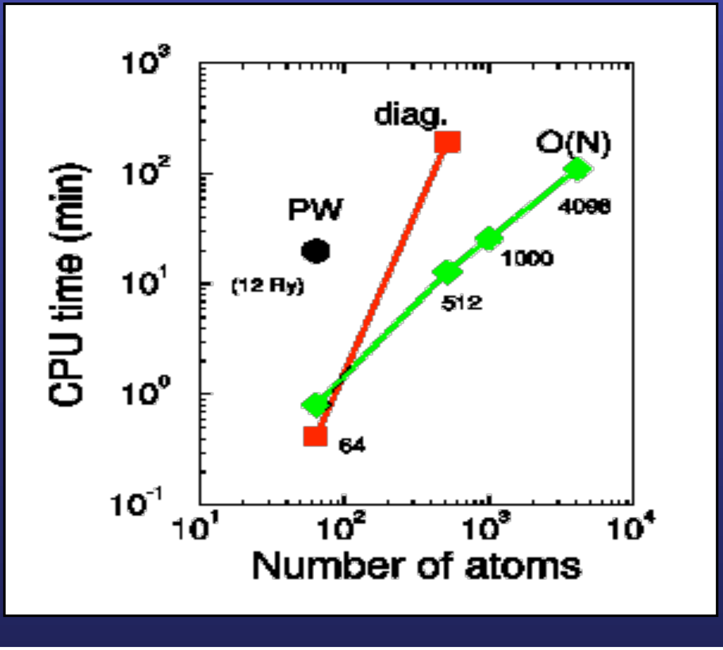
A code for DFT simulations in large systems

Spanish Initiative for Electronic Simulations with Thousands of Atoms

Soler, Artacho, Gale, García, Junquera, Ordejón and Sánchez-Portal
J. Phys.: Cond. Matt **14**, 2745 (2002)

- Numerical pseudo-atomic orbitals (large flexibility in basis set choice)

- Implements O(N) methodology
- Atomic forces and stress → MD simulations
- Very efficient: capable of trating large systems with modest computers
- Parallelized
- Freely available for the academic community



The SIESTA Team

Emilio Artacho	*(Cambridge University)*
Julian Gale	*(Curtin Inst. of Tech., Perth)*
Alberto García	*(ICMAB, Barcelona)*
Javier Junquera	*(U. Cantabria, Santander)*
Richard Martin	*(U. Illinois, Urbana)*
Pablo Ordejón	*(ICMAB, Barcelona)*
Daniel Sánchez-Portal	*(UPV, San Sebastián)*
José M. Soler	*(UAM, Madrid)*

The SIESTA Manager

Jose Antonio Torres	*(UAM and Nanotec, Madrid)*

The impact of SIESTA

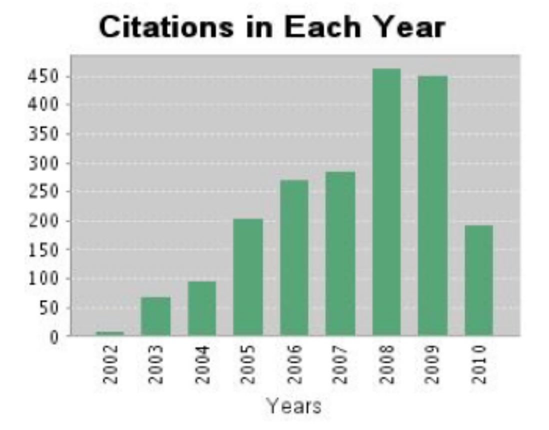
- Basic methodology paper:

  J. Soler *et al*,
  J. Phys: Condens. Matter, **14**, 2745 (2002)

- More than 4000 registered users

- Over 1500 published papers have used the code

- Over 2000 citations



Siesta resources:

Web page: http://www.uam.es/siesta

- SIESTA methodological papers
  J. Soler *et al*,
  J. Phys: Condens. Matter, **14**, 2745 (2002)
- Pseudos and basis database
- Mailing list (including past mailing archives)
- Registration and Download of sources
- User’s Guide
- Documentation of previous Tutorials and Courses

PLAN OF THE ~~COURSE~~ TALK:

Theory:

- Introduction to DFT and SIESTA
- Basis sets: Numerical PAO’s of finite range
- Numerical algorithms in SIESTA
- Orden-N methods
- Basic execution – important parameters
- Molecular Dynamics and Structural Relaxation
- Analysis, Visualization and Post-processing
- Instalation, Compilation, Parallelization

Example run (after coffee):

- Basis set: H_2O – a case study
- Molecular dynamics: H_2 on Si(001) 2x1 surface

Introduction to DFT and SIESTA

What are the main approximations?

Born-Oppenhaimer

Decouple the movement of the electrons and the nuclei.

Density Functional Theory

Treatment of the electron – electron interactions.

Pseudopotentials

Treatment of the (nuclei + core) – valence.

Basis set

To expand the wave functions: Numerical PAOS of finite range

Numerical evaluation of matrix elements

Efficient and self-consistent computations of H and S.

Supercells

To deal with periodic and non-periodic systems

DFT in practice

1. Choose a *basis set*

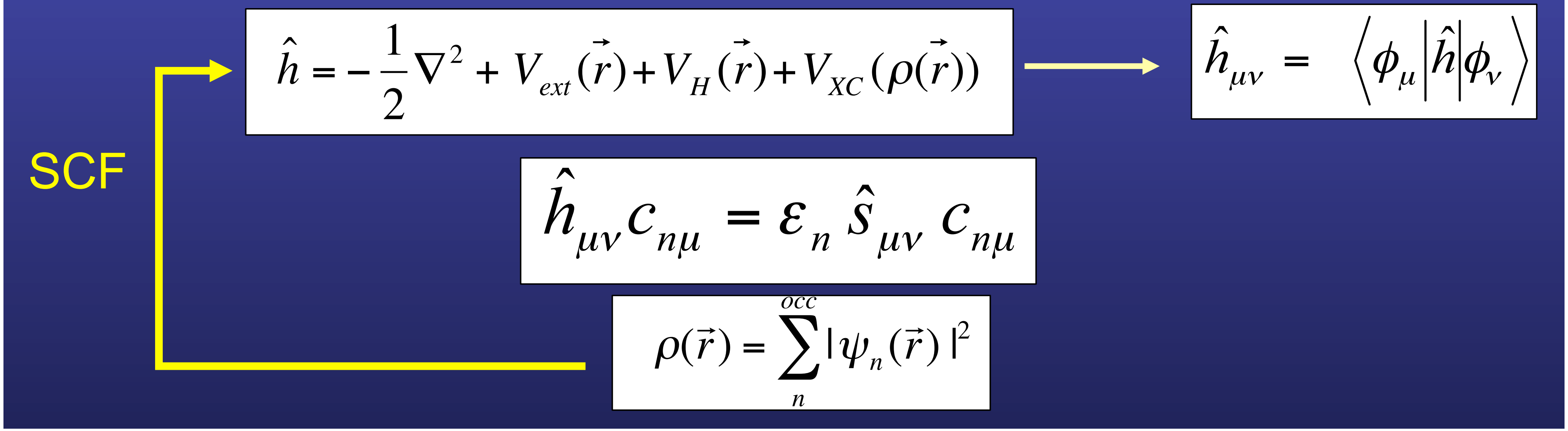
$$\psi_n(\vec{r}) = \sum_{\mu} c_{n\mu} \phi_\mu(\vec{r})$$

Plane Waves - APWs - LMTOs - Grids

Gaussians - Slaters

(Numerical) Pseudo-Atomic Orbitals

2. Solve the *self-consistent* one electron problem: Building H and obtaining the eigenstates:



$$\hat{h} = -\frac{1}{2}\nabla^2 + V_{ext}(\vec{r}) + V_H(\vec{r}) + V_{XC}(\rho(\vec{r}))$$

$$\hat{h}_{\mu\nu} = \left\langle \phi_\mu \middle| \hat{h} \middle| \phi_\nu \right\rangle$$

SCF

$$\hat{h}_{\mu\nu} c_{n\mu} = \varepsilon_n \hat{s}_{\mu\nu} c_{n\mu}$$

$$\rho(\vec{r}) = \sum_{n}^{occ} |\psi_n(\vec{r})|^2$$

Capabilities

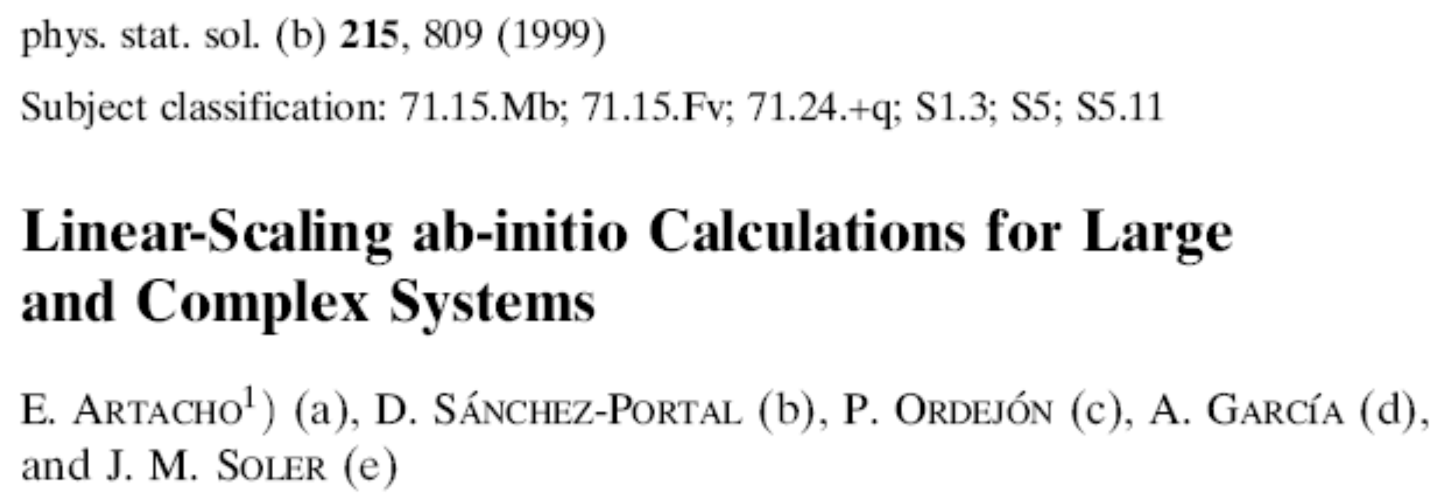
siesta

- **Electronic structure information**
  - Band structures (k-point sampling)
  - Population analysis
  - Charge distributions
  - Electrostatic Potentials
  - Density of States
  - Spin distributions
  - Non-collinear spin states
  - STM image simulation....
- **Atomic forces and stress**
  - Relaxations
    - Atomic coordinates
    - Cell shape & size
  - Phonons, elastic constants, ...
  - Molecular Dynamics:
    - E, V
    - T, V (Nose Thermostat)
    - P (Parrinello-Rahman)
    - T, P
- **New features (3.0beta)**
  - Non-equilibrium electronic transport (TranSIESTA)
  - Van der Waals functional (Langreth-Lundqvist)
  - Virtual Crystal Approximation
  - Filters to reduce the ‘egg-box’ effect
- **Upcoming release**
  - Hybrid QM/MM module (finite and periodic)
  - Real-time TD-DFT
  - Spin-orbit coupling
  - Massively parallel performance

Basis Sets:

Pseudo-Atomic orbitals of finite range

Main references on Basis Sets for SIESTA

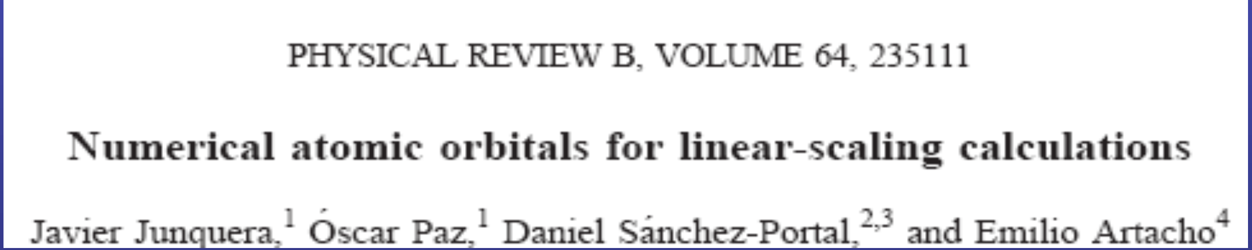


phys. stat. sol. (b) **215**, 809 (1999)

Subject classification: 71.15.Mb; 71.15.Fv; 71.24.+q; S1.3; S5; S5.11

Linear-Scaling ab-initio Calculations for Large and Complex Systems

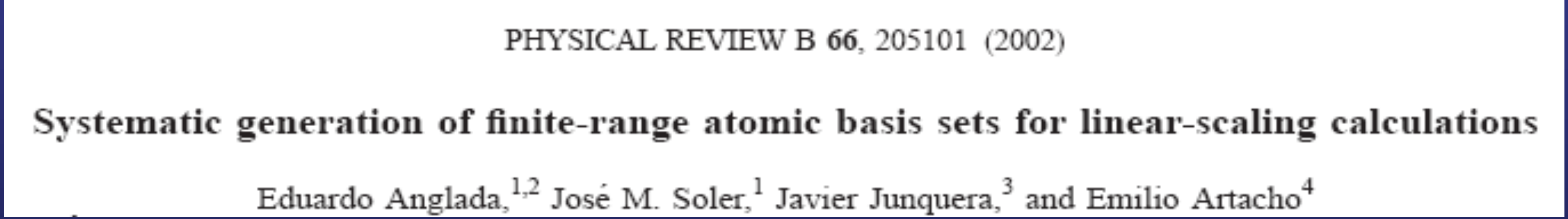
E. Artacho[1]) (a), D. Sánchez-Portal (b), P. Ordejón (c), A. García (d), and J. M. Soler (e)



PHYSICAL REVIEW B, VOLUME 64, 235111

Numerical atomic orbitals for linear-scaling calculations

Javier Junquera,[1] Óscar Paz,[1] Daniel Sánchez-Portal,[2,3] and Emilio Artacho[4]



PHYSICAL REVIEW B **66**, 205101 (2002)

Systematic generation of finite-range atomic basis sets for linear-scaling calculations

Eduardo Anglada,[1,2] José M. Soler,[1] Javier Junquera,[3] and Emilio Artacho[4]

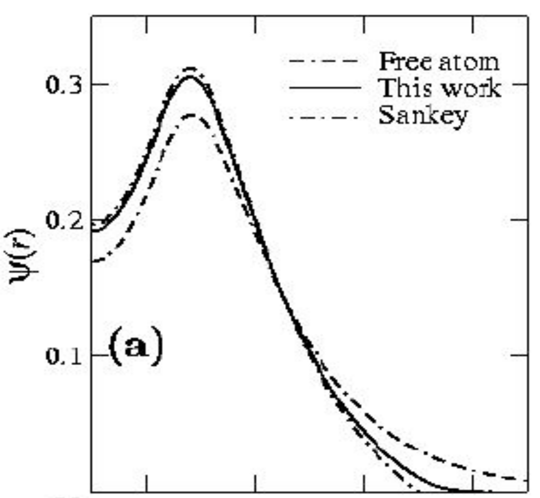
Atomic orbitals:

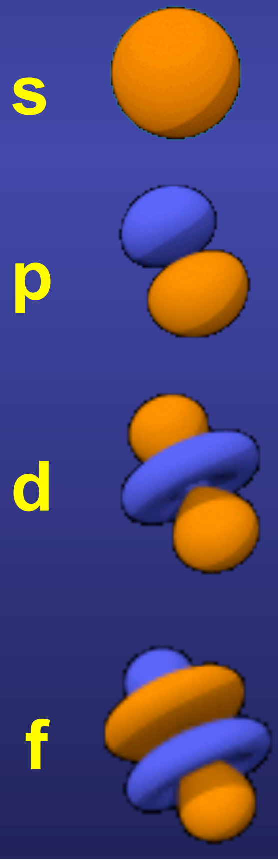
LCAO: $\psi_n(\vec{r}) = \sum_{\mu} c_{n\mu}\phi_\mu(\vec{r})$

$$\phi_{Ilmn}(\vec{r}) = R_{Iln}(|\vec{r}_I|)\,Y_{lm}(\hat{r}_I)$$

Radial part:
degree of freedom to play with

Spherical harmonics:
well defined (fixed) objects





Size: Number of orbitals for a given *lm n*

Range: Spatial extension of the orbitals

Shape: of the radial part

Atomic orbitals: advantages and pitfalls

$$\phi_{Ilmn}(\vec{r}) = R_{Iln}(|\vec{r}_I|)\,Y_{lm}(\hat{r}_I)$$

ADVANTAGES

- Very efficient (number of basis functions needed is usually very small).
- Large reduction of CPU time and memory
- Straightforward physical/chemical interpretation (population analysis, projected density of states,…)
- They can achieve very high accuracy

DISADVANTAGES

- Equations and codes are more complex
- Lack of systematic for convergence (non unique way of enlarge the basis set)
- Human and computational effort searching for a good basis set before facing a realistic project.
- Depend on the atomic position (Pulay terms).
- Basis Set Superposition Errors

Numerical Pseudo-atomic orbitals

Numerical solution of the Kohn-Sham Hamiltonian for the **isolated pseudoatom** with the **same approximations** (xc, pseudos) as for the condensed system

$$\left(-\frac{1}{2r}\frac{d^2}{dr^2}r+\frac{l(l+1)}{2r^2}+V_l\left(r\right)\right)R_l\left(r\right)=\varepsilon_l R_l\left(r\right)$$

This equation is solved in a radial grid using Numerov’s method

(Pseudo) Atomic Orbitals

with finite range

siesta

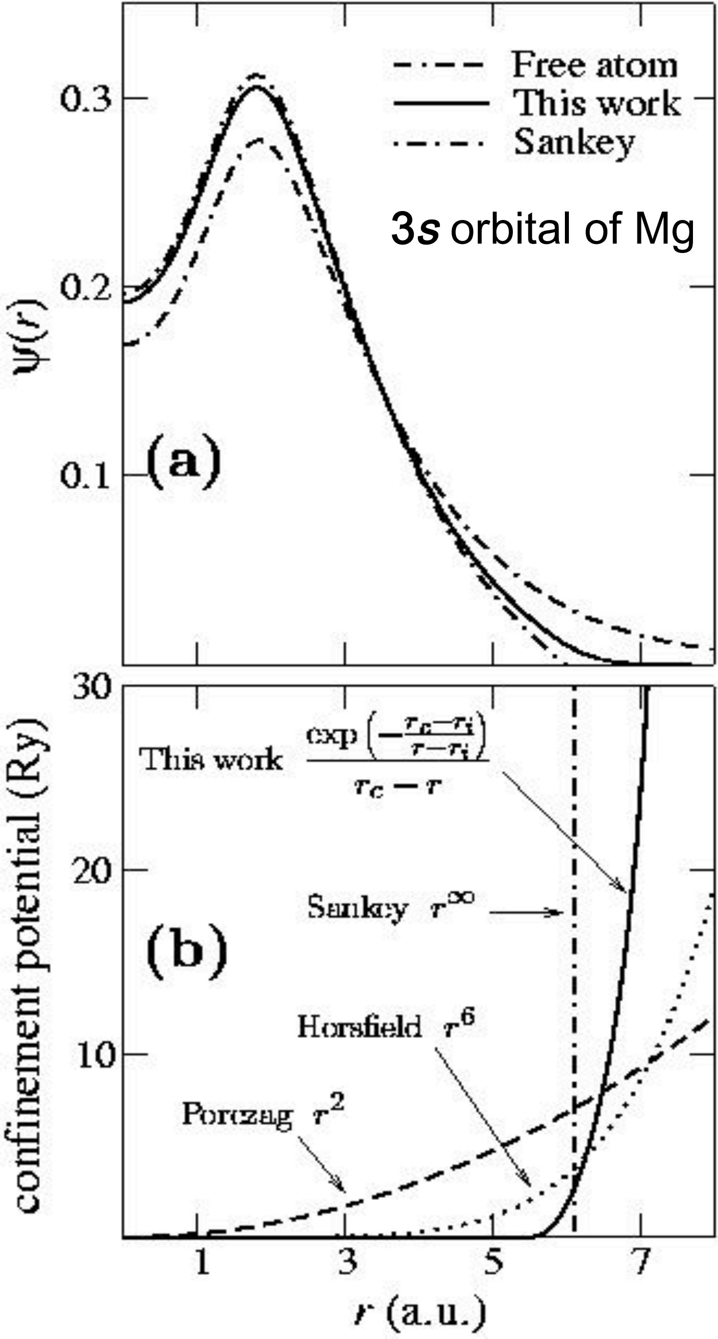
Sankey & Niklewski, Phys. Rev. B **41** 3979 (89)

Hard wall potential confinement (FIREBALLS)

Artacho *et al.*, Phys. Stat. Sol. **215**, 809 (99)

J. Junquera *et al*, Phys. Rev. B **64**, 235111 (01)

E. Anglada *et al.*, Phys. Rev. B **66**, 205101 (02)

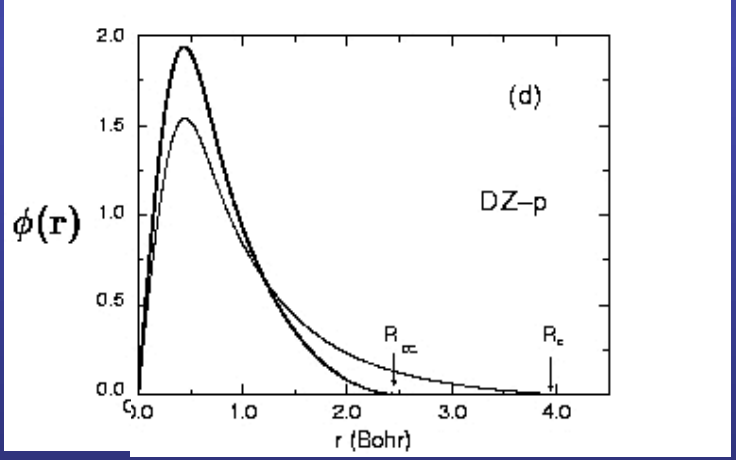


Radial and Angular flexibility

$$\phi_{Ilmn}\left(\vec{r}\right) = R_{Iln}\left(\left|\vec{r}_I\right|\right) Y_{lm}\left(\hat{r}_I\right)$$

- Minimal bases: One radial function per occupied shell in the free atom

Single-ζ (eg: Si: one 3s orbital and three 3p orbitals)



- Several radial functions to describe an atomic shell (same angular part):

Multiple-ζ

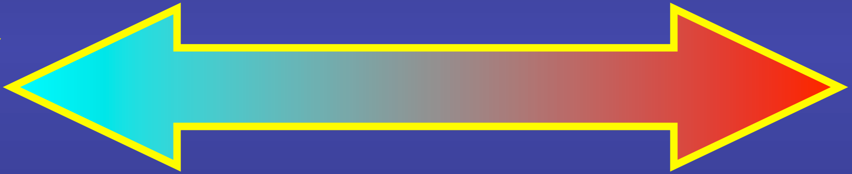
- Higher angular momenta:

Polarization Functions

Size (number of basis set per atom)

Depending on the required accuracy and

available computational power



Quick exploratory
calculations

Highly converged
calculations

Minimal basis set

(single-ζ; SZ)

Multiple-ζ

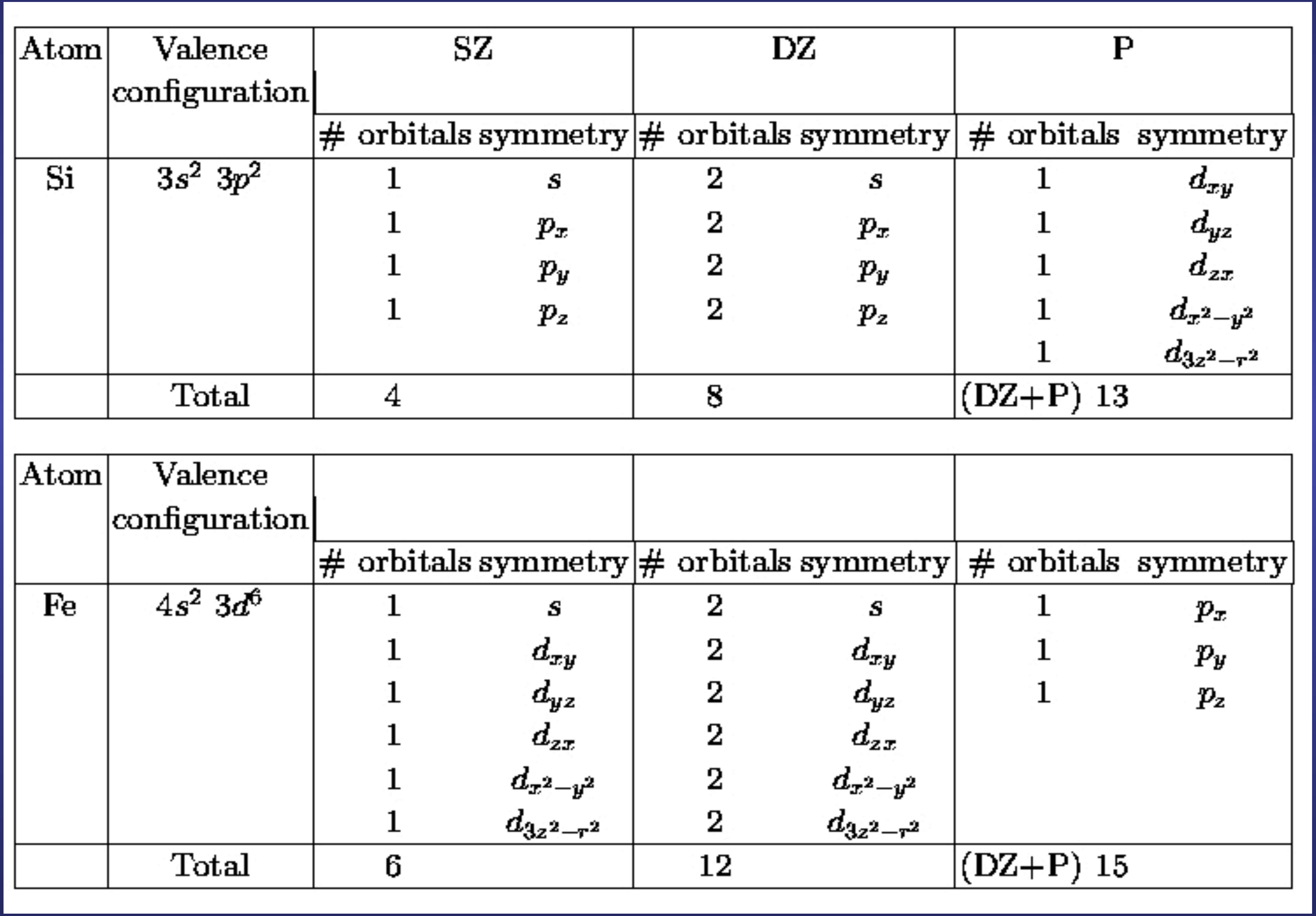
+

Polarization

+

Diffuse orbitals

Improving the quality of the basis ⇒ more atomic orbitals per atom

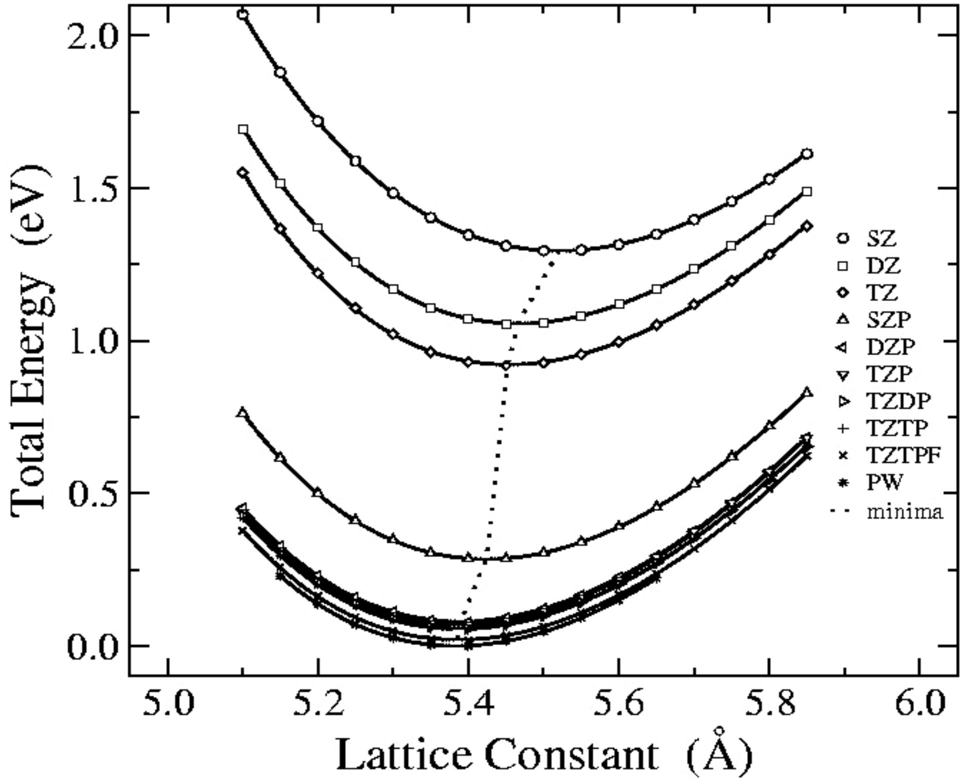


Atom	Valence configuration	SZ		DZ		P	
		# orbitals	symmetry	# orbitals	symmetry	# orbitals	symmetry
Si	$3s^2\ 3p^2$	1	s	2	s	1	d_{xy}
		1	p_x	2	p_x	1	d_{yz}
		1	p_y	2	p_y	1	d_{zx}
		1	p_z	2	p_z	1	$d_{x^2-y^2}$
						1	$d_{3z^2-r^2}$
	Total	4		8		(DZ+P) 13	

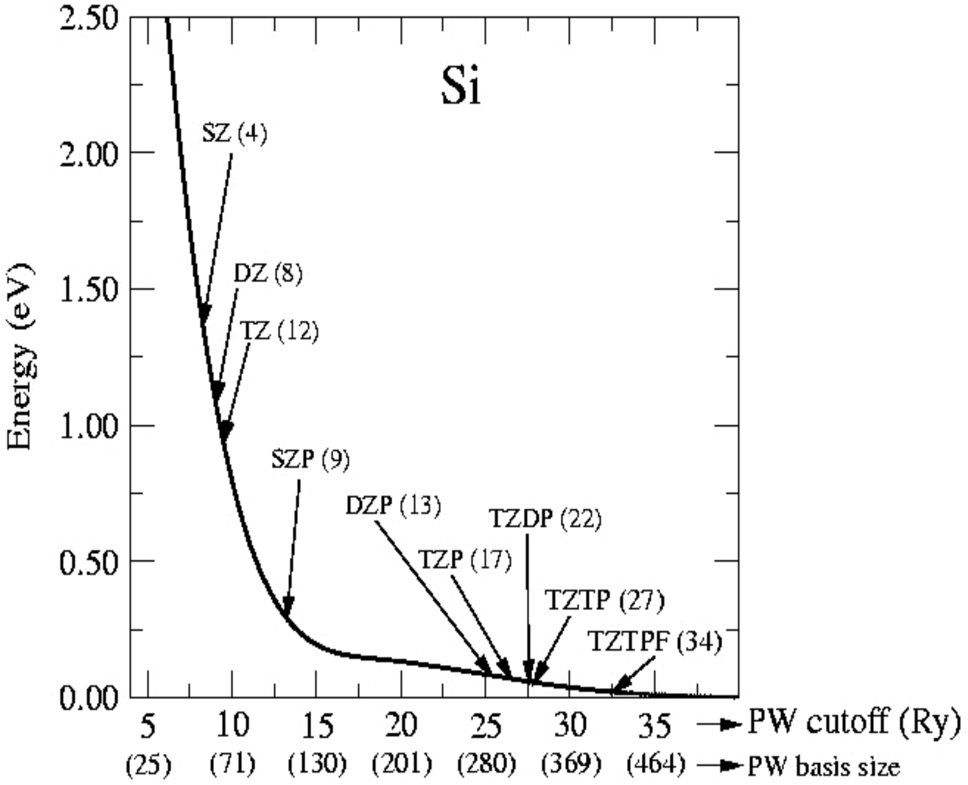
Atom	Valence configuration						
		# orbitals	symmetry	# orbitals	symmetry	# orbitals	symmetry
Fe	$4s^2\ 3d^6$	1	s	2	s	1	p_x
		1	d_{xy}	2	d_{xy}	1	p_y
		1	d_{yz}	2	d_{yz}	1	p_z
		1	d_{zx}	2	d_{zx}		
		1	$d_{x^2-y^2}$	2	$d_{x^2-y^2}$		
		1	$d_{3z^2-r^2}$	2	$d_{3z^2-r^2}$		
	Total	6		12		(DZ+P) 15	

Convergence as a function of the size of the basis set: Bulk Si

Cohesion curves



PW and NAO convergence



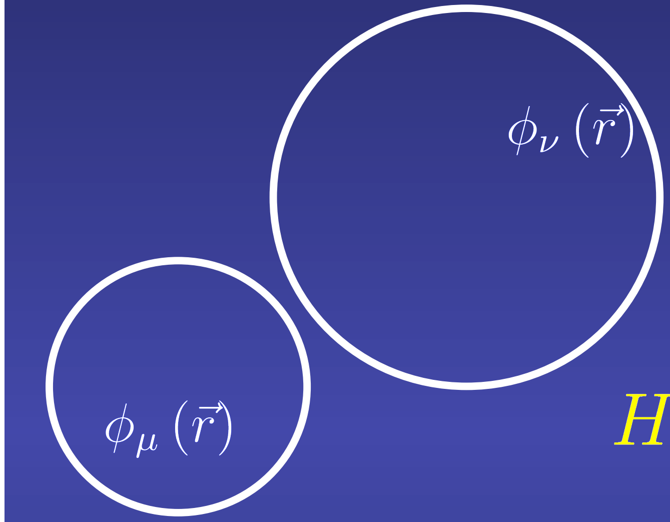
Atomic orbitals show nice convergence with respect the size

Polarization orbitals very important for convergence (more than multiple-ζ)

Double-ζ plus polarization equivalent to a PW basis set of 26 Ry

Range: the spatial extension of the atomic orbitals

Order(N) methods ⇒ locality, that is, a finite range for matrix and overlap matrices



If the two orbitals are sufficiently far away

$$S_{\nu\mu} = \langle \phi_\nu \mid \phi_\mu \rangle = \int d\vec{r}\ \phi_\nu^*(\vec{r})\,\phi_\mu(\vec{r}) = 0$$

$$H_{\nu\mu} = \langle \phi_\nu \mid \hat{H} \mid \phi_\mu \rangle = \int d\vec{r}\ \phi_\nu^*(\vec{r})\,\hat{H}\,\phi_\mu(\vec{r}) = 0$$

Neglect interactions:

Below a tolerance

Beyond a given scope of neighbours

Problem: introduce numerical instabilities for high tolerances.

Strictly localized atomic orbitals:

Vanishes beyond a given cutoff radius

O. Sankey and D. Niklewski, PRB 40, 3979 (89)

Problem: accuracy and computational efficiency depend on the range of the basis orbitals

How to define all the r_c in a balance way?

How to control de range of the orbitals in a balanced way: the energy shift

$$\left(-\frac{1}{2r}\frac{d^2}{dr^2}r+\frac{l(l+1)}{2r^2}+V_l\left(r\right)\right)R_l\left(r\right)=\left(\varepsilon_l+\underset{\big\uparrow}{\delta\varepsilon_l}\right)R_l\left(r\right)$$

Energy increase ≡ Energy shift

PAO.EnergyShift (energy)

Cutoff radius, r_c, = position where each orbital has the node

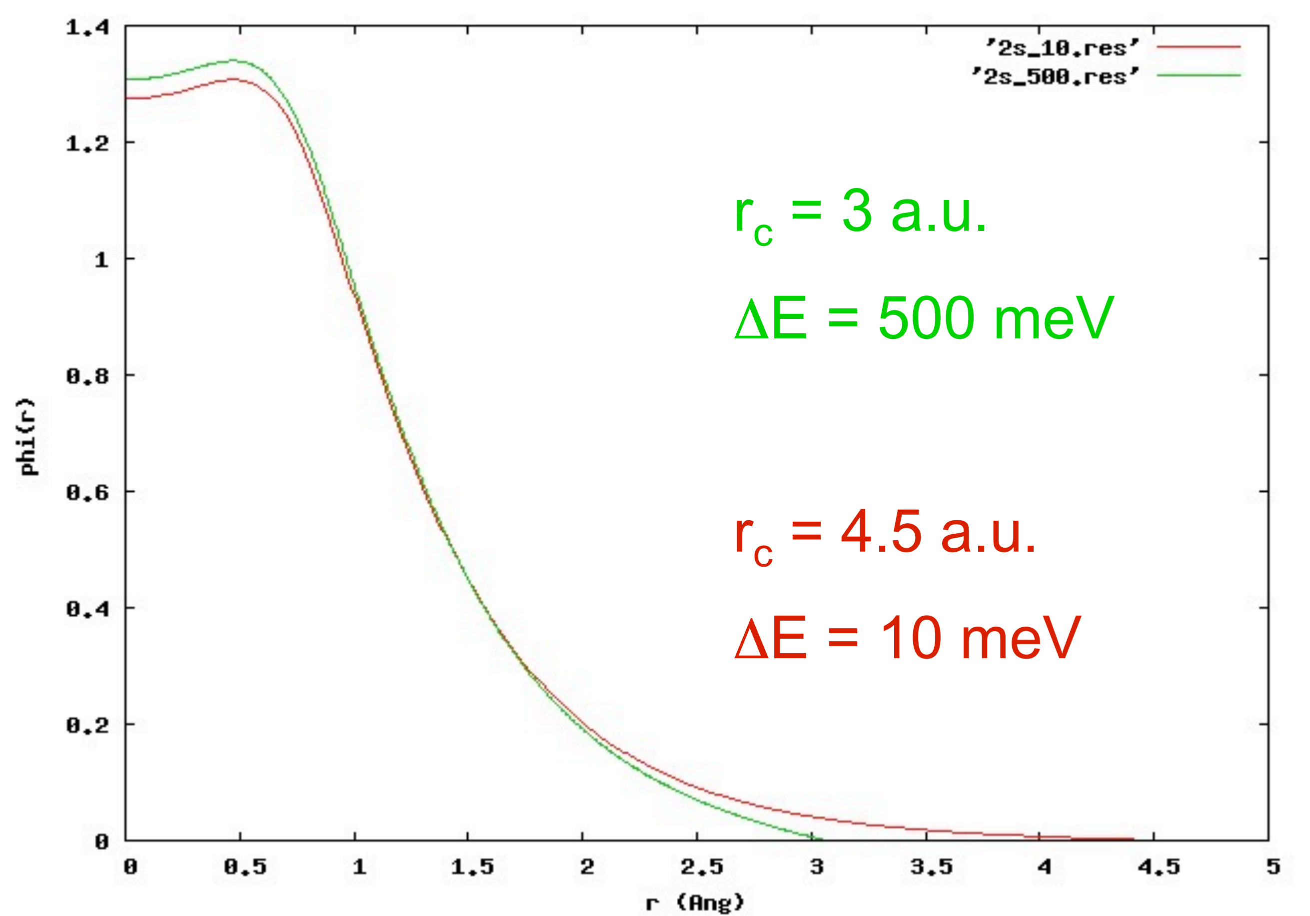
A single parameter for all cutoff radii

The larger the Energy shift, the shorter the r_cs

Typical values: 100-200 meV

E. Artacho et al. Phys. Stat. Solidi (b) 215, 809 (1999)

Shape of the orbitals: r_c



r_c = 3 a.u.

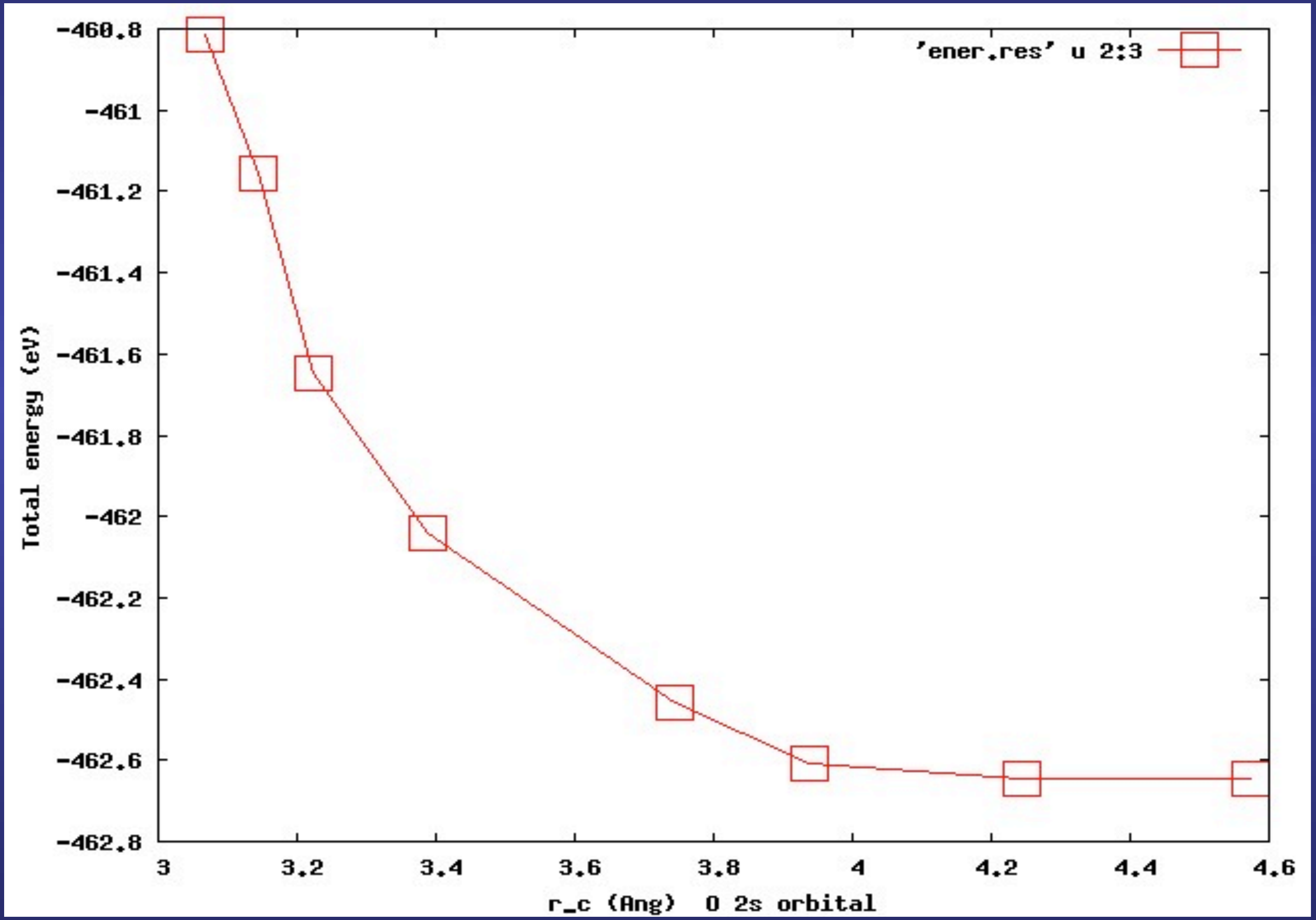
ΔE = 500 meV

r_c = 4.5 a.u.

ΔE = 10 meV

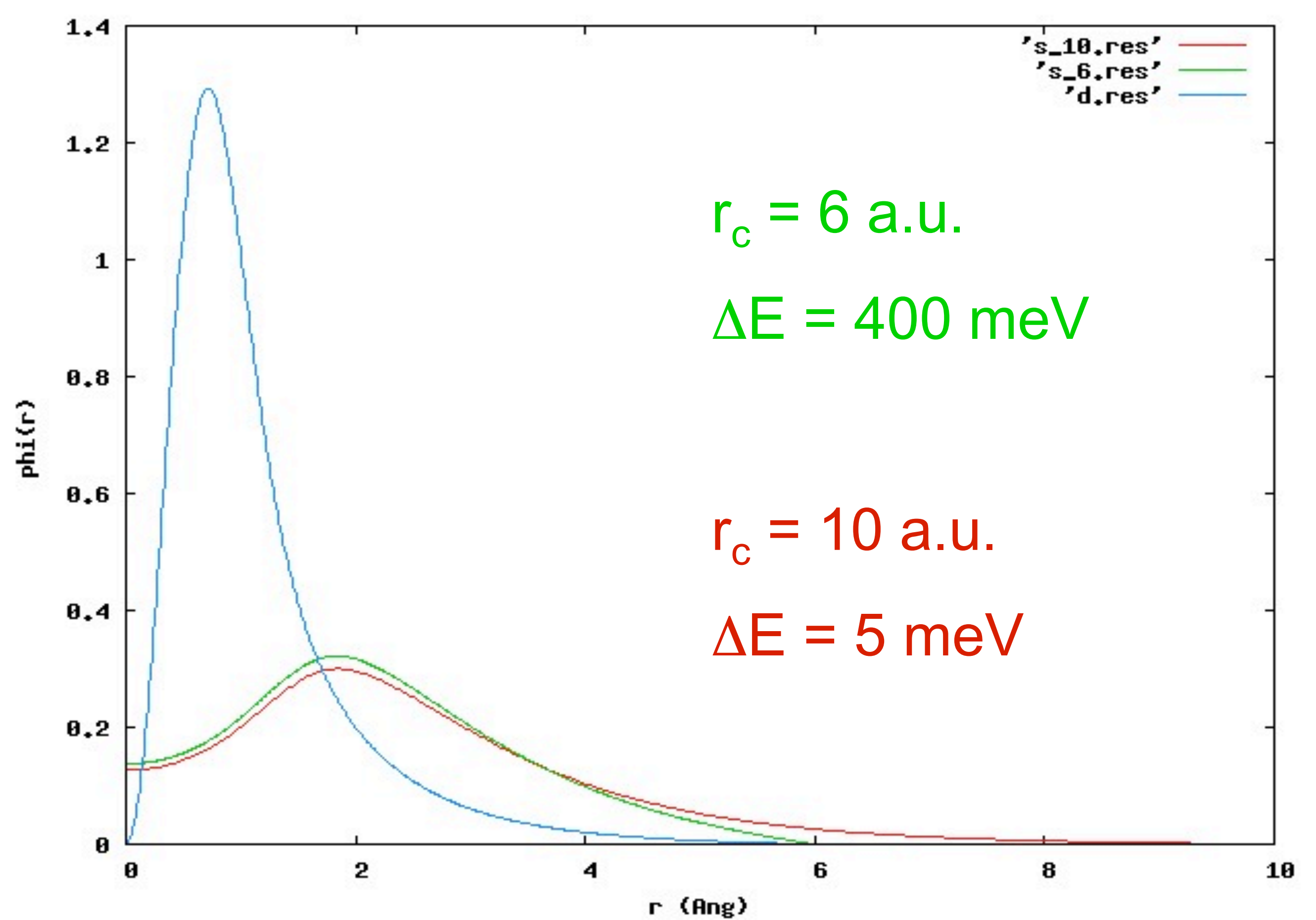
O 2s orbital

Energy vs. r_c - Molecules



H_2O

Shape of the orbitals: r_c



r_c = 6 a.u.

ΔE = 400 meV

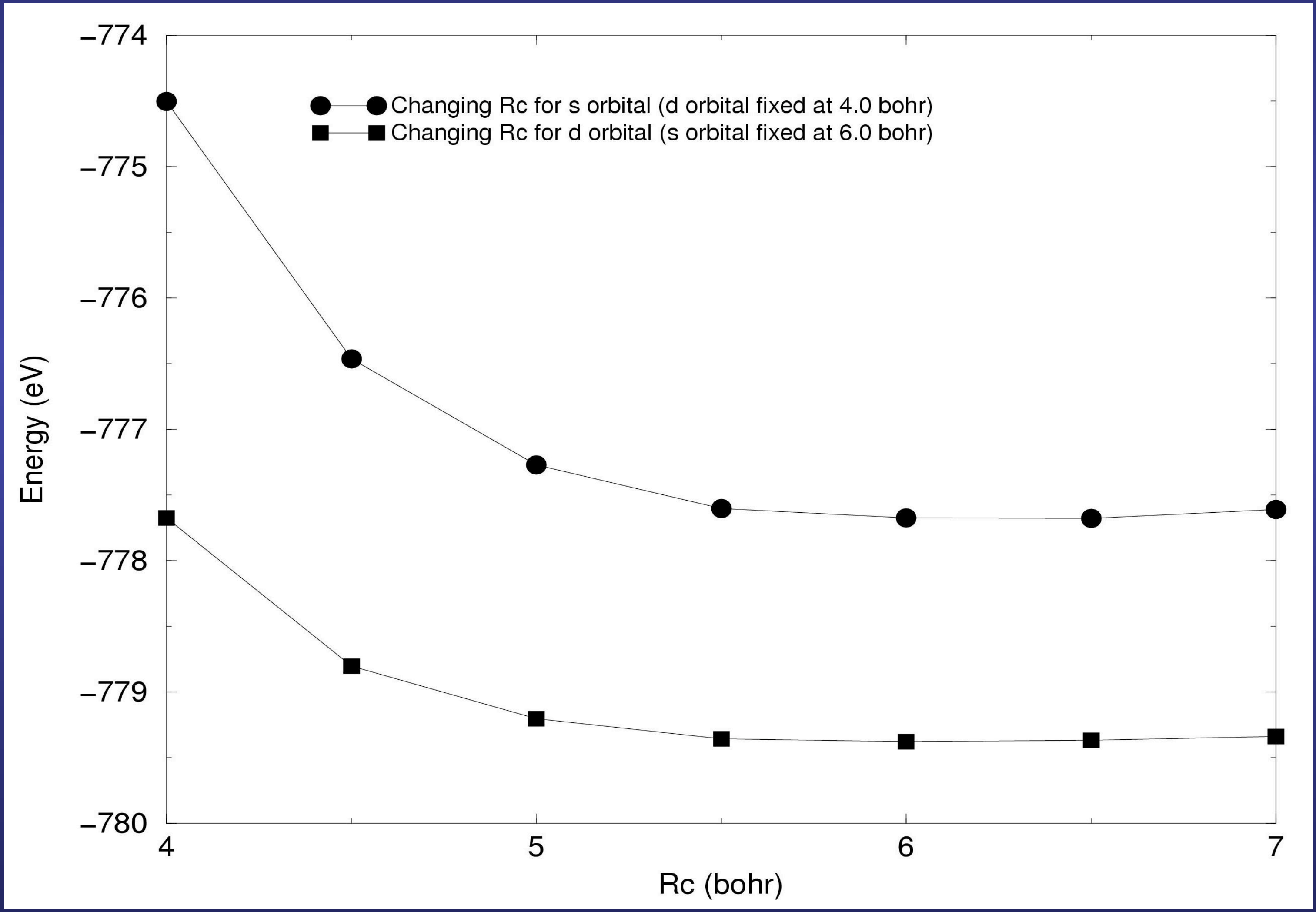
r_c = 10 a.u.

ΔE = 5 meV

Fe 3d orbital

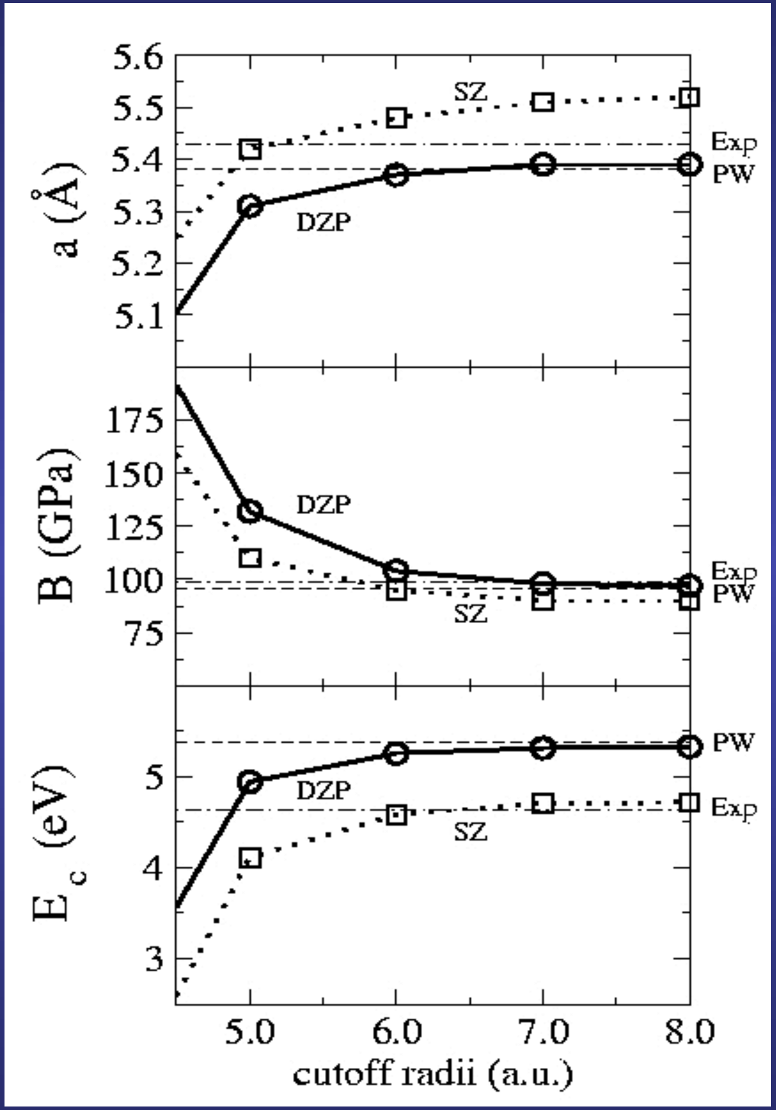
Fe 4s orbital

Energy vs. r_c - Solids



Bulk Fe

Convergence with the range



Bulk Si

J. Soler *et al.*, J. Phys: Condens. Matter, 14, 2745 (2002)

More efficient →

← **More accurate**

The shape and range might be also controlled by an extra charge and/or by a confinement potential

Extra charge δQ

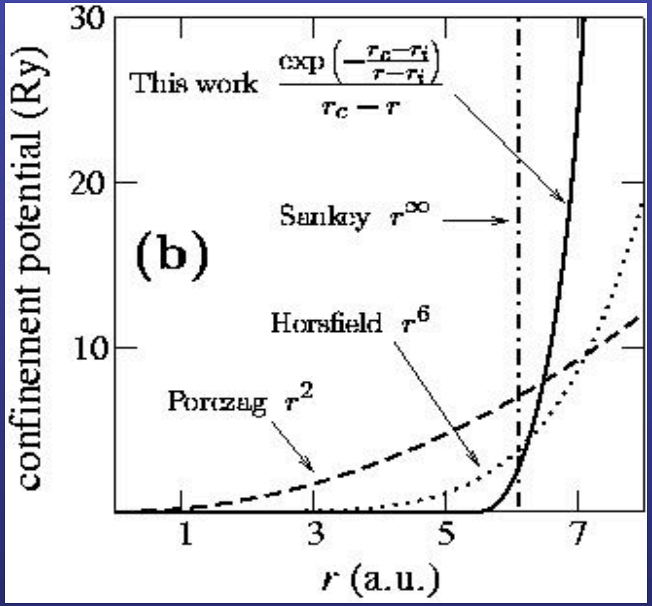
Orbitals in anions tend to be more expanded

Orbitals in cations tend to be more contracted

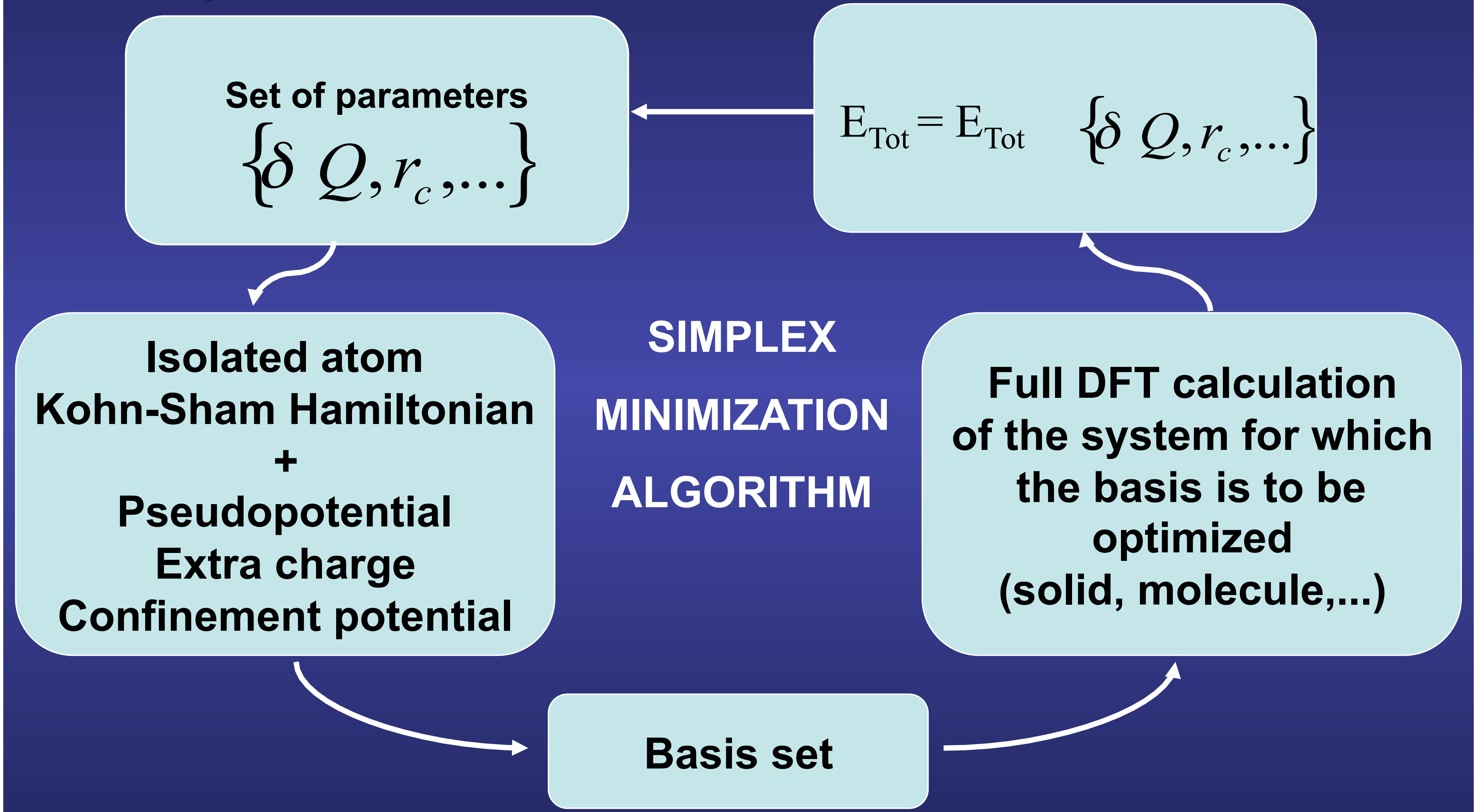
This parameter might be important in some oxides

Confinement potentials

Solve the Schrödinger equation for the isolated atom inside a confinement potential.



Optimization of the parameters that define the basis set: the Simplex code



Set of parameters

$$\{\delta Q, r_c, \ldots\}$$

$$E_{\mathrm{Tot}} = E_{\mathrm{Tot}} \{\delta Q, r_c, \ldots\}$$

Isolated atom
Kohn-Sham Hamiltonian
+
Pseudopotential
Extra charge
Confinement potential

SIMPLEX

MINIMIZATION

ALGORITHM

Full DFT calculation of the system for which the basis is to be optimized (solid, molecule,...)

Basis set

Publicly available soon…

Recap on basis sets

Choosing the basis set:

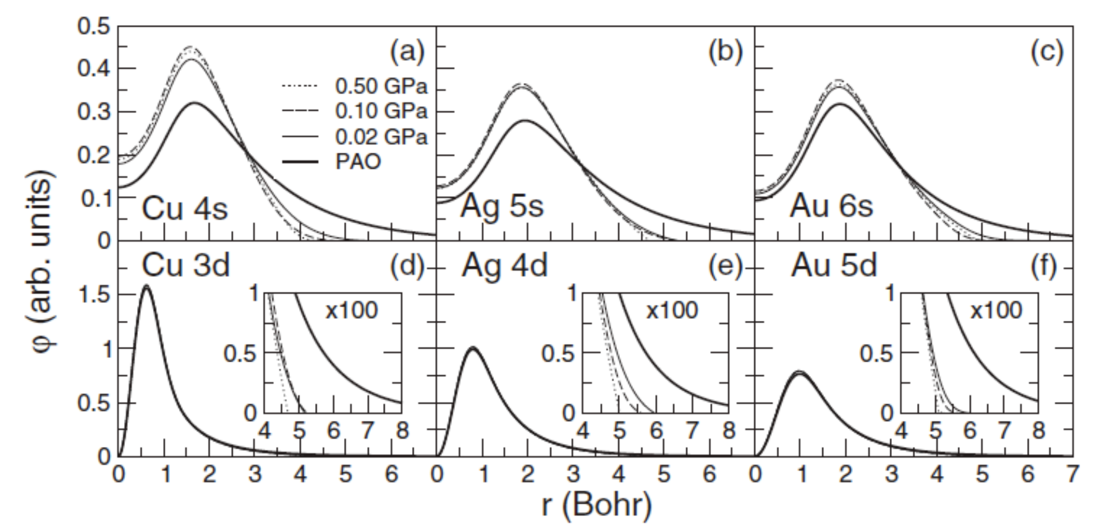
- Number of orbitals per atom:
  - # radial functions per angular momentum shell: SZ, DZ, TZ...
  - # of angular momentum shells: Polarization
- Radial cutoff: Energy shift parameter or explicit optimization
- Radial shape:
  - scheme for Multilple-Z and polarization
  - parameters defining net charge, shape of confining potentials, matching radii, etc.

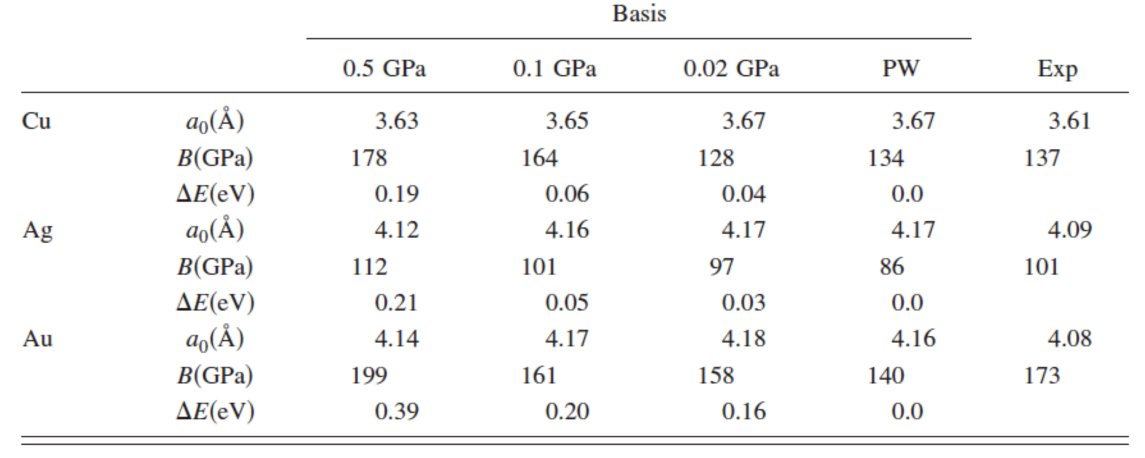
Current effort for searching for systematics.

DZP basis set, typical errors similar to those from the DFT functional or the pseudopotentials.

A Case Study: Noble Metal (111) Surfaces

- Excellent description of BULK with standard DZP bases



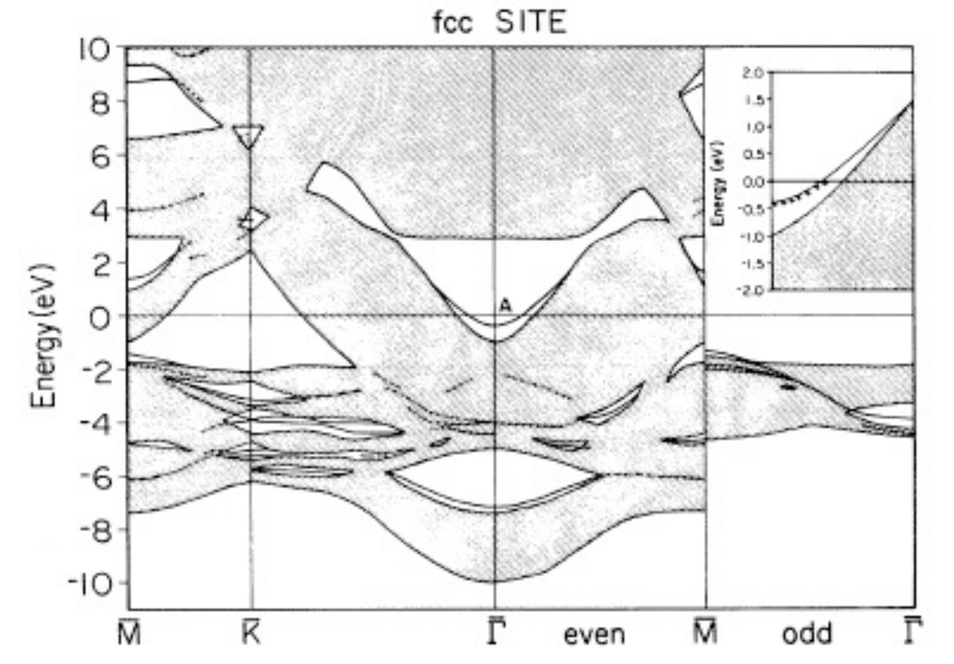


		Basis				
		0.5 GPa	0.1 GPa	0.02 GPa	PW	Exp
Cu	a_0(Å)	3.63	3.65	3.67	3.67	3.61
	B(GPa)	178	164	128	134	137
	ΔE(eV)	0.19	0.06	0.04	0.0	
Ag	a_0(Å)	4.12	4.16	4.17	4.17	4.09
	B(GPa)	112	101	97	86	101
	ΔE(eV)	0.21	0.05	0.03	0.0	
Au	a_0(Å)	4.14	4.17	4.18	4.16	4.08
	B(GPa)	199	161	158	140	173
	ΔE(eV)	0.39	0.20	0.16	0.0	

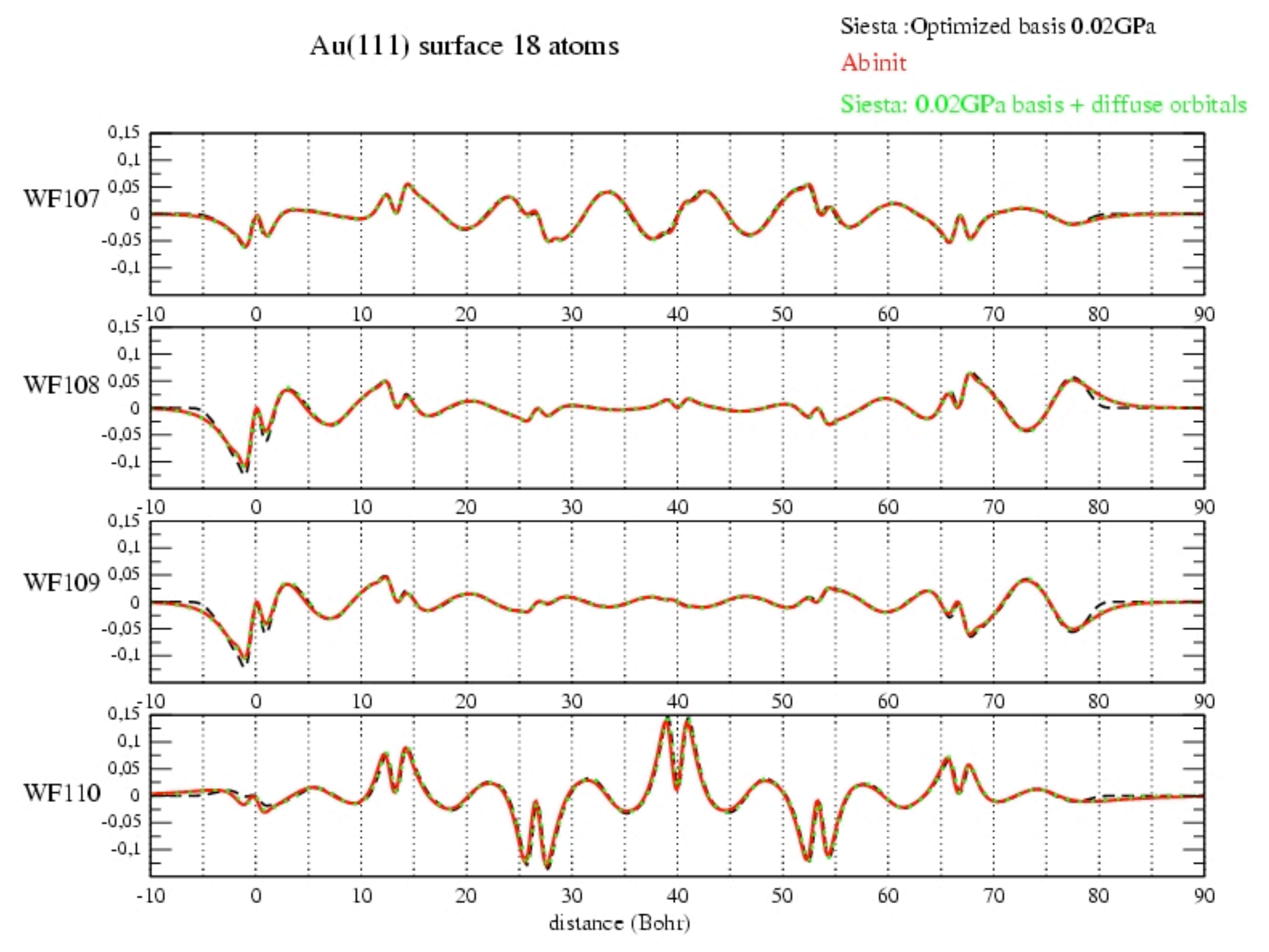
A Case Study: Noble Metal (111) Surfaces

- The decay of the wave functions into vacuum is different from that in the bulk

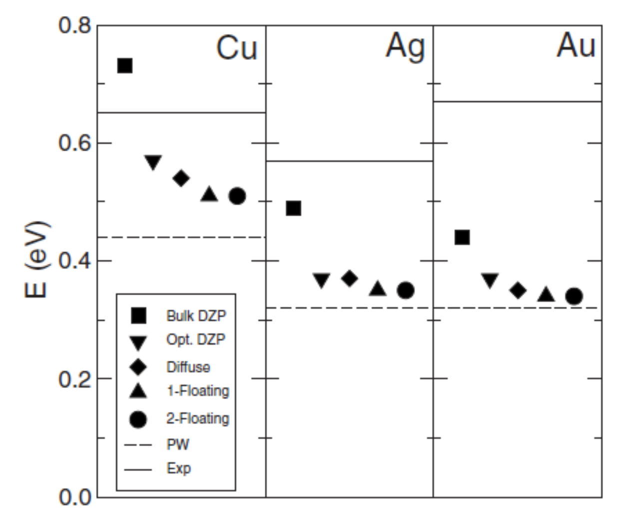
- The (111) surface shows surface states which extend into vacuum

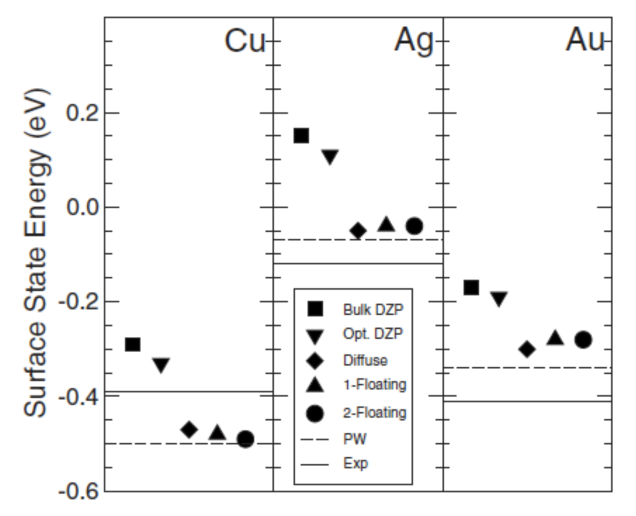


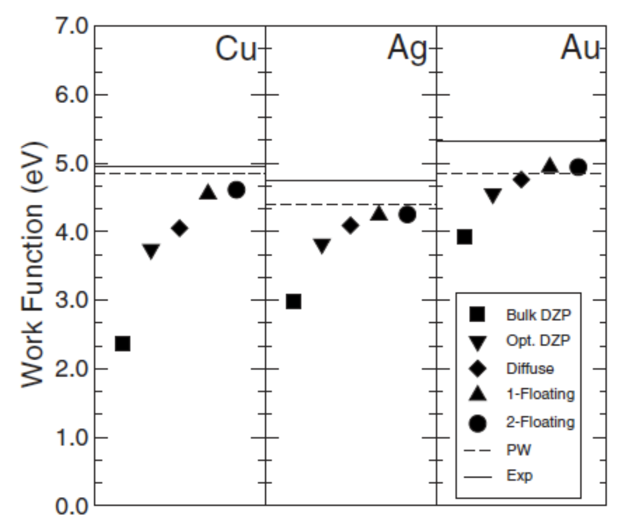
A Case Study: Noble Metal (111) Surfaces

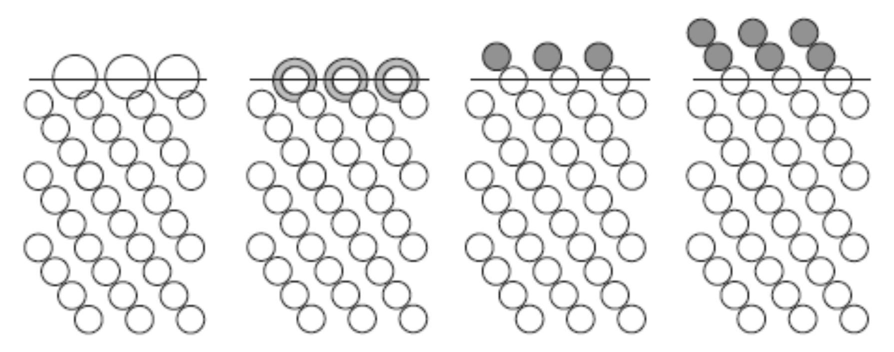


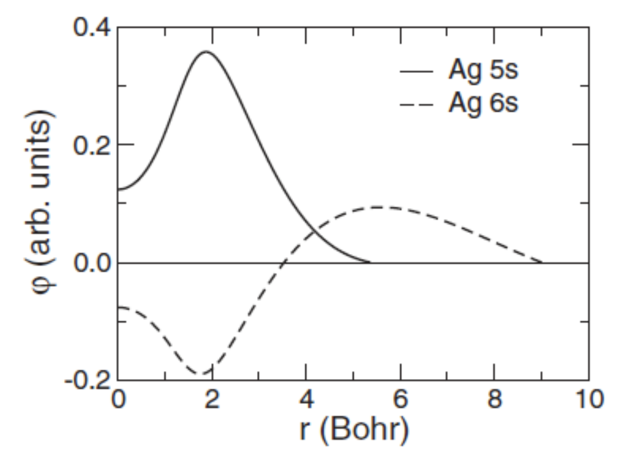
A Case Study: Noble Metal (111) Surfaces



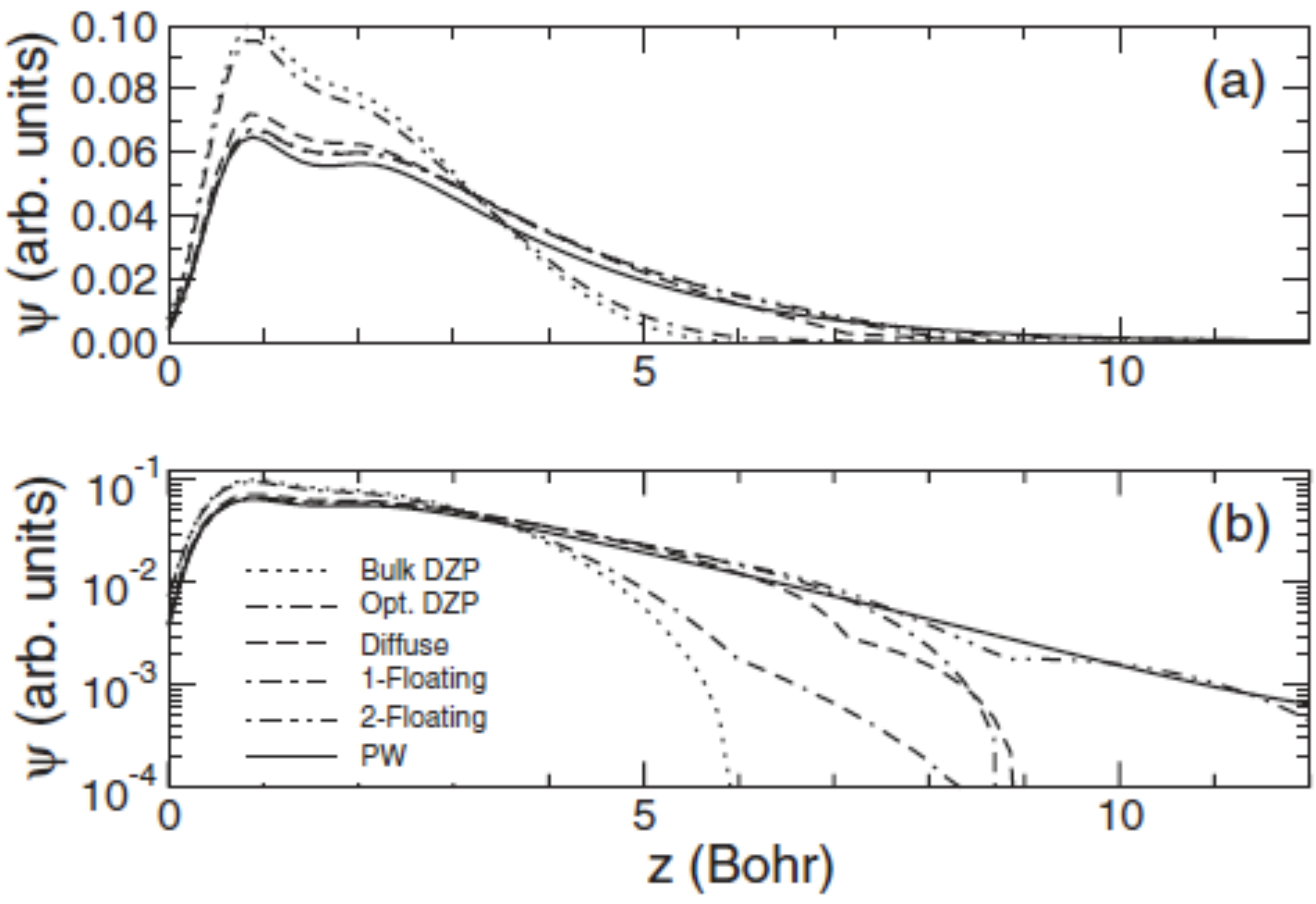





(a) Opt. DZP (b) Diffuse (c) 1–Floating (d) 2–Floating



A Case Study: Noble Metal (111) Surfaces



SIESTA Basic Execution

To run Siesta you need:

1.- Access to the executable file

2.- An input file: written in ascii (plain text) using:

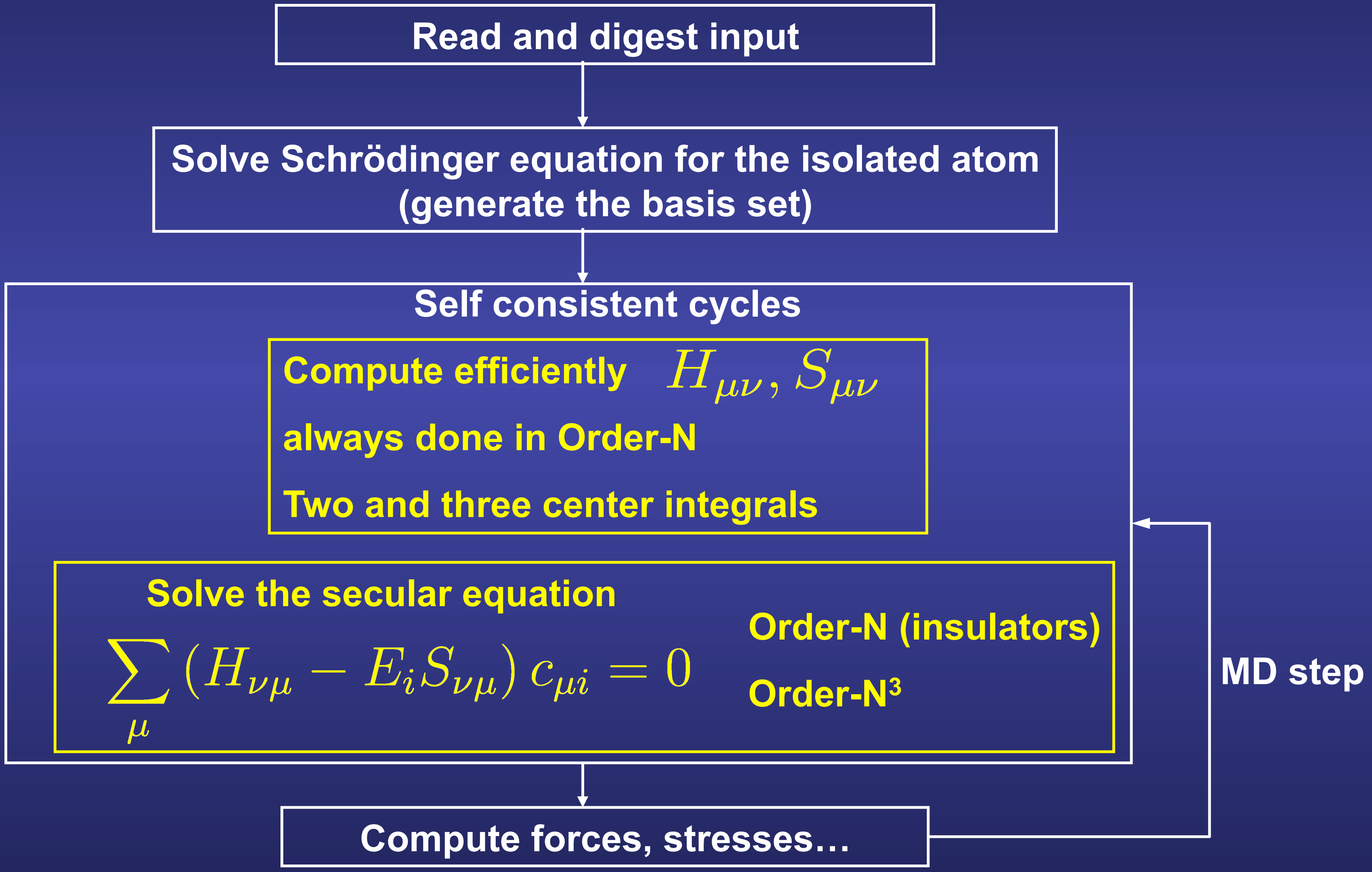
Flexible Data Format (FDF)   (A. García and J. M. Soler)

3.- A pseudopotential file for each kind of element in the input file. Two different formats:

Unformatted binary (.vps)

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

Schematic flowchart of a SIESTA run



Read and digest input

Solve Schrödinger equation for the isolated atom
(generate the basis set)

Self consistent cycles

Compute efficiently $H_{\mu\nu}, S_{\mu\nu}$

always done in Order-N

Two and three center integrals

Solve the secular equation

$$\sum_{\mu} \left(H_{\nu\mu} - E_i S_{\nu\mu} \right) c_{\mu i} = 0$$

Order-N (insulators)

Order-N^3

Compute forces, stresses…

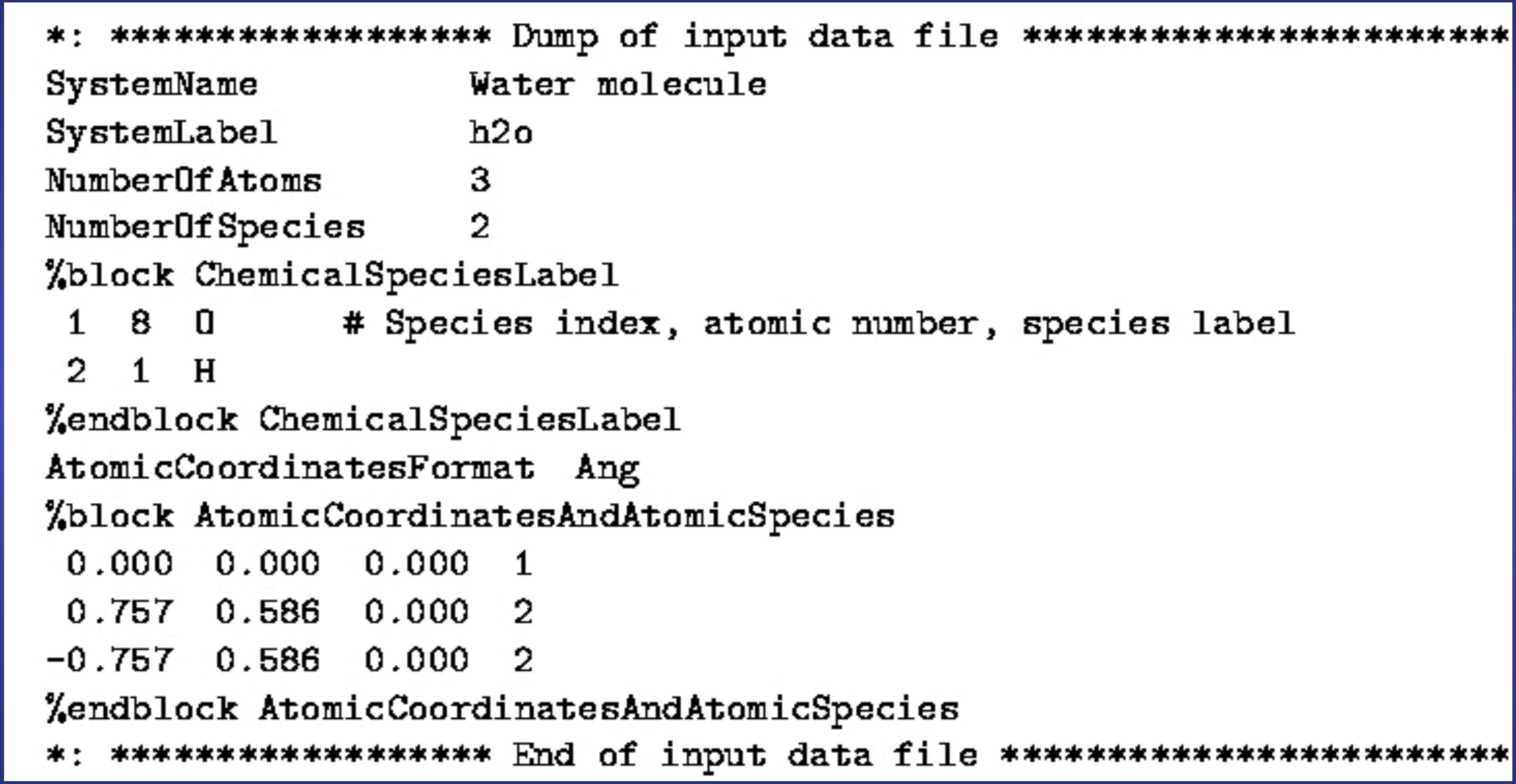
MD step

FDF

- Data can be given in any order
- Data can be omitted in favor of default values
- Syntax: ‘data label’ followed by its value

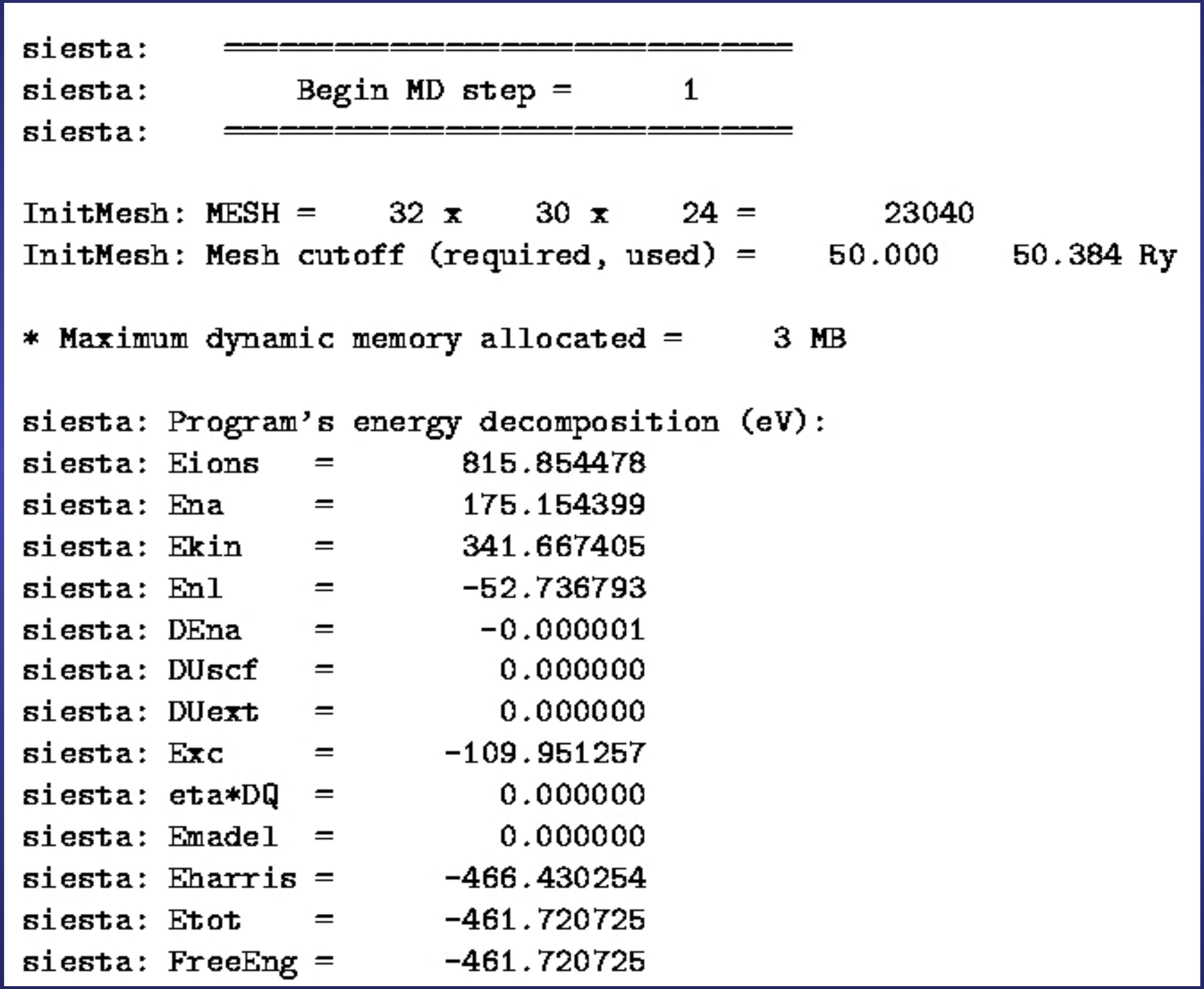
Character string:	SystemLabel	h2o
Integer:	NumberOfAtoms	3
Real:	PAO.SplitNorm	0.15
Logical:	SpinPolarized	.false.
Physical magnitudes	LatticeConstant	5.43 Ang

FDF Example (very basic info)



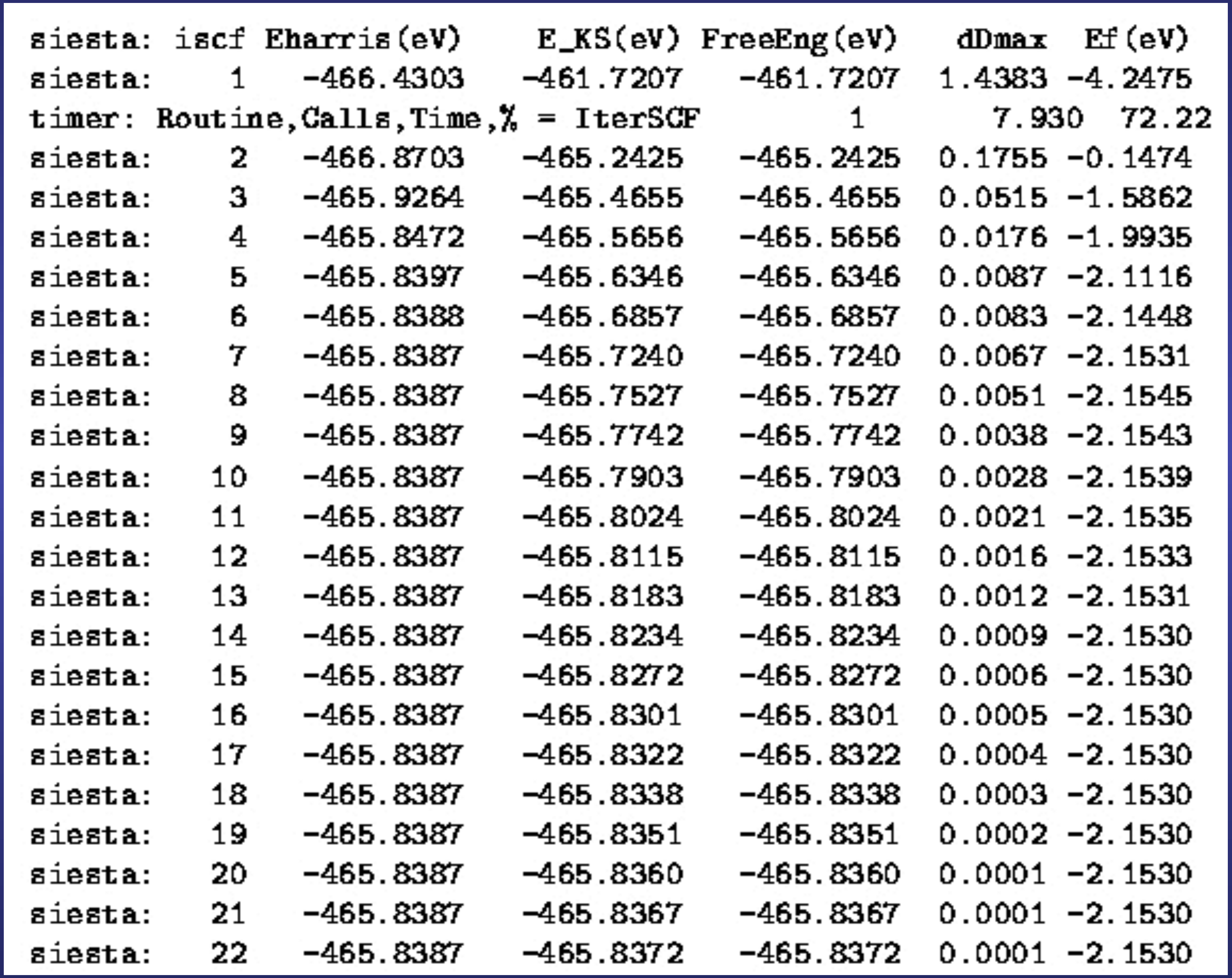
```
*: ****************** Dump of input data file ***********************
SystemName              Water molecule
SystemLabel             h2o
NumberOfAtoms           3
NumberOfSpecies         2
%block ChemicalSpeciesLabel
 1   8   O        # Species index, atomic number, species label
 2   1   H
%endblock ChemicalSpeciesLabel
AtomicCoordinatesFormat  Ang
%block AtomicCoordinatesAndAtomicSpecies
 0.000   0.000   0.000   1
 0.757   0.586   0.000   2
-0.757   0.586   0.000   2
%endblock AtomicCoordinatesAndAtomicSpecies
*: ****************** End of input data file ************************
```

Output: First MD step



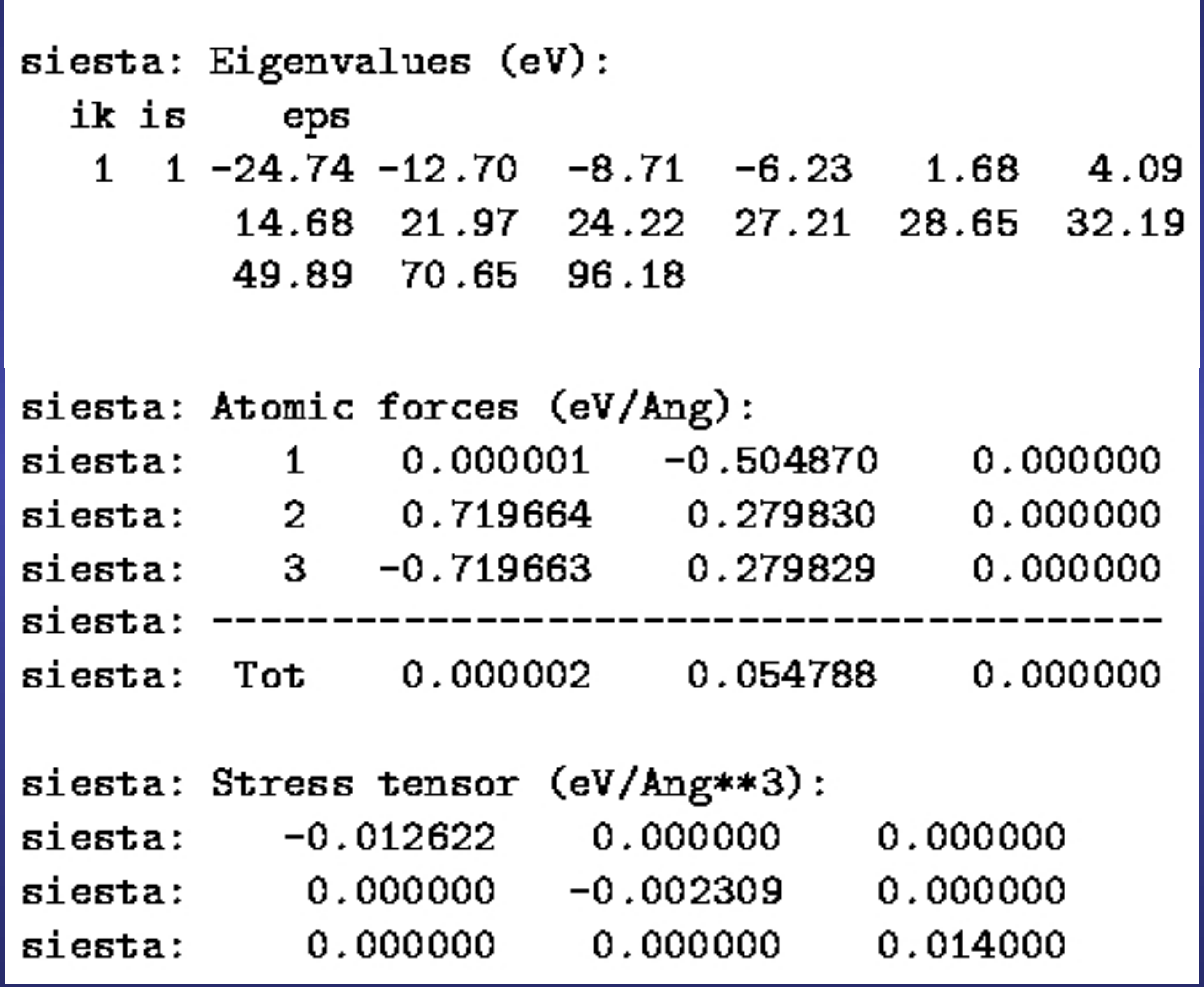
```
siesta:    ===============================
siesta:        Begin MD step =      1
siesta:    ===============================

InitMesh: MESH =    32 x    30 x    24 =       23040
InitMesh: Mesh cutoff (required, used) =    50.000    50.384 Ry

* Maximum dynamic memory allocated =     3 MB

siesta: Program's energy decomposition (eV):
siesta: Eions   =       815.854478
siesta: Ena     =       175.154399
siesta: Ekin    =       341.667405
siesta: Enl     =       -52.736793
siesta: DEna    =        -0.000001
siesta: DUscf   =         0.000000
siesta: DUext   =         0.000000
siesta: Exc     =      -109.951257
siesta: eta*DQ  =         0.000000
siesta: Emadel  =         0.000000
siesta: Eharris =      -466.430254
siesta: Etot    =      -461.720725
siesta: FreeEng =      -461.720725
```

Output: Self-consistency



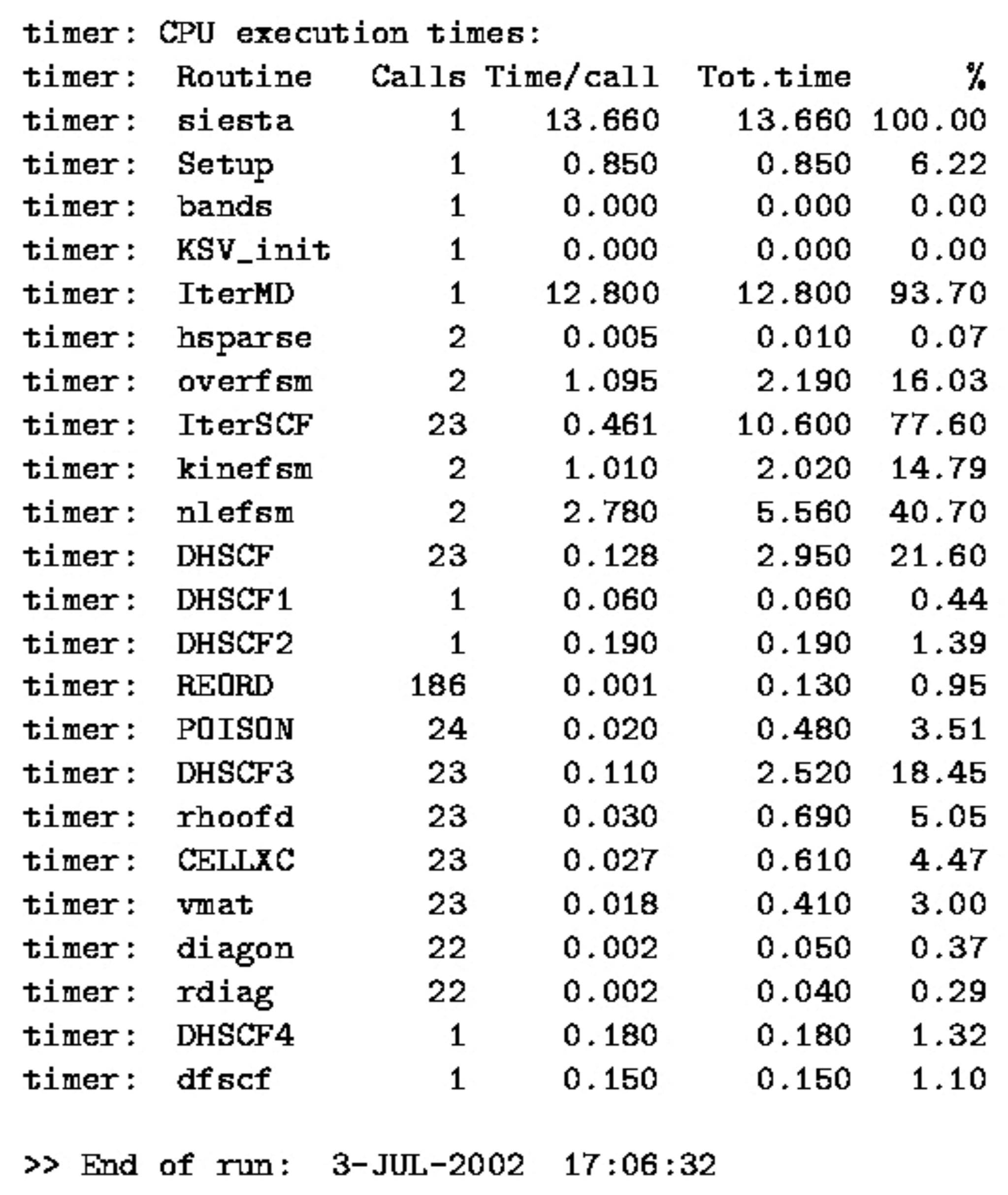
```
siesta: iscf Eharris(eV)      E_KS(eV)  FreeEng(eV)    dDmax   Ef(eV)
siesta:    1   -466.4303   -461.7207   -461.7207  1.4383 -4.2475
timer: Routine,Calls,Time,% = IterSCF          1       7.930   72.22
siesta:    2   -466.8703   -465.2425   -465.2425  0.1755 -0.1474
siesta:    3   -465.9264   -465.4655   -465.4655  0.0515 -1.5862
siesta:    4   -465.8472   -465.5656   -465.5656  0.0176 -1.9935
siesta:    5   -465.8397   -465.6346   -465.6346  0.0087 -2.1116
siesta:    6   -465.8388   -465.6857   -465.6857  0.0083 -2.1448
siesta:    7   -465.8387   -465.7240   -465.7240  0.0067 -2.1531
siesta:    8   -465.8387   -465.7527   -465.7527  0.0051 -2.1545
siesta:    9   -465.8387   -465.7742   -465.7742  0.0038 -2.1543
siesta:   10   -465.8387   -465.7903   -465.7903  0.0028 -2.1539
siesta:   11   -465.8387   -465.8024   -465.8024  0.0021 -2.1535
siesta:   12   -465.8387   -465.8115   -465.8115  0.0016 -2.1533
siesta:   13   -465.8387   -465.8183   -465.8183  0.0012 -2.1531
siesta:   14   -465.8387   -465.8234   -465.8234  0.0009 -2.1530
siesta:   15   -465.8387   -465.8272   -465.8272  0.0006 -2.1530
siesta:   16   -465.8387   -465.8301   -465.8301  0.0005 -2.1530
siesta:   17   -465.8387   -465.8322   -465.8322  0.0004 -2.1530
siesta:   18   -465.8387   -465.8338   -465.8338  0.0003 -2.1530
siesta:   19   -465.8387   -465.8351   -465.8351  0.0002 -2.1530
siesta:   20   -465.8387   -465.8360   -465.8360  0.0001 -2.1530
siesta:   21   -465.8387   -465.8367   -465.8367  0.0001 -2.1530
siesta:   22   -465.8387   -465.8372   -465.8372  0.0001 -2.1530
```

Output: Eigenvalues, forces, stress



```
siesta: Eigenvalues (eV):
  ik is     eps
   1  1 -24.74 -12.70  -8.71  -6.23   1.68   4.09
         14.68  21.97  24.22  27.21  28.65  32.19
         49.89  70.65  96.18

siesta: Atomic forces (eV/Ang):
siesta:      1     0.000001    -0.504870     0.000000
siesta:      2     0.719664     0.279830     0.000000
siesta:      3    -0.719663     0.279829     0.000000
siesta: ----------------------------------------
siesta:    Tot     0.000002     0.054788     0.000000

siesta: Stress tensor (eV/Ang**3):
siesta:     -0.012622     0.000000     0.000000
siesta:      0.000000    -0.002309     0.000000
siesta:      0.000000     0.000000     0.014000
```

Output: timer (real and cpu times)



```
timer: CPU execution times:
timer:  Routine     Calls Time/call  Tot.time       %
timer:  siesta          1    13.660    13.660  100.00
timer:  Setup           1     0.850     0.850    6.22
timer:  bands           1     0.000     0.000    0.00
timer:  KSV_init        1     0.000     0.000    0.00
timer:  IterMD          1    12.800    12.800   93.70
timer:  hsparse         2     0.005     0.010    0.07
timer:  overfsm         2     1.095     2.190   16.03
timer:  IterSCF        23     0.461    10.600   77.60
timer:  kinefsm         2     1.010     2.020   14.79
timer:  nlefsm          2     2.780     5.560   40.70
timer:  DHSCF          23     0.128     2.950   21.60
timer:  DHSCF1          1     0.060     0.060    0.44
timer:  DHSCF2          1     0.190     0.190    1.39
timer:  REORD         186     0.001     0.130    0.95
timer:  POISON         24     0.020     0.480    3.51
timer:  DHSCF3         23     0.110     2.520   18.45
timer:  rhoofd         23     0.030     0.690    5.05
timer:  CELLXC         23     0.027     0.610    4.47
timer:  vmat           23     0.018     0.410    3.00
timer:  diagon         22     0.002     0.050    0.37
timer:  rdiag          22     0.002     0.040    0.29
timer:  DHSCF4          1     0.180     0.180    1.32
timer:  dfscf           1     0.150     0.150    1.10

>> End of run:   3-JUL-2002   17:06:32
```

Saving and reading information

Some information is stored in files to restart simulations:

- Density matrix: DM.UseSaveDM
- Localized wave functions (Order-N): ON.UseSaveLWF
- Atomic positions and velocities: MD.UseSaveXV
- Conjugent gradient history (minimizations): MD.UseSaveCG

All of them are logical variables

EXTREMLY USEFUL TO SAVE LOT OF TIME!

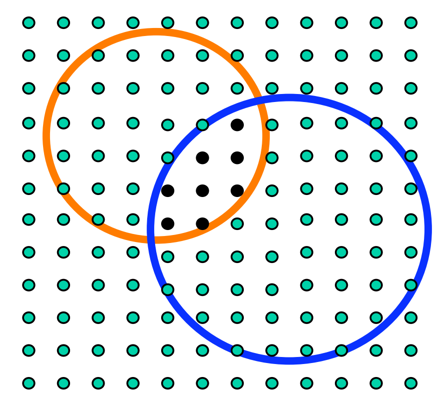
Converging the calculation:

- XC functional: LDA, GGAs
- Pseudopotential
  - Method of generation
  - Number of valence states
  - Number of angular momenta
  - Core matching radii
  - Nonlinear core corrections

- Basis set
  - Number of functions
    - Highest angular momentum
    - Number of zetas
  - Range
  - Shape (Optimized!)

- Real space mesh cutoff (V_{xc})
- Number of k-points
- Supercell size (solid & vacuum)
- Electronic temperature
- Spin polarization
- SCF convergence tolerance
- Geometry relaxation tolerance / MD temp...
- O(N) R_c and minimization tolerance

Real-space grid: Mesh cut-off



Used to compute $\rho(\mathbf{r})$ in order to calculate:

- XC potential (non linear function of $\rho(\mathbf{r})$)
- Solve Poisson equation to get Hartree potential
- Calculate three center integrals (difficult to tabulate and store)

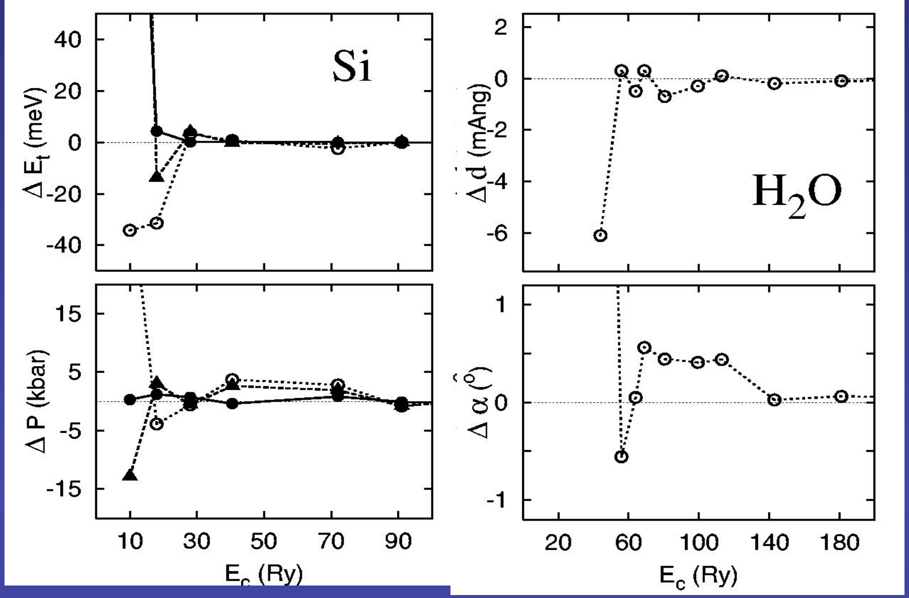
$$<\varphi_i(\mathbf{r}-R_i) \mid V_{local}(\mathbf{r}-R_k) \mid \varphi_j(\mathbf{r}-R_j)>$$

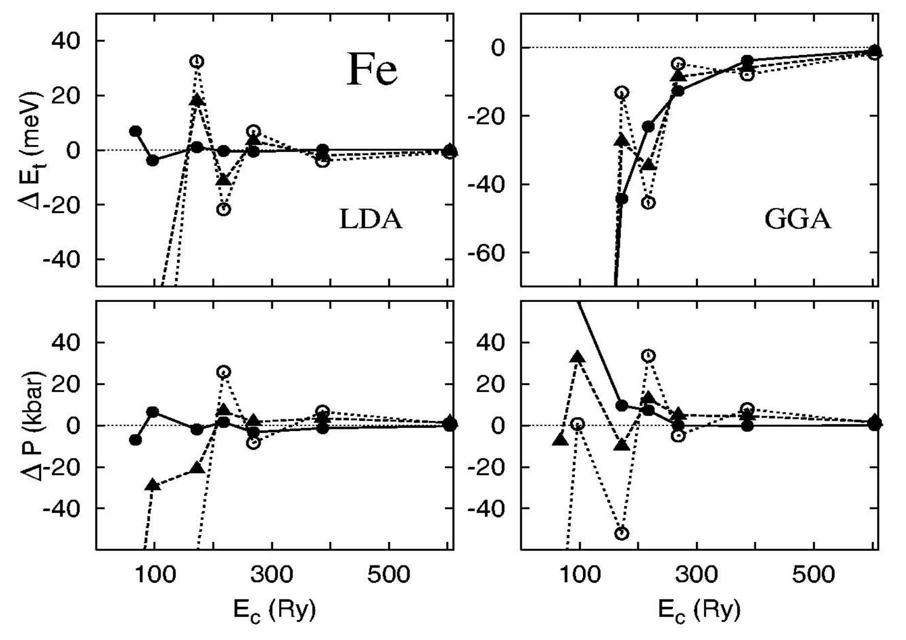
- IMPORTANT this grid is NOT part of the basis set…

  It is an AUXILIARY integration grid and, therefore, convergence of energy is not necessarily variational respect to its fineness.

- Mesh cut-off: highest energy of PW that can be represented with such grid.

Convergence with mesh cutoff

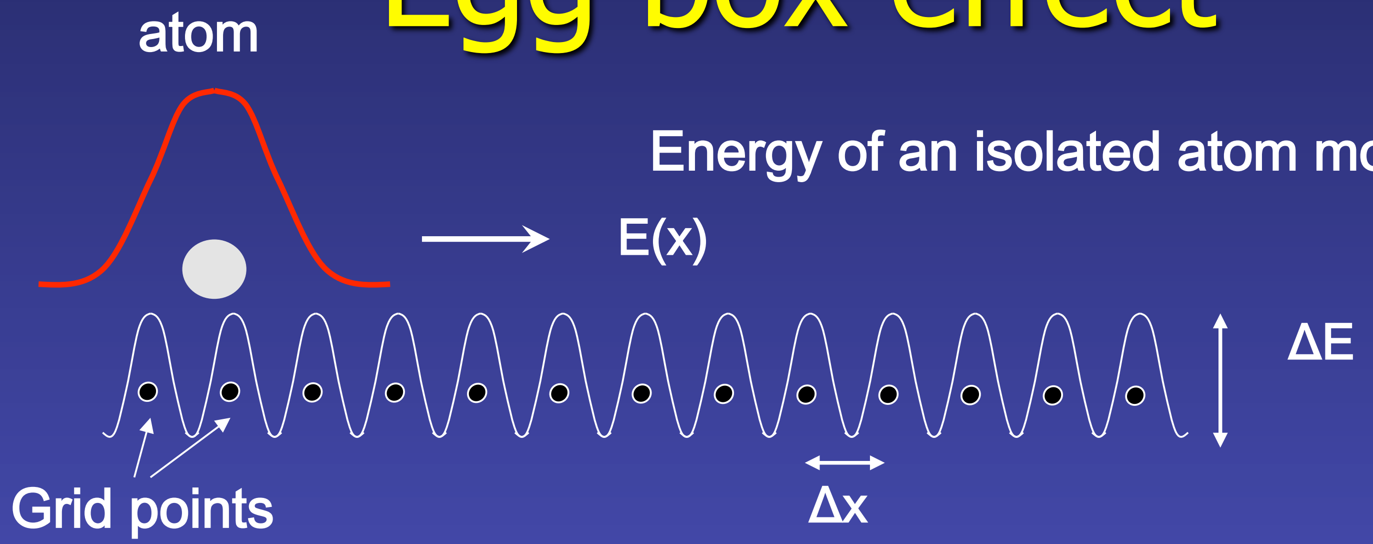




Important tips:

- Convergence is rarely achieved for less than 100 Ry.
- Values between 150 and 200 Ry provide good results in most cases
- GGA and pseudo-core require larger values than other systems
- To obtain very fine results use GridCellSampling
- Filtering of orbitals and potentials coming soon

Egg box effect



Energy of an isolated atom moving along the grid

We know that ΔE goes to zero as Δx goes to zero, but
what about the ratio ΔE/Δx?:

- Tipically covergence of forces is somewhat slowler than for the total energy
- This has to be taken into account for very precise relaxations and phonon calculations.
- Also important and related: tolerance in forces (for relaxations, etc) should not be smaller than tipical errors in the evaluation of forces.

k-point sampling

- Only time reversal symmetry used in SIESTA (k=-k)

- Convergence in SIESTA not different from other codes:

  - Metals require a lot of k-point for perfect convergence
    (explore the Diag.ParallelOverK parallel option)

  - Insulators require fewer k-points

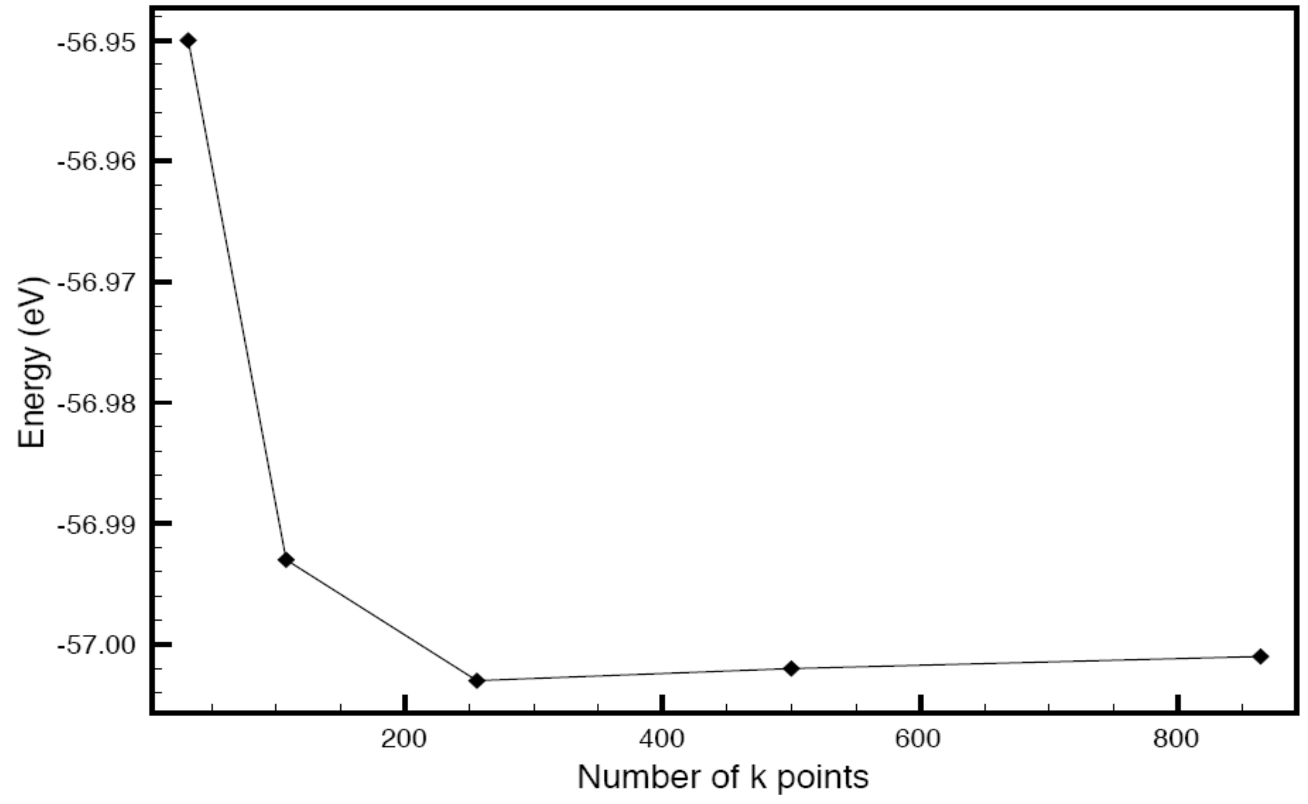
- Gamma-only calculations should be reserved to really large simulation cells

- As usual, an incremental procedure might be the most intelligent approach:

  - Density matrix and geometry calculated with a *"reasonable"* number of k-points should be close to the converged answer.

  - Might provide an excellent input for more refined calculations

k-point sampling: Al



kgrid_cutoff (Moreno and Soler, PRB 45, 13891 (1992)): Automatic generation of integration grid

kgrid_Monkhorst_Pack (Monkhorst and Pack, PRB 13, 5188 (1997)): Grid defined by hand

Convergence of the density matrix

DM.MixingWeight:

$$\rho_{in}^{n+1} = \alpha \rho_{out}^{n} + (1-\alpha)\rho_{in}^{n}$$

α is not easy to guess, has to be small (0.1-0.3) for insulator and semiconductors, tipically much smaller for metals

DM.NumberPulay (DM.NumberBroyden) : *N*

$$\rho_{in}^{n+1} = \alpha \bar{\rho}_{out}^{n} + (1-\alpha)\bar{\rho}_{in}^{n}$$

$$\left.\begin{aligned} \bar{\rho}_{in}^{n} &= \sum_{i=1}^{N} \beta_i \rho_{in}^{(n-N+i)} \\ \bar{\rho}_{out}^{n} &= \sum_{i=1}^{N} \beta_i \rho_{out}^{(n-N+i)} \end{aligned}\right\}$$

such that

$$| \bar{\rho}_{in}^{n} - \bar{\rho}_{out}^{n} |$$

is minimum

N between 3 and 7 usually gives the best results

Convergence of the density matrix

DM.Tolerance: you should stick to the default 10^{-4} or use even smaller values ……

… except in special situations:

- Preliminary relaxations
- Systems that resist complete convergence, but you are *almost* there
- in particular if the Harris energy is very well converged
- Warning: above 10^{-3} errors may be too large.
- ALWAYS CHECK THAT THINGS MAKE SENSE.

MD and Relaxations in SIESTA

Moving the atoms in SIESTA

1) Structural Relaxations: Find out positions that minimize the energy

   (Several methods: CG, dynamical quench, Broyden, ...)

2) Molecular Dynamics:

   Constant Energy (microcanonical ensamble)

   Constant Temperature (canonical ensamble)

   Constant Pressure (variable cell size/shape)

   Constant T and P

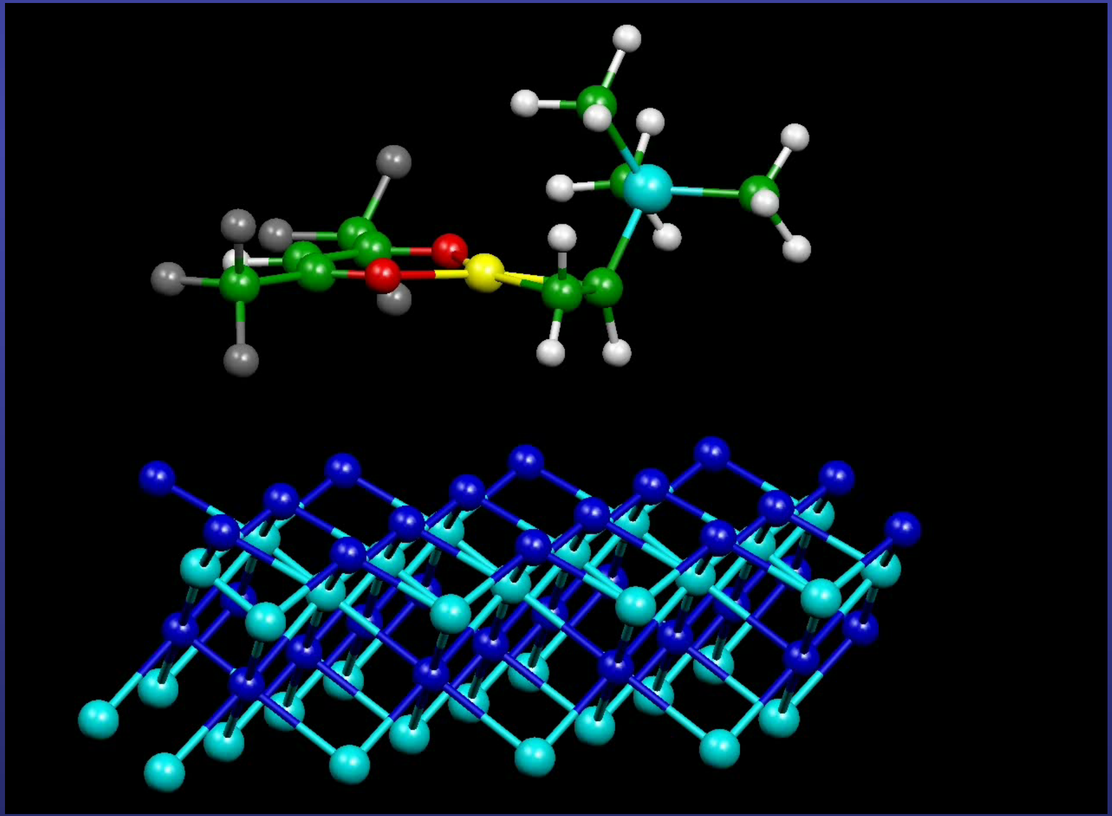
   Annealing / Quenching

3) Calculation of phonon frequencies and modes (through the Dynamical Matrix obtained by finite diferences)

Analysis, Visualization and Post-processing in SIESTA

Output information

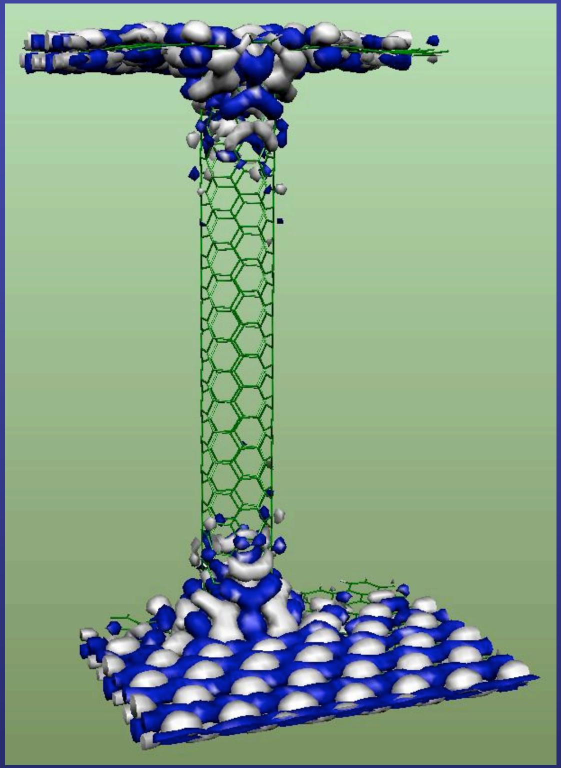
1) Electronic structure information (band structures, atomic charges, spins, ...)
2) Atomic forces; vibrational modes (through the VIBRA postprocessing tool)
3) Molecular Dynamics and Relaxation history: *.ANI files (xyz format, readable using many visualization programs, like Molekel)

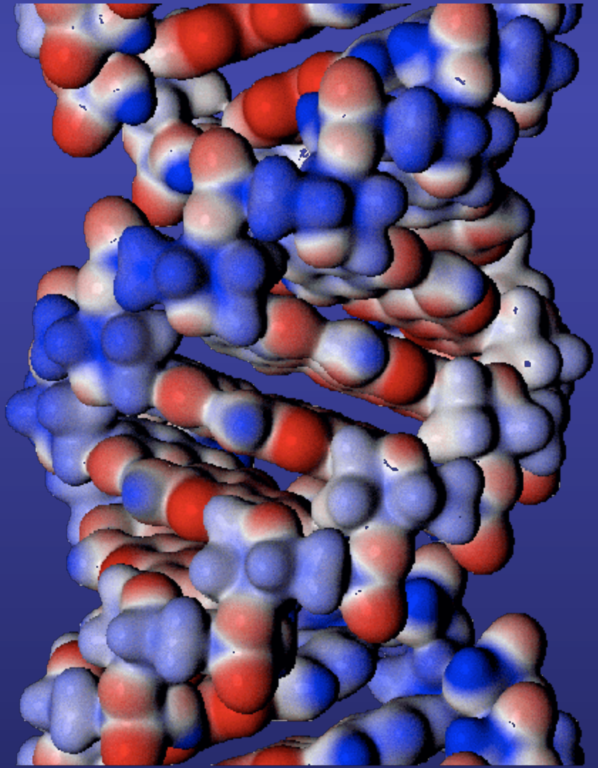


Output information

4) More sophisticated electronic information in real space (DENCHAR and other tools):

- Charge Density (total, atomic, difference)
- Potentials (electrostatic, total, local,...)
- Wave functions, including complex wfs for k-points different from Gamma





Now, just try it!!

Thank you!