Systematic convergence for realistic projects

Fast versus accurate

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Thanks to José M. Soler and A. García

Efficient density-functional calculations with atomic orbtitals: a hands-on tutorial on the SIESTA code

CECAM Tutorial

Lyon, June 18-22

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Basic strategy

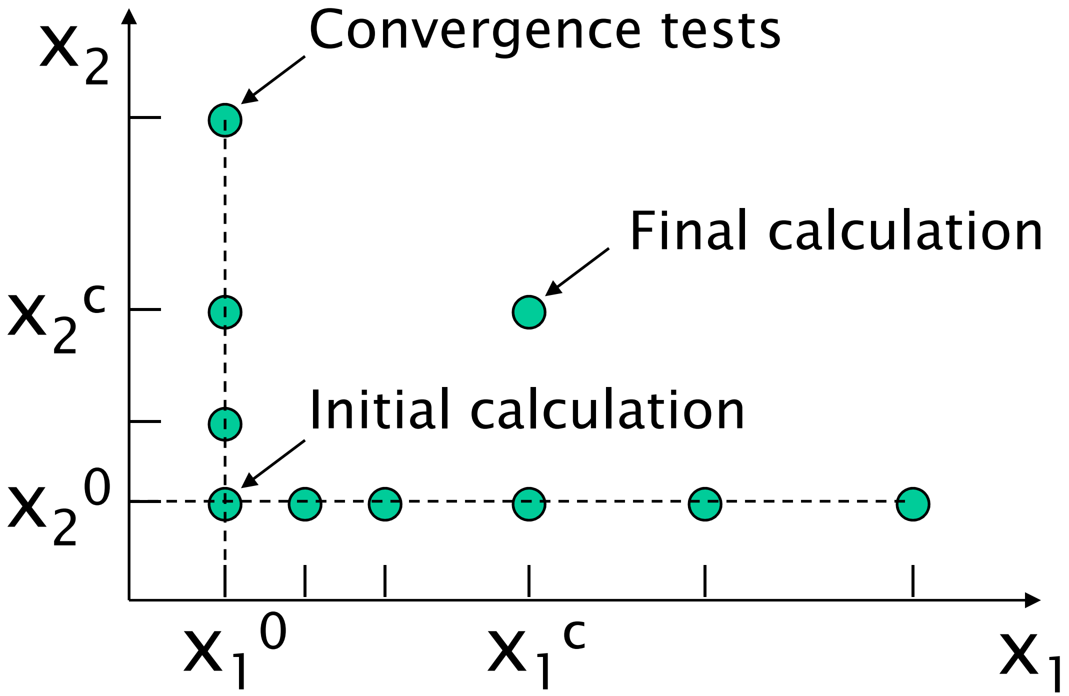
Steps of a typical research project:

1. **Exploratory-feasibility tests**
2. **Convergence tests**
3. **Converged calculations**

A fully converged calculation is impossible without convergence tests

Convergence tests

- Choose relevant magnitude(s) ***A*** of the problem (e.g. an energy barrier or a magnetic moment)
- Choose set of qualitative and quantitative parameters $\boldsymbol{x_i}$ (e.g. xc functional, number of k-points, etc)



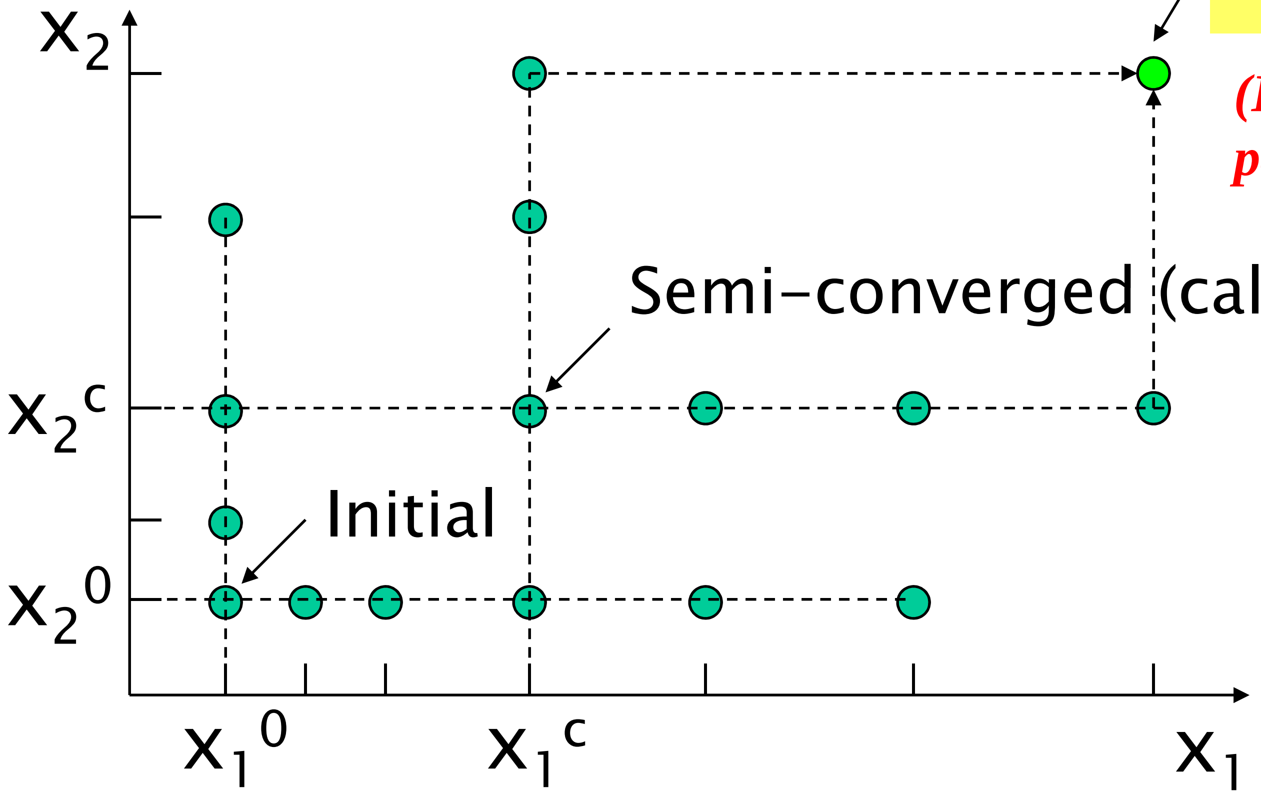
Goal: Approx. parameter independence:

$$\frac{\partial A}{\partial x_i} < our\ tolerance$$

Monitor:

- Convergence
- CPU time & memory

Multi-stage convergence



Final (extrapolated)

$$A \approx A_0 + \sum_i \frac{\partial A}{\partial x_i} \delta x_i$$

(Be careful with parameter interactions!)

Semi-converged (calculated)

Initial

Practical hints

- **Ask your objective: find the truth or publish a paper?**
- **Do not try a converged calculation from the start**
- **Start with minimum values of all x_i**
- **Do not assume convergence for any x_i**
- **Choose a simpler reference system for some tests**
- **Take advantage of error cancellations**
- **Refrain from stopping tests when results are “good”**

What determines the accuracy of your calculation?

-Variational freedom and adequacy of your basis set

-Accuracy of your pseudopotentials and appropriate definition of the “active” (valence) electrons

-DFT and used XC-functional

-Fineness of your k-sampling (specially for metals)

-Electronic temperature: not always such a good friend !

-Fineness of the real-space grid (SIESTA)

More complete parameter list

- Pseudopotential
  - Method of generation
  - Number of valence states
  - Number of angular momenta
  - Core radii
  - Nonlinear core corrections
- Number of k-points
- Electronic temperature
- XC functional: LDA, GGAs
- Harris functional vs SCF
- Spin polarization
- SCF convergence tolerance
- Supercell size (solid & vacuum)
- Geometry relaxation tolerance
  - Check of final stability
- Basis set
  - Number of functions
    - Highest angular momentum
    - Number of zetas
  - Range
  - Shape
    - Sankey
    - Optimized
- Real space mesh cutoff
  - Grid-cell sampling
- Neglect nonoverlap interactions
- O(N) minimization tolerance

Parameter interactions

$$\partial^2 A / \partial x_i \partial x_j \neq 0$$

Number of k-points:

- **Supercell size**
- **Geometry**
- **Electronic temperature**
- **Spin polarization**
- **Harris vs SCF**

Mesh cutoff:

- **Pseudopotential**
- **Nonlinear core corrections**
- **Basis set**
- **GGA**

Why basis sets of atomic orbitals?

Good things about LCAO:

-Physically motivated: very few functions can do a good job !

-Localized:

short-range interactions = sparse matrices

linear scaling algorithms become possible

more intuitive "chemistry" captured

Are atomic orbitals appropriate?

Bad things about LCAO:

-Lack of systematic convergence (as opposite to PW or grids)

-Link to the atoms:

some states (very delocalized) might be difficult to represent

easy to guess for occupied states but, what about excitations?

basis changes with atomic positions (BSSE)

Improving the quality of the basis set

Single-ζ (minimal or SZ)

One **single radial function** per angular momentum shell occupied in the free –atom

Improving the quality

Radial flexibilization:

Add **more than one** radial function within the same angular momentum than SZ

Multiple-ζ

Angular flexibilization:

Add shells of different atomic symmetry **(different l)**

Polarization

Size

Depending on the required accuracy and available computational power

Quick and dirty calculations

Highly converged calculations

Minimal basis set

(single- ζ; SZ)

Complete multiple-ζ

\+

Polarization

\+

Diffuse orbitals

HOW BAD ARE THE RESULTS WITH A SZ BASIS?

Bad!, but… not so bad as you might expect:
-bond lengths are too large
-energetics changes considerably, however, energy differences might be reasonable enough
-charge transfer and other basic chemistry is usually OK
(at least in simple systems)
-if the geometry is set to the experiment, we typically have a nice band structure for occupied and lowest unoccupied bands

When SZ basis set can be used:

-long molecular dynamics simulations
(once we have make ourselves sure that energetics is reasonable)
-exploring very large systems and/or systems with many degrees of freedom (complicated energy landscape).

Examples

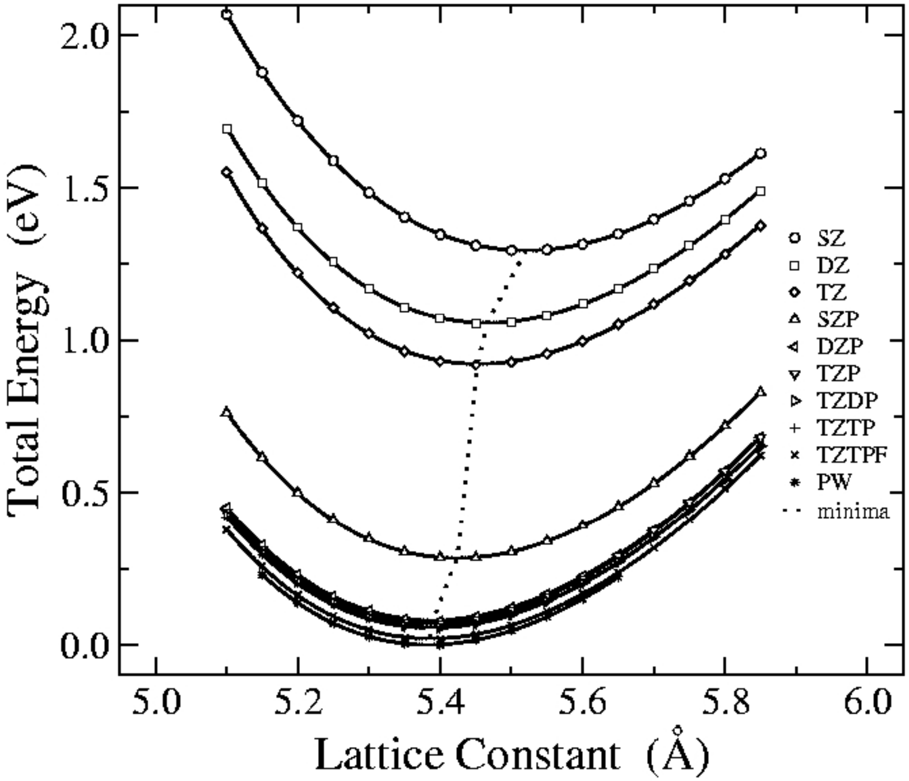
Atom	Valence configuration	SZ		DZ		P	
		# orbitals	symmetry	# orbitals	symmetry	# orbitals	symmetry
Si	$3s^2\ 3p^2$	1	s	2	s	1	d_{xy}
		1	p_x	2	p_x	1	d_{yz}
		1	p_y	2	p_y	1	d_{zx}
		1	p_z	2	p_z	1	$d_{x^2-y^2}$
						1	$d_{3z^2-r^2}$
	Total	4		8		(DZ+P) 13	

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	

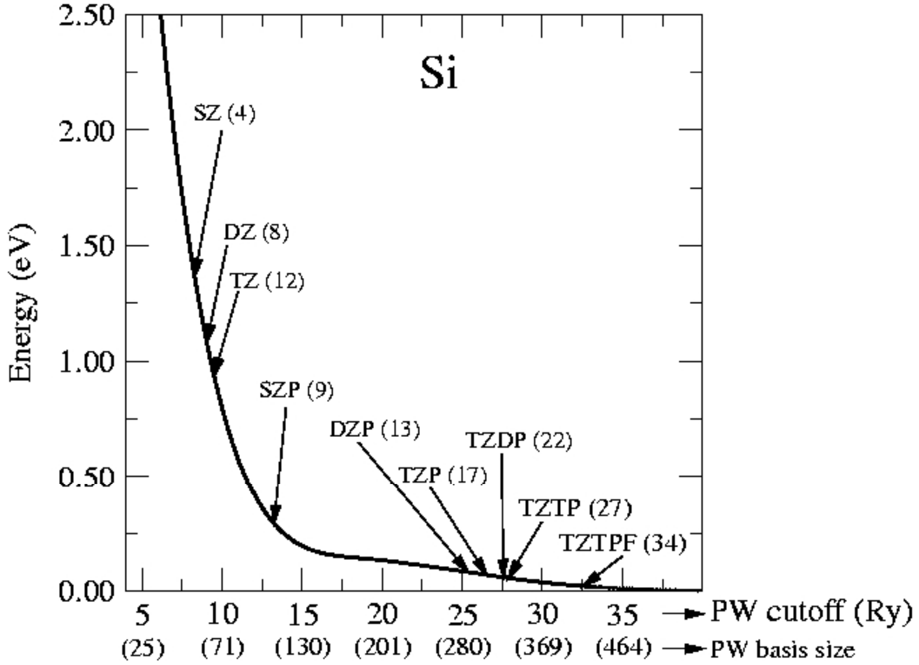
Convergence of the basis set

Bulk Si

Cohesion curves



PW and NAO convergence



Equivalent PW cutoff (E_{cut}) to optimal DZP

System	DZP # funct. per atom	PW # funct. per atom	E_{cut} (Ry)
H_2	5	11296	34
O_2	13	45442	86
Si	13	227	22
diamond	13	284	59
α-quartz	13	923	76

For molecules: cubic unit cell 10 Å of side

Range

- How to get sparse matrix for O(N)
  - Neglecting interactions below a tolerance or beyond some scope of neighbours ⇒ numerical instablilities for high tolerances.
  - **Strictly localized atomic orbitals** (zero beyond a given cutoff radius, r_c)

⇓

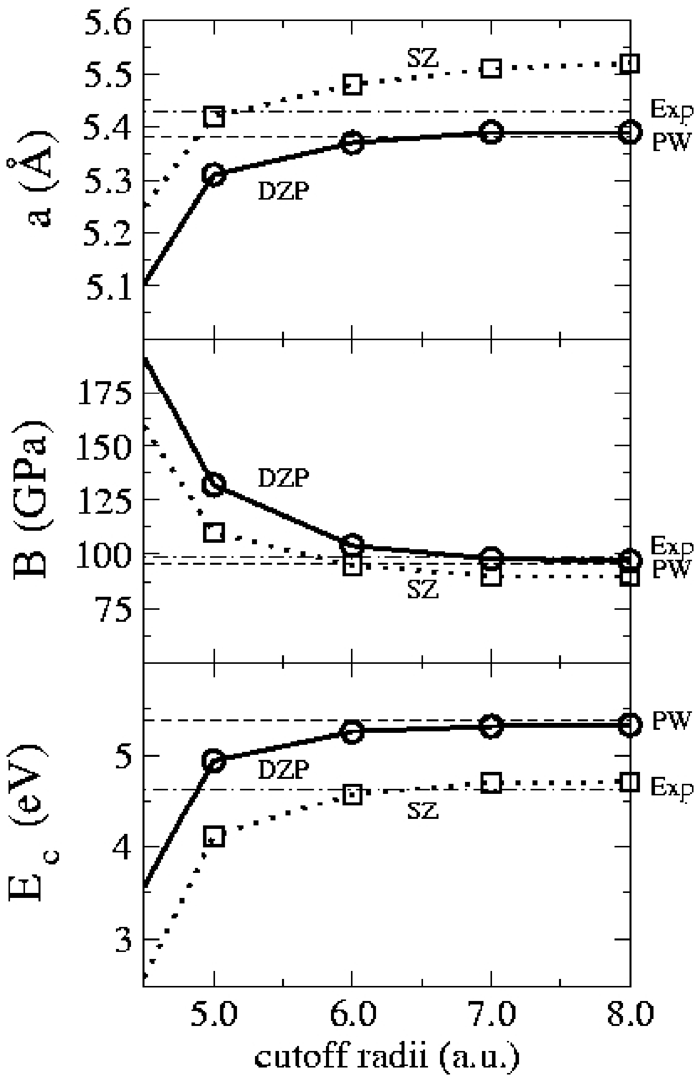
•**Accuracy** and **computational efficiency** depend on the range of the atomic orbitals

•Way to define all the cutoff radii in a **balanced way**

Convergence with the range

bulk Si

equal *s*, *p* orbitals radii



Remarks:

-Not easy to get

-Longer not better if basis set is not complet enough

-Affects cohesion, but energy differences converge better

-More relevant for surfaces, small molecules and/or adsorbates (BSSE)

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

Energy shift

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

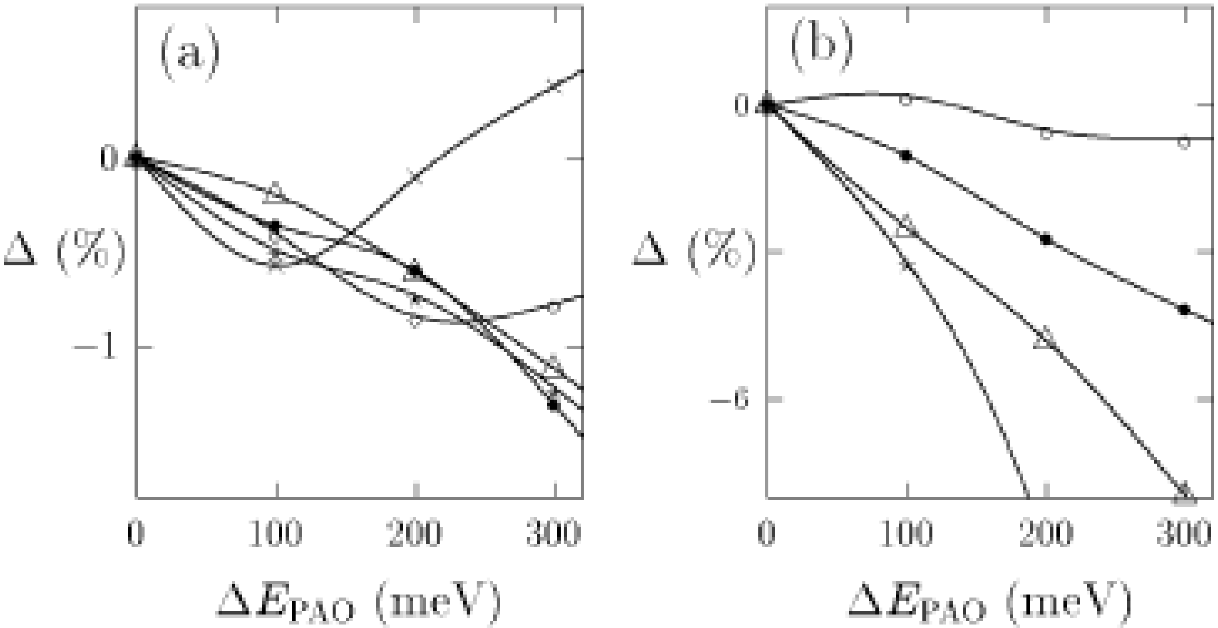
A single parameter for all cutoff radii

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

Reasonable values for practical calculations:
ΔE_{PAO} ~50-200 meV

Convergence vs Energy shift of

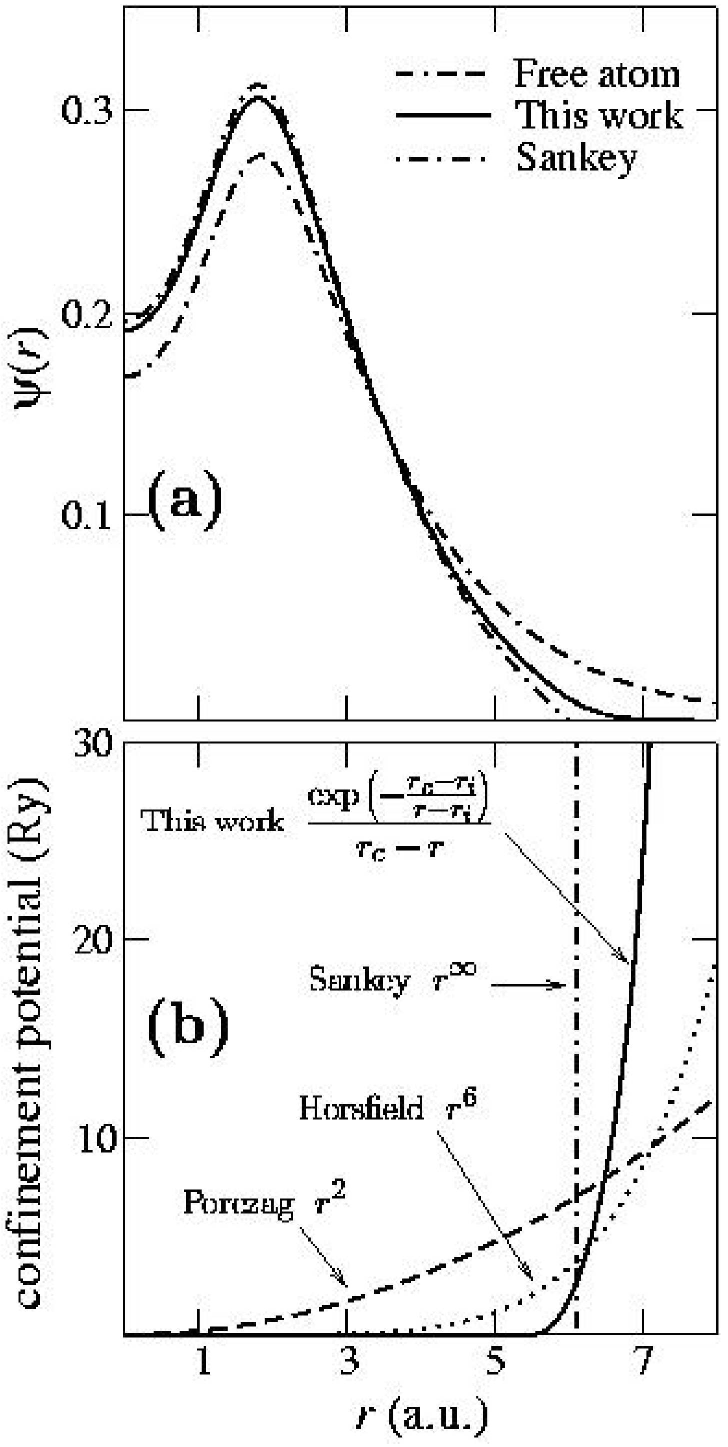
Bond lengths *Bond energies*



Soft confinement

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

3*s* of Mg in MgO for different confinement schemes



Optimized confinement potential:

- Better variational basis sets
- Removes the discontinuity of the derivative
- Coming soon to the official version

Procedure

Difference in energies involved in your problem?

- SZ: (Energy shift)

  Semiquantitative results and general trends

- DZP: automatically generated (Split Valence and Peturbative polarization)

  High quality for most of the systems.

  Good valence: well converged results ↔computational cost

  ‘Standard’

- Variational optimization

Rule of thumb in Quantum Chemistry:

A basis should always be doubled before being polarized

Convergence of the basis set

Bulk Si

	SZ	DZ	TZ	SZP	DZP	TZP	TZDP	PW	APW	Exp
a (Å)	5.52	5.46	5.45	5.42	5.39	5.39	5.39	5.38	5.41	5.43
B (GPa)	89	96	98	98	97	97	96	96	96	98.8
E_c (eV)	4.72	4.84	4.91	5.23	5.33	5.34	5.34	5.37	5.28	4.63

SZ = single-ζ

DZ= doble- ζ

TZ=triple- ζ

P=Polarized

DP=Doble-polarized

PW: Converged Plane Waves (50 Ry)

APW: Augmented Plane Waves (all electron)

System		Exp	LAPW	PW (Literature)	PW (same ps)	DZP
Au	a	4.08	4.05	4.07	4.05	4.07
	B	173	198	190	191	188
	E_c	3.81	-	-	4.19	4.03
C	a	3.57	3.54	3.54	3.53	3.54
	B	442	470	436	466	453
	E_c	7.37	10.13	8.96	8.90	8.81
Na	a	4.23	4.05	3.98	3.95	3.98
	B	6.9	9.2	8.7	8.8	9.2
	E_c	1.11	1.44	1.28	1.22	1.22
Cu	a	3.60	3.52	3.56	-	3.57
	B	138	192	172	-	165
	E_c	3.50	4.29	4.24	-	4.37

a (Å) B(GPa) E_c(eV)

Real-space grid: **Mesh cut-off**

Different from PW calculations, used to project $\rho(\mathbf{r})$ 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)

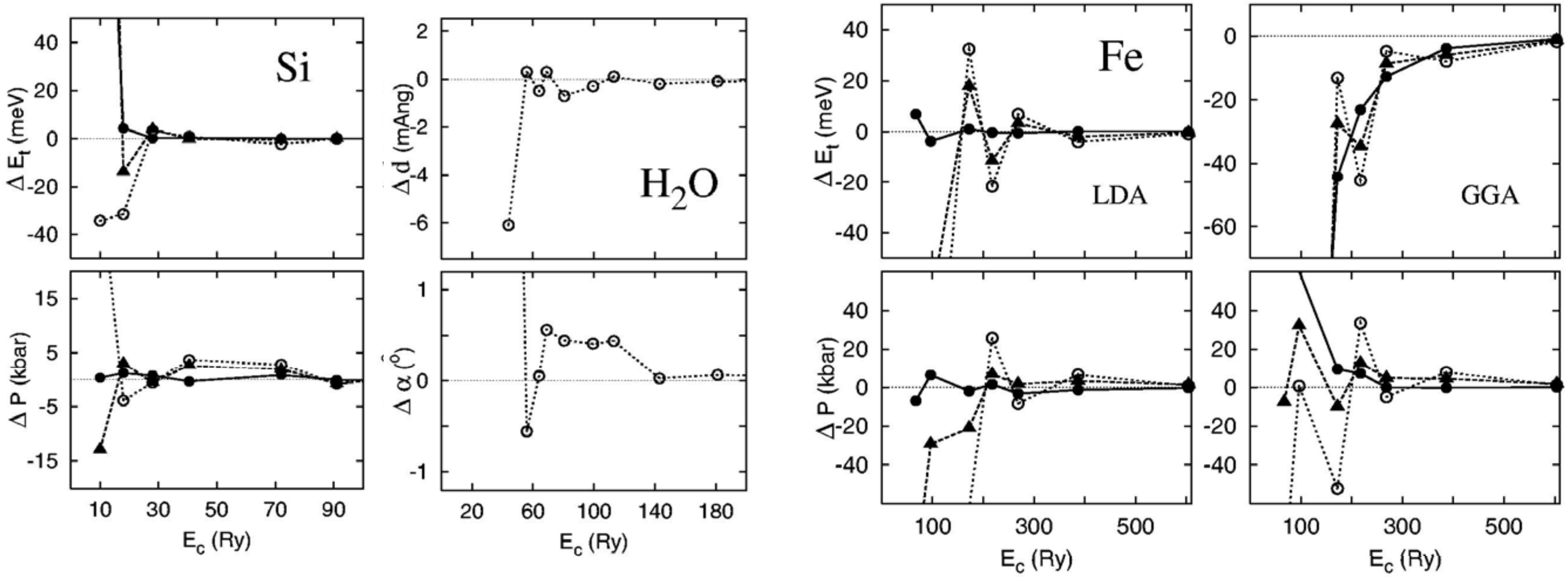
$$<\varphi_i(\mathbf{r}-\mathbf{R}_i) \mid V_{local}(\mathbf{r}-\mathbf{R}_k) \mid \varphi_j(\mathbf{r}-\mathbf{R}_j)>$$

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

is an AUXILIAR 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 of energy with the grid



Important tips:

-**Never go below 100 Ry** unless you know what you are doing.

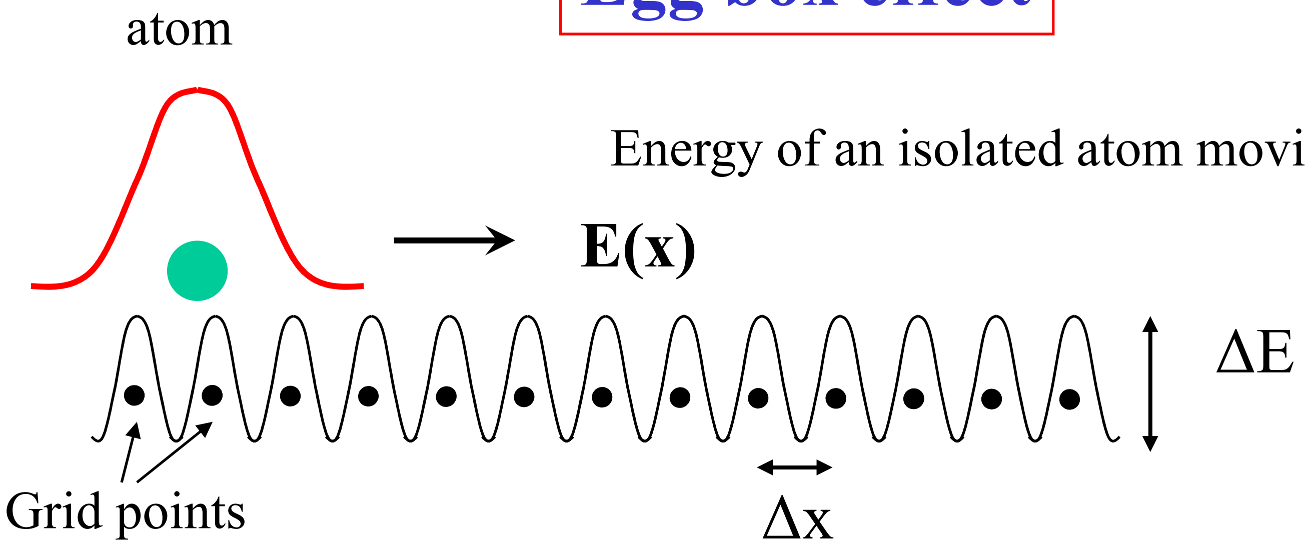
-Values between **150 and 200 Ry** provide good results in most cases

-**GGA and pseudo-core** require larger values than other systems

-To obtain very fine results use **GridCellSampling**

-Filtering of orbitals and potentials coming soon (Eduardo Anglada)

Egg box effect



Energy of an isolated atom moving along the grid

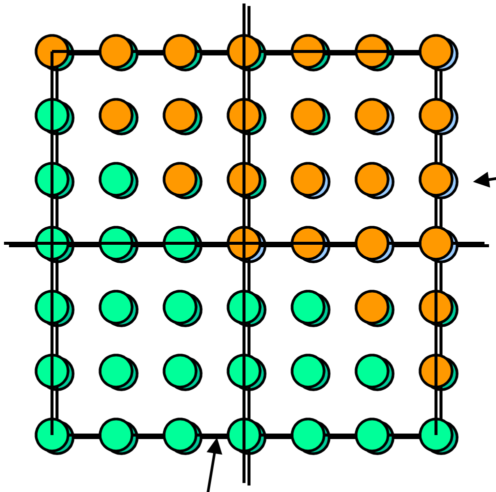
We know that ΔE goes to zero as Δx goes to zero, but
what about the ratio ΔE/Δx?:

- 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 should not be smaller than tipical errors in the evaluation of forces.

K-point sampling

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

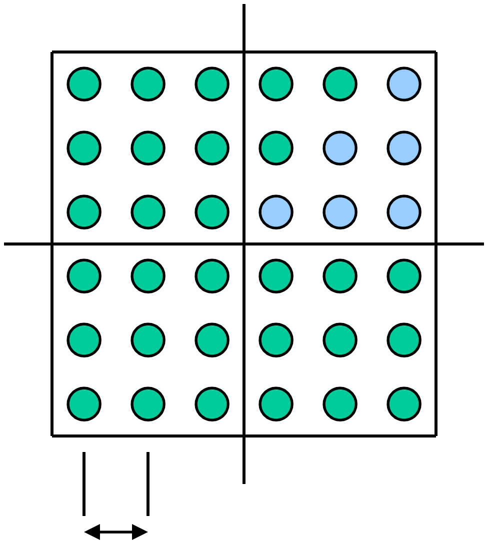
Regular k-grid



Inequivalent points

First Brillouin Zone

Monkhorst-Pack



$\Delta k \Rightarrow l_c = \pi / \Delta k$

k-sampling

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

-**Convergence in SIESTA not different from other codes:**

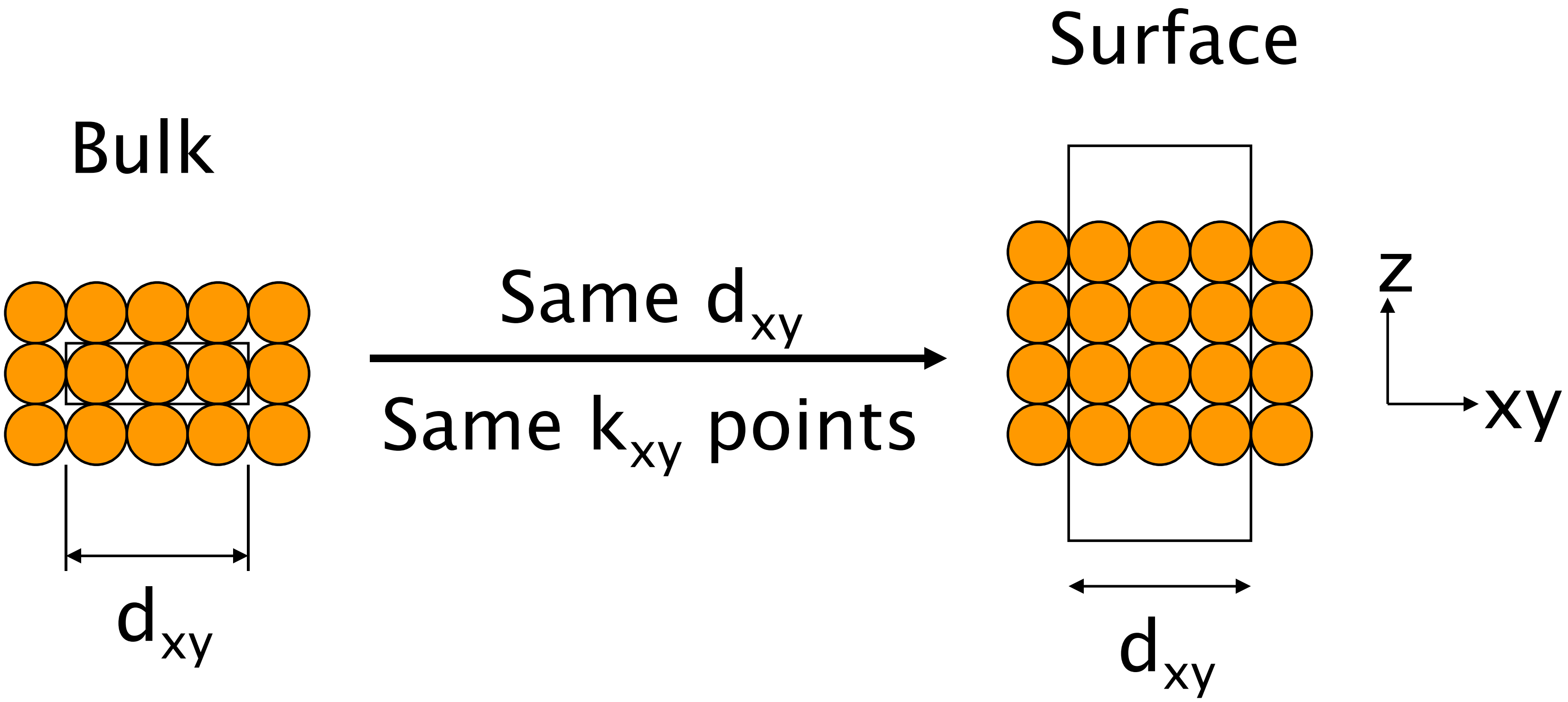
- Metals require a lot of k-point for perfect convergence
  (explore the Diag.ParallelOverK parallel option)
- Insulators require much less k-points

-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**

Surface (slab) calculations



Bulk

Surface

Same d_{xy}

Same k_{xy} points

d_{xy}

d_{xy}

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 at most 0.1-0.15 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 unless……

…you know what you are doing:

-Preliminary relaxations

-Systems that resist complete convergence but your are *almost* there

-in particular if the Harris energy is very well converged

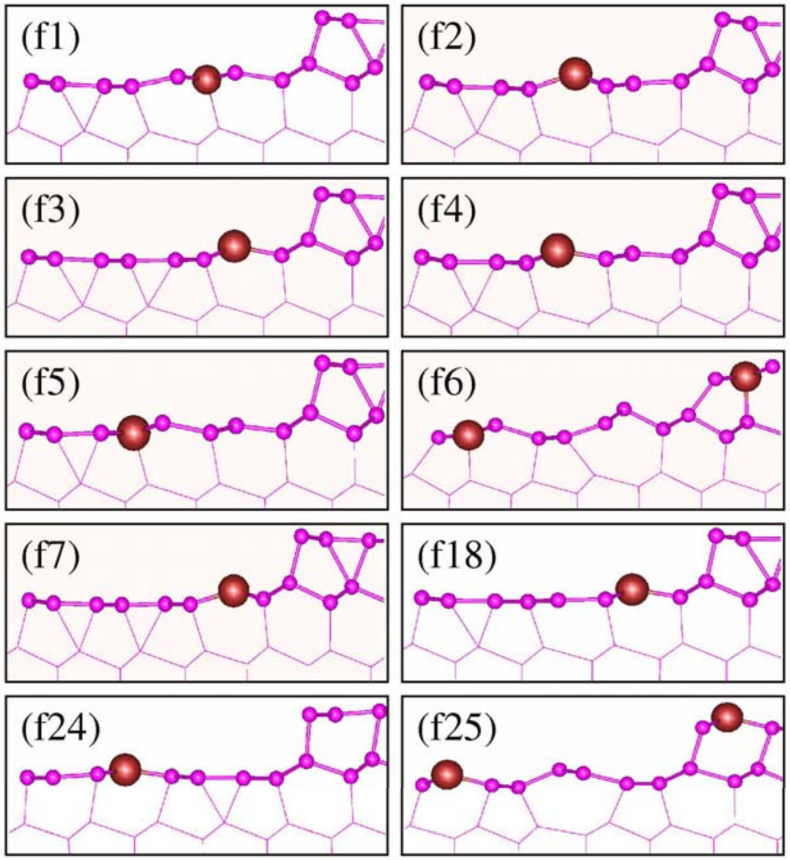
-NEVER go above 10^{-3}

-ALWAYS CHECK THAT THINGS MAKE SENSE.

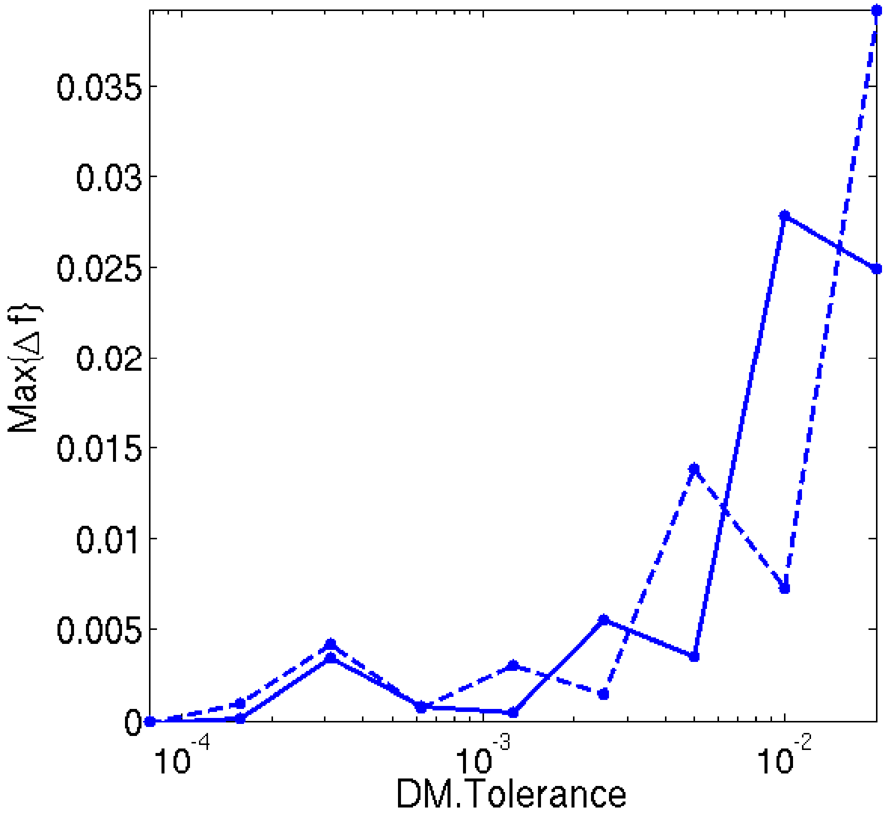
A particular case where DM.Tolerance could be reduced

Determination of the Si(553)/Au structure

More than 200 structures explored



S. Riikonen and DSP



Harris functional

$$\rho(r) = \Sigma_i |\psi_i(r)|^2$$

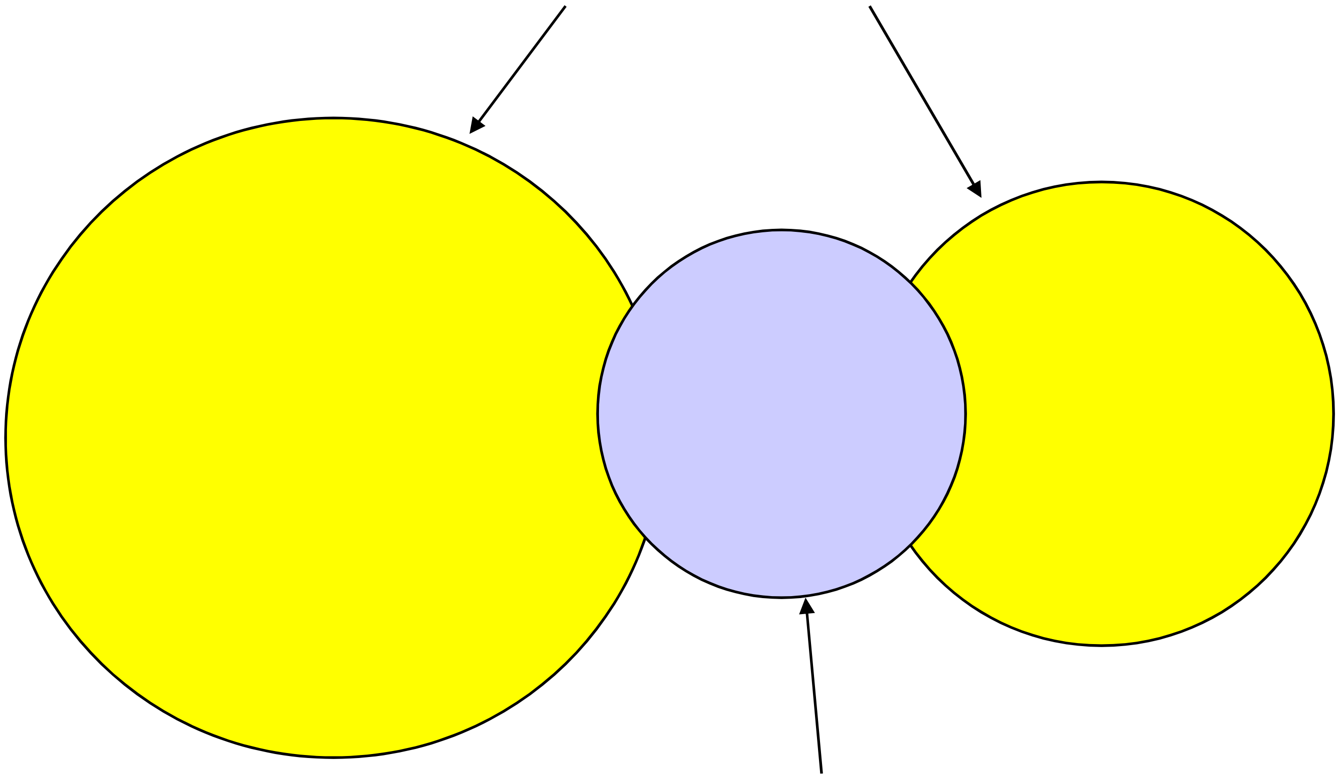
$$E_{KS}[\rho] = -(1/2)\, \Sigma_i |\nabla\psi_i(r)|^2 + \int V_{ext}(r)\, \rho(r)\, dr$$

$$+(1/2) \int V_H(r)\, \rho(r)\, dr + \int \varepsilon_{xc}(r)\, \rho(r)\, dr$$

$$E_{Harris}[\rho_{in}] = E_{KS}[\rho_{in}] + Tr[(\rho_{out}-\rho_{in})H_{in}]$$

- Much faster SCF convergence
- Usually $\rho_{in} = \Sigma\, \rho_{atoms}$ and no SCF

Neglect of non-overlap interactions



Basis orbitals

KB pseudopotential projector

Incremental approach to convergence

i) SZ basis set, 2x1 sampling, constraint relaxations,
slab with two silicon bulayers, DM.Tol=10^{-3}

only surface layer: first relax interlayer height, then relaxations with some constraints to preserve model topology.

Selecting a subset with the most stable models

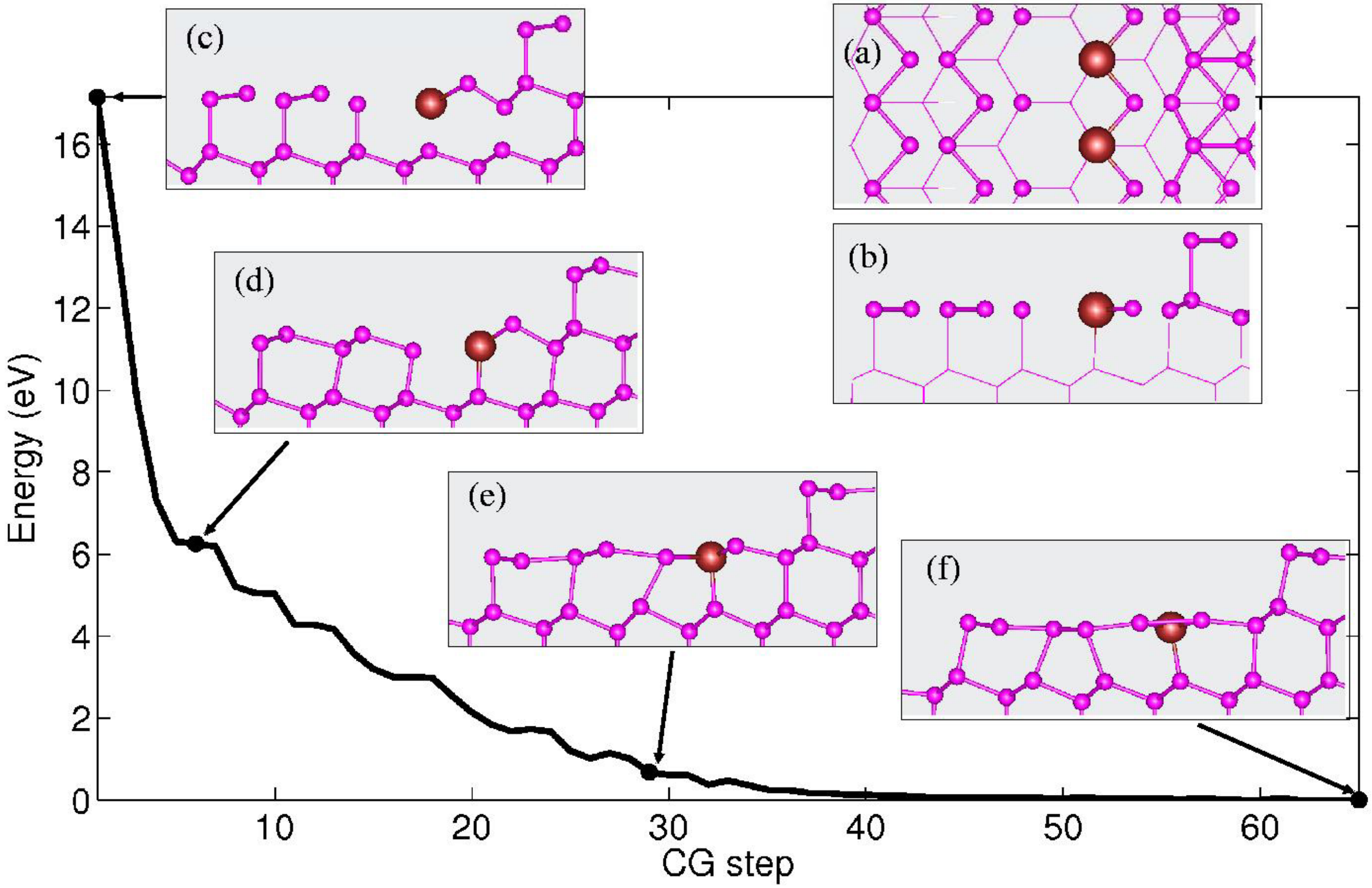
ii) DZ basis set, 8x4 sampling, full relaxation,
slab with four silicon bilayers, DM.Tol=10^{-3}
Rescaling to match DZ bulk lattice parameter

iii) DZ basis set, 8x4 sampling, full relaxation, DM.Tol=10^{-4}

iv) DZP basis set, 8x4 sampling, full relaxation, DM.Tol=10^{-4}
Rescaling to match DZ bulk lattice parameter

Automatic guess + first constraint relaxations with SZ

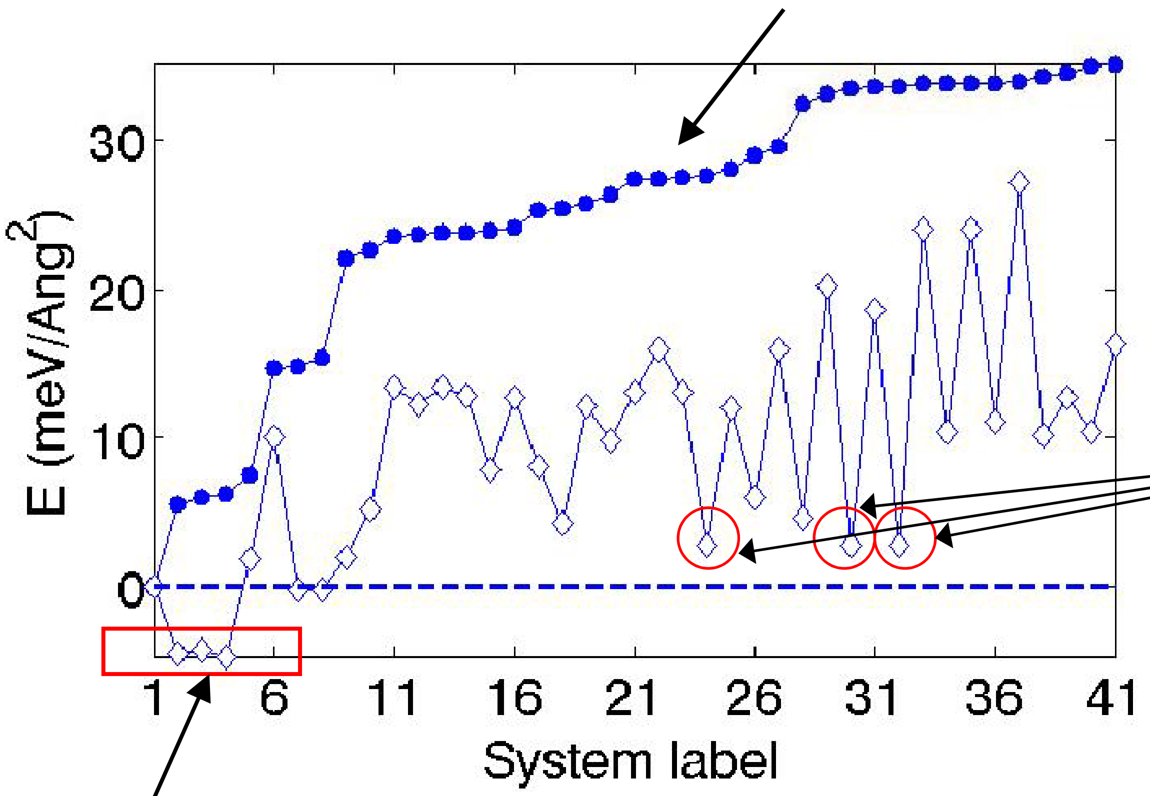
(1,2,2,1,1,0,4,1,1)



(1,2,0,2,1,1,4,1,1)

SZ energies might be a guide to select reasonable candidates, but… caution is needed!!!!

SZ: 88 initial structures converge to the 41 most stable different models



All converged to the same structure

Already DZ recovers these as the most stable structures

Finally we get quite accurate answer….

Name	ΔE (meV/Å^2)	
	SIESTA	VASP
p2*	4.85	4.93
p4*	6.44	6.54
p5*	9.51	9.13
f1	4.63	4.27
f2	0.17	-0.08
f4	0.00	0.00