CIC nanoGUNE
nanoscience cooperative research center

Basis sets for SIESTA
II. Finite support numerical bases used in SIESTA

Emilio Artacho

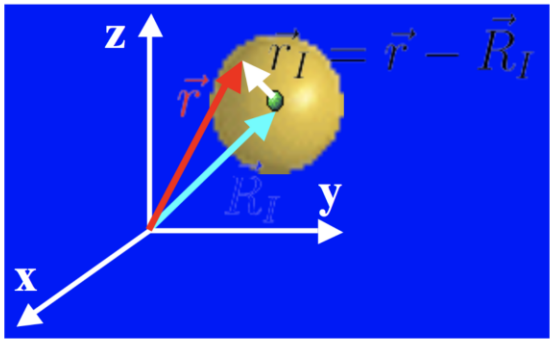
Nanogune, Ikerbasque & DIPC, San Sebastian, Spain
Cavendish Laboratory, University of Cambridge

SIESTA basis sets

ONLY REQUIREMENTS:

1. Of the general shape:

$$\phi_{Ilmn}(\mathbf{r_I}) = R_{Iln}(r)Y_{lm}(\hat{\mathbf{r}}_I)$$

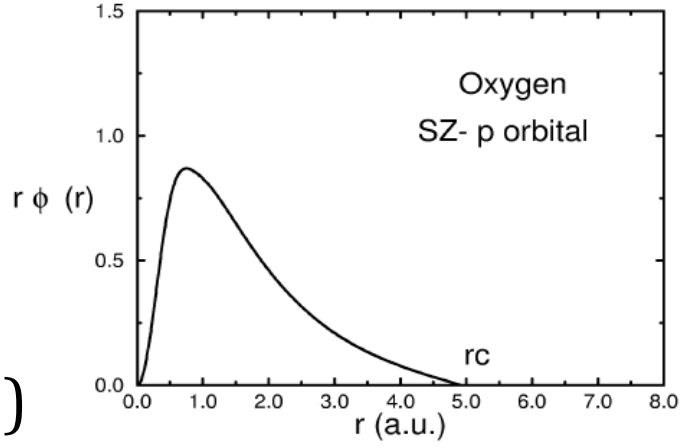


2. Of finite support:

Strictly zero beyond a cutoff radius r_c

They can be:

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



How to input basis sets for SIESTA

Choice of tier (how many), cutoff radii, and where, made by user

Choosing a tier (e.g. DZP) makes SIESTA put the corresponding amount of orbitals around each of the atoms in the cell

(not saying anything, it assumes DZP)

Radial shapes can be:

- Introduced by user

  (Basis type: "`user`"; reads a file with a table of values for *r* (discretised)
- Generated by SIESTA
  - Based on numerical solution of KS DFT on pseudoatom + modifications
  - Quite tunable
  - Depends on parameters that need to be defined by user

Various levels of automatism, and predefinition of default values for parameters

VERY IMPORTANT

- SIESTA offers tools for generating basis sets
  - of various kinds
  - at different levels of accuracy
- It has a hierarchical structure of defaults
- It even generates a decent basis without your stating anything!

BUT: It is up to you to generate the basis you need

If going to calculate for months or years,

a few days trying out bases and basis convergence is definitely worth it! It is what we do

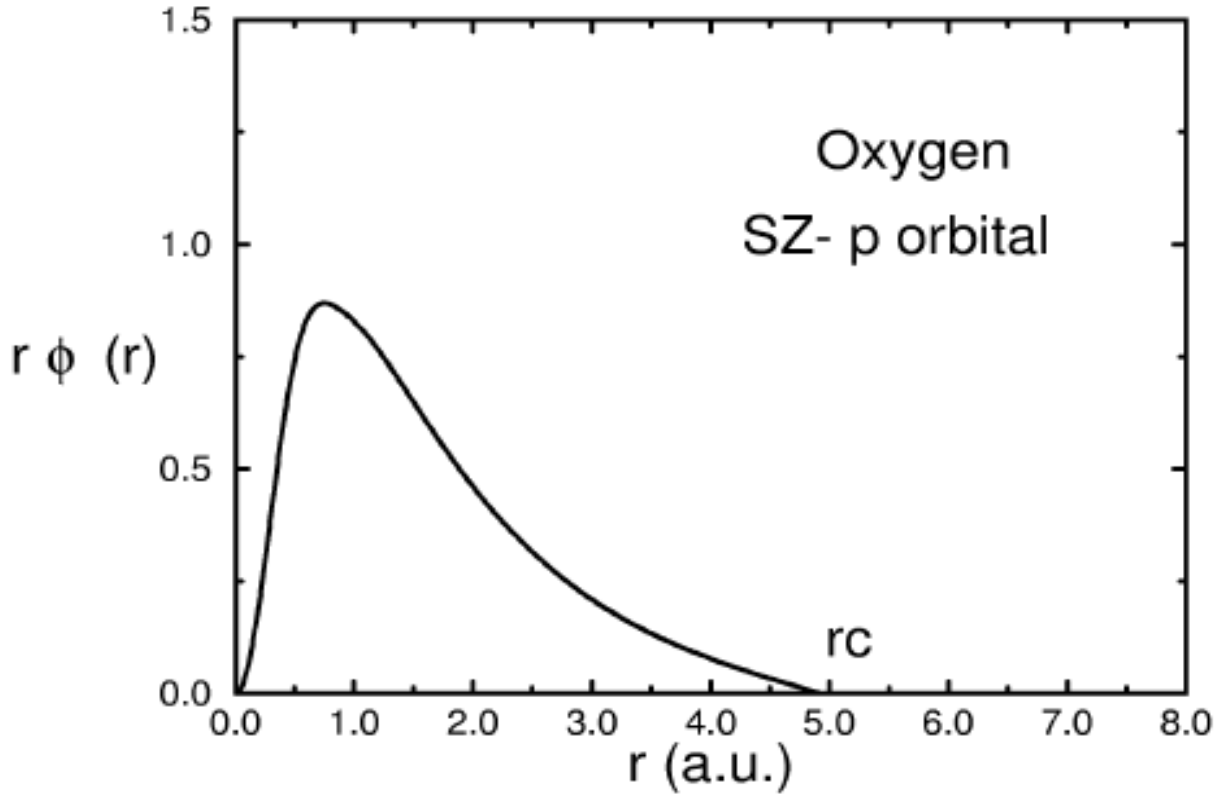
It allows you to have much more control on the results

Of course, people can share bases (depending on trust), in communities, the SIESTA mailing list etc.

Third parties can also distribute bases (e.g. Simune)

https://www.simuneatomistics.com

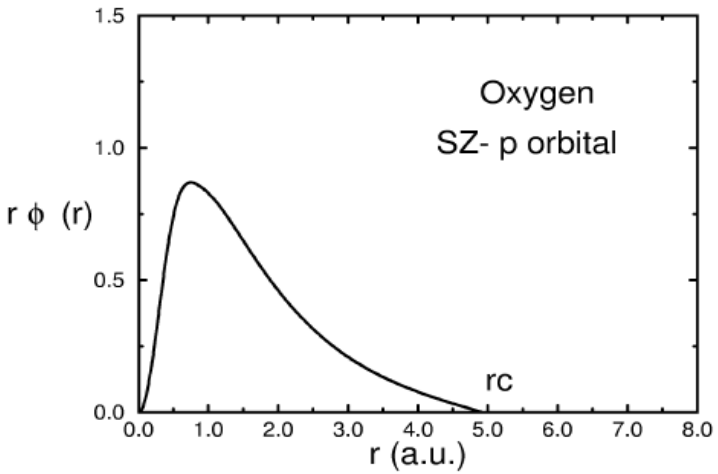
Starting: Minimal basis



Solution of KS-DFT on pseudo-atom,
under an added confinement potential

FIREBALLS O. F. Sankey & D. J. Niklewski, Phys. Rev. B 40, 3979 (1989)

Hard confining potentials



Fireballs

O F Sankey & D J Niklewski, Phys. Rev. B 1989

BUT:

A different cut-off radius for each orbital

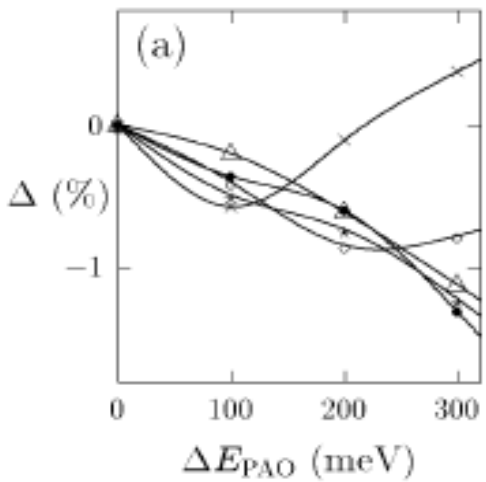
A single parameter

Energy shift

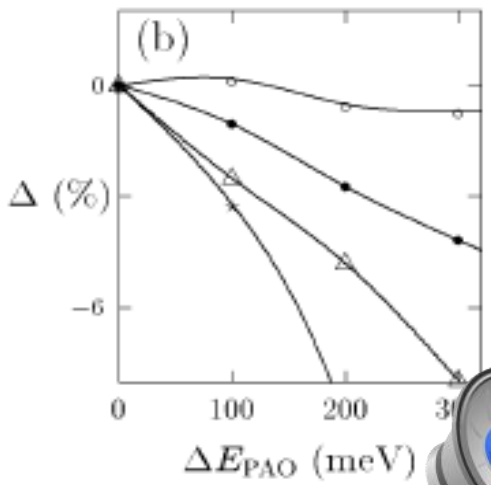
E. Artacho et al. Phys. Stat. Solidi (b) 215, 809 (1999)

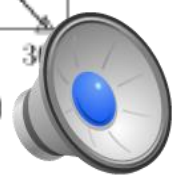
Convergence vs Energy shift of

Bond lengths



Bond energies





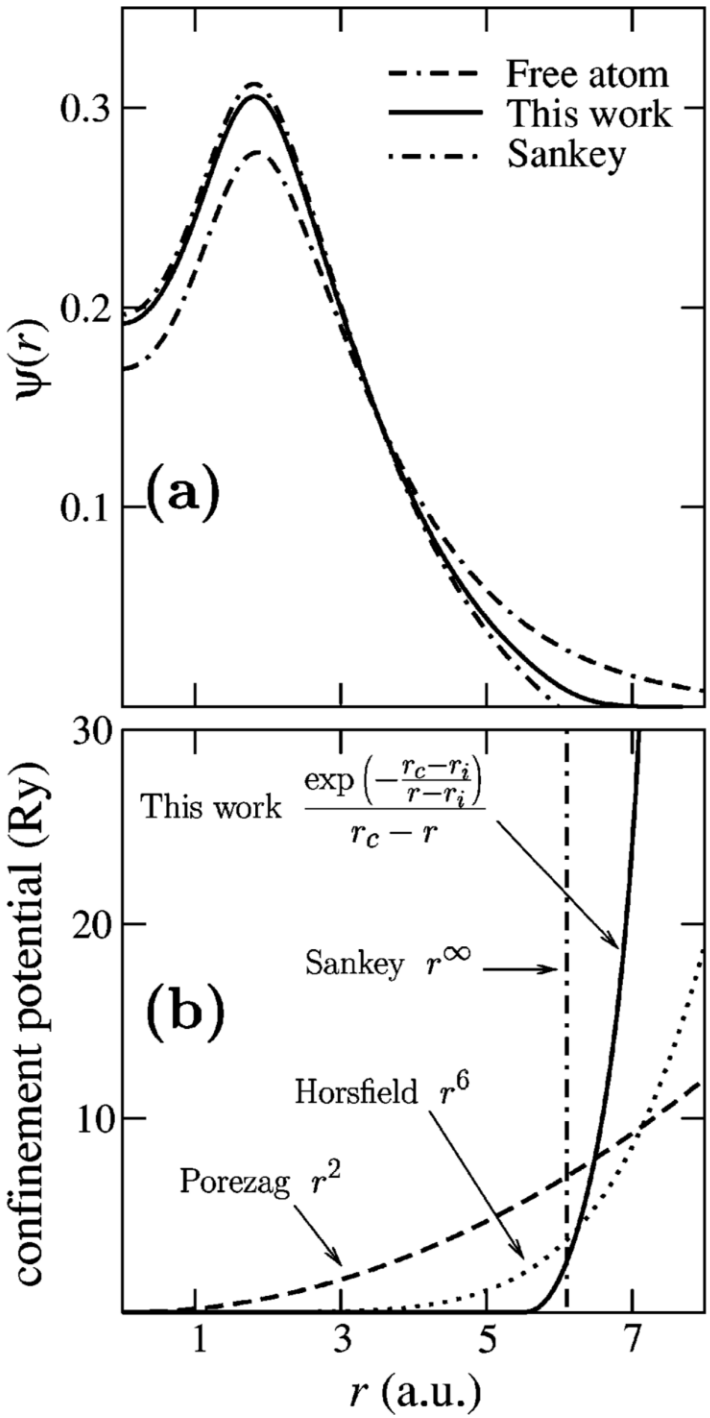
Soft confining potentials

Removing the derivative discontinuity at r_c
(and numerical inconveniences)

Better basis (variationally & for other results)

Default:

$$r_i = 0.9\, r_c$$

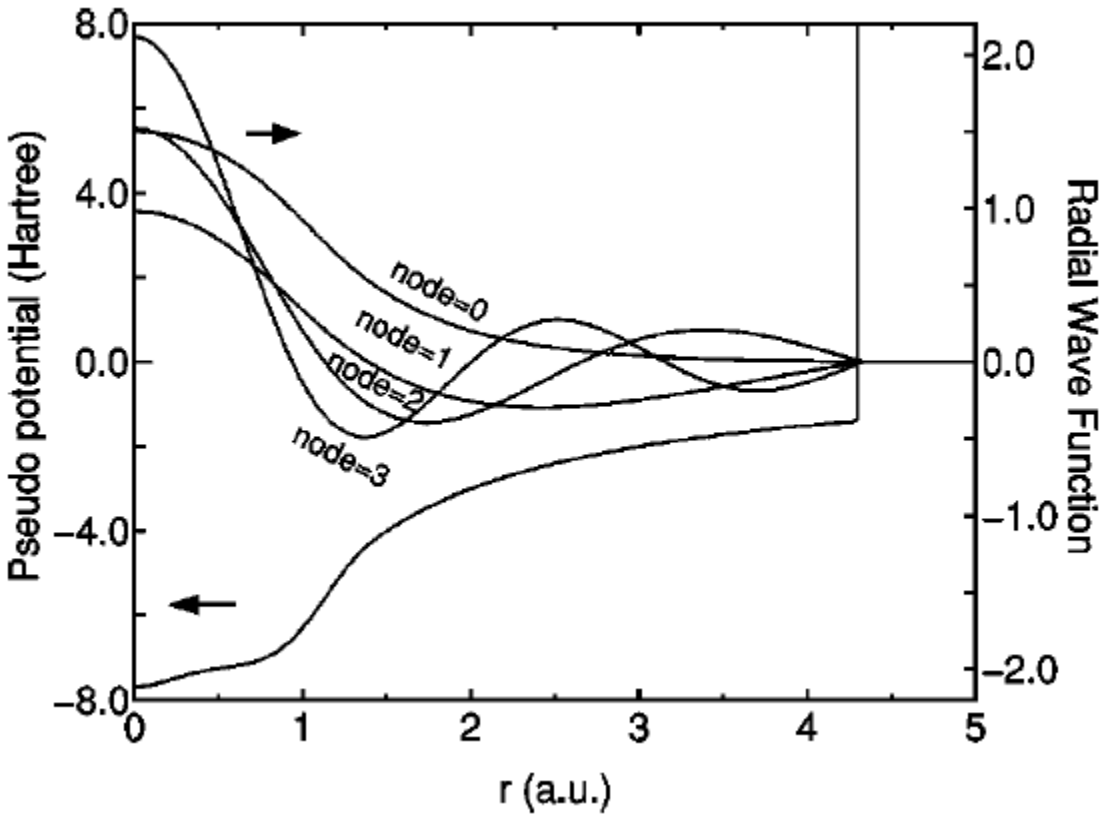


J. Junquera, O. Paz, D. Sanchez-Portal & E. Artacho, Phys. Rev. B, **64**, 235111 (2001)
E. Anglada, J. M. Soler, J. Junquera & E. Artacho, Phys. Rev. B **66**, 205101 (2002)

Also used by FHI-AIMS

Schemes to generate multiple-ζ basis sets

Use pseudopotential eigenfunctions with increasing number of nodes



T. Ozaki et al., Phys. Rev. B 69, 195113 (2004)

Advantages

Orthogonal

Asymptotically complete (within sphere)

Disadvantages

Excited states of pseudos, (usually unbound)

Efficiency depends on r_c's

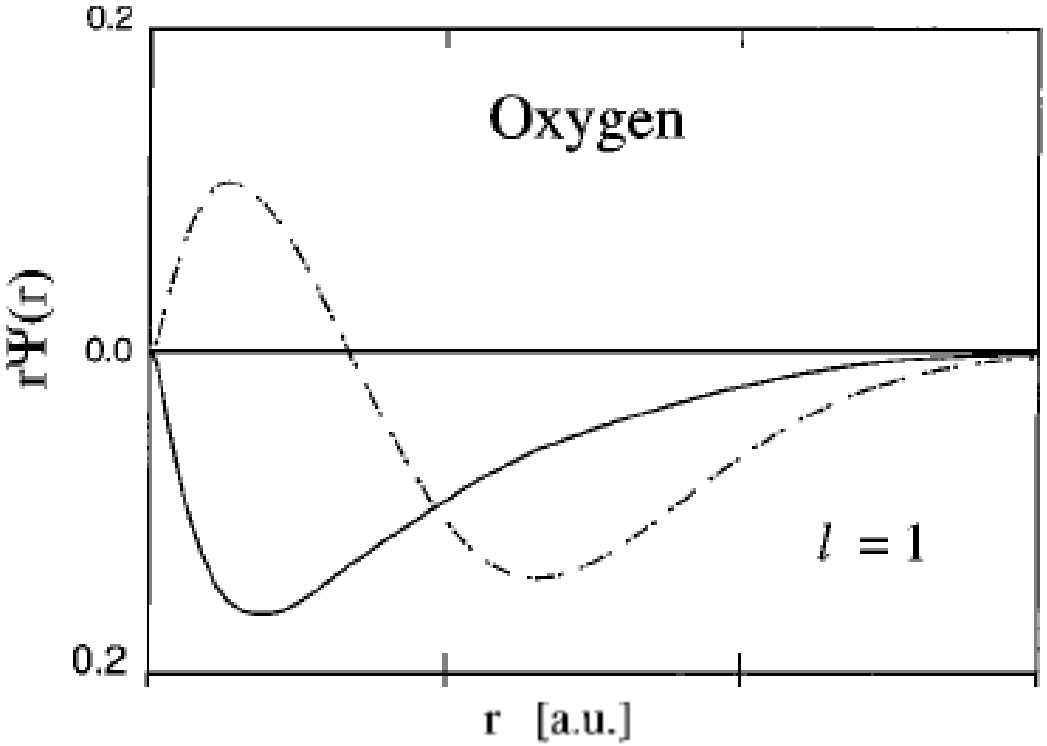
Need more than other schemes

Available in Siesta

PAO.BasisType Nodes

Schemes to generate multiple-ζ basis sets
Chemical hardness

Derivative with respect to the charge of the atom



Advantages

Orthogonal

It does not depend on any extra (variational) parameter

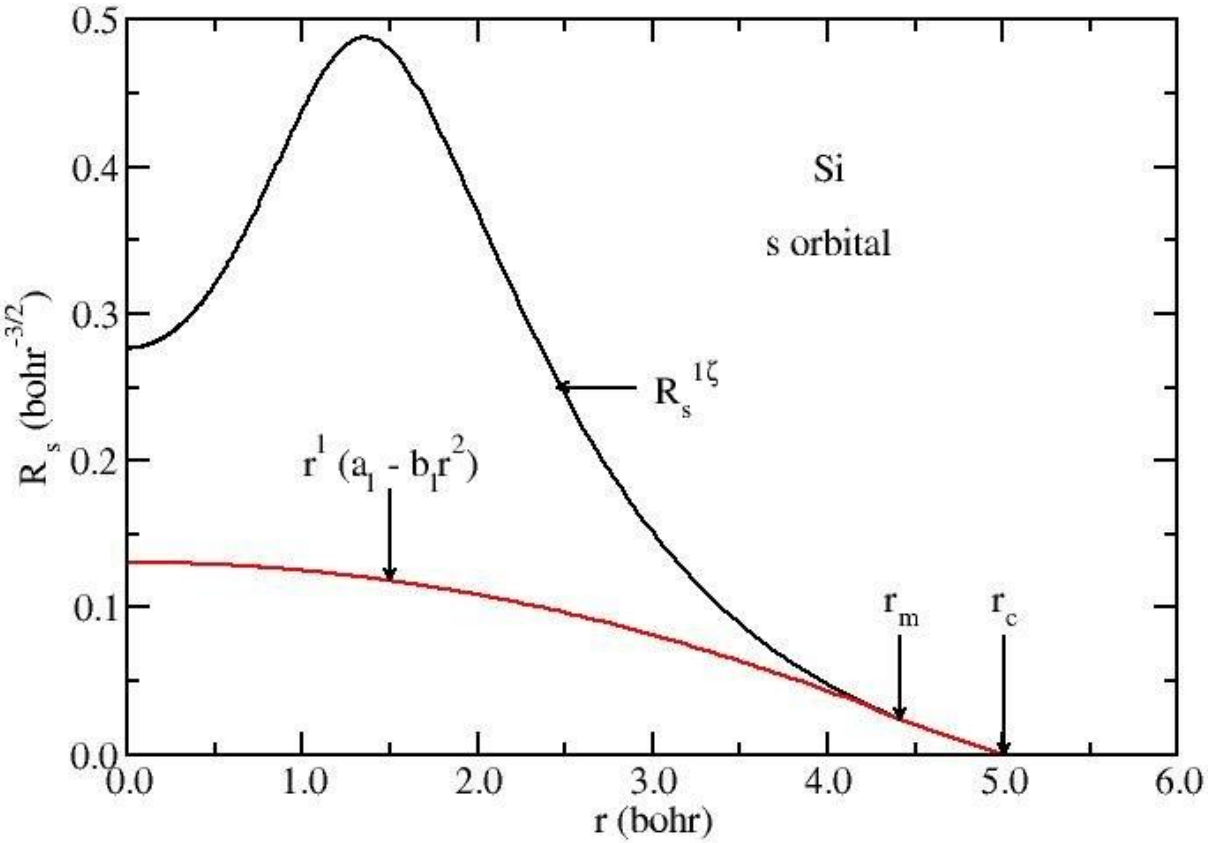
Disadvantages

Range of second-ζ equals the range of the first-ζ function

G. Lippert et al., J. Phys. Chem. 100, 6231 (1996)

Default mechanism to generate multiple-ζ in SIESTA

Our own "Split-valence" method

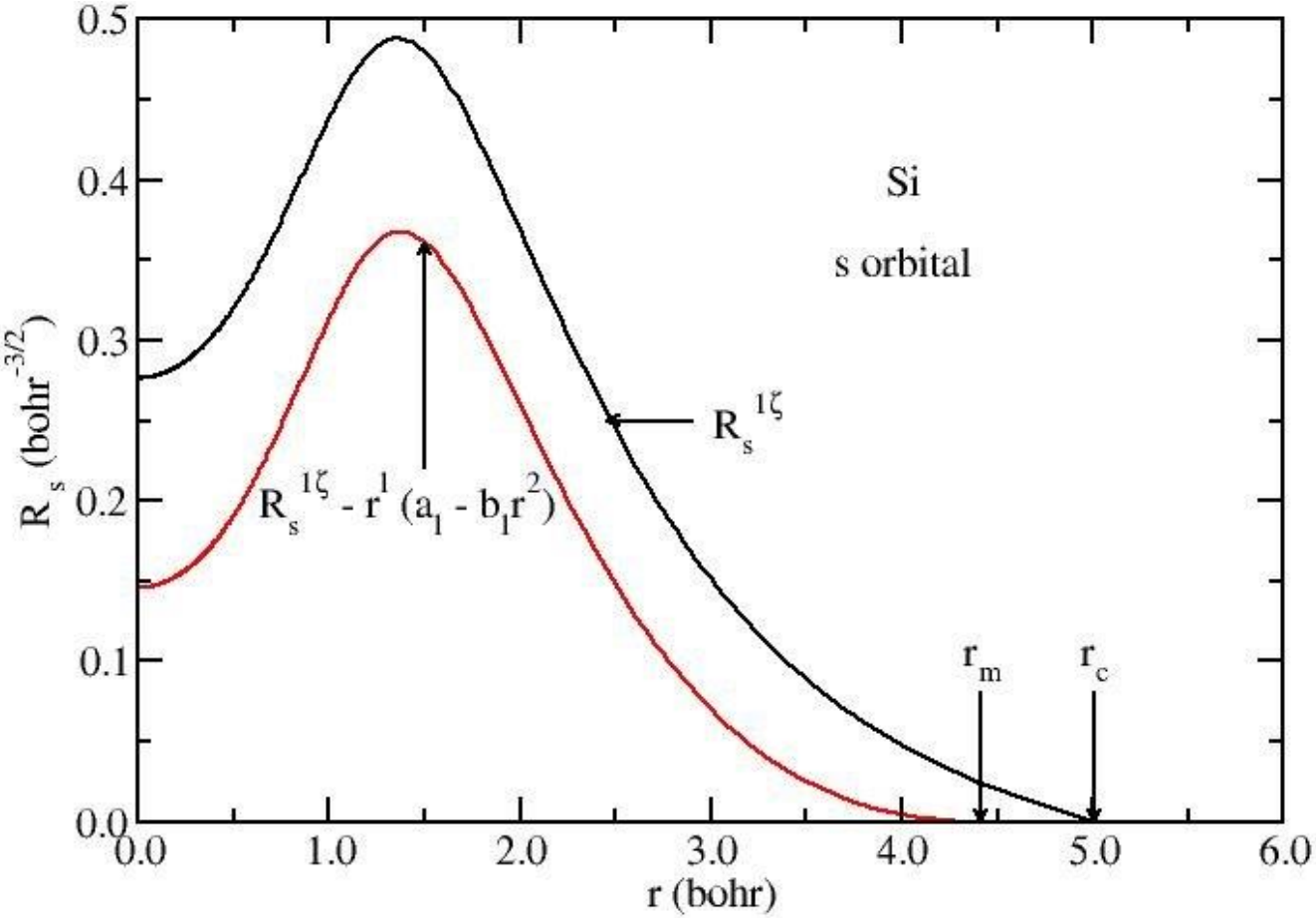


Choose r_m and continue smoothly towards the origin as $r^l \left(a_l - b_l r^2\right)$

The second-ζ function reproduces the tail of the of the first-ζ outside a radius r_m

Default mechanism to generate multiple-ζ in SIESTA

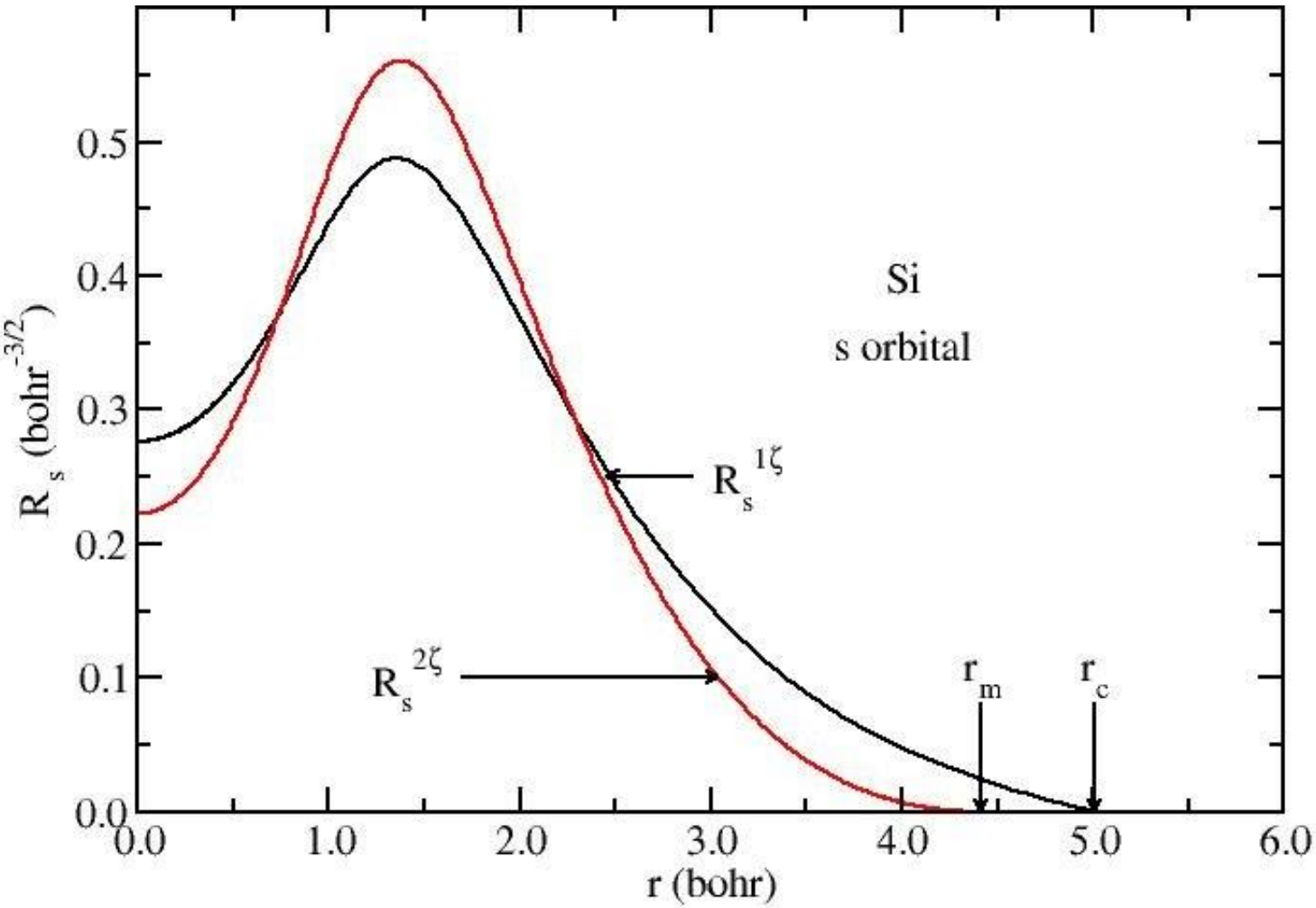
Our own "Split-valence" method



The same Hilbert space can be expanded if we use the difference, with the advantage that now the second-ζ vanishes at r_m (more efficient)

Default mechanism to generate multiple-ζ in SIESTA

Our own "Split-valence" method

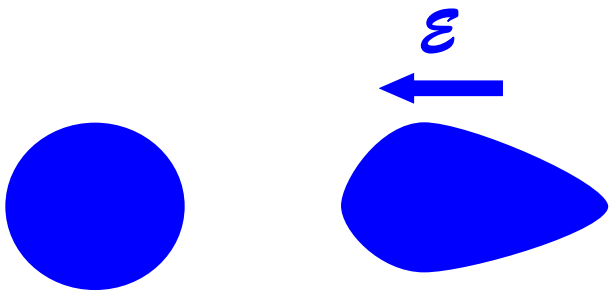


Finally, the second-ζ is normalized

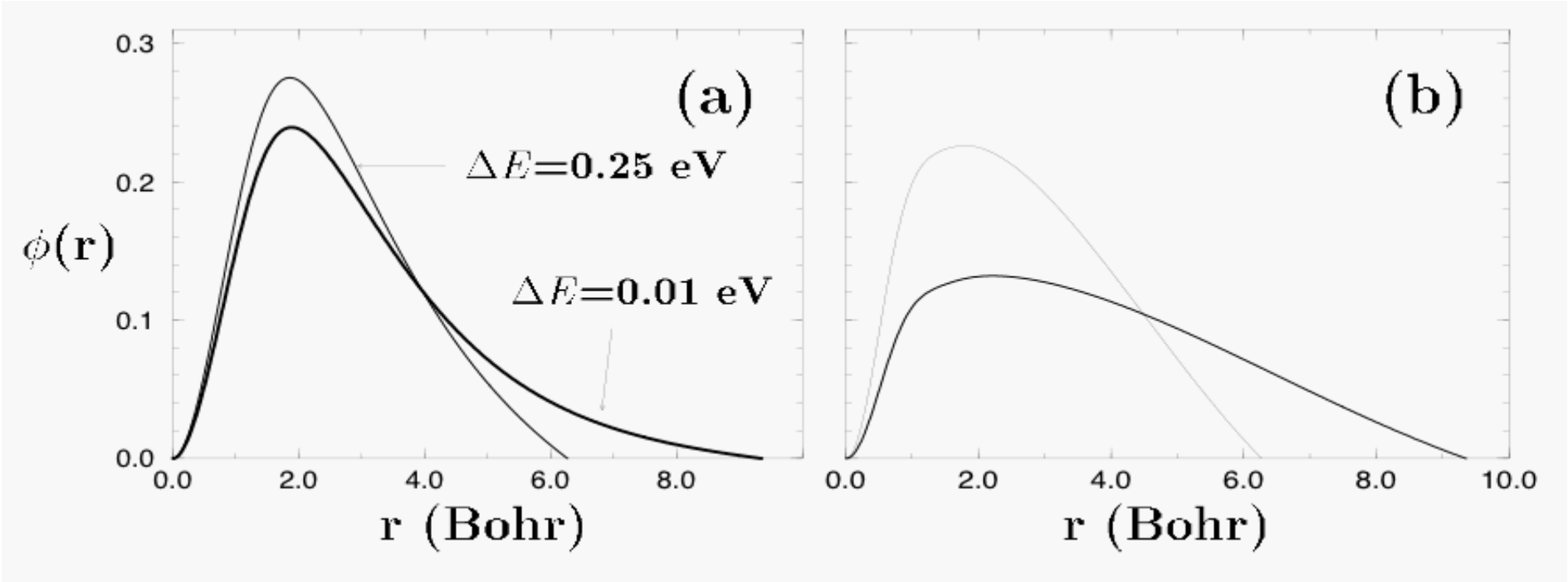
r_m controlled with PAO.SplitNorm (typical value 0.15)

Polarisation

From free pseudoatom valence eigenstates under $\mathcal{E}$ electric field



From free pseudoatom (empty) eigenstates of higher *l*



Original idea of J. M. Soler

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

How to introduce basis sets in SIESTA

Systematics with minimum set of parameters

Defaults (if nothing is specified)

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	
Confinement:	PAO.SoftDefault	false	(Hard confinement)

A decent basis set in terms of accuracy versus efficiency

How to introduce the basis set in SIESTA

Systematics with minimum set of parameters

Defaults (if nothing is specified)			But I prefer
Basis size:	PAO.BasisSize	DZP	
Range of first-zeta:	PAO.EnergyShift	0.02 Ry	50 meV
Second-zeta:	PAO.BasisType	Split	
Range of second-zeta:	PAO.SplitNorm	0.15	
Confinement:	PAO.SoftDefault	false	true
	PAO.SoftInnerRadius	0.9	

A better basis set, a bit less efficient

More direct control of the basis

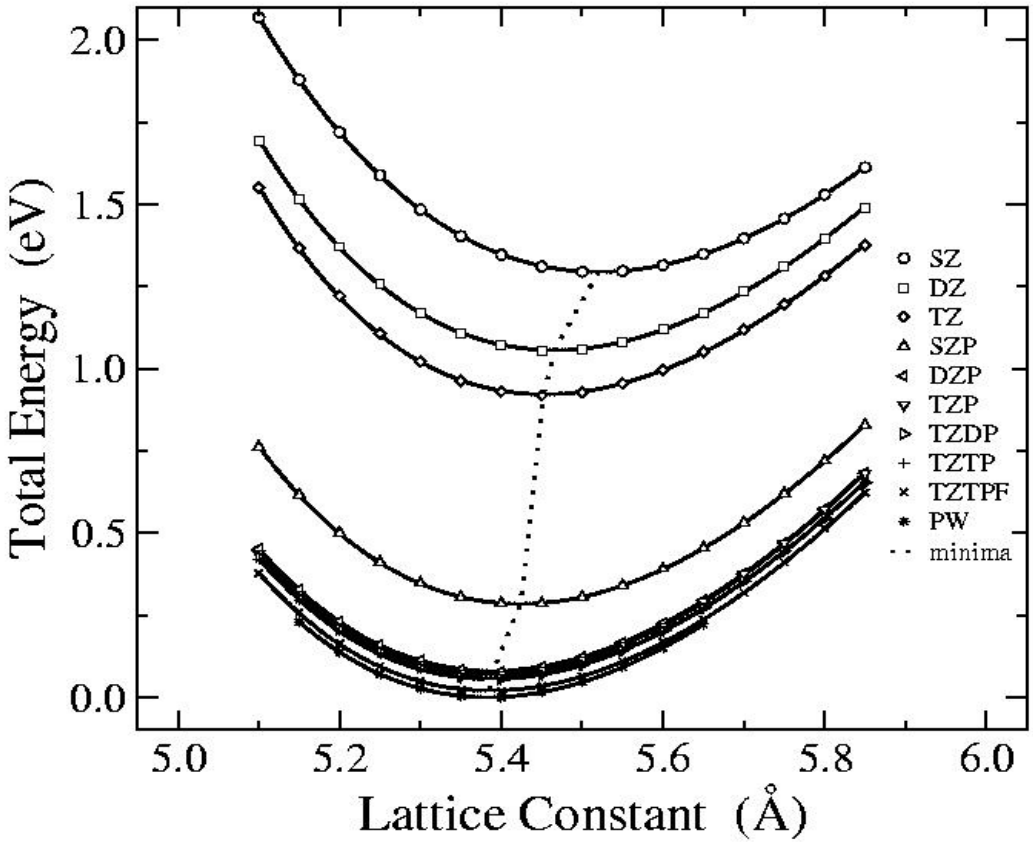
The PAO.Basis block

```
%block PAO.Basis                  # Define Basis set
H       1    +0.25                # Species label, number of l-shells, charge
 n=1    0    2                    # n, l, Nzeta
   5.000       3.000              # rc (first-zeta), rm (second-zeta)
   1.000       1.000              # scaling factors
%endblock PAO.Basis
```

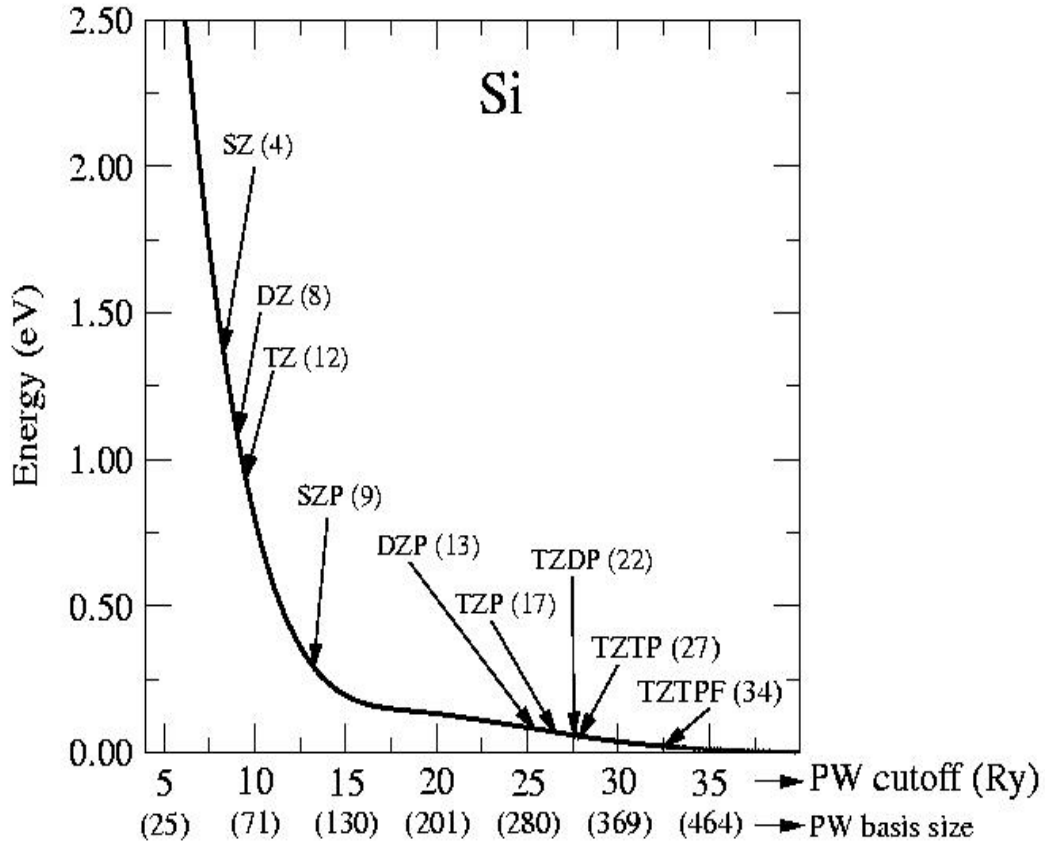
Convergence with basis set size

Bulk Si

Cohesive curves



PW and NAO convergence



Atomic orbitals show nice convergence with basis size

Polarisation orbitals important for convergence (more than multiple-ζ)

Variational optimisation

Possibility: Minimising Energy versus basis set parameters

For some reference/representative system

Simplex utility within SIESTA package to do that

But careful

Blind optimisation can result in poorly transferable bases

(I am not a fan, I prefer strategy described in F Corsetti et al, JPCM 2013)

Systematic protocol on e.g. same-species dimers (done by FHI-AIMS)

Simune has done this for SIESTA

(and please do not use basis parameters to fit to desired property values, such as structures, band gaps etc)

Convergence with basis set size

Elemental solids with GGA-PBE

		Exp.	LAPW	Other PW	PW	DZP
C	a (Å)	3.57	3.54	3.54	3.53	3.54
	B (GPa)	442	470	436	459	453
	E_c (eV)	7.37	10.13	8.96	8.89	8.81
Si	a (Å)	5.43	5.41	5.38	5.38	5.40
	B (GPa)	99	96	94	96	97
	E_c (eV)	4.63	5.28	5.34	5.40	5.31
Na	a (Å)	4.23	4.05	3.98	3.95	3.98
	B (GPa)	6.9	9.2	8.7	8.7	9.2
	E_c (eV)	1.11	1.44	1.28	1.22	1.22
Cu	a (Å)	3.60	3.52	3.56	-	3.57
	B (GPa)	138	192	172	-	165
	E_c (eV)	3.50	4.29	4.24	-	4.37
Au	a (Å)	4.08	4.05	4.07	4.05	4.07
	B (GPa)	173	198	190	195	188
	E_c (eV)	3.81	-	-	4.36	4.13

DZP basis

Similar deviations as for DFT-XC's or pseudos

PW: Converged Plane Waves with Pseudopotentials

LAPW: All electron calculations (no pseudos) with Augmented Plane Waves

Concluding

- Basis generation tools of SIESTA have been introduced
- Use them to get the basis you need