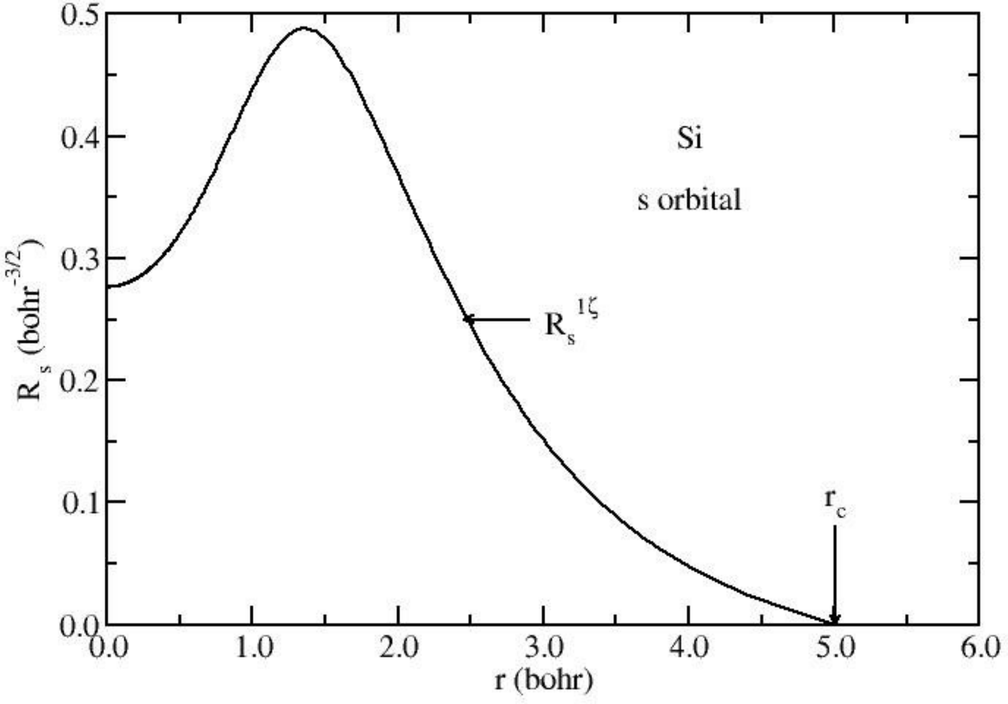
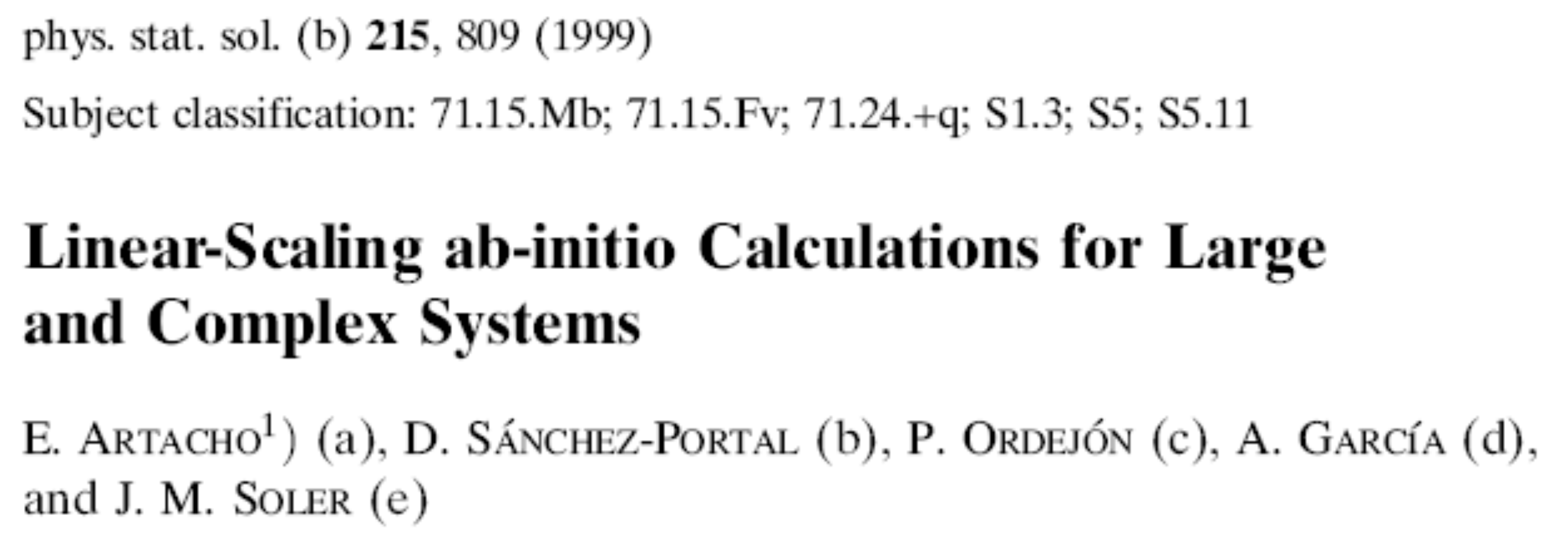
Atomic orbitals of finite range as basis sets



Javier Junquera

UNIVERSIDAD DE CANTABRIA

Most important reference followed in this lecture

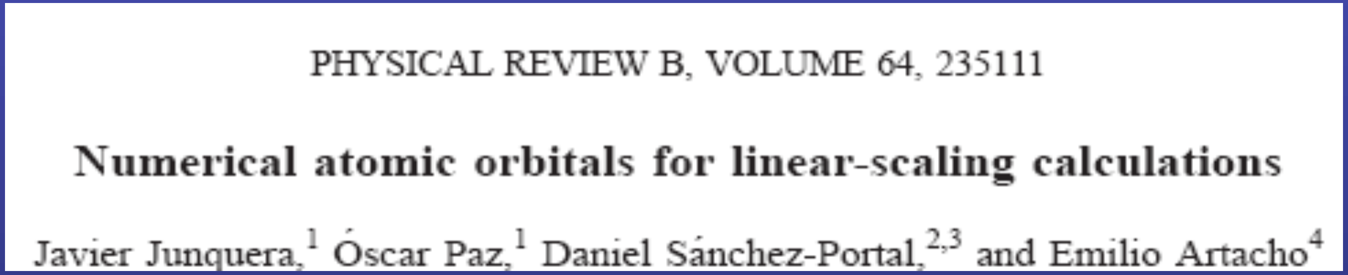


phys. stat. sol. (b) **215**, 809 (1999)

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

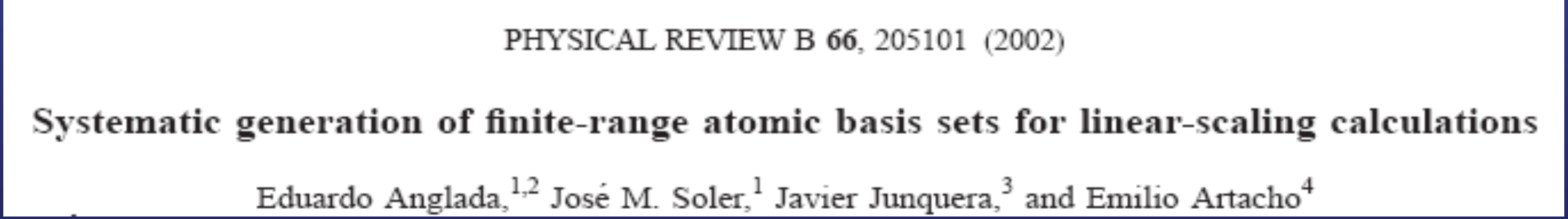
E. Artacho1) (a), D. Sánchez-Portal (b), P. Ordejón (c), A. García (d), and J. M. Soler (e)



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]

…in previous chapters:

the many body problem reduced to a problem of independent particles

One particle Kohn-Sham equation

$$\left[-\frac{1}{2}\nabla^2 + V_{eff}^{\sigma}(\vec{r})\right]\psi_i^{\sigma}(\vec{r}) = \varepsilon_i^{\sigma}\psi_i^{\sigma}(\vec{r})$$

$$V_{eff}^{\sigma}(\vec{r}) = V_{ext}(\vec{r}) + V_{Hartree}[n] + V_{xc}^{\sigma}[n^{\uparrow}, n^{\downarrow}]$$

Goal: solve the equation, that is, **find**

- the **eigenvectors**
- the **eigenvalues**

Solution: expand the eigenvectors in terms of functions of known properties **(basis)**

$$\psi_i(\vec{r}) = \sum_{\alpha} c_{i\alpha} \boxed{f_\alpha(\vec{r})}$$

basis functions

Different methods propose different basis functions

Each method has its own **advantages**:

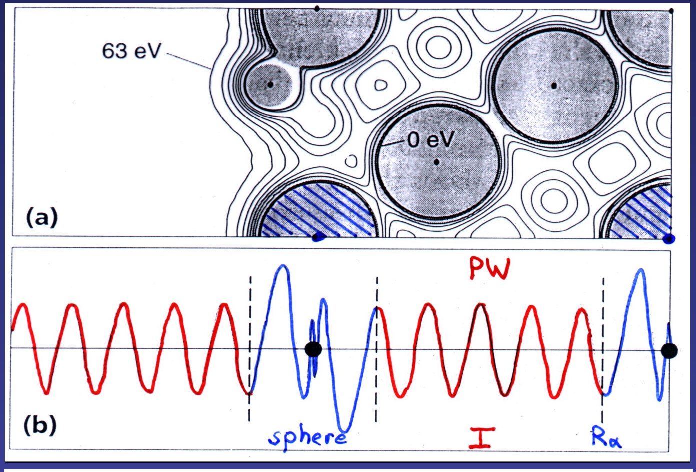
- most appropriate for a range of problems
- provide insightful information in its realm of application

Each method has its own **pitfalls**:

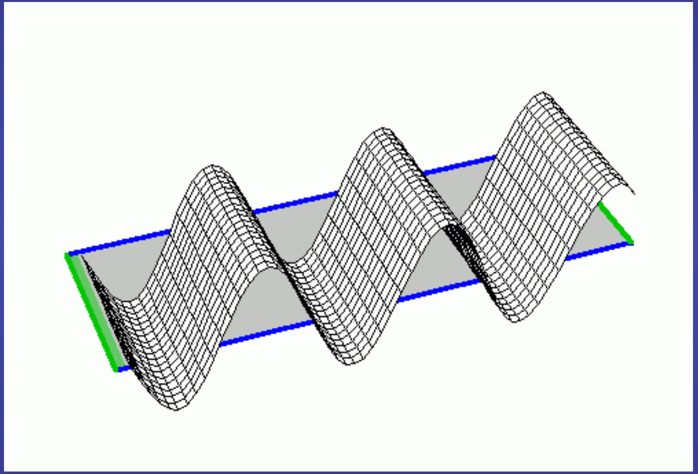
- importance to understand the method, the pros and the cons.
- what can be computed and what can not be computed

Three main families of methods depending on the basis sets

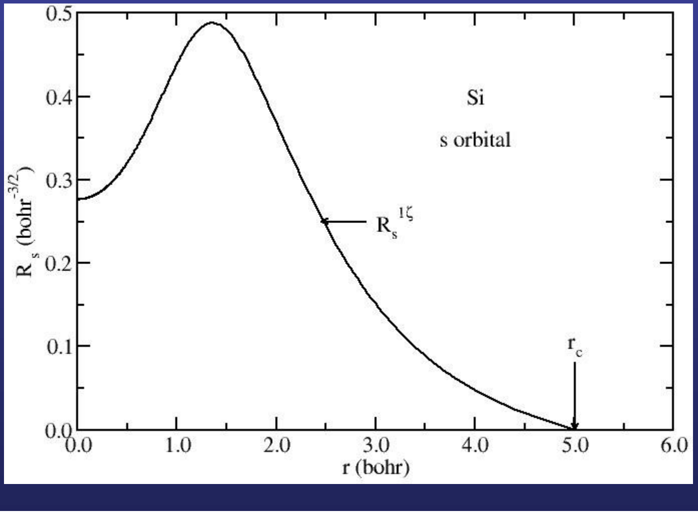
Atomic sphere methods



Plane wave and grids

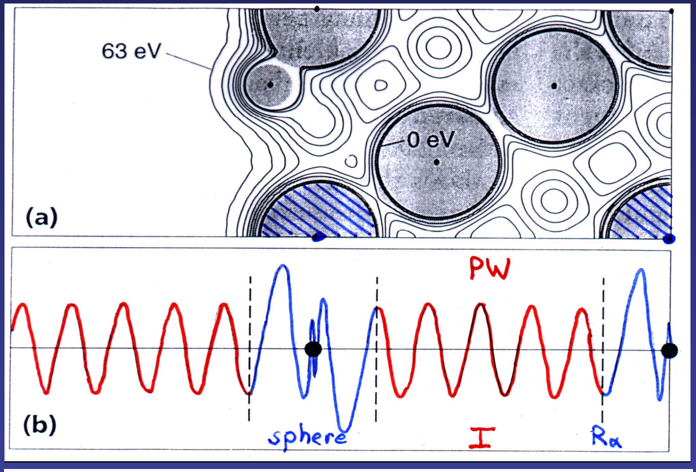


Localized basis sets

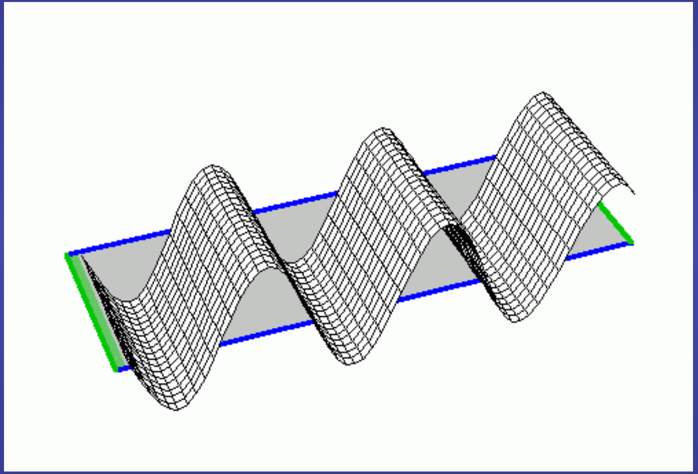


Three main families of methods depending on the basis sets

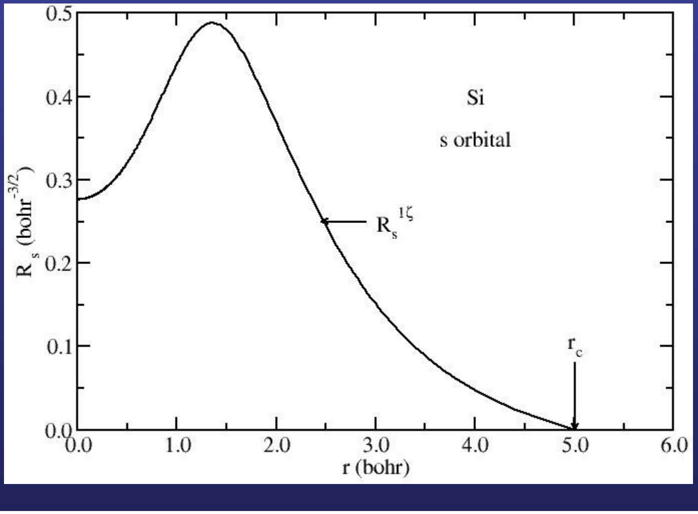
Atomic sphere methods



Plane wave and grids

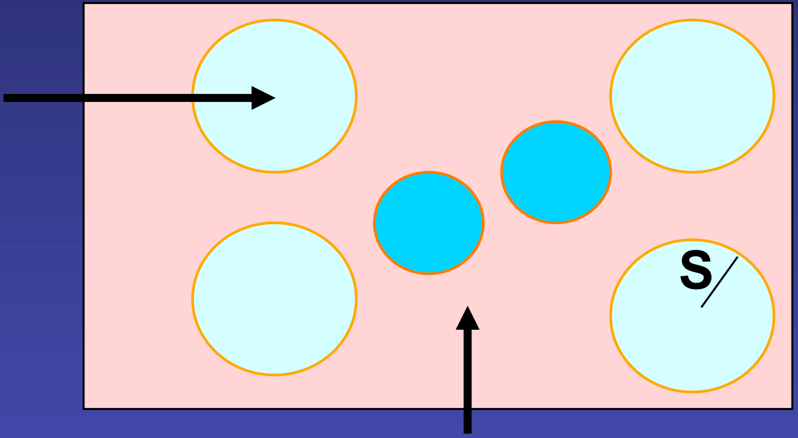


Localized basis sets

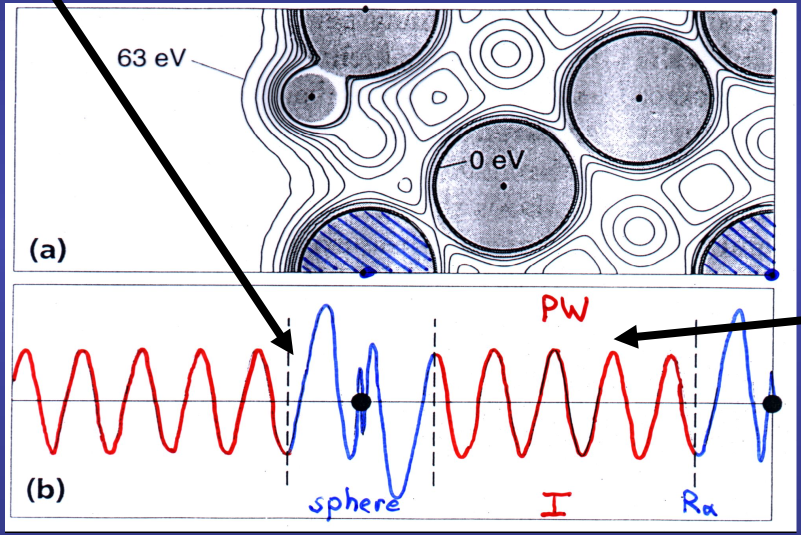


Atomic spheres methods: most general methods for precise solutions of the KS equations

General idea: divide the electronic structure problem



Efficient representation of
atomic like features near each nucleus



Smoothly varying functions
between the atoms

Courtesy of K. Schwarz

APW (Augmented Plane Waves; Atomic Partial Waves + Plane Waves)

KKR (Korringa, Kohn, and Rostoker method; Green’s function approach)

MTO (Muffin tin orbitals)

Corresponding “L” (for linearized) methods

Atomic spheres methods: most general methods for precise solutions of the KS equations

$$\psi_{i,\vec{k}}(\vec{r}) = \sum_m c_{i,m}(\vec{k})\chi^{APW}_{\vec{k}+\vec{G}_m}(\vec{r})$$

$$\chi^{APW}_{\vec{k}+\vec{G}_m}(\vec{r}) = \begin{cases} e^{i(\vec{k}+\vec{G}_m)\cdot\vec{r}} & r > S, \\ \sum_L C_L(\vec{k}+\vec{G}_m)\psi_L(\epsilon,\vec{r}) & r < S \end{cases}$$

ADVANTAGES

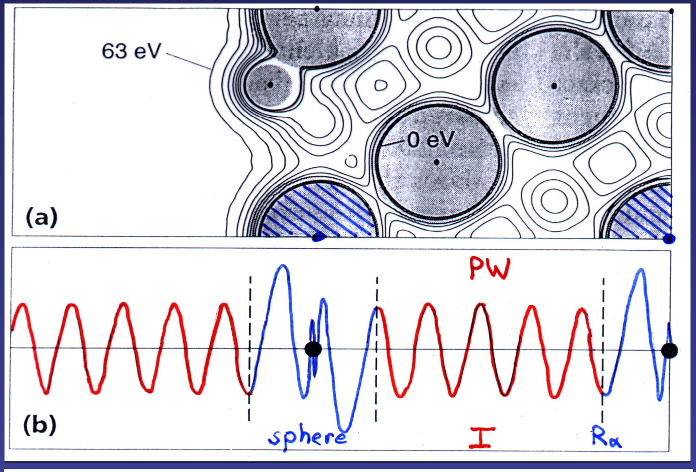
- Most accurate methods within DFT
- Asymptotically complete
- Allow systematic convergence

DISADVANTAGES

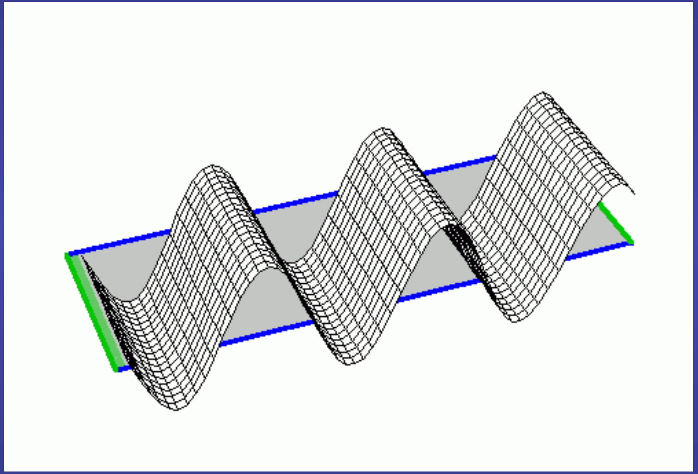
- Very expensive
- Absolute values of the total energies are very high ⇒ if differences in relevant energies are small, the calculation must be very well converged
- Difficult to implement

Three main families of methods depending on the basis sets

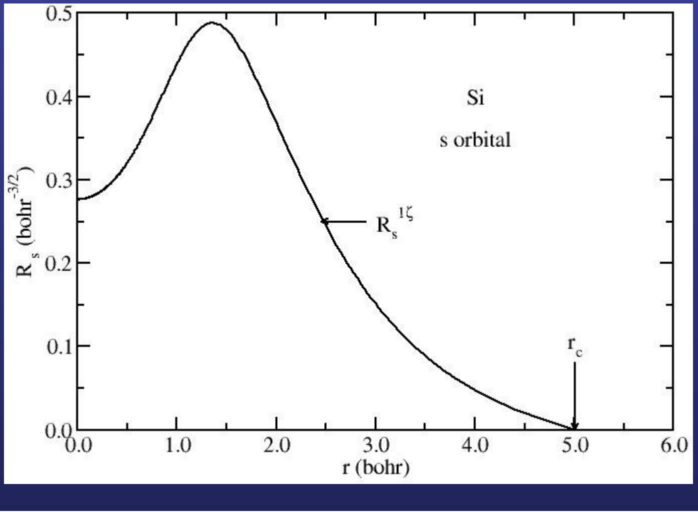
Atomic sphere methods



Plane wave and grids



Localized basis sets



Plane wave methods (intertwined with pseudopotentials)

$$\psi_{i,\vec{k}}(\vec{r}) = \sum_{\vec{g}} c_{i,\vec{g}} \left[\frac{1}{\sqrt{\Omega}} e^{i\left(\vec{k}+\vec{g}\right)\cdot\vec{r}} \right]$$

ADVANTAGES

- Very extended among physicists
- Conceptually simple (Fourier transforms)
- Asymptotically complete
- Allow systematic convergence
- Spatially unbiased (no dependence on the atomic positions)
- "Easy" to implement (FFT)

DISADVANTAGES

- Not suited to represent any function in particular
- Hundreths of plane waves per atom to achieve a good accuracy
- Intrinsic inadequacy for Order-N methods (extended over the whole system)
- Vacuum costs the same as matter
- Hard to converge for tight-orbitals (3d,…)

M. Payne et al., Rev. Mod. Phys. 64, 1045 (1992)

Matrix elements with a plane wave basis set: the overlap matrix

Plane waves corresponding to different wave vectors $\vec{G} \neq \vec{G}'$ are orthogonal

$$S^{\vec{k}}_{\vec{G}\vec{G}'} = \langle \phi^{\vec{k}}_{\vec{G}} | \phi^{\vec{k}}_{\vec{G}'} \rangle = \frac{1}{\Omega} \int_{\Omega} e^{i(\vec{G}' - \vec{G})\cdot\vec{r}} = \frac{1}{\Omega} (\Omega \delta_{\vec{G}\vec{G}'}) = \delta_{\vec{G}\vec{G}'}$$

So the overlap matrix in a plane wave basis set is the unitary matrix

Matrix elements with a plane wave basis set: the kinetic matrix elements

$$T^{\vec{k}}_{\vec{G}\vec{G}'} = -\frac{1}{2}\langle \phi^{\vec{k}}_{\vec{G}} | \vec{\nabla}^2 | \phi^{\vec{k}}_{\vec{G}'} \rangle$$

Knowing that

$$\vec{\nabla}^2 \left(\frac{1}{\sqrt{\Omega}} e^{i(\vec{k}+\vec{G}')\cdot\vec{r}} \right) = -|\vec{k}+\vec{G}'|^2 \left(\frac{1}{\sqrt{\Omega}} e^{i(\vec{k}+\vec{G}')\cdot\vec{r}} \right)$$

Then

$$\begin{aligned} T^{\vec{k}}_{\vec{G}\vec{G}'} &= -\frac{1}{2}\int \phi^{\vec{k}\,*}_{\vec{G}}(\vec{r})\vec{\nabla}^2\phi^{\vec{k}}_{\vec{G}'}(\vec{r})d\vec{r} = \frac{1}{2\Omega}|\vec{k}+\vec{G}'|^2 \int_{\Omega} e^{i(\vec{G}'-\vec{G})\cdot\vec{r}}d\vec{r} \\ &= \frac{1}{2\Omega}|\vec{k}+\vec{G}'|^2(\Omega\delta_{\vec{G}\vec{G}'}) = \frac{1}{2}|\vec{k}+\vec{G}'|^2\delta_{\vec{G}\vec{G}'} \end{aligned}$$

The kinetic term in the one-electron Hamiltonian is diagonal in reciprocal space

Matrix elements with a plane wave basis set: the effective potential matrix elements

$$V_{eff}(\vec{G},\vec{G}') = \langle \phi^{\vec{k}}_{\vec{G}} | \hat{V}_{eff} | \phi^{\vec{k}}_{\vec{G}'} \rangle = \frac{1}{\Omega} \int V_{eff}(\vec{r}) e^{-i(\vec{G}-\vec{G}')\cdot\vec{r}} d\vec{r} = \tilde{V}_{eff}(\vec{G}-\vec{G}')$$

↑

Fourier transform of the potential

If $\hat{V}_{eff}$ is a local potential, the matrix elements are independent of the wave vector $\vec{k}$ in the BZ

Time independent Schrödinger equation in a plane wave basis set

$$\hat{H}_{eff}(\vec{r})\psi_{n\vec{k}}(\vec{r}) = \left[-\frac{1}{2}\vec{\nabla}^2 + V_{eff}(\vec{r})\right]\psi_{n\vec{k}}(\vec{r}) = \varepsilon_{n\vec{k}}(\vec{r})$$

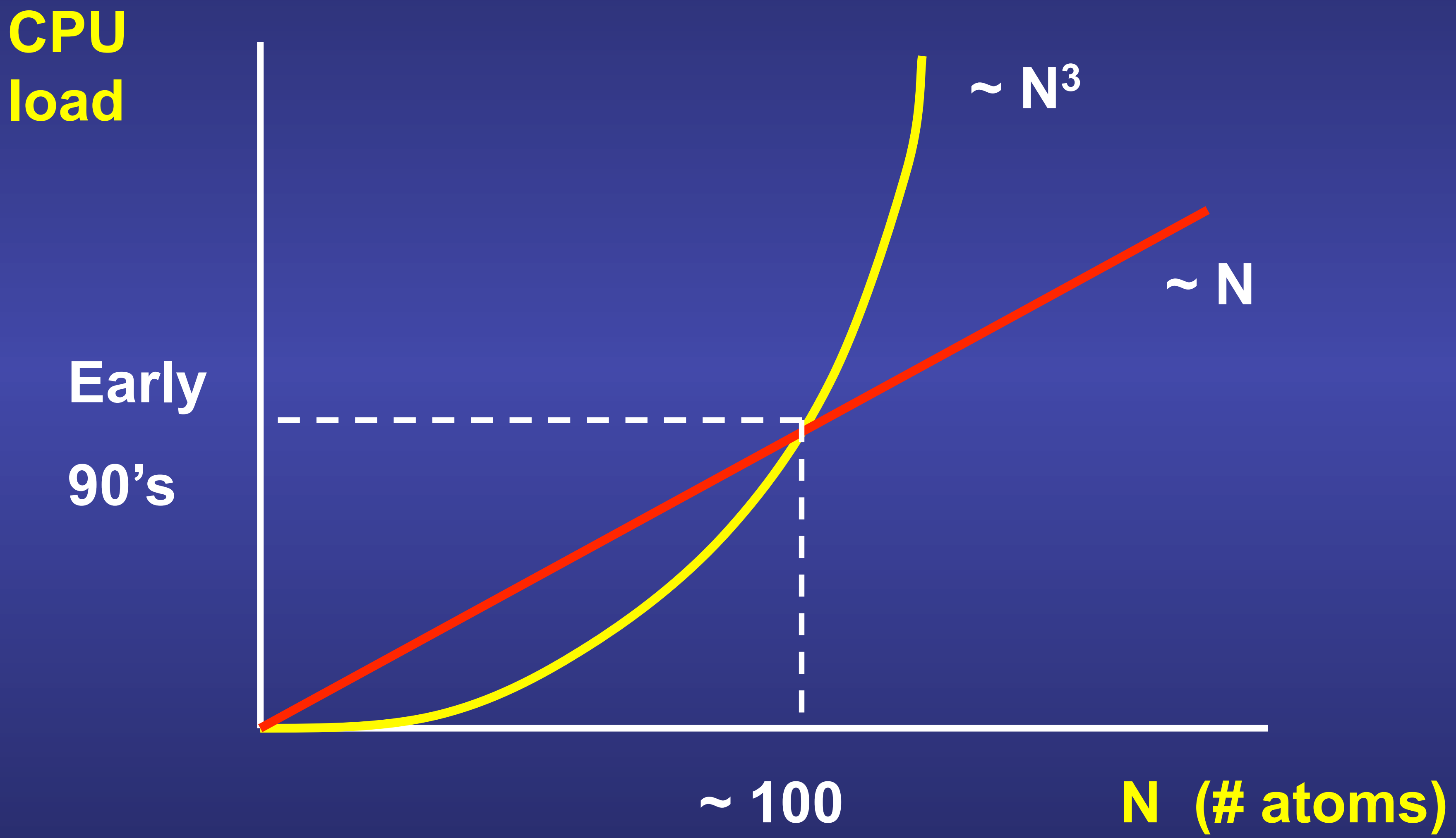
$$\phi_{\vec{G}}(\vec{r}) = \frac{1}{\sqrt{\Omega}} e^{i\vec{G}\cdot\vec{r}}$$

$$\psi_{n\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} \sum_{\vec{G}=0}^{\infty} C_{n\vec{k}}(\vec{G})\phi_{\vec{G}}(\vec{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\vec{G}=0}^{\infty} C_{n\vec{k}}(\vec{G}) e^{i(\vec{k}+\vec{G})\cdot\vec{r}}$$

$$\psi_{n\vec{k}}(\vec{r}) = \sum_{\vec{G}=0}^{\infty} C_{n\vec{k}}(\vec{G})\phi_{\vec{G}}^{\vec{k}}(\vec{G})$$

$$\phi_{\vec{G}}^{\vec{k}}(\vec{G}) = \frac{1}{\sqrt{\Omega}} e^{i(\vec{k}+\vec{G})\cdot\vec{r}}$$

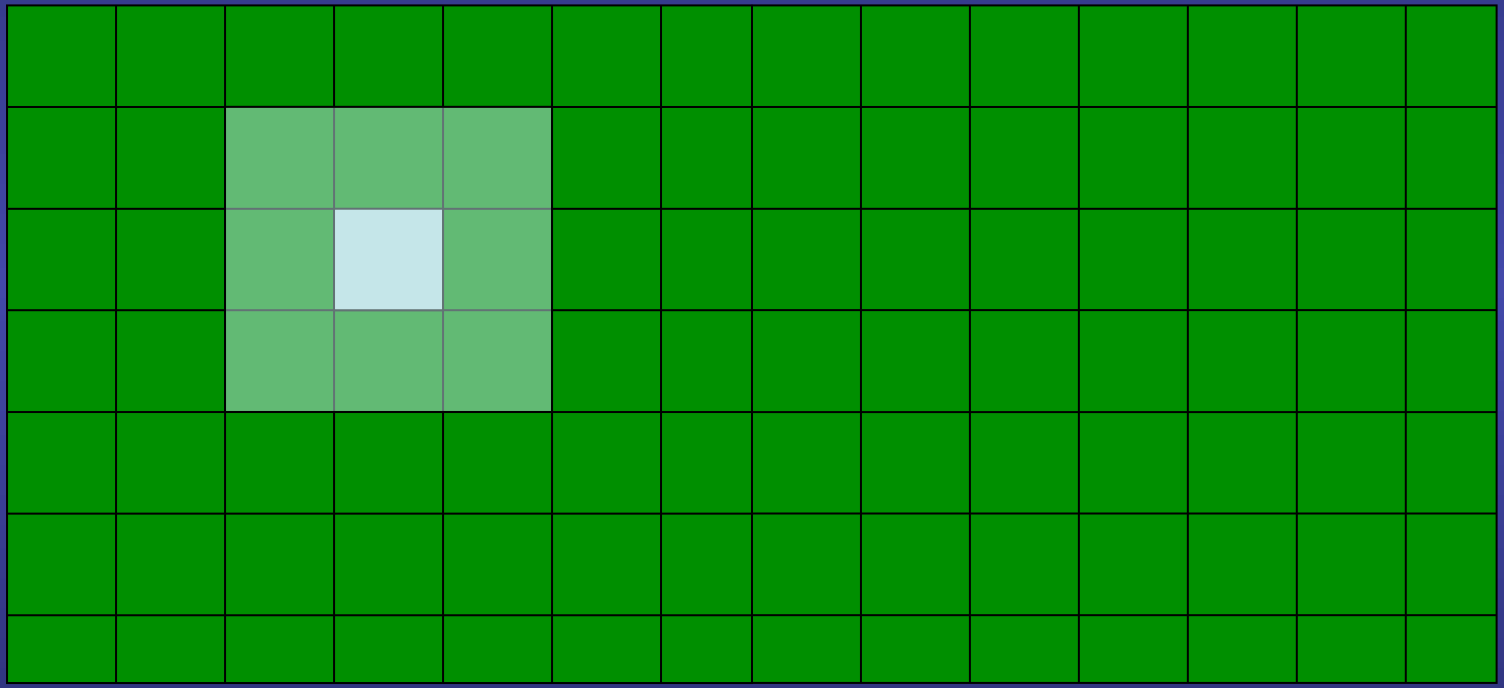
Order-N methods: The computational load scales linearly with the system size



G. Galli and M. Parrinello, Phys. Rev Lett. 69, 3547 (1992)

Locality is the key point to achieve linear scaling

Large system



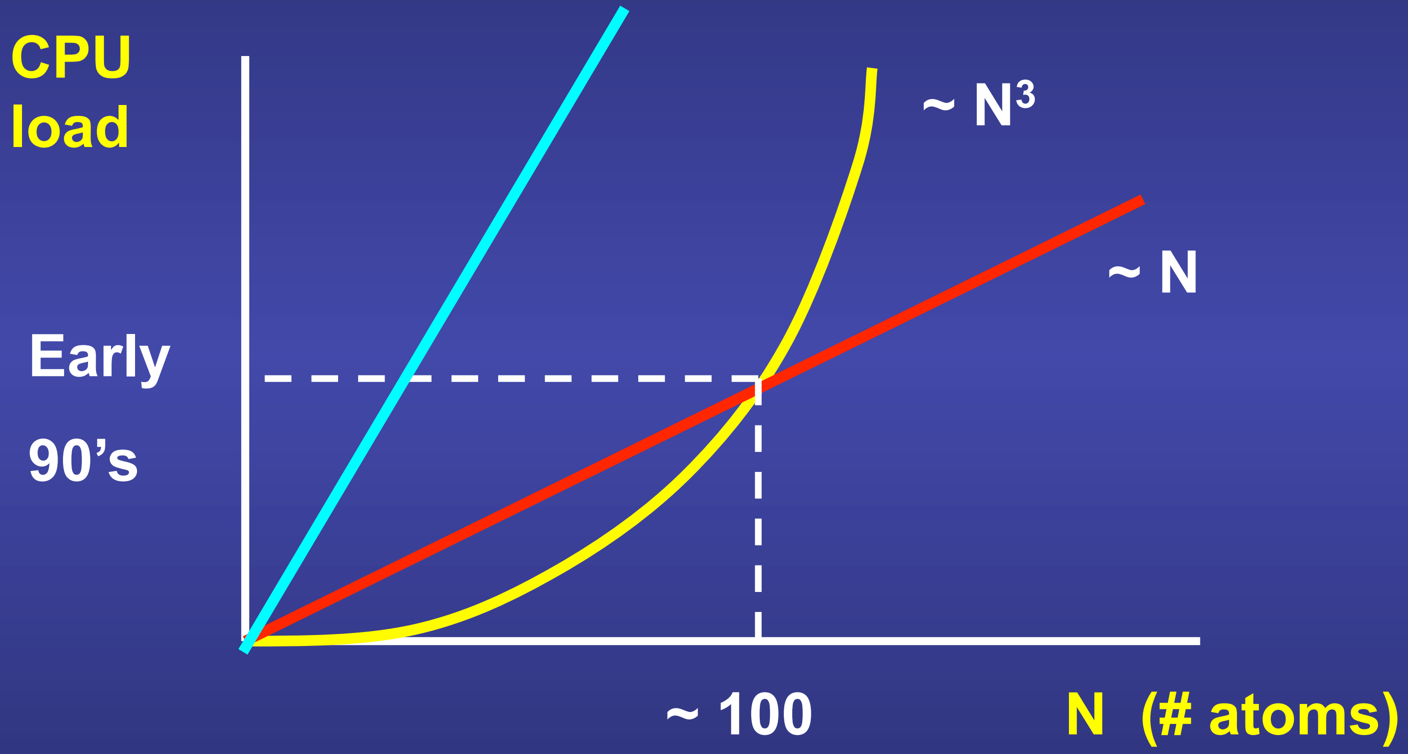
x2

"Divide and Conquer"

W. Yang, Phys. Rev. Lett. 66, 1438 (1992)

Efficient basis set for linear scaling calculations: localized, few and confined

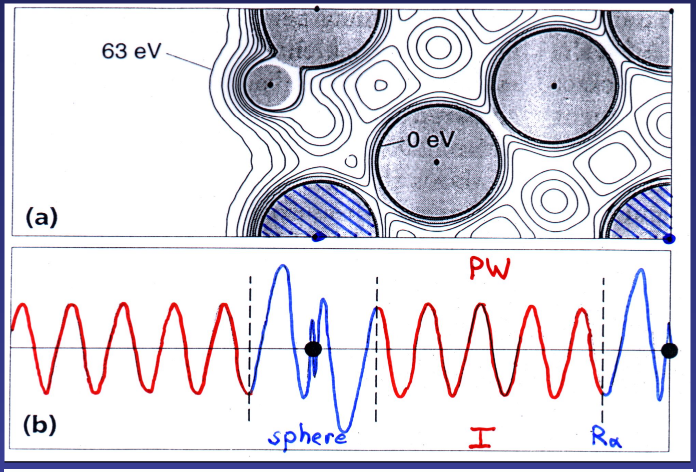
Locality ⇒ Basis set of localized functions



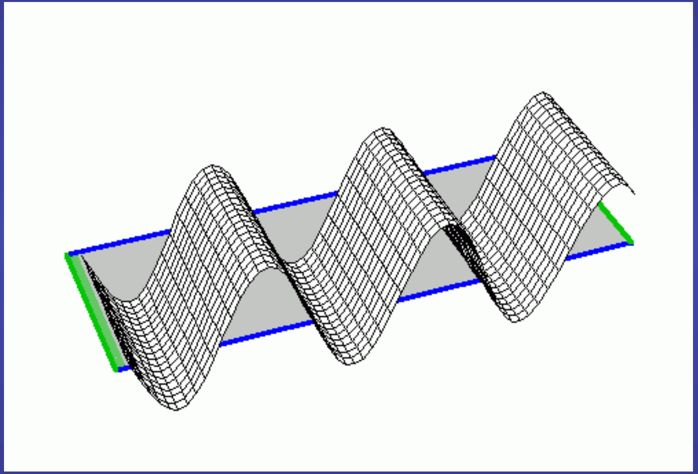
Regarding efficiency, the important aspects are:

- **NUMBER** of basis functions per atom
- **RANGE** of localization of these functions

Three main families of methods depending on the basis sets



Atomic sphere methods



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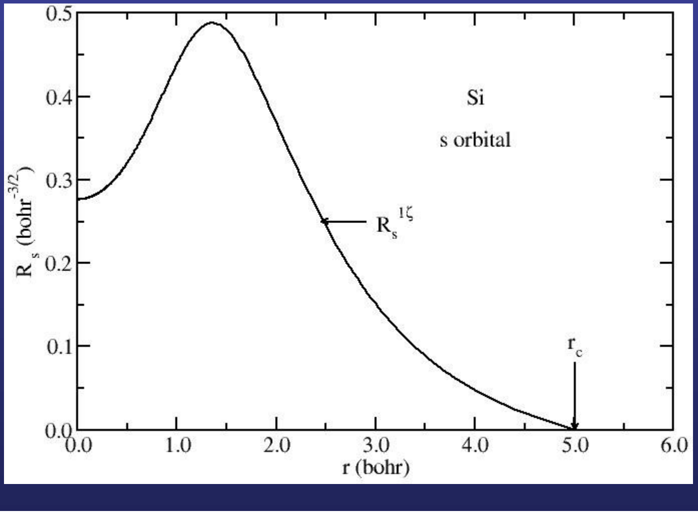
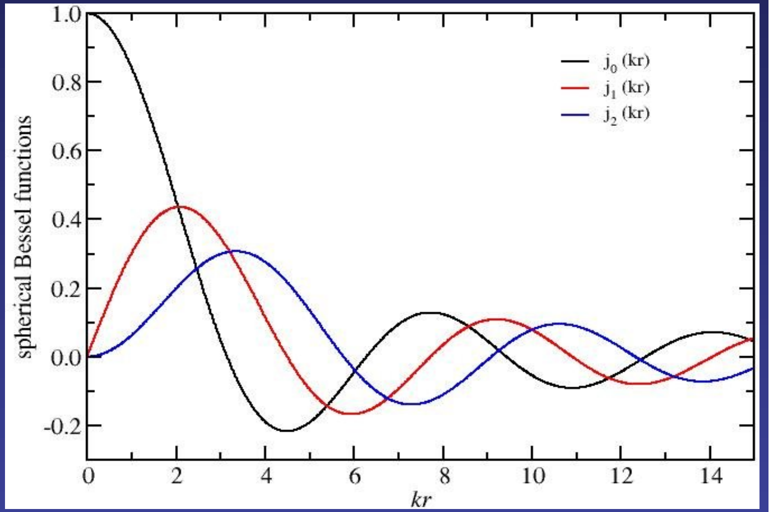


Localized basis sets

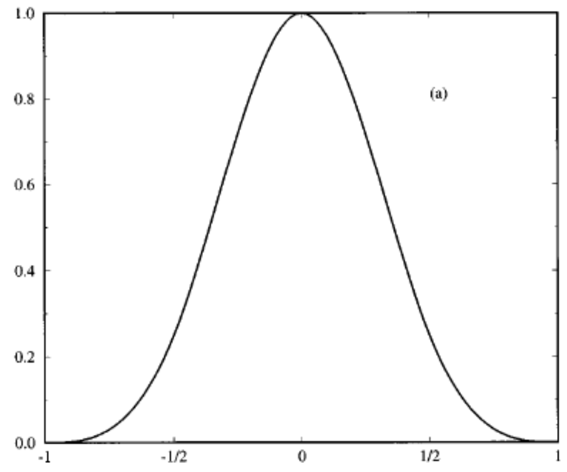
Basis sets for linear-scaling DFT
Different proposals in the literature



Bessel functions in overlapping spheres

P. D. Haynes

http://www.tcm.phy.cam.ac.uk/~pdh1001/thesis/
and references therein



3D grid of spatially localized functions: blips

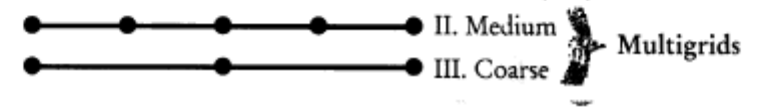
E. Hernández *et al.*, Phys. Rev. B 55, 13485 (1997)

D. Bowler, M. Gillan *et al.*, Phys. Stat. Sol. b 243, 989 (2006)

http://www.conquest.ucl.ac.uk

Real space grids + finite difference methods

J. Bernholc *et al.*



Wavelets

S. Goedecker *et al.*, Phys. Rev. B 59, 7270 (1999)

Atomic orbitals

Atomic orbitals: advantages and pitfalls

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

ADVANTAGES

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

DISADVANTAGES

- …Lack of systematic for convergence (not 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).

Atomic orbitals:
a radial function times an spherical harmonic

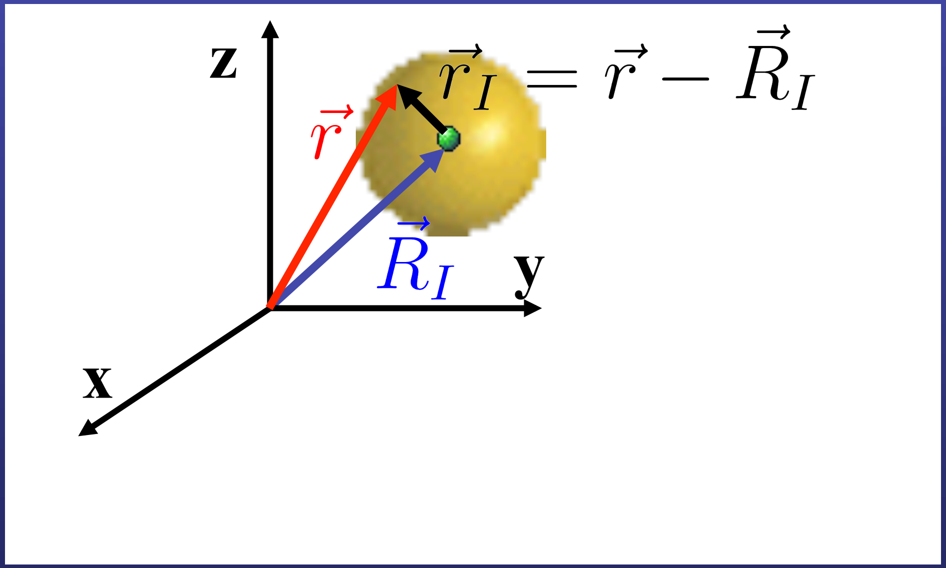
$$\phi_{Ilmn}(\vec{r}) = R_{Iln}\left(|\vec{r}_I|\right) Y_{lm}\left(\hat{r}_I\right)$$

Index of an atom

Angular momentum

Possibility of multiple orbitals with the same l,m

$$\hat{r}_I = \frac{\vec{r}_I}{|\vec{r}_I|}$$



$$\vec{r}_I = \vec{r} - \vec{R}_I$$

Atomic Orbitals: different representations

- Gaussian based + QC machinery

  G. Scuseria (GAUSSIAN),
  M. Head-Gordon (Q-CHEM)
  R. Orlando, R. Dobesi (CRYSTAL)
  J. Hutter (CP2K)

- Slater type orbitals

  Amsterdam Density Functional (ADF)

- Numerical atomic orbitals (NAO)

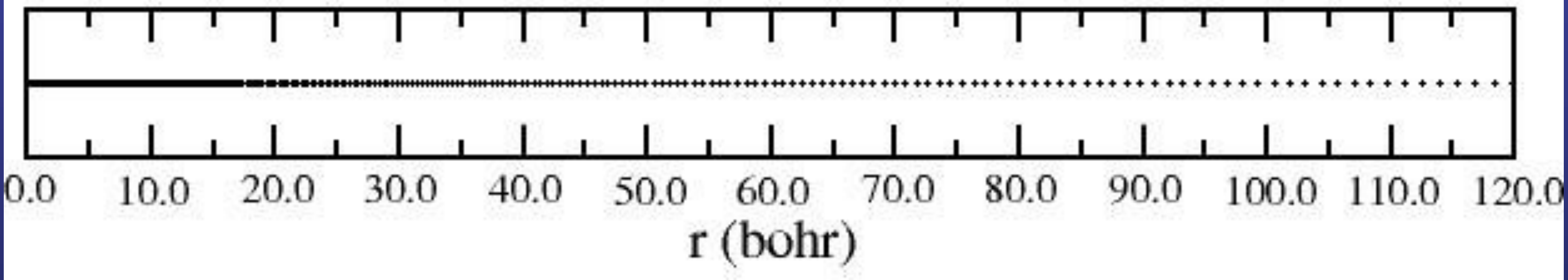
  SIESTA
  S. Kenny, A. Horsfield (PLATO)
  T. Ozaki (OpenMX)
  O. Sankey (FIREBALL)

Numerical 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 logarithmic grid using the Numerov method



Dense close at the origin where atomic quantities oscillates wildly

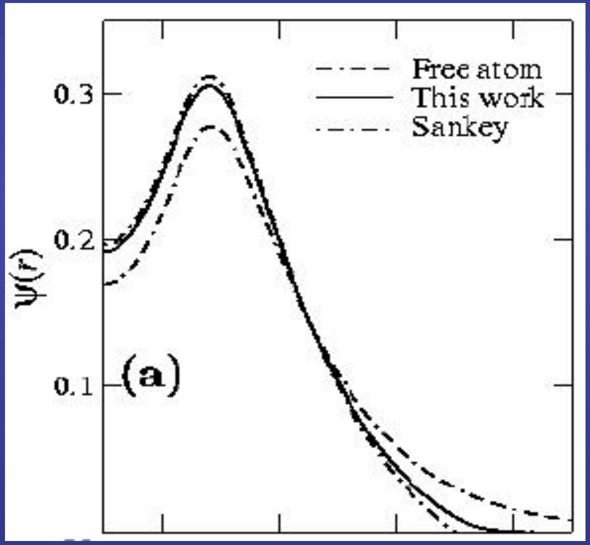
Light far away from the origin where atomic quantities change smoothly

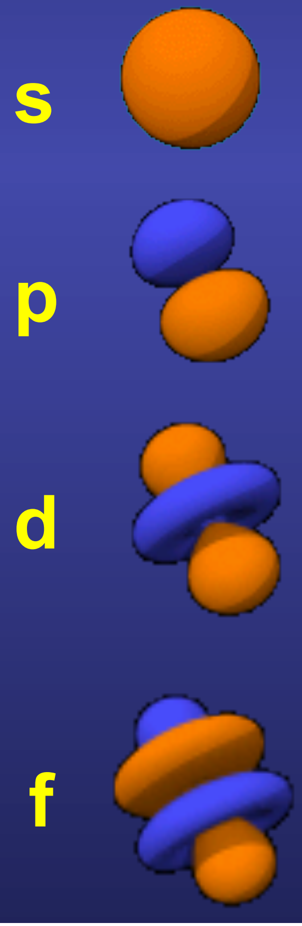
Atomic orbitals:
Main features that characterize the basis

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

Radial part:
degree of freedom to play with

Spherical harmonics:
well defined (fixed) objects





Size: Number of atomic orbitals per atom

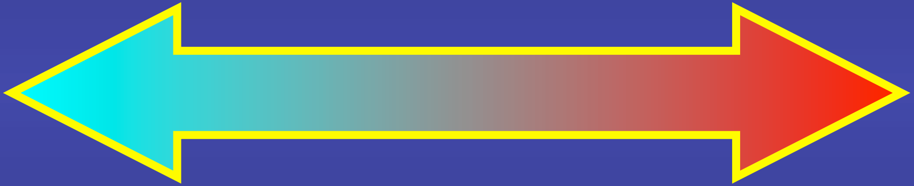
Range: Spatial extension of the orbitals

Shape: of the radial part

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

(Orbitals much more extended that the typical extension in the free atom

+ Basis optimization

Converging the basis size: from quick and dirty to highly converged calculations

Single-ζ (minimal or SZ)

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

Examples of minimal basis-set:

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

l = 0 (s)

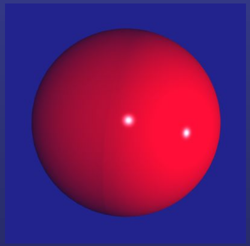
l = 1 (p)

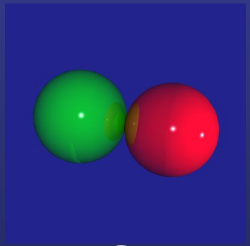
m = 0

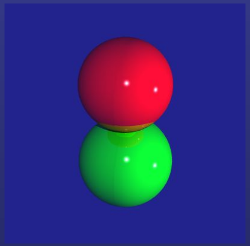
m = -1

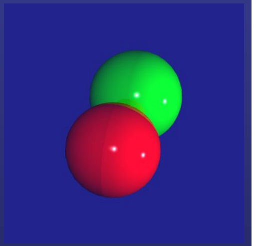
m = 0

m = +1









4 atomic orbitals per Si atom

(pictures courtesy of Victor Luaña)

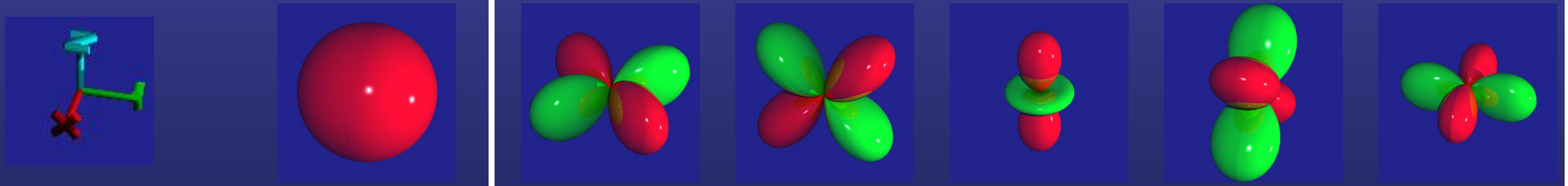
Converging the basis size: from quick and dirty to highly converged calculations

Single-ζ (minimal or SZ)

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

Examples of minimal basis-set:

Fe atomic configuration: $\underbrace{1s^2\ 2s^2\ 2p^6\ 3s2\ 3p6}_{\text{core}}$ $\underbrace{4s^2\ 3d^6}_{\text{valence}}$



$l = 0$ (s)

$m = 0$

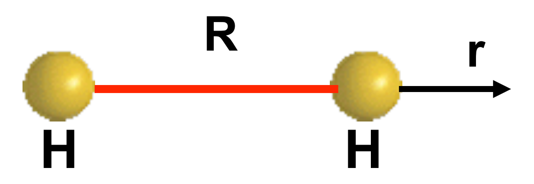
$l = 2$ (d)

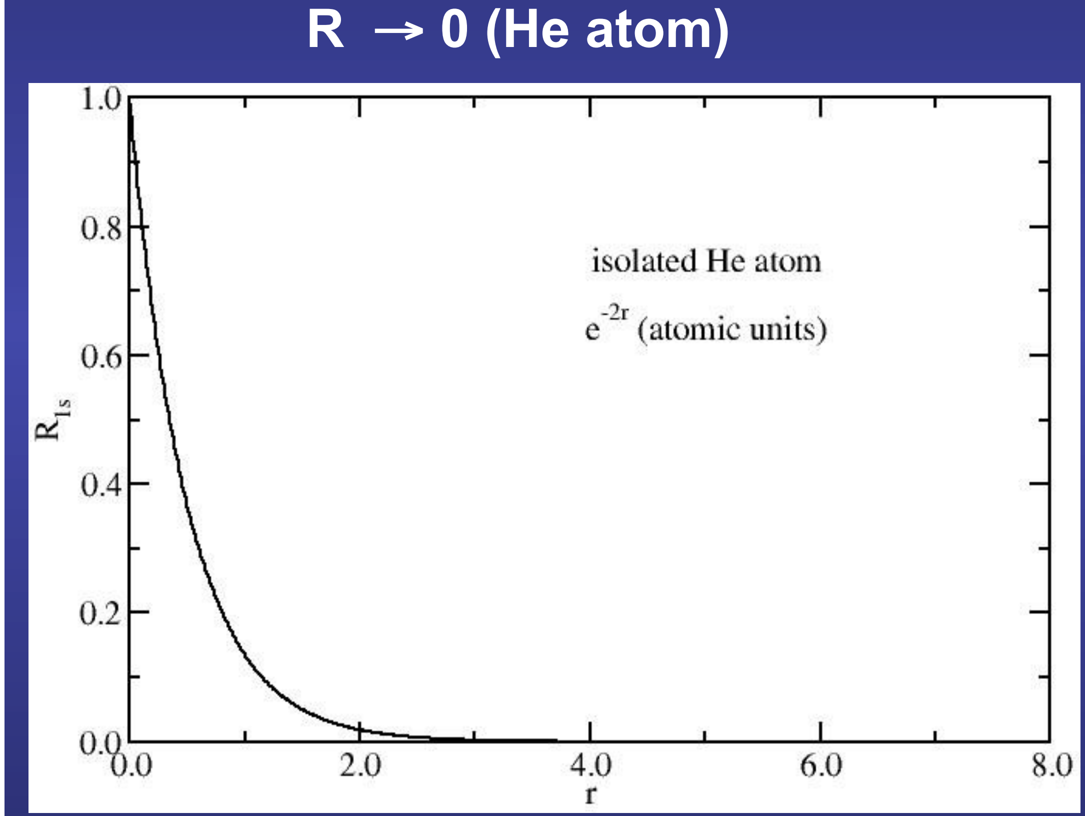
$m = -2$ $m = -1$ $m = 0$ $m = +1$ $m = +2$

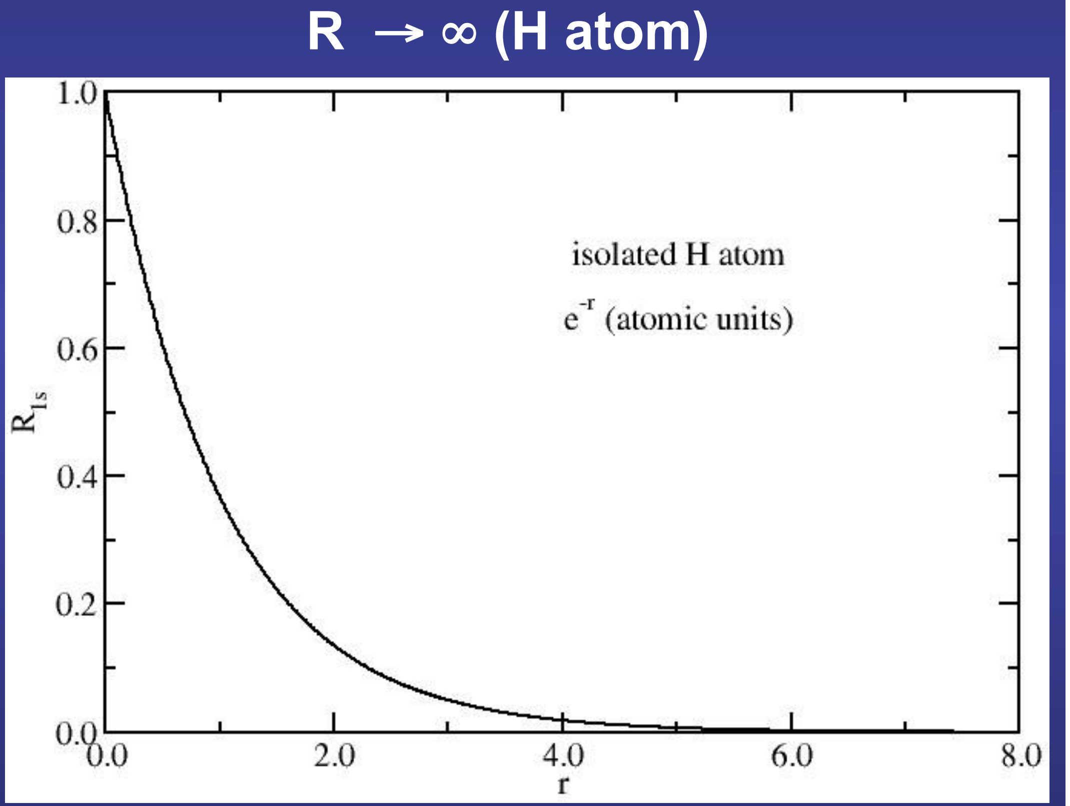
6 atomic orbitals per Fe atom

(pictures courtesy of Victor Luaña)

The optimal atomic orbitals are environment dependent







Basis set generated for isolated atoms… …
but used in molecules or condensed systems

Add flexibility to the basis to adjust to different configurations

Converging the basis size: from quick and dirty to highly converged calculations

Single-ζ (minimal or SZ)

One single radial function per angular

momentum shell occupied in the free–atom

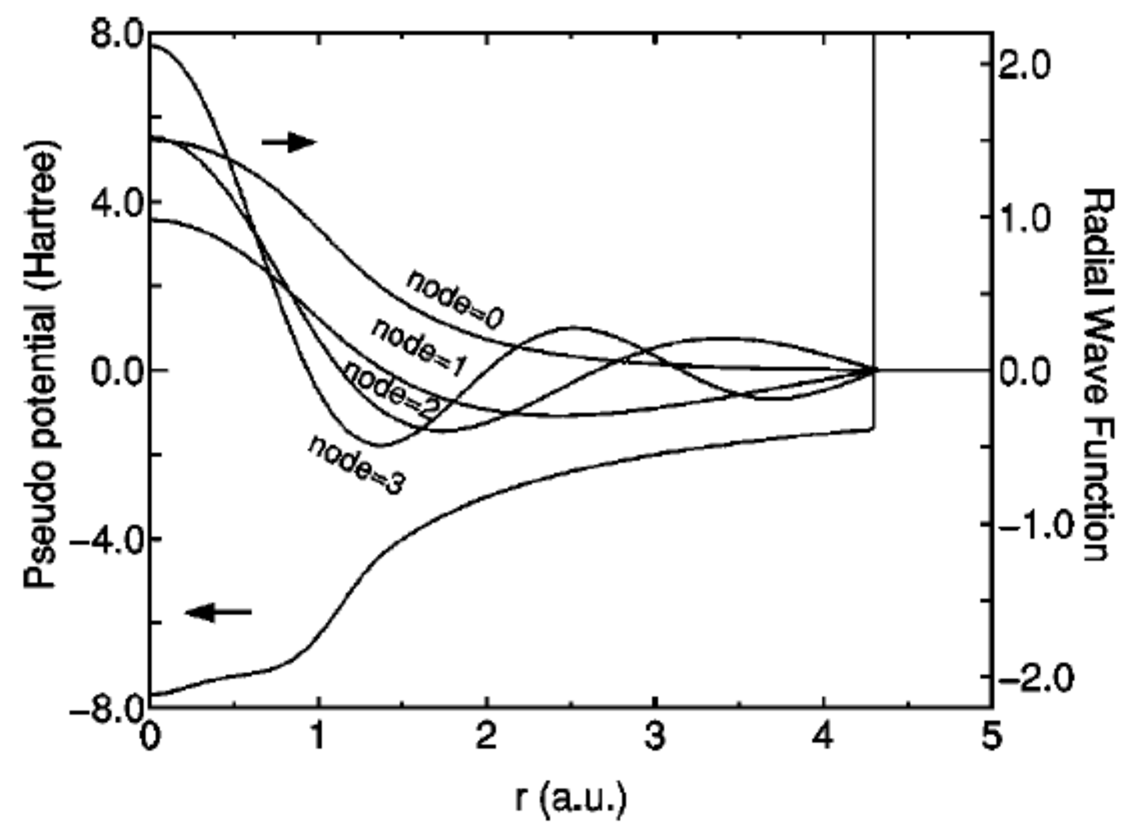
Improving the quality

Radial flexibilization:

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

Multiple-ζ

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)

http://www.openmx-square.org/

Advantages

Orthogonal

Asymptotically complete

Disadvantages

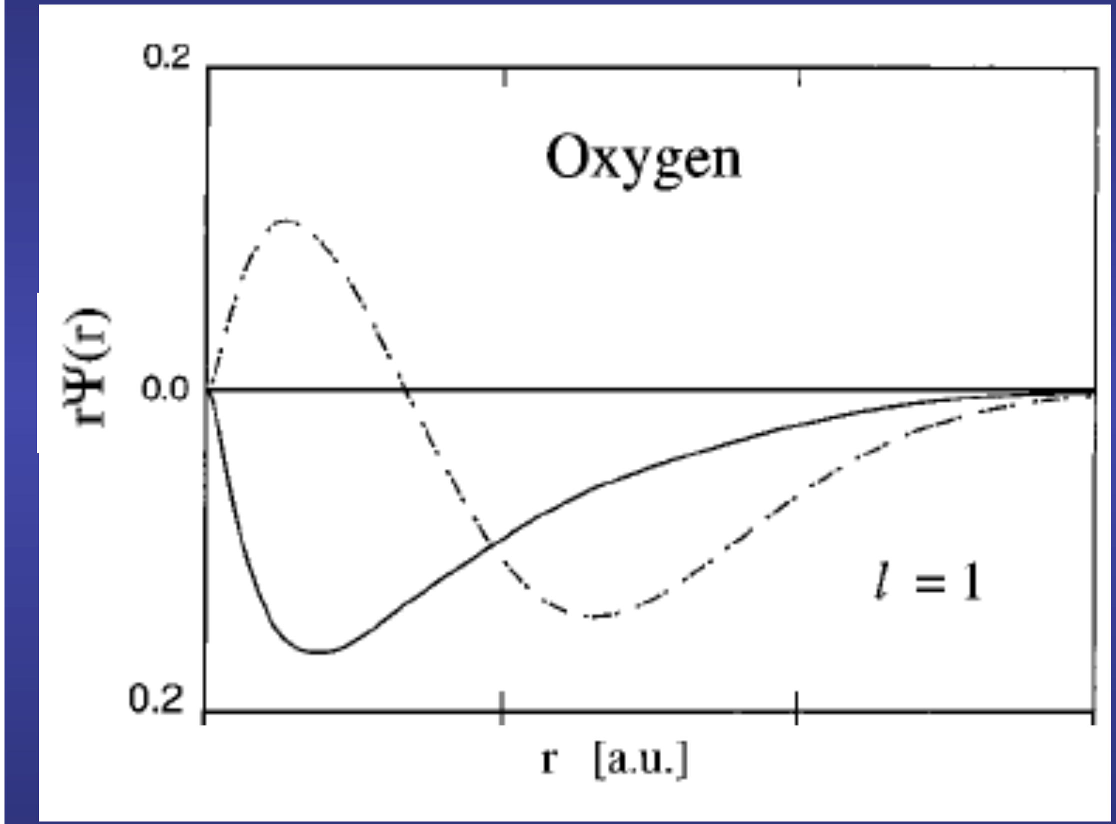
Excited states of the pseudopotentials, usually unbound

Efficient depends on localization radii

Availables in Siesta:

PAO.BasisType Nodes

Schemes to generate multiple-ζ basis sets
Chemical hardness: use derivatives with respect to the charge of the atoms



Advantages

Orthogonal

It does not depend on any variational parameter

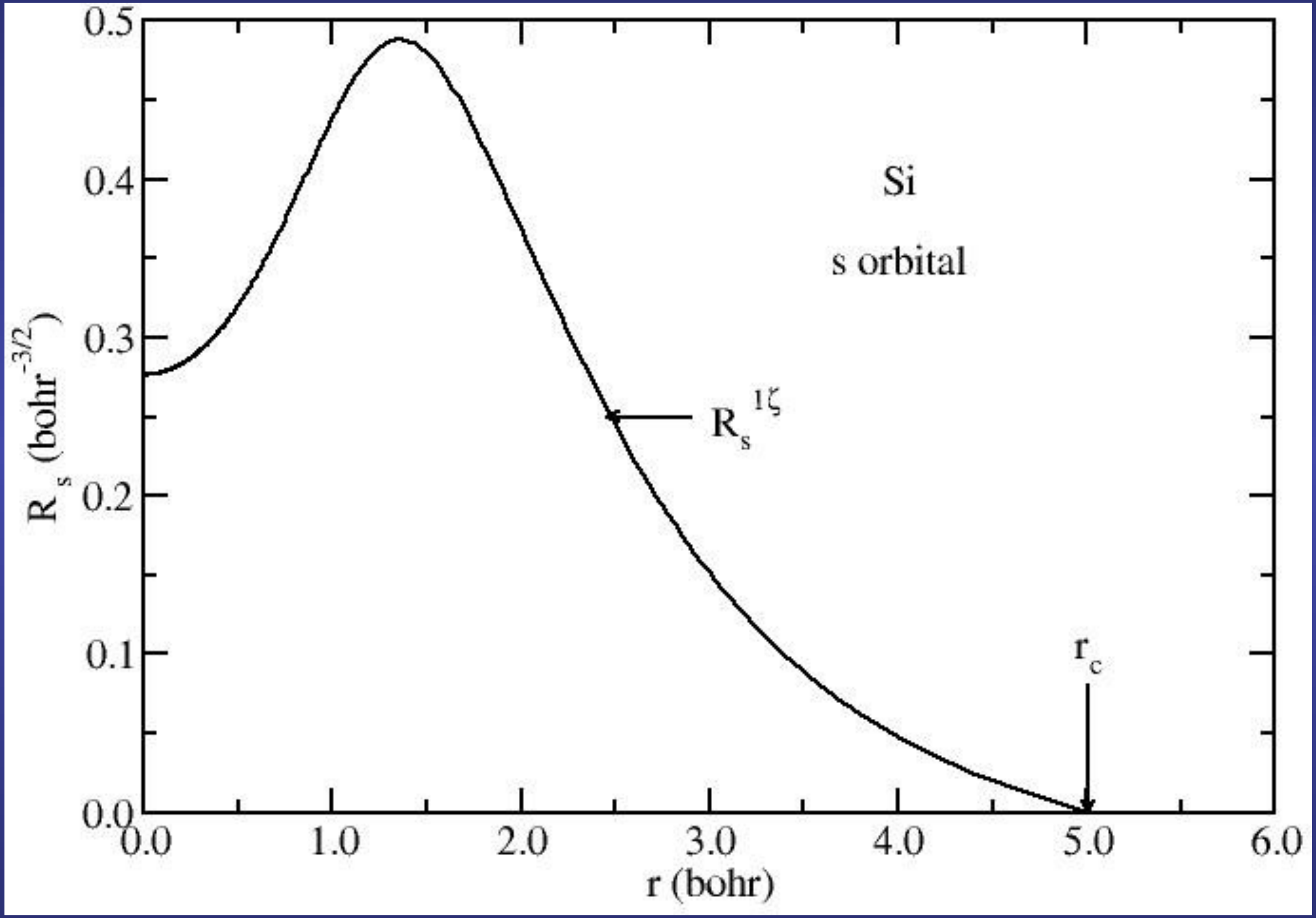
Disadvantages

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

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

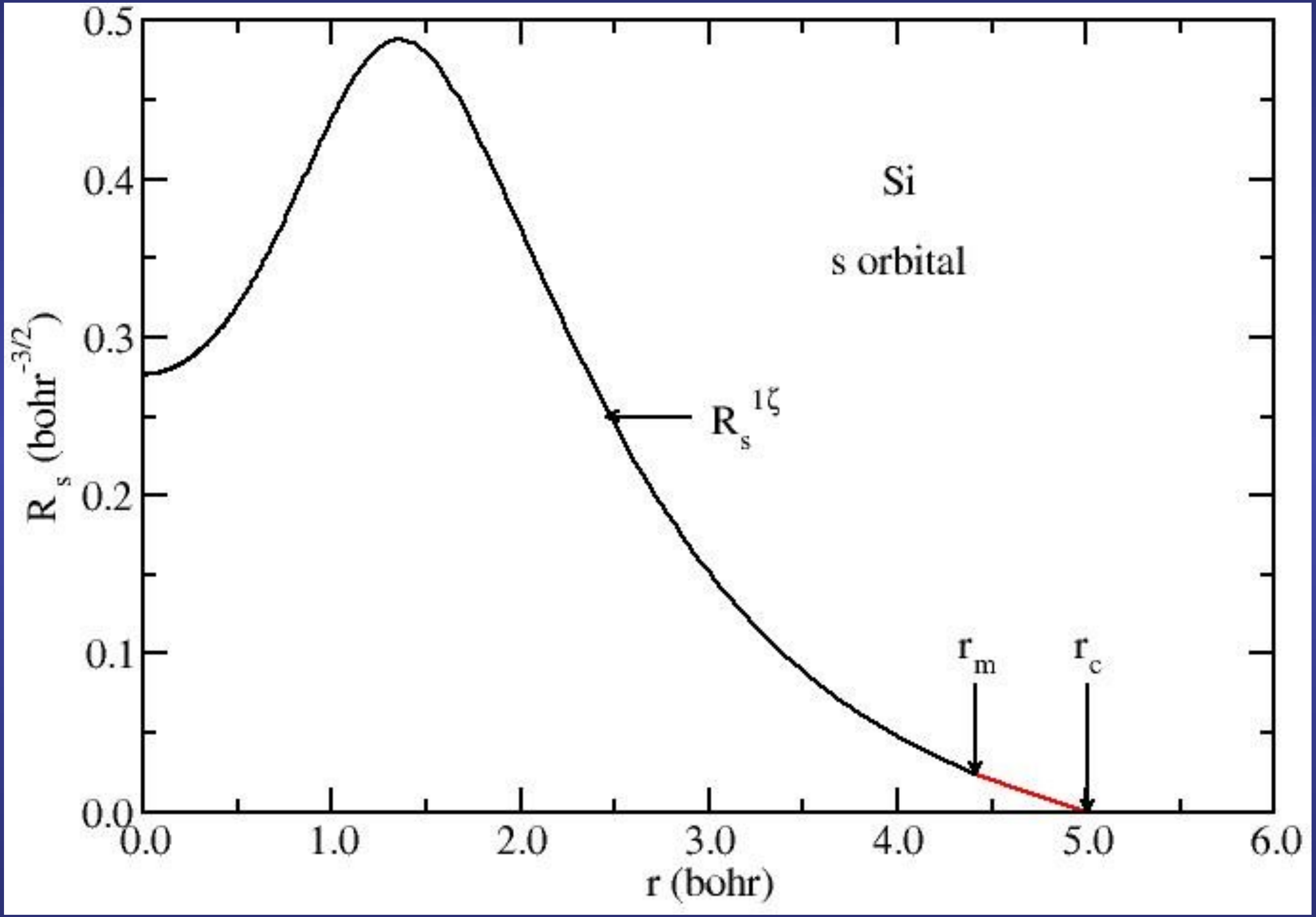
http://cp2k.berlios.de/

Default mechanism to generate multiple-ζ in SIESTA: "Split-valence" method



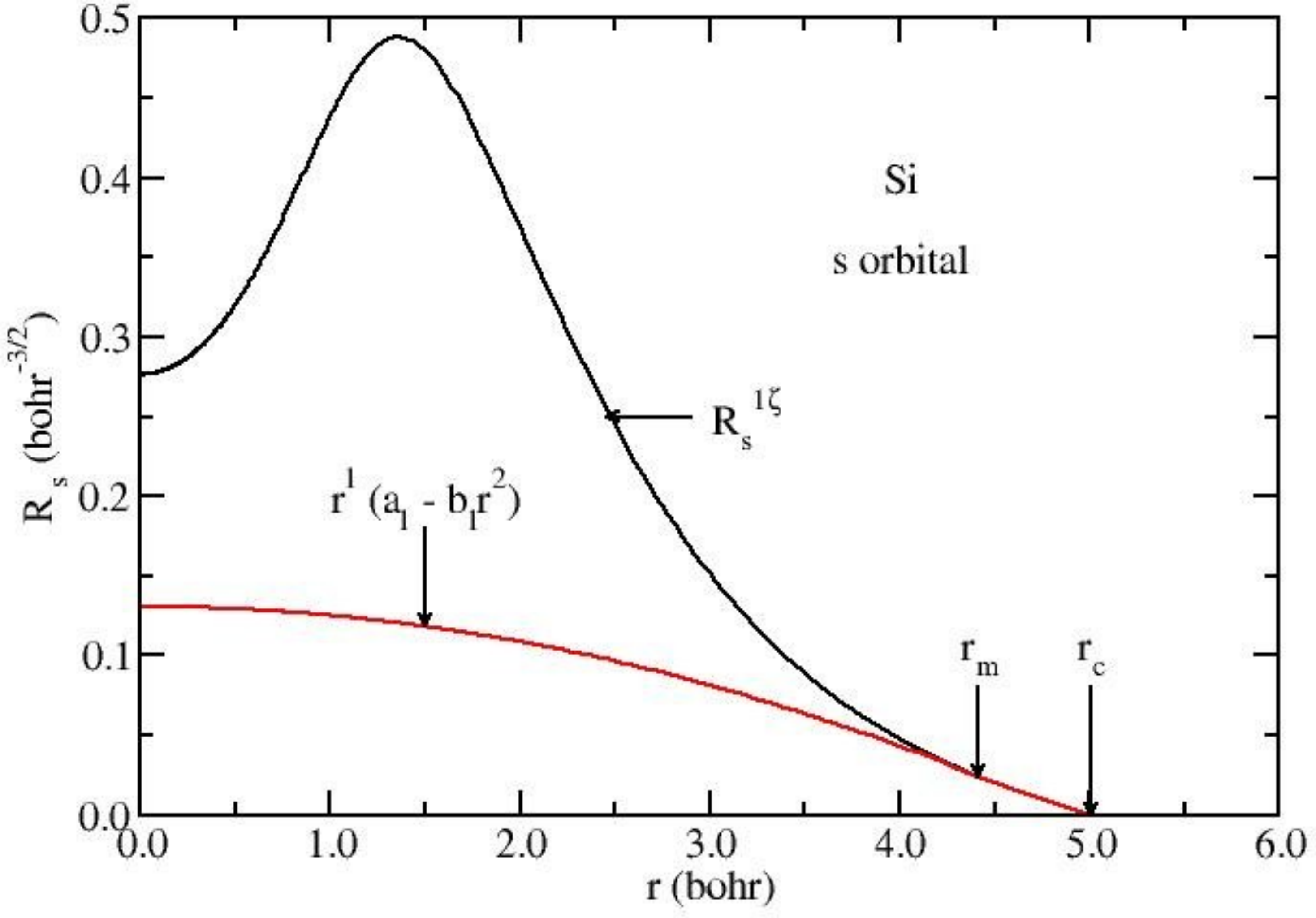
Starting from the function we want to suplement

Default mechanism to generate multiple-ζ in SIESTA: “Split-valence” method



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

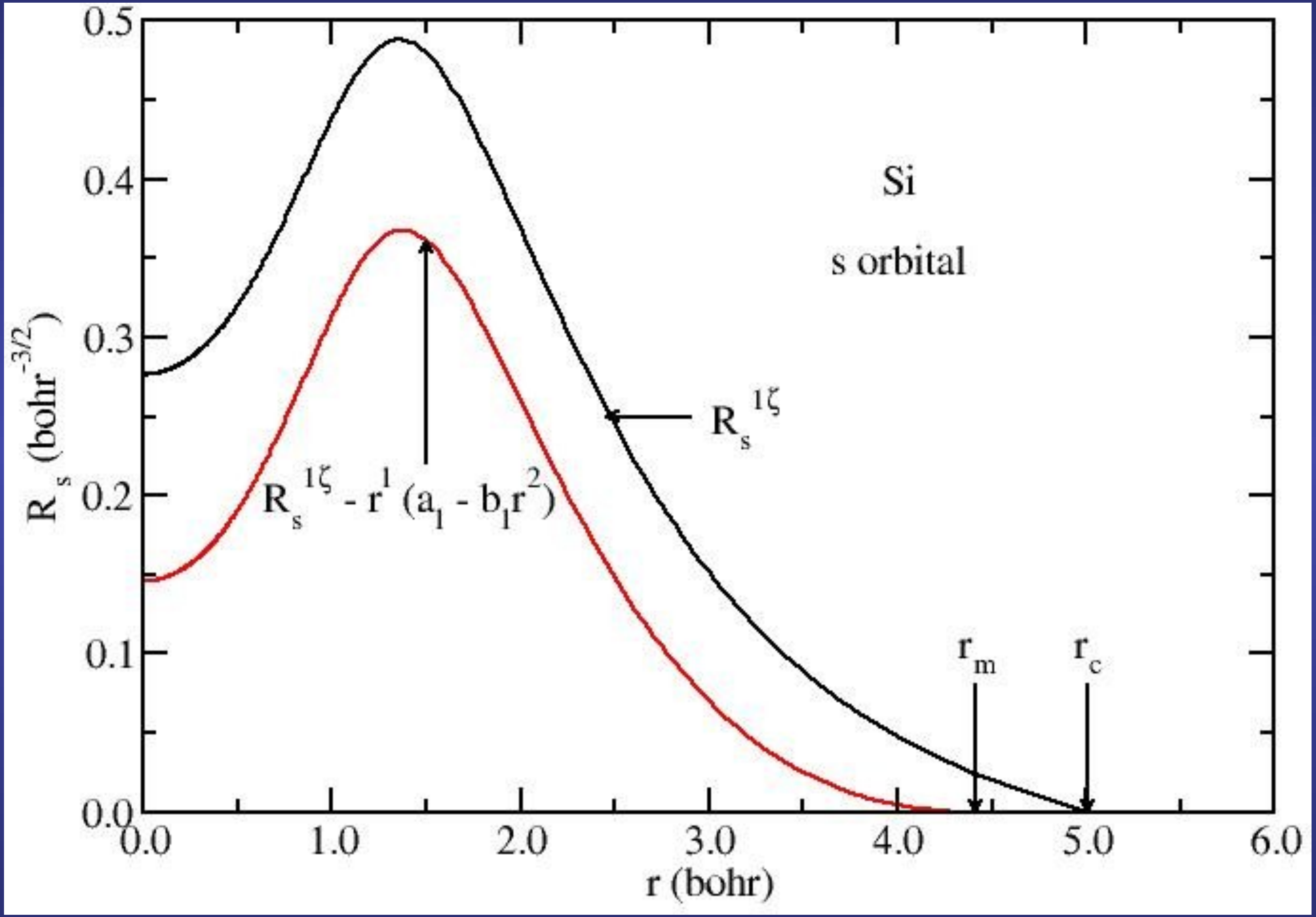
Default mechanism to generate multiple-ζ in SIESTA: "Split-valence" method



And continuous smoothly towards the origin as $r^l \left(a_l - b_l r^2 \right)$

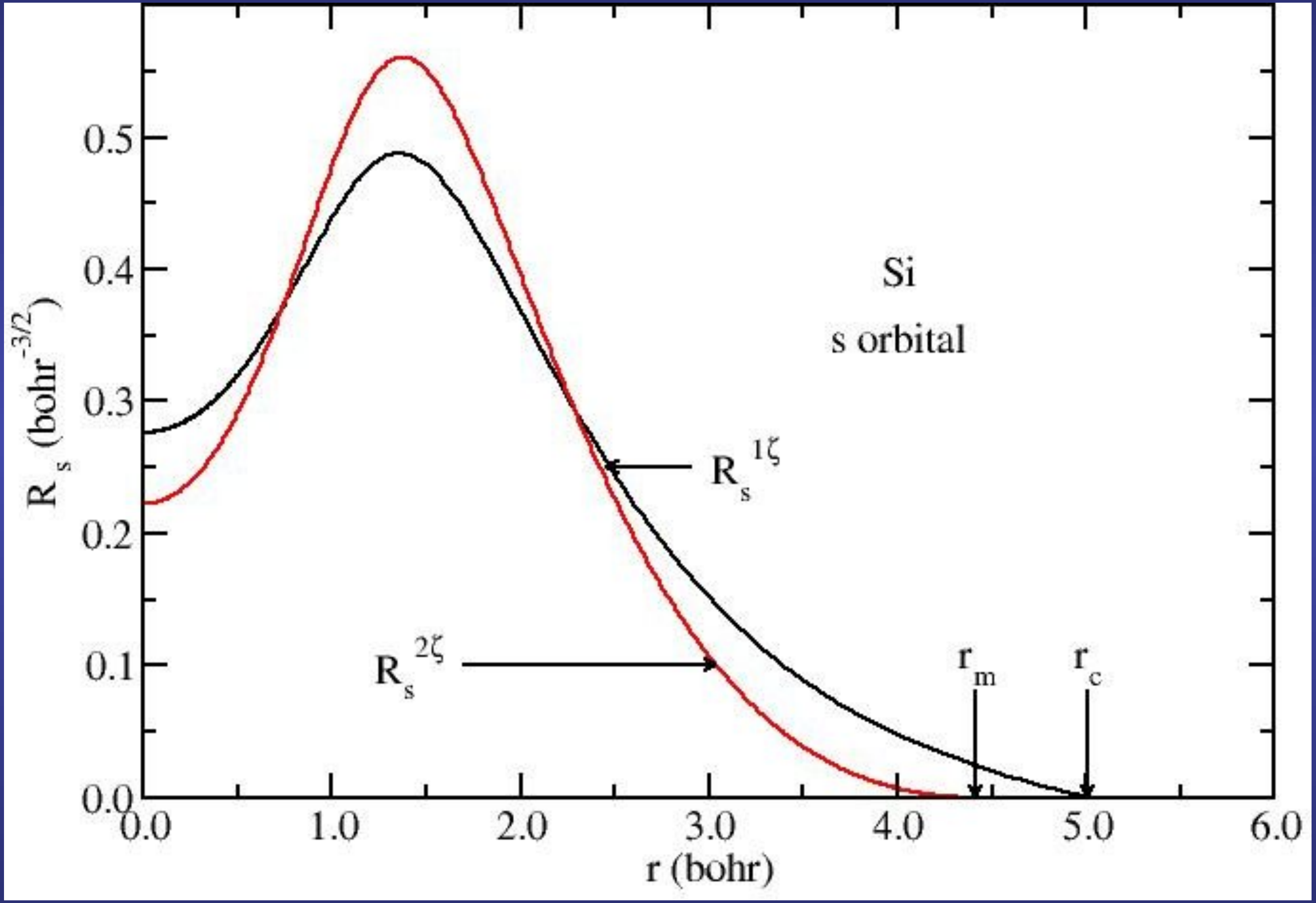
(two parameters: the second-ζ and its first derivative continuous at r_m

Default mechanism to generate multiple-ζ in SIESTA: "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)

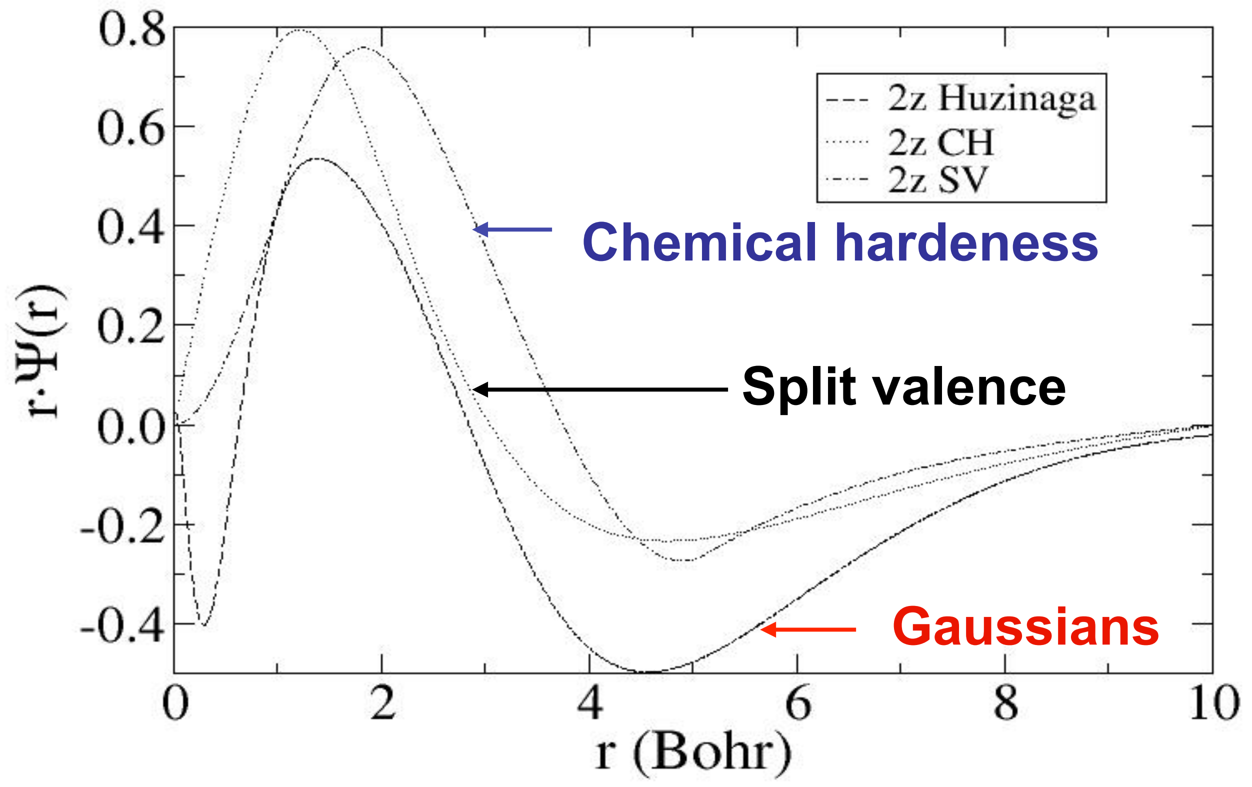
Default mechanism to generate multiple-ζ in SIESTA: "Split-valence" method



Finally, the second-ζ is normalized

r_m controlled with PAO.SplitNorm (typical value 0.15)

Both split valence and chemical hardness methods provides similar shapes for the second-ζ function



Chemical hardeness

Split valence

Gaussians

Split valence double-ζ has been orthonormalized to first-ζ orbital

SV: higher efficiency

(radius of second-ζ can be restricted to the inner matching radius)

E. Anglada, J. Junquera, J. M. Soler, E. Artacho,

Phys. Rev. B 66, 205101 (2002)

Converging the basis size: from quick and dirty to highly converged calculations

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

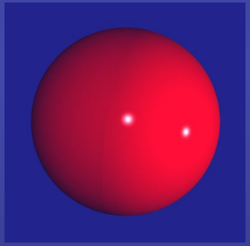
Example of adding angular flexibility to an atom

Polarizing the Si basis set

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

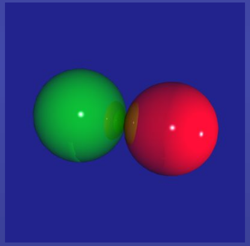
$l = 0$ (s)

$m = 0$

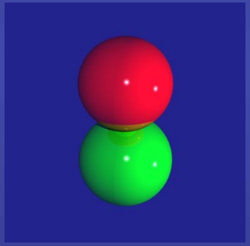


$l = 1$ (p)

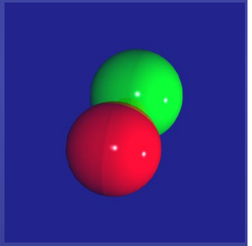
$m = -1$



$m = 0$

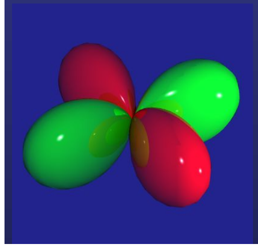


$m = +1$

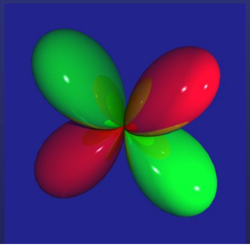


Polarize: add $l = 2$ (d) shell

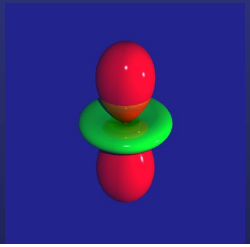
$m = -2$



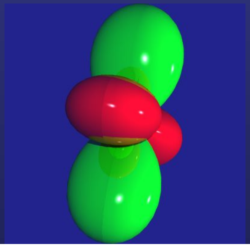
$m = -1$



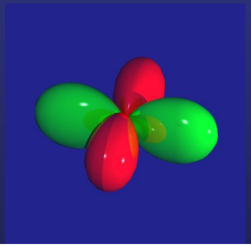
$m = 0$



$m = +1$



$m = +2$

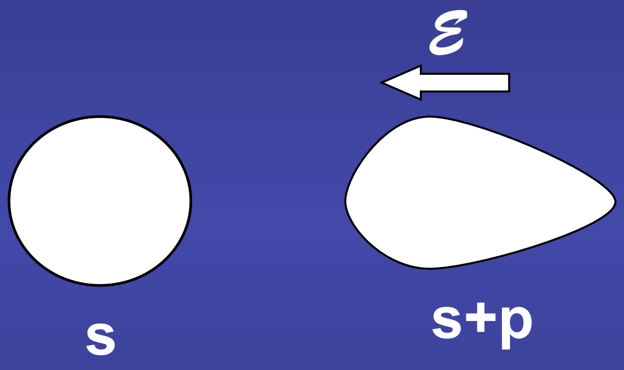


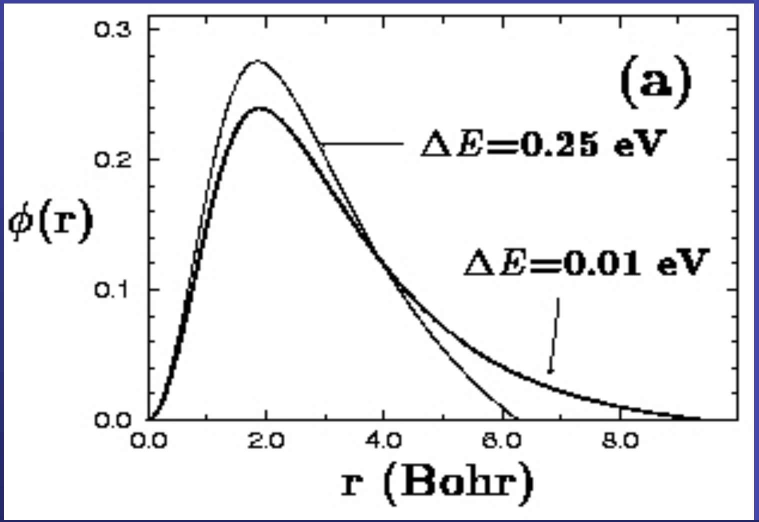
New orbitals directed in different directions with respect the original basis

Two different ways of generate polarization orbitals

Perturbative polarization

Apply a **small electric field** to the orbital we want to polarize





Si 3d

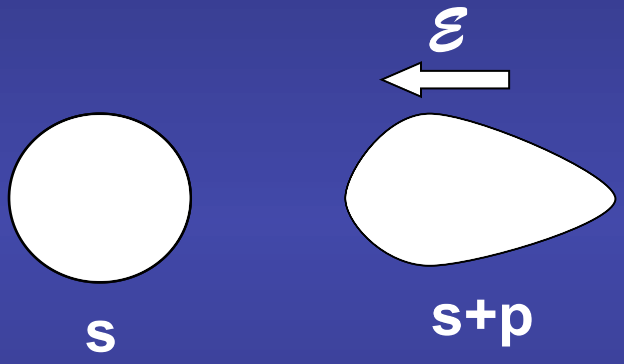
orbitals

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

Two different ways of generate polarization orbitals

Perturbative polarization

Apply a small electric field to the orbital we want to polarize

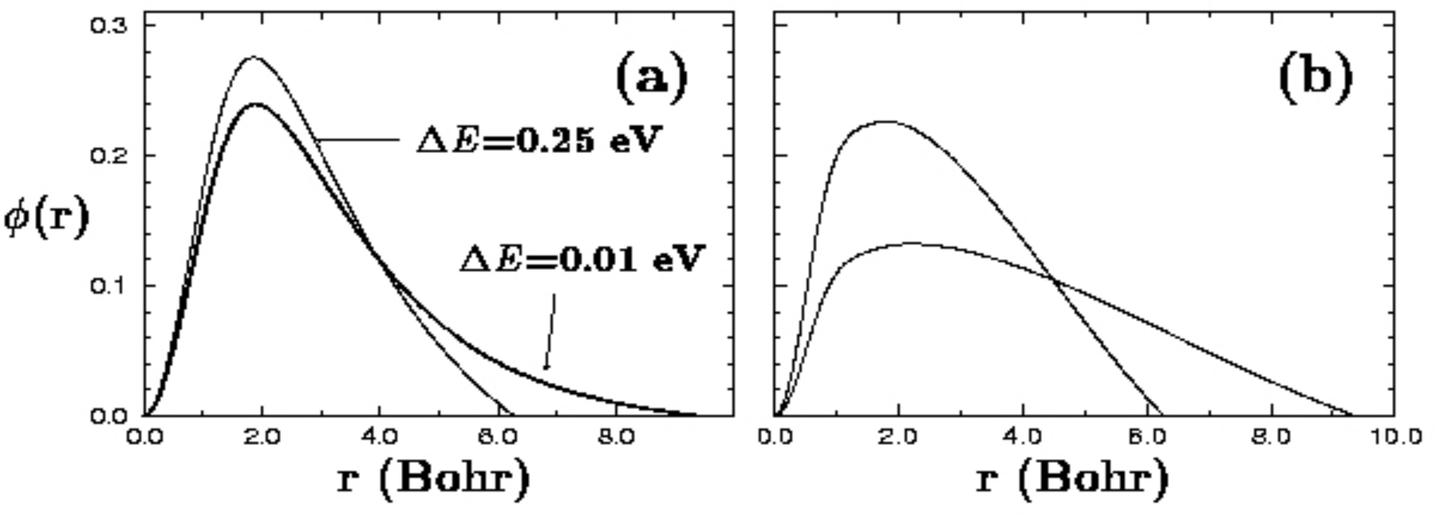


Atomic polarization

Solve Schrödinger equation for higher angular momentum

unbound in the free atom ⇒

require short cut offs

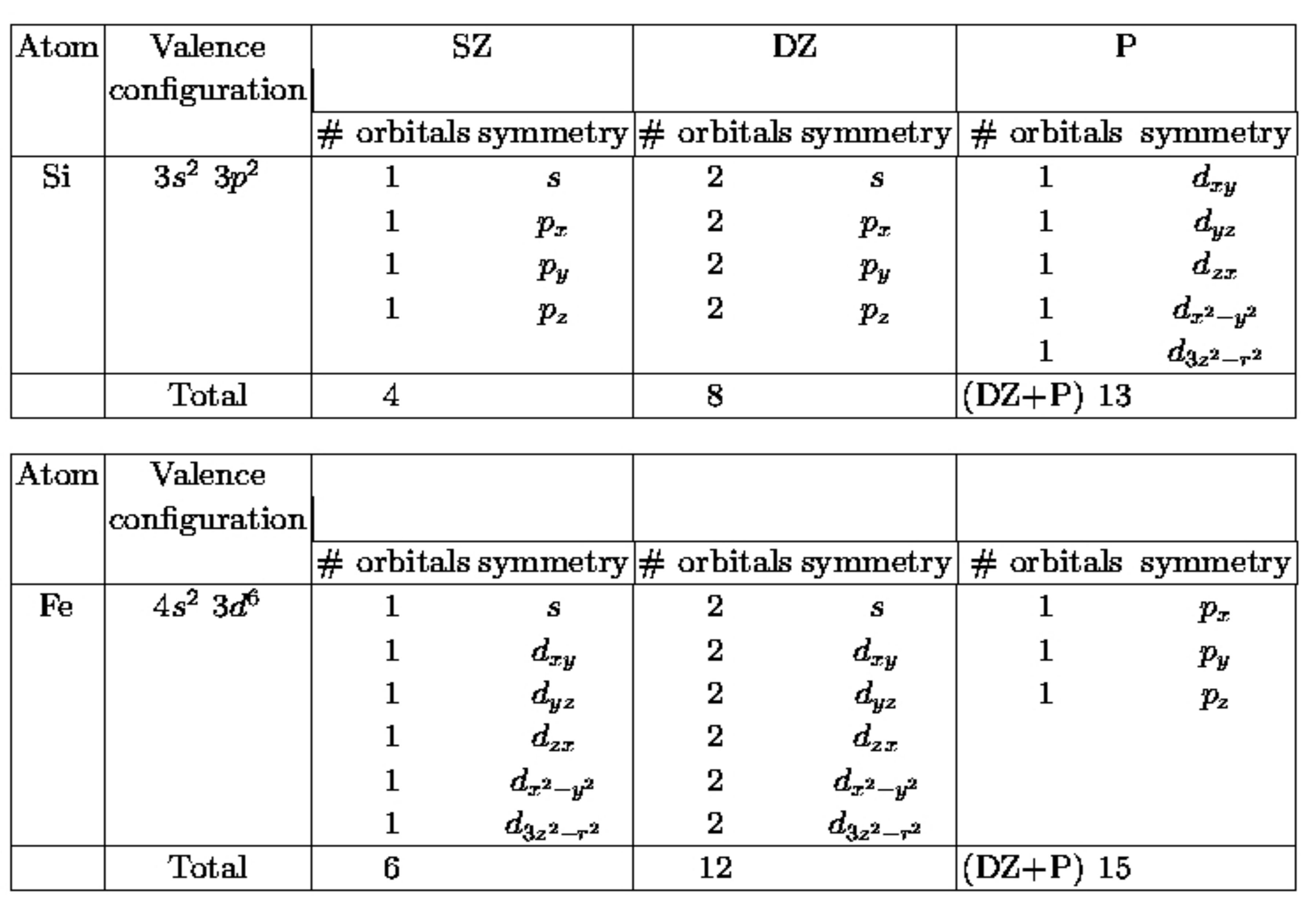


Si 3d

orbitals

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

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

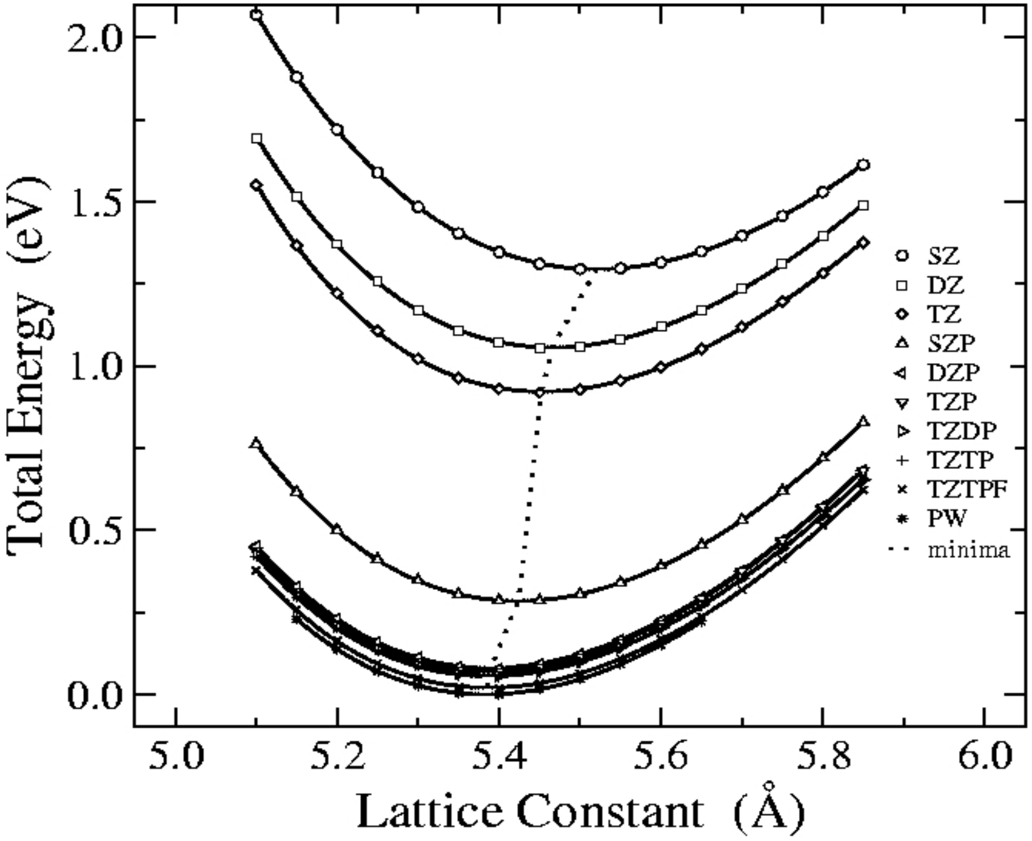


Atom	Valence configuration	SZ		DZ		P	
		# orbitals	symmetry	# orbitals	symmetry	# orbitals	symmetry
Si	$3s^2$ $3p^2$	1	s	2	s	1	d_{xy}
		1	p_x	2	p_x	1	d_{yz}
		1	p_y	2	p_y	1	d_{zx}
		1	p_z	2	p_z	1	$d_{x^2-y^2}$
						1	$d_{3z^2-r^2}$
	Total	4		8		(DZ+P) 13	

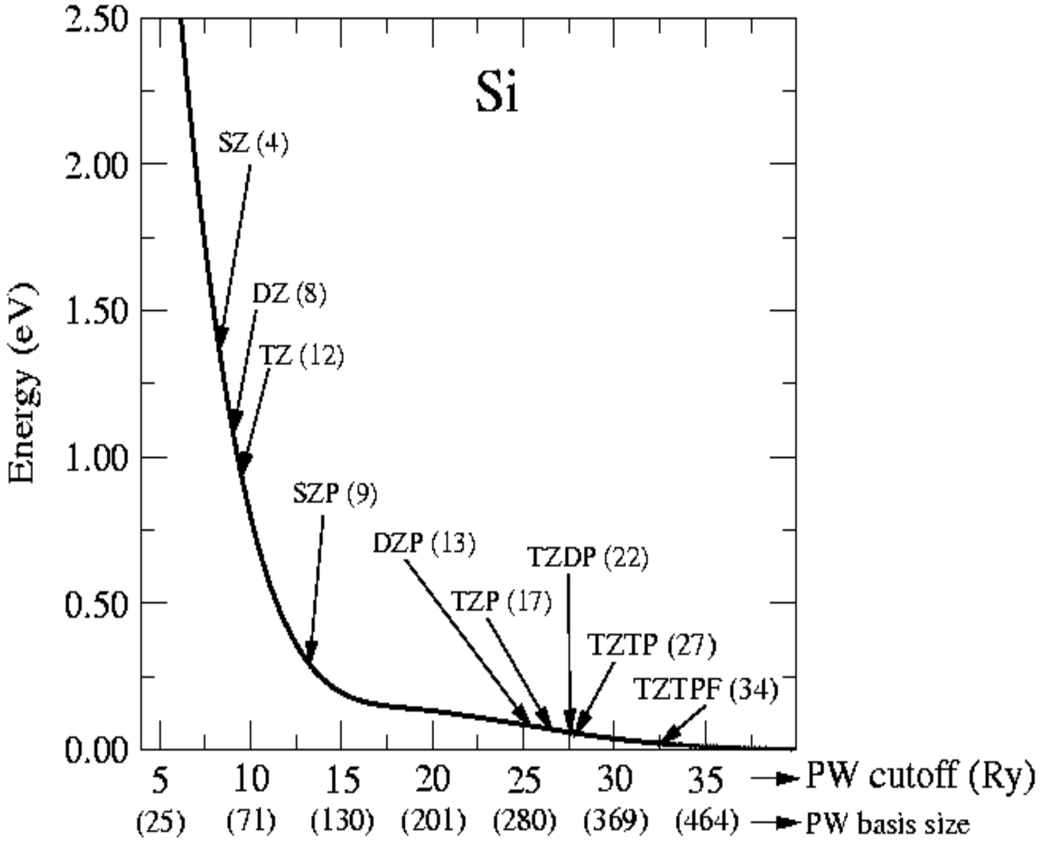
Atom	Valence configuration						
		# orbitals	symmetry	# orbitals	symmetry	# orbitals	symmetry
Fe	$4s^2$ $3d^6$	1	s	2	s	1	p_x
		1	d_{xy}	2	d_{xy}	1	p_y
		1	d_{yz}	2	d_{yz}	1	p_z
		1	d_{zx}	2	d_{zx}		
		1	$d_{x^2-y^2}$	2	$d_{x^2-y^2}$		
		1	$d_{3z^2-r^2}$	2	$d_{3z^2-r^2}$		
	Total	6		12		(DZ+P) 15	

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

Convergence as a function of the size 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

A DZP basis set introduces the same deviations as the ones due to the DFT or the pseudopotential approaches

SZ = single-ζ

DZ= doble- ζ

TZ=triple- ζ

P=Polarized

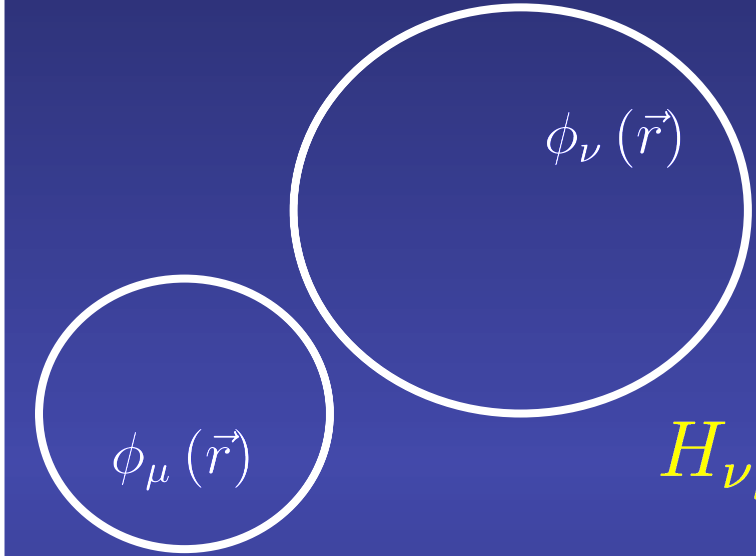
DP=Doble-polarized

PW: Converged Plane Waves (50 Ry)

APW: Augmented Plane Waves

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

Difficulty: introduce numerical instabilities for high tolerances.

Strictly localized atomic orbitals:

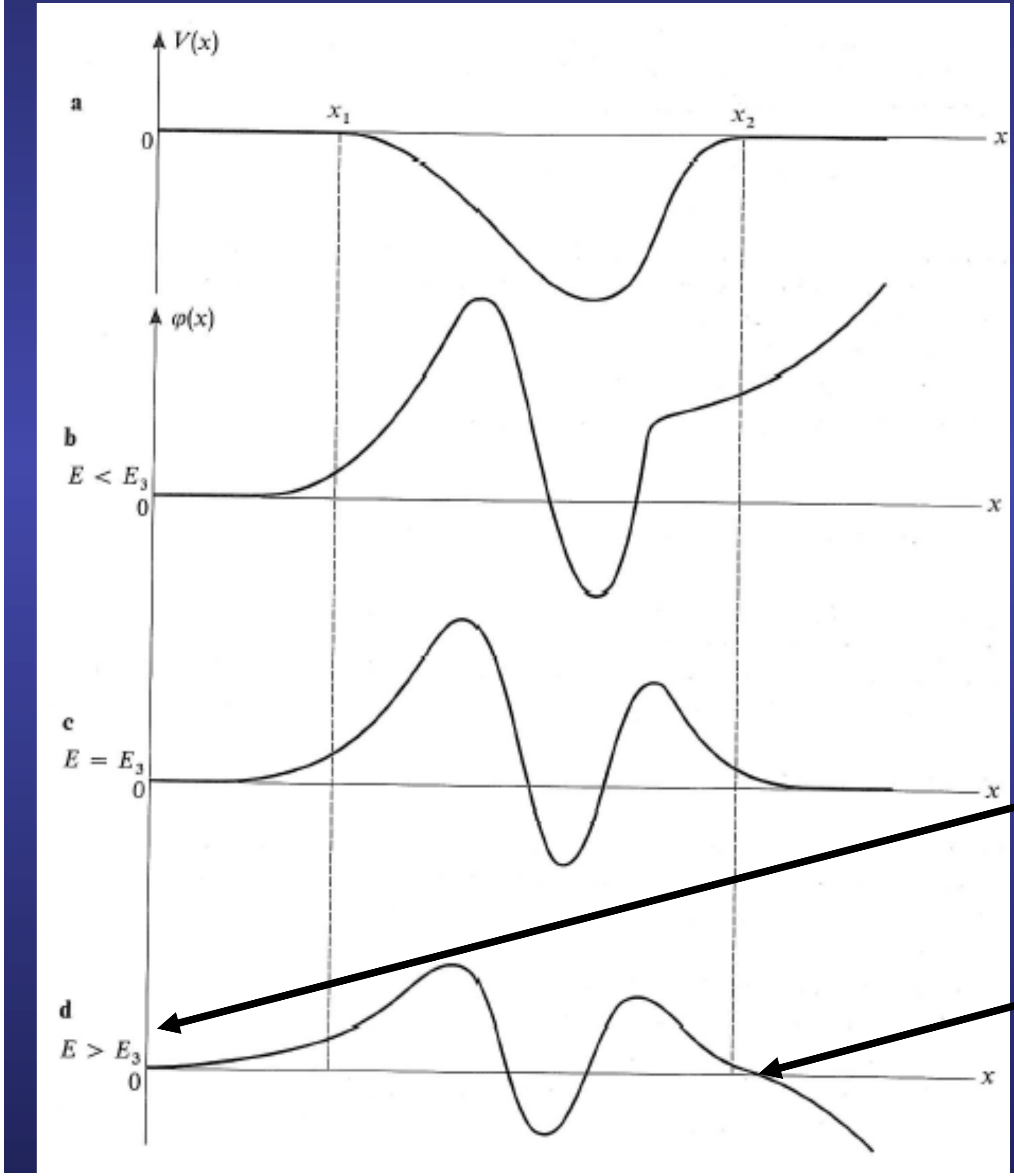
Vanishes beyond a given cutoff radius

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

Difficulty: 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 the range of the orbitals in a balanced way: the energy shift



Particle in a confinement potential:

Imposing a finite $\int_{-\infty}^{+\infty} |\phi(x)|^2 dx$ +

Continuous function and first derivative

$\Downarrow$

E is quantized (not all values allowed)

Increasing $E \Rightarrow \phi_\mu$ has a node and tends to -∞ when $x \rightarrow$ - ∞

Complement M III "Quantum Mechanics",

C. Cohen-Tannoudji *et al.*

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

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

↑

Energy increase ≡ Energy shift

PAO.EnergyShift (energy)

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

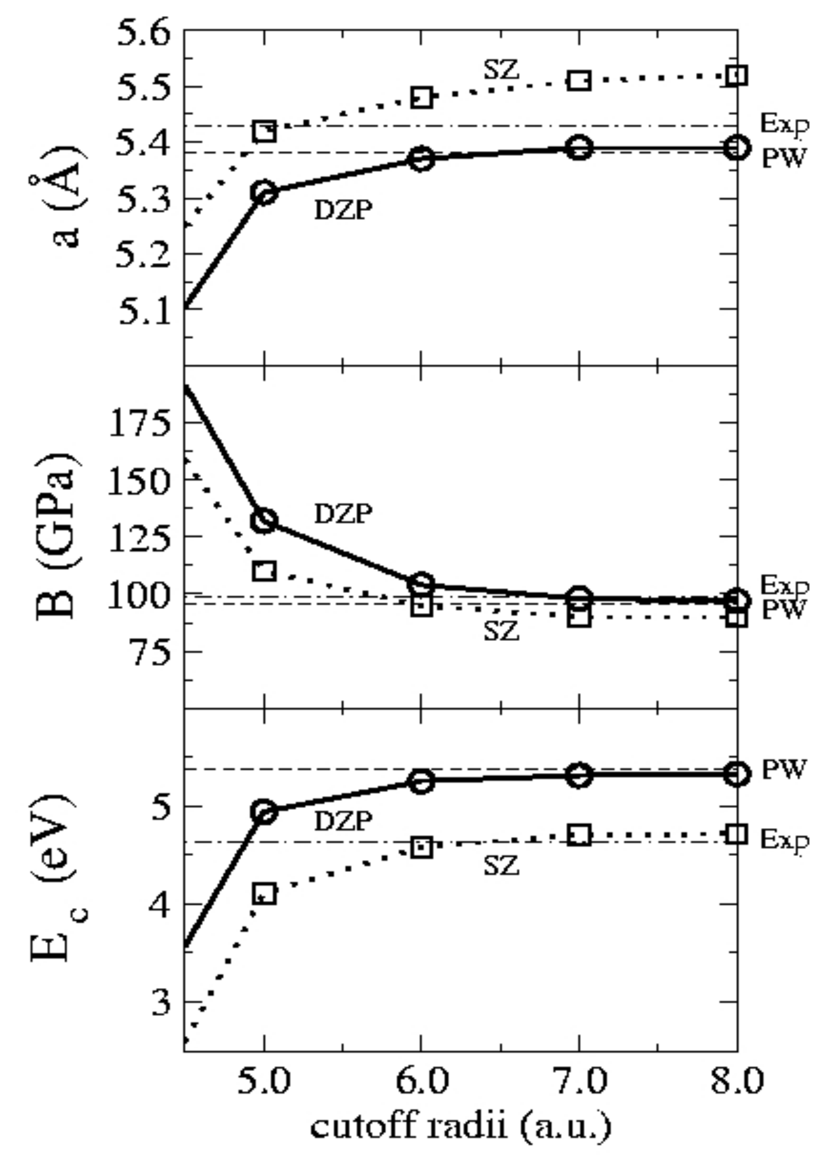
A single parameter for all cutoff radii

The larger the Energy shift, the shorter the r_c's

Typical values: 100-200 meV

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

Convergence with the range



More efficient →

← **More accurate**

Bulk Si

equal *s*, *p* orbitals radii

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

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

Extra charge δQ

Orbitals in anions tend to be more delocalized

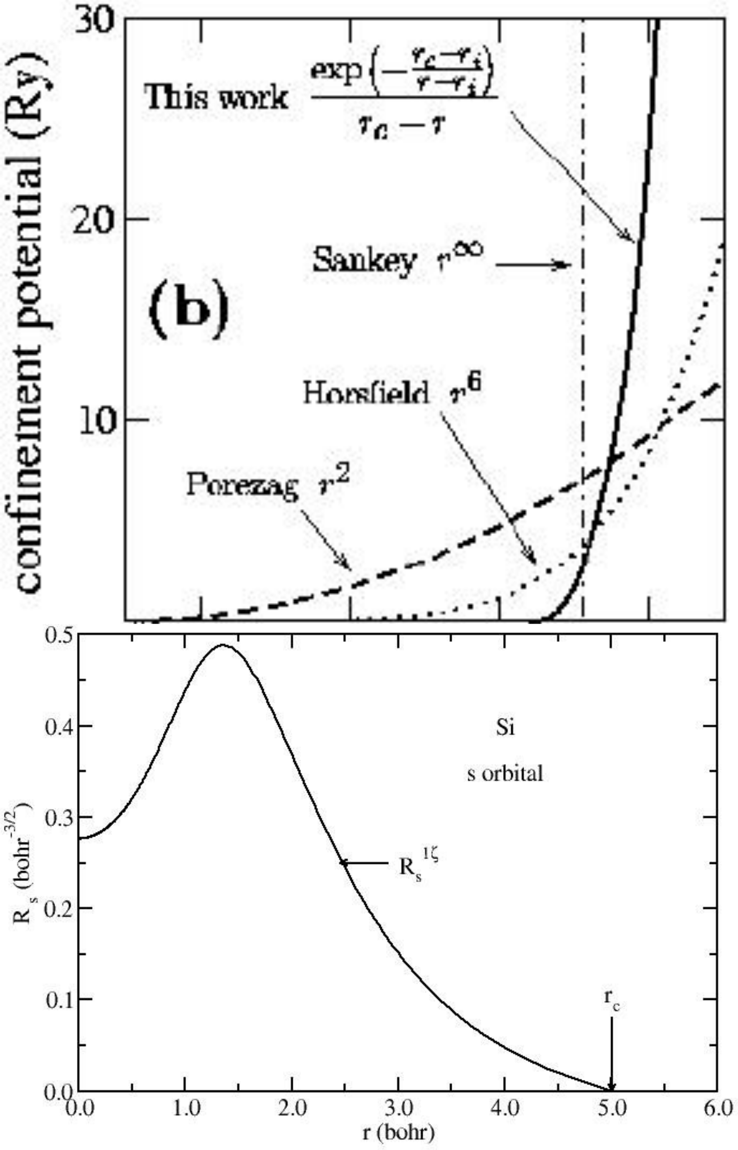
Orbitals in cations tend to be more localized

(For instance, this parameter might be important in some oxides)

Confinement potentials

Solve the Schrödinger equation for the isolated atom inside an confinement potential

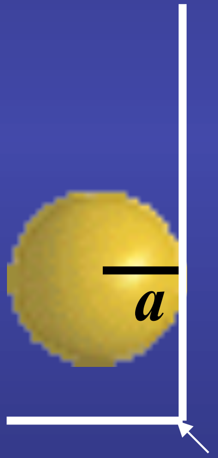
Different proposals for the confinement potentials: Hard confinement



Fireball

O. F. Sankey and D. J. Niklewski, Phys. Rev. B 40, 3979 (89)

The default in SIESTA



$$V = \infty, r \geq a$$

Determined by the energy shift

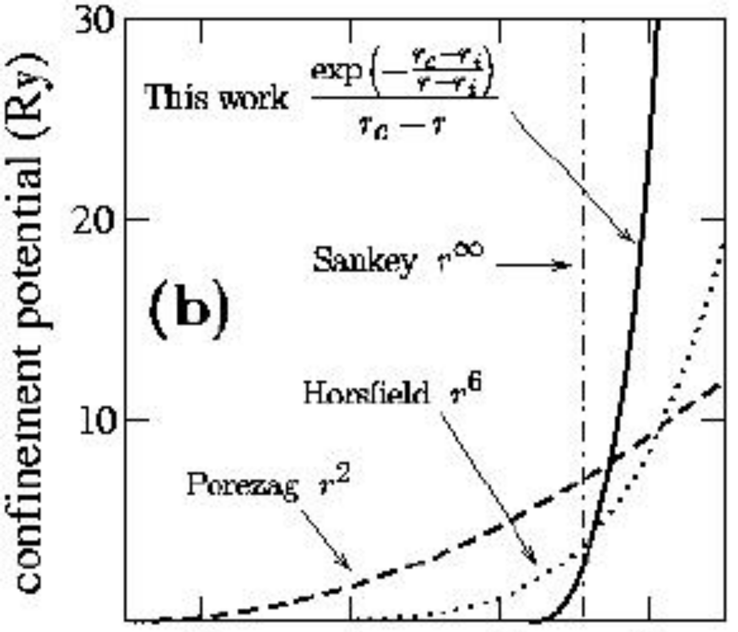
$$V = 0, r < a$$

Advantages: empirically, it works very nice

Pitfall: produces orbitals with first derivative discontinuous at r_c

problem when combined with numerical grids.

Different proposals for the confinement potentials: Polynomials



$$V(r) = V_0 r^n$$

n = 2 [D. Porezag *et al*, PRB 51, 12947 (1995)]

n = 6 [A. P. Horsfield, PRB 56, 6594 (1997))

Advantages: orbital continuous with all the derivatives continuos

Pitfall: no radius where the orbitals is strictly zero

not zero in the core regions

Different proposals for the confinement potentials: Direct modification of the wave function

$$\phi_{conf}(r) = \left(1 - e^{-\alpha(r-r_c)^2}\right)\psi_{atom}(r)$$

S. D. Kenny *et al.*, Phys. Rev. B 62, 4899 (2000)

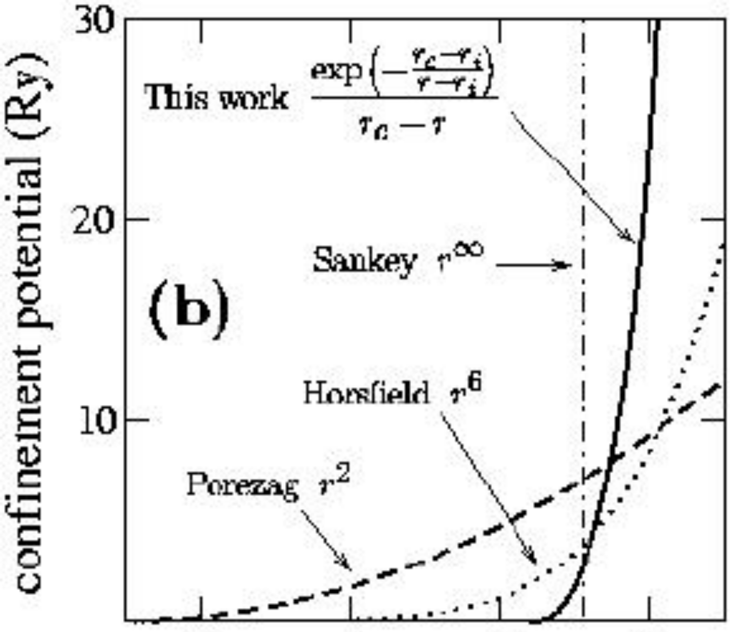
C. Elsaesser *et al*. J. Phys. Condens. Matter 2, 4371 (1990)

Advantages: strict localization beyond r_c

Pitfall: bump when α is large and r_c is small

Different proposals for the confinement potentials:

Soft-confinement potential



Available in SIESTA

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

J. Junquera *et al.*, Phys. Rev. B 64, 235111 (2001)

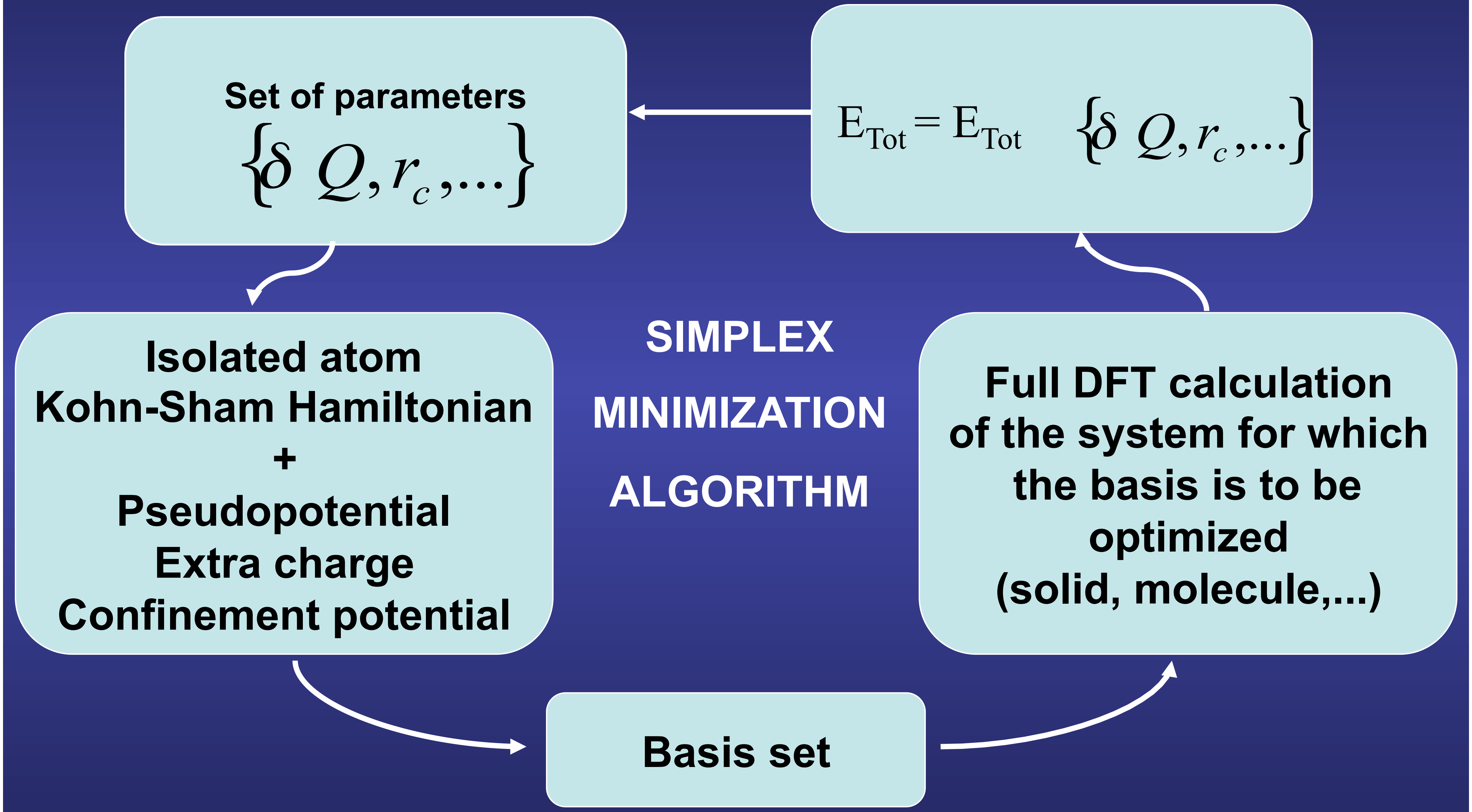
Advantages: orbital continuous with all the derivatives continuos

diverges at r_c (orbital exactly vanishes there)

zero at the core region

Pitfall: two new parameters to play with, more exploratory calculations

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



Set of parameters

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

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

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…

How to introduce the basis set in SIESTA
Effort on defining a systematic with minimum parameters

If nothing is specified: default

		Default value
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:	Hard well	

Good basis set in terms of accuracy versus efficiency

More global control on the basis with a few input variables: size and range

Size:

Basis size:

	PAO.BasisSize	**SZ**
		DZ
		SZP
		DZP

Range:

Range of first-zeta:	**PAO.EnergyShift**	**0.02 Ry**
Range of second-zeta:	**PAO.SplitNorm**	**0.15**

The larger both values, the more confined the basis functions

More specific control on 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
```

More specific control on the basis: the PAO.Basis block

Some variable might be computed automatically

```
%block PAO.Basis                   # Define Basis set
H      1    +0.25                  # Species label, number of l-shells, charge
 n=1   0    2                      # n, l, Nzeta
   0.000       0.000               # rc (first-zeta), rm (second-zeta)
   1.000       1.000               # scaling factors
%endblock PAO.Basis
```

These variables calculated from

PAO.EnergyShift and PAO.SplitNorm values

More specific control on the basis: the PAO.Basis block

Adding polarization orbitals: perturbative polarization

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

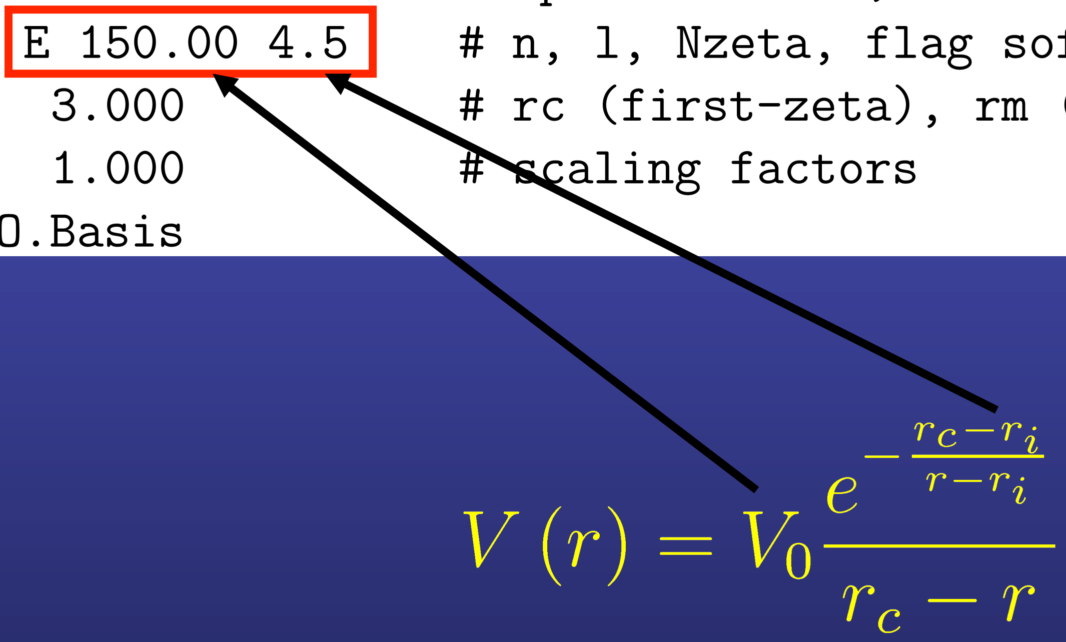
More specific control on the basis: the PAO.Basis block

Adding polarization orbitals: atomic polarization

```
%block PAO.Basis                  # Define Basis set
H        2    +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
 n=2     1    1                   # n, l, Nzeta
   5.000                          # rc (first-zeta)
   1.000                          # scaling factors
%endblock PAO.Basis
```

More specific control on the basis: the PAO.Basis block

Soft-confinement potential



```
%block PAO.Basis                # Define Basis set
H       1    +0.25              # Species label, number of l-shells, charge
 n=1    0    2 E 150.00 4.5     # n, l, Nzeta, flag soft-conf, prefactor, inner rad
   5.000       3.000            # rc (first-zeta), rm (second-zeta)
   1.000       1.000            # scaling factors
%endblock PAO.Basis
```

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

V_0 **in Ry**

r_i **in bohrs**

Recap

Numerical Atomic Orbitals

A very efficient basis set

Especially suitable for Order-N methods

Smooth transition from quick exploratory calculations to highly converged

Lack of systematic convergence

Simple handles for tuning the basis sets

Generate multiple-ζ: Split Valence

Generate polarization orbitals: Perturbative polarization

Control the range of the orbitals in a balanced way: Energy Shift

Confine the orbitals: Soft-confinement potential

A DZP basis set, the same deviations as DFT functional or Pseudo

Suplementary information

Spherical Bessel functions $j_l(kr)$, solutions of a free particle confined in a box

$$V = \infty, r \geq a$$

$$V = 0, r < a$$

Schrödinger equation for a particle inside the box

$$-\frac{\hbar^2}{2m}\nabla^2\psi\left(r,\theta,\phi\right) = E\psi\left(r,\theta,\phi\right)$$

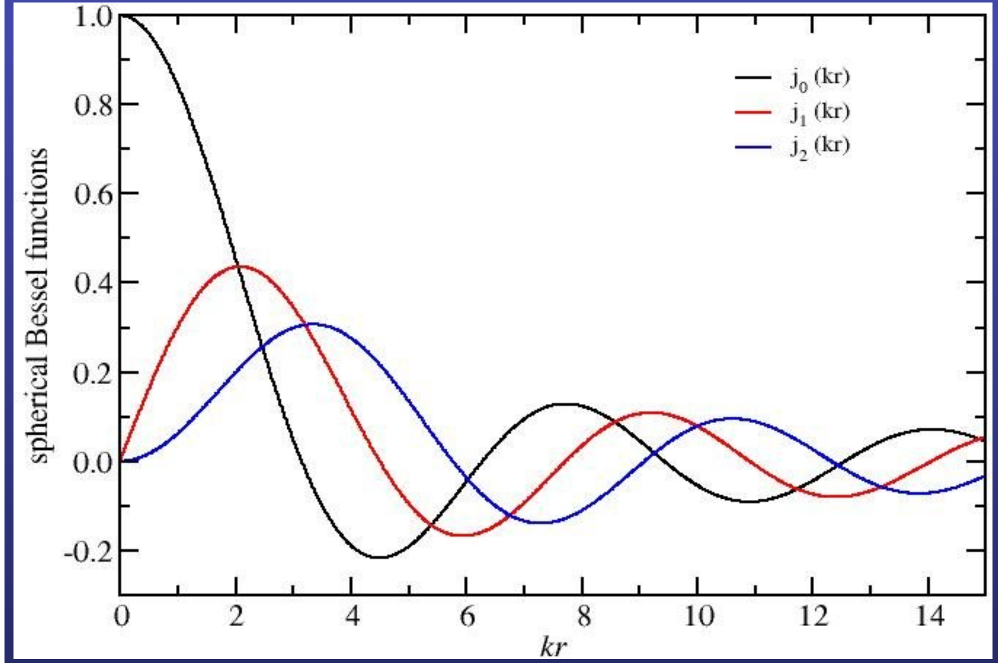
After separation of variables, the radial equation reads

$$\psi\left(r,\theta,\phi\right) = R\left(R\right)\Theta\left(\theta\right)\Phi\left(\phi\right)$$

$$\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr} + \left[k^2 - \frac{l(l+1)}{r^2}\right]R = 0$$

$$k^2 = \frac{2mE}{\hbar^2}$$

$l \in$ Z, separation variable constant



Solution of the radial equation

$$R\left(r\right) = \begin{cases} Aj_l\left(kr\right) + \xcancel{Bn_l\left(kr\right)}, & r < a \\ 0, & r \geq a \end{cases}$$

Boundary conditions: k **must satisfy** $j_l\left(ka\right) = 0$

Spherical von Neumann function, not finite at the origin