

# Efficient Materials Modelling on HPC



March 13, 2024

# Basis sets in SIESTA

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# Density Functional Theory (DFT)

## Background

## Kohn-Sham (DFT)

$$\hat{V}_{ext}(r) \iff n(r)$$
$$n(r) = \sum_i^N |\psi_i^{KS}(r)|^2$$

← N electronic states

$$\hat{H}^{KS} \psi_j^{KS}(r) = \varepsilon_j^{KS} \psi_j^{KS}(r)$$

## Basis Expansion:

$$|\psi_i\rangle = \sum_{\mu=1}^M c_{i,\mu} |\mu\rangle$$

← M basis functions

Generalised eigenvalue problem:

$$H_{\mu\nu} C_{j\nu} = \varepsilon_j S_{\mu\nu} C_{j\nu} \quad (\text{matrix form})$$

$$H_{\mu\nu} = \langle \mu | \hat{H} | \nu \rangle$$

Hamiltonian matrix

$$S_{\mu\nu} = \langle \mu | \nu \rangle$$

Overlap matrix

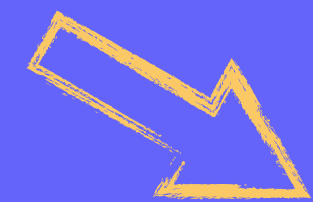
# Density Functional Theory (DFT)

## Background

## Kohn-Sham (DFT)

$$\hat{V}_{ext}(r) \iff n(r)$$

$$n(r) = \sum_i^N |\psi_i^{KS}(r)|^2$$



$$n(r) = \sum_i^N |\psi_i(r)|^2 = \sum_i^N \sum_{\mu\nu}^M c_{\mu,i} c_{\nu,i}^* \phi_{\mu}(r) \phi_{\nu}^*(r) =$$

## Density Matrix

$$= \sum_{\mu\nu} \left[ \sum_i^N c_{\mu,i} c_{\nu,i}^* \right] \phi_{\mu}(r) \phi_{\nu}^*(r) = \sum_{\mu\nu} \rho_{\mu\nu} \phi_{\mu}(r) \phi_{\nu}^*(r)$$

## Basis Expansion:

$$|\psi_i\rangle = \sum_{\mu=1}^M c_{i,\mu} |\mu\rangle$$

$$\langle r | \mu \rangle = \phi_{\mu}(r)$$

# Density Functional Theory (DFT)

## Background

## Periodic Boundary Conditions?: Bloch theorem

$$|\psi_i\rangle = \sum_{\mu=1}^M c_{i,\mu} |\mu\rangle \longrightarrow |n\vec{k}\rangle = \frac{1}{\sqrt{N}} \sum_{\mu, \vec{R}} c_{n,\mu}(\vec{k}) \cdot e^{i\vec{k}\cdot\vec{R}} |\mu\vec{R}\rangle$$

Bloch orbitals

$$|\mu\vec{k}\rangle = \frac{1}{\sqrt{N}} \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} |\mu\vec{R}\rangle$$

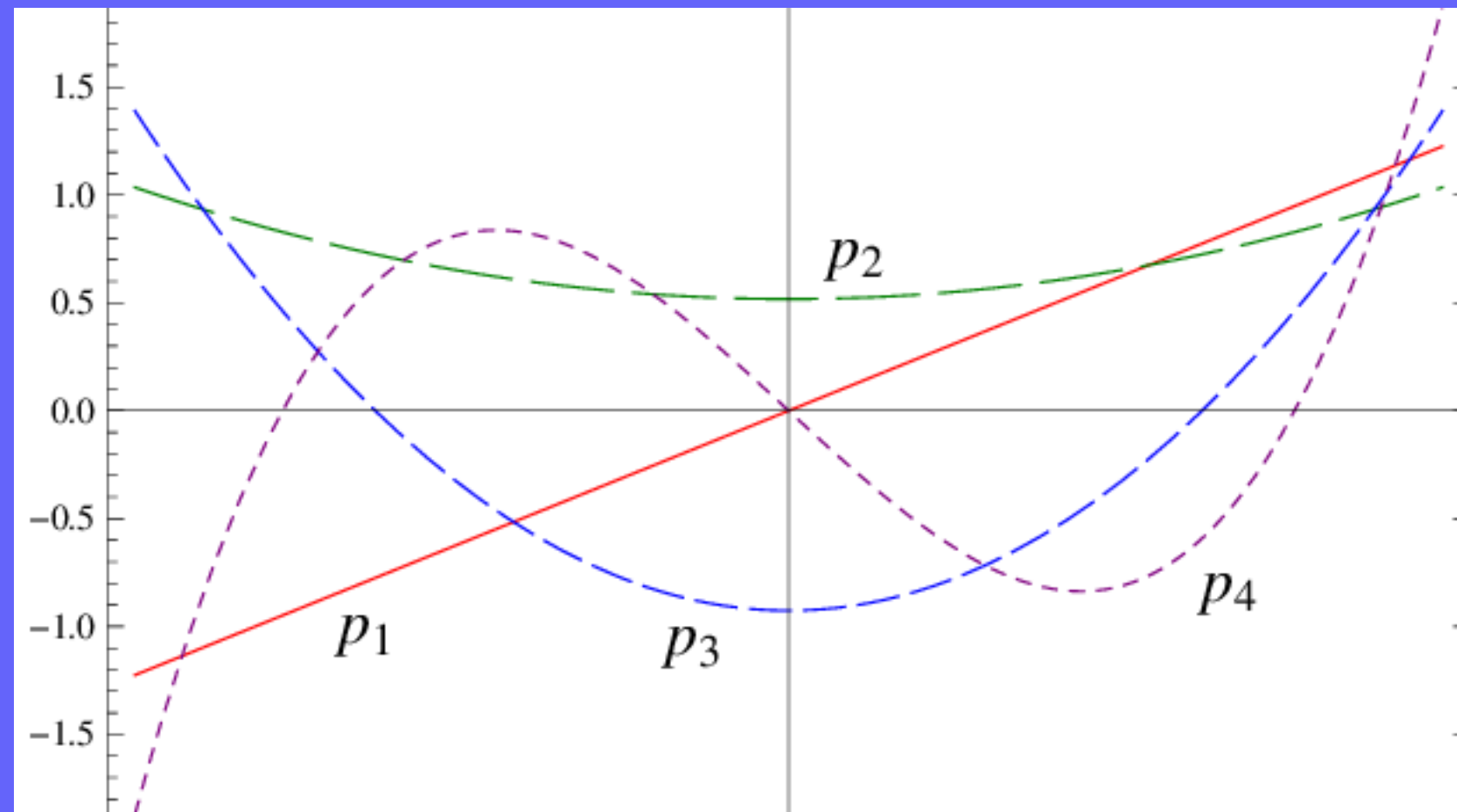
Generalised eigenvalue problem:

$$H_{\mu\nu}(\vec{k}) C_{j\nu}(\vec{k}) = \epsilon_{j,\vec{k}} S_{\mu\nu}(\vec{k}) C_{j\nu}(\vec{k})$$

$$H_{\mu\nu}(\vec{k}) = \langle \mu, \vec{k} | \hat{H} | \nu, \vec{k} \rangle = \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} \langle \mu, 0 | \hat{H} | \nu, \vec{R} \rangle$$

# What type of Basis Functions?

Representation of Hilbert space for the electronic wavefunctions



## ● Planewaves

- ▶ Good for PBC
- ▶ Systematic convergence (complete)
- ▶ Orthogonal and Spatially unbiased
- ▶ Expressions for  $H$  are simple (FFT)
- ▶ Vacuum costs as much as matter!
- ▶ Large number of PWs per electron
- ▶ Compact orbitals are harder
- ▶ Localisation ideas are not easily implemented

## ● Atomic Orbitals

## ● Other Numerical Functions:

- Wavelets,
- Bessel functions,
- Psinc's, blips,
- Augmented Plane Waves,
- Muffin-tin Orbitals, etc.

# Atomic Orbitals

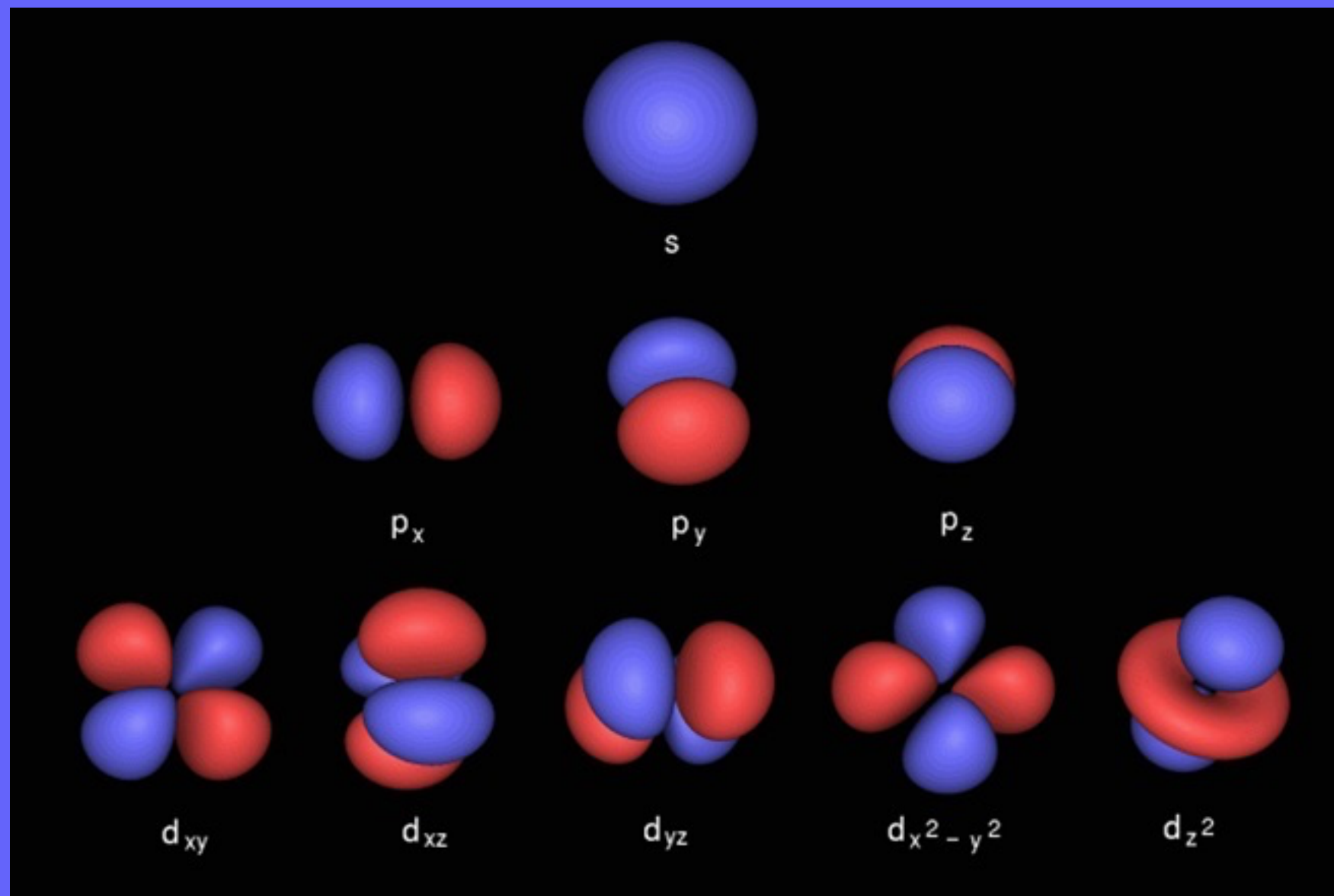
$$\langle r | \mu \rangle = \phi_{\mu}(r) \longrightarrow \phi_{\mu}(r - R_{\mu})$$

$$\phi_{\mu}(r - R_{\mu}) \longrightarrow \phi_{I l m n}(r_I) = R_{I l n}(r) Y_{l m}(\hat{r}_I)$$

Atom index  
angular momentum  
magnetic quantum number  
Multiple orbitals with same  $l m$

## LCAO methods

- Orbitals close to the solutions of the atomic problem are good approximations
- Tradition of Quantum Chemistry methods:
  - Slater-type orbitals (STO)
  - Gaussian-type orbitals (GTO)
  - Contracted Gaussian-type orbitals
  - Numerical real-space grid



# Atomic Orbitals

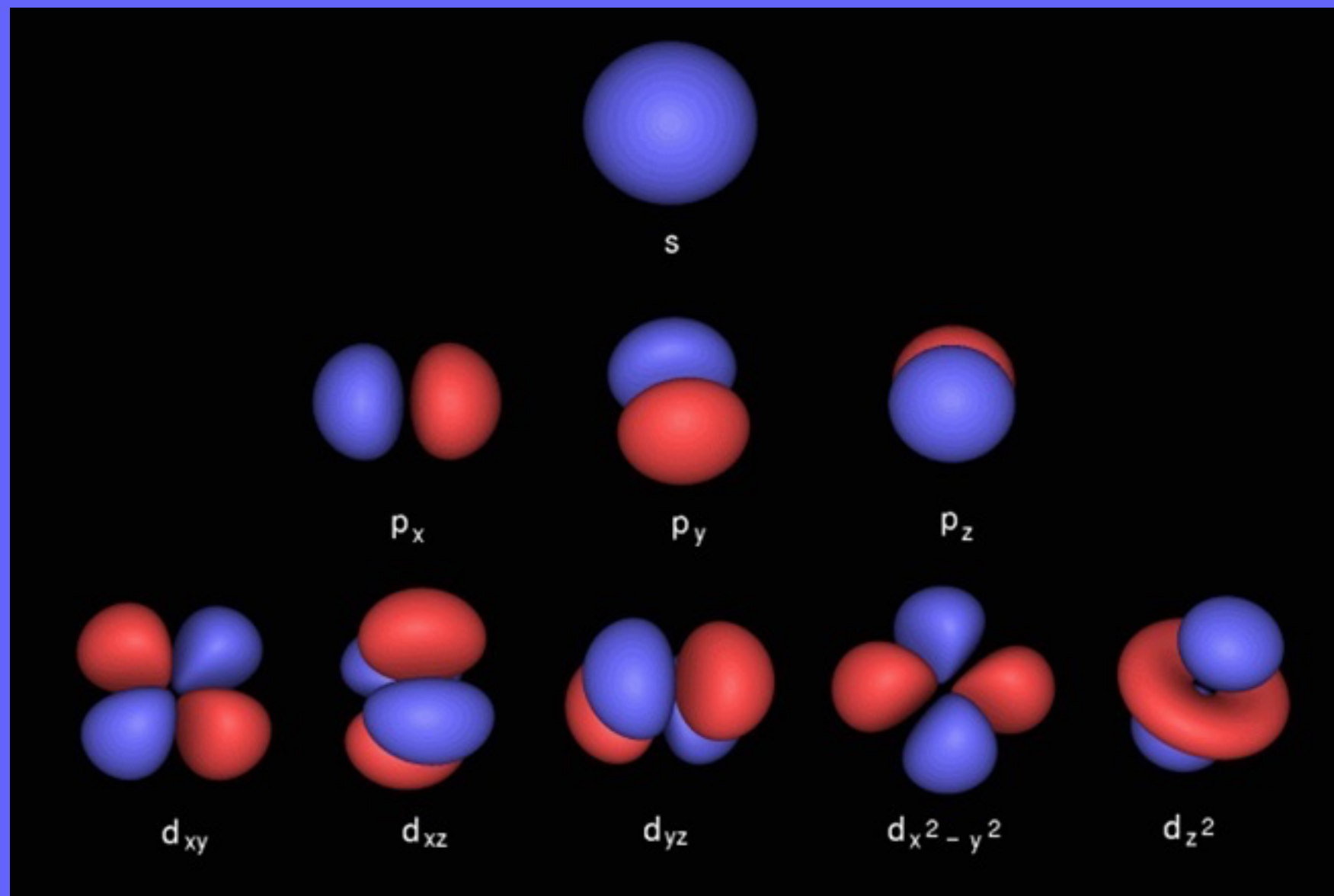
$$\langle r | \mu \rangle = \phi_{\mu}(r) \longrightarrow \phi_{\mu}(r - R_{\mu})$$

$$\phi_{\mu}(r - R_{\mu}) \rightarrow \phi_{I l m n}(r_I) = R_{I l n}(r) Y_{l m}(\hat{r}_I)$$

Atom index  
angular momentum  
magnetic quantum number  
Multiple orbitals with same  $l m$

## LCAO methods

- ▶ Very efficient in terms of number of orbitals per electrons
- ▶ Very well suited to describe localisation
- ▶ Large reduction in CPU and memory costs
- ▶ No need for periodicity
- ▶ Vacuum is almost free
- ▶ Chemical information (charge population, projected density of states, etc).
- ▶ Lack of systematics for convergence.
- ▶ Require human and computational effort to get a good basis set before use
- ▶ Spatially biased, since they are optimal for an atomic problem: Basis Set Superposition Error
- ▶ Orbitals move with atoms, which brings extra terms in forces (Pulay corrections)
- ▶ Calculation of Hamiltonian matrix elements can be quite complicated (and expensive)



# Atomic Orbitals

$$\langle r | \mu \rangle = \phi_{\mu}(r) \longrightarrow \phi_{\mu}(r - R_{\mu})$$

$$\phi_{\mu}(r - R_{\mu}) \rightarrow \phi_{Ilmn}(r_I) = R_{Il}(r) Y_{lm}(\hat{r}_I)$$

Radial flexibility

Angular flexibility

- Minimal basis, a.k.a. single- $\zeta$  (SZ)

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

- Multiple- $\zeta$

- Add more than one radial function with the same angular momentum.
- Double- $\zeta$  (DZ), Triple- $\zeta$  (TZ), quadruple- $\zeta$  (QZ), etc.

- Diffuse functions

- Add radial function on pre-existing valence shell, with longer tail than free atom

- Polarisation orbitals.

- Add new shell with larger values of  $l$
- d-orbitals for C, N, O, etc
- f-orbitals for Mn, Fe, ...



# Hierarchy of basis sets

## Standardised tiers

- General procedure:

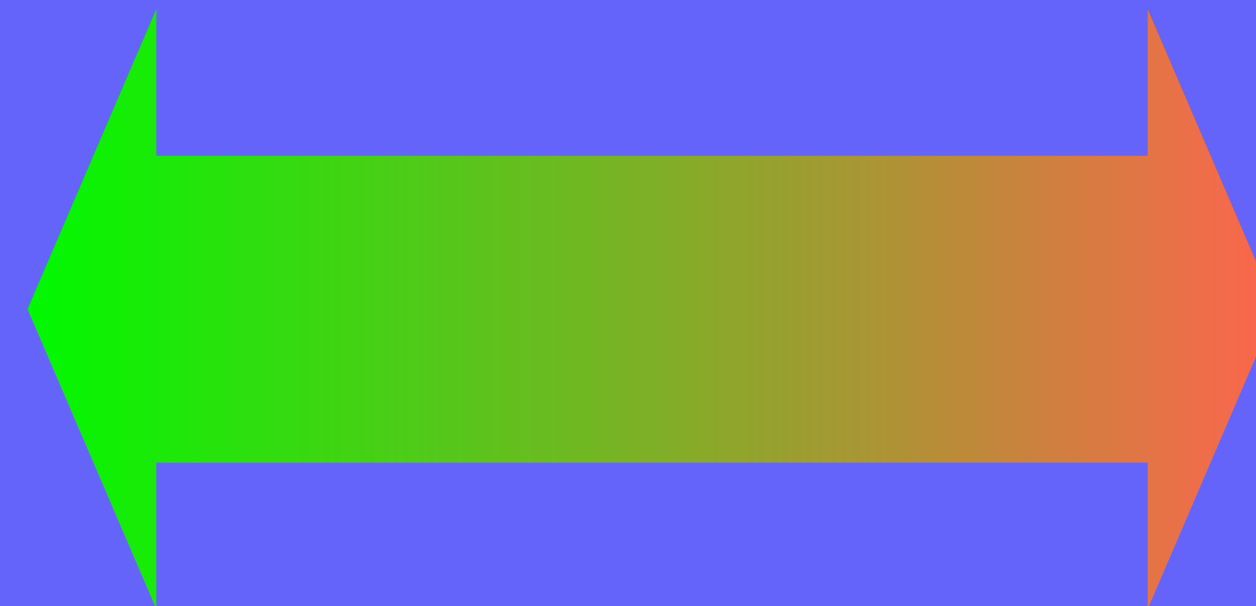
- ▶ Start from SZ
- ▶ Every step: increase both  $\zeta$  and polarisation by one

- General philosophy

- ▶ The larger the number of orbitals, the better the quality

Quick/cheap  
exploratory  
calculations

single- $\zeta$



Highly converged  
calculations

+ multiple- $\zeta$   
+ polarisation  
+ diffuse orbitals

# Hierarchy of basis sets

## Standardised tiers

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	

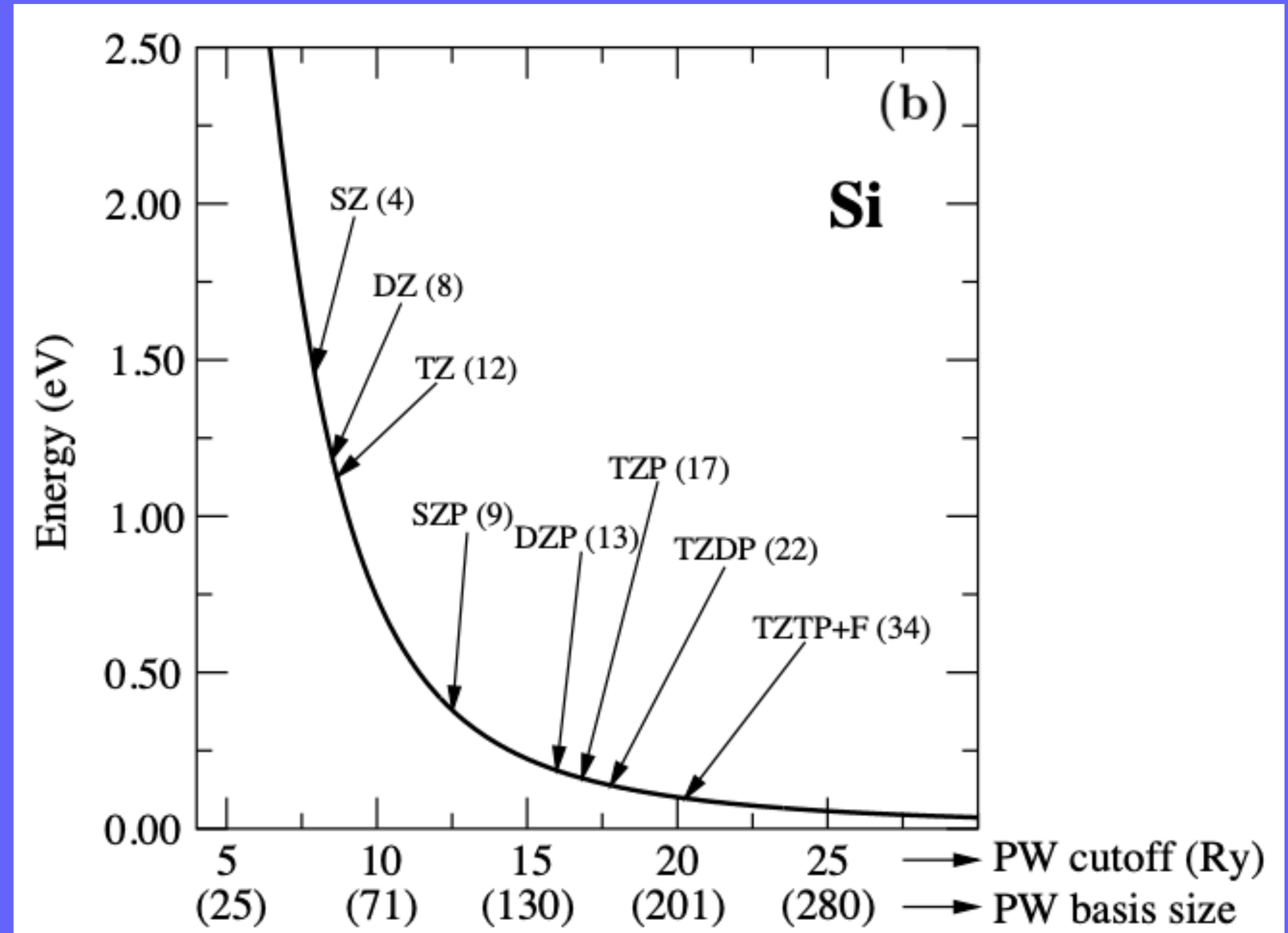
# Hierarchy of basis sets

## Convergence with size of basis set

- ▶ Polarisation orbitals are important for convergence.
- ▶ DZP basis is usually “good enough” as compared to converged PW calculations.
- ▶ Deviations are comparable to differences due to pseudopotentials or XC functionals

TABLE II. Basis comparisons for bulk Si.  $a$ ,  $B$ , and  $E_c$  stand for lattice parameter (in Å), bulk modulus (in GPa), and cohesive energy (in eV), respectively. SZ, DZ, and TZ stand for single- $\zeta$ , double- $\zeta$ , and triple- $\zeta$ . P stands for polarized, DP for doubly polarized. LAPW results were taken from Ref. 48, and the experimental values from Ref. 39.

	SZ	DZ	TZ	SZP	DZP	TZP	TZDP	PW	LAPW	Exp
$a$	5.52	5.49	5.48	5.43	5.40	5.39	5.39	5.38	5.41	5.43
$B$	85	87	85	97	97	97	97	96	96	98.8
$E_c$	4.70	4.83	4.85	5.21	5.31	5.32	5.34	5.40	5.28	4.63



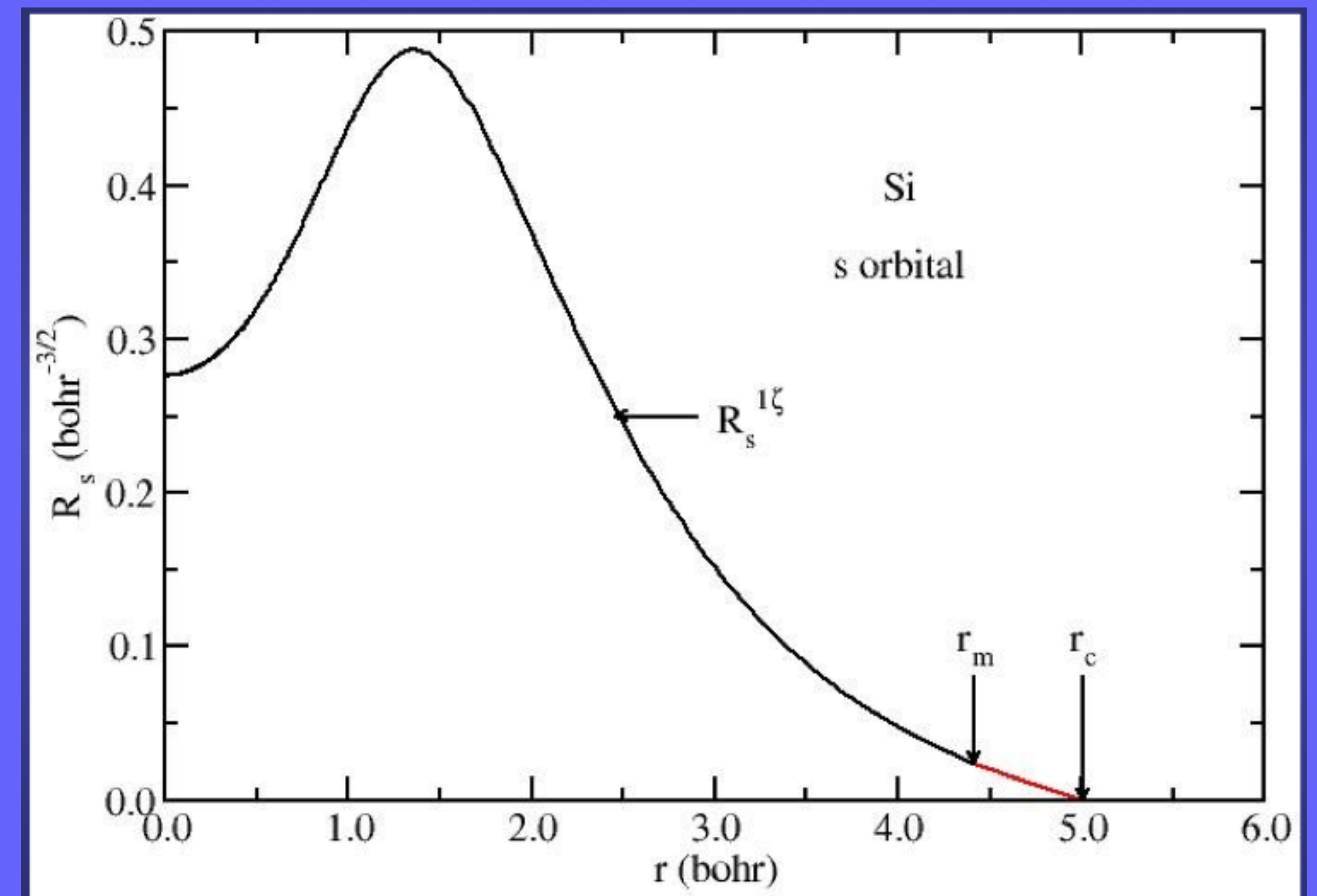
Junquera et al Phys. Rev. B 64, 235111 (2001)

# Atomic orbitals in SIESTA

► General functional form:  $\phi_{Ilmn}(r_I) = R_{Ilm}(r)Y_{lm}(\hat{r}_I)$

► Strictly localised (zero beyond a certain cutoff radii,  $r_c$ )

- ✓ As many as you want (l-shells and number of  $\zeta$ s)
- ✓ Of any (radial) shape
- ✓ Any localisation range ( $r_c$ )
- ✓ Any center (not necessarily an atom)
- ✓ **Numerical Pseudo-Atomic Orbitals (PAO)**



# Atomic orbitals in SIESTA

Radial functions  $R_{l'n}(r)$

## ● Automatically generated by SIESTA:

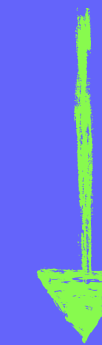
- ▶ Numerical solution of pseudoatom + “modifications”
- ▶ Depends on parameters that need to be defined by user
- ▶ Quite tunable
- ▶ Various levels of automatism, and predefinition of default values for parameters

# Strictly localised orbitals?

- Solution of Kohn–Sham DFT on pseudo-atom under an added confinement potential
- Control the range of the orbitals with one parameter:

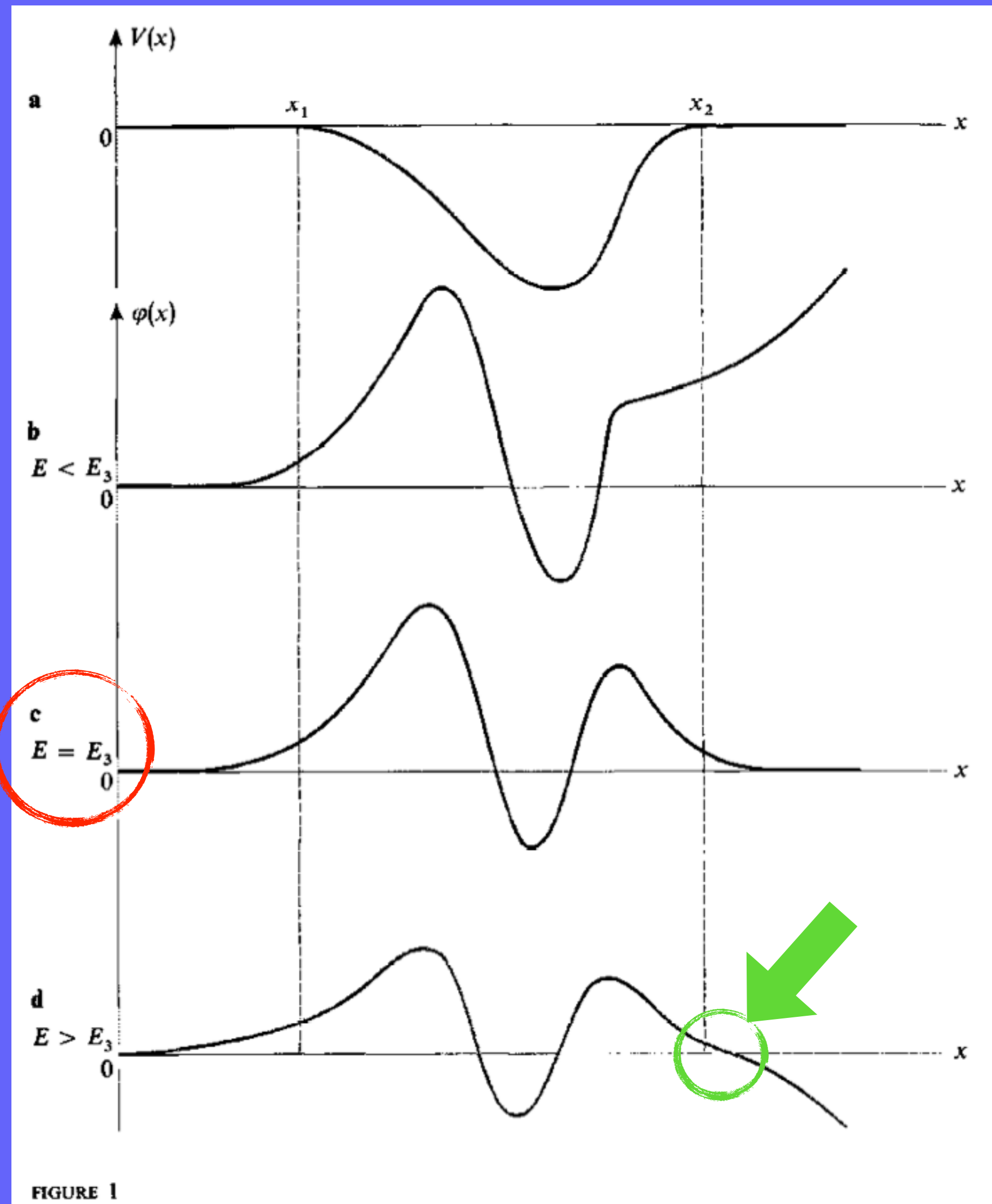
▶ FIREBALLS: O. F. Sankey & D. J. Niklewski, Phys. Rev. B 40, 3979 (1989)

▶ Energy Shift



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

# Strictly localised orbitals?



Bound states in a “potential well” of arbitrary shape

Complement M<sub>III</sub> – “Quantum Mechanics”, C. Cohen-Tannoudji et al.

$E$  is quantised and only certain values are allowed

$E >$  eigenenergy results in wfn  $\rightarrow -\infty$

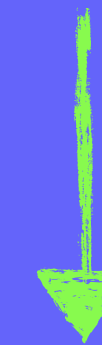
$\psi(r_c) = 0$  for certain point close to the well boundary

# Strictly localised orbitals?

- Solution of Kohn–Sham DFT on pseudo-atom under an added confinement potential
- Control the range of the orbitals with one parameter:

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

▶ Energy Shift



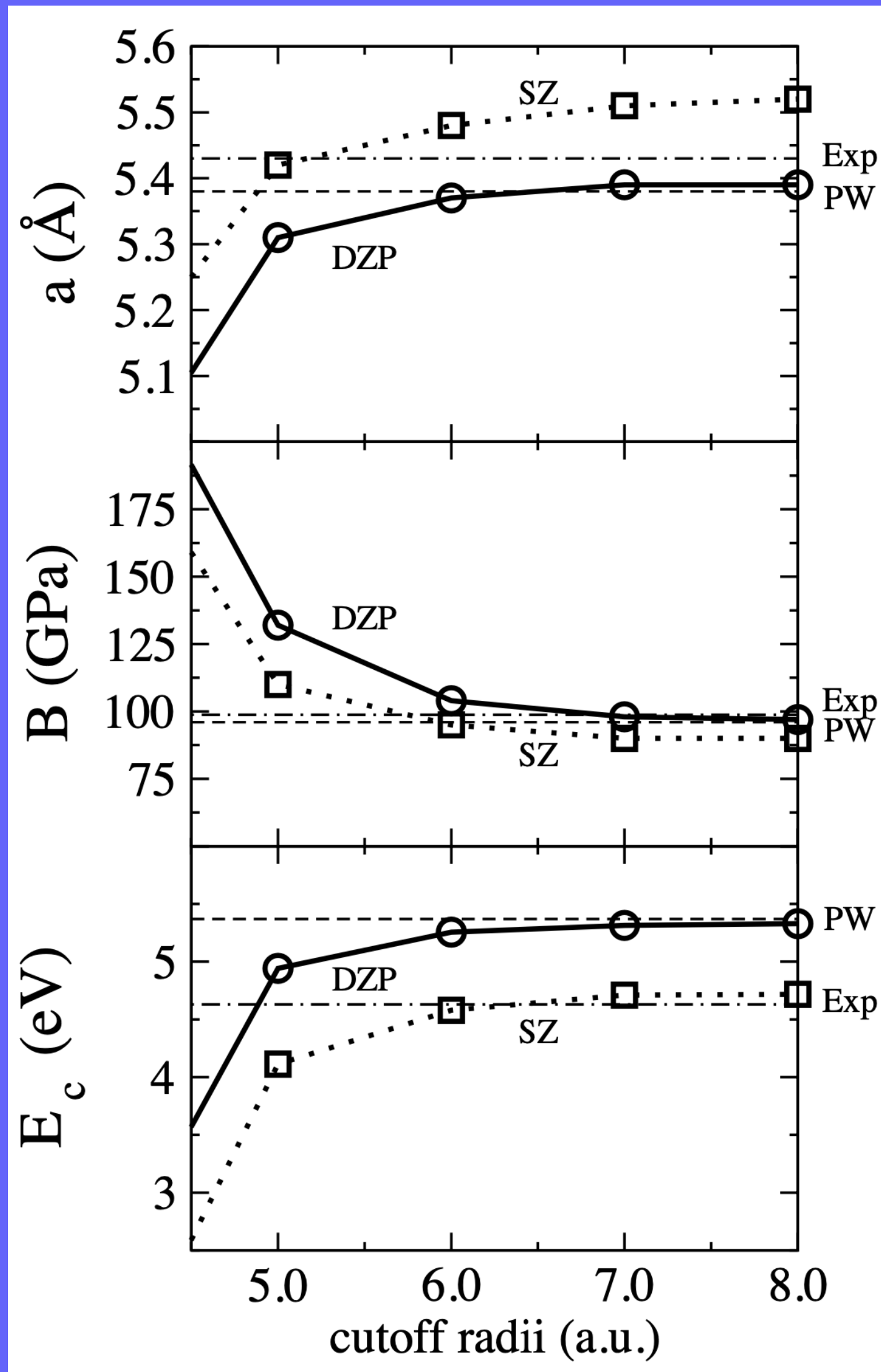
$$\left( -\frac{1}{2r} \frac{d^2}{dr^2} r + \frac{l(l+1)}{2r^2} + V_l(r) \right) R_l(r) = (\varepsilon_l + \delta\varepsilon_l) R_l(r) \quad \text{(Radial equation)}$$

The larger the Energy Shift, the shorter the  $r_c$

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



# Strictly localised orbitals?



Convergence with the cutoff radii

Larger radii  $\longrightarrow$  More accurate

VS

Shorter radii  $\longrightarrow$  More efficient (computationally)

WARNING: Basis can be optimised to get better agreement with experiments. That doesn't necessarily mean the basis set is better. There are other approximations implied (e.g. the xc functional) that could be responsible for disagreements between calculations and experiments!!

Bulk silicon – same cutoff radii for s & p orbitals

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

# Strictly localised orbitals?

## Soft-Confinement potentials

Default in SIESTA is a hard-wall potential

$$\begin{cases} V(r < a) = 0 \\ V(r \geq a) = \infty \end{cases}$$

Orbitals with discontinuous first derivative at  $r_c$

Other functional forms are possible.

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

- + orbitals with continuous derivatives
- + strictly localised (zero at  $r_c$ )
- + two parameters to optimise

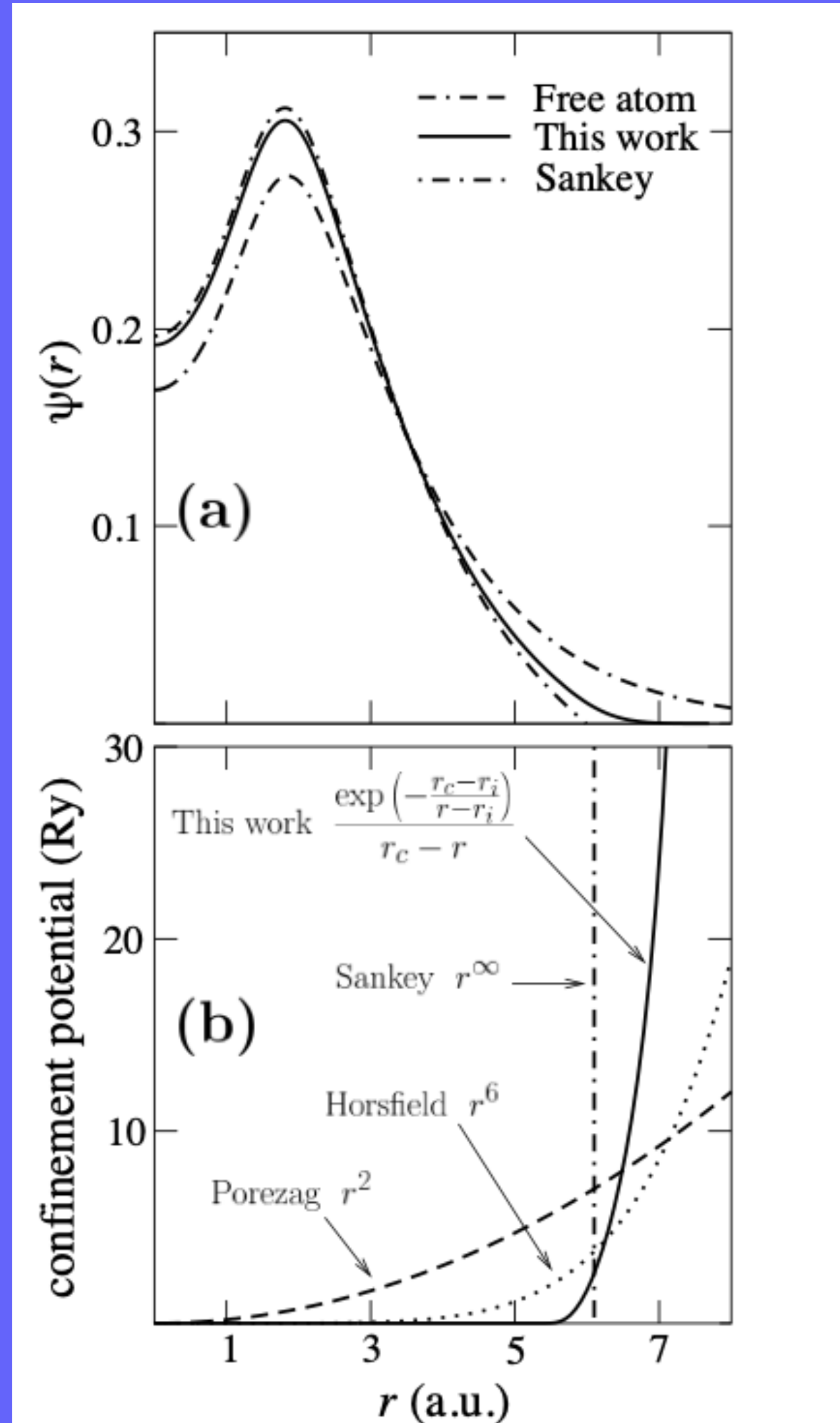
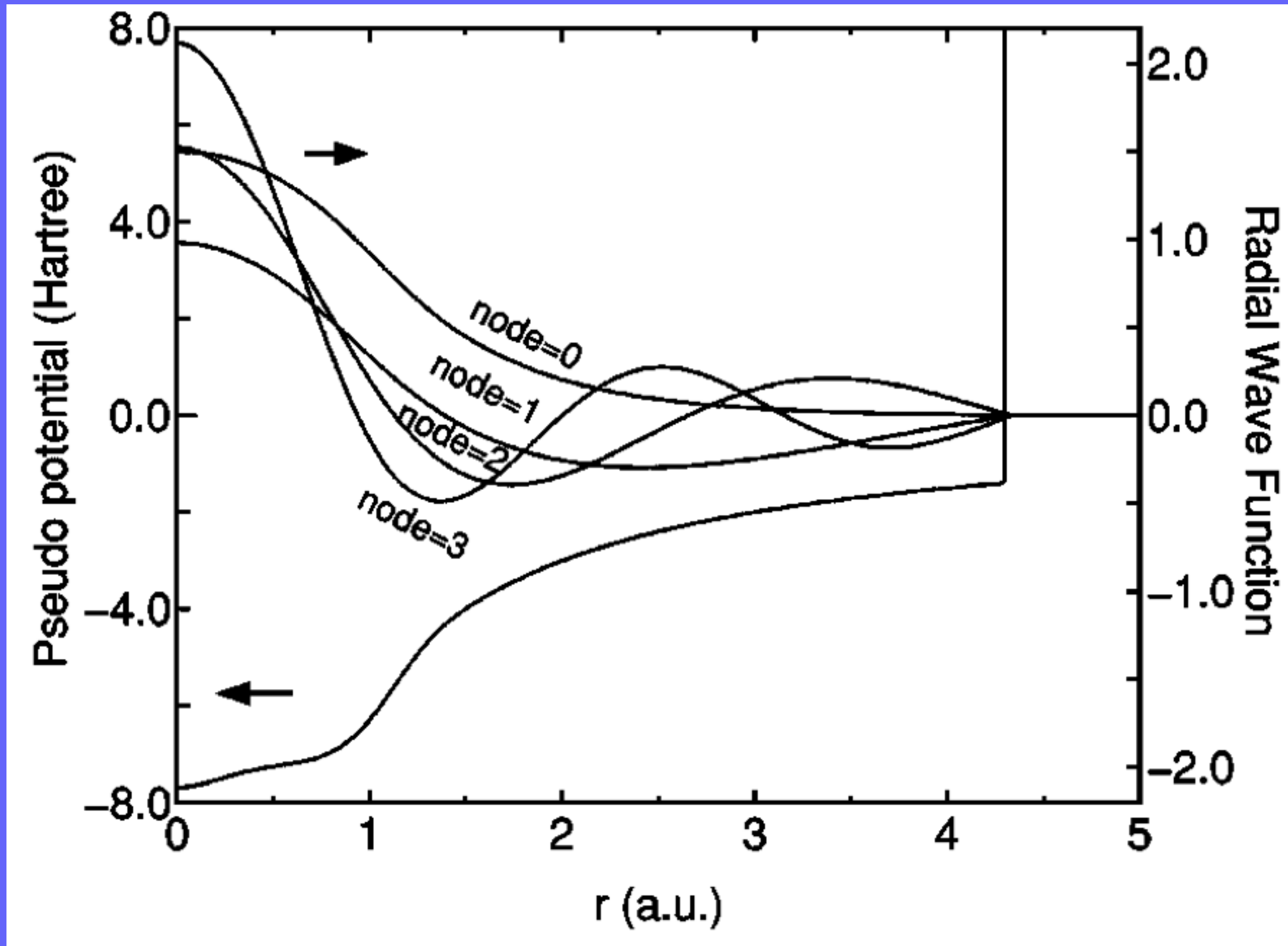


FIG. 1. Shape of the 3s orbital of Mg in MgO for the different confinement schemes (a) and corresponding potentials (b).

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

# Expanding radial flexibility

## Schemes to generate multiple- $\zeta$ basis sets



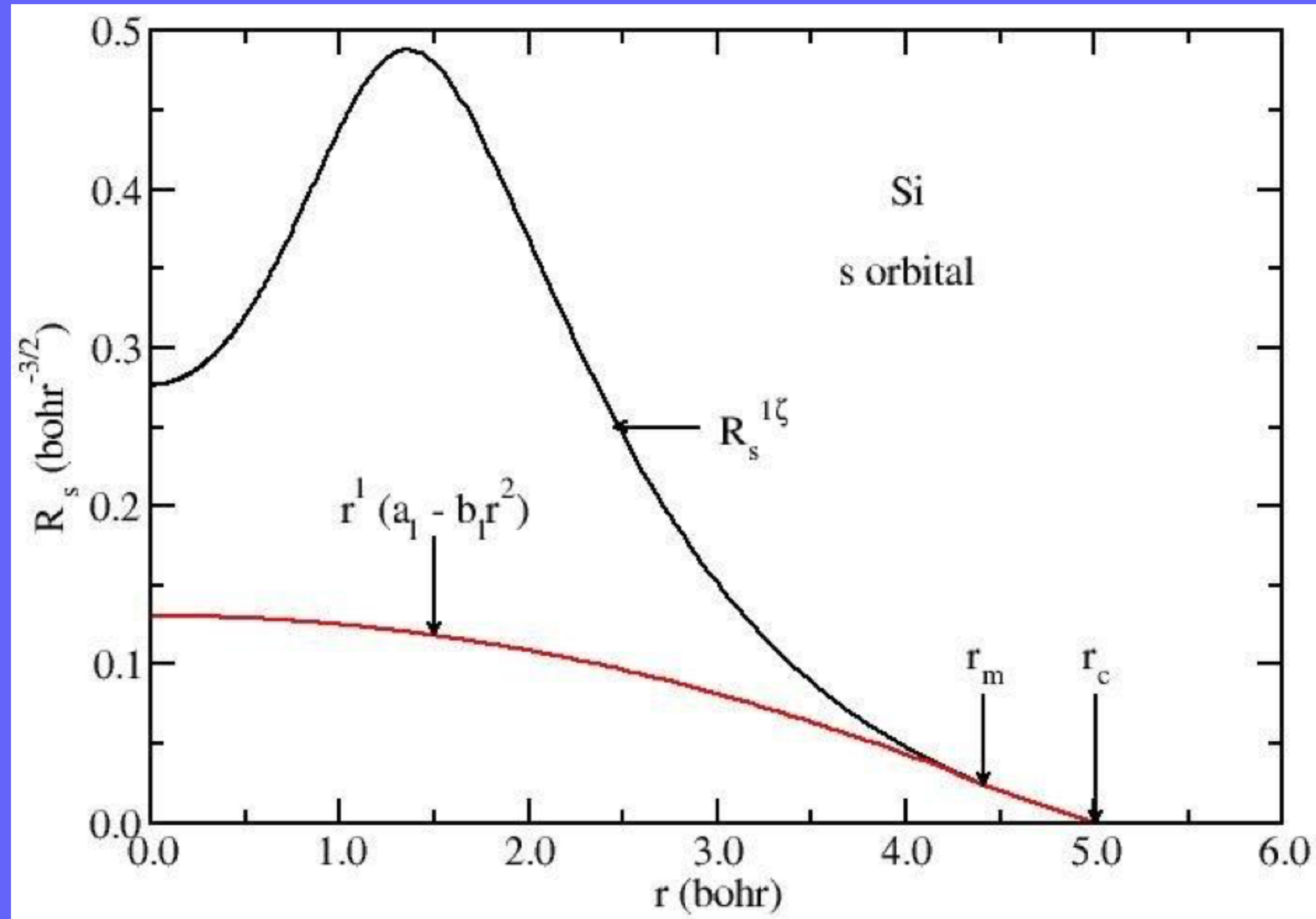
Ozaki & Kino Phys. Rev. B **69**, 195113 (2004)

Pseudoatom-wavefunctions with increasing number of nodes:

- + Orthogonality
- + Asymptotically complete (within sphere)
- unbound excited states of pseudos
- Efficiency requires longer  $r_c$

# Expanding radial flexibility

## Schemes to generate multiple- $\zeta$ basis sets

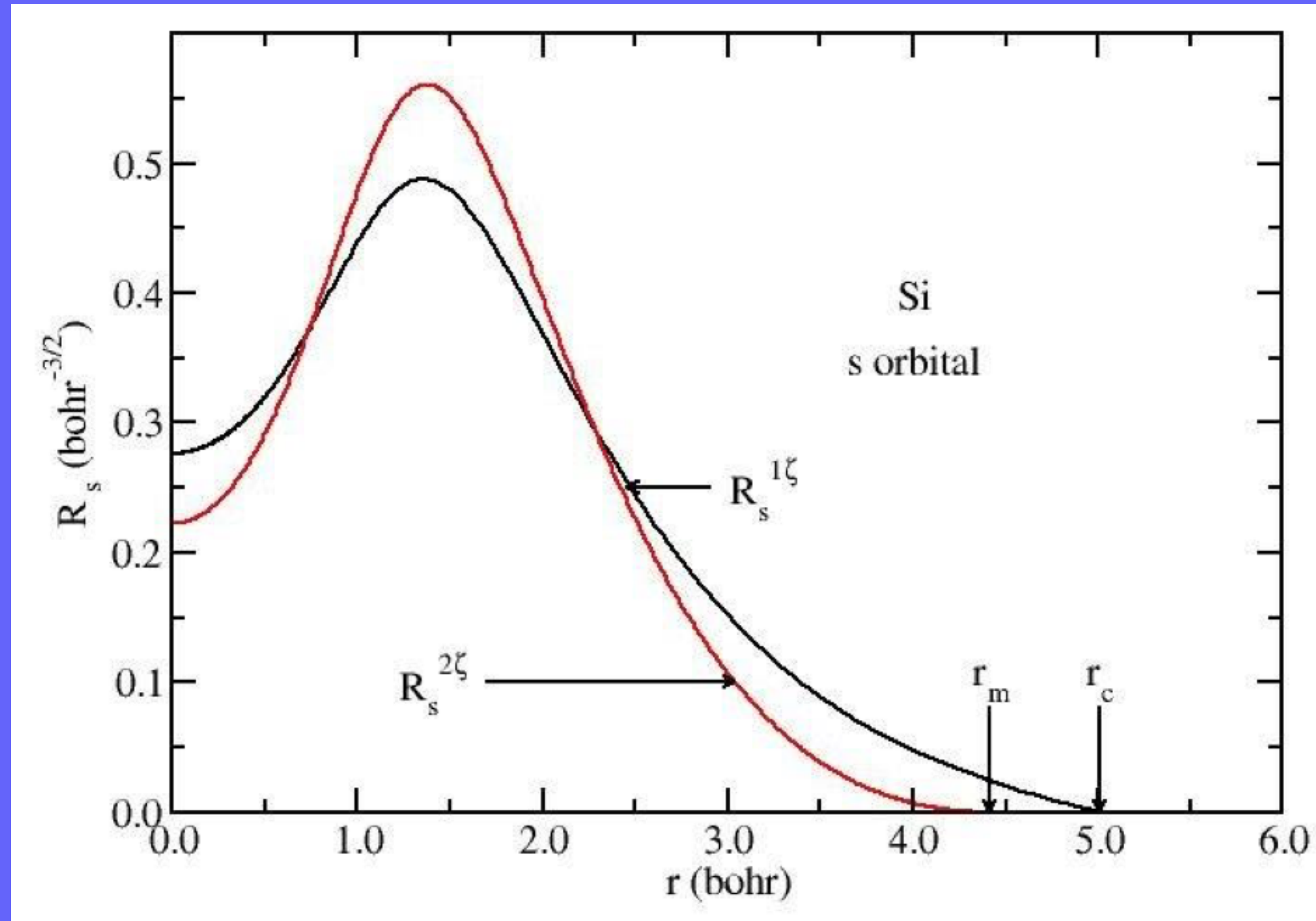


## “Split-valence” method

- ▶ Choose  $r_m$  and continue smoothly towards the origin as  $r^l(a_l - b_l r^2)$
- ▶ Two parameters: the new orbital and its first derivative must be continuous at  $r_m$
- ▶ The second- $\zeta$  is the (normalised) difference between the first- $\zeta$  and the function above.

# Expanding radial flexibility

## Schemes to generate multiple- $\zeta$ basis sets



## "Split-valence" method

- ▶ Choose  $r_m$  and continue smoothly towards the origin as  $r^l(a_l - b_l r^2)$
- ▶ Two parameters: the new orbital and its first derivative must be continuous at  $r_m$
- ▶ The second- $\zeta$  is the (normalised) difference between the first- $\zeta$  and the function above.
- ▶  $r_m$  is controlled with `PAO.SplitNorm` (default is 0.15)

# Expanding angular flexibility

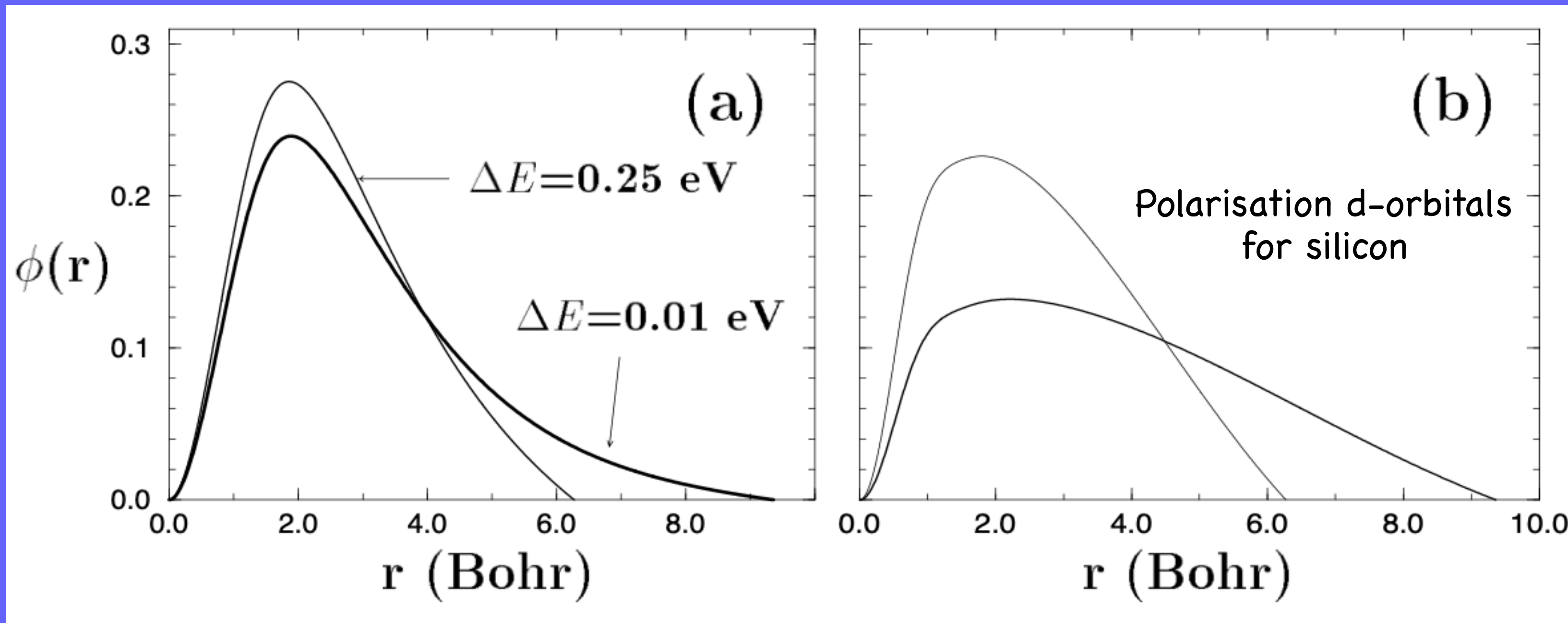
## Two schemes to generate polarization orbitals

### Perturbative polarisation

- ▶ Free pseudo atom valence orbitals under external electric field
- ▶  $l+1$  orbitals with same range of unperturbed orbitals

### Atomic polarisation

- ▶ Free pseudo atom orbitals of higher angular momentum
- ▶ Usually unbound: require short cutoffs



# Recap

## Standardised tiers

- General procedure:

- ▶ Start from SZ
- ▶ Every step: increase both  $\zeta$  and polarisation by one

Quick/cheap  
exploratory  
calculations

single- $\zeta$

- General philosophy

- ▶ The larger the number of orbitals, the better the quality

Highly converged  
calculations

+ multiple- $\zeta$   
+ polarisation  
+ diffuse orbitals

# Recap

## Standardised tiers

- General procedure:
  - ▶ Start from SZ
  - ▶ Every step: increase both  $\zeta$  and polarisation by one
- SIESTA basis
  - ▶ Multiple options to generate basis sets
  - ▶ Hierarchical structure,
  - ▶ Decent default basis...
- General philosophy
  - ▶ The larger the number of orbitals, the better the quality

Highly converged  
calculations

**BUT: optimal orbitals are  
environment-dependent!!**



# How to input basis sets?

## ● Test before going serious:

- ▶ Although the default basis is usually a good starting point, it is important that you verify it is appropriate for your system.
- ▶ If going to calculate for months or years, it is a good idea to spend a few days trying out bases and testing parameters is definitely worth it!

(C orbitals in diamond are not necessarily good for molecular CO<sub>2</sub>, or graphene)

Sometimes people can share bases in communities, the SIESTA mailing list, or third parties.

Practical session: Basis Set Optimization

# How to input basis sets?

	FDF flags	Default	Slightly better
Basis Size:	<code>PAO.BasisSize</code>	DZP	
Range of first-zeta:	<code>PAO.EnergyShift</code>	0.01 Ry	3–5 mRy
Second-zeta:	<code>PAO.BasisType</code>	Split	
Range of second-zeta:	<code>PAO.SplitNorm</code>	0.15	
Confinement:	<code>PAO.SoftDefault</code>	True	
	<code>PAO.SoftInnerRadius</code>	0.9	

# How to input basis sets?

## Better control on the basis?

```
%block PAO.BasisSize
Si    DZ
H     SZP
O     DZP
%endblock PAO.BasisSize
```

```
%block PAO.Basis
0    2
n=2  0    2    E 50.  2.5
      0.0  0.0
      1.0  1.0
n=2  1    2    P    1
      0.0  0.0
      1.0  1.0
%endblock PAO.Basis
```

```
%block PAO.Basis
0    3
n=2  0    2
      0.0  0.0
      1.0  1.0
n=2  1    2
      0.0  0.0
      1.0  1.0
n=3  2    1
      0.0
      1.0
%endblock PAO.Basis
```

Practical session: Basis Set Optimization

Efficient Materials Modelling on HPC



# Basis sets in SIESTA

Questions?

