

On-line School 2024



Nov 11, 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

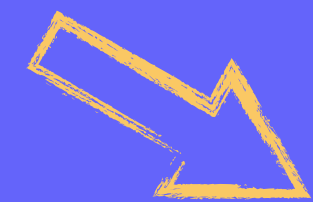
Density Functional Theory (DFT)

Background

Kohn-Sham (DFT)

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

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



Basis Expansion:

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

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

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

Density Matrix

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

Density Functional Theory (DFT)

Background

Periodic Boundary Conditions?: Bloch theorem

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

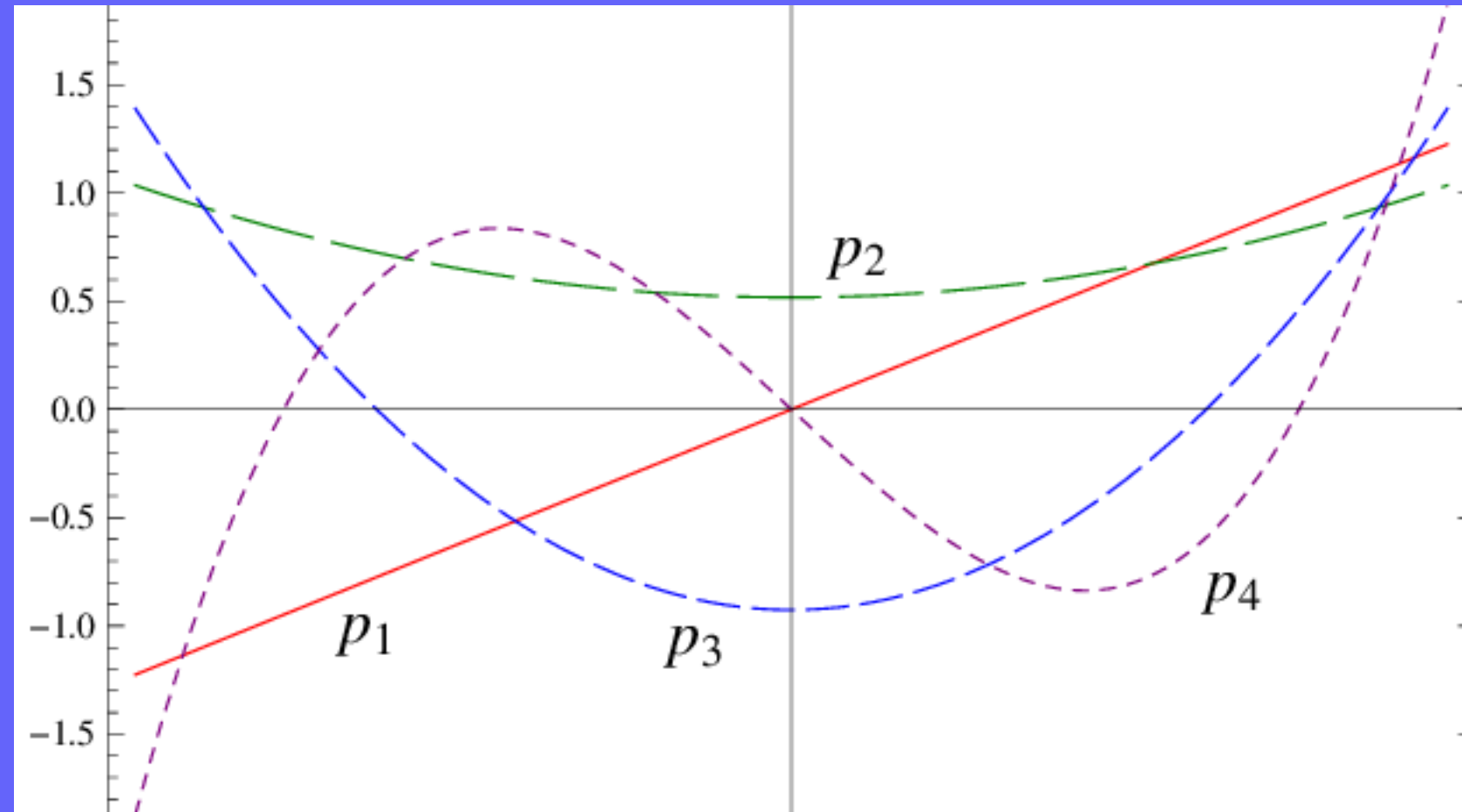
Generalised eigenvalue problem:

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

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

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

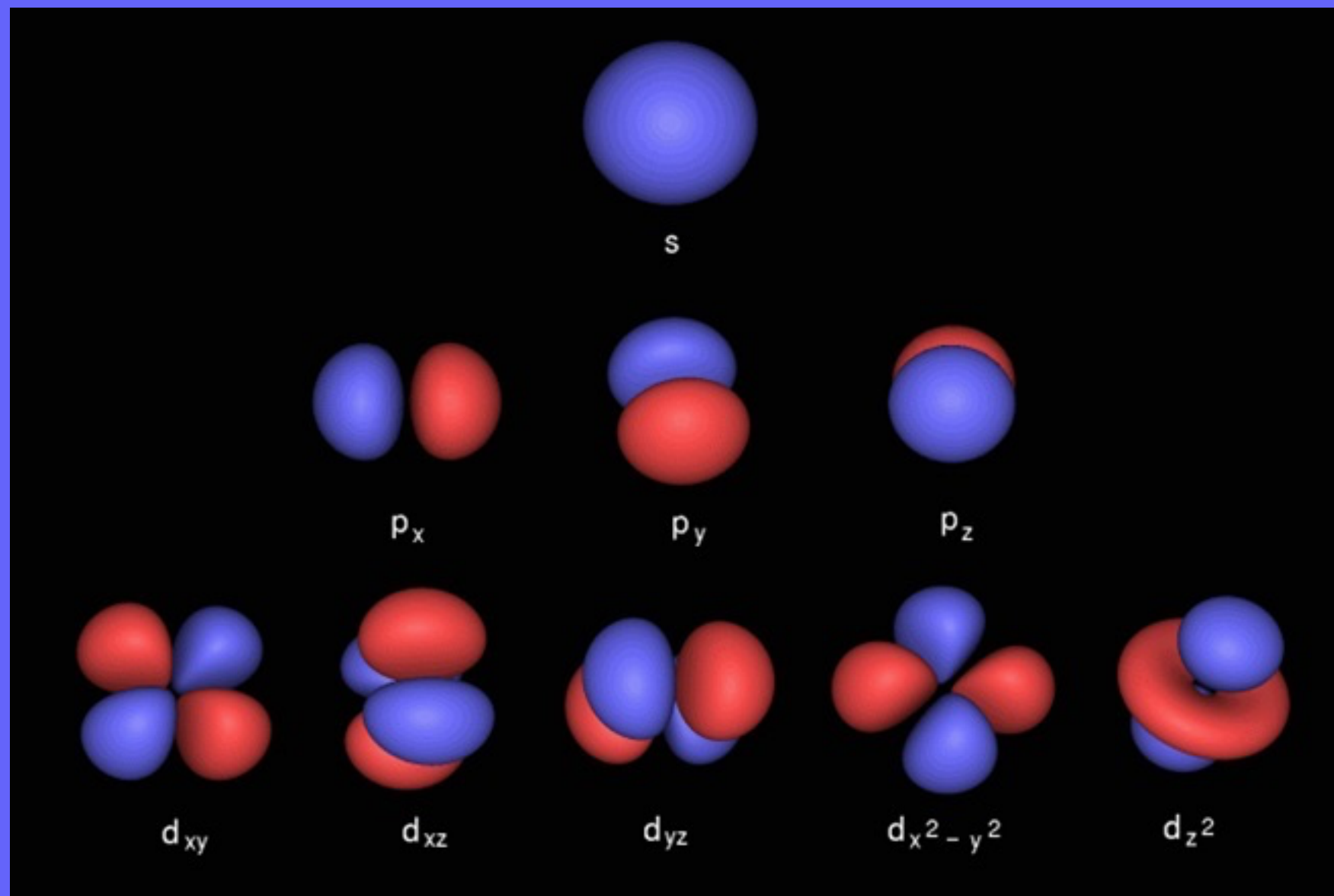
$$\langle r | \mu \rangle = \phi_{\mu}(r) \longrightarrow \phi_{\mu}(r - R_{\mu})$$

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

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

LCAO methods

- 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



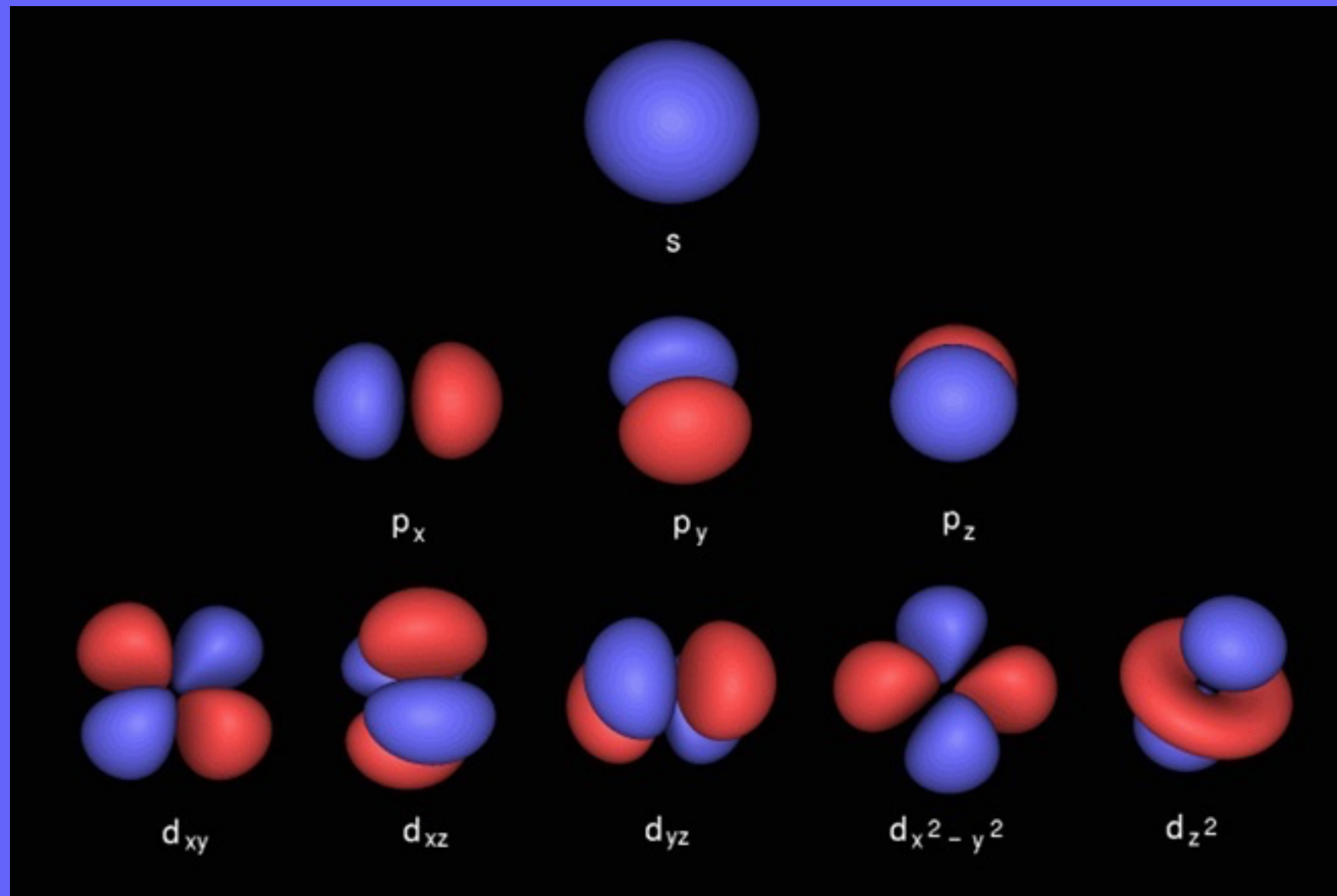
Atomic Orbitals

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

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

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

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

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

Radial flexibility

Angular flexibility

- Minimal basis, a.k.a. single- ζ (SZ)

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

- Multiple- ζ

- Add more than one radial function with the same angular momentum.
- Double- ζ (DZ), Triple- ζ (TZ), quadruple- ζ (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 ζ and polarisation by one

Quick/cheap
exploratory
calculations

single- ζ

- General philosophy

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

Highly converged
calculations

+ multiple- ζ
+ 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

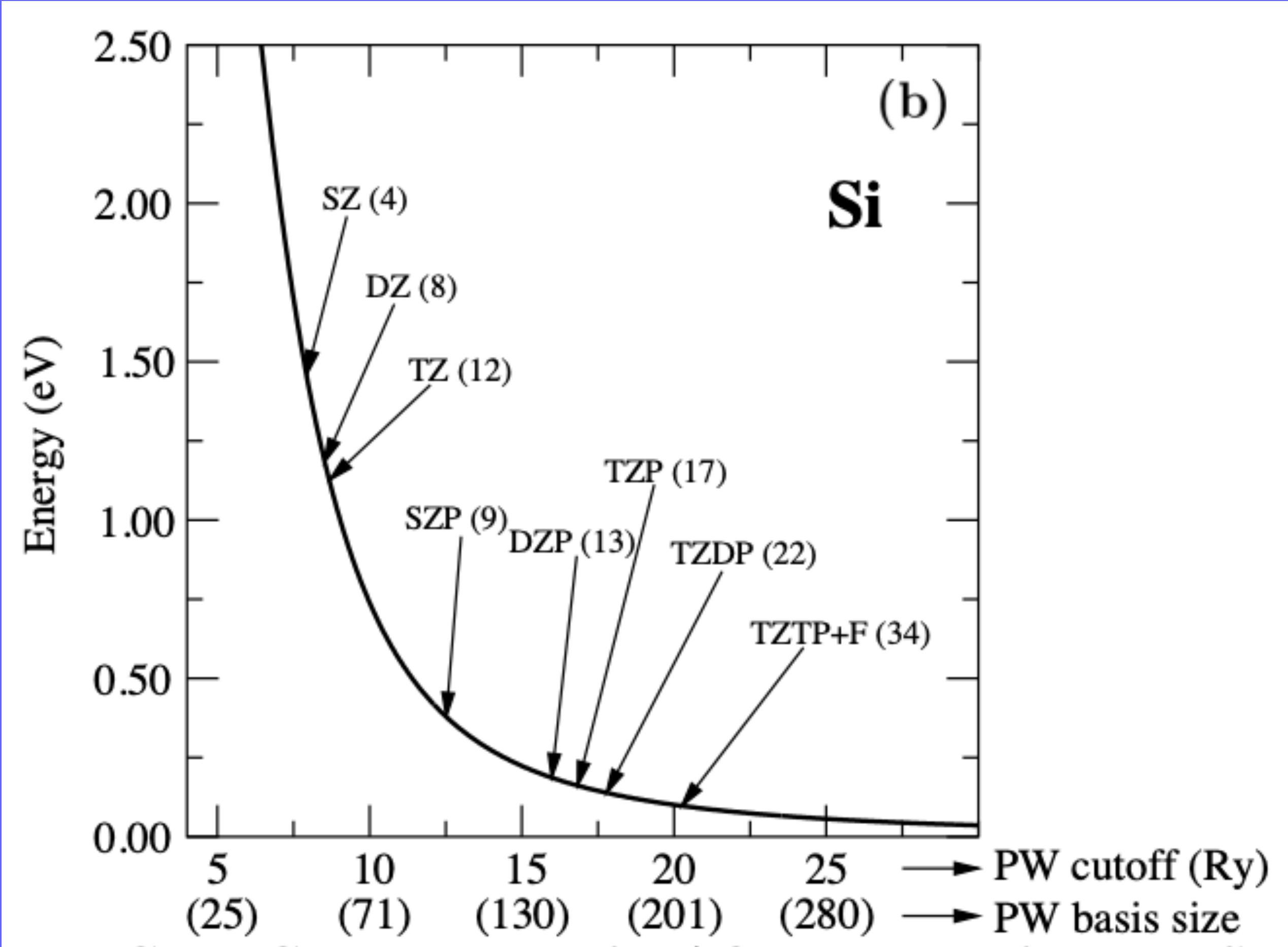
Hierarchy of basis sets

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- ζ , double- ζ , and triple- ζ . 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



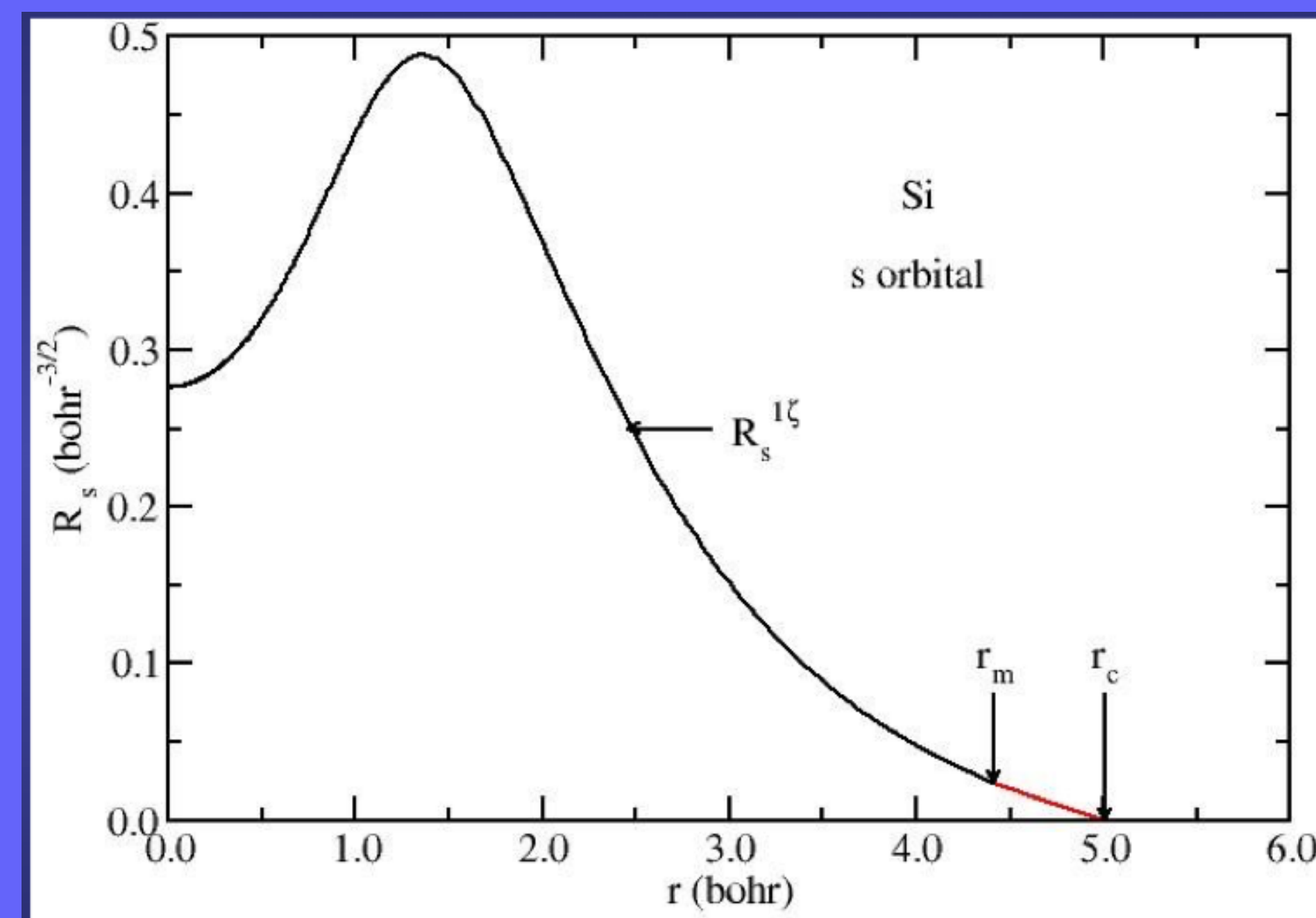
Junquera et al Phys. Rev. B 64, 235111 (2001)

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 ζ 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:

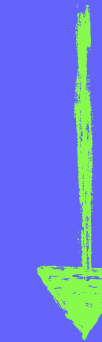
- ▶ Numerical solution of pseudoatom + “modifications”
- ▶ Depends on parameters that need to be defined by user
- ▶ Quite tunable
- ▶ Various levels of automatism, and predefinition of default values for parameters

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)

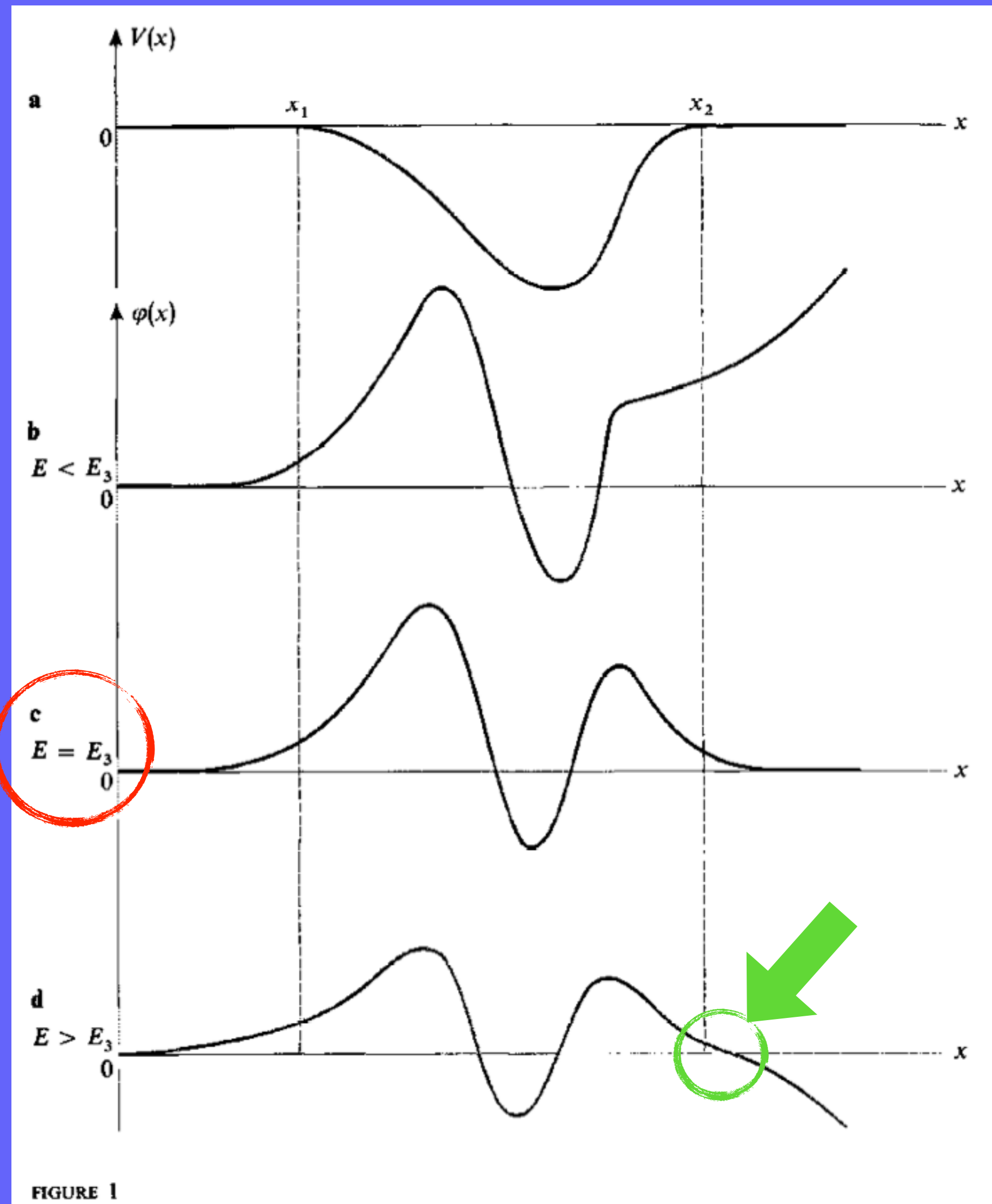
► Energy Shift



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

(Radial equation)

Strictly localised orbitals?



Bound states in a “potential well” of arbitrary shape

Complement M_{III} – “Quantum Mechanics”, C. Cohen-Tannoudji et al.

E is quantised and only certain values are allowed

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

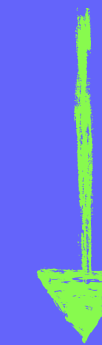
$\psi(r_c) = 0$ for certain point close to the well boundary

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

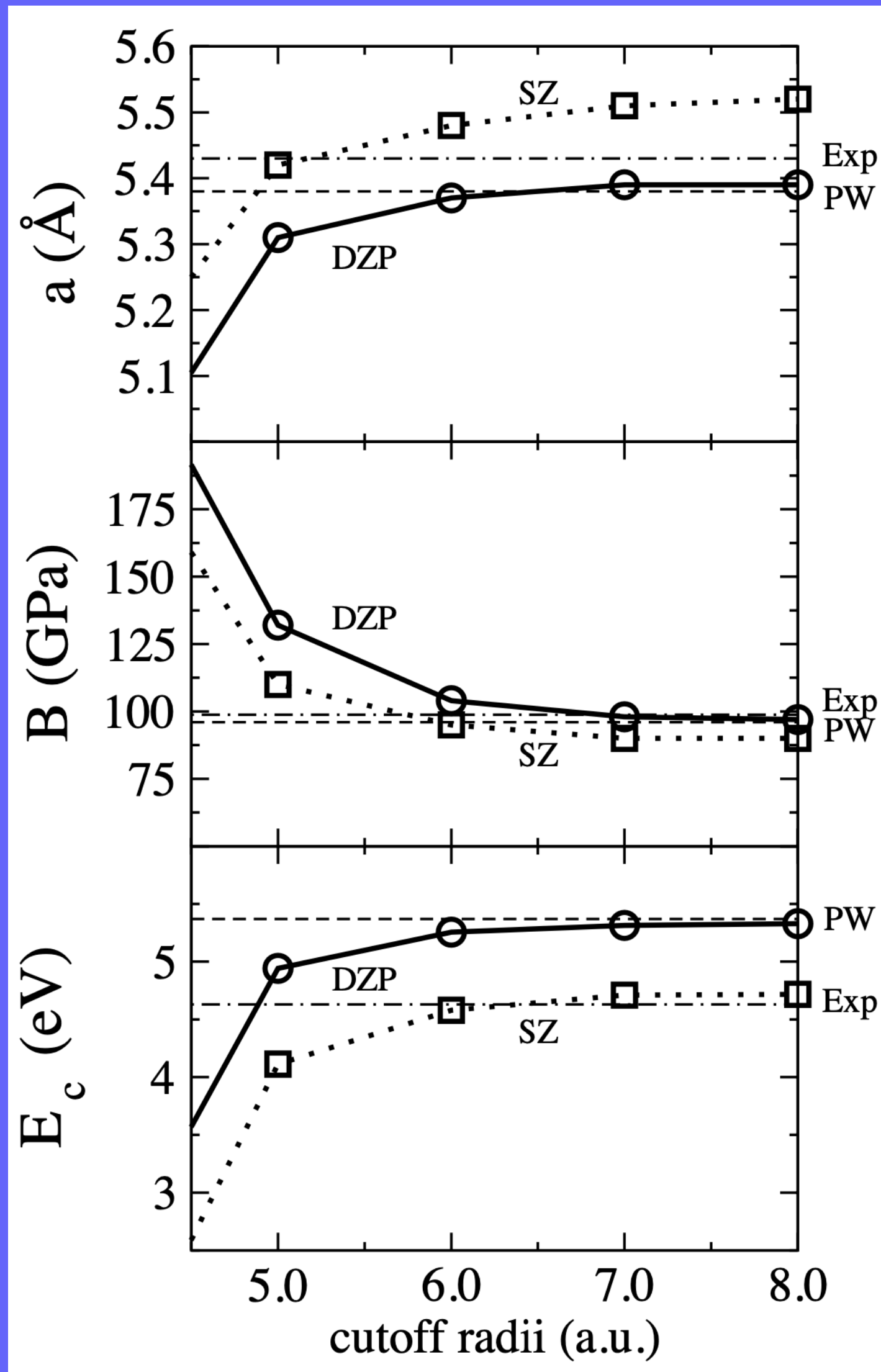


$$\left(-\frac{1}{2r} \frac{d^2}{dr^2} r + \frac{l(l+1)}{2r^2} + V_l(r) \right) R_l(r) = (\varepsilon_l + \delta\varepsilon_l) R_l(r) \quad \text{(Radial equation)}$$

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

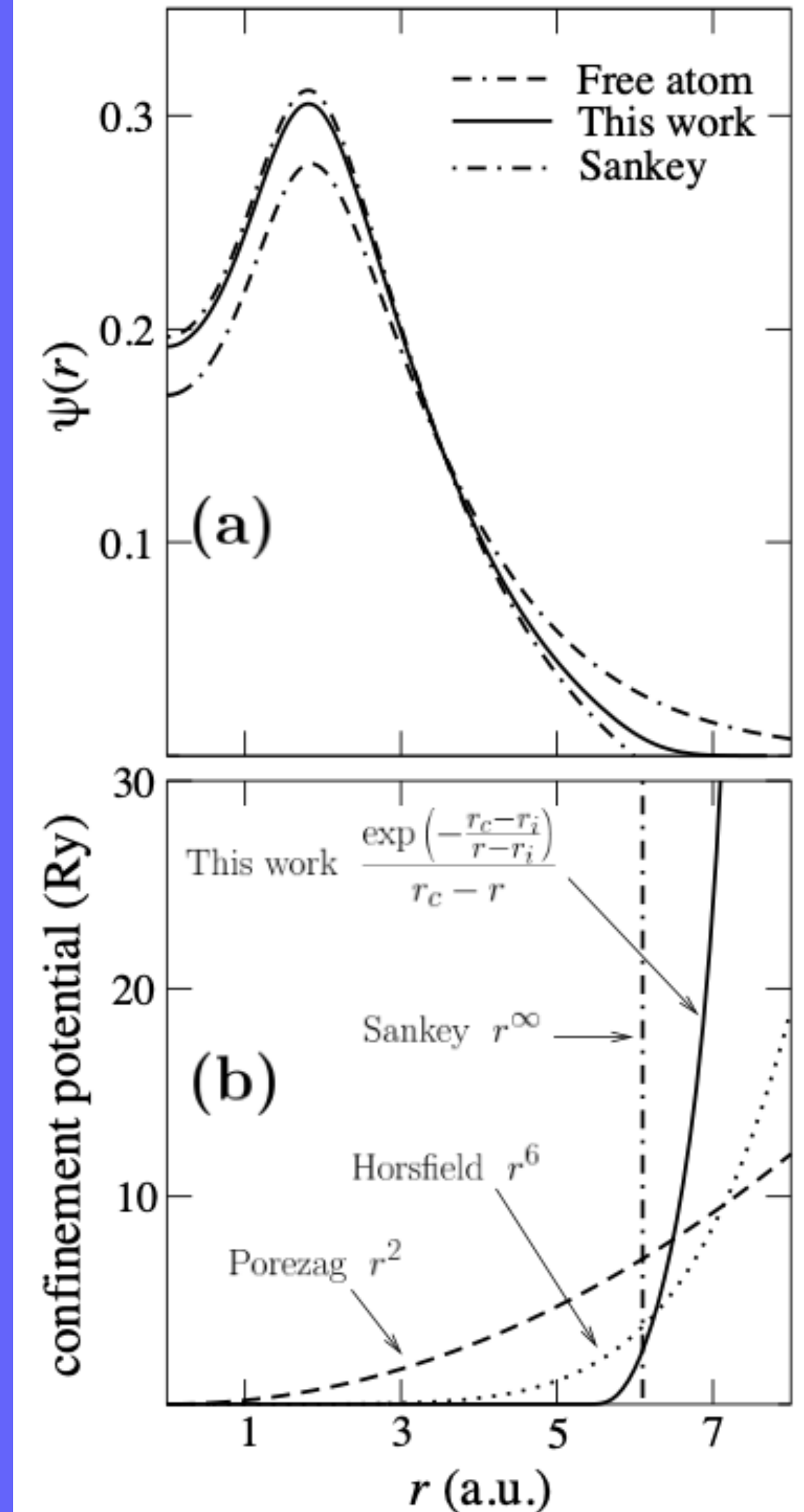
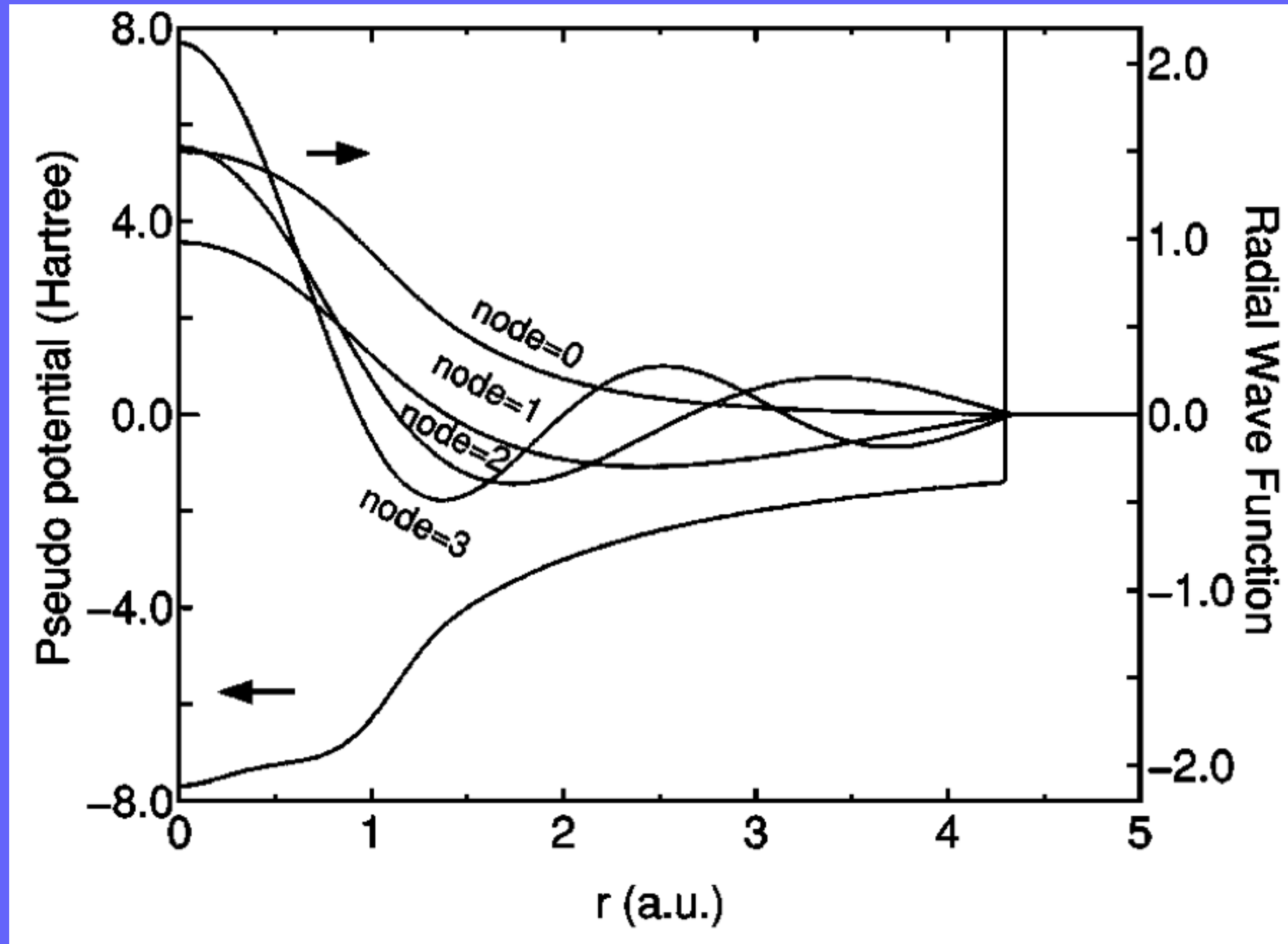


FIG. 1. Shape of the 3s orbital of Mg in MgO for the different confinement schemes (a) and corresponding potentials (b).

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

Expanding radial flexibility

Schemes to generate multiple- ζ basis sets



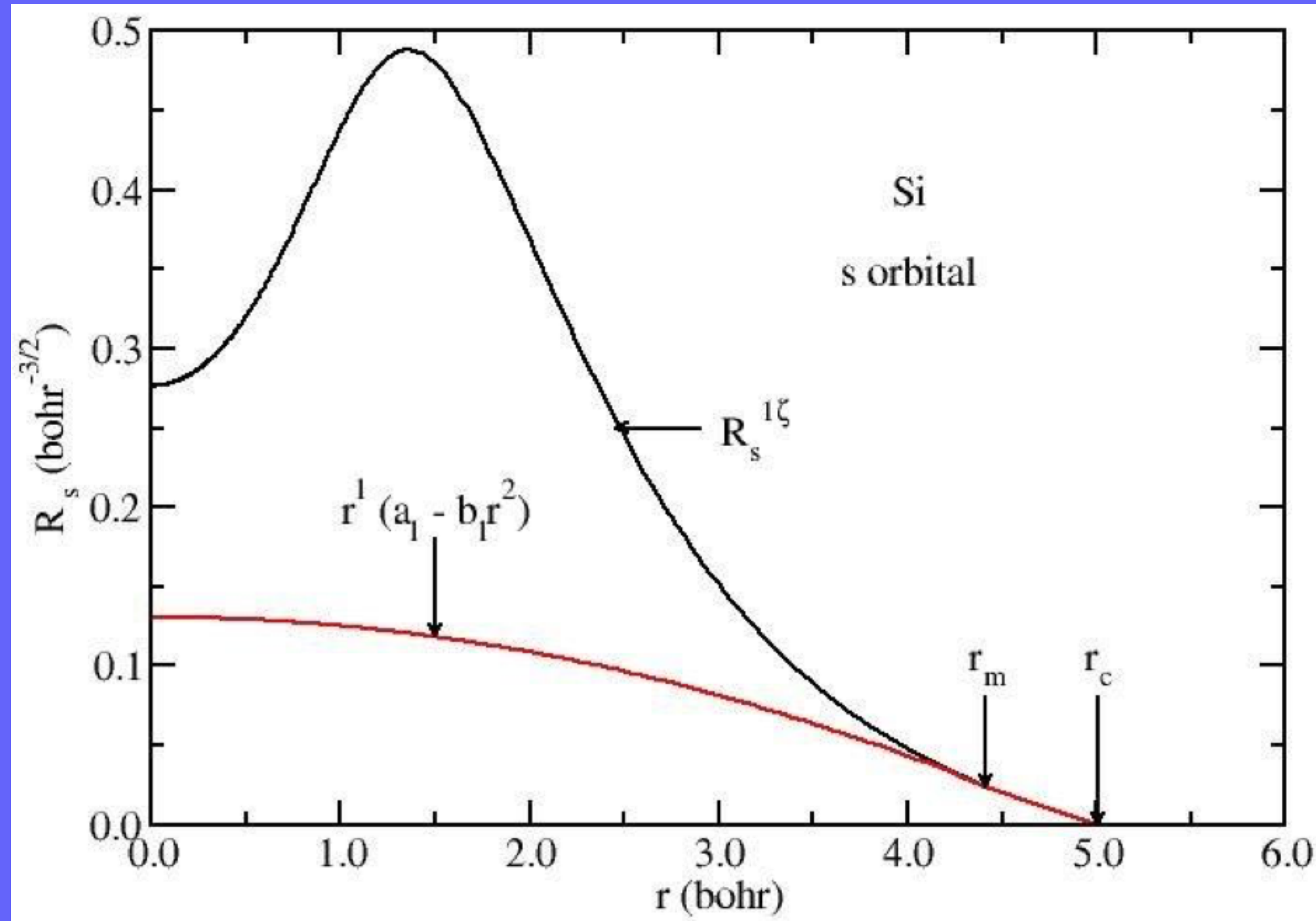
Pseudoatom-wavefunctions with increasing number of nodes:

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

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

Expanding radial flexibility

Schemes to generate multiple- ζ basis sets

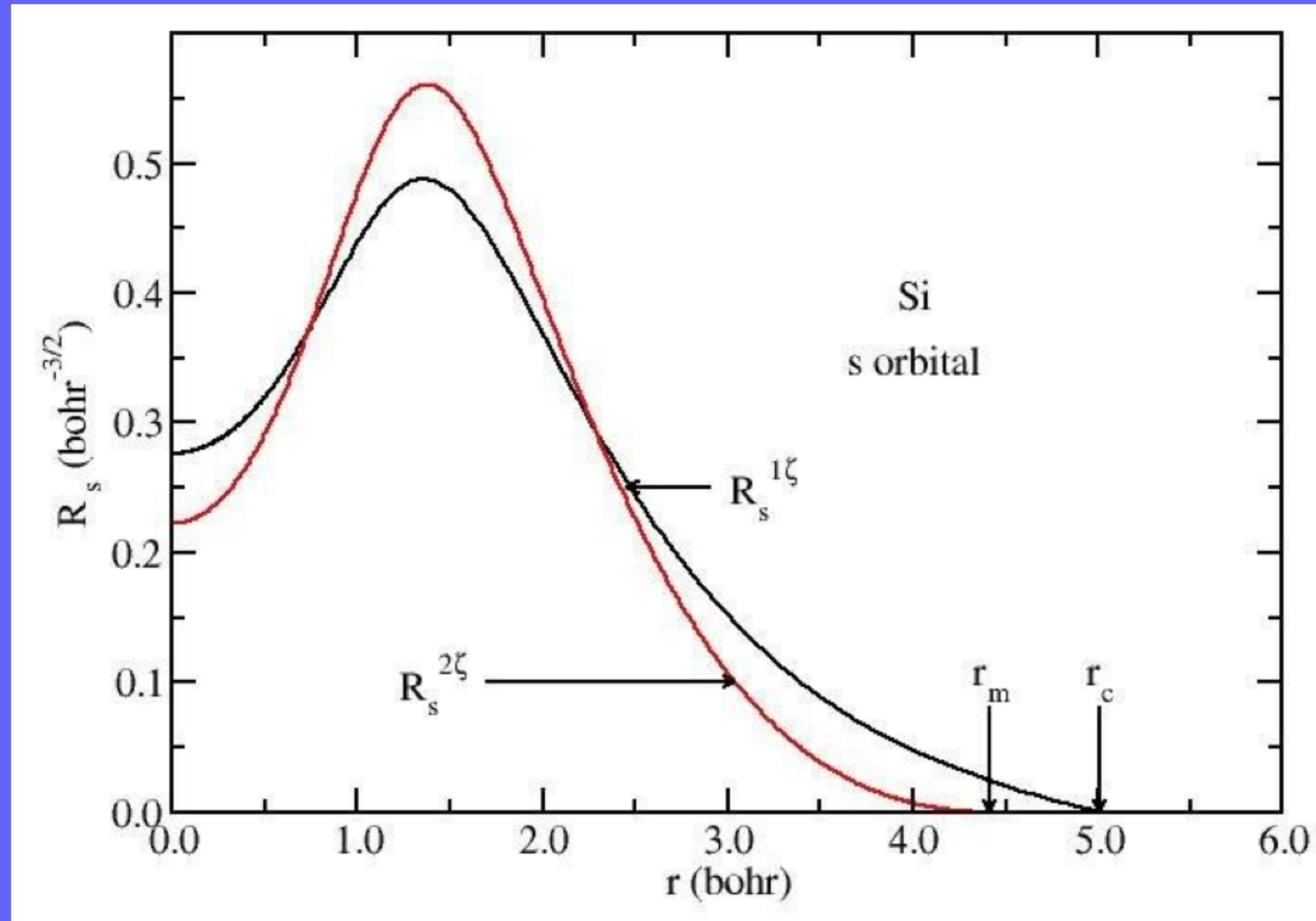


“Split-valence” method

- ▶ 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- ζ is the (normalised) difference between the first- ζ and the function above.

Expanding radial flexibility

Schemes to generate multiple- ζ 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- ζ is the (normalised) difference between the first- ζ and the function above.
- ▶ r_m is controlled with `PAO.SplitNorm` (default is 0.15)

Expanding angular flexibility

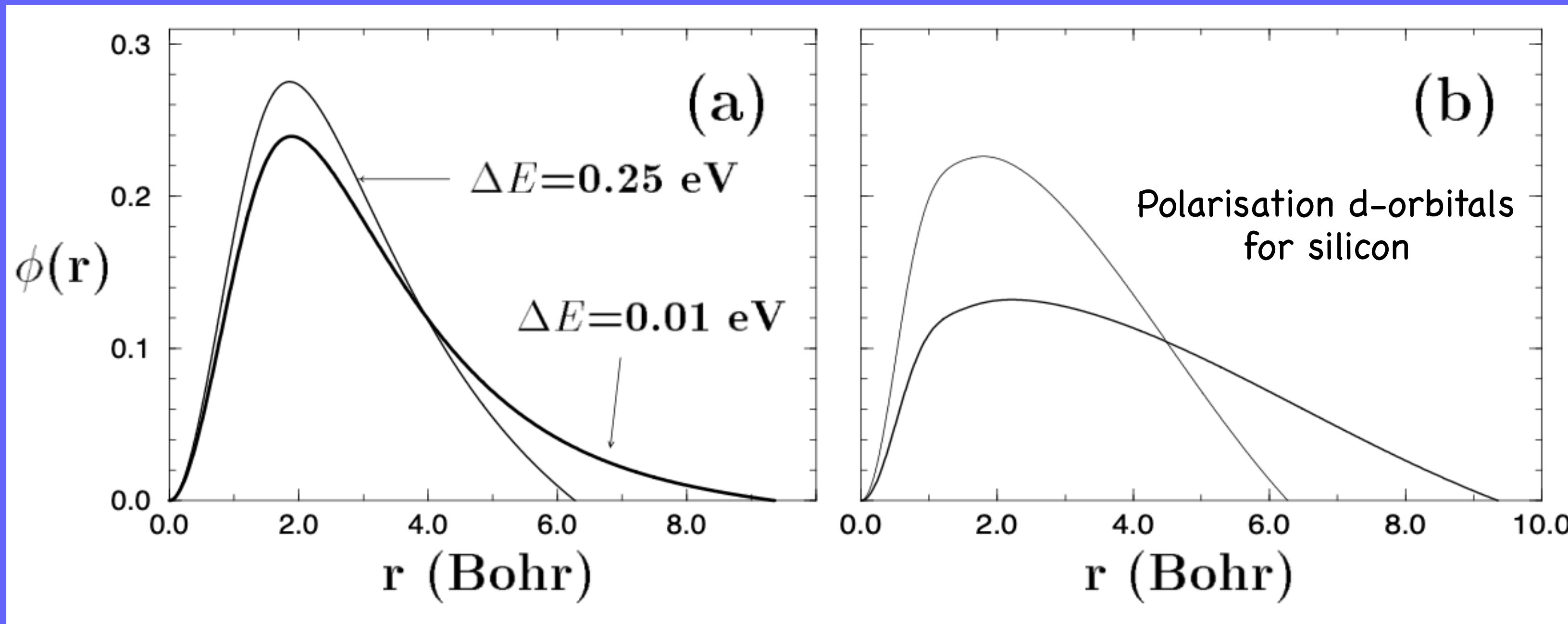
Two schemes to generate polarization orbitals

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 ζ and polarisation by one

Quick/cheap
exploratory
calculations

single- ζ



- General philosophy

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

Highly converged
calculations

+ multiple- ζ
+ polarisation
+ diffuse orbitals

Recap

Standardised tiers

- General procedure:

- Start from SZ
- Every step: increase both ζ 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!!

● 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 CO₂, 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:	PAO.BasisSize	DZP	
Range of first-zeta:	PAO.EnergyShift	0.01 Ry	3–5 mRy
Second-zeta:	PAO.BasisType	Split	
Range of second-zeta:	PAO.SplitNorm	0.15	
Confinement:	PAO.SoftDefault	True	
	PAO.SoftInnerRadius	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
  O    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
  O    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

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Basis sets in SIESTA

Questions?