

Pseudopotentials and Basis Sets



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The Kohn-Sham equations

LDA, GGA

$$E = T_o[\rho] + \int V_{ext} \rho(\vec{r}) d\vec{r} + \frac{1}{2} \int \frac{\rho(\vec{r}) \rho(\vec{r}')}{|\vec{r}' - \vec{r}|} d\vec{r} d\vec{r}' + E_{xc}[\rho]$$

1-electron equations (Kohn Sham)

vary ρ

$$\left\{ -\frac{1}{2} \nabla^2 + V_{ext}(\vec{r}) + V_C(\rho(\vec{r})) + V_{xc}(\rho(\vec{r})) \right\} \Phi_i(\vec{r}) = \varepsilon_i \Phi_i(\vec{r})$$

$$-Z/r$$

$$\int \frac{\rho(\vec{r})}{|\vec{r}' - \vec{r}|} d\vec{r}$$

$$\frac{\partial E_{xc}(\rho)}{\partial \rho}$$

$$\rho(\vec{r}) = \sum_{\varepsilon_i \leq E_F} |\Phi_i|^2$$

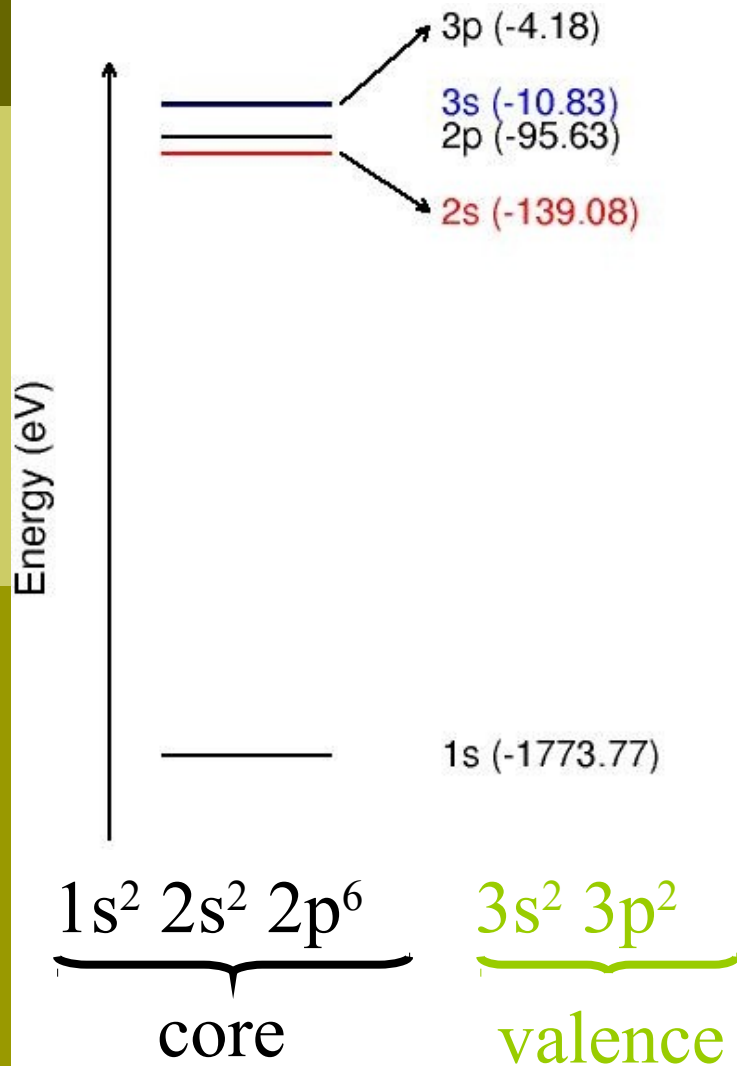
$$E_{xc}^{LDA} \propto \int \rho(r) \varepsilon_{xc}^{hom.}[\rho(r)] dr$$

$$E_{xc}^{GGA} \propto \int \rho(r) F[\rho(r), \nabla \rho(r)] dr$$

LDA } treats both,
exchange and correlation effects,
GGA } but approximately

Pseudopotential idea

Atomic Si

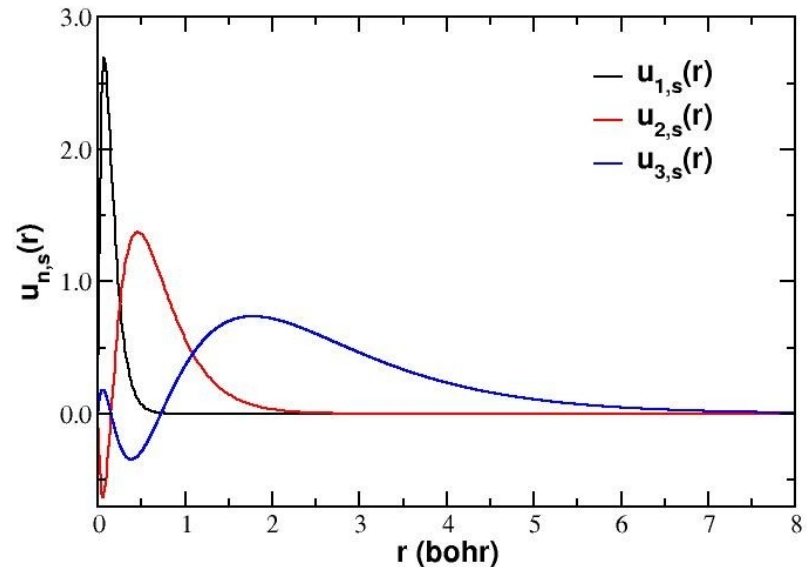


Core electrons...

highly localized

very depth energy

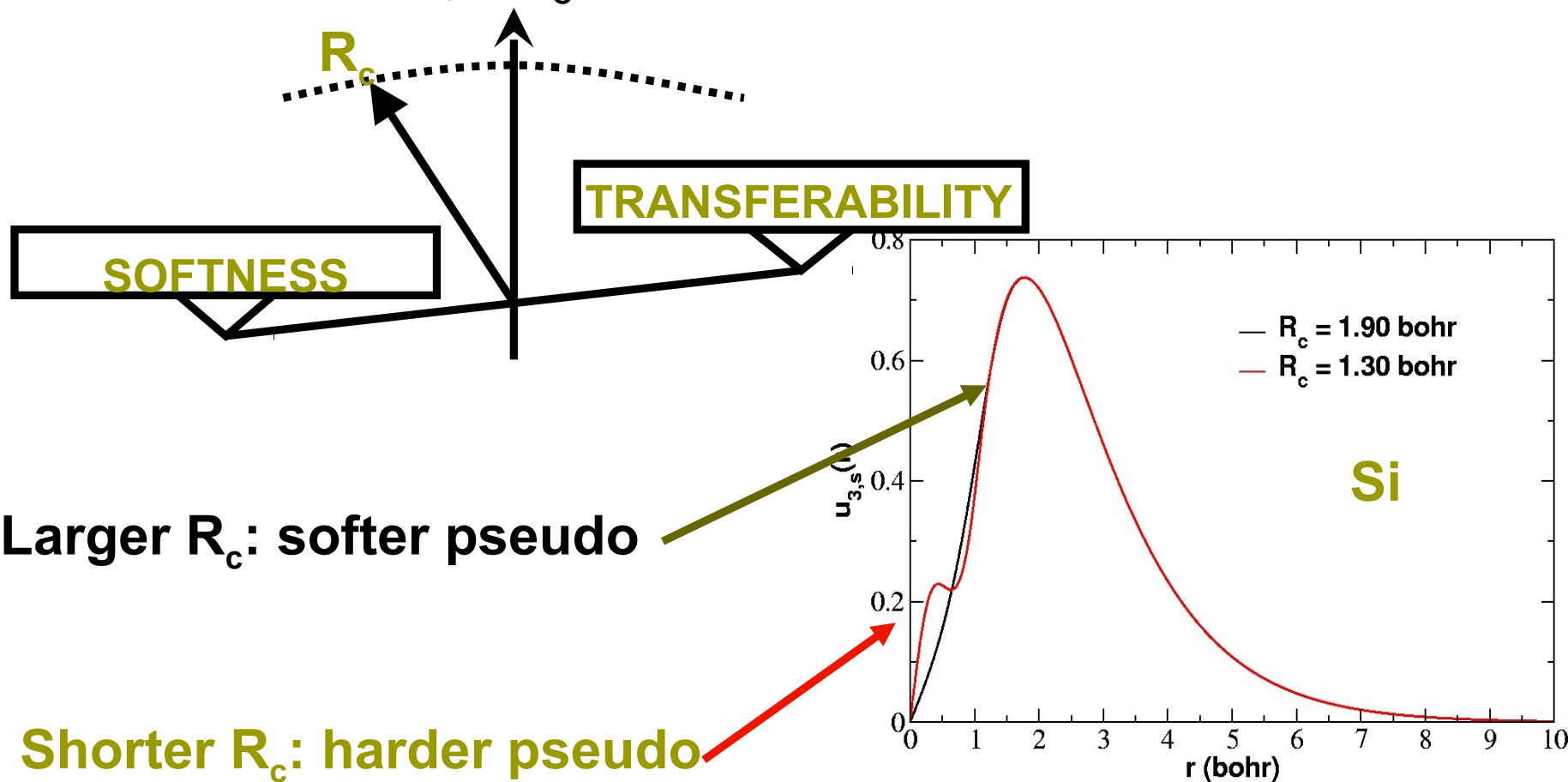
... are chemically inert



Valence wave functions must be orthogonal to the core wave functions

Cut-off radii

Balance between softness and transferability controlled by R_c



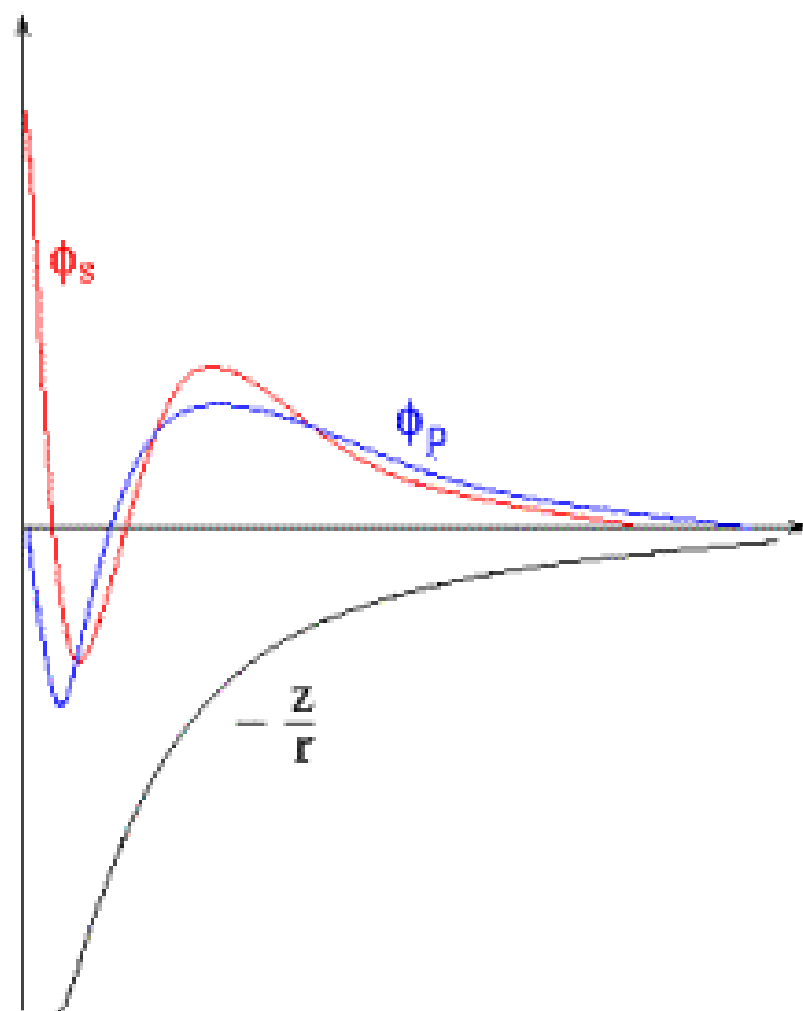
Ab initio pseudopotentials

- ❑ Need of pseudopotentials that are not derived from experimental or ad hoc parameters
- ❑ Must be generated from atomic calculations that are themselves ab initio
- ❑ Should be smooth
- ❑ Should be transferable. Transferability is a very important property of modern pseudopotentials: no need to have different pseudo's for different bonding geometries (for instance C in diamond, graphite, nanotube or fullerene structures). One pseudopotential should give results of comparable accuracy in a broad variety of chemical environments.
- ❑ The answer: **Norm Conserving Pseudopotentials (NCP)**
- ❑ Norm conserving pseudowavefunctions are normalized and solution of a model potential chosen to reproduce the valence properties of an all-electron calculation - no need to add a smooth and a hard part as in OPW
- ❑ Pseudowavefunctions are orthogonal and are thus solution of a set of K-S equation of the usual form

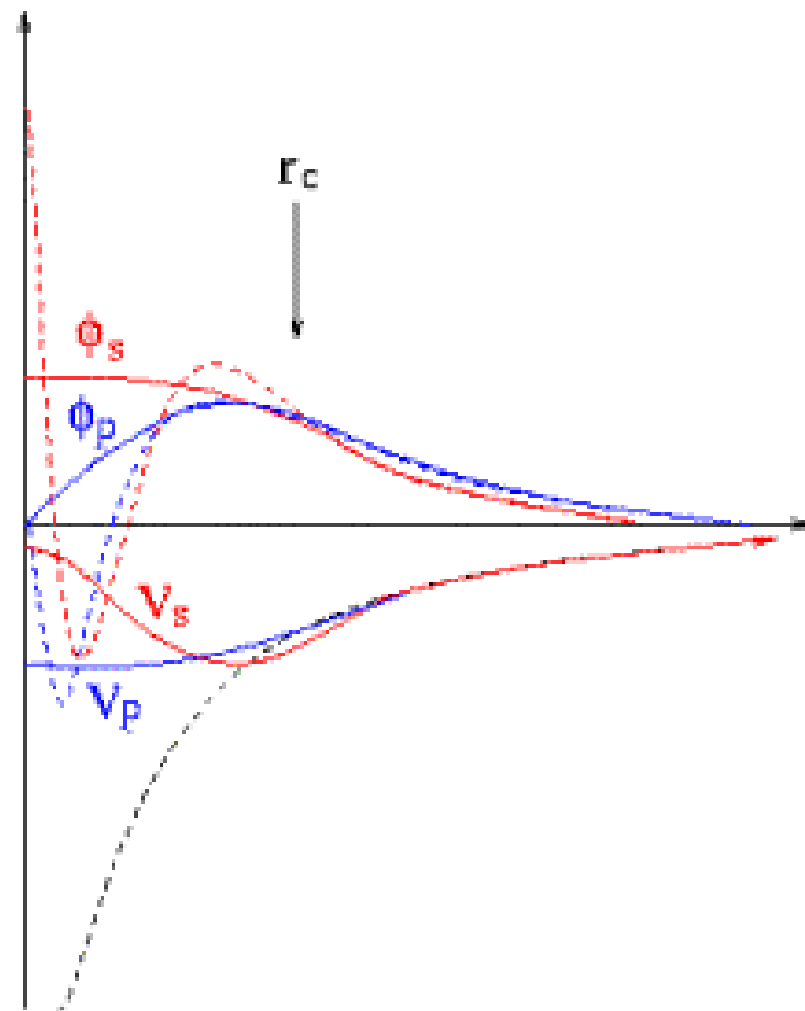
Norm conserving pseudopotentials

- Condition for a good norm-conserving pseudopotential:
 1. All-electron and pseudo valence eigenvalues agree for the chosen atomic configuration
 2. All-electron and pseudo valence wavefunction agree beyond a chosen cut-off radius, R_c
 3. The logarithmic derivatives of the all-electron and pseudo wavefunction agree at R_c
 4. The integrated charge inside R_c for each wavefunction agrees (norm conservation)
 5. The first energy derivative of the logarithmic derivatives of all-electron and pseudo wavefunctions agree at R_c
- 1. and 2. Ensure that the NCPP and the true potential are the same outside the core region
- 3. ensures that the pseudo wavefunctions satisfy continuity conditions
- 4. imposes the conservation of the charge in the core region and that the normalized pseudo-orbital and true orbital are equal outside the core region
- 5. although more obscure, it is crucial for the generation of a good, transferable ab initio pseudopotential

Original wavefunctions
and potential

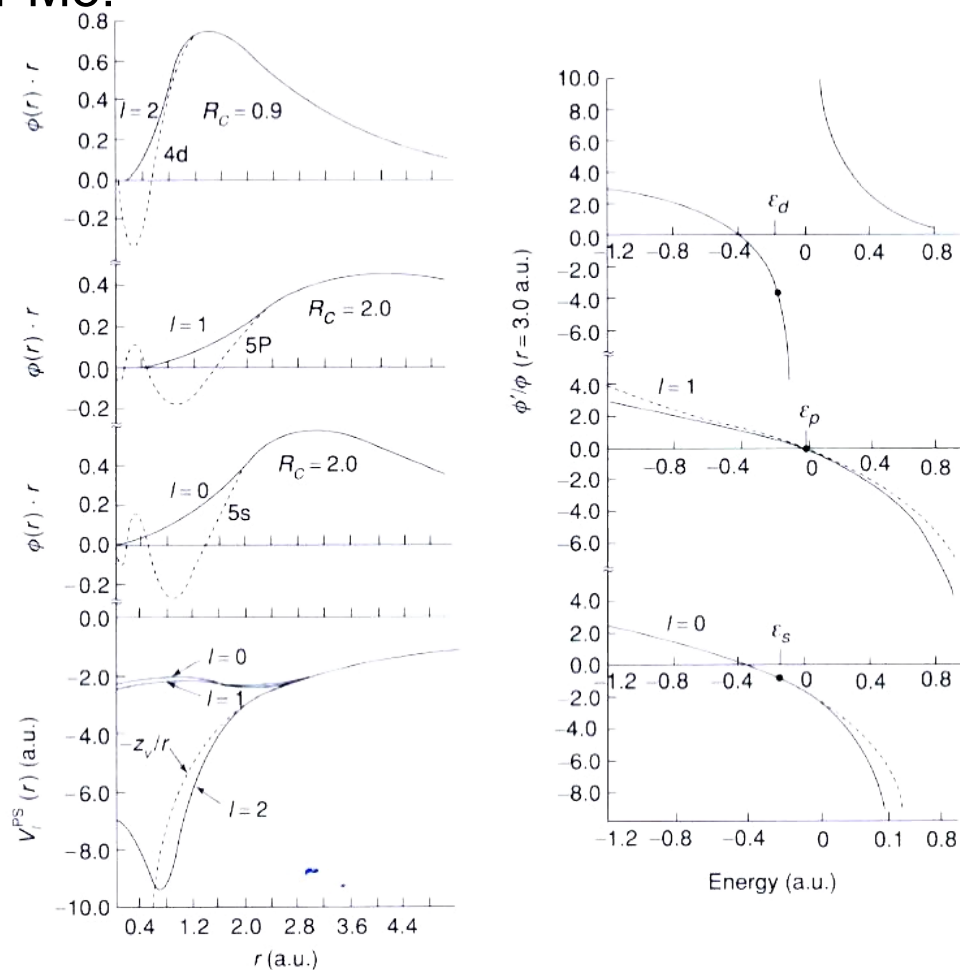


The pseudo-wavefunctions
and potentials



Norm conserving pseudopotentials

- An example: pseudopotential, pseudowavefunctions and logarithmic derivatives for Mo:



Norm conserving pseudopotentials

- How to construct a pseudopotential:
 - Solve the atomic all-electron problem for a given electronic configuration where each state l, m is treated independently
 - Ab initio self consistent calculation
 - Only approximation: choice of the exchange and correlation functional
 - Identify the valence states and generate the pseudopotentials $V_l(r)$ and pseudo-orbitals $\psi_l^{\text{ps}}(r)$
 - Various procedures can be followed to generate a pseudopotential that satisfies the criteria we gave above (Bachelet-Hamman-Schluter, Troullier-Martins, vanBarth-Car, Rappe-Rabe-Kaxiras-Joannopoulos, etc.). In general, it amounts to some kind of numerical fitting procedure within the boundaries of norm-conservation.
 - PP's are usually written as a sum of a local potential (non l -dependent) and a non-local part (l -dependent):
$$V_l(r) = V_{\text{loc}}(r) + \delta V_l(r)$$
 - The local part reproduces the behavior of the all-electron potential for large r ($r \rightarrow \infty$).

Norm conserving pseudopotentials

□ General considerations:

- There is no one “best pseudopotential” for a given atom. There might be many best choices, each optimized for some particular use.
- Accuracy and transferability generally lead to the choice of a small cut-off radius. “Hard” pseudopotentials, more oscillations since we want to describe accurately the behavior near the ion. Demanding on the dimension of the PW basis set!
- Smoothness generally leads to a choice of a larger cut-off radius. “Soft” pseudopotentials can be described well by fewer basis functions

Different methods to generate norm-conserving pseudopotential

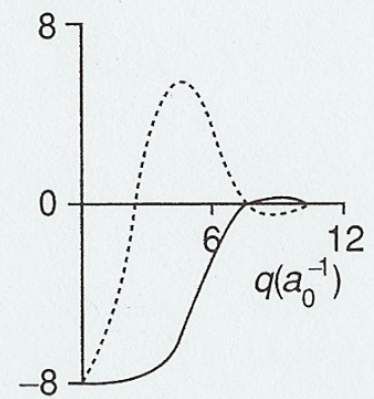
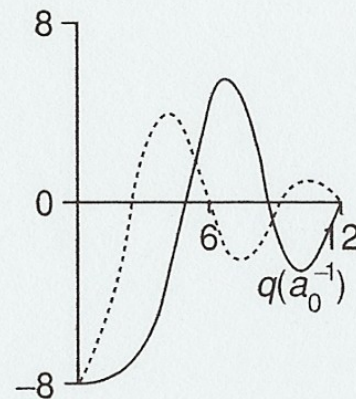
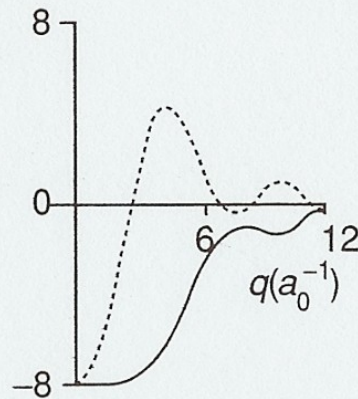
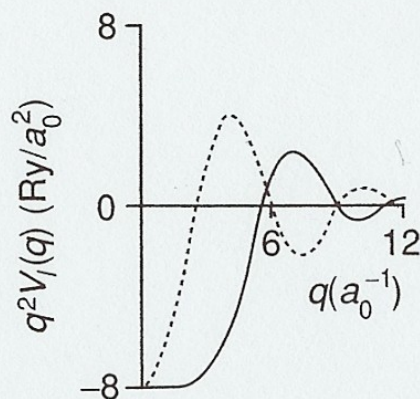
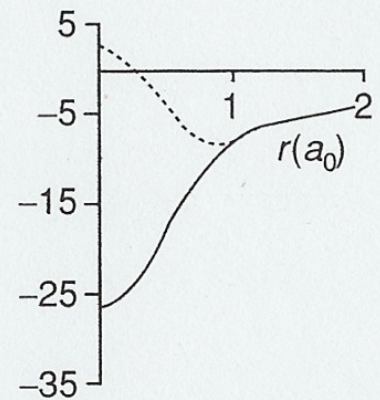
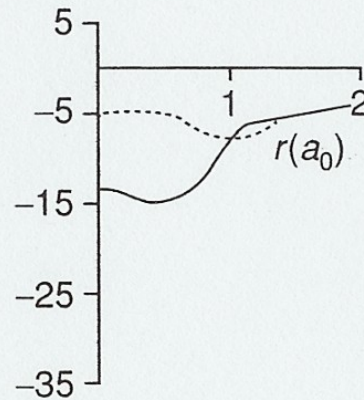
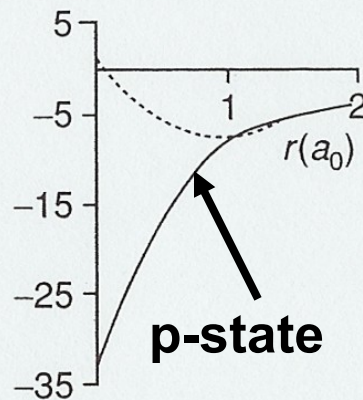
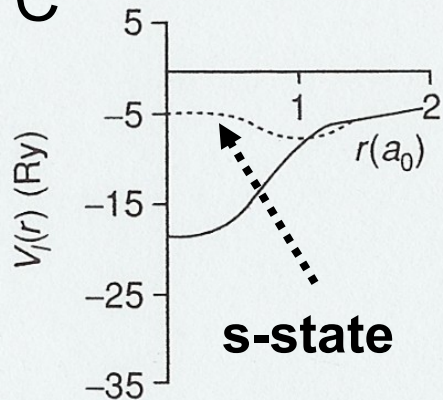
Troullier-Martins

Kerker

Haman-Schlüter-
Chiang

Vanderbilt

C



The “*atom*” program

“pseudopotential generation” label

xc flavor

```
#
# Pseudopotential generation for Silicon
# pg: simple generation
#
pg Silicon
tm2 3.0 # PS flavor, logder R
n=Si c=car # Symbol, XC flavor,{ |r|s}
0.0 0.0 0.0 0.0 0.0 0.0
3 4 # norbs_core, norbs_valence
3 0 2.00 0.00 # 3s2
3 1 2.00 0.00 # 3p2
3 2 0.00 0.00 # 3d0
4 3 0.00 0.00 # 4f0
1.90 1.90 1.90 1.90 0.00 0.00
#
# Last line (above):
# rc(s) rc(p) rc(d) rc(f) rcore_flag rcore
#
#23456789012345678901234567890123456789012345678901234567890
```

valence shells

#core orbitals

$$n$$

1

Valence configuration

Cutoff radii

Procedure (I)

- Run the shell script (pg.sh)

```
pg.sh Si.tm2.inp
```

```
==> Output data in directory Si.tm2
```

```
==> Pseudopotential in Si.tm2.vps and Si.tm2.psf (and maybe in Si.tm2.xml)
```

- Check contents of new directory (Si.tm2)

```
$ ls Si.tm2
```

AECHARGE	AEWFNR3	PSLOGD3	PSPOTR3	PSWFNR3	charge.gplot
AELOGD0	CHARGE	PSPOTQ0	PSWFNQ0	RHO	charge.gps
AELOGD1	INP	PSPOTQ1	PSWFNQ1	SCRPSPOTR0	pots.gplot
AELOGD2	OUT	PSPOTQ2	PSWFNQ2	SCRPSPOTR1	pots.gps
AELOGD3	PSCHARGE	PSPOTQ3	PSWFNQ3	SCRPSPOTR2	pseudo.gplot
AEWFNR0	PSLOGD0	PSPOTR0	PSWFNR0	SCRPSPOTR3	pseudo.gps
AEWFNR1	PSLOGD1	PSPOTR1	PSWFNR1	VPSFMT	pt.gplot
AEWFNR2	PSLOGD2	PSPOTR2	PSWFNR2	VPSOUT	pt.gps

- Plot the pseudo-potentials/orbitals

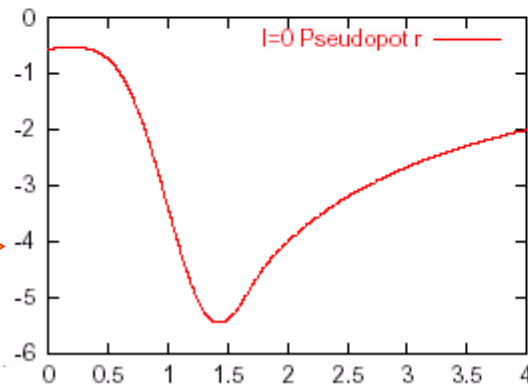
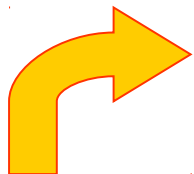
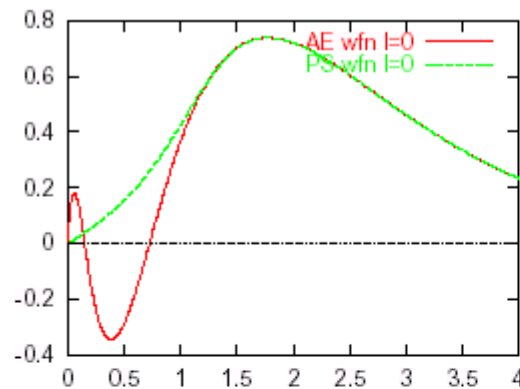
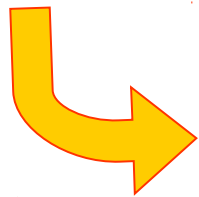
```
$ cd Si.tm2
```

```
$ gnuplot pseudo.gps
```

```
==> Postscript output in pseudo.ps
```

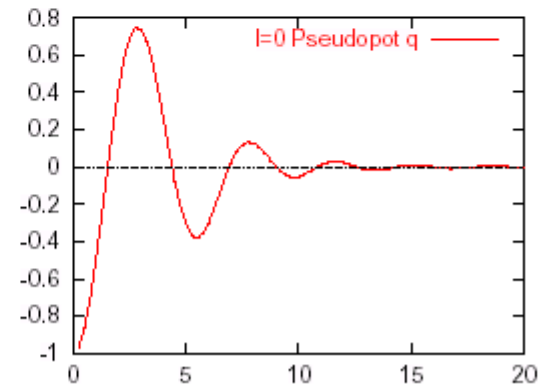
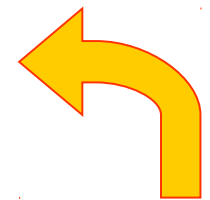
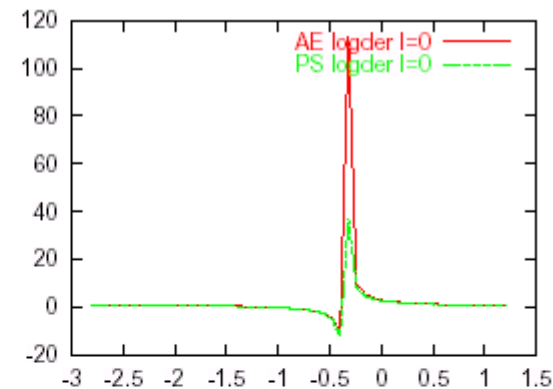
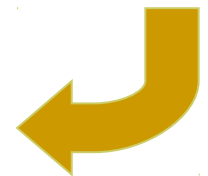
Procedure (II)

Pseudo-wave
function



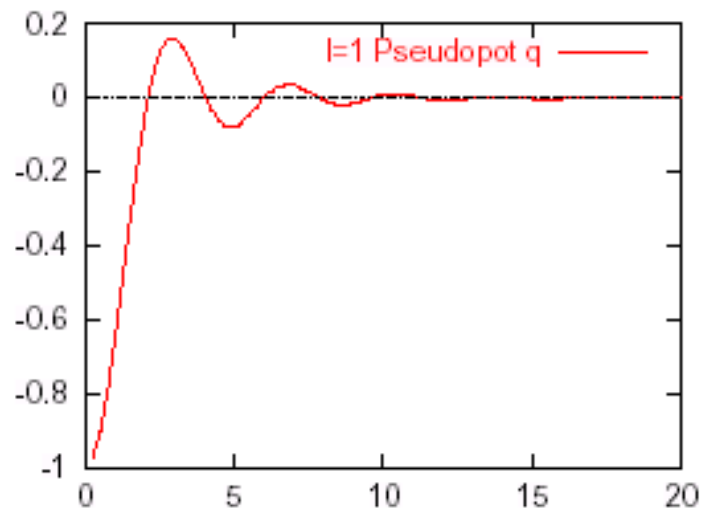
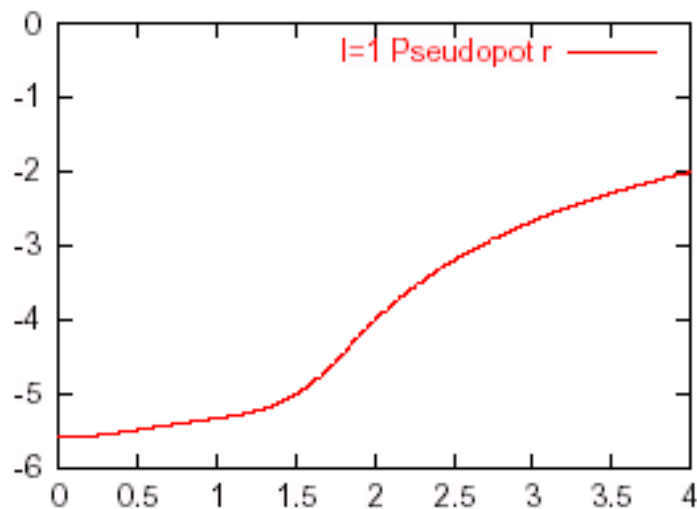
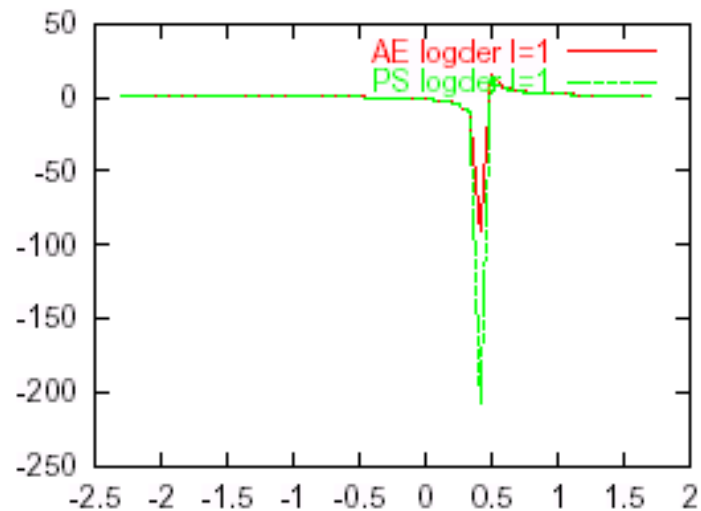
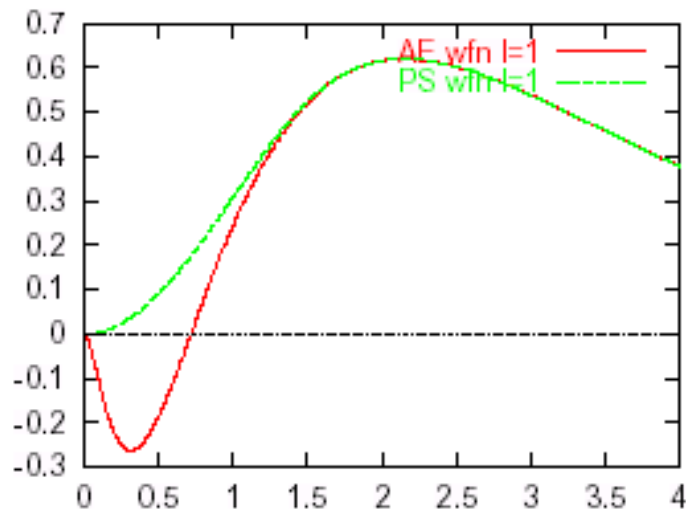
Pseudopotential

Logarithmic
derivative



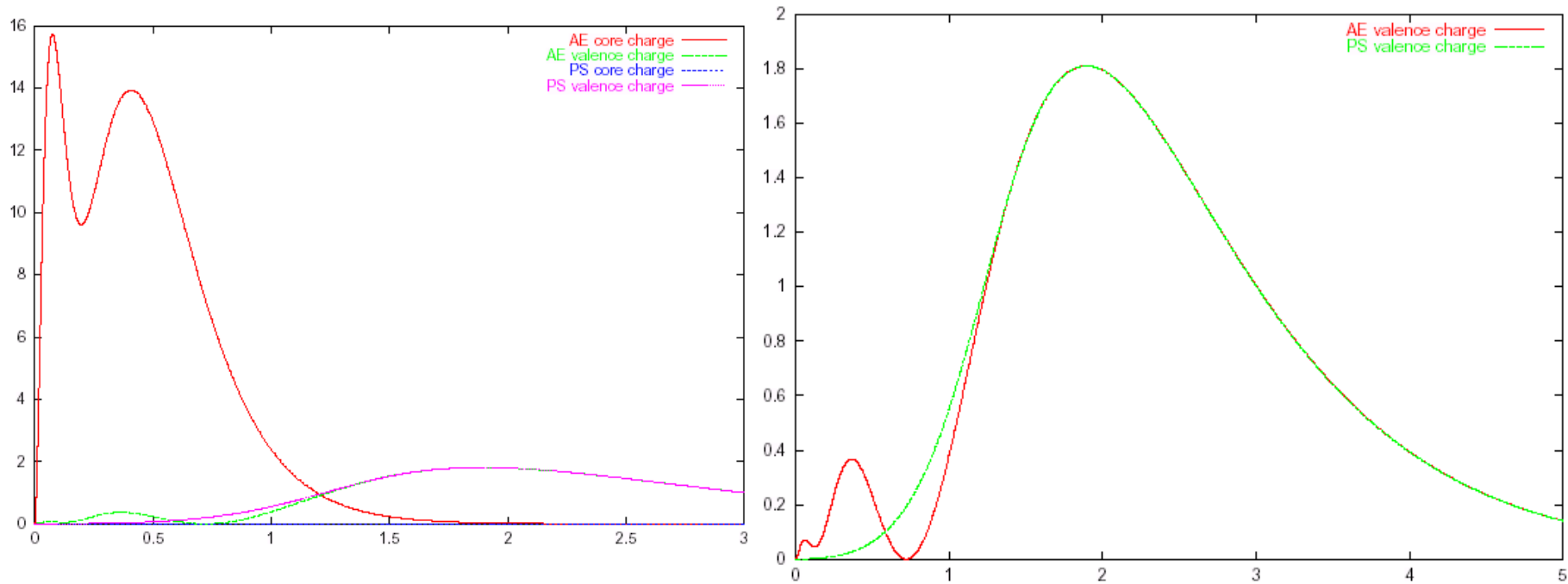
Radial
Fourier-T

Procedure (III)



Radial charge distribution:

- Compare all-electron with pseudo-charge



Pseudopotential testing (I)

The *all-electron* ([ae.sh](#)) and *pseudo-test* ([pt.sh](#)) scripts:

```
ae Si Test -- 3s0 3p3 3d1
Si   ca
    0.0
  3   3
  3   0      0.00
  3   1      3.00
  3   2      1.00
```

```
pt Si Test -- 3s0 3p3 3d1
Si   ca
    0.0
  3   3
  3   0      0.00
  3   1      3.00
  3   2      1.00
```

[run script](#) [input](#) [pseudopotential to test](#)

```
sh ../pt.sh Si.test.inp Si.tm2.vps
Output data in directory Si.test-Si.tm2...
```

Pseudopotential testing (II)

```
$ cd Si.test-Si.tm2
```

```
$ ls [A-Z]*
```

```
AECHARGE  AEFN1R1  CHARGE  OUT      PTWFNR0  PTWFNR2  VPSIN
AEWFNR0    AEFN1R2  INP      PTCHARGE PTWFNR1  RHO
```

```
$
```

```
$ ## EIGENVALUE TEST
```

```
$
```

```
$ grep '&v' OUT
```

```
ATM3      11-JUL-02  Si Test -- 3s0 3p3 3d1
3s   0.0    0.0000    -1.14358268      3.71462770
3p   0.0    3.0000    -0.60149474      2.68964513
3d   0.0    1.0000    -0.04725203      0.46423687
```

*A transferable pseudo will
reproduce the AE energy levels
and wave functions in arbitrary
environments*

```
-----
ATM3      11-JUL-02  Si Test -- 3s0 3p3 3d1
1s   0.0    0.0000    -1.14353959      0.56945741
2p   0.0    3.0000    -0.59931810      0.95613808
3d   0.0    1.0000    -0.04733135      0.45664551
-----
```

Pseudopotential testing (III)

- Compute the energy of two different configurations E_{C1} E_{C2}
- Compute the difference in energy $\Delta E = E_{C2} - E_{C1}$
- For the pseudopotential to be transferible: $\Delta E^{AE} = \Delta E^{PS}$

&d total energy differences in series

&d	1	2	3	4	5
&d 1	0.0000				
&d 2	0.4308	0.0000			
&d 3	0.4961	0.0653	0.0000		
&d 4	0.9613	0.5305	0.4652	0.0000	
&d 5	1.4997	1.0689	1.0036	0.5384	0.0000

ΔE^{AE}

→ **3s² 3p² (reference)**

→ **3s² 3p¹ 3d¹**

→ **3s¹ 3p³**

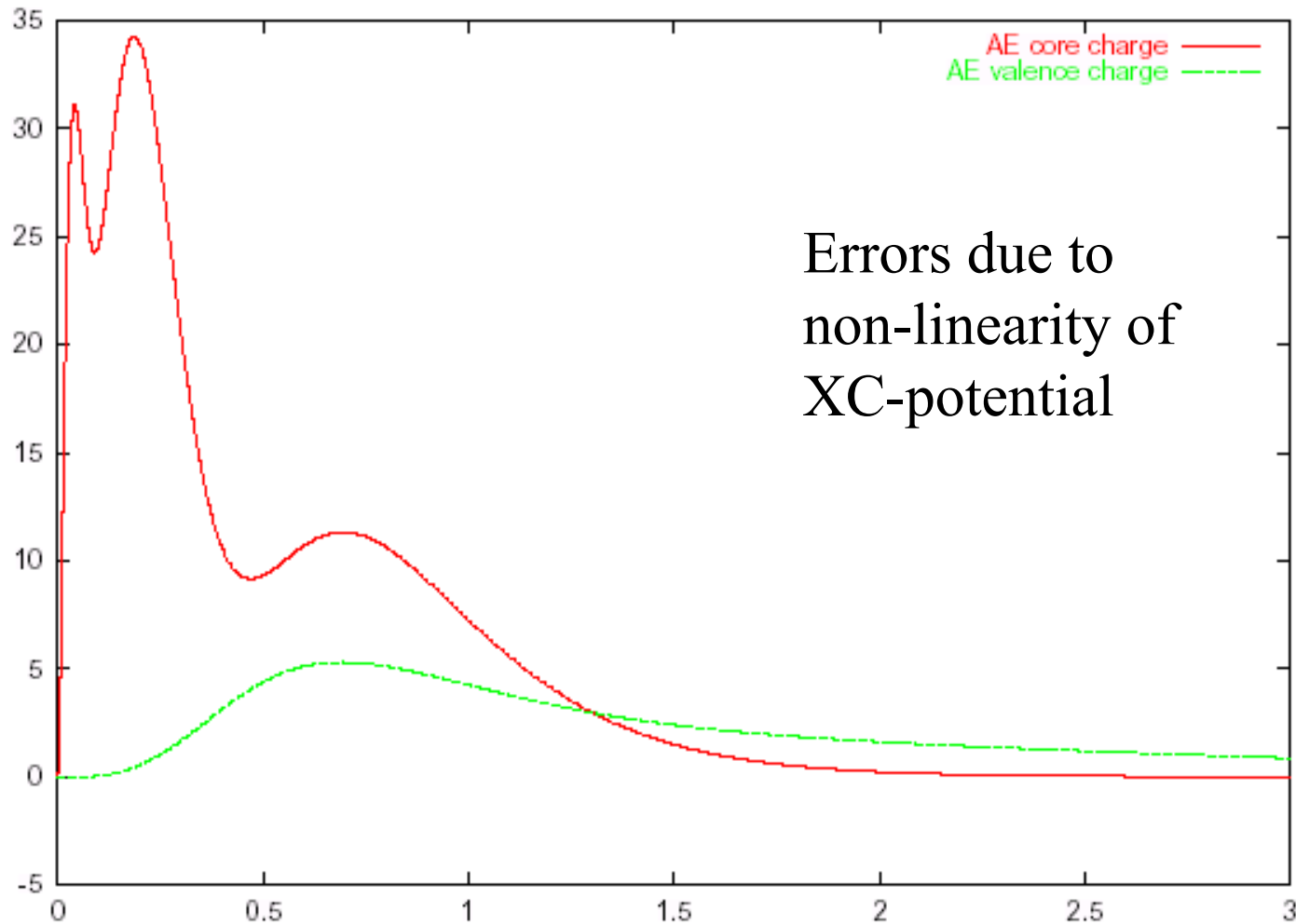
→ **3s¹ 3p² 3d¹**

→ **3s⁰ 3p³ 3d¹**

&d	1	2	3	4	5
&d 1	0.0000				
&d 2	0.4299	0.0000			
&d 3	0.4993	0.0694	0.0000		
&d 4	0.9635	0.5336	0.4642	0.0000	
&d 5	1.5044	1.0745	1.0051	0.5409	0.0000

ΔE^{PS}

Large core-valence overlap



Non-linear core corrections

Standard pseudopotential unscreening: Valence charge only

$$V^{ps} = V_{scr}^{ps}[\rho_v](r) - V_H[\rho_v](r) - V_{xc}[\rho_v](r)$$

However...

$$V_{xc}[\rho_v + \rho_c](r) \neq V_{xc}[\rho_v](r) + V_{xc}[\rho_c](r)$$

Core-correction

$$\tilde{V}_{xc} = V_{xc}[\rho_v] + \{V_{xc}[\rho_v + \rho_c] - V_{xc}[\rho_v]\}$$

Keep core charge in pseudopotential generation

$$V^{ps}(r) = V_{scr}^{ps}[\rho_v + \rho_c](r) - V_H[\rho_v](r) - V_{xc}[\rho_v + \rho_c](r)$$

PCC input file

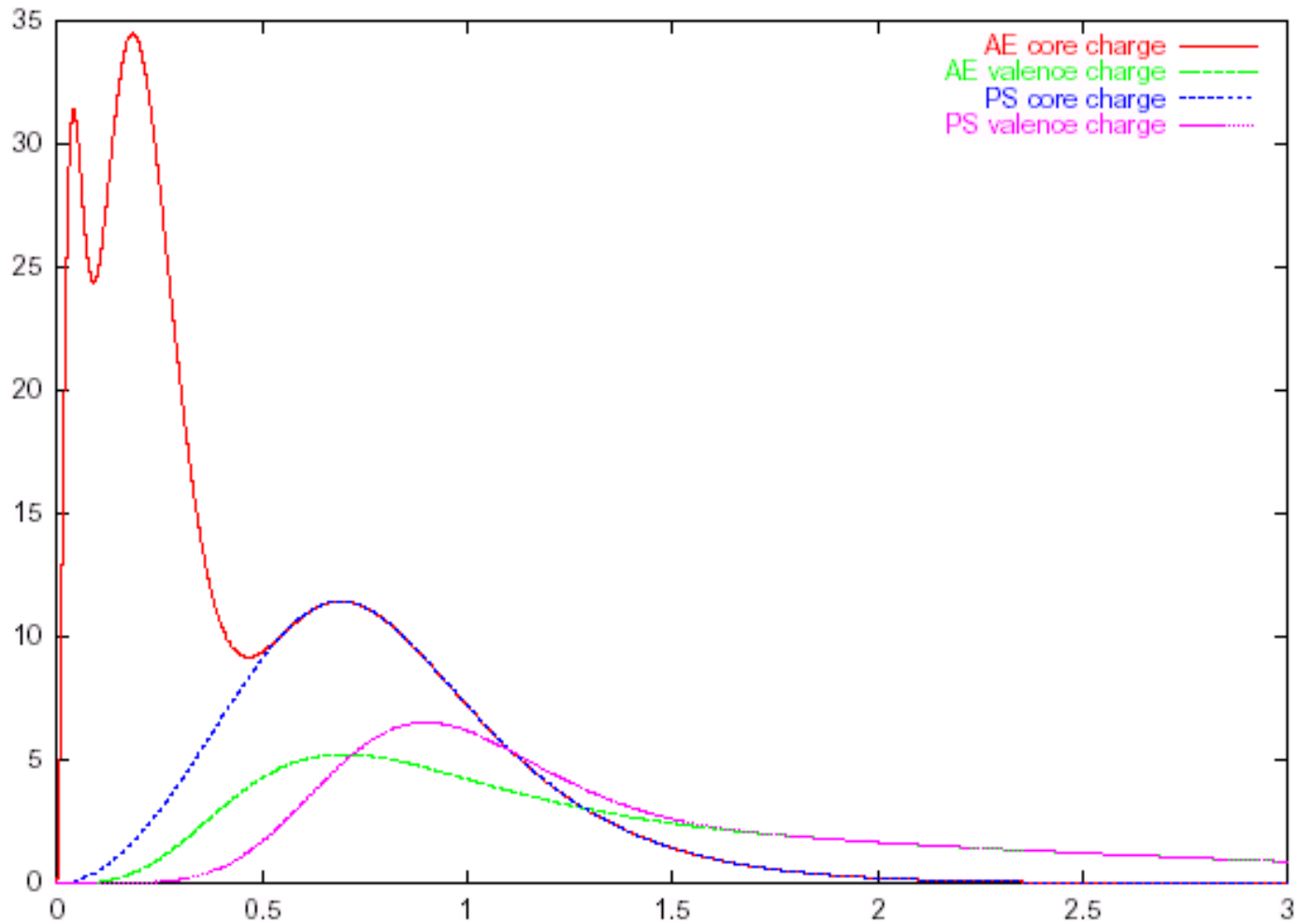
New flag



```
#
# PS generation with core corrections
# GGA (Perdew-Burke-Ernzerhof) XC , relativistic
#
pe Fe, GGA, rcore=0.70
tm2 3.0
n=Fe c=pbr
0.0 0.0 0.0 0.0 0.0 0.0
5 4
4 0 2.00 0.00 # 4s2
4 1 0.00 0.00 # 4p0
3 2 6.00 0.00 # 3d6
4 3 0.00 0.00 # 4f0
2.00 2.00 2.00 2.00 0.00 0.70
#
# Radius of pseudocore
```

The input file defines a pseudopotential (PS) generation for Iron (Fe) using the GGA (Perdew-Burke-Ernzerhof) exchange-correlation functional, relativistic treatment, and core corrections. The 'pe' flag is highlighted as a new flag. The 'rcore=0.70' parameter is also highlighted, with a vertical line indicating it corresponds to the 'Radius of pseudocore'.

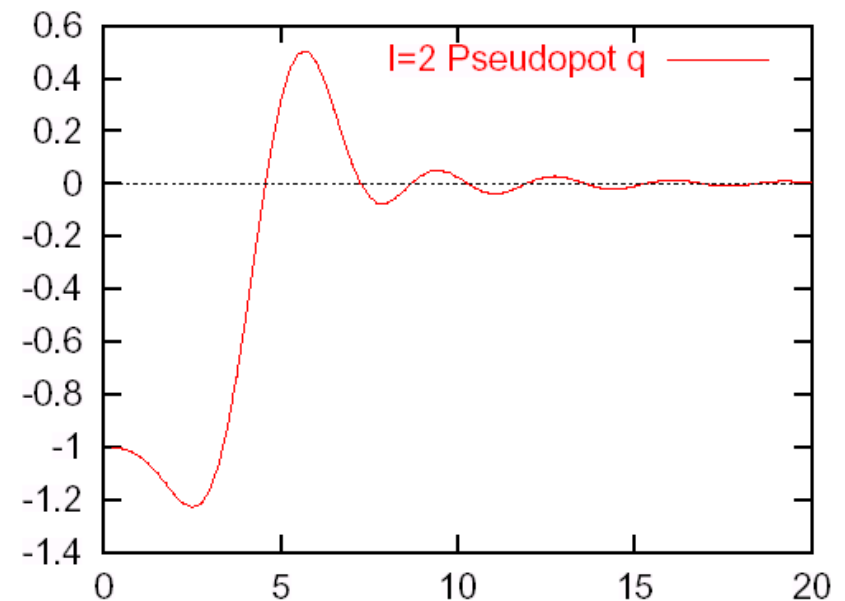
Pseudo-core & pseudo-valence charge



Smooth Fourier Transform

The real-space grid required fineness depends on how you define the pseudopotential. The *meshcutoff* parameter can be determined from the Fourier Transform.

$$\text{Cutoff} = (q_{\max})^2$$

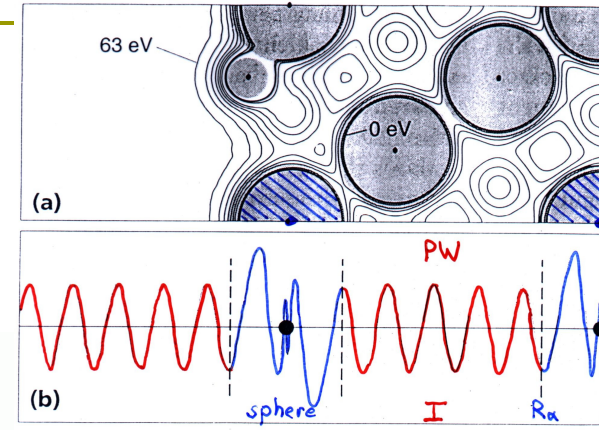


Basis generation

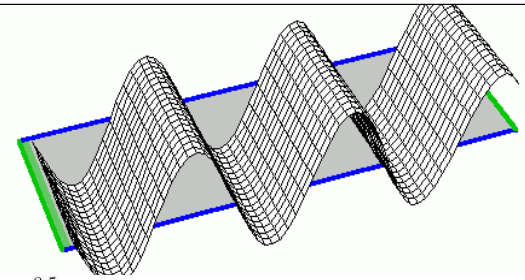


Three main families of methods depending on the basis sets

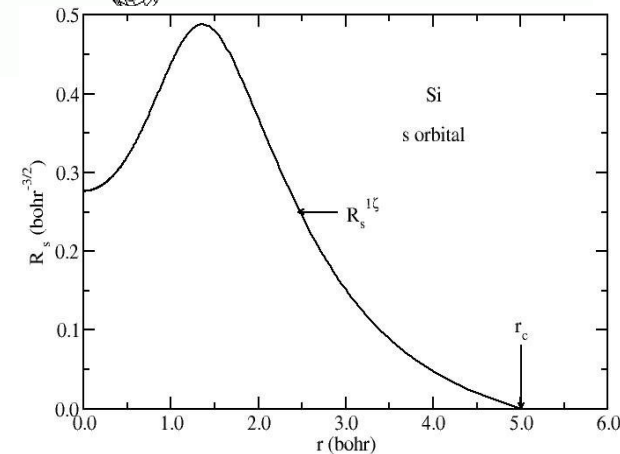
Atomic sphere methods



Plane wave and grids

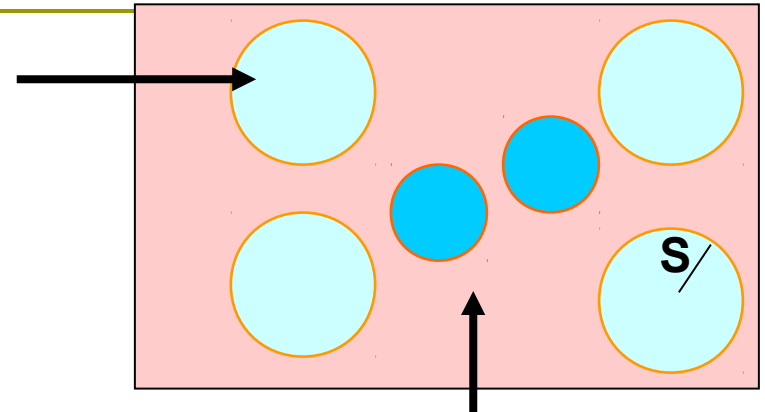
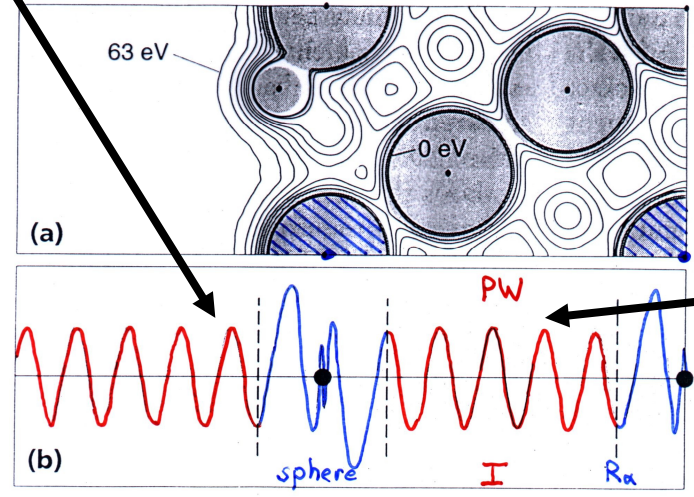


Localized basis sets



Atomic spheres methods:

Efficient representation of atomic like features near each nucleus



Smoothly varying functions between the atoms

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 Method

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

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

ADVANTAGES

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

DISADVANTAGES

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

Plane wave methods (intertwined with pseudopotentials)

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

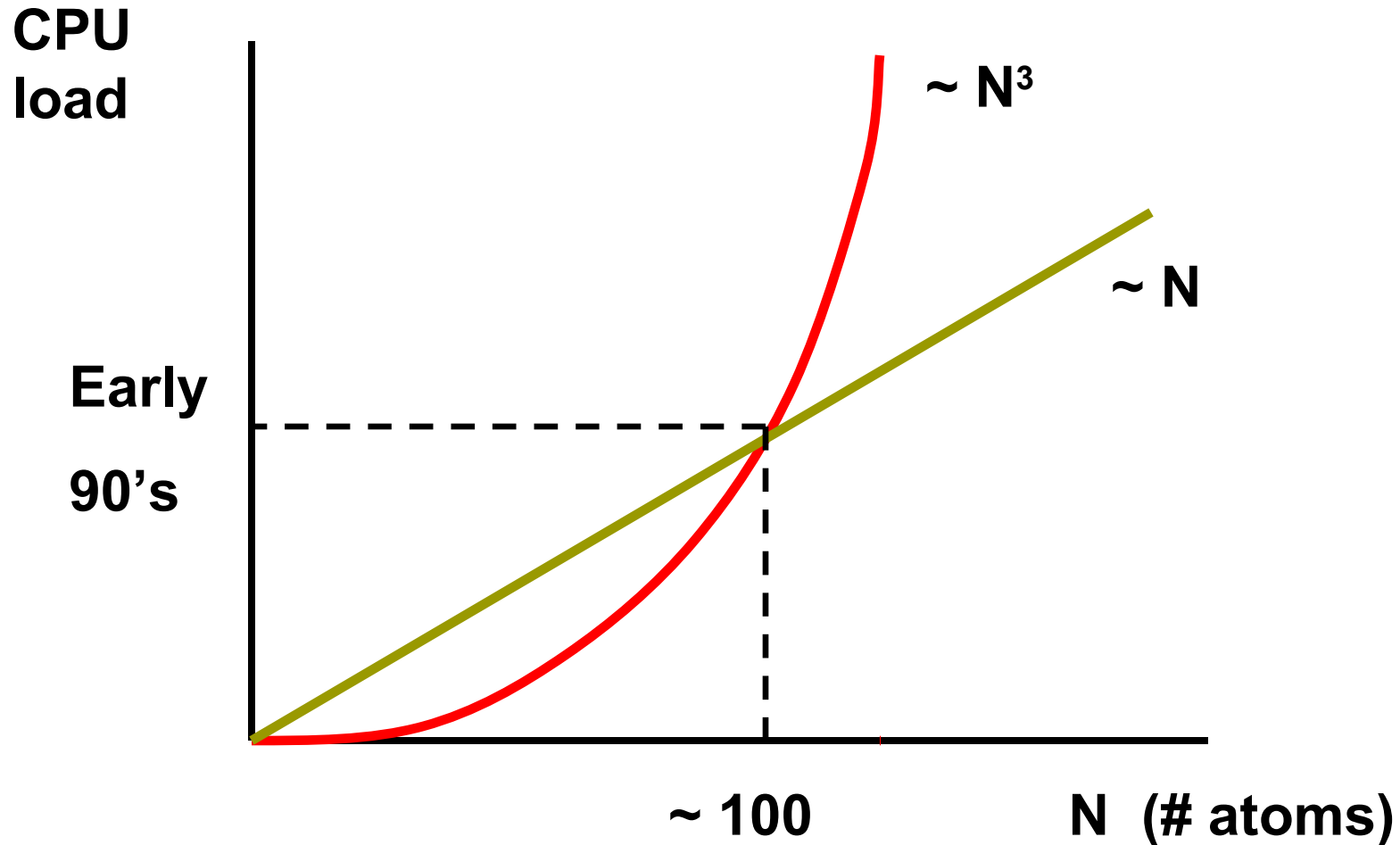
ADVANTAGES

- 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 wave functions per atom to achieve a good accuracy
- Intrinsic inadequacy for Order-N methods (extended over the whole system)

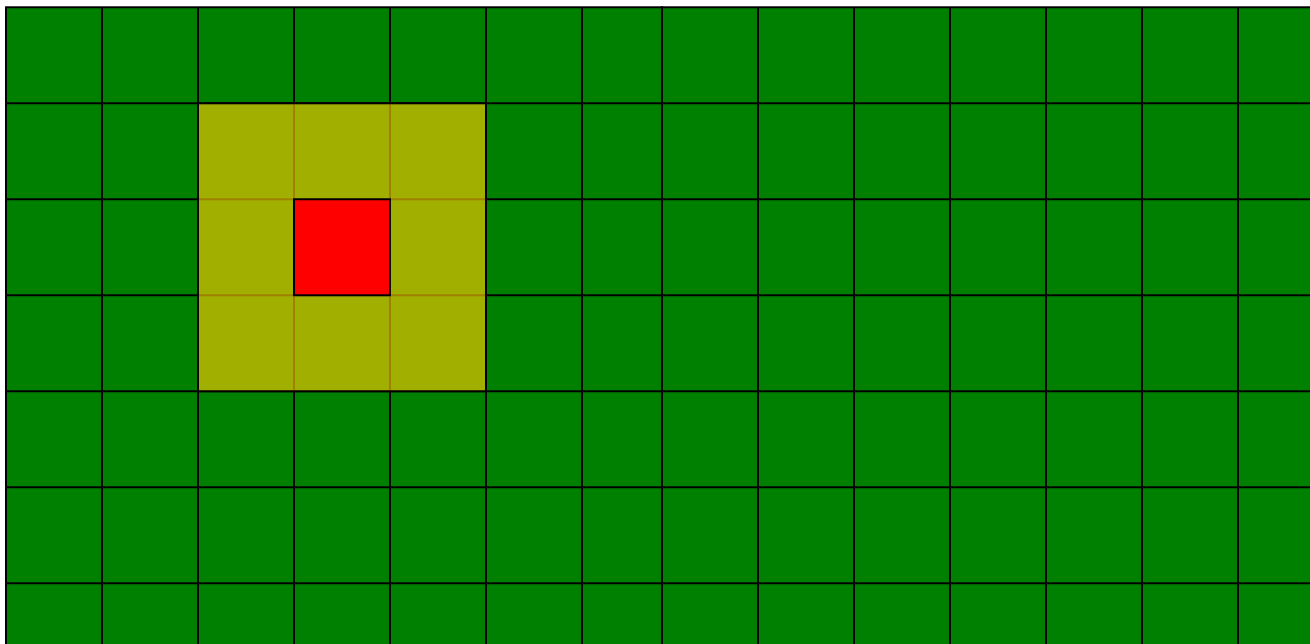
Order-N methods: The computational load scales linearly with the system size



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

Key for linear-scaling: LOCALITY

Large system



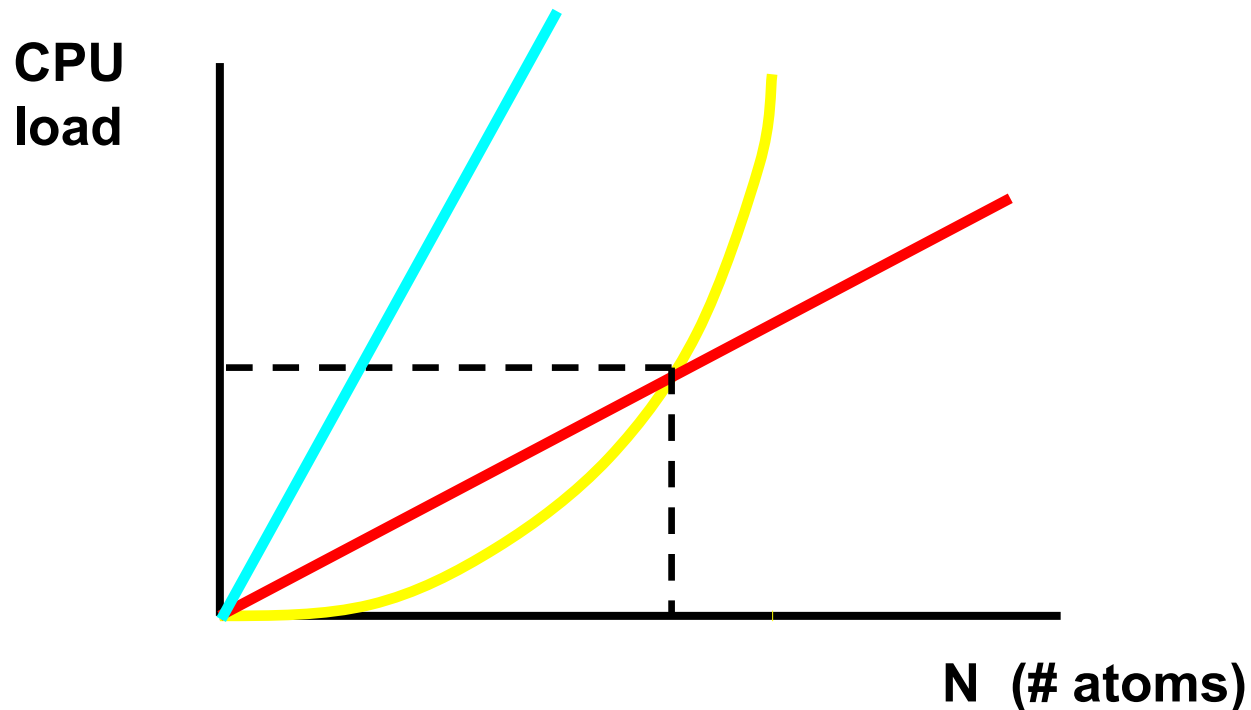
x2

“Divide and Conquer”

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

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

Locality $\Rightarrow$ Basis set of localized functions



Regarding efficiency, the important aspects are:

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

Atomic orbitals: advantages and pitfalls

$$\phi_{Ilmn}(\vec{r}) = R_{Il n}(|\vec{r}_I|) Y_{lm}(\hat{r}_I)$$

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,...)
- They can achieve very high accuracies...

DISADVANTAGES

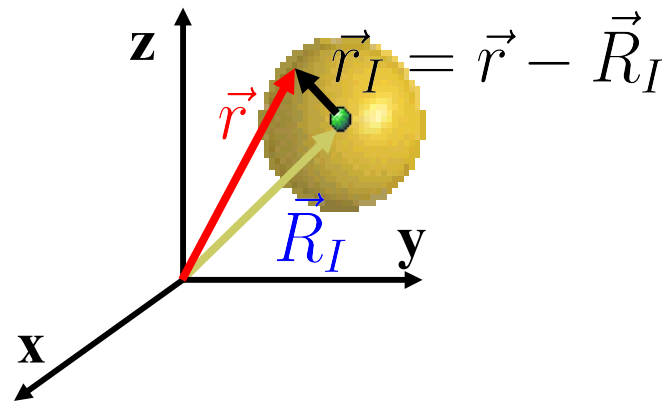
- ...Lack of systematic for convergence (not unique way of enlarge the basis set)
- Human and computational effort searching for a good basis set before facing a realistic project.
- Depend on the atomic position (Pulay terms).

a radial function times an spherical harmonic

$$\phi_{I l m n}(\vec{r}) = R_{I l n}(|\vec{r}_I|) Y_{l m}(\hat{r}_I)$$

Diagram illustrating the components of the atomic orbital wavefunction $\phi_{I l m n}(\vec{r})$:

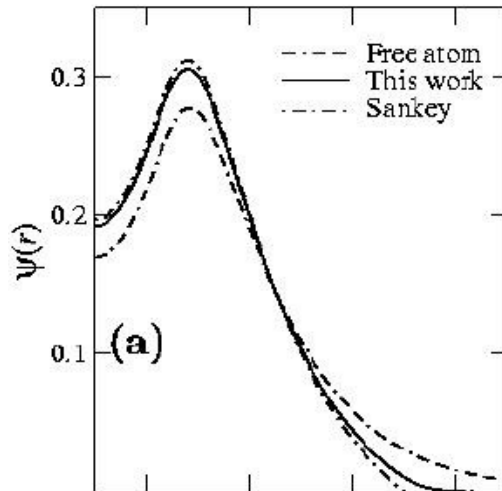
- Index of an atom**: Points to the index I in the wavefunction.
- Angular momentum**: Points to the indices l and m in the wavefunction.
- Possibility of multiple orbitals with the same l, m** : Points to the index n in the wavefunction.
- Unit vector definition**: $\hat{r}_I = \frac{\vec{r}_I}{|\vec{r}_I|}$



Atomic orbitals: Main features that characterize the basis

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

Radial part:
degree of freedom to play with



Size: Number of atomic orbitals per atom

Range: Spatial extension of the orbitals

Shape: of the radial part

Spherical harmonics:
well defined (fixed)
objects

s



p



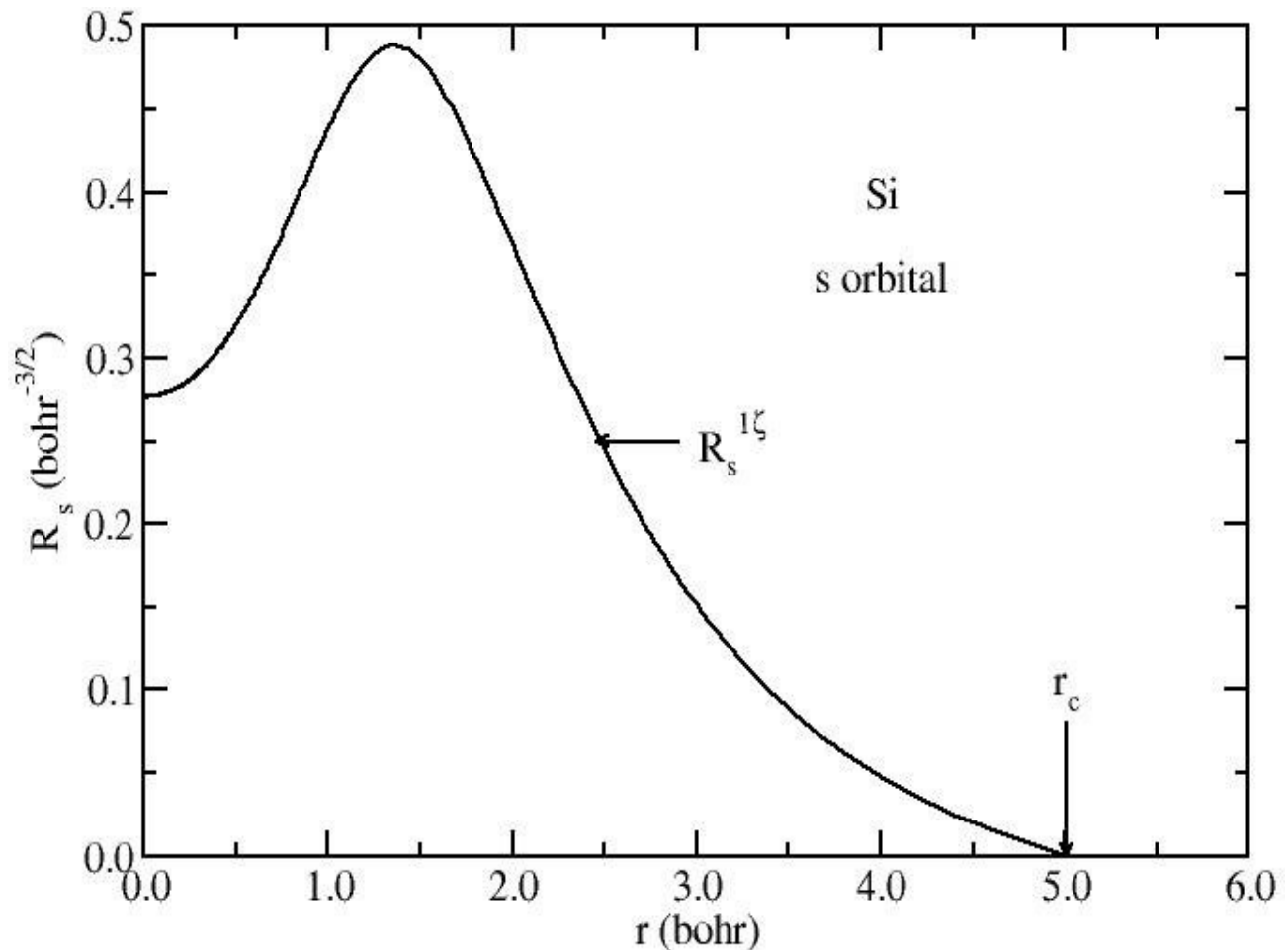
d



f

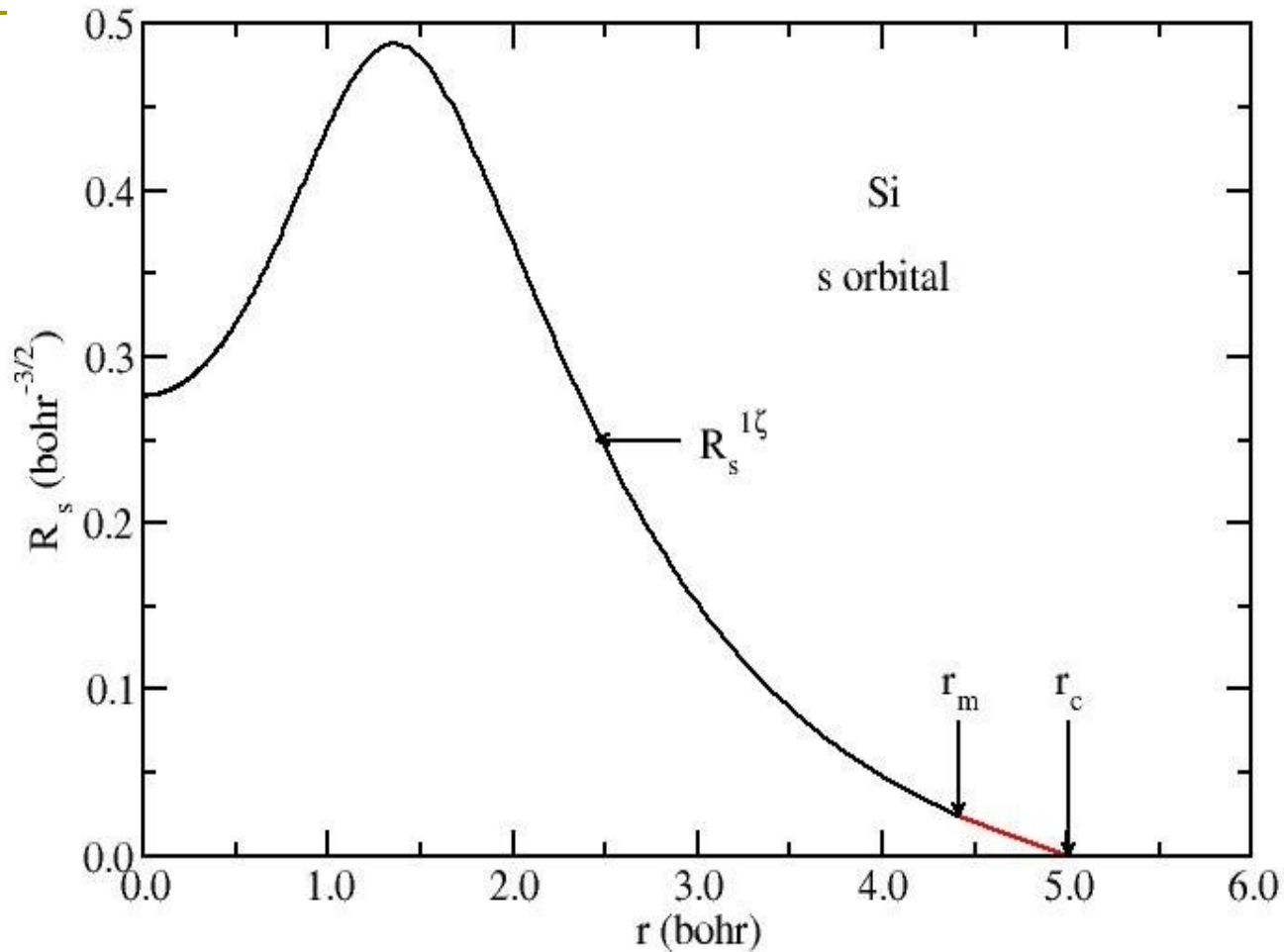


Default mechanism to generate multiple- ζ in SIESTA: “Split-valence” method



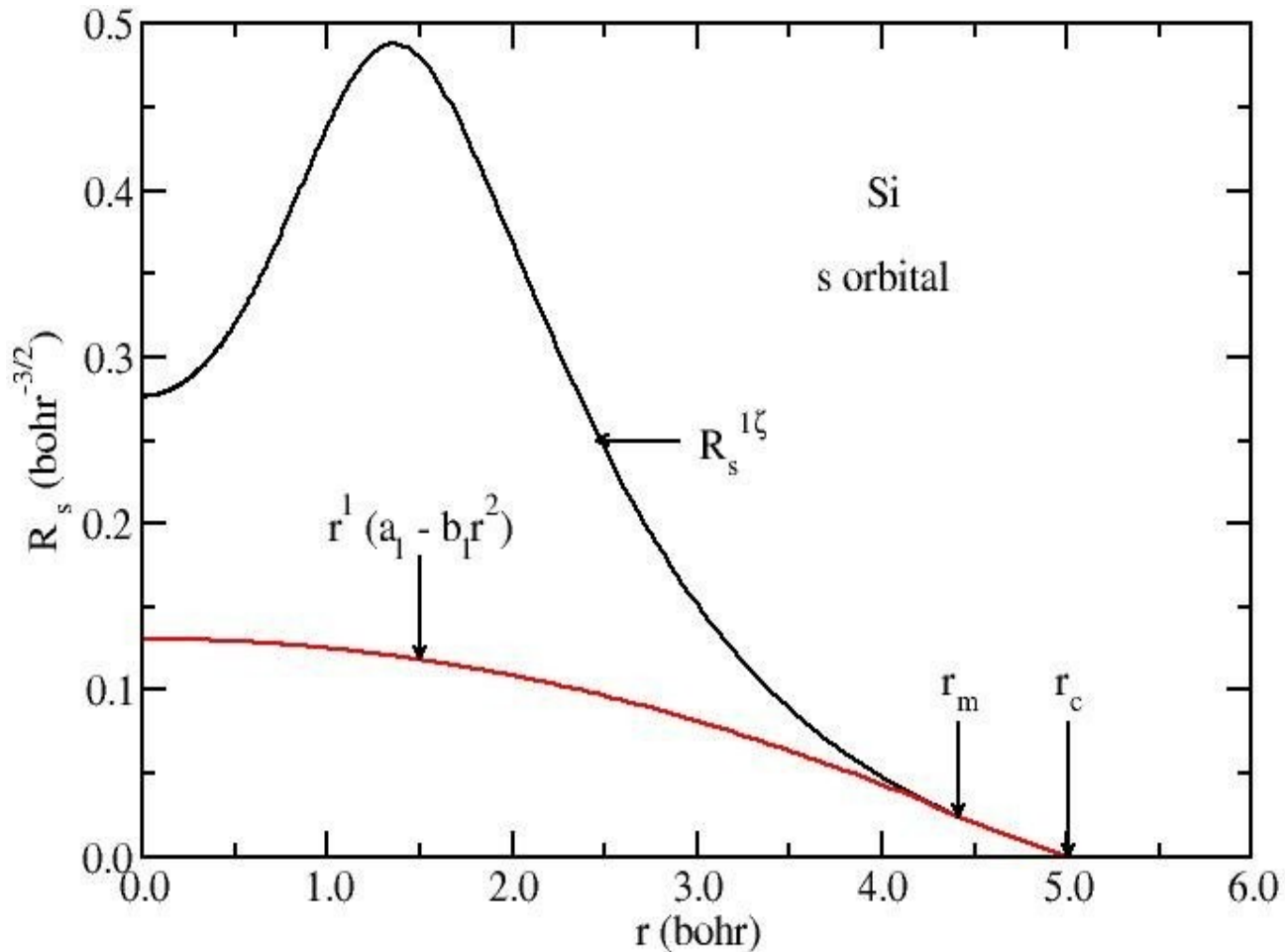
Starting from the function we want to supplement

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

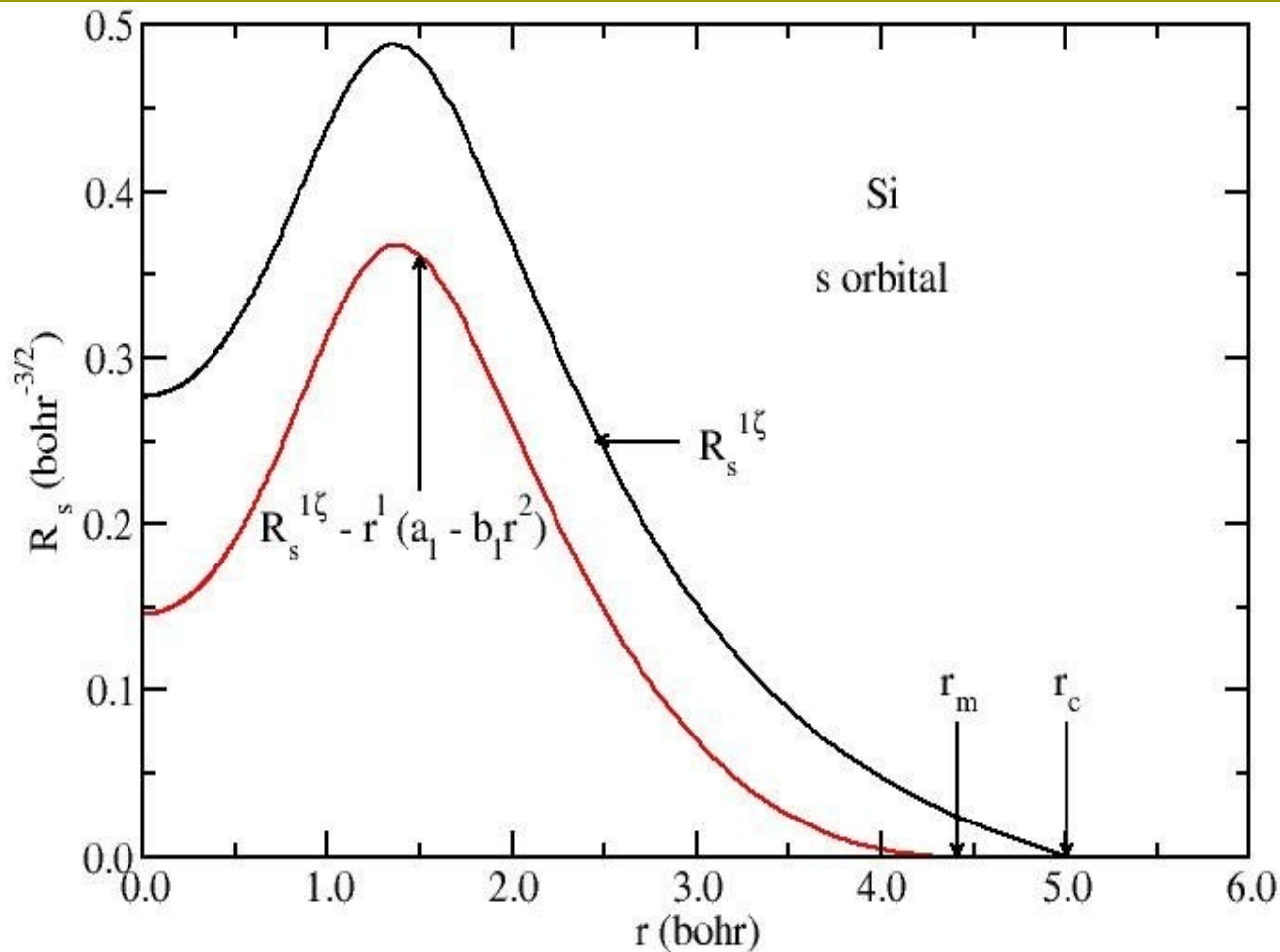
Default mechanism to generate multiple- ζ in SIESTA: “Split-valence” method



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

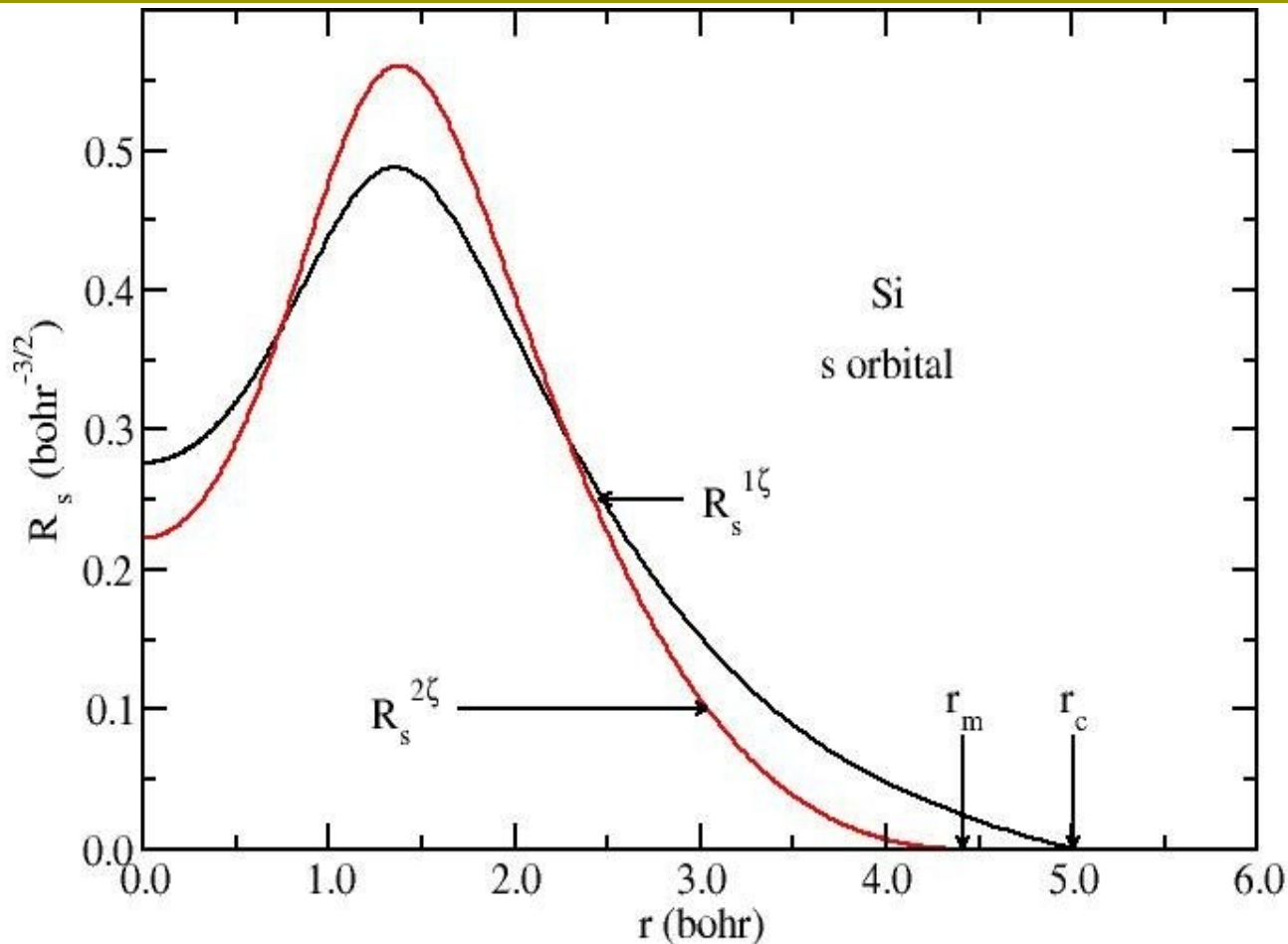
(two parameters: the second- ζ and its first derivative continuous at r_m)

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

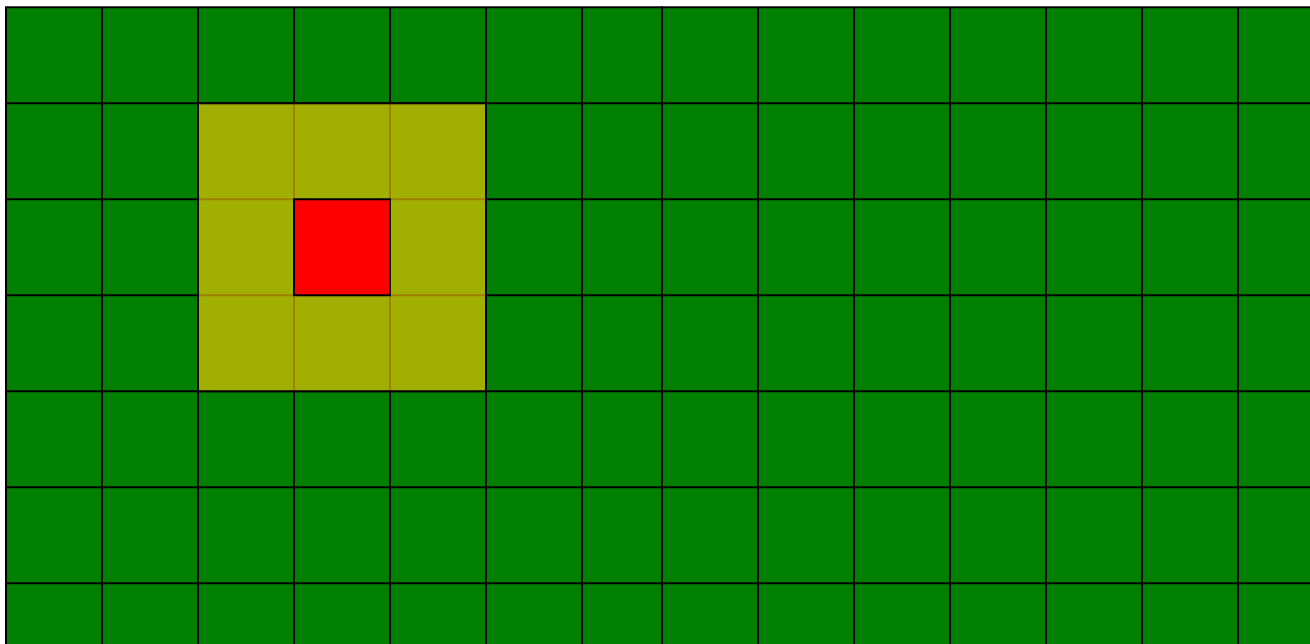


Finally, the second- ζ is normalized

r_m controlled with PAO.SplitNorm (typical value 0.15)

Key for linear-scaling: LOCALITY

Large system



x2

“Divide and Conquer”

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

Atomic Orbitals

$$\phi_{Ilm}(\vec{r}) = R_{Il}(r_I) Y_{lm}(\hat{r}_I) \quad \vec{r}_I = \vec{r} - \vec{R}_I$$

- Numerical Atomic Orbitals (NAOs): *Numerical solution of the KS Hamiltonian for the isolated pseudoatom with the same approximations (xc, pseudos) as for the condensed system*

- Very efficient
- Lack of systematic for convergence
- Main features:
 - **Size** or number of functions
 - **Range** of localization of these functions
 - **Shape** or functional form used.

Basis Size (I)

Depends 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

Basis Size (II): improving

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

Single- ζ
(minimal or SZ)

Improving the
quality

A diagram illustrating the improvement of basis quality. At the top center is the text 'Single- ζ (minimal or SZ)'. Below it, the text 'Improving the quality' is written in red. Two yellow arrows point downwards from this central text to two separate boxes. The left box is titled 'Radial flexibilization:' and describes adding more than one radial function within the same angular momentum shell, labeled 'Multiple- ζ '. The right box is titled 'Angular flexibilization:' and describes adding shells of different angular momentum, labeled 'Polarization'.

Radial flexibilization:

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

Multiple- ζ

Angular flexibilization:

Add shells of different angular
momentum

Polarization

Examples

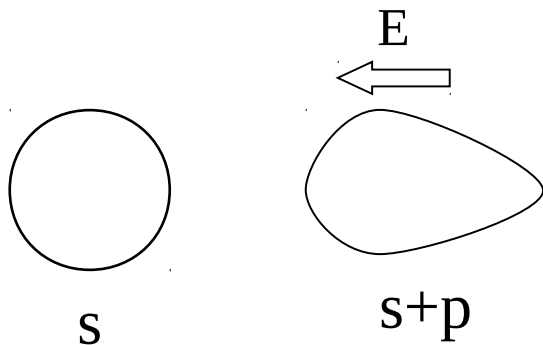
Atom	Valence configuration	SZ	DZ	P
		# orbitals symmetry	# orbitals symmetry	# orbitals symmetry
Si	$3s^2 3p^2$	1 s	2 s	1 d_{xy}
		1 p_x	2 p_x	1 d_{yz}
		1 p_y	2 p_y	1 d_{zx}
		1 p_z	2 p_z	1 $d_{x^2-y^2}$
				1 $d_{3z^2-r^2}$
	Total	4	8	(DZ+P) 13

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

Basis Size (III): Polarization

Perturbative polarization

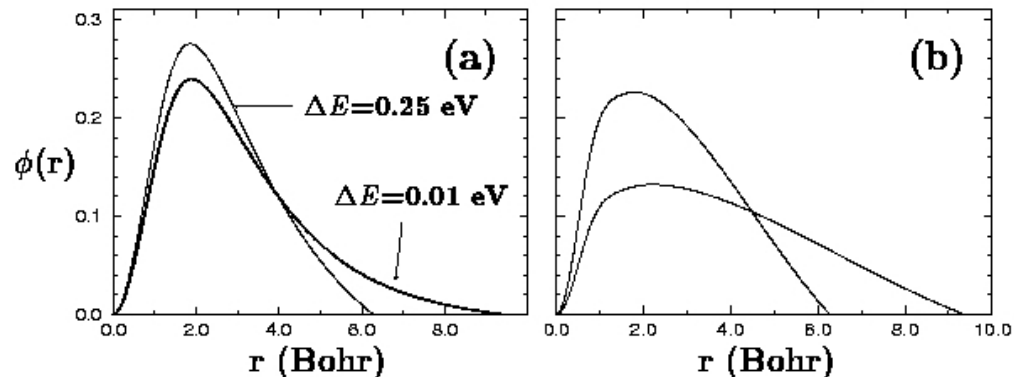
Apply a **small E field** to the orbital we want to polarize



Atomic polarization

Solve Schrödinger equation for **higher angular momentum**

unbound in the free atom
⇒ require short cut offs

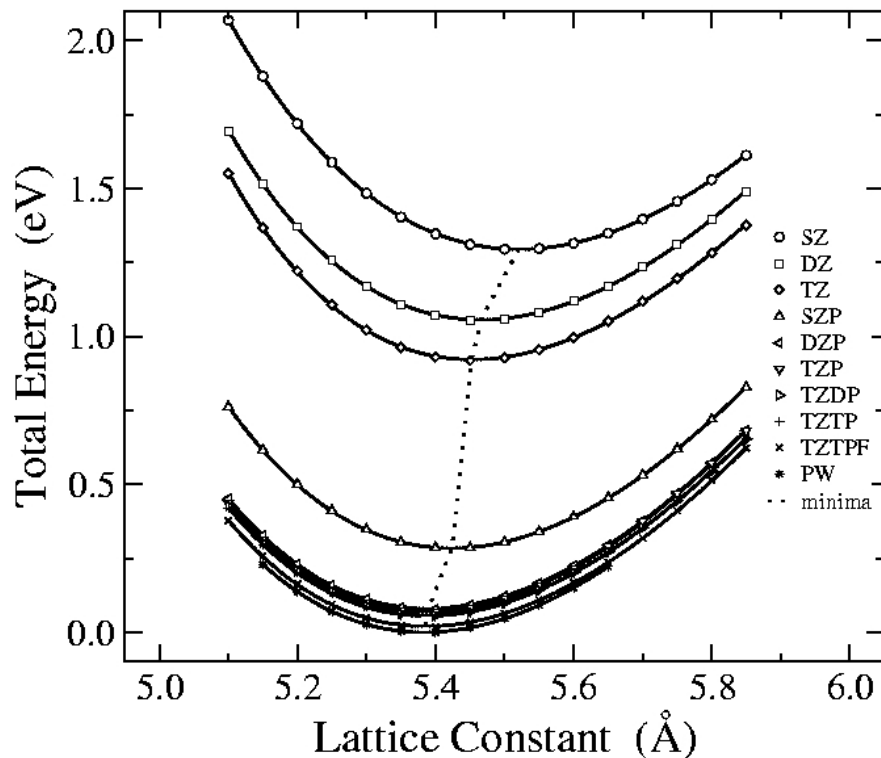


Si 3d
orbitals

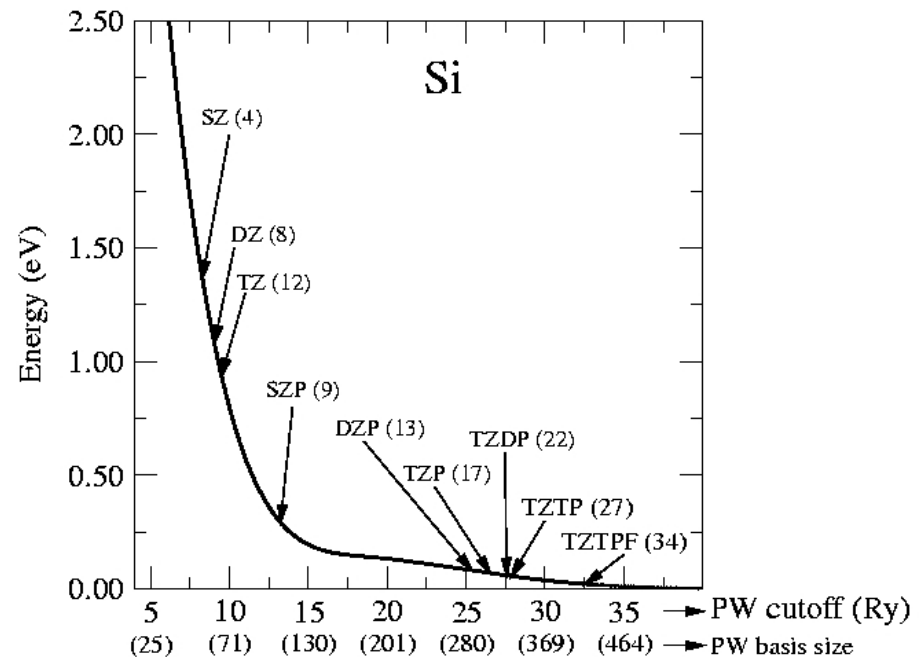
Basis Size (IV): Convergence

Bulk Si

Cohesion curves



PW and NAO convergence



J. Junquera et. al. PRB **64**, 235111 (2001).

Range (I): How to get sparsity for $O(n)$

- *Neglecting interactions* below a tolerance or beyond some scope of neighbours $\Rightarrow$ numerical instabilities 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.

Range (II): Energy Shift

Easy approach to define the cutoff radii for the NAOs:

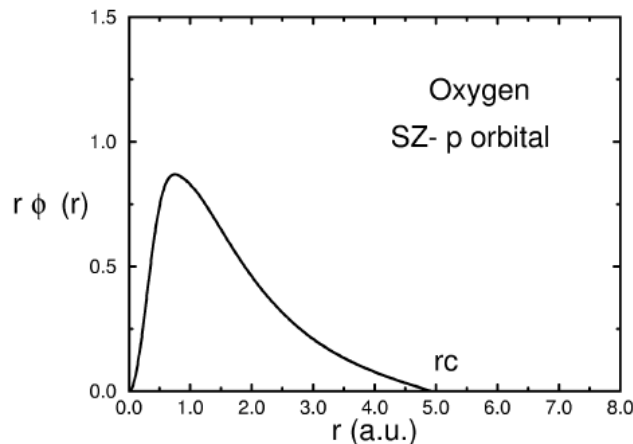
$$\left(-\frac{1}{2r} \frac{d^2}{dr^2} r + \frac{l(l+1)}{2r^2} + V_l(r) \right) \phi_l(r) = (\varepsilon_l + \delta\varepsilon_l) \phi_l(r)$$

A single parameter for all cutoff radii...

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

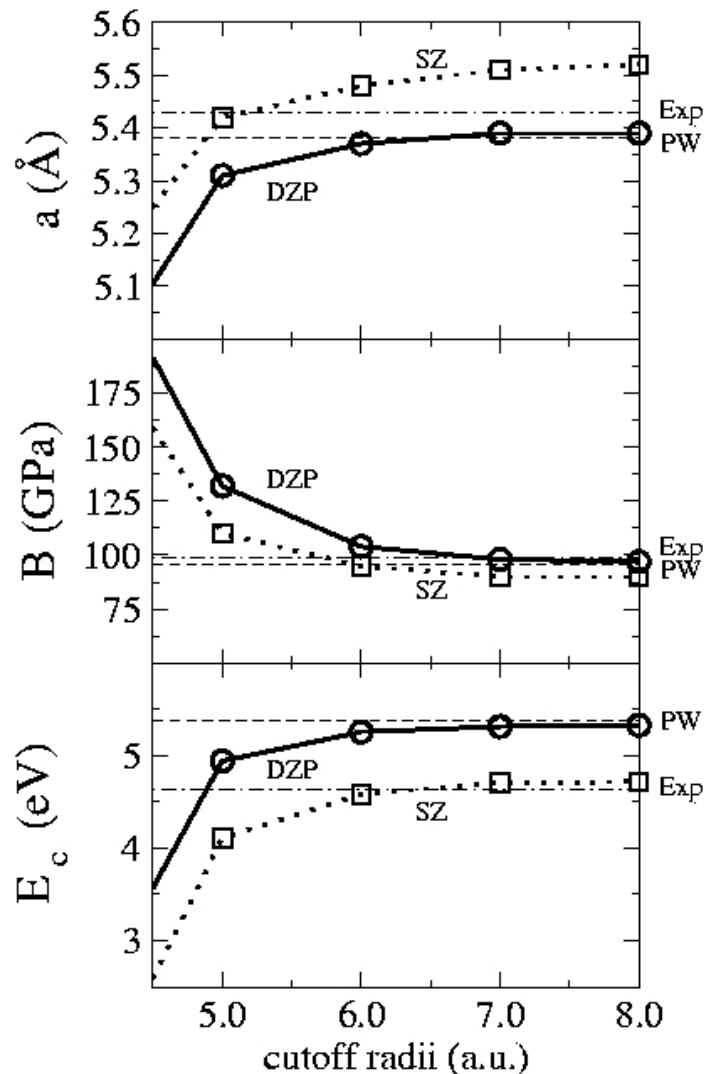
Fireballs

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



...BUT, a different cutoff radius for each orbital

Range (II): Convergence



Bulk Si

equal s , p orbitals radii

Shape (I)

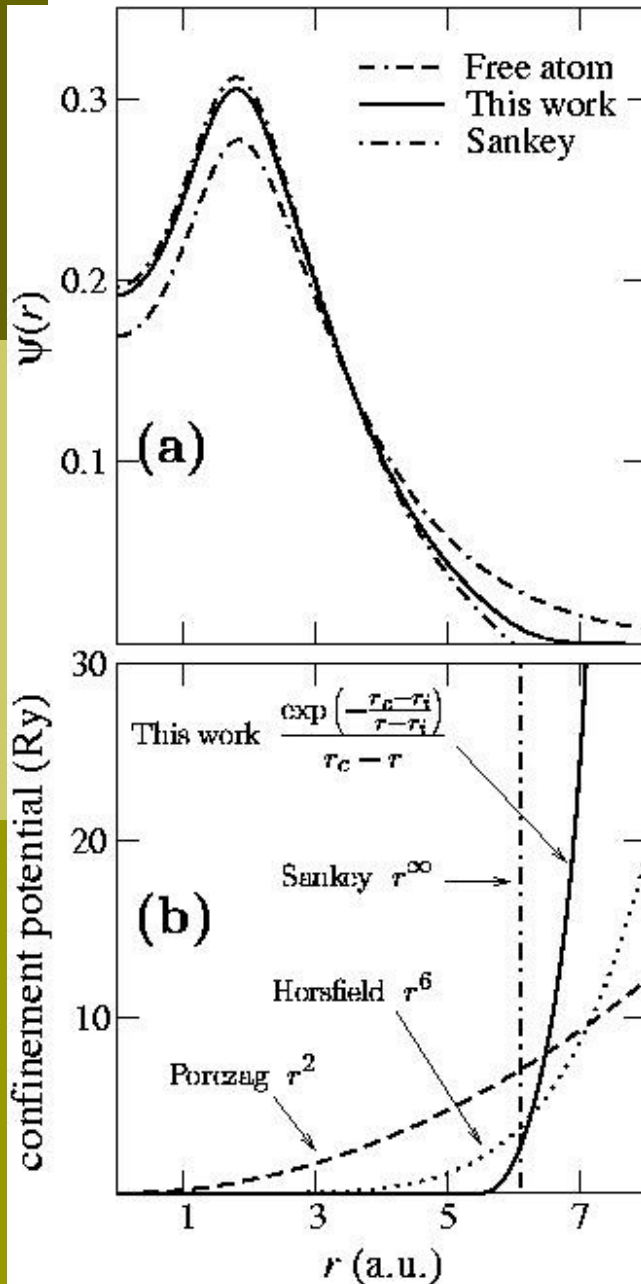
The radial function shape is mainly determined by the pseudopotential.

Extra parameters can be introduced to add flexibility:

- δQ : extra charge per atomic specie.
- **Confinement** : imposed separately for each angular momentum shell.

Soft confinement

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



Shape of the optimal 3s orbital of Mg in MgO for different schemes

Corresponding optimal confinement potential

- Better variational basis sets
- Removes the discontinuity of the derivative

PAO.Basis (I)

shells

Add polarization

```
%block PAO.Basis
Cu      2
4s → n=4  0  2 P  1
      5.500  5.200 ← Rc
      1.000  1.000
3d → n=3  2  2
      4.991  3.541 ← Rc
      1.000  1.000 ← 2nd ζ
1st ζ
%endblock PAO.Basis
```

Define Basis set
Species label, number of l-shells
n, l, Nzeta, Polarization, NzetaPol

n, l, Nzeta

PAO.Basis (II): new generation

```
%block PAO.Basis
Cu 3 0.10660
n=4 0 1 E 5.78489 0.96502
5.10647
1.00000
n=4 1 1 E 2.51950 0.48813
4.97570
1.00000
n=3 2 1 E 4.30968 3.07629
4.99958
1.00000
%endblock PAO.Basis
```

charge

Define Basis set

V_c

r_c

Polarization orbital

Procedure

1. Check the difference in energies involved in your problem
2. For semiquantitative results and general trends use SZ
3. Improve the basis:
 - Automatic DZP (Split Valence & Perturbative Polarization):
 - High quality for most systems
 - Good valence between well converged results & computational cost
 - 'Standard'
 - Rule of thumb in Quantum Chemistry: « *a basis should always be doubled before being polarized* ».
4. Functional optimization of the basis

Pseudos & Basis repository

- Pseudopotentials and basis sets available in the SIESTA web page: www.icmab.es/siesta
 - Uploaded by users
 - input files to generate them
 - Plots of the radial functions
 - Documentation of the tests done
 - Author's contact information
 - The PAO is pseudopotential-dependent.
- Check also in the user's mailing list.