



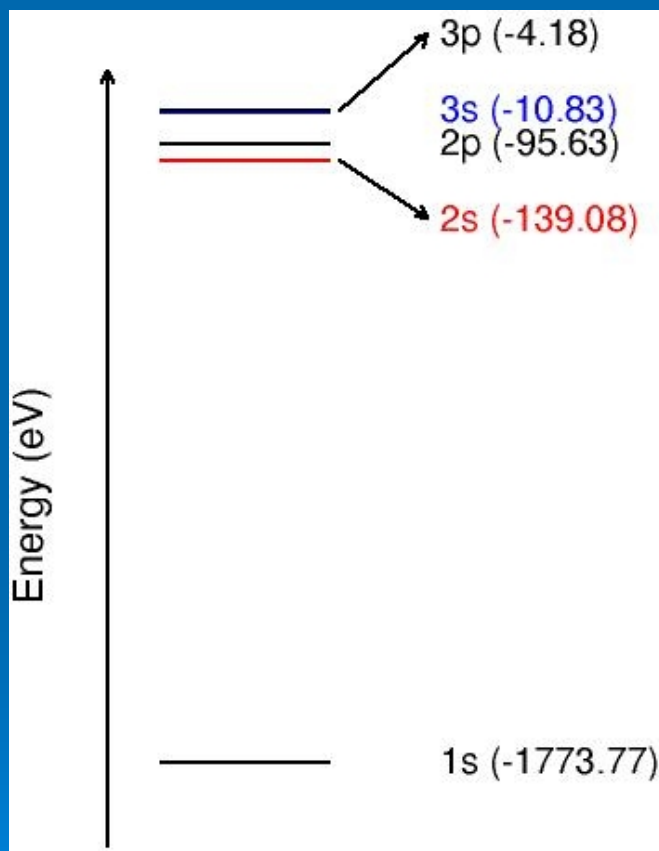
# Pseudopotentials and Basis Sets

How to generate and test them



# Pseudopotential idea

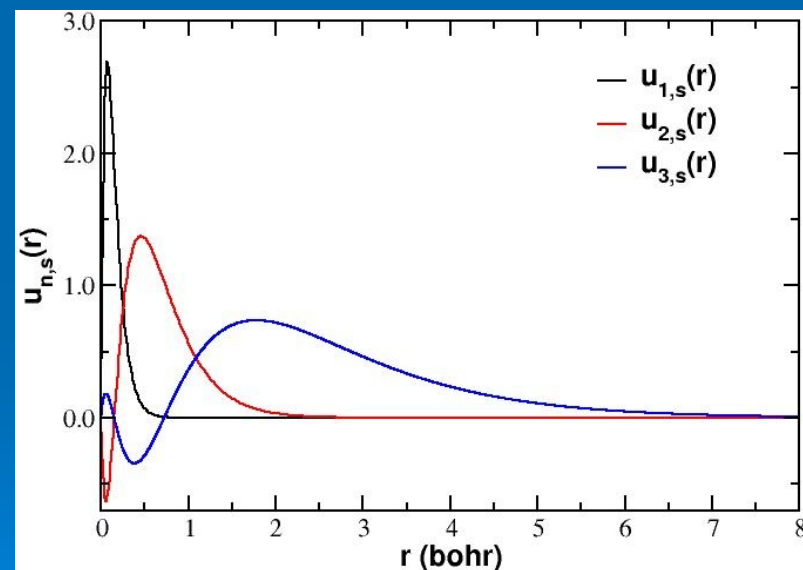
## Atomic Si



## Core electrons...

highly localized  
very deep energy

... are chemically inert



$1s^2 2s^2 2p^6$   
core

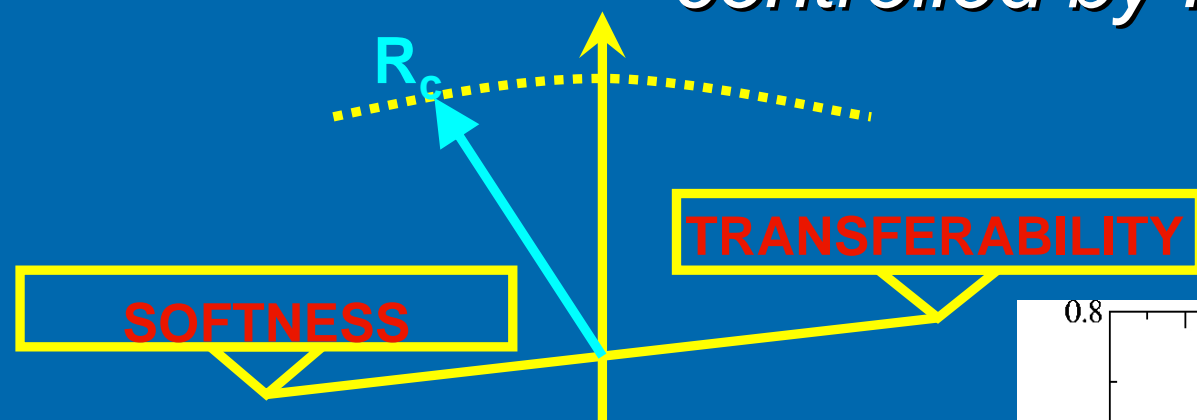
$3s^2 3p^2$   
valence

Valence wave functions must be orthogonal to the core wave functions



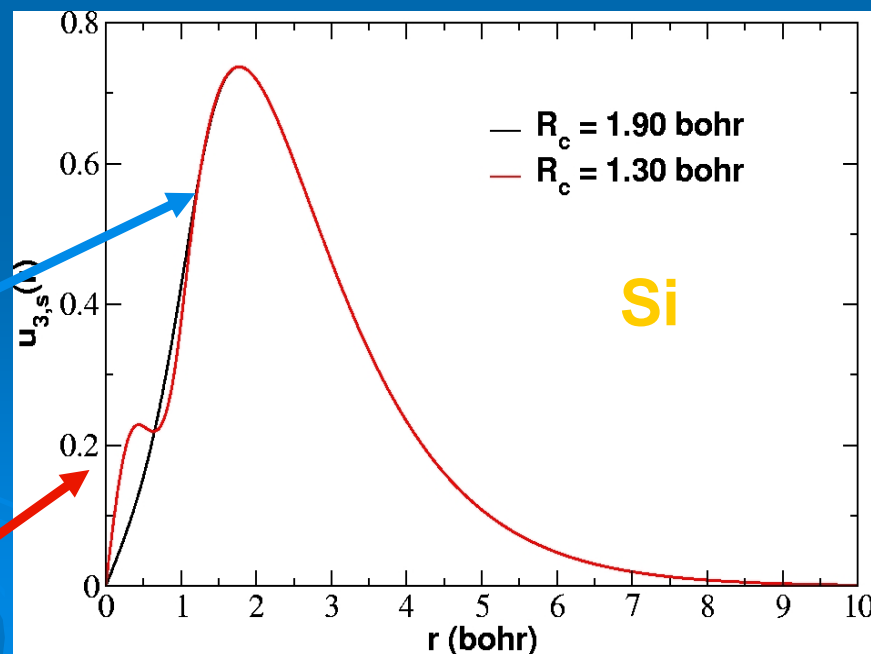
# Cut-off radii

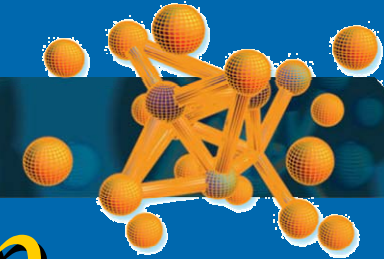
*Balance between softness and transferability  
controlled by  $R_c$*



Larger  $R_c$ : softer pseudo

Shorter  $R_c$ : harder pseudo





# The “atom” program

“pseudopotential generation” label

xc flavor

# valence shells

# core orbitals

$n$

$l$

Valence configuration

Cutoff radii

```
#
# 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
# norbs_core, norbs_valence
3 4 # 3s2
3 0 2.00 0.00 # 3p2
3 1 2.00 0.00
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
#
#234567890123456789012345678901234567890123456789012345678901234567890
```



# Procedure (I)

- Run the shell script (pg.sh)

```
$ pg.sh Si.tm2.inp  
Calculation for Si.tm2 completed. Output in directory Si.tm2
```

- Check contents of new directory (Si.tm2)

```
$ ls Si.tm2  
AECHARGE  AEFNR3  PSLOGD3  PSPOTR3  PSWFNR3  charge.gplot  
AELOGD0   CHARGE  PSPOTQ0  PSWFNQ0  RHO       charge.gps  
AELOGD1   INP     PSPOTQ1  PSWFNQ1  SCRPSPTR0 pots.gplot  
AELOGD2   OUT     PSPOTQ2  PSWFNQ2  SCRPSPTR1 pots.gps  
AELOGD3   PSCHARGE PSPOTQ3  PSWFNQ3  SCRPSPTR2 pseudo.gplot  
AEWFNR0   PSLOGD0 PSPOTR0  PSWFNR0  SCRPSPTR3 pseudo.gps  
AEWFNR1   PSLOGD1 PSPOTR1  PSWFNR1  VPSFMT    pt.gplot  
AEWFNR2   PSLOGD2 PSPOTR2  PSWFNR2  VPSOUT    pt.gps
```

- Plot the pseudo-potentials/orbitals

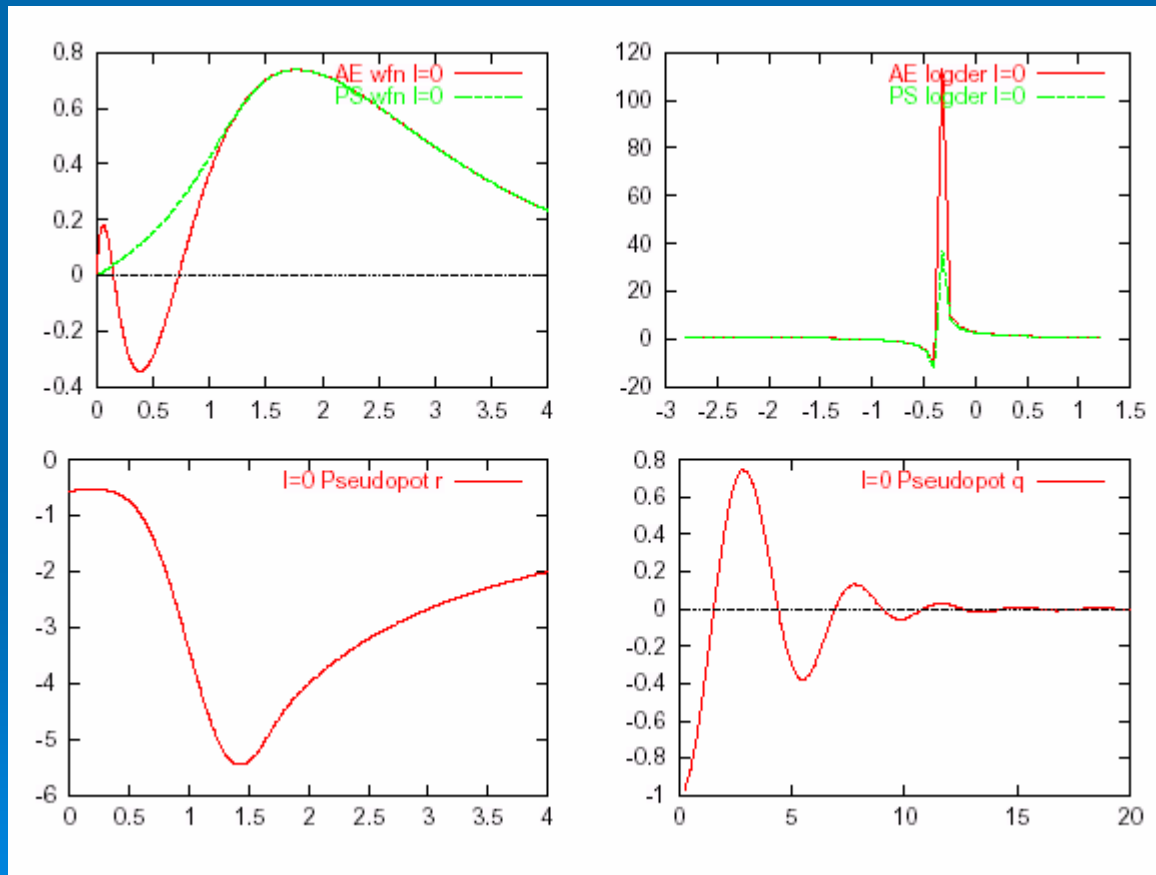
```
$ cd Si.tm2
```

```
$ gnuplot pseudo.gps  
==> Postscript output in pseudo.ps
```

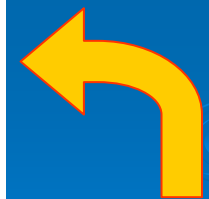
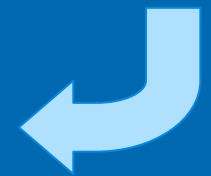


# Procedure (II)

Pseudo-wave  
function



Logarithmic  
derivative

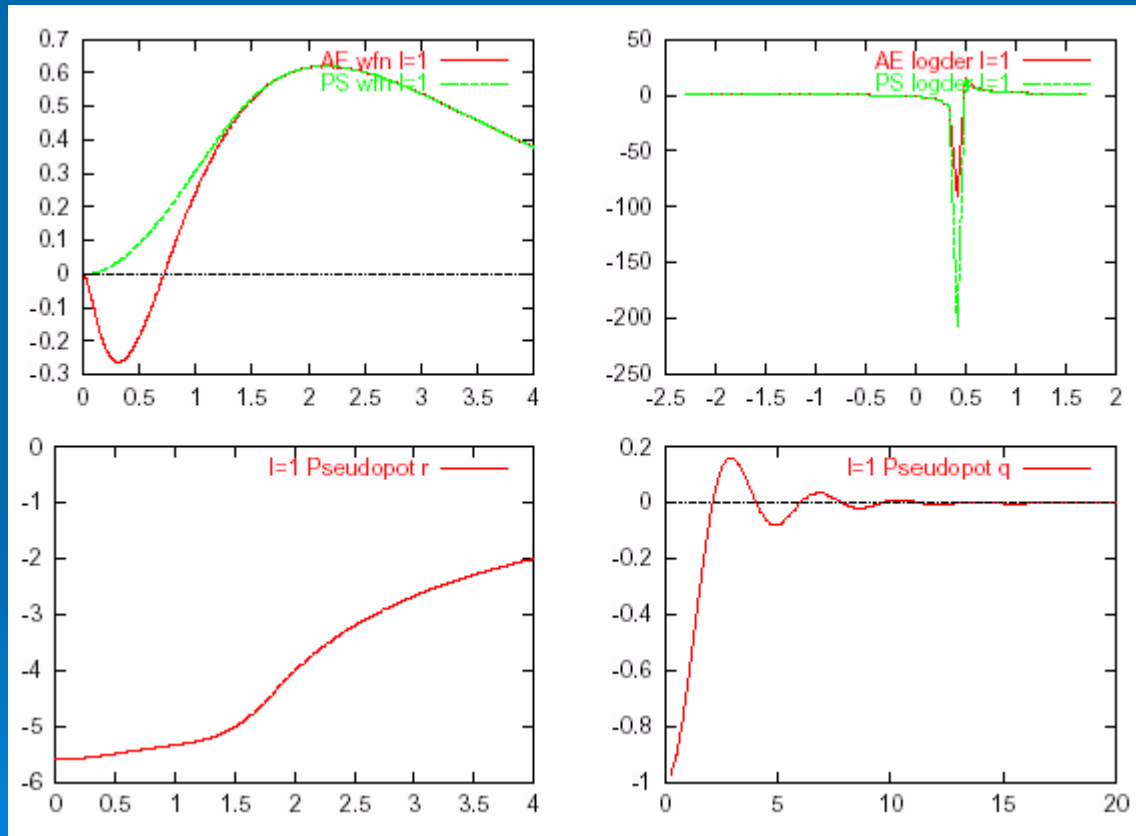


Radial  
Fourier-T

Pseudopotential



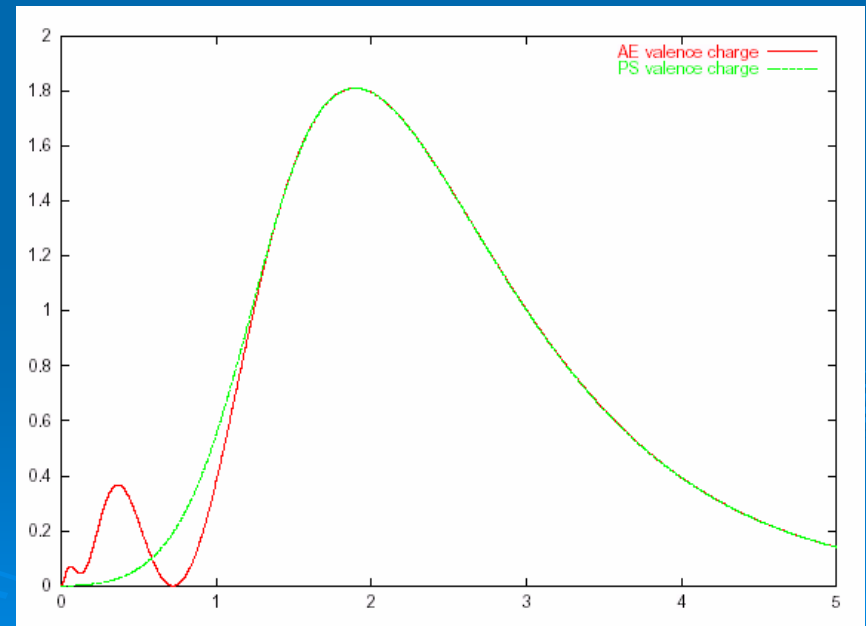
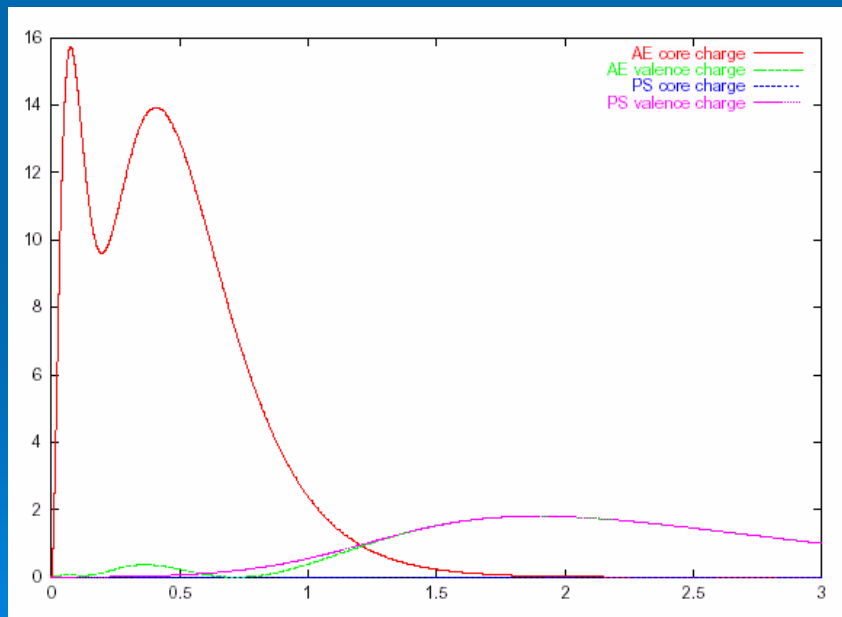
# Procedure (III)





# 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  AEFWNR1  CHARGE  OUT          PTWFNR0  PTWFNR2  VPSIN
AEWFNR0   AEFWNR2  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
-----
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
-----
```

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



# 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

$\Delta E^{AE}$

- $3s^2 3p^2$  (reference)
- $3s^2 3p^1 3d^1$
- $3s^1 3p^3$
- $3s^1 3p^2 3d^1$
- $3s^0 3p^3 3d^1$

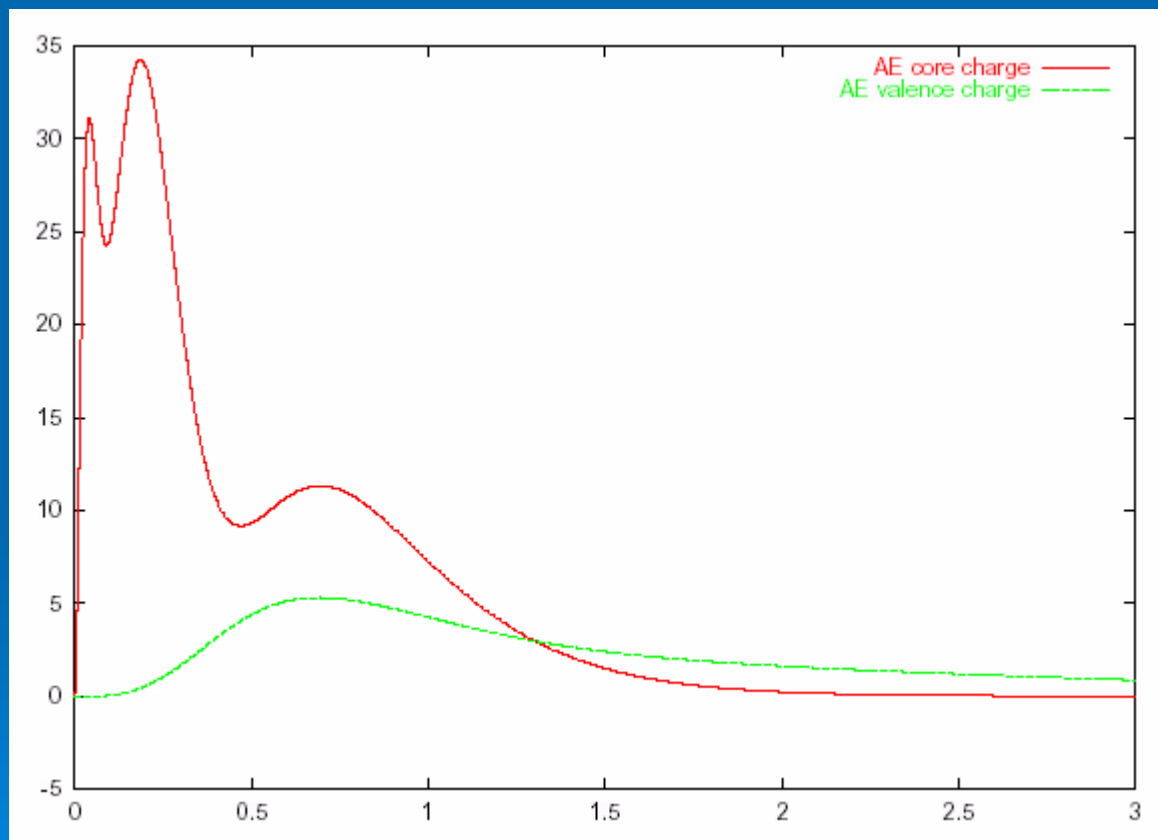
&d	1	2	3	4	5
&d 1	0.0000				
&d 2	0.4299	0.0000			
&d 3	0.4993	0.0694	0.0000		
&d 4	0.9635	0.5336	0.4642	0.0000	
&d 5	1.5044	1.0745	1.0051	0.5409	0.0000

$\Delta E^{PS}$





# Large core-valence overlap



Errors due to  
non-linearity of  
XC-potential



# 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

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



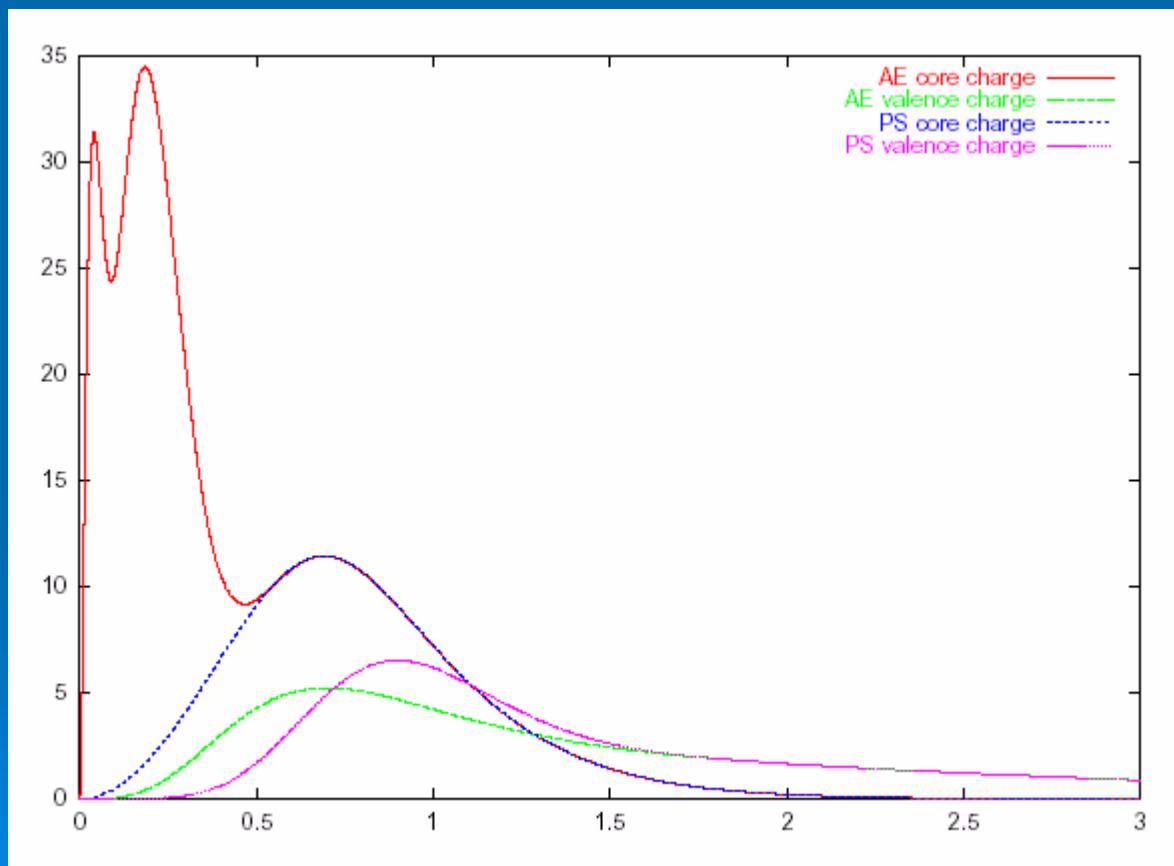
# PCC input file

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
```



# Pseudo-core & pseudo-valence charge

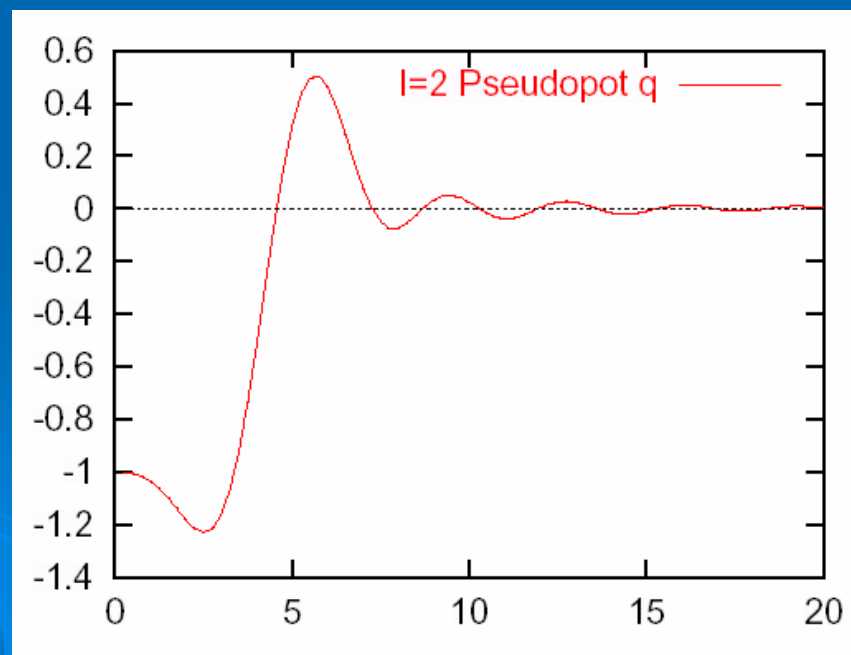




# Smooth Fourier Transform

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

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







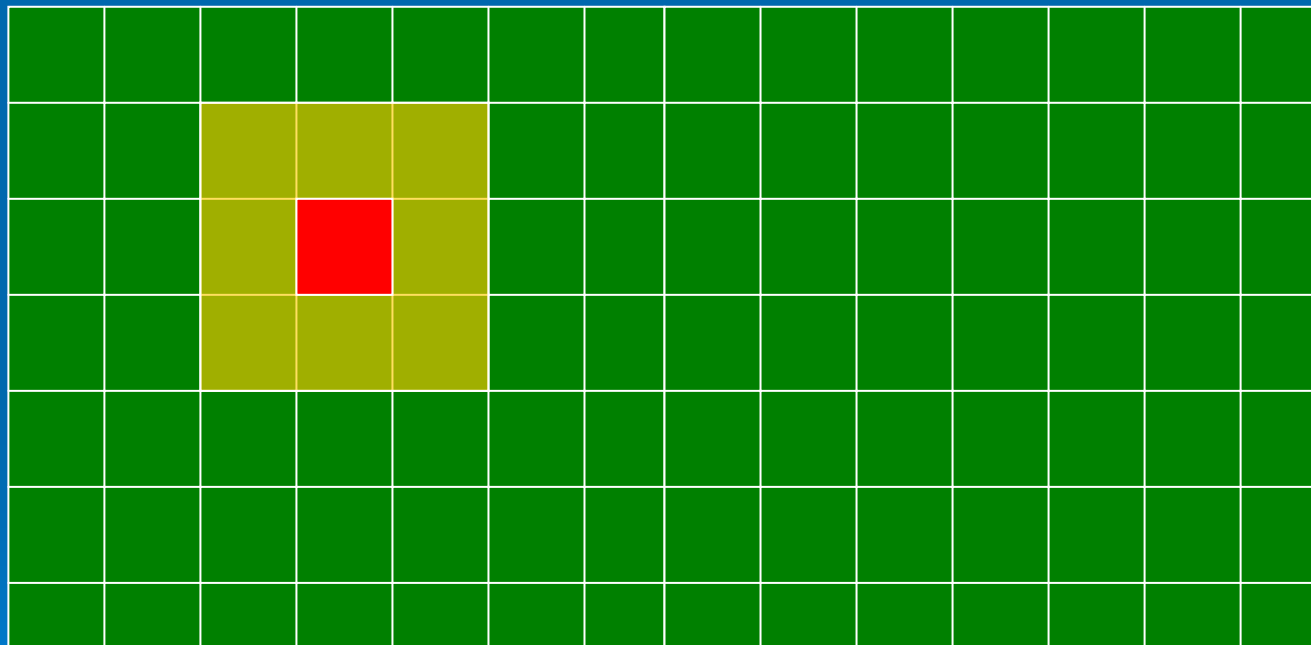
# Basis generation





# Key for linear-scaling: LOCALITY

*Large system*



*“Divide and Conquer”*

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

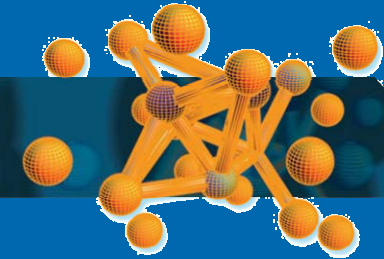


# Atomic Orbitals

$$\phi_{l m}(\vec{r}) = R_{l}(r_I) Y_{l m}(\hat{r}_I) \quad \vec{r}_I = \vec{r} - \vec{R}_I$$

• 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.



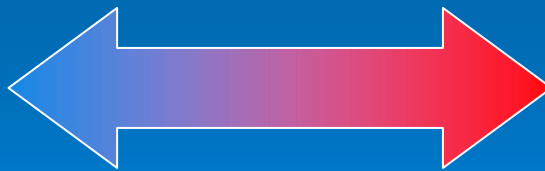
# Basis Size (I)

Depends on the required accuracy and available computational power

Quick and dirty calculations

Highly converged calculations

Minimal basis set  
(single- $\zeta$ ; SZ)



Complete multiple- $\zeta$   
+  
Polarization  
+  
Diffuse orbitals



# Basis Size (II): improving

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

Single- $\zeta$   
(minimal or SZ)

Improving the  
quality?



## Radial flexibilization:

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

**Multiple- $\zeta$**

## Angular flexibilization:

Add shells of different angular momentum

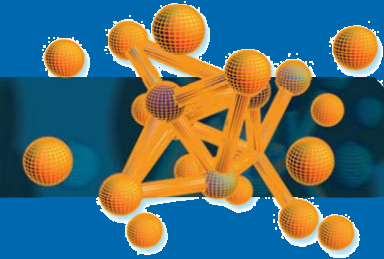
**Polarization**

# 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	

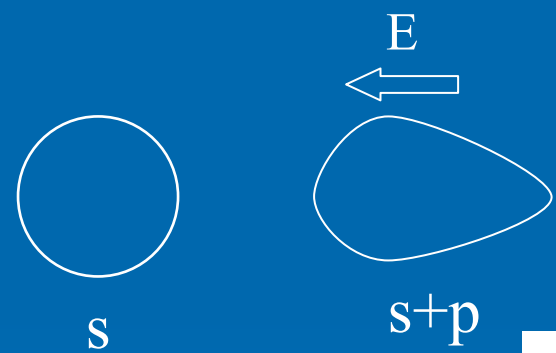
Atom	Valence configuration						
		# orbitals	symmetry	# orbitals	symmetry	# orbitals	symmetry
Fe	$4s^2 3d^6$	1	$s$	2	$s$	1	$p_x$
		1	$d_{xy}$	2	$d_{xy}$	1	$p_y$
		1	$d_{yz}$	2	$d_{yz}$	1	$p_z$
		1	$d_{zx}$	2	$d_{zx}$		
		1	$d_{x^2-y^2}$	2	$d_{x^2-y^2}$		
		1	$d_{3z^2-r^2}$	2	$d_{3z^2-r^2}$		
	Total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



# Basis Size (III): Polarization

## Perturbative polarization

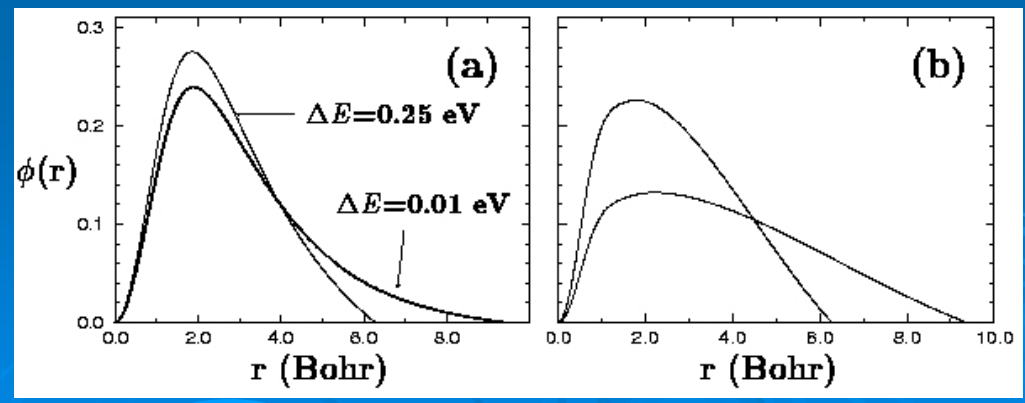
Apply a small E field to the orbital we want to polarize



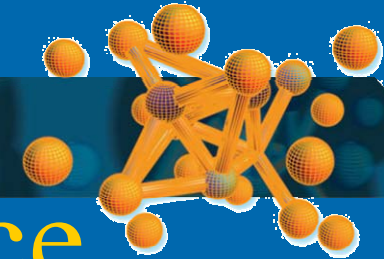
## Atomic polarization

Solve Schrödinger equation for higher angular momentum

unbound in the free atom  
⇒ require short cut offs



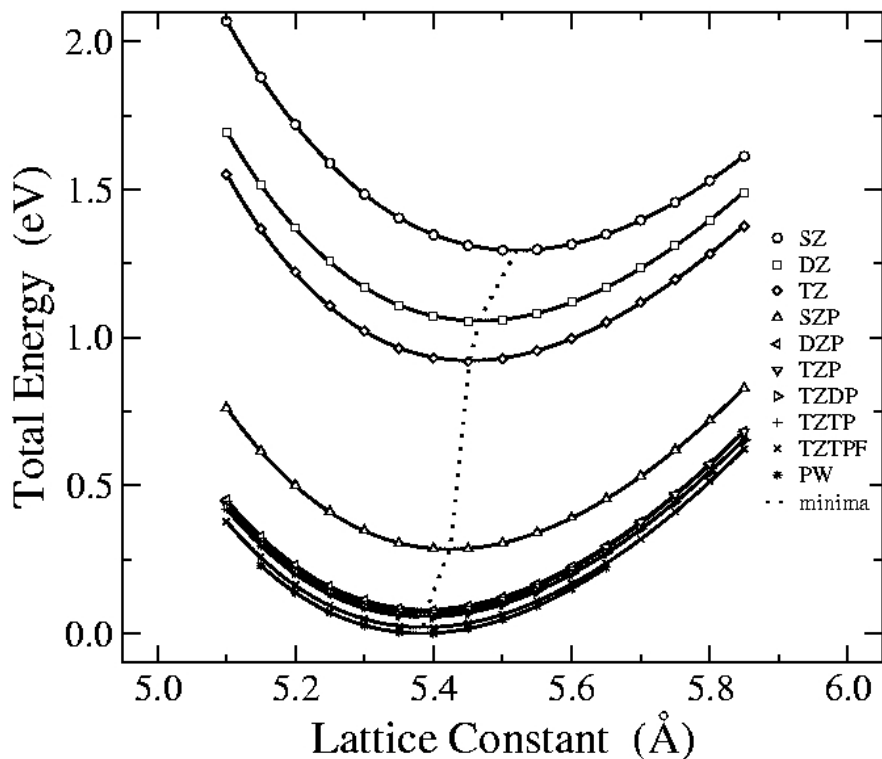
Si 3d orbitals



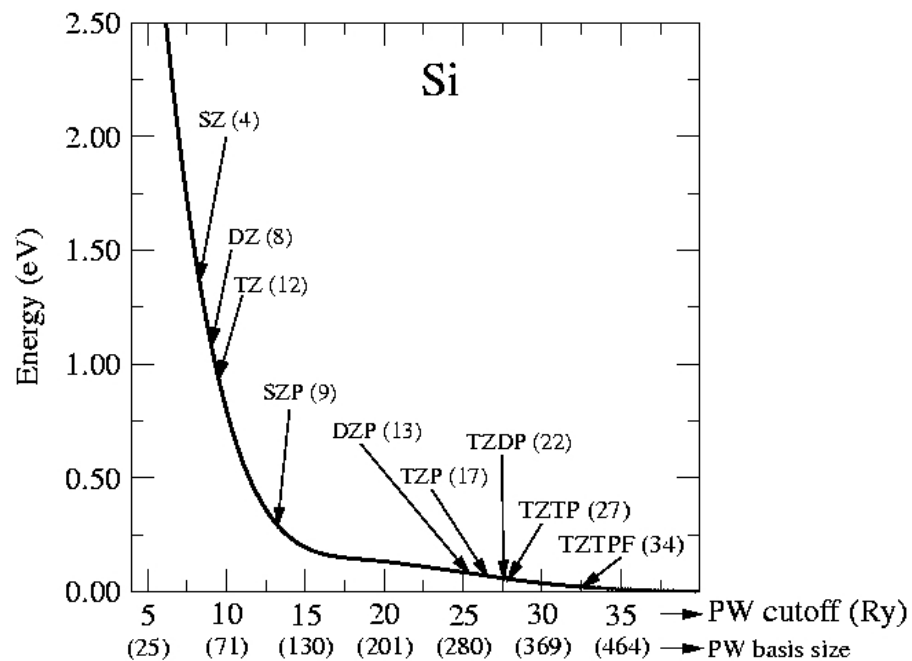
# Basis Size (IV): Convergence

## Bulk Si

### Cohesion curves



### PW and NAO convergence







## 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.



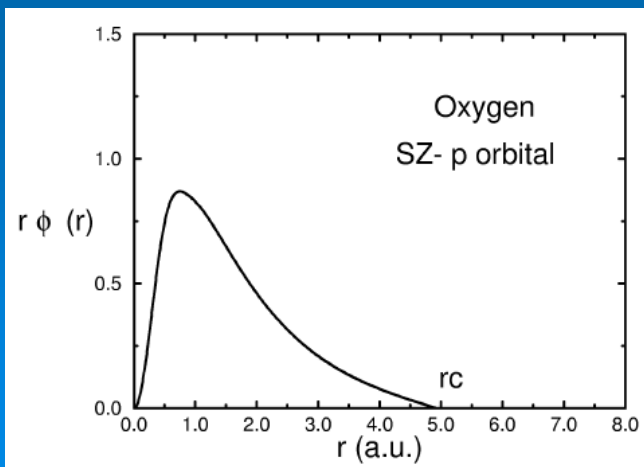
# Range (II): Energy Shift

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...*

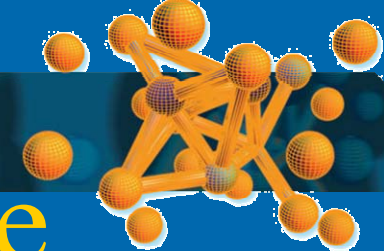
E. Artacho et al. *Phys. Stat. Solidi (b)* 215, 809 (1999)



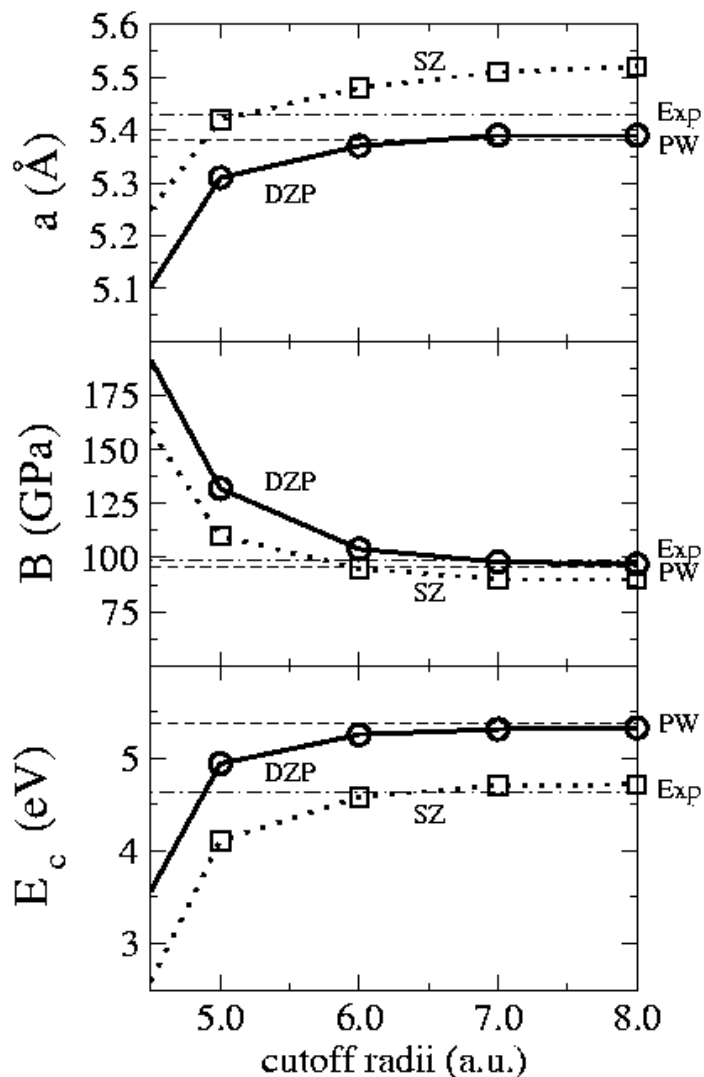
*Fireballs*

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:

- **$\delta Q$**  : extra charge per atomic specie.
- **Confinement** : imposed separately for each angular momentum shell.



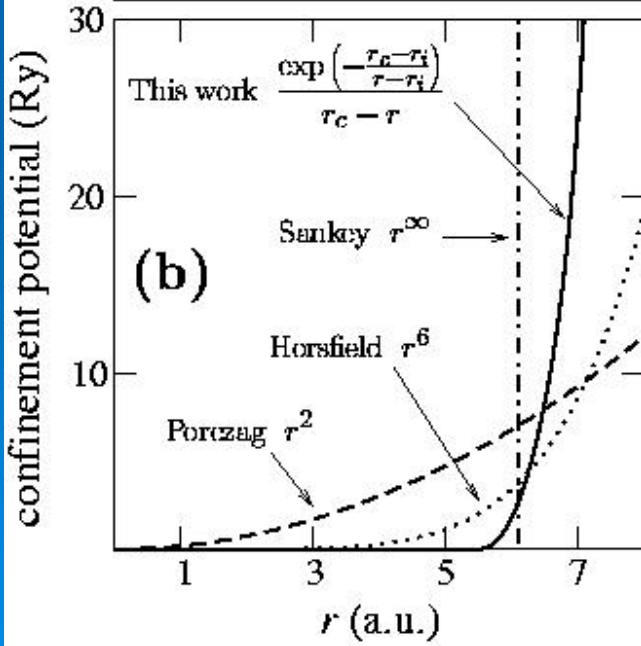
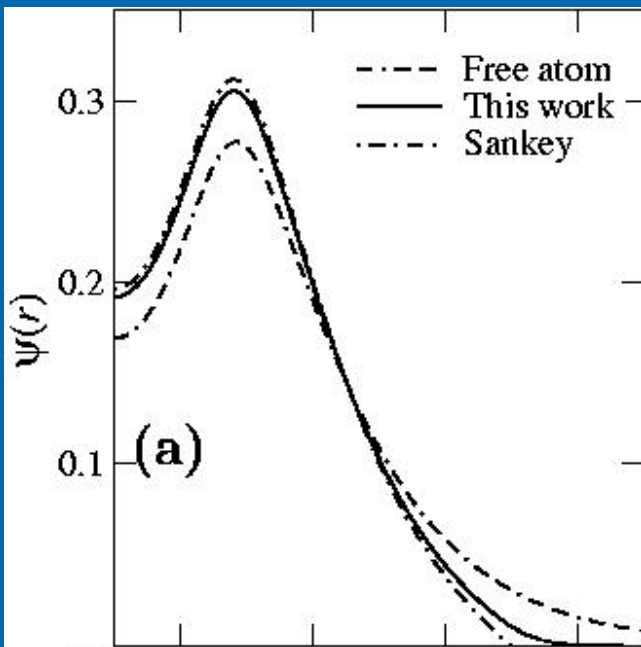


# Shape (II)

## Soft confinement

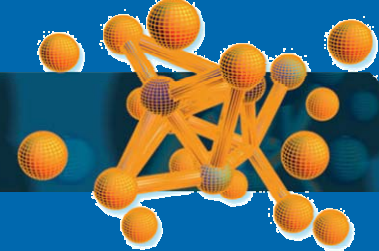
(J. Junquera *et al*, Phys. Rev. B **64**, 235111 (01) )

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
%endblock PAO.Basis
    
```

*1<sup>st</sup> ζ*

# 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
    
```

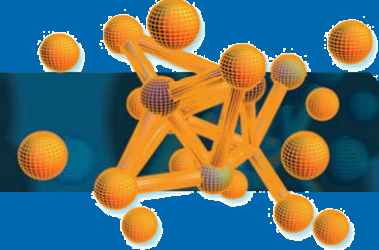
charge

# 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.uam.es/siesta](http://www.uam.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.