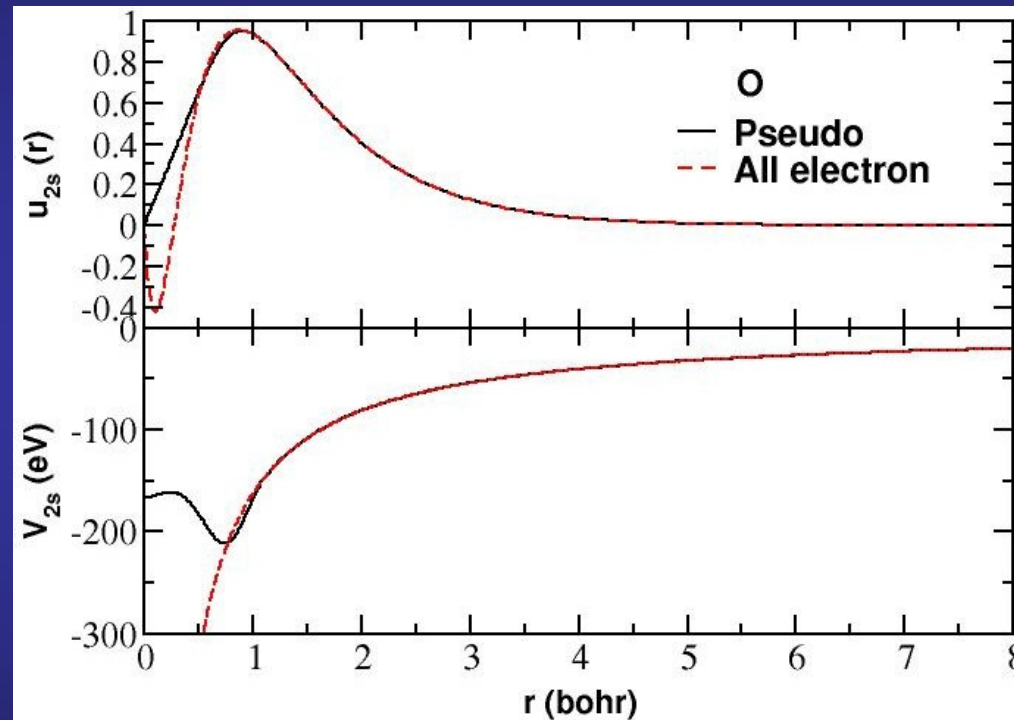# Norm-conserving pseudopotentials and basis sets in electronic structure calculations

Javier Junquera

Universidad de Cantabria

Outline

Pseudopotentials

Why pseudopotential approach is useful

Orthogonalized Plane Waves (1940)

Pseudopotential transformation (1959)

Norm-conserving pseudopotentials (1979)

Basis sets

Plane Waves

Localized Orbitals
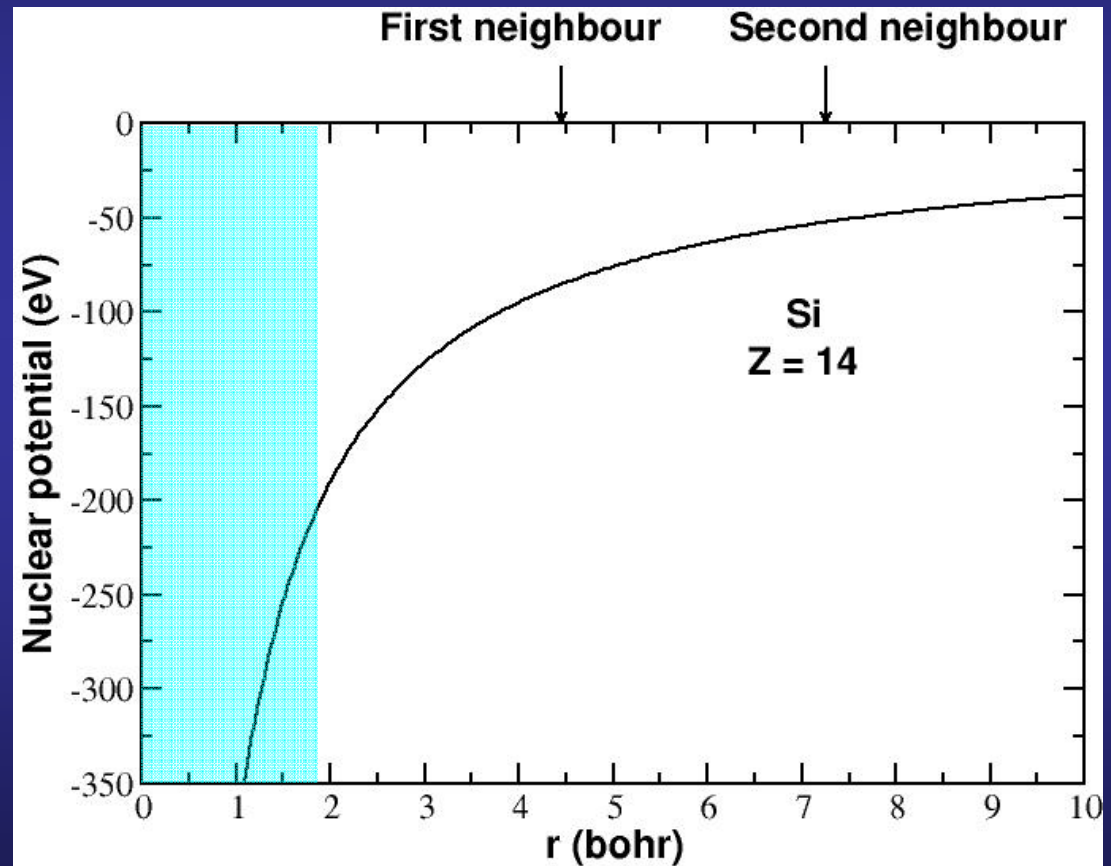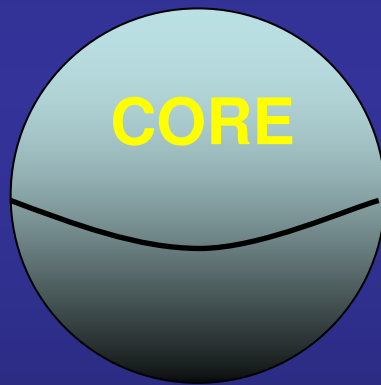
Numerical Atomic Orbitals

Atomic calculation using DFT:
Solving the Schrodinger-like equation

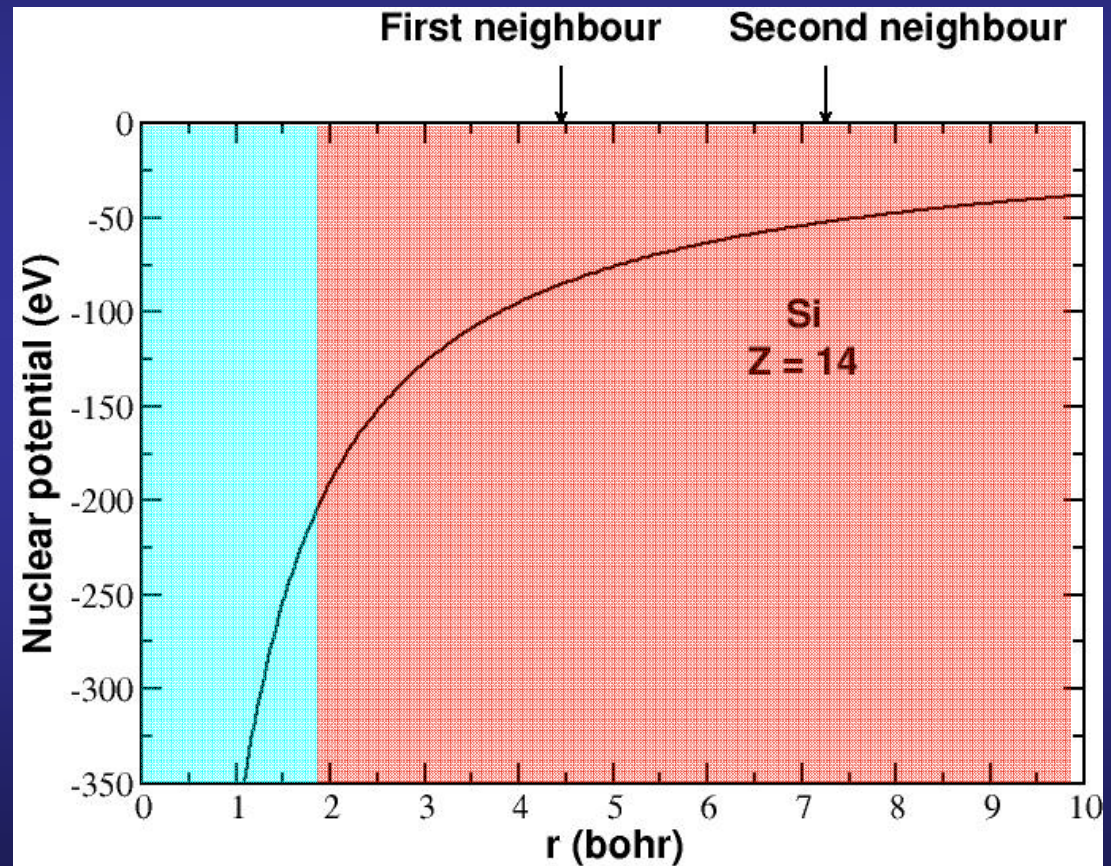**One particle Kohn-Sham equations**

$$\left(\hat{T} + \hat{V}_{ion-e} + \hat{V}_H + \hat{V}_{xc} \right) \psi_i = \varepsilon_i \psi_i$$

$$-\frac{Ze}{r}$$

Difficulty: how to deal accurately with both the core and valence electrons

Difficulty: how to deal accurately with both the core and valence electrons

Core eigenvalues are much deeper than valence eigenvalues

3p (-4.18)

3s (-10.83)
2p (-95.63)

2s (-139.08)

Valence

Core

1s (-1773.77)
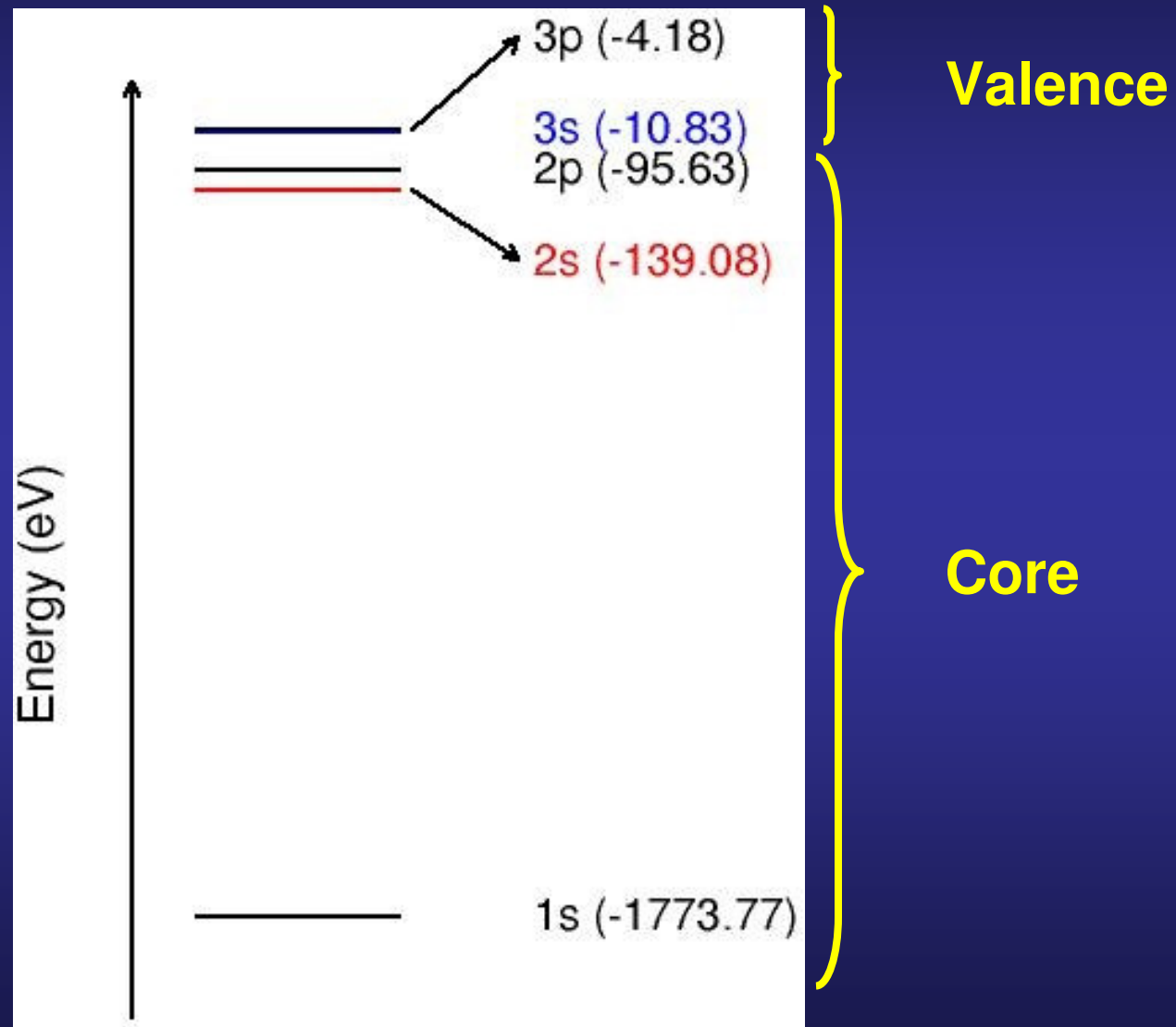
Energy (eV)

Atomic Si

Core wavefunctions are very localized around the nuclei
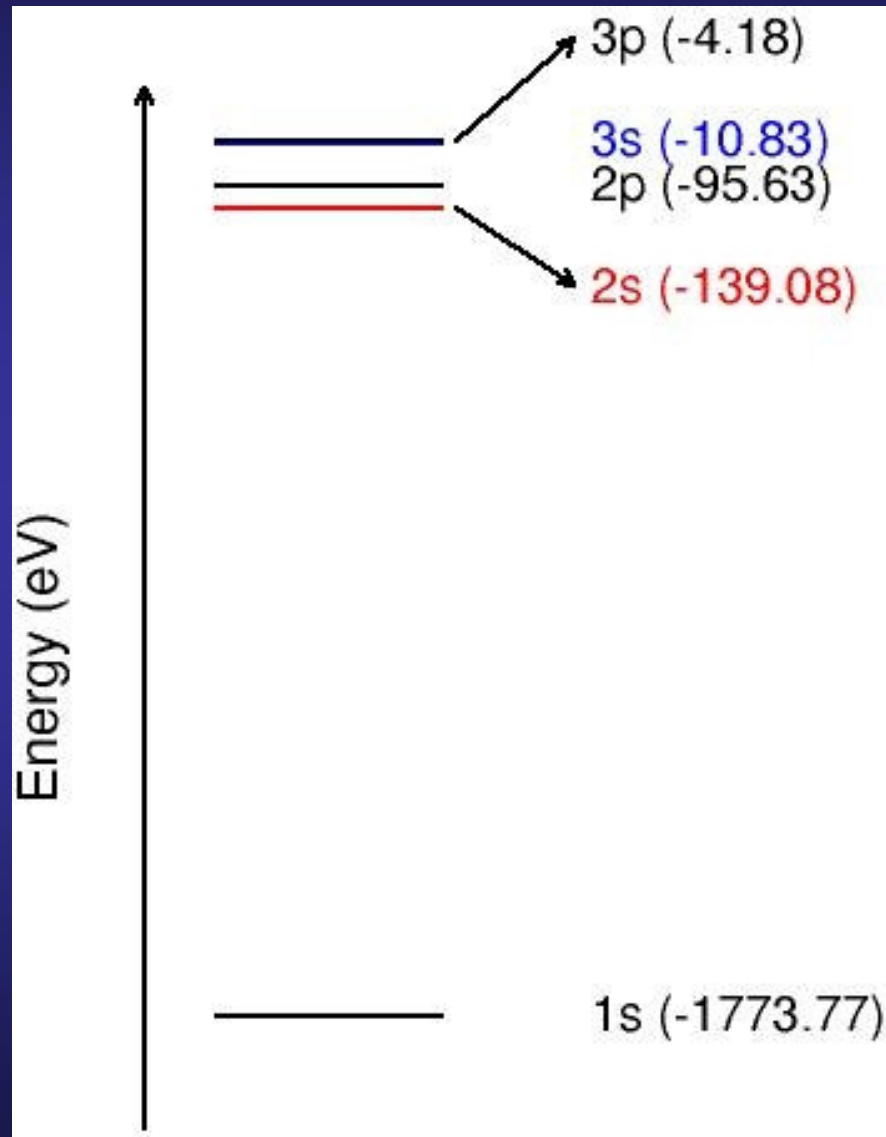
3p (-4.18)

3s (-10.83)
2p (-95.63)

2s (-139.08)

1s (-1773.77)

Energy (eV)

Atomic Si

$u_{1,s}(r)$

$u_{n,s}(r)$

r (bohr)

Core wavefunctions are very localized around the nuclei

Atomic Si
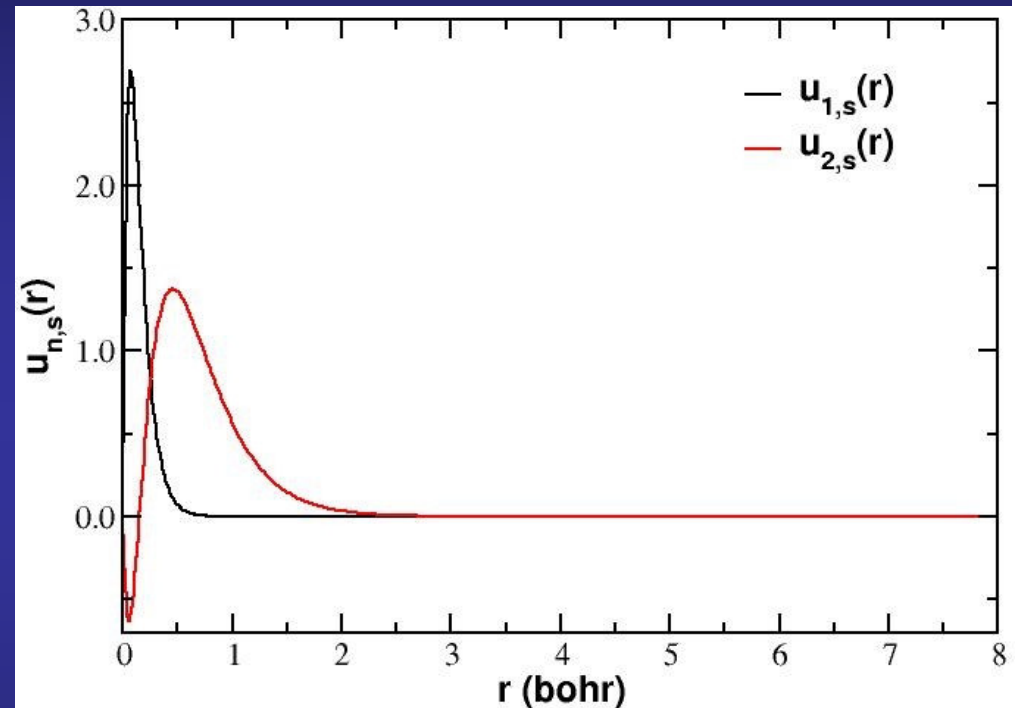
Core electrons…

highly localized

very depth energy

… are chemically inert

Core electrons are chemically inert
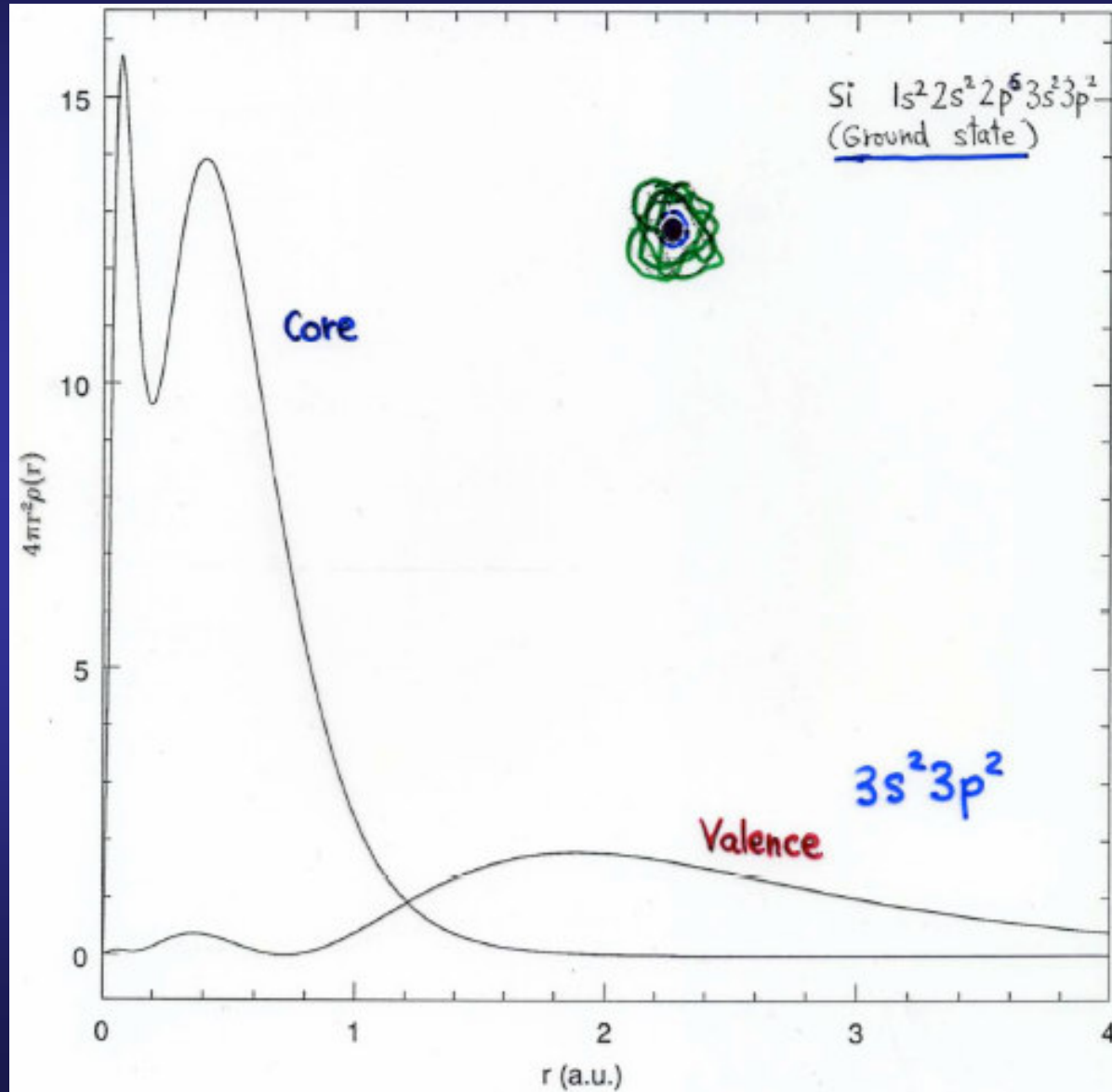
Core electrons are chemically inert
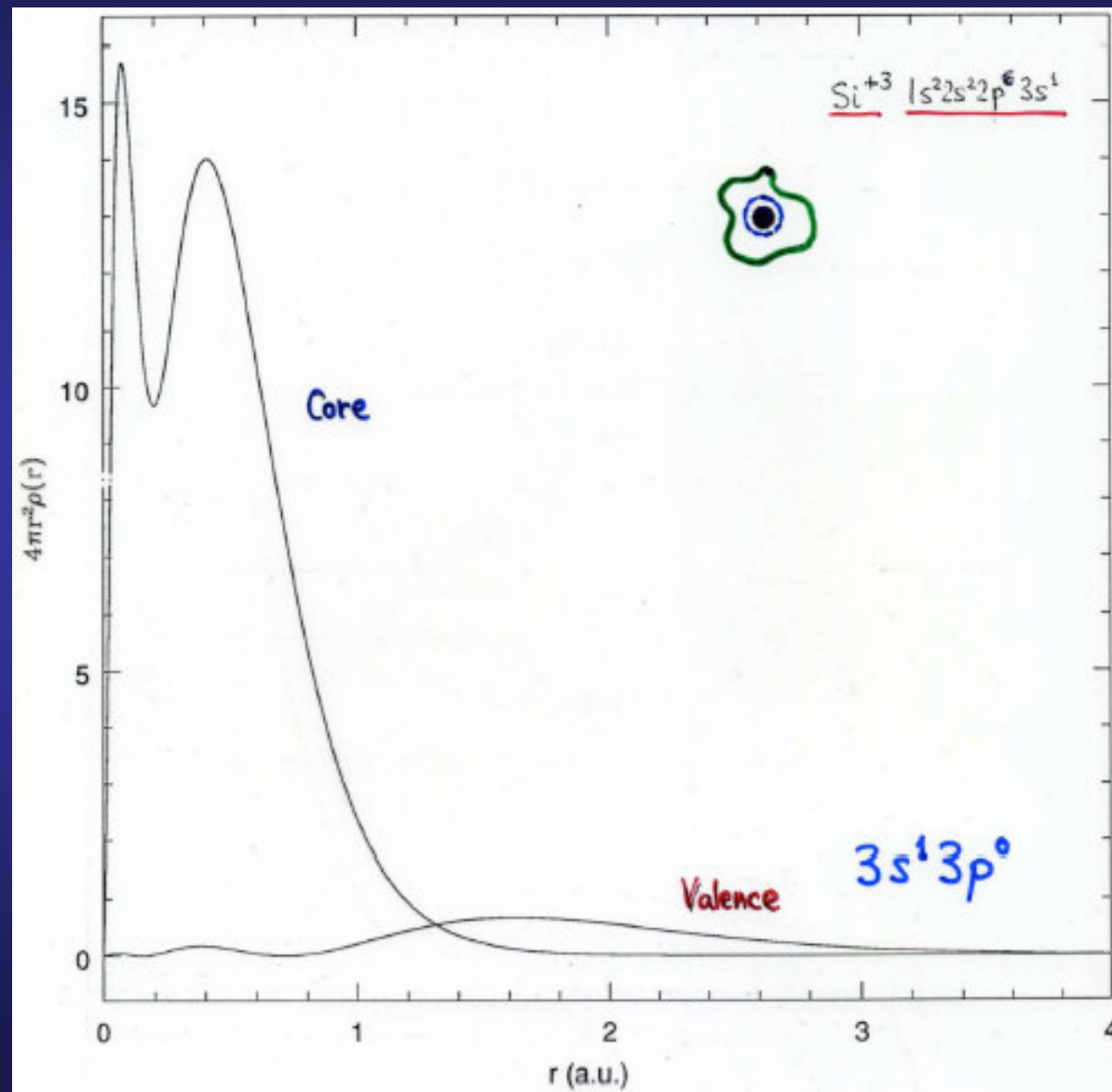
Valence wave functions must be orthogonal to the core wave functions

Atomic Si

Core electrons…

highly localized

very depth energy

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Valence wave functions must be orthogonal to the core wave functions

3p (-4.18)

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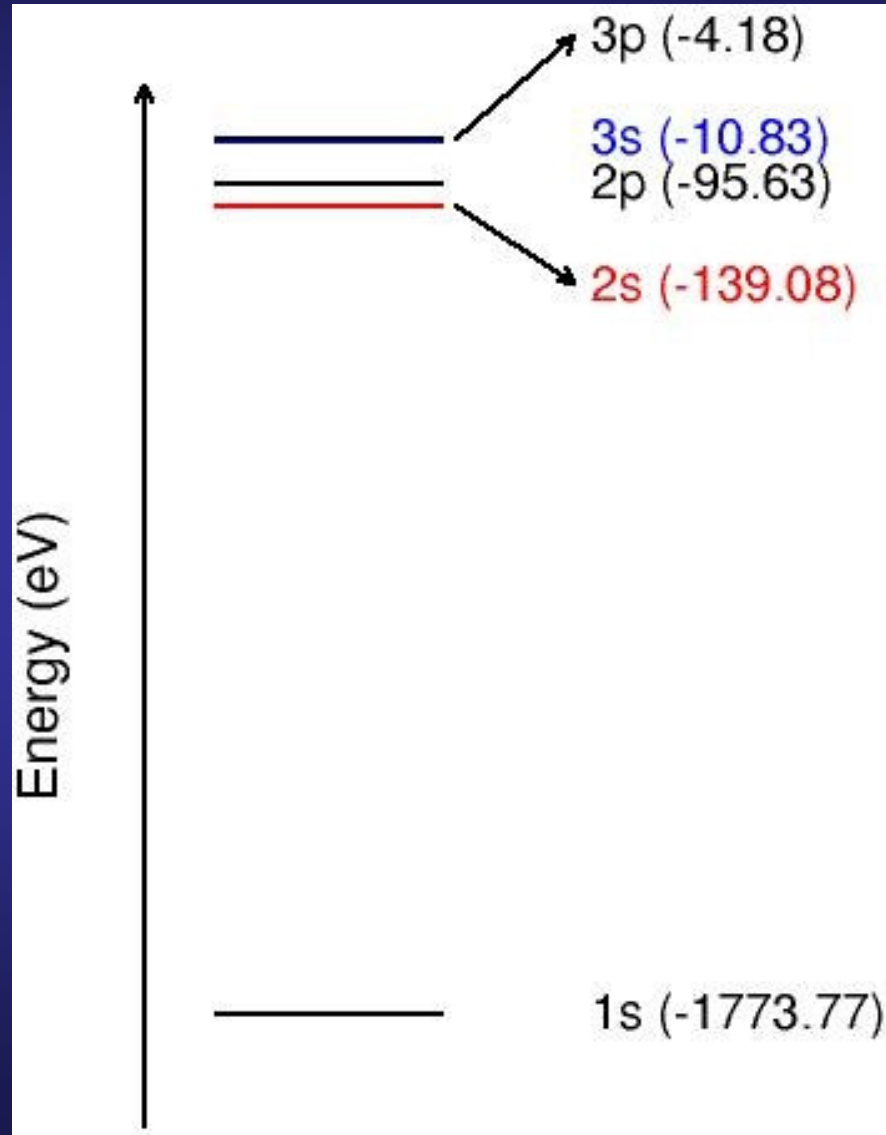
Atomic Si
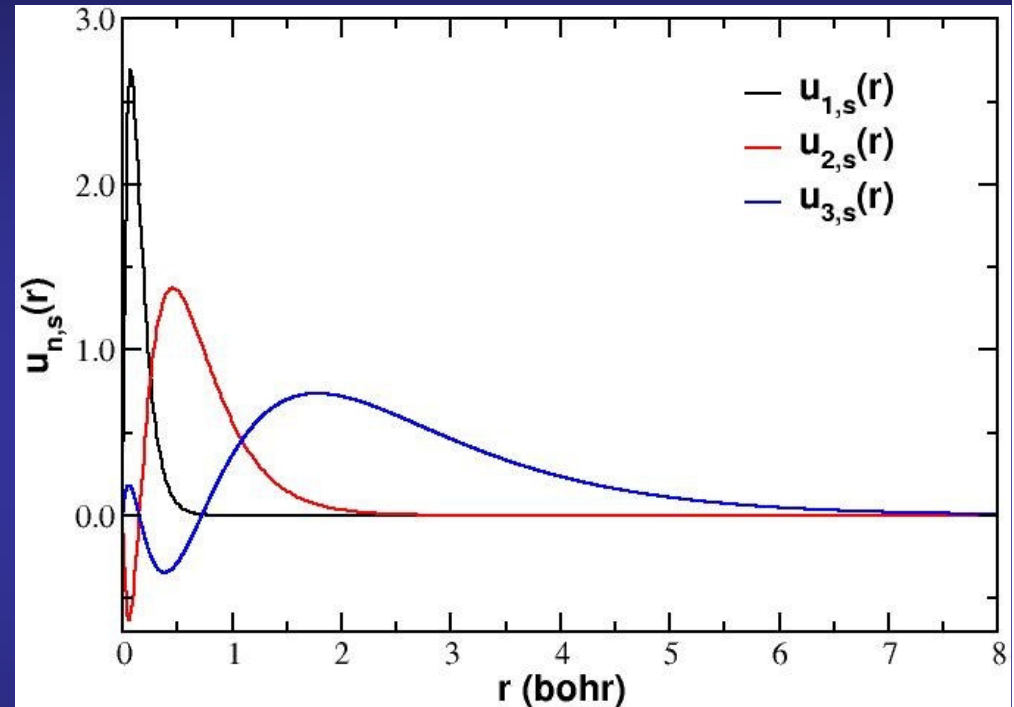
Core electrons…

highly localized

very depth energy

… are chemically inert

Fourier expansion of a valence wave function has a great contribution of short-wave length
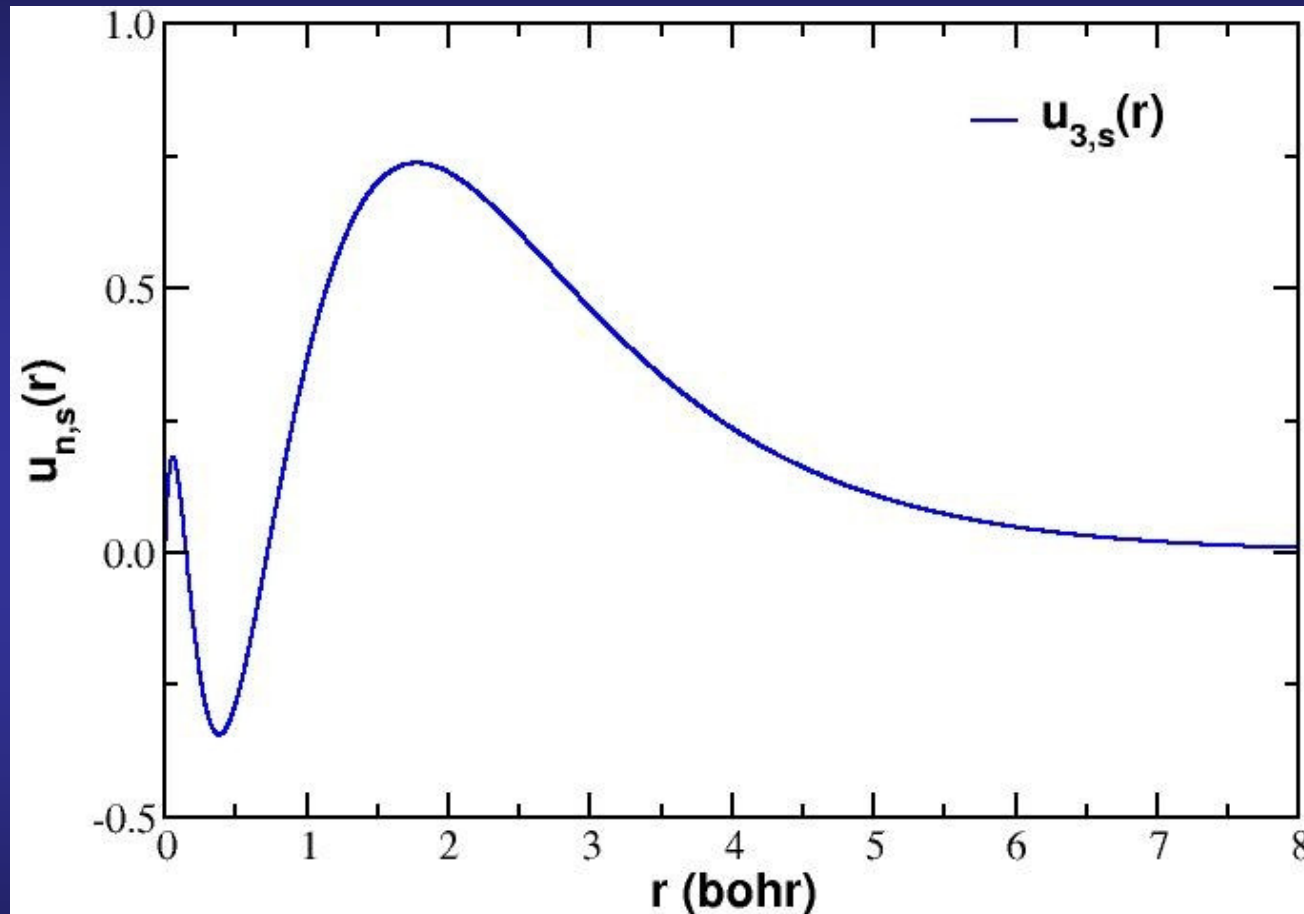
To get a good approximation we would have to use a large number of plane waves.

Pseudopotential idea:

Core electrons are chemically inert

(only valence electrons involved in bonding)

Core electrons make the calculation more expensive

more electrons to deal with

orthogonality with valence $\Rightarrow$ poor convergence in PW

Core electrons main effect: screen nuclear potential

Idea:

Ignore the dynamics of the core electrons (freeze them)

And replace their effects by an effective potential

Orthogonalized Plane Waves (OPW) take into account effects of the cores upon valence electrons

$$\chi_{\vec{k}}^{OPW}(\vec{r}) = \frac{1}{\sqrt{\Omega}} \left[e^{i\vec{k}\cdot\vec{r}} - \sum_j \langle v_j | \vec{k} \rangle v_j(\vec{r}) \right]$$

$$\langle v_j | \vec{k} \rangle \equiv \int d\vec{r} \, v_j(\vec{r}) e^{i\vec{k}\cdot\vec{r}}$$

$v_j(\vec{r})$ are functions localized around each nucleus

(typically the core orbitals)

Example of the OPW method:
Valence function with a 3s character close to the nucleus

$\psi_{\vec{k}}$

r
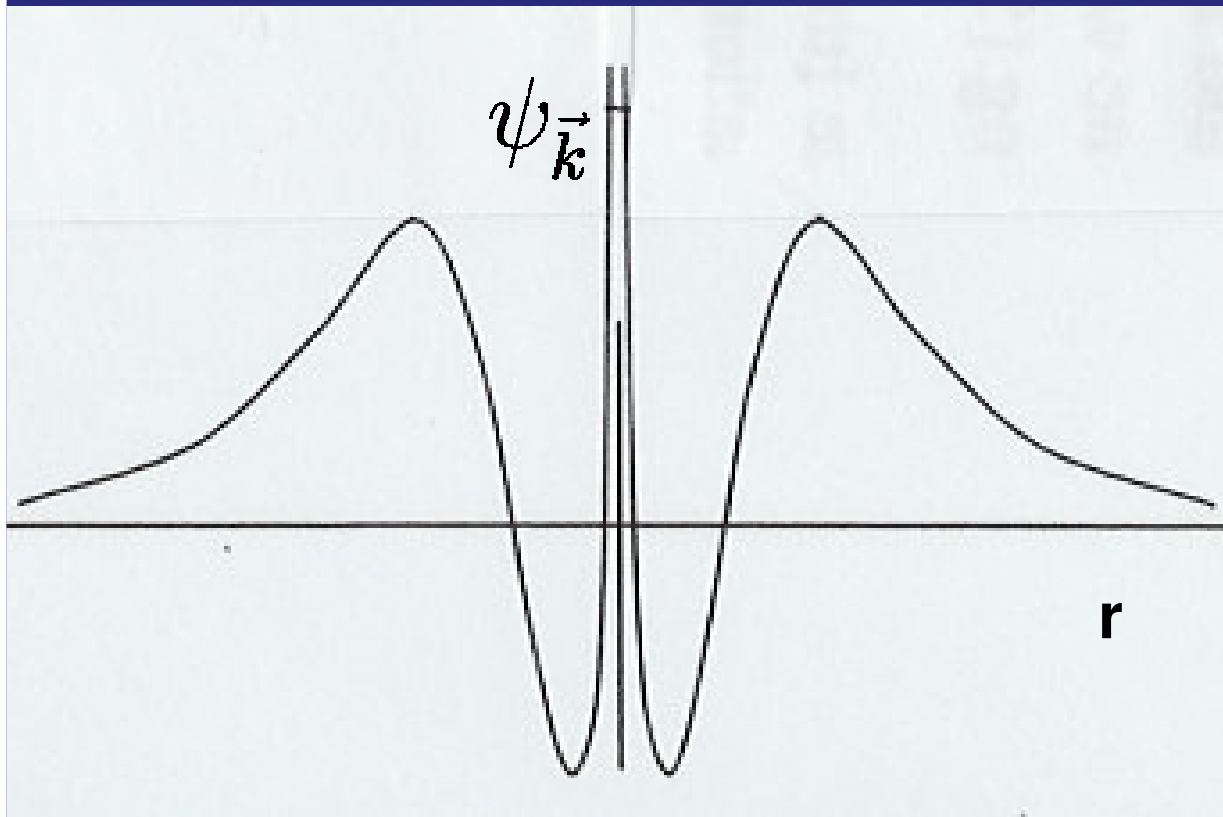
Orthogonal to 1s and 2s

Rapidly varying function close to the nuclei

⇓

Poor convergence in PW

R. M. Martin, Electronic structure, Basic Theory and Practical Methods, Cambridge University Press, Cambridge, 2004

Orthogonalizing the function to the core functions we get a smoother wave function.

$$\tilde{\psi}_{\vec{k}}(\vec{r}) = \psi_{\vec{k}}(\vec{r}) - \sum_{j,\nu} \alpha_{j,\nu} v_j(\vec{r} - \vec{R}_\nu)$$

$\underbrace{\phantom{\alpha_{j,\nu} v_j(\vec{r} - \vec{R}_\nu)}}$ **Atomic core functions**
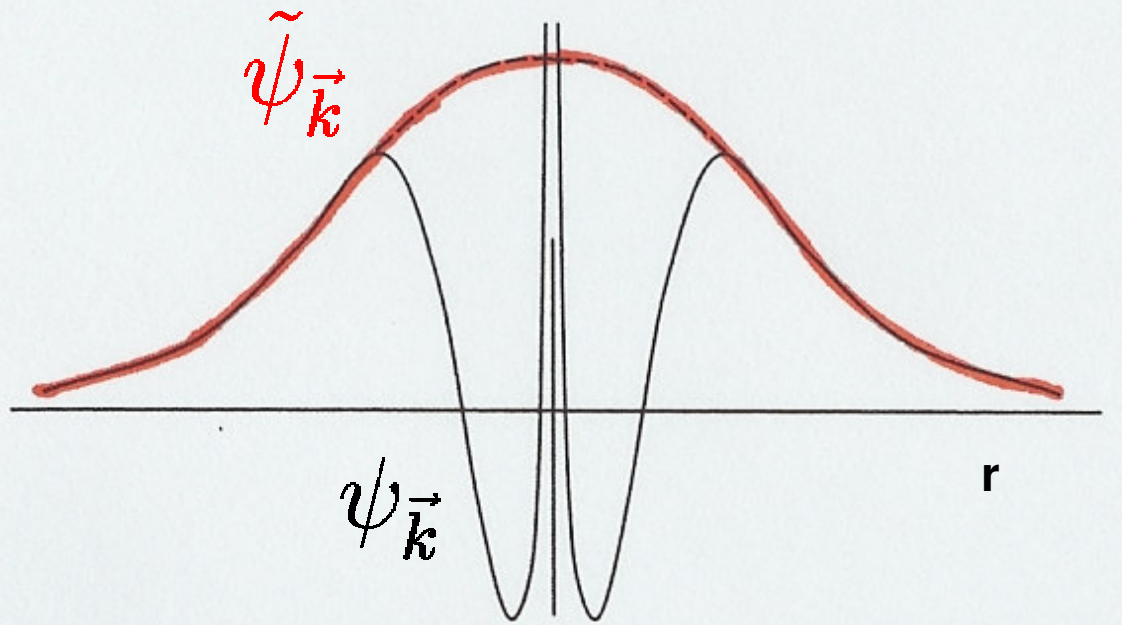
Fourier series for $\tilde{\psi}_{\vec{k}}$
converge rapidly

$\tilde{\psi}_{\vec{k}}$

$\psi_{\vec{k}}$

r

The wave function can be expanded in a rapidly convergent serie of orthogonalized plane waves!!

$$\tilde{\psi}_{\vec{k}}(\vec{r}) = \psi_{\vec{k}}(\vec{r}) - \sum_{j,\nu} \alpha_{j,\nu} v_j(\vec{r} - \vec{R}_\nu)$$

$$\tilde{\psi}_{\vec{k}}(\vec{r}) = \sum_{\vec{g}} \frac{\beta_{\vec{g}}}{\sqrt{\Omega}} e^{i(\vec{k}+\vec{g})\cdot\vec{r}}$$

$$\Downarrow \qquad \langle v_l | \psi_{\vec{k}} \rangle \approx 0$$

$$\psi_{\vec{k}}(\vec{r}) \approx \sum_{\vec{g}} \beta_{\vec{g}} \chi_{\vec{k}+\vec{g}}^{OPW}(\vec{r})$$

The OPW method is the prescience of all the modern pseudopotential and PAW methods

Distinguishes between core and valence electrons

Divides the space into a smooth part and a localized part

Requires the solution of the Schrodinger equation for the isolated atom

Much rapid convergence of the wave functions with the number of plane waves

The pseudopotential transformation:
Seeking for the wave equation of the "smooth"

Replace the OPW form of the wave function into the Schrödinger equation

$$\psi_i^v(\vec{r}) = \tilde{\psi}_i^v(\vec{r}) - \sum_j \left\langle \psi_j^c | \tilde{\psi}_i^v \right\rangle \psi_j^c(\vec{r})$$

$$\hat{H}\psi_i^v(\vec{r}) = \left[-\frac{1}{2}\nabla^2 + V(\vec{r}) \right] \psi_i^v(\vec{r}) = \varepsilon_i^v \psi_i^v(\vec{r})$$

$$\Downarrow$$

Equation for the smooth part, with a non local operator

$$\hat{H}^{PKA}\tilde{\psi}_i^v(\vec{r}) \equiv \left[-\frac{1}{2}\nabla^2 + \hat{V}^{PKA} \right] \tilde{\psi}_i^v(\vec{r}) = \varepsilon_i^v \tilde{\psi}_i^v(\vec{r})$$

The original potential is replaced by a weaker non-local pseudopotential

$$\hat{V}^{PKA} = V + \hat{V}^{R}$$

$$\hat{V}^{R}\tilde{\psi}_i^v(\vec{r}) = \sum_j (\varepsilon_i^v - \varepsilon_j^c)\left\langle \psi_j^c | \tilde{\psi}_i^v \right\rangle \psi_j^c(\vec{r})$$

Advantages

Repulsive

$$\varepsilon_i^v - \varepsilon_j^c > 0$$

$$\Downarrow$$

V^{PKA} is much weaker than the original potential V(r)

The original potential is replaced by a weaker non-local pseudopotential

$$\hat{V}^{PKA} = V + \hat{V}^R$$

$$\hat{V}^R \tilde{\psi}_i^v(\vec{r}) = \sum_j (\varepsilon_i^v - \varepsilon_j^c) \left\langle \psi_j^c \middle| \tilde{\psi}_i^v \right\rangle \psi_j^c(\vec{r})$$

Advantages

Repulsive

$$\varepsilon_i^v - \varepsilon_j^c > 0$$

$$\Downarrow$$

V^{PKA} is much weaker than the original potential V(r)

Spatially localized

vanishes where $\psi_j^c = 0$

Disadvantages

Non-local operator

$$\left\langle \psi_j^c \middle| \tilde{\psi}_i^v \right\rangle = \int d\vec{r'} \, \psi_j^c(\vec{r'}) \tilde{\psi}_i^v(\vec{r'})$$

The original potential is replaced by a weaker non-local pseudopotential

J. C. Phillips and L. Kleinman, Phys. Rev. 116, 287 (1959)

$$\hat{V}^{PKA} = V + \hat{V}^{R}$$

$$\hat{V}^{R}\tilde{\psi}_i^v(\vec{r}) = \sum_j (\varepsilon_i^v - \varepsilon_j^c)\left\langle \psi_j^c \middle| \tilde{\psi}_i^v \right\rangle \psi_j^c(\vec{r})$$

Advantages	**Disadvantages**
Repulsive	**Non-local operator**
$$\varepsilon_i^v - \varepsilon_j^c > 0$$	$\tilde{\psi}_i^v$ **are not orthonormal**
$\Downarrow$	
V^{PKA} is much weaker than the original potential V(r)	$\hat{V}^R$ **is not smooth**
Spatially localized	**l-dependent**
vanishes where $\psi_j^c = 0$	

**Fundamental idea of pseudopotential:
"Replace one problem with another"**

The properties of the wave function outside the scattering region can be reproduced over a wide range of energies by another potential chosen to have more desirable properties.

The pseudopotential can be chosen to be both weaker and smoother

The pseudopotential is not unique.

There exists many different pseudopotential

Model ion potential constructed by fitting experiments or from first-principles
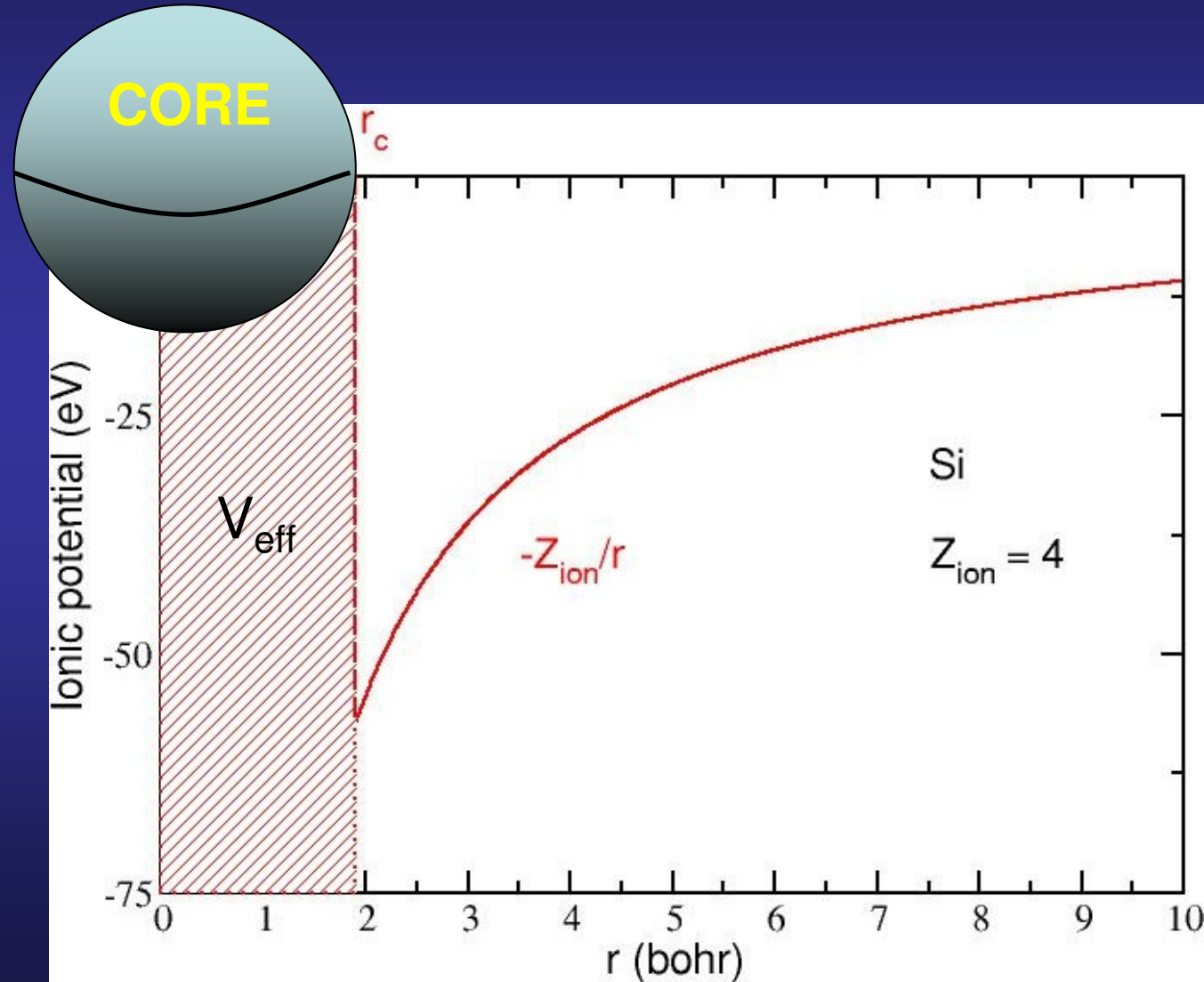
Model ion potential constructed by fitting experiments or from first-principles

Model potentials
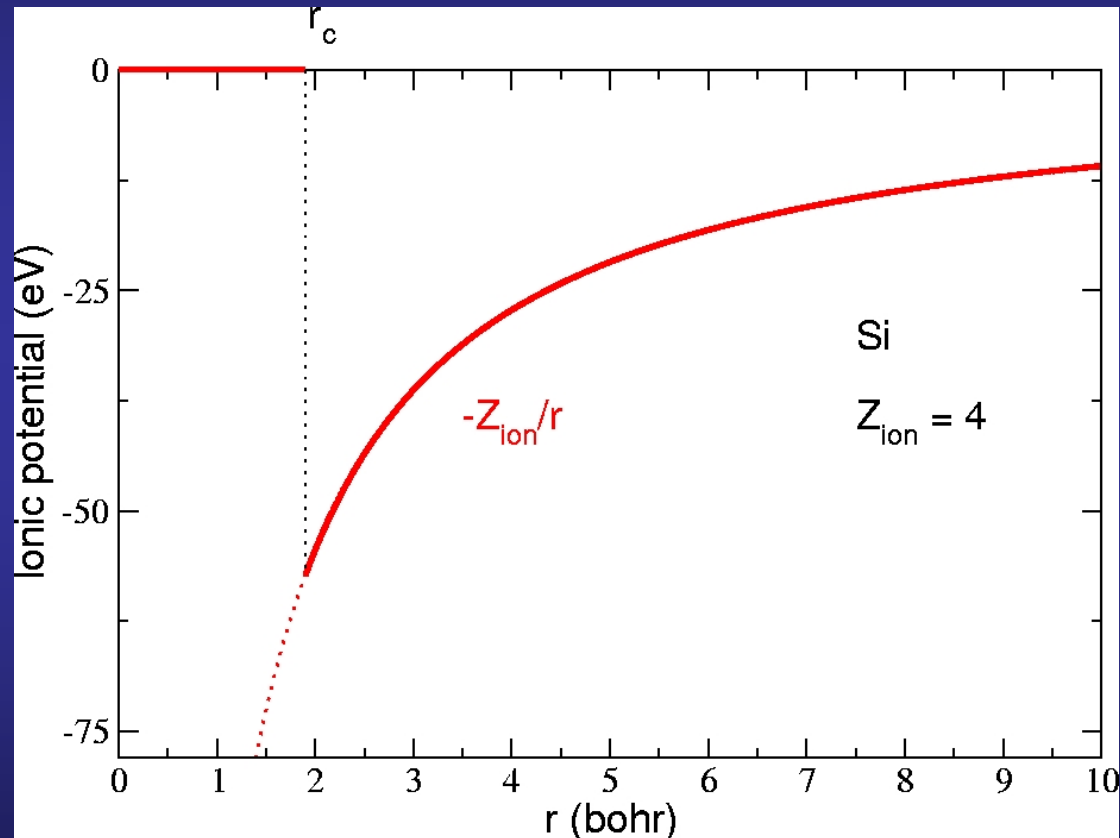
Empty core

N. W. Ashcroft, Phys. Lett. 23, 48 (1966)

Empirical pseudopotential method (EPM): from expt. input to the whole band structure

Band structure of GaAs

-adsorption edge

-reflectivity features

T. C. Chiang *et al.*, Phys. Rev. B 21, 3513 (1980)
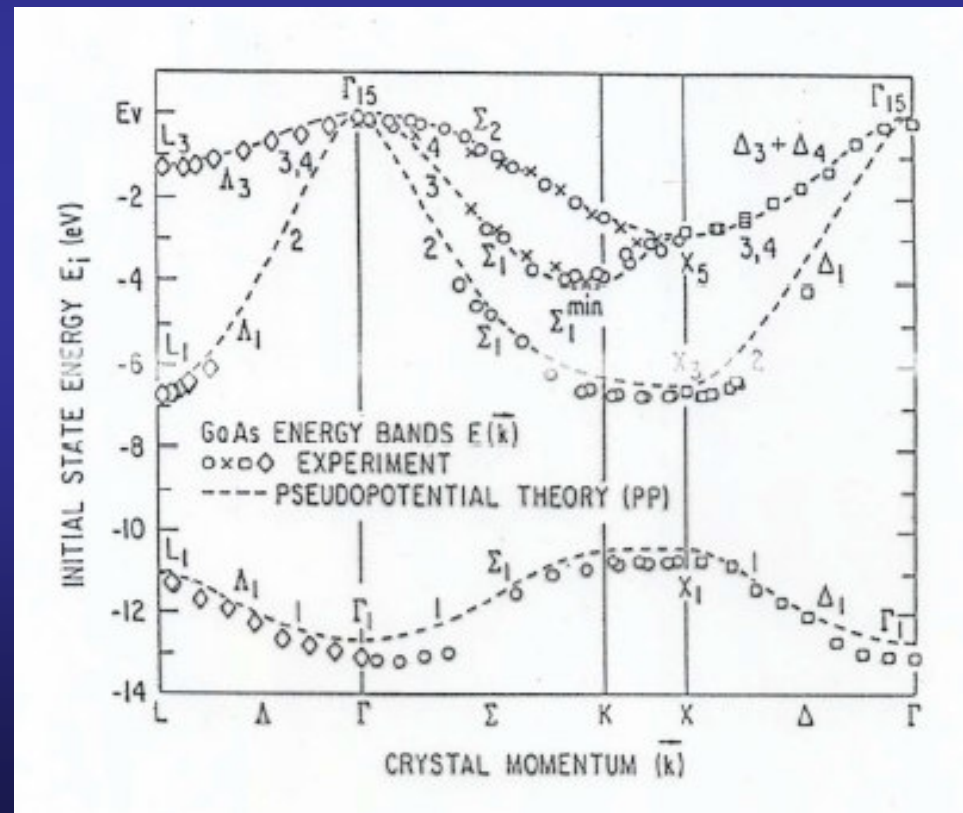
Ab-initio pseudopotential method: fit the valence properties calculated from the atom
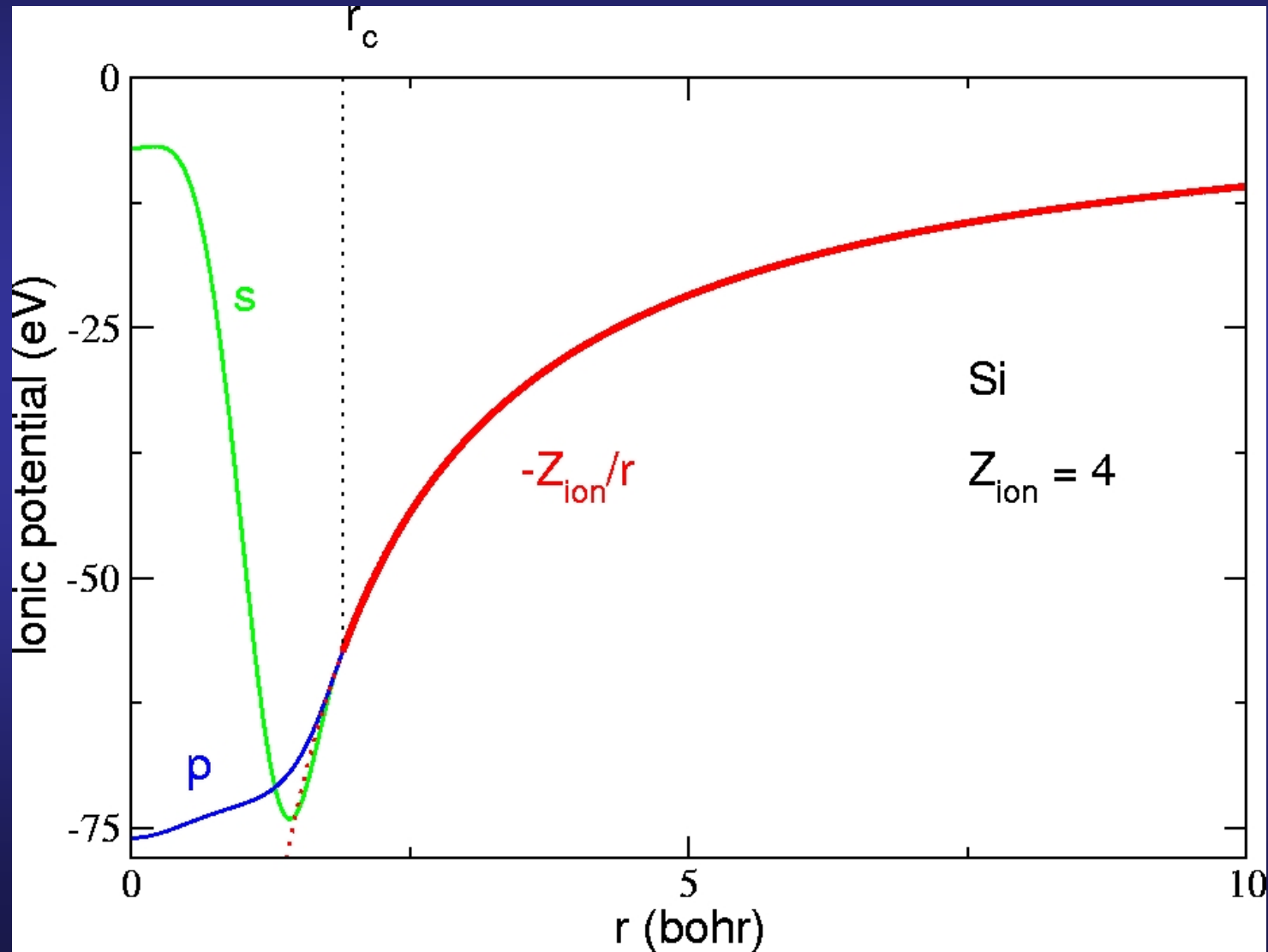
List of requirements for a good norm-conserving pseudopotential:

Choose an atomic reference configuration   Si: $\underbrace{1s^2\ 2s^2\ 2p^6}_{\text{core}}$ $\underbrace{3s^2\ 3p^2}_{\text{valence}}$
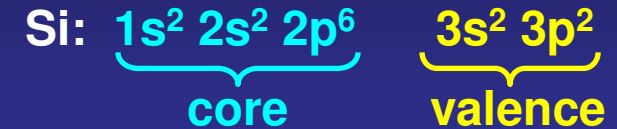
1. All electron and pseudo valence eigenvalues agree for the chosen reference configuration
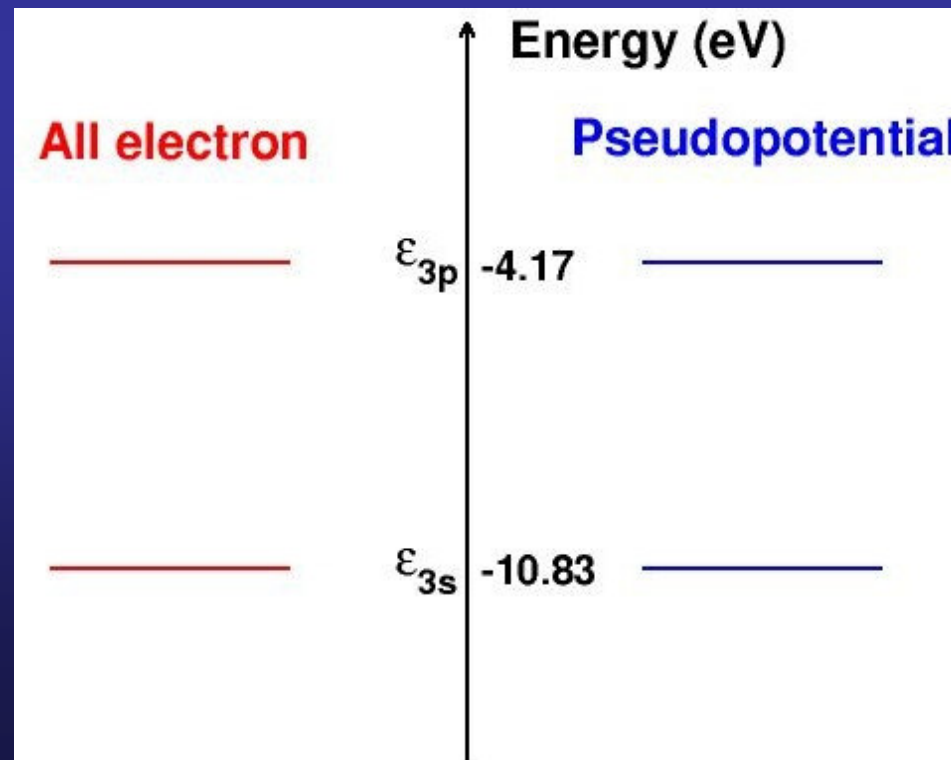
List of requirements for a good norm-conserving pseudopotential:

Choose an atomic reference configuration   Si: $1s^2\ 2s^2\ 2p^6$ $3s^2\ 3p^2$

core   valence
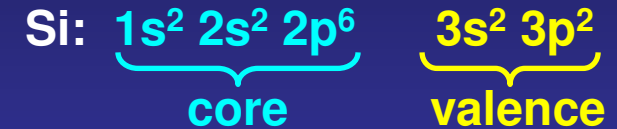
2. All electron and pseudo valence wavefunctions agree beyond a chosen cutoff radius R_c (might be different for each shell)
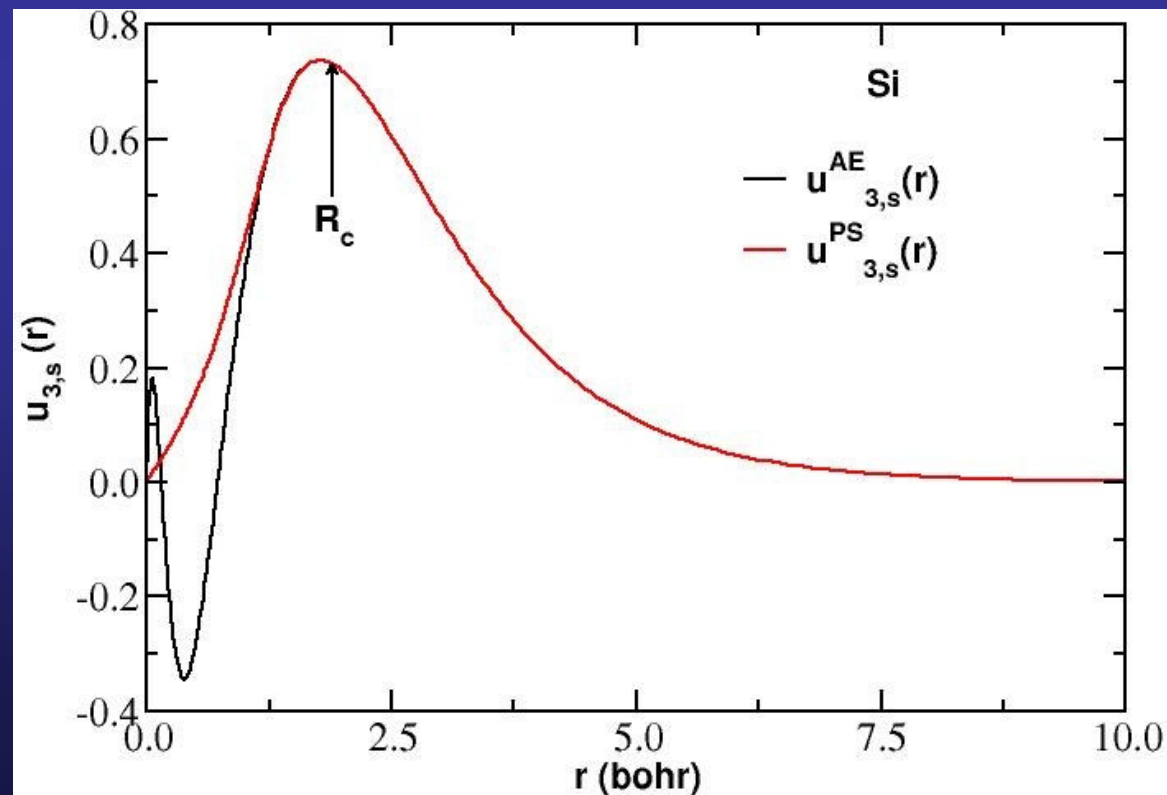
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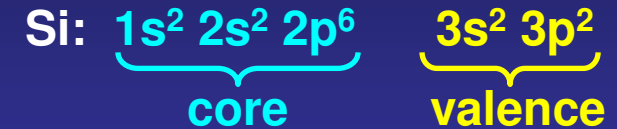
3. The logarithmic derivatives of the all-electron and pseudowave functions agree at R_c

$$D_l(\varepsilon, r) \equiv r\frac{\psi_l'(\varepsilon, r)}{\psi_l(\varepsilon, r)} = r\frac{d}{dr}ln\left[\psi_l(\varepsilon, r)\right]$$

List of requirements for a good norm-conserving pseudopotential:

Choose an atomic reference configuration   Si: $\underbrace{1s^2\ 2s^2\ 2p^6}_{\text{core}}\ \underbrace{3s^2\ 3p^2}_{\text{valence}}$
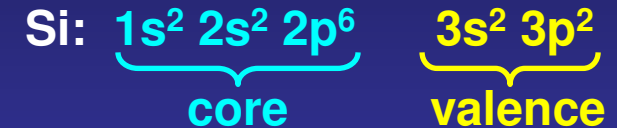
4. The integrals from 0 to *r* of the real and pseudo charge densities agree for *r* > R$_c$ for each valence state

$$Q_l = \int_0^{R_c} dr\, r^2 \left| \psi_l(r) \right|^2$$

Q_l **is the same for** ψ_l^{PS} **as for the all electron radial orbital** ψ_l

$\Downarrow$

- Total charge in the core region is correct

- Normalized pseudoorbital is equal to the true orbital outside of R$_c$

List of requirements for a good norm-conserving pseudopotential:

Choose an atomic reference configuration   Si: $\underbrace{1s^2\ 2s^2\ 2p^6}_{\text{core}}\ \underbrace{3s^2\ 3p^2}_{\text{valence}}$
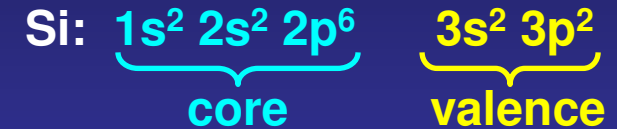
5. The first energy derivative of the logarithmic derivatives of the all-electron and pseudo wave functions agrees at R_c

Central point due to Hamann, Schlüter and Chiang:

Norm conservation [(4)] $\Rightarrow$ (5)

$$2\pi \left[(r\psi)^2 \frac{d}{d\varepsilon} \frac{d}{dr} ln\psi \right]_R = 4\pi \int_0^R r^2 \psi^2 dr$$

Equality of AE and PS energy derivatives of the logarithmic derivatives essential for transferability

Atomic Si
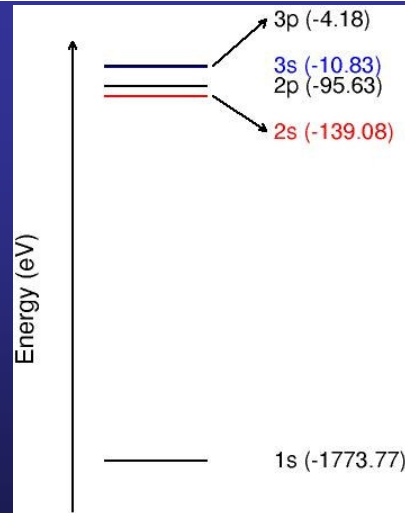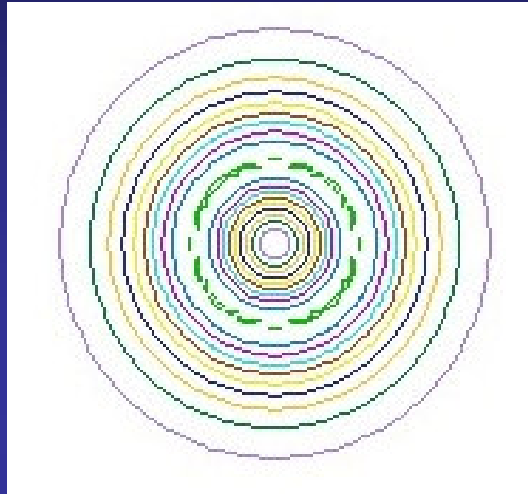
Bulk Si
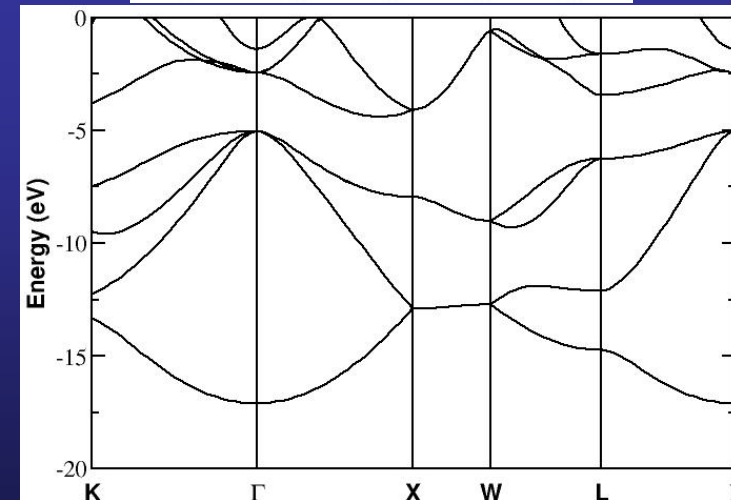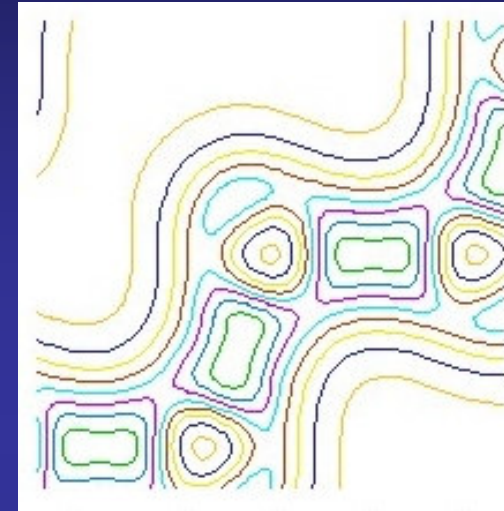
If condition 5 is satisfied, the change in the eigenvalues to linear order in the change in the potential is reproduced

Generation of *l*-dependent norm-conserving pseudopotential

All electron self consistent atomic calculation

Each state l,m treated independently

Identify the valence states

Freedom (different approaches)

Generate the pseudopotential $V_{l,total}(r)$ and pseudoorbitals $\psi_l^{PS}(r)$

$V_{l,total}(r)$ screened pseudopotential acting on valence electrons

"Unscreened" by substracting from the total potential $V_{Hxc}^{PS}(r)$

$$V_l(\vec{r}) \equiv V_{l,total}(\vec{r}) - V_{Hxc}^{PS}(\vec{r})$$

Different methods to generate norm-conserving pseudopotential

Troullier-Martins **Kerker** **Haman-Schlüter-Chiang** **Vanderbilt**
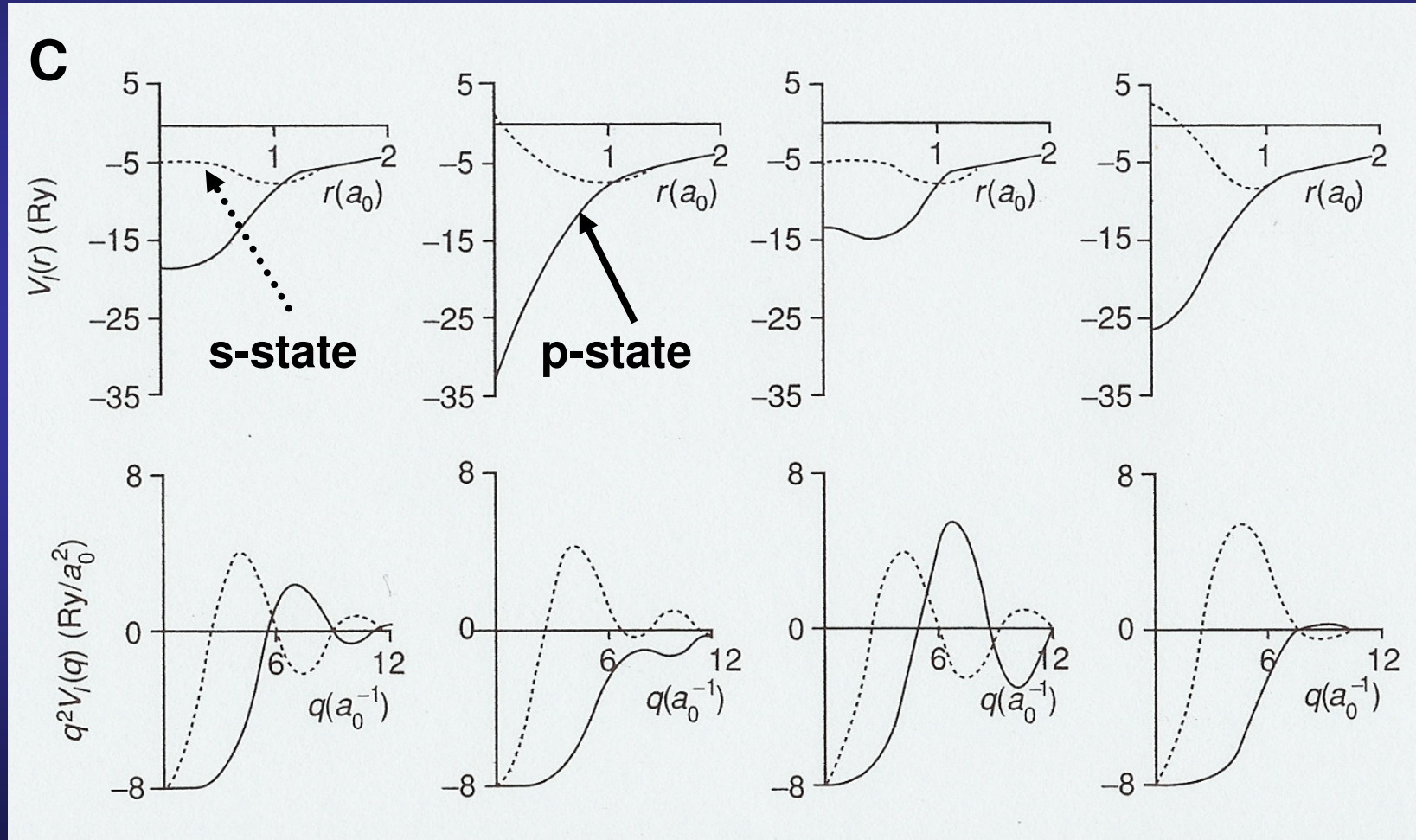
s-state

p-state

R. M. Martin, Electronic structure, Basic Theory and Practical Methods, Cambridge University Press, Cambridge, 2004
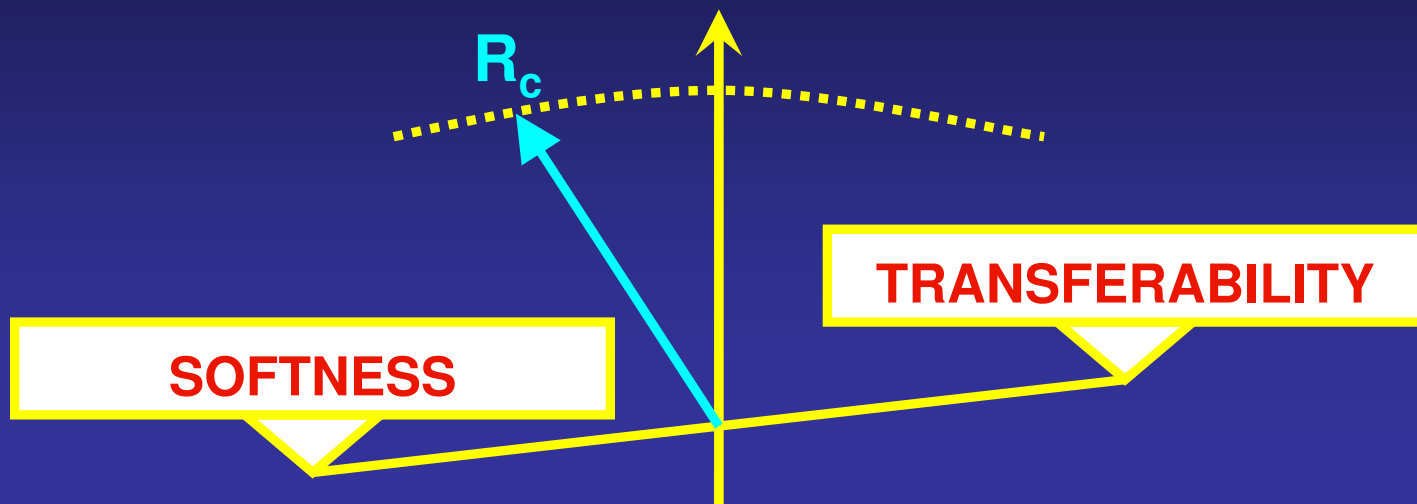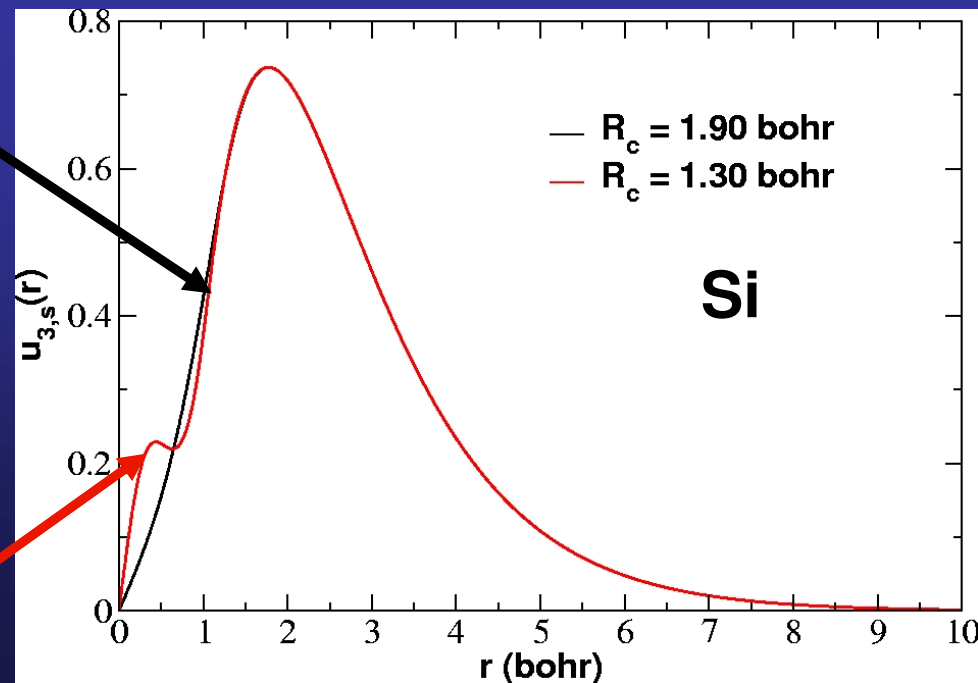
A transferable pseudo will reproduce the AE energy levels and wave functions in arbitrary environments

- 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: $\Delta E^{AE} = \Delta E^{PS}$

total energy differences in series

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

ΔE^{AE}

total energy differences in series

	1	2	3	4	5
1	0.0000				
2	0.4304	0.0000			
3	0.4958	0.0654	0.0000		
4	0.9602	0.5297	0.4643	0.0000	
5	1.4970	1.0666	1.0012	0.5369	0.0000

ΔE^{PS}

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

Problematic cases: first row elements 2p and 3d elements

O: $1s^2$ $\underbrace{2s^2\ 2p^4}$

core valence
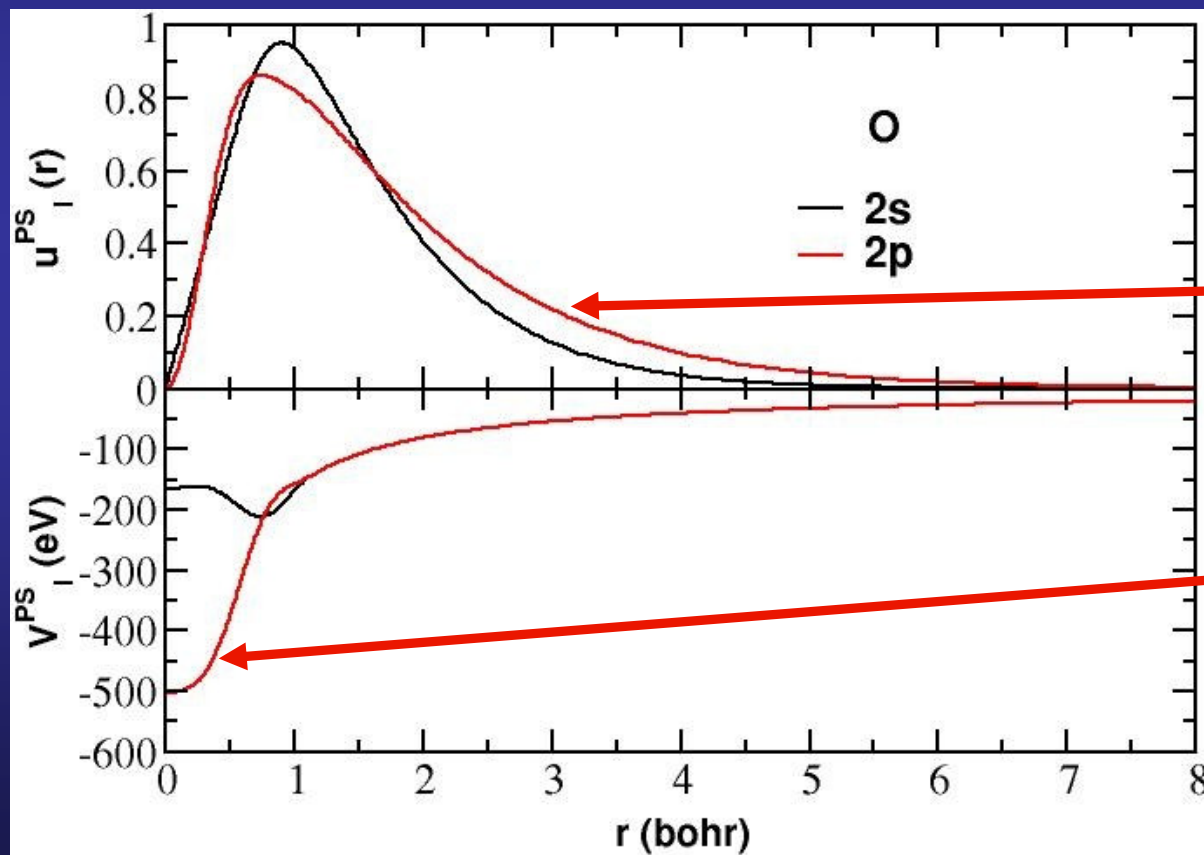
No nodes because there are no p states to be orthogonal to

pseudopotential is hard

Conclusions

- Core electrons…

  highly localized and very depth energy

  … are chemically inert

- Pseudopotential idea

  Ignore the dynamics of the core electrons (freeze them)

  And replace their effects by an effective potential

- Pseudopotentials are not unique

  there might be many "best choices"

- Two overall competing factors: transferability vs hardness

- Norm conservation helps transferability

- Always test the pseudopotential in well-known situations

Outline

Pseudopotentials

Why pseudopotential approach is useful

Orthogonalized Plane Waves (1940)

Pseudopotential transformation (1959)

Norm-conserving pseudopotentials (1979)

Basis sets

Plane Waves

Localized Orbitals

Numerical Atomic Orbitals

Any function can be expanded as a sum of plane waves (Fourier expansion)

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

ADVANTAGES

- Conceptually simple

- Asymptotically complete

- Allow systematic convergence

- "Easy" to implement (FFT)

DISADVANTAGES

- Not suited to represent any function in particular

- Hundreths of wave functions per atom to achieve a good accuracy

- Not well suited for Order-N methods

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

Order-N methods: The computational load scales linearly with the system size
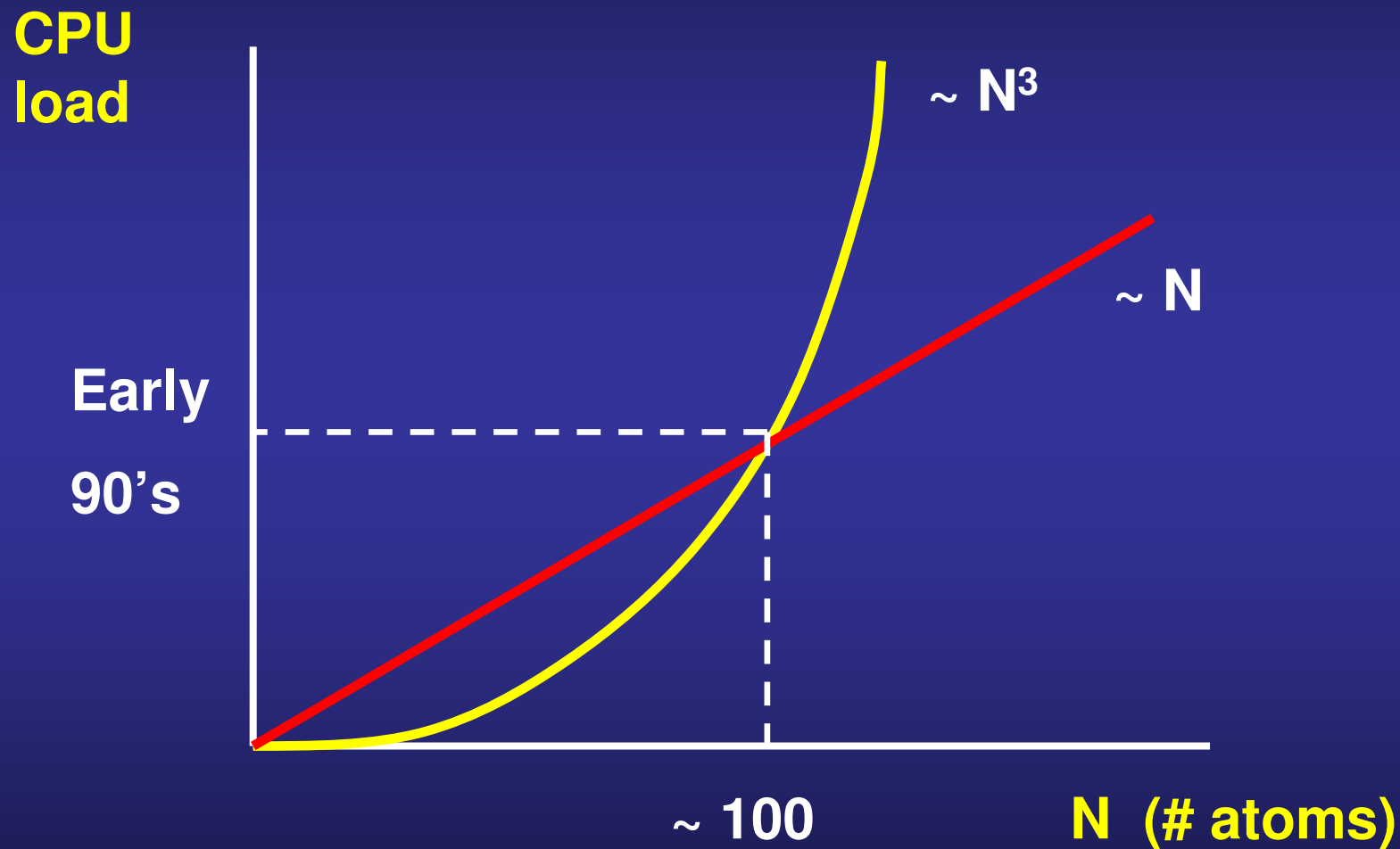
G. Galli and M. Parrinello, Phys. Rev Lett. 69, 3547 (1992)

Locality is the key point to achieve linear scaling

Large system

x2
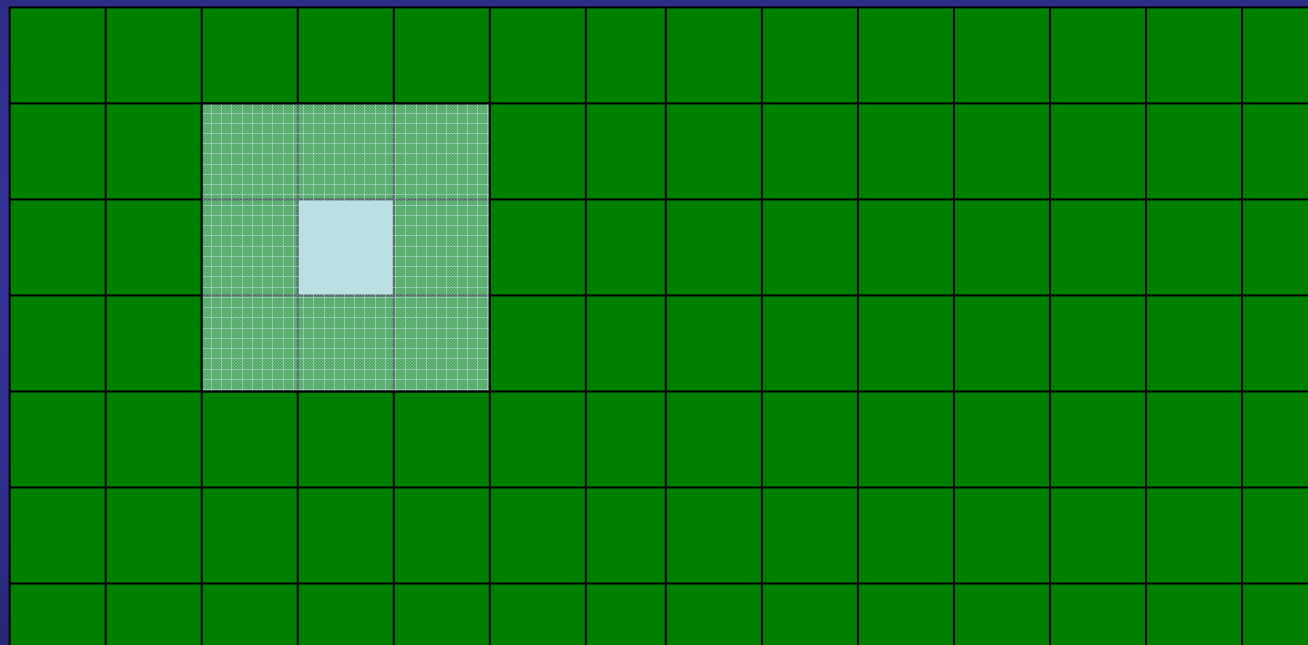
"Divide and Conquer"

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

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

Locality $\Rightarrow$ **Basis set of localized functions**

CPU load

$\sim N^3$

$\sim N$

Early 90's

~ 100

N (# atoms)
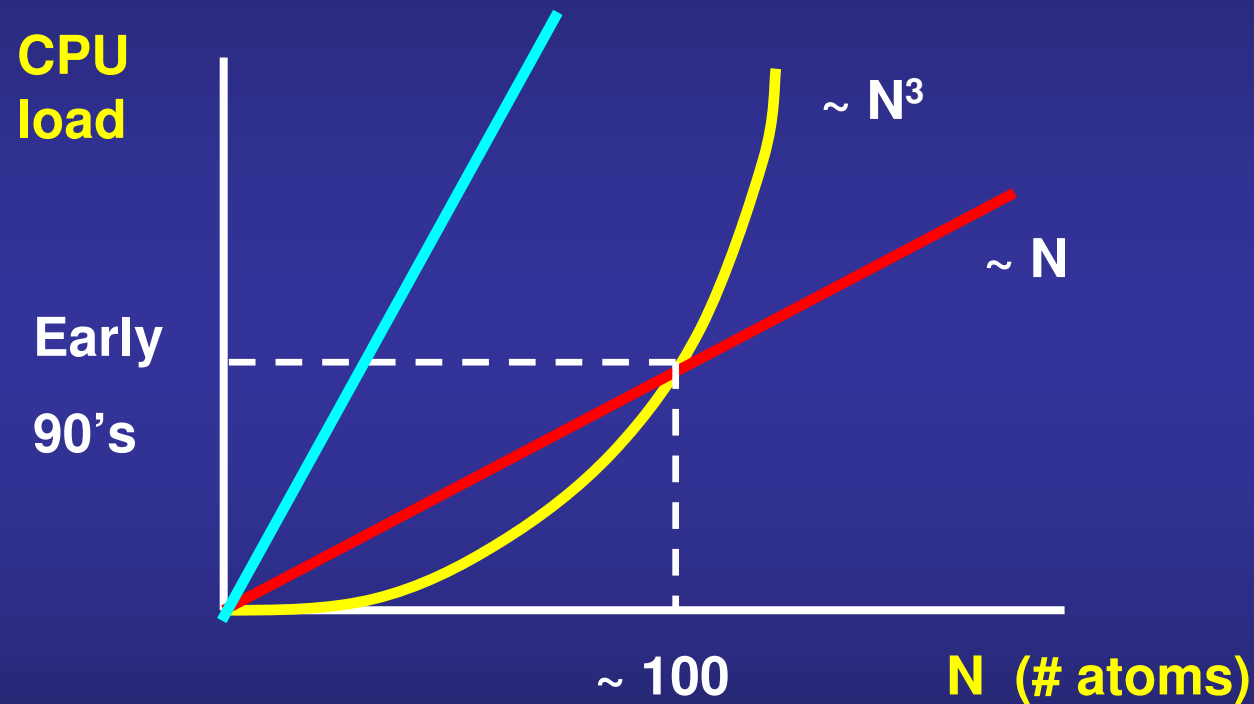
Regarding efficiency, the important aspects are:
- **NUMBER** of basis functions per atom
- **RANGE** of localization of these functions

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

- **Bessel functions in ovelapping spheres**

  P. Haynes & M. Payne

- **B-splines in 3D grid**

  D. Bowler & M. Gillan

- **Finite-differences (nearly O(N))**

  J. Bernholc

- **Linear Combination of Atomic Orbitals**

Main features of the Atomic Orbitals: the pros and the cons

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

- **Very efficient**

- **Lack of systematic for convergence**

- **Main features:**
  - Size
  - Range
  - Shape

Atomic Orbitals: different representations

– Gaussian based + QC machinery

G. Scuseria (GAUSSIAN),

M. Head-Gordon (Q-CHEM)

R. Orlando, R. Dobesi (CRYSTAL)

- Numerical atomic orbitals (NAO)

SIESTA

S. Kenny &. A Horsfield (PLATO)

T. Ozaki (ABRED)

O. Sankey (FIREBALL)

Numerical solution of the Kohn-Sham Hamiltonian for the isolated pseudoatom with the same approximations (xc,pseudos) as for the condensed system

Our method

Linear-scaling DFT based on NAOs (Numerical Atomic Orbitals)

P. Ordejon, E. Artacho & J. M. Soler , Phys. Rev. B 53, R10441 (1996)

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

- Born-Oppenheimer   (relaxations, mol.dynamics)
- DFT   (LDA, GGA)
- Pseudopotentials   (norm conserving, factorised)
- Numerical atomic orbitals as basis   (finite range)
- Numerical evaluation of matrix elements   (3D grid)

Implemented in the SIESTA program

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

Size (number of basis set per atom)

Depending on the required accuracy and available computational power

Quick and dirty **calculations**

Highly converged calculations

Minimal basis set

(single-ζ; SZ)

Multiple-ζ

+

Polarization

+

Diffuse orbitals

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

Examples of different sizes of basis sets

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 of the basis set with Si

Bulk Si

Cohesion curves
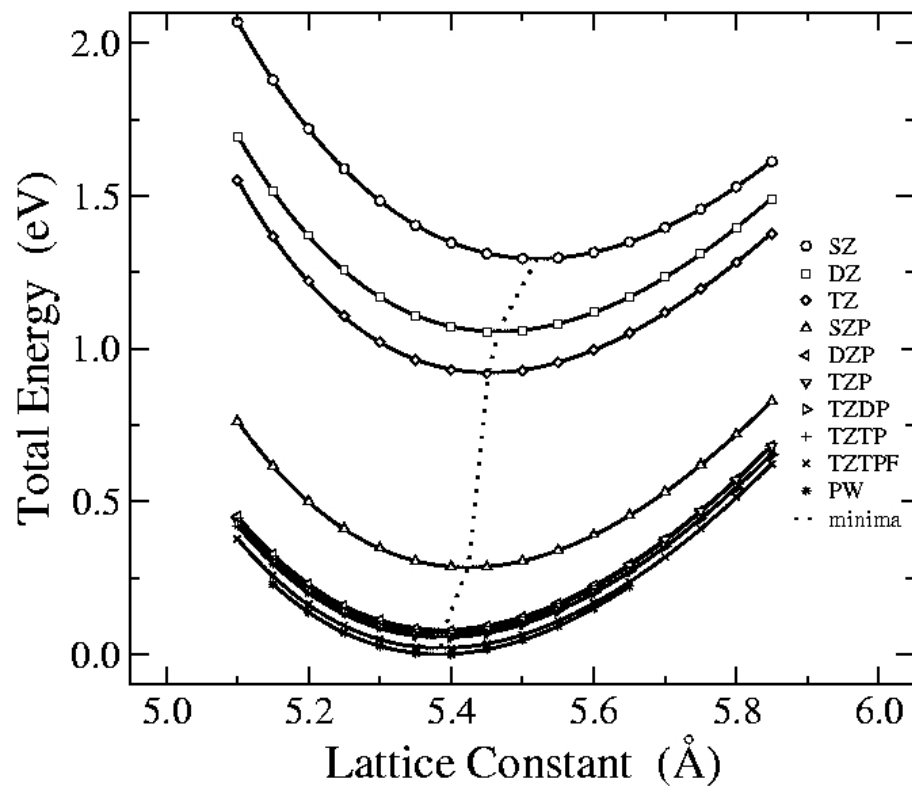
PW and NAO convergence
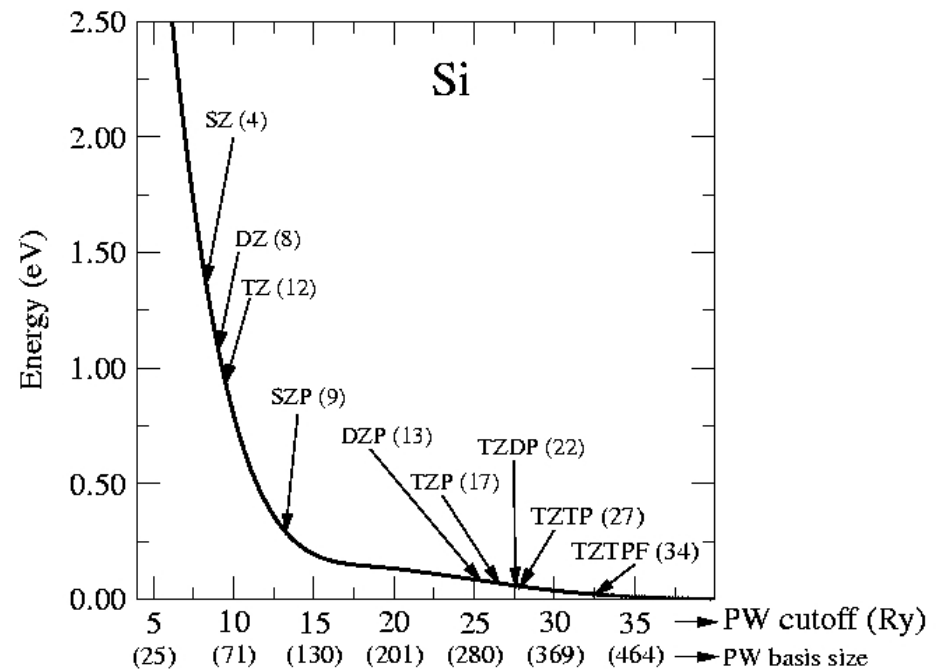
Convergence of the basis set with Si

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

SZ = single-ζ P=Polarized

DZ= doble- ζ DP=Doble-polarized

TZ=triple- ζ

PW: Converged Plane Waves (50 Ry)

APW: Augmented Plane Waves

Range (spatial length of the basis functions)

- **How to get sparse matrix for O(N)**

    - **Neglecting interactions below a tolerance or beyond some scope of neighbours $\Rightarrow$ numerical instablilities for high tolerances.**

    - **Strictly localized atomic orbitals (zero beyond a given cutoff radius, r_c)**

$$\Downarrow$$

- Accuracy and computational efficiency depend on the range of the atomic orbitals

- Way to define all the cutoff radii in a balanced way

Convergence with the range

Bulk Si

equal *s*, *p* orbitals radii

J. Soler *et al.*, J. Phys: Condens. Matter, 14, 2745 (2002)
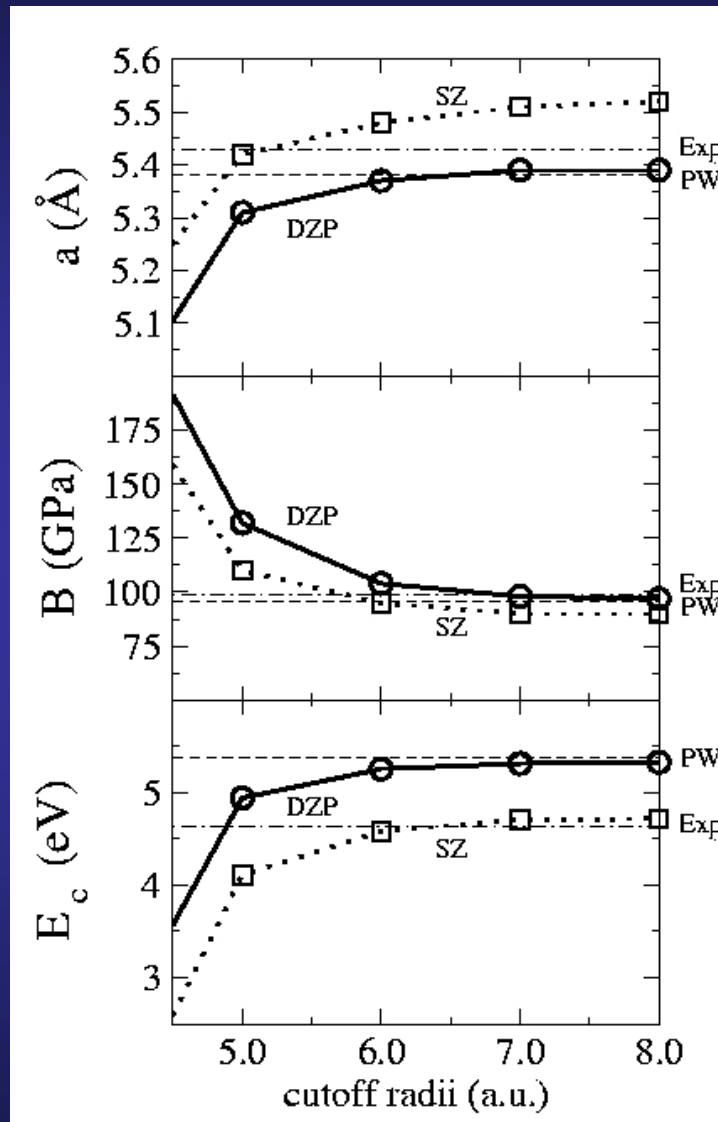
Equivalent PW cutoff (E_{cut}) to optimal DZP

System	DZP # funct. per atom	PW # funct. per atom	E_{cut} (Ry)
H_2	5	11296	34
O_2	13	45442	86
Si	13	227	22
diamond	13	284	59
α-quartz	13	923	76

For molecules: cubic unit cell 10 Å of side

(J. Junquera *et al*, Phys. Rev. B, 64, 23511 (2001))

System		Exp	LAPW	PW (Literature)	PW (same ps)	DZP
Au	a	4.08	4.05	4.07	4.05	4.07
	B	173	198	190	191	188
	E_c	3.81	-	-	4.19	4.03
C	a	3.57	3.54	3.54	3.53	3.54
	B	442	470	436	466	453
	E_c	7.37	10.13	8.96	8.90	8.81
Na	a	4.23	4.05	3.98	3.95	3.98
	B	6.9	9.2	8.7	8.8	9.2
	E_c	1.11	1.44	1.28	1.22	1.22
Cu	a	3.60	3.52	3.56	-	3.57
	B	138	192	172	-	165
	E_c	3.50	4.29	4.24	-	4.37

a (Å)   B(GPa) E_c(eV)

Conclusions

- Within the pseudopotential framework, many different choices of basis:

  - PW

  - Real space grids

  - Localized basis sets

- Plane waves (PW):

  - Asymptotically complete with systematic convergence.

  - Easy to implement

  - Not suited for Order-N

- Atomic orbitals:

  - No systematic convergence.

  - From "quick and dirty" to highly converged

  - Order-N

Different schemes to double the basis set

- **Quantum Chemistry: Split Valence**

$$\phi_\mu^{CGF}(\vec{r}) = \sum_i c_{i,\mu} \varphi_i(\varsigma_i, \vec{r})$$

Slowest decaying (most extended) gaussian (φ)

- **Nodes:**

  Use excited states of atomic calculations

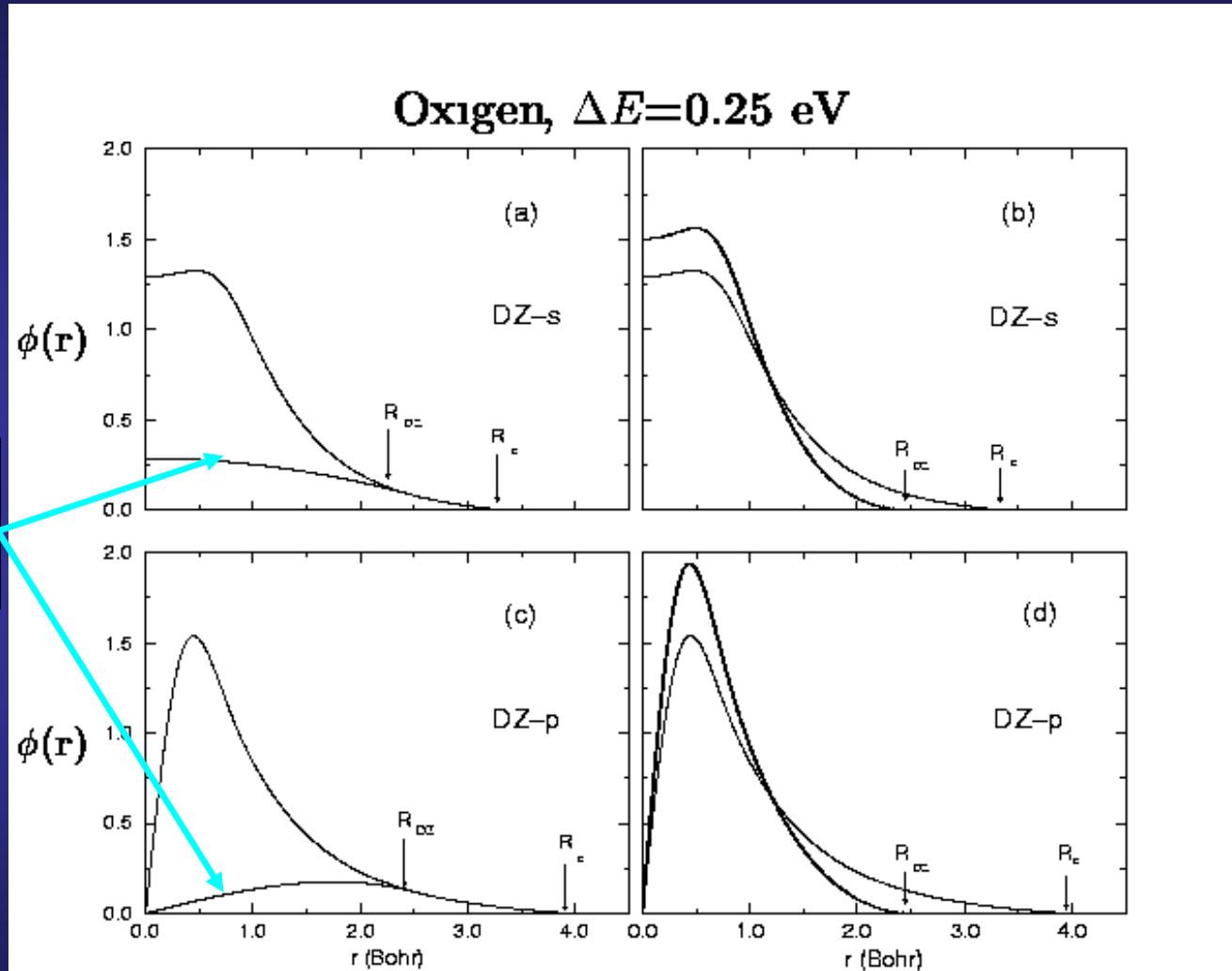 **Orthogonal, asympotically complete but inefficient**

  Only works for tight confinement

- **Chemical hardness:**

  Derivative of the first-ζ respect the atomic charge.

- **SIESTA: extension of the Split Valence to NAO.**

Split valence in NAO formalism

$$r^l\left(a-br^2\right)$$

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

Split valence - Chemical hardness
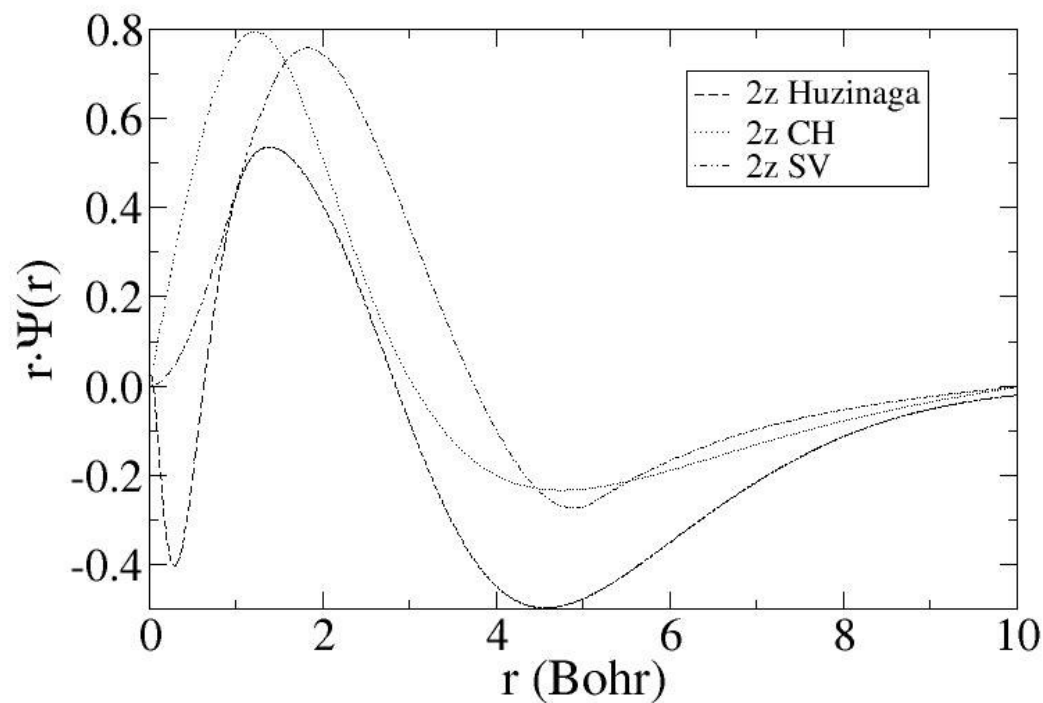
- **Similar shapes**

- **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)

Two different ways of generate polarization orbitals

Perturbative polarization

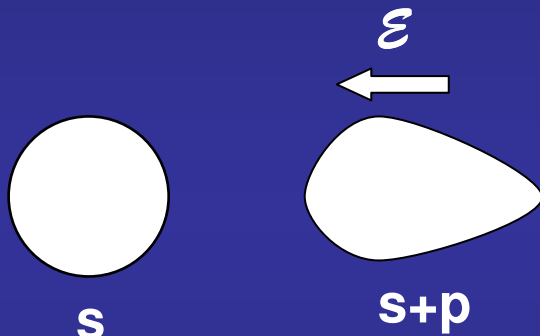**Apply a small electric field to the orbital we want to polarize**

$\mathcal{E}$

s

s+p

Atomic polarization

Solve Schrödinger equation for higher angular momentum

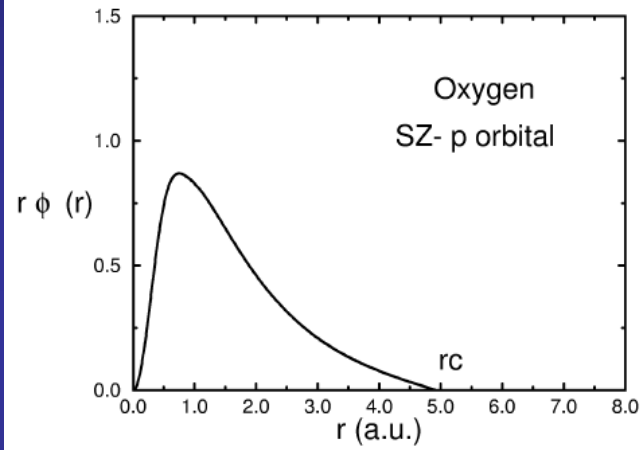unbound in the free atom $\Rightarrow$

require short cut offs

Si 3d

orbitals

(a) $\Delta E = 0.25$ eV
$\Delta E = 0.01$ eV
$\phi(r)$
r (Bohr)

(b)
r (Bohr)

E. Artacho *et al.*, Phys. Stat. Sol. (b), 215, 809 (1999)
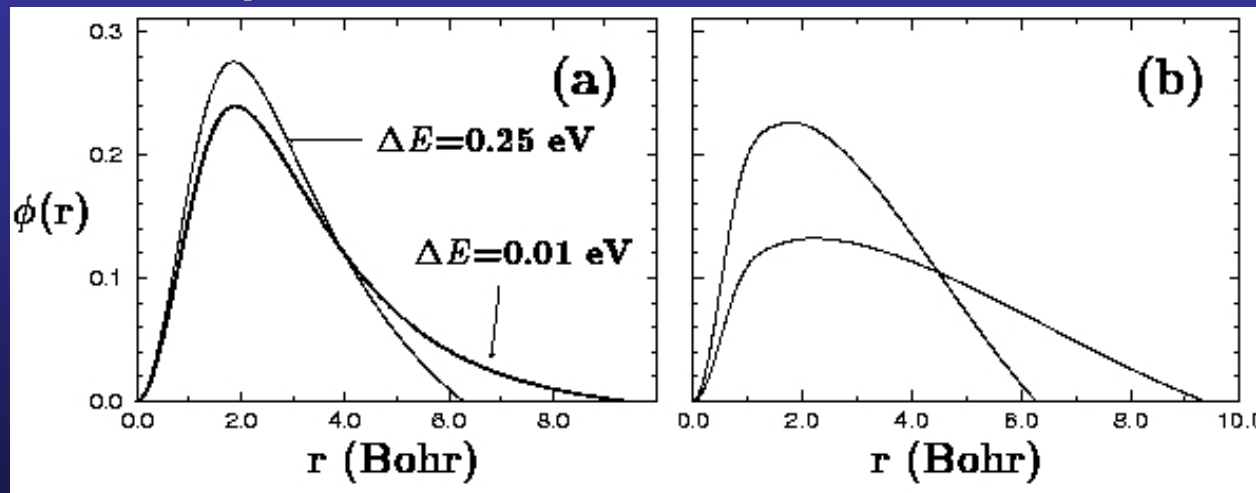
Energy shift: cutting the orbitals in a balance way

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

Oxygen
SZ- p orbital

$r\phi(r)$

rc

r (a.u.)

A single parameter for all cutoff radii

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

Convergence vs Energy shift of
Bond lengths   Bond energies

Δ (%)

ΔE_{PAO} (meV)

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

But:

A different cut-off radius for each orbital
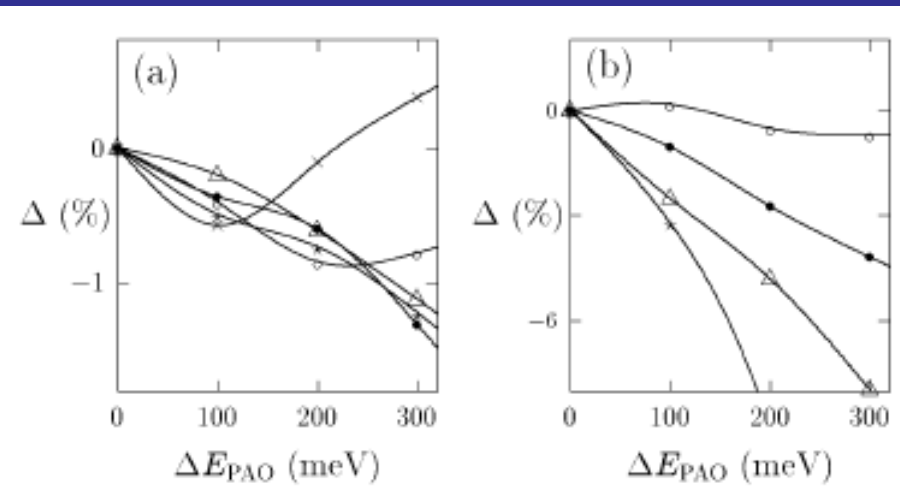
Transferability: α-quartz

	Exp[a]	PW[b]	PW[c]	PW[d]	PW[e]	DZP
$a(\text{Å})$	4.92	4.84	4.89	4.81	4.88	4.85
$c(\text{Å})$	5.41	5.41	5.38	5.32	5.40	5.38
$d^1_{Si-O}(\text{Å})$	1.605	1.611	1.60	1.605	-	1.611
$d^1_{Si-O}(\text{Å})$	1.614	1.617	1.60	1.605	-	1.611
$\alpha_{Si-O-Si}(\text{deg})$	143.7	140.2	-	139.0	-	140.0

Si basis set optimized in c-Si

O basis set optimized in water molecule

a Levien *et al*, Am. Mineral, 65, 920 (1980)

b Hamann, Phys. Rev. Lett., 76, 660 (1996)

c Sautet (using VASP, with ultrasoft pseudopotential)

d Rignanese *et al*, Phys. Rev. B, 61, 13250 (2000)

e Liu *et al*, Phys. Rev. B, 49, 12528 (1994) (ultrasoft pseudopotential)

System	Basis	Properties		
MgO		**a (Å)**	**B(GPa)**	**E$_c$(eV)**
	Transfer	4.13	157	11.81
	Opt	**4.10**	**167**	**11.87**
	PW	**4.10**	**168**	**11.90**
	Exp	**4.21**	**152**	**10.30**
Graphite		**a (Å)**	**c (Å)**	**ΔE(meV)**
	Transfer	2.456	6.50	38
	Exp	**2.456**	**6.674**	**23**
H$_2$O		**d$_{O-H}$ (Å)**	**θ$_{H-O-H}$(deg)**	**E$_b$(eV)**
	Transfer	0.975	105.0	12.73
	Opt	**0.972**	**104.5**	**12.94**
	PW	**0.967**	**105.1**	**13.10**
	LAPW	**0.968**	**103.9**	**11.05**
	Exp	**0.958**	**104.5**	**10.08**