Université de Liège

Numerical Atomic Orbitals: An efficient basis for Order-N ab-initio simulations

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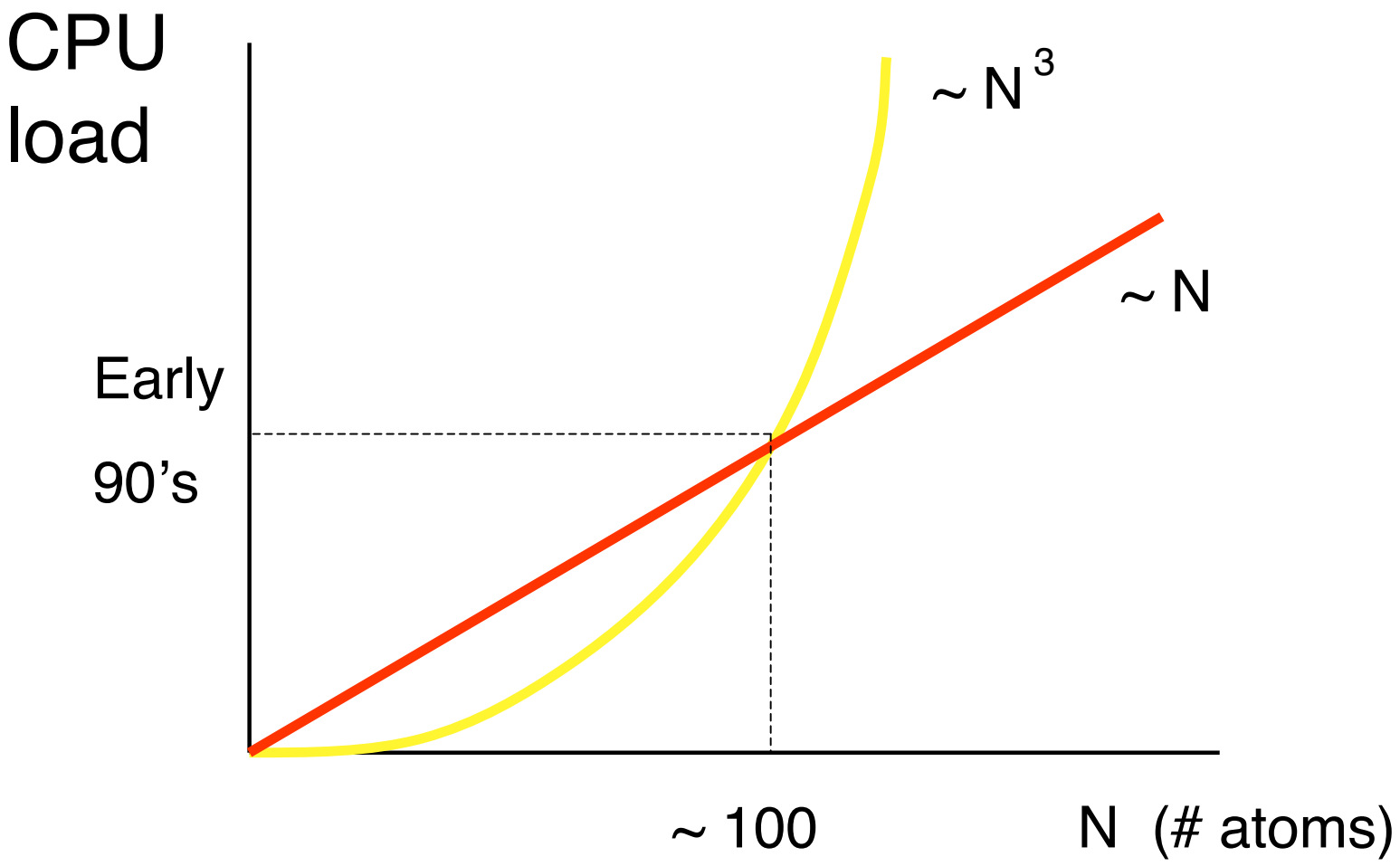
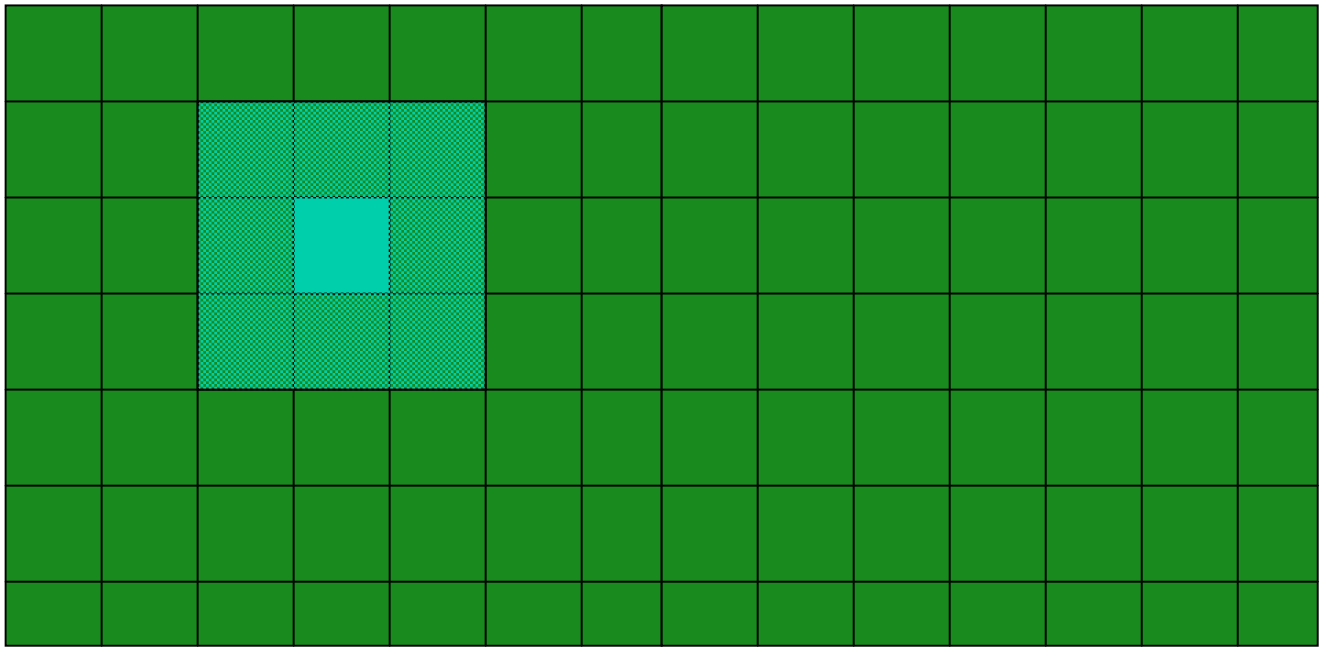
LINEAR SCALING



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

KEY: LOCALITY

Large system



x2

"Divide and Conquer"

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

- In order to get efficiency, two aspects of the basis are important:
  - NUMBER of basis functions per atom
  - RANGE of localization of these functions
- Some proposals for self-consistent DFT O(N) :
  - 'blips'
  - Bessels
  - Finite differences
  - Gaussians
  - Atomic orbitals
    - Very efficient
    - Less straight forward variational convergence
    - Freedom : RADIAL SHAPE

Atomic Orbitals

- Very efficient
- Lack of systematic for convergence
- Main features:
  - Size
  - Range $\phi_{Ilm}(\vec{r}) = R_{Il}(r_I) Y_{lm}(\hat{r}_I) \qquad \vec{r}_I = \vec{r} - \vec{R}_I$
  - Shape

- Numerical Atomic Orbitals (NAOs):

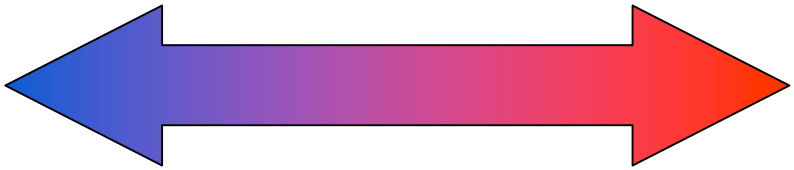
Numerical solution of the Kohn-Sham Hamiltonian
for the isolated pseudoatom
with the same approximations (xc, pseudos) as for the
condensed system

Size

Depending on the required accuracy and available computational power

Quick and dirty calculations

Highly converged calculations



Minimal basis set

(single- □; SZ)

Complete multiple-□

+

Polarization

+

Diffuse orbitals

Converging the basis size

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

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	

How to double the basis set

Different schemes to generate Double-ζ:

- Quantum Chemistry: Split Valence $\phi_{\zeta}^{CGF}(\vec{r}) = \sum_i c_{i,\zeta}\phi_i(\zeta_i,\vec{r})$

  Slowest decaying (most extended) gaussian (ζ).

- Nodes: Use excited states of atomic calculations.

  Orthogonal, asympotically complete but inefficient

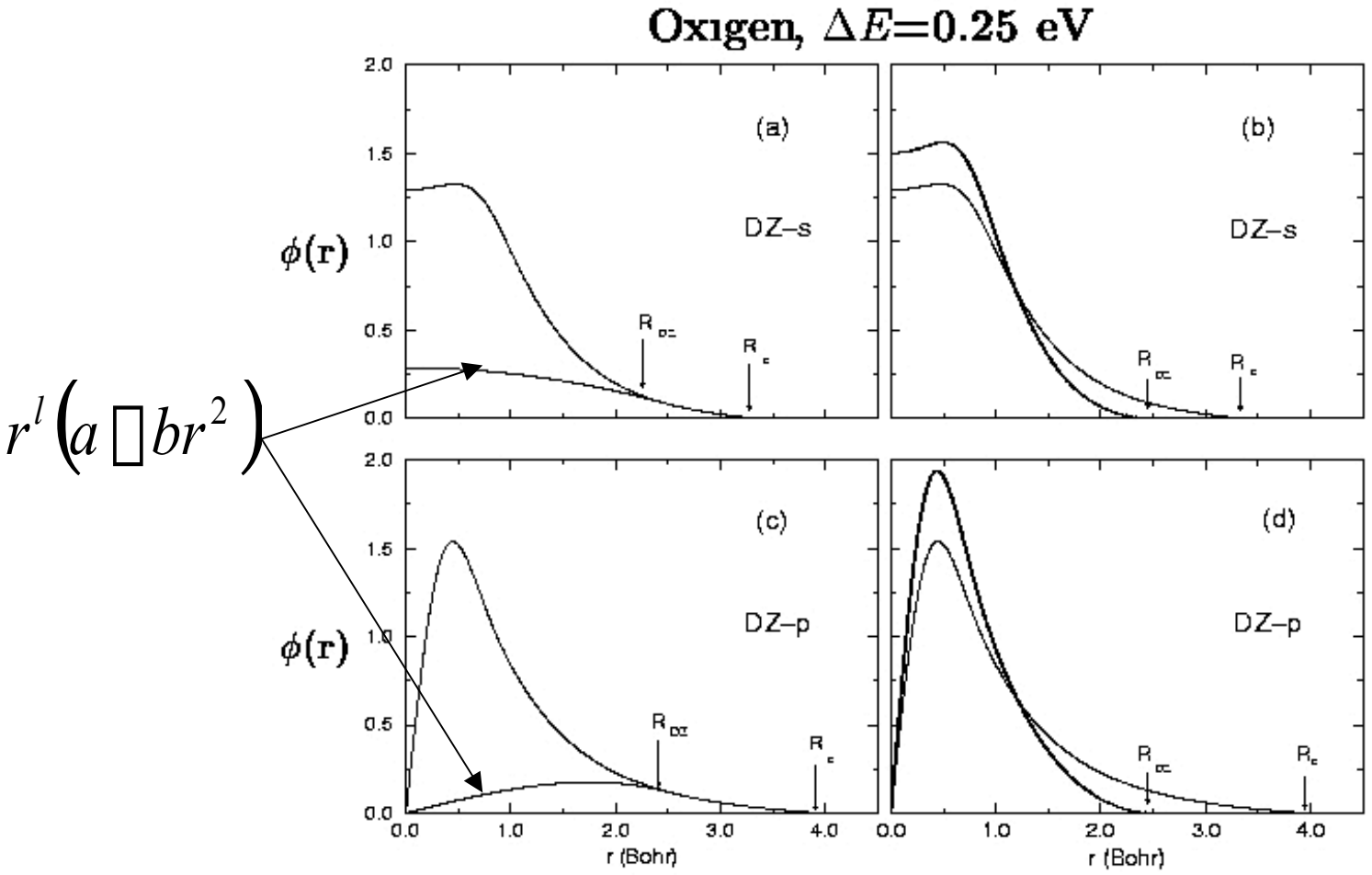
  Only works for tight confinement

- Chemical hardness: Derivative of the first-ζ respect

  the atomic charge.

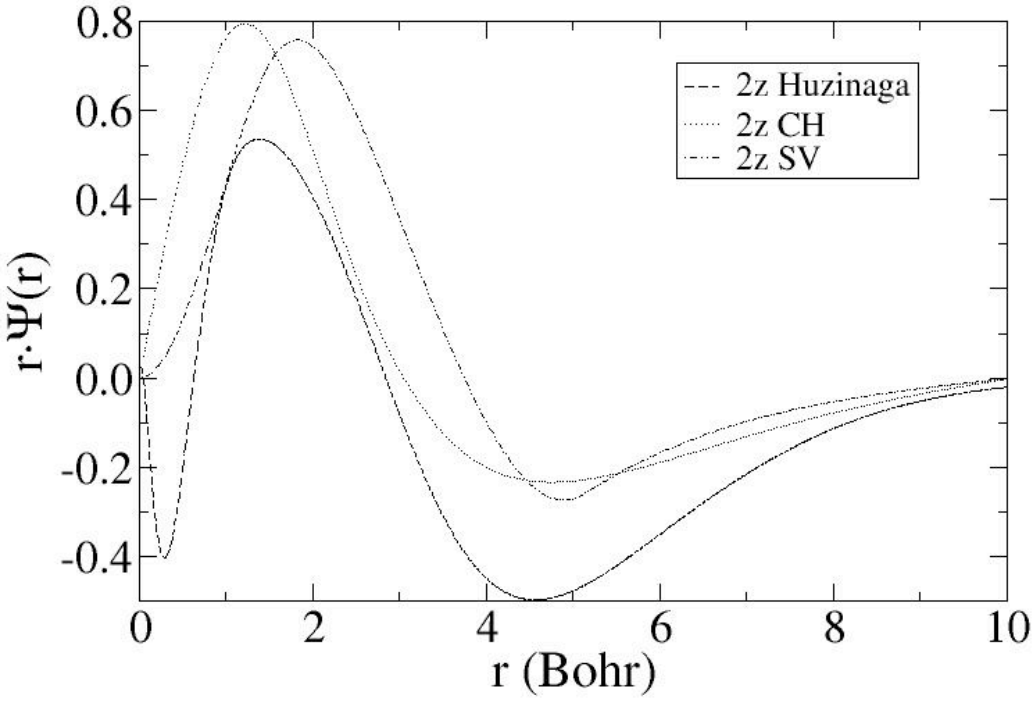
- SIESTA: extension of the Split Valence to NAO.

Split valence in NAO formalism



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

Split valence - Chemical hardness



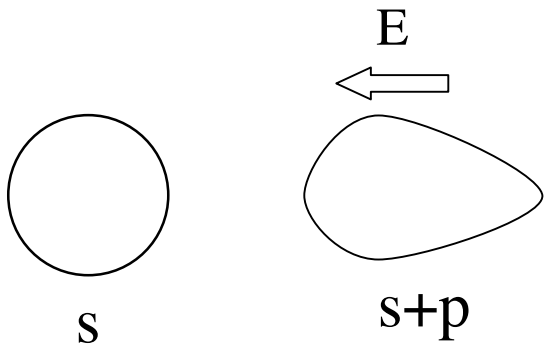
- Similar shapes
- SV: higher efficiency (radius of second-□ can be restricted to the inner matching radius)

E. Anglada *et al*, submitted to Phys. Rev. B

Polarization orbitals

Perturbative polarization

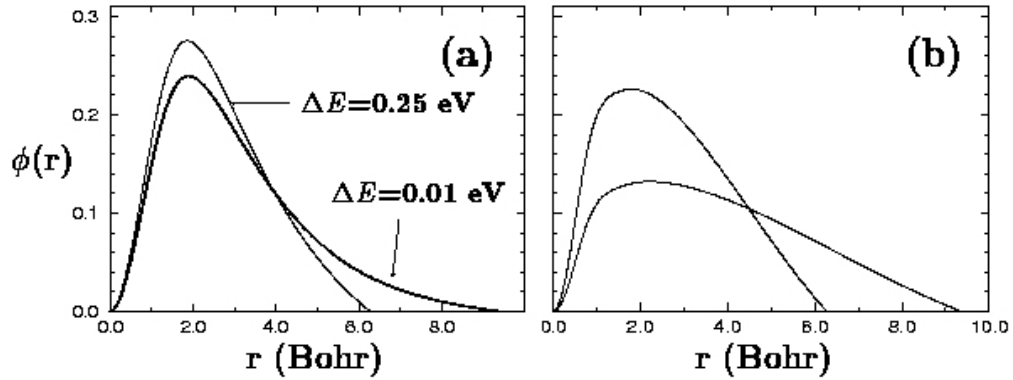
Apply a small electric field to the orbital we want to polarize



Atomic polarization

Solve Schrödinger equation for higher angular momentum

unbound in the free atom require short cut offs



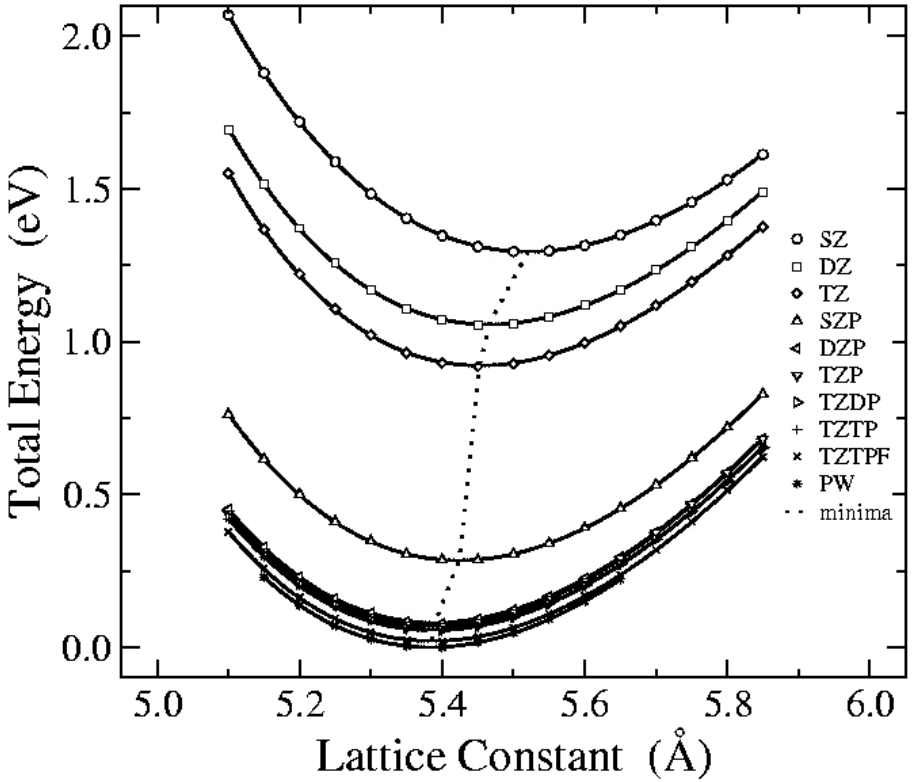
Si 3d orbitals

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

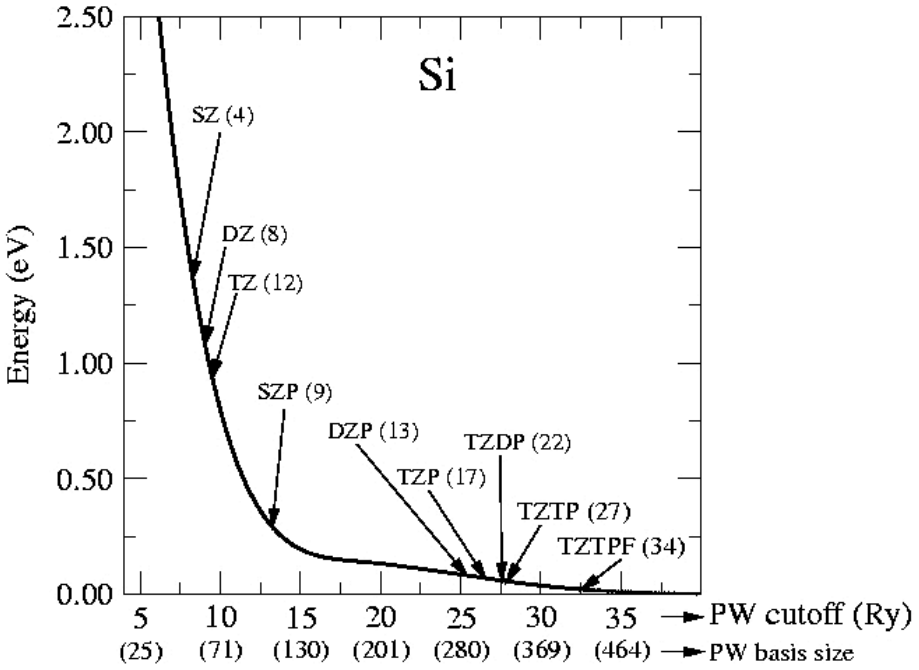
Convergence of the basis set

Bulk Si

Cohesion curves



PW and NAO convergence



Range

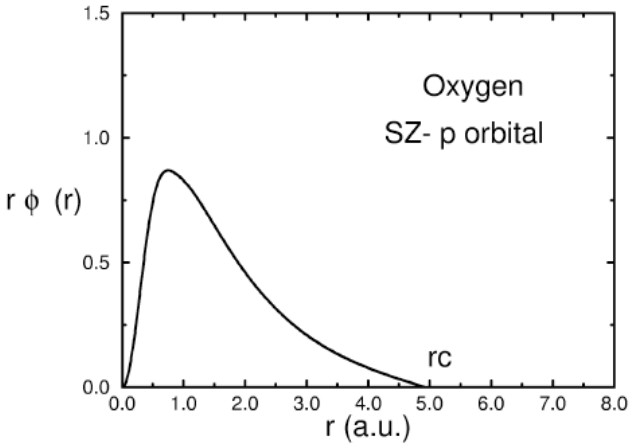
- How to get sparse matrix for O(N)
  - Neglecting interactions below a tolerance or beyond some scope of neighbours numerical instablilities for high tolerances.
  - **Strictly localized atomic orbitals** (zero beyond a given cutoff radius, r_c)

•**Accuracy** and **computational efficiency** depend on the range of the atomic orbitals

•Way to define all the cutoff radii in a **balanced way**

Energy shift

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



Fireballs

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

BUT:

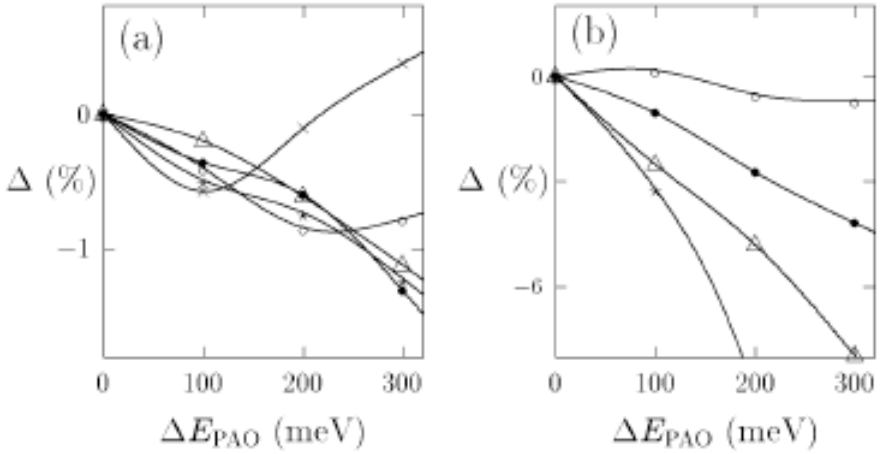
A different cut-off radius for each orbital

A single parameter for all cutoff radii

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

Convergence vs Energy shift of

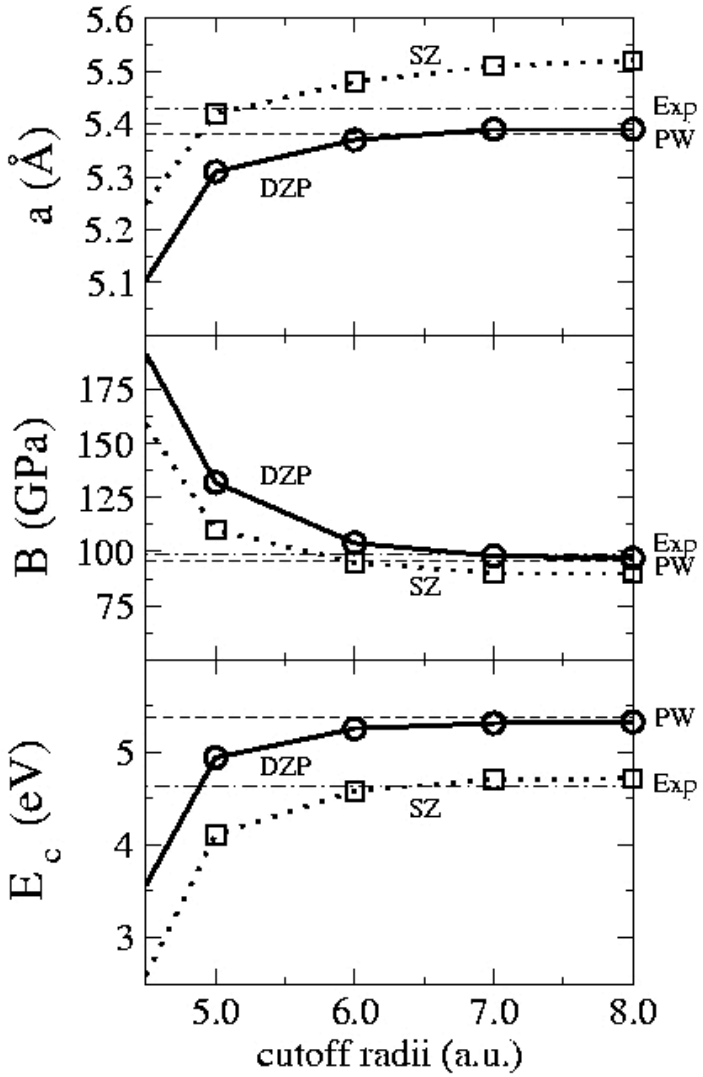
Bond lengths *Bond energies*



Convergence with the range

bulk Si

equal *s*, *p* orbitals radii



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

Range and shape

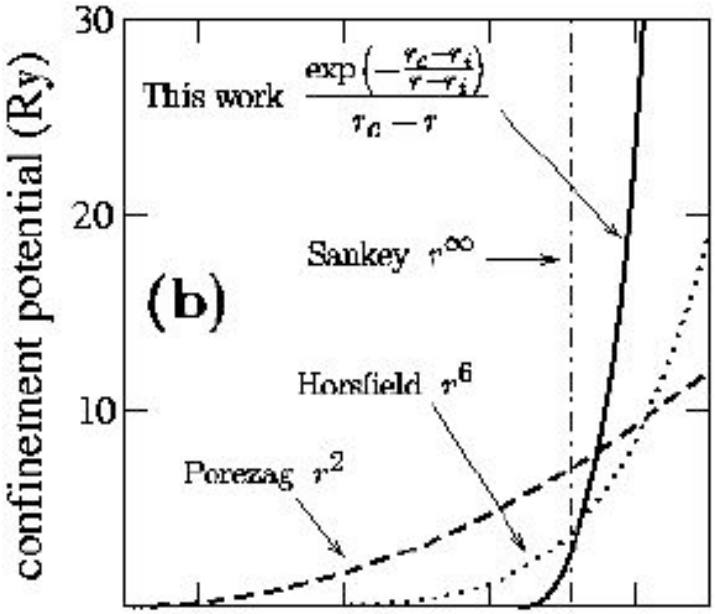
ΔQ : extra charge per atomic specie

Confinement: imposed separately
per angular momentum shell

Confinement

- **Hard confinement** (Sankey et al, PRB 40, 3979 (1989))
  - Orbitals: discontinuos derivative at r_c
- **Polinomial:** $V(r) = V_0 r^n$
  - n = 2 (Porezag *et al*, PRB **51**, 12947 (95))
  - n = 6 (Horsfield, PRB **56**, 6594 (97))
  - No radius where the orbital is stricly zero
  - Non vanishing at the core region
- **Direct modification of the wf:**
  - Bump for large α and small r_c
- **New proposal:**
  - Flat at the core region
  - Continuos
  - Diverges at r_c

  (J. Junquera *et al*,
  Phys. Rev. B, **64**, 23511 (01))



$$\rho_{conf}(r) = \left(1 - e^{-\alpha/(r-r_c)^2}\right)\rho_{atom}(r)$$

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

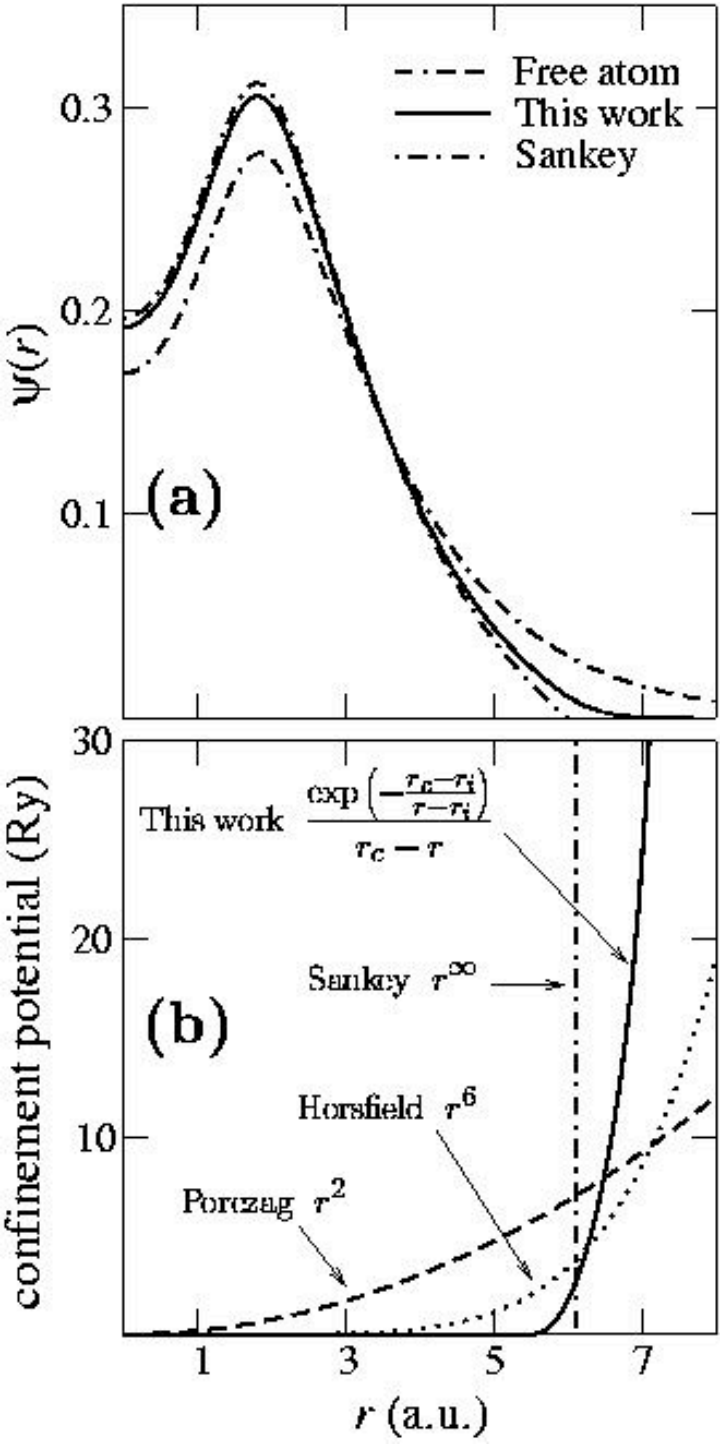
Soft confinement

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

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

Corresponding optimal confinement potential

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



Comparison of confinement schemes

Mg and **O** basis sets **variationally optimized** for **all** the **schemes**

MgO	SZ			DZP		
Basis scheme	a (Å)	B (GPa)	E_c (eV)	a (Å)	B (GPa)	E_c (eV)
Unconfined	4.25	119	6.49			
Sankey	4.17	222	10.89	4.12	165	11.82
Direct modification	4.16	228	11.12	4.12	163	11.84
Porezag	4.18	196	11.17	4.09	183	11.83
Horsfield	4.15	221	11.26	4.11	168	11.86
This work	4.15	226	11.32	4.10	167	11.87
PW (100 Ry)				4.10	168	11.90
Exp				4.21	152	10.3

Procedure

Difference in energies involved in your problem?

- SZ: (Energy shift)

  Semiquantitative results and general trends

- DZP: automatically generated (Split Valence and Peturbative polarization)

  High quality for most of the systems.

  Good valence: well converged results computational cost

  'Standard'

- Variational optimization

  Rule of thumb in Quantum Chemistry:

  A basis should always be doubled before being polarized

Convergence of the basis set

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-□

DZ= doble- □

TZ=triple- □

P=Polarized

DP=Doble-polarized

PW: Converged Plane Waves (50 Ry)

APW: Augmented Plane Waves (all electron)

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
□-quartz	13	923	76

For molecules: cubic unit cell 10 Å of side

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)

Transferability: □-quartz

	Exp[a]	PW[b]	PW[c]	PW[d]	PW[e]	DZP
a(Å)	4.92	4.84	4.89	4.81	4.88	4.85
c(Å)	5.41	5.41	5.38	5.32	5.40	5.38
d^1_{Si-O}(Å)	1.605	1.611	1.60	1.605	-	1.611
d^1_{Si-O}(Å)	1.614	1.617	1.60	1.605	-	1.611
□$_{Si-O-Si}$(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)	□E(meV)
	Transfer	**2.456**	**6.50**	**38**
	PW	2.457	6.72	24
	Exp	2.456	6.674	23
H_2O		d_{O-H} (Å)	□$_{H-O-H}$(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

Conclusions

- Basis sets of Numerical Atomic Orbitals (NAO) have been optimized
- Performance of NAO basis sets of modest size, as DZP, is very satisfactory, being the errors comparable to the ones due to the DFT or pseudopotential
- The bases obtained show enough transferability

Our method

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

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

- *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

D. Sanchez-Portal, P. Ordejon, E. Artacho & J. M. Soler
Int. J. Quantum Chem. 65, 453 (1997)

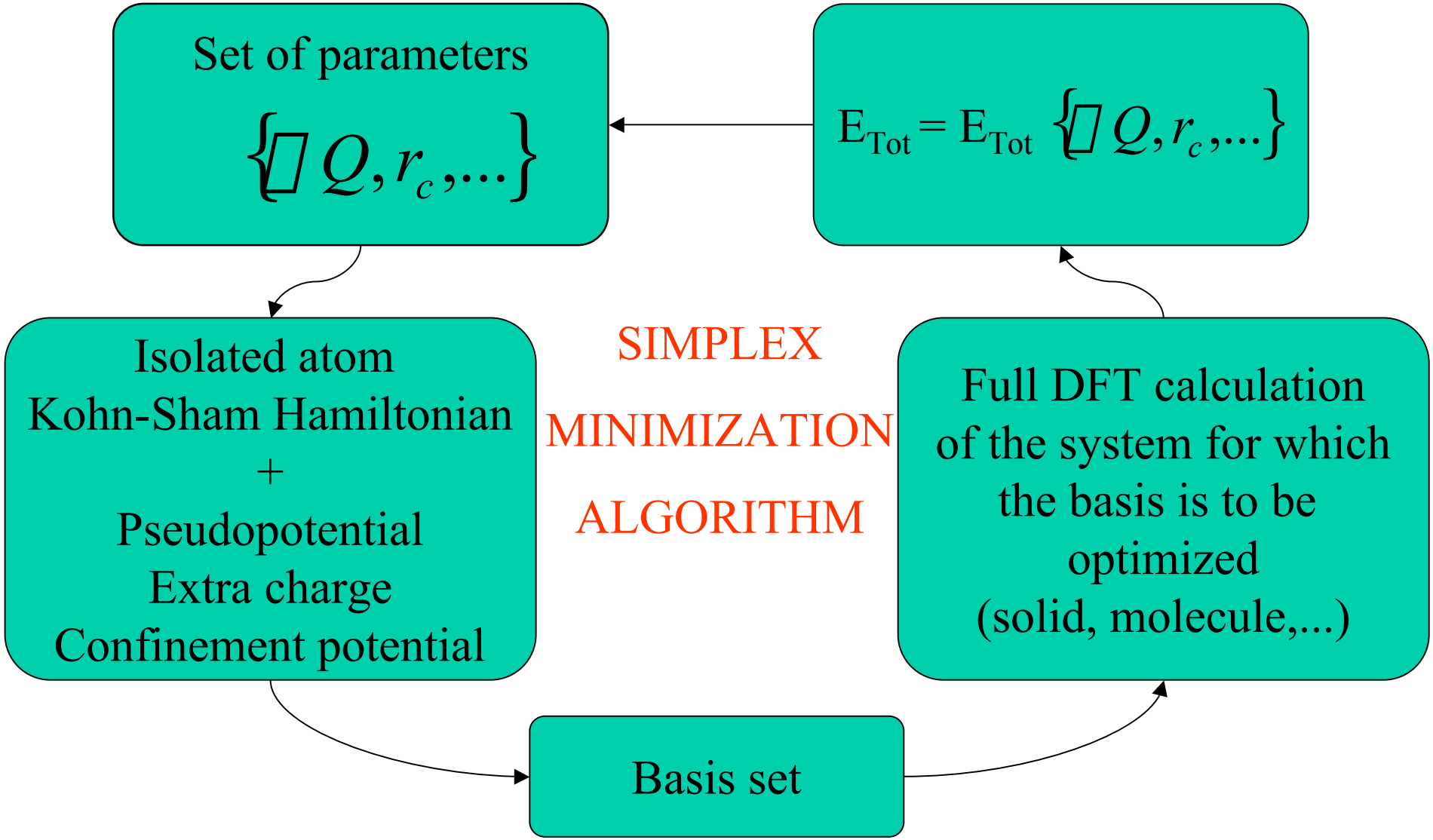
How to enlarge the basis set

- **Simple-ζ: One single radial function** per angular momentum shell occupied in the free –atom
- **Radial flexibilization: Multiple-ζ**

  Add **more than one** radial function
  - Pseudopot. eigenfunctions with increasing number of nodes
  - Atomic eigenstates for different ionization states
  - Derivatives of the radial part respect the occupation
  - Split valence
- **Angular flexibilization: Polarization**

  Add shells of **higher l**
  - Atomic
  - Perturbative

Optimization Procedure



Optimization Procedure (I)

- **Range** and **shape** of the orbitals: defined by a **set of parameters**:
  - Per atomic species: global Q
  - Confinement impossed separately per angular momentum shell. The parameters depend on the scheme used to confine:
    - Hard confinement: r_c
    - Polinomial confinement: V_0
    - Direct modification of the wave function: r_c,
    - This work: r_c, r_i, V_0
  - For each beyond the first, the matching radius r_m

Optimization procedure(II)

Parameters for an optimization of Si, DZP quality

Scheme	Potential	s	p	d	Extra charge	number param.
Sankey	$\left(\frac{r}{r_c}\right)^{\square}$	r_c-1□ r_m-2□	r_c-1□ r_m-2□	r_c-1□	□Q	6
Porezag	$V_0 r^2$	V_0-1□ r_m-2□	V_0-1□ r_m-2□	V_0-1□	□Q	6
Horsfield	$V_0 r^6$	V_0-1□ r_m-2□	V_0-1□ r_m-2□	V_0-1□	□Q	6
Kenny	$1 \square e^{\square / (r \square r_c)^2}$	r_c-1□ □ –1□ r_m-2□	r_c-1□ □ –1□ r_m-2□	r_c-1□ □ –1□	□Q	9
This work	$V_0 \frac{e^{\square \frac{r_c \square r_i}{r \square r_i}}}{r_c \square r}$	r_c-1□ r_i-1□ V_0-1□ r_m-2□	r_c-1□ r_i-1□ V_0-1□ r_m-2□	r_c-1□ r_i-1□ V_0-1□	□Q	12

Cutting the atomic orbitals

$$H = E_{Total} + \underbrace{pV}_{\text{Penalty for long range orbitals}}$$

$$V = \prod_{l} r_c^3(l)$$

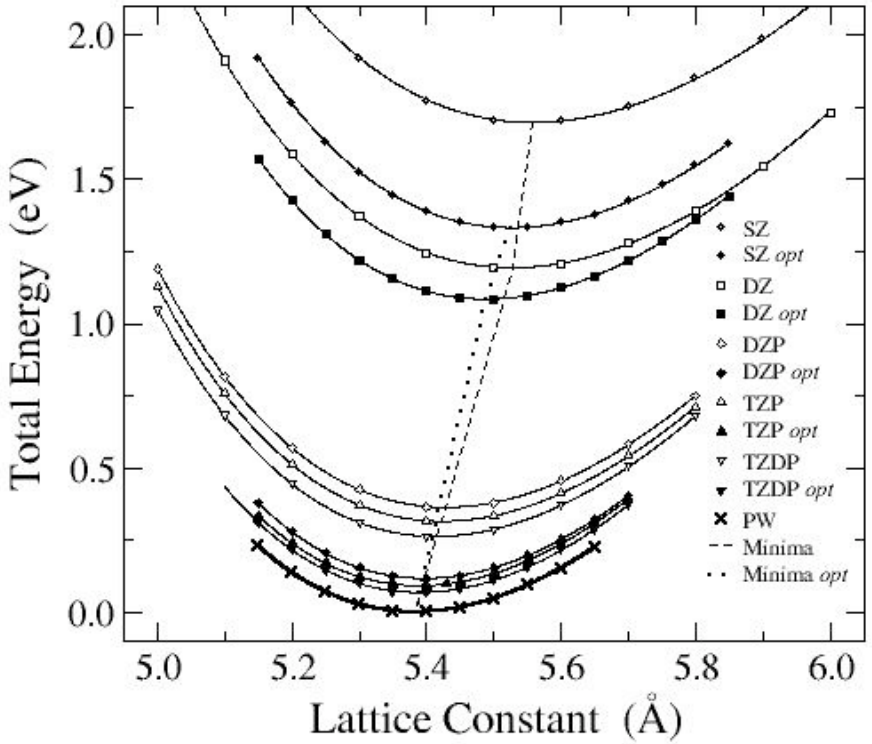
$$p \equiv \textbf{\textit{pressure}}$$

- Optimize the *enthalpy* in the condensed system
- Just one parameter to define all the cutoff radii: the **pressure**

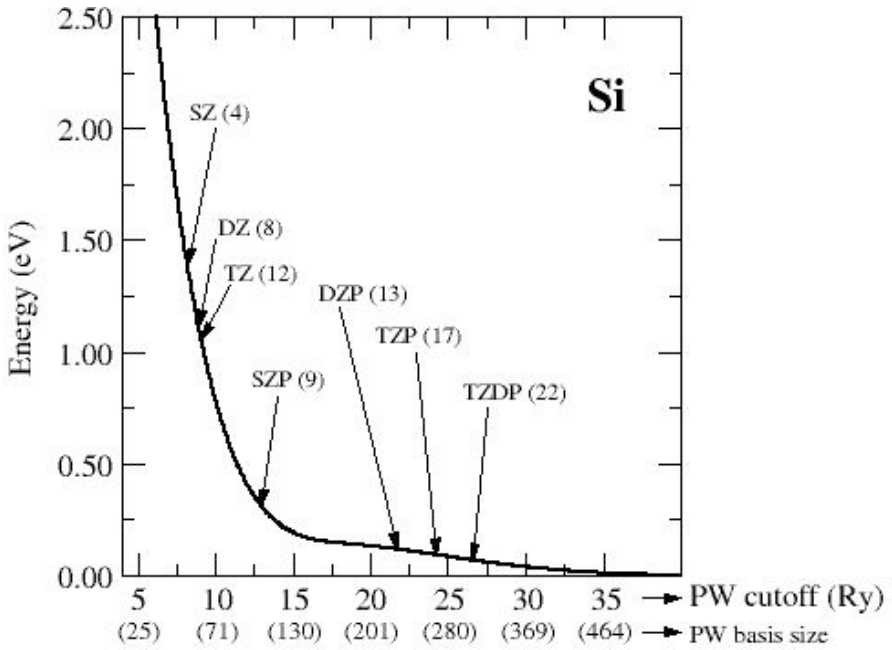
Convergence of the basis set

Bulk Si

Cohesion curves



PW and NAO convergence



Tightening the basis confinement in □-quartz

r_c^{Si} (a.u.) s p d	r_c^{O} (a.u.) s p d	a (Å)	c (Å)	d^1_{Si-O} (Å)	d^1_{Si-O} (Å)	□$_{Si-O-Si}$ (deg)
8.0 8.0 8.0	8.0 8.0 8.0	4.85	5.38	1.611	1.612	140.0
6.0 6.0 6.0	8.0 8.0 8.0	4.85	5.35	1.607	1.608	140.0
6.0 6.0 6.0	5.0 5.0 5.0	4.74	5.29	1.610	1.610	134.0
6.0 6.0 6.0	4.5 4.5 4.5	4.69	5.26	1.610	1.610	132.0
6.0 6.0 6.0	5.0 6.5 4.0	4.84	5.36	1.607	1.608	139.7
5.6 6.3 4.2	4.0 5.3 2.8	4.81	5.34	1.607	1.610	138.2

Si basis set optimized in c-Si

O basis set optimized in water molecule