The SIESTA method for electronic structure calculations

Spanish

Initiative for

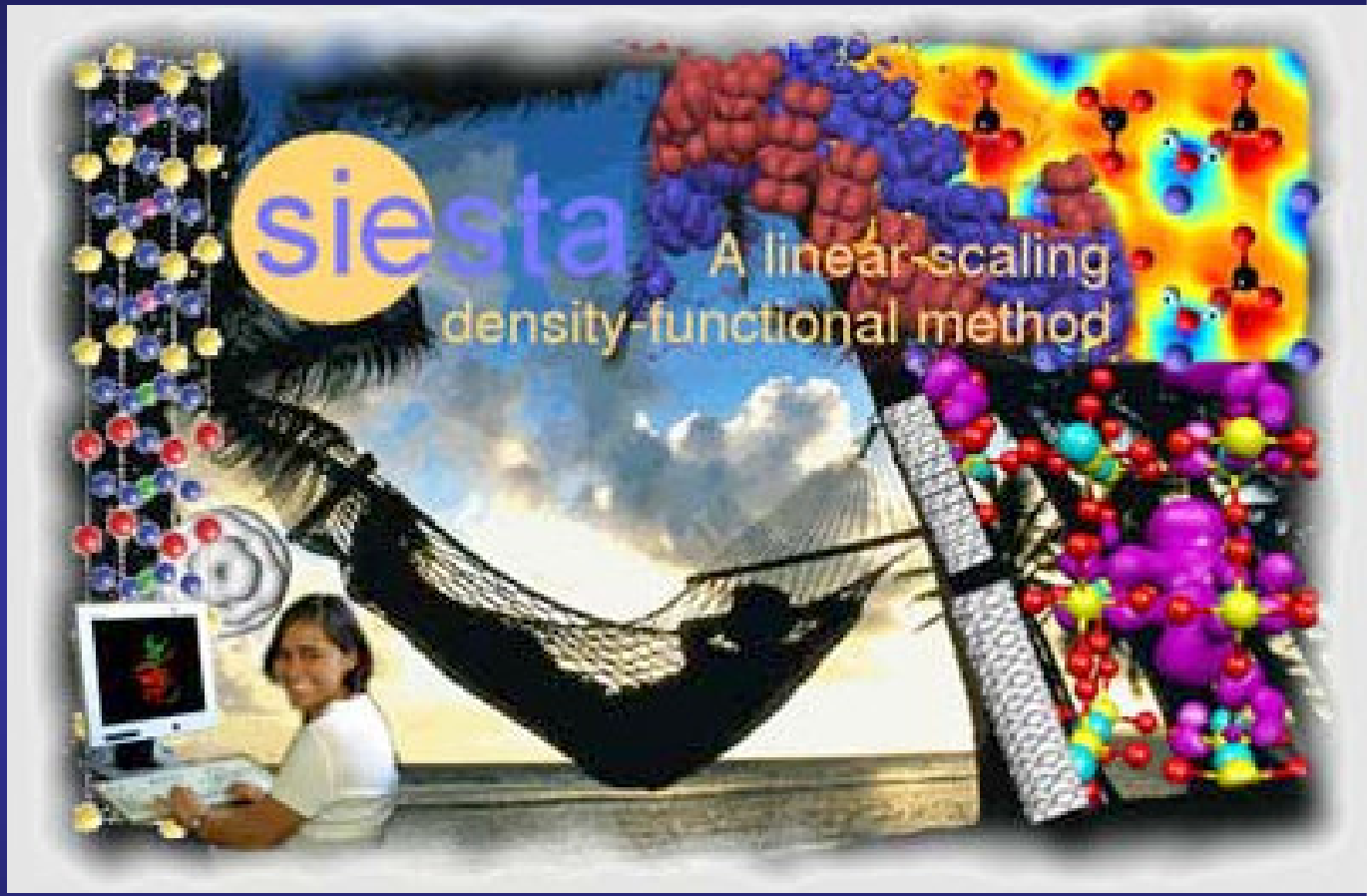
Electronic

Simulations with

Thousand of

Atoms

http://www.uam.es/siesta



Javier Junquera

UC
UNIVERSIDAD
DE CANTABRIA

What is SIESTA?

(http://www.uam.es/siesta)

Is both a **method** and its **computer program implementation** to simulate molecules and solids at the atomic scale.

Performs **electronic structure calculations: solves** numerically the **quantum mechanical equations** that rules the behaviour of the electrons

Performs **molecular dynamics** simulations of physical and chemical processes that occur at the atomic scale.

EVERYTHING FROM FIRST-PRINCIPLES OR *AB-INITIO*

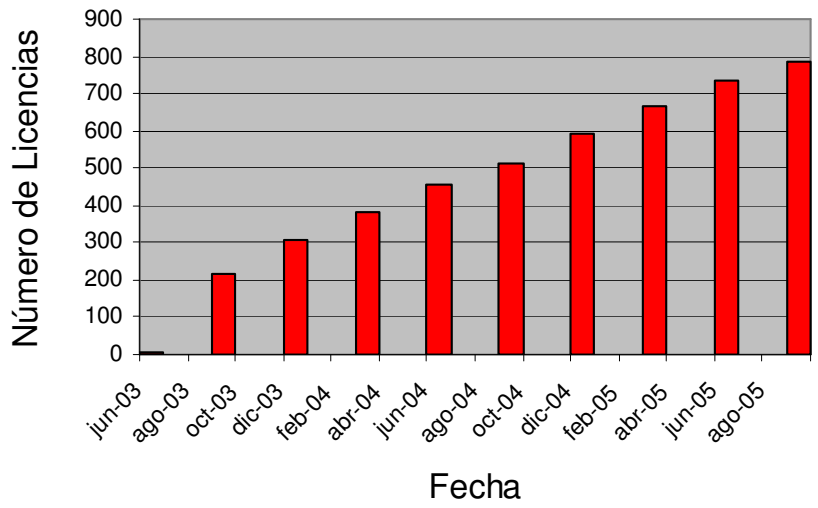
Who are the members of the SIESTA core?

Collaboration between different Condensed Matter groups, with a strong Spanish contribution

Emilio Artacho	University of Cambridge (United Kingdom)
Julian D. Gale	Curtin University of Technology (Australia)
Alberto García	ICMAB (CSIC; Barcelona)
Javier Junquera	Universidad de Cantabria
Richard M. Martin	University of Illinois at Urbana-Champaign
Pablo Ordejón	ICMAB (CSIC; Barcelona)
Daniel Sánchez-Portal	DIPC (CSIC; San Sebastián)
José M. Soler	Universidad Autónoma de Madrid
José M. Cela's group	Barcelona Supercomputing Center

International impact of SIESTA

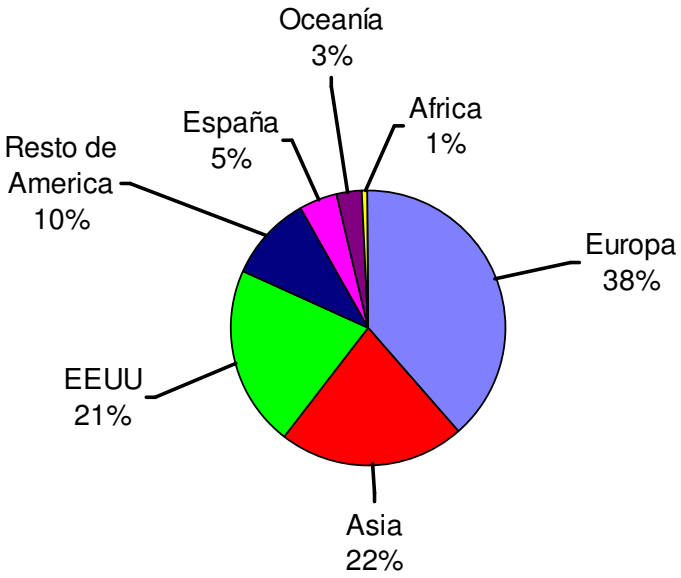
Figura 1: Licencias Académicas de SIESTA v. 1.3



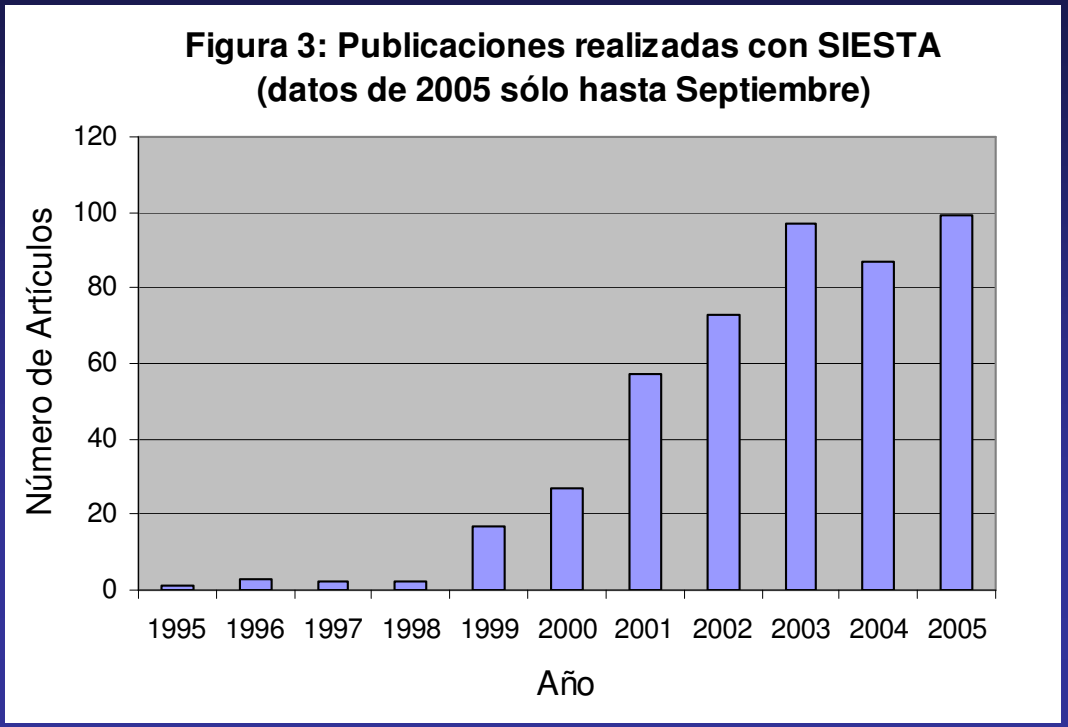
Steadily growth of the number of users

Presence in the five continents

Figura 2: Distribución geográfica de Licencias



More than 500 publications using the code



Review	Impact factor	Number of papers
Nature	32,182	4
Science	31,853	2
Nature Materials	13,531	2
Phys. Rev. Lett.	7,218	46
Phys. Rev. B	3,075	168

Most important reference followed in this lecture

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **14** (2002) 2745–2779 PII: S0953-8984(02)30737-9

The SIESTA method for *ab initio* order-N materials simulation

José M Soler[1], Emilio Artacho[2], Julian D Gale[3], Alberto García[4], Javier Junquera[1,5], Pablo Ordejón[6] and Daniel Sánchez-Portal[7]

Goal: Describe properties of matter from theoretical methods firmly rooted in fundamental equations

Quantum Mechanics: Schrödinger equation (assuming no relativistic)

$$i\hbar \frac{\partial \Psi\left(\{\vec{x}_i\},\{\vec{R}_\alpha\};t\right)}{\partial t} = \hat{H}\Psi\left(\{\vec{x}_i\},\{\vec{R}_\alpha\};t\right)$$

Coordinates of electron i $\vec{x}_i$ comprise

- Space coordinates $\vec{r}_i$
- Spin coordinates σ_i

Electromagnetism: Coulomb's law

$$\hat{H} = \hat{T} + \hat{V}_{Coulomb}$$

For a pair of charged particles

$$\hat{V}_{Coulomb} = \frac{q_i q_j}{|\vec{r}_i - \vec{r}_j|}$$

A closer look to the hamiltonian:
A difficult interacting many-body system.

$$\hat{H} = \sum_i -\frac{\hbar^2}{2m_e}\nabla_i^2$$

Kinetic energy operator for the electrons

$$-\sum_{i,\alpha}\frac{Z_\alpha e^2}{\mid \vec{r}_i - \vec{R}_\alpha \mid}$$

Potential acting on the electrons due to the nuclei

$$+\frac{1}{2}\sum_{i\neq j}\frac{e^2}{\mid \vec{r}_i - \vec{r}_j \mid}$$

Electron-electron interaction

$$+\sum_\alpha -\frac{\hbar^2}{2M_\alpha}\nabla_\alpha^2$$

Kinetic energy operator for the nuclei

$$+\frac{1}{2}\sum_{\alpha\neq\beta}\frac{Z_\alpha Z_\beta e^2}{\mid \vec{R}_\alpha - \vec{R}_\beta \mid}$$

Nucleus-nucleus interaction

What are the main approximations?

Born-Oppenhaimer

Decouple the movement of the electrons and the nuclei.

Density Functional Theory

Treatment of the electron — electron interactions.

Pseudopotentials

Treatment of the (nuclei + core) — valence.

Basis set

To expand the eigenstates of the hamiltonian.

Numerical evaluation of matrix elements

Efficient and self-consistent computations of H and S.

Solve the secular equation

Supercells

To deal with periodic systems

What are the main approximations?

Born-Oppenhaimer

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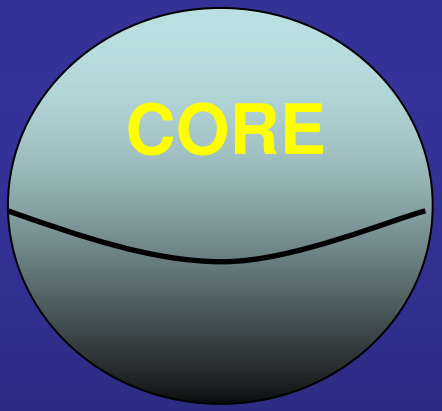
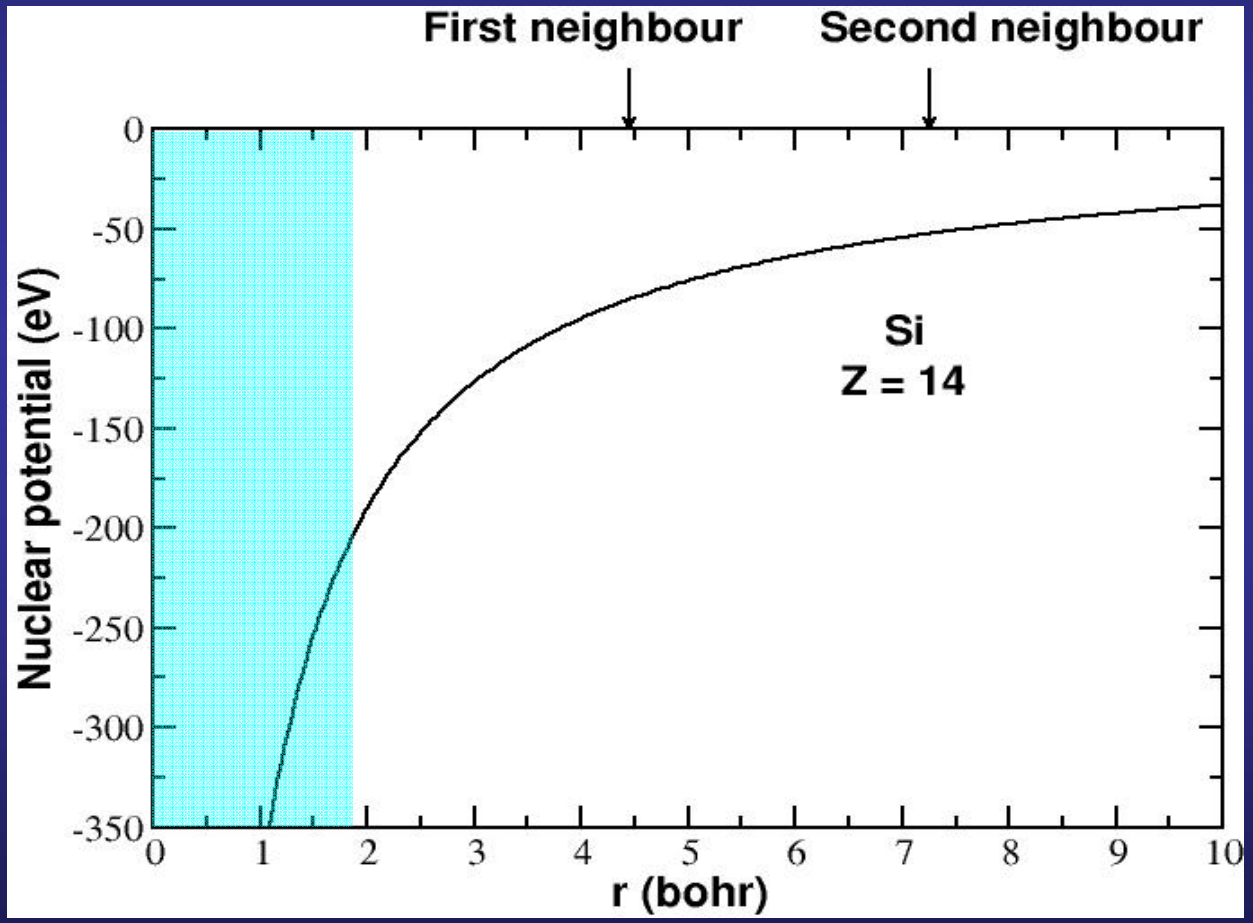
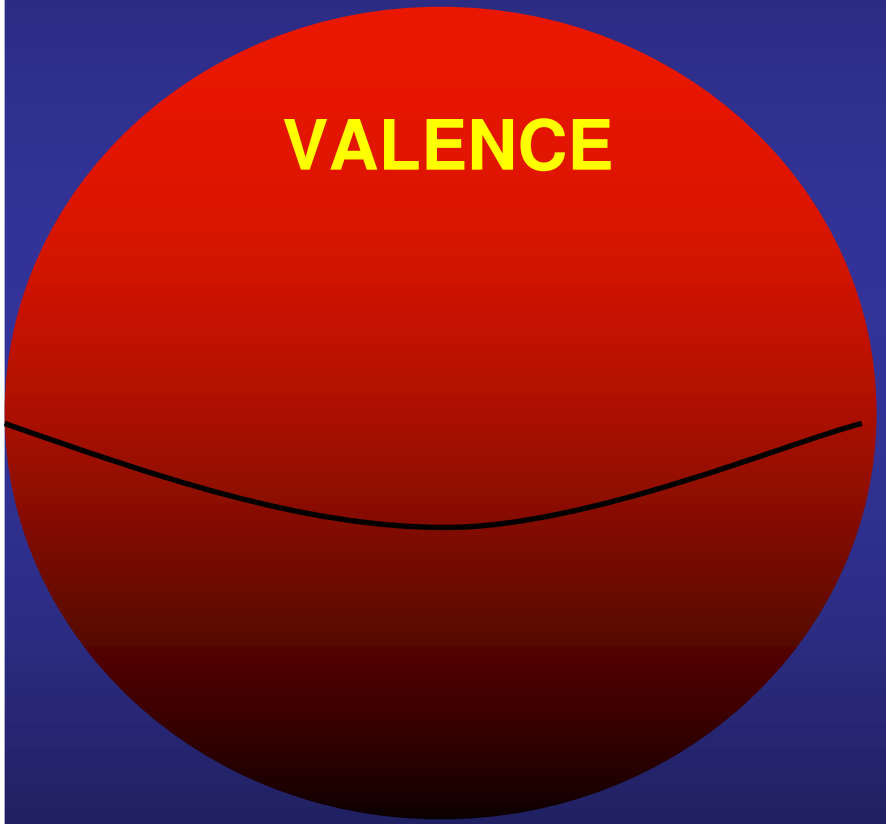
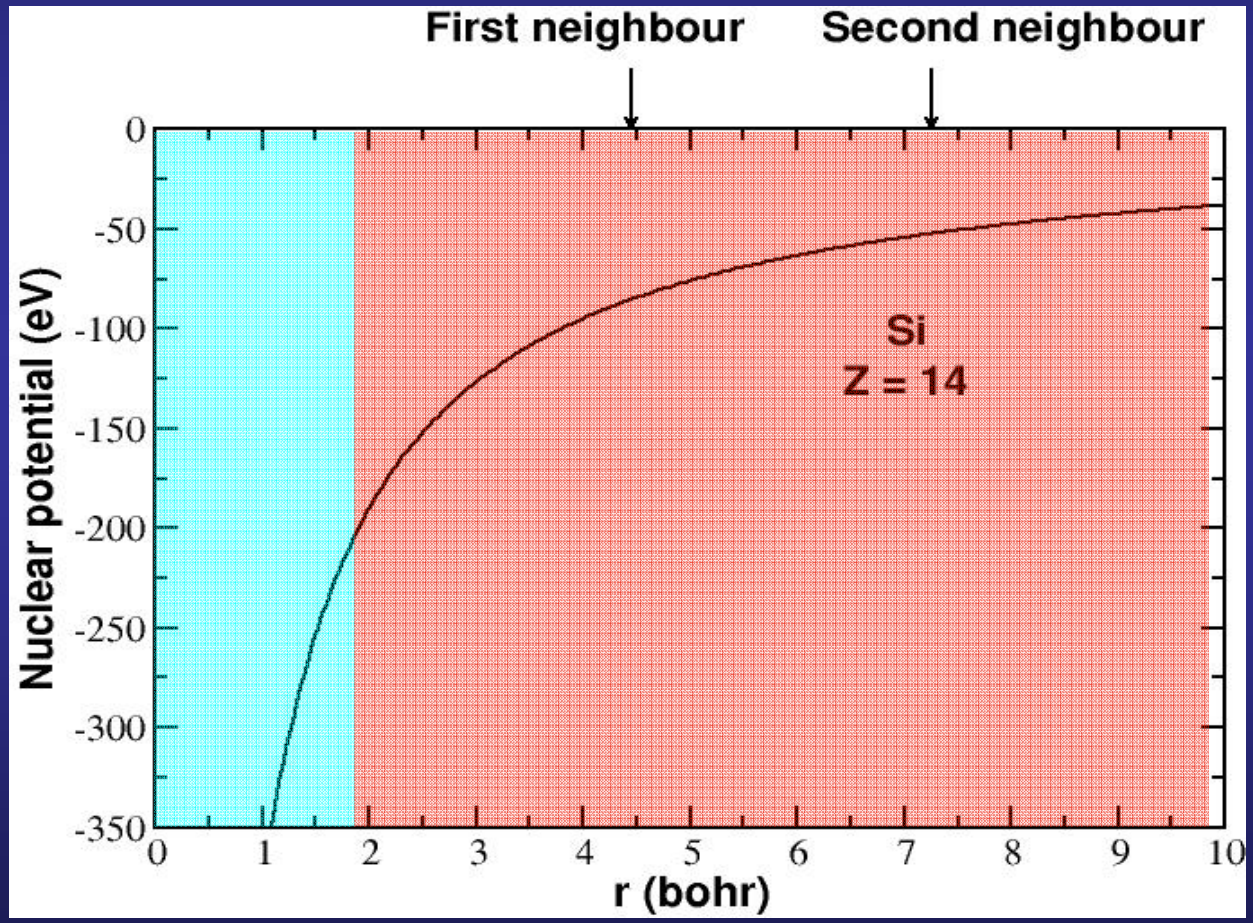
Difficulty: how to deal accurately with both the core and valence electrons





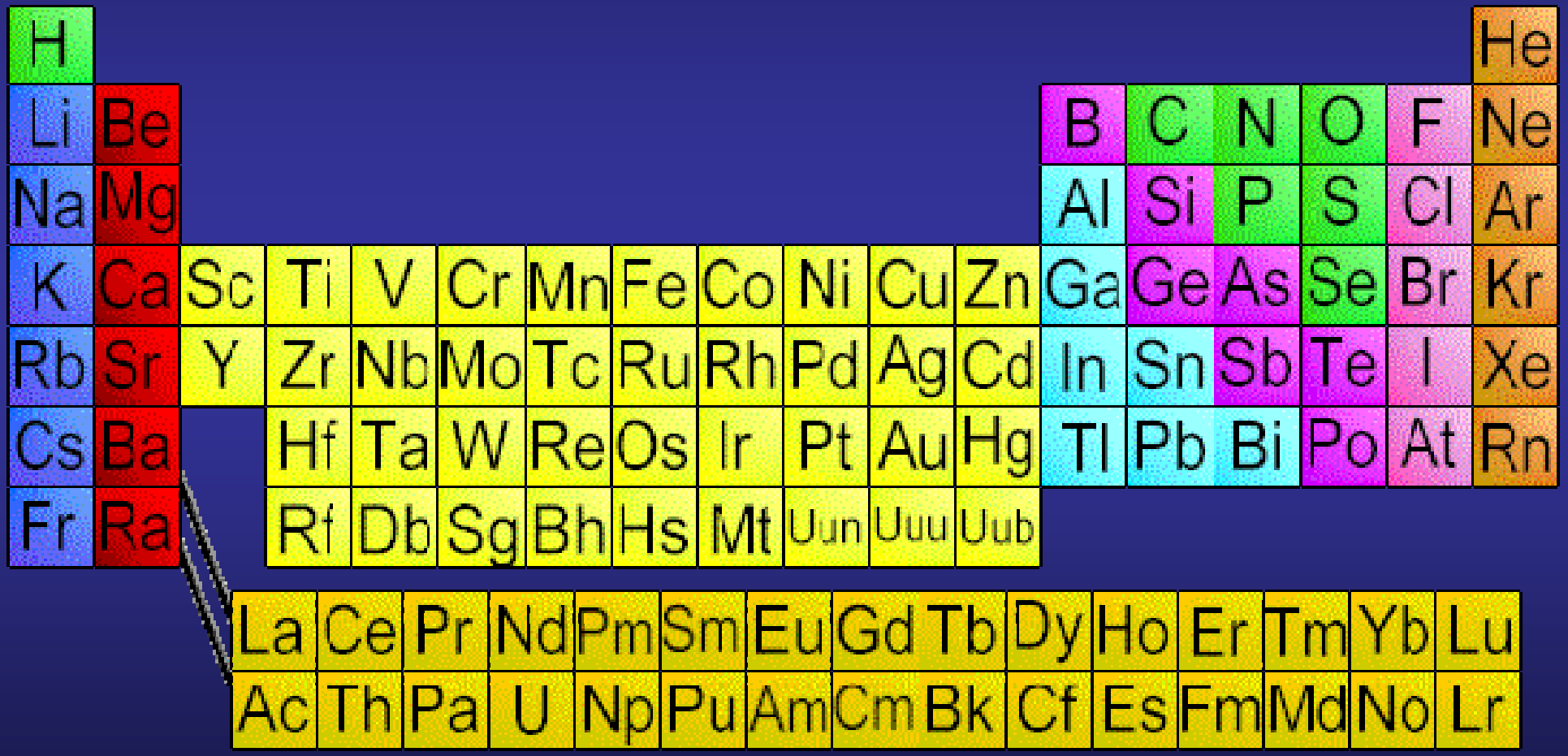
Difficulty: how to deal accurately with both the core and valence electrons



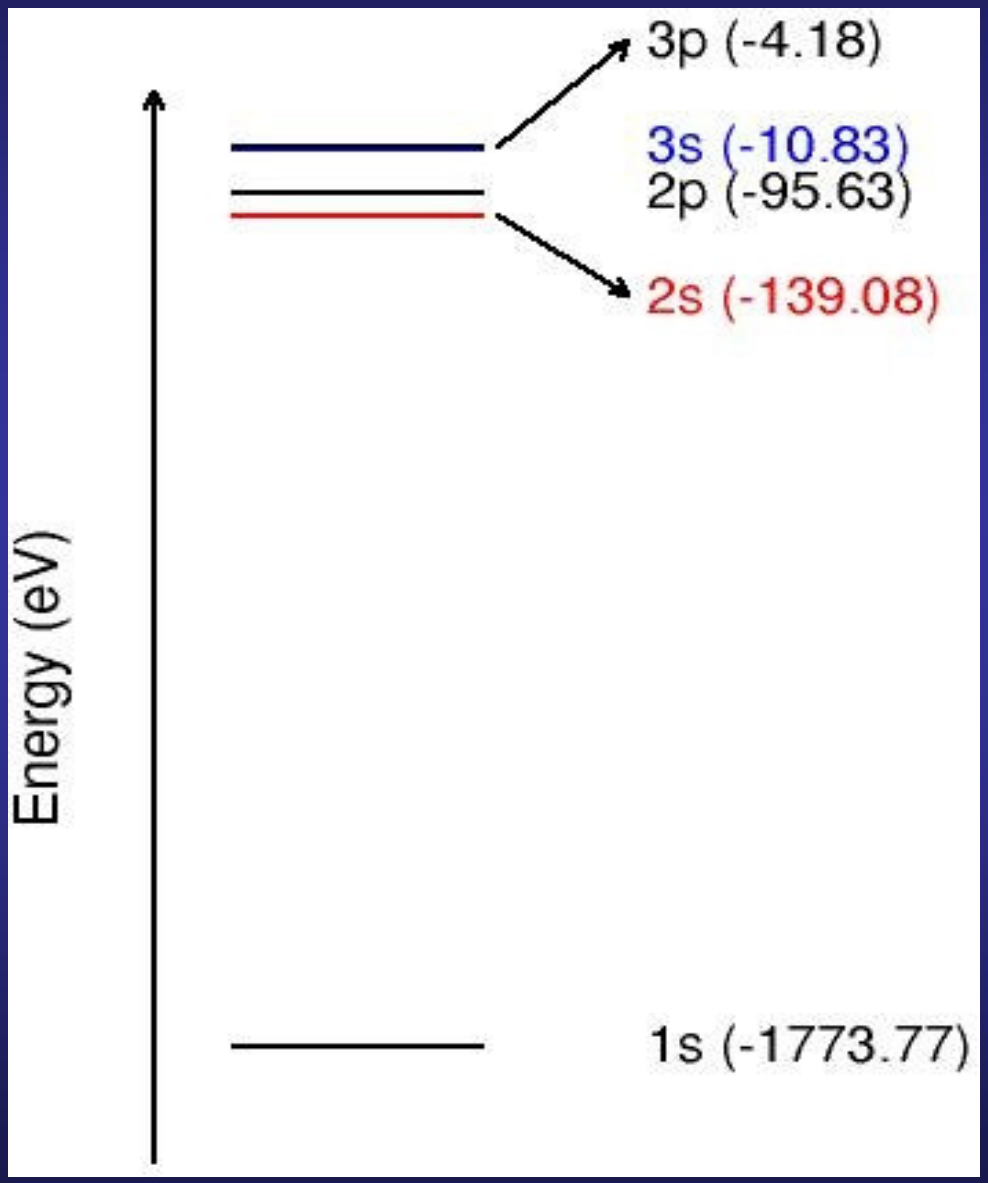


Si atomic configuration: $1s^2\ 2s^2\ 2p^6$ $3s^2\ 3p^2$

core valence

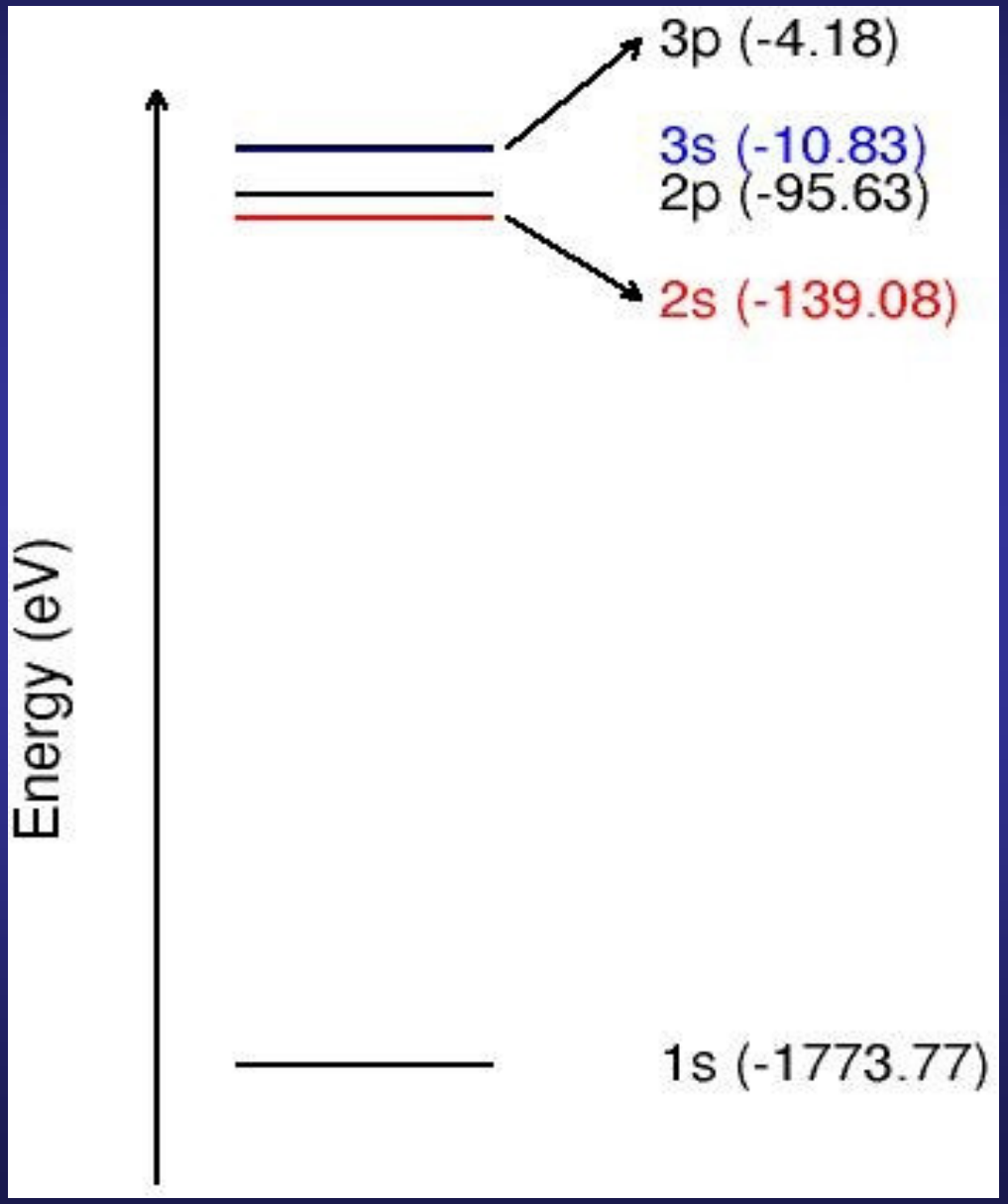


Core eigenvalues are much deeper than valence eigenvalues

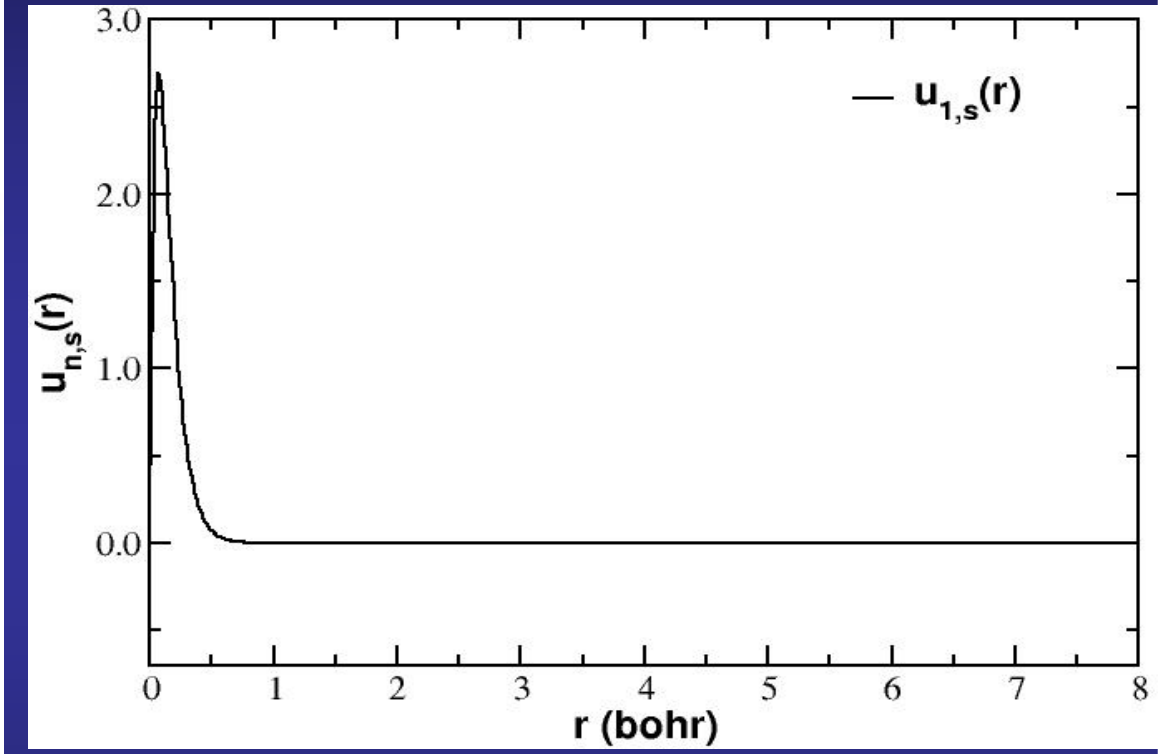


Atomic Si

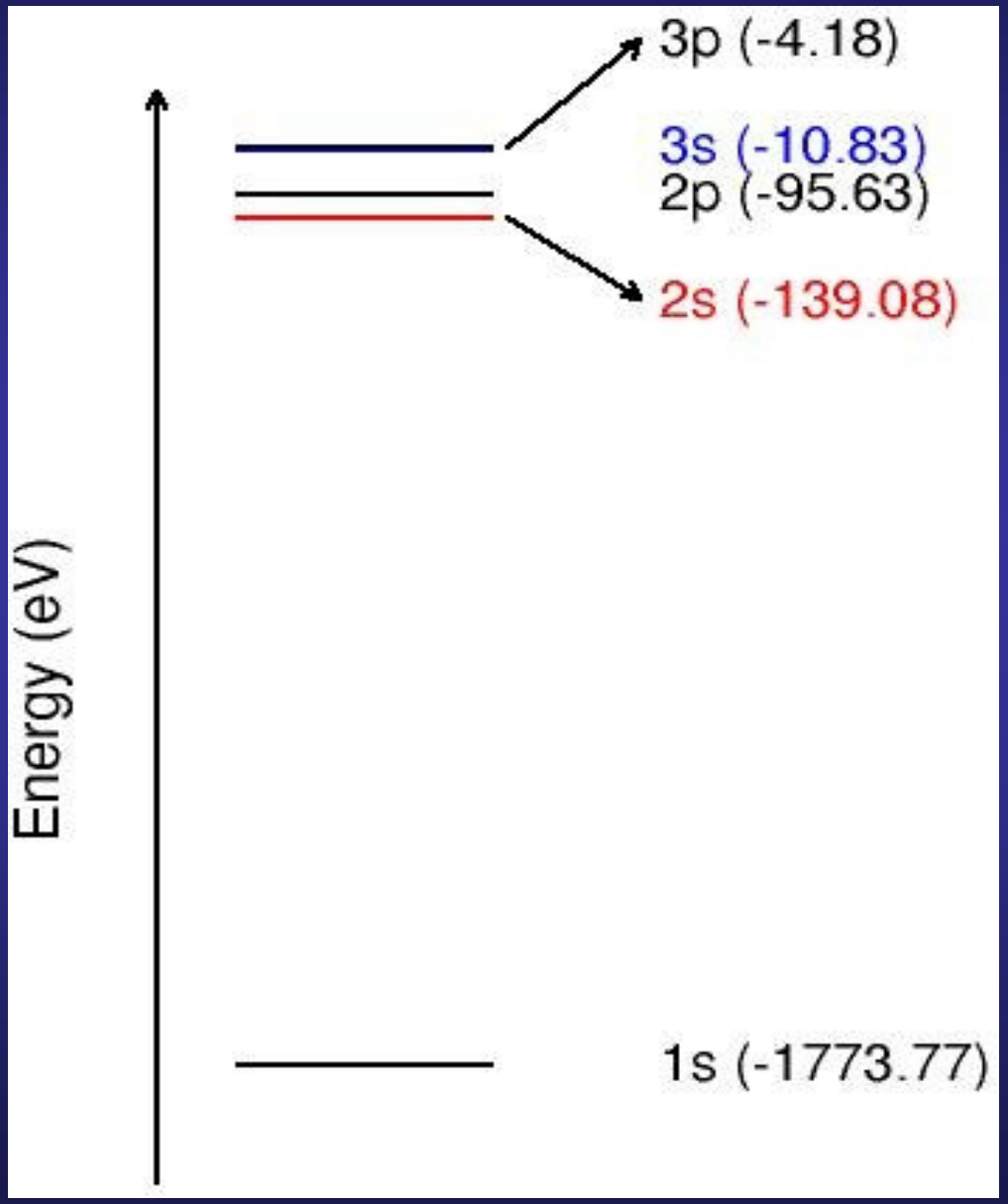
Core wavefunctions are very localized around the nuclei



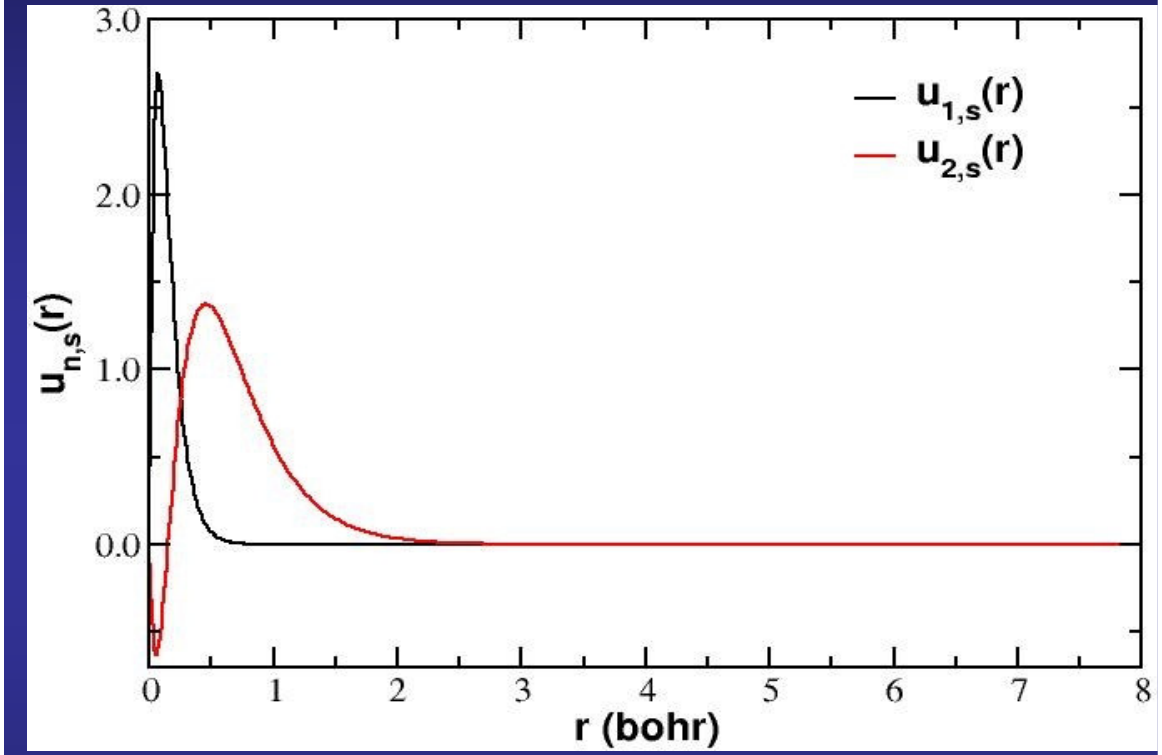
Atomic Si



Core wavefunctions are very localized around the nuclei



Atomic Si



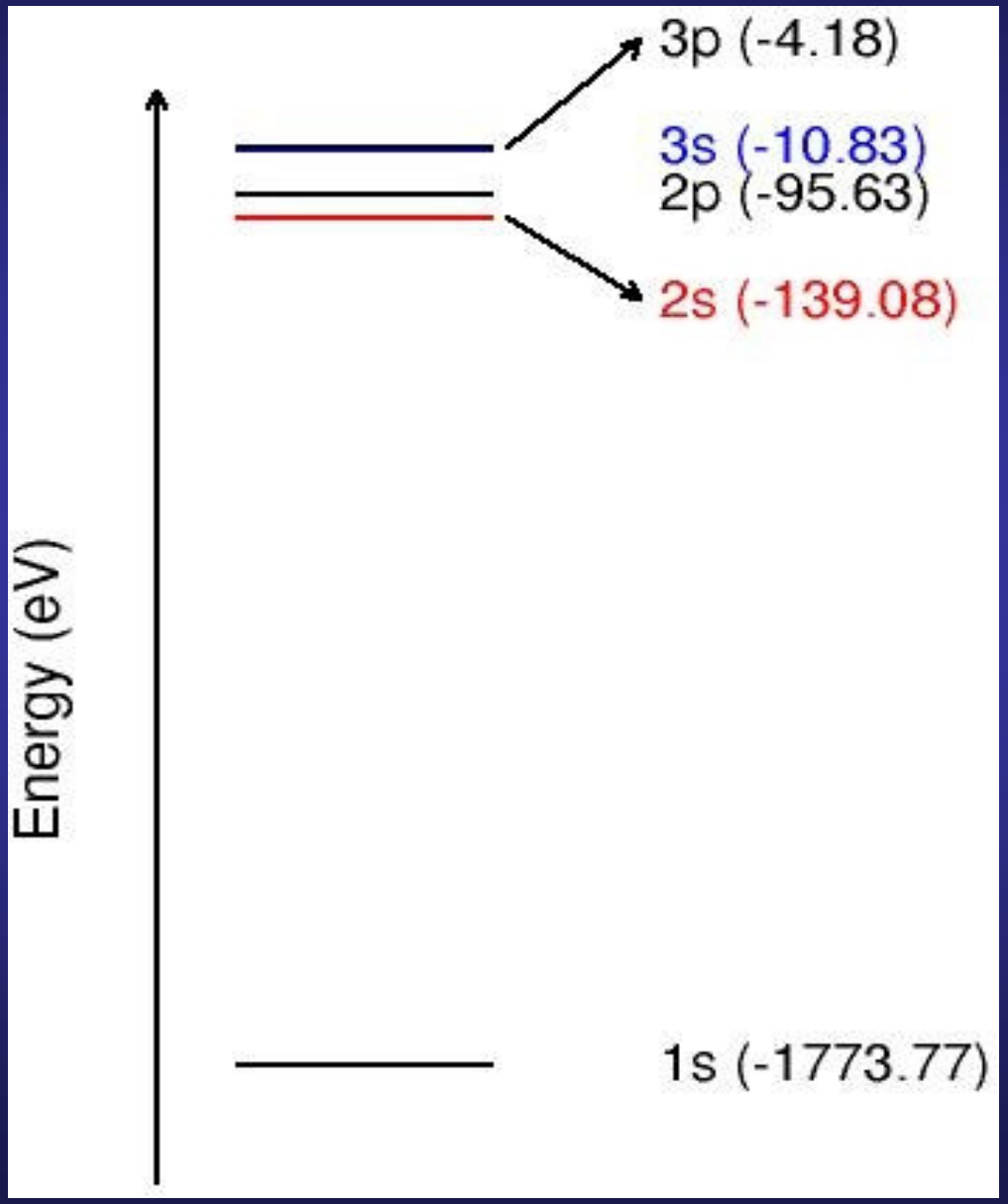
Core electrons…

highly localized

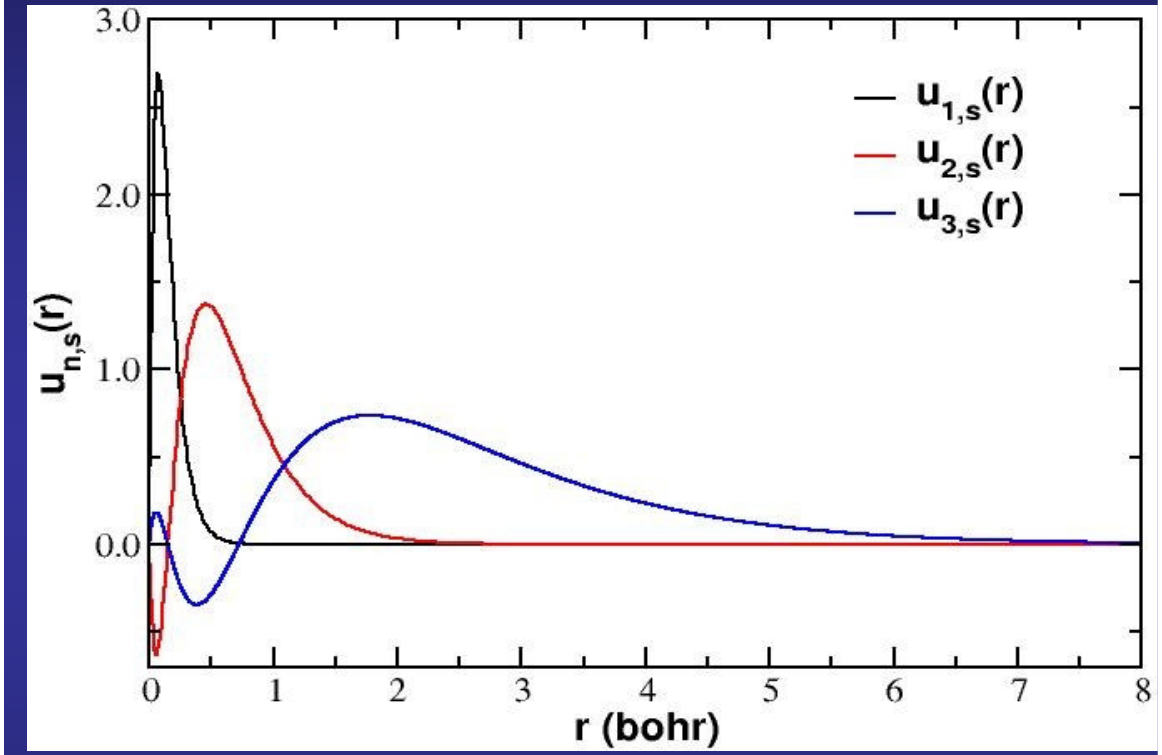
very depth energy

… are chemically inert

Valence wave functions must be orthogonal to the core wave functions



Atomic Si



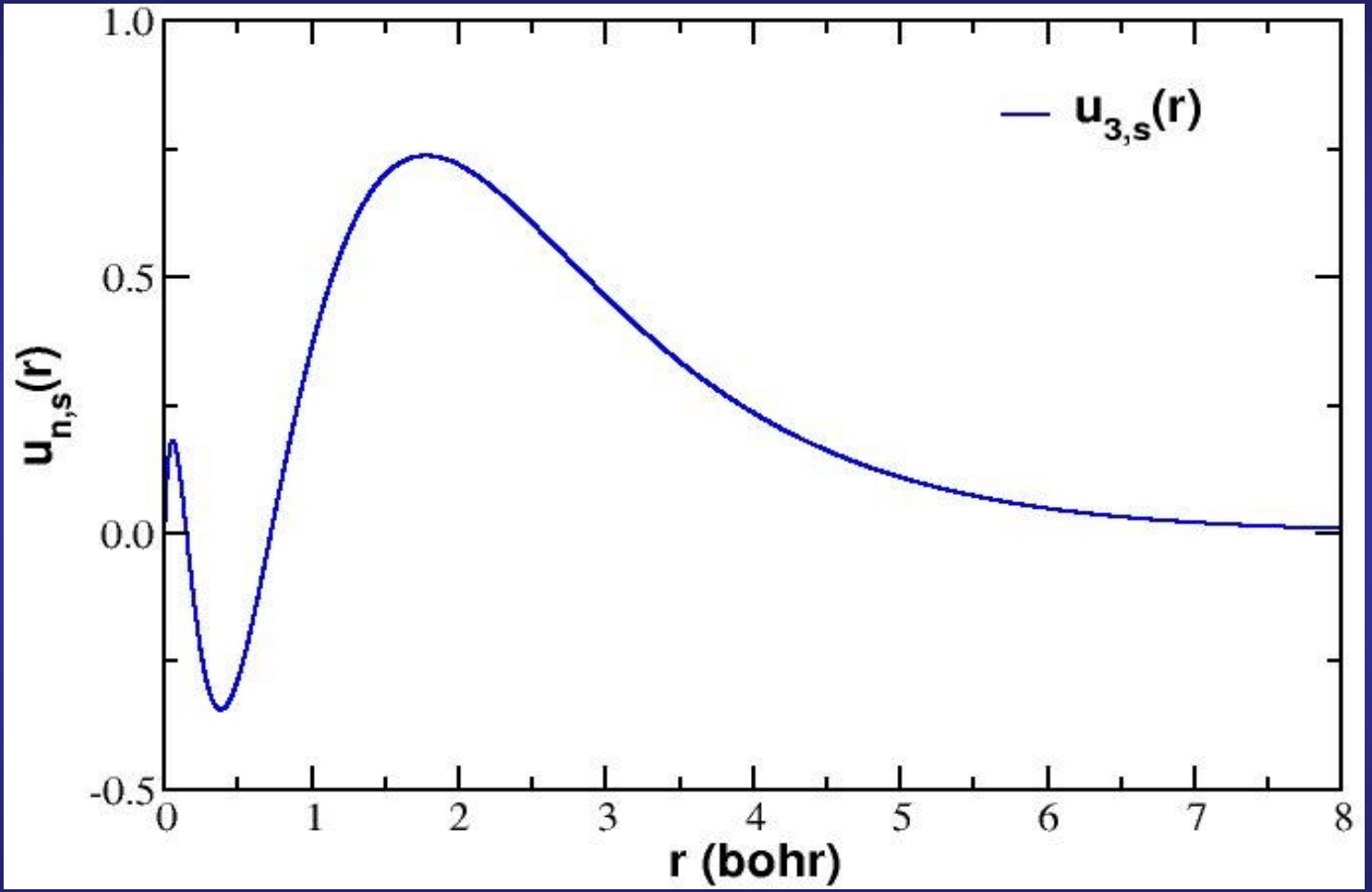
Core electrons…

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

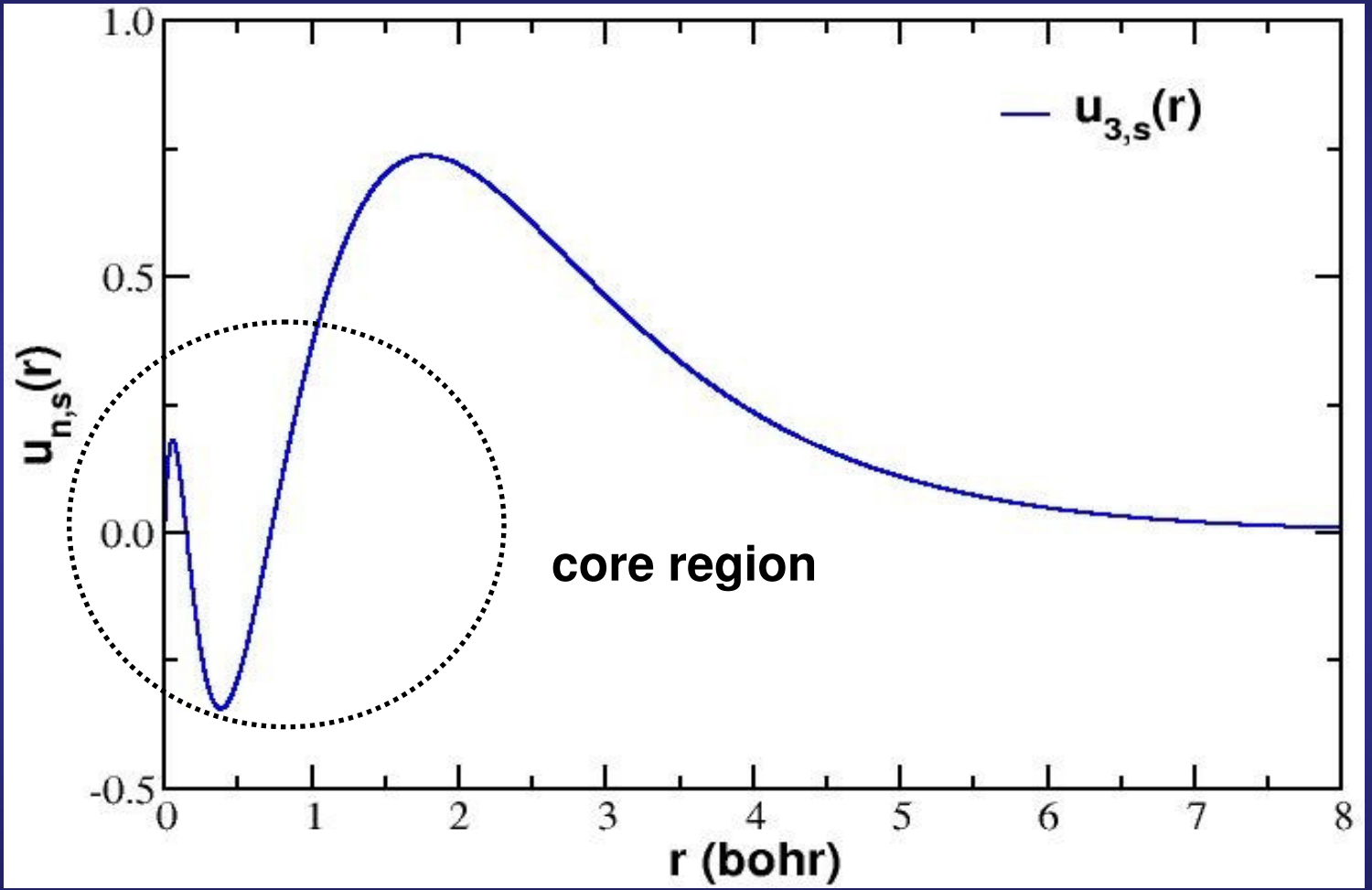
Core electrons main effect: screen nuclear potential

Idea:

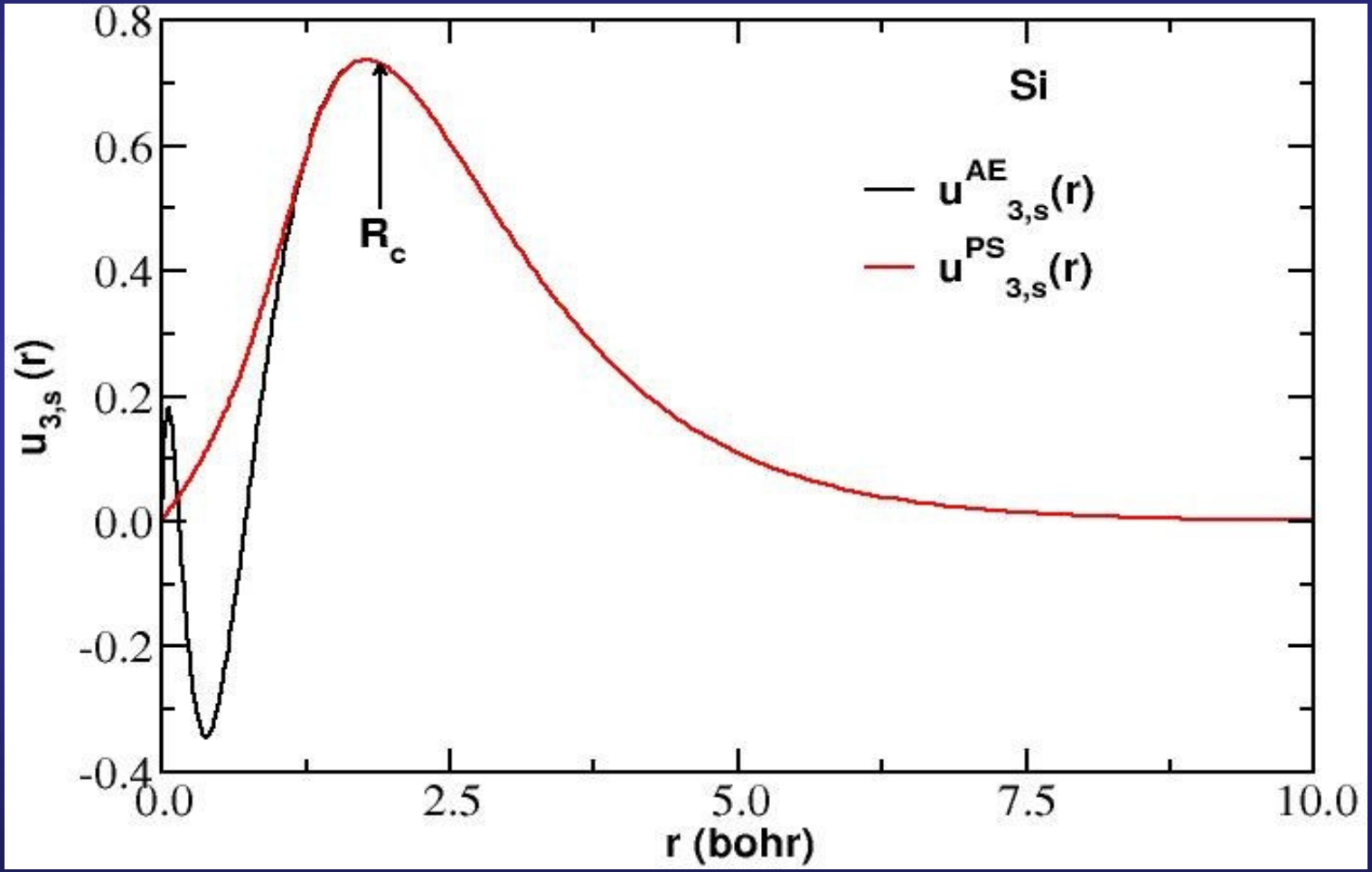
Ignore the dynamics of the core electrons (freeze them)

And replace their effects by an effective potential

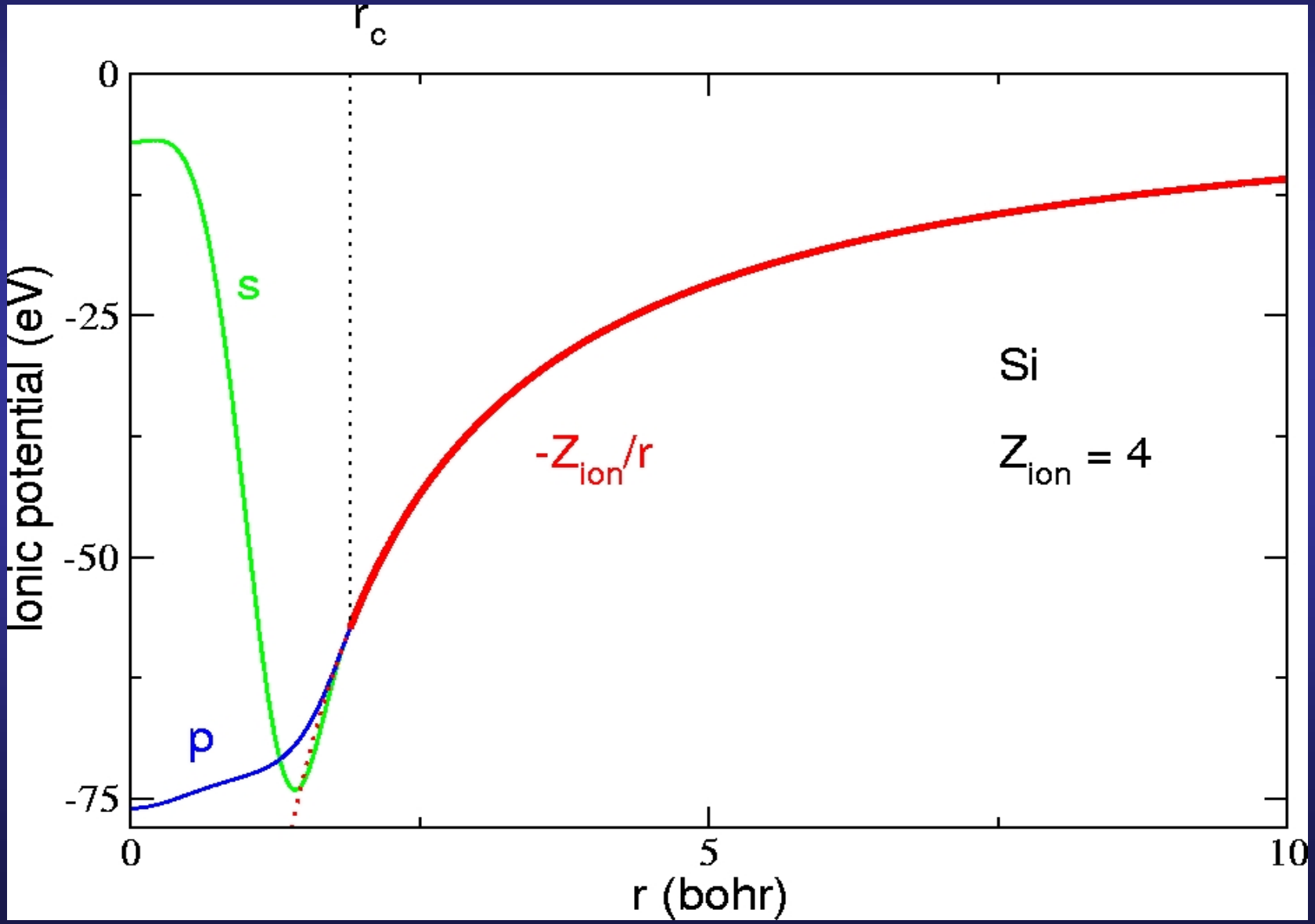
The nodes are imposed by orthogonality to the core states



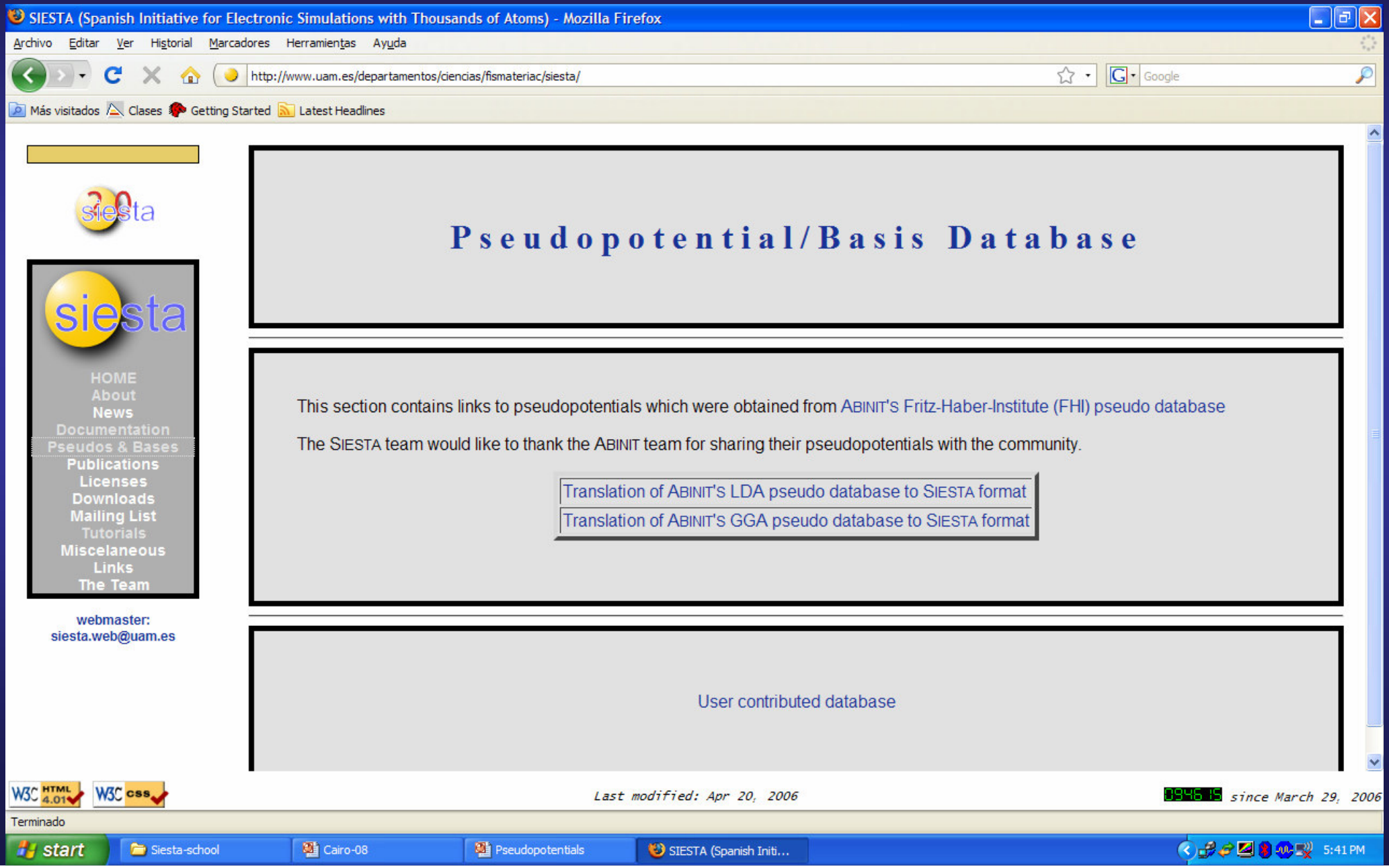
Idea, eliminate the core electrons by ironing out the nodes



Ab-initio pseudopotential method: fit the valence properties calculated from the atom



A good starting point: pseudopotentials tabulated in the SIESTA web page



Warning:

Before use a pseudopotential for production, test it

Independent of SIESTA or any other code

What are the main approximations?

Born-Oppenhaimer

Decouple the movement of the electrons and the nuclei.

Density Functional Theory (talk by Notker Roesch)

Treatment of the electron — electron interactions.

Pseudopotentials

Treatment of the (nuclei + core) — valence.

Basis set

To expand the eigenstates of the hamiltonian.

Numerical evaluation of matrix elements

Efficient and self-consistent computations of H and S.

Solve the secular equation

Supercells

To deal with periodic systems

Most important reference followed in this lecture

phys. stat. sol. (b) **215**, 809 (1999)

Subject classification: 71.15.Mb; 71.15.Fv; 71.24.+q; S1.3; S5; S5.11

Linear-Scaling ab-initio Calculations for Large and Complex Systems

E. ARTACHO[1]) (a), D. SÁNCHEZ-PORTAL (b), P. ORDEJÓN (c), A. GARCÍA (d), and J. M. SOLER (e)

PHYSICAL REVIEW B, VOLUME 64, 235111

Numerical atomic orbitals for linear-scaling calculations

Javier Junquera,[1] Óscar Paz,[1] Daniel Sánchez-Portal,[2,3] and Emilio Artacho[4]

PHYSICAL REVIEW B **66**, 205101 (2002)

Systematic generation of finite-range atomic basis sets for linear-scaling calculations

Eduardo Anglada,[1,2] José M. Soler,[1] Javier Junquera,[3] and Emilio Artacho[4]

the many body problem reduced to a problem of independent particles

One particle Kohn-Sham equation

$$\left[-\frac{1}{2}\nabla^2 + V^{\sigma}_{eff}\left(\vec{r}\right)\right]\psi^{\sigma}_i\left(\vec{r}\right) = \varepsilon^{\sigma}_i\psi^{\sigma}_i\left(\vec{r}\right)$$

$$V^{\sigma}_{eff}\left(\vec{r}\right) = V_{ext}\left(\vec{r}\right) + V_{Hartree}[n] + V^{\sigma}_{xc}[n^{\uparrow}, n^{\downarrow}]$$

Goal: solve the equation, that is, **find**

- the **eigenvectors**
- the **eigenvalues**

Solution: expand the eigenvectors in terms of functions of known properties **(basis)**

$$\psi_i\left(\vec{r}\right) = \sum_{\alpha} c_{i\alpha} f_{\alpha}\left(\vec{r}\right)$$

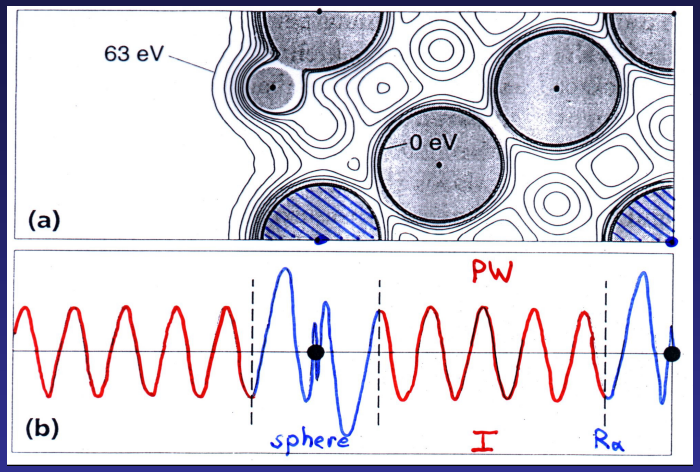
basis functions

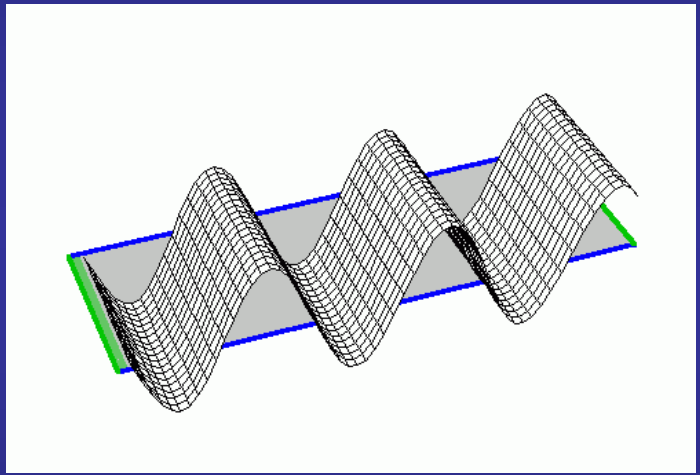
Three main families of methods depending on the basis sets

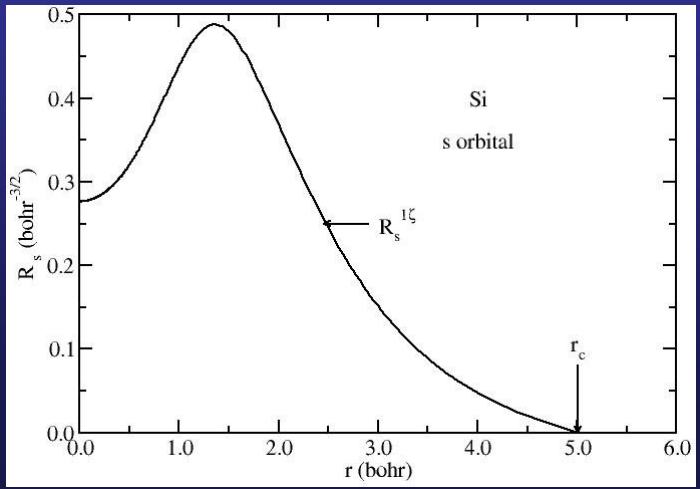
Atomic sphere methods

Plane wave and grids

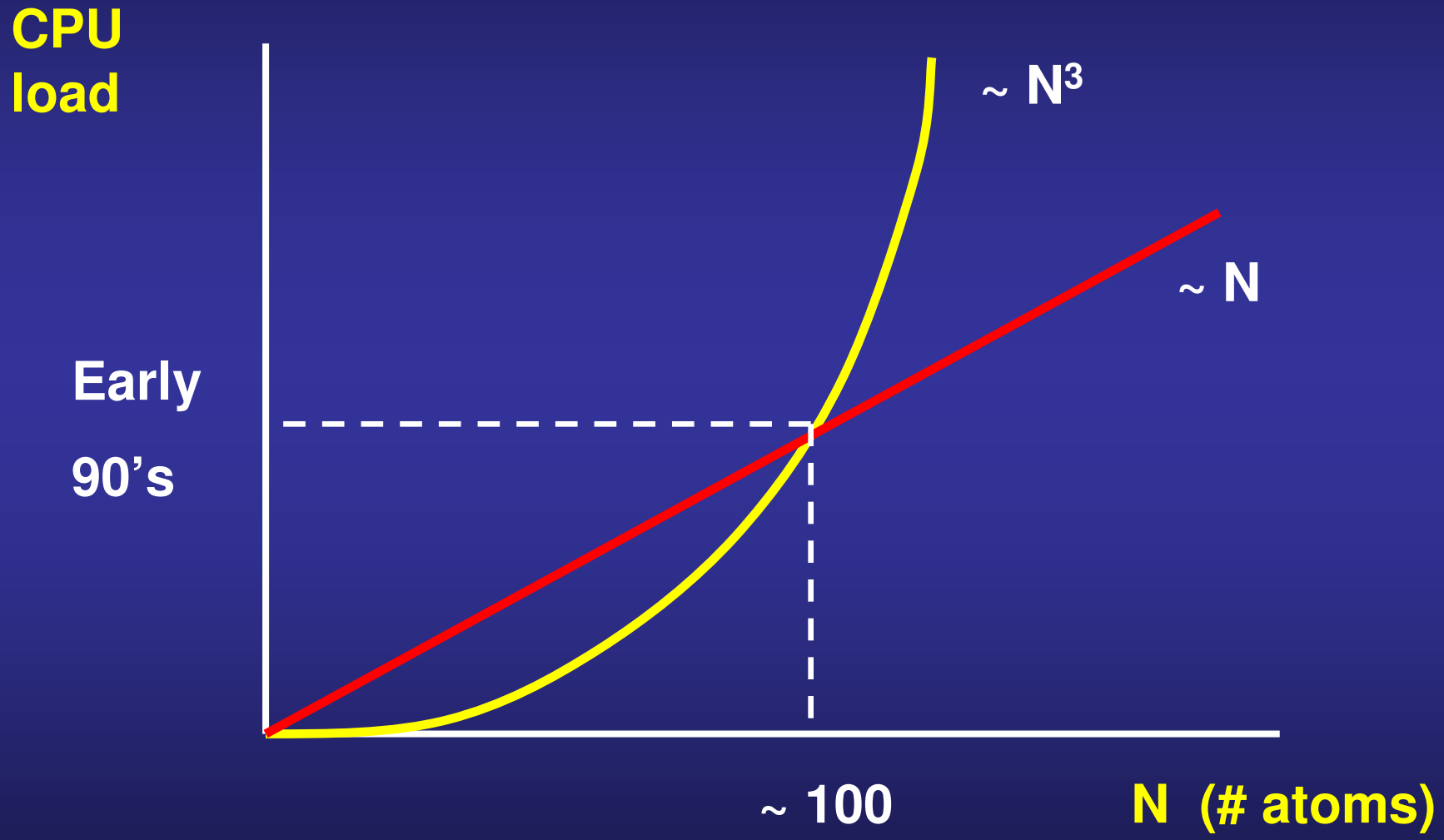
Localized basis sets







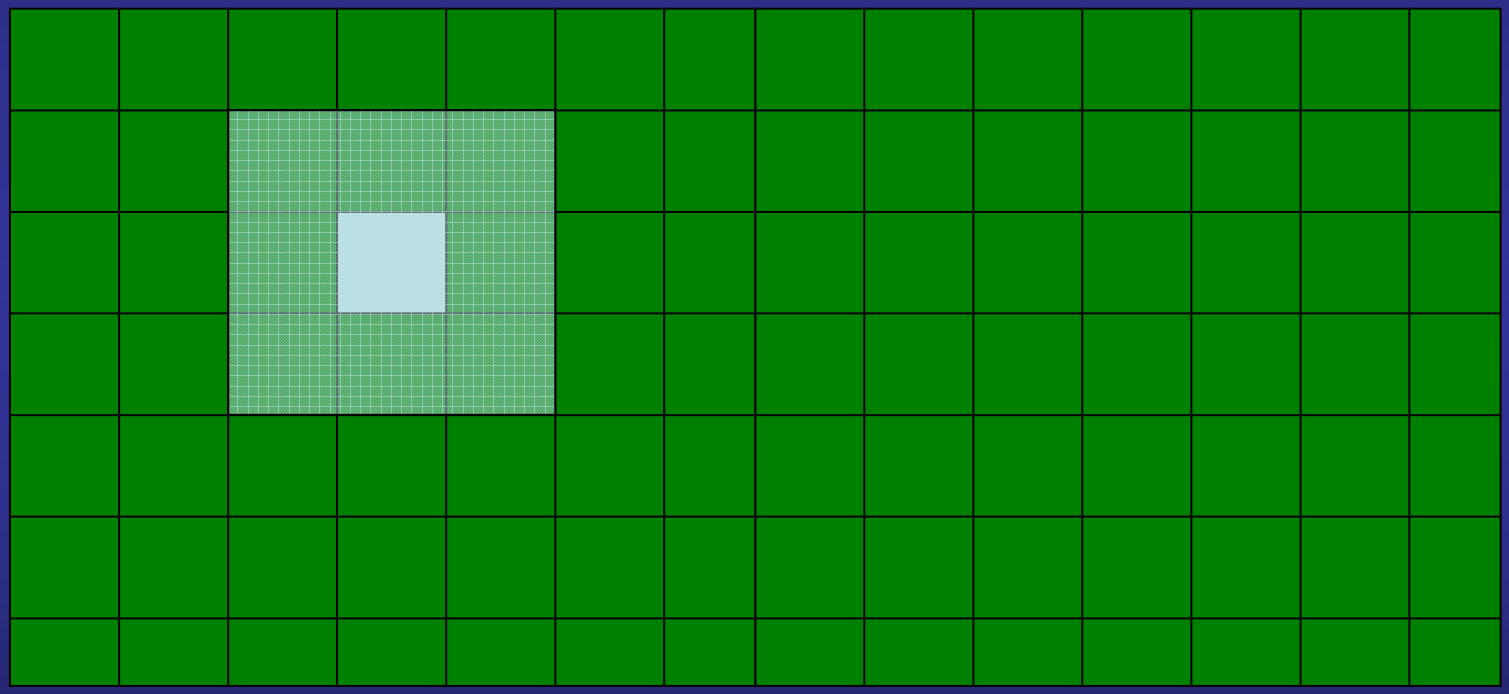
Order-N methods: The computational load scales linearly with the system size



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

Locality is the key point to achieve linear scaling

Large system



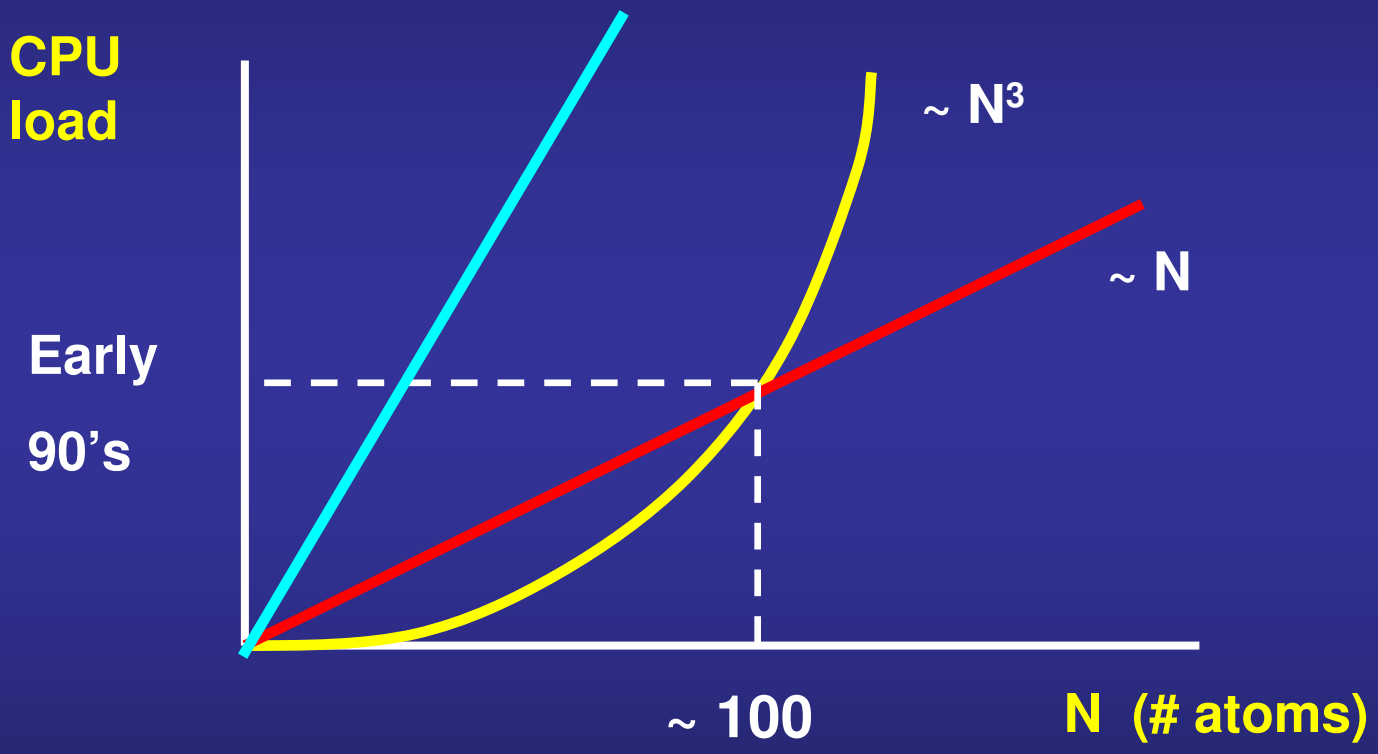
x2

"Divide and Conquer"

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

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

Locality ⇒ 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

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

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).

Atomic orbitals:
a radial function times an spherical harmonic

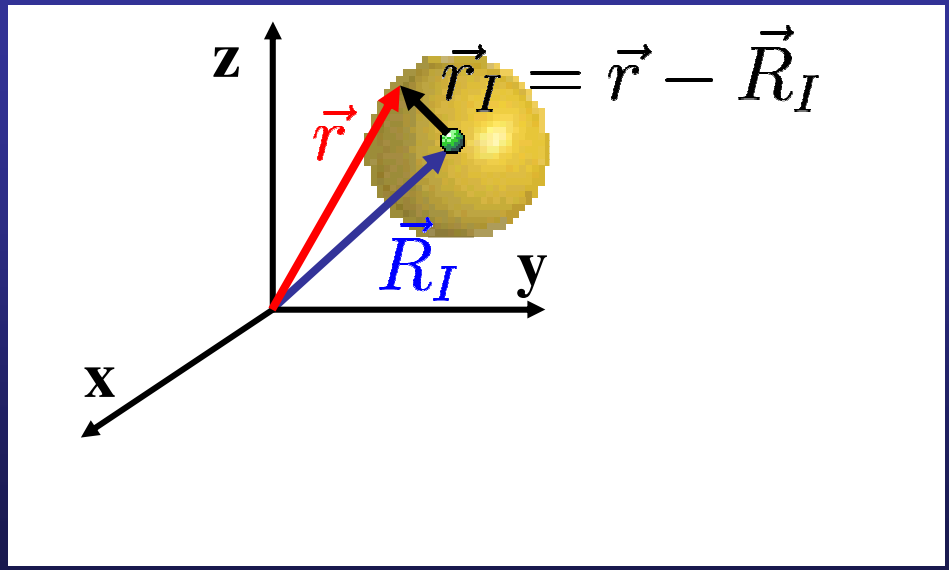
$$\phi_{Ilmn}(\vec{r}) = R_{Iln}(|\vec{r}_I|)\, Y_{lm}(\hat{r}_I)$$

Index of an atom

Angular momentum

Possibility of multiple orbitals with the same l,m

$$\hat{r}_I = \frac{\vec{r}_I}{|\vec{r}_I|}$$

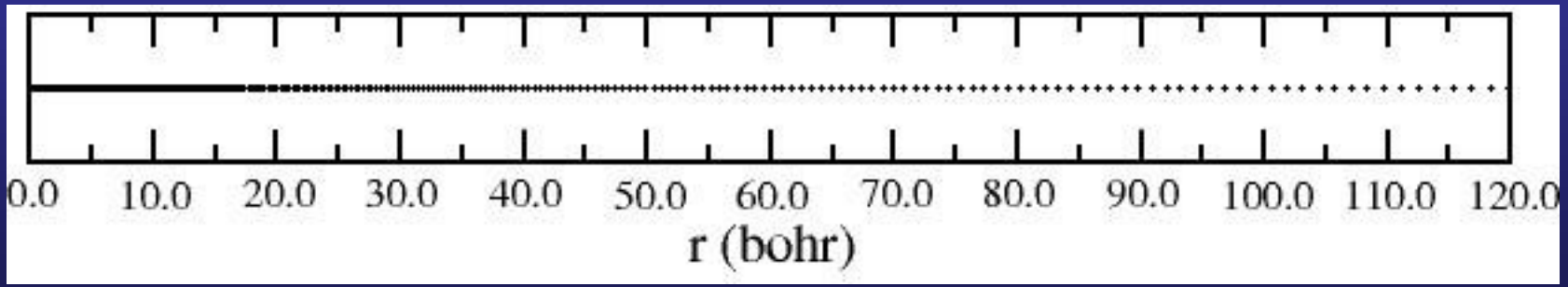


Numerical atomic orbitals

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

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

This equation is solved in a logarithmic grid using the Numerov method



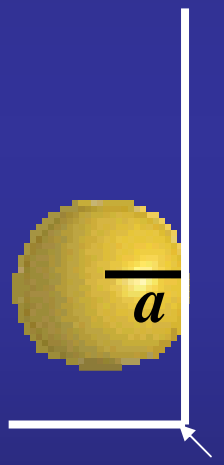
Dense close at the origin where atomic quantities oscillates wildly

Light far away from the origin where atomic quantities change smoothly

In SIESTA: strictly localized numerical atomic orbitals

The Schrödinger equation for the isolated atom is solved within a confinement potential that forces the orbital to be extrivtly zero beyond a given rc.

The default in SIESTA



$V = \infty, r \geq a$

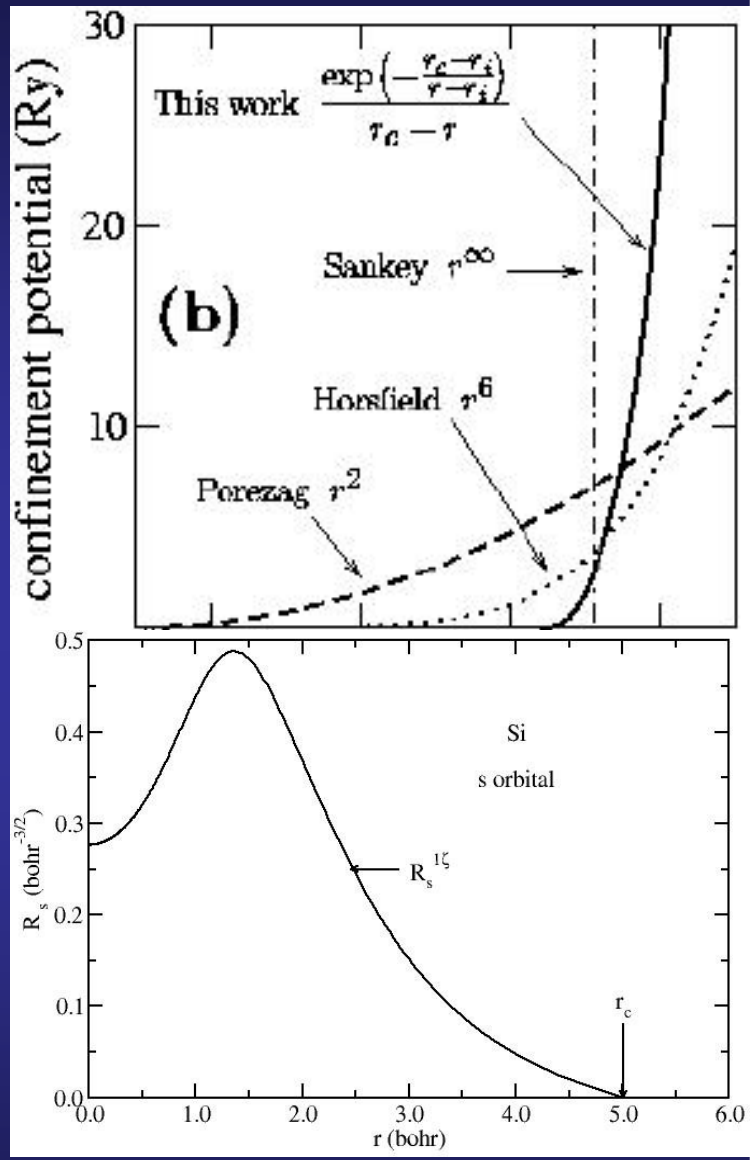
Determined by the energy shift

$V = 0, r < a$

Fireball

O. F. Sankey and D. J. Niklewski, Phys. Rev. B 40, 3979 (89)

Empirically, it works very nice



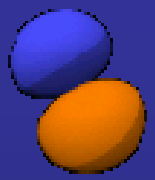
Atomic orbitals:
Main features that characterize the basis

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

Spherical harmonics:
well defined (fixed) objects

s

p



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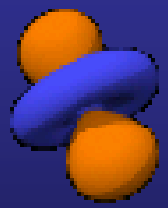

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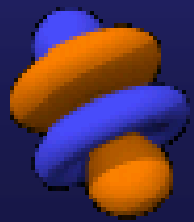


We use real spherical harmonics for computational efficiency

$$Y_{lm}(\theta,\varphi) = C_{lm} P_l^m(cos\theta) \begin{cases} sin(m\varphi) & \text{if } m < 0 \\ cos(m\varphi) & \text{if } m \geq 0 \end{cases}$$

Normalization factors

Associated Legendre polynomials

l = 0

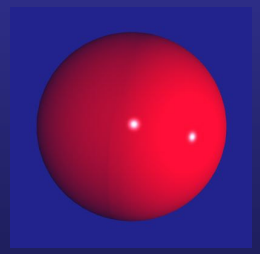
l = 1

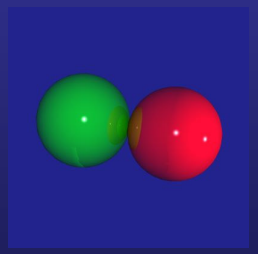
m = 0

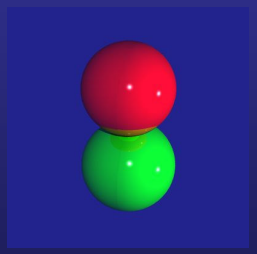
m = -1

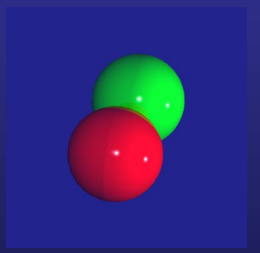
m = 0

m = +1







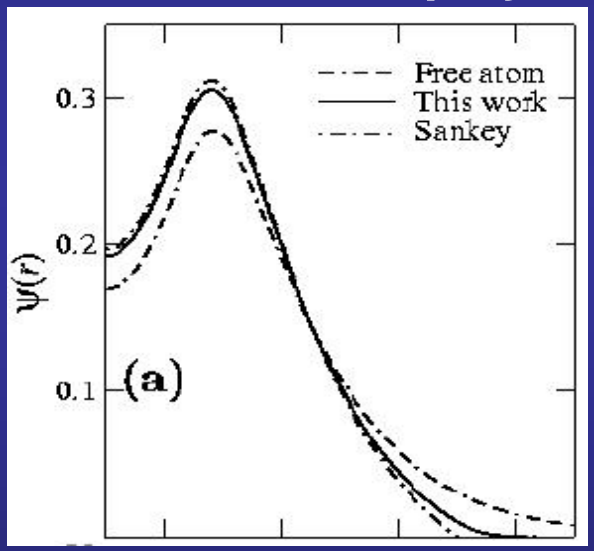


Pictures courtesy of Victor Luaña

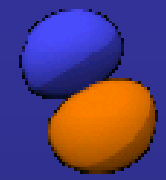
Atomic orbitals:
Main features that characterize the basis

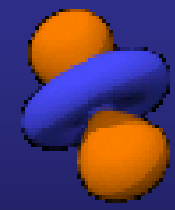
$$\phi_{Ilmn}(\vec{r}) = R_{Iln}(|\vec{r}_I|)\, Y_{lm}(\hat{r}_I)$$

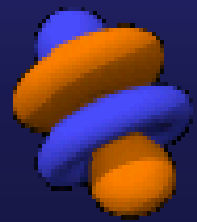
Radial part:
degree of freedom to play with



Spherical harmonics:
well defined (fixed) objects







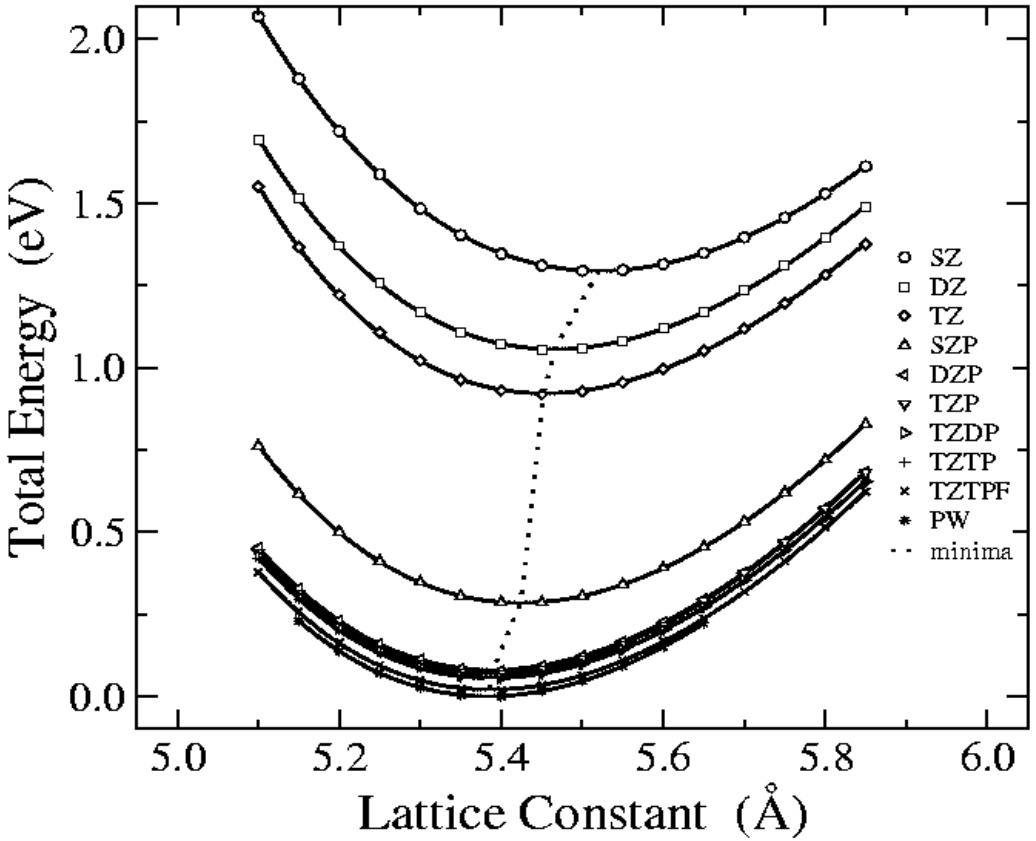
Size: Number of atomic orbitals per atom

Range: Spatial extension of the orbitals

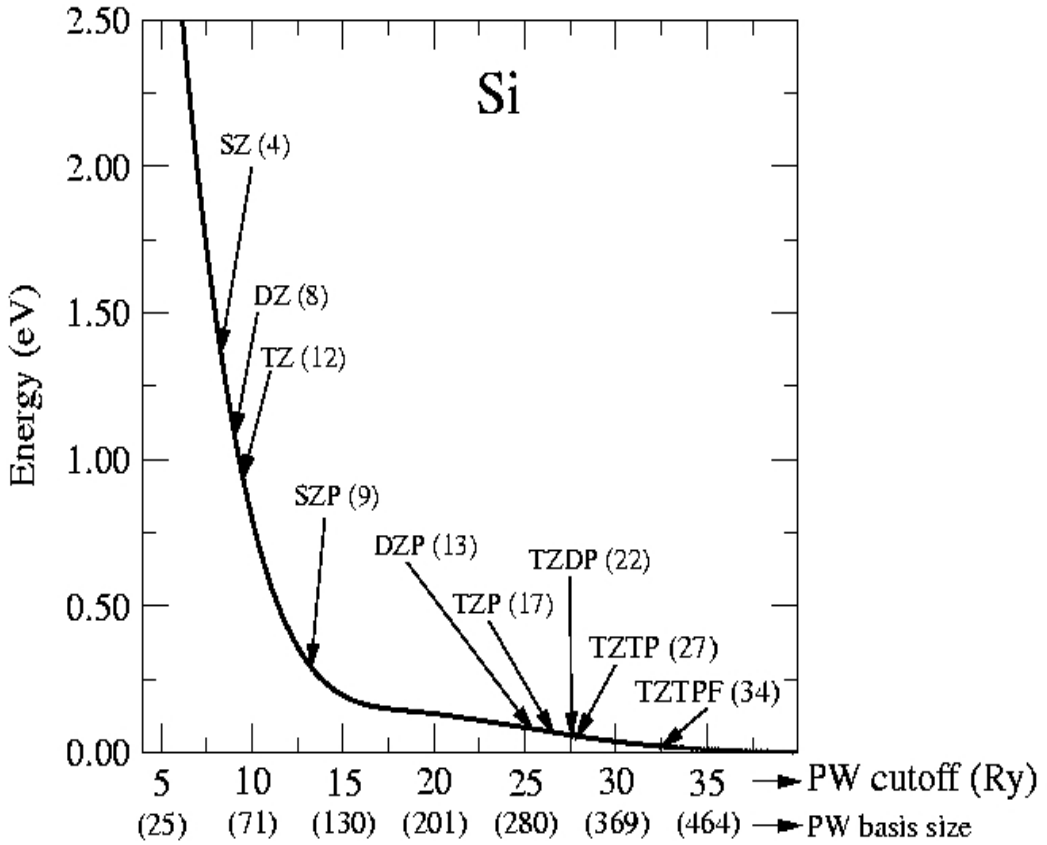
Shape: of the radial part

Convergence as a function of the size of the basis set: Bulk Si

Cohesion curves



PW and NAO convergence



Atomic orbitals show nice convergence with respect the size

Polarization orbitals very important for convergence (more than multiple-ζ)

Double-ζ plus polarization equivalent to a PW basis set of 26 Ry

Convergence as a function of the size 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		5.28	4.63

A DZP basis set introduces the same deviations as the ones due to the DFT or the pseudopotential approaches

SZ = single-ζ

DZ= doble- ζ

TZ=triple- ζ

P=Polarized

DP=Doble-polarized

PW: Converged Plane Waves (50 Ry)

APW: Augmented Plane Waves

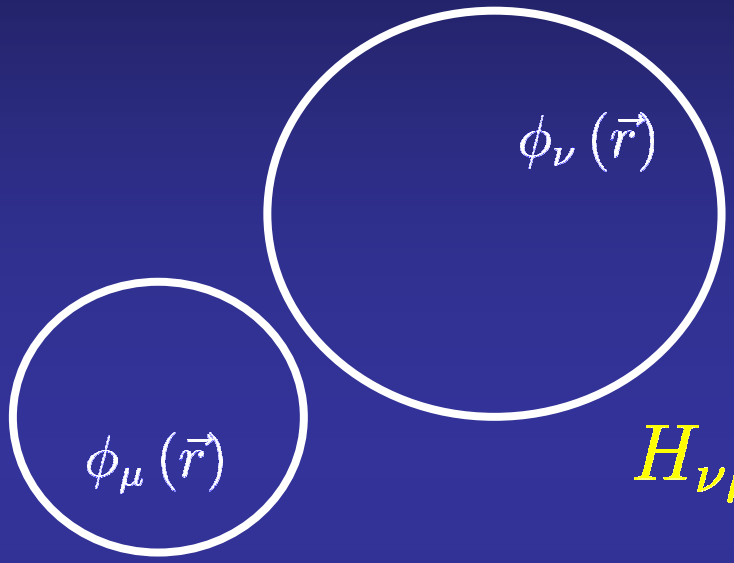
Convergence as a function of the size of the basis set

		Exp	LAPW	Other PW	PW	DZP
Au	a	4.08[a]	4.05[b]	4.07[c]	4.05	4.07
	B	173[a]	198[b]	190[c]	191	188
	E_c	3.81[a]	-	-	4.19	4.03
MgO	a	4.21[d]	4.26[e]	-	4.10	4.11
	B	152[d]	147[e]	-	168	167
	E_c	10.30[d]	10.40[e]	-	11.90	11.87
C	a	3.57[a]	3.54[f]	3.54[g]	3.53	3.54
	B	442[a]	470[f]	436[g]	466	453
	E_c	7.37[a]	10.13[f]	8.96[g]	8.90	8.81
Si	a	5.43[a]	5.41[h]	5.38[g]	5.38	5.40
	B	99[a]	96[h]	94[g]	96	97
	E_c	4.63[a]	5.28[h]	5.34[g]	5.37	5.31
Na	a	4.23[a]	4.05[i]	3.98[g]	3.95	3.98
	B	6.9[a]	9.2[i]	8.7[g]	8.8	9.2
	E_c	1.11[a]	1.44[j]	1.28[g]	1.22	1.22
Cu	a	3.60[a]	3.52[b]	3.56[g]	-	3.57
	B	138[a]	192[b]	172[g]	-	165
	E_c	3.50[a]	4.29[k]	4.24[g]	-	4.37
Pb	a	4.95[a]	-	4.88	-	4.88
	B	43[a]	-	54	-	64
	E_c	2.04[a]	-	3.77	-	3.51

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

Range: the spatial extension of the atomic orbitals

Order(N) methods ⇒ locality, that is, a finite range for matrix and overlap matrices



If the two orbitals are sufficiently far away

$$S_{\nu\mu} = \langle \phi_\nu \mid \phi_\mu \rangle = \int d\vec{r}\ \phi_\nu^*(\vec{r})\,\phi_\mu(\vec{r}) = 0$$

$$H_{\nu\mu} = \langle \phi_\nu \mid \hat{H} \mid \phi_\mu \rangle = \int d\vec{r}\ \phi_\nu^*(\vec{r})\,\hat{H}\phi_\mu(\vec{r}) = 0$$

Neglect interactions:

Below a tolerance

Beyond a given scope of neighbours

Problem: introduce numerical instabilities for high tolerances.

Strictly localized atomic orbitals:

Vanishes beyond a given cutoff radius

O. Sankey and D. Niklewski, PRB 40, 3979 (89)

Problem: accuracy and computational **efficiency depend** on the **range** of the basis orbitals

How to define all the r_c in a **balance way**?

How to control de range of the orbitals in a balanced way: the energy shift

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

Energy increase ≡ Energy shift

PAO.EnergyShift (energy)

Cutoff radius, r_c, = position where each orbital has the node

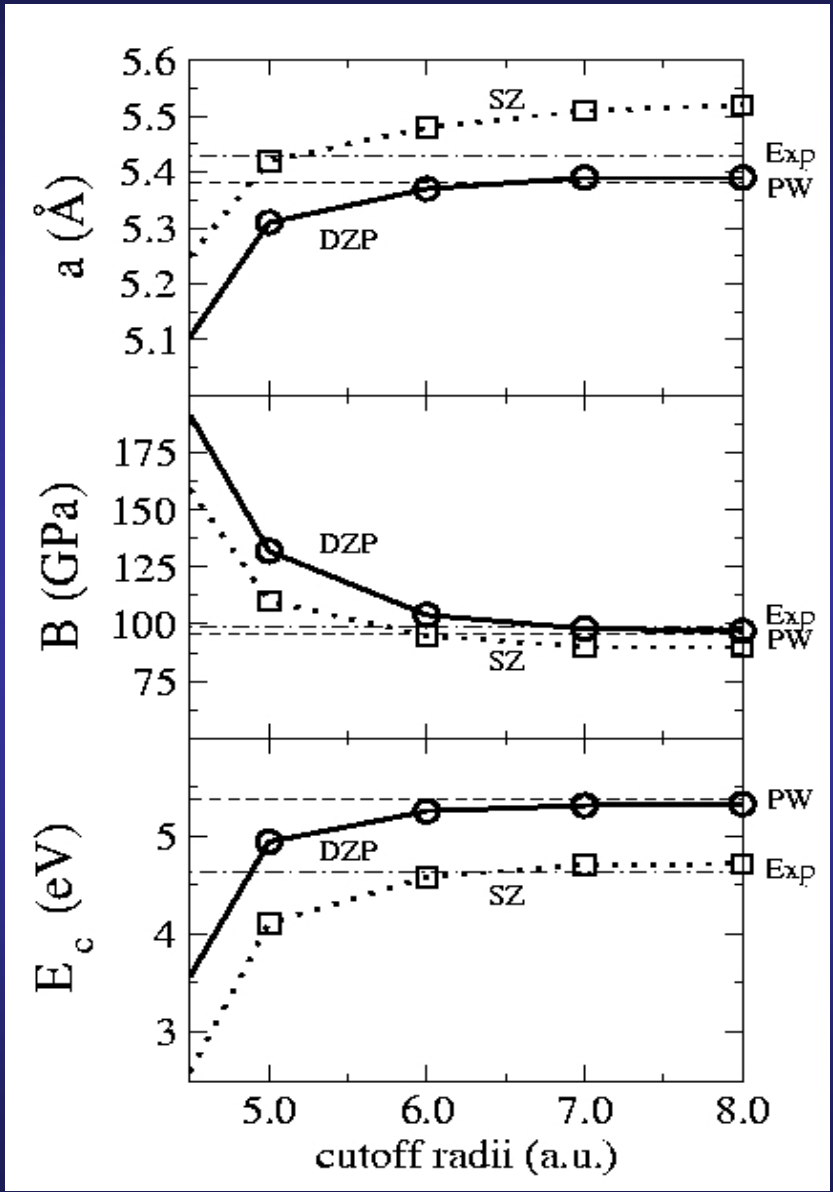
A single parameter for all cutoff radii

The larger the Energy shift, the shorter the r_cs

Typical values: 100-200 meV

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

Convergence with the range



More efficient →

← More accurate

Bulk Si

equal *s*, *p* orbitals radii

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

How to introduce the basis set in SIESTA
Effort on defining a systematics with minimum parameters

If nothing is specified: default

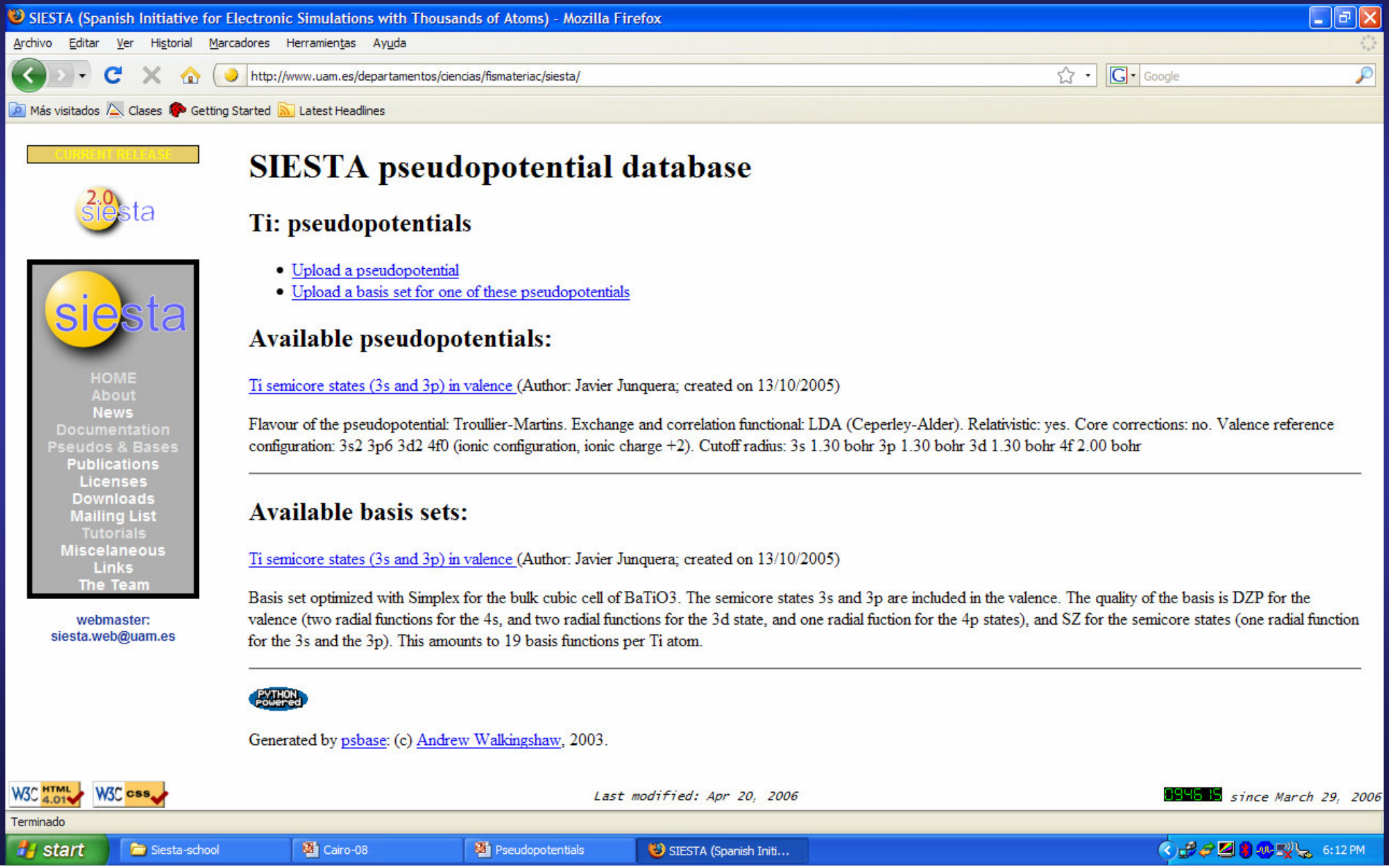
Basis size:	PAO.BasisSize	DZP
Range of first-zeta:	PAO.EnergyShift	0.02 Ry
Second-zeta:	PAO.BasisType	Split
Range of second-zeta:	PAO.SplitNorm	0.15
Confinement:	Hard well	

Good basis set in terms of accuracy versus efficiency

The user has the freedom to play with these parameters

Recently: used variationally optimized basis set

As with the pseudopotentials, there is a list of contributed basis sets



What are the main approximations?

Born-Oppenhaimer

Decouple the movement of the electrons and the nuclei.

Density Functional Theory (talk by Notker Roesch)

Treatment of the electron — electron interactions.

Pseudopotentials

Treatment of the (nuclei + core) — valence.

Basis set

To expand the eigenstates of the hamiltonian.

Numerical evaluation of matrix elements

Efficient and self-consistent computations of H and S.

Solve the secular equation

Supercells

To deal with periodic systems

Goal: solve the one-particle Kohn-Sham Schrödinger-like equation

$$\hat{H}\psi_i(\vec{r}) = E_i\psi_i(\vec{r})$$

Expansion of the eigenvectors in a basis of localized atomic orbitals

$$\psi_i(\vec{r}) = \sum_\mu \phi_\mu(\vec{r})\, c_{\mu i}$$

where the coefficients $c_{\mu i} = \langle \tilde{\phi}_\mu \,|\, \psi_i \rangle$, and $\tilde{\phi}_\mu$ are the dual orbital of ϕ_μ : $\langle \tilde{\phi}_\mu \,|\, \phi_\nu \rangle = \delta_{\mu\nu}$

Introducing the expansion into the Kohn-Sham equation, we arrive to the **secular equation**

$$\sum_\mu (H_{\nu\mu} - E_i S_{\nu\mu})\, c_{\mu i} = 0$$

$$S_{\nu\mu} = \langle \phi_\nu \,|\, \phi_\mu \rangle = \int d\vec{r}\ \phi_\nu^*(\vec{r})\, \phi_\mu(\vec{r})$$

$$H_{\nu\mu} = \langle \phi_\nu \,|\, \hat{H} \,|\, \phi_\mu \rangle = \int d\vec{r}\ \phi_\nu^*(\vec{r})\, \hat{H}\phi_\mu(\vec{r})$$

The one-particle Kohn-Sham hamiltonian

$$\hat{H} = \hat{T} + \sum_{\alpha} \hat{V}_{\alpha}^{PS} + V^{H}(\vec{r}) + V^{xc}(\vec{r})$$

Transforming the semilocal pseudopotential form into the fully nonlocal separable Kleinman-Bylander form

$$\hat{V}^{PS} = V^{local}(\vec{r}) + \hat{V}^{KB}$$

$$V^{local}(\vec{r}) \rightarrow -\frac{Z_{val}}{r}$$

$$\hat{V}^{KB} = \sum_{l=0}^{l_{max}^{KB}} \sum_{m=-l}^{l} \sum_{n=1}^{N_l^{KB}} |\chi_{lmn}^{KB}\rangle v_{ln}^{KB} \langle \chi_{lmn}^{KB}|$$

The standard Kohn-Sham one-electron hamiltonian might be written as

$$\hat{T} + \sum_{\alpha} V_{\alpha}^{local}(\vec{r}) + \sum_{\alpha} V_{\alpha}^{KB} + V^{H}(\vec{r}) + V^{xc}(\vec{r})$$

Kinetic energy operator

$$\hat{T} = -\frac{1}{2}\nabla^2$$

Hartree potential

$$V^{H}(\vec{r}) = \int d\vec{r}\,' \frac{\rho(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|}$$

Exchange-correlation potential

(Assume LDA approach)

$$V^{xc}(\vec{r}) = V^{xc}[\rho(\vec{r})]$$

Electronic charge density =

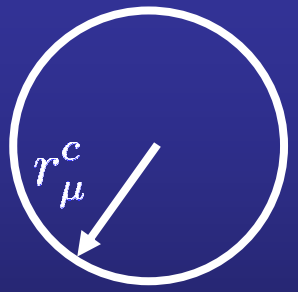
sum of spherical atomic densities +

deformation charge density (bonding)

$$\rho(\vec{r}) = \rho^{atom}(\vec{r}) + \delta\rho(\vec{r})$$

$$\rho^{atom}(\vec{r}) = \sum_I \rho_I^{atom}(\vec{r})$$

Populate basis function with appropriate valence atomic charges



$\phi_\mu(\vec{r})$

ρ_I^{atom} exactly vanishes beyond $r_I^c = \max_l r_{Il}^c$

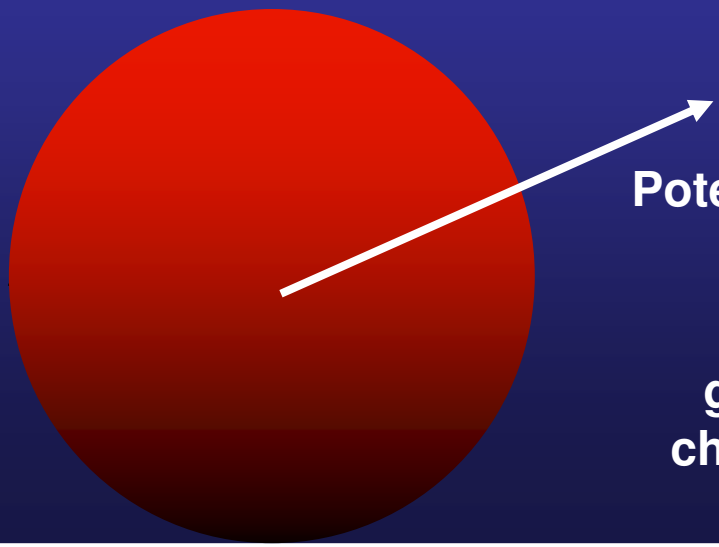
The local part is screened by the potential generated by an atomic electron density

$$V^H(\vec{r}) = \int d\vec{r}\,' \frac{\rho(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} = \int d\vec{r}\,' \frac{\rho^{atom}(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} + \int d\vec{r}\,' \frac{\delta\rho(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} \equiv V^{atom}(\vec{r}) + \delta V^H(\vec{r})$$

Neutral atom potential

$$V^{local}(\vec{r}) \rightarrow -\frac{Z_{val}}{r}$$

$$V_I^{NA}(\vec{r}) \equiv V_I^{local}(\vec{r}) + V_I^{atom}(\vec{r})$$

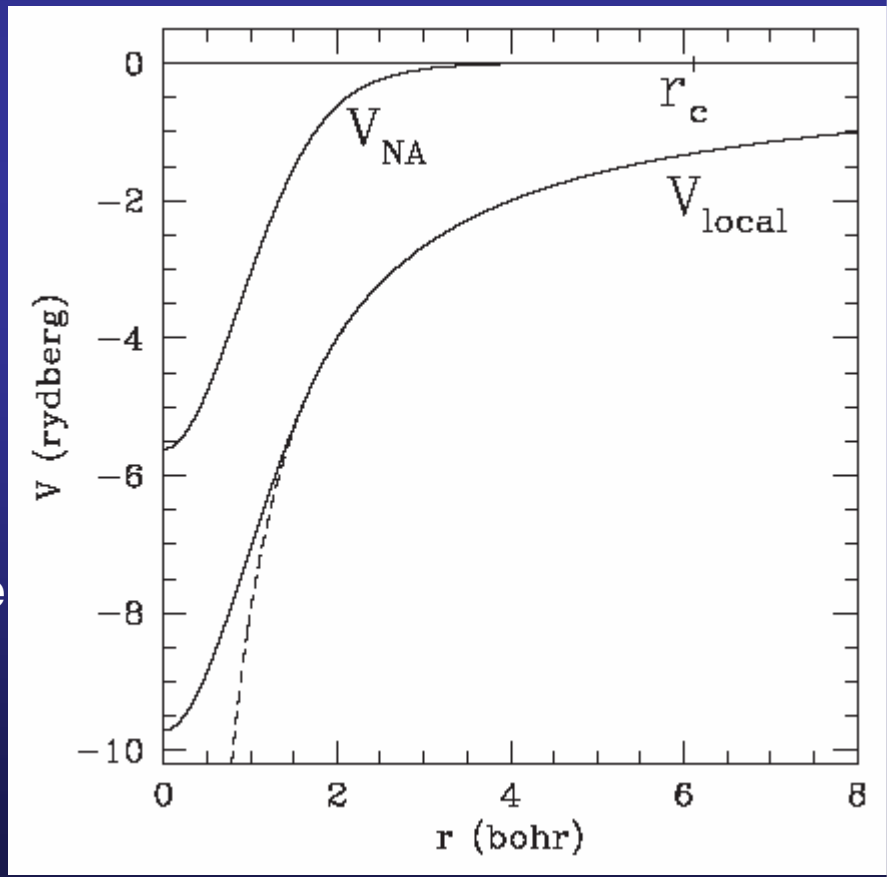


$$V_I^{NA}(\vec{r}) = 0$$

Potential outside the sphere vanishes

(Gauss theorem ⇒ generated by the total charge inside the sphere = 0 if neutral atom)

Vanishes exactly ar r_c



The hamiltonian computed in SIESTA, combination of two and three center matrix elements

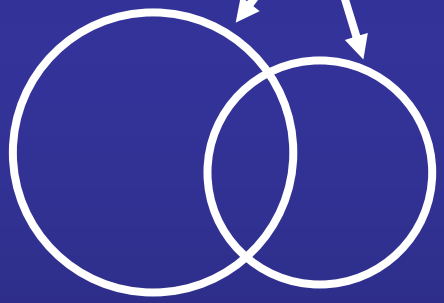
Two center integrals

Three center integrals

$$\hat{H} = \hat{T} + \hat{V}^{NL} + V^{NA}(\vec{r}) + \delta V^{H}(\vec{r}) + V^{xc}(\vec{r})$$

$\langle \phi_\nu | \nabla^2 | \phi_\mu \rangle$

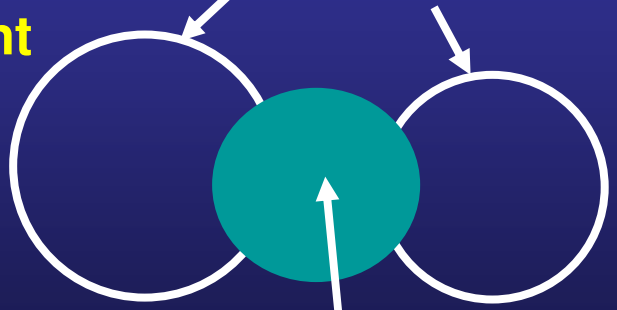
Basis orbitals



Non self-consistent

$\langle \phi_\nu | \chi^{KB}_{lmn} \rangle \langle \chi^{KB}_{lmn} | \phi_\mu \rangle$

Basis orbitals



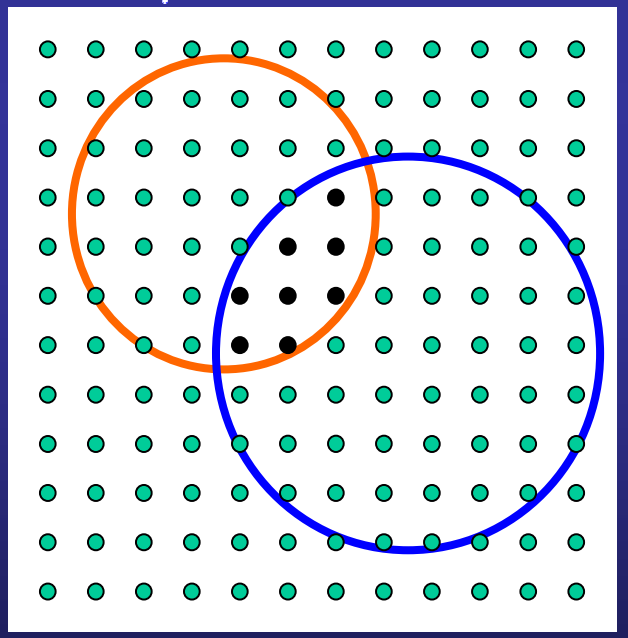
KB pseudopotential projector

Computed in reciprocal space and tabulated

$\langle \phi_\nu | V(\vec{r}) | \phi_\mu \rangle$

$\phi_\mu(\vec{r})$

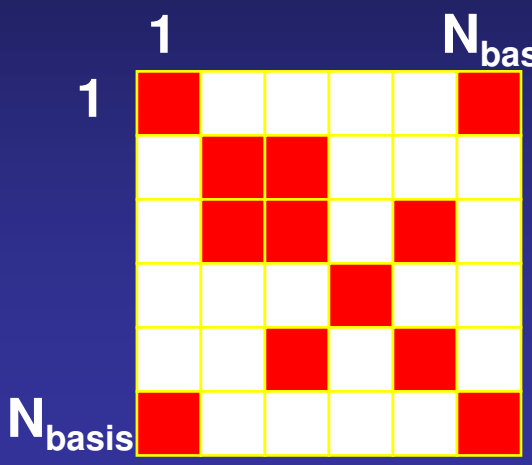
Self-consistent

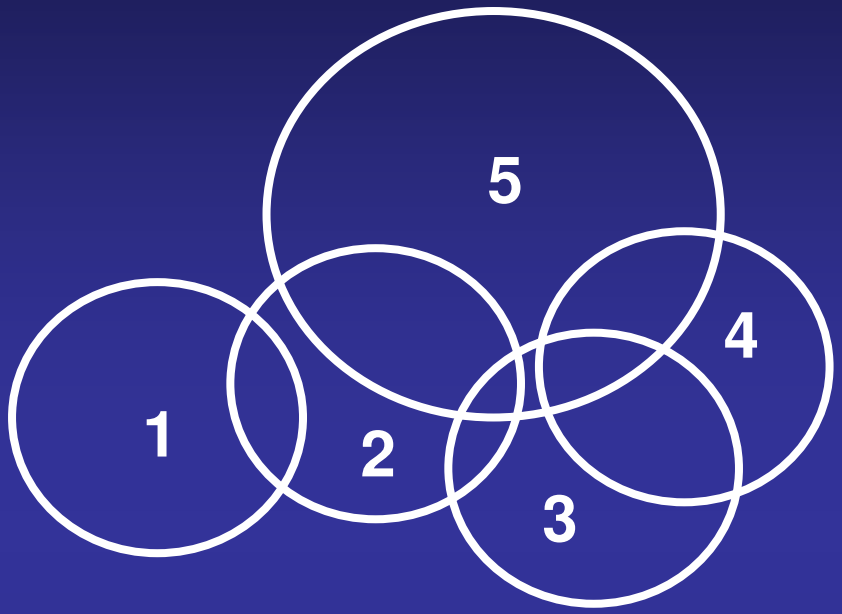


$\phi_\nu(\vec{r})$

Three-dimensional real space grid

Order-N methods rely heavily on the sparsity of the Hamiltonian and overlap matrices





1 with 1 and 2

2 with 1,2,3, and 5

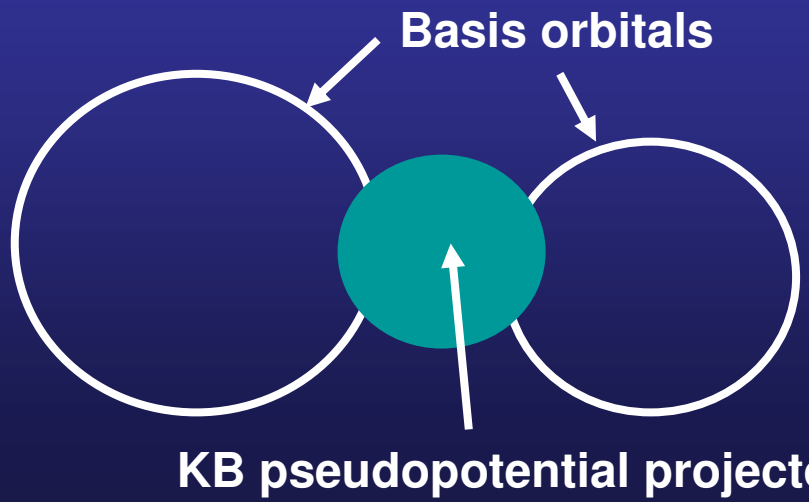
3 with 2,3,4, and 5

4 with 3,4 and 5

5 with 2,3,4, and 5

Sparse ≡ many entrances of the matrix are zero

Non-overlap interactions



$S_{\mu\nu}$ and $H_{\mu\nu}$ are sparse

$\rho_{\mu\nu}$ is not strictly sparse but only a sparse subset is needed

Two center integrals are calculated in Fourier space

Two center integrals (i. e. the overlap) have a form like

$$S_{12}(\vec{R}) \equiv \langle \psi_1 \mid \psi_2 \rangle = \int_{all\ \ space} d\vec{r}\ \psi_1^*(\vec{r})\,\psi_2(\vec{r}+\vec{R})$$

ψ_1, ψ_2 might be atomic orbitals, KB projectors or other functions centered on atoms

$S_{12}(\vec{R})$ can be seen as a convolution: in 1D $f * g \equiv \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} g(y)\, f(x-y)\, dy$

Arfken, Mathematical Methods for Physicist, Ch 15.5

Take the Fourier transform of one of the functions

$$\psi(\vec{k}) = \frac{1}{(2\pi)^{3/2}} \int \psi(\vec{r})\, e^{-i\vec{k}\cdot\vec{r}} d\vec{r}$$

The Fourier transform of a convolution in real space is a product in reciprocal space

$$S_{12}(\vec{R}) = \int d\vec{k}\ \psi_1^*(\vec{k})\psi_2(\vec{k})e^{-i\vec{k}\cdot\vec{R}}$$

Two center integrals are calculated in Fourier space

$$S_{12}(\vec{R}) = \int d\vec{k}\ \psi_1^*(\vec{k})\psi_2(\vec{k})e^{-i\vec{k}\cdot\vec{R}}$$

For each pair of functions they are calculated and stored in a fine radial grid (2500 Ry) as a function of R_i, up to the maximum distance $R_{max} = r_1^c + r_2^c$

The value at arbitrary distances can be obtained by accurate cubic spline interpolation (once obtained, the fine grid does not suppose a penalty in execution time, since interpolation effort is independent of the number of grid points).

The density matrix, a basic ingredient of SIESTA

Expansion of the eigenvectors in a basis of localized atomic orbitals

$$\psi_i(\vec{r}) = \sum_\mu \phi_\mu(\vec{r})\, c_{\mu i}$$

where the coefficients $c_{\mu i} = \langle \tilde{\phi}_\mu \,|\, \psi_i \rangle$, and $\tilde{\phi}_\mu$ are the dual orbital of ϕ_μ : $\langle \tilde{\phi}_\mu \,|\, \phi_\nu \rangle = \delta_{\mu\nu}$

The electron density is given by

$$\rho(\vec{r}) = \sum_i n_i \,|\, \psi_i(\vec{r}) \,|^2$$

Occupation of state ψ_i

Inserting the expansion into the definition of the density

$$\rho(\vec{r}) = \sum_{\mu\nu} \rho_{\mu\nu} \phi^*_\nu(\vec{r})\, \phi_\mu(\vec{r})$$

where, with $c_{i\nu} \equiv c^*_{\nu i}$, the **density matrix** is defined

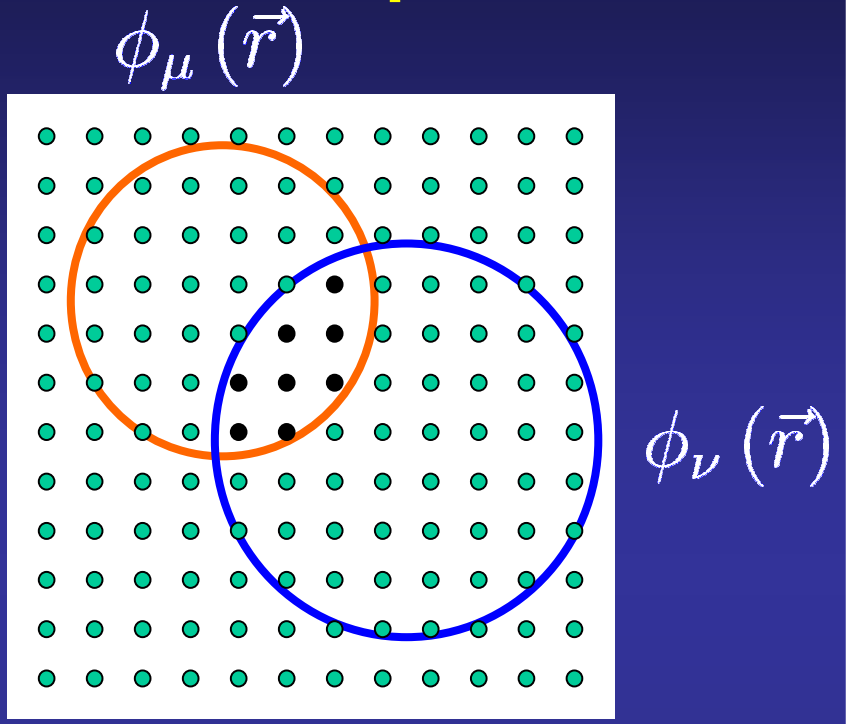
$$\rho_{\mu\nu} = \sum_i c_{\mu i} n_i c_{i\nu}$$

Control convergence SCF

Restart calculations

Three dimensional grid to compute Hartree, exchange correlation and neutral atom potentials

$$\rho(\vec{r}) = \sum_{\mu\nu} \rho_{\mu\nu} \phi_\nu^*(\vec{r}) \phi_\mu(\vec{r})$$



Find all the atomic orbitals that do not vanish at a given grid point

(in practice, interpolate the radial part from numerical tables)

Once the density is known, we compute the potentials

EVERYTHING O(N)

$$\rho(\vec{r}) \rightarrow V^{xc}(\vec{r})$$

$$\delta\rho(\vec{r}) = \rho(\vec{r}) - \rho_{atoms}(\vec{r})$$

$$\delta\rho(\vec{r}) \xrightarrow{FFT} \delta V^H(\vec{r})$$

The Poisson equation is solved in the real space grid by FFTs

$$\nabla^2 V^H(\vec{r}) = -4\pi\rho(\vec{r})$$

Since the unit cell is periodic (naturally or artifically), we can expand the density in a Fourier series

$$\rho(\vec{r}) = \sum_{\vec{G}} \rho(\vec{G}) e^{i\vec{G}\cdot\vec{r}} \Rightarrow V^H(\vec{r}) = \sum_{\vec{G}} V^H(\vec{G}) e^{i\vec{G}\cdot\vec{r}}$$

In reciprocal space, the differential Poisson equation is nothing else than a division

$$V^H(\vec{G}) = -4\pi \frac{\rho(\vec{G})}{|\vec{G}|^2}$$

Once the coefficients of the potential are known in reciprocal space, Fourier transform back to real space

$$\rho(\vec{r}) \xrightarrow{FFT} \rho(\vec{G}) \longrightarrow V^H(\vec{G}) \xrightarrow{IFFT} V^H(\vec{r})$$

FFT scales as $N \log(N)$

However is cost is negligible and has no influence on the overall scaling properties.

Multigrid techniques (by Oswaldo Diéguez) coming soon

Generalized Gradient Approximation, the derivative of the charge computed numerically

$$V_{xc}^{GGA}(\vec{r}) = \frac{\delta E^{GGA}\left[\rho(\vec{r}\,'), |\nabla\rho(\vec{r}\,')|\right]}{\delta\rho(\vec{r})}$$

$$V_{xc}^{GGA}\left(\rho(\vec{r}), |\nabla\rho(\vec{r})|, \nabla^2\rho(\vec{r}), \nabla\rho(\vec{r})\cdot\nabla|\nabla\rho(\vec{r})|\right)$$

Density gradient need not be provided, since they are calculated numerically using the density at the grid points

$$\frac{\partial\rho}{\partial x} = \frac{\rho_{i+1}-\rho_{i-1}}{x_{i+1}-x_{i-1}} \Rightarrow E_{xc}^{GGA}(\rho_1, \rho_2, \ldots)$$

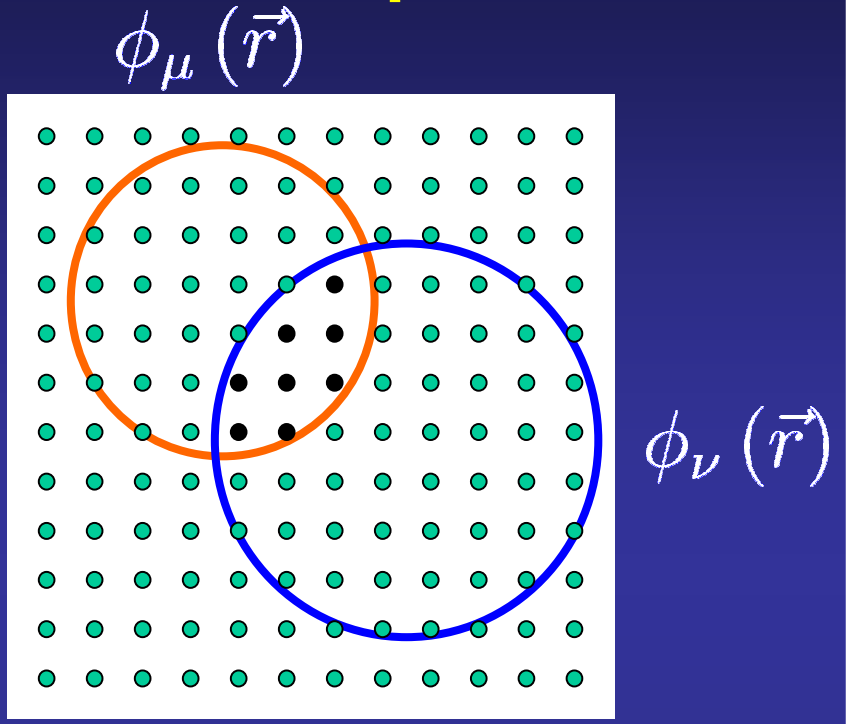
A finer grid is required for GGA

$$V_{xc}^{GGA}(\vec{r}_i) \equiv \frac{\partial E_{xc}^{GGA}}{\partial\rho_i}$$

L. C. Balbás et al., Phys. Rev. B 64, 165110 (2001)

Three dimensional grid to compute Hartree, exchange correlation and neutral atom potentials

$$\rho\left(\vec{r}\right) = \sum_{\mu\nu} \rho_{\mu\nu} \phi_{\nu}^{*}\left(\vec{r}\right) \phi_{\mu}\left(\vec{r}\right)$$



Finally, we add together all the grid contributions and perform the integral

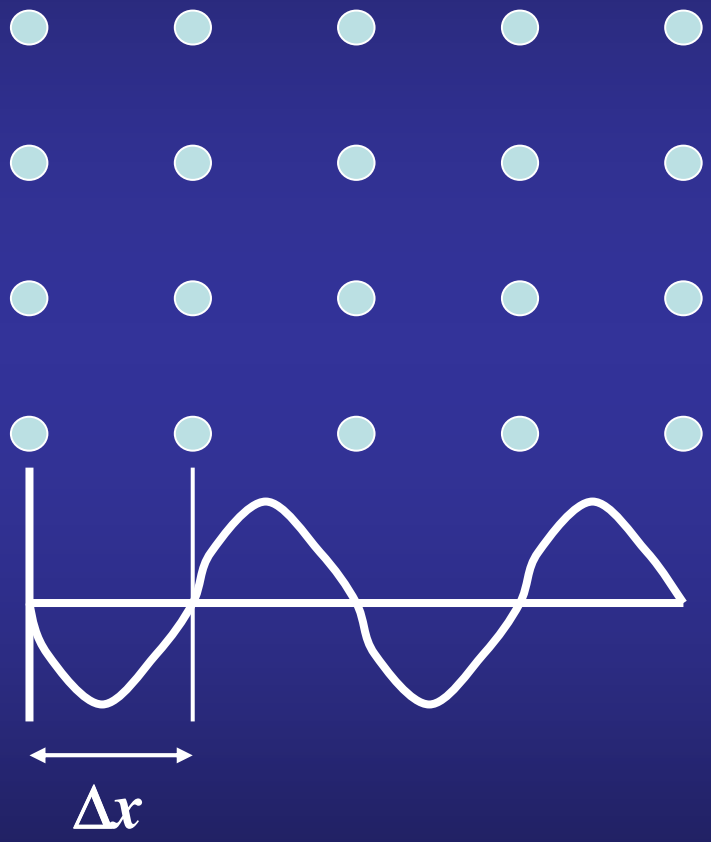
$$V\left(\vec{r}\right) = V^{NA}\left(\vec{r}\right) + \delta V^{H}\left(\vec{r}\right) + V^{xc}\left(\vec{r}\right)$$

$$\int d\vec{r}\ \phi_{\nu}^{*}\left(\vec{r}\right) V\left(\vec{r}\right) \phi_{\nu}\left(\vec{r}\right) \approx \sum_{i} \phi_{\nu}^{*}\left(\vec{r}\right) V\left(\vec{r}\right) \phi_{\nu}\left(\vec{r}\right) \Delta\vec{r}$$

Volume per grid point

Fineness of the grid controlled by a single parameter, the "MeshCutoff"

E_{cut} : maximum kinetic energy of the plane waves that can be represented in the grid without aliasing



$$\Delta x \Longrightarrow k_c = \frac{\pi}{\Delta x} \Longrightarrow E_c = \frac{\hbar^2 k_c^2}{2m_e}$$

In the grid, we represent the density ⇒ grid cutoff not directly comparable with the plane wave cutoff to represent wave functions

(Strictly speaking, the density requires a value four times larger)

What are the main approximations?

Born-Oppenhaimer

Decouple the movement of the electrons and the nuclei.

Density Functional Theory (talk by Notker Roesch)

Treatment of the electron — electron interactions.

Pseudopotentials

Treatment of the (nuclei + core) — valence.

Basis set

To expand the eigenstates of the hamiltonian.

Numerical evaluation of matrix elements

Efficient and self-consistent computations of H and S.

Solve the secular equation

Supercells

To deal with periodic systems

Once the hamiltonian and the overlap matrices are build, we have to solve the Schrodinger equation

$$\begin{bmatrix} H \end{bmatrix}\begin{bmatrix} C \end{bmatrix} = E_{n\vec{k}}\begin{bmatrix} S \end{bmatrix}\begin{bmatrix} C \end{bmatrix}$$

Order-N

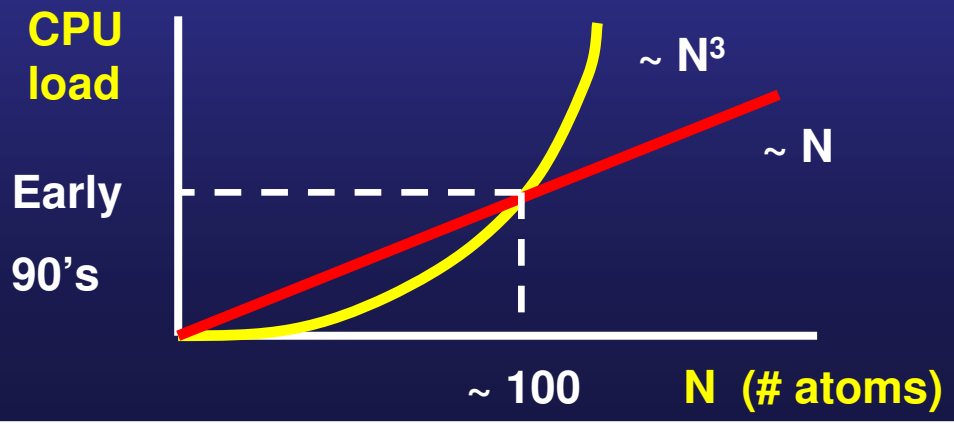
Minimization of an energy functional

Not valid for metals or “dirty” gap systems

Order-N^3

Standard diagonalization techniques

Both eigenvectors and eigenvalues available



If diagonalization, the generalized eigenvalue problem is solved using standard mathematical libraries

$$\underset{N\times N}{\left[\,H\,\right]}\underset{N\times 1}{\left[\,C\,\right]} = E_{n\vec{k}}\underset{N\times N}{\left[\,S\,\right]}\underset{N\times 1}{\left[\,C\,\right]}$$

Serial:

BLAS

LAPACK

Parallel:

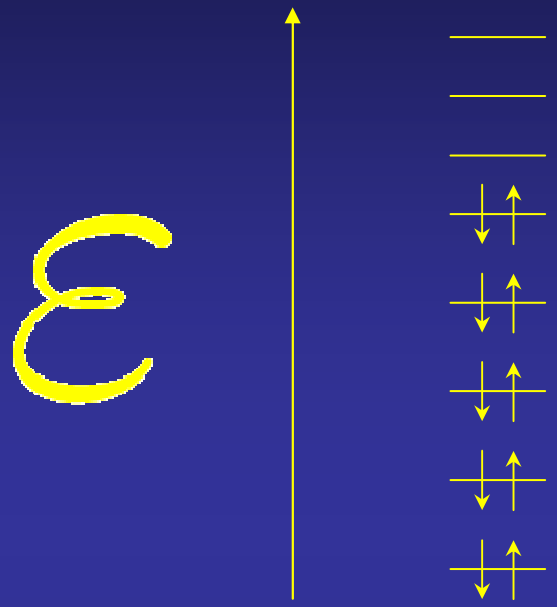
BLACS

SCALAPACK

Freely available in http://www.netlib.org

Most machine vendors have their own implementations available for their own platforms (acml, mkl,…).

The one-particle eigenstates are filled following the "Aufbau" principle: from lower to higher energies



$$n^{\sigma}(\vec{r}) = \sum_{i} f_i^{\sigma} \left|\psi_i^{\sigma}(\vec{r})\right|^2$$

Occupation numbers

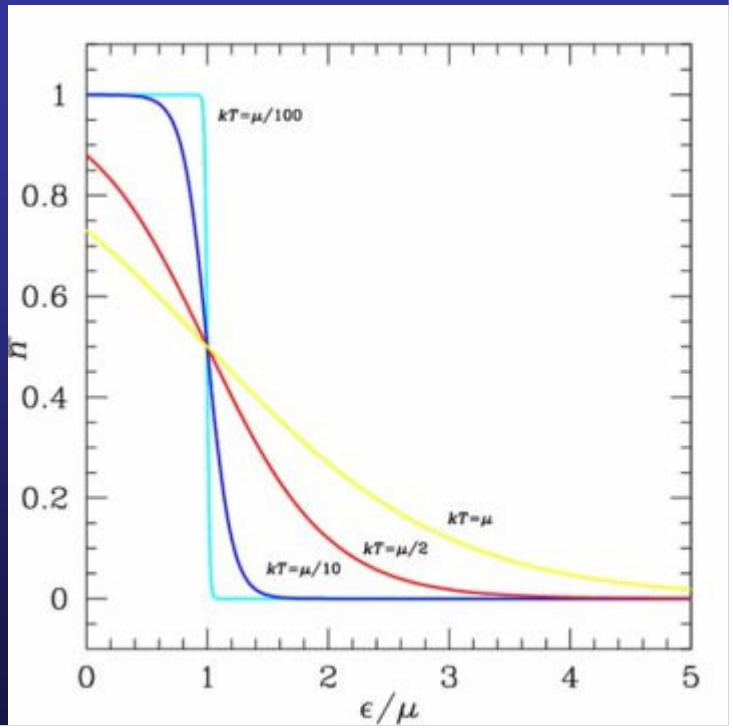
The ground state has one (or two if spin independent) in each of the orbitals with the lowest eigenvalues

A smearing of the electronic occupation might be done:

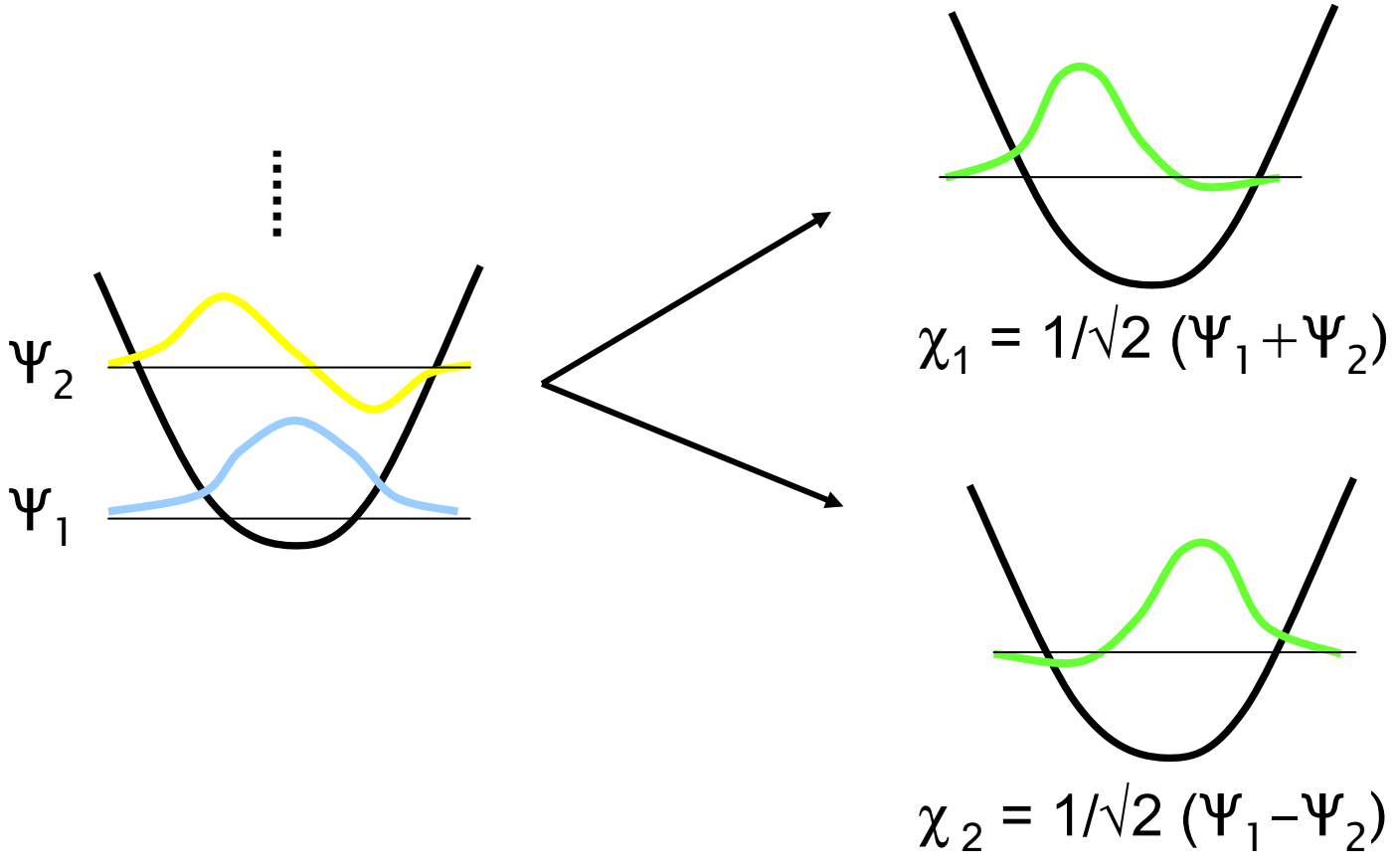
Fermi-Dirac (OccupationFunction FD)

ElectronicTemperature

Methfessel Paxton (OccupationFunction MP)



Locality of Wave Functions



$$\left|\chi^{occ}\right\rangle = \mathbf{U}\left|\psi^{occ}\right\rangle$$

Wannier functions (crystals)

Localized Molecular Orbitals (molecules)

Locality of Wave Functions

Energy:

$$E = \langle \psi_1 | H | \psi_1 \rangle + \langle \psi_2 | H | \psi_2 \rangle = Tr_{occ}(H)$$

Unitary Transformation: $\{|\psi_i\rangle\} \rightarrow \{|\chi_i\rangle\}$

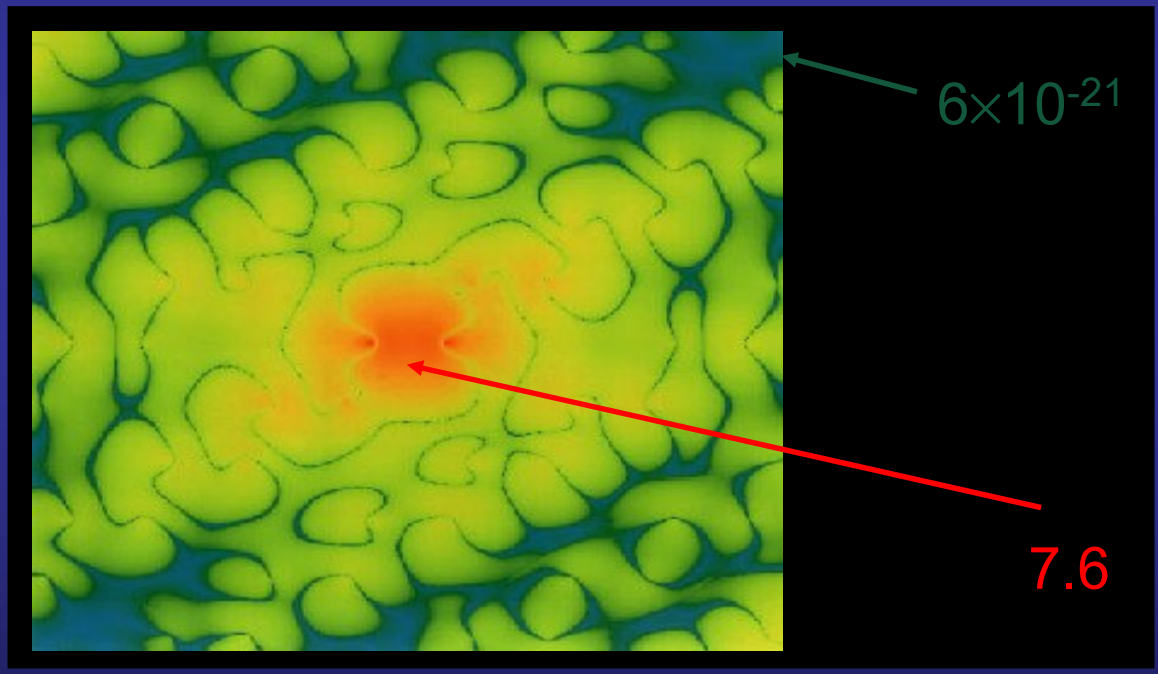
$$E = Tr_{occ}(H) = \langle \chi_1 | H | \chi_1 \rangle + \langle \chi_2 | H | \chi_2 \rangle$$

We do NOT need eigenstates!

We can compute energy with Loc. Wavefuncs.

Locality of Wave Functions

Exponential localization (insulators):

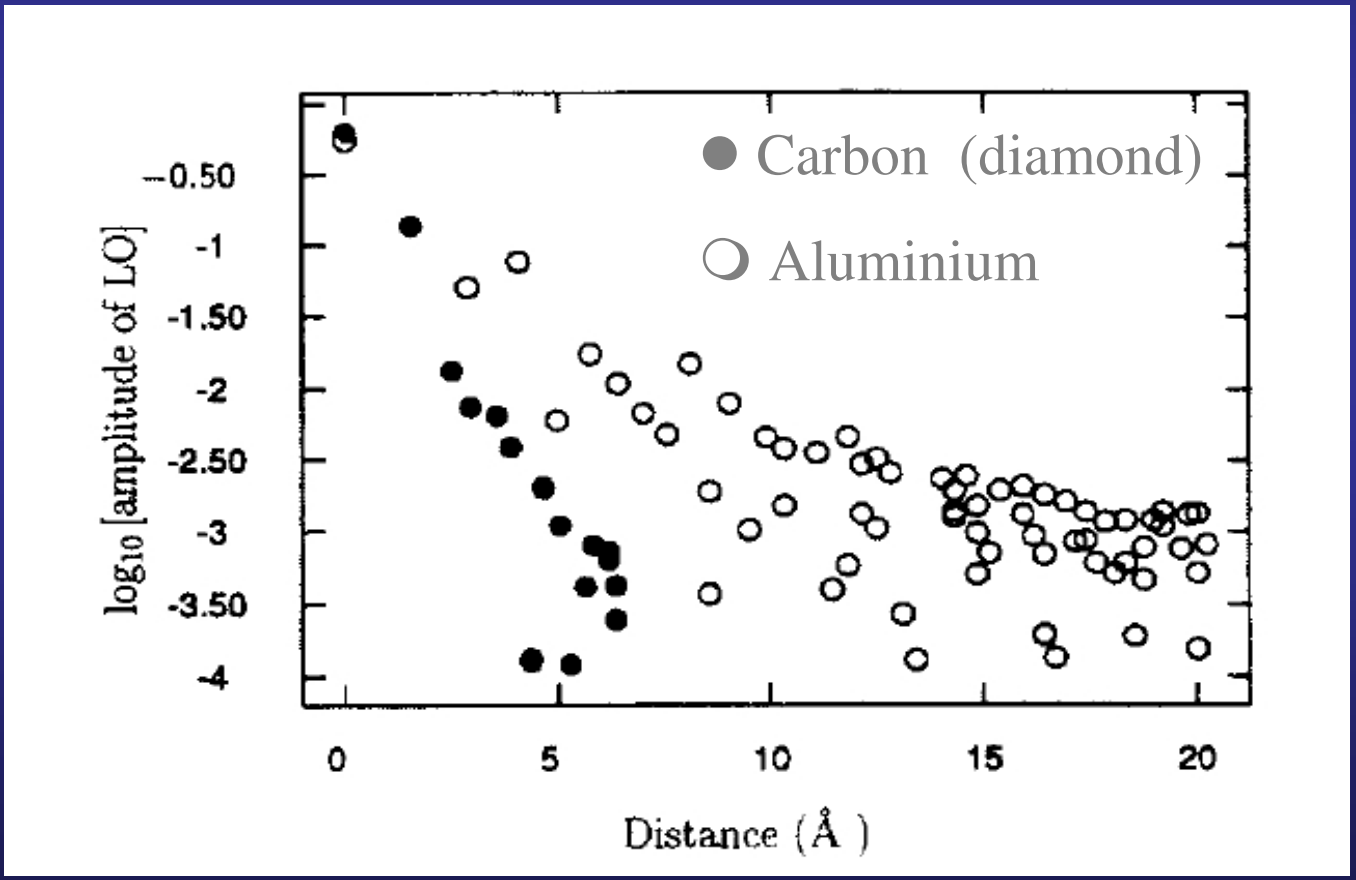


Wannier function in Carbon (diamond)

Drabold et al.

Locality of Wave Functions

Insulators vs Metals:



Goedecker & Teter, PRB 51, 9455 (1995)

Order-N functionals

Kim, Mauri & Galli, PRB 52, 1640 (1995)

Idea: derive a functional that, when minimized, would lead to the correct ground state energy, but with the constraints would not need to be explicitly included

Constraints: orthonormalization of the one-electron wave function.

no computation of the inverse of the overlap matrix

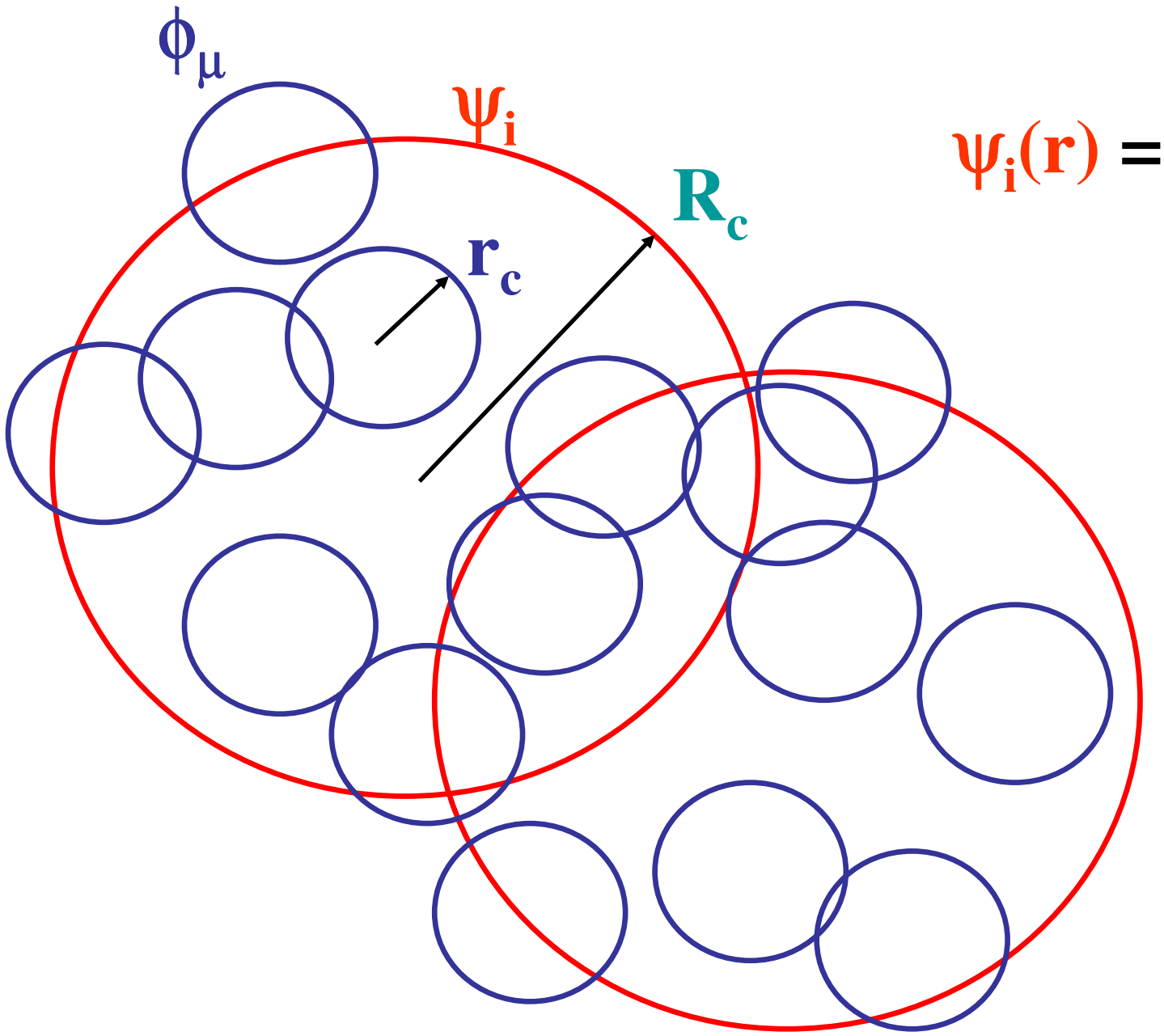
Functional of Ordejon-Mauri

$E_{OM} = \mathrm{Tr}_{occ}[(2I - S)H]$ # states = # electron pairs

Functional of Kim-Mauri-Galli

$E_{KMG} = \mathrm{Tr}^{+}_{occ}[(2I - S)(H - \eta S)]$ # states > # electron pairs

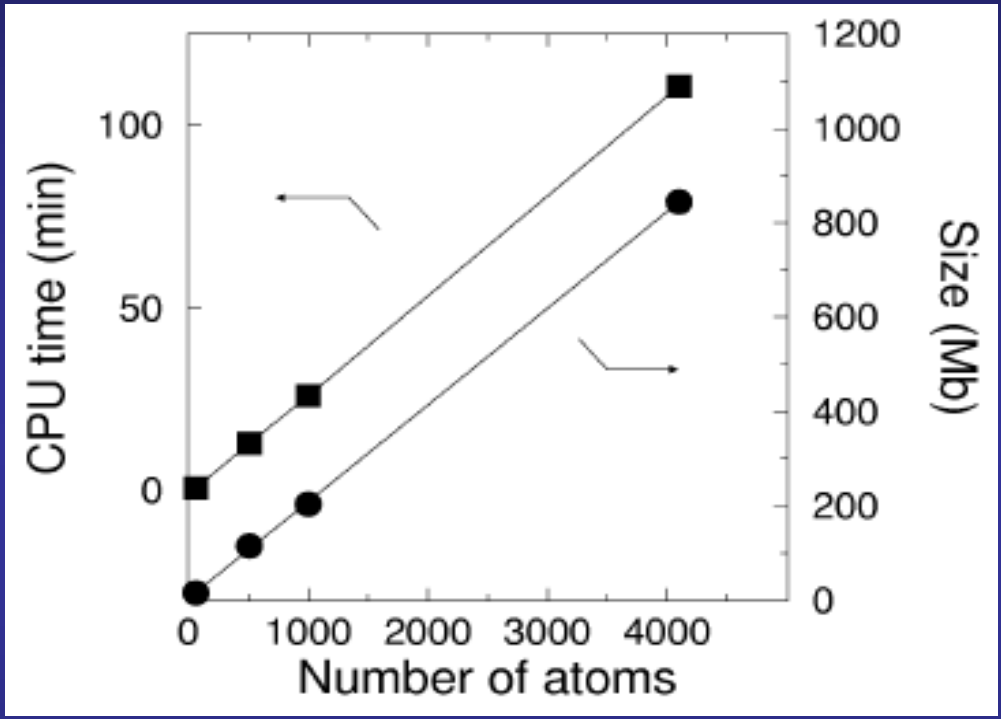
Minimization is done with respect a set of specially truncated wave functions, allowed to be non-zero only in a particular region of space

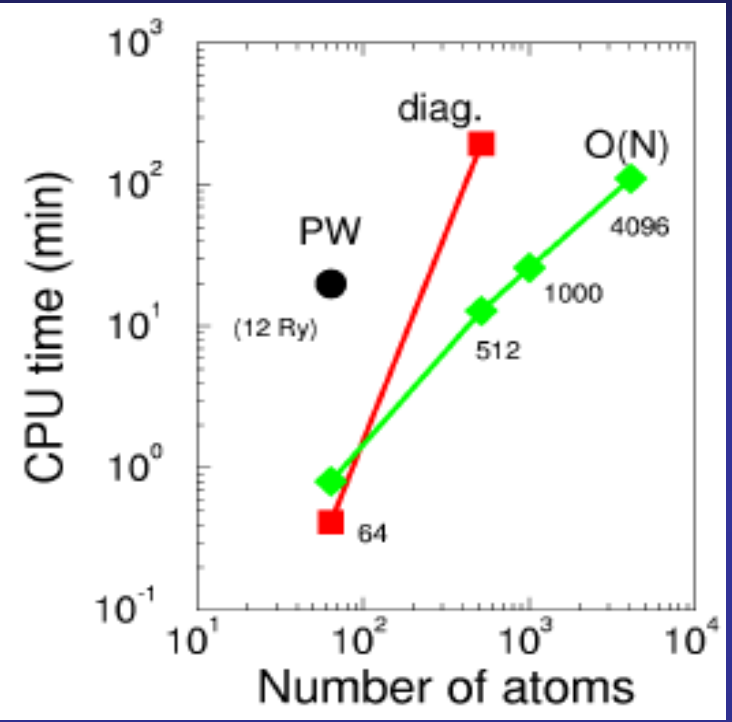


$$\psi_i(\mathbf{r}) = \Sigma_\mu \, c_{i\mu} \, \phi_\mu(\mathbf{r})$$

Actual linear scaling

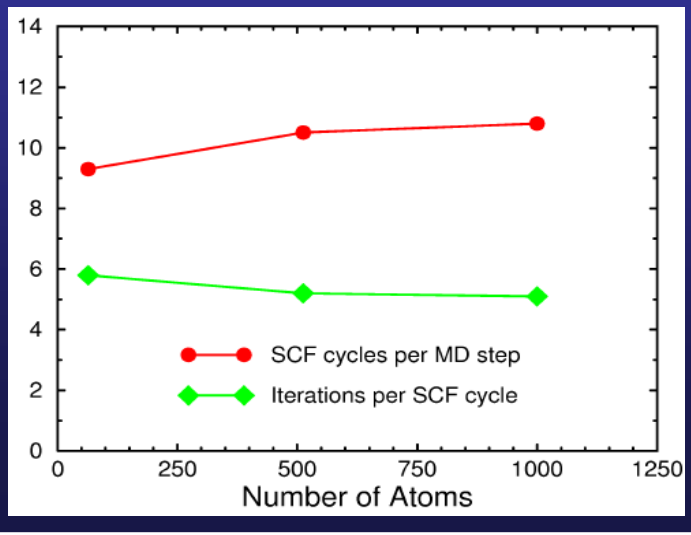
c-Si supercells, single-ζ



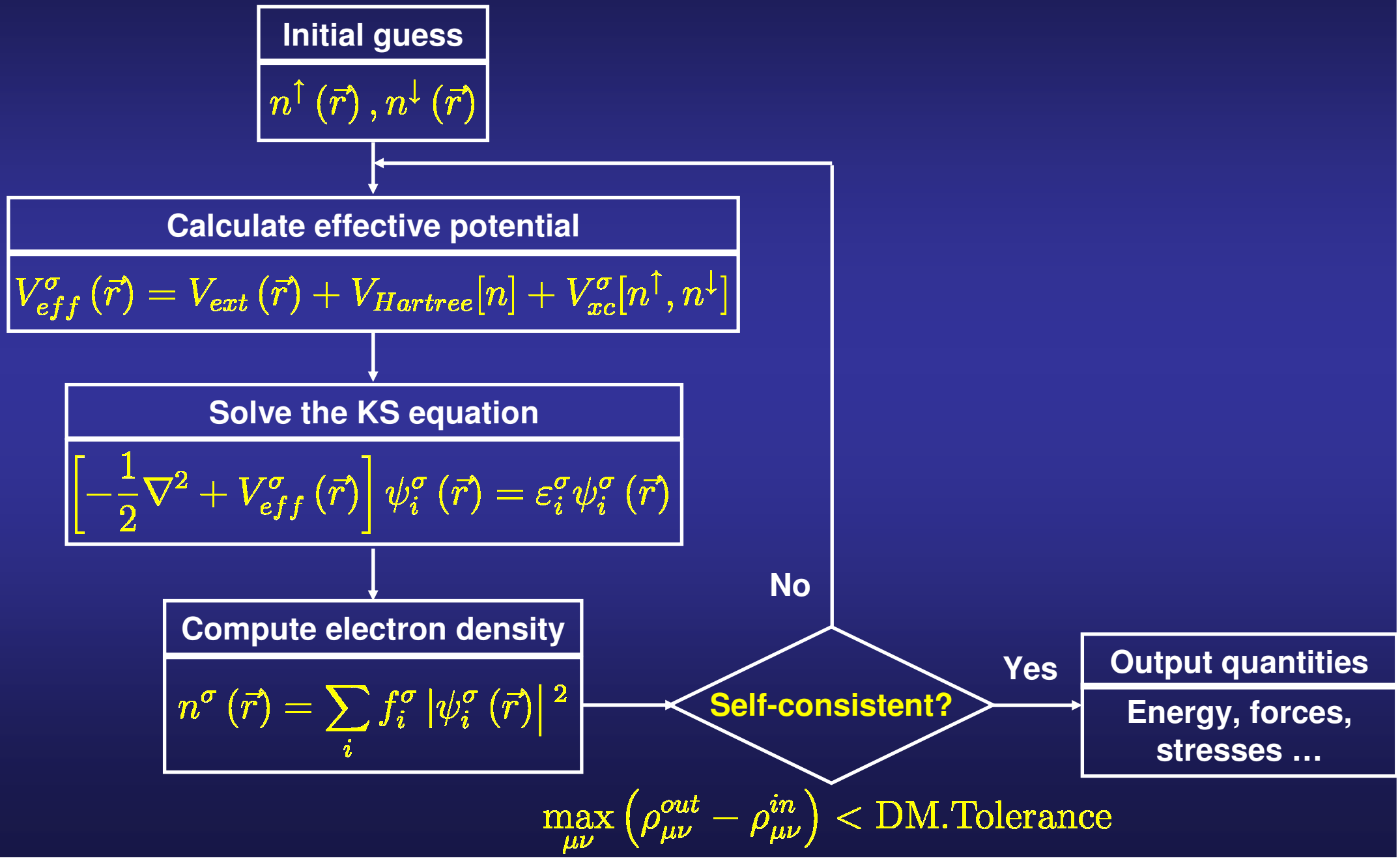


Single Pentium III 800 MHz. 1 Gb RAM

132.000 atoms in 64 nodes



The Kohn-Sham equations must be solved self-consistently
The potential (input) depends on the density (output)



The Kohn-Sham total energy can be written as a sum of the band structure (BS) energy + 'double-count' corrections

$$E^{BS} = \sum_i n_i \langle \psi_i \mid \hat{H} \mid \psi_i \rangle = \sum_{\mu\nu} H_{\mu\nu}\rho_{\nu\mu} = Tr\left(H\rho\right)$$

After SCF

Eigenvectors of the Hamiltonian

$$E^{KS} = \sum_{\mu\nu} H_{\mu\nu}\rho_{\nu\mu} - \underbrace{\frac{1}{2}\int V^H\left(\vec{r}\right)\rho\left(\vec{r}\right)d\vec{r} + \int\left[\varepsilon^{xc}\left(\vec{r}\right) - V^{xc}\left(\vec{r}\right)\right]\rho\left(\vec{r}\right)d\vec{r} + \sum_{IJ}\frac{Z_I Z_J}{R_{IJ}}}$$

Functionals of the electron density and atomic positions

Kohn-Sham energy in SIESTA

$$E^{KS} = \sum_{\mu\nu} T_{\mu\nu}\rho_{\nu\mu}$$ **Ekin**

$$+ \sum_{\mu\nu} V^{KB}_{\mu\nu}\rho_{\nu\mu}$$ **Enl**

$$+ \frac{1}{2}\sum_{IJ} U^{NA}_{IJ}(R_{IJ})$$
$$+ \sum_{I<J} \delta U^{local}_{IJ}(R_{IJ})$$ } **Ena**

$$- \sum_{I} U^{local}_{I}$$ **Eions**

$$+ \int V^{NA}(\vec{r})\,\delta\rho(\vec{r})\,d\vec{r}$$ **DEna**

$$+ \frac{1}{2}\int \delta V_H(\vec{r})\delta\rho(\vec{r})d\vec{r}$$ **DUscf**

$$+ \int \varepsilon^{xc}(\vec{r})\,\rho(\vec{r})\,d\vec{r}$$ **Exc**

```
siesta: Program's energy decomposition (eV):
siesta: Eions   =       380.802124
siesta: Ena     =       114.848182
siesta: Ekin    =        81.633888
siesta: Enl     =        29.327240
siesta: DEna    =         4.386897
siesta: DUscf   =         0.250143
siesta: DUext   =         0.000000
siesta: Exc     =       -65.086299
siesta: eta*DQ  =         0.000000
siesta: Emadel  =         0.000000
siesta: Ekinion =         0.000000
siesta: Eharris =      -215.442072
siesta: Etot    =      -215.442072
siesta: FreeEng =      -215.442072
```

+ Sum extra terms if a net charge (Emadel), an external electric field (DUext), Order-N solver (eta*DQ) are used, or if the nuclei are moving (Ekinion)

Atomic forces and stresses obtained by direct diferentiation of the energy expression

$$\vec{F}_I = -\frac{\partial E^{KS}}{\partial \vec{R}_I}$$

$$\sigma_{\alpha\beta} = \frac{\partial E^{KS}}{\partial \epsilon_{\alpha\beta}}$$

$\epsilon_{\alpha\beta} \equiv \text{strain tensor}$

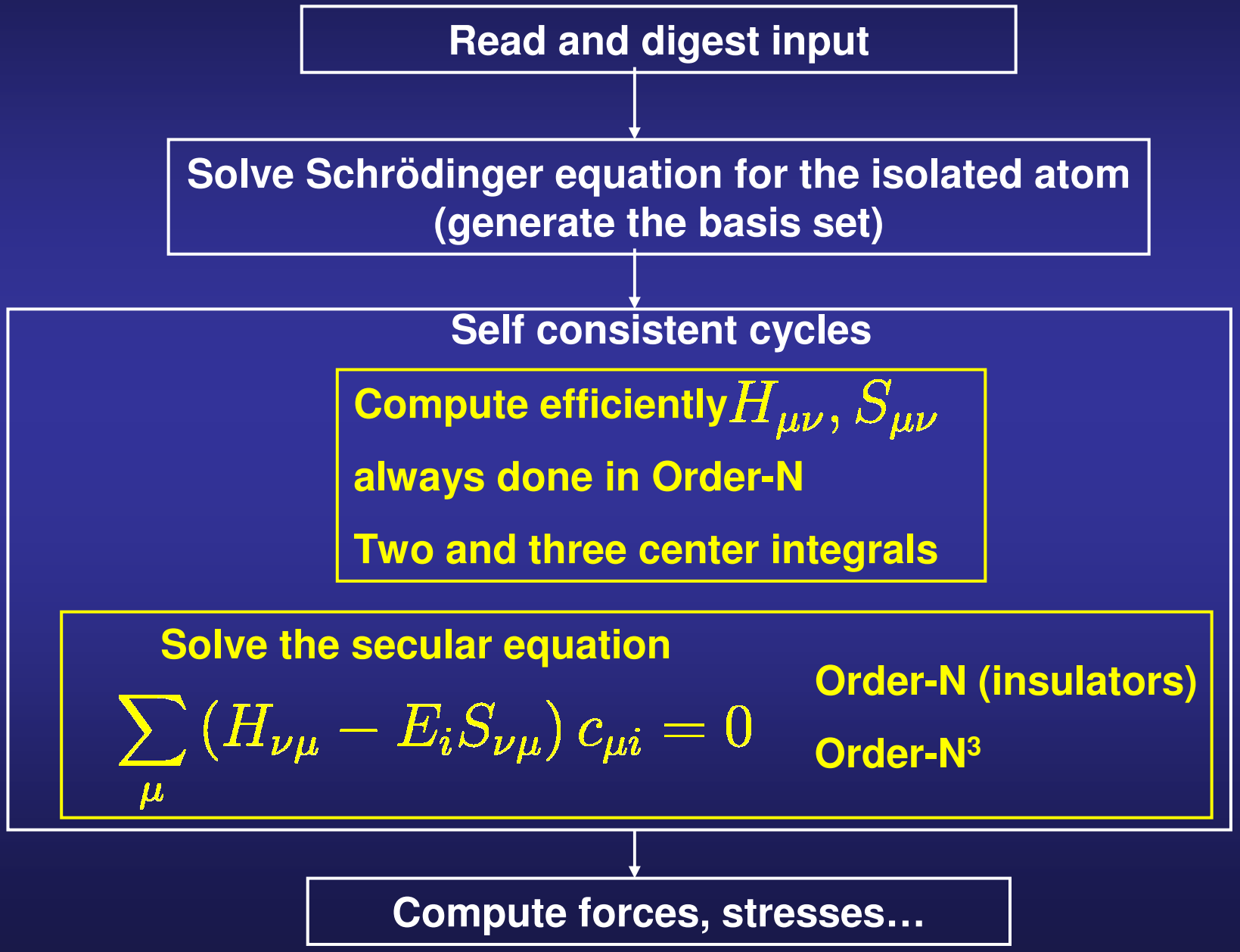
"One piece of energy $\Rightarrow$ one piece of force and stress"

Calculated as the **analytical derivatives** of the energy

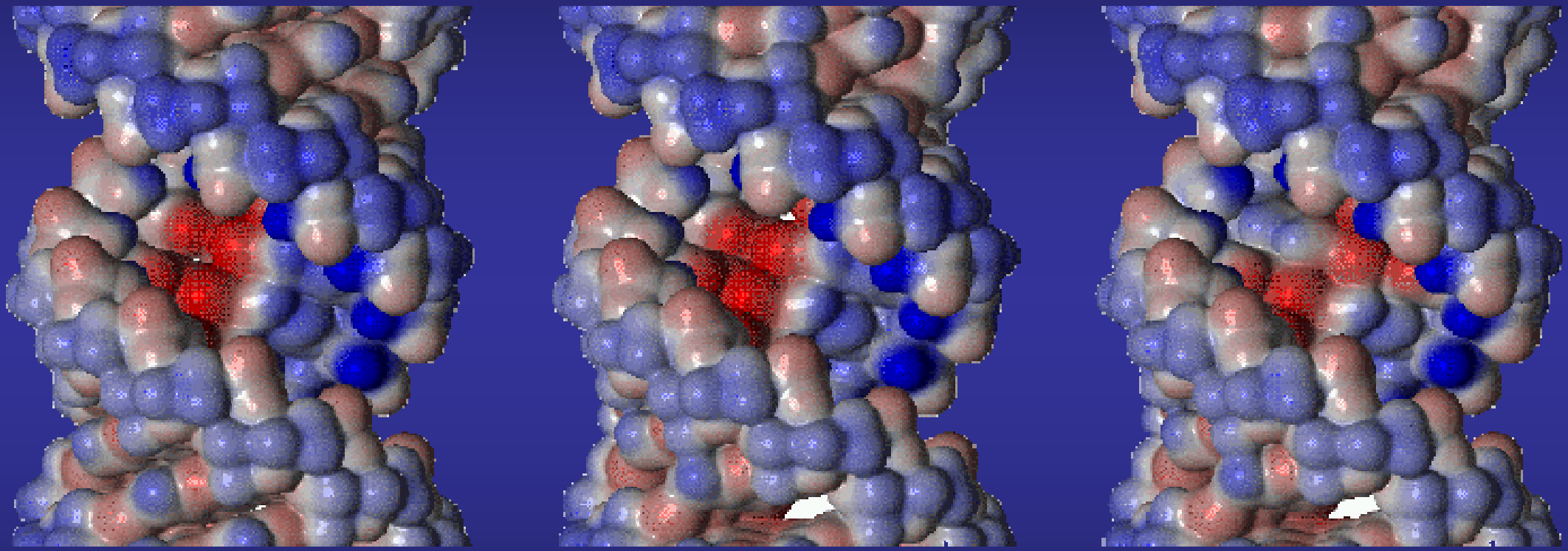
Pulay corrections, related with the dependency of the basis set on atomic positions, **automatically included**

Calculated **only** in the **last self-consistent step**

Recap: schematic flowchart of SIESTA



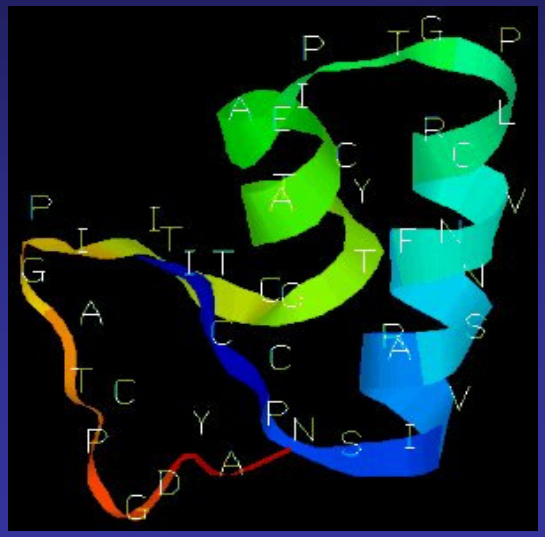
The efficiency of Siesta allows the treatment of systems with an unprecedent number of atoms in the simulation box

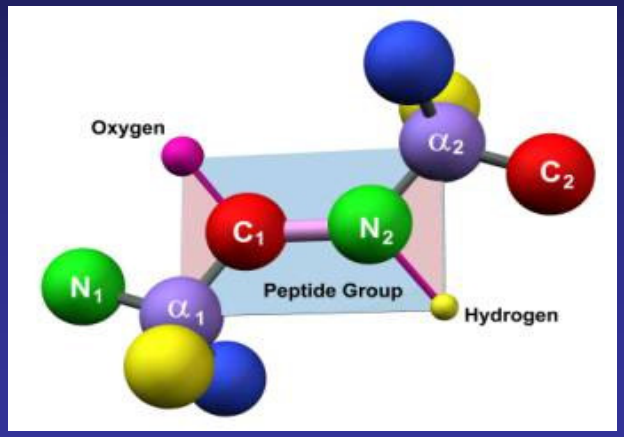


Electronic structure of the double helix of DNA

715 atoms in a work station Digital Alpha

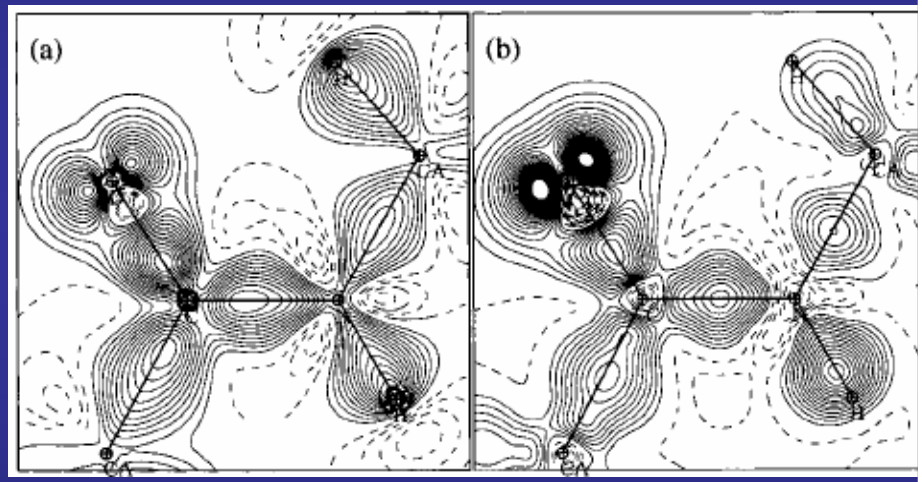
Deformation of the charge density in the peptidic bond of crambine





46 aminoacids; 642 atoms

Average of all the peptidic bonds



X-ray difraction

DFT (Siesta)

PERGAMON

Solid State Communications 116 (2000) 395–400

solid state communications

www.elsevier.com/locate/ssc

Electron density in the peptide bonds of crambin

M.V. Fernández-Serra[a,*], J. Junquera[a], C. Jelsch[b], C. Lecomte[b], E. Artacho[c]

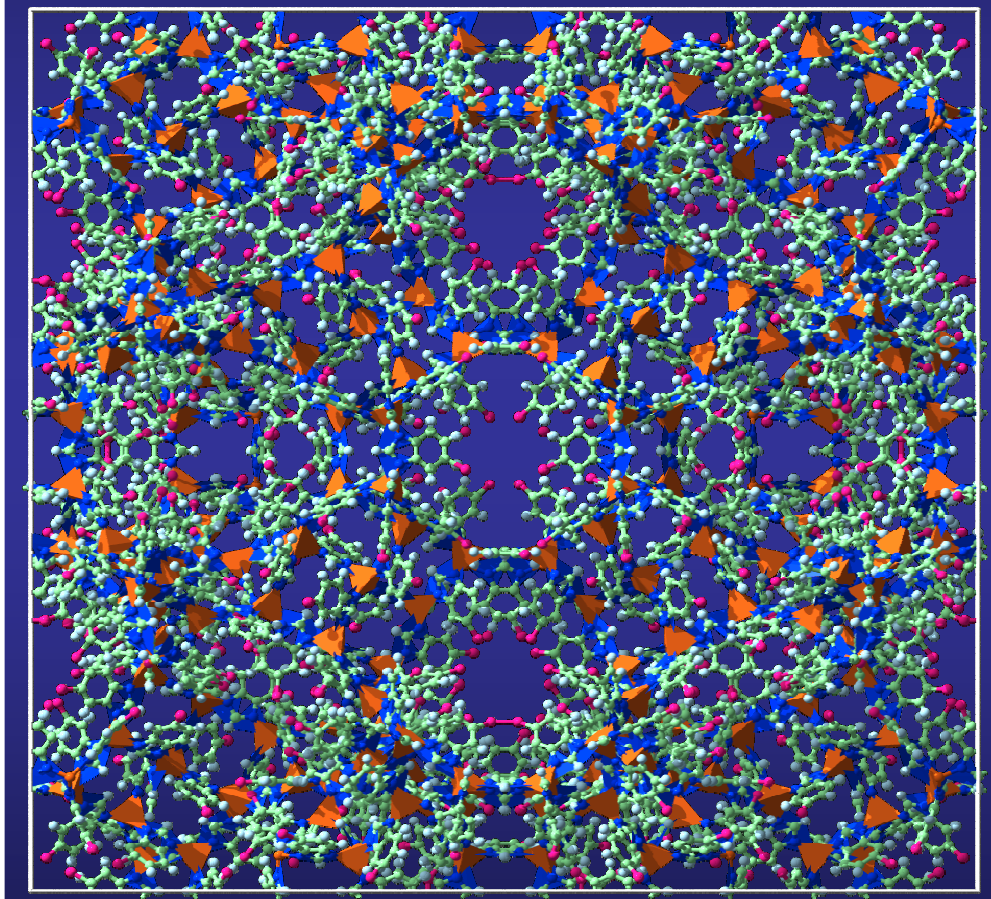
General results in good agreement with X-ray analysis

DZP basis set is accurate enough for the description

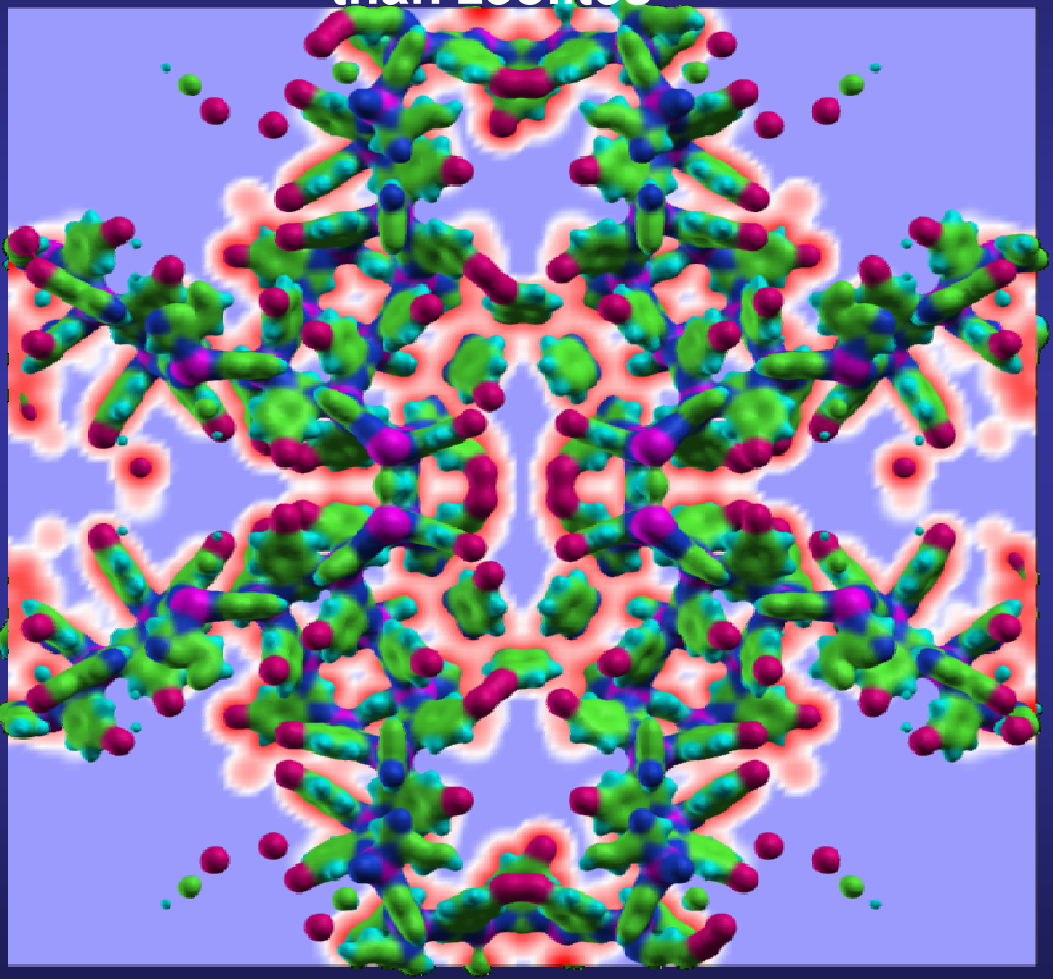
Large/complex materials: Metal Organic Frameworks

B.O. Cankurtaran, J.D. Gale & M.J. Ford, J. Phys. Cond. Mat., 20, 294208 (2008)

Large space of empty space inside for gas adsorption



Lighter and easy to functionalize than zeolites



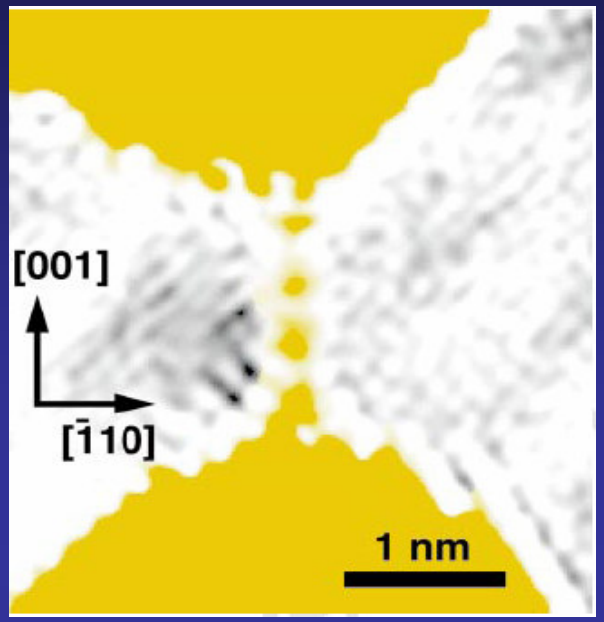
Largest calculation to date with SIESTA:
524,288 atoms -> 2,000,000 basis fns

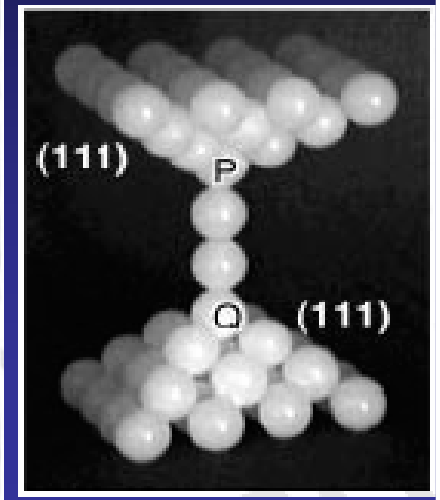
Structure of monoatomic gold wires

NATURE | VOL 395 | 22 OCTOBER 1998 | www.nature.com

Quantized conductance through individual rows of suspended gold atoms

Hideaki Ohnishi*, Yukihito Kondo* & Kunio Takayanagi*†

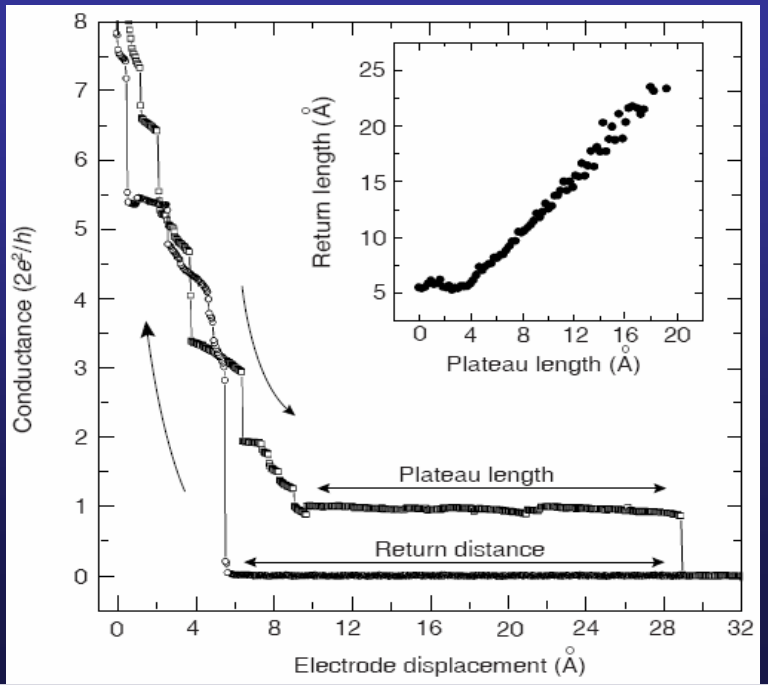




NATURE | VOL 395 | 22 OCTOBER 1998 | www.nature.com

Formation and manipulation of a metallic wire of single gold atoms

A. I. Yanson*, G. Rubio Bollinger†, H. E. van den Brom*, N. Agraït† & J. M. van Ruitenbeek*

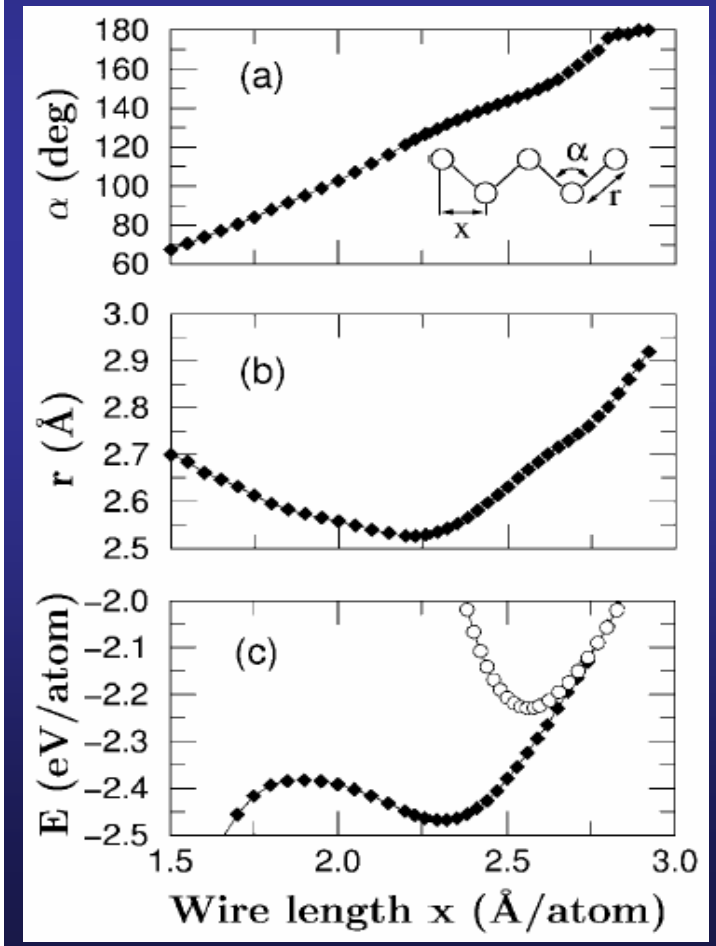


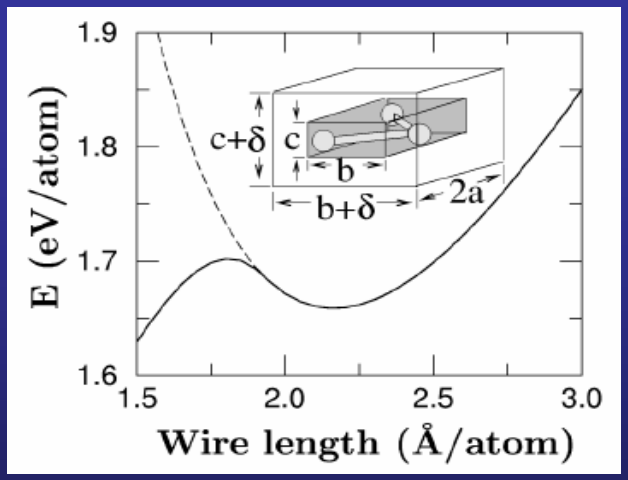
Structure of monoatomic gold wires

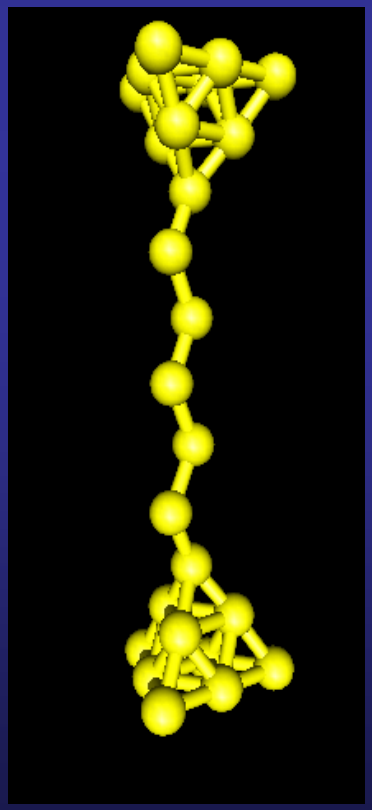
VOLUME 83, NUMBER 19 PHYSICAL REVIEW LETTERS 8 NOVEMBER 1999

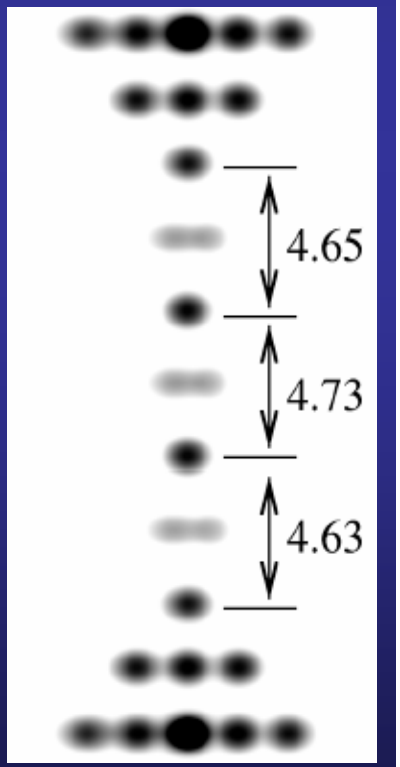
Stiff Monatomic Gold Wires with a Spinning Zigzag Geometry

Daniel Sánchez-Portal,[1] Emilio Artacho,[2] Javier Junquera,[2] Pablo Ordejón,[3] Alberto García,[4] and José M. Soler[2]









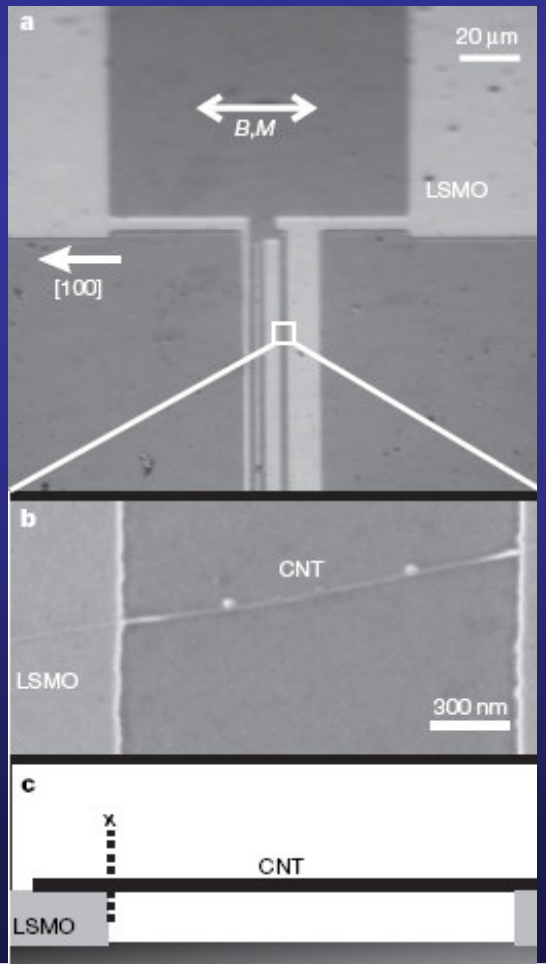
Nanospintronics:

Nanotubes to transport spin

nature Vol 445|25 January 2007|doi:10.1038/nature05507

Transformation of spin information into large electrical signals using carbon nanotubes

Luis E. Hueso[1]†, José M. Pruneda[2,3]†, Valeria Ferrari[4]†, Gavin Burnell[1]†, José P. Valdés-Herrera[1,5], Benjamin D. Simons[4], Peter B. Littlewood[4], Emilio Artacho[2], Albert Fert[6] & Neil D. Mathur[1]



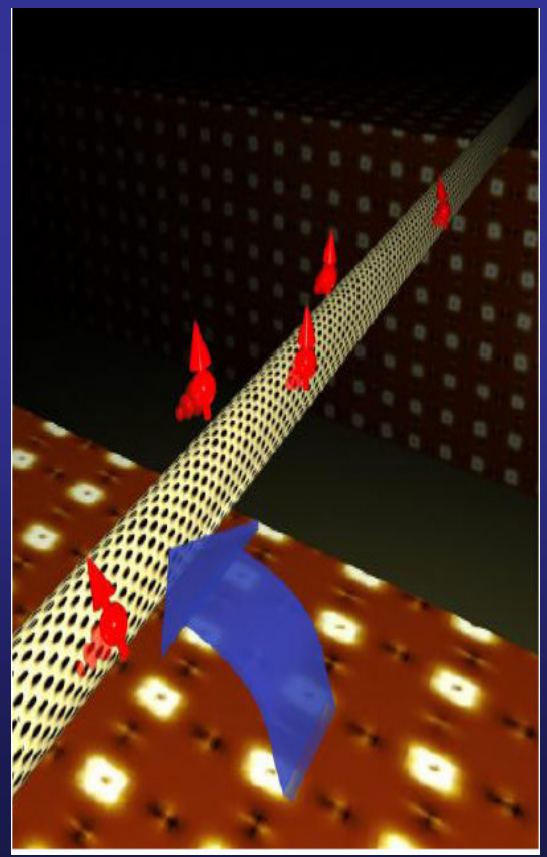
Inject spins in a nonmagnetic material

Transport this spin over distances of thousands of nm

Detect the spin at the other end of the device with a large enough electric signal

Magnetoresistance

$$MR = \frac{\Delta R}{R_P} \equiv \frac{R_{AP} - R_P}{R_P}$$



Nanospintronics:

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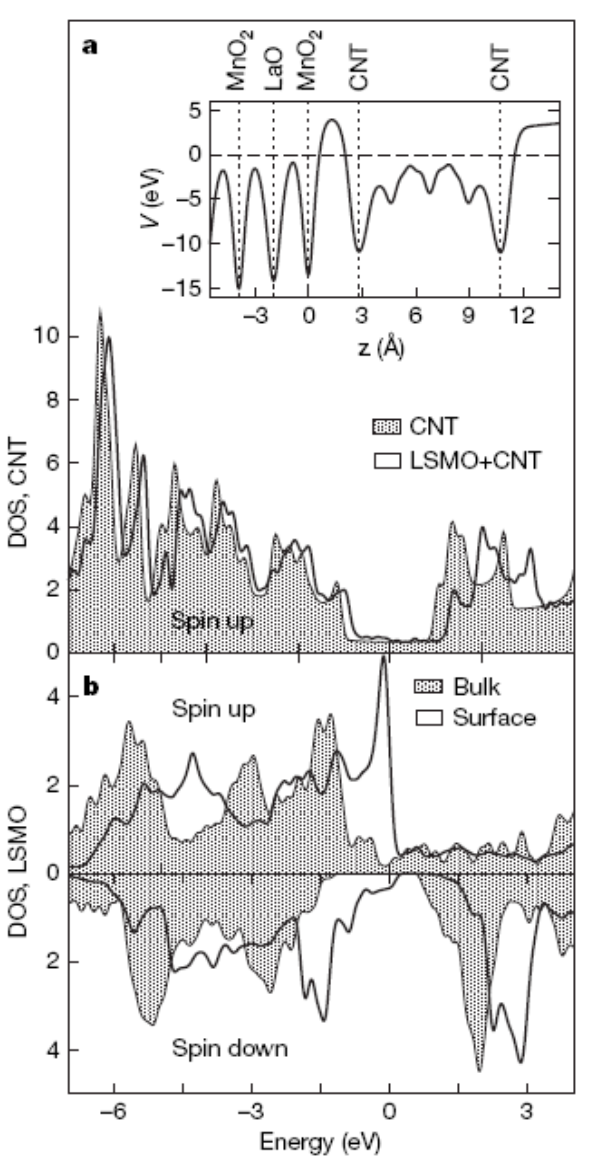

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Luis E. Hueso[1]†, José M. Pruneda[2,3]†, Valeria Ferrari[4]†, Gavin Burnell[1]†, José P. Valdés-Herrera[1,5], Benjamin D. Simons[4], Peter B. Littlewood[4], Emilio Artacho[2], Albert Fert[6] & Neil D. Mathur[1]

Energy barrier at the CNT/LSMO interface, but the ratio kinetic energy and the barrier width suggest a relatively high transmission probability

Carbon nanotube (CNT) not significantly altered when contacted by $La_{0.7}Sr_{0.3}MnO_3$ (LSMO)

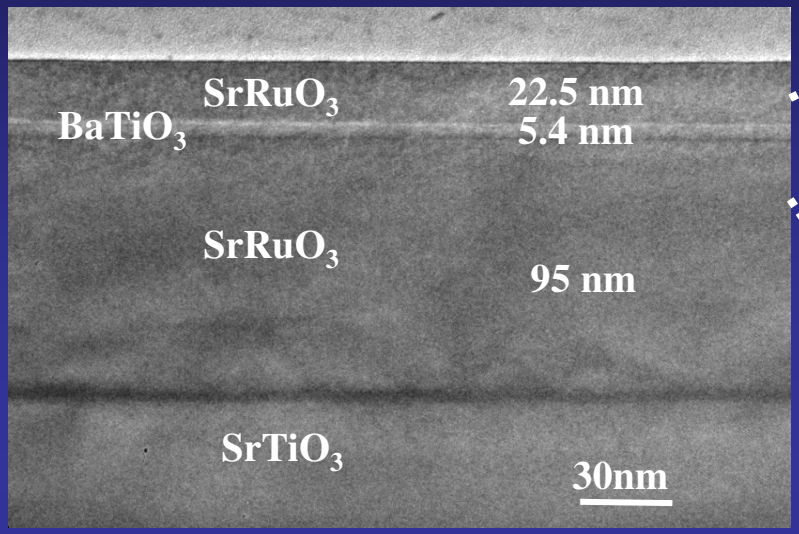
The LSMO surface is highly spin polarized

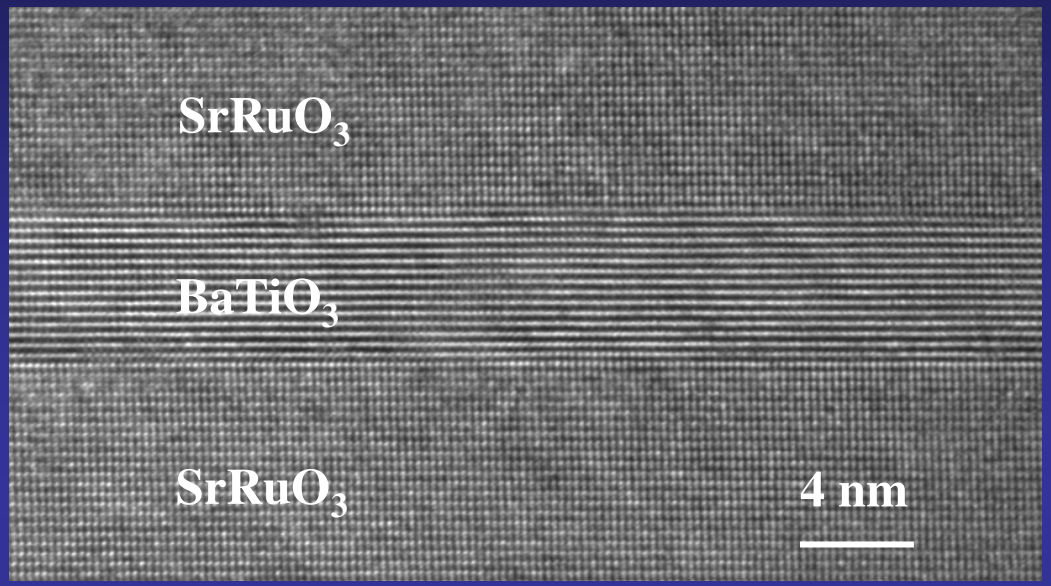
$$MR = \frac{\Delta R}{R_P} \equiv \frac{R_{AP} - R_P}{R_P}$$

61 % at 5 K

Previous devices limited to ~0.1-1 %

First simulation on a realistic ferroelectric capacitor: existence of a critical thickness for ferroelectricity





NATURE | VOL 422 | 3 APRIL 2003 | www.nature.com/nature

Critical thickness for ferroelectricity in perovskite ultrathin films

Javier Junquera & Philippe Ghosez

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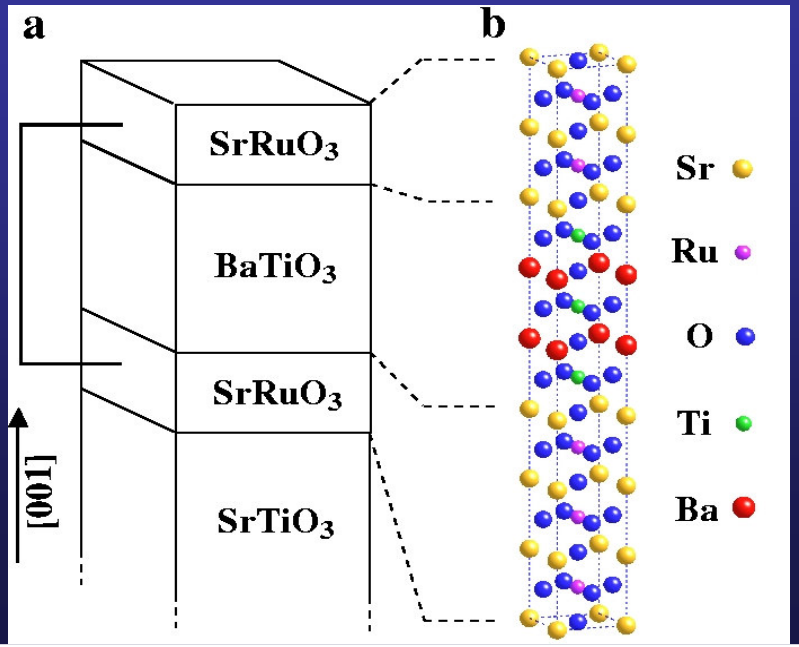
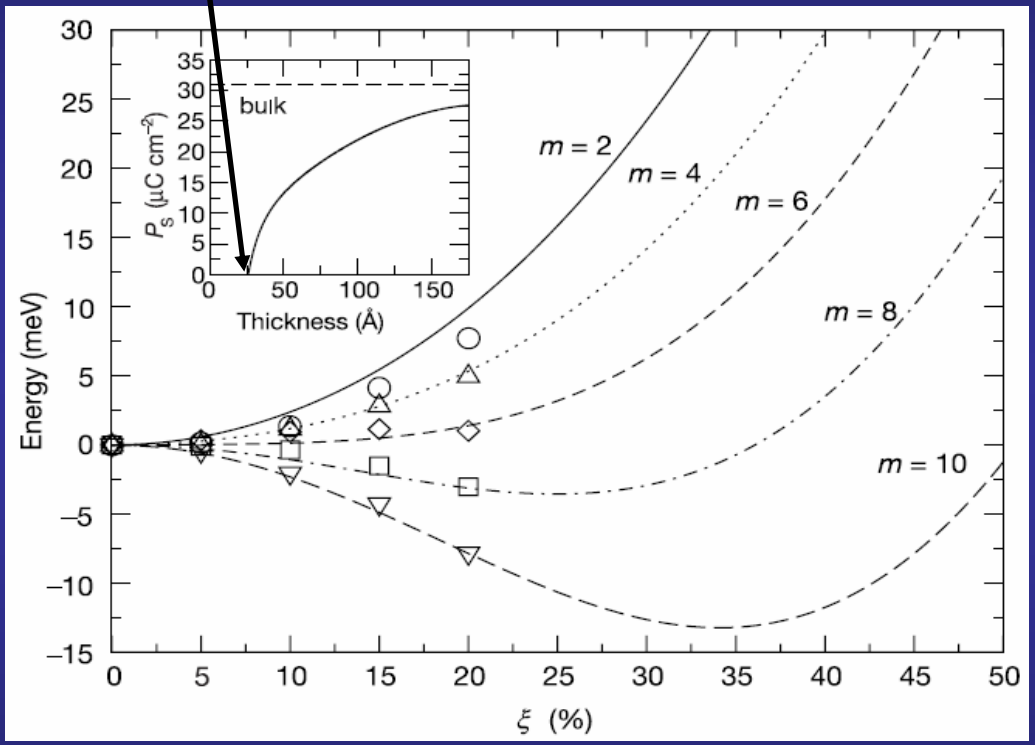
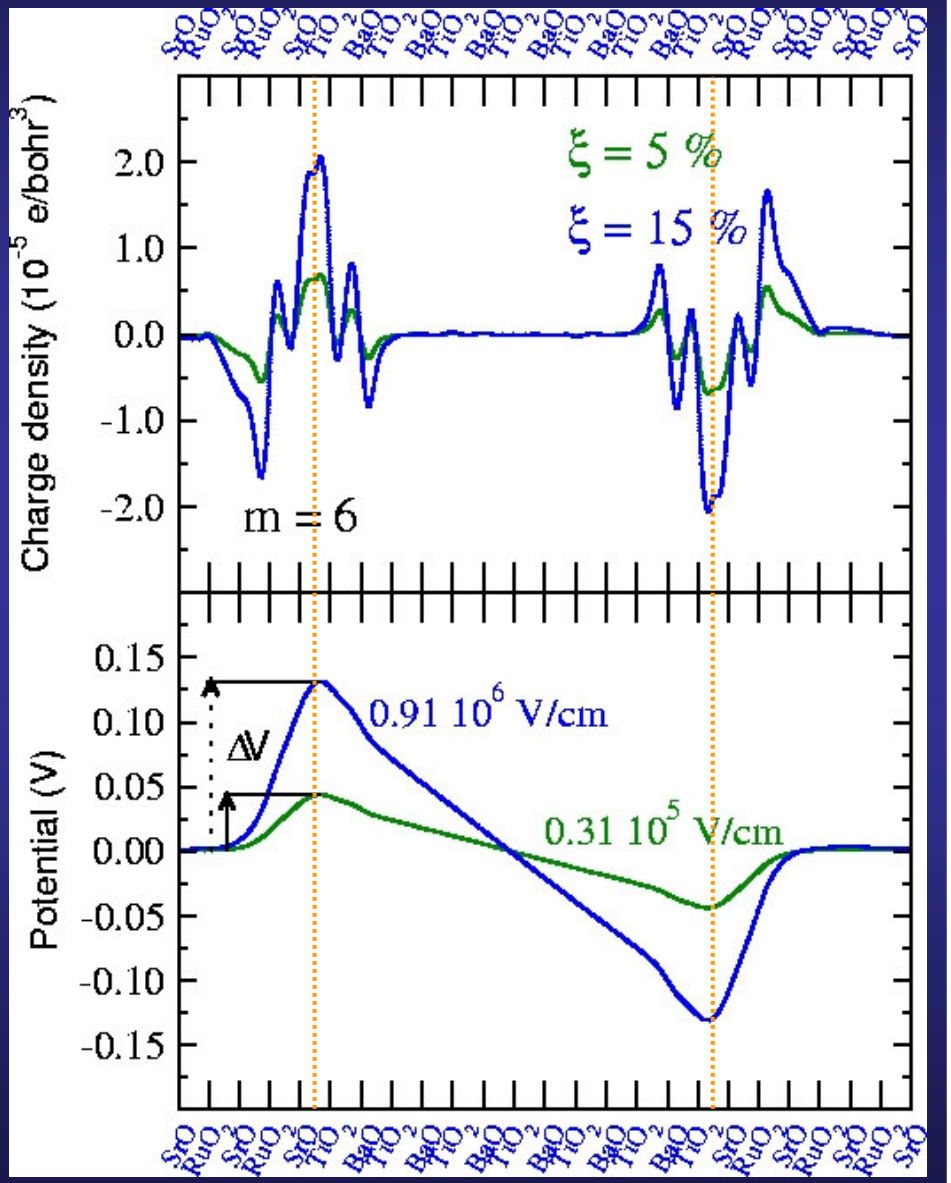
253 citas



The critical thickness is due to the incomplete screening of polarization charge: the depolarizing field

$t_c \approx$ 24 Å (6 celdas unidad)





Depolarizing field:

- **Directaly proportional to the polarization.**
- **Inversely proportional to the thickness.**

J. Junquera and Ph. Ghosez, Nature 422, 506 (2003)

SIESTA availability

- Free to academics
- Free to Government labs engaged in academic & ethical research
- Small charge to industry
- All get source code

SIESTA current status

- New versions about to be released
  - Massively parallel re-write (Barcelona Supercomputer Centre)
  - Van der Waals version
  - TranSIESTA included (PRB, 65, 165401 (2002))
  - LDA + U
  - Z-matrices
  - Broyden optimisation
  - SIESTA as a subroutine / CamposASE (http://www.fysik.dtu.dk/campos/ASE)
  - Many enhancements / new properties

SIESTA next version…

- New order N solvers
  - Divide and conquer
    - (*J. Phys. Cond. Matter*, 20, 294208 (2008))
  - Li, Nunes, Vanderbilt
  - Density matrix purification
- Filterets
- Time Dependent Density Functional Theory (TDDFT)
- Spin-orbit
- Response of periodic dielectrics to electric field
- Calculation of optical properties
- Simulation of STM images

Example of input

H_2O molecule: example of a very simple input file

Go to the directory where the exercise of the H_2O molecule is included

Inspect the input file, h2o.fdf

Examine in detail the different input variables, more information at

http://www.icmab.es/siesta and follow the link Documentations, Manual

```
SystemName          Water molecule
SystemLabel         h2o
NumberOfAtoms       3
NumberOfSpecies     2

%block ChemicalSpeciesLabel
 1  8  O      # Species index, atomic number, species label
 2  1  H
%endblock ChemicalSpeciesLabel

AtomicCoordinatesFormat  Ang
%block AtomicCoordinatesAndAtomicSpecies
 0.000   0.000   0.000  1
 0.757   0.586   0.000  2
-0.757   0.586   0.000  2
%endblock AtomicCoordinatesAndAtomicSpecies
```

Number of different species and atoms present in the unit cell

List of different species

Position of the atoms

Example of a first-principles simulation: no input from experiment

Input of example
MgO an ionic solid that crystallizes in the rocksalt structure

Go to the directory where the exercise of the bands of MgO is included

Inspect the input file, MgO.fdf

```
SystemName Magnesium Oxide Crystal
SystemLabel              MgO

NumberOfAtoms            2
NumberOfSpecies          2

%block Chemical_Species_Label
  1   12   Mg
  2    8    0
%endblock Chemical_Species_Label

LatticeConstant     4.117 Ang
%block LatticeVectors
  0.000  0.500  0.500
  0.500  0.000  0.500
  0.500  0.500  0.000
%endblock LatticeVectors

AtomicCoordinatesFormat Fractional
%block AtomicCoordinatesAndAtomicSpecies
  0.000  0.000  0.000   1
  0.500  0.500  0.500   2
%endblock AtomicCoordinatesAndAtomicSpecies

%block kgrid_Monkhorst_Pack
  6  0  0  0.5
  0  6  0  0.5
  0  0  6  0.5
%endblock kgrid_Monkhorst_Pack
```

More information at the Siesta web page http://www.icmab.es/siesta and follow the link Documentations, Manual

The equilibrium lattice constant within LDA has been computed for you…

Rocksalt structure:

FCC lattice

+ a basis of two atoms

Sampling in k in the first Brillouin zone to achieve self-consistency

Recap on SIESTA

- First-principles method and Fortran-90 implementation code
- Based on Density Functional Theory
- Norm-conserving pseudopotential
- Strictly localized Numerical Atomic Orbital as the basis set
- Matrix elements of the Hamiltonian and Overlap matrices always computed in Order-N.
- Solution of the Hamiltonian, in Order-N or standard diagonalization.
- Freely available for the academic community

More information at: http://www.uam.es/siesta

http://personales.unican.es/junqueraj