Materials Science from First Principles:
Materials Scientist Toolbox

Start: 2025/11/03 | End: 2025/11/07 | Location: Paris, France

HANAMI

cecam
Centre Européen de Calcul Atomique et Moléculaire

Density Functional Theory and the siesta code

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Program

2. The SIESTA code

- What is SIESTA? Main characteristics
- The Kohn-Sham Equations in a basis set
- The LCAO approach: (Pseudo) atomic orbital bases
- PAOs with finite support
- Radial and Angular components of the basis, and how to improve the solution
- The SCF Cycle and its two main steps:
    - Building H – some details
    - Solving the KS eqs to find the density - some solvers
- Periodic boundary conditions and BZ sampling
- SCF convergence – mixing algorithms

Main characteristics

- Standard DFT
- Fast for large systems => from O(N^3) to Order-N
- From ”quick & dirty” to highly accurate

Methods and approximations

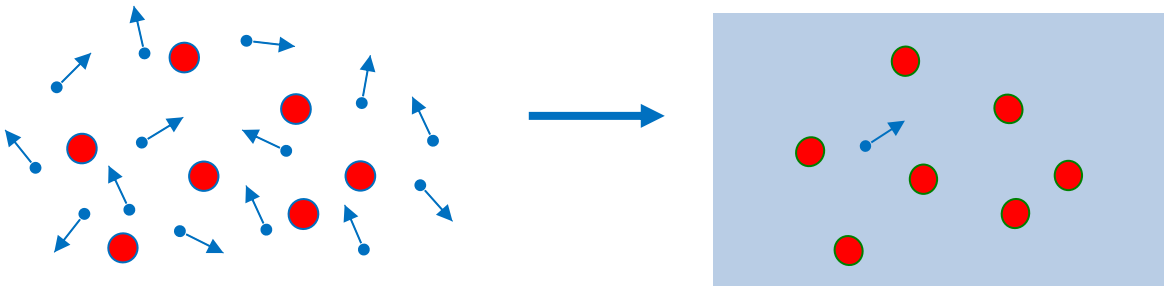
- Norm-conserving pseudopotentials
- Basis of numerical atomic orbitals
- Uniform real-space grid
- Several solvers (diag, PEXSI, Order-N, Greens Functions, …)

Introduction to basics only

(SIESTA can do many more things than presented here!)

Kohn – Sham formulation

Interacting electrons: As if *non-interacting* electrons in an *effective potential* (Kohn-Sham Ansatz)

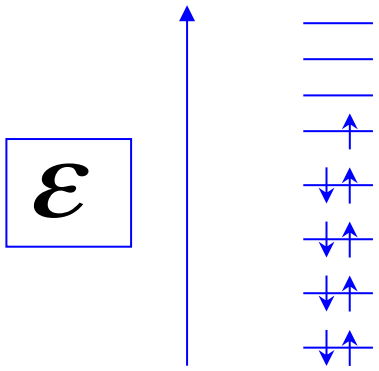


$$\hat{h}\psi_n(\vec{r}) = \varepsilon_n \psi_n(\vec{r})$$

$$n(\vec{r}) = \sum_n^{occ} \left|\psi_n(\vec{r})\right|^2$$

$$H_{eff} = -\frac{1}{2}\nabla^2 + V_{eff}(r) =$$

$$= -\frac{1}{2}\nabla^2 + V_{ext}(r) + V_H(r) + V_{xc}(r)$$



Expand KS states in a basis

Basis set: $\{|e_\mu\rangle,\ \mu = 1 \ldots \mathcal{N}\}$ $\quad \phi_\mu(\mathbf{r}) = \langle \mathbf{r}|e_\mu\rangle$

Schrödinger (Kohn-Sham) eq. $H|\psi_n\rangle = E_n|\psi_n\rangle$ becomes

$$\sum_\nu H_{\mu\nu} C_{\nu n} = E_n \sum_\nu S_{\mu\nu} C_{\nu n}$$

where

$$|\psi_n\rangle = \sum_\mu |e_\mu\rangle\, C_{\mu n}\,, \quad H_{\mu\nu} = \langle e_\mu|H|e_\nu\rangle\,, \quad \text{and } S_{\mu\nu} = \langle e_\mu|e_\nu\rangle\,,$$

$$n(\mathbf{r}) = \sum_n^{\text{occ}} |\psi_n(\mathbf{r})|^2 = \sum_n^{\text{occ}} \psi_n(\mathbf{r})\psi_n^*(\mathbf{r}) = \sum_n^{\text{occ}} \sum_{\mu,\nu} C_{\mu n}\phi_\mu(\mathbf{r})\, C_{\nu n}^*\phi_\nu^*(\mathbf{r})$$

$$= \sum_{\mu,\nu} \rho_{\mu\nu}\phi_\mu(\mathbf{r})\,\phi_\nu^*(\mathbf{r}) \quad \text{where} \quad \rho_{\mu\nu} \equiv \sum_n^{\text{occ}} C_{\mu n} C_{\nu n}^*$$

Basis set – LCAO – atomic orbitals

Numerical (pseudo)atomic orbitals (PAOs)
& real spherical harmonics

$$\phi_{\zeta lm}(r,\theta,\varphi) = R_{\zeta}(r)Y_{lm}(\theta,\varphi)$$

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

$$l=1,\ \ m=-1,0,+1 \quad\Rightarrow\quad p_y, p_z, p_x$$

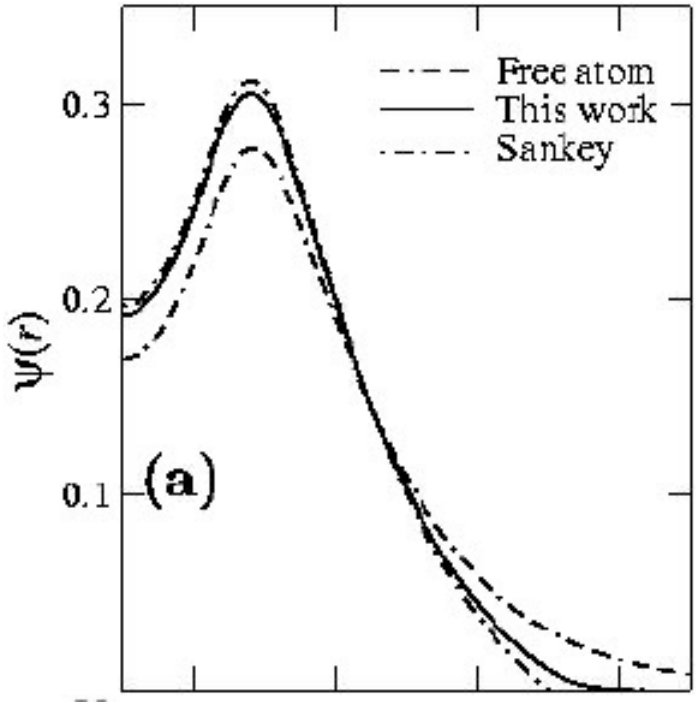
Finite-support atomic orbitals as basis

s

p

d

f



Strictly localised

(zero beyond cut-off radius)

Finite-support atomic orbitals as basis

s

p

d

f

Only 2 conditions

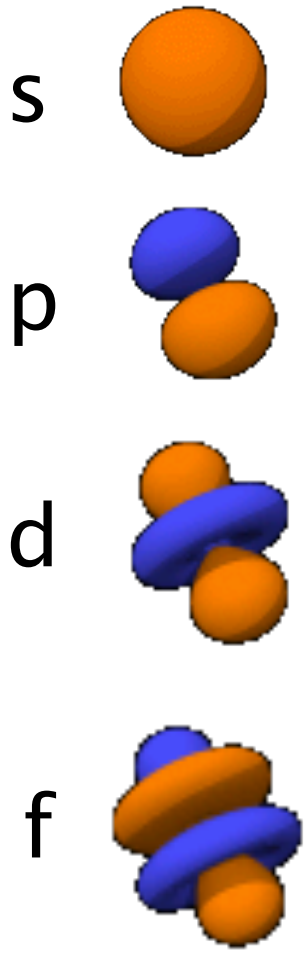
1. $\phi_{\zeta lm}(r,\theta,\varphi) = R_{\zeta}(r)Y_{lm}(\theta,\varphi)$
2. Finite range

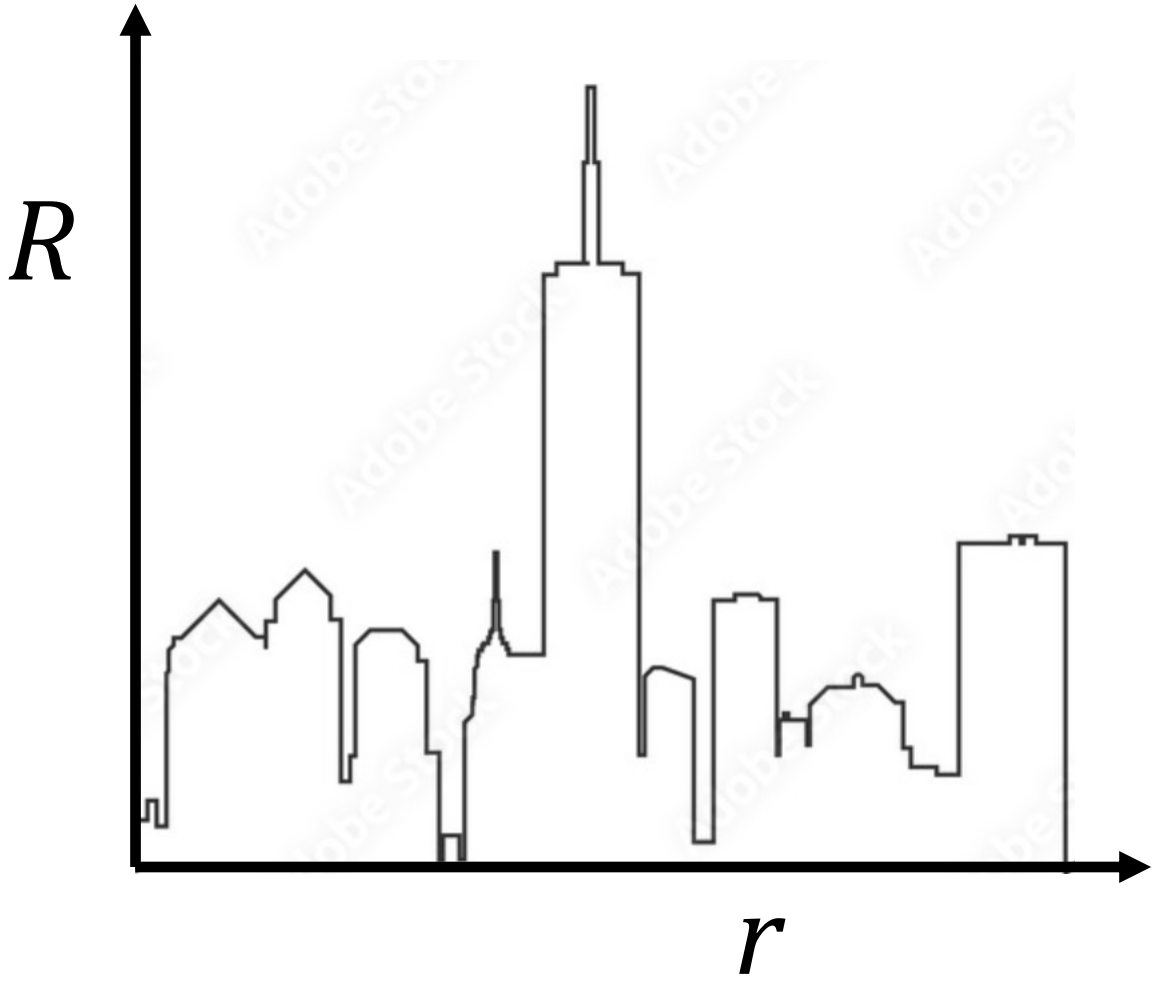
User decides

- How many centres
- Where to put them (on atoms or not)
- How many angular momenta
- How many for each ang. momentum
- Each radial shape

Finite-support atomic orbitals as basis

$$\phi_{\zeta lm}(r,\theta,\varphi) = R_{\zeta}(r)Y_{lm}(\theta,\varphi)$$





Basis Size: how many orbitals?

$$\phi_{\zeta lm}(r,\theta,\varphi) = R_{\zeta}(r)Y_{lm}(\theta,\varphi)$$

- How many angular components?

s p d f ….

- How many radial functions for each angular component?

***Quick exploratory* calculations**

Minimal basis set

(single-ζ; SZ)

Highly converged calculations

Multiple-ζ
+
Polarization
+
Diffuse orbitals

Minimal Bases (SZ)

$$\phi_{\zeta lm}(r,\theta,\varphi) = R_{\zeta}(r)Y_{lm}(\theta,\varphi)$$

- Minimal bases: One radial function per occupied shell in the free atom

  Single-ζ (or SZ) (eg: Si: one 3s orbital and three 3p orbitals)

Numerical (pseudo)atomic orbitals (PAOs)

$$\phi_{\zeta lm}(r,\theta,\varphi) = R_{\zeta}(r)Y_{lm}(\theta,\varphi)$$

Solution of the Schrödinger Eq. in the atom with a given pseudopotential …

▸ Energy Shift

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

… with a confining potential

- Strictly confined atomic orbitals, either with a hard or a soft confinement (user's choice)
- Several ways to define the confinement radii
- CPU and accuracy depend on r_c → need to check!

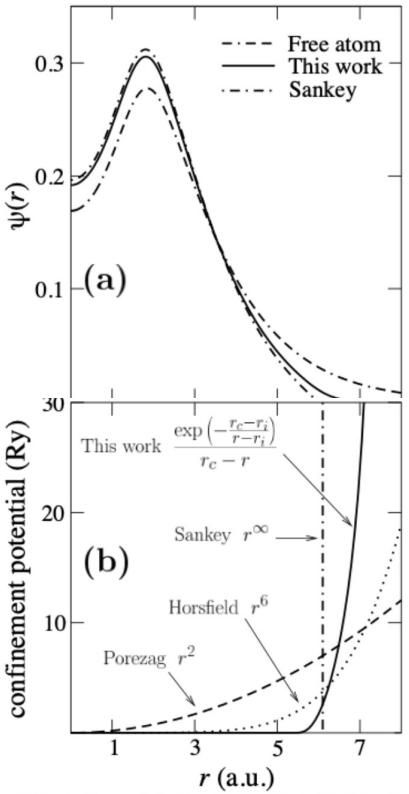


FIG. 1. Shape of the 3s orbital of Mg in MgO for the different confinement schemes (a) and corresponding potentials (b).

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

Minimal Bases (SZ)

$$\phi_{\zeta lm}(r,\theta,\varphi) = R_{\zeta}(r)Y_{lm}(\theta,\varphi)$$

- Minimal bases: One radial function per occupied shell in the free atom

  Single-ζ (or SZ) (eg: Si: one 3s orbital and three 3p orbitals)

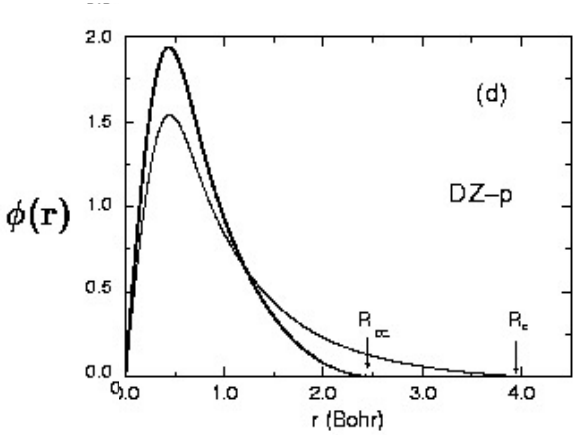
- How do we improve upon the SZ? (common wisdom in QC community)
  1. Increasing the number of radial functions for each angular component
  2. Increasing the number of angular components
  3. Introducing diffuse radial functions
  4. Introducing off-site orbitals

Radial flexibility

$$\phi_{\zeta lm}(r,\theta,\varphi) = R_{\zeta}(r)Y_{lm}(\theta,\varphi)$$

- Minimal bases: One radial function per occupied shell in the free atom

  Single-ζ (or SZ) (eg: Si: one 3s orbital and three 3p orbitals)



- Several radial functions to describe an atomic shell (same angular part):

  Multiple-ζ:

  Double-ζ Triple-ζ …..

SIESTA has several ways to define the shape of the second, third, … functions (advanced users)

More Angular Components

$$\phi_{\zeta lm}(r,\theta,\varphi) = R_{\zeta}(r)Y_{lm}(\theta,\varphi)$$

- "Polarization" orbitals
  Orbitals with higher angular momentum than those occupied in the free atom

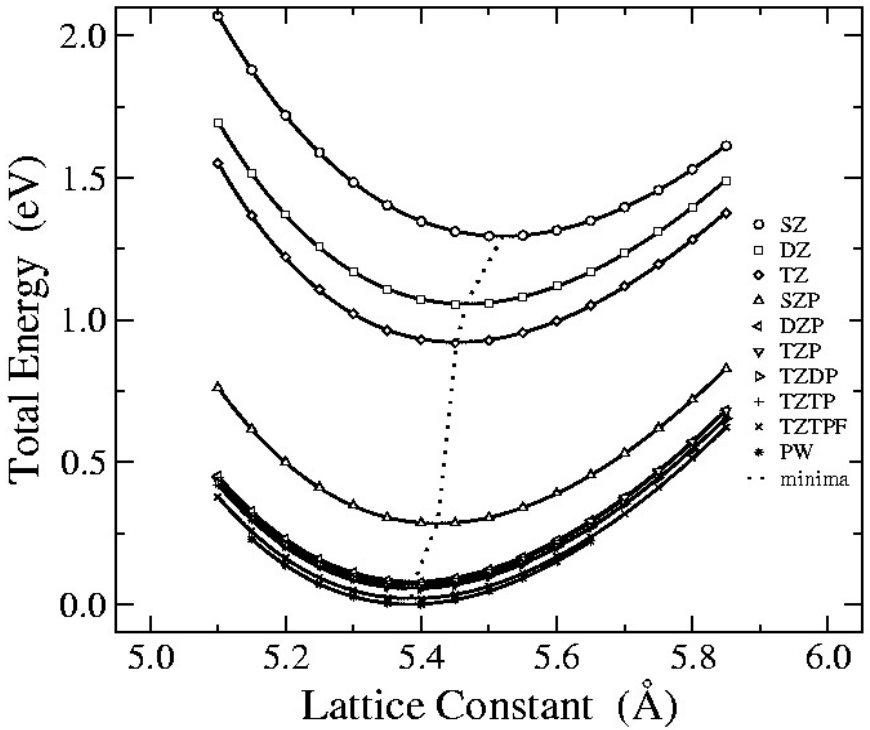
Atom	Valence configuration	SZ		DZ		P	
		# orbitals	symmetry	# orbitals	symmetry	# orbitals	symmetry
Si	$3s^2\ 3p^2$	1	s	2	s	1	d_{xy}
		1	p_x	2	p_x	1	d_{yz}
		1	p_y	2	p_y	1	d_{zx}
		1	p_z	2	p_z	1	$d_{x^2-y^2}$
						1	$d_{3z^2-r^2}$
	Total	4		8		(DZ+P) 13	

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	

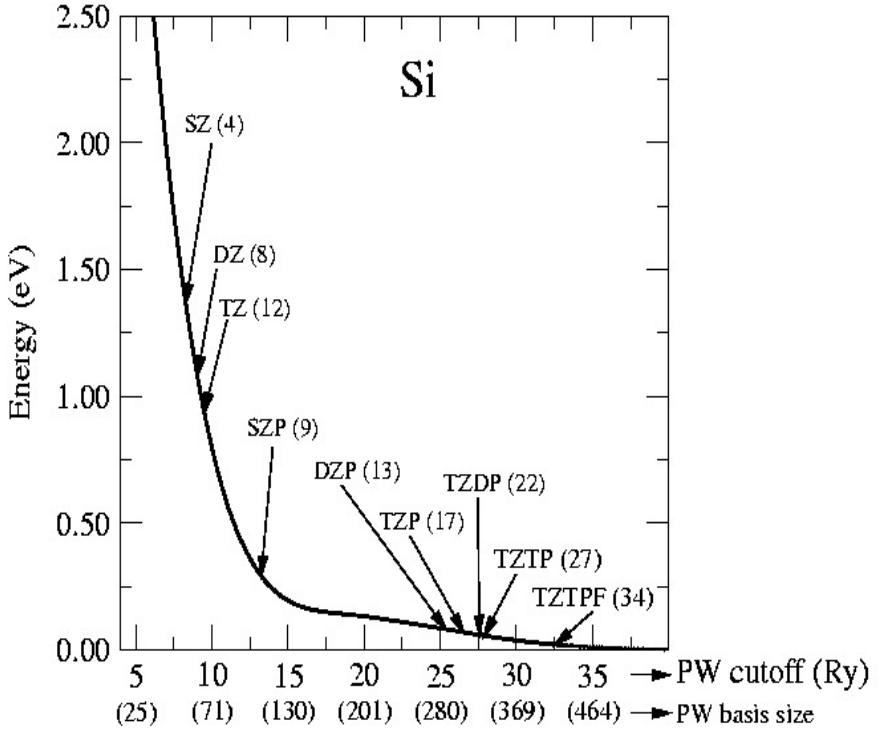
SIESTA has several ways to define the "polarization" orbitals (advanced users)

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

Cohesion curves



PW and NAO convergence

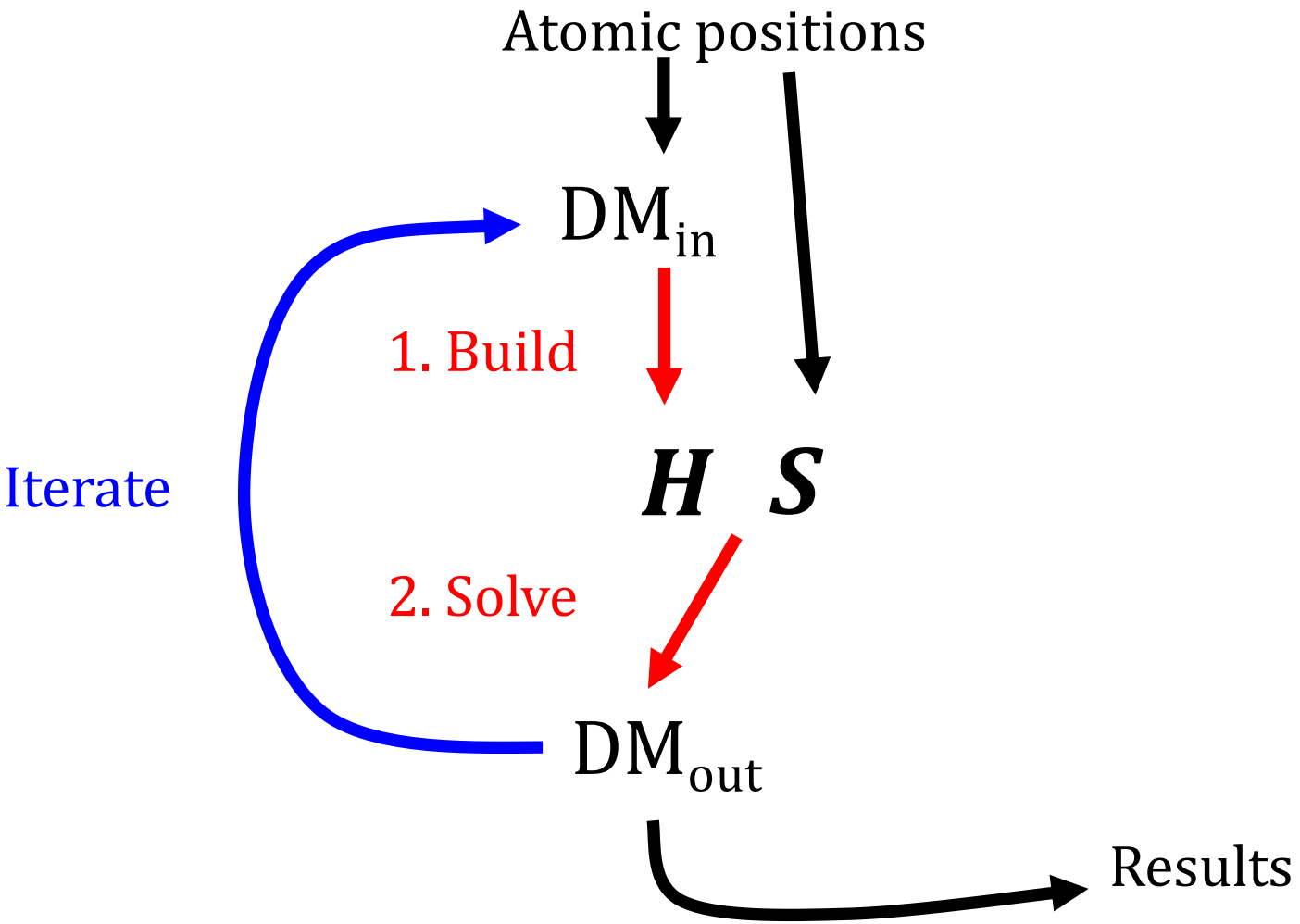


Atomic orbitals show nice convergence with respect the size

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

Double-ζ plus polarization is typically an excellent choice (compromise between accuracy and cost)

Computational Effort: Two steps and SCF cycle



1. Building: Computing H (and S)

J. Phys.: Condens. Matter **14** (2002) 2745–2779

$$H = T + V_{\text{ion}}(\mathbf{r}) + V_{\text{nl}} + V_{\text{H}}(\mathbf{r}) + V_{\text{xc}}(\mathbf{r})$$

Long range

Electronic charge density of the neutral atom

$$\rho_{SCF}(r) = \rho_o(r) + \delta\rho(r)$$

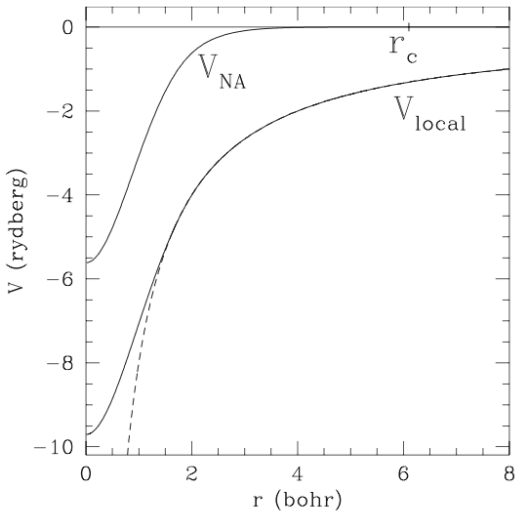
$$V_{\text{na}}(r) = V_{\text{ion}}(r) + V_{\text{H}}[\rho_{\text{o}}(r)]$$ Neutral-atom potential

$$\delta V_{\text{H}}(\mathbf{r}) = V_{\text{H}}[\rho_{\text{SCF}}(\mathbf{r})] - V_{\text{H}}[\rho_{\text{o}}(\mathbf{r})] = V_{\text{H}}[\delta\rho(\mathbf{r})]$$

$$H = T + V_{\text{nl}} + V_{\text{na}}(\mathbf{r}) + \delta V_{\text{H}}(\mathbf{r}) + V_{\text{xc}}(\mathbf{r})$$

Two-center integrals

Grid integrals



1. Building (a)
Two-center integrals

Convolution theorem

$$S(\mathbf{R}) \equiv \langle \phi_1 | \phi_2 \rangle = \int \phi_1(\mathbf{r})\, \phi_2(\mathbf{r}-\mathbf{R})\, d\mathbf{r}$$

$$\phi(\mathbf{k}) = \frac{1}{(2\pi)^{2/3}} \int \phi(\mathbf{r})\, e^{-i\mathbf{kr}}\, d\mathbf{r}$$

$$S(\mathbf{R}) = \int \phi_1(\mathbf{k})\, \phi_2(\mathbf{k})\, e^{i\mathbf{kR}}\, d\mathbf{k}$$

$T = -(1/2)\,\nabla^2$

$V_{\mathrm{nl}} = \sum_\alpha |\chi_\alpha\rangle\, \varepsilon_\alpha\, \langle\chi_\alpha|$ Kleinman-Bylander

1. Building (b): on a real-space grid

(discretise space)

$$\langle \varphi_\mu | V | \varphi_\nu \rangle = \int \varphi_\mu(r) V(r) \varphi_\nu(r) dr$$

$$\approx \sum_i \varphi_\mu(r_i) V(r_i) \varphi_\nu(r_i)$$

$$\psi_i(r) = \sum_\mu c_{i\mu} \varphi_\mu(r)$$

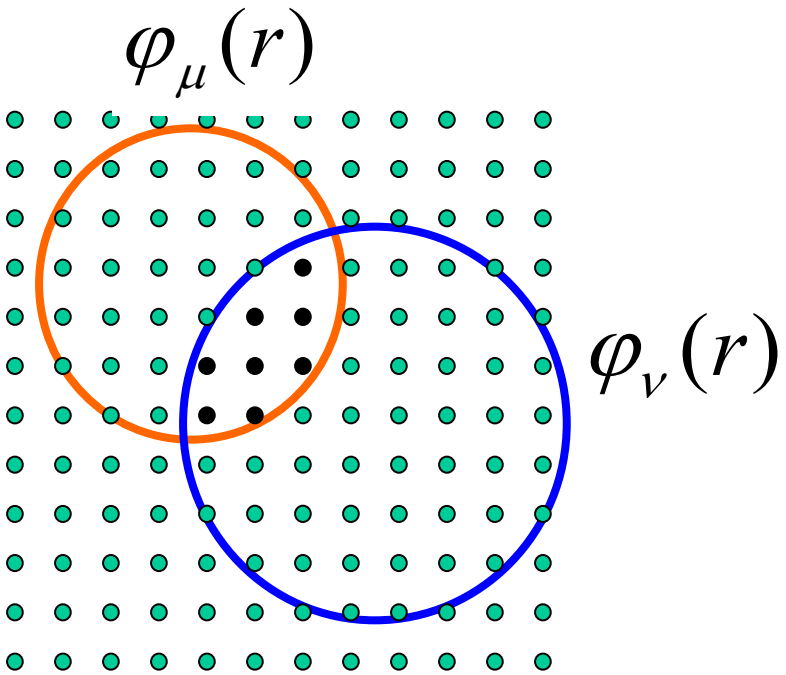
$$\rho_{\mu\nu} = \sum_i c_{i\mu} c_{i\nu}$$

$$\rho(r) = \sum_i \psi_i^2(r) = \sum_{\mu\nu} \rho_{\mu\nu} \varphi_\mu(r) \varphi_\nu(r)$$

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

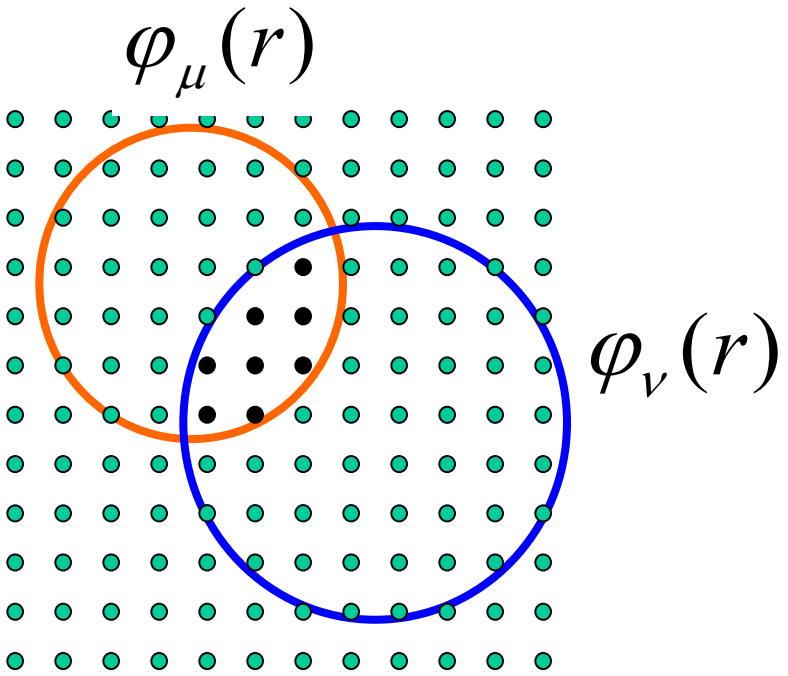
$$\rho(r) \rightarrow V_{xc}(r)$$

$$\delta\rho(r) \underset{FFT}{\rightarrow} \delta V_H(r)$$



1. Building (b): on a real-space grid

(discretise space)



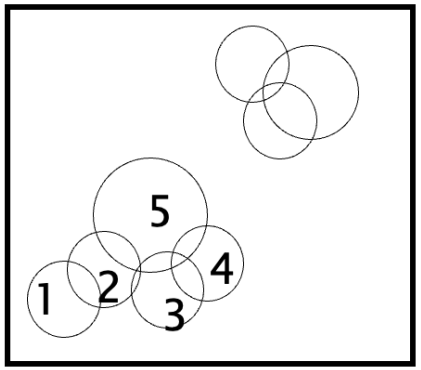
- The grid spacing should be small enough, and that depends on each system.
- Grid spacing defined by the Energy Cutoff – E_{cut} (Ry) like in plane waves (maximum kinetic energy of plane waves that can be represented in the grid)

$$\Delta x \Rightarrow k_c = \pi/\Delta x \Rightarrow E_{cut} = h^2 k_c^2 / 2m_e$$

- Important convergence parameter in SIESTA
- Calculation of all matrix elements is O(N) for large systems!

$$\hat{h}_{\mu\nu} = \left\langle \varphi_\mu \middle| \hat{h} \middle| \varphi_\nu \right\rangle$$

Sparse Matrices



Poisson equation

$$\nabla^2 V_H(r) = -4\pi\,\rho(r)$$

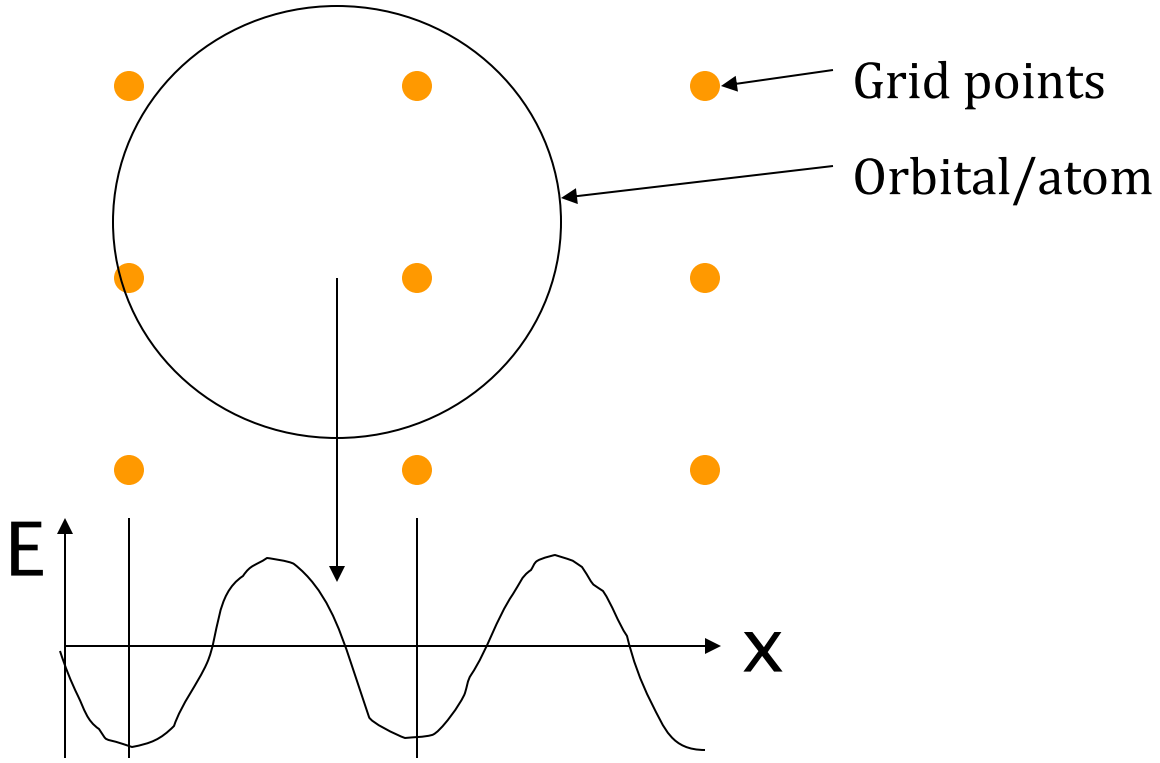
$$\rho(r) = \sum_G \rho_G\, e^{iGr} \quad \Rightarrow \quad V_H(r) = \sum_G V_G\, e^{iGr}$$

$$V_G = -4\pi\,\rho_G / G^2$$

$$\rho(r) \xrightarrow{\text{FFT}} \rho_G \rightarrow V_G \xrightarrow{\text{FFT}} V_H(r)$$

- SIESTA (normally) uses periodic boundary conditions
- Net charge compensated by uniform background
- Spurious interactions between 'images'

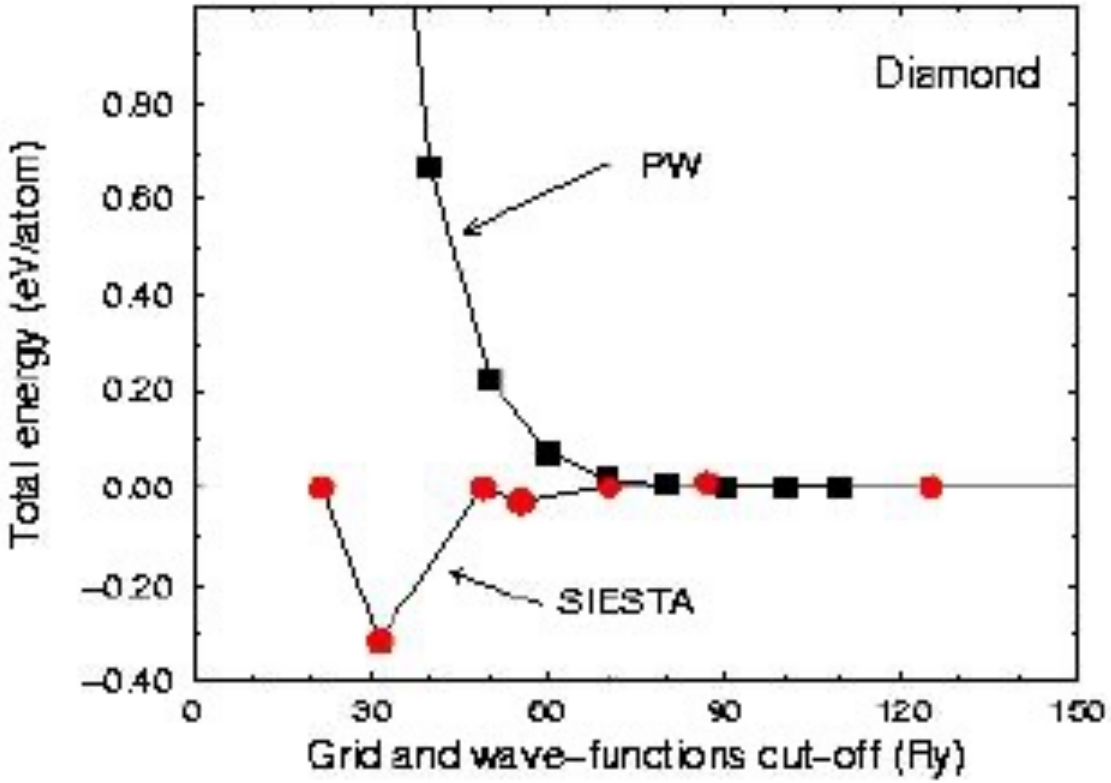
Egg-box effect



Higher effects on forces than on energy

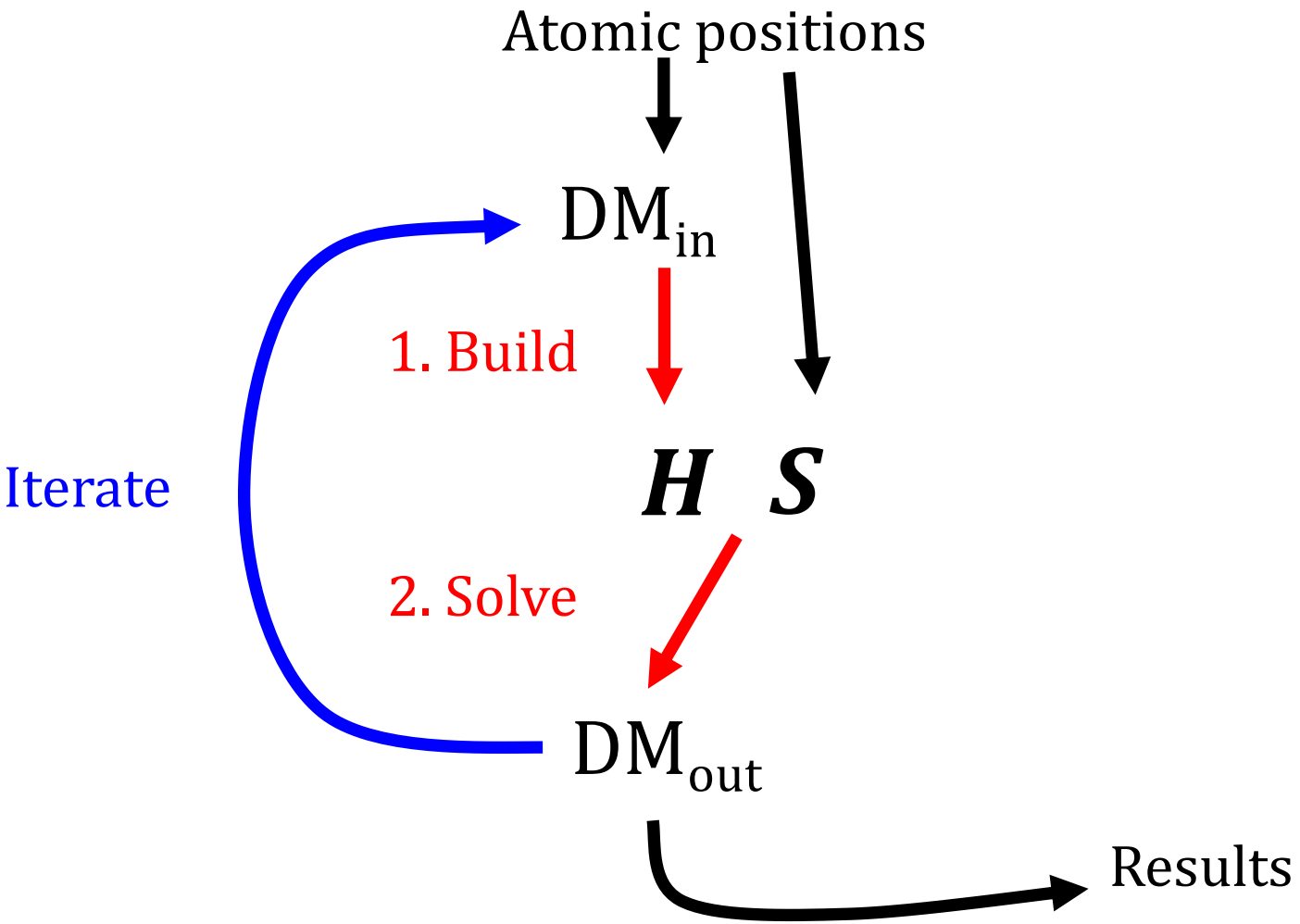
Grid-cell sampling

Grid fineness convergence



$$E_{cut} = (\pi / \Delta x)^2$$

Computational Effort: Two steps and SCF cycle



Expand KS states in a basis

Basis set: $\{|e_\mu\rangle,\ \mu = 1 \ldots \mathcal{N}\}$ $\quad \phi_\mu(\mathbf{r}) = \langle \mathbf{r}|e_\mu\rangle$

Schrödinger (Kohn-Sham) eq. $H|\psi_n\rangle = E_n|\psi_n\rangle$ becomes

where

$$\sum_\nu H_{\mu\nu} C_{\nu n} = E_n \sum_\nu S_{\mu\nu} C_{\nu n}$$

$$|\psi_n\rangle = \sum_\mu |e_\mu\rangle\, C_{\mu n}\,, \quad H_{\mu\nu} = \langle e_\mu|H|e_\nu\rangle\,, \quad \text{and } S_{\mu\nu} = \langle e_\mu|e_\nu\rangle\,,$$

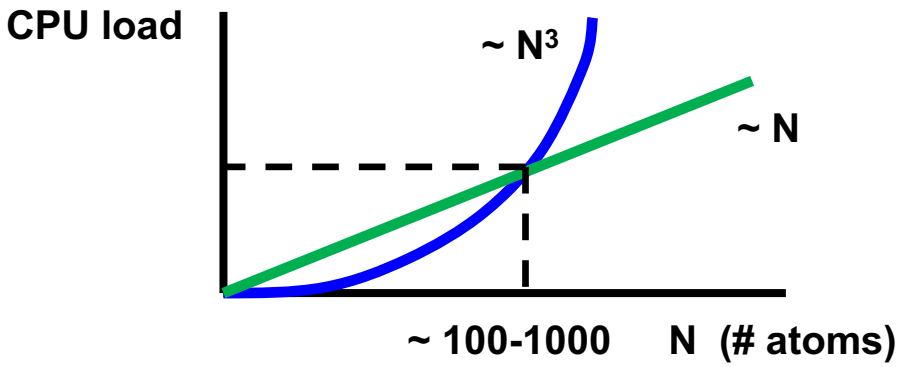
$$n(\mathbf{r}) = \sum_n^{\text{occ}} |\psi_n(\mathbf{r})|^2 = \sum_n^{\text{occ}} \psi_n(\mathbf{r})\psi_n^*(\mathbf{r}) = \sum_n^{\text{occ}} \sum_{\mu,\nu} C_{\mu n}\phi_\mu(\mathbf{r})\, C_{\nu n}^*\phi_\nu^*(\mathbf{r})$$

$$= \sum_{\mu,\nu} \rho_{\mu\nu}\phi_\mu(\mathbf{r})\,\phi_\nu^*(\mathbf{r}) \quad \text{where} \quad \rho_{\mu\nu} \equiv \sum_n^{\text{occ}} C_{\mu n} C_{\nu n}^*$$

Once the hamiltonian and the overlap matrices are built, we have to solve the Schrodinger Eq.

$$\sum_{\nu} H_{\mu\nu} C_{\nu n} = E_n \sum_{\nu} S_{\mu\nu} C_{\nu n}$$

$N \times N \quad N \times 1 \qquad\qquad N \times N \quad N \times 1$



Order-N³

Standard diagonalization techniques

Very well optimized libraries (in parallel too)

Exact (to machine precission)

Both eigenvectors and eigenvalues available

Order-N

Minimization of an energy functional…

…. or direct computation of density matrix

Eigenvalues and eigenvectors **not** available

Some (locality) approximations

Not valid for metals or “dirty” gap systems

Linear algebra libraries are essential for this step, as it is the dominant one for medium and large systems

Once the hamiltonian and the overlap matrices are built, we have to solve the Schrodinger Eq.

$$\sum_{\nu} H_{\mu\nu} C_{\nu n} = E_n \sum_{\nu} S_{\mu\nu} C_{\nu n}$$

$N \times N$ $N \times 1$ $N \times N$ $N \times 1$

Order-N^3

Diagonalization:

Generalized Eigenvalue Problem

Serial:

BLAS

LAPACK

Parallel:

BLACS

SCALAPACK

ELPA: alternative transformation sequence + optimizations **https://elpa.mpcdf.mpg.de/**

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

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

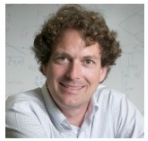
Once the hamiltonian and the overlap matrices are built, we have to solve the Schrodinger Eq.

Solver strategies for performance and features: Use external libraries

ELSI initiative to integrate solver libraries

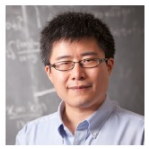
Alberto García
ICMAB–CSIC

https://elsi-interchange.org

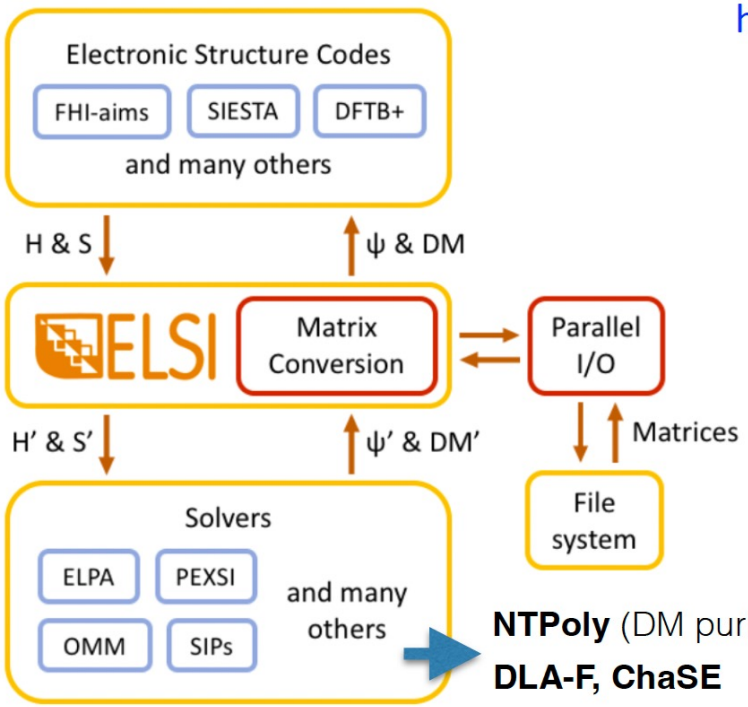


Volker Blum, Duke

Lin Lin, Berkeley



Jiangfen Lu, Duke



NTPoly (DM purification, O(N))
DLA-F, ChaSE

Interface in Siesta:

Collaboration with
Victor Yu

MAX DRIVING THE EXASCALE TRANSITION

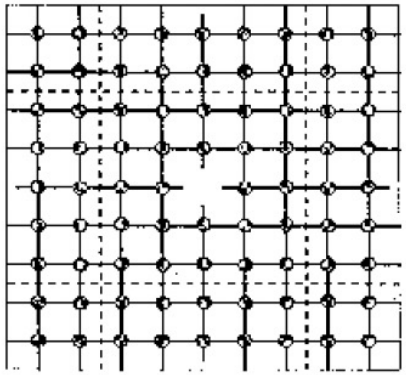
Periodic Boundary Conditions (PBC)

Atoms in the unit cell are **periodically repeated throughout space** along the lattice vectors

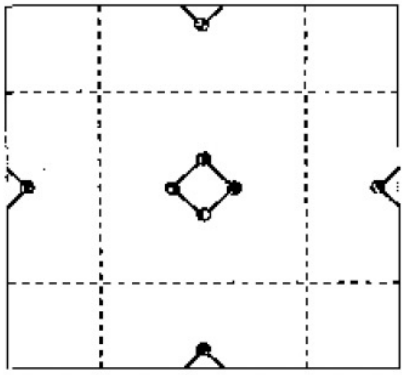
Periodic systems and crystalline solids:

Aperiodic systems: Supercell approximation

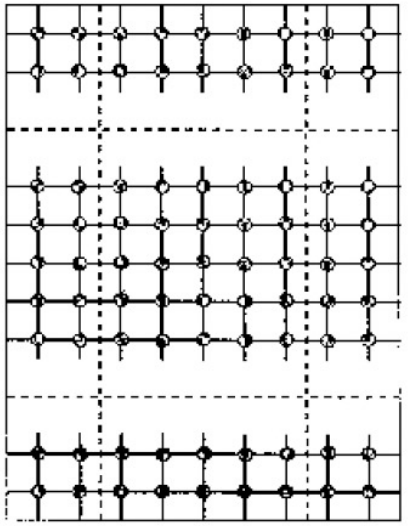
Defects



Molecules



Surfaces



M. C. Payne *et al*, Rev. Mod. Phys., **64**, 1045 (92)

k-sampling

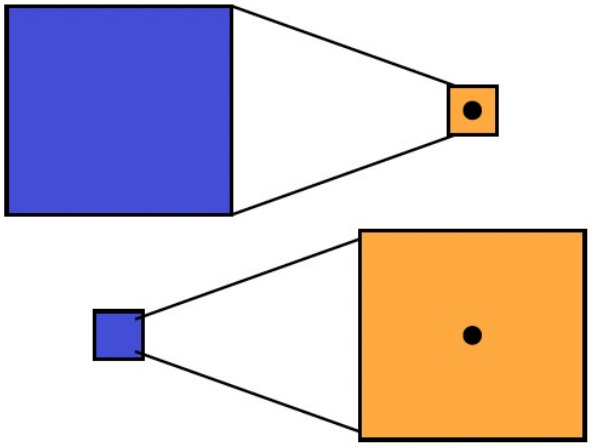
Many magnitudes require integration of functions over the Brillouin zone (BZ)

$$\rho(\vec{r}) = \sum_i \int_{BZ} d\vec{k} n(\vec{k}) \left|\psi_i(\vec{k})\right|^2$$

In practice: integral ⟶ sum over a finite uniform grid

Essential for:

Small systems Metals Magnetic systems



Real space Reciprocal space

Good description of the Bloch states at the Fermi level

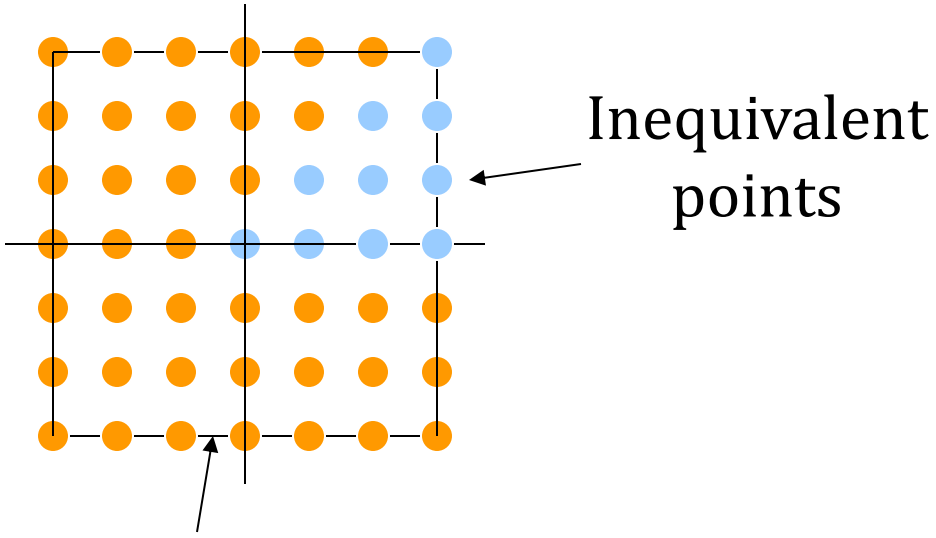
Even in insulators:

Perovskite oxides

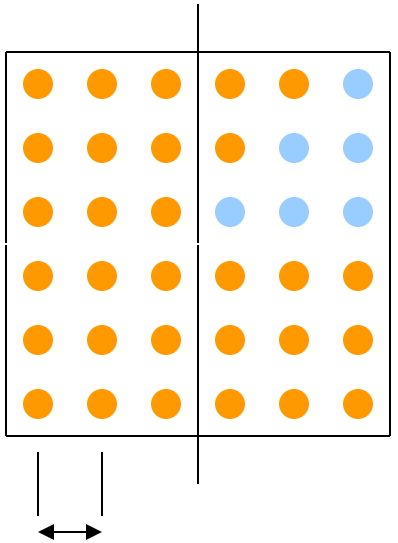
k-point sampling

(fineness of grid in *k*-space)

Regular k-grid



Monkhorst-Pack



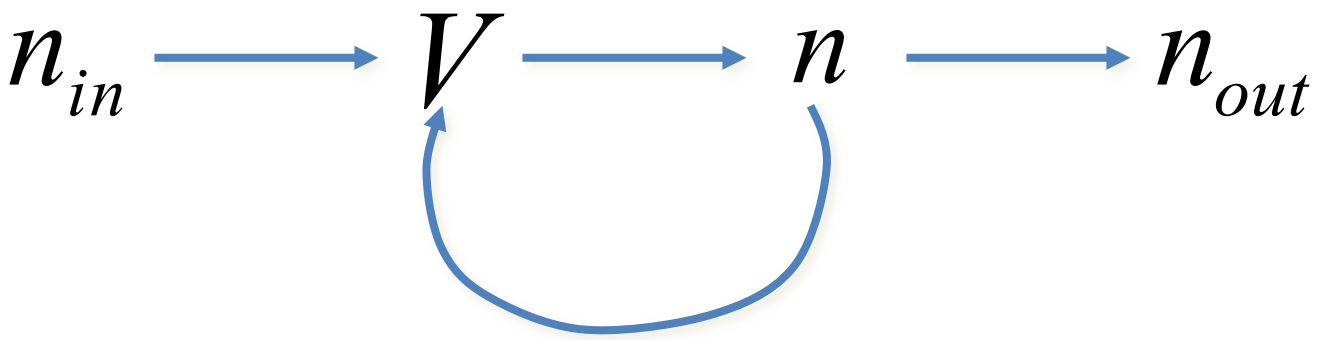
$\Delta k \Rightarrow L_c = \pi/\Delta k$

L_c = 'length cutoff'

Self-consistency

PROBLEM: The potential (input)

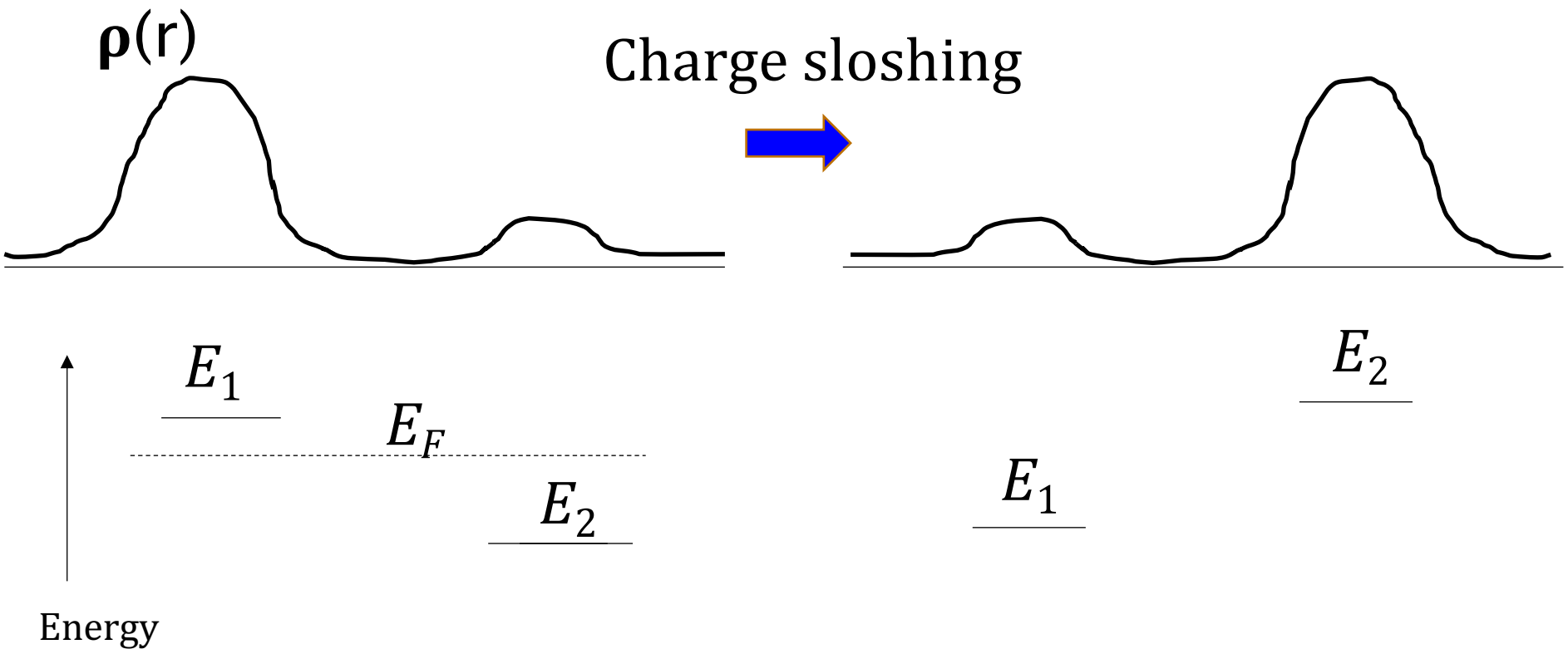
depends on the density (output)



$$|\, n_n - n_{n-1} \,| > \varepsilon$$

Selfconsistency convergence

SCF cycle: $\boldsymbol{\rho}(r) \rightarrow V(r) \rightarrow \boldsymbol{\rho}(r)$



Moderated by electronic temperature

Linear mixing

$$\rho_n^{in}(\mathrm{r}) \rightarrow \rho_n^{out}(\mathrm{r})$$

$$\rho_{n+1}^{in}(\mathrm{r}) = \alpha\rho_n^{out}(\mathrm{r}) + (1-\alpha)\rho_n^{in}(\mathrm{r})$$

- Large α: larger amount of output, faster convergence, but instabilities appear beyond some critical value (system-dependent)
- Smaller α: smaller amount of output, slower convergence, but more stable
- In practice: find the optimal α – as large as possible but convergent
- You can choose to mix the charge or the Hamiltonian

Pulay mixing

$$\rho_n^{in}(\mathrm{r}) \rightarrow \rho_n^{out}(\mathrm{r})$$

$$\delta\rho_n(\mathrm{r}) = \rho_n^{out}(\mathrm{r}) - \rho_n^{in}(\mathrm{r})$$

$$\rho_{n+1}^{in}(\mathrm{r}) = \sum_{k=n-m}^{n} c_k \{\alpha \rho_n^{out}(\mathrm{r}) + (1 - \alpha)\rho_n^{in}(\mathrm{r})\}$$

$$\delta\rho_{n+1}(\mathrm{r}) = \sum_{k=n-m}^{n} c_k \delta\rho_k(\mathrm{r}) = min$$

Important choices:

1. The Pseudopotential and the DFT functional
2. The basis set
    - Size - SZ, DZ, DZP, …;
    - Confinement radii

3. The solution method / libraries (diag)
4. The real space grid and the k-point sampling
5. SCF parameters

Thank you!

Questions? pablo.ordejon@icn2.cat