

Introduction to the code's structure

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

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

Daniel Sánchez-Portal

Javier Junquera

José M. Soler

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 Soler¹, Emilio Artacho², Julian D Gale³, Alberto García⁴,
Javier Junquera^{1,5}, Pablo Ordejón⁶ and Daniel Sánchez-Portal⁷**

Atomic units

$$e = m_e = \hbar = 1$$

$$\text{atomic mass unit} = m_e$$

$$\text{atomic length unit} = 1 \text{ Bohr} = 0.5292 \text{ \AA}$$

$$\text{atomic energy unit} = 1 \text{ Hartree} = 27.2 \text{ eV}$$

$$\text{SIESTA energy unit} = 1 \text{ Ry} = 0.5 \text{ Hartree} = 13.6 \text{ eV}$$

$$H_k = -\frac{1}{2} \nabla^2$$

$$V(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3 \mathbf{r}'$$

$$\rho(\mathbf{r}) \equiv n(\mathbf{r}) > 0$$

Basis sets and secular equation (Gamma point)

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

Expansion of the eigenvectors in a basis of localized atomic orbitals

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

Inserting the expansion of the eigenvector into the Kohn-Sham equation

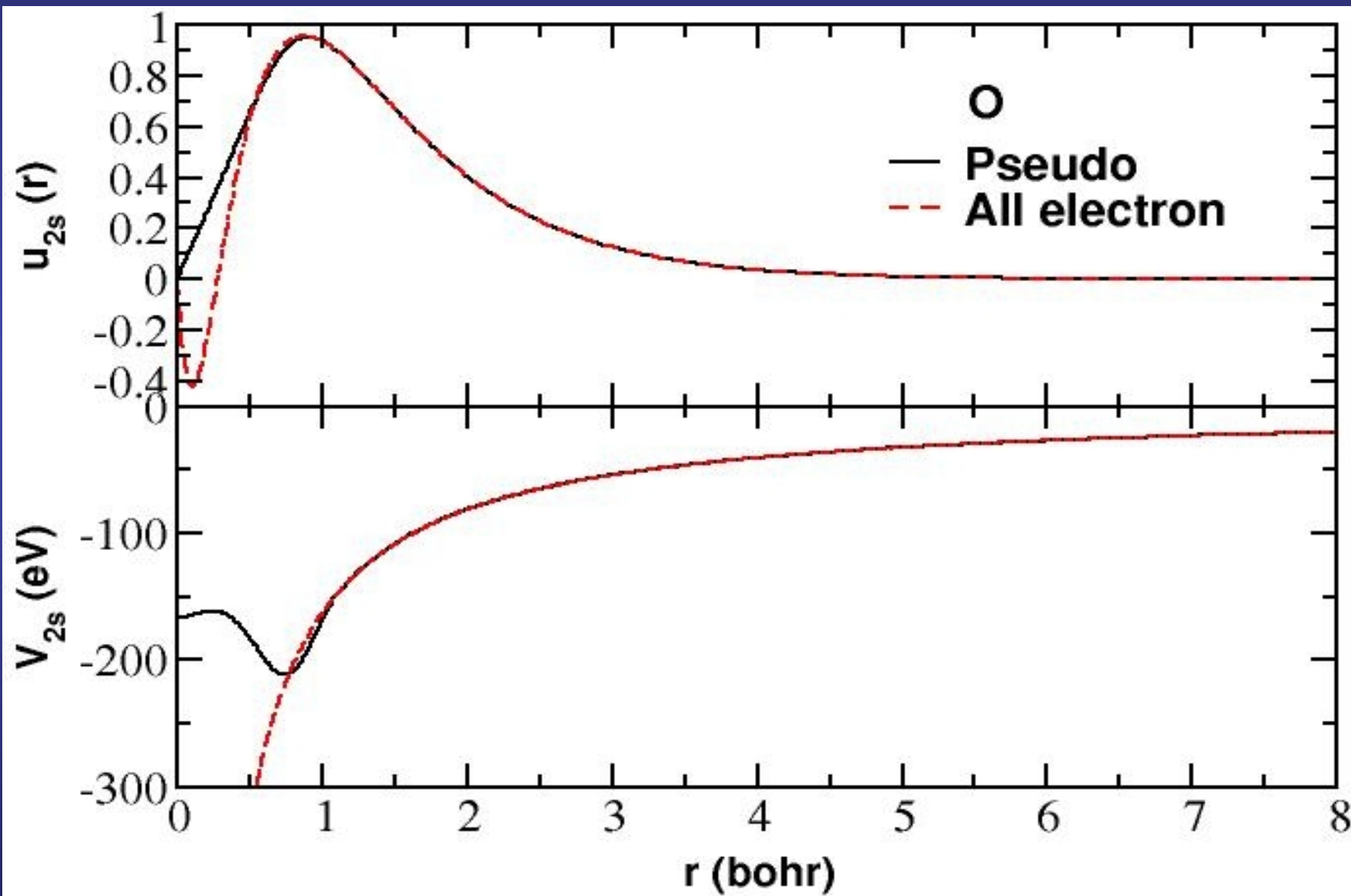
$$\sum_{\mu} c_{\mu i} \hat{H} \phi_{\mu}(\vec{r}) = E_i \sum_{\mu} c_{\mu i} \phi_{\mu}(\vec{r})$$

Multiplying by ϕ_{ν}^* at the left in both sides and integrating over all space

$$\sum_{\mu} c_{\mu i} \int d\vec{r} \phi_{\nu}^*(\vec{r}) \hat{H} \phi_{\mu}(\vec{r}) = E_i \sum_{\mu} c_{\mu i} \int d\vec{r} \phi_{\nu}^*(\vec{r}) \phi_{\mu}(\vec{r})$$

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

Norm-conserving pseudopotentials in electronic structure calculations



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

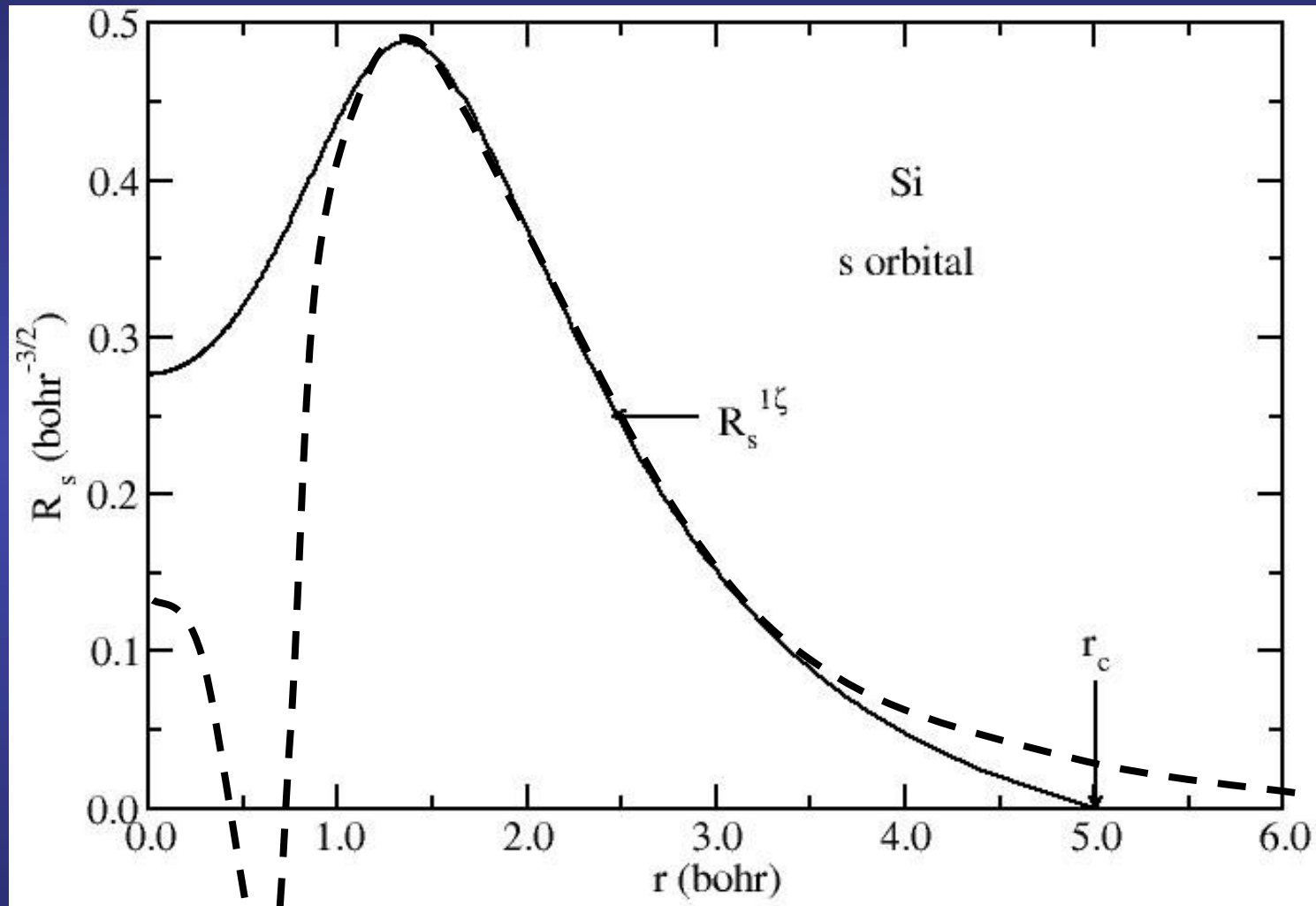
$$\left(-\frac{1}{2r} \frac{d^2}{dr^2} r + \frac{l(l+1)}{2r^2} + V_l(r) \right) R_l(r) = \varepsilon_l R_l(r)$$

Screened pseudopotential

$$\varepsilon_l + \delta\varepsilon_l$$

Energy shift
150-50 meV

Example of a first- ζ function for Si



Converging the basis size: from quick and dirty to highly converged calculations

Single- ζ (minimal or SZ)

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



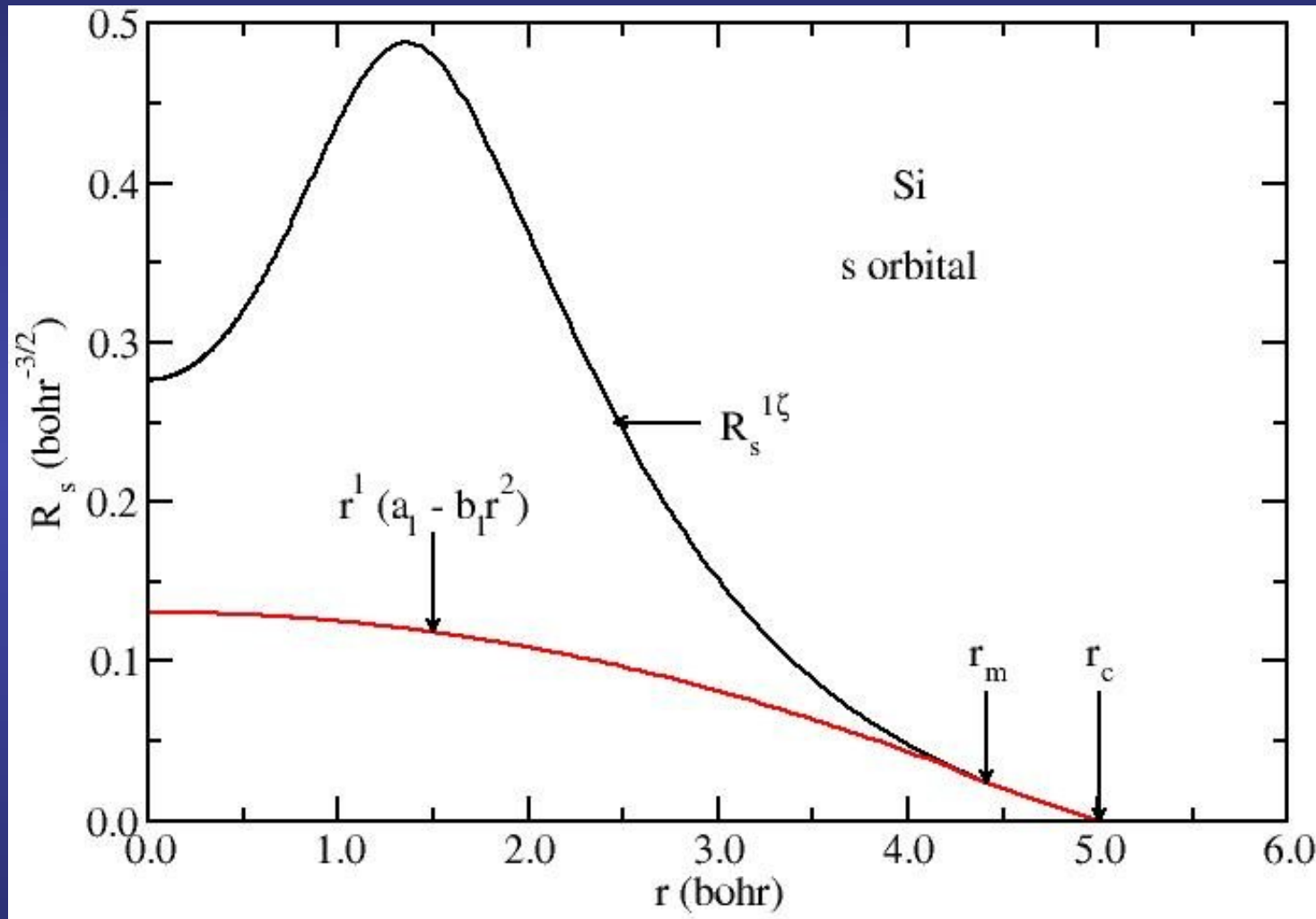
Improving the quality

Radial flexibilization:

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

Multiple- ζ

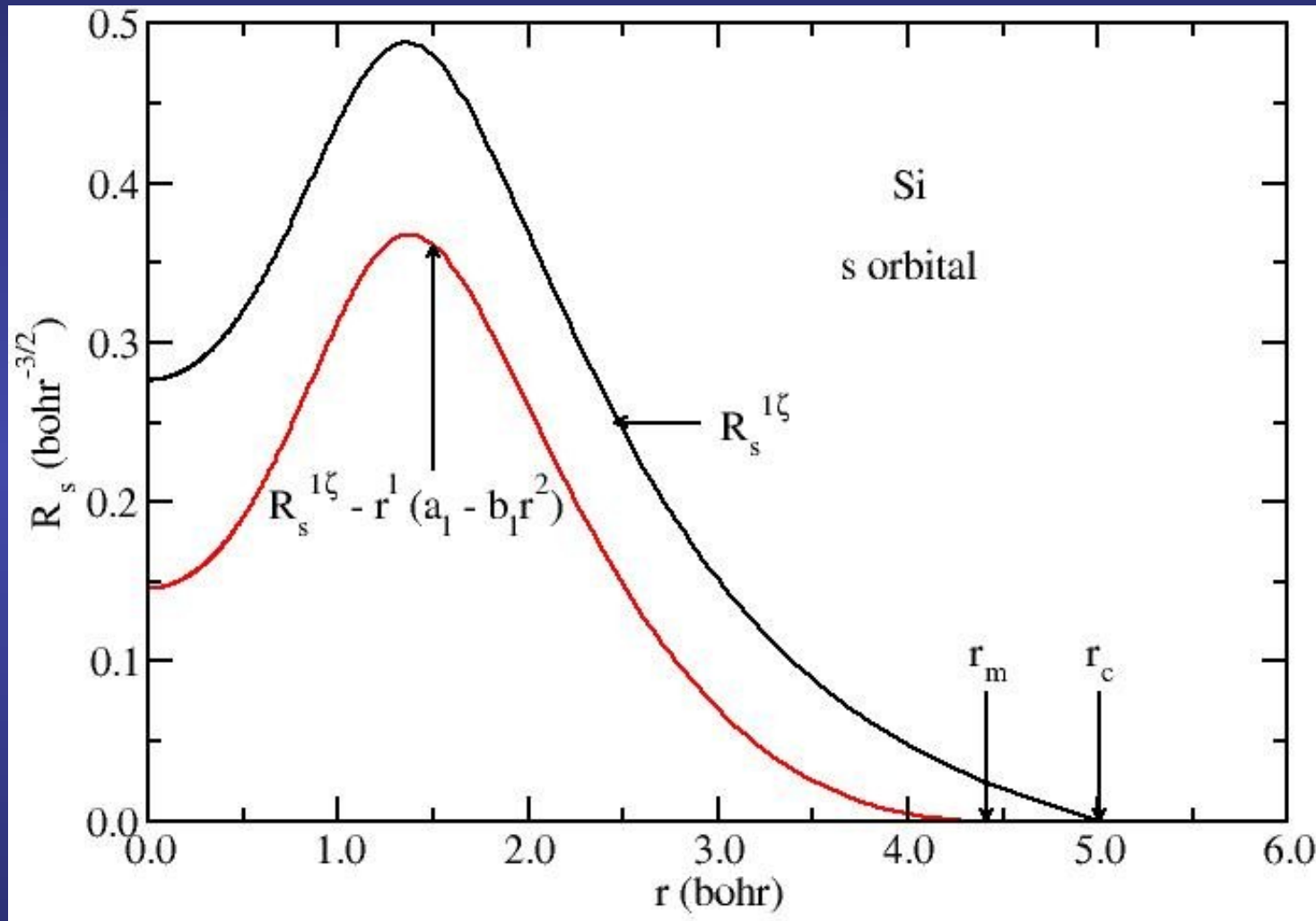
Default mechanism to generate multiple- ζ in SIESTA: “Split-valence” method



And continuous smoothly towards the origin as $r^l (a_l - b_l r^2)$

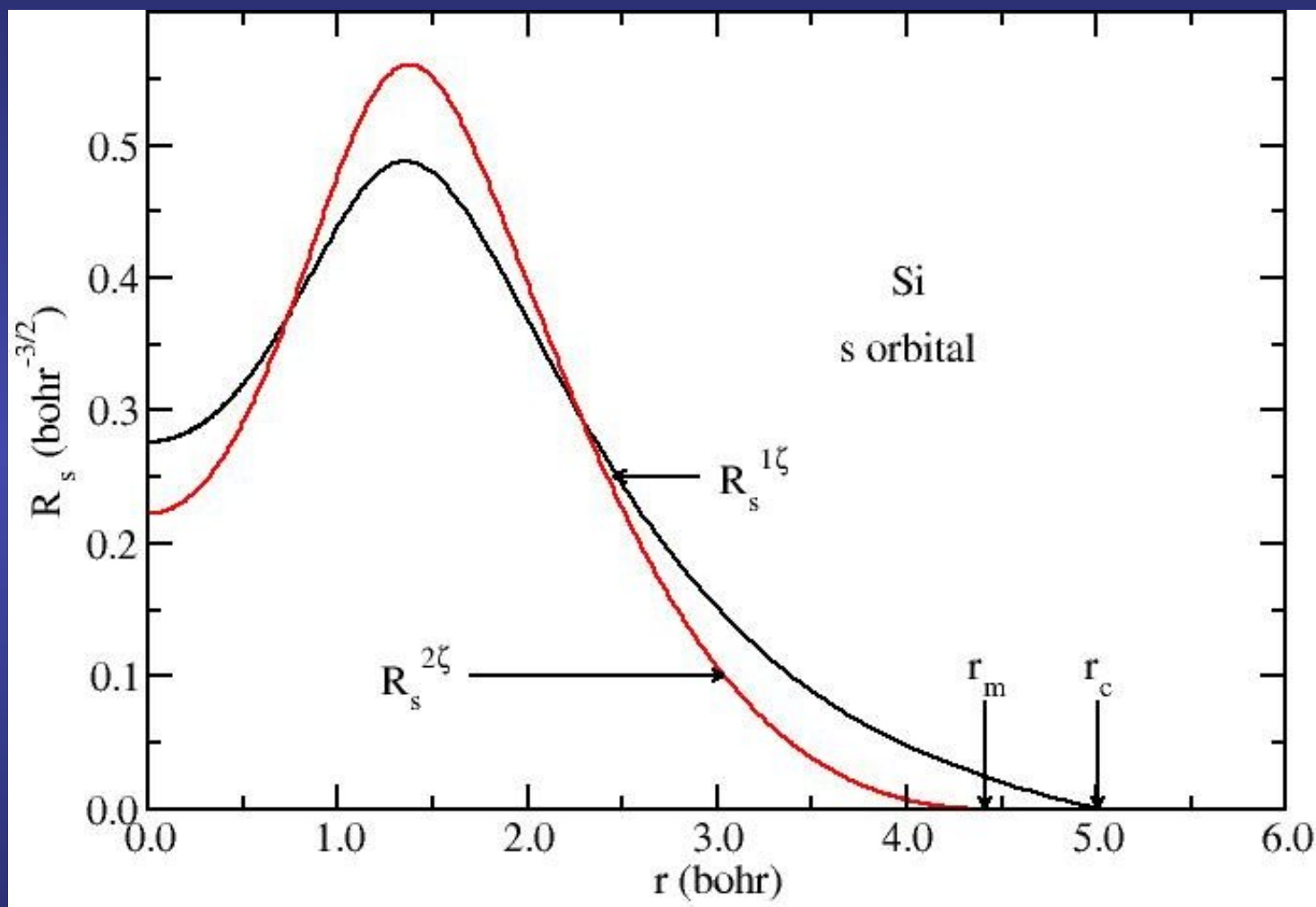
(two parameters: the second- ζ and its first derivative continuous at r_m)

Default mechanism to generate multiple- ζ in SIESTA: “Split-valence” method



The same Hilbert space can be expanded if we use the **difference**, with the advantage that now the second- ζ vanishes at r_m (more efficient)

Default mechanism to generate multiple- ζ in SIESTA: “Split-valence” method



Finally, the second- ζ is normalized

r_m controlled with **PAO.SplitNorm** (typical value 0.15)

Converging the basis size: from quick and dirty to highly converged calculations

Single- ζ (minimal or SZ)

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

Improving the quality



Radial flexibilization:

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

Multiple- ζ

Angular flexibilization:

Add shells of different atomic
symmetry (different l)

Polarization

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 = 272 meV
Second-zeta:	PAO.BasisType	Split
Range of second-zeta:	PAO.SplitNorm	0.15
Confinement:	Hard well	
Charge state:	Neutral atom	

Reasonably good basis set in terms of accuracy versus efficiency

More global control on the basis with a few input variables: size and range

Size:

Basis size:

PAO.BasisSize

SZ

DZ

SZP

DZP

Range:

Range of first-zeta:

PAO.EnergyShift

0.02 Ry

Range of second-zeta:

PAO.SplitNorm

0.15

The larger both values, the more confined the basis functions

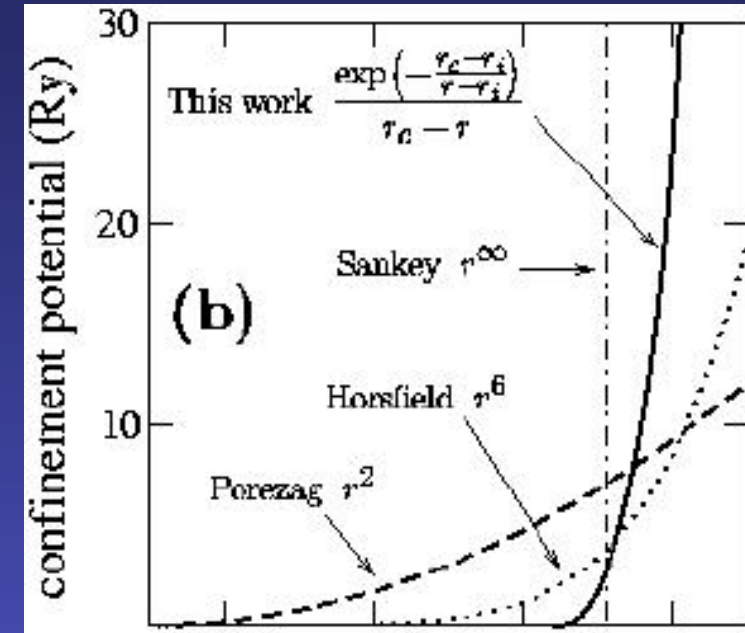
Also possible to control all parameters related to basis set generation using more complex input options

Different proposals for the confinement potentials: Shoft-confinement potential

Available in SIESTA

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

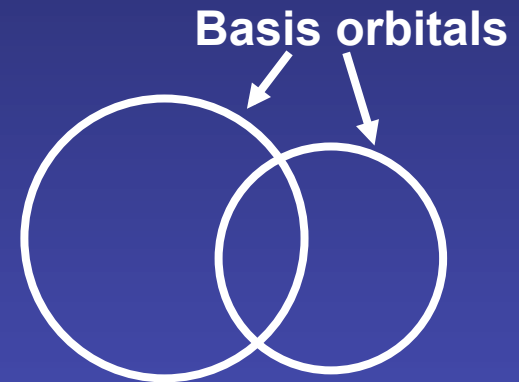
J. Junquera *et al.*, Phys. Rev. B 64, 235111 (2001)



Advantages: orbital continuous with all the derivatives continuous
diverges at r_c (orbital exactly vanishes there)
zero at the core region

Pitfall: two new parameters to play with, more exploratory calculations

Using a localized basis set allows reducing the scaling of the calculation (both computational time and storage)



$O(N)$ number of non-zero elements

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

The one-particle Kohn-Sham hamiltonian

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

Kinetic energy operator

Hartree potential

Exchange-correlation potential

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

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

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

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

Long range

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

Electronic charge density =

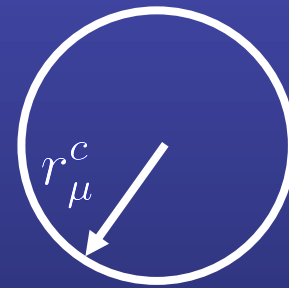
sum of spherical atomic densities +

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 $r_I^c = \max_l r_{Il}^c$

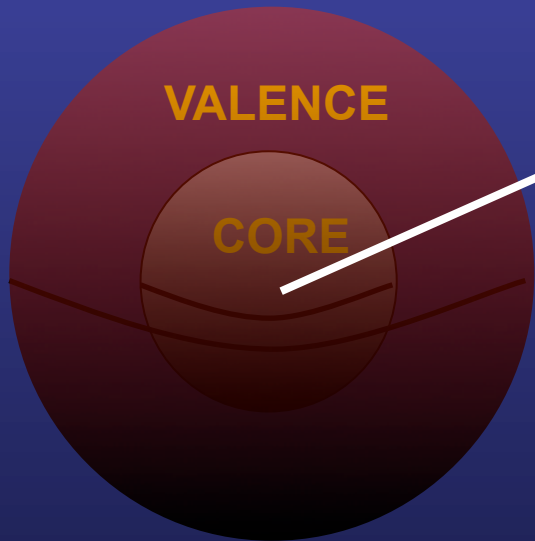
The local part is screened by the potential generated by an atomic electron density

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

Neutral atom potential

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

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

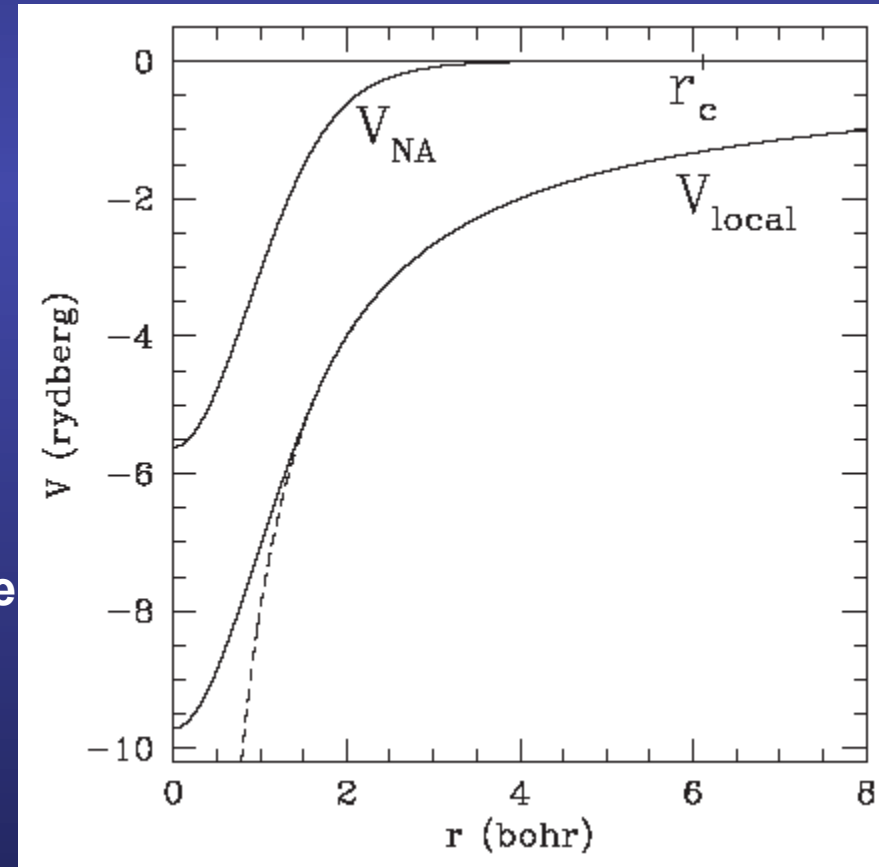


$$V_I^{NA}(\vec{r}) = 0$$

Potential outside the sphere vanishes

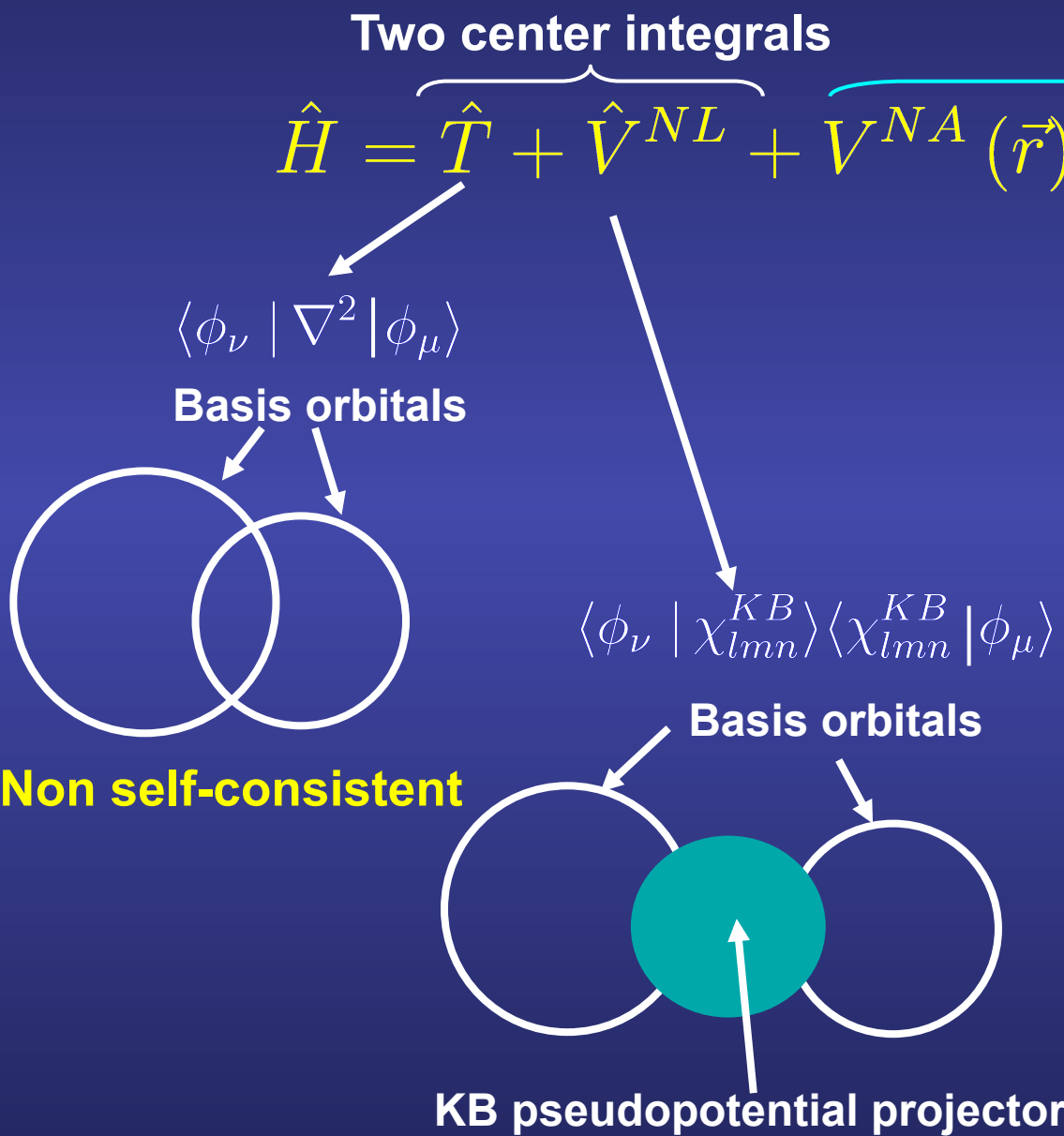
(Gauss theorem \Rightarrow generated by the total charge inside the sphere = 0 if neutral atom)

Vanishes exactly at r_c

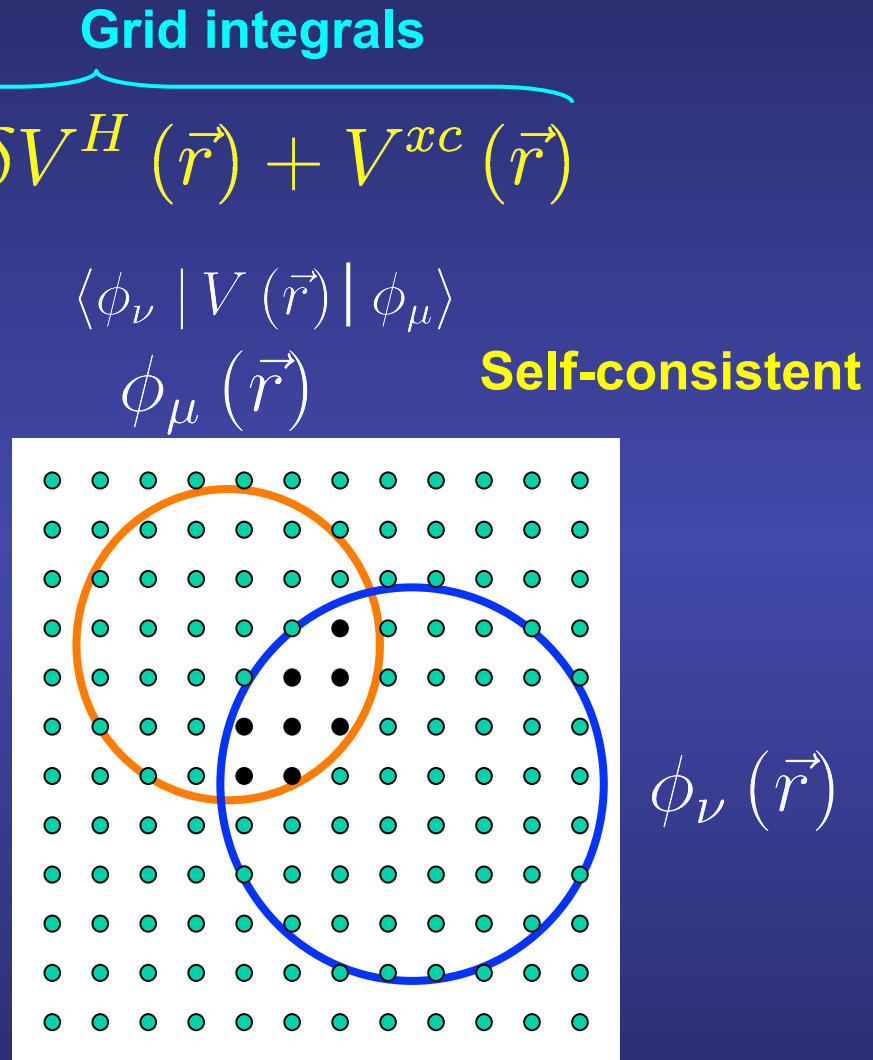


The hamiltonian computed in SIESTA, combination of two and three center matrix elements

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

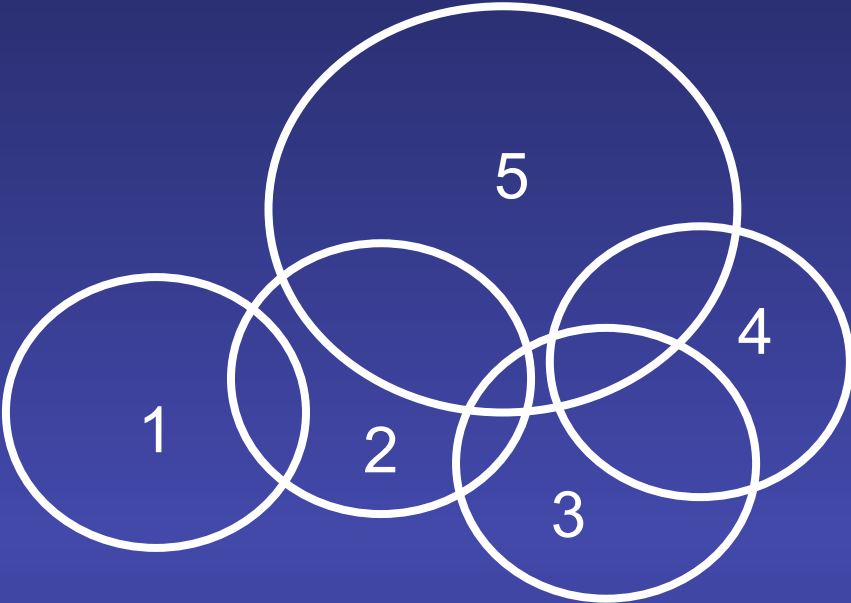
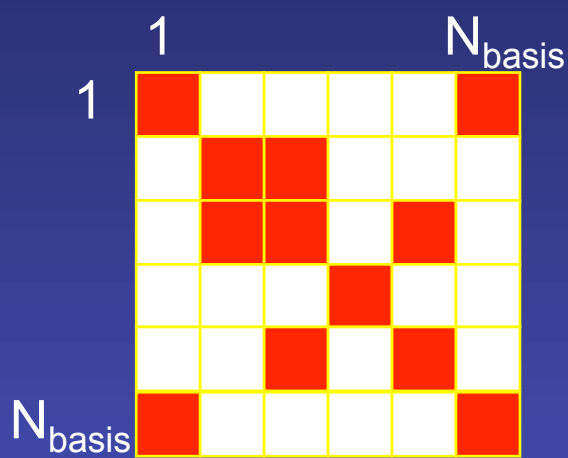


Computed in reciprocal space and tabulated



Three-dimensional real space grid

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

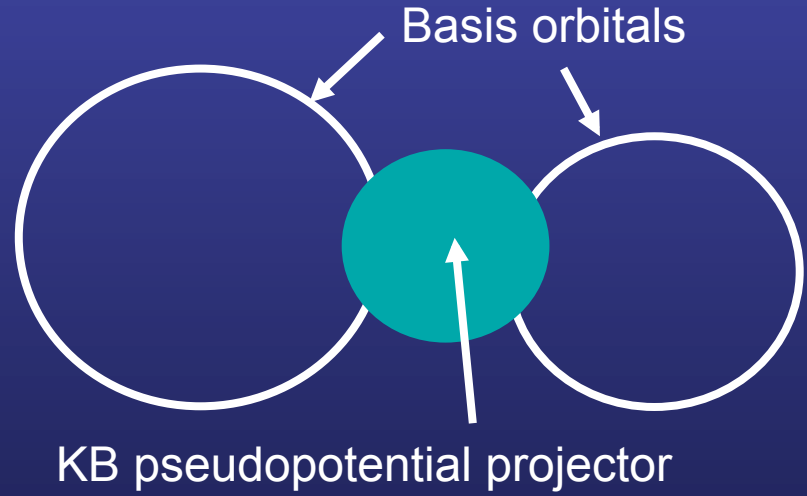


- 1 with 1 and 2
- 2 with 1,2,3, and 5
- 3 with 2,3,4, and 5
- 4 with 3,4 and 5
- 5 with 2,3,4, and 5

Sparse = many entries of the matrix are zero

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

Non-overlap interactions



Two center integrals are calculated in Fourier space (using radial FFT)

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

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

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

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

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).

We use real spherical harmonics for computational efficiency

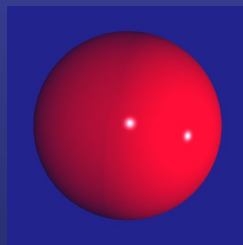
$$Y_{lm}(\theta, \varphi) = C_{lm} P_l^m(\cos\theta) \begin{cases} \sin(m\varphi) & \text{if } m < 0 \\ \cos(m\varphi) & \text{if } m \geq 0 \end{cases}$$

Normalization factors

Associated Legendre polynomials

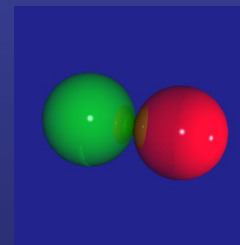
$l = 0$

$m = 0$

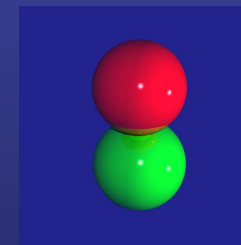


$l = 1$

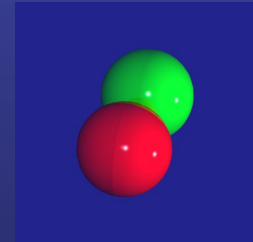
$m = -1$



$m = 0$



$m = +1$



Pictures courtesy of Victor Luaña

The density matrix, a basic ingredient of SIESTA

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

“Partial” calculation of the density matrix and the work on the grid

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

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

$$E_B = \sum_{\mu\nu} \rho_{\mu\nu} H_{\nu\mu}$$

Only those elements of $\rho_{\mu\nu}$ such that $S_{\mu\nu}$ or $H_{\mu\nu}$ are non-zero

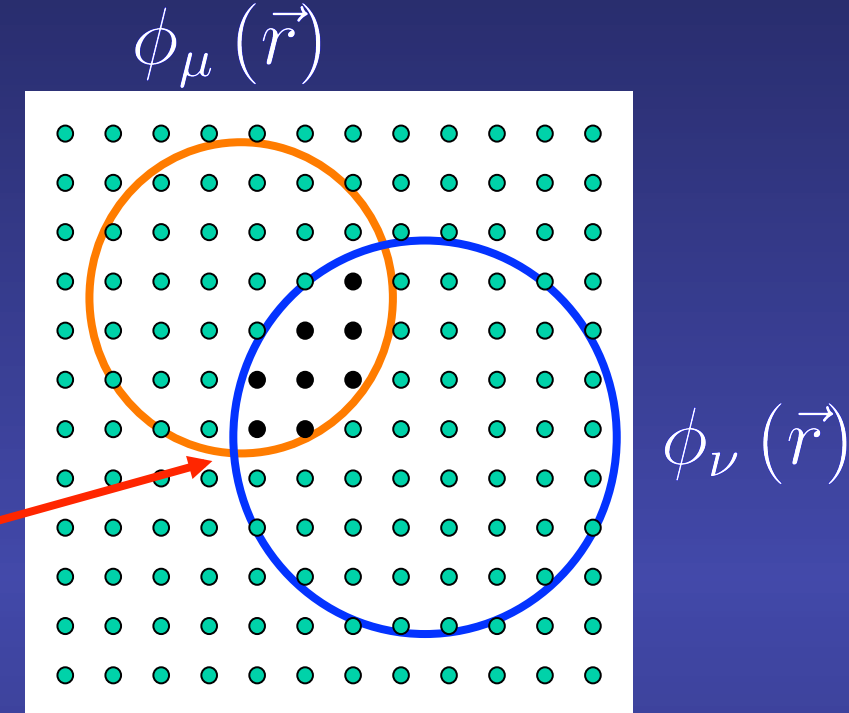
Only those elements of $\rho_{\mu\nu}$ such that μ and ν have some overlap

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

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

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

$\rho(r)$ only in those grid points where it is not trivially zero



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)

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

$$\delta\rho(\vec{r}) = \rho(\vec{r}) - \rho_{atoms}(\vec{r}) \quad \delta\rho(\vec{r}) \xrightarrow{FFT} \delta V^H(\vec{r})$$

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 artificially), we can expand the density in a Fourier series

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

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

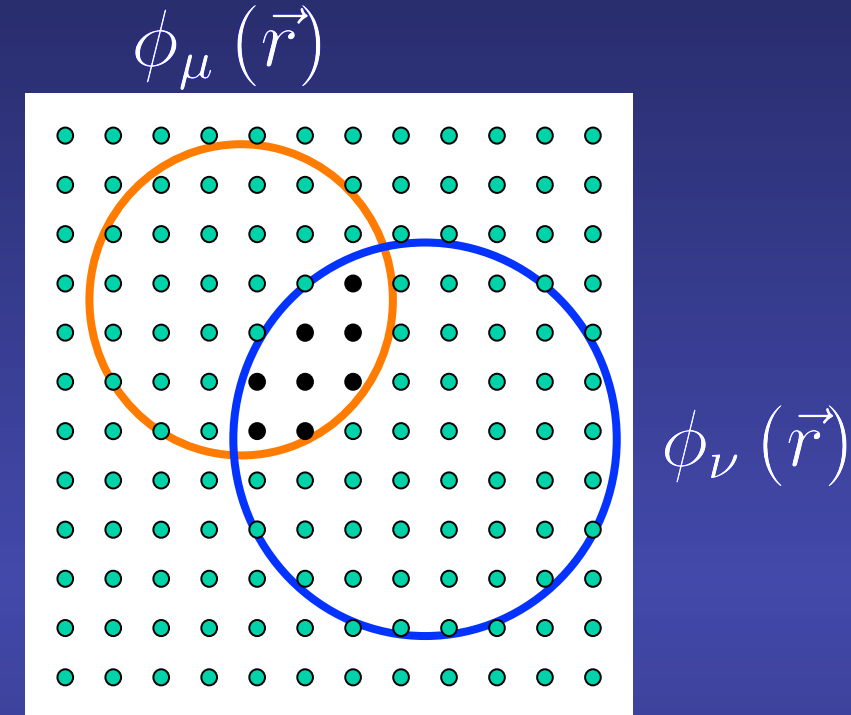
FFT scales as $N \log(N)$

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

Multigrid techniques also available, although there are seldom competitive with FFT. However, they allow treating isolated charged systems exactly.

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

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



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

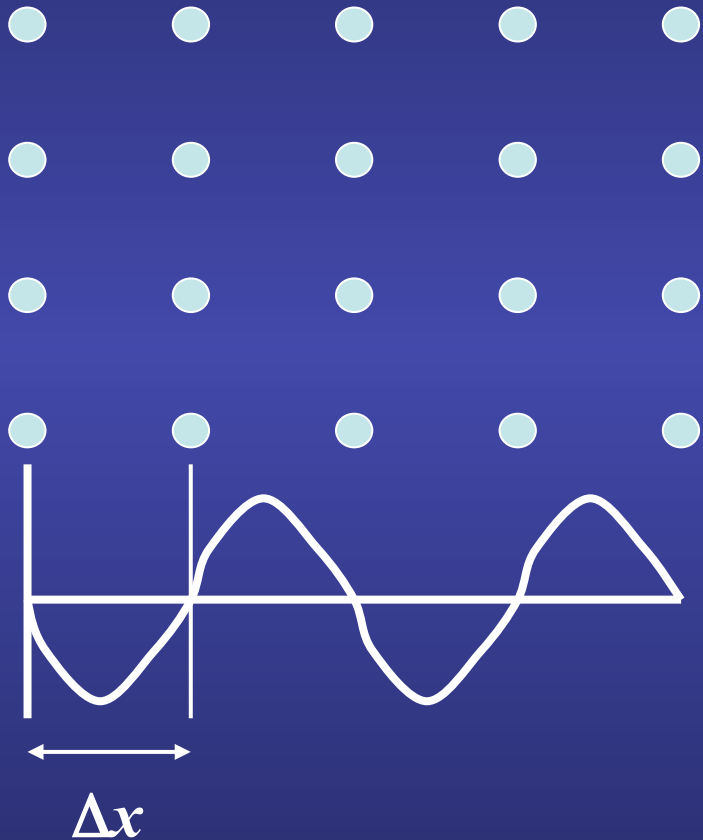
$$V(\vec{r}) = V^{NA}(\vec{r}) + \delta V^H(\vec{r}) + V^{xc}(\vec{r})$$

$$\int d\vec{r} \phi_{\nu}^*(\vec{r}) V(\vec{r}) \phi_{\nu}(\vec{r}) \approx \sum_i \phi_{\nu}^*(\vec{r}) V(\vec{r}) \phi_{\nu}(\vec{r}) \Delta\vec{r}$$

Volume per grid point

Fineness of the grid controlled by a single parameter, the “mesh cutoff”

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



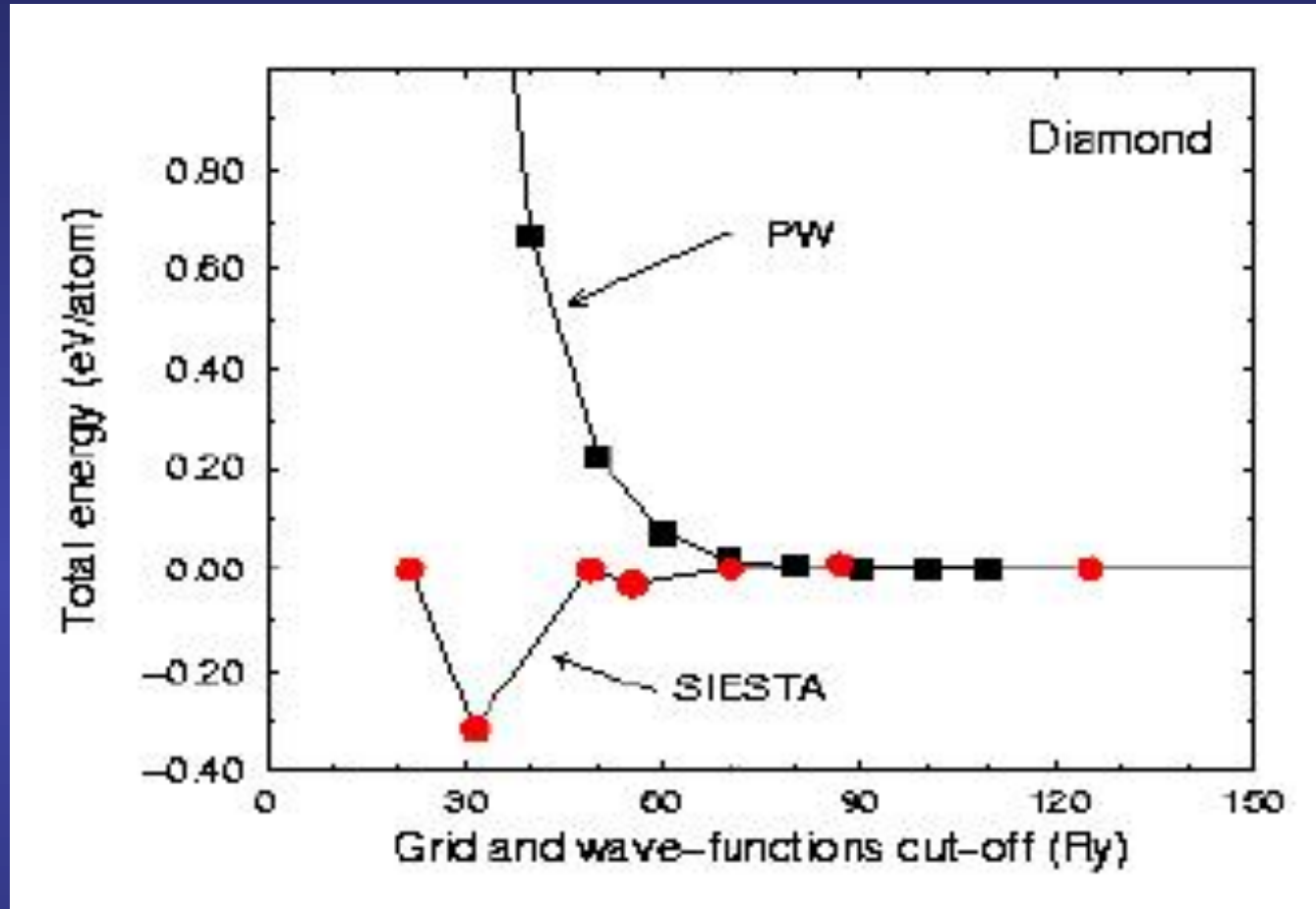
$$\Delta x \implies k_c = \frac{\pi}{\Delta x} \implies E_c = \frac{\hbar^2 k_c^2}{2m_e}$$

In the **grid**, we represent the **density** \Rightarrow grid cutoff **not directly comparable**

with the **plane wave cutoff** to represent wave functions

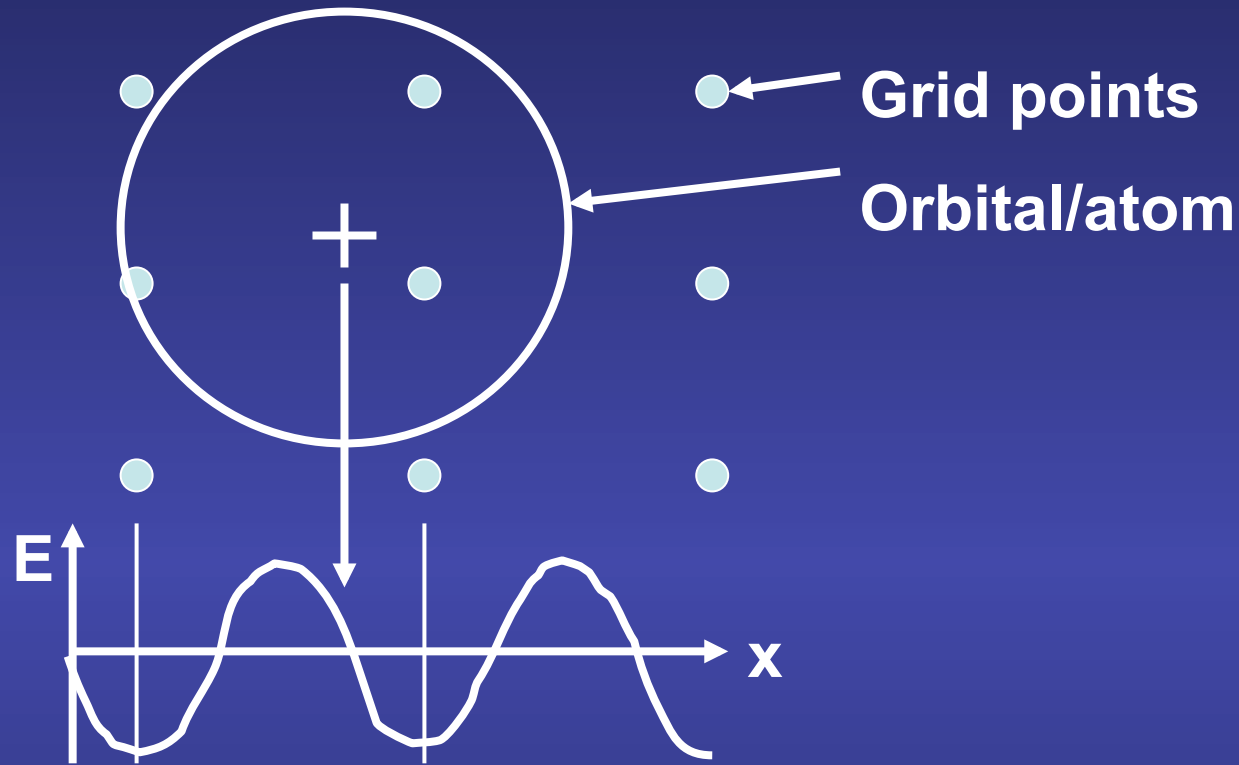
(Strictly speaking, the density requires a value four times larger)

Convergence of the results with the mesh cutoff



$$E_{cut} = \left(\frac{\pi}{\Delta x} \right)^2$$

The grid breaks traslation symmetry, the “eggbox” effect



Affects more to forces than to energy

Solutions:

- Increase cutoff (computational effort in time and memory)
- “Grid-cell sampling”
- Filter the atomic orbitals [E. Anglada *et al.* Phys. Rev. B 73, 115122 (2006)]

Once the hamiltonian and the overlap matrices have been built, we have to solve the Schrodinger equation

$$\begin{pmatrix} H \\ N \times N \end{pmatrix} \begin{pmatrix} C \\ N \times 1 \end{pmatrix} = E_{n\vec{k}} \begin{pmatrix} S \\ N \times N \end{pmatrix} \begin{pmatrix} C \\ N \times 1 \end{pmatrix}$$

Order-N

Order-N³

Minimization of an energy functional

Standard diagonalization techniques

Not valid for metals or “dirty” gap systems

Both eigenvectors and eigenvalues available

Recent SIESTA versions have available other possibilities:

- Iterative diagonalization $N^2 \times N_{\text{occ}}$
- PEXSI algorithm N^2
- RT-TDDFT
- ...

~ 100

N (# atoms)

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

$$\begin{pmatrix} H \\ N \times N \end{pmatrix} \begin{pmatrix} C \\ N \times 1 \end{pmatrix} = E_{n\vec{k}} \begin{pmatrix} S \\ N \times N \end{pmatrix} \begin{pmatrix} C \\ N \times 1 \end{pmatrix}$$

Serial:

BLAS

LAPACK

Parallel:

BLACS

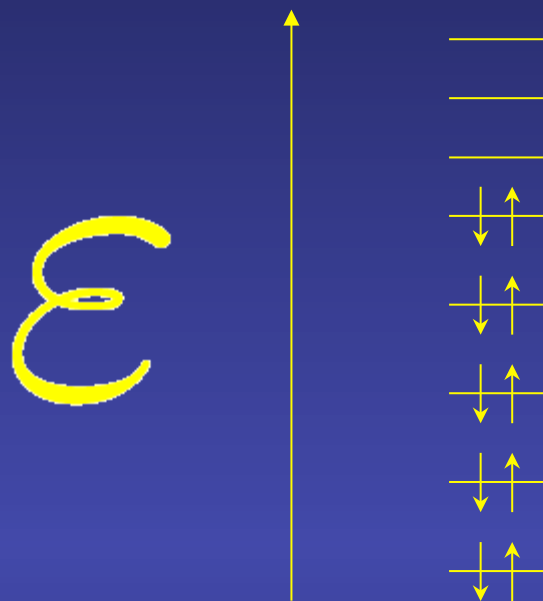
SCALAPACK

ELPA (over orbitals,
Gamma point, no SO)

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



$$n^\sigma(\vec{r}) = \sum_i f_i^\sigma |\psi_i^\sigma(\vec{r})|^2$$

Occupation numbers

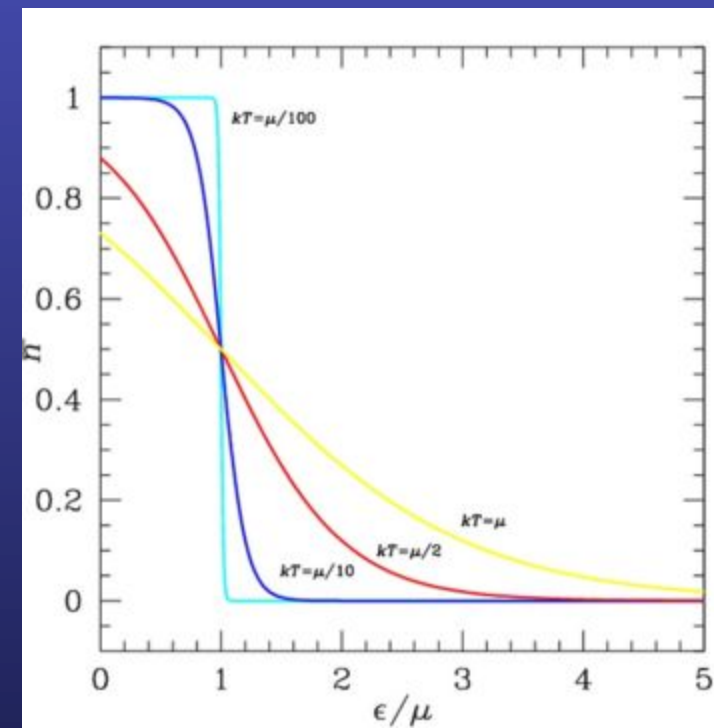
The ground state has one (or two if spin independent) in each of the orbitals with the lowest eigenvalues

A smearing of the electronic occupation might be done:

Fermi-Dirac (Occupation Function FD)

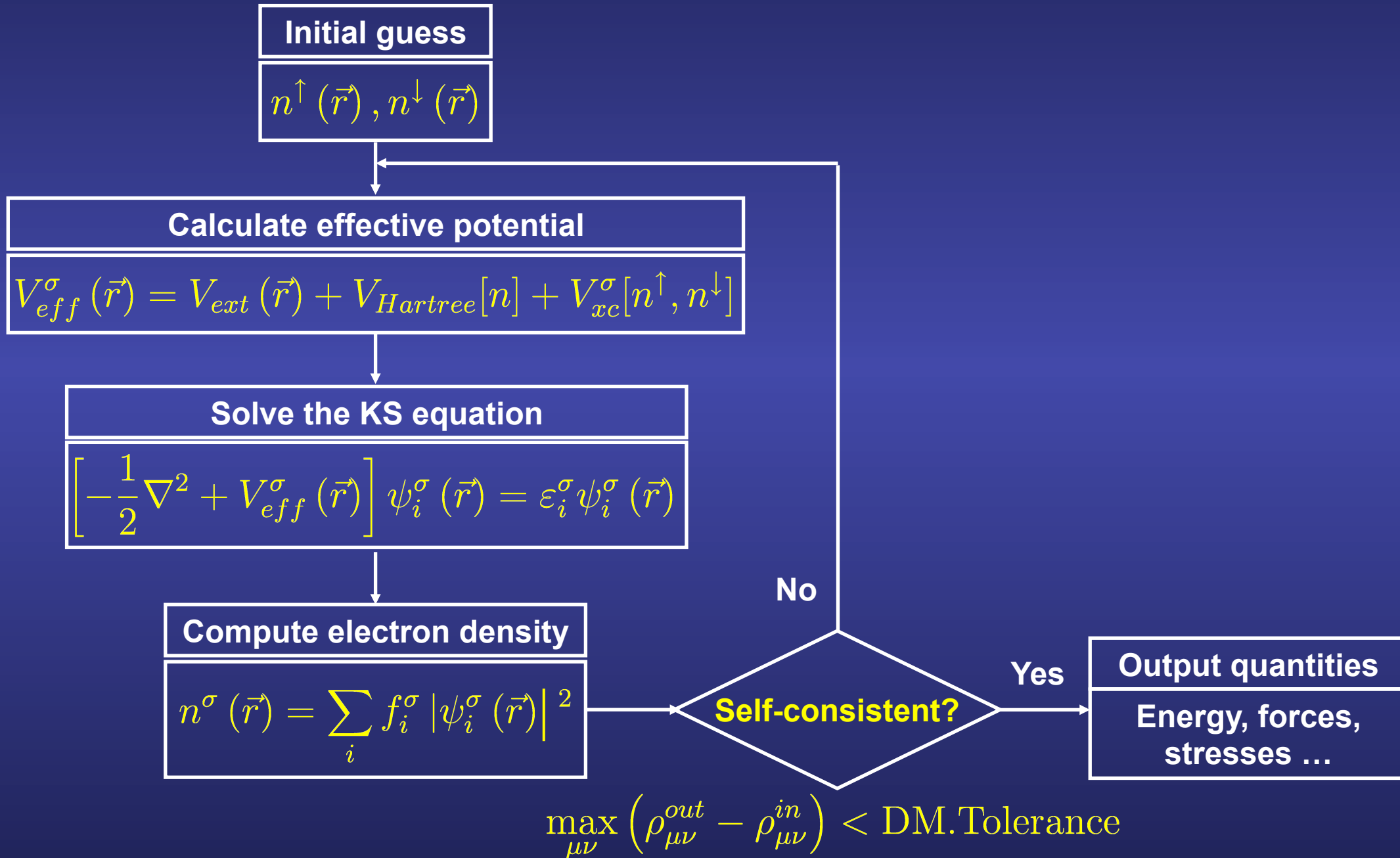
Electronic Temperature

Methfessel Paxton (Occupation Function MP)



The Kohn-Sham equations must be solved self-consistently

The potential (input) depends on the density (output)



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

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

$$\sigma_{\alpha\beta} = \frac{\partial E^{KS}}{\partial \epsilon_{\alpha\beta}} \quad \epsilon_{\alpha\beta} \equiv \text{strain tensor}$$

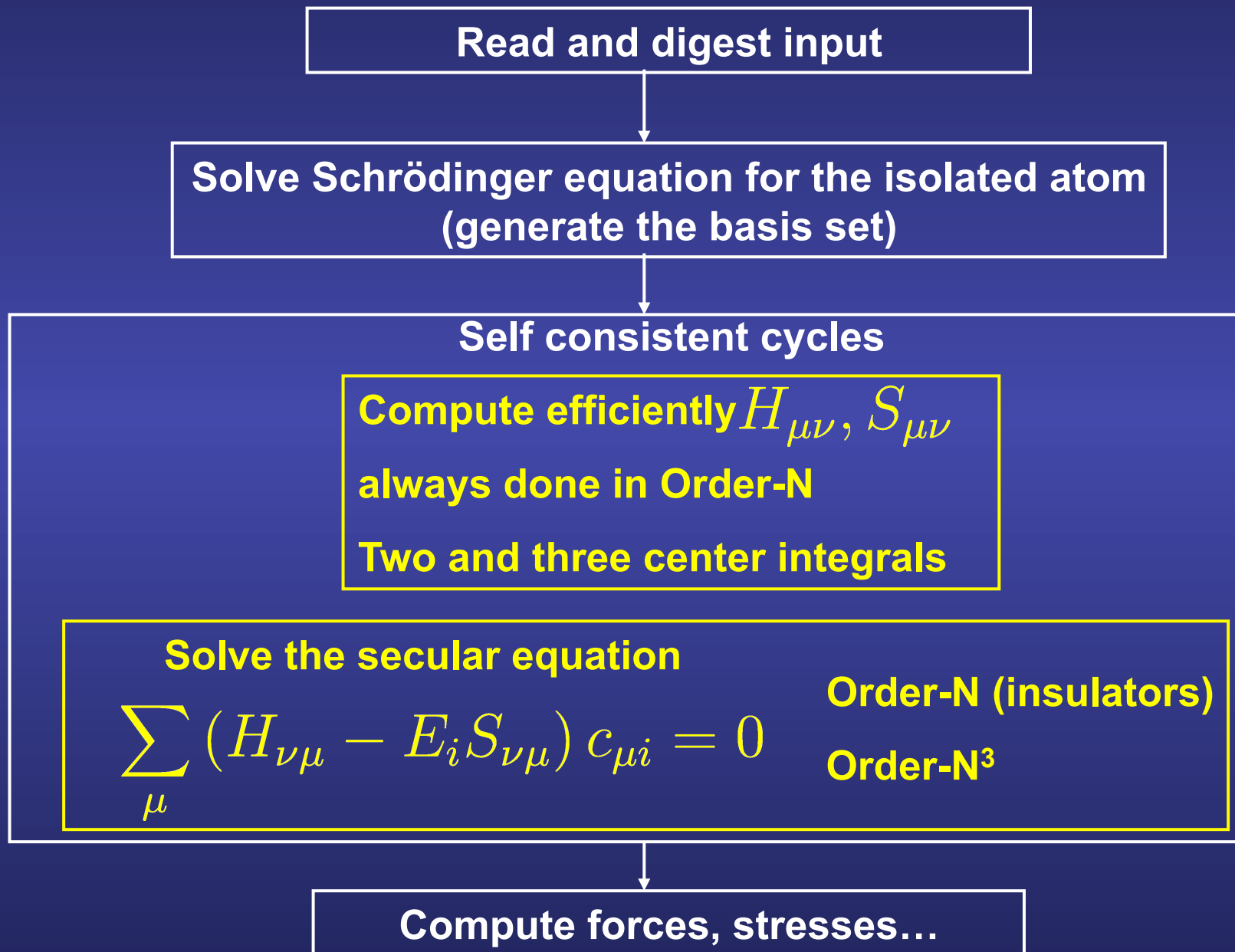
“One piece of energy \Rightarrow one piece of force and stress”

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



Supplementary information

Two center integrals are calculated in Fourier space

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

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

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

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

Fourier transform of the atomic orbitals

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

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

The goal now is to compute the Fourier coefficients of the atomic functions

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

Introducing the plane wave expansion in spherical harmonics and operating

$$e^{i\vec{k} \cdot \vec{r}} = \sum_{l=0}^{\infty} \sum_{m=-l}^l 4\pi i^l j_l(kr) Y_{lm}^*(\hat{k}) Y_{lm}(\hat{r})$$

$$\psi(\vec{k}) = \sum_{l=0}^{l_{max}} \sum_{m=-l}^l \psi_{lm}(k) Y_{lm}(\hat{k})$$

$$\psi_{lm}(k) = \sqrt{\frac{2}{\pi}} (-i)^l \int_0^{\infty} r^2 j_l(kr) \psi_{lm}(kr) dr$$

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 artificially), 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 its 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

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

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

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

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

A finer grid is required for GGA

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