Code structure: calculation of matrix elements of H and S. Direct diagonalization

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

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

Javier Junquera

José M. Soler

UC UNIVERSIDAD DE CANTABRIA

UAM

Most important reference followed in this lecture

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

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

Expansion of the eigenvectors in a basis of localized atomic orbitals

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

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

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

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

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

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

Derivation of the secular equation at Gamma

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**

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

Transposing everything to the left hand side term

$$\sum_{\mu} \left(\int d\vec{r} \; \phi_{\nu}^{*}(\vec{r}) \hat{H} \phi_{\mu}(\vec{r}) - E_i \int d\vec{r} \phi_{\nu}^{*}(\vec{r}) \phi_{\mu}(\vec{r}) \right) c_{\mu i} = 0$$

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)

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

$$\rho^{atom}\left(\vec{r}\right) = \sum_{I} \rho_I^{atom}\left(\vec{r}\right)$$

r_μ^c $\phi_\mu\left(\vec{r}\right)$

Populate basis function with appropriate valence atomic charges

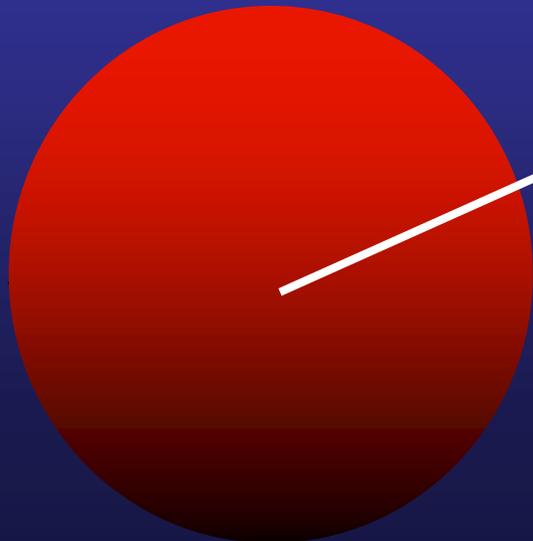ρ_I^{atom} **exactly vanishes beyond** $r_I^c = \max_l r_{Il}^c$

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

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

Neutral atom potential

Vanishes exactly ar r_c

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

$$V_I^{NA}\left(\vec{r}\right) \equiv V_I^{local}\left(\vec{r}\right) + V_I^{atom}\left(\vec{r}\right)$$
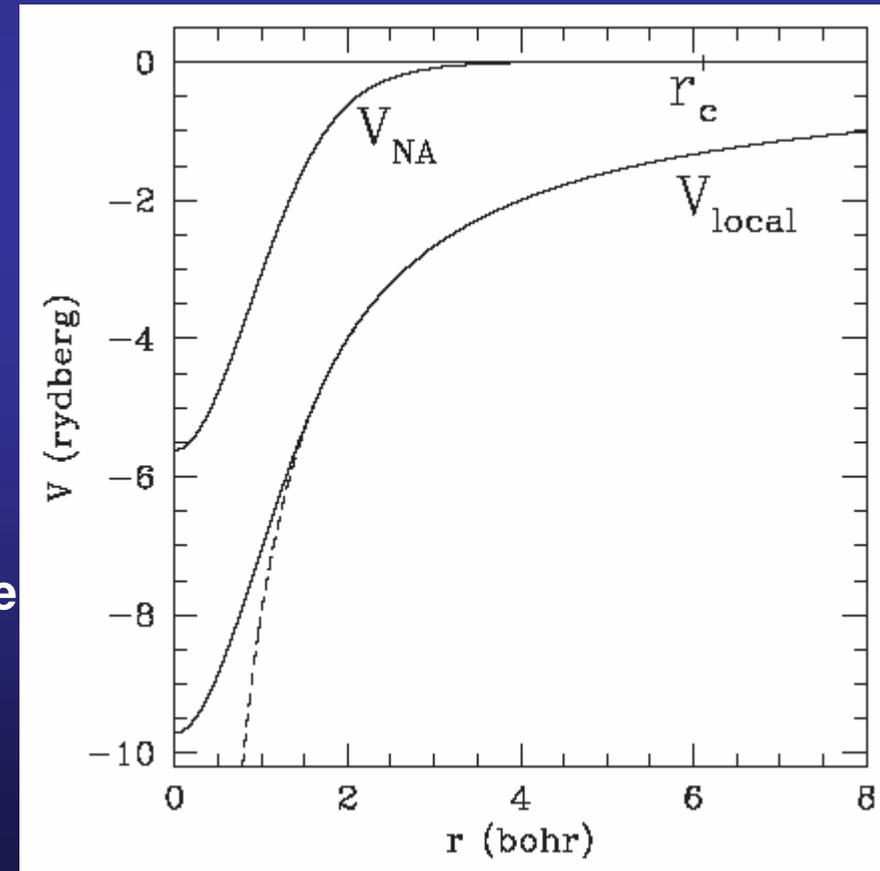
$$V_I^{NA}\left(\vec{r}\right) = 0$$

Potential outside the sphere vanishes

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

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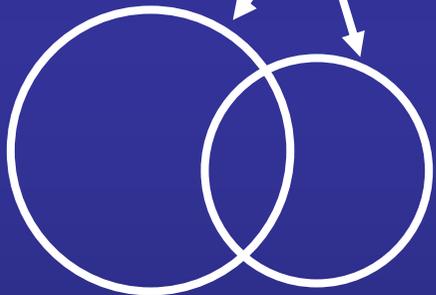
Two center integrals

Three center integrals

$$\hat{H} = \hat{T} + \hat{V}^{NL} + V^{NA}(\vec{r}) + \delta V^{H}(\vec{r}) + V^{xc}(\vec{r})$$
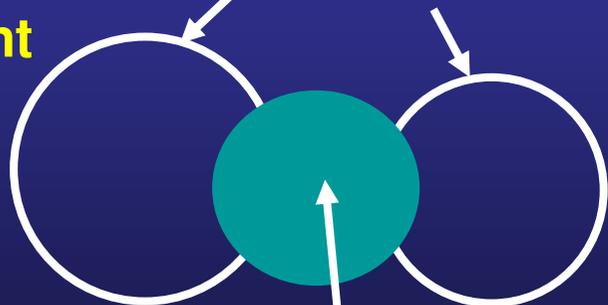
$\langle \phi_\nu | \nabla^2 | \phi_\mu \rangle$

Basis orbitals

Non self-consistent

$\langle \phi_\nu | \chi_{lmn}^{KB} \rangle \langle \chi_{lmn}^{KB} | \phi_\mu \rangle$
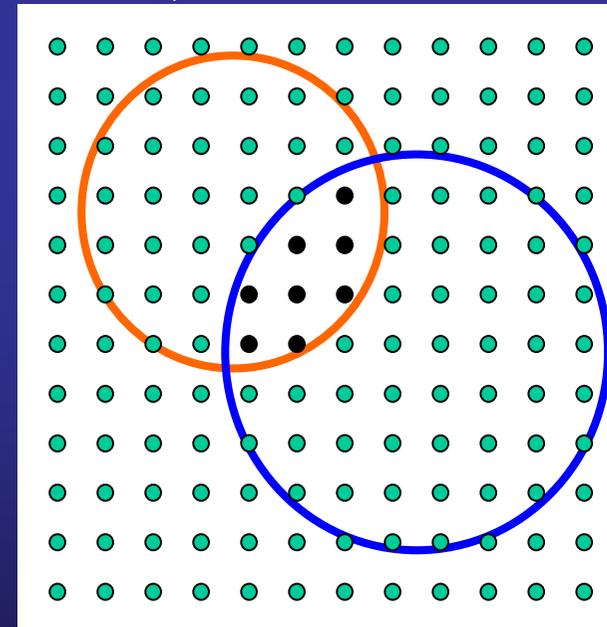
Basis orbitals

KB pseudopotential projector

Computed in reciprocal space and tabulated

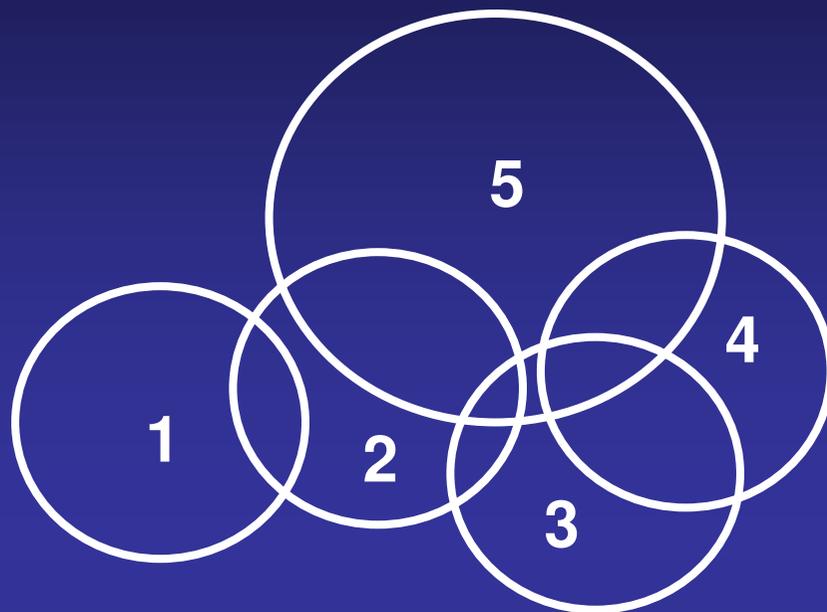$\langle \phi_\nu | V(\vec{r}) | \phi_\mu \rangle$

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

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

Sparse ≡ many entrances of the matrix are zero
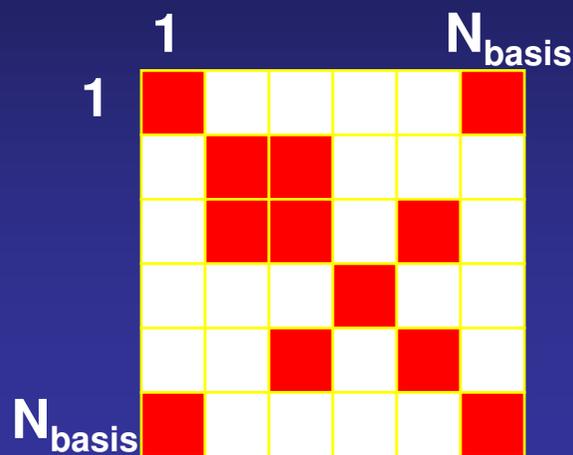
1 with 1 and 2

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

Non-overlap interactions

Basis orbitals

KB pseudopotential projector

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

$\rho_{\mu\nu}$ is not strictly sparse but only a sparse subset is needed
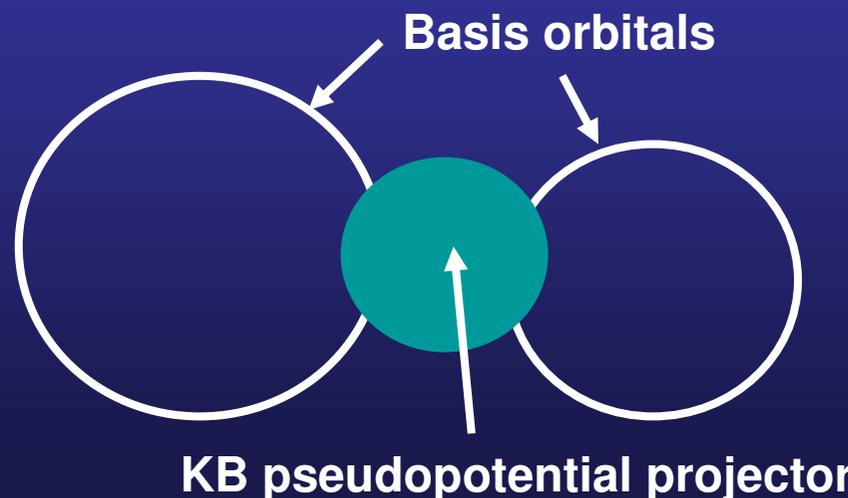
Two center integrals are calculated in Fourier space

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 $\quad f * g \equiv \dfrac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} g(y)\, f(x - y)\, dy$

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).

We use real spherical harmonics for computational efficiency
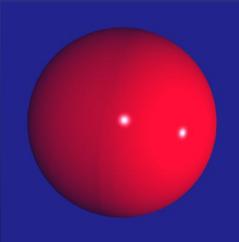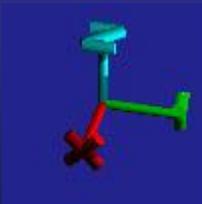
$$Y_{lm}(\theta, \varphi) = C_{lm} P_l^m(cos\theta) \begin{cases} sin(m\varphi) & \text{if } m < 0 \\ cos(m\varphi) & \text{if } m \geq 0 \end{cases}$$

Normalization factors

Associated Legendre polynomials

l = 0

l = 1

m = 0
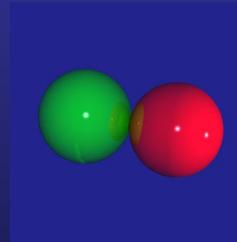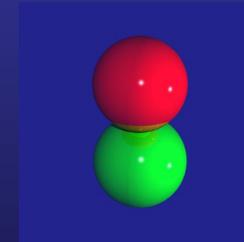
m = -1 m = 0 m = +1

Pictures courtesy of Victor Luaña

The density matrix, a basic ingredient of SIESTA

Expansion of the eigenvectors in a basis of localized atomic orbitals

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

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

The electron density is given by

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

↑

Occupation of state ψ_i

Inserting the expansion into the definition of the density

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

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

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

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

$$\phi_\nu\left(\vec{r}\right)$$
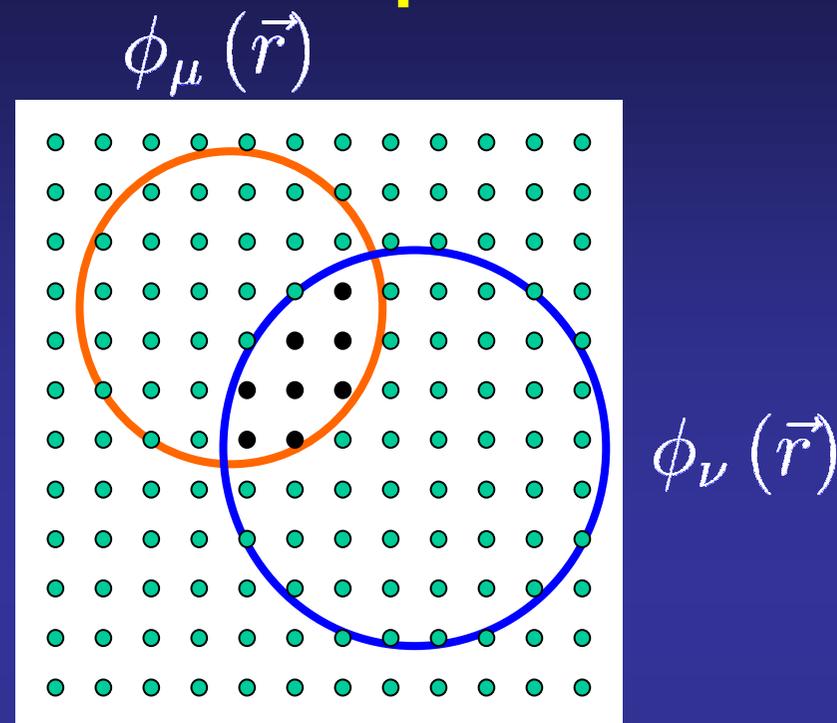
Find all the atomic orbitals that do not vanish at a given grid point

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

Once the density is known, we compute the potentials

EVERYTHING O(N)

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

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

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

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

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

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

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

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

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

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

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

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

Density gradient need not be provided, since they are calculated numerically using the density at the grid points
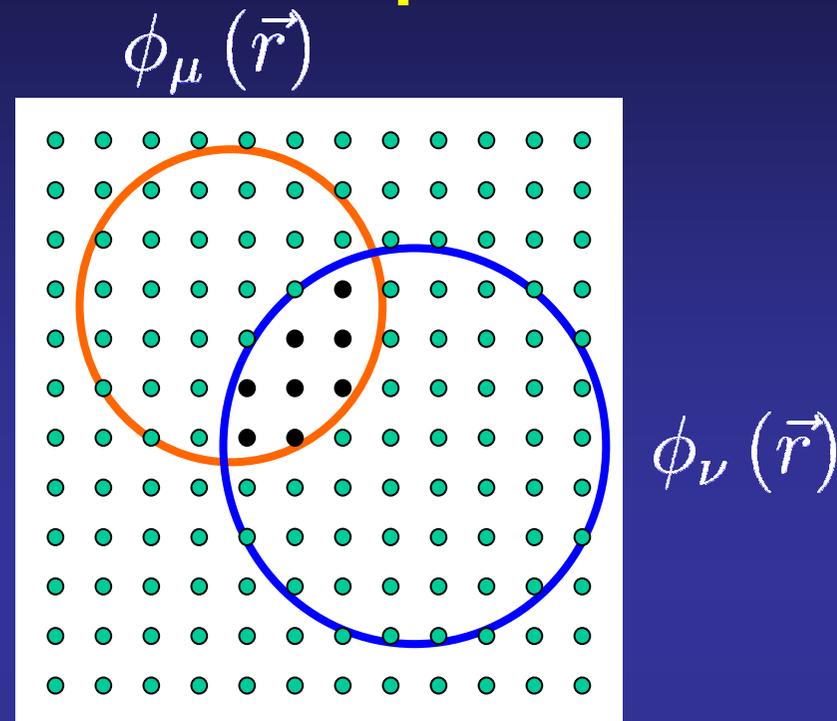
$$\frac{\partial\rho}{\partial x} = \frac{\rho_{i+1} - \rho_{i-1}}{x_{i+1} - x_{i-1}} \Rightarrow E_{xc}^{GGA}\left(\rho_1, \rho_2, \ldots\right)$$

A finer grid is required for GGA

$$V_{xc}^{GGA}\left(\vec{r_i}\right) \equiv \frac{\partial E_{xc}^{GGA}}{\partial\rho_i}$$

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

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

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

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

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

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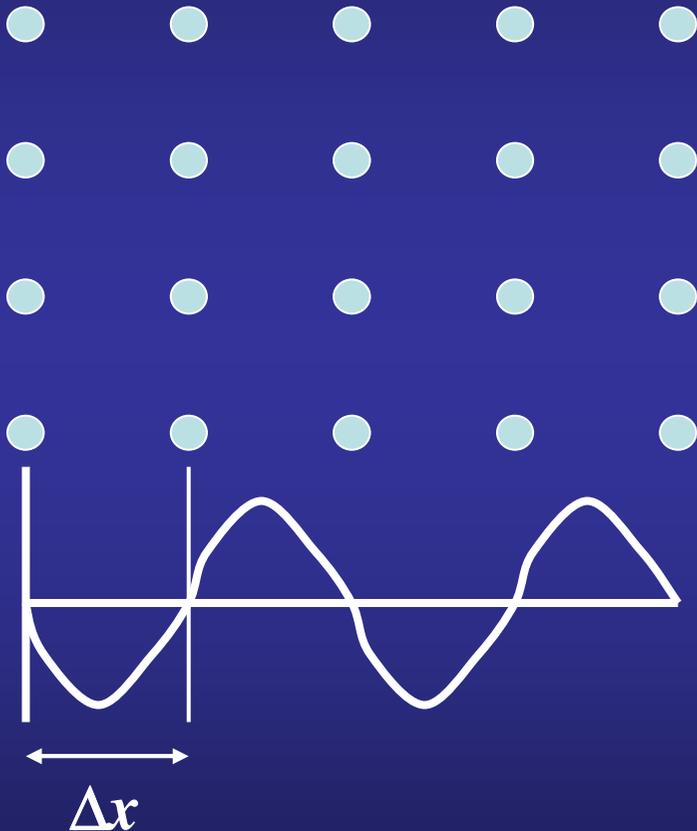
$$\Delta x \implies k_c = \frac{\pi}{\Delta x} \implies E_c = \frac{\hbar^2 k_c^2}{2 m_e}$$

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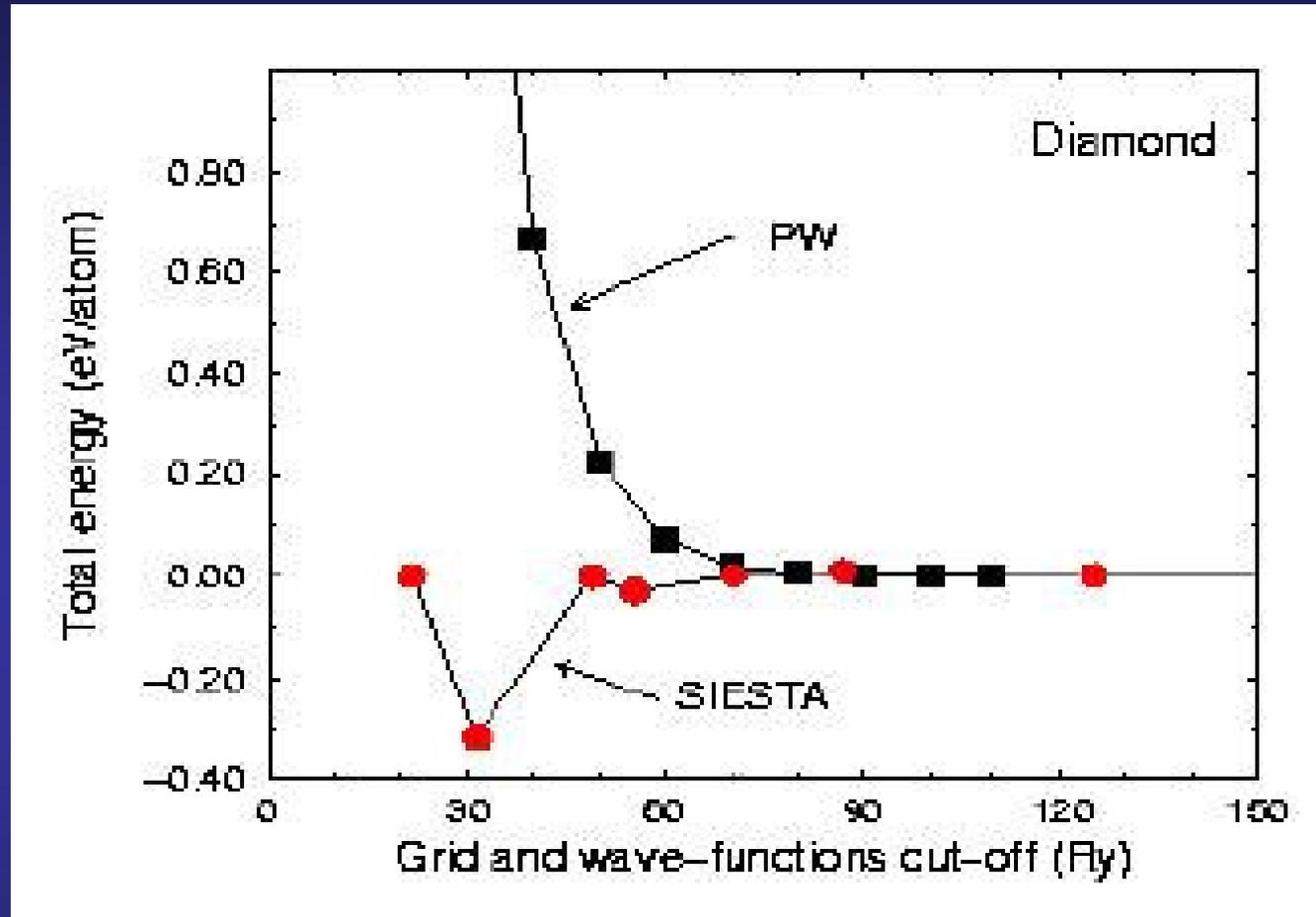
$$E_{cut} = \left(\frac{\pi}{\Delta x} \right)^2$$

The grid breaks traslation symmetry, the "eggbox" effect

Grid points

Orbital/atom

E

X
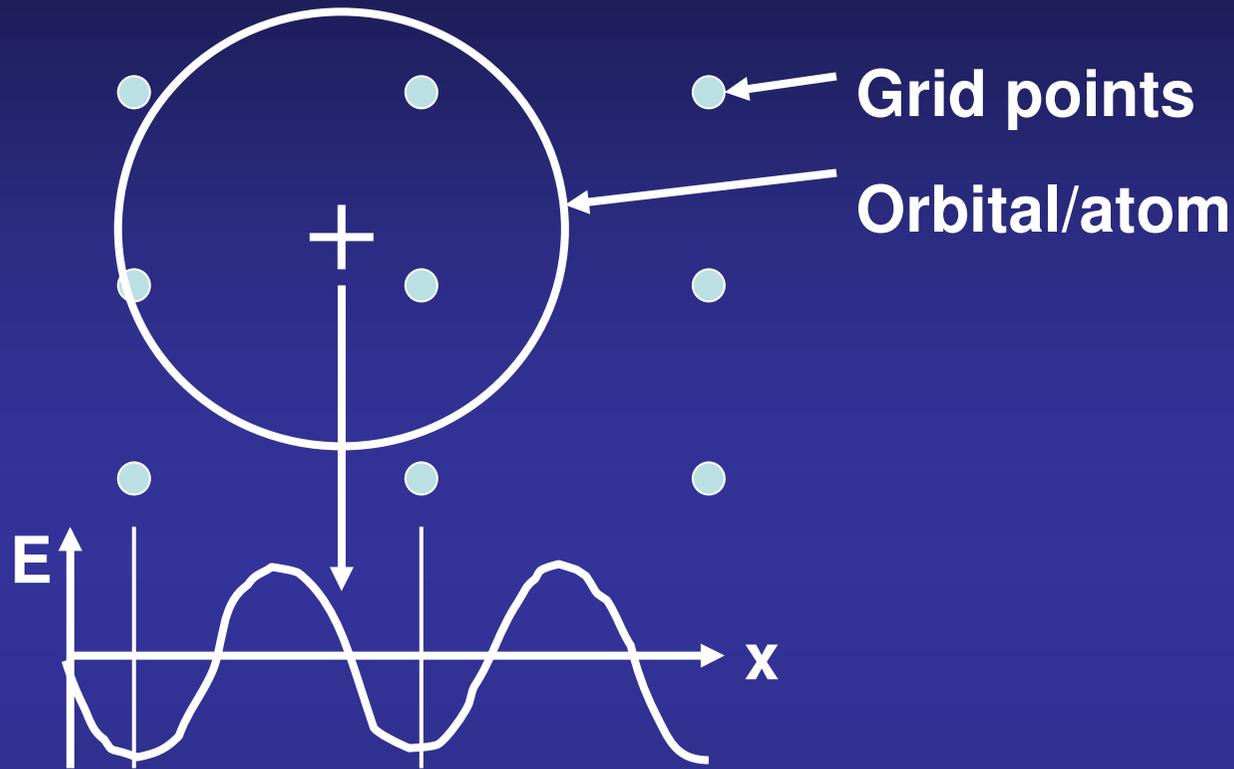
Affects more to forces than to energy

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 are build, we have to solve the Schrodinger equation

$$\left[H \right] \left[C \right] = E_{n\vec{k}} \left[S \right] \left[C \right]$$

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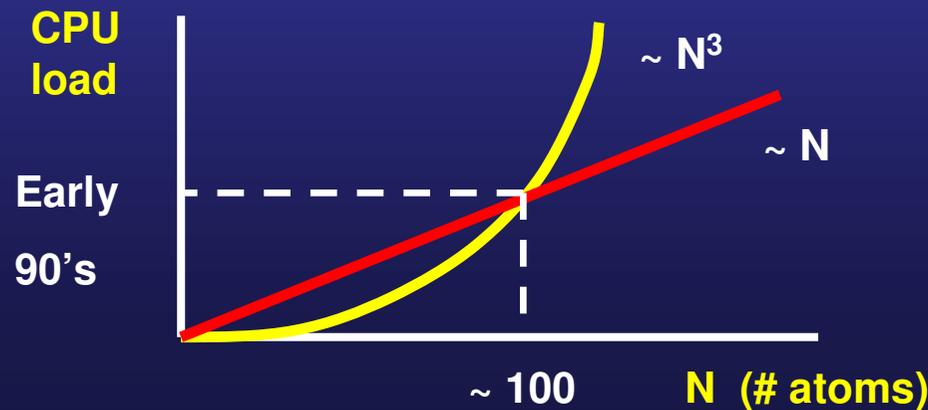
If diagonalization, the generalized eigenvalue problem is solved using standard mathematical libraries

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

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

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)

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

Initial guess

$$n^\uparrow(\vec{r}), n^\downarrow(\vec{r})$$

Calculate effective potential

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

Solve the KS equation

$$\left[-\frac{1}{2}\nabla^2 + V_{eff}^\sigma(\vec{r})\right]\psi_i^\sigma(\vec{r}) = \varepsilon_i^\sigma\psi_i^\sigma(\vec{r})$$

Compute electron density

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

Self-consistent?

No

Yes

Output quantities

Energy, forces, stresses …

$$\max_{\mu\nu}\left(\rho_{\mu\nu}^{out} - \rho_{\mu\nu}^{in}\right) < \mathrm{DM.Tolerance}$$
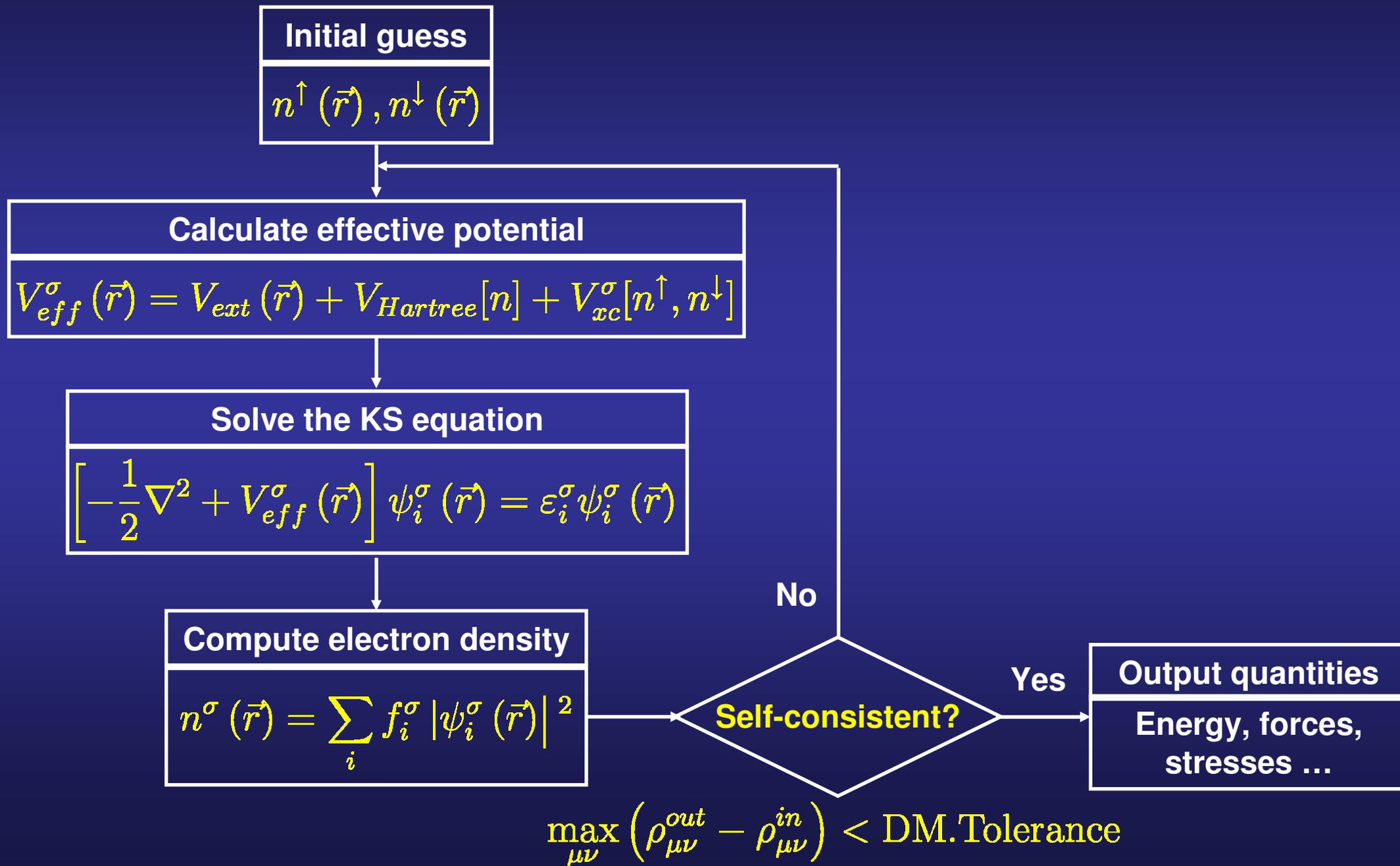
The Kohn-Sham total energy can be written as a sum of the band structure (BS) energy + 'double-count' corrections

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

After SCF

Eigenvectors of the Hamiltonian

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

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**

$$\left.\begin{array}{l} + \dfrac{1}{2} \sum_{IJ} U^{NA}_{IJ} (R_{IJ}) \\[2em] + \sum_{I<J} \delta U^{local}_{IJ} (R_{IJ}) \end{array}\right\}$$ **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

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

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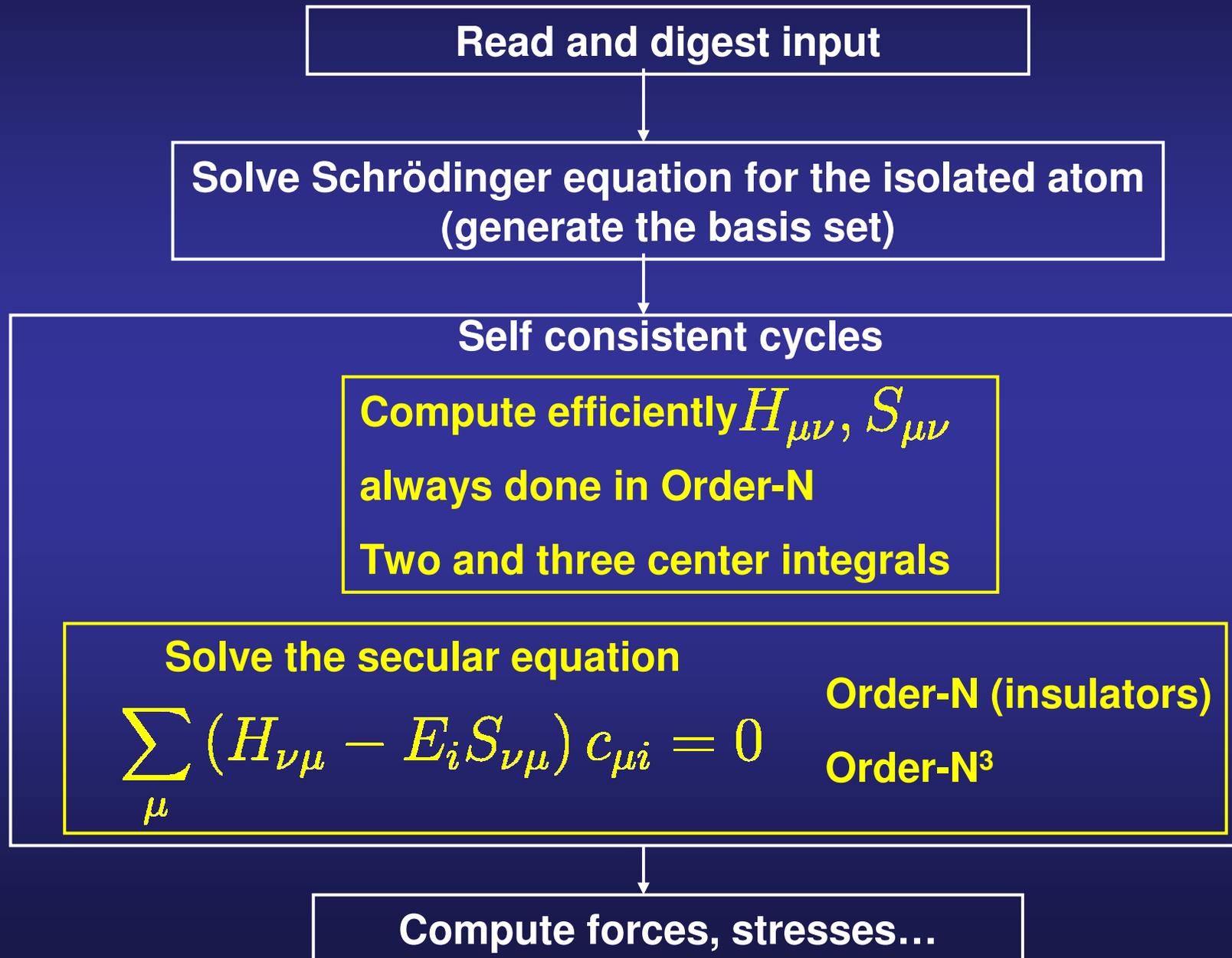
$$\epsilon_{\alpha\beta} \equiv \text{strain tensor}$$

"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

Read and digest input

Solve Schrödinger equation for the isolated atom
(generate the basis set)

Self consistent cycles

Compute efficiently $H_{\mu\nu}, S_{\mu\nu}$

always done in Order-N

Two and three center integrals

Solve the secular equation

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

Order-N (insulators)

Order-N³

Compute forces, stresses…

Suplementary information

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

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

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

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