DFT / SIESTA algorithms

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References

http://siesta.icmab.es → Documentation → Tutorials

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]

Atomic units

$e = m_e = \hbar = 1$

atomic mass unit $= m_e$

atomic length unit $=$ 1 Bohr $=$ 0.5292 Ang

atomic energy unit $=$ 1 Hartree $=$ 27.2 eV

SIESTA energy unit $=$ 1 Ry $=$ 0.5 Hartree $=$ 13.6 eV

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

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

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

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

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

Hartree potential

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

Exchange-correlation potential

(Assume LDA approach)

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

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

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

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

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

Exchange-correlation functional

Spin dependency:

- Unpaired electrons
- Non-singlet states
- Ferromagnetic solids

$$E_{xc}\left[\rho_{\uparrow}(\mathbf{r}),\rho_{\downarrow}(\mathbf{r})\right] \Rightarrow V_{xc}^{\uparrow\downarrow}(\mathbf{r})$$

fdf labels:

- SpinPolarized
- FixSpin
- TotalSpin
- XC.Functional
- XC.Authors

Local density approximation (LDA):

$$V_{xc}\left(\rho(\mathbf{r})\right)$$

- Unambiguous and purely nonempirical
- Generally bonds too short and strong
- Frequently too crude

Generalized gradient approximation (GGA):

$$V_{xc}\left(\rho(\mathbf{r}),\left|\nabla\rho(\mathbf{r})\right|\right)$$

- Many flavours with same functional form but different approximations
- Versions optimized for molecules OR for solids
- Generally bonds somewaht long and weak but much better than LDA
- Tendency to overestimate high-spin states
- Underestimates weak bonds (vdW)

Van der Waals functionals (VDW):

$$V_{xc}(\mathbf{r}) = \int K\left(\rho(\mathbf{r}),\nabla\rho(\mathbf{r}),\rho(\mathbf{r}'),\nabla\rho(\mathbf{r}'),\left|\mathbf{r}-\mathbf{r}'\right|\right) d^3\mathbf{r}'$$

- Much better for weak vdW interactions
- vdW bonds systematically too long

Solving Schrödinger's 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

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

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

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

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

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

Transposing everything to the left hand side term

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

Solving Schrödinger’s equation

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

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

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

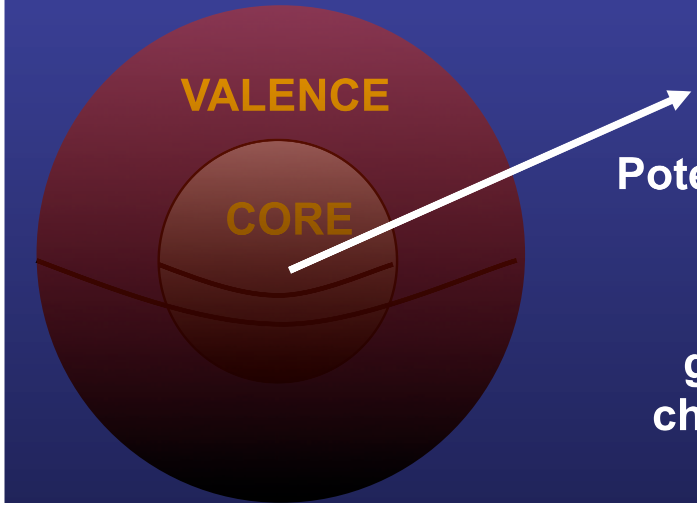
The neutral-atom potential

$$\rho(\mathbf{r}) = \rho_{atom}(\mathbf{r}) + \delta\rho(\mathbf{r}) \quad \Rightarrow \quad V_H(\mathbf{r}) = V_H^{atom}(\mathbf{r}) + \delta V_H(\mathbf{r})$$

Neutral atom potential

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

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

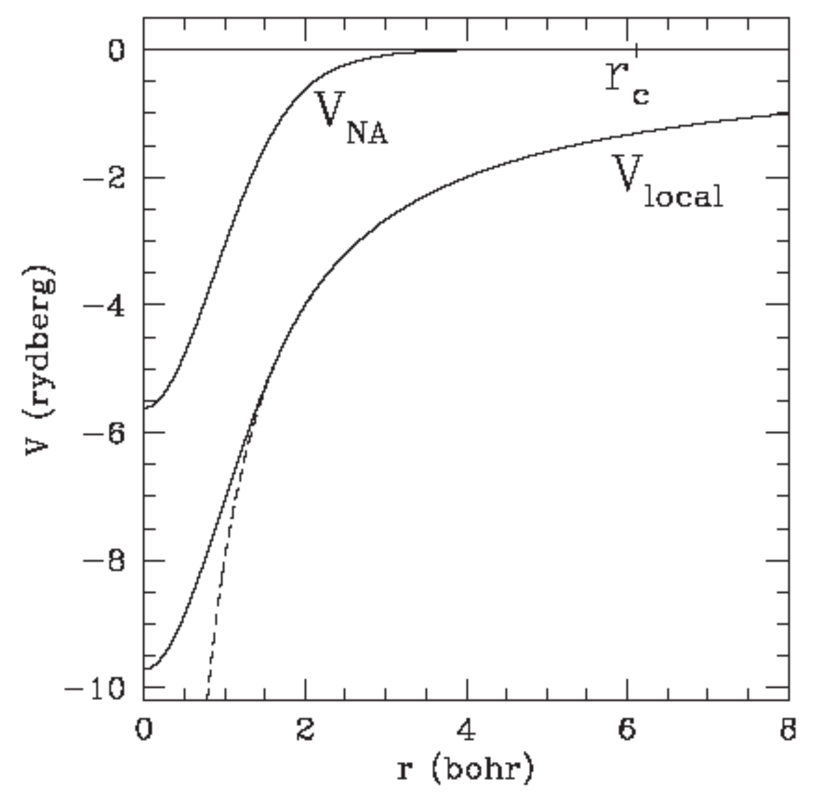


$$V_I^{NA}(\vec{r}) = 0$$

Potential outside the sphere vanishes

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

Vanishes exactly ar r_c



Real spherical harmonics

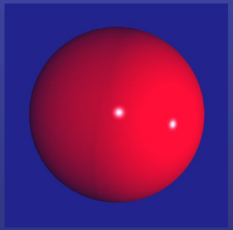
$$Y_{lm}(\theta,\varphi) = C_{lm} P_l^m(cos\theta) \begin{cases} sin(m\varphi) & \text{if } \; m < 0 \\ cos(m\varphi) & \text{if } \; m \geq 0 \end{cases}$$

Normalization factors

Associated Legendre polynomials

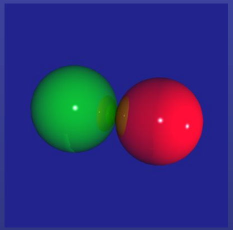
***l* = 0**

***m* = 0**

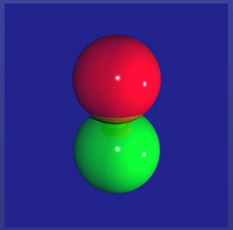


***l* = 1**

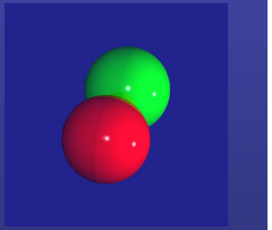
***m* = -1**



***m* = 0**



***m* = +1**



Pictures courtesy of Victor Luaña

siesta.ORB_INDX output file

siesta.ORB_INDX   output file

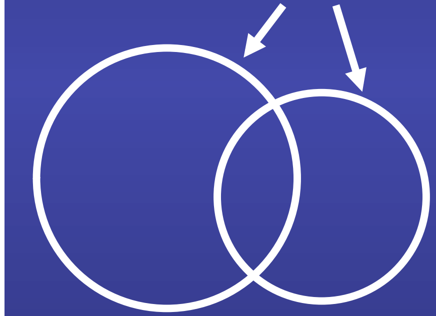
```
    92      92 = orbitals in unit cell and supercell. See end of file.

   io     ia is   spec iao  n  l  m  z  p          sym     rc    isc     iuo
    1      1  1      O   1  2  0  0  1  F            s  4.574  0  0  0     1
    2      1  1      O   2  2  0  0  2  F            s  2.639  0  0  0     2
    3      1  1      O   3  2  1 -1  1  F           py  6.175  0  0  0     3
    4      1  1      O   4  2  1  0  1  F           pz  6.175  0  0  0     4
    5      1  1      O   5  2  1  1  1  F           px  6.175  0  0  0     5
    6 ...

Column codes:
  io = Orbital index in supercell
  ia = Atom to which orbital belongs
  is = Atomic species index
spec = ...
```

Two- and three-center matrix elements

$$\hat{H} = \overbrace{\hat{T} + \hat{V}^{NL}}^{\text{Two center integrals}} + \overbrace{V^{NA}\left(\vec{r}\right) + \delta V^{H}\left(\vec{r}\right) + V^{xc}\left(\vec{r}\right)}^{\text{Three center integrals}}$$

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

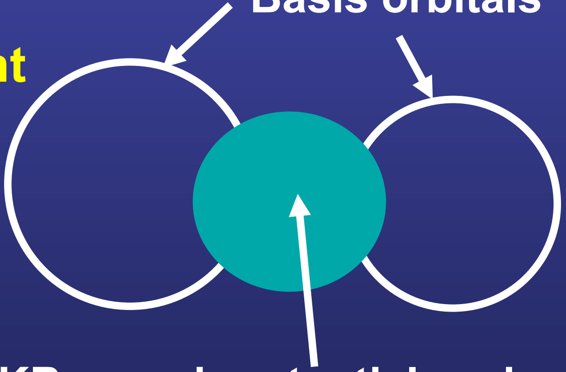
Basis orbitals



Non self-consistent

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

Basis orbitals



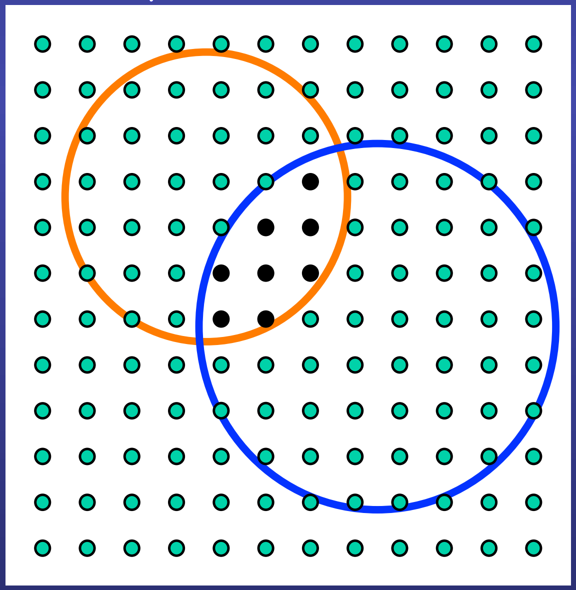
KB pseudopotential projector

Computed in reciprocal space and tabulated

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

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

Self-consistent



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

Three-dimensional real space grid

The density matrix, a basic ingredient of SIESTA

Expansion of the eigenvectors in a basis of localized atomic orbitals

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

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

Occupation of state ψ_i

Inserting the expansion into the definition of the density

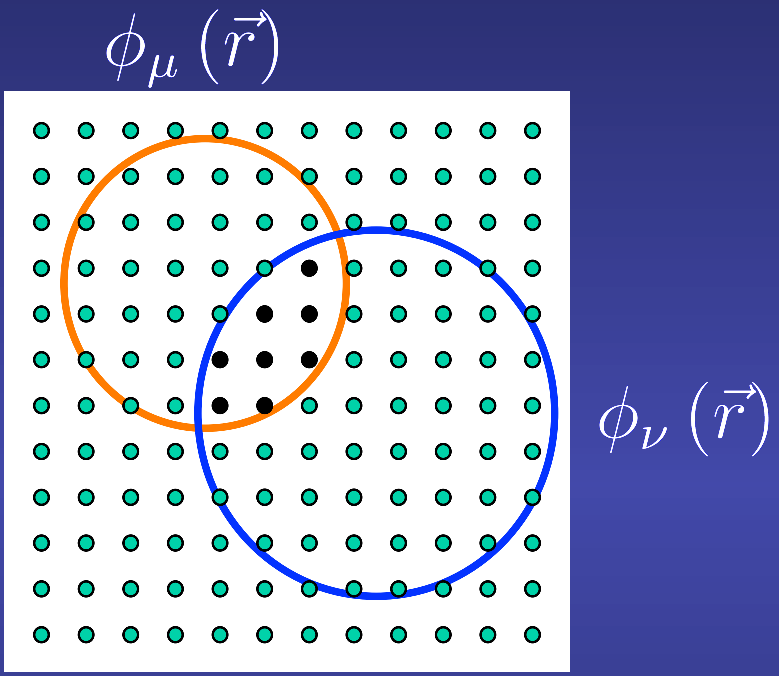
$$\rho\left(\vec{r}\right) = \sum_{\mu\nu} \rho_{\mu\nu} \phi_{\nu}^{*}\left(\vec{r}\right) \phi_{\mu}\left(\vec{r}\right)$$

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

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

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

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



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

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

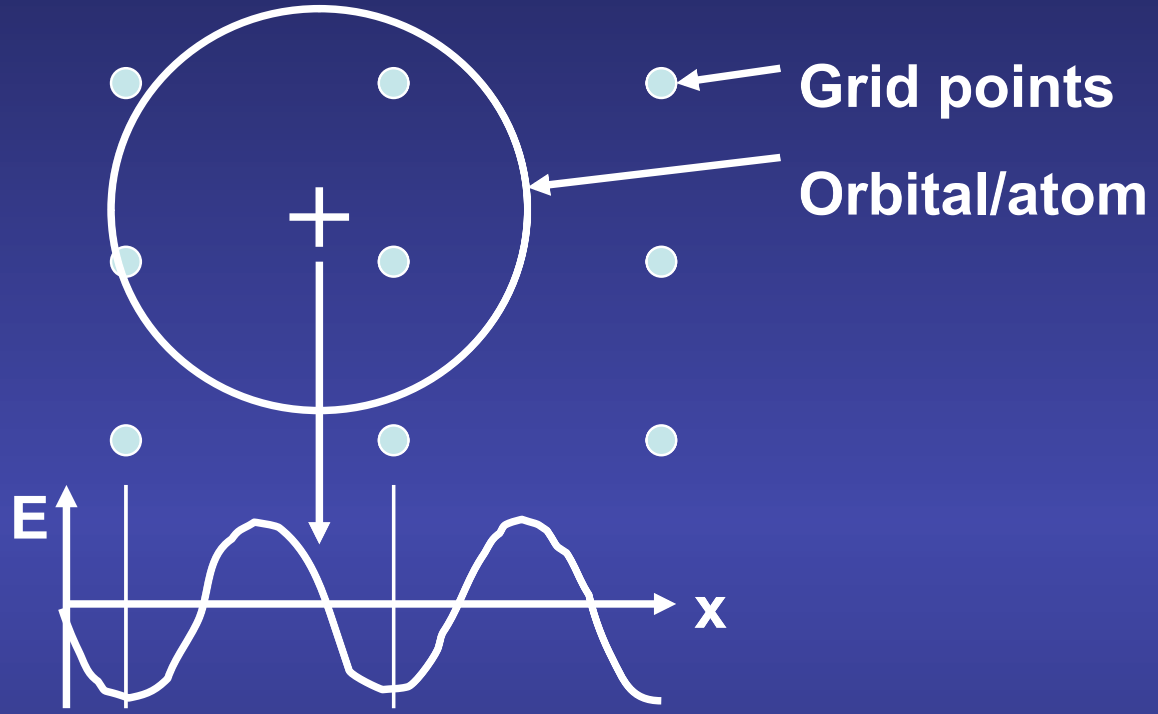
$$\delta\rho\left(\vec{r}\right)\xrightarrow{FFT}\delta V^{H}\left(\vec{r}\right)$$

$$\boxed{\rho_{xc}(\vec{r})=\rho(\vec{r})+\delta\rho_{nlcc}(\vec{r})}$$

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

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

The grid breaks traslation symmetry, the “eggbox” effect



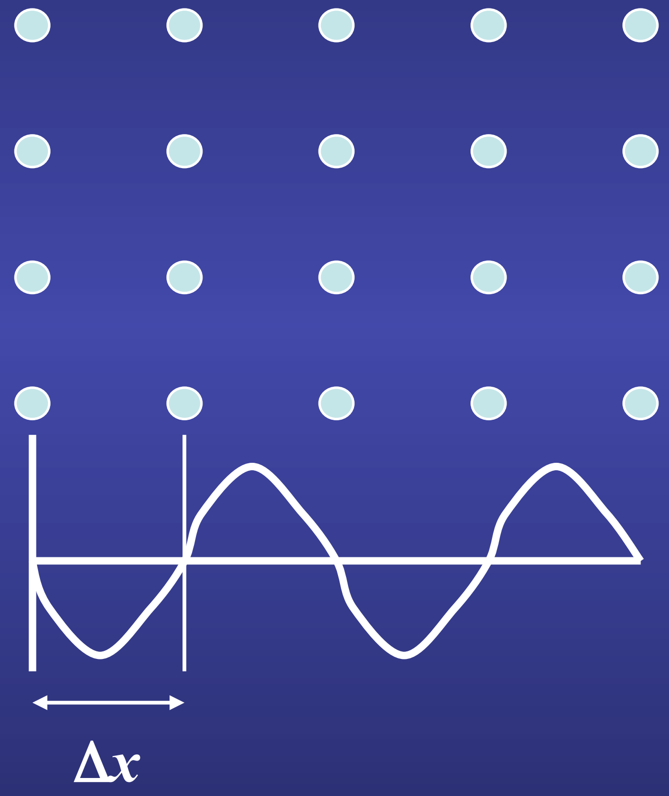
Affects more to forces than to energy

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)]

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



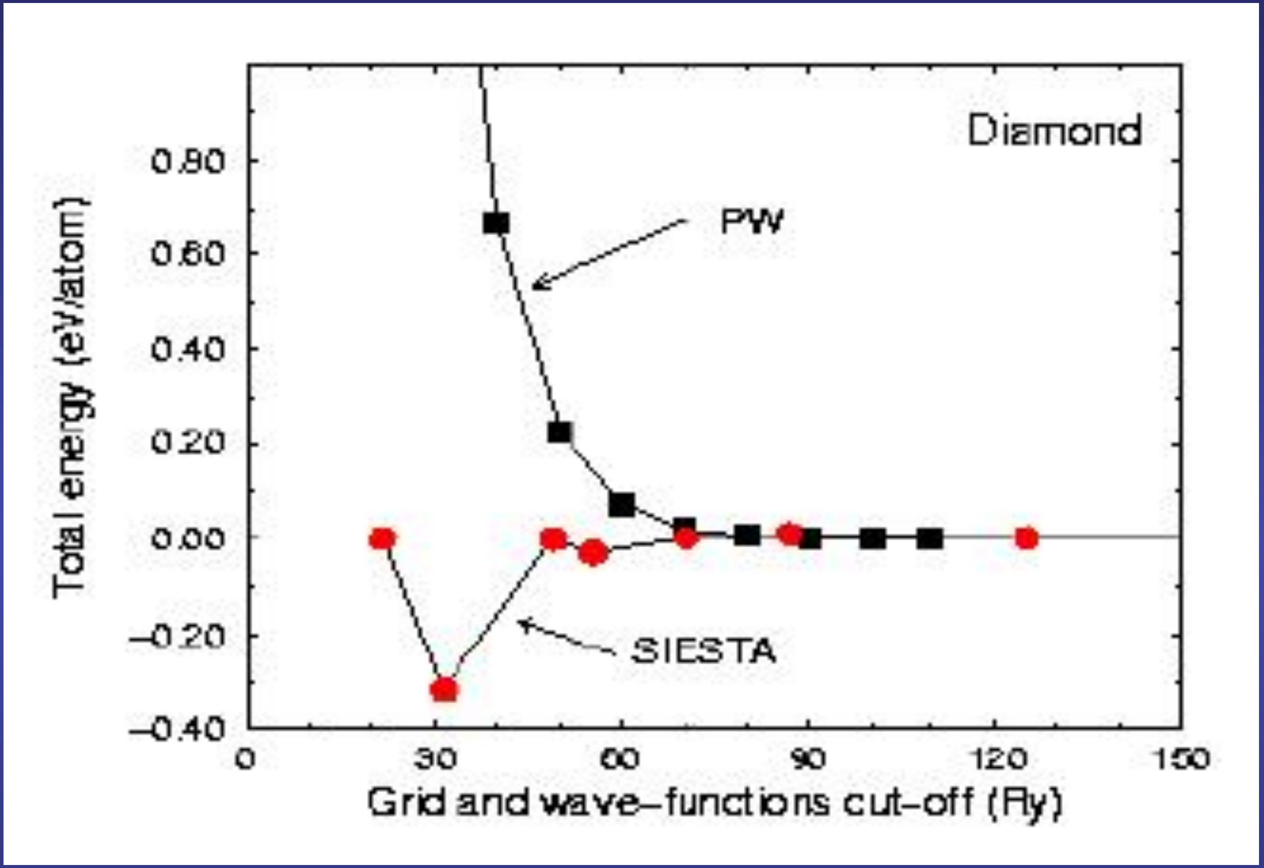
$$\Delta x \Longrightarrow k_c = \frac{\pi}{\Delta x} \Longrightarrow E_c = \frac{\hbar^2 k_c^2}{2m_e}$$

fdf label:
- MeshCutoff

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)

Convergence of the results with the grid cutoff



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

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

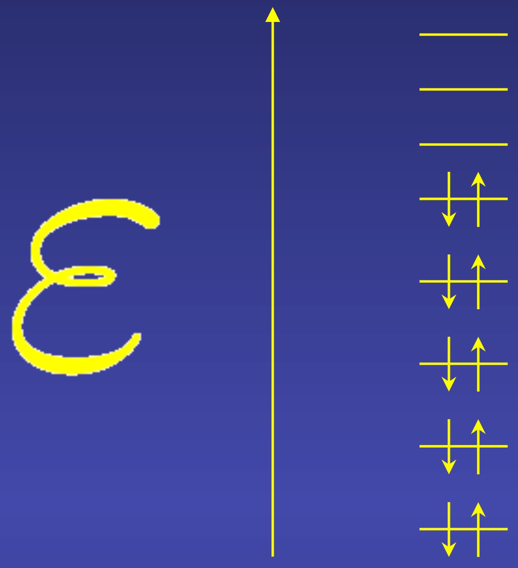
$$\underset{N \times N}{\begin{pmatrix} & & \\ & H & \\ & & \end{pmatrix}} \underset{N \times 1}{\begin{pmatrix} \\ C \\ \\ \end{pmatrix}} = E_{n\vec{k}} \underset{N \times N}{\begin{pmatrix} & & \\ & S & \\ & & \end{pmatrix}} \underset{N \times 1}{\begin{pmatrix} \\ C \\ \\ \end{pmatrix}}$$

Serial:	**Parallel:**
BLAS	BLACS
LAPACK	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



$$n^{\sigma}\left(\vec{r}\right) = \sum_{i} \underset{\big\downarrow}{f_{i}^{\sigma}} \left|\psi_{i}^{\sigma}\left(\vec{r}\right)\right|^{2}$$

Occupation numbers

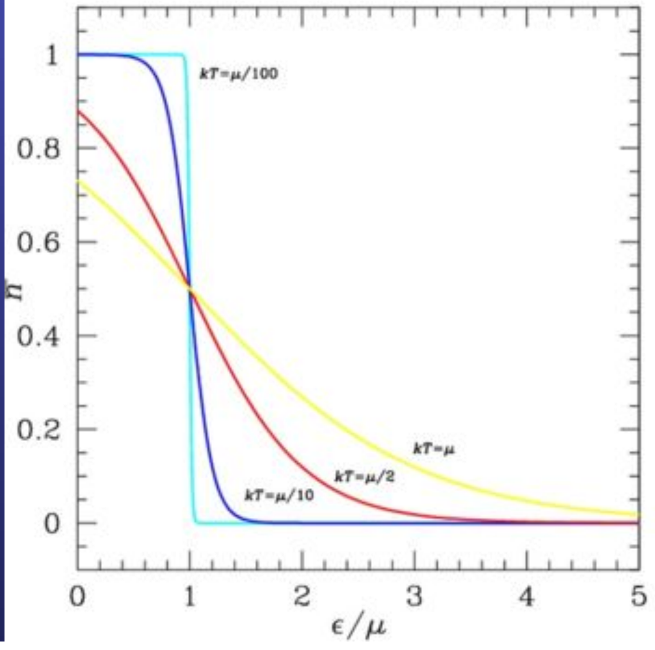
The ground state has one (or two if spin independent) in each of the orbitals with the lowest eigenvalues

A smearing of the electronic occupation might be done:

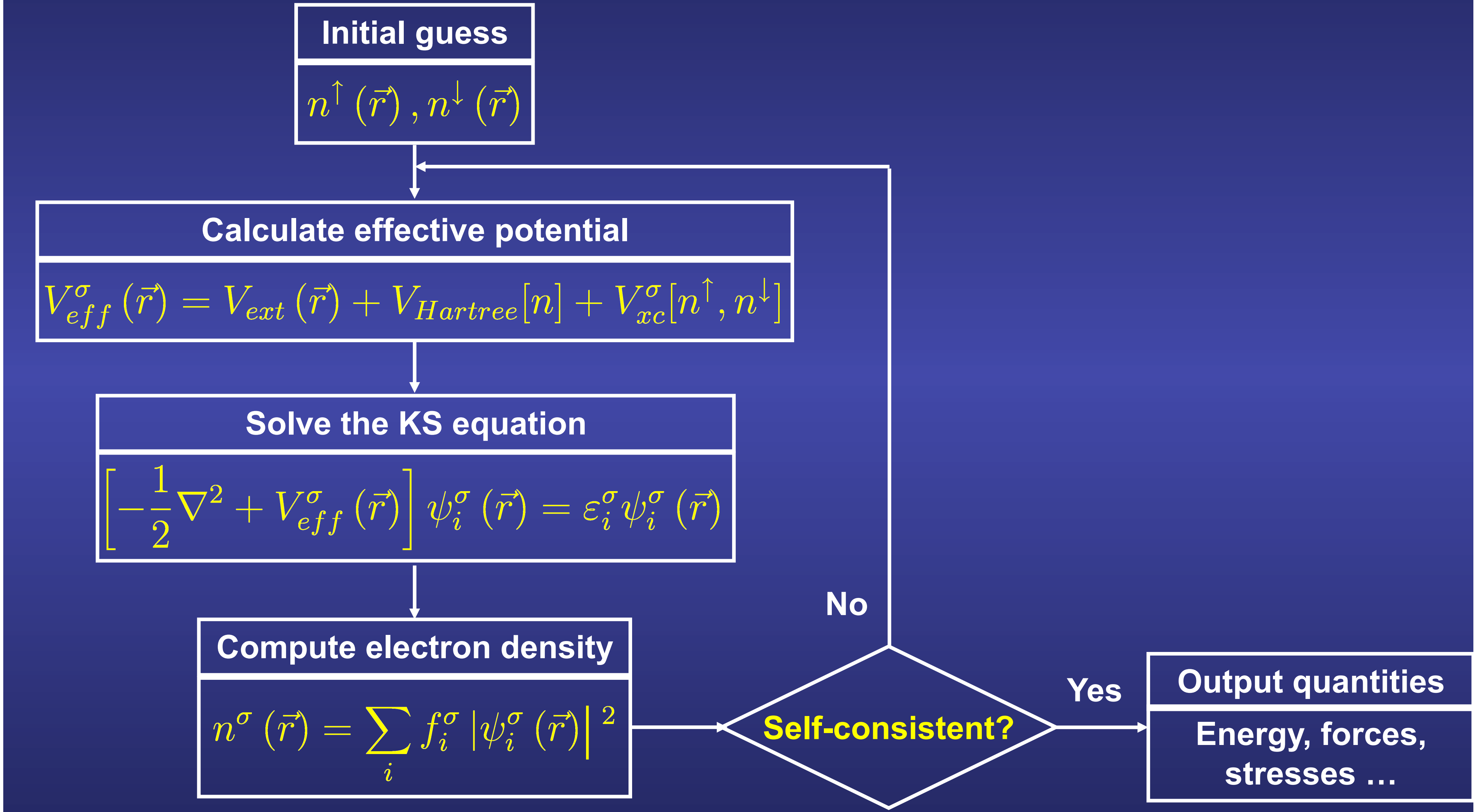
Fermi-Dirac (OccupationFunction FD)

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

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

Solve the KS equation

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

Compute electron density

$$n^{\sigma}(\vec{r}) = \sum_i f^{\sigma}_i \left|\psi^{\sigma}_i(\vec{r})\right|^2$$

Self-consistent?

No

Yes

Output quantities

Energy, forces, stresses …

$$\max_{\mu\nu}\left(\rho^{out}_{\mu\nu} - \rho^{in}_{\mu\nu}\right) < \mathrm{DM.Tolerance}$$

SCF convergence

Charge sloshing:

$E_1<E_2 \;\Rightarrow\; n_1>n_2 \;\Rightarrow\; E_1>E_2 \;\Rightarrow\; n_1<n_2$

Simple mixing:

$\rho_{n+1} = (1-w)\,\rho^{in} + w\,\rho^{out}$

Pulay mixing:

$\rho^{in} \rightarrow \rho^{out} = \rho^{in} + \Delta\rho$

$\Delta\rho_{n+1} = w_{n-2}\,\Delta\rho_{n-2} + w_{n-1}\,\Delta\rho_{n-1} + w_n\,\Delta\rho_n = \min$

$\rho_{n+1} = w_{n-2}\,\rho_{n-2} + w_{n-1}\,\rho_{n-1} + w_n\,\rho_n + w\,\rho^{out}$

fdf labels:

- ElectronicTemperature
- OccupationFunction
- MixHamiltonian
- DM.UseSaveDM
- DM.MixingWeight
- DM.NumberPulay
- DM.Tolerance
- MaxSCFiterations

Kohn-Sham energy in SIESTA

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

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

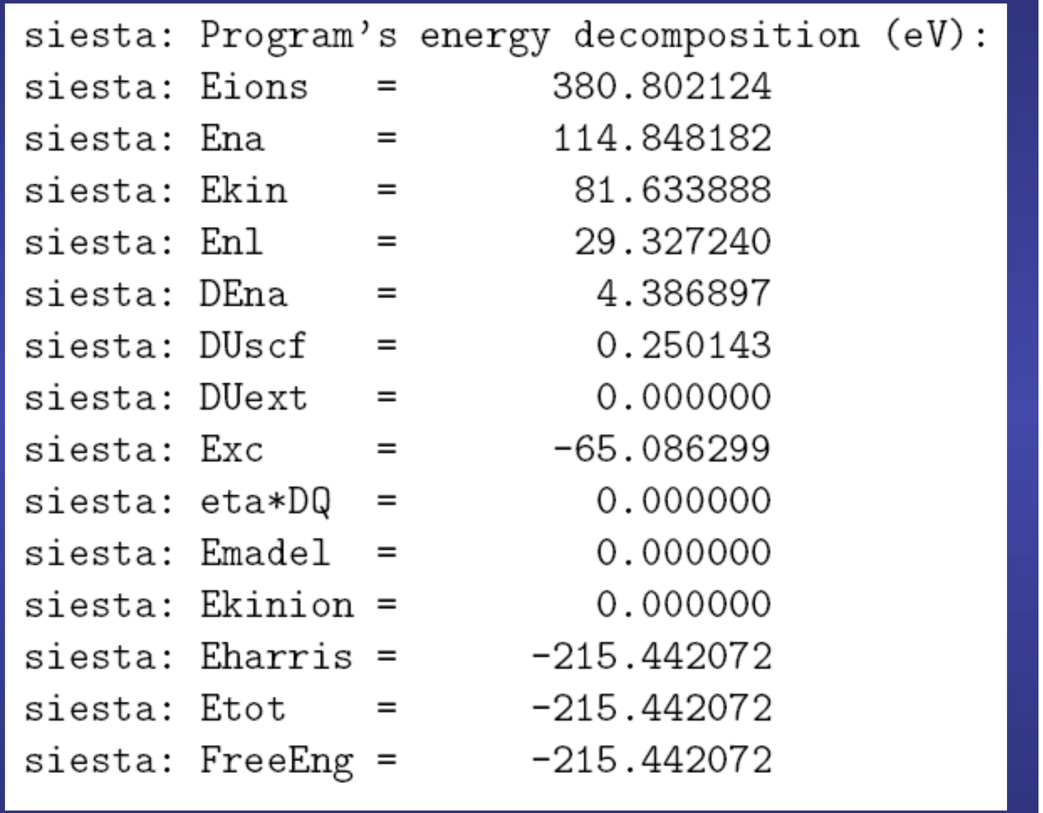
$$\left.\begin{array}{l} +\dfrac{1}{2}\displaystyle\sum_{IJ} U^{NA}_{IJ}\left(R_{IJ}\right) \\ +\displaystyle\sum_{I<J} \delta U^{local}_{IJ}\left(R_{IJ}\right) \end{array}\right\} \qquad \textbf{Ena}$$

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

$$+\int V^{NA}\left(\vec{r}\right)\delta\rho\left(\vec{r}\right)d\vec{r} \qquad \textbf{DEna}$$

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

$$+\int \varepsilon^{xc}\left(\vec{r}\right)\rho\left(\vec{r}\right)d\vec{r} \qquad \textbf{Exc}$$



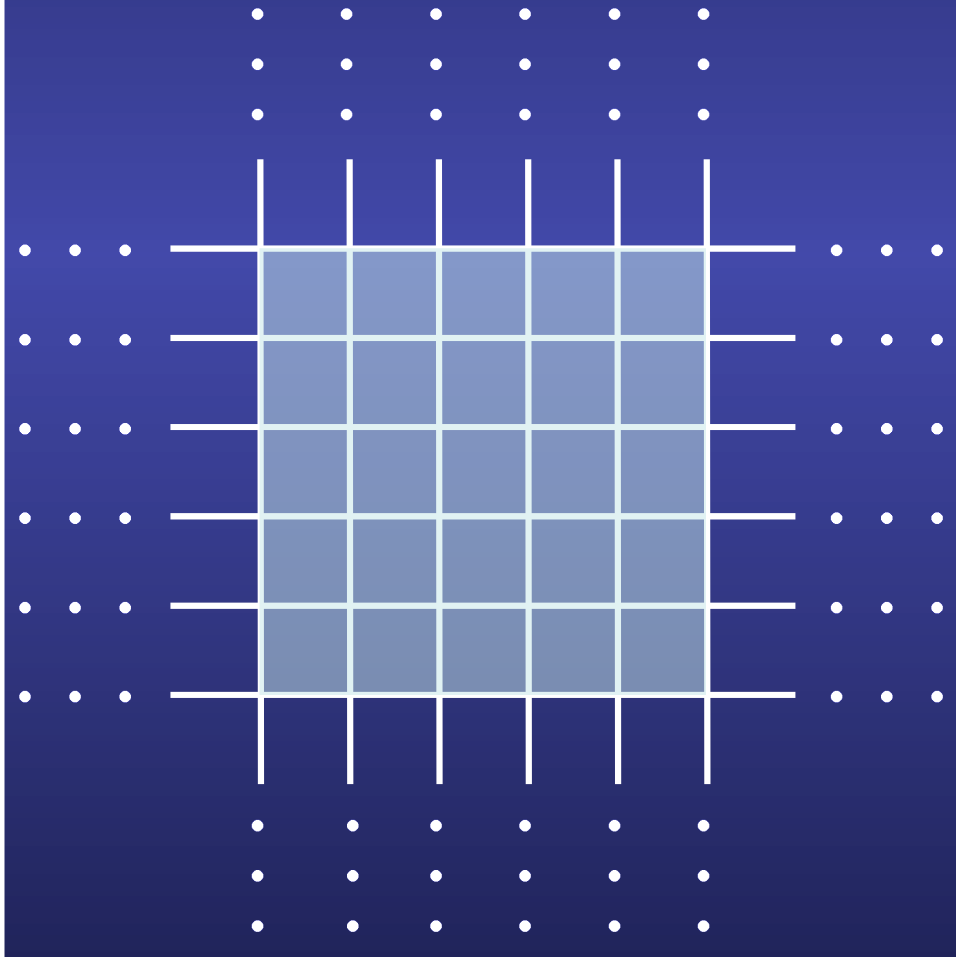
```
siesta: Program's energy decomposition (eV):
siesta: Eions   =       380.802124
siesta: Ena     =       114.848182
siesta: Ekin    =        81.633888
siesta: Enl     =        29.327240
siesta: DEna    =         4.386897
siesta: DUscf   =         0.250143
siesta: DUext   =         0.000000
siesta: 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)

How can we simulate an infinite periodic solid?
Periodic (Born-von Karman) boundary conditions

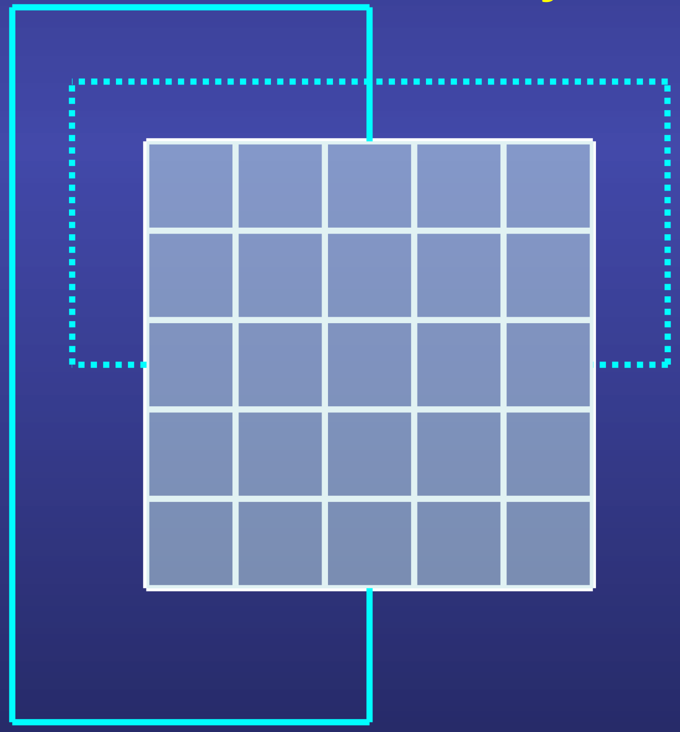
We should expect that the bulk properties to be unaffected by the presence of its surface.

A natural choice to emphasize the inconsequence of the surface by disposing of it altogether

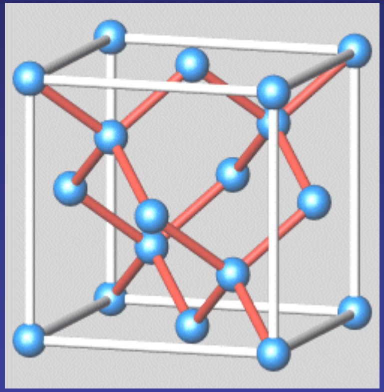


Supercell +

Born-von Karman boundary conditions



Electrons in a periodic potential



$$V(\vec{r}) = V(\vec{r} + \vec{R})$$

Bloch Theorem:

$$\psi_{n,\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u_{n,\vec{k}}(\vec{r})$$

$$u_{n,\vec{k}}(\vec{r} + \vec{R}) = u_{n,\vec{k}}(\vec{r})$$

Periodicity in reciprocal space

$\vec{G}$ ≡Reciprocal lattice vector

$$\left\{ \begin{array}{l} \psi_{n,\vec{k}+\vec{G}}(\vec{r}) = \psi_{n,\vec{k}}(\vec{r}) \\ \\ \varepsilon_{n,\vec{k}+\vec{G}} = \varepsilon_{n,\vec{k}} \end{array} \right.$$

Instead of computing an infinite number of electronic wave functions

Finite number of wave functions at an infinite number of k-points in the 1BZ

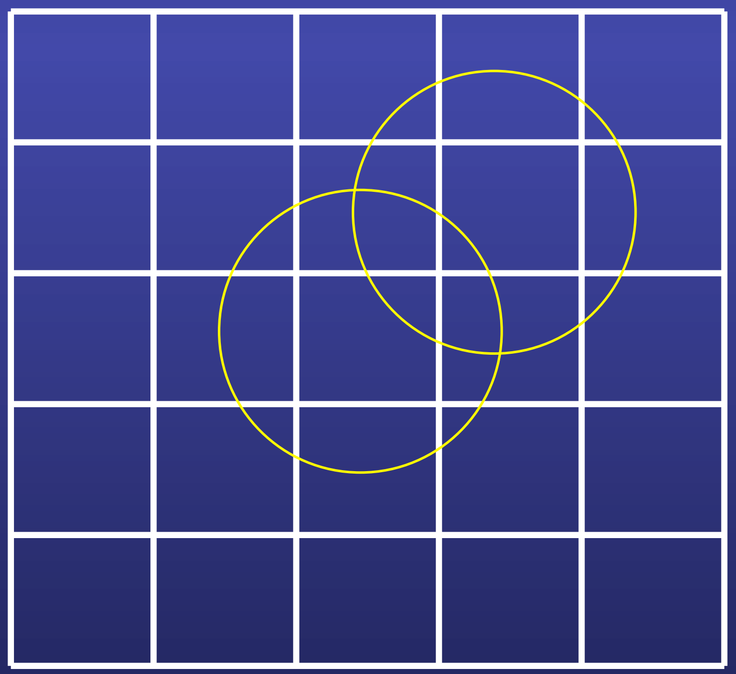
K-dependent matrix elements

$$\psi_{\mathbf{k}j}(\mathbf{r}) = \sum_{\mu\mathbf{R}} c_{\mu\mathbf{k}j}\,\phi_{\mu\mathbf{R}}(\mathbf{r})\,e^{i\mathbf{k}(\mathbf{R}+\mathbf{r}_{\mu})}$$

$$\sum_{\nu}\left(H_{\mu\nu\mathbf{k}} - E_{j}\,S_{\mu\nu\mathbf{k}}\right)c_{\nu\mathbf{k}j} = 0$$

$$H_{\mu\nu\mathbf{k}} = \sum_{\mathbf{R}'}\left\langle \phi_{\mu\mathbf{R}}\middle|\mathbf{H}\middle|\phi_{\nu\mathbf{R}'}\right\rangle e^{i\mathbf{k}(\mathbf{R}+\mathbf{r}_{\mu}-\mathbf{R}'-\mathbf{r}_{\nu})}$$

$$S_{\mu\nu\mathbf{k}} = \sum_{\mathbf{R}'}\left\langle \phi_{\mu\mathbf{R}} \mid \phi_{\nu\mathbf{R}'}\right\rangle e^{i\mathbf{k}(\mathbf{R}+\mathbf{r}_{\mu}-\mathbf{R}'-\mathbf{r}_{\nu})}$$



SIESTA supercell

Many magnitudes require integration of Bloch functions over Brillouin zone (1BZ)

Charge density

$$\rho(\vec{r}) = \sum_i \int_{BZ} n_i(\vec{k}) |\psi_{i\vec{k}}(\vec{r})|^2 d\vec{k}$$

Band structure energy

$$E_{BS} = \sum_i \int_{BZ} n_i(\vec{k}) \varepsilon_i(\vec{k}) d\vec{k}$$

In principle: we should know the eigenvalues and/or eigenvectors at all the k-points in the first BZ

In practice: electronic wave functions at k-points that are very close together will be almost identical $\Rightarrow$

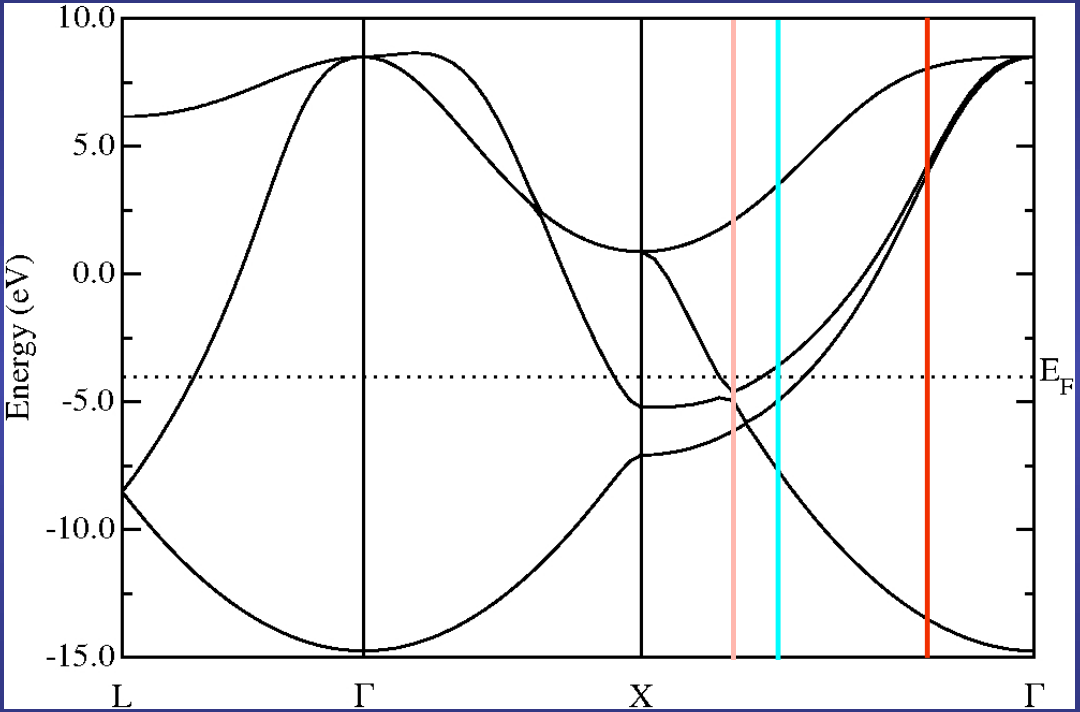
It is possible to represent electronic wave functions over a region of k-space by the wave function at a single k-point.

$$\int d\vec{k} \longrightarrow \sum_{\vec{k}} \Delta\vec{k}$$

Fermi surface sampling for metallic systems

The determination of the Fermi level might be delicate for metallic systems

Band structure of bulk Al



For this k-point, three bands are occupied

For this k-point, two bands are occupied

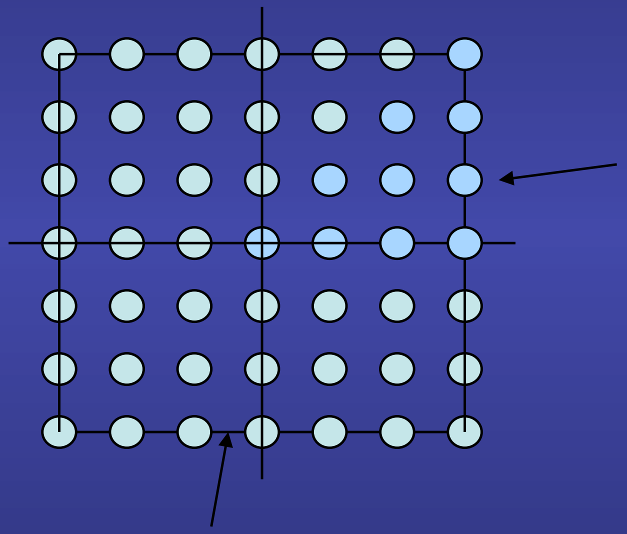
For this k-point, one band is occupied

Slightly different choices of k-points can lead to bands entering or exiting the sum, depending if a given eigenvalue is above or below the Fermi level.

For a sufficiently dense Brillouin zone sampling, this should not be a problem

K-point sampling

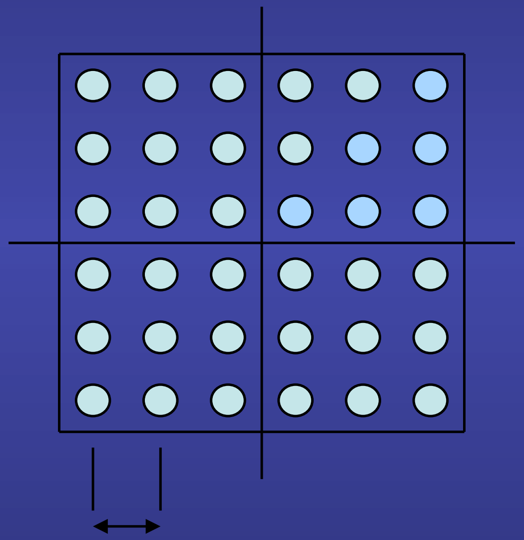
Regular k-grid



Inequivalent points

First Brillouin Zone

Monkhorst-Pack



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

How to set up the k-point sampling in Siesta

Variables that control the fineness of the grid

kgrid_cutoff

```
kgrid_cutoff        10.0 Ang
```

A real-space radius that plays a role equivalent to the plane-wave cutoff in real space grids

(Moreno and Soler 92)

kgrid_Monkhorst_Pack

```
%block kgrid_Monkhorst_Pack
     4    0    0   0.5
     0    4    0   0.5
     0    0    4   0.5
%endblock kgrid_Monkhorst_Pack
```

The origin of the k-grid might be displaced to reduce the number of inequivalent k-points

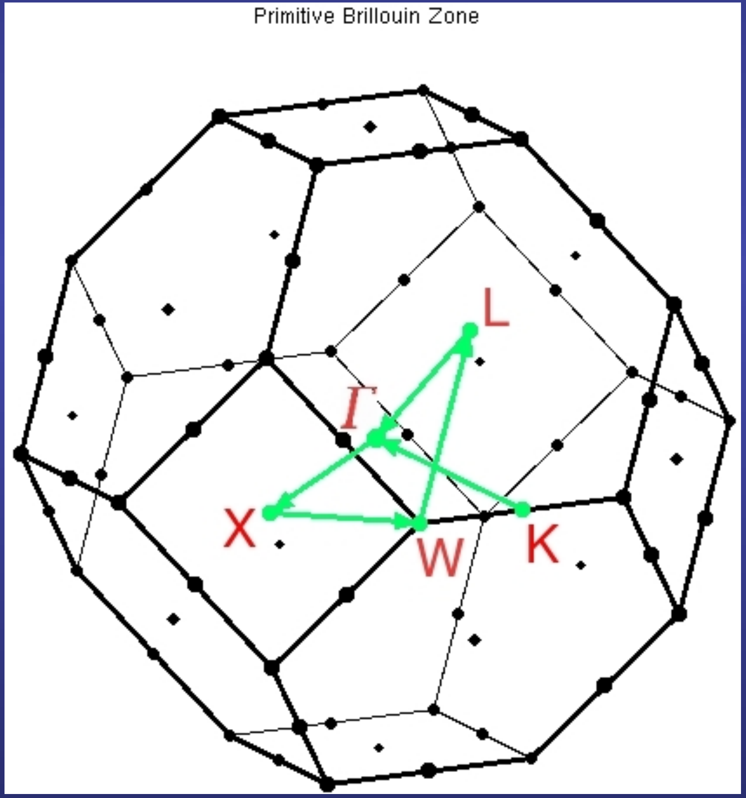
Comparing energies of structures having different symmetries: take care of BZ samplings

The BZ sampling of all the structures must be sampled with the same accuracy

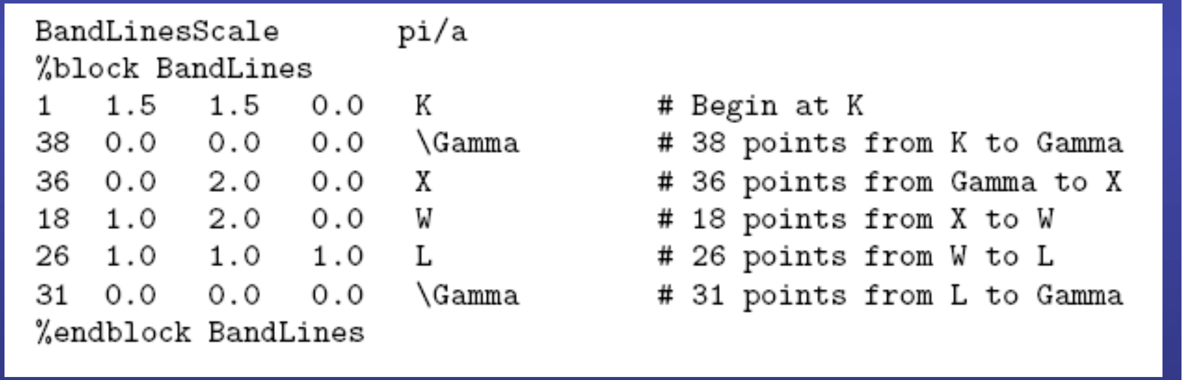
Since for unit cells of different shapes it is not possible to choose exactly the same k-point sampling, a usual strategy is to try and maintain the same density of k-points

Once SCF has been achieved, we compute the bands along the high symmetry points in the First-Brillouin zone

First-Brillouin zone of a FCC ,
with the high symmetry points



New variables to plot the band structure



```
BandLinesScale        pi/a
%block BandLines
1    1.5    1.5    0.0    K              # Begin at K
38   0.0    0.0    0.0    \Gamma         # 38 points from K to Gamma
36   0.0    2.0    0.0    X              # 36 points from Gamma to X
18   1.0    2.0    0.0    W              # 18 points from X to W
26   1.0    1.0    1.0    L              # 26 points from W to L
31   0.0    0.0    0.0    \Gamma         # 31 points from L to Gamma
%endblock BandLines
```