Université de Liège

Introduction to run Siesta

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Our method

Linear-scaling DFT based on NAOs (Numerical Atomic Orbitals)

P. Ordejon, E. Artacho & J. M. Soler , Phys. Rev. B 53, R10441 (1996)

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

- *Born-Oppenheimer (relaxations, mol.dynamics)*
- *DFT (LDA, GGA)*
- *Pseudopotentials (norm conserving,factorised)*
- *Numerical atomic orbitals as basis (finite range)*
- *Numerical evaluation of matrix elements (3Dgrid)*

Implemented in the SIESTA program

D. Sanchez-Portal, P. Ordejon, E. Artacho & J. M. Soler
Int. J. Quantum Chem. 65, 453 (1997)

To run Siesta you need:

1.- Access to the executable file

2.- An input file

Flexible Data Format (FDF) (A. García and J. M. Soler)

3.- A pseudopotential file for each kind of element in the input file

Unformatted binary (.vps)

Formatted ASCII (.psf) (more transportable and easy to look at)

Siesta package:

- Src: Sources of the Siesta code
- Docs: Documentation and user conditions

  User's Guide (siesta.tex)
- Pseudo: ATOM program to generate and test pseudos

  (A. García; *Pseudopotential and basis generation*, Tu 12:00)
- Examples: fdf and pseudopotentials input files for simple systems
- Utils: Programs or scripts to analyze the results

The input file

Main input file:

- Physical data of the system
- Variables to control the approximations
- Flexible Data Format (FDF)

  developped by A. García and J. M. Soler

FDF (I)

- Data can be given in any order
- Data can be omitted in favour of default values
- Syntax: 'data label' followed by its value

Character string:	SystemLabel	h2o
Integer:	NumberOfAtoms	3
Real:	PAO.SplitNorm	0.15
Logical:	SpinPolarized	.false.
Physical magnitudes	LatticeConstant	5.43 Ang

FDF (II)

- Labels are case insensitive and characters -_. are ignored

  LatticeConstant is equivalent to lattice_constant

- Text following # are comments

- Logical values: T , .true. , true , yes

  F , .false. , false , no

- Character strings, NOT in apostrophes

- Complex data structures: blocks

  %block label

  …

  %endblock label

FDF (III)

- Physical magnitudes: followed by its units.

  Many physical units are recognized for each magnitude

  (Length: m, cm, nm, Ang, bohr)

  Automatic conversion to the ones internally required.

- You may 'include' other FDF files or redirect the search to another file

Basic input variables

1.- General system descriptors

2.- Structural and geometrical variables

3.- Functional and solution mehod

4.- Convergence of the results

5.- Self-consistency

(Basis set generation related variables:

A. García; *Pseudopotential and basis generation*, Tu 12:00)

General system descriptor

SystemName: descriptive name of the system

```
SystemName    Si bulk, diamond structure
```

SystemLabel: nickname of the system to name output files

```
SystemLabel    Si
```

(After a succesful run, you should have files like

Si.DM : Density matrix

Si.XV: Final positions and velocities

...)

Structural and geometrical variables

NumberOfAtoms: number of atoms in the simulation

```
NumberOfAtoms     2
```

NumberOfSpecies: number of different atomic species

```
NumberOfSpecies   1
```

ChemicalSpeciesLabel: specify the different chemical species.

```
%block ChemicalSpeciesLabel
     1      14     Si
%endblock ChemicalSpeciesLabel
```

ALL THESE VARIABLES ARE MANDATORY

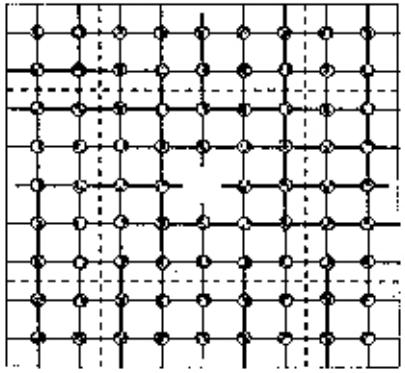
Periodic Boundary Conditions (PBC)

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

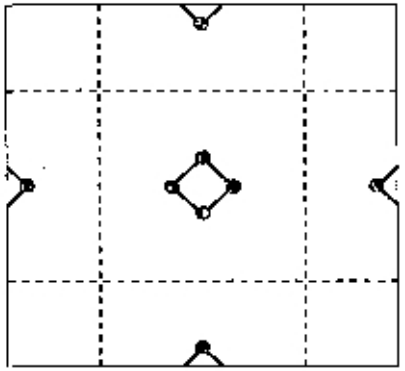
Periodic systems and crystalline solids:

Aperiodic systems: Supercell approximation

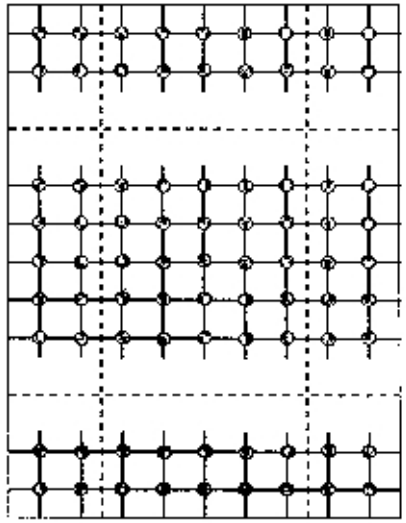
Defects



Molecules



Surfaces



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

Lattice Vectors

LatticeConstant: real length to define the scale of the lattice vectors

```
LatticeConstant       5.43 Ang
```

LatticeParameters: Crystallograhic way

```
%block LatticeParameters
    1.0  1.0  1.0  60.  60.  60.
%endblock LatticeParameters
```

LatticeVectors: read as a matrix, each vector being a line

```
%block LatticeVectors
    0.0   0.5   0.5
    0.5   0.0   0.5
    0.5   0.5   0.0
%endblock LatticeVectors
```

Atomic Coordinates

AtomicCoordinatesFormat: format of the atomic positions in input:

Bohr: cartesian coordinates, in bohrs

Ang: cartesian coordinates, in Angstroms

ScaledCartesian: cartesian coordinates, units of the lattice constant

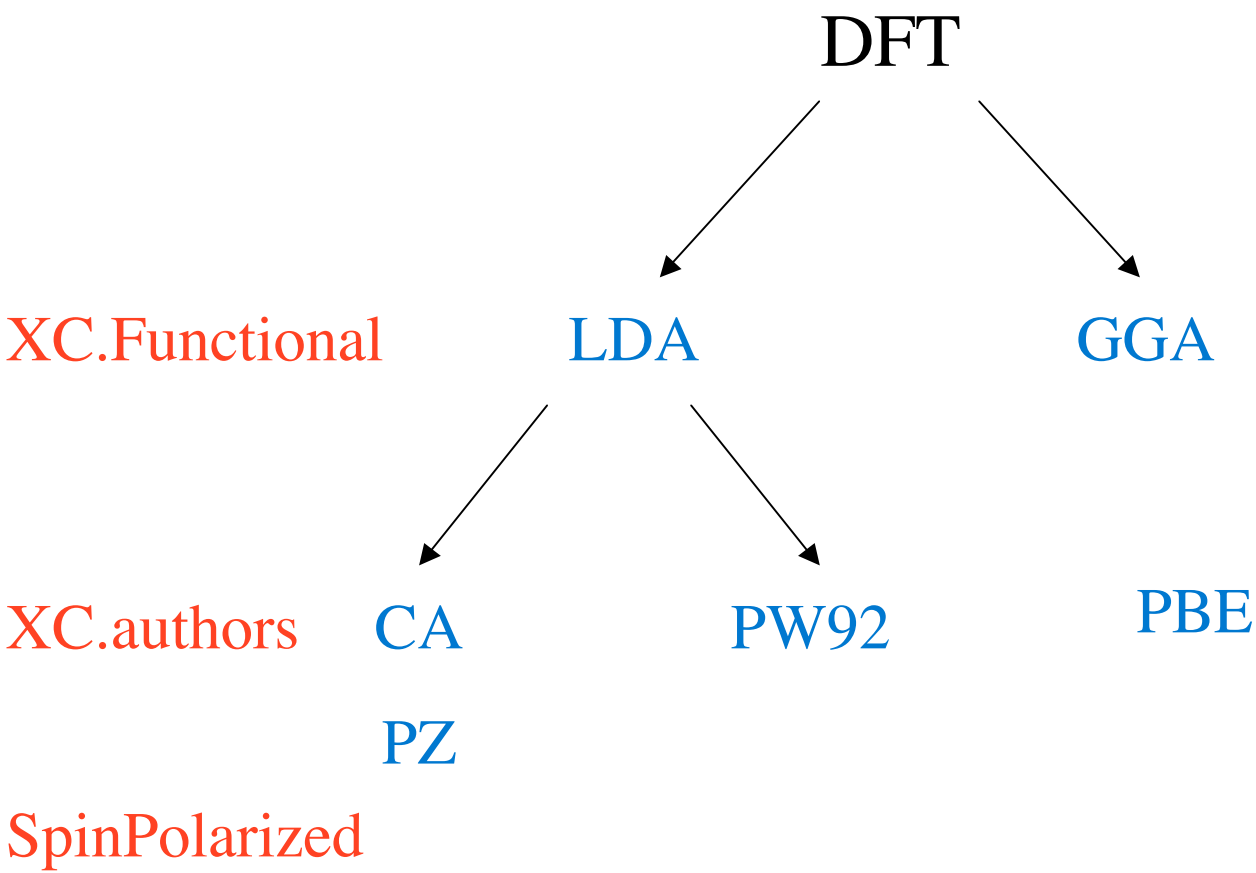
Fractional: referred to the lattice vectors

```
AtomicCoordinatesFormat      Fractional
```

AtomicCoordinatesAndAtomicSpecies:

```
%block AtomicCoordinatesAndAtomicSpecies
  0.00   0.00   0.00   1
  0.25   0.25   0.25   1
%endblock AtomicCoordinatesAndAtomicSpecies
```

Functional



DFT ≡ Density Functional Theory

LDA ≡ Local Density Approximation

GGA ≡ Generalized Gradient Approximation

CA ≡ Ceperley-Alder

PZ ≡ Perdew-Zunger

PW92 ≡ Perdew-Wang-92

PBE ≡ Perdew-Burke-Ernzerhof

Solution method

From the atomic coordinates and the unit cell

$$\left\{\vec{R}, \vec{a}\right\}$$

Order *N* operations

Hamiltonian, *H*, and Overlap, *S*, matrices

$$(H - \varepsilon S)C = 0$$

SolutionMethod diagon Order-N

E. Artacho, *Running with Order-N*,
Wed 11:40

k-sampling

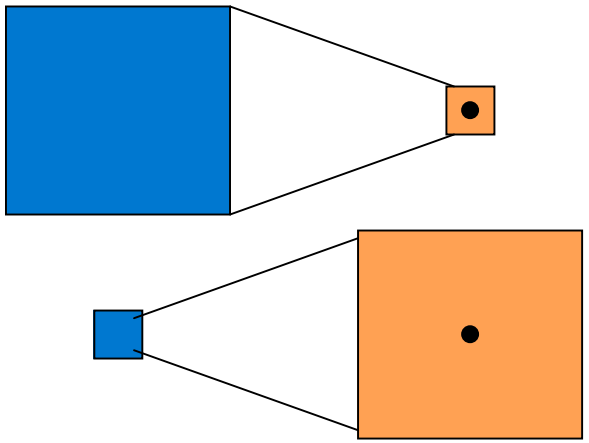
Many magnitudes require integration of Bloch functions over Brillouin zone (BZ)

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

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 same insulators:

Perovskite oxides

k-sampling

Spetial set of k-points: **Accurate results** for a **small #** k-points:

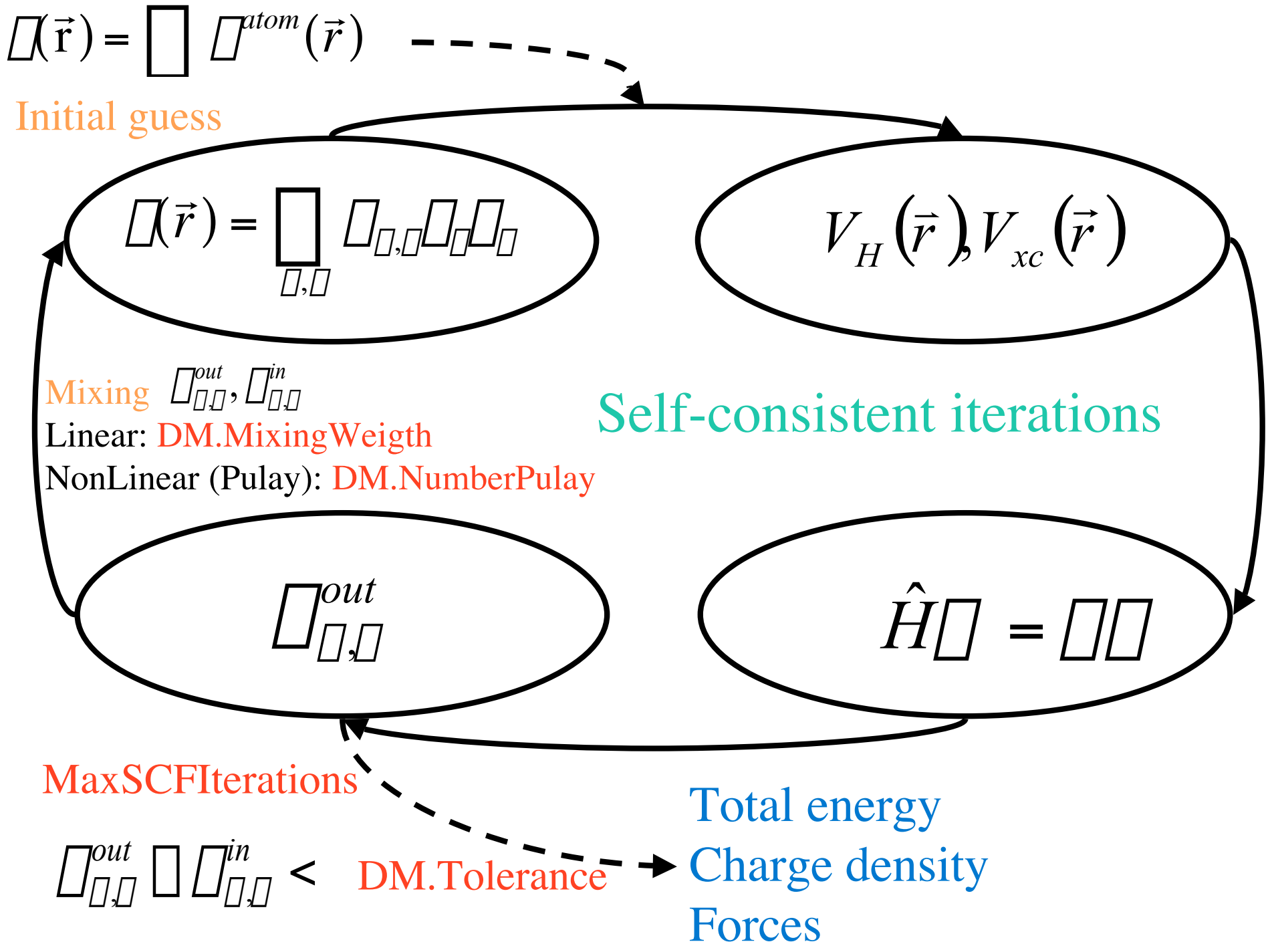
Baldereschi, Chadi-Cohen, Monkhorst-Pack

kgrid_cutoff:

```
kgrid_cutoff        10.0 Ang
```

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
```


Initial guess
Self-consistent iterations
Mixing
Linear: DM.MixingWeigth
NonLinear (Pulay): DM.NumberPulay
MaxSCFIterations
DM.Tolerance
Total energy
Charge density
Forces

How to run Siesta

To run the serial version:

[path]siesta < myinput.fdf > myoutput &

To see the information dumped in the

output file during the run:

tail –f myoutput

Output: the header

```
SIESTA 1.2.3 -- [iorho parallel fix/O(N)] (Nov 20, 2001)
Architecture  : lahey
Compiler flags: lf95 -O --warn --quiet --tpp --ntrace
SERIAL version

* Running in serial mode
>> Start of run:  3-JUL-2002  17:06:18
```

Output: dumping the input file

```
*: ******************** Dump of input data file ************************
SystemName          Water molecule
SystemLabel         h2o
NumberOfAtoms       3
NumberOfSpecies     2
%block ChemicalSpeciesLabel
 1   8   O      # Species index, atomic number, species label
 2   1   H
%endblock ChemicalSpeciesLabel
AtomicCoordinatesFormat  Ang
%block AtomicCoordinatesAndAtomicSpecies
 0.000   0.000   0.000   1
 0.757   0.586   0.000   2
-0.757   0.586   0.000   2
%endblock AtomicCoordinatesAndAtomicSpecies
*: ******************** End of input data file ************************
```

Output: processing the input

```
prinput: *****
coor: Atomic-coordinates input format  =     Cartesian coordinates
coor:                                        (in Angstroms)
redata: Number of spin components        =     1
redata: Long output                      =     F
redata: Number of Atomic Species         =     2
redata: Charge density info will appear in .RHO file
redata: Write Mulliken Pop.              =     NO
redata: Mesh Cutoff                      =    50.0000  Ry
redata: Net charge of the system         =     0.0000 |e|
redata: Max. number of SCF Iter          =    50
redata: Mixing is linear
redata: Mix DM in first SCF step ?       =     F
redata: Write Pulay info on disk?        =     F
redata: New DM Mixing Weight             =     0.2500
redata: No kicks to SCF
redata: DM Mixing Weight for Kicks       =     0.5000
redata: DM Tolerance for SCF             =     0.000100
redata: Use continuation files for DM    =     F
redata: Neglect nonoverlap interactions  =     F
redata: Method of Calculation            =     Diagonalization
redata: Electronic Temperature           =     0.0019  Ry
redata: Fix the spin of the system       =     F
redata: Dynamics option                  =     Verlet MD run
redata: Initial MD time step             =     1
redata:   Final MD time step             =     1
redata: Length of MD time step           =     1.0000  fs
redata: Length of MD time step           =     1.0000  fs
redata: Initial Temperature of MD run    =     0.0000  K
redata: Perform a MD quench              =     F
redata: ***********************************************************
```

Output: coordinates and k-sampling

```
siesta: Atomic coordinates (Bohr) and species
siesta:      0.00000   0.00000   0.00000  1        1
siesta:      1.43052   1.10738   0.00000  2        2
siesta:     -1.43052   1.10738   0.00000  2        3

siesta: Automatic unit cell vectors (Ang):
siesta:    7.286412    0.000000    0.000000
siesta:    0.000000    5.746952    0.000000
siesta:    0.000000    0.000000    5.621012

siesta: System type = molecule
...

siesta: System type = bulk

siesta: k-grid: Number of k-points =   196
siesta: k-grid: Cutoff             =    14.021 Ang
siesta: k-grid: Supercell and displacements
siesta: k-grid:    7   0   0      0.000
siesta: k-grid:    0   7   0      0.000
siesta: k-grid:    0   0   7      0.000
```

Output: First MD step

```
siesta:     ============================
siesta:         Begin MD step =      1
siesta:     ============================

InitMesh: MESH =    32 x    30 x    24 =       23040
InitMesh: Mesh cutoff (required, used) =    50.000    50.384 Ry

* Maximum dynamic memory allocated =     3 MB

siesta: Program's energy decomposition (eV):
siesta: Eions   =       815.854478
siesta: Ena     =       175.154399
siesta: Ekin    =       341.667405
siesta: Enl     =       -52.736793
siesta: DEna    =        -0.000001
siesta: DUscf   =         0.000000
siesta: DUext   =         0.000000
siesta: Exc     =      -109.951257
siesta: eta*DQ  =         0.000000
siesta: Emadel  =         0.000000
siesta: Eharris =      -466.430254
siesta: Etot    =      -461.720725
siesta: FreeEng =      -461.720725
```

Output: Self-consistency

```
siesta: iscf Eharris(eV)    E_KS(eV) FreeEng(eV)   dDmax  Ef(eV)
siesta:    1   -466.4303   -461.7207   -461.7207  1.4383 -4.2475
timer: Routine,Calls,Time,% = IterSCF        1       7.930  72.22
siesta:    2   -466.8703   -465.2425   -465.2425  0.1755 -0.1474
siesta:    3   -465.9264   -465.4655   -465.4655  0.0515 -1.5862
siesta:    4   -465.8472   -465.5656   -465.5656  0.0176 -1.9935
siesta:    5   -465.8397   -465.6346   -465.6346  0.0087 -2.1116
siesta:    6   -465.8388   -465.6857   -465.6857  0.0083 -2.1448
siesta:    7   -465.8387   -465.7240   -465.7240  0.0067 -2.1531
siesta:    8   -465.8387   -465.7527   -465.7527  0.0051 -2.1545
siesta:    9   -465.8387   -465.7742   -465.7742  0.0038 -2.1543
siesta:   10   -465.8387   -465.7903   -465.7903  0.0028 -2.1539
siesta:   11   -465.8387   -465.8024   -465.8024  0.0021 -2.1535
siesta:   12   -465.8387   -465.8115   -465.8115  0.0016 -2.1533
siesta:   13   -465.8387   -465.8183   -465.8183  0.0012 -2.1531
siesta:   14   -465.8387   -465.8234   -465.8234  0.0009 -2.1530
siesta:   15   -465.8387   -465.8272   -465.8272  0.0006 -2.1530
siesta:   16   -465.8387   -465.8301   -465.8301  0.0005 -2.1530
siesta:   17   -465.8387   -465.8322   -465.8322  0.0004 -2.1530
siesta:   18   -465.8387   -465.8338   -465.8338  0.0003 -2.1530
siesta:   19   -465.8387   -465.8351   -465.8351  0.0002 -2.1530
siesta:   20   -465.8387   -465.8360   -465.8360  0.0001 -2.1530
siesta:   21   -465.8387   -465.8367   -465.8367  0.0001 -2.1530
siesta:   22   -465.8387   -465.8372   -465.8372  0.0001 -2.1530
```

Output: Eigenvalues, forces, stress

```
siesta: Eigenvalues (eV):
  ik is    eps
   1  1 -24.74 -12.70  -8.71  -6.23   1.68   4.09
        14.68  21.97  24.22  27.21  28.65  32.19
        49.89  70.65  96.18


siesta: Atomic forces (eV/Ang):
siesta:     1     0.000001   -0.504870    0.000000
siesta:     2     0.719664    0.279830    0.000000
siesta:     3    -0.719663    0.279829    0.000000
siesta: ----------------------------------------
siesta:  Tot     0.000002    0.054788    0.000000

siesta: Stress tensor (eV/Ang**3):
siesta:    -0.012622    0.000000    0.000000
siesta:     0.000000   -0.002309    0.000000
siesta:     0.000000    0.000000    0.014000
```

Output: Total energy

```
siesta: Fermi energy =      -2.152975 eV

siesta: Program's energy decomposition (eV):
siesta:-Eions   =    -815.854478
siesta: Ena     =     175.154399
siesta: Ekin    =     350.784945
siesta: Enl     =     -61.958840
siesta: DEna    =      -1.777979
siesta: DUscf   =       0.727284
siesta: DUext   =       0.000000
siesta: Exc     =    -112.912881
siesta: eta*DQ  =       0.000000
siesta: Emadel  =       0.000000
siesta: Ekinion =       0.000000
siesta: Eharris =    -465.839084
siesta: Etot    =    -465.837551
siesta: FreeEng =    -465.837551

siesta: Final energy (eV):
siesta:       Kinetic =     350.784945
siesta:       Hartree =     382.616610
siesta:    Ext. field =       0.000000
siesta:   Exch.-corr. =    -112.912881
siesta:  Ion-electron =   -1072.820417
siesta:       Ion-ion =     -13.505807
siesta:       Ekinion =       0.000000
siesta:         Total =    -465.837551
```

Output: timer

```
timer: CPU execution times:
timer:  Routine    Calls Time/call  Tot.time      %
timer:  siesta         1    13.660    13.660 100.00
timer:  Setup          1     0.850     0.850   6.22
timer:  bands          1     0.000     0.000   0.00
timer:  KSV_init       1     0.000     0.000   0.00
timer:  IterMD         1    12.800    12.800  93.70
timer:  hsparse        2     0.005     0.010   0.07
timer:  overfsm        2     1.095     2.190  16.03
timer:  IterSCF       23     0.461    10.600  77.60
timer:  kinefsm        2     1.010     2.020  14.79
timer:  nlefsm         2     2.780     5.560  40.70
timer:  DHSCF         23     0.128     2.950  21.60
timer:  DHSCF1         1     0.060     0.060   0.44
timer:  DHSCF2         1     0.190     0.190   1.39
timer:  REORD        186     0.001     0.130   0.95
timer:  POISON        24     0.020     0.480   3.51
timer:  DHSCF3        23     0.110     2.520  18.45
timer:  rhoofd        23     0.030     0.690   5.05
timer:  CELLXC        23     0.027     0.610   4.47
timer:  vmat          23     0.018     0.410   3.00
timer:  diagon        22     0.002     0.050   0.37
timer:  rdiag         22     0.002     0.040   0.29
timer:  DHSCF4         1     0.180     0.180   1.32
timer:  dfscf          1     0.150     0.150   1.10

>> End of run:  3-JUL-2002  17:06:32
```

Saving and reading information (I)

Some information is stored by Siesta to restart simulations from:

- Density matrix: DM.UseSaveDM
- Localized wave functions (Order-N): ON.UseSaveLWF
- Atomic positions and velocities: MD.UseSaveXV
- Conjugent gradient history (minimizations): MD.UseSaveCG

All of them are logical variables

EXTREMLY USEFUL TO SAVE LOT OF TIME!

Saving and reading information (II)

Information needed as input for various post-processing programs,

for example, to visualize:

- Total charge density: SaveRho
- Deformation charge density: SaveDeltaRho
- Electrostatic potential: SaveElectrostaticPotential
- Total potential: SaveTotalPotential
- Local density of states: LocalDensityOfStates
- Charge density contours: WriteDenchar
- Atomic coordinates: WriteCoorXmol and WriteCoorCerius

All of them are logical variables

Analyzing the electronic structure (I)

- **Band structure** along the high symetry lines of the BZ

  BandLineScale: scale of the k vectors in BandLines

  ```
  BandLineScale      pi/a
  ```

  BandLines: lines along with band energies are calculated.

  ```
  %block BandLines
      1    1.000   1.000   1.000   L
     20    0.000   0.000   0.000   \Gamma
     25    2.000   0.000   0.000   X
     30    2.000   2.000   2.000 \Gamma
  %endblock BandLines
  ```

Analyzing the electronic structure (II)

•**Density of states**: total and projected on the atomic orbitals

- Compare with experimental spectroscopy
- Bond formation
- Defined as:

$$g(\epsilon) = \sum_i \sum_{\mathbf{k}} \delta(\epsilon - \epsilon_i(\mathbf{k})) \simeq \sum_i \sum_{\mathbf{k}} \frac{1}{\sigma\sqrt{\pi}} exp\left(-\frac{(\epsilon - \epsilon_i(\mathbf{k}))^2}{\sigma^2}\right)$$

ProjectedDensityOfStates:

```
%block ProjectedDensityOfStates
    -20.00   10.00   0.200  500  eV
%endblock ProjectedDensityOfStates
```

Analyzing the electronic structure (III)

- **Population analysis: Mulliken** prescription

  - Amounts of charge on an atom or in an orbital inside the atom

  - Bond formation

  - Be careful, very dependent on the basis functions

WriteMullikenPop

WriteMullikenPop 0 = None

1 = Atomic and orbitals charges

2 = 1 + atomic overlap pop.

3 = 2 + orbital overlap pop.

Tools (I)

- Various **post-processing programs**:

  -PHONONS:

    -Finite differences: VIBRA (P. Ordejón)

    -Linear response: LINRES (J. M. Alons-Pruneda et al.)

    -Interphase with Phonon program (Parlinsky)

  -Visualize of the CHARGE DENSITY and POTENTIALS

    -3D: PLRHO (J. M. Soler)

    -2D: CONTOUR (E. Artacho)

    -2D: DENCHAR (J. Junquera)

Tools (II)

-TRANSPORT PROPERTIES:

-TRANSIESTA (M. Brandbydge *et al.*)

-PSEUDOPOTENTIAL and BASIS information:

-PyAtom (A. García)

-ATOMIC COORDINATES:

-Sies2arc (J. Gale)