GEOMETRY OPTIMIZATION **15/May/2025**

The objective is to optimize/relax (=obtain minimum energy state) of a molecule and a crystal structure. This is related (but not equal) to the official SIESTA tutorial:
https://docs.siesta-project.org/projects/siesta/en/latest/tutorials/basic/structure-optimization/

Start by creating a GitHub repository for the SIESTA case studies (today and forthcoming sessions).
Upload the obtained results at your **GitHub** for use in future sessions.

1. Geometry optimization of a molecule

1.1 Generation of coordinates

a) We will start by creating a molecule of our choice using VMD Molefacture option. In VMD, go to *Extensions - Modelling – Molefacture.*

The coordinate file for the molecule can also be created with other programs such as Avogadro or using a python library such as ASE. Also, there are repositories with molecular coordinates.

b) Now you have several options to create new molecules (from small ones to big polymers) and modify existing ones adding functional groups. Let us start creating a benzene molecule by going to *Build - Add independent fragment.*

c) Save your molecule in xyz and pdb formats in a new folder (for example with name "build_molecule").

d) Modify the benzene molecule, by replacing a H atom by a functional group of your choice and save the new molecule.

e) Let us convert the xyz files to fdf format for SIESTA. Open a terminal (*you need sisl installed*) and use the sgeom command: https://sisl.readthedocs.io/en/latest/scripts/sgeom.html

sgeom benzene.xyz benzene.fdf

Unfortunately it is not possible to visualize fdf files with VMD and verify the conversion. But this can be easily done in **python** using **sisl** as we did before with:

```
import sisl as si
molecula=si.Geometry.read("benzene.fdf")
print(molecula)
molecula.plot()
```

1.2 Energy Minimization

a) In order to perform a simulation with SIESTA we will need the following files:

- **Coordinates** of the structure to be simulated in **fdf format**
- Script containing **SIESTA commands** for the calculation in **fdf format**.
- **Pseudopotentials** for all chemical elements

Prepare a new folder (**input**) with all the necessary files.

Examples of fdf scripts for executing Energy Minimization for molecules and crystals are available at https://github.com/jfaraudo/SIESTA_examples. Download one appropriate for molecules.

Curated Pseudopotentials for all chemical elements can be downloaded from here: https://www.pseudo-dojo.org/

b) Revise the fdf script and once ready run a SIESTA calculation. Before running the calculation is advisable to copy the **input** folder into a new folder (**run**) and execute the calculation in this run folder. To run SIESTA in the background:

nohup siesta optimization.fdf > optimization.log &

1.3 Analyse the Energy Minimization

a) Once the simulation has finished, check the results. Open the trajectory file (ANI file) with VMD and look at the changes in the structure (for example measure how bonds change).

b) Verify the changes in the Potential Energy, which can be plotted from the MDE file. Has the calculation converged to a final result?

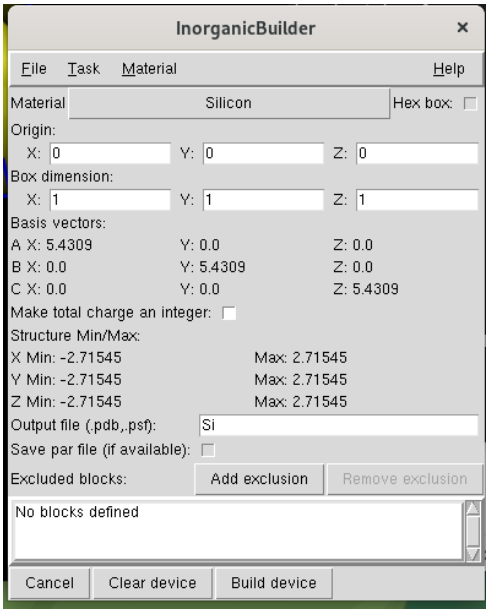
c) A critical parameter in the Energy minimization was the MD.MaxForceTol parameter. Try another simulation, increasing or reducing this parameter and compare the results.

2. Geometry relaxation of a crystal

The case of a crystal differs form that of a molecule because we typically need to optimize not only atomic coordinates but also the cell vectors. This requires additional options in SIESTA.

2.1 Generation of coordinates

a) We will start by creating a crystal of our choice using VMD Inorganic builder option. In VMD, go to *Extensions - Modelling – Inorganic Builder.*



b) Select Build a new device. A Window similar to the left image will open. As Material select *Silicon*. Create a structure with a single unit cell (8 atoms).

c) Save the coordinates in *xyz* format in a new *build_crystal* folder.

d) Convert the *xyz* format to *fdf* as we did before.

d) Open the *fdf* file to verify wether the automatic conversion has saved correctly the crystal lattice. You will see that sisl has added a lot of empty space **which is not correct for a 3D crystal**. Remove that vacuum by hand using the cell vectors provided by VMD (**what happens for a 2D material?**)

2.2 Energy Minimization

Proceed as before in 1.2 but now use a fdf file appropiate for optimization with variable cell.

2.3 Analyse the Energy Minimization

a) Once the simulation has finished, check the results as before. Open the trajectory file (ANI file) with VMD and look at the changes in the structure.

b) Verify changes in the relevant quantities which are now *Potential Energy, Volume and Pressure* (why now we monitor more quantities?).

c) A critical parameter in the Energy minimization was the MD.MaxStressTol. Try another simulation, increasing or reducing this parameter and compare the results. For example, you can try try with 0.1 GPa or 0.001 GPa.

d) Another critical parameter for the calculation is the sampling of k points in reciprocal space:

```
%block kgrid_Monkhorst_Pack
  3  0  0  0.0
  0  3  0  0.0
  0  0  3  0.0
%endblock kgrid_Monkhorst_Pack
```

Try using, instead of 3x3x3 (=27 points) a larger or smaller number of k points. What happens?