Practical 3 – Geometry Optimization

Learning Objectives

- Build your own `.cell` and `.param` files to control CASTEP
- Learn how to do both fixed-cell and variable-cell geometry optimizations
- Learn how to download structures from online databases and convert to CASTEP cell files

Exercise 1 - H_2 dimer

Build your own `H2.cell` and `H2.param` files *from scratch* to compute the bond length of an H_2 molecule in the gas phase.

Hint: You can use `castep --help` to assist you with finding the appropriate input parameters. You can also use the input files from previous practicals as a guide.

Consider:

- How big does your box need to be?
- Do you want the size of your box to vary?
- Set your initial H-H distance to 1 Angstrom.
- Set **`basis_precision=FINE`** in the `.param` file (an alternative way to specify the cut-off energy).
- What k-point sampling do you need for this computation?
- Set the appropriate value for **`task`** in the `.param` file).
- If you do not specify a pseudopotential file then CASTEP will build its own 'on-the-fly'.

Run CASTEP on your input files and see what it thinks is the equilibrium bond length of H2. Study the `.castep` file carefully and make sure you understand everything that is going on!

The experimental H2 bond length is about 0.74 Angstroms and the vibrational frequency is about 4395 cm^{-1}

Explore the various parameters and see how close you can get! Which parameters have the biggest effect and why?

Exercise 2

Run a geometry optimisation on silicon, using a copy of the Si2 input files from the previous tutorials as a starting point for your input files.

Set CASTEP's parameters to perform a geometry optimisation to find the equilibrium lattice parameters and ionic positions, using:

- **`task : geometry optimisation`**
- **`cut_off_energy : 160 eV`** (you will need to remove any existing **`basis_precision`** setting)
- **`XC_functional : PBE`**
- **`kpoints_MP_grid 8 8 8`** (in the `.cell` file)

(NB these input files have already been optimised for the LDA exchange-correlation (XC) functional, so we are changing to the PBE functional which will have a different optimal lattice parameter.)

This time there will be extra output in the `.castep` file associated with the stress and the changing cell vectors. Study this file carefully and make sure you understand everything that is going on!

NB As you want CASTEP to change the lattice vectors, CASTEP will do a finite basis-set correction (FBSC) which will calculate and print out dEtotal/dlog(Ecut). This is used to correct for the change in energy due to the change in basis set size when the lattice vectors change. A value of dEtotal/dlog(Ecut) greater than 0.1 eV/atom is large, and a sign of incomplete convergence. What should you do to improve the convergence?

The experimental lattice constant of Si is 3.84 Angstrom - how does your value compare?

Exercise 3 - Extensions

Try some systems you are interested in! You can download structures from various databases including http://psds.ac.uk usually in a common format such as `.cif`. There are various CASTEP file format converters, such as `cif2cell` (that is included by the `module load phys/CASTEP` command) that you can use to generate an appropriate `.cell` file.

`cif2cell -h`	gives you the built-in help
`cif2cell my.cif -p castep`	converts my.cif to my.cell

See the cif2cell.pdf manual for more information.