Vibrational Spectroscopy Practical 2:

The aims of today's session are to introduce you to running larger-scale CASTEP jobs on supercomputer clusters, creation of input files for and setup of CASTEP jobs, and analysis of the results using standalone tools. In order to achieve results without waiting too long for jobs to complete the initial runs will be small ones, but the aim by the end of this afternoon should be to set up a larger and more significant run to execute overnight, for analysis in tomorrow's practical session. Today's session will entirely comprise insulators or semiconductors.

You may need to consult the CASTEP phonon users guide, which may be accessed at

http://www.tcm.phy.cam.ac.uk/castep/Phonons_Guide/Castep_Phonons.html

The practical will be conducted using the *redqueen* service. Once logged on you must issue the command

```
module load castep/training
```

to get access to course software. You will find example files in

```
/home/system/software/redqueen/castep-course/Examples
```

and pseudpotential files in

```
/home/system/software/redqueen/castep-course/PSPOTS
```

A. Γ-Point phonon in h-BN

The first exercise will take you through the construction of a Γ point phonon calculation and the generation of a simple model infrared spectrum of a semiconductor. It will also introduce you to the use of some additional analysis and visualisation tools. These calculations should be run on one of the dedicated high-performance cluster systems – Lagavulin (at Durham) or Redqueen (at Oxford Supercomputer Centre) as the runs would take too long on the PCs. Please see the separate instructions for logging on to these systems and transferring files to and from the OUCS PC system.

BN is one of a family of Nitride semiconductors, which occurs in cubic zincblende (c-BN), hexagonal wurtzite (w-BN) and graphite-like hexagonal (w-BN) polymorphs. We will calculate the phonons, infrared spectrum and raman spectrum of h-BN.

Your starting point will be the structure which is provided in a pdb file named *h-BN.pdb* which you can copy from the shared K drive on the windows system. There are several ways to use this to initialise a CASTEP calculation. The first is to import the structure into Materials Studio. But since you are already proficient at that, the input files for this exercise should be constructed by hand. The Phonons manual (http://www.tcm.phy.cam.ac.uk/castep/Phonons_Guide/Castep_Phonons.html) contains a very similar example for a different polymorph of BN. You can translate the .pdb file into a skeleton .cell file using the *pdb2cell* script. This is installed on the K drive in the windows system, but is probably easier to use on the linux cluster *redqueen*. Copy the .pdb file over to redqueen and run the command

```
pdb2cell h-BN.pdb > h-BN.cell
```

after loading the appropriate course module. Then edit the .cell file using one of the text editors installed on the system. If you are not familiar with any then I suggest *nano*, but *vi* and *emacs* are also installed. The file prepared by “pdb2cell” contains the structure, but will need additional keywords to initialise a CASTEP run. For now just add the keyword

```
symmetry_generate
```

on an extra line, and save the result.

But first you will observe that there is a problem with this .cell file. The atoms in this structure should be located at crystallographic special positions such as (1/3,2/3,1/4). However this is only satisfied to rather low precision in the .cell file generated from the .pdb. This situation causes problems for the symmetry handling in CASTEP phonon calculations. We recommend that symmetries are satisfied to 1 part in 10^{-7} or better to avoid trouble.

There is a tool to analyse this in the academic CASTEP toolset, which you should run as

```
symmetry_snap h-BN
```

which will (a) indicate the symmetry precision and (b) attempt to produce a new version of the .cell with symmetries satisfied to higher precision. (In Materials Studio there is a button in the symmetry finder to do the same.)

Please edit your .cell file and change the fractional co-ordinates to specify the relevant numbers of 1/3, 2/3,1/4 and 3/4 to at least 8 decimal places. Rerun “symmetry_snap” to check that you have done this correctly.

Now you are ready to add some additional information to the .cell file to prepare for a CASTEP run. You should add a specification of the pseudopotentials to use

```
%BLOCK SPECIES_POT
 B b-krlda1.recpot
 N n-optlda1.recpot
%ENDBLOCK SPECIES_POT
```

the k-point set to use – remove the Gamma-only block KPOINT_LIST and replace with the line

```
kpoint_mp_grid 7 7 4
```

and one to specify a gamma-point *phonon* wavevector

```
phonon_kpoint_mp_grid 1 1 1
```

Congratulations. You have set up the .cell file by hand. To actually run you will need copies of the pseudopotential files ”b-krlda.recpot” and “n-optlda1.recpot” which can be copied from the shared K drive area. There is also a .param file “h-BN.param” provided containing the setup to specify the phonon run.

Once you have in place the <seed>.cell and <seed>.param files, and the pseudopotentials, you are ready to submit the CASTEP job. This is done using our general script:

```
castepsub -5 -n 16 h-BN
```

which requests a 16-processor parallel run using CASTEP version 5. Use the “qstat” command to monitor the progress of your calculation. When it has finished, you can examine the output file h-BN.castep and find the frequencies. What you see is explained further in the Phonons user guide on the WWW. There is also a machine-readable file h-BN.phonon which contains the frequences, but also the eigenvectors which we will analyse.

Analysis of h-BN phonon output.

We will use the academic tools to visualise the modes using the free Jmol visualiser. Jmol will read a file of “XYZ” format containing the phonon eigenvector data. You may create this on redqueen using the following command to read the .phonon file:

```
phonon2xyz h-BN.phonon > h-BN.xyz
```

Use secure file transfer to copy this xyz file back to the PC where Jmol is installed. Start jmol and bring up a console window from the right-mouse menu. Then type the Jmol command to load your XYZ file

```
 load h-BN.xyz {3 3 2} unitcell {2.504    2.504    6.660  90.00  90.00 120.00} PACKED
```

(You may need to supply a full pathname for Jmol to find the .xyz file). Note that while you can read in the xyz file from Jmol's File menu, you need the additional opitions of the command line to add the unit cell and display additional periodic repeats.

You can then use the “Tools-Vibrate” menu to turn on mode animation, and navigate the modes. Can you see from the mode eigenvectors which modes are ir active and which are raman active? Do you agree with the ir and raman activity printed in the .castep file?

Generation of ir spectrum

The easiest way to generate a simple model ir spectrumis to use the “dos.pl” tool. To run this in the most effective way and audomatically display a plot, you will need to be running an X windows server on the PC. In that case the command

```
  dos.pl -ir -xg h-BN.phonon
```

will generate a plot script and use the “xmgrace” plotting program to display it. You can create a GNUPLOT script instead of xmgrace by changing the “-xg” flag to “-gp”. Alternatively you can generate a GNUPLOT script without plotting by

```
  dos.pl -ir -gp -np h-BN.phonon > h-BN-phonon.plt
```

You can then copy the “h-BN-phonon.plt” back to the PC and read this into GNUPLOT.

Raman spectrum

The calculation of a raman intensities is fairly expensive compared to infrared matrix elements and it is therefore not turned on by default. To enable this, add the keyword

```
  calculate_raman : true
```

to the h-BN.param file, and resubmit the job. This will take around 10 minutes to run on redqueen. You can then use the “-raman” flag of dos.pl to generate and plot a raman spectrum.

B. Molecular modes in benzene

The next part of this practical is to compute the modes and spectrum of a molecule and compare the result with a calculation of a molecular crystal. Our example is benzene. You are supplied with pdb files describing a benzene molecule and of a cif structure describing a high-pressure crystalline polymorph, phase III. These are in both the shared K drive on the PC system and in the course directory on redqueen.

First run the isolated molecule calculation. Using the methods of the previous section generate a .cell file for a single molecule calculation. There are a few other considerations to take into account for an isolated molecule calculation.

1. The size of the simulation cell governs the interactions between periodic copies of the molecule and should be large enough that these are negligible.
2. The shape of the simulation cell governs the crystallographic point groups allowed in the handling of the symmetry. It should be chosen to be commensurate (as far as possible) with the molecular point group to maximise the use of symmetry. In the case of benzene it should obviously be hexagonal, and I recommend a box 8A by 8A by 4A.

3. Recall that there is no electronic dispersion for a molecule, so only a single electronic k-point is needed. The general rule is that all “molecule in a box” calculations should use the Γ point only as CASTEP uses special performance optimisations in this case.

For simplicity use the local density approximation, the standard library pseudopotentials C_00.recpot and H_00.recpot and a plane-wave cutoff of 600 eV.

In benzene not all atoms are on special symmetry sites so you should first perform a geometry optimisation. Then set up a follow-on calculation to compute the Gamma point phonons. The Phonons User Guide on the WWW should help you fill in the details, but please ask if you are stuck.

Benzene Phase III: The next stage is to compute the gamma point phonon modes of the molecular crystal of benzene in the high pressure polymorph, Phase III. You are supplied with a .cif file. The easiest way to generate the .cell file is to use Materials Studio. However you will have to tweak the settings to get a calculation comparable to the molecule. You should use a 2x2x2 grid of electronic k-points, as dispersion is nonzero in this molecular crystal. Make sure that symmetry is detected and enabled. Use the same .param file as for the molecular case to ensure the settings are the same.

Once these calculations have completed you should generate a phonon DOS and ir spectra as in the previous practical and compare the molecule with the molecular crystal. You can also use phonon2xyz and Jmol to identify the modes.

Are all your frequencies positive? If not, can you suggest why not? Try investigating the effect of decreasing the geometry optimisation tolerance GEOM_FORCE_TOL. How does this change the frequencies?

C. Phonon dispersion using interpolation in NaH

From Γ point only calculations we now explore the whole of the Brilllouin zone of phonon wavevectors. Our example is the rocksalt-structured hydride, NaH which should run quickly enough to return results in a few minutes. Based on previous exercises, lectures and the user manual, you should be able to set up and run a DFPT phonon dispersion calculation and display a well converged set of dispersion curves.

Some suitable settings are

- The primitive fcc unit cell of the B1 rocksalt structure has a=b=c=3.393405, α=β=γ=60°, with the Na ion at (0,0,0) and the H ion at (1/2,1/2,1/2). This is a high-symmetry structure so it is important to instruct CASTEP to generate and use the full symmetry set.
- Use norm-conserving pseudopotentials *na-krlda1.recpot, h-optlda1.recpot* with a cutoff of 550 eV
- A suitable phonon qpoint grid for the interpolation is an offset 4x4x4 grid

```
phonon_kpoint_mp_grid 4 4 4
phonon_kpoint_mp_offset 0.125 0.125 0.125
```

- A suitable list of points for the fine q-point path for FCC is

```
%block phonon_fine_kpoint_path
  0.0 0.0 0.0   ! Gamma
  0.5 0.5 0.0   ! X (along Delta
  1.0 1.0 1.0   ! Gamma (Sigma )
  0.5 0.5 0.5   ! L (Delta)
  0.5 0.75 0.25 ! W (Q)
```

```
    0.5 0.5 0.0   ! X (Z)
%endblock phonon_fine_kpoint_path
```

You will first need to perform a k-point convergence test. For a phonon calculation, convergence of the *forces* is an appropriate test criterion. Since all of the ions are on symmetry positions the forces are zero by symmetry. Try to think of a way around this obstacle. And adopt a suitable compromise between accuracy and run-time.

C.II Phonon DOS using interpolation

The task here is to use the NaH example to compute and display not a dispersion curve but a density of states. This will exploit CASTEPs interpolation functionality, and you will be able to compute a good DOS without the need the repeat the expensive electronic structure calculation. To do this you will need to set up a calculation neatly identical to your previous one but with two differences.

1. The calculation should be set up as a continuation. If your previous run wrote a .check file named “NaH-disp.check” for example, then the param file should contain the line

   continuation : NaH-disp.check

2. Instead of a %block phonon_fine_kpoint_list in the .cell file, you can specify a grid

   phonon_fine_kpoint_mp_grid 16 16 16

You can run CASTEP on just 1-4 processors for this (omitting the “-n” argument to the castepsub command should work).

You can try this several times with different fine q-point grids.

This will produce a .castep and .phonon file as before. You may analyse the .phonon file and generate a DOS using the “dos.pl” script

```
dos.pl -xg NaH-dos.phonon
```

(again, an X server running on the PC will be needed for grace to display) .

Finally you can use these same results to generate a predicted INS spectrum using the A-Climax program. See separate instructions for more details.

D. Phonon dispersion of a larger/more complex system.

All of the examples so far have been chosen to be deliberately small and quick. However we have access to most of the redqueen cluster overnight, which will allow you to run a more serious calculation overnight and analyse the results tomorrow. This. is an open ended exercise so you should probably discuss the feasibility and details with a tutor.

This exercise is intended to explore the DFPT phonon functionality, so please restrict consideration to insulating or semiconducting (or even molecular) systems and norm-conserving pseudopotentials. We can find suitable potentials for much of the periodic table.

If you don't have a test case of your own, then I suggest a full dispersion calculation of alpha quartz, in the structure you have worked on before, or have a browse in the Materials Studio structures library.