Electronic Structure Theory
Exercise 5

Due: Friday Week 6, 12pm

1 Aims

In this exercise, you will use the Quantum ESPRESSO (QE) density functional theory package to calculate more advanced ground-state properties of different materials. These include electronic densities of states and band structures, estimates of pressure-induced phase transitions, and estimates of elastic constants.

You will perform these calculations on materials you have already encountered, silicon, quartz, and the α- and β-phases of tin.

2 Instructions

2.1 Preparations

Log into ARCHER2. Copy the QE input file archive into an appropriate sub-directory of your user account and unpack it. Also remember to look up your convergence test results from the previous exercise, for both silicon and the two tin allotropes.

```
user@login:~> tar -zxvf  input_files.tar.gz
user@login:~>   cd Exercise-5/inputs
```

Have a look at the QE input files and job scripts. These are set up to perform SCF calculations very much like you did in the previous exercise. You will need to edit the input files (maybe automated through a more sophisticated job script?) as described in more detail below.

3 Tasks

3.1 Silicon elastic properties

We want to estimate (some of) the components of the elastic constants tensor c_{ij} of silicon. In particular, we want to determine c_{11} and c_{12}. To this end, we will impose anisotropic strains on the silicon structure (this is different from the isotropic volume changes we have used in the last exercise) and monitor the resulting stresses. The strain we want to impose (see week 5 lecture) is along the [100] or, equivalently, the [001] direction. This will break the cubic symmetry of the silicon structure, and we thus need to describe it in a tetragonal setting.

3.1.1 Different Bravais lattices, same answer

Verify that QE gives the same total energy per silicon atom no matter the setting for the Bravais lattice. Modify the input file `si.scf-van.in` to represent the *same* face-centered cubic structure through (i) a rhombohedral lattice (`ibrav=5`); (ii) a simple cubic lattice (`ibrav=1`); and (iii) a tetragonal lattice (`ibrav=6`). In each case, modify the cell parameters needed and the number and positions of the silicon atoms in the unit cell to ensure you model the *same* three-dimensional crystal. Make sure you use the equilibrium volume you obtained with the Vinet EOS fit in the previous exercise. The total energy per atom should not deviate by more than 1 mRy between these different settings (some differences from the k-point grids might remain). Include the respective relevant sections of the input files (most easily the `&system` and `ATOMIC_POSITIONS` sections) in your submission.

3.1.2 Putting on the squeeze

For this task use the *tetragonal* description of silicon. The input file needs two additional lines in the `&control` section to calculate the stress tensor and forces on the atoms:

```
&control
    ...
    tstress = .true.,
    tprnfor = .true.
/
```

Now perform a set of SCF calculations where you modify the c/a ratio, which is 1.0 for the cubic structure, to simulate compressive and tensile strains along the c axis. This corresponds to a finite strain rate ϵ_{33}. Cover a range of strain rates approximately $\pm 1\%$. For each strain, retrieve the components of the stress tensor σ_{ij} from the output file. Plot σ_{11} and σ_{33} against the strain rate ϵ_{33}, and use linear fits to obtain the derivatives $\partial \sigma_{ij}/\partial \epsilon_{33}$. These are equal to the elastic constants c_{13} and c_{33}, which by symmetry are equal to (and usually denoted as) c_{12} and c_{11}, respectively. How do the values you obtain compare to experimental data?

3.2 Electronic density of states and band structure

Beyond performing simple SCF cycles, we want to study the materials' electronic structure by calculating their electronic densities of states (DOS) and band structures. The relevant input file collections are in the `dos` and `bands` subdirectories.

DOS calculations are done as described in week 5's lectures: first, we perform a SCF calculation to obtain the electronic charge density, which completely defines the Kohn-Sham Hamiltonian; then, we perform a non-SCF calculation on a much denser k-point mesh (i.e., a simple diagonalization of the Kohn-Sham matrix across a larger number of wave vectors); and finally, a postprocessing step to extract the DOS from the eigenvalue data. This sequence is automated in the job script `job-dos.bash`.

For band structure calculations, as with the DOS, one performs a SCF calculation to determine the electronic Hamiltonian, then uses that to perform a non-SCF calculation, but now along a special path in the Brillouin zone. The choice of path depends on the Bravais lattice, which determines the shape of the Brillouin zone. See Figure 1 for the Brillouin zone of the primitive unit cell of quartz (space group $P3_221$ has a hexagonal lattice), diamond (space group $Fm\bar{3}m$ means a face-centered cubic lattice) and β-Sn (space group $I4_1/amd$ means a body-centered tetragonal lattice, here with $c < a$). The figure also shows the special points and their coordinates. An example for a meaningful path around the edge of the irreducible wedge of the Brillouin zone of quartz is given in `quartz.bands.in`.

Now calculate the electronic DOS and band structure of quartz, α- and β-tin. Use the ultrasoft pseudopotentials for SiO_2. In all systems, use plane wave cutoffs and SCF k-point grids you have found to be sufficient in the previous exercise: total energy of quartz converged to 1 meV/SiO_2; energy difference between α- and β-Sn converged to 1 meV/Sn.

1. Calculate the electronic DOS of quartz, α- and β-tin. I have provided sample input files for β-tin. Use those as templates to put together input files for both quartz and α-tin. What k-point grids are necessary in the non-SCF step to converge the features of the DOS's? Aim to minimize numerical noise while retaining all significant DOS features. Adjust the Gaussian broadening width or produce results using the tetrahedron interpolation method by adapting the postprocessing inputs `beta-sn.pp_dos.in`, etc.

2. Calculate the electronic band structures of quartz, α- and β-tin. A postprocessing step will convert the electronic band structure to a data file that can be plotted easily. This sequence has been prepared in `job-bands.bash`. I have provided sample input files (which need adjusting in the plane wave cutoff and SCF k-point grid) for quartz. Use these as templates to put together input files for α- and β-Sn. In those, you should track the following pathways through their respective Brillouin zones:

    - α-Sn: $\Gamma - X - W - K - \Gamma - L$
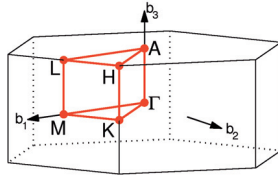   - β-Sn: $\Gamma - X - M - \Gamma - Z - N - P - Z_1 - \Gamma$

Table 13
Symmetry **k**-points of HEX.

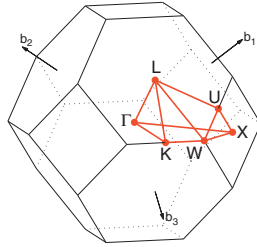| $\times\mathbf{b}_1$	$\times\mathbf{b}_2$	$\times\mathbf{b}_3$		$\times\mathbf{b}_1$	$\times\mathbf{b}_2$	$\times\mathbf{b}_3$	
0	0	0	Γ	1/3	1/3	0	K
0	0	1/2	A	1/2	0	1/2	L
1/3	1/3	1/2	H	1/2	0	0	M

Table 3
Symmetry **k**-points of FCC lattice.

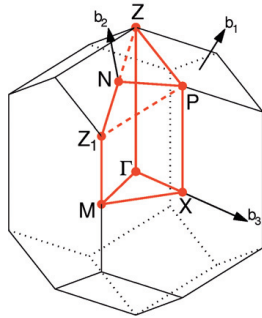| $\times\mathbf{b}_1$	$\times\mathbf{b}_2$	$\times\mathbf{b}_3$		$\times\mathbf{b}_1$	$\times\mathbf{b}_2$	$\times\mathbf{b}_3$	
0	0	0	Γ	5/8	1/4	5/8	U
3/8	3/8	3/4	K	1/2	1/4	3/4	W
1/2	1/2	1/2	L	1/2	0	1/2	X

Table 6
Symmetry **k**-points of BCT$_1$ lattice.

$\times\mathbf{b}_1$	$\times\mathbf{b}_2$	$\times\mathbf{b}_3$		$\times\mathbf{b}_1$	$\times\mathbf{b}_2$	$\times\mathbf{b}_3$	
0	0	0	Γ	0	0	1/2	X
−1/2	1/2	1/2	M	η	η	$-\eta$	Z
0	1/2	0	N	$-\eta$	$1-\eta$	η	Z_1
1/4	1/4	1/4	P				
$\eta = (1 + c^2/a^2)/4$							

Figure 1: Brillouin zone (left) and special points coordinates (right) of a hexagonal (top), face-centered cubic (middle), and body-centered tetragonal Bravais lattice (bottom). From Comp. Mat. Sci. 49, 299-312 (2010).

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3. After the calculations, plot the electronic band structures next to the DOS's, and discuss whether they agree with each other. Which of the systems studied has a bandgap, and which is a metal? Does this agree qualitatively with reality, and how do fundamental band gaps compare to experimental values? The Fermi energy for each system, which separates occupied and empty states, can be found in the DOS calculations.

3.3 Tin's phases and transitions

We want to use the method of common tangents to estimate a phase transition pressure between α- and β-Sn. To that end, generate $E(V)$ curves for both tin phases around their respective equilibrium lattice constants. Note that β-Sn has an internal degree of freedom, the c/a ratio in its tetragonal crystal structure. This is set as parameter `celldm(3)` in the input file. We will ignore the volume dependence of c/a and leave this value unchanged; hence, for both phases, rescale the total volume by changing `celldm(1)` just as you did last week for the equation of state of silicon.

Once all calculations have finished, fit both $E(V)$ curves to one of the equations of state, and compare equilibrium volumes and bulk moduli to literature values. Next, fit a common tangent to both curves. What is its slope, and thus your predicted transition pressure between α- and β-Sn? How does the volume collapse ΔV at the transition compare with experiment, which finds $\Delta V \sim 20\%$?

4 Submission

Submit a summary of your results, addressing the questions posed in the previous section. Submit a single document (preferrably PDF) including tabulated data, figures, and discussion.

5 Marking Scheme

- Si elastic constants: unit cells, data and fits, comparison to experiment. [10]

- DOS for all compounds: Non-SCF k-point grid for DOS; Gaussian smearing vs tetrahedron method; discussion. [10]

- Band structures: agreement with DOS; qualitative interpretation; comparison to experiment. [10]

- Sn-EOS: $E(V)$ data and fits for α- and β-Sn, comparison to experiment, estimate of transition pressure and volume collapse. [10]

Total marks: 40, count for 20% of the course grade.