

## Theoretical Material Science: Exercise Sheet 5

Please hand in solutions by: **Tuesday, May 30**, start of the exercise class

The following description is only a skeleton description of the task. A more detailed description of the tasks to be performed is provided separately. The actual task will be performed using a general-purpose electronic structure code, installed in a virtual machine (VM). See [http://www.itp.tu-berlin.de/fileadmin/a3233/upload/SS17/TMS/Howto\\_UsingVirtualMachine.pdf](http://www.itp.tu-berlin.de/fileadmin/a3233/upload/SS17/TMS/Howto_UsingVirtualMachine.pdf) for detailed instructions on how to install/use the VM. We will begin the exercise together during class. Any remaining parts should be done as homework.

### Exercise 13 (4 points): Brillouin zone integrals

In periodic solids, Bloch's theorem tells us that a good quantum number to count "states" is the crystal momentum  $\mathbf{k}$ , whose unique values are confined to the first Brillouin zone. For integrated quantities, this means that the usual sums over states  $i$  are replaced by an integral over all  $\mathbf{k}$  and different states  $n$  that correspond to the same  $\mathbf{k}$ :

$$\sum_i [\dots] \rightarrow \sum_n \int_{\mathbf{k} \text{ in 1. BZ}} d^3k [\dots]$$

For any quantity that is an average over states—for example, the total energy or the electron density—the  $k$ -space integral must be carried out explicitly, and with sufficient accuracy. Investigate the influence of a finite  $k$ -space integration grid for Si:

- For the diamond phase of Si, at the experimental lattice parameter  $a=5.43 \text{ \AA}$ , and using density-functional theory in the local-density approximation, calculate and plot the convergence of the cohesive energy with the integration quality of the Brillouin zone. How many integration points are needed for good convergence (few meV)? Is the convergence of the total energy variational with integration quality?
- For a given  $k$ -space integration grid, plot (i) the three-dimensional electron density  $n(\mathbf{r})$  and (ii) the electron density *difference* to a simple superposition of free atom densities. What is the predominant density change compared to simple free atoms, and does it match your physical intuition?
- For each  $k$  grid, the code gives you an estimate of the highest occupied state, the lowest unoccupied state, and their difference—the equivalent of the "band gap," but computed in Kohn-Sham theory. Is this "Kohn-Sham band gap" large enough compared to experiment? How does it evolve with improving integration quality of the Brillouin zone? What can you learn from the (approximate) location of the lowest unoccupied state in  $k$ -space?

### Exercise 14 (8 points): Cohesive properties: Will the stable phase(s) please stand up?

One of the fundamental questions in materials science is this: Given one or more chemical elements in a certain proportion, which stable structure will they form? The ability of density functional theory (DFT) in the local-density approximation (LDA) to predict, without any empirical parameters, the phase stability and materials parameters of real solids, marked a breakthrough in quantum-mechanics based computational materials science.

At  $T=0$  and  $p=0$ , the quantity that determines phase stability is the total energy  $E(V)$ , which has the following functional form: ("Murnaghan equation of state"):

$$E(V) = E_0 + \frac{B_0 V}{B'_0} \left[ \frac{(V_0/V)^{B'_0}}{B'_0 - 1} + 1 \right] - \frac{B_0 V_0}{B'_0 - 1} \quad (1)$$

In other words,  $E$  is related to the volume  $V$  by the following material properties defined at zero pressure:  $E_0$ , the equilibrium energy,  $V_0$ , the equilibrium volume,  $B_0$ , the bulk modulus at zero pressure, and its pressure derivative  $B'_0 = \left( \frac{\partial B}{\partial p} \right)_T$  at  $p = 0$ . The bulk modulus ( $B$ ) of a solid is defined as:

$$B = -V \left( \frac{\partial P}{\partial V} \right) = -V \left( \frac{\partial^2 E}{\partial V^2} \right) \quad (2)$$

In this exercise, we take  $E$  to be the energy at the Born-Oppenheimer surface, and neglect vibrations and finite-temperature effects.

a)  $E(V)$  of the diamond phase of Si.

- (i) For a set of five different unit cell volumes (lattice parameters), compute  $E(V)$  for diamond Si. Use DFT-LDA and a  $12 \times 12 \times 12$   $k$ -point integration grid.
- (ii) By fitting to Eq. (1), determine  $E_0$ ,  $V_0$ , and  $B_0$ .
- (iii) Compare your results to the following experimentally known parameters ( $T=0$ ): Lattice parameter  $a_0=5.43 \text{ \AA}$ ,  $B_0=98.9 \text{ GPa}$ , cohesive energy  $E_{\text{coh}}=4.63 \text{ eV/atom}$ . What are the trends? How do they match the expected properties of LDA? For Si and LDA, use the energy of the spherically symmetric free atom (ensemble average with fractional occupation numbers) as a reference in  $E_{\text{coh}}$ .

b) Other phases of Si.

At Earth atmospheric conditions, Si assumes the diamond structure, but at different conditions, other structures could exist. We here consider fcc and bcc Si.

- (i) Find the fcc and bcc lattice parameter values that correspond to the same Si-Si nearest-neighbour distance as in the experimental diamond structure.
- (ii) Beginning from these rough estimates, use a  $12 \times 12 \times 12$   $k$ -point grid and a Gaussian broadening of 0.1 eV about the Fermi level to find the equilibrium lattice parameters, bulk modulus, and cohesive energy for fcc Si and bcc Si as a function of volume.
- (iii) Only for the calculated lowest-energy geometry, verify the  $k$ -space convergence explicitly by using a  $24 \times 24 \times 24$   $k$ -point grid. How good is the convergence? Inspect the printed highest occupied and lowest unoccupied levels: Are fcc and bcc Si semiconductors or metals?
- (iv) Plot the cohesive energy of all three phases into the same graph, as a function of the unit cell volume per atom. According to LDA, which is the most stable phase? Does the prediction agree with experiment? Under pressure, do you expect fcc or bcc Si to become stable?

**Exercise 15** (4 points): *Trends for cohesive properties in LDA*

Use the same strategy as in the preceding exercise to determine the cohesive properties of

- a) GaAs
- b) ZnSe

Both materials (important semiconductors!) crystallize in the zincblende phase: The same lattice as the diamond phase, but two different elements occupy the two atomic sites. Consider only the zincblende structure, and only  $12 \times 12 \times 12$   $k$ -point grids. Use the free atom reference energies in the detailed instructions as a reference. Compare to the following  $T=0$  experimental values:

Material	$a$ [ $\text{\AA}$ ]	$B_0$ [GPa]	$E_{\text{coh}}$ [eV/atom]
GaAs	5.648	75.6	3.31
ZnSe	5.668	64.7	2.19

What are the trends that you would expect from DFT-LDA? Do the results match your expectations?