Computational Solid State Physics
Second part (DFT)

Makeup Exam, January 13th 2024

In this makeup test you will employ the DFT code `quantum espresso` to calculate some simple electronic structure properties of zincblende semiconductors with chemical formula AB. You have two hours to solve the assignment; you can consult any books, notes and internet websites, but communicating with other students by any means is strictly forbidden (your test will be invalidated in that case). **The use of AI tools like `ChatGPT` is strictly prohibited and will result in test invalidation.**
At the end of the four hours submit your report as a single PDF (named 'NAME_SURNAME.pdf') via email to `lilia.boeri@uniroma1.it`. Include all input files in a separate zipped attachment (named 'NAME_SURNAME_inputs.zip'). Use the subject line: 'Computational Solid State Physics Make up - NAME SURNAME.'" Please note that NAME SURNAME indicate YOUR name and surname, respectively. **At the beginning of your pdf file, please write down your name, surname, matricule number and group number.**

► **Exercise:** In this exercise, we will analyze the electronic properties of zincblende II-VI and III-V semiconductors, which are critical materials in research and industry, due to their unique electronic and optical properties. III-V semiconductors, like GaAs and InP, are essential for high-speed electronics, optoelectronics, and photovoltaics, offering superior electron mobility and efficient light emission. II-VI semiconductors, such as CdTe and ZnSe, are widely used in solar cells, lasers, and infrared devices, benefiting from their tunable band gaps and excellent optoelectronic characteristics. This enables advancements in telecommunications, renewable energy, and sensor technologies.

1 Preliminary steps:

- Download and unzip the archive `pseudo2.tar.gz` from the e-learning website of the course. The archive contains GGA Norm-Conserving pseudopotentials from the Pseudo-dojo website for selected elements of the periodic table.
- Each student has been assigned a different *student number*, as indicated in the student list file on elearning.
- Consult Table 1 to see what combination of elements corresponds to your student number. Each combination of elements defines a different binary compound with chemical formula AB for which you should perform calculations as described in the text.
- Download also the file `CdTe.scf.in`, which contains the input file for a QE self-consistent calculation for a II-VI zincblende semiconductor (CdTe).

2 Electronic properties of zincblende semiconductors:

2.1 Initial Structure Setup and Convergence of the Relevant Input Parameters:

1. Edit the `CdTe.scf.in` input file, replacing Cd and Te with the A and B atoms contained in the table. Answer the following question:
   - What is the underlying Bravais lattice?
   - What are the reciprocal lattice vectors and the basis vectors of atoms A and B (write them down explicitly).
   - How many valence electrons does your system contain?
2. Once you have verified that your input file is correctly set up, run all convergence tests required to attain an accuracy on the total energy of at least 10 meV/atom. Produce a separate plot for each convergence test, with a short explanation (max 50 words for each plot).

2.2 Structural Relaxation:

Starting from the lattice constant of CdTe, you now have to relax your structure to ambient pressure (0 GPa) to obtain the theoretical equilibrium structure.

1. What is the theoretical pressure calculated by `quantum espresso` for the structure you set up?
2. If you had to relax the structure by hand, without using `quantum espresso` relaxation routines, what would you do?
3. Once you are sure that your calculation has reached the theoretical equilibrium volume, write down the final value of the volume and the corresponding lattice constant.
4. Is it larger or smaller than that of CdTe? Can you guess why?
5. **Hint:** To make sure that your relaxation has really converged to the actual equilibrium structure, re-run a second relaxation starting from the final structure of the first relaxation.

2.3 Band Structure and Density of States:

Having determined the theoretical equilibrium structure we will now compute the corresponding electronic properties.

1. Compute the electronic band structure and Density of States of your zincblende semiconductor. For the band structure, use the $W - L - \Gamma - X - W - L$ path – A list of special k points for the fcc crystal is provided in the Appendix.
2. Based on your plots, answer the following questions:
   - Is your system a metal or an insulator? Why?
   - In case there is a band gap, how large is it? Is it a direct or indirect gap? What does it mean?
   - Do you think the actual experimental band gap will be smaller or larger than the one you computed? Why?

2.4 Atomic Displacements and Forces:

You will now displace one of the two atoms along the bond direction, compute the resulting forces, and relax the structure back to its equilibrium shape. Answer the following questions:

1. Answer the following preliminary questions:
   - How many bonds does each A atom form to B atoms and vice-versa? How long are they? What are the bond directions?
   - Displace the atom in the origin by f $0.05 \times \sqrt{3}$ times the lattice constant along the body diagonal. How do you do it?
2. Compute the resulting forces: what are the magnitude and direction of the force? What will happen when you let the structure relax?
3. Relax the structure using `quantum espresso` relaxation routine. Answer the following questions:
   - How many steps does it take to converge to the equilibrium structure?
   - Produce a plot of the variation of the energy and of the forces during the relaxation, as a function of the displacement. Comment your results (max. 100 words).

3 Appendix

3.1 Brillouin zone and special k points:

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

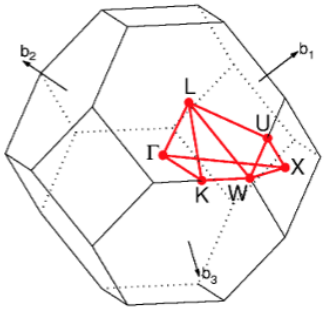

Figure 2: Brillouin zone of FCC lattice. Path: Γ-X-W-K-Γ-L-U-W-L-K|U-X. An example of band structure using this path is given in Figure 27.

3.2 Combinations of elements/structures for each student:

Group Number	Element A	Element B	Group Number	Element A	Element B
1	Ga	Sb	15	Zn	O
2	Cd	Te	16	Al	Sb
3	In	Sb	17	B	P
4	Al	As	18	Cd	Se
5	In	P	19	Ga	N
6	Zn	S	20	Zn	Se
7	Ga	P	21	B	As
8	Zn	Te	22	Ga	As
9	In	N	23	Cd	S
10	Al	N	24	B	N
11	Cd	O	25	Zn	Te
12	B	Sb	26	Al	P
13	Al	S	27	Ga	Sb
14	Ga	As	28	In	N

Tabella 1: List of element pairs – A cation, B anion – for each group.