

Computational Solid State Physics

2nd Midterm (DFT)

Midterm Exam, December 16th 2024

In this midterm exam you will employ the DFT code `quantum espresso` to calculate some simple electronic structure properties of hypothetical binary compounds with chemical formula AB , and simulate the effect of vacancies. You have four 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 Midterm - NAME SURNAME.' Please note that NAME SURNAME indicate YOUR name and surname, respectively.

► **Exercise:** In this exercise, we will compute the electronic properties of hypothetical compounds formed by placing two elements A and B in the rocksalt structure. The rocksalt structure is common for ionic compounds and consists of two interpenetrating fcc lattices, one for the anion (A) and one for the cation (B). This structure maximizes electrostatic attraction between the anion and cation. A classical example is sodium chloride (table salt, NaCl), where Na acts as a cation, losing one electron (Na^+) and Cl as an anion (Cl^-). A picture of the crystal structure is shown in Fig.1 of the Appendix.

1 Preliminary steps:

- Download and unzip the archive `pseudo.zip` 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.

2 Electronic properties of hypothetical AB compounds in the rock-salt structure:

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

1. The structural parameters of the rocksalt structure are contained in the Appendix. Before setting it up, answer the following questions:
 - What is the space group number? What is the underlying Bravais lattice?
 - How many inequivalent Wyckoff positions are occupied? What is their multiplicity? Are they fixed or free? What is the point group? - To answer these questions you can consult the Bilbao crystallographic group entry attached to this document.
 - What is the difference between space and point group? (max. 100 words).
2. Using the structural data provided in the Appendix, set up an initial input file for a **quantum espresso** calculation for your *AB* binary compound in the rocksalt crystal structure. The file should contain all parameters needed to run a standard self-consistent calculation. To make sure your initial guess of the structure is not too far from the optimal structure at ambient pressure, you should choose your initial lattice parameter **rescaling** the experimental lattice constant of NaCl, which is 5.64 Å, by the sum of of the atomic radii of the *A* and *B* elements, provided in table 2.
3. 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:

In the second part of the exercise we will relax the crystal structure of the AB crystal to ambient pressure (0 GPa), to obtain the theoretical equilibrium structure.

1. Explain briefly (max 100 words) what is meant by structural relaxation, and how **quantum espresso** computes forces acting on individual atoms and on the unit cell (pressure/stress).
2. What is the theoretical pressure calculated by **quantum espresso** for the initial structure you set up? What are the forces acting on the atoms? Do you expect your final volume to be larger or smaller than the initial one?
3. Provide a plot that you would use to monitor the structural relaxation, with a short (max 100 words) description, explaining which quantities you decided to monitor and why.
4. **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.
5. **Hint:** if your pc is too slow and the relaxation is taking too long, stop it and reduce the k grid. Write down in your report that you had to do this due to slow convergence.
6. 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.

2.3 Electronic Properties:

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 AB crystal. A list of special k points for the fcc crystal is provided in the Appendix. Based on your plots, answer the following questions:
 - How many bands are filled in your system? Is this consistent with the number of valence electrons?
 - Are there any semicore states in your system? What are they? Why can you have/not have semicore states in a DFT/psp calculation? (max. 100 words)
 - Is your system a metal or an insulator? How can you answer this question based on your results?

3 Vacancies:

In the second part of the exercise we will simulate the creation of *vacancies* in the AB crystal using a supercell. Vacancies are point defects that occur when one or more atoms are removed from a crystal lattice. This can introduce localized electronic states, altering conductivity, and facilitating ion migration. Hence, vacancies can influence mechanical properties by affecting dislocations, thermal properties by scattering phonons, and chemical reactivity by enabling diffusion and catalysis. Understanding vacancies is essential for studying conductivity, strength, thermal performance, and catalytic behavior in materials.

In this exercise, we will simulate vacancies by removing one A atom from the cubic conventional cell of the fcc lattice. We will first construct the cubic cell, and then remove one atom to create the vacancy.

3.1 Construction of the conventional cell:

The conventional cell of the fcc lattice is cubic, and contains more atoms (and formula units) than the primitive one.

1. Construct the cubic conventional cell and answer the following questions:
 - What are the lattice constant and volume of the conventional cell? What is their relation to the fcc one?
 - How many atoms are there in the conventional cell? How many formula units? What is the difference?
 - Write down the coordinates of all atoms in the conventional cell, and explain how you obtained them.
 - How many A nearest neighbours does each B atom have? (and vice-versa). What is their relative distance?
2. Setup a self-consistent input file for quantum espresso. Run the self-consistent calculation and explain how you can make sure that your conventional cell is correctly set up, based on your previous results in the primitive fcc cell (max 100 words).

3. **Hint:** Calculations in the conventional cell might take very long on slow computers. Run all self-consistent calculations with a 2 2 2 k grid. If needed, you can also reduce the kinetic energy cutoff.
4. **Hint:** If the energy oscillates, increase the energy convergence threshold by one order of magnitude and reduce the mixing parameter as follows:

```
&ELECTRONS
  conv_thr = 1e-04
  mixing_beta = 0.4
```

3.2 Vacancies

We will now introduce a vacancy, removing the *A* atom at the origin from the conventional unit cell.

1. Setup the input file for a self-consistent calculation for a single *A* vacancy in the conventional unit cell, run it and answer the following questions:
 - What is the concentration of vacancies in the structure you just set up?
 - What is the number of electrons? Why?
 - Compute the forces/stresses acting on the structure with the vacancy. How large are they? Is this result expected? Why? (100 words).
 - Produce a 2D plot of the charge density of the cubic conventional cell with and without vacancies, using the following input file for the `pp.x` program of the `quantum espresso` distribution (you may need to edit directory and file names):

```
&INPUTPP
prefix='BeNc'
plot_num=0
outdir='./tmp'
filplot='cubic.2d.dat'
&end

&PLOT
  iflag = 2,                ! 2D planar plot
  output_format = 7,        ! Output format for 2D grid (gnuplot format)
  fileout = 'cubic_001.gnuplot', ! File to store the plane data
  nx = 100, ny = 100,       ! Grid points in x and y (adjust as needed)
  e1(1) = 2.0, e1(2) = 0.0, e1(3) = 0.0, ! First vector (along [100])
  e2(1) = 0.0, e2(2) = 2.0, e2(3) = 0.0, ! Second vector (orthogonal to [010])
  x0(1) = -1.0, x0(2) = -1.0, x0(3) = 0.0 ! Origin of the plane
/
&end
```

You can run `pp.x` by typing `pp.x <input_file >output_file` in your terminal. This file generates a 2D plot of the charge density in the [001] plane, in a square centered on the origin.

- `pp.x` generates a file with three columns containing $x, y, f(x, y)$, which can be plotted by gnuplot or by a simple python script, like the script `plot2d_vac.py` on elearning.
- Once you have succeeded in generating a plot for both the crystal with and without vacancies, discuss the differences you see, and whether they are consistent with what you would expect based on the electronegativity values reported in table 2.

4 Appendix

4.1 Definition of the structure:

Chemical Formula: AB
Space Group (Bravais Lattice): 225
Atomic coordinates (*WyckoffPositions*): A (4a) B (4b)

4.2 Primitive Cell and Brillouin zone:

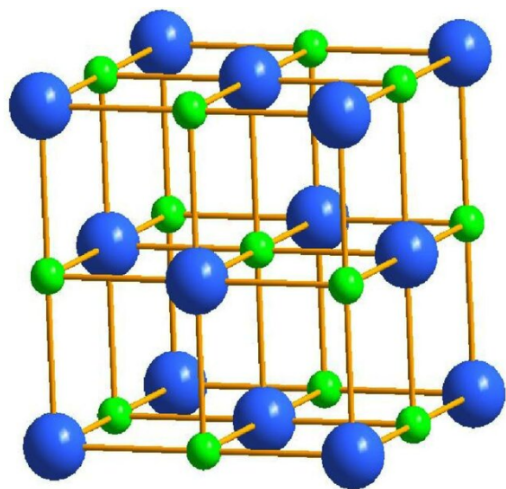


Table 3: Symmetry **k**-points of FCC lattice.

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

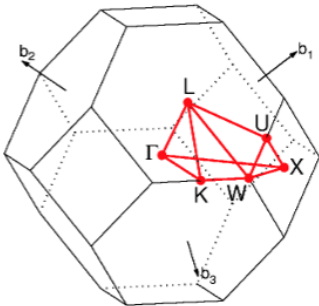


Figure 2: Brillouin zone of FCC lattice. Path: Γ -X-W-K- Γ -L-U-W-L-K|U-X. An example of band structure using this path is given in Figure 27.

Figura 1: (Left) Rocksalt crystal structure; (Right) Brillouin zone and special k points of the fcc lattice.

4.3 Combinations of elements/structures for each student:

St. Number	Element A	Element B	St. Number	Element A	Element B
1	Al	O	21	Na	F
2	H	C	22	Be	Cl
3	H	F	23	Be	S
4	H	N	24	Al	Cl
5	H	P	25	Be	B
6	Be	S	26	Mg	N
7	Li	Cl	27	Li	S
8	Na	O	28	Al	C
9	Mg	F	29	Na	P
10	Al	S	30	Mg	O
11	Al	Cl	31	Li	F
12	H	O	32	Na	C
13	Be	N	33	Be	F
14	Li	P	34	Mg	S
15	Al	F	35	Al	P
16	Na	S	36	Na	N
17	Mg	Cl	37	H	Cl
18	Be	C	38	Li	C
19	Al	N	39	Al	O
20	Li	O	40	Mg	P

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

4.4 Periodic Table

Element	$\mathbf{R}_{at}(\text{pm})$	Electronegativity
Hydrogen	53	2.20
Lithium	167	0.98
Beryllium	112	1.57
Boron	87	2.04
Carbon	67	2.55
Nitrogen	56	3.04
Oxygen	48	3.44
Fluorine	42	3.98
Sodium	190	0.93
Magnesium	145	1.31
Aluminum	118	1.61
Silicon	111	1.90
Phosphorus	98	2.19
Sulfur	88	2.58
Chlorine	79	3.16

Tabella 2: Atomic Radii (\mathbf{R}_{at}) and Pauling Electronegativity of Selected Elements

Wyckoff Positions of Group *Fm-3m* (No. 225)

Multiplicity	Wyckoff letter	Site symmetry	Coordinates
			(0,0,0) + (0,1/2,1/2) + (1/2,0,1/2) + (1/2,1/2,0) +
192	l	1	(x,y,z) (-x,-y,z) (-x,y,-z) (x,-y,-z) (z,x,y) (z,-x,-y) (-z,-x,y) (-z,x,-y) (y,z,x) (-y,z,-x) (y,-z,-x) (-y,-z,x) (y,x,-z) (-y,-x,-z) (y,-x,z) (-y,x,z) (x,z,-y) (-x,z,y) (-x,-z,-y) (x,-z,y) (z,y,-x) (z,-y,x) (-z,y,x) (-z,-y,-x) (-x,-y,-z) (x,y,-z) (x,-y,z) (-x,y,z) (-z,-x,-y) (-z,x,y) (z,x,-y) (z,-x,y) (-y,-z,-x) (y,-z,x) (-y,z,x) (y,z,-x) (-y,-x,z) (y,x,z) (-y,x,-z) (y,-x,-z) (-x,-z,y) (x,-z,-y) (x,z,y) (-x,z,-y) (-z,-y,x) (-z,y,-x) (z,-y,-x) (z,y,x)
96	k	.m	(x,x,z) (-x,-x,z) (-x,x,-z) (x,-x,-z) (z,x,x) (z,-x,-x) (-z,-x,x) (-z,x,-x) (x,z,x) (-x,z,-x) (x,-z,-x) (-x,-z,x) (x,x,-z) (-x,-x,-z) (x,-x,z) (-x,x,z) (x,z,-x) (-x,z,x) (-x,-z,-x) (x,-z,x) (z,x,-x) (z,-x,x) (-z,x,x) (-z,-x,-x)
96	j	m..	(0,y,z) (0,-y,z) (0,y,-z) (0,-y,-z) (z,0,y) (z,0,-y) (-z,0,y) (-z,0,-y) (y,z,0) (-y,z,0) (y,-z,0) (-y,-z,0) (y,0,-z) (-y,0,-z) (y,0,z) (-y,0,z) (0,z,-y) (0,z,y) (0,-z,-y) (0,-z,y) (z,y,0) (z,-y,0) (-z,y,0) (-z,-y,0)
48	i	m.m 2	(1/2,y,y) (1/2,-y,y) (1/2,y,-y) (1/2,-y,-y) (y,1/2,y) (y,1/2,-y) (-y,1/2,y) (-y,1/2,-y) (y,y,1/2) (-y,y,1/2) (y,-y,1/2) (-y,-y,1/2)
48	h	m.m 2	(0,y,y) (0,-y,y) (0,y,-y) (0,-y,-y) (y,0,y) (y,0,-y) (-y,0,y) (-y,0,-y) (y,y,0) (-y,y,0) (y,-y,0) (-y,-y,0)
48	g	2.m m	(x,1/4,1/4) (-x,3/4,1/4) (1/4,x,1/4) (1/4,-x,3/4) (1/4,1/4,x) (3/4,1/4,-x) (1/4,x,3/4) (3/4,-x,3/4) (x,1/4,3/4) (-x,1/4,1/4) (1/4,1/4,-x) (1/4,3/4,x)
32	f	.3m	(x,x,x) (-x,-x,x) (-x,x,-x) (x,-x,-x) (x,x,-x) (-x,-x,-x) (x,-x,x) (-x,x,x)
24	e	4m. m	(x,0,0) (-x,0,0) (0,x,0) (0,-x,0) (0,0,x) (0,0,-x)
24	d	m.m m	(0,1/4,1/4) (0,3/4,1/4) (1/4,0,1/4) (1/4,0,3/4) (1/4,1/4,0) (3/4,1/4,0)
8	c	-43m	(1/4,1/4,1/4) (1/4,1/4,3/4)
4	b	m-3m	(1/2,1/2,1/2)
4	a	m-3m	(0,0,0)