PHYS4450 Solid State Physics Problem Set 2 Due: 20 February 2013 (Wednesday)

All problem sets should be handed in not later than 5pm on the due date. Drop your assignment in the Box labelled PHY4450 in SC 213 (Year 1 teaching laboratory).

Important: You MUST attached a SIGNED declaration on academic honesty to every problem set. Homework without a signed declaration form will NOT be graded. A form is attached at the end of the Problem Set.

Please work out the steps of the calculations in detail.

2.0 *Reading Assignment:* For the first part of the course on crystal structures, bonding, and structure determination, read Kittel's Chapters 1-3 and/or early sections of Chapter 3 in Christman's book. There is always a chapter (or sections) on bonding in standard SSP textbooks. The materials in such chapters were covered in Quantum Physics I/II. You should read the relevant chapters/sections for a review. Also, read the sections on Reciprocal Lattices and X-ray diffraction. Chapter 3 of the book by Ibach (see book list and revised in University Library) gives a thorough and readable discussion on "Diffraction from Periodic Structures" with an appendix on experimental techniques. We started the second part on Lattice Vibrations. It is covered in Chapter 4 of Kittel's and Christman's books, but our treatment will be more thorough. It will also be useful to review by yourself the statistical physics of a collection of quantum oscillators.

2.1 (This problem is a continuation of Problem 1.5 on the structure of graphene and **similar to SQ5 and SQ6**. It is also meant to be educational and serves as a review on several basic concepts.) Refer to the figure in Problem Set 1 and the figures in this Problem Set. Graphene is a two-dimensional honeycomb array of carbon atoms forming (see figure). The nearest-neighboring separation is 1.42Å. (**See SQ5 & SQ6.**)

(a) From Problem 1.5, you should have known that the underlying lattice is the hexagonal lattice given in a separate figure (see figure). Let $\hat{x}$ and $\hat{y}$ be two unit vectors in the x-direction and y-direction on a 2D plane, respectively. In SQ6, the TA chose a set of primitive vectors. Here, to unify the choice, I marked another set of two primitive vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ on the attached figure (which are chosen intentionally to be different from the solutions to SQ5 and SQ6). Write down $\mathbf{a}_1$ and $\mathbf{a}_2$ in terms of the separation a (see figure) and the two unit vectors $\hat{x}$ and $\hat{y}$. Also, find a in units of Å. This will be the direct lattice in this problem. We will go over various concepts based on this direct lattice.

(b) The vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ defines a parallelogram, which is a primitive unit cell. Sketch this primitive unit cell and find the area of the primitive unit cell. [Since we have a 2D system, we are talking about area rather than volume.]

(c) In handling 2D systems, it is convenient to introduce an additional or auxiliary $\mathbf{a}_3 = \hat{z}$, which is a unit vector perpendicular to the plane of the system. Using the formula in getting the "volume" of a primitive unit cell in terms of $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$, find the "volume" of a primitive unit cell. [Compare results with (b). You should keep track of the units, i.e., when you are asked about the volume of the primitive cell, then it is a volume; but when you are asked about the area of the 2D primitive cell, then it is an area. That is to say, when you include a $\mathbf{a}_3$ into the problem, be very clear in your mind about what you are calculating.]

(d) Back to the direct lattice. Take any lattice point and construct the Wigner-Seitz cell. Check that the area is that of a primitive unit cell.

(e) With $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$, construct the vectors $\mathbf{b}_1$, $\mathbf{b}_2$, and $\mathbf{b}_3$. Using $\mathbf{b}_1$ and $\mathbf{b}_2$ as primitive vectors, dot out the reciprocal lattice on a SEPARATE page. Since there are only 5 possible lattice types in 2D, the reciprocal lattice must also belong to one of these types. Identify the lattice type of the reciprocal lattice. [Note: $\hat{x}$ and $\hat{y}$ defined the x and y directions.]

(f) Using $\mathbf{b}_1$ and $\mathbf{b}_2$ to form a parallelogram, this is a primitive cell of the reciprocal lattice. Find the "area" of this primitive cell. How is this area related to the area of the primitive cell in the direct lattice (result in (b))? [Note: Compare with general relation between the volumes of primitive unit cells in direct space and reciprocal space. Recall that we are dealing with a 2D system.]

(g) Go back to the direct lattice. Sketch a set of parallel crystal planes (try some less trivial ones). Identify the Miller's indices (hk) or (hk0). [Why is the third index "0"?]

(h) Go to the graph of the reciprocal lattice in part (f). Draw a reciprocal lattice vector $\mathbf{G}(hk) = h\mathbf{b}_1 + k\mathbf{b}_2$, for (hk) in part (h).

(i') Just do this in private (don't need to write down anything, but the TA can check this readily from your graphs). Put the two graphs together and look at them through strong light, do you see that the reciprocal lattice $\mathbf{G}(hk)$ is perpendicular to the set of planes you drew in part (h)? Convince yourself that $\mathbf{G}(hk)$ is the shortest reciprocal lattice vector with this property and other reciprocal lattice vectors $n\mathbf{G}(hk)$ with n being an integer ($\neq 0$) also carry the same property.

(i) (Brillouin zones) Use the picture for the reciprocal lattice. Take a point, draw lines to the neighboring points (don't stop at the nearest neighbors, draw lines farther away from the point), and drop perpendicular bisecting lines. It will then emerge an area in the reciprocal space (k-space) that is closer to the chosen point than any other points in the reciprocal lattice. This region is called the *first Brillouin zone* (1st BZ) of the direct lattice. Identify (e.g., use a color pencil to highlight) the first Brillouin zone.

Justify the following statement: The first Brillouin zone of the direct lattice is the Wigner-Seitz cell of the reciprocal lattice.

You may wonder why the region is called the "first" Brillouin zone, are there "second" and "third" Brillouin zones and so on? Now, look at your sketch again. There are patches of regions beyond the 1st BZ that can be identified as "second nearest" to the chosen point. They are usually **disjoint** patches. Together, they form the *second Brillouin zone.* They have several properties. The areas of the patches ADD UP to the same area as the 1st BZ and thus a primitive unit cell in the reciprocal space. More, one can translate the patches back into the region of the 1st BZ by some reciprocal lattice vector $\mathbf{G}$ (see must be $\mathbf{G}$!). From your picture, identify the second Brillouin zone (coloring the patches) and indicate which $\mathbf{G}$'s needed in translating the patches back to the 1st BZ. Check also that the area of the 2nd BZ is the same as that of the 1st BZ.

(j) Don't need to do anything. Read the whole problem again and see if you follow all the steps and all the relationships between the direct lattice and the reciprocal lattice? Keep in mind the 1st BZ of graphene. We will need it in future discussions, e.g., in lattice vibrations and energy bands. **Keep a copy of this problem and your answer as an appendix to Chapter IV.**

2.2 Find a picture of a fcc lattice (using the conventional unit cell) and identify the (111)planes. Let a be the cube edge of the conventional unit cell. There are lattice points on a (111) plane and thus there is a certain concentration of lattice points on the plane (e.g., number of points per unit area). Next, consider a simple cubic lattice with a cube edge $\overline{a}$ and identify the (110) planes. Again, there are lattice points on a (110) plane and there is a certain concentration of lattice points on the plane. If the concentrations of lattice points in the two systems happen to be the same, find the ratio $\overline{a}/a$.

2.3 **Self-Study on cohesive energy II – Cohesive energy of ionic crystals.** This is a continuation of Problem 1.1, in which we studied the cohesive energy in molecular crystals where the relevant interaction is the Van der Waals interaction. Here, we deal with **IONIC crystals**. This turns out to be an interesting and not-so-easy problem numerically. The ideas in Problem 1.1 are still applicable.

(a) To appreciate the "difficulty", we start with a two-dimensional (2D) ionic crystal. Let there be two types of ions, with +e charge (cations) and -e charge (anions). Draw a lattice of this 2D ionic crystal so that every cation has 4 nearest neighboring anions and every anion has 4 nearest neighboring cations, and the (equilibrium) nearest neighbor separation is r_0. [Optional (no bonus of course!): How would you formally describe this crystal structure?]

(b) There are actually two kinds of interactions here. One is the long range Coulomb interaction between the ions, and another is a short-range (i.e., effective only when two ions are very close to each other) repulsion that acts only between nearest neighboring ions. For the moment, let's consider ONLY the Coulomb interaction. From the crystal structure, write down the separations between nearest neighbors, next nearest neighbors, next-next nearest neighbors, ... up to next-(5 times) nearest neighbors (i.e., altogether, 6 separations). Let u_c be the coulomb energy PER ION. Show that u_c is given by:

$$u_c = \frac{1}{2} \cdot \frac{e^2}{4\pi\epsilon_0 r_0} \left(-4 + \frac{4}{\sqrt{2}} + 2 - \frac{8}{\sqrt{5}} + other\, two\, terms + \cdots \right). \tag{1}$$

One can work out as many terms as possible and sum them to convergence to get u_c.
The short-range repulsion can be represented by a term of the form A/r_0^{12}. Thus, the energy PER ION is given by

$$u = u_c + \frac{4A}{r_0^{12}}, \tag{2}$$

where the factor 4 in the repulsive term comes from the four nearest neighbors of an ion. (Remark: You have seen such $+1/r^n$ repulsive part in Problem 1.1.]

(c) Now, consider the number in the brackets in Eq.(1). To illustrate the difficulty, list a table for the sum. In the table, list the value inside the brackets if we retain only one term (the first term), two terms, three terms, ... up to 6 terms.

Here is the point. Look at the running total of the sum. Do you see that the numbers are going up and down, instead of having a clear trend of converging to some number. In fact, it does not look like that it is a converging sum at all! This is the **difficulty of handling IONIC crystals.** Series of this type are called **Madelung Sums**, after the German physicist Erwin Madelung who studied the problem in 1918. The sum does converge! **Important Point:** Look at the sum. The sum is a property of the **crystal structure**, as real-material parameters such as r_0 has been taken out as the pre-factor. That is to say, the same "Madelung constant" works for materials that take on the same crystal structure.

(d) Optional (**with** bonus point): Inspect how to write down more terms for the farther ions. Write a computer program to sum up a thousand terms to a few thousand terms. For a thousand term or so, you may get a number close to -1.6. [Note: This is not an accurate number. If you sum up a few thousand terms, you will get a more accurate number.]

(e) For those who don't do the optional part (d), let's say the number converges to -1.6. Find an expression for the equilibrium separation r_0. And then obtain an expression for the cohesive energy per ion u in the form of something times e^2/r_0. Remark: To turn it into **cohesive energy per mole** U, argue that $U = 2N_A u$, where N_A is the Avogadro number. [For example, in Kittel, the cohesive energy of NaCl is quoted as 774 $kJ\ mol^{-1}$.]

As a physics student, you should see the universality in achieving an equilibrium separation between ions or atoms (or between nucleons in nucleus). We need a short-range repulsive part and a long-range attractive part in the energy, combined they give a minimum in energy at some equilibrium separation.

Remark: Possible interesting extension/not even optional – An interesting (but not easy) extension is to consider an array of electric dipoles. In this case, one may similarly consider the potential energy for a dipole moment due to the interactions with the other dipole moments in the periodic array. It turns out that there are some non-trivial mathematical tricks. One way to do it is to use what is called the Ewald sum (what is it?), after the same Ewald as in the Eward construction related to X-ray diffraction. This is a nice short project.

2.4 **Self-study on cohesive energy III – Cohesive energy of** ***NaCl*****.** Next, we extend the study in Problem 2.3 to three-dimensional ionic crystals. Take NaCl as our example and follow the ideas in Problem 2.3. Find out the crystal structure. Let r_0 be the nearest neighbor separation (i.e., between cation and anion).

(a) Identify the separations between nearest neighbors, next-nearest neighbors, next-next-nearest neighbors, and next-next-next nearest neighbors (4 separations altogether). Show that the Coulomb energy PER ION is given by:

$$u_c = \frac{1}{2} \cdot \frac{e^2}{4\pi\epsilon_0 r_0} \, (a\, sum\, of\, numbers) , \tag{3}$$

and write down 4 terms in the brackets.

(b) Make a list of running total of the sum, by including one term, two terms, three terms, and four terms.

Look at the numbers. Again, it is not sure at all that there is a trend to convergence! The situation is actually worse than the 2D case. Even including a few thousand terms, there is only some sign of convergence! Madelung showed that this number indeed converges. Note that the number is specific to the crystal structure under consideration (but independent of the actual materials forming the ions). You may find some Madelung constants for different structures on Wikipedia.

For NaCl type structure, the sum turns out to give $M = -1.748$, which is called the **Madelung constant of the NaCl type structure.**

(c) Including a short-range repulsive term of an ion with its 6 nearest neighbors, the cohesive energy per ion can be written as

$$u = u_c + \frac{6A}{r_0^{12}}. \tag{4}$$

The last term is the "12"-term (repulsive term) in the 6-12 potential or the Van der Waals potential. Using the given Madelung constant, show that the equilibrium nearest neighbor separation can be expressed as

$$r_0 = \left(\frac{576 A \pi \epsilon_0}{+1.748 e^2} \right)^{1/11} . \tag{5}$$

Hence, show that the cohesive energy PER ION is given by

$$u = \frac{-1.602 e^2}{8\pi\epsilon_0 r_0}. \tag{6}$$

(d) Solid state physics deals with real stuffs! The above result says that if we know r_0 (e.g., from experimental data), then we can estimate the cohesive energy per ion. For different ionic crystals with the same structure, Eq.(6) works. Thus, different values of r_0 will give different u.

Consider NaCl. Let's estimate r_0 from the following data. The mass density of NaCl is 2165 $kg\ m^{-3}$. One mole of Na has a mass of 22.99 $\times 10^{-3}$ kg, and one mole of Cl has a mass of 35.45 $\times 10^{-3}$ kg. Show that $r_0 \approx 2.82 \times 10^{-10}$ m (i.e., Angstrom scale). [Hint: Find the mass of one chemical formula unit of NaCl, and then find the volume occupied by one chemical formula unit in terms of r_0. Then you can get r_0.] Hence, find u for NaCl in units of J/ion and eV per ion.

(e) Obtain U, the cohesive energy **PER MOLE** of NaCl. Compare your result with the numbers 774 $kJ\ mol^{-1}$ cited in books (e.g. in Kittel's Chapter 3). [Remark for physics students: Try to turn the 774 $kJ\ mol^{-1}$ into eV. Sounds strange you may think! Not quite – think about how many eV when multiplied by N_A (Avogadro's number) and turned the result to J would give 774 $kJ\ mol^{-1}$? The answer is very familiar and the value is typical of ionic and covalent bonds in molecular physics. Try it!]

Remark: Problems 1.1, 2.3, and 2.4 collectively complete the discussion on cohesive energy of solids, *c.f.* Kittel's Chapter 3. This is also related to the idea of bonding and binding energy of a molecule discussed in your Quantum Physics courses.

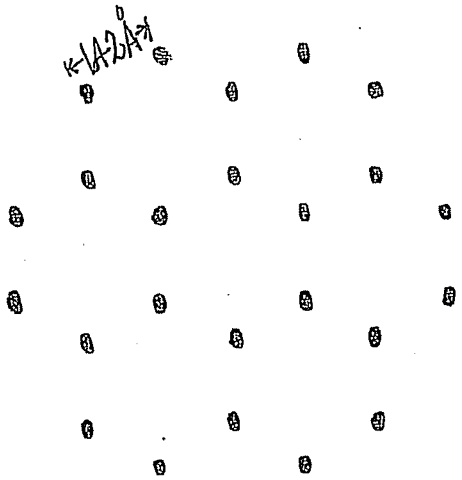
2.5 Write down a proof that clearly show the Bragg condition follows from the Laue condition. [Hint: Read class notes. The point here is that you should think it through carefully. The Bragg condition carries d, θ, n and λ. The Laue condition carries $\mathbf{s}$, $\mathbf{s}'$, and $\mathbf{G}$ (and apparently no "n"). So, it is not at all obvious that they are telling us the same thing!]

2.6 **Normal modes in 1D Triatomic Chain.** Read the early sections of Chapter VI on Lattice Vibrations, in particular on 1D diatomic chain. Now generalize the treatment to a 1D chain of the form ...A-B-C-A-B-C-A-B-C..., where A, B, C refer to atoms with masses M_A, M_B, and M_c, respectively. The period is a (what does it mean?). Discuss the vibrational modes dispersion relations $\omega(q)$. [You may need to define the details of the problem, e.g., how many spring constants you want to introduce, etc. It is like writing a section on this topic in a textbook.]

Important: You must attach a signed copy of the following declaration to your homework. You may also download the form in the website listed below.

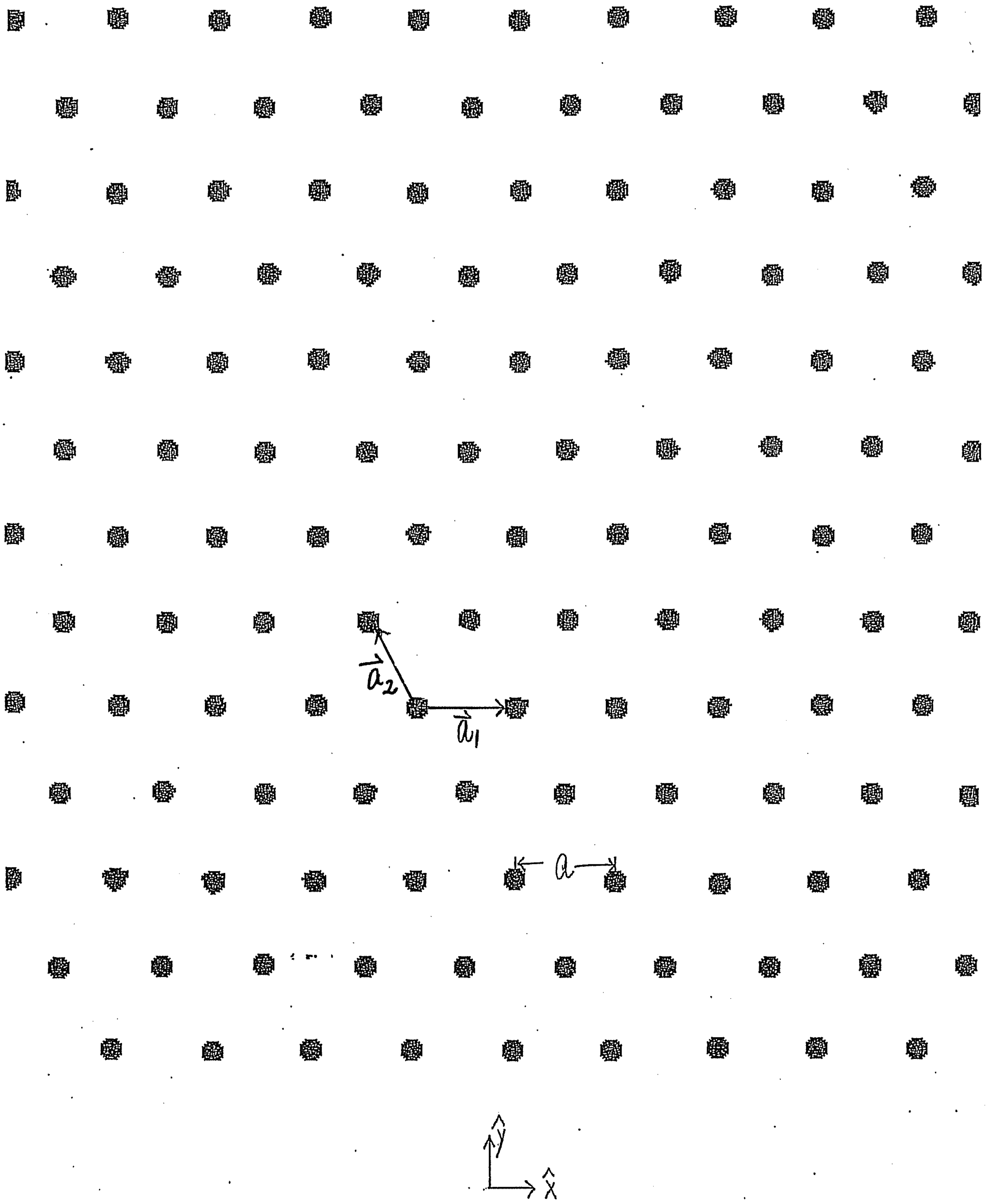
I declare that the assignment here submitted is original except for source material explicitly acknowledged, and that the same or related material has not been previously submitted for another course. I also acknowledge that I am aware of University policy and regulations on honesty in academic work, and of the disciplinary guidelines and procedures applicable to breaches of such policy and regulations, as contained in the website http//www.cuhk.edu.hk/policy/academichonesty.

Signature	Date
Name	Student ID
Course code	Course title



Graphene – carbon atoms in honeycomb structure

[See also the figure in Problem Set 1]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