

Electronic Structure - Fudan - 2010 - Homework 1 Solutions

There may be mistakes! Let me know if you find an error in the statement of a problem or solution!

GRADING: Total 25 points; 5 points for each problem

Problem 5 is difficult - graded easy if you tried

MISTAKES: There are two mistakes. EXTRA POINTS given for finding the mistakes.
See below.

1. Crystals

Give the Bravais lattice and the basis for:

- (a) A line of atoms spaced by a , $X - - X - - X - - X - -$
 Solution: The Bravais lattice is the set of points spaced by a :
 $\odot - - \odot - - \odot - - \odot - -$, and the basis is X
- (b) If the above crystal is dimerized, this is alternating short and long bonds $X - X - - - X - X - - -$. Give two ways to choose the basis.
 Solution: For parts b,c, and d the Bravais lattice is the same: points spaced by $2a$, $\odot - - - - \odot - - - - \odot - - - - \odot - - - -$
 Basis: $X - X$ or $X - - - - X$
- (c) A line of atoms spaced by equal distance a with alternating A and B atoms $A - - B - - A - - B - -$. Give two ways to choose the basis.
 Solution: See above for Bravais lattice. Basis: $A - - B$ or $B - - A$
- (d) If there is the combination of both alternating A and B atoms and alternating short and long bonds. Give two ways to choose the basis.
 Solution: See above for Bravais lattice. Basis: $A - B$ or $B - - - - A$
- (e) A two dimensional graphene crystal with the distance between atoms denoted by D .
 Solution: The basis is two atoms spaced by D and the Bravais lattice is hexagonal with primitive lattice vectors of length $\sqrt{3}D$ at a 60 degree angle. See figures in lecture for orinettaion.
- (f) A NaCl crystal with the side of conventional cell having length a .
 Solution: FCC with basis $(0, 0, 0)$ and $(0, 0, \frac{1}{2}a)$
- (g) A Si crystal with the side of conventional cell having length a .
 Solution: FCC with basis $(0, 0, 0)$ and $(\frac{1}{4}a, \frac{1}{4}a, \frac{1}{4}a)$

2. Reciprocal lattice

- (a) Show explicitly that fcc and bcc lattices are reciprocal to one another.
 Solution: This can be demonstrating that the vectors obey the relation $\mathbf{a}_i \cdot \mathbf{b}_i = 1$ and $\mathbf{a}_i \cdot \mathbf{b}_j = 0$ for $i \neq j$. That is, $\mathbf{a}_1$ is perpendicular to $\mathbf{b}_2$ and $\mathbf{b}_3$, etc. See Lect 2, slide 21, where it asks you to show that the vectors obey the relation on slide 19.

For example: consider the fcc vector $\mathbf{a}_1 = (0, \frac{1}{2}, \frac{1}{2})$. The dot products with the bcc vectors $\mathbf{b}_1 = (-1, 1, 1)$, $\mathbf{b}_2 = (1, -1, 1)$ and $\mathbf{b}_3 = (1, 1, -1)$ are: $\mathbf{a}_1 \cdot \mathbf{b}_1 = 1$, $\mathbf{a}_1 \cdot \mathbf{b}_2 = 0$ and $\mathbf{a}_1 \cdot \mathbf{b}_3 = 0$.

Also a solution with cross product formulas is just as good.

- (b) For the two-dimensional graphene lattice, show that the reciprocal space lattice is hexagonal and that it is rotated with respect to the real space lattice. What is the angle of rotation?

Solution: 30 degrees. This can be seen by drawing the vectors as in Lect. 2, slide 20. Also 90 degrees is correct because we can have 30 plus any multiple of 60 in a hexagonal lattice.

3. Density of electrons

The local density approximation is best for high densities of electrons. The density can be characterized by r_s , the radius of a sphere that has the average volume per electrons: $(4\pi/3)r_s^3 = 1/n$ where n is the density. Note that n is the density counting both up and down spin electrons. Typical values in solids are $\approx 2 - 4$ in units of the bohr radius a_0 . For $r_s > \approx 5$, the electrons may become highly correlated.

- (a) Consider an fcc crystal with a denoting the length of the side of the conventional cube, show that $r_s = \frac{a}{2}(\frac{3}{2\pi Z})^{1/3}$ where Z is the number of electrons per cell.
- (b) For the valence electrons in diamond carbon, show that your result in the previous exercise gives $r_s \approx 2.0$ in units of the bohr radius a_0 .

Solution: There is a mistake: the value of $r_s \approx 2.0$ is for Si. For carbon it should be $r_s \approx 1.3$. (Extra credit given to anyone who found the correct answer with the correct reasoning!) For carbon the answer is found using the lattice constant $a = 3.57\text{\AA}$ and $Z = 8$ valence electrons per cell.

4. Special points

Special points are designed to evaluate the integral over periodic functions $f(k)$ as the sum over only a few points. We can use the fact that all the properties of bands are periodic in k with periodic volume equal to the Brillouin zone (BZ). Examples: The average of eigenvalues ϵ_k is needed for the total energy per cell; the total density $n(r)$ normalized to one electron per band in the cell (2 electrons counting spin) is the integral of the density of the eigenfunction at wavevector k , $|\psi_k(r)|^2$. We can find the average of $f(k)$ by summing over a fine grid, but we can do this much more efficiently for smooth periodic functions. Since bands functions are smooth they can always be represented by a Fourier series $f(k) = A_0 + A_1 \cos(ka) + A_2 \cos(2ka) + A_3 \cos(3ka) + \dots$. Often $f(k)$ can be represented by a very small number of Fourier components with $A_i = 0$ for all $i > n_{max}$. However, we do not know the values of $A_0, A_1, \dots$ in advance; we need to find the average A_0 by calculating $f(k)$ at points k in the BZ. Special points are chosen so that the average of each cosine function is zero for $0 < i, n$, so that the average of $f(k)$ gives the desired value A_0 .

- a. For a one-dimensional crystal with cell length a , show that the average of $f(k)$ over the Brillouin zone (BZ) is given correctly by $\frac{1}{2}(f(\frac{1}{4}\frac{\pi}{a}) + f(\frac{3}{4}\frac{\pi}{a}))$, if f is given by the

Fourier components $f(k) = A_0 + A_1 \cos(ka) + A_2 \cos(2ka) + A_3 \cos(3ka)$ and all higher Fourier components are zero.

Solution: The sums vanish for each of the terms A_1 , A_2 , and A_3 for the two k points; thus the sum is simply A_0 which is the average value of $f(k)$.

b. However, there is an error if higher Fourier components are not negligible. What is the error due to a term $A_4 \cos(4ka)$?

Solution: Adding the two terms gives $A_0 - A_4$, so that the error is $-A_4$.

c. Extend the arguments to a two dimensional square lattice with side a where we consider a function $f(k_x, k_y) = A_{00} + A_{10} \cos(k_x a) + A_{01} \cos(k_y a) + A_{1,1} \cos(k_x a + k_y a) + \dots$. Consider the three points $(1/4, 1/4)$, $(3/4, 3/4)$ and $(1/4, 3/4)$, where $(1/4, 3/4)$ is weighted by a factor of 2 since it actually represents two equivalent points $(1/4, 3/4)$ and $(1/4, 1/4)$. Show that this is sufficient to correctly give the average A_{00} for all Fourier components up through $(3, 3)$, where a is the square edge. ASK PROF. MARTIN IF IT IS NOT CLEAR WHAT YOU NEED TO DO IN THIS EXERCISE.

Solution: THERE IS A MISTAKE. (I confused two problems. My apologies.) These points do NOT give the correct result. The points should be ONLY two points: $(1/4, 1/4, 1/4)$ and $(3/4, 3/4, 3/4)$. Full credit to anyone who found the correct result with the four points given in the problem. EXTRA POINT FOR ANYONE WHO FOUND THE CORRECT POINTS.

The actual solution is long to write out but it is simply the sum of the cosine terms for each order.

5. "Force Theorem" ("Hellmann-Feynman theorem")

In his undergraduate thesis, Feynman showed that the force on any nucleus is simply the charge of the nucleus times the electric field at the site of the nucleus due to the electron density $n(r)$ and the other nuclei. This is obvious if the electron density does not change as one nucleus is given an infinitesimal displacement. But in fact the electrons respond, the wavefunction changes, etc.

The object of this problem is to show that if the electrons are in their ground state, these complicated changes in the electron state do not affect the force. This can be done in extremely difficult ways or by a very easy argument. DO NOT SPEND A LONG TIME ON THIS - ASK PROF. MARTIN IF THIS SEEMS DIFFICULT.

Hint: All changes in the electrons are described by the changes in their ground state wavefunction as the atom is displaced. However, we know something about ground state wavefunction; it is the function that gives the lowest energy. This is sufficient to find the desired result.

Solution 1: A general argument. If all the degrees of freedom are at equilibrium, then there is no change in energy to linear order, and thus no contribution to the force which is the linear change in energy as the nucleus is displaced. Full credit if you state this clearly.

Solution 2. A proof given in many texts using the wavefunction: $E = \langle \Psi | H | \Psi \rangle$ and

$$\frac{dE}{dR} = \langle \Psi | \frac{dH}{dR} | \Psi \rangle + \langle \frac{d\Psi}{dR} | H | \Psi \rangle + \langle \Psi | H | \frac{d\Psi}{dR} \rangle.$$

The only term in H that depends upon R is the potential due to that nucleus. Thus the first term is the expectation value of the force on that nucleus. As stated in the hint, the proof requires that there be no contribution due to changes in Ψ . This can be proven by noting that Ψ is an eigenfunction $H\Psi = E\Psi$, so that the last two terms can be written

$$\langle \frac{d\Psi}{dR} | H | \Psi \rangle + \langle \Psi | H | \frac{d\Psi}{dR} \rangle = E \left[\langle \frac{d\Psi}{dR} | \Psi \rangle + \langle \Psi | \frac{d\Psi}{dR} \rangle \right] = E \frac{d}{dR} \langle \Psi | \Psi \rangle = 0,$$

where the last equality follows because Ψ is normalized and $\langle \Psi | \Psi \rangle$ does not change with the displacement of a nucleus.

Solution 3: A shorter proof very similar to solution 2, but using DFT where E is a functional $E[n] = E_{internal} + \int V_{ext}(r)n(r)$.

$$\frac{dE}{dR} = \int \frac{dV_{ext}(r)}{dR} n(r) + \int \frac{\delta E}{\delta n(r)} \frac{dn(r)}{dR}$$

The first term is the direct force the involves only the density and the second vanishes since $\frac{\delta E}{\delta n(r)} = 0$ for the ground state.