

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

Physics Department

8.231: Physics of Solids I

Due in Ses #11

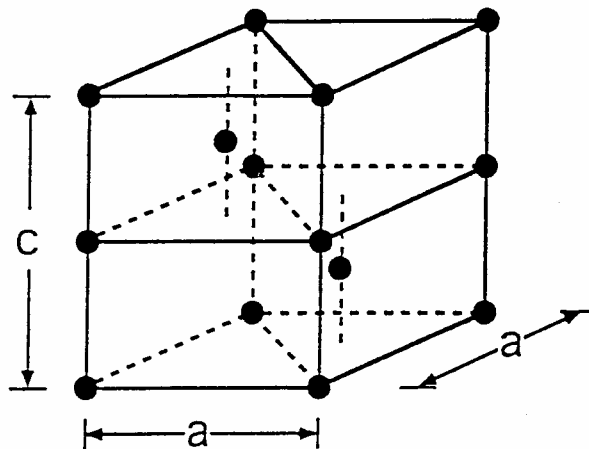
Problem Set #2

Problem 1: Americium

The figure below shows a primitive unit cell of one crystalline form of the element

Americium. The space lattice is hexagonal with $\vec{a}_1 = a\hat{x}$, $\vec{a}_2 = \frac{1}{2}a\hat{x} + \frac{\sqrt{3}}{2}a\hat{y}$, and

$\vec{a}_3 = c\hat{z}$. The basis is (000) , $(\frac{2}{3} \frac{2}{3} \frac{1}{4})$, $(00\frac{1}{2})$, and $(\frac{1}{3} \frac{1}{3} \frac{3}{4})$.



- Find the reciprocal lattice vectors \vec{G} . Describe in words and sketch the reciprocal lattice.
- Sketch the first Brillouin zone. Give values for the important dimensions.
- Find the structure factors associated with the points (100) , (001) , and (120) of the reciprocal lattice.
- What is the ratio of the scattering intensity corresponding to (120) to that corresponding to (100) ?

Problem 2: Width of a Diffraction Peak

The fundamental mathematical concept involved in diffraction from crystals is that the Fourier transform of a lattice of points (three dimensional delta functions) in one domain is a lattice of points in the transform domain. We will examine this concept in one dimension, and in the process determine the width of the diffraction peak when the sample is finite in extent.

We will consider the Fourier transform of an array of delta functions separated by a distance a along the x axis. It will be instructive to begin with a finite array containing $M+1$ delta functions distributed symmetrically about the origin (M is an even integer).

$$n(x) = \sum_{m=-M/2}^{M/2} \delta(x - ma)$$
$$F(\Delta k) \equiv \int_{-\infty}^{\infty} n(x) e^{-i\Delta k x} dx = \sum_{m=-M/2}^{M/2} e^{-im\Delta k a}$$

a) By doing the sum, show that

$$F(\Delta k) = \frac{\sin(\frac{1}{2}(M+1)\Delta k a)}{\sin(\frac{1}{2}\Delta k a)}.$$

It may help to recall that

$$\sum_{n=0}^{N-1} x^n = \frac{1-x^N}{1-x}.$$

b) The function you found in a) has principal maxima whenever Δk is an integer multiple of $2\pi/a$. What is the height at a principal maximum? What is the area under the peak in the vicinity of each principal maximum? Use these facts to

argue that in the limit $M \rightarrow \infty$, $F(\Delta k)$ approaches

$$\frac{2\pi}{a} \sum_{j=-\infty}^{\infty} \delta(\Delta k - j \frac{2\pi}{a}).$$

c) The scattered intensity is proportional to $|F|^2$ and from a)

$$|F|^2 = \frac{\sin^2(\frac{1}{2}(M+1)\Delta k a)}{\sin^2(\frac{1}{2}\Delta k a)}.$$

Some of you who remember your 8.03 will recognize the intensity pattern due to $M+1$ identical, equally spaced antennae. For $M \gg 1$, sketch the function near a maximum. What is the full width of the peak at half its maximum; in particular, how does the width depend on the total width of the array, aM ? What is the area under the function in the vicinity of one of these peaks? Check to see that the integrated intensity under a peak is proportional to the number of elements in the array.

Problem 3: Form Factor for Atomic Hydrogen

For the hydrogen atom in its ground state, the number density is $n(r) = (\pi a_0^3)^{-1} \exp(-2r/a_0)$, where a_0 is the Bohr radius. Show that the form factor is

$$f_G = 16/(4 + G^2 a_0^2)^2.$$

Problem 4: Reciprocal Lattice of Conventional Verses Primitive Unit Cells

a) Why are there fewer reciprocal lattice points \vec{G} in a given volume of Fourier space if the unit cell of the crystal lattice is primitive than if the unit cell is non-primitive?

b) In view of a), how can the allowed reflections from a given structure be independent of the choice of the unit cell of the crystal lattice?

Problem 5: Indium

Indium crystallizes in a body centered tetragonal lattice. For the conventional unit cell the lattice parameters are $a=3.244\text{\AA}$ and $c=4.938\text{\AA}$, and the basis is $(000), (\frac{1}{2} \frac{1}{2} \frac{1}{2})$.

The primitive translation vectors are

$$\vec{a}_1 = \frac{a}{2}\hat{x} + \frac{a}{2}\hat{y} + \frac{c}{2}\hat{z}$$

$$\vec{a}_2 = \frac{a}{2}\hat{x} + \frac{a}{2}\hat{y} - \frac{c}{2}\hat{z}$$

$$\vec{a}_3 = \frac{a}{2}\hat{x} - \frac{a}{2}\hat{y} - \frac{c}{2}\hat{z}$$

- a) Make a careful sketch of the conventional unit cell. What is its volume?
- b) Make a careful sketch of the primitive unit cell defined by the above vectors. What is its volume?
- c) Make a careful sketch of the Wigner-Seitz cell. Note that $c > \sqrt{2}a$.
- d) Find the primitive translation vectors of the reciprocal lattice. What lattice type is the reciprocal lattice? Be careful here. Is the lattice that you suggest one of the 14 Bravais lattices shown in the handout?
- e) Find, and make a carefully labeled sketch of, the first Brillouin zone.
- f) How many atoms are there in the primitive unit cell of this structure? How many atoms are there in the basis associated with the primitive cell? What does this imply about the structure factor for each point in reciprocal space? Test your hypothesis by finding an expression for the structure factor referred to the

cartesian coordinates of the conventional tetragonal cell. Evaluate it at a few points on your reciprocal lattice.

Problem 6: Van der Waals Interaction Between Harmonic Oscillators

This problem is an expanded version of the discussion of the van der Waals interaction given in Chapter 3 of Kittel. The object is to study a model of the van der Waals interaction that can be treated analytically. It complements the perturbation treatment of the van der Waals interaction between two hydrogen atoms discussed in class.

a) Consider a single isolated one dimensional harmonic oscillator at radian frequency ω_0 in which a mass m is displaced an amount x from its equilibrium position. Look up the wavefunction for the ground state and use it to find the probability density $p(x)$ that the particle will be found a distance x from the equilibrium position. The resulting probability density will have the form of a Gaussian random variable with zero mean:

$$p(x) = \frac{1}{(2\pi\sigma_0^2)^{1/2}} e^{-\frac{x^2}{2\sigma_0^2}},$$

where σ_0 is the characteristic length associated with the ground state distribution.

Find an expression for σ_0 in terms of h , m , and ω_0 .

Now consider two identical harmonic oscillators with centers separated by a distance R . Let each oscillator be a dipole consisting of a stationary charge $|e|$ at the center and a mobile charge $-|e|$. The two mobile charges are located at distances x_1 and x_2 from their respective partners.

b) Write down the Hamiltonian \mathbf{H}_0 for the two oscillators without taking into account the electrostatic interaction between the charges. Find the two particle wavefunction $\psi(x_1, x_2)$ and the corresponding two particle probability density $p(x_1, x_2)$. When the joint density separates, $p(x_1, x_2) = p(x_1)p(x_2)$, the two variables are statistically independent. Is this the case here? Find the following averages: $\langle x_1 \rangle$, $\langle x_1^2 \rangle$, and $\langle x_1 x_2 \rangle$.

c) Determine the interaction Hamiltonian \mathbf{H}_1 for the four charges. Assuming that $|x_1|$ and $|x_2|$ are both much smaller than R , show that through terms of second order

$$\mathbf{H}_1 \approx -\frac{2e^2 x_1 x_2}{4\pi\epsilon_0 R^3}.$$

Show that this is what would be expected for the interaction of two one-dimensional dipole moments $p_1 = -|e|x_1$ and $p_2 = -|e|x_2$.

d) Show that the transformation to normal coordinates

$$x_s = \frac{1}{\sqrt{2}}(x_1 + x_2), \quad x_a = \frac{1}{\sqrt{2}}(x_1 - x_2)$$

allows the total Hamiltonian $\mathbf{H} = \mathbf{H}_0 + \mathbf{H}_1$ to be separated into a sum of symmetric and antisymmetric contributions.

e) Show that the frequencies of the two new oscillators, ω_s and ω_a , are given by

$$\omega_s = \omega_0(1-\zeta)^{1/2}, \quad \omega_a = \omega_0(1+\zeta)^{1/2}$$

where the small dimensionless parameter ζ can be written as

$$\zeta = 2 \frac{(\text{coulomb energy of two charges } |e| \text{ separated by } R)}{(\text{ground state energy of an unperturbed oscillator})} \frac{\sigma_0^2}{R^2}.$$

f) The ground state of the interacting system corresponds to each of the two new oscillators being in its ground state. Find an expression for the amount by which the interaction decreases the total energy of the system. Show that through terms of third order in ζ the binding energy is given by $\frac{1}{8}\hbar\omega_0\zeta^2$. Show that this energy is proportional to R^{-6} . This is the separation dependence characteristic of the van der Waals interaction. ←

g) Find the two particle wavefunction $\psi(x_s, x_a)$ and the corresponding two particle probability density $p(x_s, x_a)$ associated with the new variables. Use the result to show that $\langle x_1 \rangle = \langle x_2 \rangle = 0$. The physically important fact is that the breaking of the left-right symmetry about each core has **not** caused dipole moments to develop at those cores.

h) Show that $\langle x_1 x_2 \rangle = \frac{1}{2}\sigma_0^2\zeta$. The physical interpretation is that although the mean of the two displacements is zero, the motion of the two charges is **correlated** and that correlated motion is responsible for the lowering of the energy!

i) Part g) shows that x_s and x_a are statistically independent variables [even better, they are Gaussian with zero mean]. For the physically relevant variables x_1 and x_2 , however, part h) shows that we are not so lucky: they are correlated. It is possible to do a change in variables and convert the joint probability density for x_s and x_a to a joint density for x_1 and x_2 . From that one can then determine the conditional probability density $p(x_2 | x_1)$ that particle 2 will be found at x_2 given that particle 1 is known to be at x_1 [note that in this function x_2 is the variable and x_1 is a parameter]. The steps involved are completely straight forward, but

the actual algebra can become tedious. I have done the calculation for you, and the resulting conditional probability density is

$$p(x_2 | x_1) = \frac{1}{(2\pi\sigma_0^2)^{1/2}} e^{-\frac{(x_2 - 1/2\zeta x_1)^2}{2\sigma_0^2}}$$

Make a sketch of this function and interpret the result.

Problem 7: sp^2 Hybridization

a) Find the three linear combination of s , p_x and p_y atomic orbitals necessary to form sp^2 orbitals in three planar bonding directions.

- i) Assume the input orbitals are normalized and orthogonal. Assume the same for the hybrid orbitals.
- ii) Assume the coefficients in the expansion are real.
- iii) Point one of the hybrid orbitals maximally in the x direction.
- iv) Make use of symmetry.

Make a sketch of the resulting orbitals assuming one is in the $n=2$ shell.

b) Consider the benzene molecule. Assume the $1s$ states belong to the atomic cores. This accounts for 2 of the 6 electrons from each carbon. How should the $2sp^2$ hybrid orbitals be used to form pairwise bonds to the hydrogens and between carbon neighbors? These bonds should account for another 3 electrons per carbon.

c) Now use the remaining $2p_z$ states on each carbon to further bind the molecule. Make a giant molecular orbital out of a linear combination of all 6 atomic states, one centered at each carbon site. By symmetry the magnitude of each of the six coefficients must be equal in a given molecular orbital, hence the coefficients can

differ only in phase. The phase must advance uniformly as one goes from one site to the next, and must come back to the starting value when the circuit is completed.

$$\Psi_k(r) = \sum_{m=0}^5 c_k e^{im\phi_k} \psi(r-r_m)$$

The six allowed values of the phase are $\phi_k = 0, \pm\pi/3, \pm2\pi/3, \text{ and } \pi$. Which of these hybrid orbitals should have the lowest energy and which the highest? Which of the orbitals will be bonding and which antibonding? Which will be degenerate? Which will be filled in the benzene molecule? Will benzene be paramagnetic?