Problems for Solid State Physics
(3rd year course B.VI)

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These problems are based substantially on those prepared and distributed by Prof S.H. Simon in Hilary Term 2015.

Suggested schedule:

- Problem Set 1: Hilary Term Week 3
- Problem Set 2: Hilary Term Week 5
- Problem Set 3: Hilary Term Week 7
- Problem Set 4: Hilary Term Vacation

‡ Denotes crucial problems that you need to be able to do in your sleep.
* Denotes problems that are slightly harder.

Problem Set 1

Einstein, Debye, Drude, and Free Electron Models

1.1. **Einstein Solid**

(a) **Classical Einstein Solid (or “Boltzmann” Solid)**

Consider a single harmonic oscillator in three dimensions with Hamiltonian

$$H = \frac{\mathbf{p}^2}{2m} + \frac{k}{2}\mathbf{x}^2$$

▷ Calculate the classical partition function

$$Z = \int \frac{\mathbf{dp}}{(2\pi\hbar)^3} \int \mathbf{dx}\, e^{-\beta H(\mathbf{p},\mathbf{x})}$$

Note: in this problem **p** and **x** are three dimensional vectors (they should appear bold to indicate this unless your printer is defective).

▷ Using the partition function, calculate the heat capacity $3k_B$.

▷ Conclude that if you can consider a solid to consist of N atoms all in harmonic wells, then the heat capacity should be $3Nk_B = 3R$, in agreement with the law of Dulong and Petit.

(b) **Quantum Einstein Solid**

Now consider the same Hamiltonian quantum mechanically.

▷ Calculate the quantum partition function

$$Z = \sum_j e^{-\beta E_j}$$

where the sum over j is a sum over all Eigenstates.

▷ Explain the relationship with Bose statistics.

▷ Find an expression for the heat capacity.

▷ Show that the high temperature limit agrees with the law of Dulong of Petit.

▷ Sketch the heat capacity as a function of temperature.

1.2. **Debye Theory**

(a)‡ State the assumptions of the Debye model of heat capacity of a solid.

▷ Derive the Debye heat capacity as a function of temperature (you will have to leave the final result in terms of an integral that cannot be done analytically).

▷ From the final result, obtain the high and low temperature limits of the heat capacity analytically.

You may find the following integral to be useful
$\int_0^\infty dx \frac{x^3}{e^x-1} = \sum_{n=1}^\infty \int_0^\infty x^3 e^{-nx} = 6\sum_{n=1}^\infty \frac{1}{n^4} = \frac{\pi^4}{15}$
By integrating by parts this can also be written as $\int_0^\infty dx \frac{x^4 e^x}{(e^x-1)^2} = \frac{4\pi^4}{15}$

(b) The following table gives the heat capacity C for potassium iodide (KI) as a function of temperature.

▷ Discuss, with reference to the Debye theory, and make an estimate of the Debye temperature.

T(K)	0.1	1.0	5	8	10	15	20
C (J K $^{-1}$ mol $^{-1}$)	8.5×10^{-7}	8.6×10^{-4}	1.2×10^{-1}	5.9×10^{-1}	1.1	2.8	6.3

1.3. **Drude Theory of Transport in Metals**

(a) Assume a scattering time τ and use Drude theory to derive an expression for the conductivity of a metal.

(b) Define the resistivity matrix $\underset{\sim}{\rho}$ as $\vec{E} = \underset{\sim}{\rho}\vec{j}$.

▷ Use Drude theory to derive an expression for the matrix $\underset{\sim}{\rho}$ for a metal in a magnetic field. (You might find it convenient to assume $\vec{B}$ parallel to the $\hat{z}$ axis. The under-tilde notation means that the quantity $\underset{\sim}{\rho}$ is a matrix.)

▷ Invert this matrix to obtain an expression for the conductivity matrix $\underset{\sim}{\sigma}$.

(c) Define the Hall coefficient.

▷ Estimate the magnitude of the Hall voltage for a specimen of sodium in the form of a rod of rectangular cross section 5 mm by 5 mm carrying a current of 1 A in a magnetic field of 1T orthogonal to the direction of the current. The density of sodium atoms is roughly 1 g/cm^3, and sodium has atomic mass of roughly 23 u. You may assume that there is one free electron per sodium atom (Sodium has *valence* one).

▷ What practical difficulties would there be in measuring the Hall voltage and resistivity of such a specimen (and how might these difficulties be addressed).

(d) What properties of metals does Drude theory not explain well?

(e)* Consider now an applied AC field $\vec{E} \sim e^{i\omega t}$ which induces an AC current $\vec{j} \sim e^{i\omega t}$. Modify the above calculation (in the presence of a magnetic field) to obtain an expression for the complex AC conductivity matrix $\underset{\sim}{\sigma}(\omega)$. For simplicity in this case you may assume that the metal is very clean, meaning that $\tau \to \infty$, and you may assume that $\vec{E} \perp \vec{B}$. You might again find it convenient to assume $\vec{B}$ parallel to the $\hat{z}$ axis. (This problem might look hard, but if you think about it for a bit, it isn't really much harder than what you did above!)

▷ At what frequency is there a divergence in the conductivity?

▷ What does this divergence mean? (When τ is finite, the divergence is cut off).

▷ Explain how could one use this divergence (known as the cyclotron resonance) to measure the mass of the electron. (In fact, in real metals, the measured mass of the electron is generally not equal to the well known value $m_e = 9.1095 \times 10^{-31}$ kg. This is a result of *band structure* in metals, which we will explain later in the course.)

1.4. **Fermi Surface in the Free Electron (Sommerfeld) Theory of Metals**

(a)‡ Explain what is meant by the Fermi energy, Fermi temperature and the Fermi surface of a metal.

(b)‡ Obtain an expression for the Fermi wavevector and the Fermi energy for a gas of electrons (in 3D).

▷ Show that the density of states at the Fermi surface, dN/dE_F can be written as $3N/2E_F$.

(c) Estimate the value of E_F for sodium [As above, the density of sodium atoms is roughly 1 g/cm^3, and sodium has atomic mass of roughly 23 u. You may assume that there is one free electron per sodium atom (Sodium has *valence* one)]

(d) Now consider a two dimensional Fermi gas. Obtain an expression for the density of states at the Fermi surface.

1.5. **Velocities in the Free Electron Theory**

(a) Assuming that the free electron theory is applicable: show that the speed v_F of an electron at the Fermi surface of a metal is $v_F = \frac{\hbar}{m}(3\pi^2 n)^{1/3}$ where n is the density of electrons.

(b) Show that the mean drift speed v_d of an electron in an applied electric field E is $v_d = |\sigma E/(ne)|$, where σ is the electrical conductivity, and show that σ is given in terms of the mean free path λ of the electrons by $\sigma = ne^2\lambda/(mv_F)$.

(c) Assuming that the free electron theory is applicable to copper:

(i) calculate the values of both v_d and v_F for copper at 300 K in an electric field of 1 V m^{-1} and comment on their relative magnitudes.

(ii) estimate λ for copper at 300 K and comment upon its value compared to the mean spacing between the copper atoms.

Copper is monovalent, meaning there is one free electron per atom. The density of atoms in copper is $n = 8.45 \times 10^{28}$ m^{-3}. The conductivity of copper is $\sigma = 5.9 \times 10^{7}$ $\Omega^{-1}\mathrm{m}^{-1}$ at 300 K.

1.6. **Physical Properties of the Free Electron Gas**

In both (a) and (b) you may always assume that the temperature is much less than the Fermi temperature.

(a)‡ Give a simple but approximate derivation of the Fermi gas prediction for heat capacity of the conduction electrons in metals

(b)‡ Give a simple (not approximate) derivation of the Fermi gas prediction for magnetic susceptibility of the conduction electrons in metals. Here susceptibility is $\chi = dM/dH = \mu_0 dM/dB$ at small H and is meant to consider the magnetization of the electron spins only.

(c) How are the results of (a) and (b) different from those for a classical gas of electrons?

▷ What other properties of metals may be different from the classical prediction?

(d) The experimental heat capacity of potassium metal at low temperatures has the form:

$$C = (\gamma T + \alpha T^3)$$

where $\gamma = 2.08\,\mathrm{mJ\,mol^{-1}\,K^{-2}}$ and $\alpha = 2.6\,\mathrm{mJ\,mol^{-1}\,K^{-4}}$.

▷ Explain the origin of each of the two terms in this expression.

▷ Make an estimate of the Fermi energy for potassium metal.

Problem Set 2

Chemical Bonding, Thermal Expansion, Normal Modes, Phonons in 1d

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2.1. Chemical Bonding

(a) Qualitatively describe five different types of chemical bonds and why they occur.

▷ Describe which combinations of what types of atoms are expected to form which types of bonds (make reference to location on the periodic table).

▷ Describe some of the qualitative properties of materials that have these types of bonds.

(Yes, you can just copy the table out of the notes, but the point of this exercise is to learn the information in the table!)

(b) Describe qualitatively the phenomenon of Van der Waals forces. Explain why the force is attractive and proportional to $1/R^7$ where R is the distance between two atoms.

(c) The ionization energy of a sodium (Na) atom is 5.14 eV. The electron affinity of a chlorine (Cl) atom is 3.62 eV. The bond length of a sodium-chloride *molecule* (i.e., one Na atom and one Cl atom) is 0.236 nm. Assuming the cohesive energy is purely Coulomb energy, calculate the total energy released when a Na atom and a Cl atom come together to form an NaCl molecule. The actual experimental value is 4.26 eV. Qualitatively account for the sign of your error.

2.2. Covalent Bonding in Detail*

(a) **Linear Combination of Atomic Orbitals (LCAO)** In class we considered two atoms each with a single atomic orbital. We called the orbital $|1\rangle$ around nucleus 1 and $|2\rangle$ around nucleus 2. More generally we may consider any set of wavefunctions $|n\rangle$ for $n = 1, \ldots, N$. For simplicity, let us assume this basis is orthonormal $\langle n|m\rangle = \delta_{n,m}$

Let us write a trial wavefunction for our ground state as

$$|\Psi\rangle = \sum_n \phi_n |n\rangle$$

This is known as a linear combination of atomic orbitals (LCAO). We would like to find the lowest energy wavefunction we can construct in this form, that is the best approximation to the actual ground state wavefunction. (The more states we use in our basis, generally, the more accurate our results will be).

We claim that the the ground state is given by the solution of the effective Schroedinger equation

$$\mathcal{H}\,\boldsymbol{\phi} = E\,\boldsymbol{\phi} \tag{1}$$

where $\boldsymbol{\phi}$ is the vector of N coefficients ϕ_n, and $\mathcal{H}$ is the N by N matrix

$$\mathcal{H}_{n,m} = \langle n|H|m\rangle$$

with H the Hamiltonian of the full system we are considering.

To prove this, let us construct the energy

$$E = \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle}$$

▷ Show that minimizing this energy with respect to each ϕ_n gives the same eigenvalue equation, Eq. (1). (Caution: ϕ_n is generally complex! If you are not comfortable with complex differentiation, write everything in terms of real and imaginary parts of each ϕ_n). Similarly, the second eigenvalue of the effective Schroedinger equation will be an approximation to the first excited state of the system.

This technique is know as the molecular orbital approach, or the LCAO (linear combination of atomic orbitals) approach. It is used heavily in numerical simulation of molecules. However, more generally, one cannot assume that the basis set of orbitals is orthonormal. (See problem 6.5 from the book for handling the LCAO without this assumption.)

(b) **Two-orbital covalent bond** Let us return to the case where there are only two orbitals in our basis. This pertains to a case where we have two identical nuclei and a single electron which will be shared between them to form a covalent bond. We write the full Hamiltonian as

$$H = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r} - \mathbf{R_1}) + V(\mathbf{r} - \mathbf{R_2}) = K + V_1 + V_2$$

where V is the Coulomb interaction between the electron and the nucleus, R_1 is the position of the first nucleus and R_2 is the position of the second nucleus. Let ϵ be the energy of the atomic orbital around one nucleus in the absence of the other. In other words

$$\begin{aligned}(K + V_1)|1\rangle &= \epsilon|1\rangle \\ (K + V_2)|2\rangle &= \epsilon|2\rangle\end{aligned}$$

Define also the cross-energy element

$$V_{\text{cross}} = \langle 1|V_2|1\rangle = \langle 2|V_1|2\rangle$$

and the hopping matrix element

$$t = -\langle 1|V_2|2\rangle = -\langle 1|V_1|2\rangle$$

These are not typos!

▷ Why can we write V_{cross} and t equivalently using either one of the expressions given on the right hand side?

▷ Show that the eigenvalues of our Schroedinger equation Eq. 1 are given by

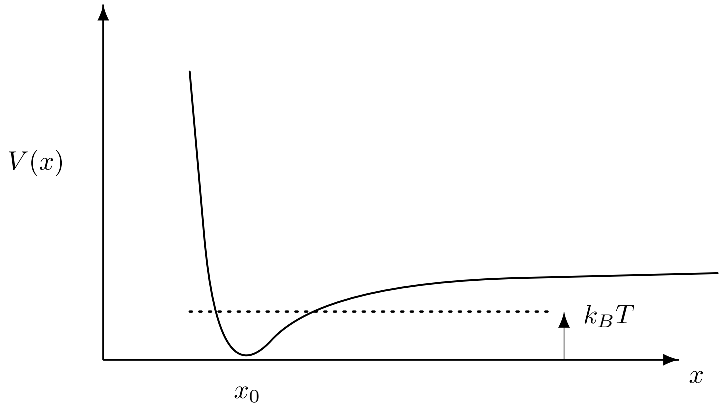
$$E = \epsilon + V_{\text{cross}} \pm |t|$$

▷ Argue (perhaps using Gauss's law) that V_{cross} should roughly cancel the repulsion between nuclei, so that, in the lower eigenstate the total energy is indeed lower when the atoms are closer together.

▷ This approximation must fail when the atoms get sufficiently close. Why?

2.3. **Potentials Between Atoms**

As a model of thermal expansion, we study the distance between two nearest neighbour atoms in an anharmonic potential that looks roughly like this



where x is the distance between the two neighbouring atoms. This potential can be expanded around its minimum as

$$V(x) = \frac{\kappa}{2}(x - x_0)^2 - \frac{\kappa_3}{3!}(x - x_0)^3 + \ldots \tag{2}$$

where the minimum is at position x_0 and $\kappa_3 > 0$. For small energies, we can truncate the series at the cubic term. (Note we are defining the energy at the bottom of the well to be zero here).

A very accurate approximate form for inter-atomic potentials (particularly for inert atoms such as helium or argon) is given by the so-called Lennard-Jones potential

$$V(x) = 4\epsilon\left[\left(\frac{\sigma}{x}\right)^{12} - \left(\frac{\sigma}{x}\right)^{6}\right] + \epsilon \tag{3}$$

where ϵ and σ are constants that depend on the particular atoms we are considering.

$\triangleright$ What is the meaning of the exponent 6 in the second term of this expression (i.e., why is the exponent necessarily chosen to be 6).

$\triangleright$ By expanding Eq. (3) around its minimum, and comparing to Eq. (2), calculate the values of the coefficients x_0, κ, and κ_3 for the Lennard-Jones potential in terms of the constants ϵ and σ.

2.4. **Classical Model of Thermal Expansion**

In classical statistical mechanics, we write the expectation of x as

$$\langle x \rangle_\beta = \frac{\int dx\, x\, e^{-\beta V(x)}}{\int dx\, e^{-\beta V(x)}}$$

Although one cannot generally do such integrals for arbitrary potential $V(x)$ as in Eq. 2, one can expand the exponentials as

$$e^{-\beta V(x)} = e^{-\frac{\beta\kappa}{2}(x-x_0)^2}\left[1 + \frac{\beta\kappa_3}{6}(x - x_0)^3 + \ldots\right]$$

and let limits of integration go to ±∞.

$\triangleright$ Why is this expansion of the exponent and the extension of the limits of integration allowed?

$\triangleright$ Use this expansion to derive $\langle x \rangle_\beta$ to lowest order in κ_3, and hence show that the coefficient of thermal expansion is

$$\alpha = \frac{1}{L}\frac{dL}{dT} \approx \frac{1}{x_0}\frac{d\langle x \rangle_\beta}{dT} = \frac{1}{x_0}\frac{k_B\,\kappa_3}{2\kappa^2}$$

with k_B Boltzmann's constant.

$\triangleright$ In what temperature range is the above expansion valid?

$\triangleright$ While this model of thermal expansion in a solid is valid if there are only two atoms, why is it invalid for the case of a many-atom chain? (Although actually it is not so bad as an approximation!)

2.5. Normal Modes of a One Dimensional Monatomic Chain

(a)‡ Explain what is meant by "normal mode" and by "phonon".

$\triangleright$ Explain briefly why phonons obey Bose statistics.

(b)‡ Derive the dispersion relation for the longitudinal oscillations of a one dimensional mass-and-spring crystal with N identical atoms of mass m, lattice spacing a, and spring constant κ. (Motion of the masses is restricted to be in one dimension).

(c)‡ Show that the mode with wavevector k has the same pattern of mass displacements as the the mode with wavevector $k + 2\pi/a$. Hence show that the dispersion relation is periodic in reciprocal space (k-space).

$\triangleright$ How many *different* normal modes are there?

(d)‡ Derive the phase and group velocities and sketch them as a function of k.

$\triangleright$ What is the sound velocity?

$\triangleright$ Show that the the sound velocity is also given by $v_s = \sqrt{\beta^{-1}/\rho}$ where ρ is the chain density and β is the compressibility.

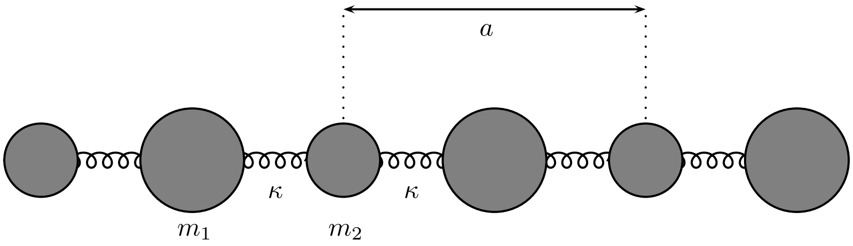
(e) Find the expression for $g(\omega)$, the density of states of modes per angular frequency.

$\triangleright$ Sketch $g(\omega)$.

(f) Write an expression for the heat capacity of this one dimensional chain. You will inevitably have an integral that you cannot do analytically.

(g) Show that at high temperature the law of Dulong-Petit (for one dimension) is recovered.

2.6. **Normal modes of a One Dimensional Diatomic Chain**



(a) What is the difference between an acoustic mode and an optical mode?

▷ Describe how particles move in each case.

(b) Derive the dispersion relation for the longitudinal oscillations of a one dimensional *diatomic* mass-and-spring crystal where the unit cell is of length a and each unit cell contains one atom of mass m_1 and one atom of mass m_2 connected together by springs with spring constant κ (all springs are the same, and motion of particles is in one dimension only).

(c) Determine the frequencies of the acoustic and optical modes at $k = 0$ as well as at the Brillouin zone boundary.

▷ Determine the sound velocity and show that the group velocity is zero at the zone boundary.

▷ Show that the the sound velocity is also given by $v_s = \sqrt{\beta^{-1}/\rho}$ where ρ is the chain density and β is the compressibility.

(d) Sketch the dispersion in both reduced and extended zone scheme.

▷ If there are N unit cells, how many different normal modes are there?

▷ How many *branches* of excitations are there? (I.e., in reduced zone scheme, how many modes are there there at each k).

(e) What happens when $m_1 = m_2$?

2.7. **One Dimensional Tight Binding Model**

(a) **Monatomic Solid:** Consider a one-dimensional tight binding model of electrons hopping between atoms. Let the distance between atoms be called a, and here let us label the atomic orbital on atom n as $|n\rangle$ for $n = 1 \ldots N$ (and you may assume periodic boundary conditions, and you may assume $\langle n|m\rangle = \delta_{nm}$). Suppose there is an on-site energy ϵ and a hopping matrix element $-t$. In other words, suppose $\langle n|H|m\rangle = \epsilon$ for $n = m$ and $\langle n|H|m\rangle = -t$ for $n = m \pm 1$.

▷ Derive and sketch the dispersion curve for electrons. (Hint: Use the effective Schroedinger equations of problem 2.2.a. The resulting equation should look very similar to that of problem 2.5. above.)

▷ How many different eigenstates are there in this system?

▷ What is the effective mass of the electron near the bottom of this band?

▷ What is the density of states?

▷ If each atom is monovalent (it donates a single electron) what is the density of states at the fermi surface?

$\triangleright$ Estimate the heat capacity of the system at low temperature.

$\triangleright$ What is the heat capacity if each atom is divalent? What about the spin susceptibility?

(b) **Diatomic Solid:** Now consider a model of a diatomic solid as such

$$-A-B-A-B-A-B-$$

Suppose that the onsite energy of type A is different from the onsite energy of type B. I.e, $\langle n|H|n\rangle$ is ϵ_A for n being on a site of type A and is ϵ_B for n being on a site of type B. (All hopping matrix elements $-t$ are still identical to each other).

$\triangleright$ Calculate the new dispersion relation. (This is extremely similar to problem 2.6. above. If you are stuck, try studying that problem again.)

$\triangleright$ Sketch this dispersion relation in both the reduced and extended zone schemes.

$\triangleright$ What happens in the "atomic" limit when t becomes very small.

$\triangleright$ What is the effective mass of an electron near the bottom of the lower band?

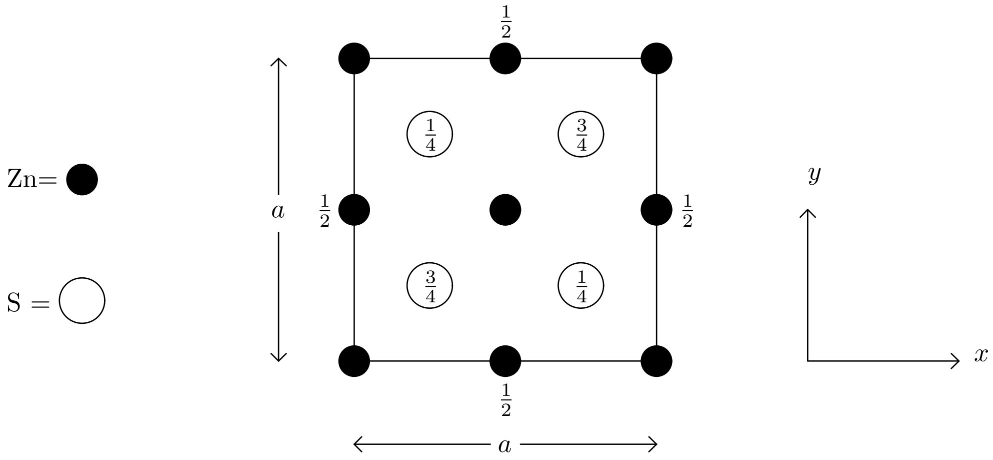
$\triangleright$ If each atom (of either type) is monovalent, is the system a metal or an insulator?

$\triangleright$ What happens if $\epsilon_A = \epsilon_B$?

Problem Set 3

Crystal Structure, Reciprocal Lattice, and Scattering

3.1. **Crystal Structure**



The diagram above shows a plan view of a structure of cubic ZnS (zinc blende) looking down the z axis. The numbers attached to some atoms represent the heights of the atoms above the $z = 0$ plane expressed as a fraction of the cube edge a. Unlabeled atoms are at $z = 0$ and $z = a$.

(a) What is the Bravais lattice type?

(b) Describe the basis.

(c) Given that $a = 0.541$ nm, calculate the nearest-neighbor Zn-Zn, Zn-S, and S-S distances.

(d) Copy the drawing above, and show the [210] direction and the set of (210) planes.

(e) Calculate the spacing between adjacent (210) planes.

3.2. **Directions and Spacings of Crystal Planes**

▷ Explain briefly what is meant by the terms “crystal planes” and “Miller indices.”

▷ Show that the general direction $[hkl]$ in a cubic crystal is normal to the planes with Miller indices (hkl).

▷ Is the same true in general for an orthorhombic crystal?

▷ Show that the spacing d of the (hkl) set of planes in a cubic crystal with lattice parameter a is

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \ .$$

▷ What is the generalization of this formula for an orthorhombic crystal?

3.3. ‡**Reciprocal Lattice**

(a) Define the term Reciprocal Lattice.

(b) Show that if a lattice in three dimensions has primitive lattice vectors $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$ then primitive lattice vectors for the reciprocal lattice can be taken as

$$\begin{aligned}
\mathbf{b}_1 &= 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} \\
\mathbf{b}_2 &= 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} \\
\mathbf{b}_3 &= 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}
\end{aligned}$$

What is the proper formula in two dimensions?

(c) Define "tetragonal" and "orthorhombic" lattices. For an orthorhombic lattice, show that $|\mathbf{b}_j| = 2\pi/|\mathbf{a}_j|$. Hence, show that the length of the reciprocal lattice vector $\mathbf{G} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$ is equal to $2\pi/d$, where d is the spacing of the (hkl) planes (see question 3.2.).

3.4. **Reciprocal Lattice and X-ray Scattering**

A two-dimensional rectangular crystal has a unit cell with sides $a_1 = 0.468$ nm and $a_2 = 0.342$ nm. A collimated beam of monochromatic X-rays with wavelength 0.166 nm is used to examine the crystal.

(a) Draw to scale a diagram of the reciprocal lattice.

▷ Label the reciprocal lattice points for indices in the range $0 \leq h \leq 3$ and $0 \leq k \leq 3$.

(b) Calculate the magnitude of the wavevectors $\mathbf{k}$ and $\mathbf{k}'$ of the incident and reflected X-ray beams, and hence construct on your drawing the "scattering triangle" corresponding to the Laue condition $\Delta\mathbf{k} = \mathbf{G}$ for diffraction from the (210) planes. (The scattering triangle includes $\mathbf{k}$, $\mathbf{k}'$ and $\Delta\mathbf{k}$.)

(c) Draw the first and second Brillouin zones using the Wigner-Seitz construction.

3.5. ‡ **X-ray scattering II**

$BaTiO_3$ has a primitive cubic lattice and a basis with atoms having fractional coordinates

Ba	[0,0,0]		
Ti	$[\frac{1}{2}, \frac{1}{2}, \frac{1}{2}]$		
O	$[\frac{1}{2}, \frac{1}{2}, 0]$,	$[\frac{1}{2}, 0, \frac{1}{2}]$,	$[0, \frac{1}{2}, \frac{1}{2}]$

▷ Sketch the unit cell.

▷ Show that the X-ray structure factor for the $(00l)$ Bragg reflections is given by

$$S_{hkl} = f_{\mathrm{Ba}} + (-1)^l f_{\mathrm{Ti}} + \left[1 + 2(-1)^l\right] f_{\mathrm{O}} \tag{1}$$

where f_{Ba} is the atomic form factor for Ba, etc.

▷ Calculate the ratio I_{002}/I_{001}, where I_{hkl} is the intensity of the X-ray diffraction from the (hkl) planes. You may assume that the atomic form factor is proportional to atomic number (Z), and neglect its dependence on the scattering vector. [$Z_{\mathrm{Ba}} = 56$, $Z_{\mathrm{Ti}} = 22$, $Z_{\mathrm{O}} = 8$]

3.6. ‡ X-ray scattering and Systematic Absences

(a) Explain what is meant by “lattice constant” for a cubic crystal structure.

(b) Explain why X-ray diffraction may be observed in first order from the (110) planes of a crystal with a body-centred cubic (BCC) lattice, but not from the (110) planes of a crystal with a face-centred cubic (FCC) lattice.

▷ Derive the general selection rules for which planes are observed in BCC and FCC lattices.

(c) Show that these selection rules hold independent of what atoms are in the primitive unit cell, so long as the lattice is BCC or FCC respectively.

(d) A collimated beam of monochromatic X-rays of wavelength 0.162 nm is incident upon a powdered sample of the cubic metal palladium. Peaks in the scattered X-ray pattern are observed at angles of 42.3°, 49.2°, 72.2°, 87.4° and 92.3° from the direction of the incident beam.

▷ Identify the lattice type.

▷ Calculate the lattice constant.

▷ If you assume there is only a single atom in the basis, how well does this lattice constant agree with the known data that the density of palladium is 12023 kg m^{-3}? [Atomic mass of palladium = 106.4].

(e) How could you improve the precision with which the lattice constant is determined?

3.7. ‡ Neutron Scattering

(a) X-ray diffraction from sodium hydride (NaH) established that the Na atoms are arranged on a face-centred cubic lattice.

▷ Why is it difficult to locate the positions of the H atoms using X-rays?

The H atoms were thought to be displaced from the Na atoms either by $[\frac{1}{4}, \frac{1}{4}, \frac{1}{4}]$ or by $[\frac{1}{2}, \frac{1}{2}, \frac{1}{2}]$, to form the ZnS (zincblende) structure or NaCl (sodium chloride) structure, respectively. To distinguish these models a neutron powder diffraction measurement was performed. The intensity of the Bragg peak indexed as (111) was found to be much larger than the intensity of the peak indexed as (200).

▷ Write down expressions for the structure factors S_{hkl} for neutron diffraction assuming NaH has

(i) the sodium chloride (NaCl) structure,

(ii) the zinc blende (ZnS) structure.

▷ Hence, deduce which of the two structure models is correct for NaH. [Nuclear scattering length of Na $= 0.363 \times 10^{-5}$ nm; nuclear scattering length of H $= -0.374 \times 10^{-5}$ nm]

(b) How does one produce monochromatic neutrons for use in neutron diffraction experiments?

▷ What are the main differences between neutrons and X-rays?

▷ Explain why (inelastic) neutron scattering is well suited for observing phonons, but X-rays are not.

Problem Set 4

Band Structure, Semiconductor Physics, and Magnetism

4.1. **Number of States in the Brillouin Zone**

A specimen in the form of a cube of side L has a primitive cubic lattice whose mutually orthogonal primitive lattice vectors have length a. Show that the number of different allowed $\vec{k}$-states within the first Brillouin zone equals the number of primitive unit cells forming the specimen (do not consider spin). One may assume periodic boundary conditions, although it is worth thinking about whether this still holds for hard-wall boundary conditions as well.

4.2. **‡Nearly Free Electron Model**

Consider an electron in a weak periodic potential in one dimension $V(x) = V(x + a)$. Write the periodic potential as

$$V(x) = \sum_G e^{iGx} V_G$$

where the sum is over the reciprocal lattice $G = 2\pi n/a$, and $V_G^* = V_{-G}$ assures that the potential $V(x)$ is real.

(a) Explain why for k near to a Brillouin zone boundary (such as k near π/a) the electron wavefunction should be taken to be

$$\psi = Ae^{ikx} + Be^{i(k+G)x} \tag{1}$$

where G is a reciprocal lattice vector such that $|k|$ is close to $|k + G|$.

(b) For an electron of mass m with k exactly at a zone boundary, use the above form of the wavefunction to show that the eigenenergies at this wavevector are

$$E = \frac{\hbar^2 k^2}{2m} + V_0 \pm |V_G|$$

where G is chosen so $|k| = |k + G|$.

▷ Give a qualitative explanation of why these two states are separated in energy by $2|V_G|$.

▷ Give a sketch (don't do a full calculation) of the energy as a function of k in both the extended and the reduced zone schemes.

(c) *Now consider k close to, but not exactly at, the zone boundary. Give an expression for the energy $E(k)$ correct to order $(\delta k)^2$ where δk is the wavevector difference of k to the zone boundary wavevector.

▷ Calculate the effective mass of an electron at this wavevector.

(d) Consider a two dimensional square lattice with one divalent atom per unit cell. If the periodic potential is very very weak, you can consider the electrons to be free and to form a circular Fermi sea. Using the intuition from above (as well as the result of 4.1. above) sketch the Fermi surface for weak, medium, and strong periodic potentials.

▷ Roughly how strong should the periodic potential be for the system to be no longer a metal?

4.3. **Band Theory**

(a) Give a brief description of the formation of electron bands in crystals including reference to the atomic structure of the constituent atoms.

(b) Explain the following:

(i) sodium, which has 2 atoms in a BCC (conventional cubic) unit cell, is a metal;

(ii) calcium, which has 4 atoms in a FCC (conventional cubic) unit cell, is a metal;

(iii) diamond, which has 8 atoms in a FCC (conventional cubic) unit cell with a basis, is an electrical insulator, whereas silicon and germanium, which have similar structures, are semiconductors.

▷ Why is diamond transparent?

(c) A two-dimensional material has a square lattice with lattice constant $a = 0.3$ nm. The dispersion relations for electron energies in the conduction and valence bands are given by

$$\begin{aligned}\epsilon_c(\mathbf{k}) &= 6 - 2(\cos k_x a + \cos k_y a)\\ \epsilon_v(\mathbf{k}) &= -2 + (\cos k_x a + \cos k_y a)\end{aligned}$$

where energies are given here in units of eV. Sketch ϵ_c and ϵ_v for the direction $k_x = k_y$.

▷ Indicate the value and position of the minimum band gap.

▷ Show that close to the conduction and valence band edges, contours of constant energy are circles in k-space and..

▷ .. determine the effective masses of both the electrons and the holes.

▷ Sketch the density of states as a function of energy for the whole of both the conduction and the valence band.

(d) Using a tight-binding Hamiltonian, explain where the above dispersion relations come from.

4.4. **Law of Mass Action and Doping of Semiconductors**

(a) Assume that the band gap energy E_g is much greater than the temperature $k_B T$. Derive expressions for the density of electrons (n) and for the density of holes (p) and for the product np. Show that in a pure semiconductor at a fixed T, the product np depends only on the density of states in the conduction band and the density of states in the valence band (through their effective masses), and on the band gap energy. You may need to use the integral $\int_0^\infty dx\, x^{1/2} e^{-x} = \sqrt{\pi}/2$.

(b) The band gaps of silicon and germanium are 1.1 eV and 0.75 eV respectively. You may assume the effective masses for Silicon and Germanium are isotropic, roughly the same, and are roughly 0.5 of the bare electron mass for both electrons and holes. (Actually the effective masses are not quite the same, and furthermore the effective masses are both rather anisotropic, but we are just making a rough estimates here.)

▷ Estimate the conduction electron concentration for intrinsic (undoped) silicon at room temperature.

▷ Make a rough estimate of the maximum concentration of ionized impurities that will still allow for this “intrinsic” behavior.

▷ Estimate the conduction electron concentration for germanium at room temperature.

(c) The graph in Figure 1 shows the relationship between charge-carrier concentration for a certain n-doped semiconductor.

▷ Estimate the bandgap for the semiconductor and the concentration of donor ions.

▷ Describe in detail an experimental method by which this data could have been measured and suggest possible sources of experimental error.

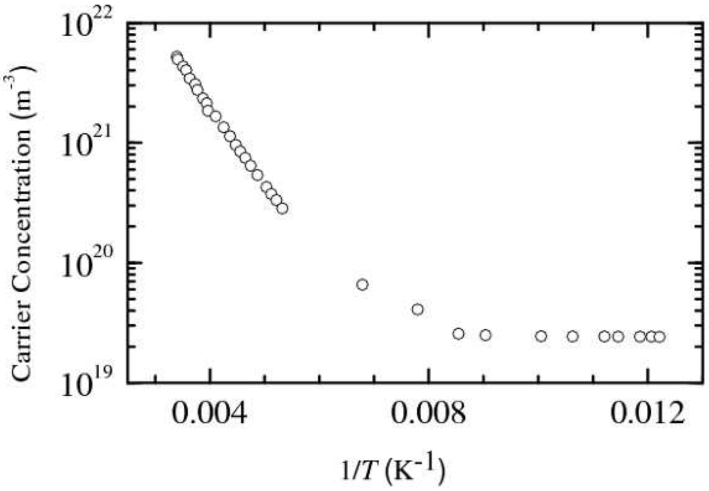


FIG. 1. Figure for Problem 4.4.

4.5. **More about Semiconductors**

(a) In semiconductor physics what is meant by a “hole” and why is it useful?

(b) An electron near the top of the valence band in a semiconductor has energy

$$E = -10^{-37}|\vec{k}|^2$$

where E is in J and k is in m^{-1}. An electron is removed from a state $\vec{k} = (2 \times 10^8\,\mathrm{m}^{-1})\hat{x}$ where $\hat{x}$ is the unit vector in the x-direction. For a hole, calculate (including the sign):

- (i) the effective mass;
- (ii) the energy;
- (iii) the momentum;
- (iv) the velocity.

(v) If there is a density $p = 10^5\,\mathrm{m}^{-3}$ of such holes all having almost exactly this same momentum, calculate the current density and its sign.

(c)Show that the chemical potential in an intrinsic semiconductor lies in the middle of the gap at low temperature.

▷ Explain how the chemical potential varies with temperature if the semiconductor is doped with (i) donors (ii) acceptors.

(d) A direct gap semiconductor is doped to produce a density of 10^{23} electrons/m^3. Calculate the hole density at room temperature given that the gap is 1.0 eV, and the effective mass of carriers in the conduction and valence band are 0.25 and 0.4 electron masses respectively. Hint: use the result of problem 4.4.a.

4.6. ‡ General Magnetism

(a) Explain qualitatively why some atoms are paramagnetic and others are diamagnetic with reference to the electronic structure of these materials.

(b) Define the terms Ferromagnetism, Antiferromagnetism, Ferrimagnetism, and Itinerant Ferromagnetism.

▷ Write down an example of a Hamiltonian which would have each one of these as its ground state.

(c) Use Hund's rules and the Aufbau principle to determine L, S, and J for the following isolated atoms:

(i) Sulfur (S) atomic number = 16

(ii) Vanadium (V), atomic number = 23

(iii) Zirconium (Zr), atomic number = 40

(iv) Xenon (Xe), atomic number = 54

(v) Dysprosium (Dy), atomic number = 66

4.7. ‡ Para and Diamagnetism

Manganese (Mn, atomic number = 25) forms an atomic vapour at 2000 K with vapour pressure 10^5 Pa. You can consider this vapour to be an ideal gas.

(a) Determine L, S, and J for an isolated manganese atom. Determine the paramagnetic contribution to the (Curie) susceptibility of this gas at 2000 K.

(b) In addition to the Curie susceptibility, the manganese atom will also have some diamagnetic susceptibility due to its filled core orbitals. Determine the Larmor diamagnetism of the gas at 2000 K. You may assume the atomic radius of a manganese atom is one angstrom.

Make sure you know the derivations of all the formulas you use!

4.8. ‡ Weiss Mean Field Theory of the Ferromagnet

Consider the spin-1/2 ferromagnetic Heisenberg Hamiltonian on the cubic lattice

$$\mathcal{H} = -\frac{J}{2}\sum_{\langle i,j\rangle} \mathbf{S}_i \cdot \mathbf{S}_j + g\mu_B \mathbf{B} \sum_i \mathbf{S}_i \tag{2}$$

Here, $J > 0$, the sum indicated with $\langle i,j\rangle$ means summing over i and j being neighbouring sites of the cubic lattice, and $\mathbf{B}$ is the externally applied magnetic field (which we will assume is in the $\hat{z}$ direction for simplicity). The factor of 1/2 out front is included so that each pair of spins is counted only once. Each site i is assumed to have a spin $\mathbf{S}_i$ of spin $S = 1/2$. Here μ_B is the conventional Bohr magneton defined to be positive. The fact that the final term has a + sign out front is from the fact that the electron charge is negative, therefore the magnetic moment opposes the spin direction. If one were to assume that these were nuclear spins the sign would be reversed (and the magnitude would be much smaller due to the larger nuclear mass).

(a) Focus your attention on one particular spin $\mathbf{S}_i$, and write down an effective Hamiltonian for this spin, treating all other variables $\mathbf{S}_j$ with $j \neq i$ as expectations $\langle \mathbf{S}_j \rangle$ rather than operators.

(b) Calculate $\langle \mathbf{S}_i \rangle$ in terms of the temperature and the fixed variables $\langle \mathbf{S}_j \rangle$ to obtain a mean-field self-consistency equation.

▷ Write the magnetization $M = |\mathbf{M}|$ in terms of $\langle \mathbf{S} \rangle$ and the density of spins.

(c) At high temperature, find the susceptibility $\chi = dM/dH = \mu_0 dM/dB$ in this approximation.

(d) Find the critical temperature in this approximation.

$\triangleright$ Write the susceptibility in terms of this critical temperature.

(e) Show graphically that in zero external field ($\mathbf{B} = 0$), below the critical temperature, there are solutions of the self consistency equation with $M \neq 0$.

4.9. **Ground States**

Consider the spin-1/2 Heisenberg Hamiltonian from Problem 4.8. Let us take $\mathbf{B}$ to be in the $-\hat{z}$ direction, and assume a cubic lattice.

It will be useful to remember that

$$\mathbf{S_i} \cdot \mathbf{S_j} = \frac{1}{2}(S_i^+ S_j^- + S_i^- S_j^+) + S_i^z S_j^z$$

(a) For $J > 0$, i.e., for the case of a ferromagnet, intuition tells us that the ground state of this Hamiltonian should simply have all spins aligned. Consider such a state. Show that this is an eigenstate of the Hamiltonian Eq. 2 and find its energy.

(b) For $J < 0$, the case of an antiferromagnet, one might expect that, at least for $\mathbf{B} = 0$, the state where spins on alternating sites point in opposite directions might be an eigenstate.

$\triangleright$ Show that, in fact, this state is not an eigenstate of the Hamiltonian. Can you identify a state that is?