Problems for Solid State Physics
(3rd Year Course 6)
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"Everything should be made as simple as possible, but no simpler."

— Frequently attributed to Albert Einstein

Actual quote:

"It can scarcely be denied that the supreme goal of all theory is to make the irreducible basic elements as simple and as few as possible without having to surrender the adequate representation of a single datum of experience"

— Albert Einstein, lecture delivered at Oxford 10 June 1933

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

Annotations Regarding which problems are worth studying for the final exam.

Problem Set 1

Einstein, Debye, Drude, and Free Electron Models

1.1. **Einstein Solid**

Classical Einstein Solid (or "Boltzmann" Solid): Consider a single harmonic oscillator in three dimensions with Hamiltonian

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

The classical calculation has never been examined on the condensed matter exam

Calculate the classical partition function

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

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.

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.

(See also problem A.1.1. for more on the same topic)

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.

Debye theory is examined frequently!

(b) The following table gives the heat capacity C for KCl 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

For part (a) you may find the following integral to be useful

$$\int_0^\infty dx \frac{x^3}{e^x - 1} = \sum_{n=1}^\infty \int_0^\infty x^3 e^{-nx} = 6 \sum_{n=1}^\infty \frac{1}{n^4} = \frac{\pi^4}{15}$$

Alternately, you may find useful the form

$$\int_0^\infty dx \frac{x^4 e^x}{(e^x - 1)^2} = \frac{4\pi^4}{15}$$

which you can derive from the first by integrating by parts.

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.

Basic Drude theory has been examined lots. Make sure to know how it works for semiconductors too.

(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.) Invert this matrix to obtain an expression for the conductivity tensor.

(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 5mm by 5mm carrying a current of 1A in a magnetic field of 1T. The density of sodium atoms is roughly 1 gram/cm^3, and sodium has atomic mass of roughly 23. What practical difficulties would there be in measuring the Hall voltage and resistivity of such a specimen (and how might these difficulties be addressed). You may assume that there is one free electron per sodium atom (Sodium has *valence* one).

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

Finite frequency Drude is probably too hard for an exam

(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.) 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.

This would be a very standard exam question

(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 [The density of sodium atoms is roughly 1 gram/cm^3, and sodium has atomic mass of roughly 23. 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**

This is a standard exam question too

(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 300K in an electric field of 1 V m^{-1} and comment on their relative magnitudes.

(ii) estimate λ for copper at 300K 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 300K.

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 electron in metals

More standard material. Very examinable.

(b)‡ Give a simple (not approximate) derivation of the Fermi gas prediction for magnetic susceptibility of the conduction electron 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 that of 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:

$$C = (2.08\,T + 2.6\,T^3)\mathrm{mJ\,mol^{-1}\,K^{-1}}$$

where T is in Kelvin. Explain the origin of each of the two terms in this expression and make an estimate of the Fermi energy for potassium metal.

A lot of things near the beginning of this problem set are officially on the syllabus, but are unlikely to appear on the exam because they are new to the syllabus (chemical bonding, thermal expansion, normal modes). However, phonons are really crucial to know very well.

Problem Set 2

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

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This much detail of chemical bonding has never been examined. It supposedly is now added to the syllabus, but unlikely to appear I would think.

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.

(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.

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

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

Not likely to show up on an exam, for same reason as above.

Although part b is pretty simple and is nice to know.

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!). 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. In problem A.2.1. we properly consider a non-orthonormal basis.

(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

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

and the hopping matrix element

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

(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

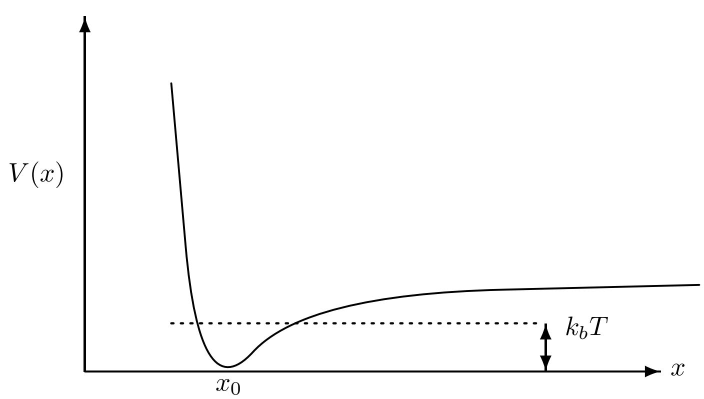
$$E = \epsilon + V_{cross} \pm |t|$$

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. Thermal Expansion

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

Thermal expansion is mandated by IOP to be part of syllabus. It has never been examined, but might be worth knowing something about it.



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

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

where the minimum is at position x_0 and $\kappa_3 > 0$. For small energies, we can truncate the series at the cubic term.

(a) **Classical model:** 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, 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 $\pm\infty$ (why is this allowed?) 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. In what temperature range is the above expansion valid?

(b) **Quantum model:** In quantum mechanics we write a Hamiltonian

$$H = H_0 + V$$

The quantum model is FAR too hard for any exam. Probably this problem will be removed in future years.

where

$$H_0 = \frac{p^2}{2m} + \frac{\kappa}{2}(x-x_0)^2$$

is the Hamiltonian for the free Harmonic oscillator, and V is the perturbation

$$V = -\frac{\kappa_3}{6}(x-x_0)^3 + \ldots$$

where we will throw out quartic and higher terms. What value of m should be used here?

(i)** (Note: You can solve parts ii and iii below even if you cannot solve this part).

Use perturbation theory to show that to lowest order in κ_3

$$\langle n|x|n\rangle = x_0 + E_n\kappa_3/(2\kappa^2) \qquad (2)$$

where $|n\rangle$ is the eigenstate of the Harmonic oscillator whose energy is

$$E_n = \hbar\omega(n + \frac{1}{2}) + \mathcal{O}(\kappa_3) \qquad n \geq 0$$

with $\omega = \sqrt{\kappa/m}$.

(ii) Note that even when the oscillator is in its ground state, the expectation of x deviates from x_0. Physically why is this?

(iii)* Use, Eq. 2 to calculate the quantum expectation of x at any temperature. We write

$$\langle x \rangle_\beta = \frac{\sum_n \langle n|x|n\rangle e^{-\beta E_n}}{\sum_n e^{-\beta E_n}}$$

Derive the coefficient of thermal expansion. Examine the high temperature limit and show that it matches that of part a above. In what range of temperatures is our perturbation expansion valid? In light of the current quantum calculation, when is the above classical calculation valid?

(c) 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?

2.4. Classical Normal Modes to Quantum Eigenstates

I'd love to see this on an exam, since it is pretty fundamental to the idea of a phonon.

But this sort of thing has never been examined before on the cond-mat exams.

For this reason, I don't think the examiners would want to test it this year.

Also some people were upset about too much quantum mechanics in this course, so I expect the examiners would shy away from quantum-ish problems.

But just to give my two cents, solid state physics IS quantum mechanics and don't let anyone tell you any differently.

So there.

In class we stated, without proof that a classical normal mode becomes a quantum eigenstate. Here we prove this fact for a simple diatomic molecule in a potential well. (See also problem A.1.1.)

Consider two particles, each of mass m in one dimension, connected by a spring (K), at the bottom of a potential well (with spring constant k). We write the potential energy as

$$U = \frac{k}{2}(x_1^2 + x_2^2) + \frac{K}{2}(x_1 - x_2)^2$$

Write the classical equations of motion. Transform into relative $x_{rel} = (x_1 - x_2)$ and center of mass $x_{cm} = (x_1 + x_2)/2$ coordinates.

(a) Show that in these transformed coordinates, the system decouples, thus showing that the two normal modes have frequencies

$$\begin{aligned} \omega_{cm} &= \sqrt{k/m} \\ \omega_{rel} &= \sqrt{(k + 2K)/m} \end{aligned}$$

Note that since there are two initial degrees of freedom, there are two normal modes.

Now consider the quantum mechanical version of the same problem. The Hamiltonian is

$$H = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + U(x_1, x_2)$$

Again transform into relative and center of mass coordinates. Define the corresponding momenta are given by $p_{rel} = (p_1 - p_2)/2$ and $p_{cm} = (p_1 + p_2)$.

(b) Show that $[p_\alpha, x_\gamma] = -i\hbar\delta_{\alpha,\gamma}$ where α and γ take the values cm or rel.

(c) In terms of these new coordinates show that the Hamiltonian decouples into two independent harmonic oscillators with the same eigenfrequencies ω_{cm} and ω_{rel}. Conclude that the spectrum of this system is

$$E_{n_{rel}, n_{cm}} = \hbar\omega_{rel}(n_{rel} + \frac{1}{2}) + \hbar\omega_{cm}(n_{cm} + \frac{1}{2})$$

where n_{cm} and n_{rel} are nonnegative integers.

(d) At temperature T what is the expectation of the energy of this system?

In problem A.2.4. the principle that normal modes become quantum eigenstates is proven in more generality.

2.5. Normal Modes of a One Dimensional Monatomic Chain

(a)‡ Explain what is meant by "normal mode" and by "phonon". Explain briefly why phonons obey Bose statistics.

You better know this problem inside and out.

(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).

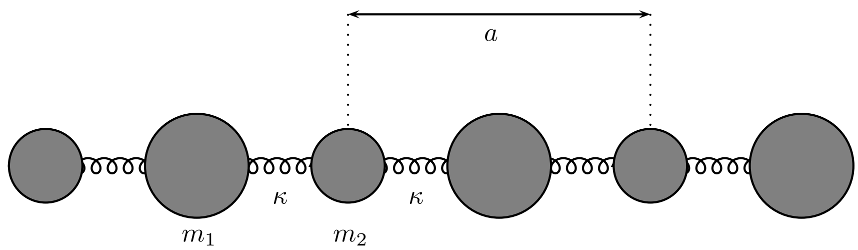
(c)‡ Show that the mode with wavevector k has the same pattern of mass displacements as the the mode with wavevector $k + 2\pi/a$. Hence show that the dispersion relation is periodic in reciprocal space (k-space).

(d)‡ Derive the phase and group velocities and sketch them as a function of k. What is the sound velocity? 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. Sketch $g(\omega)$.

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

Same for this problem
You better be able to
do this in your sleep.



(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 energies of the acoustic and optical modes at $k = 0$ as well as at the Brillioun 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.

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

2.7. **One Dimensional Tight Binding Model**

Monatomic tight bindnig
has been examined before
at least qualitatively.

Really at least (a)
should not cause you
trouble.

(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). 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) 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? What then is the Pauli paramagentic (spin) susceptibility of the system? (See problem 1.6.). What is the spin susceptibility if each atom is divalent?

Part B caused a lot of
difficulty. It would likely
be too hard for an exam

The point of this was just
to show that diatomic
tight binding was just
like problem 2.6 above.
But almost no one got this,
so conclude it is too advanced.

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

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

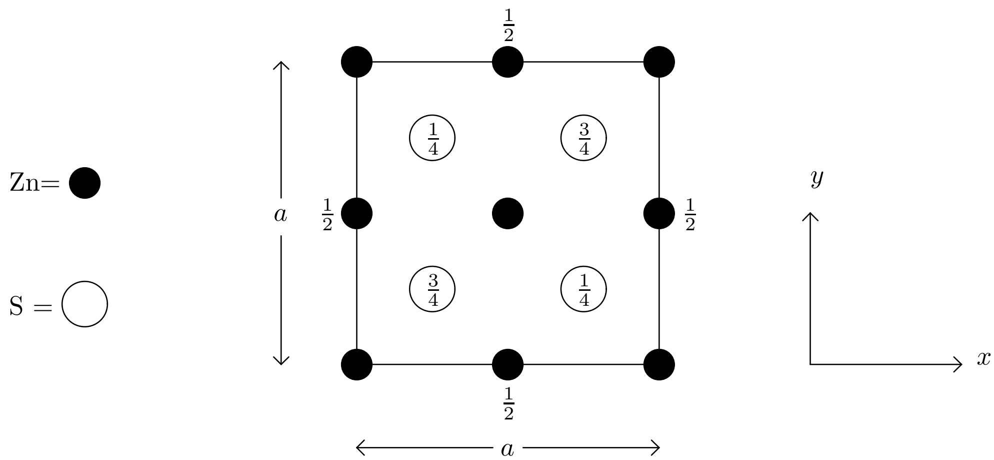
Suppose that the onsite energy of type A is different from the onsite energy of type B. I.e, $\langle n|H|n\rangle$ is ϵ_A for n being on a site of type A and is ϵ_B for n being on a site of type B. (All hopping matrix elements $-t$ are still identical to each other). Calculate the new dispersion relation. Sketch this dispersion relation in both the reduced and extended zone schemes. What happens in the "atomic" limit when t becomes very small. What is the effective mass of an electron near the bottom of the lower band? If each atom (of either type) is monovalent, is the system a metal or an insulator?

Problem Set 3

Crystal Structure, Reciprocal Lattice, and Scattering

3.1. **Crystal Structure**

Very standard exam question



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**

Very standard exam question.

Explain briefly what is meant by the terms "Crystal Planes" and "Miller Indices" for the case where the axes of a lattice are all mutually orthogonal to each other.

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**

Same.

(a) Define the term Reciprocal Lattice.

(b) Show that if a lattice in 3d has primative basis vectors $\mathbf{a_1}$, $\mathbf{a_2}$ and $\mathbf{a_3}$ then primative basis vectors for the reciprocal lattice can be taken as

$$\mathbf{b_1} = 2\pi \frac{\mathbf{a_2} \times \mathbf{a_3}}{\mathbf{a_1} \cdot (\mathbf{a_2} \times \mathbf{a_3})} \qquad (1)$$

$$\mathbf{b_2} = 2\pi \frac{\mathbf{a_3} \times \mathbf{a_1}}{\mathbf{a_1} \cdot (\mathbf{a_2} \times \mathbf{a_3})} \quad (2)$$

$$\mathbf{b_3} = 2\pi \frac{\mathbf{a_1} \times \mathbf{a_2}}{\mathbf{a_1} \cdot (\mathbf{a_2} \times \mathbf{a_3})} \quad (3)$$

What is the proper formula in 2d?

(c) Define tetragonal and orthorhombic. 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 of wavelength of 0.166 nm is used to examine the crystal.

Know this too.

(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

Know this inside out.

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

$$S_{hkl} = f_{Ba} + (-1)^l f_{Ti} + \left[1 + 2(-1)^l\right] f_O \quad (4)$$

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**

Know this in your sleep.

(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 lattice, but not from the (110) planes of a crystal with a face-centred cubic 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, and calculate the lattice constant and the nearest-neighbor distance. How well does this distance 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**

Know this like the back of your hand.

(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 (zinc blende) 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, and (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 appropriate for observing phonons, but x-rays are not.

Problem Set 4

Band Structure and Semiconductor Physics

4.1. Number of States in the Brillioun Zone

This has been examined (not recently though)

A specimen in the form of a cube of side L has a primitive cubic lattice whose mutually orthogonal fundamental translation vectors have length a. Show that the number of different allowed $\vec{k}$-states within the first Brillouin zone equals the number of 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

This is examined roughly every year.

You should be able to do this problem in varying levels of detail.

You shoudl be able to give qualitative answers if it is asked for as such.

AND you should be able to do the detailed derivations if that is asked for.

(Giving the detailed derivation when only qualitative results are asked for would get full marks, but waste precious time).

Part (c) you should probably know how to do in a pinch, and you should know what the results should be. Unlikely they would ask for it.

Part d is crucial

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 Brillioun zone boundary (such as k near π/a) the electron wavefunction should be taken to be

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

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 of divalent atoms. 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

You better know this.

(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?

Part c was an exam problem

(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

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

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.

part d was not on the exam I think..I suspect if tight binding shows up it will be in 1d only.

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

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

This is a standard exam question.

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

(b) 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. The band gaps of Silicon and Germanium are 1.1 eV and 0.75 eV respectively. Assume the effective masses for Silicon and Germanium are isotropic, roughly the same, and are roughly .5 of the bare electron mass. (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 estimate).

(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.

4.5. **More about Semiconductors**

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

This was an exam question.

(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 Joules 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. Calculate (i) The effective mass (ii) the energy (iii) the momentum (iv) the velocity of the hole and giving the sign for each one. (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)Explain why 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.

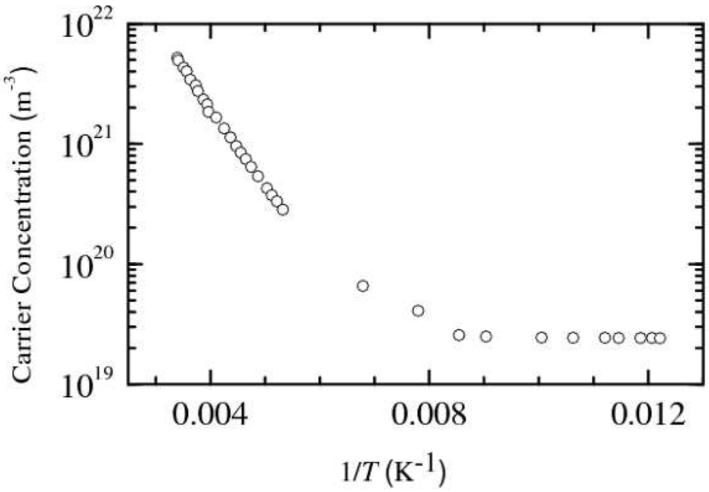
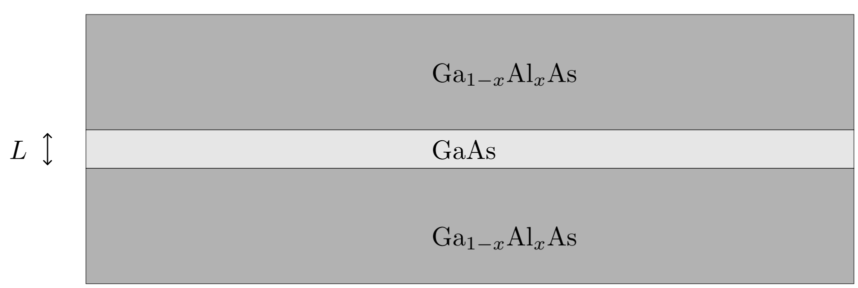


FIG. 1: Figure for Problem 4.4.

(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 carries 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. **Semiconductor Quantum Well**

(a) A quantum well is formed from a layer of GaAs of thickness L nm, surrounded by layers of $Ga_{1-x}Al_xAs$. Sketch the shape of the potential for the electrons and holes. What approximate value of L is required if the band gap of the quantum well is to be 0.1 eV larger than that of GaAs bulk material? You may assume that the band gap of the $Ga_{1-x}Al_xAs$ is substantially larger than that of GaAs. (The electron (hole) effective mass in GaAs is 0.068 m_e (0.45 m_e) where m_e is the mass of the electron.) (b) *What might this structure be useful for? How would it be possible to n-dope this structure so that electrons accumulate in the well region of the structure, but away from impurities. Why would this be useful?



4.6 is complicated. Officially it is on the syllabus. But most of device physics has been removed from the syllabus, so it seems unlikely that this will appear. (particularly part b is unlikely to be examined).

Problem Set 5

Magnetism and Mean Field Theory

This could appear.

5.1. ‡ **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) The wavefunction of an electron bound to an impurity in n-type silicon is hydrogenic in form. Estimate the impurity contribution to the diamagnetic susceptibility of a Si crystal containing 10^{20} m^{-3} donors given that the electron effective mass $m* = 0.4m_e$ and the relative permitivity is $\epsilon_r = 12$. Make sure you know the derivation of the formula you use!

Mean field theory has appeared many many times.

5.2. ‡ **Weiss Mean Field Theory of the Ferromagnet** Consider the spin-1/2, ferromagnetic Heisenberg Hamiltonian on the cubic lattice

$$\mathcal{H} = -\frac{J}{2}\sum_{<i,j>} \mathbf{S_i}\cdot\mathbf{S_j} - g\mu_B \mathbf{B}\sum_i \mathbf{S_i} \tag{1}$$

Here, $J > 0$, with the sum indicated with $< i, j >$ means summing over i and j being neighboring 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. (Here μ_B is the conventional Bohr magneton). 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 $S = 1/2$.

(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. 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 $M \neq 0$.

(f) Repeat parts (a)-(d) but now assuming there is an $S = 1$ spin on each site.

Bragg-williams has never appeared on an exam.

I think it is safe to assume it will not appear.

5.3. **Bragg-Williams Approximation**

This problem provides a different approach to obtaining the Weiss mean-field equations. For simplicity we will again assume spin 1/2 variables on each site.

Assume there are N lattice sites in the system. Let the average spin value be $\langle S_i \rangle = m$. Thus the probability the probability of a spin being an up spin is $P_\uparrow = 1/2 + m$ whereas the probability of any spin being a down spin is $P_\downarrow = 1/2 - m$. The total number of up spins or down spins is then $NP_\uparrow$ and $NP_\downarrow$ respectively where there are N total lattice sites in the system.

(a) Consider first a case where sites do not interact with each other. In the micro-canonical ensemble, we can count the number of configurations (microstates) which have the given number of spin ups and spin downs (determined by m). Using $S = k_b \ln \Omega$ calculate the entropy of the system in the large N limit.

(b) Assuming all sites have independent probabilities $P_\uparrow$ and $P_\downarrow$ of pointing up and down respectively, calculate the probability that two neighboring sites will point in the same direction and the probability that two neighboring sites will point in opposite directions. Use this result to calculate the an approximation to the expectation of the Hamiltonian. Note: This is not an exact result, as in reality, sites that are next to each other will have a tendency to have the same spin because that will lower their energies, but we have ignored this effect here.

(c) Putting together the results of (a) and (b) above, derive the approximation to the free energy

$$F = E - TS = Nk_bT\left[(\frac{1}{2}+m)\log(\frac{1}{2}+m) + (\frac{1}{2}-m)\log(\frac{1}{2}-m)\right] - g\mu_B B_z N m - JNZm^2/2$$

where Z is the number of neighbors each spin has, and we have assumed the external field to be in the $\hat{z}$ direction.

(d) Extremize this expression with respect to the variable m to obtain the same mean field equations as above. Below the critical temperature note that there are three solutions of the mean field equations. By examining the second derivative of F with respect to m, show that the $m = 0$ solution is actually a maximum of the Gibbs energy rather than a minimum. Sketch $F(m)$ both above and below the critical temperature for $B = 0$. At nonzero B?

5.4. **Mean Field Theory for the Antiferromagnet**

Mean field antiferro HAS appeared on exams.

For this exercise we use the Molecular Field (Weiss Mean Field) approximation for the spin-1/2 *Antiferromagnetic* model on a 3 dimensional cubic lattice. The full Hamiltonian is exactly that of Eq. 1 above, except that now we have $J < 0$, so neighboring spins want to point in opposite directions. (Compared to a Ferromagnet where $J > 0$ and neighboring spins want to point in the same direction). For simplicity let us assume that the external field points in the $\hat{z}$ direction.

At mean field level, the ordered ground state of this Hamiltonian will have alternating spins pointing up and down respectively. Let us call the sublattices of alternating sites, sublattice A and sublattice B respectively (i.e, A sites have lattice coordinates (i, j, k) with $i + j + k$ odd whereas B sites have lattice coordinates with $i + j + k$ even).

In Mean field theory the interaction between neighboring spins is replaced by an interaction with an average spin. Let $m_A = \langle S^z \rangle_A$ be the average value of the spins on sub-lattice A, and $m_B = \langle S^z \rangle_B$ be the average value of the spins on sub-lattice B. (We assume that these are also oriented in the $\pm\hat{z}$ direction).

(a) Write the mean field Hamiltonian for a single site on sublattice A and the mean field Hamiltonian for a single site on sublattice B.

(b) Derive the mean-field self consistency equations

$$m_A = \frac{1}{2}\tanh(\beta[JZm_B + g\mu_B B]/2)$$
$$m_B = \frac{1}{2}\tanh(\beta[JZm_A + g\mu_B B]/2)$$

with $\beta = 1/(k_bT)$. Recall that $J < 0$.

(c) Let $B = 0$. Reduce the two self-consistency equations to a single self consistency equation. (Hint: Use symmetry to simplify! Try plotting m_A versus m_B).

(d) Assume $m_{A,B}$ are small near the critical point and expand the self consistency equations. Derive the critical temperature T_c below which the system is antiferromagnetic (i.e., $m_{A,B}$ become nonzero).

(e) How does one detect antiferromagnetism experimentally?

(f) In this mean-field approximation, the magnetic susceptibility can be written as

$$\chi = (N/2) g \mu_0 \mu_B \lim_{B \to 0} \frac{\partial (m_A + m_B)}{\partial B}$$

(why the factor of 1/2 out front?).

Derive this susceptibility for $T > T_c$ and write it in terms of T_c. Compare your result with the analogous result for a ferromagnet. (Problem 5.2.). In fact, it was this type of measurement that first suggested the existence of antiferromagnets!

I can't imagine g would ever be on an exam. (Much too hard).

(g)* Derive a similar expression for the susceptibility below T_c and write the final result in terms of T_c and in terms of $m_A(T)$. Give a sketch of the susceptibility at all T.

5.5. **Ground States and Spin Waves**

(a) Consider the spin-1 Heisenberg Hamiltonian from Problem 5.2.. Let us take $\mathbf{B}$ to be in the $\hat{z}$ direction, and assume a cubic lattice.

Spin waves are new to the syllabus.

I suspect you can safely ignore them this year.

(a.i) 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. 1 and find its energy.

(a.ii) 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. Unfortunately, this is not precisely true. Consider such an state of the system. Show that the state in question is not an eigenstate of the Hamiltonian. Although the intuition of alternating spins on alternating sites is not perfect, it becomes reasonable for systems with large spins S. For smaller spins (like spin 1/2) one needs to consider these so-called "quantum fluctuations". (We will not do that here).

Hint for parts (i) and (ii):

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

(b) For the spin-S ferromagnet particularly for large S, our "classical" intuition is fairly good and we can use simple approximations to examine the excitation spectrum above the ground state.

First recall the Heisenberg equations of motion for any operator

$$i\hbar \frac{d\hat{O}}{dt} = [\hat{O}, \mathcal{H}]$$

with $\mathcal{H}$ the Hamiltonian (Eq. 1 with $\mathbf{S_i}$ being a spin S operator).

(b.i) Derive equations of motion for the spins in the Hamiltonian Eq. 1. Show that one obtains

$$\hbar \frac{d\mathbf{S_i}}{dt} = \mathbf{S_i} \times \left(J \sum_j \mathbf{S_j} + g\mu_b \mathbf{B} \right) \quad (2)$$

where the sum is over sites j that neighbor i.

(b.ii) In the ferromagnetic case, particularly if S is large, we can treat the spins as not being operators, but rather as being classical variables. In the ground state, we can set all $\mathbf{S_i} = \hat{z}S$ (Assuming $\mathbf{B}$ is in the $\hat{z}$ direction so the ground state has spins aligned in the $\hat{z}$ direction). Then to consider excited states, we can perturb around this solution by writing

$$\begin{aligned} S_i^z &= S - \mathcal{O}((\delta S)^2/S) \\ S_i^x &= \delta S_i^x \\ S_i^y &= \delta S_i^y \end{aligned}$$

where we can assume δS^x and δS^y are small compared to S. Expand the equations of motion (Eq. 2) for small perturbation to obtain equations of motion that are linear in δS_x and δS_y

(b.iii) Further assume wavelike solutions

$$\begin{aligned} \delta S_i^x &= A_x e^{i\omega t - i\mathbf{k}\cdot\mathbf{r}} \\ \delta S_i^y &= A_y e^{i\omega t - i\mathbf{k}\cdot\mathbf{r}} \end{aligned}$$

Plugging this form to your derived equations of motion, show that the dispersion curve for "spin-waves" of a ferromagnet is given by $\hbar\omega = |F(\mathbf{k})|$ where

$$F(\mathbf{k}) = S\left[J(6 - 2[\cos(k_x a) + \cos(k_y a) + \cos(k_z a)]) + g\mu_b B\right]$$

How might these spin waves be detected in an experiment?

5.6. **Itinerant Ferromagnetism**

(a.i) Review 1: For a three dimensional tight binding model on a cubic lattice, calculate the effective mass in terms of the hopping matrix element t between nearest neighbors and the lattice constant a.

Itinerant ferromag and hubbard model is new to the course.

In future years I hope it will be examined. I think because it has not been examined in the past I suspect it is safe to ignore it for this year.

(a.ii) Review 2: Assuming the density n of electrons in this tight binding band is very low, one can view the electrons as being free electrons with this effective mass m^*. For a system of spinless electrons show that the total energy per unit volume (at zero temperature) is given by

$$E/V = nE_{min} + Cn^{5/3}$$

where E_{min} is the energy of the bottom of the band. Calculate the constant C.

(b) Let the density of spin-up electrons be $n_\uparrow$ and the density of spin-down electrons be $n_\downarrow$ we can write these as

$$\begin{aligned} n_\uparrow &= (n/2)(1+\alpha) \quad (3) \\ n_\downarrow &= (n/2)(1-\alpha) \quad (4) \end{aligned}$$

where the total magnetization of the system is given by

$$M = \mu_b n \alpha$$

Using the result of part (a), fixing the total density of electrons in the system n, calculate the total energy of the system per unit volume as a function of α. Expand your result to fourth order in α. Show that $\alpha = 0$ gives the lowest possible energy. Argue that this remains true to all orders in α

(c) Now consider adding a Hubbard interaction term

$$H_{hubbard} = U \sum_i N_\uparrow^i N_\downarrow^i$$

with $U \geq 0$ where N_σ^i is the number of electrons of spin σ on site i.

Calculate the expectation value of this interaction term given that the up and down electrons form fermi seas with densities $n_\uparrow$ and $n_\downarrow$ as given by Eqns. 3 and 4 above. Write this energy in terms of α.

(d) Adding together the kinetic energy calculated in part b with the interaction energy calculated in part c, determine the value of U for which it is favorable for α to become nonzero. For values of U not too much bigger than this value, calculate the magnetization as a function of U. Explain why this calculation is only an approximation.

(e) Consider now a two dimensional tight binding model on a square lattice with a Hubbard interaction. How does this alter the result of part (d)?

5.7. **Antiferromagnetism in the Hubbard Model**

Anitferr in the hubbard model almost certainly won't appear.

Some people were upset that this was on the syllabus at all. So it would likely be too controversial to have it on an exam.

Consider a tight binding model with hopping t and a strong Hubbard interaction.

$$H_{hubbard} = U \sum_i N_\uparrow^i N_\downarrow^i$$

(a) If there is one electron per site, if the interaction term U is very strong, explain qualitatively why the system must be an insulator.

(b) On a square lattice, with one electron per site, and large U, use second order perturbation theory to determine the energy difference between the ferromagnetic state and the antiferromagnetic state. Which one is lower energy?

Some Revision Problems

Know this

6.1. Debye Theory

Use the Debye approximation to determine the specific heat of a two dimensional solid as a function of temperature. State your assumptions. You will need to leave your answer in terms of an integral that generally one cannot do. At high T, show the specific heat goes to a constant and find that constant. At low T, show that $C_v = KT^n$ Find n. Find K in terms of a definite integral. If you are brave you can try to evaluate the integral, but you will need to leave your result in terms of the Riemann zeta function $\zeta(s) = \sum_{n=1}^{\infty} n^{-s}$.

Hmmm... would be a suprising question .. but maybe could appear as one of those last little bits

6.2. Debye Theory II

Physicists should be good at making educated guesses: Guess the element with the highest Debye temperature. The lowest? You might not guess the ones with the absolutely highest or lowest temperatures, but you should be able to get close.

6.3. Free Electron Theory

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

Standard exam question.

(b) Show that the kinetic energy of a free electron gas in 3D is $(3/5)NE_F$ where E_F is the fermi energy.

Part d would never appear. Too hard.

(c) Consider a two dimensional electron gas. Derive an expression for the density of states.

(d) *Calculate the specific heat at low temperature of this two dimensional electron gas. The following integral may be useful:

$$\int_{-\infty}^{\infty} dx \frac{x^2 e^x}{(e^x+1)^2} = \frac{\pi^2}{3}$$

6.4. Vibrations I

This woudl be an interesting exam question that could appear I suppose.

(a) Consider a 1 dimensional mass and spring model of a crystal. Write down the dispersion curve $\omega(k)$ for this model (this should be easy by this time). Now write an expression for the specific heat of this 1 dimensional chain. You will inevitably have an integral that you cannot do.

(b)* However, you can expand exponentials for high temperature to obtain a high temperature approximation. It should be obvious that the high temperature limit should give heat capacity $C = k_B$ per atom (the law of Dulong-Petit in one dimension). By expanding to next nontrivial order, show that

$$C/N = k_B(1 - A/T^2 + \ldots)$$

where

$$A = \frac{\hbar^2 k}{6m}$$

where m is the atomic mass and k is the spring constant.

This has appeared on exams before. (perhaps before 2004 though).

Woudl be a good question.

6.5. **Vibrations II** Consider a 1 dimensional spring and mass model of a crystal. Generalize this model to include springs not only between neighbors but also between second nearest neighbors. Let the spring constant between neighbors be called κ_1 and the spring constant between second neighbors be called κ_2. Let the mass of each atom be M.

(a) Calculate the dispersion curve $\omega(k)$ for this model.

(b) Determine the sound wave velocity, Show the group velocity vanishes at the Brillouin zone boundary.

6.6. **Reciprocal Lattice**

Should know this.

Show that the reciprocal lattice of a FCC (face-centered-cubic) lattice is a BCC (body-centered-cubic) lattice. Correspondingly show that the reciprocal lattice of a BCC lattice is an FCC lattice. If an FCC lattice has conventional unit cell with lattice constant a, what is the lattice constant for the conventional unit cell of the reciprocal BCC lattice?

Consider now an orthorhombic face-centered lattice with conventional lattice constants a_1, a_2, a_3. What it the reciprocal lattice now?

6.7. **Scattering**

Should be easy

The Bragg angles of a certain reflection off of copper Is 47.75° at 20°C but is 46.60° at 1000°C. What is the coefficient of linear expansion of copper? (Note: the Bragg angle θ is half of the measured diffraction (deflection) angle 2θ).

6.8. **More scattering**

Should know this. Very standard exam question.

KCl and KBr are alkali-halides with the same crystal structure as NaCl: fcc cubic with Na at (0,0,0) and Cl at (1/2,1/2,1/2). KBr shows X-ray diffraction peaks from planes (111) (200) (220) (331) (222) (400)(331)(420), but KCl shows peaks only at (200)(220)(222)(400)(420). Why might this be true?

6.9. **Semiconductors**

Know this

Describe experiments to determine the following properties of a semiconductor sample: (i) sign of the majority carrier, (ii) carrier concentration (assume that one carrier type is dominant), (iii) band gap, (iv) effective mass (v) mobility of the majority carrier.

This has appeared in the past, and is still on syllabus but often when it was examined it was part of a device-like question -- which is no longer examinable

6.10. **More Semiconductors**

Outline the absorption properties of a semiconductor and how these are related to the band gap. Explain the significance of the distinction between a direct and an indirect semiconductor. What region of the optical spectrum would be being studied for a typical semiconducting crystal?

6.11. **Yet More Semiconductors**

Similar to 6.10

Outline a model with which you could estimate the energy of electron states introduced by donor atoms into an n-type semiconductor. Write down an expression for this energy, explaining why the energy levels are very close to the conduction band edge.

6.12. **Magnetism**

Explain briefly the origin of diamagnetism and paramagnetism in atoms.

Standard Exam question

Consider a crystal of volume V composed of N identical atoms. Each atom has spin 1/2 and $g = 2$. Assume neighboring atoms do not interact, derive an expression for the paramagnetic susceptibility as a function of temperature in the high temperature limit. Explain how this system might be used to make a refrigerator. In reality what limits how well this works?

Discuss what is meant by "quenching" of orbital angular momentum and its consequences for paramagnetism.

Quenching is examinable, and has appeared.

This was an exam question (when it was on the exam it had a great big error!).

6.13. **Mean field theory**

(a) β-Brass is an alloy containing equal numbers of of Cu and Zn atoms. Above a temperature of 730K, the atoms are arranged randomly on a body centered cubic lattice. Below 730K, the lattice becomes simple cubic with Cu atoms largely on the (0,0,0) position and the Zn atoms largely at the (1/2,1/2,1/2) position in the unit cell. The energy of the crystal depends on the occupancy of the sites and is given by

$$E = \frac{1}{2}\sum_{i,j} J\sigma_i\sigma_j$$

where $\sigma_i = +1$ if the site is occupied by a Cu atom and $\sigma_i = -1$ if the site is occupied by a Zn atom. Here the sum is restricted to nearest neighbors. Using mean field approximation show that

$$\langle|\sigma|\rangle = \tanh(zJ\langle|\sigma|\rangle)$$

what is z ? (b) Estimate the magnitude of J (c) Explain, in detail, how this ordering could be observed.

Additional Problems

More problems associated with Problem Set 1

A.1.1. **Diatomic Einstein Solid***

Having studied problem 1.1., consider now a solid made up of diatomic molecules. We can (very crudely) model this as a two particles in three dimensions, connected to each other with a spring, both in the bottom of a harmonic well.

Too hard

$$H = \frac{\mathbf{p_1}^2}{2m_1} + \frac{\mathbf{p_2}^2}{2m_2} + \frac{k}{2}\mathbf{x_1}^2 + \frac{k}{2}\mathbf{x_2}^2 + \frac{K}{2}(\mathbf{x_1} - \mathbf{x_2})^2$$

Here k is the spring constant holding both particles in the bottom of the well, and K is the spring constant holding the two particles together. Assume that the two particles are distinguishable atoms.

(a) Analogous to problem 1.1. above, calculate the classical partition function and show that the heat capacity is again $3k_B$ per particle (i.e., $6k_B$ total).

(b)Analogous to problem 1.1. above, calculate the quantum partition function and find an expression for the heat capacity. Sketch the heat capacity as a function of temperature if $K \gg k$.

(c)** How does the result change if the atoms are indistinguishable?

For this problem you may find it useful to transform to relative and center-of-mass coordinates. If you find this difficult, for simplicity you may assume that $m_1 = m_2$.

A.1.2. **Another review of free electron theory**

What is the *free electron model* of a metal. Define *Fermi energy* and *Fermi temperature*.

Why do metals held at room temperature feel cold to the touch even though their Fermi temperatures are much higher than room temperature?

This was an exam question.

A d-dimensional sample with volume L^d contains N electrons and can be described as a free electron model. Show that the Fermi energy is given by

$$E_F = \frac{\hbar^2}{2mL^2}(Na_d)^{2/d}$$

Find the numerical values of a_d for $d = 1, 2$, and 3.

Show also that the density of states at the Fermi energy is given by

$$g(E_F) = \frac{Nd}{2L^d E_F}$$

Assuming the free electron model is applicable, estimate the Fermi energy and Fermi temperature of the following materials:

(a) Copper, a monovalent metal (with face-centered-cubic structure) having four atoms per unit cell, where the side of a unit cell has length 0.361 nm.

(b) A one dimensional organic conductor which has unit cell of length 0.8 nm, where each unit cell contributes one mobile electron.

A.1.3. **Heat Capacity of a Free Electron Gas****

Too hard.

In problem 1.6..a we approximated the heat capacity of a free electron gas (in 3d). Calculate an exact expression for the specific heat of a metal at low temperature. Caution, be careful to account for the fact that the chemical potential is a function of temperature. Note: you will run into some nasty integrals. If you cannot evaluate these integrals you can rewrite them as series whose summation is known.

More problems associated with Problem Set 2

A.2.1. **LCAO Done Right**

(a) In problem 2.2. we introduced the method of linear combination of Atomic orbitals. In that problem we assumed that our basis of orbitals is orthonormal. In this problem we will relax this assumption.

Too hard.

Consider now many orbitals on each atom (and potentially many atoms). Let us write

$$|\psi\rangle = \sum_{i=1}^{N} \phi_i |i\rangle$$

for an arbitrary number N of orbitals. Let us write the N by N overlap matrix $\mathcal{S}$ whose elements are

$$\mathcal{S}_{i,j} = \langle i|j\rangle$$

In this case do NOT assume that $\mathcal{S}$ is diagonal.

Using a similar method as in problem 2.2., derive the new "Schroedinger equation"

$$\mathcal{H}\boldsymbol{\phi} = E\mathcal{S}\boldsymbol{\phi} \quad (1)$$

With the same notation for $\mathcal{H}$ and ϕ as in problem 2.2.. This equation is known as a "generalized eigenvalue problem" because of the $\mathcal{S}$ on the right hand side.

(b)** Let us now return to the situation with only two atoms and only one orbital on each atom but such that $\langle 1|2\rangle = \mathcal{S}_{1,2} \neq 0$. Without loss of generality we may assume $\langle i|i\rangle = 1$ and $S_{1,2}$ is real. If the atomic orbitals are s-orbitals then we may assume also that t is real and positive (why?).

Use the above Eq. 1 to derive the eigenenergies of the system. Argue again the the energy gained in the bonding orbital is sufficient to overcome the repulsion between nuclei.

A.2.2. **LCAO and the Ionic-Covalent Crossover**

Would be interesting but almost certainly not this appearing this year.

(a) For problem 2.2..b consider now the case where the atomic orbitals $|1\rangle$ and $|2\rangle$ have unequal energies $\epsilon_{0,1}$ and $\epsilon_{0,2}$. As the difference in these two energies increases show that the bonding orbital becomes more localized on the lower energy atom. (For simplicity you may use the orthogonality assumption $\langle 1|2\rangle = 0$). Explain how this calculation can be used to describe a crossover between covalent and ionic bonding.

A.2.3. **Van der Waals Bonding in Detail***

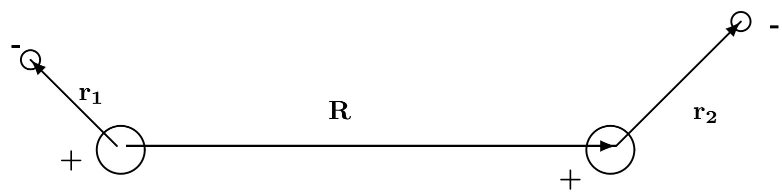
(a) *Here we will do a much more precise calculation of the van der Waals force between two hydrogen atoms. First, let the position of the two nuclei be separated by a vector $\mathbf{R}$ as

Too hard.

shown in the figure. Let us write the Hamiltonian for both atoms (assuming fixed positions of nuclei) as

$$\begin{aligned} H &= H_0 + H_1 \\ H_0 &= \frac{\mathbf{p_1}^2}{2m} + \frac{\mathbf{p_2}^2}{2m} - \frac{e^2}{4\pi\epsilon_0|\mathbf{r_1}|} - \frac{e^2}{4\pi\epsilon_0|\vec{r}_2|} \\ H_1 &= \frac{e^2}{4\pi\epsilon_0|\mathbf{R}|} + \frac{e^2}{4\pi\epsilon_0|\mathbf{R}+\mathbf{r_1}+\mathbf{r_2}|} - \frac{e^2}{4\pi\epsilon_0|\mathbf{R}+\mathbf{r_1}|} - \frac{e^2}{4\pi\epsilon_0|\mathbf{R}+\mathbf{r_2}|} \end{aligned}$$

as shown in the figure



Here H_0 is the Hamiltonian for two noninteracing hydrogen atoms, and H_1 is the interaction between the atoms.

Without loss of generality, let us assume that $\mathbf{R}$ is in the $\hat{x}$ direction. Show that for large $\vec{R}$ and small $\vec{r}_i$, the interaction Hamiltonian can be written as

$$H_1 = \frac{e^2}{4\pi\epsilon_0|\mathbf{R}|^3}(z_1 z_2 + y_1 y_2 - 2x_1 x_2) + \mathcal{O}(1/R^4)$$

where x_i, y_i, z_i are the components of $\mathbf{r_i}$. Show that this is just the interaction between two dipoles.

(b) **Perturbation Theory:** The eigenvalues of H_0 can be given as the eigenvalues of the two atoms separately. Recall that the eigenstates of hydrogen are written in the usual notation as $|n, l, m\rangle$ and have energies $E_n = -\mathrm{Ry}/n^2$ with $\mathrm{Ry} = me^4/(32\pi^2\epsilon_0^2\hbar^2) = e^2/(8\pi\epsilon_0 a_0)$ the Rydberg (Here $l \geq 0$, $|m| \leq l$ and $n \geq l+1$). Thus the eigenstates of H_0 are written as $|n_1, l_l, m_1; n_2, l_2, m_2\rangle$ with energies $E_{n_1,n_2} = -\mathrm{Ry}(1/n_1^2 + 1/n_2^2)$. The ground state of H_0 is $|1,0,0;1,0,0\rangle$. Perturbing H_0 with the interaction H_1, show that to first order in H_1 there is no change in the ground state energy. Thus conclude that the leading correction to the energy ground state energy is proportional to $1/R^6$ (and hence the force is proportional to $1/R^7$). Recalling second order perturbation theory show that we have a correction to the total energy given by

$$\delta E = \sum_{n_1,n_2,l_1,l_2,m_1,m_2} \frac{|<1,0,0;1,0,0|\; H_1 \;|n_1, l_l, m_1; n_2, l_2, m_2\rangle|^2}{E_{0,0} - E_{n_1,n_2}}$$

Show that the force must be attractive.

(c)* **Bounding the binding energy:** First, show that the numerator in this expression is zero if either $n_1 = 1$ or $n_2 = 1$. Thus the smallest E_{n_1,n_2} that appears in the denominator is $E_{2,2}$. If we replace E_{n_1,n_2} in the denominator with $E_{2,2}$ then the $|\delta E|$ we calculate will be greater than than the $|\delta E|$ in the exact calculation. On the other hand, if we replace E_{n_1,n_2} by 0, then we the $|\delta E|$ will always be less than the δE of the exact calculation. Make these replacements, and perform the remaining sum by identifying a complete set. Derive the bound

$$\frac{6e^2 a_0^5}{4\pi\epsilon_0 R^6} \leq |\delta E| \leq \frac{8e^2 a_0^5}{4\pi\epsilon_0 R^6}$$

You will need the matrix element for a hydrogen atom

$$\langle 1,0,0|x^2|1,0,0\rangle = a_0^2$$

where $a_0 = 4\pi\epsilon_0\hbar^2/(me^2)$ is the Bohr radius. (This last identity is easy to derive if you remember that the ground state wavefunction of a hydrogen atom is proportional to $e^{-r/2a_0}$).

A.2.4. **General Proof That Normal Modes Become Quantum Eigenstates** This proof generalizes the argument given in problem 2.4.. Consider a set of N particles $a = 1,\ldots N$ with masses m_p interacting via a potential

Too hard.

$$U = \frac{1}{2}\sum_{a,b} x_a V_{a,b} x_b$$

where x_a is the deviation of the position of particle a from its equilibrium position and V can be taken (without loss of generality) to be a symmetric matrix. (Here we consider a situation in 1d, however, we will see that to go to 3d we just need to keep track of 3 times as many coordinates).

(i) Defining $y_a = \sqrt{m_a}x_a$ show that the classical equations of motion may be written as

$$\ddot{y}_a = -\sum_b S_{a,b}\, y_b$$

where

$$S_{a,b} = \frac{1}{\sqrt{m_a}} V_{a,b} \frac{1}{\sqrt{m_b}}$$

Thus show that the solutions are

$$y_a^{(m)} = e^{-i\omega_m t} s_a^{(m)}$$

where ω_m is the m^{th} eigenvalue of the matrix S with corresponding eigenvector $s_a^{(m)}$. These are the N normal modes of the system.

(ii) Recall the orthogonality relations for eigenvectors of hermitian matrices

$$\sum_a [s_a^{(m)}]^*[s_a^{(n)}] \;=\; \delta_{m,n} \tag{2}$$

$$\sum_m [s_a^{(m)}]^*[s_b^{(m)}] \;=\; \delta_{a,b} \tag{3}$$

Since S is symmetric as well as hermitian, the eigenvectors can be taken to be real. Construct the transformed coordinates

$$Y^{(m)} \;=\; \sum_a s_a^{(m)} x_a \sqrt{m_a} \tag{4}$$

$$P^{(m)} \;=\; \sum_a s_a^{(m)} p_a/\sqrt{m_a} \tag{5}$$

show that these coordinates have canonical commutations

$$[P^{(m)}, Y^{(n)}] = -i\hbar\delta_{n,m} \tag{6}$$

and show that in terms of these new coordinates the Hamiltonian is rewritten as

$$H = \sum_m \left[\frac{1}{2}[P^{(m)}]^2 + \frac{1}{2}\omega_m^2 [Y^{(m)}]^2 \right] \tag{7}$$

Conclude that the quantum eigenfrequencies of the system are also ω_m. (Can you derive this result from the prior two equations?)

More problems associated with Problem Set 3

A.3.1. **And More X-ray scattering**

Would be a good exam problem.

A sample of Aluminum powder is put in an Debye-Scherrer X-ray diffraction device. The incident X-ray radiation is from Cu-Ka Xray transition (this just means that the wavelength is l = 1.54 Angstrom)

The following scattering angles were observed:

19.48° 22.64° 33.00° 39.68° 41.83° 50.35° 57.05° 59.42°

Given also that the atomic weight of Al is 27, and the density is 2.7 g/cm^3, use this information to calculate Avagadros number. How far off are you? What causes the error?

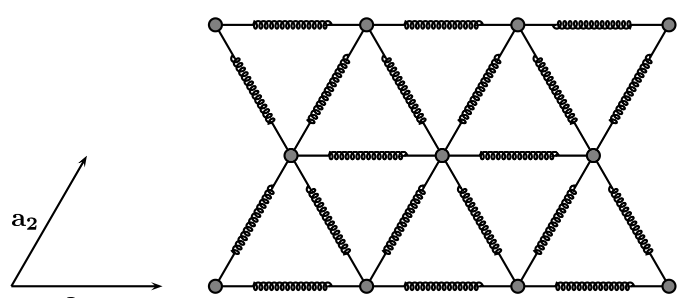
A.3.2. **Still More X-ray scattering**

Woudl be a nice exam question

The unit cell dimension for a particular b.c.c. solid is 2.4 Angstrom. Two orders of diffraction are observed. What is the minimum Energy of the neutrons? At what T would such neutrons be dominant If the distribution is Maxwell Boltzmann.

A.3.3. **Phonons in 2d**

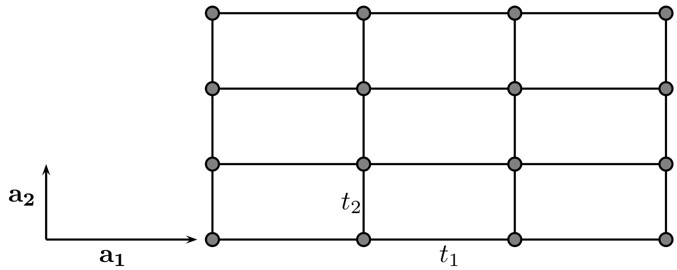
Too hard probably



Consider a mass and spring model of a two dimensional triangular lattice (assume the lattice is extended infinitely in all directions). Assume that each mass is attached to each of its 6 neighbors by equal springs of equal length. Find the first Brillouin zone. Calculate the dispersion curve $\omega(\mathbf{k})$.

A.3.4. **Tight Binding in 2d**

Similarly too hard.



Consider a rectangular lattice in 2 dimensions with lattice constants a_1 in the horizontal direction and a_2 in the vertical direction. Describe the first Brillioun zone for this lattice.

Now imagine a tight binding model where there is one orbital at each lattice site, and where the hopping matrix element is $\langle n|H|m\rangle = t_1$ if sites n and m are neighbors in the horizontal direction and is $= t_2$ if n and m are neighbors in the vertical direction. Calculate the dispersion relation for this tight binding model. What does the dispersion relation look like near the bottom of the band?

A.3.5. **Diatomic Tight Binding Model: Peierls disortion**

Consider a chain made up of all the same type of atom, but in such a way that the spacing between atoms alternated as long-short-long-short as follows

Too hard.

$$-A = A - A = A - A = A-$$

In a tight binding model, the shorter bonds (marked with $=$) will have hopping matrix element $t_{short} = t(1+\epsilon)$ whereas the longer bonds marked with $-$ have hopping matrix element $t_{long} = t(1-\epsilon)$. Calculate the tight-binding energy spectrum of this chain. (The onsite energy ϵ is the same on every atom). Expand your result to linear order in ϵ. Suppose the lower band is filled and the upper band is empty (what is the valence of each atom in this case?). Calculate the total ground state energy of the filled lower band, and show it decreases linearly with increasing ϵ.

Now consider a chain of equally spaced identical A atoms connected together with identical springs with spring constant κ. Show that making a distortion whereby every other spacing is shorter by δx costs energy proportional to $(\delta x)^2$. Conclude that for a chain with the valence discussed above, a distortion of this sort will occur spontaneously. This is known as a Peierls distortion.

More problems associated with Problem Set 4

A.4.1. p-n junction

This was a very standard exam question for years and years -- it showed up almost every year. I removed it from the syllabus.

[Note: Presumably p-n junction is not supposed to be on the syllabus, but for years it was a standard question.]

Explain the origin of the depletion layer in an abrupt p-n junction and discuss how the junction causes rectifcation to occur. Stating your assumptions, show that the total width w of the depletion layer of a p-n junction is:

$$w = w_n + w_p$$

where

$$w_n = \left(\frac{2\epsilon_r \epsilon_0 N_A \phi_0}{e N_D (N_A + N_D)} \right)^{1/2}$$

and a similar expression for w_p Here ϵ_r is the relative permittivity and N_A and N_D are the acceptor and donor densities per unit volume, while ϕ_0 is the difference in potential across the p-n junction with no applied voltage. Calculate the total depletion charge and infer how this changes when an additional voltage, V ,is applied.

What is the differential capacitance of the diode and why might it be useful to use a diode as a capacitor in an electronic circuit?

More problems associated with Problem Set 5

A.5.1. **Spin J Paramagnet**

Given the hamiltonian for a system of noninteracting spin-J atoms

Might be nice to know how to do this.

$$\mathcal{H} = -\tilde{g}\mu_B \mathbf{B} \cdot \mathbf{J}$$

Determine the magnetization as a function of B and T. Show that the susceptibility is given by

$$\chi = \frac{\rho \mu_0 (\tilde{g}\mu_B)^2}{3} \frac{J(J+1)}{k_B T}$$

where ρ is the density of spins.

A.5.2. **Correction to Mean Field**

Too hard.

Consider the spin-1/2 Ising Ferromagnet on a cubic lattice in d dimensions. When we consider mean field theory, we treat exactly a single spin σ_i and the $z = 2d$ neighbors on each side will be considered to have an average spin $\rightarrow \langle \sigma \rangle$. The critical temperature you calculate should be $k_b T_c = Jz/4$.

To improve on mean field theory, we can instead treat a block of two connected spins σ_i and $\sigma_{i'}$ where the neighbors outside of this block are assumed to have the average spin $\rightarrow \langle \sigma \rangle$. Each of the spins in the block has $2d - 1$ such averaged neighbors. Use this improved mean field theory to write a new equation for the critical temperature (it will be a transcendental equation). Is this improved estimate of the critical temperature higher or lower than that calculated in the more simple mean-field model?