

# Exam - Solid State Physics 1

Friday, 3<sup>rd</sup> of November 2017 14:00-17:00

This is a closed book exam. You are not allowed to bring books, notes *etc.* You can use a basic or scientific calculator, but no other electronic equipment having capabilities to display the course content.

Do not forget to indicate your full name and student number on **each** sheet. Please write in a clear way!

The exam has 5 questions with a total of 100 points plus 10 bonus points.

This exam has been drafted by J. Ye and verified by G. Blake

Date: 30/10/2016

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J. Ye

G. Blake

## 1) Crystal structure and diffraction (20 points)

- a. Draw all possible 2D Bravais lattices (5p). For each case specify the two lattice vectors  $\mathbf{a}$  and  $\mathbf{b}$  and the angle  $\theta$  between them.
- b. Write down the expression of **Bragg's law** (3p) and illustrate how to derive it (2p).
- c. Briefly explain the meaning of structure factor, atomic form factor and their influence on X-ray diffraction (5p). If the basis of a Bravais lattice comprises more than one atom, what will be the general trend for the diffraction pattern (showing more or less different spots) as the number of atoms in the basis increases (5p).

## Solutions

a. Bravais lattices are

1-fold: Oblique

$$a_1 \neq a_2; \beta$$

2-fold + mirror:

Centered rectangular  $a_1 \neq a_2; \beta = 90^\circ$

2-fold: Rectangular

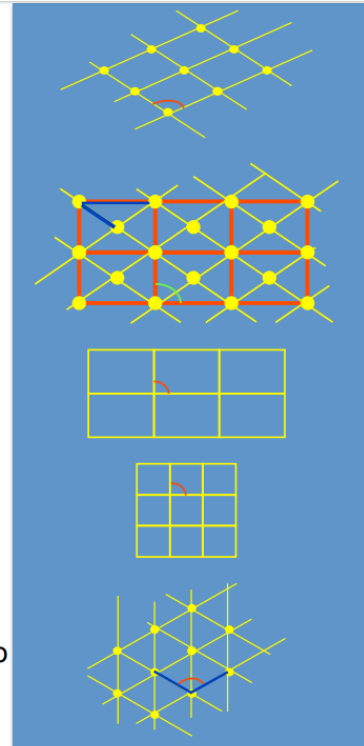
$$a_1 \neq a_2; \beta = 90^\circ$$

4-fold: Square

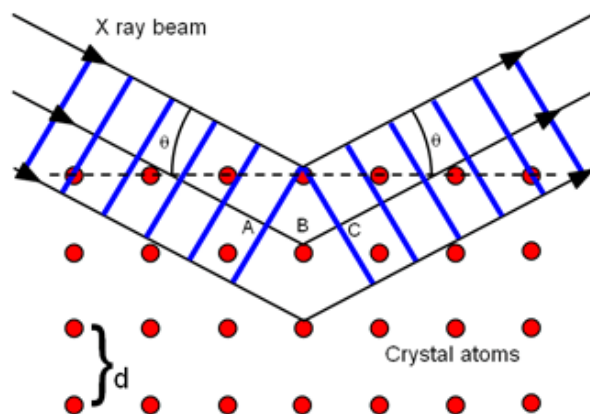
$$a_1 = a_2; \beta = 90^\circ$$

6-fold: Hexagonal

$$a_1 = a_2; \beta = 120^\circ$$



b. A set of parallel atomic planes spaced  $d$  apart. X-rays are incident at an angle  $\theta$  are reflected at successive layers of atoms. For any arbitrary angle  $\theta$  emergent rays are not in phase. Diffraction (constructive interference) only occurs when the path difference of the ray  $AB + BC = 2d \sin\theta$  is an integer number  $n$  of wavelength  $\lambda$ .



So that:  $2d \sin\theta = n\lambda$ , where  $n$  – order of the diffraction,  $\theta$  – Bragg angles. Bragg reflection occurs only for wavelength  $\lambda \leq 2d$ ,  $\theta = 90^\circ$  in extreme case. Otherwise the above relation cannot be satisfied.

c. **Structure factor** is a scattering amplitude of a single cell. The structure factor is a particularly useful tool in the interpretation of interference patterns obtained in X-ray, electron and neutron diffraction experiments. It is given by

$$S_{\mathbf{G}} = \sum_j f_j \exp(-i\mathbf{G} \cdot \mathbf{r}_j), \text{ (expression was not necessary here)}$$

where  $f_j = \int dV n_j(\boldsymbol{\rho}) \exp(-i\mathbf{G} \cdot \boldsymbol{\rho})$  integrated over all space,  $\boldsymbol{\rho} = \mathbf{r} - \mathbf{r}_j$ .

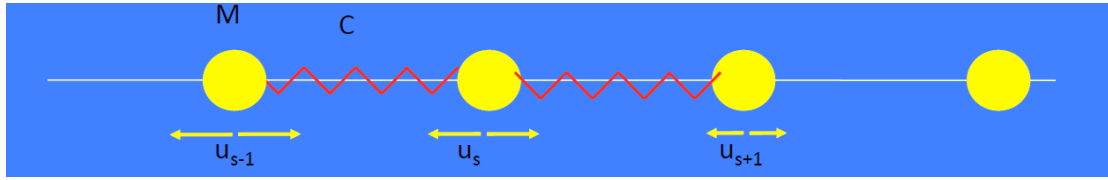
(expression was not necessary here)

$f_j$  is an **atomic form factor** and is a measure of the scattering amplitude of a wave by an isolated atom (or molecule like in case of crystalline fullerene). The atomic form factor depends on atom, bond and angle, thus is different for each basis atom. The common feature of all form factors is that they involve a Fourier transform of a spatial density distribution  $n_j(\boldsymbol{\rho})$  of the scattering object from real space to momentum space.

Additional atoms in the basis can only further reduce crystal symmetry, therefore extra diffraction will appear.

## 2) Phonons and thermal properties (20 points).

Calculate the normal mode of a linear monoatomic chain, where the force constant between nearest-neighbor atoms is  $C$ , the mass of each atom is  $M$ , and the nearest-neighbor separation is  $a$ .



- Show that the dispersion relation is  $\omega(k) = \left(\frac{4C}{M}\right)^{\frac{1}{2}} \left| \sin\left(\frac{ka}{2}\right) \right|$  (start from equation of motion,  $F = Ma$ , consider only the nearest neighbor interactions) (6p).
- Sketch in the dispersion relation in the first Brillouin zone (2p).
- Show that the density of modes for this system is  $D(\omega) = \frac{2N}{\pi} \frac{1}{\sqrt{\omega_m^2 - \omega^2}}$ , where  $N$  is the total number of atoms in the chain, and  $\omega_m$  is the maximum (or Debye) frequency (4p).
- Find the heat capacity of monoatomic chain when  $k \rightarrow 0$  (in this case the dispersion relation reduces to  $\omega = vk$ ) and  $\hbar\omega \gg k_B T$  (4p).
- Qualitatively sketch the differences of dispersion relations between mono- and diatomic chains (1p). Argue from the point of zone folding that if periodicity of the lattice doubles due to either two different masses or two different force constants, how will the  $\omega(k)$  relationship evolve (3p).

### Solution

- Consider 1D chain as shown on the picture:

We assume that the force on ion  $s$  caused by displacement of ion  $s + p$  is proportional to the difference  $u_{s+p} - u_s$  of their displacement. Let's consider only nearest-neighbor interactions with  $p = \pm 1$ . The total force on  $s$  from ions  $s \pm 1$ :

$$F_s = C(u_{s+1} - u_s) + C(u_{s-1} - u_s)$$

The equation of motion of an ion  $s$  is

$$M \frac{d^2 u_s}{dt^2} = C(u_{s+1} + u_{s-1} - 2u_s)$$

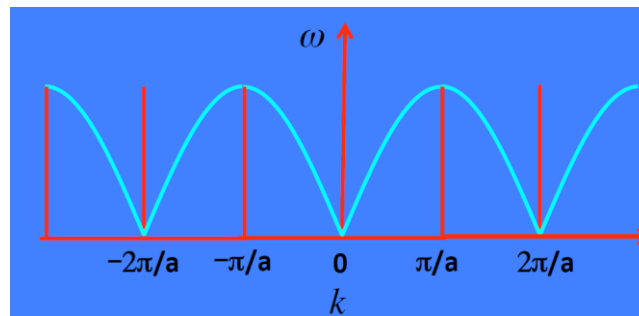
Where  $M$  is the mass of ion,  $C$  is the force constant. Since the equation is the same at each  $s$ , the solution must have the same form at each  $s$  differing only by a phase factor:  $u_s(t) = u \cdot e^{ikas} \cdot e^{-i\omega t}$ .

$$-\omega^2 M = C[e^{ika} + e^{-ika} - 2]$$

By substitution  $2\cos ka = e^{ika} + e^{-ika}$  we can obtain

$$\omega^2 = \frac{2C}{M}(1 - \cos ka) = \frac{4C}{M} \sin^2 \frac{ka}{2} \Rightarrow \omega(k) = \sqrt{\frac{4C}{M}} \left| \sin \frac{ka}{2} \right|$$

b. Then dispersion relation is:



c. if the total length of the chain is  $L$ , then the allowed values of  $k$  are

$$-\frac{\pi}{a} < k = n \frac{2\pi}{L} \leq \frac{\pi}{a}$$

The maximum frequency is then  $\omega_{max} = 2 \left( \frac{C}{M} \right)^{\frac{1}{2}}$

The number of states in the interval  $dk$  is  $D(k)dk = dk \cdot \frac{L}{2\pi}$ , so the number of states in the

interval  $d\omega$  is  $D(\omega)d\omega = 2D(k) \cdot \frac{dk}{d\omega} d\omega$ , which gives the DOS

$$D(\omega) = \frac{2L}{a\pi} \frac{1}{\omega_{max} \left| \cos \frac{ka}{2} \right|} = \frac{2N}{\pi} \cdot \frac{1}{\sqrt{\omega_{max}^2 - \omega^2}}$$

d. In the linear regime (low  $\omega$ ) DOS can be calculated as in c by taking into an account  $\omega = vk$ .  $D(\omega) = \frac{L}{\pi v}$ . Heat capacity is  $C = \frac{dU}{dT}$ , where  $U$  is the total energy of system:

$$U = \int_0^{\omega_{max}} D(\omega) \frac{\hbar\omega}{e^{\frac{\hbar\omega}{k_B T}} - 1} d\omega$$

Taking into an account that  $\hbar\omega \gg kT$  and DOS we can find

$$U = \frac{L}{\pi v} \int_0^{\omega_{max}} \hbar\omega \cdot e^{-\frac{\hbar\omega}{k_B T}} d\omega$$

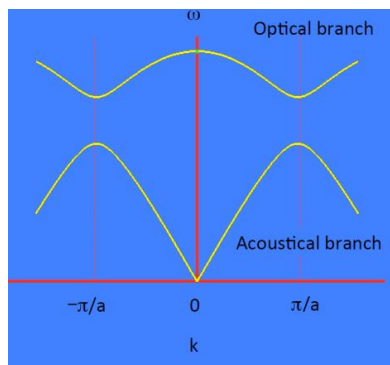
Then heat capacity is

$$C = \frac{L}{\pi v} \int_0^{\omega_{max}} \hbar\omega \cdot \frac{d}{dT} \left( e^{-\frac{\hbar\omega}{k_B T}} \right) d\omega = \frac{L}{\pi v} \int_0^{\omega_{max}} \hbar\omega \cdot \frac{\hbar\omega}{k_B T^2} \cdot e^{-\frac{\hbar\omega}{k_B T}} d\omega$$

By substituting  $x = \frac{\hbar\omega}{k_B T}$  we can estimate

$$C = \frac{Lk_B^2 T}{\pi v \hbar} \int_0^{\infty} x^2 e^{-x} dx = 2 \frac{Lk_B^2 T}{\pi v \hbar}$$

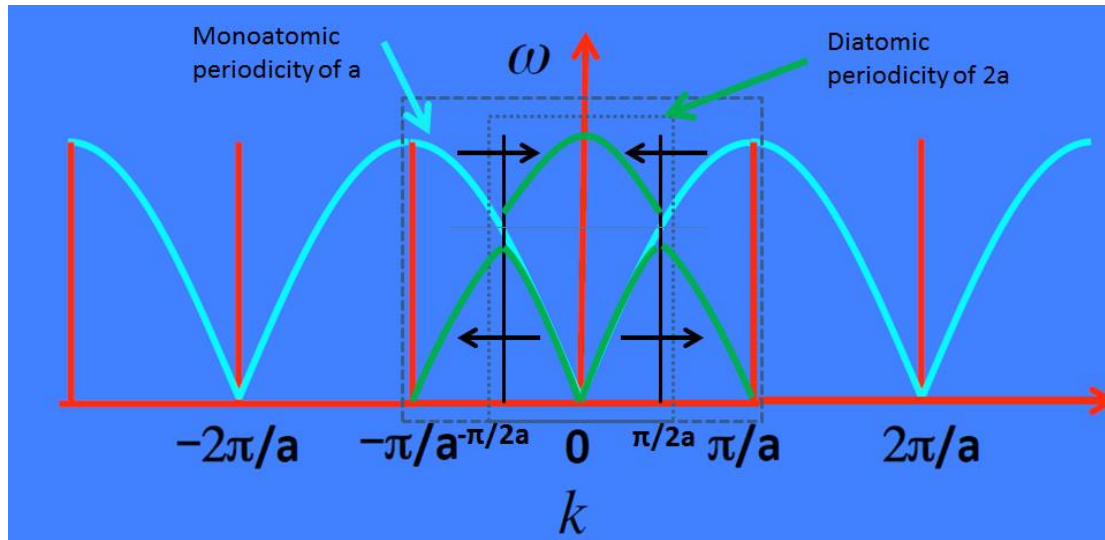
e. In the case of diatomic chain we should expect a formation of optical phonon branch. Dispersion relation would have a gap at zone boundary.



In case of diatomic 1D chain periodicity is doubled. Lattice constant increases from  $a$  to  $2a$ , this leads to reduced size of 1<sup>st</sup> BZ from  $\frac{2\pi}{a}$  to  $\frac{\pi}{a}$ . Part of dispersion relation that belong to

$\left[-\frac{\pi}{a}, -\frac{\pi}{2a}\right]$  and  $\left[\frac{\pi}{2a}, \frac{\pi}{a}\right]$  becomes 2<sup>nd</sup> BZ. By applying zone folding we can obtain optical

branch of dispersion relation of diatomic chain. Gap opened on the new boundary is due to Bragg reflection.



### 3) Free electron and Fermi gas (20 points + 4 bonus points)

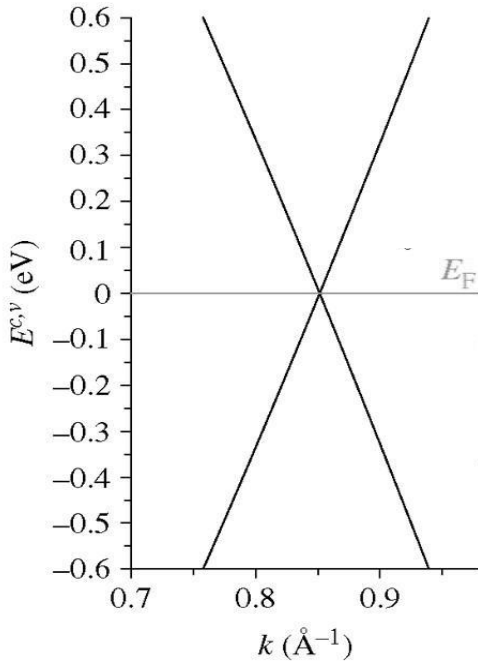
*Graphene* is a monolayer of carbon atoms arranged in a honeycomb lattice exhibiting very special electronic properties. Close to the Fermi level, graphene shows a linear dispersion relations:  $E = \pm \hbar v_F k$ , where  $v_F$  is the Fermi velocity and  $k$  is the wavevector. As shown in the figure below, this dispersion relations has two branches as indicated by  $\pm$  sign. The two branches are degenerate at Fermi level  $E_F$ , (the energy of the Fermi level was chosen as  $E_F = 0$ ).

- Explain what is Fermi surface (2p) Give an example of Fermi surface of free electron gas in 1D, 2D and 3D case (2p).
- Derive the expression for the 2D density of states (DOS)  $D(E)$  per unit area of graphene (5p). Compare the DOS of graphene with that of a 2D free electron gas and explain the origin of the difference in  $D(E)$  (3p).
- Sketch  $D(E)$ ,  $f(E)$  and  $D(E) \cdot f(E)$  as a function of  $E$  for the case of zero temperature (3p) and a finite temperature  $T$  (3p). The Fermi-Dirac distribution is given by  $f(E) = \frac{1}{1 + \exp\left(\frac{E - E_F}{k_B T}\right)}$ .

d. At finite temperature  $T$

- Determine the rough energy range with respect to the Fermi level that accommodates most thermally excited electrons (2p).
- Calculate the number of electrons that are thermally excited in this process.

(Hint:  $\int_0^1 \frac{x}{1+e^x} dx \approx \frac{1}{6}$ ) (4p bonus).



### Solutions

- a. The Fermi surface is the surface of constant energy  $E_F$  in  $\mathbf{k}$  space. The Fermi surface separates the unfilled orbitals from the filled orbitals, at absolute zero. The electrical properties of the metal are determined by the volume and shape of the Fermi surface, because the current is due to changes in the occupancy of states near the Fermi surface. Examples of the Fermi surface of free electron gas in 1D, 2D and 3D can be section, circle and a sphere with radius  $E_F$  correspondingly.
- b.  $E = \pm \hbar v_F k$ ,  $\frac{dE}{dk} = \pm \hbar v_F$ ,  $k = \pm \frac{E}{\hbar v_F}$

For the positive branch,

$$D_+(E) = \frac{1}{A} \left| \frac{dN}{dE} \right| = \frac{1}{A} \left| \frac{dN}{dk} \cdot \frac{dk}{dE} \right| = \frac{1}{A} \left| 2 \cdot \frac{A}{2\pi} \cdot \frac{k}{\hbar v_F} \right| = \frac{|E|}{\pi(\hbar v_F)^2}$$

For the negative branch we can derive the same expression, therefore,

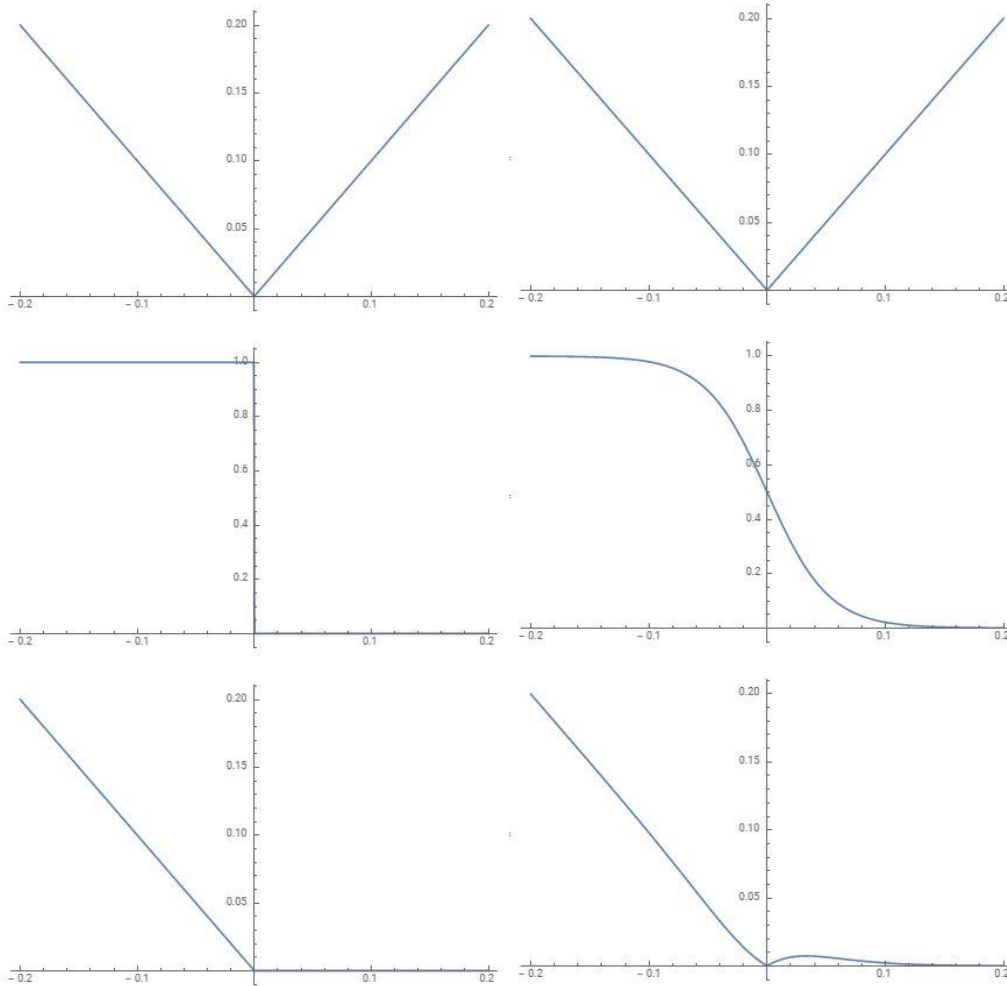
$$D(E) = \frac{2|E|}{\pi(\hbar v_F)^2}$$

As you may notice, although graphene is a 2D system it's DOS is linear as a function of energy. This differs from the case of 2D free electron gas, where DOS is constant in energy. Such a difference originates from linear dispersion relation of

graphene  $E = \pm \hbar v_F k$  and quadratic  $E = \frac{\hbar^2 k^2}{2m^*}$  for the case of free electron gas .



c. From top to bottom you can find  $D(E)$ ,  $f(E)$  and  $D(E) \cdot f(E)$  for electrons. Left and right column describing the cases of  $T = 0$  and  $T > 0$ . Please note that  $E_F = 0$  as indicated on dispersion relation graph of graphene and separates filled and unfilled Dirac cone.



d.

- i. Most thermally excited electrons can be found in a range between  $E_F$  and  $E_F + k_B T$ .
- ii.

$$n = \int_{E_F}^{E_F + k_B T} D(E) \cdot f(E) dE = \frac{2}{\pi(\hbar v_F)^2} \int_{E_F}^{E_F + k_B T} \frac{E}{1 + \exp\left(\frac{E - E_F}{k_B T}\right)} dE$$

use  $x = \frac{E - E_F}{k_B T}$ , then  $E = k_B T x + E_F$ ,  $dE = k_B T dx$ , the integral becomes:

$$\frac{2}{\pi(\hbar v_F)^2} \int_0^1 \frac{k_B T x + E_F}{1 + e^x} k_B T dx$$

$$\begin{aligned}
&= \frac{2k_B T}{\pi(\hbar v_F)^2} \left( k_B T \int_0^1 \frac{x}{1+e^x} dx + \epsilon_F \int_0^1 \frac{1}{1+e^x} dx \right) \\
&\approx \frac{(k_B T)^2}{3\pi(\hbar v_F)^2} + \frac{2k_B T E_F}{\pi(\hbar v_F)^2} \int_0^1 \frac{e^{-x}}{1+e^{-x}} dx \\
&\approx \frac{(k_B T)^2}{3\pi(\hbar v_F)^2} + 0.37 \frac{2k_B T E_F}{\pi(\hbar v_F)^2}
\end{aligned}$$

Since  $E_F = 0$ , only the first term is needed. If you take  $E_F = 0$  from the beginning of the calculation, you should also arrive to the first term. By taking for example room temperature and  $v_F \approx \frac{1}{300}c$ , where  $c$  is a speed of light we can get

$$\begin{aligned}
n &\approx \frac{(1.38 \cdot 10^{-23} \cdot 300)^2}{3 \cdot 3.14 (1.05 \cdot 10^{-34} \cdot 3 \cdot 10^{10} / 300)^2} \approx \frac{(4.14 \cdot 10^{-21})^2}{9.42 \cdot (1.05 \cdot 10^{-26})^2} \\
&\approx 1.65 \cdot 10^{10} \text{ cm}^{-2}
\end{aligned}$$

#### 4) Magnetism and superconductivity (20 points + 3 bonus points)

- a. Consider an ion that has an outer shell of  $3d^3$ . Apply the Hund's rules to find the ground state of this ion (3p). Write your answer in atomic notation (2p).
- b. Considering the spin paramagnetism in metals, what happens to the energy band when metal is subjected to magnetic field  $\mathbf{B}$ ? Draw corresponding energy diagram (3p). Calculate the magnetization  $M$  of such a system ( $N$  electrons) in terms of  $\mu_B$  (3p).
- c. Some materials undergo superconducting transition when cooled below the superconducting transition temperature. Qualitatively describe the differences between a superconductor and a perfect conductor when they are placed in the magnetic field (4 points).
- d. An organic molecule has a triplet ( $S = 1$ ) excited states above a singlet ( $S = 0$ ) ground state with an energy gap  $\Delta$ .
  - i. Draw the energy diagram of this molecule before and after applying magnetic field  $\mathbf{B}$ , and label the energy of each level (2p).
  - ii. Find the expectation value of the magnetic moment  $\langle \mu \rangle$  of this molecule in a magnetic field  $\mathbf{B}$  (3p).
  - iii. Show that for a system with  $N$  of such molecules in a volume  $V$ , the susceptibility at the limit of high temperature is independent of  $\Delta$  (Hint: use the canonical partition function  $Z = \sum_i e^{-\frac{E_i}{k_B T}}$ ) (3p bonus).

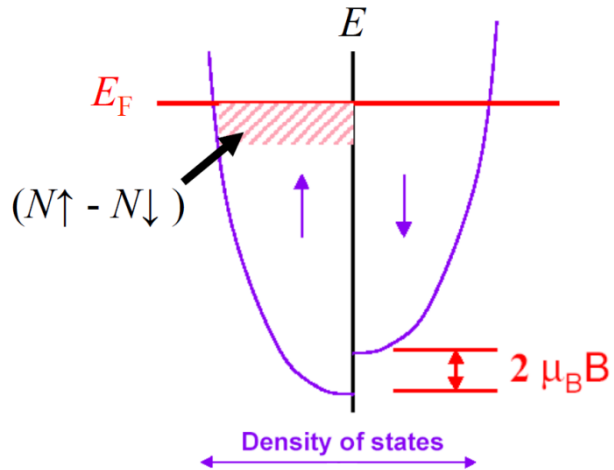
## Solutions

a.  $L_Z: 2, 1, 0, -1, -2, S = 3/2 \rightarrow 2S + 1 = 4, L = 3 \rightarrow F, J = |L - S| = 3/2$  The ground state is  ${}^4F_{3/2}$ .

b. Spin up electrons (parallel to field) are shifted opposite to spin down electrons (antiparallel to  $B$  field), and the energy shift is determined by Zeeman energy  $\Delta E = \pm\mu_B B$ . Such a shift cause a net magnetization of a metal, since the total amount of aligned spins is larger than the amount of antiparallel spins.

$$M = \mu_B(N_\uparrow - N_\downarrow) = \mu_B \frac{1}{2} D(E_F) 2\mu_B B$$

This is a way to measure the density of states.

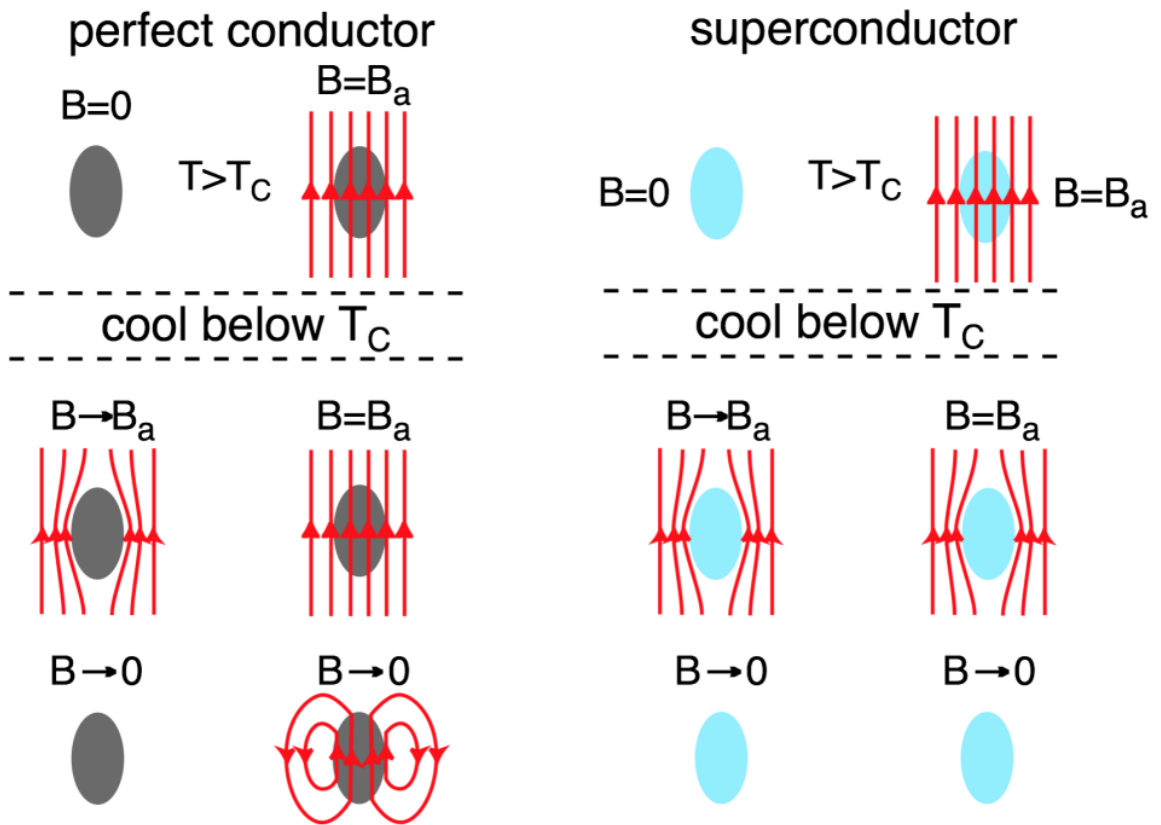


c. Perfect conductor is a material with zero resistance. Suppose this property appears below some critical temperature  $T_C$ . Above  $T_C$  it behaves like a normal metal.

Inside a perfect conductor  $\vec{E} = \vec{0}$ , we have  $\frac{\partial \vec{B}}{\partial t} = 0$ . Magnetic field is "frozen".

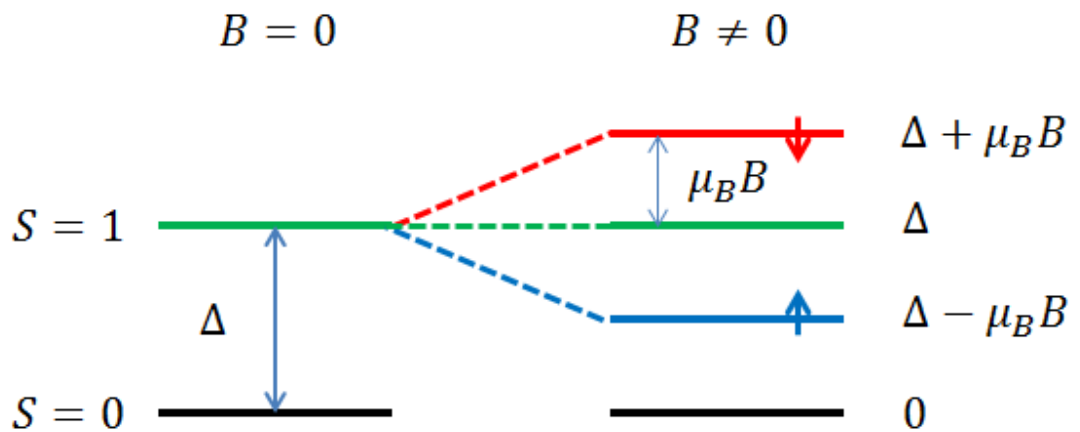
Therefore, if initially there was no magnetic field applied, but it was applied on the later stage (below  $T_C$ ) magnetic field will not penetrate inside. If initially there was magnetic field  $B_a$  applied and cooled below  $T_C$  it will remain to have  $B_a$  inside even after removal of external field (since  $\frac{\partial \vec{B}}{\partial t} = 0$ ).

In contrast to perfect conductor there is a superconductor, which resistance also goes to 0 below critical temperature  $T_C$ . In superconductor Meissner effect takes place when it's subjected to magnetic field. No matter how the sample was cooled, magnetic field is expelled from the interior of superconductor. Only zero resistance cannot explain such a behavior as you see for the case of perfect conductor. The Meissner effect suggest that perfect diamagnetism is an essential property of superconductor.



d.

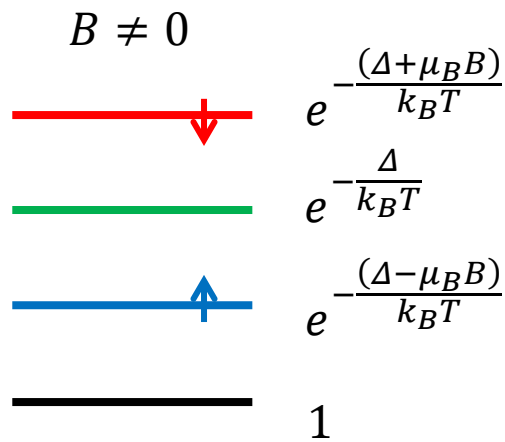
i. Energy diagram of molecule before and after magnetic field is applied.



ii.  $\langle \mu \rangle$  can be found by taking into account population expectations of spin up and spin down states as following

$$\langle \mu \rangle = \mu_B \frac{e^{-\frac{(\Delta - \mu_B B)}{k_B T}} - e^{-\frac{(\Delta + \mu_B B)}{k_B T}}}{Z}$$

$$Z = 1 + e^{-\frac{(\Delta - \mu_B B)}{k_B T}} + e^{-\frac{\Delta}{k_B T}} + e^{-\frac{(\Delta + \mu_B B)}{k_B T}}$$



iii. At high temperatures  $e^{-\frac{\Delta}{k_B T}} \rightarrow 1$  and

$$\langle \mu \rangle \rightarrow \mu_B \cdot \frac{\left(1 + \frac{\mu_B B}{k_B T} - \dots\right) - \left(1 - \frac{\mu_B B}{k_B T} + \dots\right)}{1 + 1 + \left(1 + \frac{\mu_B B}{k_B T} - \dots\right) + \left(1 - \frac{\mu_B B}{k_B T} + \dots\right)} = \frac{\mu_B^2 B}{2k_B T}$$

$$\chi = \frac{N \mu_B^2}{2V k_B T}$$

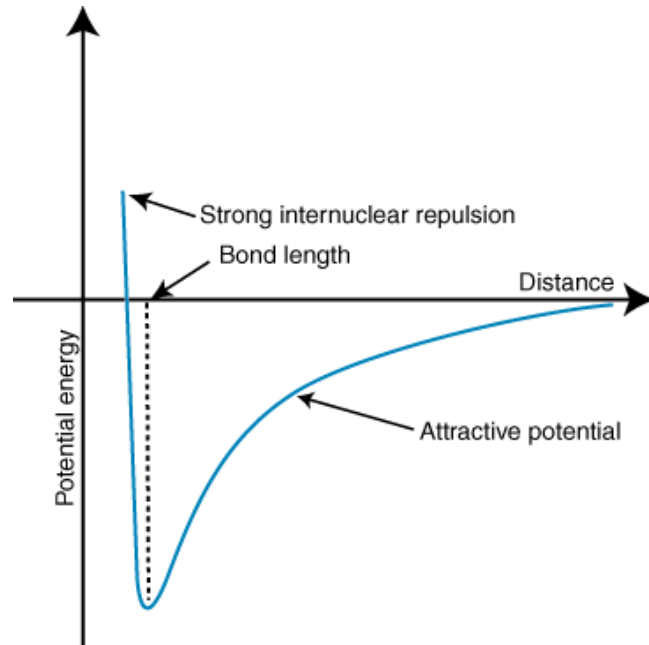
### 5) General concepts (20 points + 3 bonus points)

- Name at least three typical crystalline bindings (3p) and sketch the general interatomic potential as a function of the distance between the two atoms (1p).
- The resistivity of metal is highly dependent on scattering processes. Which scattering processes take place in a metal (2p)? Sketch the corresponding resistivity as a function of temperature and mark the different temperature regions (4p).
- Discuss the concept of effective mass and give a corresponding expression (3p). Explain what it physically means when the effective mass of an electron is negative (2p bonus).
- Sketch the energy diagram of a typical  $p$  and  $n$  doped semiconductors before and after placing them into contact (4p). Sketch the  $I - V$  dependence of a typical  $p-n$  junction when forward or reverse bias is applied across the junction (1p bonus).
- Use the diagram you drew in question **d** to explain how light emitting diode works (3p).

## Solutions:

- a. There are four types of crystalline bindings, van der Waals, ionic, metallic, covalent. Also see Kittel P48. You get the **2 points** for correctly naming at least two of the four.

The interatomic potential-distance relation is shown in the figure, here we are looking at: the general shape of the curve (**0.5 p**), the negative potential minimum at bond length (**0.5 p**), the curvature for the attractive potential part (**0.5 p**), and the limits at 0 and infinite distance (**0.5 p**).



- b. See Kittel P148-P150. The electrical resistivity of most metals is dominated at room temperature (300K) by collisions of the conduction electrons with lattice **phonons (1 p)** and at low temperature (4K) by collision with **impurity (1 p)** atoms and mechanical imperfections in the lattice.

The resistance can be calculated as following,

$$\rho = \frac{m}{ne^2\tau} = \frac{m}{ne^2} \left( \frac{1}{\tau_{phonon}} + \frac{1}{\tau_{impurity}} \right)$$

$$\frac{1}{\tau_{phonon}} \propto n_{phonon}, \quad \frac{1}{\tau_{impurity}} \propto n_{impurity}$$

$$n_{phonon} = \int_0^{\omega_D} D(\omega) f(\omega) d\omega$$

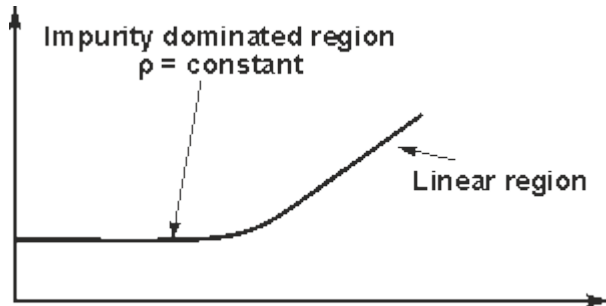
The impurity concentration is usually very small and does not depend on temperature, therefore for most cases it is the phonons that dominate the process. Only at very low temperature when the phonon concentration is extremely low, the impurity scattering dominates.

At high temperature,  $n_{phonon} \propto T$ , so  $\rho \propto T$ ; (**0.5 p**)

At low temperature,  $n_{phonon} \propto T^3$ , so  $\rho \propto T^3$  (**0.5 p**)

At very low temperature,  $n_{\text{phonon}} = \text{const.}$ , therefore  $\rho = \text{const.}$  (1 p)

See the plot below. (2 p)



You don't have to write down any formula for this questions. We only look at if you remember the temperature dependence of phonon concentration, and if you realize the dominance of impurity scattering at very low temperature.

c. The expression of effective mass is, (2 p)

$$m^* = \frac{\hbar^2}{\frac{d^2E}{dk^2}}$$

Or

$$\frac{1}{m^*} = \frac{1}{\hbar^2} \frac{d^2E}{dk^2}$$

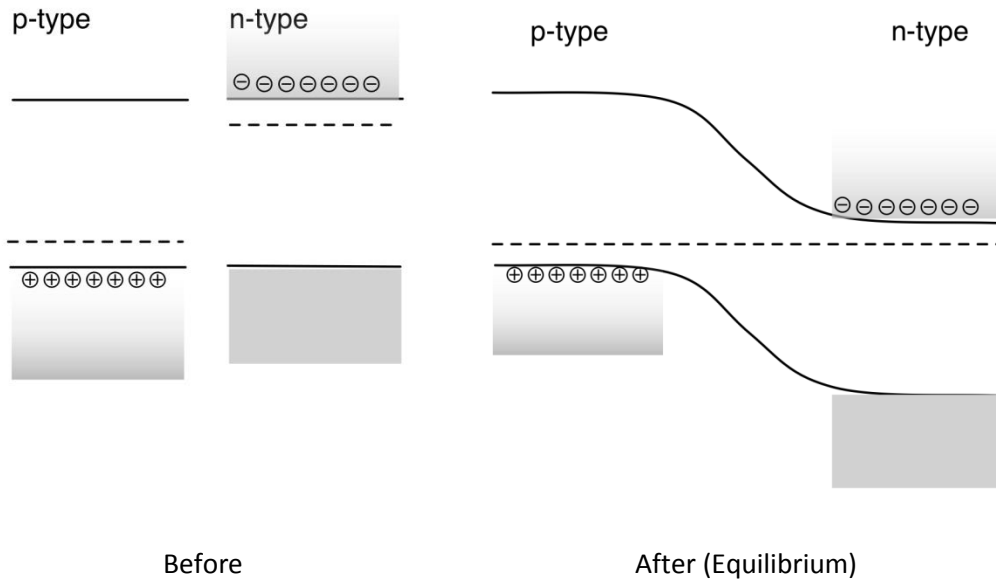
This concept is created for to describe the movement of nearly-free electrons in crystals, as analogous to the mass of a free electron. It shows how and how much an electron in a crystal will react to an external field. The fact that the effective mass is different from a free electron mass is due to the interaction of the electron wave and the lattice. You get 1 point for correctly introduce the concept, it doesn't have to be the same as stated above.

For the concept of negative effective mass, you can explain in the language of momentum transfer between the electrons and the lattice, for this please refer to Kittel P199, and Figure 11 on that page. You can also think in the language of the group velocity of the electron waves. From equation 27 on P198, we see that a negative effective mass means that, when applied an positive external field (force  $F$ ), the group velocity of the wave decelerates. In this process each single electron is still accelerated by the field, however due to the interaction of the periodic lattice, the group velocity appear to be decelerating. You can compare this to a rotating wheel, when the rotation accelerates, it could happen that for an observer, the wheel appears to be decelerating, or even rotating backwards.

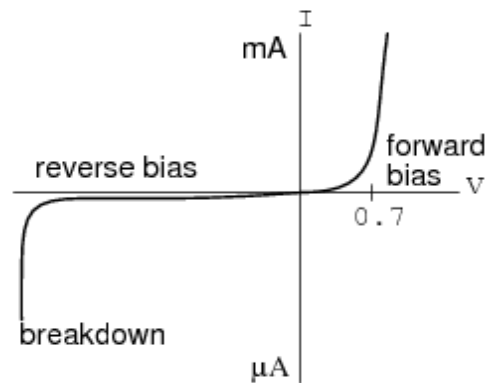
You get the 2 bonus points for using either way to explain the negative effective mass.

d. For this question we are looking at:

Before putting them together, the Fermi level for each case (2 p), after putting them together, the alignment of the Fermi level (1 p) and the band bending (1 p). Figures as shown below:



For a p-n junction the I-V curve is shown below, you get 1 bonus point for showing the shape of the curve. You do not have to show the breakdown at the high reverse bias.



e. See Kittel P511. A light emitting diode works by applying an electric field to a p-n junction to push both electrons and holes to the p-n interface so that they can recombine and emit photons. As shown in the figure below, the p-type side is applied positive bias, effectively lowering its Fermi level. Whereas at the n-type side the Fermi level is raised by applying a negative field. The energy difference between the Fermi levels is now  $eV$ , where  $V$  is the applied voltage. The change of the Fermi levels changes the balance between drift and diffusive electrons and now



electrons and holes can both move across the junction, therefore recombine and emit photons. You get **2 points** for explaining the charge recombination process and **1 point** for mentioning the shift of Fermi levels.

