

Structure of Matter 2

Re-exam August 21, 2012. Room 5419.0013, Kapteynborg, 9.00-12.00.

- ◇ Write your name and student number on each sheet you use.
- ◇ Read the problems carefully and give complete, clear, and readable answers. Illegible answers will be discarded.
- ◇ You are allowed to use your books, lecture slides and your notes. Use of a calculator is allowed.
- ◇ The exam has 4 problems.

Problem 1

Please give concise, but precise answers to the following questions.

- i The optical density of a solution is $OD = 0.25$. What is the fraction of light transmitted through this solution?

(4 pts)

$$T = 10^{-OD} = 0.56, \text{ so } 56 \%$$

- ii Why is it not possible to use a two level system as a laser medium?

(4 pts)

One can not reach population inversion, the probability of stimulated emission and absorption are at best equal. Hence no light amplification can occur.

- iii Calculate the rotational constant \tilde{B} (in cm^{-1}) for a water molecule for rotations around the 2-fold symmetry axis. The HOH bond angle is $\theta = 104.5^\circ$, the HO bond length is $r = 95.4$ pm.

(4 pts)

The distance of each H atom to the rotational axis is $r_H = r \sin(\theta/2) = 95.4 \cdot 10^{-12} \cdot \sin(52.25) = 7.54 \cdot 10^{-11}$ m. The moment of inertia is $I = 2 * m_H \cdot r_H^2 = 1.9 \cdot 10^{-47}$ kg m² (oxygen is on the axis, so does not contribute). The rotational constant is $\tilde{B} = \frac{h}{4\pi c I} = 14.66$ cm⁻¹

- iv Name four types of bonding which may occur in molecules or solids, and give a typical example compound in which this bonding occurs.

(4 pts)

Covalent bonding (H₂), ionic bonding (NaCl), metallic bonding (Fe), van der Waals bonding (graphite).

- v The vibrational frequency of the hydrogen molecule is 4400 cm⁻¹. Give an estimate for the vibrational frequency of the tritium (³H) molecule.

(4 pts)

The reduced mass is 3 times as heavy, so the vibrational frequency will be about $\sqrt{3}$ times lower, *i.e.* $\sim 2540 \text{ cm}^{-1}$.

- vi Do you expect the molecule-ion H_2^+ to have a higher or a lower vibrational frequency than the neutral H_2 molecule? Explain your answer!

(4 pts)

Lower because the bond strength is lower and bond length larger. As a result the second derivative of the binding potential will be smaller.

- vii Describe the process called 'spin state switching' which occurs in certain magnetic molecular materials.

(4 pts)

This is the process in which the electronic configuration of a magnetic ion (for instance a 3d element like Mn or Fe) changes from a high spin to a low spin state (*e.g.* for Fe^{2+} from $S = 2$ to $S = 0$). This can happen when the Hund's coupling energy is comparable to the crystal field strength (For Fe^{2+} the $S = 0$ state is not complying with Hund's rules, the four electrons are all in the lowest d-levels rather than each in a separate orbital all with the same spin direction).

- viii How do the electrons in a Cooper pair in a conventional superconductor overcome the repulsive Coulomb interaction between them?

(4 pts)

Through coupling with phonons. A cartoon like picture is that one electron polarises the lattice, creating a local positively charged area which then attracts the other electron (after the first one is gone, the lattice reacts much more slowly).

Problem 2

- i Draw the structures of $BeCl_2$ and H_2O . Are the structures different? Why? Which of the two molecules is polar?

(4 pts)

$BeCl_2$ is a linear molecule since there are no lone pairs and we have sp hybridization. In H_2O the hybridization is sp^3 since there are 2 lone pairs. The presence of the 2 lone pairs, and in particular their repulsion, favours a non-linear alignment of the 2 hydrogen atoms.

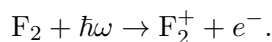
Only H_2O is polar, because of the non-linear geometry.

- ii Consider a molecular crystal composed of molecules AB_2 . Suppose that this crystal has two structural phases: In the phase 1 the molecules are linear while in the phase 2 the B-A-B angle differs from π . What would you expect when comparing the vibrational spectra of the 2 phases?

(4 pts)

The number of vibrational modes differs between the phases. In particular, when AB_2 is linear there is one librational (rotational) mode less. So, when going from phase 2 to phase 1, one of the modes should disappear.

iii In a photoionization experiment an electron is emitted from an F_2 molecule according to



Is there a difference in the equilibrium bond length between F_2 and F_2^+ ?

Do you think that the molecule in the final state would be in an vibrationally excited state or in the vibrational ground state?

What is the difference between this process and the Franck-Condon one? Do you expect fluorescence?

(4 pts)

F_2^+ is formed when F_2 loses an antibonding electron, so we would expect F_2^+ to have a shorter bond than F_2 .

The vertical transition of the photoionization will leave the molecular ion with a stretched bond relative to its equilibrium bond length. A stretched bond means a vibrationally excited molecular ion, hence a stronger transition to a vibrationally excited state than to the vibrational ground state of the cation.

In the Franck-Condon process the transition is between 2 electronic states like F_2 to F_2^* . Here we do not expect fluorescence since there is no excited electron in final state of F_2^+ .

iv The vibrational ground-state wavefunction of a molecule, $\Phi(x)$, is given by

$$\Phi(x) = \begin{cases} 0 & \text{for } x < -a \\ B & \text{for } -a \leq x \leq a \\ 0 & \text{for } x > a \end{cases}$$

Normalize this wavefunction.

What is the Franck-Condon factor for a transition to the vibrational state $\Phi'(x) = \Phi(x - y)$ when $y = a$?

Sketch the Franck-Condon factor for transitions between the vibrational ground states as a function of y .

(5 pts)

First calculate the normalization factor B from $|\Phi|^2 = 1$.

$$1 = \int \Phi^2 dx = 2aB^2 \text{ so that } B = \frac{1}{\sqrt{2a}}$$

$$S(0,0) = \int_0^a \Phi \Phi' dx = \int_0^a B^2 dx = \frac{1}{2}$$

The Franck-Condon factor shows a triangular shape centered around $y = 0$. $S(0,0) = 0$ when $|y| = 2a$. Between $y = -2a$ and $y = 0$ it increases linearly from 0 to 1 at $y = 0$. Between $y = 0$ and $y = 2a$ it decreases linearly from 1 to 0 at $y = 2a$.

Problem 3

The physics of a two dimensional electron gas has shown many surprises in the past, including the integer and fractional quantum hall effects. A realization of such a two dimensional electron gas is found at the interface between GaAs and $\text{Al}_x\text{Ga}_{1-x}$ in a so-called heterostructure. Consider a two dimensional metal as a sheet of dimensions $L \times L$ in the free electron approximation.

- i The wavevector $\vec{k} = (k_x, k_y)$ will be quantized. Give an expression for the allowed wavevectors.

(3 pts)

Assume periodic boundary conditions so that $e^{ik_x x} = e^{ik_x(x+L)}$. Then $e^{ik_x L} \equiv 1$ or $k_x = n_x \frac{2\pi}{L}$ with $n_x = 0, 1, 2, \dots$. Similarly for k_y : $k_y = n_y \frac{2\pi}{L}$ with $n_y = 0, 1, 2, \dots$

- ii Make a drawing of \vec{k} -space, indicating the lattice of allowed wavevectors. Draw also the Fermi-level in this diagram, and indicate which part of the states in \vec{k} -space are occupied at $T = 0$ K.

(3 pts)

Square lattice of allowed k-points spaced in k_x and k_y direction by $2\pi/L$. The Fermi-level is a circle centred around zero, all states within the circle are occupied at zero temperature, those outside are not occupied.

- iii The Fermi wavevector, k_F , is the wavevector of the highest (in energy) occupied state. Assume that the electron density is n (unit cm^{-2}). Derive an equation for the Fermi vector as a function of the electron density.

(3 pts)

Number of states within a disk of radius k :

$$N(k) = 2 \frac{\text{surface of the disk}}{\text{area per k-state}} = 2 \frac{\pi k^2}{\left(\frac{2\pi}{L}\right)^2} = L^2 \frac{k^2}{2\pi}$$

where the factor 2 accounts for the spin degeneracy. So $n = N(k)/L^2 = \frac{k^2}{2\pi}$, or $k_F = \sqrt{2\pi n}$.

- iv A typical charge density in a GaAs/AlGaAs heterostructure is 10^{11} electrons/ cm^2 . What is the value of the Fermi energy for this density (The effective mass of the electrons can be taken as the free electron mass.)?

Can one approximate the behaviour of the electron gas in this heterostructure using the ground state properties?

(4 pts)

$k_F = \sqrt{2\pi 10^{11}} \approx 7.9 \cdot 10^7 \text{ m}^{-1}$. $E_F = \frac{\hbar^2 k_F^2}{2m} \approx 3.8 \cdot 10^{-23} \text{ J}$. This corresponds to a temperature $T_F = \frac{E_F}{k_B} \approx 2.8 \text{ K}$, hence a ground state approximation is not appropriate for the room temperature behaviour.

v Derive an equation for the density of states as a function of energy E per unit area.

(4 pts)

$$D(k) = \frac{1}{L^2} \frac{dN(k)}{dk} = \frac{k}{\pi},$$

using $E = \frac{\hbar^2 k^2}{2m}$ one finds

$$D(E) = \frac{dN}{dk} \left(\frac{dE}{dk} \right)^{-1} = \frac{k}{\pi} \frac{m}{\hbar^2 k} = \frac{m}{\pi \hbar^2}.$$

vi Derive an equation for the heat capacity of this two dimensional electron gas in the limit $T \gg E_F/k_b$ (k_b is the Boltzmann constant). *hint:* $\int_0^\infty \frac{x}{e^x+1} dx = \frac{\pi^2}{12}$

(4 pts)

In this case the Fermi-Dirac distribution can be approximated as

$$f(E, T) = \frac{1}{e^{\frac{E}{k_b T}} + 1}$$

The total energy of the gas is $U = \int_0^\infty E \cdot f(E) \cdot D(E) dE$:

$$U = \int_0^\infty E \cdot \frac{1}{e^{\frac{E}{k_b T}} + 1} \cdot \frac{m}{\pi \hbar^2} dE = \frac{m}{\pi \hbar^2} (k_b T)^2 \int_0^\infty \frac{\frac{E}{k_b T}}{e^{\frac{E}{k_b T}} + 1} d\frac{E}{k_b T} = \frac{\pi}{12} \frac{m}{\hbar^2} (k_b T)^2.$$

The heat capacity is then

$$C_v = \frac{dU}{dT} = \frac{\pi}{6} \frac{m}{\hbar^2} k_b^2 T.$$

Problem 4

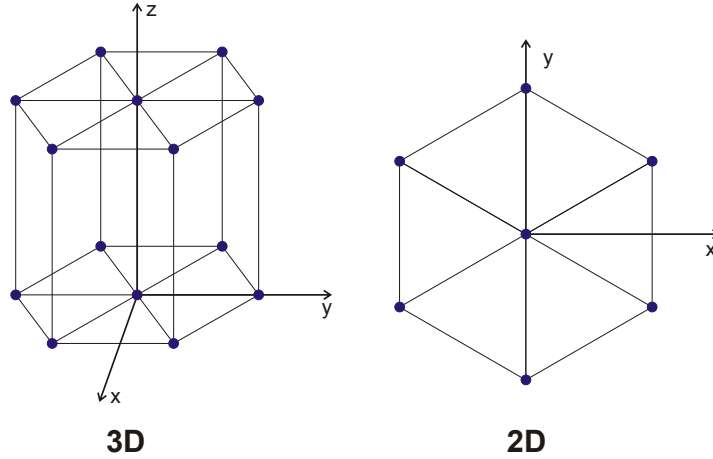
The figure below shows the real space lattices of a hexagonal crystal in two and three dimensions. In three dimensions the primitive cell is spanned by the following three vectors:

$$\vec{a}_1 = \frac{\sqrt{3}}{2} a \cdot \vec{e}_x + \frac{a}{2} \cdot \vec{e}_y,$$

$$\vec{a}_2 = -\frac{\sqrt{3}}{2} a \cdot \vec{e}_x + \frac{a}{2} \cdot \vec{e}_y,$$

$$\vec{a}_3 = c \cdot \vec{e}_z,$$

with $\vec{e}_x = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}$, $\vec{e}_y = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}$, and $\vec{e}_z = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$; and $\|\vec{a}_1\| = \|\vec{a}_2\| = a$ and $\|\vec{a}_3\| = c$ as lattices constants.



Schematic drawing of the hexagonal lattice in 3D (left) and 2D (right).

- i Show that the volume of the primitive unit cell in the three dimensional structure is $(\frac{\sqrt{3}}{2})a^2 \cdot c$. (4 pts)

The volume of the primitive cell is:

$$V = (\vec{a}_1 \times \vec{a}_2) \cdot \vec{a}_3 = \left(\frac{\sqrt{3}}{2}a \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \times -\frac{\sqrt{3}}{2}a \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \right) \cdot c \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} = \frac{\sqrt{3}}{2}a^2 \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \cdot c \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} = \frac{\sqrt{3}}{2}a^2 \cdot c.$$

- ii Make a drawing of the Wigner-Seitz-cell for the two dimensional case in the x-y-plane. Describe your procedure!

(4 pts)

The cell may be chosen by first picking a lattice point, e.g. the one at the origin of the x-y-plane. Then, lines are drawn to all 6 adjacent lattice points. At the midpoint of each line, another line is drawn normal to each of the first set of lines. The result is again a hexagon.

- iii Prove that the reciprocal lattice is also a hexagonal lattice with vectors $\vec{b}_1 = \frac{2\pi}{\sqrt{3}a} \cdot \vec{e}_x + \frac{2\pi}{a} \cdot \vec{e}_y$, $\vec{b}_2 = -\frac{2\pi}{\sqrt{3}a} \cdot \vec{e}_x + \frac{2\pi}{a} \cdot \vec{e}_y$, and $\vec{b}_3 = \frac{2\pi}{c} \cdot \vec{e}_z$.

(4 pts)

The vectors of the reciprocal lattice are:

$$\begin{aligned} \vec{b}_1 &= \frac{2\pi}{V}(\vec{a}_2 \times \vec{a}_3) = \frac{2\pi}{V} \left(-\frac{\sqrt{3}}{2}a \cdot \vec{e}_x + \frac{a}{2} \cdot \vec{e}_y \right) \times c \cdot \vec{e}_z = \frac{4\pi}{\sqrt{3}a} \left(\frac{1}{2} \cdot \vec{e}_x + \frac{\sqrt{3}}{2} \cdot \vec{e}_y \right) \\ \vec{b}_2 &= \frac{2\pi}{V}(\vec{a}_3 \times \vec{a}_1) = \frac{2\pi}{V} \times c \cdot \vec{e}_z \times \left(\frac{\sqrt{3}}{2}a \cdot \vec{e}_x + \frac{a}{2} \cdot \vec{e}_y \right) = \frac{4\pi}{\sqrt{3}a} \left(-\frac{1}{2} \cdot \vec{e}_x + \frac{\sqrt{3}}{2} \cdot \vec{e}_y \right) \\ \vec{b}_3 &= \frac{2\pi}{V}(\vec{a}_1 \times \vec{a}_2) = \frac{2\pi}{V} \left(\frac{\sqrt{3}}{2}a \cdot \vec{e}_x + \frac{a}{2} \cdot \vec{e}_y \right) \times \left(-\frac{\sqrt{3}}{2}a \cdot \vec{e}_x + \frac{a}{2} \cdot \vec{e}_y \right) = \frac{2\pi}{c} \cdot \vec{e}_z \end{aligned}$$

One famous example of a hexagonal lattice is the semiconductor GaN, which is often used as material for light-emitting diodes (LEDs) or lasers.

iv How are energy bands in metals, semiconductors and insulators formed?

(4 pts)

The electrons of a single isolated atom occupy atomic orbitals, which form a discrete set of energy levels. If several atoms are brought together into a molecule, their atomic orbitals split due to interactions into separate molecular orbitals each with a different energy. This produces a number of molecular orbitals proportional to the number of valence electrons. When a large number of atoms are brought together to form a solid, the number of orbitals becomes exceedingly large. Consequently, the difference in energy between them becomes very small. Thus, in solids the levels form continuous bands of energy rather than the discrete energy levels of the atoms in isolation. However, due to the periodicity of the crystal potential, some intervals of energy contain no orbitals leading to the formation band gaps.

v Describe in short words the terms direct and indirect semiconductors! Why do you need a direct semiconductor for the use in LEDs?

(4 pts)

In direct semiconductors the maximum of the valence band and the minimum of the conduction band have the same momentum (k-value). A direct transition of charge carriers between the two bands is possible. In indirect semiconductors the maximum of the valence band and the minimum of the conduction band do not have the same k-value: a direct transition is not possible. For optical transitions these materials need the adsorption or emission of an additional phonon to overcome the momentum difference. The involvement of the phonon makes this process much less likely to occur in a given span of time, which is why radiative recombination is far slower in indirect band gap materials than direct band gap ones. To obtain efficient light generation in a LED one needs a direct transition.

A list of some fundamental constants, definitions and relations

Constant	Symbol	Approximate Value
Speed of light in vacuum	c	3.00×10^8 m/s
Permeability of vacuum	μ_0	12.6×10^{-7} H/m
Permittivity of vacuum	ϵ_0	8.85×10^{-12} F/m
Magnetic flux quantum	$\phi_0 = \frac{h}{2e}$	2.07×10^{-15} Wb
Electron charge	e	1.602176×10^{-19} C
Electron mass	m_e	9.11×10^{-31} kg
Proton mass	m_p	1.673×10^{-27} kg
Neutron mass	m_n	1.675×10^{-27} kg
Proton-electron mass ratio	$\frac{m_p}{m_e}$	1836
Boltzman constant	k_b	$1.3806503 \times 10^{-23}$ m ² kg s ⁻² K ⁻¹
Boltzman constant [cm ⁻¹]	k_b	0.6950356 cm ⁻¹
planck constant/ 2π	\hbar	1.05457×10^{-34} J s
atomic mass unit (a.m.u.)	amu	$1.66053886 \times 10^{-27}$ kg
electron volt to Joule	1 eV	1.602176×10^{-19} J
electron volt to wavenumber	1 eV	8065.395 cm ⁻¹
wavenumber to frequency	1 cm ⁻¹	29.98 GHz