

Structure of Matter 2

Exam July 9th, 2013. 5412.0025, 14.00-17.00.

- o Write your name and student number on each sheet you use.
- o Read the problems carefully and give **complete, clear, and readable answers**. Illegible answers will be discarded.
- o The exam has problems. The max. points per question are indicated.
- o Answers may be given in Dutch or English.

Problem 1

A molecular orbital can accommodate a maximum of _____ electron(s).

a. one b. two c. four d. six e. twelve

(0.5 pts)

How many s atomic orbitals and p atomic orbital(s) must be mixed to produce sp^3 hybrid orbitals?

(1 pt)

Explain what electronegativity is and how this property determines which bond is formed between atoms. Discuss one example.

(2.5 pts)

Solution

- A molecular orbital contains maximum 2 electrons, so b is the correct answer.
- 1 s orbital and 3 p orbitals
- Electronegativity is a measure of the tendency of an atom in a molecule or aggregate of atoms to attract electrons. (1 point)
Ionic bonds form between atoms of electronegativity difference of 2 or greater. (1 pt) Ex. Fluorine, which have a strong attraction for electrons are said to be highly electronegative. Alkali atoms, such as caesium, which have little electron-attracting ability have low electronegativities. Caesium fluoride CsF has an ionic bond. (0.5 pts) (others obviously also give you points if correct)

Problem 2

i) Which of the following molecules may show a pure rotational microwave spectrum and why: (a) N_2 , (b) LiF, (c) CH_4 , (d) CH_3Cl , (e) CH_2Cl_2 ? (2 pts)

ii) Calculate the wavenumber of the $J = 4 \leftarrow 3$ transition in the pure rotational spectrum of $^{14}N^{16}O$. The equilibrium bond length is 115 pm, $\tilde{F}(J) = \tilde{B}J(J + 1)$, $hc\tilde{B} = \frac{\hbar^2}{2I}$ (3 pts)

Solution

i) Polar molecules show a pure rotational absorption spectrum. Therefore the polar molecules need to be selected based on their well-known structures. The polar molecules are: (b) LiF, (d) CH_3Cl , (e) CH_2Cl_2 .

ii) Frequency should be $2(J + 1)B$, or $8B(J+1)$, where B is the rotational constant. [1 pt]

$$I = \mu r_o^2 \\ = (14.003 \times 15.995) / (14.003 + 15.995) \times (1.66054 \times 10^{-27}) \times (115 \times 10^{-12})^2$$

$$\begin{aligned}
&= 1.6397 \times 10^{-46} \text{ kgm}^2 \\
B &= h / (8\pi^2 I c) \\
&= 6.626 \times 10^{-34} / (8\pi^2 \times 1.6397 \times 10^{-46} \times 3 \times 10^{10}) \\
&= 6.626 \times 10^{-34} / 3.88 \times 10^{-34} = 1.706 \text{ cm}^{-1} \\
\nu_3 \rightarrow 4 &= 2(1.706)(3+1) \\
&= 13.65 \text{ cm}^{-1}
\end{aligned}$$

Problem 3

The transmission through a 2 mm cell of a solution containing 100 molecules per μm^3 is 28%. Calculate the molar absorption coefficient. What will the transmission be through a 4.5 mm cell?

(3 pts)

Solution

The Beer-Lambert law is:

$$\log T = -\epsilon [J] l \quad \text{so} \quad \epsilon = \frac{-1}{[J] l} \log T$$

The molar concentration corresponding to 100 molecule per cubic μm is:

$$\frac{n}{V} = \frac{100}{6.022 \cdot 10^{23} \text{ mol}^{-1}} * \frac{(10^6 \mu\text{m} \cdot \text{m}^{-1})^3}{(1.0 \mu\text{m}^3)(10 \text{ dm} \cdot \text{m}^{-1})^3} = 1.7 \cdot 10^{-7} \text{ mol} / \text{dm}^3.$$

$$\epsilon = \frac{-1}{(1.7 \cdot 10^{-7} \text{ mol} \cdot \text{dm}^{-3}) * 0.2 \text{ cm}} \log 0.28 = 1.6 \cdot 10^7 \text{ mol}^{-1} \cdot \text{dm}^3 \cdot \text{cm}^{-1}.$$

Now that we have ϵ , we can calculate T of this solution with any size of the cell:

$$T = 10^{-\epsilon [J] l} = 10^{-1.6 \cdot 10^7 \text{ mol}^{-1} \text{ dm}^3 \cdot 0.45 \cdot 1.7 \cdot 10^{-7} \text{ mol} \text{ dm}^{-3}} = 6\%.$$

Problem 4

- i) In solids we distinguish bonds by where the electrons go with respect to their host atoms – please
- name the 4 types of bonds that can be formed,
 - say where the electrons go with respect to their host atoms for each type of bonding
 - which place each type of bonding has on a scale of strength (1 weakest, 4 strongest)
 - give an example for each type.

(4 pts)

ii) The potential energy for a pair of inert gas atoms separated by a distance r may be written as the Lennard-Jones potential:

$$U_{\text{pair}}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

Explain the physical origin of these two terms.

(2 pts)

Solution:

- i)
- 1 - Van der Waals bonding; electrons localised around atoms; example: rare gas solid
 - 2 - Covalent bonding; electrons shared with neighbouring atoms; example: diamond
 - 3 - Metallic bonding; electrons free to move throughout the crystal; example: copper
 - 4 - Ionic bonding; electrons transferred to adjacent atom or received from adjacent atom; example: NaCl.
- ii) The term proportional to r^{-12} corresponds to the repulsive energy term arising from the Pauli principle, the term $\propto r^{-6}$ is instead the Van der Waals attractive term which stems from the interaction between the instantaneous dipole in one atom and induced dipole in its neighbour.

Problem 5

- i) What defines a perfect solid? (List at least four of the properties of a perfect solid.) (2 pts)
- ii) You observe concentric rings consisting of spots in a diffraction pattern. What can you conclude from this regarding the structure and the orientation of your sample. (2 pts)
- iii) For the {1 2 3} plane, calculate the absolute value of scattering vector Δk for given lattice parameters, $a = 0.98 \text{ nm}$; $b = 0.8 \text{ nm}$ and $c = 0.67 \text{ nm}$ with Laue equations. How does the k vector change if you double the wavelength of your x-rays? (2 pts)

Solution: i) A perfect solid is an infinite single crystal (*i.e.* it possesses no external surfaces, no grain boundaries) with no holes (no internal surfaces). It has perfect purity or perfect stoichiometry. Every atom must occupy a lattice site – no atom is out of place, there are no empty lattice sites (no missing atoms). The perfect solid is at a temperature of absolute zero (no excitations). [0.5 pts for each property]

The material is polycrystalline. [1 pt] In fact, when the X-ray beam passes through a polycrystal it will produce a diffraction pattern equivalent to that produced by a beam passing through series of single crystals of various orientations. The diffraction pattern will therefore look like a superposition of single crystal spot patterns: a series of concentric rings resulting from many spots very close together at various rotations around the centre beam spot. From the diffraction rings one can also determine the type of crystal structure and the "lattice parameter".

One cannot determine the orientation of a polycrystal, since there is no single orientation and flipping or turning the polycrystal will yield the same ring pattern. [1 pt]

iii) For the (1 2 3) plane, calculate the absolute value of scattering vector Δk for given lattice parameters, $a = 0.98 \text{ nm}$; $b = 0.8 \text{ nm}$ and $c = 0.67 \text{ nm}$ with Laue equations.

$$d_{hkl} = \frac{2\pi}{|\vec{G}_{hkl}|} \quad \Delta\vec{k} = \vec{G}_{hkl}$$

$$|\Delta\vec{k}| = |\vec{G}_{hkl}| = 2\pi \sqrt{\left(\frac{h}{a}\right)^2 + \left(\frac{k}{b}\right)^2 + \left(\frac{l}{c}\right)^2} = 32.8 \text{ nm}^{-1} \quad [1 \text{ pt}]$$

$$k = \frac{2\pi}{\lambda} \quad \text{Doubling the wavelength will halve the } k \text{ vector.} \quad [1 \text{ pt}]$$

Problem 6

Gallium arsenide has a band gap of 1.40 eV. At what wavelength does it start to absorb? (Remember that 1 eV = 1.6019x10⁻¹² erg). (1 pt)

Solution: The band gap determines threshold of continuous optical absorption at ν_{gap} , therefore since $h\nu_{gap} = 1.40 \text{ eV} \times 1.6019 \times 10^{-12} \text{ erg} = 2.24 \times 10^{-12} \text{ erg}$, and since $h = 6.6254 \times 10^{-27} \text{ erg s}$, $\nu_{gap} = 2.24 \times 10^{-12} \text{ erg} / 6.6254 \times 10^{-27} \text{ erg s} = 0.3381 \times 10^{15} \text{ s}^{-1}$;

$$\nu_{gap} = c/\lambda \Rightarrow \lambda = c/\nu_{gap} = 3.0 \times 10^8 \text{ m s}^{-1} / 0.3381 \times 10^{15} \text{ s}^{-1} = 8.87 \times 10^{-7} \text{ m} = 887 \text{ nm}.$$

Problem 7

(a) What is the physical meaning of the first Brillouin zone in relation to the phonon dispersion relation? (1 pt)

(b) The dispersion relation for longitudinal phonons in a 2D lattice is given by:

$$\omega(q) = \sqrt{\frac{4C}{M}} \left| \sin\left(\frac{qa}{2}\right) \right|$$

What is the sound velocity? (2 pts)

(c) Write down the conservation laws for collision between neutron and phonon. What is an Umklapp process? (2 pts)

Solution: (a) The excitations are labelled by a wavevector q and are periodic functions of q in reciprocal space. All the excitations are counted if one considers only q inside the Brillouin zone (BZ). The excitations for q outside the BZ are identical to those inside and are not independent excitations.

(b) The group velocity is the slope of ω vs q : $v_q = \frac{d\omega}{dq}$ (0.5pts)

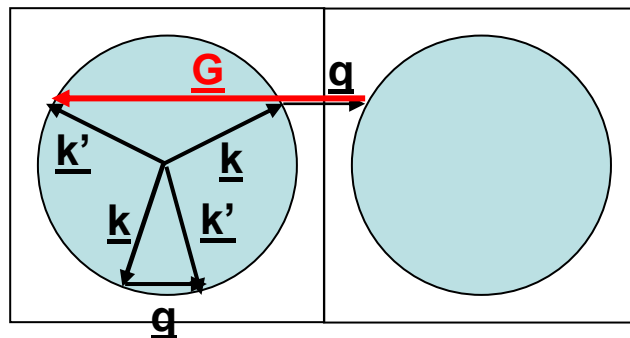
$$\omega(q) = \sqrt{\frac{4C}{M}} \left| \sin\left(\frac{qa}{2}\right) \right|$$

$$v_q = \sqrt{\frac{Ca^2}{M}} \left| \cos\left(\frac{qa}{2}\right) \right|$$

For $q \rightarrow 0$ $v_q = \sqrt{\frac{Ca^2}{m}}$ (1 pt) (0.5pts)

If you defined the group velocity correctly as the derivative and you considered an approximation of the cos for $q \rightarrow 0$ you get the full points.

(c) Both energy and momentum have to be conserved: if $\hbar\omega$ and \mathbf{k} are the energy and the momentum of the neutron before collision and $\hbar\omega'$ and \mathbf{k}' those after collision and $\hbar\Omega$ and \mathbf{q} are the energy and momentum of the phonon, for energy conservation $\hbar\omega' = \hbar\omega \pm \hbar\Omega$ for momentum conservation $\mathbf{k}' = \mathbf{k} \pm \mathbf{q}$. An Umklapp process additionally involves a reciprocal lattice vector \mathbf{G} : Normal collision: the wavevector of the neutron after collision is $\mathbf{k}' = \mathbf{k} + \mathbf{q}$ (bottom of drawing) Umklapp: Happens when the sum of the wave vectors of the incoming neutron and the phonon lies outside the Brillouin zone: a reciprocal lattice vector intervenes at well, with energy and wave vector conservation, resulting in backscattering of the neutron: $\mathbf{k}' = \mathbf{k} + \mathbf{q} + \mathbf{G}$ (top of drawing) – of course if you explained this only for scattering between phonons as seen in the lecture, the point is given also.



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/2 π	\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

Periodic Table of Elements

For elements with no stable isotopes, the mass number of the isotope with the longest half-life is in parentheses.

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