

Structure of Matter 2

Exam June 21st, 2013. Arletta Jacobshal 02 , 14.00-17.00.

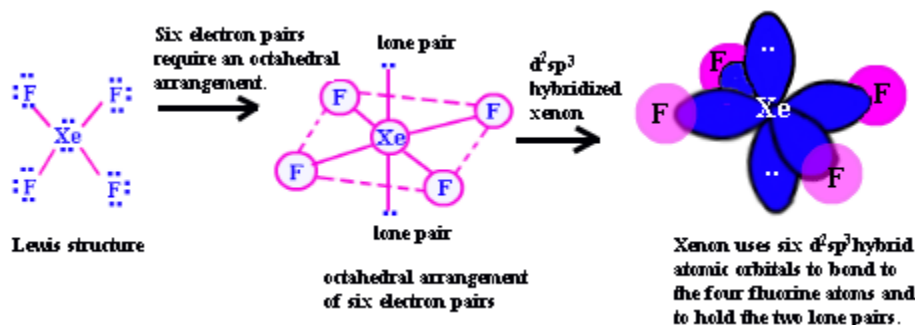
- o Write your name and student number on each sheet you use.
- o Read the problems carefully and give **complete, clear, and readable answers**. Illegible answers will be discarded.
- o The exam has 8 problems. The max. points per question are indicated.
- o Answers may be given in Dutch or English.

Problem 1

- i) According to valence bond theory, which orbitals on bromine atoms overlap in the formation of the bond in Br₂? (1 pt)
- ii) What is the hybridization of the central atom of the XeF₄ molecule? How many lone pairs of electrons does the molecule have? (2 pts)
- iii) Please complete the following sentence with the possible answers below:
A typical double bond
- a. is stronger and shorter than a single bond
 - b. consists of one σ bond and one π bond
 - c. imparts rigidity to a molecule
 - d. consists of two shared electron pairs
 - e. All of the above answers are correct. (1 pt)

Solution

- . The 4p orbitals on bromine atoms overlap in the formation of the bond in Br₂
- . the hybridization of the central atom of the XeF₄ molecule is sp³d²; the molecule has 2 lone pairs



Of the 5s and 5p electrons in the outermost orbit of Xe, two of the 5p orbital electrons get excited to the vacant 5 d orbital resulting in 4 unpaired hybridized electrons, 2 in 5p and 2 in 5d orbitals.

- . e. All of the above answers concerning a typical double bond are correct.

Problem 2

The RbH molecule can be described quite well by a Morse oscillator with potential $V = hcD_e\{1 - e^{-a(R-R_e)}\}^2$ where $hcD_e = 3.79 \text{ eV}$. Solving the Schrödinger equation for the Morse potential yields for the permitted energy levels:

$$G(v) = \left(v + \frac{1}{2}\right)\tilde{\nu} - \left(v + \frac{1}{2}\right)^2 \chi_e \tilde{\nu}$$

- i) For Rb¹H, $\tilde{\nu} = 936.8 \text{ cm}^{-1}$, and $\chi_e \tilde{\nu} = 14.16 \text{ cm}^{-1}$
Calculate the dissociation energy hcD_0 of the Rb-¹H molecule. (2 pts)
- ii) Calculate the dissociation energy if we replace the ¹H atom with ²H (deuterium). (3 pts)

Solution:

i)

$$\begin{aligned} hcD_0 &= hcD_e - G(0) \\ &= hcD_e - \frac{1}{2}\tilde{\nu} - \frac{1}{4}\chi_e \tilde{\nu} \\ &= 3.79 - \frac{1}{2} * 936.8 * 1.239 \cdot 10^{-4} - \frac{1}{4} 14.16 * 1.239 \cdot 10^{-4} = 3.73 \text{ eV} \end{aligned}$$

[1 pt for the right equation, 1 pt for the correct result]

- ii) if we replace the H atom with D, the effective mass increased by a factor $\frac{85.47+1}{85.47+2} = 1.98$.

Since the wavenumber scales with $1/\sqrt{m_{\text{eff}}}$, we can find the new wavenumbers $\tilde{\nu} = 936.8/\sqrt{1.98} = 665.75 \text{ cm}^{-1}$, and $\chi_e \tilde{\nu} = 14.16/\sqrt{1.98} = 10.06 \text{ cm}^{-1}$. So again we have

$$\begin{aligned} hcD_0 &= hcD_e - G(0) \\ &= hcD_e - \frac{1}{2}\tilde{\nu} - \frac{1}{4}\chi_e \tilde{\nu} \\ &= 3.79 - \frac{1}{2} * 665.75 * 1.239 \cdot 10^{-4} - \frac{1}{4} 10.06 * 1.239 \cdot 10^{-4} = 3.75 \text{ eV} \end{aligned}$$

[1 pt for the right effective mass, also given if the atomic mass for Rb was only approximately correct, 1 pt for knowing that the wavenumber scales with $1/\sqrt{m_{\text{eff}}}$, 1 pt for the correct result]

Problem 3

What properties does the molecule have to satisfy for

- i) pure rotational transitions;
- ii) rotational Raman transitions;
- iii) infrared absorption activity?
- iv) Give the exclusion rule for vibrational modes.

(1 pt each, total 4 pts)

Solution

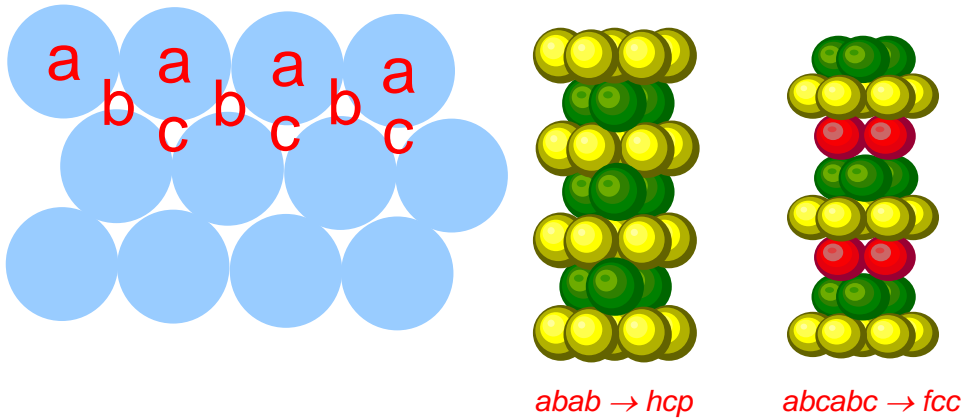
- i) For pure rotation transitions, the molecule must be polar.
- ii) For Rotational Raman transitions, the molecule must be anisotropically polarizable.
- iii) For a molecule to be Infrared active the motion corresponding to a normal mode should be accompanied by a change of dipole moment
- iv) If the molecule has a centre of symmetry, then no modes can be both infrared and Raman active.

Problem 4

- i) Explain the difference between the hexagonal close-packed and the face-centred cubic structure. (2 pts)
- ii) Name 2 examples each for
 - a hexagonal close-packed structure
 - diamond structure (2 pt)
- iii) Define the first and the second Brillouin zone of a square lattice (2D); include drawing. (2 pt)

Solution:

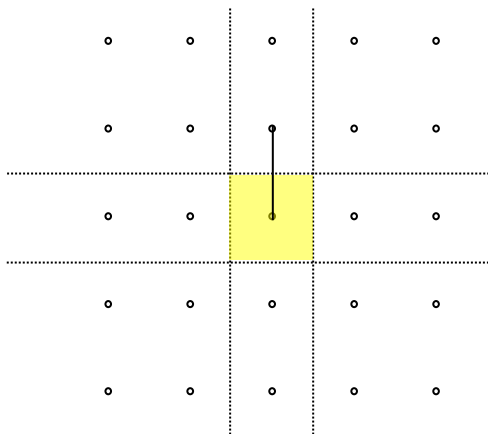
i) Both are close packed lattices formed by stacking atoms on hexagonal basal plane:



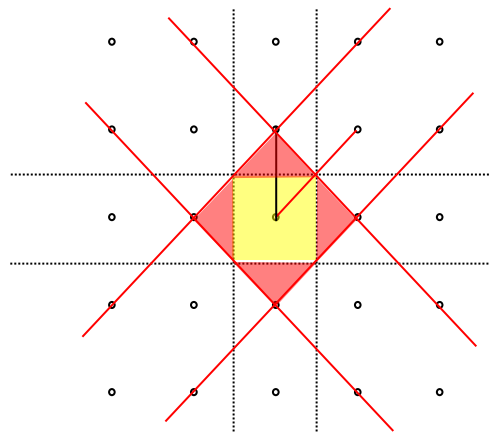
ii) hcp: H, He, N, Be, Mg, Co, Zn, Sc, Ti, Y, Zr, Tc, Ru, Cd, Hf, Re, Os, Tl, Pr, Gd, Tb, Dy, Ho, Er, Lu
 diamond: C, Ge, Si, Zn

iii) The 1st BZ is the primitive unit cell of the reciprocal lattice and is constructed in the same way as the Wigner-Seitz cell for the lattice in real space. The 2nd BZ is constructed in a similar way but considering the 2nd nearest neighbours:

First BZ



Second BZ



Problem 5

A soft X-ray source with Gd anode emits x-rays with a wavelength of 6,7 nm. A chemist asks if his organic crystal built up of large molecules and with the orthogonal unit vectors $a = 11,4 \text{ nm}$; $b=12\text{nm}$ and $c=13,5\text{nm}$ can be investigated by x-ray diffraction. Is it possible to investigate the (123) plane with this X-ray source?

(3 pts)

Solution: For the (1 2 3) plane, calculate the absolute value of scattering vector Δk for given lattice parameters, $a = 11.4 \text{ nm}$; $b = 12 \text{ nm}$ and $c = 13.5 \text{ nm}$ with Laue equations. [1 pt]

$$d = \frac{1}{\sqrt{\frac{1^2}{11.4\text{nm}^2} + \frac{2^2}{12\text{nm}^2} + \frac{3^2}{13.5\text{nm}^2}}} = 3.38\text{nm} \quad [0.5 \text{ pts}]$$

$$d_{\min} = \frac{6.7\text{nm}}{2} = 3.35\text{nm} \quad [0.5 \text{ pts}]$$

So a result is possible as $3.38 \text{ nm} > 3.35\text{nm}$ [1 pt]

Problem 6

The energy near a valence band edge is given by $E_k = -1 \times 10^{-26} k^2 \text{ ergs}$ (nearly free electron approximation).

- (a) Calculate the effective mass of an electron in the orbital $k = 1 \times 10^7 k_x \text{ cm}^{-1}$. Give the sign and the magnitude of the effective mass.

(2 pts)

Solution: $E = \frac{\hbar^2}{2m^*} k^2$ where m^* is the effective mass. Comparing with the given value of the energy $E_k = -1 \times 10^{-26} k^2 \text{ ergs}$, one deduces for the effective mass of the electron

$$-1 \times 10^{-26} = \frac{\hbar^2}{2m^*} \Rightarrow m_e^* = -\frac{\hbar^2}{2 \times 10^{-26}} = -\frac{(1.05 \times 10^{-27})^2}{2 \times 10^{-26}} = -0.55 \times 10^{-28} \text{ erg.s}^2 . m^{-2}$$

- (b) If this electron is removed and the band is otherwise full, what is the effective mass (sign and magnitude) of the hole?

(1 pt)

Solution: since the effective mass of the hole is minus that of the electron,

$$m_h^* = 0.55 \times 10^{-28} \text{ erg.s}^2 . m^{-2}$$

- (c) What is the direction and the magnitude of the wave vector of the hole?

(1 pt)

$$\text{Solution: } k_h = -k_e \Rightarrow k_e = 1 \times 10^7 \hat{k}_x \text{ cm}^{-1}; k_h = -1 \times 10^7 \hat{k}_x \text{ cm}^{-1}$$

Problem 7

(a) Gallium arsenide has a band gap of 1.40 eV. At what wavelength does it start to absorb?

(1 pt)

*The band gap determines threshold of continuous optical absorption at ν_{gap} , therefore since $h\nu_{\text{gap}} = 1.40 \text{ eV} \times 1.6019 \times 10^{-12} \text{ erg} = 2.24 \times 10^{-12} \text{ erg}$, and since $h = 6.6254 \times 10^{-27} \text{ erg s}$, $\nu_{\text{gap}} = 2.24 \times 10^{-12} \text{ erg} / 6.6254 \times 10^{-27} \text{ erg s} = 0.3381 \times 10^{15} \text{ s}^{-1}$;
 $\nu_{\text{gap}} = c/\lambda \Rightarrow \lambda = c/\nu_{\text{gap}} = 3.0 \times 10^8 \text{ m s}^{-1} / 0.3381 \times 10^{15} \text{ s}^{-1} = 8.87 \times 10^{-7} \text{ m} = 887 \text{ nm}$.*

Problem 8

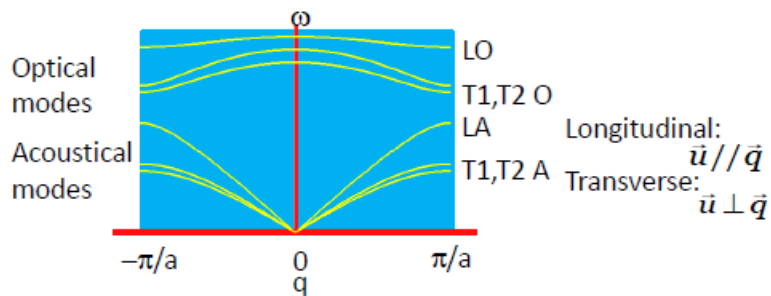
What is the necessary and sufficient condition to have optical branches in the phonon dispersion curves?

(1 pt)

Draw the phonon dispersion curves for such a crystal and label the curves.

(2 pts)

Solution: The number of optical branches is given by $3s-3$ where s is the number of atoms in the basis of the crystal structure, hence $s \geq 2$ to have optical branches.



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

period	group																							
	1*																	18						
	Ia																	VIIIb						
																		0						
1	H																	He						
2	Li	Be																	B	C	N	O	F	Ne
3	Na	Mg	Al	Si	P	S	Cl	Ar																
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr						
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe						
6	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn						
7	Fr	Ra	Ac	****	****	****	****	****	****	****	****	****	****	****	****	****	****	****						
			58	59	60	61	62	63	64	65	66	67	68	69	70	71								
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu								
			90	91	92	93	94	95	96	97	98	99	100	101	102	103								
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr								