

# Structure of Matter 2

Exam June 18, 2012. Tentamenhal 02, Blauwborgje 4, 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 simple calculator is allowed.
- ◇ The exam has 4 problems.
- ◇ The max. points per question are indicated. Grade is calculated from (total # pts + 10)/100.
- ◇ Answers may be given in dutch or english.

## Problem 1

- i In LCAO theory hybrid orbitals are formed by linear combination of degenerate orbitals  $\psi_{ni}$  with the same main quantum number  $n$ , and hence the same energy  $E_n$  ( $H\psi_{ni} = E_n\psi_{ni}$ ). Show that the energy of the hybrid wavefunction  $\Phi = \sum_i \alpha_i \psi_{ni}$  is also equal to  $E_n$ . [5 PTS]

$$\begin{aligned} H\Phi &= H \sum_i \alpha_i \psi_{ni} \\ H\Phi &= \sum_i \alpha_i H\psi_{ni} \\ H\Phi &= \sum_i \alpha_i E_n \psi_{ni} \\ H\Phi &= E_n \sum_i \alpha_i \psi_{ni} \\ H\Phi &= E_n \Phi. \end{aligned}$$

- ii Why are hybrid orbitals not built from orbitals with different main quantum number? [5 PTS]

These are not eigenstates of the Hamilton operator.

- iii By mixing  $s$ ,  $p_x, p_y$  and  $p_z$  4  $sp^3$  hybrid orbital are formed, yielding a tetragonal molecular structure.  $\text{AsCl}_5$  is an example where a  $d$  orbital is also used: it is called  $sp^3d$  hybridization. Discuss the geometry of the  $\text{AsCl}_5$  molecule. How many electrons are there in each orbitals? How many lone pairs are there? [5 PTS]

The hybridization of  $sp^3d$  orbitals will result in 5 new orbitals. The structure is the same as  $\text{PCl}_5$ : 2  $sp$  like orbitals along the + and - z-direction, and 3 orbitals in the x-y plane (with  $120^\circ$  angles between them). These 5 orbitals will each share 1 electron with one of the chlorines. So there are 10 shared electrons and no lone pair.

- iv Which of the following molecules do you think would exist:  $\text{PCl}_5$ ,  $\text{AsBr}_5$ ,  $\text{NCl}_5$ ? Explain your answer. [5 PTS]

The orbital structure of  $PCl_5$  and  $AsBr_5$  is similar to  $AsCl_5$ , so one expects them to exist. The highest occupied orbitals of N have main quantum number  $n = 2$ , and since there is no  $d$ -orbital in this case  $sp^3d$  hybridization will not be possible.  $NCl_5$  will probably not exist.

- v A photon with an energy  $E$  interacts with a molecule. The ionization potential of the molecule is  $I$ , the energetically highest vibrational mode has energy  $\Omega$ . Discuss what kind of information we can obtain using photon energies a)  $E \leq \Omega$ ; b)  $\Omega < E < I$ ; c)  $E > I$ .

[5 PTS]

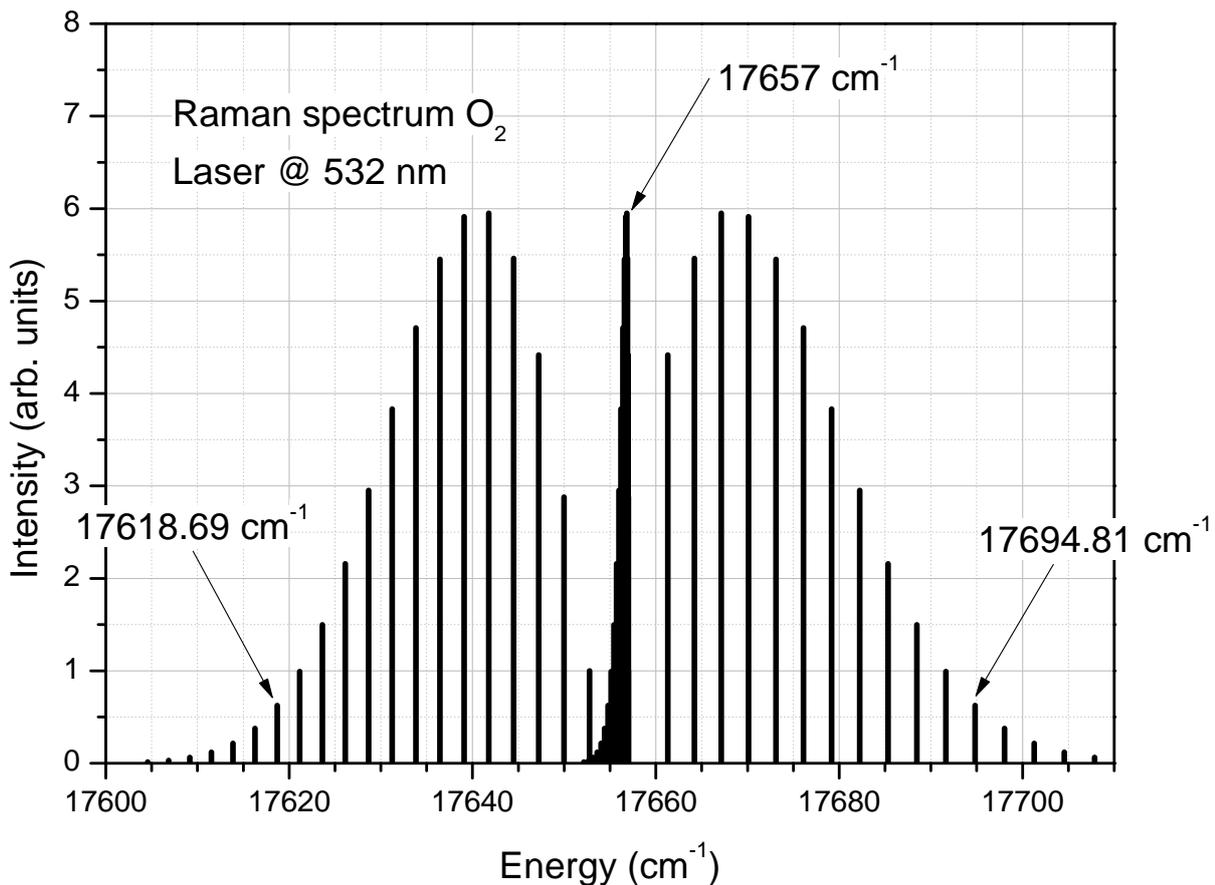
a) The only possible process is direct absorption. This will give information on the rotational and vibrational degrees of freedom. b) One possible process is inelastic (Raman) scattering yielding information on the rotational and vibrational degrees of freedom (though usually not the same as in a) due to the difference in selection rules). In addition, information will be obtained on the electronically excited states through absorption. c) In principle Raman scattering is still possible, but since usually the ionization cross section is much higher it is much more likely that a photoemission process occurs. Hence we obtain information on the ionization potential.

- vi Is the vibrational structure observed in the optical absorption spectrum reflecting vibrations of the excited state or of the ground state? Why? [5 PTS]

Excited state. The initial state is predominantly the vibrational ground state, the final state is typically a vibrationally (and electronically) excited state.

## Problem 2

The figure below shows the ro-vibrational Raman spectrum of oxygen gas recorded using an excitation laser with a wavelength of 532 nm.



i Discuss the origin of the peaks you observe [2 PTS]

Central strong dense set of lines at  $17657\text{ cm}^{-1}$  originates from Stokes transitions in which the vibrational quantum number changes by 1 ( $\Delta\nu = 1$ ) and the rotational quantum number does not change ( $\Delta J = 0$ ).

The set of lines at lower energy correspond to  $\Delta\nu = 1$  and simultaneously  $\Delta J = +2$ .

The set of lines at lower energy correspond to  $\Delta\nu = 1$  and simultaneously  $\Delta J = -2$ .

ii The graph shows only a limited energy range. Do you expect that there will be other active Raman modes in different energy range(s)? If so, what is their origin? [3 PTS]

$O_2$  has only one vibrational mode, for which the Stokes scattering is displayed in the graph. There will also be anti-Stokes scattering of this rovibrational band around  $19940\text{ cm}^{-1}$ . The only other modes are the pure librational which Stokes and anti-Stokes scattering are found in the region  $\pm 50\text{ cm}^{-1}$  around the laser energy.

iii What is the force constant of the molecular bond in oxygen? [3 PTS]

The laser energy is  $\omega_i = 10^7/532 = 18797 \text{ cm}^{-1}$ . The vibrational frequency is therefore  $\omega_0 = 18797 - 17657 = 1140 \text{ cm}^{-1}$  ( $f_0 = 34.1772 \text{ THz}$ ). The frequency  $f_0$  equals  $\frac{1}{2\pi} \sqrt{K/m_{eff}}$ , with  $m_{eff}$  the effective mass ( $= 0.5m_{oxygen} = 8 \text{ amu} = 1.328 \times 10^{-26} \text{ kg}$ ), and  $K$  the force constant. So,  $K = (2\pi f_0)^2 \times m_{eff} = 612.4 \text{ Nm}^{-1}$ .

*Note that the real frequency of the oxygen vibration is  $1554 \text{ cm}^{-1}$ , leading to  $K=1177 \text{ N/m}$ .*

- iv For two of the smaller outer peaks of the spectrum the energy is indicated on the graph. Use these frequencies to calculate the bondlength in the vibrationally excited state. [6 PTS]

The bondlength can be determined from the rotational constant  $B_1$  in the excited state. The total energy of a combined rotational and vibrational state is given by

$$S(n, J) = \left( n + \frac{1}{2} \right) \omega_0 + B_n \cdot J(J+1),$$

where  $B_n$  is the rotational constant of the molecule in vibrational state  $n$ .

For stokes transitions we have:

$$\Delta n = 1, \Delta J = -2 \text{ (O-branch)}$$

$$\omega = \omega_i - [S(n+1, J-2) - S(n, J)] = \omega_i - \omega_0 + (B_0 - B_1)J^2 + (B_0 + 3B_1)J - 2B_1$$

$$\Delta n = 1, \Delta J = 0 \text{ (Q-branch)}$$

$$\omega = \omega_i - [S(n+1, J) - S(n, J)] = \omega_i - \omega_0 + (B_0 - B_1)J^2 + (B_0 - B_1)J$$

$$\Delta n = 1, \Delta J = -2 \text{ (S-branch)}$$

$$\omega = \omega_i - [S(n+1, J+2) - S(n, J)] = \omega_i - \omega_0 + (B_0 - B_1)J^2 + (B_0 - 5B_1)J - 6B_1$$

For a given initial rotational state  $J$  the difference between the corresponding O and S branch transitions are then

$$8B_1J + 4B_1$$

. We now only have to count which  $J$  the indicated peaks correspond to (for the S-branch the first mode corresponds to  $J = 0$ , for the S-branch to  $J = 2$ ). We find  $J = 13$ , therefore the rotational constant is  $B_1 = \frac{17694.81 - 17618.69}{8 \cdot 13 + 4} = 0.7048 \text{ cm}^{-1}$ . The rotational constant (in  $\text{cm}^{-1}$ ) for a homonuclear diatomic molecule is given by:

$$B = \frac{\hbar}{4\pi c I} = \frac{\hbar}{4\pi c m r_1^2}$$

From this one finds

$$r_1 = \sqrt{\frac{\hbar}{4\pi c m B_1}} = 122 \text{ pm}$$

v Find the bond length of the oxygen molecule in the vibrational ground state. [4 PTS]

For this one can take either the energy of the transition from  $J = 13$  in the O- or S-branch. For the O-branch we have:

$$\omega_i - \omega_0 + (B_0 - B_1)J^2 + (B_0 + 3B_1)J - 2B_1 =$$

$$18797 - 1140 + (B_0 - 0.7048) \cdot 13^2 + (B_0 + 3 \cdot 0.7048) \cdot 13 - 2 \cdot 0.7048 = 17694.81$$

so that  $B_0 = 0.7189 \text{ cm}^{-1}$ . Using  $\frac{B_1}{B_0} = \frac{r_0^2}{r_1^2}$  one finds that there is about 1 % difference  $r_0 = 121 \text{ pm}$ .

vi Estimate the temperature of the gas from the Raman spectrum [4 PTS]

The intensity is proportional to the occupation of the modes which is in a Boltzmann approximation ( $T \gg E_{rot}$ ) given by

$$N_J \propto N(2J + 1)e^{-hcB \cdot J(J+1)/k_b T}$$

The maximum intensity is found for

$$J_{max} = \sqrt{\frac{kT}{2hcB_0}} - \frac{1}{2}$$

leading to

$$T = \frac{hcB(4J_{max}^2 + 4J_{max} + 1)}{2k_b} = 50 \frac{hcB_0}{k_b} \approx 50K$$

with  $J_{max} \approx 4.5$  found from the graph.

### Problem 3

The real space lattice of a simple cubic (sc) crystal is given by the three vectors:  $\vec{a}_1 = a \cdot \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}$ ,

$\vec{a}_2 = a \cdot \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}$ , and  $\vec{a}_3 = a \cdot \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$ , with  $a$  as lattice constant (= side length of the unit cell).

i Proof that the reciprocal lattice of a sc lattice with vectors  $\vec{a}_1, \vec{a}_2, \vec{a}_3$  is again a sc lattice with vectors  $\vec{b}_1, \vec{b}_2, \vec{b}_3$  by using the well-known relations between real space and reciprocal space lattices. [4 PTS]

From the definition of the reciprocal lattice, the vectors  $\vec{b}_1$ ,  $\vec{b}_2$ , and  $\vec{b}_3$  can be calculated. The vector  $\vec{b}_1$  is defined as  $\vec{b}_1 = 2\pi \frac{(\vec{a}_2 \times \vec{a}_3)}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}$ . If we insert the values of the real space vectors  $\vec{a}_1$ ,  $\vec{a}_2$ ,  $\vec{a}_3$  we therefore get:

$$\vec{b}_1 = 2\pi \frac{(\vec{a}_2 \times \vec{a}_3)}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} = 2\pi \frac{a^2 \cdot \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}}{a \cdot \underbrace{\begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \cdot \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}}_{=(1+0+0)=1} \cdot a^2} = 2\pi \frac{a^2}{a^3} \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} = \frac{2\pi}{a} \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}. \quad \text{The}$$

vectors  $\vec{b}_2$  and  $\vec{b}_3$  can be calculated analogously.

ii How many atoms per unit cell are there in (a) a sc lattice, (b) a bcc lattice, and (c) a fcc lattice? [4 PTS]

(a) There are 8 atoms at the corners of each unit cell, each of which is part of 8 unit cells. So:  $8 \times 1/8 = 1$ . There is 1 atom per unit cell.

(b) In addition to the corner atoms, there is 1 atom in the center of the unit cell. So:  $(8 \times 1/8) + 1 = 2$ . There are 2 atoms per unit cell.

(c) In addition to the corner atoms, there are 6 atoms in the center of the side planes of the unit cell. Each of these atoms is part of 2 unit cells. So:  $(8 \times 1/8) + (6 \times 1/2) = 4$ . There are 4 atoms in every fcc unit cell.

iii Calculate the packing density of the sc lattice. Assume that the atoms are spheres which are touching each other; i.e. the radii  $r$  of the spheres are given by  $r = a/2$ . Remember: The volume of one sphere (i.e. atom) is  $V_{sphere} = \frac{4}{3} \cdot \pi \cdot r^3$ . [3 PTS]

The volume of one sphere (i.e. atom) is  $V_{sphere} = \frac{4}{3} \cdot \pi \cdot r^3$ . The volume of the cube is  $V_{cube} = a^3 = (2r)^3 = 8r^3$ .

Since we only have one atom per unit cell, the filled fraction is simply:

$f = \frac{\frac{4}{3} \cdot \pi \cdot r^3}{8r^3} = 0.524$ . So, 52.4% of the space is occupied.

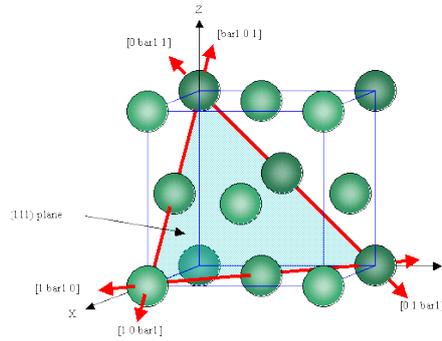
iv Find the Miller indices of the planes that intersect the crystallographic axes at the distances (a)  $(6x, 3y, 2z)$  and (b)  $(1x, 1y, 1z)$ . Assuming a cubic lattice with  $a = 0.5 \text{ nm}$ , what are the lattice plane distances for these two planes? [4 PTS]

To determine the Miller indices of the lattice planes, we have to take the inverse of the intersects with the crystallographic axes and multiply them with a number so that each value is an integer number. (a) The inverse of the intersects  $(6x, 3y, 2z)$  are  $1/6$ ,  $1/3$ , and  $1/2$ . If we multiply with 6 we gain for the Miller indices: 1, 2, and 3. So, the lattice plane is the (123) plane.

(b) The inverse of the intersects  $(1x, 1y, 1z)$  are 1, 1, and 1. We do not have to multiply. So, also the Miller indices are 1, 1, and 1. The corresponding lattice plane is the (111) plane.

In a cubic lattice the lattice plane distance is calculated with:  $d_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2}}$ . For the present cases we get:  $d_{123} = \frac{a}{\sqrt{1^2+2^2+3^2}} = \frac{0.5 \text{ nm}}{\sqrt{14}} = 0.1336 \text{ nm}$  and  $d_{111} = \frac{a}{\sqrt{1^2+1^2+1^2}} = \frac{0.5 \text{ nm}}{\sqrt{3}} = 0.2887 \text{ nm}$ .

- v Draw a (3D) unit cell of a cubic lattice including the latter of the two planes of the previous question. Which rotational symmetry does this plane have? [3 PTS]



In the figure above a fcc unit cell with a (111) plane is shown. It gets obvious that the (111) plane has a threefold symmetry/ a triangular shape.

- vi How many atoms are there on this particular plane (per unit cell) in (a) a sc lattice, (b) a bcc lattice, (c) a fcc lattice? From your findings, can you guess why this plane is a special one in a fcc lattice? [3 PTS]

As can be seen from the above figure, there are 6 atoms per unit cell on the (111) plane in the fcc lattice. For a sc and a bcc lattice there are only 3 atoms on this plane. Hence, the (111) planes in the fcc lattice are equivalent to the closely packed layers of the ccp (cubic close-packed) structure.

Remark: In terms of fractional atoms: SC & BCC 3/8 atoms; FCC 15/8 atoms. This is not the usual way of expressing the number of atoms in the plane, but for this exam considered correct.

## Problem 4

The dispersion relation of single particle charge excitations in a cubic superconductor (lattice constant  $a$ ) is given by  $E(k) = \sqrt{\alpha^2 \cdot k^4 + \Delta^2}$

- i Derive an equation for the density of states of these excitations, assuming that each state  $k$  is spin degenerate [5 PTS]

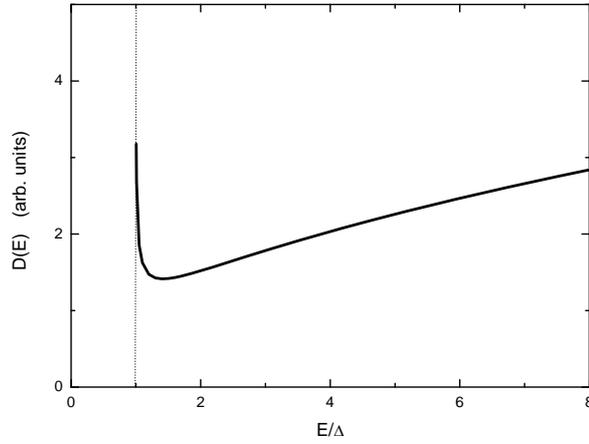
$$N(k) = 2 \cdot \frac{\frac{4}{3}\pi k^3}{\left(\frac{\pi}{a}\right)^3}$$

$$\frac{\partial N(k)}{\partial k} = V \cdot \frac{8k^2}{\pi^2}$$

$$D(E) = \frac{\partial N(E)}{\partial E} = \frac{\partial N(k)}{\partial k} \cdot \left(\frac{\partial E(k)}{\partial k}\right)^{-1} = V \frac{8k^2}{\pi^2} \cdot \frac{1}{2} \frac{\sqrt{\alpha^2 k^4 + \Delta^2}}{\alpha^2 k^3}$$

$$D(E) = 4V \frac{E}{\pi^2 \alpha [\alpha^2 (E^2 - \Delta^2)]^{1/4}}$$

ii Sketch the density of states as a function of energy [2 PTS]



iii For  $\Delta = 0$  the dispersion reduces to the free electron result. Can you give an expression for  $\alpha$ ? [5 PTS]

$$\alpha = \frac{\hbar^2}{2m^*}$$

iv Can you give a physical interpretation to  $\Delta$ ? [5 PTS]

$\Delta$  is the superconducting energy gap parameter

## A list of some fundamental constants, definitions and relations

Constant	Symbol	Approximate Value
Speed of light in vacuum	$c$	$3.00 \times 10^8$ m/s
Permeability of vacuum	$\mu_0$	$12.6 \times 10^{-7}$ H/m
Permittivity of vacuum	$\epsilon_0$	$8.85 \times 10^{-12}$ F/m
Magnetic flux quantum	$\phi_0 = \frac{h}{2e}$	$2.07 \times 10^{-15}$ Wb
Electron charge	$e$	$1.602176 \times 10^{-19}$ C
Electron mass	$m_e$	$9.11 \times 10^{-31}$ kg
Proton mass	$m_p$	$1.673 \times 10^{-27}$ kg
Neutron mass	$m_n$	$1.675 \times 10^{-27}$ kg
Proton-electron mass ratio	$\frac{m_p}{m_e}$	1836
Boltzman constant	$k_b$	$1.3806503 \times 10^{-23}$ m <sup>2</sup> kg s <sup>-2</sup> K <sup>-1</sup>
Boltzman constant [cm <sup>-1</sup> ]	$k_b$	$0.6950356$ cm <sup>-1</sup>
planck constant/2 $\pi$	$\hbar$	$1.05457 \times 10^{-34}$ J s
atomic mass unit (a.m.u.)	amu	$1.66053886 \times 10^{-27}$ kg
electron volt to Joule	1 eV	$1.602176 \times 10^{-19}$ J
electron volt to wavenumber	1 eV	$8065.395$ cm <sup>-1</sup>
wavenumber to frequency	1 cm <sup>-1</sup>	29.98 GHz