Structure of Matter II, 2020
Thursday 18 July 2020, 8.30-11.30
Write your name and student number on every sheet
Scan/photograph your answers and upload 1 pdf document

PROBLEM 1. Molecular orbital theory [13 pts]

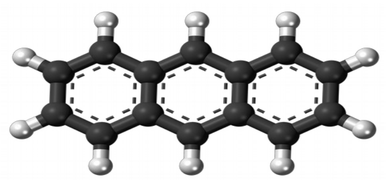
a) What are the hybridization of all the atoms in CO_3^{2-}? Draw the orbitals. **(4 pts)**
b) Consider the molecular orbital diagram of O_2 and N_2. How are they different? **(2 pts)**
c) Explain why the bonding π-orbitals are denoted as π_u while the bonding σ-orbitals are denoted as σ_g. **(3 pts)**
d) In molecular bond theory, the p-orbitals form only *one* bonding and anti-bonding σ-orbital, while they form *two* bonding and anti-bonding π-orbitals. Why? Schematically draw how the σ-orbitals and π-orbitals are constructed from the atomic p-orbitals. **(4 pts)**

PROBLEM 2 - Heteronuclear diatomic molecules [10 pts]

a) Consider the molecule HCl. Write down the wavefunction of this bond in terms of *c*-coefficients and atomic orbital wavefunctions. What can you say about the coefficients? **(3 pts)**
b) Which atomic orbitals of the two atoms form this bond? **(1 pt)**
c) Draw the molecular orbital diagram for the HCl molecule. The drawing should include labelled atomic and molecular orbitals and include electrons in the appropriate orbitals. **(4 pts)**
d) The variation principle can be used to find the coefficients c_a and c_b using the secular equations. What can you say about the magnitude of the Coulomb integrals α_H and α_{Cl}? **(2 pts)**

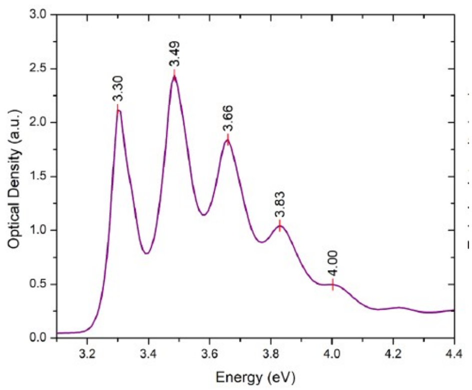
PROBLEM 3. SPECTROSCOPY [7 pts]

Consider the anthracene molecule:



a) How many vibrational degrees of freedom does the anthracene molecule, above, have? **[1 pt]**

Use the following UV/Vis spectrum to answer questions b and c:



b. Which experiment leads to such a spectrum? What is the energy spacing between peaks in wavenumbers, what does it correspond to? What other technique would reveal the same information? **[4 pts]**
c. Draw an energy diagram summarizing what happens, using the labels S_0 for the ground state S_1 for the excited state, $\hbar\omega$ the value from question b and the peaks themselves. **[2 pts]**

PROBLEM 4. Electronic transitions [11pt]

a. Make a schematic drawing of the operation of a 4-level laser and describe its operation based on the drawing. Why can a 2-level system not be a laser? **[4pt]**

b. Explain the Franck-Condon principle and make a suitable drawing to support your answer. **[3pt]**

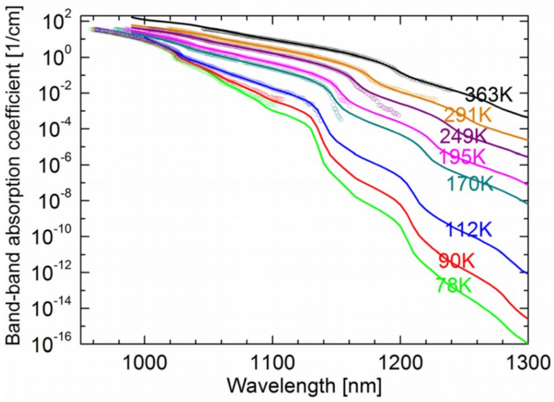
c. What is the reason for the difference between phosphorescence and fluorescence? Make a suitable drawing to support your answer. **[4pt]**

PROBLEM 5. Crystals and lattices [14 pts]

a. Calculate the reciprocal lattice vectors of an orthorhombic lattice with sides *a*, *b*, and *c* $(\vec{a_1} = a\hat{x},\ \vec{a_2} = b\hat{y},\ \vec{a_3} = c\hat{z})$ **[2pts]**

Given a 3D hexagonal lattice with constants *a* and *c* and direct lattice vectors:
$\vec{a_1} = a\hat{x},\ \vec{a_2} = \frac{1}{2}a\hat{x} + \frac{\sqrt{3}}{2}a\hat{y},\ \vec{a_3} = c\hat{z}$
b. Calculate the reciprocal lattice vectors **[3 pts]**
c. Given that *a* = 0.2 nm, what length should *c* be to make the hexagonal lattice close packed? **[4 pts]**
d. Calculate the packing fraction (the fraction of the unit cell filled, assuming that atoms are solid spheres) for a hexagonal close packed lattice. **[2 pts]**
e. Suppose an electron bundle with a wavelength of 0.14 nm hits the hexagonal lattice and scatters off a (001) plane. At which angle with respect to the inbound X-ray beam does the first order diffracted wave leave the sample? (use *a* = 0.25 nm and *c* = 0.41 nm as lattice constants.) **[3 pts]**

PROBLEM 6. Semiconductors and phonons [10 pts]
The laws of the conservation of energy and that of momentum are fundamental physical laws. We have seen in this course that the energy is conserved when a molecule or a semiconductor absorbs a photon. In this question, you will derive why the absorption of silicon changes with temperature. The graph below (adapted from: H.T. Nguyen, *et al.*, J. Appl. Phys. **115**, 043710 (2014).) shows how the absorption coefficient of silicon changes with temperature. Clearly, at lower temperatures, silicon absorbs less across all wavelengths.



a) Calculate the energy and momentum carried by a photon with a wavelength of 1200 nm. **[2pts]**
b) A typical phonon frequency is 10^{12} Hz. What is the energy in meV of such a phonon? **[2 pts]**
c) The speed of sound in silicon is 2200 m/s. Calculate the momentum of a phonon in silicon with a frequency of 10^{12} Hz. **[2 pts]**

Hopefully, you have found that the momentum of a typical phonon (calculated under c) is much lager than that of a photon (a). On the other hand, the energy of a photon that might be absorbed by silicon (a) has a much larger energy that of a typical phonon in silicon.

A simplified sketch of the band structure (energy-*k* relationship) of silicon is shown below. Clearly, in order to promote an electron from the maximum of the valence band (1) to the minimum of the conduction band (2) requires more than just the absorption of a photon.

d) Based on the above discussion, explain which other particle is needed and how this explains the temperature dependence of the absorption coefficient of silicon. **[4 pts].**

Now take pictures of your answers, convert them to a single pdf document, and upload the file.