

IMPERIAL COLLEGE LONDON

**BSc and MSci DEGREES – JANUARY 2013, for Internal Students of the
Imperial College of Science, Technology and Medicine**

**This paper is also taken for the relevant examination for the
Associateship**

ADVANCED CHEMISTRY THEORY IIA

Physical Chemistry

Monday 07th January 2013, 09:30-11:00

**PLEASE NOTE THAT IT IS DEPARTMENTAL POLICY THAT THESE
EXAM QUESTIONS MAY REQUIRE UNDERSTANDING OF ANY PRIOR
CORE COURSE.**

**USE A SEPARATE ANSWER BOOK FOR EACH QUESTION.
WRITE YOUR CANDIDATE NUMBER ON EACH ANSWER
BOOK.**

2.P3 – Electronic Properties of Solids

Answer part a) and **EITHER** part b) or part c) of this question.

a) Answer **ALL** parts of this question.

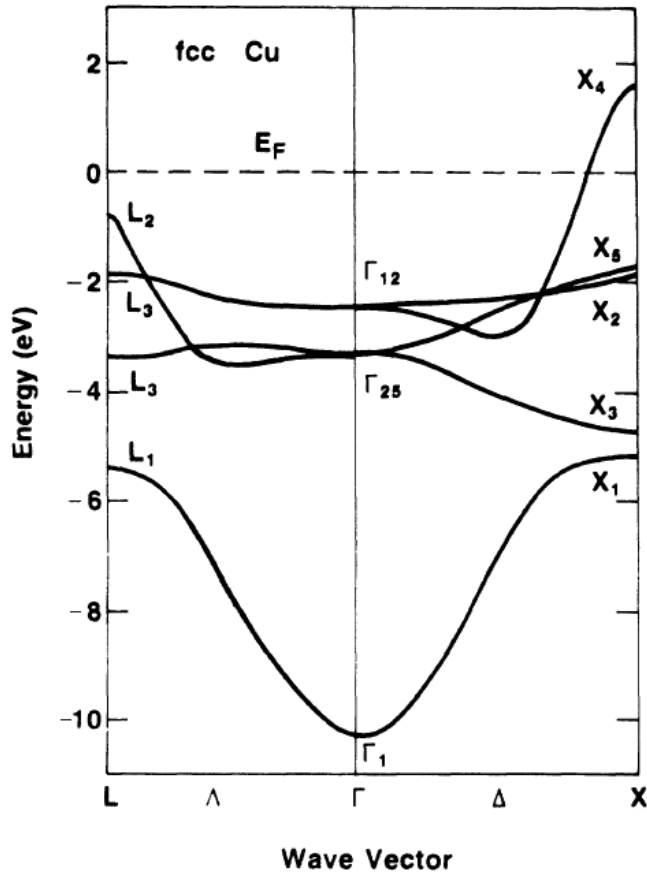
In copper mining, copper is first extracted from rocks using a solution based on sulphuric acid. In this solution, the copper is present as Cu^{2+} ions, which is then deposited onto metallic electrodes as Cu^0 (elemental copper) by electrochemical reduction. After some time, a thick layer of copper forms, which can be scraped off the electrode surface for further processing (e.g. turning it into copper wires). The copper layer may be several centimetres thick at this stage.

- i) For the copper sample described above, draw the Density-of-States (DOS) as a function of energy E , based on the free-electron model. Briefly explain how the $\text{DOS}(E)$ function depends on the dimensionality of the metal and justify your choice for the drawing. In the same drawing, indicate the Density-of-Occupied States (DOOS) and the Fermi level. What is the physical meaning of the area under the $\text{DOOS}(E)$ curve? Label all axes carefully.
- ii) The figure on page 2 shows a band diagram for copper. Explain the shape of the lowest band between symmetry points Γ and X , using the LCAO approach for a linear chain of atoms and a suitable orbital basis set. Draw orbital diagrams for the highest and the lowest electronic levels and indicate whether the interactions are bonding or anti-bonding in nature.

(8 marks)

(5 marks)

QUESTION CONTINUED OVERLEAF



from: Chelikowsky/Chou, Physical Review B 1988, 38, 7966

b) Answer **ALL** parts of this question.

The heat capacity C of metals has two contributions, namely an electronic part and a phonon part.

- i) Write down an expression for C as a function of temperature T and define all terms. In which temperature range does the electronic part dominate and why?

(4 marks)

QUESTION CONTINUED OVERLEAF

- ii) The following table contains $C(T)$ data for bulk gold. Plot the data in a manner suitable to extract the temperature coefficients for the electronic and the phonon components, respectively. Estimate their numerical value based on your drawing.

T [K]	C [mJ/(molK)]
0.2	0.15
0.7	0.8
1.2	2.6
1.9	8.4
2.4	15.6
2.6	19.4

(4 marks)

- iii) Why is the measured heat capacity for a three-dimensional electron gas much smaller than what the classical ideal gas model would predict? What is the approximate ratio between the two values?

(4 marks)

c) Answer **ALL** parts of this question.

The number of electrons in the conduction band, N_e , of a semiconducting material is calculated from the following integral:

$$N_e = \int_{E_c}^{\infty} \text{DOS}(E) \cdot f(E) dE$$

‘ E ’ is the energy and E_c the energy corresponding to the bottom of the conduction band; $\text{DOS}(E)$ the density of states function and $f(E)$ the Fermi function.

- Write down the Fermi function and define all terms. Derive a simplified expression for the Fermi function for $E - \mu \gg k_B T$.
(4 marks)
- Draw the Fermi function $f(E)$ and the simplified version on the same diagram. Label the drawing appropriately.
(4 marks)
- Using the simplified expression for the Fermi function you have derived above, write down an integral expression for N_e for a two-dimensional semiconductor of area A . Solve the integral.
(4 marks)

2.P6 – Quantum Chemistry

UNLESS OTHERWISE STATED YOU MAY OMIT NORMALISATION CONSTANTS IN YOUR ANSWER TO THIS QUESTION.

Answer part a) and **EITHER** part b) or part c) of this question.

a) Answer **ALL** parts of the question.

- i) Explain what is meant by a minimal basis set, and list the atomic orbitals that must be included in the minimal basis set for the homonuclear diatomic molecules Li_2 to F_2 .
(2 marks)
- ii) Draw a labelled energy level diagram for the ten molecular orbitals of C_2 .
(4 marks)
- iii) Using appropriate rules to simplify your LCAO expansions, write down approximate expressions for the $1\pi_g$ and $3\sigma_u$ molecular orbitals in C_2 . Note, you should allow for mixing between the 2s and relevant 2p atomic orbitals.
(4 marks)
- iv) Which is higher in energy (less stable) the $1\pi_u$ or the $3\sigma_g$ state? How does this compare with the situation in O_2 ?
(3 marks)
- v) Explain what effect removal of an electron (ionisation) will have on the bond strength of C_2 .
(2 marks)

b) Answer **ALL** parts of the question.

- i) Explain briefly what is meant by the pi electron approximation for conjugated systems.
(3 marks)
- ii) State the Hückel approximations, defining clearly in your answer the symbols α and β .
(4 marks)
- iii) Write down the secular determinant for butadiene in the Hückel approximation in terms of α and β , and hence obtain the orbital energies. You may wish to use the result:

$$\begin{vmatrix} b & a & 0 & 0 \\ a & b & a & 0 \\ 0 & a & b & a \\ 0 & 0 & a & b \end{vmatrix} \cong \left(b - \frac{a}{2}(1 + \sqrt{5})\right) \left(b + \frac{a}{2}(1 + \sqrt{5})\right) \left(b - \frac{a}{2}(1 - \sqrt{5})\right) \left(b + \frac{a}{2}(1 - \sqrt{5})\right)$$

(3 marks)

QUESTION CONTINUED OVERLEAF

c) Answer **ALL** parts of the question

- i) In the independent particle approximation, the molecular wave function for H_2 may be constructed from the $1\sigma_g$ and $1\sigma_u$ molecular orbitals of H_2^+ . Accounting fully for spin and using the $1\sigma_g$ and $1\sigma_u$ molecular orbitals only, write down wave functions for the S_0 and S_1 singlet states and the three T_1 triplet states. Label each state clearly. (4 marks)
- ii) By considering what happens to the space parts of the S_1 and T_1 wave functions when the two electrons are close together, explain which is lower in energy (more stable) the S_1 state or the T_1 state? (3 marks)
- iii) What implication does your answer to cii) have for ground-state B_2 ? (3 marks)