

IMPERIAL COLLEGE LONDON

**BSc and MSci DEGREES – JANUARY 2011, 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

Wednesday 12th January 2011, 09:30-11:00

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

Year 2/0111

Turn Over

2.P6 – Quantum Chemistry Part 2

Answer **ANY TWO** parts of this question.

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

For the following cyclic systems C_6H_6 , C_8H_8 and $C_{10}H_{10}$

- i) Calculate the Huckel Molecular Orbital (MO) energies for each molecule and draw the respective energy level diagram for each molecule. (6 marks)
- ii) Calculate the delocalisation energies for each molecule. (3 marks)
- iii) Comment on the relative separations of the MO's. Indicate whether each molecule is aromatic. (3 ½ marks)

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

For $CH_2=CH-CH=CH-CH=CH-CH_2\bullet$

- i) Construct the Huckel secular determinant identifying the approximations used. (3 ½ marks)
- ii) Find the Huckel MO energies for the HOMO and LUMO. (3 marks)
- iii) Find the Huckel MO's for the HOMO and LUMO and qualitatively draw their forms. (6 marks)

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

- i) Explain the origin and use of the Born-Oppenheimer approximation in quantum chemistry. (3 marks)
- ii) Describe how the Hamiltonian for an atom differs from that for a homonuclear diatomic molecule. (3 marks)
- iii) With the aid of an MO diagram explain why He_2^+ is a stable molecular species, which is observed experimentally, whilst He_2 is not. (4 marks)
- iv) Explain what is meant by the term electron correlation. (2 ½ marks)

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.

- i) For a three-dimensional metallic conductor at room temperature, prepare three separate diagrams plotting the density-of-states $\text{DOS}(E)$; the Fermi function $f(E)$; and the density of occupied states $\text{DOOS}(E)$. ‘ E ’ is the energy of the electrons. Label the plots appropriately and be as accurate as possible in preparing the drawings.

(4 marks)

- ii) At $T = 0$ K, all electronic states above the Fermi energy E_F are empty. Thus, the total number of electrons N in a conductor is obtained by integrating the $\text{DOOS}(E)$ up to E_F .

$$N = \int_0^{E_F} \frac{(2 \cdot m^3)^{\frac{1}{2}}}{\pi^2 \cdot \hbar^3} \cdot V \cdot E^{\frac{1}{2}} dE$$

‘ m ’ is the (effective) mass of the electron (take $9.11 \cdot 10^{-31}$ kg); ‘ V ’ is the sample volume; \hbar ($\hbar = h/(2 \cdot \pi)$) with $h = 6.626 \cdot 10^{-34}$ J·s).

Calculate an expression for E_F as a function of electron density. A typical alkali metal has an electron density of $2.5 \cdot 10^{28} \text{ m}^{-3}$. Calculate the value of E_F in units of eV and compare it to the thermal energy at room temperature. Do thermal effects have a strong influence on the energy of electrons at the Fermi level?

(6 marks)

QUESTION CONTINUED OVERLEAF

- iii) The (free) electrons in a conductor obey the Pauli Exclusion Principle; they constitute a so-called 'Fermi gas'. Calculate the mean energy $\langle E \rangle$ of the electrons in the Fermi gas as a function of E_F from

$$\langle E \rangle = \frac{\int_0^{E_F} \left(E \cdot \frac{1}{E^2} \right) dE}{\int_0^{E_F} \left(\frac{1}{E^2} \right) dE}$$

Based on a typical value of E_F (you can either use the value calculated in ii) or use another specific example you can remember), how does the value of $\langle E \rangle$ compare with the mean energy of a classical thermal gas at room temperature? (Hint: Assume that the classical thermal gas has three degrees of freedom, each of which contributed $0.5 \cdot k_B \cdot T$ of energy.)

Note that the difference between the two values is merely a manifestation of the Pauli Exclusion Principle.

(6 marks)

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

The free-electron model was successful in explaining a number of physical properties of solids, especially for simple alkali metals. One of the most important failures, however, is that it cannot account for the existence of band gaps.

- i) Why do band gaps emerge? What is the fundamental physical effect that needs to be incorporated in the theory? (Hint: This modification leads to the nearly-free-electron theory.)

(3 marks)

- ii) For a simple metal, draw dispersion curves $E(k)$ of an s-band for the free-electron model and the nearly-free-electron model (with parts of the 2nd Brillouin zone) on the same diagram and label the curves appropriately (include the Fermi level, the Fermi wave vector etc.). Also indicate the energy difference between the free-electron and the nearly-free-electron model at the band edge.

(3 marks)

- iii) Application of an electric field E_{el} alters the electron distribution and thus the $E(k)$ diagram. Illustrate the effect by drawing two-dimensional $E(k_x, k_y)$ plots: one for $E_{el} = 0$ and another one for $E_{el} > 0$, where the electric field acts in the x-direction only. Are all electrons affected by the electric field or only a fraction of them?

(3 marks)

QUESTION CONTINUED OVERLEAF

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

The electric conductivity of a metal decreases with increasing temperature; a semiconductor shows the opposite behaviour (conductivity increases with increasing temperature).

i) Explain this observation with help of appropriate diagrams.

(3 marks)

ii) Silicon is an intrinsic semiconductor with a band gap of 1.1 eV. Calculate the probability, $f(E)$, of finding an electron at the bottom of the conduction band at $T = 300$ K. Note: You do not need to calculate the number of conduction electrons; the DOS is not needed here.

(3 marks)

iii) The resistivity of a semiconducting material typically decreases upon illumination with light. Explain this observation using a suitable band diagram.

(3 marks)