IMPERIAL COLLEGE LONDON

BSc and MSci DEGREES – JANUARY 2012, 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

Thursday 12th January 2012, 14:00-15:30

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.

2P6 – Quantum Chemistry Part 2

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 this question.

    i) Explain why the total wave function for indistinguishable particles must be either symmetric or antisymmetric with respect to particle exchange.

       (3 marks)

    ii) State whether electrons are described by symmetric or antisymmetric wave functions. In the specific case of two-particle wave functions, explain how spin and space wave functions can be combined to give a complete wave function that has the required symmetry properties.

       (3 marks)

    iii) Explain why $\alpha(1)\beta(2)$ and $\beta(1)\alpha(2)$ are not acceptable spin wave functions and state how they may be combined to yield acceptable wave functions.

       (2 marks)

    iv) Using the independent electron model, write down the four possible wave functions for the first excited state of H_2, taking into account both space and spin.

       (3 marks)

    v) How do the energies of the four wave functions from iv) compare in the independent particle model?

       (1 mark)

    vi) Explain why in reality the triplet state is always lower in energy than the corresponding singlet state.

       (3 marks)

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

   i)   Using a minimal basis set, and making use of appropriate rules to simplify your LCAO expansions, write down approximate expressions for the $2\sigma_g$ and $1\pi_u(x)$ molecular orbitals in O_2.

   (4 marks)

   ii) Draw a labelled energy level diagram for the ten molecular orbitals of O_2.

   (4 marks)

   iii) Explain why O_2 is paramagnetic.

   (2 marks)

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

   i)   Write down the secular equation for hydrogen in terms of the Coulomb integral H_{AA}, the exchange integral H_{AB}, the overlap integral S_{AB}, the orbital energy E and the orbital weighting coefficients c_A and c_B.

   (4 marks)

   ii) Use your expression from i) to obtain expressions for the energies of the $1\sigma_g$ and $1\sigma_u$ molecular orbitals.

   (4 marks)

   iii) Describe briefly in words the connection between the secular equation and the variational principle.

   (2 marks)

2.P3 – Electronic Properties of Solids

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

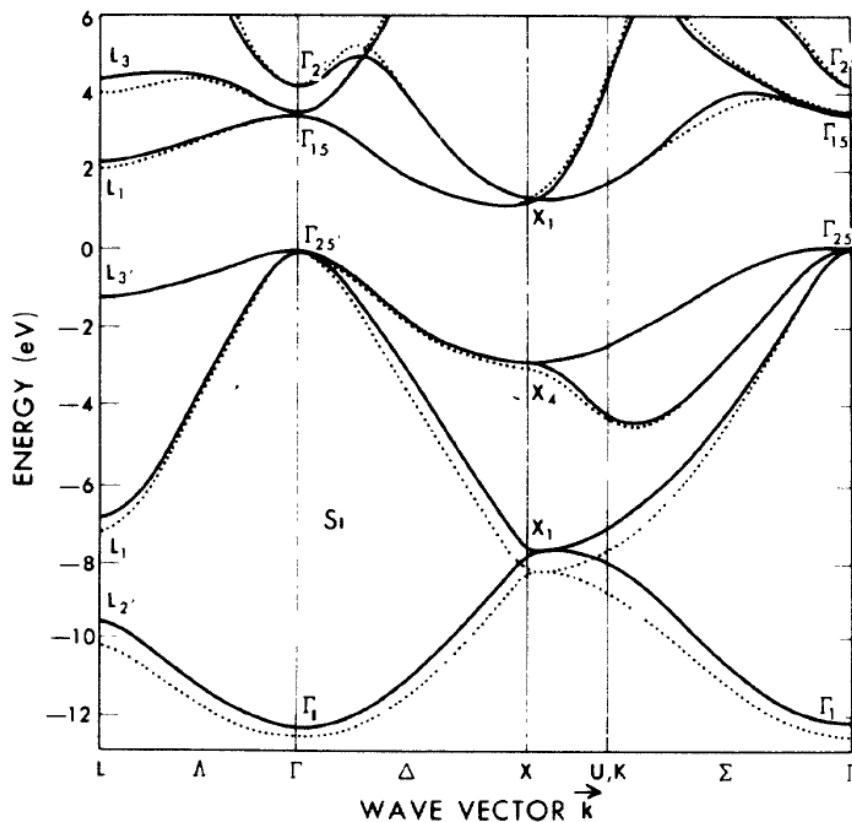a) Answer **ALL** parts of this question.

Silicon is the most important semiconducting material in the world and forms the basis of computer chip technology. Producing high-purity silicon is of central importance in this context.

i) What is the raw starting material for the fabrication of Silicon wafers in the semiconductor industry? Write down all seven processing steps involved in the production of Si wafers, as discussed in the lectures, including correct chemical formulas where appropriate.

(8 marks)

ii) The band structure diagram of Si is depicted below (taken from Chelikowsky and Cohen, Phys. Rev. B 1974, 10, 5095). Use the copy of the diagram provided to you and indicate on it the band gap as well as the Fermi level. Explain the difference between a direct and an indirect band gap material and give an example for each one. Name a physical property where this difference manifests itself and explain why this is so.

(5 marks)

Please ignore the dotted lines and the indexed symmetry points (L_1, L_2,..., Γ_{25}...) in the diagram.

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

In the nearly free electron approximation, electrons of a certain energy are reflected back and forth between two nuclei and are hence trapped. This results in two possible states of different energy, similar to bonding and anti-bonding states in molecular orbital theory. The wave function of the lower energy state is

$$\Psi_+(x,t) = A \cdot \exp\left(i \cdot \left(n \cdot \frac{\pi}{a} \cdot x - \omega \cdot t\right)\right) + B \cdot \exp\left(i \cdot \left(-n \cdot \frac{\pi}{a} \cdot x - \omega \cdot t\right)\right)$$

where $k = n \cdot \pi / a$.

    i) What is the physical reason for the energy difference between the two states?

(2 marks)

    ii) Based on the physical model, what can you infer about the relative magnitude of A and B? What do these two parameters stand for?

(2 marks)

    iii) Show mathematically that the probability density $\rho = \Psi^* \Psi$ at a given point x is indeed independent of time, as expected for a trapped electron.

The following relations may be useful (Euler's equation; $i = \sqrt{-1}$):

$\exp(-ix) = \cos(x) - i \cdot \sin(x)$
$\exp(ix) = \cos(x) + i \cdot \sin(x)$

(8 marks)

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

i) Write down a definition (in words) of the Fermi function $f(E)$ and the Density-of-States function $DOS(E)$. What does each of them tell you about an electronic system? Give a mathematical definition of the total number of electrons N_e (in a band), in terms of $f(E)$ and $DOS(E)$.

(2 marks)

ii) Define the term "Fermi surface" and draw the Fermi surface of an ideal, two-dimensional free-electron metal. What is the difference between k-points inside and outside the Fermi surface?

(2 marks)

iii) Derive an expression for the number of electrons N_e in the conduction band of a two-dimensional intrinsic semiconductor. Note that the electron energy E ranges from the bottom of the conduction band at E_c to infinity. The Fermi level is in the centre of the band gap between valence and conduction band.

(4 marks)

Hint: Simplify the Fermi function taking into account $E\text{-}E_F \gg k_BT$, before you start calculating N_e itself.

The DOS(E) in two dimensions is given by $DOS(E)_{2D} = \frac{m \cdot A}{\pi \cdot \hbar^2}$

where m is the effective mass of the electron ($9.11 \cdot 10^{-31}$ kg) and A is the area of the conductor ($A = x \cdot y$; $x = y = 100$ nm). $\hbar$ is the reduced Planck's constant, $\hbar = 1.055 \cdot 10^{-34}$ Js.

iv) Calculate N_e given that the band gap is 0.2 eV and $T = 298$ K. Remember that Boltzmann's constant $k_B = 1.38 \cdot 10^{-23}$ JK^{-1}.

(4 marks)