**IMPERIAL COLLEGE LONDON**

**BSc and MSci DEGREES – JANUARY 2014, 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**

**Tuesday 14th January 2014, 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.**

**Year 2/0114 Turn Over**

**2.P3 – Electronic Properties of Solids**

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

1. Answer **ALL** parts of this question.

Polythiophene is an example of a conducting polymer, i.e. an organic material with semiconducting or metallic properties. A section of the underivatized polymer chain is shown below. The band gap of such a material is on the order of 3 to 3.5 eV, depending on the chain length.



1. Based on the chemical structure, what type of electrons do you expect to determine the electric and optical properties of the material? Justify your answer.

(4 marks)

1. Focusing on the carbon atoms only, suggest a simple model within the Linear Combination of Atomic Orbitals (LCAO) approximation to describe the electronic structure of a single polythiophene chain and justify your choice. Use a suitable basis set to construct the valence and the conduction bands. Draw the atomic orbital configurations for the lowest electronic state in the valence band and the highest electronic state in the conduction band.

(6 marks)

1. The electrical conductivity of pure polythiophene is relatively low. Suggest a general strategy to increase the electrical conductivity of this material, and give a specific example.

(3 marks)

1. Answer **BOTH** parts of this question.

Free electron theory is surprisingly successful, given the simplifications on which it is based, but it also has severe limitations in many respects.

1. List three failures of the free electron theory and give one illustrative example in each case.

(6 marks)

QUESTION CONTINUED OVERLEAF

1. In nearly free electron theory, electrons at the Brillouin zone boundary are standing waves, due to electron scattering at the nuclei. This results in the formation of two distinct states with electron density distributions *+* and *-*. Write down the mathematical expressions for *+*(*x*) and *-*(*x*), derived for a one-dimensional chain of atoms in the *x*-direction, and define all terms. Plot *+* and *-* as a function of *x* for *k* = /*a*, along with the electron density distribution for a freely travelling wave. Explain why the electron energy is different for the three cases.

(6 marks)

1. Answer **ALL** parts of this question.
2. Write down the Fermi-Dirac distribution formula ('Fermi function') and define all terms.

(3 marks)

1. Sketch the Fermi function for different temperatures and comment on the result.

(3 marks)

1. The heat capacity of an ideal electron gas of *N* electrons is *C* = (3/2)*kB*·*N* per unit volume. Experimental values for common metals at room temperature are usually only ~ 1% of this value. Explain this observation and illustrate this for case of Al (*EF* = 11.6 eV, *T* = 300 K).

(4 marks)

1. In a real metal at room temperature, there is another important contribution to the overall heat capacity. State what this is and explain why it makes a negligible contribution at very low temperatures.

(2 marks)

**2.P6 – Quantum Chemistry**

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

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

1. Answer **ALL** parts of this question.
2. Explain what is meant by a minimal basis set, and state which atomic orbitals must be included in the minimal basis set for the hydrogen molecular ion H2+.

(2 marks)

1. Assuming a minimal basis set, write down in matrix form the secular equation for H2+ in terms of the Coulomb integral H­AA, the exchange integral HAB, the overlap integral SAB, the orbital energy *E* and the orbital weighting coefficients *c*A and *c*B. Write down expressions for H­AA, HAB and SAB in terms of the Hamiltonian and the atomic orbitals of the minimal basis set.

(4 marks)

1. Explain why the determinant of the secular matrix must equal zero in order to obtain a physically realistic wave function. Using this condition, obtain energies for the 1g and 1u molecular orbitals of H2+.

(4 marks)

1. By solving the secular equation, obtain expressions for the 1g and 1u molecular orbitals in terms of the atomic orbitals of the minimum basis set.

(3 mark)

1. Answer **ALL** parts of this question.
2. Using the independent particle approximation, write down space wave functions for the ground state and excited states of H2 in terms of the 1g and 1u molecular orbitals of H2+. State whether each space wave function is symmetric or antisymmetric with respect to particle exchange.

(4 marks)

1. For each space wave function in b) i) draw an indicative energy level diagram, showing the occupancies of the 1g and 1u molecular orbitals. Hence, using the independent particle approximation, write down the energy of each space wave function.

(2 marks)

QUESTION CONTINUED OVERLEAF

1. Write down the four allowed spin wave functions for a two-electron system in terms of *α* and *β*, stating whether each wave function is symmetric or antisymmetric with respect to particle exchange.

(2 marks)

1. Combine your spin and space wave functions from b) i) and b) iii) to obtain total wave functions for the ground state and excited states of the H2 molecule. Comment on the symmetry of these total wave functions with respect to particle exchange.

(4 marks)

1. Answer **ALL** parts of this question.
2. State the Hückel approximations, defining clearly in your answer the meaning of the Hückel parameters and .

(4 marks)

1. The allyl radical depicted below has formula C3H5 and may be considered to be a propylene molecule that has lost a hydrogen atom from the methyl end. Each carbon atom is assumed to be sp2 hybridized, contributing one pz electron to the pi bond. Write down an expression for the Hückel matrix in terms of and , and hence determine the energies of the three pi molecular orbitals.



You may wish to use the result:

(6 marks)

1. Using your result from c) ii) write down the total energy of the pi electrons in the ground-state of the allyl radical.

(2 marks)