IMPERIAL COLLEGE LONDON

BSc and MSci DEGREES – JANUARY 2015, 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 15th January 2015, 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.

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.

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) Electrons belong to a class of elementary particles known as Fermions – what does this mean in relation to your answer to a) part i)?

(1 mark)

iii) For the specific case of two-electron wave functions, explain how spin and space wave functions can be combined to give a complete wave function with the required symmetry properties.

(2 marks)

iv) Discuss whether each of the following is an acceptable spin wave function. Explain how the unacceptable spin wave functions may be combined to obtain acceptable spin wave functions :

$$\alpha(1)\alpha(2)$$

$$\alpha(1)\beta(2)$$

$$\beta(1)\alpha(2)$$

$$\beta(1)\beta(2)$$

(2 marks)

v) In the independent electron approximation, four of the six possible molecular wave functions of H_2^+ are degenerate. Write down expressions for each of these four degenerate wave functions, taking into account both space and spin.

(4 marks)

vi) Explain how electron-electron interactions affect the energies of the four wave functions in a) part v).

(2 marks)

QUESTION CONTINUED OVERLEAF

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

i) Write down in $\hat{T}, \hat{V}$ notation the **full** Hamiltonian for the H_2^+ molecule. Your expression should include both the electron and the nuclei.

(2 marks)

ii) State the Born-Oppenheimer approximation and use it to obtain an expression for the H_2^+ electronic Hamiltonian in $\hat{T}, \hat{V}$ notation.

(3 marks)

iii) Using your expression from bii) write down an expression for the electronic Hamiltonian of the H_2^+ molecule in terms of the electron mass m_e, the nuclear separation R_{AB}, the distance r_A of the electron from nucleus A and the distance r_B of the electron from nucleus B. (Your answer should include all relevant fundamental constants). Comment on the signs of each of the four terms.

(6 marks)

c) Answer **ALL** parts of this 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 cyclobutadiene (C_4H_4) in the Hückel approximation in terms of α, β and E, and hence obtain the orbital energies. You may wish to use the result:

$$\begin{vmatrix} a & b & 0 & b \\ b & a & b & 0 \\ 0 & b & a & b \\ b & 0 & b & a \end{vmatrix} = a^2(a^2 - 4b^2)$$

(3 marks)

iv) What is the delocalisation energy for cyclobutadiene in the Hückel approximation, i.e. how does the average energy per electron in the ground-state of cyclobutadiene compare to the average energy per electron in the ground-state of ethene?

(1 mark)

2.P9 – Photochemistry

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

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

i) With the aid of a suitable diagram define the terms internal conversion, intersystem crossing, fluorescence and phosphorescence. Clearly indicate on your diagram singlet and triplet states.

(5 marks)

ii) Explain what is meant by oscillator strength.

(2 marks)

iii) A dye molecule has a natural radiative lifetime of 35 ns. In a solution, this dye has a fluorescence lifetime of 900 ps. Calculate the fluorescence quantum yield.

(2 marks)

iv) Solutions of naphthalene and halogenated naphthalenes were found to have the following photophysical data.

	Fluorescence quantum yield	Phosphorescence quantum yield
Naphthalene	0.55	0.06
1-bromo Naphthalene	2×10^{-3}	0.27
1-iodo Naphthalene	5×10^{-4}	0.38

Explain the origin of the different fluorescence and phosphorescence yields for these three compounds.

(6 marks)

QUESTION CONTINUED OVERLEAF

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

i) Derive the Stern-Volmer equation for bimolecular quenching.

(5 marks)

ii) The emission lifetimes of a dye molecule were measured as function of dissolved oxygen concentration in solution. The data obtained from these studies is given in the table below.

$[O_2]/(10^{-2}\ moldm^{-3})$	0	2.2	5.6	8.1	11
τ / (10^{-9} s)	2.5	1.6	0.9	0.7	0.6

From these data determine the quenching rate constant.

(5 marks)

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

i) With the aid of suitable diagrams and equations describe the three main energy transfer mechanisms.

(6 marks)

ii) A donor-bridge-acceptor energy relay has been prepared to test Forster energy transfer theory. The donor moiety has an emission quantum yield of 80% in solution, which is reduced to 30% when covalently bound to the acceptor. Assuming a Forster radius of 4.5 nm for the donor / acceptor pair estimate the length of the bridge.

(4 marks)