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 IIIA

Physical Chemistry

Tuesday 11th January 2011, 14:00-17:00

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

3.P2 – 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 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) Using appropriate rules to simplify your LCAO expansions, write down approximate expressions for the $1\pi_u$ and $3\sigma_g$ in B_2. Note, you should allow for mixing between the 2s and relevant 2p atomic orbitals.

   (4 marks)

   iii) Draw a labelled energy level diagram for the ten molecular orbitals of B_2.

   (4 marks)

   iv) Comment on the ordering of the $1\pi_u$ and $3\sigma_g$ states and explain why this differs from the situation in F_2.

   (3 mark)

   v)   Explain what effect removal of an electron (ionisation) will have on the bond strength of B_2.

   (2 marks)

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

   i)   Write down in matrix form the secular equation for H_2^+ 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 part i) to obtain expressions for the energies of the $1\sigma_g$ and $1\sigma_u$ molecular orbitals.

   (4 marks)

   iii) By considering the effect on the overlap integral, explain how the energy difference between the $1\sigma_g$ and $1\sigma_u$ molecular orbitals will depend on the spacing of the nuclei.

   (2 marks)

QUESTION CONTINUED OVERLEAF

c) Answer **ALL** parts of this 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 $1\sigma_u$ 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) If the energies of the $1\sigma_g$ and $1\sigma_u$ molecular orbitals of H_2^+ are $E_{\sigma g}$ and $E_{\sigma u}$, respectively, use the independent electron model to obtain expressions for the energies of the S_0, S_1 and T_1 states.

   (1 mark)

   iii) What happens to the space parts of the S_1 and T_1 wave functions when the two electrons are close together? What implication does this have for the relative energies of the S_1 and T_1 states?

   (4 marks)

   iv) State Hund's first rule and explain how this arises naturally from your answer to iii).

   (1 mark)

3.P3 – Molecular Reaction Dynamics

Answer any **TWO** of the three parts a), b) **AND** c) of this question.

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

   i) A Morse potential can be used to describe the interaction between two atoms or molecules. Draw a one-dimensional potential energy surface that could describe such an interaction, labelling all axes and marking (1) the equilibrium separation, (2) the dissociation limit and (3) the repulsive potential.

   (3 marks)

   ii) Using drawings of potential energy surfaces, justify the following statements:
      1. Translational energy is most effective for passage across an "early" barrier in the entrance channel, whereas even reactant vibrational energy far in excess of the barrier height may be ineffective in causing a reaction.
      2. A "late" barrier is best surmounted by vibrational rather than translational energy of reactants.

   (6.5 marks)

   iii) Explain the Hammond postulate.

   (3 marks)

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

   i) To study the dynamics of a chemical reaction it is necessary to employ a triggering mechanism to initiate the reaction. Briefly discuss three triggering techniques, highlighting their advantages and limitations.

   (6.5 marks)

   ii) The rate of electron transfer between a particular electron acceptor and electron donor embedded in a protein is found to be 8.74×10^6 s^{-1}. The edge-to-edge distance between them is 1.23 nm. Assuming activationless electron transfer, estimate the electron tunnelling coefficient of the protein environment. Define each symbol used, and explain any approximations that you have made.

   (6 marks)

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

   i) A diatomic molecule has a stretching vibration with wavenumber 3000 cm^{-1}. Estimate the duration of an optical pulse that would be required to create a vibrational wavepacket.

   (3 marks)

   ii) Explain the difference in time dependent behaviour of a vibrational eigenstate and a vibrational wavepacket. Demonstrate mathematically that the average bond length of the molecule is not time dependent in one case, but is in the other, and show explicitly the mathematical form of this time dependence. Define each symbol used in the derivation.

   (9.5 marks)

3.P9 – Photochemistry

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

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

    i) A porphyrin has a singlet excited state lifetime of 3 ns. The quantum yield of triplet formation is 30 %. What is the rate constant for intersystem crossing from the singlet excited state to the triplet state?

        (2 marks)

    ii) Which molecule would you expect to exhibit the highest fluorescence yield, Zinc Porphyrin or Platinum Porphyrin? Justify your answer.

        (2 marks)

    iii) With the aid of a suitable diagram define the terms internal conversion and intersystem crossing. Indicate on this diagram the $S_0{}^0 \rightarrow S_1{}^2$ and $T_1{}^0 \rightarrow S_0{}^3$ optical transitions.

        (5 marks)

    iv) Explain the origin of the Franck Condon principle and how it leads to the appearance of vibrational structure in an electronic transition. Your answer should include references to potential energy surfaces, vibrational wavefunctions and the Franck Condon Overlap Integral.

        (6 marks)

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

    i) Derive the Stern-Volmer equation for bimolecular emission quenching defining all terms used.

        (4 marks)

ii) The phosphorescence of compound **A** in ethanol is quenched by the addition of compound **B**. The following phosphorescence yields were measured as a function of the concentration of **B**.

[B] / (10^{-3} mol dm^{-3})	0	1	2
ϕ_0/ϕ	1	1.7	2.5

Assuming that the quenching reaction is diffusion controlled and the rate constant has a value of 10^{10} M^{-1}s^{-1}, determine the lifetime of the triplet state of compound **A.**

(3 marks)

iii) Describe the mechanism of Type 2 photodynamic action.

(3 marks)

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

i) With reference to suitable equations, describe the Förster energy transfer mechanism.

(5 marks)

ii) A protein has been internally modified to contain both a donor and acceptor. The free donor dye has a lifetime of 5.5 ns and the lifetime of the donor in the presence of the acceptor is 3.7 ns. If the Forster radius (R_o) for the donor and acceptor pair is 5.4 nm what is the spatial separation between the donor and the acceptor?

(5 marks)