

**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**

**Inorganic Chemistry**

**Monday 09<sup>th</sup> January 2012, 09:30-11:00**

**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.**

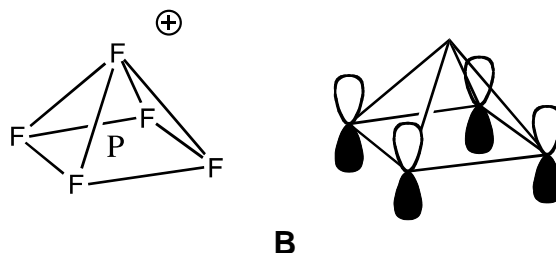
## 2I.1 – Molecular Orbitals in Inorganic Chemistry

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

- a) Construct and **annotate** a valence MO diagram for  $I_3^-$  ( $D_{\infty h}$  point group). Use as fragments the two terminal I atoms ( $I-\bullet-I$ ) and a central I atom ( $\bullet-I-\bullet$ ), assume that the MOs do not undergo mixing.

(17 marks)

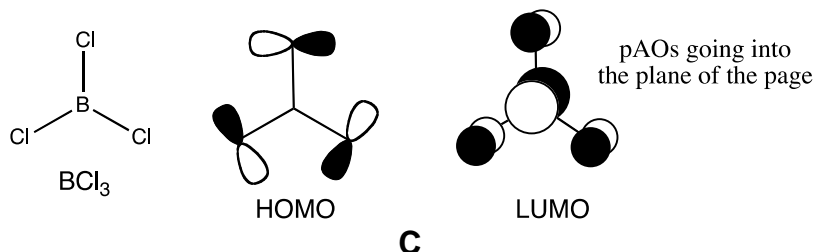
- b) Square pyramidal  $[PF_5]^+$  belongs to the  $C_{4v}$  point group. Use the projection formula to determine the  $b_1$  symmetry wavefunction using as your basis the **basal plane**  $p_z$  atomic orbitals, **B**. Show your working. The molecular orbital wavefunction does not need to be normalised. Draw the molecular orbital associated with the wavefunction.



(8 marks)

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

The HOMO and LUMO of trigonal planar  $BCl_3$  are given below, **C**



- i) Draw the expected HOMO and LUMO for  $BF_3$  (1 mark)
- ii) Determine the symmetry label for the HOMO of  $BF_3$ . (1 mark)
- iii) On your diagram of the HOMO and LUMO for  $BF_3$  annotate those features important in evaluating the bonding character of these MOs (3 marks)
- iv) Assume  $BF_3$  undergoes distortion into a trigonal pyramidal geometry. Draw the new LUMO and use your diagram to explain why this MO is stabilised or destabilised. (3 marks)

## 2IS.1 – NMR and EPR Spectroscopy

Answer part a) and any **TWO** parts from b), c) and d) of this question.

- a) A laboratory notebook contains the following brief partial comments, **I-III**, about the  $^1\text{H}$  NMR spectra of the square planar metal complexes **A-C**.

**I** Shows a doublet of triplets with satellites centred at about -15 ppm.

**II** Shows a triplet centred near -15 ppm.

**III** Shows a triplet with satellites centred at about -15 ppm.

**A** *trans*-[PtH(Cl)(PEt<sub>3</sub>)<sub>2</sub>]    **B** *trans*-[PdH(Cl)(PEt<sub>3</sub>)<sub>2</sub>]    **C** [PtH(PEt<sub>3</sub>)<sub>3</sub>]ClO<sub>4</sub>

- i) Assign the correct spectral description to each compound giving reasons for your answers.

(3 marks)

- ii) Sketch each spectrum and label couplings using the  $^nJ_{X-Y}$  notation.

(9 marks)

- iii) Comment on the relative magnitude of the couplings present in your sketches

(3 marks)

(Assume that  $^1\text{H}$  and  $^{31}\text{P}$  are both 100% abundant,  $I = 1/2$ ;  $^{195}\text{Pt}$  is 33% abundant,  $I = 1/2$ ; no other nuclei present significantly affect the spectra.)

- b) Sketch and label the couplings seen in the epr (esr) spectra of the trigonal planar radicals shown below.

i) (t-Bu)<sub>3</sub>Ge•

ii) (t-Bu)<sub>3</sub>Sn•

(Assume that  $^{73}\text{Ge}$  is 8% abundant,  $I = 9/2$ ;  $^{117}\text{Sn}$  and  $^{119}\text{Sn}$  are both 8% abundant  $I = 1/2$ ; no other nuclei present significantly affect the spectra.)

(5 marks)

QUESTION CONTINUED OVERLEAF

- c) NMR properties for two metal nuclei are given below. Describe the problems associated with recording NMR spectra from each nucleus. Can any of these problems be overcome, and if so how?

Nucleus	Spin (I)	Natural abundance (%)	Gyromagnetic ratio ( $\gamma$ ) ( $10^7 \text{ rad T}^{-1} \text{ s}^{-1}$ )
$^{59}\text{Co}$	7/2	100	6.137
$^{187}\text{Os}$	1/2	1.64	0.616

(5 marks)

- d) The  $^{14}\text{N}$  spectra and some associated data for a series of nitrogen compounds in aqueous solution (except for  $\text{NH}_3$  which was recorded as a neat liquid) are shown below in **A** (Emsley, Feeney, Sutcliffe, Vol 2. p. 1038). The spectra have all been shifted to be centred at 0 ppm.

Compare and contrast the spectra in **A** below, giving reasons for the lineshapes and number of signals.

(Assume that  $^1\text{H}$  is 100% abundant,  $I = 1/2$ ;  $^{14}\text{N}$  is 100% abundant,  $I = 1$ ; no other nuclei present significantly affect the spectra.)

(5 marks)

