The character of the irreducible representation A_1 in the C_{3v} point group is given below

	E	$2C_3$	$3\sigma v$
A1	1	1	1

Identify one irreducible representation orthogonal to A_1 among the following.

	E	$2C_3$	$3\sigma v$
Γ1	1	−1	1
Γ2	2	−1	0
Γ3	2	0	−1
Γ4	1	−1	−1

(iii) Sketch the products of the composite operation $\sigma_v C_2$ on pyridazine and pyrimidine.

5 marks

(1c) Simplify the following operations:

(i) $\sigma_h C_2 i^2$ (ii) $\sigma^2 i^8$ (iii) $\sigma_h C_{12}^4 i^4$ **5 marks**

(2a) C_{2h} point group has four symmetry classes and thus, four irreducible representations, which are partly listed in the table below. Derive the missing characters and labels (I – X) on the table. Provide necessary calculations/explanations to support your answers.

C_{2h}	E	C_2	i	σ_h
A_g	1	1	? (I)	? (II)
? (III)	1	-1	1	? (IV)
? (V)	? (VI)	1	? (VII)	-1
B_u	? (VIII)	? (IX)	? (X)	1

10 marks

(2b) D_{2h} molecules have the symmetry elements E, $C_{2(z)}$, $C_{2(y)}$, $C_{2(x)}$, i, $\sigma_{(xy)}$, $\sigma_{(xz)}$ and $\sigma_{(yz)}$.

(i) Write the 3 x 3 transformation matrix for each of the operations.

8 marks

(ii) Write the 3 x 3 transformation matrix for the $\sigma_{(xy)}C_{2(z)}$ operation.

2 marks

SECTION TWO – QUANTUM MECHANICS OF MOLECULES

3. a. – State the Born – Oppenheimer approximation and express it mathematically.

b. Write explicitly the Schrodinger equation for the hydrogen molecule ion.

c. Assume that, for a real system, a real wavefunction is a linear combination of two orthonormal basis functions where the energy integrals are as follows:

$$H_{11} = -15(\text{arbitrary energy units}),\ H_{22} = -4,\ \textit{and}\ H_{12} = H_{21} = -1$$

Given that for the orthonormal wavefunctions, $S_{11} = S_{22} = 1$ and $S_{12} = S_{21} = 0$

Evaluate the approximate energies of the real system, and determine the coefficients of the expansion: $\psi = c_1\phi_1 + c_2\phi_2$

OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE, NIGERIA

DEPARTMENT OF CHEMISTRY

2014/2015 SESSION (RAIN SEMESTER)

MID-SEMESTER EXAMINATION

CHM 310: GROUP THEORY AND QUANTUM MECHANICS OF MOLECULES

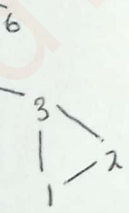
TIME: 1 HR **FEBRUARY, 2016**

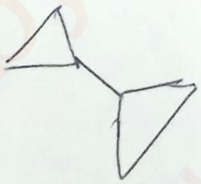
Answer all questions

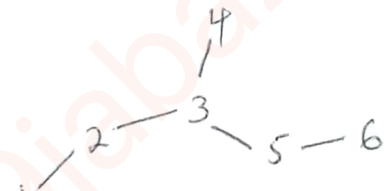
For a one-electron ***heteronuclear*** diatomic molecule the values of some relevant integrals are as given below:

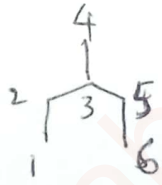
$\int \phi_A \hat{H} \phi_A \, d\tau$ = -2 a.u., $\int \phi_B \hat{H} \phi_B \, d\tau$ = -1 a.u., $\int \phi_A \hat{H} \phi_B \, d\tau$ = -0.5 a.u., $\int \phi_A \phi_B \, d\tau$ = 1/3

where ϕ_A and ϕ_B are normalised set of basis functions for an LCAO wave function. Find the lowest energy that can be computed from the LCAO wave function $\Psi = c_1\phi_A + c_2\phi_B$ and the normalised wave function.









OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE, NIGERIA

DEPARTMENT OF CHEMISTRY

2014/2015 SESSION (RAIN)

MID-SEMESTER EXAMINATION

CHM 310: GROUP THEORY AND QUANTUM MECHNICS OF MOLECULES

TIME: 1 HR **FEBRUARY, 2016**

Answer all questions

Given that the secular equation $(H_{11} - W)c_1 + (H_{12} - WS_{12})c_2 = 0$ has two roots W_1 and W_2. If $W_1 = \frac{H_{11}+H_{12}}{1+S_{12}}$ and $W_2 = \frac{H_{11}-H_{12}}{1-S_{12}}$ determine the value of c_1 and c_2 for the lower energy root.

(**Hint**: H_{12} is negative)

OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE, NIGERIA
BSc (CHEMISTRY) DEGREE EXAMINATION
2014/2015 Rain Semester

CHM 310 –GROUP THEORY AND QUANTUM MECHANICS OF MOLECULES

TIME ALLOWED: 2 hours **DATE: April, 2016**

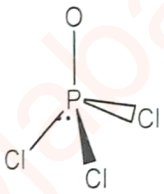
INSTRUCTION: Answer each section in separate booklets.

SECTION A

Answer question 1 and any other one question in this section.

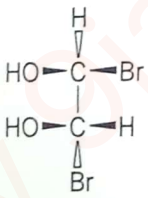
1. (a) List all the symmetry elements and with well-drawn diagram locate as many as possible the elements in the following molecules:

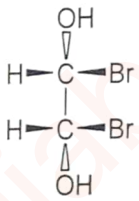
i ii

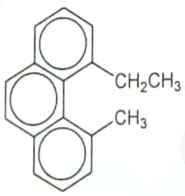


(b) Which of the following molecules are optically active (Give reason(s))? For those which are inactive, state which elements that make the molecule inactive

i. ii. iii

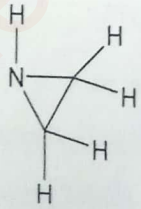




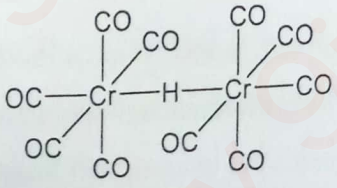


(c) Classify the following molecules into point groups using Schonfile notation. (Give the details of how you arrived at the final answer).

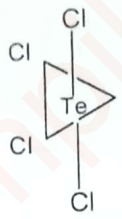
(i) Trans-1-bromo-2chlorethylene



(ii) Aziridine



(iii) $HCr_2(CO)_{10}$



(iv)

(v) O=C=C=O (linear)

(d) (i) Using Molecular orbital theory, deduce which of the following molecules and ions will be most stable.

O_2, O_2^+ and O_2^{2-}

(ii) Give the spectroscopic state for the following molecule/ion: O_2, and O_2^+.(Show how you arrived at each state)

(e) The D_6 point group has the following character table.

D_6 group	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$
A_1	1	1	1	1	1	1
A_2	1	1	1	1	x	-1
B_1	1	Y	1	-1	1	-1
B_2	1	-1	1	-1	-1	1
E_1	2	1	-1	a	0	0
E_2	b	-1	-1	2	0	0

(i) Complete the irreducible representation for B_1 and E_1. i.e find x,y,a and b. (Show how you arrived at the answer).

(ii) Explain the meaning of Mulliken symbols, A, B and E.

30 marks

2. Analysis of the x,y and z coordinates of each atom in boron trichloride (BCl_3) - D_{3h} gives the following representation.

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
Γ	12	0	-2	4	-2	2

(i) Using character table given, reduce Γ to its irreducible representations

(ii) Classify the irreducible representations into translational, rotational and vibrational modes.

(iii) Which vibrational modes are infrared and Raman active?

10 marks

3. For the hydrogen molecule-ion, if the normalized wave functions are

$$\psi_g = (2+2S)^{-1/2}(\phi_a + \phi_b) \text{ and } \psi_u = (2-2S)^{-1/2}(\phi_a - \phi_b)$$

for the bonding and anti-bonding orbitals, prove that the energies for bonding and anti-bonding are:

$$E_g = E_H + \frac{1}{R}(1+S)^{-1}(\varepsilon_{aa} + \varepsilon_{ab}) \text{ and } E_u = E_H + \frac{1}{R}(1-S)^{-1}(\varepsilon_{aa} - \varepsilon_{ab})$$

$$\text{where } \varepsilon_{aa} = \int \phi_a \left(-\frac{1}{r_a}\right)\phi_a d\tau \text{ and } \varepsilon_{ab} = \int \phi_a \left(-\frac{1}{r_b}\right)\phi_b d\tau$$

Show all integral expressions and give the physical interpretation of the integral(s). Assume the atomic orbitals ϕ_a and ϕ_b of the two hydrogen atoms are normalized. State any other assumptions made. [Hint: Electronic Hamiltonian for H_2^+ in atomic unit is $H = -\frac{1}{2}\nabla^2 - \frac{1}{r_a} - \frac{1}{r_b} + \frac{1}{R}$]

10 marks

Character table for D_{3h}

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$	
A_1'	1	1	1	1	1	1	$x^2 + y^2, z^2$
A_2'	1	1	−1	1	1	−1	R_z
E'	2	−1	0	2	−1	0	$(x, y)(x^2 - y^2, xy)$
A_1''	1	1	1	−1	−1	−1	
A_2''	1	1	−1	−1	−1	1	z
E''	2	−1	0	−2	1	0	(R_x, R_y)

SECTION B

Answer question 4 and any other one question in this section

4 (a) Give the Huckel molecular orbital (HMO) diagrams for the following allyl systems and calculate their bond and delocalisation energies: (i) $C_3H_5^+$ (ii) $C_3H_5^{\cdot}$ (iii) $C_3H_5^-$

(b) Give the normalised bonding and antibonding HMO wavefunctions of an allyl system.

(c) What is the significance of the HMO coefficient?

(d) Normalise each of the following symmetry orbital (SO) functions of NH_3 molecule,

i) $\psi_{A_1} = 1/3\,(s_1 + s_2 + s_3)$ ii) $\psi_{E_1} = 1/6\,(2s_1 - s_2 - s_3)$ and iii) $\psi_{E_2} = 1/4b\,(s_2 - s_3)$

(e) Give the character table of irreducible representation of water molecule that adds up only A_1, B_1 and B_2 symmetry types.

20 marks

5 (a) Calculate the bond and delocalisation energies of cyclobutadiene. From your results, determine whether the molecule is stable or not.

(b) Elucidate the skeletal carbon structures corresponding to each of the following determinantal matrices (i) and (ii):

i) $$\begin{vmatrix} x & 1 & 1 & 0 & 0 & 0 \\ 1 & x & 1 & 0 & 0 & 0 \\ 1 & 1 & x & 1 & 0 & 0 \\ 0 & 0 & 1 & x & 1 & 1 \\ 0 & 0 & 0 & 1 & x & 1 \\ 0 & 0 & 0 & 1 & 1 & x \end{vmatrix}$$

ii) $$\begin{vmatrix} x & 1 & 0 & 0 & 0 & 0 \\ 1 & x & 1 & 0 & 0 & 0 \\ 0 & 1 & x & 1 & 1 & 0 \\ 0 & 0 & 1 & x & 0 & 0 \\ 0 & 0 & 1 & 0 & x & 1 \\ 0 & 0 & 0 & 0 & 1 & x \end{vmatrix}$$

c) What are the applications of Quantum mechanics?

15 marks

6 (a) For H_2 molecular system, given the expressions below for J, K and S, calculate the values of E corresponding to each value of R, for R values in the range $1.0 \leq R \leq 10.0$ a.u using the equation $E = 2E_H - \frac{2(J+K)}{1+S} + J + \frac{1}{R}$, and taking E_H to be 0.0 a.u.

$J = \frac{1}{R}[1 - (1+R)e^{-2R}]$, $K = (1+R)e^{-R}$, $S = \left(1 + R + \frac{R^2}{3}\right)e^{-R}$

(b) Plot the E values obtained in **6 (a)** above against R, and determine the following: (i) equilibrium bondlength and (ii) the dissociation energy D_e.

15 marks

OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE

B.Sc. Chemistry Degree Examination

Part III

RAIN SEMESTER EXAMINATION, 2015/2016 SESSION

CHM 310 –GROUP THEORY AND QUANTUM MECHANICS OF MOLECULES

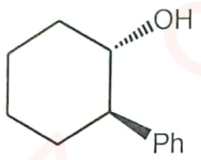
March, 2017 Time: 2hr 30mins

- Answer all questions, each section in a separate booklet

SECTION A

1a. List the symmetry elements and locate with diagram as many of them as possible in the following molecules.

(i)

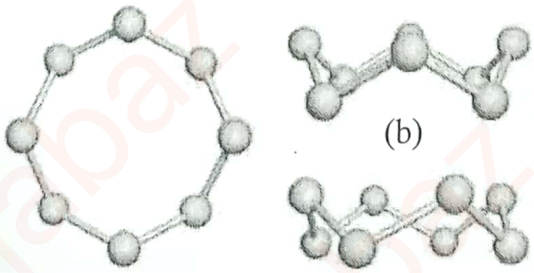


(ii)

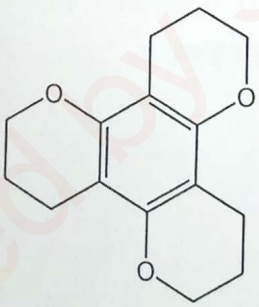
(iii) H_2

b. Determine the point group of each of the following molecules stating clearly how you arrived at your answers.

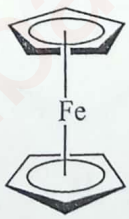
(i) The 3-D cyclic structure of S_8 molecule shown below



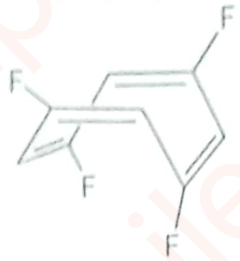
(ii)



(iii) Staggered ferrocene



(iv) 1,3,5,7-tetraflurocyclooctatetraene



c. For compound Eclipsed ferrocene:
   i. What is the order of the group?
   ii. List the various classes and give the number of classes in the point group.

2a. State the Great Orthogonality theorem and define all the notations used in the theorem.

b. The C_{2h} character table is written in part below

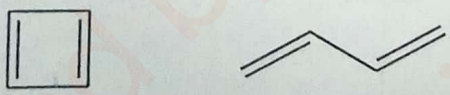
C_{2h}	E	C_2	i	σ_h
A_g	1	1	1	1
A_u	1	1	-1	-1
B_g	1	-1	1	-1
B_u	1	-1	-1	1

   i. Taking the C_2 axis as the z axis, and σ_h to be the xy plane, to what representations do x belong in C_{2h} symmetry?
   ii. To what representations do the d_{xy} orbitals belong in C_{2h} symmetry? Show how you arrived at the representations in both.

c. For this molecule, CH_3Cl (Methyl Chloride):
   i. generate the reducible representation,
   ii. using the appropriate character table, decompose it to irreducible representations, and
   iii. state the vibrational modes that are Infrared and Raman active. **(35 marks)**

SECTION B

3. (a) Construct the Hückel Molecular Orbital (HMO) diagrams for the following conjugated systems and calculate their delocalization energies.



I **II**

(b) From your results in 3(a), predict the stability of each molecule giving the reason(s), and state whether they can be synthesized in the laboratory or not under normal condition.

(c) Given that the bonding (Ψ_B), non-bonding (Ψ_N) and anti-bonding (Ψ_A) MO wave functions of molecule **I** are:

$\Psi_B = \frac{1}{2}\Phi_1 + \frac{1}{2}\Phi_2 + \frac{1}{2}\Phi_3 + \frac{1}{2}\Phi_4$, $\Psi_N = \frac{1}{\sqrt{2}}\Phi_1 - \frac{1}{\sqrt{2}}\Phi_3$ (doubly degenerate) and $\Psi_A = \frac{1}{2}\Phi_1 - \frac{1}{2}\Phi_2 + \frac{1}{2}\Phi_3 - \frac{1}{2}\Phi_4$ respectively, determine whether there are any of these orbitals which can undergo transitions between one another, and calculate the corresponding ΔE value(s) between them.

(d) calculate the wavelength (in terms of β) of an (HOMO-1) → LUMO transition with ΔE of $2.24|\beta|$ J. ($h = 6.626 \times 10^{-34}$ J.s, $c = 3.0 \times 10^{8}$ ms^{-1}). In which of the butadienes **I** and **II** (in 3a above) will this transition occur? **(25 marks)**

4. (a) Elucidate the skeletal carbon structure corresponding to each of the following determinantal matrices:

i)
$$\begin{vmatrix} x & 1 & 0 & 0 & 0 & 0 \\ 1 & x & 1 & 0 & 0 & 1 \\ 0 & 1 & x & 1 & 0 & 0 \\ 0 & 0 & 1 & x & 1 & 0 \\ 0 & 0 & 0 & 1 & x & 1 \\ 0 & 1 & 0 & 0 & 1 & x \end{vmatrix}$$

ii)
$$\begin{vmatrix} x & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 \\ 1 & x & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & x & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & x & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & x & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 1 & x & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & x & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & x & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & x & 1 \\ 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & x \end{vmatrix}$$

(b) The one-electron ion, H_2^+, has the wave function $\psi = c_1\phi_1 + c_2\phi_2$, where ϕ_1, ϕ_2 are normalized 1s orbitals and c_1, c_2 are coefficients of the linear combination of the two hydrogen atomic orbitals,

i) what is the physical interpretation of c_1, c_2?

ii) what is the normalization restriction on the values of c_1, c_2? (i.e give an equation that links c_1 to c_2) **(10 marks)**

C_3	E	$2C_3$		
A	1	1	z, R_z	$x^2 + y^2$, z^2
E	2	−1	(x, y), (R_x, R_y)	$(x^2 - y^2, xy)$, (xz, yz)

C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	$x^2 + y^2$, z^2
A_2	1	1	−1	R_z	
E	2	−1	0	(x, y), (R_x, R_y)	$(x^2 - y^2, xy)$, (xz, yz)

C_{3h}	E	$2C_3$	σ_h	$2S_3$		
A'	1	1	1	1	R_z	$x^2 + y^2$, z^2
E'	2	−1	2	−1	(x, y)	$(x^2 - y^2, xy)$
A''	1	1	−1	−1	z	
E''	2	−1	−2	1	(R_x, R_y)	(xz, yz)

D_3	E	$2C_3$	$3C_2$		
A_1	1	1	1		$x^2 + y^2$, z^2
A_2	1	1	−1	z, R_z	
E	2	−1	0	(x, y), (R_x, R_y)	$(x^2 - y^2, xy)$, (xz, yz)

Department of Chemistry, Faculty of Science

OBAFEMI AWOLOWO UNIVERSITY

ILE-IFE, NIGERIA

RAIN SEMESTER, 2016/2017 SESSION

CHM 310: GROUP THEORY AND QUANTUM MECHANICS OF MOLECULES

JANUARY 2018 **TIME: $1\frac{1}{4}$ HR**

1. Given that the secular equation $(H_{AA} - E)c_1 + (H_{AB} - ES_{AB})c_2 = 0$ has two roots E_1 and E_2. If $E_1 = (H_{AA} + H_{AB})/(1 + S_{AB})$ and $E_2 = (H_{AA} - H_{AB})/(1 - S_{AB})$, determine the values of c_1 and c_2 for the lower energy root. (**15 marks**)

2. The values of some relevant integrals for a one-electron *heteronuclear* diatomic molecule are given below:

$\int \phi_A \hat{H} \phi_A d\tau = -2$ a.u. , $\int \phi_B \hat{H} \phi_B d\tau = -1$ a.u. , $\int \phi_A \hat{H} \phi_B d\tau = -0.5$ a.u. , $\int \phi_A \phi_B d\tau = 1/3$ a.u., where ϕ_A and ϕ_B are normalized set of basis functions for an LCAO wave function. Find the lowest energy that can be computed from the normalized LCAO wave function and, the c_1 and c_2 in the wave function corresponding to this energy. (**15 marks**)

(**Hint**: For the LCAO, $\Psi = c_1\phi_A + c_2\phi_B$)

OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE

B.Sc. Chemistry Degree Examination

Part III

RAIN SEMESTER EXAMINATION 2017/2018 SESSION

CHM 310 –GROUP THEORY AND QUANTUM MECHANICS OF MOLECULES

December, 2018 Time: 1 hr

1. (a) Given that the secular equation $(H_{AA} - E)c_1 + (H_{AB} - ES_{AB})c_2 = 0$ for a normalized wave function has two roots E_1 and E_2. If $E_1 = (H_{AA} + H_{AB})/(1 + S_{AB})$ and $E_2 = (H_{AA} - H_{AB})/(1 - S_{AB})$, determine the values of c_1 and c_2 for the lower energy root.

[5 marks]

(b) The values of some relevant integrals for a one-electron ***heteronuclear*** diatomic molecule are given below:

$\int \phi_A \hat{H} \phi_A d\tau = -2$ a.u., $\int \phi_A \hat{H} \phi_B d\tau = -0.5$ a.u, $\int \phi_B \hat{H} \phi_B d\tau = -1$ a.u, $\int \phi_A \phi_B d\tau = \frac{1}{3}$ a.u

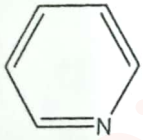
where ϕ_A and ϕ_B are normalized set of basis functions for an LCAO wave function. Find the minimum electronic energy for this system and the corresponding normalized wave function. (**Hint**: For the LCAO, $\Psi = c_1\phi_A + c_2\phi_B$)

[10 marks]

2. (a) Simplify the following symmetry operations:

(i) $C_{10}^5 C_8^4$ (ii) $\sigma^5 i^4$ (iii) S_5^5 (iv) $C_6^5 C_{12}^2 i^5$

(b) List the basic symmetry elements present in each of the following molecules/objects. Hence, determine their point group using the Schoeflies symbols:



(i)

B_5H_9 (Square pyramidal)

(ii)

a fluorescent lamp

(iii)

(iv)

3. (a) Draw all the possible isomeric structure(s) of diiodobenzene that correspond(s) to:
(i) zero dipole moment (ii) non-zero dipole moment.
(b) Show the directions of bonds polarity and the direction of the overall dipole moment in the structures with non-zero dipole.
(c) Determine the point group of each of the molecules in 3(a) above.

[15 marks]

OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE, NIGERIA

DEPARTMENT OF CHEMISTRY

2018/2019 SESSION

MID-RAIN SEMESTER EXAMINATION

CHM 310: GROUP THEORY AND QUANTUM MECHANICS OF MOLECULES

TIME ALLOWED: 1½ HRS **NOVEMBER, 2019**

Instructions: Attempt all questions

1 (a) Construct the Hückel Molecular Orbital (HMO) diagrams for the following conjugated systems and calculate their delocalization energies.

I

II

(b) From your results in 1(a), predict the stability of each molecule giving the reason(s), and state whether they can be synthesized in the laboratory under normal condition or not.

2(a) Given that the bonding (Ψ_B), non-bonding (Ψ_N) and antibonding (Ψ_A) MO wave functions of molecule I are respectively

$\Psi_B = \frac{1}{2}\phi_1 + \frac{1}{2}\phi_2 + \frac{1}{2}\phi_3 + \frac{1}{2}\phi_4$, $\Psi_N = \frac{1}{\sqrt{2}}\phi_1 - \frac{1}{\sqrt{2}}\phi_3$ (doubly degenerate) and

$\Psi_A = \frac{1}{2}\phi_1 - \frac{1}{2}\phi_2 + \frac{1}{2}\phi_3 - \frac{1}{2}\phi_4$. Determine whether there can be any coupling interactions (transitions) between any of the orbitals, and calculate the corresponding ΔE value(s).

15 marks

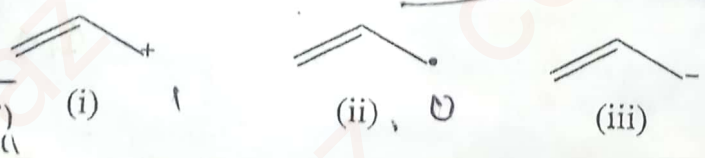
OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE, NIGERIA
DEPARTMENT OF CHEMISTRY
B.Sc. Degree (Chemistry) Examination Part III
CHM 310: Group Theory and Quantum Mechanics of Molecules
2018/2019 Rain Semester

TIME ALLOWED: 2½ hours **DATE: December, 2019**

INSTRUCTION: Attempt all questions. Answer each section in separate booklets

SECTION A

1(a) Construct the Hückel molecular orbital (HMO) diagrams for the following allyl systems and calculate their π-bond and resonance stabilization energies:



(i) (ii) (iii)

(b) From the results obtained in **1(a)**, predict the stability of each allyl system.

(c) Deduce the normalized bonding (ψ_B), nonbonding (ψ_N) and antibonding (ψ_A) HMO wavefunctions of any of the allyl systems described in **1(a)**.

(d) From the deduced molecular orbital (MO) wavefunctions in **1(c)**, determine whether there can be any coupling interaction (transitions) between the orbitals and calculate the corresponding ΔE value(s), taking the allyl (*i*) as prototype and assuming that a mirror plane is placed on the middle carbon of this system (*i*).

[15 marks]

2(a) Normalize the following orbital function for a molecule of the type AB_3: $\psi_{1/3} = 1/3(\phi_1 + \phi_2 + \phi_3)$.

(b) Show that the spin function, $\chi(s) = \alpha(1)\beta(2) - \alpha(2)\beta(1)$ associated with the antisymmetric wavefunction of a two-electron molecular system is an eigenfunction of the spin operator $\hat{S}^2$.

(c) Elucidate the skeletal carbon structures corresponding to each of the following determinantal matrices (i) and (ii):

(i)

	1	2	3	4	5	6
1	x	1	1	0	0	0
2	1	x	1	0	0	0
3	1	1	x	1	0	0
4	0	0	1	x	1	1
5	0	0	0	1	x	1
6	0	0	0	1	1	x

(ii)

	1	2	3	4	5	6
1	x	1	0	0	0	0
2	1	x	1	0	0	0
3	0	1	x	1	1	0
4	0	0	1	x	0	0
5	0	0	1	0	x	1
6	0	0	0	0	1	x

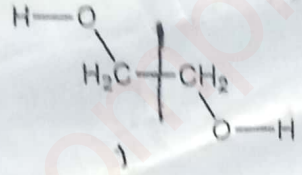
(d) What is the significance of the HMO coefficient?

[15 marks]

SECTION B

(3a) List all the symmetry elements that exist in each of the following molecules

(i) 1,3-dichlorobenzene (ii) 1,4-dichlorobenzene

(iii) 

(iv) BH_3 (planar)

(3b) Based on the symmetry elements listed in **3(a)** above, deduce

(i) the point groups of the molecules.

(ii) with reason, which of the molecules have non-zero dipole moment.

(3c) Write a 3X3 matrix representing each of the following operations in the point group C_{3h}

(i) E (ii) C_3 (iii) C_3^2 (iv) σ_h (or σ_{xy}) and (v) S_3

[17 Marks]

(4a) The four irreducible representations of the point group C_{2h} are partially provided in the character table below.

C_{2h}	E	C_2	i	σ_h
A_g				
B_g				
A_u				
B_u	1	-	-	1

(i) What are the order and class of the group?

(ii) Briefly explain the nomenclature of the irreducible representations, i.e. A_g, B_g, A_u, and B_u.

(iii) Copy the table and supply the missing characters. Provide reasons and/or show necessary calculations for arriving at each character.

(4b) O_2, O_2^+, O_2^- and O_2^{2-} all belong to the D_{2h} symmetry group. The respective bond lengths of the species are 1.2074 Å, 1.1227 Å, 1.2800 Å, and 1.4900 Å.

(i) Write the ground state molecular electronic configuration for each of the species.

(ii) Deduce the bond order for each of the species and hence, arrange the species in increasing order of stability.

(iii) Correctly assign the species as either diamagnetic or paramagnetic. Give reason(s) for your answers.

[18 Marks]

Department of Chemistry

OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE

Part III B.Sc. Chemistry Degree Examination

RAIN SEMESTER EXAMINATION, 2022/2023 SESSION

CHM 310 – Group Theory and Quantum Mechanics of Molecules

DATE: 11TH JULY, 2024 **TIME ALLOWED: 2½ Hrs**

INSTRUCTION: Attempt All Questions. Provide answers to new questions on a fresh page. Do not muddle up your answers. Constant: 1 Debye = 3.335×10^{-30} C m

SECTION A

1. (a.) Describe how molecular orbitals are formed using the molecular orbital theory for molecular structure

   (b.) From (a) above, explain what you understand by:

   i. Bonding orbital

   ii. Antibonding orbital

   (c.) Normalize the molecular orbital $\psi_A + \lambda\psi_B$ in terms of the parameter λ and the overlap integral S.

   (d.) Arrange the species O_2^+, O_2, O_2^-, O_2^{2-} in order of increasing bond length.

2. (a.) With appropriate mathematical expression(s) only, define the following terms:

   i. Coulomb integral

   ii. Resonance integral

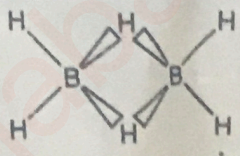
   iii. Overlap integral

   (b.) What are the approximations involved in the Hückel molecular orbital theory in terms of the resonance and overlap integrals.

   (c.) For a hypothetical heteronuclear molecule XY, the X-Y bond moment is 0.68 D and the bond length is 1.34 Å. Write out the expression for the LCAO molecular wavefunction, based on the LCAO approach, for this molecule.

SECTION B

3. (a) Draw the following chemical structures and mark out with a line, their principal axes of rotation. List all the symmetry elements and determine their point groups.

   (i) $H_2C{=}C{=}CH_2$ (ii) $H_2C{=}C{=}C{=}CH_2$ (iii)  (iv) ammonia

   (b) What is the order of the group determined for each of the chemical structures in 3(a)?

(c) Which of the following molecules: BH_2Cl, CH_3Cl, NH_2Cl, and HOCl will possess a C_2 axis of symmetry?

(d) (i) What is the result of the operation $\sigma_{xy}C_2^x\begin{bmatrix}x\\y\\z\end{bmatrix}$, where C_2^x is a 180° rotation about the x axis and σ_{xy} is a reflection through the x-y plane? Hint: Assume $\begin{bmatrix}x\\y\\z\end{bmatrix}$ to be the position vector of a certain molecule in space.

(ii) Which of the following symmetry operations; σ_{xz}, σ_{yz}, C_2^y, and C_2^z, is equivalent to the result of the transformation in 3(d)(i) ?

[15 marks]

4. (a) Simplify the operation $\sigma_{xy}S_4^z$; given that S_4^z is a four-fold improper rotation about z axis and σ_{xy} is a reflection through the x-y plane.
   (b) Show that $S_2 = C_2^z\sigma_{xy} = i$ using the matrix method.
   (c) Define the following Mulliken symbols: (i) A_1 (ii) B_2 (iii) A_u (iv) B_g
   (d) The character table of the point group C_{2v} are partially provided below:

C_{2v}	E	C_2	σ_v	σ_v'	Linear and rotational functions	Quadratic function
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2		1	-1		R_z	xy
B_1		-1		-1	x, R_y	xz
B_2			-1	1	y, R_x	yz

(i) Copy and supply the missing characters. Provide the reasons and/or show the necessary calculation for arriving at each missing value.
(ii) Using the completed character table, and given that it is the same as the irreducible representation for water molecule, determine (by showing all the calculation steps) the number of IR and Raman active modes in water.

[15 marks]

OBAFEMI AWOLOWO UNIVERSITY, ILE IFE, NIGERIA

DEPARTMENT OF CHEMISTRY

CHM 310 - GROUP THEORY AND QUANTUM MECHANICS OF MOLECULES

TEST ON QUANTUM MECHANICS OF MOLECULES

TIME ALLOWED - 50 MINUTES

a. The Schrödinger equation for the hydrogen molecule can be written in the form:

$$\hat{H}\psi(r_1, r_2, R) = E_{el}\psi(r_1, r_2, R)$$

i. Explain each term in the equation above with the aid of a suitable diagram

ii. Write the complete expression for the Hamiltonian for a hydrogen molecule

b. The bond energy in C_2^- is 2.2 eV greater than that of C_2 but the bond energy of O_2^- is 1.1 eV less than that of O_2. Explain this difference.

c. The Huckel molecular orbital approximation gave the following solutions for the secular equations associated with 1,3-butadiene as:

$$\frac{\alpha - E}{\beta} = \pm 1.62 \text{ and } \pm 0.618$$

i. Draw the energy level diagram arising from the Huckel molecular orbital approximations for this molecule [Hint: Both α and β are negative]

ii. If the corresponding molecular orbital wavefunctions are:

$$\psi_1 = 0.372\phi_1 + 0.602\phi_2 + 0.602\phi_3 + 0.372\phi_4$$
$$\psi_2 = 0.602\phi_1 + 0.372\phi_2 - 0.372\phi_3 - 0.602\phi_4$$
$$\psi_3 = 0.602\phi_1 - 0.372\phi_2 - 0.372\phi_3 + 0.602\phi_4$$
$$\psi_4 = 0.372\phi_1 - 0.602\phi_2 + 0.602\phi_3 - 0.372\phi_4.$$

Calculate the electron density on each carbon atom.

QBAFEMI AWOLOWO UNIVERSITY, ILE-IFE, NIGERIA
DEPARTMENT OF CHEMISTRY
B.Sc. Degree (Chemistry) Examination Part III
CHM 310: Group Theory and Quantum Mechanics of Molecules
2023/2024 Rain Semester

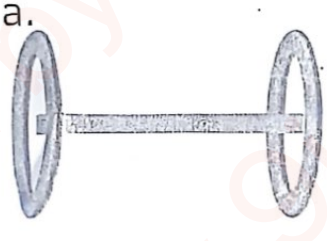
TIME ALLOWED: 30 mins **DATE:** June, 2025

INSTRUCTION: Attempt all questions.

1.) List all the symmetry elements in the following molecular materials and suggest their correct point groups;

b. BH_3 (planar) c. NH_3

a.



by any means possible

2.) Show that S_2 is equivalent to i.

OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE, NIGERIA
B.Sc. (CHEMISTRY) DEGREE EXAMINATION
RAIN SEMESTER EXAMINATION, 2023/2024 SESSION

CHM 310: Group Theory and Quantum Mechanics of Molecules

TIME ALLOWED: $2\frac{1}{2}$ **Hrs** **DATE: Friday, 11th July 2025**

INSTRUCTIONS: Attempt All Questions. Provide answers to new questions on a fresh page. Do not muddle up your answers.

CONSTANT: $h = 6.626 \times 10^{-34}$ J s; $c = 2.998 \times 10^{8}$ m s^{-1}; 1 Debye $= 3.335 \times 10^{-30}$ C m; 1eV = 8065.54 cm^{-1}

SECTION A

1. (a) Explain the following terms (NOT MORE THAN TWO LINES EACH)

i. Bond dissociation energy
ii. Bond length
iii. Bond order
iv. How (i) and (ii) are related to (iii) **[4 marks]**

(b) Suppose that a diatomic molecule *XZ* contains a single σ bond. The binding energy of an electron in the valence shell of atom X is -10.0 eV. Spectroscopically it is observed that promotion of an electron to the antibonding state leads to an absorption band at 16,100 cm^{-1}. Using a value of 0.10 for the overlap integral, determine

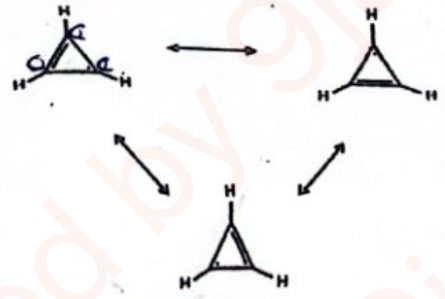
i. the value of the exchange integral. **[10 marks]**
ii. the actual energies of the bonding and antibonding states. **[4 marks]**

2. (a) Write the mathematical expression for the following:

i. Coulomb integral
ii. Exchange integral
iii. Overlap integral **[4 marks]**

(b) Write the complete Hamiltonian for the hydrogen molecule ion, H_2^+, with the aid of a suitable diagram.

(c) For the cyclopropenyl system depicted below;



i. Give the form of the secular determinant for this system [Hint: $x = (\alpha - E)/\beta$] **[3 marks]**

ii. Obtain and solve the characteristic equation for the secular determinant in (i) above [Hints: Try rational roots] **[3 marks]**

iii. Draw the molecular orbital energy diagram for the radical, cation and the anion, showing the occupancy **[6 marks]**

iv. If the corresponding molecular orbital wave functions are:

$$\psi_1 = \frac{1}{\sqrt{3}}(\phi_1 + \phi_2 + \phi_3)$$

$$\psi_2 = \frac{1}{\sqrt{6}}(2\phi_1 - \phi_2 - \phi_3)$$

$$\psi_3 = \frac{1}{\sqrt{2}}(\phi_2 - \phi_3)$$

Find the electron density for each of the carbon atoms in the cyclopropenyl CATION **[6 marks]**

SECTION B

3. (a) Draw the following chemical structures and mark out with a line, their principal axes of rotation. List all the symmetry elements and determine their point groups.

(i.) BF_3 (planar) (ii.) CO_2 (iii.) trans-1,2-dichloroethene

(b) What is the order of the group determined for each of the chemical structures in 3(a)?

(c) Which of the following molecules: H_2O_2 (skew conformation), $CHCl_3$, C_2H_4, and NOCl will possess a C_2 axis of symmetry?

(d) (i) Given a molecular position vector $\vec{r} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}$, evaluate the effect of the combined symmetry operation $C_2^y \sigma_{yz} i\vec{r}$, where i is an inversion through the position vector, σ_{yz} is reflection through the yz-plane and C_2^y is a 180° rotation about the y-axis. Provide the final coordinates of the transformed vector and show whether the following order, $\sigma_{yz} C_2^y i$, $i\sigma_{yz} C_2^y$, and $\sigma_{yz} i C_2^y$, of applying the operations affect(s) the outcome. Hint: Consider $\vec{r}$ as the spatial coordinate of an atom within a molecular framework.

[15 marks]

4. (a) In not more than five lines, explain what is meant by a *group* in quantum mechanics.

(b) Show that $S_1 = \sigma$ using any one method that is most convenient for you.

(c) The character table of cis-1,2-dichloroethene is partially provided below:

C_{2v}	E	C_2	σ_v (xz)	σ_v' (yz)	Linear and rotational functions	Quadratic function
A_1	1	1	a	1	z	x^2, y^2, z^2
A_2	1	1	-1	b	R_z	xy
B_1	1	-1	c	-1	x, R_y	xz
B_2	1	d	-1	1	y, R_x	yz

(i) Copy and supply the missing characters, showing the necessary calculation to arriving at the correct missing value.

(ii) Using the completed character table, determine (by showing all the calculation involved) the number of IR and Raman active modes in cis-1,2-dichloroethene.

(d) Provide the matrix equivalent of an S_3 operation.

[15 marks]

$1 + 1 + 1 + b = 0$

$2 - 1 + b = 0$

$1 + b = 0$

$b = -1$

1	1	1	1
1	1	−1	−1

+	+	+
+	−	+
−	+	−
−	−	+

$$\begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

E	C_n	i	σ_n	S_n
3	$2\cos\theta + 1$	−3	1	$2\cos\theta - 1$