Chemistry 6330

Fall Semester 1 2019

Midterm Exam

Name: Key

Question 1: ________ pts / 20 pts

Question 2: ________ pts / 25 pts

Question 3: ________ pts / 25 pts

Question 4: ________ pts / 10 pts

Question 5: ________ pts / 10 pts

Question 6: ________ pts / 10 pts

TOTAL: _______ PTS / 100 PTS

Name: Key

(1) [20 pts] Consider a group of order 7.

(a) [15 pts] Build a group multiplication table for the group.

{E, A, B, C, D, F, G}

	E	A	B	C	D	F	G
E	E	A	B	C	D	F	G
A	A	B	C	D	F	G	E
B	B	C	D	F	G	E	A
C	C	D	F	G	E	A	B
D	D	F	G	E	A	B	C
F	F	G	E	A	B	C	D
G	G	E	A	B	C	D	F

(b) [3 pts] Is this group cyclic? Justify your answer by showing your work.

Yes; a cyclic group is one in which all elements commute. This is true above, e.g. AB = BA = C, CF = A = FC, etc.

(c) [2 pts] How many subgroups are in this group?

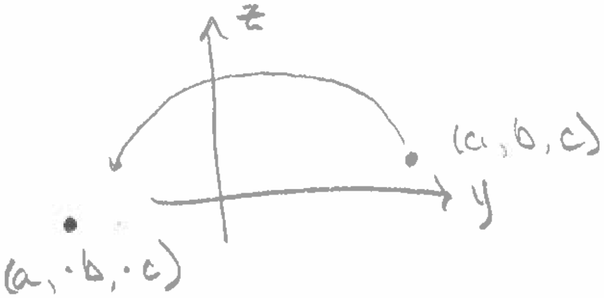
The order of a sub-group, g, must be an integer divisor of the order of the larger group, h.

Given h=7, a prime number, only 7 and 1 are possible values for g. Given h=7, g=7 is just the group, and the element {E} is the only one which completes a group of order 1.

Name: Key

(2) [25 pts] Consider the symmetry elements C_2^x and σ_z.

(a) [3 pts] Consider a rotation about the C_2^x axis operating on a general Cartesian point (a,b,c). What is the Cartesian coordinate of the transformed point? Show your work.

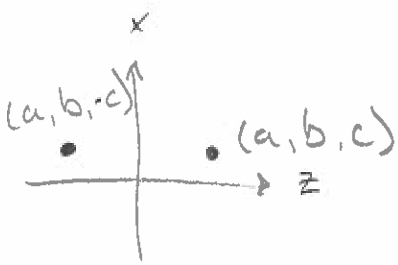


$$\begin{bmatrix} a \\ b \\ c \end{bmatrix} \rightarrow \begin{bmatrix} a \\ -b \\ -c \end{bmatrix}$$

(b) [3 pts] What is the transformation matrix for applying this C_2^x operator?

$$\underset{3\times 3}{\begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}} \underset{3\times 1}{\begin{bmatrix} a \\ b \\ c \end{bmatrix}} \longrightarrow \underset{3\times 1}{\begin{bmatrix} a \\ -b \\ -c \end{bmatrix}}$$

(c) [3 pts] Consider reflection through the σ_z plane operating on a general Cartesian point (a,b,c). What is the Cartesian coordinate of the transformed point? Show your work.



$\sigma_z = \sigma_{xy}$

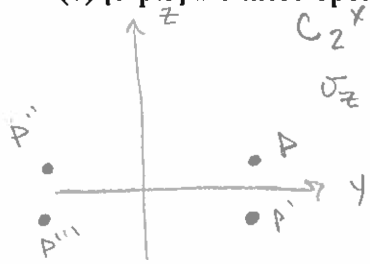
$$\begin{bmatrix} a \\ b \\ c \end{bmatrix} \longrightarrow \begin{bmatrix} a \\ b \\ -c \end{bmatrix}$$

(d) [3 pts] What is the transformation matrix for applying the σ_z operator?

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} a \\ b \\ c \end{bmatrix} \longrightarrow \begin{bmatrix} a \\ b \\ -c \end{bmatrix}$$

Name: Key

(e) [3 pts] Do these operations commute? Show your work.



$C_2^x \cdot \sigma_z(P) \rightarrow C_2^x(P') \rightarrow P''$

$\sigma_z \cdot C_2^x(P) \rightarrow \sigma_z(P''') \rightarrow P''$

Yes, they commute

$C_2^x \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}\begin{bmatrix} a \\ b \\ c \end{bmatrix} \rightarrow \begin{bmatrix} a \\ -b \\ -c \end{bmatrix}$

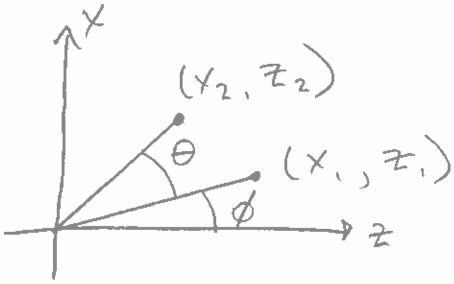
$\sigma_z \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}\begin{bmatrix} a \\ -b \\ -c \end{bmatrix} \rightarrow \begin{bmatrix} a \\ -b \\ c \end{bmatrix}$

OR

$\sigma_z \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}\begin{bmatrix} a \\ b \\ c \end{bmatrix} \rightarrow \begin{bmatrix} a \\ b \\ -c \end{bmatrix}$

$C_2^x \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}\begin{bmatrix} a \\ b \\ -c \end{bmatrix} \rightarrow \begin{bmatrix} a \\ -b \\ c \end{bmatrix}$

(f) [10 pts] Derive the generalized transformation matrix for a C_n rotation around the y axis. Show your work.



$x_1 = r\sin\phi$

$z_1 = r\cos\phi$

$$x_2 = r\sin(\theta+\phi) = \underbrace{r\sin\phi}_{x_1}\cos\theta + \underbrace{r\cos\phi}_{z_1}\sin\theta = x_1\cos\theta + z_1\sin\theta$$

$$z_2 = r\cos(\theta+\phi) = \underbrace{r\cos\phi}_{z_1}\cos\theta - \underbrace{r\sin\phi}_{x_1}\sin\theta = z_1\cos\theta - x_1\sin\theta$$

$$\underset{2\times2}{\begin{bmatrix} ? \end{bmatrix}}\begin{bmatrix} x_1 \\ z_1 \end{bmatrix} = \begin{bmatrix} x_1\cos\theta + z_1\sin\theta \\ -x_1\sin\theta + z_1\cos\theta \end{bmatrix} = \begin{bmatrix} x_2 \\ z_2 \end{bmatrix}$$

$$? = \begin{bmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{bmatrix}$$

Now include y axis. under C_n^y, y value does not change, so $y_1 = y_2$

$$\begin{bmatrix} \cos\theta & 0 & \sin\theta \\ 0 & 1 & 0 \\ -\sin\theta & 0 & \cos\theta \end{bmatrix}\begin{bmatrix} x_1 \\ y_1 \\ z_1 \end{bmatrix} = \begin{bmatrix} x_2 \\ y_1 \\ z_2 \end{bmatrix}$$

Generalizing for a C_n $\longrightarrow$ $\begin{bmatrix} \cos\frac{2\pi}{n} & 0 & \sin\frac{2\pi}{n} \\ 0 & 1 & 0 \\ -\sin\frac{2\pi}{n} & 0 & \cos\frac{2\pi}{n} \end{bmatrix}$

Name: Key

(3) (a) [20 pts] A blank character table for the D_{3h} symmetry point group is shown below. Use your knowledge of the properties of groups and representations to generate the five irreducible representations A_1, A_2, B_1, B_2, and E. Show your work (i.e. explain how you arrived at answers)!

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	(xz,yz)
E''	2	-1	0	-2	1	0	(R_x,R_y)	

→ The sum of the squares of the characters under "E" give dimensions. A reps → 1, E reps → 2 (2 pts.)

→ "A" indicates symmetry w.r.t. PAR, which is C_3 in D_{3h} point group. All "A" reps have 1 under $2C_3$ column (2pts.)

→ 1 subscript indicates symmetry w.r.t. $C_2 \perp C_3$. A_1' and A_1'' get "1" under $3C_2$, A_2' and A_2'' get -1. (2 pts.)

→ ' indicates $\chi > 0$ under σ_h, '' indicates $\chi < 0$ under σ_h. A_1' and A_2' get 1, A_1'' and A_2'' get -1, E' must be a positive character and E'' must be negative (2 pts.)

→ A_1' is a fully symmetric rep, all characters are 1 (2pts

→ Use orthogonality to complete the remaining 1-D reps. (5pts

Ex. $\Gamma^{A_1'} \cdot \Gamma^{A_2'}$ $0 = (1)(1)(1) + (2)(1)(1) + (3)(1)(-1) + (1)(1)(1) + (2)(1)(x) + (3)(1)(y)$

$0 = 1 + 2x + 3y$, x and y must be ± 1

Only possibility is $x = +1, y = -1$

(Cont. on scratch paper)

Name: Key

(b) [5 pts] Consider the partially filled out character table for the D_{3d} symmetry point group, shown below. Fill in the Mullikan symbols for each irreducible representation (Γ_1-Γ_6). Justify your answers below.

D_{3d}	D_{3d}	E	2 C_3	3 C_2	i	2 S_6	$3\sigma_d$		
Γ_1	A_{1g}	1	1	1	1	1	1		$x^2 + y^2, z^2$
Γ_2	A_{2g}	1	1	-1	1	1	-1	R_z	
Γ_3	E_g	2	-1	0	2	-1	0	(R_x, R_y)	$(x^2 - y^2, xy)$ (xz,yz)
Γ_4	A_{1u}	1	1	1	-1	-1	-1		
Γ_5	A_{2u}	1	1	-1	-1	-1	1	z	(xz,yz)
Γ_6	E_u	2	-1	0	-2	1	0	(x,y)	

- Under E column, the dimensions of the matrices are given. Γ_3 and Γ_6 are two-dimensional and receive the symbol "E".

- Γ_1, Γ_2, Γ_4, and Γ_5 are one-dimensional and will receive "A" or "B" symbols. The P.A.R. in the D_{3d} point group is the C_3-axis. All four Γ_n have "+1" under the C_3 column, therefore all are "A"

- 1 vs 2 must be determined for the one-dimensional reps. This is determined by a $C_2 \perp C_3$. Γ_1 and Γ_4 are symmetric w.r.t. C_2 and therefore get "1" subscript. Γ_2 and Γ_5 are antisymmetric w.r.t. C_2 and get "2"

- g vs. u is determined by symmetry w.r.t. i operation. Γ_{1-3} have positive values and receive "g", Γ_{4-6} have negative values and receive "u".

→ Use orthogonality and the rule that the sum of the squares of characters in a rep., multiplied by the coefficient in front of classes, must equal h to complete the 2-D reps. (5pts)

Ex. Fill in the E' rep in a way that satisfies the rule above, $\sum_R \{\chi_i(R)\}^2 = h$

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
E'	2	1	1	1	1	0

Check orthogonality with A_1':

$\Gamma^{A_1'} \cdot \Gamma^{E'}$ $\quad 0 = (1)(1)(2) + (2)(1)(1) + (3)(1)(1) + (1)(1)(1) + (2)(1)(1) + (3)(1)(0)$

$0 = 2 + 2 + 3 + 1 + 2$

Now manipulate signs to satisfy above equation, remembering χ under σ_h must be positive.

$0 = 2 + -2 + -3 + 1 + 2$ ✓

E' rep now looks like:

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
E'	2	-1	-1	1	1	0

Check orthogonality with A_2':

$\Gamma^{A_2'} \cdot \Gamma^{E'}$ $\quad 0 = (1)(1)(2) + (2)(1)(-1) + (3)(-1)(-1) + (1)(1)(1) + (2)(1)(1) + (3)(-1)(0)$

$0 \neq 2 + -2 + 3 + 1 + 2$

E' is not orthogonal to A_2' in this configuration.

Return to attempt to fill in characters in a manner that satisfies $\sum_R \{\chi_i(R)\}^2 = h$

Name: ______________________________

ADDITIONAL BLANK PAPER FOR WORK - Do not turn in final answers on this sheet.

One possibility is to move the "1" under $3C_2$ to $3\sigma_v$ and put a "0" below $3C_2$. This would satisfy $\sum_R \{\chi_i(R)\}^2 = h$ but upon inspection of the characters of A_2' the same issue of orthogonality would be encountered.

The only other possibility is:

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
E'	2	1	0	2	1	0

$1 \cdot 2^2 + 2 \cdot 1^2 + 3 \cdot 0^2 + 1 \cdot 2^2 + 2 \cdot 1^2 + 3 \cdot 0^2 = 12 = h$ ✓

Check orthogonality with A_1':

$\Gamma^{A_1'} \cdot \Gamma^{E'}$ $\quad 0 = (1)(1)(2) + (2)(1)(1) + (3)(1)(0) + (1)(1)(2) + (2)(1)(1) + (3)(1)(0)$

$0 = 2 + 2 + 0 + 2 + 2 + 0$

Manipulate signs - note that E and σ_h must be positive

$0 = 2 + -2 + 0 + 2 + -2 + 0$ ✓

E' rep is now:

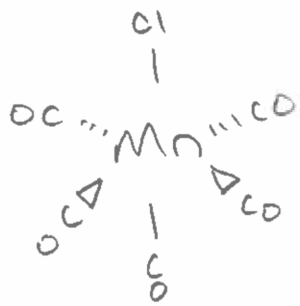
D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
E'	2	-1	0	2	-1	0

Verify that this rep is orthogonal with the other 1-D reps (it is), then repeat the process with E''.

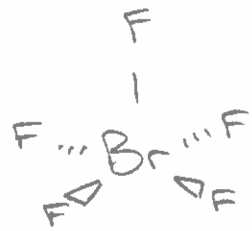
Name: Key

(4) [10 pts] Consider the C_{4v} symmetry point group.

(a) [2 pts] Draw a molecule that exhibits C_{4v} symmetry.



$[MnCl(CO)_5]$



BrF_5

etc.

(b) [8 pts] Identify all the symmetry elements and symmetry operations of the molecule (it may help to draw them on the molecule).

$E \quad \underbrace{C_4 \quad C_4^3}_{2C_4} \quad C_2 \quad \underbrace{\sigma_v \quad \sigma_v'}_{2\sigma_v} \quad \underbrace{\sigma_d \quad \sigma_d'}_{2\sigma_d}$

Name: Key

(5) [10 pts] The following questions pertain to the D_{4d} point group (character table included).

(a) [2 pts] Find the direct product $E_2 \bullet A_2$.

E_2	2	0	-2	0	2	0	0
A_2	1	1	1	1	1	-1	-1
$E_2 \bullet A_2$	2	0	-2	0	2	0	0

(b) [2 pts] Find the direct product $E_1 \bullet E_3$.

E_1	2	$\sqrt{2}$	0	$-\sqrt{2}$	-2	0	0
E_3	2	$-\sqrt{2}$	0	$\sqrt{2}$	-2	0	0
$E_1 \bullet E_3$	4	-2	0	-2	4	0	0

(c) [6 pts] Reduce your answer in (b) to a sum of irreducible representations.

$B_1: \frac{1}{16}[(1)(1)(4) + (2)(-1)(-2) + 0 + (2)(-1)(-2) + (1)(1)(4) + 0 + 0] = 1$

$B_2: \frac{1}{16}[(1)(1)(4) + (2)(-1)(-2) + 0 + (2)(-1)(-2) + (1)(1)(4) + 0 + 0] = 1$

$E_2: \frac{1}{16}[(1)(2)(4) + (2)(0)(-2) + 0 + (2)(0)(-2) + (1)(2)4) + 0 + 0] = 1$

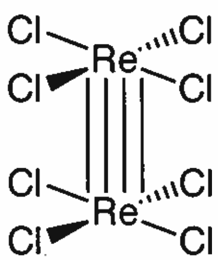
All other reps. equal 0.

$E_1 \bullet E_3 = B_1 + B_2 + E_2$

Name: Key

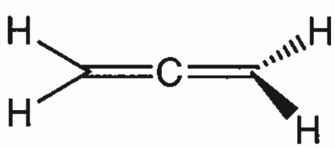
(6) |10 pts; 2 pts ea| Assign point groups to the following molecules:

(a) NH_3 $\boxed{C_{3v}}$



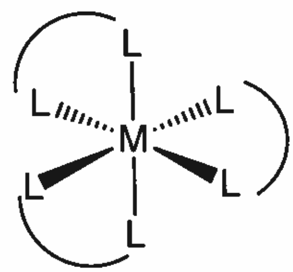
(b)

$\boxed{D_{4h}}$



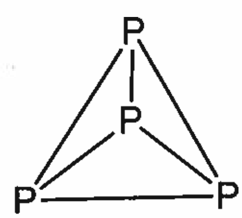
(c)

$\boxed{D_{2d}}$



(d)

$\boxed{D_3}$



(e)

$\boxed{T_d}$

Name: ______________________________

Selected Character Tables

C_{2h}	E	C_2	i	σ_h		
A_g	1	1	1	1	R_z	x^2, y^2, z^2, xy
B_g	1	−1	1	−1	R_x, R_y	xz, yz
A_u	1	1	−1	−1	z	
B_u	1	−1	−1	1	x, y	

D_2	E	$C_2(z)$	$C_2(y)$	$C_2(x)$		
A	1	1	1	1		x^2, y^2, z^2
B_1	1	1	−1	−1	z, R_z	xy
B_2	1	−1	1	−1	y, R_y	xz
B_3	1	−1	−1	1	x, R_x	yz

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$		
A_g	1	1	1	1	1	1	1	1		x^2, y^2, z^2
B_{1g}	1	1	−1	−1	1	1	−1	−1	R_z	xy
B_{2g}	1	−1	1	−1	1	−1	1	−1	R_y	xz
B_{3g}	1	−1	−1	1	1	−1	−1	1	R_x	yz
A_u	1	1	1	1	−1	−1	−1	−1		
B_{1u}	1	1	−1	−1	−1	−1	1	1	z	
B_{2u}	1	−1	1	−1	−1	1	−1	1	y	
B_{3u}	1	−1	−1	1	−1	1	1	−1	x	

D_{4d}	E	$2S_8$	$2C_4$	$2S_8^3$	C_2	$4C_2'$	$4\sigma_d$		
A_1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_2	1	1	1	1	1	-1	-1	R_z	
B_1	1	-1	1	-1	1	1	-1		
B_2	1	-1	1	-1	1	-1	1	z	
E_1	2	$\sqrt{2}$	0	$-\sqrt{2}$	-2	0	0	(x,y)	
E_2	2	0	-2	0	2	0	0		(x^2-y^2, xy)
E_3	2	$-\sqrt{2}$	0	$\sqrt{2}$	-2	0	0	(R_x,R_y)	(xz,yz)