Chemistry 6330

Winter Quarter 2018

Midterm Exam

Name: Key

Question 1: ________ pts / 15 pts

Question 2: ________ pts / 10 pts

Question 3: ________ pts / 20 pts

Question 4: ________ pts / 15 pts

Question 5: ________ pts / 25 pts

Question 6: ________ pts / 15 pts

TOTAL: _______ **PTS / 100 PTS**

Average: 80
High: 98
Low: 36

$\geq$ 90 : 8
80 - 89 : 6
70 - 79 : 3
60 - 69 : 5
50 - 59 : 1
$<$50 : 1

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(1) [15 pts] Consider a mathematical group.

2pts (a) [8 pts] List the properties that define a group.

1. The product of any two elements in a group must also be a member of the group → Closure

pts

2. There must be an identity element, E, which commutes with all elements of the group and, upon multiplication leaves the element unchanged.

pts

3. The Associative Law of Multiplication must hold: $(AB)C = A(BC)$

pts

4. Every element of the group must have a reciprocal that is also a member of the group → If $S^{-1} = R$, then $SR = RS = E$

(b) [3 pts] What is a subgroup?

A group of order lower than the larger group's order. If a group of order "h" contains a subgroup of order "g", $\frac{h}{g}$ = an integer

(c) [4 pts] What is a class?

A class is a complete set of elements in a group that are conjugates of one another, as related by a similarity transform.

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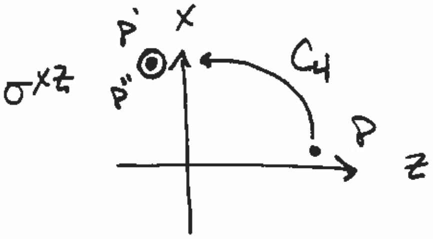
(2) [10 pts] Suppose that a S_4 rotation about the y-axis operates on a general Cartesian point (a,b,c).

(a) [7 pts] What is the Cartesian coordinate of the transformed point? Show your work.

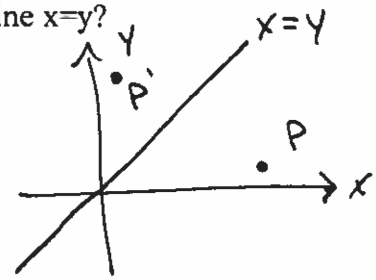


$$\underset{P}{(a,b,c)} \xrightarrow{C_4(y)} \underset{P'}{(c,b,-a)}$$

$$\underset{P'}{(c,b,-a)} \xrightarrow{\sigma^{xz}} \underset{P''}{(c,-b,-a)}$$

$$(a,b,c) \xrightarrow{S_4(y)} \boxed{(c,-b,-a)}$$

(b) [3 pts] What is the general 3x3 matrix for a reflection through a plane that contains the z-axis and the line x=y?



$P \rightarrow (a,b,c)$

$P' \rightarrow (b,a,c)$

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

$$? = \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

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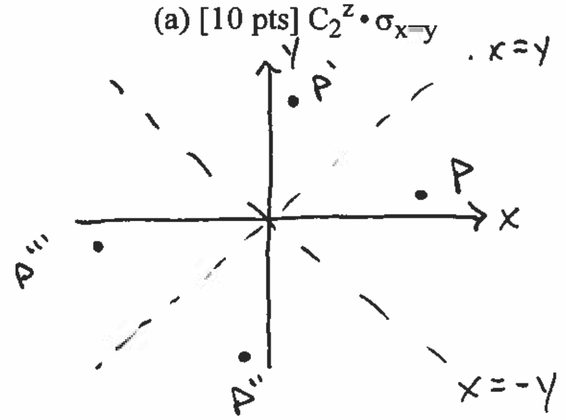
(3) [20 pts] For the following products of symmetry operations, determine (i) a single symmetry operation that is equal to the product and (ii) if the symmetry operations commute.

(a) [10 pts] $C_2^z \cdot \sigma_{x=y}$



$\sigma^{x=y}(P) \rightarrow P'$; $C_2(z)(P') \rightarrow P''$

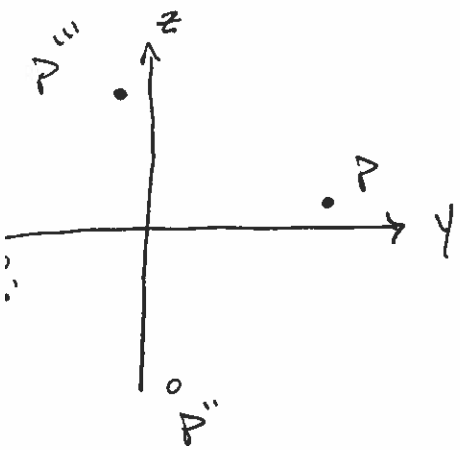
$C_2(z) \cdot \sigma^{x=y} = \boxed{\sigma^{x=-y}}$

$C_2(z)(P) \rightarrow P'''$; $\sigma^{x=y}(P''') \rightarrow P''$

$\sigma^{x=y} \cdot C_2(z) = \boxed{\sigma^{x=-y}}$

(i) $\sigma^{x=-y}$ (ii) Commute? Yes

(b) [10 pts] $C_4^x \cdot i$



$i(P) \rightarrow P'$; $C_4(x)(P') \rightarrow P''$

$C_4(x) \cdot i = \boxed{S_4^3(x)}$

$C_4(x)(P) \rightarrow P'''$; $i(P''') \rightarrow P''$

$i \cdot C_4(x) = \boxed{S_4^3(x)}$

(i) $S_4^3(x)$ (ii) Commute? Yes

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(4) [15 pts] A blank character table for the D_{2d} 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_{2d}	E	$2S_4$	C_2	$2C_2'$	$2\sigma_d$		
A_1	1	1	1	1	1		x^2+y^2, z^2
A_2	1	1	1	-1	-1	R_z	
B_1	1	-1	1	1	-1		x^2-y^2
B_2	1	-1	1	-1	1	z	xy
E	2	0	-2	0	0	(x,y) (R_x,R_y)	(xz,yz)

A or B indicates 1-D rep, E indicates 2-D rep.

A_1 → fully symmetric rep.

"A" indicates symmetric w.r.t. P.A.R. (S_4), "B" is antisymmetr

Subscript "1" indicates symmetric w.r.t. ⊥ C_2 (C_2'), "2" is antisymmetric

$\Gamma_m \cdot \Gamma_n = 0$, where $m \neq n$

$A_1 \cdot \Gamma_{B_1} = 0 = (1)(1)(1) + (2)(1)(-1) + (1)(1)(x) + (2)(1)(1) + (2)(1)(y)$

1   -2   1x   2   2y

x must be +1   y must be -1

$A_1 \cdot \Gamma_{B_2} = 0 = (1)(1)(1) + (2)(1)(-1) + (1)(1)(x) + (2)(1)(-1) + (2)(1)(y)$

1   -2   1x   -2   2y

x must be +1   y must be +1

$A_1 \cdot \Gamma_{A_2} = 0 = (1)(1)(1) + (2)(1)(1) + (1)(1)(x) + (2)(1)(-1) + (2)(1)(y)$

1   2   1x   -2   2y

x must be +1   y must be -1

Checking orthogonality between Γ_E and all other reps, the only values possible are "-2" under C_2 and zeroes elsewhere

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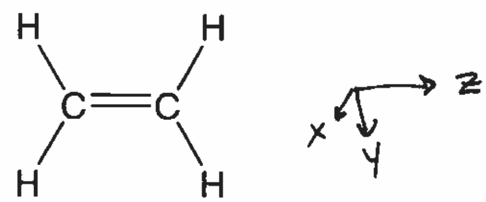
(5) [25 pts] Consider ethene drawn below.



(a) [6 pts] Identify all the symmetry elements and symmetry operations of the molecule (it may help to draw them on the molecule)

E, $C_2(x)$, $C_2(y)$, $C_2(z)$, i, σ^{xz}, σ^{yz}, σ^{xy}

(b) [4 pts] What is the point group of ethene? D_{2h}

(c) [10 pts] Write the representation for transposing the four H atoms in ethene.

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	σ^{xy}	σ^{xz}	σ^{yz}
Γ_H	4	0	0	0	0	0	0	4

(d) [5 pts] Is the representation in part (c) reducible or irreducible? Explain your answer.

Yes; no irr. rep. in the D_{2h} character table has a dimension of 4. Thus, the rep. in part c must be the sum of other irr. reps.

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(6) [15 pts] The following questions pertain the D_{4h} point group (character table included).

(a) [10 pts] Find the direct product $E_u \bullet E_u$ and reduce to a sum of irreducible representations.

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
$E_u \cdot E_u$	4	0	4	0	0	4	0	4	0	0

Can reduce using $\frac{1}{h} \sum_i a_i \chi_i(R) \chi_i(\Gamma_{E_u \cdot E_u})$, but upon inspection of the D_{4h} character table the only combination of irr. reps. that can sum to the above reducible rep. is:

$$\Gamma_{E_u \cdot E_u} = A_{1g} + A_{2g} + B_{1g} + B_{2g}$$

(b) [5 pts] Show that the irreducible representations B_{2g} and E_g are orthogonal to one another.

If orthogonal, dot product must be 0.

$$B_{2g} \cdot \Gamma_{E_g} = (1)(1)(2) + 0 + (1)(1)(-2) + 0 + 0 + (1)(1)(2) + 0 + (1)(1)(-2) + 0 + 0$$

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

$$= 0 \checkmark$$

They are orthogonal.