Mathematical Methods in Chemistry, Part I
Symmetry and Group Theory
Midterm Exam

April 17, 2023

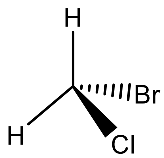
Name:

2 h to complete the exam. Total number of points: 33.

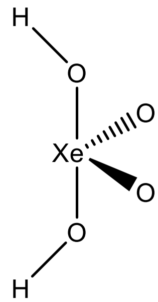
Please note that this is not an open-book exam. Only the material handed out with the exam questions may be used. You are allowed to use a non-programmable calculator, but the calculator will be checked during the exam. Computers or molecular modeling kits are not permitted. Do not write with a pencil or a fountain pen that can be erased. Please have your photo ID ready.

1) Determine the point group of the following molecules and objects. (10 points)

A



B



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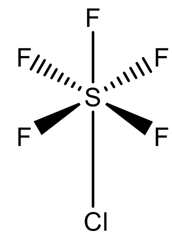

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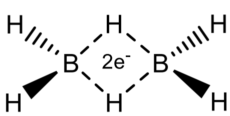

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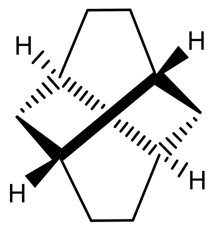
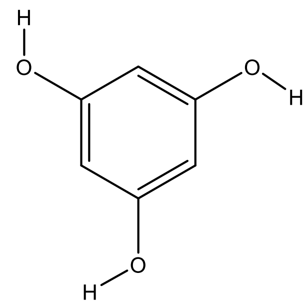
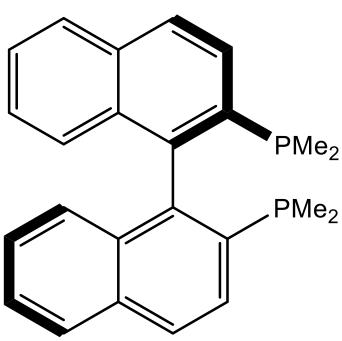


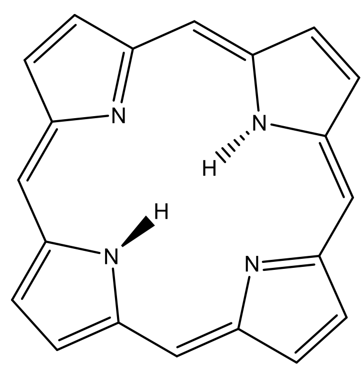
F



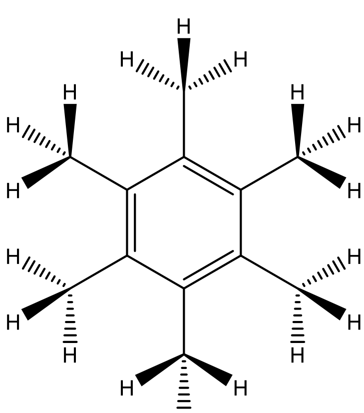
G



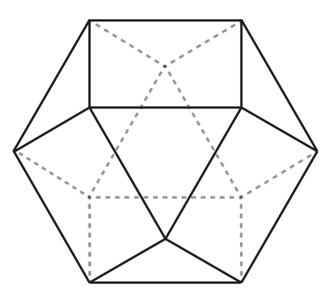
H



I



J



A: C_s

(1 point)

B: C_{2v}

(1 point)

C: C_{4v}

(1 point)

D: D_{2h}

(1 point)

E: D_2

(1 point)

F: C_{3h}

(1 point)

G: C_2

(1 point)

H: C_{2h}

(1 point)

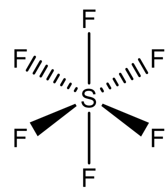
I: D_{3d}

(1 point)

J: O_h

(1 point)

2) Construct a qualitative molecular orbital diagram for SF_6. (10 points total)



For the basis functions, use the 3s and 3p orbitals of the sulfur atom as well as a 2p orbital on each fluorine atom that is pointing towards the sulfur.

a) Draw the molecular orbital diagram. Make sure to add symmetry labels to each molecular orbital in your diagram and populate the orbitals with electrons. (7 points)

Point group: O_h **(1 point)**

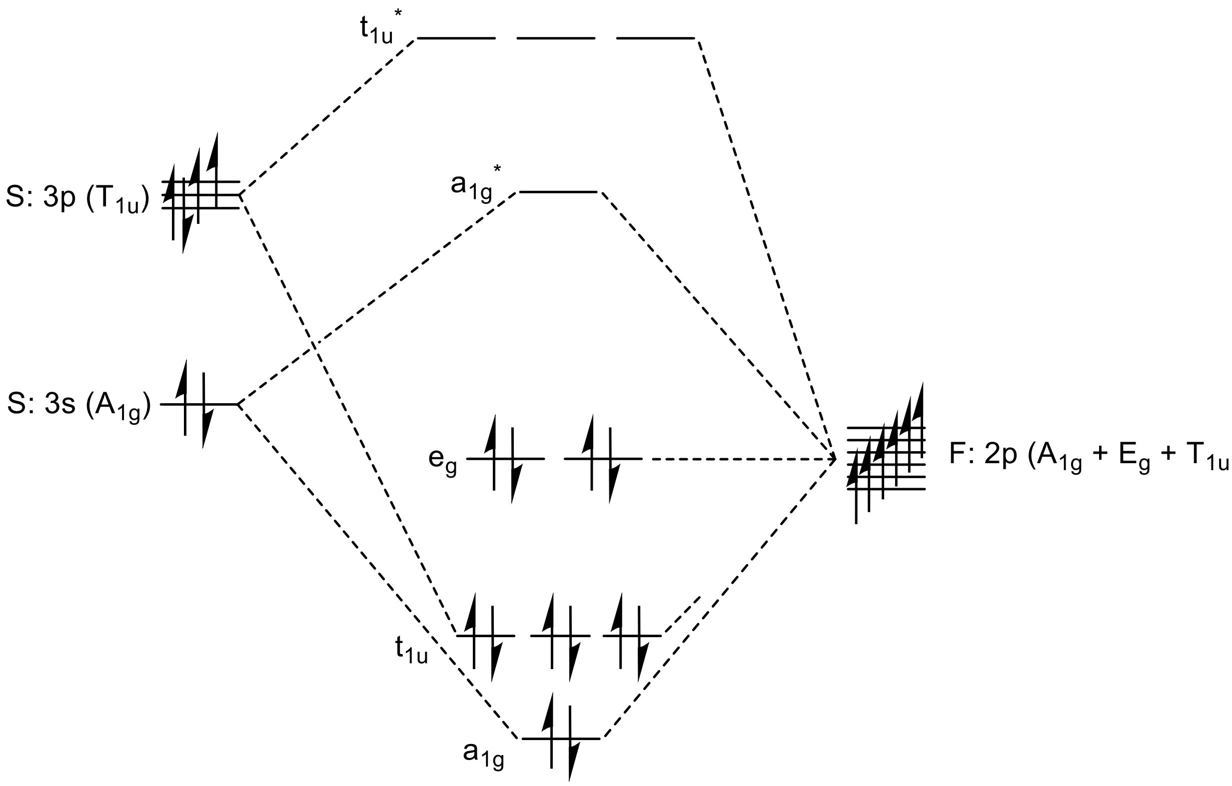
Symmetry species of the sulfur orbitals **(1 point)**

S 3s orbital: A_{1g}
S 3p orbitals: T_{1u}

Symmetry species of the F 2p orbitals pointing towards the sulfur **(2 points)**

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
$\Gamma_{2p,F} = A_{1g} + E_g + T_{1u}$	6	0	0	2	2	0	0	0	4	2

We obtain the following molecular orbital diagram. **(3 points)**



(2 points for the correct structure of the diagram,
0.5 points for populating the molecular orbitals with electrons correctly,
0.5 points for labeling the molecular orbitals correctly)

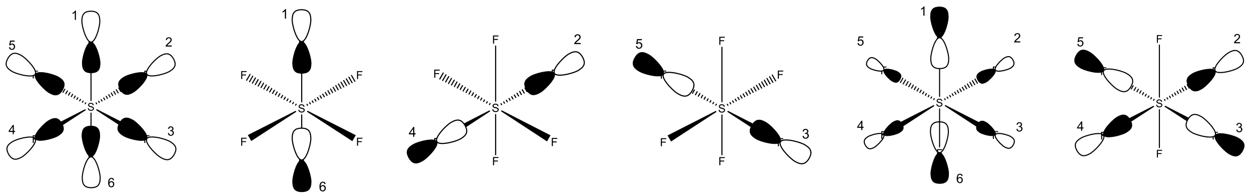
b) Determine the symmetry adapted linear combinations for the six fluorine 2p orbitals that are pointing towards the sulfur and draw them. (3 points)

The symmetry adapted linear combinations can be found by comparing with atomic orbitals on the sulfur atom of the same symmetry.

$$\sigma_{2p,F}(A_{1g}) = p_1 + p_2 + p_3 + p_4 + p_5 + p_6,$$

$$\sigma_{2p,F}(T_{1u})_1 = p_1 - p_6,$$
$$\sigma_{2p,F}(T_{1u})_2 = p_2 - p_4,$$
$$\sigma_{2p,F}(T_{1u})_3 = p_3 - p_5,$$

$$\sigma_{2p,F}(E_g)_1 = p_2 + p_3 + p_4 + p_5 - 2p_1 - 2p_6,$$
$$\sigma_{2p,F}(E_g)_2 = p_2 + p_4 - p_3 - p_5.$$



$\sigma_{2p,F}(A_{1g})$ $\sigma_{2p,F}(T_{1u})_1$ $\sigma_{2p,F}(T_{1u})_2$ $\sigma_{2p,F}(T_{1u})_3$ $\sigma_{2p,F}(E_g)_1$ $\sigma_{2p,F}(E_g)_2$

(3 points)

3) The quaternion group $Q = \{1, -1, a, -a, b, -b, c, -c\}$ is a group with respect to multiplication. (13 points total)

The quaternions, which can be understood as an extension of complex numbers, satisfy the relations

$$a^2 = b^2 = c^2 = -1$$

and

$$abc = -1.$$

a) Write down the group multiplication table of the quaternion group. (4 points)

While multiplication of the quaternions is associative, do not assume that it is commutative.

Hint: If you struggle to figure out the products of the quaternions, you might want to solve problem 3d) first and then use the result to solve this problem. You can also use the information provided in d) to verify your result.

Q	*1*	*-1*	*a*	*-a*	*b*	*-b*	*c*	*-c*
1	1	-1	a	-a	b	-b	c	-c
-1	-1	1	-a	a	-b	b	-c	c
a	a	-a	-1	1	c	-c	-b	b
-a	-a	a	1	-1	-c	c	b	-b
b	b	-b	-c	c	-1	1	a	-a
-b	-b	b	c	-c	1	-1	-a	a
c	c	-c	b	-b	-a	a	-1	1
-c	-c	c	-b	b	a	-a	1	-1

The blue blocks follow from the definition $a^2 = b^2 = c^2 = -1$.

The inverses are given by $a^{-1} = -a,\ b^{-1} = -b, c^{-1} = -c$.

Using the inverses, we can then use $abc = -1$ to deduce $ab = c,\ bc = a,\ ca = b$ and fill in the rest of the table.

b) Demonstrate that $\boldsymbol{Q = \{1, -1, a, -a, b, -b, c, -c\}}$ is a group with respect to multiplication. Is the group Abelian? (2.5 points)

1) The group is complete since the group multiplication table shows that multiplication of each two elements generates another element of the group.
2) There is a neutral element, *i.e.* 1.
3) Each element has an inverse.
4) The associative law is satisfied.

(2 points)

5) The group is not Abelian since the multiplication table is not symmetric, *e.g.*, $ab = c$, but $ba = -c$.

(0.5 points)

c) Determine the classes of Q. (2 points)

Hint: You can also use the information provided in d) to solve this problem.

The classes are given by $\{1\}, \{-1\}, \{\pm a\}, \{\pm b\}, \{\pm c\}$.

d) The elements a, b, and c of the quaternion group can be represented with the following two-dimensional matrices.

1	-1	a	b	c	-a	-b	-c
…	…	$\begin{pmatrix} i & 0 \\ 0 & -i \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & i \\ i & 0 \end{pmatrix}$	…	…	…

Express the remaining elements of the quaternion group with two-dimensional matrices in order to obtain a two-dimensional representation of the quaternion group. (1 point)

1	-1	a	b	c	-a	-b	-c
$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} i & 0 \\ 0 & -i \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & i \\ i & 0 \end{pmatrix}$	$\begin{pmatrix} -i & 0 \\ 0 & i \end{pmatrix}$	$\begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & -i \\ -i & 0 \end{pmatrix}$

e) The two-dimensional representation obtained in d) is irreducible. Based on this information, construct the character table for the quaternion group. (3.5 points)

Since there are 5 classes, there must be 5 irreducible representations (Rule 5). **(0.5 points)**

The totally symmetric representation must be one of them. **(0.5 points)**

Furthermore, we can calculate the characters of the two-dimensional representation Γ_5 that is given in d). Hence, 3 irreducible representations are missing. **(0.5 points)**

Q	1	-1	± a	± b	± c
Γ_1	1	1	1	1	1
Γ_2	x_1	x_4	x_7	x_{10}	x_{13}
Γ_3	x_2	x_5	x_8	x_{11}	x_{14}
Γ_4	x_3	x_6	x_9	x_{12}	x_{15}
Γ_5	2	-2	0	0	0

From Rule 1, we obtain the dimensions of the remaining representations from

$$1^2 + 2^2 + x_1^2 + x_2^2 + x_3^2 = 8$$

so that $x_1 = x_2 = x_3 = 1$. **(0.5 points)**

Q	1	-1	± a	± b	± c
Γ_1	1	1	1	1	1
Γ_2	1	x_4	x_7	x_{10}	x_{13}
Γ_3	1	x_5	x_8	x_{11}	x_{14}
Γ_4	1	x_6	x_9	x_{12}	x_{15}
Γ_5	2	-2	0	0	0

Rule 2 states that the sum of the squares of the characters of an irreducible representation is equal to the order of the group, for example

$$1^2 + x_4^2 + 2x_7^2 + 2x_{10}^2 + 2x_{13}^2 = 8.$$

Hence, all remaining variables have to be ±1. **(0.5 points)**

Q	1	-1	± a	± b	± c
Γ_1	1	1	1	1	1
Γ_2	1	±1	±1	±1	±1
Γ_3	1	±1	±1	±1	±1
Γ_4	1	±1	±1	±1	±1
Γ_5	2	-2	0	0	0

From Rule 3, we know that two different rows of the character table are orthogonal. In order for the representation Γ_2, Γ_3 and Γ_4 to be orthogonal to the Γ_5 representation, their second character has to be 1. **(0.5 points)**

Since the Γ_2, Γ_3, and Γ_4 representations also have to be mutually orthogonal, we can complete the character table as follows. **(0.5 points)**

Q	1	-1	± a	± b	± c
Γ_1	1	1	1	1	1
Γ_2	1	1	1	-1	-1
Γ_3	1	1	-1	1	-1
Γ_4	1	1	-1	-1	1
Γ_5	2	-2	0	0	0