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

April 17, 2024

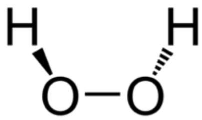
Name:

2 h to complete the exam. Total number of points: 38.

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.

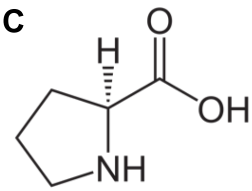
1) Determine the point group of the following molecules and objects. (12 points)

A

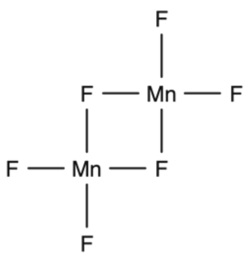


B

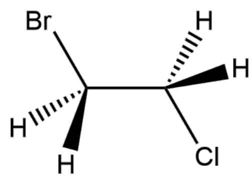
C



D



E



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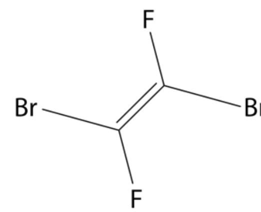
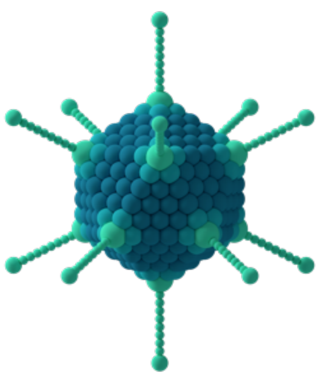
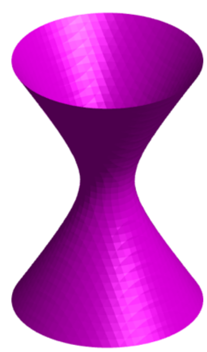


G



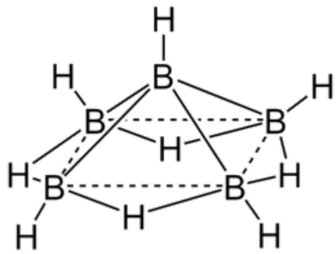
Adenovirus

H

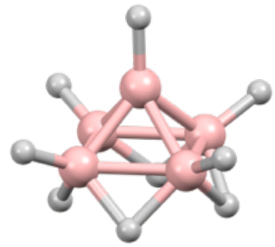


$$\frac{x^2}{a^2} + \frac{y^2}{b^2} - \frac{z^2}{c^2} = 1$$

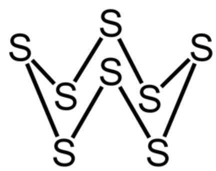
I

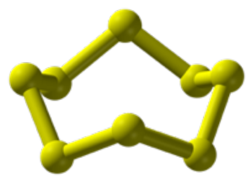


Pentaborane(9)

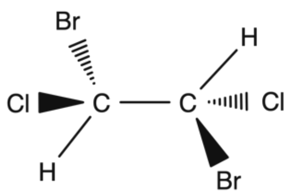


J

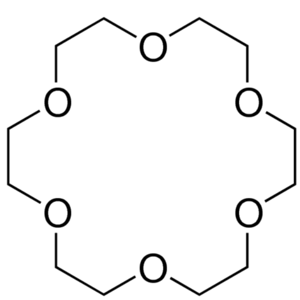




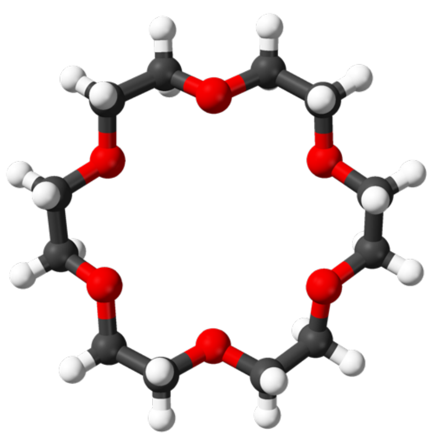
K



L



18-Crown-6



Solution:

A: C_2

B: $D_{\infty h}$

C: C_1

D: D_{2h}

E: C_s

F: C_{2h}

G: I, (full points for I_h, which is not quite correct)

H: $D_{\infty h}$

I: C_{4v}

J: D_{4d}

K: C_i

L: S_6 (full points for D_{3d}, which is not quite correct)

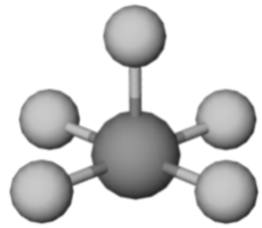
(12 points)

2) Determine all subgroups of the points groups C_{4v}, C_i, C_{2h}, D_{2h}. (2 points)

Solution:
C_{4v} has subgroups $C_4, C_{2v}, C_2, C_s, C_1$
C_i has subgroup C_1
C_{2h} has subgroups C_2, C_s, C_i, C_1
D_{2h} has subgroups $D_2, C_{2h}, C_{2v}, C_2, C_s, C_i, C_1$

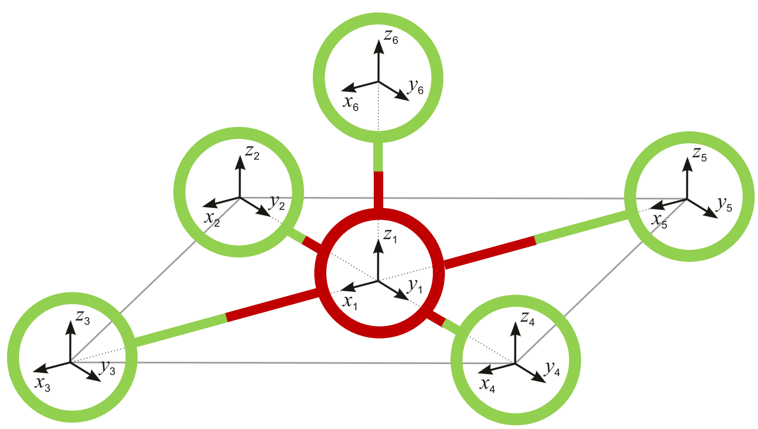
(2 points)

3) BrF_5 has a square pyramidal geometry. How many peaks do you expect to find in the IR and Raman spectrum? (10 points)



Point group C_{4v}. **(1 point)**

We use the displacement vectors of all atoms as a basis for a reducible representation. An example of how to arrange the displacement vectors is shown below.



We obtain the following characters. **(3 points)**

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$
Γ_{tot}	18	2	-2	4	2

The character table gives us the irreducible representations for the translations and rotations, $\Gamma_{trans} = A_1 \oplus E$ and $\Gamma_{rot} = A_2 \oplus E$, respectively. **(1 point)**

After subtraction, we are left with the representation for the vibrations Γ_{vib}

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$
Γ_{tot}	18	2	-2	4	2
$-\Gamma_{trans}$	-3	-1	1	-1	-1
$-\Gamma_{rot}$	-3	-1	1	1	1
Γ_{vib}	12	0	0	4	2

Using the reduction formula, we obtain $\Gamma_{vib} = 3A_1 \oplus 2B_1 \oplus B_2 \oplus 3E$. **(3 points)**

IR active modes must belong to the same symmetry species as one of the Cartesian coordinates x, y, of z, *i.e.* A_1 and E. We therefore obtain 6 peaks in the IR spectrum for the 3 A_1 and the 3 doubly degenerate E vibrations.

Raman active modes must have the same symmetry species as one of the products of the Cartesian coordinates, *i.e.* A_1, B_1, B_2, and E. We therefore obtain 9 peaks in the Raman spectrum for the 3 A_1, the 2 B_1, the B_2, and the 3 doubly degenerate E vibrations.

(2 points)

4) Assume that $\{\psi_1, \psi_2\}$ is a basis of a representation Γ of the group G and consider the direct product $\Gamma \otimes \Gamma$. The symmetrized part of the direct product contains the following three functions

$$\left\{\boldsymbol{\psi_1\psi_1}, \tfrac{1}{2}(\boldsymbol{\psi_1\psi_2} + \boldsymbol{\psi_2\psi_1}), \boldsymbol{\psi_2\psi_2}\right\},$$

which form a basis for another representation Γ_s.

Note that in this notation $\psi_1\psi_2 = \psi_1(r_1)\psi_2(r_2)$ and $\psi_2\psi_1 = \psi_2(r_1)\psi_1(r_2)$, where r_1 and r_2 are coordinates in three-dimensional space.

Show that the character χ_{Γ_s} of this representation for an operation R is given by the following formula

$$\chi_{\Gamma_s}(\boldsymbol{R}) = \tfrac{1}{2}[\chi_\Gamma(\boldsymbol{R})^2 + \chi_\Gamma(\boldsymbol{R}^2)],$$

where χ_Γ represents the character of the representation Γ. (7 points total)

In the basis $\{\psi_1, \psi_2\}$ let R be given by $R = \begin{pmatrix} a & b \\ c & d \end{pmatrix}$. We have to find a representation of the matrix R under the basis B. The matrix R maps the first basis vector ψ_1 to $a\psi_1 + b\psi_2$ and the second basis vector to $c\psi_1 + d\psi_2$.

(1 point)

Then, in the new basis B, it holds:

$$\psi_1\psi_1 \longmapsto (a\psi_1 + b\psi_2)(a\psi_1 + b\psi_2) = a^2\psi_1\psi_1 + \ldots$$

$$\psi_2\psi_2 \longmapsto (c\psi_1 + d\psi_2)(c\psi_1 + d\psi_2) = d^2\psi_2\psi_2 + \ldots$$

$$\psi_1\psi_2 + \psi_2\psi_1 \longmapsto (a\psi_1 + b\psi_2)(c\psi_1 + d\psi_2) + (c\psi_1 + d\psi_2)(a\psi_1 + b\psi_2)$$
$$= ad\psi_1\psi_2 + bc\psi_2\psi_1 + cb\psi_1\psi_2 + da\psi_2\psi_1 + \ldots$$

(3 points)

Therefore,

$$\chi_{\Gamma_s}(R) = a^2 + d^2 + \tfrac{1}{2}(ad + bc + cb + da).$$

(1 point)

And since the characters of corresponding matrices are:

$$\chi(R)^2 = (a + d)^2 = a^2 + d^2 + 2ad,$$
$$\chi(R^2) = a^2 + d^2 + 2bc,$$

we prove that

$$\chi_{\Gamma_s}(R) = \frac{1}{2}[\chi(R)^2 + \chi(R^2)].$$

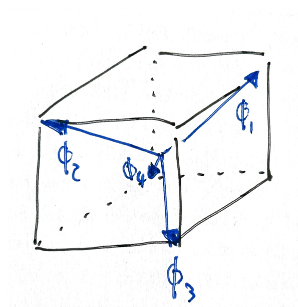
(2 points)

5) In class, we have used symmetry to construct a qualitative MO diagram of CH_4. For the minimal basis, we used the 2s and 2p orbitals on the carbon atom. Show that we would have obtained the same result if we had instead used four sp^3 hybridized orbitals on the carbon.

To this end, show that the sp^3 orbitals give rise to SALCs of the same symmetry species as the 2s and 2p orbitals. Determine the SALCs of the sp^3 orbitals. Finally, show that these SALCs are identical to the 2s and the 2p orbitals. (7 points total)

In class, we have seen that the 2s orbital belongs to the A_1 representation and the p orbitals to the T_2 representation in T_d. **(1 point)**

If we take the four sp^3 orbitals as a basis (schematically indicated below),



we obtain the following representation

	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
$\Gamma_{sp3} = A_1+T_2$	4	1	0	0	2

which contains the A_1 and the T_2 representations, to which the 2s and 2p orbitals give rise.

(2 points)

For the corresponding SALCs of the sp^3 orbitals, we can easily guess the following mutually orthogonal SALCs by comparing with the character table (neglecting normalization constants).

$$\Phi_{A_1} = \Phi_1 + \Phi_2 + \Phi_3 + \Phi_4$$
$$\Phi_{T_2,1} = \Phi_1 - \Phi_2 + \Phi_3 - \Phi_4$$
$$\Phi_{T_2,2} = \Phi_1 - \Phi_2 - \Phi_3 + \Phi_4$$
$$\Phi_{T_2,3} = \Phi_1 + \Phi_2 - \Phi_3 - \Phi_4$$

(2 points)

If we express the sp^3 orbitals as (mutually orthogonal) linear combinations of the s and p orbitals (again neglecting normalization)

$$\Phi_1 = s + p_x + p_y + p_z$$
$$\Phi_2 = s - p_x - p_y + p_z$$
$$\Phi_3 = s + p_x - p_y - p_z$$
$$\Phi_4 = s - p_x + p_y - p_z$$

(1 point)

we can then show that

$$\Phi_{A_1} = s$$
$$\Phi_{T_2,1} = p_x$$
$$\Phi_{T_2,2} = p_y$$
$$\Phi_{T_2,3} = p_z$$

(1 point)