CHEM 190 and CHEM 290

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Homework No. 8
Due May 31 in class

1. **Textbook Chapter 6 No. 108**
2. **Textbook Chapter 6 No. 110**
3. **Textbook Chapter 6 No. 118**
4. **Textbook Chapter 6 No. 131**
5. **Textbook Chapter 6 No. 137**

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THE FOLLOWING ARE GROUP THEORY SAMPLE PROBLEMS, TOGETHER WITH THE SORT OF INFORMATION THAT WE WILL PROVIDE ON THE EXAM. WE ARE ASKING YOU TO TURN IT IN MAY 31 RATHER THAN JUNE 7 SO THAT WE CAN GET YOU THE SOLUTIONS EARLY ENOUGH FOR YOU TO HAVE PLENTY OF TIME TO GO OVER THEM.

SOME IMPORTANT THEOREMS FROM GROUP THEORY

$$\sum_R (R_\alpha)^*_{ij}(R_\beta)_{i'j'} = \frac{g}{d_\alpha^{1/2} d_\beta^{1/2}} \delta_{\alpha\beta}\delta_{ii'}\delta_{jj'}$$

$$\sum_R (\chi_R^{\Gamma_\alpha})^* \chi_R^{\Gamma_\beta} = g\delta_{\alpha\beta}$$

$$n_\beta = \frac{1}{g}\sum_R (\chi_R^{\Gamma_\beta})^* \chi_R^{\Gamma}$$

$$P_{\Gamma_\alpha} = \sum_R (\chi_R^{\Gamma_\alpha})^* R$$

1. **NOTE**: This problem is much like (but not exactly like) several problems on a previous homework, but the way things are laid out gives you a notion of how questions might be asked on the exam. The following questions revolve around the $\mathcal{C}_{3v}$ group, whose character table is the following:

$\mathcal{C}_{3v}$	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

(a) What is the order of this group?

A basis for a representation Γ of C_{3v} consists of the infinitesimal displacements of the H atoms of NH_3. These may be drawn as coordinate systems centered on each hydrogen atom, with the x axis in each case pointing radially, the y axis in each case pointing tangentially, and the z axis in each case pointing out of the paper (see drawing). We will use this coordinate system for the next few questions. **NOTE**: The similar representation used on the previous homework was 12-dimensional and included the coordinates of N. If we are only interested in the vibrational and rotational motions of the molecule and are not interested in the translational motion of the whole molecule, we can just imagine "sitting" on the center of mass at N and then the coordinates of N do not matter.

(b) What is the dimensionality of this representation?

(c) Find the matrices for C_3 and σ_v in this representation. Use the basis vectors in the following order:

$$x_1 \quad x_2 \quad x_3 \quad y_1 \quad y_2 \quad y_3 \quad z_1 \quad z_2 \quad z_3$$

(d) From the result of **(c)** (or however you wish to do it) construct the characters of this representation to fill in the blanks under the character table:

C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0
Γ	__	__	__

(e) How many times does each irreducible representation of C_{3v} occur in Γ?

(f) One form of the irreducible representation E of C_{3v} was given in class. In this representation the element C_3 has the form

$$C_3 = \begin{pmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{pmatrix}$$

Write C_3 for the NH_3 problem in block diagonal form.

(g) Construct the projection operator P_E for C_{3v}.

(h) Apply the projection operator P_E to the basis vector z_1 and thereby obtain a linear combination of the original basis vectors that transforms as the *representation* E.

(i) Find the characters of the direct-product representation $E \times E$.

(j) What irreducible representations may the $E \times E$ representation be reduced to?

(**k**) In a particular four-dimensional representation of $E \times E$, the matrix for C_3 is

$$C_3 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1/2 & -\sqrt{3}/2 \\ 0 & 0 & \sqrt{3}/2 & -1/2 \end{pmatrix}$$

What is a possible form of the four by four matrix for σ_v in this representation?

2. One form of the two-dimensional irreducible representation of the group C_{3v} was given in class:

$$\mathrm{E} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \qquad \mathrm{C}_3 = \begin{pmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{pmatrix} \qquad \mathrm{C}_3^2 = \begin{pmatrix} -1/2 & \sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{pmatrix}$$

$$\sigma_v = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} \qquad \sigma_{v'} = \begin{pmatrix} 1/2 & -\sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{pmatrix} \qquad \sigma_{v''} = \begin{pmatrix} 1/2 & \sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{pmatrix}$$

Suppose that this representation is associated with the basis

$$\text{Basis} = (a \quad b).$$

Now we wish to construct another *equivalent* irreducible representation in the basis

$$\text{New Basis} = (1/\sqrt{2})(a + b \quad a - b).$$

What are the appropriate matrices for C_3 and for σ_v in this new representation?

3. A four-dimensional representation of the group C_4 is constructed by using a basis $(a\ b\ c\ d)$ as follows (don't confuse the name of the group with the operations in the group!):

$$(a \quad b \quad c \quad d)\ \mathrm{E} = (a \quad b \quad c \quad d)$$

$$(a \quad b \quad c \quad d)\ \mathrm{C}_4 = (b \quad c \quad d \quad a)$$

$$(a \quad b \quad c \quad d)\ \mathrm{C}_2 = (c \quad d \quad a \quad b)$$

$$(a \quad b \quad c \quad d)\ \mathrm{C}_4^3 = (d \quad a \quad b \quad c)$$

(a) Construct the corresponding 4×4 matrices.

(b) Use your results to construct the **CHARACTER TABLE** for C_4. **Useful reminder**: $\mathrm{C}_2 = \mathrm{C}_4^2$, that is, all the elements of this group are powers of C_4.