12.E: Group Theory - The Exploitation of Symmetry (Exercises)

A Libretexts Textmap organized around McQuarrie and Simon's textbook
Physical Chemistry: A Molecular Approach

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These are homework exercises to accompany Chapter 12 of McQuarrie and Simon's "Physical Chemistry: A Molecular Approach" Textmap.

Q12.1

Normalize the following equation:

$$\psi(x) = Zxe^{-kx^2} \tag{12.E.1}$$

S12.1

$$\int_{-\infty}^{\infty} \psi(x)^* \psi(x) dx \tag{12.E.2}$$

$$1 = Z^2 \frac{1}{4} \sqrt{\frac{\pi}{2}} \alpha^{\frac{-3}{2}} \tag{12.E.3}$$

$$Z^2 = 4\sqrt{\frac{2}{\pi}} \left(\frac{m\omega}{2\hbar}\right)^{3/2} \tag{12.E.4}$$

notes:

When I integrated $(xe^{-kx^2})^2$ the answer had an erf term in it. I think that the normalization of this specific function is more complex than was intended

Q12.3

List the symmetry elements for the bent molecule H_2O.

S12.3

Identity element E, two reflection planes σ_{xz} and σ_{yz}, one 2-fold rotation axis C_2, and it belongs to the point group C_2v.

Q12.4

Verify that an ethene molecule has the symmetry elements given in Table 12.2.

S12.4

The point group of ethene is D_{2h}. The identity of element is given. There are three C_2 axes and three vertical axes.

Q12.5

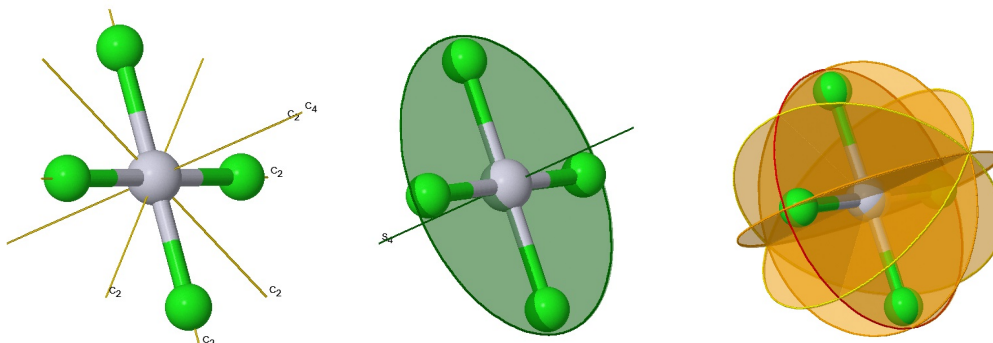Verify that a water molecule has the symmetry elements given in Table 12.2.

S12.5

The point group of water is C_{2v}. A water molecule contains the symmetry elements E, C_2, and $2\sigma_v$. Water contains a two- fold C_2 axis through the oxygen molecule located directly on the Z axis. Water also contains two vertical planes of symmetry. The first mirror plane cuts vertically through all three molecules, H-O-H. The second mirror plane cuts through the water molecule perpendicular to the other vertical plane. The C_2 axis lies along the intersection of the two σ planes.

Q12.6

What is the point group of tetrachloropalladate [PdCl$_4$]$^{2-}$ and show the symmetry elements.

S12.6

The symmetry elements for tetrachloropalladate are $E, i, C_4, 4C_2, S_4, \sigma_h, 2\sigma_v, 2\sigma_d$.

(left): proper rotations (C_2 and C_4), (center) improper S_4 rotation, (right) reflection planes (σ_h σ_d and σ_h)

Q12.31

Considering the allyl anion, $CH_2CHCH_2^-$, which belongs to the C_{2v} point group, calculate the Huckel secular determinant using $|\psi_1\rangle, |\psi_2\rangle$, and $|\psi_3\rangle$ (2_{pz} on each carbon atom). Then find the reducible representation for the allyl anion using $|\psi_j\rangle$ as the basis.

Show that the reducible representation $\Gamma = A_2 + 2B_1$. What does this say about the expected secular determinant? Now, use the generating operator (Equation 13.2) to derive three symmetry orbitals for the allyl anion. Normalize them and calculate the Huckel secular determinant equation and solve for the π electron energies.

S12.31

Applying the Huckel theory to the allyl anion yields the secular determinant given as

$$\begin{vmatrix} \alpha - E & \beta & 0 \\ \beta & \alpha - E & \beta \\ 0 & \beta & \alpha - E \end{vmatrix} = 0 \tag{12.E.5}$$

Dividing the matrix by β and using the variable $x = \dfrac{\alpha - E}{\beta}$, we can solve a determinant of the form:

$$\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} = 0 \tag{12.E.6}$$

Expanding this determinant gives the equation

$$x^3 - 2x = 0 \tag{12.E.7}$$

Solving this equation gives $x = 0, \pm\sqrt{2}$.

The reducible representation can be found by looking at the four operators in the C_{2v} point group, which are $E, C_2, \sigma_v, \sigma_v'$. The operator E leaves all three orbitals unchanged (reducible representation of 3). The C_{2v} operator inverts just one of the orbitals (a reducible representation of -1). The σ_v operator leaves just one of the orbitals unchanged but does not invert any (reducible representation of 1). Lastly, the σ_v' operator inverts all three orbitals (reducible representation of -3). Thus, the reducible representation of the C_{2v} point group is

$$\Gamma = 3 \quad -1 \quad 1 \quad -3$$

Using equation 12.23, we find the irreducible representations to be

$$a_{A_1} = \frac{1}{4}(3 - 1 + 1 - 3) = 0 \tag{12.E.8}$$

$$a_{A_2} = \frac{1}{4}(3 - 1 - 1 + 3) = 1 \tag{12.E.9}$$

$$a_{B_1} = \frac{1}{4}(3 + 1 + 1 + 3) = 2 \tag{12.E.10}$$

$$a_{B_2} = \frac{1}{4}(3 + 1 - 1 - 3) = 0 \tag{12.E.11}$$

We therefore yield the reducible representation $\Gamma = A_2 + 2B_1$. This result shows us that the secular determinant can be written in either a 1 x 1 or 2 x 2 block diagonal form corresponding to the A_2 or B_1 representation, respectively. The three symmetry orbitals are found by

$$P_{A_2}\psi_1 = \frac{1}{4}(\psi_1 - \psi_3 - \psi_3 + \psi_1) \propto \psi_1 - \psi_3 \tag{12.E.12}$$

$$P_{B_1}\psi_1 = \frac{1}{4}(\psi_1 + \psi_3 + \psi_3 + \psi_1) \propto \psi_1 + \psi_3 \tag{12.E.13}$$

$$P_{B_1}\psi_2 = \frac{1}{4}(\psi_2 + \psi_2 + \psi_2 + \psi_2) = \psi_2 \tag{12.E.14}$$

using generating operators for A_2 and B_1.

The three normalized symmetry orbitals are

$$\Phi_1 = \frac{1}{\sqrt{2}}(\psi_1 - \psi_3) \tag{12.E.15}$$

$$\Phi_2 = \psi_2 \tag{12.E.16}$$

$$\Phi_3 = \frac{1}{\sqrt{2}}(\psi_1 + \psi_3) \tag{12.E.17}$$

Thus, these three orbitals give the symmetry elements below.

$$H_{11} = \frac{1}{2}(2\alpha) = \alpha \tag{12.E.18}$$

$$H_{22} = \alpha \tag{12.E.19}$$

$$H_{33} = \frac{1}{2}(2\alpha) = \alpha \tag{12.E.20}$$

$$H_{12} = \frac{1}{2}(\beta - \beta) = 0 \tag{12.E.21}$$

$$H_{13} = \frac{1}{2}(\alpha - \alpha) = 0 \tag{12.E.22}$$

$$H_{23} = \frac{1}{\sqrt{2}}(2\beta) = \sqrt{2}\beta \tag{12.E.23}$$

$$S_{11} = S_{22} = S_{33} = 1 \tag{12.E.24}$$

$$S_{12} = S_{13} = S_{23} = 0 \tag{12.E.25}$$

This gives the secular determinant

$$\begin{vmatrix} \alpha - E & 0 & 0 \\ 0 & \alpha - E & \sqrt{2}\beta \\ 0 & \sqrt{2}\beta & \alpha - E \end{vmatrix} = 0 \tag{12.E.26}$$

Dividing the matrix by β and using the variable $x = \frac{\alpha - E}{\beta}$, we can solve a determinant of the form:

$$\begin{vmatrix} x & 0 & 0 \\ 0 & x & \sqrt{2} \\ 0 & \sqrt{2} & x \end{vmatrix} = 0 \tag{12.E.27}$$

which gives roots $x = 0, \pm\sqrt{2}$. Using the substitution that $x = \dfrac{\alpha - E}{\beta}$, we get the energies to be

$$E_1 = \alpha - \sqrt{2}\beta \tag{12.E.28}$$

$$E_2 = \alpha \tag{12.E.29}$$

$$E_3 = \alpha + \sqrt{2}\beta \tag{12.E.30}$$

Q12.32

How will the secular determinant for SF_6 look if we use group theory to generate symmetry orbitals?

S12.32

The reducible representation for an octahedral is

$$\begin{array}{cccccccccccc} O_h & E & 8C_3 & 6C_2 & 6C_4 & 3C_2 & i & 6S_4 & 8S_6 & 3\sigma_h & 6\sigma_d \\ \Gamma & 6 & 0 & 0 & 2 & 2 & 0 & 0 & 0 & 4 & 2 \end{array} \tag{12.E.31}$$

Use this equation:

$$a_i = \frac{1}{h}\sum \chi(\hat{R})\chi_i(\hat{R}) \tag{12.E.32}$$

to get:

$$a_E = \frac{1}{10}\left(6 + 2 + 2 + 4 + 2\right) \tag{12.E.33}$$

However, the reducible representation is better represented in a table format:

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
Γ	6	0	0	2	2	0	0	0	4	2

Q12.33

Apply the *Great Orthogonality Theorem,*

$$\sum_{\hat{R}} \Gamma_i(\hat{R})_{nm}\Gamma_{ij}(\hat{R})_{n'm'} = \frac{h}{d_i}\delta_{ij}\delta_{mm'}\delta_{nn'} \tag{12.E.34}$$

,

to C_{3v} point group given in which

$$\Gamma_E = [E_1 E_2 E_3 E_4 E_5 E_6] \tag{12.E.35}$$

where

$$E_1 = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \tag{12.E.36}$$

$$E_2 = \begin{bmatrix} -1/2 & -\sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{bmatrix} \tag{12.E.37}$$

$$E_3 = \begin{bmatrix} -1/2 & \sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{bmatrix} \tag{12.E.38}$$

$$E_4 = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \tag{12.E.39}$$

$$E_5 = \begin{bmatrix} -1/2 & \sqrt{3}/2 \\ \sqrt{3}/2 & 1/2 \end{bmatrix} \tag{12.E.40}$$

$$E_6 = \begin{bmatrix} -1/2 & -\sqrt{3}/2 \\ -\sqrt{3}/2 & 1/2 \end{bmatrix} \tag{12.E.41}$$

(h is the number of elements of Γ_i and d_i is the length of the diagonal of the matrix element of Γ_i)

S12.33

If we assume that $i = j = E_i$ and that $m = m', n = n'$, the general equation looks like

$$\sum_{\hat{R}} [\Gamma_E(\hat{R})_{nm}]^2 \tag{12.E.42}$$

we must to pick the same element of each matrix, square it, and add them all together. All of them should equal $/frachl = 3$.

$$\sum_{\hat{R}} [\Gamma_E(\hat{R})_{11}]^2 = 1 + 1/4 + 1/4 + 1 + 1/4 + 1/4 = 3 \tag{12.E.43}$$

$$\sum_{\hat{R}} [\Gamma_E(\hat{R})_{12}]^2 = 0 + 3/4 + 3/4 + 0 + 3/4 + 3/4 = 3 \tag{12.E.44}$$

$$\sum_{\hat{R}} [\Gamma_E(\hat{R})_{21}]^2 = 0 + 3/4 + 3/4 + 0 + 3/4 + 3/4 = 3 \tag{12.E.45}$$

$$\sum_{\hat{R}} [\Gamma_E(\hat{R})_{22}]^2 = 1 + 1/4 + 1/4 + 1 + 1/4 + 1/4 = 3 \tag{12.E.46}$$

for unequal cases,($m \neq m'$ and $n \neq n'$) we can use the products of the elements and they should sum to zero.

$$\sum_{\hat{R}} \Gamma_E(\hat{R})_{11}\Gamma_E(\hat{R})_{12} = 0 + \sqrt{3}/4 - \sqrt{3}/4 + 0 - \sqrt{3}/4 + \sqrt{3}/4 = 0 \tag{12.E.47}$$

$$\sum_{\hat{R}} \Gamma_E(\hat{R})_{11}\Gamma_E(\hat{R})_{21} = 0 - \sqrt{3}/4 + \sqrt{3}/4 + 0 - \sqrt{3}/4 + \sqrt{3}/4 = 0 \tag{12.E.48}$$

$$\sum_{\hat{R}} \Gamma_E(\hat{R})_{12}\Gamma_E(\hat{R})_{21} = 0 - 3/4 - 3/4 + 0 + 3/4 + 3/4 = 0 \tag{12.E.49}$$

$$\sum_{\hat{R}} \Gamma_E(\hat{R})_{12}\Gamma_E(\hat{R})_{22} = 1 + 1/4 + 1/4 - 1 - 1/4 - 1/4 = 0 \tag{12.E.50}$$

$$\sum_{\hat{R}} \Gamma_E(\hat{R})_{21}\Gamma_E(\hat{R})_{22} = 0 - \sqrt{3}/4 + \sqrt{3}/4 + 0 + \sqrt{3}/4 - \sqrt{3}/4 = 0 \tag{12.E.51}$$

Q12.34

Using the Great Orthogonality Theorem, let $i = j$, $m = n$, and $m' = n'$ and sum over n and n' to show that

$$\sum_{\hat{R}} [\chi_j(\hat{R})]^2 = h \tag{12.E.52}$$

.

S12.34

Recall that $\chi_j(\hat{R})$ is defined as the character of the jth irreducible representation of $\hat{R}$, which in terms of matrix elements, is given by

$$\chi_i(\hat{R}) = \sum_m \Gamma_i(\hat{R})_{mm} \tag{12.E.53}$$

We now use the **great orthogonality theorem** to find the summed equation:

$$\sum_{\hat{R}} \Gamma_i(\hat{R})_{mn} \Gamma_j(\hat{R})_{m'n'} = \frac{h}{l_i} \delta_{ij} \delta_{mm'} \delta_{nn'} \tag{12.E.54}$$

Let $i = j$, $m = n$, and $m' = n'$. Then

$$\sum_{\hat{R}} \Gamma_i(\hat{R})_{nn} \Gamma_i(\hat{R})_{n'n'} = \frac{h}{l_i} \delta_{nn'} \tag{12.E.55}$$

$$\sum_{\hat{R}} \sum_{n} \Gamma_i(\hat{R})_{nn} \sum_{n'} \Gamma_i(\hat{R})_{n'n'} = \frac{h}{l_i} \delta_{nn'} \tag{12.E.56}$$

$$\sum_{\hat{R}} [\chi_i(\hat{R})]^2 = \frac{h}{l_i} = h \tag{12.E.57}$$

Q12.35

Determine the character table for C_i which has the symmetry elements E and i.

S12.35

Because there are two symmetry elements, there are two rows to the character table also to have a 2x2. The first row is completely symmetric to both operations while the second is antisymmetric with respect to the inversion center. Therefore, the character table is as shown below.

	E	i
A_g	1	1
A_u	1	-1

Q12-36

The C_i point group character table is given by

Ci	E	i
Ag	+1	+1
Au	+1	-1

Show that the basis for this point group are the even and odd functions over an interval (-a,a). Evaluate the integrals of this basis set using group theory in order to establish symmetry principles.

S12-36

Applying the inversion operator to a function,

$$i f_{even} = f_{even} \tag{12.E.58}$$

$$i f_{odd} = -f_{odd} \tag{12.E.59}$$

This demonstrates that f(even) belongs to Ag and f(odd) belongs to Au. As a result these functions are a basis of the C_i point group.

$$S_{ij} = \int \phi_i^* \phi_j d\tau \tag{12.E.60}$$

$$RS_{ij} = \int R\phi_i^* R\phi_j d\tau = S_{ij} = \int \phi_i^* \phi_j d\tau \tag{12.E.61}$$

with the value of Sij unchanged by the symmetry operation of the point group.

$$S_{ij} = \int_{-a}^{a} f_{even}(x) f_{even}(x) dx \tag{12.E.62}$$

$$iS_{ij} = \int_{-a}^{a} i f_{even}(x) i f_{even}(x) dx = \int_{-a}^{a} f_{even}(x) f_{even}(x) dx = 1 \tag{12.E.63}$$

$$S_{ij} = \int_{-a}^{a} f_{odd}(x) f_{odd}(x) dx \tag{12.E.64}$$

$$iS_{ij} = \int_{-a}^{a} i f_{odd}(x) i f_{odd}(x) dx = \int_{-a}^{a} -f_{odd}(x) - f_{odd}(x) dx = 1 \tag{12.E.65}$$

$$S_{ij} = \int_{-a}^{a} f_{even}(x) f_{odd}(x) dx \tag{12.E.66}$$

$$iS_{ij} = \int_{-a}^{a} i f_{even}(x) i f_{odd}(x) dx = -\int_{-a}^{a} f_{even}(x) f_{odd}(x) dx = 0 \tag{12.E.67}$$

12.37

Derive the symmetry orbitals for the pi- orbitals of butadiene by applying the generating operator

$$P_j = \frac{d_j}{h} \sum_{R} \chi_j(R) R \tag{12.E.68}$$

to the atomic 2pz orbital on each carbon atom. Identify the irreducible representation to which each resulting symmetry orbital belong. Derive the Huckel secular determinant.

S12.37

Butadiene belongs to the C2h point-group. Denote the 2pz orbital on

$$C_i \tag{12.E.69}$$

by

$$\psi_i \tag{12.E.70}$$

$$P\psi_1 = \frac{1}{4} \sum_{R} \chi(R) R \tag{12.E.71}$$

$$= \frac{1}{4}[(1)E\psi_1 + (1)C_2\psi_1 + (1)i\psi_1 + (1)\sigma\psi_1] \tag{12.E.72}$$

$$= \frac{1}{4}(\psi_1 + \psi_4 - \psi_4 + \psi_2) = 0 \tag{12.E.73}$$

Similarly,

$$P\psi_2 = \frac{1}{4}(\psi_2 + \psi_3 - \psi_3 - \psi_2) = 0 \tag{12.E.74}$$

$$P\psi_2 = \frac{1}{4}(\psi_2 + \psi_3 - \psi_3 - \psi_2) = 0 \tag{12.E.75}$$

Using Psi 1 and 2 (things get very confusing after this line, especially the part of the equation "=0 $\alpha\psi_1 - \psi_4$? -RM)

$$P\psi_1 = \frac{1}{4}(\psi_1 - \psi_4 - \psi_4 + \psi_1) = 0\alpha\psi_1 - \psi_4 \tag{12.E.76}$$

$$P\psi_2 = \frac{1}{4}(\psi_2 - \psi_3 - \psi_3 + \psi_2) = 0\alpha\psi_2 - \psi_3 \tag{12.E.77}$$

$$P\psi_3 = \frac{1}{4}(\psi_1 + \psi_4 + \psi_4 + \psi_1) = 0\alpha\psi_1 + \psi_4 \tag{12.E.78}$$

$$P\psi_4 = \frac{1}{4}(\psi_2 + \psi_3 + \psi_3 + \psi_2) = 0\alpha\psi_2 + \psi_3 \tag{12.E.79}$$

$$P\psi_1 = \backslash\hat{\ } P\psi_2 = 0 \tag{12.E.80}$$

The process isnt very clear as to how you got to the solution...perhaps explain a little better how the math works.

Q12.41

An arbitrary tetrahedral molecule (AB_4) belonging to the T_d point group has the reducible representation: Γ = 4 1 0 0 2. Show that:

  a. the symmetry elements of the point group give this representation, and
  b. it can be reduced as $\Gamma = A_1 + T_2$.

Finally, prove that an **sp^3** orbital with **T$_d$** symmetry can be formed.

S12.41

a.) Applying the symmetry elements, we see that:

- $\hat{E}$ leaves all 4 bonds unmoved
- $\hat{C}_3$ leaves 1 bond unmoved
- $\hat{C}_2$ leaves 0 bonds unmoved
- $\hat{S}_4$ leaves 0 bonds unmoved
- $\hat{\sigma}_d$ leaves 2 bonds unmoved

The result is the reducible representation Γ = 4 1 0 0 2.

b.) Rewriting the symmetry elements in terms of the irreducible representations, we see that:

- $\alpha_{A_1} = \dfrac{1}{24}(4+8+0+0+12) = 1$
- $\alpha_{A_2} = \dfrac{1}{24}(4+8+0+0-12) = 0$
- $\alpha_{E} = \dfrac{1}{24}(8-8+0+0+0) = 0$
- $\alpha_{T_1} = \dfrac{1}{24}(12+0+0+0-12) = 0$
- $\alpha_{T_2} = \dfrac{1}{24}(12+0+0+0+12) = 1$

Using α as a coefficient and taking the sum of these 5 equations, we can rewrite the reducible representation as $\Gamma = A_1 + T_2$.

c.) The 2 p orbitals all have T_2 symmetry for a T_d molecule, so they can combine to form a hybrid T_2 orbital. All s orbitals are totally symmetric due to their spherical shape, making them A_1. Summing the 3 p orbitals and an s orbital will give a hybrid orbital of the desired $A_1 + T_2$ symmetry.

-Interesting question. I like the explanation on how an Sp3 orbital with T_2 symmetry can be formed

Q12.42

Consider an octahedral molecule XY6 whose point group is O$_h$. Prove the irreducible representation of O$_h$ is Γ = A$_{1g}$ + E$_g$ + T$_{1u}$.

S12.43

$$a_{A_{1g}} = \frac{1}{48}\left(6+0+0+12+6+0+0+0+12+12\right) = 1 \qquad (12.E.81)$$

$$a_{A_{2g}} = \frac{1}{48}\left(6+0+0-12+6+0+0+0+12-12\right) = 0$$

$$a_{E_g} = \frac{1}{48}\left(12+0+0+0+12+0+0+0+24+0\right) = 1$$

$$a_{T_{1g}} = \frac{1}{48}\left(18+0+0+12-6+0+0+0-12-12\right) = 0$$

$$a_{T_{2g}} = \frac{1}{48}\left(18+0+0-12-6+0+0+0-12+12\right) = 0$$

$$a_{A_{1u}} = \frac{1}{48}\left(6+0+0+12+6+0+0+0-12-12\right) = 0$$

$$a_{A_{2u}} = \frac{1}{48}\left(6+0+0-12+6+0+0+0-12+12\right) = 0$$

$$a_{E_u} = \frac{1}{48}\left(12+0+0+0+12+0+0+0-24+0\right) = 0$$

$$a_{T_{1u}} = \frac{1}{48}\left(18+0+0+12-6+0+0+0+12+12\right) = 1$$

$$a_{T_{2u}} = \frac{1}{48}\left(18+0+0-12-6+0+0+0+12-12\right) = 0$$

$= \Gamma = A_{1g} + E_g + T_{1u}.$

Q12.43

Consider an octahedral molecule XY6 whose point group is O_h. Prove the irreducible representation of O_h is $\Gamma = A_{1g} + E_g + T_{1u}$.

S12.43

$$a_{A_{1g}} = \frac{1}{48}\left(6+0+0+12+6+0+0+0+12+12\right) = 1 \qquad (12.E.82)$$

$$a_{A_{2g}} = \frac{1}{48}\left(6+0+0-12+6+0+0+0+12-12\right) = 0$$

$$a_{E_g} = \frac{1}{48}\left(12+0+0+0+12+0+0+0+24+0\right) = 1$$

$$a_{T_{1g}} = \frac{1}{48}\left(18+0+0+12-6+0+0+0-12-12\right) = 0$$

$$a_{T_{2g}} = \frac{1}{48}\left(18+0+0-12-6+0+0+0-12+12\right) = 0$$

$$a_{A_{1u}} = \frac{1}{48}\left(6+0+0+12+6+0+0+0-12-12\right) = 0$$

$$a_{A_{2u}} = \frac{1}{48}\left(6+0+0-12+6+0+0+0-12+12\right) = 1$$

$$a_{E_u} = \frac{1}{48}\left(12+0+0+0+12+0+0+0-24+0\right) = 0$$

$$a_{T_{1u}} = \frac{1}{48}\left(18+0+0+12-6+0+0+0+12+12\right) = 1$$

$$a_{T_{2u}} = \frac{1}{48}\left(18+0+0-12-6+0+0+0+12-12\right) = 0$$

Therefore, the irreducible representation becomes $\Gamma = A_1 + A_2 + E$