Symmetry and Condensed Matter Physics
A Computational Approach
Solution Manual

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1
Symmetry and physics

1.1 Exercises

1.1 Write down and solve the equations of motion for the system of masses and springs shown in Fig. 1.5. Assume both masses to be equal and all springs to have the same force constant. Show that the eigenvalues for the energy are given by $\omega^2 m = k,\ 3k$, from which the eigenvectors can be found to be in agreement with the results obtained purely by symmetry arguments. Must all three force constants be equal for this result to be obtained? Can you decide based on symmetry arguments alone?

1.2 Write the equations of motion for exercise 1.1 in the form $M\mathbf{u} = -\omega^2 m\mathbf{u}$, where M is a matrix. Use the two eigenvectors found in the text,

$$\mathbf{u}_1 = \begin{pmatrix} 1 \\ 1 \end{pmatrix} \qquad \text{and} \qquad \mathbf{u}_2 = \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

to construct the matrix

$$S = \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix},$$

where the first column of the matrix is given by $\mathbf{u}_1$ and the second column by $\mathbf{u}_2$. Find S^{-1} and then diagonalize M according to

$$S^{-1}MS = \lambda I,$$

where I is the unit matrix, to find the eigenvalues λ.

1.3 Find the function generated by C_4 acting on the function $xf(r)$.

1.4 Show that the operation $S_n^{n/2} = I$ for $n/2$ odd. Show that for even n, S_n implies the existence of $C_{n/2}$.

1.5 Consider the case of an n-fold principal axis. Show that the introduction of a 2-fold symmetry axis perpendicular to it implies the coexistence of n equivalent axes for n odd, and the coexistence of n/2 equivalent axes for n even.

1.6 Introduce diagonal reflection planes, σ_d, in the previous problem and show, using the 3-dimensional defining matrices for a σ_d plane and a neighboring 2-fold axis U, that the product $U\sigma_\mathrm{d} = S_\mathrm{n}$.

1.7 Show that the determinant of an improper rotation is -1.

1.8 Obtain the 3-dimensional rotation matrix for the C_2 axis joining two opposite edges of a tetrahedron, shown in figure 1.1. Note that the origin of the coordinate system is the centroid of the tetrahedron. (Hint: Start with a 2-fold rotation about the z-axis, then use a counterclockwise rotation about the x-axis to transform the axis to its final position, as shown in the figure.)

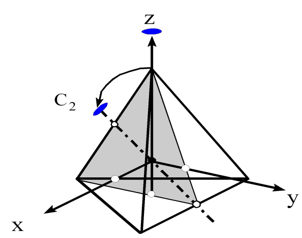

Fig. 1.1. A C_2 rotation about an axis bisecting opposite edges of a tetrahedron.

1.9 Using the results of the previous problem, find the new function generated by the function operator $\hat{C}_2$ acting on $zf(r)$.

1.10 Obtain the 3-dimensional rotation matrix for the operation $C_3[111]$ shown in figure 1.2. (Hint: Start with a 3-fold rotation axis along the z-direction, followed by rotating the axis counterclockwise, by 45° about the y-axis; and, finally, rotate the axis counterclockwise by 45° about the z-axis.)

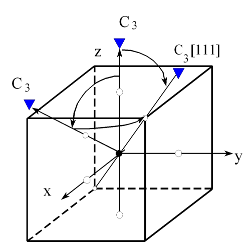

Fig. 1.2. A C_3 rotation about a [111] body-diagonal axis of a cube.

1.2 Solutions

1.1 The equation of motion are

$$\left.\begin{aligned} m\,\frac{d^2x_1}{dt^2} &= \kappa\left(x_2 - 2x_1\right) \\ m\,\frac{d^2x_2}{dt^2} &= \kappa\left(x_1 - 2x_2\right) \end{aligned}\right\} \quad \Rightarrow \quad \begin{pmatrix} \dfrac{2\kappa}{m} - \omega^2 & \dfrac{-\kappa}{m} \\ \dfrac{-\kappa}{m} & \dfrac{2\kappa}{m} - \omega^2 \end{pmatrix} \begin{bmatrix} x_1 \\ x_2 \end{bmatrix} = 0 \tag{1.1}$$

where we assumed a harmonic time-dependence. The characteristic equation is

$$\left(\frac{2\kappa}{m} - \omega^2\right)^2 = \left(\frac{\kappa}{m}\right)^2 \quad \Rightarrow \quad \omega^2 = \frac{\kappa}{m}, \frac{3\kappa}{m}$$

Eigenvectors

$$\omega^2 = \frac{\kappa}{m} : \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ 1 \end{bmatrix}; \qquad \omega^2 = \frac{3\kappa}{m} : \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ -1 \end{bmatrix}$$

The resulting eigenvectors obtain as long as the system is symmetric about the center. This can be achieved by keeping the outer spring constants at κ and setting the middle one to κ'; the eigenvalues will become $\omega^2 = \kappa/m$, $(\kappa + 2\kappa')/m$.

1.2 $S^{-1} = S$, and normalizing

$$S = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}$$

we obtain

$$\frac{1}{2} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \begin{pmatrix} 2\kappa & -\kappa \\ -\kappa & 2\kappa \end{pmatrix} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} = \begin{pmatrix} \kappa & 0 \\ 0 & 3\kappa \end{pmatrix}$$

1.3 The operation C_4 is given by

$$C_4 = \begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix}$$

and we have

$$\hat{C}_4\left(x f(r)\right) = \left(C_4^{-1}\, x\, f(C_4^{-1} r)\right) = y f(r)$$

1.4 The operation $S_n = C_n \sigma_h$, hence, for $n/2$ odd we have

$$S_n^{n/2} = C_n^{n/2}\, \sigma_h^{n/2} = C_2 \sigma_h = I$$

1.5 The existence of a 2-fold axis U perpendicular to C_n implies the existence of equivalent 2-fold axes $U^{(m)} = C_n^{-m} U C_n^m,\ m = 0, \ldots, n-1$. For n odd there n distinct axes $U^{(m)}$, while for n even the values m and $n-m$ define the same axis; hence there only $n/2$ 2-fold axes perpenducular to C_n.

1.6 If we take the 2-fold axis to be along the x-axis, then its matrix is

$$U^{(x)} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

An adjacent diagonal reflection plane can be generated by rotating a σ_y plane by π/n about the z-axis, namely,

$$\begin{aligned} \sigma_{\mathrm{d}} &= \begin{bmatrix} \cos(\pi/n) & -\sin(\pi/n) & 0 \\ \sin(\pi/n) & \cos(\pi/n) & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} \cos(\pi/n) & \sin(\pi/n) & 0 \\ -\sin(\pi/n) & \cos(\pi/n) & 0 \\ 0 & 0 & 1 \end{bmatrix} \\ &= \begin{bmatrix} \cos(2\pi/n) & \sin(2\pi/n) & 0 \\ \sin(2\pi/n) & -\cos(2\pi/n) & 0 \\ 0 & 0 & 1 \end{bmatrix} \end{aligned}$$

The product

$$\begin{aligned} U^{(x)} \cdot \sigma_{\mathrm{d}} &= \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} \cos(2\pi/n) & \sin(2\pi/n) & 0 \\ \sin(2\pi/n) & -\cos(2\pi/n) & 0 \\ 0 & 0 & 1 \end{bmatrix} \\ &= \begin{bmatrix} \cos(2\pi/n) & \sin(2\pi/n) & 0 \\ -\sin(2\pi/n) & \cos(2\pi/n) & 0 \\ 0 & 0 & 1 \end{bmatrix} = C_n \, \sigma_h = S_n \end{aligned}$$

1.7 The determinant of an improper rotation $S_n = C_n \sigma_h$ is given by

$$\det(S_n) = \det\big(C_n \cdot \sigma_h\big) = \det(C_n) \cdot \det(\sigma_h) = 1 \times (-1) = -1$$

1.8 The rotation C_2 is obtained as

$$
\begin{aligned}
C_2 &= C_3^{(x)} C_2^{(z)} C_3^{(x)} \\
&= \begin{bmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix} \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix} \\
&= \begin{bmatrix} -1 & 0 & 0 \\ 0 & \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix}
\end{aligned}
$$

1.9 Applying $\hat{C}_2$ to the function $\psi = zf(r)$ yields

$$
\hat{C}_2 \psi = \left(C_2\, z\right) f(C_2 r) = \begin{bmatrix} -1 & 0 & 0 \\ 0 & \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix} \begin{bmatrix} 0 \\ 0 \\ z \end{bmatrix} f(r) = \left(-\frac{\sqrt{3}}{2} y - \frac{1}{2} z\right) f(r)
$$

1.10

2

Symmetry and group theory

2.1 Exercises

Note on the problems: Problems 1 through 15 range from those which help in developing an understanding of the *theory* of groups to those which are in the nature of finger exercises and help in developing familiarity with group theory and some dexterity in performing the mathematical manipulations of group theory. Problems 17 and 18 are crucial. The solution to problem 16 provides the basis for the remaining computational methods that follow in later chapters. Problem 19 provides a check on the program developed in problem 18. Problems 20 through 25 provide an introduction to crystallographic point-groups. They should all be read and thought about, and at least a few of them carried to completion. Geometric figures are provided to elucidate the properties of these point-groups. The vertices of the figures are numbered sequentially, to facilitate the construction of permutation operations associated with the groups. In addition to the particular questions posed in each problem, apply the program developed in problem 18 to each of problems 20 through 25.

2.1 Convert the following permutation from bracket notation to cycle notation.

$$\begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 & 7 \\ 6 & 5 & 2 & 3 & 4 & 1 & 7 \end{pmatrix}$$

2.2 Convert (163275) to bracket notation.

2.3 Given permutation operators p and q defined by

$$p = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 & 7 \\ 1 & 7 & 4 & 5 & 3 & 2 & 6 \end{pmatrix} \qquad q = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 & 7 \\ 5 & 1 & 2 & 4 & 3 & 7 & 6 \end{pmatrix},$$

(a) Find the product pq in bracket notation.

(b) Use the `Permute` function defined in *Mathematica*, or any other computer language code you develop, to carry out the permutation product.

2.4 Repeat problem 2.3 for the following pairs of permutation operators
(a) $p = (567),\ q = (2673)$,
(b) $p = (246)(37),\ q = (143)(56)$.

Write the products pq in cycle notation. Try to do this by sight without writing out the implicit cycles in p or q.

2.5 Find the inverse and degree of each of the following permutation operations, by long-hand, using the *Mathematical*function `InversePermutation`, or developing your own code in C or FORTRAN:

$$p = \begin{pmatrix} 1 & 2 & 3 \\ 1 & 3 & 2 \end{pmatrix}\ q = \begin{pmatrix} 1 & 2 & 3 \\ 3 & 2 & 1 \end{pmatrix}\ r = \begin{pmatrix} 1 & 2 & 3 & 4 \\ 4 & 3 & 1 & 2 \end{pmatrix}$$

$$s = \begin{pmatrix} 1 & 2 & 3 & 4 \\ 2 & 1 & 4 & 3 \end{pmatrix}\ t = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 \\ 5 & 4 & 1 & 2 & 3 \end{pmatrix}$$

$$u = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 & 7 \\ 1 & 4 & 7 & 6 & 3 & 2 & 5 \end{pmatrix}\ v = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 & 7 \\ 6 & 5 & 2 & 3 & 4 & 7 & 1 \end{pmatrix}$$

$$w = (12)(34657)$$

2.6 Show that the permutations of n objects, which form the symmetric group $\mathcal{S}_{\mathrm{n}}$ is of order $n!$.

2.7 Show for the symmetric group $\mathcal{S}_3$ that elements with the same form of decomposition into cycles belong to the same class. In generating the classes augment the above computer functions, or codes, with the *Mathematical*function `ToCycle[p]`, or an equivalent.

2.8 Determine the classes of the symmetric group $\mathcal{S}_4$.

2.9 Show that the number of element nc_i of a class $\mathcal{C}_i$ of a finite group $\mathcal{G}$, divides its order, i.e. g/nc_i is an integer.

2.10 Show that the set comprised of all inverses of the elements of a class $\mathcal{C}_i$ of a group $\mathcal{G}$ is also a class of $\mathcal{G}$, which we may denote by $\mathcal{C}_j = \mathcal{C}_i^{-1}$. Such classes are called *mutually reciprocal classes*. If a class contains its own inverse elements it is called a *self-inverse class*.

2.11 Consider the isomorphic realizations C_{4v} and $\mathcal{D}_4$ of the square. These realization groups contain 8 elements:

$$E, C_4, C_4^{-1}, C_2, \sigma_1(C_2'^1), \sigma_2(C_2'^2), \sigma_1'(C_2''^2), \sigma_2'(C_2''^2).$$

In addition to the identity operation we find in each realization 4-fold rotations and reflections (or 2-fold rotations). However, if we examine the class structure of these realization groups we find: $\mathcal{C}_1 = \{E\}$, $\mathcal{C}_2 = \{C_4, C_4^{-1}\}$, $\mathcal{C}_3 = C_2$, $\mathcal{C}_4 = \{\sigma_1(C_2'^1), \sigma_2(C_2'^2)\}$, $\mathcal{C}_5 =$

$\{\sigma_1'(C_2''^2), \sigma_2'(C_2''^2)\}$. A close examination of the nature of the operations in these groups reveals that the reflections (or 2-fold rotations) in different classes are not mutually reachable by any of the group elements.

2.12 Prove that if class $\mathcal{C}_j$ contains the inverse of element R in class $\mathcal{C}_i$, then $\mathcal{C}_j$ must be comprised of all the inverse elements of $\mathcal{C}_i$, and $\mathrm{nc}(j) = \mathrm{nc}(i)$, where $\mathrm{nc}(i)$ is the number of elements in class $\mathcal{C}_i$. An *ambivalent* class is a class that is its own inverse.

2.13 Find the class multiplication coefficients h_{ijk} for the groups $C_{3\mathrm{v}}$ and C_{4v}.

2.14 Show that the following general relations are satisfied by the class multiplication coefficients.

(i) $\mathrm{h}_{ijk} = \mathrm{h}_{jik}$ (This is equivalent to proving that $\mathcal{C}_i X = X\mathcal{C}_i$ for all elements X. Let X range over all elements in $\mathcal{C}_j$.)

(ii) $\sum_{k=1}^{\mathrm{ncl}} \mathrm{h}_{ijk}\,\mathrm{h}_{klm} = \sum_{k=1}^{\mathrm{ncl}} \mathrm{h}_{jlk}\,\mathrm{h}_{ikm}$

(iii) $\mathrm{nc}(i)\,\mathrm{nc}(j) = \sum_{k=1}^{ncl} h_{ijk}\,\mathrm{nc}(k)$.

(iv) $\mathrm{h}_{ijk} = \mathrm{h}_{\bar{i}\bar{j}\bar{k}}$

(v) $\mathrm{nc}(k)\ \mathrm{h}_{ijk} = \mathrm{nc}(i)\ \mathrm{h}_{k\bar{j}i} = \mathrm{nc}(i)\ \mathrm{h}_{j\bar{k}\bar{i}} = \mathrm{nc}(j)\ \mathrm{h}_{i\bar{k}\bar{j}}$

(vi) $\mathrm{h}_{ij1} = \mathrm{nc}(i)\ \delta_{i\bar{j}}$ where $\mathrm{nc}(i)$ is the number of elements in class $\mathcal{C}_i$ and where bars denote the inverse class. That is, $\mathcal{C}_{\bar{i}}$ is a class that contains the inverses of the elements of class $\mathcal{C}_i$. Note, that the third subscript on h, here, is the number 1, not the letter l.

(vii) Show that a mapping of one group onto another can be completely specified by the action of the mapping on the generators of the larger group.

2.15 Prove the group rearrangement theorem.

2.16 Prove the class rearrangement theorem.

2.17 Prove that the set of integers $1, 2, 3, \ldots, (k-1)$ form a group of order (k-1) under ordinary multiplication *modulo* k. Note: Two integers m and n are equal, *modulo* k, if $m = n + jk$, where j is an integer.

Multiplication, modulo a prime number, plays an important role in Dixon's method for determining the characters of irreducible representations.

2.18 Write a a general computer program, guided by the outlines in the text, which makes use of the minimal set of group generators to

(i) generate the group elements in permutation form,

(ii) construct the corresponding Cayley tables,

(iii) generate the inverse elements,

(iv) generate the classes and class arrays, specified in Section 3.1,

(v) generate the class multiplication matrices

2.19 Use the program from the previous problem to obtain the group multiplication tables for the point-groups $C_{3\mathrm{v}}$, C_{4v}, C_{5v}.

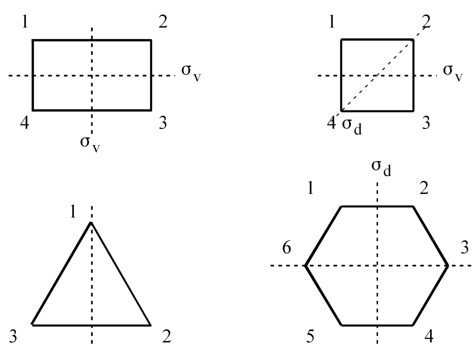

Fig. 2.1. Clockwise from top left: Symmetries of the point-groups $\mathcal{C}_{2\mathrm{v}}$, $\mathcal{C}_{4\mathrm{v}}$, $\mathcal{C}_{6\mathrm{v}}$, and $\mathcal{C}_{3\mathrm{v}}$, respectively.

The surface nets of figure 2.5 can be modified by replacing the n reflection planes σ_{v} with n 2-fold rotation axes C_2 that are perpendicular to the principal C_n axis, and by replacing the n reflection planes σ_{d} with n 2-fold C_2' axes, giving rise to the dihedral symmetry groups $\mathcal{D}_{\mathrm{n}}$ shown in figure 2.6, which are isomorphic to the $\mathcal{C}_{\mathrm{nv}}$ groups.$\mathcal{D}_{\mathrm{n}}$ shown in figure 2.6, which are isomorphic to the $\mathcal{C}_{\mathrm{nv}}$ groups.

2.20 Figure 2.5 shows the primitive meshes corresponding to allowed two-dimensional surface lattices (nets). The vertices are sequentially numbered, clockwise. Also shown, are the allowed types of reflection planes, designated by σ_{v} and σ_d.

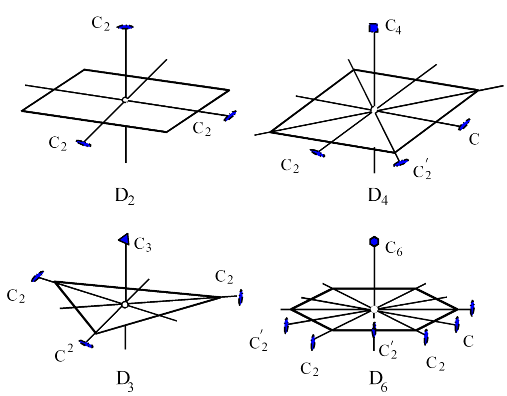

Fig. 2.2. Symmetries of the dihedral groups $\mathcal{D}_2$, $\mathcal{D}_4$, $\mathcal{D}_3$, and $\mathcal{D}_6$.

(a) Find all the physically realizable point-symmetry operations for the four meshes of figure 2.5. Write out these symmetry operations as permutations of the vertex numbering, in cycle notation. (Note that there are 4, 8, 6, and 12 operations for these meshes, respectively; and that the identity operation and the rotations maintain the clockwise ordering of the labeling. The mirror reflections change the labeling to counterclockwise.)

b) Why aren't the remaining permutations, like (1324) for C_{4v}, symmetry operations?

2.21 Figure 2.7 shows the primitive (Wigner-Seitz) cells for lattices with symmetry involving a *major* axis of rotation and a horizontal reflection plane σ_h, that is, a reflection plane perpendicular to the major axis. These *improper* point symmetry groups are designated $\mathcal{C}_{nh}$, where n = 2, 3, 4, 6.

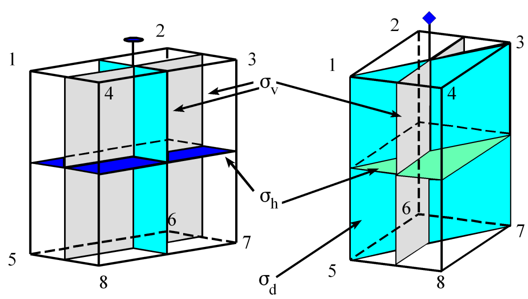

Fig. 2.3. Primitive cells with $\mathcal{C}_{nh}$ symmetries.

Show that these groups have the following properties:

(i) Since groups with even n include the 2-fold rotation $C_2 = C_n^{n/2}$, by taking the major axis along the z-direction, and defining the C_2 and σ_h by the 3-dimensional rotation matrices, show that

$$C_2\sigma_h = \sigma_h C_2 = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} = I,$$

which is just the matrix that defines the inversion symmetry operation $\mathbf{r} \to -\mathbf{r}$. Thus, $\mathcal{C}_{nh}$ *symmetries with even n contain the inversion operation, i.e., the corresponding primitive cell have a center of inversion. Groups with odd n do not contain the inversion.*

(ii) For n=1, the group $\mathcal{C}_{1h}$ is comprised of the identity E and σ, and is usually denoted by $\mathcal{C}_s$. Thus, show that we can express the $\mathcal{C}_{nh}$ groups as the outer products

$$\mathcal{C}_{nh} = \mathcal{C}_n \otimes \mathcal{C}_s \ ,$$

containing 2n elements.

(iii) Each has 2n classes.

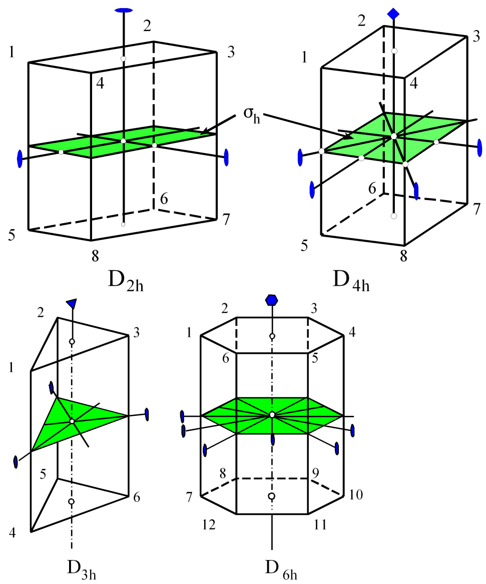

Fig. 2.4. Primitive cells with $\mathcal{D}_{\rm nh}$ symmetries

2.22 When the dihedral groups $\mathcal{D}_{\rm n}$ are augmented by a $\sigma_{\rm h}$ reflection plane, perpendicular to the major axis, as shown in Fig. 2.8, we obtain the improper point-groups $\mathcal{D}_{\rm nh}$. Again, I is an element of the group, only if n is even. Show that the $\mathcal{D}_{\rm n}$ point-groups have the following properties:

(i) The group order is 4n.
(ii) They contain n $\sigma_{\rm v}$ reflection planes, in addition to the n C_2 rotations.
(iii) $\sigma_{\rm h}$ commutes with all the elements of the group. Hence we can express these groups as

$$\mathcal{D}_{\rm nh} = \mathcal{D}_{\rm n} \otimes \mathcal{C}_{\rm s} \ .$$

2.23 In Figure 2.9, we show the case of augmenting $\mathcal{D}_{\rm n}$ by a vertical $\sigma_{\rm d}$ reflection plane that bisects the angle between two neighboring C_2 axes. The ensuing groups are designated $\mathcal{D}_{\rm nd}$.

Show that

(i) the operation

$$C_2\sigma_{\rm d} = S_{\rm 2n} \ ,$$

where C_2 is one of the neighboring 2-fold axes.

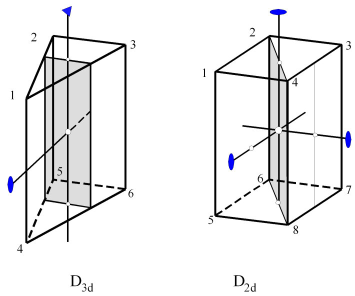

Fig. 2.5. Primitive cells with $\mathcal{D}_{\mathrm{nd}}$ symmetries.

(ii) for n odd, there is one σ_{d} plane perpendicular to one of 2-fold axes, and that, in this case, the group can be expressed as

$$\mathcal{D}_{\mathrm{nd}} = \mathcal{D}_{\mathrm{n}} \otimes \mathcal{C}_i \ .$$

2.24 Figure 2.10 shows two regular tetrahedra with symmetries T and T$_d$.

(a) For the tetrahedron shown with point-group symmetry T, write out the symmetry operations in cycle notation for the various rotations about the axes that pass through an apex of the tetrahedron and the center of the opposite face. These consist of rotations denoted by C_3 and C_3^2. Do the same for symmetry operations that consist of rotations about a 2-fold axis that passes through the midpoint of one edge, the center of the tetrahedron, and the midpoint of the opposite edge. Show that these 11 operations together with the identity form a group, the T group.

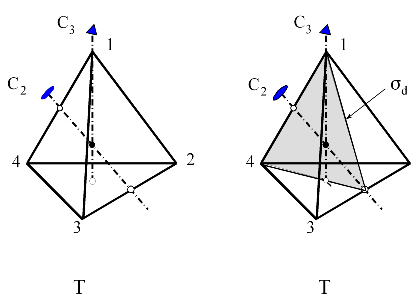

Fig. 2.6. Primitive cells with tetrahedral symmetries T and T$_d$.

(b) In addition to the operation of part (a), the tetrahedron with point-group symmetry T$_d$ shows reflection planes that pass through one edge of the tetrahedron and bisect the opposite edge. Each of these reflection planes contains one 2-fold and two 3-fold axes, and bisects the angle between the remaining two 2-fold axes, thus designated σ_{d}.

Show that each σ_d plane converts the 2-fold axis it contains into a 4-fold rotary reflection axes S_4.

Write out the symmetry operations corresponding to the reflections σ_d in cycle form. Expand the group of part (a) by including these symmetry operations in the group. Note that this *requires* the inclusion of other symmetry operations to complete the group, an example being (1234) = (14)(123), which corresponds to a rotation followed by a reflection. This group is designated T_d.

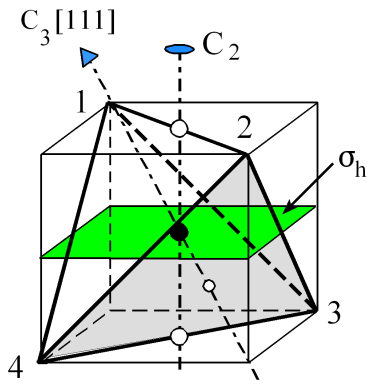

Fig. 2.7. Primitive cell with T_h tetrahedral symmetries.

(c) Figure 2.11 shows the primitive cell with T_h symmetry. In this figure the 3-fold axes are rotated to coincide with the body diagonals of a cube. One of the 2-fold axes is now along the z-axis. The σ_h reflection planes are perpendicular to the 2-fold axes and bisect the angles between the 3-fold axes. Carry out all the steps stated in parts (a) and (b).

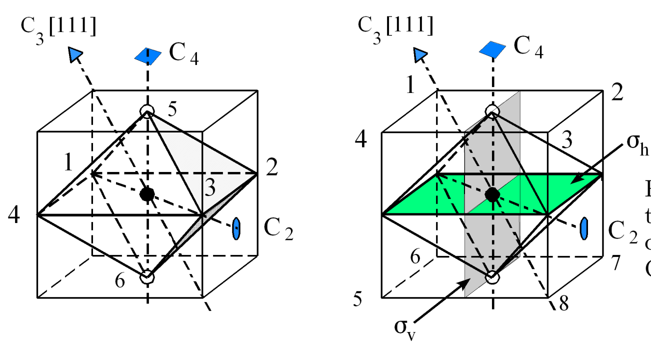

Fig. 2.8. The octahedral primitive cell with O and O_h symmetries.

2.25 Figure 2.12 shows the primitive cell with O and O_h symmetry. O is comprised of allowed rotation and reflection operation except σ_h, it has 24 operations. Obviously, O_h contains σ_h. Carry out all the steps stated in parts (a) and (c) of the previous problem for these two octahedral groups.

2.2 Solutions

2.1 (16)(2543)

2.2 $\begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 & 7 \\ 6 & 7 & 2 & 4 & 1 & 3 & 5 \end{pmatrix}$

2.3 a) $\tilde{q} = \begin{pmatrix} 2 & 3 & 5 & 4 & 1 & 7 & 6 \\ 1 & 2 & 3 & 4 & 5 & 6 & 7 \end{pmatrix}$

$$pq = \begin{pmatrix} 2 & 3 & 5 & 4 & 1 & 7 & 6 \\ 1 & 7 & 4 & 5 & 3 & 2 & 6 \end{pmatrix} = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 & 7 \\ 3 & 1 & 7 & 5 & 4 & 6 & 2 \end{pmatrix}$$

b) `Permute[{1, 7, 4, 5, 3, 2, 6},{5, 1, 2, 4, 3, 7, 6}]`

`={3, 1, 7, 5, 4, 6, 2}`

2.4 a) $\tilde{q} = \begin{pmatrix} 1 & 2 & 3 & 4 & 6 & 7 & 5 \\ 1 & 2 & 3 & 4 & 5 & 6 & 7 \end{pmatrix}$

$$pq = \begin{pmatrix} 1 & 6 & 2 & 4 & 5 & 7 & 3 \\ 1 & 2 & 3 & 4 & 7 & 5 & 6 \end{pmatrix} = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 & 7 \\ 1 & 3 & 6 & 4 & 7 & 2 & 5 \end{pmatrix}$$

Cycles: (236)(57)

b) $\tilde{q} = \begin{pmatrix} 4 & 2 & 1 & 3 & 6 & 5 & 7 \\ 1 & 2 & 3 & 4 & 5 & 6 & 7 \end{pmatrix}$

$$pq = \begin{pmatrix} 4 & 2 & 1 & 3 & 6 & 5 & 7 \\ 1 & 6 & 7 & 2 & 5 & 4 & 3 \end{pmatrix} = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 & 7 \\ 7 & 6 & 2 & 1 & 4 & 5 & 3 \end{pmatrix}$$

Cycles: (1732654)

2.5 $p^{-1} = p; \quad q^{-1} = q; \quad r^{-1} = \begin{pmatrix} 1 & 2 & 3 & 4 \\ 3 & 4 & 2 & 1 \end{pmatrix}; \quad s^{-1} = s;$

$$t^{-1} = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 \\ 3 & 4 & 5 & 2 & 1 \end{pmatrix}; \qquad u^{-1} = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 & 7 \\ 1 & 6 & 5 & 2 & 7 & 4 & 3 \end{pmatrix};$$

$$v^{-1} = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 & 7 \\ 7 & 3 & 4 & 5 & 2 & 1 & 6 \end{pmatrix}; \qquad w^{-1} = (12)(43756)$$

2.6 $\mathcal{S}_3 : \begin{cases} E = (1)(2)(3),\ C_3 = (123),\ C_3^{-1} = (132), \\ \sigma_1 = (12),\ \sigma_2 = (23),\ \sigma_3 = (31) \end{cases}$

2.7

2.8 $\{E\}$,

$\{(12), (13), (14), (23), (24), (34)\}$,

$\{(12)(34), (13)(24), (14)(23)\}$,

$\{(123), (124), (132), (134), (142), (143), (234), (243)\}$

$\{(1234), (1243), (1324), (1342), (1423), (1432)\}$.

2.9 In the conjugation operation $SUS^{-1} = V$, where S, U, $V \in \mathcal{G}$, either $V \equiv U$, and U is in a class by itself, or $V \not\equiv U$ i.e. distinct from U. Accordingly, if we define the class sum for $\mathcal{C}_i$

$$\sum_{U \in \mathcal{C}_i} U$$

containing $nc(i)$ distinct elements, then we find that

$$S \left(\sum_{U \in \mathcal{C}} U \right) S^{-1} = \left(\sum_{U \in \mathcal{C}} U \right)$$

We consider any two elements U, V of some class $\mathcal{C}$ of a group $\mathcal{G}$, related by the conjugation $V = SUS^{-1}$, $S \in \mathcal{G}$, then

$$\sum_{R \in \mathcal{G}} RVR^{-1} = \sum_{R \in \mathcal{G}} RSUS^{-1}R^{-1} = \sum_{R \in \mathcal{G}} (RS)U(RS)^{-1} = \sum_{R \in \mathcal{G}} RUR^{-1}$$

by the group rearrangement theorem. Moreover,

$$S \sum_{R \in \mathcal{G}} RVR^{-1} = \sum_{R \in \mathcal{G}} SRUR^{-1}S^{-1}S = \sum_{R \in \mathcal{G}} (SR)U(SR)^{-1}S = \sum_{R \in \mathcal{G}} RUR^{-1}S$$

or

$$S\left(\sum_{R\in\mathcal{G}} RVR^{-1}\right)S^{-1} = \sum_{R\in\mathcal{G}} RUR^{-1}$$

i.e. it contains the same

Thus,

2.10 Consider the mutually inverse elements $UU^{-1} = E$, and the conjugation $RUR^{-1} = V$, where U and V belong to the same class $\mathcal{C}_i$, then

$$V^{-1} = \left(RUR^{-1}\right)^{-1} = RU^{-1}R^{-1}$$

thus, U^{-1} and V^{-1} belong to the same class $\mathcal{C}_j$. If $V^{-1} \in \mathcal{C}_i$, then $U^{-1} \in \mathcal{C}_i$ and $\mathcal{C}_i$ is a self-inverse class.

2.11 There is no conjugation operation in the group that would take one set of reflections (U rotations) into the other, since there is no $\pi/4$ rotation about the z-axis.

2.12 See Exercise 2.10.

2.13 For $\mathcal{C}_{3\mathrm{v}}$, see example 2.7. $\mathcal{C}_{4\mathrm{v}}$ has five classes

$$\mathcal{C}_1 = \{E\},\ \mathcal{C}_2 = \{C_2\},\ \mathcal{C}_3 = \{C_4,\ C_4^{-1}\},\ \mathcal{C}_4 = \{\sigma_1,\ \sigma_2\},\ \mathcal{C}_5 = \{\sigma_1^{\mathrm{d}},\ \sigma_2^{\mathrm{d}}\}$$

The class multiplications are

$$\begin{aligned}
&\mathcal{C}_1\,\mathcal{C}_i = \mathcal{C}_i\,\mathcal{C}_1 = \mathcal{C}_i,\\
&\mathcal{C}_2^2 = \mathcal{C}_1,\quad \mathcal{C}_2\,\mathcal{C}_3 = \mathcal{C}_3,\quad \mathcal{C}_2\,\mathcal{C}_4 = \mathcal{C}_4,\quad \mathcal{C}_2\,\mathcal{C}_5 = \mathcal{C}_5,\\
&\mathcal{C}_3^2 = 2\mathcal{C}_1 + 2\mathcal{C}_2,\quad \mathcal{C}_3\,\mathcal{C}_2 = \mathcal{C}_3,\quad \mathcal{C}_3\,\mathcal{C}_4 = 2\mathcal{C}_5,\quad \mathcal{C}_3\,\mathcal{C}_5 = 2\mathcal{C}_4,\\
&\mathcal{C}_4^2 = 2\mathcal{C}_1 + 2\mathcal{C}_2,\quad \mathcal{C}_4\mathcal{C}_2 = \mathcal{C}_4,\quad \mathcal{C}_4\mathcal{C}_3 = 2\mathcal{C}_5,\quad \mathcal{C}_4\,\mathcal{C}_5 = 2\mathcal{C}_3,\\
&\mathcal{C}_5^2 = 2\mathcal{C}_1 + 2\mathcal{C}_2,\quad \mathcal{C}_5\,\mathcal{C}_2 = \mathcal{C}_5,\quad \mathcal{C}_5\,\mathcal{C}_3 = 2\mathcal{C}_4,\quad \mathcal{C}_5\,\mathcal{C}_4 = 2\mathcal{C}_3
\end{aligned}$$

2.14

(i) Using $X\,\mathcal{C}_i = \mathcal{C}_i\,X,\ \forall X \in \mathcal{G}$ then

$$\sum_{X_j\in\mathcal{C}_j} X_j\,\mathcal{C}_i = \mathcal{C}_j\,\mathcal{C}_i = \mathcal{C}_i \sum_{X_j\in\mathcal{C}_j} X_j = \mathcal{C}_i\,\mathcal{C}_j$$

hence $h_{ijk} = h_{jik}$

(ii)

(iii)

(iv)

(v)

(vi)

(vii)

2.15 Since each element of the group appears only once in any row or column, then multiplying any row by one element of the group should not introduce any redundancies, but only rearanges the elements as they appear in the row.

2.16 We define the class sum for $\mathcal{C}_i$

$$\sum_{U_i \in \mathcal{C}_i} U$$

containing $nc(i)$ distinct elements, then we find that

$$S\left(\sum_{U_i \in \mathcal{C}_i} U_i\right) S^{-1} = \sum_{U_i \in \mathcal{C}_i} SU_iS^{-1} = \sum_{V_i \in \mathcal{C}_i} V_i$$

where $V_i = SU_iS^{-1} \in \mathcal{C}_i$, and twe obtain a set of nc(i) distinct elements of $\mathcal{C}_i$.

2.17 Denote the set of number $1, 2, 3 \ldots, (k-1)$ by $\mathcal{S}$, then

$$(i * j) \mod k = l \in \mathcal{S},\ \forall\, i, j \in \mathcal{S}, \quad \text{Closure}$$

$$(i * j) \mod k = 1 \ \Rightarrow\ i * j = mk + 1,\ \text{or}\ j = \frac{mk+1}{i} < k$$

2.18 Mathematica program:

```
<< "Combinatorica`"
Print["GROUP T"];
g = 12;
Print["GROUP ORDER: ", g];
(* GENERATE THE GROUP ELEMENTS IN PERMUTATION FORM *)
i = 1;
lgen = 3;
L = {Range[4], {4, 3, 2, 1}, {1, 4, 2, 3}};
Print["GROUP GENERATORS: ", L];
(* L is the list of group elements in permutation form.  *)
f := Permute[L[[i]], L[[j]]]
While[TrueQ[Length[L] < g],
```

```
      For[i = 1, i < g, i++,
          For[j = 1, j < (Length[L] + 1), j++,
              Switch[FreeQ[L, f], True,
                    AppendTo[L, f]
                    ]
              ]
          ]
      ];
Print["GROUP ELEMENTS: ", L];

(* GENERATE INVERSE ELEMENTS *)

(* LI is list of inverse elements of L in permutation form.*)

Print["MULTIPLICATION TABLE"];
(* m is the multiplication table.*)
m = TableForm[MultiplicationTable[L, Permute]];

(* LI1 is list of the inverse elements of L in number form.*)

LI1 = {1};
For[i = 2, i < g + 1, i++,
     For[j = 1, j < g + 1, j++,
         Switch[TrueQ[m[[1, i, j]] == 1], True,
                AppendTo[LI1, j]
                ]
         ]
     ];
Print["INVERSE ELEMENTS; ", LI1]
(* GENERATE THE GROUP CLASSES . *)

(* LC is the list of classes where
   LC[i,j] is the jth element of class i,
   nc is the number of classes.  *)
```

```
LC = {{1}};
i = 1;
nc = 1;
f := m[[1, m[[1, j, i]], LI1[[j]]]];
Block[{p = Range[g], C1 = {}}, p[[1]] = 0;
      While[Apply[Plus, p]!= 0, i = i + 1;
            Switch[TrueQ[p[[i]]!= 0], True,
                   C1 = {i}; p[[i]] = 0;
                   For[j = 2, j < g + 1, j++,
                       Switch[FreeQ[C1, f], True,
                              AppendTo[C1, f];
                              p[[f]] = 0]];
                              AppendTo[LC, C1];
                              nc = nc + 1;
                              C1 = {}
                              ]
                       ]
                   ];
Print["NUMBER OF CLASSES: ", nc]
Print["CLASSES: ", LC];
(* indc[i] is the class to which element i belongs.  *)

Do[j = 1;
   While[j <= nc,
         Switch[MemberQ[LC[[j]], i], True,
                indc[i] = j; j = nc + 1,
                False,
                j = j + 1
                ]
```

```
        ], {i, 1, g}
   ];
Print["CLASS OF ELEMENT I: ",
MatrixForm[indexc = Array[indc, {g}]]]

(* GENERATE THE CLASS MULTIPLICATION MATRICES *)

(* a[i,j,k] is the class multiplication matrix.*)

Print["CLASS MULTIPLICATION MATRICES"];
Do[a[i, j, k] = 0, {i, 1, nc}, {j, 1, nc}, {k, 1, nc}];
Do[a[1, i, i] = 1; a[i, 1, i] = 1, {i, 1, nc}];
s := m[[1, LC[[i, l]], LC[[j, k]]]];
Do[
   For[l = 1, l < Length[LC[[i]]] + 1, l++,
       For[k = 1, k < Length[LC[[j]]] + 1, k++,
           For[m1 = 1, m1 < nc + 1, m1++,
               Switch[MemberQ[LC[[m1]], s], True,
                      a[i, j, m1] = a[i, j, m1] + 1
                      ]
               ]
           ]
       ];
   Do[a[i, j, m1] = a[i, j, m1]/Length[LC[[m1]]],
       {m1, 1, nc}
       ],
{i, 2, nc}, {j, 2, nc}
]
Print["CLASS MULTIPLICATION MATRICES: ",
MatrixForm[h = Array[a, {nc, nc, nc}]]]
```

2.19 $\mathcal{C}_{3v}$

GROUP ORDER: 6

GROUP ELEMENTS: $\{E = 1 = \{1,2,3\},\ C_3 = 2 = \{2,3,1\},\ C_3^{-1} = 3 = \{2,1,3\},$
$\sigma_1 = 4 = \{3,1,2\},\ \sigma_2 = 5 = \{3,2,1\},\ \sigma_3 = 6 = \{1,3,2\}\}$

MULTIPLICATION TABLE:

1	2	3	4	5	6
2	4	5	1	6	3
3	6	1	5	4	2
4	1	6	2	3	5
5	3	2	6	1	4
6	5	4	3	2	1

INVERSE ELEMENTS: $\{1, 4, 3, 2, 5, 6\}$

NUMBER OF CLASSES: 3

CLASSES: $\{\{1\},\ \{2, 4\},\ \{3, 6, 5\}\}$

CLASS OF ELEMENT I:

1	2	3	4	5	6
1	2	3	2	3	3

CLASS MULTIPLICATION MATRICES:

$$H^{(1)} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix},\ H^{(2)} = \begin{pmatrix} 0 & 2 & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 2 \end{pmatrix},\ H^{(3)} = \begin{pmatrix} 0 & 0 & 3 \\ 0 & 0 & 3 \\ 1 & 2 & 0 \end{pmatrix}$$

$\mathcal{C}_{4v}$

GROUP ORDER: 8

GROUP GENERATORS: $\{E = 1 = \{1,2,3,4\},\ C_4 = 2 = \{4,1,2,3\},\ \sigma_1^d = 3 = \{3,2,1,4\}\}$

GROUP ELEMENTS: $\{E = 1 = \{1,2,3,4\},\ C_4 = 2 = \{4,1,2,3\},\ \sigma_1^d = 3 = \{3,2,1,4\},$
$C_2 = 4 = \{3,4,1,2\},\ \sigma_x = 5 = \{2,1,4,3\},\ C_4^{-1} = 6 = \{2,3,4,1\},$
$\sigma_2^d = 7 = \{1,4,3,2\},\ \sigma_y = 8 = \{4,3,2,1\}\}$

MULTIPLICATION TABLE

1	2	3	4	5	6	7	8
2	4	5	6	7	1	8	3
3	8	1	7	6	5	4	2
4	6	7	1	8	2	3	5
5	3	2	8	1	7	6	4
6	1	8	2	3	4	5	7
7	5	4	3	2	8	1	6
8	7	6	5	4	3	2	1

INVERSE ELEMENTS: $\{1,6,3,4,5,2,7,8\}$

NUMBER OF CLASSES: 5

CLASSES: $\{\{1\},\ \{2,6\},\ \{3,7\},\ \{4\},\ \{5,8\}\}$

CLASS OF ELEMENT I: $\begin{matrix} 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 \\ 1 & 2 & 3 & 4 & 5 & 2 & 3 & 5 \end{matrix}$

CLASS MULTIPLICATION MATRICES:

$$\mathtt{H}^{(1)} = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{pmatrix},\ \mathtt{H}^{(2)} = \begin{pmatrix} 0 & 2 & 0 & 0 & 0 \\ 1 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 2 \\ 0 & 2 & 0 & 0 & 0 \\ 0 & 0 & 2 & 0 & 0 \end{pmatrix},\ \mathtt{H}^{(3)} = \begin{pmatrix} 0 & 0 & 2 & 0 & 0 \\ 0 & 0 & 0 & 0 & 2 \\ 1 & 0 & 0 & 1 & 0 \\ 0 & 0 & 2 & 0 & 0 \\ 0 & 2 & 0 & 0 & 0 \end{pmatrix},$$

$$\mathtt{H}^{(4)} = \begin{pmatrix} 0 & 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{pmatrix},\ \mathtt{H}^{(5)} = \begin{pmatrix} 0 & 0 & 0 & 0 & 2 \\ 0 & 0 & 2 & 0 & 0 \\ 0 & 2 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 2 \\ 1 & 0 & 0 & 1 & 0 \end{pmatrix}$$

$\mathcal{C}_{5\mathtt{v}}$

GROUP ORDER: 10

GROUP GENERATORS: $\{E = 1 = \{1,2,3,4,5\},\ C_5 = 2 = \{5,1,2,3,4\},\ \sigma_2 = 3 = \{3,2,1,5,4\}\}$

GROUP ELEMENTS: $\{E = 1 = \{1,2,3,4,5\},\ C_5 = 2 = \{5,1,2,3,4\},$
$\sigma_2 = 3 = \{3,2,1,5,4\},\ C_5^2 = 4 = \{4,5,1,2,3\},$
$\sigma_4 = 5 = \{2,1,5,4,3\},\ C_5^3 = 6 = \{3,4,5,1,2\},$
$\sigma_1 = 7 = \{1,5,4,3,2\},\ C_5^4 = 8 = \{2,3,4,5,1\},$
$\sigma_3 = 9 = \{5,4,3,2,1\},\ \sigma_5 = 10 = \{4,3,2,1,5\}\}$

MULTIPLICATION TABLE:

1	2	3	4	5	6	7	8	9	10
2	4	5	6	7	8	9	1	10	3
3	10	1	9	8	7	6	5	4	2
4	6	7	8	9	1	10	2	3	5
5	3	2	10	1	9	8	7	6	4
6	8	9	1	10	2	3	4	5	7
7	5	4	3	2	10	1	9	8	6
8	1	10	2	3	4	5	6	7	9
9	7	6	5	4	3	2	10	1	8
10	9	8	7	6	5	4	3	2	1

INVERSE ELEMENTS: $\{1,8,3,6,5,4,7,2,9,10\}$

NUMBER OF CLASSES: 4

CLASSES: $\{\{1\},\ \{2,8\},\ \{3,7,10,5,9\},\ \{4,6\}\}$

CLASS OF ELEMENT I:

1	2	3	4	5	6	7	8	9	10
1	2	3	4	3	4	3	2	3	3

CLASS MULTIPLICATION MATRICES:

$$\mathtt{H}^{(1)} = \begin{pmatrix}1&0&0&0\\0&1&0&0\\0&0&1&0\\0&0&0&1\end{pmatrix},\ \mathtt{H}^{(2)} = \begin{pmatrix}0&2&0&0\\1&0&0&1\\0&0&2&0\\0&1&0&1\end{pmatrix},\ \mathtt{H}^{(3)} = \begin{pmatrix}0&0&5&0\\0&0&5&0\\1&2&0&2\\0&0&5&0\end{pmatrix},\ \mathtt{H}^{(4)} = \begin{pmatrix}0&0&0&2\\0&1&0&1\\0&0&2&0\\1&1&0&0\end{pmatrix}$$

2.20

$$C_{2\mathtt{v}}:\ E=(1)(2)(3)(4),\ C_2=(24)(13),\ \sigma_x=(12)(34),\ \sigma_y=(14)(23)$$

$$C_{4\mathtt{v}}:\ E=(1)(2)(3)(4),\ C_4=(1234),\ C_4^{-1}=(1432),\ C_2=(24)(13),$$
$$\sigma_x=(12)(34),\ \sigma_y=(14)23),\ \sigma_1^{\mathtt{d}}=(13),\ \sigma_2^{\mathtt{d}}=(24)$$

$$C_{3\mathtt{v}}:\ E=(1)(2)(3),\ C_3=(123),\ C_3^{-1}=(132),\ \sigma_1=(23),\ \sigma_2=(34),\ \sigma_3=(12),$$

$$C_{6\mathtt{v}}:\ E=(1)(2)(3)(4)(5)(6),\ C_6=(123456),\ C_6^{-1}=(165432),$$
$$C_3=(135)(246),\ C_3^{-1}=(153)(264),\ C_2=(14)(25)(36),$$
$$\sigma_1^{\mathtt{v}}=(12)(36)(45),\ \sigma_2^{\mathtt{v}}=(14)(23)(56),\ \sigma_3^{\mathtt{v}}=(16)(25)(34),$$
$$\sigma_1^{\mathtt{d}}=(26)(35),\ \sigma_2^{\mathtt{d}}=(13)(46),\ \sigma_3^{\mathtt{d}}=(15)(24)$$

2.21 (i) Since both $\sigma_h = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$ and $C_2 = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$ are diagonal matrices, they commute; and

$$\sigma_h C_2 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

(ii) $\mathcal{C}_n$ is a cyclic group of order n. Taking $\sigma \equiv \sigma_h$, the outer product is comprised of the elements $E \times C_n^i$ and $\sigma_h \times C_n^i$, $i = 0, \ldots n-1$. $\mathcal{C}_{\mathtt{nh}}$ contains $2n$ elements.

(iii) $\mathcal{C}_n$ is abelian, and $\sigma_h \times C_n^i = C_n^i \times \sigma_h$, hence the group $\mathcal{C}_{\mathtt{nh}}$ is abelian and contains $2n$ classes.

2.22 (i) For n even, $D_{\mathtt{n}}$ contains the n elements of the point-group $\mathcal{C}_n$, two inequvalent sets of two-fold rotations U_k and U_k', each containing $n/2$ elements.

$$D_{\mathtt{nh}} = E \times D_{\mathtt{n}} + \sigma_{\mathtt{h}} \times D_{\mathtt{n}}$$

and, thus, contains $4n$ elements.

(ii) We consider the representative two-fold rotation $U = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$, then

$$\sigma_{\mathtt{h}} U = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

which is a σ_v type reflection.

(iii) $\sigma_{\mathtt{h}}$ is diagonal, hence, it commutes with all the elements of $D_{\mathtt{n}}$, and we write

$$\mathcal{D}_{\mathrm{nh}} = \mathcal{D}_{\mathrm{n}} \otimes \mathcal{C}_{\mathrm{s}}.$$

2.23 (i) We consider $\mathcal{D}_4$, and take $U = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$ and $\sigma_{\mathtt{d}} = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$

$$U \sigma_{\mathtt{d}} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} = \sigma_{\mathtt{h}} C_4 = S_8$$

(ii) A reflection plane that bisects the angle between two U-axes of $\mathcal{D}_\mathrm{n}$ overlaps passes through another U-axis, in which case, we obtain a $\mathcal{D}_\mathrm{nh}$ group. Thus, a σ_d plane can only be perpendicular to a U-axis. Taking the U-axis to be along the y-axis, we get

$$U\,\sigma_\mathrm{d} \;=\; \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \;=\; \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \;=\; \mathfrak{I}$$

and since $\mathfrak{I}$ commutes with all elements of $\mathcal{D}_\mathrm{n}$, we write

$$\mathcal{D}_\mathrm{nd} \;=\; \mathcal{D}_\mathrm{n} \otimes \mathcal{C}_\mathrm{i}$$

2.24 (a) The group elements in cycle notation are

(234), (243), (134), (143), (124), (142), (123), (132)

(14)(32), (12)(34), (13)(24)

GROUP: T

```
GROUP ORDER: 12
GROUP GENERATORS:
```
$\big\{E = 1 = \{1,2,3,4\},\, U_1 = 2 = \{4,3,2,1\},$
$C_3^{(1)} = 3 = \{1,4,2,3\}\big\}$

```
GROUP ELEMENTS:
```
$\big\{\big\{E = 1 = \{1,2,3,4\},\, U_1 = 2 = \{4,3,2,1\},$
$C_3^{(1)} = 3 = \{1,4,2,3\},\; C_3^{(3)} = 4 = \{4,1,3,2\},$
$C_3^{(2)} = 5 = \{3,2,4,1\},\; C_3^{2(1)} = 6 = \{1,3,4,2\},$
$C_3^{2(4)} = 7 = \{3,1,2,4\},\; C_3^{(3)} = 8 = \{2,4,3,1\},$
$U_2 = 9 = \{2,1,4,3\},\; C_3^{(4)} = 10 = \{2,3,1,4\},$
$C_3^{(2)} = 11 = \{4,2,1,3\},\; U_3 = 12 = \{3,4,1,2\}\big\}$

MULTIPLICATION TABLE

1	2	3	4	5	6	7	8	9	10	11	12
2	1	4	3	10	11	8	7	12	5	6	9
3	5	6	7	8	1	9	2	4	11	12	10
4	10	11	8	7	2	12	1	3	6	9	5
5	3	7	6	11	12	2	9	10	8	1	4
6	8	1	9	2	3	4	5	7	12	10	11
7	11	12	2	9	5	10	3	6	1	4	8
8	6	9	1	12	10	5	4	11	2	3	7
9	12	10	5	4	8	11	6	1	3	7	2
10	4	8	11	6	9	1	12	5	7	2	3
11	7	2	12	1	4	3	10	8	9	5	6
12	9	5	10	3	7	6	11	2	4	8	1

INVERSE ELEMENTS: $\{1, 2, 6, 8, 11, 3, 10, 4, 9, 7, 5, 12\}$
NUMBER OF CLASSES: 4
CLASSES: $\{\{1\}, \{2, 12, 9\}, \{3, 10, 4, 5\}, \{6, 7, 8, 11\}\}$

CLASS OF ELEMENT I:

1	2	3	4	5	6	7	8	9	10	11	12
1	2	3	3	3	4	4	4	2	3	4	2

CLASS MULTIPLICATION MATRICES:

$$\mathtt{H}^{(1)} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}, \mathtt{H}^{(2)} = \begin{pmatrix} 0 & 3 & 0 & 0 \\ 1 & 2 & 0 & 0 \\ 0 & 0 & 3 & 0 \\ 0 & 0 & 0 & 3 \end{pmatrix}, \mathtt{H}^{(3)} = \begin{pmatrix} 0 & 0 & 0 & 4 \\ 0 & 0 & 0 & 4 \\ 1 & 3 & 0 & 0 \\ 0 & 0 & 4 & 0 \end{pmatrix}, \mathtt{H}^{(4)} = \begin{pmatrix} 0 & 0 & 4 & 0 \\ 0 & 0 & 4 & 0 \\ 0 & 0 & 0 & 4 \\ 1 & 3 & 0 & 0 \end{pmatrix}$$

(b) We take the U-axis along the z-direction, and σ in the yz-plane, we then get

$$U\,\sigma = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

(12), (13), (14), (23), (24), (34)

(c)

2.25

3

Group representations: Concepts

3.1 Exercises

3.1 Replace the dots in figure 3.2 with ones, and fill the blank squares with zeroes; show that the resultant matrices satisfy the group multiplication rules of Table 2.1.

3.2 Consider an equilateral triangle with sides of unit length. The triangle is in the *xy*-plane with its center of gravity at the origin and the coordinates of its apices being

$$(0, \sqrt{3}/3), (1/2, -\sqrt{3}/6), (-1/2, -\sqrt{3}/6).$$

Show that the first apex is taken into the second apex by a clockwise rotation of 120 deg. Let C_3 be the operator which rotates the triangle clockwise by 120 deg. Show that the *transpose* of C_3 is the operator $\widehat{C}_3$ which, operating on the *function* represented by the vector directed from the origin to the second apex, generates a new function represented by the vector from the origin to the first apex.

3.3 Show that the set of matrices analogous to the one in (3.16) do not satisfy the group multiplication table give in Table 2.3.

3.4 Show that the set of function operator matrices as illustrated by (3.16) for $\widehat{C}_3$ do not satisfy the group multiplication table.

3.5 Consider $x^2 - y^2$ and xy as two possible basis functions for the group $C_{3\mathrm{v}}$. Writing $x = r\cos\phi$, $y = r\sin\phi$, show that one must use $2xy$ rather than xy as a basis function in order that $x^2 - y^2$ and $2xy$ have the same normalization and thus lead to a unitary matrix representation of $C_{3\mathrm{v}}$.

3.6 The ammonia molecule, NH_3, belongs to the point-group $C_{3\mathrm{v}}$. Consider three functions $\{f_A,\ f_B,\ f_C\}$ that describe the three valence bonds connecting the N atom with the three H atoms. The operation of $\widehat{C}_3$ on the valence bond functions can be described by

$$\widehat{C}_3(f_A\ f_B\ f_C) = (f_A\ f_B\ f_C)\begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}.$$

Find the remaining matrices that provide a matrix representation based on the three valence bond functions. Check that the matrices actually obey the group multiplication table.

We assume the original basis set to be normalized as well as being orthogonal. Now consider three new (orthonormal) basis functions (vectors) that are linear combinations of the original set:

$$\begin{aligned} \phi_1 &= \frac{1}{\sqrt{3}}(f_A + f_B + f_C) \\ \phi_2 &= \frac{1}{\sqrt{6}}(f_A + f_B - 2f_C) \\ \phi_3 &= \frac{1}{\sqrt{2}}(f_A - f_B) \end{aligned}$$

Construct a matrix S whose columns (corresponding to $\{\phi_1,\ \phi_2,\ \phi_3\}$) are the coefficients of the original basis functions $\{f_A,\ f_B,\ f_C\}$. Perform the similarity transformation $S^{-1}\widehat{M}S$ for each matrix representative of $C_{3\text{v}}$ based on the original basis set to find the new transformed representation relative to the transformed basis set. What can be said about the new-found representation?

3.2 Solutions

3.1

3.2

3.3

3.4

3.5 In polar coordinates, we have

$$\begin{aligned} x^2 - y^2 &= r^2\left(\cos^2\phi - \sin^2\phi\right) = r^2\cos(2\phi) \\ xy &= r^2 \sin\phi\,\cos\phi = \frac{r^2}{2}\,\sin(2\phi) \end{aligned}$$

It is then obvious that in order to have the same normalization with respect to ϕ the second function must be $2xy$.

3.6 The representation Γ engendered by the basis function set $\{f_A,\ f_B,\ f_c\}$ is

$$\Gamma(E) = \begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix} \quad \Gamma(C_3) = \begin{pmatrix}0&0&1\\1&0&0\\0&1&0\end{pmatrix} \quad \Gamma(C_3^2) = \begin{pmatrix}0&1&0\\0&0&1\\1&0&0\end{pmatrix}$$

$$\Gamma(\sigma_1) = \begin{pmatrix}1&0&0\\0&0&1\\0&1&0\end{pmatrix} \quad \Gamma(\sigma_2) = \begin{pmatrix}0&0&1\\0&1&0\\1&0&0\end{pmatrix} \quad \Gamma(\sigma_3) = \begin{pmatrix}0&1&0\\1&0&0\\0&0&1\end{pmatrix}$$

The transfromation is

$$S = \frac{1}{\sqrt{6}} = \begin{pmatrix}\sqrt{2}&1&\sqrt{3}\\\sqrt{2}&1&-\sqrt{3}\\\sqrt{2}&-2&0\end{pmatrix}$$

$S^{-1}\,MS$ blockdiagonalizes the Γ representation

$$\Gamma(E) = \begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix} \quad \Gamma(C_3) = \begin{pmatrix}1&0&0\\0&-0.5&\sqrt{3}/2\\0&-\sqrt{3}/2&-0.5\end{pmatrix} \quad \Gamma(C_3^2) = \begin{pmatrix}1&0&0\\0&-0.5&-\sqrt{3}/2\\0&\sqrt{3}/2&-0.5\end{pmatrix}$$

$$\Gamma(\sigma_1) = \begin{pmatrix}1&0&0\\0&-0.5&\sqrt{3}/2\\0&\sqrt{3}/2&0.5\end{pmatrix} \quad \Gamma(\sigma_2) = \begin{pmatrix}1&0&0\\0&-0.5&-\sqrt{3}/2\\0&-\sqrt{3}/2&0.5\end{pmatrix} \quad \Gamma(\sigma_3) = \begin{pmatrix}1&0&0\\0&1&0\\0&0&-1\end{pmatrix}$$

4
Group representations: Formalism and methodology

4.1 Exercises

4.1 Show that a similarity transformation relating two equivalent unitary Irreps, must be unitary, if its determinant is 1, i.e. if it is unimodular.

4.2 Use Schur's lemma to demonstrate that all the Irreps of an abelian group are one dimensional. Hence the number of Reps equals the order of the group.

4.3 Show that the character is invariant under a similarity transformation.

4.4 Prove the character orthogonality relationship

$$\sum_{\alpha} {}^{(\alpha)}\chi(\mathcal{C}_i)\ {}^{(\alpha)}\chi^*(\mathcal{C}_j) \;=\; \frac{g}{n_c(j)}\ \delta_{ij}\ ,$$

for the complete set of unitary Irreps of a group G. This is useful for checking the orthonormality of columns in a character table such as in Table 3.2. Hint: Use the first orthogonality relation to demonstrate the unitarity of the matrix

$$U_{\alpha i} \;=\; \left(\frac{n_c(i)}{g}\right)^{1/2}\ {}^{(\alpha)}\chi(\mathcal{C}_i), \qquad UU^* \;=\; E\,,$$

hence, show that simple commutation of this product yields the second orthogonality relation.

4.5 Show that

$$\sum_{R\in\mathcal{G}} {}^{(\mu)}\chi(R) \;=\; 0,$$

for any Irrep (μ) of $\mathcal{G}$ except the identity Irrep.

4.6 Since the characters form an orthogonal set of vectors, as described by (4.33) and (4.34), multiply (4.37) on both sides by ${}^{(\alpha')}\chi(\widehat{R}^{-1})$, sum over group elements $\widehat{R}$, collect elements into classes and obtain (4.40).

4.7 Use Burnside's method to determine the Irreps and characters of the point-group $\mathcal{C}_3$. Do not use a computer program, rather work it out by hand.

4.8 Construct the character table for the group C_{4v} following the steps of example 4.2.

4.9 Construct the character table for the tetrahedral point-group $\mathcal{T}$.

4.10 Construct the class matrices for the 2-dimensional Irrep of the group C_{4v}:

$$E = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \; C_4 = \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}, \; C_4^{-1} = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}, \; C_2 = \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix},$$

$$\sigma_x = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \; \sigma_y = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}, \; \sigma_1' = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \; \sigma_2' = \begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix}.$$

Show that they commute with all the corresponding matrix operators of the group. Hence, according to Schur's lemma they should have the form of a constant (the Dirac character) times the 2-dimensional unit matrix. Diagonalize these class matrices and obtain the corresponding Dirac characters.

4.11 Show that a necessary and sufficient condition for the irreducibility of a Rep (α) of a finite group $\mathcal{G}$ is

$$\frac{1}{g} \sum_{R \in \mathcal{G}} \left| {}^{(\alpha)}\chi(R) \right|^2 = 1 .$$

4.12 Transform the permutations obtained in problem 2.16 for the point-group C_{4v} into matrix form, and show that it forms a matrix Rep of C_{4v} of dimension 4. Show that this Rep is reducible. Determine the multiplicities of the Irreps of C_{4v} in this Rep.

4.13 Determine the multiplicities of the three Irrep of $C_{3\mathrm{v}}$ in its regular Rep.

4.2 Computational Projects

(i) Write a program to generate the regular Rep. Check that the matrix representatives for $C_{3\mathrm{v}}$ are given correctly by 3.49).

(ii) (a) Augment the class multiplication matrices program, developed in chapter 2, with matrix diagonalization capabilities (either by using diagonalization subroutines, or using *Mathematical* functions such as `Eigenvalues[m], Eigenvectors[m], or Eigensystem[m]`).

(b) Use this new program to calculate the Dirac characters of the groups: $\mathcal{C}_{6v},\ \mathcal{D}_{3h},\ \mathcal{T}_d$.

(c) Determine the dimensionality of the respective Irreps.

(d) Use (4.47) to construct the corresponding irreducible character tables.

4.3 Solutions

4.1 Consider two equivalent Irreps Γ and Γ', related by a similarity transformation S, such that

$$\Gamma'(R) = S^{-1}\,\Gamma(R)\,S$$

and

$$\chi'(R) = \chi(R)$$

This is established by the trace identity

$$\mathrm{Tr}\big(ABC\big) = \mathbf{Tr}\big(BCA\big)$$

Thus,

$$\mathrm{Tr}\big(S^{-1}\,\Gamma(R)\,S\big) = \mathrm{Tr}\big(\Gamma(R)\,S\,S^{-1}\big)$$

$$\sum_k \Gamma'_{kk}(R) = \sum_{klj} (S^{-1})_{kl}\,\Gamma_{lj}(R)\,S_{jk} = \sum_k \Gamma_{kk}(R)$$

4.2

4.3 This is again established by the trace identity

$$\mathrm{Tr}\big(ABC\big) = \mathbf{Tr}\big(BCA\big)$$

Thus,

$$\mathrm{Tr}\big(S^{-1}\,\Gamma(R)\,S\big) = \mathrm{Tr}\big(\Gamma(R)\,S\,S^{-1}\big) = \mathrm{Tr}\big(\Gamma(R)\big)$$

4.4

4.5 We use the character orthogonality theorem, and choose the identity Irrep and the Irrep (μ), we obtain

$$\sum_{R\in\mathcal{G}} {}^{(\mu)}\chi(R) = 0,$$

4.6

4.7

4.8

4.9 We choose the class multiplication matrices

$$\mathtt{H}^{(2)} = \begin{pmatrix} 0 & 3 & 0 & 0 \\ 1 & 2 & 0 & 0 \\ 0 & 0 & 3 & 0 \\ 0 & 0 & 0 & 3 \end{pmatrix}, \ \mathtt{H}^{(3)} = \begin{pmatrix} 0 & 0 & 0 & 4 \\ 0 & 0 & 0 & 4 \\ 1 & 3 & 0 & 0 \\ 0 & 0 & 4 & 0 \end{pmatrix}$$

derived in problem 2.24. $\mathtt{H}^{(2)}$ has only one nondegenerate eigenvalue with corresponding eigenvector $\big(-3, 1, 0, 0\big)$ $\mathtt{H}^{(3)}$ has 4 nondegenerate eigenvalues

$$^{(1)}\Gamma:\ \lambda = 4 \ \Rightarrow\ \text{Eigenvector } [1,1,1,1] \ \Rightarrow\ \text{Normalized Eigenvector } [1,1,1,1]$$
$$^{(2)}\Gamma:\ \lambda = 4e^{i\pi/3} \ \Rightarrow\ \text{Eigenvector } [e^{-i\pi/3}, e^{-i\pi/3}, e^{i\pi/3}, 1] \ \Rightarrow\ \text{Normalized Eigenvector } [1,1,e^{-i\pi/3}, e^{i\pi/3}]$$
$$^{(3)}\Gamma:\ \lambda = 4e^{-i\pi/3} \ \Rightarrow\ \text{Eigenvector } [e^{i\pi/3}, e^{i\pi/3}, e^{-i\pi/3}, 1] \ \Rightarrow\ \text{Normalized Eigenvector } [1,1,e^{i\pi/3}, e^{-i\pi/3}]$$
$$^{(4)}\Gamma:\ \lambda = 0 \ \Rightarrow\ \text{Eigenvector } [1,-1/3,0,0]$$

It is straightforward to see that $d_1 = d_2 = d_3 = 1$;

$$d_4^2 = \frac{12}{1 + (3/9)} = 9$$

and

$$^{(4)}\chi(1) = 3,\ ^{(4)}\chi(2) = -1,\ ^{(4)}\chi(3) = 0,\ ^{(4)}\chi(4) = 0.$$

The character table of $\mathcal{T}$ is

Table 4.1. *Character table of the point-group $\mathcal{T}$*

	E	$3U$	$4C_3$	$4C_3^{-1}$
$^{(1)}\Gamma$	1	1	1	1
$^{(2)}\Gamma$	1	1	$e^{i2\pi/3}$	$e^{-i2\pi/3}$
$^{(3)}\Gamma$	1	1	$e^{-i2\pi/3}$	$e^{i2\pi/3}$
$^{(4)}\Gamma$	3	-1	0	0

4.10 The class matrices are

$$\mathcal{C}_1 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad \mathcal{C}_2(C_4) = \mathcal{C}_4(\sigma) = \mathcal{C}_5(\sigma') = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix}, \quad \mathcal{C}_3 = \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = 1 \times \mathbb{I}, \quad \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix} = 0 \times \mathbb{I}, \quad \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix} = -1 \times \mathbb{I}$$

hence all class matrices commute with all ${}^{(5)}\Gamma$ matrices. The corresponding Dirac characters are

$$\lambda_1 = 1, \quad \lambda_2 = \lambda_4 = \lambda_5 = 0, \quad \lambda_3 = -1$$

4.11 From the character orthogonality theorem two Irreps, (α) and (β), of a finite group $\mathcal{G}$, have to satisfy the relation

$$\sum_{R \in \mathcal{G}} {}^{(\alpha)}\chi(R)\, {}^{(\beta)}\chi^*(R) = g\, \delta_{\alpha\beta},$$

hence, for a Rep (α)

$$\sum_{R \in \mathcal{G}} \left| {}^{(\alpha)}\chi(R) \right|^2 = g$$

is a necessary and sufficient condition for (α) to be an Irrep of $\mathcal{G}$.

4.12

4.13

5

Dixon's Method for Computing Group Characters

5.1 Solutions

4.1

6
Group action and symmetry projection operators

6.1 Exercises

6.1 Determine the orbits, stabilizers and strata of the action of

$$\mathcal{G} := \left\{ \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \begin{pmatrix} 1- & 0 \\ 0 & 1 \end{pmatrix}, \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}, \right\},$$

on the xy-plane.

6.2 With reference to example 6.3, to which rows of ${}^{(3)}\Gamma$ do the functions $\{yz,\, xy\}$ belong, if any?

6.3 The valence electron orbitals of a water molecule consist of one $1s$-orbitals on each H atom, and the 3-fold degenerate $2p$ orbital manifold centered on the O atom. Under the $\mathcal{C}_{2v}$ symmetry group operations the permutations among the atoms are the same as those considered in example 6.. However the function-space is now different it consists of electron wavefunctions.

(i) Determine the Rep engendered by $\mathcal{C}_{2v}$ on the set of electron states.
(ii) Derive the symmetry-adapted states of the water molecule.

6.4 The ammonia molecule NH_3 has $\mathcal{C}_{3\text{v}}$ symmetry. Determine:

(i) Its symmetry-adapted vibrational modes.
(ii) Its symmetry-adapted molecular orbitals. (Again, consider s-orbitals centered on the H atoms, and a p-manifold on the N atom.

In the following problems we consider molecules which contain carbon atoms. The 4 valence electrons of a carbon atom occupy both the $2s$ and $2p$ states, which have to be included in each set of orbitals of these molecules.

6.5 Repeat problem 4 for the case of a planar molecule of the form AB_3, such as ${CO_3}^{2-}$, which has $\mathcal{D}_{3h}$ symmetry.

6.6 In the methane molecule CH_4, the C atom is located at the center of a tetrahedron, while the H atoms are at its apices.

6.7 Repeat problem 4 for the benzene molecule. It consists of 6 carbon atoms forming the apices of a hexagon and 6 hydrogen atoms bound radially, thus having $\mathcal{D}_{6h}$ symmetry.

6.2 Solutions

6.1

6.2

6.3 The engendered representation is

$$E = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{pmatrix} \quad C_2 = \begin{pmatrix} 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & -1 & \\ 0 & 0 & 0 & 0 & 1 \end{pmatrix}$$

$$\sigma_x = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{pmatrix} \quad \sigma_y = \begin{pmatrix} 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{pmatrix}$$

Table 6.1. Character Table for $\mathcal{C}_{2\text{v}}$

	E	C_2	σ_x	σ_y
${}^{(1)}\Gamma$	1	1	1	1
${}^{(2)}\Gamma$	1	1	-1	-1
${}^{(3)}\Gamma$	1	-1	1	-1
${}^{(4)}\Gamma$	1	-1	-1	1

Next, we construct the Irrep projection matrices using the following simple program:

```
P1 = (E + C2 + Sigmax + Sigmay)/4;
P2 = (E + C2 - Sigmax - Sigmay)/4;
P3 = (E - C2 + Sigmax - Sigmay)/4;
P4 = (E - C2 - Sigmax + Sigmay)/4;
Eigensystem[P1]
Eigensystem[P2]
Eigensystem[P3]
Eigensystem[P4]
```

The resulting eigenvalues and eigenvectors are:

$$ {}^{(1)}\mathcal{P} = \begin{pmatrix} \frac{1}{2} & \frac{1}{2} & 0 & 0 & 0 \\ \frac{1}{2} & \frac{1}{2} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{pmatrix} \qquad \begin{cases} \text{Eigenvalues :} & 1,1,0,0,0 \\ \text{Eigenvectors :} & \{0,0,0,0,1\},\{1,1,0,0,0\}, \\ & \{0,0,0,1,0\},\{0,0,1,0,0\},\{-1,1,0,0,0\} \end{cases} $$

$$ {}^{(2)}\mathcal{P} = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix} \qquad \begin{cases} \text{Eigenvalues :} & 0,0,0,0,0 \\ \text{Eigenvectors :} & \{0,0,0,0,1\},\{0,0,0,1,0\}, \\ & \{0,0,1,0,0\},\{0,1,0,0,0\},\{1,0,0,0,0\} \end{cases} $$

$$ {}^{(3)}\mathcal{P} = \begin{pmatrix} \frac{1}{2} & -\frac{1}{2} & 0 & 0 & 0 \\ -\frac{1}{2} & \frac{1}{2} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix} \qquad \begin{cases} \text{Eigenvalues :} & 1,1,0,0,0 \\ \text{Eigenvectors :} & \{\{0,0,0,1,0\},\{-1,1,0,0,0\}, \\ & \{0,0,0,0,1\},\{0,0,1,0,0\},\{1,1,0,0,0\} \end{cases} $$

$$ {}^{(4)}\mathcal{P} = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix} \qquad \begin{cases} \text{Eigenvalues :} & 1,0,0,0,0 \\ \text{Eigenvectors :} & \{0,0,1,0,0\},\{0,0,0,0,1\}, \\ & \{0,0,0,1,0\},\{0,1,0,0,0\},\{1,0,0,0,0\} \end{cases} $$

Selecting the eigenvectors corresponding to eigenvalue of unity, we obtain the following symmetry-adapted vectors:

$$^{(1)}\Gamma : \quad \begin{bmatrix} 0 & 0 & 0 & 0 & 1 \\ 1 & 1 & 0 & 0 & 0 \end{bmatrix}$$

$$^{(2)}\Gamma : \quad \text{None}$$

$$^{(3)}\Gamma : \quad \begin{bmatrix} 0 & 0 & 1 & 0 & 0 \\ -1 & 1 & 0 & 0 & 0 \end{bmatrix}$$

$$^{(4)}\Gamma : \quad \begin{bmatrix} 0 & 0 & 1 & 0 & 0 \end{bmatrix}$$

6.4(i) The symmetry-adapted vibrational modes of NH_3 are derived in Chapter 15.

(ii) The representation of $\mathcal{C}_{3\mathrm{v}}$ engendered by the atomic orbitals is

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

$$C_3 = \begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1/2 & -\sqrt{3}/2 & 0 \\ 0 & 0 & 0 & \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \quad \sigma_1 = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}$$

$$\sigma_2 = \begin{pmatrix} 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1/2 & \sqrt{3}/2 & 0 \\ 0 & 0 & 0 & \sqrt{3}/2 & 1/2 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \quad \sigma_3 = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1/2 & -\sqrt{3}/2 & 0 \\ 0 & 0 & 0 & -\sqrt{3}/2 & 1/2 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}$$

where we ordered the atomic orbital basis set as $s(H_1)$, $s(H_2)$, $s(H_3)$, $px(N)$, $p_y(N)$, $p_z(N)$.

Table 6.2. Character Table for $\mathcal{C}_{3\mathrm{v}}$

	E	C_3, C_3^2	σ_1, σ_2, σ_3
$^{(1)}\Gamma$	1	1	1
$^{(2)}\Gamma$	1	1	-1
$^{(3)}\Gamma$	2	-1	0

Next, we construct the class matrices and the Irrep projection matrices using the following simple program:

```
c2=c3x+c32x

c3=s1x+s2x+s3x

p1=(ex+c2+c3)/6

p2=(ex+c2-c3)/6

p3=(2ex-c2)/6

Eigensystem[p1]

Eigensystem[p2]

Eigensystem[p3]
```

The class matrices are

$$\mathcal{C}_2 = \begin{pmatrix} 0 & 1 & 1 & 0 & 0 & 0 \\ 1 & 0 & 1 & 0 & 0 & 0 \\ 1 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 2 \end{pmatrix} \qquad \mathcal{C}_3 = \begin{pmatrix} 1 & 1 & 1 & 0 & 0 & 0 \\ 1 & 1 & 1 & 0 & 0 & 0 \\ 1 & 1 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 3 \end{pmatrix}$$

$$
{}^{(1)}\mathcal{P} = \begin{pmatrix} \frac{1}{3} & \frac{1}{3} & \frac{1}{3} & 0 & 0 & 0 \\ \frac{1}{3} & \frac{1}{3} & \frac{1}{3} & 0 & 0 & 0 \\ \frac{1}{3} & \frac{1}{3} & \frac{1}{3} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \qquad \begin{cases} \text{Eigenvalues :} & 1,1,0,0,0,0 \\ \text{Eigenvectors :} & \{0,0,0,0,0,1\},\{1,1,1,0,0,0\},\{0,0,0,0,1,0\}, \\ & \{0,0,0,1,0,0\},\{-1,0,1,0,0,0\},\{-1,1,0,0,0,0\} \end{cases}
$$

$$
{}^{(2)}\mathcal{P} = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \qquad \begin{cases} \text{Eigenvalues :} & 0,0,0,0,0,0 \\ \text{Eigenvectors :} & \{0,0,0,0,0,1\},\{0,0,0,0,1,0\},\{0,0,0,1,0,0\}, \\ & \{0,0,1,0,0,0\},\{0,1,0,0,0,0\},\{1,0,0,0,0,0\} \end{cases}
$$

$$
{}^{(3)}\mathcal{P} = \begin{pmatrix} \frac{2}{3} & -\frac{1}{3} & -\frac{1}{3} & 0 & 0 & 0 \\ -\frac{1}{3} & \frac{2}{3} & -\frac{1}{3} & 0 & 0 & 0 \\ -\frac{1}{3} & -\frac{1}{3} & \frac{2}{3} & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \qquad \begin{cases} \text{Eigenvalues :} & 1,1,1,1,0,0 \\ \text{Eigenvectors :} & \{0,0,0,1,0,0\},\{0,0,0,0,1,0\}, \\ & \{\frac{1}{\sqrt{2}},-\frac{1}{\sqrt{2}},0,0,0,0\}, \\ & \{-\frac{1}{\sqrt{6}},-\frac{1}{\sqrt{6}},\sqrt{\frac{2}{3}},0,0,0\}, \\ & \{-\frac{1}{\sqrt{3}},-\frac{1}{\sqrt{3}},-\frac{1}{\sqrt{3}},0,0,0\},\{0,0,0,0,0,1\} \end{cases}
$$

Selecting the eigenvectors corresponding to eigenvalue of unity, we obtain the following symmetry-adapted vectors:

$$
{}^{(1)}\Gamma : \quad \begin{bmatrix} 1 & 1 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}
$$

$$
{}^{(2)}\Gamma : \quad \text{None}
$$

$$
{}^{(3)}\Gamma : \quad \begin{bmatrix} \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} & 0 & 0 & 0 & 0 \\ -\frac{1}{\sqrt{6}} & -\frac{1}{\sqrt{6}} & \sqrt{\frac{2}{3}} & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \end{bmatrix}
$$

6.5 The point group $\mathcal{D}_{3h}$ has elements:

$$
E,\, C_3,\, C_3^2,\, U_1,\, U_2,\, U_3, \sigma_h,\, \sigma_1,\, \sigma_2,\, \sigma_3, S_3, S_3^{-1}
$$

If we consider the ${CO_3}^{2-}$ as an example of a AB_3 molecule, we will simplify the problem by treating the four p_z-orbitals on the C and O atoms separately, since they do not interact with the remaining orbitals. That leaves us with a Hilbert space of dimension 9. The Rep engendered on this space is:

$$\begin{matrix} E \\ \sigma_h \end{matrix} = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}, \quad \begin{matrix} C_3 \\ S_3^{-1} \end{matrix} = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} \\ 0 & 0 & 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & 0 & 0 \end{pmatrix},$$

$$\begin{matrix} C_3^{-1} \\ S_3 \end{matrix} = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} \\ 0 & 0 & 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 \end{pmatrix}, \quad \begin{matrix} U_1 \\ \sigma_1 \end{matrix} = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \end{pmatrix},$$

$$\begin{matrix} U_2 \\ \sigma_2 \end{matrix} = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}, \quad \begin{matrix} U_3 \\ \sigma_3 \end{matrix} = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{2} & \frac{\sqrt{3}}{2} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} \\ 0 & 0 & 0 & 0 & 0 & \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & 0 & 0 \end{pmatrix}$$

Table 6.3. Character Table for $\mathcal{D}_{3\mathrm{h}}$

	E	σ_h	$2C_3$	$2S_3$	$3U$	$3\sigma_v$
$^{(1)}\Gamma$	1	1	1	1	1	1
$^{(2)}\Gamma$	1	1	1	1	-1	-1
$^{(3)}\Gamma$	1	-1	1	-1	1	-1
$^{(4)}\Gamma$	1	-1	1	-1	-1	1
$^{(5)}\Gamma$	2	-2	-1	1	0	0
$^{(6)}\Gamma$	2	2	-1	-1	0	0

The class matrices are

$$\mathcal{C}_3 = \begin{pmatrix} 2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} & -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ 0 & 0 & 0 & 0 & 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} & \frac{\sqrt{3}}{2} & -\frac{1}{2} \\ 0 & 0 & 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ 0 & 0 & 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} \\ 0 & 0 & 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} & -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 \\ 0 & 0 & 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} & \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 \end{pmatrix}$$

$$U = \begin{pmatrix} 3 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & \frac{1}{2} & -\frac{\sqrt{3}}{2} & \frac{1}{2} & \frac{\sqrt{3}}{2} \\ 0 & 0 & 0 & 0 & 1 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} & \frac{\sqrt{3}}{2} & -\frac{1}{2} \\ 0 & 0 & 0 & \frac{1}{2} & -\frac{\sqrt{3}}{2} & \frac{1}{2} & \frac{\sqrt{3}}{2} & -1 & 0 \\ 0 & 0 & 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} & \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 1 \\ 0 & 0 & 0 & \frac{1}{2} & \frac{\sqrt{3}}{2} & -1 & 0 & \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ 0 & 0 & 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 1 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$$

$$
{}^{(1)}\mathcal{P} = \begin{pmatrix}
1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \frac{1}{3} & -\frac{1}{2\sqrt{3}} & -\frac{1}{6} & \frac{1}{2\sqrt{3}} & -\frac{1}{6} \\
0 & 0 & 0 & 0 & -\frac{1}{2\sqrt{3}} & \frac{1}{4} & \frac{1}{4\sqrt{3}} & -\frac{1}{4} & \frac{1}{4\sqrt{3}} \\
0 & 0 & 0 & 0 & -\frac{1}{6} & \frac{1}{4\sqrt{3}} & \frac{1}{12} & -\frac{1}{4\sqrt{3}} & \frac{1}{12} \\
0 & 0 & 0 & 0 & \frac{1}{2\sqrt{3}} & -\frac{1}{4} & -\frac{1}{4\sqrt{3}} & \frac{1}{4} & -\frac{1}{4\sqrt{3}} \\
0 & 0 & 0 & 0 & -\frac{1}{6} & \frac{1}{4\sqrt{3}} & \frac{1}{12} & -\frac{1}{4\sqrt{3}} & \frac{1}{12}
\end{pmatrix}
$$

$$
\begin{cases}
\text{Eigenvalues :} & 1,1,0,0,0,0,0,0,0 \\
\text{Eigenvectors :} & \left\{0,0,0,0,-2,\sqrt{3},1,-\sqrt{3},1\right\}, \{1,0,0,0,0,0,0,0,0\}, \left\{0,0,0,0,\frac{1}{2},0,0,0,1\right\}, \\
& \left\{0,0,0,0,-\frac{\sqrt{3}}{2},0,0,1,0\right\}, \left\{0,0,0,0,\frac{1}{2},0,1,0,0\right\}, \left\{0,0,0,0,\frac{\sqrt{3}}{2},1,0,0,0\right\}, \\
& \{0,0,0,1,0,0,0,0,0\}, \{0,0,1,0,0,0,0,0,0\}, \{0,1,0,0,0,0,0,0,0\}
\end{cases}
$$

$$
{}^{(2)}\mathcal{P} = \begin{pmatrix}
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & \frac{1}{3} & 0 & -\frac{1}{6} & \frac{1}{2\sqrt{3}} & -\frac{1}{6} & -\frac{1}{2\sqrt{3}} \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & -\frac{1}{6} & 0 & \frac{1}{12} & -\frac{1}{4\sqrt{3}} & \frac{1}{12} & \frac{1}{4\sqrt{3}} \\
0 & 0 & 0 & \frac{1}{2\sqrt{3}} & 0 & -\frac{1}{4\sqrt{3}} & \frac{1}{4} & -\frac{1}{4\sqrt{3}} & -\frac{1}{4} \\
0 & 0 & 0 & -\frac{1}{6} & 0 & \frac{1}{12} & -\frac{1}{4\sqrt{3}} & \frac{1}{12} & \frac{1}{4\sqrt{3}} \\
0 & 0 & 0 & -\frac{1}{2\sqrt{3}} & 0 & \frac{1}{4\sqrt{3}} & -\frac{1}{4} & \frac{1}{4\sqrt{3}} & \frac{1}{4}
\end{pmatrix}
$$

$$
\begin{cases}
\text{Eigenvalues :} & 1,0,0,0,0,0,0,0,0 \\
\text{Eigenvectors :} & \left\{0,0,0,-\frac{2}{\sqrt{3}},0,\frac{1}{\sqrt{3}},-1,\frac{1}{\sqrt{3}},1\right\}, \left\{0,0,0,\frac{\sqrt{3}}{2},0,0,0,0,1\right\}, \left\{0,0,0,\frac{1}{2},0,0,0,1,0\right\}, \\
& \left\{0,0,0,-\frac{\sqrt{3}}{2},0,0,1,0,0\right\}, \left\{0,0,0,\frac{1}{2},0,1,0,0,0\right\}, \{0,0,0,0,1,0,0,0,0\}, \\
& \{0,0,1,0,0,0,0,0,0\}, \{0,1,0,0,0,0,0,0,0\}, \{1,0,0,0,0,0,0,0,0\}
\end{cases}
$$

$$
{}^{(6)}\mathcal{P} = \begin{pmatrix}
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & \frac{2}{3} & 0 & \frac{1}{6} & -\frac{1}{2\sqrt{3}} & \frac{1}{6} & \frac{1}{2\sqrt{3}} \\
0 & 0 & 0 & 0 & \frac{2}{3} & \frac{1}{2\sqrt{3}} & \frac{1}{6} & -\frac{1}{2\sqrt{3}} & \frac{1}{6} \\
0 & 0 & 0 & \frac{1}{6} & \frac{1}{2\sqrt{3}} & \frac{2}{3} & 0 & \frac{1}{6} & -\frac{1}{2\sqrt{3}} \\
0 & 0 & 0 & -\frac{1}{2\sqrt{3}} & \frac{1}{6} & 0 & \frac{2}{3} & \frac{1}{2\sqrt{3}} & \frac{1}{6} \\
0 & 0 & 0 & \frac{1}{6} & -\frac{1}{2\sqrt{3}} & \frac{1}{6} & \frac{1}{2\sqrt{3}} & \frac{2}{3} & 0 \\
0 & 0 & 0 & \frac{1}{2\sqrt{3}} & \frac{1}{6} & -\frac{1}{2\sqrt{3}} & \frac{1}{6} & 0 & \frac{2}{3}
\end{pmatrix}
$$

$$
\begin{cases}
\text{Eigenvalues :} & 1,1,1,1,1,1,0,0,0 \\
\text{Eigenvectors :} & \left\{0,0,0,\frac{\sqrt{3}}{2},\frac{1}{2},0,0,0,1\right\}, \left\{0,0,0,\frac{1}{2},-\frac{\sqrt{3}}{2},0,0,1,0\right\}, \left\{0,0,0,-\frac{\sqrt{3}}{2},\frac{1}{2},0,1,0,0\right\}, \\
& \left\{0,0,0,\frac{1}{2},\frac{\sqrt{3}}{2},1,0,0,0\right\}, \{0,0,1,0,0,0,0,0,0\}, \{0,1,0,0,0,0,0,0,0\}, \\
& \left\{0,0,0,-\frac{\sqrt{3}}{2},-\frac{1}{2},\frac{\sqrt{3}}{2},-\frac{1}{2},0,1\right\}, \left\{0,0,0,-\frac{1}{2},\frac{\sqrt{3}}{2},-\frac{1}{2},-\frac{\sqrt{3}}{2},1,0\right\}, \{1,0,0,0,0,0,0,0,0\}
\end{cases}
$$

Symmetry-adapted vectors

$$\begin{array}{ccccccccc} \mathrm{C} & \mathrm{C} & \mathrm{C} & \mathrm{O}^1 & \mathrm{O}^1 & \mathrm{O}^2 & \mathrm{O}^2 & \mathrm{O}^3 & \mathrm{O}^3 \\ s & p_x & p_y & p_x & p_y & p_x & p_y & p_x & p_y \end{array}$$

$$^{(1)}\Gamma : \quad \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -2 & \sqrt{3} & 1 & -\sqrt{3} & 1 \end{bmatrix}$$

$$^{(2)}\Gamma : \quad \begin{bmatrix} 0 & 0 & 0 & -\frac{2}{\sqrt{3}} & 0 & \frac{1}{\sqrt{3}} & -1 & \frac{1}{\sqrt{3}} & 1 \end{bmatrix}$$

$$^{(6)}\Gamma : \quad \begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{2} & \frac{\sqrt{3}}{2} & 1 & 0 & 0 & 0 \end{bmatrix}$$

6.6 The carbon atom does not permute with any of the hydrogens under the operations of $\mathcal{T}_d$. Thus, we find that the carbon s-state engenders the identity Irrep $^{(1)}\Gamma$, while the p-state manifold engenders the vector Irrep $^{(5)}\Gamma$, given in table 6.4.

The Rep engendered by the $1s$-states of the four hydrogen atoms is just the permutations generated by the operations of $\mathcal{T}_d$ on the these atoms. We start by generating the permutations among the four tetrahedral apecies where the hydrogen atoms reside. For the sake of completeness we will also generate the vector Rep of $\mathcal{T}_d$.

Program

Generators : C_{2z}, C_{2x}, σ_{xy}, C_3^{xyz}

```
<<Combinatorica`
g = 24;NG = 5;
L = { Range [4],{2,1,4,3},{3,4,1,2},{1,2,4,3},{2,3,1,4}};
R = {{{1,0,0},{0,1,0},{0,0,1}},{{-1,0,0},{0,-1,0},{0,0,1}},{{1,0,0},{0,-1,0},{0,0,-1}},
{{0,-1,0},{-1,0,0},{0,0,1}},{{0,0,1},{1,0,0},{0,1,0}}};
 Array [ Rot ,{3,3}];
Do [B = R[[i]]; Rot [i]= B, {i,1, NG }];
```

```
f: =  Permute [L[[i]],L[[j]]]; nel = NG ;
While [ TrueQ [ Length [L] < g],
        For [i=2,i < g,i++,
              For [j=2,j < ( Length [L]+1),j++,
                   Switch [ FreeQ [L,f], True ,
                             AppendTo [L,f]; nel ++; Rot [ nel ]= Rot [i]. Rot [j]
                            ]]]]; Print [L];
  Print ["Rotation Matrices of Group Elements: "]
 Do [
       Print ["R(",i,") = ",MatrixForm[Rot[i]],",",
             " R(",i+1,") = ",MatrixForm[Rot[i+1]],",",
             " R(",i+2,") = ",  MatrixForm [ Rot [i+2]],",",
             "   R(  ",i+3,") = ", MatrixForm [ Rot [i+3]]
             ],
       {i,1,g-3,4}
       ];
 X = 0* IdentityMatrix [4]; Perm = {};
Do[ AppendTo [ Perm , X ], {i,1,g}];
Do [ B = X ;
      Do [
            B [[j,L[[i,j]]]] = 1, {j,1,4}
             ]; Perm [[i]]+ = B, {i,1,g}
      ];
 Do [
       Print [
              "P(",i,") = ",MatrixForm[Perm[[i]]],",",
               " P(",i+1,") = ",MatrixForm[Perm[[i+1]]],",",
               " P(",i+2,") = ", MatrixForm[Perm[[i+2]]],",",
               " P(",i+3,") = ",MatrixForm[Perm[[i+3]]]
               ],  {i,1,g-3,4}
       ]
```

```
NM = {{1},{5,8,10,12,18,20,22,24},{2,3,6},{9,11,13,15,17,23},{4,7,14,16,19,21}};
xi = {{1,1,1,-1,-1},{2,-1,2,0,0},{3,0,-1,1,-1},{3,0,-1,-1,1}};
 Class = {};
Do [
      Cls =X;
      Do [
             Cls+ = Perm[[NM[[i,j]]]],{j,1, Length [NM[[i]]]}
             ] ; AppendTo [ Class , Cls ],{i,1,5}
       ];
Do [ Print [ MatrixForm [ Class [[i]]]],{i,1,5}];
Pr  = Class[[1]];
Do [ Pr+ = Class[[i]],{i,2,5}];Pr =Pr/24;
 Print[ MatrixForm[ Pr ]]; Eigensystem[ Pr  ]
Pr2 = xi[[1,1]]* Class[[1]];
Do [ Pr2+ =  xi [[1,i]]* Class [[i]],{i,2,5}]; Pr2 = Pr2/24;
 Print [ MatrixForm [ Pr2 ]]; Eigensystem [ Pr2 ]
Pr3 = xi [[2,1]]* Class [[1]];
Do [ Pr3+ =  xi[[2,i]]* Class [[i]],{i,2,5}]; Pr3 = Pr3/12;
 Print [ MatrixForm [ Pr3 ]]; Eigensystem [ Pr3 ]
Pr4 = xi [[3,1]]* Class [[1]];
Do [Pr4+ = xi [[3,i]]* Class [[i]],{i,2,5}]; Pr4 = Pr4/8;
 Print [ MatrixForm [ Pr4 ]]; Eigensystem [ Pr4 ]
Pr5 = xi [[4,1]]* Class [[1]];
 Do [Pr5+ = xi [[4,i]]* Class [[i]],{i,2,5}]; Pr5 = Pr5/8;
 Print [ MatrixForm [ Pr5 ]]; Eigensystem [ Pr5 ]
```

Group Permutations:

$\{\{1,2,3,4\},\{2,1,4,3\},\{3,4,1,2\},\{1,2,4,3\},\{2,3,1,4\},\{4,3,2,1\},\{2,1,3,4\},\{1,4,2,3\},$
$\{3,4,2,1\},\{4,1,3,2\},\{4,3,1,2\},\{3,2,4,1\},\{2,4,1,3\},\{1,3,2,4\},\{3,1,4,2\},\{4,2,3,1\},$
$\{2,3,4,1\},\{3,1,2,4\},\{3,2,1,4\},\{2,4,3,1\},\{1,4,3,2\},\{4,2,1,3\},\{4,1,2,3\},\{1,3,4,2\}\}$

Rotation Matrices of Group Elements:

$$\begin{matrix}\mathrm{R}(1)\\ E\end{matrix} = \begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix},\quad \begin{matrix}\mathrm{R}(2)\\ U_z\end{matrix} = \begin{pmatrix}-1&0&0\\0&-1&0\\0&0&1\end{pmatrix},\quad \begin{matrix}\mathrm{R}(3)\\ U_x\end{matrix} = \begin{pmatrix}1&0&0\\0&-1&0\\0&0&-1\end{pmatrix},\quad \begin{matrix}\mathrm{R}(4)\\ \sigma_{xy}\end{matrix} = \begin{pmatrix}0&-1&0\\-1&0&0\\0&0&1\end{pmatrix}$$

$$\begin{matrix}\mathrm{R}(5)\\ C_3^{xyz}\end{matrix} = \begin{pmatrix}0&0&1\\1&0&0\\0&1&0\end{pmatrix},\quad \begin{matrix}\mathrm{R}(6)\\ U_y\end{matrix} = \begin{pmatrix}-1&0&0\\0&1&0\\0&0&-1\end{pmatrix},\quad \begin{matrix}\mathrm{R}(7)\\ \sigma x\bar{y}\end{matrix} = \begin{pmatrix}0&1&0\\1&0&0\\0&0&1\end{pmatrix},\quad \begin{matrix}\mathrm{R}(8)\\ C_3^{\bar{x}yz}\end{matrix} = \begin{pmatrix}0&0&-1\\-1&0&0\\0&1&0\end{pmatrix},$$

$$\begin{matrix}\mathrm{R}(9)\\ S_4^{z}\end{matrix} = \begin{pmatrix}0&-1&0\\1&0&0\\0&0&-1\end{pmatrix},\quad \begin{matrix}\mathrm{R}(10)\\ C_3^{2x\bar{y}z}\end{matrix} = \begin{pmatrix}0&0&1\\-1&0&0\\0&-1&0\end{pmatrix},\quad \begin{matrix}\mathrm{R}(11)\\ S_4^{3z}\end{matrix} = \begin{pmatrix}0&1&0\\-1&0&0\\0&0&-1\end{pmatrix},\quad \begin{matrix}\mathrm{R}(12)\\ C_3^{2xy\bar{z}}\end{matrix} = \begin{pmatrix}0&0&-1\\1&0&0\\0&-1&0\end{pmatrix}$$

$$\begin{matrix}\mathrm{R}(13)\\ S_4^{3x}\end{matrix} = \begin{pmatrix}-1&0&0\\0&0&-1\\0&1&0\end{pmatrix},\quad \begin{matrix}\mathrm{R}(14)\\ \sigma_{y\bar{z}}\end{matrix} = \begin{pmatrix}1&0&0\\0&0&1\\0&1&0\end{pmatrix},\quad \begin{matrix}\mathrm{R}(15)\\ \sigma_{yz}\end{matrix} = \begin{pmatrix}1&0&0\\0&0&-1\\0&-1&0\end{pmatrix},\quad \mathrm{R}(16)\, S_4^{x} = \begin{pmatrix}-1&0&0\\0&0&1\\0&-1&0\end{pmatrix}$$

$$\begin{matrix}\mathrm{R}(17)\\ S_4^{3y}\end{matrix} = \begin{pmatrix}0&0&1\\0&-1&0\\-1&0&0\end{pmatrix},\quad \begin{matrix}\mathrm{R}(18)\\ C_3^{2xyz}\end{matrix} = \begin{pmatrix}0&1&0\\0&0&1\\1&0&0\end{pmatrix},\quad \begin{matrix}\mathrm{R}(19)\\ \sigma_{\bar{x}z}\end{matrix} = \begin{pmatrix}0&0&1\\0&1&0\\1&0&0\end{pmatrix},\quad \begin{matrix}\mathrm{R}(20)\\ C_3^{xy\bar{z}}\end{matrix} = \begin{pmatrix}0&1&0\\0&0&-1\\-1&0&0\end{pmatrix}$$

$$\begin{matrix}\mathrm{R}(21)\\ S_4^{y}\end{matrix} = \begin{pmatrix}0&0&-1\\0&-1&0\\1&0&0\end{pmatrix},\quad \begin{matrix}\mathrm{R}(22)\\ C_3^{x\bar{y}z}\end{matrix} = \begin{pmatrix}0&-1&0\\0&0&1\\-1&0&0\end{pmatrix},\quad \begin{matrix}\mathrm{R}(23)\\ \sigma_{xz}\end{matrix} = \begin{pmatrix}0&0&-1\\0&1&0\\-1&0&0\end{pmatrix},\quad \begin{matrix}\mathrm{R}(24)\\ C_3^{x\bar{y}z}\end{matrix} = \begin{pmatrix}0&-1&0\\0&0&-1\\1&0&0\end{pmatrix}$$

Permutation Matrices for the Hydrogen Atoms:

$$\mathrm{P}(1) = \begin{pmatrix}1&0&0&0\\0&1&0&0\\0&0&1&0\\0&0&0&1\end{pmatrix},\quad \mathrm{P}(2) = \begin{pmatrix}0&1&0&0\\1&0&0&0\\0&0&0&1\\0&0&1&0\end{pmatrix},\quad \mathrm{P}(3) = \begin{pmatrix}0&0&1&0\\0&0&0&1\\1&0&0&0\\0&1&0&0\end{pmatrix},\quad \mathrm{P}(4) = \begin{pmatrix}1&0&0&0\\0&1&0&0\\0&0&0&1\\0&0&1&0\end{pmatrix}$$

$$\mathrm{P}(5) = \begin{pmatrix}0&1&0&0\\0&0&1&0\\1&0&0&0\\0&0&0&1\end{pmatrix},\quad \mathrm{P}(6) = \begin{pmatrix}0&0&0&1\\0&0&1&0\\0&1&0&0\\1&0&0&0\end{pmatrix},\quad \mathrm{P}(7) = \begin{pmatrix}0&1&0&0\\1&0&0&0\\0&0&1&0\\0&0&0&1\end{pmatrix},\quad \mathrm{P}(8) = \begin{pmatrix}1&0&0&0\\0&0&0&1\\0&1&0&0\\0&0&1&0\end{pmatrix},$$

$$P(9) = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}, \quad P(10) = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}, \quad P(11) = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}, \quad P(12) = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \end{pmatrix},$$

$$P(13) = \begin{pmatrix} 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}, \quad P(14) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}, \quad P(15) = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \end{pmatrix}, \quad P(16) = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}$$

$$P(17) = \begin{pmatrix} 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \end{pmatrix}, \quad P(18) = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}, \quad P(19) = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}, \quad P(20) = \begin{pmatrix} 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}$$

$$P(21) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}, \quad P(22) = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}, \quad P(23) = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}, \quad P(24) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \end{pmatrix}$$

Table 6.4. Character Table for $\mathcal{T}_{\mathrm{d}}$

	E	$8C_3$	$3U$	$6S_4$	$6\sigma_{\mathrm{d}}$
$^{(1)}\Gamma$	1	1	1	1	1
$^{(2)}\Gamma$	1	1	1	-1	-1
$^{(3)}\Gamma$	2	-1	2	0	0
$^{(4)}\Gamma$	3	0	-1	1	-1
$^{(5)}\Gamma$	3	0	-1	-1	1

$$Classmatrix(1) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}, \; Classmatrix(2) = \begin{pmatrix} 2 & 2 & 2 & 2 \\ 2 & 2 & 2 & 2 \\ 2 & 2 & 2 & 2 \\ 2 & 2 & 2 & 2 \end{pmatrix},$$

$$Classmatrix(3) = \begin{pmatrix} 0 & 1 & 1 & 1 \\ 1 & 0 & 1 & 1 \\ 1 & 1 & 0 & 1 \\ 1 & 1 & 1 & 0 \end{pmatrix}, \; Classmatrix(4) = \begin{pmatrix} 0 & 2 & 2 & 2 \\ 2 & 0 & 2 & 2 \\ 2 & 2 & 0 & 2 \\ 2 & 2 & 2 & 0 \end{pmatrix}$$

$$Classmatrix(5) = \begin{pmatrix} 3 & 1 & 1 & 1 \\ 1 & 3 & 1 & 1 \\ 1 & 1 & 3 & 1 \\ 1 & 1 & 1 & 3 \end{pmatrix}$$

$${}^{(1)}\mathcal{P} = \begin{pmatrix} \frac{1}{4} & \frac{1}{4} & \frac{1}{4} & \frac{1}{4} \\ \frac{1}{4} & \frac{1}{4} & \frac{1}{4} & \frac{1}{4} \\ \frac{1}{4} & \frac{1}{4} & \frac{1}{4} & \frac{1}{4} \\ \frac{1}{4} & \frac{1}{4} & \frac{1}{4} & \frac{1}{4} \end{pmatrix}$$

$$\begin{cases} \text{Eigenvalues :} & 1, 0, 0, 0 \\ \text{Eigenvectors :} & \{1, 1, 1, 1\}, \{-1, 0, 0, 1\}, \{-1, 0, 1, 0\}, \{-1, 1, 0, 0\} \end{cases}$$

$${}^{(2)}\mathcal{P} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$$

$$\begin{cases} \text{Eigenvalues :} & 0, 0, 0, 0 \\ \text{Eigenvectors :} & \{0, 0, 0, 1\}, \{0, 0, 1, 0\}, \{0, 1, 0, 0\}, \{1, 0, 0, 0\} \end{cases}$$

$${}^{(3)}\mathcal{P} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$$

$$\begin{cases} \text{Eigenvalues :} & 0, 0, 0, 0 \\ \text{Eigenvectors :} & \{0, 0, 0, 1\}, \{0, 0, 1, 0\}, \{0, 1, 0, 0\}, \{1, 0, 0, 0\} \end{cases}$$

$$^{(4)}\mathcal{P} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$$

$$\begin{cases} \text{Eigenvalues :} & 0, 0, 0, 0 \\ \text{Eigenvectors :} & \{\{0,0,0,1\},\{0,0,1,0\},\{0,1,0,0\},\{1,0,0,0\} \end{cases}$$

$$^{(5)}\mathcal{P} = \begin{pmatrix} \frac{3}{4} & -\frac{1}{4} & -\frac{1}{4} & -\frac{1}{4} \\ -\frac{1}{4} & \frac{3}{4} & -\frac{1}{4} & -\frac{1}{4} \\ -\frac{1}{4} & -\frac{1}{4} & \frac{3}{4} & -\frac{1}{4} \\ -\frac{1}{4} & -\frac{1}{4} & -\frac{1}{4} & \frac{3}{4} \end{pmatrix}$$

$$\begin{cases} \text{Eigenvalues :} & 1, 1, 1, 0 \\ \text{Eigenvectors :} & \{-1,0,0,1\},\{-1,0,1,0\},\{-1,1,0,0\},\{1,1,1,1\} \end{cases}$$

Symmetry-adapted vectors

$$^{(1)}\Gamma : \quad \begin{bmatrix} 1 & 1 & 1 & 1 \end{bmatrix}$$

$$^{(5)}\Gamma : \quad \begin{bmatrix} -1 & 0 & 0 & 1 \\ -1 & 0 & 1 & 0 \\ -1 & 1 & 0 & 0 \end{bmatrix}$$

6.7 **(* C_6, C_{2x}, I *)**

```
<<Combinatorica`
g = 24; NG = 4;
L = { Range [12], {6,1,2,3,4,5,12,7,8,9,10,11}, {7,12,11,10,9,8,1,6,5,4,3,2}, {10,11,12,7,8,9,4,5,6,1,2,3}};
R = {{{1,0,0},{0,1,0},{0,0,1}},{{1/2,Sqrt[3]/2,0},{-Sqrt[3]/2,1/2,0},{0,0,1}},
     {{1,0,0},{0,-1,0},{0,0,-1}},{{-1,0,0},{0,-1,0},{0,0,-1}}};Array[Rot,{3,3}];
Do [B = R[[i]]; Rot [i] = B,{i,1, NG }];
f:= Permute [L[[i]],L[[j]]]; nel = NG ;
While [ TrueQ [ Length [L]<g],
      For [i=2,i<g,i++,
          For [j=2,j<( Length [L]+1),j++,
              Switch [ FreeQ [L,f], True , AppendTo [L,f];
```

```
                    nel ++; Rot [ nel ] = Rot[i]. Rot [j];bc=R[[i]].R[[j]];
                   AppendTo[R,bc]]]]];
 Print [L];
  Print ["Rotation Matrices of Group Elements: "]
 Do[
     Print["R(",i,") = ",MatrixForm[Rot[i]],",",
         " R(",i+1,") = ",MatrixForm[Rot[i+1]],",",
         " R(",i+2,") = ", MatrixForm[Rot[i+2]],",",
         " R(",i+3,") = ",MatrixForm[Rot[i+3]]
         ],
     {i,1,g-3,4}
     ]; X=0* IdentityMatrix [6]; Perm = {}; Do[ AppendTo [ Perm ,X],{i,1,g}];
Do [B=X;
     Do [
        Switch [L[[i,j]]¡7, True ,B[[j,L[[i,j]]]]=1, False , cb =L[[i,j]]-6;B[[j, cb ]]=1],{j,1,6}
              ]; Perm [[i]]+=B,{i,1,g}
 ];
(* Transformation of s-orbitals *)
 Do [
  Print ["P(",i,") = ",MatrixForm[Perm[[i]]],",",
 " P(",i+1,") = ",MatrixForm[Perm[[i+1]]],",",
 " P(",i+2,") = ", MatrixForm[Perm[[i+2]]],",",
 " P(",i+3,") = ",MatrixForm[Perm[[i+3]]]
 ], {i,1,g-3,4}
 ] ;
 ] ; pz={};
(* Transformation of pz-orbitals *)
Do[pp=Perm[[i]]*R[[i,3,3]];AppendTo[pz,pp],{i,1,g}];
Do[
 Print["Ppz(",i,") = ",MatrixForm[pz[[i]]],",",
 " Ppz(",i+1,") = ",MatrixForm[pz[[i+1]]],",",
```

```
 " Ppz(",i+2,") = ", MatrixForm[pz[[i+2]]],",",
 " Ppz(",i+3,") = ",MatrixForm[pz[[i+3]]]
 ], {i,1,g-3,4}
 ] ;
 NM ={{1},{2,14},{5,11},{8},{3,9,15},{6,12,17},{4},{7,18},{10,16},{13},{19,21,23},{20,22,24}};
xi = {{1,1,1,1,-1,-1,1,1,1,1,-1,-1},{1,-1,1,-1,1,-1,1,-1,1,-1,1,-1},{1,-1,1,-1,-1,1,1,-1,1,-1,-1,1},
     {2,1,-1,-2,0,0,2,1,-1,-2,0,0},{2,-1,-1,2,0,0,2,-1,-1,2,0,0},{1,1,1,1,1,1,-1,-1,-1,-1,-1,-1},
     {1,1,1,1,-1,-1,-1,-1,-1,-1,1,1},{1,-1,1,-1,1,-1,-1,1,-1,1,-1,1},{1,-1,1,-1,-1,1,-1,1,-1,1,1,-1},
     {2,1,-1,-2,0,0,-2,-1,1,2,0,0},{2,-1,-1,2,0,0,-2,1,1,-2,0,0}};
 Class = {};
Do [
 Cls = X;
 Do [ Cls+ = Perm [[ NM [[i,j]]]],{j,1, Length [ NM [[i]]]}
 ] ; AppendTo [ Class , Cls ],{i,1,12}
 ];
Do[ Print [ MatrixForm [ Class [[i]]]],{i,1,12}];
Pr  = Class [[1]];
Do [Pr + = Class [[i]],{i,2,12}];Pr  = Pr/24; Print [ MatrixForm [Pr ]]; Eigensystem [Pr ]
Do [
 Pr2 = xi [[i,1]]* Class [[1]];
 Do [ Pr2 + = xi [[i,j]]* Class [[j]],{j,2,12}]; Pr2 = xi [[i,1]]* Pr2 ;
 Pr2 = Pr2/24; Print [ MatrixForm [ Pr2 ]]; Print [ Eigensystem [ Pr2 ]],{i,1,11}
 ]
Claspz={};
Do[
 Clpz=X;
 Do[Clpz+=pz[[NM[[i,j]]]],{j,1,Length[NM[[i]]]}
 ] ;AppendTo[Claspz,Clpz],{i,1,12}
 ];
Do[
 Print["Clpz(",i,") = ",MatrixForm[Claspz[[i]]],",",
```

```
    " Clpz(",i+1,") = ",MatrixForm[Claspz[[i+1]]],",",
    " Clpz(",i+2,") = ", MatrixForm[Claspz[[i+2]]],",",
    " Clpz(",i+3,") = ",MatrixForm[Claspz[[i+3]]]
    ], {i,1,9,4}
    ] ;
   Pr =Claspz[[1]];
   Do[Pr +=Claspz[[i]],{i,2,12}];Pr =Pr /24;Print[MatrixForm[Pr ]];Eigensystem[Pr ]
Do[
    Pr2=xi[[i,1]]*Claspz[[1]];
 Do[
    Pr2+=xi[[i,j]]*Claspz[[j]],{j,2,12}
    ];Pr2=Pr2*xi[[i,1]];Pr2=Pr2/24;Print[MatrixForm[Pr2]];Print[Eigensystem[Pr2]],{i,1,11}]
```

Group Permutations:

{{1,2,3,4,5,6,7,8,9,10,11,12},{6,1,2,3,4,5,12,7,8,9,10,11},{7,12,11,10,9,8,1,6,5,4,3,2},
{10,11,12,7,8,9,4,5,6,1,2,3},{5,6,1,2,3,4,11,12,7,8,9,10},{8,7,12,11,10,9,2,1,6,5,4,3},
{9,10,11,12,7,8,3,4,5,6,1,2},{4,5,6,1,2,3,10,11,12,7,8,9},{9,8,7,12,11,10,3,2,1,6,5,4},
{8,9,10,11,12,7,2,3,4,5,6,1},{3,4,5,6,1,2,9,10,11,12,7,8},{10,9,8,7,12,11,4,3,2,1,6,5},
{7,8,9,10,11,12,1,2,3,4,5,6},{2,3,4,5,6,1,8,9,10,11,12,7},{11,10,9,8,7,12,5,4,3,2,1,6},
{12,7,8,9,10,11,6,1,2,3,4,5},{12,11,10,9,8,7,6,5,4,3,2,1},{11,12,7,8,9,10,5,6,1,2,3,4},
{4,3,2,1,6,5,10,9,8,7,12,11},{3,2,1,6,5,4,9,8,7,12,11,10},{2,1,6,5,4,3,8,7,12,11,10,9},
{1,6,5,4,3,2,7,12,11,10,9,8},{6,5,4,3,2,1,12,11,10,9,8,7},{5,4,3,2,1,6,11,10,9,8,7,12}}

Rotation Matrices of Group Elements:

$$\begin{matrix}\mathrm{R}\ (1)\\ \mathrm{E}\end{matrix} = \begin{pmatrix}1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1\end{pmatrix}, \begin{matrix}\mathrm{R}\ (2)\\ \mathrm{C}_6\end{matrix} = \begin{pmatrix}\frac{1}{2} & \frac{\sqrt{3}}{2} & 0\\ -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0\\ 0 & 0 & 1\end{pmatrix}, \begin{matrix}\mathrm{R}\ (3)\\ \mathrm{U}_1\end{matrix} = \begin{pmatrix}1 & 0 & 0\\ 0 & -1 & 0\\ 0 & 0 & -1\end{pmatrix},$$

$$\begin{array}{c}\mathrm{R}\ (4)\\ \mathrm{I}\end{array} = \begin{pmatrix}-1 & 0 & 0\\ 0 & -1 & 0\\ 0 & 0 & -1\end{pmatrix},\ \begin{array}{c}\mathrm{R}\ (5)\\ \mathrm{C}_3\end{array} = \begin{pmatrix}-\frac{1}{2} & \frac{\sqrt{3}}{2} & 0\\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0\\ 0 & 0 & 1\end{pmatrix},\ \begin{array}{c}\mathrm{R}\ (6)\\ \mathrm{U}_{d1}\end{array} = \begin{pmatrix}\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0\\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0\\ 0 & 0 & -1\end{pmatrix},$$

$$\begin{array}{c}\mathrm{R}\ (7)\\ \mathrm{S}_3\end{array} = \begin{pmatrix}-\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0\\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0\\ 0 & 0 & -1\end{pmatrix},\ \begin{array}{c}\mathrm{R}\ (8)\\ \mathrm{C}_2\end{array} = \begin{pmatrix}-1 & 0 & 0\\ 0 & -1 & 0\\ 0 & 0 & 1\end{pmatrix},\ \begin{array}{c}\mathrm{R}\ (9)\\ \mathrm{U}_2\end{array} = \begin{pmatrix}-\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0\\ -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0\\ 0 & 0 & -1\end{pmatrix},$$

$$\begin{array}{c}\mathrm{R}\ (10)\\ \mathrm{S}_6\end{array} = \begin{pmatrix}\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0\\ \frac{\sqrt{3}}{2} & \frac{1}{2} & 0\\ 0 & 0 & -1\end{pmatrix},\ \begin{array}{c}\mathrm{R}\ (11)\\ \mathrm{C}_3^2\end{array} = \begin{pmatrix}-\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0\\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0\\ 0 & 0 & 1\end{pmatrix},\ \begin{array}{c}\mathrm{R}\ (12)\\ \mathrm{U}_{d2}\end{array} = \begin{pmatrix}-1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & -1\end{pmatrix}$$

$$\begin{array}{c}\mathrm{R}\ (13)\\ \sigma_{\mathrm{h}}\end{array} = \begin{pmatrix}1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & -1\end{pmatrix},\ \begin{array}{c}\mathrm{R}\ (14)\\ \mathrm{C}_6^{-1}\end{array} = \begin{pmatrix}\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0\\ \frac{\sqrt{3}}{2} & \frac{1}{2} & 0\\ 0 & 0 & 1\end{pmatrix},\ \begin{array}{c}\mathrm{R}\ (15)\\ \mathrm{U}_3\end{array} = \begin{pmatrix}-\frac{1}{2} & \frac{\sqrt{3}}{2} & 0\\ \frac{\sqrt{3}}{2} & \frac{1}{2} & 0\\ 0 & 0 & -1\end{pmatrix},$$

$$\begin{array}{c}\mathrm{R}\ (16)\\ \mathrm{S}_6^2\end{array} = \begin{pmatrix}\frac{1}{2} & \frac{\sqrt{3}}{2} & 0\\ -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0\\ 0 & 0 & -1\end{pmatrix},\ \begin{array}{c}\mathrm{R}\ (17)\\ \mathrm{U}_{d3}\end{array} = \begin{pmatrix}\frac{1}{2} & \frac{\sqrt{3}}{2} & 0\\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0\\ 0 & 0 & -1\end{pmatrix},\ \begin{array}{c}\mathrm{R}\ (18)\\ \mathrm{S}_3^2\end{array} = \begin{pmatrix}-\frac{1}{2} & \frac{\sqrt{3}}{2} & 0\\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0\\ 0 & 0 & -1\end{pmatrix},$$

$$\begin{array}{c}\mathrm{R}\ (19)\\ \sigma_{\mathrm{d1}}\end{array} = \begin{pmatrix}-1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1\end{pmatrix},\ \begin{array}{c}\mathrm{R}\ (20)\\ \sigma_1\end{array} = \begin{pmatrix}-\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0\\ -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0\\ 0 & 0 & 1\end{pmatrix},\ \begin{array}{c}\mathrm{R}\ (21)\\ \sigma_{\mathrm{d2}}\end{array} = \begin{pmatrix}\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0\\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0\\ 0 & 0 & 1\end{pmatrix},$$

$$\begin{array}{c}\mathrm{R}\ (22)\\ \sigma_2\end{array} = \begin{pmatrix}1 & 0 & 0\\ 0 & -1 & 0\\ 0 & 0 & 1\end{pmatrix},\ \begin{array}{c}\mathrm{R}\ (23)\\ \sigma_{\mathrm{d3}}\end{array} = \begin{pmatrix}\frac{1}{2} & \frac{\sqrt{3}}{2} & 0\\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0\\ 0 & 0 & 1\end{pmatrix},\ \begin{array}{c}\mathrm{R}\ (24)\\ \sigma_3\end{array} = \begin{pmatrix}-\frac{1}{2} & \frac{\sqrt{3}}{2} & 0\\ \frac{\sqrt{3}}{2} & \frac{1}{2} & 0\\ 0 & 0 & 1\end{pmatrix}$$

Since the *s*-orbital engenders the identity Irrep, the *s*-orbitals of both species engender the site permutation matrices.

Site Permutations:

$$\mathrm{P}\ (1) = \begin{pmatrix}1 & 0 & 0 & 0 & 0 & 0\\ 0 & 1 & 0 & 0 & 0 & 0\\ 0 & 0 & 1 & 0 & 0 & 0\\ 0 & 0 & 0 & 1 & 0 & 0\\ 0 & 0 & 0 & 0 & 1 & 0\\ 0 & 0 & 0 & 0 & 0 & 1\end{pmatrix},\ \mathrm{P}\ (2) = \begin{pmatrix}0 & 0 & 0 & 0 & 0 & 1\\ 1 & 0 & 0 & 0 & 0 & 0\\ 0 & 1 & 0 & 0 & 0 & 0\\ 0 & 0 & 1 & 0 & 0 & 0\\ 0 & 0 & 0 & 1 & 0 & 0\\ 0 & 0 & 0 & 0 & 1 & 0\end{pmatrix},\ \mathrm{P}\ (3) = \begin{pmatrix}1 & 0 & 0 & 0 & 0 & 0\\ 0 & 0 & 0 & 0 & 0 & 1\\ 0 & 0 & 0 & 0 & 1 & 0\\ 0 & 0 & 0 & 1 & 0 & 0\\ 0 & 0 & 1 & 0 & 0 & 0\\ 0 & 1 & 0 & 0 & 0 & 0\end{pmatrix},$$

$$P(4) = \begin{pmatrix} 0&0&0&1&0&0\\ 0&0&0&0&1&0\\ 0&0&0&0&0&1\\ 1&0&0&0&0&0\\ 0&1&0&0&0&0\\ 0&0&1&0&0&0 \end{pmatrix},\ P(5) = \begin{pmatrix} 0&0&0&0&1&0\\ 0&0&0&0&0&1\\ 1&0&0&0&0&0\\ 0&1&0&0&0&0\\ 0&0&1&0&0&0\\ 0&0&0&1&0&0 \end{pmatrix},\ P(6) = \begin{pmatrix} 0&0&0&0&0&1\\ 0&0&0&0&1&0\\ 0&0&0&1&0&0\\ 0&0&1&0&0&0\\ 0&1&0&0&0&0\\ 1&0&0&0&0&0 \end{pmatrix},$$

$$P(7) = \begin{pmatrix} 0&0&1&0&0&0\\ 0&0&0&1&0&0\\ 0&0&0&0&1&0\\ 0&0&0&0&0&1\\ 1&0&0&0&0&0\\ 0&1&0&0&0&0 \end{pmatrix},\ P(8) = \begin{pmatrix} 0&0&0&1&0&0\\ 0&0&0&0&1&0\\ 0&0&0&0&0&1\\ 1&0&0&0&0&0\\ 0&1&0&0&0&0\\ 0&0&1&0&0&0 \end{pmatrix},\ P(9) = \begin{pmatrix} 0&0&0&0&1&0\\ 0&0&0&1&0&0\\ 0&0&1&0&0&0\\ 0&1&0&0&0&0\\ 1&0&0&0&0&0\\ 0&0&0&0&0&1 \end{pmatrix},$$

$$P(10) = \begin{pmatrix} 0&1&0&0&0&0\\ 0&0&1&0&0&0\\ 0&0&0&1&0&0\\ 0&0&0&0&1&0\\ 0&0&0&0&0&1\\ 1&0&0&0&0&0 \end{pmatrix},\ P(11) = \begin{pmatrix} 0&0&1&0&0&0\\ 0&0&0&1&0&0\\ 0&0&0&0&1&0\\ 0&0&0&0&0&1\\ 1&0&0&0&0&0\\ 0&1&0&0&0&0 \end{pmatrix},\ P(12) = \begin{pmatrix} 0&0&0&1&0&0\\ 0&0&1&0&0&0\\ 0&1&0&0&0&0\\ 1&0&0&0&0&0\\ 0&0&0&0&0&1\\ 0&0&0&0&1&0 \end{pmatrix}$$

$$P(13) = \begin{pmatrix} 1&0&0&0&0&0\\ 0&1&0&0&0&0\\ 0&0&1&0&0&0\\ 0&0&0&1&0&0\\ 0&0&0&0&1&0\\ 0&0&0&0&0&1 \end{pmatrix},\ P(14) = \begin{pmatrix} 0&1&0&0&0&0\\ 0&0&1&0&0&0\\ 0&0&0&1&0&0\\ 0&0&0&0&1&0\\ 0&0&0&0&0&1\\ 1&0&0&0&0&0 \end{pmatrix},\ P(15) = \begin{pmatrix} 0&0&1&0&0&0\\ 0&1&0&0&0&0\\ 1&0&0&0&0&0\\ 0&0&0&0&0&1\\ 0&0&0&0&1&0\\ 0&0&0&1&0&0 \end{pmatrix},$$

$$P(16) = \begin{pmatrix} 0&0&0&0&0&1\\ 1&0&0&0&0&0\\ 0&1&0&0&0&0\\ 0&0&1&0&0&0\\ 0&0&0&1&0&0\\ 0&0&0&0&1&0 \end{pmatrix},\ P(17) = \begin{pmatrix} 0&1&0&0&0&0\\ 1&0&0&0&0&0\\ 0&0&0&0&0&1\\ 0&0&0&0&1&0\\ 0&0&0&1&0&0\\ 0&0&1&0&0&0 \end{pmatrix},\ P(18) = \begin{pmatrix} 0&0&0&0&1&0\\ 0&0&0&0&0&1\\ 1&0&0&0&0&0\\ 0&1&0&0&0&0\\ 0&0&1&0&0&0\\ 0&0&0&1&0&0 \end{pmatrix},$$

$$P(19) = \begin{pmatrix} 0&0&0&1&0&0\\ 0&0&1&0&0&0\\ 0&1&0&0&0&0\\ 1&0&0&0&0&0\\ 0&0&0&0&0&1\\ 0&0&0&0&1&0 \end{pmatrix},\ P(20) = \begin{pmatrix} 0&0&0&0&1&0\\ 0&0&0&1&0&0\\ 0&0&1&0&0&0\\ 0&1&0&0&0&0\\ 1&0&0&0&0&0\\ 0&0&0&0&0&1 \end{pmatrix},\ P(21) = \begin{pmatrix} 0&0&0&0&0&1\\ 0&0&0&0&1&0\\ 0&0&0&1&0&0\\ 0&0&1&0&0&0\\ 0&1&0&0&0&0\\ 1&0&0&0&0&0 \end{pmatrix},$$

$$P(22) = \begin{pmatrix} 1&0&0&0&0&0\\ 0&0&0&0&0&1\\ 0&0&0&0&1&0\\ 0&0&0&1&0&0\\ 0&0&1&0&0&0\\ 0&1&0&0&0&0 \end{pmatrix},\ P(23) = \begin{pmatrix} 0&1&0&0&0&0\\ 1&0&0&0&0&0\\ 0&0&0&0&0&1\\ 0&0&0&0&1&0\\ 0&0&0&1&0&0\\ 0&0&1&0&0&0 \end{pmatrix},\ P(24) = \begin{pmatrix} 0&0&1&0&0&0\\ 0&1&0&0&0&0\\ 1&0&0&0&0&0\\ 0&0&0&0&0&1\\ 0&0&0&0&1&0\\ 0&0&0&1&0&0 \end{pmatrix}$$

Class matrices:

$$\text{Class}(1) = \begin{pmatrix} 1&0&0&0&0&0\\ 0&1&0&0&0&0\\ 0&0&1&0&0&0\\ 0&0&0&1&0&0\\ 0&0&0&0&1&0\\ 0&0&0&0&0&1 \end{pmatrix}, \text{Class}(2) = \begin{pmatrix} 0&1&0&0&0&1\\ 1&0&1&0&0&0\\ 0&1&0&1&0&0\\ 0&0&1&0&1&0\\ 0&0&0&1&0&1\\ 1&0&0&0&1&0 \end{pmatrix}, \text{Class}(3) = \begin{pmatrix} 0&0&1&0&1&0\\ 0&0&0&1&0&1\\ 1&0&0&0&1&0\\ 0&1&0&0&0&1\\ 1&0&1&0&0&0\\ 0&1&0&1&0&0 \end{pmatrix},$$

$$\text{Class}(4) = \begin{pmatrix} 0&0&0&1&0&0\\ 0&0&0&0&1&0\\ 0&0&0&0&0&1\\ 1&0&0&0&0&0\\ 0&1&0&0&0&0\\ 0&0&1&0&0&0 \end{pmatrix}, \text{Class}(5) = \begin{pmatrix} 1&0&1&0&1&0\\ 0&1&0&1&0&1\\ 1&0&1&0&1&0\\ 0&1&0&1&0&1\\ 1&0&1&0&1&0\\ 0&1&0&1&0&1 \end{pmatrix}, \text{Class}(6) = \begin{pmatrix} 0&1&0&1&0&1\\ 1&0&1&0&1&0\\ 0&1&0&1&0&1\\ 1&0&1&0&1&0\\ 0&1&0&1&0&1\\ 1&0&1&0&1&0 \end{pmatrix},$$

$$\text{Class}(7) = \begin{pmatrix} 0&0&0&1&0&0\\ 0&0&0&0&1&0\\ 0&0&0&0&0&1\\ 1&0&0&0&0&0\\ 0&1&0&0&0&0\\ 0&0&1&0&0&0 \end{pmatrix}, \text{Class}(8) = \begin{pmatrix} 0&0&1&0&1&0\\ 0&0&0&1&0&1\\ 1&0&0&0&1&0\\ 0&1&0&0&0&1\\ 1&0&1&0&0&0\\ 0&1&0&1&0&0 \end{pmatrix}, \text{Class}(9) = \begin{pmatrix} 0&1&0&0&0&1\\ 1&0&1&0&0&0\\ 0&1&0&1&0&0\\ 0&0&1&0&1&0\\ 0&0&0&1&0&1\\ 1&0&0&0&1&0 \end{pmatrix},$$

$$\text{Class}(10) = \begin{pmatrix} 1&0&0&0&0&0\\ 0&1&0&0&0&0\\ 0&0&1&0&0&0\\ 0&0&0&1&0&0\\ 0&0&0&0&1&0\\ 0&0&0&0&0&1 \end{pmatrix}, \text{Class}(11) = \begin{pmatrix} 0&1&0&1&0&1\\ 1&0&1&0&1&0\\ 0&1&0&1&0&1\\ 1&0&1&0&1&0\\ 0&1&0&1&0&1\\ 1&0&1&0&1&0 \end{pmatrix}, \text{Class}(12) = \begin{pmatrix} 1&0&1&0&1&0\\ 0&1&0&1&0&1\\ 1&0&1&0&1&0\\ 0&1&0&1&0&1\\ 1&0&1&0&1&0\\ 0&1&0&1&0&1 \end{pmatrix}$$

$$^{(1)}\mathcal{P} = \begin{pmatrix} \frac{1}{6}&\frac{1}{6}&\frac{1}{6}&\frac{1}{6}&\frac{1}{6}&\frac{1}{6}\\ \frac{1}{6}&\frac{1}{6}&\frac{1}{6}&\frac{1}{6}&\frac{1}{6}&\frac{1}{6}\\ \frac{1}{6}&\frac{1}{6}&\frac{1}{6}&\frac{1}{6}&\frac{1}{6}&\frac{1}{6}\\ \frac{1}{6}&\frac{1}{6}&\frac{1}{6}&\frac{1}{6}&\frac{1}{6}&\frac{1}{6}\\ \frac{1}{6}&\frac{1}{6}&\frac{1}{6}&\frac{1}{6}&\frac{1}{6}&\frac{1}{6}\\ \frac{1}{6}&\frac{1}{6}&\frac{1}{6}&\frac{1}{6}&\frac{1}{6}&\frac{1}{6} \end{pmatrix}$$

$$\begin{cases} \text{Eigenvalues :} & 1, 0, 0, 0, 0, 0 \\ \text{Eigenvectors :} & \{1,1,1,1,1,1\}, \{-1,0,0,0,0,1\}, \{-1,0,0,0,1,0\}, \\ & \{-1,0,0,1,0,0\}, \{-1,0,1,0,0,0\}, \{-1,1,0,0,0,0\} \end{cases}$$

$$
{}^{(6)}\mathcal{P} = \begin{pmatrix}
\frac{1}{3} & -\frac{1}{6} & -\frac{1}{6} & \frac{1}{3} & -\frac{1}{6} & -\frac{1}{6} \\
-\frac{1}{6} & \frac{1}{3} & -\frac{1}{6} & -\frac{1}{6} & \frac{1}{3} & -\frac{1}{6} \\
-\frac{1}{6} & -\frac{1}{6} & \frac{1}{3} & -\frac{1}{6} & -\frac{1}{6} & \frac{1}{3} \\
\frac{1}{3} & -\frac{1}{6} & -\frac{1}{6} & \frac{1}{3} & -\frac{1}{6} & -\frac{1}{6} \\
-\frac{1}{6} & \frac{1}{3} & -\frac{1}{6} & -\frac{1}{6} & \frac{1}{3} & -\frac{1}{6} \\
-\frac{1}{6} & -\frac{1}{6} & \frac{1}{3} & -\frac{1}{6} & -\frac{1}{6} & \frac{1}{3}
\end{pmatrix}
$$

$$
\begin{cases}
\text{Eigenvalues :} & 1,1,0,0,0,0 \\
\text{Eigenvectors :} & \{-1,0,1,-1,0,1\},\{-1,1,0,-1,1,0\},\{1,1,0,0,0,1\}, \\
 & \{0,-1,0,0,1,0\},\{-1,0,0,1,0,0\},\{1,1,1,0,0,0\}
\end{cases}
$$

$$
{}^{(9)}\mathcal{P} = \begin{pmatrix}
\frac{1}{6} & -\frac{1}{6} & \frac{1}{6} & -\frac{1}{6} & \frac{1}{6} & -\frac{1}{6} \\
-\frac{1}{6} & \frac{1}{6} & -\frac{1}{6} & \frac{1}{6} & -\frac{1}{6} & \frac{1}{6} \\
\frac{1}{6} & -\frac{1}{6} & \frac{1}{6} & -\frac{1}{6} & \frac{1}{6} & -\frac{1}{6} \\
-\frac{1}{6} & \frac{1}{6} & -\frac{1}{6} & \frac{1}{6} & -\frac{1}{6} & \frac{1}{6} \\
\frac{1}{6} & -\frac{1}{6} & \frac{1}{6} & -\frac{1}{6} & \frac{1}{6} & -\frac{1}{6} \\
-\frac{1}{6} & \frac{1}{6} & -\frac{1}{6} & \frac{1}{6} & -\frac{1}{6} & \frac{1}{6}
\end{pmatrix}
$$

$$
\begin{cases}
\text{Eigenvalues :} & 1,0,0,0,0,0 \\
\text{Eigenvectors :} & \{-1,1,-1,1,-1,1\},\{1,0,0,0,0,1\},\{-1,0,0,0,1,0\}, \\
 & \{1,0,0,1,0,0\},\{-1,0,1,0,0,0\},\{1,1,0,0,0,0\}
\end{cases}
$$

$$
{}^{(11)}\mathcal{P} = \begin{pmatrix}
\frac{1}{3} & \frac{1}{6} & -\frac{1}{6} & -\frac{1}{3} & -\frac{1}{6} & \frac{1}{6} \\
\frac{1}{6} & \frac{1}{3} & \frac{1}{6} & -\frac{1}{6} & -\frac{1}{3} & -\frac{1}{6} \\
-\frac{1}{6} & \frac{1}{6} & \frac{1}{3} & \frac{1}{6} & -\frac{1}{6} & -\frac{1}{3} \\
-\frac{1}{3} & -\frac{1}{6} & \frac{1}{6} & \frac{1}{3} & \frac{1}{6} & -\frac{1}{6} \\
-\frac{1}{6} & -\frac{1}{3} & -\frac{1}{6} & \frac{1}{6} & \frac{1}{3} & \frac{1}{6} \\
\frac{1}{6} & -\frac{1}{6} & -\frac{1}{3} & -\frac{1}{6} & \frac{1}{6} & \frac{1}{3}
\end{pmatrix}
$$

$$
\begin{cases}
\text{Eigenvalues :} & 1,1,0,0,0,0 \\
\text{Eigenvectors :} & \{1,0,-1,-1,0,1\},\{-1,-1,0,1,1,0\},\{-1,1,0,0,0,1\}, \\
 & \{0,1,0,0,1,0\},\{1,0,0,1,0,0\},\{1,-1,1,0,0,0\}
\end{cases}
$$

The missing Irreps have null projection operators. The symmetry-adapted vectors for the s-orbitals are

$$
A_{1g}\left({}^{(1)}\Gamma\right) : \begin{bmatrix} 1 & 1 & 1 & 1 & 1 & 1 \end{bmatrix}
$$

$$
E_{2g}\left({}^{(6)}\Gamma\right) : \begin{bmatrix} -1 & 0 & 1 & -1 & 0 & 1 \\ -1 & 1 & 0 & -1 & 1 & 0 \end{bmatrix}
$$

$$B_{1u}\left({}^{(9)}\Gamma\right) : \begin{bmatrix} -1 & 1 & -1 & 1 & -1 & 1 \end{bmatrix}$$

$$E_{1u}\left({}^{(11)}\Gamma\right) : \begin{bmatrix} 1 & 0 & -1 & -1 & 0 & 1 \\ -1 & -1 & 0 & 1 & 1 & 0 \end{bmatrix}$$

Rep engendered by the p_z orbitals

$$\text{Ppz}(1) = \begin{pmatrix} 1&0&0&0&0&0\\0&1&0&0&0&0\\0&0&1&0&0&0\\0&0&0&1&0&0\\0&0&0&0&1&0\\0&0&0&0&0&1 \end{pmatrix}, \text{Ppz}(2) = \begin{pmatrix} 0&0&0&0&0&1\\1&0&0&0&0&0\\0&1&0&0&0&0\\0&0&1&0&0&0\\0&0&0&1&0&0\\0&0&0&0&1&0 \end{pmatrix}, \text{Ppz}(3) = \begin{pmatrix} -1&0&0&0&0&0\\0&0&0&0&0&-1\\0&0&0&0&-1&0\\0&0&0&-1&0&0\\0&0&-1&0&0&0\\0&-1&0&0&0&0 \end{pmatrix},$$

$$\text{Ppz}(4) = \begin{pmatrix} 0&0&0&-1&0&0\\0&0&0&0&-1&0\\0&0&0&0&0&-1\\-1&0&0&0&0&0\\0&-1&0&0&0&0\\0&0&-1&0&0&0 \end{pmatrix}, \text{Ppz}(5) = \begin{pmatrix} 0&0&0&0&1&0\\0&0&0&0&0&1\\1&0&0&0&0&0\\0&1&0&0&0&0\\0&0&1&0&0&0\\0&0&0&1&0&0 \end{pmatrix}, \text{Ppz}(6) = \begin{pmatrix} 0&0&0&0&0&-1\\0&0&0&0&-1&0\\0&0&0&-1&0&0\\0&0&-1&0&0&0\\0&-1&0&0&0&0\\-1&0&0&0&0&0 \end{pmatrix}$$

$$\text{Ppz}(7) = \begin{pmatrix} 0&0&-1&0&0&0\\0&0&0&-1&0&0\\0&0&0&0&-1&0\\0&0&0&0&0&-1\\-1&0&0&0&0&0\\0&-1&0&0&0&0 \end{pmatrix}, \text{Ppz}(8) = \begin{pmatrix} 0&0&0&1&0&0\\0&0&0&0&1&0\\0&0&0&0&0&1\\1&0&0&0&0&0\\0&1&0&0&0&0\\0&0&1&0&0&0 \end{pmatrix}, \text{Ppz}(9) = \begin{pmatrix} 0&0&0&0&-1&0\\0&0&0&-1&0&0\\0&0&-1&0&0&0\\0&-1&0&0&0&0\\-1&0&0&0&0&0\\0&0&0&0&0&-1 \end{pmatrix}$$

$$\text{Ppz}(10) = \begin{pmatrix} 0&-1&0&0&0&0\\0&0&-1&0&0&0\\0&0&0&-1&0&0\\0&0&0&0&-1&0\\0&0&0&0&0&-1\\-1&0&0&0&0&0 \end{pmatrix}, \text{Ppz}(11) = \begin{pmatrix} 0&0&1&0&0&0\\0&0&0&1&0&0\\0&0&0&0&1&0\\0&0&0&0&0&1\\1&0&0&0&0&0\\0&1&0&0&0&0 \end{pmatrix}, \text{Ppz}(12) = \begin{pmatrix} 0&0&0&-1&0&0\\0&0&-1&0&0&0\\0&-1&0&0&0&0\\-1&0&0&0&0&0\\0&0&0&0&0&-1\\0&0&0&0&-1&0 \end{pmatrix}$$

$$\text{Ppz}(13) = \begin{pmatrix} -1&0&0&0&0&0\\0&-1&0&0&0&0\\0&0&-1&0&0&0\\0&0&0&-1&0&0\\0&0&0&0&-1&0\\0&0&0&0&0&-1 \end{pmatrix}, \text{Ppz}(14) = \begin{pmatrix} 0&1&0&0&0&0\\0&0&1&0&0&0\\0&0&0&1&0&0\\0&0&0&0&1&0\\0&0&0&0&0&1\\1&0&0&0&0&0 \end{pmatrix}, \text{Ppz}(15) = \begin{pmatrix} 0&0&-1&0&0&0\\0&-1&0&0&0&0\\-1&0&0&0&0&0\\0&0&0&0&0&-1\\0&0&0&0&-1&0\\0&0&0&-1&0&0 \end{pmatrix}$$

$$\text{Ppz}(16) = \begin{pmatrix} 0&0&0&0&0&-1\\-1&0&0&0&0&0\\0&-1&0&0&0&0\\0&0&-1&0&0&0\\0&0&0&-1&0&0\\0&0&0&0&-1&0 \end{pmatrix}, \text{Ppz}(17) = \begin{pmatrix} 0&-1&0&0&0&0\\-1&0&0&0&0&0\\0&0&0&0&0&-1\\0&0&0&0&-1&0\\0&0&0&-1&0&0\\0&0&-1&0&0&0 \end{pmatrix}, \text{Ppz}(18) = \begin{pmatrix} 0&0&0&0&-1&0\\0&0&0&0&0&-1\\-1&0&0&0&0&0\\0&-1&0&0&0&0\\0&0&-1&0&0&0\\0&0&0&-1&0&0 \end{pmatrix}$$

$$\mathrm{Ppz}(19) = \begin{pmatrix} 0&0&0&1&0&0\\ 0&0&1&0&0&0\\ 0&1&0&0&0&0\\ 1&0&0&0&0&0\\ 0&0&0&0&0&1\\ 0&0&0&0&1&0 \end{pmatrix}, \quad \mathrm{Ppz}(20) = \begin{pmatrix} 0&0&0&0&1&0\\ 0&0&0&1&0&0\\ 0&0&1&0&0&0\\ 0&1&0&0&0&0\\ 1&0&0&0&0&0\\ 0&0&0&0&0&1 \end{pmatrix}, \quad \mathrm{Ppz}(21) = \begin{pmatrix} 0&0&0&0&0&1\\ 0&0&0&0&1&0\\ 0&0&0&1&0&0\\ 0&0&1&0&0&0\\ 0&1&0&0&0&0\\ 1&0&0&0&0&0 \end{pmatrix},$$

$$\mathrm{Ppz}(22) = \begin{pmatrix} 1&0&0&0&0&0\\ 0&0&0&0&0&1\\ 0&0&0&0&1&0\\ 0&0&0&1&0&0\\ 0&0&1&0&0&0\\ 0&1&0&0&0&0 \end{pmatrix}, \quad \mathrm{Ppz}(23) = \begin{pmatrix} 0&1&0&0&0&0\\ 1&0&0&0&0&0\\ 0&0&0&0&0&1\\ 0&0&0&0&1&0\\ 0&0&0&1&0&0\\ 0&0&1&0&0&0 \end{pmatrix}, \quad \mathrm{Ppz}(24) = \begin{pmatrix} 0&0&1&0&0&0\\ 0&1&0&0&0&0\\ 1&0&0&0&0&0\\ 0&0&0&0&0&1\\ 0&0&0&0&1&0\\ 0&0&0&1&0&0 \end{pmatrix}$$

The corresponding class matrices are

$$\mathrm{Clpz}(1) = \begin{pmatrix} 1&0&0&0&0&0\\ 0&1&0&0&0&0\\ 0&0&1&0&0&0\\ 0&0&0&1&0&0\\ 0&0&0&0&1&0\\ 0&0&0&0&0&1 \end{pmatrix}, \quad \mathrm{Clpz}(2) = \begin{pmatrix} 0&1&0&0&0&1\\ 1&0&1&0&0&0\\ 0&1&0&1&0&0\\ 0&0&1&0&1&0\\ 0&0&0&1&0&1\\ 1&0&0&0&1&0 \end{pmatrix}, \quad \mathrm{Clpz}(3) = \begin{pmatrix} 0&0&1&0&1&0\\ 0&0&0&1&0&1\\ 1&0&0&0&1&0\\ 0&1&0&0&0&1\\ 1&0&1&0&0&0\\ 0&1&0&1&0&0 \end{pmatrix},$$

$$\mathrm{Clpz}(4) = \begin{pmatrix} 0&0&0&1&0&0\\ 0&0&0&0&1&0\\ 0&0&0&0&0&1\\ 1&0&0&0&0&0\\ 0&1&0&0&0&0\\ 0&0&1&0&0&0 \end{pmatrix}, \mathrm{Clpz}(5) = \begin{pmatrix} -1&0&-1&0&-1&0\\ 0&-1&0&-1&0&-1\\ -1&0&-1&0&-1&0\\ 0&-1&0&-1&0&-1\\ -1&0&-1&0&-1&0\\ 0&-1&0&-1&0&-1 \end{pmatrix}, \quad \mathrm{Clpz}(6) = \begin{pmatrix} 0&-1&0&-1&0&-1\\ -1&0&-1&0&-1&0\\ 0&-1&0&-1&0&-1\\ -1&0&-1&0&-1&0\\ 0&-1&0&-1&0&-1\\ -1&0&-1&0&-1&0 \end{pmatrix},$$

$$\mathrm{Clpz}(7) = \begin{pmatrix} 0&0&0&-1&0&0\\ 0&0&0&0&-1&0\\ 0&0&0&0&0&-1\\ -1&0&0&0&0&0\\ 0&-1&0&0&0&0\\ 0&0&-1&0&0&0 \end{pmatrix}, \quad \mathrm{Clpz}(8) = \begin{pmatrix} 0&0&-1&0&-1&0\\ 0&0&0&-1&0&-1\\ -1&0&0&0&-1&0\\ 0&-1&0&0&0&-1\\ -1&0&-1&0&0&0\\ 0&-1&0&-1&0&0 \end{pmatrix}, \mathrm{Clpz}(9) = \begin{pmatrix} 0&-1&0&0&0&-1\\ -1&0&-1&0&0&0\\ 0&-1&0&-1&0&0\\ 0&0&-1&0&-1&0\\ 0&0&0&-1&0&-1\\ -1&0&0&0&-1&0 \end{pmatrix}$$

$$\mathrm{Clpz}(10) = \begin{pmatrix} -1&0&0&0&0&0\\ 0&-1&0&0&0&0\\ 0&0&-1&0&0&0\\ 0&0&0&-1&0&0\\ 0&0&0&0&-1&0\\ 0&0&0&0&0&-1 \end{pmatrix}, \quad \mathrm{Clpz}(11) = \begin{pmatrix} 0&1&0&1&0&1\\ 1&0&1&0&1&0\\ 0&1&0&1&0&1\\ 1&0&1&0&1&0\\ 0&1&0&1&0&1\\ 1&0&1&0&1&0 \end{pmatrix}, \quad \mathrm{Clpz}(12) = \begin{pmatrix} 1&0&1&0&1&0\\ 0&1&0&1&0&1\\ 1&0&1&0&1&0\\ 0&1&0&1&0&1\\ 1&0&1&0&1&0\\ 0&1&0&1&0&1 \end{pmatrix}$$

$$^{(4)}\mathcal{P} = \begin{pmatrix} \frac{1}{6}&-\frac{1}{6}&\frac{1}{6}&-\frac{1}{6}&\frac{1}{6}&-\frac{1}{6}\\ -\frac{1}{6}&\frac{1}{6}&-\frac{1}{6}&\frac{1}{6}&-\frac{1}{6}&\frac{1}{6}\\ \frac{1}{6}&-\frac{1}{6}&\frac{1}{6}&-\frac{1}{6}&\frac{1}{6}&-\frac{1}{6}\\ -\frac{1}{6}&\frac{1}{6}&-\frac{1}{6}&\frac{1}{6}&-\frac{1}{6}&\frac{1}{6}\\ \frac{1}{6}&-\frac{1}{6}&\frac{1}{6}&-\frac{1}{6}&\frac{1}{6}&-\frac{1}{6}\\ -\frac{1}{6}&\frac{1}{6}&-\frac{1}{6}&\frac{1}{6}&-\frac{1}{6}&\frac{1}{6} \end{pmatrix}$$

$$\begin{cases} \text{Eigenvalues :} & 1, 0, 0, 0, 0, 0 \\ \text{Eigenvectors :} & \{-1, 1, -1, 1, -1, 1\}, \{1, 0, 0, 0, 0, 1\}, \{-1, 0, 0, 0, 1, 0\}, \\ & \{1, 0, 0, 1, 0, 0\}, \{-1, 0, 1, 0, 0, 0\}, \{1, 1, 0, 0, 0, 0\} \end{cases}$$

$$^{(5)}\mathcal{P} = \begin{pmatrix} \frac{1}{3} & \frac{1}{6} & -\frac{1}{6} & -\frac{1}{3} & -\frac{1}{6} & \frac{1}{6} \\ \frac{1}{6} & \frac{1}{3} & \frac{1}{6} & -\frac{1}{6} & -\frac{1}{3} & -\frac{1}{6} \\ -\frac{1}{6} & \frac{1}{6} & \frac{1}{3} & \frac{1}{6} & -\frac{1}{6} & -\frac{1}{3} \\ -\frac{1}{3} & -\frac{1}{6} & \frac{1}{6} & \frac{1}{3} & \frac{1}{6} & -\frac{1}{6} \\ -\frac{1}{6} & -\frac{1}{3} & -\frac{1}{6} & \frac{1}{6} & \frac{1}{3} & \frac{1}{6} \\ \frac{1}{6} & -\frac{1}{6} & -\frac{1}{3} & -\frac{1}{6} & \frac{1}{6} & \frac{1}{3} \end{pmatrix}$$

$$\begin{cases} \text{Eigenvalues :} & 1, 1, 0, 0, 0, 0 \\ \text{Eigenvectors :} & \{1, 0, -1, -1, 0, 1\}, \{-1, -1, 0, 1, 1, 0\}, \{-1, 1, 0, 0, 0, 1\}, \\ & \{0, 1, 0, 0, 1, 0\}, \{1, 0, 0, 1, 0, 0\}, \{1, -1, 1, 0, 0, 0\} \end{cases}$$

$$^{(8)}\mathcal{P} = \begin{pmatrix} \frac{1}{6} & \frac{1}{6} & \frac{1}{6} & \frac{1}{6} & \frac{1}{6} & \frac{1}{6} \\ \frac{1}{6} & \frac{1}{6} & \frac{1}{6} & \frac{1}{6} & \frac{1}{6} & \frac{1}{6} \\ \frac{1}{6} & \frac{1}{6} & \frac{1}{6} & \frac{1}{6} & \frac{1}{6} & \frac{1}{6} \\ \frac{1}{6} & \frac{1}{6} & \frac{1}{6} & \frac{1}{6} & \frac{1}{6} & \frac{1}{6} \\ \frac{1}{6} & \frac{1}{6} & \frac{1}{6} & \frac{1}{6} & \frac{1}{6} & \frac{1}{6} \\ \frac{1}{6} & \frac{1}{6} & \frac{1}{6} & \frac{1}{6} & \frac{1}{6} & \frac{1}{6} \end{pmatrix}$$

$$\begin{cases} \text{Eigenvalues :} & 1, 0, 0, 0, 0, 0 \\ \text{Eigenvectors :} & \{1, 1, 1, 1, 1, 1\}, \{-1, 0, 0, 0, 0, 1\}, \{-1, 0, 0, 0, 1, 0\}, \\ & \{-1, 0, 0, 1, 0, 0\}, \{-1, 0, 1, 0, 0, 0\}, \{-1, 1, 0, 0, 0, 0\} \end{cases}$$

$$^{(12)}\mathcal{P} = \begin{pmatrix} \frac{1}{3} & -\frac{1}{6} & -\frac{1}{6} & \frac{1}{3} & -\frac{1}{6} & -\frac{1}{6} \\ -\frac{1}{6} & \frac{1}{3} & -\frac{1}{6} & -\frac{1}{6} & \frac{1}{3} & -\frac{1}{6} \\ -\frac{1}{6} & -\frac{1}{6} & \frac{1}{3} & -\frac{1}{6} & -\frac{1}{6} & \frac{1}{3} \\ \frac{1}{3} & -\frac{1}{6} & -\frac{1}{6} & \frac{1}{3} & -\frac{1}{6} & -\frac{1}{6} \\ -\frac{1}{6} & \frac{1}{3} & -\frac{1}{6} & -\frac{1}{6} & \frac{1}{3} & -\frac{1}{6} \\ -\frac{1}{6} & -\frac{1}{6} & \frac{1}{3} & -\frac{1}{6} & -\frac{1}{6} & \frac{1}{3} \end{pmatrix}$$

$$\begin{cases} \text{Eigenvalues :} & 1, 1, 0, 0, 0, 0 \\ \text{Eigenvectors :} & \{-1, 0, 1, -1, 0, 1\}, \{-1, 1, 0, -1, 1, 0\}, \{1, 1, 0, 0, 0, 1\}, \\ & \{0, -1, 0, 0, 1, 0\}, \{-1, 0, 0, 1, 0, 0\}, \{1, 1, 1, 0, 0, 0\} \end{cases}$$

The symmetry-adapted vectors are

$$B_{2g} : \begin{bmatrix} 1 & -1 & 1 & -1 & 1 & -1 \end{bmatrix}$$

$$E_{1g} : \begin{bmatrix} 1 & 0 & -1 & -1 & 0 & 1 \\ -1 & -1 & 0 & 1 & 1 & 0 \end{bmatrix}$$

$$A_{2u} : \begin{bmatrix} 1 & 1 & 1 & 1 & 1 & 1 \end{bmatrix}$$

$$E_{2u} : \begin{bmatrix} 1 & 0 & -1 & 1 & 0 & -1 \\ 1 & -1 & 0 & 1 & -1 & 0 \end{bmatrix}$$

Rep engendered by p_x, p_y:

$$\mathrm{Rxy}(1) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \ \mathrm{Rxy}(2) = \begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}, \ \mathrm{Rxy}(3) = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \ \mathrm{Rxy}(4) = \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$\mathrm{Rxy}(5) = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}, \ \mathrm{Rxy}(6) = \begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}, \ \mathrm{Rxy}(7) = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}, \ \mathrm{Rxy}(8) = \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$\mathrm{Rxy}(9) = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}, \ \mathrm{Rxy}(10) = \begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}, \ \mathrm{Rxy}(11) = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}, \ \mathrm{Rxy}(12) = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$$

$$\mathrm{Rxy}(13) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \ \mathrm{Rxy}(14) = \begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}, \ \mathrm{Rxy}(15) = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}, \ \mathrm{Rxy}(16) = \begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$$

$$\mathrm{Rxy}(17) = \begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}, \ \mathrm{Rxy}(18) = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}, \ \mathrm{Rxy}(19) = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}, \ \mathrm{Rxy}(20) = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$$

$$\mathrm{Rxy}(21) = \begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}, \ \mathrm{Rxy}(22) = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \ \mathrm{Rxy}(23) = \begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}, \ \mathrm{Rxy}(24) = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$$

The corresponding Rep engendered by the full set of p_x, p_y of the benzene molecule is

$$
\mathrm{Pxy}(1) = \begin{pmatrix}
1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1
\end{pmatrix},
$$

$$
\mathrm{Pxy}(2) = \begin{pmatrix}
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{2} & \frac{\sqrt{3}}{2} \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{\sqrt{3}}{2} & \frac{1}{2} \\
\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
-\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0
\end{pmatrix}
$$

$$
\mathrm{Pxy}(3) = \begin{pmatrix}
1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0
\end{pmatrix},
$$

$$
\mathrm{Pxy}(4) = \begin{pmatrix}
0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 \\
-1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0
\end{pmatrix}
$$

$$
\mathrm{Pxy}(5)=\begin{pmatrix}
0&0&0&0&0&0&0&0&-\frac{1}{2}&\frac{\sqrt{3}}{2}&0&0\\
0&0&0&0&0&0&0&0&-\frac{\sqrt{3}}{2}&-\frac{1}{2}&0&0\\
0&0&0&0&0&0&0&0&0&0&-\frac{1}{2}&\frac{\sqrt{3}}{2}\\
0&0&0&0&0&0&0&0&0&0&-\frac{\sqrt{3}}{2}&-\frac{1}{2}\\
-\frac{1}{2}&\frac{\sqrt{3}}{2}&0&0&0&0&0&0&0&0&0&0\\
-\frac{\sqrt{3}}{2}&-\frac{1}{2}&0&0&0&0&0&0&0&0&0&0\\
0&0&-\frac{1}{2}&\frac{\sqrt{3}}{2}&0&0&0&0&0&0&0&0\\
0&0&-\frac{\sqrt{3}}{2}&-\frac{1}{2}&0&0&0&0&0&0&0&0\\
0&0&0&0&-\frac{1}{2}&\frac{\sqrt{3}}{2}&0&0&0&0&0&0\\
0&0&0&0&-\frac{\sqrt{3}}{2}&-\frac{1}{2}&0&0&0&0&0&0\\
0&0&0&0&0&0&-\frac{1}{2}&\frac{\sqrt{3}}{2}&0&0&0&0\\
0&0&0&0&0&0&-\frac{\sqrt{3}}{2}&-\frac{1}{2}&0&0&0&0
\end{pmatrix},
$$

$$
\mathrm{Pxy}(6)=\begin{pmatrix}
0&0&\frac{1}{2}&-\frac{\sqrt{3}}{2}&0&0&0&0&0&0&0&0\\
0&0&-\frac{\sqrt{3}}{2}&-\frac{1}{2}&0&0&0&0&0&0&0&0\\
\frac{1}{2}&-\frac{\sqrt{3}}{2}&0&0&0&0&0&0&0&0&0&0\\
-\frac{\sqrt{3}}{2}&-\frac{1}{2}&0&0&0&0&0&0&0&0&0&0\\
0&0&0&0&0&0&0&0&0&0&\frac{1}{2}&-\frac{\sqrt{3}}{2}\\
0&0&0&0&0&0&0&0&0&0&-\frac{\sqrt{3}}{2}&-\frac{1}{2}\\
0&0&0&0&0&0&0&0&\frac{1}{2}&-\frac{\sqrt{3}}{2}&0&0\\
0&0&0&0&0&0&0&0&-\frac{\sqrt{3}}{2}&-\frac{1}{2}&0&0\\
0&0&0&0&0&0&\frac{1}{2}&-\frac{\sqrt{3}}{2}&0&0&0&0\\
0&0&0&0&0&0&-\frac{\sqrt{3}}{2}&-\frac{1}{2}&0&0&0&0\\
0&0&0&0&\frac{1}{2}&-\frac{\sqrt{3}}{2}&0&0&0&0&0&0\\
0&0&0&0&-\frac{\sqrt{3}}{2}&-\frac{1}{2}&0&0&0&0&0&0
\end{pmatrix}
$$

$$
\mathrm{Pxy}(7)=\begin{pmatrix}
0&0&0&0&-\frac{1}{2}&-\frac{\sqrt{3}}{2}&0&0&0&0&0&0\\
0&0&0&0&\frac{\sqrt{3}}{2}&-\frac{1}{2}&0&0&0&0&0&0\\
0&0&0&0&0&0&-\frac{1}{2}&-\frac{\sqrt{3}}{2}&0&0&0&0\\
0&0&0&0&0&0&\frac{\sqrt{3}}{2}&-\frac{1}{2}&0&0&0&0\\
0&0&0&0&0&0&0&0&-\frac{1}{2}&-\frac{\sqrt{3}}{2}&0&0\\
0&0&0&0&0&0&0&0&\frac{\sqrt{3}}{2}&-\frac{1}{2}&0&0\\
0&0&0&0&0&0&0&0&0&0&-\frac{1}{2}&-\frac{\sqrt{3}}{2}\\
0&0&0&0&0&0&0&0&0&0&\frac{\sqrt{3}}{2}&-\frac{1}{2}\\
-\frac{1}{2}&-\frac{\sqrt{3}}{2}&0&0&0&0&0&0&0&0&0&0\\
\frac{\sqrt{3}}{2}&-\frac{1}{2}&0&0&0&0&0&0&0&0&0&0\\
0&0&-\frac{1}{2}&-\frac{\sqrt{3}}{2}&0&0&0&0&0&0&0&0\\
0&0&\frac{\sqrt{3}}{2}&-\frac{1}{2}&0&0&0&0&0&0&0&0
\end{pmatrix},
$$

$$
\mathrm{Pxy}(8)=\begin{pmatrix}
0&0&0&0&0&0&-1&0&0&0&0&0\\
0&0&0&0&0&0&0&-1&0&0&0&0\\
0&0&0&0&0&0&0&0&-1&0&0&0\\
0&0&0&0&0&0&0&0&0&-1&0&0\\
0&0&0&0&0&0&0&0&0&0&-1&0\\
0&0&0&0&0&0&0&0&0&0&0&-1\\
-1&0&0&0&0&0&0&0&0&0&0&0\\
0&-1&0&0&0&0&0&0&0&0&0&0\\
0&0&-1&0&0&0&0&0&0&0&0&0\\
0&0&0&-1&0&0&0&0&0&0&0&0\\
0&0&0&0&-1&0&0&0&0&0&0&0\\
0&0&0&0&0&-1&0&0&0&0&0&0
\end{pmatrix}
$$

$$\mathrm{Pxy}(9) = \begin{pmatrix} 0 & 0 & 0 & 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{\sqrt{3}}{2} & \frac{1}{2} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 & 0 & 0 \end{pmatrix},$$

$$\mathrm{Pxy}(10) = \begin{pmatrix} 0 & 0 & \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{\sqrt{3}}{2} & \frac{1}{2} \\ \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$$

$$\mathrm{Pxy}(11) = \begin{pmatrix} 0 & 0 & 0 & 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} \\ -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix},$$

$$\mathrm{Pxy}(12) = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \end{pmatrix}$$

$$
\text{Pxy}(13) = \begin{pmatrix}
1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1
\end{pmatrix},
$$

$$
\text{Pxy}(14) = \begin{pmatrix}
0 & 0 & \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{2} & -\frac{\sqrt{3}}{2} \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{\sqrt{3}}{2} & \frac{1}{2} \\
\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0
\end{pmatrix}
$$

$$
\text{Pxy}(15) = \begin{pmatrix}
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
-\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{\sqrt{3}}{2} & \frac{1}{2}
\end{pmatrix},
$$

$$
\text{Pxy}(16) = \begin{pmatrix}
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{2} & \frac{\sqrt{3}}{2} \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{\sqrt{3}}{2} & \frac{1}{2} \\
\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
-\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0
\end{pmatrix}
$$

$$
\mathrm{Pxy}(17) = \begin{pmatrix}
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{2} & \frac{\sqrt{3}}{2} \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0
\end{pmatrix},
$$

$$
\mathrm{Pxy}(18) = \begin{pmatrix}
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} \\
-\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
-\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & 0 & 0
\end{pmatrix}
$$

$$
\mathrm{Pxy}(19) = \begin{pmatrix}
0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
-1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0
\end{pmatrix},
$$

$$
\mathrm{Pxy}(20) = \begin{pmatrix}
0 & 0 & 0 & 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
-\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
-\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{\sqrt{3}}{2} & \frac{1}{2} \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 & 0 & 0
\end{pmatrix}
$$

$$
\mathrm{Pxy}(21) = \begin{pmatrix}
0 & 0 & \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
-\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{2} & -\frac{\sqrt{3}}{2} \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0
\end{pmatrix},
$$

$$
\mathrm{Pxy}(22) = \begin{pmatrix}
1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0
\end{pmatrix}
$$

$$
\mathrm{Pxy}(23) = \begin{pmatrix}
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{2} & \frac{\sqrt{3}}{2} \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0
\end{pmatrix},
$$

$$
\mathrm{Pxy}(24) = \begin{pmatrix}
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
-\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{\sqrt{3}}{2} & \frac{1}{2}
\end{pmatrix}
$$

$$\mathrm{Clpxy}(1) = \begin{pmatrix} 1&0&0&0&0&0&0&0&0&0&0&0\\ 0&1&0&0&0&0&0&0&0&0&0&0\\ 0&0&1&0&0&0&0&0&0&0&0&0\\ 0&0&0&1&0&0&0&0&0&0&0&0\\ 0&0&0&0&1&0&0&0&0&0&0&0\\ 0&0&0&0&0&1&0&0&0&0&0&0\\ 0&0&0&0&0&0&1&0&0&0&0&0\\ 0&0&0&0&0&0&0&1&0&0&0&0\\ 0&0&0&0&0&0&0&0&1&0&0&0\\ 0&0&0&0&0&0&0&0&0&1&0&0\\ 0&0&0&0&0&0&0&0&0&0&1&0\\ 0&0&0&0&0&0&0&0&0&0&0&1 \end{pmatrix},$$

$$\mathrm{Clpxy}(2) = \begin{pmatrix} 0&0&\frac{1}{2}&-\frac{\sqrt{3}}{2}&0&0&0&0&0&0&\frac{1}{2}&\frac{\sqrt{3}}{2}\\ 0&0&\frac{\sqrt{3}}{2}&\frac{1}{2}&0&0&0&0&0&0&-\frac{\sqrt{3}}{2}&\frac{1}{2}\\ \frac{1}{2}&\frac{\sqrt{3}}{2}&0&0&\frac{1}{2}&-\frac{\sqrt{3}}{2}&0&0&0&0&0&0\\ -\frac{\sqrt{3}}{2}&\frac{1}{2}&0&0&\frac{\sqrt{3}}{2}&\frac{1}{2}&0&0&0&0&0&0\\ 0&0&\frac{1}{2}&\frac{\sqrt{3}}{2}&0&0&\frac{1}{2}&-\frac{\sqrt{3}}{2}&0&0&0&0\\ 0&0&-\frac{\sqrt{3}}{2}&\frac{1}{2}&0&0&\frac{\sqrt{3}}{2}&\frac{1}{2}&0&0&0&0\\ 0&0&0&0&\frac{1}{2}&\frac{\sqrt{3}}{2}&0&0&\frac{1}{2}&-\frac{\sqrt{3}}{2}&0&0\\ 0&0&0&0&-\frac{\sqrt{3}}{2}&\frac{1}{2}&0&0&\frac{\sqrt{3}}{2}&\frac{1}{2}&0&0\\ 0&0&0&0&0&0&\frac{1}{2}&\frac{\sqrt{3}}{2}&0&0&\frac{1}{2}&-\frac{\sqrt{3}}{2}\\ 0&0&0&0&0&0&-\frac{\sqrt{3}}{2}&\frac{1}{2}&0&0&\frac{\sqrt{3}}{2}&\frac{1}{2}\\ \frac{1}{2}&-\frac{\sqrt{3}}{2}&0&0&0&0&0&0&\frac{1}{2}&\frac{\sqrt{3}}{2}&0&0\\ \frac{\sqrt{3}}{2}&\frac{1}{2}&0&0&0&0&0&0&-\frac{\sqrt{3}}{2}&\frac{1}{2}&0&0 \end{pmatrix}$$

$$\mathrm{Clpxy}(3) = \begin{pmatrix} 0&0&0&0&-\frac{1}{2}&-\frac{\sqrt{3}}{2}&0&0&-\frac{1}{2}&\frac{\sqrt{3}}{2}&0&0\\ 0&0&0&0&\frac{\sqrt{3}}{2}&-\frac{1}{2}&0&0&-\frac{\sqrt{3}}{2}&-\frac{1}{2}&0&0\\ 0&0&0&0&0&0&-\frac{1}{2}&-\frac{\sqrt{3}}{2}&0&0&-\frac{1}{2}&\frac{\sqrt{3}}{2}\\ 0&0&0&0&0&0&\frac{\sqrt{3}}{2}&-\frac{1}{2}&0&0&-\frac{\sqrt{3}}{2}&-\frac{1}{2}\\ -\frac{1}{2}&\frac{\sqrt{3}}{2}&0&0&0&0&0&0&-\frac{1}{2}&-\frac{\sqrt{3}}{2}&0&0\\ -\frac{\sqrt{3}}{2}&-\frac{1}{2}&0&0&0&0&0&0&\frac{\sqrt{3}}{2}&-\frac{1}{2}&0&0\\ 0&0&-\frac{1}{2}&\frac{\sqrt{3}}{2}&0&0&0&0&0&0&-\frac{1}{2}&-\frac{\sqrt{3}}{2}\\ 0&0&-\frac{\sqrt{3}}{2}&-\frac{1}{2}&0&0&0&0&0&0&\frac{\sqrt{3}}{2}&-\frac{1}{2}\\ -\frac{1}{2}&-\frac{\sqrt{3}}{2}&0&0&-\frac{1}{2}&\frac{\sqrt{3}}{2}&0&0&0&0&0&0\\ \frac{\sqrt{3}}{2}&-\frac{1}{2}&0&0&-\frac{\sqrt{3}}{2}&-\frac{1}{2}&0&0&0&0&0&0\\ 0&0&-\frac{1}{2}&-\frac{\sqrt{3}}{2}&0&0&-\frac{1}{2}&\frac{\sqrt{3}}{2}&0&0&0&0\\ 0&0&\frac{\sqrt{3}}{2}&-\frac{1}{2}&0&0&-\frac{\sqrt{3}}{2}&-\frac{1}{2}&0&0&0&0 \end{pmatrix},$$

$$\mathrm{Clpxy}(4) = \begin{pmatrix} 0&0&0&0&0&0&-1&0&0&0&0&0\\ 0&0&0&0&0&0&0&-1&0&0&0&0\\ 0&0&0&0&0&0&0&0&-1&0&0&0\\ 0&0&0&0&0&0&0&0&0&-1&0&0\\ 0&0&0&0&0&0&0&0&0&0&-1&0\\ 0&0&0&0&0&0&0&0&0&0&0&-1\\ -1&0&0&0&0&0&0&0&0&0&0&0\\ 0&-1&0&0&0&0&0&0&0&0&0&0\\ 0&0&-1&0&0&0&0&0&0&0&0&0\\ 0&0&0&-1&0&0&0&0&0&0&0&0\\ 0&0&0&0&-1&0&0&0&0&0&0&0\\ 0&0&0&0&0&-1&0&0&0&0&0&0 \end{pmatrix}$$

$$\mathrm{Clpxy}(5) = \begin{pmatrix} 1 & 0 & 0 & 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 \\ 0 & -1 & 0 & 0 & -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 & \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 \\ 0 & 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 & 1 & 0 \\ 0 & 0 & -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 & \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 & 0 & -1 \\ -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 & 1 & 0 & 0 & 0 \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 & \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 & 1 & 0 & 0 & 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ 0 & 0 & \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 & 0 & -1 & 0 & 0 & -\frac{\sqrt{3}}{2} & \frac{1}{2} \\ -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 & 1 & 0 & 0 & 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 \\ \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 & 0 & -1 & 0 & 0 & -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ 0 & 0 & 0 & -1 & 0 & 0 & -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 & \frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix},$$

$$\mathrm{Clpxy}(6) = \begin{pmatrix} 0 & 0 & \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & -1 & 0 & 0 & 0 & \frac{1}{2} & \frac{\sqrt{3}}{2} \\ 0 & 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & 0 & 1 & 0 & 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} \\ \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & -1 & 0 & 0 & 0 & \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & 0 & 1 & 0 & 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 & 0 & \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 & \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ 0 & 0 & 0 & 1 & 0 & 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} \\ -1 & 0 & 0 & 0 & \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 & \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 \\ 0 & 1 & 0 & 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 \\ 0 & 0 & \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 & \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & -1 & 0 \\ 0 & 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & 0 & 1 \\ \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 & \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & -1 & 0 & 0 & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & 0 & 1 & 0 & 0 \end{pmatrix}$$

$$\mathrm{Clpxy}(7) = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 \\ -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix},$$

$$\mathrm{Clpxy}(8) = \begin{pmatrix} 0 & 0 & 0 & 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ 0 & 0 & 0 & 0 & 0 & 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} \\ -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 \\ 0 & 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ 0 & 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} \\ -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & 0 & 0 \end{pmatrix}$$

$$\mathrm{Clpxy}(9) = \begin{pmatrix}
0 & 0 & \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{2} & \frac{\sqrt{3}}{2} \\
0 & 0 & \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{\sqrt{3}}{2} & \frac{1}{2} \\
\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 & \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 & 0 \\
-\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 & \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 & \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 \\
0 & 0 & -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 & \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 & \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 \\
0 & 0 & 0 & 0 & -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 & \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 & \frac{1}{2} & -\frac{\sqrt{3}}{2} \\
0 & 0 & 0 & 0 & 0 & 0 & -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 & \frac{\sqrt{3}}{2} & \frac{1}{2} \\
\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 \\
\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0
\end{pmatrix},$$

$$\mathrm{Clpxy}(10) = \begin{pmatrix}
1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1
\end{pmatrix}$$

$$\mathrm{Clpxy}(11) = \begin{pmatrix}
0 & 0 & \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & -1 & 0 & 0 & 0 & \frac{1}{2} & \frac{\sqrt{3}}{2} \\
0 & 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & 0 & 1 & 0 & 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} \\
\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & -1 & 0 & 0 & 0 & \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 \\
-\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & 0 & 1 & 0 & 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 \\
0 & 0 & -1 & 0 & 0 & 0 & \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 & \frac{1}{2} & -\frac{\sqrt{3}}{2} \\
0 & 0 & 0 & 1 & 0 & 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} \\
-1 & 0 & 0 & 0 & \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 & \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 \\
0 & 1 & 0 & 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 \\
0 & 0 & \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 & \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & -1 & 0 \\
0 & 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & 0 & 1 \\
\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 & \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & -1 & 0 & 0 & 0 \\
\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & 0 & 1 & 0 & 0
\end{pmatrix},$$

$$\mathrm{Clpxy}(12) = \begin{pmatrix}
1 & 0 & 0 & 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 \\
0 & -1 & 0 & 0 & -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 & \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 \\
0 & 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 & 1 & 0 \\
0 & 0 & -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 & \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 & 0 & -1 \\
-\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 & 1 & 0 & 0 & 0 \\
-\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 & \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 & 0 & -1 & 0 & 0 \\
0 & 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 & 1 & 0 & 0 & 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\
0 & 0 & \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 & 0 & -1 & 0 & 0 & -\frac{\sqrt{3}}{2} & \frac{1}{2} \\
-\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 & 1 & 0 & 0 & 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 \\
\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 & 0 & -1 & 0 & 0 & -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} \\
0 & 0 & 0 & -1 & 0 & 0 & -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 & \frac{\sqrt{3}}{2} & \frac{1}{2}
\end{pmatrix}$$

$$
{}^{(1)}\mathcal{P} = \begin{pmatrix}
\frac{1}{6} & 0 & \frac{1}{12} & -\frac{1}{4\sqrt{3}} & -\frac{1}{12} & -\frac{1}{4\sqrt{3}} & -\frac{1}{6} & 0 & -\frac{1}{12} & \frac{1}{4\sqrt{3}} & \frac{1}{12} & \frac{1}{4\sqrt{3}} \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\frac{1}{12} & 0 & \frac{1}{24} & -\frac{1}{8\sqrt{3}} & -\frac{1}{24} & -\frac{1}{8\sqrt{3}} & -\frac{1}{12} & 0 & -\frac{1}{24} & \frac{1}{8\sqrt{3}} & \frac{1}{24} & \frac{1}{8\sqrt{3}} \\
-\frac{1}{4\sqrt{3}} & 0 & -\frac{1}{8\sqrt{3}} & \frac{1}{8} & \frac{1}{8\sqrt{3}} & \frac{1}{8} & \frac{1}{4\sqrt{3}} & 0 & \frac{1}{8\sqrt{3}} & -\frac{1}{8} & -\frac{1}{8\sqrt{3}} & -\frac{1}{8} \\
-\frac{1}{12} & 0 & -\frac{1}{24} & \frac{1}{8\sqrt{3}} & \frac{1}{24} & \frac{1}{8\sqrt{3}} & \frac{1}{12} & 0 & \frac{1}{24} & -\frac{1}{8\sqrt{3}} & -\frac{1}{24} & -\frac{1}{8\sqrt{3}} \\
-\frac{1}{4\sqrt{3}} & 0 & -\frac{1}{8\sqrt{3}} & \frac{1}{8} & \frac{1}{8\sqrt{3}} & \frac{1}{8} & \frac{1}{4\sqrt{3}} & 0 & \frac{1}{8\sqrt{3}} & -\frac{1}{8} & -\frac{1}{8\sqrt{3}} & -\frac{1}{8} \\
-\frac{1}{6} & 0 & -\frac{1}{12} & \frac{1}{4\sqrt{3}} & \frac{1}{12} & \frac{1}{4\sqrt{3}} & \frac{1}{6} & 0 & \frac{1}{12} & -\frac{1}{4\sqrt{3}} & -\frac{1}{12} & -\frac{1}{4\sqrt{3}} \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
-\frac{1}{12} & 0 & -\frac{1}{24} & \frac{1}{8\sqrt{3}} & \frac{1}{24} & \frac{1}{8\sqrt{3}} & \frac{1}{12} & 0 & \frac{1}{24} & -\frac{1}{8\sqrt{3}} & -\frac{1}{24} & -\frac{1}{8\sqrt{3}} \\
\frac{1}{4\sqrt{3}} & 0 & \frac{1}{8\sqrt{3}} & -\frac{1}{8} & -\frac{1}{8\sqrt{3}} & -\frac{1}{8} & -\frac{1}{4\sqrt{3}} & 0 & -\frac{1}{8\sqrt{3}} & \frac{1}{8} & \frac{1}{8\sqrt{3}} & \frac{1}{8} \\
\frac{1}{12} & 0 & \frac{1}{24} & -\frac{1}{8\sqrt{3}} & -\frac{1}{24} & -\frac{1}{8\sqrt{3}} & -\frac{1}{12} & 0 & -\frac{1}{24} & \frac{1}{8\sqrt{3}} & \frac{1}{24} & \frac{1}{8\sqrt{3}} \\
\frac{1}{4\sqrt{3}} & 0 & \frac{1}{8\sqrt{3}} & -\frac{1}{8} & -\frac{1}{8\sqrt{3}} & -\frac{1}{8} & -\frac{1}{4\sqrt{3}} & 0 & -\frac{1}{8\sqrt{3}} & \frac{1}{8} & \frac{1}{8\sqrt{3}} & \frac{1}{8}
\end{pmatrix}
$$

$$
\begin{cases}
\text{Eigenvalues :} & 1,0,0,0,0,0,0,0,0,0,0,0 \\
\text{Eigenvectors :} & \left\{\frac{2}{\sqrt{3}},0,\frac{1}{\sqrt{3}},-1,-\frac{1}{\sqrt{3}},-1,-\frac{2}{\sqrt{3}},0,-\frac{1}{\sqrt{3}},1,\frac{1}{\sqrt{3}},1\right\}, \left\{-\frac{\sqrt{3}}{2},0,0,0,0,0,0,0,0,0,0,1\right\}, \\
& \left\{-\frac{1}{2},0,0,0,0,0,0,0,0,0,1,0\right\}, \left\{-\frac{\sqrt{3}}{2},0,0,0,0,0,0,0,0,1,0,0\right\}, \\
& \left\{\frac{1}{2},0,0,0,0,0,0,0,1,0,0,0\right\}, \{0,0,0,0,0,0,0,1,0,0,0,0\}, \\
& \{1,0,0,0,0,0,1,0,0,0,0,0\}, \left\{\frac{\sqrt{3}}{2},0,0,0,0,1,0,0,0,0,0,0\right\}, \\
& \left\{\frac{1}{2},0,0,0,1,0,0,0,0,0,0,0\right\}, \left\{\frac{\sqrt{3}}{2},0,0,1,0,0,0,0,0,0,0,0\right\}, \\
& \left\{-\frac{1}{2},0,1,0,0,0,0,0,0,0,0,0\right\}, \{0,1,0,0,0,0,0,0,0,0,0,0\}
\end{cases}
$$

$$
{}^{(2)}\mathcal{P} = \begin{pmatrix}
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & \frac{1}{6} & \frac{1}{4\sqrt{3}} & \frac{1}{12} & \frac{1}{4\sqrt{3}} & -\frac{1}{12} & 0 & -\frac{1}{6} & -\frac{1}{4\sqrt{3}} & -\frac{1}{12} & -\frac{1}{4\sqrt{3}} & \frac{1}{12} \\
0 & \frac{1}{4\sqrt{3}} & \frac{1}{8} & \frac{1}{8\sqrt{3}} & \frac{1}{8} & -\frac{1}{8\sqrt{3}} & 0 & -\frac{1}{4\sqrt{3}} & -\frac{1}{8} & -\frac{1}{8\sqrt{3}} & -\frac{1}{8} & \frac{1}{8\sqrt{3}} \\
0 & \frac{1}{12} & \frac{1}{8\sqrt{3}} & \frac{1}{24} & \frac{1}{8\sqrt{3}} & -\frac{1}{24} & 0 & -\frac{1}{12} & -\frac{1}{8\sqrt{3}} & -\frac{1}{24} & -\frac{1}{8\sqrt{3}} & \frac{1}{24} \\
0 & \frac{1}{4\sqrt{3}} & \frac{1}{8} & \frac{1}{8\sqrt{3}} & \frac{1}{8} & -\frac{1}{8\sqrt{3}} & 0 & -\frac{1}{4\sqrt{3}} & -\frac{1}{8} & -\frac{1}{8\sqrt{3}} & -\frac{1}{8} & \frac{1}{8\sqrt{3}} \\
0 & -\frac{1}{12} & -\frac{1}{8\sqrt{3}} & -\frac{1}{24} & -\frac{1}{8\sqrt{3}} & \frac{1}{24} & 0 & \frac{1}{12} & \frac{1}{8\sqrt{3}} & \frac{1}{24} & \frac{1}{8\sqrt{3}} & -\frac{1}{24} \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & -\frac{1}{6} & -\frac{1}{4\sqrt{3}} & -\frac{1}{12} & -\frac{1}{4\sqrt{3}} & \frac{1}{12} & 0 & \frac{1}{6} & \frac{1}{4\sqrt{3}} & \frac{1}{12} & \frac{1}{4\sqrt{3}} & -\frac{1}{12} \\
0 & -\frac{1}{4\sqrt{3}} & -\frac{1}{8} & -\frac{1}{8\sqrt{3}} & -\frac{1}{8} & \frac{1}{8\sqrt{3}} & 0 & \frac{1}{4\sqrt{3}} & \frac{1}{8} & \frac{1}{8\sqrt{3}} & \frac{1}{8} & -\frac{1}{8\sqrt{3}} \\
0 & -\frac{1}{12} & -\frac{1}{8\sqrt{3}} & -\frac{1}{24} & -\frac{1}{8\sqrt{3}} & \frac{1}{24} & 0 & \frac{1}{12} & \frac{1}{8\sqrt{3}} & \frac{1}{24} & \frac{1}{8\sqrt{3}} & -\frac{1}{24} \\
0 & -\frac{1}{4\sqrt{3}} & -\frac{1}{8} & -\frac{1}{8\sqrt{3}} & -\frac{1}{8} & \frac{1}{8\sqrt{3}} & 0 & \frac{1}{4\sqrt{3}} & \frac{1}{8} & \frac{1}{8\sqrt{3}} & \frac{1}{8} & -\frac{1}{8\sqrt{3}} \\
0 & \frac{1}{12} & \frac{1}{8\sqrt{3}} & \frac{1}{24} & \frac{1}{8\sqrt{3}} & -\frac{1}{24} & 0 & -\frac{1}{12} & -\frac{1}{8\sqrt{3}} & -\frac{1}{24} & -\frac{1}{8\sqrt{3}} & \frac{1}{24}
\end{pmatrix}
$$

$$
\begin{cases}
\text{Eigenvalues :} & 1,0,0,0,0,0,0,0,0,0,0,0 \\
\text{Eigenvectors :} & \left\{0,2,\sqrt{3},1,\sqrt{3},-1,0,-2,-\sqrt{3},-1,-\sqrt{3},1\right\}, \left\{0,-\frac{1}{2},0,0,0,0,0,0,0,0,0,1\right\}, \\
& \left\{0,\frac{\sqrt{3}}{2},0,0,0,0,0,0,0,0,1,0\right\}, \left\{0,\frac{1}{2},0,0,0,0,0,0,0,1,0,0\right\}, \\
& \left\{0,\frac{\sqrt{3}}{2},0,0,0,0,0,0,1,0,0,0\right\}, \{0,1,0,0,0,0,0,1,0,0,0,0\}, \\
& \{0,0,0,0,0,0,1,0,0,0,0,0\}, \left\{0,\frac{1}{2},0,0,0,1,0,0,0,0,0,0\right\}, \\
& \left\{0,-\frac{\sqrt{3}}{2},0,0,1,0,0,0,0,0,0,0\right\}, \left\{0,-\frac{1}{2},0,1,0,0,0,0,0,0,0,0\right\}, \\
& \left\{0,-\frac{\sqrt{3}}{2},1,0,0,0,0,0,0,0,0,0\right\}, \{1,0,0,0,0,0,0,0,0,0,0,0\}
\end{cases}
$$

$$
{}^{(6)}\mathcal{P} = \begin{pmatrix}
\frac{1}{3} & 0 & -\frac{1}{12} & \frac{1}{4\sqrt{3}} & \frac{1}{12} & \frac{1}{4\sqrt{3}} & -\frac{1}{3} & 0 & \frac{1}{12} & -\frac{1}{4\sqrt{3}} & -\frac{1}{12} & -\frac{1}{4\sqrt{3}} \\
0 & \frac{1}{3} & -\frac{1}{4\sqrt{3}} & -\frac{1}{12} & -\frac{1}{4\sqrt{3}} & \frac{1}{12} & 0 & -\frac{1}{3} & \frac{1}{4\sqrt{3}} & \frac{1}{12} & \frac{1}{4\sqrt{3}} & -\frac{1}{12} \\
-\frac{1}{12} & -\frac{1}{4\sqrt{3}} & \frac{1}{3} & 0 & -\frac{1}{12} & \frac{1}{4\sqrt{3}} & \frac{1}{12} & \frac{1}{4\sqrt{3}} & -\frac{1}{3} & 0 & \frac{1}{12} & -\frac{1}{4\sqrt{3}} \\
\frac{1}{4\sqrt{3}} & -\frac{1}{12} & 0 & \frac{1}{3} & -\frac{1}{4\sqrt{3}} & -\frac{1}{12} & -\frac{1}{4\sqrt{3}} & \frac{1}{12} & 0 & -\frac{1}{3} & \frac{1}{4\sqrt{3}} & \frac{1}{12} \\
\frac{1}{12} & -\frac{1}{4\sqrt{3}} & -\frac{1}{12} & -\frac{1}{4\sqrt{3}} & \frac{1}{3} & 0 & -\frac{1}{12} & \frac{1}{4\sqrt{3}} & \frac{1}{12} & \frac{1}{4\sqrt{3}} & -\frac{1}{3} & 0 \\
\frac{1}{4\sqrt{3}} & \frac{1}{12} & \frac{1}{4\sqrt{3}} & -\frac{1}{12} & 0 & \frac{1}{3} & -\frac{1}{4\sqrt{3}} & -\frac{1}{12} & -\frac{1}{4\sqrt{3}} & \frac{1}{12} & 0 & -\frac{1}{3} \\
-\frac{1}{3} & 0 & \frac{1}{12} & -\frac{1}{4\sqrt{3}} & -\frac{1}{12} & -\frac{1}{4\sqrt{3}} & \frac{1}{3} & 0 & -\frac{1}{12} & \frac{1}{4\sqrt{3}} & \frac{1}{12} & \frac{1}{4\sqrt{3}} \\
0 & -\frac{1}{3} & \frac{1}{4\sqrt{3}} & \frac{1}{12} & \frac{1}{4\sqrt{3}} & -\frac{1}{12} & 0 & \frac{1}{3} & -\frac{1}{4\sqrt{3}} & -\frac{1}{12} & -\frac{1}{4\sqrt{3}} & \frac{1}{12} \\
\frac{1}{12} & \frac{1}{4\sqrt{3}} & -\frac{1}{3} & 0 & \frac{1}{12} & -\frac{1}{4\sqrt{3}} & -\frac{1}{12} & -\frac{1}{4\sqrt{3}} & \frac{1}{3} & 0 & -\frac{1}{12} & \frac{1}{4\sqrt{3}} \\
-\frac{1}{4\sqrt{3}} & \frac{1}{12} & 0 & -\frac{1}{3} & \frac{1}{4\sqrt{3}} & \frac{1}{12} & \frac{1}{4\sqrt{3}} & -\frac{1}{12} & 0 & \frac{1}{3} & -\frac{1}{4\sqrt{3}} & -\frac{1}{12} \\
-\frac{1}{12} & \frac{1}{4\sqrt{3}} & \frac{1}{12} & \frac{1}{4\sqrt{3}} & -\frac{1}{3} & 0 & \frac{1}{12} & -\frac{1}{4\sqrt{3}} & -\frac{1}{12} & -\frac{1}{4\sqrt{3}} & \frac{1}{3} & 0 \\
-\frac{1}{4\sqrt{3}} & -\frac{1}{12} & -\frac{1}{4\sqrt{3}} & \frac{1}{12} & 0 & -\frac{1}{3} & \frac{1}{4\sqrt{3}} & \frac{1}{12} & \frac{1}{4\sqrt{3}} & -\frac{1}{12} & 0 & \frac{1}{3}
\end{pmatrix}
$$

$$
\begin{cases}
\text{Eigenvalues :} & 1,1,1,1,0,0,0,0,0,0,0,0 \\
\text{Eigenvectors :} & \left\{-\frac{\sqrt{3}}{2},-\frac{1}{2},0,0,0,-1,\frac{\sqrt{3}}{2},\frac{1}{2},0,0,0,1\right\}, \left\{-\frac{1}{2},\frac{\sqrt{3}}{2},0,0,-1,0,\frac{1}{2},-\frac{\sqrt{3}}{2},0,0,1,0\right\}, \\
& \left\{-\frac{\sqrt{3}}{2},\frac{1}{2},0,-1,0,0,\frac{\sqrt{3}}{2},-\frac{1}{2},0,1,0,0\right\}, \left\{\frac{1}{2},\frac{\sqrt{3}}{2},-1,0,0,0,-\frac{1}{2},-\frac{\sqrt{3}}{2},1,0,0,0\right\}, \\
& \left\{\frac{\sqrt{3}}{2},\frac{1}{2},\frac{\sqrt{3}}{2},-\frac{1}{2},0,0,0,0,0,0,0,1\right\}, \left\{\frac{1}{2},-\frac{\sqrt{3}}{2},-\frac{1}{2},-\frac{\sqrt{3}}{2},0,0,0,0,0,0,1,0\right\}, \\
& \{0,0,0,1,0,0,0,0,0,1,0,0\}, \{0,0,1,0,0,0,0,0,1,0,0,0\}, \\
& \{0,1,0,0,0,0,0,1,0,0,0,0\}, \{1,0,0,0,0,0,1,0,0,0,0,0\}, \\
& \left\{-\frac{\sqrt{3}}{2},-\frac{1}{2},-\frac{\sqrt{3}}{2},\frac{1}{2},0,1,0,0,0,0,0,0\right\}, \left\{-\frac{1}{2},\frac{\sqrt{3}}{2},\frac{1}{2},\frac{\sqrt{3}}{2},1,0,0,0,0,0,0,0\right\}
\end{cases}
$$

$$
{}^{(9)}\mathcal{P} = \begin{pmatrix}
\frac{1}{6} & 0 & -\frac{1}{12} & \frac{1}{4\sqrt{3}} & -\frac{1}{12} & -\frac{1}{4\sqrt{3}} & \frac{1}{6} & 0 & -\frac{1}{12} & \frac{1}{4\sqrt{3}} & -\frac{1}{12} & -\frac{1}{4\sqrt{3}} \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
-\frac{1}{12} & 0 & \frac{1}{24} & -\frac{1}{8\sqrt{3}} & \frac{1}{24} & \frac{1}{8\sqrt{3}} & -\frac{1}{12} & 0 & \frac{1}{24} & -\frac{1}{8\sqrt{3}} & \frac{1}{24} & \frac{1}{8\sqrt{3}} \\
\frac{1}{4\sqrt{3}} & 0 & -\frac{1}{8\sqrt{3}} & \frac{1}{8} & -\frac{1}{8\sqrt{3}} & -\frac{1}{8} & \frac{1}{4\sqrt{3}} & 0 & -\frac{1}{8\sqrt{3}} & \frac{1}{8} & -\frac{1}{8\sqrt{3}} & -\frac{1}{8} \\
-\frac{1}{12} & 0 & \frac{1}{24} & -\frac{1}{8\sqrt{3}} & \frac{1}{24} & \frac{1}{8\sqrt{3}} & -\frac{1}{12} & 0 & \frac{1}{24} & -\frac{1}{8\sqrt{3}} & \frac{1}{24} & \frac{1}{8\sqrt{3}} \\
-\frac{1}{4\sqrt{3}} & 0 & \frac{1}{8\sqrt{3}} & -\frac{1}{8} & \frac{1}{8\sqrt{3}} & \frac{1}{8} & -\frac{1}{4\sqrt{3}} & 0 & \frac{1}{8\sqrt{3}} & -\frac{1}{8} & \frac{1}{8\sqrt{3}} & \frac{1}{8} \\
\frac{1}{6} & 0 & -\frac{1}{12} & \frac{1}{4\sqrt{3}} & -\frac{1}{12} & -\frac{1}{4\sqrt{3}} & \frac{1}{6} & 0 & -\frac{1}{12} & \frac{1}{4\sqrt{3}} & -\frac{1}{12} & -\frac{1}{4\sqrt{3}} \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
-\frac{1}{12} & 0 & \frac{1}{24} & -\frac{1}{8\sqrt{3}} & \frac{1}{24} & \frac{1}{8\sqrt{3}} & -\frac{1}{12} & 0 & \frac{1}{24} & -\frac{1}{8\sqrt{3}} & \frac{1}{24} & \frac{1}{8\sqrt{3}} \\
\frac{1}{4\sqrt{3}} & 0 & -\frac{1}{8\sqrt{3}} & \frac{1}{8} & -\frac{1}{8\sqrt{3}} & -\frac{1}{8} & \frac{1}{4\sqrt{3}} & 0 & -\frac{1}{8\sqrt{3}} & \frac{1}{8} & -\frac{1}{8\sqrt{3}} & -\frac{1}{8} \\
-\frac{1}{12} & 0 & \frac{1}{24} & -\frac{1}{8\sqrt{3}} & \frac{1}{24} & \frac{1}{8\sqrt{3}} & -\frac{1}{12} & 0 & \frac{1}{24} & -\frac{1}{8\sqrt{3}} & \frac{1}{24} & \frac{1}{8\sqrt{3}} \\
-\frac{1}{4\sqrt{3}} & 0 & \frac{1}{8\sqrt{3}} & -\frac{1}{8} & \frac{1}{8\sqrt{3}} & \frac{1}{8} & -\frac{1}{4\sqrt{3}} & 0 & \frac{1}{8\sqrt{3}} & -\frac{1}{8} & \frac{1}{8\sqrt{3}} & \frac{1}{8}
\end{pmatrix}
$$

$$
\begin{cases}
\text{Eigenvalues :} & 1,0,0,0,0,0,0,0,0,0,0,0 \\
\text{Eigenvectors :} & \left\{-\frac{2}{\sqrt{3}},0,\frac{1}{\sqrt{3}},-1,\frac{1}{\sqrt{3}},1,-\frac{2}{\sqrt{3}},0,\frac{1}{\sqrt{3}},-1,\frac{1}{\sqrt{3}},1\right\}, \left\{\frac{\sqrt{3}}{2},0,0,0,0,0,0,0,0,0,0,1\right\}, \\
& \left\{\frac{1}{2},0,0,0,0,0,0,0,0,0,1,0\right\}, \left\{-\frac{\sqrt{3}}{2},0,0,0,0,0,0,0,0,1,0,0\right\}, \\
& \left\{\frac{1}{2},0,0,0,0,0,0,0,1,0,0,0\right\}, \{0,0,0,0,0,0,0,1,0,0,0,0\}, \\
& \{-1,0,0,0,0,0,1,0,0,0,0,0\}, \left\{\frac{\sqrt{3}}{2},0,0,0,0,1,0,0,0,0,0,0\right\}, \\
& \left\{\frac{1}{2},0,0,0,1,0,0,0,0,0,0,0\right\}, \left\{-\frac{\sqrt{3}}{2},0,0,1,0,0,0,0,0,0,0,0\right\}, \\
& \left\{\frac{1}{2},0,1,0,0,0,0,0,0,0,0,0\right\}, \{0,1,0,0,0,0,0,0,0,0,0,0\}
\end{cases}
$$

$$
{}^{(10)}\mathcal{P} = \begin{pmatrix}
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & \frac{1}{6} & -\frac{1}{4\sqrt{3}} & -\frac{1}{12} & \frac{1}{4\sqrt{3}} & -\frac{1}{12} & 0 & \frac{1}{6} & -\frac{1}{4\sqrt{3}} & -\frac{1}{12} & \frac{1}{4\sqrt{3}} & -\frac{1}{12} \\
0 & -\frac{1}{4\sqrt{3}} & \frac{1}{8} & \frac{1}{8\sqrt{3}} & -\frac{1}{8} & \frac{1}{8\sqrt{3}} & 0 & -\frac{1}{4\sqrt{3}} & \frac{1}{8} & \frac{1}{8\sqrt{3}} & -\frac{1}{8} & \frac{1}{8\sqrt{3}} \\
0 & -\frac{1}{12} & \frac{1}{8\sqrt{3}} & \frac{1}{24} & -\frac{1}{8\sqrt{3}} & \frac{1}{24} & 0 & -\frac{1}{12} & \frac{1}{8\sqrt{3}} & \frac{1}{24} & -\frac{1}{8\sqrt{3}} & \frac{1}{24} \\
0 & \frac{1}{4\sqrt{3}} & -\frac{1}{8} & -\frac{1}{8\sqrt{3}} & \frac{1}{8} & -\frac{1}{8\sqrt{3}} & 0 & \frac{1}{4\sqrt{3}} & -\frac{1}{8} & -\frac{1}{8\sqrt{3}} & \frac{1}{8} & -\frac{1}{8\sqrt{3}} \\
0 & -\frac{1}{12} & \frac{1}{8\sqrt{3}} & \frac{1}{24} & -\frac{1}{8\sqrt{3}} & \frac{1}{24} & 0 & -\frac{1}{12} & \frac{1}{8\sqrt{3}} & \frac{1}{24} & -\frac{1}{8\sqrt{3}} & \frac{1}{24} \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & \frac{1}{6} & -\frac{1}{4\sqrt{3}} & -\frac{1}{12} & \frac{1}{4\sqrt{3}} & -\frac{1}{12} & 0 & \frac{1}{6} & -\frac{1}{4\sqrt{3}} & -\frac{1}{12} & \frac{1}{4\sqrt{3}} & -\frac{1}{12} \\
0 & -\frac{1}{4\sqrt{3}} & \frac{1}{8} & \frac{1}{8\sqrt{3}} & -\frac{1}{8} & \frac{1}{8\sqrt{3}} & 0 & -\frac{1}{4\sqrt{3}} & \frac{1}{8} & \frac{1}{8\sqrt{3}} & -\frac{1}{8} & \frac{1}{8\sqrt{3}} \\
0 & -\frac{1}{12} & \frac{1}{8\sqrt{3}} & \frac{1}{24} & -\frac{1}{8\sqrt{3}} & \frac{1}{24} & 0 & -\frac{1}{12} & \frac{1}{8\sqrt{3}} & \frac{1}{24} & -\frac{1}{8\sqrt{3}} & \frac{1}{24} \\
0 & \frac{1}{4\sqrt{3}} & -\frac{1}{8} & -\frac{1}{8\sqrt{3}} & \frac{1}{8} & -\frac{1}{8\sqrt{3}} & 0 & \frac{1}{4\sqrt{3}} & -\frac{1}{8} & -\frac{1}{8\sqrt{3}} & \frac{1}{8} & -\frac{1}{8\sqrt{3}} \\
0 & -\frac{1}{12} & \frac{1}{8\sqrt{3}} & \frac{1}{24} & -\frac{1}{8\sqrt{3}} & \frac{1}{24} & 0 & -\frac{1}{12} & \frac{1}{8\sqrt{3}} & \frac{1}{24} & -\frac{1}{8\sqrt{3}} & \frac{1}{24}
\end{pmatrix}
$$

$$
\begin{cases}
\text{Eigenvalues :} & 1,0,0,0,0,0,0,0,0,0,0,0 \\
\text{Eigenvectors :} & \left\{0,-2,\sqrt{3},1,-\sqrt{3},1,0,-2,\sqrt{3},1,-\sqrt{3},1\right\}, \left\{0,\frac{1}{2},0,0,0,0,0,0,0,0,0,1\right\}, \\
& \left\{0,-\frac{\sqrt{3}}{2},0,0,0,0,0,0,0,0,1,0\right\}, \left\{0,\frac{1}{2},0,0,0,0,0,0,0,1,0,0\right\}, \\
& \left\{0,\frac{\sqrt{3}}{2},0,0,0,0,0,0,1,0,0,0\right\}, \{0,-1,0,0,0,0,0,1,0,0,0,0\}, \\
& \{0,0,0,0,0,0,1,0,0,0,0,0\}, \left\{0,\frac{1}{2},0,0,0,1,0,0,0,0,0,0\right\}, \\
& \left\{0,-\frac{\sqrt{3}}{2},0,0,1,0,0,0,0,0,0,0\right\}, \left\{0,\frac{1}{2},0,1,0,0,0,0,0,0,0,0\right\}, \\
& \left\{0,\frac{\sqrt{3}}{2},1,0,0,0,0,0,0,0,0,0\right\}, \{1,0,0,0,0,0,0,0,0,0,0,0\}
\end{cases}
$$

$$
{}^{(11)}\mathcal{P} = \begin{pmatrix}
\frac{1}{3} & 0 & \frac{1}{12} & -\frac{1}{4\sqrt{3}} & \frac{1}{12} & \frac{1}{4\sqrt{3}} & \frac{1}{3} & 0 & \frac{1}{12} & -\frac{1}{4\sqrt{3}} & \frac{1}{12} & \frac{1}{4\sqrt{3}} \\
0 & \frac{1}{3} & \frac{1}{4\sqrt{3}} & \frac{1}{12} & -\frac{1}{4\sqrt{3}} & \frac{1}{12} & 0 & \frac{1}{3} & \frac{1}{4\sqrt{3}} & \frac{1}{12} & -\frac{1}{4\sqrt{3}} & \frac{1}{12} \\
\frac{1}{12} & \frac{1}{4\sqrt{3}} & \frac{1}{3} & 0 & \frac{1}{12} & -\frac{1}{4\sqrt{3}} & \frac{1}{12} & \frac{1}{4\sqrt{3}} & \frac{1}{3} & 0 & \frac{1}{12} & -\frac{1}{4\sqrt{3}} \\
-\frac{1}{4\sqrt{3}} & \frac{1}{12} & 0 & \frac{1}{3} & \frac{1}{4\sqrt{3}} & \frac{1}{12} & -\frac{1}{4\sqrt{3}} & \frac{1}{12} & 0 & \frac{1}{3} & \frac{1}{4\sqrt{3}} & \frac{1}{12} \\
\frac{1}{12} & -\frac{1}{4\sqrt{3}} & \frac{1}{12} & \frac{1}{4\sqrt{3}} & \frac{1}{3} & 0 & \frac{1}{12} & -\frac{1}{4\sqrt{3}} & \frac{1}{12} & \frac{1}{4\sqrt{3}} & \frac{1}{3} & 0 \\
\frac{1}{4\sqrt{3}} & \frac{1}{12} & -\frac{1}{4\sqrt{3}} & \frac{1}{12} & 0 & \frac{1}{3} & \frac{1}{4\sqrt{3}} & \frac{1}{12} & -\frac{1}{4\sqrt{3}} & \frac{1}{12} & 0 & \frac{1}{3} \\
\frac{1}{3} & 0 & \frac{1}{12} & -\frac{1}{4\sqrt{3}} & \frac{1}{12} & \frac{1}{4\sqrt{3}} & \frac{1}{3} & 0 & \frac{1}{12} & -\frac{1}{4\sqrt{3}} & \frac{1}{12} & \frac{1}{4\sqrt{3}} \\
0 & \frac{1}{3} & \frac{1}{4\sqrt{3}} & \frac{1}{12} & -\frac{1}{4\sqrt{3}} & \frac{1}{12} & 0 & \frac{1}{3} & \frac{1}{4\sqrt{3}} & \frac{1}{12} & -\frac{1}{4\sqrt{3}} & \frac{1}{12} \\
\frac{1}{12} & \frac{1}{4\sqrt{3}} & \frac{1}{3} & 0 & \frac{1}{12} & -\frac{1}{4\sqrt{3}} & \frac{1}{12} & \frac{1}{4\sqrt{3}} & \frac{1}{3} & 0 & \frac{1}{12} & -\frac{1}{4\sqrt{3}} \\
-\frac{1}{4\sqrt{3}} & \frac{1}{12} & 0 & \frac{1}{3} & \frac{1}{4\sqrt{3}} & \frac{1}{12} & -\frac{1}{4\sqrt{3}} & \frac{1}{12} & 0 & \frac{1}{3} & \frac{1}{4\sqrt{3}} & \frac{1}{12} \\
\frac{1}{12} & -\frac{1}{4\sqrt{3}} & \frac{1}{12} & \frac{1}{4\sqrt{3}} & \frac{1}{3} & 0 & \frac{1}{12} & -\frac{1}{4\sqrt{3}} & \frac{1}{12} & \frac{1}{4\sqrt{3}} & \frac{1}{3} & 0 \\
\frac{1}{4\sqrt{3}} & \frac{1}{12} & -\frac{1}{4\sqrt{3}} & \frac{1}{12} & 0 & \frac{1}{3} & \frac{1}{4\sqrt{3}} & \frac{1}{12} & -\frac{1}{4\sqrt{3}} & \frac{1}{12} & 0 & \frac{1}{3}
\end{pmatrix}
$$

$$
\begin{cases}
\text{Eigenvalues :} & 1,1,1,1,0,0,0,0,0,0,0,0 \\
\text{Eigenvectors :} & \left\{\frac{\sqrt{3}}{2},\frac{1}{2},0,0,0,1,\frac{\sqrt{3}}{2},\frac{1}{2},0,0,0,1\right\}, \left\{\frac{1}{2},-\frac{\sqrt{3}}{2},0,0,1,0,\frac{1}{2},-\frac{\sqrt{3}}{2},0,0,1,0\right\}, \\
& \left\{-\frac{\sqrt{3}}{2},\frac{1}{2},0,1,0,0,-\frac{\sqrt{3}}{2},\frac{1}{2},0,1,0,0\right\}, \left\{\frac{1}{2},\frac{\sqrt{3}}{2},1,0,0,0,\frac{1}{2},\frac{\sqrt{3}}{2},1,0,0,0\right\}, \\
& \left\{-\frac{\sqrt{3}}{2},-\frac{1}{2},\frac{\sqrt{3}}{2},-\frac{1}{2},0,0,0,0,0,0,0,1\right\}, \left\{-\frac{1}{2},\frac{\sqrt{3}}{2},-\frac{1}{2},-\frac{\sqrt{3}}{2},0,0,0,0,0,0,1,0\right\}, \\
& \{0,0,0,-1,0,0,0,0,0,1,0,0\}, \{0,0,-1,0,0,0,0,0,1,0,0,0\}, \\
& \{0,-1,0,0,0,0,0,1,0,0,0,0\}, \{-1,0,0,0,0,0,1,0,0,0,0,0\}, \\
& \left\{-\frac{\sqrt{3}}{2},-\frac{1}{2},\frac{\sqrt{3}}{2},-\frac{1}{2},0,1,0,0,0,0,0,0\right\}, \left\{-\frac{1}{2},\frac{\sqrt{3}}{2},-\frac{1}{2},-\frac{\sqrt{3}}{2},1,0,0,0,0,0,0,0\right\}
\end{cases}
$$

The missing Irreps have null projection operators. The symmetry-adapted vectors for the p_x, p_y-orbitals are

$$
\begin{array}{lc}
p & \begin{array}{cccccccccccc} x_1 & y_1 & x_2 & y_2 & x_3 & y_3 & x_4 & y_4 & x_5 & y_5 & x_6 & y_6 \end{array} \\
A_{1\mathrm{g}}\left({}^{(1)}\Gamma\right): & \left[\begin{array}{cccccccccccc} 2 & 0 & 1 & -\sqrt{3} & -1 & -\sqrt{3} & -2 & 0 & -1 & \sqrt{3} & 1 & \sqrt{3} \end{array}\right] \\
A_{2\mathrm{g}}\left({}^{(2)}\Gamma\right): & \left[\begin{array}{cccccccccccc} 0 & 2 & \sqrt{3} & 1 & \sqrt{3} & -1 & 0 & -2 & -\sqrt{3} & -1 & -\sqrt{3} & 1 \end{array}\right] \\
E_{2\mathrm{g}}\left({}^{(6)}\Gamma\right): & \begin{bmatrix} -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & 0 & -1 & \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 & 0 & 1 \\ -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 & -1 & 0 & \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & 1 & 0 \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & -1 & 0 & 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 1 & 0 & 0 \\ \frac{1}{2} & \frac{\sqrt{3}}{2} & -1 & 0 & 0 & 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 1 & 0 & 0 & 0 \end{bmatrix} \\
B_{1\mathrm{u}}\left({}^{(9)}\Gamma\right): & \left[\begin{array}{cccccccccccc} -2 & 0 & 1 & -\sqrt{3} & 1 & \sqrt{3} & -2 & 0 & 1 & -\sqrt{3} & 1 & \sqrt{3} \end{array}\right] \\
B_{2\mathrm{u}}\left({}^{(10)}\Gamma\right): & \left[\begin{array}{cccccccccccc} 0 & -2 & \sqrt{3} & 1 & -\sqrt{3} & 1 & 0 & -2 & \sqrt{3} & 1 & -\sqrt{3} & 1 \end{array}\right] \\
E_{2\mathrm{u}}\left({}^{(11)}\Gamma\right): & \begin{bmatrix} \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 & 0 & 1 & \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 & 0 & 1 \\ \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & 1 & 0 & \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & 1 & 0 \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 1 & 0 & 0 & -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 1 & 0 & 0 \\ \frac{1}{2} & \frac{\sqrt{3}}{2} & 1 & 0 & 0 & 0 & \frac{1}{2} & \frac{\sqrt{3}}{2} & 1 & 0 & 0 & 0 \end{bmatrix}
\end{array}
$$

Table 6.5. Character Table for $\mathcal{D}_{6h}$

		E	$2C_6$	$2C_3$	C_2	$3U$	$3U_d$	I	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$
A_{1g}	${}^{(1)}\Gamma$	1	1	1	1	1	1	1	1	1	1	1	1
A_{2g}	${}^{(2)}\Gamma$	1	1	1	1	-1	-1	1	1	1	1	-1	-1
B_{1g}	${}^{(3)}\Gamma$	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1
B_{2g}	${}^{(4)}\Gamma$	1	-1	1	-1	-1	1	1	-1	1	-1	-1	1
E_{1g}	${}^{(5)}\Gamma$	2	1	-1	-2	0	0	2	1	-1	-2	0	0
E_{2g}	${}^{(6)}\Gamma$	2	-1	-1	2	0	0	2	-1	-1	2	0	0
A_{1u}	${}^{(7)}\Gamma$	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1
A_{2u}	${}^{(8)}\Gamma$	1	1	1	1	-1	-1	-1	-1	-1	-1	1	1
B_{1u}	${}^{(9)}\Gamma$	1	-1	1	-1	1	-1	-1	1	-1	1	-1	1
B_{2u}	${}^{(10)}\Gamma$	1	-1	1	-1	-1	1	-1	1	-1	1	1	-1
E_{1u}	${}^{(11)}\Gamma$	2	1	-1	-2	0	0	-2	-1	1	2	0	0
E_{2u}	${}^{(12)}\Gamma$	2	-1	-1	2	0	0	-2	1	1	-2	0	0

7
Construction of the irreducible representations

7.1 Exercises

7.1 In chapter 2 or 3 it was found that the matrix

$$S = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ i & -i \end{pmatrix}$$

diagonalized the matrix $\hat{C}_3^2$. Use the inverse process to "undiagonalize" the set of six matrices found in example 7.2 and show that this similarity transformation produces a set of six matrices that form an Irrep of the group $C_{3\mathrm{v}}$ which differs from (2.3) only in having opposite signs for the elements of the matrices $\sigma_1,\ \sigma_2,\ \sigma_3$.

7.2 Solutions

4.1

8

Product groups and product representations

8.1 Exercises

8.1 Show that if $\mathcal{H}_2 \subset \mathcal{H}_1 \subset \mathcal{G}$, and $\mathcal{H}_2 \lhd \mathcal{G}$ is an invariant subgroup of $\mathcal{G}$, then it is also an invariant subgroup of $\mathcal{H}_2$, i.e. $\mathcal{H}_2 \lhd \mathcal{H}_1$. If $\mathcal{H}_1$ is the largest invariant subgroup of $\mathcal{G}$, i.e. maximal in $\mathcal{G}$, it is called the **normalizer** of $\mathcal{H}_2$ in $\mathcal{G}$.

8.2 Show that the converse of problem 1 does not necessarily hold, and give an example where it is not true.

8.3 Prove that the number of pairs of inequivalent conjugate Irreps of a finite group is equal to the number of pairs of reciprocal classes.

8.4 Determine the subgroups of $\mathcal{D}_4$, and identify the invariant ones. Derive the factor groups of its invariant subgroups.

8.5 Determine the subgroups of the symmetric group $\mathcal{S}_4$, and identify the invariant subgroups among them. Derive the corresponding factor groups.

8.6 Construct the character table of $\mathcal{D}_{4h}$ from that of $\mathcal{D}_4$.

8.7 Generalize the previous problem for the point-groups $\mathcal{D}_{nh}$ and $\mathcal{C}_{nh}$.

8.8 **Subduction of representations**

Consider the vector Irrep of $\mathcal{O}(3)$, namely ${}^{(j=1)}\Gamma^{-}$.

(i) Now select among the infinitely uncountable set of operators those that correspond to $\mathcal{C}_{4v}$, which comprise 4- and 2-fold rotations about the z-axis, the two reflections planes xz and yz, and in the two vertical diagonal reflection planes intersecting with the xy plane through the lines $x = y$ and $x = -y$, respectively.

(ii) Show that this set of matrices forms a group isomorphic to $\mathcal{C}_{4v}$, i.e. they form a faithful representation of $\mathcal{C}_{4v}$.

(iii) Decompose this representation in terms of the Irreps of $\mathcal{C}_{4v}$, and obtain the corresponding reduction coefficients $\left\langle {}^{(j=1)}\Gamma^- \,\middle|\, {}^{(i)}\Gamma \right\rangle$.

This procedure is known as *subduction*, and will discussed in the following chapter.

8.9 **Symmetrization of a second-rank tensor**

Consider a second-rank tensor associated with a 3-dimensional system with $\mathcal{C}_{4v}$ symmetry. Use the fact that the $\mathcal{O}(3)$ Irrep of the tensor is given by ${}^{(j=1)}\Gamma^- \otimes {}^{(j=1)}\Gamma^-$, and obtain its CG-series in terms of the Irreps of $\mathcal{C}_{4v}$.

8.10 What would be the outcome of the second-rank tensor symmetrization had the symmetry of the system been $\mathcal{D}_4$ rather than $\mathcal{C}_{4v}$?

8.11 Repeat the symmetrization of the second-rank tensor if the symmetry of the system is $\mathcal{C}_{3\mathrm{v}}$.

8.12 Consider the tetrahedral point-group $23\,(\mathcal{T})$, which contains 4-axis 3-fold oerations $\{C_3^i, C_3^{-1,i}\}$, $i = 1-4$, and 3 2-fold axes, U^i bisecting opposite edges of the tetrahedron.

(i) Show that it has one invariant subgroup, and determine the corresponding factor group.
(ii) Show that $23\,(\mathcal{T})$ can be constructed from the outer-product of the invariant subgroup with its factor group.
(iii) Construct its character table with the help of the above results.

8.13 Consider the self-direct-product of the 3-dimensional Irrep T of $23\,(\mathcal{T})$, with generators

$$C_3^{xyz} = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}; \quad C_2^z = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

23 has the character table

(i) Determine the CG series.
(ii) Determine the CGCs.

8.14 Derive the steps that lead to CGCs given in Example 8.17 for the Irreps ${}^{(2)}\Gamma$ and ${}^{(3)}\Gamma$ of $\mathcal{C}_{3\mathrm{v}}$.

8.15 Derive the results given in Example 8.18 for the CGCs $\left(\begin{array}{c|c} 55 & \sigma \\ ik & 1 \end{array} \right)$, $\sigma = 1, 2, 3, 4$, of $\mathcal{C}_{4v}$.

8.2 Solutions

8.1 A normal subgroup $\mathcal{H}_2$ of $\mathcal{G}$ satisfies the condition

$$R\,\mathcal{H}_2\,R^{-1} = \mathcal{H}_2, \quad \forall\, R \in \mathcal{G}$$

By definition, all the elements of the subgroup $\mathcal{H}_1$ are also elements of $\mathcal{G}$, hence

$$S\,\mathcal{H}_2\,S^{-1} = \mathcal{H}_2, \quad \forall\, S \in \mathcal{H}_1$$

which is the condition that $\mathcal{H}_2 \lhd \mathcal{H}_1$.

8.2 Here the normal subgroup $\mathcal{H}_2$ of $\mathcal{H}_1$ satisfies the condition

$$S\,\mathcal{H}_2\,S^{-1} = \mathcal{H}_2, \quad \forall\, S \in \mathcal{H}_1$$

But, it does not necessarily satisfy the condition

$$R\,\mathcal{H}_2\,R^{-1} = \mathcal{H}_2, \quad \forall\, R \in \mathcal{G}$$

since not every R is to be found in $\mathcal{H}_1$. The group $\mathcal{T}$ contains the subgroup $\mathcal{D}_2$ which is invariant in $\mathcal{T}$; it is comprised of E and three two-fold rotations. $\mathcal{D}_2$ contains three invariant subgroups, each comprised of E and one two-fold rotations, however, these subgroups are not invariant in $\mathcal{T}$.

8.4 We write the elements of $\mathcal{D}_4$ as E, C_4, C_4^{-1}, C_2, U_x, U_y, U_{xy}, $U_{barx\bar{y}}$. $\mathcal{D}_4$ is of order 8; hence, it has subgroups of index 2 and 4:

$$\text{Subgroups of index 2}: \begin{cases} \mathcal{C}_4: & E,\, C_4,\, C_2,\, C_4^{-1} \\ \mathcal{D}_2: & E,\, C_2,\, U_x,\, U_y \\ \mathcal{D}_2^{\mathrm{d}}: & E,\, C_2,\, U_{xy},\, U_{\bar{x}\bar{y}} \end{cases} \quad [4pt]\text{Subgroups of index 4}: \begin{cases} \mathcal{C}_2: & E,\, C_2 \\ \mathcal{C}_2: & E,\, U_x \\ \mathcal{C}_2: & E,\, U_y \\ \mathcal{C}_2: & E,\, U_{xy} \\ \mathcal{C}_2: & E,\, U_{\bar{x}\bar{y}} \end{cases}$$

All subgroups of index 2 are normal subgroups with factor groups

$$\frac{\mathcal{D}_4}{\mathcal{C}_4} = \mathcal{C}_4,\, U_x\,\mathcal{C}_4$$
$$\frac{\mathcal{D}_4}{\mathcal{D}_2} = \mathcal{D}_2,\, U_x\,\mathcal{D}_2$$
$$\frac{\mathcal{D}_4}{\mathcal{D}_2^{\mathrm{d}}} = \mathcal{D}_2^{\mathrm{d}},\, C_4\,\mathcal{D}_2^{\mathrm{d}}$$

are

8.5 We write the elements of $\mathcal{S}_4$ as

(1)(2)(3)(4), (12), (13), (14), (23), (24), (34), (12)(34), (13)(24), (14)(23), (123), (124),

(132), (134), (142), (143), (234), (243), (1234), (1243), (1324), (1342), (1423), (1432)

$\mathcal{S}_4$ is of order 24, thus, it has subgroups of index 2, 3, 4, 6, 8, and 12.

Subgroups of index 2 :$\mathcal{T}$: (1)(2)(3)(4), (12)(34), (13)(24), (14)(23), (123), (124), (132), (134), (142), (143), (234), (243)

Subgroups of index 3 :$\mathcal{T}$: (1)(2)(3)(4), (1234), (1432), (13)(24), (13), (12)(34), (24), (14)(23)

Subgroups of index 4 :4 subgroups isomorphic to $\mathcal{S}_3$, groups of permutations of 3 of the 4 objects

Subgroups of index 6 : $\begin{cases} \text{3 subgroups isomorphic to the cyclic group } \mathcal{C}_4 \\ \mathcal{V}_4 = (1)(2)(3)(4),\ (12)(34),\ (13)(24),\ (14)(23) \end{cases}$

8.6 The character table of $\mathcal{D}_4$ is

Table 8.1. *Character table of* $\mathcal{D}_4$

	E	C_4	C_2	U	U_d
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
B_1	1	-1	1	1	-1
B_2	1	-1	1	-1	1
E	2	0	-2	0	0

Since

$$\mathcal{D}_{4\mathrm{h}} = \mathcal{D}_4 \otimes \mathcal{C}_{\mathrm{i}}$$

and $\mathcal{C}_s$ has the character table we obtain the character table of as

Table 8.2. *Character table of* $\mathcal{C}_{\mathrm{i}}$

	E	I
$^{(+)}\Gamma$	1	1
$^{(-)}\Gamma$	1	-1

Table 8.3. *Character table of* $\mathcal{D}_{4\mathrm{h}}$

	E	C_4	C_2	U	U_d	I	S_4	σ_h	σ	σ_d
A_{1g}	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1
E_g	2	0	-2	0	0	2	0	-2	0	0
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1
E_u	2	0	-2	0	0	-2	0	2	0	0

8.7 For n even, the order of the group is $g = 2n$ we set $n = 2\ell$; then we have:

(i) An n-fold rotation axis, with the n rotations falling into $\ell + 1$ classes: $\{E\}$, $\{C_2\}$, $\{C_n, C_n^{-1}\}$, $\{C_n^2, C_n^{-2}\}$, ...

(ii) For the $\mathcal{D}_{\mathrm{nh}}$ groups, we have n 2-fold rotation axes lying in a plane perpendicular to the n-fold axis, U-axes. They are divided into two classes: one class is comprised of the U axes that pass through the apices of an n-polygon and the second class of the perpendicular bisectors of the polygon edges.

(iii) The generating relations are

$$C_n^n = U^2 = E, C_nU = UC_n^{-1}$$

For the $\mathcal{C}_{\mathrm{nh}}$ groups, we replace the n 2-fold axes by n σ_v reflection planes.

In all, we have $\ell + 3$ classes.

Both group types have the cyclic group $\mathcal{C}_n$ as an invariant subgroup with index 2; its factor group is isomorphic with $\mathcal{C}_i$. $\mathcal{C}_n$ has n 1-dimensional Irreps of the form

$$^{(m)}\Gamma(C_n) = e^{-i2m\pi/n}, \quad 0 \leq m \leq n-1$$

Thus, if define a basis function $^{(m)}\eta$ for Irrep m, we can construct a 2-dimensional Irrep by defining a partner basis function $^{(m)}\zeta = U\,^{(m)}\eta$ and obtain

$$U\,^{(m)}\zeta = {}^{(m)}\eta,\ ^{(m)}\eta = {}^{(m)}\zeta,\ C_n\,^{(m)}\zeta = UC_n^{-1}\,^{(m)}\eta = e^{i2m\pi/n}\,^{(m)}\zeta$$

Thus we engender the 2-dimensional Irrep of $\mathcal{D}_\mathrm{n}$

$$ {}^{(m)}E(C_n) \;=\; \begin{pmatrix} e^{-i2m\pi/n} & 0 \\ 0 & e^{i2m\pi/n} \end{pmatrix}, \; {}^{(m)}E(U) \;=\; \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} $$

There are $\ell - 1$ such Irreps defined with $1 \le m \le \ell - 1$; the 2-dimensional Reps engendered from $m > \ell - 1$ are either equivalent or reducible.

This leaves us with four 1-dimensional Irreps. We construct the Irreps A_1 and A_2 using the Irrep ${}^{(0)}\Gamma$ of $\mathcal{C}_\mathrm{n}$ and the two Irreps of the factor group $\mathcal{C}_i$, namely

$$ \begin{aligned} A_1(C_n) \;&=\; A_1(U) \;= 1 \\ A_2(C_n) \;&=\; 1, \; A_2(U) \;=\; -1 \end{aligned} $$

To construct the remaining two Irreps we use the invariant subgroup

$$ \mathcal{C}_\ell \;=\; E,\, C_n^2,\, C_n^4,\, C_n^6,\, \ldots,\, C_n^{n-2} $$

with index 4. Its factor group is isomorphic with $\mathcal{D}_2$, with cosets

$$ \mathcal{C}_\ell,\, C_n\,\mathcal{C}_\ell,\, U\,\mathcal{C}_\ell,\, U_d\,\mathcal{C}_\ell $$

Its has the four 1-dimensional Irreps shown in Table 8.4.

Table 8.4. *Character table of the factor group*

	E	C_n	U	U_d
${}^{(1)}\Gamma(A_1)$	1	1	1	1
${}^{(2)}\Gamma(A_2)$	1	1	-1	-1
${}^{(3)}\Gamma(B_1)$	1	-1	1	-1
${}^{(4)}\Gamma(B_2)$	1	-1	-1	1

It is clear from Table 8.4 that the first two Irreps will just induce A_1 and A_2 we have just constructed, but with B_1 and B_2 we can induce the remaining Irreps as

$$ \begin{aligned} B_1(C_{2i}) \;&=\; B_1(U) \;= 1,\; B_1(C_{2i+1}) = B_1(U_d) \;= -1, \\ B_1(C_{2i}) \;&=\; B_1(U_d) \;= 1,\; B_1(C_{2i+1}) = B_1(U) \;= -1, \end{aligned} $$

The Irreps of $\mathcal{D}_\mathrm{nh}$ can then be constructed using the Irreps of $\mathcal{C}_i$ given in Table 8.2.

8.8 (i) The subduced Rep is

$$E = \begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix}, C_4 = \begin{pmatrix}0&-1&0\\1&0&0\\0&0&1\end{pmatrix}, C_4^{-1} = \begin{pmatrix}0&1&0\\-1&0&0\\0&0&1\end{pmatrix}, C_2 = \begin{pmatrix}-1&0&0\\0&-1&0\\0&0&1\end{pmatrix},$$

$$\sigma_x = \begin{pmatrix}-1&0&0\\0&1&0\\0&0&1\end{pmatrix}, \sigma_y = \begin{pmatrix}1&0&0\\0&-1&0\\0&0&1\end{pmatrix}, \sigma_{xy} = \begin{pmatrix}0&1&0\\1&0&0\\0&0&1\end{pmatrix}, \sigma_{x\bar{y}} = \begin{pmatrix}0&-1&0\\-1&0&0\\0&0&1\end{pmatrix}$$

(ii) Matrix multiplication can be used to show that the subduced Rep is faithful

(iii) Examination of the matrices of (i) reveals that they all have the same block-diagonal form, and that we can decompose these matrices into

$$^{(1)}\Gamma(A_1):\; E = 1,\, C_4 = 1,\, C_4^{-1} = 1,\, C_2 = 1,\, \sigma_x = 1,\, \sigma_y = 1,\, \sigma_{xy} = 1,\, \sigma_{x\bar{y}} = 1$$

$$^{(5)}\Gamma(E):\; \begin{pmatrix}1&0\\0&1\end{pmatrix}, C_4 = \begin{pmatrix}0&-1\\1&0\end{pmatrix}, C_4^{-1} = \begin{pmatrix}0&1\\-1&0\end{pmatrix}, C_2 = \begin{pmatrix}-1&0\\0&-1\end{pmatrix},$$

$$\sigma_x = \begin{pmatrix}-1&0\\0&1\end{pmatrix}, \sigma_y = \begin{pmatrix}1&0\\0&-1\end{pmatrix}, \sigma_{xy} = \begin{pmatrix}0&1\\1&0\end{pmatrix}, \sigma_{x\bar{y}} = \begin{pmatrix}0&-1\\-1&0\end{pmatrix}$$

8.9 We learned from problem 8.8 that the vector Rep

$$^{(j=1)}\Gamma^- \downarrow \mathcal{C}_{4\mathrm{v}} = {}^{(1)}\Gamma(A_1) \oplus {}^{(5)}\Gamma(E)$$

Thus,

$$\begin{aligned} ^{(j=1)}\Gamma^- \otimes {}^{(j=1)}\Gamma^- &= \left({}^{(1)}\Gamma(A_1) \oplus {}^{(5)}\Gamma(E)\right) \otimes \left({}^{(1)}\Gamma(A_1) \oplus {}^{(5)}\Gamma(E)\right) \\ &= 2\,{}^{(1)}\Gamma(A_1) \oplus {}^{(2)}\Gamma(A_2) \oplus {}^{(3)}\Gamma(B_1) \oplus {}^{(4)}\Gamma(B_2) \oplus 2\,{}^{(5)}\Gamma(E) \end{aligned}$$

where we have used Chapter 8 Table 8.4.

8.10 Since $\mathcal{D}_4$ is isomorphic with $\mathcal{C}_{4\mathrm{v}}$ they should have the same CG series.

8.11 The subduced Rep is

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

$$\sigma_1 = \begin{pmatrix}-1&0&0\\0&1&0\\0&0&1\end{pmatrix}, \sigma_2 = \begin{pmatrix}-1/2&-\frac{\sqrt{3}}{2}&0\\-\frac{\sqrt{3}}{2}&1/2&0\\0&0&1\end{pmatrix}, \sigma_3 = \begin{pmatrix}-1/2&\frac{\sqrt{3}}{2}&0\\\frac{\sqrt{3}}{2}&1/2&0\\0&0&1\end{pmatrix}$$

$$^{(j=1)}\Gamma^- \downarrow \mathcal{C}_{3\mathrm{v}} = {}^{(1)}\Gamma(A_1) \oplus {}^{(3)}\Gamma(E)$$

and using Table 8.2 of Chapter 8, we get

$$^{(j=1)}\Gamma^{-} \otimes {}^{(j=1)}\Gamma^{-} = 2\,{}^{(1)}\Gamma(A_1) \oplus {}^{(2)}\Gamma(A_2) \oplus 3\,{}^{(3)}\Gamma(E)$$

8.12 Group Permutations:

$$\{\{1,2,3,4\},\{2,1,4,3\},\{3,2,1,4\},\{4,3,2,1\},\{2,3,1,4\},\{3,2,4,1\},$$
$$\{1,4,2,3\},\{4,1,3,2\},\{3,1,2,4\},\{4,2,1,3\},\{1,3,4,2\},\{2,4,3,1\},$$

Rotation Matrices of Group Elements:

$$\begin{matrix}\mathrm{R}(1)\\ E\end{matrix} = \begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix},\quad \begin{matrix}\mathrm{R}(2)\\ U_z\end{matrix} = \begin{pmatrix}-1&0&0\\0&-1&0\\0&0&1\end{pmatrix},\quad \begin{matrix}\mathrm{R}(3)\\ U_x\end{matrix} = \begin{pmatrix}1&0&0\\0&-1&0\\0&0&-1\end{pmatrix},\quad \begin{matrix}\mathrm{R}(4)\\ U_y\end{matrix} = \begin{pmatrix}-1&0&0\\0&1&0\\0&0&-1\end{pmatrix},$$

$$\begin{matrix}\mathrm{R}(5)\\ C_3^{xyz}\end{matrix} = \begin{pmatrix}0&0&1\\1&0&0\\0&1&0\end{pmatrix},\quad \begin{matrix}\mathrm{R}(6)\\ C_3^{\bar{x}yz}\end{matrix} = \begin{pmatrix}0&0&-1\\-1&0&0\\0&1&0\end{pmatrix},\quad \begin{matrix}\mathrm{R}(7)\\ C_3^{2x\bar{y}z}\end{matrix} = \begin{pmatrix}0&0&1\\-1&0&0\\0&-1&0\end{pmatrix},\quad \begin{matrix}\mathrm{R}(8)\\ C_3^{2xy\bar{z}}\end{matrix} = \begin{pmatrix}0&0&-1\\1&0&0\\0&-1&0\end{pmatrix}$$

$$\begin{matrix}\mathrm{R}(9)\\ C_3^{2xyz}\end{matrix} = \begin{pmatrix}0&1&0\\0&0&1\\1&0&0\end{pmatrix},\quad \begin{matrix}\mathrm{R}(10)\\ C_3^{xy\bar{z}}\end{matrix} = \begin{pmatrix}0&1&0\\0&0&-1\\-1&0&0\end{pmatrix},\quad \begin{matrix}\mathrm{R}(11)\\ C_3^{x\bar{y}z}\end{matrix} = \begin{pmatrix}0&-1&0\\0&0&-1\\1&0&0\end{pmatrix},\quad \begin{matrix}\mathrm{R}(12)\\ C_3^{x\bar{y}z}\end{matrix} = \begin{pmatrix}0&-1&0\\0&0&1\\-1&0&0\end{pmatrix},$$

It has four classes

$$\begin{aligned}\mathcal{C}_1 &= \{E\},\\ \mathcal{C}_2 &= \{\{2,3,1,4\},\{3,2,4,1\},\{1,4,2,3\},\{4,1,3,2\}\}\\ \mathcal{C}_3 &= \{\{3,1,2,4\},\{4,2,1,3\},\{1,3,4,2\},\{2,4,3,1\}\}\\ \mathcal{C}_4 &= \{\{2,1,4,3\},\{3,2,1,4\},\{4,3,2,1\}\}\end{aligned}$$

The normal subgroup is

Table 8.5. *Character table of $\mathcal{T}/\mathcal{N}$*

	$\mathcal{N}$	$\{123\}\mathcal{N}$	$\{321\}\mathcal{N}$
$^{(1)}\Gamma$	1	1	1
$^{(2)}\Gamma$	1	ω	ω^2
$^{(3)}\Gamma$	1	ω^2	ω

$$\mathcal{N} = \{\{1,2,3,4\},\{2,1,4,3\},\{3,2,1,4\},\{4,3,2,1\}$$

with factor group

$$\frac{\mathcal{T}}{\mathcal{N}} = \mathcal{N},\ \{2,3,1,4\}\mathcal{N},\ \{3,1,2,4\}\mathcal{N}$$

isomorphic to $\mathcal{C}_3$ with the character table in Table 8.5.

Since $\mathcal{T}$ has four classes, it has four Irreps, and since $\sum_\mu d_\mu^2 = 12$ we must have three 1-dimensional and one 3-dimensional Irreps. The mapping defined in Table 8.5 gives the three 1-dimensional Irreps as

Table 8.6. *Character table of $\mathcal{T}$*

	E	U	C_3	C_3^{-1}
$^{(1)}\Gamma$	1	1	1	1
$^{(2)}\Gamma$	1	1	ω	ω^2
$^{(3)}\Gamma$	1	1	ω^2	ω
$^{(4)}\Gamma$	3	-1	0	0

8.13 The characters of the outer products are

	E	U	C_3	C_3^{-1}
$^{(4)}\Gamma \otimes {}^{(4)}\Gamma$	9	1	0	0

It is then straightforward to obtain the frequencies:

$$\langle 4\otimes 4|1\rangle = \langle 4\otimes 4|2\rangle = \langle 4\otimes 4|3\rangle = 1, \quad \langle 4\otimes 4|4\rangle = 2$$

The CG series is

$$^{(4)}\Gamma \otimes {}^{(4)}\Gamma = {}^{(1)}\Gamma \oplus {}^{(2)}\Gamma \oplus {}^{(3)}\Gamma \oplus 2\,{}^{(4)}\Gamma$$

(* Generators: C_{2z}, C_3^{xyz} *)

```
<<Combinatorica`
g=12;NG=3;
L={Range[4],{2,1,4,3},{2,3,1,4}};
```

```
R={{{1,0,0},{0,1,0},{0,0,1}},{{-1,0,0},{0,-1,0},{0,0,1}},{{0,0,1},{1,0,0},{0,1,0}}};
Array[Rot,{3,3}];
Do[B=R[[i]];Rot[i]=B,{i,1,NG}];
f:=Permute[L[[i]],L[[j]]];nel=NG;
While[TrueQ[Length[L]¡g],
        For[i=2,i¡g,i++,
              For[j=2,j¡(Length[L]+1),j++,
                    Switch[FreeQ[L,f],
                              True,AppendTo[L,f];nel++;
                              Rot[nel]=Rot[i].Rot[j];
                              bc=R[[i]].R[[j]];AppendTo[R,bc]
                              ]]]];Print[L];
 Print["Rotation Matrices of Group Elements: "]
 Do[
 Print["R(",i,") = ",MatrixForm[Rot[i]],",",
 " R(",i+1,") = ",MatrixForm[Rot[i+1]],",",
 " R(",i+2,") = ", MatrixForm[Rot[i+2]],",",
 " R(",i+3,") = ",MatrixForm[Rot[i+3]]
 ],
 {i,1,g-3,4}
 ];
NM={{1},{2,9,12},{3,4,5,10},{6,7,8,11}};ω = (−1/2 + i √3/2);
xi={{1, 1, 1, 1}, {1, 1, ω, ω^2} , {1, 1, ω^2, ω} , {3, −1, 0, 0}};
 Outpr={};
Do[ Rnu=R[[i]];
 vx=KroneckerProduct[Rnu,Rnu];
AppendTo[Outpr,vx],{i,1,g}];
Do[
 Print["OP(",i,") = ",MatrixForm[Outpr[[i]]],",",
 " OP(",i+1,") = ",MatrixForm[Outpr[[i+1]]],",",
 " OP(",i+2,") = ", MatrixForm[Outpr[[i+2]]],",",
```

```
" OP(",i+3,") = ",MatrixForm[Outpr[[i+3]]]
], {i,1,g-3,4}
] ;
X=0*IdentityMatrix[9];Class={};
Do[Cls=X;
Do[Cls+=Outpr[[NM[[i,j]]]],{j,1,Length[NM[[i]]]}
] ;AppendTo[Class,Cls],{i,1,4}
];
Do[Print[MatrixForm[Class[[i]]]],{i,1,4}];
Do[
Pr2=xi[[i,1]]*Class[[1]];
Do[
Pr2+=xi[[i,j]]*Class[[j]],{j,2,4}
];Pr2=Pr2*xi[[i,1]];Pr2=Pr2/12;Print[MatrixForm[Pr2]];Print[N[Eigensystem[Pr2]]],{i,1,4}];
```

{{1,2,3,4},{2,1,4,3},{2,3,1,4},{1,4,2,3},{3,2,4,1},{3,1,2,4},
{2,4,3,1},{1,3,4,2},{3,4,1,2},{4,1,3,2},{4,2,1,3},{4,3,2,1}}

Rotation Matrices of Group Elements:

$$\mathrm{R}(1) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad \mathrm{R}(2) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad \mathrm{R}(3) = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}, \quad \mathrm{R}(4) = \begin{pmatrix} 0 & 0 & -1 \\ -1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}$$

$$\mathrm{R}(5) = \begin{pmatrix} 0 & 0 & 1 \\ -1 & 0 & 0 \\ 0 & -1 & 0 \end{pmatrix}, \quad \mathrm{R}(6) = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}, \quad \mathrm{R}(7) = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & -1 \\ -1 & 0 & 0 \end{pmatrix}, \quad \mathrm{R}(8) = \begin{pmatrix} 0 & -1 & 0 \\ 0 & 0 & 1 \\ -1 & 0 & 0 \end{pmatrix}$$

$$\mathrm{R}(9) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}, \quad \mathrm{R}(10) = \begin{pmatrix} 0 & 0 & -1 \\ 1 & 0 & 0 \\ 0 & -1 & 0 \end{pmatrix}, \quad \mathrm{R}(11) = \begin{pmatrix} 0 & -1 & 0 \\ 0 & 0 & -1 \\ 1 & 0 & 0 \end{pmatrix}, \quad \mathrm{R}(12) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

$$
\mathrm{OP}(1) = \begin{pmatrix}1&0&0&0&0&0&0&0&0\\0&1&0&0&0&0&0&0&0\\0&0&1&0&0&0&0&0&0\\0&0&0&1&0&0&0&0&0\\0&0&0&0&1&0&0&0&0\\0&0&0&0&0&1&0&0&0\\0&0&0&0&0&0&1&0&0\\0&0&0&0&0&0&0&1&0\\0&0&0&0&0&0&0&0&1\end{pmatrix}, \quad \mathrm{OP}(2) = \begin{pmatrix}1&0&0&0&0&0&0&0&0\\0&1&0&0&0&0&0&0&0\\0&0&-1&0&0&0&0&0&0\\0&0&0&1&0&0&0&0&0\\0&0&0&0&1&0&0&0&0\\0&0&0&0&0&-1&0&0&0\\0&0&0&0&0&0&-1&0&0\\0&0&0&0&0&0&0&-1&0\\0&0&0&0&0&0&0&0&1\end{pmatrix},
$$

$$
\mathrm{OP}(3) = \begin{pmatrix}0&0&0&0&0&0&0&0&1\\0&0&0&0&0&0&1&0&0\\0&0&0&0&0&0&0&1&0\\0&0&1&0&0&0&0&0&0\\1&0&0&0&0&0&0&0&0\\0&1&0&0&0&0&0&0&0\\0&0&0&0&0&1&0&0&0\\0&0&0&1&0&0&0&0&0\\0&0&0&0&1&0&0&0&0\end{pmatrix}, \quad \mathrm{OP}(4) = \begin{pmatrix}0&0&0&0&0&0&0&0&1\\0&0&0&0&0&0&1&0&0\\0&0&0&0&0&0&0&-1&0\\0&0&1&0&0&0&0&0&0\\1&0&0&0&0&0&0&0&0\\0&-1&0&0&0&0&0&0&0\\0&0&0&0&0&-1&0&0&0\\0&0&0&-1&0&0&0&0&0\\0&0&0&0&1&0&0&0&0\end{pmatrix},
$$

$$
\mathrm{OP}(5) = \begin{pmatrix}0&0&0&0&0&0&0&0&1\\0&0&0&0&0&0&-1&0&0\\0&0&0&0&0&0&0&-1&0\\0&0&-1&0&0&0&0&0&0\\1&0&0&0&0&0&0&0&0\\0&1&0&0&0&0&0&0&0\\0&0&0&0&0&-1&0&0&0\\0&0&0&1&0&0&0&0&0\\0&0&0&0&1&0&0&0&0\end{pmatrix}, \quad \mathrm{OP}(6) = \begin{pmatrix}0&0&0&0&1&0&0&0&0\\0&0&0&0&0&1&0&0&0\\0&0&0&1&0&0&0&0&0\\0&0&0&0&0&0&0&1&0\\0&0&0&0&0&0&0&0&1\\0&0&0&0&0&0&1&0&0\\0&1&0&0&0&0&0&0&0\\0&0&1&0&0&0&0&0&0\\1&0&0&0&0&0&0&0&0\end{pmatrix},
$$

$$
\mathrm{OP}(7) = \begin{pmatrix}0&0&0&0&1&0&0&0&0\\0&0&0&0&0&-1&0&0&0\\0&0&0&-1&0&0&0&0&0\\0&0&0&0&0&0&0&-1&0\\0&0&0&0&0&0&0&0&1\\0&0&0&0&0&0&1&0&0\\0&-1&0&0&0&0&0&0&0\\0&0&1&0&0&0&0&0&0\\1&0&0&0&0&0&0&0&0\end{pmatrix}, \quad \mathrm{OP}(8) = \begin{pmatrix}0&0&0&0&1&0&0&0&0\\0&0&0&0&0&-1&0&0&0\\0&0&0&1&0&0&0&0&0\\0&0&0&0&0&0&0&-1&0\\0&0&0&0&0&0&0&0&1\\0&0&0&0&0&0&-1&0&0\\0&1&0&0&0&0&0&0&0\\0&0&-1&0&0&0&0&0&0\\1&0&0&0&0&0&0&0&0\end{pmatrix},
$$

$$
\mathrm{OP}(9) = \begin{pmatrix}1&0&0&0&0&0&0&0&0\\0&-1&0&0&0&0&0&0&0\\0&0&1&0&0&0&0&0&0\\0&0&0&-1&0&0&0&0&0\\0&0&0&0&1&0&0&0&0\\0&0&0&0&0&-1&0&0&0\\0&0&0&0&0&0&1&0&0\\0&0&0&0&0&0&0&-1&0\\0&0&0&0&0&0&0&0&1\end{pmatrix}, \quad \mathrm{OP}(10) = \begin{pmatrix}0&0&0&0&0&0&0&0&1\\0&0&0&0&0&0&-1&0&0\\0&0&0&0&0&0&0&1&0\\0&0&-1&0&0&0&0&0&0\\1&0&0&0&0&0&0&0&0\\0&-1&0&0&0&0&0&0&0\\0&0&0&0&0&1&0&0&0\\0&0&0&-1&0&0&0&0&0\\0&0&0&0&1&0&0&0&0\end{pmatrix},
$$

$$
\mathrm{OP}(11) = \begin{pmatrix}0&0&0&0&1&0&0&0&0\\0&0&0&0&0&1&0&0&0\\0&0&0&-1&0&0&0&0&0\\0&0&0&0&0&0&0&1&0\\0&0&0&0&0&0&0&0&1\\0&0&0&0&0&0&-1&0&0\\0&-1&0&0&0&0&0&0&0\\0&0&-1&0&0&0&0&0&0\\1&0&0&0&0&0&0&0&0\end{pmatrix}, \quad \mathrm{OP}(12) = \begin{pmatrix}1&0&0&0&0&0&0&0&0\\0&-1&0&0&0&0&0&0&0\\0&0&-1&0&0&0&0&0&0\\0&0&0&-1&0&0&0&0&0\\0&0&0&0&1&0&0&0&0\\0&0&0&0&0&1&0&0&0\\0&0&0&0&0&0&-1&0&0\\0&0&0&0&0&0&0&1&0\\0&0&0&0&0&0&0&0&1\end{pmatrix}
$$

$$Class(1) = \begin{pmatrix} 1&0&0&0&0&0&0&0&0\\ 0&1&0&0&0&0&0&0&0\\ 0&0&1&0&0&0&0&0&0\\ 0&0&0&1&0&0&0&0&0\\ 0&0&0&0&1&0&0&0&0\\ 0&0&0&0&0&1&0&0&0\\ 0&0&0&0&0&0&1&0&0\\ 0&0&0&0&0&0&0&1&0\\ 0&0&0&0&0&0&0&0&1 \end{pmatrix}, \; Class(2) = \begin{pmatrix} 3&0&0&0&0&0&0&0&0\\ 0&-1&0&0&0&0&0&0&0\\ 0&0&-1&0&0&0&0&0&0\\ 0&0&0&-1&0&0&0&0&0\\ 0&0&0&0&3&0&0&0&0\\ 0&0&0&0&0&-1&0&0&0\\ 0&0&0&0&0&0&-1&0&0\\ 0&0&0&0&0&0&0&-1&0\\ 0&0&0&0&0&0&0&0&3 \end{pmatrix},$$

$$Class(3) = \begin{pmatrix} 0&0&0&0&0&0&0&0&4\\ 0&0&0&0&0&0&0&0&0\\ 0&0&0&0&0&0&0&0&0\\ 0&0&0&0&0&0&0&0&0\\ 4&0&0&0&0&0&0&0&0\\ 0&0&0&0&0&0&0&0&0\\ 0&0&0&0&0&0&0&0&0\\ 0&0&0&0&0&0&0&0&0\\ 0&0&0&0&4&0&0&0&0 \end{pmatrix}, \; Class(4) = \begin{pmatrix} 0&0&0&0&4&0&0&0&0\\ 0&0&0&0&0&0&0&0&0\\ 0&0&0&0&0&0&0&0&0\\ 0&0&0&0&0&0&0&0&0\\ 0&0&0&0&0&0&0&0&4\\ 0&0&0&0&0&0&0&0&0\\ 0&0&0&0&0&0&0&0&0\\ 0&0&0&0&0&0&0&0&0\\ 4&0&0&0&0&0&0&0&0 \end{pmatrix}$$

$$^{(1)}\mathcal{P} = \begin{pmatrix} \frac{1}{3}&0&0&0&\frac{1}{3}&0&0&0&\frac{1}{3}\\ 0&0&0&0&0&0&0&0&0\\ 0&0&0&0&0&0&0&0&0\\ 0&0&0&0&0&0&0&0&0\\ \frac{1}{3}&0&0&0&\frac{1}{3}&0&0&0&\frac{1}{3}\\ 0&0&0&0&0&0&0&0&0\\ 0&0&0&0&0&0&0&0&0\\ 0&0&0&0&0&0&0&0&0\\ \frac{1}{3}&0&0&0&\frac{1}{3}&0&0&0&\frac{1}{3} \end{pmatrix}$$

$$\begin{cases} \text{Eigenvalues :} & 1, 0, 0, 0, 0, 0, 0, 0, 0. \\ \text{Eigenvectors :} & \{1, 0, 0, 0, 1, 0, 0, 0, 1\}, \{-1, 0, 0, 0, 0, 0, 0, 0, 1\}, \{0, 0, 0, 0, 0, 0, 0, 1, 0\}, \\ & \{0, 0, 0, 0, 0, 0, 1, 0, 0\}, \{0, 0, 0, 0, 0, 1, 0, 0, 0\}, \{-1, 0, 0, 0, 1, 0, 0, 0, 0\}, \\ & \{0, 0, 0, 1, 0, 0, 0, 0, 0\}, \{0, 0, 1, 0, 0, 0, 0, 0, 0\}, \{0, 1, 0, 0, 0, 0, 0, 0, 0\} \end{cases}$$

$$
{}^{(2)}\mathcal{P} = \begin{pmatrix}
\frac{1}{3} & 0 & 0 & 0 & \frac{1}{3}\left(-\frac{1}{2}+\frac{i\sqrt{3}}{2}\right)^2 & 0 & 0 & 0 & \frac{1}{3}\left(-\frac{1}{2}+\frac{i\sqrt{3}}{2}\right) \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\frac{1}{3}\left(-\frac{1}{2}+\frac{i\sqrt{3}}{2}\right) & 0 & 0 & 0 & \frac{1}{3} & 0 & 0 & 0 & \frac{1}{3}\left(-\frac{1}{2}+\frac{i\sqrt{3}}{2}\right)^2 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\frac{1}{3}\left(-\frac{1}{2}+\frac{i\sqrt{3}}{2}\right)^2 & 0 & 0 & 0 & \frac{1}{3}\left(-\frac{1}{2}+\frac{i\sqrt{3}}{2}\right) & 0 & 0 & 0 & \frac{1}{3}
\end{pmatrix}
$$

$$
\begin{cases}
\text{Eigenvalues}: & 1,0,0,0,0,0,0,0,0 \\
\text{Eigenvectors}: & \{-\frac{1}{2}+\frac{i\sqrt{3}}{2},0,0,0,-\frac{1}{2}-\frac{i\sqrt{3}}{2},0,0,0,1\},\{\frac{1}{2}-\frac{i\sqrt{3}}{2},0,0,0,0,0,0,0,1\},\{0,0,0,0,0,0,0,1,0\}, \\
& \{0,0,0,0,0,0,1,0,0\},\{0,0,0,0,0,1,0,0,0\},\{\frac{1}{2}+\frac{i\sqrt{3}}{2},0,0,0,1,0,0,0,0\}, \\
& \{0,0,0,1,0,0,0,0,0\},\{0,0,1,0,0,0,0,0,0\},\{0,1,0,0,0,0,0,0,0\}
\end{cases}
$$

$$
{}^{(3)}\mathcal{P} = \begin{pmatrix}
\frac{1}{3} & 0 & 0 & 0 & \frac{1}{3}\left(-\frac{1}{2}+\frac{i\sqrt{3}}{2}\right) & 0 & 0 & 0 & \frac{1}{3}\left(-\frac{1}{2}+\frac{i\sqrt{3}}{2}\right)^2 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\frac{1}{3}\left(-\frac{1}{2}+\frac{i\sqrt{3}}{2}\right)^2 & 0 & 0 & 0 & \frac{1}{3} & 0 & 0 & 0 & \frac{1}{3}\left(-\frac{1}{2}+\frac{i\sqrt{3}}{2}\right) \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\frac{1}{3}\left(-\frac{1}{2}+\frac{i\sqrt{3}}{2}\right) & 0 & 0 & 0 & \frac{1}{3}\left(-\frac{1}{2}+\frac{i\sqrt{3}}{2}\right)^2 & 0 & 0 & 0 & \frac{1}{3}
\end{pmatrix}
$$

$$
\begin{cases}
\text{Eigenvalues}: & 1,0,0,0,0,0,0,0,0 \\
\text{Eigenvectors}: & \{-\frac{1}{2}-\frac{i\sqrt{3}}{2},0,0,0,-\frac{1}{2}+\frac{i\sqrt{3}}{2},0,0,0,1\},\{\frac{1}{2}+\frac{i\sqrt{3}}{2},0,0,0,0,0,0,0,1\},\{0,0,0,0,0,0,0,1,0\}, \\
& \{0,0,0,0,0,0,1,0,0\},\{0,0,0,0,0,1,0,0,0\},\{\frac{1}{2}-\frac{i\sqrt{3}}{2},0,0,0,1,0,0,0,0\}, \\
& \{0,0,0,1,0,0,0,0,0\},\{0,0,1,0,0,0,0,0,0\},\{0,1,0,0,0,0,0,0,0\}
\end{cases}
$$

$$
{}^{(4)}\mathcal{P} = \begin{pmatrix}
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0
\end{pmatrix}
$$

$$
\begin{cases}
\text{Eigenvalues}: & 1,1,1,1,1,1,0,0,0 \\
\text{Eigenvectors}: & \{0,0,0,0,0,0,0,1,0\},\{0,0,0,0,0,0,1,0,0\},\{0,0,0,0,0,1,0,0,0\}, \\
& \{0,0,0,1,0,0,0,0,0\},\{0,0,1,0,0,0,0,0,0\},\{0,1,0,0,0,0,0,0,0\}, \\
& \{0,0,0,0,0,0,0,0,1\},\{0,0,0,0,1,0,0,0,0\},\{1,0,0,0,0,0,0,0,0\}
\end{cases}
$$

$$
\begin{aligned}
{}^{(1)}\Gamma &= \begin{bmatrix} 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 \end{bmatrix} \\
{}^{(2)}\Gamma &= \begin{bmatrix} \frac{1}{2} - i\frac{\sqrt{3}}{2} & 0 & 0 & 0 & \frac{1}{2} + i\frac{\sqrt{3}}{2} & 0 & 0 & 0 & -1 \end{bmatrix} \\
{}^{(3)}\Gamma &= \begin{bmatrix} \frac{1}{2} + i\frac{\sqrt{3}}{2} & 0 & 0 & 0 & \frac{1}{2} - i\frac{\sqrt{3}}{2} & 0 & 0 & 0 & -1 \end{bmatrix} \\
{}^{(4)}\Gamma_1 &= \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \end{bmatrix} \\
{}^{(4)}\Gamma_2 &= \begin{bmatrix} 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}
\end{aligned}
$$

8.14 The CGCs can be calculated with the aid of the following relations

$$
\left(\begin{array}{c|c} \mu\nu & \sigma \\ ik & m \end{array} \right) \left(\begin{array}{c|c} \sigma & \mu\nu \\ n & jl \end{array} \right) = \frac{d_\sigma}{g} \sum_{R\in\mathcal{G}} {}^{(\mu)}\Gamma_{ij}(R)^{(\nu)}\Gamma_{kl}(R)^{(\sigma)}\Gamma^*_{mn}(R)
$$

$$
\left| \left(\begin{array}{c|c} \mu\nu & \sigma \\ ik & m \end{array} \right) \right|^2 = \frac{d_\sigma}{g} \sum_{R\in\mathcal{G}} {}^{(\mu)}\Gamma_{ii}(R)\,{}^{(\nu)}\Gamma_{kk}(R)\,{}^{(\sigma)}\Gamma^*_{mm}(R)
$$

Remembering that the Irreps of $\mathcal{C}_{3\mathrm{v}}$ are

Table 8.7. *Irreps of* $\mathcal{C}_{3\mathrm{v}}$

	E	σ	C_3
${}^{(1)}\Gamma\,(A_1)$	1	1	1
${}^{(2)}\Gamma\,(A_2)$	1	-1	1
${}^{(3)}\Gamma\,(E)$	2	0	-1

and that the matrices of ${}^{(3)}\Gamma\,(E)$ are

$$
E = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix},\ \sigma_1 = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix},\ \sigma_2 = \begin{pmatrix} 1/2 & -\sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{pmatrix},
$$

$$
\sigma_3 = \begin{pmatrix} 1/2 & \sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{pmatrix},\ C_3 = \begin{pmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{pmatrix},\ C_3^{-1} = \begin{pmatrix} -1/2 & \sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{pmatrix}
$$

We obtain for ${}^{(2)}\Gamma\,(A_2)$

$$\left|\begin{pmatrix} 33 & 2 \\ 11 & 1 \end{pmatrix}\right|^2 = \left|\begin{pmatrix} 33 & 2 \\ 22 & 1 \end{pmatrix}\right|^2 = \frac{1}{6}\left[1-1-\frac{1}{4}-\frac{1}{4}+\frac{1}{4}+\frac{1}{4}\right] = 0$$

$$\left|\begin{pmatrix} 33 & 2 \\ 12 & 1 \end{pmatrix}\right|^2 = \frac{1}{6}\left[0+0+\frac{3}{4}+\frac{3}{4}+\frac{3}{4}+\frac{3}{4}\right] = \frac{1}{2},$$

$$\begin{pmatrix} 33 & 2 \\ 12 & 1 \end{pmatrix}\begin{pmatrix} 33 & 2 \\ 21 & 1 \end{pmatrix} = \frac{1}{6}\left[0+0-\frac{3}{4}-\frac{3}{4}-\frac{3}{4}-\frac{3}{4}\right] = -\frac{1}{2}$$

$$\begin{pmatrix} 33 & 2 \\ ik & 1 \end{pmatrix} = \frac{1}{\sqrt{2}}\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}$$

$$\left|\begin{pmatrix} 33 & 3 \\ 11 & 1 \end{pmatrix}\right|^2 = \frac{1}{3}\left[1-1-\frac{1}{8}-\frac{1}{8}+\frac{1}{8}+\frac{1}{8}\right] = 0$$

$$\left|\begin{pmatrix} 33 & 3 \\ 11 & 2 \end{pmatrix}\right|^2 = \frac{1}{3}\left[1+1-\frac{1}{8}-\frac{1}{8}-\frac{1}{8}-\frac{1}{8}\right] = \frac{1}{2}$$

$$\left|\begin{pmatrix} 33 & 3 \\ 22 & 1 \end{pmatrix}\right|^2 = \frac{1}{3}\left[1-1+\frac{1}{8}+\frac{1}{8}-\frac{1}{8}-\frac{1}{8}\right] = 0$$

$$\left|\begin{pmatrix} 33 & 3 \\ 22 & 2 \end{pmatrix}\right|^2 = \frac{1}{3}\left[1+1-\frac{1}{8}-\frac{1}{8}-\frac{1}{8}-\frac{1}{8}\right] = \frac{1}{2}$$

$$\left|\begin{pmatrix} 33 & 3 \\ 12 & 1 \end{pmatrix}\right|^2 = \frac{1}{3}\left[1+1-\frac{1}{8}-\frac{1}{8}-\frac{1}{8}-\frac{1}{8}\right] = \frac{1}{2}$$

$$\left|\begin{pmatrix} 33 & 3 \\ 12 & 2 \end{pmatrix}\right|^2 = \frac{1}{3}\left[1-1+\frac{1}{8}+\frac{1}{8}-\frac{1}{8}-\frac{1}{8}\right] = 0$$

$$\begin{pmatrix} 33 & 3 \\ 11 & 2 \end{pmatrix}\begin{pmatrix} 3 & 33 \\ 2 & 22 \end{pmatrix} = \frac{1}{3}\left[0+0-\frac{3}{8}-\frac{3}{8}-\frac{3}{8}-\frac{3}{8}\right] = -\frac{1}{2}$$

$$\begin{pmatrix} 33 & 3 \\ 12 & 1 \end{pmatrix}\begin{pmatrix} 3 & 33 \\ 1 & 21 \end{pmatrix} = \frac{1}{3}\left[0+0+\frac{3}{8}+\frac{3}{8}+\frac{3}{8}+\frac{3}{8}\right] = \frac{1}{2}$$

$$\begin{pmatrix} 33 & 3 \\ ik & 1 \end{pmatrix} = \frac{1}{\sqrt{2}}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

$$\begin{pmatrix} 33 & 3 \\ ik & 2 \end{pmatrix} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

8.15 The CG series is

$${}^{(5\otimes 5)}\Gamma = {}^{(1)}\Gamma \oplus {}^{(2)}\Gamma \oplus {}^{(3)}\Gamma \oplus {}^{(4)}\Gamma,$$

is comprised of 1-dimensional Irreps only. The matrices for Irrep ${}^{(5)}\Gamma$ are

$$
{}^{(5)}\Gamma(E) = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}, \qquad {}^{(5)}\Gamma(C_{2x}) = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix},
$$

$$
{}^{(5)}\Gamma(C_{2y}) = \begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix}, \qquad {}^{(5)}\Gamma(C_{2z}) = \begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix},
$$

$$
{}^{(5)}\Gamma(C_{4z}) = \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix}, \qquad {}^{(5)}\Gamma(C_{4z}^{-1}) = \begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix},
$$

$$
{}^{(5)}\Gamma(C_{2xy}) = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \qquad {}^{(5)}\Gamma(C_{2\bar{x}\bar{y}}) = \begin{bmatrix} 0 & -1 \\ -1 & 0 \end{bmatrix}.
$$

Following the procedure and notation of the previous problem, we obtain

$$
\begin{aligned}
\left|\left(\begin{array}{c|c} 55 & 1 \\ 11 & 1 \end{array}\right)\right|^2 &= \left|\left(\begin{array}{c|c} 55 & 1 \\ 22 & 1 \end{array}\right)\right|^2 = \frac{1}{8}\,[1+1+1+1+0+0+0+0] = \frac{1}{2} \\
\left(\begin{array}{c|c} 55 & 1 \\ 11 & 1 \end{array}\right)\left(\begin{array}{c|c} 1 & 55 \\ 1 & 12 \end{array}\right) &= \frac{1}{8}\sum {}^{(5)}\Gamma_{11}\,{}^{(5)}\Gamma_{12} = 0 \\
\left(\begin{array}{c|c} 55 & 1 \\ 11 & 1 \end{array}\right)\left(\begin{array}{c|c} 1 & 55 \\ 1 & 22 \end{array}\right) &= \frac{1}{8}\sum {}^{(5)}\Gamma_{12}^2 = \frac{1}{8}\,[0+0+0+0+1+1+1+1] = \frac{1}{2} \\
\left(\begin{array}{c|c} 55 & 1 \\ ik & 1 \end{array}\right) &= \frac{1}{\sqrt{2}}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \\
\left|\left(\begin{array}{c|c} 55 & 2 \\ 11 & 1 \end{array}\right)\right|^2 &= \left|\left(\begin{array}{c|c} 55 & 2 \\ 22 & 1 \end{array}\right)\right|^2 = \frac{1}{8}\,[1+1+1+1+0+0+0+0] = \frac{1}{2} \\
\left(\begin{array}{c|c} 55 & 2 \\ 11 & 1 \end{array}\right)\left(\begin{array}{c|c} 2 & 55 \\ 1 & 12 \end{array}\right) &= \frac{1}{8}\sum {}^{(5)}\Gamma_{11}\,{}^{(5)}\Gamma_{12}\,{}^{(2)}\Gamma = 0 \\
\left(\begin{array}{c|c} 55 & 2 \\ 11 & 1 \end{array}\right)\left(\begin{array}{c|c} 2 & 55 \\ 1 & 22 \end{array}\right) &= \frac{1}{8}\sum {}^{(5)}\Gamma_{12}^2\,{}^{(2)}\Gamma = \frac{1}{8}\,[0+0+0+0+1+1+1+1] = \frac{1}{2} \\
\left(\begin{array}{c|c} 55 & 2 \\ ik & 1 \end{array}\right) &= \frac{1}{\sqrt{2}}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}
\end{aligned}
$$

$$\left|\begin{pmatrix} 55 & 3 \\ 11 & 1 \end{pmatrix}\right|^2 = \left|\begin{pmatrix} 55 & 3 \\ 22 & 1 \end{pmatrix}\right|^2 = \frac{1}{8}\,[1+1+1+1+0+0+0+0] = \frac{1}{2}$$

$$\begin{pmatrix} 55 & 3 \\ 11 & 1 \end{pmatrix}\begin{pmatrix} 3 & 55 \\ 1 & 12 \end{pmatrix} = \frac{1}{8}\sum {}^{(5)}\Gamma_{11}\,{}^{(5)}\Gamma_{12}\,{}^{(3)}\Gamma = 0$$

$$\begin{pmatrix} 55 & 3 \\ 11 & 1 \end{pmatrix}\begin{pmatrix} 3 & 55 \\ 1 & 22 \end{pmatrix} = \frac{1}{8}\sum {}^{(5)}\Gamma_{12}^2\,{}^{(3)}\Gamma = \frac{1}{8}\,[0+0+0+0+1+1+1+1] = \frac{1}{2}$$

$$\begin{pmatrix} 55 & 3 \\ ik & 1 \end{pmatrix} = \frac{1}{\sqrt{2}}\begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}$$

$$\left|\begin{pmatrix} 55 & 4 \\ 11 & 1 \end{pmatrix}\right|^2 = \left|\begin{pmatrix} 55 & 4 \\ 22 & 1 \end{pmatrix}\right|^2 = \frac{1}{8}\,[1+1+1+1+0+0+0+0] = \frac{1}{2}$$

$$\begin{pmatrix} 55 & 4 \\ 11 & 1 \end{pmatrix}\begin{pmatrix} 4 & 55 \\ 1 & 12 \end{pmatrix} = \frac{1}{8}\sum {}^{(5)}\Gamma_{11}\,{}^{(5)}\Gamma_{12}\,{}^{(4)}\Gamma = 0$$

$$\begin{pmatrix} 55 & 4 \\ 11 & 1 \end{pmatrix}\begin{pmatrix} 4 & 55 \\ 1 & 22 \end{pmatrix} = \frac{1}{8}\sum {}^{(5)}\Gamma_{12}^2\,{}^{(4)}\Gamma = \frac{1}{8}\,[0+0+0+0+1+1+1+1] = \frac{1}{2}$$

$$\begin{pmatrix} 55 & 4 \\ ik & 1 \end{pmatrix} = \frac{1}{\sqrt{2}}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

9
Induced representations

9.1 Exercises

9.1 Show explicitly that the set of matrices $\mathbf{M}^*$ in (**??**) obeys the group multiplication table for $\mathcal{C}_{3\mathrm{v}}$.

9.2 Carry out all the steps to assure yourself that the results of (9.33) are correct. Show explicitly that the set of matrices obeys the group multiplication table for $\mathcal{C}_{4v}$.

9.3 Prove (9.30).

9.4 Consider the symmetric group $\mathcal{S}_4$ of order 24; it has 5 classes and 2 normal subgroups, as was determined in problem 4.5. Use the normal subgroup isomorphic to $\mathcal{T}$ to induce Irreps of $\mathcal{S}_4$.

9.5 Consider the isomorphic point-groups $\mathcal{C}_{2nv}$ and $\mathcal{D}_{2n}$.

(i) Show that their order is $4n$.
(ii) Show that $\mathcal{D}_4$ and $\mathcal{D}_6$ have 5 and 7 classes.
(iii) Generalize these results by showing that for an arbitrary n there correspond $n+3$ classes and hence $n+3$ Irreps.
(iv) Describe the nature of the different classes.
(v) Show that the Irrep dimension sum-rule uniquely determines the dimensionality of the Irreps.
(vi) Determine the invariant subgroup of either $\mathcal{C}_{2nv}$ or $\mathcal{D}_{2n}$.
(vii) Use this normal subgroup and its factor group to construct the group Irreps.

9.6 Consider the $\mathcal{C}_{(2n+1)v}$ and $\mathcal{D}_{2n+1}$ type point-groups.

(i) Show that their order is $4n+2$.
(ii) Show that they have $n+2$ classes.
(iii) Describe the nature of the different classes.

(iv) Show that the Irrep dimension sum-rule uniquely determines the dimensionality of the Irreps.
(v) Determine the invariant subgroup of either $\mathcal{C}_{2nv}$ or $\mathcal{D}_{2n}$.
(vi) Use this normal subgroup and its factor group to construct the group Irreps.

9.7 The proper cubic point-group 432 $(\mathcal{O})$ contains the tetrahedral point-group 23 $(\mathcal{T})$ as a normal subgroup. From the 4 Irreps of 23, derived in problem 8.12 of chapter 8, construct the Irreps of 432.
9.8 Use the Irreps of the normal subgroup $\mathcal{C}_4 \lhd \mathcal{D}_4$ to induce the latter's Irreps.

9.2 Solutions

9.1 Just carry out matrix multiplication to verify the group properties.
9.2
9.3
9.4
9.5 Parts (i) through (ii) have were covered in Problem 8.7.

(iv) Since we have $n+3$ classes, the number of Irreps is also $n+3$. We write the Irrep dimension sum-rule as

$$4n \;=\; 1 + \sum_{\mu=2}^{n+3} d_\mu^2$$

For $n = 1$ the Irrep sum rule required that all Irreps be 1-dimensional. For larger n the sum-rule does not allow for Irreps of dimension greater than 2. The sum rule is then uniquely satisfied with four 1-dimensional Irreps and $n-1$ 2-dimensional Irreps.

Parts (v) and (vi) were also solved in Problem 8.7.

9.7 We have

$$\frac{\mathcal{O}}{\mathcal{T}} = \mathcal{C}_{\mathrm{s}} \;=\; \mathcal{T} \,\oplus\, U_d\,\mathcal{T}$$

where

$$U_d\,\mathcal{T} \;=\; 6U_d,\, 6C_4$$

The Irreps of $\mathcal{C}_{\mathrm{s}}$ are given in Table 8.2.

(i) ${}^{(1)}\Delta\,(A)$ is self-conjugate, hence, $\mathcal{L}_{II} = \mathcal{O}$, $\mathcal{L}_I = \mathcal{C}_{\mathrm{s}}$. We can induce two Irreps of $\mathcal{O}$ from the Irrep A, namely,

Table 9.1. *Character table of $\mathcal{T}$*

		E	U	C_3	C_3^{-1}
A	$^{(1)}\Delta$	1	1	1	1
E	$^{(2)}\Delta$	1	1	ω	ω^2
	$^{(3)}\Delta$	1	1	ω^2	ω
T	$^{(4)}\Delta$	3	-1	0	0

	E	$6C_4$	$3C_2$	$8C_3$	$6U_d$
$^{(1)}\Gamma\,(A_1)$	1	1	1	1	1
$^{(2)}\Gamma\,(A_2)$	1	-1	1	1	-1

(ii) Next, we find that Irreps $^{(2)}\Gamma$ and $^{(3)}\Gamma$ of $\mathcal{T}$ form a two-pronged orbit under conjugation by elements of $\mathcal{O}$, for example, we get

$$^{(2)}\Delta\,(U_d^{xy}\,C_3^{xyz}\,U_d^{xy}) \;=\; ^{(2)}\Delta\,(C_3^{xyz}) \;=\; \omega^* \;=\; ^{(3)}\Delta\left(C_3^{y\bar{z}\bar{x}}\right)$$

Thus, they have $\mathcal{L}_{II} = \mathcal{T}$, $\mathcal{L}_I = E$. We need to determine the ground Rep matrices with respect to $\mathcal{L}_{II} = \mathcal{T}$ for the generators of $\mathcal{O} = E\,\mathcal{T} \oplus U_d\mathcal{T}$, namely, C_3^{xyz}, C_{2x}, U_d^{xy}.

$$M\,(C_3^{xyz}) \;=\; \begin{pmatrix} EC_3^{xyz}E & EC_3^{xyz}U_d^{xy} \\ U_d^{xy}C_3^{xyz}E & U_d^{xy}C_3^{xyz}U_d^{xy} \end{pmatrix} \;=\; \begin{pmatrix} ^{(2)}\Delta\,(C_3^{xyz}) & 0 \\ 0 & ^{(3)}\Delta\,(C_3^{xyz}) \end{pmatrix}$$
$$\;=\; \begin{pmatrix} \omega & 0 \\ 0 & \omega^* \end{pmatrix}$$
$$M\,(C_{2x}) \;=\; \begin{pmatrix} EC_{2x}E & EC_{2z}U_d^{xy} \\ U_d^{xy}C_{2x}E & U_d^{xy}C_{2x}U_d^{xy} \end{pmatrix} \;=\; \begin{pmatrix} ^{(2)}\Delta\,(C_{2x}) & 0 \\ 0 & ^{(3)}\Delta\,(C_{2x}) \end{pmatrix}$$
$$\;=\; \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$
$$M\,(U_d^{xy}) \;=\; \begin{pmatrix} EU_d^{xy}E & EU_d^{xy}U_d^{xy} \\ U_dU_d^{xy}E & U_d^{xy}U_d^{xy}U_d^{xy} \end{pmatrix} \;=\; \begin{pmatrix} 0 & ^{(2)}\Delta\,(E) \\ ^{(3)}\Delta\,(E) & 0 \end{pmatrix}$$

(iii) The Irrep T contains the matrices

$$^{(4)}\Delta\,(C_{2x}) \;=\; \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix},\; ^{(4)}\Delta\,(C_3^{xyz}) \;=\; \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}$$

Under the conjugation with U_d^{xy} we obtain

$$U_d^{xy}\,C_{2x}\,U_d^{xy} \;=\; C_{2y},\; U_d^{xy}\,C_3^{xyz}\,U_d^{xy} \;=\; C_3^{y\bar{z}\bar{x}}$$

or

$$^{(4)}\Delta\,(U_d^{xy}\,C_{2x}\,U_d^{xy}) \;=^{(4)}\; \Delta\,(C_{2y}) \;=\; \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix},$$

$$^{(4)}\Delta\,(U_d^{xy}\,C_3^{xyz}\,U_d^{xy}) \;=\; ^{(4)}\Delta\left(C_3^{y\bar{z}\bar{x}}\right) \;=\; \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & -1 \\ -1 & 0 & 0 \end{pmatrix}$$

We see that the characters of the conjugate Irrep are the same as of $^{(4)}\Delta$ itself. Hence, $^{(4)}\Delta$ is self-conjugate, and $\mathcal{L}_{II} = \mathcal{O}$, $\mathcal{L}_I = \mathcal{C}_{\mathrm{s}}$.

Now, we determine the matrix representative of U_d^{xy}, say U that satifies

$$\begin{aligned} ^{(4)}\Delta\,(C_{2y}) \;&=\; U^{-1}\,{}^{(4)}\Delta\,(C_{2x})\,U \\ ^{(4)}\Delta\left(C_3^{y\bar{z}\bar{x}}\right) \;&=\; U^{-1}\,{}^{(4)}\Delta\left(C_3^{y\bar{z}\bar{x}}\right)\,U \\ U^2 \;&=\; (U_d^{xy})^2 \;=\; \mathbb{I} \end{aligned}$$

which yields

$$U_d^{xy} \;=\; \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

10

Crystallographic Symmetry and Space-Groups

10.1 Exercises

10.1 Use the integers 1, 2, 3, etc. to label each of the lattice points in Fig. 12a whose x-coordinates are such that $x \geq 0$. Perform the space-group operation $(C_4^- \,|\mathbf{t})$ on each of these numbered lattice points and label the resulting lattice points by 1', 2', etc. Find the new origin such that the space group operations $(C_4^- \,|\mathbf{t})$ just carried out can be described as pure rotations about the new origin.

10.2 Show that body-centered and face-centered tetragonal lattices are equivalent.

10.3 Derive the a-holohedry matrices of the generators C_{4z}, C_{3xyz}, $\mathfrak{I}$ of the face-centered cubic structure.

10.4 Sketch the unit cell of figure 10.13 as viewed along the screw axis. With the use of the solid and open circles to distinguish atoms in the basal plane from those in the mid-plane, identify the glide plane. What is the Seitz operator that takes atom 1 to the position of atom 2?

10.5 Show that for the 2-dimensional space-group $p2mg$

$$\left(\sigma_x \middle| \boldsymbol{\tau}\right)\, \left(\sigma_y \middle| \boldsymbol{\tau}\right)\, \mathbf{r} \;=\; \left(\sigma_x \sigma_y \middle| \boldsymbol{\tau} + \sigma_x\, \boldsymbol{\tau}\right)\, \mathbf{r} \;=\; -\mathbf{r}.$$

Show explicitly that $\left(\sigma_x \middle| \boldsymbol{\tau}\right)\, \left(\sigma_y \middle| \boldsymbol{\tau}\right)$ is its own inverse.

10.6 Explain the difference between the crystallographic point-groups $3m$ and $m3$. Explain why that $m3\,(\mathcal{T}_h)$ is not holohedral despite the fact that it contains a center of inversion.

10.7 Explain the reason that no face-centered lattices appear in the tetragonal system.

10.8 Show that monoclinic I (body-centered) lattices are possible, but not new; that is, show that $2C$ is not a distinct lattice but that $2A$ and $2B$ are.

10.9 Use the reasoning presented in §5.2.1 to demonstrate that symmetry operations involving improper rotations cannot be accompanied by a nonprimitive translation $\boldsymbol{\tau}$, except $\bar{2}(S_2)$.

10.10 Discuss the reasons for the classification of the point-groups $\mathcal{C}_{3h}$ and $\mathcal{S}_6$ among the hexagonal and trigonal systems.

10.11 Write down an explicit form of the following Seitz operators:

(i) a c-glide plane at $x, 1/4, z$,
(ii) a 2_1 axis along $[0, y, 1/4]$
(iii) an n-glide plane at $x, 0, z$
(iv) a 4_2 axis along $[1/4, 0, z]$.

Discuss the action of the following sequence of symmetry operations:

i. (a) followed by (b),
ii. (c) followed by (d)

on the point (x, y, z). Repeat the argument when the sequence of operations are reversed.

10.12 Enumerate all n-glide plane operators that appear in the space-group $P4nc\,(\mathbb{C}_{4v}^6)$, #104. Show that there are two types of non-primitive translations, namely, $(\mathbf{b}+\mathbf{c})/2$ and $(\mathbf{a}+\mathbf{b}+\mathbf{c})/2$. Discuss the action of these glide planes on a point x, y, z.

10.13 Write down the Seitz operator form for the symmetry operations effecting the following mappings:

$$\begin{aligned}
(x, y, z) &\longrightarrow (1/2-x, 1/2-x, 1/2+z) \\
(x, y, z) &\longrightarrow (1/2+z, 1/2-y, +z) \\
(1/4+x, 1/4+y, 1/4+z) &\longrightarrow (1/2+x, y, 1/2+z) \\
(y-x, y, 2/3-z) &\longrightarrow (y-x, -x, 1/3+z)
\end{aligned}$$

10.14 Discuss the action of the operations of the non-symmorphic space-group $P\frac{4_2}{m}\frac{2_1}{n}\frac{2}{m}$ of the rutile structure, presented in §6.5.2, on a wave-function $\psi(x, y, z)$.

10.15 What are the crystallographic point-groups and the site-symmetry of the (a) Wyckoff position for the following space-groups: $P\bar{4}m2$, $P\bar{4}c2$, $P3m1$, $R\bar{3}c$, and 123?

10.16 Consider the space-group $Pban$. Write out all the essential symmetry operations with respect to a *fixed* origin taken at

(i) the intersection of the 2-fold axes,
(ii) a center of inversion.

10.17 The matrices representing an n-glide plane operation normal to a, and an a-glide plane operation normal to b are

$$\begin{pmatrix} \bar{1} & 0 & 0 & 0 \\ 0 & 1 & 0 & 1/2 \\ 0 & 0 & 1 & 1/2 \\ 0 & 0 & 0 & 1 \end{pmatrix}, \qquad \begin{pmatrix} 1 & 0 & 0 & 1/2 \\ 0 & \bar{1} & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

Determine the nature and orientation of the symmetry operator arising from the combination of the two operators given.

10.18 Consider a crystallographic point-group rotation operation $R \in \mathbb{P} \subset \mathcal{SO}(3)$. Next, consider a unit sphere centered about the origin; the axis of rotation of R intersects the sphere at two points, its *poles of rotation*. Each element of $\mathcal{SO}(3)$ has two such poles.

We consider two poles p_1 and p_2 as *equivalent* if they are related through some $R \in \mathbb{P}$ by

$$p_2 = R\,p_1.$$

This definition allows us through the action of $\mathbb{P}$ to define a stabilizer $\mathcal{G}_p \subset \mathbb{P}$ of a pole p as

$$p = \mathcal{G}_p\,p.$$

(i) Expand $\mathbb{P}$ in terms of cosets of $\mathcal{G}_p$.
(ii) How many poles are equivalent to p, in other words, what is the size of the equivalence class of p?
(iii) Enumerate the subgroups of $\mathbb{P}$ conjugate to $\mathcal{G}_p$.
(iv) How many elements of $\mathbb{P}$ there are in the union of all conjugate subgroups of $\mathcal{G}_p$ other than the identity?
(v) Excluding the identity, show that equating the number of non-identity elements $\mathbb{P}$ to the total number of non-identity elements in all the equivalence classes of poles leads to the relation

$$2\left(1 - \frac{1}{p}\right) = \sum_{i=1}^{m} \left(1 - \frac{1}{g_p^m},\right)$$

where p is the order of $\mathbb{P}$, m is the total number of distinct equivalent pole classes, and g_p the order of $\mathcal{G}_p$.

(vi) The above relation can be used to determine all possible finite subgroups of $\mathcal{SO}(3)$:

(a) Show that the limits of ∞ and 2 that can be imposed on p lead to the inequalities

$$2 > 2(1-(1/p) > 1, \quad 1 > (1-(1/g_p^m)) \geq 1/2.$$

(b) Show, by considering the inequality

$$p \geq g_p \geq 2,$$

that the only possible values m can assume are 2 and 3.

(c) Show that the case of $m = 2$ leads to cyclic point-groups.

(d) Show that for the case of $m = 3$, the relation

$$\frac{1}{n_1} + \frac{1}{n_2} + \frac{1}{n_3} = 1 + \frac{2}{N} > 1$$

with $n_1 \geq n_2 \geq n_3$, requires that $n_3 = 2$.

(e) Show that the inequality $n_1 \geq n_2 \geq n_3$ would then require that n_2 takes on the values 2 and 3 only.

(f) What values can n_1 assume for $n_2 = n_3 = 2$? Show that the corresponding groups are $\mathcal{D}_n$.

(g) Repeat part (iv) for $n_2 = 3$. What are the corresponding point-groups?

10.19 The perovskite structure, with the formula ABX_3 (A and B are cations and X anions) belongs to the space-group $Pm3m$ ($\mathcal{O}_h^1$. The unit cell coordinates of orbit representative atoms are:

$$\begin{aligned} &\text{A}: \quad \text{at} \quad (1/2, 1/2, 1/2) \\ &\text{B}: \quad \text{at} \quad (0, 0, 0) \\ &\text{X}: \quad \text{at} \quad (1/2, 0, 0) \end{aligned}$$

(i) Identify the corresponding Wyckoff positions, and determine the new coordinates if the origin is moved to the A cation site.

(ii) Determine the appropriate space-subgroup and its type that emerge when:

(a) The A and B cations are displaced, by differing amounts, along the [001] direction.

(b) The A and B cations are displaced, by differing amounts, along the [110] direction.

(c) The A and B cations are displaced, by differing amounts, along the [111] direction.

(d) neighboring coplanar anion octahedra are rotated in opposite directions about their z-axes.

10.20 Determine the Wyckoff positions for the space-group $P23\,(T^1)$. (B& C).

10.21 Both the graphite and wurtzite (AB) structures belong to the space-group $P\,6_3mc\;(\mathcal{C}_{6v}^4)$. Their unit cell coordinates are given in the table below.

Graphite			Wurtzite	
(0,0,0)	(0,0,1/2)	A	(1/3,2/3,0)	(2/3,1/3,1/2)
(1/3,2/3,0)	(2/3,1/3,1/2)	B	(1/3,2/3,u)	(2/3,1/3,u+1/2)

Determine their respective Wyckoff positions.

10.2 Solutions

10.1

10.2 If we first consider a face-centered lattice we write its basis vectors as

$$\mathbf{a}_1 = \frac{a}{2}\,\hat{\mathbf{x}} + \frac{a}{2}\,\hat{\mathbf{y}}, \quad \mathbf{a}_2 = \frac{a}{2}\,\hat{\mathbf{x}} + \frac{c}{2}\,\hat{\mathbf{z}}, \quad \mathbf{a}_3 = \frac{a}{2}\,\hat{\mathbf{y}} + \frac{c}{2}\,\hat{\mathbf{z}}$$

Rotation by $\pi/4$ about the c-axis yields

$$\hat{\mathbf{x}} = \frac{1}{\sqrt{2}}\,\hat{\mathbf{x}}' + \frac{1}{\sqrt{2}}\,\hat{\mathbf{y}}',\ \hat{\mathbf{y}} = -\frac{1}{\sqrt{2}}\,\hat{\mathbf{x}}' + \frac{1}{\sqrt{2}}\,\hat{\mathbf{y}}',\ \hat{\mathbf{z}}' = \hat{\mathbf{z}}$$

Thus,

$$\begin{aligned}
\mathbf{a}_1 &= \frac{a}{2}\left(\frac{1}{\sqrt{2}}\,\hat{\mathbf{x}}' + \frac{1}{\sqrt{2}}\,\hat{\mathbf{y}}'\right) + \frac{a}{2}\left(-\frac{1}{\sqrt{2}}\,\hat{\mathbf{x}}' + \frac{1}{\sqrt{2}}\,\hat{\mathbf{y}}'\right) = a'\,\hat{\mathbf{y}}' \\
\mathbf{a}_2 &= \frac{a}{2}\left(\frac{1}{\sqrt{2}}\,\hat{\mathbf{x}}' + \frac{1}{\sqrt{2}}\,\hat{\mathbf{y}}'\right) + \frac{c}{2}\,\hat{\mathbf{z}}' = \frac{a'}{2}\,\hat{\mathbf{x}}' + \frac{a'}{2}\,\hat{\mathbf{y}}' + \frac{c}{2}\,\hat{\mathbf{z}}' \\
\mathbf{a}_3 &= \frac{a}{2}\left(-\frac{1}{\sqrt{2}}\,\hat{\mathbf{x}}' + \frac{1}{\sqrt{2}}\,\hat{\mathbf{y}}'\right) + \frac{c}{2}\,\hat{\mathbf{z}}' = -\frac{a'}{2}\,\hat{\mathbf{x}}' + \frac{a'}{2}\,\hat{\mathbf{y}}' + \frac{c}{2}\,\hat{\mathbf{z}}'
\end{aligned}$$

where $a' = a/\sqrt{2}$.

10.3 The primitive basis of the fcc lattice is

$$\mathbf{a}_1 = \frac{a}{2}\,(\hat{\mathbf{x}} + \hat{\mathbf{y}})\,, \quad \mathbf{a}_2 = \frac{a}{2}\,(\hat{\mathbf{x}} + \hat{\mathbf{z}})\,, \quad \mathbf{a}_3 = \frac{a}{2}\,(\hat{\mathbf{y}} + \hat{\mathbf{z}})$$

Under the action of C_{4z} we obtain

$$\begin{bmatrix}\hat{\mathbf{x}}\\ \hat{\mathbf{y}}\\ \hat{\mathbf{z}}\end{bmatrix} = \begin{pmatrix}0 & 1 & 0\\ -1 & 0 & 0\\ 0 & 0 & 1\end{pmatrix}\begin{bmatrix}\hat{\mathbf{x}}'\\ \hat{\mathbf{y}}'\\ \hat{\mathbf{z}}'\end{bmatrix} = \begin{bmatrix}\hat{\mathbf{y}}'\\ -\hat{\mathbf{x}}'\\ \hat{\mathbf{z}}'\end{bmatrix}$$

Thus,

$$\left.\begin{aligned}\mathbf{a}_1' &= \tfrac{a}{2}\left(\hat{\mathbf{y}}' - \hat{\mathbf{x}}'\right)\\ \mathbf{a}_2' &= \tfrac{a}{2}\left(\hat{\mathbf{y}}' + \hat{\mathbf{z}}'\right)\\ \mathbf{a}_3' &= \tfrac{a}{2}\left(-\hat{\mathbf{x}}' + \hat{\mathbf{z}}'\right)\end{aligned}\right\} \Rightarrow \begin{pmatrix}0 & -1 & 1\\ 0 & 0 & 1\\ -1 & 0 & 1\end{pmatrix}$$

Under the action of C_3^{xyz} we obtain

$$\begin{bmatrix}\hat{\mathbf{x}}\\ \hat{\mathbf{y}}\\ \hat{\mathbf{z}}\end{bmatrix} = \begin{pmatrix}0 & 1 & 0\\ 0 & 0 & 1\\ 1 & 0 & 0\end{pmatrix}\begin{bmatrix}\hat{\mathbf{y}}'\\ \hat{\mathbf{z}}'\\ \hat{\mathbf{x}}'\end{bmatrix} = \begin{bmatrix}\hat{\mathbf{y}}'\\ \hat{\mathbf{x}}'\\ \hat{\mathbf{z}}'\end{bmatrix}$$

Thus,

$$\left.\begin{aligned}\mathbf{a}_1' &= \tfrac{a}{2}\left(\hat{\mathbf{y}}' + \hat{\mathbf{z}}'\right)\\ \mathbf{a}_2' &= \tfrac{a}{2}\left(\hat{\mathbf{y}}' + \hat{\mathbf{x}}'\right)\\ \mathbf{a}_3' &= \tfrac{a}{2}\left(\hat{\mathbf{z}}' + \hat{\mathbf{x}}'\right)\end{aligned}\right\} \Rightarrow \begin{pmatrix}0 & 0 & 1\\ 1 & 0 & 0\\ 0 & 1 & 0\end{pmatrix}$$

As for the action of $\mathfrak{I}$, it is easy to show that it engenders the matrix

$$\begin{pmatrix}-1 & 0 & 0\\ 0 & -1 & 0\\ 0 & 0 & -1\end{pmatrix}$$

10.4

10.5

$$\left(\sigma_x\middle|\boldsymbol{\tau}\right)\,\left(\sigma_y\middle|\boldsymbol{\tau}\right)\,\mathbf{r} \;=\; \left(\sigma_x\sigma_y\middle|\boldsymbol{\tau} + \sigma_x\,\boldsymbol{\tau}\right)\,\mathbf{r}$$

But

$$\boldsymbol{\tau} + \sigma_x\,\boldsymbol{\tau} \;=\; \left(E + \sigma_x\right)\boldsymbol{\tau} \;=\; \begin{pmatrix}0 & 0\\ 0 & 2\end{pmatrix}\begin{bmatrix}\frac{1}{2}\\ \frac{1}{2}\end{bmatrix} \;=\; \begin{bmatrix}0\\ 1\end{bmatrix}$$

which is a primitive lattice vector. Hence,

$$\left(\sigma_x\sigma_y\middle|\boldsymbol{\tau} + \sigma_x\,\boldsymbol{\tau}\right)\,\mathbf{r} \;=\; \left(C_2\middle|\mathbf{0}\right)\,\mathbf{r} \;=\; \begin{pmatrix}-1 & 0\\ 0 & -1\end{pmatrix}\,\mathbf{r} \;=\; -\mathbf{r}$$

10.6 The crystallographic point group $3m$ is just $\mathcal{C}_{3\mathrm{v}}$ which contains the six operations E, C_3, C_3^{-1}, σ_1, σ_2, σ_3.

On the other hand, $m3$ is the tetrahedral group $\mathcal{T}_{\mathrm{h}}$, it contains the operations: E, $4C_3$, $4C_3^{-1}$, $3U$, I, $4S_6, 4S_6^{-1}$, $3\sigma_h$. Although $m3$

contains the inversion operation it is a subgroup of the full cubic group $\mathcal{O}_{\rm h}$ which also contains the inversion operation and is the holohedral point group.

10.7 It was shown in problem 10.2 that a face-centered F-lattice is equivalent to a body-centrered I-lattice. Since the I-lattice has a smaller volume than the F-lattice, the latter is usually ignored.

10.8 The monoclinic structure has a $\mathcal{C}_{\rm 2h}$ holohedry. The 2-fold axis of rotation is usually taken along the c-direction. This, in turn, requires that the c-axis be perpendicular to the a- and b-axes, and that the σ_h lies in the ab-plane. The only restriction on the **a**-**b** angle is that it should be different from $\pi/2$.

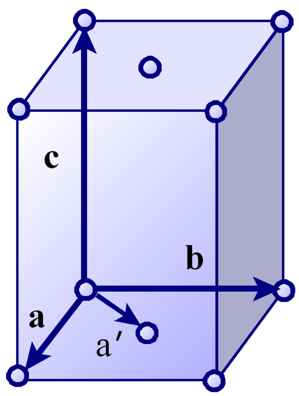

Fig. 10.1. Transformation of a $2C$ monoclinic lattice to a P monoclinic lattice.

Now, a $2C$-structure can be simply reduced to a P-structure replacing, say the **a** primitive basis vector by $\mathbf{a}'$ that connects the lattice point at the origin to the C-centered lattice point, as shown in figure 10.1; this changes the magnitude of **a** and the **a**-**b** angle, but the new structure still satisfies the monoclinic conditions and has a smaller primitive cell volume.

This is not the case for $2A$ or $2B$ centering. If we try to construct a P-lattice by introducing basis vectors that connect the origin-point to the A- or B-centered point we lose the monoclinic conditions. Yet, we know that the lattice posses a 2-fold axis of symmetry. Thus, we conclude that this lattice system has an orthorhombic unit cell which contains multiple primitive cells.

The body-centered configuration can be easily transformed to a $2B$ centered lattice as shown in figure 10.2.

10.9 As was shown in Chapter 1, only the improper rotations S_2, S_3, S_4

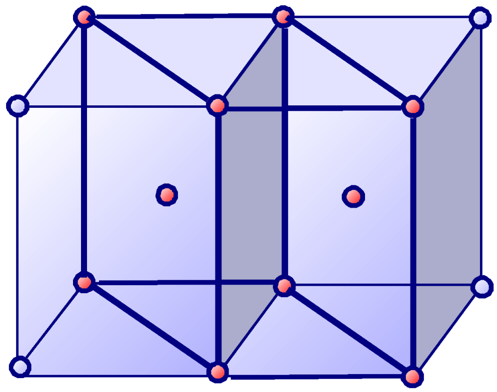

Fig. 10.2. Transformation of an I-monoclinic lattice to a $2B$ monoclinic lattice.

and S_6 are allowed in crystalline structures. It was also shown that they have the form

$$S_2 = I, \quad S_3 = IC_6^{-1}, \quad S_4 = IC_4^{-1}, \quad S_6 = IC_3^{-1}$$

Now, we consider the case

$$\begin{aligned}&\left(S_3 | \boldsymbol{\tau}_\parallel\right)^6 = (E | \mathbf{0})\\ &\boldsymbol{\tau}_\parallel + IC_6^{-1}\boldsymbol{\tau}_\parallel + C_3^{-1}\boldsymbol{\tau}_\parallel + IC_2\boldsymbol{\tau}_\parallel + C_3\boldsymbol{\tau}_\parallel + IC_6\boldsymbol{\tau}_\parallel = \mathbf{0}\end{aligned}$$

which gives

$$3(E + I)\boldsymbol{\tau}_\parallel = 0 \times \boldsymbol{\tau}_\parallel = \mathbf{0}$$

Consequently, we can choose $\boldsymbol{\tau}_\parallel = \mathbf{0}$.

10.10 Although the point group $\mathcal{C}_{3\mathrm{h}}$ has only a 3-fold proper rotation axis, it contains improper rotations of S_3 type. Such operations can be written as

$$S_3 = \sigma_h C_3 = IC_2C_3 = IC_6^{-1}$$

which involve a 6-fold axis of rotation.

By contrast, the point group $\bar{6}\,\mathcal{S}_6$ does not contain a 6-fold axis of proper rotation, but instead contains improper rotatation of the S_6 type which have the form

$$S_6 = \sigma_h C_6 = IC_2C_6 = IC_3^{-1}$$

10.11

10.12 The space group $P4nc$ contains the operations

$$E = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}, \; C_2 = \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}, \; C_4 = \begin{pmatrix} 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}, \; C_4^2 = \begin{pmatrix} 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix},$$

$$\sigma_x = \begin{pmatrix} -1 & 0 & 0 & 1/2 \\ 0 & 1 & 0 & 1/2 \\ 0 & 0 & 1 & 1/2 \end{pmatrix}, \; \sigma_y = \begin{pmatrix} 1 & 0 & 0 & 1/2 \\ 0 & -1 & 0 & 1/2 \\ 0 & 0 & 1 & 1/2 \end{pmatrix}, \; \sigma_{xy} = \begin{pmatrix} 0 & 1 & 0 & 1/2 \\ 1 & 0 & 0 & 1/2 \\ 0 & 0 & 1 & 1/2 \end{pmatrix}, \; \sigma_{\bar{x}\bar{y}} = \begin{pmatrix} 0 & -1 & 0 & 1/2 \\ -1 & 0 & 0 & 1/2 \\ 0 & 0 & 1 & 1/2 \end{pmatrix}$$

The choice of the nonprimitive translation vector $\boldsymbol{\tau} = \left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right)$ is based on having a common origin. However, the glide planes σ_x and σ_y coincide with the yz and xz planes, respectively. Hence the component of $\boldsymbol{\tau}$ perpendicular to these planes can be removed by an origin shift. This leads to

$$\left(\sigma_x \middle| 0, \frac{1}{2}, \frac{1}{2}\right), \; \left(\sigma_y \middle| \frac{1}{2}, 0, \frac{1}{2}\right)$$

10.13

10.14 In the rutile structure example Of §6.5.2, we were given the coset representatives of the symmetry operations as

$$(E|\mathbf{0}), \; (C_2|\mathbf{0}), \; (U_{xy}|\mathbf{0}), \; (U_{\bar{x}y}|\mathbf{0}), \; (I|\mathbf{0}), \; (\sigma_h|\mathbf{0}), \; (\sigma_{xy}|\mathbf{0}), \; (\sigma_{\bar{x}y}|\mathbf{0}),$$
$$(C_4|\boldsymbol{\tau}), \; (C_4^{-1}|\boldsymbol{\tau}), \; (U_x|\boldsymbol{\tau}), \; (U_y|\boldsymbol{\tau}), \; (S_4|\boldsymbol{\tau}), \; (S_4^{-1}|\boldsymbol{\tau}), \; (\sigma_x|\boldsymbol{\tau}), \; (\sigma_y|\boldsymbol{\tau}),$$

where the nonprimitive vectors $\boldsymbol{\tau} = (\mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3)/2$ are associate with the origin taken at the center of the unit cell, namely, $(1/2, 1/2, 1/2)$, or at $(0, 0, 0)$. These points comprise the Wyckoff (a)-position.

The action of these operations on the wavefunction $\Psi(x, y, z)$ can be written as

$(E\|\mathbf{0})$ $\Psi(x, y, z)$,	$(I\|\mathbf{0})$ $\Psi(\bar{x}, \bar{y}, \bar{z})$,	$(C_2\|\mathbf{0})$ $\Psi(\bar{x}, \bar{y}, z)$,	$(\sigma_h\|\mathbf{0})$ $\Psi(x, y, \bar{z})$.
$(\sigma_{\bar{x}y}\|\mathbf{0})$ $\Psi(y, x, z)$,	$(U_{xy}\|\mathbf{0})$ $\Psi(y, x, \bar{z})$,	$(\sigma_{xy}\|\mathbf{0})$ $\Psi(\bar{y}, \bar{x}, z)$,	$(U_{\bar{x}y}\|\mathbf{0})$ $\Psi(\bar{y}, \bar{x}\bar{z})$.
	$(U_y\|\boldsymbol{\tau})$ $\Psi\left(\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z\right)$,	$(U_x\|\boldsymbol{\tau})$ $\Psi\left(\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z\right)$	
	$(\sigma_y\|\boldsymbol{\tau})$	$(\sigma_x\|\boldsymbol{\tau})$	

$\Psi\left(\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z\right)$,	$\Psi\left(\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z\right)$.
$(S_4\|\boldsymbol{\tau})$ $\Psi\left(\frac{1}{2}+y, \frac{1}{2}-x, \frac{1}{2}-z\right)$,	$(C_4^{-1}\|\boldsymbol{\tau})$ $\Psi\left(\frac{1}{2}+y, \frac{1}{2}-x, \frac{1}{2}+z\right)$.
$(S_4^{-1}\|\boldsymbol{\tau})$ $\Psi\left(\frac{1}{2}-y, \frac{1}{2}+x, \frac{1}{2}-z\right)$,	$(C_4\|\boldsymbol{\tau})$ $\Psi\left(\frac{1}{2}-y, \frac{1}{2}+x, \frac{1}{2}+z\right)$.

10.15 The following table shows Wyckoff (a)-position and its site-symmetry for the space-groups listed:

Space-group	Point-group	Wyckoff (a)-position	Site-symmetry
$P\bar{4}m2$	$\bar{4}m2$	$(0,0,0)$	$\bar{4}m2$
$P\bar{4}c2$	$\bar{4}m2$	$\left(0,0,\frac{1}{4}\right)$, $\left(0,0,\frac{3}{4}\right)$	$222\,.$
$P31m$	$31m$	$(0,0,z)$	$3m\,.$
$R\bar{3}c$	$\bar{3}m$	$\left(\frac{1}{4},\frac{1}{4},\frac{1}{4}\right)$, $\left(\frac{3}{4},\frac{3}{4},\frac{3}{4}\right)$	32
	$\bar{3}m$	$\left(0,0,\frac{1}{4}\right)$, $\left(0,0,\frac{3}{4}\right)$	32
$P23$	23	$(0,0,0)$	$23\,.$

10.16 We obtain for the stated choices of origin:

(i) Origin at the intersection of the 2-fold axes

$$E = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}, \; C_2 = \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}, \; U_y = \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \end{pmatrix}, \; U_x = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \end{pmatrix},$$

$$I = \begin{pmatrix} -1 & 0 & 0 & \frac{1}{2} \\ 0 & -1 & 0 & \frac{1}{2} \\ 0 & 0 & -1 & 0 \end{pmatrix}, \; \sigma_z = \begin{pmatrix} 1 & 0 & 0 & \frac{1}{2} \\ 0 & 1 & 0 & \frac{1}{2} \\ 0 & 0 & -1 & 0 \end{pmatrix}, \; \sigma_y = \begin{pmatrix} 1 & 0 & 0 & \frac{1}{2} \\ 0 & -1 & 0 & \frac{1}{2} \\ 0 & 0 & 1 & 0 \end{pmatrix}, \; \sigma_x = \begin{pmatrix} -1 & 0 & 0 & \frac{1}{2} \\ 0 & 1 & 0 & \frac{1}{2} \\ 0 & 0 & 1 & 0 \end{pmatrix},$$

(ii) A center of inversion

$$E = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}, \; C_2 = \begin{pmatrix} -1 & 0 & 0 & \frac{1}{2} \\ 0 & -1 & 0 & \frac{1}{2} \\ 0 & 0 & 1 & 0 \end{pmatrix}, \; U_y = \begin{pmatrix} -1 & 0 & 0 & \frac{1}{2} \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \end{pmatrix}, \; U_x = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & \frac{1}{2} \\ 0 & 0 & -1 & 0 \end{pmatrix},$$

$$I = \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \end{pmatrix}, \; \sigma_z = \begin{pmatrix} 1 & 0 & 0 & \frac{1}{2} \\ 0 & 1 & 0 & \frac{1}{2} \\ 0 & 0 & -1 & 0 \end{pmatrix}, \; \sigma_y = \begin{pmatrix} 1 & 0 & 0 & \frac{1}{2} \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}, \; \sigma_x = \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & 1 & 0 & \frac{1}{2} \\ 0 & 0 & 1 & 0 \end{pmatrix},$$

10.17 The two operations can be written as

$$\left(\sigma_x \middle| 0, \frac{1}{2}, \frac{1}{2}\right) \left(\sigma_y \middle| \frac{1}{2}, 0, 0\right) = \left(\sigma_x \sigma_y \middle| \left(0, \frac{1}{2}, \frac{1}{2}\right) + \sigma_x \left(\frac{1}{2}, 0, 0\right)\right)$$

$$= \left(C_{2z} \middle| -\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right)$$

10.18 (i) $\mathbb{P} = \sum_{i=1}^{p/g_p} \mathtt{R}_i \, \mathcal{G}_p$.

(ii) The number of equivalent poles is equal to the index of $\mathcal{G}_p$ in $\mathbb{P}$; thus, the size of the equivalence class $\mathtt{C}_m$ of pole m is

$$c_m = \frac{p}{g_p^m}$$

(iii) For every $p_i = R_i \, p_1$ there corresponds a conjugate subgroup $\mathcal{G}_{p_i} = R_i \, \mathcal{G}_{p_1} \, R_i^{-1}$.

(iv) The order of $\mathbb{P}$ can be expressed as

$$p = g_p^m c_m$$

Moreover, there are $g_p^m - 1$ and $p - 1$ non-identity elements in $\mathcal{G}_{p_m}$ and $\mathbb{P}$, respectively. Thus, in total we have

$$\sum_{m=1}^{\ell} c_m \left(g_p^m - 1\right)$$

non-identity elements, where ℓ is the number of distinct pole classes. Now, since each rotation element has two poles, we get

$$p - 1 = \frac{1}{2} \sum_{m=1}^{\ell} c_m \left(g_p^m - 1\right)$$

or

$$2\left(1 - \frac{1}{p}\right) = \sum_{m=1}^{\ell} \left(1 - \frac{1}{g_p^m}\right) \tag{10.1}$$

(v) For $p = \infty$, the lhs of (10.1) becomes equal to 2, while for $p = 2$ it is equal to 1. Since $p < \infty$, i.e. finite, we obtain

$$2 > 2\left(1 - \frac{1}{p}\right) \geq 1 \tag{10.2}$$

and since $p \geq g_p^m \geq 2$ and $g_p^m < \infty$, we get

$$1 > \left(1 - \frac{1}{g_p^m}\right) \geq \frac{1}{2} \tag{10.3}$$

(vi) We have

$$2 - \frac{2}{p} = \ell - \sum_{m=1}^{\ell} \frac{1}{g_p^m} \Rightarrow \frac{2}{p} = \sum_{m=1}^{\ell} \frac{1}{g_p^m} - \left(\ell - 2\right)$$

ℓ must be greater than 1, since for $\ell = 1$, inequality (10.2) requires that the lhs of (10.1) be ≥ 1, while inequality (10.3) requires that the rhs be < 1. Again, for $4 \leq \ell$ inequality (10.2) requires that the lhs of (10.1) be < 2, while inequality (10.3) requires that the rhs be ≥ 2. Hence ℓ can assume only the values 2 and 3.

(vii) For $\ell = 2$ we have

$$\frac{2}{p} = \frac{1}{g_p^1} + \frac{1}{g_p^2}$$

But since $\dfrac{1}{g_p^1} \geq \dfrac{1}{p}$, and $\dfrac{1}{g_p^2} \geq \dfrac{1}{p}$,

$$g_p^1 = g_p^2 = p \geq 2$$

In this case there are two inequivalent poles, each has the point group $\mathbb{P}$ as its stabilizer. Since every rotation has two poles, we recognize these groups as cyclic rotation point groups $\mathcal{C}_n$. The crystallographic point groups among them are n=2, 3, 4, and 6.

(viii) For $\ell = 3$, (10.1) gives

$$1 + \frac{2}{p} = \frac{1}{g_p^1} + \frac{1}{g_p^2} + \frac{1}{g_p^3} > 1 \tag{10.4}$$

Assuming $g_p^1 \geq g_p^2 \geq g_p^3$, and setting $g_p^3 \geq 3$ we find that

$$\frac{1}{g_p^1} + \frac{1}{g_p^2} + \frac{1}{g_p^3} \leq 1$$

which contradicts (10.4); hence, g_p^3 must be equal to 2.

(ix) For $\ell = 3$ and $g_p^3 = 2$ we obtain

$$\frac{1}{g_p^1} + \frac{1}{g_p^2} > \frac{1}{2} + \frac{2}{p}$$

For $g_p^1 \geq g_p^2$, $g_p^2 \geq 4$ we find that

$$\frac{1}{g_p^1} + \frac{1}{g_p^2} \leq \frac{1}{2} < \frac{1}{2} + \frac{2}{p}$$

hence g_p^2 can only assume the values 2 and 3.

(x) Setting $g_p^2 = g_p^3 = 2$, we obtain

$$p = 2g_p^1 \geq 4, \quad g_p^1 = 2, 3, 4, \ldots$$

Here, the stabilizer of pole p_1, $\mathcal{G}_p^1$ is a cyclic group. A second pole, p_2, of the rotation axis is in the pole equivalence class of p_1, since it can be obtained from p_1 by a 2-fold rotation in either $\mathcal{G}_p^2$ or $\mathcal{G}_p^3$. There g_p^1 poles in each of the inequivalent pole classes corresponding $\mathcal{G}_p^2$ and $\mathcal{G}_p^3$. It is now obvious that the point group $\mathbb{P}$ is one of the dihedral point groups.

(xi) For $g_p^2 = 3$, $g_p^3 = 2$ we have

$$\frac{1}{g_p^1} - \frac{1}{6} = \frac{2}{p} \Rightarrow p = \frac{12g_p^1}{6 - g_p^1}$$

Thus, setting

(a) $g_p^1 = 3$, we obtain $p = 12$. This is just the tetrahedral point group $\mathcal{T}$ of order 12. It contains 3 pole classes : 2 with 4 poles of 3-fold rotations and 1 with 6 poles of 2-fold rotations.

(b) $g_p^1 = 4$, we obtain $p = 24$. This is the octahedral point group $\mathcal{O}$ of order 24. It has 3 pole classes : one contains 6 poles of 4-fold rotations, the second has 8 poles of 3-fold rotations, and the third has 12 poles of 2-fold rotations.

(c) $g_p^1 = 5$, we obtain $p = 60$. This is the icosahedral point group of order 60.

10.19.(a) The Wyckoff positions occupied by the perovskite atoms are

A : (1/2, 1/2, 1/2) is the (b) Wyckoff position,

B : (0, 0, 0) is the (a) Wyckoff position,

C : (1/2, 0, 0) is the (d) Wyckoff position,

10.19.(b) The emerging space subgroups are

(i) For A at (0, 0, u) and B at (1/2, 1/2, 1/2+w) the structure becomes noncentrosymmetric. It has a 4-fold rotation symmetry only about the z-axis, and thus tetragonal symmetry emerges. Moreover, since $u \neq w$ the structure does not possess 2-fold symmetry axes or a mirror plane normal to the z-axis. Thus, the point group symmetry reduces to $\mathcal{C}_{4\mathrm{v}}$, and since the primitive cell basis vectors are left invariant the subgroup is the t-equal $P4mm$ $\left(\mathcal{C}_{4\mathrm{v}}^1\right)$.

(ii) For A at (u, u, 0) and B at (1/2+w, 1/2+w, 1/2) the 4-fold symmetries are completely lost. The only rotational symmetry left is a 2-fold axis along the [110]-direction, plus two mirror planes: a σ_z and a $\sigma_{\bar{x}\bar{y}}$. Thus, the space subgroup is the symmorphic and t-equal $C2mm$ $\left(\mathcal{C}_{2\mathrm{v}}^{14}\right)$

(iii) For A at (u, u, u) and B at (1/2+w, 1/2+w, 1/2+w) $R3m$ $\left(\mathcal{C}_{3\mathrm{v}}^5\right)$

(iv) For A at (u, 0, 0) and B at (1/2+w, 1/2, 1/2)

10.20 The Wyckoff positions for the space group $P23$ are given in the following table

Table 10.2: Wyckoff Positions of Space Group $P23$ $\left(T^1\right)$

Multiplicity	Wyckoff Letter	Site Symmetry	Coordinates
(x,y,z), (-x,-y,z), (-x,y,-z), (x,-y,-z)			
12	j	1	(z,x,y), (z,-x,-y), (-z,-x,y), (-z,x,-y)
			(y,z,x), (-y,z,-x), (y,-z,-x), (-y,-z,x)

Table 10.2: Continued

6	i	2..	(x,1/2,1/2), (-x,1/2,1/2), (1/2,x,1/2) (1/2,-x,1/2), (1/2,1/2,x), (1/2,1/2,-x)
6	h	2..	(x,1/2,0), (-x,1/2,0), (0,x,1/2), (0,-x,1/2), (1/2,0,x), (1/2,0,-x)
6	g	2..	(x,0,1/2), (-x,0,1/2), (1/2,x,0), (1/2,-x,0), (0,1/2,x), (0,1/2,-x)
			(x,0,0), (-x,0,0), (0,x,0),
6	f	2..	(0,-x,0), (0,0,x), (0,0,-x)
4	e	.3.	(x,x,x), (-x,-x,x), (-x,x,-x), (x,-x,-x)
3	d	222..	(1/2,0,0), (0,1/2,0), (0,0,1/2)
3	c	222..	(0,1/2,1/2), (1/2,0,1/2), (1/2,1/2,0)
1	b	23.	(1/2,1/2,1/2)
1	a	23.	(0,0,0)

10.21 The Wyckoff positions for graphite and wurtzite are given in the table below.

System	Atomic Positions		Wyckoff Position
Graphite	(0,0,0)	(0,0,1/2)	(a)
	(1/3,2/3,0)	(2/3,1/3,1/2)	(b)
Wurtzite	(1/3,2/3,0)	(2/3,1/3,1/2)	(b)
	(1/3,2/3,u)	(2/3,1/3,u+1/2)	(b)

11
Space groups: Irreps

11.1 Exercises

11.1 Show that the action of a space-group operation $\big(R|\mathbf{w}\big)$ on a planewave $\exp\big(i\mathbf{k}\cdot\mathbf{r}\big)$, leads to

$$\big(R|\mathbf{w}\big)\ \exp\big(i\mathbf{k}\cdot\mathbf{r}\big) \;=\; \exp\big(iR\,\mathbf{k}\cdot(\mathbf{r}-\mathbf{w})\big).$$

11.2 The choice of coset representatives is not unique. Show that if we replace the coset representative C_4^- by σ_d^2 we find, for example,

$$\mathbf{M}^*\left(C_4^+\right) \;=\; \begin{pmatrix} 0 & 0 & 0 & \sigma_v^1 \\ 0 & 0 & E & 0 \\ E & 0 & 0 & 0 \\ 0 & \sigma_v^1 & 0 & 0 \end{pmatrix}$$

Because we have used nonstandard coset representatives that do not form a group, the modified ground representation contains a mix of matrix elements from $\mathcal{P}_\Delta$. Nonetheless, the set of matrices obtained, $\mathbf{M}^*\left(R\right)$, still obey the group multiplication table for $\mathcal{C}_{4v}$.

11.3 Show that $\mathbb{T}_\mathbf{k}$ is a normal subgroup of $\mathbb{S}_\mathbf{k}$ and of $\mathbb{T}$.

11.4 Consider the 2-dimensional square net; show that

(i) The translation subgroup of the wave vector $\mathbb{T}_{\bar{\Delta}}$ is a subset of all translation vectors $(m_x a, m_y a) \in \mathbb{T}$ that satisfy the condition

$$\mathbb{T}_{\bar{\Delta}} \equiv \big\{(E\big|(m_1 a, m_y a)\big\};\quad m_1 a k \;=\; 2n\pi,\ \text{and}\ \forall\, m_y.$$

with cosets of $\mathbb{S}_{\bar{\Delta}}$

$$\mathbb{T}_{\bar{\Delta}}, (E\big|(ma,0))\mathbb{T}_{\bar{\Delta}}, (\sigma_v\big|(ma,0))\mathbb{T}_{\bar{\Delta}};\quad m \neq\ m_1$$

which form the quotient group $\mathcal{Q}_{\bar{\Delta}}$.

(ii) The translation subgroup of the wave vector $\mathbb{T}_\Sigma$ is the subgroup

$$\mathbb{T}_\Sigma \equiv \left\{ (E \big| (m_1 a, m_2 a) \right\}; \quad (m_1 + m_2) ak \; = \; 2n\pi.$$

with cosets of $\mathbb{S}_\Sigma$

$$\mathbb{T}_\Sigma, (E \big| (ma, m'a))\mathbb{T}_\Sigma, (\sigma_d \big| (ma, m'a))\mathbb{T}_\Sigma; \quad m{+}m'a \neq \; m_1{+}m_2$$

which form the quotient group $\mathcal{Q}_\Sigma$.

(iii) The translation subgroup of the wave vector $\mathbb{T}_M$ is the subgroup

$$\begin{aligned} \mathbb{T}_M \;\; &\equiv \;\; \left\{ (E \big| (m_1 a, m_2 a) \right\}; \quad m_1 + m_2 \text{ even}, \\ &= \;\; \left\{ (E \big| \mathbf{t}_e) \right\}. \end{aligned}$$

with cosets of $\mathbb{G}_M$

$$(R_{i\mathbf{k}} \big| (0,0))\mathbb{T}_M, (R_{i\mathbf{k}} \big| (a,0))\mathbb{T}_M, (R_{i\mathbf{k}} \big| (0,a))\mathbb{T}_M$$

which form the quotient group $\mathcal{Q}_M$.

11.5 Consider the 2-dimensional space-group $p4mm$ presented in §11.2.2.1. Determine:

(i) the two 4-dimensional Irreps for the Σ line.
(ii) the 2-dimensional Irrep of for the M-point.

11.6 Consider the 2D symmorphic space-group $p\,6mm$.

(i) Determine its reciprocal lattice basis and determine the relative orientation of its Brillouin zone, shown in figure, to its Wigner-Seitz cell.
(ii) For wavevectors at: $\bar{\Gamma}$, $\bar{\Delta}$, $\bar{\Sigma}$, M, and K, determine:

(a) the star of the wavevector.
(b) The wavevector point-subgroup.
(c) The corresponding point-subgroup Irreps.
(d) The corresponding ground Rep.

11.7 Repeat part (b) of the previous problem for the space-group $P\,d3m$, and the symmetry points Γ, Δ, Λ, Σ, X, L, W, and K.

11.8 Use Herrings method to obtain the Irreps of the rutile structure, $P\dfrac{4_2}{m}\dfrac{2_1}{n}\dfrac{2}{m}$, at the X-point.

11.9 Consider the space-group $P23\,(T^1)$. Determine the star of $\mathbf{k}_\Gamma$ and $\mathbf{k}_M$, their ground Reps and the Irreps of their little groups.

11.10 The translation group of the wave vector $\mathbb{T}_Y$ is the subgroup

$$\mathbb{T}_Y \equiv \left\{(E\big|(m_1 a, m_2 a)\right\}; \quad m_2 k a \;=\; (2n - m_1)\pi. \tag{11.1}$$

with cosets of $\mathbb{G}_Y$

$$\mathbb{T}_Y, (\,E\big|(ma,0))\mathbb{T}_Y, (C_2\big|(ma,0))\mathbb{T}_Y; \quad m \neq \; m_1$$

which form the quotient group $\mathcal{Q}_Y$.

11.11 The translation group of the wave vector $\mathbb{T}_\Sigma$ is the subgroup

$$\mathbb{T}_X \equiv \left\{(\,E\big|(m_1 a, m_y a)\right\}; \quad m_1 \text{ even and } \forall m_y. \tag{11.2}$$

with cosets of $\mathbb{G}_X$

$$\mathbb{T}_X, (\,E\big|(a,0))\mathbb{T}_X, (\,C_2\big|(a,0))\mathbb{T}_X, (\,\sigma_v^1\big|(a,0))\mathbb{T}_X, (\,\sigma_v^2\big|(a,0))\mathcal{T}_X \tag{11.3}$$

which form the quotient group $\mathcal{Q}_\Sigma$.

11.12 Show that (**??**) can be generalized for the case of the more general space-group operator $\left(R\big|t\right)$.

11.13 Given two vectors, $\mathbf{k}$ and $\mathbf{t}$, and a rotation operator R with inverse R^{-1}, show that the angle between the vectors $R\mathbf{k}$ and $\mathbf{t}$ equals the angle between the vectors $\mathbf{k}$ and $R^{-1}\mathbf{t}$. Thus

$$\mathbf{k} \cdot R^{-1}\mathbf{t} = R\mathbf{k} \cdot \mathbf{t}.$$

11.14 Show that in two dimensions, the glide and a two-fold screw axis are identical.

11.15 Find the elements of the point-group $\mathcal{P}$ for the two-dimensional non-symmorphic crystal of figure. 4. Show that the elements of $\mathcal{P}$ actually form a group. Show that the point-group is not a subgroup of the space-group because of the existence of a glide plane.

11.16 Find the elements of the little-group of the wave vector, $\mathbb{S}_\mathbf{k}$, for the nonsymmorphic crystal of figure. 4, for each of the $\mathbf{k}$-values (labeled by $\mathbf{\Gamma}$, $\mathbf{\Delta}$, $\cdots$) in figure. 11*b*.

11.17 Find the elements of the point-group $\mathcal{P}_\mathbf{k}$, for the nonsymmorphic crystal of figure. 4, for each of the $\mathbf{k}$-values (labeled by $\mathbf{\Gamma}$, $\mathbf{\Delta}$, $\cdots$, in figure 7b.

11.18 Consider the space-groups associated with the fcc lattice.

(i) Determine the stars of $\mathbf{k}$ at the X, L, W points on the surface of the BZ.

(ii) The diamond structure belongs to the space-group $Fd3m$. Use Herrings method to obtain the corresponding Irreps at the above points.

(iii) Repeat problem for the hcp structure at the BZ surface points M, K, A.

11.2 Solutions

4.1

12

Time-reversal symmetry: color groups and the Onsager relations

12.1 Exercises

12.1 Demonstrate that the time-reversal operator commutes with the inversion operator and all proper rotation operators. [Hint: write the rotation operator in terms of the angular momentum **J**.]

12.2 Use Table 7 to generate the elements of the following double point-groups, and then determine their Irreps:

(i) $\mathfrak{D}3$.
(ii) $\mathfrak{D}4$.
(iii) $\mathfrak{D}222$.
(iv) $\mathfrak{D}32$.
(v) $\mathfrak{D}\bar{4}2m$.

12.3 Consider the crystallographic point-groups $\dfrac{n}{m}\,\dfrac{2}{m}\,\dfrac{2}{m}$, $n = 1$, 2, 4 and 6.

(i) Enumerate all subgroups of index 2 in each of these point-groups.
(ii) Determine the corresponding dichromatic groups.

12.4 CoF_2 has the rutile structure in its paramagnetic phase, with gray space-group $P\,\dfrac{4_2}{mnm}\,\underline{1}$. In the antiferromagnetic phase, the spins align along the z-axis with the corner spins pointing opposite to the spin at the center of the unit cell.

(i) Determine the appropriate dichromatic space-group associated with that phase, and identify its unitary subgroup. [Refer to Example 12.5]
(ii) Discuss the changes that occur to the Wyckoff site-symmetries of $P\,\dfrac{4_2}{mnm}$, listed in chapter 10 §6.5.2.

(iii) Identify the Brillouin zone of the unitary space-subgroup, and compare its high-symmetry points and lines with those of the primitive tetragonal zone associated with $P\,\dfrac{4_2}{mnm}$.

12.5 Consider the composite dichromatic/translation operator $\mathcal{C}\,\hat{\mathbf{a}}_i$, where $\mathbf{a}_i$, $i = 1, 2$ is a translation basis vector.

(i) Simplify the product

$$\prod_{i=1}^{2} (\mathcal{C}\,\hat{\mathbf{a}}_i)^{m_i}\,,$$

for $(\sum_i\, m_i)$ even and odd, bearing in mind that $\mathcal{C}^2 = E$, and that the two operators commute.

(ii) Since the elements R of the lattice holohedry also commute with $\mathcal{C}$, namely $R\,\mathcal{C} = \mathcal{C}\,R$, show that

$$R\,\mathcal{C}\,\mathbf{t}_1\,R^{-1} \;=\; \mathcal{C}\,\mathbf{t}_2, \qquad \mathbf{t}_1,\, \mathbf{t}_2 \,\in\, \mathbb{T}.$$

(iii) Show that the basis sets $(\mathcal{C}\,\hat{\mathbf{a}}_1,\, \hat{\mathbf{a}}_2)$ and $(\mathcal{C}\,\hat{\mathbf{a}}_1,\, \mathcal{C}\,\hat{\mathbf{a}}_2)$ produce equivalent lattices

12.6 Determine the translation vectors $\boldsymbol{\tau}_0$ that produce each of the 2-dimensional dichromatic lattices of figure 4.

12.7 Write down the Seitz operator that would represent a dichromatic screw axis operation involving an n-fold rotation. Use this form to determine the allowed values of n for dichromatic nonsymmorphic space-groups.

12.8 Use the Irreps of $\mathfrak{D}32$, obtained in problem 2 above, to derive the CoIrreps of $\mathfrak{D}\,\underline{3m}$ and to identify the extra degeneracies associated with each.

12.9 Consider a Co^{2+} ion in a CoO crystal. The free ion has a ^4F configuration, that is $L = 3$, $S = 3/2$. In the crystal it has octahedral site-symmetry. Derive the ensuing splitting when:

(i) we neglect the spin angular momentum,

(ii) we include the spin angular momentum.

12.10 In their high temperature paramagnetic phase, CoF_2 and NiF_2 belong to the grey group $P\,\dfrac{4_2}{mnm}\underline{1}$. Below their respective Néel temperatures they become antiferromagnetic; CoO has the dichromatic group $P\,\dfrac{\underline{4_2}}{mn\underline{m}}$, while NiF_2 exhibits additional weak ferromagnetism and has the dichromatic group $P\,n\underline{nm}$. The free ions Ni^{2+} and Co^{2+}

have ground state configurations $^3F_4$ and $^4F_{9/2}$, respectively. Discuss the ensuing crystal field splittings for each of these crystals.

12.2 Solutions

4.1

13

Tensors and Tensor Fields

13.1 Exercises

13.1 Consider the case where the symmetry point-group of a system possesses two conjugate inequivalent Irreps ${}^1E$ and ${}^2E$. A basis for such a pair is usually given in the form $x_1 \pm i x_2$. Now, suppose that the system exhibits a phenomenon where two of its physical properties, $(x_1,\, x_2)$ and $(y_1,\, y_2)$, form two bases for such a pair of Irreps, namely, $x_1 \pm i x_2$ and $y_1 \pm i y_2$, which in turn are related by tensors

$$y_1 + i y_2 \;=\; \mathfrak{T}\,(x_1 + i x_2), \qquad y_1 - i y_2 \;=\; \mathfrak{T}^*\,(x_1 - i x_2).$$

(i) Determine the tensor that relates the physical vectors $\mathbf{X} = [x_1,\, x_2]$ and $\mathbf{Y} = [y_1,\, y_2]$.

(ii) What happens when that tensor is intrinsically symmetric?

13.2 Consider the wurtzite structure with $6mm\,(\mathcal{C}_{6v})$ point-group symmetry. Determine the number of independent parameters in:

(i) The polarization tensor.

(ii) The piezoelectric tensor.

(iii) The Hall tensor.

(iv) The elasticity tensor.

13.3 Determine the nonvanishing components of the piezoelectric tensor for a crystal with point-group symmetry $2\,(\mathcal{C}_2)$. How would you extrapolate your results to crystals with $\mathbb{P} = 222\,(\mathcal{D}_2)$?

13.4 Quartz crystals are commonly used as piezoelectric transducers. It has $\mathbb{P} = 32\,(\mathcal{D}_3)$.

(i) Follow the procedure of Example 13.7 to show that its piezoelectric tensor has the form

$$\begin{bmatrix} p_{11} & -p_{11} & 0 & p_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & -p_{14} & -2p_{11} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

(ii) Determine the electric field orientation that can produce expansion/contraction along the x_1-axis.

13.2 Solutions

4.1

14
Electronic Properties of Solids

14.1 Exercises

14.1 Derive an expression for the electron energy band dispersion of a monovalent bcc metal, such as Na, using only first-neighbor terms in (**??**).

14.2 Describe the motion in real space of free electrons in each of the eight free electron states just referred to.

14.3 Verify that the free-electron energy bands of Fig. 12.4 are correct.

14.4 Show that the X point in Figure 13.4 occurs at $2\pi/a$ and not at π/a, as it does for a one-dimensional crystal. What is the reason for the difference?

14.5 Show that the eigenfunction coefficients, $C_{\mathbf{k}-\mathbf{G}}$, for wave functions at the W point of the Brillouin zone for the fcc lattice, using the eigenvalues of are as given in table 1.

14.7 Verify (**??**) and (**??**).

14.8 Solve for the eigenvalues and eigenfunctions at the X point. Identify the splittings. Find the symmetrized wave functions. etc. Do the L point? We already have the $\mathbf{G}$ vectors. Choose an energy?

14.9 Show that the matrix element of v_{ps}^{KKRZ} between plane waves is

$$V_{ps,GG'}^{\mathrm{KKRZ}} = V_{\mathbf{GG}'} + \frac{4\pi R_c}{\Omega} \sum_l (2l+1) \left[L_l - \kappa \frac{j_l'(\kappa R_c)}{j_l(\kappa R_c)} \right] \times j_l\big(|\mathbf{k}-\mathbf{G}|R_c\big)\, j_l\big(|\mathbf{k}-\mathbf{G}'|R_c\big)\, P_l(\cos\theta_{\mathbf{GG}'}), \quad (14.1)$$

and that the term in square bracket in (2.6.40) can be written as

$$-(1/\kappa)[Rj_l(\kappa R)]^{-2} \tan\eta_l', \quad (14.2)$$

in terms of the modified phase shift η_l' defined by

$$\cot\eta_l' = \cot\eta_l - n_l(\kappa R_c)/j_l(\kappa R_c), \quad (14.3)$$

The proof follows readily from (2.6.31) by using the Wronskian identity $x^2(jn' - j'n) = 1$.

14.2 Solutions

4.1

15

Dynamical Properties of Molecules, Solids and Surfaces

15.1 Exercises

15.1 NaCl belongs to the space group $Fm3m\,(O_h^5)$. The Na^+-Cl^- bond has $C_{4\text{v}}$ symmetry, while the Na-Na and Cl-Cl bonds mm. Determine the forms of the force constant matrices corresponding to these two bond-types.

15.2 **The rigid ion model**: One of the early models for the dynamics of alkali halides, proposed by Born, considers an interionic potential of the form

$$\Phi(\kappa\kappa'|r) \;=\; \frac{Z_\kappa\, Z_{\kappa'}\, e^2}{r} + a_{\kappa\kappa'}\, e^{-br} \;=\; \Phi^{(C)}(r) + \Phi^{(R)}(r)$$

where the last term is the short-range Born-Mayer type nearest-neighbor repulsive potential. Consider, here, the case of NaCl, $Na^{+1}(\kappa = 1)$ and $Cl^{-1}(\kappa = 2)$, with $Z_1 = 1$ and $Z_2 = -1$.

(i) Show that the energy per primitive cell is given by

$$\Phi_0 \;=\; -\alpha\,\frac{e^2}{r_0} + 6\Phi^{(R)}$$

where $r_0 = 2.1\text{Å}$ is the nearest-neighbor distance in NaCl, and

$$\alpha \;=\; \sum_j \frac{\pm 1}{\rho_{0j}}$$

is the Madelung constant. The (+) sign involve even neighbors and the (-) sign odd ones, and $\rho_{0j} = r_{0j}/r_0$.

(ii) The equilibrium value r_0 is obtained by setting $\left.\frac{d\Phi(r)}{dr}\right|_{r_0} = 0$. Writing

$$\left(\frac{1}{r}\frac{d\Phi^{(R)}(r)}{dr}\right)_{r_0} \;=\; \frac{e^2}{2r_0^3}\,B,$$

where $2r_0^3 = v_a$ is the primitive cell volume, use the equilibrium condition to express B in terms of α.

(iii) Calculate α for NaCl with the aid of a simple program.

(iv) Given that the pressure is expressed as

$$P = -\frac{\partial \Phi}{\partial v_a} = -\frac{1}{6r^2}\frac{\partial \Phi}{\partial r},$$

show that the comressibility κ_B is given by

$$\frac{1}{\kappa_B} = -v_a \left.\frac{\partial P}{\partial v_a}\right|_{r_0} = \frac{1}{18r_0}\left[-2\alpha\frac{e^2}{r_0^3} + \frac{3}{2}A\frac{e^2}{r_0^3}\right] = \frac{1}{12r_0^4}\,[A + 2B]\,,$$

where we set

$$\left.\frac{d^2\Phi^{(R)}}{dr^2}\right|_{r_0} = \frac{e^2}{v_a}A.$$

Express A in terms of α and κ_B.

(v) Given that $\kappa_B = 4.16 \times 10^{-12}\text{cm}^2/\text{dyne}$, and the value you obtained for α, evaluate A

15.3 (i) Derive expressions for the force constants

$$\Phi^{(R)}_{\alpha\beta}\begin{pmatrix} 0l \\ \kappa\kappa' \end{pmatrix} = \frac{\partial^2\Phi^{(R)}(0\kappa; l\kappa')}{\partial x_\alpha \partial x_\beta}$$

in terms of A and B defined in Exercise 15.1.

(ii) Obtain an expression for $R_{\alpha\beta}(\kappa\kappa'|\mathbf{q})$, the short-range contribution to the dynamical matrix. Remember that because the ionic sites have inversion symmetry, all $R_{\alpha\beta}(\kappa\kappa'|\mathbf{q})$ are real.

(iii) Use the Ewald summation method to evaluate $C_{\alpha\beta}(\kappa\kappa'|\mathbf{q})$ for $\mathbf{q} = [00\xi]$, i.e. the Δ-direction.

(iv) Show that as $\xi \to 0$

$$C_{zz}(\kappa\kappa'|\mathbf{0}) = \frac{8\pi e^2}{3v_0},\; C_{xx}(\kappa\kappa'|\mathbf{0}) = C_{yy}(\kappa\kappa'|\mathbf{0}) = -\frac{4\pi e^2}{3v_0}$$

(v) Show that the corresponding optic modes are

$$\mu\,\omega_L^2 = \frac{e^2}{v_0}(A + 2B) + \frac{8\pi e^2}{3v_0}, \quad \mu\omega_T^2 = \frac{e^2}{v_0}(A + 2B) - \frac{4\pi e^2}{3v_0}$$

(vi) Use the expressions you obtained for $\overleftrightarrow{\mathbf{R}}$ and $\overleftrightarrow{\mathbf{C}}$ to otain the phonon dispersion curves along the Δ-direction for NaCl, in the rigid ion model.

15.4 **Phonon dispersion curves in diamond**: Diamond belongs to the nonsymorphic space group $Fd\bar{3}m$.

(i) As we demonstrated in Appendix 1, the macroscopic electric field is associated with a dipole-moment array that arises from atomic displacements. We may express the polarization density as

$$\mathbf{P} = \sum_{l\kappa} \overleftrightarrow{\mathbf{A}}(l\kappa) \cdot \mathbf{u}(l\kappa)$$

where, as usual, $\mathbf{u}(l\kappa)$ is the displacement from equilibrium position $\mathbf{R}(l\kappa)$. Diamond has two atoms per primitive cell ([000], a/4[1,1,1]). Use the property of invariance under arbitrary dispacement, together with $S = (I|\boldsymbol{\tau})$ to show that diamond has no macroscopic polarization associated with its $\mathbf{q} = \mathbf{0}$ modes.

(ii) The nearest-neighbor (nn) bond $[000] - a/4[1,1,1]$, second-nn bond $[000]-a/2[1,1,0]$ and third nn bond $[000]-a/4[-1,-1,-3]$ have bond-symmetry groups $3m$, mm and m, respectively. Derive the corresponding symmetry adapted force-constant matrices.

(iii) Use appropriate coset representatives to obtain force-constant matrices belonging to the remaining orbit members of each bond.

(iv) Construct the dynamical matrix in terms of the force-constant matrices obtained above.

(v) Show that the acoustic and optical modes at the Γ-point, i.e. $\mathbf{q} = \mathbf{0}$, have Γ_{15}^{-} and Γ_{25}^{+} symmetries of O_{h} the factor group of O_{h}^{7}. Construct the symmetry-adapted vectors using the corresponding projection operators. (Note that in this case the symmetry-adapted vectors are actually the eigenvectors!)

(vi) The group of the wavevector along the Δ-direction ($\mathbf{q} = [q,0,0]$) is $\mathbb{S}_{\Delta} = 4mm \otimes \mathcal{T}$, and the corresponding character table is given in table 15.1. Use table 15.1 to obtain compatibility relations between Γ and Δ. Show that the eigenvalue problem reduces to two 1×1 and two 2×2 matrices, and determine the coresponding eignevalues.

(vii) Repeat the above steps for the Σ and Λ directions.

(viii) Use the longwavelength limit of the expression you obtained for the dynamical matrix, to derive the relations between the elastic constants and force-constants of diamond. (Use the relations developed in §15.3.4.3)

Table 15.1. *Character table of* $\mathbb{S}_\Delta$

	Δ_1	Δ_2	Δ_2'	Δ_1'	Δ_5
$(E\|\mathbf{0})$	1	1	1	1	1
$(U_x\|\mathbf{0})$	1	1	1	1	1
$(C_{4,x}, C_{4,x}^{-1}\|\boldsymbol{\tau})$	ζ	$-\zeta$	$-\zeta$	ζ	0
$(\sigma_y, \sigma_z\|\boldsymbol{\tau})$	ζ	ζ	$-\zeta$	$-\zeta$	0
$(\sigma_{yz}, \sigma_{\bar{y}z}\|\mathbf{0})$	1	-1	1	-1	0

$\zeta = \exp[-iqa/4]$.

15.2 Solutions

4.1

16
Experimental measurements and selection rules

16.1 Exercises

16.1 $LiNbO_3$ belongs to the space group $R3c\,(C^6_{3\mathrm{v}})$, #161; its generators are $(C_3|\mathbf{0})$, $(\sigma_{\mathrm{d}}|\boldsymbol{\tau})$, with $\boldsymbol{\tau} = (1/2, 1/2, 1/2)$. It has two formulas per primitive cell. The primitive lattice basis is $(2/3, 1/3, 1/3)$, $(-1/3, 1/3, 1/3)$, $(-1/3, -2/3, 1/3)$ with respect to hexagonal axes: $a = 5.15$Å, $c = 13.86$Å. The atomic positions in the rhombohedral primitive cell are given in table 16.1.

Table 16.1. *The positions of the 10 atoms in the rhombohedral primitive cell*

Atom	positions
Nb	$(0,0,w)\,,\ \left(0,0,\frac{1}{2}+w\right)$
Li	$\left(0,0,\frac{1}{3}+w'\right),\ \left(0,0,\frac{5}{6}+w'\right)$
O	$\left(\frac{1}{3}-v,u-v,\frac{5}{12}\right),\ \left(v-u,\frac{1}{3}-u,\frac{5}{12}\right),\ \left(-\frac{1}{3}+u,-\frac{1}{3}+v,\frac{5}{12}\right),$
	$\left(-\frac{1}{3}-v,-u,\frac{7}{12}\right),\ \left(u,-\frac{1}{3}+u-v,\frac{7}{12}\right),\ \left(\frac{1}{3}-u+v,\frac{1}{3}+v,\frac{7}{12}\right)$

$w = 0.0186,\ w' = -0.0318,\ u = 0.0492,\ v = 0.0113.$

(i) Determine the symmetries of the phonon modes at the Γ-point.
(ii) Determine the symmetries of the acoustic modes at the Γ-point.
(iii) Determine the Raman active modes.
(iv) Derive the inelastic neutron scattering selection rules for $\mathbf{q}$ along a 3-fold axis.

16.2 The rutile family includes FeF_2 and MgF_2. It belongs to the space-group $P4_2/mnm$ (D_{4h}^{14}, #136); its generators are $(U_x|\boldsymbol{\tau})$, $(C_4|\boldsymbol{\tau})$, $(I|\mathbf{0})$, with $\boldsymbol{\tau} = (a/2, a/2, c/2)$.

(i) Determine the symmetries of the phonon modes at the Γ-point.
(ii) Determine the symmetries of the acoustic modes at the Γ-point.
(iii) Determine the Raman active modes.
(iv) Derive the inelastic neutron scattering selection rules for **q** along the Δ- and Σ-directions.

16.3 Repeat exercise 16.2 for α HgI_2, which belongs to the space group $P4_2/nmc$, (D_{4h}^{15}), #137); its generators are $(U_x|\boldsymbol{\tau})$, $(C_4|\boldsymbol{\tau})$, $(I|\boldsymbol{\tau})$, with $\boldsymbol{\tau} = (a/2, a/2, c/2)$. The primitive cell contains two formulas with positions given in table 16.2

Table 16.2. *The positions of the 6 atoms in the primitive cell*

Atom	positions
Hg	$(0,0,0)$, $\left(\frac{1}{2},\frac{1}{2},\frac{1}{2}\right)$
I	$\left(0,\frac{1}{2},u\right)$, $\left(-\frac{1}{2},0,-u\right)$, $\left(0+u,\frac{1}{2},\frac{1}{2}+u\right)$, $\left(-\frac{1}{2},0,\frac{1}{2}-u\right)$.

$u = 0.14$.

16.2 Solutions

4.1

17

Landau's Theory of Phase Transitions

17.1 Exercises

17.1 Consider systems that belong to the Bravais class $P4mm$:

(i) Determine the points in the Brillouin zone that satisfy the Lishitz condition.
(ii) Derive the corresponding $\mathbb{P}_{\mathbf{k}}$.

17.2 Consider a crystal with cubic symmetry. It was shown in table 15.9 that the two elastic strain components

$$\eta \propto 2\varepsilon_{33} - \varepsilon_1 - \varepsilon_{22}; \quad \xi \propto \varepsilon_1 - \varepsilon_{22},$$

form a basis for the cubic Irrep Γ_{12}.

Show that third-degree invariants of this Irrep do not vanish; and hence, these two strain components cannot drive a second-order phase transition to a t-equal tetragonal structure [**?**].

17.3 Determine the integrity basis of the 3-dimensional Rep of the dihedral point-group $\mathcal{D}_6$, with Rep matrix generators

$$C_2 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}; \quad C_6 = \begin{pmatrix} 1/2 & -\sqrt{3}/2 & 0 \\ \sqrt{3}/2 & 1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

17.4 Gadolinium molybdate, $Gd_2(Mo_4)_3$, undergoes a phase transition from a $P\bar{4}2_1m$ to a $Pba2$ space-group symmetry at 160°C. It involves the poin-group change $\bar{4}2m \Rightarrow mm2$. It also involves a reduction in translational syymetry From a P-tetragonal $\mathbb{T}_0$ with basis $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ (along 4-fold symmetry axis), to another P-tetragonal $\mathbb{T}$ with $\mathbf{a}'_1 = \mathbf{a}_1 - \mathbf{a}_2$, $\mathbf{a}'_2 = \mathbf{a}_1 + \mathbf{a}_2$, $\mathbf{a}'_3 = \mathbf{a}_3$, with $\mathbb{T}_0 : \mathbb{T} = 2$, giving $\mathbb{S}_0 : \mathbb{S} = 4$.

(a) Identify ${}^\star\mathbf{k}$.
(b) Derive the Irreps of ${}^\star\mathbf{k}$.

(c) Determine the corresponding kernel and image groups.

(d) Enumerate the possible low-symmetry space-groups, and identify the Irrep corresponding to the phase transition in $Gd_2(Mo_4)_3$.

(e) Use the integrity basis for $\mathbf{C}_4$ to construct $\Delta\Phi$

(f) We notice that P_3 of the electric polarization tensor, and ε_{12} the shear component of the strain tensor are invariant under the point-group operations of $Pba2$. This suggests that the emerging low-symmetry phase can support ferroelectricity and a shear distortion. Write down a $\Delta\Phi'$ in these variables as secondary OPs (SOP), as well as $\Delta\Phi_c$, the terms coupling the primary and secondary OPs.

(g) Describe the procedure of obtaining the minima of $\Delta\Phi$.

17.5 Determine the possible magnetic arrangement associated with the point-group $4mm$, $4\underline{mm}$, $\underline{4}m\underline{m}$, $\underline{4m}m$.

17.2 Solutions

4.1

18

Incommensurate Systems and Quasi-Crystals

18.1 Solutions