

Group Theory in Spectroscopy

The group theory in this textbook will be treated in a practical way, as one of many useful tools rather than as a field of abstract mathematics.¹

Quite a lot of what we will be discussing in this appendix was invented by Evariste Galois. He was only 21, when he died in a duel. Galois spent his last night writing down his group theory.

Evariste Galois (1811–1832), a French mathematician, created also many fundamental ideas in the theory of algebraic equations



Our goal will be to predict the selection rules in the ultraviolet (UV), visual (VIS), and infrared (IR) molecular spectra.

We will try to be concise, but examples need explanations, and there are few amateurs of dry formulas.

Group

Imagine a set of elements $\hat{R}_i, i = 1, 2, \dots, g$. We say that they form a group G of the order² g , if the following four conditions are satisfied:

¹ Symmetry may be viewed either as beautiful or primitive. It seems that from the psychological point of view, the symmetry stresses people's longing for simplicity, order, and understanding. On the other hand, symmetry means less information and hence often a kind of wearingly dull stimuli. Possibly an interplay of these two opposite features leads us to consider as beautiful what has a *broken* symmetry. The trees and the leaves exhibit broken symmetry and look beautiful. Ancient architects knew the secrets of creating beautiful buildings, which relied on symmetry breaking, which is substantial but almost invisible from distance.

² g may be finite or infinite. In practical applications in this Appendix, g will be always finite.

1. There exists an operation called *multiplication*, $\hat{R}_i \cdot \hat{R}_j$, which associates with every pair of the elements of G another element of G ; i.e., $\hat{R}_i \cdot \hat{R}_j = \hat{R}_k$. Hereafter, the multiplication $\hat{R}_i \cdot \hat{R}_j$ will be denoted simply as $\hat{R}_i \hat{R}_j$. Thus, the elements can be multiplied by each other, and the result always belongs to the group.
2. The multiplication is associative³; i.e., for any three elements of G , we have $\hat{R}_i(\hat{R}_j \hat{R}_k) = (\hat{R}_i \hat{R}_j) \hat{R}_k$.
3. Among $\hat{R}_i \in G$, there exists an *identity* element, denoted by \hat{E} , which has a handy property: $\hat{R}_i \hat{E} = \hat{R}_i$ and $\hat{E} \hat{R}_i = \hat{R}_i$ for any i .
4. To each \hat{R}_i we can find such an element of G (denoted as \hat{R}_i^{-1} , called the *inverse* element with respect to \hat{R}_i), that $\hat{R}_i \hat{R}_i^{-1} = \hat{E}$; also $\hat{R}_i^{-1} \hat{R}_i = \hat{E}$.

Example 1. A Four-Element Group

The elements $1, -1, i, -i$, with the operation chosen as the ordinary multiplication of numbers, form a group of order 4. Indeed, any product of these numbers gives one of them. Here is the corresponding multiplication table

		Second in the product			
		1	-1	i	$-i$
First in the product	1	1	-1	i	$-i$
	-1	-1	1	$-i$	i
	i	i	$-i$	-1	1
	$-i$	$-i$	i	1	-1

Note the following:

Abelian Group:

The table is *symmetric* with respect to the diagonal. A group with symmetric multiplication table is called *Abelian*.

The associativity requirement is, of course, satisfied. The unit element is 1. You can always find an inverse element. Indeed, for 1, it is 1; for -1, it is -1; for i , it is $-i$; and for $-i$, it is i . Thus, all conditions are fulfilled, and $g = 4$.

Example 2. Group of Integers

Let us take G as the set of integers with the “*multiplication*” being the regular addition of numbers. Let us check. The sum of two integers is an integer, so the requirement 1 is satisfied. The operation is associative, because the addition is. The unit element is, of course, 0. The inverse element to an integer means the opposite number. Thus, G is a group of order $g = \infty$.

³ Thanks to that, the expressions similar to $\hat{R}_i \hat{R}_j \hat{R}_k$ have an unambiguous meaning.

Example 3. Group of Non-singular Matrices

All non-singular $n \times n$ matrices⁴ with matrix multiplication as the operation form a group. Let us look at this now. Multiplication of a non-singular matrix A (i.e., $\det A \neq 0$) by a non-singular matrix B gives a non-singular matrix $C = AB$, because $\det C = \det A \det B \neq 0$. The unit element is the unit matrix $\mathbf{1}$, and the inverse element exists (this is why we needed the non-singularity) and is equal to A^{-1} . Also, from the matrix multiplication rule, we have $(AB)C = A(BC)$. This is a group of the order ∞ .

Example 4. Group of Unitary Matrices $U(n)$

In particular, all the unitary $n \times n$ matrices form a group with matrix multiplication as the group multiplication operation. Let us take a look at this. Any such multiplication is feasible, and the product represents a unitary matrix (if matrices U_1 and U_2 are unitary—i.e., $U_1^\dagger = U_1^{-1}$ and $U_2^\dagger = U_2^{-1}$ —then $U = U_1 U_2$ is also unitary because $U^{-1} = U_2^{-1} U_1^{-1} = U_2^\dagger U_1^\dagger = (U_1 U_2)^\dagger = U^\dagger$), matrix multiplication is associative, the identity element means the $n \times n$ unit matrix, and the inverse matrix is $U^{-1} = U^\dagger \equiv (U^T)^*$ always exists. In physics, this group is called $U(n)$.

Example 5. $SU(n)$ Group

The group $SU(n)$ for $n \geq 2$, which is famous in physics, is defined as the subset of $U(n)$ of such matrices U that $\det U = 1$ with the same multiplication operation.⁵ Indeed, since $\det(U_1 U_2) = \det U_1 \det U_2$, then multiplication of any two elements of the $SU(n)$ gives an element of $SU(n)$. Also of great importance in physics is the $SO(n)$ group, which is the $SU(n)$ group with real (i.e., orthogonal) matrices.

Unitary Versus Symmetry Operation

Let us take the so-called $SO(3)$ group of all rotations of the coordinate system in 3-D (the *Cartesian 3-D Euclidean space*; see [Appendix B](http://booksite.elsevier.com/978-0-444-59436-5) available at booksite.elsevier.com/978-0-444-59436-5, p. e7). The rotation operators acting in this space will be denoted by \hat{R} and defined as follows: the operator \hat{R} acting on a vector \mathbf{r} produces the vector $\hat{R}\mathbf{r}$:

$$\hat{R}\mathbf{r} = \mathbf{R}\mathbf{r}, \quad (\text{C.1})$$

where⁶ \mathbf{R} represents an orthogonal matrix of dimension 3. The orthogonality guarantees that the transformation preserves the vector dot (or scalar) products (and therefore their lengths as well).

⁴ See [Appendix A](http://booksite.elsevier.com/978-0-444-59436-5) available at booksite.elsevier.com/978-0-444-59436-5.

⁵ Recall (see [Appendix A](http://booksite.elsevier.com/978-0-444-59436-5) available at booksite.elsevier.com/978-0-444-59436-5) that for a unitary matrix U , one has $\det U = \exp(i\phi)$. For orthogonal matrices (i.e., the unitary ones with all the elements real), $\det U = \pm 1$. This does not mean that the $SU(n)$ is composed of the orthogonal matrices only. For instance, all the four 2×2 matrices:

$$\begin{Bmatrix} 1 & 0 \\ 0 & 1 \end{Bmatrix}, \begin{Bmatrix} -1 & 0 \\ 0 & -1 \end{Bmatrix}, \begin{Bmatrix} 0 & i \\ i & 0 \end{Bmatrix}, \begin{Bmatrix} 0 & -i \\ -i & 0 \end{Bmatrix}$$

have determinants that are equal to 1 and belong to $SU(2)$, while only the first two belong to $SO(2)$.

⁶ The point in 3-D space is indicated by the vector $\mathbf{r} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}$.

Let us take an arbitrary function $f(\mathbf{r})$ of the position \mathbf{r} . Now, for each of the operators \hat{R} , let us construct the corresponding operator $\hat{\mathcal{R}}$ that *moves in space the function without its deformation*. Generally, we obtain another function, which means that $\hat{\mathcal{R}}$ *operates in the Hilbert space*. The construction of the operator $\hat{\mathcal{R}}$ is based on the following prescription:

$$\hat{\mathcal{R}}f(\mathbf{r}) = f(\hat{R}^{-1}\mathbf{r}). \quad (\text{C.2})$$

This means that displacement in space of the function $f(\mathbf{r})$ is equivalent simply to leaving the function intact, but performing instead the *inverse displacement of the coordinate system*.⁷

The operators $\hat{\mathcal{R}}$ rotate functions without their deformation; therefore, they preserve the scalar products in the Hilbert space and are unitary. They form a group isomorphic with the group of operators \hat{R} , because they have the same multiplication table as the operators \hat{R} : if $\hat{R} = \hat{R}_1\hat{R}_2$. Then $\hat{\mathcal{R}} = \hat{\mathcal{R}}_1\hat{\mathcal{R}}_2$, where $\hat{\mathcal{R}}_1f(\mathbf{r}) = f(\hat{R}_1^{-1}\mathbf{r})$ and $\hat{\mathcal{R}}_2f(\mathbf{r}) = f(\hat{R}_2^{-1}\mathbf{r})$. Indeed,⁸ $\hat{\mathcal{R}}f = (\hat{\mathcal{R}}_1\hat{\mathcal{R}}_2)f(\mathbf{r}) = f(\hat{R}_2^{-1}\hat{R}_1^{-1}\mathbf{r}) = f(\hat{R}^{-1}\mathbf{r})$.

Unitary Versus Symmetry Operation

A unitary operation is a symmetry operation of the function $f(\mathbf{r})$, when $\hat{\mathcal{R}}f(\mathbf{r}) = f(\mathbf{r})$.

Example 6. Rotation of a Point

The operator $\hat{R}(\alpha; z)$ of rotation of the point with the coordinates x, y, z by angle α about the axis z gives the point with the coordinates x', y', z' (Fig. C.1a):

$$\begin{aligned} x' &= r \cos(\phi + \alpha) = r \cos \phi \cos \alpha - r \sin \phi \sin \alpha = x \cos \alpha - y \sin \alpha, \\ y' &= r \sin(\phi + \alpha) = r \sin \phi \cos \alpha + r \cos \phi \sin \alpha = x \sin \alpha + y \cos \alpha, \\ z' &= z, \end{aligned}$$

⁷ Motion is relative. Let us concentrate on a rotation by angle α . The result is the same if either of the following is true:

- The coordinate system stays still, but the point rotates by angle α .
- The point does not move, while the coordinate system rotates by angle $-\alpha$.

What if function $f(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ is to be rotated? Then we will do the following: $\hat{\mathcal{R}}f(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = f(\hat{R}^{-1}\mathbf{r}_1, \hat{R}^{-1}\mathbf{r}_2, \dots, \hat{R}^{-1}\mathbf{r}_N)$.

⁸ This result is correct, but the routine of notation works here in a misleading way when suggesting that $(\hat{\mathcal{R}}_1\hat{\mathcal{R}}_2)f(\mathbf{r})$ and $f(\hat{R}_1^{-1}\hat{R}_2^{-1}\mathbf{r})$ means the same. The correct result is derived in the following way. First, from the definition, we have $\hat{\mathcal{R}}_2f(\mathbf{r}) = f(\hat{R}_2^{-1}\mathbf{r}) \equiv g_2(\mathbf{r})$. Then, we get $(\hat{\mathcal{R}}_1\hat{\mathcal{R}}_2)f(\mathbf{r}) = \hat{\mathcal{R}}_1[\hat{\mathcal{R}}_2f(\mathbf{r})] = \hat{\mathcal{R}}_1g_2(\mathbf{r}) = g_2(\hat{R}_1^{-1}\mathbf{r}) = \hat{\mathcal{R}}_2f(\hat{R}_1^{-1}\mathbf{r}) = f(\hat{R}_2^{-1}\hat{R}_1^{-1}\mathbf{r})$.

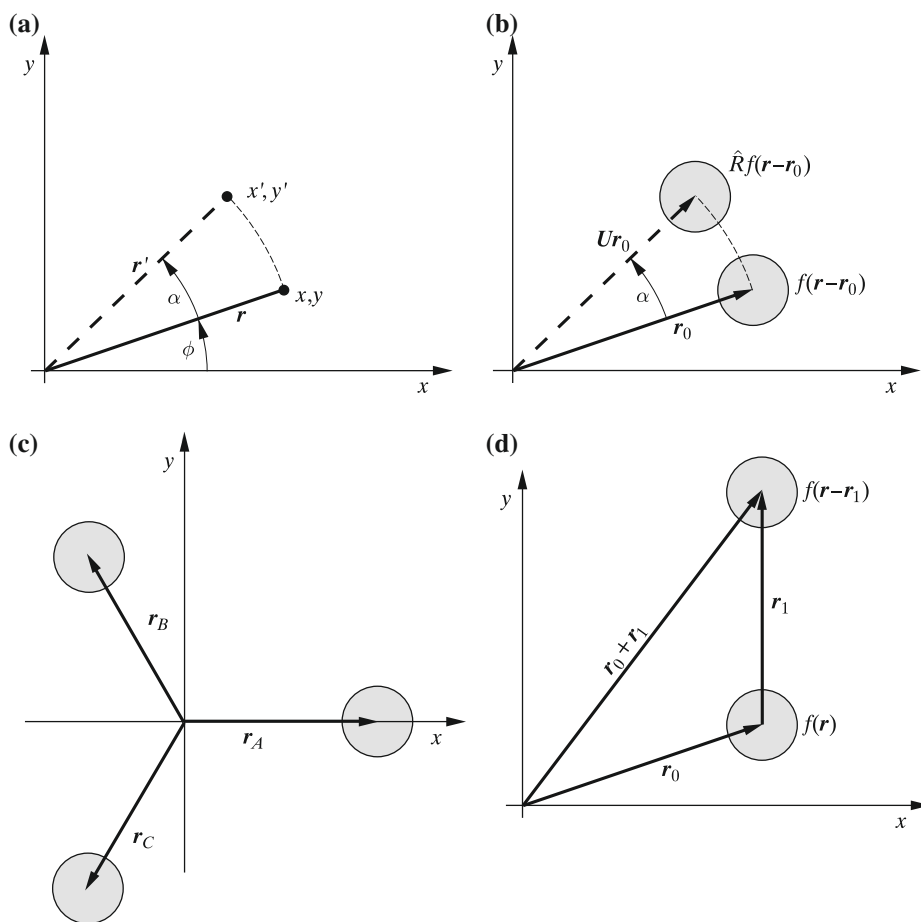


Fig. C.1. Examples of an isometric operation. (a) Unitary operation: rotation of a point by angle α about the axis z . The old position of the point is indicated by the vector r , the new position by r' (of the same length). (b) Unitary operation: rotation of the function $f(r - r_0)$ by the angle α about the axis z . As a result, we have the function $f(r - Ur_0)$, which in general represents a function that differs from $f(r - r_0)$. (c) The unitary operation that represents a symmetry operation: rotation by the angle $\alpha = 120^\circ$ of the function $f(r) = \exp[-|r - r_A|^2] + \exp[-|r - r_B|^2] + \exp[-|r - r_C|^2]$, where the vectors r_A, r_B, r_C are of the same length and form the mercedes trademark (the angle 120°). The new function is identical to the old one. (d) Translational operator by the vector r_1 : $\hat{R}(r_1) f(r) = f(\hat{R}^{-1}r) = \exp[-|\hat{R}^{-1}r - r_0|^2] = \exp[-|r - r_1 - r_0|^2] = \exp[-|r - (r_1 + r_0)|^2] = f(r - r_1)$; i.e., the function shifted in space by the vector r_1 with respect to the original function.

the corresponding transformation matrix of the old to the new coordinates, therefore, is

$$U = \begin{bmatrix} \cos \alpha & -\sin \alpha & 0 \\ \sin \alpha & \cos \alpha & 0 \\ 0 & 0 & 1 \end{bmatrix}.$$

We obtain the same new coordinates, if the point stays still, while the coordinate system rotates in the opposite direction (i.e., by the angle $-\alpha$).

Example 7. Rotation of an Atomic Orbital

Let us construct a single spherically symmetric Gaussian orbital $f(\mathbf{r}) = \exp[-|\mathbf{r} - \mathbf{r}_0|^2]$ in the Hilbert space for one electron. Let the atomic orbital be centered in the point indicated by the vector \mathbf{r}_0 . The operator $\hat{\mathcal{R}}(\alpha; z)$ has to carry out rotation of a function⁹ by the angle α about the axis z (Fig. C.1b), which corresponds to a rotation in the Hilbert space.¹⁰ According to the definition of a rotation, what we need is $\hat{\mathcal{R}}f(\mathbf{r}) = f(\hat{R}^{-1}\mathbf{r})$. Since the operator \hat{R} corresponds to the matrix U , then \hat{R}^{-1} corresponds to U^{-1} . The last matrix is simply

$$U^{-1} = U^T = \begin{bmatrix} \cos \alpha & \sin \alpha & 0 \\ -\sin \alpha & \cos \alpha & 0 \\ 0 & 0 & 1 \end{bmatrix}.$$

We obtain the following chain of transformations

$$\begin{aligned} f(\hat{R}^{-1}\mathbf{r}) &= \exp\left[-|\hat{R}^{-1}\mathbf{r} - \mathbf{r}_0|^2\right] \\ &= \exp\left[-|\hat{R}^{-1}\mathbf{r} - \hat{R}^{-1}\hat{R}\mathbf{r}_0|^2\right] \\ &= \exp\left[-\langle \hat{R}^{-1}\mathbf{r} - \hat{R}^{-1}\hat{R}\mathbf{r}_0 | \hat{R}^{-1}\mathbf{r} - \hat{R}^{-1}\hat{R}\mathbf{r}_0 \rangle\right] \\ &= \exp\left[-\langle \hat{R}\hat{R}^{-1}\mathbf{r} - \hat{R}\hat{R}^{-1}\hat{R}\mathbf{r}_0 | \mathbf{r} - \hat{R}\mathbf{r}_0 \rangle\right] \\ &= \exp\left[-\langle \mathbf{r} - \hat{R}\mathbf{r}_0 | \mathbf{r} - \hat{R}\mathbf{r}_0 \rangle\right] \\ &= \exp\left[-|\mathbf{r} - \hat{R}\mathbf{r}_0|^2\right]. \end{aligned}$$

Thus, the center of the orbital underwent the rotation and therefore $\hat{\mathcal{R}}f(\mathbf{r})$ represents indeed the spherically symmetric orbital¹¹ displaced by angle α .

⁹ This orbital represents our *object* to rotate by α . The coordinate system rests unchanged, while the object moves. The job will be done by the operator $\hat{\mathcal{R}}(\alpha; z)$.

¹⁰ We will obtain another function because it is centered differently.

¹¹ The definition $\hat{\mathcal{R}}f(\mathbf{r}) = f(\hat{R}^{-1}\mathbf{r})$ can transform anything: from the spherically symmetric Gaussian orbital through a molecular orbital (recall that it can be represented by the LCAO expansion) until the Statue of Liberty! Indeed, do you want to rotate the Statue of Liberty? Then leave the Statue in peace, but transform (in the opposite way) your Cartesian coordinate system!

More general transformations, allowing deformation of objects, also could be described by the formula $\hat{\mathcal{R}}f(\mathbf{r}) = f(\hat{R}^{-1}\mathbf{r})$, but the operator \hat{R} would be non-unitary.

Since *in general* for any value of angle α , function $\exp[-|\mathbf{r} - U\mathbf{r}_0|^2]$ is not equal to $\exp[-|\mathbf{r} - \mathbf{r}_0|^2]$, unitary operation $\hat{\mathcal{R}}$ is *not* a symmetry operation of the object.

If, however, $\alpha = 2\pi n$, $n = 0, \pm 1, \pm 2, \dots$, then $\hat{\mathcal{R}}f(\mathbf{r}) = f(\mathbf{r})$ and $\hat{\mathcal{R}}(2\pi n; z)$ is¹² a symmetry operation.

Example 8. Rotation of a Particular Sum of Atomic Orbitals

Let us take an example of a *sum* of three spherically symmetric Gaussian orbitals:

$$f(\mathbf{r}) = \exp[-|\mathbf{r} - \mathbf{r}_A|^2] + \exp[-|\mathbf{r} - \mathbf{r}_B|^2] + \exp[-|\mathbf{r} - \mathbf{r}_C|^2],$$

where vectors $\mathbf{r}_A, \mathbf{r}_B, \mathbf{r}_C$ are of the same length and form the mercedes sign (angles equal to 120°); see Fig. C.1c. Let us take operator $\hat{\mathcal{R}}(\alpha = 120^\circ; z)$ corresponding to the matrix \mathbf{U} of rotation by 120° . Application of $\hat{\mathcal{R}}$ to function $f(\mathbf{r})$ is equivalent to¹³

$$\begin{aligned} f(\hat{\mathcal{R}}^{-1}\mathbf{r}) &= \exp\left[-|\hat{\mathcal{R}}^{-1}\mathbf{r} - \mathbf{r}_A|^2\right] + \exp\left[-|\hat{\mathcal{R}}^{-1}\mathbf{r} - \mathbf{r}_B|^2\right] + \exp\left[-|\hat{\mathcal{R}}^{-1}\mathbf{r} - \mathbf{r}_C|^2\right] \\ &= \exp\left[-|\mathbf{r} - \hat{\mathcal{R}}\mathbf{r}_A|^2\right] + \exp\left[-|\mathbf{r} - \hat{\mathcal{R}}\mathbf{r}_B|^2\right] + \exp\left[-|\mathbf{r} - \hat{\mathcal{R}}\mathbf{r}_C|^2\right]. \end{aligned}$$

From the figure (or from the matrix), we have $\hat{\mathcal{R}}\mathbf{r}_A = \mathbf{r}_B$; $\hat{\mathcal{R}}\mathbf{r}_B = \mathbf{r}_C$; $\hat{\mathcal{R}}\mathbf{r}_C = \mathbf{r}_A$. This gives

$$\hat{\mathcal{R}}f(\mathbf{r}) = \exp[-|\mathbf{r} - \mathbf{r}_B|^2] + \exp[-|\mathbf{r} - \mathbf{r}_C|^2] + \exp[-|\mathbf{r} - \mathbf{r}_A|^2] = f(\mathbf{r}).$$

We have obtained our old function. $\hat{\mathcal{R}}(\alpha = 120^\circ; z)$ is therefore the *symmetry* operation¹⁴ $f(\mathbf{r})$.

$\hat{\mathcal{R}}(\alpha = 120^\circ; z)$ represents a symmetry operation, not only for the function f , but also for other objects, that would have the *symmetry of the equilateral triangle*.

Example 9. Rotation of a Many-Electron Wave Function

If in the last example we took a three-electronic function as a *product* of the Gaussian orbitals $f(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \exp[-|\mathbf{r}_1 - \mathbf{r}_A|^2] \cdot \exp[-|\mathbf{r}_2 - \mathbf{r}_B|^2] \cdot \exp[-|\mathbf{r}_3 - \mathbf{r}_C|^2]$, then after applying $\hat{\mathcal{R}}(\alpha = 120^\circ; z)$ to f , we would obtain using an almost identical procedure

¹² The transformed and non-transformed orbitals coincide.

¹³ We use the result from the last example.

¹⁴ Note, that e.g., if one of the 1s orbitals had the opposite sign, then the function $f(\mathbf{r})$ would not have the symmetry of the equilateral triangle, although it would be invariant too with respect to *some* of the operations of the equilateral triangle.

$\hat{\mathcal{R}}f(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = f(\hat{\mathcal{R}}^{-1}\mathbf{r}_1, \hat{\mathcal{R}}^{-1}\mathbf{r}_2, \hat{\mathcal{R}}^{-1}\mathbf{r}_3) = \exp[-|\mathbf{r}_1 - \mathbf{r}_B|^2] \cdot \exp[-|\mathbf{r}_2 - \mathbf{r}_C|^2] \cdot \exp[-|\mathbf{r}_3 - \mathbf{r}_A|^2]$, which represents a completely different function than the original one $f(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$. Thus, $\hat{\mathcal{R}}$ does not represent any symmetry operation for $f(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$. If, however, we took a symmetrized function [e.g., $\tilde{f}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \sum_P \hat{P} f(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$, where \hat{P} permutes the centers A, B, C, and the summation goes over all permutations] we would obtain \tilde{f} , which would turn out to be symmetric with respect to $\hat{\mathcal{R}}$ ($\alpha = 120^\circ; z$).

Example 10. Translation

Translation cannot be represented as a matrix transformation (C.1). It is however an *isometric operation*; i.e., it preserves the distances among the points of the transformed object. This is sufficient for us. Let us enlarge the set of the allowed operations in the 3-D Euclidean space by isometry. Similarly, as in the case of rotations, let us define a shift of the *function* $f(\mathbf{r})$. A shift of the *function* $f(\mathbf{r})$ by vector \mathbf{r}_1 is such a transformation $\hat{\mathcal{R}}(\mathbf{r}_1)$ (in the Hilbert space), that the new function $\tilde{f}(\mathbf{r}) = f(\mathbf{r} - \mathbf{r}_1)$. As an example, let us take the function $f(\mathbf{r}) = \exp[-|\mathbf{r} - \mathbf{r}_0|^2]$ and shift it by the vector \mathbf{r}_1 . Translations obey the known relation (C.2): $\hat{\mathcal{R}}(\mathbf{r}_1) f(\mathbf{r}) = f(\hat{\mathcal{R}}^{-1}\mathbf{r}) = \exp[-|\hat{\mathcal{R}}^{-1}\mathbf{r} - \mathbf{r}_0|^2] = \exp[-|\mathbf{r} - \mathbf{r}_1 - \mathbf{r}_0|^2] = \exp[-|\mathbf{r} - (\mathbf{r}_1 + \mathbf{r}_0)|^2] = f(\mathbf{r} - \mathbf{r}_1)$. The function $f(\mathbf{r})$ had been concentrated around the point \mathbf{r}_0 , while the new function $\hat{\mathcal{R}}(\mathbf{r}_1) f(\mathbf{r})$ is concentrated around the point indicated by the vector $\mathbf{r}_1 + \mathbf{r}_0$, i.e., the function has been shifted by \mathbf{r}_1 (Fig. C.1d). This transformation is (similar to the case of rotations) a unitary one because the scalar product between two functions f_1 and f_2 shifted by the same operation is preserved: $\langle f_1(\mathbf{r}) | f_2(\mathbf{r}) \rangle = \langle f_1(\mathbf{r} - \mathbf{r}_1) | f_2(\mathbf{r} - \mathbf{r}_1) \rangle$.

Symmetry Group of the Ammonia Molecule

Imagine a model of the NH_3 molecule (trigonal pyramide), as shown in Fig. C.2. A student sitting at the table plays with the model. We look at the model, then close our eyes for a second, and open them again. We see that the coordinate system, the model, and its position with respect to the coordinate system look exactly the same as before. Could the student change the model position? Yes, he could. He could, for example, rotate the model about the z -axis (perpendicular to the table) by 120° , he might exchange two NH bonds in the model, he may also do nothing. Whatever the student could do is called a *symmetry operation*.

Let us make a list of all the symmetry operations allowed for the ammonia molecule. To this end, let us label the vortices of the triangle by a, b, c and locate it in such a way as to coincide the triangle center with the origin of the coordinate system, and the y axis indicated the vortex a .

Now, let us check whether the operations given in Table C.1 form a group. Four conditions have to be satisfied. The first condition requires the existence of a “multiplication” in the group, and that the product of any two elements gives an element of the group: $\hat{R}_i \hat{R}_j = \hat{R}_k$. The elements will be the symmetry operations of the equilateral triangle. The product $\hat{R}_i \hat{R}_j = \hat{R}_k$

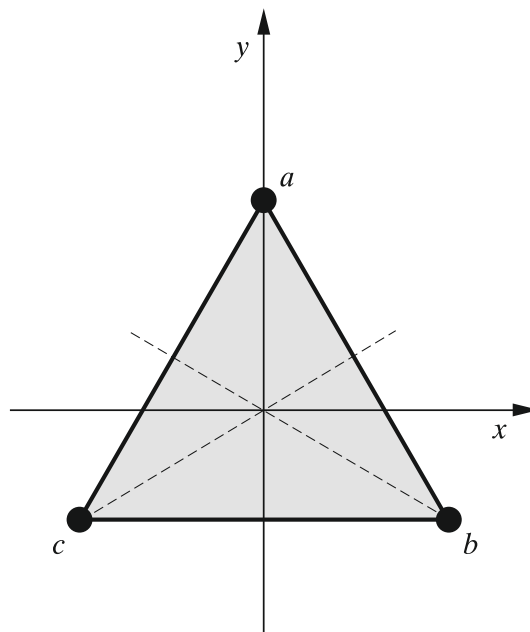


Fig. C.2. The equilateral triangle and the coordinate system. Positions a , b , and c are occupied by hydrogen atoms, and the nitrogen atom is (symmetrically) above the plane.

Table C.1. Symmetry operations of the ammonia molecule (the reflections pertain to the mirror planes perpendicular to the triangle shown in Fig. C.2, and going through the center of the triangle).

Symbol	Description	Symbolic Explanation
\hat{E}	Do nothing	$\hat{E} \begin{bmatrix} a \\ c \ b \end{bmatrix} = \begin{bmatrix} a \\ c \ b \end{bmatrix}$
\hat{A}	Reflection in the plane going through point a shown in Fig. C.2	$\hat{A} \begin{bmatrix} a \\ c \ b \end{bmatrix} = \begin{bmatrix} a \\ b \ c \end{bmatrix}$
\hat{B}	Reflection in the plane going through point b shown in Fig. C.2	$\hat{B} \begin{bmatrix} a \\ c \ b \end{bmatrix} = \begin{bmatrix} c \\ a \ b \end{bmatrix}$
\hat{C}	Reflection in the plane going through point c shown in Fig. C.2	$\hat{C} \begin{bmatrix} a \\ c \ b \end{bmatrix} = \begin{bmatrix} b \\ c \ a \end{bmatrix}$
\hat{D}	Rotation by 120° clockwise	$\hat{D} \begin{bmatrix} a \\ c \ b \end{bmatrix} = \begin{bmatrix} c \\ b \ a \end{bmatrix}$
\hat{F}	Rotation by -120° counterclockwise	$\hat{F} \begin{bmatrix} a \\ c \ b \end{bmatrix} = \begin{bmatrix} b \\ a \ c \end{bmatrix}$

means that the operation \hat{R}_k gives the same result as applying the operation \hat{R}_j to the triangle *first*, and *then* the result is subject to the operation \hat{R}_i . In this way, the “multiplication table” shown in Table C.2 can be obtained.

Table C.2. Group multiplication table.

		Second in the product						
		\hat{R}_j	\hat{E}	\hat{A}	\hat{B}	\hat{C}	\hat{D}	\hat{F}
First in the product	\hat{R}_i							
	\hat{E}	\hat{E}	\hat{A}	\hat{B}	\hat{C}	\hat{D}	\hat{F}	
	\hat{A}	\hat{A}	\hat{E}	\hat{D}	\hat{F}	\hat{B}	\hat{C}	
	\hat{B}	\hat{B}	\hat{F}	\hat{E}	\hat{D}	\hat{C}	\hat{A}	
	\hat{C}	\hat{C}	\hat{D}	\hat{F}	\hat{E}	\hat{A}	\hat{B}	
	\hat{D}	\hat{D}	\hat{C}	\hat{A}	\hat{B}	\hat{F}	\hat{E}	
	\hat{F}	\hat{F}	\hat{B}	\hat{C}	\hat{A}	\hat{E}	\hat{D}	

Further, using Table C.2, we may check whether the operation is associative. E.g., we check whether $\hat{A}(\hat{B}\hat{C}) = (\hat{A}\hat{B})\hat{C}$. The left side gives $\hat{A}(\hat{B}\hat{C}) = \hat{A}\hat{D} = \hat{B}$. The right-hand side gives $(\hat{A}\hat{B})\hat{C} = \hat{D}\hat{C} = \hat{B}$. It agrees, and it will agree for all the other entries in the table.

The unit operation is \hat{E} , as it is seen from the table, because multiplying by \hat{E} does not change anything: $\hat{E}\hat{R}_i = \hat{R}_i\hat{E} = \hat{R}_i$. Also, using the table again, we can find the inverse element of any of the elements. Indeed, $\hat{E}^{-1} = \hat{E}$, because \hat{E} times just \hat{E} equals \hat{E} . Further, $\hat{A}^{-1} = \hat{A}$ because \hat{A} times \hat{A} equals \hat{E} , etc., $\hat{B}^{-1} = \hat{B}$, $\hat{C}^{-1} = \hat{C}$, $\hat{D}^{-1} = \hat{F}$, and $\hat{F}^{-1} = \hat{D}$.

Thus, all the requirements are fulfilled and all these operations form a group of order $g = 6$. Note that in this group, the operations do not necessarily commute; e.g., $\hat{C}\hat{D} = \hat{A}$, but $\hat{D}\hat{C} = \hat{B}$ (the group is not Abelian).

Classes

The group elements can be all divided into disjoint sets called *classes*. A class (to put it first in a simple way) represents a set of the operations that are similar in a common sense; e.g., three reflection operations \hat{A} , \hat{B} and \hat{C} constitute one class, the rotations \hat{D} and \hat{F} form the second class, and the third class is simply the element \hat{E} . Now, let us look at the precise definition.

Class

A class is the set of elements that are conjugate one to another. An element \hat{R}_i is conjugate with \hat{R}_j , if we can find in the group G such an element (let us denote it by \hat{X}), that $\hat{X}^{-1}\hat{R}_j\hat{X} = \hat{R}_i$.

Then, of course, the element \hat{R}_j is a conjugate to \hat{R}_i as well. We check that by multiplying \hat{R}_i from the left by $\hat{X} = \hat{Y}^{-1}$, and from the right by $\hat{X}^{-1} = \hat{Y}$ (what yields $\hat{Y}^{-1}\hat{R}_i\hat{Y} = \hat{X}\hat{R}_i\hat{X}^{-1} = \hat{X}\hat{X}^{-1}\hat{R}_i\hat{X}\hat{X}^{-1} = \hat{E}\hat{R}_i\hat{E} = \hat{R}_i$).

Let us make a little exercise using our Table C.2. We have $\hat{X}^{-1}\hat{E}\hat{X} = \hat{X}^{-1}\hat{X}\hat{E} = \hat{E}\hat{E} = \hat{E}$ for each $\hat{X} \in G$; i.e., \hat{E} represents only a class. Further, making $\hat{X}^{-1}\hat{A}\hat{X}$ for all possible \hat{X} gives:

$$\begin{aligned}\hat{E}^{-1}\hat{A}\hat{E} &= \hat{E}\hat{A}\hat{E} = \hat{A}\hat{E} = \hat{A} \\ \hat{A}^{-1}\hat{A}\hat{A} &= \hat{A}\hat{A}\hat{A} = \hat{E}\hat{A} = \hat{A} \\ \hat{B}^{-1}\hat{A}\hat{B} &= \hat{B}\hat{A}\hat{B} = \hat{F}\hat{B} = \hat{C} \\ \hat{C}^{-1}\hat{A}\hat{C} &= \hat{C}\hat{A}\hat{C} = \hat{D}\hat{C} = \hat{B} \\ \hat{D}^{-1}\hat{A}\hat{D} &= \hat{F}\hat{A}\hat{D} = \hat{B}\hat{D} = \hat{C} \\ \hat{F}^{-1}\hat{A}\hat{F} &= \hat{D}\hat{A}\hat{F} = \hat{B}\hat{F} = \hat{C}.\end{aligned}$$

This means that \hat{A} belongs to the same class together with \hat{B} and \hat{C} . Now, we will create some conjugate elements to \hat{D} and \hat{F} :

$$\begin{aligned}\hat{A}^{-1}\hat{D}\hat{A} &= \hat{A}\hat{D}\hat{A} = \hat{B}\hat{A} = \hat{F} \\ \hat{B}^{-1}\hat{D}\hat{B} &= \hat{B}\hat{D}\hat{B} = \hat{C}\hat{B} = \hat{F} \\ \hat{C}^{-1}\hat{D}\hat{C} &= \hat{C}\hat{D}\hat{C} = \hat{A}\hat{C} = \hat{F}\end{aligned}$$

etc. Thus, \hat{D} and \hat{F} make a class. Therefore, the group under consideration consists of the following classes: $\{\hat{E}\}\{\hat{A}, \hat{B}, \hat{C}\}\{\hat{D}, \hat{F}\}$.

It is always so: the group is a sum of the disjoint classes.

Representations

A representation of the group is a g -element sequence of the square matrices (of the same dimension; each element of the group is associated to a matrix), such that the matrices have the multiplication table consistent with the multiplication table of the group.

By “consistency,” we mean the following. To each element of the group, one assigns a square matrix (of the same dimension for all elements). If the multiplication table for the group says that $\hat{R}_i\hat{R}_j = \hat{R}_k$, then the matrix corresponding to \hat{R}_i times the matrix that corresponds to \hat{R}_j is the matrix that corresponds to \hat{R}_k . If this agrees for all \hat{R} , then we say that the matrices form a representation.¹⁵

We may create many group representations; see Table C.3.

¹⁵ More formally, a representation is a *homomorphism of the group into the above set of matrices*.

Table C.3. Several representations of the equilateral triangle symmetry group.

Repr.	Group Elements					
	\hat{E}	\hat{A}	\hat{B}	\hat{C}	\hat{D}	\hat{F}
Γ_1	1	1	1	1	1	1
Γ_2	1	-1	-1	-1	1	1
Γ_3	$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$	$\begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix}$	$\begin{bmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix}$	$\begin{bmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix}$	$\begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix}$	$\begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix}$
Γ_4	$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$	$\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$	$\begin{bmatrix} -1 & 0 & 0 \\ 0 & \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix}$	$\begin{bmatrix} -1 & 0 & 0 \\ 0 & \frac{1}{2} & \frac{\sqrt{3}}{2} \\ 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix}$	$\begin{bmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix}$	$\begin{bmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix}$

The easiest thing is to see that Γ_1 satisfies the criterion of being a representation (the matrices have dimension 1; i.e., they are numbers). After looking at Γ_2 for a while, we will say the same. Multiplying the corresponding matrices, we will prove that for Γ_3 and Γ_4 . For example, for Γ_3 , the product of the matrices \hat{B} and \hat{C} gives the matrix corresponding to the operation \hat{D} :

$$\begin{bmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix} \begin{bmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix} = \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix};$$

i.e., the same as for the operations themselves. If we had more patience, we would show that equally easily for the whole multiplication table of the group. Note that

there are many representations of a group.

There is also another interesting thing to note. Let us take a point with the coordinates $(x, y, 0)$ and see what will happen to it when the symmetry operations are applied (the coordinate system rests, while the point itself moves). The identity operation \hat{E} leads to the following transformation matrix:

$$\begin{bmatrix} x' \\ y' \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \end{bmatrix}.$$

The results of the other operations are characterized by the following transformation matrices (you may check that step by step):

$$\hat{A} : \begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix} \quad \hat{B} : \begin{bmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix} \quad \hat{C} : \begin{bmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix}$$

$$\hat{D} : \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix} \quad \hat{F} : \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix}.$$

Note, that the matrices obtained are identical to those of the representation Γ_3 . Thus, by transforming the coordinates of a point, we have generated a representation of the symmetry.

By transforming anything (coordinates of a point, vectors, functions) using the symmetry operations and collecting the results in the form of matrices, we always obtain a representation of the group.

Characters of Representation

For any representation Γ , we may define the vector $\chi^{(\Gamma)}$ of dimension g , having as elements the traces of the representation matrices $\Gamma(\hat{R}_i)$:

$$\text{Tr}\Gamma = \sum_i \Gamma_{ii} \quad (\text{C.3})$$

$$\chi^{(\Gamma)} \equiv \begin{bmatrix} \text{Tr}\Gamma(\hat{R}_1) \\ \text{Tr}\Gamma(\hat{R}_2) \\ \dots \\ \text{Tr}\Gamma(\hat{R}_g) \end{bmatrix} \equiv \begin{bmatrix} \chi^{(\Gamma)}(\hat{R}_1) \\ \chi^{(\Gamma)}(\hat{R}_2) \\ \dots \\ \chi^{(\Gamma)}(\hat{R}_g) \end{bmatrix}. \quad (\text{C.4})$$

The number $\chi^{(\Gamma)}(\hat{R}_i)$ is called the *character of the representation* Γ that corresponds to the operation \hat{R}_i . The characters of representations will play the most important role in application of the group theory to spectroscopy.

Irreducible Representations

To tell what an irreducible representation is, let us define first what are called *reducible representations*.

A representation is called *reducible* if its matrices can be transformed into the so-called *block form* by using the transformation $\mathbf{P}^{-1}\Gamma(\hat{R}_i)\mathbf{P}$ for every matrix $\Gamma(\hat{R}_i)$, where \mathbf{P} is a non-singular matrix.

In a block form, the nonzero elements can be only in the square blocks located on the diagonal (see Fig. C.3).

If using the same \mathbf{P} , we can transform each of the matrices $\Gamma(\hat{R}_i)$ and obtain the same block form, then the representation is called *reducible*.

If we do not find such a matrix (because it does not exist), then the representation is irreducible. If we carry out the transformation $\mathbf{P}^{-1}\Gamma(\hat{R}_i)\mathbf{P}$ (*similarity transformation*) for $i = 1, 2, \dots, g$ of a representation, the new matrices also form a representation Γ' called *equivalent* to Γ .

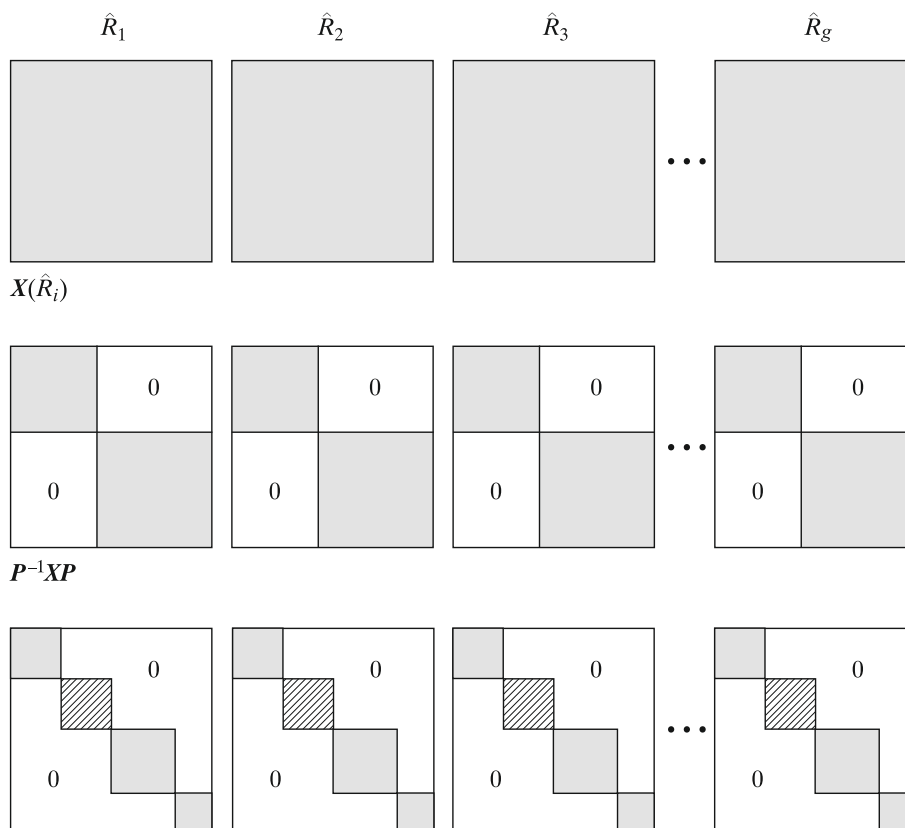


Fig. C.3. Reducible representation, block form, and irreducible representation. In the first row, the matrices $\Gamma(\hat{R}_i)$ are displayed that form a *reducible representation* (each matrix corresponds to the symmetry operation \hat{R}_i); the matrix elements are in general nonzero. The central row shows a representation Γ' equivalent to the first one; i.e., related by a similarity transformation (with matrix \mathbf{P}). The new representation exhibits a block form; i.e., in this particular case each matrix has two blocks of zeros that are identical in all matrices. The last row shows an equivalent representation Γ'' that corresponds to the smallest square blocks (of nonzeros); i.e., the maximum number of the blocks, of the form identical in all the matrices. Not only Γ , Γ' , and Γ'' are representations of the group, but also any sequence of individual blocks (as that shadowed) is a representation. Thus, Γ'' is decomposed into the four irreducible representations.

This is easy to show. Indeed, the group operations \hat{R}_i and \hat{R}_j correspond to the matrices $\Gamma(\hat{R}_i)$ and $\Gamma(\hat{R}_j)$ in the original representation and to $\Gamma'(\hat{R}_i) = \mathbf{P}^{-1}\Gamma(\hat{R}_i)\mathbf{P}$ and $\Gamma'(\hat{R}_j) = \mathbf{P}^{-1}\Gamma(\hat{R}_j)\mathbf{P}$ in the equivalent representation (we will check in a moment whether this is indeed a representation). The product $\Gamma'(\hat{R}_i)\Gamma'(\hat{R}_j)$ equals $\mathbf{P}^{-1}\Gamma(\hat{R}_i)\mathbf{P}\mathbf{P}^{-1}\Gamma(\hat{R}_j)\mathbf{P} = \mathbf{P}^{-1}\Gamma(\hat{R}_i)\Gamma(\hat{R}_j)\mathbf{P}$; i.e., the matrix $\Gamma(\hat{R}_i)\Gamma(\hat{R}_j)$ transformed by a *similarity transformation*, so everything goes with the same multiplication table. Thus, the matrices $\Gamma'(\hat{R}_i)$ form also a representation (Γ'). This means that we can create as many representations as we wish, it is sufficient to change the matrix \mathbf{P} , and this is easy (since what we want is its singularity, i.e., the \mathbf{P}^{-1} matrix has to exist).

The blocks are square matrices. It turns out the set of the first blocks $\Gamma_1(\hat{R}_1), \Gamma_1(\hat{R}_2), \dots, \Gamma_1(\hat{R}_g)$ (each block for one operation) is a representation, the set of the second blocks

$\Gamma_2(\hat{R}_1), \Gamma_2(\hat{R}_2), \dots, \Gamma_2(\hat{R}_g)$ forms a representation as well, etc. So it is sufficient to see what happens when we multiply two matrices in the same block form. The matrix product has the same block form and a particular block results from multiplication of the corresponding blocks of the matrices that are being multiplied. This is sufficient to treat each set of the blocks as a representation.¹⁶

In particular, the maximum decomposition into blocks leads, of course, to the blocks that are not decomposable anymore, and represent therefore the *irreducible representations*.

Properties of the Irreducible Representations

For two irreducible representations α and β , the following *group orthogonality theorem* is satisfied¹⁷:

$$\sum_i [\Gamma^{(\alpha)}(\hat{R}_i)]_{mn} [\Gamma^{(\beta)}(\hat{R}_i)]_{m'n'}^* = \frac{g}{n_\alpha} \delta_{\alpha\beta} \delta_{mm'} \delta_{nn'}, \quad (\text{C.5})$$

where $\Gamma^{(\alpha)}(\hat{R})$ and $\Gamma^{(\beta)}(\hat{R})$ denote the matrices that correspond to the group element \hat{R} (m, n and m', n' determine the elements of the matrices), the summation goes over all the group elements, and n_α is the dimension of the irreducible representation α ; i.e., the dimension of the matrices that form the representation. The symbol $*$ means the complex conjugation¹⁸. The

¹⁶ Let us explain this with an example. We have two square matrices of dimension 4: \mathbf{A} and \mathbf{B} , both having the block form:

$$\mathbf{A} = \begin{bmatrix} \mathbf{A}_1 & \mathbf{0} \\ \mathbf{0} & \mathbf{A}_2 \end{bmatrix}, \quad \mathbf{B} = \begin{bmatrix} \mathbf{B}_1 & \mathbf{0} \\ \mathbf{0} & \mathbf{B}_2 \end{bmatrix} \quad \text{with}$$

$$\mathbf{A}_1 = \begin{bmatrix} 3 & 1 \\ 1 & 2 \end{bmatrix}, \quad \mathbf{A}_2 = \begin{bmatrix} 2 & 2 \\ 2 & 3 \end{bmatrix}, \quad \mathbf{B}_1 = \begin{bmatrix} 1 & 3 \\ 3 & 2 \end{bmatrix}, \quad \mathbf{B}_2 = \begin{bmatrix} 2 & 1 \\ 1 & 2 \end{bmatrix}.$$

Let us check that $\mathbf{C} = \mathbf{AB}$ has the same block form:

$$\mathbf{C} = \begin{bmatrix} \mathbf{C}_1 & \mathbf{0} \\ \mathbf{0} & \mathbf{C}_2 \end{bmatrix}$$

and that (what is particularly important for us) $\mathbf{C}_1 = \mathbf{A}_1\mathbf{B}_1$ and $\mathbf{C}_2 = \mathbf{A}_2\mathbf{B}_2$. Indeed, multiplying \mathbf{AB} , we have

$$\mathbf{C} = \begin{bmatrix} 6 & 11 & 0 & 0 \\ 7 & 7 & 0 & 0 \\ 0 & 0 & 6 & 6 \\ 0 & 0 & 7 & 8 \end{bmatrix} \quad \text{i.e.,} \quad \begin{bmatrix} 6 & 11 \\ 7 & 7 \end{bmatrix} = \mathbf{C}_1, \quad \begin{bmatrix} 6 & 6 \\ 7 & 8 \end{bmatrix} = \mathbf{C}_2.$$

Hence, indeed $\mathbf{C}_1 = \mathbf{A}_1\mathbf{B}_1$ and $\mathbf{C}_2 = \mathbf{A}_2\mathbf{B}_2$

¹⁷ For the proof, see H. Eyring, J. Walter, and G.E. Kimball, *Quantum Chemistry*, (New York, Wiley: 1944).

¹⁸ This is important only for the complex representations Γ .

symbols δ denote the Kronecker deltas; i.e., $\delta_{\alpha\beta} = 1$, if $\alpha = \beta$ and $\delta_{\alpha\beta} = 0$, if $\alpha \neq \beta$. The word *orthogonality* in the name of the theorem is related to the following observation. We create two g -dimensional vectors: one composed of the components $[\Gamma^{(\alpha)}(\hat{R}_i)]_{mn}$, the other vector from $[\Gamma^{(\beta)}(\hat{R}_i)]_{m'n'}^*$, $i = 1, 2, \dots, g$. The group orthogonality theorem says the following:

- If $\alpha \neq \beta$, then the vectors are orthogonal.
- If $m \neq m'$ or $n \neq n'$, the two vectors are orthogonal as well. The formula kills everything, except the two irreducible representations are identical and we choose as the vector components *the same* elements.

Characters of Irreducible Representations

The most important consequence of the group orthogonality theorem is the equation

$$\sum_i \chi^{(\alpha)}(\hat{R}_i) \chi^{(\beta)}(\hat{R}_i)^* = g \delta_{\alpha\beta}, \quad (\text{C.6})$$

where $\chi^{(\alpha)}(\hat{R}_i)$ is a character of the *irreducible representation* α corresponding to the symmetry operation \hat{R}_i . Equation (C.6) in view of Eq. (C.3) may be rewritten as a scalar product in a unitary space (see [Appendix B](http://booksite.elsevier.com/978-0-444-59436-5) available at booksite.elsevier.com/978-0-444-59436-5)

$$\langle \chi^{(\beta)} | \chi^{(\alpha)} \rangle = g \delta_{\alpha\beta}. \quad (\text{C.7})$$

Equation (C.7) can be obtained from the group orthogonality theorem after setting $m = n$ and $m' = n'$, and then summing up over m and m' :

$$\begin{aligned} \langle \chi^{(\beta)} | \chi^{(\alpha)} \rangle &= \sum_i \sum_m \sum_{m'} [\Gamma^{(\alpha)}(\hat{R}_i)]_{mm} [\Gamma^{(\beta)}(\hat{R}_i)]_{m'm'}^* \\ &= \frac{g}{n_\alpha} \delta_{\alpha\beta} \sum_m \sum_{m'} (\delta_{mm'})^2 = \frac{g}{n_\alpha} \delta_{\alpha\beta} n_\alpha = g \delta_{\alpha\beta}. \end{aligned}$$

Decomposing Reducible Representation into Irreducible Ones

It is important that

equivalent representations have identical characters

because the trace of a matrix is invariant with respect to any similarity transformation. Indeed, for two equivalent representations Γ and Γ' for any \hat{R}_i , we have $\Gamma'(\hat{R}_i) = \mathbf{P}^{-1}\Gamma(\hat{R}_i)\mathbf{P}$, which gives

$$\begin{aligned}\chi^{(\Gamma')}(\hat{R}_i) &= \sum_m (\mathbf{P}^{-1}\Gamma(\hat{R}_i)\mathbf{P})_{mm} = \sum_{mkl} P_{mk}^{-1}\Gamma_{kl}P_{lm} = \sum_{kl} \Gamma_{kl} \sum_m P_{lm}P_{mk}^{-1} \\ &= \sum_{kl} \Gamma_{kl}(\mathbf{P}\mathbf{P}^{-1})_{lk} = \sum_{kl} \Gamma_{kl}\delta_{lk} = \sum_k \Gamma_{kk} = \chi^{(\Gamma)}(\hat{R}_i).\end{aligned}$$

In particular, the character of a representation is the same as its block form (with the maximum number of blocks that correspond to the irreducible representations):

$$\chi(\hat{R}_i) = \sum_{\alpha} a(\alpha)\chi^{(\alpha)}(\hat{R}_i), \quad (\text{C.8})$$

or, in other words,

$$\chi = \sum_{\alpha} a(\alpha)\chi^{(\alpha)}, \quad (\text{C.9})$$

where $a(\alpha)$ is a natural number telling us how many times the irreducible representation α appears in the block form. The above formula comes from the very definition of the trace (a sum of the diagonal elements).

We will need another property of the characters. Namely,

the characters corresponding to the elements of a class are equal.

Indeed, two elements of the group \hat{R}_i and \hat{R}_j that belong to the same class are related to one another by the relation $\hat{R}_i = X^{-1}\hat{R}_jX$, where X is an element of the group. The same multiplication table is valid for the representations (from the definition of the representation); thus

$$\Gamma(\hat{R}_i) = \Gamma(X^{-1})\Gamma(\hat{R}_j)\Gamma(X) = [\Gamma(X)]^{-1}\Gamma(\hat{R}_j)\Gamma(X). \quad (\text{C.10})$$

This concludes the proof because in such a case, the matrices $\Gamma(\hat{R}_i)$ and $\Gamma(\hat{R}_j)$ are related by a similarity transformation and therefore have identical characters. From now on, we can write $\chi(C)$ instead of $\chi(\hat{R})$, where C denotes a class to which operation \hat{R}_i belongs.

Equation (C.8) can be now modified appropriately. It can be rewritten as

$$\langle \chi^{(\beta)} | \chi^{(\alpha)} \rangle = \sum_C n_C \chi^{(\alpha)}(C) \chi^{(\beta)}(C)^* = \sum_C [\sqrt{n_C} \chi^{(\alpha)}(C)] [\sqrt{n_C} \chi^{(\beta)}(C)^*] = g \delta_{\alpha\beta}, \quad (\text{C.11})$$

where C stands for the class, and n_C tells us how many operations belong to the class. Such a notation reminds us that the numbers $[\sqrt{n_C} \chi^{(\alpha)}(C)]$ for a fixed α and changing class C may be treated as the components of a vector (its dimension is equal to the number of classes) and, that the vectors that correspond to different irreducible representations are orthogonal. The

dimension of the vectors is equal to the number of classes – say, k . Since the number of the orthogonal vectors, each of dimension k , cannot exceed k , then the number of the different irreducible representations is equal to the number of the classes.

In future applications, it will be of key importance to find a natural number $a(\alpha)$ that tells us how many times the irreducible representation α is encountered in a reducible representation. The formula for $a(\alpha)$ is the following:

$$a(\alpha) = \frac{1}{g} \sum_C n_C \chi(C) \chi^{(\alpha)}(C)^* \quad (\text{C.12})$$

The proof is simple. From the scalar product of both sides of Eq. (C.9) with the vector $\chi^{(\beta)}$ after using Eq. (C.7), one obtains $\langle \chi^{(\beta)} | \chi \rangle = \sum_{\alpha} a(\alpha) \langle \chi^{(\beta)} | \chi^{(\alpha)} \rangle = \sum_{\alpha} a(\alpha) g \delta_{\alpha\beta} = a(\beta)g$ or $a(\alpha) = \frac{1}{g} \langle \chi^{(\alpha)} | \chi \rangle$. This is the formula sought because the characters are the same for all operations of the same class.

Note that

to find $a(\alpha)$, it is sufficient to know the *characters* of the representations, the representations themselves are not necessary.

Tables of Characters of the Irreducible Representations

Any textbook on application of group theory in molecular spectroscopy contains tables of characters of irreducible representations, which correspond to various symmetry groups of molecules.¹⁹

Before we can apply the group theory to a particular molecule, we have to find the above mentioned table of characters. To this end, note the following:

- The Born–Oppenheimer approximation is used, so the positions of the nuclei are fixed in space (geometry).
- Looking at the geometry, we make a list of all the symmetry operations that transform it into itself.
- We identify the corresponding symmetry group.²⁰

¹⁹ The tables have been constructed by considering possible symmetries (symmetry groups), creating suitable matrix representations, using similarity transformations to find the irreducible representations, summing up the diagonal elements we end up with the character tables in question.

²⁰ This may be done by using a flowchart; e.g., what is given in P.W. Atkins, *Physical Chemistry*, 6th ed., Oxford University Press, Oxford (1998).

Table C.4. Examples of the symmetry group for a few molecules in their ground-state optimum geometry.

Molecule	Group
H ₂ O	C _{2v}
NH ₃	C _{3v}
CH ₄	T _d
Benzene	D _{6h}
Naphthalene	D _{2h}

In order to find the proper table, we may use Schoenflies notation for the symmetry²¹ (there are also some other notations):

- \hat{E} Means a symbol of the identity operation (i.e., do nothing).
- \hat{C}_n Rotation by angle $\frac{2\pi}{n}$ about the n - fold symmetry axis.
- \hat{C}_n^m Rotation by $\frac{2\pi m}{n}$ about the n -fold symmetry axis
- $\hat{\sigma}_v$ Reflection in the plane going through the axis of the highest symmetry
- $\hat{\sigma}_h$ Reflection in the plane perpendicular to the axis of the highest symmetry
- \hat{i} Inversion with respect to the center of symmetry
- \hat{S}_n Rotation by angle $\frac{2\pi}{n}$ about the n -fold symmetry axis with subsequent reflection in the plane perpendicular to it
- \hat{S}_n^m Rotation by angle $\frac{2\pi m}{n}$ about the n -fold symmetry axis with subsequent reflection in the plane perpendicular to it.

The set of the symmetry operations forms the symmetry group. The symmetry groups also have their special symbols. In Table C.4 the Schoenflies notation of the symmetry groups of some simple molecules is given (in their geometry corresponding to the energy minimum).

A molecule may be much more complicated, but often its symmetry is identical to that of a simple molecule (e.g., one of those reported in the table).

When we finally identify the table of characters suitable for the molecule under consideration, it is time to look at it carefully. For example, for the ammonia molecule, we find the table of characters shown in Table C.5.

In the upper-left corner, the name of the group is displayed (C_{3v}). In the same row, the symmetry operations are listed (in this case \hat{E} , $\hat{\sigma}_v$, \hat{C}_3).²² The operations are collected in classes, and the number of such operations in the class is given: the identity operation (\hat{E}) forms the

²¹ Artur Moritz Schoenflies (1853–1928), German mathematician and professor at the universities in Göttingen, Königsberg, and Frankfurt am Main. Schoenflies proved (independent of J.S. Fiodorow and W. Barlow) the existence of the complete set of 230 space groups of crystals.

²² These are the same symmetry operations as discussed on p. e23.

Table C.5. C_{3v} group table of characters.

C_{3v}	\hat{E}	$3\hat{\sigma}_v$	$2\hat{C}_3$		
A_1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	-1	1	R_z	
E	2	0	-1	$(x, y)(R_x, R_y)$	$(x^2 - y^2, xy)(xz, yz)$

first class, the three reflection operations (hence $3\hat{\sigma}_v$, before called $\hat{A}, \hat{B}, \hat{C}$) corresponding to the planes that contain the threefold symmetry axis, *two* rotation operations (hence, $2\hat{C}_3$, called before \hat{D} and \hat{F}) about the threefold symmetry axis (by 120° and by 240° , or -120° , the rotation by 360° is identical to \hat{E}).

In the second and later rows, we have information about the irreducible representations, with one row for each representation. The number of the irreducible representations is equal to the number of classes (three in our case); i.e., the table of characters is square. On the left side, we have the symbol of the representation informing us about its dimension (if the symbol is A, then the dimension is 1; if it is E, then the dimension is 2; and if T, then it is 3). Thus, the letter E unfortunately plays a double role in the table: as the identity operation \hat{E} , and as E, the symbol of an irreducible representation. In a given row (irreducible representation), the number below the symbol of class is the corresponding character. For the identity operation \hat{E} , the corresponding matrices are unit matrices, the calculated character is therefore equal to the dimension of the irreducible representation.

Of great importance is the simplest representation possible: just all the characters equal to 1 (in our case, A_1). It will be called the fully symmetric representation.

Example 11. Decomposition of a Reducible Representation

Let us find how the reducible representation Γ_4 from p. e28 may be decomposed into the irreducible representations. First of all, we see from Eq. (C.12) that what one needs are characters rather than the representations themselves. The characters $\chi^{(\Gamma_4)}$ are calculated by summing up the diagonals of the matrix representations for the corresponding classes, $\chi^{(\Gamma_4)} : 3$ (class \hat{E}), -1 (class $\hat{\sigma}_v$), 0 (class \hat{C}_3). Let us first ask how many times (a_{A_1}) the irreducible representation A_1 is encountered in Γ_4 . The characters of A_1 (Table C.5) are 1, 1, 1 for the corresponding classes. The number of the operations in the classes is respectively $n_C : 1, 3, 2$. From Eq. (C.12), we find $a(A_1) = \frac{1}{6} (1 \cdot 3 \cdot 1 + 3 \cdot (-1) \cdot 1 + 2 \cdot 0 \cdot 1) = 0$. Similarly, we find $a(A_2) = \frac{1}{6} (1 \cdot 3 \cdot 1 + 3 \cdot (-1) \cdot (-1) + 2 \cdot 0 \cdot 1) = 1$ and $a(E) = \frac{1}{6} (1 \cdot 3 \cdot 2 + 3 \cdot (-1) \cdot 0 + 2 \cdot 0 \cdot (-1)) = 1$. Thus, we may write that $\Gamma_4 = A_2 + E$. This exercise will be of great help when the selection rules in spectroscopy will be considered.

Projection Operator on an Irreducible Representation

Soon we will need information on whether a particular function exhibits certain symmetry properties of the system under consideration. To this end, we will need certain projection operators:

$$\hat{P}^{(\alpha)} = \frac{n_\alpha}{g} \sum_i \chi^{(\alpha)*}(\hat{R}_i) \hat{R}_i \quad (\text{C.13})$$

represents the projection operator that projects on the space of such functions that transform according to the irreducible representation $\Gamma^{(\alpha)}$.

This means that either $\hat{P}^{(\alpha)} f$ transforms according to the irreducible representation $\Gamma^{(\alpha)}$ or we obtain zero. In order to be a projection operator, $\hat{P}^{(\alpha)}$ has to satisfy²³

$$\hat{P}^{(\alpha)} \hat{P}^{(\beta)} = \delta_{\alpha\beta} \hat{P}^{(\alpha)}. \quad (\text{C.14})$$

We can also prove that

$$\sum_\alpha \hat{P}^{(\alpha)} = 1, \quad (\text{C.15})$$

where the summation goes over all irreducible representations of the group.

²³ This means that two functions that transform according to *different* irreducible representations are orthogonal, and that a projection of an already projected function changes nothing. Here is the proof. After noting that $\hat{R}\hat{S} = \hat{Q}$, or $\hat{S} = \hat{R}^{-1}\hat{Q}$, we have

$$\begin{aligned} \hat{P}^{(\alpha)} \hat{P}^{(\beta)} &= \frac{n_\alpha n_\beta}{g^2} \sum_{\hat{R}, \hat{S}} \chi^{(\alpha)*}(\hat{R}) \chi^{(\beta)*}(\hat{S}) \hat{R} \hat{S} \\ &= \frac{n_\alpha n_\beta}{g^2} \sum_{\hat{Q}} \hat{Q} \sum_{\hat{R}} \chi^{(\alpha)*}(\hat{R}) \chi^{(\beta)*}(\hat{R}^{-1} \hat{Q}). \end{aligned}$$

Note, that

$$\chi^{(\beta)*}(\hat{R}^{-1} \hat{Q}) = \sum_k \Gamma_{kk}^{(\beta)*}(\hat{R}^{-1} \hat{Q}) = \sum_k \sum_l \Gamma_{kl}^{(\beta)*}(\hat{R}^{-1}) \Gamma_{lk}^{(\beta)*}(\hat{Q}).$$

After inserting this result, we have

$$\begin{aligned} \hat{P}^{(\alpha)} \hat{P}^{(\beta)} &= \frac{n_\alpha n_\beta}{g^2} \sum_{\hat{Q}} \hat{Q} \sum_{\hat{R}} \sum_m \Gamma_{mm}^{(\alpha)*}(\hat{R}) \sum_k \sum_l \Gamma_{kl}^{(\beta)*}(\hat{R}^{-1}) \Gamma_{lk}^{(\beta)*}(\hat{Q}) \\ &= \frac{n_\alpha n_\beta}{g^2} \sum_{\hat{Q}} \hat{Q} \sum_{\hat{R}} \sum_{k,l,m} \Gamma_{mm}^{(\alpha)*}(\hat{R}) \Gamma_{lk}^{(\beta)}(\hat{R}) \Gamma_{lk}^{(\beta)*}(\hat{Q}) \\ &= \frac{n_\alpha n_\beta}{g^2} \sum_{\hat{Q}} \hat{Q} \sum_{k,l,m} \Gamma_{lk}^{(\beta)*}(\hat{Q}) \sum_{\hat{R}} [\Gamma_{mm}^{(\alpha)*}(\hat{R}) \Gamma_{lk}^{(\beta)}(\hat{R})], \end{aligned}$$

Transformation of a Function According to Irreducible Representation

The right part of the character table such as Table (C.5) contains the symbols x , y , z , $(x^2 - y^2)$, xy , R_x , R_y , R_z . These symbols will be needed to establish the selection rules in spectroscopy (UV-VIS, IR, Raman). They pertain to the coordinate system (the z -axis coincides with the axis of the highest symmetry). Let us leave the symbols R_x , R_y , R_z alone for the moment.

We have some polynomials in the rows of the table. *The polynomials transform according to the irreducible representation that corresponds to the row.*²⁴ If a polynomial (displayed in a row of the table of characters) is subject to the projection $\hat{P}^{(\alpha)}$, then the following is true:

- If α does not correspond to the row, then we obtain 0.
- If α corresponds to the row, then we obtain either the polynomial itself (if the irreducible representation has dimension 1), or, if the dimension of the irreducible representation is greater than 1, a linear combination of the polynomials given in the same row (in parentheses).

If function f transforms according to a 1-D irreducible representation, the function is an eigenfunction of all the symmetry operators \hat{R} , with the corresponding eigenvalues $\chi^{(\alpha)}(\hat{R})$.

Let us come back to R_x , R_y , R_z . Imagine R_x , R_y , R_z as oriented circles perpendicular to a rotation axis (i.e., x , y , or z) that symbolize rotations about these axes. For instance, the operation \hat{E} and the two rotations \hat{C}_3 leave the circle R_z unchanged, while the operations $\hat{\sigma}_v$ change its orientation to the opposite one; hence R_z transforms according to the irreducible representation A_2 . It turns out that R_x and R_y transform under the symmetry operations into their linear combinations and therefore correspond to a 2-D irreducible representation (E).

Group Theory and Quantum Mechanics

Representation Basis

If in a molecule we have two equivalent²⁵ nuclei, then this *always* results from a molecular symmetry; i.e., at least one symmetry operation exchanges the positions of these two nuclei.

because from the unitary character of the representation matrices $\Gamma^{(\beta)}(\hat{R}^{-1})$ and $\Gamma^{(\beta)}(\hat{R})$, we have $\Gamma_{kl}^{(\beta)*}(\hat{R}^{-1}) = \Gamma_{lk}^{(\beta)}(\hat{R})$. From the group theorem of orthogonality (Eq. (C.5)), we have

$$\begin{aligned} \hat{P}^{(\alpha)} \hat{P}^{(\beta)} &= \frac{n_\alpha n_\beta}{g^2} \frac{g}{n_\alpha} \sum_Q \hat{Q} \sum_{k,l,m} \Gamma_{lk}^{(\beta)*}(\hat{Q}) \delta_{ml} \delta_{mk} \delta_{\alpha\beta} \\ &= \delta_{\alpha\beta} \frac{n_\alpha}{g} \sum_Q \hat{Q} \sum_m \Gamma_{mm}^{(\alpha)*}(\hat{Q}) \\ &= \delta_{\alpha\beta} \frac{n_\alpha}{g} \sum_Q \chi^{(\alpha)*}(\hat{Q}) \hat{Q} = \delta_{\alpha\beta} \hat{P}^{(\alpha)}, \end{aligned}$$

which we wanted to show; see Eq. (C.13).

²⁴ Recall the definition of the symmetry operation given on p. e20: $\hat{R}f(\mathbf{r}) = f(\mathbf{r})$, where $\hat{R}f(\mathbf{r}) = f(\hat{R}^{-1}\mathbf{r})$.

²⁵ That is, they are equivalent with respect to physical and chemical properties.

There is no reason at all that electrons like one of such nuclei more than the other one.²⁶ Let us focus on molecular orbitals calculated for a fully symmetric Fock operator.²⁷ Therefore,

each molecular orbital has to be such that when making a square of it, the electron density is the same on the equivalent nuclei.

What will happen, however, with the *molecular orbital itself*? Squaring it removes information about its sign. The signs at both atoms may be the same (symmetric orbital), but they may also be opposite²⁸ (antisymmetric orbital). For example, the bonding orbital for the hydrogen molecule is symmetric with respect to reflection in the plane perpendicular to the internuclear axis²⁹ and going through its center, while the antibonding orbital is antisymmetric with respect to the operation.

We know how to apply the symmetry operations on molecular orbitals (p. e20) and transforming them to other functions.

²⁶ This may not be true for non-stationary states. The reason is simple. Imagine a long polymer molecule with two equivalent atoms at its ends. If one of them is touched by the tip of the tunnel microscope and one electron is transferred to the polymer, a non-stationary asymmetric electron state is created.

²⁷ Limiting ourselves to molecular orbitals is not essential in this case.

²⁸ This pertains to non-degenerate orbital levels. For a degenerate level, any linear combination of the eigenfunctions (associated to the same level) is also an eigenfunction as good as those that entered the linear combination. A symmetry operation acting on an orbital gives another orbital corresponding to the same energy. In such a case, the squares of both orbitals in general do not exhibit the symmetry of the molecule. However, we can find a linear combination of both, such that its square preserves the symmetry.

²⁹ Let us see what it really means in a very *formal* way (it may help us in more complicated cases). The coordinate system is located in the middle of the internuclear distance (on the x -axis, the internuclei distance equal to $2A$). The bonding orbital $\varphi_1 = N_1(a + b)$ and the antibonding orbital $\varphi_2 = N_2(a - b)$, where N are the normalization constants, the $1s$ atomic orbitals have the following form:

$$a \equiv \frac{1}{\sqrt{\pi}} \exp[-|\mathbf{r} - \mathbf{A}|] = \frac{1}{\sqrt{\pi}} \exp\left[-\sqrt{(x - A)^2 + y^2 + z^2}\right],$$

$$b \equiv \frac{1}{\sqrt{\pi}} \exp[-|\mathbf{r} + \mathbf{A}|] = \frac{1}{\sqrt{\pi}} \exp\left[-\sqrt{(x + A)^2 + y^2 + z^2}\right],$$

$$\mathbf{A} = (A, 0, 0).$$

The operator $\hat{\sigma}$ of the reflection in the plane $x = 0$ corresponds to the following unitary transformation matrix of the coordinates $\mathbf{U} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$. Therefore, the inverse matrix $\mathbf{U}^{-1} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$; i.e., the transformation $\mathbf{U}^{-1}\mathbf{r}$ means $x \rightarrow -x$, $y \rightarrow y$, $z \rightarrow z$, what transforms $a \rightarrow b$ and $b \rightarrow a$. Hence,

$$\hat{\sigma}(a + b) = (b + a) = (a + b)$$

$$\hat{\sigma}(a - b) = (b - a) = -(a - b).$$

In both cases, the molecular orbital represents an eigenfunction of the symmetry operator with the eigenvalue $+1$ and -1 , respectively.

Under such a symmetry operation, the orbital either remains unchanged (as the abovementioned bonding one), or changes the sign (as the antibonding one),

or, if the orbital level is degenerate, we may obtain another function. This function corresponds to the same energy because when applying any symmetry operation, we only exchange equivalent nuclei, which otherwise are on equal footing in the Hamiltonian.

If we obtain another orbital (φ_2), then we may begin to play with it by applying all the symmetry operations. Some operations will lead to the same (new) orbital (sometimes with the opposite sign) after some other operations, we obtain the old orbital φ_1 (sometimes with the opposite sign) and sometimes these operations will lead to the *third* orbital φ_3 . Then, we apply the symmetry operations to the third orbital, etc. until a final set of orbitals is obtained, whose orbitals transform into themselves when subjected to the symmetry operations. The set of such linearly independent orbitals $\varphi_i, i = 1, \dots, n$ we may treat as the basis set in a vector space.

All the results of applying the operation $\hat{\mathcal{R}}_i$ on the orbitals are collected in a transformation matrix \mathbf{R}_i , where $\boldsymbol{\varphi} = \begin{bmatrix} \varphi_1 \\ \dots \\ \varphi_n \end{bmatrix}$:

$$\hat{\mathcal{R}}_i \boldsymbol{\varphi} = \mathbf{R}_i^T \boldsymbol{\varphi}. \quad (\text{C.16})$$

The matrices $\mathbf{R}_i, i = 1, 2, \dots, g$ form the n -dimensional representation (in general reducible) of the symmetry group of the molecule.

Indeed, let us see what happens if we apply the operation $\hat{\mathcal{T}} = \hat{\mathcal{R}}_1 \hat{\mathcal{R}}_2$ to the function φ_i :

$$(\hat{\mathcal{R}}_1 \hat{\mathcal{R}}_2) \varphi_i = \hat{\mathcal{R}}_1 \mathbf{R}_2^T \boldsymbol{\varphi} = \mathbf{R}_2^T \hat{\mathcal{R}}_1 \boldsymbol{\varphi} = \mathbf{R}_2^T \mathbf{R}_1^T \boldsymbol{\varphi} = (\mathbf{R}_1 \mathbf{R}_2)^T \boldsymbol{\varphi}.$$

This means that all the matrices \mathbf{R}_i form a representation.

Basis of a Representation

A set of the linearly independent functions φ_i , that served to create the representation forms a *basis of the representation*.

The basis need not have been composed of the orbitals; it could be expressions like x, y, z or $x^2, y^2, z^2, xy, xz, yz$ or any linearly independent functions, provided they transform into themselves under symmetry operations. We may begin from an atomic orbital, and after applying the symmetry operations soon will obtain a basis set that contains this orbital and all the other equivalent ones.

Decomposition of a Function into Irreducible Representation Components

Let us take a function f belonging to a Hilbert space. Since $\sum_{\alpha} \hat{P}^{(\alpha)} = 1$ [see Eq. (C.15)], where α goes over all the irreducible representations of the group, then f can be written as a sum of its components $f^{(\alpha)}$, with each component (belonging to the corresponding subspace of the Hilbert space) transforming according to the irreducible representation α :

$$f = 1 \cdot f = \sum_{\alpha} \hat{P}^{(\alpha)} f = \sum_{\alpha} f^{(\alpha)}. \quad (\text{C.17})$$

In view of Eq. (C.14), the components $f^{(\alpha)}$ and $f^{(\beta)}$ are automatically orthogonal if $\alpha \neq \beta$.

Example 12. Decomposition of a Function

Let us take three hydrogen atoms in the configuration of equilateral triangle, and assume that we are in the simplest version of the molecular orbitals in the LCAO MO approximation; i.e., the atomic basis set is composed of the three $1s$ orbitals a , b , and c centered on the three nuclei. Let us check whether the following functions:

$$\begin{aligned} u_1 &= a + b + c \\ u_2 &= b - c \\ u_3 &= a - c, \end{aligned}$$

form a basis to a (reducible) representation. If the symmetry operations are applied to a , b , and c , then they transform into each other (cf. Fig. C.2), and the results obtained are easily shown as linear combinations of the functions u_1 , u_2 , and u_3 (with \mathbf{R}_i^T as transformation matrices). For example, $\hat{A}u_1 = a + b + c = u_1$, $\hat{A}u_2 = -b + c = -u_2$, $\hat{A}u_3 = a - b = -u_2 + u_3$. Hence,

$$\mathbf{A}^T = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & -1 & 1 \end{bmatrix}. \quad (\text{C.18})$$

In this way [see Eq. (C.16)] we obtain \mathbf{R}_i as

$$\mathbf{E} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}; \mathbf{A} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & -1 \\ 0 & 0 & 1 \end{bmatrix}; \mathbf{B} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & -1 & -1 \end{bmatrix}; \quad (\text{C.19})$$

$$\mathbf{C} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix}; \mathbf{D} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & -1 & -1 \end{bmatrix}; \mathbf{F} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & -1 \\ 0 & 1 & 0 \end{bmatrix}. \quad (\text{C.20})$$

Let us check that $\mathbf{DF} = \mathbf{E}$ and $\mathbf{AD} = \mathbf{B}$; i.e., exactly as for the operations: $\hat{D}\hat{F} = \hat{E}$, $\hat{A}\hat{D} = \hat{B}$, and so on. Thus, this is a representation—moreover, this is a representation that is already *in a block form* because u_1 transforms always in itself, while u_2 and u_3 mix among themselves. It

can be shown that this mixing cannot be avoided by any choice of u . Hence, u_1 alone represents a basis of a 1-D irreducible representation (A_1 , which is seen from the characters corresponding to the first block 1×1), while u_2 and u_3 form a basis of a 2-D irreducible representation (E). Note that from the mathematical form of the functions u , it follows that u_2 and u_3 have to correspond to the same energy and this energy is different from that corresponding to u_1 . The conclusion is that a , b , and c form a basis for a reducible representation, while their linear combinations u_1 and $\{u_2, u_3\}$ form the basis sets of two irreducible representations: A_1 and E. Any function that is a linear combination of a , b , and c can be represented as a linear combination of u_1 , u_2 , and u_3 as well.

The same symmetry orbitals can be obtained by using the projection operators of Eq. (C.13). Let us take any one of the functions a , b , or c (the result does not depend on this choice); e.g., function a . In view of a beautiful equilateral triangle, such a function is no doubt a really deformed object that does not take care of making the three vortices of the triangle equivalent. Let us see whether such a function has any component that transforms according to the irreducible representation A_1 . To this end, let us use the projection operator $\hat{P}^{(A_1)}$ [Eq. (C.13) and the table of characters on p. e37]: $\hat{P}^{(A_1)}a = \frac{1}{6}(a + b + c + a + b + c) = \frac{1}{3}(a + b + c)$. Thus, there *is* a fully symmetric component³⁰ in a . Now, let us use the same orbital a to obtain: $\hat{P}^{(A_2)}a = \frac{1}{6}(a + b + c - a - b - c) = 0$. This means that a does not contain anything that transforms according to A_2 . Now is the turn of the irreducible representation E: $\hat{P}^{(E)}a = \frac{2}{6}(2a - b - c + 0 \cdot a + 0 \cdot b + 0 \cdot c) = \frac{1}{3}[2(a - c) - (b - c)]$. We obtain a linear combination of u_2 and u_3 .

If the projections were made for the function b , then we would obtain a trivial repetition³¹ of the irreducible representations A_1 and A_2 and a non-trivial result for the irreducible representation E: $\hat{P}^{(E)}b = \frac{2}{6}(2b - a - c + 0 \cdot a + 0 \cdot b + 0 \cdot c) = \frac{1}{3}[2(b - c) - (a - c)]$. This is just another linear combination of u_2 and u_3 . These two functions are therefore inseparable and form a basis for a 2-D *irreducible* representation.

Decomposition into Irreducible Representations

Any function that is a linear combination of the basis functions of a *reducible* representation can be decomposed into a linear combination of the basis functions of those *irreducible* representations that form the reducible representation.

³⁰ This sentence carries a simple message: that by mixing symmetric objects, we may obtain an asymmetric one; e.g., the asymmetric function $a + 2b$ can be represented by a linear combination $u_1 + u_2$, with both functions transforming according to irreducible representation of the symmetry group.

³¹ $\hat{P}^{(A_1)}b = \frac{1}{3}(a + b + c)$ and $\hat{P}^{(A_2)}b = 0$.

The Most Important Point

The Most Important Point so Far

The wave functions corresponding to an energy level have the following characteristics:

- They *form a basis of an irreducible representation* of the symmetry group of the molecule, or in other words, they transform according to this irreducible representation.
- The dimension of the representation is equal to the degeneracy of the energy level.

This is how it should be, because if a symmetry operation acts on an eigenfunction of the Hamiltonian, we will have only two possibilities: (1) we obtain the same function to the accuracy of the sign (which in the case of a 1-D representation is by definition irreducible); (2) another function *corresponding to the same energy* (because of the same physical situation). Acting on the function obtained and repeating the whole procedure we will arrive finally to a set of n linearly independent functions that correspond to the same energy (a basis of a n -dimensional irreducible representation).

This means (see Fig. C.4) that

the energy levels may be labeled by tags, each tag corresponds to a single irreducible representation. This will be of fundamental importance when the selection rules in spectroscopy will be considered.

We usually have plenty of the energy levels, while the number of the irreducible representation is small. Thus, there will be in general a lot of levels with the same labels. This result was first obtained by Eugene Wigner. The group theory will not tell us about how many levels correspond to a particular irreducible representation, or what energy they correspond to.

Integrals Important in Spectroscopy

Direct Product of Irreducible Representations

We are approaching the application of group theory in optical transitions in spectroscopy. The most important issue will be a decision whether an integral is zero or nonzero. If the integral is zero, then the transition is forbidden, while if it is nonzero, then it is allowed. To make such a decision, we have to use what is known as the *direct product of irreducible representations*. Imagine basis functions $\{\varphi_i\}$ and $\{\psi_j\}$ that correspond to irreducible representations α and β of

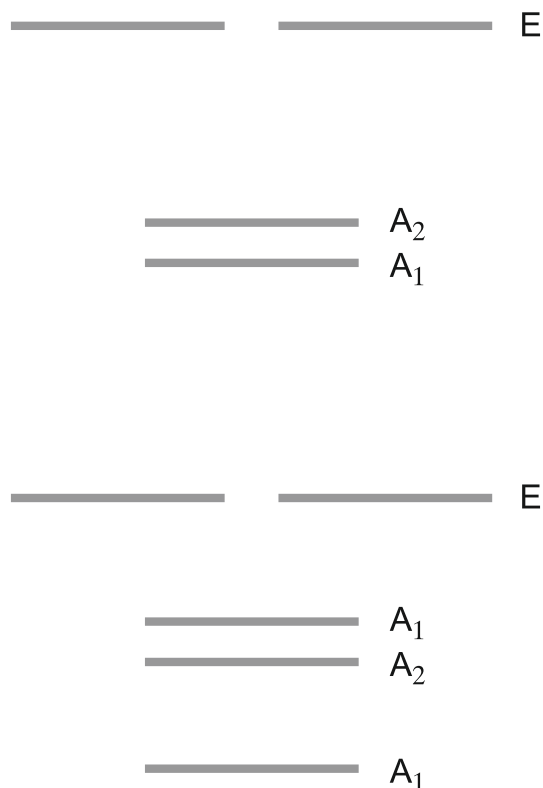


Fig. C.4. Each energy level corresponds to an irreducible representation of the symmetry group of the Hamiltonian. Its linearly independent eigenfunctions that correspond to a given level form a basis of the irreducible representation, or in other words, transform according to this representation. The number of the basis functions is equal to the degeneracy of the level.

the symmetry group of a molecule. Let us make a set $\{\varphi_i \psi_j\}$ of all possible products of them (i.e., the Cartesian product).

Direct Product

The products $\{\varphi_i \psi_j\}$ when subject to symmetry operations lead (as usual) to a representation, we call it the *direct product* $\Gamma^\alpha \times \Gamma^\beta$ of the irreducible representations Γ^α and Γ^β .

The functions $\{\varphi_i \psi_j\}$ form a basis set of the representation (reducible in general). We obtain the matrices of the representations as usual by applying symmetry operations:

$$\begin{aligned} \hat{R} [\varphi_i(\mathbf{r}) \psi_j(\mathbf{r})] &= \varphi_i(\hat{R}^{-1}\mathbf{r}) \psi_j(\hat{R}^{-1}\mathbf{r}) = \sum_k U_{ik}^{(\alpha)} \varphi_k \sum_l U_{jl}^{(\beta)} \psi_l = \sum_{kl} U_{ik}^{(\alpha)} U_{jl}^{(\beta)} \varphi_k \psi_l \\ &= \sum_{kl} Z_{ij,kl} \varphi_k \psi_l, \end{aligned}$$

where $U_{ik}^{(\gamma)}$ are the matrix elements of the irreducible representation γ , $Z_{ij,kl} = U_{ik}^{(\alpha)} U_{jl}^{(\beta)}$. Of course,

the dimension of this representation is the product of the dimensions of the representations α i β , because this is the number of the functions $\varphi_k \psi_l$.

The characters of the representation can be easily obtained from the characters of the irreducible ones, just we have to multiply the latter ones:

$$\chi^{(\alpha \times \beta)}(\hat{R}) = \chi^{(\alpha)}(\hat{R}) \chi^{(\beta)}(\hat{R}). \quad (\text{C.21})$$

Indeed, the formula is justified by

$$\begin{aligned} \chi(\hat{R}) &= \sum_{kl} Z_{kl,kl} = \sum_{kl} U_{kk}^{(\alpha)} U_{ll}^{(\beta)} = \left(\sum_k U_{kk}^{(\alpha)} \right) \left(\sum_l U_{ll}^{(\beta)} \right) \\ &= \chi^{(\alpha)}(\hat{R}) \chi^{(\beta)}(\hat{R}). \end{aligned} \quad (\text{C.22})$$

This rule can be naturally generalized for a larger number of the irreducible representations in the direct product (just multiply the characters of the irreducible representations). We will have a product of three irreducible representations shortly.

When Is an Integral Bound to Be Zero?

Everybody knows how to calculate the integral

$$\int_{-1}^{+1} x dx = \left[\frac{x^2}{2} \right]_{-1}^{+1} = \frac{1}{2} - \frac{1}{2} = 0.$$

Note, however, that we can tell what the value of the integral is without calculating, just by looking at the integrand. Indeed, the integrand is odd with respect to the transformation $x \rightarrow -x$; i.e., the plot of the integral is an antisymmetric function with respect to the reflection in the plane perpendicular to x at $x = 0$. The integration limits are symmetric with respect to that point. An integral means the surface under the plot; therefore, what we gain for $x > 0$, we lose for $x < 0$, and the integral will be exactly zero.

The force of the group theory relies on the fact that even having a complicated integrand, we are able to tell immediately whether the integral *is* equal to zero. This will allow us to predict whether an optical transition is allowed or forbidden.

We have to stress that these conclusions will be valid independent of the approximations used to compute the molecular wave functions. The reason is that they follow from the symmetry, which is identical for the exact and approximate wave functions.

The previous example can be generalized. Let us take the integral

$$\int f_{\alpha} f_{\beta} f_{\gamma} \cdots d\tau, \quad (\text{C.23})$$

where $f_{\alpha}, f_{\beta}, f_{\gamma}, \dots$ transform according the irreducible representations $\Gamma^{(\alpha)}, \Gamma^{(\beta)}, \Gamma^{(\gamma)}, \dots$, respectively, of a symmetry group, and the integration is over the whole space.

When does the Integral Equal Zero?

If a representation (which in general is reducible), being the direct product of the irreducible representations $\Gamma^{(\alpha)}, \Gamma^{(\beta)}, \Gamma^{(\gamma)}, \dots$, does not contain the fully symmetric representation (that one with all its characters equal 1), then the integral equals zero.

We have been working so hard with symmetry groups, operations, characters, etc. This result is precisely what we wanted to accomplish in this appendix. The essence of the theorem is very simple. The product $f_{\alpha} f_{\beta} f_{\gamma} \dots$ transforms according to the (in general *reducible*) representation, which is the direct product of the irreducible representations $\Gamma^{(\alpha)}, \Gamma^{(\beta)}, \Gamma^{(\gamma)}, \dots$. This means that according to Eq. (C.17), the integrand $f_{\alpha} f_{\beta} f_{\gamma} \dots$ can be represented as a linear combination of the basis functions of all the irreducible representations: $f_{\alpha} f_{\beta} f_{\gamma} \dots = \sum_{\mu} g_{\mu}$, where g_{μ} transforms according to the irreducible representation $\Gamma^{(\mu)}$. Therefore, the integral [Eq. (C.23)] is a sum of the integrals

$$\int f_{\alpha} f_{\beta} f_{\gamma} \dots d\tau = \sum_{\mu} \int g_{\mu} d\tau, \quad (\text{C.24})$$

each with the integrand transforming to an *irreducible* representation $\Gamma^{(\mu)}$. Let us take one of these integrals: $\int g_{\mu} d\tau$. Note that the integration is over the whole space (i.e., the integration limits are symmetric). If the integrand g_{μ} were antisymmetric with respect to one or more symmetry operations, the integral would automatically equal zero (the same argument as for $\int x dx$). From this, it follows that all integrals in the sum would be zero except that single one that contains the integrand transforming according to the fully symmetric representation.³²

There are two special cases of this theorem that are important to this discussion.

³² Only for the fully symmetric representation are all the characters equal to 1, and therefore the corresponding function does not change under symmetry operations.

Two Special Cases

$\int f_\alpha f_\beta d\tau = \delta_{\alpha\beta} A$; i.e., in order to have the integral not vanish, we have to have $\Gamma^{(\alpha)} = \Gamma^{(\beta)}$.

The proof is very simple and relies on the fact that the characters of the fully symmetric irreducible representation equal 1. We can calculate the number of times, $a(A)$, that the fully symmetric representation A is present in the direct product $\Gamma^{(\alpha)} \times \Gamma^{(\beta)}$ from the following formula:

$$\begin{aligned} a(A) &= \frac{1}{g} \sum_i \chi^{(\alpha \times \beta)}(\hat{R}_i) \chi^{(A)}(\hat{R}_i)^* \\ &= \frac{1}{g} \sum_i \chi^{(\alpha \times \beta)}(\hat{R}_i) = \frac{1}{g} \sum_i \chi^{(\alpha)}(\hat{R}_i) \chi^{(\beta)}(\hat{R}_i)^* = \delta_{\alpha\beta}. \end{aligned} \quad (\text{C.25})$$

This means that the fully symmetric representation is always present in $\Gamma^{(\alpha)} \times \Gamma^{(\alpha)}$, and therefore the integral does not vanish.³³

Let us take the integral

$$\int f_\alpha f_\beta f_\gamma d\tau, \quad (\text{C.26})$$

where $f_\alpha, f_\beta, f_\gamma$ transform according to the irreducible representations α, β, γ . In order to have the non-vanishing integral, the direct product $\Gamma^{(\alpha)} \times \Gamma^{(\beta)}$ must contain the representation $\Gamma^{(\gamma)}$.

This means that in order to have Eq. (C.26) not vanish, the function $f_\alpha f_\beta$ decomposes [Eq. (C.17)] in such a way that there is a nonzero component belonging to $\Gamma^{(\gamma)}$. If this happens, according to the previous case, a component of the integrand will transform according to the fully symmetric representation, what will keep the expression (C.26) from vanishing.

Selection Rules for Electronic Transitions (UV-VIS)

The selection rules will be shown taking an example of pyrazine and its monoprotonated- and diprotonated ions (Fig. C.5).

³³ It is easy to understand. What transforms according to $\Gamma^{(\alpha)} \times \Gamma^{(\alpha)}$ is a product of two (in general different) functions, each belonging to $\Gamma^{(\alpha)}$. This means that the function behaves in a very special way (typical for $\Gamma^{(\alpha)}$) under the symmetry operations (e.g., changes sign under \hat{R}_1), while other operations leave it unchanged. If we have a product of two such functions, then this means that the product does not change at all under \hat{R}_1 (and, of course, the other operations); i.e., transforms according to the fully symmetric operation. This is why the fully symmetric representation is always present in $\Gamma^{(\alpha)} \times \Gamma^{(\alpha)}$.

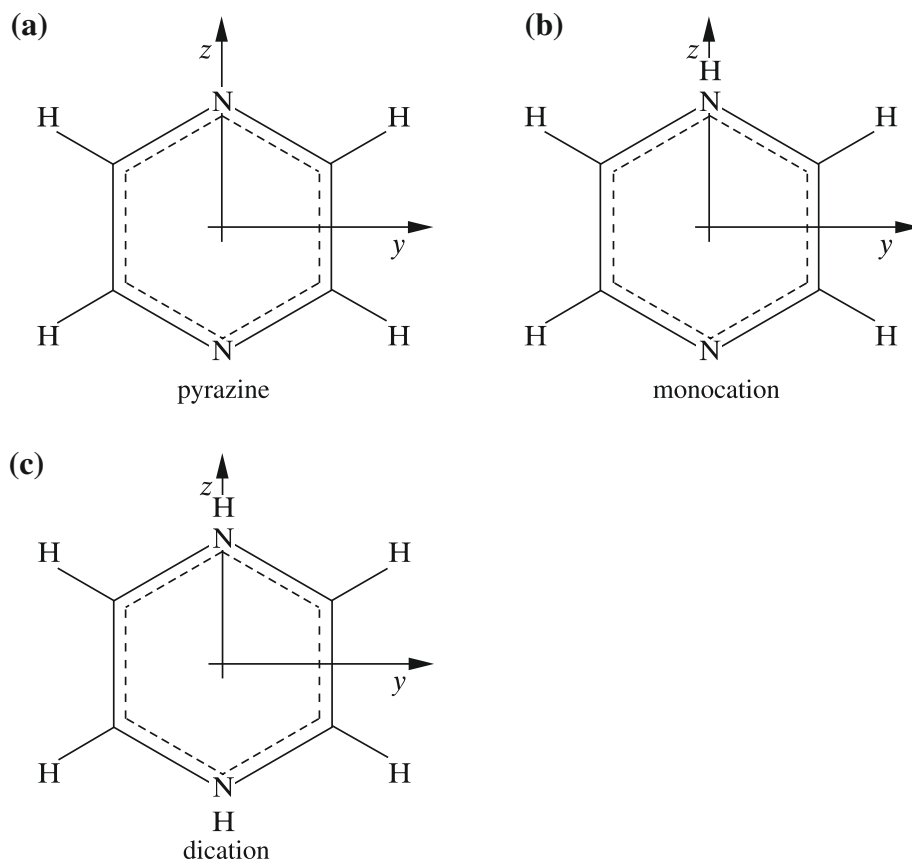


Fig. C.5. The pyrazine (a) and its monoprotonated- (b) and diprotonated (c) derivatives. The x -axis is perpendicular to the ring plane, the y -axis is in the ring plane perpendicular to the NN axis, and the z -axis means the NN axis.

A glimpse on the chemical formulas is sufficient to tell, that the monocation of the pyrazine has the same symmetry as H_2O that corresponds to the symmetry group C_{2v} (see Table C.4), while the pyrazine and its diprotonated derivative have the symmetry identical with that of the naphthalene; i.e., D_{2h} . Let us focus first on the last case.

Example 13. Pyrazine and Its Diprotonated Derivative

Every book on group theory contains the table of characters of the symmetry group D_{2h} (see Table C.6; the x -axis perpendicular to the plane of the molecule, and z goes through the nitrogen atoms).

From Table C.6, we see³⁴ that what we call *irreducible representations* represent *distinct rhythms* of pluses and minuses, which after making the square, give the fully symmetric behavior.

³⁴ Note that all the irreducible representations of the symmetry group of the molecules under consideration are 1-D, so their energy levels are non-degenerate.

Table C.6. D_{2h} group table of characters.

D_{2h}	\hat{E}	$\hat{C}_2(z)$	$\hat{C}_2(y)$	$\hat{C}_2(x)$	\hat{i}	$\hat{\sigma}(xy)$	$\hat{\sigma}(xz)$	$\hat{\sigma}(yz)$	
A_g	1	1	1	1	1	1	1	1	x^2, y^2, z^2
B_{1g}	1	1	-1	-1	1	1	-1	-1	R_z xy
B_{2g}	1	-1	1	-1	1	-1	1	-1	R_y xz
B_{3g}	1	-1	-1	1	1	-1	-1	1	R_x yz
A_u	1	1	1	1	-1	-1	-1	-1	
B_{1u}	1	1	-1	-1	-1	-1	1	1	z
B_{2u}	1	-1	1	-1	-1	1	-1	1	y
B_{3u}	1	-1	-1	1	-1	1	1	-1	x

All the electronic states of the pyrazine and its diprotonated derivative can be labeled by the irreducible representation labels: $A_g, B_{1g}, B_{2g}, B_{3g}, A_u, B_{1u}, B_{2u}, B_{3u}$.

We may ask at this point, what are the selection rules for the state-to-state optical transitions? Are all the transitions allowed, or are some of them forbidden? From the theory of the electromagnetic field (cf. Chapters 2 and 12), it follows that the probability of the transition between the states k and l is proportional to $|\mu_{kl}(x)|^2$, to $|\mu_{kl}(y)|^2$, or to $|\mu_{kl}(z)|^2$, respectively,³⁵ with

$$\begin{aligned}\mu_{kl}(x) &= \int \psi_k^* \hat{\mu}_x \psi_l d\tau \\ \mu_{kl}(y) &= \int \psi_k^* \hat{\mu}_y \psi_l d\tau \\ \mu_{kl}(z) &= \int \psi_k^* \hat{\mu}_z \psi_l d\tau,\end{aligned}\tag{C.27}$$

where ψ stand for the electronic states k and l ; $\hat{\mu}_x, \hat{\mu}_y, \hat{\mu}_z$ are the operators of the molecular dipole moment components³⁶ (e.g., $\hat{\mu}_z = \sum_i q_i z_i$); and, q_i is the electric charge of the particle (electron or nucleus) having its z component equal to z_i . Since we will decide, by using group theory, whether this integral³⁷ vanishes or not, what will count is that μ_x transforms exactly the same way that the coordinate x does. The integrand $\psi_k^* \hat{\mu}_x \psi_l$ transforms as the direct product of the three irreducible representations: that of ψ_k , that of $\hat{\mu}_x$ and that of ψ_l .

³⁵ Depending on the electromagnetic wave polarization along axes x or y or z axes. From the equality $|\mu_{kl}(x)|^2 = |\mu_{lk}(x)|^2$, and similarly for y and z , it follows that the optical excitation and the corresponding deexcitation have the same probability.

³⁶ This may look alarming because the operator depends on the choice of the coordinate system (cf. see Appendix X available at booksite.elsevier.com/978-0-444-59436-5). Do not worry, though—everything is all right. Even if the dipole moment depends on such a choice, any two choices give the dipole moments that differ by a *constant vector*. This vector, being a constant, can be shifted outside the integral and the integral itself will become zero, because ψ_k and ψ_l are orthogonal. Thus, to our delight, light absorption does not depend on the choice of the coordinate system.

³⁷ The integration goes over all the electronic coordinates.

Excitations from the Ground State

Suppose we do the following:

- Have a molecule in its ground state ψ_k (thus, belonging to the fully symmetric irreducible representation A_g)
- Immobilize the molecule in space (say, in crystal),
- Introduce the coordinate system in the way described above,
- Irradiate the molecule with a light polarized along the x -axis

Then, we ask to *which states the molecule can be excited*. The direct product of A_g and the irreducible representation to which x belongs decomposes into some irreducible representations. For the allowed optical transition, we have to find among them the irreducible representation to which ψ_l belongs (just recall that $\int f_\alpha f_\beta d\tau = \delta_{\alpha\beta} A$). Only then will the integrand contain something that has a chance to be transformed according to the fully symmetric representation. The x -coordinate belongs to the representation B_{3u} (see the last column of Table C.6). Therefore, let us see what represents the direct product $A_g \times B_{3u}$. We have Eq. (C.12) for the integer $a(\alpha)$ that is a number of the irreducible representations α in a given reducible representation. Let us compute this number for the (in general reducible) representation being the direct product and all the irreducible representations α . In this particular case, the direct product is³⁸ $A_g \times B_{3u}$. We have

$$\begin{aligned} a(A_g) &= \frac{1}{8}[1 \times 1 + 1 \times (-1) + 1 \times (-1) + 1 \times 1 + 1 \times (-1) + 1 \times 1 \\ &\quad + 1 \times 1 + 1 \times (-1)] = 0 \\ a(B_{1g}) &= \frac{1}{8}[1 \times 1 + 1 \times (-1) + (-1) \times (-1) + (-1) \times 1 \\ &\quad + 1 \times (-1) + 1 \times 1 + (-1) \times 1 \\ &\quad + (-1) \times (-1)] = 0 \end{aligned}$$

etc., all equaling zero, and finally

$$\begin{aligned} a(B_{3u}) &= \frac{1}{8}(1 \times 1 + (-1) \times (-1) + (-1) \times (-1) + 1 \times 1 + (-1) \times (-1) + 1 \times 1 \\ &\quad + 1 \times 1 + (-1) \times (-1)] = 1, \end{aligned}$$

³⁸ The characters of $A_g \times B_{3u}$ are as follows (in the order of the symmetry operations in the table of characters):
 1 -1 -1 1 -1 1 1 -1;
 i.e., they are identical to those of the (it turned out ...irreducible) representation B_{3u} . Such a product is a 100 percent banality to make. Just in the table of characters, one finger goes horizontally over the characters of A_g (all they are equal to ...1), while the second finger moves similarly over the characters of B_{3u} ; and we multiply what the first finger shows by that, which indicates the second one. The result is the character of the direct product $A_g \times B_{3u}$, which in this case turns out to be exactly the character of B_{3u} . This is why we may expect that $a(\alpha)$ will all be zero except $a(B_{3u}) = 1$.

exactly as we have expected. Thus, we can write³⁹

$$A_g \times B_{3u} = B_{3u}.$$

Now only those ψ_l are allowed in optical transitions (from the ground state A_g) that are labeled by B_{3u} , because only the direct product $B_{3u} \times B_{3u}$ may contain the fully symmetric irreducible representation A_g . Thus, the transitions $A_g \Rightarrow B_{3u}$ as well as $B_{3u} \Rightarrow A_g$ are allowed, if the light is polarized along x ; i.e., perpendicularly to the ring of the molecule.

Now, let us take the light polarized along y ; i.e., within the molecular plane, perpendicularly to the N-N line. This time, we are interested in the irreducible representations that arise from $A_g \times B_{2u}$, because y transforms according to B_{2u} . Very similar to before [by analyzing $a(\alpha)$], we find that

$$A_g \times B_{2u} = B_{2u}.$$

This means that now the allowed states are of the B_{2u} type.

Similarly, for the polarization along z (z belongs to B_{1u}), i.e., along the nitrogen-nitrogen direction, we have

$$A_g \times B_{1u} = B_{1u}.$$

Thus, for polarization parallel to the NN axis of the molecule, the absorption may occur from the ground state to any state of the B_{1u} type (and *vice versa*).

Nothing more can be said when basing solely on the group theory. One will not get any information about the energies of the transitions, as well as about the corresponding intensities. In order to get this additional (and important) information, we have to take pains and work hard to solve the Schrödinger equation, rather than count on some easy profits obtained by primitive multiplication of integers (as in the group theory). To obtain the intensities, we have to calculate the transition moment integrals μ_{kl} . However, the group theory, just by excluding from the spectrum a lot of transitions (forbidden ones), provides a lot of important information on the symmetry of the molecule. Table C.7 collects the calculated light frequencies⁴⁰ ($\bar{\nu}$ in wave numbers, or cm^{-1} , $\nu = c\bar{\nu}$, where ν is the usual frequency), the so-called oscillator strengths f_{kl} (in a.u.) are as follows:

$$f_{kl} = \frac{4\pi c}{3} \nu |\mu_{kl}|^2, \quad (\text{C.28})$$

as well as the polarization of light for excitations from the electronic ground state for the pyrazine and the pyrazine monocation. It is seen that the left side of Table C.7 is consistent with the selection rules derived above. Indeed, a large f_{kl} corresponds only to those transitions from the ground state of the pyrazine that have been predicted as allowed (B_{1u} , B_{2u} and B_{3u}). Also the predicted polarization agrees with the observed ones.

³⁹ We may say that the fully symmetric representation plays a role of unity in the multiplication of irreducible representations.

⁴⁰ J. Koput, unpublished results.

Table C.7. Wave numbers ($\bar{\nu}$, in cm^{-1}), oscillator strengths (f_{kl}) and light polarization (in parentheses).

Pyrazine			Pyrazine Monocation		
Excited State	$\bar{\nu}$	f_{kl}	Excited State	$\bar{\nu}$	f_{kl}
B_{3u}	28960	0.015(x)	B_1	27440	0.007(x)
B_{2u}	36890	0.194(y)	B_2	34130	0.280(y)
B_{2g}	38890	0.0	A_2	45100	0.0
A_u	41710	0.0	A_1	49720	0.126(z)
B_{1u}	49800	0.183(z)	B_1	57380	0.012(x)
B_{1g}	57070	0.0	A_2	57710	0.0
B_{1u}	57420	0.426(z)	A_1	58210	0.625(z)
A_u	60170	0.0	A_2	59830	0.0
B_{2g}	60970	0.0	B_2	60370	0.010(y)

Excitations from an Excited State

Calculations for the absorption from the ground state were particularly simple. Now, let us see whether anything will be more complicated for the transitions from an excited state of the B_{2g} type of symmetry. We are going to calculate $a(\alpha)$ (for every α) for the following representations:

$$\begin{aligned} \text{for polarization along } x: & \quad B_{2g} \times B_{3u} \\ \text{for polarization along } y: & \quad B_{2g} \times B_{2u} \\ \text{for polarization along } z: & \quad B_{2g} \times B_{1u}. \end{aligned}$$

The characters of the representation $B_{2g} \times B_{3u}$ are the following (Table C.6, the first finger goes along B_{2g} , the second – along B_{3u} , etc.)

$$1 \quad -1 \quad -1 \quad -1 \quad -1 \quad 1 \quad 1$$

and are identical with the characters of B_{1u} . Hence, even without any calculation of $a(\alpha)$, we have $B_{2g} \times B_{3u} = B_{1u}$. Thus, the transitions (for the polarization along x) are allowed only to the states labeled by B_{1u} , because otherwise there is no chance to obtain a fully symmetric integrand. Similarly, by multiplying B_{2g} and B_{2u} , we obtain the following characters of $B_{2g} \times B_{2u}$:

$$1 \quad 1 \quad 1 \quad 1 \quad -1 \quad -1 \quad -1 \quad -1$$

and this is identical to the characters of A_u , so $B_{2g} \times B_{2u} = A_u$. If the polarization of the light is along y , then the only excitations (or deexcitations) possible are to the states belonging to A_u . Finally, for the polarization along z , we find the characters of $B_{2g} \times B_{1u}$:

$$1 \quad -1 \quad -1 \quad 1 \quad -1 \quad 1 \quad 1 \quad -1$$

that turn out to be those of B_{3u} . This means that $B_{2g} \times B_{1u} = B_{3u}$ and that the transitions are possible only to the states belonging to B_{3u} .

Table C.8. C_{2v} group characters.

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

Example 14. Pyrazine Monocation

As to the selection rules, nothing was said so far about the pyrazine monocation. We will be interested in excitations from the electronic ground state (as in Table C.7). The pyrazine monocation corresponds to the symmetry group C_{2v} (shown in Table C.8).

The ground state belongs to the fully symmetric irreducible representation A_1 . Since (as before) we begin by excitations from the ground state, then let us see which irreducible representations arise from $A_1 \times B_1$ (for the x polarization of light, see Table C.8; x transforms according to B_1), $A_1 \times B_2$ (for the y polarization) and $A_1 \times A_1$ (for the z polarization). We calculate the characters of $A_1 \times B_1$ by multiplying 1 by

$$1 \quad -1 \quad 1 \quad -1,$$

and checking in Table C.8 that these correspond to B_1 (it has to be like that because the characters of A_1 all equal 1); i.e., $A_1 \times B_1 = B_1$. Similarly, even without immediate checking, we see that $A_1 \times B_2 = B_2$ and $A_1 \times A_1 = A_1$. In this way, the following allowed transitions from the ground state (A_1) have been predicted:

- for polarization along x : $A_1 \rightarrow B_1$;
- for polarization along y : $A_1 \rightarrow B_2$;
- for polarization along z : $A_1 \rightarrow A_1$.

Now we are able to compare the spectrum for the pyrazine and for its monocation, as shown in Table C.7. Attaching a proton to the pyrazine (creating its monocation) does not look like something that would ruin the UV-VIS spectrum. We might expect that the frequencies of the bands, and even their intensities, should be somehow similar in both molecules. As we can see from the Table C.7, the frequencies are similar indeed, although in the middle of the table, the deviations are quite significant. For both molecules, there are forbidden ($f_{kl} = 0$) and allowed ($f_{kl} \neq 0$) transitions. Note that what is allowed for the pyrazine is also allowed for its cation; the light polarization coincides; and even the values of f_{kl} are similar (we took into account that the transition to B_{1u} in pyrazine with the frequency 49800 cm^{-1} corresponds to the transition to A_1 in the monocation with the frequency 49720 cm^{-1}). In the monocation, there are some additional transitions allowed: to B_1 and to B_{2g} . This is quite understandable because the number of symmetry operations for the monocation is smaller, and forbidding results from molecular symmetry. If a molecule had no symmetry operations at all (except of course the identity symmetry), all transitions would be allowed.

Thus, with practically no effort, we find the selection rules in UV-VIS for any molecule we want.

Selection Rules in IR and Raman Spectra

The selection rules derived above pertained to electronic transitions, where the positions of the nuclei were fixed in space. Now a change of the vibrational states of the molecule will be considered, while the electronic state is assumed to be unchanged. The vibrations of a molecule are related to its vibrational levels (each of them corresponding to an irreducible representation) and the corresponding vibrational wave functions, and the IR spectrum results from transitions between such levels. Fig. C.6 shows the energy levels of three normal modes.

In the harmonic approximation, the problem of small amplitude vibrations (discussed in Chapters 6 and 7) reduces to the $3N - 6$ normal modes (N is the number of atoms in the molecule). Each of the normal modes may be treated as an independent harmonic oscillator. A normal mode moves all the atoms with a certain frequency about their equilibrium positions

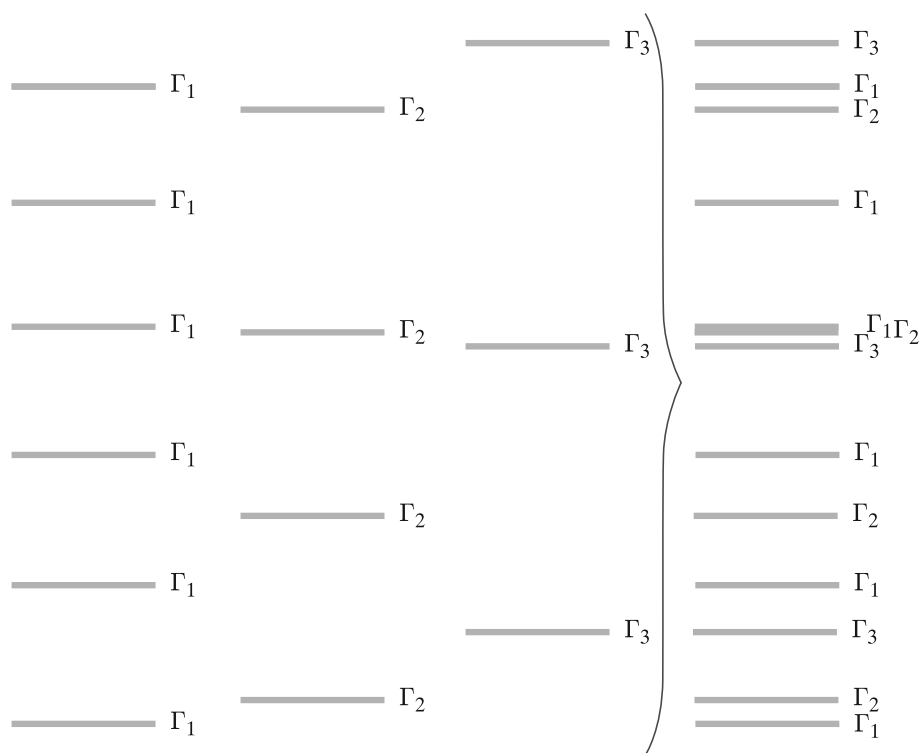


Fig. C.6. Small amplitude harmonic vibrations of a molecule (N atoms) are described by $3N - 6$ independent harmonic oscillators (normal modes). Each normal mode is characterized by an irreducible representation. A scheme of the vibrational energy levels of three normal modes corresponding to the irreducible representations Γ_1 , Γ_2 , Γ_3 . The modes have different frequencies, so the interlevel separations are different for all of them (but equal for a given mode due to the harmonic potential). On the right side, all these levels are shown together.

in a concerted motion (the same phase). The relative deviations (i.e., the ratios of the amplitudes) of the vibrating atoms from the equilibrium are characteristic for the mode, while the deviation itself is obtained from them by multiplication by the corresponding normal mode coordinate $Q \in (-\infty, \infty)$. The value $Q = 0$ corresponds to the equilibrium positions of all the atoms, Q and $-Q$ correspond to two opposite deviations of any atom from its equilibrium position.

Each normal mode belongs to an irreducible representation of the symmetry group of the molecule. What does it really mean? In any mode, the displacements of the *equivalent* atoms from the equilibrium have the same absolute value, although they may differ by sign.

We assume that small atomic deviations satisfy the symmetry requirements of the symmetry group of the molecule (valid for all atoms in the equilibrium positions) and transform according to the irreducible representation, to which the normal mode belongs. Squaring the deviations destroys information about their signs; i.e., the absolute values of the deviations of the equivalent atoms are the same. This means that the squares of deviations transform according to the fully symmetric representation of the group.

To establish the vibrational selection rules let us define first the vibrational states of $3N - 6$ harmonic oscillators (normal modes). The ground state of the system is no doubt the state, in which *every* normal mode i is in its ground state, $\psi_{i,0}$. The ground-state wave function of the i th normal mode reads as (p. 186)

$$\psi_{i,0} = N_0 \exp(-a_i Q_i^2), \quad (\text{C.29})$$

where $a_i > 0$ is a constant, and Q_i is the normal mode coordinate. Whatever this normal mode is, the wave function contains the *square* of Q_i ; i.e., the sign of the deviations of the equivalent atoms is *irrelevant*.

The squares of the deviations and therefore function $\psi_{i,0}$ itself transform independently of i .

Let us denote this fully symmetric irreducible representation by A_1 . The wave function of the first *excited state* of a normal mode has the form

$$\psi_{i,1} = N_1 Q_i \exp(-a_i Q_i^2), \quad (\text{C.30})$$

and we see that $\psi_{i,1}$ transforms exactly as the coordinate Q_i does; i.e., according to that irreducible representation to which the normal mode belongs (because Q_i^2 in the exponent and therefore the exponent itself both belong to the fully symmetric representation). In the harmonic approximation, the total vibrational wave function of the system of $3N - 6$ normal (i.e.,

independent) oscillators can be written as

$$\psi_0^{osc} = \psi_{1,0}\psi_{2,0}\psi_{3,0}\dots\psi_{3N-6,0}, \quad (\text{C.31})$$

the zeros in the indices mean that all the modes are in their ground states. This means that ψ_0^{osc} transforms according to the representation being the direct product $A_1 \times A_1 \times A_1 \times \dots \times A_1 = A_1$ (a banality, all the characters of A_1 are equal 1). Now, let us focus on the excited states of the $3N - 6$ vibrational modes. The excited states may be quite complex, but the most important (and the simplest) ones are those with all the normal modes in their ground states except a single mode that is in its first excited state. A transition from the many-oscillator ground state to such an excited state is called a *fundamental transition*. The intensities of the fundamental transitions are at least by one order of magnitude larger than others. This is why we will focus on the selection rules for such transitions. Let us take one of these singly excited states (with the first mode excited):

$$\psi_1^{osc} = \psi_{1,1}\psi_{2,0}\psi_{3,0}\dots\psi_{3N-6,0}. \quad (\text{C.32})$$

The function $\psi_{1,1}$ corresponding to the first excited state transforms according to the irreducible representation Γ , to which the normal mode 1 belongs. Thus, ψ_1^{osc} transforms according to $\Gamma \times A_1 \times A_1 \times A_1 \times \dots \times A_1 = \Gamma$; i.e., it belongs to the same irreducible representation as $\psi_{1,1}$ does. Of course, if the only excited mode were the i th one, then the many-oscillator wavefunction would belong to the same irreducible representation as the wavefunction of the particular oscillator does. We will need this result soon.

IR Selection Rules

Let us consider a molecule having a fixed position in a Cartesian coordinate system. To excite the molecule, the IR light (because the separation of the vibrational levels corresponds to the infrared region) is used that is polarized along the x -axis. The electromagnetic theory says that what decides the intensity of the absorption is the square of the transition integral⁴¹

$$\int \psi_0^{osc} \hat{\mu}_x \psi_1^{osc} d\tau, \quad (\text{C.33})$$

where $\hat{\mu}_x$ stands for the dipole moment component x . The selection rules mean to establish which integrals of that kind will be zero for symmetry reasons. To this end, what we need is information about the irreducible representations to which ψ_0^{osc} , $\hat{\mu}_x$, ψ_1^{osc} belong.⁴² Since ψ_0^{osc} transforms according to A_1 , the integral to survive the function ψ_1^{osc} has to belong to the same irreducible representation as $\hat{\mu}_x$ (and therefore x itself). It was shown that ψ_1^{osc} belongs to the same irreducible representation to which the normal mode 1 belongs. In other words, the rule is as follows:

⁴¹ The integration goes over the coordinates of the nuclei.

⁴² We are going to analyze the direct product of these three representations. If it contains the fully symmetric representation, then the integral is not zero.

Selection Rule in IR

the transition from the ground state is allowed for those normal modes that transform as x , where x is the direction of the light polarization. It also will be similar for the light polarization along y and z .

Raman Selection Rules

The physics of the Raman spectra⁴³ is different: rather than direct absorption, this is a light scattering (in the UV-VIS region) on molecules. It turns out that besides the light the source is emitting, we detect also quanta of the energy lower or higher by $h\nu$, where ν is a vibrational frequency of the molecule. For the Raman scattering to be nonzero, at least one of the following integrals should be nonzero:

$$\int \psi_0^{osc} \hat{\alpha}_{qq'} \psi_1^{osc} d\tau, \quad (\text{C.34})$$

where $\hat{\alpha}_{qq'}$ with $q, q' = x, y, z$ is a component of the polarizability tensor, that transforms as one of the following [cf., Eq. (12.42), p. 744]: $qq' = x^2, y^2, z^2, xy, xz, yz$ or their linear combinations (this information is available in the tables of characters). An identical reasoning as before leads to the conclusion that

the normal mode excited in a fundamental transition has to belong to the same irreducible representation as the product qq' .

It remains to be seen to *which irreducible representations the normal modes belong*. The procedure consists of two stages.

Stage 1. The global Cartesian coordinate system is chosen. In this system, we draw the equilibrium configuration of the molecule, with the atoms numbered. On each atom, a local Cartesian coordinate system is located with the axes parallel to those of the global one. For each atom we draw the arrows of its displacements along x , y and z oriented toward the positive values ($3N$ displacements all together), assuming that the displacements of equivalent atoms have to be the same. When symmetry operations are applied, these displacements transform into themselves⁴⁴ and therefore form a basis set of a (reducible) representation Γ of the symmetry

⁴³ Chandrasekhar Venkata Raman (1888–1970), was an Indian physicist and professor at the University of Calcutta and at the Indian Scientific Institute in Bangalore. Raman discovered in 1928 light scattering that has been accompanied by a change of frequency (by frequency of molecular vibrations). In 1930, Raman received the Nobel Prize “for his work on the scattering of light and for the discovery of the effect named after him.”

⁴⁴ For example, a displacement of an atom along x under a symmetry operation turns out to be a displacement of another atom.

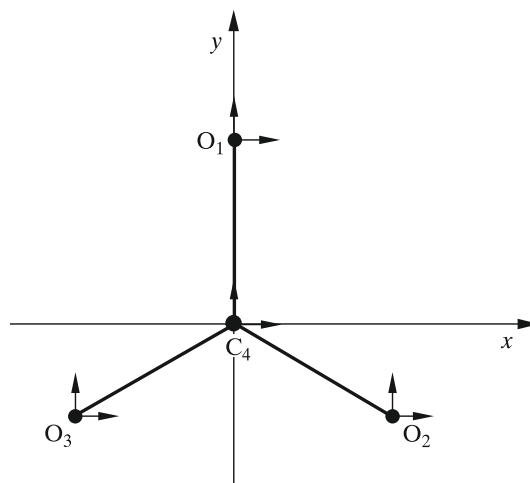


Fig. C.7. The carbonate anion CO_3^{2-} , the coordinate system used, and the versors describing the displacements of the atoms.

group of the molecule (in its equilibrium position). This representation will be decomposed into the irreducible representations.

Stage 2. The reducible representation describes the genuine (internal) vibrations as well as the six apparent vibrations (three translations and three rotations). The apparent vibrations can be easily eliminated by throwing away (from the total reducible representation) those irreducible representations that correspond to x , y , z (translations) and R_x , R_y , R_z (rotations). What the latter ones are, we know from the corresponding table of characters. To summarize, the abovementioned reducible representation has to be decomposed into the irreducible ones. The decomposition yields $\Gamma = a(\Gamma_1)\Gamma_1 + a(\Gamma_2)\Gamma_2 + a(\Gamma_3)\Gamma_3 \dots$. From this decomposition, we have to subtract (in order to eliminate the apparent vibrations) all the irreducible representations the x , y , z , R_x , R_y and R_z belong to.

After the two stages, we are left with a number of the irreducible representations that pertain to the genuine vibrations.⁴⁵ Only after that can we establish the vibrational selection rules according to the same procedure that has been used before. All this will be shown in a simple example of the carbonate anion CO_3^{2-} that in its equilibrium configuration corresponds to the D_{3h} symmetry group (see Fig. C.7).

Example 15. IR and Raman Spectra of the Carbonate Anion

In order to decompose a reducible representation into the irreducible representations, we do not need the reducible representation be given in details. It is sufficient to know its characters (p. e35). These characters are easy to deduce just by considering what happens to the displacement vectors along x_i , y_i , and z_i (for atom i) under all the symmetry operations. What

⁴⁵ These are internal motions. Note that some of these genuine vibrations may correspond to rotations of the functional groups in the molecule.

will simplify greatly our task is that *only the diagonal* elements of the matrices of the reducible representation contribute to the characters. This is how it looks in practice.

Class	The character of the corresponding matrix
E	$\chi(E) = 12$ <i>Justification:</i> Each versor transforms into itself. Hence, each diagonal element equals 1, and the number of them equals 3 times the number of atoms = 12.
$2C_3$	$\chi(C_3) = 0$ <i>Justification:</i> 0 from the oxygens, because they transform into other oxygens. For the carbon: $+1(\text{from } z_4) + \cos 120^\circ(\text{from } x_4) + \cos 120^\circ(\text{from } y_4) = 0$.
$3C_2$	$\chi(C_2) = -2$ <i>Justification:</i> It is sufficient to consider only one of the operations of the class; other ones will have the same character. Let us take the rotation about the C_2 axis going through O_1 and C. Then the only versors that transform into themselves (eventually changing sign, then the contribution to the character is -1) are those related to O_1 and C. We have $\chi(C_2) = -1(\text{from } z_4) + (-1)(\text{from } z_1) - 1(\text{from } x_1) - 1(\text{from } x_4) + 1(\text{from } y_1) + 1(\text{from } y_4) = -2$.
σ_h	$\chi(\sigma_h) = 4$ <i>Justification:</i> The contribution from each atom will be the same; i.e., χ will be equal to 4 times the contribution from a single atom, the latter one equals $-1(\text{from } z) + 1(\text{from } x) + 1(\text{from } y) = 1$.
$2S_3$	$\chi(S_3) = -2$ <i>Justification:</i> Only C gives a contribution, which is equal to $-1(\text{from } z_4) - \frac{1}{2}(\text{from } x_4) - \frac{1}{2}(\text{from } y_4) = -2$.
$3\sigma_v$	$\chi(\sigma_v) = 2$ <i>Justification:</i> Let us take only a single operation from the class—this one, which represents the reflection in the plane going through O_1 and C_4 . Then the contributions to χ are the same for both these atoms, and one of them gives $-1(\text{from } x) + 1(\text{from } z) + 1(\text{from } y) = 1$.

Thus, the characters of the reducible representation have been found. In order to decompose the representation, we have to know the table of characters for the D_{3h} symmetry group, shown in Table C.9.

Let us write down (in the same order as in Table C.9) the characters of the reducible representation just found:

$$12 \quad 0 \quad -2 \quad 4 \quad -2 \quad 2.$$

Now, let us find (p. e35), how many times $[a(\alpha)]$ the irreducible representation α is present in the reducible representation (a sum over classes: the number of operations in the class \times the calculated character \times the character of the irreducible representation):

$$a(A'_1) = \frac{1}{12}[1 \times 12 \times 1 + 2 \times 0 \times 1 + 3 \times (-2) \times 1 + 1 \times 4 \times 1 + 2 \times (-2) \times 1 + 3 \times 2 \times 1] = 1$$

Similarly, we find (knowing only how to multiply such numbers as 1, 2, 3) that

$$a(A'_2) = 1, a(E') = 3, a(A''_1) = 0, a(A''_2) = 2, a(E'') = 1.$$

This means that the reducible representation in question decomposes into

$$\Gamma = A'_1 + A'_2 + 3E' + 2A''_2 + E''. \quad (\text{C.35})$$

Table C.9. Characters of the irreducible representations of the symmetry group D_{3h} .

D_{3h}	\hat{E}	$2\hat{C}_3$	$3\hat{C}_2$	$\hat{\sigma}_h$	$2\hat{S}_3$	$3\hat{\sigma}_v$		
A'_1	1	1	1	1	1	1		$x^2 + y^2, z^2$
A'_2	1	1	-1	1	1	-1	R_z	
E'	2	-1	0	2	-1	0	x, y	$x^2 - y^2, xy$
A''_1	1	1	1	-1	-1	-1		
A''_2	1	1	-1	-1	-1	1	z	
E''	2	-1	0	-2	1	0	R_x, R_y	xz, yz

From the table of characters, we see that the apparent vibrations (see the irreducible representations corresponding to $x, y, z, R_x, R_y,$ and R_z) belong to A''_2, E', A'_2, E'' . After subtracting them from Γ , we obtain the irreducible representations that correspond to the genuine vibrations:

$$A'_1, A''_2, 2E';$$

i.e., one vibration of symmetry A'_1 (and a certain frequency ν_1), two vibrations (each doubly degenerate) of symmetry E' (they differ by frequency, $\nu_3 \neq \nu_4$), and one vibration of A''_2 symmetry (corresponding to frequency ν_2).

Selection Rules for IR Spectra:

Therefore, we expect the following selection rules for the fundamental transitions in the IR spectrum for the CO_3^{2-} anion:

- x and y belong to representation E' , so frequencies ν_3 and ν_4 are active in IR.
- z belongs to representation A''_2 , so frequency ν_2 is active in IR.

Selection Rules for Raman Spectra

For the Raman spectra, we expect the following selection rules. Vibrations with the following frequency will be active:

- ν_1 , because $x^2 + y^2$ and z^2 belong to A'_1
- ν_3 and ν_4 , because $x^2 - y^2$ and xy belong to E' ,

while the vibration of the frequency ν_2 will be inactive in the Raman spectroscopy because none of the polarizability components (symbolized by $x^2, y^2,$ etc.) belongs to A''_2 .

The results are collected in Table C.10 (sign “+” = active vibration, sign “-” = inactive vibration, the polarization of the light is shown in parentheses).

Table C.10. Transitions in CO_3^{2-} that are active (+) in the IR and in the Raman spectra.

Representation	ν	IR (Polarization)	Raman
A'_1	ν_1	–	+
A''_2	ν_2	+(z)	–
E'	ν_3	+(circular)	+
E'	ν_4	+(circular)	+

As seen from Table C.10, in the case of the carbonate anion, the vibration ν_1 is inactive in IR, but active in the Raman spectroscopy, while the opposite is true for ν_2 . The vibrations with the frequencies ν_3 and ν_4 are active both in IR and Raman spectra.

Exclusion Rule

If the molecule under study has the center of symmetry, then the *exclusion rule* is valid; i.e., the vibrations that are active in IR are inactive in the Raman spectrum, and *vice versa*.

This follows from the fact that in that case, x , y , and z belong to different irreducible representations than x^2 , y^2 , z^2 , xy , xz , and yz . Indeed, the x , y , and z are antisymmetric with respect to the inversion operation, whereas x^2 , y^2 , z^2 , xy , xz , yz , or their combinations are symmetric with respect to inversion. This guarantees that they belong to *different* irreducible representations for a molecule, with the center of inversion the vibrations active in IR are inactive in Raman spectra and *vice versa*.

When the Selection Rules Fail?

When deriving the selection rules, the following assumptions have been made:

- The molecule is *isolated*.
- Elements are represented by *the same isotope*.
- The molecule is in a *stationary state*.
- The vibrations have *small amplitudes*.
- The vibrations are *harmonic*.
- The electromagnetic field interacts with the molecule only through the *electric field–molecule* interaction.
- In the interaction of the molecule with the electromagnetic field, only the *dipole transitions* are involved.⁴⁶

⁴⁶ That is, the electric field of the electromagnetic wave within the molecule is assumed to be *uniform*. Then, the only term in the Hamiltonian related to the light–molecule interaction is $-\hat{\mu}\mathcal{E}$, where $\hat{\mu}$ stands for the dipole moment operator of the molecule and \mathcal{E} is the electric field intensity.

However, in practice, the molecule is never isolated. In particular, the interactions it undergoes in liquid or solid state are sufficiently strong to deform the molecule. As a result, we have to deal with a population of molecules (especially in a liquid), each in a different geometry, which are usually devoid of *any particular symmetry* (for a single molecule, this means a non-stationary state), although the molecule is not far from the perfect symmetry (“*broken symmetry*”).

Suppose that the molecule under consideration *is* indeed isolated. In a substance, we have usually several isotopomers, with different distributions of the isotopes in the molecules. In most cases, this also means a broken symmetry. *A broken symmetry means that the selection rules in principle are not applicable.*

In practice, a broken symmetry means that the selection rules cause only a *small intensity of the forbidden transitions with respect to the allowed ones.*

When considering electronic transitions, we assumed that the molecule stays in its equilibrium geometry, often with high symmetry. This may be the most probable configuration,⁴⁷ but the vibrations and rotations deform it. An electronic excitation is fast and usually undergoes a molecular geometry that differs slightly from the most probable and most symmetric one. This will cause a transition that is forbidden for the perfectly symmetric geometry, to have a non-negligible intensity.

Deriving the selection rules for the IR and Raman spectra, we assumed that the equivalent atoms can differ only by the *sign* of the deviation from the equilibrium position, but its absolute value is the same. This is how it would be for a harmonic oscillator. An anharmonicity introduces, therefore, another reason why a (harmonically) forbidden transition will have a non-negligible intensity.

The electromagnetic field has its electric and magnetic components. The selection rules that we have derived did not take into account the presence of the magnetic field. Taking into account the magnetic field introduces some additional selection rules. Also, the wavelength of an electromagnetic wave in the UV-VIS region is of the order of thousands of angstroms, whereas the length of the molecule is usually of the order of a few angstroms. This means that the assumption that the electric field of the electromagnetic wave is uniform looks good, but the field is not perfectly uniform. The deviations will be small but nonzero. Taking this into account by including further terms besides $-\hat{\mu}\mathcal{E}$, we obtain the interaction of the electric field gradient with the quadrupole moment of the molecule, as well as further terms. This also weakens the selection rules found.

⁴⁷ The maximum of the ground-state probability density for the *harmonic* oscillator corresponds indeed just to the equilibrium geometry. This is why the selection rules work at all (although in an approximate way).

Despite these complications, the group theory allows for understanding the basic features of the molecular spectra. It works sometimes even if the molecule under study has no symmetry at all because of a substituent that breaks it. Some electronic or vibrational excitations are of a local spatial character and pertain to a portion of the molecule that is (nearly) symmetric. Due to that, some optical transitions that are allowed, because the molecule as a whole does not have any symmetry,⁴⁸ will still have a very low intensity.

⁴⁸ But they would be forbidden if the portion in question represented a separate molecule and were symmetric.