Chapter 5. Geometrical Symmetry

Notes:

- *Most of the material presented in this chapter is taken from Bunker and Jensen (2005), Chap. 3, and Atkins and Friedman, Chap. 5.*

5.1 Symmetry Operations

We have already encountered many operators that can act on a quantum mechanical system (or any kind of system for that matter). Sometimes the operator will transform the state of the system, but it may also happen that it will leave it unaltered in the case where the state corresponds to an eigenvector of the operator. The latter situation happens when the operator in question is a so-called **symmetry operator**. This concept can be extended to other situations. We will consider in Chapter 6 sets of symmetry operations that leave the Hamiltonian of a system unchanged. Alternatively, one can investigate ensembles of operations that leave the geometrical shape of a system or an object (e.g., a molecule at equilibrium) unaffected. These are the types of operators with which we are concerned in this chapter.

As we are concerned with rigid objects of different geometrical shapes anchored at a given point (the centre of symmetry), we do not take into account any possible translational symmetry and only consider symmetry operators that compose the so-called **point groups** (see below). There are five types of such operators that can leave the geometrical appearance of objects unchanged, with five corresponding kinds of **symmetry elements**. An element either is a point, a line, or a plane with respect to which the symmetry operation is effected. The different operations and elements are listed in Table 5-1.

Table 5-1 – The five type of symmetry operations and elements.

Operation	Description	Element
E	The **identity** operation	The object itself
C_n	An n**-fold rotation**, a rotation by $2\pi/n$ about an axis of symmetry	The axis of symmetry
σ	A **reflection** in a mirror plane	The plane of mirror symmetry
i	An **inversion** through a centre of symmetry	The centre of symmetry
S_n	An n**-fold improper rotation** about an axis of improper rotation	The axis of improper rotation

An object, or a molecule, can have more than one axis of symmetry. For example, a molecule such as the H_3^+ ion has one three-fold axis of symmetry (C_3) perpendicular to the plane of the molecule, and three two-fold axes (C_2) going through one nucleus and the centre of symmetry (see Figure 5-1). In a case such as this one, the axis associated with the operation C_n of largest value n (C_3 in this case) is called the **principal axis**. An n-fold symmetry axis will generate $(n-1)$ rotations $C_n, C_n^2, \ldots, C_n^{n-1}$. A rotation C_n^k is right-handed in the usual sense (i.e., the right thumb points in the direction of the corresponding symmetry axis and the rotation sense follows the other fingers).

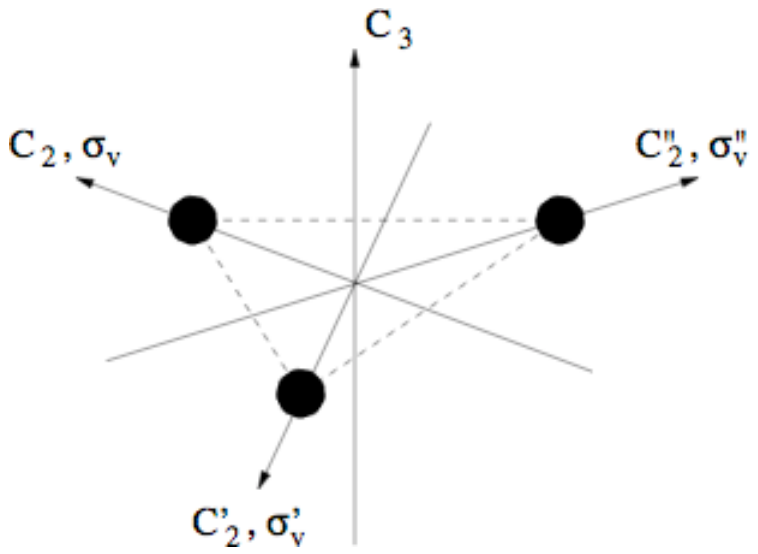

Figure 5-1 – The H_3^+ ion (allowing for the projection) with its symmetries and symmetry elements. There is one three-fold axis of symmetry C_3 (the principal axis), three two-fold axes C_2, and three mirror or reflection planes σ_v; other symmetry operations are discussed in the text. Note that all the symmetry elements intersect at one point; hence the name point groups.

As is apparent from Figure 5-1, the H_3^+ ion also possesses three mirror (or reflection) planes denoted by σ_v (other symmetry operations for this molecule will be discussed later). A mirror plane is called a **vertical plane** σ_v when it contains the principal axis, and it is called a **horizontal plane** σ_h when it is perpendicular to the principal axis. A **dihedral plane** σ_d is a vertical plane that bissects two C_2 axes that are perpendicular to the principal axis.

The inversion i operation consists of taking each point through the centre of symmetry to an equal distance in the opposite direction. The H_3^+ ion is obviously not symmetric under this transformation, as the inverted position of a given nucleus is not the original position of another nucleus composing the molecule.

An improper rotation S_n is the composite of a C_n rotation followed by a horizontal reflection σ_h in a plane perpendicular to the n-fold axis, or vice-versa. That is,

$$S_n = C_n\sigma_h = \sigma_h C_n. \tag{5.1}$$

It is often the case (specifically when n is even) that neither of the latter two operators alone will be a symmetry operation, but their aforementioned combination will be. The reader should verify, for example, that the methane molecule (CH_4) possesses three S_4 axes but no C_4 and σ_h operators. It can be verified that the improper rotations S_1 and S_2 are equivalent to the horizontal reflection and inversion operations, respectively.

5.2 The Classification of Molecules through Point Groups

Upon studying a molecule such as the H_3^+ ion of Figure 5-1, it will be advantageous to list all of its symmetry operations into an ensemble. When this is accomplished, for any molecule, it is found that the resulting ensemble can be associated with the so-called **point group** to which the molecule "belongs". The different point groups are often identified with their dominant symmetry features, as follows

1. *The groups* C_1, C_s, *and* C_i. These groups respectively consist of the identity E alone, the identity and a reflection σ, and the identity and the inversion i.
2. *The groups* C_n. These groups consist of the identity and an n-fold rotation.
3. *The groups* C_{nv}. Each of these groups contains the elements of the corresponding C_n group, as well as n vertical reflections σ_v. A special case is that of the $C_{\infty v}$ group of heteronuclear diatomic molecules (e.g., CO).
4. *The groups* C_{nh}. Each of these groups contains the elements of the corresponding C_n group, as well as a horizontal reflection σ_h and whatever other new operations brought about by its multiplication with the elements of C_n (see the definition of a point group below).
5. *The groups* D_n. Each of these groups contains the elements of the corresponding C_n group, as well as n C_2 rotations perpendicular to the n-fold principal axis and whatever other new operations brought about by multiplications between these elements.
6. *The groups* D_{nh}. Each of these groups contains the elements of the corresponding D_n group, as well as a horizontal reflection σ_h and whatever other new operations brought about by multiplications between these elements. A special case is that of the $D_{\infty h}$ group which includes homonuclear diatomic molecules.
7. *The groups* D_{nd}. Each of these groups contains the elements of the corresponding D_n group, as well as n dihedral reflections σ_d and whatever other new operations brought about by multiplications between these elements.
8. *The groups* S_n. These groups consist of the identity and an n-fold improper rotation S_n, as well as whatever other new operations brought about by multiplications between these elements. Only even values of n need to be considered, as a S_n group with an odd n is equivalent to the corresponding C_{nh} group.
9. *The cubic and icosahedral groups*. Each of these groups contains more than one n-fold rotation with $n \geq 3$. The cubic groups are either tetrahedral (labeled T) or octahedral (labeled O). The point group T_d is that of the regular tetrahedron and of the methane molecule CH_4; T is the same group but without the reflections; T_h is a tetrahedral group with an inversion. The point group O_h is that of the regular octahedron and of the sulphur hexafluoride molecule SF_6, for example; O is the same group but without the reflections. The point group I_h is that of the regular octahedron and of the buckminsterfullerene molecule C_{60}; I is the same group but without the inversion.

10. *The full rotation group* R_3 *or* K. This group contains all the possible rotations (an infinite number of them) through any axis that passes through the centre of a molecule. It is also the symmetry group of the sphere.

The point group of a given molecule will be determined by first identifying all of its symmetry operations, and then comparing against the list of known point groups. This will be easily accomplished with the help of the algorithm presented in Figure 5-2. Let us work out, for example, the point group of the H_3^+ ion. Beside the identity element, this molecule possesses not only, as stated before, a C_3 principal axis of symmetry with its associated C_3 and C_3^2 elements, three C_2 rotations with their respective axis perpendicular to the principal axis of symmetry (and connecting the centre of symmetry to one hydrogen nucleus), but also three σ_v reflections (each associated with a plane containing a hydrogen nucleus), one horizontal reflection σ_h, as well as two improper rotations S_3 $(= C_3\sigma_h)$. The point group of the H_3^+ ion therefore consists of the following ensemble

$$\text{point group of } H_3^+ = \left\{E, C_3, C_3^2, C_2, C_2', C_2'', \sigma_h, S_3, S_3^2, \sigma_v, \sigma_v', \sigma_v''\right\}. \qquad (5.2)$$

Simply answering the questions contained in the chart of Figure 5-2 quickly reveals that the point group of this molecule is D_{3h}. It is in principle possible to do the same for any molecule. One must, however, be careful that in certain cases some symmetry operations may not be obvious at first sight and could be omitted. It is often preferable to verify that the products of every pair of symmetry operations result in another operation also present in the ensemble. The reason for this becomes apparent when one considers the formal definition of a group; which we now do.

5.2.1 **The Definition of a Group**

Although we will postpone the study of the **theory of groups** to the next chapter, it will be to our advantage to introduce the concept of a mathematical group.

A careful examination of the symmetry operations associated with the geometry of a given molecule would reveal that they fulfill the conditions set forth by the mathematical theory of groups, or **group theory**. That is, the set composed of all the symmetry operations of a molecule forms a group, in the mathematical sense. The formal definition of a group is as follows

1. The identity E is an operator of the set.
2. The operators multiply associatively; i.e., given three operators R, S and T, then it is true that $(RS)T = R(ST)$.
3. If R and S are two operators of the set, then RS is also an operator contained in the set.
4. The inverse of each operator is a member of the set.

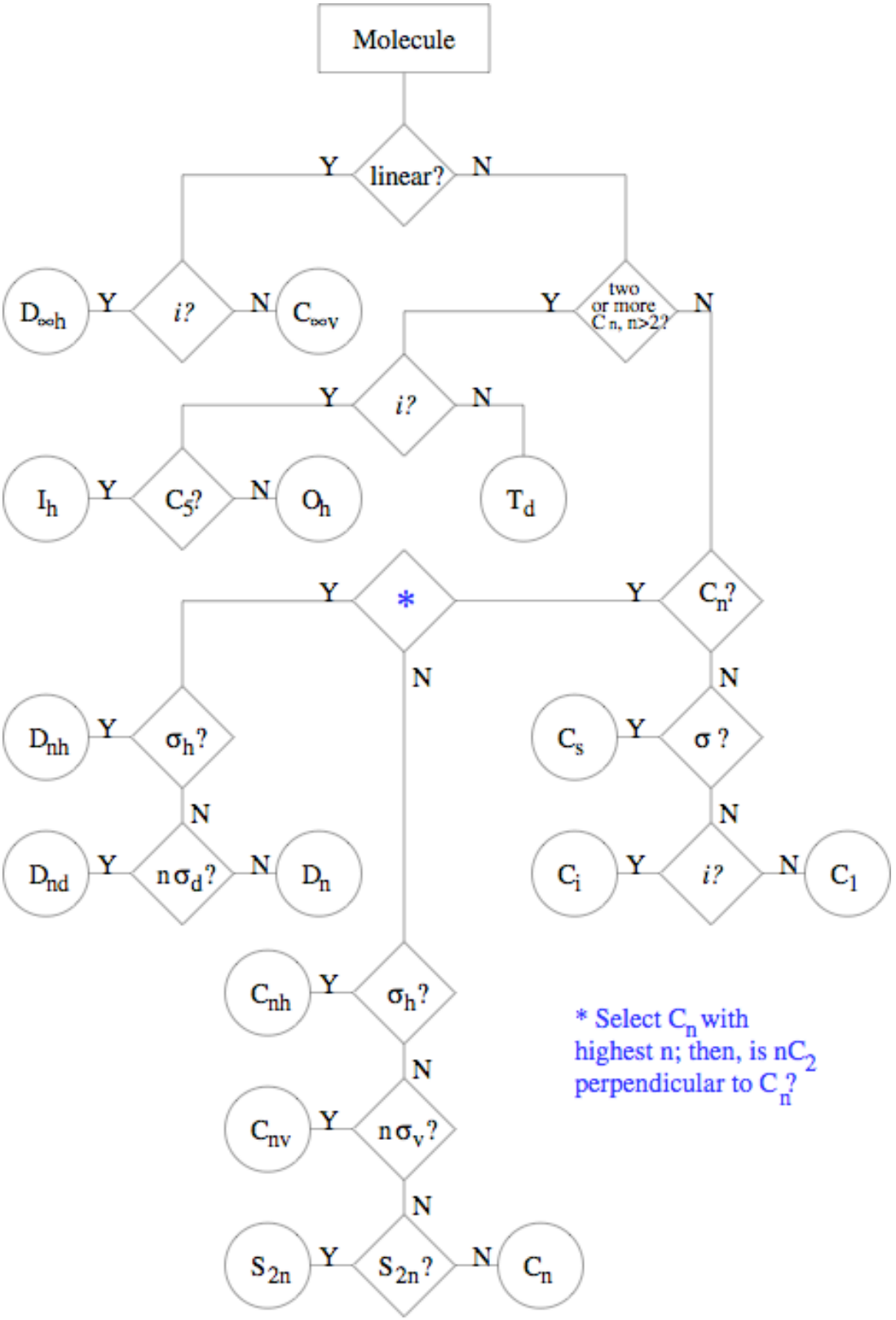

Figure 5-2 – An algorithm to determine the point group of a molecule (from Atkins and Friedman).

For example, we can verify that the ensemble of equation (5.2) associated with the H_3^+ ion indeed satisfies these conditions. Although the first condition is obviously met, the second and third conditions can be verified more easily if we produce the so-called **multiplication table** for the group. This table is obtained by listing the results of every product between two operators of the group, as shown in Table 5-2.

Table 5-2 – The multiplication table for the point group of the H_3^+ ion (i.e., D_{3h}). The table is calculated by first applying the operator of the top row and then the operator of the left column.

	E	C_3	C_3^2	C_2	C_2'	C_2''	σ_h	S_3	S_3^2	σ_v	σ_v'	σ_v''
E	E	C_3	C_3^2	C_2	C_2'	C_2''	σ_h	S_3	S_3^2	σ_v	σ_v'	σ_v''
C_3	C_3	C_3^2	E	C_2''	C_2	C_2'	S_3	S_3^2	σ_h	σ_v''	σ_v	σ_v'
C_3^2	C_3^2	E	C_3	C_2'	C_2''	C_2	S_3^2	σ_h	S_3	σ_v'	σ_v''	σ_v
C_2	C_2	C_2'	C_2''	E	C_3	C_3^2	σ_v	σ_v'	σ_v''	σ_h	S_3	S_3^2
C_2'	C_2'	C_2''	C_2	C_3^2	E	C_3	σ_v'	σ_v''	σ_v	S_3^2	σ_h	S_3
C_2''	C_2''	C_2	C_2'	C_3	C_3^2	E	σ_v''	σ_v	σ_v'	S_3	S_3^2	σ_h
σ_h	σ_h	S_3	S_3^2	σ_v	σ_v'	σ_v''	E	C_3	C_3^2	C_2	C_2'	C_2''
S_3	S_3	S_3^2	σ_h	σ_v''	σ_v	σ_v'	C_3	C_3^2	E	C_2''	C_2	C_2'
S_3^2	S_3^2	σ_h	S_3	σ_v'	σ_v''	σ_v	C_3^2	E	C_3	C_2'	C_2''	C_2
σ_v	σ_v	σ_v'	σ_v''	σ_h	S_3	S_3^2	C_2	C_2'	C_2''	E	C_3	C_3^2
σ_v'	σ_v'	σ_v''	σ_v	S_3^2	σ_h	S_3	C_2'	C_2''	C_2	C_3^2	E	C_3
σ_v''	σ_v''	σ_v	σ_v'	S_3	S_3^2	σ_h	C_2''	C_2	C_2'	C_3	C_3^2	E

The fact that every cell in Table 5-2 contains an operator originally contained in the set tells us that condition 3 is indeed satisfied. Condition 2 can be verified using this same table. For example, let us consider the following operation

$$\left(C_3\sigma_v\right)S_3^2 = \sigma_v''S_3^2 = C_2', \tag{5.3}$$

but since

$$C_3\left(\sigma_vS_3^2\right) = C_3C_2'' = C_2', \tag{5.4}$$

then $\left(C_3\sigma_v\right)S_3^2 = C_3\left(\sigma_vS_3^2\right)$, as required. The same can be proved for any other association of three operators from the point group. The last condition concerning the existence of the inverse for every symmetry operation in the group can be asserted by the one-time appearance of the identity operation in every row and column. It is in fact possible to show that every operator of the group should appear once and only once in every row and column of the multiplication table. One last comment should be made concerning the results shown in Table 5-2. It is the fact that the different symmetry

operations are effected using space-fixed axes. That is, in the product, say, $C_2\sigma_v$ the axes relative to which the molecule is oriented are not changed by the first operation (i.e., σ_v), only the orientation of the molecule in space is affected. Therefore, the following operation (i.e., σ_v) is also done with respect to the same set of axes.

Finally, although we know from the chart of Figure 5-2 that linear molecules in their equilibrium configuration can either belong to the $C_{\infty v}$ or $D_{\infty h}$, it can also be shown that

- A molecule with one, and only one, C_n- or S_n-axis with a finite $n \geq 3$ is a symmetric top.
- A molecule with more than one C_n-axis with a finite $n \geq 3$ is a spherical top.
- A molecule with no rotational symmetry axis or only C_2 axes only is an asymmetric top.

It follows from these that the ammonia molecule NH_3 (one C_3-axis), the methane molecule CH_4 (four C_3-axis), and the water molecule (one C_2-axis) are symmetric, spherical, and asymmetric tops, respectively.