Molecular Symmetry

I. WHAT IS SYMMETRY AND WHY IT IS IMPORTANT?

Some object are "more symmetrical" than others. A sphere is more symmetrical than a cube because it looks the same after rotation through any angle about the diameter. A cube looks the same only if it is rotated through certain angels about specific axes, such as 90^o, 180^o, or 270^o about an axis passing through the centers of any of its opposite faces, or by 120^o or 240^o about an axis passing through any of the opposite corners.

Here are also examples of different molecules which remain the same after certain symmetry operations: NH_3, H_2O, C_6H_6, $CBrClF$. In general, an action which leaves the object looking the same after a transformation is called a **symmetry operation**. Typical symmetry operations include **rotations**, **reflections**, and **inversions**. There is a corresponding **symmetry element** for each symmetry operation, which is the **point**, **line**, or **plane** with respect to which the symmetry operation is performed. For instance, a rotation is carried out around an axis, a reflection is carried out in a plane, while an inversion is carried our in a point.

We shall see that we can classify molecules that possess the same set of symmetry elements, and grouping together molecules that possess the same set of symmetry elements. This classification is very important, because it allows to make some general conclusions about molecular properties without calculation. Particularly, we will be able to decide if a molecule has a dipole moment, or not and to know in advance the degeneracy of molecular states. We also will be able to identify overlap, or dipole moment integrals which necessary vanish and obtain selection rules for transitions in polyatomic molecules.

II. SYMMETRY OPERATIONS

The classification of objects according to symmetry elements corresponding to operations that leave **at least one common point unchanged** gives rise to the **point groups**. These are **five kinds of symmetry operations** and **five kinds of symmetry elements** of this kind. These symmetry operations are as follows.

- The **identity**, E, consists of doing nothing: the corresponding symmetry element is an entire object. In general, any object undergo this symmetry operation. The example of the molecule which has only the identity symmetry operation is $C_3H_6O_3$, DNA, and $CHClBrF$.

- The **n-fold rotation** about an **n-fold axis of symmetry**, C_n is a rotation through the angle $360^o/n$. Particularly, the operation C_1 is a rotation through 360^o which is equivalent to the identity E. H_2O molecule has one twofold axis, C_2. NH_3 molecule has one threefold axis, C_3 which is associated with two symmetry operations: 120^o rotation C_3 and 240^o (or -120^o) rotation C_3^2. C_6H_6 molecule has one sixfold axis C_6 and six twofold axes C_2. If a molecule possess several rotational axes, then the one of them with the greatest value of n is called the **principal axis**. All linear molecules including all diatomics has C_∞ axis because rotation on any angle remains the molecule the same.

- The **reflection** in a **mirror plane**, σ may contain the principal axis of a molecule, or be perpendicular to it. If the plane contains the principal axis, it is called **vertical** and denoted σ_v. For instance, H_2O molecule has two vertical planes of symmetry and NH_3 molecule has tree. A vertical mirror plane which bisects the angle between two C_2 axes is called a **dihedral plane** and is denoted by σ_d. If the plane of symmetry is perpendicular to the principal axis, it is called **horizontal** and denoted σ_h. For instance, C_6H_6 molecule has a C_6 principal axis and a horizontal mirror plane.

- The **inversion** through the **center of symmetry** is the operation which transforms all coordinates of the object according to the rule: $(x, y, z) \rightarrow (-x, -y, -z)$. For instance, a sphere, or a cube has a center of inversion, but H_2O, and NH_3 have not. C_6H_6 molecule has a center of inversion.

- The **n-fold improper rotation** about an **n-fold axis of symmetry**, S_n is a combination of two successive transformations. The first transformation is a rotation through $360^o/n$ and the second transformation is a reflection through a plane perpendicular to the axis of the rotation. Note, that neither operation alone needs to be a symmetry operation. For instance, CH_4 molecule has three S_4 axes.

III. THE SYMMETRY CLASSIFICATION OF MOLECULES

In order to classify molecules according to symmetry one can list their symmetry elements and collect together the molecules with the same list of elements. More precisely, we can collect together the molecules which belong to the same **group**.

A. Definition of the Group

According to the **group theory**, the symmetry operations are the members of a group if they satisfy the following **group axioms**:

1. The successive application of two operations is equivalent to the application of a member of the group. In other words, if the operations A and B belong to the same group then $A \cdot B = C$, where C is also the operation from the same group. Note, that in general $A \cdot B \neq B \cdot A$.
2. One of the operations in the group is the identity operation E. This means that $A \cdot E = E \cdot A = A$.
3. The reciprocal of each operation is a member of the group: if A belongs to a group, then $A^{-1} = B$, where B is also the member of the group. Note, that $A \cdot A^{-1} = A^{-1} \cdot A = E$.
4. Multiplication of the operations is associative: $A \cdot B \cdot C = (A \cdot B) \cdot C = A \cdot (B \cdot C)$.

B. Point Groups

Particularly we will consider the following point groups which molecules can belong to.

1. The groups C_1, C_i, and C_s. A molecule belongs to the group C_1 if it has no elements other than identity E. Example: DNA. A molecule belongs to the group C_i, if it consist of two operations: the identity E and the inversion i. Example: meso-tartaric acid. A molecule belongs to the group C_s, if it consists of two elements: identity E and a mirror plane σ. Example: OHD.

2. The group C_n. A molecule belongs to the group C_n if it has a n-fold axis. Example: H_2O_2 molecule belongs to the C_2 group as it has the elements E and C_2.

3. **The group C_{nv}.** A molecule belongs to the group C_{nv} if in addition to the identity E and a C_n axis, it has n vertical mirror planes σ_v. Examples: H_2O molecule belongs to the C_{2v} group as it has the symmetry elements E, C_2, and two vertical mirror planes which are called σ_v and σ_v'. The NH_3 molecule belongs to the C_{3v} group as it has the symmetry elements E, C_3, and three σ_v planes. All heteroatomic diatomic molecules and OCS belong to the group $C_{\infty v}$ because all rotations around the internuclear axis and all reflections across the axis are symmetry operations.

4. **The group C_{nh}.** A molecule belongs to the group C_{nh} if in addition to the identity E and a C_n axis, it has a horizontal mirror plane σ_h. Example: butadiene C_4H_6, which belongs to the C_{2h} group, while $B(OH)_3$ molecule belongs to the C_{3h} group. Note, that presence of C_2 and σ_h operations imply the presence of a center of inversion. Thus, the group C_{2h} consists of a C_2 axis, a horizontal mirror plane σ_h, and the inversion i.

5. **The group D_n.** A molecule belongs to the group D_n if it has a n-fold principal axis C_n and n two-fold axes perpendicular to C_n. D_1 is of cause equivalent with C_2 and the molecules of this symmetry group are usually classified as C_2.

6. **The group D_{nd}.** A molecule belongs to the group D_{nh} if in addition to the D_n operations it possess n dihedral mirror planes σ_d. Example: The twisted, 90^o allene belongs to D_{2d} group while the staggered confirmation of ethane belongs to D_{3d} group.

7. **The group D_{nh}.** A molecule belongs to the group D_{nh} if in addition to the D_n operations it possess a horizontal mirror plane σ_h. As a consequence, in the presence of these symmetry elements the molecule has also necessarily n vertical planes of symmetry σ_v at angles $360^o/2n$ to one another. Examples: BF_3 has the elements E, C_3, $3C_2$, and σ_h and thus belongs to the D_{3h} group. C_6H_6 has the elements E, C_6, $3C_2$, $3C_2'$ and σ_h and thus belongs to the D_{6h} group. All homonuclear diatomic molecules, such as O_2, N_2, and others belong to the $D_{\infty h}$ group. Another examples are ethene C_2H_4 (D_{2h}), CO_2 ($D_{\infty h}$), C_2H_2 ($D_{\infty h}$).

8. **The group S_n.** A molecule belongs to the group S_n if it possess one S_n axis. Example: tetraphenylmethane which belongs to the group S_4. Note, that the group S_2 is the same as C_i, so such molecules have been classified before as C_i.

9. The cubic groups. There are many important molecules with more than one principal axes, for instance, CH_4 and SF_6. Most of them belong to the cubic groups, particularly to **tetrahedral groups** T, T_d, and T_h, or to the **octahedral groups** O and O_h. If the object has the rotational symmetry of the tetrahedron, or octahedron, but has no their planes of reflection, then it belongs to the simpler groups T, or O. The group T_h is based on T, but also has a center of inversion.

10. The full rotational group R_3. This group consists of infinite number of rotational axes with all possible values of n. It is the symmetry of a sphere. All atoms belong to this symmetry group.

C. Group Multiplication Table

Let us consider the symmetry group of NH_3 molecule. These are:

- a 3-fold axis, associated with two symmetry operations: C_3^+ (+120^o rotation) and C_3^- (-120^o rotation).
- 3 σ_v vertical planes, σ_v, σ_v', and σ_v'' associated with tree mirror reflections.

Now we add to these five symmetry operations the identity operator E and show that all six symmetry operations joint a group. Particularly, it is easy to see that $C_3^+C_3^- = E$, where the identity operation E can be considered as a "product" of the two rotation operators operations C_3^+ and C_3^-. It can also be seen that $\sigma_{va}C_3^+ = \sigma_{vb}$ and $C_3^+\sigma_{va} = \sigma_{vc}$. Following this procedure we can build the "multiplication table" presented below.

According to the Table I, the "product" of each two symmetry transformations from six E, C_3^+, C_3^-, σ_v, σ_v', and σ_v'' is equivalent to one of these transformations. It is clearly seen that the third and the fourth conditions of the group are also valid. Thus, these six operators build a group. This group is known as C_{3v} group. The total number of operations in a group is called the **group order**. Therefore, the order of C_{3v} is 6.

Let us consider the symmetry group of H_2O molecule. The symmetry elements are:

- a 2-fold axis, associated with the symmetry operation: C_2 .
- two σ_v vertical planes, σ_v, and σ_v' associated with two mirror reflections.

TABLE I: **Multiplication Table for the C_{3v} Group**

	E	C_3^+	C_3^-	σ_v	σ_v'	σ_v''
E	E	C_3^+	C_3^-	σ_v	σ_v'	σ_v''
C_3^+	C_3^+	C_3^-	E	σ_v'	σ_v''	σ_v
C_3^-	C_3^-	E	C_3^+	σ_v''	σ_v	σ_v'
σ_v	σ_v	σ_v''	σ_v'	E	C_3^-	C_3^+
σ_v'	σ_v'	σ_v	σ_v''	C_3^+	E	C_3^-
σ_v''	σ_v''	σ_v'	σ_v	C_3^-	C_3^+	E

Now we add to these four symmetry operations the identity operator E and show that all six symmetry operations joint a group. The "multiplication table" presented below.

TABLE II: **Multiplication Table for the C_{2v} Group**

	E	C_2	σ_v	σ_v'
E	E	C_2	σ_v	σ_v'
C_2	C_2	E	σ_v'	σ_v
σ_v	σ_v	σ_v'	E	C_2
σ_v'	σ_v'	σ_v	C_2	E

According to the Table II, the "product" of each two symmetry transformations from six E, C_2, σ_v, and σ_v' is equivalent to one of these transformations. It is clearly seen that the third and the fourth conditions of the group are also valid. Thus, these four operators build a group. This group is known as C_{2v} group. The group order of C_{2v} is 4.

Each point group is characterized by each own multiplication table.

D. Some Consequences of Molecular Symmetry

As soon point the group of a molecule is identified, some statements about its properties can be done.

1. Polarity

As we have already discussed a **polar molecule** is one having a permanent electric dipole moment. For instance these are $NaCl$, O_3, NH_3, and many others. It is known that the rotational absorption transitions can occur only in polar molecules. The group theory give important instructions, how the molecular symmetry is related to the molecular polarity. For instance, if a molecule belongs to the group C_n, where $n > 1$, then it cannot have a component of the dipole moment perpendicular to the symmetry axis, because a dipole moment which exist in one direction perpendicular to the axis is cancelled by an opposing dipole. A dipole moment in these molecules can be only parallel to the molecular axis. The same is valid for **any** of the C_{nv} group molecule. The molecules which belongs to all other groups, but C_s, cannot have a permanent dipole moment, because they always have symmetry operations transforming one end of the molecule into another. **Thus, only the molecules which belong to the C_n, C_{nv}, or C_s group can have a permanent dipole moment.**

2. Chirality

A **chiral molecule** is that cannot be transformed to itself with any **mirror transformation**. An **achiral molecule** can be transformed to itself with a **mirror transformation**. Chiral molecules are important because they are **optically active** in the sense that they can rotate the plane of polarized light passing through the molecular sample. A molecule may be chiral only if it **does not have an axis of improper rotation S_n**. Note, that the molecule with a center of inversion i belongs to S_2 group and thus cannot be chiral. Similarly, because $S_1 = \sigma$, **any molecule with a mirror plane is achiral.**

IV. SYMMETRY OF MOLECULAR VIBRATIONS

Vibrational movement in polyatomic molecules is much more complicated than that of the diatomics. That is because much greater number of possible **degrees of freedom** of a polyatomic molecule. For instance, if there are N nuclei we need $3N$ coordinates to describe their motion. However, if we want to study the vibrational motion of a molecule, we are not interested in the translational motion of the system as a whole, which can be described completely by tree coordinates of the **molecular center of mass**, X_c, Y_c, Z_c. Therefore, $3N-3$ coordinates are sufficient for fixing the **relative** positions of all N nuclei with respect to the molecular center of mass.

The motion relative the center of mass includes the rotation of the molecule. The rotation alone can also be described by 3 coordinates, which are usually the two polar angles which fix a certain direction in the molecule and the angle of rotation about that direction. Thus, $3N-6$ coordinates are left for describing the relative motion of the nuclei with fixed orientation of the system as a whole, in other words, we have $3N-6$ **vibrational degrees of freedom**. However, for **linear molecules** two coordinates, for instance, the two angles of the internuclear axis, are sufficient for describing the rotation and therefore for linear molecules we have $3N-5$ vibrational degrees of freedom.

When the molecule is in its equilibrium configuration, the coordinates of nucleus i in the molecular x, y, z coordinate frame are written x_i^e, y_i^e, z_i^e and, at a displacement configuration, the Cartesian vibrational displacement coordinates are given by:

$$\Delta x_i = (x_i - x_i^e) \qquad \Delta y_i = (y_i - y_i^e) \qquad \Delta z_i = (z_i - z_i^e) \tag{1}$$

A. The Vibrational Hamiltonian

The classical expression for the vibrational energy, using molecular-fixed x, y, z coordinates $(u_1, u_2, ...u_{3N}) = (\Delta x_i, \Delta y_i, ...\Delta z_N)$ is

$$E_{vib} = \frac{1}{2}\sum_{i=1}^{3N} m_i \dot{u}_i^2 + V_N(u_i), \tag{2}$$

where $V_N(u_i)$ is the potential energy which is zero at the equilibrium together with its first derivative. The Taylor's series expansion about the equilibrium is

$$V_N = \frac{1}{2}\sum_{i,j=1}^{3N} k_{ij} u_i u_j + \frac{1}{6}\sum_{i,j,k=1}^{3N} k_{i,j,k} u_i u_j u_k + \frac{1}{24}\sum_{i,j,k,l=1}^{3N} k_{i,j,k,l} u_i u_j u_k u_l + \cdots, \tag{3}$$

where $k_{ij}, k_{i,j,k}$ and $k_{i,j,k,l}$ are **force constants**.

The lowest order terms in the expansion are quadratic and for small displacement only these terms can be preserved in eq. (3), while all other terms can be neglected. Corresponding expression for the potential V_N^0 is called the **harmonic-oscillator approximation**. In the harmonic-oscillator approximation the vibrational energy can be written as

$$E_{vib}^0 = \frac{1}{2}\sum_{i=1}^{3N} m_i \dot{u}_i^2 + \frac{1}{2}\sum_{i,j=1}^{3N} k_{i,j} u_i u_j, \tag{4}$$

where $k_{i,j}$ are harmonic force constants.

B. Normal Vibrational Modes

A standard result from classical mechanics is that the vibrational energy of a N-body harmonic oscillator (4) can be written in terms of $3N-6$ mass-weighted linear combinations of the u_j which are called **vibrational normal coordinates** Q_r:

$$E_{vib}^0 = \frac{1}{2}\sum_{r=1}^{3N-6} [\dot{Q}_r^2 + \lambda_r Q_r^2], \tag{5}$$

where

$$m_i^{1/2} u_i = \sum_{r=1}^{3N} l_{ui,r} Q_r. \tag{6}$$

The quantum mechanical Hamiltonian of a vibrating polyatomic molecule can be obtained from eq.(5) by replacing the classical variables Q_r and $\dot{Q}_r$ by their quantum mechanical analogues. Great advantage of the vibrational energy expression in eq.(5) is that there is no cross terms in the potential energy. Therefore, the solution (wavefunction) of the corresponding Schrödinger equation is greatly simplified as can be presented as a product of the **normal mode wavefunctions** which are known solution of the harmonic oscillator problem:

$$\Phi_{vib} = \Phi_{v1}(Q_1)\Phi_{v2}(Q_2)\ldots\Phi_{v3N-6}(Q_{3N-6}). \tag{7}$$

The corresponding vibrational energy E_{vib} is a sum of the each normal mode energy

$$E_{vib} = E_{v1} + E_{v2} + \cdots + E_{v3N-6}, \tag{8}$$

where $E_{vk} = \omega_{ek}(v_k + 1/2)$.

Each of the $3N-6$ $(3N-5)$ vibrational normal coordinate Q_r describes a **collective normal mode of vibration**.

In general, any vibrational of the molecular system may be represented as a superposition of normal vibrations with suitable amplitudes. Within each of the normal mode k all nuclei move with **the same frequency** ν_k according to simple harmonic motion. Two, or more normal modes are **degenerate** if they all have the same frequency.

As an example, consider vibration of a mass suspended by an elastic bar of rectangular cross section. If mass is displaced slightly from its equilibrium position in the x direction and then left, it will carry our simple harmonic in this direction with a frequency

$$\nu_x = \frac{1}{2\pi}\sqrt{\frac{k_x}{m}}, \tag{9}$$

where k_x is a force constant in the x direction.

If mass is displaced slightly from its equilibrium position in the y direction and then left, it will carry our simple harmonic in this direction with a frequency

$$\nu_y = \frac{1}{2\pi}\sqrt{\frac{k_y}{m}}, \tag{10}$$

where k_y is a force constant in the y direction.

If mass is displaced in a direction different from x and y, it will not carry out a simple harmonic oscillation, but more complicated type of motion, so named *Lissajous motion.* This is because the restoring force F whose components are $F_x = -k_x x$ and $F_y = -k_y y$ is not directed toward the origin since $k_x \neq k_y$. However, this motion can be always presented as linear superposition of two simple harmonic motions of different frequency:

$$x = x_0 \cos 2\pi\nu_x t, \qquad y = y_0 \cos 2\pi\nu_y t, \tag{11}$$

where x_0, y_0 are coordinates of initial position of the mass (point A).

C. Symmetry of Normal Vibrations

We will now consider the effect of symmetry operations on the normal vibrations. Mathematically there are two equivalent ways of carrying out a symmetry operation. We may either keep the coordinate frame fixed and transform the molecule (for instance, reflecting, or rotating the positions of nuclei), or we can keep the positions of nuclei and refer them to the transformed coordinate frame (reflected, or rotated). Following G.Herzberg, we chouse here the former way.

1. Effect of Symmetry Operations on Non-Degenerate Vibrations

For a given non-degenerate normal vibration ν_r, there is only one possible way of displacement coordinates of the atoms. As the symmetry operation acts simultaneously on all atom displacements, it can only either simultaneously change signs of all displacement coordinates u_i, or remain them unchanged. Thus, a non-degenerate vibration **can only be symmetric**, **or antisymmetric** with respect to any symmetry operation which is permitted by the **symmetry of the molecule**. The former means that $Q_r' = Q_r$ and the latter means that $Q_r' = -Q_r$, where the primed coordinates are the ones after the symmetry operation.

For example, for the formaldehyde molecule, H_2CO the reflection over the plane xz perpendicular to the molecular plane leaves the normal modes ν_1, ν_2, ν_3, and ν_6 the same, whereas inverts directions of all displacement vectors for the modes ν_4 and ν_5. In a similar way it can be seen that all vibrations but ν_6 are symmetric with respect to the molecular plane, while ν_6 is antisymmetric. Finally, the vibrations ν_4, ν_5, and ν_6 are antisymmetric with respect to the rotation by π about the two-fold XY axis.

2. Effect of Symmetry Operations on Degenerate Vibrations

Let us consider the normal vibrations of a linear triatomic molecule, like CO_2. The two vibrations ν_{2a} and ν_{2b} are obviously degenerate with each other. They are **antisymmetric** with respect to an **inversion** at a center of symmetry as is the vibration ν_3. Another possible symmetry operation is rotation C_∞^φ by an arbitrary angle φ about the internuclear axis. This rotation leaves the vibrations ν_1 and ν_3 unchanged, however, both ν_{2a} and ν_{2b} are changes by more than just a sign. In other words, the vibrations ν_{2a} and ν_{2b} are **neither symmetric, nor antisymmetric with respect to the rotation** C_∞^φ. The displacement normal coordinates **after** the rotation Q_{2a}', Q_{2b}' can be expressed over the normal coordinates **before** the rotation Q_{2a}, Q_{2b} as

$$Q_{2a}' = Q_{2a}\cos\varphi + Q_{2b}\sin\varphi \tag{12}$$

$$Q_{2b}' = -Q_{2a}\sin\varphi + Q_{2b}\cos\varphi \tag{13}$$

Therefore, degenerate vibrations, in general, **transformed under a symmetry operation as a linear combination of each other**. This result is valid for any number of the degenerate vibrations and any type of symmetry operations involved.

V. SYMMETRY OF VIBRATION AND ELECTRONIC WAVEFUNCTIONS

Since a vibrational eigenfunction is a function of the normal coordinates, its behavior with respect to symmetry operations depends on the symmetry behavior of the normal coordinates.

A. Molecules with Non-Degenerate Vibrations

The total vibrational wavefunction of a molecule can be always written as a product of the **normal mode wavefunctions** which are known solution of the harmonic oscillator problem, see eq. (7). The i-th harmonic oscillator wavefunction can be presented as

$$\Phi_{vi}(Q_i) = N_{vi} e^{-\frac{\alpha_i}{2} Q_i^2} H_{vi}(\sqrt{\alpha_i} Q_i), \tag{14}$$

where $H_{vi}(\sqrt{\alpha_i} Q_i)$ is the Hermit polynomial of the v_i-th degree and $\alpha_i = \omega_i / h$.

If a non-degenerate vibration Q_i is **symmetric** with respect to a symmetry operation A (that is $\hat{A} \cdot Q_i = Q_i$), the wavefunction $\Phi_{vi}(Q_i)$ in eq. (14) is also **symmetric** for all values of the quantum number v_i (that is, $\hat{A} \cdot \Phi_{vi}(Q_i) = \Phi_{vi}(Q_i)$). If a non-degenerate vibration Q_i is **antisymmetric** with respect to this symmetry (that is $\hat{A} \cdot Q_i = -Q_i$), the wavefunction $\Phi_{vi}(Q_i)$ behaves as $\hat{A} \cdot \Phi_{vi}(Q_i) = \Phi_{vi}(-Q_i) = (-1)^{v_i} \Phi_{vi}(Q_i)$. Therefore, for **antisymmetric** vibration mode Q_i the wavefunction $\Phi_{vi}(Q_i)$ can be either symmetric, or antisymmetric depending of the value of the quantum number v_i.

In case if all normal vibrations are non-degenerate, the **total** vibrational eigenfunction Φ in eq. (7) will be **symmetric** with respect to a given symmetry operation when the **number of component antisymmetric wave functions** $\Phi_{vi}(Q_i)$ is **even**. The total eigenfunction Φ will be **antisymmetric** when the number of component antisymmetric wave functions $\Phi_{vi}(Q_i)$ is **odd**.

Important result: Total vibrational eigenfunctions, corresponding to a non-degenerate vibration **must** be either symmetric, or antisymmetric with respect to the symmetry operations of the group. The symmetric, or antisymmetric behavior of the total wavefunction can be relatively easy obtained considering its explicit form which is a product of the eigenfunctions of harmonic oscillators corresponding to different normal vibration modes.

B. Molecules with Degenerate Vibrations

If a molecule has a doubly degenerate vibrations they have the same frequencies $\omega_1 = \omega_2 = \omega_i$ and the formula for the term values can be written as

$$G(v_1, v_2) = \omega_1(v_1 + \frac{1}{2}) + \omega_2(v_2 + \frac{1}{2}) = \omega_i(v_i + 1), \tag{15}$$

where $v_i = v_1 + v_2$ can be treated as a new vibrational quantum number.

The corresponding total vibrational eigenfunction can be written as (see eq. (14))

$$\Phi_i = N_{vi} e^{-\frac{\alpha_i}{2}(Q_1^2 + Q_2^2)} H_{v1}(\sqrt{\alpha_i} Q_1) H_{v2}(\sqrt{\alpha_i} Q_2), \tag{16}$$

where $\alpha_i = \omega_i / h$.

If $v_1 = v_2 = v_i = 0$, than $H_0(\sqrt{\alpha_i} Q) = constant$ and there is only one function Φ_i in eq. (16). **Thus, the zero-point vibrational** $v_i = 0$ **does not introduce a degeneracy.** In this case, the same relations apply as in the previous section.

If the degenerate vibration if excited by only one quantum, we have either $v_1 = 1, v_2 = 0$, or $v_1 = 0, v_2 = 1$ for which the wavefunctions Φ_i in eq. (16) are not the same. That is, there are two eigenfunctions for the state $v_i = v_1 + v_2 = 1$ with the energy $G_{vi} = 2\omega_i$, see eq. (15). Therefore, the state v_i is doubly degenerate. Note, that any linear combination of the two wavefunctions in eq. (16) is also an eigenfunction of the same energy level.

If two quanta are excited ($v_i = 2$), we may have either $v_1 = 2, v_2 = 0$, or $v_1 = 1, v_2 = 1$, or $v_1 = 0, v_2 = 2$, that is there is a triple degeneracy. In general, the degree of degeneracy if v_i quanta of the double degenerate vibration are excited, is equal to $v_i + 1$.

Important result: Total vibrational eigenfunctions, corresponding to a degenerate vibration are neither symmetric, nor antisymmetric, but can in general be transformed under a symmetry operation as a linear combination of each other. However, there is only one zero-point $v = v_1 = v_2 = 0$ vibration wavefunction Φ_0 which must be either symmetric, or antisymmetric under a symmetry operation.

VI. CHARACTER TABLES

According to the Scrödinger equation

$$\hat{H}_{vib}\Phi_k = E_k\Phi_k, \tag{17}$$

each eigenfunction Φ is associated with a certain energy level E_k.

Therefore, molecular eigenfunctions and energy levels can be labelled with a symmetry index k which indicates the point symmetry group of the molecule.

The **quantitative characteristic of the labelling** is a **character table** which shows the behavior of the molecular wavefunctions under the symmetry operations of the molecular symmetry point group. Since only certain combinations of symmetry elements occur in the various point groups and since some of their symmetry elements are consequence of others, **only certain combinations of symmetry properties of the vibrational (and electronic) wavefunctions are possible**. Following Mulliken, in the molecular spectroscopy these combinations of symmetry properties are called **symmetry types**, or **species**. In the formal **group theory** the same combinations are called **irreducible representations** of the group.

As an example we first consider the **character table** of the C_s symmetry group which is shown in Table III

TABLE III: **Character Table for the C_s Group**

C_s	E	$\sigma(xy)$	$h = 2$
A'	$+1$	$+1$	x, y
A''	$+1$	-1	z

Here the first line shows the symmetry operations of the group, E and $\sigma(xy)$, where (xy) indicates the reflection mirror plain. The first column indicates the irreducible representations of the group A' and A'', while $+1$ and -1 is used for indication the symmetric and antisymmetric behavior of the wavefunctions with respect to the corresponding symmetry operation. Note, that in every normal vibration and eigenfunction there are species (irreducible representations) which are **symmetric under all symmetry operations** permitted within a group. These species are called **totally symmetric** and usually indicated by A, or A_1, or A'. Particularly for the C_s group the totally symmetric species is indicated by A' and presented in the second line in Table III. It is seen, that the group C_s has two species, A' and A''.

The last column in the table indicate the **group order**, $h = 2$ and the simple functions of the coordinates x, y, z which belongs to a certain irreducible representation. These functions are very important, because they represent the symmetry of p_x, p_y, and p_x atomic orbitals which as we know are used for building the molecular orbitals. Therefore, these coordinates provide a simple way of understanding which species a normal mode, or wavefunction belongs to.

For instance, consider the plane, but non-linear molecule of hydrazoic acid, N_3H which belongs to the C_s group. It has, according to Table III normal vibrations which are symmetric, or antisymmetric with respect to the molecular plane. During the former, all atoms remain in the plane, during the latter, they move in lines perpendicular to the plane.

As another example consider the **character table** of the C_{2v} symmetry group which is shown in Table IV

TABLE IV: **Character Table for the C_{2v} Group**

C_{2v}	E	C_2	σ_v	σ'_v	$h = 4$	
A_1	$+1$	$+1$	$+1$	$+1$	z	x^2, y^2, z^2
A_2	$+1$	$+1$	-1	-1		xy
B_1	$+1$	-1	$+1$	-1	x	xz
B_2	$+1$	-1	-1	$+1$	y	yz

As seen from Table IV, the C_{2v} group has four species (irreducible representations). The totally symmetric species is called in this case A_1. Each of the other A_2, B_1 and B_2 species are used to denote one-dimensional (non-degenerate) representations. A is used if the character under the principal rotation is $+1$, while B is used if the character is -1. If other higher dimensional representations are permitted, letter E denotes a two-dimensional irreducible representation and T denotes a three-dimensional representation. The symmetry species A_1, A_2, B_1, and B_2 summarize the symmetry properties of the vibrational, or electronic molecular wavefunctions of a for polyatomic molecule. They are analogue to the symmetry labels Σ, Π, Δ which are used for diatomic molecules.

As an example we consider normal vibrations of the formaldehyde molecule H_2CO which belongs to the group C_{2v}. It is seen that the three normal vibrations ν_1, ν_2, and ν_3 are totally symmetric and thus belong to species A_1. The vibrations ν_4 and ν_5 belong to species B_1 (if we call the plane of the molecule the xz plane), and ν_6 belongs to species B_2. **There is no normal vibration of species A_2 in this case**. However, in more complicated molecules belonging to the same group there also can be normal vibrations belonging to species A_2.

Let us now consider the symmetry of electronic orbitals. As we know, lowercase Greek letters σ, π, etc are used for denoting the symmetries of orbitals in **diatomic** molecules. Similarly, the lowercase Latin letters a_1, a_2, b_1, and b_2 are used for denote the symmetry of orbitals in **polyatomic** molecules which belong to the A_1, A_2, B_1, and B_2 irreducible representations, respectively. Alternatively, one says that the wavefunctions a_1, a_2, b_1, and b_2 **span** the irreducible representations A_1, A_2, B_1, and B_2. The functions in the 5-th and 6-th columns in Table IV represent the symmetry of different p and d atomic orbitals which **span** a certain irreducible representation.

For instance, the symmetry of electronic wavefunctions in the H_2O molecule are as follows. The atomic orbitals of the O atom are: $O2p_x$, $O2p_y$, and $O2p_z$. Assuming that the molecular plane is YZ we can see that the orbital $O2p_x$ change sign under a 180^0 rotation, C_2 and under the reflection σ_v', but remains the same under the reflection σ_v. Therefore, this orbital belongs to the B_1 irreducible representation. As we shall see, any molecular orbital built from this atomic orbital will be a b_1 orbital. It can also be seen in the similar way that $O2p_y$ orbital changes sign under C_2, but remain the same after σ_v', thus it belongs to B_2 and can contribute to b_2 molecular orbital. Similarly, it can be shown that $O2p_z$ belongs to the A_1 irreducible representation.

Finally, consider the **character table** of the C_{3v} symmetry group which is shown in Table V

TABLE V: **Character Table for the C_{3v} Group**

C_{3v}	E	$2C_3$	$3\sigma_v$	$h = 6$	
A_1	$+1$	$+1$	$+1$	z	z^2, $x^2 + y^2$
A_2	$+1$	$+1$	-1		
E	$+2$	-1	0	(x, y)	$(xz,\, x^2 - y^2)$, (xz, yz)

There are several new features of the Character Table V compared with the Character Tables III and IV.

First of all, the number of symmetry operations $h = 6$ is now not equal to the number of possible irreducible representations (3). That is because, some of the symmetry operations in Table V can be combined into **classes**, which means that they are of the same type (for example, rotations) and can be transferred into one another by a symmetry operation of the same group. For instance, the 3-fold rotations C_3^+ and C_3^- belong to the same **class** because the can be transformed to each other by reflection in the bisecting plane. Therefore, these two rotations are put to the same cell in Table V. Also three vertical planes of mirror reflection σ_v, σ_v', and σ_v'' belong to the same class because they can be transformed to each other by 3-fold rotation. All these mirror planes are put to another cell in Table V.

There is an important theorem of group theory states that:

Number of symmetry species is equal to the number of classes.

There are **three classes** of symmetry operations in C_{3v} group shown in the first line in Table V and, therefore, there are **three symmetry species** which are shown in the first column. It is seen that all elements of each symmetry class have the same symmetry characters.

Secondly, the symmetry species E in Table V is a **double degenerate** one. These species cannot be characterized simply by +1, or −1, as for non-degenerate case. As we know, the wavefunctions which belong to a degenerate vibration are **neither symmetric**, **nor antisymmetric** with respect to the symmetry operation of the group, but in general can be transformed as a linear combination of each other as

$$\begin{aligned} \Phi'_{v1} &= d_{11}\Phi_{v1} + d_{12}\Phi_{v2} + d_{13}\Phi_{v3} + \cdots, \\ \Phi'_{v2} &= d_{21}\Phi_{v1} + d_{22}\Phi_{v2} + d_{23}\Phi_{v3} + \cdots, \\ \Phi'_{v3} &= d_{31}\Phi_{v1} + d_{32}\Phi_{v2} + d_{33}\Phi_{v3} + \cdots, \\ \cdots &= \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots, \end{aligned} \tag{18}$$

where the primed wavefunctions in the *lhs* are ones **after** the symmetry operation while the non-primed wavefunctions in the *rhs* are the initial ones. In case of a double-degenerate state the number of the wavefunctions and the number of equations in eq. (18) is of cause equal to two.

It can be shown, that for characterization of the behavior of the degenerate eigenfunctions under symmetry operations it is sufficient to label every symmetry operation with the value

$$\chi = d_{11} + d_{22} + d_{33} + \cdots \tag{19}$$

which is the sum of the diagonal expansion coefficients in the set of equations in eq. (18).

The values χ in eq. (19) (as well as $\lambda = \pm 1$ symmetric indices for non-degenerate species) are called **characters of the irreducible representation.** These characters are given in the third line in Table V. As you can see the characters of the degenerate eigenfunctions are not limited by the values ±1, but can take **other integer numbers including zero**.

Note, that the character of identity operator E **is always equal to the degeneracy of the state**. Therefore, for a C_{3v} molecule any orbitals with a symmetry label a_1 and a_2 is non-degenerate, while a doubly degenerate pair of orbitals belong to e representation. Because there is not characters greater than 2 in Table V we can assume that no triply degenerate orbitals can occur in any C_{3v} molecule.

So far, we dealt with the symmetry classification of individual atomic orbitals. It is important to note that the same technique may be applied to **the linear combinations of atomic orbitals** which are used for building the **molecular orbitals**. **This allows to**

classify the molecular energy states and molecular orbitals with respect to the symmetry transformations of the molecule.

As an example, we consider the linear combinations of electronic wavefunctions which belong to different representations in Table V.

Particularly, for NH_3 case the combination

$$s_1 = s_a + s_b + s_c, \tag{20}$$

where s_a, s_b, and s_c are s-orbitals of three hydrogen atoms, belongs to the species a_1.

The combinations

$$\begin{aligned} s_2 &= -s_a + \frac{1}{2}(s_b + s_c) \\ s_3 &= s_b - s_c \end{aligned} \tag{21}$$

belongs to the doubly degenerate species e.

For proving this statement let us consider the transformation of the combinations in eq. (21) under C_3^+ and σ_v symmetry operations of the group

Rotation C_3^+:

$$\begin{aligned} s_2' &= -s_b + \frac{1}{2}(s_c + s_a) \\ s_3' &= s_c - s_a \end{aligned} \tag{22}$$

This can be easily proved from eqs. (21) and (22) that

$$\begin{aligned} s_2' &= -\frac{1}{2}s_2 - \frac{3}{4}s_3 \\ s_3' &= s_2 - \frac{1}{2}s_3 \end{aligned} \tag{23}$$

Reflection σ_v: (over the plane containing $N - H_a$ bond)

$$\begin{aligned} s_2' &= -s_a + \frac{1}{2}(s_b + s_c) = s_2 \\ s_3' &= s_c - s_b = -s_3 \end{aligned} \tag{24}$$

Similar expressions can be obtained for the symmetry operations C_3^-, σ_v', and σ_v''. It is seen that the wavefunctions s_2 and s_3 are transformed as a linear combination of each other and thus span the species E.

A. Vanishing Integrals

The character tables provide a quick and convenient way of judging whether an overlap, or transition integral is necessary zero.

Let us consider the overlap integral

$$I = \int f_1 f_2 \, d\tau, \tag{25}$$

where f_1 and f_2 are two atomic, or molecular orbitals.

The integral I is always a **scalar** value which means that it does not changes under any symmetry transformations of the molecule. The volume element $d\tau$ is also a scalar as it is invariant under any coordinate transformations. Therefore, the product $f_1 f_2$ must also **remain unchanged** by **any symmetry operations of the molecular point group**. If the integrand changes its sign under a symmetry operation, the integral I is necessary zero, because its positive part will necessary cancel its positive part. As we know, the the irreducible representation which **is equivalent in the molecular point group** is **totally symmetric representation** A_1. Thus, the integral I differs from zero only if the **integrand** $f_1 f_2$ spans the symmetry species A_1.

If the symmetry species of the functions f_1 and f_2 are known, the group theory provides a formal procedure which can be used for determination of the symmetry species of the product $f_1 f_2$. **Particularly, the character table of the product $f_1 f_2$ can be obtained just by multiplication of the characters from the character tables of the functions f_1 and f_2 corresponding to a certain symmetry operator.**

As an example we consider the product of the $f_1 = s_N$ orbital of the N atom and the linear combination of three hydrogen atom orbitals, $f_2 = s_1$ in eq. (20) in NH_3 molecule, each of the orbitals spans A_1 species:

$$\begin{aligned} f_1 &: \;\; 1 \;\; 1 \;\; 1 \\ f_2 &: \;\; 1 \;\; 1 \;\; 1 \\ f_1 f_2 &: \;\; 1 \;\; 1 \;\; 1 \end{aligned} \tag{26}$$

It is evident from eq. (26) and the table V , that the product $f_1 f_1$ also spans A_1 and therefore, the in integral I in eq. (25) in this case is **not necessary equal to zero**. Therefore, bonding and antibonding molecular orbitals **can be formed from linear combinations of s_N and s_1**.

The procedure of finding the irreducible representation of the product of two representations Γ_1 and Γ_2 is written as **direct product of irreducible representations** $\Gamma_1 \times \Gamma_2$ and and for the example above can be written as $A_1 \times A_1 = A_1$.

As another example, we consider the product of the $f_1 = s_N$ orbital of the N atom in NH_3 and $f_2 = s_3$, where $s_3 = s_B - s_C$ is the linear combination of the hydrogen atom wavefunctions from eq. (21). Now one function spans the A_1 species and another the E species. The product table of characters is

$$\begin{array}{rcrrr} f_1 & : & 1 & 1 & 1 \\ f_2 & : & 2 & -1 & 0 \\ f_1 f_2 & : & 2 & -1 & 0 \end{array} \tag{27}$$

The product characters 2, -1, 0 are those of the E species alone and therefore, the integral must be zero. Therefore, bonding and antibonding molecular orbitals **cannot be formed from linear combinations of s_N and s_3**. The direct product of the representations in this case is written as $A_1\times$ E = E.

The general rule is that **only orbitals of the same symmetry species may have nonzero overlap** and therefore, **form bonding and antibonding combinations**. This result makes a direct link between the group theory and construction of molecular orbitals from atomic orbitals by the LCAO procedure we discussed in previous chapter. Indeed, the molecular orbitals can be formed only from a particular set of atomic orbitals with nonzero overlap. These molecular orbitals are usually labelled with a lower-case letter corresponding to the symmetry species. For instance, the (s_N, s_1) molecular orbitals are called a_1 if they are bonding and a_1^* if they are antibonding.

Note, that the relationship between the symmetry species of the atomic orbitals and their product, in general, is not as simple as in eqs. (26) and (27). As an example, let us consider the linear combinations s_2 and s_3 in eq. (21) which both have symmetry species E. As we know the $N(2s)$ atomic orbital cannot be used together with each of them for building the bonding and antibonding molecular orbitals. However, the $N2p_x$ and $N2p_y$ atomic orbitals also belong to the E species in C_{3v} (see Character Table V) and thus are suitable because they may have a nonzero overlap with s_2 and s_3. This construction can be verified by multiplying the characters as

$$\begin{aligned} f_1 &: \quad 2 \quad -1 \quad 0 \\ f_2 &: \quad 2 \quad -1 \quad 0 \\ f_1 f_2 &: \quad 4 \quad\ \ 1 \quad\ 0 \end{aligned} \tag{28}$$

It can be easily verified from eq. (28) by making summation of characters in Table V that E × E = $A_1 + A_2 +$ E. The product $f_1 f_2$ in eq. (28) contains the totally symmetric species A_1 and, therefore, the corresponding integral may have a nonzero value.

B. Vanishing Dipole Moment Integrals and Selection Rules

The integrals of the form

$$I = \int f_1 f_2 f_3 \, d\tau \tag{29}$$

are very important in quantum mechanics as they include **transition matrix elements**.

For **dipole** transitions in molecules under influence of electromagnetic radiation, f_1 and f_3 are the molecular wavefunctions of the initial and the final quantum states and f_2 is a component of the molecular dipole moment, μ_x, μ_y, or μ_z. In case of **electronic transitions**, the components of the dipole moment are just the coordinates of the optical electron, x, y, and z.

The conditions when the transition matrix elements (29) **are necessary zero** lead to the **transition selection rules**. As shown in the previous section, the integral (29) can be nonzero only if the product $f_1 f_2 f_3$ **spans totally symmetric representation** A_1**, or its equivalent**. In order to test whether this condition is fulfilled, the characters of all three functions should be multiplied together and the resulting characters should be analyzed.

As an example, let us investigate whether an electron in an a_1 orbital in H_2O can make an electric dipole transition to a b_1 orbital. Having in mind that H_2O molecule belong to the C_{2v} group, we should examine all three x, y, and z components of the transition dipole moment. Reference to the C_{2v} character table in Table IV shows that these three components transform as B_1, B_2, and A_1, respectively. The calculation runs as shown in Table VI.

TABLE VI: **Optical Transition in Water**

	x-component				y-component				z-component			
	E	C_2	σ_v	σ_v'	E	C_2	σ_v	σ_v'	E	C_2	σ_v	σ_v'
$f_1(B_1)$	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1
f_2	1	-1	1	-1	1	-1	-1	1	1	1	1	1
$f_3(A_1)$	1	1	1	1	1	1	1	1	1	1	1	1
$f_1 f_2 f_3$	1	1	1	1	1	1	-1	-1	1	-1	1	-1

It is seen that the product with $f_2 = x$ spans A_1, the product with $f_2 = y$ spans A_2, and the product with $f_2 = z$ spans B_1. Thus, only the x-component of the transition dipole moment may be nonzero. Therefore, we conclude that the electric dipole transition between a_1 and b_1 is allowed and that x-polarization of the radiation can be absorbed, or emitted in this transition. Note that the electric vector of this radiation is **perpendicular** to the molecular plane.

Continuing this analysis we can build similar table for any of the a_1, a_2, b_1, and b_2 orbitals of the C_{2v} symmetry molecule and for all x, y, and z directions of the transition dipole moment. The result is that the $B_1 \leftrightarrow B_2$ and $A_1 \leftrightarrow A_2$ transitions are forbidden, while the transition between all other states are allowed for certain component of the dipole moment each. Particularly, the transitions between the states of the same symmetry $A_1 \leftrightarrow A_1$, $B_1 \leftrightarrow B_1$, ets. are possible for z component of the dipole moment which is parallel to the C_2 axis, while the transitions between different symmetry states are possible either for x, or y components of the dipole moment. Other selection rules can be obtained using a similar procedure for all other molecular symmetry groups.

The obtained selection rules for a C_{2v} molecule are analogues of the $\Sigma \leftrightarrow \Sigma$, $\Pi \leftrightarrow \Pi$, ($\Delta M = 0$) and $\Sigma \leftrightarrow \Pi$ ($\Delta M = \pm 1$) selection rules for the electronic transitions in diatomic molecules we studied before.