Chapter 3

A Theoretical Background of Spectroscopic Analysis

In this chapter I would present the theoretical background necessary for an elucidation of the analysis of data which is acquired through experimental techniques in Chapter 2 and whose implications are discussed in Chapter 4.

3.1 Optical Absorption Spectra of Benzene and Polystyrene

3.1.1 Electronic Spectroscopy and Symmetry

I shall begin with a brief discussion on molecular orbital theory to understand the correlation between molecular structure of a sample with its electronic spectra and assign the molecular states (i.e., electronic states in molecule).

The qualitative molecular orbital theory (MO) discussed here will form a foundation for my study of electronic spectroscopy. It should be stressed that there is a variety of ways to treat the electronic structure of molecules and I am taking a rather naive qualitative approach chosen to emphasize the symmetry of molecular orbitals. This discussion can give the idea of distribution of electrons in a given molecule, relative energies of the
molecular orbitals and how the electron distribution changes upon going to some low-
lying excited electronic states.

Here the treatment of molecular orbital theory, and electronic spectroscopy will make
extensive use of molecular symmetry. Although the vast majority of molecules in their
entirety have no symmetry at all, but many of them do have local symmetry. Consider the
"representative" large molecule in Figure 3.1. The molecule as a whole is not only devoid
of symmetry, it is a mess. But if we focus our attention on the iron surrounded by four
nitrogen atoms in an approximately square arrangements, we have found a region pos-
sessing useful local symmetry. For many purpose, only the iron atom and its four nearest
neighbours need be considered to understand the spectroscopic behaviour of this region
of the molecule. Many small molecules do possess real symmetry. We must understand
the behaviour of these small molecules before we try to understand big ones. Many of
the properties of, say, a benzene ring are nearly the same whether we are looking at free
benzene or a phenyl ring bound to a large molecule (in my work, a polymer, polystyrene).
The properties of free benzene are easier to understand if we make use of its symmetry.
What we learn about benzene can then be transferred to the phenyl substituent [112].

Figure 3.1: A representative large molecule.
3.1.2 Electronic states in benzene molecule

States for Hydrogen Molecule-Ion: Molecular Orbitals

The hydrogen atom is the basic model for atomic orbitals. So I shall begin with hydrogen molecule-ion as the basic model for molecular orbitals and then I pass on to the more complicated polyatomic molecule, benzene. This molecule is of my concern because the sample I have studied in my thesis is polystyrene, where \( \pi \) electrons are only associated with pendant benzene rings of the polystyrene molecule (shown in Chapter 1), and electronic spectra of polystyrene in 350 to 150 nm wavelength range, where only \( \pi \) electrons are involved, (Figure 2.7) follow those of benzene [113,114].

![Figure 3.2: A system of two nuclei of masses \( m_A \) and \( m_B \), and charges \( +Z_A \) and \( +Z_B \), and an electron of mass \( m_e \) and charges \( -e \). The distances between the particles are \( R \), \( r_A \), and \( r_B \). For hydrogen molecule-ion \( Z_A = Z_B = 1 \).](image)

Since the nuclei are several thousand times more massive than the electrons and therefore will move much more slowly than the electrons, according to Born-Oppenheimer approximation we can consider that nuclei are fixed at separation \( R \) and only the electron is allowed to move. With the aid of Figure 3.2 the Hamiltonian of hydrogen molecule-ion \((Z_A = Z_B = 1)\) can then be written as

\[
H = -\left(\frac{\hbar^2}{2m_e}\right)\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 R_A} - \frac{e^2}{4\pi\varepsilon_0 r_B} + \frac{e^2}{4\pi\varepsilon_0 R} \tag{3.1}
\]

The energy states of the Hamiltonian can be obtained by using variation theorem according to which, first a reasonable form of the solution (or wavefunction) with some adjustable parameter is guessed and then energy of the guessed wavefunction is minimized by varying
the parameters. Let us guess a wavefunction that is some linear combination of the 1s atomic orbitals (LCAO) of the two isolated atoms whose nuclei are A and B.

\[ \psi = c_1 \phi_{1sA} + c_2 \phi_{1sB} \]  \hspace{1cm} (3.2)

where, \( \phi_{1sA} = \phi_{1sA}(r_A) \); \( \phi_{1sB} = \phi_{1sB}(r_B) \). The functions \( \phi_{1sA} \) and \( \phi_{1sB} \) are already normalized and each is a solution of the Schrödinger equation for atoms A or B, i.e., for atom A

\[ H_A = -\left( \frac{\hbar^2}{2m_e} \right) \nabla^2 - \frac{e^2}{4\pi \varepsilon_0 r_A} \]

\[ H_A \phi_{1sA} = E_A \phi_{1sA} \]

\[ \int_{-\infty}^{\infty} \phi_{1sA}^* \phi_{1sA} \, dr = 1 \]  \hspace{1cm} (3.3)

Normalizing \( \psi \) using a normalization constant \( N \),

\[ 1 = \int_{-\infty}^{\infty} (N\psi)^* (N\psi) \, dr \]

\[ N = (c_1^2 + c_2^2 + 2c_1c_2S_{1sA1sB})^{-1/2} \]  \hspace{1cm} (3.4)

where

\[ S_{1sA1sB} = S = \int_{-\infty}^{\infty} \phi_{1sA} \phi_{1sB} \, dr \]  \hspace{1cm} (3.5)

\( S_{1sA1sB} \) is the overlap integral, physically it is a measure of the volume in which there is electron density from both atoms. The maximum value of any overlap integral is unity, when the two orbitals completely coincide.

Now the energy of the molecular orbital

\[ E = \int_{-\infty}^{\infty} (N\psi)^* H(N\psi) \, dr \]

\[ = \frac{c_1^2 H_{AA} + c_2^2 H_{BB} + 2c_1c_2 H_{AB}}{c_1^2 + c_2^2 + 2c_1c_2 S} \]  \hspace{1cm} (3.6)
Here, $H_{AA} = \int \phi_{1A}^* \phi_{1A} d\tau$, $H_{BB} = \int \phi_{1B}^* \phi_{1B} d\tau$ are called Coulomb integrals and $H_{AB} = \int \phi_{1A}^* \phi_{1B} d\tau$, $H_{BA} = \int \phi_{1B}^* \phi_{1A} d\tau$ are called exchange integrals and all Hamiltonians are Hermitian, i.e., $H_{ij} = H_{ji}$. We have assumed the coefficients to be real.

To minimize $E$ with respect to the coefficients $c_1$ and $c_2$, we have

$$\frac{\partial E}{\partial c_1} = \frac{c_1(H_{AA} - E) + c_2(H_{AB} - ES)}{c_1^2 + c_2^2 + 2c_1c_2S} = 0$$
$$\frac{\partial E}{\partial c_2} = \frac{c_1(H_{AB} - ES) + c_2(H_{BB} - E)}{c_1^2 + c_2^2 + 2c_1c_2S} = 0$$

Equations (3.7) can be solved only if

$$\begin{vmatrix}
H_{AA} - E & H_{AB} - ES \\
H_{AB} - ES & H_{BB} - E
\end{vmatrix} = 0$$

(3.9)

When the condition in Equation (3.9) is met, the lowest energy possible for the wave function in Equation (3.2) is achieved.

For homonuclear diatomic molecule, i.e., A and B identical, $H_{AA} = H_{BB} = \alpha$; $H_{AB} = H_{BA} = \beta$; but $H_{AB} \neq H_{AA}$ (because the exchange integral, $H_{AB}$, involves wave functions at two centres (A and B) and the Coulomb integral, $H_{AA}$, involves functions at only one centre).

$$E = E_{\pm} = \frac{H_{AA} - H_{AB}}{1 \pm S} = \frac{\alpha \pm \beta}{1 \pm S}$$

(3.10)

Note that relative to the energy of an electron at infinity, the values of $\alpha$ and $\beta$ are negative. They represent stabilizing interactions. Corresponding bonding ($\psi_b$) and antibonding ($\psi^*$)
orbitals are:

\[ \psi_b = \frac{1}{\sqrt{2 + 2S}} [\phi_{1s_A} + \phi_{1s_B}] \]

\[ \psi^* = \frac{1}{\sqrt{2 - 2S}} [\phi_{1s_A} - \phi_{1s_B}] \]

Figure 3.3: The energy levels described by Equation (3.10)

In this way every linear combination of two identical atomic orbitals (AOs) gives two molecular orbitals (MOs), one higher and the other lower in energy than the AOs [112].

**A. Important principles guiding construction of molecular orbitals:**

(i) The AOs must have the same symmetry properties with respect to certain symmetry elements of the molecule. (For two orbitals to form a molecular orbital, they must have the same symmetry about the internuclear axis).

(ii) The energies of AO must be comparable and should overlap as much as possible.

(iii) Each possible molecular orbital must form a basis for some irreducible representation of the point group of the molecule.

**B. Important principles guiding spectral assignment:**

(i) Starting with a given number of atomic orbitals, we must generate that same number of molecular orbitals.

(ii) 'g' or 'u' symmetry property: \( \psi \) has 'g' ('u') symmetry if it is symmetric (antisymmetric) with respect to inversion through the centre of molecule.

(iii) '+1' or '-1' symmetry property: This concerns the symmetry of \( \psi \) with respect to
3.1. Optical Absorption Spectra of Benzene and Polystyrene

reflection across any \((\sigma_v)\) plane containing the internuclear axis (for diatomic molecule).
\(\psi\) has '+ ('-) symmetry if it is symmetric (antisymmetric) with respect to this reflection.
(iv) For a given molecule \(\pi \rightarrow \pi^*\) transitions are relatively more intense than the \(n \rightarrow \pi^*\) transitions where \(n\) electrons play no part in the bonding and remain associated with the atom contributing them (see Figure 2.7).

Energy estimation of Molecular Orbitals (MOs) by Hückel Method: Benzene Molecule

With an arsenal of drastic approximations it is possible to estimate the energies of molecular orbitals in a fairly simple manner. The Hückel method is generally used for systems of \(\pi\) electrons (although the method can be extended to include sigma bonds). In a molecule where the highest filled and lowest unoccupied orbitals are \(\pi\) orbitals, such as formaldehyde, ethylene, buta-1,3-diene and benzene, energy estimation by approximate MO method due to Hückel is most useful. Since I have already mentioned above that, from a spectroscopic point of view I am only concerned about the ground state and excited states of the benzene molecule, I will discuss here first the steps of Hückel treatment in general case and then specifically the case of benzene molecule under the Hückel treatment [112,115].

The Hückel molecular orbital method is basically a extension of LCAO method (discussed in previous section for hydrogen molecule ion) to polyatomic molecule. In this treatment here the sigma frameworks of hydrocarbons are completely ignored, only the \(\pi\) orbitals are treated.

The secular determinant of the general type:

\[
\begin{vmatrix}
H_{11} - E & H_{12} - ES_{12} & \cdots & H_{1n} - ES_{1n} \\
H_{12} - ES_{12} & H_{22} - E & \cdots & H_{2n} - ES_{2n} \\
\vdots & \vdots & \ddots & \vdots \\
H_{1n} - ES_{1n} & H_{2n} - ES_{2n} & \cdots & H_{nn} - E
\end{vmatrix} = 0
\]

(3.13)
where, $H_{nn}$, $H_{mn}$ (for $m \neq n$), and $S_{mn}$ (for $m \neq n$) are the Coulomb integral, resonance integral, and overlap integral respectively. $E$ is the Molecular Orbital (MO) energy. The determinant (3.13) is abbreviated to $|H_{mn} - ES_{mn}| = 0$, where, $S_{mn} = 1$ for $m=n$.

For $\pi$ electron system Hückel approximations are as follows:

1. Only electrons in $\pi$ orbitals are considered, those in $\sigma$-orbitals being neglected, i.e.,
   
   $H_{ij} = \int (2p_i)H(2p_j) \, dr$.

2. It is assumed that, for $m \neq n$, $S_{mn} = 0$ implying no overlap of atomic orbitals even for nearest neighbour atoms.

3. When $m = n$, $H_{nn}$, coulomb integral is assumed to be same for each atom and is given the symbol $\alpha$, i.e., $H_{nn} = \alpha$

4. When $m \neq n$, resonance integral $H_{mn}$ is assumed to be same for any pair of directly bonded atoms and is given the symbol $\beta$, i.e., $H_{mn} = \beta$.

5. When $m$ and $n$ are not directly bonded $H_{mn} = 0$

The $\pi$-electron wavefunctions in the Hückel method are given by (as in Equation (3.2) for LCAO MOs of a diatomic molecule)

$$\psi = \sum \xi_i \phi_i$$  \hspace{1cm} (3.14)

now $\phi_i$ are only those AO s, very often $2p$ on $C$, $N$, $O$, which are involved in the $\pi$ MOs.

In the case of benzene, Hückel treatment of the six $2p$ orbitals on the carbon atoms
and perpendicular to the plane of the ring leads to the secular determinant

\[
\begin{vmatrix}
  x & 1 & 0 & 0 & 0 & 1 \\
 1 & x & 1 & 0 & 0 & 0 \\
 0 & 1 & x & 1 & 0 & 0 \\
 0 & 0 & 1 & x & 1 & 0 \\
 0 & 0 & 0 & 1 & x & 1 \\
 1 & 0 & 0 & 0 & 1 & x \\
\end{vmatrix} = 0
\] (3.15)

where, \( \frac{\alpha - \beta}{\beta} = x \)

Solution of determinant (3.15) is \( x = \pm 1, \pm 1, \pm 2 \) i.e., \( E = \alpha \pm \beta, \alpha \pm \beta, \alpha \pm 2\beta \). So there are six energy states of which \( E = \alpha + \beta \) and \( E = \alpha - \beta \) are both doubly degenerate. The corresponding six MO wavefunctions will be obtained from

\[
\psi = \Sigma c_i \phi_i = c_1 2p_1 + c_2 2p_2 + c_3 2p_3 + \ldots + c_6 2p_6
\] (3.16)

To find out the symmetry species of \( \pi \) MOs of benzene, I have to discuss in brief the point group symmetry of benzene, corresponding character table, reducible representation of benzene in this point group and from these, extraction of irreducible representation by using the character table of the point group. The terms used here will be clear after the following discussion.

Benzene, shown in Figure 3.4, in respect to its symmetry, belongs to the point group \( D_{6h} \). The symbol “\( D_{nh} \)” tells us that we need a \( C_n \) axis (i.e., the \( n \)-fold axis of rotation), \( n \perp C_2 \) axes, and a horizontal mirror plane which, by definition, is perpendicular to the principal axis where, as a point of nomenclature, the axis of highest order in a point group is called the principal axis. These symmetry elements will then generate \( n \) vertical mirror planes. Following the above nomenclature benzene has \( D_{6h} \) symmetry (see Figure 3.4). Here \( C_6 \) axis is the principal axis. The six \( \perp C_2 \) axes fall into two classes, designated \( C_2' \) and \( C_2'' \) depending on whether they pass through vertices or bisect sides of the hexagonal...
molecules respectively. The six vertical mirror planes also fall into two classes, designated \( \sigma_v \) and \( \sigma_d \) corresponding to the \( \perp C_2 \) axis nomenclature. By convention, \( \sigma_v \) and \( C_2' \) are defined to be colinear, and \( \sigma_d \) and \( C_2'' \) have to be colinear. Further, \( \sigma_v \) and \( C_2' \) will pass through as many atoms as possible, whereas \( \sigma_d \) and \( C_2'' \) will pass through a few atoms as possible. This convention is illustrated for benzene in Figure 3.4.

![Numbering and symmetry elements of benzene](image)

**Figure 3.4: Numbering and symmetry elements of benzene**

Matrices can be used as representations of symmetry operations. As an example, for simplicity I consider the point group \( C_{2h} \) and a vector, \( \overrightarrow{v} \), which starts at the origin and terminates at the point \((x_1, y_1, z_1)\) and use a \( 3 \times 3 \) matrix to represent the effect of the symmetry operations of this group on this vector. Let the \( C_2 \) axis be the \( z \) axis. Beside \( C_2 \) operation some other operations in this group are \( E \) (identity operation), \( i \) (inversion operation), \( \sigma_h \) (reflection operation, mentioned above) etc. The operation \( E \), the identity operation, does nothing to the vector, so the representation of \( E \) is written as follows:

\[
\begin{bmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{bmatrix}
\begin{bmatrix}
x_1 \\
y_1 \\
z_1
\end{bmatrix} =
\begin{bmatrix}
x_1 \\
y_1 \\
z_1
\end{bmatrix}
\]

(3.17)
Inversion operation \((i)\) changes each coordinates into minus itself:

\[
\begin{bmatrix}
-1 & 0 & 0 \\
0 & -1 & 0 \\
0 & 0 & -1 \\
\end{bmatrix}
\begin{bmatrix}
x_1 \\
y_1 \\
z_1 \\
\end{bmatrix}
=
\begin{bmatrix}
-x_1 \\
-y_1 \\
-z_1 \\
\end{bmatrix}
\]

(3.18)

\(\sigma_h\) operation leaves the \(x\) and \(y\) coordinates unchanged but changes \(z\) to \(-z\).

\[
\begin{bmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & -1 \\
\end{bmatrix}
\begin{bmatrix}
x_1 \\
y_1 \\
z_1 \\
\end{bmatrix}
=
\begin{bmatrix}
x_1 \\
y_1 \\
-z_1 \\
\end{bmatrix}
\]

(3.19)

The \(C_2\) rotation (2-fold rotation) operation leaves \(z\) alone but changes \(x\) and \(y\). I will derive the new \(x\) and \(y\) coordinates in a general way which will be applicable to rotation through any angle \(\theta\). Considering the rotation of the vector \(\vec{r}_1(x_1, y_1)\) through the angle \(\theta\) to give the vector \(\vec{r}_2(l, \alpha)\) or \(\vec{r}_2(x_2, y_2)\), I have

\[
x_1 = l \cos \alpha
\]

(3.20)

\[
y_1 = l \sin \alpha
\]

The rotated vector has coordinates

\[
x_2 = l \cos(\theta - \alpha) = x_1 \cos \theta + y_1 \sin \theta
\]

(3.21)

\[
y_2 = -l \cos(\theta - \alpha) = -x_1 \sin \theta + y_1 \cos \theta
\]
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In matrix-vector language, it can be written as

\[
\begin{bmatrix}
\cos \theta & \sin \theta \\
-\sin \theta & \cos \theta
\end{bmatrix}
\begin{bmatrix}
x_1 \\
y_1
\end{bmatrix}
= \begin{bmatrix}
x_2 \\
y_2
\end{bmatrix}
\]

(3.22)

The matrix \( R_\theta \) is a representation of a rotation through the angle \( \theta \). A \( C_2 \) rotation is a rotation through \( \theta = 2\pi/2 = \pi \) and \( \cos \pi = -1 \), \( \sin \pi = 0 \); so the \( C_2 \) matrix is

\[
\begin{bmatrix}
-1 & 0 & 0 \\
0 & -1 & 0 \\
0 & 0 & 1
\end{bmatrix}
\begin{bmatrix}
x_1 \\
y_1 \\
z_1
\end{bmatrix}
= \begin{bmatrix}
x_1 \\
y_1 \\
z_1
\end{bmatrix}
\]

(3.23)

These then constitute the symmetry operations of \( C_{2v} \) point group in matrix representations. Now I shall discuss the meaning and requirement of Characters and Character Tables of any point group and will give specifically those of \( D_{6h} \) point group in Table 3.1.

The matrix form of any symmetry operation on a molecule of a given point group can be decomposed to its basic irreducible components. The symmetry species of the molecular orbitals (MOs) of the given molecule is related with the symmetry of these irreducible representations [112]. Instead of working with such irreducible representation, things can be make simpler by working with characters of irreducible representations.

The character of a matrix is the trace of the matrix. Table 3.1 represents the character table for the point group \( D_{6h} \). Across the top row is the complete set of operation of the group. Every operation presented here has been explained except \( S_n \). This is an improper rotation, it consists of an \( (n\text{-fold}) \) rotation followed by a reflection through the plane perpendicular to the axis of rotation. Down the left column are the names of the irreducible representations. The number of irreducible representations is equal to the number of classes of operations of the point group. The symbols “\( 2C_3 \)” and “\( 3\sigma_v \)”
mean that there are two operations in the class containing \( C_3 \) and three operations in the class containing \( \sigma_v \) (for detail see page 48-49 of ref. [112]). The full character table, for example the \( D_{6h} \) table (Table 3.1), is divided into several areas. The main part contains the characters. On the left are the names of the irreducible representations, known as Mulliken symbols. Conventionally, the letters \( A, B, E, \) and \( T \) are used. \( A \) and \( B \) are one-dimensional, \( E \) is two-dimensional and \( T \) is three-dimensional. The dimension of an irreducible representation is the dimension of any of its matrices (the numbers of rows or columns in the matrix). Since the representation of the operation \( E \) is always the identity matrix, the character of \( E \) is always the dimension of the irreducible representation. For example, for a two-dimensional irreducible representation, \( E \), the character (or trace) of identity operation, \( E \), is 2. The difference between \( A \) and \( B \) is that the character under the principal rotational operation, \( C_n \), is always +1 for \( A \) and -1 for \( B \) representations. The subscripts 1, 2, 3, etc., which may appear with \( A, B, E \) or \( T \) can be considered arbitrary labels, where the maximum value of the subscript for a given representation will be equal to the number of probable symmetry configurations maintaining the condition of this representation, while \( g \) (gerade) or \( u \) (ungerade) representation is symmetric or

<p>| Table 3.1: Character Table of point group ( D_{6h} ) |</p>
<table>
<thead>
<tr>
<th>( D_{6h} )</th>
<th>( E )</th>
<th>( 2C_6 )</th>
<th>( 2C_3 )</th>
<th>( C_2 )</th>
<th>( 3C'_2 )</th>
<th>( i )</th>
<th>( 2S_3 )</th>
<th>( 2S_6 )</th>
<th>( \sigma_v )</th>
<th>( 3\sigma_d )</th>
<th>( 3\sigma_e )</th>
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</table>

\[ R_x, R_y, R_z \]
\[ (xz, yz) \]
\[ (x^2 + y^2, z^2) \]
\[ (x^2 - 3y^2) \]
\[ y(3x^2 - y^2) \]
\[ (xz^2, yz^2) \]
\[ (xy, z(x^2 - y^2)) \]

Chapter. A Theoretical Background of Spectroscopic Analysis
antisymmetric respectively with respect to inversion as mentioned earlier. The three columns on the right side of the table contain basis functions (Three columns corresponds to simple, quadratic and cubic basis functions) for the irreducible representations (see page 50-54 of ref. [112] for detail). As an example, Table 3.1 shows that \( z \) forms a basis for the irreducible representation \( A_{2u} \) in the group \( D_{6h} \) because the characters of \( z \) are same as that of \( A_{2u} \). In a similar way \( x \) and \( y \) together form a basis for the two-dimensional irreducible representation, \( E_{1u} \). The symmetry of these two bases \( z \) and \( (x, y) \) will be used later in forthcoming section to decide symmetry of the dipole moment operator for \( \pi \) orbital electronic transition of benzene. Other symbols in the character table are the rotations about the \( x, y, \) and \( z \) axes, called \( R_x, R_y, \) and \( R_z \). For example, \( E, C_6, C_3 \) operations leave the direction of rotation about the \( z \) axis unchanged while the two reflection \( \sigma_d \) and \( \sigma_v \) reverse the sense of rotation. So the characters of \( R_z \) under operations \( E, C_6, C_3, \sigma_d \) and \( \sigma_v \) are 1, 1, 1, -1, and -1 respectively. \( x, y \) and \( z \) together form the representation \( \Gamma_{x,y,z} \) shown at the bottom of the character table, the characters of this representation are the sum of those of the two bases \( z \) and \( (x, y) \). This representation is particularly important in case of vibrational spectroscopy (see page 141 of ref. [112] for detail).

I shall next examine the benzene molecule with its irreducible representations and its Hückel energy levels. Considering basis atomic orbitals as one \( 2p \) orbital from each carbon atom in the \( \pi \) network of six carbon atom in benzene (Figure 3.4) we can get the reducible representation as shown in Table 3.2. This representation can be decomposed to give four irreducible representations using character table 3.1, i.e., Table 3.2 gives the sum of these irreducible representations (see page 55-57 of ref. [112] for detail) as \( (b_{2g} + e_{1g} + a_{2u} + e_{2u}) \). These four irreducible representations tell us immediately that

<table>
<thead>
<tr>
<th>( D_{6h} )</th>
<th>( E )</th>
<th>( 2C_6 )</th>
<th>( 2C_3 )</th>
<th>( C_2 )</th>
<th>( 3C_2' )</th>
<th>( 3C_2'' )</th>
<th>( i )</th>
<th>( 2S_3 )</th>
<th>( 2S_5 )</th>
<th>( \sigma_h )</th>
<th>( 3\sigma_d )</th>
<th>( 3\sigma_v )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 6C(2p_z) )</td>
<td>6</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-6</td>
<td>0</td>
<td>2</td>
</tr>
</tbody>
</table>
there will be only four different \( \pi \) energy levels, that means two sets of molecular orbitals will be degenerate, since from six atomic orbitals we will expect six MOs. The \( \pi \) MO wave functions and corresponding symmetry species of benzene according to the Table 3.1 are shown in Figure 3.5. Dotted lines shown in this figure indicate nodes, i.e., the points where the wave functions change sign and the probabilities go to zero. The Hückel \( \pi \)

![Figure 3.5: \( \pi \) orbitals of benzene. Dotted lines are nodes. In each case the \( C(2p_z) \) orbitals perpendicular to the plane of the molecule are presented, going into and out of the page.](image)

energy levels and corresponding MOs for benzene are shown in Figure 3.6. The energy increases with the number of nodal planes perpendicular to the ring.

The ground configuration of benzene is obtained by putting the six electrons, which were originally in 2\( p_z \) AOs on the carbon atoms (z axis perpendicular to the ring), into the lower energy MOs, taking into account the fact that an \( e_{1g} \) or \( e_{2u} \) orbital is doubly degenerate and can accommodate four electrons, giving

\[
\cdots (1a_{2u})^2(1e_{1g})^4 \rightarrow ^1A_{1g}
\]  

(3.24)

This is a totally symmetric singlet state. As for all molecules with occupied orbitals that are all filled, the ground state is a totally symmetric singlet state.

The first excited configuration is obtained by promoting an electron from an \( e_{1g} \) to an \( e_{2u} \) orbital (see Figure 3.6), resulting in

\[
\cdots (1a_{2u})^2(1e_{1g})^3(1e_{2u})^1
\]  

(3.25)
3.1. Optical Absorption Spectra of Benzene and Polystyrene

Figure 3.6: Hückel π energy level diagram for benzene. At extreme left and middle Hückel π energy levels and corresponding MOs and their symmetry. At the extreme right more complete MO diagram shows that the σ bonding orbitals overlap the lowest π bonding orbital in energy.

the states arising from this configuration are the same as those from \( \cdots \cdot (1a_{2u})^2(1e_{1g})^1(1e_{2u})^1 \), as a single vacancy in \( e_{1g} \) can be treated as like an electron.

Now the symmetry species \( \Gamma(\Psi^o_e) \), where superscript ‘o’ stands for orbital, of the orbital part of the electronic wave function corresponding to a particular configuration is given by

\[
\Gamma(\Psi^o_e) = \prod_i \Gamma(\Psi_i) \tag{3.26}
\]

where \( \prod_i \Gamma(\Psi_i) \) stands for the product, over all elements \( i \), of the symmetry species of all occupied MOs \( \Psi_i \). Since filled orbitals need not be considered as they only have the effect of multiplying the result by the totally symmetric species, effectively product is only over all partially filled MOs. This product can be directly obtained from direct product table for a given point group.

So the symmetry species \( \Gamma(\Psi^o_e) \) of the orbital part of the electronic wavefunction for
the first excited state (expression (3.25)) is obtained from

\[
\Gamma(\Psi^e) = e_{1g} \times e_{2u} = B_{1u} + B_{2u} + E_{1u}
\]  

(3.27)

Table 3.3, direct product table for \(D_{6h}\) point group, is used here to get the result. It is to be noted that the \(g - u\) selection rules \((g \times g = g; g \times u = u; u \times u = g)\) are added here.

<table>
<thead>
<tr>
<th>(D_{6h})</th>
<th>(A_1)</th>
<th>(A_2)</th>
<th>(B_1)</th>
<th>(B_2)</th>
<th>(E_1)</th>
<th>(E_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A_1)</td>
<td>(A_1)</td>
<td>(A_2)</td>
<td>(B_1)</td>
<td>(B_2)</td>
<td>(E_1)</td>
<td>(E_2)</td>
</tr>
<tr>
<td>(A_2)</td>
<td>(A_1)</td>
<td>(B_2)</td>
<td>(B_1)</td>
<td>(E_1)</td>
<td>(E_2)</td>
<td></td>
</tr>
<tr>
<td>(B_1)</td>
<td>(A_1)</td>
<td>(A_2)</td>
<td>(E_2)</td>
<td>(E_1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(B_2)</td>
<td>(A_1)</td>
<td>(E_2)</td>
<td>(E_1)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(E_1)</td>
<td></td>
<td>(A_1 + [A_2] + E_2)</td>
<td>(B_1 + B_2 + E_1)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(E_2)</td>
<td></td>
<td>(A_1 + [A_2] + E_2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

As the two electrons (or one electron and one vacancy) in the partially occupied orbitals may have parallel \((S = 1)\) or antiparallel \((S = 0)\) spins, there are six states arising from the excited configuration (expression (3.25)) shown in Figure 3.7.

Figure 3.7: Partial state diagram of benzene.
3.1.3 Molecular Optical Response

A molecular system subjected to an external electromagnetic field will respond to this by changing its state, accompanied by changes in the electromagnetic field. The absorption spectrum describes how much energy (or how many photons of a given energy) is taken out of the external beam due to excitation of the molecular system to a higher quantum state, and is given by

\[ A(w) = \sum_f |\langle f | \hat{\mu}_e \cdot \mathbf{e} | g \rangle|^2 \delta(E_f - E_g - hw) \] (3.28)

Here, \( \mathbf{e} \) is the polarization vector of the light. \( |g\rangle \) denotes the state of the molecule before the light was turned on (taken it to be the ground state), while \( |f\rangle \) is summed over all molecular excited states. The quantities \( E_g \) and \( E_f \) denote the energies of these states, while \( w \) is the frequency of the incident light wave. The delta function reflects conservation of energy: the absorption only occurs if the photon energy is resonant with one of the molecular transitions. Thus, the absorption spectrum shows a series of delta peaks. In practice, these peaks will not be infinitely sharp, as a consequence of the fact that the excited states have a finite lifetime. The width of each peak is determined by the inverse lifetime of the excited state involved. In gases, this may be dominated by the spontaneous-emission lifetime, while in molecules that occur in condensed phases (solutions, glasses, crystals) this lifetime is dominated by dephasing times imposed by interactions with dynamic degrees of freedom in the environment. The *area under each of the absorption peaks* gives the so-called (oscillator) strength of the transition. As seen from Eqn. (3.28), the strength is just given by the absolute value squared of the transition dipole moment, i.e., the matrix element of the dipole moment between the ground state and the final state. So the strength of each peak is given by the square of the transition dipole moment projected along the direction of the polarization of the light wave. For dipole forbidden transitions, this dipole moment vanishes and there will not be any absorption peak to be seen associated with the transition.
I have discussed the formalism to construct various electronic excited states of molecules. In many situations, it is useful and sufficient to consider each molecule as just a two-level system, having a ground state and a single excited state. This is the case if one of the many possible transitions in the molecules has an oscillator strength that dominates all others and if light of frequencies that are close to this dominant transition are used.

**Intensities of Spectral transitions**

Selection rules of transition can explain the intensities of the spectral transitions from ground state. As discussed earlier the probability that a transition between two states will be induced by the oscillating electric field of a light wave is proportional to the square of the transition moment integral.

For an electronic transition, the transition moment integral

\[ M = \int \psi_e^* \psi \, d\tau_n \int \psi_e^* \mu_e \psi \, d\tau_s \int \psi_e^* \psi \, d\tau_s \]  

(3.29)

\[ = \int \psi_e^* \psi_e^* \mu_e \psi_e \psi_e \, d\tau_e \int \psi_e^* \psi_e \, d\tau_s \]  

(3.30)

where the prime denotes an excited state and \( \mu_e \) is the dipole moment operator, depends only on electron coordinates. Eqn. (3.29) is the basis of the electronic selection rules. If any of the integrals is zero, the transition is formally forbidden. \( \int \psi_e^* \psi \, d\tau_n \) is identified as *Frank-Condon factor* (Frank-Condon factor is actually usually taken as the square of the integral), representing the overlap of vibrational wave functions of the ground and excited electronic states, is not necessarily zero because the two vibrational wave functions do not belong to the same electronic state and therefore need not be orthogonal. \( \int \psi_e^* \mu_e \psi_e \, d\tau_e \) is the basis of orbital selection rules and \( \int \psi_e^* \psi_e \, d\tau_s \) is the basis of spin selection rules. Spin selection rules state that the integral \( \int \psi_e^* \psi_e \, d\tau_s \) must be nonzero if the transition is to be allowed. So a transition is spin-allowed if and only if the multiplicities of the two states involved are identical, i.e., if the spin symmetry, written as left superscript of the state, of excited and ground states are same. The spin selection rule is the strictest of the...
electronic selection rules. An electronic transition is orbitally-allowed if and only if triple direct product $\Gamma(\psi_e^*) \times \Gamma(\hat{\mu}_e) \times \Gamma(\psi_e)$ contains totally symmetric irreducible representation of the point group of the molecule. It should be immediately obvious that for a totally symmetric ground state, only transitions to excited states which have the same symmetry as at least one of the components of the dipole moment operator will be orbitally-allowed. Eqn. (3.29) can be rearranged as Eqn. (3.30), where $\int \psi_e^* \psi_r^* \hat{\mu}_e \psi_e \psi_r \, dr_{en}$ is the basis of vibronic selection rules. In the preceding discussion of orbital selection rules, only 0-0 ("pure electronic") transitions are considered for which both $\psi_\nu$ and $\psi_e$ are totally symmetric. In Eqn. (3.30) vibrational and electronic integrals are combined to allow for the case in which $\psi_\nu$ or $\psi_e$ is not totally symmetric. If by coupling an orbitally-forbidden electronic transition with a vibrational transition of the molecule, the selection rules can be satisfied and some intensity can be expected, such a transition is called vibronically allowed. Spin allowed, vibronically allowed but orbitally forbidden transitions exhibit intensities between those of fully allowed and spin forbidden transitions.

As discussed in a previous section for benzene, dipole moment operator $\hat{\mu}_e$ transforms as $a_2u(z) + e_{1u}(x, y)$ in the point group $D_{oh}$ (as discussed before, when discussing the character table). To see whether the electronic transitions to different states from the ground state of benzene are allowed or forbidden with respect to spin, orbital and vibronic selection rules, the triple direct product has to be calculated for each transition. I have shown below the electronic transitions for benzene and their corresponding characters and molar absorptivity ($a$, in Litre $Mole^{-1} cm^{-1}$, used in Eqn. (2.17) of Chapter 2) in tabular form. Here the triple direct products are calculated using Table 3.3.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Transition moment factor</th>
<th>Nature of transition</th>
<th>Approx. range of $a$ ($LM^{-1} cm^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{1g} \rightarrow 1E_{1u}$</td>
<td>singlet $\rightarrow$ singlet transition</td>
<td>spin allowed,</td>
<td>$10^2 - 10^5$</td>
</tr>
</tbody>
</table>

$E_{1u} \left( \begin{array}{c} a_{2u} \\ e_{1u} \end{array} \right) A_{1g}= \left( \begin{array}{c} e_{1g} \\ 0 \end{array} \right)$ orbitally allowed.
3.1. Optical Absorption Spectra of Benzene and Polystyrene

\[ \begin{align*}
A_{1g} \rightarrow ^1B_{1u} & \quad \text{singlet} \rightarrow \text{singlet transition} \quad \text{spin allowed,} \quad 10^0 - 10^3 \\
B_{1u} & \left( \begin{array}{c} a_{2u} \\ e_{1u} \end{array} \right) A_{1g} = \left( \begin{array}{c} b_{2g} \\ e_{2g} \end{array} \right) \quad \text{orbitally forbidden,}
\end{align*} \]

\[ \begin{align*}
B_{1u}e_{2g} & \left( \begin{array}{c} a_{2u} \\ e_{1u} \end{array} \right) A_{1g}a_{1g} = \left( \begin{array}{c} e_{1g} \\ a_{1g} + a_{2g} + e_{2g} \end{array} \right) \quad \text{vibronically allowed (by vibration of } e_{2g} \text{ or } b_{2g} \text{ symmetry).}
\end{align*} \]

\[ \begin{align*}
B_{1u}b_{2g} & \left( \begin{array}{c} a_{2u} \\ e_{1u} \end{array} \right) A_{1g}a_{1g} = \left( \begin{array}{c} a_{1g} \\ e_{1g} \end{array} \right) \quad \text{vibration of } e_{2g} \text{ or } b_{1g} \text{ symmetry).}
\end{align*} \]

\[ \begin{align*}
A_{1g} \rightarrow ^1B_{2u} & \quad \text{singlet} \rightarrow \text{singlet transition} \quad \text{spin allowed,} \quad 10^0 - 10^3 \\
B_{2u} & \left( \begin{array}{c} a_{2u} \\ e_{1u} \end{array} \right) A_{1g} = \left( \begin{array}{c} b_{1g} \\ e_{2g} \end{array} \right) \quad \text{orbitally forbidden,}
\end{align*} \]

\[ \begin{align*}
B_{2u}e_{2g} & \left( \begin{array}{c} a_{2u} \\ e_{1u} \end{array} \right) A_{1g}a_{1g} = \left( \begin{array}{c} e_{1g} \\ a_{1g} + a_{2g} + e_{2g} \end{array} \right) \quad \text{vibronically allowed (by vibration of } e_{2g} \text{ or } b_{1g} \text{ symmetry).}
\end{align*} \]

\[ \begin{align*}
B_{2u}b_{1g} & \left( \begin{array}{c} a_{2u} \\ e_{1u} \end{array} \right) A_{1g}a_{1g} = \left( \begin{array}{c} a_{1g} \\ e_{1g} \end{array} \right) \quad \text{vibration of } e_{2g} \text{ or } b_{1g} \text{ symmetry).}
\end{align*} \]

\[ \begin{align*}
A_{1g} \rightarrow ^3B_{1u} & \quad \text{singlet} \rightarrow \text{triplet transition} \quad \text{spin forbidden,} \quad 10^{-5} - 0 \\
& \quad \text{orbitally forbidden, vibronically allowed.}
\end{align*} \]

Vibrations of benzene include some of \( e_{2g} (\nu_{12}) \) and \( b_{2g} (\nu_4, \nu_5) \) symmetry, but none of \( b_{1g} \) symmetry (see Table for Vibrational Frequencies of Benzene in [112], page 387).

From these table and above discussion the benzene spectrum at ultraviolet-visible range (corresponds to \( \pi \rightarrow \pi^* \) transitions) can be assigned and the energy of each excited state with respect to its ground state can be determined from its corresponding peak position in wavelength or photon energy, as shown in Figure 3.8.

Armed with the theoretical tools provided above I shall now attempt a reconstruction of the optical spectrum of polystyrene. I have mentioned in Section 3.1.1, optical absorp-
3.1. Optical Absorption Spectra of Benzene and Polystyrene

Figure 3.8: Spectrum of benzene in gas phase.

Figure 3.9: Spectrum of atactic polystyrene film on quartz substrate (quartz is transparent in spectral region shown here).

Absorption spectra of polystyrene will follow the benzene molecule spectra at ultraviolet energy range specifically at 150-300nm wavelength (or 4-8eV energy) range, as in polystyrene phenyl-groups are attached as side-group to the C—C— backbone chain by saturated or σ-bonds (see Chapter 1 for detail) that have no major effect on the spectrum at the above mentioned energy range. Hence polystyrene spectra can be assigned correctly [113] (Figure 3.9) from the shift of peak positions and peak splitting with respect to the gas phase spectra of benzene where benzene is treated as individual molecule. The associated correlation between benzene rings in polystyrene can also be determined and in the
3.2 Optical properties of molecular aggregates

In the previous section I have discussed the optical response of individual molecule or dilute solutions, where interactions between two solute molecules can be neglected. If the solution is made denser, molecules that are kept in close proximity may form molecular aggregates due to electrostatic forces (for instance, van der Waals interactions). The class of molecular aggregates with a red-shifted absorption band are referred to as J-aggregates. The narrow absorption band with a large intensity (oscillator strength) is the most characteristic property of these systems. Collective optical response of the molecules that form the aggregates is the basic interest in this section. Here collective properties mean that the optical response of aggregates is fundamentally different from the addition of the optical response of the individual molecules that make up the aggregate. This behaviour results from the collective Frenkel excitons that describe the excited states and the optical response of the aggregates. From the point of view of my interest intermolecular charge transfer is neglected. This implies that excitations in which, after annihilation from ground-state, an electron is created in an excited orbital of a different molecule (charge transfer excitons or Wannier excitons), are not considered. The excitation, in which the ground-state hole and the excited-state electron are always on the same molecule, is called the Frenkel exciton. It is a simple excitation, as we only need one coordinate to describe it the positions of electron and hole being the same. Compared to this, in the case of possible charge transfer, the positions of electron and hole should be considered as two separate degree of freedom, complicating the description, as the exciton acquires internal degrees of freedom through the relative motion of electron and hole. The Frenkel exciton limit is valid in the case of strong electron-hole attraction in combination with weak electron hopping between neighbouring molecules, i.e., weak charge overlap. This is usually understood to be the case in van der Waals bound molecular systems [12,116]. Molec-
3.2. Optical properties of molecular aggregates

.. aggregates belong to this class of materials. I shall begin discussions on theoretical aspects of optical properties of molecular aggregate with an outline about treatment of the simplest possible molecular aggregate: the 'physical dimer'.

3.2.1 Optical response of 'physical dimers'

If the solution is made dense, two molecules that are kept in close proximity due to electrostatic forces may become coupled. The word 'physical dimer' has been used to describe this situation in which two identical molecules are closer to each other in a particular spatial arrangement than to other like molecules but do not form a chemical bond between themselves. The transition dipoles of these molecules will interact with each other, leading to collective eigenstates. In order to understand the optical response of such a physical dimer, these collective eigenstates have to be found.

I shall start from the simple situation of two two-level molecules, which have no permanent dipoles in their ground state or in their excited states, labeled 1 and 2, respectively, with equal transition energies \( w_0 \) (setting \( \hbar = 1 \)). The transition dipoles are given by \( \mu_1 \) and \( \mu_2 \), which will be assumed equal in magnitude (\( \mu \)), but possibly different in orientation (Figure 3.10a). If the nature of the molecular electronic orbital of one molecule is not strongly affected by the presence of the other, as is appropriate for molecular systems with small charge overlap, the electronic states of the dimer can be described on a basis of the following four normalized states: \( |g \rangle \), which is the state where both molecules are in their ground state; \( |1 \rangle \), which is the state in which molecule 1 is excited and molecule 2 is in its ground state; \( |2 \rangle \), in which only molecule 2 is excited; \( |12 \rangle \) in which both molecules are excited. In the absence of intermolecular interactions, these four states are eigenstates of the pair with energies, respectively, 0, \( w_0 \), \( w_0 \) and \( 2w_0 \) (Figure 3.10b). The interactions between the transitions dipoles, however, will lead to mixing of these four states. These interactions fall into two classes. The first class is the resonant transfer interaction, it describes the transfer of the excitation from one molecule to the other and may be written
Figure 3.10: (a) Transition dipoles of the individual molecules 1 and 2 in a dimer and of the dimer eigenstates |+⟩ and |−⟩. (b) Level diagram of a homogeneous dimer before (left) and after (right) taking the transfer interaction J into account. (c) Exciton splitting in dimers of various geometries. Orientations of monomer transition dipoles are represented by short arrows. Dipole-forbidden transitions are denoted by dotted lines. See text for other symbols.

\[ H_{res} = J(|2⟩⟨1| + |1⟩⟨2|) \]  

(3.31)

Here \( J \) is known as the excitation transfer interaction, which in the point-dipole approximation is given by

\[ J = \frac{(\mu_1 \cdot \mu_2)|r_{12}|^2 - 3(\mu_1 \cdot r_{12})(\mu_2 \cdot r_{12})}{|r_{12}|^5} \]  

(3.32)

where \( r_{12} \) is the relative position vector of the two molecules. The resonant interaction mixes the degenerate states |1⟩ and |2⟩. The second class of interactions are the non resonant ones, in which either both molecules are simultaneously excited or de-excited. I will discuss resonant interaction in detail since only linear optical response of the molecular
aggregates is of my concern and two photon process, which affect both molecules involve nonlinear optical responses.

The two new eigenstates resulting from the mixing, of the singly excited states, arising from the resonant interaction are given by

\[ |\pm\rangle = \frac{|1\rangle \pm |2\rangle}{\sqrt{2}} \]  

(3.33)

with energies \( E_\pm = w_0 \pm J \). This reflects the well-known linear splitting of two degenerate states upon coupling them (see Figure 3.10(b)).

In the language of molecular aggregates, these two states are referred to as one-exciton states (or Frenkel exciton states), as they describe states in which the molecules share one excitation quantum. In the same language, the state \( |12\rangle \) is called a two-exciton state. The one-exciton states of the homogeneous dimer are \textit{delocalized}, the probability of excitation is spread evenly over both molecules. The states differ only in the relative phase of the excitation amplitude on both molecules.

In order to determine the optical response of the dimer, the total transition dipoles from the ground state to each one of the three excited states \( |+, -\rangle \), and \( |12\rangle \) have to be found. The total dipole operator is given by

\[ \mathbf{M} = \mathbf{\mu}_1 + \mathbf{\mu}_2 \]  

(3.34)

It is a simple matter to calculate the matrix elements of this operator:

\[ \langle \pm | \mathbf{M} | g \rangle = (\mu_1 \pm \mu_2)/\sqrt{2} \]  

(3.35)

from which it is seen (using \( |\mu_1| = |\mu_2| \)) that these transitions are polarized perpendicular to each other (Figure 3.10(a)). Thus, the one-exciton states give rise to two peaks in the absorption spectrum, which are separated by a frequency \( 2|J| \) and which have an intensity ratio \( I_+ / I_- = (1 + \cos \alpha)/(1 - \cos \alpha) \), with \( \alpha \) the angle between the transition dipoles \( \mu_1 \)
3.2. Optical properties of molecular aggregates

In the language of exciton theory, these two transitions are known as Davydov components and the frequency splitting between them as Davydov splitting [12, 116, 117]. In addition to these two states, a doubly excited state or two-exciton state exists, which cannot be excited from the ground state by absorption of a single photon, so it does not give rise to a linear absorption contribution.

It is useful to consider the special situation where both molecular dipoles, in addition to having equal magnitude, also have equal orientation, i.e., for translationally equivalent molecules, the transition moments are either parallel or antiparallel ($\alpha = 0^\circ$ or $180^\circ$), with the consequence that for one of these configurations, either $M_+$ or $M_- = 0$, so only one excited state of the dimer is optically dipole allowed. This situation occurs in $J$-aggregates where $\alpha = 0$. For other values of $\alpha$ both excited states have non zero transition moments, and the difference of their transition energies provides a direct measure of the magnitude of $J$ since, $|E_- - E_+| = 2|J|$. Here it should be remembered the dimer state $|+\rangle$ is of lower energy when $J < 0$. Figure 3.10(c) illustrates the dipole-allowed transitions in dimers of various geometries, where $E_0$ ($E_m$) denotes the monomer ground (excited) state energy while $E''$ ($E'$) denotes the higher (lower) level of the split excited state of the 'physical dimer'. $M''$ ($M'$) corresponds to moment for the ground $\rightarrow$ $E''$ (ground $\rightarrow$ $E'$) transition [118].

The above mentioned situation for the case of completely homogeneous physical dimer cannot be expected in practice. For an inhomogeneous physical dimer where transition frequencies of two molecules in the dimer are different, say $w_1$ and $w_2$, the Hamiltonian of the molecules coupled by the transfer interaction equation (Eqn. (3.31)), on the basis of the states $|1\rangle$ and $|2\rangle$ is given by [12]

$$H = \begin{pmatrix} w_1 & J \\ J & w_2 \end{pmatrix} = \frac{w_1 + w_2}{2} 1 + \left( \begin{array}{cc} \frac{w_1 - w_2}{2} & J \\ J & -\frac{w_1 - w_2}{2} \end{array} \right)$$

(3.36)

Diagonalization of this matrix gives the one-exciton eigenstates. It is clear from the second term in the right-hand side of Eqn. (3.36) that the nature of these eigenstates is determined

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by a competition between the energy difference \((w_1 - w_2)/2\) and the interaction \(J\). In the limit of large inhomogeneity, \(|(w_1 - w_2)/2| \gg |J|\), the interaction is not strong enough to yield appreciable mixing of the states \(|1\rangle\) and \(|2\rangle\). The excited states are localized on just one of the two molecules and, being simply the single-molecule excited states, they both have the single-molecule oscillator strength given by \(\mu^2\). The absorption spectrum of such a single dimer would exhibit two absorption peaks with position \(w_1\) and \(w_2\), respectively, and equal intensity. In the opposite limit, with \(|(w_1 - w_2)/2| \ll |J|\), the eigenstates are identical to the completely delocalized collective dimer states \(|+\rangle\) and \(|-\rangle\) as defined earlier. The energies of these states are given by

\[
E_\pm^i = \frac{w_1 + w_2}{2} \pm J
\]

The absorption spectrum for an individual dimer is in this limit given by two peaks, with average position \((w_1 + w_2)/2\) and separated by the Davydov splitting \(2|J|\), while the oscillator strengths are determined by the angle \(\alpha\) between the dipoles, as discussed earlier.

Thus far, the absorption spectrum of individual inhomogeneous dimers has been considered, but the most typical experimental situation is the absorption spectrum of an ensemble of inhomogeneous dimers. If \(\sigma\) determines the width of the transition frequency distribution it may be considered a measure of the amount of “static disorder” in the sample. In case of large disorder, \(\sigma \gg |J|\). Then most dimers will be in the large disorder limit and the ensemble spectrum is identical to the spectrum obtained from an ensemble of non-interacting molecules, exhibiting one Gaussian absorption peak (neglecting dynamic effect) of FWHM \(\sqrt{8ln2} \sigma \approx 2.35\sigma\). In the opposite case of weak disorder, \(\sigma \ll |J|\), the vast majority of the dimers will be in the weak-inhomogeneity limit, carrying delocalized one-exciton states. The absorption spectrum of the ensemble contains two Gaussian peaks which are correlated at the frequencies \(w_0 \pm |J|\), respectively, and which both have a FWHM \(2.35\sigma/\sqrt{2}\). The narrowing of the absorption peaks relative to the single-molecule
3.2. Optical properties of molecular aggregates

spectrum by a factor of $\sqrt{2}$ is called exchange narrowing [119]. Physically, it originates from the simple fact that in the weak-disorder limit, the eigenstates are delocalized and, thus, average over the individual inhomogeneous offsets of the two molecules in the dimer. If these two offsets are uncorrelated, this averaging process tends to eliminate large deviations from the overall mean value. It should be noted that the narrow line width should only be expected for the Davydov component with the lowest energy, as the higher state will tend to rapidly relax to the lower one, leading to lifetime broadening.

3.2.2 Linear Optical Properties of Linear J-aggregates

Now I consider a linear chain of $N$ identical, equidistant, polarizable, two-level (separated by energy $\varepsilon$) molecules, at positions $r_1, \ldots, r_N$, coupled to a multimode electromagnetic field of wave vector $k = |k| = \varepsilon/c$ with their transition dipoles, each of magnitude $\mu_{\text{mono}}$, all parallel to each other and making an angle $\theta$ with the local axis of the chain (see Figure 3.11). Neglecting phonons and restricting to states with at most one excitation on the chain, this system is described by the exciton Hamiltonian [120]

$$H = \sum_n \left( \langle \varepsilon \rangle + D_n \right) |n\rangle \langle n| + \sum_{n,m} J_{nm} |m\rangle \langle n|$$

(3.38)

Here $|n\rangle$ denotes the state where molecule $n (n = 1, \ldots, N)$ is excited and all other molecules are in the ground state. $\langle \varepsilon \rangle$ stands for the average molecular excitation energy.

Figure 3.11: Schematic picture of a linear aggregate of $N$ equidistant two-level molecules with parallel transition dipoles of magnitude $\mu_{\text{mono}}$. The angle between the dipoles and the chain is $\theta$. For $\theta < 54.7^\circ$, the intermolecular dipole interaction is negative and the aggregate is a J-aggregate.
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and $D_n$ is the (static) inhomogeneous offset energy of molecule $n$, reflecting the effect of disorder imposed by the surrounding host medium or diagonal disorder as mentioned in case of physical dimers. $J_{nm}$ is the transfer interaction (intermolecular interaction) between the molecules $n$ and $m$, separated by distance $r_{nm}$ given by [121],

$$J_{nm} = \frac{\mu_{nm}^2}{r_{nm}^3} [1 - 3\cos^2 \theta \cos(kr_{nm}) - \frac{\mu_{mono}^2}{r_{nm}^3} [1 - 3\cos^2 \theta \sin(kr_{nm}) - \frac{\mu_{mono}^2}{r_{nm}^3} [1 - \cos^2 \theta \cos(kr_{nm})] (3.39)$$

It should be noted that in expression (3.39), the very general restriction of the case in which the molecules are confined to a region small in comparison to the transition wavelength [122,123] is removed, and the expression takes into account the frequency shifts due to electromagnetic coupling between the molecules. This is important for the case of polymers where the molecular size is not small compared to the excitation wavelength.

For the aggregates with length $L$ small compared to the optical wavelength, such as the 'physical dimers', $kL \ll 1$, and Eqn. (3.39) reduces to [12]

$$J_{nm} = \frac{\mu_{mono}^2}{r_{nm}^3} [1 - 3\cos^2 \theta] (3.40)$$

For perfectly ordered linear chain systems ($D_n = 0$), $r_n = na$ and $d = Na$, where $a$ is the average distance between nearest neighbour molecules and $d$ is the film thickness. In one-dimensional systems, approximating the long-range dipole-dipole interaction by a nearest-neighbour one is not too bad an approximation, certainly if one is mostly interested in the essential physics; for quantitative fits to experiment, even in linear systems the long-range nature may be of importance. If I consider the resonant transfer interaction to be active only between nearest neighbours i.e., $J_{nm} = J$, for $|n - m| = 1$, $J_{nm} = 0$, otherwise, the Hamiltonian in Eqn. (3.38) can be diagonalized exactly, leading to the eigenfunctions

$$|\psi_j\rangle = \left(\frac{2}{N+1}\right)^{1/2} \sum_{n=1}^{N} \sin \left(\frac{\pi j n}{N+1}\right) |n\rangle (3.41)$$
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with the energies [12]

\[ E_j = \varepsilon + 2J \cos \left( \frac{\pi j}{N + 1} \right) \simeq \varepsilon + 2J \cos \left( \frac{\pi j}{a + 1} \right) \]  

(3.42)

Here, \( j = 1, 2, \ldots, N \) denotes the quantum number of the state. Clearly all states are delocalized standing waves of excitation on the chain, with the \( j \)-th state having \( j - 1 \) nodes. For \( N = 2 \), the above solution reduces to the state \(|\pm\rangle\) of the dimer, separated by \(2|J|\). With growing \( N \), the one-exciton band develops a width \(4|J|\), centred around the molecular frequency \(\varepsilon\). The oscillator strength between the ground state and the one-exciton \( j \) state is given by [124]

\[ \mu_{j,0} = |\langle j|M|0\rangle|^2 = \frac{1 - (-1)^j}{2} \frac{2\mu_{\text{monomer}}^2}{N + 1} \cot^2 \frac{\pi j}{2(N + 1)} \]  

(3.43)

Analysis of this result yields that oscillator strength for \( j = 1 \) state contains an overwhelming part of the total oscillator strength \(N\mu_{\text{monomer}}^2\), leading to domination of the absorption spectrum by this state. The absorption of \( J \)-aggregates occurs at the bottom of the band, giving sharp absorption peaks, that allow for a more detailed study and description. The sharp absorption band of \( J \)-aggregates is generally known as the \( J \)-band.

I shall use all these results extensively in Chapter 4 to analyse the optical absorption spectra of polystyrene film under one dimensional confinement.