MOLECULAR INTERACTIONS AND ELECTRONIC SPECTRA

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PREFACE

This book is an introduction to the mechanisms of various molecular interactions as studied mainly by molecular electronic absorption and emission spectra and partly by infrared spectra. We are concerned mainly with complex organic molecules having π-electron system whose electronic behaviors have been studied extensively.

Many fine monographs have already been published concerning the quantum theory of molecular electronic structures as well as those pertaining to the molecular electronic spectra and including molecular interactions. However, to our knowledge, there is no introductory book which summarizes all the important topics of molecular interactions such as hydrogen bonding, charge transfer, solute–solvent interactions, both in the ground and in the excited electronic states, and the energy transfer phenomena. This book is an attempt to give, from a unified viewpoint, a general and introductory interpretation for these phenomena.

Chapters 1 to 3 give elementary descriptions and summaries of the quantum theories of molecular electronic structures as well as the electronic absorption and emission spectra since the knowledge of these fundamental theories seems to be important and necessary to understand the thoretical background of molecular interaction phenomena. Chapter 4 deals with the radiationless transition caused by interactions between electrons and nuclear vibrations as well as spin–orbit interaction. The mechanisms of the radiationless transitions are being studied quite extensively at present. Chapter 5 gives a brief account of the mechanisms and experimental examples of the intermolecular electronic excitation transfer in fluid solutions and in solids.

Chapter 6 gives a systematic account of electron donor–acceptor complexes. Namely, the interpretation of the nature of the electron donor–acceptor interactions as put forth by Mulliken, the classification of the donors and acceptors, and the electronic absorption and luminescence spectra of the complexes are discussed from various viewpoints. In Chapter 7, the mechanisms of hydrogen bonding and its effect on the electronic absorption and emission spectra as well as on the infrared spectra are discussed. Chapter 7 is rather closely connected with Chapter 6 because the hydrogen bonding would be ascribed to the electron donor–acceptor interactions between the proton donor and acceptor. Throughout these chapters we paid particular attention to discussing charge transfer theory and related phenomena along with the development of theory and experiment.

Chapter 8 gives general interpretations and experimental examples of the solvent effects on the electronic absorption and fluorescence spectra. This is a topic that is difficult to omit because the mechanisms of solute-solvent interactions are essential to the understanding of the chemical and physical processes in solution. And, it is known that the experimental application of these theories to explain the solvent effect on absorption and emission spectra of organic compounds gives reliable information about molecular electronic structures in ground and excited states.

In the last chapter, we discuss the excimer formation and related processes which arise only in electronically excited states. The mechanisms of the excimer formation between two identical molecules, as well as that between different molecules, are also closely connected with the discussions in the other chapters because the main part of the binding energy in the excimers seems to be ascribable to the electronic delocalization between the partners in the excimer. In addition to this, a systematic discussion is given for the luminescence quenching reactions in solution, in relation to the excimer formation–decomposition processes. The atomistic or electronic mechanisms of the luminescence quenching processes are now being studied quite intensively. One of the important mechanisms of the luminescence quenching reactions is the intermolecular electron transfer process, which is also closely connected with the discussions given in the other chapters.

Although the experimental results for the molecular interactions of the complex organic molecules are quite complicated, we have tried to interpret the phenomena from a unified viewpoint as far as possible in order that the readers can easily understand the basic concepts for discussing various aspects of the molecular interactions. Thus, because our purpose is not to write a review article for each topic in molecular interactions, but to make a systematic interpretation of the molecular interactions on the grounds of molecular electronic structure, our selection of the references is not complete.

Because molecular interaction studies are now rapidly progressing, both theoretically and experimentally, some parts of this book may require some revision in the future. However, the most fundamental views expressed throughout this book will not in all probability change.

This book can be used as a reference book for the advanced undergraduate students or graduate students. Also, we hope that it will be of some help to research workers interested in the field of the molecular interactions and molecular electronic spectra.

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Chapter 1

ELEMENTS OF QUANTUM MECHANICS

It is necessary to use quantum mechanics for the description of the microscopic phenomena. We summarize here elementary principles of quantum mechanics and some elementary formulas which will be used in this book.

1-1. SCHRÖDINGER EQUATION

Let us consider the dynamical state of an electron moving under the influence of a potential $V(\mathbf{r})$. In quantum mechanics the dynamical state of this system is described by the wave function $\Psi(\mathbf{r}, t)$, and the observable quantities such as energies and momentums are expressed by operators which operate on the wave functions. The total energy E of the system can be expressed by using the momentum $\mathbf{p}$ which is canonically conjugate to the coordinate $\mathbf{r}$, as follows:

$$E = \mathscr{H} = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r}) \tag{1-1}$$

$\mathscr{H}$ is called the Hamiltonian of the dynamical system. We replace the momentum by the differential operators.

$$p_x \rightarrow \frac{\hbar}{i}\frac{\partial}{\partial x}, \qquad p_y \rightarrow \frac{\hbar}{i}\frac{\partial}{\partial y}, \qquad p_z \rightarrow \frac{\hbar}{i}\frac{\partial}{\partial z} \tag{1-2}$$

In general, the state of a system changes with time, and the dynamical equation of motion including this time variation is written as

$$i\hbar \frac{\partial \Psi(\mathbf{r}, t)}{\partial t} = \mathscr{H}\Psi(\mathbf{r}, t) \tag{1-3}$$

Equation (1-3) is the fundamental equation of quantum mechanics, the Schrödinger equation. In other words, in the quantum mechanical translation of the classical equation,

$$E = \mathscr{H}(\mathbf{p}, \mathbf{r}) \tag{1-4}$$

we replace the energy and momentum by the operators, according to the correspondence rule

$$E \rightarrow i\hbar\frac{\partial}{\partial t}, \qquad \mathbf{p} \rightarrow \frac{\hbar}{i}\nabla \tag{1-5}$$

where ∇ is the vector operator, $\nabla = \left(\mathbf{i}\frac{\partial}{\partial x} + \mathbf{j}\frac{\partial}{\partial y} + \mathbf{k}\frac{\partial}{\partial z}\right)$, where **i**, **j**, and **k** are unit vectors.

The generalization of this procedure to the many particle system is straightforward. The total energy of this system is

$$E = \mathscr{H}(\mathbf{r}_1 \cdots \mathbf{r}_j \cdots \mathbf{r}_n, \mathbf{p}_1 \cdots \mathbf{p}_j \cdots \mathbf{p}_n) \tag{1-6}$$

By using the correspondence rule (1-5), the Schrödinger equation may be written as

$$i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r}_1 \cdots \mathbf{r}_n, t) = \mathscr{H}\left(\mathbf{r}_1 \cdots \mathbf{r}_n, \frac{\hbar}{i}\frac{\partial}{\partial \mathbf{r}_1} \cdots \frac{\hbar}{i}\frac{\partial}{\partial \mathbf{r}_n}\right)\Psi(\mathbf{r}_1 \cdots \mathbf{r}_n, t) \tag{1-7}$$

Let us consider a complex atom with a nucleus of charge Ze and mass M, and Z electrons. The Schrödinger equation for this system may be written as

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}&\Psi(\mathbf{R}, \mathbf{r}_1 \cdots \mathbf{r}_z, t) \\ &= \left[-\frac{\hbar^2}{2M}\Delta_R - \frac{\hbar^2}{2m}\sum_{j=1}^{Z}\Delta_j - \sum_{j=1}^{Z}\frac{Ze^2}{|\mathbf{R} - \mathbf{r}_j|} + \sum_{j<k}\frac{e^2}{|\mathbf{r}_j - \mathbf{r}_k|}\right] \\ &\quad \cdot \Psi(\mathbf{R}, \mathbf{r}_1 \cdots \mathbf{r}_z, t) \end{aligned} \tag{1-8}$$

where **R** is the nuclear coordinate, **r** is the electronic coordinate, and Δ is the Laplacian operator div · grad = $(\nabla \cdot \nabla)$; i.e.,

$$\Delta_R = \frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2} + \frac{\partial^2}{\partial Z^2}. \qquad \Delta_j = \frac{\partial^2}{\partial x_j^2} + \frac{\partial^2}{\partial y_j^2} + \frac{\partial^2}{\partial z_j^2}$$

For a complex molecule, the equation becomes

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} &\Psi(\mathbf{R}_1 \cdots \mathbf{R}_N, \mathbf{r}_1 \cdots \mathbf{r}_n, t) \\ &= \left[-\sum_{i=1}^{N} \frac{\hbar^2}{2M_i} \Delta_i - \frac{\hbar^2}{2m} \sum_{j=1}^{n} \Delta_j - \sum_{i=1}^{N} \sum_{j=1}^{n} \frac{Z_i e^2}{|\mathbf{R}_i - \mathbf{r}_j|} \right. \\ &\quad \left. + \sum_{i<l} \frac{Z_i \cdot Z_l}{|\mathbf{R}_i - \mathbf{R}_l|} + \sum_{j<h} \frac{e^2}{|\mathbf{r}_j - \mathbf{r}_h|} \right] \\ &\quad \cdot \Psi(\mathbf{R}_1 \cdots \mathbf{R}_N, \mathbf{r}_1 \cdots \mathbf{r}_n, t) \end{aligned} \tag{1-9}$$

where

$$\Delta_i = \frac{\partial^2}{\partial X_i^2} + \frac{\partial^2}{\partial Y_i^2} + \frac{\partial^2}{\partial Z_i^2}$$

When the Hamiltonian $\mathscr{H}$ does not explicitly depend upon the time (i.e., the system is conservative), we can get a solution representing a state of well-defined energy $E = \hbar\omega$, where ω is the angular frequency of the wave Ψ. This relation between the energy of the system and the angular frequency of the wave is the fundamental postulate of the matter wave, which has the form $\exp[i(\mathbf{Kr} - \omega t)]$. **K** is the wave vector of the matter wave. Therefore, we can assume that

$$\Psi(\mathbf{r}, t) = \Psi(\mathbf{r})e^{-i\omega t} = \Psi(\mathbf{r})e^{-iEt/\hbar} \tag{1-10}$$

Substituting (1-10) into Eq. (1-3), we get

$$\mathscr{H}\Psi(\mathbf{r}) = E\Psi(\mathbf{r}) \tag{1-11}$$

This is the time-independent Schrödinger equation. When Eqs. (1-10) and (1-11) hold, the system is said to be in a stationary state. When we are considering the electronic "energy levels" of atoms and molecules, the relevant wave functions are those of stationary states.

1-2. Physical Quantities and Hermitean Operators

If a dynamical variable F represents a physical quantity, it is a real function of the **r** and **p** because the results of measurements of F are real quantities. In other words, the operator F must be Hermitean. If F is Hermitean, Eq. (1-12) holds, where Φ_m and Φ_n are any two functions of the function space in which the operator F acts:

$$F_{mn} = \int \Phi_m^* F \Phi_n \, dv = \int \Phi_n^* F^* \Phi_m \, dv = F_{nm}^* \tag{1-12}$$

We can show easily that the Hamiltonian and momentums are Hermitean. Note that

$$H_{mn} \cdot H_{nm} = |H_{mn}|^2, \qquad \text{where } H_{mn} = \int \Phi_m^* \mathscr{H} \Phi_n \, dv$$

It is well known in quantum mechanics that one cannot attribute a precise position to a particle because of the spatial extension of the associated wave function $\Psi(\mathbf{r})$. We can only define the probability of finding the particle in a given region of space when we make a measurement of position. The probability of finding a particle in a small volume $dv = dx\,dy\,dz$ at $\mathbf{r}(x, y, z)$ may be given by

$$P(\mathbf{r})\, dv = |\Psi(\mathbf{r})|^2 \, dv \tag{1-13}$$

The integration of Eq. (1-13) over whole space must be unity, leading to the normalization of Ψ:

$$N \equiv \int |\Psi(\mathbf{r})|^2 \, dv = 1 \tag{1-14}$$

In the case of a many-particle system, the probability of finding the first particle in $dv(1)$, the second one in $dv(2)$, and the nth one in $dv(n)$ may be written as

$$\begin{aligned} P(\mathbf{r}_1, \mathbf{r}_2 \cdots r_n)\, dv(1) \cdots dv(n) &= |\Psi(\mathbf{r}_1 \cdots \mathbf{r}_n)|^2 \, dv(1) \cdots dv(n) \\ &= |\Psi(\mathbf{r}_1 \cdots \mathbf{r}_n)|^2 \, dv \end{aligned} \tag{1-15}$$

The normalization condition is

$$N \equiv \int |\Psi(\mathbf{r}_1 \cdots \mathbf{r}_n)|^2 \, dv = 1 \tag{1-16}$$

We can easily show that the integral N in Eqs. (1-14) and (1-16) is independent of time (i.e., $(dN/dt) = 0$) from the Hermitean property of the Hamiltonian.

Let us consider the eigenvalue equation

$$F\Phi_m = a_m \Phi_m \qquad (m = 1, 2, \ldots) \tag{1-17}$$

Equation (1-17) means that when the observed value of F is a_m, the system is in the state Φ_m, a_m is the mth eigenvalue, and Φ_m is the mth eigenfunction of F.

In general, we can expand an arbitrary function Ψ (which is not an eigenfunction of F) in terms of Φ_m:

$$\Psi = \sum_m c_m \Phi_m \tag{1-18}$$

In this case the probability of finding the system in state Φ_n may be given by

$$P_n = \frac{|c_n|^2}{\sum_m |c_m|^2} \tag{1-19}$$

Now, if a_n and a_m are different eigenvalues of the Hermitean operator F, the corresponding eigenfunctions Φ_n and Φ_m are orthogonal to each other. This is easily proved as follows: Because

$$\int [F\Phi_m]^*\Phi_n \, dv = a_m \int \Phi_m^* \Phi_n \, dv,$$

$$\int \Phi_m^* F\Phi_n \, dv = a_n \int \Phi_m^* \Phi_n \, dv \qquad \text{and} \qquad \int [F\Phi_m]^*\Phi_n \, dv = \int \Phi_m^* F\Phi_n \, dv,$$

$$(a_n - a_m) \int \Phi_m^* \Phi_n \, dv = 0$$

Therefore $$\int \Phi_m^* \Phi_n \, dv = 0$$

In some cases, a may be a degenerate eigenvalue; i.e., there may be n eigenfunctions $\Phi^{(1)}, \Phi^{(2)} \cdots \Phi^{(n)}$ for the same a value ($n \geq 2$). From the viewpoint of the preceding arguments, the degenerate eigenfunctions are not necessarily orthogonal to each other. However, we can form appropriate linear combinations of these functions to transform them to an orthogonal set of function $\varphi^{(1)}, \varphi^{(2)} \cdots \varphi^{(n)}$ as follows: First we take $\varphi^{(1)} = \Phi^{(1)}$. We define $\varphi^{(2)}$ by

$$\varphi^{(2)} = c_1\Phi^{(1)} + c_2\Phi^{(2)} \tag{1-20}$$

and orthogonalize $\varphi^{(2)}$ to $\varphi^{(1)}$:

$$\int \varphi^{(1)*}\varphi^{(2)} \, dv = c_1 \int \Phi^{(1)*}\Phi^{(1)} \, dv + c_2 \int \Phi^{(1)*}\Phi^{(2)} \, dv = 0$$

We assume here that the $\Phi^{(i)}$ are normalized; then

$$\int \varphi^{(1)*}\varphi^{(2)} \, dv = c_1 + c_2 \int \Phi^{(1)*}\Phi^{(2)} \, dv = 0 \tag{1-21}$$

From (1-21) the ratio $r = c_1/c_2$ can be determined. With this ratio r and the normalization condition for $\varphi^{(2)}$, we can determine the coefficients c_1 and c_2. Similarly, we put

$$\varphi^{(3)} = d_1\Phi^{(1)} + d_2\Phi^{(2)} + d_3\Phi^{(3)} \tag{1-22}$$

and determine the coefficients d_1, d_2, and d_3 in such a way that $\varphi^{(3)}$ is normalized and orthogonal to $\varphi^{(1)}$ and $\varphi^{(2)}$. We repeat this procedure until we get $\varphi^{(n)}$.

Summarizing the argument above with regard to the orthonormality of the eigenfunctions, for all eigenfunctions of an operator F we may write

$$\int \Phi_m^* \Phi_n \, dv = \delta_{mn} \tag{1-23}$$

where δ_{mn} is the Kronecker delta.

Now the probability that the system has the eigenvalue a_n, as given in Eq. (1-19), may be written, owing to the orthonormality of functions, as

$$P_n = \left| \int \Phi_n^* \Psi \, dv \right|^2 = c_n^* c_n = |c_n|^2 \qquad \text{(1-24}$$

assuming that Ψ is normalized. The (statistical) mean value of the quantity F when the system is in state Ψ may be given by

$$\langle F \rangle = \sum_n a_n P_n = \sum_n a_n c_n^* c_n = \sum_n a_n |c_n|^2 \tag{1-25}$$

In general, the mean value of F is defined by

$$\langle F \rangle = \int \Psi^* F \Psi \, dv \tag{1-26}$$

We can see easily that Eq. (1-26) reduces to Eq. (1-25) as follows:

$$\begin{aligned} \int \Psi^* F \Psi \, dv &= \int \Psi^* F \left(\sum c_n \Phi_n \right) dv \\ &= \sum_n a_n c_n \int \Psi^* \Phi_n \, dv = \sum_n a_n c_n c_n^* = \sum_n a_n |c_n|^2 \end{aligned}$$

1-3. Commutators and Uncertainty Relations

For the product of momentum and the conjugate coordinate ($p_x \cdot x$, for example), we have the following relation:

$$\begin{aligned} p_x x \Psi &= -i\hbar \frac{\partial}{\partial x} x \Psi = -i\hbar\Psi - x i\hbar \frac{\partial}{\partial x} \Psi \\ &= -i\hbar\Psi + x p_x \Psi \qquad p_x x - x p_x = -i\hbar \end{aligned} \tag{1-27}$$