Shu Hotta

Mathematical Physical Chemistry

Practical and Intuitive Methodology

Second Edition

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To my wife Kazue
and
To the memory of Roro

Preface to the Second Edition

This book is the second edition of *Mathematical Physical Chemistry*. Mathematics is a common language of natural science including physics, chemistry, and biology. Although the words mathematical physics and physical chemistry (or chemical physics) are commonly used, mathematical physical chemistry sounds rather uncommon. Therefore, it might well be reworded as the mathematical physics for chemists. The book title could have been, for instance, "*The Mathematics of Physics and Chemistry*" accordingly, in tribute to the famous book that was written three-quarters of a century ago by H. Margenau and G. M. Murphy. Yet, the word mathematical physical chemistry is expected to be granted citizenship, considering that chemistry and related interdisciplinary fields such as materials science and molecular science are becoming increasingly mathematical.

The main concept and main theme remain unchanged, but this book's second edition contains the theory of analytic functions and the theory of continuous groups. Both the theories are counted as one of the most elegant theories of mathematics. The mathematics of these topics is of a somewhat advanced level and something like a "sufficient condition" for chemists, whereas that of the first edition may be a prerequisite (or a necessary condition) for them. Therefore, chemists (or may be physicists as well) can creatively use the two editions. In association with these major additions to the second edition, the author has disposed the mathematical topics (the theory of analytic functions, Green's functions, exponential functions of matrices, and the theory of continuous groups) at the last chapter of individual parts (Part I through Part IV).

At the same time, the author has also made several specific revisions including the introductory discussion on the perturbation method and variational method, both of which can be effectively used for gaining approximate solutions of various quantum-mechanical problems. As another topic, the author has presented the recent progress on organic lasers. This topic is expected to help develop high-performance light-emitting devices, one of the important fields of materials science. As in the case of the first edition, readers benefit from going freely back and forth across the whole topics of this book.

Once again, the author wishes to thank many students for valuable discussions and Dr. Shin'ichi Koizumi at Springer for giving him an opportunity to write this book.

Takatsuki, Japan Shu Hotta
October 2019

Preface to the First Edition

The contents of this book are based upon manuscripts prepared for both undergraduate courses of Kyoto Institute of Technology by the author entitled "Polymer Nanomaterials Engineering" and "Photonics Physical Chemistry" and a master's course lecture of Kyoto Institute of Technology by the author entitled "Solid-State Polymers Engineering."

This book is intended for graduate and undergraduate students, especially those who major in chemistry and, at the same time, wish to study mathematical physics. Readers are supposed to have a basic knowledge of analysis and linear algebra. However, they are not supposed to be familiar with the theory of analytic functions (i.e., complex analysis), even though it is desirable to have relevant knowledge about it.

At the beginning, mathematical physics looks daunting to chemists, as used to be the case with myself as a chemist. The book introduces the basic concepts of mathematical physics to chemists. Unlike other books related to mathematical physics, this book makes a reasonable selection of material so that students majoring in chemistry can readily understand the contents in spontaneity. In particular, we stress the importance of practical and intuitive methodology. We also expect engineers and physicists to benefit from reading this book.

In Part I and Part II, the book describes quantum mechanics and electromagnetism. Relevance between the two is well considered. Although quantum mechanics covers the broad field of modern physics, in Part I we focus on a harmonic oscillator and a hydrogen (like) atom. This is because we can study and deal with many of fundamental concepts of quantum mechanics within these restricted topics. Moreover, knowledge acquired from the study of the topics can readily be extended to practical investigation of, e.g., electronic states and vibration (or vibronic) states of molecular systems. We describe these topics by both analytic method (that uses differential equations) and operator approach (using matrix calculations). We believe that the basic concepts of quantum mechanics can be best understood by contrasting the analytical and algebraic approaches. For this reason, we give matrix representations of physical quantities whenever possible. Examples include energy

eigenvalues of a quantum-mechanical harmonic oscillator and angular momenta of a hydrogen-like atom. At the same time, these two physical systems supply us with a good opportunity to study classical polynomials, e.g., Hermite polynomials, (associated) Legendre polynomials, Laguerre polynomials, Gegenbauer polynomials, and special functions, more generally. These topics constitute one of the important branches of mathematical physics. One of the basic concepts of quantum mechanics is that a physical quantity is represented by a Hermitian operator or matrix. In this respect, the algebraic approach gives a good opportunity to get familiar with this concept. We present tangible examples for this. We also emphasize the importance of the notion of Hermiticity of a differential operator. We often encounter a unitary operator or unitary transformation alongside the notion of Hermitian operators. We show several examples of unitary operators in connection with transformation of vectors and coordinates.

Part II describes Maxwell equations and their applications to various phenomena of electromagnetic waves. These include their propagation, reflection, and transmission in dielectric media. We restrict ourselves to treating those phenomena in dielectrics without charge. Yet, we cover a wide range of important topics. In particular, when two (or more) dielectrics are in contact with each other at a plane interface, reflection and transmission of light are characterized by various important parameters such as reflection and transmission coefficients, Brewster angles, and critical angles. We should have a proper understanding not only from the point of view of basic study but also to make use of relevant knowledge in optical device applications such as a waveguide. In contrast to a concept of electromagnetic waves, light possesses a characteristic of light quanta. We present semiclassical and statistical approaches to blackbody radiation occurring in a simplified system in relation to Part I. The physical processes are well characterized by a notion of two-level atoms. In this context, we outline the dipole radiation within the framework of the classical theory. We briefly describe how the optical processes occurring in a confined dielectric medium are related to a laser that is of great importance in fundamental science and its applications. Many of basic equations of physics are descried as second-order linear differential equations (SOLDEs). Different methods were developed and proposed to seek their solutions. One of the most important methods is that of Green's functions. We present the introductory theory of Green's functions accordingly. In this connection, we rethink the Hermiticity of a differential operator.

In Part III and Part IV, we describe algebraic structures of mathematical physics. Their understanding is useful to studies of quantum mechanics and electromagnetism whose topics are presented in Part I and Part II. Part III deals with theories of linear vector spaces. We focus on the discussion of vectors and their transformations in finite-dimensional vector spaces. Generally, we consider the vector transformations among the vector spaces of different dimensions. In this book, however, we restrict ourselves to the case of the transformation between the vector spaces of same dimension, i.e., endomorphism of the space ($V^n \to V^n$). This is not only because this is most often the case with many of physical applications, but because the relevant operator is represented by a square matrix. Canonical forms of square matrices hold

an important position in algebra. These include a triangle matrix, diagonalizable matrix as well as a nilpotent matrix and idempotent matrix. The most general form will be Jordan canonical form. We present its essential parts in detail taking a tangible example. Next to the general discussion, we deal with an inner product space. Once an inner product is defined between any couple of vectors, the vector space is given a fruitful structure. An example is a norm (i.e., "length") of a vector. Also, we gain a clear relationship between Part III and Part I. We define various operators or matrices that are important in physical applications. Examples include normal operators (or matrices) such as Hermitian operators, projection operators, and unitary operators. Once again, we emphasize the importance of Hermitian operators. In particular, two commutable Hermitian matrices share simultaneous eigenvectors (or eigenstates) and, in this respect, such two matrices occupy a special position in quantum mechanics.

Finally, Part IV describes the essence of group theory and its chemical applications. Group theory has a broad range of applications in solid-state physics, solid-state chemistry, molecular science, etc. Nonetheless, the knowledge of group theory does not seem to have fully prevailed among chemists. We can discover an adequate reason for this in a preface to the first edition of *Chemical Applications of Group Theory* written by F. A. Cotton. It might well be natural that definition and statement of abstract algebra, especially group theory, sound somewhat pretentious for chemists, even though the definition of group is quite simple. Therefore, we present various examples for readers to get used to notions of group theory. The notion of mapping is important as in the case of the linear vector spaces. Aside from being additive with calculation for a vector space and multiplicative for a group, the fundamentals of calculation regulations are pretty much the same regarding the vector space and group. We describe the characteristics of symmetry groups in detail partly because related knowledge is useful for molecular orbital (MO) calculations that are presented in the last section of the book. Representation theory is probably one of the most daunting notions for chemists. Practically, however, the representation is just homomorphism that corresponds to a linear transformation in a vector space. In this context, the representation is merely denoted by a number or a matrix. Basis functions of representation correspond to basis vectors in a vector space. Grand orthogonality theorem (GOT) is a "nursery bed" of the representation theory. Therefore, readers are encouraged to understand its essence apart from the rigorous proof of the theorem. In conjunction with Part III, we present a variety of projection operators. These are very useful to practical applications in, e.g., quantum mechanics and molecular science. The final parts of the book are devoted to applications of group theory to problems of physical chemistry, especially those of quantum chemistry, more specifically molecular orbital calculations. We see how symmetry consideration, particularly the use of projection operators, saves us a lot of labor. Examples include aromatic hydrocarbons and methane.

The previous sections sum up the contents of this book. Readers may start with any part and go freely back and forth. This is because contents of many parts are interrelated. For example, we emphasize the importance of Hermiticity of differential operators and matrices. Also projection operators and nilpotent matrices appear

in many parts along with their tangible applications to individual topics. Hence, readers are recommended to carefully examine and compare the related contents throughout the book. We believe that readers, especially chemists, benefit from the writing style of this book, since it is suited to chemists who are good at intuitive understanding.

The author would like to thank many students for their valuable suggestions and discussions at the lectures. The author also wishes to thank many students for valuable discussions and Dr. Shin'ichi Koizumi at Springer for giving him an opportunity to write this book.

Kyoto, Japan Shu Hotta
October 2017

Contents

Part IV Group Theory and Its Chemical Applications

Part I
Quantum Mechanics

Quantum mechanics is clearly distinguished from classical physics whose major pillars are Newtonian mechanics and electromagnetism established by Maxwell. Quantum mechanics was first established as a theory of atomic physics that handled microscopic world. Later on, quantum mechanics was applied to macroscopic world, i.e., cosmos. A question on how exactly quantum mechanics describes the natural world and on how far the theory can go remains yet problematic and is in dispute to thisday.

Such an ultimate question is irrelevant to this monograph. Our major aim is to study a standard approach to applying Schrödinger equation to selected topics. The topics include a particle confined within a potential well, a harmonic oscillator, and a hydrogen-like atoms. Our major task rests on solving eigenvalue problems of these topics. To this end, we describe both an analytical method and algebraic (oroperator) method. Focusing on these topics, we will be able to acquire various methods to tackle a wide range of quantum-mechanical problems. These problems are usually posed as an analytical equation (i.e., differential equation) or an algebraic equation. A Hamiltonian is constructed analytically or algebraically accordingly. Besides Hamiltonian, physical quantities are expressed as a differential operator or a matrix operator. In both analytical and algebraic approaches, Hermitian property (orHermiticity) of an operator and matrix is of crucial importance. This feature will, therefore, be highlighted not only in this part but also throughout this book along with a unitary operator and matrix.

Optical transition and associated selection rules are dealt with in relation to the above topics. Those subjects are closely related to electromagnetic phenomena that are considered in PartII.

Unlike the eigenvalue problems of the abovementioned topics, it is difficult to get exact analytical solutions in most cases of quantum-mechanical problems. For this reason, we need appropriate methods to obtain approximate solutions with respect to various problems including the eigenvalue problems. In this context, we deal with approximation techniques of a perturbation method and variational method.

In the last part, we study the theory of analytic functions, one of the most elegant theories of mathematics. This approach not only helps cultivate a broad view of pure mathematics, but also leads to the acquisition of practical methodology. The last part deals with the introductory set theory and topology aswell.

Chapter 1
Schrödinger Equation and Its Application

Quantum mechanics is an indispensable research tool of modern natural science that covers cosmology, atomic physics, molecular science, materials science, and so forth. The basic concept underlying quantum mechanics rests upon Schrödinger equation. The Schrödinger equation is described as a second-order linear differential equation (SOLDE). The equation is analytically solved accordingly. Alternatively, equations of the quantum mechanics are often described in terms of operators and matrices and physical quantities are represented by those operators and matrices. Normally, they are noncommutative. In particular, the quantum-mechanical formalism requires the canonical commutation relation between position and momentum operators. One of great characteristics of the quantum mechanics is that physical quantities must be Hermitian. This aspect is deeply related to the requirement that these quantities should be described by real numbers. We deal with the Hermiticity from both an analytical point of view (or coordinate representation) relevant to the differential equations and an algebraic viewpoint (or matrix representation) associated with the operators and matrices. Including these topics, we briefly survey the origin of Schrödinger equation and consider its implications. To get acquainted with the quantum-mechanical formalism, we deal with simple examples of the Schrödinger equation.

1.1 Early-Stage Quantum Theory

The Schrödinger equation is a direct consequence of discovery of quanta. It stemmed from the hypothesis of energy quanta propounded by Max Planck (1900). This hypothesis was further followed by photon (light quantum) hypothesis propounded by Albert Einstein (1905). He claimed that light is an aggregation of light quanta and that individual quanta carry an energy E expressed as Planck constant h multiplied by frequency of light ν, i.e.,

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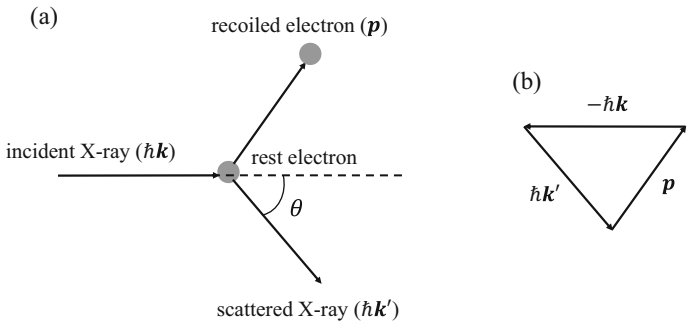

Fig. 1.1 Scattering of an X-ray beam by an electron. (**a**) θ denotes a scattering angle of the X-ray beam. (**b**) Conservation of momentum

$$E = h\nu = \hbar\omega, \tag{1.1}$$

where $\hbar \equiv h/2\pi$ and $\omega = 2\pi\nu$. The quantity ω is called angular frequency with ν being frequency. The quantity $\hbar$ is said to be a reduced Planck constant.

Also Einstein (1917) concluded that momentum of light quantum p is identical to the energy of light quantum divided by light velocity in vacuum c. That is, we have

$$p = E/c = \hbar\omega/c = \hbar k, \tag{1.2}$$

where $k \equiv 2\pi/\lambda$ (λ is wavelength of light in vacuum) and k is called wavenumber. Using vector notation, we have

$$\boldsymbol{p} = \hbar\boldsymbol{k}, \tag{1.3}$$

where $\boldsymbol{k} \equiv \frac{2\pi}{\lambda}\boldsymbol{n}$ ($\boldsymbol{n}$: a unit vector in the direction of propagation of light) is said to be a wavenumber vector.

Meanwhile, Arthur Compton (1923) conducted various experiments where he investigated how an incident X-ray beam was scattered by matter (e.g., graphite, copper). As a result, Compton found out a systematical redshift in X-ray wavelengths as a function of scattering angles of the X-ray beam (Compton effect). Moreover he found that the shift in wavelengths depended only on the scattering angle regardless of quality of material of a scatterer. The results can be summarized in a simple equation described as

$$\Delta\lambda = \frac{h}{m_{\mathrm{e}}c}(1 - \cos\theta), \tag{1.4}$$

where $\Delta\lambda$ denotes a shift in wavelength of the scattered beam; m_{e} is a rest mass of an electron; θ is a scattering angle of the X-ray beam (see Fig. 1.1). A quantity $\frac{h}{m_{\mathrm{e}}c}$ has a dimension of length and denoted by λ_{e}. That is,

$$\lambda_e \equiv h/m_e c. \tag{1.5}$$

In other words, λ_e is equal to the maximum shift in the wavelength of the scattered beam; this shift is obtained when $\theta = \pi/2$. The quantity λ_e is called an electron Compton wavelength and has an approximate value of 2.426×10^{-12} [m].

Let us derive (1.4) on the basis of conservation of energy and momentum. To this end, in Fig. 1.1 we assume that an electron is originally at rest. An X-ray beam is incident to the electron. Then the X-ray is scattered and the electron recoils as shown. The energy conservation reads as

$$\hbar\omega + m_e c^2 = \hbar\omega' + \sqrt{p^2c^2 + {m_e}^2c^4}, \tag{1.6}$$

where ω and ω' are initial and final angular frequencies of the X-ray; the second term of RHS is an energy of the electron in which p is a magnitude of momentum after recoil. Meanwhile, conservation of the momentum as a vector quantity reads as

$$\hbar\boldsymbol{k} = \hbar\boldsymbol{k}' + \boldsymbol{p}, \tag{1.7}$$

where $\boldsymbol{k}$ and $\boldsymbol{k}'$ are wavenumber vectors of the X-ray before and after being scattered; $\boldsymbol{p}$ is a momentum of the electron after recoil. Note that an initial momentum of the electron is zero since the electron is originally at rest. Here $\boldsymbol{p}$ is defined as

$$\boldsymbol{p} \equiv m\boldsymbol{u}, \tag{1.8}$$

where $\boldsymbol{u}$ is a velocity of an electron and m is given by [1].

$$m = m_e/\sqrt{1 - |\boldsymbol{u}|^2/c^2}. \tag{1.9}$$

Figure 1.1 shows that $-\hbar\boldsymbol{k}$, $\hbar\boldsymbol{k}'$, and $\boldsymbol{p}$ form a closed triangle.

From (1.6), we have

$$\left[m_e c^2 + \hbar(\omega - \omega')\right]^2 = p^2c^2 + {m_e}^2c^4. \tag{1.10}$$

Hence, we get

$$2m_e c^2\hbar(\omega - \omega') + \hbar^2(\omega - \omega')^2 = p^2c^2. \tag{1.11}$$

From (1.7), we have

$$\begin{aligned}\boldsymbol{p}^2 = \hbar^2(\boldsymbol{k} - \boldsymbol{k}')^2 &= \hbar^2\left(k^2 + k'^2 - 2kk'\cos\theta\right) \\ &= \frac{\hbar^2}{c^2}\left(\omega^2 + \omega'^2 - 2\omega\omega'\cos\theta\right),\end{aligned} \tag{1.12}$$

where we used the relations $\omega = ck$ and $\omega' = ck'$ with the third equality. Therefore, we get

$$p^2c^2 = \hbar^2\Big(\omega^2 + \omega'^2 - 2\omega\omega'\cos\theta\Big). \tag{1.13}$$

From (1.11) and (1.13), we have

$$2m_ec^2\hbar(\omega - \omega') + \hbar^2(\omega - \omega')^2 = \hbar^2\Big(\omega^2 + \omega'^2 - 2\omega\omega'\cos\theta\Big). \tag{1.14}$$

Equation (1.14) is simplified to the following:

$$2m_ec^2\hbar(\omega - \omega') - 2\hbar^2\omega\omega' = -2\hbar^2\omega\omega'\cos\theta.$$

That is,

$$m_ec^2(\omega - \omega') = \hbar\omega\omega'(1 - \cos\theta). \tag{1.15}$$

Thus, we get

$$\frac{\omega - \omega'}{\omega\omega'} = \frac{1}{\omega'} - \frac{1}{\omega} = \frac{1}{2\pi c}(\lambda' - \lambda) = \frac{\hbar}{m_ec^2}(1 - \cos\theta), \tag{1.16}$$

where λ and λ' are wavelengths of the initial and final X-ray beams, respectively. Since $\lambda' - \lambda = \Delta\lambda$, we have (1.4) from (1.16) accordingly.

We have to mention another important person, Louis-Victor de Broglie (1924) in the development of quantum mechanics. Encouraged by the success of Einstein and Compton, he propounded the concept of matter wave, which was referred to as the de Broglie wave afterward. Namely, de Broglie reversed the relationship of (1.1) and (1.2) such that

$$\omega = E/\hbar, \tag{1.17}$$

and

$$k = \frac{p}{\hbar} \qquad \text{or} \qquad \lambda = h/p, \tag{1.18}$$

where p equals $|\boldsymbol{p}|$ and λ is a wavelength of a corpuscular beam. This is said to be the de Broglie wavelength. In (1.18), de Broglie thought that a particle carrying an energy E and momentum p is accompanied by a wave that is characterized by an angular frequency ω and wavenumber k (or a wavelength $\lambda = 2\pi/k$). Equation (1.18) implies that if we are able to determine the wavelength of the corpuscular beam experimentally, we can decide a magnitude of momentum accordingly.

In turn, from squares of both sides of (1.8) and (1.9) we get

$$u = \frac{p}{m_e\sqrt{1 + (p/m_e c)^2}}. \tag{1.19}$$

This relation represents a velocity of particles of the corpuscular beam. If we are dealing with an electron beam, (1.19) gives the velocity of the electron beam. As a nonrelativistic approximation (i.e., $p/m_e c \ll 1$), we have

$$p \approx m_e u.$$

We used a relativistic relation in the second term of RHS of (1.6), where an energy of an electron E_e is expressed by

$$E_e = \sqrt{p^2c^2 + {m_e}^2c^4}. \tag{1.20}$$

In the meantime, deleting u^2 from (1.8) and (1.9) we have

$$mc^2 = \sqrt{p^2c^2 + {m_e}^2c^4}.$$

Namely, we get [1].

$$E_e = mc^2. \tag{1.21}$$

The relation (1.21) is due to Einstein (1905, 1907) and is said to be the equivalence theorem of mass and energy.

If an electron is accompanied by a matter wave, that wave should be propagated with a certain phase velocity v_p and a group velocity v_g. Thus, using (1.17) and (1.18) we have

$$\begin{aligned} v_p &= \omega/k = E_e/p = \sqrt{p^2c^2 + {m_e}^2c^4}/p > c, \\ v_g &= \partial\omega/\partial k = \partial E_e/\partial p = c^2 p/\sqrt{p^2c^2 + {m_e}^2c^4} < c, \\ v_p v_g &= c^2. \end{aligned} \tag{1.22}$$

Notice that in the above expressions, we replaced E of (1.17) with E_e of (1.20). The group velocity is thought to be a velocity of a wave packet and, hence, a propagation velocity of a matter wave should be identical to v_g. Thus, v_g is considered as a particle velocity as well. In fact, v_g given by (1.22) is identical to u expressed in (1.19). Therefore, a particle velocity must not exceed c. As for photons (or light quanta), $v_p = v_g = c$ and, hence, once again we get $v_p v_g = c^2$. We will encounter the last relation of (1.22) in Part II as well.

The above discussion is a brief historical outlook of early-stage quantum theory before Erwin Schrödinger (1926) propounded his equation.

1.2 Schrödinger Equation

First we introduce a wave equation expressed by

$$\nabla^2 \psi = \frac{1}{v^2} \frac{\partial^2 \psi}{\partial t^2}, \tag{1.23}$$

where ψ is an arbitrary function of a physical quantity relevant to propagation of a wave; v is a phase velocity of wave; ∇^2 called Laplacian is defined below

$$\nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}. \tag{1.24}$$

One of special solutions for (1.24) called a plane wave is well studied and expressed as

$$\psi = \psi_0 e^{i(\boldsymbol{k} \cdot \boldsymbol{x} - \omega t)}. \tag{1.25}$$

In (1.25), $\boldsymbol{x}$ denotes a position vector of a three-dimensional Cartesian coordinate and is described as

$$\boldsymbol{x} = (\boldsymbol{e}_1 \ \boldsymbol{e}_2 \ \boldsymbol{e}_3) \begin{pmatrix} x \\ y \\ z \end{pmatrix}, \tag{1.26}$$

where $\boldsymbol{e}_1$, $\boldsymbol{e}_2$, and $\boldsymbol{e}_3$ denote basis vectors of an orthonormal base pointing to positive directions of x-, y-, and z-axes. Here we make it a rule to represent basis vectors by a *row vector* and represent a coordinate or a component of a vector by a *column vector*; see Sect. 9.1.

The other way around, now we wish to seek a basic equation whose solution is described as (1.25). Taking account of (1.1)–(1.3) as well as (1.17) and (1.18), we rewrite (1.25) as

$$\psi = \psi_0 e^{i\left(\frac{\boldsymbol{p}}{\hbar} \cdot \boldsymbol{x} - \frac{E}{\hbar} t\right)}, \tag{1.27}$$

where we redefine $\boldsymbol{p} = (\boldsymbol{e}_1 \ \boldsymbol{e}_2 \ \boldsymbol{e}_3) \begin{pmatrix} p_x \\ p_y \\ p_z \end{pmatrix}$ and E as quantities associated with those of matter (electron) wave. Taking partial differentiation of (1.27) with respect to x, we obtain

$$\frac{\partial \psi}{\partial x} = \frac{i}{\hbar} p_x \psi_0 e^{i\left(\frac{\boldsymbol{p}}{\hbar}\cdot \boldsymbol{x} - \frac{E}{\hbar}t\right)} = \frac{i}{\hbar} p_x \psi. \tag{1.28}$$

Rewriting (1.28), we have

$$\frac{\hbar}{i}\frac{\partial \psi}{\partial x} = p_x \psi. \tag{1.29}$$

Similarly we have

$$\frac{\hbar}{i}\frac{\partial \psi}{\partial y} = p_y \psi \quad \text{and} \quad \frac{\hbar}{i}\frac{\partial \psi}{\partial z} = p_z \psi. \tag{1.30}$$

Comparing both sides of (1.29), we notice that we may relate a differential operator $\frac{\hbar}{i}\frac{\partial}{\partial x}$ to p_x. From (1.30), similar relationship holds with the y and z components. That is, we have the following relations:

$$\frac{\hbar}{i}\frac{\partial}{\partial x} \leftrightarrow p_x, \quad \frac{\hbar}{i}\frac{\partial}{\partial y} \leftrightarrow p_y, \quad \frac{\hbar}{i}\frac{\partial}{\partial z} \leftrightarrow p_z. \tag{1.31}$$

Taking partial differentiation of (1.28) once more,

$$\frac{\partial^2 \psi}{\partial x^2} = \left(\frac{i}{\hbar} p_x\right)^2 \psi_0 e^{i\left(\frac{\boldsymbol{p}}{\hbar}\cdot \boldsymbol{x} - \frac{E}{\hbar}t\right)} = -\frac{1}{\hbar^2} p_x^2 \psi. \tag{1.32}$$

Hence,

$$-\hbar^2 \frac{\partial^2 \psi}{\partial x^2} = p_x^2 \psi. \tag{1.33}$$

Similarly we have

$$-\hbar^2 \frac{\partial^2 \psi}{\partial y^2} = p_y^2 \psi \quad \text{and} \quad -\hbar^2 \frac{\partial^2 \psi}{\partial z^2} = p_z^2 \psi. \tag{1.34}$$

As in the above cases, we have

$$-\hbar^2 \frac{\partial^2}{\partial x^2} \leftrightarrow p_x^2, \quad -\hbar^2 \frac{\partial^2}{\partial y^2} \leftrightarrow p_y^2, \quad -\hbar^2 \frac{\partial^2}{\partial z^2} \leftrightarrow p_z^2. \tag{1.35}$$

Summing both sides of (1.33) and (1.34) and then dividing by $2m$, we have

$$-\frac{\hbar^2}{2m}\nabla^2\psi = \frac{\boldsymbol{p}^2}{2m}\psi \tag{1.36}$$

and the following correspondence

$$-\frac{\hbar^2}{2m}\nabla^2 \leftrightarrow \frac{\boldsymbol{p}^2}{2m}, \tag{1.37}$$

where m is the mass of a particle.

Meanwhile, taking partial differentiation of (1.27) with respect to t, we obtain

$$\frac{\partial\psi}{\partial t} = -\frac{i}{\hbar}E\psi_0 e^{i\left(\frac{\boldsymbol{p}}{\hbar}\cdot\boldsymbol{x}-\frac{E}{\hbar}t\right)} = -\frac{i}{\hbar}E\psi. \tag{1.38}$$

That is,

$$i\hbar\frac{\partial\psi}{\partial t} = E\psi. \tag{1.39}$$

As the above, we get the following relationship:

$$i\hbar\frac{\partial}{\partial t} \leftrightarrow E. \tag{1.40}$$

Thus, we have relationships between c-numbers (classical numbers) and q-numbers (quantum numbers, namely, operators) in (1.35) and (1.40). Subtracting (1.36) from (1.39), we get

$$i\hbar\frac{\partial\psi}{\partial t} + \frac{\hbar^2}{2m}\nabla^2\psi = \left(E - \frac{\boldsymbol{p}^2}{2m}\right)\psi. \tag{1.41}$$

Invoking the relationship on energy

$$(\text{Total energy}) = (\text{Kinetic energy}) + (\text{Potential energy}), \tag{1.42}$$

we have

$$E = \frac{\boldsymbol{p}^2}{2m} + V, \tag{1.43}$$

where V is a potential energy. Thus, (1.41) reads as

$$i\hbar\frac{\partial\psi}{\partial t}+\frac{\hbar^2}{2m}\nabla^2\psi=V\psi. \tag{1.44}$$

Rearranging (1.44), we finally get

$$\left(-\frac{\hbar^2}{2m}\nabla^2+V\right)\psi=i\hbar\frac{\partial\psi}{\partial t}. \tag{1.45}$$

This is the Schrödinger equation, a fundamental equation of quantum mechanics. In (1.45), we define a following Hamiltonian operator H as

$$H\equiv-\frac{\hbar^2}{2m}\nabla^2+V. \tag{1.46}$$

Then we have a shorthand representation such that

$$H\psi=i\hbar\frac{\partial\psi}{\partial t}. \tag{1.47}$$

On going from (1.25) to (1.27), we realize that quantities $\boldsymbol{k}$ and ω pertinent to a field have been converted to quantities $\boldsymbol{p}$ and E related to a particle. At the same time, whereas $\boldsymbol{x}$ and t represent a whole space-time in (1.25), those in (1.27) are characterized as localized quantities.

From a historical point of view, we have to mention a great achievement accomplished by Werner Heisenberg (1925) who propounded matrix mechanics. The matrix mechanics is often contrasted with the wave mechanics Schrödinger initiated. Schrödinger and Pau Dirac (1926) demonstrated that wave mechanics and matrix mechanics are mathematically equivalent. Note that the Schrödinger equation is described as a nonrelativistic expression based on (1.43). In fact, kinetic energy K of a particle is given by [1].

$$K=\frac{m_\mathrm{e}c^2}{\sqrt{1-(u/c)^2}}-m_\mathrm{e}c^2.$$

As a nonrelativistic approximation, we get

$$K\approx m_\mathrm{e}c^2\left[1+\frac{1}{2}\left(\frac{u}{c}\right)^2\right]-m_\mathrm{e}c^2=\frac{1}{2}\,m_\mathrm{e}u^2\approx\frac{p^2}{2m_\mathrm{e}},$$

where we used $p\approx m_\mathrm{e}u$ again as a nonrelativistic approximation; also, we used

$$\frac{1}{\sqrt{1-x}} \approx 1 + \frac{1}{2}x$$

when x (>0) corresponding to $\left(\frac{u}{c}\right)^2$ is enough small than 1. This implies that in the above case the group velocity u of a particle is supposed to be well below light velocity c. Dirac (1928) formulated an equation that describes relativistic quantum mechanics (the Dirac equation).

In (1.45) ψ varies as a function of $\boldsymbol{x}$ and t. Suppose, however, that a potential V depends only upon $\boldsymbol{x}$. Then we have

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\boldsymbol{x})\right]\psi(\boldsymbol{x},t) = i\hbar\frac{\partial\psi(\boldsymbol{x},t)}{\partial t}. \tag{1.48}$$

Now, let us assume that separation of variables can be done with (1.48) such that

$$\psi(\boldsymbol{x},t) = \phi(\boldsymbol{x})\xi(t). \tag{1.49}$$

Then, we have

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\boldsymbol{x})\right]\phi(\boldsymbol{x})\xi(t) = i\hbar\frac{\partial\phi(\boldsymbol{x})\xi(t)}{\partial t}. \tag{1.50}$$

Accordingly, (1.50) can be recast as

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\boldsymbol{x})\right]\phi(\boldsymbol{x})/\phi(\boldsymbol{x}) = i\hbar\frac{\partial\xi(t)}{\partial t}/\xi(t). \tag{1.51}$$

For (1.51) to hold, we must equate both sides to a constant E. That is, for a certain fixed point $\boldsymbol{x}_0$ we have

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\boldsymbol{x}_0)\right]\phi(\boldsymbol{x}_0)/\phi(\boldsymbol{x}_0) = i\hbar\frac{\partial\xi(t)}{\partial t}/\xi(t), \tag{1.52}$$

where $\phi(\boldsymbol{x}_0)$ of a numerator should be evaluated after operating ∇^2, while with $\phi(\boldsymbol{x}_0)$ in a denominator, $\phi(\boldsymbol{x}_0)$ is evaluated simply replacing $\boldsymbol{x}$ in $\phi(\boldsymbol{x})$ with $\boldsymbol{x}_0$**.** Now, let us define a function $\Phi(\boldsymbol{x})$ such that

$$\Phi(\boldsymbol{x}) \equiv \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\boldsymbol{x})\right]\phi(\boldsymbol{x})/\phi(\boldsymbol{x}). \tag{1.53}$$

Then, we have

$$\Phi(\boldsymbol{x}_0) = i\hbar \frac{\partial \xi(t)}{\partial t} / \xi(t). \tag{1.54}$$

If RHS of (1.54) varied depending on t, $\Phi(\boldsymbol{x}_0)$ would be allowed to have various values, but this must not be the case with our present investigation. Thus, RHS of (1.54) should take a constant value E. For the same reason, LHS of (1.51) should take a constant.

Thus, (1.48) or (1.51) should be separated into the following equations:

$$H\phi(\boldsymbol{x}) = E\phi(\boldsymbol{x}), \tag{1.55}$$

$$i\hbar \frac{\partial \xi(t)}{\partial t} = E\xi(t). \tag{1.56}$$

Equation (1.56) can readily be solved. Since (1.56) depends on a sole variable t, we have

$$\frac{d\xi(t)}{\xi(t)} = \frac{E}{i\hbar} dt \quad \text{or} \quad d \ln \xi(t) = \frac{E}{i\hbar} dt. \tag{1.57}$$

Integrating (1.57) from zero to t, we get

$$\ln \frac{\xi(t)}{\xi(0)} = \frac{Et}{i\hbar}. \tag{1.58}$$

That is,

$$\xi(t) = \xi(0) \exp(-iEt/\hbar). \tag{1.59}$$

Comparing (1.59) with (1.38), we find that the constant E in (1.55) and (1.56) represents an energy of a particle (electron).

Thus, the next task we want to do is to solve an eigenvalue equation of (1.55). After solving the problem, we get a solution

$$\psi(\boldsymbol{x}, t) = \phi(\boldsymbol{x}) \exp(-iEt/\hbar), \tag{1.60}$$

where the constant $\xi(0)$ has been absorbed in $\phi(\boldsymbol{x})$. Normally, $\phi(\boldsymbol{x})$ is to be normalized after determining the functional form (vide infra).