

## CHAPTER I

### INTRODUCTION



#### 1.1 Introduction

The hydrogen atom is a dynamical system consisting of two particles differing in charge, the proton or nucleus with positive charge (+e), and the electron with negative charge (-e) moving around the proton under the influence of attractive Coulomb potential. The old quantum theory was successful in that it could be used to calculate the energy spectrum of the hydrogen atom. When the new quantum mechanics was discovered, the physicists could calculate the energy spectrum of the hydrogen atom more precisely. Furthermore, the new quantum mechanics allowed the wave functions of the hydrogen atom to be determined exactly. It also gave rise to the concept of spin which had not existed in classical mechanics. For any mechanical system (including the spin degrees of freedom), one could set up an eigenvalue equation to find its energy spectrum, or construct a wave equation to derive its probability amplitudes if the total Hamiltonian were known.

#### 1.2 Quantization Character of the Hydrogen Spectrum

For a long time ago, the structure of the hydrogen atom had interested physicists. The first clue to our present knowledge of the quantized character of hydrogenic system and its radiations came from Balmer's discovery in 1884 of simple numerical relations between the frequencies of hydrogen line. The expression is

$$\frac{1}{\lambda} = R_H \left( \frac{1}{2^2} - \frac{1}{m^2} \right), \quad m = 3, 4, 5, \dots \quad (1.1)$$

where  $R_H$  is an empirical constant called the "Rydberg constant for hydrogen" with the approximate value

$$R_H = 1.097 \times 10^7 \text{ m}^{-1}$$

Moreover, there are other spectral series lying in the invisible spectrum. The wavelengths of them follow the relation

$$\frac{1}{\lambda} = R_H \left( \frac{1}{n^2} - \frac{1}{m^2} \right), \quad n < m \quad (1.2)$$

where  $n$  and  $m$  are integers. This general expression is known as the Ritz's combination law.

As seen from the above relation, the wavelengths of lines in the energy spectrum appear to be quantized. It was N. Bohr who could first describe the hydrogenic structure and successively developed the theory based on quantum concepts. He has made two postulates concerning the electronic structure of an atom. The first of these was that an atomic system can exist in particular stationary or quantized states, each of which corresponds to a definite energy of the system. Transitions from one stationary state to another are accompanied by the gain or loss of an amount of energy equal to the energy difference between the two states; the energy gained or lost appears as a quantum of electromagnetic radiation. The second postulate was that a radiation quantum has a frequency equal to its energy divided by Planck's constant  $h$ . These two postulates by themselves provided some insight into this Ritz's law. To obtain specific results for hydrogen, Bohr proposed a simple rule for the

selection of the circular orbits that are to constitute stationary states; the angular momentum must be an integral multiple of  $\frac{h}{2\pi}$ . A more general quantization rule was discovered independently by A. Sommerfeld, thus making possible the application of Bohr's postulates to a wider variety of atomic systems. This rule is applicable to Hamiltonian systems in which the coordinates are cyclic variables; it states that the integral of each canonical momentum with respect to its coordinate over a cycle of its motion known as the action variable  $J$  must be an integral multiple of  $h$ , i.e.,

$$J = \oint p dq = nh, \quad n = \text{integer} \quad (1.3)$$

Eq. (1.3) is often called Bohr-Sommerfeld's quantization condition.

In the Heisenberg's construction of a new mathematical formalism called matrix mechanics, which will be briefly presented in the next chapter, the above quantization condition (1.3) was expressed in another form. According to Heisenberg's idea, any given mechanical problem will be solved in the matrix formulation if we can determine the solution matrices  $\hat{q}$  and  $\hat{p}$ . In Bohr's quantum theory the functions  $q(t)$  and  $p(t)$  must satisfy the quantization condition (1.3). It can be inferred that a similar restriction must be imposed appearing in the Heisenberg's formulation. By considering the limiting conditions of the correspondence principle, it can be shown that when  $n$  is small, the matrix analogue of Bohr-Sommerfeld's quantization condition can be expressed in the form (1)

$$\hat{q}\hat{p} - \hat{p}\hat{q} = -\frac{h}{2\pi i} \mathbb{1} \quad (1.4)$$

$\mathbb{1}$  denotes unit matrix

The above relation defines a mathematical restriction which must be imposed on the matrices  $\hat{q}$  and  $\hat{p}$  of any one-dimensional mechanical system. As such, it informs us of the difference in the values of  $\hat{q}\hat{p}$  and of  $\hat{p}\hat{q}$ , and enables us to formulate definite algebraic rules of combination for the solution matrices  $\hat{q}$  and  $\hat{p}$ . The dual role played by the relation (1.4) justifies our referring to it as the commutation relation or as the "new" quantization condition in the new quantum theory.

As distinct from Hisenberg's idea, the wave mechanics of Schroedinger originated in the works of de Broglie on matter wave. Schroedinger, generalizing the motion of matter waves, discovered the equation of motion for the wave function  $\Psi$  representing a given quantum system. According to Schroedinger's postulate, the wave function is defined in configuration space as the dynamical state of the quantum system and whose wave equation is obtained by having the classical Hamiltonian operate on wave function with the energy and momentum term given by

$$E \rightarrow i\hbar \frac{\partial}{\partial t} \quad \text{and} \quad p_j \rightarrow -i\hbar \frac{\partial}{\partial q_j} \quad (1.5)$$

These two quantities, considered as operators, give the "new" quantization condition when acting on the wave function. The equation thus obtained is the Schroedinger equation of the corresponding quantum system.

In 1948 Feynman (2) proposed a new approach to quantum mechanics which expressed the propagator or the probability amplitude of a particle as a path integral over all possible histories of the system that is characterized by the Lagrangian. The dynamical information of a quantum mechanical system is contained in the wave

function. According to Feynman's ideas, the wave function can be rewritten as

$$\Psi(\vec{x}'', t'') = \int_{-\infty}^{\infty} K(\vec{x}'', \vec{x}'; t'', t') \Psi(\vec{x}', t') d^3x' \quad (1.6)$$

where  $K(\vec{x}'', \vec{x}'; t'', t')$  is called the propagator of a particle to go from  $\vec{x}'$  at time  $t'$  to  $\vec{x}''$  at time  $t''$ .

It was suggested that there are infinitely many paths along which a particle can go from the initial point to the final point under restrictive conditions that  $\vec{x}(t') = \vec{x}'$ ,  $\vec{x}(t'') = \vec{x}''$ . Each trajectory contributes to the total amplitude for going from  $\vec{x}'$  to  $\vec{x}''$ . They contribute equal amounts to the total amplitude, but contribute at different phases. The phase of the contribution from a given path is the action  $S$  for that path in units of the quantum of action  $\hbar$ . The propagator can thus be expressed in the path integral form

$$K(\vec{x}'', \vec{x}'; t'', t') = \lim_{N \rightarrow \infty} \left( \frac{2\pi i \hbar \epsilon}{m} \right)^{-3N/2} \int \dots \int \exp \left\{ \frac{i}{\hbar} \sum_{j=1}^N \left[ \frac{m}{2\epsilon} (\vec{x}_j - \vec{x}_{j-1})^2 - \epsilon V(\vec{x}_j) \right] \right\} d^3x_1 d^3x_2 \dots d^3x_{N-1} \quad (1.7)$$

or in a less restrictive notation as

$$K(\vec{x}'', \vec{x}'; t'', t') = \int_{\vec{x}'}^{\vec{x}''} e^{\frac{i}{\hbar} S[\vec{x}'', \vec{x}']} \mathcal{D}(\vec{x}(t)) \quad (1.8)$$

The above expression is called Feynman's path integral and it can be seen as a new approach to quantum mechanics.

The hydrogen atom problem is one of the most interesting problems which can be solved exactly by quantum mechanics. One may find this problem in any current textbooks on quantum mechanics. The method of wave mechanics was used to evaluate the energy spectrum and most discussion of this problem has employed this method. Only in a few places one can find the corresponding method of matrix mechanics to solve the hydrogen atom problem completely even though Pauli solved it shortly after introducing of matrix mechanics. The main reason for this absence is that Pauli's method is rather confusing and it involves several tricks in the process of mathematical derivation. The hydrogen atom problem has just also been solved within the framework of Feynman's path integral approach. This later success serves not only a theorist's academic satisfaction but it is also an illustrative confirmation that Feynman's path integral approach is an alternative formalism of quantum mechanics.

The purpose of this thesis is to reinvestigate Pauli's original work (3) on the hydrogen atom problem in order to obtain its energy spectrum. In his original paper, Pauli discussed the influence of external electric and magnetic fields of force on the hydrogen spectrum in the nonrelativistic case. In our thesis, we will merely discuss the method Pauli used to evaluate the energy spectrum since it is a physically interesting example of what can be done with quantum mechanics. It might also be illustrative of the methods needed to solve more complicated problems. In this study, we will write and simplify original expressions and formulae in a more compact form using conventional notations.

In the next chapter we will review the mathematical formalism of matrix mechanics. An illustrative solvable problem which can be performed directly by matrix mechanics, the harmonic oscillator, will be presented. In chapter III, the Lenz vector used by Pauli in his study on the hydrogen atom problem will be introduced. This vector is a constant vector for any particle moving according to a Coulomb field in a Kepler motion problem. In chapter IV, we will show the method Pauli used to examine the hydrogen spectrum from the system of matrix equations contributed by this vector. The conclusion will then be given in chapter V



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