



CHAPTER II

THREE DIMENSIONAL HYDROGEN ATOM

In this chapter the problem of the three dimensional hydrogen atom will be briefly reviewed. Starting with the discussion about the inadequacy of classical physics for describing atoms, the Bohr and the Sommerfeld relativistic theories of the hydrogen atom are then studied in Section 2.2. The latter portion of this chapter is concerned with the nonrelativistic and relativistic quantum mechanical treatments of the problem, Section 2.4 and 2.5 respectively.

2.1 INADEQUACY OF CLASSICAL PHYSICS FOR DESCRIBING ATOM.

It is well-known that classical physics, as represented by Newtonian mechanics and Maxwell's laws of electromagnetism, works marvelously well for the analysis of the behavior of macroscopic objects in terms of empirically determined laws of force. But as soon as we enter the world of the atom, new phenomena appear, requiring new concepts for their analysis and description.

Rutherford's discovery of the atomic nucleus in 1911 made it quite clear that by classical physics alone it is quite impossible to understand the most essential properties of atoms - the stability in atomic structure and the properties of the radiation sent out from atoms. According to Rutherford's model, an atom consists of a heavy positively charged nucleus of dimensions very small compared to the atom itself surrounded by a system of light electrons kept together

by the inverse square attractive Coulomb force from the nucleus.

Let us consider the atom which composes of a nucleus and one electron, i.e., the hydrogenic atom. For convenience such atom will be called the hydrogen atom with the understanding that the number of proton in the nucleus is now equal to Z (atomic number). From classical mechanics, the electron in the hydrogen atom would describe an elliptical or circular orbit about the nucleus, similar to that of the earth about the sun. The electron would therefore experience centripetal acceleration. Moreover, the orbit representing any state of motion lies in the plane, since the force acting on the electron at any instant is the central force. According to classical electrodynamics, the acceleration of the charged particle would lead to the emission of light with frequencies equal to the mechanical frequency of the particle in its orbit, and to multiples of this as overtones. With the emission of energy, the radius of the orbit would diminish - the electron would slowly spiral into the nucleus - and the mechanical frequency would change. Hence, according to classical physics, the emitted light should show a wide range of frequencies. This is not at all what is observed. The radiation emitted by the hydrogen atom is confined to spectral lines of sharply defined frequencies, and, moreover, these frequencies are not related to one another by integral factors, as overtones. Instead, there is observed a new and unexpected connection between the frequencies, called Reitz's combination law of spectroscopy,

$$\frac{1}{\lambda} = R_H \left(\frac{1}{n^2} - \frac{1}{m^2} \right), \quad n > m, \quad n, m = \text{integers} \quad (2.1)$$

where R_H is an empirical constant called the Rydberg constant.

2.2 THE OLD QUANTUM THEORY.

2.2.1 BOHR'S THEORY OF HYDROGEN ATOM.

The first formulation of the principle of the quantum theory that could immediately account for the stability in atomic structure and the properties of the radiation sent out from atoms was proposed in 1913 by Bohr in the form of two postulates (26);

- (1) Among the conceivably possible states of motion in an atomic system there exist a number of so-called stationary states which, in spite of the fact that the motion of the particles in these states obeys the laws of classical mechanics to a considerable extent, possess a peculiar, mechanically unexplainable stability, of such a sort that every permanent change in the motion of the system must consist in a complete transition from one stationary state to another.
- (2) While in contradiction to the classical electromagnetic theory no radiation takes place from the atom in the stationary states themselves, a process of transition between two stationary states can be accompanied by the emission of electromagnetic radiation, which will have the same properties as that which would be sent out according to the classical theory from an electrified particle executing an harmonic vibration with constant frequency. This frequency ν has, however, no simple relation to the motion of the particles of the atom, but is given by the relation

$$h\nu = E' - E''$$

where h is Planck's constant, and E' and E'' are the values of the energy of the atom in the two stationary states that form the initial and final states of the radiation process. Conversely, irradiation of the atom with electromagnetic waves of this frequency can lead to an absorption process, where by the atom is transformed back from the latter stationary state to the former.

It follows from the first postulate that in Bohr's theory the motion of the electron in the stationary states is the motion in a plane.

In calculating the energy of the stationary states of the hydrogen atom Bohr imagined that the electron orbits in the stationary states are represented by circles, although the theory places no restriction on the eccentricity of the orbit. He also used the assumption that for orbits of very large diameter the frequency of the emitted light should correspond to the frequency of the orbiting electron, which was a prediction of classical physics. This "correspondence principle" led to the intriguing conclusion that for a stationary state designated by the integer n the angular momentum of the orbiting electron is equal to $(nh/2\pi)$. Hence the angular momentum, like the energy, can change only in discrete steps. This "quantization" of the angular momentum is of fundamental significance ; without it the atom could radiate at any frequency and the state would no longer be stationary.

As the result of the Bohr theory, the energy of the stationary state of the hydrogen atom which is designated by the integer "quantum number" n can be expressed by means of the relation

$$E_n = -\frac{mZ^2e^4}{2\hbar^2n^2}, \quad n = 1, 2, 3, \dots, \quad (2.2)$$

where m is the Electron's rest mass (the rest mass of the nucleus is taken to be infinity), Z is the atomic number (the number of protons in the nucleus), e is the elementary charge, and \hbar is the Planck constant divided by 2π .

Bohr's theory was a great conceptual advance over the earlier theories, but it soon proved inadequate to explain the observed features of atomic spectra, even those of the simplest spectrum, that of hydrogen - although it was quite successful in predicting the position of the spectral lines of hydrogen, there remained an unexplained "fine structure" of the spectral lines. The fine structure is a splitting of the spectral lines, into several distinct components, which is found in all spectra. This splitting amounts to about one part in 10^4 and cannot be seen in spectrometers of low resolving power.

2.2.2 SOMMERFELD'S RELATIVISTIC THEORY OF HYDROGEN ATOM.

The more general quantization rules were derived in 1915 by Wilson from the theory of heat radiation and applied almost immediately by him and Sommerfeld to the hydrogen spectrum (27). These rules are applicable to Hamiltonian systems in which the coordinates are cyclic variables ; they state 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 Planck's constant, i.e.,

$$J = \oint p_q dq = n_q h, \quad n_q = \text{integer} \quad (2.3)$$

where p_q is the canonical momentum conjugate to the coordinate q ,

$$p_q = \frac{\partial L}{\partial \dot{q}} ; \quad L = \text{Lagrangian of the system.}$$

These rules are often called the " Bohr-Sommerfeld-Wilson quantization conditions".

One of the important applications of the Bohr-Sommerfeld-Wilson quantization conditions was to the case of the hydrogen atom in which it was assumed that the electron could move in elliptical orbits. This was done by Sommerfeld in an attempt to explain the fine structure of the hydrogen spectrum. Sommerfeld first evaluated the size and shape of the allowed elliptical orbits, as well as the total energy of an electron moving in such an orbit, using the formulas of classical mechanics. Describing the motion in terms of the plane polar coordinates ρ and ϕ , and applying the two quantum conditions

$$\oint p_{\phi} d\phi = n_{\phi} h, \quad n_{\phi} = 1, 2, 3, \dots, \quad (2.4a)$$

$$\oint p_{\rho} d\rho = n_{\rho} h, \quad n_{\rho} = 0, 1, 2, \dots, \quad (2.4b)$$

he found that (a) the length of the semimajor and semiminor axes, a and b , are

$$a = \frac{n^2 h^2}{mZe^2}, \quad (2.5a)$$

$$b = a(n_{\phi}/n), \quad (2.5b)$$

and that (b) the possible values of the total energy of the electron are

$$E_n = -\frac{mZ^2 e^4}{2n^2 h^2}, \quad (2.6)$$

where the quantum number n is defined by the relation

$$n = n_{\rho} + n_{\phi} = 1, 2, 3, \dots \quad (2.7)$$

For a given value of n , n_ϕ can assume only the values

$$n_\phi = 1, 2, 3, \dots, n. \quad (2.8)$$

Thus, corresponding to each value of the quantum number n there are n different allowed orbits. One of these, the circular orbit ($n_\phi=n$), is just the orbit described by the Bohr theory, the others ($n_\phi \neq n$) are elliptical. These orbits are said to be "degenerate".

Sommerfeld (28) removed the degeneracy by treating the problem with the theory of relativistic mechanics. He showed that the total energy of an electron in an orbit characterized by the quantum numbers n and n_ϕ is equal to

$$E_{n,n_\phi} = mc^2 \left[1 + \frac{Z\alpha}{(n-n_\phi) + \left[n_\phi^2 - (Z\alpha)^2 \right]^{1/2}} \right]^2 \quad (2.9a)$$

$$= mc^2 - \frac{mZ^2e^4}{2\hbar^2n^2} \left\{ 1 + \frac{(Z\alpha)^2}{n} \left[\frac{1}{n_\phi} - \frac{3}{4n} \right] \right\}, \quad (2.9b)$$

where the quantity

$$\alpha = \frac{e^2}{\hbar c} \quad (2.10)$$

is a pure number (dimensionless) called the Sommerfeld fine structure constant. Eq.(2.9b) is obtained by expanding Eq.(2.9a) in power series of $(Z\alpha)$ and keeping the terms up to the sixth order. This formula accounts quite well for the spectrum of hydrogen atom - the terms in Eq.(2.9b) in which α appears correctly accounted for the fine structure splitting of the lines of the hydrogen spectrum. Unfortunately, the Sommerfeld relativistic theory is not the correct explanation for the fine

structure of atomic spectra. We now know that the fine structure is partly due to the relativistic variation of mass with velocity, partly due to the spin of the electron which produces the so-called spin-orbit interaction.

Although the old quantum theory, which is essentially a general method of calculating quantized quantities based upon the postulates of Bohr and the correspondence principle, achieved many successes in atomic and molecular spectroscopy, it was an incomplete theory. It could not be applied to aperiodic systems, most collision and scattering problems. Furthermore, it contained errors, contradictions, and ambiguities. However, it predicted a large body of experimental results from a few simple rules, and it set the stage for the new quantum mechanics which soon replaced it.

2.3 NONRELATIVISTIC QUANTUM MECHANICS.

The founding of nonrelativistic quantum mechanics can be placed between the years of 1923 and 1927. Two equivalent formulations thereof have been proposed almost simultaneously ; Heisenberg's matrix mechanics and Schroedinger's wave mechanics. Apart from these two formulations, the third formulation of quantum mechanics , the so-called Feynman path integral approach, was proposed by Feynman in 1948 (33).

2.3.1 HEISENBERG'S MATRIX MECHANICS. (27, 29, 30)

The starting point of the Heisenberg matrix mechanics is a critical analysis of the old quantum theory. The point of view developed by Heisenberg is the following. In any physical theory one must distinguish the concepts and quantities which are physically observable, i.e., enter into the experimental results, from those which are not. The former must necessarily play a role in the theory, whereas the latter can be modified or abandoned without impairment. The notion of electron orbit is an example of the concept without experimental foundation since no experiment allows us to assert that the electron actually describes a precise orbit in the atom.

Starting exclusively from physically observable quantities, such as the frequencies and the intensities of the radiation emitted by atoms, the theory associates with each physical quantity a certain matrix. In contrast to the quantities of ordinary algebra, these matrices obey a noncommutative algebra. It is on this essential point that the new (quantum) mechanics differs from the classical mechanics. The equations of motion of the dynamical variables of a quantized system are thus equations between matrices. Following the correspondence principle, these equations of motion are formally identical to the equations of the corresponding classical system.

The method of Heisenberg's matrix mechanics has been applied to the hydrogen atom by Pauli in 1926. His treatment has recently been reinvestigated by Veerapaspong (4). By this method the total energy of the electron in the hydrogen atom is exactly

the same as that obtained from the Bohr theory, i.e.,

$$E_n = -\frac{mZ^2e^4}{2\hbar^2n^2} \quad ; n = 1, 2, 3, \dots \quad (2.2)$$

2.3.2 SCHROEDINGER'S WAVE MECHANICS. (27, 31)

Shortly after Heisenberg's discovery of matrix mechanics, Schroedinger set up independently another form of quantum mechanics - the wave mechanics. It originates in the de Broglie hypothesis on matter waves (in 1925) which states that the wave-corpucle duality is a general property of microscopic objects, and that matter, as well as light, exhibits both wave and corpuscular aspects. The speculations of de Broglie's hypothesis on the wave nature of matter were confirmed experimentally in 1927, about one year later than Schroedinger's first paper, by the work of Davisson and Germer, in which they scattered low energy electrons from a nickel crystal.

The basic of Schroedinger's investigation is the understanding that , besides the de Broglie relation between wavelength and momentum, the ture quantum mechanics must stand in the same relation to the ordinary classical mechanics that physical optics does to geometrical optics. Indeed, if one accepts the additional hypothesis that matter waves (as contrasted to electromagnetic waves) are represented by one scalar wave function U , then the Schrodinger nonrelativistic wave equation in the configuration space for the wave function U representing a given system can be deduced from the Hamiltonian of the corresponding classical system by operating on the wave function

the classical Hamiltonian with the energy and momentum terms given by

$$E \longrightarrow i\hbar \frac{\partial}{\partial t} \quad \text{and} \quad p_j \longrightarrow -i\hbar \frac{\partial}{\partial x_j} . \quad (2.11)$$

These two quantities, considered as operators, give the "new" quantization condition when acting on the wave function.

For the hydrogen atom in which the classical Hamiltonian is

$$H = \frac{p^2}{2m} - \frac{Ze^2}{r} = E , \quad (2.12)$$

the Schroedinger equation is

$$\left(-\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{r} \right) U(\vec{r}, t) = i\hbar \frac{\partial}{\partial t} U(\vec{r}, t) . \quad (2.13)$$

The solutions of this equation are well-known. The normalized wave functions are (32)

$$U_{nlm}(\vec{r}, t) = R_{nl}(r) Y_{lm}(\theta, \phi) T_n(t), \quad (2.14)$$

$$R_{nl}(\rho) = - \left(\frac{2Z}{na_0} \right)^3 \left\{ \frac{(n-1-1)!}{2n [(n+1)!]} \right\}^{1/2} \exp\left(-\frac{\rho}{2}\right) \rho^1 L_{n+1}^{2l+1}(\rho), \quad (2.15)$$

$$T_n(t) = \exp(-iE_n t/\hbar), \quad (2.16)$$

where ρ is the dimensionless variable

$$\rho = \left(\frac{2Z}{na_0} \right) r, \quad a_0 = \frac{\hbar^2}{me^2} = \text{Bohr radius}, \quad (2.17)$$

$Y_{lm}(\theta, \phi)$ and $L_{n+1}^{2l+1}(\rho)$ are the normalized spherical harmonic and the associated Laguerre polynomials respectively, and E_n is the energy eigenvalue

$$E_n = - \frac{mZ^2 e^4}{2n^2 \hbar^2}, \quad n = 1, 2, 3, \dots .$$

The three quantum numbers n , l , and m are called the "principal", the "azimuthal" or orbital angular momentum, and the "magnetic" quantum numbers respectively. When n is given l and m can be found from the following rules ;

for the restrictive n

l can be $0, 1, 2, \dots, n-2, n-1$

m can be $-(n-1), -(n-2), \dots, (n-2), (n-1)$.

Although the Heisenberg and the Schroedinger theories has different standing points and were developed by the use of different process of thought, they produced the same results for the problems treated by both theories. In fact, as Schroedinger has shown, wave mechanics and matrix mechanics are equivalent (34). They are two particular formulations of a theory which can be presented in very general terms. The setting up of the general formalism of the quantum theory is essentially due to Dirac.

2.3.3 FEYNMAN'S PATH INTEGRAL. (33)

In the Feynman path integral approach of quantum mechanics the dynamical information of a quantum mechanical system is, as in the Schroedinger wave mechanics, contained in the wave function. But in this approach the wave function is written as

$$U(\vec{x}'', t'') = \int K(\vec{x}'', \vec{x}'; t'', t') U(\vec{x}', t') d^3x' \quad (2.18)$$

where $K(\vec{x}'', \vec{x}'; t'', t')$ is called the propagator or probability amplitude of a particle to go from \vec{x}' at time t' to \vec{x}'' at time t'' . Since, quantum mechanically, there are infinitely many possible paths for a particle to go from the initial point to the final

point under restrictive conditions that $\vec{x}(t') = \vec{x}'$ and $\vec{x}(t'') = \vec{x}''$, the propagator must be the sum of contribution $\phi[\vec{x}(t)]$ from each path;

$$K(\vec{x}'', \vec{x}'; t'', t') = \sum_{\substack{\text{over all possible} \\ \text{paths from} \\ \vec{x}' \text{ to } \vec{x}''}} \phi[\vec{x}(t)]. \quad (2.19)$$

According to Feynman's idea, each path contributes equal amount, C , to the total propagator but contributes at different phase. The phase of the contribution from each path is the action S for that path in units of the quantum action \hbar , i.e.,

$$\phi[\vec{x}(t)] = C \exp\left[\frac{iS[\vec{x}(t)]}{\hbar}\right], \quad (2.20)$$

where the action S is defined by

$$S[\vec{x}(t)] = \int_{t'}^{t''} L[\vec{x}(t), \dot{\vec{x}}(t)] dt \quad (2.21)$$

with the Lagrangian

$$L[\vec{x}(t), \dot{\vec{x}}(t)] = \frac{1}{2} m \dot{\vec{x}}^2 - V(\vec{x}). \quad (2.22)$$

The propagator (2.19) then becomes

$$K(\vec{x}'', \vec{x}'; t'', t') = \sum_{\substack{\text{over all possible} \\ \text{paths from} \\ \vec{x}' \text{ to } \vec{x}''}} C \cdot \exp\left\{\frac{iS[\vec{x}(t)]}{\hbar}\right\}, \quad (2.23)$$

which, as Feynman has shown (33), can be expressed in the path integral form

$$K(\vec{x}'', \vec{x}'; t'', t') = \lim_{N \rightarrow \infty} \left(\frac{m}{2\pi i \hbar \epsilon}\right)^{3N/2} \int \dots \int \exp\left\{\frac{i}{\hbar} \sum_{j=1}^N \left[\frac{m}{2\epsilon} (\vec{x}_j - \vec{x}_{j-1})^2 - \epsilon V(\vec{x}_j)\right]\right\} d^3x_1 d^3x_2 \dots d^3x_{N-1}, \quad (2.24)$$

where $\epsilon = \left(\frac{t'' - t'}{N}\right)$, $t_0 = t'$, $t_N = t''$, $\vec{x}_0 = \vec{x}'$, and $\vec{x}_N = \vec{x}''$.

Feynman wrote this sum over all paths in a less restrictive notation as

$$K(\vec{x}'', \vec{x}'; t'', t') = \int_{\vec{x}'}^{\vec{x}''} \exp\left\{\frac{iS[x'', x']}{\hbar}\right\} \mathcal{D}[\vec{x}(t)] \quad (2.25)$$

which he called a path integral.

The hydrogen atom problem has just also been solved with in the framework of Feynman path integral (3). The results obtained from this method are exactly the same as those obtained from the Heisenberg matrix mechanics and the Schroedinger wave mechanics. In fact, it can be shown that these three approaches of quantum mechanics are equivalent (34). They are different mathematical formulations of the same physics relations.

Apparently, all the three approaches of quantum mechanics discussed above predicted the Bohr energy levels of the hydrogen atom, and hence the same wavelengths of the spectral lines. Again, the relativistic corrections had to be introduced in order to explain the fine structure splitting of the spectral lines. Moreover, in addition to the relativistic corrections, the correction due to the electron spin must also be included in the theories.

2.3.4 PAULI'S THEORY OF ELECTRON SPIN

The concept of the electron spin was introduced by Goudsmit and Uhlenbeck in 1925 to explain measurements of the spectra of alkali-metal atoms. According to their hypothesis the electron must have its own "spin" angular momentum of the magnitude of half a quantum ($\frac{\hbar}{2}$), which means that if one measures the component of this angular momentum along any direction one finds either the values $+\frac{\hbar}{2}$ or $-\frac{\hbar}{2}$, and have a magnetic moment of one Bohr magneton ($\frac{e\hbar}{2mc}$).

After the preliminary discussion of Goudsmit and Uhlenbeck, the first treatment of the electron spin was given in 1926 by Heisenberg and Jordan, who employed the formal methods of the matrix mechanics. A mathematical scheme to include the Goudsmit-Uhlenbeck hypothesis in the wave mechanics was proposed independently by Darwin and by Pauli in 1927. The method proposed by Pauli soon became standard for the discussion of all ordinary problems in atomic and molecular structure. However, none of these authors pretended to offer a theory of the origin of the electron spin, but tried to find a suitable procedure for the mathematical description of the physical ideas proposed by Goudsmit and Uhlenbeck. Since their methods do not conform to the requirements of the special theory of relativity we cannot consider them as ultimately satisfactory from the point of view of general theory. Nevertheless, the Pauli theory is a valuable first approach to the more complex theory based on the Dirac equation.

Pauli opened the way to successful wave mechanical treatment of the electron spin by the assumption of the two wave functions, i.e., he replaced the Schrodinger wave function (one single scalar function) by a pair of wave functions whose squared absolute values determine the probability density of finding the electron with its spin oriented parallel or anti-parallel to an arbitrarily chosen axis of quantization. In analog to the orbital angular momentum operator \vec{L} , he introduced the spin operator \vec{S} , represented by what were subsequently called the "Pauli matrices" which operate on the two-component wave function, a linear superposition of the two wave functions ;

$$\vec{S} = \frac{1}{2} \hbar \vec{\sigma}^P, \quad (2.26)$$

where the Pauli spin matrices $\vec{\sigma}^P = (\sigma_x^P, \sigma_y^P, \sigma_z^P)$ are the 2-by-2 matrices

$$\sigma_x^P = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \quad \sigma_y^P = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \quad \sigma_z^P = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}. \quad (2.27)$$

By studying the transformation of the component of the wave function under the rotation of the coordinate system, Pauli developed a consistent wave mechanical spin theory which explained a large number of phenomena but not the origin of the electron spin.

The main physical assumption of the Pauli theory is that the Hamiltonian describing a system of particles is just the usual Schroedinger Hamiltonian plus an additional term representing an interaction energy with the electron spin (35).

For the hydrogen atom, with in the approximations that the mass of the nucleus is infinity and that the spin of the nucleus is zero, the interaction energy arises from the interaction between the Coulomb field of the nucleus and the intrinsic magnetic moment of the moving electron and is found to be, to the first order approximation, (35),

$$H_{sp} = \frac{Ze^2 \hbar^2}{2m^2 c^2} \frac{\vec{S} \cdot \vec{L}}{r^3}, \quad (2.28)$$

where \vec{S} and \vec{L} are the spin and the orbital angular momentum of the electron respectively.

Apart from the spin-orbit interaction (2.28), the correction terms which arise from the relativistic variation of mass with velocity must also be included into the Hamiltonian in order to explain the fine structure splitting of the spectral lines. To the first order approximation, the additional term is

$$H_{rel} = - \frac{p^4}{8m^3 c^2} = - \frac{1}{2mc^2} (E^2 + V^2 - 2EV), \quad (2.29)$$

where $V = V(r) = - \frac{Ze^2}{r}$. The total Hamiltonian for the hydrogen atom is then

$$H_{tot} = \frac{p^2}{2m} + V(r) + H_{sp} + H_{rel}. \quad (2.30)$$

Since the spin and the relativistic effects are known to be small - they correspond to the fine structure splitting of the spectral lines, we may consider H_{sp} and H_{rel} as perturbing potentials and may handle the problem by perturbation methods (36).

By choosing the unperturbed wave functions to be

$$R_{nl}(r)Y_{lm}(\theta, \phi)\bar{\alpha}, \quad R_{nl}(r)Y_{lm}(\theta, \phi)\bar{\beta}, \quad (2.31)$$

where

$$\bar{\alpha} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad \bar{\beta} = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad (2.32)$$

are the spin wave functions corresponding to the states with spin-up and spin-down respectively, and using the first order perturbation theory to evaluate the first order change in energy due to H_{sp} and H_{rel} , one finds that

(a) the additional energy due to the spin-orbit interaction H_{sp} is

$$E_{nl, sp}^{(1)} = \frac{Ze^2\hbar^2}{2m^2c^2} \left\langle \frac{1}{r^3} \right\rangle \langle \vec{S} \cdot \vec{L} \rangle$$

$$= \begin{cases} 0 ; l = 0 \\ \frac{(Z\alpha)^2 |E_n|}{n(2l+1)(l+1)} ; j = l + \frac{1}{2}, l \neq 0 \\ -\frac{(Z\alpha)^2 |E_n|}{n(2l+1)l} ; j = l - \frac{1}{2}, l \neq 0 \end{cases} \quad (2.33)$$

where E_n is the unperturbed energy eigenvalue;

α is the Sommerfeld fine structure constant; l and j are the 'orbital' and the 'total' angular momentum quantum numbers, respectively,

and that (b) the additional energy due to H_{rel} is

$$E_{nl, rel}^{(1)} = \langle H_{rel} \rangle$$

$$= -\frac{(Z\alpha)^2 |E_n|}{n} \left(\frac{2}{2l+1} - \frac{3}{4n} \right). \quad (2.34)$$

Thus, to the first order approximation, the total energy of the electron is, in terms of the quantum numbers n and j ,

$$E_{nj}^{(1)} = E_n^{(0)} + E_{nj,sp}^{(1)} + E_{nj,rel}^{(1)}$$

$$= \begin{cases} -\frac{mZ^2e^4}{2\hbar^2n^2} \left(1 + \frac{(Z\alpha)^2}{n} \left[\frac{1}{j + \frac{1}{2}} - \frac{3}{4n} \right] \right), & l \neq 0 \\ -\frac{mZ^2e^4}{2\hbar^2n^2} \left(1 + \frac{(Z\alpha)^2}{n} \left[2 - \frac{3}{4n} \right] \right), & l = 0. \end{cases} \quad (2.35)$$

Comparing these results with those obtained from the Sommerfeld relativistic theory of hydrogen atom (Section 2.2.2), we see that except for the case $l = 0$, the values of the energy predicted by the above calculations are in exact agreement with those predicted by Sommerfeld. For $l = 0$, there is a discrepancy. But this discrepancy is removed by the Dirac relativistic theory, which shows that there is one more relativistic correction to the Hamiltonian - the so-called "Darwin term", whose existence we could not have guessed because it has no classical analog (see Appendix B).

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

2.4 RELATIVISTIC QUANTUM MECHANICS.

As have been mentioned in the previous section, the Pauli theory of the electron spin is an incomplete theory since it does not conform to the requirement of the special theory of relativity. It was Dirac in 1928 that found a new way of constructing a theory of quantum mechanics for the electron spin that is also consistent with the special theory of relativity (37). In the Dirac theory the electron spin appears as a natural consequence of the basic equation - the Dirac equation - rather than as a special hypothesis stipulated by experimental facts. In fact, the Dirac theory is applicable to all spin one-half particles - the Dirac particles.

2.4.1 KLEIN - GORDON EQUATION.

Actually, the Dirac equation was not the first relativistic wave equation, the so-called Klein-Gordon equation, for spin-less particles, was established before - it was proposed in 1926 independently by Schroedinger, Gordon, Fock, Klein, de Donder and Van Dungen, and Kodar. This equation is derived by inserting the usual operator substitutions, $E \rightarrow i\hbar \frac{\partial}{\partial t}$ and $\vec{p} \rightarrow -i\hbar \vec{\nabla}$, into the relativistic relation between the energy and momentum for the free particle

$$E^2 = (cp)^2 + (mc^2)^2, \quad (2.36)$$

where m is the rest mass of the particle and c is the speed of light in vacuum. This procedure yields the wave equation

$$-\hbar^2 \frac{\partial^2}{\partial t^2} U(\vec{r}, t) = (-\hbar^2 c^2 \nabla^2 + m^2 c^4) U(\vec{r}, t) \quad (2.37)$$

which has become known as the Klein-Gordon equation.

From the wave equation (2.37) a probability density P and a probability current density \vec{j} which satisfy the continuity equation

$$\vec{\nabla} \cdot \vec{j} - \frac{\partial}{\partial t} P = 0 \quad (2.38)$$

are found to be

$$P = \frac{i\hbar}{2mc^2} \left(U^* \left[\frac{\partial}{\partial t} U \right] - \left[\frac{\partial}{\partial t} U^* \right] U \right) \quad (2.39)$$

and

$$j_s = \frac{\hbar}{2mi} \left(U^* \left[\frac{\partial}{\partial x_s} U \right] - \left[\frac{\partial}{\partial x_s} U^* \right] U \right), \quad (2.40)$$

$s = 1, 2, 3.$

It should, however, be noted that P given by Eq.(2.39) is not necessarily positive and hence cannot be interpreted as a position probability density. Because of the possibility of negative P values, the Klein-Gordon equation fell into disrepute for about seven years after it was first proposed. It was only in 1934 that Pauli and Weisskopf re-established the validity of the equation by reinterpreting it as a field equation and quantizing it in the usual fashion.



2.4.2 DIRAC EQUATION.

Historically, Dirac discovered the relativistic wave equation which now bears his name while trying to overcome the difficulties of negative probability densities of the Klein-Gordon equation. According to Dirac (36) the relativistic wave equation must satisfy the following requirements :

- (1) It must allow the customary probability interpretation of the wave function to be valid. This means that it must be possible to define, from the wave equation, a probability density P which is positive definite and a probability current density \vec{j} such that the continuity equation holds between them, i.e.,

$$\vec{\nabla} \cdot \vec{j} + \frac{\partial}{\partial t} P = 0 . \quad (2.38)$$

- (2) It must be consistent with the principle of special relativity.
- (3) It must be linear in the wave function in order that the superposition principle of the quantum mechanics holds.
- (4) It must be consistent with the correspondence principle and in the nonrelativistic limit it must reduce to the standard form of quantum mechanics already found applicable at low velocities. Furthermore, in the non-quantum limit it must yield the mechanics of special relativity - this implies that, for a free particle, the wave function must obey the Klein-Gordon equation to assure that the relativistic energy - momentum relation for a free particle is satisfied.

These requirements imply the following form of the relativistic wave equation for the description of the motion of a free particle of spin- $\frac{1}{2}$ and rest mass m , the Dirac equation for a free particle,

$$H_D U(\vec{r}, t) = (c\vec{\alpha} \cdot \vec{p} + \beta mc^2) U(\vec{r}, t) = i\hbar \frac{\partial}{\partial t} U(\vec{r}, t), \quad (2.41)$$

where H_D is the Dirac Hamiltonian for a free particle

$$H_D = c\vec{\alpha} \cdot \vec{p} + \beta mc^2 = -i\hbar c (\alpha_x \frac{\partial}{\partial x} + \alpha_y \frac{\partial}{\partial y} + \alpha_z \frac{\partial}{\partial z}) + \beta mc^2, \quad (2.42)$$

$\vec{\alpha} = (\alpha_x, \alpha_y, \alpha_z)$ and β are 4-by-4 matrices satisfy the commutation relations

$$\begin{aligned} \alpha_x^2 &= 1, & \alpha_x \alpha_y + \alpha_y \alpha_x &= 0, \\ \beta^2 &= 1, & \alpha_x \beta + \beta \alpha_x &= 0, \end{aligned} \quad (2.43)$$

together with the relations obtained from these by permuting the suffixes x, y, z . The wave function $U(\vec{r}, t)$ is now a four-component wave function

$$U(\vec{r}, t) = \begin{bmatrix} U^1(\vec{r}, t) \\ U^2(\vec{r}, t) \\ U^3(\vec{r}, t) \\ U^4(\vec{r}, t) \end{bmatrix} = \begin{bmatrix} \varphi(\vec{r}, t) \\ \chi(\vec{r}, t) \end{bmatrix}, \quad (2.44)$$

where

$$\varphi(\vec{r}, t) = \begin{bmatrix} U^1(\vec{r}, t) \\ U^2(\vec{r}, t) \end{bmatrix} \quad \text{and} \quad \chi(\vec{r}, t) = \begin{bmatrix} U^3(\vec{r}, t) \\ U^4(\vec{r}, t) \end{bmatrix}. \quad (2.45)$$

The standard representation of the $\vec{\alpha}$ and β matrices, the Pauli representation, is specified in terms of the Pauli matrices (2.27),

$$\vec{\alpha} = \begin{bmatrix} 0 & \vec{\sigma}^P \\ \vec{\sigma}^P & 0 \end{bmatrix}, \quad \beta = \begin{bmatrix} I & 0 \\ 0 & -I \end{bmatrix}, \quad I = 2\text{-by-2 unit matrix.} \quad (2.46)$$

That the Dirac equation describes the particle of spin $\frac{1}{2}$ can be seen by noting that in the Dirac theory the orbital angular momentum is no longer a constant of the motion but instead there exists another operator which is a constant of the motion and can be interpreted as the total angular momentum. That operator is

$$\vec{J} = \vec{L} + \vec{S} , \quad (2.47)$$

where \vec{S} is the operator which can be interpreted as the spin angular momentum ;

$$\vec{S} = \frac{1}{2} \hbar \begin{bmatrix} \vec{\sigma}^P & 0 \\ 0 & \vec{\sigma}^P \end{bmatrix} = \frac{1}{2} \hbar \vec{\sigma}^D , \quad (2.48)$$

$$\vec{\sigma}^D = \begin{bmatrix} \vec{\sigma}^P & 0 \\ 0 & \vec{\sigma}^P \end{bmatrix} = \text{Dirac's spin matrices.} \quad (2.49)$$

Since the eigenvalues of each component of \vec{S} are $\frac{\hbar}{2}$ and $-\frac{\hbar}{2}$, it follows that the Dirac equation (2.41) is the equation which describes the spin- $\frac{1}{2}$ particle.

The Dirac equation (2.41) can be generalized to describe the motion of a charged particle of spin- $\frac{1}{2}$ in the presence of an external electromagnetic field described by a scalar potential $A_0(\vec{r}, t)$ and a vector potential $\vec{A}(\vec{r}, t)$ by making the usual replacements

$$\vec{p} \rightarrow \vec{p} - \frac{q}{c} \vec{A} , \quad i\hbar \frac{\partial}{\partial t} \rightarrow i\hbar \frac{\partial}{\partial t} - qA_0 . \quad (2.50)$$

The resulting equation is

$$H_D U(\vec{r}, t) = \left\{ c\vec{\alpha} \cdot \left(\vec{p} - \frac{q}{c} \vec{A} \right) + \beta mc^2 + qA_0 \right\} U(\vec{r}, t) = i\hbar \frac{\partial}{\partial t} U(\vec{r}, t), \quad (2.51)$$

where the potentials $A_0(\vec{r}, t)$ and $\vec{A}(\vec{r}, t)$ are evaluated at the

position of the particle. This equation can be separated with respect to the space and time coordinates provided that the scalar and vector potentials are independent of time . By putting

$$U(\vec{r}, t) = U(\vec{r}) \exp\left(-\frac{iEt}{\hbar}\right) \quad (2.52)$$

into Eq.(2.51) we obtain

$$H_D U(\vec{r}) = \left\{ c\vec{\alpha} \cdot \left(\vec{p} - \frac{q}{c} \vec{A} \right) + \beta mc^2 + qA_0 \right\} U(\vec{r}) = EU(\vec{r}) , \quad (2.53)$$

which should be referred to as the time-independent Dirac equation. The quantity E in the above equation is called the energy eigenvalue .

For the hydrogen atom , $A_0 = \frac{Ze}{r}$ and $\vec{A} = 0$, the time-independent Dirac equation takes the form

$$\left(c\vec{\alpha} \cdot \vec{p} + \beta mc^2 - \frac{Ze^2}{r} \right) U(\vec{r}) = E U(\vec{r}) , \quad (2.54)$$

which can be solved exactly (19 - 22). The bound state energy eigenvalues are found to be

$$E_{nk} = mc^2 \left[1 + \left\{ \frac{Z\alpha}{(n - |k|) + [k^2 - (Z\alpha)^2]^{1/2}} \right\}^2 \right]^{-1/2} \quad (2.55a)$$

$$= mc^2 - \frac{mc^2(Z\alpha)^2}{2n^2} - \frac{mc^2(Z\alpha)^4}{2n^4} \left(\frac{n}{|k|} - \frac{3}{4} \right) + \dots, \quad (2.55b)$$

where n is the principal quantum number, $n = 1, 2, \dots$, and k is the quantum number related to the orbital and the total angular momentum quantum numbers, l and j, through the relations

$$k = \begin{cases} -(j + \frac{1}{2}) & = -(l + 1) \text{ if } j = l + \frac{1}{2} \text{ (spin-up),} \\ (j + \frac{1}{2}) & = l \text{ if } j = l - \frac{1}{2} \text{ (spin-down).} \end{cases} \quad (2.56)$$

Eqs.(2.55) are equivalent to the formulas first derived by Sommerfeld on the basis of the old quantum theory, although the interpretation of the quantum numbers is different (and wrong) in the old theory.

The first term in the series expansion (2.55b) is the rest energy. the second term is the nonrelativistic energy. The terms in $(Z\alpha)^4$ are exactly what is obtained in the Pauli theory if a first-order perturbation calculation is used to evaluate the contribution of the sum of the following three terms (19) ;

- (i) the additional energy due to variation of mass with velocity

$$-\frac{p^4}{8m^3c^2} = -\frac{1}{2}(E - V)^2 ; \quad (2.57)$$

- (ii) the spin - orbit coupling

$$\frac{\hbar Z e^2}{4m^2 c^2} \frac{\vec{\sigma} \cdot \vec{L}}{r^3} ; \quad (2.58)$$

- (iii) the "Darwin" fluctuation term (see Appendix B)

$$-\frac{\pi \hbar^2 Z e^2}{2m^2 c^2} \delta(\vec{r}) . \quad (2.59)$$

The normalized wave functions which correspond to the bound states energy eigenvalues (2.55) are divided into two classes (19) ;

(a) for the spin-up states, i.e., $j = 1 + \frac{1}{2}$ and $k = -(l + 1)$,

$$U_{nk\bar{m}}^A(r) = \begin{bmatrix} g_{nk}(r) \sqrt{\frac{k - \bar{m} + \frac{1}{2}}{2k + 1}} Y_{-k-1, \bar{m}-\frac{1}{2}}(\theta, \phi) \\ -g_{nk}(r) \sqrt{\frac{k + \bar{m} + \frac{1}{2}}{2k + 1}} Y_{-k-1, \bar{m}+\frac{1}{2}}(\theta, \phi) \\ -if_{nk}(r) \sqrt{\frac{k + \bar{m} - \frac{1}{2}}{2k - 1}} Y_{-k, \bar{m}-\frac{1}{2}}(\theta, \phi) \\ -if_{nk}(r) \sqrt{\frac{k - \bar{m} - \frac{1}{2}}{2k - 1}} Y_{-k, \bar{m}+\frac{1}{2}}(\theta, \phi) \end{bmatrix}, \quad (2.60)$$

(b) for the spin-down states, i.e., $j = 1 - \frac{1}{2}$ and $k = l$,

$$U_{nk\bar{m}}^B(r) = \begin{bmatrix} g_{nk}(r) \sqrt{\frac{k - \bar{m} + \frac{1}{2}}{2k + 1}} Y_{k, \bar{m}-\frac{1}{2}}(\theta, \phi) \\ g_{nk}(r) \sqrt{\frac{k + \bar{m} + \frac{1}{2}}{2k + 1}} Y_{k, \bar{m}+\frac{1}{2}}(\theta, \phi) \\ -if_{nk}(r) \sqrt{\frac{k + \bar{m} - \frac{1}{2}}{2k - 1}} Y_{k-1, \bar{m}-\frac{1}{2}}(\theta, \phi) \\ -if_{nk}(r) \sqrt{\frac{k - \bar{m} - \frac{1}{2}}{2k - 1}} Y_{k-1, \bar{m}+\frac{1}{2}}(\theta, \phi) \end{bmatrix}, \quad (2.61)$$

where \bar{m} is the eigenvalue of the z-component of the total angular momentum ; $Y_{i,j}(\theta, \phi)$ is the spherical harmonics ; $g_{nk}(r)$ and $f_{nk}(r)$ are the normalized radial Dirac eigenfunctions ,

$$g_{nk}(r) = \left\{ \frac{\Gamma(2\gamma_k + \bar{n} + 1)}{4N_{nk}(N_{nk} - k) [\Gamma(2\gamma_k + 1)] 2^{\bar{n}}!} \right\}^{\frac{1}{2}} (1 + \epsilon_{nk})^{\frac{1}{2}} (2\lambda_{nk})^{3/2} \\ \exp\left(-\frac{1}{2} \lambda_{nk} r\right) (2\lambda_{nk} r)^{\gamma_k - 1} \left[\bar{n}_1 F_1(-\bar{n} + 1; 2\gamma_k + 1; 2\lambda_{nk} r) \right. \\ \left. - (N_{nk} - k) {}_1F_1(-\bar{n}; 2\gamma_k + 1; 2\lambda_{nk} r) \right], \quad (2.62)$$

$$f_{nk}(r) = - \left\{ \frac{\Gamma(2\gamma_k + \bar{n} + 1)}{4N_{nk} (N_{nk} - k) [\Gamma(2\gamma_k + 1)]^2 \bar{n}!} \right\}^{1/2} (1 - \epsilon_{nk})^{1/2} (2\lambda_{nk})^{3/2} \exp\left(-\frac{1}{2} \lambda_{nk} r\right) (2\lambda_{nk} r)^{\gamma_k - 1} \left[\bar{n} {}_1F_1(-\bar{n} + 1; 2\gamma_k + 1; 2\lambda_{nk} r) + (N_{nk} - k) {}_1F_1(-\bar{n}; 2\gamma_k + 1; 2\lambda_{nk} r) \right], \quad (2.63)$$

$$\gamma_k = \sqrt{[k^2 - (Z\alpha)^2]}; \quad \alpha = \text{Sommerfeld fine structure constant,}$$

$$\bar{n} = n - |k|,$$

$$N_{nk} = \sqrt{[(\bar{n} + \gamma_k)^2 + (Z\alpha)^2]} = \text{the "apparent" principal quantum number}$$

$$\epsilon_{nk} = \frac{E_{nk}}{mc^2}, \quad \lambda_{nk} = \frac{mcZ\alpha}{\hbar N_{nk}} = \frac{Z}{a_0 N_{nk}}, \quad a_0 = \text{Bohr radius,}$$

$$\Gamma(c) = \int_0^\infty e^{-z} z^{c-1} dz = \text{the gamma function,}$$

$${}_1F_1(a; c; z) = 1 + \frac{a}{c} z + \frac{a(a+1)}{c(c+1)} \frac{z^2}{2!} + \frac{a(a+1)(a+2)}{c(c+1)(c+2)} \frac{z^3}{3!} + \dots$$

= the confluent hypergeometric function.

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย