Study on Systems of Hydrogen Atoms in the View Point of Natural Statistical Physics

By

Yoshifumi ITO

Professor Emeritus, The University of Tokushima
Home Address : *209-15 Kamifukuman Hachiman-cho*
Tokushima 770-8073, JAPAN
e-mail address : *yoshifumi@md.pikara.ne.jp*

Abstract

In this paper, we study the derivation and the solution of Schrödinger equation of the hydrogen atoms using the theory of Natural Statistical Physics. Using these results, we study the phenomena of the spectra of hydrogen atoms and the phenomena of the stability of hydrogen atoms. Here we consider the system of hydrogen atoms for which we need not to consider the influence of the outer electro-magnetic field. This is the case where there is no influence of outer electro-magnetic field or where we can neglect the influence of the outer electro-magnetic field. In this paper, we succeeded in deriving the Schrödinger equation in the natural and reasonable way by the method of variational calculus. Thereby we can obtain the complete understanding of the phenomena of the spectra of hydrogen atoms and the phenomena of the stability of hydrogen atoms.

We remark that the model of the system of hydrogen atoms considered in this paper does not concern with the scattering state of hydrogen atoms.

In this paper, Fourier's method plays the fundamental role. For the results of this paper, we refer to Ito[16], [19], [20], [22], [24], [25], [26].

2010 Mathematics Subject Classification. Primary 82D99, 82B99, 81Q99.

1 Systems of hydrogen atoms and the formulation of the problem

In this paper, we study the derivation of the Schrödinger equation of the system of hydrogen atoms and its solutions which are necessary to analyze the natural statistical phenomena of the system of hydrogen atoms in the basis of the laws of natural statistical physics.

Using the above results, we study the spectral phenomena of the system of hydrogen atoms and the stability phenomena of hydrogen atoms as the natural statistical phenomena of the system of hydrogen atoms. Thereby we obtain the complete understanding of these phenomena.

We assume that hydrogen atoms considered here are in the bound state. Each hydrogen atom is moving in the 3-dimensional space.

One hydrogen atom is a combined system of two particles composed of one nucleus and one electron rotating around the nucleus. Here the nucleus of the hydrogen atom is composed of one proton.

This means that the nucleus and one electron are moving as a combined system under Coulomb interaction. Even though the system of hydrogen atoms is a system of two particles, the mass of an inner electron is throughly smaller than the mass of the nucleus. Therefore we analyze the phenomena using an approximating model of a system of one electron moving in a field of Coulomb potential at the point of center where the nucleus keep to rest.

Here we consider the system of hydrogen atoms for which we need not consider the influence of spin. It is the case where there is no influence of the outer electro-magnetic field or where we can neglect such an influence. This means that no factor of the outer electro-magnetic field is contained in the Schrödinger equation of the system of hydrogen atoms. Namely we study the phenomena using such an approximating model.

Each electron is moving in the field of Coulomb potential according to Newtonian dynamics. Because the masses of a proton and an electron are very small, we consider their motion neglecting the gravitational interaction.

Here we put the mass of one electron $m = m_e$, and the charge of one electron $-e$. Then the electron is moving according to the Newtonian equation of motion

$$m \frac{d^2 \boldsymbol{r}}{dt^2} = -\operatorname{grad} V(\boldsymbol{r}) = -\frac{e^2}{r^3} \boldsymbol{r}.$$

Therefore, the mechanical energy of the inner electron of one hydrogen atom

$$\mathcal{E} = \frac{1}{2m} \boldsymbol{p}^2 - \frac{e^2}{r}, \ \left(\boldsymbol{p} = m \frac{d \boldsymbol{r}}{dt} \right)$$

does not depend on the time t. The first term is the kinetic energy and the second term is the potential energy. Namely the conservative law of mechanical energy holds for each inner electron of a hydrogen atom.

Therefore each electron has its own mechanical energy. We can define the energy functional to be the expectation value of this mechanical energy for the physical system of the inner electrons of hydrogen atoms.

Using variational principle in section 3, we can derive the Schrödinger equation as Euler's equation of the variational problem. Then, this Schrödinger operator has only the negative eigenvalues in the bound state.

Using the eigenvalues

$$\mathcal{E}_n = -\frac{m_e e^4}{2\hbar^2 n^2}, \ (n = 1, 2, 3, \cdots)$$

of the Schrödinger operator, we can prove that the Bohr's law holds for the spectrum of the system of hydrogen atoms. This fact was demonstrated by virtue of the experiment of Frank-Herz in 1914. Here we put $\hbar = h/2\pi$, h being the Planck constant.

In general, the physical state of a physical system is varying toward the equilibrium state of energy or the thermal equilibrium state. Thereby we can completely understand and interpret the phenomena of stability of hydrogen atoms.

2   Laws of natural statistical physics

In general, every material particle is the natural existence which has its own mass and charge.

Because it is known that an electron has its own mass and charge by the effective measurement, it is the evidence that an electron is a material particle. Here we put the mass of an electron to be $m = m_e$ and its charge to be $-e$.

Therefore we can consider that an electron is moving by virtue of Newtonian equation of motion in the field of Coulomb potential.

On the basis of these facts, we can understand the spectral phenomena of the system of hydrogen atoms as the natural statistical phenomena.

We can consider that the nucleus of a hydrogen atom has approximately the infinite mass. Therefore, in the first approximation, the inner electron of the hydrogen atom is moving in the field of Coulomb potential $V(\boldsymbol{r}) = -\dfrac{e^2}{r}$ by virtue of Newtonian equation of motion.

Here, in order to analyze the natural statistical phenomena of the system of inner electrons of the hydrogen atoms, we establish the laws of natural statistical physics as follows.

Law I (Physical system)   The system Ω of hydrogen atoms is a set of inner electrons of hydrogen atoms. It is a probability space $(\Omega, \mathcal{B}, P)$ mathematically. Here Ω is the set of inner electrons ρ of hydrogen atoms, $\mathcal{B}$ is

σ-algebra of the family of subsets of Ω, and P is a completely additive probability measure on $\mathcal{B}$. Its elementary event is one inner electron ρ of a hydrogen atom. This is a system of one particle composed of an inner electron moving in the field of Coulomb potential.

Law II (State of physical system)   We define a natural statistical state of the system $\Omega = (\Omega, \mathcal{B}, P)$ of hydrogen atoms to be the state of natural probability distributions of the position variable $\boldsymbol{r}(\rho)$ and the momentum variable $\boldsymbol{p}(\rho)$ of inner electrons ρ of hydrogen atoms. Here $\boldsymbol{r}(\rho)$ is varying in the 3-dimensional space $\boldsymbol{R}^3$ and $\boldsymbol{p}(\rho)$ is varying in its dual space $\boldsymbol{R}^3$, where $\boldsymbol{R}^3$ is considered to be a self-dual space.

(i)   The natural probability distribution law of the position variable $\boldsymbol{r} = \boldsymbol{r}(\rho)$ is determined by an L^2-density $\psi(\boldsymbol{r})$ on $\boldsymbol{R}^3$.

(ii)   The natural probability distribution law of the momentum variable $\boldsymbol{p} = \boldsymbol{p}(\rho)$ is determined by the Fourier transform $\hat{\psi}$ of ψ. Here the Fourier transform $\hat{\psi}$ of ψ is defined by the relation

$$\hat{\psi}(\boldsymbol{p}) = (2\pi\hbar)^{-3/2} \int \psi(\boldsymbol{r}) e^{-i(\boldsymbol{p}\cdot\boldsymbol{r})/\hbar} d\boldsymbol{r},$$

$$\boldsymbol{r} = {}^t(x_1, x_2, x_3), \boldsymbol{p} = {}^t(p_1, p_2, p_3),$$

$$\boldsymbol{p} \cdot \boldsymbol{r} = p_1 x_1 + p_2 x_2 + p_3 x_3,$$

where the integral domain is the whole space. Here we put $\hbar = \dfrac{h}{2\pi}$, h being the Planck constant.

(iii)   For a Lebesgue measurable set A in $\boldsymbol{R}^3$, we put

$$\mu(A) = \int_A |\psi(\boldsymbol{r})|^2 d\boldsymbol{r}.$$

Then we have

$$\mu(A) = P(\{\rho \in \Omega; \boldsymbol{r}(\rho) \in A\}).$$

Thus $\mu(A)$ denotes the probability of the event "$\boldsymbol{r}(\rho)$ belongs to A". Thereby we have the probability space $(\boldsymbol{R}^3, \mathcal{M}_3, \mu)$. Here $\mathcal{M}_3$ denotes the family of all Lebesgue measurable sets in $\boldsymbol{R}^3$.

(iv)   For a Lebesgue measurable set B in $\boldsymbol{R}^3$, we put

$$\nu(B) = \int_B |\hat{\psi}(\boldsymbol{p})|^2 d\boldsymbol{p}.$$

Then we have
$$\nu(A) = P(\{\rho \in \Omega; \boldsymbol{p}(\rho) \in B\}).$$

Thus $\nu(B)$ denotes the probability of the event "$\boldsymbol{p}(\rho)$ belongs to B". Thereby we have the probability space $(\boldsymbol{R}^3, \mathcal{N}_3, \nu)$. Here $\mathcal{N}_3$ denotes the family of all Lebesgue measurable sets in $\boldsymbol{R}^3$.

The reason why we define the Fourier transformation in such a form in Law (II), (ii) is to meet with the necessity that the Schrödinger equation of the system of hydrogen atoms should be derived by using variational principle in section 3. The constants are chosen in order that the theoretical results coincide with some observed data of the natural statistical phenomena.

Law III (Motion of physical system) The L^2-density $\psi(\boldsymbol{r}, t)$ determining the natural probability distribution law of the position variable $\boldsymbol{r}$ at time t is determined by the time evolving Shrödinger equation. We call the time evolution the motion of the system of hydrogen atoms. The law of motion of the system of hydrogen atoms is described by the Schrödinger equation. We call this Schrödinger equation the equation of motion of the system of hydrogen atoms.

The Schrödinger equation is described in the following form :

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

We call the operator H a Schrödinger operator. H is a self-adjoint operator on a certain Hilbert space. The concrete form of this operator is determined afterward.

Here we consider that the position variable and the momentum variable and the energy variable of electrons are continuous random variables defined on the probability space made by the system of hydrogen atoms. Then the L^2-density determining the natural probability distribution law of the position variable is determined as a solution of the Schrödinger equation.

As for the laws of natural statistical physics, we refer to Ito[16], Section 2.2 and Ito[25], Section 6.2.

3 Setting of mathematical models

Now we assume that the system of hydrogen atoms considered here is a probability space $\Omega = (\Omega, \mathcal{B}, P)$. Its elementary event ρ is an inner electron of a hydrogen atom moving in the 3-dimensional space $\boldsymbol{R}^3$.

Here the force acts on the electron in the hydrogen atom by the Coulomb potential

$$V(\boldsymbol{r}) = -\frac{e^2}{r}, \ r = \|\boldsymbol{r}\|.$$

Then the mechanical energy of each inner electron ρ of a hydrogen atom is determined by the classical mechanics. Its value is

$$\frac{1}{2m}\|\boldsymbol{p}(\rho)\|^2 + V(\boldsymbol{r}(\rho)).$$

Here the mass of an electron is $m = m_e$ and its charge is $-e$.

This energy variable is considered as a natural random variable on the probability space Ω. This is a continuous random variable.

Then $\boldsymbol{r} = \boldsymbol{r}(\rho)$ and $\boldsymbol{p} = \boldsymbol{p}(\rho)$ have different values for each inner electron ρ of a hydrogen atom and, in general, its values are considered to be distributed randomly. In such a sense, $\boldsymbol{r} = \boldsymbol{r}(\rho)$ and $\boldsymbol{p} = \boldsymbol{p}(\rho)$ are considered to be random variables. Especially it is the mode of phenomena as the natural statistical phenomena that these variables are the natural random variables on the system of hydrogen atoms.

We assume that electrons in hydrogen atoms considered here are in the bound state. Therefore, the Schrödinger operator determined afterward has only the discrete spectrum.

Then, we consider that, by virtue of Law II in Section 2, the natural probability distribution law of $\boldsymbol{r} = \boldsymbol{r}(\rho)$ is determined by the L^2-density $\psi(\boldsymbol{r})$ and the natural probability distribution law of $\boldsymbol{p} = \boldsymbol{p}(\rho)$ is determined by its Fourier transform $\hat{\psi}(\boldsymbol{p})$.

Then the expectation value $\overline{E}$ of the energy variable is given as the integral using the probability measure P as follows :

$$\overline{E} = E\left[\ \frac{1}{2m}\|\boldsymbol{p}(\rho)\|^2 + V(\boldsymbol{r}(\rho)) \ \right]$$

$$= E\left[\ \frac{1}{2m}\|\boldsymbol{p}(\rho)\|^2 \ \right] + E[V(\boldsymbol{r}(\rho))]$$

$$= \int \left(\ \frac{1}{2m}\|\boldsymbol{p}\|^2 \ \right) |\hat{\psi}(\boldsymbol{p})|^2 d\boldsymbol{p} + \int V(\boldsymbol{r})|\psi(\boldsymbol{r})|^2 d\boldsymbol{r}$$

$$= \int \left\{ \ \frac{\hbar^2}{2m}\|\nabla_{\boldsymbol{r}}\psi(\boldsymbol{r})\|^2 + V(\boldsymbol{r})|\psi(\boldsymbol{r})|^2 \ \right\} d\boldsymbol{r}.$$

Here we use the Plancherel formula for the Fourier transformation. Also the integral domain is the whole space. $\nabla = \nabla_{\boldsymbol{r}}$ denotes the gradient operator with respect to $\boldsymbol{r}$.

In this paper, we define the partial derivatives of an L^2-function ψ in the sense of L^2-convergence.

Here we represent this energy expectation value by the relation

$$J[\psi] = \int \left\{ \frac{\hbar^2}{2m} \|\nabla_{\boldsymbol{r}} \psi(\boldsymbol{r})\|^2 + V(\boldsymbol{r})|\psi(\boldsymbol{r})|^2 \right\} d\boldsymbol{r}$$

We call this $J[\psi]$ the energy functional.

As the solutions of the variational problem for this functional, we have the L^2-densities ψ which are realized practically in the stationary states.

Here we consider the following variational principle and the variational problem.

Principle I (Variational principle) The L^2-density $\psi(\boldsymbol{r})$ which is realized practically in the stationary state is a stationary function for the energy functional $J[\psi]$.

Thereby, among the admissible L^2-densities $\psi(\boldsymbol{r})$ which determine the natural probability distribution laws of the position variables $\boldsymbol{r} = \boldsymbol{r}(\rho)$ of the inner electrons ρ, we choose the L^2-density $\psi(\boldsymbol{r})$ realized practically in the stationary state. These solutions determine the natural statistical phenomena observed practically.

In order to determine the stationary function for Principle I, we consider the following variational problem.

Problem I (Variational problem) Determine the stationary functions ψ of the energy functional $J[\psi]$.

4 Solutions of variational problem and the derivation of the Schrödinger equation

In this section, we study the solutions of variational problem I in section 3 and thereby we derive the Schrödinger equation.

The Schrödinger operator H has the form

$$H = -\frac{\hbar^2}{2m}\Delta - \frac{e^2}{r}.$$

Here Δ denotes the Laplacian with respect to $\boldsymbol{r}$.

This is the case where this Schrödinger operator H has only the discrete spectrum.

Now let the system of hydrogen atoms be $\Omega = (\Omega, \mathcal{B}, P)$. Its elementary event is one inner electron ρ of a hydrogen atom. We put its position variable $\boldsymbol{r} = \boldsymbol{r}(\rho) = {}^t(x_1(\rho), x_2(\rho), x_3(\rho))$, and its momentum variable $\boldsymbol{p} = \boldsymbol{p}(\rho) = {}^t(p_1(\rho), p_2(\rho), p_3(\rho))$.

We consider that the variable $\boldsymbol{r}$ moves in the space $\boldsymbol{R}^3$, and the variable $\boldsymbol{p}$ moves in the dual space $\boldsymbol{R}_3 = \boldsymbol{R}^3$. Here we identify $\boldsymbol{R}_3$ and $\boldsymbol{R}^3$.

Then, by virtue of law II in section 2, the L^2-density $\psi(\boldsymbol{r})$ determines the natural probability distribution law of the position variable $\boldsymbol{r}$, and its Fourier transform $\hat{\psi}(\boldsymbol{p})$ determines the natural probability distribution law of the momentum variable $\boldsymbol{p}$.

Therefore the energy expectation value $\overline{E}$ of the total system of hydrogen atoms is equal to

$$\overline{E} = E\left[\ \frac{1}{2m}\boldsymbol{p}(\rho)^2 - \frac{e^2}{r(\rho)}\ \right]$$

$$= \int \frac{1}{2m}\boldsymbol{p}^2|\hat{\psi}(\boldsymbol{p})|^2 d\boldsymbol{p} - \int \frac{e^2}{r}|\psi(\boldsymbol{r})|^2 d\boldsymbol{r}$$

$$= \int \left(\ \frac{\hbar^2}{2m}|\nabla\psi(\boldsymbol{r})|^2 - \frac{e^2}{r}|\psi(\boldsymbol{r})|^2\ \right)\ d\boldsymbol{r}.$$

Here the integral domain is the whole space $\boldsymbol{R}^3$, and $\nabla = \nabla_{\boldsymbol{r}}$ represents the gradient operator.

Then, for the L^2-function $\psi(\boldsymbol{r})$ on $\boldsymbol{R}^3$, we represent the energy functional $J[\psi]$ as follows :

$$J[\psi] = \int \left(\frac{\hbar^2}{2m}|\nabla\psi(\boldsymbol{r})|^2 - \frac{e^2}{r}|\psi(\boldsymbol{r})|^2 \right) d\boldsymbol{r}.$$

The domain of $J[\psi]$ is the Hilbert space of L^2-functions as follows :

$$\mathbb{D} = \left\{ \psi \in L^2; \int |\nabla\psi(\boldsymbol{r})|^2 d\boldsymbol{r} < \infty, \ \int \frac{1}{r}|\psi(\boldsymbol{r})|^2 d\boldsymbol{r} < \infty \right\}.$$

The norm $\|\psi\|$ of $\mathbb{D}$ is defined by the relation

$$\|\psi\|^2 = \int \left(\ |\psi(\boldsymbol{r})|^2 + |\nabla(\psi(\boldsymbol{r})|^2 + \frac{e^2}{r}|\psi(\boldsymbol{r})|^2\ \right)\ d\boldsymbol{r}.$$

Then $J[\psi]$ is a continuous functional on $\mathbb{D}$.

Here $\mathcal{D} = \mathcal{D}(\boldsymbol{R}^3)$ is the space of all C^∞-functions with compact support. Then $\mathcal{D}$ is dense in $\mathbb{D}$.

Then variational problem I in section 3 is fixed as follows.

Problem I (Variational problem) Determine the stationary functions ψ of the energy functional $J[\psi]$ defined on $\mathbb{D}$ under the condition

$$K[\psi] = \int |\psi(\boldsymbol{r})|^2 d\boldsymbol{r} = 1.$$

Thus we ask the stationary function using Lagrange's method of indeterminate coefficient.

$\mathcal{E}$ being an indeterminate coefficient of Lagrange, we put

$$I[\psi] = J[\psi] - \mathcal{E}(K[\psi] - 1).$$

Then the conditional stationary problem and the stationary value problem for $I[\psi]$ are equivalent.

Now we assume that we have a solution ψ of the conditional stationary value problem in the above. Then this ψ is a solution of the stationary value problem for $I[\psi]$. Then, ε being a sufficiently small real parameter, we have

$$\frac{d}{d\varepsilon}(I[\psi + \varepsilon\varphi])|_{\varepsilon=0} = 0, \tag{4.1}$$

$$\frac{d}{d\varepsilon}(I[\psi + i\varepsilon\varphi])|_{\varepsilon=0} = 0 \tag{4.2}$$

for every $\varphi \in \mathbb{D}$. Hence we have

$$\frac{\hbar^2}{2m}(\nabla\varphi, \nabla\psi) + (\varphi, V\psi) - (\varphi, \mathcal{E}\psi) = 0$$

by virtue of the equations (4.1), (4.2). Here $(\cdot, \cdot)$ denotes the inner product in L^2.

Using the Plancherel formula twice in the first term in this formula, we have

$$\left(\varphi, -\frac{\hbar^2}{2m}\Delta\psi + V\psi - \mathcal{E}\psi\right) = 0.$$

Because this holds for every $\varphi \in \mathcal{D}$, we have

$$-\frac{\hbar^2}{2m}\Delta\psi + V\psi = \mathcal{E}\psi. \tag{4.3}$$

When there exists a solution $\psi \in \mathbb{D}$ of the eigenvalue problem (4.3) which is not identically 0, $\mathcal{E}$ and ψ are called the eigenvalue and the eigenfunction of the Schrödinger operator H respectively. Especially ψ is the eigenfunction associated with the eigenvalue $\mathcal{E}$.

This is the Euler's differential equation for the conditional variational problem. We call this the Schrödinger equation.

This Schrödinger equation is the necessary condition in order that there exist the solutions of variational problem I in the above. Further we can prove the completeness of the system of solutions of this eigenvalue problem for the system of hydrogen atoms.

Then we can determine the L^2-density for the total system of hydrogen atoms completely by virtue of the eigenfunction expansion. Hence we can solve the Schrödinger equation completely. Namely, in the Theorem 5.5 in section 5, we prove that the completeness of the system of solutions of the eigenvalue

problem in the above is the sufficient condition in order to the existence of the solutions of the variational problem I in the above.

In this sense, we can obtain the information of the physical states of the system of hydrogen atoms by virtue of solving the Schrödinger equation obtained here.

5   Schrödinger equation and its solutions

The solutions of the eigenvalue problem for the Schrödinger equation of the stationary states are given in the following theorem. This is the well known facts.

Theorem 5.1   *There exist the eigenvalues $\mathcal{E}_n$, $(n = 1, 2, 3, \cdots)$ of the Schrödinger equation of the stationary states and the system $\{\psi_{nlm}(\boldsymbol{r})\}$ of its eigenfunctions associated with them. Namely we have the following equations :*

$$\left(-\frac{\hbar^2}{2m_e}\Delta - \frac{e^2}{r} \right)\psi_{nlm}(\boldsymbol{r}) = \mathcal{E}_n\psi_{nlm}(\boldsymbol{r}),$$

$$(|m| \le l,\ l = 0, 1, 2, \dots, n-1,\ n = 1, 2, 3, \cdots),$$

$$\mathcal{E}_n = -\frac{m_e e^4}{2\hbar^2 n^2},\ (n = 1, 2, 3, \cdots).$$

This system of the eigenfunctions $\{\psi_{nlm}(\boldsymbol{r})\}$ is given by the following theorem.

Theorem 5.2   *The eigenfunctions in Theorem 5.1 are given by the following equalities :*

$$\psi_{nlm}(\boldsymbol{r}) = \psi_{nlm}(r, \theta, \phi) = R_{nl}(r)Y_l^m(\theta, \phi),$$

$$R_{nl}(r) = -\left\{ \left(\frac{2}{na_0} \right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3} \right\}^{1/2} e^{s/2}s^l L_{n+l}^{(2l+1)}(s),$$

$$Y_l^m(\theta, \phi) = \sqrt{\frac{(2l+1)}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}}P_l^m(\cos\theta)e^{im\phi},$$

$$(|m| \le l,\ l = 0, 1, 2, \dots, n-1,\ n = 1, 2, 3, \cdots).$$

Here we put

$$a_0 = \frac{\hbar^2}{m_e e^2},\ s = \frac{2}{na_0}r.$$

Further, the special functions appeared in the representation of $\psi_{nlm}(\boldsymbol{r})$ are as follows: $R_{nl}(r)$ is the radial function, $L_n^{(m)}(z)$ is the associated Laguerre

polynomial, $Y_l^m(\theta, \phi)$ is the spherical function, and $P_l^m(x)$ is the associated Legendre polynomial.

Theorem 5.3 (Normalized orthogonality condition)   *For the system of eigenfunctions $\{\psi_{nlm}(\boldsymbol{r})\}$, we have the following equality*

$$\int \psi_{n'l'm'}(\boldsymbol{r})^* \psi_{nlm}(\boldsymbol{r}) d\boldsymbol{r} = \delta_{nn'} \delta_{ll'} \delta_{mm'}.$$

Here $\delta_{nn'}$ denotes Kronecker's symbol and (n, l, m) and (n', l', m') are chosen as in Theorem 5.1.

Theorem 5.4 (Completeness condition)   *Let $\mathcal{H}$ be the closed subspace spanned by the system of eigenfunctions $\{\psi_{nlm}(\boldsymbol{r})\}$ in $L^2 = L^2(\boldsymbol{R}^3)$. We use the above notation. Then, for $\psi(\boldsymbol{r}) \in \mathcal{H}$, we have the following equality*

$$\int |\psi(\boldsymbol{r})|^2 d\boldsymbol{r} = \sum_{n=1}^{\infty} \sum_{l=0}^{n-1} \sum_{m=-l}^{l} |c_{nlm}|^2,$$

$$c_{nlm} = \int \psi_{nlm}(\boldsymbol{r})^* \psi(\boldsymbol{r}) d\boldsymbol{r}.$$

Here (n, l, m) are chosen as in Theorem 5.1.

Therefore we have the following theorem of eigenfunction expansion.

Theorem 5.5 (Theorem of eigenfunction expansion)   *We consider the system of eigenfunctions $\{\psi_{nlm}(\boldsymbol{r})\}$ as in Theorem 5.1. Then, for a square integrable function $\psi(\boldsymbol{r}) \in \mathcal{H}$, we have the following equality :*

$$\psi(\boldsymbol{r}) = \sum_{n=1}^{\infty} \sum_{l=0}^{n-1} \sum_{m=-l}^{l} c_{nlm} \psi_{nlm}(\boldsymbol{r}).$$

Here the Fourier type coefficients c_{nlm} are given by the equalities :

$$c_{nlm} = \int \psi_{nlm}(\boldsymbol{r})^* \psi(\boldsymbol{r}) d\boldsymbol{r}.$$

Here (n, l, m) are chosen as in Theorem 5.1.

Especially, if $\psi(\boldsymbol{r})$ is an L^2-density, its Fourier type coefficients $\{c_{nlm}\}$ satisfy the following condition :

$$\sum_{n=1}^{\infty} \sum_{l=0}^{n-1} \sum_{m=-l}^{l} |c_{nlm}|^2 = 1.$$

Theorem 5.6   *Let $\mathcal{H}$ be as in Theorem* 5.4. *Further, let $J[\psi]$ be as in Problem* I, *and $\{\mathcal{E}_n\}$, $\{\psi_{nlm}\}$ be as in Theorem* 5.1. *Now we define the closed subspace $\mathcal{H}_n$ of $\mathcal{H}$ to be spanned by the system of eigenfunctions*

$$\{\psi_{klm}; |m| \leq l, l = 0, 1, 2, \cdots, k-1; k = n, n+1, n+2, \cdots\}.$$

Then we have the following :

$$\min_{\psi \in \mathcal{H}_n,\, \|\psi\|=1} J[\psi] = \mathcal{E}_n, \ \ J[\psi_{nlm}] = \mathcal{E}_n,$$

$$(|m| \leq l, l = 0, 1, 2, \cdots, n-1; n = 1, 2, 3, \cdots),$$

$$\mathcal{E}_1 < \mathcal{E}_2 < \cdots < \mathcal{E}_n < \cdots < 0, \ \lim_{n \to \infty} \mathcal{E}_n = 0.$$

Here the multiplicity of the eigenvalue $\mathcal{E}_n$ is equal to n^2, $(n \geq 1)$.

As for Theorem 5.6, we refer to Ito[26].

By virtue of this Theorem, we can see that the solutions $\{\psi_{nlm}\}$, $\{\mathcal{E}_n\}$ of the eigenvalue problem in Theorem 5.1 are the complete solutions of the variational problem for the energy functional $J[\psi]$. Namely this solutions give the necessary and sufficient condition in order that the variational problem is solved.

For the Schrödinger equation for the time evolution of the physical system of the system of hydrogen atoms in the bound state, we have the following theorem.

Theorem 5.7   *Let $\mathcal{H}$ be as in Theorem* 5.4. *We assume that the initial natural probability distribution law of the position variable of this system of hydrogen atoms is given by the L^2-density $\psi(\boldsymbol{r}) \in \mathcal{H}$. Then the L^2-density $\psi(\boldsymbol{r}, t)$ which determines the natural probability distribution law of the position variable at time t is given by the solution of the initial value problem for the time evolving Schrödinger equation*

$$i\hbar \frac{\partial \psi(\boldsymbol{r}, t)}{\partial t} = \left(-\frac{\hbar^2}{2m_e} \Delta - \frac{e^2}{r} \right) \psi(\boldsymbol{r}, t),$$

$$\psi(\boldsymbol{r}, 0) = \psi(\boldsymbol{r}), \ \textit{(Initial Condition)},$$

$$(\boldsymbol{r} \in \boldsymbol{R}^3, \ 0 < t < \infty).$$

Here, by using the Fourier type coefficients $\{c_{nlm}\}$ of the eigenfunction expansion of the initial condition $\psi(\boldsymbol{r})$ in Theorem 5.5, the solution $\psi(\boldsymbol{r}, t)$ in the above is given by the formula

$$\psi(\boldsymbol{r}, t) = \sum_{n=1}^{\infty} \sum_{l=0}^{n-1} \sum_{m=-l}^{l} c_{nlm} \psi_{nlm}(\boldsymbol{r}, t).$$

12

Here we put
$$\psi_{nlm}(\boldsymbol{r}, t) = \psi_{nlm}(\boldsymbol{r}) \exp\left[-i\frac{\mathcal{E}_n}{\hbar}t \right],$$
where (n, l, m) are chosen as in Theorem 5.1.

Then we have $\psi(\boldsymbol{r}, t) \in \mathcal{H}$, $(0 \le t < \infty)$.

6 The Meaning of the spectra of hydrogen atoms

By virtue of the study until section 5, we see that the system Ω of hydrogen atoms in the bound state has the following structure at time t. Namely, we have the direct sum decomposition of Ω as follows :

$$\Omega = \sum_{n=1}^{\infty} \Omega_n, \text{ (direct sum)} \tag{6.1}$$

$$p_n = P(\Omega_n), \ (n = 1, 2, \cdots),$$

$$\sum_{n=1}^{\infty} p_n = 1.$$

Further each Ω_n is decomposed into the direct sum as follows :

$$\Omega_n = \sum_{l=0}^{n-1} \sum_{m=-l}^{l} \Omega_{nlm}, \text{ (direct sum)}$$

$$P(\Omega_{nlm}) = |c_{nlm}|^2,$$

$$p_n = \sum_{l=0}^{n-1} \sum_{m=-l}^{l} |c_{nlm}|^2, \ (n = 1, 2, \cdots),$$

$$\sum_{n=1}^{\infty} p_n = \sum_{n=1}^{\infty} \sum_{l=0}^{n-1} \sum_{m=-l}^{l} |c_{nlm}|^2 = 1.$$

Then we have the following formulas, for every $A \in \mathcal{B}$

$$P(A) = \sum_{n=1}^{\infty} P(\Omega_n) P_{\Omega_n}(A)$$

$$= \sum_{n=1}^{\infty} \sum_{l=0}^{n-1} \sum_{m=-l}^{l} P(\Omega_{nlm}) P_{\Omega_{nlm}}(A).$$

13

Here $P_{\Omega_n}(A)$ and $P_{\Omega_{nlm}}(A)$ are the conditional probabilities.

Here, because we study the spectra of hydrogen atoms, we consider only the principal index n. Therefore we consider the direct sum decomposition (6.1).

Then, we have the following, for any Lebesgue measurable sets A of $\boldsymbol{R}^3$ and B of $\boldsymbol{R}_3$,

$$P_{\Omega_{nlm}}(\{\rho \in \Omega_{nlm}; \boldsymbol{r}(\rho) \in A\}) = \int_A |\psi_{nlm}(\boldsymbol{r})|^2 d\boldsymbol{r},$$

$$P_{\Omega_{nlm}}(\{\rho \in \Omega_{nlm}; \boldsymbol{p}(\rho) \in B\}) = \int_B |\hat{\psi}_{nlm}(\boldsymbol{p})|^2 d\boldsymbol{p}.$$

Therefore the energy expectation value of the proper subsystem Ω_{nlm} of hydrogen atoms is equal to

$$E_{\Omega_{nlm}}\left[\frac{1}{2m}\boldsymbol{p}(\rho)^2 - \frac{e^2}{r}\right] = J[\psi_{nlm}] = \mathcal{E}_n,$$

$$(|m| \le l, l = 0, 1, \cdots, n-1; n = 1, 2, \cdots).$$

Then, by virtue of the relation of the total system of hydrogen atoms and the proper subsystems of hydrogen atoms, the energy expectation value $\overline{E}$ of the total system of hydrogen atoms is equal to

$$\overline{E} = E\left[\frac{1}{2m}\boldsymbol{p}(\rho)^2 - \frac{e^2}{r}\right]$$

$$= \sum_{n=1}^{\infty}\sum_{l=0}^{n-1}\sum_{m=-l}^{l} P(\Omega_{nlm})E_{\Omega_{nlm}}\left[\frac{1}{2m}\boldsymbol{p}(\rho)^2 - \frac{e^2}{r}\right]$$

$$= \sum_{n=1}^{\infty}\sum_{l=0}^{n-1}\sum_{m=-l}^{l} |c_{nlm}|^2 \mathcal{E}_n = \sum_{n=0}^{\infty} \mathcal{E}_n p_n$$

$$= -\frac{m_e e^4}{2\hbar^2}\sum_{n=1}^{\infty}\frac{1}{n^2}p_n.$$

The system of hydrogen atoms in the bound state is realized as the state of mixture of the proper subsystems of hydrogen atoms at each time t. The subsystem Ω_n of hydrogen atoms with the energy expectation value $\mathcal{E}_n$ is the state of mixture of the n^2 proper subsystems Ω_{nlm} of hydrogen atoms, $(|m| \le l, l = 0, 1, \cdots, n-1)$.

The ratio of mixture of these subsystems Ω_n is determined by the sequence $\{p_n\}_{n=1}^{\infty}$.

Then, by virtue of the motion of the electrons in the hydrogen atoms according to Coulomb force, the L^2-densities $\psi_{nlm}(\boldsymbol{r}, t)$ and $\psi(\boldsymbol{r}, t)$ are varying with time t. Then the values of $\{p_n\}$ are varying with time t together with it.

Therefore each hydrogen atom composing the subsystem with the mean energy $\mathcal{E}_n$ is varying its belonging to the proper subsystems together with time t.

Thereby, when these hydrogen atoms move from the subsystem with the mean energy $\mathcal{E}_n$ to the subsystem with the mean energy $\mathcal{E}_m$, the spectral line corresponding to the difference of these mean energies

$$\mathcal{E}_n - \mathcal{E}_m$$

is observed. This coincides well with the distribution of the spectrum observed practically for the hydrogen atoms.

As the historical result, the spectrum of hydrogen atoms are known to be as follows.

Here we remember the Bohr's law established in 1913.

Bohr's law   We use the above notation. Then, ν being the oscillation number of observed light, we have the relation

$$h\nu = \mathcal{E}_n - \mathcal{E}_m.$$

Here h denotes the Planck constant.

Then, from the consideration in the above, the value of ν is equal to

$$\nu = \frac{m_e e^4}{4\pi\hbar^3}\left(\frac{1}{m^2} - \frac{1}{n^2}\right).$$

Here m_e denotes the mass of the electron.

Here, in the case $m = 2$, this result coincides with the spectral line of the visible light from the hydrogen atoms discovered by Balmer in 1885. This is now called to be the Balmer sequence.

The spectral sequences known until now are the following.

Writing by virtue of the representation of Rydberg, these are the following.

(1)   Lyman sequence (discovered in 1906) :

$$\nu = Rc\left(\frac{1}{1^2} - \frac{1}{n^2}\right), \ (n = 2, 3, \cdots).$$

(2)   Balmer sequence (discovered in 1885) :

$$\nu = Rc\left(\frac{1}{2^2} - \frac{1}{n^2}\right), \ (n = 3, 4, \cdots).$$

(3)   Paschen sequence (discovered in 1908) :

$$\nu = Rc\left(\frac{1}{3^2} - \frac{1}{n^2}\right), \ (n = 4, 5, \cdots).$$

(4) Brackett sequence (discovered in 1922) :

$$\nu = Rc\left(\frac{1}{4^2} - \frac{1}{n^2}\right), \ (n = 5, 6, \cdots).$$

(5) Pfund sequence (discovered in 1924) :

$$\nu = Rc\left(\frac{1}{5^2} - \frac{1}{n^2}\right), \ (n = 6, 7, \cdots).$$

Here R is said to be Rydberg's constant and its value is given as follows :

$$R = 1.09737 \times 10^5 \text{cm}^{-1}, \ \text{(observed value)},$$

$$Rch = 13.61\text{eV}, \ \text{(dimension of energy)}.$$

By virtue of the condition in the above, R is equal to

$$R = \frac{m_e e^4}{4\pi c\hbar^3}$$

as the theoretically evaluated value. Here, the constant c denotes the velocity of light.

By virtue of the consideration in the above, we can see that the theoretical value and the observed value of R coincide well.

The Bohr's law described in the above was demonstrated by the experiment of Franck-Hertz in 1914. By taking account of the observed data of the experiment of Franck-Hertz, it is evident that the regularity such as Bohr's law holds for the mean values $\mathcal{E}_n$ of the energy.

Thus the spectral lines of the hydrogen atoms known until now are understood and explained naturally and rationally by virtue of the theory of the natural statistical physics.

7 On the stability of the hydrogen atoms

Here we consider the problem of the stability of the hydrogen atoms.

As for the result of this section, we refer to Ito[20].

If one hydrogen atom is isolated, its electron is rotating around the nucleus and has emitted its total energy as the electro-magnetic waves. Finally this electron has fallen onto the nucleus and stops its motion relatively. Therefore the hydrogen atom does not keep its stable state.

Nevertheless the hydrogen atom existing in the nature keeps its stable state. It is the great question why is it so. This can be understood as follows by using the theory of the natural statistical physics.

In general, the physical state of a physical system moves toward the equilibrium state of the energy or the thermal equilibrium state. On the basis of this fact, we show that we can understand and explain the phenomena of stability of the hydrogen atoms completely.

If the hydrogen atoms exist collectively, the state of the system of hydrogen atoms moves toward the thermal equilibrium state. Namely, if the energy of one hydrogen atom becomes higher than the energy of the system around it, it emits the energy and moves toward the equilibrium state with the system around it. Further if the energy of one hydrogen atom becomes lower than the energy of the physical system around it, it absorbs the energy and moves toward the equilibrium state with the system around it.

This emission and absorption of the energy are observed as the spectrum of emission and the spectrum of absorption of the hydrogen atoms. By virtue of this mode of movement of the physical system, the hydrogen atoms keep their stable states.

This is the solution of the problem of stability of the hydrogen atoms.

Thus each hydrogen atom always gives and takes the heat by virtue of the mutual interaction with the surrounding hygrogen atoms and others. It is considered that the Schrödinger equation gives the state of the natural statistical distribution in such a equilibrium state. The equilibrium state does not mean that there is no interaction with the surrounding matter, but it means that the thermal equilibrium is kept under the interaction with the surrounding matter. The state of the natural statistical distribution given by the Schrödinger equation concerns only with understanding the natural statistical phenomena of the physical state under the thermal equilibrium states insistently without entering the analysis of the mutual interaction. The Schrödinger equation is the approximating model in such a sense.

References

[1]   Y. Ito, *Theory of Hypo-probability Measures*, RIMS Kôkyûroku, **558**(1985), 96-113, (in Japanese).

[2]   ———, *Linear Algebra*, Kyôritu, 1987, (in Japanese).

[3]   ———, *Analysis*, Vol. **1**, Science House, 1991, (in Japanese).

[4]   ———, *Mathematical Statistics*, Science House, 1991, (in Japanese).

[5]   ———, *New Axiom of Quantum Mechanics–Hilbert's 6th Problem–*, J. Math. Tokushima Univ., **32**(1998), 43-51.

[6]   ———, *New Axiom of Quantum Mechanics–Hilbert's 6th Problem–*, Real Analysis Symposium 1998 Takamatsu, pp.96-103, 1998.

[7] ———, *Axioms of Arithmetics*, Science House, 1999, (in Japanese).

[8] ———, *Mathematical Principles of Quantum Mechanics. New Theory*, Science House, 2000, (in Japanese).

[9] ———, *Theory of Quantum Probability*, J. Math. Tokushima Univ., **34**(2000), 23-50.

[10] ———, *Foundation of Analysis*, Science House, 2002, (in Japanese).

[11] ———, *Theory of Measure and Integration*, Science House, 2002, (in Japanese).

[12] ———, *Analysis*, Vol. **2**, Revised Ed. Science House, 2002, (in Japanese).

[13] ———, *New Quantum Theory. Present Situation and Problems*, Natural Science Research, Faculty of Integrated Arts and Sciences, The University of Tokushima, **18**(2004), 1-14, (in Japanese).

[14] ———, *New Quantum Theory. Present Situation and Problems*, Real Analysis Symposium 2004 Osaka, pp.181-199, 2004, (in Japanese).

[15] ———, *Fundamental Principles of New Quantum Theory*, Natural Science Research, Faculty of Integrated Arts and Sciences, The University of Tokushima, **19**(2005), 1-18, (in Japanese).

[16] ———, *New Quantum Theory*, Vol. **I**, Science House, 2006, (in Japanese).

[17] ———, *Black Body Radiation and Planck's Law of Radiation*, RIMS Kôkyûroku **1482**(2006), 86-100, Research Institute of Mathematical Sciences, Kyoto University, (Application of Renormalization Group in the Mathematical Sciences, 2005.9.7~9.9, Organizer Keiichi R. Ito), (in Japanese).

[18] ———, *Fundamental Principles of New Quantum Theory*, Real Analysis Symposium 2006 Hirosaki, pp.25-28, 2006, (in Japanese).

[19] ———, *Solutions of Variational Problems and Derivation of Schrödinger Equations*, Real Analysis Symposium 2006 Hirosaki, pp.29-32, 2006, (in Japanese).

[20] ———, *New Quantum Theory*, Vol. **II**, Science House, 2007, (in Japanese).

[21] ———, *New Meanings of Conditional Convergence of Integrals*, Real Analysis Symposium 2007 Osaka, pp.41-44, 2008, (in Japanese).

[22]   ———, *New Solutions of Some Variational Problems and the Derivation of Schrödinger Equations*, Complex Analysis and its Applications, Eds., Yoichi Imayoshi, Yohei Komori, Masaharu Nisio, and Ken-ichi Sakan, pp. 213-217, 2008, OMUP(Osaka Municipal University Press). (Proceedings of the 15th International Conference on Finite or Infinite Complex Analysis and Applications, July 30 ∼ August 3, 2007, Osaka City University).

[23]   ———, *Vector Analysis*, Science House, 2008, (in Japanese).

[24]   ———, *What are Happening in the Physics of Electrons, Atoms and Molecules? Physical Reality Revisited*, RIMS Kôkyûroku, **1600**(2008), 113-131, Research Institute of Mathematical Sciences of Kyoto University, Kyoto. (Symposium at RIMS of Kyoto University, Applications of Renormalization Group Methods in Mathematical Sciences, September 12 ∼ September 14, 2007, Organizer, Keiichi R. Ito).

[25]   ———, *Fundamental Principles of Natural Statistical Physics*, Science House，2009, (in Japanese).

[26]   ———, *Natural Statistical Physics* , preprint, 2009, (in Japanese).

[27]   Y. Ito and K. Kayama, *Variational Principles and Schrödinger Equations*, Natural Science Research, Faculty of Integrated Arts and Sciences, The University of Tokushima, **15**(2002), 1-7, (in Japanese).

[28]   ———, *Variational Principles and Schrödinger Equations*, RIMS Kôkyûroku, **1278**(2002), 86-95, (in Japanese).

[29]   Y. Ito, K. Kayama and Y. Kamosita, *New Quantum Theory and New Meanings of Planck's Radiatin Formula*, Natural Science Research, Faculty of Integrated Arts and Sciences, The University of Tokushima, **16**(2003), 1-10, (in Japanese).

[30]   Y. Ito and Md Sharif Uddin, *New Quantum Theory and New Meaning of Specific Heat of a Solid*, J. Math. Univ. Tokushima, **38**(2004), 17-27.

[31]   ———, *New Quantum Theory and New Meaning of Specific Heat of an Ideal Gas*, J. Math. Univ. Tokushima, **38**(2004), 29-40.