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Study on the Spectra of Hydrogen Type Ions

(Y. Ito, "Foundation of Natural Statistical Physics", Chap.17)

By

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Abstract

In this paper, we study the spectra of hydrogen type ions by using the method of Natural Statistical Physics.

As for the results in this paper, we refer to Y. Ito [20] and [44].

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1 Physical system composed of hydrogen type ions

In this section, we study the physical system of hydrogen type ions.

The simplest atom is the hydrogen atom such that one electron is rotating around the nucleus. As for the spectra of the hydrogen atom, we refer to Y. Ito [15], Chapter 13 and Y. Ito [44], Chapter 15.

As for the hydrogen type ions He^{+}, Li^{++}, Be^{+++}, $\cdots$, we study the mathematical model such as one electron is rotating around the nucleus in the

similar way as the hydrogen atom. Thereby we can understand the spectra of the hydrogen type ion.

In the case of the atom which has the several electrons, the nucleus makes the combined system with the several electrons by virtue of the action of the strong force of the nucleus in the center.

Then these electrons have the shell type structure. The mutual interaction of these electrons is considered to be the effect of the shield of the charge of the nucleus by virtue of the electrons inside this shell.

Thereby, we can analyze the spectra of the hydrogen type ion by using the similar model as the hydrogen atom.

Then some electrons move into the inside of the shell. Therefore the fluctuation of the spectra of hydrogen type ion happens to appear.

We understand and explain the observed data of the spectra of the hydrogen type ions on the bases of the laws of the natural statistical physics.

Here we consider the system of hydrogen type ions such as we need not consider the influence of the spin. They are the cases where there is not the influence of the outer electro-magnetic field or where we can neglect such an influence.

One hydrogen type ion is the combined system of two particles composed of one nucleus and one electron rotating around it. The physical system of those hydrogen type ion is an example of the system of two particles.

Each hydrogen type ion is moving in the 3-dimensional space.

Assume that the masses of the nucleus and the electron are m_1 and m_2 respectively. Further we assume that the electric charges of the nucleus and the electron are Ze and $-e$ respectively.

Here we assume $Z \geq 1$.

Then, when we consider the shell type structure of the electrons, it is necessary to consider the shield effect by this shell type structure. Thereby we must consider the electric charge of the nucleus Ze to be $Z'e$, where we must choose $Z' < Z$ properly instead of the atomic number Z. In the sequel, for the simplicity of the notation, we happen to identify Z' with Z.

Then we denote the position variables of a nucleus and an electron as $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ respectively. Then the position variable of a hydrogen type ion is expressed as $\boldsymbol{r} = (\boldsymbol{r}_1,\ \boldsymbol{r}_2)$

We denote the momentum variables of a nucleus and an electron as $\boldsymbol{p}_1$ and $\boldsymbol{p}_2$ respectively. Then the momentum variable of a hydrogen type ion is expressed as $\boldsymbol{p} = (\boldsymbol{p}_1,\ \boldsymbol{p}_2)$.

We assume that we can neglect the mutual interaction between the different hydrogen type ions.

There is the mutual interaction by virtue of the action of the potential

$$V(\boldsymbol{r}) = -\frac{Ze^2}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|}$$

between a nucleus and an electron of one hydrogen type ion.

Because the masses of a nucleus and an electron are very small, we can neglect the gravitational interaction.

Then each hydrogen type ion is moving by virtue of the Newtonian equation of motion

$$\frac{d\boldsymbol{p}}{dt} = -\mathrm{grad}\, V(\boldsymbol{r}).$$

Therefore the total energy of one hydrogen type ion

$$\sum_{i=1}^{2} \frac{1}{2m_i}|\boldsymbol{p}_i|^2 + V(\boldsymbol{r})$$

does not depend on the time t.

Here the first term denotes the kinetic energy of a hydrogen type ion and the second term denotes the potential energy of a hydrogen type ion.

Namely the conservation law of the total energy of each hydrogen type ion holds.

2 Setting of the mathematical model

In this section, we study the setting of the mathematical model for the study of the natural statistical phenomena of the spectra of the hydrogen type ions.

Here we assume that the physical system considered here is the probability space $\Omega = \Omega(\mathcal{B},\ P)$. Its elementary event ρ is one hydrogen type ion moving in the 3-dimensional space $\boldsymbol{R}^3$. This hydrogen type ion is the combined system of two particles composed of one nucleus and one electron.

Therefore the considered physical system is an example of the system of two particles.

Then the position variable $\boldsymbol{r}(\rho)$ of one hydrogen type ion ρ is the pair $\boldsymbol{r}(\rho) = (\boldsymbol{r}_1(\rho),\ \boldsymbol{r}_2(\rho))$ of the position variable $\boldsymbol{r}_1(\rho)$ of a nucleus and the position variable $\boldsymbol{r}_2(\rho)$ of an electron. Corresponding to this, the momentum variable $\boldsymbol{p}(\rho)$ of one hydrogen type ion ρ is the pair $\boldsymbol{p}(\rho) = (\boldsymbol{p}_1(\rho),\ \boldsymbol{p}_2(\rho))$ of the momentum variable $\boldsymbol{p}_1(\rho)$ of a nucleus and the momentum variable $\boldsymbol{p}_2(\rho)$ of an electron.

Then the variable $\boldsymbol{r}$ changes in the space $\boldsymbol{R}^6$ and the variable $\boldsymbol{p}$ changes in its dual space $\boldsymbol{R}_6$.

Further the variables $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ change in the space $\boldsymbol{R}^3$ and the variables $\boldsymbol{p}_1$ and $\boldsymbol{p}_2$ change in its dual space $\boldsymbol{R}_3$.

Here, since the 3-dimensional Euclidean space $\boldsymbol{R}^3$ is self-dual, we identify the Euclidean space $\boldsymbol{R}^3$ and its dual space and we denote the 3-dimensional Euclidean space and its dual space as the same symbol $\boldsymbol{R}^3$. We use the similar notation for $\boldsymbol{R}^6$ and $\boldsymbol{R}_6$.

The mutual interaction of the force of the Coulomb potential

$$V(\boldsymbol{r}) = -\frac{Ze^2}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|}$$

is working between a nucleus and an electron.

Then the total energy of each hydrogen type ion ρ is determined by virtue of the Newtonian mechanics. Its value is equal to

$$\sum_{i=1}^{2} \frac{1}{2m_i}|\boldsymbol{p}_i(\rho)|^2 + V(\boldsymbol{r}(\rho)).$$

Here the masses of a nucleus and an electron are m_1 and m_2 respectively and the electric charges of a nucleus and an electron are Ze and $-e$ respectively.

We consider that this energy variable is a natural random variable on the probability space Ω. This is a continuous random variable.

Then we consider that $\boldsymbol{r} = \boldsymbol{r}(\rho)$ and $\boldsymbol{p} = \boldsymbol{p}(\rho)$ have the different values for each hydrogen type ion ρ and, in general, these values distribute randomly. In this sense, we can consider that $\boldsymbol{r} = \boldsymbol{r}(\rho)$ and $\boldsymbol{p} = \boldsymbol{p}(\rho)$ are two random variables and it is the forms of phenomena as the natural statistical phenomena that, especially, they are the natural random variables on the physical system.

We assume that the hydrogen type ion considered here is always in the bound state. Therefore, in this case, the Schrödinger operator determined afterwards has only the negative discrete eigen-values.

Then, by virtue of Law II in Y. Ito [44], Section 2.2, the natural random distribution law of $\boldsymbol{r} = \boldsymbol{r}(\rho)$ is determined by the L^2-density $\psi(\boldsymbol{r})$ and the natural random distribution law of $\boldsymbol{p} = \boldsymbol{p}(\rho)$ is determined by its Fourier transform $\hat{\psi}(\boldsymbol{p})$.

Then we have the expectation value $\overline{E}$ of the energy variable of the total physical system as follows:

$$\begin{aligned}
\overline{E} &= E\left[\sum_{i=1}^{2} \frac{1}{2m_i}|\boldsymbol{p}_i(\rho)|^2 + V(\boldsymbol{r}(\rho))\right] \\
&= E\left[\sum_{i=1}^{2} \frac{1}{2m_i}|\boldsymbol{p}_i(\rho)|^2\right] + E\left[V(\boldsymbol{r}(\rho))\right] \\
&= \int \left(\sum_{i=1}^{2} \frac{1}{2m_i}|\boldsymbol{p}_i|^2\right)\left|\hat{\psi}(\boldsymbol{p})\right|^2 d\boldsymbol{p} + \int V(\boldsymbol{r})|\psi(\boldsymbol{r})|^2 d\boldsymbol{r} \\
&= \int \left\{\sum_{i=1}^{2} \frac{\hbar^2}{2m_i}|\nabla_{\boldsymbol{r}_i}\psi(\boldsymbol{r})|^2 + V(\boldsymbol{r})|\psi(\boldsymbol{r})|^2\right\} d\boldsymbol{r}.
\end{aligned}$$

Here we use the Plancherel's equality for the Fourier transformation. Further the integral domain is considered to be the whole space.

Then we denote this **energy expectation value** as the formula

$$J[\psi] = \int \Big\{ \sum_{i=1}^{2} \frac{\hbar^2}{2m_i} |\nabla_{\boldsymbol{r}_i} \psi(\boldsymbol{r})|^2 + V(\boldsymbol{r}) |\psi(\boldsymbol{r})|^2 \Big\} \, d\boldsymbol{r}.$$

We say that $J[\psi]$ is the **energy functional**.

We can obtain the L^2-density which is really realized as the solution of the variational problem for this functional in the stationary state.

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

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

Thereby, we can choose the L^2-density $\psi(\boldsymbol{r})$ of the natural probability distribution of the position variable $\boldsymbol{r} = \boldsymbol{r}(\rho)$ of the hydrogen type ion ρ, which is really realized in the stationary state among the admissible L^2-densities.

The L^2-density $\psi(\boldsymbol{r})$ obtained as the solution of the variational problem in the above determines the really observed natural statistical phenomena.

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

Problem I (Variational problem) Among the admissible L^2-densities ψ, determine the L^2-density ψ so that the energy functional $J[\psi]$ has the stationary value.

3 Mathematical analysis

In this section, we carry out the mathematical analysis for the mathematical model considered in Section 2.

By solving the variational problem in Section 2, we solve the Schrödinger equation in the stationary state for the system of hydrogen type ions.

We have the following Schrödinger equation

$$\Big(-\frac{\hbar^2}{2m_1}\Delta_1 - \frac{\hbar^2}{2m_2}\Delta_2 - \frac{Ze^2}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} \Big) \psi = \mathcal{E}\psi \tag{3.1}$$

as the Euler equation for the variational problem of Problem I in Section 2. Here $\mathcal{E}$ is the Lagrange's indeterminate multiplier. Further $\Delta_1 = \Delta_{\boldsymbol{r}_1}$ and $\Delta_2 = \Delta_{\boldsymbol{r}_2}$ denote the Laplace operators with respect to the variables $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ respectively.

The L^2-density ψ, which is the solution of the variational problem of Problem I, is obtained as the solution of the Schrödinger equation in the above.

By the similar consideration as same as the argument until now, we have the time-evolving Schrödinger equation

$$i\hbar\frac{\partial\psi(\boldsymbol{r},\ t)}{\partial t} =\Big(-\frac{\hbar^2}{2m_1}\Delta_1 - \frac{\hbar^2}{2m_2}\Delta_2 - \frac{Ze^2}{|\boldsymbol{r}_1-\boldsymbol{r}_2|}\ \Big)\ \psi(\boldsymbol{r},\ t).$$

When we consider the motion of the system of two particles by virtue of the Newtonian mechanics, we happen to consider it by the separation of the center of gravity. As for its outline, we refer to Y. Ito [15], Section 13.5 and Y Ito [44], Chapter 15.

Then the motion of the center of gravity is the linear motion with constant velocity.

On the other hand, the relative motion is the motion of one particle with the converted mass

$$\mu = \frac{m_1m_2}{m_1+m_2}$$

under the action of the potential $V(r)$ of the central force.

Corresponding to this, we may consider the separation of the center of gravity for the Schrödinger equation.

Then the motion of the center of gravity is considered as the motion of the system of free particles with the mass $M = m_1 + m_2$.

On the other hand, the relative motion is considered as the motion of the system of one particle composed of the micro-particles with the converted mass μ under the action of the potential $V(r)$ of the central force.

Really, the observed result of the spectra of the hydrogen type ions are the effects of this relative motion.

We consider that the effect of the motion of the center of gravity can be neglected.

Therefore, in the real, we may consider that the center of gravity is motionless.

This is a very rough approximation of the real phenomena.

Then, since the converted mass μ is nearly equal to the mass m_e of an electron, really we may consider the approximation in the following in order to solve the Schrödinger equation (3.1).

As the first approximation, we consider that a nucleus is infinitely heavy and we treat the system of hydrogen type ions as the system of particles composed of electrons in the field of Coulomb force $-\dfrac{Ze^2}{r}$.

Therefore we consider that the physical system considered here is the probability space $\Omega = \Omega(\mathcal{B},\ P)$ composed of electrons moving under the conditions in the above. This is the system of one particle.

Here we consider that a nucleus is stopped at a point and we consider the orthogonal coordinate system so that this point is the origin.

Then we denote the position variable of one electron ρ as $\boldsymbol{r} = \boldsymbol{r}(\rho)$ and the momentum variable of ρ as $\boldsymbol{p} = \boldsymbol{p}(\rho)$.

Then the variable $\boldsymbol{r}$ changes in the space $\boldsymbol{R}^3$ and the variable $\boldsymbol{p}$ changes in its dual space $\boldsymbol{R}^3$.

Here each electron is moving under the action of the potential

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

Then we have the Schrödinger equation

$$\Big(-\frac{\hbar^2}{2m_e}\Delta - \frac{Ze^2}{r} \Big)\ \psi(\boldsymbol{r}) = \mathcal{E}\psi(\boldsymbol{r})$$

which describes the stationary state of the system of electrons. Here $\Delta = \boldsymbol{\Delta}_{\boldsymbol{r}}$ denotes the Laplace operator with respect to $\boldsymbol{r}$ and we put $r = |\boldsymbol{r}|$. We denote the mass of an electron as m_e.

By deforming this, we have the equation

$$\Delta\psi + \frac{2m_e}{\hbar^2}\ \Big(\mathcal{E} + \frac{Ze^2}{r} \Big)\ \psi = 0.$$

At first, because we have

$$\lim_{r\to\infty}\ \Big(-\frac{Ze^2}{r} \Big) = 0,$$

we remark that $\mathcal{E} < 0$ holds in the bound state.

Then we put $\mathcal{E} = -|\mathcal{E}|$.

Here we consider the polar coordinate expression in the 3-dimensional space. This is expressed as follows:

$$\begin{cases} x = r\sin\,\theta\cos\,\phi, \\ \\ y = r\sin\,\theta\sin\,\phi, \\ \\ z = r\cos\,\theta, \end{cases}$$

$$(r > 0,\ 0 \le \theta \le \pi,\ 0 \le \phi < 2\pi).$$

Therefore the Jacobian of this coordinate transformation is equal to

$$J = r^2\,\sin\,\theta.$$

Then, for a function $\psi(\boldsymbol{r}) = \psi(x,\ y,\ z)$, we have the formula of the coordinate transformation of the integral

$$\int\ \psi(\boldsymbol{r})d\boldsymbol{r} = \iiint\ \psi(x,\ y,\ z)dxdydz$$

$$= \iiint\ \psi\ \Big(r\sin\,\theta\cos\,\phi,\ r\sin\,\theta\sin\,\phi,\ r\cos\,\theta \Big)\ r^2\sin\,\theta dr d\theta d\phi.$$

Here the integration domain is the whole space $\boldsymbol{R}^3$. In general, for a function $\psi(x,\ y,\ z) = \psi(r,\ \theta,\ \phi)$, the Laplace operator Δ is expressed as follows:

$$\Delta\psi = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}.$$

Therefore, if we use the polar coordinate in the above, we can separate the variable as follows:

$$\psi(r,\ \theta,\ \phi) = R(r)Y_l^m(\theta,\ \phi).$$

Then the radial function $R(r)$ is the solution of the equation

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \left\{ \frac{2m_e}{\hbar^2}\left(-|\mathcal{E}| + \frac{Ze^2}{r}\right) - \frac{l(l+1)}{r^2}\right\} R = 0.$$

Here, by the transformation of variables as follows, we rewrite this equation to the dimensionless equation:

$$s = \alpha r,\ \alpha^2 = \frac{8m_e|\mathcal{E}|}{\hbar^2},\ \lambda = \frac{Ze^2}{\hbar}\left(\frac{m_e}{2|\mathcal{E}|}\right)^{1/2}.$$

Then $R(s)$ satisfies the equation

$$\frac{1}{s^2}\frac{d}{ds}\left(s^2\frac{dR}{ds}\right) + \left(\frac{\lambda}{s} - \frac{1}{4} - \frac{l(l+1)}{s^2}\right) R = 0.$$

When s is sufficiently large, the solution behaves as $R \sim e^{-s/2}$. Thus, if we put

$$R(s) = f(s)e^{-s/2},$$

$f(s)$ satisfies the equation

$$\frac{d^2f}{ds^2} + \left(\frac{2}{s} - 1\right)\frac{df}{ds} + \left(\frac{\lambda - 1}{s} - \frac{l(l+1)}{s^2}\right) f = 0.$$

Then we determine R so that it is a L^2-function.

Now, putting

$$f(s) = s^l(a_0 + a_1s + a_2s^2 + \cdots) \equiv s^lL(s),\ a_0 \neq 0,$$

$L(s)$ satisfies the equation

$$s\frac{d^2L}{ds^2} + \left(2(l+1) - s\right)\frac{dL}{ds} + (\lambda - l - 1)L = 0.$$

Thereby, the coefficients a_ν satisfy the iteration formula

$$a_{\nu+1} = \frac{\nu + l + 1 - \lambda}{(\nu+1)(\nu+2l+2)}a_\nu.$$

Therefore we have the formula

$$\frac{a_{\nu+1}}{a_\nu} \sim \frac{1}{\nu},\ (\nu \to \infty).$$

Then, if $L(s)$ is an infinite series, we have $L(s) \sim e^s,\ (s \to \infty)$ and $R(s)$ is not a L^2-function.

Therefore, $L(s)$ must be a polynomial.

Hence, there exists a natural number n_r so that

$$\lambda = n_r + l + 1 \equiv n$$

holds.

Thereby, we see that the eigen-values $\mathcal{E}$ are equal to

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

Now we assume that the function $L_n^{(m)}(z)$ denotes the polynomial solution

$$L_n^{(m)}(z) = \frac{1}{n!} z^{-m} e^z \frac{d^n}{dz^n}(z^{n+m} e^{-z})$$

of the equation

$$z\frac{d^2}{dz^2}L_n^{(m)}(z) + (m+1-z)\frac{d}{dz}L_n^{(m)}(z) + nL_n^{(m)}(z) = 0,$$

$$(n = 0,\ 1,\ 2,\ \cdots;\ m = 1,\ 2,\ \cdots).$$

We say that this function $L_n^{(m)}(z)$ is the **Laguerr's bi-polynomial**.

Then the following normalization condition is satisfied:

$$\int_0^\infty e^{-z} z^{2l} \left[\ L_{n+l}^{(2l+1)}(z)\ \right]^2 z^2 dz = \frac{2n[(n+l)!]^3}{(n-l-1)!}.$$

Therefore, if we define the solution $R(r) = R_{nl}(r)$ as

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

$$s = \frac{2}{na_0} r,\ a_1 = \frac{a_0}{Z},\ a_0 = \frac{\hbar^2}{m_e e^2},$$

the ortho-normality condition of the radial function $R_{nl}(r)$ is satisfied in the following.

Theorem 3.1(Ortho-normality condition) *We use the notation in the above. Then we have the following equalities*:

$$\int_0^\infty R_{n'l}(r)^* R_{nl}(r) r^2 dr = \delta_{nn'},\ (n,\ n' = 1,\ 2,\ \cdots).$$

In the next, we assume that the spherical function $Y_l^m(\theta,\ \phi)$ is the simultaneous eigen-function solution of the equation

$$-\left[\ \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\ \sin\theta\frac{\partial}{\partial\theta}\ \right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\ \right]Y_l^m(\theta,\ \phi),$$

$$=l(l+1)Y_l^m(\theta,\ \phi),$$

$$-i\frac{\partial}{\partial\phi}Y_l^m(\theta,\ \phi)=mY_l^m(\theta,\ \phi),$$

$$(|m|\leq l,\ l=0,\ 1,\ \cdots,\ n-1).$$

The spherical function $Y_l^m(\theta,\ \phi)$ is expressed as

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

Then, we say that $P_l(x)$ and $P_l^m(x),\ (|x|\leq 1)$ are the **Legendre's polynomial** and the **Legendre's bi-polynomial** respectively and we define them in the following formulas respectively:

$$P_l(x)=\frac{1}{2^l l!}\frac{d^l}{dx^l}(x^2-1)^l,$$

$$P_l^m(x)=\frac{1}{2^l l!}(1-x^2)^{\frac{|m|}{2}}\frac{d^{l+|m|}}{dx^{l+|m|}}(x^2-1)^l$$

$$=(1-x^2)^{\frac{|m|}{2}}\frac{d^{|m|}}{dx^{|m|}}P_l(x),\ (|m|\leq l).$$

Then $P_l^m(x),\ (|m|\leq l)$ are the polynomial solutions of the **Legendre's associated differential equation**

$$(1-x^2)\frac{d^2}{dx^2}P_l^m(x)-2x\frac{d}{dx}P_l^m(x)$$

$$+\left(\ l(l+1)-\frac{m^2}{1-x^2}\ \right)P_l^m(x)=0.$$

For these functions, the following two ortho-normality conditions are satisfied.

Theorem 3.2 (Ortho-normality condition) *We use the notation in the above. Then we have the following equality*:

$$\int_{-1}^{1}P_l^m(x)P_{l'}^m(x)dx=\frac{2}{(2l+1)}\frac{(l+|m|)!}{(l-|m|)!}\delta_{ll'}.$$

Theorem 3.3 (Ortho-normality condition) *We use the notation in the above. Then we have the following equality*:

$$\int_0^{2\pi} d\phi \int_0^{\pi} Y_{l'}^{m'}(\theta,\ \phi)^* Y_l^m(\theta,\ \phi) \sin\theta d\theta = \delta_{ll'}\delta_{mm'}.$$

Then n is said to be a **principal index**. If we fix the principal index n, the **point index** l can takes the n values $0,\ 1,\ 2,\ \cdots, n-1$. Further, for each value of l, the **magnetic index** m can takes the $(2l+1)$ values $-l,\ -l+1,\ \cdots,\ l-1,\ l$.

Here we used to denote m as the magnetic index. Even though we denote the mass of an electron as m also, it is the convention that we venture to use the same letter.

Therefore, for one fixed value n, there are the

$$\sum_{l=0}^{n-1}(2l+1) = n^2$$

linearly independent eigen-functions and they are associated with the same eigen-value $\mathcal{E}_n$.

The $(2l+1)$ eigen-functions are degenerated for one l because the potential is spherically symmetric, and the eigen-value $\mathcal{E}_n$ is determined by only one principal index n and it does not depend on l because the potential is the Coulomb potential.

Then the eigen-functions of the system of hydrogen type ions in the stationary state are given as follows.

Namely, the eigen-functions associated with the indices $n,\ l$ and m are given with the consideration of the normalization condition as follows:

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

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

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

Here we put

$$s = \frac{2}{na_1}r,\ a_1 = \frac{a_0}{Z},\ a_0 = \frac{\hbar^2}{m_e e^2}.$$

By the consideration in the above, we have the solution of the eigen-value problem of the Schrödinger equation for the system of hydrogen type ions.

Namely, we have the following.

Theorem 3.4 (Eigen-value problem) *The function* $\psi_{nlm}(x,\ y,\ z) = \psi_{nlm}(r,\ \theta,\ \phi)$ *defined in the above is the eigen-function of the* Schrödinger *operator*

$$H = -\frac{\hbar^2}{2m_e}\Delta - \frac{Ze^2}{r}$$

associated with the eigen-value

$$\mathcal{E}_n = -\frac{m_e Z^2 e^4}{2\hbar^2 n^2} = -\frac{Z^2\hbar^2}{2m_e a_0^2}\frac{1}{n^2} = -\frac{\hbar^2}{2m_e a_1^2}\frac{1}{n^2}.$$

Namely, we have the following equality

$$\Big(-\frac{\hbar^2}{2m_e}\Delta - \frac{Ze^2}{r} \Big)\ \psi_{nlm} = \mathcal{E}_n \psi_{nlm},$$

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

Then the eigen-functions

$$\psi_{nlm}(\boldsymbol{r}) = \psi_{nlm}(x,\ y,\ z) = \psi_{nlm}(r,\ \theta,\ \phi)$$

in Theorem 3.4 satisfy the following ortho-normality condition.

Theorem 3.5(Ortho-normality condition) *We use the notation in the above. Then we have the following equalities*:

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

Further, the system of eigen-functions $\{\psi_{nlm}(\boldsymbol{r})\}$ in the above satisfies the following completeness condition.

Theorem 3.6 (Completeness condition) *We use the notation in the above. Then we have the following equalities*:

$$\sum_{n=1}^{\infty}\sum_{l=0}^{n-1}\sum_{m=-l}^{l} \psi_{nlm}(\boldsymbol{r}')^* \psi_{nlm}(\boldsymbol{r}) = \delta(\boldsymbol{r}' - \boldsymbol{r}),\ (\boldsymbol{r}'.\, \boldsymbol{r} \in \boldsymbol{R}^3).$$

Namely, the system of eigen-functions $\{\psi_{nlm}\}$ in the above is the complete ortho-normal system.

Then Theorem 3.6 is equivalent to Corollary 3.1 in the following.

Corollary 3.1 *For* $\psi(\boldsymbol{r}) \in L^2$, *we have the following equality*:

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

Here we put

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

Here the integration domain is the whole space.

Therefore we have the following eigen-function expansion theorem.

Theorem 3.7 (Eigen-function expansion theorem) *We consider the system of eigen-functions* $\{\psi_{nlm}(\boldsymbol{r})\}$ *in the above. Then, for a square integrable function* $\psi(\boldsymbol{r})$ *on* $\boldsymbol{R}^3$*, 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 coefficient c_{nlm} *is defined by the equality*

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

Here, we assume that the integration domain is the whole space $\boldsymbol{R}^3$*. Then the series on the right hand side converges in the sense of* L^2*-convergence.*

Especially, if $\psi(\boldsymbol{r})$ is a L^2-density, we have the equality

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

Thus the Fourier type coefficients $\{c_{nlm}\}$ defined in the Theorem 3.7 satisfy the condition

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

Theorem 3.8 *We put* $L^2 = L^2(\boldsymbol{R}^3)$*. Further we assume that* $J[\psi]$ *is the same as Problem* I *and* $\{\mathcal{E}_n\}$ *and* $\{\psi_{nlm}\}$ *are the same as Theorem* 3.4*. Here we denote the closed subspace*

$$\mathcal{L}\{\psi_{klm};\ |m| \leq l,\ l = 0,\ 1,\ 2,\ \cdots,\ k-1;$$

$$k = n,\ n+1,\ n+2,\ \cdots\}$$

as $\mathcal{H}_n$. Then we have the following:

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

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

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

Here the multiplicity of the eigen-value $\mathcal{E}_n$ is equal to n^2, $(n\ge 1)$.

By virtue of this Theorem, we see that the solution $\{\psi_{nlm}\}$, $\{\mathcal{E}_n\}$ of the eigen-value problem in Theorem 3.4 are the complete solution of the variational problem for the energy functional $J[\psi]$.

Here, by virtue of the inverse process of the separation of variables, we derive the time-evolving Schrödinger equation.

At first, we consider the function

$$\psi_{nlm}(\boldsymbol{r},\ t)=\psi_{nlm}(\boldsymbol{r})\exp\ \left[\ -i\frac{\mathcal{E}_n}{\hbar}t\ \right].$$

By differentiating the both sides of this equality with respect to t, we have the equality

$$i\hbar\frac{\partial\psi_{nlm}(\boldsymbol{r},\ t)}{\partial t}=\mathcal{E}_n\psi_{nlm}(\boldsymbol{r})\exp\ \left[\ -i\frac{\mathcal{E}_n}{\hbar}t\ \right].$$

Here, assuming that the Schrödinger operator H for the system of hydrogen type ions is

$$H=-\frac{\hbar^2}{2m_e}\Delta-\frac{Ze^2}{r},$$

we have the equality

$$H\psi_{nlm}(\boldsymbol{r})=\mathcal{E}_n\psi_{nlm}(\boldsymbol{r}).$$

Therefore we have the equality

$$i\hbar\frac{\partial\psi_{nlm}(\boldsymbol{r},\ t)}{\partial t}=H\psi_{nlm}(\boldsymbol{r})\cdot\exp\ \left[\ -i\frac{\mathcal{E}_n}{\hbar}t\ \right]=H\psi_{nlm}(\boldsymbol{r},\ t).$$

Now we put

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

by using the Fourier type coefficients $\{c_{nlm}\}$ of the initial condition $\psi(\boldsymbol{r})$.

Then $\psi(\boldsymbol{r},\ t)$ satisfies the equality

$$i\hbar\frac{\partial\psi(\boldsymbol{r},\ t)}{\partial t}=H\psi(\boldsymbol{r},\ t).$$

This equation is the time-evolving Schrödinger equation for the system of hydrogen type ions in the bound state.

Namely we have the following.

Theorem 3.9 *Assume that the functions $\psi(\boldsymbol{r})$ and $\psi(\boldsymbol{r},\ t)$ are given as in the above. Then $\psi(\boldsymbol{r},\ t)$ is the unique solution of the initial value problem for the time-evolving* Schrödinger *equation*

$$i\hbar\frac{\partial\psi(\boldsymbol{r},\ t)}{\partial t} =\Big(-\frac{\hbar^2}{2m_e}\Delta - \frac{Ze^2}{r}\ \Big)\ \psi(\boldsymbol{r},\ t),\ (\boldsymbol{r}\in\boldsymbol{R}^3,\ 0<t<\infty)$$

under the following condition (1):

(1) (Initial condition) *We have the equality*

$$\psi(\boldsymbol{r},\ 0)=\psi(\boldsymbol{r}),\ (\boldsymbol{r}\in\boldsymbol{R}^3).$$

By using the Plancherel's equality for the Fourier transformation, the energy functional $J[\psi]$ is expressed as follows:

$$J[\psi]=\int\ \psi(\boldsymbol{r})^*\ \Big(\ -\frac{\hbar^2}{2m_e}\Delta-\frac{Ze^2}{r}\ \Big)\ \psi(\boldsymbol{r})d\boldsymbol{r}.$$

Therefore, by virtue of Theorem 3.4, we have the equalities

$$J[\psi_{nlm}]=\mathcal{E}_n,$$

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

Then, by virtue of Theorem 3.7, we have the equality

$$\begin{aligned}J[\psi]&=\sum_{n=1}^{\infty}\sum_{l=0}^{n-1}\sum_{m=-l}^{l}|c_{nlm}|^2J[\psi_{nlm}]\\&=\sum_{n=1}^{\infty}\sum_{l=0}^{n-1}\sum_{m=-l}^{l}|c_{nlm}|^2\mathcal{E}_n\\&=-\frac{m_eZ^2e^4}{2\hbar^2}\sum_{n=1}^{\infty}\sum_{l=0}^{n-1}\sum_{m=-l}^{l}\frac{1}{n^2}|c_{nlm}|^2.\end{aligned}$$

Here, if we put

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

we have the equalities

$$J[\psi] = -\frac{m_e Z^2 e^4}{2\hbar^2} \sum_{n=1}^{\infty} \frac{1}{n^2} p_n,$$
$$0 \leq p_n \leq 1, \ (n = 1, \ 2, \ \cdots),$$
$$\sum_{n=1}^{\infty} p_n = 1.$$

4 Meaning of the spectra of hydrogen type ions

In this section, we study the natural statistical meaning of the spectral phenomena of hydrogen type ions by using the theory of natural statistical physics.

By virtue of the study until Section 3, we see that the physical system Ω composed of hydrogen type ions in the bound state has the following structure in the stationary state. Namely, Ω is decomposed into the direct sum in the following:

$$\Omega = \sum_{n=1}^{\infty} \Omega_n. \tag{4.1}$$

Then we have the equalities

$$P(\Omega_n) = p_n, \ (n = 1, \ 2, \ \cdots),$$
$$\sum_{n=1}^{\infty} p_n = 1.$$

Further, each Ω_n is decomposed into the direct sum in the following:

$$\Omega_n = \sum_{l=0}^{n-1} \sum_{m=-l}^{l} \Omega_{nlm}.$$

Then we have the equalities

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

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

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

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

Here we consider only the principal index n because we study the spectra of hydrogen type ions. Therefore we consider the direct sum decomposition (4.1). Then, for two Lebesgue measurable sets A and B in $\boldsymbol{R}^3$, we have the equalities

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

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

Therefore the energy expectation values of the proper physical subsystem Ω_{nlm} are equal to

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

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

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

$$\overline{E} = E \left[\ \frac{1}{2m_e} \boldsymbol{p}(\rho)^2 - \frac{Ze^2}{r} \ \right]$$
$$= \sum_{n=1}^{\infty} \sum_{l=0}^{n-1} \sum_{m=-l}^{l} P(\Omega_{nlm}) E_{\Omega_{nlm}} \left[\ \frac{1}{2m_e} \boldsymbol{p}(\rho)^2 - \frac{Ze^2}{r} \ \right]$$
$$= \sum_{n=1}^{\infty} \sum_{l=0}^{n-1} \sum_{m=-l}^{l} |c_{nlm}|^2 \mathcal{E}_n = \sum_{n=0}^{\infty} \mathcal{E}_n p_n$$
$$= -\frac{m_e Z^2 e^4}{2\hbar^2} \sum_{n=1}^{\infty} \frac{1}{n^2} p_n.$$

The physical system of hydrogen type ions in the bound state is realized as the composite state of the proper physical subsystems. The physical subsystem

Ω_n, whose energy expectation value is $\mathcal{E}_n$, is the composite state of the n^2 proper physical subsystems

$$\Omega_{nlm},\ (|m| \leq l,\ l = 0,\ 1,\ \cdots,\ n-1).$$

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

Then, because the electron in the hydrogen type ion is moving by virtue of Coulomb force, L^2-densities $\psi_{nlm}(\boldsymbol{r},\ t)$ is varying with time t. Then the Fourier type coefficients $\{c_{nlm}\}$ are varying with time t and, according to this, the values of $\{p_n\}$ are varying with time t.

Therefore each hydrogen type ion composing the physical subsystem with the mean energy $\mathcal{E}_n$ is changing its belonging to the proper physical subsystem with time t. According to this, when a hydrogen type ion in the subsystem of the mean energy $\mathcal{E}_n$ transverses into the subsystem of the mean energy $\mathcal{E}_m$, the spectral line corresponding to the difference

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

of these mean energies will be observed. We can consider that this spectral lines coincide well with the distribution of the observed spectra for the hydrogen type ions in the real.

As the historical facts, the spectra of the hydrogen atoms is known to be as follows.

Here we remember the Bohr's Hypotheses proposed in 1913.

Here we propose the analogy of Bohr's Hypotheses as the Bohr's Law.

Bohr's Law We use the notation in the above. Here, assume that the oscillation number of the observed light is ν. Then we have the formula

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

Here h denotes the Planck's constant.

By the study until now, the value of ν is equal to

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

Here m_e denotes the mass of an electron.

Here, in the case $m = 2$, this coincides with the spectral line of the visible line from hydrogen atoms, which is discovered by Balmer in 1885.

In the present, this is said to be the **Balmer series**.

The spectral series known until now are the following. According to the Pydberg's expression, these spectral series considered here are the following.

(1) Lyman series (discovered in 1906):

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

(2) Balmer series (discovered in 1885):

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

(3) Paschen series (discovered in 1908):

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

(4) Brackett series (discovered in 1922):

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

(5) Pfund series (discovered in 1924):

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

Here R denotes the Pydberg constant and its value is given as follows:

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

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

By the study until now, R is equal to

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

as the theoretically calculated value.

By the study in the above, the theoretical value and the actual value for R coincide well.

Thereby we can understand and explain reasonably the spectral lines of hydrogen type ions by virtue of the law of the natural statistical physics.

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