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Phenomena of Spectra of Hydrogen Atoms

By

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Abstract

In this paper, we have completely succeeded in the true understanding of the phenomena of spectra of hydrogen atoms.

This problem is the motivation of quantum mechanics 100 years ago.

But we know that the quantum mechanics is a curious theory.

In order to clear this problem, I create the theory of natural statistical physics.

In the present time, we know that we must not use the quantum mechanics.

The new age of physics starts just now.

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Introduction

In this paper, we show the new discovery of the spectral phenomena of hydrogen atoms.

This year 2025 is the 100th anniversary of the birth of quantum mechanics.

It is the motivation of quantum mechanics that we wish to understand the phenomena of spectra of hydrogen atoms.

Then, Schrödinger discovered the Schrödinger equation.

Nevertheless, as for the spectral phenomena of hydrogen atoms, many problems were left in the framework of the quantum mechanics.

I succeeded in the true physical understanding of the spectral phenomena of hydrogen atoms by creating the theory of natural statistical physics. We have succeeded in the complete solution of this problem after 100 years.

In each hydrogen atom constructing a system of hydrogen atoms, an electron is rotating around the nucleus by virtue of the Newtonian equation under the Coulomb interaction.

Thereby, each hydrogen atom radiates and absorbs the electro-magnetic waves. Thereby, the spectra of hydrogen atoms are observed.

We have only this as a real physical phenomenon .

As for the results in this paper, we refer to Ito [1], chapter 15 and Ito [2], chapter 7.

Here I am most grateful to my wife Mutuko for her help of typesetting of this manuscript.

1 Physical system of hydrogen atoms

In this section, we study and understand the observed data of spectra of hydrogen atoms on the basis of the laws of natural statistical physics.

Here we consider the system of hydrogen atoms. Here we may neglect the influence of their spins.

These are the cases where there is not the influence of the outer electro-magnetic field or where we can neglect those influence.

One hydrogen atom is the combined system of one proton and one electron. In a hydrogen atom, one electron is rotating around this proton.

Then, the problem is the study of the natural statistical phenomena of this physical system. We study this problem by using the theory of natural statistical physics.

The physical system is the set of such hydrogen atoms. This is an example of the system of two particles.

Each hydrogen atom is moving in the 3-dimensional space.

We assume that the masses of a proton and an electron are m_1 and m_2 respectively.

Then we assume that the electric charges of a proton and an electron are e and $-e$ respectively.

Then, we express the position variables of a proton and an electron as $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ respectively. Then the position variable of the hydrogen atom is expressed as

$$\boldsymbol{r} = (\boldsymbol{r}_1, \boldsymbol{r}_2).$$

We express the momentum variables of a proton and an electron as $\boldsymbol{p}_1$ and $\boldsymbol{p}_2$ respectively. Then the momentum variable of a hydrogen atom is expressed as

$$\boldsymbol{p} = (\boldsymbol{p}_1, \boldsymbol{p}_2).$$

Here we neglect the interaction of force among the different hydrogen atoms.

The interaction of force is acting on the proton and the electron of one hydrogen atom by virtue of the Coulomb potential

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

Since the masses of a proton and an electron are small, we assume that we can neglect their gravitational interaction.

Then each hydrogen atom is moving by virtue of Newtonian equation

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

Therefore, the mechanical energy of one hydrogen atom is equal to

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

Here the first term is the kinetic energy of the hydrogen atom and the second term is its potential energy. Namely we have the conservation law of the mechanical energy of each hydrogen atom.

2 Setting of the mathematical model

In this section, we set the mathematical model for the natural statistical phenomena of the spectra of hydrogen atoms.

We assume that the physical system is the set of hydrogen atoms. This physical system $\Omega = \Omega(\mathcal{B}, P)$ is assumed to be the probability space.

Its elementary event ρ is one hydrogen atom. This hydrogen atom is the combined system of one proton 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 atom ρ is the combined system $\boldsymbol{r}(\rho) = (\boldsymbol{r}_1(\rho), \boldsymbol{r}_2(\rho))$ of the position variable $\boldsymbol{r}_1(\rho)$ of one proton and the position variable $\boldsymbol{r}_2(\rho)$ of one electron.

Corresponding to this, the momentum variable $\boldsymbol{p}(\rho)$ of one hydrogen atom ρ is the combined system $\boldsymbol{p}(\rho) = (\boldsymbol{p}_1(\rho), \boldsymbol{p}_2(\rho))$ of the momentum variable $\boldsymbol{p}_1(\rho)$ of one proton and the momentum variable $\boldsymbol{p}_2(\rho)$ of one electron.

Then, the variable $\boldsymbol{r}$ changes in the space $\boldsymbol{R}^6$ and the variable $\boldsymbol{p}$ changes in the 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 the dual space $\boldsymbol{R}_3$.

Here, since the 3-dimensional Euclidean space $\boldsymbol{R}^3$ is self-dual, we identify the space $\boldsymbol{R}^3$ and its dual space $\boldsymbol{R}_3$. Then we denote the 3-dimensional Euclidean space and its dual space with the same symbol $\boldsymbol{R}^3$.

A proton and an electron interact by virutue of the Coulomb potential

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

Then the mechanical energy of each hydrogen atom ρ is determined by virtue of Newtonian mechanics.

Its value is equal to

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

Here, the masses of the proton and the electron are m_1 and m_2 respectively and the electric charges of the proton and the electron are e 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 $\boldsymbol{r} = \boldsymbol{r}(\rho)$ and $\boldsymbol{p} = \boldsymbol{p}(\rho)$ obtain the values corresponding to every hydrogen atom respectively.

Thus, in general, we can consider that their values are distributed in the random manner.

In these senses, we may consider that $\boldsymbol{r} = \boldsymbol{r}(\rho)$ and $\boldsymbol{p} = \boldsymbol{p}(\rho)$ are random variables.

Further, since, especially, they are the natural random variables defined on the physical system Ω, these are the forms of phenomena as the natural statistical phenomena.

Then, as the natural statistical phenomena, the dependence on the space and the time of the position variable and the momentum variable of hydrogen atoms and, thereby, the probability distribution laws of the position variable and the momentum variable are determined legally.

This is why the motion of the proton and the electron of a hydrogen atom is determined by virtue of the law of Newtonian equation of motion.

Here we consider that the hydrogen atoms are usually in the bound state.

Therefore, the Schrödinger operator has only the negative discrete eigenvalues. They are determined afterward.

Then, by virtue of the law II in Ito[1], section 2.2, 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, as the expectation value $\overline{E}$ of the energy variable of the total physical system is obtained in the following :

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

Here we use the Planeherel formula for the Fourier transformation. Further, we consider that the integration domain is the total space.

Then, we denote this energy expectation value as

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

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

Here, in order to choose the L^2-density $\psi(\boldsymbol{r})$ determined really in the equilibrium state or the stationary state among the admissible L^2- densities $\psi(\boldsymbol{r})$ which determine the natural probability distribution law of the position variable $\boldsymbol{r} = \boldsymbol{r}(\rho)$ of the hydrogen atom ρ, 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 equilibrium state is the stationary function of the energy functional $J[\psi]$.

In order to determine the stationary function in the principle, 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 its stationary value.

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

3 Mathematical analysis

In this section, we consider 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 atoms and the time-evolving Schrödinger equation .

As the Euler equation for the variation problem in Problem I in section 2, we obtain the Schödinger equation

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

Here $\mathcal{E}$ is the Lagrange's indeterminate multiplier. Further, $\Delta_1 = \Delta_{\boldsymbol{r}_1}$ and $\Delta_2 = \Delta_{\boldsymbol{r}_2}$ are Laplace operators with respect to the variables $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ respectively.

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

By the similar consideration as the discussion until now, we can derive the time- evolving Schrödinger equation

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

When we consider the mecanical motion of the system of two particles, we happen to consider the motion of the center of gravity by its separation.

Then the motion of the center of gravity is the linear uniform motion.

Corresponding to this, the relative motion of the system of two particles is considered as the motion of one particle with the converted mass

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

under the action of the potential $V(r)$ of the central force. Corresponding to this, we can consider the separation of the motion of center of gravity in the Schödinger equation.

Then, the motion of the center of gravity is considered as the motion of the system of free particles with the mass $M = m_1 + m_2$. Against to this, the relative motion of the system of two particles is considered as the motion of the system of one particle with the converted mass μ under the action of the potential $V(r)$ of the central force.

Really, the observation of the spectra of the hydrogen atom is the effect of this relative motion. The effect of the motion of the center of gravity can be neglected.

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

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

In the first approximation, we consider that the proton is infinitely heavy and we consider that the hydrogen atom is the system of one particle of one electron in the field of Coulonb force.

Therefore, we consider that the physical system considered here is the probability space

$$\Omega = \Omega(\mathcal{B}, P)$$

composed of electrons moving under the condition in the above.

This is the system of one particle.

Then, we consider 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 $\boldsymbol{r}$ moves in the space $\boldsymbol{R}^3$ and the variable $\boldsymbol{p}$ moves in its dual space $\boldsymbol{R}^3$.

Then, each electron moves under the action of the potential

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

Then the Schrödinger equation describing the stationary states of the system of free electrons is given by the formula

$$\Big(-\frac{\hbar^2}{2m}\Delta - \frac{e^2}{r} \Big)\, \psi(\boldsymbol{r}) = \mathcal{E}\psi(\boldsymbol{r}).$$

Here $\Delta = \boldsymbol{\Delta_r}$ denotes the Laplacian operator with respect to $\boldsymbol{r}$ and we put $r = |\boldsymbol{r}|$. We denote the mass of an electron as m.

Then, by solving the Schrödinger equation in the stationary state, we determine the eigenvalues $\mathcal{E}_n$ and the system of the corresponding eigenfunctions ψ_{nlm}.

In the sequel, we prepare the symbols in order to solve this eigenvalue problem. We write the results in the theorem. Then, the eigenvalue $\mathcal{E}$ is equal to

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

Now, we define the polynomial functions $L_n^{(m)}(z)$ by the formulas

$$L_n^{(m)}(z) = \frac{1}{n!} z^{-m} e^z \frac{d^n}{dz^n}(z^{n+m}e^{-z}), (n = 1, 2, \cdots, m = 1, 2, \cdots).$$

We say this function $L_n^{(m)}(z)$ as Laguerre's bi-polynomial.

Then we have the normalization conditions in the following:

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

Thereby, we define the solution

$$R(r) = R_{nl}(r)$$

by the formula

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

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

Then the function $R_{nl}(r)$ satisfies the orthonormalization condition in the following.

Theorem 3.1(Orthonormalization condition)
In the notation in the above, we have the equalities in the following:

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

In the next, we define the spherical function $Y_l^m(\theta, \phi)$ by the formulas

$$Y_l^m(\theta,\phi) = \sqrt{\frac{(2l+1)}{4\pi} \frac{(l-|m|)!}{(l+|m|)!}} P_l^n(\cos\theta) e^{im\theta}, (l = 0, 1, \cdots, n-1, |m| \leq l).$$

Then we call that $P_l(x)$ and $P_l^m(x), (|x| < 1))$ are Laguerre's polynomial and Laguerre's bi-polynomial and we define them by the formulas in the following:

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

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

As for these, we have two orthonormalization conditions in the following.

Theorem 3.2 (orthonormalization condition). In the notation in the above, we have the equalities in the following:

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

Theorem 3.3 (Orthonormalization condition) In the notation in the aboves, we have the equalities in the following:

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

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

Here it is ordinary to use m as the magnetic index. Although we denote m for the mass of an electron, it is a convention to venture to use the same letter. Therefore, for a fixed value of n, we have the number

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

of the linearly independent eigenfunctions and they attach to the same eigenvalue $\mathcal{E}_n$.

For one l, the $(2l+1)$-eigenfunctions are degenerated because we have the special reason why the potential is spherically symmetric.

The eigenvalue $\mathcal{E}_n$ is determined by only one principal index n and independent of l since the potential is the Coulomb potential especially.

Then the eigenfunctions in the stationary state of the system of hydrogen atoms are determined in the following.

Namely, the eigenfunction corresponding to the indices n, l and m is determined in the following:

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

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

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

by considering the normalization conditions. Here we assume

$$n \geq 1, 0 \leq l \leq n-1, |m| \leq l.$$

Here we put

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

By virtue of the above, we can solve the eigenvalue problem of the Schrödinger equations for the system of hydrogen atoms.

Namely, we have the following.

Theorem 3.4 (Eigenvalue problem)

The function $\psi_{nlm}(x, y, z) = \psi_{nlm}(r, \theta, \phi)$ defined in the above is the eigenfunction of the Schrödinger operator

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

associated to the eigenvalue

$$\mathcal{E}_n = -\frac{me^4}{2\hbar^2 n^2}.$$

Namely, we have the equalities

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

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

Then the eigenfunction

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

of Theorem 3.4 satisfies the orthonomality condition.

Theorem 3.5 By virtue of the notation in the above, we have the 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 eigenfunctions $\{\psi_{nlm}(\boldsymbol{r})\}$ in the above satisfies the completeness condition in the following.

Theorem 3.6 (Completeness) By virtue of the notation in the above, we have the equality in the following:

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

Theorem 3.7 (Theorem of eigenfunction expansion) We consider the system of eigenfunctions $\{\psi_{nlm}(\boldsymbol{r})\}$ in the above.

Then, for a square integrable function $\psi(\boldsymbol{r})$ on $\boldsymbol{R}^3$, we have the equality in the following:

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

Here the Fourier coefficient c_{nlm} is defined by the formula

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

Here we assume that the integration domain is the entire space. Then the series in the right hand side converges in the sense of L^2-convergence.

Especially we assume that $\psi(\boldsymbol{r})$ is a L^2-density. Then we have the equality

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

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

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

Here we follow the inverse of the method of separation of variables. Then, we deduce the time-evolving Schrödinger equation.

At first, we consider the function

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

By differentiating partially both sides of this equation by t partially, we have the equality

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

Here we define the Schrödinger operator H for the system of hydrogen atoms as

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

Then we have the equality

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

Therefore we have the equality

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

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

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

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

This equation is the Schrödinger equation for the certain system of hydrogen atoms in the stationary state.

Namely we have the following .

Theorem 3.8 Assume that the functions $\psi(\boldsymbol{r})$ and $\psi(\boldsymbol{r},t)$ as above. Then, $\psi(\boldsymbol{r},t)$ is the solution of the initial value problem

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

$$\psi(\boldsymbol{r},0) = \psi(\boldsymbol{r}), \text{(initial condition)},$$

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

for the time-evolving Schrödinger equation.

By using the Plancherel equality for the Fourier transformation, the energy functional $J[\psi]$ is expressed in the following:

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

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

$$J[\psi_{nlm}] = \mathcal{E}_n, (n = 1, 2, \cdots ; l = 0, 1, \cdots , n-1; |m| \leq l).$$

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

$$J[\psi] = \sum_{n=1}^{\infty} \sum_{\psi=0}^{n-1} \sum_{m=-l}^{l} |c_{nlm}|^2 J[\psi_{nlm}]$$

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

$$= -\frac{me^4}{2\hbar^2} \sum_{n=1}^{\infty} \sum_{l=0}^{n-1} \sum_{m=-l}^{l} \frac{1}{n^2}|c_{nlm}|^2.$$

Here, we put

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

Then we have the equalities

$$J[\psi] = -\frac{me^4}{2\hbar^2} \sum_{n=1}^{\infty} \frac{1}{n^2} p_n,$$

$$0 \leq p_n \leq 1, (n = 1, 2, \cdots),$$

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

4 Phenomena of the spectra of hydrogen atoms

In this section, by using the theory of natural statistical physics, we study the natural statistical meaning of the phenomena of the spectra of hydrogen atoms.

By virtue of the study in sections 1∼ 3, we have the fundamental proposition 4.1 in the following.

Here the **fundamental proposition** is the statement on the physical phenomena concerning the system of hydrogen atoms.

Fundamental Proposition 4.1

We can see that the physical system Ω of hydrogen atoms has the following structure in the stationary state.

Namely Ω is the direct decomposition in the following:

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

Here we have the formulas

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

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

Further each Ω_n is decomposed as the direct sum in the following:

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

Then we have the formulas in the following:

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

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

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

Then we have the fundamental proposition 4.2 in the following.

Fundamental Proposition 4.2

For every $A \in \mathcal{B}$, we have the equality

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

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

Here, since we study the spectra of hydrogen atoms, we consider only the principal index n. Therefore we consider the direct sum decomposition(4.1) of Ω,

Then, for the domains A and B of $\boldsymbol{R}^3$, we have the equalities:

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

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

Therefore, we have the fundamental proposition 4.3 in the following.

Fundamental Proposition 4.3

The energy expectation value of the excited state Ω_{nlm} is equal to

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

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

Then, by virtue of the relation of the physical system Ω and the excited states Ω_{nlm}, the energy expectation value of the physical system Ω is equal to

$$\overline{E} = E\ \Big[\ \frac{1}{2m}\boldsymbol{p}(p)^2 - \frac{e^2}{r}\ \Big] = \sum_{n=1}^{\infty} \sum_{l=0}^{n-1} \sum_{m=-l}^{l} |c_{nlm}|^2 \mathcal{E}_n$$

$$= \sum_{n=l}^{\infty} \mathcal{E}_n p_n = -\frac{me^4}{2\hbar^2} \sum_{n=1}^{\infty} \frac{1}{n^2} p_n.$$

Therefore we have the fundamental proposition 4.4.

Fundamental Proposition 4.4

The physical system Ω of hydrogen atoms in the stationary state is realized as the mixed state of the excited states. The excited state Ω_n of the energy expectation value $\mathcal{E}_n$ is the mixed states of the n^2 excited states $\Omega_{nlm}, (l = 0, 1, \cdots, n-1; |m| \leq l)$.

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

5 Consideration

By virtue of the analysis in this paper, we understood the phenomena of the spectra of hydrogen atoms.

Then the L^2-densities $\psi_{nlm}(\boldsymbol{r},t)$ and $\psi(\boldsymbol{r},t)$ are varying with time t by the reason why an electron in the hydrogen atom is moving by virtue of Newtonian equation of motion under the Coulomb force. Then the Fourier type coefficients $\{c_{nlm}\}$ are varying with time, and thereby, the values $\{p_n\}$ are varying with time.

Therefore, the mechanical energy of each hydrogen atom is varying with time. At each time, the physical system Ω of the hydrogen atoms is the mixed system of the excited systems $\Omega_n, (n \geq 1)$ as in the Fundamental Proposition 4.4.

Thus the belonging to each excited state Ω_n is varying.

As for each electron in each hydrogen atom, the electron is rotating around the proton by virtue of Coulomb force.

Thereby, the kinetic energy of the electron in the hydrogen atom is varying by the absorption and the radiation of the electro-magnetic waves. The system of hydrogen atoms with such electrons is the mixed system of the excited systems with the energy expectation values each wise at every time. Thereby the spectra are observed by virtue of Bohr's law.

Then we do not say that each electron transits discontinuously from one excited state to another excited state.

Since an electron in each hydrogen atom is rotating continuously by virtue of Newtonian equation of motion, the energy of each electron is varying continuously.

At each time, the energy expectation values of the excited states are discrete as a whole.

Then we have Bohr's rule about the relations of the energy expectation values and the spectra of hydrogen atoms.

Thereby, for the excited state Ω_n with the mean energy $\mathcal{E}_n$ and the exited state Ω_m with the mean energy $\mathcal{E}_m$, we can observe the spectral line according to the difference of these mean energies

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

This is well identified with the spectral distribution observed really for the hydrogen atoms.

As the historical facts, we know that the spectra of the hydrogen atoms are in the following.

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

Bohr's law We use the notation in the above. Then, when we define the frequency of the observed light as ν, we have the relation

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

Here h denotes the Planck's constant.

By virtue of the consideration until now, 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 is identified with the spectral lines of the visible light absorbes or radiates from the hydrogen atoms.

This was discovered by Balmer in 1885.

This is, so called today, the **sequence of Balmer's type**.

The spectral sequences known until now are as follows.

By expressing these by virtue of Rydberg's expression, we have the following.

(1) Lyman series (discovered in 1906);

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

(2) Balmer series (discovered in 1885);

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

(3) Paschen series (discovered in 1908);

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

(4) Brackett series (discovered in 1922);

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

(5) Pfund series (discovered in 1924);

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

Here R denotes the Rydberg 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.

The Bohr's law in the above was discovered as the hypothesis.

At first, in 1914, this was proved by Frank-Hertz's experiment. By virtue of the consideration of the observed data of Frank-Hertz's experiment, it is proved that we have the regularity such as Bohr's hypothesis. Thereby, Bohr's hypothesis is established as Bohr's law.

Thereby we can understand and explain reasonably the spectral lines of hydrogen atoms known until now by virtue of the law of the natural statistical physics.

As a result, it is only the fact that the electron is rotating around the proton by virtue of Newtonian equation of motion by Coulomb interaction in the hydrogen atom.

Thereby, in the system Ω of hydrogen atoms, each hydrogen atom radiates or absorbs the electro-magnetic waves according the large or small quantity of its kinetic energy.

This is the reason why, by virtue of the principle of balancing of the energy, each hydrogen atom absorbs or radiates the electro-magnetic wave according to the size of their energy.

This arises as the phenomena of acceleration or slowdown of the rotation of the electron. Then we observe the spectra of hydrogen atoms by virtue of Bohr's law.

If we consider only one hydrogen atom, it continues to radiate the electro-magnetic waves by virtue of rotation of the electron around the proton, and finally, the rotation of the electron around the proton will stop. If it happens to be so, the considered system of the proton and the electron cannot exist as the hydrogen atom.

Nevertheless, when we really consider the system of hydrogen atoms, each hydrogen atom radiates and absorbs the electro-magnetic waves between the hydrogen atoms and the surroundings by virtue of the principle of balancing of the energy. Thereby, its electron can continues the rotation.

Therefore, in the system of hydrogen atoms, the electron in each hydrogen atom can continue the rotation without stopping.

Thus, when we study the phenomena by using the natural statistical physics, we can see clearly that the phenomena of the spectra of hydrogen atoms arise by the rotation of the electrons around the protons.

It is the big discovery that we can see concretely the true phase of the physical phenomena.

References

[1] Yoshifumi Ito, *Foundation of Natural Statistical Physics*, preprint, 2016.

[2] ——, *Fundamental Principles of Physics*, preprint, 2025.

[3] ——, *Reality of Showing Signs of Physical Phenomena*, preprint, 2025.