Angular Momentum
and its Expectation Value

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1   Introduction

In this paper, we study the angular momenta of inner electrons of hydrogen atoms. Especially we calculate the expectation values of angular momenta of the system of inner electrons of hydrogen atoms. Thereby we clarify the structure of the system of hydrogen atoms.

We study these phenomena as the natural statistical phenomena

These natural statistical phenomena are caused by the **family** of inner electrons of hydrogen atoms but not by a **single** inner electron of a hydrogen atom.

Here we use the theory of natural statistical physics.

We remark that the natural statistical physics is not quantum mechanics.

The theory of natural statistical physics is the very new theory originated by me. Thus these results are the very new ones.

For these results, we refer to Ito [29], Chapter 4.

2   Mathematical Model

At first, we give a mathematical model for the system of hydrogen atoms, we consider the system of hydrogen atoms as the family of hydrogen atoms, each electron of which is moving in the Coulomb potential

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

with its center at the nucleus of the hydrogen atom.

Each electron is moving according to Newtonian equation of motion by virtue of the causality laws.

As a mathematical model, this physical system is the system of inner electrons of hydrogen atoms which are moving in the Coulomb potential with its center at the origin.

We denote this system of inner electrons of hydrogen atoms by

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

In this paper, we call this physical system to be the system of hydrogen atoms.

Each electron ρ has its position variable $\boldsymbol{r} = \boldsymbol{r}(\rho)$ and its momentum variable $\boldsymbol{p} = \boldsymbol{p}(\rho)$.

When we consider the family of electrons, each electron has its own values of $\boldsymbol{r}$ and $\boldsymbol{p}$ individually. When we consider these situation of the phenomenon, we ask how the values of the variables $\boldsymbol{r}$ and $\boldsymbol{p}$ are distributed. When we study this problem, we use the framework of the probability space Ω and the random variables defined on Ω as a mathematical model.

Therefore, when we study the natural statistical phenomena of the physical system of hydrogen atoms, we assume that Ω is a probability space, whose elementary event is an inner electron ρ of a hydrogen atom, and that the variables $\boldsymbol{r} = \boldsymbol{r}(\rho)$ and $\boldsymbol{p} = \boldsymbol{p}(\rho)$ are the vector valued random variables defined on Ω.

Further each electron ρ has its angular momentum

$$\boldsymbol{L} = \boldsymbol{r} \times \boldsymbol{p} = {}^t(L_x, L_y, L_z).$$

Here we consider the variable $\boldsymbol{L} = \boldsymbol{L}(\rho)$ to be the vector valued random variable defined on Ω.

In this case, each electron ρ has the total energy

$$\mathcal{E}(\rho) = \frac{1}{2m_e}\boldsymbol{p}(\rho)^2 - \frac{e^2}{r},$$

where m_e and e denote the mass and the electric charge of the electron respectively.

In general, a physical quantity is a function $F(\boldsymbol{r}, \boldsymbol{p})$ of the variables $\boldsymbol{r}$ and $\boldsymbol{p}$.

In a certain case, this is a vector valued function.

This is considered to be a natural random variable defined on Ω.

We calculate the expectation value of the angular momentum of the system of inner electrons of hydrogen atoms.

3   What is the Problem?

Here we have the fundamental question :

What are the probability distribution laws of the variables $\boldsymbol{r} = \boldsymbol{r}(\rho)$ **and** $\boldsymbol{p} = \boldsymbol{p}(\rho)$.

The answer is this:

The probability distribution laws of the variables $\boldsymbol{r} = \boldsymbol{r}(\rho)$ **and** $\boldsymbol{p} = \boldsymbol{p}(\rho)$ **are given as the natural statistical distribution laws.**

This is the characteristic point of the theory of natural statistical physics.

By virtue of the laws of natural statistical physics, the probability distribution law of the variable $\boldsymbol{r} = \boldsymbol{r}(\rho)$ is determined by the L^2-density ψ which is a solution of Schrödinger equation of the system of hydrogen atoms.

Then the probability distribution law of the variable $\boldsymbol{p} = \boldsymbol{p}(\rho)$ is determined by the Fourier transform $\hat{\psi}$ of ψ.

Here we define the Fourier transformation of ψ as follows:

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

where we put

$$\boldsymbol{r} = {}^t(x,y,z), \quad \boldsymbol{p} = {}^t(p_x,p_y,p_z), \quad \boldsymbol{p}\cdot\boldsymbol{r} = p_x x + p_y y + p_z z.$$

Here we give the fundamental relations in the natural probability distribution laws in the following:

$$P(\{\rho \in \Omega; \boldsymbol{r}(\rho) \in A\}) = \int_A |\psi(\boldsymbol{r})|^2 d\boldsymbol{r},$$

and

$$P(\{\rho \in \Omega; \boldsymbol{p}(\rho) \in B\}) = \int_B |\hat{\psi}(\boldsymbol{p})|^2 d\boldsymbol{p}.$$

Here A and B are Lebesgue measurable sets in $\boldsymbol{R}^3$.

Further the natural probability distribution law of the variable $(x(\rho), p_y(\rho))$ is determined by the partial Fourier transform $\hat{\psi}(x, p_y, z)$ as the marginal distribution of the simultaneous distribution of the variables $(x(\rho), p_y(\rho), z(\rho))$.

Here the partial transformation of ψ is defined in the following relation:

$$\hat{\psi}(x, p_y, z) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \psi(x, y, z)e^{-ip_y y/\hbar}dy.$$

The other marginal distributions are defined similarly.

Thereby, by using the natural probability distribution law of the variable $(x(\rho), p_y(\rho))$ as the marginal distribution, the expectation value of the z-component L_z of the angular momentum is calculated by the following formula

$$E[L_z] = \int_\Omega L_z(\rho)dP(\rho) = \frac{\hbar}{i} \int \psi(\boldsymbol{r})^* \left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x} \right) \psi(\boldsymbol{r})d\boldsymbol{r}.$$

In the right hand side of the above equality, the operator expression is formal and used only for the benefit of the mathematical calculation. Further, we remark that this operator expression has no physical meaning.

For L_x, L_y, $L^2 = L_x^2 + L_y^2 + L_z^2$, we calculate their expectation values in the same way.

We remark that the derivatives of the L^2-functions ψ are calculated in the sense of L^2-convergence. We call these the L^2-derivatives of ψ.

4   Derivation of Schrödinger Equation

Here we consider the derivation of Schrödinger equation of the system of hydrogen atoms.

In order to derive the Schrödinger equation of the system of hydrogen atoms, we consider the mathematical model under the following situations.

Here a hydrogen atom is a combined system of a hydrogen nucleus and its inner electron. We call this state of hydrogen atom to be the bound state. Thus, here, we do not study the scattering state of a hydrogen atom because we consider just a system of inner electrons of hydrogen atoms.

Namely, in the scattering state of a hydrogen atom, the electron cannot be considered the inner electron of the hydrogen atom.

Schrödinger equation of the system of hydrogen atoms is obtained by **the variational principle** and the solution of **the variational problem** for the energy expectation value.

We call this energy expectation value for an admissible L^2-density the energy functional $J[\psi]$ of ψ.

Then the L^2-density ψ is the stationary function of the energy functional $J[\psi]$.

Here $J[\psi]$ is given by

$$J[\psi] = \int \psi(\mathbf{r})^* \left(-\frac{\hbar^2}{2m_e}\Delta - \frac{e^2}{r} \right) \psi(\mathbf{r})d\mathbf{r}.$$

Namely,

$$J[\psi] = \overline{E} = E\left[\frac{1}{2m_e}\mathbf{p}(\rho)^2 - \frac{e^2}{r} \right].$$

Namely, this is equal to the expectation value of the total energy

$$\mathcal{E}(\rho) = \frac{1}{2m_e}\mathbf{p}(\rho)^2 - \frac{e^2}{r}$$

with respect to an admissible L^2-density ψ exactly in the mathematical sense.

Here we give the variational principle as follows.

Variational Principle

L^2-density which is realized really in the stationary state is a stationary function of the energy functional $J[\psi]$.

Then we give the variational problem as follows.

Variational Problem

Determine the L^2-density ψ which takes a stationary value of the energy functional $J[\psi]$ among all admissible L^2-densities ψ.

This stationary function ψ satisfies the Schrödinger equation as the Euler equation

$$\left[-\frac{\hbar^2}{2m_e}\Delta - \frac{e^2}{r} \right] \psi = \mathcal{E}\psi.$$

Here $\mathcal{E}$ is the energy eigenvalue.

Here, we put

$$H = -\frac{\hbar^2}{2m_e}\Delta - \frac{e^2}{r}, \quad \Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}.$$

When we consider the L^2-solution of Schrödinger equation, it satisfies Schrödinger equation concidering the L^2-derivatives of the L^2-solution. As for the concept of L^2-derivatives of an L^2-function, we refer to Ito [24].

5 Eigenfunctions and Eigenvalues

In the stationary state, Eigenfunctions and Eigenvalues of Schrödinger equation are given by the following:

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

$$\hat{\boldsymbol{L}}^2\psi_{nlm}(\boldsymbol{r}) = l(l+1)\hbar^2\psi_{nlm},$$

$$\hat{L}_z\psi_{nlm}(\boldsymbol{r}) = m\hbar\psi_{nlm},$$

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

Here, we put

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

Formally we give the operator expressions

$$\hat{L}_x = \frac{\hbar}{i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right),$$

$$\hat{L}_y = \frac{\hbar}{i}\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right),$$

$$\hat{L}_z = \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right).$$

$$\hat{\boldsymbol{L}} = {}^t(\hat{L}_x, \hat{L}_y, \hat{L}_z) = \frac{\hbar}{i}(\boldsymbol{r} \times \nabla),$$

$$\hat{\boldsymbol{L}}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2.$$

Of course, these operator expressions have no physical meanings.

The system of eigenfunctions is the complete orthonormal system in some Hilbert space $\mathcal{H}$.

$\mathcal{H}$ is defined to be the closed subspace of $L^2 = L^2(\boldsymbol{R}^3)$ spanned by $\{\psi_{nlm}\}$. Namely we have

$$\mathcal{H} = \mathcal{L}(\{\psi_{nlm}\}) \subset L^2 = L^2(\boldsymbol{R}^3).$$

Here, as is well known, we define the function $\psi_{nlm}(\boldsymbol{r})$ in the following:

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

Here the radial function $R_{nl}(r)$ is defined as follows:

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

where we put

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

The function $L_n^m(z)$ is the associated polynomial of Laguerre.

The spherical harmonic function $Y_l^m(\theta, \phi)$ is defined as follows:

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

where the Legendre's bi-function $P_l^m(z)$ is defined as follows:

$$P_l^m(z) = (1-z^2)^{|m|} \frac{d^{|m|} P_l(z)}{dz^{|m|}}, \quad (-1 < z < 1),$$

and the Legendre's function $P_l(z)$ is defined as follows:

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

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

6 Eigenfunction Expansion

Eigenfunction expansion in the space $\mathcal{H}$ is given in the following:

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

$$c_{nlm} = \int \psi_{nlm}(r)^* \psi(r) dr$$

Here we assume $\psi(r) \in \mathcal{H}$, and we assume that

$$\int |\psi(r)|^2 dr = 1,$$

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

hold. These equalities are the conditions of the L^2-densities.

Now, we put

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

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

Then $\psi(r, t)$ is the solution of the Cauchy problem

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

$$\psi(r, 0) = \psi(r),$$

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

7 Expectation Values

We calculate the expectation values of some physical quantities.
We have the expectation value of the energy as follows:

$$\int \psi_{nlm}(\boldsymbol{r})^* H \psi_{nlm}(\boldsymbol{r}) d\boldsymbol{r}) = \mathcal{E}_n = -\frac{m_e e^4}{2\hbar^2 n^2},$$

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

$$E\left[-\frac{1}{2m_e}\boldsymbol{p}(\rho)^2 - \frac{e^2}{r}\right] = \int \psi(\boldsymbol{r})^* H \psi(\boldsymbol{r}) d\boldsymbol{r}$$

$$= \sum_{n=1}^{\infty}\sum_{l=0}^{n-1}\sum_{m=-l}^{l} |c_{nlm}|^2 \mathcal{E}_n = -\frac{m_e e^4}{2\hbar^2}\sum_{n=1}^{\infty}\sum_{l=0}^{n-1}\sum_{m=-l}^{l} \frac{1}{n^2}|c_{nlm}|^2.$$

We have the expectation values of the angular momentum as follows:

$$\int \psi_{nlm}(\boldsymbol{r})^* \hat{\boldsymbol{L}}^2 \psi_{nlm}(\boldsymbol{r}) d\boldsymbol{r}) = l(l + 1)\hbar^2,$$

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

$$E[\boldsymbol{L}^2] = \int \psi(\boldsymbol{r})^* \hat{\boldsymbol{L}}^2 \psi(\boldsymbol{r}) d\boldsymbol{r} = \hbar^2 \sum_{n=1}^{\infty}\sum_{l=0}^{n-1}\sum_{m=-l}^{l} l(l + 1)|c_{nlm}|^2.$$

At last, we have the expectation value of the z-component of the angular momentum as follows:

$$\int \psi_{nlm}(\boldsymbol{r})^* \hat{L}_z \psi_{nlm}(\boldsymbol{r}) d\boldsymbol{r}) = m\hbar,$$

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

$$E[L_z] = \int \psi(\boldsymbol{r})^* \hat{L}_z \psi(\boldsymbol{r}) d\boldsymbol{r} = \hbar \sum_{n=1}^{\infty}\sum_{l=0}^{n-1}\sum_{m=-l}^{l} m|c_{nlm}|^2.$$

8 Structure of the System of Hydrogen Atoms

Now we show that the system of hydrogen atoms Ω in the bound state has the following structure in the stationary state.
Namely, we have the direct sum decomposition in the following :

$$\Omega = \sum_{n=1}^{\infty}\Omega_n, = \sum_{n=1}^{\infty}\sum_{l=0}^{n-1}\Omega_{nl} = \sum_{n=1}^{\infty}\sum_{l=0}^{n-1}\sum_{m=-l}^{l}\Omega_{nlm},$$

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

$$\Omega_{nl} = \sum_{m=-l}^{l} \Omega_{nlm},$$

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

$$p_{nl} = P(\Omega_{nl}) = \sum_{m=-l}^{l} |c_{nlm}|^2,$$

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

We decompose Ω in the above form according to the eigenvalues of the self-adjoint operators H, L^2 and L_z.

Then we consider the complete orthonormal system $\{\psi_{nlm}\}$ of the eigenfunctions of the Schrödinger equation in the bound state and denote the Fourier type coefficients of the eigenfunction expansion of an L^2-density as $\{c_{nlm}\}$.

The energy expectation of the proper subsystem Ω_{nlm} is equal to

$$E_{\Omega_{nlm}}(\mathcal{E}(\rho)) = \int \psi_{nlm}(r)^* H \psi_{nlm}(r) dr = \mathcal{E}_n,$$

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

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

$$\overline{E} = E(\mathcal{E}(\rho)) = -\frac{me^4}{2\hbar^2} \sum_{n=1}^{\infty} \frac{1}{n^2} p_n.$$

Therefore the system of hydrogen atoms in the bound state is realized as the mixed system of proper subsystems. The subsystem Ω_n with the energy expectation $\mathcal{E}_n$ is the mixed system of n^2 proper subsystems

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

The ratio of mixing of those subsystems Ω_n is equal to the ratio of the sequence $\{p_n\}_{n=1}^{\infty}$.

Then, because the electron in a hydrogen atom is moving by the action of Coulomb force, L^2-densities $\psi_{nlm}(r, t)$ and $\psi(r, t)$ are varying with time variation. Then the Fourier type coefficients $\{c_{nlm}\}$ are also varying with time variation. Accompanying with this, the values of $\{p_n\}$ are also varying with time variation.

Therefore, each hydrogen atom which composes the proper subsystem with mean energy $\mathcal{E}_n$ varies its belonging to some proper subsystem according to time variation.

This is the meaning of energy expectation values of the system of hydrogen atoms.

Next we study the meaning of the expectation value of angular momentum of the system of hydrogen atoms.

The expectation value of angular momentum L^2 of the proper subsystem Ω_{nlm} is equal to

$$E_{\Omega_{nlm}}[L^2] = \int \psi_{nlm}(r)^* \hat{L}^2 \psi_{nlm}(r) dr = l(l + 1)\hbar^2.$$

The expectation value of angular momentum $\boldsymbol{L}^2$ of the total system Ω is also equal to

$$E[\boldsymbol{L}^2] = \hbar^2 \sum_{n=1}^{\infty} \sum_{l=0}^{n-1} \sum_{m=-l}^{l} l(l+1)|c_{nlm}|^2.$$

The expectation value of the z-component L_z of angular momentum of the proper subsystem Ω_{nlm} is equal to

$$E_{\Omega_{nlm}}[L_z] = m\hbar.$$

The expectation value of the z-component L_z of angular momentum of the total system Ω is also equal to

$$E[L_z] = \hbar \sum_{n=1}^{\infty} \sum_{l=0}^{n-1} \sum_{m=-l}^{l} m|c_{nlm}|^2.$$

This is the meaning of the expectation values of angular momentum of the system of hydrogen atoms.

In the stationary state, the total system Ω of hydrogen atoms is the mixed system of proper subsystems

$$\{\Omega_{nlm}; |m| \le l, \ 0 \le l \le n-1, \ n \ge 1\}.$$

The ratio of this mixing is equal to the ratio of

$$\{p_{nlm}; |m| \le l, \ 0 \le l \le n-1, \ n \ge 1\}.$$

Then, the proper subsystem Ω_{nlm} is the subsystem of hydrogen atoms with the expectation value of energy $\mathcal{E}_n$, the expectation value of angular momentum $l(l+1)\hbar^2$, and the expectation value of the z-component of angular momentum $m\hbar$.

The proper subsystem of hydrogen atoms Ω_n with the expectation value of energy $\mathcal{E}_n$ is the mixed system of proper subsystems

$$\{\Omega_{nlm}; |m| \le l, \ 0 \le l \le n-1\}.$$

The ratio of this mixing is equal to the ratio of

$$\{p_{nlm}; |m| \le l, \ 0 \le l \le n-1\}.$$

The proper subsystem of hydrogen atoms Ω_{nl} with the expectation value of energy $\mathcal{E}_n$ and the expectation value of angular momentum $l(l+1)\hbar^2$ is the mixed system of proper subsystems

$$\{\Omega_{nlm}; |m| \le l\}.$$

The ratio of this mixing is equal to the ratio of

$$\{p_{nlm}; |m| \le l\}.$$

Therefore the belonging of each hydrogen atom to some proper subsystem is varying according to time variation.

Such a phase of varitation of the state of hydrogen atoms is known by solving the Schrödinger equation.

For the precise consideration, we refer to Ito [29], Chapter 4.

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