Visualization and analysis of electronic fine structure electron cloud

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Abstract: Electron spin and orbital interaction outside the nucleus is a classical and important problem in quantum mechanics. In this paper, a simplified model is constructed for the phenomenon of atomic energy level splitting in weak magnetic field in quantum mechanics, and the wave function of the fine structure of hydrogen-like atoms under perturbation is derived. According to the probability interpretation of quantum mechanics, we obtain the probability density function of the fine structure electron cloud of hydrogen-like atoms. The Monte Carlo selection method is used to sample, and the electron cloud images under different quantum numbers are drawn by Mathematica software. The experimental results are explained regularly, so that people can intuitively understand the distribution of electron cloud in three-dimensional space.

1. Introduction

The existence of the external field will add some energy disturbances on the basis of the ideal Coulomb potential, which will change the Hamiltonian operator, resulting in the shift of the energy level or the splitting of the degenerate energy level [1,2]. Most quantum mechanics textbooks only give a rough transition image of the energy level splitting of sodium atoms, and do not give a complete and intuitive three-dimensional electron cloud image. Moreover, the fine structure is relatively abstract. Beginners only understand the outline of the electron cloud distribution area by reading the fine structure wave function given in the textbook, and do not understand the density of the electron cloud. It is difficult to understand the influence of spin on the spatial distribution of hydrogen-like atom electron cloud.

With the popularization and application of computer numerical simulation in physics teaching, teachers can use computer software to draw hydrogen atom electron cloud images, making the probability density distribution of electron cloud more intuitive. Zhao Yunfang used Matlab as a development tool and used the point-by-point scanning method to draw the contour map of the probability distribution of the ground state and each excited state of the hydrogen atom [3]. Li Jinhai analyzed the distribution of electron probability density in hydrogen atom by numerical calculation, and made some discussions different from the traditional understanding [4]. In recent years, Cao Yuhan analyzed the distribution of electron probability density in hydrogen atom based on Monte

Carlo method, which provides an algorithm for the visualization of electron cloud image in perturbation system[5]. In this paper, starting from the Hamiltonian under the interaction of electron spin and orbit of hydrogen-like atoms, the wave function solution under the zero-order approximation is obtained by using the perturbation theory in the degenerate case, and a series of random numbers are generated by Monte Carlo method to simulate various simulated electron clouds. Using Mathematica software, we visualize the three-dimensional distribution of electron clouds of hydrogen-like atoms from different spin directions, making the image more intuitive and helpful for beginners to understand the knowledge of fine structure. Based on the Monte Carlo electron cloud sampling program, we can visualize the three-dimensional electron cloud by setting the quantum number of the wave function.

1.1 Wave function of fine structure of hydrogen-like atom

In order to simplify the model, this paper discusses the Hamiltonian of a hydrogen-like atom in the absence of an external field if the energy of the interaction between the electron spin and the orbit is not considered.

$$\widehat{H_0} = -\frac{h^2}{2m_e}\nabla^2 + U(r) \tag{1}$$

The uncoupled basis vectors L_2, L_z and S_z are chosen to represent, and they are all commutative with H_0. They have common eigenfunctions:

$$\psi_{nlm_lm_s}(r,\theta,\varphi,s_z) = R_{nl}(r)Y_{lm_l}(\theta,\varphi)x_{m_s} \tag{2}$$

J = L + S can also be introduced to represent the total angular momentum operator of electrons. The coupling basis vectors L_2, J_2 and J_z are chosen to represent, which are commutative with H_0, and they have commoneigenfunctions.

$$\psi_{nlm_lm_s}(r,\theta,\varphi,s_z) = R_{nl}(r)u_{ljm}(\theta,\varphi,s_z) \tag{3}$$

Now we consider the energy of spin-orbit interaction. The Hamiltonian of the system is written as

$$\widehat{H} = -\frac{h^2}{2m_e}\nabla^2 + U(r) + \xi(r)\hat{L}\cdot\hat{S} = \widehat{H_0} + \widehat{H'} \tag{4}$$

In the formula, the shielding of extranuclear electrons to the nucleus is not considered for hydrogen-like atoms.

$$\begin{cases} \widehat{H'} = \xi(r)\hat{L}\cdot\hat{S} = \frac{1}{2m_e^2c^2}\frac{1}{r}\frac{dU}{dr} \\ U(r) = -\frac{Ze_s^2}{r} \end{cases} \tag{5}$$

The ξ (r) L·S term in the Hamiltonian is called spin-orbit coupling. Because of the existence of this term, neither L_z nor S_z is commutative with H, and the state of the electron should be represented by other quantum numbers. On the other hand, by

$$\hat{J}^2 = (\hat{L}+\hat{S})^2 = \hat{L}^2 + \hat{S}^2 + 2\hat{L}\cdot\hat{S}, \hat{S}^2 = \frac{3}{4}h^2 \tag{6}$$

Then

$$\hat{L}\cdot\hat{S} = \frac{1}{2}\left[\hat{J}^2 - L^2 - \frac{3}{4}h^2\right] \tag{7}$$

Therefore, J_2, J_z, L_2 are all commutative with H, j, m and l are suitable for describing the state of electrons, where the state of electrons is determined by the four quantum numbers n, l, j and m. The

relationship between $\Psi_{n,l,l+1/2,m}$ and $\Psi_{n,l,l+1/2,m}$ is shown below

$$\left|j_1, \frac{1}{2}, j_1 + \frac{1}{2}, m\right\rangle = \left[\frac{j_1+m+\frac{1}{2}}{2j_1+1}\right]^{\frac{1}{2}} \left|j_1, m - \frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right\rangle + \left[\frac{j_1-m+\frac{1}{2}}{2j_1+1}\right]^{\frac{1}{2}} \left|j_1, m + \frac{1}{2}, \frac{1}{2}, -\frac{1}{2}\right\rangle \tag{8}$$

$$\left|j_1, \frac{1}{2}, j_1 - \frac{1}{2}, m\right\rangle = -\left[\frac{j_1-m+\frac{1}{2}}{2j_1+1}\right]^{\frac{1}{2}} \left|j_1, m - \frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right\rangle + \left[\frac{j_1+m+\frac{1}{2}}{2j_1+1}\right]^{\frac{1}{2}} \left|j_1, m + \frac{1}{2}, \frac{1}{2}, -\frac{1}{2}\right\rangle \tag{9}$$

By multiplying the two sides of the coordinate representation and the s_z representation basis vector to the left, we obtain

$$\psi_{n,\,l,\,l+\frac{1}{2},\,m}(r,\theta,\varphi,s_z) = \left(\frac{l+m+\frac{1}{2}}{2l+1}\right)^{\frac{1}{2}} R_{nl}(r)Y_{lm-\frac{1}{2}}(\theta,\varphi)x_{\frac{1}{2}} + \left(\frac{l-m+\frac{1}{2}}{2l+1}\right)^{\frac{1}{2}} R_{nl}(r)Y_{lm+\frac{1}{2}}(\theta,\varphi)x_{-\frac{1}{2}} \tag{10}$$

$$\psi_{n,\,l,\,l-\frac{1}{2},\,m}(r,\theta,\varphi,s_z) = -\left(\frac{l-m+\frac{1}{2}}{2l+1}\right)^{\frac{1}{2}} R_{nl}(r)Y_{lm-\frac{1}{2}}(\theta,\varphi)x_{\frac{1}{2}} + \left(\frac{l+m+\frac{1}{2}}{2l+1}\right)^{\frac{1}{2}} R_{nl}(r)Y_{lm+\frac{1}{2}}(\theta,\varphi)x_{-\frac{1}{2}} \tag{11}$$

Through the above discussion, we get the fine structure wave function in the case of $l > 0$, and we can discuss the probability distribution in different states.

For example, the states $\Psi_{n,l,l+1/2,m}$ are written as the linear superposition of the spin-up state $x_{1/2}$ and the spin-down state $x_{-1/2}$. According to the statistical interpretation of the wave function, the probabilities that the system is partially in the spin-up state $x_{1/2}$ and the spin-down state $x_{-1/2}$ are

$$W x_{\frac{1}{2}} = [(\frac{l+m+\frac{1}{2}}{2l+1})^{\frac{1}{2}} R_{nl}(r)Y_{lm-\frac{1}{2}}(\theta,\varphi)x_{\frac{1}{2}}]^2 \tag{12}$$

$$W x_{-\frac{1}{2}} = [(\frac{l-m+\frac{1}{2}}{2l+1})^{\frac{1}{2}} R_{nl}(r)Y_{lm+\frac{1}{2}}(\theta,\varphi)x_{-\frac{1}{2}}]^2 \tag{13}$$

When the hydrogen-like atom is in the spin-up state $x_{1/2}$, the probability that the electron is located around any point in space is

$$W(r,\theta,\varphi) = [(\frac{l+m+\frac{1}{2}}{2l+1})^{\frac{1}{2}} R_{nl}(r)Y_{lm-\frac{1}{2}}(\theta,\varphi)x_{\frac{1}{2}}]^2 r^2 \sin\theta \, dr d\theta d\varphi \tag{14}$$

We can obtain the probability density function of the radial and angular parts by separating the variables of the volume element probability.

$$W_R(r) = R_{nl}(r)^2 r^2 \tag{15}$$

$$W_\Theta(\delta) = \frac{l+m+\frac{1}{2}}{2l+1} Y_{lm-\frac{1}{2}}(\theta,\varphi)^2 \sin\theta \tag{16}$$

1.2 The random number of the first kind of selection sampling

The electrons of hydrogen-like atoms are around the nucleus according to a certain probability distribution, and have a certain probability density distribution function. In order to simulate the distribution of hydrogen-like atomic electrons in three-dimensional space, the first kind of selection method in Monte Carlo method is selected for sampling. The space coordinates of the wave function are r, θ, φ, and the separable variable of the wave function is the product of the single variable radial function R(r) and a spherical harmonic function Y^m_l (θ,φ). Then we sample according to the corresponding function, and get the random location of the electrons in turn. We use the first kind

of selection method can only select random numbers in a finite interval, but the sampling interval of the radial distribution function is close to infinity. In order to meet the selection range of the first type of selection method, we need to limit the value range of r. By adjusting the different value intervals, we finally retain 80 % of the electrons in the r direction can be taken to the corresponding interval, and the value range of r is determined to be $[0, r_m]$, where the interval is truncated to ensure that the electron cloud image is relatively complete.

Firstly, we select r by the following steps:

1) The expression $W_R(r)$ of the probability density function of electron is written, and the maximum value M in the range $[0, r_m]$ is obtained.

2) A random number $\delta = r_m * x1$ with uniform distribution in $[0, r_m]$ is constructed by selecting a uniform random number x1 in the interval $[0,1]$.

3) Then the random number x_2 in the uniform $[0,1]$ interval is selected to determine whether $x_2 \leq W_R(\delta)/M$ is satisfied. If the above inequality is satisfied, the next step is performed; if not satisfied, return to the previous step.

4) Select $x_3 = \delta$ as the sampling value.
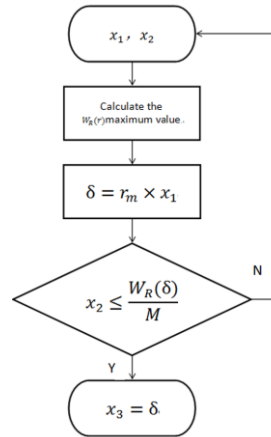
The flowchart is shown in Fig 1.

Figure 1: Radial sampling block diagram

Next, we sample the θ:

1) The radial probability density function $W_\Theta(\theta)$ of electron is written, and the maximum value M in the range of $[0, \pi]$ is obtained.

2) Select the random number x_1 in the uniform interval $[0,1]$, and construct the random number $\delta = \pi * x_1$ uniformly distributed in $[0, \pi]$.

3) Select the random x_2 of the uniform $[0,1]$ interval to determine whether $x_2 \leq W_\Theta(\theta)/M$ is satisfied. If the above inequality is satisfied, the next step is performed; if not satisfied, return to the previous step.

4) Select $x_3 = \delta$ as the sampling value.
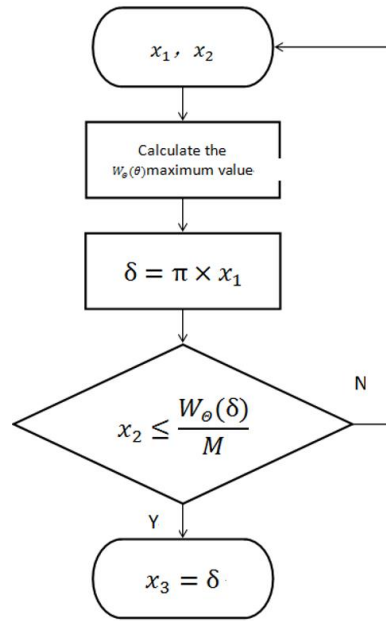
The flowchart is shown in Fig 2.

Figure 2: Radial sampling block diagram

Finally, the random number in the direction of φ is extracted. Because φ is uniformly distributed in [0,2π], we directly sample φ uniformly to obtain a set of sampling values.

Through the selection sampling method, we can get three sets of independent arrays { r_i }, { θ_i }, { φ_i }.Construct the three sets of sampling values into the spatial coordinates of the electron (r_i, θ_i, φ_i), and then use Mathematica to represent the scatter points with rectangular coordinates, and finally get the spatial coordinates of the electron (x_i, y_i, z_i).

2. Result

2.1 Visualization of the fine structure of hydrogen-like atoms

We design and compile the program according to the above principles and block diagram, and use Mathematica software to visualize the electronic cloud. The electron cloud image output by Mathematica software is not limited by the size of quantum number, and a set of quantum numbers of any size and consistent with the value range can be input.

It is easy to observe the wave function of the fine structure of hydrogen-like atoms. The wave function consists of two parts: spin-up $x_{1/2}$ and spin-down $x_{-1/2}$. We select the upward and downward parts of the wave function respectively. Blue is used to label the spin-up electron cloud, and red is used to label the spin-down electron cloud. Finally, two electron cloud images with different orientations are combined for analysis and comparison.

In the image of the electron cloud, each marker point represents the possible spatial position of the electron. Studying the distribution of electron clouds can roughly observe the density of points in a region. The denser the points in the selected area, the greater the probability of electrons appearing in this area. The dark color indicates that the point concentration is large and the probability density is large. However, we summarize the law by comparing the electron cloud images under different quantum number values, and must use the probability density distribution histogram image to analyze and explain.

2.2 Analysis

From the previous analysis, we can know that when n and l are determined, j can take two semi-integer values: j = l ± 1 / 2. There are two energy levels with the same quantum number nl, corresponding to two wave function expressions. The two wave functions can be treated as the product of constant, radial function and angular function, and the expressions have similar composition. The radial functions of the four states of the two wave functions are determined by the quantum number nl, which is exactly the same. The angular function m is two integer values adjacent to j, and the spin-down state is l + 1 and l respectively than the spin-up state.

After nl is determined, the two electron clouds with opposite m have the same shape and position, and the only difference is the rotation direction of the electron around the z axis.

The following six groups of pictures show the electron distribution and probability distribution histograms of five groups of sodium atom fine structure electron cloud spin up state and spin down state and superposition state.
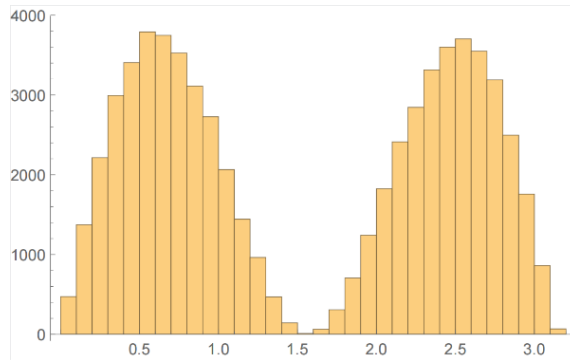

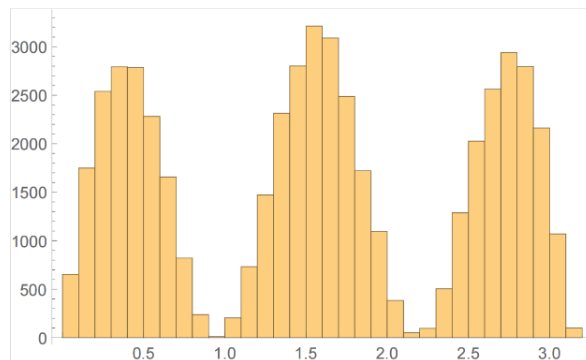Figure 3: l = 1, m = 0 elevation probability distribution histogram

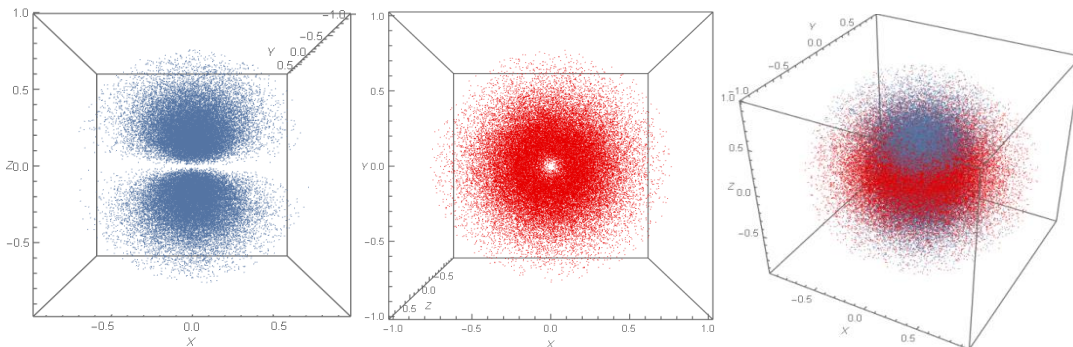Figure 4: l = 2, m = 0 elevation probability distribution histogram

Figure 5: Electron cloud distribution map of helium atom n = 2, l = 1, m = 0.5
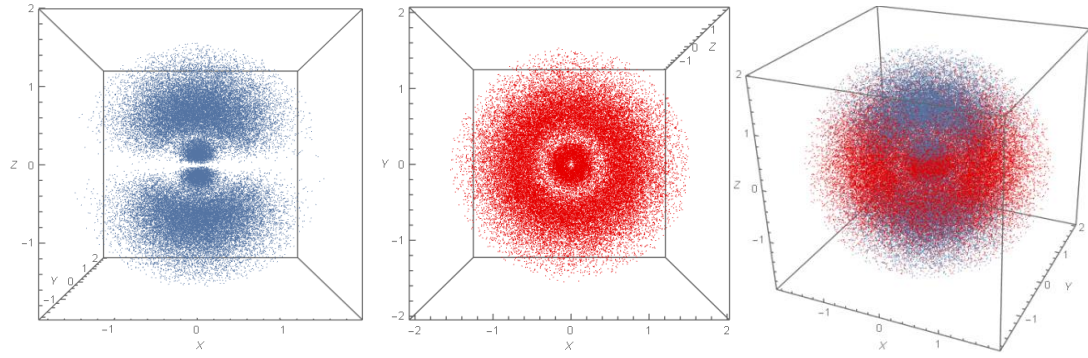
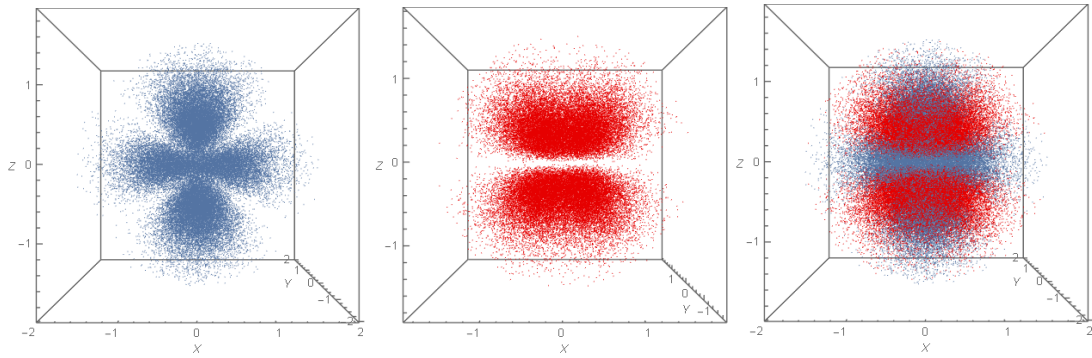Figure 6: Sodium atoms take n = 2, l = 1, m = -0.5 electron cloud distribution map

Figure 7: Sodium atoms take n = 3, l = 2, m = 0.5 electron cloud distribution map

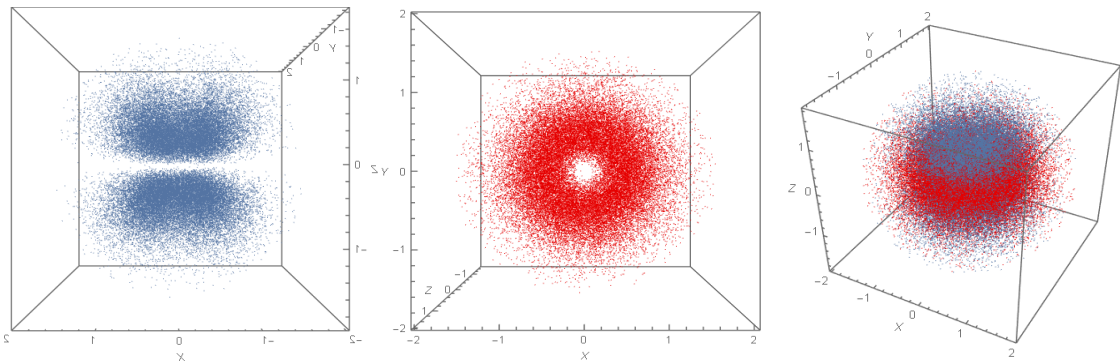Figure 8: Electron cloud distribution map of sodium atom n = 3, l = 2, m = 1.5

By comparing the above set of images, it can be found that when l = 1, it can be seen from Fig 3 that there are two peaks in the elevation probability density function, which is reflected in Figs 5-7 that the electron cloud shape is similar to a dumbbell divided into two parts, because the different values of m are divided into inconsistent extension directions. When n = 2, l = 1, m = 0.5, the electronic cloud image can be abstracted as the superposition of spindles and concentric rings distributed up and down along the z-axis. When n = 3, l = 1, m = 0.5, the electronic cloud image can be abstracted as the superposition of a dumbbell-shaped distribution along the z axis and two concentric rings with different inner diameters.

When l = 2, the distribution shape of the electron cloud is not the traditional spindle shape, because the radial probability distribution of the electron is also considered, and the total probability distribution is the product of the two [6]. When l = 2, Fig 4 shows that the elevation angle probability density function has three peaks. We can see that the electron cloud distribution in Figure 8 presents three relatively concentrated areas at different elevation angles in space.

When m is 0.5, the number of spin-up and spin-down petals is the same, and the petal angle and

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shape are different. When m ≥ 1.5, the number of spin-down electron cloud petals is 2.

3. Summary

In this paper, the wave function solution of the fine structure of sodium atom spectrum is obtained. Using the first kind of selection method, Mathematica software is used to draw the three-dimensional space visualization image of the electron cloud of each energy level of the hydrogen-like atom. In the experiment, we cannot directly observe the distribution of the atomic electron cloud. However, in this paper, the electron clouds with different quantum numbers of atomic energy level splitting in three-dimensional space are simulated by visual simulation program. The intuitive visualization of the fine structure wave function of the hydrogen-like atom spectrum is of great help to the classroom teaching of quantum theory and students ' understanding and mastery of abstract concepts in quantum mechanics [7-10]. It provides a feasible research idea for studying the influence of perturbation on the probability distribution of microscopic particle electron cloud.

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