

A Three-Dimensional Representation of Born's Probability Densities of Hydrogen Atomic Orbitals in Glass Blocks

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We report here a novel method of visualization to record Born's probability densities in glass blocks by the use of a recently developed three-dimensional laser technique. Conventional visualization methods cannot simultaneously show all the characteristic features of an atomic orbital, whereas a real image in a glass block in the present study allows us to recognize both the shape of the orbital and its wave character, such as the existence of spherical, planar and/or conical nodes, at the same time. One can take this block in one's hands and observe it from an arbitrary direction, to gain clearly the whole image of probability density in it. To show a physical image of the behavior of an electron in an atom is profitable for the understanding of atomic orbitals. This method is the most appropriate to understand images of "the probability density".

Keywords: Hydrogen atomic orbital, Born's probability density, Electron clouds, 3-D visualization, Laser sculpture method

1 Introduction

The Schrödinger equation (1) describing the behavior of an electron in a hydrogen atom takes the form

$$\left[-\frac{\hbar^2}{8\pi^2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) - \frac{e^2}{r} \right] \chi = E\chi, \quad (1)$$

where \hbar , m , e , and r are Planck's constant, the mass of an electron, the elementary charge, and the distance of the electron from the nucleus. The atomic nucleus lies on the origin, and x , y , z are the coordinates of the electron. The exact solutions of equation (1) are well known to be expressed as wavefunctions χ_{1s} , χ_{2s} , \dots , χ_{2p} , χ_{3p} , \dots , χ_{3d} , χ_{4d} , \dots , and their energy values E_n are determined by the principal quantum number n . The wavefunctions of a single electron are usually referred to as orbitals, and their squares are called electron clouds. For almost eight decades, scientists have been exploring how to represent the physical meaning of the solutions of the Schrödinger equation [1]. In 1926, Max Born proposed that the square of the wavefunction gives the probabil-

ity density of finding an electron [2]. Suppose we could photograph the position of a single electron at any particular instant; three-dimensional (3-D) photography would enable us to assign coordinates to the electron [3]. The probability density would be represented as an accumulation of particles in a 3-D space. This concept is widely accepted; however, there is not yet any method to visualize the image of the probability density in a "real" 3-D space.

Although a vast number of methods of orbital visualization have already been reported [4–13], most of them are two-dimensional (2-D) projections of 3-D pictures. Shading or 3-D rotation technique helps us to image 3-D pictures from 2-D projections. Real 3-D representations such as solid models also exist [4]. Even if they accurately describe the shape of an orbital, they are not sufficient by themselves. Their sharp boundaries often mislead beginners that the electron moves along the surface. They are far from being suitable images of "electron clouds" or "probability density". A laser sculpture method in a glass block has been employed for reproduc-

ing the boundary surface features of the atomic orbitals [5]. This paper deals with a novel application of the laser technique to visualize the “real” 3-D probability densities of the hydrogen atomic orbitals.

2 Methods

By some improvements of previously reported programs [6, 7] for 2-D electron clouds, we developed a C-language computer program to calculate the probability densities of hydrogen atomic orbitals in a 3-D space. The probable points (x, y, z coordinates) where we could find a single electron were determined by the rejection method [14]. The practical processes are as follows.

- (i) Let $f(x, y, z)$ be a squared wavefunction. For example, $f(x, y, z)$ of the hydrogen 1s atomic orbital is expressed by

$$\chi_{1s}^2 = \frac{1}{\pi} \exp(-2r), \quad (2)$$

$$\text{where } r = (x^2 + y^2 + z^2)^{1/2}. \quad (3)$$

- (ii) The variables $x, y,$ and z are defined in the range of $-R/2$ to $R/2$ according to the size of the orbital.
- (iii) A parameter M is so chosen that it is slightly larger than the maximum value of $f(x, y, z)$.
- (iv) By utilizing uniform random numbers u_i ($0.0 \leq u_i \leq 1.0$), the value F of $f(x, y, z)$ at a trial point P ($x = v_1, y = v_2, z = v_3$) is calculated,

$$\text{where } v_i = R \times u_i - \frac{R}{2} \quad (i = 1, 2, 3). \quad (4)$$

- (v) If $F > M \times u_i$ ($i = 4$),
the point P is accepted, otherwise, rejected.

- (vi) Procedures (iv and v) are repeated to get a desired number of probable points.

In the $f(x, y, z)$ expressed by equation (2), M was 0.319 au^{-3} and R was 12 au ($1 \text{ au} = 52.92 \text{ pm}$). The CPU time taken to collect 50000 probable points for this orbital was only 18 s (on Octane, R12000, SGI Inc.). The collected data were sculptured as 50000 small points in a glass block, with a size of $60 \times 60 \times 60 \text{ mm}^3$, by using laser equipment (Rofin-Baasel RMS OSC-10).

3 Results and Discussion

In a typical textbook, the hydrogen 1s orbital (χ_{1s}) is represented as a spherical isosurface having a constant

function value or a boundary surface that captures a certain percentage of the probability of the 1s wavefunction. This method represents well the symmetric character of the χ_{1s} orbital. However, it is impossible to represent the characteristic features of the hydrogen 2s orbital (χ_{2s}) by the same technique. As shown in Figure 1(a), there exist two isosurfaces having an absolute function value of $0.027 \text{ au}^{-3/2}$; one has a radius of $r_1 = 1.44 \text{ au}$ (point A), and the other has a radius of $r_2 = 4.00 \text{ au}$ (point C). When we draw the isosurfaces in a cube of $R = 8 \text{ au}$, only the outer surface ($r_2 = 4.00 \text{ au}$) can be detected (Figure 1(b)), and the inner surface ($r_1 = 1.44 \text{ au}$) is completely hidden by the outer surface. This is the most disadvantageous aspect of the isosurface representation. To avoid this disadvantage, a semi-transparent [8] or mesh [9] technique is sometimes adopted. For the same purpose, animation to look into the inner part of the orbital was reported [10]. When the cube size R is taken smaller than 8 au , the inner surface ($r_1 = 1.44 \text{ au}$) appears (Figure 1(c), Figure 1(d)). The outer surface disappears at $R = 4 \text{ au}$ (Figure 1(e)).

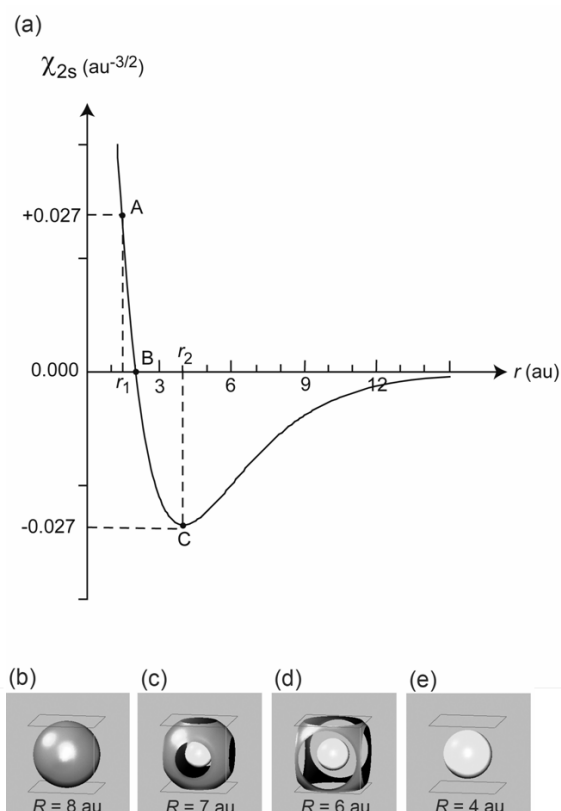


Figure 1. Characteristic features of the hydrogen 2s orbital; (a): function value of χ_{2s} orbital against distance r from atomic nucleus. Points A and C correspond to the radii of two concentric sphere shells having the same absolute value of $0.027 \text{ au}^{-3/2}$. Point B ($r = 2.00 \text{ au}$) corresponds to the radius of the nodal sphere; (b)-(e): snapshots of an animation of hydrogen χ_{2s} isosurfaces in a cube of $R \times R \times R \text{ au}^3$. By changing the display region R , the inner shell is shown.

For a representation of the inner information of the probability density of an atomic orbital, the cross section [6, 7, 11] of the electron clouds is useful (Figure 2(a-c)). Circular cross sections of spherical nodes (strictly, nodes of the original orbital, not of the square of it) are clearly shown as dark circles in Figure 2(b) and Figure 2(c). Figure 2(d) shows the images of the 3-D probability densities of the hydrogen 1s to 3s orbitals in the present study. At a glance, they look like the cross sections in Figure 2(a), Figure 2(b), and Figure 2(c), respectively, because they are 2-D projected photographs of the original pictures in 3-D glass blocks. The original ones are basically different from the cross sections from the following two standpoints. First, the present model is a “real” 3-D orbital in 3-D space; on the other hand, the cross section representation is a 2-D picture of the 3-D orbital. Second, one can take this model in one’s hands and examine it closely from every direction. This is the most advantageous feature of this model. One can easily image the

3-D spherical shapes of the s orbitals, and not the 2-D circles or disks; one can recognize the inner information including the spherical nodes, which are concentric spherical shells instead of circular lines. It must be noted that the present visualization method is the first one to display both the shape of an orbital, which is characteristic of the isosurface technique, and the inner information which is characteristic of the cross section approach.

Figure 3(a) shows the images of the 3-D probability densities of the hydrogen $2p_z$ to $4p_z$ orbitals in glass blocks. One can recognize the planar node (Figure 3(a)) and the spherical node (Figure 3(a), center and right) at the same time. The similarity of the shape of each p_z orbital is also recognized. In the conventional isosurface representations (Figure 3(b)-Figure 3(d)), the spherical nodes are hard to recognize from the view along the z axis (Figure 3(c), Figure 3(d), bottom), because the outer surface in $3p_z$ or $4p_z$ completely hides the inner surfaces.

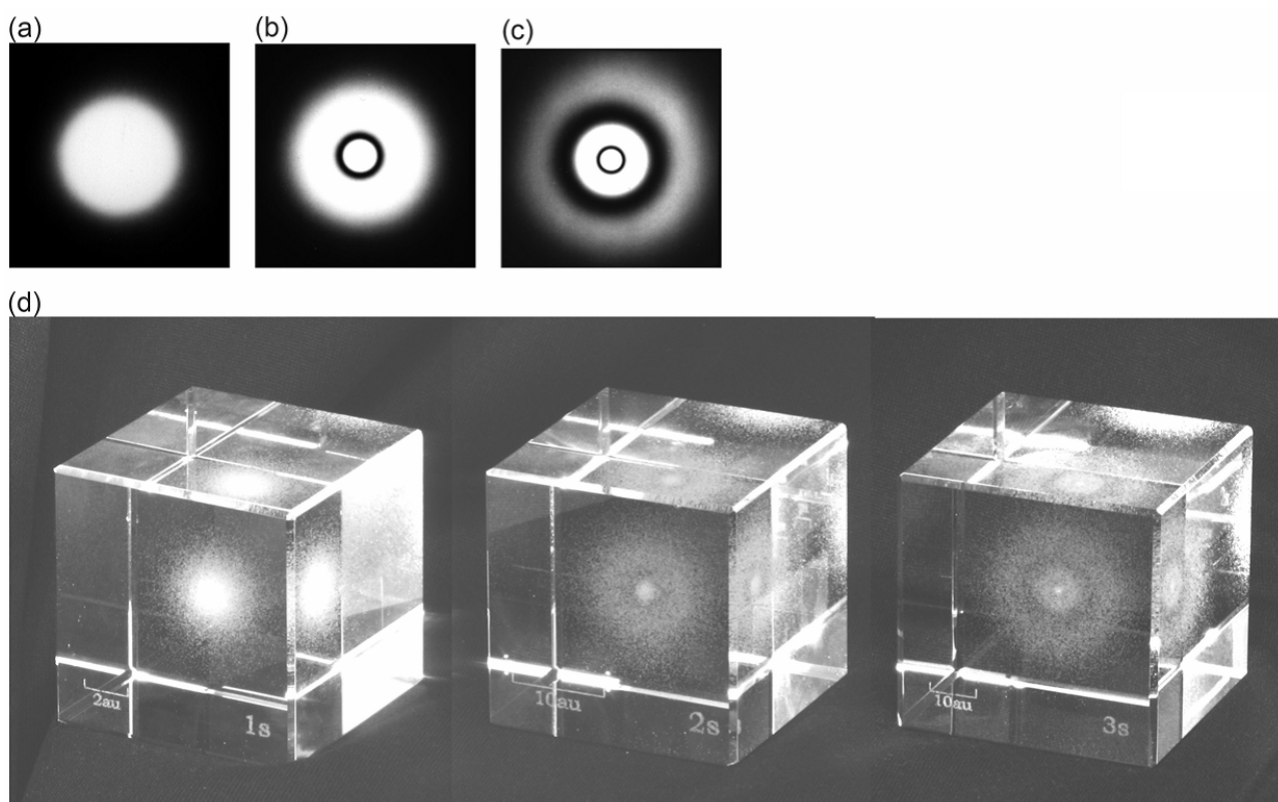


Figure 2. Representations of the probability density of hydrogen s orbitals. Among the probability densities of the cross section of hydrogen 1s (a), 2s (b), and 3s (c) orbitals [7], the inner nodes are represented in (b) and (c). Images of the 3-D probability densities of hydrogen 1s, 2s, and 3s orbitals in a glass block show the spherical shape of the orbitals together with the inner nodes (d).

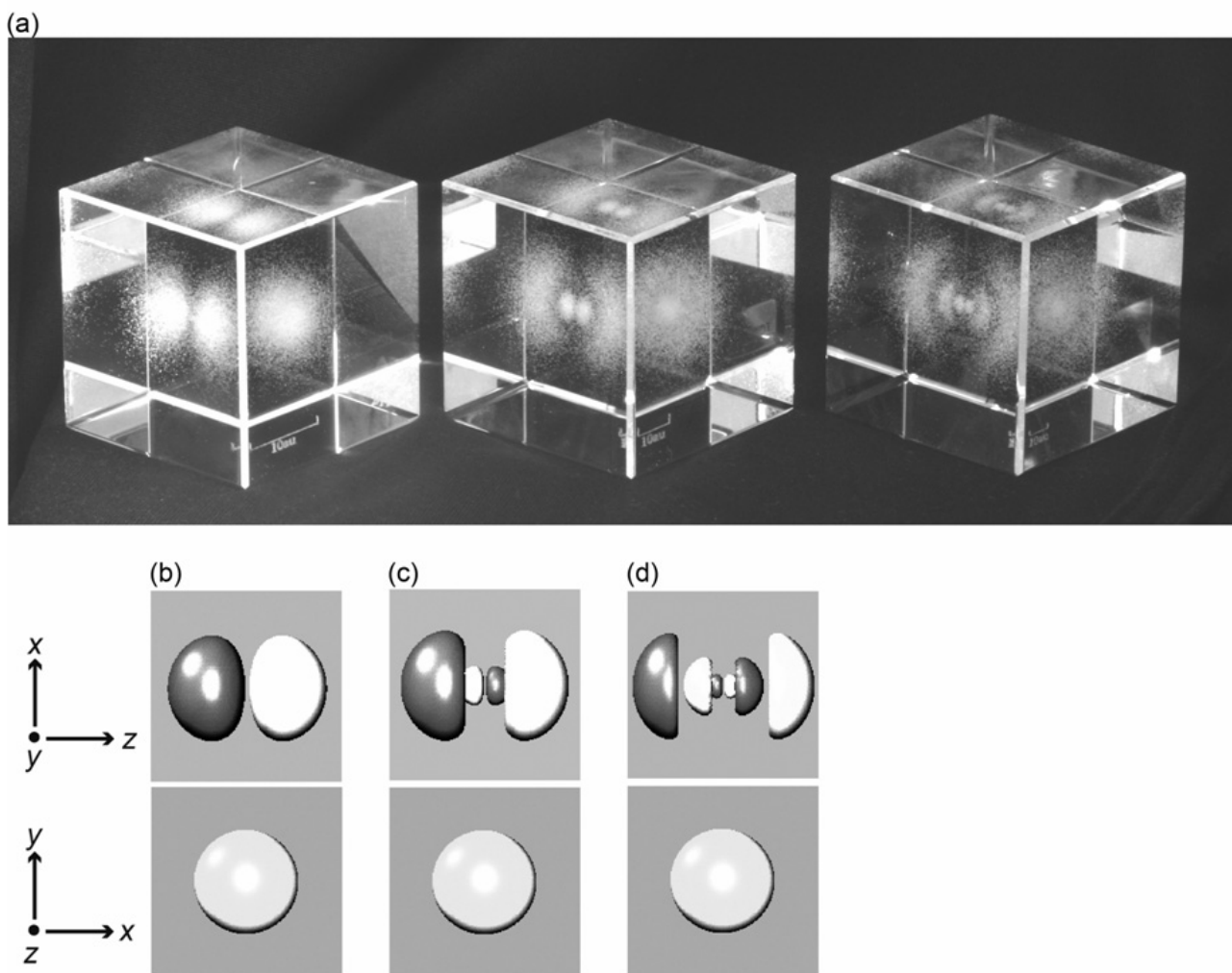


Figure 3. Comparison of probability density representations with the isosurface technique of hydrogen p_z orbitals. Images of the 3-D probability densities of hydrogen $2p_z$, $3p_z$, and $4p_z$ orbitals in a glass block are shown in (a). Isosurfaces of hydrogen $2p_z$, $3p_z$, and $4p_z$ atomic orbitals are represented in (b), (c) and (d), respectively. The views from the z axis ((b)-(d) bottom) are essentially identical.

The 3-D probability density of the hydrogen $3d_{3z^2-r^2}$ orbital in the present study (Figure 4(a)) seems to have no torus (doughnut), which is the characteristic shape of the isosurface representation (Figure 4(b)). This difference in orbital shape is based on the fact that the plot of probability density is obtained for the whole space in the cube, whereas the isosurface technique represents only surfaces having the same absolute function value. Some applications of orbital visualization are freely available on the Internet: "Atom in a box" [12], "Hydrogen Atom Viewer" [13], and so on. For example, "Atom in a box" is a piece of public domain software, presented by Dauger Research Inc., to visualize hydrogen atomic orbitals. This program traces a ray of light through a 3-D cloud density that represents the probability density of wavefunctions

and presents the results in real-time. The representation of $3d_{3z^2-r^2}$ by this program gave a picture that was almost the same as Figure 4(a). The familiar isosurface representation of $3d_{3z^2-r^2}$ (Figure 4(b)) is only a "mental model". The actually existing shape is that of "Atom in a box" or the present study (Figure 4(a)). "Atom in a box" is an excellent program to represent a 3-D probability density with high speed (up to 48 frames per second [12]). The rotation with high speed of electron clouds compensates for the 2-D output on a cathode ray tube or on a liquid crystal display; nevertheless, it is essentially a virtual method to image a 3-D object from a 2-D output. It is complicated to image a shape by rotating the picture on the display with a mouse and it is impossible to observe the whole shape at a glance.

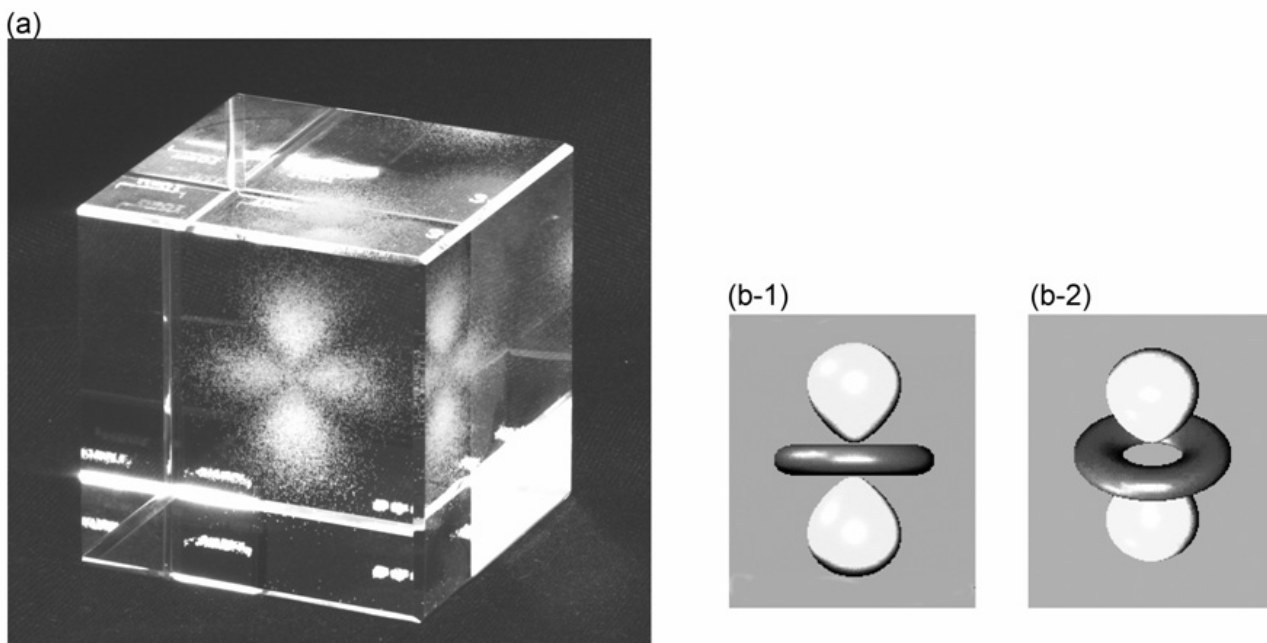


Figure 4. Representations of the hydrogen $3d_{3z^2-r^2}$ orbital. The probability density in a glass block is shown in (a). Conventional isosurface representations, (b-1) and (b-2), differ from the real 3-D picture in (a).

Exactly speaking, “clouds” are not an appropriate expression for a single electron. Schrödinger interpreted that the square of a wavefunction represents the electron density [15]. This description, which sometimes appears even in recent papers [16–18], considers a mass of “clouds” having mass and electric charge. If an electron is described as “clouds”, the Schrödinger equation (1) for hydrogen atomic orbitals must contain an expression of electron repulsion. But it does not include any such term. If we could detect a single electron, it would give us only a single particle image. We can never detect a fragment of a cloud. The representation of electron density has proved to be very useful in practice. However, it cannot be justified so rigorously as the probability density interpretation [3]. The present study agrees with the above discussion because the probability density defined by Born [2] is represented as an accumulation of detected particles.

4 Conclusion

The real image of an atomic orbital is produced by means of a novel method of visualization to record Born’s probability densities in glass blocks by the use of a recently developed three-dimensional laser technique. Solid models or the isosurface method are suitable for the represen-

tation of the shape of an orbital, while the cross section is suitable for the representation of the inner information. These conventional methods of visualization cannot simultaneously show all the characteristic features of a hydrogen atomic orbital. Furthermore, we cannot exclude the possibility that such models give us an incorrect image for an atomic orbital as shown in the hydrogen $3d_{3z^2-r^2}$ orbital. On the other hand, a real image in a glass block in the present study can be freely taken in our hands, to visualize the shape and the existence of inner information about the probability density. This is the first example that allows us to recognize both the shape of the orbital and its wave character, such as the existence of spherical, planar and/or conical nodes, at the same time.

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