

Visualizing Atomic Orbitals With Spin ½

Lloyd Watts
September 15, 2022

Abstract – Spherical Harmonics are a fundamental component of the solution of the Schrödinger Equation for the Hydrogen Atom. It is common to plot tables of these functions to aid in understanding the shape and form of electron wavefunctions in the various quantum states. Unfortunately, the Schrödinger Equation does not account for Electron Spin, so these orbital plots do not represent the correct number of quantum states, and they do not correctly represent the shape and form of real Hydrogen Atom wavefunctions, which do have Spin Up and Spin Down states. In this paper, we develop a new visualization for Atomic Orbitals that correctly represents the Spin Up and Spin Down states. These Orbitals have a direct and obvious relationship to the Periodic Table of Elements.

1. Introduction

The solution of the Schrödinger Equation for the Hydrogen Atom is [1]:

$$\psi_{n\ell m}(r, \theta, \varphi) = \sqrt{\left(\frac{2}{na_0^*}\right)^3 \frac{(n-\ell-1)!}{2n(n+\ell)!}} e^{-\rho/2} \rho^\ell L_{n-\ell-1}^{2\ell+1}(\rho) Y_\ell^m(\theta, \varphi)$$

where the Spherical Harmonic function is given by [2]:

$$Y_\ell^m(\theta, \varphi) = (-1)^m \sqrt{\frac{(2\ell+1)}{4\pi} \frac{(\ell-m)!}{(\ell+m)!}} P_\ell^m(\cos \theta) e^{im\varphi}$$

Since the Spherical Harmonic function contains all of the angular dependencies, it is common to plot tables of the Spherical Harmonic Functions as shown in Figure 1 [3] to aid in understanding the shape and form of electron wavefunctions in the various quantum states. Unfortunately, the Schrödinger Equation does not account for Electron Spin, so these orbital plots do not represent the correct number of quantum states, and they do not correctly represent the shape and form of real Hydrogen Atom wavefunctions, which do have Spin Up and Spin Down states. For each one of the orbital plots, the reader is expected to understand that there is a corresponding Spin Up ($s=+\frac{1}{2}$) and Spin Down ($s=-\frac{1}{2}$) state, but there does not appear to be a common way to visualize what those Spin Up and Spin Down states look like. The purpose of this paper is to develop a meaningful way to visualize those Spin Up and Spin Down states.

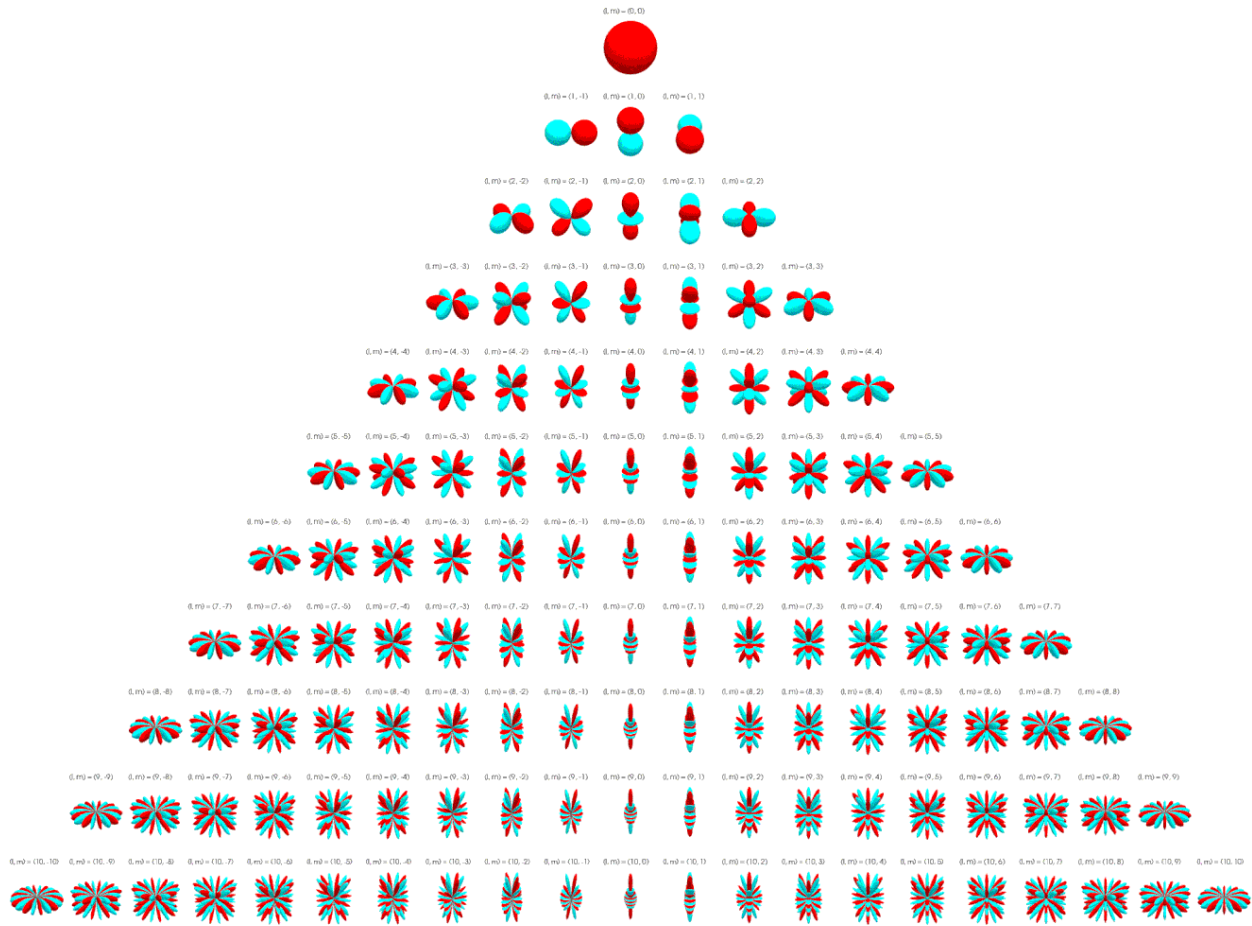


Figure 1: Conventional visualization of Real Spherical Harmonics [3]. Red indicates positive Real part, Cyan indicates negative Real part. These states are shown for different values of quantum numbers l and m , as indicated in the solution to the Schrödinger equation. But in a real Hydrogen atom, for each value of l and m , there is a Spin Up ($s = +1/2$) and Spin Down ($s = -1/2$) state, which are not shown in the diagram.

2. The Spin $\frac{1}{2}$ Property as developed by Pauli

The full development and justification of Spin $\frac{1}{2}$ requires the Dirac equation and its corresponding solution for the Hydrogen Atom [4]. But the essential properties of Spin $\frac{1}{2}$ were first developed by Pauli in 1927 [5], based on mathematics earlier developed by Cartan in 1913 [6]. For the purposes of this paper, it is sufficient to extend the Schrödinger Hydrogen Atom solution to show the Spin Up and Spin Down states by appending the corresponding Pauli Spinor:

$$\psi_{n\ell m\uparrow}(r, \theta, \varphi) = \sqrt{\left(\frac{2}{na_0^*}\right)^3 \frac{(n-\ell-1)!}{2n(n+\ell)!}} e^{-\rho/2} \rho^\ell L_{n-\ell-1}^{2\ell+1}(\rho) Y_\ell^m(\theta, \varphi) \begin{Bmatrix} 1 \\ 0 \end{Bmatrix}$$

$$\psi_{n\ell m\downarrow}(r, \theta, \varphi) = \sqrt{\left(\frac{2}{na_0^*}\right)^3 \frac{(n-\ell-1)!}{2n(n+\ell)!}} e^{-\rho/2} \rho^\ell L_{n-\ell-1}^{2\ell+1}(\rho) Y_\ell^m(\theta, \varphi) \begin{Bmatrix} 0 \\ 1 \end{Bmatrix}$$

And now our goal will be to develop a way to visualize the angular part of the wavefunctions, including the Spherical Harmonics and the Spin Up and Spin Down Pauli Spinors:

$$Y_\ell^m(\theta, \varphi) \begin{Bmatrix} 1 \\ 0 \end{Bmatrix}$$

$$Y_\ell^m(\theta, \varphi) \begin{Bmatrix} 0 \\ 1 \end{Bmatrix}$$

To do this, we need to know the properties of the Pauli Spinors, as they would apply to an electron wavefunction. At first glance, by their notation, they appear to simply be some kind of vector. But they are much more complicated than that. The essential properties of the Pauli Spinors are:

- The action of a rotation on a spinor is always double-valued. In modern terms, this presents the special unitary group SU(2) as a double cover of SO(3) [7].
- a spinor transforms to its negative when the space is continuously rotated through a complete turn from 0° to 360° [8].
- a spinor is invariant to rotations of 720° [8].

3. A Visual Representation of the Spin ½ Property

In Figure 2, we show a simple demonstration of the Spin ½ property applied to a wave loop [9]. On the left side of the figure, we see a normal wave loop with 12 cycles, without the Spin ½ property. It connects back around to itself after 12 cycles of the wave. Each point on the loop is visited once as the wave travels around the loop to connect back with itself. On the right side of the figure, we have wave loops with 12.5 cycles (Spin + ½) and 11.5 cycles (Spin - ½), respectively. After one full loop, the waves do not connect back to themselves (transformed to its negative after rotation by 360°); the wave has to go around twice to reconnect back to itself (invariant to rotation by 720°). Each point on the loop is visited twice before the wave connects back to itself (double cover). These Spin ½ waves satisfy all three properties of the Pauli Spinors as described above.

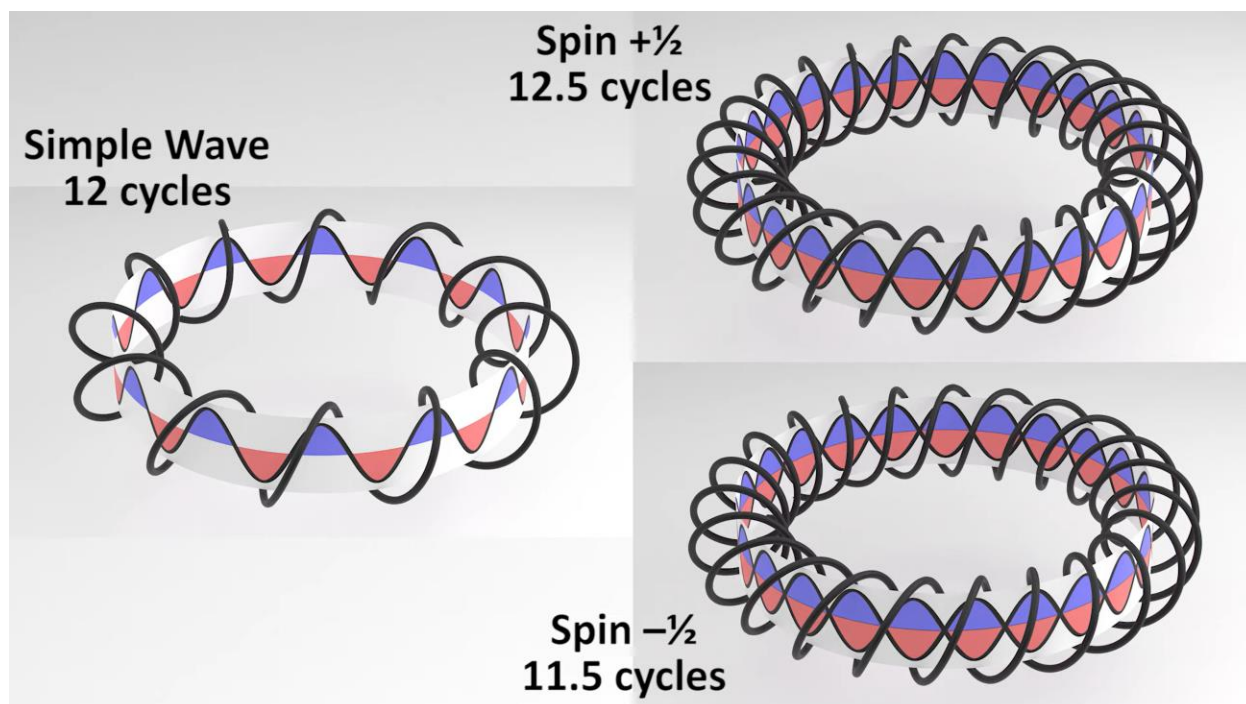


Figure 2: Applying the properties of Spin $+\frac{1}{2}$ and Spin $-\frac{1}{2}$ to a complex wavefunction configured in a loop [9]. On the left, we have a wavefunction with 12 cycles, connected back onto itself in a loop. The complex wavefunction is represented by the black helix; the real part of the wave is represented by the blue and red wave. The wave connects back to itself after 12 cycles. On the right, we have Spin $+\frac{1}{2}$ and Spin $-\frac{1}{2}$, with 12.5 and 11.5 cycles respectively. After one full loop, these wavefunctions do not connect back to themselves; they have to go around twice to connect back to themselves. Because they go around twice, they create a double-valued wave. Each point on the loop is “double-covered” by the wave.

4. A Visual Representation of Atomic Orbitals with Spin $\frac{1}{2}$

Now we need a way to apply this visualization concept to an atomic orbital, which is a three-dimensional wavefunction, not just to a wave loop. In Figure 3 on the left side, we show the conventional view of the Spherical Harmonic function with $l=12$ and $m=12$. The actual function being plotted is

$$\psi = \frac{5 \sqrt{\frac{676039}{\pi}} \operatorname{Re} \left[e^{12 i \phi} \sin[\theta]^{12} \right]}{4096}$$

This wavefunction has a total of 12 cycles, where each cycle of the wave has a positive half-cycle (red lobe) and negative half-cycle (cyan lobe). There are a total of exactly 24 lobes, in alternating red/cyan sequence, perfectly spaced, indicating a simple wavefunction that goes through 12 cycles as it goes around the vertical z axis.

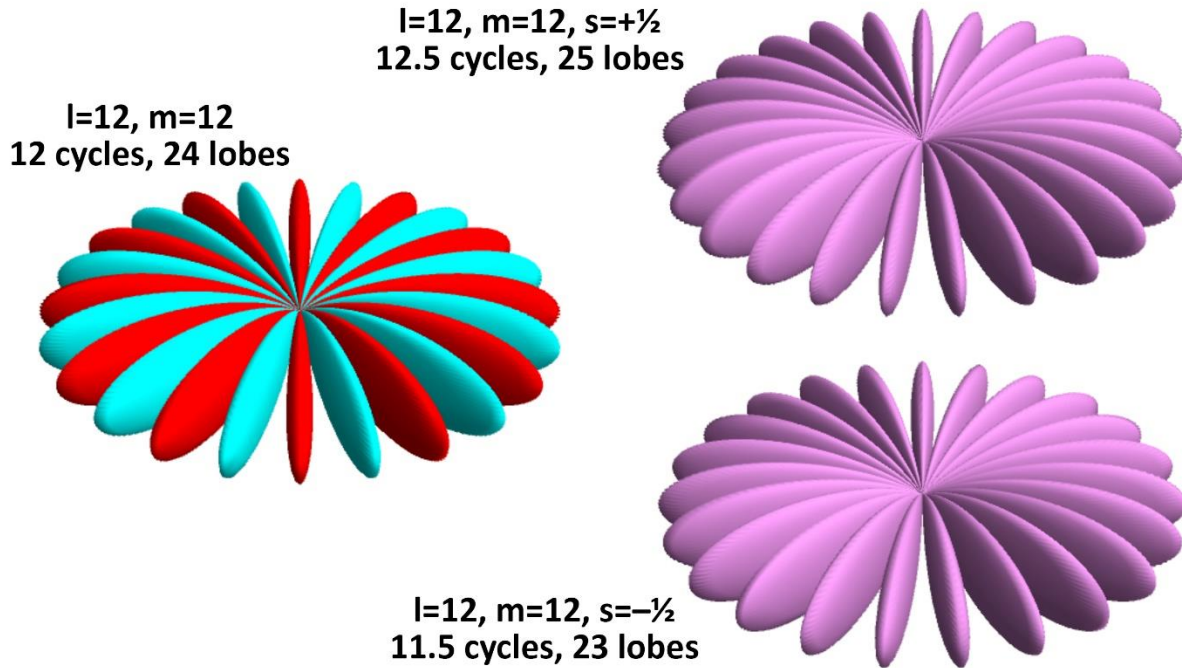


Figure 3: Applying the properties of Spin + $\frac{1}{2}$ and Spin - $\frac{1}{2}$ to a Spherical Harmonic function with $l=12$ and $m=12$. On the left, we have the conventional Spherical Harmonic plot with 12 cycles around the vertical z axis. The positive half-cycles of the function are colored red; the negative half-cycles are colored cyan. There are a total of 12 cycles, with 24 lobes, in an alternating red/cyan sequence. On the right, we have Spin + $\frac{1}{2}$ and Spin - $\frac{1}{2}$ variations. The Spin + $\frac{1}{2}$ variation has 12.5 cycles, and 25 lobes. The Spin - $\frac{1}{2}$ variation has 11.5 cycles, and 22 lobes. After one full loop around the vertical z axis, these wavefunctions do not connect back to themselves; they have to go around twice to connect back to themselves. Because they go around twice, they create a double-valued wave. Each point on the loop is “double-covered” by the wave. For this reason, each lobe is both positive and negative, so we cannot color each lobe red or cyan. We choose the lavender color to indicate a double-valued lobe, both positive and negative.

Now let us consider the Spin + $\frac{1}{2}$ case, in the upper right part of Figure 3. The actual function being plotted is:

$$\text{psiUp} = \frac{5 \sqrt{\frac{676039}{\pi}} \operatorname{Re} \left[e^{\frac{25 i \phi}{2}} \sin[\theta]^{12} \right]}{4096}$$

i.e., we have replaced $e^{12 i \phi}$ with $e^{25 i \phi / 2}$, thus giving the wavefunction an extra half-cycle of phase accumulation around the vertical z axis, thus making the wavefunction double-valued everywhere.

The function of the Spin + ½ operator is to map

$$\text{Spin } +1/2: e^{im\phi} \rightarrow e^{i(m+1/2)\phi}$$

Since the wavefunction has an odd number of half-cycles (25), and thus an odd number of lobes, we cannot color the nodes red and cyan, for positive and negative lobes. Each lobe is double-valued, both positive and negative. So we choose a new lavender color to represent a double-valued positive-and-negative value.

Similarly, we consider the Spin – ½ case in the bottom right part of Figure 3. The actual function being plotted is:

$$\text{psiDown} = \frac{5 \sqrt{\frac{676039}{\pi}} \operatorname{Re} \left[e^{\frac{23 i \phi}{2}} \sin[\phi]^{12} \right]}{4096}$$

i.e., we have replaced $e^{12 i \phi}$ with $e^{23 i \phi/2}$, thus giving the wavefunction one less half-cycle of phase accumulation around the vertical z axis, thus making the wavefunction double-valued everywhere.

The function of the Spin – ½ operator is to map

$$\text{Spin } -1/2: e^{im\phi} \rightarrow e^{i(m-1/2)\phi}$$

Since the wavefunction has an odd number of half-cycles (23), and thus an odd number of lobes, we again use the new lavender color to represent a double-valued positive-and-negative value.

Thus, we have defined a graphical convention for the Spin + ½ and Spin – ½ wavefunctions. They will always have an odd number of half-cycles or lobes, and they will be colored lavender to indicate that they are double-valued.

5. A Special Case: The Ground State $l=0, m=0$

The ground state, $l=0$ and $m=0$, is a special case, and it is instructive to examine it in detail in Figure 4. On the left side of the figure, we see a normal wave loop with 0 cycles, without the Spin ½ property. It connects back around to itself after 0 cycles of the wave, i.e. it is a constant value all the way around the loop. Each point on the loop is visited once as the wave travels around the loop to connect back with itself. On the right side of the figure, we have wave loops with 0.5 cycles (Spin + ½) and -0.5 cycles (Spin – ½), respectively. After one full loop, the waves do not connect back to themselves (transformed to its negative after rotation by 360°); the wave has to go around twice to reconnect back to itself (invariant to rotation by 720°). Each point on the loop is visited twice before the wave connects back to itself (double cover). These Spin ½ waves satisfy all three properties of the Pauli Spinors as described above. Each wave effectively makes a Mobius strip, but the two waves are not identical; they differ in their chirality (direction of twist). Notice that the real part of the Spin ½ loops has a single node, where the magnitude of the real part goes to zero.

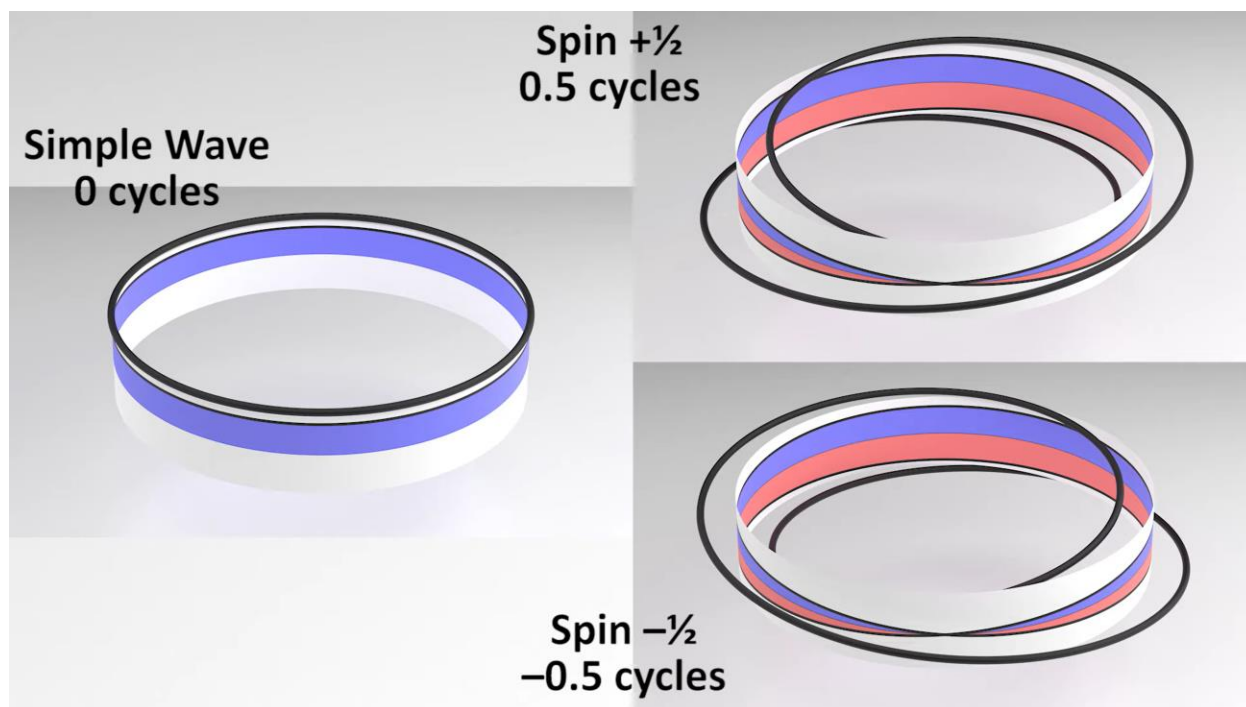


Figure 4: The special case of the Ground State, where $l=0$ and $m=0$. On the left, we have a wavefunction with 0 cycles, connected back onto itself in a loop. The wave connects back to itself after 0 cycles, i.e. it is a constant value all the way around the loop. On the right, we have Spin $+\frac{1}{2}$ and Spin $-\frac{1}{2}$, with 0.5 and -0.5 cycles respectively. After one full loop, these wavefunctions do not connect back to themselves; they have to go around twice to connect back to themselves. Because they go around twice, they create a double-valued wave. Each point on the loop is “double-covered” by the wave. Each wave effectively makes a Mobius strip, but the two waves are not identical; they differ in their chirality (direction of twist). Notice that the real part of the Spin $\frac{1}{2}$ loops has a single node, where the magnitude of the real part goes to zero.

Now we will apply this visualization concept to the ground state atomic orbital. In Figure 5 on the left side, we show the conventional view of the Spherical Harmonic function with $l=0$ and $m=0$. The actual function being plotted is

$$\psi = \frac{1}{2\sqrt{\pi}}$$

This wavefunction has a total of 0 cycles, with constant amplitude, so it is colored red. There are 0 lobes.

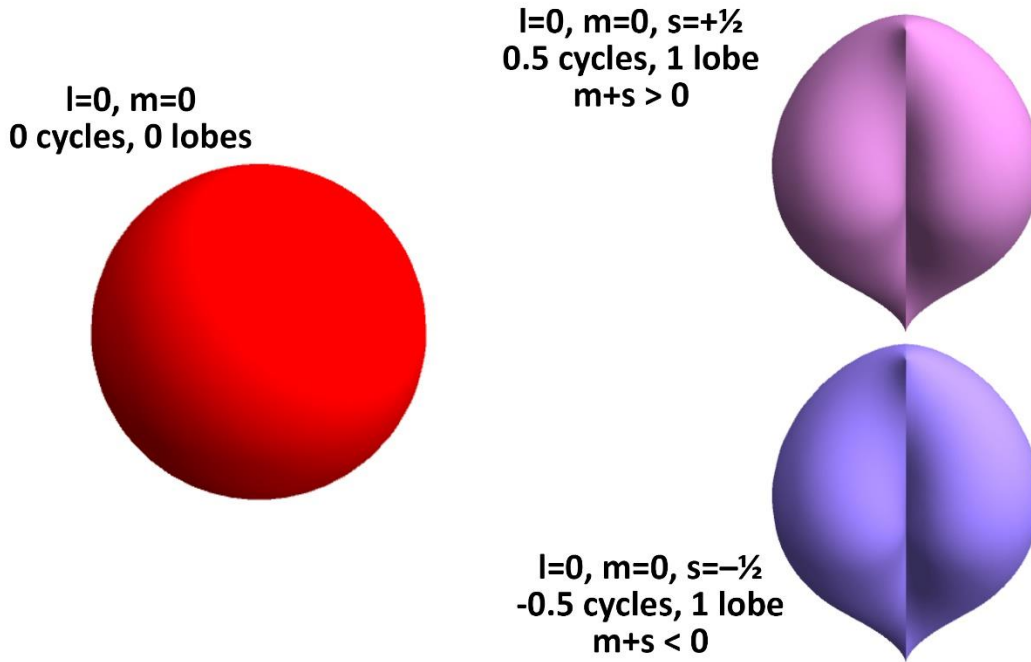


Figure 5: Applying the properties of Spin + $\frac{1}{2}$ and Spin - $\frac{1}{2}$ to a Spherical Harmonic function with $l=0$ and $m=0$ (Ground State). On the left, we have the conventional Spherical Harmonic plot with 0 cycles around the vertical z axis, i.e. constant amplitude. The function is single-valued and positive everywhere, so it is colored red. There are a total of 0 cycles, with 0 lobes. On the right, we have Spin + $\frac{1}{2}$ and Spin - $\frac{1}{2}$ variations. The Spin + $\frac{1}{2}$ variation has 0.5 cycles, and 1 lobe, with positive chirality, because $m+s>0$. The Spin - $\frac{1}{2}$ variation has -0.5 cycles, and 1 lobe, with negative chirality, because $m+s<0$. After one full loop around the vertical z axis, these wavefunctions do not connect back to themselves; they have to go around twice to connect back to themselves. Because they go around twice, they create a double-valued wave. Each point on the loop is “double-covered” by the wave. For this reason, each lobe is both positive and negative, so we cannot color each lobe red or cyan. We choose the lavender color to indicate a double-valued lobe, when the chirality is positive ($m+s>0$). We choose the violet color to indicate a double-valued lobe, when the chirality is negative ($m+s<0$).

Now let us consider the Spin + $\frac{1}{2}$ case, in the upper right part of Figure 5. The actual function being plotted is:

$$\psi_{\text{Up}} = \frac{\text{Re} \left[e^{\frac{i\phi}{2}} \right]}{2\sqrt{\pi}}$$

i.e., we have replaced 1 with $e^{i\phi/2}$, thus giving the wavefunction an extra half-cycle of phase accumulation around the vertical z axis, thus making the wavefunction double-valued everywhere.

This function is double-valued, with positive chirality, so we choose the same lavender color as previously to represent a double-valued positive-and-negative value.

Similarly, we consider the Spin – ½ case in the bottom right part of Figure 5. The actual function being plotted is:

$$\text{psiDown} = \frac{\text{Re} \left[e^{-\frac{i\phi}{2}} \right]}{2\sqrt{\pi}}$$

i.e., we have replaced 1 with $e^{-i\phi/2}$, thus giving the wavefunction a negative half-cycle of phase accumulation around the vertical z axis (negative chirality, since $m+s<0$), thus making the wavefunction double-valued everywhere. We choose the violet color to represent a double-valued positive-and-negative value with negative chirality.

6. A Table of Atomic Orbitals with Spin ½

Now we can generate a new table of Hydrogen Orbitals which explicitly represent these Spin Up and Spin Down states, as shown in Figure 6. For each conventional red/cyan even-lobed Spherical Harmonic, we will have a pair of variations, one with Spin + ½ and one with Spin – ½. The variations will be colored lavender ($m+s>0$) or violet ($m+s<0$). This new table has the correct number of quantum states (twice as many as the conventional table), and it properly displays them as lavender or violet odd-lobed double-valued states with the Spin ½ property.

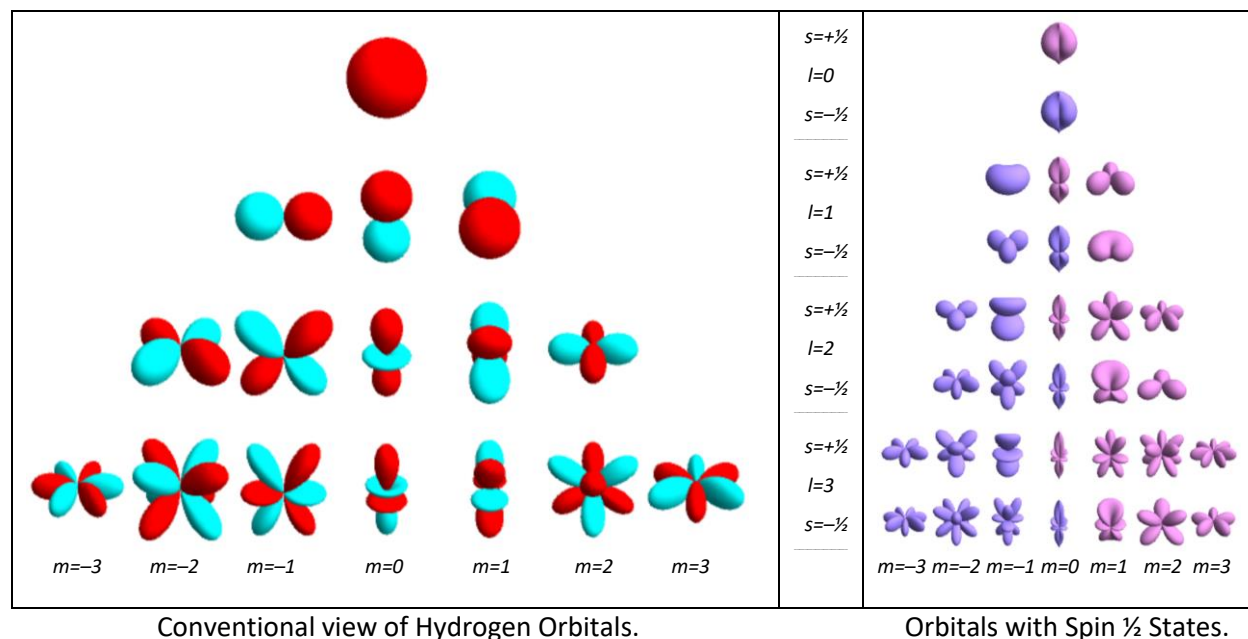


Figure 6: Comparing the conventional view of Hydrogen Orbitals (no representation of Spin states) with the new Hydrogen Orbitals which explicitly represent the Spin Up and Spin Down states, showing them as double-valued spinors with odd numbers of azimuthal lobes. Lavender for positive chirality ($m+s>0$), Violet for negative chirality ($m+s<0$).

Now we can state the general rule for mapping the conventional Spherical Harmonics Orbitals to the new corrected Orbitals. Recall the definition of the Spherical Harmonic function:

$$Y_{\ell}^m(\theta, \varphi) = (-1)^m \sqrt{\frac{(2\ell+1)(\ell-m)!}{4\pi(\ell+m)!}} P_{\ell}^m(\cos \theta) e^{im\varphi}$$

The Spin $\frac{1}{2}$ operator makes the following mappings:

$$\text{Spin } +1/2: Y_{\ell}^m(\theta, \phi) \rightarrow Y_{\ell}^m(\theta, \phi) e^{i\phi/2}$$

$$\text{Spin } -1/2: Y_{\ell}^m(\theta, \phi) \rightarrow Y_{\ell}^m(\theta, \phi) e^{-i\phi/2}$$

Note also that this mapping properly gives the correct total angular momentum in the Spin $+\frac{1}{2}$ and Spin $-\frac{1}{2}$ states:

$$j = l + s = l \pm \frac{1}{2}$$

Finally, we can also use this mapping and visualization technique to apply to the small component (negative energies) of the Dirac Hydrogen Atom.

7. Relationship to the Periodic Table of the Elements

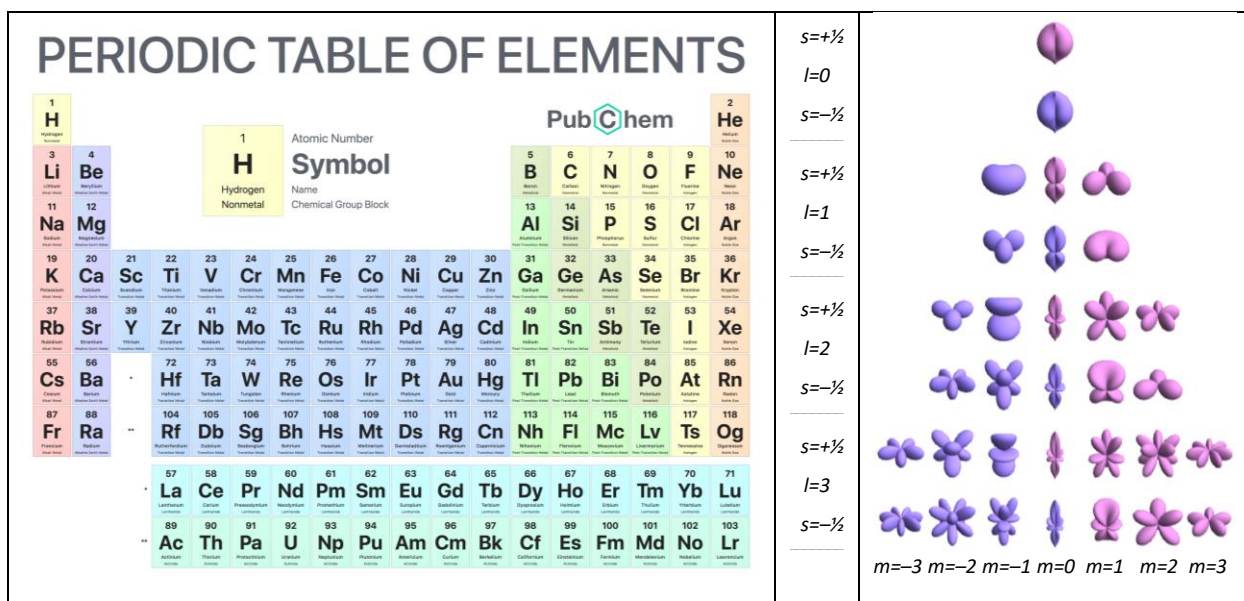
Now that we have the correct number of quantum states represented in the graphical table of Orbitals, the relationship to the Periodic Table of the Elements [10] is now very direct and obvious, as shown in Figure 7. The major rows of the Orbital table for $l=0, 1, 2, 3$, contain 2, 6, 10, and 14 states, respectively. We can map these states easily to the rows of the Periodic Table.

The first row of the Periodic Table contains 2 elements: Hydrogen (H) and Helium (He). These correspond to the 2 quantum states in the first row $l=0$ of the Orbital Table, for $n=1$.

The second row of the Periodic Table contains 8 elements: Li, Be, B, C, N, O, F, Ne. These correspond to $n=2$, taking the 2 quantum states in first row $l=0$, and the 6 quantum states in the second row $l=1$, for a total of $2+6=8$ elements in the second row of the Periodic Table.

The third row of the Periodic Table contains 8 elements: Na, Mg, Al, Si, P, S, Cl and Ar. These correspond to $n=3$, taking the 2 quantum states in first row $l=0$, and the 6 quantum states in the second row $l=1$, for a total of $2+6=8$ elements in the third row of the Periodic Table. Note that the 10 quantum states for $l=2$ (Transition Metals) do NOT appear in the third row, because their energy levels are higher than the $n=4$ states for Potassium (K) and Calcium (Ca).

The fourth row of the Periodic Table contains 18 elements: K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, and Kr. These correspond to $n=4$, taking the 2 quantum states in first row $l=0$, and the 6 quantum states in the second row $l=1$, AND to $n=3$, taking the 10 quantum states in the third row $l=2$, for a total of $2+6+10=18$ elements in the fourth row of the Periodic Table.



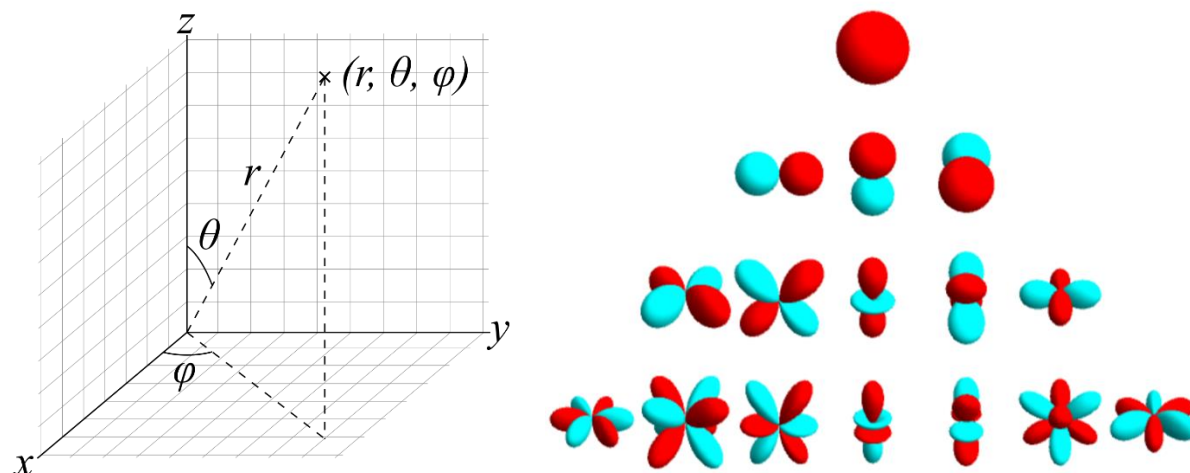
Periodic Table of Elements.

Orbitals with Spin $\frac{1}{2}$ States.

Figure 7: Comparing the Periodic Table of Elements [10] with the new Hydrogen Orbitals which explicitly represent the Spin Up and Spin Down states. The number of Orbital states in each row (2, 6, 10, 14) now has a direct and obvious mapping to the number of elements in each row and section of the Periodic Table.

8. Generality of the Spin Operator

All of these visualizations build on the established conventions shown in Figures 8 and 9.



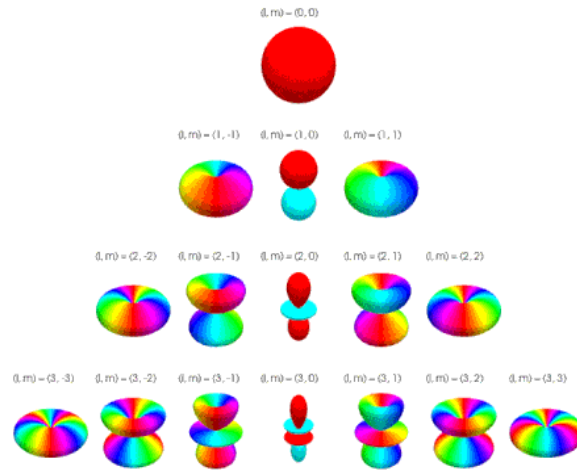


Figure 9: Alternate representation, showing complex magnitude as radius, and phase as hue [11]. Note in the animated references, rotations are shown about the z axis.

In these established conventions, the z axis is chosen for convenience to be the axis of rotation that corresponds to the angular momentum of the orbital state. Of course, in a given row of these tables, we have an orthogonal basis set which can be linearly combined to create other equivalent basis sets that correspond to other axis orientations. Without loss of generality, it is conventional to choose a canonical orientation with the z axis pointing vertically, with the x-y plane positioned horizontally. And in this convention, the angular momentum of the orbital state corresponds to rotations about the z axis. This can be seen directly by looking at the $m=0$ state in each row. In the animated reference plots [11], that state is not rotating about the z axis; it has zero angular momentum. And of course, if we were to consider rotations of that state about the x or y axes, it would have non-zero angular momentum. But we know that the $m=0$ has zero angular momentum. Therefore, we do not need to consider rotations about the x and y axes. Without loss of generality, the standard visualizations of the spherical harmonics use a coordinate system that is aligned in a specific and convenient way with the angular momentum of the orbital states.

Now, in the present work, we are trying to extend these visualizations to include the Spin $\frac{1}{2}$ property. Pauli's Spin Operator transforms as spinors over all rotations, not just rotations about the z axis, and of course there is nothing special about any particular direction in space. So, do we have to show that our spinor states transform as spinors over all rotations?

No, we do not. Without loss of generality, we have chosen a coordinate system with the z axis aligned with the orientation of the Hydrogen Atom's axis of angular momentum. The atom has angular momentum in a particular direction, not all directions at any time. And by convention, we align the z axis of our coordinate system with that particular direction. And now, we must consider that one particular rotation – following the wavefunction around the z axis is what led us to propose that we needed an extra half-cycle of phase accumulation to achieve the Spin $\frac{1}{2}$ behavior. Put simply, the angular momentum provides the rotation that causes the spin operator to operate.

Summarizing the logic of the argument:

- By convention, and without loss of generality, the standard visualizations align the z axis with the axis of angular momentum of the atom.
- Therefore, the atom is rotating (has angular momentum) about the z axis in the ϕ direction.
- The angular momentum about the z axis in the ϕ direction provides the rotation that causes the spin operator to operate.
- Therefore, for the purpose of these visualizations, the spin operator is only operating for rotations about the z axis in the ϕ direction. We must define the spin operator for in terms of the angle ϕ :

$$\text{Spin } +1/2: Y_l^m(\theta, \phi) \rightarrow Y_l^m(\theta, \phi) e^{i\phi/2}$$

$$\text{Spin } -1/2: Y_l^m(\theta, \phi) \rightarrow Y_l^m(\theta, \phi) e^{-i\phi/2}$$

- And we do not have to consider rotations about any other axis, because the atom is not rotating (has no angular momentum) about any other axis.

9. Conclusions

We have developed a new way of visualizing Hydrogen Atomic Orbitals which properly depicts the correct number of quantum states, including Spin Up and Spin Down. It uses a functional mapping which adds or removes a half-cycle of phase accumulation in the azimuthal direction, resulting in an orbital wavefunction representation which is double-valued, with an odd number of azimuthal lobes, as required by the definition of the Spin $\frac{1}{2}$ property. These quantum states have a direct and obvious relationship to the elements in the Periodic Table of Elements.

References

- [1] https://en.wikipedia.org/wiki/Hydrogen_atom#Schr%C3%B6dinger_equation
- [2] https://en.wikipedia.org/wiki/Spherical_harmonics
- [3] https://en.wikipedia.org/wiki/Table_of_spherical_harmonics
- [4] https://en.wikipedia.org/wiki/Hydrogen_atom#Mathematical_summary_of_eigenstates_of_hydrogen_atom
- [5] Pauli, Wolfgang (1927). "Zur Quantenmechanik des magnetischen Elektrons". *Zeitschrift für Physik*. 43 (9–10): 601–632. Bibcode:1927ZPhy...43..601P. doi:10.1007/BF01397326. S2CID 128228729
- [6] Cartan, Élie (1913). "Les groupes projectifs qui ne laissent invariante aucune multiplicité plane". *Bull. Soc. Math. Fr.* 41: 53–96. doi:10.24033/bsmf.916.
- [7] https://en.wikipedia.org/wiki/Spinors_in_three_dimensions.
- [8] <https://en.wikipedia.org/wiki/Spinor>.
- [9] Lloyd Watts, "Demonstration of Spin $\frac{1}{2}$ for an Electron Wavefunction", <https://youtu.be/gTdlvG1FVxc>.
- [10] PubChem Periodic Table of the Elements, <https://pubchem.ncbi.nlm.nih.gov/periodic-table/>.
- [11] Animated version of conventional view of Hydrogen Orbitals (Real Part of Spherical Harmonics), showing rotation about the z axis:
https://en.wikipedia.org/wiki/Table_of_spherical_harmonics#/media/File:Real_Spherical_Harmonics_Figure_Table_Complex_Radial_Magnitude.gif
See also the Complex Radial plots, also showing rotation about the z axis.
https://en.wikipedia.org/wiki/Table_of_spherical_harmonics#/media/File:Complex_Spherical_Harmonics_Figure_Table_Complex_Radial_Magnitude.gif