1280: Shape of atomic orbitals

(Factors that determine the shape of atomic orbitals and mathematical expressions of atomic orbitals)

Key words: Phase change of wave function; quantum numbers and nodes of wave function; relationship between phase change and energy; functional form of atomic orbitals; principal quantum number; azimuthal quantum number; magnetic quantum number; average distance from nucleus to electron

The shape of an atomic orbital is that of a wave function. Although no one has ever seen it, it is expressed as a mathematical function, so its shape can be illustrated.

The shape of a wave function is determined by the dimension and quantum number. Regarding the relationship between wave functions and quantum numbers, let's look at a one-dimensional wave function. The wave function of a particle confined between the origin 0 and *L* on the *x*-coordinate is,

$\psi(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)$, while its energy (*E*) is, $E = \frac{n^2h^2}{8mL^2}$ $\quad n = 1,2,3,\cdots$

Here, *n* is the quantum number, *h* is Planck's constant, and *m* is the mass of the electron. If we plot the wave function for *n*=1 to 3, it looks like the figure below. If the upper part is the +phase, the lower part is the -phase..

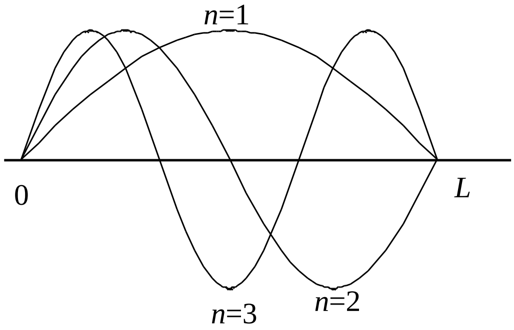

Figure 1. Shape of a one-dimensional wave function

[Phase reversal accompanies an increase in energy]

The lowest energy wave function has no phase reversal (node) (this is also true for atomic orbitals, where the 1s orbital has no node). And the important thing is that when the quantum number for the coordinate increases by one, the phase is reversed, one node is added, and the energy becomes higher.

[Wave functions of hydrogen atoms (atomic orbitals)]

Let's look at the atomic orbitals of hydrogen atoms. The wave functions of the atomic orbitals of hydrogen atoms are shown in the following table (how to calculate them is beyond the scope of this course, so we will omit it.

Table 1. Hydrogen atom orbital functions (*ρ*= (*Z*/*a*$_0$)*r*) *a*$_0$ is the Bohr radius 0.52918 Å, and for hydrogen atoms, Z=1. H. Eyring, J. Walter, G. E. Kimball, “Quantum Chemistry”, John Wiley & Sons, NY, p.85.)

n	*l*	*m*	
1	0	0	$\psi_{1s} = \frac{1}{\sqrt{\pi}}\left(\frac{z}{a_0}\right)^{3/2} e^{-\rho}$
2	0	0	$\psi_{2s} = \frac{1}{4\sqrt{2\pi}}\left(\frac{z}{a_0}\right)^{3/2} (2-\rho)e^{-\rho/2}$
2	1	0	$\psi_{2p_z} = \frac{1}{4\sqrt{2\pi}}\left(\frac{z}{a_0}\right)^{3/2} \rho e^{-\rho/2}\cos\theta$
2	1	±1	$\psi_{2p_x} = \frac{1}{4\sqrt{2\pi}}\left(\frac{z}{a_0}\right)^{3/2} \rho e^{-\rho/2}\sin\theta\cos\phi$ $\psi_{2p_y} = \frac{1}{4\sqrt{2\pi}}\left(\frac{z}{a_0}\right)^{3/2} \rho e^{-\rho/2}\sin\theta\sin\phi$
3	0	0	$\psi_{3s} = \frac{2}{81\sqrt{3\pi}}\left(\frac{z}{a_0}\right)^{3/2} (27-18\rho+2\rho^2)e^{-\rho/3}$
3	1	0	$\psi_{3p_z} = \frac{2}{81\sqrt{\pi}}\left(\frac{z}{a_0}\right)^{3/2} (6\rho-\rho^2)e^{-\rho/3}\cos\theta$
3	1	1	$\psi_{3p_x} = \frac{2}{81\sqrt{\pi}}\left(\frac{z}{a_0}\right)^{3/2} (6\rho-\rho^2)e^{-\rho/3}\sin\theta\cos\phi$ $\psi_{3p_y} = \frac{2}{81\sqrt{\pi}}\left(\frac{z}{a_0}\right)^{3/2} (6\rho-\rho^2)e^{-\rho/3}\sin\theta\sin\phi$
3	2	0	$\psi_{3d_{x^2}} = \frac{1}{81\sqrt{6\pi}}\left(\frac{z}{a_0}\right)^{3/2} \rho^2 e^{-\rho/3}(3\cos^2\theta-1)$

3	2	±1	$\psi_{3d_{xz}} = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{z}{a_0}\right)^{3/2}\rho^2 e^{-\rho/3}\sin\theta\cos\theta\cos\phi$ $\psi_{3d_{yz}} = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{z}{a_0}\right)^{3/2}\rho^2 e^{-\rho/3}\sin\theta\cos\theta\sin\phi$
3	2	±2	$\psi_{3d_{x^2-y^2}} = \frac{1}{81\sqrt{2\pi}}\left(\frac{z}{a_0}\right)^{3/2}\rho^2 e^{-\rho/3}\sin^2\theta\cos 2\phi$ $\psi_{3d_{xy}} = \frac{1}{81\sqrt{2\pi}}\left(\frac{z}{a_0}\right)^{3/2}\rho^2 e^{-\rho/3}\sin^2\theta\sin 2\phi$

In the 1*s* atomic orbital ($n = 1$, $l = m = 0$), the part before *e* is a constant, so $e^{-\rho}$ is a function of only ρ, that is, *r*. It reaches a maximum value of 1 when the distance from the origin is 0. In other words, it is a spherical function centered on the origin.

Similarly, let's look at the 2*s* atomic orbital ($n = 2$, $l = m = 0$). If you remove the constant part, it is $(2-\rho)e^{-\rho/2}$. The phase is reversed at $\rho = 2$, and a node appears. In the 3*s* orbital, the solution to $2\rho^2-18\rho+27=0$ has two nodes, where ρ is approximately 1.91 and 7.10.

Let's look at the shape of the 2*p* atomic orbital ($n = 2$, $l = 1$). First, when $m = 0$, the wave function excluding the constant term is $\rho e^{-\rho/2}\cos\theta$. There is a node at the origin ($\rho=0$). θ is the angle with the *z*-axis, so $\theta = 90^\circ$, i.e. the wave function is zero on the *xy* plane. $\rho e^{-\rho/2}$ is a spherical function, and is multiplied by $\cos\theta$, so there is a constriction at $\theta = 90^\circ$. In other words, we can see that the shape of this orbital is a function that spreads out like a dumbbell along the *z*-axis.

Similarly, let's look at the cases where $m = -1$ and 1. They are multiplied by $\sin\theta\cos\phi$ and $\sin\theta\sin\phi$, respectively. The former represents the *x*-axis and the latter the *y*-axis, and we can see that there are nodes in the *yz* plane and *xz* plane, respectively.

We can estimate the shape of the atomic orbital using this procedure, but as the quantum numbers increase, the shape of the wave function becomes extremely complex.

[Average distance from atomic nucleus to electrons]

I won't go into how to calculate it here, but the average distance from the nucleus to the electron ($\bar{r}$) is given by the following formula. The azimuthal quantum number (*l*) is involved. Even with the same principal quantum number, the larger the azimuthal quantum number, the smaller the distance from the atomic nucleus.

$$\bar{r} = \frac{a_0 n^2}{z}\left\{\frac{3}{2} - \frac{l(l+1)}{2n^2}\right\}$$

[Overview of atomic orbitals]

An overview of *s*, *p*, *d*, and *f* type atomic orbitals is shown below.

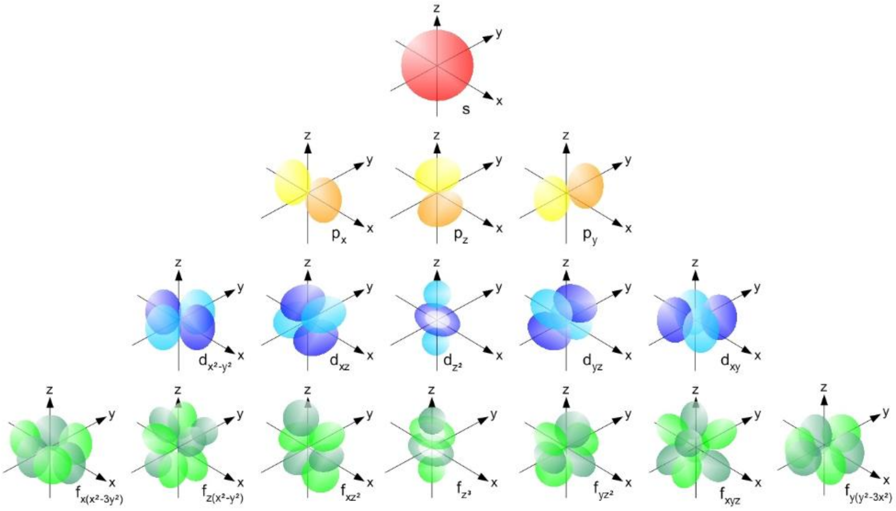

Figure1. The general shapes of *s*, *p*, *d*, and *f* orbitals. The *s* and orbitals have an internal structure due to (a) phase change(s) as *n* increases. For example, the 2*s* orbital is a double structure that overlaps a single sphere. The 3*p* orbital has a double dumbbell structure. (This figure is quoted fromhttps://energywavetgeiry.com/)