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Short Communication

On the Atomic Structure

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Abstract

In recent years, it has been recognized that treatment of the spectral problem should be associated with closed orbits. This paper proves that the closed orbit obtained by Bohr using numerical algebraic equation is reasonable both mathematically and physically and that the de Broglie wavelength of the electron in the hydrogen atom is equal to the circumference of its orbit. By Bohr model and de Broglie's matter-wave thought, some quantization conditions, electronic transition formulae, a mechanism and details of emitting photon wave train, a filling order of electrons in the periodic table, and Madelung rule have been deduced theoretically. We solve the Löwdin's challenge problem.

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Introduction

In recent years, I have found that there may be two important problems in current basic physics that need to be revised [1]. First, a law that needs to be corrected is Newton's first law, which is one of the few physical laws that can be described solely in language. The three versions of Newton's Principia were all written in Latin, and there is a paragraph describing the first law as follows:

"Corpus omne perseverare in statu suo quiescendi vel movendi uniformiter in directum, nisi quatenus a viribus impressis cogitur statum illum mutare." [2].

The underlined part is 'stationary or moving at a uniform speed in a certain direction'. Two years after Newton's death, British mathematician Mott translated it as 'stationary or uniform linear motion'. The small literal difference in this translation will have a huge impact on the definition of inertia in physics. Newton's original intention of inertia does not exclude rotational motion, but Mott's translation explicitly excludes rotation from inertia. Macroscopically, the orbital motion of planets or satellites, and microscopically, the rotational motion of electrons in atoms, according to the original meaning of Newtonian Latin, should belong to inertial motion, which does not require external driving or external doing work. Using the authority of Newton's laws, the fundamental properties of the most common forms of motion in the universe were denied by Mott. So far, Mott's translated version is still used in our physics textbooks. Nowadays, people often ask what the driving force behind planetary orbital motion is? Some people mistakenly regard universal gravity as the driving force of planetary orbital motion, and naturally mistake Coulomb force for the driving force of electron motion around the nucleus.

Second, a thing that needs to be revised is that the formula for kinetic energy in theoretical physics should be changed to Leibniz kinetic energy or centrifugal kinetic energy mv^2. And the Coriolis kinetic energy of $½mv^2$ should only be retained for use as an approximate and convenient formula in applied physics and engineering mechanics. After using Leibniz kinetic energy or centrifugal kinetic energy mv^2 in theoretical physics, the energy relationship will be consistent with celestial motion systems, and the kinetic energy formula (mv^2) at low speeds can also be consistent with the mass-energy relationship formula ($E=mc^2$) at high speeds; There can also be a clear energy relationship when studying atomic structure [3].

Discrete spectra require Bohr's closed orbit

Since the papers of Bohr (1913), Sommerfeld (1916) and de Broglie (1923) were published, the study of atomic structure and quantum theory has entered a new era. However, a century later, the radiation mechanism and details for atomic spectrum are still missing in the existing theory; Lö wdin's challenge problem involving the filling of electronic levels still not really solved [4]

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Closed orbitals are necessary to obtain discrete spectra

In 2020, Horodenko of Clemson University pointed out that Demkov and Ostrovsky (D-O) "believed that, in spite of the indistinguishability of electrons, Bohr's (circular orbits) and, later on, Sommerfeld's (elliptical orbits) treatment of hydrogen atom (Sommerfeld, 1934), is essential for obtaining the discrete spectrum of multielectron atom since the semiclassical-classical methods of treatment of the spectral problem should be associated with closed orbits" [4].

In measurements of "the absorption spectrum of hydrogen atoms to levels near the ionization threshold in a strong magnetic field", Haggerty and Delos fined that "the absorption rate has sinusoidal fluctuations which are correlated with closed classical orbits of the electron". [5] It can be shown that each closed classical orbit of an electron generates a peak in a recurrence spectrum at the action of the orbit. Consequently, the recurrence spectrum provides a quantum picture of classical behavior.[6] "circular states have found applications in cavity quantum electro-dynamics, metrology, collisions, and intense radiation field dynamics".[7]

Is it a death radius or a true radius of the ground state ?

The wave equation for dealing with hydrogen atom is established based on the following formula

$$E = T + V(r) \qquad (1\text{-}A)$$

where *E, T* and *V (r)* represent the total energy, kinetic energy and potential energy of the electron, respectively. The formula (1-A) may be written in terms of momentum p or of wave functions ψ and operators as,

$$E = \frac{p^2}{2m} + V(r) = \frac{p^2}{2m} + \frac{-ke^2}{r} \quad \text{or}$$

$$E\psi = [-\frac{\hbar^2}{2m}\nabla^2 + V(r)]\ \psi \qquad (2)$$

where *m, e, k, r* and $\hbar$ are the electron mass, the electron or proton charge, the coulomb constant, the orbital radius of the electron, and the reduced Planck constant, respectively. By solving the wave equation, we get that the ground state energy of the hydrogen atom is *-13.6 eV*, the orbital radius *r* of the electron can vary from *0* to ∞, and the probability of the electron appearing at the Bohr radius r_B is the largest. $r_B = 5.3 \times 10^{-11}$ m.

The wave equation has serious wrong in dealing with hydrogen atom. Sandhu, G. S pointed out in 2018 that when a ground state electron reaches $2r_B$ (1.06×10^{-10} m), its kinetic energy term will become zero [8]. Now, we analyze the situation of zero kinetic energy in the current theory.

Because there is an attractive potential energy between an electron and a proton, it is usually taken as a negative value, and the potential energy at the point $r = 2r_B$ is

$$-\frac{ke^2}{r} = -\frac{8.99\times10^9\times(1.6\times10^{-19})^2}{1.06\times10^{-10}} = -2.17\times10^{-18}\ \text{(J)} \quad \text{or} \quad -13.6\ \text{eV} \qquad (3)$$

Then, a numerical relationship in formula (1-A) is

$$r = 2r_B$$

$$E \quad = \quad T \quad + \quad V(r) \qquad (1\text{-}B)$$

$$-13.6\ \text{eV} \quad ? \quad -13.6\ \text{eV}$$

According to the current theory, formula (1-B) shows that the electronic kinetic energy (*T*) must be zero. This means that when an electron moves to the $2r_B$, it must die, and no any of kinetic energy is allowed for the electron. Therefore, the $2r_B$ is an unavoidable radius of electron death in current theory. Hereinafter referred to as death radius.

Obviously, there are serious problems in the current theory. So, where's the problem now?

The ground state energy (-13.6 *eV*) of hydrogen atom is reliable, because it is the ionization energy of hydrogen atom, which is an experimental data. It is verified that the potential energy calculated by equation (3) is also correct.

Then, according to understanding to the electron, we can roughly calculate its kinetic energy *T*.

The kinetic energy term in the formula (2) can be expressed by the momentum p and electronic mass m. The classical expression for momentum is $p = mv$. Since Bohr's circular orbit was replaced by wave function, the electron velocity v has always been a hidden variable in quantum mechanics, and has never given a definite value. Used the product of the velocity of light (c) and the fine structure constant (α), Sommerfeld calculated the electronic velocity. By Sommerfeld's formula, we get

$$v = \alpha c = (2.998/137)\times10^8\, m/s = 2.188\times10^6\, m/s \qquad (4)$$

Although Sommerfeld's electron velocity is not used in quantum mechanics, we can roughly estimate the kinetic energy of the electron.

$$T = \frac{1}{2}mv^2 = \frac{1}{2}\times9.109\times10^{-31}\times(2.188\times10^6)^2 = 2.180\times10^{-18}\text{(J)} \quad \text{or} \quad 13.6\ \text{eV} \qquad (5)$$

In order to facilitate comparison, we add the calculation result of formula (5) to the "?" in formula (1-B). we obtained

$$r = 2r_B$$

$$E \quad = \quad T \quad + \quad V(r) \qquad (1\text{-}C)$$

$$-13.6\ \text{eV} \quad 13.6\ \text{eV} \quad -13.6\ \text{eV}$$

Obviously, the equation in formula (1-C) is not valid. For the equation to hold, either E or T must be zero. If $E \neq 0$, the above electron death is inevitable; If the electron does not die, $E = 0$. Obviously, formula (1-A) or (2) in the current theory is wrong. Why does the solution of wave equation has such wrong?

The wave equation is established to describe the quantization phenomenon of the micro world. The energy, radius and angular momentum of electron in a hydrogen atom are quantized. In other words, these physical quantities can only take certain specific values, not continuous functions. Therefore, mathematically, they cannot be directly differentiated or integrated. However, in the process of solving the wave equation using a method of separating variables, a radial distribution function whose radius can be changed continuously is wrongly introduced to replace the quantized radius. Therefore, a wave function solution with a continuously varying radius, or a cotton candy shaped electron cloud with a radius from *0* to ∞, is obtained. That the continuous change of radial distribution function violates the quantum principle causes above wrong. How should we correct the wrong formula (1-A) or (2)?

According to a research of Ehrlich in 2017 [9], the orbital radius of the ground state hydrogen atom should be twice the Bohr radius r_B, that is,

$$r = 2r_B \qquad (6)$$

So, is the double Bohr radius a death radius or a true radius of the ground state? When $r = 2r_B$, the kinetic energy of an electron is numerically equal to its potential energy, as well as its ionization energy. The sum of the kinetic energy and potential energy of the electron is zero, indicating that the ground state hydrogen atom no longer has any energy that can be released, and its total energy E_{tot} is the lowest. Therefore, $r = 2r_B$, and

$E_{tot} = 0$ are a best constraints on the ground state hydrogen atom. The relationship between the energies of a ground state hydrogen atom is as follows

$$\begin{cases} E=V(r)=-T \\ \frac{p^2}{2m}+\frac{-ke^2}{r}=0 \end{cases} \quad (7)$$

Obviously, the ionization energy of hydrogen is not the total energy of the electron, and the radius calculated by Bohr is half smaller. **Therefore, the energy E_n of *n*th energy level of a hydrogen atom should also be the ionization energy of the electron at this energy level, not its total energy.**

According to the fact that the potential energy of the electron in a ground state hydrogen atom, numerically, is equal to its kinetic energy, we can solve the hydrogen atom according to Bohr's idea.

$$\frac{ke^2}{r}=\frac{1}{2}m\upsilon^2 \quad (8)$$

Although a ground state can no longer release electromagnetic radiation, it can absorb photons. The electron is bound in an atom, and its motion state has a characteristics of circular oscillation. Therefore, we rewrite formula (8) into a form with circular oscillation characteristics.

$$\frac{ke^2}{r}=\frac{1}{2}m\upsilon\omega r \quad (9)$$

According to the quantization conditions used by Bohr and de Broglie

$$m\upsilon r_B = \frac{h}{2\pi} \quad (10)$$

where h is the Planck constant. By equations (6) and (10), we can get

$$m\upsilon r = \frac{h}{\pi} \quad (11)$$

By equations (8) and (11), we get

$$\upsilon=\frac{2\pi ke^2}{h} \quad (12)$$

By equations (10) and (12), we get

$$r_B = \frac{h^2}{4\pi^2 mke^2} \quad (13)$$

Substitute equation (11) into equation (9) to get

$$\frac{ke^2}{r}=\frac{h\omega}{2\pi}=h\nu \quad (14)$$

where ν is the circular vibration frequency. According to Planck's energy quantum formula, we obtain the ground state energy of hydrogen atom with circular vibration

$$E=h\nu=\frac{ke^2}{r} \quad (15)$$

The formula $r = 2r_B = 1.06\times10^{-10}$ m is substituted into equation (15), and the binding energy is taken as a negative value to obtain an energy value that is exactly the same as formula (3), Bohr model and quantum mechanics, namely, -13.6 eV. Importantly, we prove that the closed orbit obtained by Bohr using numerical algebraic equation is reasonable both mathematically and physically.

Note that differentiation and integration are not used in the whole process here. Energy E and radius r are both taken as determined values, not as continuous functions.

The de Broglie's standing wave thought is scientific basis of quantum theory

The quantization proposed by Bohr in 1913 is just a hypothesis. After ten years, de Broglie found a scientific basis for quantization, that is, a standing wave principle in physics.

The essence of de Broglie's matter wave

According to de Broglie's thought of matter wave [8],"all microscopic particles in motion are accompanied by a wave-like propagation associated with the particle. This wave-phenomenon associated with the moving particle is characterized as matter-waves which are expected to be localized in the vicinity of the particle. " Each matter wave exists in a form of a standing wave packet and propagates in the same phase with matter (particle). In physics, standing wave must have a specific-numerical wavelength. The particle is not only the center of its wave packet, but also a wave source of its matter wave. However, people's understanding deviated from an original meaning of de Broglie matter wave [8], and it is "remaining profoundly misunderstood and incomplete until the now fading end of the twentieth century"[10].

In order to correctly understand the essence of de Broglie's matter wave, we first consider a matter wave formula proposed by de Broglie [8,10].

$$\lambda_d=\frac{h}{p}=\frac{h}{m\upsilon} \quad (16)$$

where λ_d is the wavelength of the matter wave. For a ground state hydrogen atom, its matter wave must be a standing wave. Therefore, in formula (16) both λ_d and h are constants. Then, the p or $m\upsilon$ must also be a constant. The λ_d equivalent to the wavelength of a circular oscillation wave, i.e, $\lambda_d = 2\pi r_d$. Here, we call r_d de Broglie's radius for a circular wave oscillation. That is

$$\lambda_d = 2\pi r_d = \frac{h}{m\upsilon} \quad (17)$$

By equations (12) and (17), we obtain

$$r_d=\frac{\lambda_d}{2\pi}=\frac{h}{2\pi m\cdot\upsilon}=\frac{h}{2\pi m}\cdot\frac{h}{2\pi ke^2}=\frac{h^2}{4\pi^2 mke^2} \quad (18)$$

The r_d obtained by the formula (18), here, is completely consistent with that the expression of Bohr radius, r_B, in formula (13), that is, $r_d = r_B$, which is very important because it proves a relationship of the standing wave wavelength, λ, with Bohr radius, r_B.

$$\lambda_d = 2\pi r_B \quad (19)$$

Now, we have a completely clear understanding for essence of the de Broglie matter wave of the electron in a ground state hydrogen atom. It turns out that the matter wave is a periodic oscillation wave of electron rotating around a nucleus. Its wavelength is equal to the circumference of Bohr circular orbit, and its frequency is equal to the rotation frequency of the electron.

As shown in Figure-1, the center of a de Broglie wave packet is consistent with the instantaneous position (e) of the electron and propagates in the same phase with the electron. Along this circular orbital, amplitude and intensity of the matter wave are the largest at point e and the smallest at point p opposite the nucleus.

It should be noted that de Broglie's wavelength formula is based on Bohr model in that years. Therefore, as expressed in formula (18), the de Broglie's radius, like the Bohr radius, is one half of the ground state radius of hydrogen atom.

Standing waves are quantization

In Physics, a standing waves are periodic oscillatory waves. No matter taking length or time as coordinates, the standing wave can return to its starting point in the same waveform state after one cycle. Then, it starts a new cycle from the starting point. This characteristic of standing wave limits that its wavelength can only be a length of specific value or constant rather than a length of any continuous change. That is, the wavelength of standing wave has a characteristics of quantization.

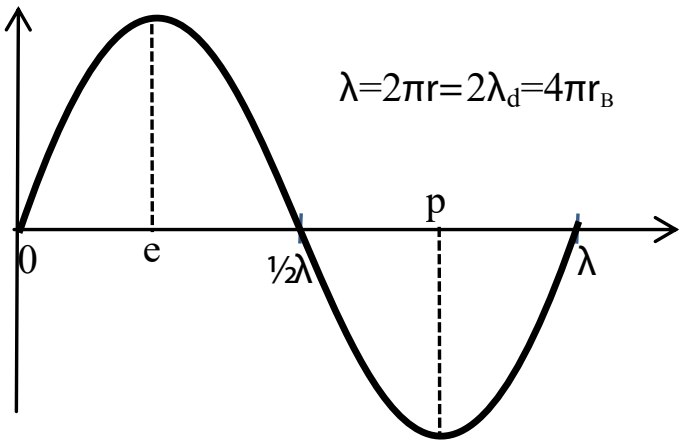

Figure 1. *Schematic diagram of de Broglie matter wave for an electron in ground state hydrogen atom. e is the instantaneous position of the electron, and p is the orbital position opposite the nucleus.*

The wavelength of a standing wave can only increase or decrease with the integral multiple of a reference wavelength. Namely

$\lambda_n = n\lambda$ or $r_n = nr$ (both λ and r are minimum values) $n = 1, 2, 3, \cdots$

$\lambda_z = \frac{1}{z}\lambda$ or $r_z = \frac{1}{z}r$ (both λ and r are maximum values) $z = 1, 2, 3, \cdots$

In quantum mechanics, n is called main quantum number. Here, z is equivalent to a number of nuclear charges. When the wavelength of a standing wave increases by an integral multiple, the term on the right-hand sides of equations (16) and (17) will also increase by an integral multiple. If we still use Bohr radius , we get

$$\lambda_{dn} = n\lambda_d = \frac{nh}{p} = \frac{nh}{m\upsilon} \quad \text{or} \quad m\upsilon\lambda_{dn} = nm\upsilon\lambda_d = nh \qquad (21)$$

Using $\lambda_{dn} = 2\pi r_{dn}$, by formula (21) we obtain Bohr's quantization condition of angular momentum

$$m\upsilon\lambda_{dn} = m\upsilon(2\pi r_{dn}) = nh \quad \text{or} \quad m\upsilon r_{dn} = m\upsilon r_{Bn} = \frac{nh}{2\pi} \qquad (22)$$

When considering Bohr's "half frequency problem", we get from equation (6)

$$m\upsilon r_n = 2m\upsilon r_{Bn} = 2m\upsilon r_{dn} = \frac{nh}{\pi} \qquad (23)$$

Equation (23-45) shows that the minimum orbital angular momentum of hydrogen atom is a constant, h/π, (of course, according to Bohr model, it is $h/2\pi$, or $\hbar$) and other values are integer multiples of this minimum value. This result fully conforms to the usual quantization rules.

Energy level formula of hydrogen atom

For any energy level of a hydrogen atom labeled with n, it can be obtained from formula (9)

$$\frac{ke^2}{r_n} = \frac{1}{2}m\upsilon r_n\omega_n \qquad (24)$$

where ω_n is an angular velocity of nth electron orbital. If its orbital frequency is v_n, then $\omega_n = 2\pi v_n$. We have proved in the previous article[11],

$$r_n = nr. \qquad (25)$$

Substitute equation (23) into equation (24) and using equation (25), we get

$$\frac{ke^2}{nr} = \frac{nh\omega_n}{2\pi} = n\hbar\omega_n = nhv_n \qquad (26)$$

According to Planck's energy quantization rule and the habit of taking negative bound energy, $\hbar\omega_n = hv_n = -E_n$, we get

$$E_n = -\frac{1}{n^2}\frac{ke^2}{r} = -\frac{1}{n^2}\times 2.178\times 10^{-18}\text{J} = -\frac{1}{n^2}\times 13.6\text{ eV} \qquad (27)$$

Equation (27) and its derivation process are easy to lead to the misunderstanding that the radius increases with n^2. In fact, Bohr has this misunderstanding. In each steady state, the formula $\omega_n \cdot r_n = \upsilon$ is valid; When an electron transitions between different stationary states, with the absorption or release of energy, there are the following relationships.

$$\omega_n = \frac{\omega}{n^2}; \quad \text{or} \quad \omega_n = \frac{ke^2}{n^2 r} \qquad (28)$$

Note that the radius is not proportional to n^2, but ω_n is inversely proportional to n^2.

Orbital shape and orbital angular momentum of each energy level for hydrogen atom

There is only one electron in hydrogen atom, and all of energy levels are degenerate states for the same n. Only the ground state orbit with $n = 1$ is a circular orbit, and all of other excited state orbits are formed by photon excitation, so they are elliptical orbits. The shape of each orbits is shown in Figure 2.

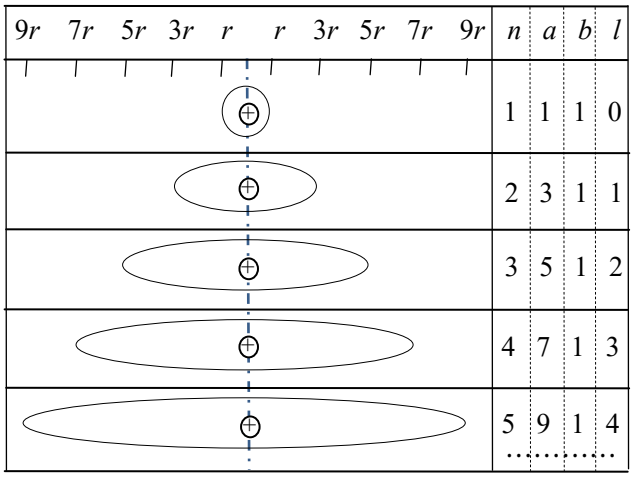

Figure 2. *Schematic diagram of orbital shapes and orbital parameters in hydrogen atom.*

In Figure 2, a and b represent long radius and short radius of each elliptical orbital respectively, and

$$n=\frac{a+b}{2};\quad l=\frac{a-b}{2} \qquad (29)$$

where n is the ratio of the average radius of an ellipse with the radius of its ground state orbital, and corresponds to the principal quantum number in quantum mechanics; l is the eccentricity of the ellipse orbital and corresponds to the angular quantum number in quantum mechanics. Their orbital angular momentum is

$$M_n=n\cdot\frac{h}{\pi}=\frac{a+b}{2}\cdot\frac{h}{\pi} \qquad (30)$$

It should be pointed out again that for an elliptical orbital obtained here, the nucleus is located at the center of the ellipse. This is different from Sommerfeld's elliptical orbital. His elliptical orbit is similar to a planetary orbit in the solar system, and the atomic nucleus is located at a focus of the ellipse.

Convergence radius of wavepacket in ground state hydrogen atom

The matter wave of moving electron in a ground state hydrogen atom is a standing wave in wavepacket form. Figure-3 shows that such a moving electron moves counterclockwise in a circular orbital with orbital radius, r_0, and its speed, υ. The wavepacket moves with the electron together, and its wave source is the electron. The velocity of the wave source is the speed at which the electron rotates, $\upsilon = \omega r$. The motion of the wave is in the same phase with the electronic motion and has the same ω. The wave velocity, U, at any wave point (R) in an instantaneous wave packet is proportional to radius R, i.e. $U = \omega R$. But, U is not the velocity of the electron, υ. The wave velocity U increases with the increase of radius R and it will not increase after reaching a maximum at the radius R_c. At maximum wave velocity U_c, $U_c = c = \omega R_c$. Because the motion of electrons is in the same phase (ω) with the motion of waves, so there is

$$\frac{\upsilon}{r}=\frac{U}{R}=\frac{c}{R_c}=\omega \qquad (31)$$

where r is the radius of the ground state orbital of hydrogen atom.

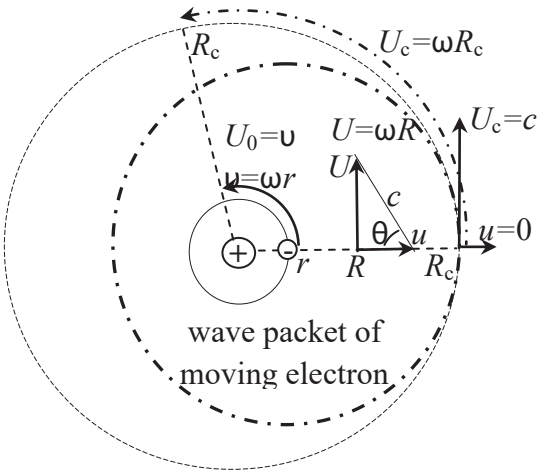

Figure 3. *Boundary trajectory of dynamic wave packet. The wave velocity is in the same phase (ω) with the source velocity, and the maximum value of the wave velocity is equal to the speed of light (c)*

$$R_c=\frac{c}{\upsilon}\cdot r=\frac{r}{\alpha}$$
$$=137.0\times1.059\times10^{-10}\,\text{m}\;=\;14.5\,\text{nm} \qquad (32)$$

where α is the fine structure constant. The thick dashed circle in figure-4 shows the wave packet of instantaneous moving electron. (R_C-r) is an instantaneous convergence radius of the wave packet, and R_C is the maximum convergence radius of the ground state hydrogen atom. The wave packet is centered on an instantaneous position of the electron, not the proton.

Because the wave velocity at any wave point is in the same phase with a source velocity and the radial velocity (u) is perpendicular to wave velocity (U), the greater the radius (R), the greater the U, and the smaller the u. By the wave-velocity triangle in the Figure-3, it can be seen that a following relationship exists

$$u=\sqrt{c^2-U^2} \qquad (33)$$

At the radius R_c, the wave velocity reaches the maximum, $U = c$, and $u = 0$. This result shows that the wave packet of the matter wave of a moving electron converges at the radius R_c and no longer propagates outside the sphere in a radial direction. This R_c sphere is a maximum-convergence boundary of the wave packets of the matter wave, which is consistent with an idea that the matter wave of the electron in a ground state hydrogen atom is a standing wave. Therefore, we call R_c an electromagnetic radius for ground state hydrogen atom [12].

It can be proved by the above principle that when a photon propagates at the speed of light in a vacuum, its velocity component in all directions excepted the propagation direction is zero. Therefore, when a photon propagates in a uniform medium, its energy does not diverge or lose, and moves in the form of overall energy quantum. This is consistent with Einstein's photon theory.

When a particle moves in a straight line, the wave velocity is equal to its source velocity. When a particle moves on a circle with the radius (r), the wave points in different positions have different wave velocities. When a wave point is at the position of the wave source, the wave velocity is equal to the source velocity; If a wave point is outside the circumference, the wave velocity is greater than the source velocity; If a wave point is located within the circumference, the wave velocity is less than the source velocity. The wave velocity is directly proportional to a distance (R) from the wave point to the center of the big circle.

For the matter wave formed by moving electron in the ground state hydrogen atom, at R_c, along the radial direction the energy flux density of the wave decreases to zero. The points where the energy flux density is zero constitute a convergent boundary surface of the wave packet. Therefore, within the convergent boundary surface of an isolated hydrogen atom, there are fluctuations of positive and negative electric fields, but outside the boundary surface, there is a neutral space around the atom. This surface fluctuates dynamically.

Quantization of wave packet surface area

The standing wave principle shows that not only the energy, angular momentum and orbital radius of the electron are quantized, but the surface area of the wave packet is quantized also. For the ground state hydrogen atom, there is a fixed factor, α^2, between the convergence surface area $4\pi R_C^2$ of the wave packet and the spherical area $4\pi r^2$ at the orbital radius r, and both are quantized. For simplicity, we only consider the change

of spherical area at the orbital radius. When the radius increases from r to rn, the spherical area of space increases from $S=4\pi r^2$ to $S_n=4\pi r_n^2$. Because $r_n=nr$; $S_n=n^2S$. Obviously, the spatial sphere S_n at r_n must have n^2 quantized wavelets to be covered, that is, n^2 orbits.

For example, when the radius (or wavelength) increases to 2 times, its spatial surface area will increase to 4 times, and 4 sub waves are required to fill the surface area; When the radius (or wavelength) increases to 3 times, its spatial surface area will increase to 9 times, requiring 9 sub waves; When the radius (or wavelength) increases to n times, its total area will increase to n^2 times, requiring n^2 subwaves.

For spherical space, only n^2 sub wave group can form a complete spherical surface, and a complete and stable group wave convergence surface will make the system more stable. The quantization rule of wave packet surface area is very important to study the electronic configuration in multi electron atoms.

Electronic transition and Emission of photon wave train

For steady-state hydrogen atom, wavelength, radius, angular momentum, energy and wave packet area are quantized. They are not continuous functions and cannot be differentiated and integrated. However, in the process of absorption or emission of hydrogen atomic spectral lines, the electron will transition between two energy levels. A transition process often takes nanosecond or even longer, and the electron needs to rotate around the nucleus millions of times or more. The better the monochromaticity of the spectral line, the longer the transition time, and the more times the electron rotates. In the process of electron transition, wavelength, radius, angular momentum, energy, wave packet area and even quantum number become continuously variable functions. Therefore, when studying the radiation mechanism and details, the continuous quantity during the transition can be differentiated and integrated.

Non-quantized changes during the transition

An electron in low-energy orbit will transition to high-energy level when it absorbs a photon. The mechanism and details of the electron absorbing radiation have been discussed in detail by the author [11]. If a transition process occurs between n_1 and n_2, then, there must be a "quantum number" that can be continuous change from n_1 to n_2. This continuously variable positive number between n_1 and n_2 is represented by g, i.e $n_1 \le g \le n_2$, or $n_2 \le g \le n_1$. Although n_1 and n_2 must be positive integers, the g does not have to be integers. All of E, r and g can change continuously between n_1 and n_2, and can be differentiable and integrable using calculus formulae.

For a transition process, the formula (27) can be rewritten as

$$E=-\frac{ke^2}{g^2r} \qquad (n_1 \le g \le n_2, \text{ or } n_2 \le g \le n_1) \qquad (34)$$

By taking differentiation for the formula (34) , we obtain

$$dE=-d\left(\frac{ke^2}{rg^2}\right)=\frac{2ke^2}{rg^3}dg \qquad (n_1 \le g \le n_2, \text{ or } n_2 \le g \le n_1) \qquad (35)$$

If an electron transition starts from $g=n_1$ and ends at $g=n_2$, the photon energy absorbed is

$$\Delta E=\int_{E_1}^{E_2} dE=\int_{n_1}^{n_2}\frac{2ke^2}{rg^3}\cdot dg=\frac{-ke^2}{rg^2}\Big|_{g_1=n_1}^{g_2=n_2}=\frac{ke^2}{r}\cdot\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right) \qquad (36)$$

For a transition to absorb photon, $\Delta E>0$, and $n_2>n_1$. For a transition to release photon, $\Delta E<0$, and $n_2<n_1$. The photon frequency is

$$v=\frac{|\Delta E|}{h}=\frac{ke^2}{hr}\times\left|\frac{1}{n_1^2}-\frac{1}{n_2^2}\right|=\left|\frac{1}{n_1^2}-\frac{1}{n_2^2}\right|\times 3.287\times10^{15}\,s^{-1} \qquad (37)$$

The ratio of the constant in equation (37) to the speed of light is the Rydberg constant.

Emission of photon wave train in hydrogen spectrum

In 1913, Bohr pointed out that "it has not been possible to observe more than 12 lines of the Balmer series in experiments with vacuum tubes, while 33 lines are observed in the spectra of some celestial bodies", …. "the diameter of the orbit of the electron in the different stationary states is proportional to τ_2. For $\tau = 12$ the diameter is equal to 1.6×10^{-6} cm., or equal to the mean distance between the molecules in a gas at a pressure of about 7 mm. mercury; for $\tau = 33$ the diameter is equal to 1.2×10^{-5} cm., corresponding to the mean distance of the molecules at a pressure of about 0.02 mm. mercury."[13] The *"τ"* used by Bohr is the principal quantum number n we use today. His "the mean distance" is equivalent to "mean free path" of gas molecules in his vacuum tube.

When 12 spectral lines of Balmer series are observed, it is equivalent to $n_2=14$; When 33 spectral lines are observed, it is equivalent to $n_2=35$. Bohr's observation shows that the quantum.

When 12 spectral lines of Balmer series are observed, it is equivalent to $n_2=14$; When 33 spectral lines are observed, it is equivalent to $n_2=35$. Bohr's observation shows that the quantum number n of the highest excited state of hydrogen atom in vacuum tube is not infinite, but limited by the mean free path in gas. Mean free path is a thermodynamic concept, which refers to the average distance traveled by molecules between two consecutive collisions in thermal motion. The lower the temperature, pressure and density of the gas, the greater the mean free path.

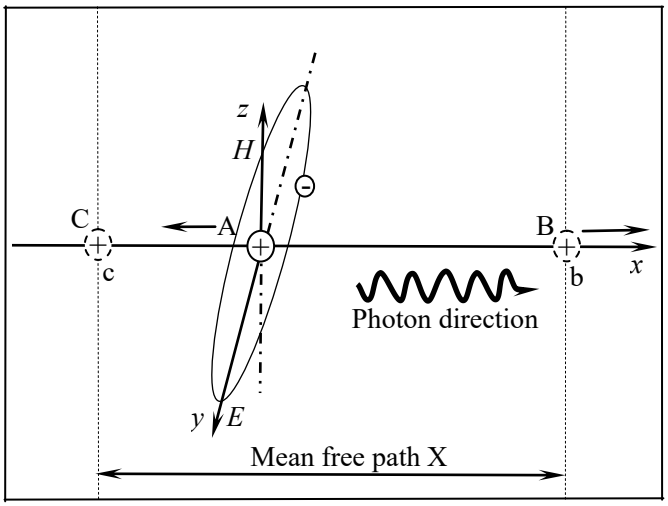

Figure 4. *Details of photon radiation. The elliptical orbit of atom A is on the xy plane, and the long axis is distributed along the y axis. The orbital angular momentum or magnetic field direction is in the z axis direction. In a free path from b to c, atom A completes the emission of a photon wave train, and the photon propagates along the x direction.*

The mean free path not only limits the longest diameter of the elliptical orbit of the highest excited state, but also limits the time history of the emitted photon wave train. As shown in Figure-4, the hydrogen atom A in the excited state collides with particle B at point *b* along the *x* direction. If the long axis of the orbit, the orbital angular momentum and the free path of A are exactly orthogonal, an effective collision may occur. B atoms often do not satisfy the condition of orthogonality in three directions. Therefore, in an effective collision, only A emits photon.

Effective collision is the beginning of emitting photon wave train. The collision makes the A reverse direction move along the -*x* axis, and the emitted photon wave train propagates along the +*x* direction. When A reaches point c, it collides with particle C and the emission of photon wave train ends. The distance between b and c is the free path of A. The emission of a photon wave train is completed in a free path. The head and tail of a photon wave train always differ by one wavelength.

Which low energy level does the electron go to in the transition?

In the spectral tube, the hydrogen atoms in each excited state with hydrogen molecule are in the common thermal motion equilibrium. They obey to the Maxwell-Boltzmann statistics. When the temperature, pressure and the total number of atoms remain unchanged, the atoms at each energy level have a certain probability distribution. So which low-energy level does an electron in the high-energy level want to jump to?

Once the photon wave train starts emitting, its frequency has been determined. Therefore, the frequency of emitted photons depends on the effective collision at the beginning. We can determine the choice of transition by the momentum conservation of effective collision process. Under the same conditions, the higher the energy level of the excited state, the larger the collision cross section and the greater the momentum of the atom. Momentum is conserved during collision, but two atoms can exchange momentum. It can be seen from Fig.-5 that the momentum p_B of atom B is exchanged to atom A in the collision. The momentum p_A of atom A is exchanged to atom B, but atom B only receives a part of this momentum, p_1, and the another part p_2 is carried by the photon wave train. The sum of these two parts is still equal to the momentum of atom A before the collision, $p_A = p_1 + p_2$. Of course, this momentum separation is accompanied by whole emission process of the photon wave train and completed in a free path.

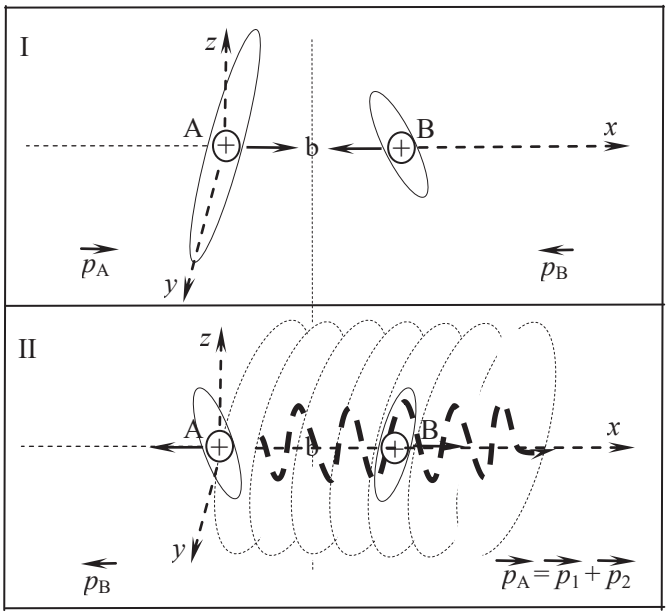

Figure 5. *Schematic diagram of photon wave train emission triggered by an effective collision. (I) is before the collision and (II) is after the collision. Momentum is conserved before and after collision. By collision, the momentum of atom A is exchanged to atom B, which is divided into particle momentum and photon momentum.*

In thermal motion, we assume that atom A is in an excited state of $n = 5$. There are four options for its transition to low-energy orbit of $n = 4$, 3, 2 and 1, respectively. If atom B is the ground state before the collision, atom A will also become the ground state after the photon wave train is emitted, and the emitted spectral line is in the ultraviolet region. If A encounters an atom B with $n = 2$, atom A will also transition to the low energy level of $n = 2$ after momentum exchange, and the emitted spectral line is a γ line of Balmer series. Which low energy level to transition to depends entirely on the energy level state of B atom before effective collision.

Fine spectrum of hydrogen atom

Due to the existence of orbital angular momentum and spin angular momentum, each hydrogen atom has its own specific magnetic field direction. This magnetic field direction is evenly divided in the collision equilibrium of thermal motion, resulting in quantized distribution. The larger and narrower the eccentricity of the orbit, the smaller the quantized population in space. However, the larger the collision cross section, the greater the effective collision probability

This specific atomic magnetic field orientation will affect the fine spectrum of hydrogen atoms. Therefore, the fine spectrum describes the interaction between different atoms, not the motion state of electron in an isolated hydrogen atom.

Orbital eccentricity and electronic filling order in multi electron atoms

Both the filling order of orbits and the arrangement of elements in the periodic table are important challenges that must face for any atomic structure model. As early as 1930, Janet organized the elements in periods of constant $n+l$, and obtained the sequence of period doubling: 2-2-8-8-18-18-32-32. Six years later, Madelung rule is proposed. This rule can be described as: "*With increasing Z, the orbitals are filled in order of increasing n+l = N. For fixed N, the orbitals are filled in order of increasing n*".[1] So far, the Madelung rule has not yet been derived from quantum mechanics or other fundamental physical principles.[14] Because the Madelung rule is empirical and requires a theoretical explanation, that find a way to derive the Madelung rule ab initio has become a famous "Löwdin's challenge problem". Löwdin's challenge problem returns the problem to the starting point of deriving the closed orbit from the spherical Coulomb potential. The obstacles caused by spherical Coulomb potential have been eliminated in this paper now. The Madelung rule is deduced below.

The *n*th layer can have n^2 orbitals at most

In Section 2.6, we have proved that a spatial sphere with radius *nr* can be fully covered by total surface area of n^2 sub wave packet. For a multi electron atom, *n* is equivalent to its electron layer and a sub wave packet is equivalent to an orbit.

That is, the *n*th electron layer can have up to n^2 orbitals. So how are these n^2 orbitals allocated?

By comparison, the value of the long radius of the elliptic orbit is quantized, and can only take 1*r*, 3*r*, 5*r*, … , (2*n*-1)*r*. The sum from item 1 to item *n* is n^2r. According to this law, the n^2 orbitals of the *n*th layer can be composed by 1, 3, 5,..., (2*n*-1) orbitals, and they can be regarded as electron sublayers. The *n*th electron layer can have at most *n* sublayers, and the *n*th sublayer has (2*n*-1) orbits. In this paper, the spectral symbols, *s, p, d, f*, ..., used in quantum mechanics are still used to represent these sublayers. The *s* sublayer has only one orbit, the *p* sublayer has three orbits, the *d* sublayer has five orbits, and the *f* sublayer has seven orbits. The rest can be done in the same manner.

One orbital can hold up to two electrons at most

Since Dirac proposed electron spin, the problem that each orbit can hold up to two electrons has been determined. If an orbit already contains two electrons, A and B, with opposite spins, the third electron C, no matter what kind of spin it has, is either repelled by the A electron or repelled by the B electron. So this is just the idea that the most electrons that you can have in a single orbital is two electrons, and that the *n*th electron layer can hold up to $2n^2$ electrons.

Ground-state electronic configuration is determined by orbital long radii rather than energy levels

Our research shows that for multi electron atoms, the angular quantum number l used in quantum mechanics is actually equivalent to the orbital eccentricity in this paper. By equation (29), we get,

$$n+l=\frac{a+b}{2}+\frac{a-b}{2}=a\ ; \qquad (38)$$

$$n-l=\frac{a+b}{2}-\frac{a-b}{2}=b \qquad (39)$$

Equation (39) shows that for the same *n*, the greater the eccentricity *l*, the smaller *b*, the closer it is to the nucleus at the short radius, and the greater the influence of the change of nuclear charge.

For the existing 7-periodic table, the eccentricity ($b\sim a$) values of all orbits occupied by electrons in multi electron atoms are listed in Table-1.

Figure 6 shows the shapes of 4*s*, 4*p*, 4*d* and 4*f* orbits and their eccentricity *l* values in multi electron atoms.

When an electron enters an atom from the outside, it always enters the orbital with the shortest long radius (*a*). That is, when we take a look at it from the outside, an electron always enters the orbital closest to the nucleus first rather than the orbital with the lowest energy. Of course, the order of electron loss during ionization is the opposite, and the electrons in the orbital with the longest radius are the most likely to lose first. An energy level is determined by its principal quantum number *n*, and the long radius *a* of an orbital is determined by *n*+*l*. At this point, although the filling order of electrons is consistent with Madelung's (*n*+*l* =*N*) rule, the Madelung rule is guessed, and the relationship between his (*n*+*l*) value and energy level is not clear.

Table 1. *Eccentricity of elliptical orbits (b~ a)*

n	*l* = 0	*l* = 1	*l* = 2	*l* = 3	
	s(*b*~ *a*)	*p*(*b*~ *a*)	*d*(*b*~ *a*)	*f*(*b*~ *a*)	$n=\frac{a+b}{2}$
1	1~1				
2	2~2	1~3			
3	3~3	2~4	1~5		
4	4~4	3~5	2~6	1~7	$l=\frac{a-b}{2}$
5	5~5	4~6	3~7	2~8	
6	6~6	5~7	4~8		
7	7~7	6~8			

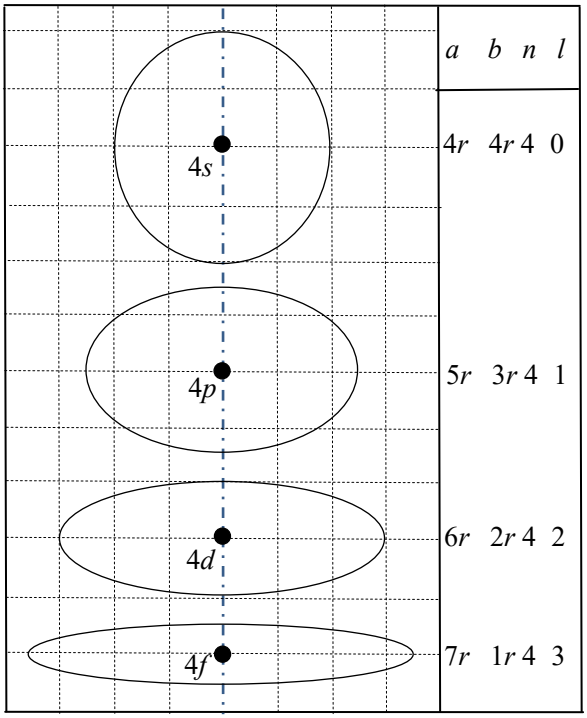

Figure 6. *Schematic diagram for shapes of the orbitals occupied by electrons in multi electron atoms. The nucleus is at the midpoint of every elliptical orbital rather than one of its focus. focal points.*

"Demkov and Ostrovsky developed an atomic physics model that incorporates the Madelung rule, but by replacing the quantization of level energies with quantization of coupling constants at zero energy." [1] Obviously, their *n*+*l* value defaults to the order of energy levels, which is obviously inappropriate.

Factors affecting orbital eccentricity

For hydrogen atoms, only the ground state orbitals are circular. Because the photon is a transverse wave, it only polarizes the electron in the transverse direction, pushing the orbit further along the transverse direction, making the excited state orbits elliptical. Therefore, all excited state orbits of hydrogen atom are elliptical, and its eccentricity is generated by photon excitation. [11]

For multi electron atoms in the ground state, the formation of elliptical orbits is obviously different from that of hydrogen atoms. The orbital eccentricity mainly depends on two factors. first factor is the weak effective nuclear charge; Second factor is in the same electron layer, the shielding and repulsion from the inner sublayer electrons.

Weak effective nuclear charge refers to those cases where the effective nuclear charge is approximately 1. The electron filling order with Z in the periodic table just belongs to this case. In the atom of the same element, the eccentricity *l* of different orbitals is quantized. But for different elements and different internal electronic configurations, *l* is only a relative value. For

the same sublayer orbit, the smaller the number of effective nuclear charges Z*, the greater the orbital eccentricity *l*; The larger Z*, the smaller *l*. When Z* →∞, *l* → 0, the orbit tends to be circular.

For the *i*th electron, the repulsion of other electrons *j* is equivalent to shielding off part of the nuclear charge. Therefore, we can use the shielding coefficient σ_{ij} to indicate. The effective nuclear charge felt by the *i*th electron is [15]

$$Z_i^* = Z - \sum_{j=1} \sigma_{ij} \qquad (40)$$

where Z is the number of nuclear charges. If *j* is an electron in outer layer , it has little shielding effect on the inner-layer electron *i*, σ_{ij} = 0; If *j* is an inner-layer electron, it can be considered to be completely shielded for the outer-layer electron *i*, σ_{ij} = 1. Therefore, the electron interaction between different electron sublayers in the same electron layer is the main content for our quantitative research. The inner-sublayer electron always occupies better orbital space, position and orientation than the outer-sublayer electron. In order to avoid the shielding and space obstruction of electrons in the inner sublayer, the outer-sublayer orbit deforms and produces eccentricity. Because the eccentricity is produced by the action of electrons in the inner sublayer, if only the nuclear charge is increased without increasing electrons, the change of eccentricity is negative.

Eccentricity *l* is quantized. For *s* orbital, there is no the inner-sublayer electron, and its eccentricity is *l* = 0. The *p* orbitals can be only affected by the *s* orbital electrons, so their orbital eccentricities are *l* = 1. The *d* orbitals can be affected by two inner sublayers (*s* and *p*), and their eccentricities are *l* = 2. The *f* orbitals can be affected by three internal sublayers (*s*, *p* and *d*), so their eccentricities are *l* = 3. The rest can be done in the same manner.

The two electrons in the filled *s* orbital lead to the eccentricity of Δ*l* = + 1 for the *p*, *d*, *f* and other outer-sublayer orbitals. The filled six *p* electrons lead to the eccentricity of Δ*l* = + 1 for *d*, *f* and other outer-sublayer orbitals. The filled 10 *d* electrons lead to the eccentricity of Δ*l* = + 1 for the *f* and other outer-sublayer orbitals. The filled 14 *f* electrons lead to the eccentricity of Δ*l* = +1 for other outer-sublayer orbitals. The rest can be done in the same manner.

In the same electron layer, the electrons in an outer sublayer have little effect on the orbitals of an inner sublayer, Δ*l* = 0, and the effect of the electrons in an inner sublayer on an outer sublayer is Δ*l*=+1. According to the numerical variation law of quantization, we can get that in the same sublayer, when its electron number increases to a full sublayer, the influence on the orbital eccentricity in this sublayer should be Δ*l*= +0.5. Specific to each sublayer, the *s* orbital has no eccentricity. The total influence of six electrons in the *p* sublayer is Δ*l*= +0.5, and the influence of each electron is Δ*l*= +0.5/6. The total influence of 10 electrons in *d* sublayer is Δ*l*= +0.5, and the influence of each electron is Δ*l*= +0.05. The total influence of 14 electrons in *f* sublayer is Δ*l*= +0.5, and the influence of each electron is Δ*l*= +0.5/14. If only the nuclear charge is increased without increasing the electron, the effect of each additional nuclear charge corresponding to the *d* sublayer is Δ*l*= -0.05, and that corresponding to the *f* sublayer is Δ*l*= -0.5/14.

Because the radius of *ns* orbital is smaller or similar to the long radius of (*n*-1)*d* and (*n*-2)*f* orbitals, the influence of the two nuclear charges increasing with *ns* on the eccentricity of (*n*-1)*d* and (*n*-2)*f* orbitals is Δl_s = - 1.0, and each nuclear charge changes by Δl_s = - 0.5.

Theoretical derivation of Hund's Rule

The filling order of electrons for equivalent orbitals is determined by two main factors. That is, the electronic spin and the change in long radius *a*.

1. For electronic spin, if the spin direction of the second electron is opposite (antiparallel), it will pair with the first electron and the two electrons occupy the same orbital. If second electron spins parallel, it will occupy another empty-equivalent orbital.
2. For change in long radius *a*, according to formula (38), *a* = *n* + *l*. When an empty-equivalent orbital is occupied by a single electron, its *a* will increase with *l* but its *n* remains unchanged. For example, the *a* of a *p* orbital will increase by 0.5/6, the *a* of a *d* orbital will increase by 0.5/10, and the *a* of a *f* orbital will increase by 0.5/14.

Because the long radius of an empty orbital is shorter than that of an electron occupied orbital, a second electron will occupy a new equivalent empty orbital with parallel spin. So does the third electron. In this way, we have theoretically derived the Hund's Rule, in which electrons always occupy as many equivalent orbitals as possible with single electron state.

"Energy level interleaving" phenomenon

For the first three-periodic elements in the periodic table the filling order of electron accords in the simple order of *a* = *n*+*l* in formula (38), $(1s)^2 \rightarrow (2s)^2 \rightarrow (2p)^6 \rightarrow (3s)^2 \rightarrow (3p)^6$. When filling is over, it just reaches element 18, argon.

Before and after element 19 in the periodic table , in a case of low effective nuclear charge, the radius of 4*s* orbital is smaller or similar than that of 3*d* orbital. Therefore, an effect of nuclear charge or electron by 4*s* on the 3*d* orbital eccentricity is the same as that of the same electron layer. For the elements of in fourth period, "a phenomenon of $E_{4s} < E_{3d}$" appears when they are filled according to "the concept of the energy level order". It is customary to think that "energy level interleaving" has

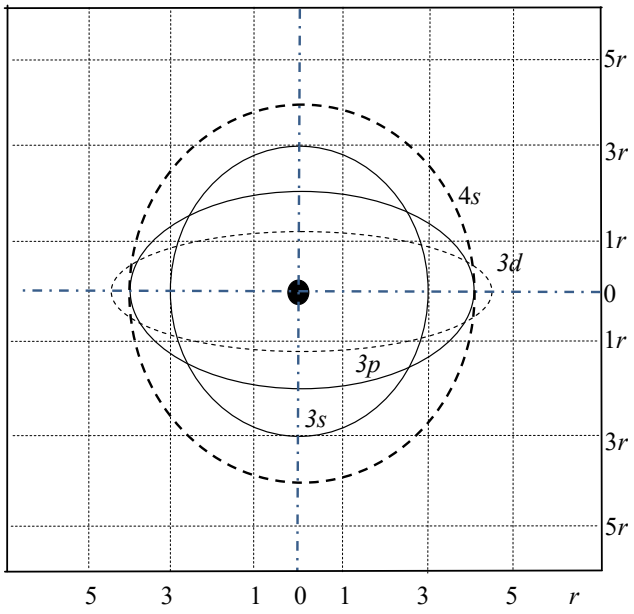

Figure 7. *Schematic diagram of the outermost two-layer orbital shapesforpotassium atom. Their long radii, a4s < a3d,resulting the last electron to fill the 4sorbit.*

occurred. But in fact, only a change in their long radius affects their filling order.

As shown in Figure 7, element 19, K, before a last electron filling, for a 4*s* orbital, $a_{4s}=b_{4s}=4$. The effect of nuclear charge corresponding to 4*s* increase on 3*d* orbital eccentricity is, Δl_s = -0.5×1 = -0.5. Eccentricity of 3*d* orbital l_{3d} = 2 - 0.5 = 1.5. Therefore, $a_{3d}=n+l$=3+1.5=4.5. Obviously $a_{3d} > a_{4s}$. So the last electron of potassium enters its 4*s* orbital rather than 3*d* orbital.

For element 20, Ca , its atomic kernel [Ar] already contains 18 electrons. Δl_s = -0.5×2 = -1. As a result, l_{3d} = 2 - 1 = 1.0. $a_{3d} = n+l$= 3+1.0=4.0. Although $a_{3d} = a_{4s}$, it seems that the 19th electron filling the 4*s* orbital is equivalent to filling the 3*d* orbital. But, after filling the 4*s* orbital, a_{4s} remains unchanged, while after filling the 3*d* orbital, a_{3d} will rise (> 4.0). Therefore, the 19th and 20th electrons are filled into 4*s* orbital rather than 3*d* orbital. As a result, the electronic configuration of Ca atom is $[Ar](3d)^0(4s)^2$.

For element 21, the electronic configuration of Sc^{3+} is $[Ar](3d)^0(4s)^0$. It has three effective nuclear charges, Δl_s = -0.5×2= -1; Δl_{3d} = -0.05×1= -0.05. l_{3d} = 2 - 1 - 0.05 = 0.95. $a_{3d} = n+l$= 3+0.95=3.95. $\because a_{4s} > a_{3d}$. $\therefore$ the 19th electron of Sc fills the 3*d* orbital and increases a_{3d} from 3.95 to 4.00. Similarly to calcium, the 20th and 21st electrons of Sc will fill the 4*s* orbital. The electronic configuration of Sc is $[Ar](3d)^1(4s)^2$.

For element 22, the electronic configuration of Ti^{4+} is $[Ar](3d)^0(4s)^0$. It has four effective nuclear charges, Δl_s = -0.5×2= -1。Δl_{3d} = -0.05×2= -0.10。l_{3d} = 2 - 1- 0.10 = 0.90。$a_{3d} = n+l$= 3+0.9=3.9. $\because a_{4s} > a_{3d}$. $\therefore$ the 19th electron fills the 3*d* orbit and increases a_{3d} from 3.9 to 3.95, which is still less than a_{4s}. So the 20th electron still fills the 3*d* orbit, and a_{3d} increases to 4.0. Similar to above, the 21st and 22nd electrons of Ti will fill the 4*s* orbital. The electronic configuration of Ti is $[Ar](3d)^2(4s)^2$. Because the last four electrons of titanium are filled with $(3d)^2$ first and then $(4s)^2$, it is inevitable to lose $(4s)^2$ first and then $(3d)^2$ in chemical reaction. According to the Hund's Rule deduced theoretically in this paper, the two 3*d* electrons of Ti occupy two different 3*d* orbits with parallel spins. The impact of the Hund's Rule is the same below and will not be repeated.

For the element 23, the electronic configuration of V^{5+} is $[Ar](3d)^0(4s)^0$. It has five effective nuclear charges, Δl_s = -0.5×2= -1. Δl_{3d} = -0.05×3= -0.15. l_{3d} = 2 - 1 - 0.15 = 0.85. $a_{3d} = n+l$= 3+0.85=3.85. $\because a_{4s} > a_{3d}$. $\therefore$ first three electrons can be filled into 3*d* orbits continuously, and a_{3d} increases continuously from 3.85 to 4.0. The last two electrons will fill the 4*s* orbital. The electronic configuration of V atom is $[Ar](3d)^3(4s)^2$. Because the last five electrons of vanadium atom are filled with $(3d)^3$ first and then $(4s)^2$, it is inevitable to lose $(4s)^2$ first and then $(3d)^3$ in chemical reaction.

It should be emphasized again that for the transition elements, the reversal of the electron filling order between *ns* and (*n*-1)*d* orbitals is not due to the reversal of the energy level order between them, but due to the change of the long radius of the (*n*-1)*d* orbitals.

Special cases in transition elements

There are many "special cases" among the three transition systems, lanthanides and actinides. The long radius of the orbital is affected by the eccentricity *l*, which is not invariable and decreases with the increase of the number of effective nuclear charges. Let's first consider the special cases in three transition systems.

For element 24, the electronic configuration of Cr atom is $[Ar](3d)^5(4s)^1$ rather than $(3d)^4(4s)^2$. In the current textbooks, it is explained by the special case of Hund's Rule that half full or complete full is a more stable state. However, we find that this is not the case. Take the half full state as an example. If d^5 or f^7 is a more stable state, then, d^{5-1} or f^{7-1} and d^{5+1} or f^{7+1} should be the second stable configuration. However, among the three transition systems, lanthanides and actinides, we can only find that element 24 Cr and element 42 Mo have the valence electron configuration of $(n\text{-}1)d^5ns^1$, and the configurations of $(n\text{-}1)d^6ns^1$ and $(n\text{-}2)f^7ns^1$ or f^8 do not exist at all. Therefore, we question the causes of this rule.

We believe that in equivalent orbitals, when fewer orbitals are occupied, such as one, the wave packet of the orbital has an expansion phenomenon. The larger the eccentricity of an orbital, the more obvious this expansion. As the number of orbitals occupied by electrons increases, the expansion of orbitals will be restrained. When it is close to half full or complete full, this restraint (or inhibition) will reach the maximum. When the expansion is restrained, the eccentricity will be reduced. This inhibition effect is represented by the coefficient F_i, and a negative value is taken to reduce the orbital eccentricity. It has a similar periodic change law before half full or complete full. The stronger the effective nuclear charge, the greater the inhibition effect, the more negative F_i. In different periods, the effective nuclear charge and F_i are different.

The anomaly of electron filling order for elements in *d* block in periodic table occurs between (*n*-1)*d* and *ns*. The radius of *ns* orbital is not affected by expansion or inhibition. Therefore, the change of (*n*-1)*d* orbital eccentricity $l_{(n-1)d}$ becomes the main reason affecting the electron filling order. Its change is mainly affected by several factors, but the change is quantized.

Among the transition elements in the fourth period, 3*d* orbital is the first added *d* orbital, and its space is relatively crowded. However, it is not affected by other factors. It has a similar change law before and after half full, and only has a moderate inhibitory effect F_i. After the gradual increase of four elements, F_i reaches a quantization unit (-0.05). For each additional orbital occupied by electron, F_i = -0.05/4 = -0.0125. $l_{3d}=2+\Delta l_s+\Delta l_{3d}+F_i$. According to formula

$$N_1=[4-(n+l)_{3d}]/0.05 \qquad (41)$$

where N_1 is electron number that atom of an element can hold in its 3*d* orbitals. The long radius of the 3*d* orbitals of elements 19-30 and the number of 3*d* electrons, N_1, are listed in Table-2. N_2 is the number of *d* electrons obtained from N_1 by the tail removal method. The calculated value N_2 is consistent with the experimental value N_3. As a result, for the fourth period elements only chromium and copper have $(4s)^1$ configuration.

For the transition elements of the fifth period, there are two main factors that make the 4*d* orbital have a strong inhibitory effect. First, with the increase of orbital radius, the space congestion of 4*d* orbitals is significantly alleviated than that of 3*d* orbitals. After continuity three elements, it has reached a quantum unit (-0.05), and each element changes -0.05/3 (or -0.0167). Second, there is an influence of the same layer 4*f* empty orbitals outside the 4*d* sublayer, F_{f0}. The F_{f0} only affects those particularly crowded orbitals in the inner sublayer, that is, it only affects the 4*d* orbitals after half full. Due to the contraction of 4*d* orbitals, the influence of F_{f0} is enhanced, and among elements 44-46 reach one quantum unit (-0.05) after half full. Then

$$l_{4d}=2+\Delta l_s+\Delta l_{4d}+F_i+F_{f0} \qquad (42)$$

Table 3. *Comparison of long radii of 5s and 4d orbits in the fifth periodic elements*

element	37Rb	38Sr	39Y	40Zr	41Nb	42Mo	43Tc	44Ru	45Rh	46Pd	47Ag	48Cd
structure	$4d^0 5s^1$	$4d^0 5s^2$	$4d^1 5s^2$	$4d^2 5s^2$	$4d^4 5s^1$	$4d^5 5s^1$	$4d^5 5s^2$	$4d^7 5s^1$	$4d^8 5s^1$	$4d^{10} 5s^0$	$4d^{10} 5s^1$	$4d^{10} 5s^2$
Δl_s	-0.5	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1
Δl_{4d}	0	0	-0.05	-0.10	-0.15	-0.20	-0.25	-0.30	-0.35	-0.40	-0.45	-0.50
F_i	0	0	-0.017	-0.033	-0.050	-0.050	0	-0.017	-0.033	-0.050	-0.050	0
F_{4f0}								-0.05	-0.05	-0.05	0	0
l_{4d}	1.5	1	0.9333	0.867	0.80	0.75	0.750	0.633	0.567	0.50	0.50	0.50
N_1	0	0	1.334	2.66	4	5	5	7.34	8.66	10	10	10
N_2	0	0	1	2	4	5	5	7	8	10	10	10
N_3	0	0	**1**	**2**	**4**	**5**	**5**	**7**	**8**	**10**	**10**	**10**

$N_1=[5-(n+l)_{4d}]/0.05$

Table 4. *Comparison of long radii of 6s and 5d orbits in the sixth periodic elements*

element	55Cs	56Ba	57La	72Hf	73Ta	74W	75Re	76Os	77Ir	78Pt	79Au	80Hg
structure	$5d^0 6s^1$	$5d^0 6s^2$	$5d^1 6s^2$	$5d^2 6s^2$	$5d^3 6s^2$	$5d^4 6s^2$	$5d^5 6s^2$	$5d^6 6s^2$	$5d^7 6s^2$	$5d^9 6s^1$	$5d^{10} 6s^1$	$5d^{10} 6s^2$
Δl_s	-0.5	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1
Δl_{5d}	0	0	-0.05	-0.10	-0.15	-0.20	-0.25	-0.30	-0.35	-0.40	-0.45	-0.50
F_{5f0}							0	-0.017	-0.033	-0.05	-0.05	0
l_{5d}	1.5	1.0	0.95	0.90	0.85	0.80	0.75	0.683	0.617	0.550	0.50	0.50
N_1	0	0	1	2	3	4	5	6.34	7.66	9	10	10
N_2	0	0	1	2	3	4	5	6	7	9	10	10
N_3	0	0	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**9**	**10**	**10**

$N_1=[6-(n+l)_{5d}]/0.05$

Table-3 lists the calculated values of the number of electrons that can be accommodated in 4*d* for the elements 37-48. The calculated value N_2 is consistent with the experimental value N_3. There are six special cases in the fifth period elements, in which Nb, Mo, Ru, Rh and Ag all have $(4s)^1$ configuration, and Pd has $(4s)^0$ configuration.

For the transition elements of the 6th period, there have been full $(n\text{-}2)f$ orbitals. Because the long radius of $(n\text{-}2)f$ orbitals is approach to that of $(n\text{-}1)d$ orbitals, the interaction between them has become the mainstream. The shielding and repulsion of 4*f* electrons to 5*d* orbitals or 5*f* electron to 6*d* orbital will lead to the almost disappearance of the F_i for 5*d* or 6*d* orbitals. Only the influence of 5*f* or 6*f* empty orbit on the 5*d* or 6*d* sublayer in the same layer, F_{f0}, affects them. After half full, for elements 76-79, the F_{5f0} gradually reach one quantum unit (-0.05). Table-4 lists the calculated values of the number of electrons that can be accommodated in the 5*d* orbitals of elements 55-80. The calculated value N_2 is consistent with the experimental value N_3. In the special cases for the sixth period elements, only Pt and Au still maintain the $(6s)^1$ configuration. The transition elements of the 7th period are similar to those of the 6th period.

By Table-2 to Table-4, it can be seen that the calculation results fully explain all 10 special cases of three transition systems.

Electron filling order of lanthanides and actinides

In the "energy level interleaving phenomenon" of lanthanides and actinides, the *ns* orbital has no eccentricity change. Unlike the *ns* orbitals, the $(n\text{-}2)f$ and $(n\text{-}1)d$ orbitals not only have almost the same long radius, but also have a similar rate of change with the increase of nuclear charge. Due to the beginning of filling, empty $(n\text{-}2)$ *f* and $(n\text{-}1)$ *d* orbitals appear at the same time, which results a more empty space and increases a gap between their long radii and the *ns* orbital radius. Therefore, the crossing of the filling orders for lanthanides and actinides mainly occurs between $(n\text{-}2)f$ and $(n\text{-}1)d$ orbitals, and there is no $(ns)^1$ configuration. In contrast, $(n\text{-}2)f$ is an inner orbital, and its expansion effect is main effect in their interactions; $(n\text{-}1)d$ is the outer orbit, and its inhibition effect is main effect in their interactions.

Lanthanide and pre lanthanide elements

Table-5 lists the calculated values of a_{5d} and a_{4f} for elements 55 to 70 in the sixth period. Because lanthanides start from the empty 4*f* orbitals, they do not form a large shielding and repulsion effect on the 5*d* orbital. Therefore, the F_i for 5*d* orbitals can be ignored in the calculation. Only the 4*f* orbits for 57 La and 58 Ce at the beginning and 64 element Gd after half full expand slightly, and the long radius of the orbitals increases slightly, marked with "+" in the a_{4f} value of table-5. With the

Table 5. *Comparison of long radii between 5d and 4f orbits in the sixth periodic elements*

element	55Cs	56Ba	57La	58Ce	59Pr	60Nd	61Pm	62Sm	63Eu	64Gd	65Tb	66Dy	67Ho	68Er	69Tm	70Yb
structure	$5d^0 6s^1$	$5d^0 6s^2$	$5d^1 6s^2$	$5d^1 6s^2$	$5d^0 6s^2$	$5d^0 6s^2$	$5d^0 6s^2$	$5d^0 6s^2$	$5d^0 6s^2$	$5d^1 6s^2$	$5d^0 6s^2$	$5d^0 6s^2$	$5d^0 6s^2$	$5d^0 6s^2$	$5d^0 6s^2$	$5d^0 6s^2$
	$4f^0$	$4f^0$	$4f^0$	$4f^1$	$4f^3$	$4f^4$	$4f^5$	$4f^6$	$4f^7$	$4f^7$	$4f^9$	$4f^{10}$	$4f^{11}$	$4f^{12}$	$4f^{13}$	$4f^{14}$
Δl_s	-0.5	-1	-1	-1	-1	-1	-1									
Δl_{5d}	0	0	-0.05	-0.10	-0.15	-0.20	-0.25									
a_{5d}	**6.5**	**6.0**	**5.95**	**5.90**	**5.85**	**5.80**	**5.75**									
Δl_s	-0.5	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1
Δl_{4f}	0	0	-0.04+	-0.07+	-0.11	-0.14	-0.18	-0.21	-0.25	-0.29	-0.32	-0.36	-0.39	-0.43	-0.46	-0.50
a_{4f}	**6.5**	**6.0**	**5.96+**	**5.93+**	**5.89**	**5.86**	**5.82**	**5.79**	**5.75**	**5.71+**	**5.68**	**5.64**	**5.61**	**5.57**	**5.54**	**5.50**

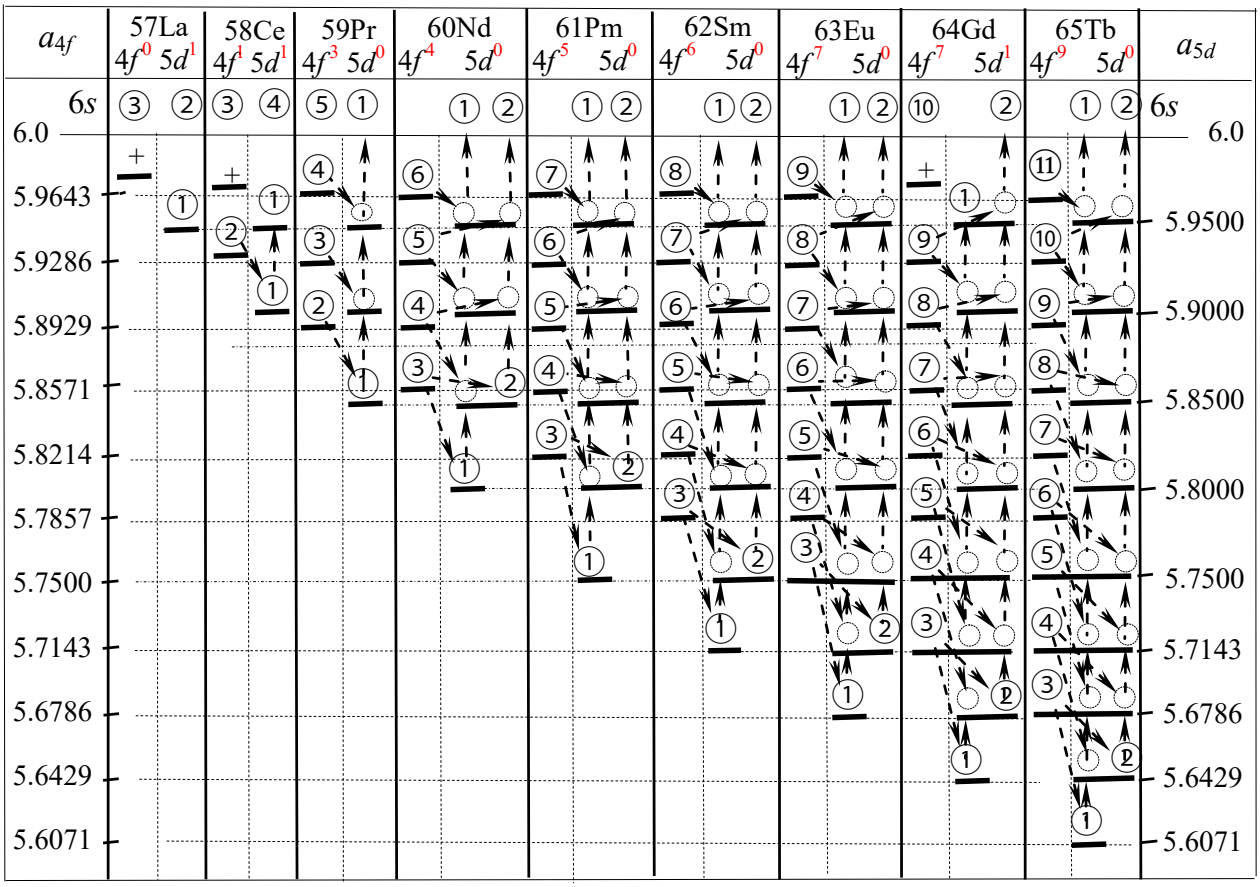

Figure 8. *Electron filling order of the Lanthanides.*

increase of the number of nuclear charges and 4*f* electrons, the shielding and repulsion of 4*f* electrons on 5*d* orbitals appear and increase gradually. When a_{5d} and a_{4f} reach the intersection of 5.75, the Δl_{5d} of 5*d* orbitals has almost been offset.

Fig.-8 shows the filling order of valence layer electrons of elements 57-65. In the Figure, the sequence number of filled electrons is represented by circled numbers. Several examples of the electron filling order of some elements are as follows.

The atomic kernel [Xe] of element 57 La has been contained 54 electrons. For La^{3+}, a_{5d}=5.95, a_{4f}= 5.96+ >5.96, any electron cannot enter 4*f* orbitals. Therefore, electron ① enters a 5*d* orbital with a_{5d}= 5.95. The electrons ② and ③ can only enter the 6*s* orbital. As a result, the electronic configuration of La is [Xe]$4f^0 5d^1 6s^2$.

For element 58, the atomic kernel [Xe] of Ce has been contained 54 electrons. For Ce^{4+}, a_{5d} =5.90, a_{4f} =5.93+. An electron ① enters a 5*d* orbital with a_{5d} = 5.90. Electron ② enters a 4*f* orbital with a_{4f} = 5.93+, which elevates the a_{5d} of the electron ① from 5.90 to 5.95. At this time, neither 4*f* nor 5*d* can enter next electron. As a result, electron ③ and electron ④ enter 6*s* orbital, and the electronic configuration of Ce is [Xe]$4f^1 5d^1 6s^2$.

For Pr^{5+} of element 59, a_{5d}=5.85, a_{4f} =5.89. The electron ① enters a 5*d* orbital with a_{5d} = 5.85. Electron ② enters first 4*f* robital with a_{4f} 5.89, which elevates the a_{5d} of electron ① from 5.85 to 5.90. Electron ③ enters second 4*f* orbital with a_{4f} = 5.93, while elevates the a_{5d} of electron ① from 5.90 to 5.95. The electron ④ enters third 4*f* orbital with a_{4f} = 5.96, while elevates

Table 6. *Comparison of long radii between 6d and 5f orbits in the seventh periodic elements*

element	87Fr	88Ra	89Ac	90Th	91Pa	92U	93Np	94Pu	95Am	96Cm	97Bk	98Cf	99Es	100Fm	101Md	102No
structure	$7s^1$	$7s^2$	$6d^17s^2$	$6d^27s^2$	$6d^17s^2$	$6d^17s^2$	$6d^17s^2$	$6d^07s^2$	$6d^07s^2$	$6d^17s^2$	$6d^07s^2$	$6d^07s^2$	$6d^07s^2$	$6d^07s^2$	$6d^07s^2$	$6d^07s^2$
			$5f^0$	$5f^0$	$5f^2$	$5f^3$	$5f^4$	$5f^6$	$5f^7$	$5f^7$	$5f^9$	$5f^{10}$	$5f^{11}$	$5f^{12}$	$5f^{13}$	$5f^{14}$
Δl_s	-0.5	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1
Δl_{6d}	0	0	-0.05	-0.10	-0.15	-0.20	-0.25	-0.30	-0.35	-0.40	-0.45	-0.50				
F_i			-0.0125	-0.0250	-0.0375	-0.0500										
l_{6d}	1.5	1.0	0.9375	0.8750	0.8125	0.7500										
a_{6d}	7.5	7.0	6.9375	6.8750	6.8125	6.7500										
Δl_s	-0.5	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1
Δl_{5f}			-0.0357	-0.0714	-0.1071	-0.1429	-0.1786	-0.2143	-0.2500	-0.2857	-0.3214	-0.3571	-0.3929	-0.4286	-0.4643	-0.5000
l_{5f}	2.5	2	1.96	1.93	1.89	1.86	1.82	1.79	1.75	1.71	1.68	1.64	1.61	1.57	1.54	1.50
a_{5f}	7.5	7.0	6.964+	6.929+	6.893+	6.857+	6.821+	6.7857	6.7500	6.714+	6.6786	6.6429	6.6071	6.5714	6.5357	6.5000

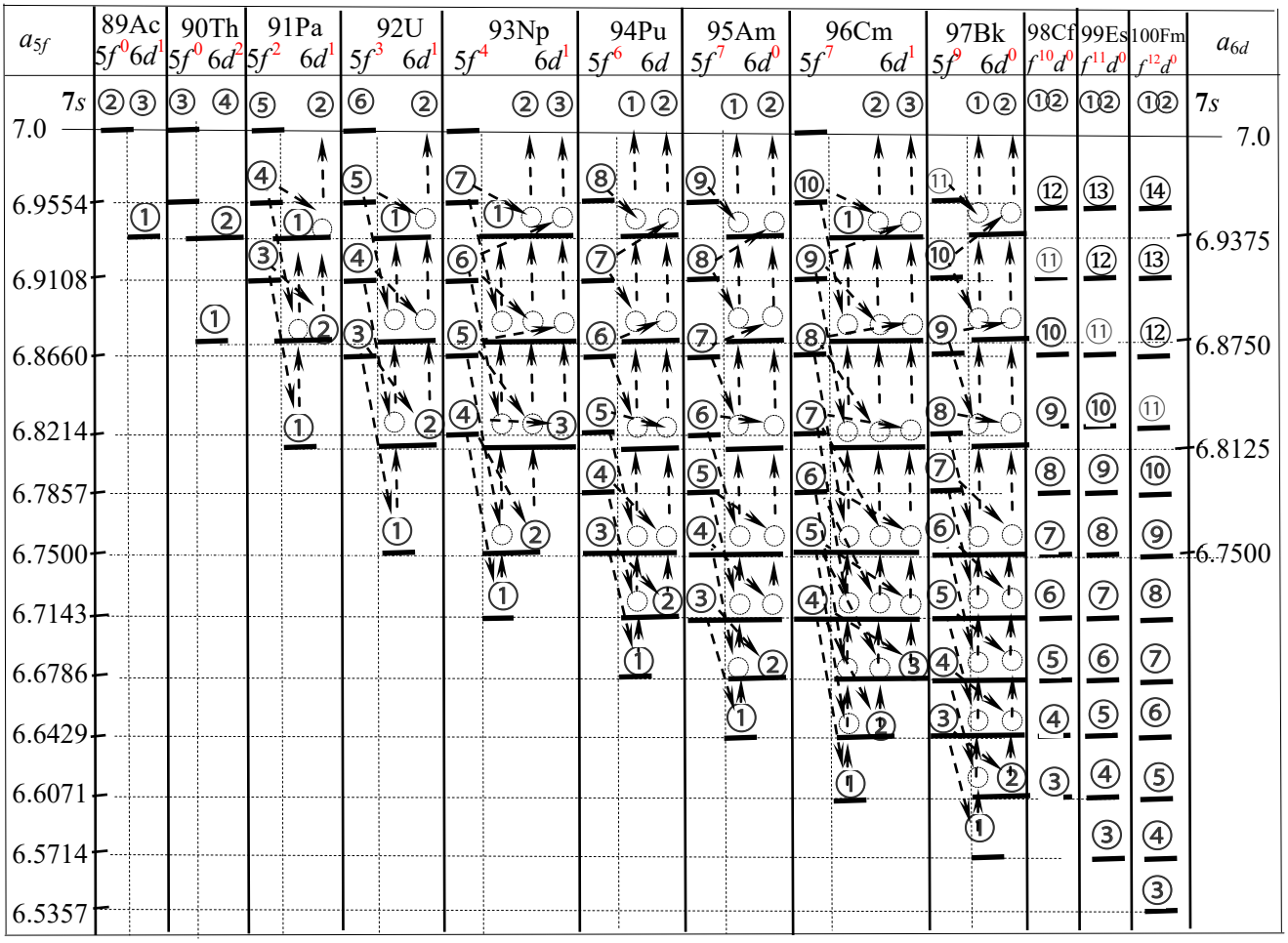

Figure 9. *Electron filling order of the actinides*

electron ① from 5.95 to 6*s* orbital. The electron ⑤ enters 6*s* orbital also. As a result, the electronic configuration of Pr is [Xe]$4f^3 5d^0 6s^2$.

From element 60 Nd to element 63 Eu, due to the shielding effect of the inner 4*f* electrons on the outer 5*d* orbitals, all of the 5*d* orbitals have no space to fill the electrons, and are all in the $5d^0$ state.

At element 64 Gd, the long radius of first 4*f* orbital increases slightly due to the expansion effect after the 4*f* orbitals are half full. As a result, the electron ① can finally remain in the 5*d* orbital. As a result, the electronic configuration of Gd is [Xe]$4f^7 5d^1 6s^2$.

By element 65 Tb, the expansion effect first 4*f* orbital after the half full has basically disappeared. As a result, the electronic configuration of element Tb is [Xe]$4f^9 5d^0 6s^2$.

With the increase in atomic number, the inhibitory effect of 4*f* orbital expansion becomes larger and larger. Before the 4*f* orbitals are fully filled, the 5*d* orbitals have no chance to contain electron. There are three special cases in the sixth periodic elements, 57La, 58Ce, and 64Gd.

Actinides and pre actinides

For the seventh periodic actinides, the shielding and repulsion between electrons affecting the filling order mainly occur between 6*d* and 5*f* orbitals. Although their long radii are similar, their short radii are quite different, i.e

$$a_{6d} \simeq a_{5f}; \quad b_{6d} \gg b_{5f}; \qquad (43)$$

Therefore, the influence of 4*f* orbital electrons filled in the inner layer on 5*f* orbitals is much greater than that on 6*d* orbitals. In addition, the expansion effect of actinide 5*f* orbitals is significantly greater than that of lanthanide 4*f* orbitals, and there are empty outer sublayer *g* orbitals outside the 5*f* orbitals (F_{5g0}). The combination of these effects is mainly reflected in element 89-93 before half full and element 96 after half full. In Table-6, the a_{5f} values of these elements are marked with a "+".

Compared with 5*f* orbitals, the expansion inhibition effect (F_i) of 6*d* orbitals becomes prominent. From 89 to 92, the F_i increases to one quantum unit (-0.05), and each element changes (-0.0125). With the gradual increase of 5*f* electrons in the inner layer, by element 93, the F_i of 6*d* orbitals disappears. The intersection occurs at a_{6d}=6.75 for element 92 and a_{5f}=6.75 for element 95. Table-6 lists the long radius changes of 6*d* and 5*f* orbitals in atoms of elements 87 to 102. Figure 9 shows the valence layer electron filling order of atoms from elements 89 to 100. There are six special cases in lanthanides, 89Ac, 90Th, 91Pa, 92U, 93Np, and 96Cm.

Conclusion

For the treatment of hydrogen atoms, calculus can only be used to the transition process of electron rather than steady state. The orbital parameters describing each steady state are some determined and quantized values, not continuous functions. Therefore, Bohr's use of numerical algebraic manipulation to deal with ground state hydrogen atoms is reasonable both mathematically and physically. The standing wave principle in physics is the theoretical basis of the quantization of micro particles. Bohr's quantization hypothesis can be deduced from de Broglie's thought of matter wave. Combining Bohr model with de Broglie's idea. A new atomic structure model with closed orbits can be established.

As a result, the rotation frequency of the electron is equal to the frequency of the matter wave and can directly correspond to the radiation frequency. A realistic process of electron rotation and photon radiation can be imagined directly, and a luminous particle in the gas completes the emission of a photon wave train by a free path; The details of photon radiation through momentum exchange in effective collision can be directly imagined; The long radius of the orbitals determines the filling order of electrons, so as to solve the filling problem of electrons in the order of periodic table. By this paper, Madelung rule has be deduced directly from theory, and the "Löwdin's challenge problem" has be solved.

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