GENERAL CHEMISTRY Lesson 1-4 Electrons in atoms.

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Planetary (Rutherford) model of atoms says that the major part of atomic material is concentrated in the atomic center (a nucleus), which consists of positive protons and neutral neutrons. Negatively charged (and light) electrons are orbiting around positively charged (and heavy) nucleus, and the negative charge of the electronic shell is compensated by the positive charge of the nucleus, so the net atomic charge is zero. The number of electrons (and, accordingly, of protons) is equal to the element's atomic number (i.e. its position in the Mendeleev's table).

Rutherford explained electron's motion in atoms in the same way planetary motion in the Solar system is explained. When a planet is orbiting the Sun (or another star), it is being attracted by the star, so it is constantly falling to the star's center. However, as the planet has some initial velocity, the resulting trajectory is not directed to the star. The planet's trajectory is curved (due to the star's gravitation force), so the resulting trajectory is a circle (or an ellipse), so



Figure 1: A planet orbiting the Sun (A), and an electron orbiting atomic nucleus in the Rutherford model (B).

the planet will never fall onto its star. The only force affecting the star is, therefore, a gravity force, and the trajectory is curved (i.e. it is not directed to the star's center) because the planed, due to its inertia, resists to a sharp trajectory change. In other words, the circular shape of the orbit is a result of two opposite effects: attractive force between the planed and the star, and the planet's inertia.

When we compare the Sun - Earth system and the electron - nucleus system, we see that an electron is being attracted by the nucleus not due to its mass, but due to its charge (in other words, the force acting between the nucleus and the electron is Coulomb force, not gravity¹). Everything else is the same: due to its inertia, electron resists to the Coulomb force, and, instead of falling on the nucleus, orbits around it.

That is a brief summary of what we have learned by now. Does this information shed any light on chemical properties of elements? I am not sure. Does this model explain physical properties of atoms and their structure? No. In other words, although Rutherford model and the discovery of the atomic nucleus composition were a major breakthrough, neither chemists nor physicists were satisfied with them. Physicists criticized this model especially strongly, because it lead to several paradoxes classical physics was unable to explain.

1 Paradoxes of the Rutherford model.

1.1 Why atoms are spherical?

As early experiments with X-rays demonstrated, atoms in crystalline materials have an approximately spherical shape, and there is a serious reason to believe that observation is general. Meanwhile, if we look at our Solar system, as well as other stellar systems, you will see the orbit of each planet is planar, and all orbits are in the same plain. Similarly, if electrons are moving in atoms as described at the fig 1b, why atoms are not discs?

Question 1. Take a look at the crystal of sodium chloride and try to explain how can we conclude that sodium and chlorine atoms are not discs.

1.2 Why atoms have a specific size?

We know that different orbits are allowed for a planed orbiting a star. Indeed, numerous extrasolar planetary systems have been found during the last decade where planets of similar size are rotating either very closely to their Suns, or they were very far from them. A satellite can be placed at any circular orbit about the Earth by providing it with an appropriate velocity. Similarly, Rutherford model and Coulomb theory applies no limitations on the radius of electron orbits. However, it was established experimentally that atoms of a certain type are totally identical to each other, and, accordingly, their radii are *absolutely* equal. That implies that, for some unclear reason, electrons in every atom "know" about the orbit they are allowed to occupy: thus, *all* hydrogen atoms in the Universe have *exactly* the same radius, and that is true for any other element.

Rutherford's model provides no explanation for this fact.

¹Actually, there is a gravity force between nuclei and electrons, however, due to low masses of nuclei and electrons, this force is many orders of magnitude smaller than Coulomb force. That is why gravitation is being neglected during the calculations of atomic structure.

1.3 Why electrons do not fall onto a nucleus?

This question was the most intriguing questions physicists started to ask immediately after the Rutherford's model was proposed. Indeed, why? On the figures 1 **a** and **b**, the planet and electron, accordingly, are affected by a single force (attraction force). According to the second Newton's law, that means their motion is an *accelerated motion*. In general, any curved motion is accelerated, and the acceleration is directed to the center of curvature. Why that fact became a source of problems in atomic physics? The reason was simple: according to the electromagnetic theory, any accelerated motion of a charged object (and an electron is a charged particle) generates an electromagnetic wave; depending on the magnitude of acceleration, it can be a visible light, or radio wave, X-rays, UV light, etc.

Moreover, emission of electromagnetic waves by electrons moving along a circular orbit is among the best ways to produce very bright X-rays radiation. In many research centers, for example, in the Brookhaven National Lab (which is very close to us), a particle accelerator (synchrotron, Fig. 4) is used specially as a source of extremely bright X-rays. The source provides highly uniform and concentrated X-rays that are needed for structural studies of biological molecules and other materials.

However, when light (or X-rays, or radio waves, etc) is produced, it carries some energy. Where does this energy come from? If the source of light is an electron moving along a curved trajectory, this energy comes from electron's energy of motion, i.e. its kinetic energy. In other words, when an electron moving along a circular orbit emits light,



Figure 2: Emission of light (orange arrows) by a charged body moving along a circular orbit.

its energy decreases, which means it is loosing its speed. In synchrotrons, the loss of speed is compensated by special electromagnets that are continuously "pushing" electrons forward, so the constant speed is maintained. Without that, electrons would quickly come to almost a full stop.



Figure 3: Collapse of Rutherford's atom.

The Rutherford's atom where electron is making a circle around a nucleus can be considered as a "small synchrotron", the only difference is that there no extarnal energy source to maintain electron's kinetic energy. That means the electron orbiting the nucleus would be constantly emitting electromagnetic waves (i.e. light, UV radiation, etc) and its velocity would decrease gradually until the electron fall onto the nucleus. Computation of that process had been made that demonstrated Rutherford atom would live less than a tiny fraction of a second, and then collapse in a bright burst of light.

That is the third and the major paradox of the Rutherford's atomic model.

Question 2. Explain why deceleration of an electron will lead to its falling onto the nucleus as shown on the Fig. 3.



Figure 4: New synchrotron in BNL. The circular building contains a vacuum tunnel where electrons are running with the speed close to the speed of light. The rectangular buildings attached to the circle are the labs where the X-ray experiments are made.

2 Planck's equation

In 1874, a young talented student Max Planck arrived to Munich to study physics. Soon after that, he had a conversation with his professor, Philipp von Jolly, who told him that there is no point for such a talented person as Planck to devote himself to physics. "In this field, almost everything is already discovered, and all that remains is to fill a few holes," - von Jolly said. Fortunately for us, Planck was undeterred by these words, and two decades later he made a discovery that demonstrated these "few holes" were actually a window to a totally new physics.

Max Plank's devoted his efforts to filling of one of these "few holes", concretely, he was trying to explain the mechanism of light emission by hot bodies. The major difficulty he was struggling with was the prediction made by classical physical theory. This theory predicted all hot or even warm bodies should shine brightly in a blue, UV and even X-ray range of electromagnetic spectrum. Obviously, for everybody who saw our Sun, which is yellow, not blue, is obvious this prediction of classical physics was blatantly wrong.

In 1900, Planck published an article where he made a paradoxical conclusion: all problems with the description of light emission by hot bodies could be resolved if we assume the emission of light occurs not continuously, but in small "wave packets", each of which carries the energy equal to:

$$E = h\nu$$

where E is a minimal amount of energy some electromagnetic wave (light, radio wave, X-ray

wave, etc) can carry, ν is the frequency of this wave, and h - a fundamental constant, called "Planck's constant" (about $10^{-30}J \cdot s$). In other words, the minimal energy that can be transferred between two bodies by a very long radio wave with the frequency of 1 Hz (one oscillation per second) is $10^{-30}J$ (or h/1s), whereas the minimal amount of energy a green light can carry is about $6 \cdot 10^{-16}J$ (frequency of green light is around $6 \cdot 10^{14}Hz$). Planck dubbed this amount "a quantum"², thereby implying that light should be considered not as a continuous wave, but as a stream of some "particle-waves" (quanta). According to Planck, this formula is universal, which means it is valid for any kind of electromagnetic radiation, and, even more generally, to any case of energy transfer between two bodies.

Since Planck's constant is *very* small, the energy a single quantum can carry is also small: If we compare the energy of a green light quantum $(6 \cdot 10^{-16}J)$ with the energy produced by a poppy seed (its mass is 0.3 milligram) falling from a table on a floor (elevation is ca 1 m, so the energy is $3 \cdot 10^{-7}J$), we see the latter is one billion times greater. However, taking into account that there are about 10^{-16} atoms in a poppy seed, we can conclude the energy of a single green light quantum is much greater than the energy one molecule would produce when it falls down from the table to the floor. Accordingly, the energy one quantum of green light carries is *much* greater than the energy needed to force one moderate size molecule jump from a floor to a table.

Why is that fact so important? That means when we consider the world of small objects (molecules, atoms, electrons or other elementary particles), we must take into account that energy transfer between these objects occurs not continuously, but in discrete portions. When scientists estimated a magnitude of momentum of electrons in atoms (and, therefore, electron's acceleration), they concluded that the frequency of photons these electrons should emit roughly corresponded to the frequency of visible light. As we have demonstrated above, the energy the visible light quantum carries is small, but not negligible when we are talking about atom size particles, and especially electrons. Actually, it is comparable with the energy of an average electron in atoms.

One of the most important consequences of that is the following:

When an electron is losing energy via light emission, it is not "spiraling down" along some smooth curved trajectory as shown on Fig 3. It falls onto the nucleus in several discrete steps. The electron jumps from the upper orbit to the next lower orbit, than it jumps even lower, and each step is achieved by emission of a discrete light quanta with energy $E = h\nu$ as shown of Fig 5.

Two important s arise from this conclusion. The **first question** is: how can we calculate the actual frequency ν of the photons the electron produces when it jumps from one orbit to another? The *second question* is even more crazy: if we assume an electron cannot spiral down, and it exists either at some upper orbit or some lower orbit, how does the process of transition occur? Indeed, if we describe an electron that moves between orbits using the same approach we use to describe, e.g. a space ship, we must conclude that before the electron arrived to the lower orbit, it mush reach the midpoint, before the midpoint is reached, the electron must reach a quarterpoint, and so on, an so forth. That reminds a famous Zeno's

²This word has the same root as "quantity". It means "a certain amount".

aporia, the aporia we discussed last year³ The same can also be said as follows: "If an electron can occupy just some discrete orbits in an atom, and intermediate orbits are not allowed, where the electron exists during the process of transition between the orbits?"

These two questions became the subject of interest of a German physicist Werner Heisenberg. In early 1920s, he decided to develop a rigorous mathematical description of the process of electron jumps between orbits. Using an advanced mathematical apparatus, he gave an answer to the first question, and, more importantly, came to a totally paradoxical conclusion that is now known as an *uncertainty principle*. This principle laid a foundation for the modern quantum mechanics, and, in particular, it gave the answer to the question where an electron is when it is jumping from one orbit to another.



Figure 5: Stepvise fall of an electron on a nucleus. A dashed curve is a "classical" trajectory.

3 Uncertainty principle

The uncertainty principle can be explained as follows. If we want to know a position (coordinate) of some physical

object with accuracy Δx (which means the coordinate of this object is $x \pm \Delta x$), and, at the same time we want to determine this object's *momentum*⁴, the minimal possible uncertainties (Δx and Δp , accordingly) are determined by this equation:

$$\Delta p \cdot \Delta x \geqslant \frac{\hbar}{2}$$

The new constant, \hbar , is the Planck's constant divided by 2π . \hbar is called "reduced Planck constant", we will use it in our future calculations. At the first glance, there is no direct connection this formula and the question about electron's movement in an atom. The linkage becomes obvious when we take into account that all early attempts physicists made to explain atomic structure were the attempts to describe *trajectories* of electrons in atoms. In contrast, the above formula means *electrons, as well as any small particles, have no trajectory at all.*

To understand how can this statement be derived from the uncertainty principle and the above inequation, let's remember what does "trajectory" mean. *Trajectory* is a path some object follows when it is moving through space. In other words, when some object is moving, and we can trace its path, we say: "the trajectory of this object is known, because we always can say where this object is and where it is moving to." The same can be said in more scientific terms: both coordinate and velocity (or momentum) of an object can be determined, which allows us to predict where this object will be in the next moment, and, if we know all

³This aporia says: "Motion cannot exist because before that which is in motion can reach its destination, it must reach the midpoint of its course, but before it can reach the middle, it must reach the quarterpoint, but before it reaches the quarterpoint, it first must reach the eightpoint, etc. Hence, motion can never start."

⁴Momentum (p) is the product of object's mass and velocity: p = mv.

forces acting upon this object, we theoretically can calculate its trajectory in distant future. This is a core idea of classical (Newtonian) mechanics, and numerous calculations made by physicists and especially astronomers demonstrated that this idea works perfectly is our big world. Calculations of celestial bodies' motions are especially impressive: astronomers predict trajectories of planets, asteroids, satellites or space ships with astonishing accuracy. However, Heisenberg's uncertainty principle limits a possibility to trace trajectories. Indeed, the concept of trajectory implies we can know *exact* coordinate and *exact* velocity of any object of interest, and this assumption works in our big world. For example, if we speak about, for example, a 1 kg stone, we can say its coordinate is exactly known when the error in coordinate determination is less than e.g. 1 micrometer. That means $\Delta x = 10^{-6}$. According to the uncertainty principle, the error in momentum is greater than $\frac{\hbar}{\cdot 10^{-6}}$, and, taking into account that h is very small, the error in momentum determination is negligible. Since momentum is a product of velocity and mass, the velocity of a 1 kg stone can also be determined with a very high precision.

Question 3. What is the lowest limit of momentum uncertainty of a 1 kg rock if its coordinate in know with 1 micrometer accuracy? Do calculation using the uncertainty principle formula and known value of Planck constant.

It would be correct to say that modern measurement technique does not allow us to achieve the precision limits when the uncertainty principle becomes detectable for large size objects (the objects with the mass of several grams and more). That means, we can safely claim we *are* able to measure both velocity and position of any macroscopic objects virtually precisely, in other words we *do* know where they are and where they are moving, so, in full accordance with classical mechanics, trajectories of macroscopic bodies can be traced virtually precisely.

A situation becomes totally different when we are dealing with small bodies (electrons, protons, etc) with the mass of 10^{-32} gram or less and the sizes of 10^{-10} or less). In that case, the uncertainty principle starts to play a significant role: if the position of an electron is known with accuracy of 10^{-10} m (the size of a hydrogen atom), the standard deviation of electron's momentum is comparable with the momentum itself, which means it is totally impossible to predict its trajectory. The latter fact explains the puzzle of electron's jumps between orbits: if no trajectory exists for an electron, all Zeno style speculations are not applicable to electron transitions: it does not need to reach a midpoint during the transition between the orbits.

The uncertainty principle also explains why electrons do not fall onto the nucleus. The answer is obvious: electrons cannot fall onto the nucleus because they are already there. They are almost in the nucleus, but the standard deviation from their position corresponds to the radius of the lowest orbit: their position is in the nucleus $\pm \Delta x$. If they come closer, that means they are confined in a smaller volume, so their Δp grows, and in the next moment they will fly away, and their distance from the nucleus increases. However, that will lead to the drop of electron's kinetic energy, electrons decelerate, and fall back to the nucleus, and this dance lasts forever, so some minimal average distance between an electron and a nucleus is maintained.

4 Uncertainty principle and a radius of a hydrogen atom

In this section we will see how the atomic radius of a hydrogen atom (i.e. the radius of its lowest orbit) is calculated. To do that, we use only four fundamental physical constants (the Planck's constant, Coulomb constant, electron mass and charge) and the universal equations for kinetic and potential energy. We will do that step by step to demonstrate your current level of knowledge is totally sufficient for doing that. Try to understand each step, because it will help you to see how physicists are thinking.

Step 1. Consider a hydrogen atom's nucleus (a proton) having a coordinate 0, 0, 0 (x = 0, y = 0, z = 0), and assume its electron fell on the nucleus, which means its coordinate is also 0, 0, 0. Since electron's position cannot be determined with absolute accuracy, every time when we try to visualize this electron, we will find it not exactly in the nucleus, but in a close proximity to it. For simplicity, let's ignore all axes but the x axis, and let's discuss only electron's x coordinate. After each measurement we will find the electron not at x = 0, but at some x_i . Obviously, the *average* of all x_i is zero (the electron has already fallen on the nucleus), but instantaneous x_i may be slightly greater or smaller (the electron is right of the nucleus or left to it. In that situation, what is the most probable distance between the electron and the nucleus? Obviously, it is not zero. To calculate the distance, take a square of all x_i , add them, and take a square root of the sum (a square is always non-negative, so the average is always greater than zero). In mathematics, we write it like this⁵

$$R = \sqrt{\frac{\sum_{i=1}^{N} x_i^2}{N}}$$

Since the above mathematical equation is used to calculate a standard deviation⁶, it is correct to say that R (the average distance of the electron from the nucleus) is actually an standard deviation of this electron from its average position (in the nucleus), in other words,

$$R = \Delta x$$

and this Δx is the same Δx we used in a formulation of the Uncertainty principle.

We can use the same approach to describe Δp . Electron's momentum can be positive or negative (it is moving to the left and to the right, but on average it is zero (which means electron stays near the nucleus). To calculate the average *deviation* of electron's momentum from its zero value, we use the same universal approach: take a square of each instantaneous values of momentum, p_i , and calculate the square root of the average value.

$$Average\Delta p = \sqrt{\frac{\sum_{i=1}^{N} p_i^2}{N}}$$

⁵This notation means: "for each i, starting from 1 to N, take a square of each x_i , calculate the average value of x_i^2 and take its square root".

⁶Strictly speaking, it is true for large N only, but that is what we need.

Following the same logic we applied to the description of the average electron's distance from the nucleus, we conclude average Δp is the average *magnitude* of electron's momentum $(p_{average})$, and it is equal to Δp in the uncertainty principle formula.

Remember, for a macroscopic observer, average electron's position is exactly in the nucleus and its average momentum in exactly zero. However, whereas the electron is not flying away from the nucleus, it experiences some random motions back and forward, and the average value of the *magnitude* (length) of the momentum's vector is $mv = \Delta p$.

At the end of this step, we found that for an electron orbiting the nucleus its Δx and Δp (as defined by the uncertainty principle) are actually equal to the radius of its orbit and the average magnitude of its momentum. To find this radius, we need to draw the energy equation.

Step 2. For this step, we use two universal physical rules:

- 1. Any physical system tries to minimize its energy: it will be evolving until the lowest energy state is achieved. The lowest electron orbit is the lowest energy state, so we need to draw the energy equation to find the parameters of electron orbit that correspond to energy minimum.
- 2. For a physical object that has no internal structure (no internal parts) the total energy is a sum of its kinetic energy T (which depends on how fast the object is moving) and potential energy U (which depends on a position of this object in space). Since an electron has no internal structure, this rule is totally applicable to it.

Obviously, Δx (or R, which is the same in our case) has a relation to electron's potential energy (because it tells about the distance between a nucleus and an electron), and Δp defines its kinetic energy (because it depends on electron's speed). Potential energy of the system where only Coulomb forces are acting can be calculated according to the equation:

$$U = -\frac{ke^2}{R}$$

Where k is Coulomb coefficient, e is an elementary charge, and R is the average distance that we discussed above. A minus sign is added because the charge of an electron is -e, and the charge of a proton is e.

Kinetic energy is always equal to:

$$T = \frac{mv^2}{2}$$

or

$$T = \frac{p^2}{2m}$$

because p = mv, where m is electron mass. In our case, $mv = \Delta p$, so

$$T = \frac{\Delta p^2}{2m}$$

Now we can write the equation of total energy:

$$E = T + U = \frac{\Delta p^2}{2m} - \frac{ke^2}{R}$$

We found the equation that describes electron's energy in an atom as a function of two variables, Δp and R. Now we need to find the value of R that corresponds to the minimal energy state.

Step 2b. Before we started, one more problem should be resolved: The above equation contains two variables, and that makes calculations difficult. Fortunately, these two variables are not independent, so we can express one of them through another, which allows us to get rid of one variable. We want to find R, so let's get rid of Δp . The Uncertainty principle says that

$$\Delta p \cdot \Delta x \geqslant \frac{\hbar}{2}$$

so in the lowest energy state (lowest possible Δx and Δp) we can write:

$$\Delta p \cdot \Delta x \approx \hbar$$

which means

$$\Delta p = \frac{\hbar}{\Delta x} = \frac{\hbar}{R}$$

Now we replace Δp with $=\frac{\hbar}{R}$ in our energy equation, and we get:

$$E = T + U = \frac{\hbar^2}{2R^2m} - \frac{ke^2}{R}$$

In we denote $\frac{\hbar^2}{2m}$ as A and ke^2 as B, the last equation transforms into this:

$$E = \frac{A}{R^2} - \frac{B}{R}$$

so the last thing we have to do is to find R that corresponds to the minimal value of E (energy).

Congratulations! We found the energy equation (that is the standard way physicists approach most problems: if a situation is unclear, draw the energy equation). The remaining steps require just basic math knowledge.

Step 3.

To obtain the atomic radius, we need to find the value of R that corresponds to the lowest value of energy. Does this minimum exist? Sure. If you look at kinetic energy, you see it grows when R approaches zero (its square is in a denominator). In contrast, potential energy *decreases* when the radius drops. Definitely, some minimum should exist. Let's find it.

Two ways to find R exist. Using a standard handbook (or Google), we can obtain the values of π , e, k, m, and h, we can just do a series of calculations of energy for different R. The results to these calculations are shown at the fig. 6. The total energy minimum corresponds to the distance of $5 \cdot 10^{-11}m$, which is approximately a half of experimentally measured diameter of a hydrogen atom $(1.1 \cdot 10^{-10}m)$. In other words, our prediction is astonishingly accurate.

For our calculations, weused just an assumption that the uncertainty principle is valid, and that the electron exists in the atom in its most stable (lowest energy) state (or, in other words, that it fell on a nucleus). The calculations we made reproduce the exper*imentally observed results* (the atomic radius of a hydrogen atom), which means our assumptions are cor-That is very imrect. portant, because we haven't learned just one more interesting fact, we learned how to obtain new knowledge. And, now we see that calculations made using the



Figure 6: Total energy (red curve) of an electron calculated using our equation for different orbit radii. A minimal value (shown by an arrow) corresponds to the radius of $5 \cdot 10^{-11} m$.

quantum theory are not something overwhelmingly crazy, something that you can never understand. It would be very good is you read and understood the above text, because it tells about much more important thing than just atomic radius of a hydrogen atom.

Step 3b. This is an optional step, you can skip it, but for those who wants to know more about computations in physics this part may be useful.

Another method to obtain R exists, it is much more elegant, it provides much more accurate results, and, importantly, it represents some important trick physicists use to solve a wide range of problems. This method requires some familiarity with calculus to convert the energy equation into the energy growth equation. Fortunately, you don't have to know calculus for that, you just need to understand one simple fact:

When some mathematical function reaches its minimum, its growth rate becomes zero. That means to find a minimal value of a mathematical function we need to find a point where its growth rate is zero.

We can do that using one rule:

For a function:

$$fx = Ax^n$$

the equation of its growth is:

$$qrowth = nAx^{n-1}$$

Using this rule, we transform the final equation from the previous step:

$$E = \frac{\hbar^2}{2R^2m} - \frac{ke^2}{R}$$

and we get this:

$$growth = -2\frac{\hbar^2}{2R^3m} + \frac{ke^2}{R^2}$$

Remember, we are interested to find only one point, namely, the point where the growth is zero, so the left part of this equation becomes zero:

$$0 = -2\frac{\hbar^2}{2R^3m} + \frac{ke^2}{R^2}$$

and, in a simplified form,

$$\frac{\hbar^2}{R^3m} = \frac{ke^2}{R^2}$$

or even simpler:

$$\frac{\hbar^2}{Rm} = ke^2$$

(note, all of that are just trivial algebraic transformations).

Now we rearrange the equation to get R, and we are done:

$$R = \frac{\hbar^2}{ke^2m}$$

If we put the values of π , e, k, m, and h into this formula, we get $5.3 \cdot 10^{-11}m$, and this value corresponds to the experimentally observed atomic radius of hydrogen perfectly.

Now we can safely conclude we explained the most intriguing puzzle of an atom: why electrons do not fall onto a nucleus.

Question 4. Using the last formula for the atomic radius of a hydrogen atom, calculate the radius of a single positively charged helium atom (the atom with one electron and a helium nucleus) and the radius of a lithium atom with a double positive charge. Do you see any interesting dependence?

Homework

Read the CW materials and answer Questions 1-4 in the text.

If you have any questions, feel free to ask.

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