Inorganic Chemistry

Atomic orbitals

March 26, 2018

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).

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 serious contradictions. Before we start to discuss them, let's look at the standard planetary system (which served as an analogy for the Rutherford model).

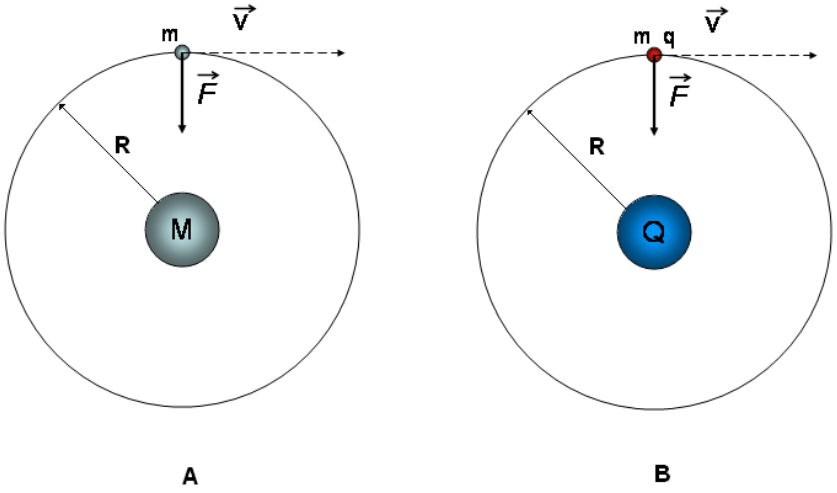

Figure 1: A planet orbiting the Sun (A), and an electron orbiting atomic nucleus in Rutherford model (B).

1 Paradoxes of the Rutherford mode.

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, since the planet has some initial velocity, the resulting trajectory is not directed to the star. Although the planet's trajectory is curved (due to the star's gravitation force), the resulting trajectory is a circle, so 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 mass and velocity, 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.

According to Rutherford, the effects acting inside the atom are essentially the same with one exception. The 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 gravity[1]). Everything else is the same: due to its initial velocity and inertia, electron resists to the Coulomb force, and its trajectory becomes circular. However, this model led to three serious physical paradoxes it failed to explain. They are as follows.

1.1 If the Rutherford model is valid, why electrons do not fall onto a nucleus?

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 *accelerated motion*. Whereas it does not leads to any problem in the first case (planets are electrically neutral), in creates serious problems for such a charged body as electron. We know that accelerated motion of a charge created a variable magnetic field. A variable magnetic field produces two effects. Firstly, it creates a variable electric field (which, by turn, creates variable magnetic field, which, by turn ... I believe you already realized I am describing a mechanism of generation of electromagnetic waves: light, radio waves, etc). Secondly (and concurrently), the variable magnetic field created by the accelerated charge produces a force that *decelerates* the charge that has begotten it. The net result of these two effects is that *acceleration of any electrical charge leads to emission of electromagnetic radiation, which took some energy from that charge.*

Figure 2: A death of the "Rutherford atom".

What does it mean in a context of the Rutherford model? That means *the electron rotating the nucleus would be constantly emitting electromagnetic waves (i.e. light, UV radiation, etc) and, since the emitted light would carry part of electron's kinetic energy, its*

[1]Actually, 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.

velocity would decrease gradually, and it would eventually fall onto the nucleus. Computation of that process had been made that demonstrated Rutherford atom would live less than a second.

That is a first paradox of the Rutherford model.

1.2 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. Similarly, if electrons are moving in atoms as described at the fig 1b, there is no reason for them to orbit randomly (which is necessary for an orbit to be spherical). In connection to that, it is absolutely unclear why atoms are not planar.

That is a second paradox of the Rutherford model.

1.3 Why atoms have a specific size?

Based on the fig 1a we can conclude different orbits are allowed for a planed orbiting a star. Indeed, it can rotate closer to the star (in that case its velocity must be higher to compensate a greater gravity force), or it can occupy remote orbit (in that case it will move slower). In other words, an infinite set of two parameters, planet's velocity and orbit's radius, is allowed for a planed. Indeed, numerous extrasolar planetary systems have been found during the last decade where the planet of similar size are rotating either very closely to their Suns, or they were very far from them. Interestingly, 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. That is absolutely unclear, and that is the third puzzle of the Rutherford model.

2 Bohr atomic theory.

A person who made the first attempt to address above paradoxes was a great Danish physicist Niels Bohr.

What is important in these considerations? We just demonstrated that energy of electron is the only necessary parameter to describe electron's orbit. In other words, we don't need to know electron's velocity or any force acting upon it. Its energy is the only characteristic we need to know.

Based on that, Niels Bohr decided to circumvent the weaknesses of the Rutherford model by *postulating* the following rules:

1. Electrons in atoms orbit the nucleus[2]

2. The electrons can only orbit stably, in certain orbits.[3] Other orbits are unstable, and

[2]He *decided* electrons can orbit the nucleus without falling on them, although he couldn't explain why.
[3]Bohr called them "stationary orbits".

electrons will fall down from them onto one os stationary orbits.

3. Electrons can jump from one allowed orbit to another only by gaining and loosing energy in a form of electromagnetic radiation (i.e. light)[4] Emission and absorption of the energy occurs in some finite portions, hence the radii of allowed orbits have some discrete values, which depend on the atom type.

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[4]Actually, in our world, every energy transfer, with few exceptions, proceeds via emission and absorption of electromagnetic waves.