

INORGANIC CHEMISTRY

Quanta and quantum mechanics

April 15, 2018

Now we are ready to discuss the effects that prevent electrons from falling on nuclei, and the effects explain atomic structure. Before we started, it is useful to remind you a wisdom that was discovered nearly two thousands years ago. These words belong to ancient alchemist and philosopher Hermes Trismegistus ("thrice-greatest Hermes"), who is believed to be one of prototypes of Jesus Christ. His *Emerald Tablet* contains a very interesting statement:

Whatever is below is similar to that which is above. Through this the marvels of the work of one thing are procured and perfected.

Translated to our modern language, these words mean that the same laws of nature governs the processes on the Earth and the Heaven, or, more generally speaking, that the laws of nature are universal. This idea seems obvious to most Western thinkers, however, it is absolutely non-trivial. Thus, in most Eastern cultures this idea is absent.

It would be correct to say that this short statement is one of the starting points all scientific knowledge originated from.

Why are we talking about that? Because the idea that the laws of Nature are universal means that no specific effects exists inside atoms that are responsible for existence of electron shells, orbitals, chemical bonds, etc., and all of that can be deduced from general laws of Physics. However, as we already demonstrated during previous lessons, these laws are unable to explain atomic structure. The reason why that happens is in one physical effect that is very hard to detect in our "big" world (the world where the average size of objects is more than 1 millimeter and the mass is more than 1 milligram). this effect become detectable when we are dealing with very small objects or when we are trying too measure very small distances. Today, we will talk about that.

1 Energy, force and waves

As we know, all processes that take place in our Universe occur due to four types interactions: gravity, electromagnetism, strong, and weak interactions. We also know that last two interactions take place only at very short distances (comparable to the size of atomic nucleus). Gravity forces have almost no effect on interaction between moderate size objects (atoms, molecules, cells, humans): the attraction between two 1 kg weights can barely be detected using even very sophisticated modern instruments, and gravitational forces between smaller

objects cannot be detected at all¹. That means, everything around us: atoms, molecules, living organisms, artificial mechanisms, winds, chemical reactions, phase transitions, heat, elasticity, turbulence, and many many other phenomenae are the result of electromagnetic interactions. The essence of electromagnetic effects can be described as follows: *when some object changes its position (i.e. accelerates), it produces an electromagnetic wave that takes part of its mechanical energy. If another charged object is around, it absorbs this wave, and, accordingly, obtains the energy the first object lost.*

This mechanism is *the only mechanism of energy transfer between two objects*. For example, when two balls collide, their deformation takes place initially, so the electrons in one atom move relatively to the electrons in other atoms. That leads to a perurbation of electrical fields around these atoms, and electromagnetic waves are produced. These wave become absorbed by other atoms in these balls, and the mechanical energy becomes transfered from one ball to another.

If you try to think about other physucal phenomena where energy transfer occurs, you will see that the mechanism is always the same: electromagnetic waves are produced by one physical body, and then they are absorbed by another body that is in a contact with the first body. That explains all elastic interactions, friction forces, viscosity, heat transfer, etc.

In the cases when we are dealing with an isolated body, the waves generated are not absorbed: they fly away, and we see them as radio waves, IR, ultraviolet, visible light, X-rays, etc.

That is how physics works. By the way, the same principles works for strong and weak interactions. The only difference is that these interactions are mediated not by electromagnetic, but other waves. Last year, a Nobel prize was awarded for discovery of gravitational waves, which demonstrates that the gravitational interactions also occurs via emission/absorption of waves (in that case, gravitational waves).

Now we are ready to ask a very important question: *are there any limitations on the amount of energy these waves can carry?* This question is very important, because the first man who asked this question made a revolution in modern Physics that lead to discovery of a new discipline called Quantum Mechanics.

2 Planck's constant and 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 explanation the mechanism of light emission by hot bodies. The major difficulty physicists were struggling with was the prediction the classical physical theory made about this process: it predicted all hot or even warm bodies should shine brightly in a blue, UV and even X-ray range of electromagnetic spectrum. Obviously,

¹That does not mean it does not exist, we just unable to detect it using a modern technique.

for everybody who saw our Sun, which is yellow, not blue, is obvious the 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.

Planck’s formula tells us that some minimal amount of energy exists that can be transferred between two objects. This amount depends on the frequency of the wave that performs that transfer, and is equal to $h\nu$. This energy is called “a quantum”, and the concept of quantum is the major difference between Planck’s theory and classical physics. Accordingly, this new physics is called “quantum mechanics”.

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.

3 Spring pendulum and the Bottle Imp

A spring pendulum is a weight attached to an elastic spring. When we pull the weight, it starts to oscillate around the equilibrium position. Because of friction, the pendulum is gradually losing energy, the amplitude of oscillations goes down, and finally oscillations stop. Such a pendulum is a good model for many systems: for example, any object held by drips can be considered a pendulum (a weight compressed between two elastic springs). An atom

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

where electrons are orbiting around a nucleus is also a pendulum, if we remember that there is a deep connection between harmonic oscillations and circular motion.

Because of friction, every macroscopic pendulum is gradually losing energy, the amplitude of oscillations goes down, and finally oscillations stop.

Now imagine a situation when the friction forces are totally eliminated: a pendulum is placed in a vacuum chamber, and a spring is “ideal”, which means there is no internal friction there. Will such a pendulum oscillate forever?

No. The weight is composed of atoms, and the atoms are composed of negative electrons and positive nuclei. During the oscillations, electromagnetic waves will be produced, and these waves will take part of pendulum’s energy, so the oscillations will gradually decay. For a heavy pendulum, this process will be very slow. However, when a pendulum is light, a situation is significantly different.

Let’s consider a pendulum is made from just one electron, and a spring is made of two parallel plate with a negative charge. Both plates repel the electron, which is trapped in a gap between them. The electron is kind of squeezed in electrostatic grips, and we may think about it as of an exotic version of a spring pendulum. Like for any other pendulum, the oscillation frequency depends on two parameters: the mass of electron (m_e) and the spring constant. In this particular case, the spring constant depends on the charge on the plates, q , so the dependence will be :

$$\nu \sim \frac{q}{m_e}$$

If the electron oscillates with a frequency ν , it produced the electromagnetic wave of the same frequency, which carries some energy. This wave takes the energy from this electron, so the amplitude and energy of its oscillations goes down. It cannot go down gradually, however, because the minimal portion of energy case is $E = h\nu$. That means, the amplitude of electron’s oscillations will decrease discretely, in a limited number of finite size steps (see Fig).

3.1 Bottle Imp and zero oscillations

To understand the importance of this fact, let’s talk about the Bottle Imp story. In this story, the magic bottle can change an owner only when the current owner sells it, and it always must be sold for a lower price that the purchase price was. Theoretically, this process can last forever, because the bottle can always be sold for a fraction of an original price. In practice, the situation is different, because a real price is always measured in some integer number of coins, which means the bottle stops changing an owner in the US (for example) when its price becomes one cent. (It is possible, however, to move to some other country with cheaper currency, but it also is just a temporary solution, because the process will stop anyway, despite the fact that the bottle’s price is still not a zero.)

I believe, the analogy between this bottle and the oscillating electron is obvious: the Fig shows a situation when the electron lost almost all its energy, but it continues to oscillate, because the remaining energy is lower than $h\nu$. The electron simply *cannot* get rid of this energy, because the electromagnetic wave of this frequency can carry the energy that is at least $h\nu$, so these oscillations will last *forever*.

This state resembles a situation when the Bottle costs just one cent: it still has some price, but nobody can buy it, because it is impossible to pay less than one cent.

To take away the remaining energy from the electron, we need to decrease the frequency of oscillations, which depends on two things: electron's mass (which we cannot change) and the electric charge of the plates. If we decrease the charge, we are "loosing the grips": the oscillations become slower, but their amplitude increases. *That is tantamount to "moving to a country where the smallest monetary unit costs less than 1 cent"*. Indeed, now the minimal amount of energy the electron can lose is $h\nu_1$, and, since $\nu_1 < \nu$, this amount is smaller than the energy electron currently has.

However, even in this case there will be some minimal energy the electron cannot get rid of. To take all energy away, we will have to "release the grips": to remove the electric charge from plates. Indeed, that will make the oscillation frequency equal to zero, thereby allowing the electron to lose all its energy. What is important here is the fact that *only the electron, or any other object, whose position is not restricted in space, can lose all energy and come to full stop. However, that would mean, we will never know its exact position in space.* This conclusion is very important, and it has a direct relation to the major question we are trying to answer: to the question about atomic structure.

3.2 Pendulum, Bottle Imp, and Atom

Why are we devoting so much attention to the pendulum? because it is a good model for many physical systems. Taking into account that there is a deep connection between the pendulum oscillations and circular motion, our conclusion about the electron confined between two negatively charged plates is totally applicable to the electron that is being attracted by a positively charged nucleus, i.e. to the electron in an atom. The only difference is that instead of oscillation frequency we use orbital period (the time needed to make one turn).

In other words, when the electron is falling down onto the nucleus, it is losing energy in portions, and finally arrives to the lowest possible orbit. The key feature of this orbit is that the energy of the electron on that orbit is smaller than $h\frac{1}{t}$, where t is a time needed to make one revolution, so the electron simply is incapable of getting rid of this residual energy.

That is an explanation of the reason why the lowest orbit exists in every atom.

Homework

Read the text and propose figures that should be added to it to make it more readable. I will add the best figures to the text.

My e-mail is mark.lukin@gmail.com

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