Course of lectures «Contemporary Physics: Part2»

Lecture Nº10

Atomic Physics. Atomic Spectra of Gases. Early Models of the Atom. Bohr's Model of the Hydrogen Atom. The Quantum Model of the Hydrogen Atom. The Wave Functions for Hydrogen.

All objects emit thermal radiation characterized by a *continuous* distribution of wavelengths. In sharp contrast to this continuous distribution spectrum is the *discrete* line spectrum observed when a low-pressure gas undergoes an electric discharge. Observation and analysis of these spectral lines is called **emission spectroscopy**.



Another form of spectroscopy very useful in analyzing substances is **absorption spectroscopy.** An absorption spectrum is obtained by passing white light from a continuous source through a gas or a dilute solution of the element being analyzed. The absorption spectrum consists of a series of dark lines superimposed on the continuous spectrum of the light source.



The lines shown in color are in the visible range of wavelengths. Ultraviolet λ (nm) 656.3 486.1 364.6 410.2 434.1

This line is the shortest wavelength line and is in the ultraviolet region of the electromagnetic spectrum. In 1885, a Swiss schoolteacher, Jacob Balmer Johann (1825–1898), found an empirical equation that correctly predicted the wavelengths of four visible emission lines of hydrogen: H_a (red), H_{β} (bluegreen), H_{γ} (blue-violet), and H_{δ} (violet). The four visible lines occur at the wavelengths 656.3 nm, 486.1 nm, 434.1 nm, and 410.2 nm. The complete set of lines is called the **Balmer series.**

$$\frac{1}{\lambda} = R_{\rm H} \left(\frac{1}{2^2} - \frac{1}{n^2} \right) \quad n = 3, 4, 5, \dots$$

Other lines in the spectrum of hydrogen were found following Balmer's discovery. These spectra are called the Lyman, Paschen, and Brackett series after their discoverers. The wavelengths of the lines in these series can be calculated through the use of the following empirical equations:

$$\frac{1}{\lambda} = R_{\rm H} \left(1 - \frac{1}{n^2} \right) \quad n = 2, 3, 4, \dots$$
$$\frac{1}{\lambda} = R_{\rm H} \left(\frac{1}{3^2} - \frac{1}{n^2} \right) \quad n = 4, 5, 6, \dots$$
$$\frac{1}{\lambda} = R_{\rm H} \left(\frac{1}{4^2} - \frac{1}{n^2} \right) \quad n = 5, 6, 7, \dots$$

No theoretical basis existed for these equations; they simply worked. The same constant R_H appears in each equation, and all equations involve small integers.

Early Models of the Atom

The electrons are small negative charges at various locations within the atom.

The positive charge of the atom is distributed continuously in a spherical volume.

$$\vec{F}(r) = \frac{e}{4\pi\varepsilon_0 R^3} \vec{r} \qquad (0 \le r \le R),$$

$$\vec{f} = (-e)\vec{F} = -\frac{e^2}{4\pi\varepsilon_0 R^3}\vec{r} = -k\vec{r}$$

$$\omega = \sqrt{\frac{k}{m}} = \sqrt{\frac{e^2}{4\pi\varepsilon_0 mR^3}}$$

$$R = \sqrt[3]{\frac{e^2}{4\pi\varepsilon_0 m\omega^2}}$$

 $R \approx 3 \cdot 10^{-10}$ м

Early Models of the Atom





Early Models of the Atom

Because the accelerating electron radiates energy, the size of the orbit decreases until the electron falls into the nucleus.



Two basic difficulties exist with Rutherford's planetary model. As we previously an atom emits (and absorbs) certain characteristic frequencies of electromagnetic radiation and no others, but the Rutherford model cannot explain this phenomenon. A second difficulty is that Rutherford's electrons are undergoing a centripetal acceleration. According to Maxwell's theory of electromagnetism, centripetally accelerated charges revolving with frequency fshould radiate electromagnetic waves of frequency f. Unfortunately, this classical model leads to a prediction of self-destruction when applied to the atom. As the electron radiates, energy is carried away from the atom, the radius of the electron's orbit steadily decreases, and its frequency of revolution increases. This process would lead to an ever-increasing frequency of emitted radiation and an ultimate collapse of the atom as the electron plunges into the nucleus.

Bohr combined ideas from Planck's original quantum theory, Einstein's concept of the photon, Rutherford's planetary model of the atom, and Newtonian mechanics to arrive at a semiclassical model based on some revolutionary ideas. The postulates of the Bohr theory as it applies to the hydrogen atom are as follows:

1. The electron moves in circular orbits around the proton under the influence of the electric force of attraction as shown in Figure.



2. Only certain electron orbits are stable. When in one of these stationary states, as Bohr called them, the electron does not emit energy in the form of radiation, even though it is accelerating. Hence, the total energy of the atom remains constant and classical mechanics can be used to describe the electron's motion. Bohr's model claims that the centripetally accelerated electron does not continuously emit radiation, losing energy and eventually spiraling into the nucleus, as predicted by classical physics in the form of Rutherford's planetary model.

3. The atom emits radiation when the electron makes a transition from a more energetic initial stationary state to a lower-energy stationary state. This transition cannot be visualized or treated classically. In particular, the frequency f of the photon emitted in the transition is related to the change in the atom's energy and is not equal to the frequency of the electron's orbital motion. The frequency of the emitted radiation is found from the energy-conservation expression

$$E_i - E_f = hf$$

where E_i is the energy of the initial state, E_f is the energy of the final state, $E_i > E_f$

4. The size of an allowed electron orbit is determined by a condition imposed on the electron's orbital angular momentum: the allowed orbits are those for which the electron's orbital angular momentum about the nucleus is quantized and equal to an integral multiple of $\hbar = h/2\pi$

$$m_e vr = n\hbar$$
 $n = 1, 2, 3, ...$

where m_e is the electron mass, v is the electron's speed in its orbit, and r is the orbital radius.

 $m_e v^2$

r

The orbiting electron is allowed to be only in specific orbits of discrete radii. Using these four postulates, let's calculate the allowed energy levels and find quantitative values of the emission wavelengths of the hydrogen atom.

$$U = k_e q_1 q_2 / r = -k_e e^2 / r$$

0

$$E = K + U = \frac{1}{2}m_ev^2 - k_e\frac{e^2}{r}$$

 $\frac{k_e e^2}{m_e r}$

the kinetic energy of the electron is

$$K = \frac{1}{2}m_e v^2 = \frac{k_e e}{2}$$

 $k_e e^2$

The following expression for the total energy of the atom:

$$E = -\frac{k_e e^2}{2r} v^2$$
$$r_n = \frac{n^2 \hbar^2}{m_e k_e e^2} \eta$$

The electron is shown in the lowest-energy orbit, but it could be in any of the allowed orbits.

 $4a_0$

 $9a_0$

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The orbit with the smallest ratio corresponds to n = 1 and has the

$$a_0 = \frac{\hbar^2}{m_e k_e e^2} = r_n = n^2 a_0 = n^2 (0.052)$$

The quantization of orbit radii leads to energy quantization. Substituting $r_n = n^2 a_0$

$$E_n = -\frac{k_e e^2}{2a_0} \left(\frac{1}{n^2}\right) \quad n = 1, 2, 3, \dots$$

Inserting numerical values into this expression, we find that

$$E_n = -\frac{13.606 \text{ eV}}{n^2}$$
 $n = 1, 2, 3, \dots$

We can calculate the frequency of the photon emitted when the electron makes a transition from an outer orbit to an inner orbit:

$$f = \frac{E_i - E_f}{h} = \frac{k_e e^2}{2a_0 h} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

Because the quantity measured experimentally is wavelength, it is convenient to use $c=f\lambda$ to express this Equation in terms of wavelength: $\frac{1}{\lambda} = \frac{f}{c} = \frac{k_e e^2}{2a_0 hc} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$

Remarkably, this expression, which is purely theoretical, is *identical* to the general form of the empirical relationships discovered by Balmer and Rydberg:

$$\frac{1}{\lambda} = R_{\rm H} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

The colored arrows for the Balmer series indicate that this series results in the emission of visible light.



Soon after Bohr demonstrated that these two quantities agree to within approximately 1%, this work was recognized as the crowning achievement of his new quantum theory of the hydrogen atom. Furthermore, Bohr showed that all the spectral series for hydrogen have a natural interpretation in his theory. The different series correspond to transitions to different final states characterized by the quantum number n_{f}

Bohr showed that many mysterious lines observed in the spectra of the Sun and several other stars could not be due to hydrogen but were correctly predicted by his theory if attributed to singly ionized helium. In general, the number of protons in the nucleus of an atom is called the **atomic number** of the element and is given the symbol Z. To describe a single electron orbiting a fixed nucleus of charge +Ze, Bohr's theory gives

$$r_{n} = (n^{2}) \frac{a_{0}}{Z}$$

$$E_{n} = -\frac{k_{e}e^{2}}{2a_{0}} \left(\frac{Z^{2}}{n^{2}}\right) \quad n = 1, 2, 3, \dots$$

Bohr's Correspondence Principle

In our study of relativity, we found that Newtonian mechanics is a special case of relativistic mechanics and is usable only for speeds much less than *c*. Similarly,

quantum physics agrees with classical physics when the difference between quantized levels becomes vanishingly small.

This principle, first set forth by Bohr, is called the **correspondence principle.**

The formal procedure for solving the problem of the hydrogen atom is to substitute the appropriate potential energy function into the Schrödinger equation, find solutions to the equation, and apply boundary conditions. The potential energy function for the hydrogen atom is that due to the electrical interaction between the electron and the proton:

$$U(r) = -k_e \frac{e^2}{r}$$

The mathematics for the hydrogen atom is more complicated than that for the particle in a box because the atom is three-dimensional and U depends on the radial coordinate r. If the time-independent Schrudinger equation is extended to three-dimensional rectangular coordinates, the result is

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right) + U\psi = E\psi$$

 $\psi(r, \theta, \phi) = R(r)f(\theta)g(\phi)$

The first quantum number, associated with the radial function R(r) of the full wave function, is called the **principal quantum number** and is assigned the symbol n.

$$E_n = -\left(\frac{k_e e^2}{2a_0}\right)\frac{1}{n^2} = -\frac{13.606 \text{ eV}}{n^2}$$
 $n = 1, 2, 3, \dots$

The **orbital quantum number**, symbolized *l* comes from the differential equation for f(u) and is associated with the orbital angular momentum of the electron. The **orbital magnetic quantum number** *m*, arises from the differential equation for g(f). Both *l* and *m*, are integers.

The application of boundary conditions on the three parts of the full wave function leads to important relationships among the three quantum numbers as well as certain restrictions on their values:

The values of *n* are integers that can range from 1 to ∞ . The values of ℓ are integers that can range from 0 to n - 1. The values of m_{ℓ} are integers that can range from $-\ell$ to ℓ .

Quantum Number	Name	Allowed Values	Number of Allowed States
n	Principal quantum number	1, 2, 3,	Any number
l	Orbital quantum number	$0, 1, 2, \ldots, n-1$	n
m_ℓ	Orbital magnetic quantum number	$-\ell$, $-\ell$ + 1,, 0,, ℓ - 1, ℓ	$2\ell + 1$

Three Quantum Numbers for the Hydrogen Atom

Atomic Shell Notations

Atomic Subshell Notations

n	Shell Symbol	l	Subshell Symbol
1	K	0	S
2	L	1	p
3	M	2	d
4	N	3	f
5	О	4	g
6	Р	5	h

The Wave Functions for Hydrogen

Because the potential energy of the hydrogen atom depends only on the radial distance r between nucleus and electron, some of the allowed states for this atom can be represented by wave functions that depend only on r. For these states, f(u) and g(f) are constants. The simplest wave function for hydrogen is the one that describes the 1s state and is designated $\psi_{1s}(r)$:

$$\psi_{1s}(r) = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$$

$$|\psi_{1s}|^2 = \left(\frac{1}{\pi a_0^3}\right) e^{-2r/a_0}$$

 $P(r) dr = |\psi|^2 dV = |\psi|^2 4\pi r^2 dr$

The Wave Functions for Hydrogen

Therefore, the radial probability density function is $P(r) = 4\pi r^2 |\psi|^2$

the radial probability density function for the hydrogen atom in its ground state:

$$P_{1s}(r) = \left(\frac{4r^2}{a_0^3}\right)e^{-2r/a_0}$$

The Wave Functions for Hydrogen

The probability has its maximum value when r equals the Bohr radius a_0 .

In this representation, the darkest color, representing the maximum probability, occurs at the Bohr radius.

 $=a_0$

