Models of an atom and old quantum theory

Classical models of atoms

Thompson's model

- Chemical elements differ by the number Z of electrons in their atoms. Atoms are electrically neutral, so that the charge $-Ze$ of all electrons in an atom must be compensated by additional positive charge Ze.

- Thompson modeled an atom as a sphere of radius $\sim 1\text{Å}$ (typical atom radius) filled uniformly by a cloud of positive charge Ze. Inside this cloud there are Z point-like electrons which sit still at their equilibrium positions determined by Coulomb forces. Under various circumstances, for example at by raising temperature, electrons can be excited into vibrating or orbiting motion. Such accelerated motion of charge leads to emission of electromagnetic radiation according to Maxwell equations, which can qualitatively explain why atoms radiate. The model can also describe ejection of electrons from atoms.

- By itself, this kind of an atom is not stable according to the laws of electrodynamics. Some unknown forces must rigidly maintain the spatial distribution of the positive charge. Furthermore, Rutherford's experiment, which experimentally observed discrete atomic radiation spectra, proved this model incorrect.

Rutherford's model

- Rutherford conducted the first scattering experiment to probe the internal structure of atoms. A beam of α particles was collimated by a pair of diaphragms and let to pass through a thin foil of some substance, typically a metal. Since α particles are energetic Helium nuclei produced by radioactive decay of some materials, they have positive charge $2e$ and mass much larger than the electron mass. Therefore, α particles can scatter from the positive charge in atoms due to Coulomb forces, while scattering from electrons can be neglected.

- In principle, α particles can interact electrostatically with many atoms as they pass through the foil and scatter in various directions. The incoming collimated beam becomes divergent upon incidence on the foil. A fluorescent screen can be placed some distance away from the foil to detect deflected α particles at an arbitrary angle θ with respect to the direction of the incident beam. This allows the measurement of the number of α particles which get deflected at any given angle.

- Thompson's model predicted that most α particles would be scattered at small angles θ. Namely, atoms are close-packed in a solid foil, so that the individual atom's clouds of positive charge would more or less touch, leading to a roughly uniform positive charge distribution inside the material. Electric fields produced by such a distribution of charge are too small to deflect a fast and heavy α particle by a large angle, even after interactions with many atoms.

- Rutherford found, however, a significant number of α particles scattering at large angles. There were even particles which scattered by 180° (bounced back). This implied large electric fields inside the solid, created by highly concentrated positive charge attached to non-negligible mass. Furthermore, the number of α particles scattered by large angles was found to be proportional to the thickness of the solid, consistent with rare large angle scattering events which randomly occur at only one atom on the path of an α particle.

- Rutherford's experiment discovered atomic nucleus: a highly concentrated positive charge of appreciable mass. Therefore, Rutherford models an atom as a small massive core (nucleus) carrying positive charge Ze with Z light electrons of charge $-e$ orbiting around it (in analogy of planets orbiting around the Sun).

- Detailed measurements of the numbers of α particles deflected by different angles allows estimating the size of a nucleus. These estimates yielded a radius $D \sim 10^{-14}\text{m}$, whereas the size of an atom is of

the order of 10^{-10}m $= 1$Å (obtained from the density of a typical solid, atomic weight and Avogadro's number). Most of an atom's mass is inside its nucleus, roughly the number of protons and neutrons times the atomic mass unit $u = 1.66 \times 10^{-27}$Kg. Mass of an electron is roughly 9.1×10^{-31}Kg, which is about 1836 times smaller than the mass of a proton. The size of an atom is determined by the size of electron orbitals around the nucleus.

- Rutherford's model is much better than Thompson's, but still not adequate. Classical electrodynamics predicts that a Rutherford's atom cannot be stable. Electrons orbiting around a nucleus must radiate electromagnetic waves because their motion is accelerated. In this manner they must loose energy and eventually slow down and fall on the nucleus (in about 10^{-12}s). A stable atom would be rather similar to the Thompson's atom, but of much smaller size ($\sim 10^{-14}$m) than observed. The resolution of these difficulties in classical physics comes about in the similar manner as in the earlier examples of quantization.

Old quantum theories of atoms

Atomic spectra

- Spectrum is analyzed by passing light through a narrow slit and then through a prism or grating. Components of light at different wavelengths refract at different angles in the prism and can be spatially resolved on a screen placed some distance away from the prism. White light produces a continuous rainbow pattern of colors at the screen.

- Atoms in a gas can be excited out of equilibrium by electric discharge through the gas. Internal motion of electrons is accelerated, so atoms emit radiation as they fall back to equilibrium. The spectrum of this radiation can be analyzed using a prism. One finds that the radiation emitted by atoms contains only certain discrete wavelengths, showing up as narrow separated lines on the screen. Every type of atom has its own pattern of wavelengths, or lines.

- Absorption spectrum is similar. When white light is passed through a transparent substance, the spectrum analysis shows that radiation at a discrete set of frequencies is absorbed. However, the absorption spectrum is a subset of the emission spectrum.

- The first measured atomic spectra are those of Hydrogen. The wavelengths λ of Hydrogen emission lines were experimentally found to be

$$\frac{1}{\lambda} = R_H \left(\frac{1}{m^2} - \frac{1}{n^2} \right)$$

where $R_H = 10967757.6 \pm 1.2$m^{-1} is Rydberg constant (determined by data fitting), and m and n are integers. All choices of m and n satisfying $n > m \geq 1$ give possible wavelengths of the Hydrogen emission spectrum. Historically, m labels named series of lines:

$$
\begin{aligned}
m &= 1 \quad \dots \quad \text{Lyman (ultraviolet)} \\
m &= 2 \quad \dots \quad \text{Balmer (near ultraviolet and visible)} \\
m &= 3 \quad \dots \quad \text{Pachen (infrared)} \\
m &= 4 \quad \dots \quad \text{Brackett (infrared)} \\
m &= 5 \quad \dots \quad \text{Pfund (infrared)}
\end{aligned}
$$

Each series consists of many lines corresponding to different n. As $n \to \infty$, the limiting wavelength converges to a finite value $\lambda \to R_H^{-1} m^2$ below which the spectrum becomes continuous. The absorption spectrum normally consists of only the Lyman series, but at very high temperatures (such as on a star surface) the lines from Balmer series can be observed.

- For Alkali atoms (Li, Na, K...) the emission spectrum was empirically found to be:

$$\frac{1}{\lambda} = R \left(\frac{1}{(m-a)^2} - \frac{1}{(n-b)^2} \right)$$

where R is the Rydberg constant for a particular element, n and m are integers, while a and b are constants which depend on the series m. $R \approx (1 \pm 0.0005)R_H$ was found to systematically and slightly increase with atomic weight.

- Other atoms, and molecules, have in general very complicated spectra. However, spectral lines are extremely robust and can be used to determine which atom or molecule they belong to. This allows precise measurements of the composition of gases, even if they are very far from us such as stars and interstellar gas clouds. Furthermore, we can determine the relative velocity of emitting gasses with respect to us by finding out how the spectrum is shifted due to Doppler effect.

Bohr's postulates and model of atoms

- Bohr supplemented the Rutherford's model of atoms with a few postulates which aimed to explain the observed discrete spectra. These postulates were motivated by the successful explanations of blackbody radiation spectra and photoelectric effect in terms of energy quantization, which clearly finds its incarnation in atomic spectra.

- 1$^{\text{st}}$ postulate: Electrons move in circular orbitals around the nucleus as determined by classical electrodynamics, that is Coulomb forces.
  2$^{\text{nd}}$ postulate: The electron's angular momentum must be an integer multiple of $\hbar = h/2\pi$ in a stable orbital.
  3$^{\text{rd}}$ postulate: An electron moving in a stable orbital does not radiate and lose energy.
  4$^{\text{th}}$ postulate: Radiation is emitted (or absorbed) if an electron switches from one to another stable orbital.

- These postulates define Bohr's model of an atom, which turns out to be applicable for Hydrogen atoms ($Z = 1$) and ions containing only one electron such as singly ionized Helium ($Z = 2$), doubly ionized Lithium ($Z = 3$), etc.

- The postulated quantization of angular momentum leads to electron energy quantization. Consider an electron (of mass m and charge $-e$) orbiting a nucleus of charge Ze and mass $M \gg m$. If the electron velocity is v and the orbit radius is r, the Coulomb force gives rise to centripetal acceleration of the orbiting electron:

$$\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r^2} = \frac{mv^2}{r}$$

The electron's angular momentum L is quantized according to the 2$^{\text{nd}}$ postulate:

$$L = mvr = n\hbar$$

If we substitute v from the quantization condition into the first equation, we obtain:

$$\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r^2} = \frac{m}{r}\left(\frac{n\hbar}{mr}\right)^2$$

It follows that:

$$r = \frac{4\pi\epsilon_0\hbar^2}{mZe^2}n^2$$

$$v = \frac{n\hbar}{mr} = \frac{Ze^2}{4\pi\epsilon_0\hbar}\frac{1}{n}$$

The orbiting electron has kinetic energy E_{kin} and potential energy E_{pot}:

$$E_{kin} = \frac{mv^2}{2} = \frac{m}{2}\left(\frac{Ze^2}{4\pi\epsilon_0\hbar}\right)^2\frac{1}{n^2}$$

$$E_{pot} = -\frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r} = -\frac{Ze^2}{4\pi\epsilon_0}\frac{mZe^2}{4\pi\epsilon_0\hbar^2}\frac{1}{n^2} = -m\left(\frac{Ze^2}{4\pi\epsilon_0\hbar}\right)^2\frac{1}{n^2}$$

The potential energy is negative because the force between the nucleus and the electron is attractive. We see that $E_{pot} = -2E_{kin}$. The total electron energy is:

$$E_n = E_{kin} + E_{pot} = -\frac{m}{2} \left(\frac{Ze^2}{4\pi\epsilon_0\hbar} \right)^2 \frac{1}{n^2}$$

Energy is quantized and specified by an integer quantum number n.

- The 4$^{\text{th}}$ postulate determines the atomic radiation spectra. If an atom is de-excited from a state with energy E_i to a state with lower energy E_f it emits radiation which must carry energy $E_i - E_f$:

$$h\nu = \frac{hc}{\lambda} = E_i - E_f = \frac{m}{2} \left(\frac{Ze^2}{4\pi\epsilon_0\hbar} \right)^2 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

where n_i and n_f are the quantum numbers for the initial and final atom state respectively. We see that this reproduces the empirically observed discrete spectra of Hydrogen if one identifies the Rydberg constant with:

$$R(Z) = \frac{m}{2hc} \left(\frac{Ze^2}{4\pi\epsilon_0\hbar} \right)^2$$

For Hydrogen, $R_H = R(Z = 1)$.

- The above discussion assumes that the nucleus is heavy enough to remain immobile as an electron orbits around it. In reality, both the nucleus and the electron orbit about their center of mass. The equation of motion can be written in the center-of-mass frame and then it describes a particle with reduced mass μ orbiting around the fixed center of mass at the origin. Bohr's angular momentum quantization should be formulated in the center-of-mass frame for the total angular momentum of the nucleus and the electron. This corrects the Rydberg constant by replacing m with $\mu = mM/(m + M)$, where M is the nucleus mass.

- The state with quantum number $n = 1$ has the lowest possible energy according to Bohr's model. This is the so called *ground-state*. An atom can live in its ground-state indefinitely long because it cannot emit any more photons of radiation. All other states are called *excited*. An excited atom can emit photons and fall eventually back to its ground-state. Several photons with appropriate discrete frequencies can be emitted in the process. The de-excitation process appears to be random, and a statistical collection of photons emitted at the allowed discrete wavelengths is what yields a pattern of spectral lines in the prism experiment. Absorption is a reversed process: an incoming photon can excite an atom if it has a correct discrete wavelength to satisfy energy conservation. Since most atoms are in their ground-state in normal conditions, only the Lyman series of absorption lines is observed ($n_i = 1$).

Sommerfeld's postulates and model of atoms

- All atomic spectra have additional fine structure: each spectral line discussed above is split into several closely spaced lines. Sommerfeld attempted to explain the fine structure of Hydrogen by extending Bohr's model to allow elliptical orbitals of electrons.

- The basis for Sommerfeld's model is the Wilson-Sommerfeld quantization rule. The state of any system which carries oscillatory motion can be described by a set of appropriate canonical coordinates q_i which are periodic functions of time. There is a canonical momentum p_i associated with each canonical coordinate q_i. Canonical coordinates and momenta are a convenient way to generalize the formalism of expressing equations of motion in classical mechanics. For example, regular position and momentum are good canonical variables describing a free particle, while angle and angular momentum are good canonical coordinates describing a system constrained to only rotational motion. The Wilson-Sommerfeld quantization condition is:

$$(\forall i) \quad \oint p_i dq_i = n_i h$$

where n_i are integers and the integral is evaluated over one period of the oscillatory motion..

- This rule is a generalization of all quantization conditions encountered so far. This can be illustrated for any linear harmonic oscillator with inertia (mass) m, coordinate q and momentum p whose equation of motion at given energy E is:

$$\frac{p^2}{2m} + \frac{m\omega^2 q^2}{2} = E$$

This is nothing but the conservation of energy for an oscillating system. For a mechanical oscillator, that is a particle of mass m on a spring of stiffness k, one derives this equation from Newton's laws and finds $\omega = \sqrt{k/m}$. However, many other systems, including electromagnetic radiation, can be formally described by the same equation if one appropriately interprets the canonical variables p and q, and the inertia m. Since the canonical momentum is related to the coordinate by:

$$p = m\frac{dq}{dt}$$

we find the following solution:

$$q = q_0 \sin(\omega t)$$
$$p = p_0 \cos(\omega t)$$
$$p_0 = m\omega q_0$$

Which after substitution in the equation of motion yields:

$$p_0 = m\omega q_0 = \sqrt{2mE}$$

(we used $\sin^2 \alpha + \cos^2 \alpha = 1$ in the last line). The motion is oscillatory with frequency $\nu = \omega/2\pi$, and the period is $T = \nu^{-1} = 2\pi\omega^{-1}$. Substituting this in the Wilson-Sommerfeld's quantization condition we get:

$$\oint p dq = \int_{t=0}^{T} p(t)\frac{dq(t)}{dt}dt = p_0 q_0 \omega \int_{t=0}^{T} \cos^2(\omega t)dt = 2\pi \times \frac{p_0 q_0}{2} = 2\pi \times \frac{2mE}{2m\omega} = \frac{E}{\nu} = nh$$

This is nothing but the Planck's quantization rule.

- In the case of atoms, elliptical electron orbitals require two pairs of canonical variables. One choice of electron's canonical coordinates is the distance r from the nucleus, and the azimuthal angle θ in the orbit plane. The corresponding canonical momenta are $p_r = m \times dr/dt$ and the angular momentum L respectively. The Bohr's quantization condition follows from the Wilson-Sommerfeld's rule applied to the second set of variables:

$$\oint L d\theta = L \int_0^{2\pi} d\theta = 2\pi L = n_\theta h \qquad \Longrightarrow \qquad L = n_\theta \hbar$$

- Since electrons are allowed to move in elliptical trajectories and the orbit radius is not constant, the quantization of L does not by itself imply the quantization of energy like in Bohr's model. There are many different allowed elliptical orbitals, having different energies for the same value of L. The other quantization condition on r and p_r is necessary to generate energy quantization. Skipping the tedious derivation, we just note the result:

$$E = -\frac{\mu}{2}\left(\frac{Ze^2}{4\pi\epsilon_0\hbar}\right)^2 \frac{1}{(n_r + n_\theta)^2}$$

which is the same as in the Bohr's model (the Bohr's quantum number is $n_r + n_\theta$).

- Note that there are different orbitals which have the same energy (varying n_θ for fixed $n = n_\theta + n_r$). These states are said to be *degenerate*. The degeneracy stemming from Coulomb forces is special and characteristic to only forces which fall off as the inverse square of distance.

- Relativistic effects due to fast electron motion in atoms are small, but sufficient to lift the above degeneracy. This produces the fine structure of atomic spectra which Sommerfeld was seeking to explain ($n = n_\theta + n_r$):

$$E = -\frac{\mu}{2} \left(\frac{Ze^2}{4\pi\epsilon_0 \hbar} \right)^2 \frac{1}{n^2} \left[1 + \frac{\alpha^2 Z^2}{n} \left(\frac{1}{n_\theta} - \frac{3}{4n} \right) \right]$$

Here,

$$\alpha = \frac{1}{4\pi\epsilon_0} \frac{e^2}{\hbar c} \approx \frac{1}{137}$$

is the so called fine structure constant which characterizes the strength of electromagnetic interactions.

Wave mechanics of electrons in atoms

- While successful for Hydrogen, Bohr's and Sommerfeld's models appear to artificially introduce the angular momentum quantization condition simply to achieve agreement with experiments. However, some of these quantization conditions are quite natural in the de Broglie's matter wave mechanics.

- Consider an electron moving on a circular orbit around the nucleus. If the orbit radius is r and electron's velocity v, the angular momentum is $L = mvr$. The orbit perimeter $2\pi r$ contains $n = 2\pi r/\lambda$ full wavelengths λ of the electron's de Broglie wave. Here, $\lambda = h/p$ by the de Broglie's postulate, where $p = mv$ is electron's momentum. We see that $n = 2\pi r \times mv/h = L/\hbar$. Therefore, Bohr's quantization rule is equivalent to the requirement that an electron's orbit perimeter contain an integer number of de Broglie's wavelengths.

- This has physical significance. If an electron is to be described as wave, its wavefunction $\psi(x) = \exp(2\pi i x/\lambda)$ along any trajectory must be single-valued everywhere in space. The phase of a wave is periodic in space, and the spatial period is the wavelength λ. Consider the wavefunction along the perimeter of a circular orbit with radius r. Start at some point $x = 0$ and go a full circle $x = l = 2\pi r$ along the orbit. The ending point is the same as the starting one, so the wavefunction must be single-valued:
$$\psi(l) = \psi(0) \qquad \Longrightarrow \qquad \exp(2\pi i l/\lambda) = 1$$
This can be satisfied only if the perimeter l is an integer multiple of the wavelength λ.

- Sommerfeld's rules are a good generalization if every aspect of particle motion always has wave-like properties. The good agreement with experimental observations implies the validity of this hypothesis. However, the quantization schemes so far are unable to relate to the de Broglie's picture in all circumstances. For example, we can't tell yet where the rule for radial coordinates and momenta comes from. The full answer to these questions was given by Schrodinger.