12.2: Bohr Model of the Hydrogen Atom

With the use of spectroscopy in the late 19th century, it was found that the radiation from hydrogen, as well as other atoms, was emitted at specific quantized frequencies. It was the effort to explain this radiation that led to the first successful quantum theory of atomic structure, developed by Niels Bohr in 1913. He developed his theory of the hydrogenic (one-electron) atom from four postulates:

1. *An electron in an atom moves in a circular orbit about the nucleus under the influence of the Coulomb attraction between the electron and the nucleus, obeying the laws of classical mechanics.*
2. *Instead of the infinity of orbits which would be possible in classical mechanics, it is only possible for an electron to move in an orbit for which its orbital angular momentum L is and integral multiple of $\hbar$.*
3. *Despite the fact that it is constantly accelerating, an electron moving in such an allowed orbit does not radiate electromagnetic energy. Thus, its total energy \(E\) remains constant.*
4. *Electromagnetic radiation is emitted if an electron, initially moving in an orbit of total energy E_i, discontinuously changes its motion so that it moves in an orbit of total energy \(E_f\). The frequency of the emitted radiation ν is equal to the quantity \(E_i-E_f\) divided by \(h\).* [1]

The third postulate can be written mathematically

$$L = n\hbar$$
$$n = 1, 2, 3, \ldots$$

For an electron moving in a stable circular orbit around a nucleus, Newton's second law reads

$$\frac{Ze^2}{r^2} = m\frac{v^2}{r} \tag{12.2.1}$$

where v is the electron speed, and r the radius of the orbit. Since the force is central, angular momentum should be conserved and is given by $L = |\mathbf{r} \times \mathbf{p}| = mvr$. Hence from the quantization condition of of the third postulate

$$mvr = n\hbar. \tag{12.2.2}$$

Equations $12.2.1$ and $12.2.2$ therefore give two equations in the two unknowns r and v. These are easily solved to yield

$$r = \frac{n^2\hbar^2}{mZe^2} = \frac{n^2}{Z}a_0$$
$$v = \frac{Ze^2}{n\hbar} = \frac{Z}{n}\alpha c$$

where

$$\alpha \equiv \frac{e^2}{\hbar c} \approx \frac{1}{137} \tag{12.2.3}$$

is a dimensionless number known as the fine-structure constant for reasons to be discussed later. Hence αc is the speed of the electron in the Bohr model for the hydrogen atom $(Z = 1)$ in the ground state $(n = 1)$. Since this is the maximum speed for the electron in the hydrogen atom, and hence $v \ll c$ for all n, the use of the classical kinetic energy seems appropriate. From equation 8, one can then write the kinetic energy,

$$K = \frac{1}{2}mv^2 = \frac{Ze^2}{2r}, \tag{12.2.4}$$

and hence the total energy, [2]

$$E = K + V = \frac{Ze^2}{2r} - \frac{Ze^2}{r} = -\frac{Ze^2}{2r}. \tag{12.2.5}$$

Having solved for r as equation 10, one can then write

$$E = -\frac{mZ^2e^4}{2\hbar^2}\frac{1}{n^2} = -\frac{mc^2}{2}(Z\alpha)^2\frac{1}{n^2}. \tag{12.2.6}$$

Numerically, the energy levels for a hydrogenic atom are

$$E=-13.6\mathrm{eV}\frac{Z^2}{n^2} \tag{12.2.7}$$

One correction to this analysis is easy to implement, that of the finite mass of the nucleus. The implicit assumption previously was that the electron moved around the nucleus, which remained stationary due to being infinitely more massive than the electron. In reality, however, the nucleus has some finite mass M, and hence the electron and nucleus both move, orbiting about the center of mass of the system. It is a relatively simple exercise in classical mechanics to show one can transform into the rest frame of the nucleus, in which frame the physics remains the same except for the fact that the electron acts as though it has a mass

$$\mu=\frac{mM}{m+M}, \tag{12.2.8}$$

which is less than m and is therefore called the reduced mass. One can therefore use μ in all equations where m appears in this analysis and get more accurate results. With this correction to the hydrogen energy levels, along with the fourth Bohr postulate which gives the radiative frequencies in terms of the energy levels, the Bohr model correctly predicts the observed spectrum of hydrogen to within three parts in 10^5.

Along with this excellent agreement with observation, the Bohr theory has an appealing aesthetic feature. One can write the angular momentum quantization condition as

$$L=pr=n\frac{h}{2\pi}, \tag{12.2.9}$$

where p is the linear momentum of the electron. Louis de Broglie's theory of matter waves predicts the relationship $p=h/\lambda$ between momentum and wavelength, so

$$2\pi r=n\lambda. \tag{12.2.10}$$

That is, the circumference of the circular Bohr orbit is an integral number of de Broglie wavelengths. This provided the Bohr theory with a solid physical connection to previously developed quantum mechanics.

Unfortunately, in the long run the Bohr theory, which is part of what is generally referred to as the old quantum theory, is unsatisfying. Looking at the postulates upon which the theory is based, the first postulate seems reasonable on its own, acknowledging the existence of the atomic nucleus, established by the scattering experiments of Ernest Rutherford in 1911, and assuming classical mechanics. However, the other three postulates introduce quantum-mechanical effects, making the theory an uncomfortable union of classical and quantum-mechanical ideas. The second and third postulates seem particularly ad hoc. The electron travels in a classical orbit, and yet

its angular momentum is quantized, contrary to classical mechanics. The electron obeys Coulomb's law of classical electromagnetic theory, and yet it is assumed to not radiate, as it would classically. These postulates may result in good predictions for the hydrogen atom, but they lack a solid fundamental basis.

The Bohr theory is also fatally incomplete. For example, the WilsonSommerfeld quantization rule, of which the second Bohr postulate is a special case, can only be applied to periodic systems. The old theory has no way of approaching non-periodic quantum-mechanical phenomena, like scattering. Next, although the Bohr theory does a good job of predicting energy levels, it predicts nothing about transition rates between levels. Finally, the theory is really only successful for one-electron atoms, and fails even for helium. To correct these faults, one needs to apply a more completely quantum-mechanical treatment of atomic structure, and such an approach is used in Schrödinger theory.

Footnote

[1] The reader may notice that $E=-K$, as a natural consequence of the virial theorem of classical mechanics.

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