VOLUME-18   Part B and C

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VIII. Atomic and Molecular Physics

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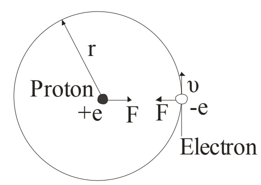
VIII.1. Quantum states of an electron in an atom

1.1. ELECTRON ORBITS

The Rutherford model of the atom, so convincingly confirmed by experiment, pictures a tiny, massive, positively charged nucleus surrounded at a relatively great distance by enough electrons to render the atom electrically neutral as a whole. The electrons cannot be stationary in this model, because there is nothing that can keep them in place against the electric force pulling them to the nucleus. If the electrons are in motion, however, dynamically stable orbits like those of the planets around the sun are possible.



Let us look at the classical dynamics of the hydrogen atom, whose single electron makes it the simplest of all atoms. We assume a circular electron orbit for convenience, though it might as reasonably be assumed to be elliptical in shape. The centripetal force.

$$F_c = \frac{m\upsilon^2}{r}$$

Holding the electron in an orbit r from the nucleus is provided by the electric force

$$F_e = \frac{1}{4\pi\epsilon_0}\frac{e^2}{r^2}$$

between them. The condition for a dynamically stable orbit is

$$F_c = F_e$$

$$\frac{m\upsilon^2}{r} = \frac{1}{4\pi\epsilon_0}\frac{e^2}{r^2} \quad \ldots 1$$

The electron velocity υ is therefore related to its orbit radius r by the formula

Electron velocity $\upsilon = \frac{e}{\sqrt{4\pi\epsilon_0 mr}}$ …2

The total energy E of the electron in a hydrogen atom is the sum of its kinetic and potential energies, which are

$$KE = \frac{1}{2}mv^2 \quad PE = -\frac{e^2}{4\pi\epsilon_0 r}$$

(The minus sign follows from the choice of $PE = 0$ at $r = \infty$, that is, when the electron and proton are infinitely far apart.) Hence

$$E = KE + PE = \frac{mv^2}{2} - \frac{e^2}{4\pi\epsilon_0 r}$$

Substituting for v from Equation (4.4) gives

$$E = \frac{e^2}{8\pi\epsilon_0 r} - \frac{e^2}{4\pi\epsilon_0 r}$$

Total energy of hydrogen atom

$$E = \frac{-e^2}{8\pi\epsilon_0 r} \qquad \ldots 3$$

The total energy of the electron is negative. This holds for every atomic electron and reflects the fact that it is bound to the nucleus. If E were greater than zero, an electron would not follow a closed orbit around the nucleus. The energy E is not a property of the electron alone but is a property of the system of electron + nucleus.

Example 4.1

Experiments indicate that 13.6 eV is required to separate a hydrogen atom into a proton and an electron; that is, its total energy is E = –13.6 eV. Find the orbital radius and velocity of the electron in hydrogen atom.

Solution

Since 13.6 eV = 2.2 $\times 10^{-18}$ J, from Equation (4.5)

$$r = -E = \frac{e^2}{8\pi\epsilon_0 E} = -\frac{(1.6\times10^{-19}C)^2}{(8\pi)(8.85\times10^{-12}F/m)(-2.2\times10^{-18}J)}$$

$$= 5.3 \times 10^{-11} m$$

An atomic radius of this magnitude agrees with estimates made in other ways. The electron's velocity can be found from Equation (4.4):

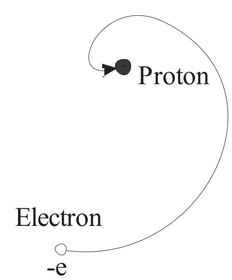
$$\upsilon = \frac{e}{\sqrt{4\pi\varepsilon_0 mr}} = \frac{1.6\times10^{-19}C}{(4\pi)(8.85\times10^{-12}F/m)(9.1\times10^{-31}kg)(5.3\times10^{-11}m)}$$

$$= 2.2\times10^{6}\,m/s$$

Since $\upsilon \ll c$, we can ignore special relativity when considering the hydrogen atom.

The failure of classical physics

The analysis above is a straightforward application of Newton's laws ofmotion and coulomb's law of electric force—both pillars of classical physics—and is in accord with the experimental observation that atoms are stable. However, it is no in accord with electromagnetic theory—another pillar of classical physics—which predicts that accelerated electric charges radiate energy in the form of em waves. An electron pursuing a curved path is accelerated and therefore should continuously lose energy, spiraling into the nucleus in a fraction of a second



But atoms do not collapse. This contradiction further illustrates what we saw in the previous two chapters: The laws of physics that are valid in the macroworld do not always hold true in the microworld of the atom.

Is Rutherford's Analysis Valid?

An interesting question comes up at this point. When he derived his scattering formula, Rutherford used the same laws of physics that prove such dismal failures when applied to atomic stability. Might it not be that this formula is not correct nucleus surrounded by distant electrons? This is not a trivial point. It is a curious coincidence that the quantum-mechanical analysis of alpha particle scattering by thin foils yields precisely the same formula that Rutherford found.

To verify that a classical calculation ought to be at least approximately correct, we note that the de Broglie wavelength of an alpha particle whose speed is 2.0×10^{7} m/s is

$$\lambda = \frac{h}{mv} = \frac{6.63\times10^{-34}\,J.s}{(6.6\times10^{-27}\,kg)(2.0\times10^{7}\,m/s)}$$

$$=5.0 \times 10^{-15} m$$

As we saw, the closest an alpha particle with this wavelength ever gets to a gold nucleus is 3.0 $\times 10^{-14}$m, which is six de Broglie wavelengths. It is therefore just reasonable to regard the alpha particle as a classical particle in the interaction. We are correct in thinking of the tom in terms of Rutherford's model, though the dynamics of the atomic electrons—which is another matter—requires a non-classical approach.

Classical physics fails to provide a meaningful analysis of atomic structure because it approaches nature in terms of "pure" particles and "pure" waves. In reality particles and waves have many properties in common, though the smallness of Planck's constant makes the wave-particle duality imperceptible in the macroworld. The usefulness of classical physics decreases as the scale of the phenomena under study deceases, and we must allow for the particle behavior of waves and the wave behavior of particles to understand the atom. In the rest of this chapter we shall see how the Bohr atomic model, which combines classical and modern notions, accomplished part of the latter task. Not until we consider the atom from the point of view of quantum mechanics, which makes no compromise with the intuitive notions we pick up in our daily lives, will we find a really successful theory of the atom.

1.2. ATOMIC SPECTRA

Spectral series

A century ago the wavelengths in the spectrum of an element were found to fall into sets called spectral series. The first such series was discovered by J.J. Blamer in 1885 in the course of a study of the visible part of the hydrogen spectrum. In the Blamer series the line with the longest wavelength, 656.3 nm, is designatedH_α, the next, whose wavelength is 486.3 nm, is designatedH_β, and so on. As the wave-length decreases, the lines are found closer together and weaker in intensity until the series limit at 364.6 nm is reached, beyond which there are no further separate lines but only a faint continuous spectrum. Blamer's formula for the wavelengths of this series is

Blamer $$\frac{1}{\lambda} = R\left(\frac{1}{2^2} - \frac{1}{n^2}\right) \quad n = 3,4,5,\ldots \qquad \ldots1$$

The quantity R, known as the Rydberg constant, has the value

Rydberg constant $R = 1.097 \times 10^{7} m^{-1} = 0.01097 nm^{-1}$

The H_α line corresponds to $n = 3$, the H_β line to $n = 4$, and so on. The series limit corresponds to $n = \infty$, so that it occurs at a wavelength of 4/R, in agreement with experiment.

The Blamer series contains wavelengths in the visible portion of the hydrogen spectrum. The spectral lines of hydrogen in the ultraviolet and infrared regions fall into several other series. In the ultraviolet the Lyman series contains the wavelengths given by the formula

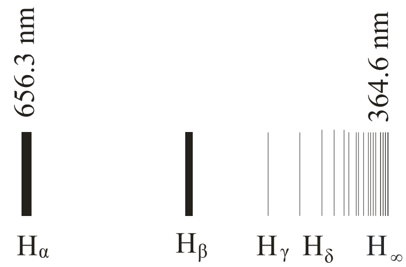


Figure 4.10 The Blamer series of hydrogen.

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