Chapter 3. The Structure of the Atom

Notes:

- *Most of the material in this chapter is taken from Thornton and Rex, Chapter 4.*

3.1 The Atomic Models of Thomson and Rutherford

Determining the structure of the atom was the next logical question to address following the discovery of the electron by J. J. Thomson. It was already established the number of electrons within an atom was essentially half of the atom's mass number (i.e., the ratio of the atom's mass to that of hydrogen). Since the electron was also known and measured to be much less massive than the atom, it was expected that mass of the positively charged component of the atom would be significant (relatively speaking; the atoms were known to be electrically neutral). Understanding the structure of the atom was also desirable when considering that, at that time, chemists had identified more than 70 different kinds of atoms. One would then be hopeful that these different atomic realisations could be explained within the context of a theory resting on simple "rules," which would define the structure of atoms.

Thomson proposed a model where the positive charge within an atom is uniformly distributed within a sphere of appropriate size, with the electrons somehow localized within this volume; this is the so-called "plum-pudding" model. Thomson then theorized that when the atom is heated up the electrons are randomly accelerated and responsible for the emission of radiation. The electrons' lower mass implied that their motion would be more important than the heavier positive charges and therefore more apt to produce

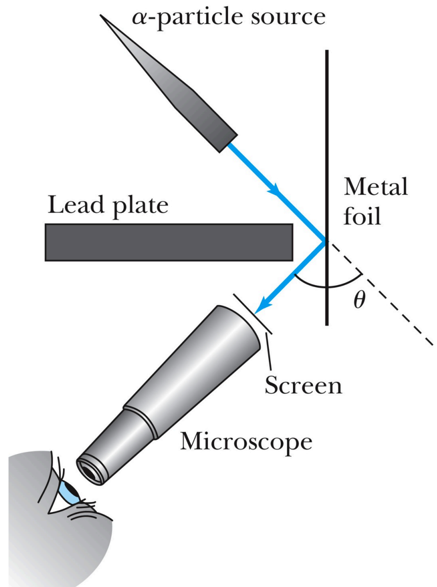

Figure 1 – Schematic of the scattering experience performed in Rutherford's laboratory to investigate the atomic structure.

radiation. Despite the apparent simplicity of his model, Thomson never was able to calculate the spectrum of hydrogen with it. This model eventually had to be abandoned.

This would be made evident from the work of **Ernest Rutherford** (1871-1937) who would use his newly established experimental method of bombarding α particles (i.e., helium nuclei) onto thin target materials. The main evidence came from the fact that his team's experiment on gold-leaf targets revealed the backward scattering (i.e., at more than 90°; see Figure 1) for some incident α particles. Since Thomson's model would imply that the α particles should go through the positive charge of the atom basically unimpeded (that component corresponds to the "pudding" in the model) the scattering could only be the result of collisions between the α particles and the electrons populating the atoms. The impossibility that the backward scattering resulted from such collisions can be verified as follows.

We calculate the maximum scattering angle stemming from the elastic collision between one α particle and an electron, choosing a reference frame where the electron is initially at rest. Of course, we must impose the conservations of energy and linear momentum before and after the collision

$$\begin{aligned}\frac{1}{2}m_\alpha v_\alpha^2 &= \frac{1}{2}m_\alpha v_\alpha'^2 + \frac{1}{2}m_\mathrm{e} v_\mathrm{e}'^2 \\ \underbrace{m_\alpha \mathbf{v}_\sigma}_{\text{initial}} &= \underbrace{m_\alpha \mathbf{v}_\alpha' + m_\mathrm{e}\mathbf{v}_\mathrm{e}'}_{\text{final}}.\end{aligned} \tag{3.1}$$

It can be shown (and you have seen in your first-year physics course) that the solution to this problem, when combining these two equations, is

$$\begin{aligned}\mathbf{v}_\alpha' &= \frac{m_\alpha - m_\mathrm{e}}{m_\alpha + m_\mathrm{e}}\mathbf{v}_\alpha \\ \mathbf{v}_\mathrm{e}' &= \frac{2m_\alpha}{m_\alpha + m_\mathrm{e}}\mathbf{v}_\alpha.\end{aligned} \tag{3.2}$$

For this case we have $m_\alpha / m_\mathrm{e} \simeq 4 \times 1837 \gg 1$ and equations (3.2) simplify to

$$\begin{aligned}\mathbf{v}_\alpha' &\simeq \mathbf{v}_\alpha \\ \mathbf{v}_\mathrm{e}' &\simeq 2\mathbf{v}_\alpha.\end{aligned} \tag{3.3}$$

That is, the α particle basically overruns the electron as if nothing was standing in its way. More precisely, we calculate for the change in momentum for each particle

$$\begin{aligned}\Delta\mathbf{p}_\alpha &= m_\alpha\left(\mathbf{v}'_\alpha - \mathbf{v}_\alpha\right)\\ &= -\frac{2m_\alpha m_\mathrm{e}}{m_\alpha + m_\mathrm{e}}\mathbf{v}_\alpha\\ &\simeq -2m_\mathrm{e}\mathbf{v}_\alpha\\ \Delta\mathbf{p}_\mathrm{e} &= -\Delta\mathbf{p}_\alpha.\end{aligned} \tag{3.4}$$

The absolute maximum scattering angle (as defined in Figure 1) will happen when these changes in momenta are all oriented in a direction normal to the initial velocity of the α particle. We then find that

$$\begin{aligned}\theta &= \tan^{-1}\left(\frac{\Delta p_\alpha}{m_\alpha v_\alpha}\right)\\ &\simeq \tan^{-1}\left(\frac{2m_\mathrm{e}}{m_\alpha}\right)\\ &\simeq 0.016^\circ.\end{aligned} \tag{3.5}$$

We must however consider the fact that one α particle will collide with more than one electron as it scatters against the thin gold-leaf target. But these collisions are all statistically independent, i.e., they will all be randomly oriented on a cone of opening angle 2θ. The angle resulting from one scattering event can therefore be decomposed into two components about perpendicular axes. For example, if we choose the direction of the incident α particle as along the z-axis, i.e., $\mathbf{v}_\alpha = v_\alpha\mathbf{e}_z$, then we have

$$\boldsymbol{\theta} = \theta_x\mathbf{e}_x + \theta_y\mathbf{e}_y. \tag{3.6}$$

The random composition of the different angles implies that the mean angle about a given axis is on average zero, but the standard deviation will be determined as follows, say, for the x-axis,

$$\theta_{x,N}^2 = N\theta_x^{\,2}, \tag{3.7}$$

after N statistically independent collisions (this is an example of a *random walk*). The same rule applies for the y-axis, such that the standard deviation of the total angle is

$$\begin{aligned}\theta_N^2 &= N\left(\theta_x^2 + \theta_y^2\right)\\ &= N\theta^2.\end{aligned} \tag{3.8}$$

For Rutherford's experiment the gold-leaf was $\tau = 6\times10^{-7}\,\mathrm{m}$ thick; we must use this information to approximately calculate N. Using the atomic data for gold we can determine the density of atoms n in the leaf as

$$\begin{aligned} n &= \left(6.02\times10^{23}\,\frac{\text{atoms}}{\text{mol}}\right)\left(\frac{1\text{ mol}}{197\text{g}}\right)\left(\frac{19.3\text{g}}{\text{cm}^3}\right) \\ &= 5.9\times10^{29}\,\text{atoms/m}^3, \end{aligned} \tag{3.9}$$

which implies that one atom occupies on average a volume of $1/\left(5.9\times10^{29}\right)\text{m}^3$. The linear distance between atoms is therefore approximately the cubic root of this value, i.e., $d \simeq 2.6\times10^{-10}\,\text{m}$. It then follows that

$$N \simeq \frac{\tau}{d} = 2{,}300 \text{ atoms}, \tag{3.10}$$

and

$$\begin{aligned} \theta_N &= \sqrt{N}\theta \\ &\simeq \sqrt{2{,}300}\cdot 0.016^\circ \\ &\simeq 0.8^\circ. \end{aligned} \tag{3.11}$$

This value is evidently completely inconsistent with backward scattering. This prompted Rutherford to conclude that his results were not in agreement with Thomson's atomic model. In fact, looking at the first of equations (3.2) we find that a backward scattering will be more likely to happen if we replace the mass of the electron by a larger one. It is straightforward to verify that backward scattering is very likely if the mass of the target is $49m_\alpha$ (i.e., approximately the atomic mass of gold). For example, the final speed of the α particle is $v'_\alpha \simeq -0.85v_\alpha$ for a one-dimensional collision. Rutherford then proposed a new model where the atom is mostly empty space with the charge (positive or negative; his experiment could not determine the position of the electrons) concentrated at the centre: the *nucleus*.

3.1.1 Rutherford Scattering

Rutherford could quantitatively follow up on his proposition on the presence of an atomic central charge by making further scattering experiments using his α particles bombarding technique and making the following assumptions:

1. The targets (initially at rest) are much more massive than the α particles and, therefore, do not recoil; this implies that the magnitude of the initial and final momenta of the incident particles are the same.
2. The α particles scatter off only one target (i.e., the target foil is very thin).
3. The incident and target particles can be treated as point masses.
4. The only force involved in the scattering is the (electrostatic) Coulomb force.

A diagram for a given collision is shown in Figure 2; such process is called *Coulomb* or *Rutherford scattering*. The important parameters are shown in the figure: b is the *impact*

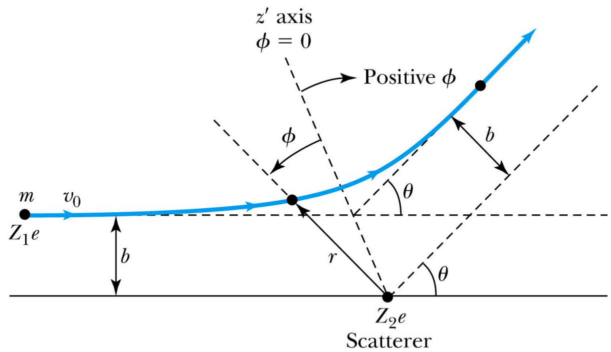

Figure 2 – Rutherford scattering of a α particle off a massive target.

parameter, θ is the *scattering angle*, Z_1e and Z_2e are the charges of the incident and target particles, respectively, and the instantaneous distance r of the incident particle to the target can be parameterised with the angle ϕ, which is set to zero at the collisional symmetry axis (the z'-axis). Because the angular momentum is also conserved (and the target does not move or recoil) the magnitude of the angular momentum of the α particle is the same before and after the scattering at

$$L = mv_0 b, \tag{3.12}$$

with v_0 is the initial speed of the α particle, and it also implies that the scattering event takes place in a plane. Rutherford was able to derive an equation relating the impact parameter b and the scattering angle θ, which we demonstrate here.

The change in momentum of the α particle is given by

$$\Delta\mathbf{p} = \mathbf{p}_f - \mathbf{p}_i \tag{3.13}$$

where the only difference between the initial and final vectors is in their direction, as they both have a magnitude of mv_0. We then write

$$\Delta\mathbf{p} = mv_0\left\{\left[\cos(\theta) - 1\right]\mathbf{e}_x + \sin(\theta)\mathbf{e}_y\right\}, \tag{3.14}$$

with the x and y axes being horizontal and vertical in Figure 2, respectively. It follows that

$$\begin{aligned}\Delta p &= mv_0\sqrt{\left[\cos(\theta) - 1\right]^2 + \sin^2(\theta)}\\ &= mv_0\sqrt{2\left[1 - \cos(\theta)\right]}\\ &= mv_0\sqrt{2\left[2\sin^2(\theta/2)\right]}\\ &= 2mv_0\sin(\theta/2),\end{aligned} \tag{3.15}$$

since more generally

$$\begin{aligned}\sin(a)\sin(b) &= \frac{1}{2}\left[\cos(a-b)-\cos(a+b)\right]\\ \cos(a)\cos(b) &= \frac{1}{2}\left[\cos(a-b)+\cos(a+b)\right]\\ \sin(a)\cos(b) &= \frac{1}{2}\left[\sin(a-b)+\sin(a+b)\right].\end{aligned} \tag{3.16}$$

We can further use equations (3.14)-(3.16) to write

$$\begin{aligned}\Delta\mathbf{p} &= mv_0\left[-2\sin^2(\theta/2)\mathbf{e}_x + 2\sin(\theta/2)\cos(\theta/2)\mathbf{e}_y\right]\\ &= \Delta p\left[-\sin(\theta/2)\mathbf{e}_x + \cos(\theta/2)\mathbf{e}_y\right]\\ &= \Delta p\mathbf{e}_{z'}\end{aligned} \tag{3.17}$$

The last equation follows from the fact that, according to Figure 2, the z'-axis makes an angle of $(\pi-\theta)/2$ relative to the negative (horizontal) x-axis, which then means that

$$\begin{aligned}\mathbf{e}_{z'} &= -\cos\left[(\pi-\theta)/2\right]\mathbf{e}_x + \sin\left[(\pi-\theta)/2\right]\mathbf{e}_y\\ &= -\sin(\theta/2)\mathbf{e}_x + \cos(\theta/2)\mathbf{e}_y.\end{aligned} \tag{3.18}$$

The instantaneous Coulomb force felt by the α particle is

$$\mathbf{F} = \frac{1}{4\pi\varepsilon_0}\frac{Z_1 Z_2 e^2}{r^2}\mathbf{e}_r, \tag{3.19}$$

which is related to $\Delta\mathbf{p}$ in the last of equations (3.17) through

$$\Delta\mathbf{p} = \int F\cos(\phi)\mathbf{e}_{z'}\,dt, \tag{3.20}$$

from the definition of the angle ϕ. We can therefore write

$$\begin{aligned}\Delta p &= 2mv_0\sin(\theta/2)\\ &= \frac{Z_1 Z_2 e^2}{4\pi\varepsilon_0}\int_{-\infty}^{\infty}\frac{\cos(\phi)}{r^2}dt.\end{aligned} \tag{3.21}$$

But the magnitude of the angular momentum of a point mass m equals its moment of inertia mr^2 times its angular speed $d\phi/dt$, and from equation (3.12) we write

$$mr^2 \frac{d\phi}{dt} = mv_0 b, \tag{3.22}$$

which can be inserted in equation (3.21) to yield

$$\begin{aligned} 2mv_0 \sin(\theta/2) &= \frac{Z_1 Z_2 e^2}{4\pi\varepsilon_0} \int_{-\infty}^{\infty} \frac{\cos(\phi)}{v_0 b (dt/d\phi)} dt \\ &= \frac{Z_1 Z_2 e^2}{4\pi\varepsilon_0 v_0 b} \int_{\phi_i}^{\phi_f} \cos(\phi) d\phi. \end{aligned} \tag{3.23}$$

The limits integration are simply related through $\phi_i = -\phi_f$, since the z'-axis is the axis of symmetry, and from our previous discussion (following equation (3.17)) we know that

$$\phi_i = -\frac{\pi - \theta}{2}. \tag{3.24}$$

Equation (3.23) now transforms to

$$\begin{aligned} 2mv_0 \sin(\theta/2) &= \frac{Z_1 Z_2 e^2}{4\pi\varepsilon_0 v_0 b} \sin(\phi)\Big|_{-\phi_f}^{\phi_f} \\ &= \frac{Z_1 Z_2 e^2}{4\pi\varepsilon_0 v_0 b} \left[2\sin\left(\frac{\pi - \theta}{2}\right) \right] \\ &= \frac{Z_1 Z_2 e^2}{4\pi\varepsilon_0 v_0 b} 2\cos\left(\frac{\theta}{2}\right), \end{aligned} \tag{3.25}$$

or

$$\begin{aligned} b &= \frac{Z_1 Z_2 e^2}{4\pi\varepsilon_0 m v_0^2} \cot\left(\frac{\theta}{2}\right) \\ &= \frac{Z_1 Z_2 e^2}{8\pi\varepsilon_0 K} \cot\left(\frac{\theta}{2}\right). \end{aligned} \tag{3.26}$$

with K the kinetic energy of the α particle. But in order to compare with experiments it is desirable to transform this equation to determine the number of α particles $N(\theta)$ scattered at angle θ. To do so we first consider N_s the number of targets of volume density n contained with a foil of thickness t and area A

$$N_s = ntA. \tag{3.27}$$

The probability of scattering f for an incident particle equals this number of targets times their cross-section σ (i.e., their subtended area) divided by the total area. That is,

$$f = \frac{ntA\sigma}{A} = nt\sigma. \tag{3.28}$$

We now associate the cross-section σ to the area πb^2, i.e., $\sigma = \pi b^2$, for scattering through an angle θ or more, since this angle increases with a smaller impact parameter (see Figure 2 and equation (3.26)). The probability of scattering then becomes

$$f = \pi nt\left(\frac{Z_1 Z_2 e^2}{8\pi\varepsilon_0 K}\right)^2 \cot^2\left(\frac{\theta}{2}\right). \tag{3.29}$$

But since a detector located at an angle θ will have a finite resolution (or width) $d\theta$ associated with a set of impact parameters contained within the range $[b, b+db]$ we need to calculate $f(\theta + d\theta) - f(\theta) \simeq \left[f(\theta) + (df/d\theta)d\theta\right] - f(\theta) = df$, which is

$$df = -\pi nt\left(\frac{Z_1 Z_2 e^2}{8\pi\varepsilon_0 K}\right)^2 \cot\left(\frac{\theta}{2}\right)\sin^{-2}\left(\frac{\theta}{2}\right)d\theta. \tag{3.30}$$

The number of scatterings per unit area at θ is then simply the product of incident particles N_i of impact parameters in the range $[b, b+db]$ and $|df|$ divided by the area containing these particles (see Figure 3)

$$\begin{aligned} N(\theta) &= \frac{N_i|df|}{dA} \\ &= \frac{N_i\pi nt\left(\frac{Z_1 Z_2 e^2}{8\pi\varepsilon_0 K}\right)^2 \cot\left(\frac{\theta}{2}\right)\sin^{-2}\left(\frac{\theta}{2}\right)d\theta}{2\pi r^2 \sin(\theta)d\theta} \\ &= \frac{N_i nt}{16}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 \frac{Z_1^2 Z_2^2}{r^2 K^2 \sin^4(\theta/2)}, \end{aligned} \tag{3.31}$$

since, from the last of equations (3.16), $2\sin(\theta) = \sin(\theta/2)\cos(\theta/2)$. This the *Rutherford scattering equation*, which was found to perfectly match the experimental data obtained by his research team. This confirmed his proposition that the atom contained a compact central charge.

Exercises

1. (Ch. 4, Prob. 5 in Thornton and Rex.) Calculate the impact parameter for scattering a 7.7-MeV α particle from gold at an angle of (a) 1° and (b) 90°.

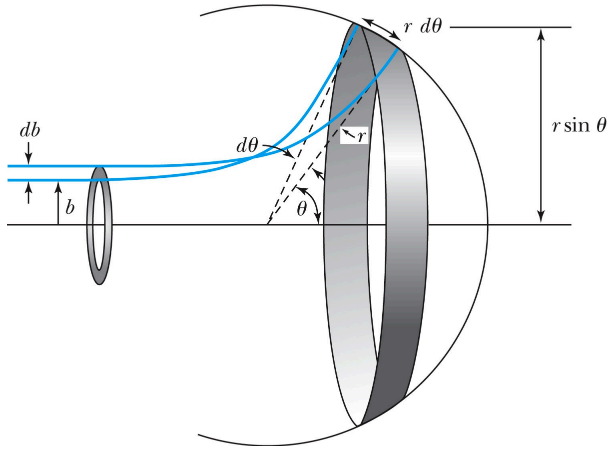

Figure 3 – The area covered by incident particles with impact parameters contained within $b+db$.

Solution.

The α particle and gold nucleus have $Z_1 = 2$ and $Z_2 = 79$, respectively, to be inserted in equation (3.26) for $\theta = 1^\circ$

$$\begin{aligned} b &= \frac{Z_1 Z_2 e^2}{8\pi\varepsilon_0 K}\cot\left(\frac{\theta}{2}\right) \\ &= \frac{(2)(79)\left(1.44\times10^{-9}\ \text{eV}\cdot\text{m}\right)}{2\left(7.7\times10^{6}\ \text{eV}\right)}\cot\left(0.5^\circ\right) = 1.69\times10^{-12}\ \text{m} \end{aligned} \tag{3.32}$$

and for $\theta = 90^\circ$

$$b = \frac{(2)(79)\left(1.44\times10^{-9}\ \text{eV}\cdot\text{m}\right)}{2\left(7.7\times10^{6}\ \text{eV}\right)}\cot\left(45^\circ\right) = 1.48\times10^{-14}\ \text{m}. \tag{3.33}$$

We used $e^2/\left(4\pi\varepsilon_0\right) = 1.44\times10^{-9}\ \text{eV}\cdot\text{m}$ to obtain these equations.

2. (Ch. 4, Prob. 7 in Thornton and Rex.) For aluminum ($Z_2 = 13$) and gold ($Z_2 = 79$) targets, what is the ratio of α particle scattering at any angle for equal numbers of scattering nuclei per unit area?

Solution.

The number of scatterings at an angle θ can be obtain from equation (3.31) with

$$N(\theta)=\frac{N_i nt}{16}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\frac{Z_1^2 Z_2^2}{r^2K^2\sin^4(\theta/2)}, \tag{3.34}$$

where nt represents the number of targets per unit area. Then the ratio of α particle scattering at any angle is

$$\frac{N_{\mathrm{Au}}}{N_{\mathrm{Al}}}=\frac{n_{\mathrm{Au}}t_{\mathrm{Au}}Z_{\mathrm{Au}}^2}{n_{\mathrm{Al}}t_{\mathrm{Al}}Z_{\mathrm{Al}}^2}=\frac{79^2}{13^2}=36.93, \tag{3.35}$$

since it is assumed that the numbers of scattering nuclei per unit area are the same $n_{\mathrm{Au}}t_{\mathrm{Au}}=n_{\mathrm{Al}}t_{\mathrm{Al}}$.

3. (Ch. 4, Prob. 12 in Thornton and Rex.) Consider the scattering of an α particle from the positively charged part of the Thomson plum-pudding model. Let the kinetic energy from the α particle be K (nonrelativistic) and let the atomic radius be R. (a) Assuming that the maximum Coulomb force acts on the α particle for a time $\Delta t = 2R/v$ (where v is the initial speed of the α particle), show that the largest scattering angle we can expect from a single atom is

$$\theta\simeq\frac{e^2}{4\pi\varepsilon_0}\frac{Z_1Z_2}{KR}. \tag{3.36}$$

(b) Evaluate θ for an 8.0-MeV α particle scattering from a gold atom of radius 0.135 nm.

Solution.

(a) The maximum Coulomb force is at the surface can be calculated by putting all the charge at the centre of the sphere and is therefore equal to $Z_1Z_2e^2/4\pi\varepsilon_0R^2$, with $Z_1=2$. Then

$$\begin{aligned}\Delta p &= F\Delta t\\ &=\frac{Z_1Z_2e^2}{4\pi\varepsilon_0R^2}\frac{2R}{v}\\ &=\frac{e^2}{4\pi\varepsilon_0}\frac{2Z_1Z_2}{Rv}.\end{aligned} \tag{3.37}$$

Using the same argument as that leading to equation (3.5) we find the maximum angular deflection, for small angles, with

$$\begin{aligned}\theta \simeq \tan\theta &= \frac{\Delta p}{p} \\ &\simeq \frac{1}{mv}\frac{e^2}{4\pi\varepsilon_0}\frac{2Z_1Z_2}{Rv} \\ &\simeq \frac{e^2}{4\pi\varepsilon_0}\frac{Z_1Z_2}{KR}.\end{aligned} \tag{3.38}$$

(b) For an 8.0-MeV α particle scattering from a gold atom ($Z_2 = 79$) of radius 0.135 nm we find that

$$\theta = \frac{(2)(79)(1.44\ \text{eV}\cdot\text{nm})}{(8\ \text{MeV})(0.135\ \text{nm})} = 2.11\times10^{-4}\ \text{rad} = 0.012^\circ. \tag{3.39}$$

3.2 The Classical Atomic Model

Rutherford's theory of α particle scattering and the corresponding experimental results allowed physicists to establish that the atom was composed of a nucleus harbouring the positive charge of the atom and electrons surrounding it (Rutherford scattering equation (3.31) yields information on Z_2 the charge of the nucleus, while the experimental determination of the scattering angles confirmed that it is massive and concentrated). Although these results clearly excluded Thomson's plum-pudding model, it did not completely rule out a classical model.

Indeed, Thomson had previously considered a "planetary model" with a positively charged nucleus at the centre with orbiting electrons. As we will later see this is very close in structure to early quantum mechanical models, but it could easily be shown to be untenable according to classical physics. If we take for example the hydrogen atom composed of a proton nucleus and a single orbiting electron, then we can calculate the Coulomb force binding the electron to the proton with

$$\mathbf{F} = -\frac{e^2}{4\pi\varepsilon_0 r^2}\mathbf{e}_r, \tag{3.40}$$

where $\mathbf{e}_r$ is the unit vector directed from the proton to the electron. For the atom to be in equilibrium, this force must be counteracted by the centrifugal acceleration (times the electron mass m) due to the orbital motion of the electron

$$-\frac{e^2}{4\pi\varepsilon_0 r^2} + \frac{mv^2}{r} = 0, \tag{3.41}$$

or, for the electron kinetic energy,

$$
\begin{aligned}
K &= \frac{1}{2}mv^2 \\
&= \frac{1}{2}\frac{e^2}{4\pi\varepsilon_0 r} \\
&= -\frac{1}{2}U,
\end{aligned}
\tag{3.42}
$$

with U the potential energy due to the Coulomb interaction. It therefore follows that the total energy of the electron is negative with

$$
\begin{aligned}
E &= K + U \\
&= -\frac{1}{2}\frac{e^2}{4\pi\varepsilon_0 r} < 0.
\end{aligned}
\tag{3.43}
$$

This negative value indicates that the electron is on a *bound orbit* about the nucleus.

But we also know from Maxwell's laws that the electron must radiate electromagnetic energy as it is accelerating on its orbit (to constantly change its direction of motion and stay on a circular orbit). From the conservation of energy its total orbital energy must become more negative, and we see from equation (3.43) that the size of its orbit r decreases accordingly. This is shown schematically in Figure 4. This scenario is evidently flawed as the electron would eventually collapse on the proton and the atom would cease to exist. This was another spectacular failure for classical physics…

Exercises

4. (Ch. 4, Prob. 14 in Thornton and Rex.) The radius of a hydrogen nucleus is believed to be about $1.2\times10^{-15}\,\mathrm{m}$. (a) If an electron rotates around the nucleus at that radius, what would be its speed according to the planetary model? (b) What would be the total

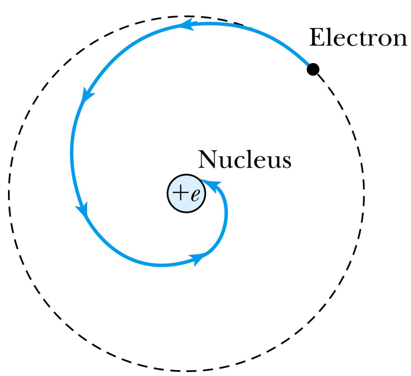

Figure 4 – The orbit of the electron about a proton for a *classical* hydrogen atom.

mechanical energy? (c) Are these reasonable?

Solution.

(a) According to equation (3.42) we have

$$\begin{aligned} v &= \sqrt{\frac{e^2}{m4\pi\varepsilon_0 r}} = \sqrt{\frac{e^2}{4\pi\varepsilon_0}} \cdot \frac{c}{\sqrt{mc^2 r}} \\ &= \frac{c\sqrt{1.44\times10^{-9}\ \text{eV}\cdot\text{m}}}{\sqrt{(511\ \text{keV})(1.2\times10^{-15}\ \text{m})}} \\ &= 1.53c. \end{aligned} \tag{3.44}$$

(b) According to equation (3.43) we write

$$\begin{aligned} E &= -\frac{1}{2}\frac{e^2}{4\pi\varepsilon_0 r} \\ &= -\frac{1.44\times10^{-9}\,\text{eV}\cdot\text{m}}{2\cdot1.2\times10^{-15}\,\text{m}} \\ &= -600\ \text{keV}. \end{aligned} \tag{3.45}$$

(c) Clearly the speed calculated in (a) is impossible as it is greater than the speed of light, and the energy in (b) is far too great compared to the ionization potential of hydrogen (i.e., 13.6 eV).

3.3 The Bohr Model of the Hydrogen Atom

Niels Bohr (1885-1962) was certainly one of the greatest physicists of the twentieth century, and arguably one of the best ever. Like Einstein he was one of the first to recognize the importance of Planck's quantum hypothesis, but he also pushed it further and with more far-reaching consequences than anybody else. He was a bold thinker who could see through the challenges classical physics faced and came up with imaginative solutions based on the nascent quantum theory. When considering the failure of the atomic classical model Bohr proposed four general assumptions or postulates, which he could then use to explain much of the experimental data known at the time:

1. To avoid the in-spiral motions of electrons orbiting a nucleus (see Figure 4), Bohr postulated that *stationary states* existed in atoms where electrons could stay on stable orbits. The electrons would therefore not radiate electromagnetic energy when occupying a stationary state.
2. The emission or absorption of radiation can only occur when an electron makes a transition between two stationary states. If we denote these states by the subscripts '1' and '2', then Bohr asserted that the difference in the energy of the two states is quantized with

$$E = E_1 - E_2 = hf, \tag{3.46}$$

where h is the Planck constant and f the frequency of the radiation emitted or absorbed. This hypothesis is then consistent with Einstein's earlier work on the quantization of radiation (i.e., the notion of the photon) and the photoelectric effect.

3. The classical laws of physics only apply to stationary states, not to the transitions between them.
4. Finally, not only is the energy between stationary states quantized but so is the angular momentum of the electron-nucleus system, with levels that are multiples of $\hbar \equiv h/2\pi$.

We can follow Bohr and calculate the following fundamental relations and quantities for the hydrogen atom. We first consider the angular momentum of the orbiting electron and equate it to the quantized level of the system's stationary state (the nucleus is much more massive than the electron and we will neglect its contribution at present)

$$L = mrv = n\hbar, \tag{3.47}$$

with r the radius of the orbit (assumed circular), v the speed of the electron, and $n = 1, 2, 3, \ldots$ the *principal quantum number*. Using this relation and equation (3.42) we find that

$$\begin{aligned} v^2 &= \frac{e^2}{4\pi\varepsilon_0 mr} \\ &= \frac{n^2\hbar^2}{m^2r^2}, \end{aligned} \tag{3.48}$$

This relation, in turn, allows us the define the *Bohr radius* when $n = 1$

$$\begin{aligned} a_0 &= \frac{4\pi\varepsilon_0\hbar^2}{me^2} \\ &= 0.53\times10^{-10}\,\text{m}, \end{aligned} \tag{3.49}$$

from which we determine the other permitted orbital radii for stationary states

$$r_n = \frac{4\pi\varepsilon_0 n^2\hbar^2}{me^2} = n^2 a_0. \tag{3.50}$$

Bohr was thus able to determine a fundamental a_0 for the hydrogen atom, entirely based on fundamental constants, that was in excellent agreement with the experimental data already existent at the time (in 1913). This size, i.e., the Bohr radius, corresponds to the *ground state* of the hydrogen atom (when $n = 1$), while stationary states for $n > 1$ are called *excited states*. The energy associated with stationary states are given, from equations (3.43) and (3.50),

$$\begin{aligned} E_n &= -\frac{e^2}{8\pi\varepsilon_0 r_n} \\ &= -\frac{e^2}{8\pi\varepsilon_0 a_0 n^2} \equiv -\frac{E_0}{n^2}, \end{aligned} \tag{3.51}$$

with the energy of the ground state

$$\begin{aligned} E_0 &= \frac{e^2}{8\pi\varepsilon_0 a_0} \\ &= \frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 = 13.6\ \text{eV}. \end{aligned} \tag{3.52}$$

We can also use the second of Bohr's four assumptions to calculate the frequency or the wavelength of the radiation emitted as a result of a transition between two stationary states of principal quantum numbers n_u and n_l with

$$\begin{aligned} \frac{1}{\lambda} &= \frac{E_\mathrm{u} - E_\mathrm{l}}{hc} \\ &= -\frac{E_0}{hc}\left(\frac{1}{n_\mathrm{u}^2} - \frac{1}{n_\mathrm{l}^2}\right) \\ &= R_\infty\left(\frac{1}{n_\mathrm{l}^2} - \frac{1}{n_\mathrm{u}^2}\right), \end{aligned} \tag{3.53}$$

with

$$\begin{aligned} R_\infty &= \frac{E_0}{hc} \\ &= \frac{m}{4\pi c\hbar^3}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 = 1.097373\times 10^7\,\mathrm{m}^{-1}. \end{aligned} \tag{3.54}$$

Bohr had thus succeeded in theoretically deriving the Rydberg equation, established experimentally in 1890, and confirming the value of the Rydberg constant R_∞ (see equation (2.11) of Chapter 2 of the lecture notes). The small discrepancy between Bohr's theoretical value and the experimental determination of Rydberg can be explained by taking into account the mass of the proton. Furthermore, Bohr's theory could be used to predict the presence of then unknown spectral lines, which were eventually verified experimentally.

Finally, another fundamental parameter can be established by considering the orbital speed of the electron. Using equations (3.48) and (3.50) we find that

$$\begin{aligned} v_n &= \frac{1}{n}\frac{\hbar}{ma_0} \\ &= \frac{1}{n}\frac{e^2}{4\pi\varepsilon_0\hbar}. \end{aligned} \tag{3.55}$$

Focusing on the speed of the ground state at $n=1$ and dividing it by the speed of light we get a unit-less parameter

$$\begin{aligned} \alpha \equiv \frac{v_1}{c} &= \frac{\hbar}{ma_0c} \\ &= \frac{e^2}{4\pi\varepsilon_0\hbar c} \simeq \frac{1}{137}, \end{aligned} \tag{3.56}$$

which is the so-called *fine structure constant*.

3.3.1 The Correspondence Principle

It was highly difficult for several physicists at the start of the twentieth century to accept the new quantum physics at face value and equally troubling that it should be assigned with any kind of physical reality. On the one hand, classical physics was incredibly successful in describing the macroscopic world as we see and feel it, while on the other it appeared that the new experiments could only be "explained" within the context of the theories of Planck, Einstein, and Bohr.[1] This apparent paradox was lessened by the fact that the classical and quantum realms dealt with scales that were worlds apart. For example, consider the scale of the Bohr radius (i.e., on the order of $10^{-10}\,\text{m}$) to those we experience on a daily basis. Although such could be the hope that both worlds would "coexist independently" in this manner, common sense would also dictate that there must exist a domain where the two realities must merge. After all, nature cannot be both classical and quantum at the same time, in view of their very different characters.

Bohr was acutely aware of this issue and proposed *The Correspondence Principle* as a guideline:

In the limits where classical and quantum theories should agree, the quantum theory must reduce to the classical result.

This is not to be interpreted as a "concession" made by the new generation of physicists

[1] Incidentally, we now know, as physicists of that generation were about to realise, that Bohr's theory of the hydrogen atom was not correct. But it provided the basics elements that would guide the elaboration of the successful, modern theory of quantum mechanics.

to make the quantum theory more palatable… But it should be understood in the context where one transitions from the quantum to the classical domain. Alternatively the Correspondence Principle could be stated such that *the behaviour of quantum systems must reproduce the results of classical physics in the large-quantum-number limit*. This will be made clearer with the following example.

According to equations (3.46) and (3.51) the angular frequency of the radiation resulting from an atomic transition between two adjacent stationary states can be calculated with

$$\begin{aligned}\omega_{\mathrm{q}} &= -\frac{E_0}{\hbar}\left[\frac{1}{(n+1)^2} - \frac{1}{n^2}\right] \\ &= \frac{E_0}{\hbar}\left[\frac{2n+1}{n^2(n+1)^2}\right].\end{aligned} \tag{3.57}$$

To find the large-quantum-number limit, we choose an arbitrarily large value for n such that we can approximate equation (3.57) to

$$\begin{aligned}\omega_{\mathrm{q}} &\simeq \frac{2E_0}{n^3\hbar} \\ &\simeq \frac{m}{n^3\hbar^3}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2.\end{aligned} \tag{3.58}$$

This equation should reproduce the corresponding classical result as for such a large value for the principal quantum number the difference in energy associated with the two stationary states is much smaller than that of the ground state (i.e., $E_{n+1} - E_n \ll E_0$).

Classically, the frequency of the radiation ω_{c} is the same as that of the acceleration of the electron responsible for the emission of electromagnetic waves. We therefore write

$$\omega_{\mathrm{c}} = \frac{v}{r}, \tag{3.59}$$

which is simply the reciprocal of the time taken to complete one orbit (i.e., the period). The classical relation for the orbital speed is obtained with equation (3.42) (or equivalently through the first of (3.48))

$$v = \left(\frac{e^2}{4\pi\varepsilon_0 mr}\right)^{1/2} \tag{3.60}$$

such that

$$\omega_c = \left(\frac{e^2}{4\pi\varepsilon_0 m r^3} \right)^{1/2}. \tag{3.61}$$

As can be verified by examining the different quantities composing it, this equation is entirely classical in nature, i.e., the Planck constant is not part of it.

To establish the correspondence between equations (3.58) and (3.61), we note that the quantity $n\hbar$ present (to the third power) in the quantum mechanical equation is nothing more than the angular momentum of the electron. We therefore first establish the following correspondence

$$n\hbar \to mvr = \left(\frac{mre^2}{4\pi\varepsilon_0} \right)^{1/2}. \tag{3.62}$$

Inserting this result in equation (3.58) we have

$$\begin{aligned} \omega_q &\to m \left(\frac{4\pi\varepsilon_0}{mre^2} \right)^{3/2} \left(\frac{e^2}{4\pi\varepsilon_0} \right)^2 \\ &\to \left(\frac{e^2}{4\pi\varepsilon_0 m r^3} \right)^{1/2} = \omega_c, \end{aligned} \tag{3.63}$$

which is what we sought to establish in agreement with the Correspondence Principle.

3.3.2 The Limitations of the Bohr Model

As we stated before, the Bohr model of the hydrogen atom was not the final answer to the problem of atomic structure but an important, successful, and fruitful first step. His main successes were covered in the previous sections, but there were also some shortcomings that made it clear that further refinements were needed. First, the wavelength for the different spectral lines that could be experimentally verified for the hydrogen atom, it was found that the previous equation (3.53) was not perfect but that small discrepancies existed between theory and experiment. However, these could easily be corrected by taking the finite mass of the proton into account; Bohr's theory effectively approximated the proton's mass as infinite (see the Second Problem List). More importantly, the following limitations of the Bohr model were eventually recognised:

1. Although it could be successfully applied to other one-electron atoms (e.g., He^+, Li^{2+}, etc.), it did not work for more complicated atoms, not even the next simplest atom, helium.
2. It was not able to account for the intensity of spectral lines, or the fact they could split into sets of so-called *fine structure lines* when subjected to external magnetic or electric fields, for example.
3. It could not explain the binding of atoms into molecules.

4. Finally, it was eventually discovered that the atomic ground state has an orbital angular momentum of zero and not $\hbar$, as assumed by Bohr.

These difficulties were eventually conquered, but only when the full quantum theory was established in the decade or two that followed.

Exercises

5. (Ch. 4, Prob. 19 in Thornton and Rex.) The Ritz combination rules express the relationships between the observed frequencies of the optical emission spectra. Prove one of the more important ones:

$$f\left(\mathbf{K}_\alpha\right)+f\left(\mathbf{L}_\alpha\right)=f\left(\mathbf{K}_\beta\right), \tag{3.64}$$

where $\mathbf{K}_\alpha$ and $\mathbf{K}_\beta$ refer to the Lyman series and $\mathbf{L}_\alpha$ to the Balmer series of hydrogen (see Figure 5).

Solution.

According to equation (3.53) the frequency of a transition for a one-electron atom is given by

$$f=\frac{c}{\lambda}=Z^2Rc\left(\frac{1}{n_l^2}-\frac{1}{n_u^2}\right), \tag{3.65}$$

where Z is the charge of the nucleus and R the Rydberg constant associated to the atom.

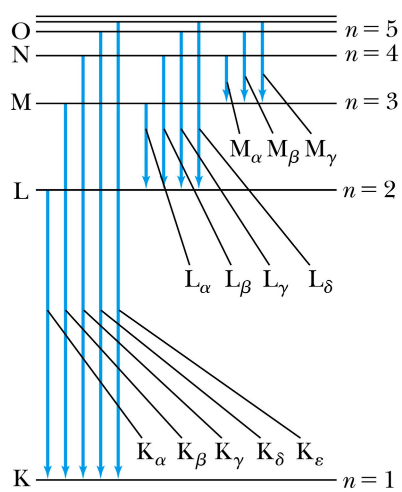

Figure 5 – The different "shells" (i.e., K, L, M, etc.) of the hydrogen atom and their associated transitions.

Referring to the figure we have

$$\begin{aligned} f(\mathbf{K}_\alpha) &= Z^2 Rc\left(1-\frac{1}{4}\right) \\ f(\mathbf{K}_\beta) &= Z^2 Rc\left(1-\frac{1}{9}\right) \\ f(\mathbf{L}_\alpha) &= Z^2 Rc\left(\frac{1}{4}-\frac{1}{9}\right), \end{aligned} \tag{3.66}$$

which yield equation (3.65) since $\left(1-1/4\right)+(1/4-1/9)=1-1/9$.

6. (Ch. 4, Prob. 29 in Thornton and Rex.) A hydrogen atom exists in an excited state for typically $10^{-8}\,\mathrm{s}$. How many revolutions would an electron make in a $n=3$ state before decaying?

Solution.

We know from equation (3.55) that

$$v_n = \frac{\hbar}{nma_0}. \tag{3.67}$$

But the number of revolutions N in a time interval t is given by

$$\begin{aligned} N &= \frac{vt}{2\pi r_n} \\ &= \left(\frac{\hbar}{nma_0}\right)\left(\frac{t}{2\pi n^2 a_0}\right) \\ &= \frac{\hbar t}{2\pi m n^3 a_0^2}, \end{aligned} \tag{3.68}$$

which for $t=10^{-8}\,\mathrm{s}$ yields $N=2.38\times10^{6}$.