

2 The structure of the atom

To understand how 20th century physics revealed the structure of the atom we must first consider how atoms were viewed at the end of the 19th century

- The atom was thought to be an indivisible unit of matter – a view that had changed little since the first expression of the idea by Democritus and Leucippus (c.400BC).
- The organisation of atoms corresponding to different elements into the Periodic Table (Mendeleev 1869) explained much of known inorganic chemistry at the time and predicted the existence of new elements.
- Though individual atoms had never been observed directly, scientists had a pretty accurate estimate of their size $\sim 10^{-10}$ m. Once you know Avogadro's number (the number of atoms per mole $N_A = 6.02 \times 10^{23}$ atoms mole $^{-1}$) it is straightforward. Consider iron, it has a molar mass $M_{mol} = 55.847 \times 10^{-3}$ kg and a density of $\rho = 7.874 \times 10^3$ kgm $^{-3}$. Therefore one mole of iron is contained within a volume of

$$V_{mol} = \frac{M_{mol}}{\rho} = \frac{55.847 \times 10^{-3}}{7.874 \times 10^3} = 7.09 \times 10^{-6} \text{ m}^3. \quad (1)$$

If we assume that each atom in solid iron is almost touching its neighbours then the size of an individual iron atom is obtained from

$$N_A = \frac{V_{mol}}{\frac{4}{3}\pi r_{atom}^3} \Rightarrow r_{atom} = \sqrt[3]{\frac{3}{4\pi} \frac{V_{mol}}{N_A}} = 5 \times 10^{-11} \text{ m}. \quad (2)$$

However, towards the end of the 19th century a growing body of evidence was accumulating that suggested that atoms corresponding to the known chemical elements did not constitute indivisible building blocks of nature.

- The discovery of the electron. As mentioned previously, the electron is about 2,000 times less massive than the Hydrogen atom. However, electrons could be liberated from metal elements via thermionic or field emission. Clearly, if negative electrons can be liberated from neutral atoms, there must remain some undiscovered positive component to the atom.
- Indeed, it was noted during experiments designed to study cathode rays (electrons) that positive “rays” of varying q/m could also be produced and studied. These so-called “canal rays” were ions – neutral atoms from which one or more electrons had been stripped.
- Atomic line spectra (Section 2.5). When basic chemical elements are burned in a flame or ionised via electrical emission they emit radiation in the form of narrow spectral lines – definitely not blackbodies. In the case of Hydrogen the spectral lines are explained by simple geometric series in wavelength – the Balmer series being the first to be observed. What could exist inside the Hydrogen atom to create such an ordered series?

- Radioactivity. Certain radioactive elements emit particles and are transformed into new chemical elements. The emitted particles – named α and β particles by Rutherford – and radiation – X and γ –rays suggest physical processes at work within the atom. The transmutation of elements via radioactive decay suggests that atoms are not immutable objects.

2.1 The $\alpha\beta\gamma$ of radioactivity

In 1896 Henri Becquerel discovered that certain uranium salts would darken photographic plates. He had discovered natural radioactivity or the spontaneous emission of nuclear radiation. Radioactivity does not form a detailed part of this course. However, it is useful to develop a basic understanding of radioactive processes and terminology. The most important concepts are the following:

1. Radioactive emission takes three forms, originally called α , β and γ rays (the classification was originally based upon the ability of each ray to penetrate matter).
 - In 1904 Rutherford demonstrated that α -rays were the doubly charged ion of Helium, approximately four times more massive than a singly charged Hydrogen atom. We now state more precisely that an α particle is a Helium nucleus consisting of two protons and two neutrons (the neutron was only discovered in 1932). An example of α particle decay sees Uranium-230 decay to Thorium-226 (the number refers to the atomic mass of the isotope) upon emission of an α particle, i.e.



Note that α decay reduces the atomic or proton number Z of the element by two units. Emitted α particles from a given element are almost mono-energetic. Overall, α particle kinetic energies are observed 1 – 8 MeV.

- Beta decay sees a radioactive element emit a β particle. The β particle was subsequently demonstrated to be a highly energetic electron (several hundred keV). We now know that β decay results from the decay of a neutron to produce a proton and an electron. Various conservation laws require the production of a third particle – an anti-neutrino (only discovered in 1956) – in order for β decay to proceed, i.e.



An example of β decay sees Carbon-14 decay to Nitrogen-14, i.e.



Note that β decay increases the atomic number of the element by one unit.

- Gamma decay sees an atomic nucleus in an excited state rearrange its internal structure and emit a γ ray – a very energetic photon. For example, consider the β decay of Cobalt-60 to produce an excited nuclear state of Nickel-60



where the asterisk indicates an excited state. The Nickel nucleus de-excites by emitting two γ ray photons of energy 1.17 MeV and 1.33 MeV respectively, i.e.



2. Radioactive decay causes atoms of one element to be transmuted into those of another element. In 1902, Rutherford and Soddy confirmed that the decay of Uranium via α emission produced Thorium. This was the first time that the transmutation of one element to another had ever been observed.
3. Individual decay events can only be predicted via the probability to decay in a given time interval (this probability-based description alone was a problem for classical physics). The decay of large samples of radioactive atoms are described by simple statistical expressions. Given a sample of radioactive material we observe a number of decay events per unit time – a quantity we define as the **activity** of the sample. If we have a sample of N radioactive atoms, we define the activity R as

$$R = -\frac{dN}{dt}. \quad (8)$$

Experiment demonstrates the activity of a radioactive samples falls off exponentially with time. We explain this as follows: given a sample of $N(t)$ atoms at a time t , we define λ as the **decay constant** which describes the probability per unit time that a particular atom undergoes a decay event. The activity of the sample may then be written as

$$R = \lambda N(t). \quad (9)$$

The number dN of atoms decaying during a time interval dt is

$$dN(t) = -Rdt = -\lambda N(t)dt \quad (10)$$

$$\int \frac{dN}{N} = -\int \lambda dt \quad (11)$$

$$\ln N = -\lambda t + \text{constant} \quad (12)$$

$$N(t) = e^{-\lambda t + \text{constant}} \quad (13)$$

$$N(t) = N_0 e^{-\lambda t}, \quad (14)$$

where we define $N(t = 0) = N_0$ in order to determine the value of the integration constant. The activity of a radioactive sample may then be written as

$$R(t) = \lambda N(t) = \lambda N_0 e^{-\lambda t} = R_0 e^{-\lambda t}, \quad (15)$$

which decays according to an exponential drop-off as determined experimentally. The relationship between the decay constant describing the activity of a sample and the more commonly quoted **half life** $t_{1/2}$ of a sample may be understood via the relation

$$N(t_{1/2}) = \frac{N_0}{2} = N_0 e^{-\lambda t_{1/2}}. \quad (16)$$

4. Radioactive elements often decay through a series of intermediate steps before reaching a stable element. Consider the decay series from Thorium to Lead (Figure 1).

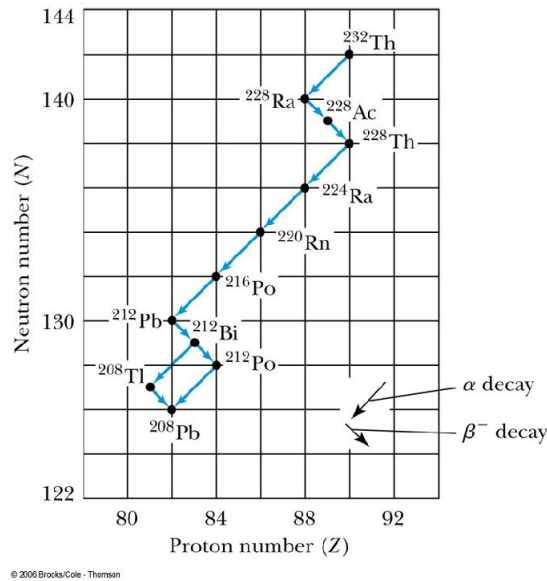


Figure 1: The main decay path from $^{226}_{90}\text{Th}$ to Lead.

2.2 The atomic models of Thomson and Rutherford (T-Rex p.128)

The discovery of the electron precipitated a flurry of new theories regarding the structure of the atom. The basic observational facts regarding the structure of the atom can be summarised as follows:

- Thomson characterized the electron as a charged particle in 1897 and Millikan confirmed the unit of electronic charge in 1909.

- Atoms were known to be electrically neutral whereas electrons are negatively charged.
- Electrons can be stripped away from atoms to generate positively charged atoms – ions.
- Atoms can be characterized by their relative atomic weight. The number of electrons in an atom is approximately half the number represented by the relative atomic weight.
- Therefore atoms must contain, in addition to a certain distribution of negatively charged electrons, a equal distribution of positive charge.

Thomson’s model of the atom consisted of a positively charged mass of size $\sim 10^{-10}\text{m}$ containing a distribution of much smaller electrons. The electrons would have to be distributed about the atom to form a stable distribution of electromagnetic forces. Although Thomson atoms would emit light when heated – the embedded electrons would oscillate thermally about their equilibrium positions – Thomson could not reproduce observed atomic line spectra.

The essence of the problem is how to look *inside* the atom. The approach taken by Rutherford and his collaborators formed the basis for almost every experiment in elementary particle physics since: fire a projectile at the thing you are interested in and see what happens!

Rutherford brought together a number of researchers and experimental techniques in his laboratory: Rutherford himself had won the Nobel prize in 1908 for demonstrating that α -particles are doubly ionized Helium nuclei. Hans Geiger had recently invented a simple apparatus to count radioactive decay particles – when an α -particle enters the gas filled detector chamber it ionizes atoms in the gas and permits an electrical spark to cross the chamber and generate an audible “click”.

The basis of the Rutherford scattering experiment is as follows (see T-Rex Figure 4.2): a beam of α -particles is fired at a thin gold screen (we shall see in Section 2.3 that the high atomic number of gold generates a large scattering angle). A Geiger counter can then be swept around the gold screen to measure the intensity of scattered α -particles as a function of angle.

In the Thomson model of the atom the gold screen should appear to the α -particle as an almost continuous sheet of positive charge with some small negative charges embedded within. Apart from some very small angle scattering events with the atomic electrons (see T-Rex Example 4.1), the α -particle should simply “punch through” the low density sheet of positive charge.

The observed results were completely unexpected: most α -particles passed straight through the gold screen with almost no deviation. However a small fraction were scattered through a large angle, some through almost 180° . The interpretation is that the positive charge contained within the atom must be contained in some small volume (assumed to be at the centre) of the atom – the atomic nucleus.

T-Rex Example 4.1: Electrons cannot scatter α -particles

Consider T-Rex Figures 4.3 and 4.4. An α -particle of mass M_α and velocity v_α encounters a stationary electron of mass m_e . The scattered α -particle has a velocity of v'_α and the electron recoils with a velocity v'_e .

The α -particle scattering angle can be computed from the vector change of its (non-relativistic) momentum (T-Rex figure 4.4), i.e.

$$M_\alpha \vec{v}_\alpha = M_\alpha \vec{v}'_\alpha + m_e \vec{v}'_e. \quad (17)$$

Therefore

$$\Delta \vec{p}_\alpha = M_\alpha \vec{v}_\alpha - M_\alpha \vec{v}'_\alpha = m_e \vec{v}'_e. \quad (18)$$

As the α -particle is approximately 7,000 times more massive than the electron, in a head-on collision (maximum momentum change) the recoil electron velocity $v'_e \approx 2v_\alpha$ and $\Delta p_{max} = 2m_e v_\alpha$.

As mentioned above, maximum momentum transfer occurs for a head-on collision. However, we can calculate a generous upper limit to the α -particle scattering angle by setting the maximum momentum change perpendicular to the incident α -particle, i.e.

$$\theta_{max} = \frac{\Delta p_\alpha}{p_\alpha} = \frac{2m_e v_\alpha}{M_\alpha v_\alpha} = \frac{2m_e}{M_\alpha} = 2.7 \times 10^{-4} \text{ rad} = 0.016^\circ. \quad (19)$$

Note that we are correctly using the small angle approximation here. The rest of T-Rex Example 4.1 goes on to demonstrate that if an incident α -particle scattered from *every electron* in *every atom* in a thin gold foil target the maximum scattering angle would be about 7° .

2.3 Rutherford scattering in detail

Rutherford scattering is an example of **Coulomb scattering**: the incident α -particle never actually strikes the atomic nucleus. Instead the Coulomb force between the positively charged α -particle and atomic nucleus is what causes the α -particle to deviate from its trajectory. Rutherford and Geiger used α -particle beams with kinetic energies in the range 5–8 MeV. More energetic particle beams probe the effects of different forces, such as the strong nuclear force.

Several assumptions are required to formulate the **Rutherford scattering equation**:

1. The target nucleus is sufficiently massive that no recoil occurs. This implies that the KE of the α -particle remains unchanged before and after scattering.
2. The target is sufficiently thin that only one scattering event occurs per α -particle.
3. The incident α -particle and target nucleus are sufficiently small to be considered point masses and charges.

4. Only the Coulomb force acts. As the Coulomb force is a central, point-like force, the angular momentum of the α -particle is conserved and the scattering geometry can be reduced to a plane.

To investigate Rutherford scattering numerically we consider the following: a charged particle of mass m , charge Z_1e and velocity v_0 is incident upon a target material characterised by particles of charge Z_2e . The *impact parameter* b is the minimum projected separation between the particle and the target. Finally, the angle θ between the incident and deflected particle trajectory is referred to as the *scattering angle*. See T-Rex Figure 4.6.

The analysis proceeds as follows:

1. We must first obtain a relationship between *impact parameter* b and *scattering angle* θ . Consideration of T-Rex Figure 4.7 indicates what we might expect: incident particles with small impact parameters will experience greater Coulomb forces and will be scattered through larger angles.
2. When firing α -particles at a gold screen we cannot know individual impact parameters in advance. Therefore, we must consider the statistics of a beam (large number) of incident α -particles and compute the distribution of scattered particles as a function of angle θ .

Starting with point (1) we define the position of the α -particle using spherical coordinates as r , the distance from the target nucleus, and ϕ , the azimuthal angle. The angle $\phi = 0$ corresponds to the location of r_{min} the minimum separation between incident α -particle and the target nucleus. The change in α -particle momentum is given by the impulse:

$$\Delta\vec{p} = \int \vec{F}_{\Delta p} dt, \quad (20)$$

where $\vec{F}_{\Delta p}$ is the component of force acting along $\Delta\vec{p}$.

The change in α -particle momentum is simply the vector difference between the incident (initial) and scattered (final) momentum (T-Rex Figure 4.8)

$$\Delta\vec{p} = \vec{p}_f - \vec{p}_i. \quad (21)$$

Consideration of the vector geometry of T-Rex Figure 4.8 shows that the magnitude Δp of the vector $\Delta\vec{p}$ is

$$\Delta p = 2mv_0 \sin \frac{\theta}{2}. \quad (22)$$

The vector $\Delta\vec{p}$ is directed along the z -axis (this can be visualised in T-Rex Figure 4.7). Therefore, we require the Coulomb force \vec{F} along the instantaneous direction of the position vector \vec{r} (the

vector describing the separation between the α -particle and the nucleus – we use the symbol \hat{e}_r), i.e.

$$\vec{F} = \frac{1}{4\pi\epsilon_0} \frac{Z_1 Z_2 e^2}{r^2} \hat{e}_r. \quad (23)$$

The component of force along the unit vector defining the momentum change is

$$F_{\Delta p} = \vec{F} \cdot \Delta\hat{p} = F \cos \phi. \quad (24)$$

We now have expressions for the magnitudes of the vectors $\Delta\vec{p}$ and $\vec{F}_{\Delta p}$ that can be substituted into Equation 20 to obtain

$$\Delta p = 2mv_0 \sin \frac{\theta}{2} = \int F \cos \phi \, dt = \frac{Z_1 Z_2 e^2}{4\pi\epsilon_0} \int \frac{\cos \phi}{r^2} \, dt. \quad (25)$$

We solve for the unknown functional form of r by returning to the condition that instantaneous angular momentum is conserved, i.e.

$$\begin{aligned} mr^2 \frac{d\phi}{dt} &= mv_0 b \\ r^2 &= \frac{v_0 b}{d\phi/dt}. \end{aligned} \quad (26)$$

Inserting this relation back into Equation 25 generates

$$\begin{aligned} 2mv_0 \sin \frac{\theta}{2} &= \frac{Z_1 Z_2 e^2}{4\pi\epsilon_0} \int \frac{\cos \phi \, d\phi}{v_0 b} \, dt \\ &= \frac{Z_1 Z_2 e^2}{4\pi\epsilon_0 v_0 b} \int_{\phi_i}^{\phi_f} \cos \phi \, d\phi. \end{aligned} \quad (27)$$

The integration occurs over an initial angle ϕ_i and final angle ϕ_f . Scattering is symmetric about the z -axis, therefore $\phi_i = -\phi_f$ and the sum of all three angles $-\phi_i + \phi_f + \theta = \pi$. Then $\phi_i = -(\pi - \theta)/2$ and $\phi_f = +(\pi - \theta)/2$. Rearranging Equation 27 yields

$$\frac{8\pi\epsilon_0 m v_0^2 b}{Z_1 Z_2 e^2} \sin \frac{\theta}{2} = \int_{-(\pi-\theta)/2}^{+(\pi-\theta)/2} \cos \phi \, d\phi = 2 \cos \frac{\theta}{2}. \quad (28)$$

We then rearrange this equation to obtain the required relationship between b and θ

$$b = \frac{Z_1 Z_2 e^2}{4\pi\epsilon_0 m v_0^2} \cot \frac{\theta}{2} = \frac{Z_1 Z_2 e^2}{8\pi\epsilon_0 K} \cot \frac{\theta}{2}, \quad (29)$$

where $K = mv_0^2/2$ is the kinetic energy of the (non-relativistic) incident α -particle.

This analysis is particularly useful as it illustrates the approach used to understand a range of scattering phenomena arising from a central force. We now consider point (2): determining the range of scattering angles produced by a beam of α -particles scattered with a range of impact parameters.

We start by defining $\sigma = \pi b^2$ as the *cross section* for scattering an incident particle through an angle equal to θ or greater (T-Rex Figure 4.9).

Next we must consider what fraction of a given target screen is covered by the cross sections of individual nuclei contained within the screen. The total number of nuclei is equal to the total number of atoms. The number of atoms per unit volume is

$$n = \frac{\rho N_A N_M}{M_{mol}} \text{ atoms m}^{-3}, \quad (30)$$

where N_A is Avogadro's number (molecules per mole), N_M is the number of atoms per molecule and M_M is the molar mass. In a thin foil screen of thickness t and area A the total number of nuclei available to scatter incident particles is

$$N_s = ntA. \quad (31)$$

We are now in a position to consider what fraction of the area of the screen will scatter incident α -particles by an angle of θ or greater. This fraction may be expressed as

$$\begin{aligned} f &= \frac{\text{total cross section of scattering nuclei}}{\text{total area of screen}} = \frac{ntA\sigma}{A} \\ &= nt\sigma = nt\pi b^2 \\ f &= \pi nt \left(\frac{Z_1 Z_2 e^2}{8\pi\epsilon_0 K} \right)^2 \cot^2 \frac{\theta}{2}. \end{aligned} \quad (32)$$

T-Rex Example 4.2

What is the fraction of 7.7 MeV α -particles deflected by an angle of 90° or greater from a gold foil of thickness 10^{-6}m ?

We require n to substitute into Equation 32. The density of gold is $19.3 \times 10^3 \text{ kg m}^{-3}$ and the atomic weight is $0.197 \text{ kg mol}^{-1}$. Therefore

$$n = \frac{(19.3 \times 10^3 \text{ kg m}^{-3})(6.02 \times 10^{23} \text{ atoms mol}^{-1})}{0.197 \text{ kg mol}^{-1}} = 5.90 \times 10^{28} \text{ atoms m}^{-3}. \quad (33)$$

and

$$f = \pi(5.90 \times 10^{28} \text{ atoms m}^{-3})(10^{-6} \text{ m}) \times \dots$$

$$\begin{aligned}
& \times \left[\frac{(79)(2)(1.6 \times 10^{-19} \text{ C})^2(9 \times 10^9 \text{ Nm}^2\text{C}^{-2})}{2(7.7 \text{ MeV})(1.6 \times 10^{-13} \text{ J MeV}^{-1})} \right]^2 \\
& \times (\cot 45^\circ)^2 \\
& = 4 \times 10^{-5}
\end{aligned} \tag{34}$$

or one α -particle in 25,000 is deflected beyond and angle of 90° .

End of T-Rex Example 4.2

We have applied Equation 32 to compute the fractional intensity of particles scattered from an incident beam by an angle greater than θ . However, this is not quite what is required; the intensity of scattered α -particles is measured using a Geiger counter (or similar device). The detector subtends a given angle $d\theta$ and the detector aperture corresponds to a given physical area. For a given incident beam of N_i particles we require the number of particles scattered into an angle θ to $\theta + d\theta$ per unit area. Differentiating Equation 32 yields

$$df = -\pi n t \left(\frac{Z_1 Z_2 e^2}{8\pi\epsilon_0 K} \right)^2 \cot \frac{\theta}{2} \csc^2 \frac{\theta}{2} d\theta. \tag{35}$$

T-Rex Figure 4.12 shows the geometry of a scattering event. The number of particles scattered into a ring of angular width $d\theta$ is $N_i |df|$. The physical area of the ring is $dA = (rd\theta)(2\pi r \sin \theta) = 2\pi r^2 \sin \theta d\theta$. Therefore, the required quantity, the number of particles $N(\theta)$ scattered per unit area into a ring at a scattering angle θ is

$$\begin{aligned}
N(\theta) &= \frac{N_i |df|}{dA} = \frac{N_i \pi n t \left(\frac{Z_1 Z_2 e^2}{8\pi\epsilon_0 K} \right)^2 \cot \frac{\theta}{2} \csc^2 \frac{\theta}{2} d\theta}{2\pi r^2 \sin \theta d\theta} \\
N(\theta) &= \frac{N_i n t}{16} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \frac{Z_1^2 Z_2^2}{r^2 K^2 \sin^4(\theta/2)}.
\end{aligned} \tag{36}$$

This is the **Rutherford scattering equation**. The main points are

- The scattering angle is proportional to the square of the atomic number of both the incident and target nucleus – bigger target nuclei scatter more effectively.
- The number of scattered particles is inversely proportional to the square of the KE of the incident particle – more energetic particles are scattered less effectively.
- The scattering angle follows a clear angular relationship – $\sin^4(\theta/2)$ – this can be confirmed experimentally.

- Scattering is proportional to target thickness for thin targets.

T-Rex Figure 4.13 shows the experimentally determined relationship between scattering intensity and scattering angle – the Rutherford formula is an exact fit. The above analysis is essentially classical in approach. However, the clear success in explaining atomic scattering phenomena provides compelling evidence that the positive charge associated with atoms is concentrated in an almost point-like (relative to the total size of the atom) central nucleus.

T-Rex Examples 4.4 and 4.5

Rutherford noted deviations from Equation 36 for 7.7 MeV α -particles ($Z_1 = 2$) scattering from aluminium ($Z_2 = 13$) at angles close to 180° . He correctly assumed that this might be due to the two nuclei approaching each other at sufficiently small distance that the original assumptions associated with the interaction break down. What can we learn from the experiment about the possible size of the atomic nucleus?

At $\theta = 180^\circ$ the α -particle approaches the target nucleus, comes to a stop at r_{min} – when the incident α -particle KE equals the Coulomb potential, and is then scattered exactly backwards. First we obtain an expression for r_{min} by equating the the kinetic and potential energy terms at closest approach, i.e.

$$\begin{aligned} \text{KE}_\alpha &= \frac{(Z_1 e)(Z_2 e)}{4\pi\epsilon_0 r_{min}} \\ r_{min} &= \frac{Z_1 Z_2 e^2}{4\pi\epsilon_0 \text{KE}_\alpha}. \end{aligned} \quad (37)$$

Inserting values appropriate to the experiment, we obtain

$$\begin{aligned} r_{min} &= \frac{(2)(13)(1.6 \times 10^{-19} \text{ C})^2(9 \times 10^9 \text{ Nm}^2\text{C}^{-2})}{(7.7 \text{ MeV})(1.6 \times 10^{-13} \text{ J MeV}^{-1})} \\ &= 4.9 \times 10^{-15} \text{ m}. \end{aligned} \quad (38)$$

as an upper limit of the sum of the radii of the ^4He and aluminium nuclei.

2.4 A “classical” model of the atom

Experimental results indicate that an atom consists of a central positively charged nucleus (of size $\leq 10^{-15}\text{m}$) surrounded by one or more electrons that provide the atom with an effective size of order 10^{-10}m . This understanding of the atom was arrived at via experiment and the application of some classical physical analysis.

However, would such a “classical” atom be stable? T-Rex Figure 4.5 shows a very basic, schematic view of a classical atom. A number of scientists at the time thought that the atomic electrons would

be in “orbit” about the central nucleus – with the centripetal force arising from their circular motion exactly balancing the inward Coulomb attraction (T–Rex Section 4.3). However, this picture of the atom is not stable:

- Circular motion involves a continuous acceleration toward the centre of motion and, as we saw with X–ray production (and known from classical physics), an accelerated electron emits radiation in the form of photons.
- The orbiting electron should emit a continuous stream of photons as it spirals to the centre and collides with the positive nucleus.
- The only alternative is to postulate that the electrons do not orbit the nucleus but occupy fixed positions – held in place by some as yet unknown force.

As we shall see in Section 2.6, Bohr refined this model by applying some simple “quantum” rules (actually Bohr’s model is a very intuitive mix of classical and quantum physics). However, it is only fair to note at this stage that any picture of the atom that shows electrons happily whizzing around the nucleus, either supported by classical forces or quantum rules, is just that – a picture. As we shall see in Lectures 3, 4 and 5, we can apply mathematics to develop a predictive quantum model of the atom (and other particles) but any connection between the theory and the concept of “reality” is still debated hotly – we return to this issue when we discuss the Copenhagen interpretation of quantum mechanics.

2.5 Line spectra

Before describing the Bohr model of the atom in detail, we will review the phenomenon of atomic line spectra and the simple mathematical rules that can be used to describe the line series of Hydrogen in particular. Though line spectra had been observed prior to work of Rutherford and the concept of the classical atom, the process by which line spectra were created remained an unsolved riddle of atomic structure.

- Pure chemical elements in the gas phase create a characteristic emission signature when burned or excited by an electrical discharge. In addition, when a source of continuum radiation (e.g. white light) is shone through the same gas, the same spectral lines appear in absorption.
- The light from such experiments was typically observed using a diffraction grating as part of a *spectrometer* (T–Rex Figure 3.6). Light scattered from the diffraction grating generates constructive interference under the following mathematical condition

$$d \sin \theta = n\lambda, \tag{39}$$

where d is the number of line rulings per centimeter and the integer n describes the scattering order ($n = 1$ is the strongest order). When projected on a screen a spectrometer creates a map of intensity versus wavelength.

- Light from a blackbody emitter shows the characteristic spectrum described by the Planck radiation law. However, excited atomic gases do not emit continuous radiation. Instead light is emitted in a series of spectral lines that are often so narrow as to be unresolved in the wavelength direction.
- The wavelength location of the lines does not change as the temperature of the flame or energy in the electrical discharge are varied.
- Balmer was the first researcher (1885) to describe the series of line spectra arising from Hydrogen in the optical part of the spectrum. He noted that the visible lines obey the formula

$$\lambda = 364.56 \frac{k^2}{k^2 - 4} \text{ nm}, \quad (40)$$

where $k > 2$ is an integer. The series of visible Hydrogen lines is now known as the **Balmer series**. However, Equation 40 can be re-written as the **Rydberg equation** to account for the additional spectral line series observed for Hydrogen at ultraviolet and infrared wavelengths (see T-Rex Table 3.2)

$$\frac{1}{\lambda} = \frac{1}{364.56 \text{ nm}} \frac{k^2 - 4}{k^2} = \frac{4}{364.56 \text{ nm}} \left(\frac{1}{2^2} - \frac{1}{k^2} \right) = R_H \left(\frac{1}{n^2} - \frac{1}{k^2} \right), \quad (41)$$

where $R_H = 1.09776 \times 10^7 \text{ m}^{-1}$ and $k > n$ are integers. The case $n = 2$ corresponds to the Balmer series (see T-Rex Figure 3.7).

2.6 The Bohr model of the Hydrogen atom

We currently have a model of the atom that is both unstable and fails to account for observed atomic line spectra. Clearly something is wrong!

Bohr introduced Planck's constant and the idea of quantized energy states to describe the electron structure of the atom. His approach was to use classical physics wherever possible and to introduce quantum physics where experimental evidence left no alternative. In this sense the "Bohr atom" is not a truly quantum model and is therefore ultimately limited compared to the "Schroedinger atom" (Lecture 5). However, the Bohr atom is a highly intuitive model and provides a good introduction to the electron structure of the atom. Bohr produced his major works over the period 1910–1915 and his atomic theory is characterised by a number of assumptions:

- A single electron of mass m and charge $-e$ moves about the positively charged nucleus of effectively infinite mass (compared to the electron) and charge e on a circular orbit. The orbital radius a is large compared to the nuclear radius. *This is essentially the classical model described in Section 2.4.*

- The orbiting electron exists in certain “stationary” or stable states corresponding to a specific total energy. *This assumption is required as atoms are clearly stable entities.*
- The emission or absorption of light from an atom can only occur as the electron changes between two stationary states. The energy of the emitted/absorbed photon is equal to the energy difference between the two states and is given by

$$E = E_1 - E_2 = hf, \quad (42)$$

where h is Planck’s constant and f is the photon frequency. *This assumption is required to explain atomic line spectra and, if you think about it, the photo–electric effect.*

- The dynamical equilibrium of the stationary states is governed by classical physics. However, transitions between the stationary states are not. *This is basically a clause that states that classical physics alone cannot provide a reasonable description of the atom.*
- The angular momentum of the orbiting electron is an integer multiple of $\hbar = h/2\pi$. The implication is that the KE of the orbiting electron is also quantised. *This is the key “quantum” assumption – you need this to derive key observables in terms of fundamental constants and integer “quantum states”.*

When deriving the Bohr model of the atom we will use the following steps:

1. We will combine classical and quantum expressions for the orbiting electron to obtain the orbital radius of each stationary state. In doing so we will define the **Bohr radius**.
2. We will next compute the binding energy of each stationary state and note that the “most bound” or lowest energy state corresponds to the **observed ionisation potential of Hydrogen**.
3. Finally, we will look at the difference between successive energy states and derive the **Rydberg equation**.

Step 1: Towards the Bohr radius

Consider an electron orbiting a nucleus of charge $+e$. The Coulomb force experienced by the electron is

$$\vec{F}_e = \frac{-1}{4\pi\epsilon_0} \frac{e^2}{r^2} \hat{e}_r, \quad (43)$$

where the minus sign indicates that the force is attractive and \hat{e}_r is the radial unit vector. The orbiting electron experiences a centripetal force equal to mv^2/r . Equating the two forces gives

$$\begin{aligned} \frac{1}{4\pi\epsilon_0} \frac{e^2}{r^2} &= \frac{mv^2}{r} \quad \text{or} \\ v &= \frac{e}{\sqrt{4\pi\epsilon_0 mr}} \end{aligned} \quad (44)$$

Aside: it will be useful if at this stage we also derive the total energy of the orbiting electron, i.e.

$$\begin{aligned}
 E &= KE + PE = \frac{1}{2}mv^2 - \frac{e^2}{4\pi\epsilon_0 r} \\
 E &= \frac{e^2}{8\pi\epsilon_0 r} - \frac{e^2}{4\pi\epsilon_0 r} = -\frac{e^2}{8\pi\epsilon_0 r}.
 \end{aligned}
 \tag{45}$$

The total energy is negative – indicating that the electron is bound.

Now we require Bohr’s assumption that the electron angular momentum L is quantised

$$L = mvr = n\hbar, \tag{46}$$

where n is referred to as the **principal quantum number**. If we solve this equation for v and equate it to Equation 44 we obtain (using v^2 as a more convenient form) a quantised expression for the electron orbital radius

$$\begin{aligned}
 v^2 &= \frac{e^2}{4\pi\epsilon_0 mr} = \frac{n^2\hbar^2}{m^2 r^2} \\
 r_n &= \frac{4\pi\epsilon_0 n^2 \hbar^2}{me^2} \equiv n^2 a_0,
 \end{aligned}
 \tag{47}$$

where the **Bohr radius** a_0 is given by

$$\frac{4\pi\epsilon_0 \hbar^2}{me^2} = 0.53 \times 10^{-10} \text{ m}. \tag{48}$$

The smallest size possible for the Bohr hydrogen atom occurs for $n = 1$ and equals $2a_0 = 10^{-10}$ m – a good match to the inferred (and now known) size of the hydrogen atom. Atomic radius is now quantised with $n = 1$ referred to as the **ground state** and $n > 1$ referring to **excited states**.

Step 2: quantised energy states

As shown in Equation 45 the energy of a given electron state can be expressed as

$$E_n = -\frac{e^2}{8\pi\epsilon_0 r_n} = -\frac{e^2}{8\pi\epsilon_0 a_0 n^2} \equiv -\frac{E_0}{n^2}. \quad (49)$$

The energy of the lowest energy state ($n = 1$) is $E_1 = -E_0$ where

$$E_0 = \frac{e^2}{8\pi\epsilon_0 a_0} = \frac{e^2}{(8\pi\epsilon_0)} \frac{me^2}{4\pi\epsilon_0 \hbar^2} = \frac{me^4}{2\hbar^2(4\pi\epsilon_0)^2} = 13.6 \text{ eV}, \quad (50)$$

and is very close to the experimentally determined ionisation potential of hydrogen.

Step 3: photon emission and absorption – the Rydberg equation

The quantised energy states in the Bohr atom can be visualised using an **energy level diagram** (see T-Rex Figure 4.15). In this model, the emission of a photon occurs when an electron makes the transition from an upper or excited energy state $n = n_u$ to a lower energy state $n = n_l$. As assumed by Bohr, the photon energy is equal to the energy difference between the two states

$$hf = E_u - E_l. \quad (51)$$

We can re-write this equation in terms of wavelength

$$\begin{aligned} \frac{1}{\lambda} &= \frac{f}{c} = \frac{E_u - E_l}{hc} \\ &= \frac{-E_0}{hc} \left(\frac{1}{n_u^2} - \frac{1}{n_l^2} \right) = \frac{E_0}{hc} \left(\frac{1}{n_l^2} - \frac{1}{n_u^2} \right), \end{aligned} \quad (52)$$

where

$$\frac{E_0}{hc} = \frac{me^4}{4\pi c \hbar^3 (4\pi\epsilon_0)^2} \equiv R_\infty \quad (53)$$

is the Rydberg constant for an infinite nuclear mass (we shall see shortly how this must be modified for a non infinite nuclear mass) and is *almost* equal to the Rydberg constant determined from experiment. Equation 52 then becomes

$$\frac{1}{\lambda} = R_\infty \left(\frac{1}{n_l^2} - \frac{1}{n_u^2} \right). \quad (54)$$

The Bohr hydrogen atom therefore explains the observed line series of hydrogen (Lyman, Balmer, Paschen, etc.) as a series of transitions to a particular energy state, i.e. Lyman corresponds to transitions to $n = 1$, Balmer to $n = 2$, Paschen to $n = 3$, etc. (see T-Rex Figure 4.16).

2.6.1 Refinements to the Bohr model

- **Reduced mass:** as noted above, the Rydberg constant for the Bohr atom, R_∞ , is not an exact match to the value determined experimentally for hydrogen. This is because Bohr's initial assumption that the nuclear mass is effectively infinite compared to the electron. In fact the mass of the hydrogen nucleus (a single proton) is only some 2,000 times larger than the electron and – in a purely classical picture – the two bodies orbit around their common centre of mass as shown in T-Rex Figure 4.17. Without going into the details of the analysis, the only modification required to Bohr's theory is to replace the mass of the electron in all the calculations with the **reduced electron mass**

$$\mu_e = \frac{m_e M}{m_e + M} = \frac{m_e}{1 + \frac{m_e}{M}} \quad (55)$$

where m_e is the electron mass and M is the nuclear mass. The Rydberg constant for an infinite nuclear mass is replaced by R , where

$$R = \frac{\mu_e}{m_e} R_\infty. \quad (56)$$

The modified Rydberg constant agrees with the value determined from experiment. Going further, in 1932 sensitive measurements showed the presence of a weak line offset from Balmer ground state emission (referred to as $H\alpha$). This line was correctly identified as deuterium (an isotope of hydrogen containing one proton and one neutron) by computing the reduced mass modified Rydberg constant for this offset spectral series.

Example: Compute the ionisation potential of hydrogen. The masses of the electron and the proton in atomic mass units (u) are 0.000548 u, 1.07276 u respectively. We first compute the reduced mass modified Rydberg constant for hydrogen, i.e.

$$R_H = \frac{1}{1 + \frac{m_e}{m_p}} R_\infty = 0.99946 R_\infty. \quad (57)$$

The ionisation potential of hydrogen is the energy required to move the electron from the ground state ($n_l = 1$) to an unbound state ($n_u = \infty$). Manipulating Equation 54 we obtain

$$\begin{aligned} \text{Energy} &= \frac{hc}{\lambda} = hc R_H = \frac{(6.626 \times 10^{-34} \text{ Js})(2.998 \times 10^8 \text{ ms}^{-1})}{(1.6 \times 10^{-19} \text{ J eV}^{-1})} \\ &\quad \times (1.09776 \times 10^7 \text{ m}^{-1}) \\ &= 13.6 \text{ eV}. \end{aligned} \quad (58)$$

Example: Compute the wavelength of H_α emission ($n_u = 3$ to $n_l = 2$) for hydrogen and deuterium. For the hydrogen atom, the wavelength of H_α is

$$\lambda = \left[R_H \left(\frac{1}{2^2} - \frac{1}{3^2} \right) \right]^{-1} = [0.13889 R_H]^{-1} = 656.47 \text{ nm}. \quad (59)$$

Secondly, we require the reduced mass modified Rydberg constant for deuterium (one proton plus one neutron, mass = 2.013553u), i.e.

$$R_D = \frac{1}{1 + \frac{m_e}{m_d}} R_\infty = 0.99973 R_\infty. \quad (60)$$

The wavelength of H_α for deuterium is therefore

$$\lambda(H_\alpha, \text{deuterium}) = \lambda(H_\alpha, \text{hydrogen}) \frac{R_H}{R_D} = 656.29 \text{ nm}. \quad (61)$$

- **Hydrogen-like atoms:** at the base of Bohr's theory of the atom lies the classical expression for the Coulomb force (Equation 43). In taking the nuclear charge to be $+e$ the expression assumes that we are dealing with hydrogen. The equation can be modified to describe more complex atoms by inserting $+Ze$ for the nuclear charge. The Rydberg equation now becomes

$$\frac{1}{\lambda} = Z^2 R \left(\frac{1}{n_l^2} - \frac{1}{n_u^2} \right). \quad (62)$$

However, the expression is only valid for single electron ions, i.e. He^+ , Li^{++} , etc.

2.6.2 Remaining questions

- **Line splitting.** A strong electric (Stark effect) or magnetic (Zeeman effect) field applied to a gas of excited atoms splits the characteristic spectral lines into a multiple features. We introduce here the concept of the **fine structure constant**. The mass of the electron enters many of the fundamental constants used to compute the electron structure of atoms. However, to be fully consistent with Special Relativity we use the relativistic electron mass $m_r = E/c^2 = \gamma m_0$, where $\gamma = \left(\sqrt{1 - v^2/c^2} \right)^{-1}$ is the Lorentz factor and m_0 is the electron rest mass (an invariant). Clearly the ratio v/c is important in determining the relativistic mass. For the Bohr atom we may write the electron velocity of the n th energy state as

$$v_n = \frac{n\hbar}{mr_n} = \frac{1}{n} \frac{\hbar}{ma_0} = \frac{1}{n} \frac{e^2}{4\pi\epsilon_0\hbar}. \quad (63)$$

The value of v_1 is $\hbar/ma_0 = 2.2 \times 10^6 \text{ ms}^{-1}$. The fine structure constant α is defined as

$$\alpha \equiv \frac{v_1}{c} = \frac{\hbar}{ma_0c} = \frac{e^2}{4\pi\epsilon_0\hbar c} \approx \frac{1}{137}. \quad (64)$$

- Multi-electron atoms. The Bohr model can only explain hydrogen-like or single electron atoms. The line spectra of He, Li, etc. could not be explained.
- Chemistry – how many electrons per energy state? The Bohr atom states that electrons exist in stationary states or “shells” – yet it makes no prediction as to how many electrons can exist in a given shell. However, consideration of the Periodic Table (ordered by atomic number, Z) indicates that a specific number of electrons are associated with each energy state or shell. Once a given shell is filled up, extra electrons have to find room in higher energy shells. If the outer electron shell is full (a chemist would express this by saying that there are no valence electrons), the atom is typically very stable. Therefore, the atomic number of noble gases (He, Ne, Ar, Kr, Xe, Rn – remember that in a neutral atom $Z =$ number of electrons) indicates how many electrons can exist in each shell: 2, 8, 8, etc. The **Pauli exclusion principle** (see later lectures) puts this empirical result on a firm quantum footing.

2.6.3 The correspondence principle

Classical physics clearly provides an acceptable description of macroscopic physics. However, quantum physics – in this case the Bohr atom – is required for microscopic or atomic physics. Are these two fundamentally different physical worlds or does the set of classical rules make a smooth transition to the quantum world as we zoom in on small-scale physical phenomena? Bohr presented the best working rule in the form of the **Correspondence principle**, i.e.

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

To illustrate the principle, we consider the classical and quantum atomic radiation laws. Using the correspondence principle, the two theories should agree in the regime where the finite size of Planck’s constant – defining the quantum scale – is unimportant. In terms of the Bohr atom this occurs in the limit of large quantum number n .

Classical physics describes the frequency of emitted radiation from an atomic electron as the orbital frequency:

$$f_{\text{classical}} = f_{\text{orb}} = \frac{1}{2\pi} \frac{v}{r}, \quad (65)$$

where we assume that the electron moves along a circular path. Substituting the classical electron velocity in an atomic orbit (Equation 44) yields

$$f_{\text{classical}} = \frac{1}{2\pi} \left(\frac{e^2}{4\pi\epsilon_0 m r^3} \right)^{1/2}. \quad (66)$$

If we now replace r by the Bohr radius (Equation 47) we obtain

$$f_{\text{classical}} = \frac{me^4}{4\epsilon_0^2 h^3} \frac{1}{n^3}. \quad (67)$$

In the Bohr atom continuous radiation emission can be described as the result of an electron cascading through a series of adjacent energy states, i.e.

$$n + 1 \rightarrow n \rightarrow n - 1 \rightarrow \dots \quad (68)$$

The frequency of an emitted photon resulting from the transition $n + 1 \rightarrow n$ is

$$\begin{aligned} f_{Bohr} &= \frac{E_0}{h} \left[\frac{1}{n^2} - \frac{1}{(n+1)^2} \right] \\ &= \frac{E_0}{h} \left[\frac{n^2 + 2n + 1 - n^2}{n^2(n+1)^2} \right] = \frac{E_0}{h} \left[\frac{2n + 1}{n^2(n+1)^2} \right], \end{aligned}$$

which for large n becomes

$$f_{Bohr} \approx \frac{2nE_0}{hn^4} = \frac{2E_0}{hn^3}. \quad (69)$$

Inputting Bohr's expression for ground state energy E_0 shows that

$$f_{Bohr} = \frac{me^4}{4\epsilon_0^2 h^3} \frac{1}{n^3} = f_{classical}. \quad (70)$$

2.7 What drives the Periodic Table – atomic weight or atomic number?

During the period when quantum physics was being developed the chemical elements in the Periodic Table were ordered by their increasing atomic weight – at the time measured as the weight of one mole of material. The atomic number was simply the numerical order of the elements, it had no physical meaning. Several fundamental chemistry questions therefore remained unanswered: do elements exist that are lighter than Hydrogen, or do any exist between Hydrogen and Helium?

In 1913 the full impact of the Bohr atom was still unclear. However, the following ideas were beginning to be appreciated.

- Chemistry is driven both by the number of electrons in the outermost “shell” and by the total number of atomic electrons.
- As atoms display neutral charge the number of electron must be balanced by an equal number of positive charge carriers, protons, in the nucleus. Demonstrating that this was the case was the subject of the **Mosely experiment** (see below).
- The outcome of the experiment clearly demonstrated that **atomic number** Z – the number of protons in the nucleus – drove the exact ordering of the Periodic table and not **atomic weight** – the total number of protons and (currently undiscovered) neutrons in the nucleus.

Moseley was one of the first researchers to perform detailed measurements of X-ray emission from a range of chemical elements. It was already known that when various elements (mainly metals) were subject to a beam of X-rays, diffuse, secondary X-ray emission was observed whose “penetrating power” was a function of the element used – heavier elements generated more penetrating X-rays.

With the advent of X-ray diffraction spectrographs (see next topic) the wavelength of X-ray emission could be measured for the first time. Moseley demonstrated that the secondary X-ray emission coming from chemical elements was a form of spectral line emission – i.e. an atomic transition. The frequency of the brightest X-ray line for each element (labelled K_α) increased steadily with increasing atomic number of the element, i.e.

$$f_{K_\alpha} = \frac{3cR}{4}(Z - 1)^2. \quad (71)$$

We can understand Moseley’s experimental result using the Bohr atomic model: an atom of an element with the atomic number Z contains Z protons in the nucleus and Z electrons in a series of stationary states. We will learn later that the Pauli exclusion principle permits only two electrons to occupy the ground state ($n = 1$), also referred to as the “K” shell. The effect of the initial X-ray beam in Moseley’s experiment is to excite a ground state electron, moving it from the K shell to a higher energy state. At some later point the remaining electron states will re-shuffle and a $n = 2$ electron will re-occupy the vacant ground state position.

Viewing this as a Bohr atom, the electron making a transition from $n = 2$ to the ground state ($n = 1$) experiences an effective nuclear charge of $Ze - e = (Z - 1)e$ – the remaining outer electrons have no net effect. The Rydberg equation for the K_α transition can be written as

$$\begin{aligned} \frac{1}{\lambda_{K_\alpha}} &= R(Z - 1)^2 \left(\frac{1}{1^2} - \frac{1}{2^2} \right) = \frac{3}{4}R(Z - 1)^2 \\ \text{or } f_{K_\alpha} &= \frac{c}{\lambda_{K_\alpha}} = \frac{3cR}{4}(Z - 1)^2. \end{aligned} \quad (72)$$

Moseley’s result confirmed that atomic number had a physical significance – the number of nuclear protons. He mapped out the chemical elements from aluminium ($Z = 13$) to gold ($Z = 79$). In the process he re-ordered the Periodic Table (using atomic weight leads to a mis-ordering of Argon and Potassium) and he predicted the existence of three as yet undiscovered elements with $Z = 43$ (Technetium), 61 (Promethium) and 75 (Rhenium).

2.8 The Franck–Hertz experiment: atomic excitation using electrons rather than photons

- Atomic line spectra arise in emission because atomic electrons have been raised from the ground state to a higher, excited energy state. As the electron falls back to the ground level

– a lower energy and thus more stable state – a photon is emitted and ultimately observed in the spectrometer. As noted previously, emission occurs when chemical elements are burned (in an environment of fast moving ions and electrons) or shocked by a spark (a stream of fast moving electrons). Charged particles are exciting the atomic electron structure but we have no idea of *exactly* what particle properties are required to excite a given energy state.

- When atomic line spectra are observed in absorption, specific wavelengths of light, corresponding to the energy difference between pairs of electron energy states, are removed from the continuum spectrum as these photons are absorbed by the atomic electrons, raising them to higher energy states. In this case incident continuum photons are exciting the electron structure and the absorption spectrum provides a clear diagnostic of which wavelengths (i.e. energy) of light are responsible.
- Franck and Hertz were the first to study the detailed physics of atomic excitation by electrons, i.e. what electron KE is required to excite a given state. The typical apparatus used in their experiment is shown in T-Rex Figure 4.20: the variable 0–45 V potential is used to accelerate electrons to a required KE. The 1.5 V decelerating voltage is used to stop the background signal of low KE electrons from hitting the anode collector plate (without this decelerating voltage electrons with zero KE could drift to the anode and be collected, confusing the signal).
- As a greater accelerating voltage is applied, more electrons are stripped from the filament, resulting in a greater current registered in the circuit. However, this increasing trend is punctuated by a series of regularly spaced dips in the electron current, corresponding to specific electron energies (measured by the accelerating voltage – see T-Rex Figure 4.21).
- The following situation is occurring:
 1. Accelerated electrons strike the atoms of the mercury gas on their way to the anode.
 2. Most electrons strike the electron structure of the mercury atom and bounce off – the collision is elastic and the electron KE is conserved. The electron may bounce around like a pinball but it loses almost no energy in the process and is collected at the anode.
 3. However, some electrons will have just the right energy to excite one of the atomic electrons and will suffer an inelastic collision – some or all of its energy will be transferred to the atomic electron, exciting it to a higher level. The incident electron loses KE and less electrons of this energy will be collected at the anode.
 4. For the mercury atoms used by Franck and Hertz the energy difference between the ground state E_0 and the first excited state E_1 is 4.88 eV – exactly the spacing observed between the successive dips in the electron current. The transition $E_0 \rightarrow E_1$ is by far the most likely and the successive dips represent electrons suffering multiple $E_0 \rightarrow E_1$ excitation encounters.
 5. What else might one observe during the experiment?

2.9 Summary of Lecture 2

- Rutherford scattering confirms that the atom contains a positive nucleus some 100,000 times smaller than the atomic radius.
- However, the “classical” atom is clearly unstable and we are obviously missing something.
- Bohr demonstrates that hydrogen and other single electron atoms can be described using classical physics and a series of ordered, quantum energy states.
- The Bohr atom correctly describes line spectra of simple elements and the results of the Moseley and Franck–Hertz experiments.
- However, the physical significance of the principal quantum number, n , is not clear.