Atoms were proposed as smallest building blocks of matter. Since they were assumed smaller than what the human eye could see, it became necessary to look for indirect evidence for their existence. Experimental evidence generally helps confirm or refine a hypothesis.

Much of the early evidence comes from chemical experiments. Boyle’s law, \( PV = RT \) was an empirical law for which a particulate matter based explanation was provided by Bernoulli around 1750 – particles move within the matter and exert pressure when they collide, and a non-zero mean free path gives it a volume.

A major refinement was the observation of existence of definite proportions in chemical reactions: (at fixed \( P, T \))

For two (or more) reacting gases the ratios of volumes of reactants & products are always small integers (and are fixed for a given reaction).

**Dalton’s hypothesis**

- 3 indivisible smallest constituent called atoms
- all atoms of a given element are identical but different elements have different atoms
- when element A reacts with element B, \( Na/Ne \) is a small integer

**Avogadro**

Molecule is the smallest unit of a substance, which determines all properties and is composed of atoms. At fixed \( P & T \) equal volumes of different gases contain equal numbers of molecules.
Determination of Avogadro's const

From the gas laws $R = N_A k_B$

So we attempt to measure $R$ and $k_B$ independently.

- $R$ is measured as $C_p - C_v$
- Best method is by determining the velocity of sound in an acoustic resonator.
- Acoustic standing waves are set up in a spherical cavity. Resonances are picked up by tuning the source frequency.

$$R = \frac{M_{\text{gas}}}{T_{\text{gas}}} \frac{1}{\nu} \frac{f_n^2}{n^2}$$

$$\nu = \frac{C_p}{C_v} \quad n \to \text{harmonic number} \quad \nu = \frac{5}{3} \text{ for Noble gases}$$

Determination of $k_B$ by diffusion

Measure the vertical density distribution of tiny solid spheres in a liquid column.

$$n(z) = n(0) e^{-mgz/k_BT}$$

$$\frac{dn}{dz} = -n(z) \frac{mg}{k_BT}$$

Direct counting yields $k_B$ since $T$ & $m$ are separately known.

OR measure the terminal velocity and require that at equilibrium the upward and downward fluxes (due to diffusion and gravity must balance.

$$V_{\text{term}} = \frac{m - (4\pi r^3/3) \rho_L}{6\pi \eta r}$$

$$j_{\text{gravity}} = V_{\text{term}} \cdot n \quad j_{\text{diff}} =$$
Electrochemical method:
Measure the mass change in the mass of an electrode after charge $Q$ has been deposited.

$$\Delta m = \frac{Q}{e} \cdot \frac{M}{N_A}$$

$M$: molar mass
$$\frac{M}{N_A} = \text{mass of a single atom}$$

X-ray diffraction

Distance between parallel planes in a crystal lattice:

$$d_k = \alpha K \sin \alpha K$$

for $\alpha K \neq 0$

$$= a$$

for $\alpha K = 0$

Bragg diffraction gives

$$2d \sin \theta_m = m \lambda$$

for different orientations of the crystal

$$2a \sin \alpha K \sin \theta_m = m \lambda \quad (\lambda \text{ is known})$$

From these data we obtain the "best" value of $a$.

For a macroscopic crystal of size $D$ and mass $M$ there are $N = (D/a)^3$ atoms. Then

$$\frac{N_A}{N} = \frac{M_{\text{molar}}}{M_{\text{crystal}}}$$

$$N_A = \frac{M_{\text{molar}}}{M_{\text{crystal}}} \cdot \left( \frac{D}{a} \right)^3$$
Gas Discharges reveal electrical structure of atoms

Cathode rays — fluorescence imaging
deflection by a magnetic field.
deflection by an electric field
Plucker, Hittorf, Lennard, Thomson (1897)

Kanal Strahlen — opposite to cathode rays
much weaker fluorescence
minor deflection (small q/m)
⇒ existence of +ve and -ve charges within the atom
No information about the spatial structure.

SIZE OF THE ATOM BASED ON X-RAY DIFFRACTION

X-ray diffraction provides a fairly direct method.
Determine the lattice constant \( \mathbf{d} \) [or \( d_1, d_2, d_3 \) if the crystal is not cubic] and obtain \( V_E \) the volume of the elementary cell: \( V_E = d_1 d_2 d_3 \)
Let \( N_E \) be the number of atoms per elementary cell.

\[
N_E = \begin{cases} 
1 & \text{simple cubic} \\
2 & \text{bcc} \\
4 & \text{fcc}
\end{cases}
\]

The packing fractions are also easily found

\[
f = \frac{(4/3) \pi r_0^3}{(2r_0)^2} = 0.52 \quad \text{for sc}
\]
\[
f = \frac{2 \times (4/3) \pi r_0^3}{(4/\sqrt{3} \cdot r_0)^2} = 0.68 \quad \text{for bcc}
\]
\[
f = \frac{4 \times (4/3) \pi r_0^3}{(4/\sqrt{2} \cdot r_0)^2} = 0.74 \quad \text{for fcc}
\]

We then have \( \frac{4}{3} \pi r_0^3 = \frac{f V_E}{N_E} \)
Size of the H- atom based on uncertainty principle

Uncertainty \( \Delta p \Delta x \sim \hbar \)

take \( p \sim \Delta p \) at least \( r \sim \Delta x \) at least \( : \quad p \approx \frac{\hbar}{r} \)

Potential energy of the atom \( E_{\text{pot}} = -\frac{e^2}{r} \)

Kinetic energy of the electron \( E_{\text{kin}} = \frac{\hbar^2}{2mr^2} \)

Total Energy \( E = \frac{\hbar^2}{2mr^2} - \frac{e^2}{r} \)

Require that this energy is a minima

\[
\frac{dE}{dr} = 0 \Rightarrow \frac{-\hbar^2}{mr^3} + \frac{e^2}{r^2} = 0
\]

\[
\Rightarrow r = \frac{\hbar^2}{e^2 mr^2} \approx 0.53 \, \text{Å}
\]

Using this value of \( r \) gives the size of the electron

\[
E = \frac{-mc^4}{2\hbar^2 (4\pi\varepsilon_0)^2}
\]

A spherical capacitance is given as \( C = 4\pi\varepsilon_0 r \)

work done to add charge \( q = \frac{1}{2} \frac{q^2}{C} \)

Self energy of an electron \( = \frac{e^2}{8\pi\varepsilon_0 r} \)

Equate this to rest mass energy \( mc^2 \)

\[
\Rightarrow r_e = \frac{e^2}{8\pi\varepsilon_0 mc^2}
\]

electron "size" based on its charge & rest mass
GAS DISCHARGE EXPTS SHOWING CHARGED NATURE OF ATOMS

Became possible after vacuum equipment became available.

Main observation: streams of charged particles seen under suitable conditions. - Seen by fluorescent screen
Anode with a hole
Allowed sampling of the streaming particle by external B and E fields
E & B fields applied in post-anode region allowed m/q estimates to be made, based on deflection.

Glow due to fluorescence seen due to electrons emerging into air

Cathode with a hole led to the observation of low mobility positively charged stream (going opposite to cathode rays
(called Kanal Strahl or channel-rays)
**THOMSON'S MODEL**

"Raisin Cake" model with equal + & - charge density. "electrons" light, "protons" heavy.

If we consider first only the positive charges, then the electric field within the atom would be

\[ \vec{E}(r) = \vec{E}(r) = \frac{+8Ze}{4\pi R^3 \varepsilon_0} \]

The force on the electrons would be attractive, and for one such electron \( F = -eE \)

\[ \propto m_0 w^2 r \] (harmonic force)

This gives rise to the idea of a plasma frequency.

If instead of one electron we have a negative charge density, we get a similar harmonic binding force with a binding frequency

\[ \omega^2 = \frac{3Ze^2}{4\pi \varepsilon_0 m R^3} \]

To test this model consider an \( \alpha \) particles passing through the raisin cake atom.

This \( \alpha \) particle is assumed to have only \( V_{\parallel} \) initially and has an impact parameter \( b \).

Assuming small deflections, the path length through the atom is approx \[ 2 \left[ R^2 - b^2 \right]^{1/2} \]

The corresponding flight time is \[ 2 \left[ R^2 - b^2 \right]^{1/2} / V_{\parallel} \]

The instantaneous angle w.r.t. the \( \parallel \) direction \( \beta = \frac{b}{(r^2 + b^2)^{1/2}} \)

\[ \propto \frac{b}{r} \]
The force on the particle is given by

\[ F_\perp = F_r \cos \beta \]  (we neglect \parallel force)

\[ = \frac{2Ze^2}{4\pi \varepsilon_0 R^3} r \cos \beta \]

\[ \Delta v_\perp = \frac{1}{m} \int F_\perp dt \]

\[ = \frac{2Ze^2 b}{m4\pi \varepsilon_0 R^3} \propto \frac{4Zb}{m v_{\parallel}} \frac{e^2}{4\pi \varepsilon_0 R^3} \sqrt{R^2 - b^2} \]

the deflection angle is \( \sim \Delta v_\perp / v_{\parallel} \)

\[ \text{typical } \theta = \frac{4Zb_{\parallel}}{mv_{\parallel}^2} \frac{e^2}{4\pi \varepsilon_0 R^2} \sqrt{R^2 - b^2} \]

\[ \frac{d\theta}{db} = \frac{4Z}{mv_{\parallel}^2} \left( \right) [\sqrt{R^2 - b^2} - \frac{b^2}{\sqrt{R^2 - b^2}}] \rightarrow 0 \text{ for max defl.} \]

\( b \) for max defl. = \( Rb_0 \cdot R/\sqrt{2} \)

\( \text{and } \theta_{\text{max}} = 2Z ( ) R^2 / mv_{\parallel}^2 \)

\[ \overline{\theta} = \int \frac{2\pi b \, db}{\pi R^2} \theta = \frac{Ze^2}{8\varepsilon_0 Rmv_{\parallel}^2} \]

For gold, alpha 5 MeV scattering \( Z=79 \) \( R = 0.2 \text{ nm} \)

Hence \( \overline{\theta} \approx 70 \mu\text{rad} \text{ or } 27' \text{ for 1 atom} \)

For \( n \) atom multiple scattering

\[ \langle \theta \rangle = \sqrt{n} \overline{\theta} \]

For a thin foil \( \langle \theta \rangle \approx 70 \times 10^2 \mu\text{rad} \)
SCATTERING IN A CENTRAL POTENTIAL

conservation of angular momentum:
\[ \vec{L} = \mu (\vec{r} \times \vec{v}) \text{ is const} = \mu r \phi (\vec{r} \times \vec{\phi}) \]
\[ |L| = \mu r^2 \phi \text{ is a constant} \]
\[ ( \text{a}^* ) \quad L = \mu v_0 b \quad \text{where } v_0 = \text{initial velocity} \]
\[ b = \text{impact parameter} \]

conservation of energy
\[ E = \frac{1}{2} \mu v_0^2 \text{ initially} \]
\[ = \frac{1}{2} \mu v^2 + V(r) \text{ at any point on the tray} \]
\[ = \frac{1}{2 \mu} (\dot{r}^2 + r^2 \dot{\phi}^2) \]
\[ ( \text{b}^* ) \quad E = \frac{1}{2} \mu r^2 + \frac{L^2}{2mr^2} + V(r) \]

solving \( \text{a}^* \) and \( \text{b}^* \) gives
\[ \dot{r} = \left[ \frac{2}{\mu} (E_0 - V(r) - \frac{L^2}{2mr^2}) \right]^{1/2} \]
\[ [ c^* ] \]
\[ \dot{\phi} = \frac{L}{mr^2} \]
\[ [ d^* ] \]

In a real experiment it is not possible to follow the path of a single particle, but only measure a deflection. Also, \( b \) cannot in general be determined. The scattering is entirely symmetric about the point of closest approach. The net scattering angle is thus
\[ \chi = \pi - 2\phi(r_{\text{min}}) \quad [\text{i.e. } \phi \text{ at } r = r_{\text{min}}] \]
\[
\phi_{\text{rmin}} = \int_{r_{\text{min}}}^{\phi_{\text{rmin}}} \frac{d\phi}{\frac{dr}{dt}} \cdot dt \cdot dr
\]
\[
= \int_{r=\infty}^{r_{\text{rmin}}} \frac{\phi}{r} dr
\]
\[
\therefore \chi = \pi - 2 \int_{r=\infty}^{r_{\text{min}}} \frac{\phi}{r} dr = \pi - 2 \int_{r_{\text{min}}}^{\infty} \frac{\phi}{r} dr
\]
\[
= \pi - 2 \int_{r_{\text{min}}}^{\infty} \frac{L}{\mu r^2} \left( \frac{2}{\mu \Phi} \left[ E - V(r) - \frac{l^2}{2 \mu r^2} \right] \right)^{1/2} dr
\]

\[
[e^*] \quad L = \mu v_0 b^a \quad \therefore \quad L^2 = \mu^2 v_0^2 b^2 = 2 \mu b^2 E_0
\]

Hence
\[
\chi = \pi - 2b \int_{r_{\text{min}}}^{\infty} \frac{dr}{r^2 \left[ 1 - \frac{b^2}{r^2 - \frac{V(r)}{E}} \right]}
\]

\[r_{\text{min}} \text{ is given by the condition } r(\text{at } r=r_{\text{min}}) = 0\]

since the particle no longer moves towards the scatt. centre. Using \(c^*, d^*\) at and \(e^*\) we get
\[
r_{\text{min}} = \frac{b}{\left[ 1 - \frac{V(r_{\text{min}})}{E} \right]^{1/2}}
\]

If \(b=0\), \(r_{\text{min}}\) is simply given by \(|V(r_{\text{min}})| = |E|\)

\[\text{this value of } r_{\text{min}} \text{ is usually given a special symbol } D : D = \frac{Z^2 e^2}{4\pi \epsilon_0} \left( \frac{1}{2} \mu v_0^2 \right) \quad \text{for the coulomb case}\]
BASIC IDEA OF CROSS-SECTION

First define flux $F$ as:
number of particles incident per unit time per unit area on the target.

Scattering / collision deflects [or alters in some manner] some [or all!] of the incident particles.

Thus some particles are "lost" from the original flux.

The flux lost will be proportional to the incident flux, to the number density of the scatterers and the length of the path in the target. Hence

$$-dF \propto F, n_{\text{target}}, dz$$  \hspace{1cm} (with a $\text{\text{+ve}}$ sign!)

$$\therefore dF = -\sigma F n_t \, dz$$

$$\therefore F = F_0 \exp \left( -\sigma n_t z \right)$$

This is the general \hspace{1cm} \hspace{1cm} gain / absorption / scattering effect on the incident flux
\sigma has dimensions of area, hence the name cross-sec.

We may also define a differential cross-sec, $d\sigma/d\chi$, where $\chi$ is the scattering angle, as follows

DCS = "number of particles emerging at a particular angle per unit incident flux"

$$\frac{d\sigma}{d\chi} = \frac{1}{F} \frac{dN}{d\chi}$$
At any arbitrary point on the trajectory

$$F = \frac{2Z\alpha^2}{4\pi\epsilon_0 r^2} \sin\phi$$

$$\mu \frac{dv}{dt} = \frac{a}{r^2} \sin\phi = D \cdot \frac{1}{2} \mu v^2 \sin\phi$$

Angular momentum is conserved in a central force field, so

$$L = m r^2 \Phi = \frac{m r^2 \Phi}{\mu}$$

for all (\phi, r)

If the particle emerges asymptotically at an angle \(\chi\) w.r.t. the forward direction, then

$$\Phi : [\Phi = 0 \to \Phi = \pi - \chi]$$

over the same trajectory

$$v_1 : [v_1 = 0 \to v_1 = v_0 \sin \chi]$$

Hence

$$\frac{dv_1}{dt} = \frac{a}{\mu r^2} \sin\phi$$

gives us

$$\frac{dv_1}{dt} = \frac{a}{L} \frac{d\phi}{dt} \sin\phi$$

Integrating over the limits above gives

$$v_0 \sin \chi = \frac{a}{\mu v_0^2 b} \left( 1 + \cos \chi \right)$$

$$\cot \chi = \frac{\mu v_0^2 b}{2b} = \frac{2b}{D}$$

$$\chi = 2 \tan^{-1} \frac{a}{\mu v_0^2 b}$$

$$= 2 \tan^{-1} \frac{1}{2} \frac{E_{pot} (r=b)}{E_{kin} (init)}$$

$$= 2 \tan^{-1} \left[ \frac{D}{2b} \right]$$
Some numerical estimates:

\[ E_{\text{kin initial}} = 5 \text{ MeV} \quad q = 2e \quad (\alpha \text{ particle}) \]
\[ Q = 79e \quad (\text{Gold nucleus}) \]

\[ b = 2 \times 10^{-12} \text{ m} \quad \chi = 1.3^\circ \]
\[ = 2 \times 10^{-13} \text{ m} \quad \chi = 13^\circ \]
\[ = 2 \times 10^{-14} \text{ m} \quad \chi = 51^\circ \]

Corresponding cross-sections are \( \pi b^2 \) & are much smaller than the atomic area \( \pi R_o^2 \) since \( R_o \sim 10^{-10} \)

That is, large angle scattering, which occurs for small impact parameters, is very unlikely.

The scattering process is azimuthally symmetric.
The differential cross-section is defined by the following.

[A] Flux of particles is defined as the number of particles incident per unit area per unit time – denoted by \( F \)

[B] The number of particles is incident on a target with impact parameters between \( b \), \( b + db \) – denoted by \( dN(b) \)

is given by

\[ dN(b) = F \cdot 2\pi b \cdot db. \]

[C] From the scattering equation we know

\[ \cot \chi/2 = \frac{2b}{D} \quad \text{where} \quad D = \frac{ZZ'}{4\pi\varepsilon_0 \left( \frac{1}{2} \mu_0^2 \right)} \]

which gives

\[ -\frac{1}{2} \csc^2 \frac{\chi}{2} = \frac{2}{D} \frac{db}{dx} \]

Using this in [B] yields

\[ dN(b) = F \cdot 2\pi b \cdot \frac{D}{4} \frac{\csc^2 \frac{\chi}{2}}{2} \cdot dx \]

- sign dropped because it has no relevance to particle counting.
Differential cross-section is defined as

"number of particles emerging at a particular angle for unit incident flux"

\[
\frac{d\sigma}{dx} = \frac{1}{F} \frac{dN}{dx}
\]

[Equation 1]

This gives

\[
\frac{dN}{dx} = F \cdot 2\pi b \cdot \frac{D}{4} \cdot \csc^2 \frac{x}{2}
\]

Hence

\[
\frac{d\sigma}{dx} = 2\pi b \cdot \frac{D}{4} \cdot \csc^2 \frac{x}{2}
\]

Using \( \cot \frac{x}{2} = \frac{2b}{D} \) we get

\[
\frac{d\sigma}{dx} = \frac{\pi D^2}{4} \cdot \frac{\cos \frac{x}{2}}{\sin^2 \frac{x}{2}}
\]

If the scattering is azimuthally symmetric

\[
d\Omega = 2\pi \sin x \, dx
\]

\[
= 4\pi \sin^2 \frac{x}{2} \cos \frac{x}{2} \, dx
\]

From which it follows that

\[
\frac{d\sigma}{d\Omega} = \frac{D^2}{16} \frac{1}{\sin^4 \left( \frac{x}{2} \right)}
\]

In terms of particle flux and number of scattered particles emerging at a particular angle we have

\[
\frac{dN}{d\Omega} = F \frac{d\sigma}{d\Omega}
\]

The Rutherford scattering cross-section diverges as \( x \to 0 \). This corresponds to large values of \( b \). In the real experiment, however, \( 0 < b < \frac{a}{2} \) where \( a \) is the lattice const.
The total number of particles scattered into a particular solid angle is given by

\[ \frac{\Delta N}{\Delta \Omega} = \frac{d\sigma}{d\Omega} \cdot F \cdot n_{\text{target}} \cdot \frac{\text{cross-sec}}{\text{Area of beam} \times \text{thk}} \text{ of target} \]

number of target atoms intercepted

The number of target nuclei per unit area of the foil is given by

\[ \frac{\Delta N}{\Delta \Omega} = \frac{F \cdot p \cdot S}{A_m \cdot p} \cdot \frac{1}{\text{atomic number}} \cdot \frac{d\sigma}{d\Omega} \]

In the practical case, \( \Delta \Omega = \Delta S/r^2 \) where \( \Delta S \) is the surface area of the detector placed at a distance \( r \) from the foil.