

## §8.1 Atoms and Molecules

We now take for granted that matter is made out of atoms, in turn made of \_\_\_\_\_, but this understanding is fairly new.

There was early Greek speculation on matter being composed of basic units called “atoms,” attributed to Leucippus(?) (~500BCE) and Democritus (~450BCE), but they didn’t have the necessary observations to confirm or disprove their hypothesis.

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### §8.1.1 History

1738: Daniel Bernoulli proposed that the macroscopic properties of gases, such as pressure and temperature, could be explained if we assumed that gases consisted of basic particles, molecules, that were in rapid motion.

Pressure arose from bouncing of molecules off container walls, temperature from kinetic energy.

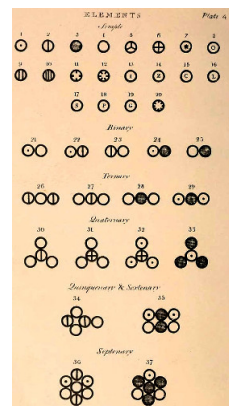
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1803: John Dalton noted chemical compounds appear to consist of integral ratios of elements. He advanced the theory that this was because elements came in basic units, atoms.

A study of tin oxides showed fixed ratios of the masses of tin to oxygen. This could be explained if tin and oxygen were made of atoms with one tin atom combining with either one or two oxygens.

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Dalton's atoms, and possible molecules



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At the time, the distinction between elements and compounds was not completely clearcut (Dalton's chart lists primary, secondary, etc., “elements”), nor was there always a distinction between atoms and molecules.

The two terms were often used interchangeably.

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1811: Avogadro proposed that equal volumes of gases at the same temperature and pressure contain equal numbers of molecules.

It followed that the relative molecular weights of any two gases are the same as the ratio of the densities of the two gases under the same conditions of temperature and pressure.

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Avogadro linked the macroscopic behavior of gases to their microscopic structure. He said that the volume of a gas at a given pressure and temperature is proportional to the number of atoms or molecules, regardless of the type of gas.

His proportionality constant, what we now call Avogadro's Number, is  $6.022 \times 10^{23}$ , giving an estimate of the smallness of molecules.

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1859: James Clerk Maxwell used ideas from statistics and probability to produce a formula that gave the distribution of molecular velocities in a gas. His formula (with later input from Boltzmann) said that the fraction of molecules in a gas with speeds between  $v$  and  $v + dv$  is

$$f(v) = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{1}{2}mv^2 \frac{1}{kT}}$$

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In 1866, Maxwell read a paper to the Royal Society:

“Theories of the constitution of bodies suppose them either to be continuous and homogeneous, or to be composed of a finite number of distinct particles or molecules.

“In certain applications of mathematics to physical questions, it is convenient to suppose bodies homogeneous . . . , but I am not aware that any theory of this kind has been proposed to account for the different properties of bodies. Indeed the properties of a body supposed to be a uniform plenum may be affirmed dogmatically, but cannot be explained mathematically.

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“Molecular theories suppose that all bodies, even when they appear to our senses homogeneous, consist of a multitude of particles, or small parts the mechanical relations of which constitute the properties of the bodies. Those theories which suppose that the molecules are at rest relative to the body may be called statical theories, and those which suppose the molecules to be in motion, even while the body is apparently at rest, may be called dynamical theories.”

At this stage, molecular/atomic theories of matter were regarded more a calculational device.

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1905: Einstein analyzed Brownian motion to show that the observed motion of pollen grains in water could directly be attributed to molecules of water in motion.

This is considered the first “direct” evidence that molecules do, in fact, exist, and that matter is indeed composed of basic particles.

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**§8.2 The Constituents of Atoms**

By the late 1800s, the distinction between atoms and molecules appears to have been understood.

Atoms were considered indivisible units of the chemical elements.

Yet, just as this was established, there were hints that the truth lay deeper.

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It was known that matter contained electric charge, liberated under the right conditions (applying voltages, for instance).

It was known that the amount of charge that could be released was proportional to mass, suggesting fixed amounts of charge/mass in elements.

13 The charge/mass ratio of the Hydrogen atom after negative charge was stripped from it was known.

14 1897: J.J. Thomson analyzed the nature of cathode rays: radiation released when gases at low pressure are subjected to voltages.

He passed the rays through combined electric and magnetic fields, and by adjusting each he worked out several properties of these rays.

Properties of cathode rays:

- They carried negative charge.
- They had mass.
- Rays from different gases all had the same charge/mass ratio.
- This ratio was  $\sim 1000$  times smaller than for Hydrogen.

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Thomson had discovered the \_\_\_\_\_, and had shown that particles less massive than the least massive atom could exist.

Later experiments by Thomson (he dropped electrons through charged clouds) established bounds on the charge of the electron:

$$1.1 \times 10^{-19} \text{ C} < |e| < 2.3 \times 10^{-19} \text{ C}$$

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1909: Robert Millikan and Harvey Fletcher refined Thomson's cloud chamber technique, using charged oil drops, to determine that all electrons have the same charge. The value they got was  $-1.592 \times 10^{-19} \text{ C}$ .

The value as of May 2019 is *exactly*  
 $-1.602176634 \times 10^{-19} \text{ C}$ .

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### §8.3 The Structure of Atoms

Once it was accepted that atoms contained sub-constituents, electrons, the question arose: how is the positive charge in an atom arranged? In other words, what is the structure of an atom?

There were several factors to consider.

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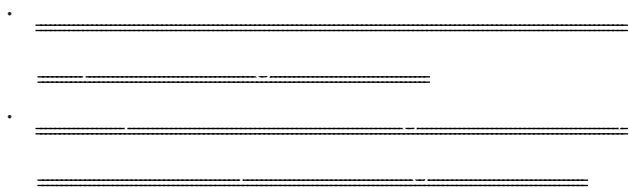


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- A normal uncharged atom had to be in stable equilibrium between



- \_\_\_\_\_ also had to be in stable equilibrium.

19 ○ Spectral lines needed to be explained.

A popular model of the atom at the time was the “plum pudding” model (Thomson et al). It had the positive charge continuously distributed, with electrons studded in it, like raisins in a pudding.

The model was stable, but it could not explain spectral lines.

Probing inside an atom was a topic of interest.

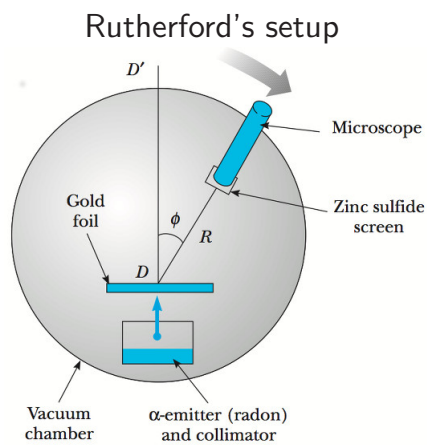
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Rutherford, in collaboration with Geiger, had investigated what happens if you shoot Helium nuclei (“alpha particles”) at thin sheets of gold foil.

Gold can be made into sheets as thin as  $4 \times 10^{-5}$  cm.

When viewed close to the incident direction, they’d found, as expected, small deflections.

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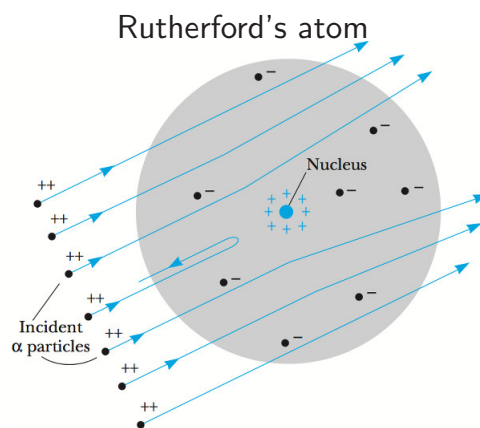


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A young researcher in the lab, Ernest Marsden needed a research project, so Rutherford offhandedly suggested he look at whether any alpha particles were deflected at large angles.

To the shock of all three, Marsden reported back that some alpha particles were deflected by angles well over  $90^\circ$ .

23 Rutherford soon realized what that meant.



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Rutherford proposed a model of the atom with a positively charged nucleus, surrounded by negatively charged electrons.

Because the charges on positive ions were known to be integral multiples of those on a Hydrogen ion (whose charge was exactly  $|e|$ ), Rutherford proposed that the nucleus contains positively charged particles that he called protons.

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A proton had an equal (in magnitude) but opposite charge as an electron, but was around 2,000 times more massive.

Rutherford also studied the kinetic energies of the deflected alpha particles far from the scattering, and equated that to their initial KE plus the potential energy at the distance of closest approach.

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The PE is

$$k \frac{(Ze)(2e)}{d_{\min}},$$

where  $Z$  is the atomic number (total positive charge in units of  $|e|$ ), and  $k$  here is Coulomb's constant.

Rutherford was able to estimate the size of the atomic nucleus at around  $10^{-14}$  m.

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Questions for Rutherford's atom:

- Atomic nuclei had charges that were  $Z$  times that of Hydrogen, but masses that were typically  $2Z$  or more the mass of a Hydrogen nucleus. What accounted for the extra mass?
- What keeps the nucleus together?
- How does the model account for spectral lines?

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Rutherford answered the first question by hypothesizing that there were neutral "particles" in a nucleus that accounted for the missing mass. he called them neutrons. But he thought of neutrons as tightly bound electron-proton pairs.

He answered the second by supposing there were complicated electrostatics at work.

29 He had no explanation for spectral lines.

### §8.4 Spectral lines

Several decades of observations had indicated that atoms of pure elements radiate (and absorb) energy only at specific sets of wavelengths, each characteristic of the element.

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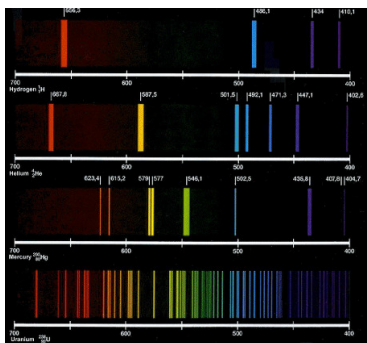
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For each value of  $n_f$ , the different allowed values of  $n_i$  gave rise to a series of spectral lines, named after the person who first studied them:

Lyman (uv):  $\sim 1906$   $n_f = 1$   $n_i = 2, 3, 4 \dots$

Balmer (vis-uv):  $\sim 1880$   $n_f = 2$   $n_i = 3, 4, 5 \dots$

Paschen (ir):  $\sim 1908$   $n_f = 3$   $n_i = 4, 5, 6 \dots$

and so forth.

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In 1913, Niels Bohr proposed a model of the H atom in which, he asserted, electrons were subject to new laws outside classical physics:

- 1) Although accelerating, they would not radiate.
- 2) They only occupied fixed energy levels (borrowing Planck's idea of resonators at fixed energies).
- 3) They could only emit or absorb quanta of fixed energy (borrowing Einstein's idea of photons).

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Emissions from Hydrogen had been particularly studied and the emission wavelengths had been empirically established to be given from

$$\frac{1}{\lambda} = R \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right),$$

$n_f = 1, 2, 3 \dots$ ,  $n_i = n_f + 1, n_f + 2 \dots$  and

$R = 1.097 \times 10^7 \text{ m}^{-1}$ , is "Rydberg's constant."

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### §8.5 The Bohr Hydrogen Atom

Rutherford and Thomson had considered what negatively charged electrons do in atoms.

They cannot stay immobile because \_\_\_\_\_  
 \_\_\_\_\_

They cannot orbit the nucleus because they are charged and they would \_\_\_\_\_  
 \_\_\_\_\_

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In greater detail, this is what Bohr asserted of the Hydrogen atom:

A] The electron moves in circular orbits about the proton under the influence of the Coulomb force of attraction.

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B] Only certain orbits are stable. In these, the electron does not radiate. The energy is fixed (stationary in time) in these orbits, and ordinary classical mechanics may be used to describe the electron's motion in them.

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C] Radiation is emitted when an electron jumps from a more energetic initial state ( $E_i$ ) to a less energetic ( $E_f < E_i$ ). This "jump" cannot be visualized classically. The frequency  $f$  of the photon emitted is independent of the frequency of the orbital motion and is given by a quantum condition

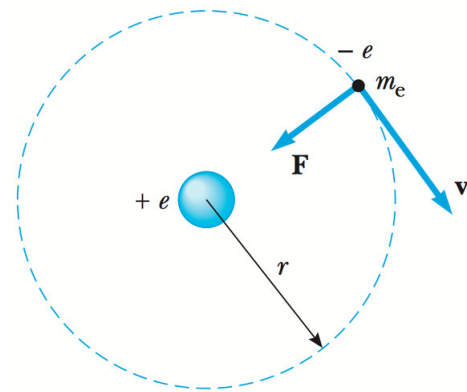
$$E_i - E_f = hf.$$

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D] The allowed electron orbits are determined by an additional quantum condition on the orbital angular momentum: the allowed orbits are those for which the electron's orbital angular momentum about the nucleus is an integral multiple of  $\hbar = h/2\pi$ :

$$m_e v r_n = n\hbar, \quad n = 1, 2, 3, \dots$$

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§8.5.1 Bohr orbits

The centripetal force on the electron in a stable orbit of radius  $r$  is provided by Coulomb's law of electrostatic attraction. Therefore,

$$\begin{array}{ccc} & = & \\ \nearrow & & \nwarrow \\ \text{Centripetal force} & & \text{Coulomb's law} \end{array}$$

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- (1) From this what is the electron KE (non-SR)?
- (2) Eliminate  $v$  above using Bohr's angular momentum quantum condition.

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(3) Solve for  $r_n$ .

$$r_n =$$

These are the allowed orbital radii.

(4) Find  $r_1 = \hbar^2 / (m_e k e^2)$ .

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§8.5.2 Bohr energy levels

(5) What is the total energy,  $E_n$ , of an electron in a Bohr orbit of radius  $r_n = n^2 r_1$ ?

$$E_n = \text{KE} + \text{PE} =$$

(6) Calculate a numerical value for  $k e^2 / 2 r_1$  in eV.

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So, the allowed energy levels of Hydrogen are

$$E_n \approx -\frac{13.6}{n^2} \text{ eV}, \quad n = 1, 2, 3 \dots$$

The values for  $n$  are examples of \_\_\_\_\_ integers that label the allowed discrete values of energy, angular momentum, etc.

For the energy quantum numbers above,  $n = 1$  is called the ground state.

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The energy levels for which  $n = 2, 3 \dots$  are called excited states.

(7) What are these levels for  $n = 2$  and  $n = 3$  in Hydrogen?

$$E_2 =$$

$$E_3 =$$

46

The limit  $n \rightarrow \infty$  corresponds to  $E_\infty = 0$ ; the value of  $E_\infty - E_1 = 13.6 \text{ eV}$  is the minimum energy needed to remove an electron from Hydrogen.

It is called the “ionization energy” and the value the Bohr model predicted agreed with experiment.

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§8.5.3 Bohr energy-level transitions

Bohr had asserted that in a transition from an energy level  $E_i$  to a lower one  $E_f$ , the radiation emitted would have a frequency  $f$  given by

$$hf = E_i - E_f.$$

Writing this in terms of wavelength ( $f = c/\lambda$ ),

$$\frac{1}{\lambda} = \frac{1}{hc} (E_i - E_f).$$

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Let  $E_i$  and  $E_f$  be energy levels with quantum numbers  $n_i$  and  $n_f$ , respectively.

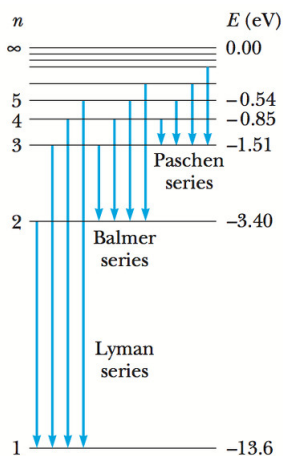
(8) Using

$$E_n = -\frac{ke^2}{2r_1} \frac{1}{n^2}$$

work out an expression for  $1/\lambda$ .

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The origin of Hydrogen spectral series in the Bohr atom.



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(10) What is the essential change needed in the discussion above to accommodate such ions?

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(9) Use

$$\frac{ke^2}{2r_1} \approx 13.6 \text{ eV} = 2.176 \times 10^{-18} \text{ J.}$$

to calculate  $\frac{ke^2}{2r_1 hc}$ .

in good agreement with the value of  $R$  in slide 32.

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### §8.6 The Bohr Model and Other Atoms

Bohr was able to extend his model to several other *single-electron ions*.

These are atoms with a nucleus of charge  $Ze$ , where  $Z$  is the atomic number, and a single electron of charge  $-e$ .

For example, ionized Helium,  $\text{He}^+$ , with  $Z = 2$ .

52

(11) What are  $r_{nZ}$ , the orbital radii for such an ion, in terms of  $r_1$ , the value for H? (See slide 43.)

(12) What are  $E_{nZ}$ , the energy levels? (Slide 44.)

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#### ADDITIONAL NOTES

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At the time there were spectral lines observed in radiation from the sun that empirically fit

$$\frac{1}{\lambda} = R \left( \frac{1}{(n_f/2)^2} - \frac{1}{(n_i/2)^2} \right).$$

which did not match known Hydrogen lines.

Understanding their origin was a puzzle.

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(13) Is there a  $Z$  that might give the right  $E_{nZ}$ ?

This was a huge triumph for the Bohr theory.

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§8.6.1 Multi-electron atoms

Here, Bohr's attempt to extend his theory faltered.

He was able to offer arguments for how electrons get added to various energy levels, and to explain some chemical properties of different atoms, but a full theory eluded him.

Part of the problem is that the classical three-(and multi-)body problem is itself unsolved.

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§8.7 **The Correspondence Principle**

Bohr built his theory by fiat, simply asserting that small systems obeyed separate laws from large ones.

He offered, however, a guiding principle for how quantum and classical theories should fit together, the correspondence principle: *Large quantum numbers should correspond to large systems, and so to classical physics.*

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Consider orbital angular momentum of an electron (circular orbit of radius  $r$ ),  $L$ , as an example:

$$L = m_e v r \quad \text{where} \quad v = \omega r.$$

It is possible to show that  $dE/dL = \omega$ . In both equations  $\omega$  is the *orbital* frequency.

But we also know, loosely, that  $dE = hf = \hbar\hat{\omega}$ , where  $\hat{\omega}$  is the angular frequency,  $f/2\pi$ , of the emitted radiation.

59

The correspondence principle asserts that for large  $n$ ,  $\omega = \hat{\omega}$ .

In other words, for large  $n$ ,

$$dE = \omega dL = \omega \hbar$$

or  $dL = \hbar$ , and it is the smallness of this that does not allow us to see the quantization of angular momentum in large-scale life.

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