Phys 3140 : Quantum Mechanics

2021

[over the course of the 19th century it became increasingly clear that all matter consists of combinations of about 100 different elements, in the form of individual atoms.

The size and masses of these atoms was unknown, and there remained some skepticism about their existence, most famously by Ernst Mach, but their relative masses were known, and this together w/ their chemical properties allowed construction of the periodic table by Mendeleev.]

[Excited atoms emit electromagnetic radiation (eg. by heating or passing a current through them the overhead fluorescent tubes contain Hg atoms which radiate in visible + UV range)

Moreover, each type of atom emits a set of characteristic discrete frequencies]

Spectrum: the set of characteristic electromagnetic frequencies/wavelengths emitted or absorbed by an element

[show image of Balmer: 656 nm, 486, 434, 410, ...]

[thick tables were compiled, allowing for identification]

Balmer (1885) and Rydberg (1888) discovered an empirical formula for the hydrogen spectrum

$$f = (3.29 \times 10^{15}\ Hz)\left(\frac{1}{n^2} - \frac{1}{m^2}\right)$$

n, m = integers
$m > n$

[show image of hydrogen]

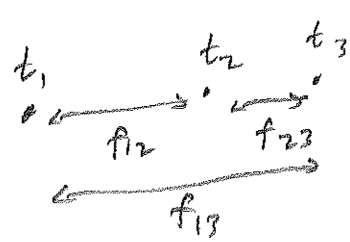
$n=1, m \geq 2$	Lyman series	(UV)	1906
$n=2, m \geq 3$	Balmer series	(visible)	1885
$n=3, m \geq 4$	Paschen series	(IR)	1908
	⋮		

[Brackett 1922 $n=4$
Pfund 1924 $n=5$
Humphreys 1953 $n=6$

No analogous simple formulas for other elements, but Ritz (1908) discovered the "combination principle"

Each atom has a series of "terms" t_n and the spectral frequencies are all given by the difference of two terms

$$f_{mn} = t_m - t_n$$



$\Rightarrow$ certain relations among frequencies, eg $f_{13} = f_{12} + f_{23}$

No explanation was known for these regularities atom = "uncuttable" but not so!

J.J. Thomson (1897) discovers first subatomic particle using a cathode ray tube.

[evacuated glass tube w/ 2 electrodes, called cathode + anode. Apply voltage, rays were seen streaming from the cathode]

"cathode rays" = electrons

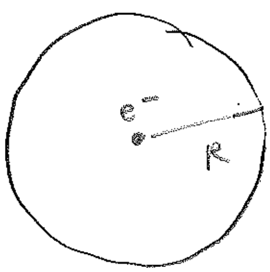
measurement of deflection of cathode rays by electric + magnetic fields showed that their mass ~ $\frac{1}{2000}$ hydrogen [lightest known atom]

[Before flat screen displays, TV's + computer monitors were called CRT's. Beam of electrons steered to different points on glass surface coated w/ phosphors that would glow

[Thomson concluded that cathode rays were constituents of atoms]

Thomson model of atom ("plum pudding model"):
pointlike negative electrons embedded in a positive jelly

Hydrogen: single e^- in equilibrium at center of uniform density positive sphere



if displace e^- $\Rightarrow$ SHM
oscillation frequency depends on m_e + R
[HW]

classical EM theory $\Rightarrow$ an oscillating charge emits EM waves w/ same frequency

[if set this equal to eg one of Balmer frequencies and solve for R $\rightarrow$ amazingly close to known size of hydrogen atom]

Problem: only one frequency rather than whole spectrum

More complicated atoms could have multiple frequencies but do not explain the Ritz principle

Rutherford (1911) disc. nucleus by bombarding gold atoms w/ α particles
($\Rightarrow$ positive charge concentrated in point-like mass)

Rutherford proposes (as alternative to Thomson model)
a planetary model of atom, w/ electrons orbiting the nucleus
[Image: AEC symbol]

hydrogen

Coulomb $|F| = \frac{Ke^2}{r^2}$ $\quad K = \frac{1}{4\pi\epsilon_0}$

[$Ke^2 = 2.307E-28$ J·m]

Assume electron in a circular orbit w/ $a = \frac{v^2}{r}$

Then $F = m_e a \Rightarrow \frac{Ke^2}{r^2} = \frac{m_e v^2}{r}$

[T = kinetic
V = potential ~~energy~~]

Velocity
① $v \sim r^{-1/2}$

Energy $E = T_e + V$ (ignore T_p because $m_p \gg m_e$)

$V = -\frac{Ke^2}{r}$

$T_e = \frac{1}{2} m_e v^2$ (assume non relativistic: check later)

$\sim \frac{1}{r}$

② $E \sim -r^{-1}$

Any (negative) energy is allowed

Orbital angular momentum $\vec{L} = \vec{r} \times \vec{p}$

circular $\Rightarrow L = m_e v r$

③ $L \sim r^{1/2}$

Orbital frequency of electron $f \sim \frac{v}{r}$

④ $f \sim r^{-3/2}$

[HW: derive exact expressions]

classical EM theory $\Rightarrow$ an orbiting charge
emits EM wave w/ same frequency (or multiples of)
as the orbital frequency

$f_{orb} \sim r^{-3/2}$

As charge radiates, it loses energy & r decreases
continuously $\Rightarrow$ continuous, not discrete, spectrum

∴ Eventually it spirals into nucleus

$\Rightarrow$ atom is unstable!

[Physicists were not impressed]

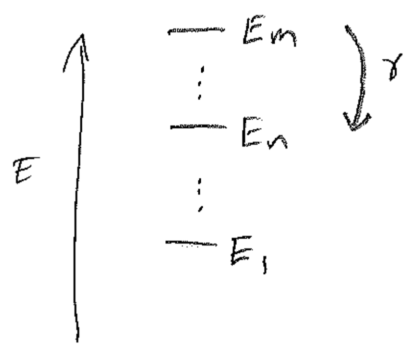
[All of this has been using classical physics

Quantum physics

Planck (1900) + Einstein (1905) propose quantization of EM radiation (blackbody radiation, photoelectric effect)

Light of frequency f consists of discrete photons w/
$E = hf$ $\qquad h$ = Planck's const = 4.14×10^{-15} eV·s.

Bohr (1913) explains Ritz's principle by postulating
(1) the energies of atoms can only have certain discrete values,
and (2) photons are emitted/absorbed in transitions between allowed energies.



Energy conservation

$$E_m = E_n + E_{photon}$$

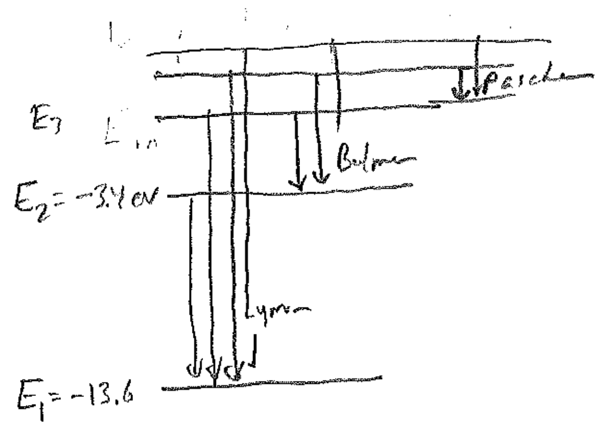
$$f_{mn} = \frac{E_{photon}}{h} = \left(\frac{E_m}{h}\right) - \left(\frac{E_n}{h}\right)$$

"terms"

For hydrogen,

$$E_n = -h \cdot (3.29 \times 10^{15}\,\mathrm{Hz}) \frac{1}{n^2}$$

$$= -\frac{(13.6\,\mathrm{eV})}{n^2}$$



To explain hydrogen energy levels

Bohr postulates that orbital angular momentum must be quantized

$L = n\hbar \qquad n = \text{integer}$

$\hbar$ = some constant related to Planck's constant

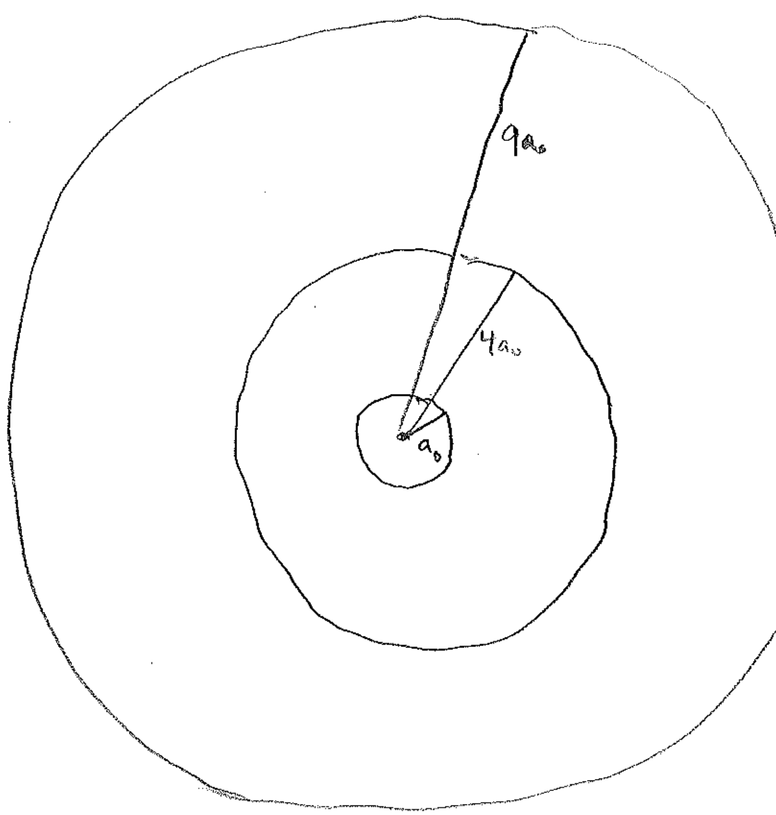
(It will turn out that $\hbar = \frac{h}{2\pi}$, but pretend we don't know)

All other parameters of Rutherford model are determined by L.

Allowed radii

recall $L \sim r^{1/2}$ so $\boxed{r_n = \left(\frac{\hbar^2}{m_e K e^2}\right) n^2}$ [HW]

min. radius r_1 = Bohr radius $a_0 = \frac{\hbar^2}{m_e K e^2} \approx \frac{1}{2}\text{Å} \quad (1\text{Å} = 10^{-10}\,\text{m})$



N.B: size of nucleus $\sim 10^{-15}\,\text{m} = 1\,\text{fm}$ much smaller than a_0

Allowed velocities

$$v_n = \left(\frac{Ke^2}{\hbar}\right)\frac{1}{n}$$ [HW: show]

Define fine structure constant $\alpha \equiv \underbrace{\frac{Ke^2}{\hbar c} \approx \frac{1}{137}}_{\text{memorize}}$

$$v_n = \frac{\alpha c}{n}$$

Non rel. assumption valid since $\frac{v}{c} = \frac{\alpha}{n} \ll 1$

[1% speed of light]

Allowed energies

$$E_n = -\underbrace{\left(\frac{m_e K^2 e^4}{2\hbar^2}\right)}_{13.6\,eV}\frac{1}{n^2}$$ [HW: show]

Allowed frequencies of orbital motion

$$f_n = \left(\frac{m_e K^2 e^4}{2\pi \hbar^3}\right)\frac{1}{n^3}$$ [HW: show]

According to classical EM theory, an orbiting electron will emit EM waves whose frequency equals the orbital frequency

$$f_n = \left(\frac{m_e K^2 e^4}{2\pi \hbar^3}\right)\frac{1}{n^3}$$

This disagrees w/ the known spectrum of hydrogen

According to Bohr, the frequencies of the emitted waves are determined by the energies of the photons emitted as the atom transitions between allowed energy levels

$$f_{mn} = \frac{E_{photon}}{h} = \frac{E_m - E_n}{h} = \frac{1}{h}\left(\frac{m_e K^2 e^4}{2\hbar^2}\right)\left(\frac{1}{n^2} - \frac{1}{m^2}\right)$$

Correspondence principle: predictions of the quantum theory must agree w/ those of classical physics when quantum #s are large

Thus: a photon emitted in a transition from state n to $n-1$ must have frequency approx. equal to orbital frequency of electron in state n as $n \to \infty$.

[Hw: show]

Bohr used this to show that $\hbar = \frac{h}{2\pi} = 1.0546 \times 10^{-34}$ J.s

and thus $f_{mn} = \underbrace{\frac{m_e K^2 e^4}{4\pi \hbar^3}}_{3.29\times10^{15}\text{ Hz}}\left(\frac{1}{n^2} - \frac{1}{m^3}\right)$ in precise agreement w/ known hydrogen spectrum!

$$\left[\quad \frac{1}{n^2} - \frac{1}{(n-1)^2} \approx \frac{2}{n^3} \quad\right]$$

Despite the fact that [the Bohr model, starting from assumption]
assuming

$L = n\hbar \qquad n \in \mathbb{Z}$

gives the correct [hydrogen energy levels (in non-rel. approx.)]

$E_n = -\frac{13.6\text{ eV}}{n^2}$

the Bohr model is fundamentally incorrect.

① Electrons do not travel in circular (or elliptical) orbits but are described by 3dim'l probability distributions

② $L \neq n\hbar$

It is true that orb. ang mom. is quantized

$L = l\hbar \qquad l \in \mathbb{Z}$

but in general l ranges from 0 to $n-1$.
[we'll see this later]

Example: ground state $(n=1)$ corresponds to a spherically symmetric probability distribution w/ angular momentum $l = 0$.

Nevertheless, Bohr model is useful for developing intuition + for rough estimates

[e.g.: Bohr radius a_0 is mean value of electron radius]

Mnemonics

Memorize $\alpha = \frac{Ke^2}{\hbar c} \sim \frac{1}{137}$

mnemonic $\alpha = \beta$ where $\beta = \frac{v}{c}$

$\Rightarrow \boxed{v_1 = \alpha c} \sim \frac{c}{137} = \frac{Ke^2}{\hbar}$

$E_1 = -\frac{1}{2}mv^2 = \boxed{-\frac{1}{2}mc^2\alpha^2} \sim \frac{511,000}{2(137)^2} \sim 13.6$

$V = -2T$

$= -\frac{mKe^2}{2\hbar^2}$

virial

$V \sim r^n$

$n\langle V\rangle = 2T$

so $n = -1$

$\Rightarrow \langle V\rangle = -2T$

$L = mvr$ so $a_0 = \frac{\hbar}{mv} = \frac{\hbar}{\alpha mc} = \frac{\text{Compton}}{\alpha}$

$= \frac{\hbar^2}{mKe^2}$

Compton $\frac{\hbar}{mc} = \frac{\hbar c}{mc^2} = \frac{197 \text{ meV fm}}{0.511 \text{ fm}} \sim 400$ fm