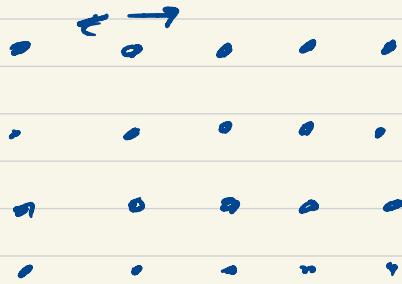


4 - Demise of Classical Physics

Apply same ideas to a solid.

Simplest possible model: perfect, ordered array of atoms



Each atom can move about its central point. Assume

Hooke's Law: $F = -kx$

k : spring constant

focus on 1-D

$$F = m\alpha = m \frac{d^2x}{dt^2} = -kx$$

$x(t)$, displacement vs time

$$\frac{d^2x}{dt^2} = -\left(\frac{k}{m}\right)x \quad \text{what is } x(t)?$$

$$x(t) = c_1 \sin c_2 t$$

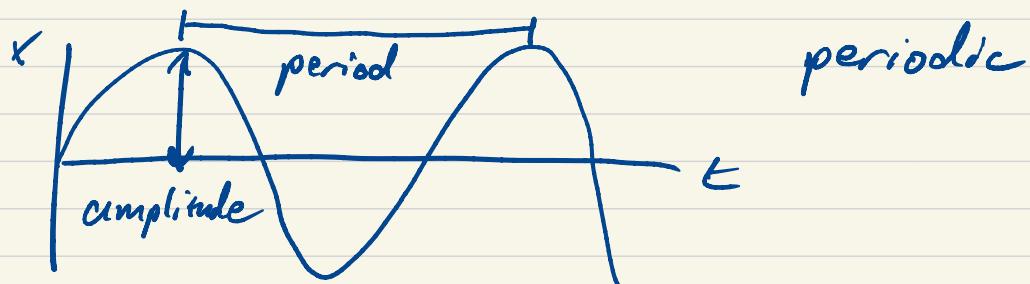
$$\frac{dx}{dt} = c_1 c_2 \cos c_2 t$$

$$\frac{d^2x}{dt^2} = -c_1 c_2^2 \sin c_2 t$$

$$-c_1 c_2^2 \sin c_2 t = -c_1 \left(\frac{k}{m}\right) \sin c_2 t$$

$$c_2^2 = \frac{k}{m} \quad c_2 = \left(\frac{k}{m}\right)^{1/2}$$

$$x(t) = c_1 \sin\left(\frac{k}{m}\right)^{1/2} t$$



$$\nu = \frac{1}{2\pi} \left(\frac{k}{m}\right)^{1/2} = \frac{\omega}{2\pi} \quad T = \frac{1}{\nu}$$

c_1 determined by initial condition
Called amplitude, A

$$x(t) = A \sin \omega t$$

Called a standing wave

Characteristic of a harmonic oscillator

Kinetic energy?

$$KE = \frac{1}{2} m v^2 = \frac{1}{2} m \left(\frac{dx}{dt} \right)^2$$

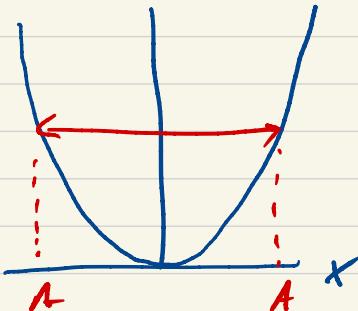
$$\frac{dx}{dt} = A \omega \cos \omega t$$

$$KE = \frac{1}{2} m A^2 \omega^2 \cos^2 \omega t$$
$$= \frac{1}{2} k A^2 \cos^2 \omega t$$

Potential energy?

$$F = -\frac{dv}{dx} = -kx \rightarrow V = \frac{1}{2} k x^2$$

parabolic potential



$$PE = \frac{1}{2} kx^2 = \frac{1}{2} kA^2 \sin^2 \omega t$$

$KE + PE$ out of phase

$$\begin{aligned} \text{Total} &= KE + PE \\ &= \frac{1}{2} kA^2 (\cos^2 \omega t + \sin^2 \omega t) \xrightarrow{\text{1}} \\ &= \frac{1}{2} kA^2 \end{aligned}$$

total energy depends only on
amplitude and characteristic k

What's expected energy at some T ?

$$\begin{aligned} \langle E \rangle &= \frac{\iint E(x, \dot{x}) e^{-E(x, \dot{x})/kT} dx d\dot{x}}{\iint e^{-E(x, \dot{x})/kT} dx d\dot{x}} \\ &= \iint \left(\frac{1}{2} m\dot{x}^2 + \frac{1}{2} kx^2 \right) \dots \end{aligned}$$

$$\langle KE \rangle + \langle PE \rangle$$

$$\frac{1}{2} k_B T + \frac{1}{2} k_B T = \underline{\underline{k_B T}}$$

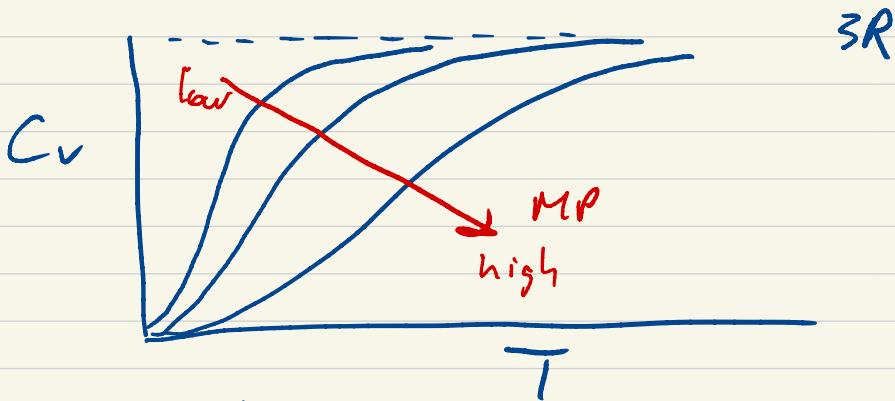
In 3-D, get $3 \cdot k_B T$ (per atom)
 $3 \cdot RT$ (per mole)

Energy linear in $T \rightarrow$

$$C_v = 3R$$

"Law" of Dulong + Petitte

How do we do?



Pure substances all follow the "law" at high T , all $\rightarrow 0$ as $T \rightarrow 0$.

Crap !! What happened?

No obvious, or unobvious, solution in classical physics.

1907 Einstein

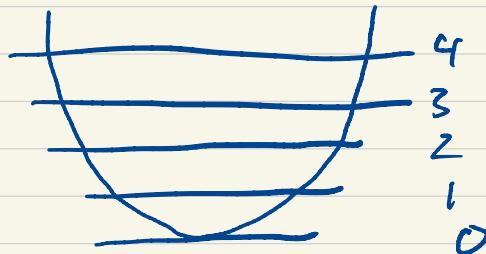
What if we said that for these vibrating atoms

$$\epsilon \propto A^2 \rightarrow \epsilon \propto \gamma$$

Also, what if only discrete, quantized values of ϵ were possible:

$$\epsilon = n\hbar\nu \quad n=0, 1, 2, \dots$$

WTF!!



The vibrating things are quantized

probability to have energy ϵ_n ?

$$P(\epsilon_n) = \frac{e^{-n\hbar\nu/kT}}{\sum_{n=0}^{\infty} e^{-n\hbar\nu/kT}}$$

$$\begin{aligned}
 \sum_i e^{-ih\nu/kT} &= \sum_{i=0}^{\infty} (e^{-h\nu/kT})^i \\
 &= \sum_{n=0}^{\infty} c^n \quad \text{geometric series} \\
 &= \frac{1}{1-c} \quad c < 1 \\
 &= \frac{1}{1-e^{-h\nu/kT}}
 \end{aligned}$$

$$P(E_n) = e^{-nh\nu/kT} (1 - e^{-h\nu/kT})$$

$$\begin{aligned}
 \langle E \rangle &= \sum_n n h\nu P(E_n) \\
 &= \frac{h\nu e^{-h\nu/kT}}{1 - e^{-h\nu/kT}}
 \end{aligned}$$

$$\boxed{\langle E \rangle = \frac{h\nu}{e^{h\nu/kT} - 1}}$$

$$C_v = \frac{d\langle E \rangle}{dT} = R \left(\frac{h\nu}{kT} \right)^2 \frac{e^{h\nu/kT}}{(e^{h\nu/kT} - 1)^2}$$

Yech!!

$$\lim_{T \rightarrow 0} C_v = 0 \quad \text{exponential in denominator dominates}$$

$$\begin{aligned} \lim_{T \rightarrow \infty} C_v &= R \left(\frac{h\nu}{kT} \right)^2 \frac{1 + h\nu/kT + \dots}{\left(1 + \frac{h\nu}{kT} - 1 - \dots \right)^2} \\ &\approx R \left(\frac{h\nu}{kT} \right)^2 \frac{1}{\left(\frac{h\nu}{kT} \right)^2} \\ &= R !! \end{aligned}$$

In 3D, $3R !!$

Gives exactly right functional behavior. High melting have high ν (or $\frac{k}{m}$), long tail; low melting vice versa.

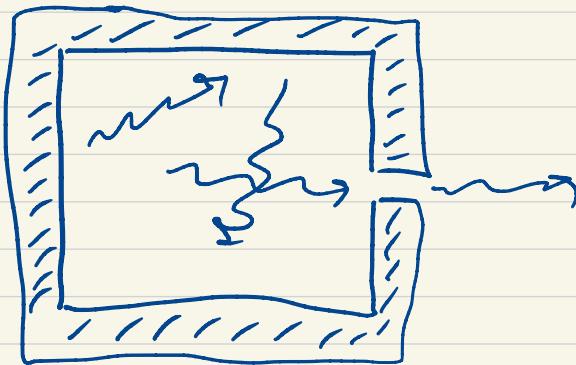
This works!! (well, almost. Debye had to fix a little.)

Something about those vibrations is quantized. But what? How?

Einstein had not pulled all this from thin air.

Blackbody radiator

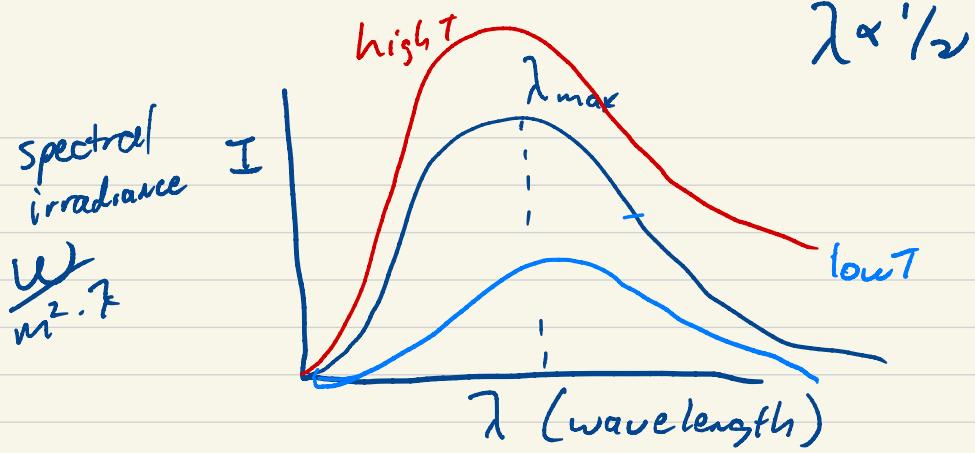
A blackbody perfectly absorbs light.
Approximated by a *Hohlraum*



Light that goes in doesn't come out
Light that does come out is thermally
equilibrated w/ box.

All objects radiate light in this way,
have some emissivity $E(\lambda)$. Hohlraum
is perfectly emissive.

(origin of radiative heat transfer)



Two key features

1) Wilhelm Wien - Wien's displacement law

$$\lambda_{\text{max}} \cdot T = \text{constant} \\ = 2.8978 \times 10^{-3} \text{ nm K}$$

<u>T (K)</u>	<u>λ_{max} (nm)</u>	
298	9700	far IR
1000	2900	near IR
2000	1400	"
4000	700	red
7000	400	blue

Heindly-dandy way of ascertaining
the temperature of an object

2) Josef Stephan - Stephan-Boltzmann law

Total flux out

$$J = \int_0^{\infty} I(\lambda, T) d\lambda = \sigma T^4$$

$$\sigma_{SB} = 5.6704 \times 10^{-8} \frac{W}{m^2 \cdot K^4}$$

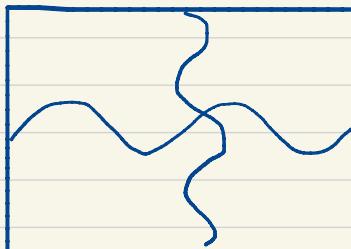
Rapidly grows with T .

This is effusion for light.

We can do that!!

Lord Rayleigh in 1900 tackled this problem.

① hohlraum is filled w/standing waves



waves that
"just fit"
 λ

② $I(\lambda, T) = \frac{\# \text{ waves}}{\lambda} \cdot \frac{\text{energy}}{\text{wave}} \cdot \text{speed}$
 $(\frac{dn}{d\lambda})$

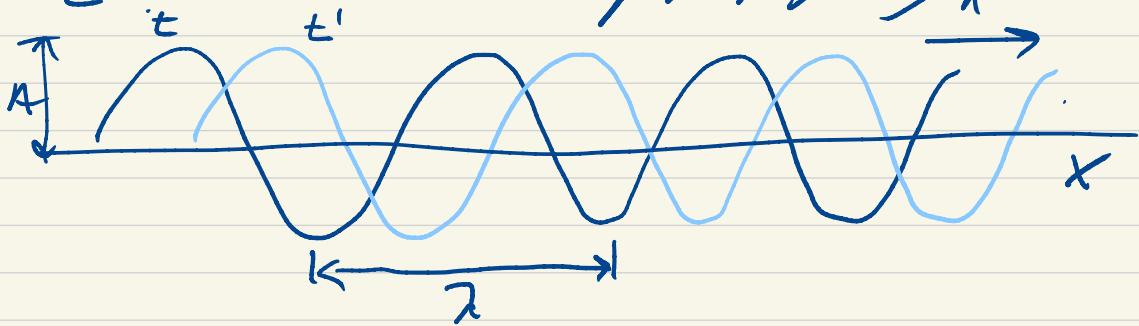
What's light? A wave!!

(Solution to general wave eq)

$$\frac{\partial^2 \psi(x, t)}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 \psi(x, t)}{\partial t^2}$$

$$\psi(x, t) = A \sin(kx - \omega t)$$

equation for a freely propagating, ^{monochromatic} wave



A : amplitude (dist)

λ : wavelength ("")

k : wavenumber ($\frac{2\pi}{\lambda}$)

T : period (time, peak to peak)

v : frequency ('/time, peaks/time)

ω : angular freq ($2\pi v$)

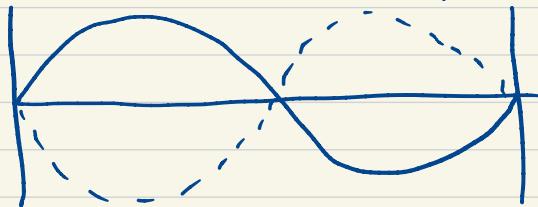
v : speed = $\lambda/T = \lambda \cdot v$

$$= \frac{2\pi}{\lambda} \cdot \frac{\omega}{2\pi} = \frac{\omega}{\lambda}$$

Already showed $E \propto A^2$
 $\langle E \rangle = k_B T$

Further, waves diffract,
 refract, interfere.

What's a "standing wave"?



"nodes"
 fixed in
 space

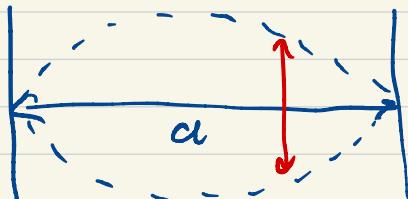
$$(\psi(x,t) = \phi(x) \chi(t))$$

$$\frac{\partial^2 \phi(x)}{\partial x^2} = -k^2 \phi(x) \quad \frac{\partial^2 \chi(t)}{\partial t^2} = -\omega^2 \chi(t)$$

$$\phi(x) = \sin kx \quad)$$

Standing wave given by

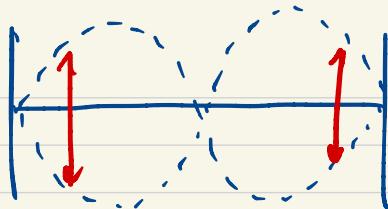
$$\phi(x) \propto \sin kx$$



$$\lambda = 2a$$

$$k = \frac{\pi}{a}$$

$$\sin \frac{\pi x}{a}$$



$$\lambda = a$$

$$k = \frac{2\pi}{a}$$

$$\sin \frac{2\pi x}{a}$$

In general $\lambda = \frac{2a}{n}$

Standing wave condition limits λ

If $a \gg \lambda$ (like in a hohlraum)

$$\frac{dn}{d\lambda} = \frac{d}{d\lambda} \frac{2a}{\lambda} = -\frac{2a}{\lambda^2}$$

$$\text{In 3-D } n = \sqrt{n_x^2 + n_y^2 + n_z^2}$$

$$\Rightarrow \frac{dn}{d\lambda} = -\frac{8\pi V}{\lambda^4}$$

or

$$-\frac{1}{V} \frac{dn}{d\lambda} = \frac{8\pi}{\lambda^4}$$

Pure
Geometry

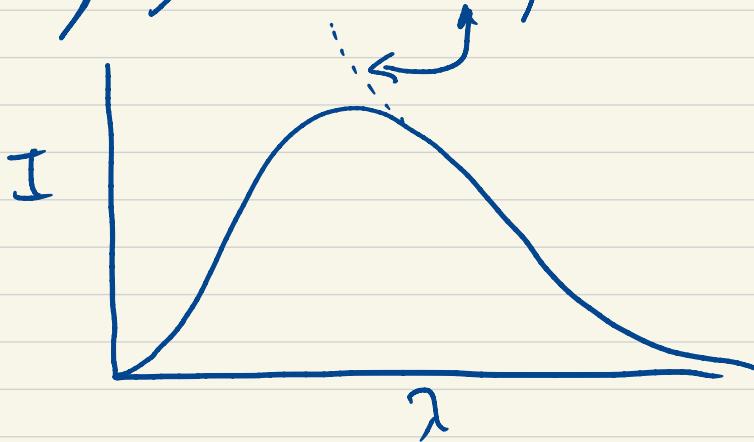
Energy/wave
→ harmonic
oscillators

$$\langle E \rangle = k_B T$$

speed of light? call it c

$$I(\lambda, T) = \frac{8\pi}{\lambda^4} \cdot k_B T \cdot c$$

Rayleigh-Jeans expression



$$J = \int I(\lambda, T) d\lambda \rightarrow \infty !!$$

Anything, at any temperature, should be radiating an infinity of energy !! At very short λ .

Called the ultraviolet catastrophe

1900 Max Planck

Made a radical suggestion.

Standing waves... sure?

$$\text{But, } E \propto \frac{1}{\lambda} \propto \nu$$

and quantized!!

$$E_n = n h \nu = n \cdot \frac{hc}{\lambda} \quad \lambda \nu = c$$

Einstein
inspiration

Exactly same math

$$\langle E \rangle = \frac{h\nu}{e^{h\nu/kT} - 1} = \frac{1}{\lambda} \frac{hc}{e^{hc/\lambda kT} - 1}$$

$$I(\lambda, T) = \frac{8\pi}{\lambda^4} \cdot \frac{1}{\lambda} \frac{hc}{e^{hc/\lambda kT} - 1} \cdot c$$

$$= \frac{8\pi}{\lambda^5} \cdot \frac{hc^2}{e^{hc/\lambda kT} - 1}$$

This works! EXACTLY!!

$$\int I(\lambda, T) d\lambda = \sigma T^4 \quad \text{Stefan-Boltzmann}$$

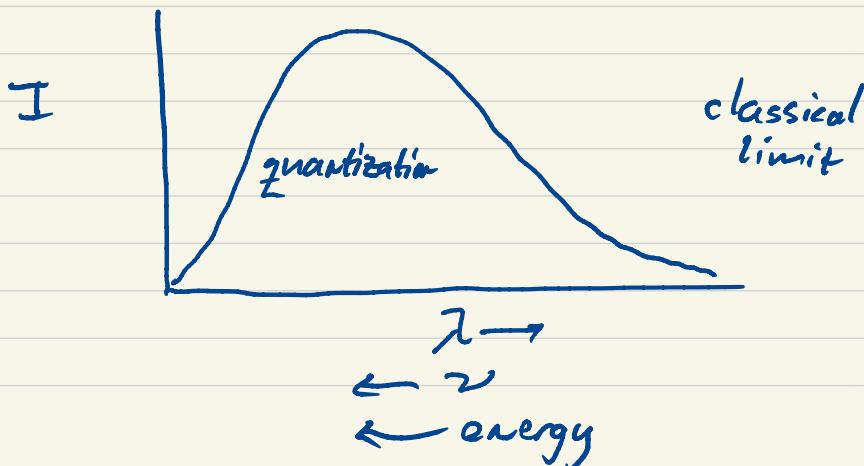
$$\frac{\partial I}{\partial \lambda} = 0 \rightarrow \lambda_{\max} T = \text{const} \quad \text{Wien's Law}$$

$$\lim_{\substack{\lambda \rightarrow 0 \\ \lambda \rightarrow \infty}} I(\lambda, T) = 0$$

$$\lim_{\substack{\lambda \rightarrow \infty \\ \lambda \rightarrow 0}} I(\lambda, T) = \frac{8\pi}{\lambda^4} \cdot kT \cdot c$$

Rayleigh-Jeans!

Planck quantized model exactly predicts BB radiation and reduces to classical limit for very long (low energy) waves.



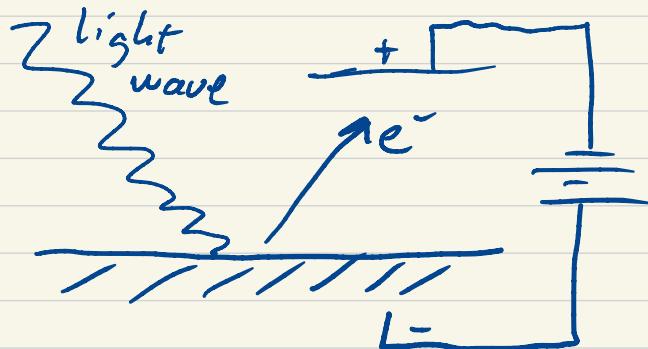
Nobel prize for you, Planck!

h called "Planck's constant" in his honor

$$h \approx 6.626 \times 10^{-34} \text{ J.s}$$

Not clear from either of these what exactly is going on. What exactly is quantized? Why?

Photoelectric effect



Shine light, electrons jump off, measure KE by observing potential to make them stop.

If light is a classical wave, $E \propto A^2$
Observation?



Intercept ("work function") different for different materials, slope always the same!

electrons (current) $\propto A^2$

1905 Einstein -

Light hitting the surface has an energy

$$E = h\nu = \frac{hc}{\lambda}$$

$$\Rightarrow KE = h\nu - w$$

characteristic of a material, corresponding to how hard it holds onto its e^-

Slope is same h !!

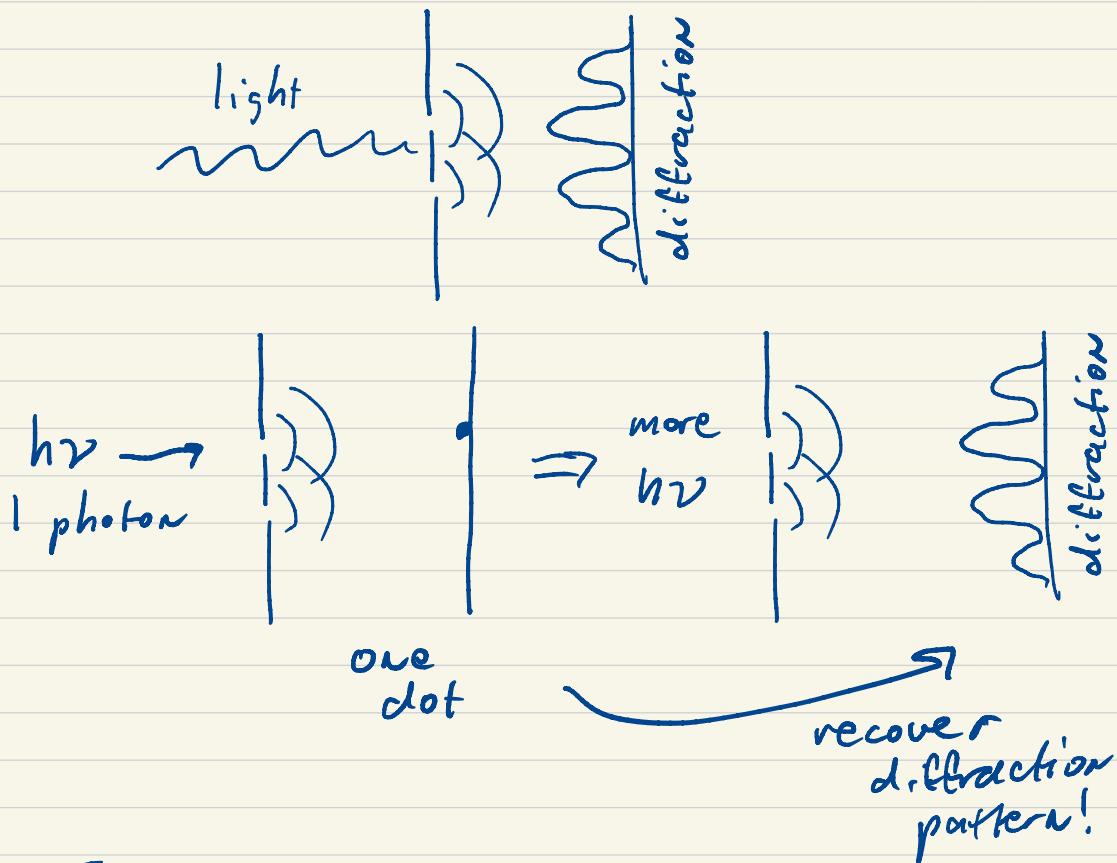
One photon is all it takes to eject an e^- . More photons, more electrons!

These are like the properties of a particle, which we call photons.

BUT, light also acts like a wave, interfering, diffracting.

DUALITY!

Double-slit experiment



Each photon interferes with itself.

Einstein's special theory of relativity demonstrates that the speed of light is a universal constant

$$c = 2.9979 \times 10^8 \text{ m/s}$$

$$\lambda\nu = c$$

Einstein model says photon has energy & momentum

$$E = h\nu = \frac{hc}{\lambda} \quad p = \frac{h}{\lambda}$$

$$hc = 1240 \text{ eV} \cdot \text{nm}$$

Compton effect ⁽¹⁹²⁷⁾ observed shift
of photon λ due to scattering off e^-

Ex 100 mW laser, $\lambda = 700 \text{ nm}$ (red)

1. energy of a photon?

$$E = \frac{hc}{\lambda} = \frac{1240 \text{ eV} \cdot \text{nm}}{700 \text{ nm}} = 1.77 \text{ eV}$$
$$= 2.84 \times 10^{-19} \frac{\text{J}}{\text{photon}}$$

2. photons/second?

$$100 \times 10^{-3} \frac{\text{J}}{\text{s}} / 2.84 \times 10^{-19} \frac{\text{J}}{\text{photon}} = 3.52 \times 10^{17} \frac{\text{ph}}{\text{s}}$$

3. photon momentum?

$$p = \frac{h}{\lambda} = \frac{6.626 \times 10^{-34} \text{ J.s}}{700 \times 10^{-9} \text{ m}} = 9.47 \times 10^{-28} \frac{\text{kg.m}}{\text{s}}$$

4. If I wore this laser, what would my acceleration be?

$$a = \frac{1}{m} \frac{dp}{dt} = \frac{9.47 \times 10^{-28} \frac{\text{kg.m}}{\text{s}} \cdot 3.52 \times 10^{17} \frac{\text{ph}}{\text{s}}}{70 \text{ kg}}$$
$$= 4.77 \times 10^{-12} \text{ m/s}^2$$

slow, not zero...

So light is particulate. Wow...

H atom spectrum

Heat up a gas of H atoms, see light emitted, not black body

Line spectrum

$$\text{Empirically } \nu = R_H \cdot c \left(\frac{1}{k^2} - \frac{1}{n^2} \right)$$

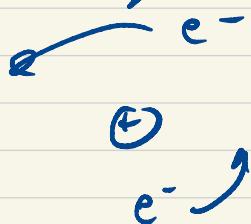
$$R_H \cdot c = 3.28805 \times 10^{15} \text{ s}^{-1} \quad \text{"Rydberg constant"}$$

$$R_H = 109677.585 \text{ cm}^{-1}$$

$k=1, n=2,3,\dots$ Lyman series (uv)

$k=2, n=3,4,\dots$ Balmer series (vis)

Rutherford — atoms have a heavy, positively charged nucleus surrounded by negatively charged electrons

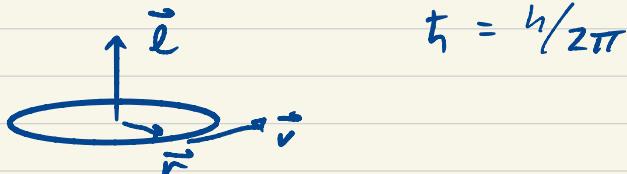


Classically, this situation is
not stable

Niels Bohr (1912 - 1913)

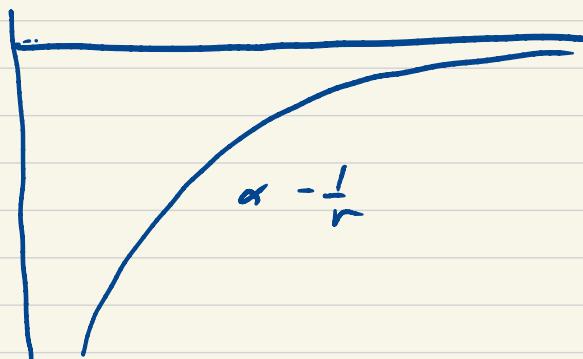
- ① electrons exist in only certain stable "orbits," or stationary states. These states have
- discrete energy
 - discrete angular momentum

$$|\vec{l}| = m \vec{r} \times \vec{v} = n \hbar \quad n = 1, 2, 3, \dots$$



$$I = m |\vec{r}|^2 \quad KE = \frac{|\vec{l}|^2}{2I} = \frac{1}{2I} n^2 \hbar^2$$

$$U = -\frac{e^2}{4\pi\epsilon_0} \cdot \frac{1}{|\vec{r}|}$$



$$\frac{n^2 \hbar^2}{2 I} - \frac{e^2}{4\pi\epsilon_0} \cdot \frac{1}{|\vec{r}|} = \text{constant } (E(n))$$

$\rightsquigarrow E_n = -E_0 \cdot \frac{1}{n^2}$ $E_0 = 13.6 \text{ eV}$

$$r_n = a_0 n^2$$

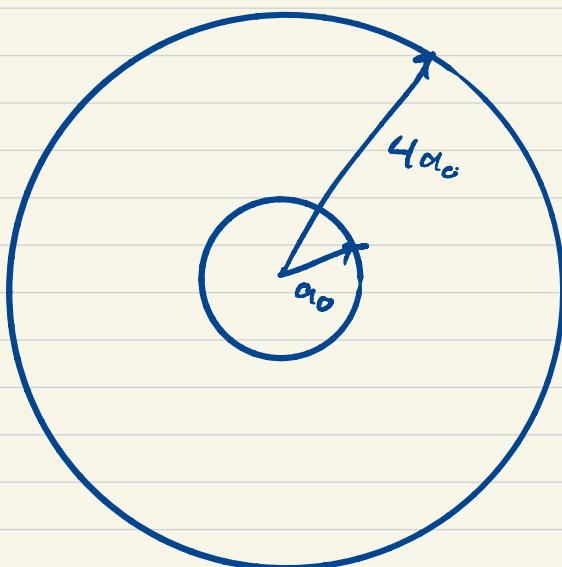
$a_0 = 0.529 \times 10^{-10} \text{ m}$
Bohr radius

$$p_n = p_0 \cdot \frac{1}{n}$$

$p_0 = 1.99 \times 10^{-24} \text{ kg} \frac{\text{m}}{\text{s}}$

Circular orbits of radius $a_0, 4a_0, \dots$

"quantized"



$$F_{\text{Coulomb}} = +\frac{e^2}{4\pi\epsilon_0} \cdot \frac{1}{|\vec{r}_F|^2}$$

$$F_{\text{centripetal}} = \frac{mv^2}{|\vec{r}|}$$

$$\Rightarrow |v| =$$

③ When an electron jumps from one state to another, it emits or absorbs a photon

$$h\nu = |E_f - E_i|$$

$$h\nu = E_0 \left| \frac{1}{k^2} - \frac{1}{n^2} \right|$$

$$\nu = \frac{E_0}{h} \left| \frac{1}{k^2} - \frac{1}{n^2} \right|$$

$$= R_H \cdot c \left| \frac{1}{k^2} - \frac{1}{n^2} \right| \quad \text{Bingo!}$$

Recovers H atom spectrum

Works for H, He⁺, Li²⁺, ...

Nothing else...

"old" QM. But why?

de Broglie relationship (1924)

Einstein's special theory of relativity says $E = mc^2$

For light, $E = hc/\lambda$

de Broglie equated $\frac{hc}{\lambda} = mc^2$

$$\frac{h}{\lambda} = mc = p$$

de Broglie postulates this relationship applies to everything

$$\lambda = \frac{h}{p}$$

$$KE = \frac{p^2}{2m} \rightarrow p = \sqrt{2mKE} \quad \lambda = \frac{h}{\sqrt{2mKE}}$$

car

1000 kg

100 km/hr

KE 3.9×10^5 J

λ 2.4×10^{-38} m

electron

9.1×10^{-31} kg

100 km/hr

3.5×10^{-28} J

2.6×10^{-5} m !!

Davison & Germer (1927)

Shine e⁻ on a nickel crystal and observe a diffraction pattern consistent with λ !

Bohr model

$$n=1 \quad p = \left(\frac{e^2}{4\pi\epsilon_0} \right) \frac{me}{\hbar}$$

$$\lambda = \frac{\hbar}{p} = 2\pi a_0$$

Circumference of orbit matches e⁻ wavelength

Standing wave!!

By end of 1920's, evident that wave-particle properties of everything, evident at small scales.