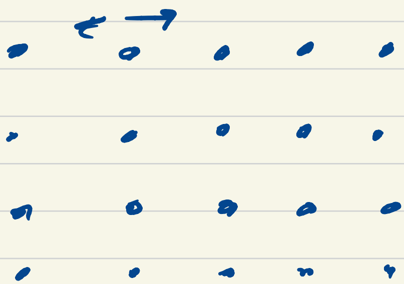
# 4 - Demise of Classical Physics

Apply same ideas to a solid. Simplest possible model: perfect, ordered array of atoms



Each atom can move about its central point. Assume <u>Hooke's</u> <u>Law</u> : $F = -kx$

$k$ : spring constant

focus on 1-D

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

$x(t)$, displacement vs time

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

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

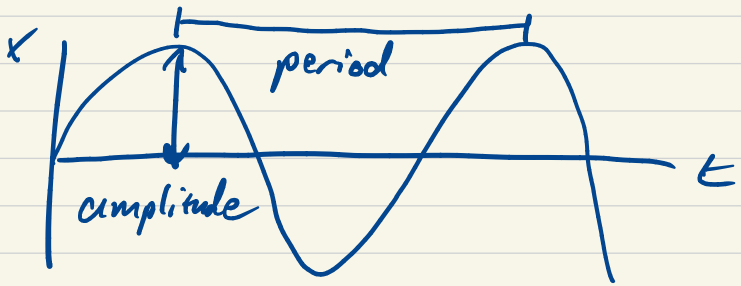
$$\frac{dx}{dt} = c_1 c_2 \cos c_2 t$$

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

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

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

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




periodic

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

$c_1$ determined by initial condition
Called amplitude, $A$

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

Called a standing wave

Characteristic of a harmonic oscillator

Kinetic energy?

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

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

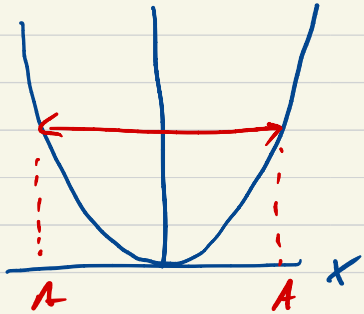
$$KE = \frac{1}{2} m A^2 \omega^2 \cos^2 \omega t$$

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

Potential energy?

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

parabolic potential



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

KE + PE out of phase

$$\text{Total} = KE + PE$$
$$= \frac{1}{2}kA^2(\underbrace{\cos^2\omega t + \sin^2\omega t}_{1})$$
$$= \frac{1}{2}kA^2$$

total energy depends only on amplitude and characteristic $k$

What's expected energy at some $T$?

$$\langle E \rangle = \frac{\iint E(x,\dot{x})\, e^{-E(x,\dot{x})/kT}\, dx\, d\dot{x}}{\iint e^{-E(x,\dot{x})/kT}\, dx\, d\dot{x}}$$

$$= \iint \left(\frac{1}{2}m\dot{x}^2 + \frac{1}{2}kx^2\right)$$

. . .

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

$$\frac{1}{2}k_BT + \frac{1}{2}k_BT = \underline{\underline{k_BT}}$$

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

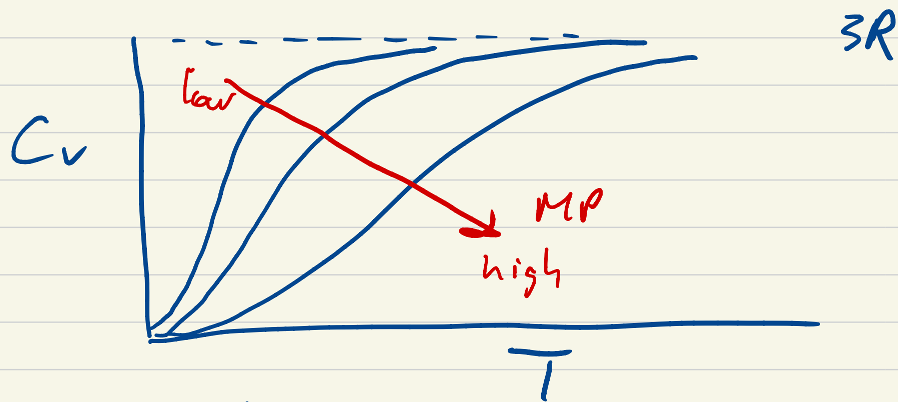
$3 \cdot RT$ (per mole)

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 $\to 0$ as $T \to 0$.

Crap!! What happened?

No obvious, or unobvious, solution in classical physics.

# 1907 Einstein

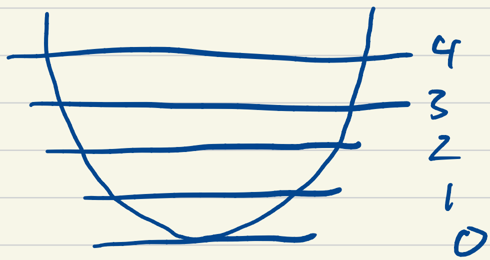
What if we said that for these vibrating atoms

$$\varepsilon \propto A^2 \longrightarrow \varepsilon \propto \nu$$

Also, what if only discrete, quantized values of $\varepsilon$ were possible:

$$\varepsilon = nh\nu \qquad n = 0, 1, 2, \ldots$$

WTF!!




The vibrating things are quantized

probability to have energy $\varepsilon_n$?

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

$$\sum_i e^{-ih\nu/kT} = \sum_{i=0}^{\infty} \left(e^{-h\nu/kT}\right)^i$$

$$= \sum_{N=0}^{\infty} c^N \qquad \text{geometric series}$$

$$= \frac{1}{1-c} \qquad c<1$$

$$= \frac{1}{1-e^{-h\nu/kT}}$$

$$P(\varepsilon_N) = \frac{e^{-Nh\nu/kT}}{1-e^{-h\nu/kT}}$$

$$\langle \varepsilon \rangle = \frac{\sum_N N h\nu\, e^{-Nh\nu/kT}}{1-e^{-h\nu/kT}}$$

$$= \frac{h\nu\, e^{-h\nu/kT}}{1-e^{-h\nu/kT}}$$

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

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

Yech!!

$$\lim_{T\to 0} C_v = 0$$ exponential in denominator dominates

$$\lim_{T\to\infty} C_v = R\left(\frac{h\nu}{kT}\right)^2 \frac{1 + h\nu/kT + \dots}{\left(1+\frac{h\nu}{kT} - 1 \dots\right)^2}$$

$$\approx R\cancel{\left(\frac{h\nu}{kT}\right)^2} \cancel{\frac{1}{(h\nu/kT)^2}}$$

$$= R!!$$

In 3D, 3R!!

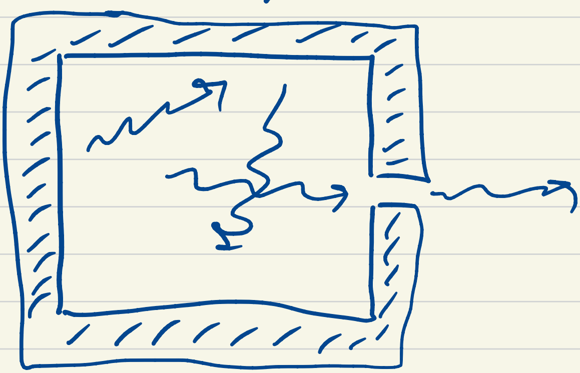
Gives exactly right functional behavior. High melting have high $\nu$ (or $\frac{k}{m}$), long tail; low melting vice versa.

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

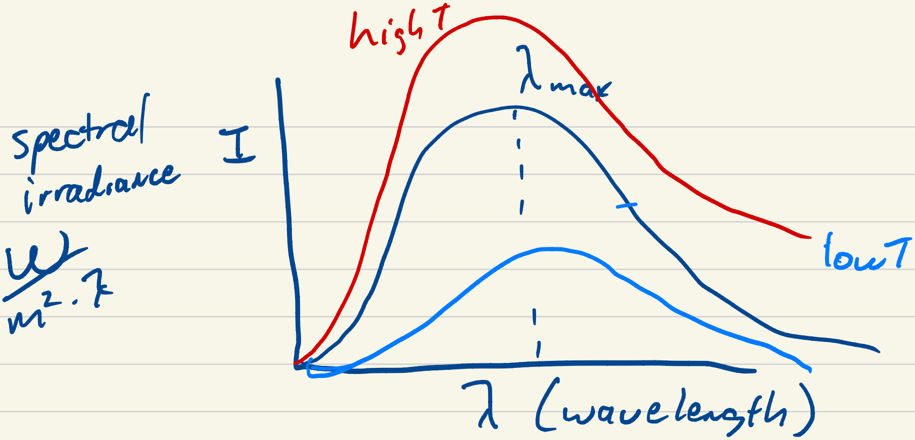
A blackbody perfectly absorbs light.
Approximated by a hohlraum



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 $\varepsilon(\lambda)$. Hohlraum is perfectly emissive.

(origin of radiative heat x'fer)




Two key features

1) Wilhelm Wien - Wien's displacement law

$$\lambda_{max} \cdot T = \text{constant}$$
$$= 2.8978 \times 10^6 \text{ nmK}$$

| $T$ (K) | $\lambda_{max}$ (nm) | |
|---|---|---|
| 298 | 9700 | far IR |
| 1000 | 2900 | near IR |
| 2000 | 1400 | " |
| 4000 | 700 | red |
| 7000 | 400 | blue |

Handy-dandy way of ascertaining the temperature of an object

2) Josef Stephan - Stephan-Boltzmann law

Total flux out

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

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

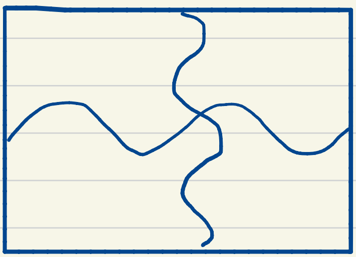
Rapidly grows with T.

This is effusion for <u>light</u>.

We can do that!!

Lord Rayleigh in 1900 tackled this problem.

1. hohlraum is filled w/ standing waves



waves that "just fit" $\lambda$

2. $I(\lambda, T) = \dfrac{\#\text{ waves}}{\lambda} \cdot \dfrac{\text{energy}}{\text{wave}} \cdot \text{speed}$

$\left(\frac{dn}{d\lambda}\right)$

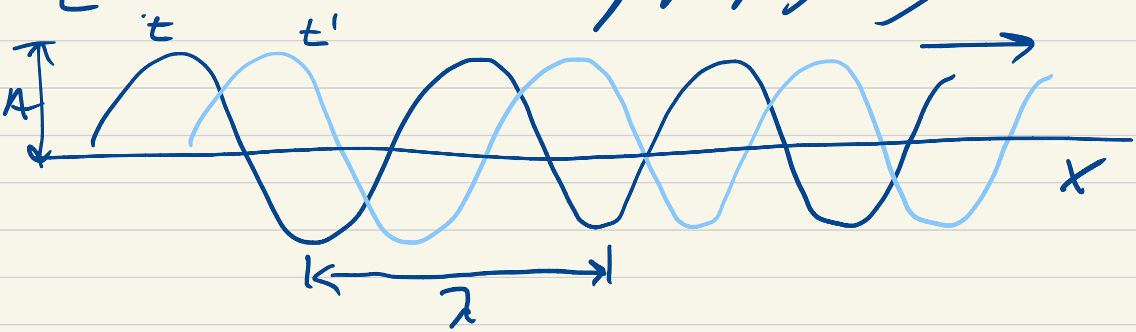
What's light? A wave!!

[ 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 propogating wave




$A$ : amplitude (dist)

$\lambda$ : wavelength ( " )

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

$T$ : period (time, peak to peak)

$\nu$ : frequency ($^1/_{\text{time}}$, peaks/time)

$\omega$ : angular freq $(2\pi\nu)$

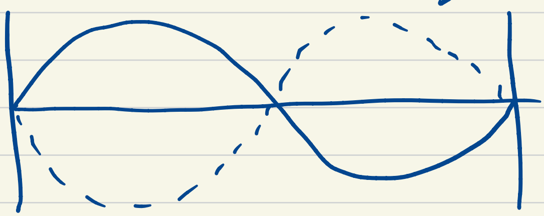
$v$ : speed $= \lambda/T = \lambda \cdot \nu$

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

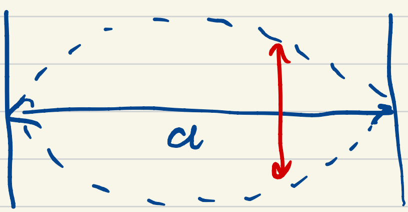
$$\left( \psi(x,t) = \phi(x)\,\chi(t) \right.$$

$$\frac{d^2\phi(x)}{dx^2} = -k^2\phi(x) \qquad \frac{d^2\chi(t)}{dt^2} = -\omega^2\chi(t)$$

$$\left. \phi(x) = \sin kx \right)$$

Standing wave given by

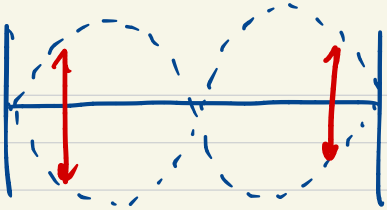
$$\phi(x) \propto \sin kx$$




$\lambda = 2a$

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

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



$\lambda = a$

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

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

Standing wave condition limits $\lambda$

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

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

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

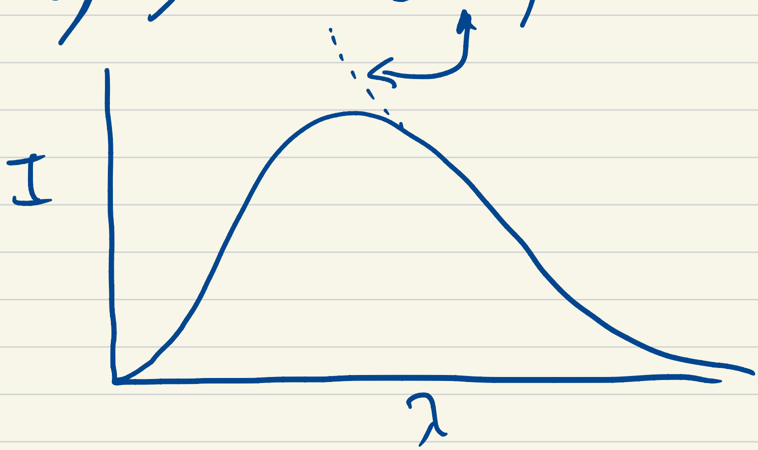
energy/wave $\langle \varepsilon \rangle = k_B T$

$\rightarrow$ harmonic oscillators

speed of light? call it c

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

Rayleigh-Jeans expression




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

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

Called the ultraviolet catastrophe

1900 Max Planck

Made a radical suggestion.

Standing waves... sure?

But, $\varepsilon \propto \frac{1}{\lambda} \propto \nu$

and quantized!!

Einstein inspiration

$$\varepsilon_n = nh\nu = n \cdot \frac{hc}{\lambda} \qquad \lambda\nu = c$$

Exactly same math

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

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

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

This works! EXACTLY!!

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

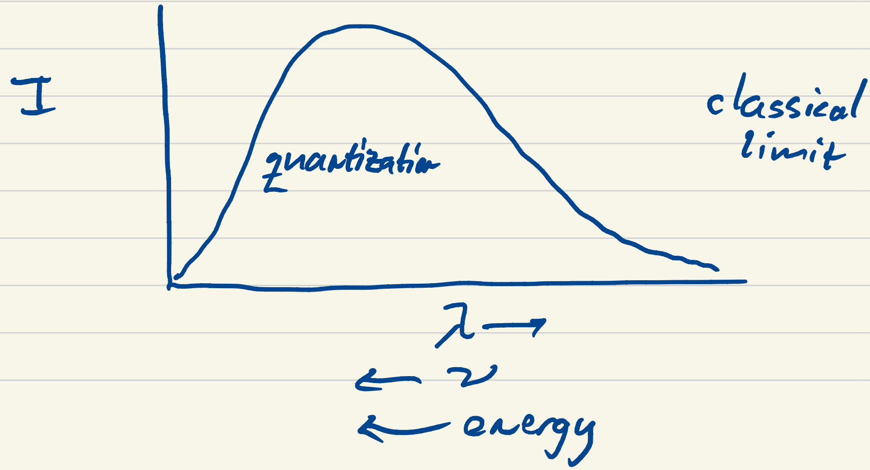
$$\frac{\partial I}{\partial \lambda} = 0 \rightarrow \lambda_{max} T = \text{const}$$ Wien's Law

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

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

Rayleigh-Jeans!

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

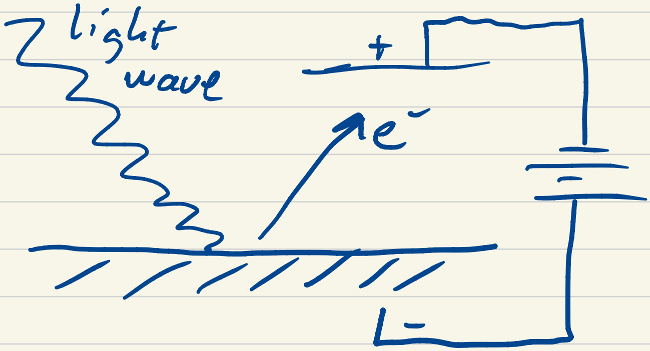


Nobel prize for you, Planck!

h called "Planck's constant" in his honor $h \approx 6.626 \times 10^{-34}\ J \cdot s$

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

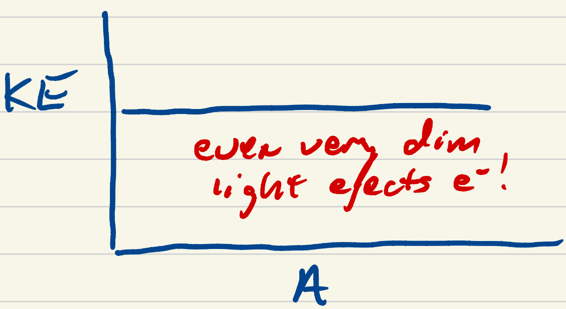
# Photoelectric effect

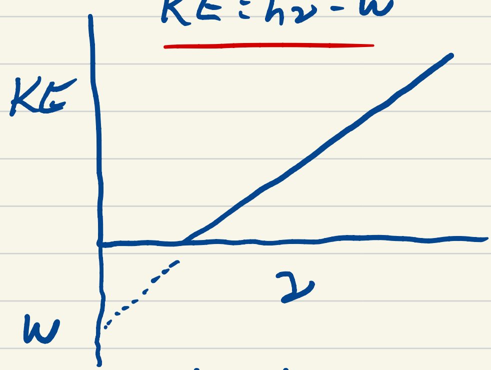



Shine light, electrons jump off, measure KE by observing potential to make them stop.

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

$KE = h\nu - W$




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

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

slope is same h!!

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

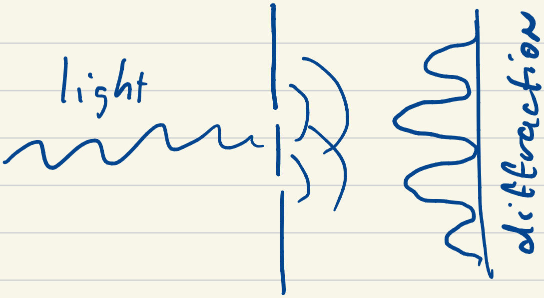
One photon is all it takes to eject an $e^-$. More photons, more electrons!

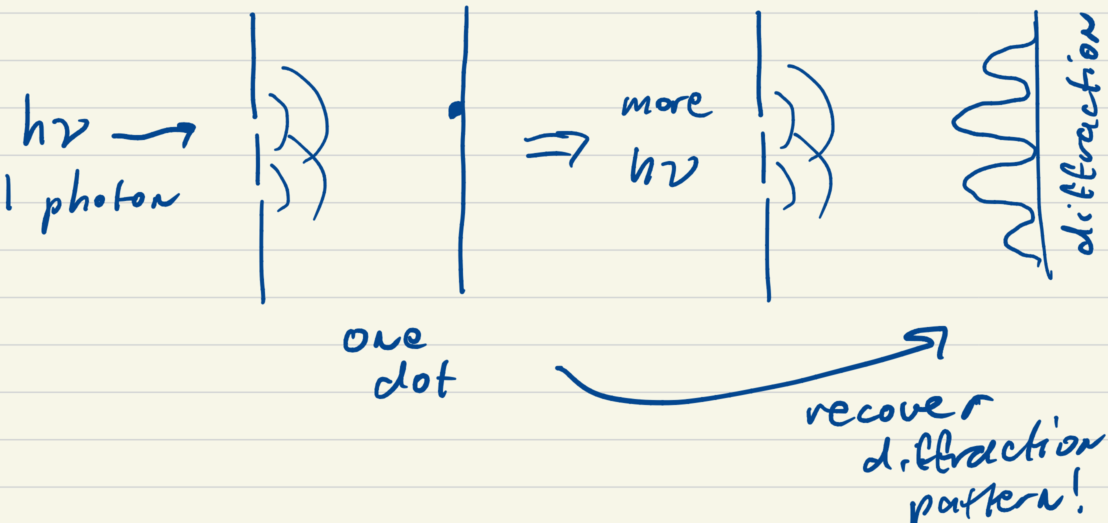
These are like the properties of a particle, which we call photons.

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

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

$$\lambda \nu = c$$

Einstein model says photon has energy & momentum

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

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

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

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

1. energy of a photon?

$$E = \frac{hc}{\lambda} = \frac{1240\,eV\cdot nm}{700\,nm} = 1.77\,eV$$

$$= 2.84\times10^{-19}\,\frac{J}{photon}$$

2. photons/second?

$$100\times10^{-3}\,J/s \Big/ 2.84\times10^{-19}\,J/photon = 3.52\times10^{17}\,\frac{ph}{s}$$

3. photon momentum?

$$p = \frac{h}{\lambda} = \frac{6.626\times10^{-34}\,J\cdot s}{700\times10^{-9}\,m} = 9.47\times10^{-28}\,kg\,m/s$$

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

$$a = \frac{1}{m}\frac{dp}{dt} = \frac{9.47\times10^{-28}\,\frac{kg\,m}{s}\cdot 3.52\times10^{17}\,ph/s}{70\,kg}$$

$$= 4.77\times10^{-12}\,m/s^2$$

slow, not zero...

So light is particulate. Wow...

## H atom spectrum

Heat up a gas of H atoms, see light emitted, <u>not</u> black body

Line spectrum

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

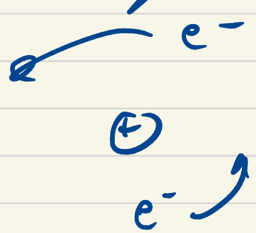
$R_H \cdot c = 3.28805 \times 10^{15}\ s^{-1}$ "Rydberg constant"

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

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

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

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



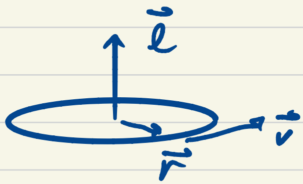

Classically, this situation is <u>not</u> <u>stable</u>

Niels Bohr (1912 - 1913)

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

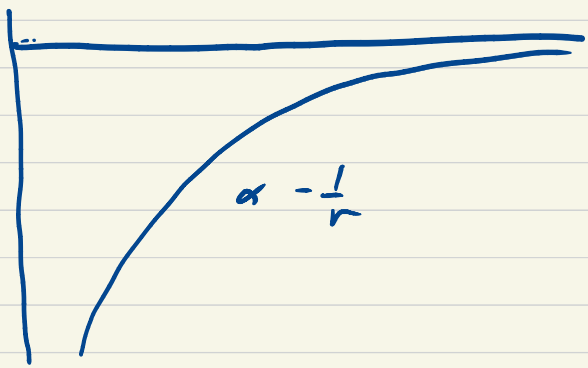
$$|\vec{\ell}| = m\vec{r} \times \vec{v} = n\hbar \qquad n = 1, 2, 3, \ldots$$

$$\hbar = h/2\pi$$




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

$$U = -\frac{e^2}{4\pi\varepsilon_0} \cdot \frac{1}{|\vec{r}|}$$



$$\frac{n^2\hbar^2}{2I} - \frac{e^2}{4\pi\varepsilon_0}\cdot\frac{1}{|\vec{r}|} = \text{constant } (E(n))$$

$\Rightarrow$

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

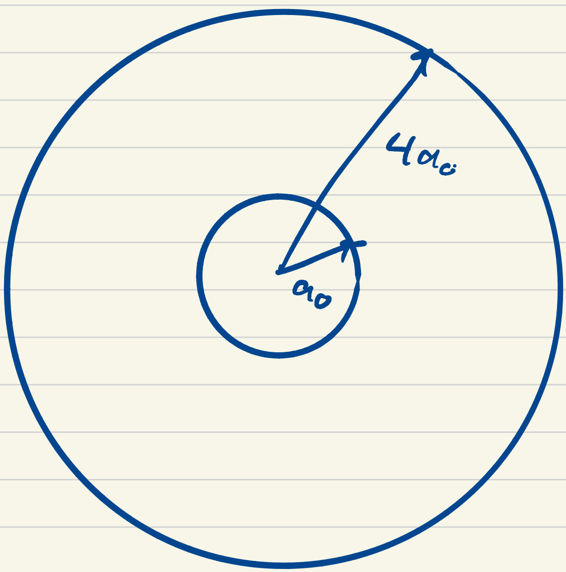
$$r_n = a_0 n^2 \qquad a_0 = 0.529\times10^{-10}\ \text{m}$$

Bohr radius

$$p_n = p_0 \cdot \frac{1}{n} \qquad p_0 = 1.99\times10^{-24}\ \text{kg}\,\frac{\text{m}}{\text{s}}$$

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

"quantized"



$$F_{coulomb} = +\frac{e^2}{4\pi\varepsilon_0} \cdot \frac{1}{|\vec{r}|^2}$$

$$F_{centripetal} = \frac{m_e v^2}{|\vec{r}|}$$

$$\Rightarrow |v| =$$

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

$$h\nu = |\mathcal{E}_f - \mathcal{E}_i|$$

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

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

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

Bingo!

Recovers H atom spectrum

Works for H, $He^+$, $Li^{2+}$, ...
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 <u>everything</u>

$$\lambda = h/p$$

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

| | <u>car</u> | <u>electron</u> |
|---|---|---|
| | 1000 kg | $9.1\times10^{-31}$ kg |
| | 100 km/hr | 100 km/hr |
| KE | $3.9\times10^{5}$ J | $3.5\times10^{-28}$ J |
| $\lambda$ | $2.4\times10^{-38}$ m | $2.6\times10^{-5}$ m !! |

Davison & Germer (1927)

Shine $e^-$ on a nickel crystal and observe a diffraction pattern consistent with $\lambda$!

Bohr model

$n = 1$ $\qquad$ $p = \left(\frac{e^2}{4\pi\varepsilon_0}\right)\frac{m_e}{\hbar}$

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

Circumference of orbit matches $e^-$ wavelength

Standing wave!!

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