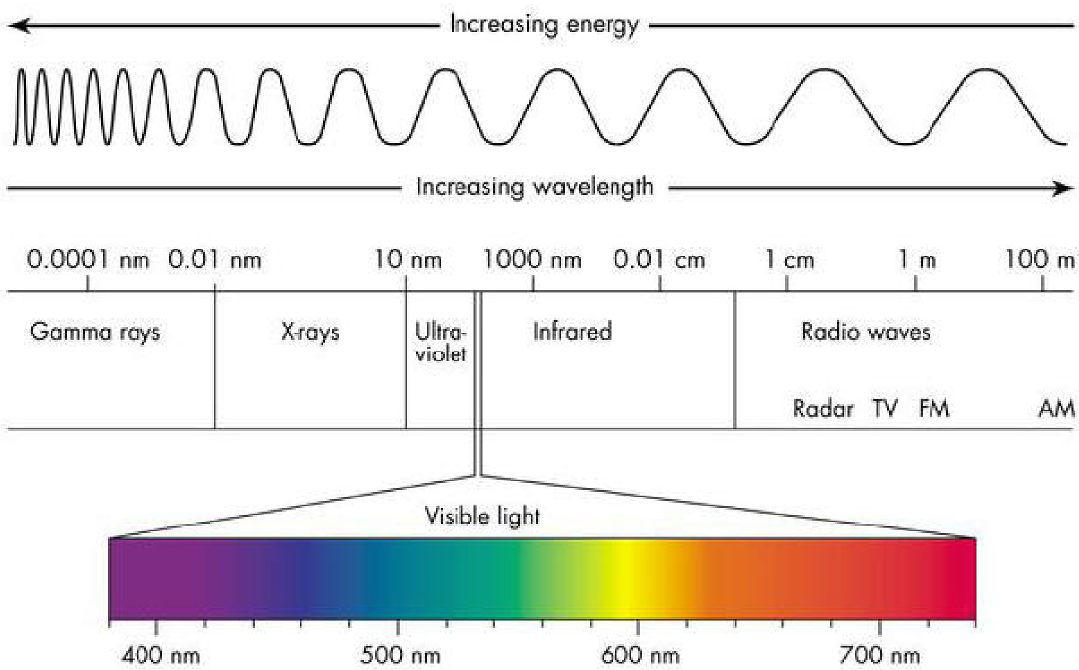
The Quantum Theory of Atoms and Molecules

Breakdown of classical physics:

Wave-particle duality

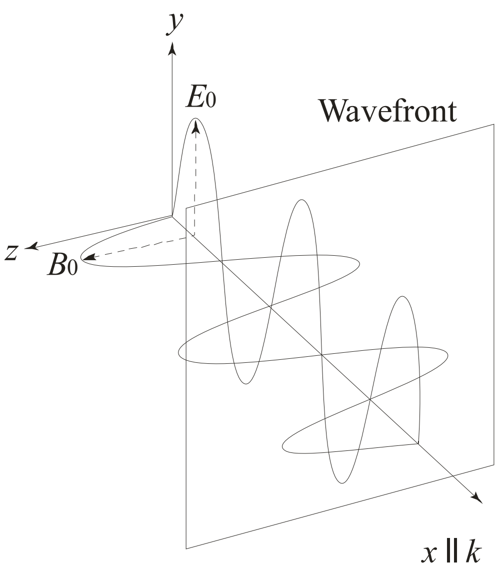
Dr Grant Ritchie

Electromagnetic waves



Remember: The speed of a wave, v, is related to its wavelength, λ, and frequency, f, by the relationship $v = f\,\lambda$.

Speed of the em wave in vacuum is a fundamental constant, with the value $c \approx 2.998\times10^{8}$ m s^{-1}.



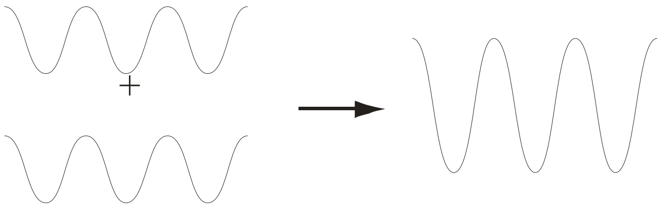
Faraday's law of induction: *A time-varying magnetic field produces an electric field*. Maxwell showed that the magnetic counterpart to Faraday's law exists, i.e. *a changing electric field produces a magnetic field*, and concluded that em waves have both electric, ***E***, and magnetic, ***B***, components.

Interference and superposition

Superposition of two linearly polarised waves, $\boldsymbol{E}_1$ and $\boldsymbol{E}_2$, of the same frequency ω leads to a wave with the following electric field distribution, $\boldsymbol{E}_{\mathrm{res}}$:

$$\begin{aligned}\boldsymbol{E}_{res} &= \boldsymbol{E}_1 + \boldsymbol{E}_2 = \boldsymbol{E}_0\left[\sin(\boldsymbol{K}\bullet\boldsymbol{r} - \omega t + \phi_1) + \sin(\boldsymbol{K}\bullet\boldsymbol{r} - \omega t + \phi_2)\right] \\ &= 2\boldsymbol{E}_0 \cos\left[\tfrac{1}{2}(\phi_1 - \phi_2)\right]\sin\left[(\boldsymbol{K}\bullet\boldsymbol{r} - \omega t + \tfrac{1}{2}(\phi_1 + \phi_2))\right]\end{aligned}$$

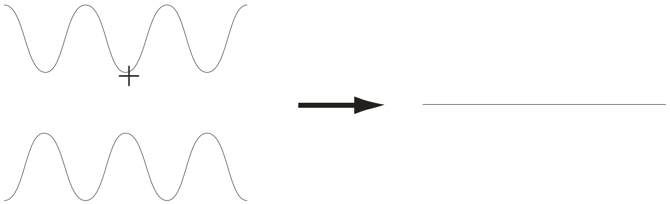
The amplitude factor dependent upon the *phase difference* $\Delta\phi = (\phi_1 - \phi_2)$ between components:



Constructive interference

Largest resultant amplitude when $\Delta\phi = n\,2\pi$ (n is an integer) $\Rightarrow$ total *constructive interference*;

By contrast, resultant wave has zero amplitude if $\Delta\phi = (2n+1)\pi \Rightarrow$ total *destructive interference*.



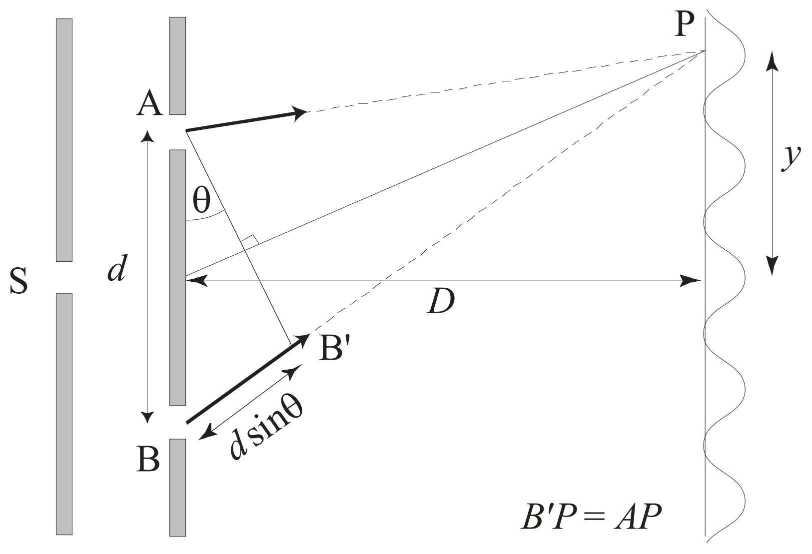
Destructive interference

Young's double slit experiment

Light passes through pinhole and illuminates two narrow slits separated by a distance *d*. WHY? (see optics notes)

Interference pattern observed on screen due to the superposition of waves originating from **both** slits.

Point *P* has maximum intensity if the two beams are totally in phase at that point so the condition for total constructive interference is:



$$BP - AP = n\lambda = d\sin\theta$$

* We have restated the condition for *constructive interference* as the case where the optical path difference (*OPD*) *between the component waves is an integral number of wavelengths*. OPD and Δϕ are related as follows:

$$\Delta\phi = \frac{2\pi}{\lambda}(OPD) = K(OPD)$$

Young’s slits continued

By assuming that $D >> y, d$ then $$\theta \approx \frac{n\lambda}{d} \Rightarrow \Delta\theta \approx \frac{\lambda}{d}$$

Position on screen: $$y = D\tan\theta \approx D\theta$$

so that separation between adjacent maxima: $$\Delta y \approx D\Delta\theta \quad \Rightarrow \quad \Delta y = \frac{\lambda D}{d}$$

Maxima occur at: $$y = 0, \pm \lambda D / d, \pm 2\lambda D / d, \ldots$$

Young's double slit experiment is an example of interference by **division of wavefront**.

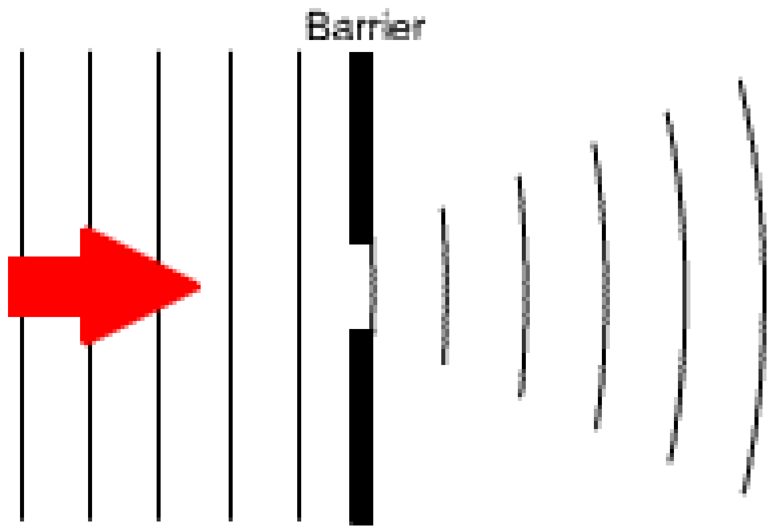
Definitely a wave phenomenon!

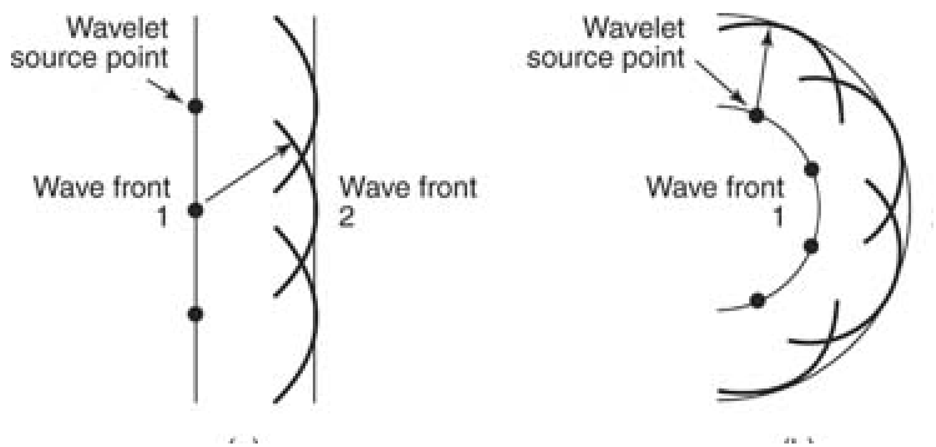
Diffraction at a single slit

Diffraction is the bending of light at the edges of objects.

Light passing through aperture and impinging upon a screen beyond has intensity distribution that can be calculated by invoking *Huygen's principle.*

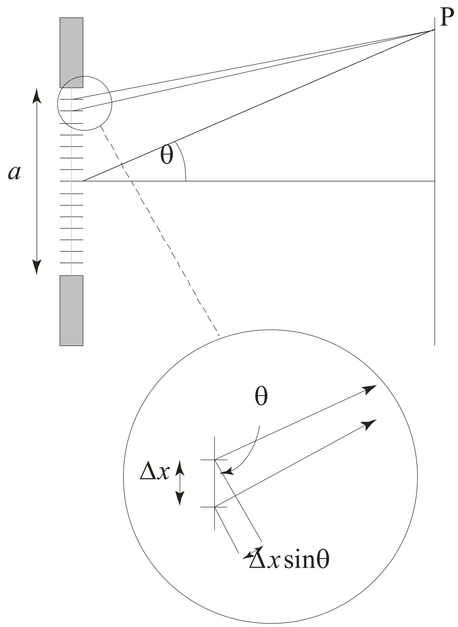
Wavefront at the diffracting aperture can be treated as a source of secondary spherical wavelets.





The single slit continued

The general expression for the minima in the diffraction pattern of a slit of width *a* is



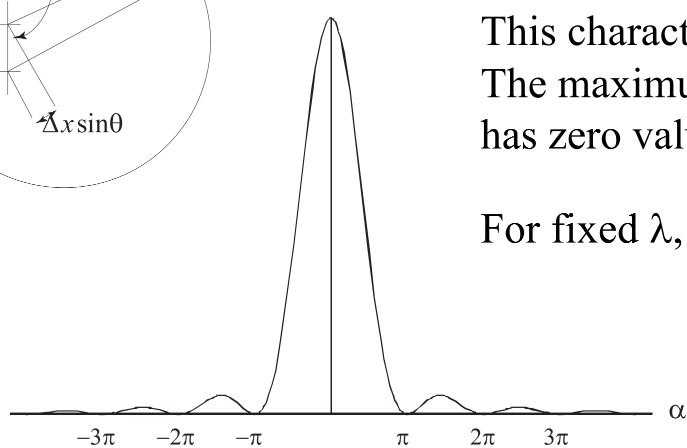
$$a \sin\theta = m\lambda$$

The intensity distribution of diffracted light, I_{res}, is

$$I_{res} = \left|E_{res}\right|^2 = I_{max}\left(\frac{\sin\alpha}{\alpha}\right)^2 \quad \text{where} \quad \alpha = \frac{\phi}{2} = \frac{\pi a}{\lambda}\sin\theta$$

This characteristic distribution is known as a *sinc function*. The maximum value of this function occurs at $\theta = 0$ and has zero values when $\alpha = \pi, 2\pi, \ldots, n\pi$.

For fixed λ, central maximum widens as slit is made narrower.



Another example of a wave phenomenon!

Photons

EM radiation is **not** continuous, in that the total energy cannot take any arbitrary value ⇒ it is *quantised*. The smallest unit of EM radiation is the *photon* and has the energy $E = h\nu$ where h is Planck's constant ($= 6.626 \times 10^{-34}$ J s).

Evidence:

1. **Thermal/Blackbody radiation**
2. **Photoelectric effect**
3. **Spectroscopy** – with quantised energy levels in atoms and molecules, spectroscopic transitions can only occur at discrete frequencies, *i.e.* with well defined energies of the photons.

As well as possessing a **well defined energy**, photons also exhibit

(a) momentum, $p = h\nu/c = h/\lambda = kh/2\pi$. – **the Compton effect, radiation pressure.**

(b) angular momentum with a value of $+ h/2\pi$ or $- h/2\pi$ around the direction of motion corresponding to right and left circularly polarised light. (See atomic spectroscopy lectures - for example, transitions between two s orbitals are *forbidden*).

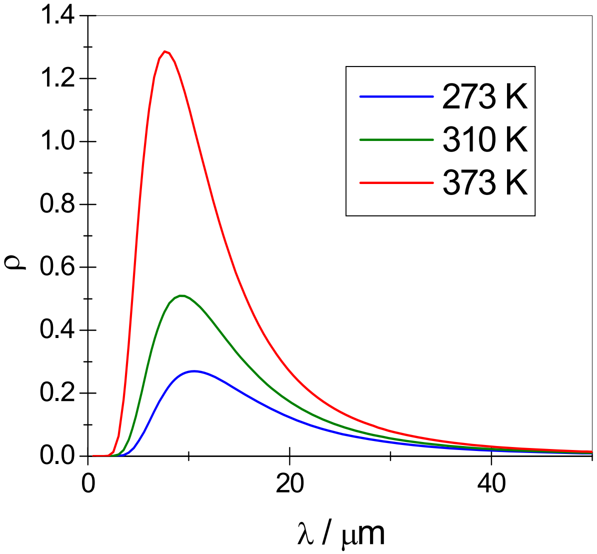
Thermal radiation I

Radiation that is given out by a body as a result of its temperature.

e.g humans emit infrared

Total rate of radiation $\propto T^4$ (Stefan's Law).

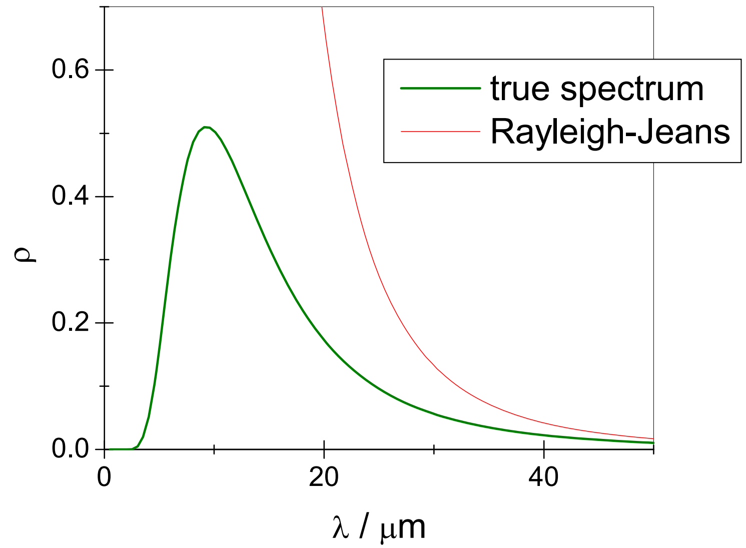
Spectrum shifts to shorter wavelengths as T increases ($\lambda_{max} T$ = const – Wien's law).



Thermal radiation II

Spectrum calculated by Rayleigh and Jeans (1900) assuming that every wavelength carried kT in energy (*equipartition*).

Experiment and theory disagree – **Ultraviolet catastrophe.**



Planck: Light comes in photons $E = nh\nu$ where $n = 1, 2, 3, \ldots$.

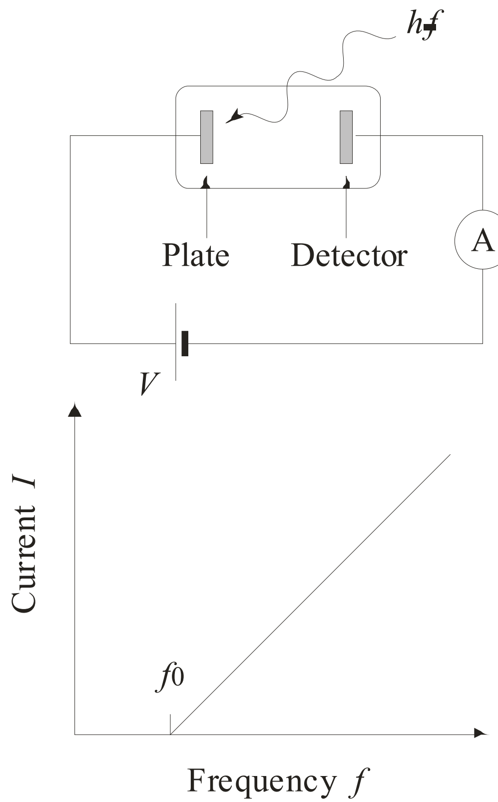
Short wavelength photons have too much energy to be supplied by thermal motions with energy ~kT. i.e $h\nu >> kT$.

Planck successfully explained the form of the thermal spectrum but had to (i) discard the wave picture of light, and (ii) introduce a new fundamental constant, h.

The Photoelectric effect (again!)

Light shining onto matter causes the emission of photoelectrons.

Note:
1. Photoelectrons are emitted instantly, whatever the intensity of the light.
2. There is a critical frequency below which no photoelectrons are emitted.
3. Maximum kinetic energy of photoelectrons increases *linearly* with frequency.



Planck's photon picture: $E = h\nu$.

The photon supplies the energy available, $\phi = h\nu_c$ (ionisation energy / work function)
For $\nu < \nu_c$, not enough energy to ionise.
For $\nu > \nu_c$, $h\nu_c$ used in ionisation, the rest is carried off by the electron as kinetic energy:
$KE_{max} = h\nu - \phi$. Basis of photoelectron spectroscopy.

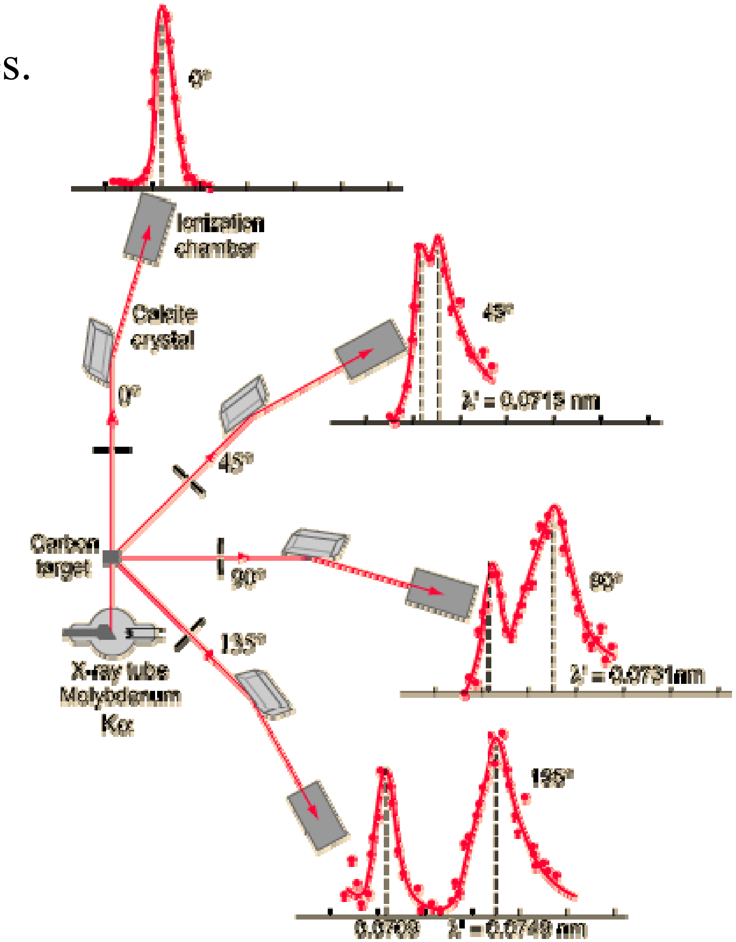
The Compton effect

Compton measured intensity of scattered X-rays from a target as a function of λ for different angles.

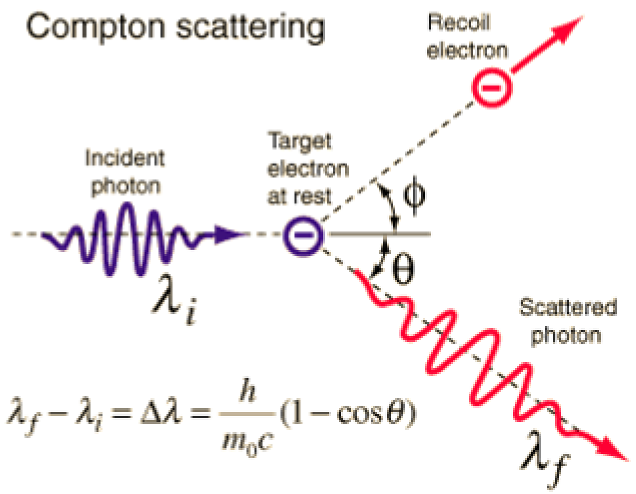
Observation: Peak in scattered radiation shifts to ***longer*** λ than source. Amount depends on θ (but not on target material).

Classical picture: Oscillating EM field causes oscillations in positions of charged particles, which re-radiate in all directions at *same frequency and wavelength as the incident radiation* ⇒ **no** shift in λ!

Momentum and energy conservation applied to collision between the photon and the electron gives correct results **IF** momentum of X-ray photons is $p = h/\lambda$!



The Compton Effect



$$\Delta\lambda = \frac{h}{m_e c}(1-\cos\theta) = \lambda_c(1-\cos\theta) \geq 0$$

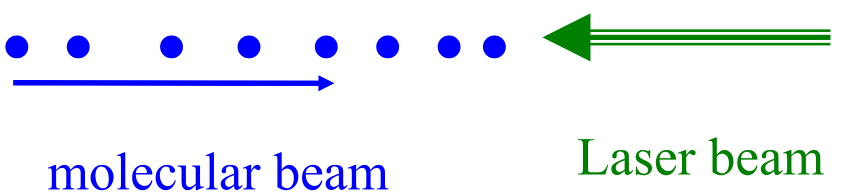
λ_c is the Compton wavelength = 2.4×10^{-12} m.

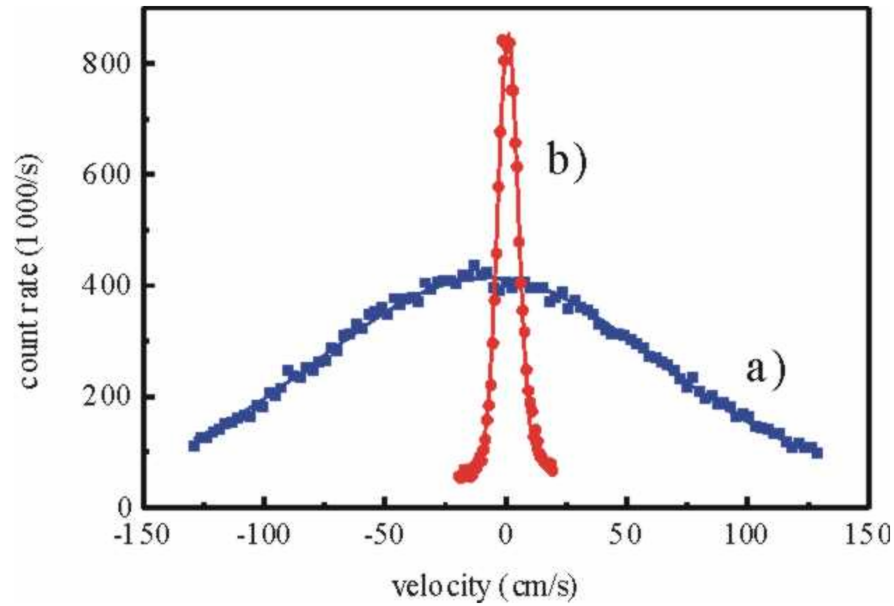
NB. At all angles there is also an **unshifted** peak and this is due to a collision between the X-ray photon and the nucleus of the atom. For this case

$$\Delta\lambda = \frac{h}{m_{nuc} c}(1-\cos\theta) \approx 0 \quad (m_{nuc} \rangle\rangle\, m_e)$$

Laser cooling

Counterpropagating beams, every photon absorbed slows atom down (re-emission in a random direction).





Velocity distribution of laser cooled calcium atoms at (a) 3 mK and (b) 6 μK.

Stationary atoms give very sharp spectra (Doppler effect)

Example: Na has an atomic absorption line at 589.6 nm. A Na atom, which is initially travelling at 400 m s^{-1} in the opposite direction to light of this wavelength, is brought to rest by the absorption of light. Calculate the number of photons absorbed.
(Prelims 2003)

It get's worse…..Matter waves

Light has both wave and particle characteristics:

Wave properties	Particle properties
Wavelength, frequency	Mass, position, velocity
Energy spread out over wavefront	Energy localised at position of the particle
Interference	No interference
Energy $\propto$ (amplitude)^2	

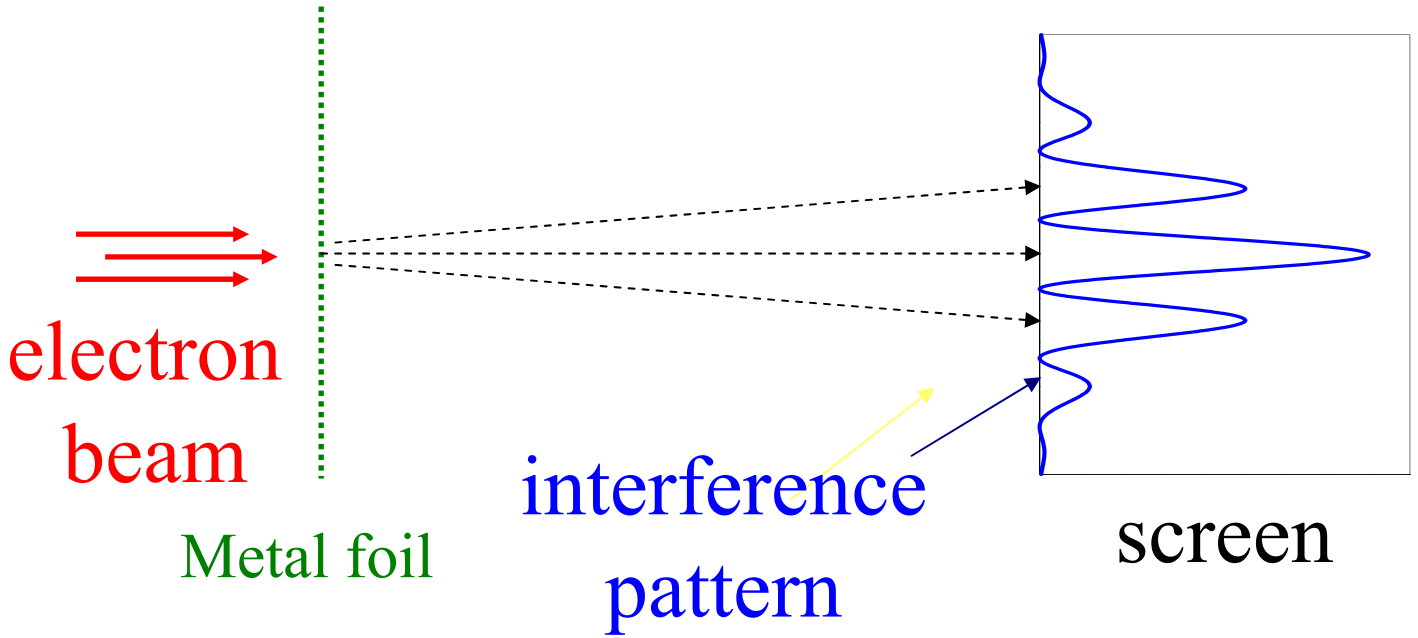
But *particles* can also have wave-like properties, with the wavelength λ related to the momentum p in the same way as for light: $p = h / \lambda$ (de Broglie).

Is this true?

Electron diffraction

Electrons can have similar λ to atomic dimensions ($\lambda \approx 10^{-10}$ m) ⇒ can use an array of atoms (crystal, metal foil) to produce an interference pattern with electrons and thus show that electrons have wave properties.

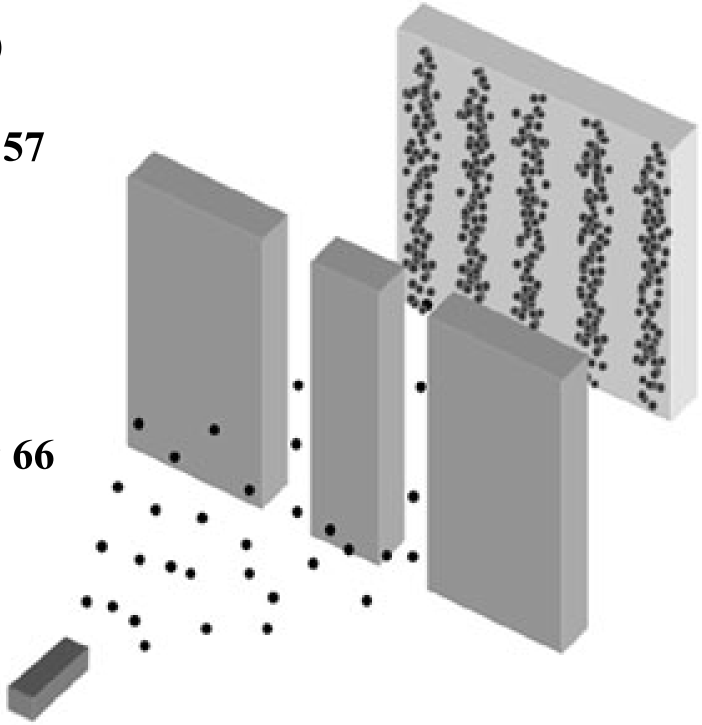
The Davisson-Germer experiment (1927).



Example: Electrons, accelerated through a potential difference of ≈100V, can be diffracted by the layers of metal atoms in a metal crystal. Comment.

The double-slit experiment with…..

•Performed with **electrons**
C. Jönsson 1961 *Zeitschrift für Physik* **161** 454-474,
(translated 1974 *American Journal of Physics* **42** 4-11)
•Performed with **single electrons**
A. Tonomura *et al.* 1989 *American Journal of Physics* **57** 117-120
•Performed with **neutrons**
A. Zeilinger *et al.* 1988 *Reviews of Modern Physics* **60** 1067-1073
•Performed with **He atoms**
O. Carnal and J. Mlynek 1991 *Physical Review Letters* **66** 2689-2692
•Performed with **C60 molecules**
M. Arndt *et al.* 1999 *Nature* **401** 680-682
•Performed with **C70 molecules**
L. Hackermüller *et al.* 2004 *Nature* **427** 711-714



2 slit single particle experiment

Only slit 1 open

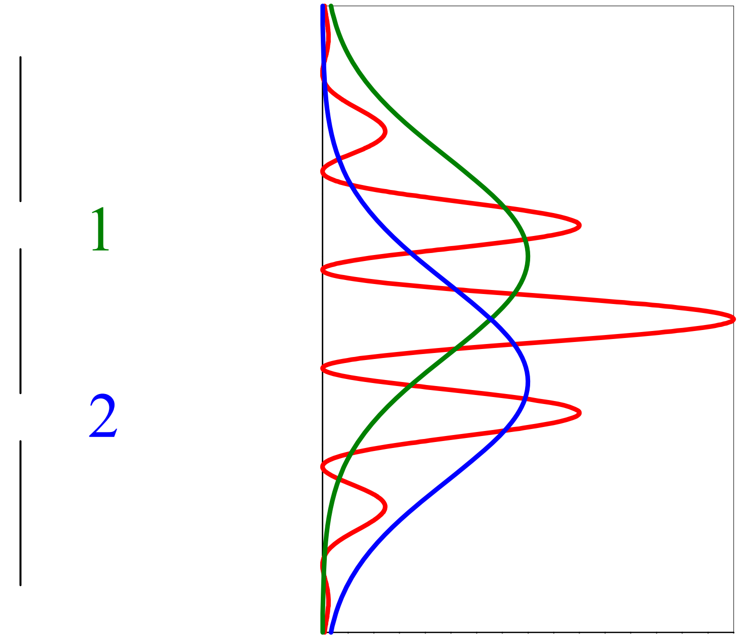
$P_1 = \psi_1^2$

Only slit 2 open

$P_2 = \psi_2^2$

Both slits open

$P_{12} = \psi_1^2 + \psi_2^2 + 2\ \psi_1\psi_2$



This observation is inexplicable in the particle picture.

Interpretation of the double slit experiment

1. The interference pattern consists of many independent events in which a particle is detected at a particular position in space on screen. A bright fringe indicates a high probability of particle being detected at that point while a dark fringe corresponds to low probability.

2. The fringe pattern required the presence of *both* slits. Covering up one slit destroys the fringes.

3. Any attempt to determine which slit the particle passes through destroys the interference pattern. We cannot see the wave-particle nature at the same time.

4. The flux of particles can be reduced so that only one particle arrives at a time $\Rightarrow$ interference fringes are still observed! Thus,

a) Wave behaviour can be shown by a single atom;

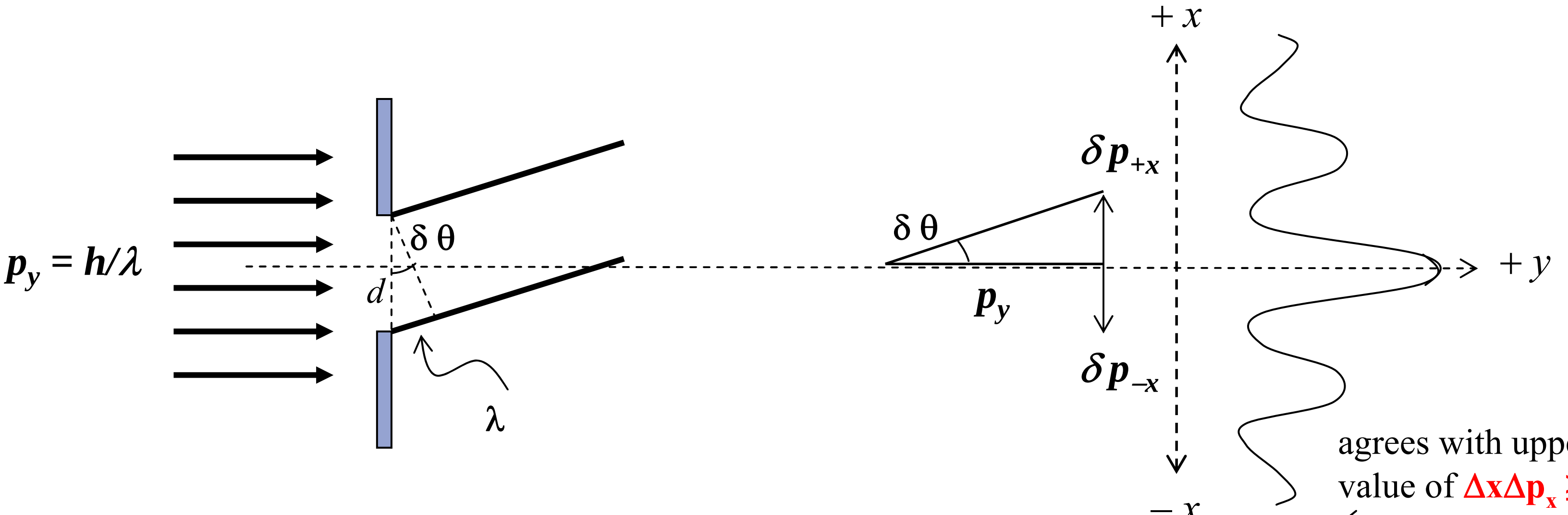
b) Each particle goes through both slits at once;

c) A matter wave can interfere with itself.

Observations also indicate that the process of measuring actually *changes* the system!

Single slit diffraction and the Heisenberg Uncertainty Principle

Wave-like behaviour of electrons, atoms etc. leads to a fundamental loss of information about their position/momentum $\Rightarrow$ compare with a trajectory in classical mechanics.



I. $\delta p_x / p_y \approx \delta\theta$

II. $\delta\theta \approx \lambda / d = h / p_y d$

III. Uncertainty through slit: $\delta x \approx d/2$.

I–II $\Rightarrow$ $\delta p_x \sim h/d$

with III $\Rightarrow$ $\delta p_x \delta x \sim h/2$

agrees with upper value of $\Delta x \Delta p_x \geq \hbar/2$

Uncertainty in ***momentum*** *along x (introduced by -partially- locating position)*

Uncertainty in ***position*** *along x*

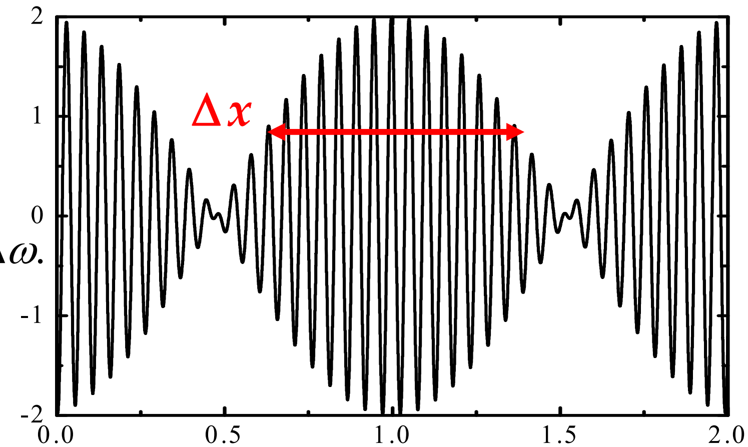
We *cannot* have simultaneous knowledge of ‘conjugate’ variables such as position and momentum (in the same direction).

How can a wave look like a particle?

Add two waves of the same amplitude but slightly different frequencies:

$$\psi = A\sin(k_1 x - \omega_1 t) + A\sin(k_2 x - \omega_2 t)$$

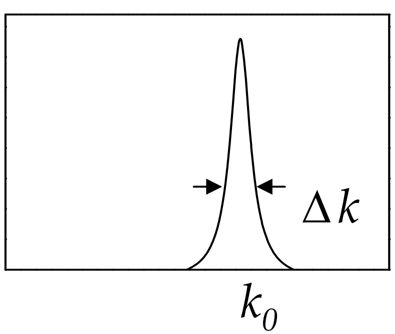
$$\longrightarrow \psi = 2A\sin(kx - \omega t)\cos(\Delta k x - \Delta\omega t)$$



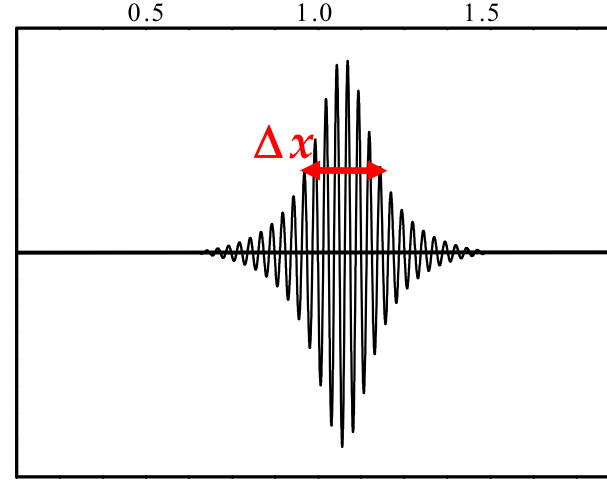
where $k_1 = k - \Delta k,\ k_2 = k + \Delta k$ and $\omega_1 = \omega - \Delta\omega,\ \omega_2 = \omega + \Delta\omega.$

Doesn't look much like a particle!

But can add more and more waves with slightly different wavevectors (different k values).



$\Rightarrow$



Wave now localised over a distance $\Delta x \Rightarrow$ *wavepacket.*

Spatial extent of wavepacket Δx inversely proportional to width of the distribution of wavevectors Δk.

Wavepackets and Heisenberg (again)

Fourier analysis shows that $\Delta k \Delta x \approx 1$. But de Broglie tells us that the uncertainty in the momentum is $\Delta p = \hbar \Delta k$, and so we arrive at the *Heisenberg uncertainty principle*:

$$\Delta p \Delta x \approx \hbar$$

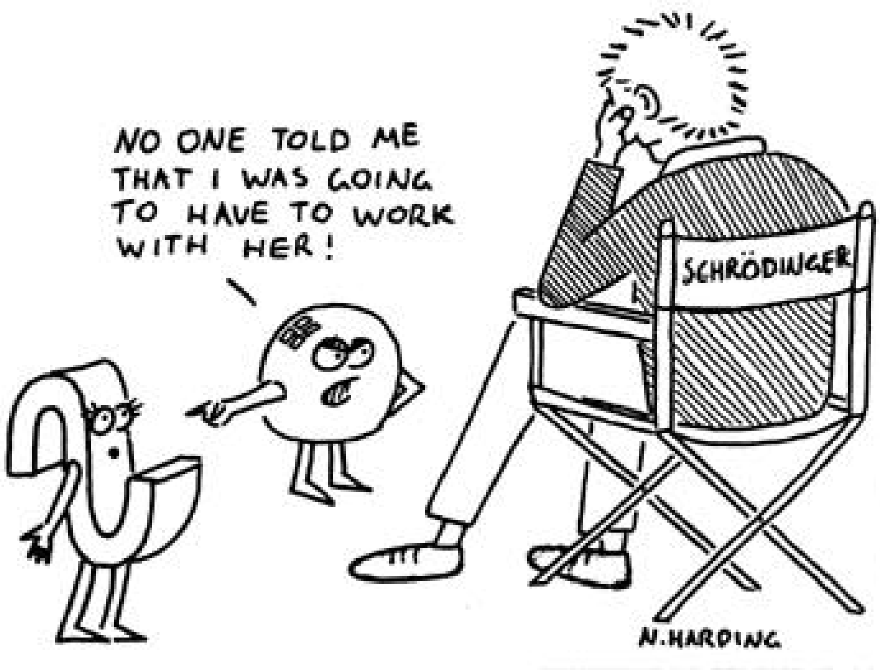
Additional points: Wavepacket picture discussed is at a single time. If we view the wavepacket passing a fixed position, we will see a very similar disturbance as a function of time. A wavepacket in the time domain is made up of waves of different angular frequencies and its width in time Δt is related to the spread in frequencies $\Delta\omega$ by the relationship $\Delta t \, \Delta\omega \approx 1$.

Multiplying by $\hbar$ we arrive at an energy-time uncertainty relation:

$$\Delta E \Delta t \approx \hbar$$

Upshot: Transitions between energy levels of atoms/molecules are not perfectly sharp in frequency $\Rightarrow$ *lifetime broadening*. See later spectroscopy and photochemistry lectures.

Summary



NO ONE TOLD ME THAT I WAS GOING TO HAVE TO WORK WITH HER!
SCHRÖDINGER
N. HARDING