

Plank got around this by suggesting that the electrons in the walls of the box vibrating at frequency  $f = \omega/(2\pi)$  can only do this in quantised units of  $E = nhf$  and we know from thermodynamics that the population at any energy level is  $N(E) = Ce^{-E/kT} = Ce^{-nhf/kT}$ . so then the average energy is

$$\begin{aligned}
 \langle E \rangle &= \frac{\int N(E)E dE}{\int N(E)dE} \\
 &= \frac{\sum_n nhfe^{-nhf/kT}}{\sum_n e^{-nhf/kT}} \\
 &\approx \frac{hfe^{-hf/kT} + 2hfe^{-2hf/kT} + 3hfe^{-3hf/kT} + 4hfe^{-4hf/kT} \dots}{e^{-hf/kT} + e^{-2hf/kT} + e^{-3hf/kT} + e^{-4hf/kT} \dots} \\
 &= \frac{hfx(1 + 2x + 3x^2 \dots)}{x + x^2 + x^3 \dots} = \frac{hfx(1-x)^{-2}}{(1-x)^{-1}} \\
 &= \frac{hfe^{-hf/kT}}{1 - e^{-hf/kT}} = \frac{hf}{e^{hf/kT} - 1}
 \end{aligned}$$

so then  $I(\lambda) \propto \langle E \rangle / \lambda^4$  so

$$\propto \frac{hf}{\lambda^4(e^{hf/kT} - 1)} = \frac{hc}{\lambda^5(e^{hc/\lambda kT} - 1)}$$

Fit to the data and get a fabulous fit!! and the value of  $h$  !!

fundamentally, what it does is reduce the number of the short wavelength states as  $e^{-nhf/kT}$  is zero for all but  $n = 0$  for  $hf \gg kT$

so this really highlights that electron energies are quantised - in atoms and in continuum states.

## 4 Quantum mechanics

we need a better theoretical framework for handling wave particle duality. We need an equation which can describe the wavelike properties of particles and the particle properties of waves

## 4.1 wave equations

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

a solution for sinusoidal waves travelling from left to right is

$$y(x, t) = A \cos(kx - \omega t) + B \sin(kx - \omega t)$$

where  $k = 2\pi/\lambda$  (wave number) and  $\omega = 2\pi f$  (angular frequency) and  $A, B$  determine the amplitude and phase of the wave

you can take the second partial derivatives w.r.t.  $x$  and  $t$  and show that this does indeed satisfy the wave equation for waves of velocity  $v = \omega/k$ , which means that  $v = 2\pi f \lambda / (2\pi) = f \lambda$

so now we need a version of the wave equation which can describe particles!

for particles, we have the de Broglie relation  $p = h/\lambda = \hbar k / (2\pi) = \hbar k$ . We know also that  $E = hf$  (from blackbody radiation) for particles. so then

$$E = hf = (h/2\pi)(2\pi f) = \hbar \omega$$

but we also know that  $E = 1/2mv^2 = p^2/(2m) = \hbar^2 k^2 / (2m)$  so our relation now between  $\omega$  and  $\lambda$  is quite different to that for waves on a string. A free particle has  $E = \hbar \omega = \hbar^2 k^2 / (2m)$

lets assume a sinusoidal wave

$$\Psi(x, t) = A \cos(kx - \omega t) + B \sin(kx - \omega t)$$

we want  $E = \hbar \omega = \hbar^2 k^2 / (2m)$ . lets do the last term first. we can get  $k^2$  by the second derivative

$$\begin{aligned} \frac{\partial^2 \Psi(x, t)}{\partial x^2} &= \frac{\partial}{\partial x} [-Ak \sin(kx - \omega t) + Bk \cos(kx - \omega t)] \\ &= -Ak^2 \cos(kx - \omega t) - Bk^2 \sin(kx - \omega t) = -k^2 \Psi(x, t) \end{aligned}$$

so we could easily justify something like

$$E\Psi(x, t) = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x, t)}{\partial x^2} = -\frac{\hbar^2}{2m} (-k^2 \Psi(x, t)) = \frac{\hbar^2 k^2}{2m} \Psi(x, t)$$

But the time bit is very different - we now want  $E = \hbar \omega$  so we can get there with only a single derivative

$$\frac{\partial \Psi(x, t)}{\partial t} = \omega[A \sin(kx - \omega t) - B \cos(kx - \omega t)]$$

what we would really like for the term in square brackets to equal  $C\Psi$ ! so if this were true then

$$[A \sin(kx - \omega t) - B \cos(kx - \omega t)] = C[A \cos(kx - \omega t) + B \sin(kx - \omega t)]$$

equating coefficients of sine we get  $A = CB$ , while for cosine its  $-B = CA$ . Divide and get  $-A/B = B/A$  i.e.  $B^2 = -A^2$  and  $B = \pm iA$ . Take the +ve root. and firstly our electron wave is COMPLEX

$$\Psi = A[\cos(kx - \omega t) + i \sin(kx - \omega t)] = Ae^{i(kx - \omega t)}$$

Secondly, we get  $C = -B/A = -i$  so  $\partial \Psi / \partial t = -iE/\hbar \Psi$ . Multiply both sides by  $i\hbar$  and get  $i\hbar \partial \Psi / \partial t = E\Psi$ . We can now put everything together and our wave equation FOR A FREE PARTICLE MOVING IN ONE DIMENSION is

$$\frac{-\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} = i\hbar \frac{\partial \Psi}{\partial t} = E\Psi$$

But we got here by thinking about the energy of a free particle, which is all kinetic. If instead we have a potential then the energy is both kinetic and potential so

$E = \hbar\omega = \hbar^2 k^2 / (2m) + U$ . We made the free particle wave into a differential equation using

$$E\Psi = \hbar\omega\Psi = \hbar^2 k^2 / (2m) \Psi$$

so now we can do this for the more general case where there is a potential as well

$$E\Psi = \hbar\omega\Psi = (\hbar^2 k^2 / (2m) + U)\Psi$$

$$\frac{-\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + U\Psi = i\hbar \frac{\partial \Psi}{\partial t} = E\Psi$$

This is the time dependent Schroedinger equation in 1 dimension.

it is linear and homogeneous so if  $\Psi_1$  and  $\Psi_2$  are two different solutions of the Schroedinger equation, then their linear sum  $\Psi = c_1\Psi_1 + c_2\Psi_2$  is also a solution.

It is also first order in the time derivative, with only  $\partial/\partial t$  rather than the  $\partial^2/\partial t^2$  of the classical wave equation. For classical waves we need both

the wave function  $\Psi$  and its first derivative  $\partial\Psi/\partial t$  in order to determine its behaviour as a function of time. Here, we only need the wave function at some time  $t_0 = 0$  in order to completely specify the subsequent behaviour of the system.