PHYSICS 2800 – 2^{nd} TERM

Outline Notes

Section 1. Basics of Quantum Physics

The approach here will be somewhat historical, emphasizing the main developments that are useful for the applications coming later for materials science. We begin with a brief (but incomplete history), just to put things into context.

1.1 Some historical background (exploring **"wave"** versus **"particle"** ideas)

Before ~ 1800:

Matter behaves as if continuous (seems to be infinitely divisible)

Light is particle-like (shadows have sharp edges; lenses described using ray tracing).

From ~ 1800 to ~ early1900s:

Matter consists of lots of particles

- measurement of e/m ratio for electron (JJ Thomson 1897)
- measurement of e for electron (Millikan 1909; he deduced mass m_e was much smaller than m_{atom})
- discovery of the nucleus (Rutherford 1913; he found that α particles could scatter at large angles from metal foil).

Light is a wave

- coherent light from two sources can interfere (Young 1801).

Just after ~ 1900:

Light is a particle (maybe)?

- photoelectric effect (explained by Einstein 1905 assuming light consists of particles)
- Compton effect (Compton 1923; he explained scattering of X-rays from electrons in terms of collisions with particles of light; needed relativity).

Matter is a wave (maybe)?

- matter has wavelike properties and can exhibit interference effects (de Broglie wave hypothesis 1923)
- the Bohr atom (Bohr 1923: he developed a model for the H-atom with only certain stable states allowed $\rightarrow$ ideas of "quantization")
- interference effects shown for electrons and neutrons (now the basis of major experimental techniques).

The present time:

Both matter and light can have both particle and wavelike properties.

This behaviour can be summed up in 2 important relations:-

♦ For the energy of the particle (photon) of light: $E = hf$ (Planck's hypothesis)
where E is the energy, f is the frequency ($= c/\lambda$ where λ is the wavelength) and h is a proportionality factor (Planck's constant).

♦ For the wavelength of a particle: $\lambda = h/p$ (de Broglie's hypothesis)
where p is the momentum and h is the same Planck's constant.

Next we look in more detail at the evidence for the particle nature of light.

1.2 The photoelectric effect

The basic idea:

When light hits the surface of a material, electrons can be emitted. If these are collected an electical current I can be measured.

The work function W:

This is the minimum energy that must be supplied to the electron for it to overcome the forces holding it inside the material, thus allowing it to escape.

What is surprising?

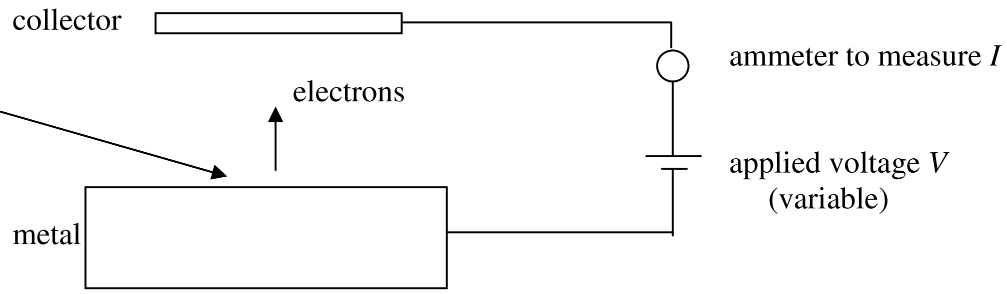
1. Electrons are only emitted if the frequency f of the light is larger than some value f_{min}, no matter how bright the light is.
2. When electrons are emitted, their energy depends on the frequency of the light, but not on the intensity.
3. If $f > f_{\text{min}}$ some electrons are emitted right away, no matter how dim the light is.

The basic explanation:

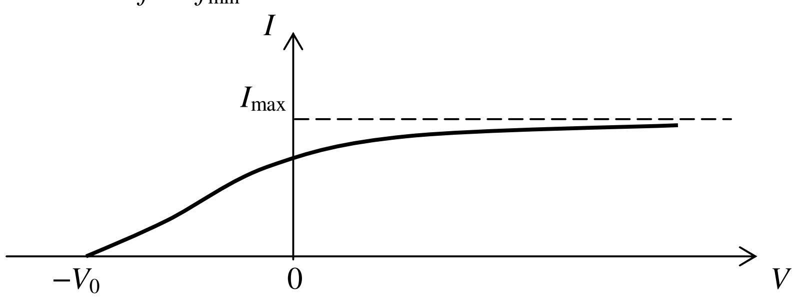
Einstein postulated that light is made up of small packages of energy (photons). He used Planck's hypothesis that $E_{\text{photon}} = hf$, where Planck's constant $h = 6.626 \times 10^{-34}$ J s.

Now we look at the details:-

The idealized experimental set-up is



Light shines on the surface; a voltage can be applied to the collector plate (detector) to attract electrons; a current I can be measured.
Typical results when $f > f_{\text{min}}$ look like



For large V, I levels off (all emitted electrons are collected). When $V = 0$ or slightly negative, I is still nonzero (because some electrons will still get to the detector if they are heading straight for it). When V is sufficiently negative, there will be a value $-V_0$ for which no electrons reach the detector. V_0 is called the "stopping potential", and it is usually measured in an experiment by adjusting V until $I = 0$.

We can explain the results using Planck's hypothesis and conservation of total (kinetic plus potential) energy:-

Time 1: photon is inside the metal surface but has not yet interacted with the electron

$$E_{\text{photon}} = hf, \quad U_e = -W, \quad K_e \sim 0$$

Time 2: photon has given all its energy to electron (and ceases to exist)

$$U_e = -W, \quad K_e = hf$$

Time 3: electron has just left the surface and is outside the metal

$$U_e = 0, \quad K_e = hf - W$$

This last result allows us to explain and find f_{min}. K_e has to be positive, and so the minimum f is when $hf_{\text{min}} = W$ (i.e. the electron just barely leaves the surface with no KE left over). Thus

$$f_{\text{min}} = W/h$$

Time 4: electron reaches the detector

Recalling that potential differences are measured in Volts and that 1 V = 1 J/C, it follows that the change of potential energy of an electron (charge $-e$) going though a potential difference V is

$$\Delta U_e = -eV$$

so when the electron reaches the detector its KE is

$$K_e = hf - W + eV$$

If we now adjust V until it is sufficiently negative ($= -V_0$) that the electrons only just stop arriving, we have

$$0 = hf - W - eV_0$$

This can be rearranged as

$$eV_0 = hf - W \qquad \rightarrow \qquad \text{This the photoelectric equation for } V_0.$$

Example 1. Assuming that a 60W bulb emits photons of average wavelength $\lambda = 600$ nm, how many photons are emitted per second?

Answer. Recall that 1 W = 1 J/s, and so

Total energy emitted per second = 60 J

Energy of each photon $= hf = hc/\lambda$

$$= \frac{(6.626\times10^{-34}\,\text{Js})(3.0\times10^{8}\,\text{m/s})}{600\times10^{-9}\,\text{m}} = 3.31\times10^{-19}\ \text{J}$$

Therefore, no. of photons emitted per second $= \dfrac{60\ \text{J}}{3.31\times10^{-19}\ \text{J}} = 1.81\times10^{20}$

Example 2. When UV light of wavelength 400 nm falls on the surface of a particular metal, a stopping potential $V_0 = 1.1$ V is needed to prevent electrons from reaching a detector.

(a) What is the maximum KE of electrons just after they have left the surface?
(b) What is the speed of those electrons?
(c) What is the work function of the metal?
(d) What will be the new value of stopping potential if light of wavelength 300 nm is used?

Answer.

(a) KE of electrons = difference in potential energy between surface and detector

$= 0 - (-eV_0) = eV_0 = (1.6 \times 10^{-19}\ \text{C})(1.1\ \text{J/C})$

$= 1.76 \times 10^{-19}\ \text{J}$

Equivalently, this can be expressed in electron-Volts as 1.1 eV. [use 1 eV $\equiv$ 1.6 $\times 10^{-19}$ J].

(b) KE $= \frac{1}{2} m_e v^2$

Therefore velocity $v = \sqrt{\dfrac{2\,\text{KE}}{m_e}} = \sqrt{\dfrac{2(1.76\times10^{-19}\ \text{J})}{9.11\times10^{-31}\ \text{kg}}}$ = 622000 m/s.

(c) From the photoelectric equation,

$$W = hf - eV_0 = \frac{(6.626\times10^{-34}\ \text{Js})(3\times10^{8}\ \text{m/s})}{400\times10^{-9}\ \text{m}} - (1.6\times10^{-19}\ \text{C})(1.1\ \text{J/C})$$

$= 3.21 \times 10^{-19}$ J (or equivalently 2.01 eV)

(d) Again, using the photoelectric equation,

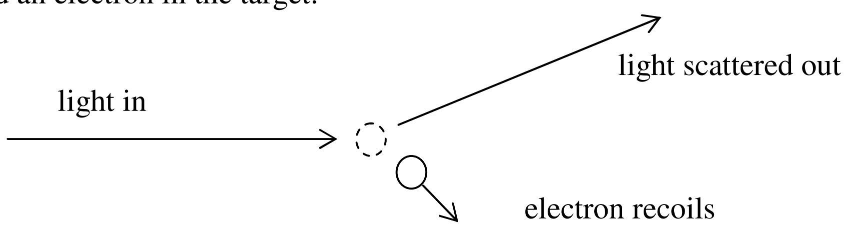
$$V_0 = \frac{hf}{e} - \frac{W}{e} = \frac{hc}{e\lambda} - \frac{W}{e}$$

$$= \frac{(6.626\times10^{-34}\ \text{Js})(3\times10^{8}\ \text{m/s})}{(1.6\times10^{-19}\ \text{C})(300\times10^{-9}\ \text{m})} - \frac{3.21\times10^{-19} J}{1.6\times10^{-19}\ \text{C}} = 2.14\ \text{V}$$

Compton scattering

This provided further major evidence for the particle nature of light:
If X-rays are directed at a target material, some will pass straight through unchanged, BUT some are scattered at an angle to the incident direction and, surprisingly, these have a *lower* frequency.

The explanation is that we can think of this event as a particle-like collision between the photon and an electron in the target.



Because the electron gains kinetic energy from the collision, the X-ray photon has lost energy when it is scattered out. Since $E_{\text{photon}} = hf$ it follows that f must decrease, as observed.

Using conservation of total energy and momentum, we could work out the change in f.

1.3 The wave properties of matter

Since light has both wave and particle properties, perhaps matter does as well (de Broglie's hypothesis). He proposed that a particle of mass m moving at speed v would have a wavelength

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

Soon afterwards, experiments were able to detect such properties, and nowadays they are important for many techniques.

- The wave nature of particles was first seen (accidentally) by Davisson and Germer. They noticed Bragg peaks in the reflection of electrons from a single Ni crystal.
- Shortly after, GP Thomson studied the diffraction pattern when electrons passed through thin Au foils.

Example 1. What is the wavelength of a snowflake (mass 1 g) falling through the air at a speed of 5 m/s?

Answer. $\lambda = \frac{h}{mv} = \frac{6.626\times10^{-34}\,\text{Js}}{(10^{-3}\,\text{kg})(5\,\text{m/s})} = 1.3\times10^{-31}\,\text{m}$

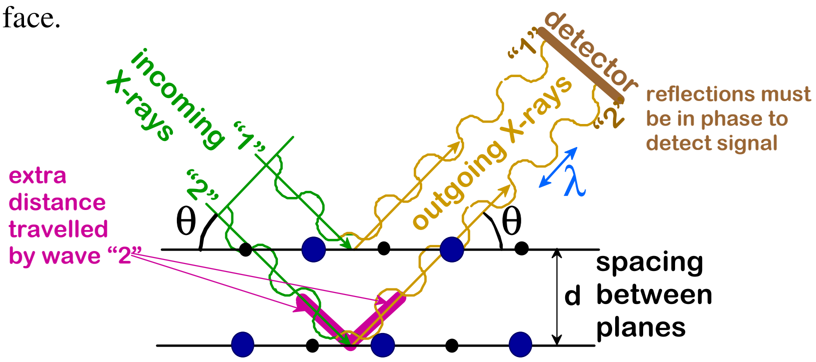
Example 2. Electrons incident on the (100) face of a fcc Ni crystal are scattered by Bragg reflection at an angle of 50^0 to the plane.

(a) What is the wavelength λ of the electrons if it is a second order Bragg process (with order $m = 2$)?
(b) What is the velocity of the electrons?
(c) What potential difference is needed to produce electrons of that speed?

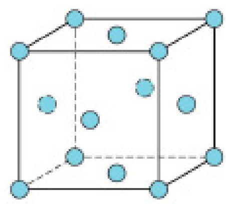
Answer. The basis of this question is Bragg's law (from last term or texbook section 3.11):

$$2d\sin\theta = m\lambda$$

where we are now told $\theta = 50^0$ and $m = 2$. Also d is the distance between planes of atoms for the (100) face.



From a sketch of the fcc structure it is easy to show that $d = a/2$ (where the cube has edges of size $a = 0.1246$ nm for Ni).



(a) $\lambda = 2(a/2)\,(\sin\theta)/2 = (a/2)\sin 50^0 = 0.0477$ nm.

(b) From de Broglie's hypothesis, $\lambda = h/p = h/(mv)$

$$\therefore \quad v = h/(m\lambda) = \frac{6.626\times10^{-34}\ \text{Js}}{(9.11\times10^{-31}\ \text{kg})(0.0477\times10^{-9}\ \text{m})} = 1.52\times10^{7}\ \text{m/s}$$

(c) These electrons have a KE $= \frac{1}{2}mv^2 = 1.06\times10^{-16}$ J. To gain this KE they must be accelerated through a potential difference of

$$\Delta V = \frac{1.06\times10^{-16}\ \text{J}}{1.6\times10^{-19}\ \text{C}} = 661\,\text{V}$$

Wave-particle duality

To summarize, we have seen that some properties of light that can only be explained by its wave nature (e.g., interference patterns) while there is also good evidence that light comes in discrete packages. Also matter, which is made up of particles, can behave in ways expected of waves.

This "duality" can be highlighted in a simple experiment: *Shine a beam of a low-intensity wave through a double slit and examine the interference pattern produced on a screen behind the slits.*

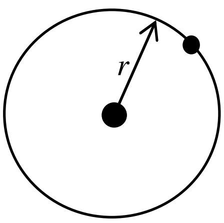
Suppose we turn the intensity down very low. The pattern will still be seen, but now we have to wait for it (it starts with just a few spots and gradually builds up to the expected pattern).

This kind of experiment can be done with either light or with particles. However, if only one particle is going through the slit arrangement at one time, what is it interfering with? A single slit would not give an interference pattern, so we have to conclude that the electron (say) interacts with *both* slits on its way to the screen. This only "makes sense" if we think of the electron as having wave-like properties.

1.4 Quantum models of simple atoms

The Rutherford atom

Recall that the Rutherford scattering experiments (using α particles directed at a metal foil) led to the conclusion that the atom has a concentrated, positively charged nucleus where most of the mass is located. The electron (if we take the simplest case of the H atom) is assumed to be in some kind of orbit (taken to be circular) under the influence of the Coulomb force of attraction.



We assume the much heavier proton in the centre does not move. From Newton's 2nd law for the radial component of the electric force (Coulomb's law) in terms of the centripetal acceleration,

$$\frac{ke^2}{r^2} = m\frac{v^2}{r}, \quad \text{giving} \quad \frac{ke^2}{r} = mv^2.$$

The total energy is therefore

$$E = \tfrac{1}{2}mv^2 - \frac{ke^2}{r} = \tfrac{1}{2}\frac{ke^2}{r} - \frac{ke^2}{r} = -\frac{ke^2}{2r}$$

Note that this is negative (and small r implies that the electron is more tightly bound).

This model (so far) has 2 major problems:

- It provides no explanation for the observation that atoms emit light of only specific wavelength. If there are no restrictions on r, it follows that E (and hence changes in E) can take any value.
- It was known that accelerated charges (the electron having centripetal acceleration) will continuously emit electromagnetic radiation (e.g. a radio antenna, a synchrotron, etc). So the electron in the atom should lose energy and the atom would be unstable.

The Bohr atom

Bohr dealt with the problems of the Rutherford atom by postulating that there are only certain orbits that the electron can occupy and that only these are stable. If the electron goes from one of these stable orbits to another stable orbit, it either absorbs or emits a photon of exactly the difference in energy (by *Planck's hypothesis*).

One way to specify the assumption about the stable orbits is to say that the circumference of the circular orbit must be an integer multiple of the de Broglie wavelengths $\lambda = h/(mv)$.

Thus it is assumed that $$2\pi r = n\frac{h}{mv} \qquad (n = 1, 2, 3, \ldots) \qquad (1)$$

We previously had another relation between v and r, namely

$$\frac{ke^2}{r} = mv^2 \qquad (2)$$

We can solve (1) for v, and then substitute this into (2) to get an expression for r. It gives

$$r = \frac{n^2\hbar^2}{ke^2m} \qquad \text{(defining } \hbar = h/2\pi\text{)}$$

The previous expression for the total energy become

$$E = -\frac{ke^2}{2r} = -\frac{k^2e^4m}{2\hbar^2}\frac{1}{n^2}$$

We will rewrite this as

$$E_n = -\frac{E^0}{n^2} \qquad \text{where the constant } E^0 = \frac{k^2e^4m}{2\hbar^2}$$

Example 1: What is (a) the radius of the H-atom with $n = 1$ (its lowest energy) and (b) what is the ionization energy?

Answer: (a) From the expression for r (taking $n = 1$):

$$r = \frac{(1)^2(6.626\times10^{-34}\,\text{Js})^2/(2\pi)^2}{(9\times10^9\,\text{Nm}^2/\text{C}^2)(1.6\times10^{-19}\,\text{C})^2(9.11\times10^{-31}\,\text{kg})} = 5.29\times10^{-11}\,\text{m} = 0.0529\,\text{nm}$$

This called the Bohr radius (and usually denoted by a_0).

(b) The ionization energy is the energy that must be supplied to separate the electron from the nucleus (i.e., its final energy will be zero). The required energy is

$$\Delta E = E_f - E_i = 0 - E_{n=1} = ke^2/2a_0$$

$$= \frac{(9\times10^9\,\text{Nm}^2/\text{C}^2)(1.6\times10^{-19}\,\text{C})^2}{2(0.0529\times10^{-9}\,\text{m})} = 2.18\times10^{-18}\,\text{J} = 13.6\,\text{eV}$$

This is in excellent agreement with the experimental value for H.

This model can be used to explain the line spectra of H by using the expression for E_n together with energy conservation and Planck's hypothesis for the energy of the emitted or absorbed photon, as shown below.

Suppose the electron undergoes a transition from a level n_i to a lower level n_f. We have

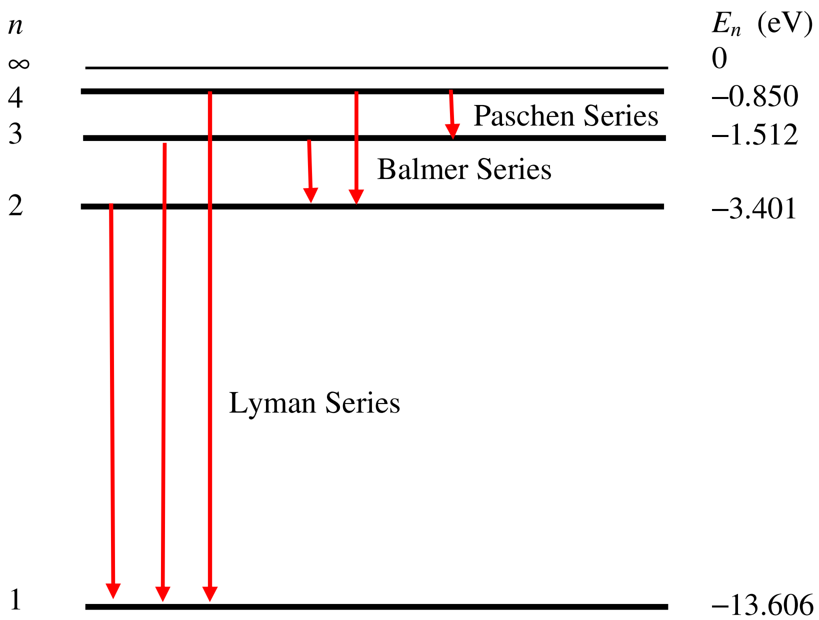
$$\text{initial energy} \quad = \quad -\frac{E^0}{n_i^2} \quad = \quad -\frac{E^0}{n_f^2} + E_{\text{photon}} \quad = \quad \text{final energy}$$

$$E_{\text{photon}} \quad = \quad E^0\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \quad = \quad hf \quad = \quad hc/\lambda$$

$$\therefore \qquad \frac{1}{\lambda} \quad = \quad \frac{E^0}{hc}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

The factor E^0/hc is called the Rydberg constant R_H (where $R_H = 1.097 \times 10^7\ \text{m}^{-1}$).

The above formula for $1/\lambda$ can be usefully interpreted in terms of an energy-level diagram (see below).



Example 2: The wavelength of one of the lines observed in the infrared part of the spectrum of H is $\lambda = 1.281\ \mu\text{m}$. To what transition does this correspond?

Answer: One way is to determine the photon energy:

$$E_{\text{photon}} \quad = \quad \frac{hc}{\lambda} \quad = \quad \frac{(6.626\times10^{-34}\,\text{Js})(3\times10^{8}\,\text{m/s})}{1.281\times10^{-6}\,\text{m}} \quad = \quad 1.55\times10^{-19}\ \text{J} \quad = \quad 0.970\,\text{eV}$$

Then we compare with an energy-level diagram (in most textbooks) to find by inspection two levels separated by this amount. Eventually, we find that

$$E_5 - E_3 \quad = \quad -0.544\ \text{eV} - (-1.512\ \text{eV}) \quad = \quad 0.968\ \text{eV}$$, which gives a fit.

Another way is to use the derived expression for $1/\lambda$ to write

$$\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) = \frac{1}{R_H \lambda} = \frac{1}{(1.097\times10^7\,\mathrm{m}^{-1})(1.281\times10^{-6}\,\mathrm{m})} = 0.0712$$

Now try various n_i and n_f until finding that

$$\frac{1}{3^2} - \frac{1}{5^2} = \frac{1}{9} - \frac{1}{25} = 0.0711 \text{ , which gives a fit.}$$

The Bohr model also works for other "one-electron" atoms (He^+, Li^{2+}, Be^{3+}, etc). We just need to repeat the calculation taking the charge on the nucleus to be Ze, where Z is the atomic number. The results are

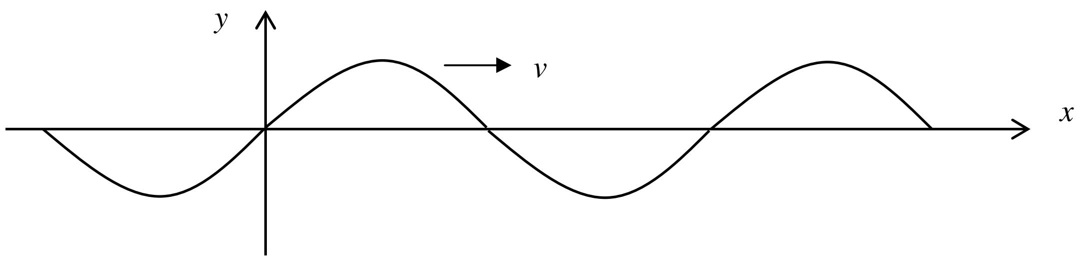
$$r_n = \frac{a_0 n^2}{Z} \quad \text{and} \quad E_n = -\frac{Z^2 E^0}{n^2}$$

It also works (with modifications) for other "H-like" systems, such as positronium and muonium (where the nucleus is replaced by a positron or a muon respectively).

However, despite the above successes, the Bohr model does not work for other atoms with more than one unpaired electron, <u>or</u> for molecules, <u>or</u> even for the H-atom when magnetic field effects are important. Hence there is a need for a new theory (Quantum Mechanics).

1.5 The quantum description of a particle

From the duality ideas, we need to develop a theory of particles in terms of waves. In "classical" physics we usually think of a traveling wave — one that (ideally, at least) is an oscillation that goes on forever. A simple example is a wave in a very long string:



Other examples are sound waves in a gas and electromagnetic waves. In all these cases there is a physical quantity that is oscillating (displacement in a string, gas pressure, the electric field, etc). They behave typically like

$$y(x,t) = A\sin(kx - \omega t) \text{ or } A\cos(kx - \omega t), \qquad \text{where } A, k \text{ and } \omega \text{ are constants.}$$

It is a function of both x and t, and it tells you what each part of the string is doing at all times. The constants are

A = amplitude
$k = 2\pi/\lambda$ = wavenumber
$\omega = 2\pi f$ = angular frequency.

It is easy to check that, when $t \rightarrow t + T = t + (1/f)$ where T is the period, a point at a given x goes through 2π rad (or 360^0) oscillation. Likewise, when $x \rightarrow x + \lambda$ for a fixed t, the wave moves through a full cycle (2π rad).

Note that $\quad \omega/k = 2\pi f(\lambda/2\pi) = f\lambda = v \quad$ (the speed of the wave)

How might we apply this to a particle? First, there is a practical problem because, if the particle's wave extends for ever with $\lambda = h/p$, then where is the particle? Presumably it is everywhere in this case, but how do we describe a localized particle like an electron? The answer is in terms of a wave packet.

As a simplified example, consider a wave that at a particular instant of time ($t = 0$, say) looks like

$$y_1(x) = A\cos(k_1 x)$$

and another wave (at the same time) with the same amplitude but slightly different k:

$$y_2(x) = A\cos(k_2 x)$$

Suppose now we superimpose the 2 waves (add them) to get the resultant:

$$y(x) = y_1(x) + y_2(x) = A\,[\cos(k_1 x) + \cos(k_2 x)]$$

We can use the trig identity that

$$\cos(a) + \cos(b) = 2\cos[\tfrac{1}{2}(a-b)]\cos[\tfrac{1}{2}(a+b)]$$

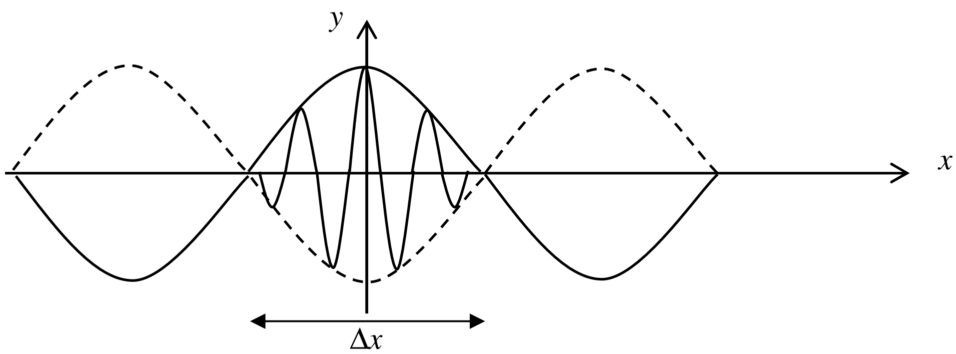
which leads to

$$y(x) = 2A\cos(\tfrac{1}{2}\Delta k\,x)\cos(\bar{k}\,x)$$

where $\quad \Delta k = k_1 - k_2 \quad$ spread of k values

$\bar{k} = (k_1 + k_2)/2 \quad$ average value of k

Consider what this looks like. There is a cosine of wavelength $2\pi/(\tfrac{1}{2}\Delta k) = 4\pi/\Delta k$, which has a large wavelength because Δk is small. This is multiplied by another cosine with a much smaller wavelength $= 2\pi/\bar{k}$.



Note that $\quad \Delta x = \tfrac{1}{2} \times$ large wavelength $= \tfrac{1}{2} \times 4\pi/\Delta k = 2\pi/\Delta k$,

and so $\quad \Delta x\,\Delta k = 2\pi \quad$ for the wave-packet.

We could generalize this process by adding more and more waves with different k (and also allowing different A), but the above argument is sufficient to give the basic idea: The envelope (wave-packet) is taken to travel at the same speed as the "particle" that it represents.

Heisenberg's Uncertainty Principle

Notice the "price" we had to pay to localize our particle:-

- The "perfect wave" (with just one value of wavelength) goes on forever. We do not know where the particle is, but we know its momentum very well:
  $$p = h/\lambda = (h/2\pi)(2\pi/\lambda) = \hbar k.$$
- In a wave-packet, there are only waves in a limited region of x, but there is a spread of k values (or momentum values).

The more localized the particle is, the less well we know its momentum. The general result is in terms of an inequality:

$$\Delta x \, \Delta p \geq \hbar/2$$

As an example of this, we remember the result that adding just 2 waves gives $\Delta x \, \Delta k = 2\pi$. Also we have $p = \hbar k$, and so $\Delta p = \hbar \Delta k$. Putting these together gives

$\Delta x \, \Delta p = 2\pi\hbar$, which satisfies the inequality in the general result.

Example: A 20 g rifle bullet and an electron both have a velocity of 500 m/s, determined to within ± 0.01 m/s. How accurately can we determine their positions?

Answer: Take the case of equality in the Uncertainty relation:

For a bullet,
$$\Delta x = \frac{\hbar}{2\Delta p} = \frac{\hbar}{2m\Delta v} = \frac{h}{4\pi m\Delta v}$$
$$= \frac{6.626\times10^{-34}\,\text{Js}}{4\pi(0.02\ \text{kg})(0.01\ \text{m/s})} = 2.6\times10^{-31}\ \text{m}$$

For an electron,
$$\Delta x = \frac{6.626\times10^{-34}\,\text{Js}}{4\pi(9.11\times10^{-31}\ \text{kg})(0.01\ \text{m/s})} = 5.8\ \text{mm}$$

1.6. The wave function and Schrödinger's equation

So far, in the case of particle waves, we have not said what physical property is oscillating. What we would like is a wave function analogous to $y(x,t) = A\cos(kx - \omega t)$ as discussed earlier for (e.g.) a wave on a string.

In QM this function is usually denoted (in 1 spatial dimension x) by $\Psi(x,t)$.

Ψ itself is not a measurable quantity!! Indeed, it turns out to be a complex number in general, i.e., it can have the form

$\Psi = a + ib$, where a and b are both real and $i^2 = -1$.

However, the modulus or amplitude (which is denoted by $|\Psi|$) of Ψ is measurable, and has the property that

$|\Psi|^2\, dx$ = probability that the particle is found in the range dx around position x.

The complex conjugate Ψ^* is used to form

$$|\Psi|^2 = \Psi^*\Psi = (a - ib)(a + ib) = a^2 + b^2$$

This is called the probability density.

In many problems in QM we are dealing with stationary states (cases where the probability density is constant in time), and it turns out that

$$\Psi(x,t) \quad = \quad \psi(x) \ \times \ [\cos(Et/\hbar) + i\sin(Et/\hbar)]$$

so the position dependence and time dependence are separated. E is the (constant) energy.

[Why is this? To get some insight we use Planck's hypothesis rewritten as:

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

Therefore the time parts involve $\cos(\omega t)$ and $\sin(\omega t)$, which is just what we expect for a wave.]

As a simple example, the wave function of a free particle can be taken as

$$\psi(x) \quad = \quad A\,[\cos(kx) + i\,\sin(kx)],$$

Note that the cos and sin functions repeats when kx is increased by 2π radians:-

$$\psi(x + \lambda) \quad = \quad A\,[\cos(kx + k\lambda) + i\,\sin(kx + k\lambda)],$$

which is the same as $\psi(x)$ if $k\lambda = 2\pi$ or $k = 2\pi/\lambda$.

Then, from de Broglie's hypothesis, $\lambda = h/p$, so $k = 2\pi p/h$. This can be written as

$$p \quad = \quad \hbar k$$

Note that the probability density of the free particle is a constant because

$$|\psi|^2 \quad = \quad \psi^*\psi \quad = \quad A\,[\cos(kx) - i\,\sin(kx)]\,A\,[\cos(kx) + i\,\sin(kx)]$$

$$= \quad A^2\,[\cos^2(kx) + \sin^2(kx)] \quad = \quad A^2 \qquad \text{(a constant)}$$

i.e., the particle is equally likely to be found anywhere.

<u>Schrödinger's equation</u>

This provides us with a way to calculate $\psi(x)$ for a stationary state with energy E. If a particle of mass m moves in 1D with a potential energy $U(x)$, then the wave function satisfies

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + U(x)\psi(x) \quad = \quad E\psi(x)$$

We cannot derive this basic equation of QM any more than we can derive Newton's 2nd Law in classical mechanics, but we can check out that it works in some special case.

Let's take the example of a free particle, i.e., no net force acts on it so $U(x)$ is a constant. We may as well choose our origin of energy such that $U(x) = 0$, so

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} \quad = \quad E\psi(x)$$

But we already know that $\psi(x) = A\,[\cos(kx) + i\,\sin(kx)]$

Differentiating once gives

$$\frac{d\psi(x)}{dx} \quad = \quad Ak\,[-\sin(kx) + i\,\cos(kx)]$$

Differentiating again gives

$$\frac{d^2\psi(x)}{dx^2} \quad = \quad Ak^2\,[-\cos(kx) - i\,\sin(kx)] \quad = \quad -k^2\psi(x)$$

Substituting this into Schrödinger's equation gives

$$-\frac{\hbar^2}{2m}(-k^2)\,\psi(x) \quad = \quad E\psi(x)\,, \qquad \text{implying} \qquad E \quad = \quad \frac{\hbar^2 k^2}{2m}$$

This is as expected because $p = \hbar k$, and so

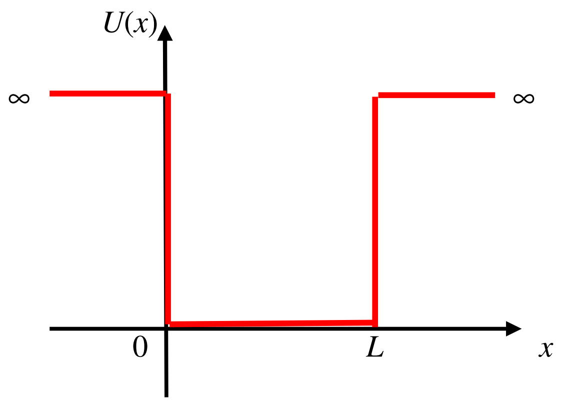
$$E \quad = \quad p^2/2m \quad = \quad (mv)^2/2m \quad = \quad ½mv^2 \qquad \text{(the usual kinetic energy).}$$

1.7 <u>Particle in a potential well</u>

A more interesting, and physically relevant, problem is to consider a particle trapped in a deep potential well, i.e., we idealize the potential energy by

$$U(x) \quad = \quad \begin{cases} \infty & x < 0 \\ 0 & 0 < x < L \\ \infty & x > L \end{cases}$$

where L is the width of the well.



We can assume that the particle lies between $x = 0$ and L, because outside this region the energy is infinite. So $\psi(x)$ is zero when $x < 0$ or $x > L$, and it remains to solve for $\psi(x)$ in the region between 0 and L. Schrödinger's equation gives

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} \quad = \quad E\,\psi(x)$$

This seems to be just the equation for a free particle, <u>except</u> that we must now take account of what happens at the <u>two boundaries</u> where $x = 0$ and $x = L$. It can be shown that $\psi(x)$ must be continuous, and hence the solution for $\psi(x)$ must vanish at $x = 0$ and $x = L$.

So let's try $\quad \psi(x) \quad = \quad A\,\sin(qx) \quad$ as a possible form of solution (q = unknown constant).
Now $\psi(x)$ automatically vanishes at $x = 0$, and to make it vanish at $x = L$ we must choose

$$qL \quad = \quad n\pi \quad \text{with} \quad n \quad = \quad 1, 2, 3, \ldots$$

Our solution is now $\quad \psi(x) \quad = \quad A\,\sin(n\pi x/L)\,, \quad$ and we must substitute this into Schrödinger's equation to find the energy:

We use $\quad \dfrac{d\psi}{dx} = A\left(\dfrac{n\pi}{L}\right)\cos(n\pi x/L) \quad$ and $\quad \dfrac{d^2\psi}{dx^2} = -A\left(\dfrac{n\pi}{L}\right)^2 \sin(n\pi x/L)$

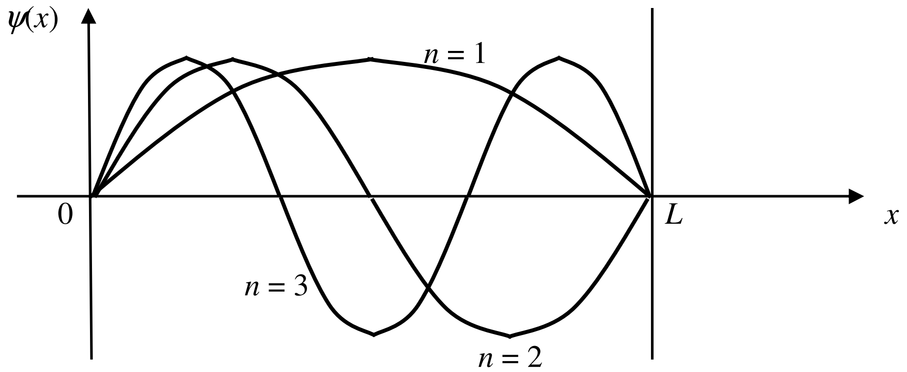
$$\therefore \quad -\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} \quad = \quad E\,\psi(x) \quad \text{implies} \quad \left(\frac{\hbar^2}{2m}\right)\left(\frac{n\pi}{L}\right)^2 A\sin(n\pi x/L) \quad = \quad E\,A\sin(n\pi x/L)$$

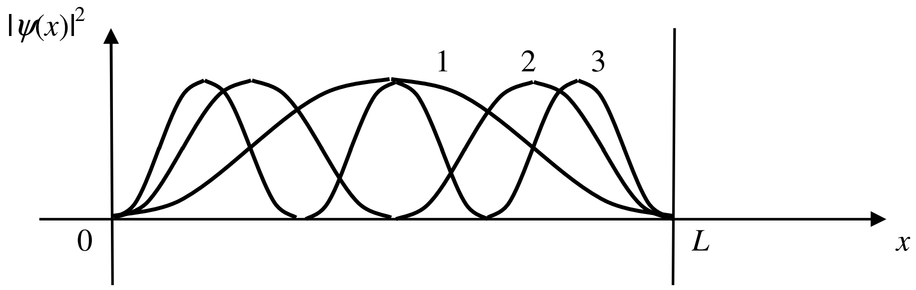
and so $\quad E \quad = \quad \left(\dfrac{h^2}{8mL^2}\right)n^2 \quad$ with $\quad n \quad = \quad 1, 2, 3, \ldots$

We find that our choice of $\psi(x)$ does work, and it leads to a set of discrete (or quantized) energy levels. Note that E is nonzero (and the particle has nonzero K.E.) even in the ground state $n = 1$.

If we want, we could calculate the overall constant A using the probability density: the total probability of finding the particle somewhere between 0 and L must be 1.

We can now sketch the form of $\psi(x)$ and $|\psi(x)|^2$ versus x from 0 to L. Note that for $n > 1$ there are points inside the well where the probability density is zero (these are called nodes).





Example: An electron is trapped in a 1D box that is 2 nm across.

(a) What will be the wavelength of the photon emitted in an energy transition between the lowest 2 levels?

(b) Estimate the speed of an electron when it is in the ground state.

Answer:

(a) The lowest transition is $n = 2$ to $n = 1$, so the photon energy will be

$$E_{\text{photon}} = \left(\frac{h^2}{8mL^2}\right)(2^2 - 1^2) = \frac{3h^2}{8mL^2} = 4.52\times10^{-20}\ \text{J} = 0.282\ \text{eV}$$

The wavelength will be

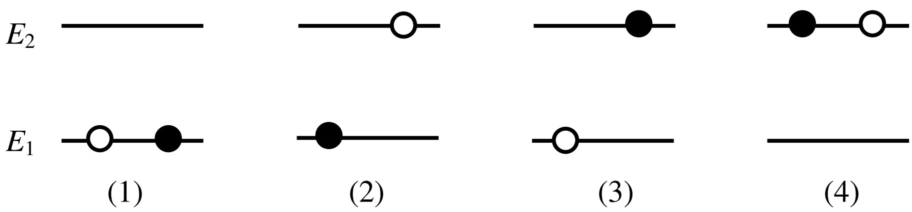
$$\lambda = c/f = hc/E_{\text{photon}} = 4.40\ \mu\text{m}$$

(b) Speed $\quad v = \dfrac{p}{m} = \dfrac{\sqrt{2mE}}{m} = \sqrt{\dfrac{2E}{m}} = \dfrac{h}{2mL} = 182000$ m/s

1.8 The Exclusion Principle

Another difficulty arising from QM is that fundamental particles are indistinguishable.

As a very simple example, consider a system with just 2 possible energy levels and containing just 2 particles. If we could distinguish between the particles, the possible ways of arranging them are



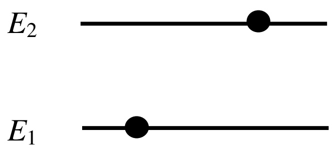
There are the four numbered possibilities in this case.

However, if the particles are indistinguishable, we cannot tell (2) from (3) and so there would seem to be only three distinct arrangements,

except that if the particles are electrons (or any other fermion) we have another rule:-

> *"**No two electrons can ever be in the same quantum state** (Pauli Exclusion Principle)".*

Thus arrangements (1) and (4) are not allowed, leaving just one possibility in this simple example:



The argument can be generalized to cases where there are more electrons and more states (and also by including effects due to electron spin).

In solids there are lots of electrons, so all the lower level states will be filled and many of the electrons will be at much higher energies.