L5: The Free Electron

Reminder: Key points from previous lectures

- we introduced kinetic energy

$$E_k = \frac{p^2}{2m}$$

- and potential energy (for a 1D HO potential)

$$E_p = \frac{1}{2}kx^2$$

- we explained how to convert classical operators into quantum mechanical operators

$$x \rightarrow x \qquad p_x \rightarrow \frac{\hbar}{i}\frac{\partial}{\partial x}$$

- we discussed *eigenvalue equations* which are equations with a special form of which the Schrödinger equation is an example, H=operator and E=constant

$$H\Psi = E\Psi$$

- we introduced our first wave equations

$$y = sin(\theta) \text{ and } y = cos(\theta)$$

Maths Prep for Today

- complex numbers can be written in polar coordinates

$$z = x + iy = r(cos\theta + isin\theta)$$

- *Euler's formula* links exponentials with sin/cos functions

$$e^{i\theta} = cos\theta + isin\theta$$

- so we can write complex numbers in an exponential format

$$z = re^{i\theta} \text{ and } z^* = re^{-i\theta}$$

- importantly a wavefunction expressed as an exponential is a function of cosθ and sinθ

In-class Activity 1

- write an expression for cosθ using the exponential form of complex numbers

The Free Particle Equation

- we start with the Schrödinger equation:

$$H = T + V$$

- we choose a 1D system that has no constraining potential (ie the *particle is free*) V(x)=0
  - we still have kinetic energy T

$$H = T + V \qquad V = 0$$

$$H = T = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$$

$$\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\right)\psi = E\psi$$

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} = E\psi$$

- the concept of a *partial differential equation* was introduced earlier
  - you are familiar with the equations for a line and for a quadratic

$$y = mx + c \qquad y = ax^2 + bx + c$$

  - another group of equations can be written for *derivatives*

$$0 = a\frac{\partial^2 f}{\partial x^2} + b\frac{\partial f}{\partial x} + cf$$

  - f is a function of one (x) or multiple variables (x,y,z)
  - the overall expression contains *differentials of increasing order*
  - we define that the equation is linear when the expression has =0
  - overall this is a *linear partial differential* equation
  - in an algebraic equation we would solve for x a variable, in a differential equation we solve for f a function
  - solving differential equations can be difficult (there are whole math courses on just this topic), I am just going to give you the solution

- the general form of the solution for a linear partial differential equation is

$$\psi = Ae^{+ikx} + Be^{-ikx}$$

where A, B and k are constants

In-class Activity 2

- confirm this is a valid solution by evaluating the Wave Equation for ψ

See also the On-Line Activity: Prove ψ is a solution

  - thus we have shown that this wavefunction "fits" the equation
  - ψ is an eigenfunction for the free particle equation, ψ is a *valid solution*

Energy and "k"

- we have shown that this equation is an *eigenvalue equation*

$$\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} = E\psi$$

$$\frac{\hbar^2}{2m}k^2\left(Ae^{ikx} + Be^{-ikx}\right) = E\left(Ae^{ikx} + Be^{-ikx}\right)$$

- and the following relationship holds

important

$$E = \frac{\hbar^2}{2m}k^2$$

  - this is very interesting! we now have a way of understanding the energy of the wavefunction
  - the energy is dependent a constant ($\hbar$), the mass of the particle and a "k" value
  - this k is not the same k as we used in the harmonic oscillator potential!
  - we can turn the equation around and find an expression for k, so k depends on the energy and mass of the particle

$$k = \left(\frac{2mE}{\hbar^2}\right)^{\frac{1}{2}}$$

  - we should understand this to mean that a particle with a *specific k* has a *specific energy*
  - our system could range over multiple energies, but each energy will correspond to a value of k and a different wavefunction solution (because of the functional form e^{ikx})

- we need to understand more about what k is, **Figure 1**
  - we know e^{ikx} can be written in terms of sin and cos functions

$$e^{ikx} = cos(kx) + isin(kx)$$

  - we know these components refer to a *real* (cos(kx)) and *imaginary* (sin(kx)) part of the wavefunction, **Figure 1a**
  - the real and imaginary parts of the wavefunction vary in sync (both have the same k)
  - typically we only draw the real part, it is assumed you know that there is an imaginary part following just behind
  - a large k means an energetic wave, short wavelength and many oscillations, **Figure 1b**
  - and a small k means a low energy wave, long wavelength and few oscillations

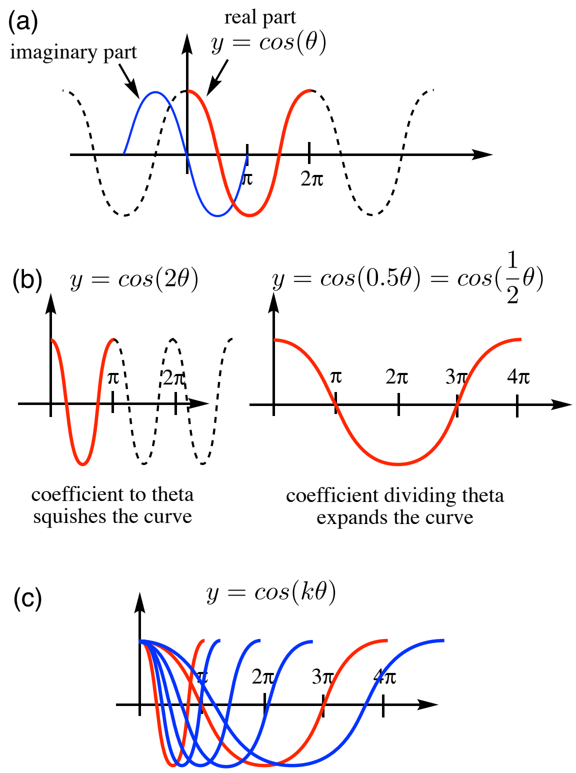


Figure 1 the wavefunction

- we have not constrained k or E in any way!
  - hence the name the "free electron"
  - the relationship allows for *continuous* values for both k and E, **Figure 1**
  - k allows the wavelength to spread over any value, it can be very small or vary long
  - this equation and its solution tell us that an electron moving through space (ie with momentum) experiencing no potential can take on any energy

Boundary Conditions

- the wavefunction solution as it stands is given below

$$\psi = Ae^{+ikx} + Be^{-ikx}$$

  - A and B are coefficients that determine the hight or amplitude of the waves
  - A and B are normally determined by the specifics of the problem as determined by *boundary conditions* (we will cover these shortly!)
  - however for a freely moving electron there are no boundary conditions, the electron is free to move in all space
  - we can also write a solution wavefunction in the sin and cos form by expanding out the exponentials

$$\psi = Ccos(kx) + iDsin(kx)$$
$$\text{where } C = A + B \text{ and } D = A - B$$

  - and we know that sin and cos curves go on infinitely (unless pinned by boundary conditions)
  - showing this equivalence is one of the end of lecture problems for you to do at home

Probability

- to find out where the particle could be we compute the *probability density* often just referred to the *probability*
- for example (suppose B=0)

$$\begin{aligned} \psi &= Ae^{ikx} \\ P(x) &= \psi^*(x)\psi(x) \\ &= Ae^{-ikx}Ae^{ikx} \\ &= A^2e^{-ikx+ikx} \\ &= A^2e^0 \\ &= A^2 \times 1 \\ &= A^2 \end{aligned}$$

  - notice the square, the probability density can never be negative, which is consistent with reality (the particle must be somewhere)
  - in this case *anywhere* we look (for any value of x) the probability of finding the particle is A^2, this *particle is delocalised*, this particle has an undefined position (but a well-defined momentum $=\hbar k$ as we will see shortly!)
  - this is consistent with the Heisenberg uncertainty principle, if the momentum is well defined the position is poorly defined.

In-class Activity 4

- what is the momentum of the wavefunction solution components?
  - hint: evaluate ψ with the momentum operator, first set B=0 and then A=0 and evaluate

On-Line Activity: Momentum of the free particle

  - thus e^{ikx} and e^{-ikx} are both *eigenfunctions* of the *momentum operator*

Momentum

- we see that the solution wavefunction is made up of two waves travelling in opposite directions, the "A" wave travels with positive $\hbar k$ momentum and the "B" wave travels with negative - $\hbar k$ momentum

$$\psi = Ae^{+ikx} + Be^{-ikx}$$

- A and B are determined by the initial conditions, so a wave might be "fired" at a target moving left to right (positive $p\psi = \hbar k\psi$) with B=0, that wave could be totally reflected by a perfect mirror and now is a wave moving right to left (negative $p\psi = -\hbar k\psi$) with A=0
- this is reminiscent of the classical wavefunctions from L3, **Figure 2**
  - if we wanted to "measure" the momentum we would need to take a large number of measurements. We would find that on average 1/2 the time a positive momentum and 1/2 the time a negative momentum, but before each individual measurement there would be no way to know which way the wave was moving!

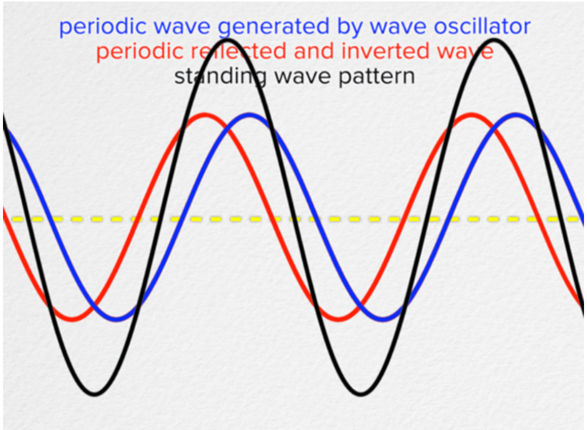


Figure 2 incoming (blue) and outgoing (red) waves interfering to give the (black) "standing: wave

- we also find that the momentum of a wave depends on k and $\hbar$, and since $\hbar$ is a constant the *momentum of a wave depends on k*
- and since k depends on the energy, k is a measure of how energetic a wave is

$$k = \left(\frac{2mE}{\hbar^2}\right)^{\frac{1}{2}}$$

- what is the momentum of the wavefunction in the sin/cos form?

$$\psi = Ccos(kx) + iDsin(kx)$$

- find this by evaluating ψ with the momentum operator, we will first set D=0

$$\begin{aligned} p\psi &= \frac{\hbar}{i}\frac{d\psi}{dx} \text{ and if } \psi = Ccos(kx) \\ &= \frac{\hbar}{i}\frac{d}{dx}Ccos(kx) \\ &= \frac{\hbar}{i}Cksin(kx) \\ &= -\hbar Cksin(kx) \\ &\neq -\hbar k\psi \end{aligned}$$

- now we have a problem!
- this wavefunction is NOT an eigenfunction of the momentum operator!!
- since cos(kx) is real this also tells us that the *wavefunction must be complex*, it cannot be totally real (nor can it be completely imaginary)
- but we can write the D=0 wavefunction in another form, which returns us to a linear superposition of waves

$$cos(x) = \frac{e^{+ix} + e^{-ix}}{2} \text{ therefore } Ccos(kx) = C(\frac{1}{2}e^{+ikx} + \frac{1}{2}e^{-ikx})$$

- can the sin and cos functional forms be solutions to the Schrodinger equation if they are not eigenfunctions of the momentum operator?
  - yes they can ... because they are eigenfunctions of H
  - they are also eigenfunctions of $\hat{p}^2$
  - they are just not eigenfunctions of p

In Reality?

- this example (of the free electron) is very unrealistic
  - we could not actually have a particle that had no interaction with any other particle
  - how would we form a wave with momentum in two directions? This would require two originating points, or reflection on a surface, both of which imply interactions with the environment
  - there are additional mathematical complications, for example we cannot integrate $\psi^*\psi$ with respect to x (this goes to ∞) and if x can go to $\pm\infty$ then it turns out A or B are zero!

Wavepackets

- we have considered creating a wave of specific defined energy, and undefined position

$$\psi = Ae^{+ikx} + Be^{-ikx} \quad E = \frac{\hbar^2}{2m}k^2$$

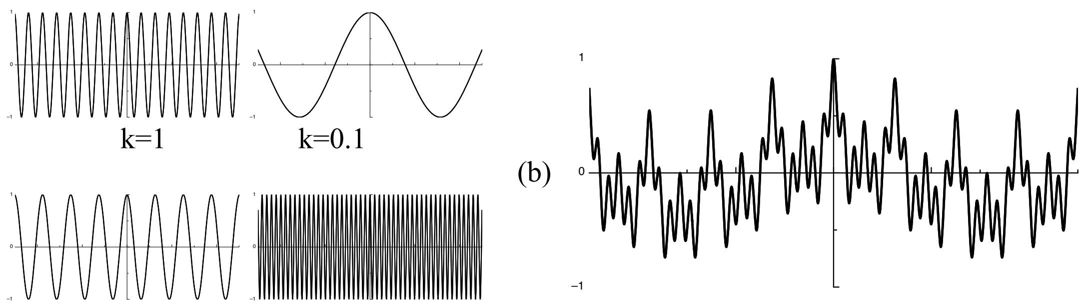
- if we allow the energy to be imprecise and therefor the momentum to be imprecise then the position becomes better defined
- the energy is mode imprecise by adding together waves of different momentum, **Figure 3**
- the wavefunction becomes a superposition of waves called a *wavepacket*

- as the number of waves with different momentum increases (ie the momentum becomes less well defined) the position of the wavepacket becomes better defined
- as an indication of what is happening, I made function that is a sum of cos curves in a graphing package, **Figure 3**
  - **Figure 4** shows the linear combination of 4 functions with the k values indicated

```
function  combine(k1,k2,k3,k4,k5,N,
      c1,c2,c3,c4,c5 :real);
var f1,f2,f3,f4,f5 :real;
begin
f1:=(1/N)*cos(k1*x);
f2:=(1/N)*cos(k2*x);
f3:=(1/N)*cos(k3*x);
f4:=(1/N)*cos(k4*x);
f5:=(1/N)*cos(k5*x);
y:=c1*f1+c2*f2+c3*f3+c4*f4+c5*f5;
end;
```

Figure 3 plotting program code

(a)



(b)

Figure 4 forming a wavepacket

- when the k values are very close to each other a wavepacket forms, **Figure 5**
  - **Figure 5a** is a *single* cos(kx) wave
  - **Figure 5b** has contributions from *four* cos(kx) curves
  - **Figure 5c** has contributions from *five* cos(kx) curves
  - **Figure 5d** has contributions from *eight* cos(kx) curves

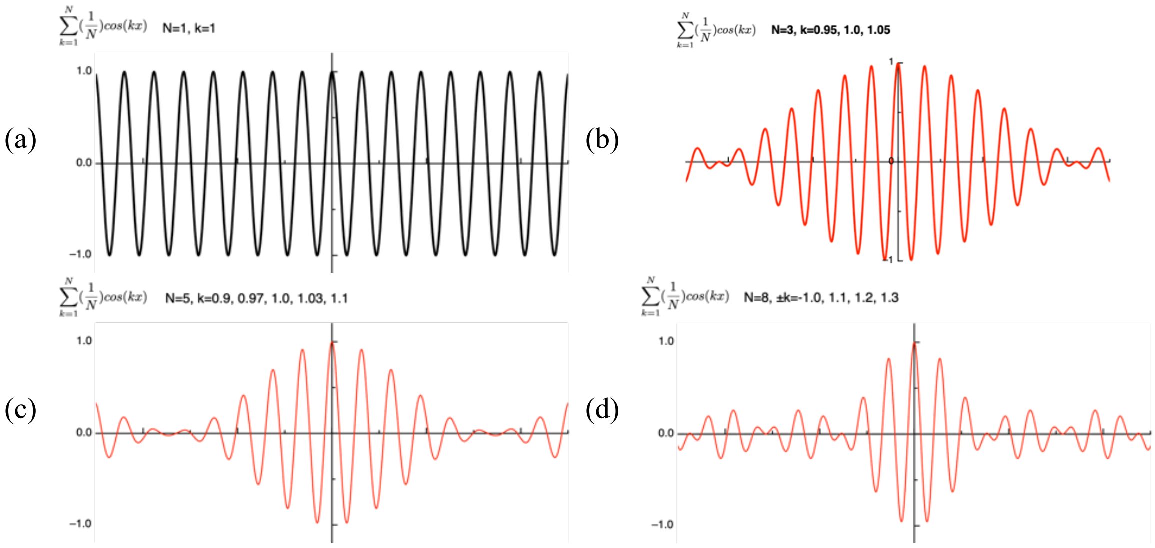


Figure 5 results for different wavepacket sums

- if an infinite number of different momentum states are combined the wavepacket becomes infinitely sharp, **Figure 6**
- **Figure 6** image from http://gisaxs.com/index.php/Wave_packet, downloaded 16 May 2021, CC By-SA 3.0 licence
- See the website! a contribution from a student Joshya Keegan who has made a small javascript simulator, add in the values of k that separated by a space.
  - try 1.1 1.2 1.3
  - make the wavepacket "tighter" with a better defined position, by spreading out the energy, try the following:
  - 1.1 1.2 1.31.4 1.5 1.6 1.7 1.8 1.9 2.0
  - 1.1 1.2 1.31.4 1.5 1.6 1.7 1.8 1.9 2.0 2.1 2.2 2.3 2.4 2.5 2.6 2.7 2.8 2.9 3.0

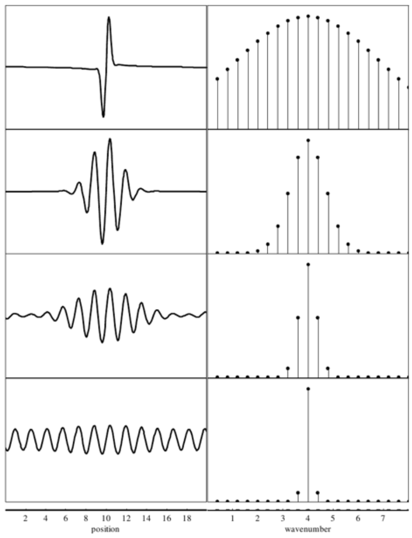


Figure 6 adding wavefunctions of different momentum, left position and right is momentum

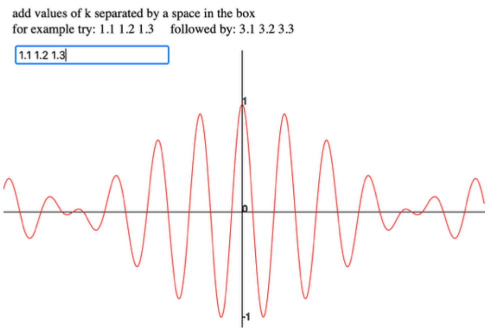


Figure 7 wavepacket simulator

Problems

- write the solution wavefunction $\psi = Ae^{+ikx} + Be^{-ikx}$ in the sin and cos form by expanding out the exponentials

- write down general expressions for and identify what each equation "tells us" about a system
  - P(x) and probability over a region/domain
  - normalisation
  - expectation value
  - eigenvalue

- expand the wavefunction $\psi = Ccos(kx) + iDsin(kx)$ into the exponential form using the expressions below, to determine A and B from $\psi = Ae^{+ikx} + Be^{-ikx}$

$$cos(x) = \frac{e^{+ix} + e^{-ix}}{2} \text{ and } sin(x) = \frac{e^{+ix} - e^{-ix}}{2i}$$

- show that the following expression of the wavefunction is also a solution to the 1D free electron equation

$$\psi = Ccos(kx) + iDsin(kx)$$

- for the wavefunction $\psi = Ae^{ikx} + Ae^{-ikx}$ the position is well defined, but the momentum is not defined. Verify that the momentum is not well defined by showing that this wavefunction is not an eigenvector of the momentum operator

- what is the probability of finding a particle at x (ie any given position) when $\psi = Ae^{+ikx}$
- what is the expectation value of the position operator for $\psi = Ae^{+ikx}$
- compare and contrast your answers to the two previous questions

- for a free wave where A=B, determine the probability function for finding the particle at any position x in space

$$\psi = Ae^{+ikx} + Be^{-ikx}$$

- what is the momentum for a free wave where A=B?