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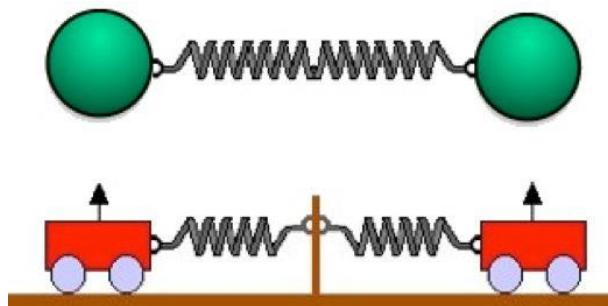
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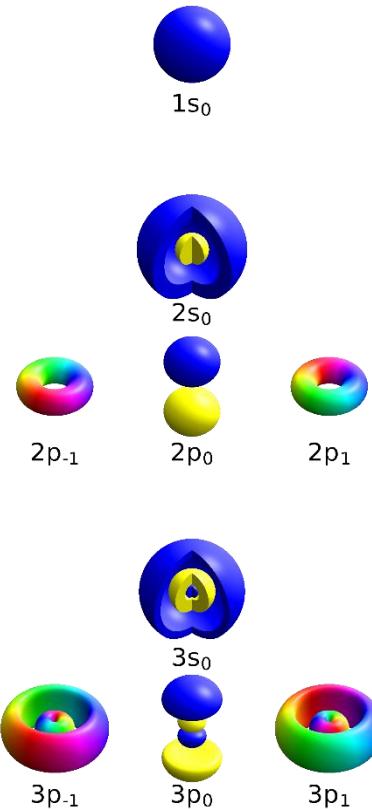
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PHY 2001 – Quantum and Statistical Mechanics

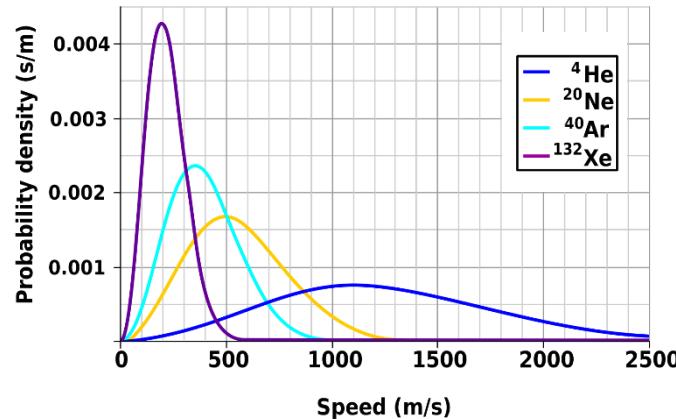
Diatom Molecular Vibrations



Atomic hydrogen orbitals



Boltzmann Distribution for Noble Gases



General Course Introduction (Still with Covid)

Delivery of the course this year will be face-to-face if possible. We will also endeavour to record lecture material if equipment is available in the room and functioning. In this case we will try to make the recordings available via Canvas within 24 hours. **CHECK CANVAS AND EMAILS REGULARLY**

- Assessment via 3 assignments (20% total), an exam in summer (60%) and 2 lab sessions (20% total)
- 3 Sections (and 3 lecturers);

QM Part 1 (4 weeks)

Dr Steven White (Me)

Please feel comfortable to ask questions either in or outside class, via email, or pop by the office (maybe not at the moment).

No such thing as a silly question

Email s.white@qub.ac.uk

Or find me in the IRCEP building first floor (same as Bell lecture theatre)
Room 01.023

QM Part 2 (3 Weeks)

Dr Satya Kar (Module Co-Ordinator)



Statistical Mechanics (5 weeks)

Dr Stuart Sim



Canvas & Updates

- We will be reviewing the teaching delivery format regularly, and are eager for feedback from students, but it is really important for everyone to stay informed so **regularly check Canvas and your emails** for any changes.
- In particular make sure you have notifications switched on. You'll then receive an email if any announcements are made.

[PHY2001 > Pages > Welcome to](#)

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Welcome to **PHY2001: Quantum and Statistical Mechanics**

This module shows how the subjects of quantum mechanics and statistical mechanics were developed in the early 20th century to supersede Classical Physics which was unable to describe many of the properties of individual atoms and ensembles of particles. The development of this "Modern Physics" underpins many other areas of Physics.

Meet the team

Dr. Steven White Dr. Satya Kar Dr. Stuart Sim

Instructor (Quantum Mechanics) Instructor (Quantum Mechanics) and Course Co-ordinator Instructor (Statistical Mechanics)

s.white@qub.ac.uk s.sim@qub.ac.uk

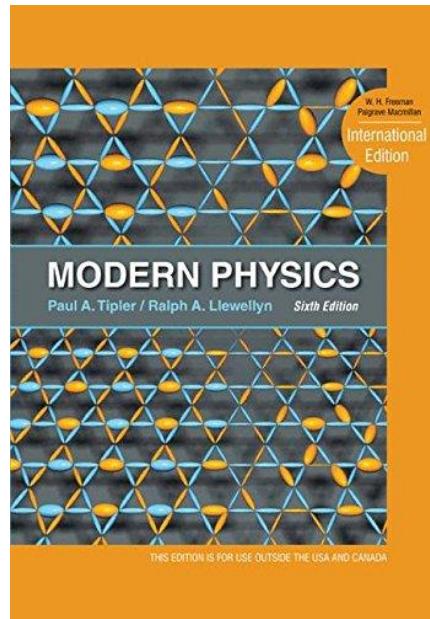
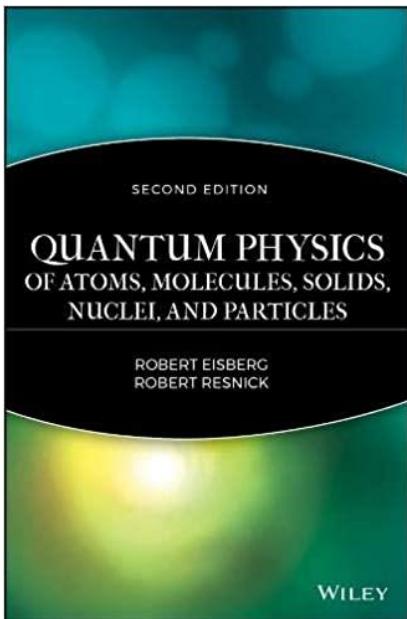
Day	Time	Venue
Monday	10 am - 11 am	Bell LT
Monday	3 pm - 4pm	Bell LT
Tuesday	12 pm - 1 pm	Bell LT
Wednesday	10 am - 11 am	Larmor LT

Lecture Times/Locations
Assessment Deadlines
(Will be made available 1 week prior)

Assignment	Week	Topic	Type	Deadline
1	5	Quantum Mechanics	Written	10 pm Mon 18th Oct
2	8	Quantum Mechanics	Written	10 pm Fri 12 Nov
3	12	Statistical Mechanics	Written	10 pm Mon 6 Dec

Recommended Textbooks for level 2 QM

- Traditionally recommended is **Eisberg** and Resnick '*Quantum Physics*'
 - 32 copies of 2nd Ed. in library – **QC174.12 EISB**
 - Excellent textbook – very detailed and thorough
- I would also recommend as a supplement '*Modern Physics*' by **Tipler** and Llewellyn.
 - 6th Ed. In Library – **QC30 TIPL**
 - Limited copies – Only 3!
 - Similar in style to level 1 textbooks

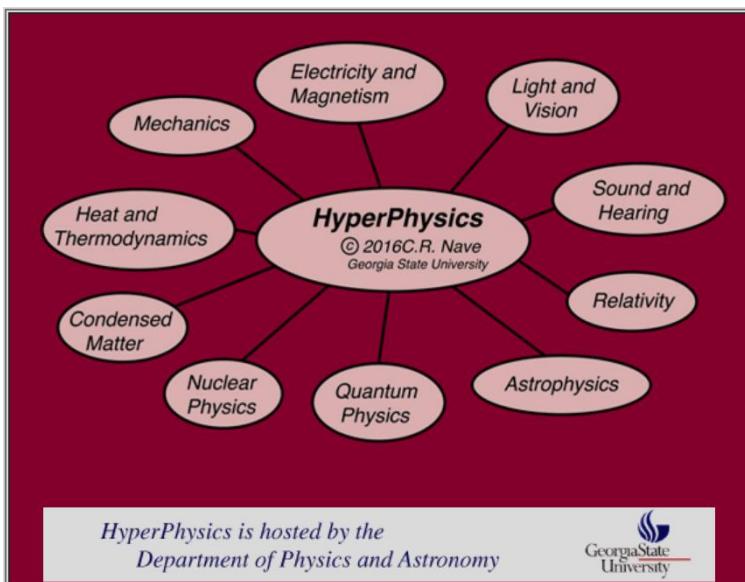


You can find copies of both books via a quick Google search on Amazon

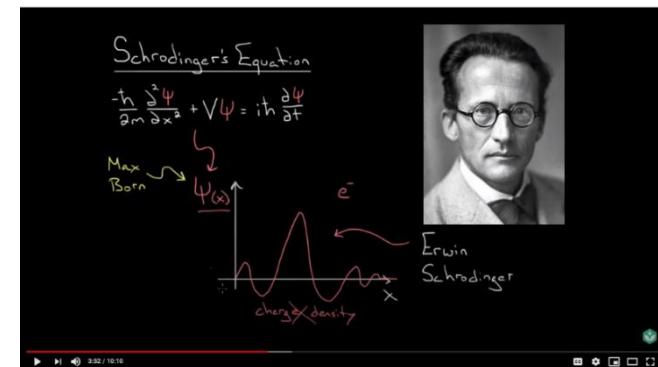
Eisberg from ~ £30 and Tipler from ~ £50

Additional Resources

- PHY1001 Notes – We will be building upon this material.
- Many online sources can complement the course as well.
- *HyperPhysics* is a great resource with short summaries on subjects.
- *YouTube* has excellent resources from full lecture courses (e.g. [MIT Quantum Physics](#)) to short videos on particular subjects, for example [Khan Academy](#)
- Search for books, websites or any other resources and find what works well for you.
- Beware though that **other sources may use different notation**, go into too much detail for second year (looking at you Wikipedia), or perhaps not enough



This screenshot shows the MIT OpenCourseWare website for "Quantum Physics I". The top navigation bar includes links for "FIND COURSES", "For Educators", "Give Now", "About", "Search", and "Search Tips". The main content area displays information for the course "Quantum Physics I", including the "COURSE HOME" tab, syllabus, calendar, and readings. A diagram illustrates a quantum optics experiment involving a beam splitter, a potential barrier V , and detectors. The right side of the page lists the "Instructor(s)" as Prof. Allan Adams, Prof. Matthew Evans, and Prof. Barton Zwiebach, with the "MIT Course Number" 8.04. It also indicates the course was "As Taught In Spring 2013" and is at the "Level Undergraduate".



Notes on the Notes

Notes for each week (i.e. 4lectures) will be posted ahead of the first lecture of the week on Canvas.

We will often go through worked examples during lectures. These will be telegraphed on the slides by empty boxes.

Worked Example XX – Calculate that using this...

Important equations, statements, etc., will have '**red boxes**'. Anything in these red boxes is very likely to come up in an assignment or exam question.

$$P(x) = \Psi(x)^* \Psi(x)$$

Blue Boxes however (or even blue text) will signify that the material is for additional understanding, and while very useful, you will **definitely not** be asked a question on it, for example application of the Schrödinger equation to a *travelling group wave function* which shows that $F = ma$ is a special case of Schrödinger.

$$\frac{d}{dt} \left(\frac{d\bar{x}}{dt} \right) = \frac{d}{dx} \left(-\frac{V(x)}{m} \right)$$

Anything in between has a reasonable chance of being asked.

Reading Suggestions

On the title slide of each lecture, there will be a summary of the learning outcomes and references to relevant sections in Eisberg (**Eis**) and Tipler (**Tip**). Occasionally I will also link to other sources. Reading Suggestions can also be found on Canvas under the '[Part One Broad Synopsis](#)' document .



MinutePhysics and
3Blue1Brown's [video](#)
on Bell's Theorem

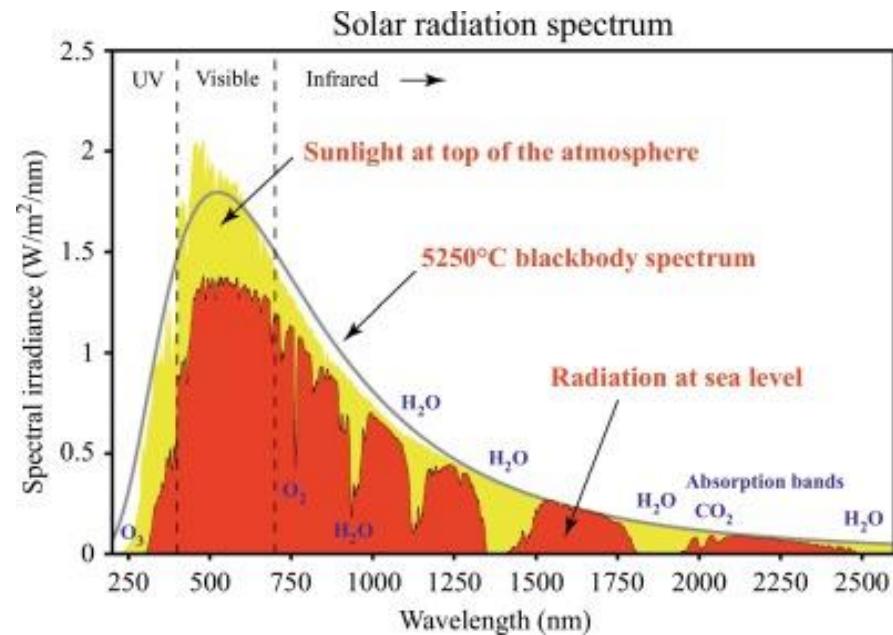
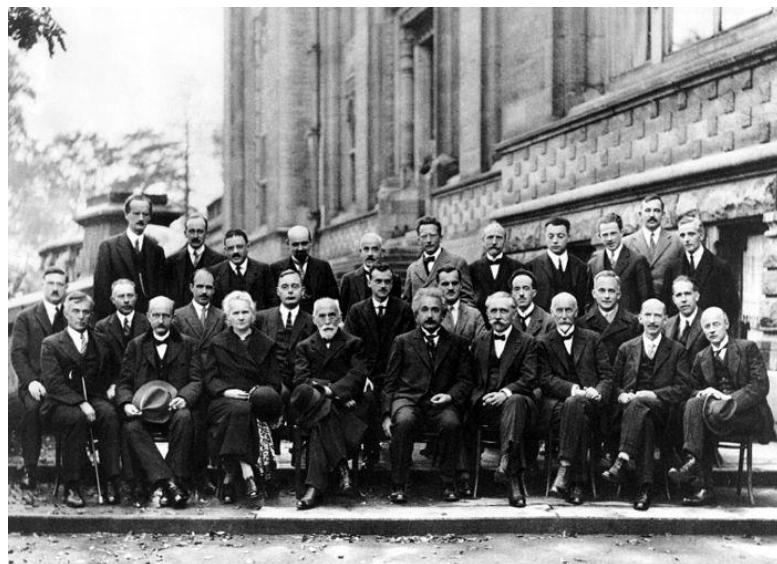
Bell's Theorem: The Quantum Venn Diagram Paradox

These slides form a **concise set of notes** and include information to obtain a good mark (65%+) in the exam or assignment. However, to really understand the topics discussed I would recommend you complement your learning by consuming material from other sources, and **reading** these two books are a great place to start.

Quantum Mechanics – Lecture 1

Learning Outcomes

- Origins of Quantum Physics Tip 3-1, 3-3
- Photoelectric Effect Recap
- Blackbody Spectra Eis 1-2, 1-3 & Tip 3-2
 - Understand what was described as the UV Catastrophe

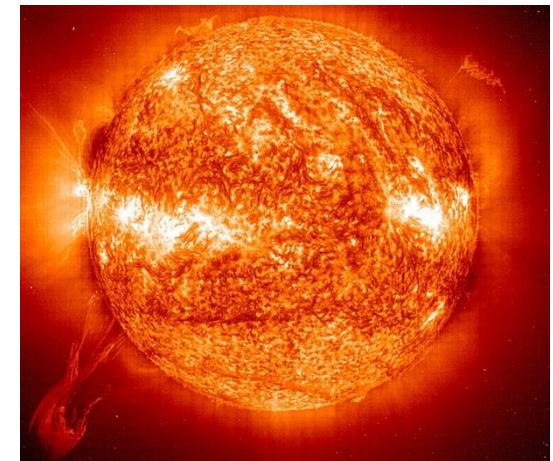


Origins of QM – Problems with Classical Physics

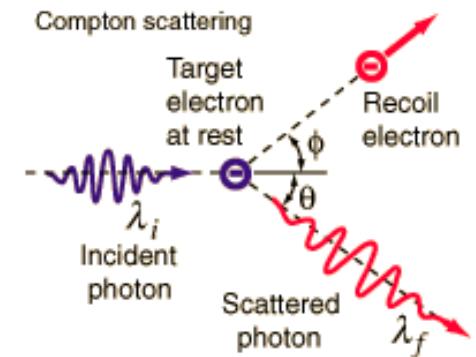
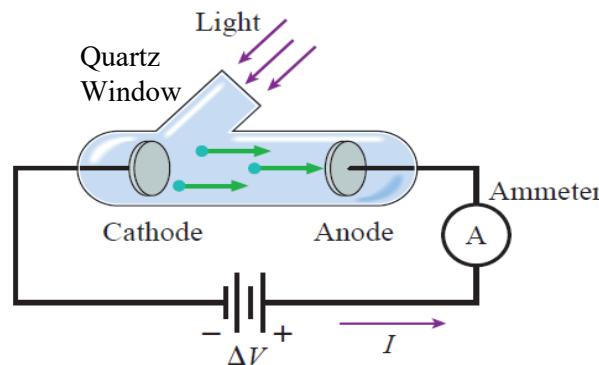
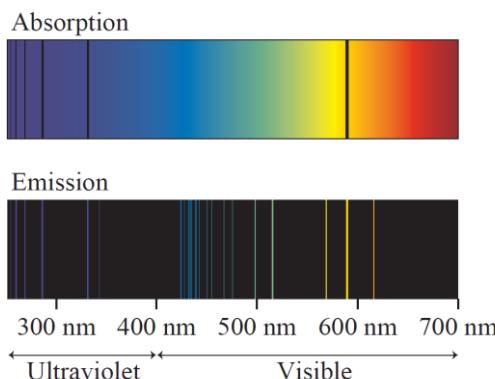
LEVEL 1 Recap

At the start of the 20th century there were four major experiments which could not be explained by the current (classical) understanding of physics:

- Continuous spectra called blackbodies - Look at this year
- Compton Scattering - Look at this year
- Atomic stability and discrete spectra - **Bohr Model & Old QM**
- The Photoelectric Effect - **Covered in some detail in Level 1**

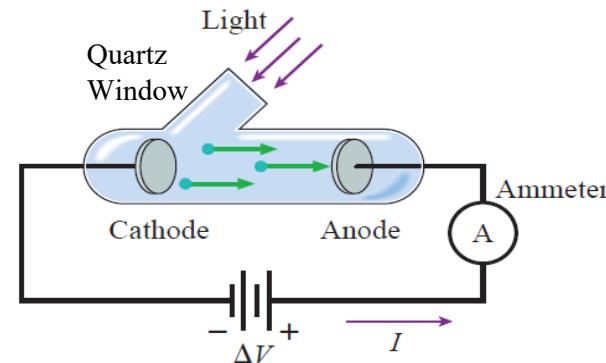


(b) Absorption and emission spectra of sodium



L1 Recap – PE Effect

Discovered in 1887 by Hertz, in the photoelectric effect, electrons can be emitted from the surface of a metal illuminated with light above a threshold frequency.



Experimental observation conflicted with classical prediction

- Stopping potential independent of light intensity, in fact, it was proportional to the light frequency.
- Emission only occurred for light above a threshold frequency.
- Emission was instantaneous, classical theory would predict a time lag of up to several minutes.

Einstein was able to explain these discrepancies by assuming the energy of the light was quantised.

$$E_\gamma = hf$$
$$eV_o = hf - \phi$$

Work Function

Stopping Voltage

The diagram shows two equations. The first equation, $E_\gamma = hf$, is enclosed in a red box. The second equation, $eV_o = hf - \phi$, is also enclosed in a red box. A purple wavy line connects the bottom equation to the top one. The word "Work Function" is written in purple next to the top equation, and "Stopping Voltage" is written in purple next to the bottom equation.

L1 Recap – Classical Physics Failing

Worked Example – Classical time lag for Photoelectric effect

A potassium plate ($\phi = 2.1 \text{ eV}$) is illuminated by a 2 W LED placed 15 cm away. Estimate, classically, the average time lag between illumination and ejection of a photoelectron. (Note: Bohr radius $a_o = 5.29 \times 10^{-11} \text{ m}$)

Discuss any assumptions

L1 Recap – Classical Physics Failing cont.

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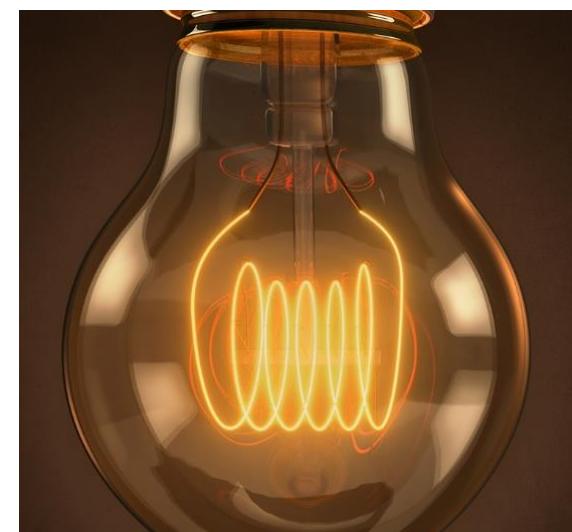
Discuss any assumptions

QM Starts With a Lightbulb

- It's sometimes said that QM started with a lightbulb – the spectrum from a filament bulb closely approximates that of a so called **blackbody**.
- When EM radiation is incident on an opaque body, some light is reflected and the rest is absorbed (i.e. no transmission).
- Electrons in the material 'feel' the electric field and are accelerated. An oscillating EM field thus drives atomic oscillations (the electrons are bound), increasing the average K.E. of the atoms, and the bulk temperature will increase.
- Accelerated charges however must emit radiation, this energy has to come from somewhere, so the average K.E. would then decrease. (See dipole radiation in E&M PHY2004 next semester).
- When the rate of absorption and emission are equal, the body is in **thermal equilibrium with its surroundings**.
- A good absorber is also a good emitter.
- A body that is a perfect absorber (and therefore also emitter) is called a **blackbody**.
- The spectrum of the emitted **thermal radiation** is heavily dependent upon the temperature
 - The peak shifts towards shorter wavelengths with increasing temperature.
 - The total power emitted, per unit area, is given by the Stefan-Boltzmann Law

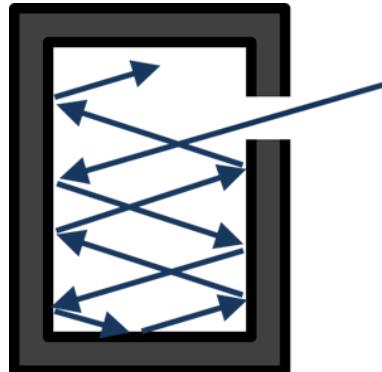
$$\frac{P}{A} = \sigma T^4$$

- $\sigma = 5.670 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$
is the Stefan-Boltzmann Constant



Classically Modelling a Blackbody Spectrum

- Our goal is to model the shape of a blackbody spectrum. First let's consider how we might construct an ideal blackbody.
- [VANTABLACK™](#) is one of the darkest materials known. Absorbs 99.65% of visible light. Can we do better?
- A cavity with a small opening is a very close approximation to a black body.
See this [video](#)



How do we model the emission from such a cavity?

- Let's assume that the cavity is in thermal equilibrium, at some temperature T and has walls with non-zero conductivity.
- The power radiated out of the hole is proportional to the **total energy density** in the cavity.

In the form of EM Radiation

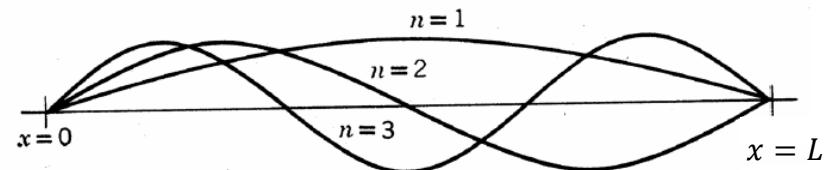
$$P \propto U$$

- Now we want to determine the spectrally dependent power radiated out of the hole, $P(\lambda)$. If $u(\lambda)d\lambda$ is the fraction of the energy density in the range $d\lambda$ then;

$$P(\lambda) \propto u(\lambda)$$

Classically Modelling a Blackbody Spectrum Cont.

- Let's look at simplified 1D case first to try and gain some intuition.
- Walls with non-zero conductivity gives a standing wave condition (transverse \vec{E} field at the wall is 0).



- The total number of modes is*
- And thus the number of modes per unit wavelength is

$$N = \frac{2L}{\lambda}$$

- If we then divide by the length of the cavity we get a more general expression for the number of modes, per unit wavelength, per unit length (of cavity) – **mode density**
- But we have two independent polarisations possible (remember these are standing EM waves) so;

$$\frac{dN}{d\lambda} = -\frac{2L}{\lambda^2}$$

$$n(\lambda) = -\frac{1}{L} \frac{dN}{d\lambda} = \frac{2}{\lambda^2}$$

$$n(\lambda) = \frac{4}{\lambda^2}$$

*Up to λ , and should really be an integer but go with it, our end goal is to get the **energy density**!

Classically Modelling a Blackbody Spectrum Cont.

- Now for a 3D cavity we have that (for details see **Eisberg Sec 1-3**);
- The energy density is just the density of modes, multiplied by the average energy per mode. This was known from classical thermodynamics to be kT , hence;

$$n(\lambda) = \frac{8\pi}{\lambda^4}$$

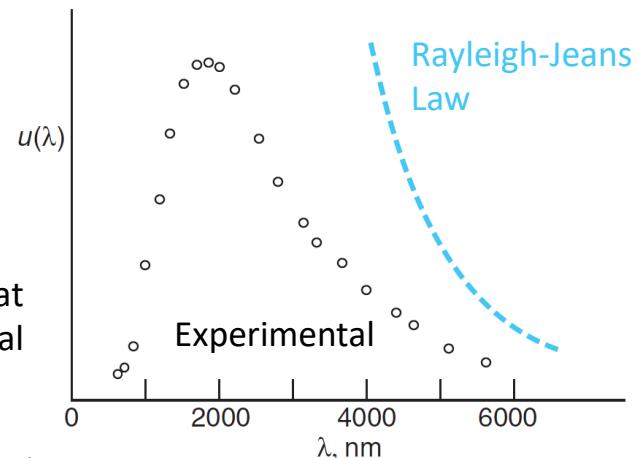
- This is called the **Rayleigh-Jeans Law**;

$$u(\lambda) = kTn(\lambda) = \frac{8\pi kT}{\lambda^4}$$

- The total power emitted is proportional to this;
- As $\lambda \rightarrow \infty$ this actually agreed quite well with observation.
- However, as $\lambda \rightarrow 0$ the energy density, and hence power emitted approached infinity!
- Clearly this was in disagreement with observation!
- In fact, this was such a massive failure of classical physics that it was called the **ultraviolet catastrophe**.

- Right:** Comparison of experimental data taken at $T=1600\text{K}$ and the corresponding classical predictions of the spectral energy density $u(\lambda)$.

$$P \propto \int_0^\infty u(\lambda) d\lambda = \int_0^\infty \frac{8\pi kT}{\lambda^4} d\lambda$$

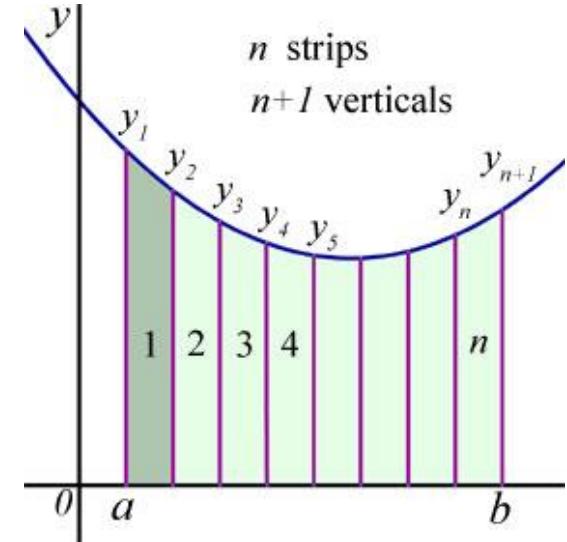


Quantum Mechanics – Lecture 2

Learning Outcomes

- Planck's Law
 - Applications
 - Using Planck's Law Eis 1-4, 1-6 & Tip 3-2
 - Example of using excel, numerical integration and Solid Angle

BlackBody Spectrum of Tungsten Filament							
Inputs				Constants			
Temperature	3000	K		Planck	6.63E-34	Js	
Min Wavelength	10	nm		Boltzmann	1.38E-23	J/K	
Max Wavelength	5000	nm		Speed of Light	3.00E+08	m/s	
BlackBody Area	3.14E-04	m^2		Stefan-Boltz.	5.67E-08	W/m^2/K	
Illumination square Edge	2.00E-02	m					
Illumination Distance	0.3	m					



Planck's Law

- Last time we saw that the Rayleigh-Jeans Law is not a valid physical model.
- In 1900 Max Planck developed a theoretical model for $u(\lambda)$ by working backwards from an **empirical fit** to data.
- He worked on the assumption that the flaw in the classical approach was the average energy per mode.
- He **postulated** that this should not equal kT but rather be a function of λ itself, and approach zero as λ does.
- Where does that kT come from in the classical expression?
- The energy distribution function is the Boltzmann Distribution function

$$f(E) = A e^{-\frac{E}{kT}}$$

*In this context,
this is the probability density
of an oscillation mode having
an energy E*

*A is called a normalisation
constant and found by
setting the integral over all
energies = 1*

- The average energy of a mode is then given by taking the weighted average, and since this is a continuous function we have;

$$\bar{E} = \int_0^{\infty} E f(E) dE = kT$$

Planck's Law cont.

- Let's show that the average energy per mode is kT . (This will be good practice for later when we will be doing lot's of integrals.)

Planck's Law Cont.

- Planck did something that at the time seemed like madness! He assumed that the oscillations can only have discrete values of energy;

$$E_n = nhf \quad n = 0, 1, 2, \dots$$

- The distribution function now became

$$f_n = Ae^{-E_n/kT}$$

- A is still found by normalisation, but this is no longer a continuous function but a series of discrete values, i.e. our normalisation value is given by;

$$\sum_{n=0}^{\infty} f_n = \sum_{n=0}^{\infty} Ae^{-E_n/kT} = 1$$

- Again, the average energy is given by the weighted mean of f_n :

$$\bar{E} = \sum_{n=0}^{\infty} E_n f_n = \sum_{n=0}^{\infty} E_n Ae^{-E_n/kT}$$

- This leads to the result that the average energy of oscillation is wavelength dependent and given by;

$$\bar{E} = \frac{hc}{\lambda} \frac{1}{e^{hc/\lambda kT} - 1}$$

Later, in statistical mechanics you will learn about the Bose-Einstein distribution function which is closely related to Planck's law

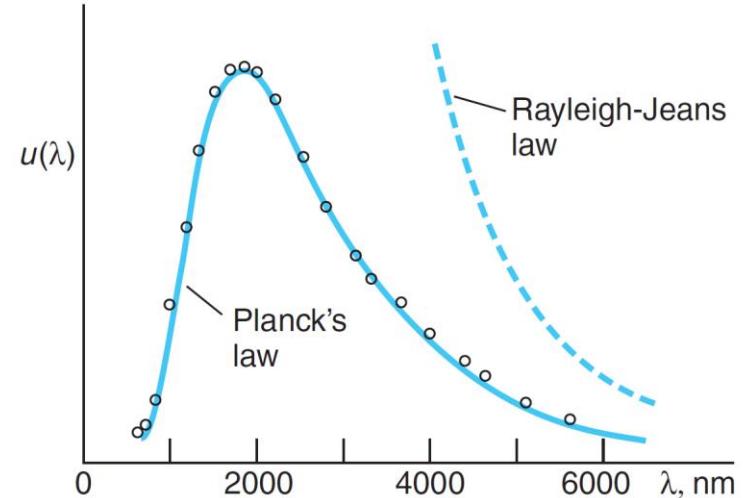
Planck's Law and Comparison with Experiment

- Remember our goal is to obtain $u(\lambda)$, the spectrally dependent energy density per unit volume, and is given by;

$$u(\lambda) = \bar{E}n(\lambda) = \bar{E} \frac{8\pi}{\lambda^4}$$

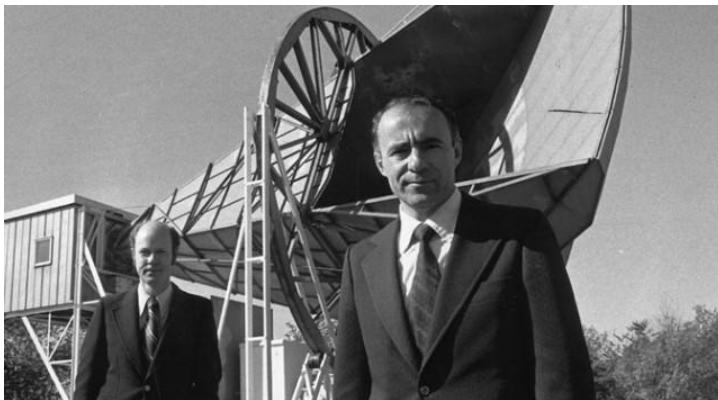
$$u(\lambda) = \frac{hc}{\lambda^5} \frac{8\pi}{e^{hc/\lambda kT} - 1}$$

- Right:** Let's look at the data for a blackbody at 1600 K again.
- Now we can see excellent agreement between Planck's law and observation.
- Planck, and many others tried to reconcile the assumption of quantisation with classical physics.
- Many physicists were not happy with the idea that quantisation was a fundamental property.
- The photoelectric effect, and many other experiments would however show that this was indeed the case.



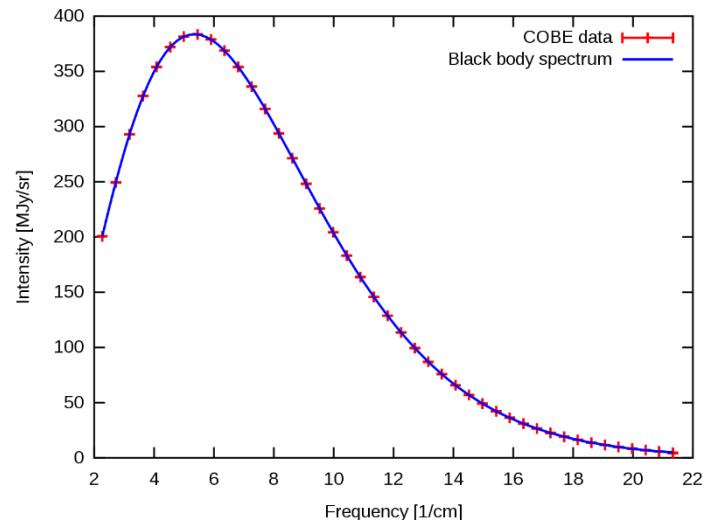
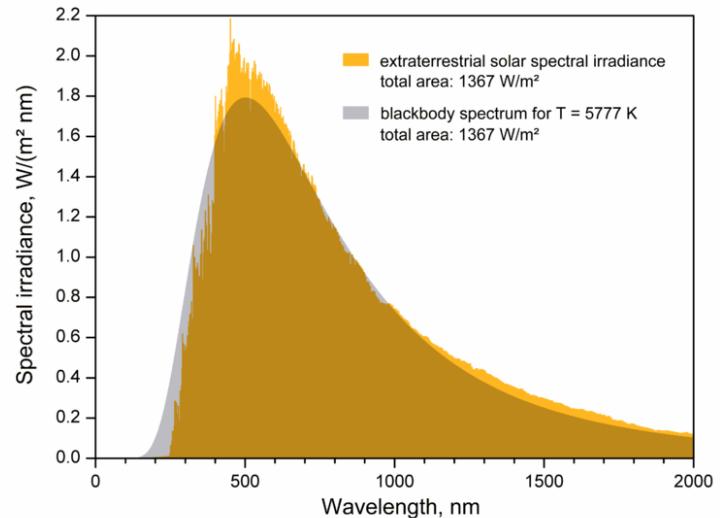
Applications of Planck's Law -CMB

- A blackbody spectrum is very sensitive to temperature ($P \propto T^4$), allowing precise measurement of, for example, solar temperatures.
- **Right:** Solar spectrum and blackbody fit. Notice the labelling of the y-axis.
- **Spectral Irradiance is the radiant flux (power) per unit wavelength (or frequency) received by a surface per unit area.**
- This can lead to some confusing units.
- A major triumph of the Big Bang theory was the prediction of a red shifted blackbody spectrum that would permeate the entire universe, the so called Cosmic Microwave Background radiation.
- Again notice the y-axis label and units here.
- Take home point here is that you should be sure of what a graph is telling you!



Left : Penzias and Wilson standing in front of the Bell Labs Horn antenna.

Right: CMB spectrum measured by COBE



Using Planck's Law

Let's do an example of using Planck's law to perform a relatively involved calculation to see how it is used in practice.

The spectral radiance of a blackbody, $B(\lambda, T)$ is given by the following equation:

A 1 cm radius tungsten plate at $T = 3000$ K is used to irradiate a square (edge = 2 cm) test piece of a solar panel. The solar panel material only absorbs visible light, which we assume it does so with 100% efficiency.

- (a) Plot the spectral radiance, in units of $\text{W m}^{-2} \text{ sr}^{-1} \text{ nm}^{-1}$ for a $T = 3000$ K blackbody.
- (b) Assuming that tungsten plate is well approximated as a blackbody, that the two plates are parallel to each other, and are separated by 30 cm, estimate the light power absorbed by the solar panel.
- (c) Would a similar panel sensitive to near-infrared radiation instead (740 – 1400 nm) be more effective?

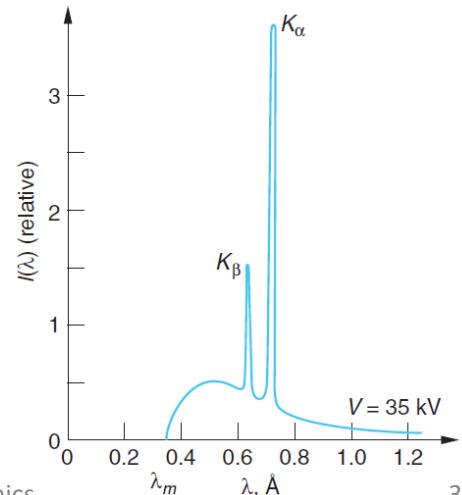
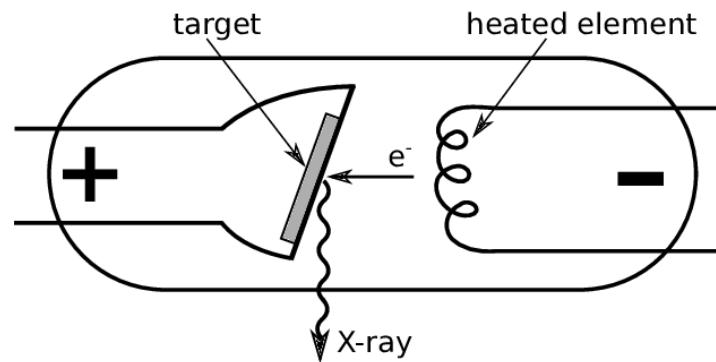
We can use Excel to plot a complicated function such as this. You can find a copy of this spreadsheet on Canvas

$$B(\lambda, T) = \frac{2hc^2}{\lambda^5} \frac{1}{e^{\frac{hc}{\lambda k_B T}} - 1}$$

Quantum Mechanics – Lecture 3

Learning Outcomes

- Producing X-rays (Eis 2-6)
 - Bremsstrahlung and Characteristic lines
- Compton Scattering (Eis 2-4, Tip 3-4)
 - Colour of the Sky



X-rays

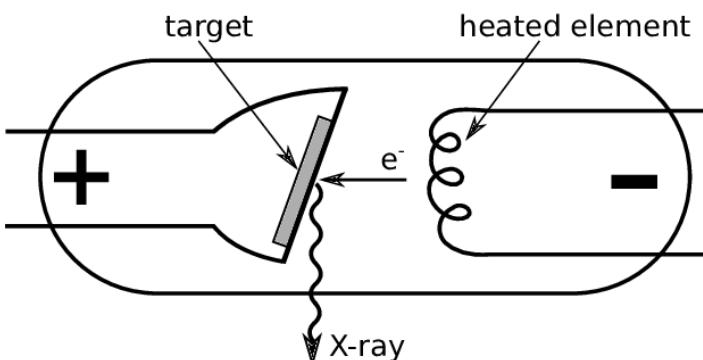
- Discovered by Röntgen in 1895
- These rays passed through many materials opaque to light and could expose photographic film.
- Could not be deflected by a magnetic field and did not exhibit ‘optical’ effects



- Labelled them x-rays due to their mysteriousness.

Left: An x-ray of Roentgen's wife's hand, only a few months after their initial discovery.

- Classical EM theory predicted that x-rays could be produced via collisions. Accelerated charges emit radiation. E.g. dipole radiation – PHY2004

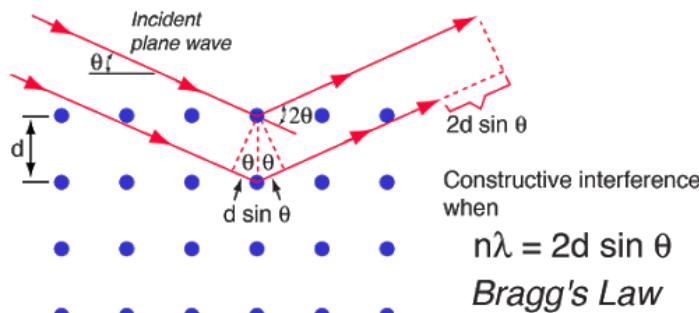


Left: Schematic of a typical x-ray tube.

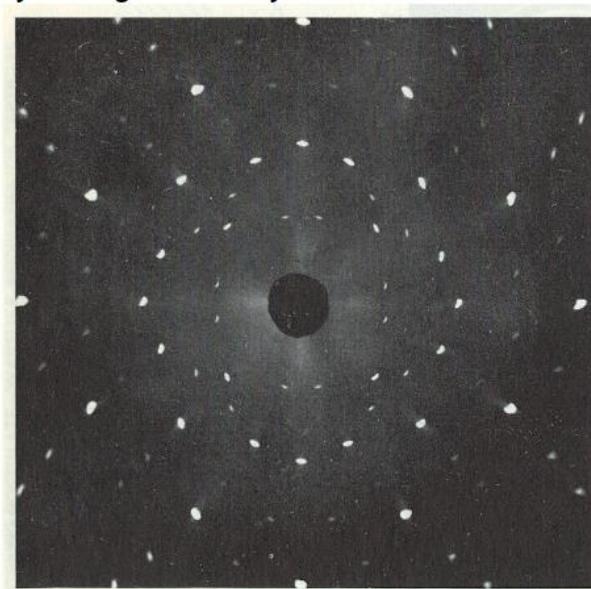
The components are sealed inside an evacuated glass tube. Electrons are ‘boiled’ off a filament by thermionic emission, and then accelerated due to a cathode anode pair connected across a high voltage power supply. These electrons then strike a moderate to high Z target producing x-rays.

Evidence that X-Rays are EM Radiation

- Experiments by people such as Max von Laue showed that x-rays had electromagnetic wave properties, albeit with much smaller wavelengths, on the order of an **Angstrom** ($1 \text{ \AA} = 10^{-10} \text{ m}$), by observing diffraction through extremely narrow slits.
- For diffraction effects to be observed $\frac{D}{\lambda} \approx 1$ where D is the size of the diffracting aperture.
- This small λ could be used to probe the structure of crystals, where the inter-atomic spacing is comparable.



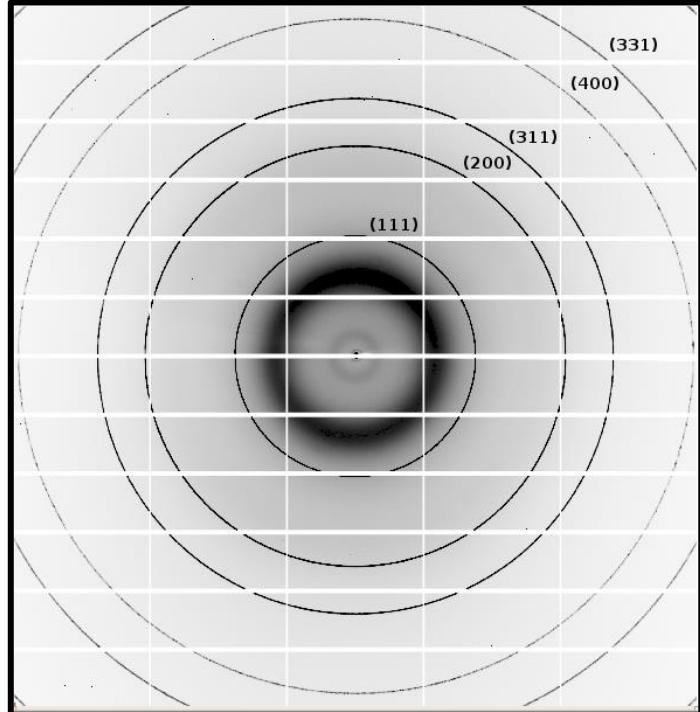
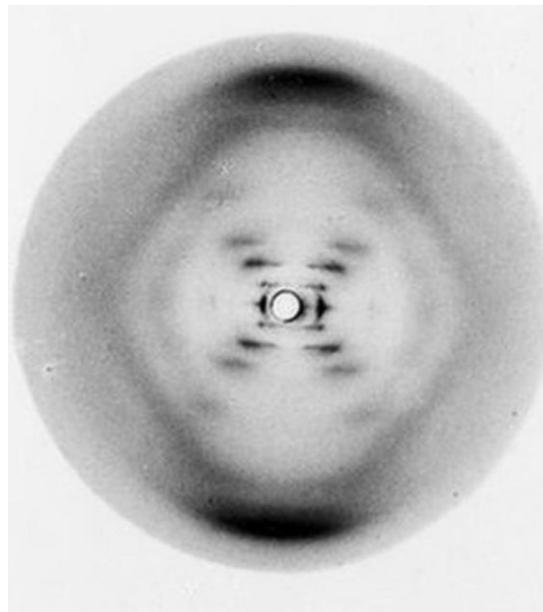
Laue pattern of x-ray diffraction
by a single NaCl crystal.



- **Above:** Bragg diffraction/reflection from a layered single crystal surface.

Complex Crystal & Poly-Crystalline Structures

- X-rays are used in a powerful technique called x-ray crystallography to determine the microscopic structure of crystalline materials.



Rosalind Franklin used x-ray diffraction to confirm the postulated double helix structure of DNA.

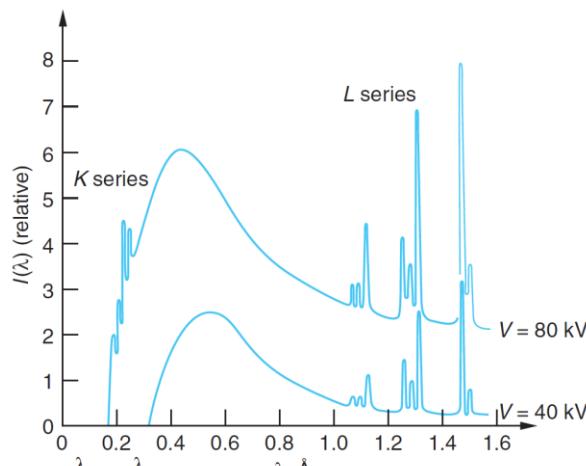
For more info see this [video](#) discussing DNA diffraction by Steve Moulds.

Powder Diffraction image of polycrystalline Si

**Techniques similar to these are used within the
centre for nanostructured media research cluster
here at QUB.**

Spectrum from an X-Ray Tube

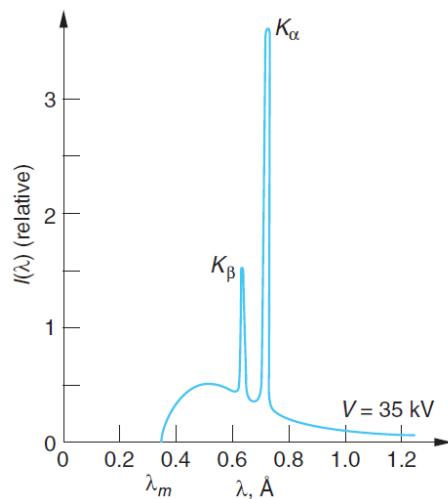
- Bragg Diffraction allows construction of an x-ray spectrometer. Similar to a grating spectrometer used for optical wavelengths.
- Measurement of the spectrally dispersed intensity distribution of the x-rays from an x-ray tube provided yet more headaches for classical physics however!



- **Left Above:** Spectrum from a tungsten ($_{74}\text{W}$) target.
- **Left Below:** Spectrum for a molybdenum ($_{42}\text{Mo}$) target.

Spectra from these tubes always showed three common features.

- 1) Sharp lines which were observed to be unique for each element and hence called the *characteristic spectrum* for that element. Notice how tungsten has more lines present.
- 2) A continuous, broad, *Bremsstrahlung* spectrum
- 3) A sharp cut-off value that was dependent upon the x-ray tube operating voltage and followed;

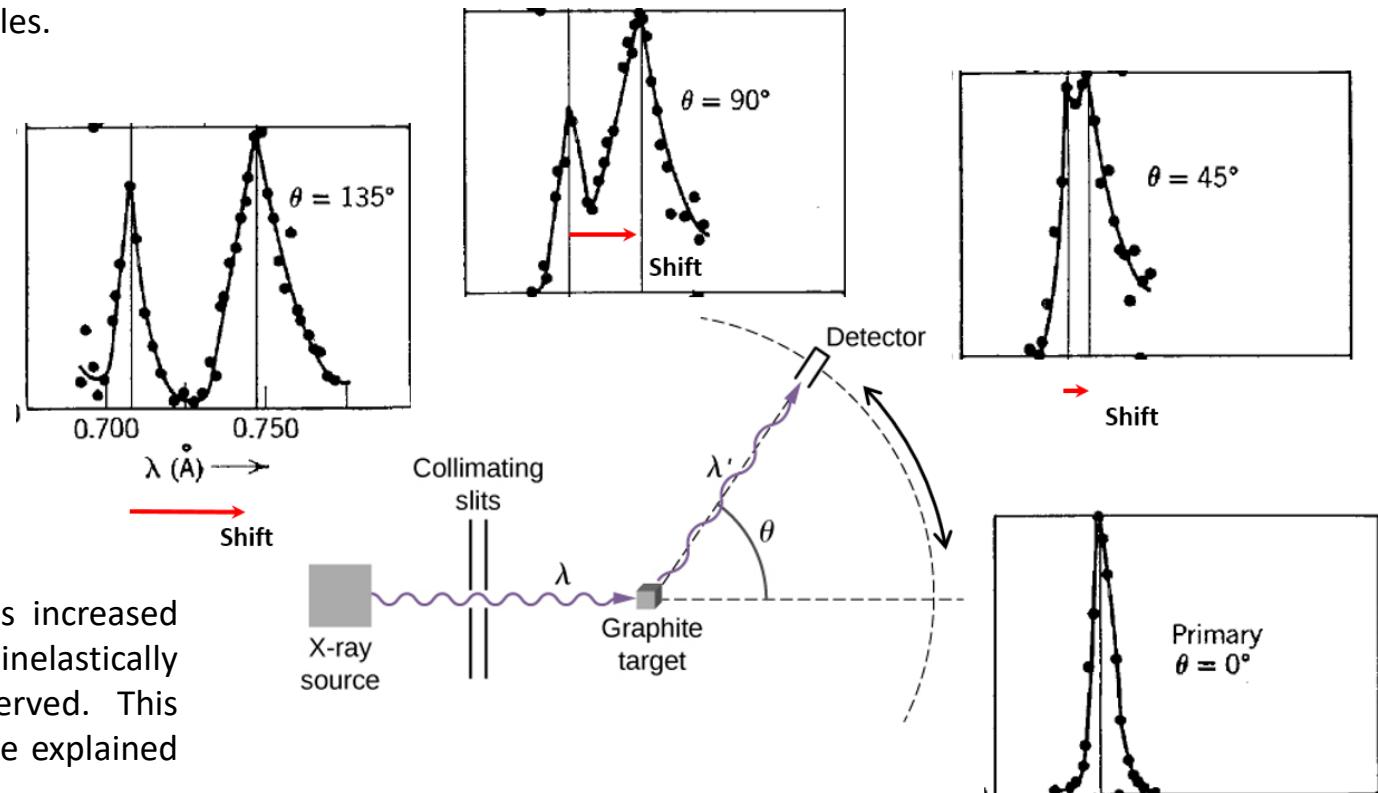


$$\lambda_m = \frac{1240}{V} \text{ nm}$$

Points 1 & 3 could not be explained by classical physics. (1 would require at least Bohr's theory of the atom and 3 can be thought of as an inverse PE effect).

Compton Effect – Labs Next Semester

- The photoelectric effect postulated that light behaved like a particle, arriving in packets of energy called photons.
- However many physicists at the time believed that this was not a fundamental property of light.
- In 1923 Arthur Compton performed an experiment that left very little doubt in the particle like nature of radiation.
- A ‘monochromatic & collimated’ source of x-rays is directed towards a low Z target and the spectrum is recorded at various scattering angles.



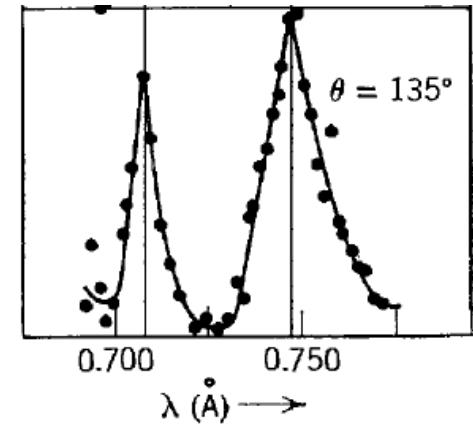
As the scattering angle was increased an elastically scattered and inelastically scattered peak were observed. This redshifted peak could not be explained using EM theory.

Compton postulated that it was due to collisions with free electrons.

Modelling the Compton Shift

Unshifted Peak

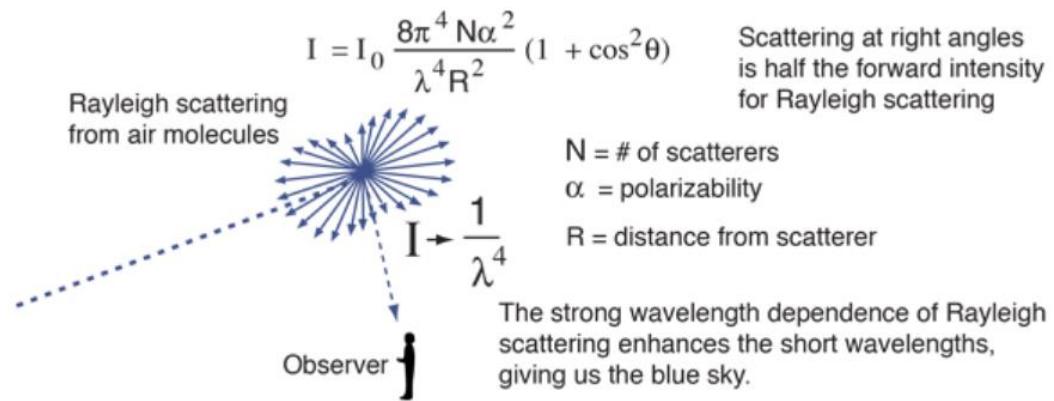
$$\Delta\lambda = \lambda_1 - \lambda_0 = \frac{h}{m_e c} (1 - \cos \theta)$$



- In the Compton Effect inelastic scattering is often **actually with weakly bound electrons**. Assumption of free electrons is reasonable though if the recoil energy is much larger than the binding energy.
- If the photon interacts with a strongly bound, core-electron then the interaction can be considered as a collision with the entire atom. Since $m_{atom} \gg m_e$ the Compton shift will be negligible and elastic scattering will be observed.
- This elastic process is actually referred to as Rayleigh scattering.

- $I(\theta) \propto \frac{1}{\lambda^4}$
- This strong affinity with shorter wavelengths is the reason the sky is blue!

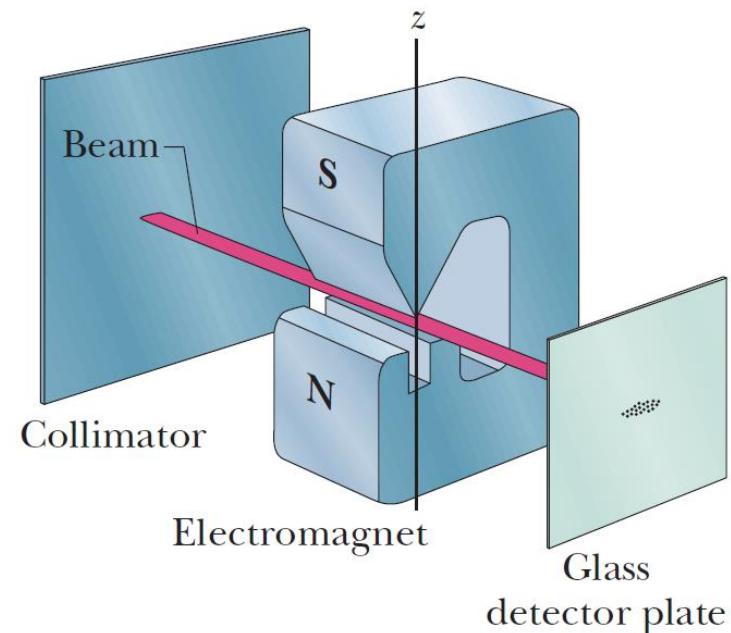
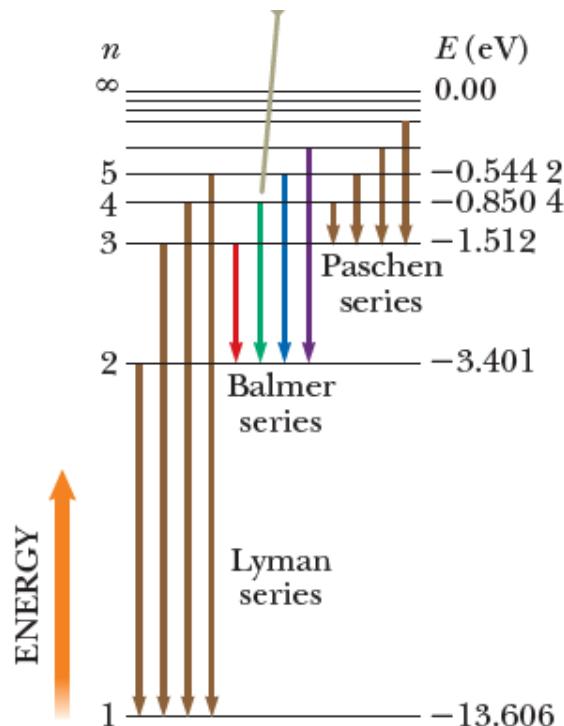
Right: Link from [hyperphysics](#) discussing the origin of the sky's colour.



Quantum Mechanics – Lecture 4

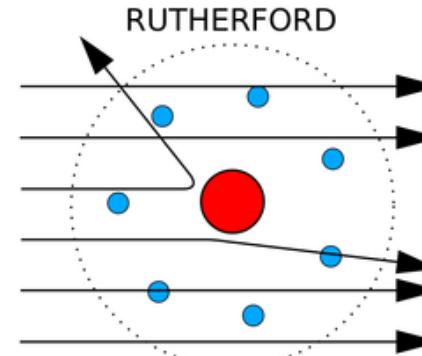
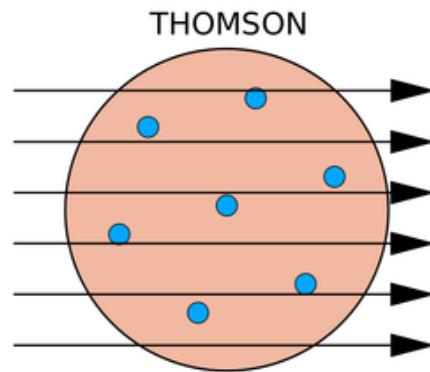
Learning Outcomes

- Recap of the Bohr Model (Eis 4-5, 4-6, and Tip 4-2, 4-3)
 - What it got right
- Stern-Gerlach Experiment (Eis 8-3, and Tip 7-4)
- Looking Ahead



Brief History of Atomic Structure

- At the start of the 20th century a viable model of atomic structure eluded science.
- Chemistry and physics had performed many experiments that led to knowledge of the atomic masses and thus radii of $\approx 10^{-10}$ m (for example Dalton, Avogadro, Milikan, Loschmidt etc).
- First attempt was by J. J. Thomson who proposed a Plum Pudding model for the atom. Electrons were embedded in a large volume of positive charge and electron stability was ensured via Gauss's law.
- In 1911 Experiments by Geiger & Marsden showed that the positive charge was contained in a very small nucleus which led to the development of Rutherford's nuclear model. However the structure and dynamics of electrons was still a mystery.
- This caused many problems in classical physics as there was no way to ensure atomic stability.



Worked Example on Maximum Nuclear Radius

- In a Rutherford scattering experiment, 7 MeV alpha particles are observed to occasionally scatter through 180° from a thin gold foil. Estimate the maximum size of the nucleus.

This requires applying some EM knowledge!

Recap:Bohr's Model

- In 1913 Bohr proposed a model which would combine the work of Planck, Einstein, and Rutherford. This semi-classical model would prove very successful at explaining some of the mysteries of the hydrogen atom and would form the basis of the old Quantum theory. However there were still some shortcomings.
- Classical physics had no way to explain either the stability of matter, or the characteristic, discrete spectra of the elements.
- Bohr suggested three key postulates to solve this issue;
 - 1) That the orbiting electrons can exist in certain stable orbits without radiating.
 - 2) An orbit is only stable if the angular momentum of the electron satisfies;

$$L = |\mathbf{r} \times \mathbf{p}| = n\hbar$$

- 3) The atom radiates when the electron makes a transition from one stationary state to another and that a photon is emitted satisfying;

$$hf = E_i - E_f$$

- These last two expressions incorporated the **quantum** ideas of Einstein and Planck and is where the model deviates from classical physics.

He also made an additional assumption, called the **Correspondence Principle**;

In the limit of large orbits and larger energies, quantum [theory] must agree with classical [theory].

- Truth time - We learned last year that a key postulate was that the orbit circumference for an electron in a hydrogen atom satisfied;

$$2\pi r = n\lambda$$

Where $\lambda = \frac{h}{p}$ is the De Broglie wavelength. This is a simplification, and doesn't really apply for our current atomic models. In these models however, **angular momentum is quantised**.

Bohr Model of the Hydrogen Atom

- When applied to the hydrogen atom great success was achieved in correctly predicting the wavelength of the hydrogen emission (and absorption spectra)

The electron is shown in the lowest-energy orbit, but it could be in any of the allowed orbits.

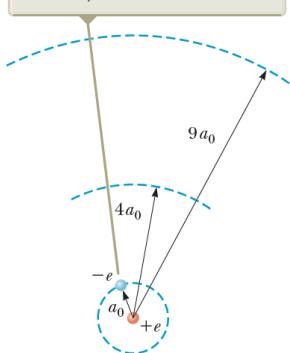


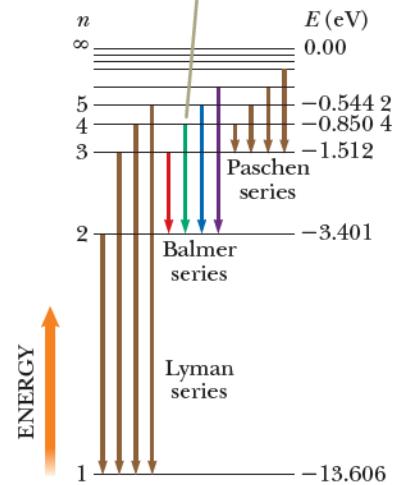
Figure 42.7 The first three circular orbits predicted by the Bohr model of the hydrogen atom.

$$E_n = -\frac{13.6 \text{ eV}}{n^2}$$

$$r_n = n^2 a_B$$

$$a_B = \frac{\hbar^2}{mk_e e^2}$$

The colored arrows for the Balmer series indicate that this series results in the emission of visible light.



- However it did not explain everything, for example;
 - Fine structure in spectra.
 - Intensity of spectral lines.
 - Could not be applied to multi-electron atoms.

A new theory for quantum physics was required, but the Bohr model did get some things correct.

Figure 42.8 An energy-level diagram for the hydrogen atom. Quantum numbers are given on the left, and energies (in electron volts) are given on the right. Vertical arrows represent the four lowest-energy transitions for each of the spectral series shown.

Successes of the Bohr Model

The general model had three major insights which are still present in modern quantum theory;

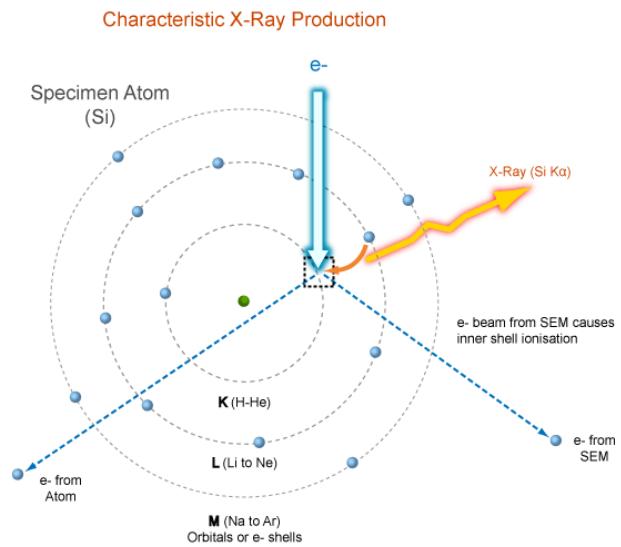
1. Stable, discrete energy states. This explained the origin of the characteristic spectra for atoms.
2. The correspondence principle. We will see later that the Schrödinger equation can be reduced to $F = ma$ for an unconfined particle.
3. The quantisation of angular momentum.

This third point was yet another bold claim in the face of common intuition and classical physics. However it has been confirmed by multiple experiments.

For example the Zeeman effect due to the quantisation of the orbiting electrons angular momentum.

And, the Stern-Gerlach experiment showing the effect of electron 'spin' undertaken in level 2 labs.

These underlying physics of these experiments will be explored more in the 2nd part of the QM course but let's take a moment to look at the SG experiment.

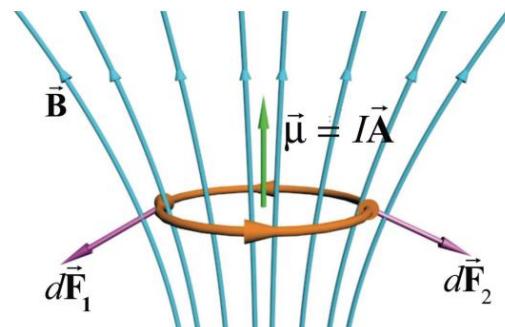
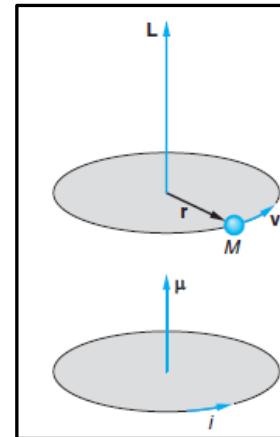


Stern-Gerlach Experiment

For any circulating charge (for example an electron orbiting a nucleus) a magnetic moment proportional to the angular momentum is produced (*Larmor Theorem*).

$$i = qf = \frac{qv}{2\pi r}$$

$$\mu = iA = \frac{qv}{2\pi r} * \pi r^2 = \frac{q}{2M} L$$



Pitfall warning: the above field distribution is inhomogeneous in more than one axis!

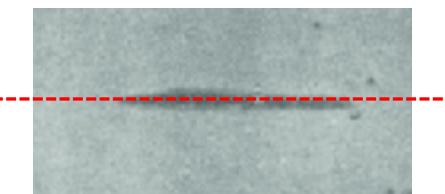
If a magnetic moment is placed in an inhomogeneous external magnetic field, it will feel a force that depends upon the gradient of the magnetic field. Consider a B-field that is only inhomogeneous in the z-direction. Then the force will be;

$$F_z = \mu_z \left(\frac{dB}{dz} \right)$$

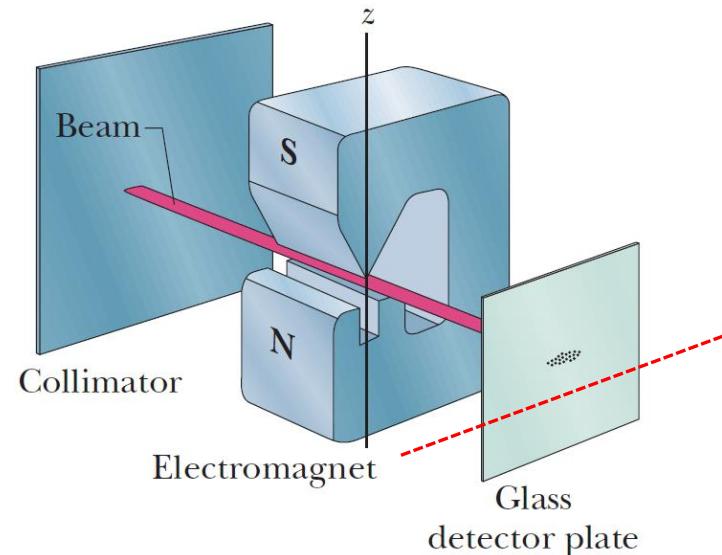
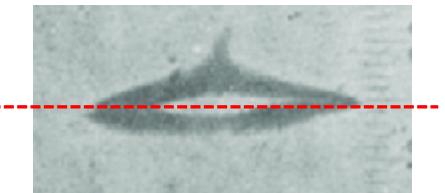
Stern-Gerlach Experiment cont.

- In the Stern-Gerlach this idea was tested. A beam of silver atoms are directed through a inhomogeneous B-field (but only in the z-direction) towards a detector.
- What would you expect to see without the field switched on?

No Field in original Experiment



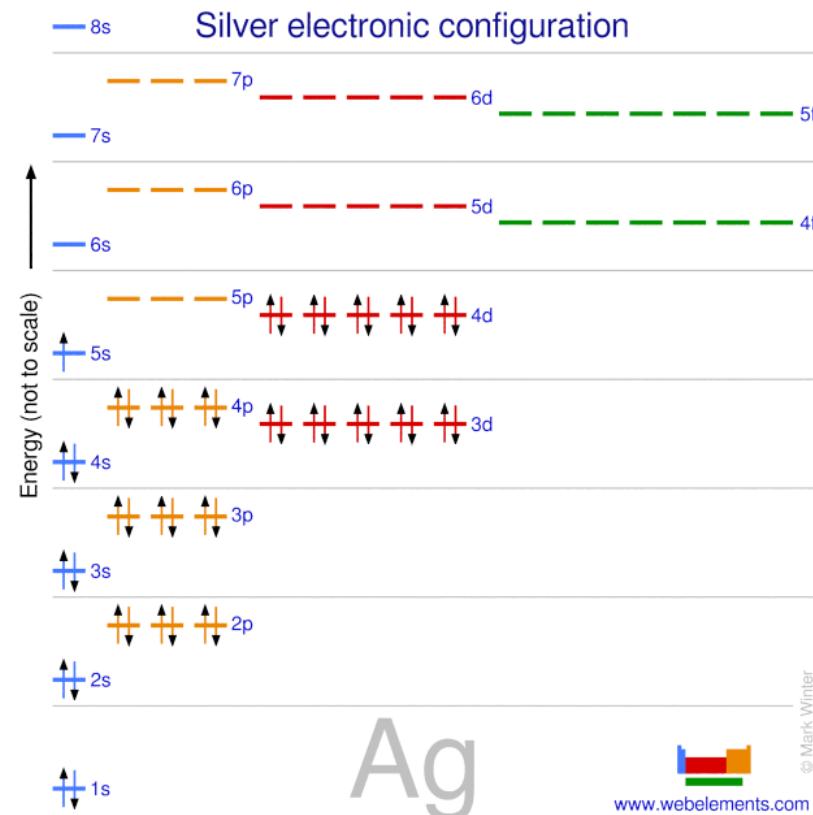
Field switched on



- What they actually saw was a separation of the beam into two distinct regions! They had chosen silver atoms deliberately because it was actually known that the *orbital angular momentum* of the atoms was zero. This implied that the electron must possess an intrinsic, quantised angular momentum, which was called spin and each electron could only possess two values, which for the z-component can be either $+\frac{\hbar}{2}$ or $-\frac{\hbar}{2}$, i.e. either spin 'up', or spin 'down'.

Stern-Gerlach Experiment cont.

- There are 47 electrons in silver. How can the total angular momentum be just two different values?
 - 46 of the silver electrons are paired up such that their spins ‘cancel’. The



Looking Ahead to the New Quantum Theory

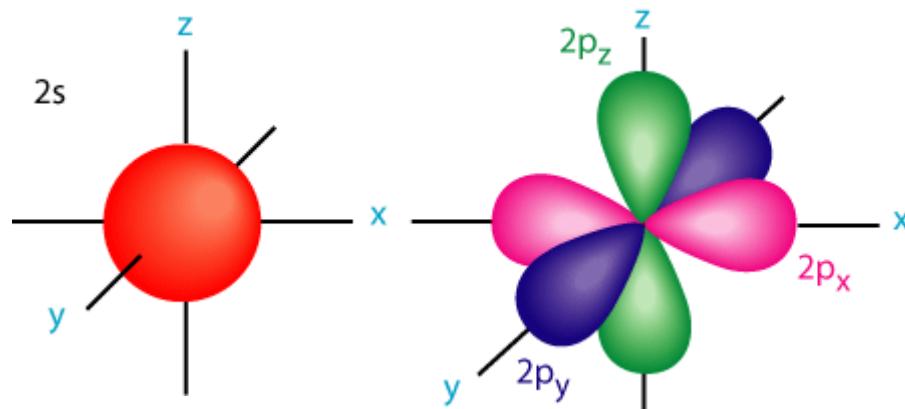
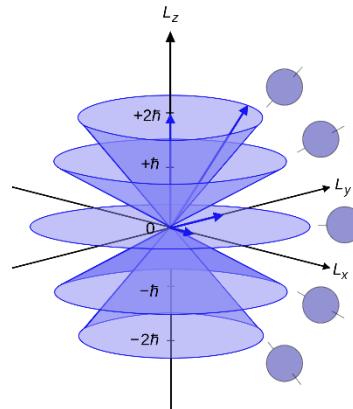
- For the rest of this course we shall discuss the first modern quantum theory based upon work by people such as De Broglie, Heisenberg and Schrödinger who assumed that matter had fundamentally wavelike properties.

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

$$\Delta x \Delta p \geq \frac{\hbar}{2}$$

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x, t)}{\partial x^2} + V(x, t)\psi(x, t) = i\hbar \frac{\partial \psi(x, t)}{\partial t}$$

- In part 2 of the QM course, with Satya, you will see that solutions of the Schrödinger equation in 3D leads to the quantization of the orbiting electrons angular momentum.

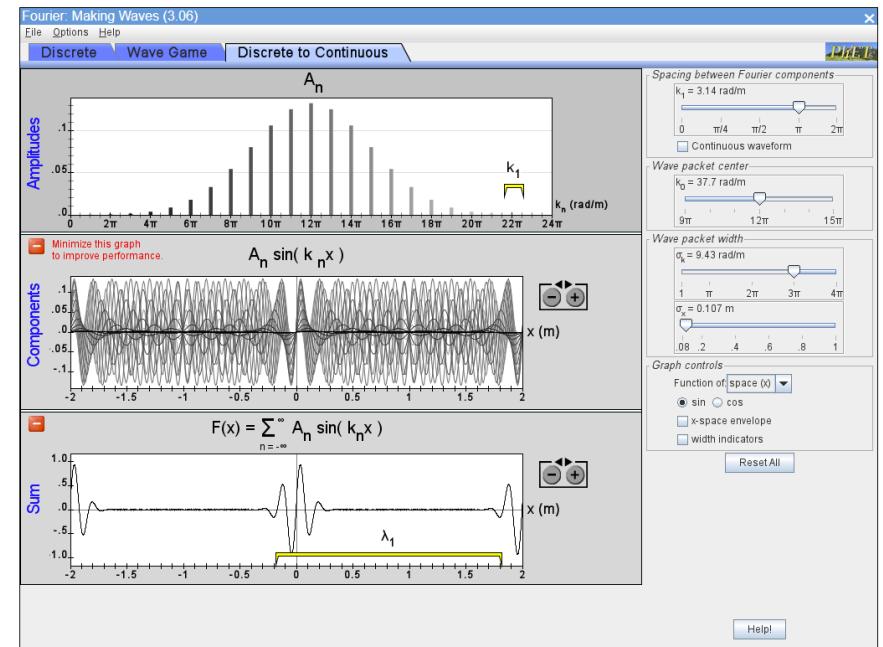


- Looking beyond level 2 you should be aware the Schrodinger approach is not the only quantum mechanical model. For example, the Dirac Equation incorporates special relativity and correctly predicts the existence of intrinsic spin for particles such as electrons, and the existence of anti-matter particles such as the positron.
 - This is often seen as the beginnings of QED (quantum electrodynamics) which describes the interaction of light and matter that is fully consistent with special relativity and quantum mechanics.

Quantum Mechanics – Lecture 5

Learning Outcomes

- Recap of the de Broglie Wavelength (Eis 3-1, and Tip 5-1)
- Planewaves and Wavepackets
- Forming Wavepackets via superposition (Eis 3-4, and Tip 5-3)
- Classical Uncertainty Relationship (Eis 3-4)



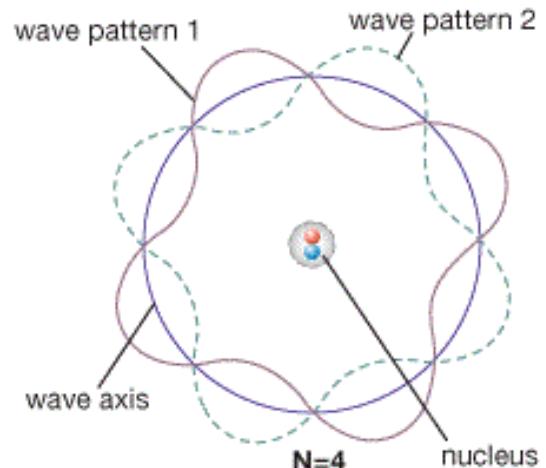
De Broglie Wavelength

- In 1924 while working on his PhD Louis De Broglie proposed that since light could exhibit particle like-behaviour, then perhaps matter would also exhibit wavelike behaviour. This symmetry in nature is summed up as;

$$f = \frac{E}{\hbar}$$

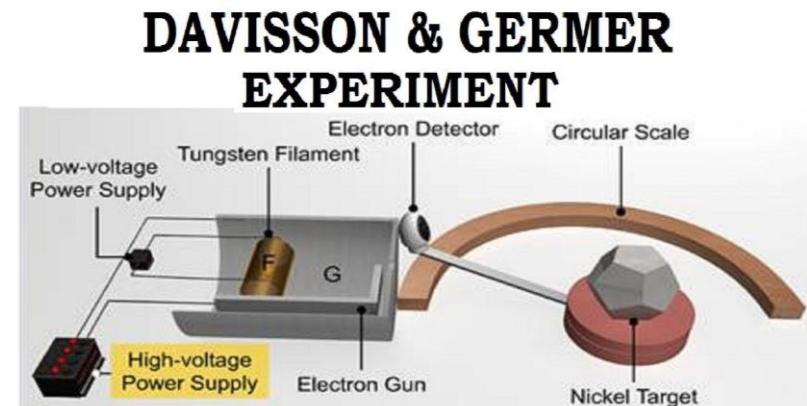
$$\lambda = \frac{\hbar}{p}$$

- In this context these equations are known as the Einstein De Broglie relationships. Notice that the first equation looks similar to the photon-energy relationship (hence the Einstein label) however to be clear, E here refers to the total energy of the particle.
- De Broglie realised that this led to a more physical interpretation of quantisation in the Bohr model for hydrogen, i.e., that the orbiting electron has a standing-wave condition. This is what we saw last year. Now while this is still not the complete picture, it led to a more appealing explanation for the existence of stationary states.
- When De Broglie proposed this idea there was no experimental observations to suggest the wave-particle duality of matter.



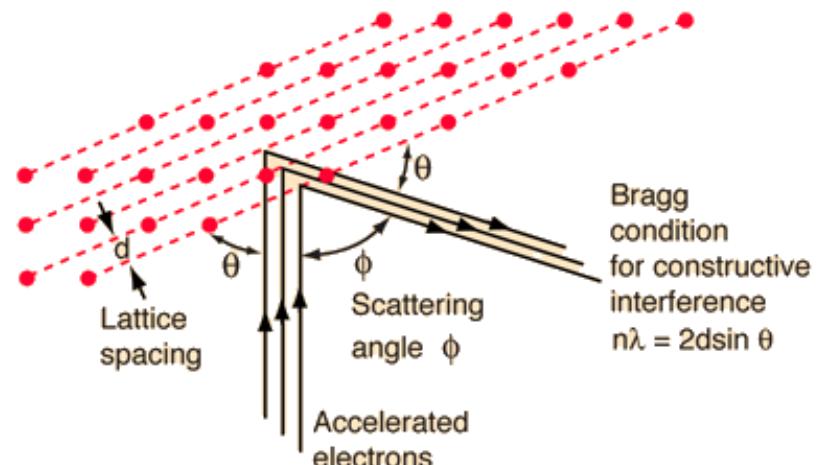
Recap : The Davisson & Germer Experiment

- In 1927 the Davisson & Germer experiment showed that electron diffraction was consistent with the De Broglie hypothesis.
- Using a beam of 54 eV electrons directed at a nickel crystal, they observed a strong scattered signal at $\phi = 50^\circ$
- This corresponded to a Bragg angle of 65°



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

- The lattice spacing for nickel was known from x-ray crystallography as $d = 0.091 \text{ nm}$
- So assuming a 1st order reflection, the corresponding wavelength of the electrons was $\lambda = 1.65 \text{ \AA}$
- **De Broglie gives $\lambda = 1.67 \text{ \AA}$**



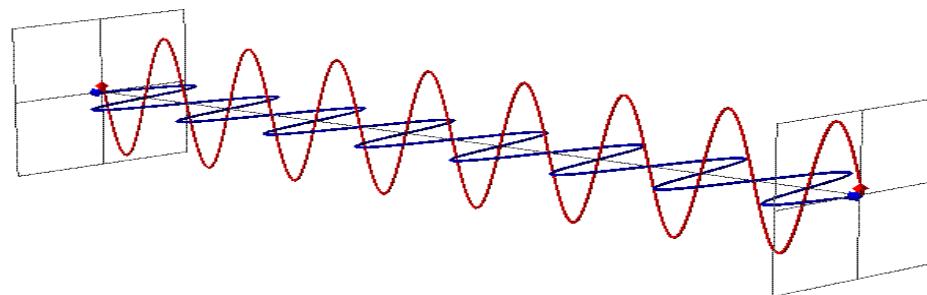
Wave-Particle Duality: EM Waves

- Experimental observations have conclusively shown that the wave-particle duality of radiation and matter is fundamental to nature.
- This prompts the question then: **For matter, what is waving?**
- Let's look at electromagnetic theory and see if we can draw an analogy in describing matter waves.
- An EM wave propagating along the x-axis can be described as;

$$E(x, t) = E_0 \sin(kx - \omega t)$$

This is a planewave
remember

- In the wave picture the intensity of radiation, $I \propto |E|^2$
- In terms of photons we can say; $I = N_\gamma h f$. In this equation N_γ is the **average** number of photons crossing a unit area per unit time.
- To unite the wave and particle models of EM radiation Einstein suggested then that $|E|^2 \propto \frac{N_\gamma}{V}$



Wave-Particle Duality: Matter

- Max Born proposed an analogous relationship for matter.
- Let's associate more than just a simple wavelength and frequency with a matter wave by using a **wavefunction ψ** to represent the particle.
- For a particle moving in the x-direction with a precise value of momentum and energy the associated wavefunction is;

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

Compare with;

$$E(x, t) = E_0 \cos(kx - \omega t)$$

- Born then said that the value of $|\Psi|^2 = \Psi^* \Psi$ will represent the probability density.
Remember that Ψ^* represents the complex conjugate (or c.c.) of Ψ .
- For 1D, this would be the **probability per unit length**. Even if Ψ is a complex function, the **probability density is a real, positive value**.
- This suggests that we can only give the probability of locating a particle in space! We cannot say exactly where it is!

Plane Wave Probability Density

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

Now the wavefunction we have here is called a plane wave (also called a harmonic wave). What is the probability density corresponding to this wavefunction?

Now the wavefunction can be complex, we can say equivalently* that the above wave is represented by;

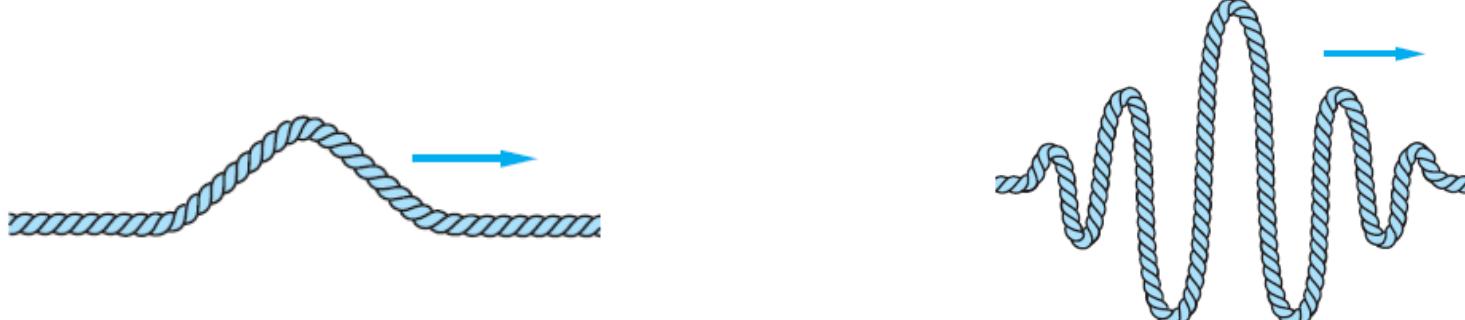
$$\Psi(x, t) = Ae^{i(kx - \omega t)}$$

What is the probability density for such a wavefunction?

$$|\Psi|^2 = \Psi(x, t) = Ae^{i(kx - \omega t)} \times Ae^{-i(kx - \omega t)} = A^2 = \text{const}$$

Our particle is equally likely to be found anywhere! Clearly this is not a good wavefunction for describing a particle localised in space. What does this mean for the probability of finding the particle anywhere?

A wave packet (or wave group) can be used to describe a pulse, i.e. a wave which has some degree of localisation in time and space.



*Euler's Formula

Plane Wave Particle Velocity

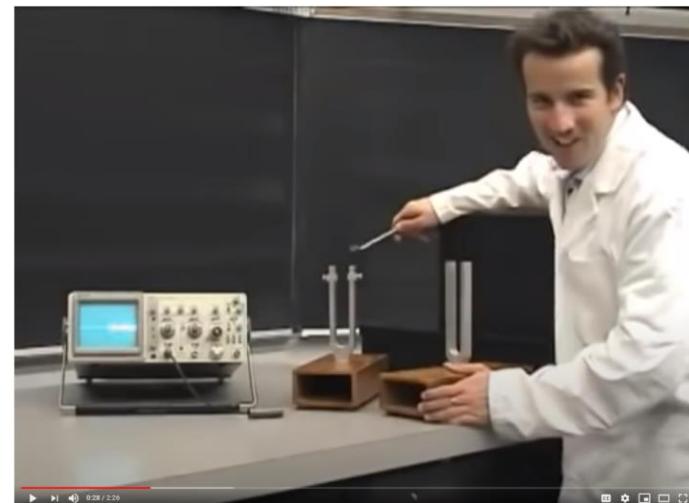
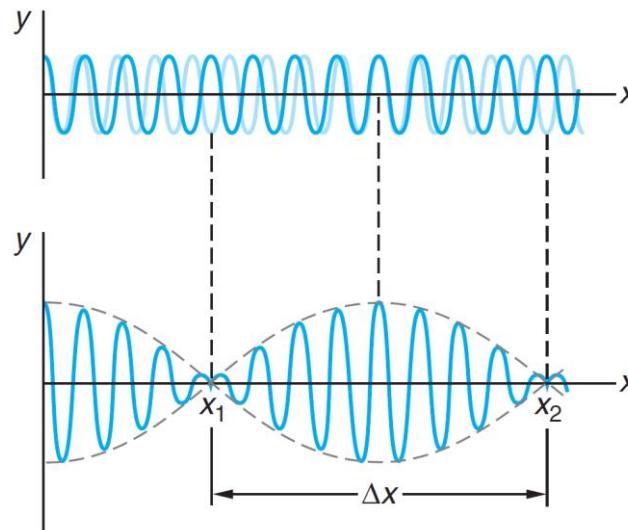
Our wavefunction should also move at the same velocity as our particle. Let's see if the plane wave description does a better job here?

Wavepacket Velocity

What would the corresponding group velocity of a wavepacket be for a wavefunction describing a particle?

Constructing Wave Packets and Uncertainty

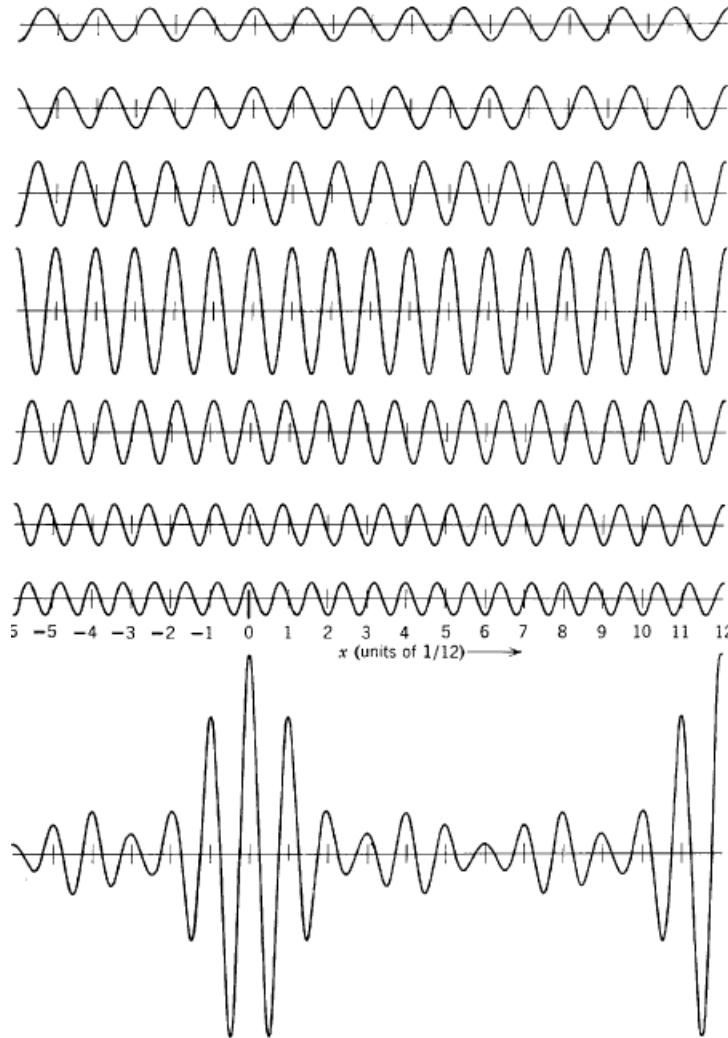
- So we have seen that a wavepacket can satisfy the requirement that a wavefunction, which represents our particle, will move at the same velocity as the particle.
- Before we look in detail at the properties of valid wavefunctions let's take some time to examine how wave packets may be constructed, and the inherent uncertainty present in this process.
- We've already seen in PHY1004 that when two waves of slightly different frequency are superimposed we get a beat pattern.
- You've probably got experience of this in the real world, for example, the slow *beating* noise on an airplane when the engines are running at slightly different speeds. ([Or lost penguins?](#)).



[Above: Demo of beats using tuning forks](#)

Constructing Wave Packets and Uncertainty Cont.

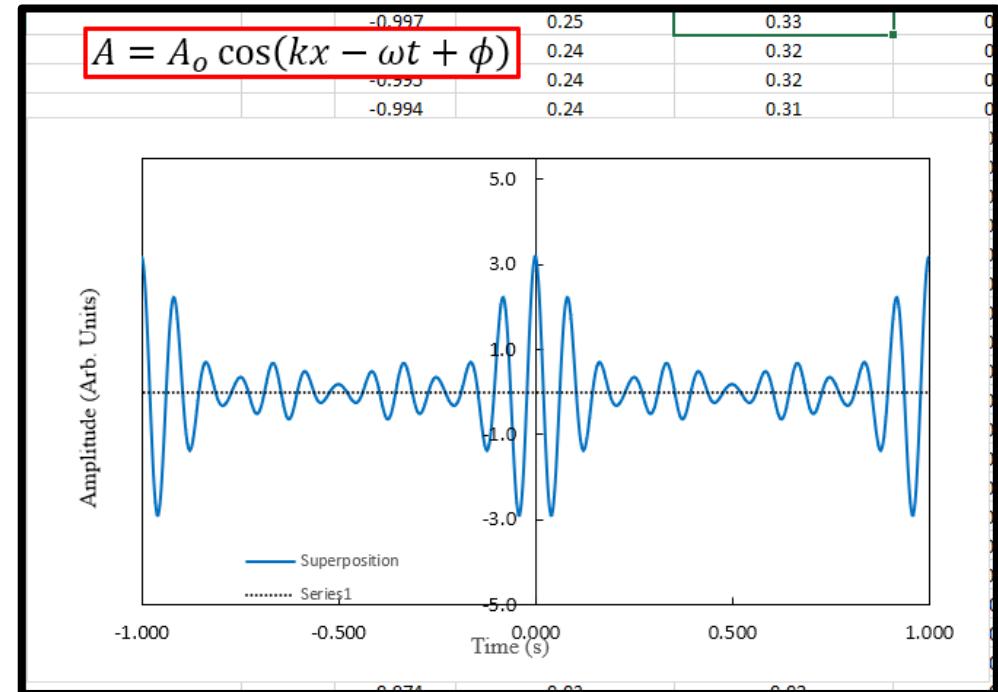
- What if we add more harmonic waves of both differing amplitude, frequency, and possibly phase together?



Left: Figure 3-9 from Eisberg and Resnick (also reproduced in Tipler 5th figure 5-16) showing the superposition of 7 harmonics.

Let's use excel to reproduce this pattern and investigate some properties of wavepacket.

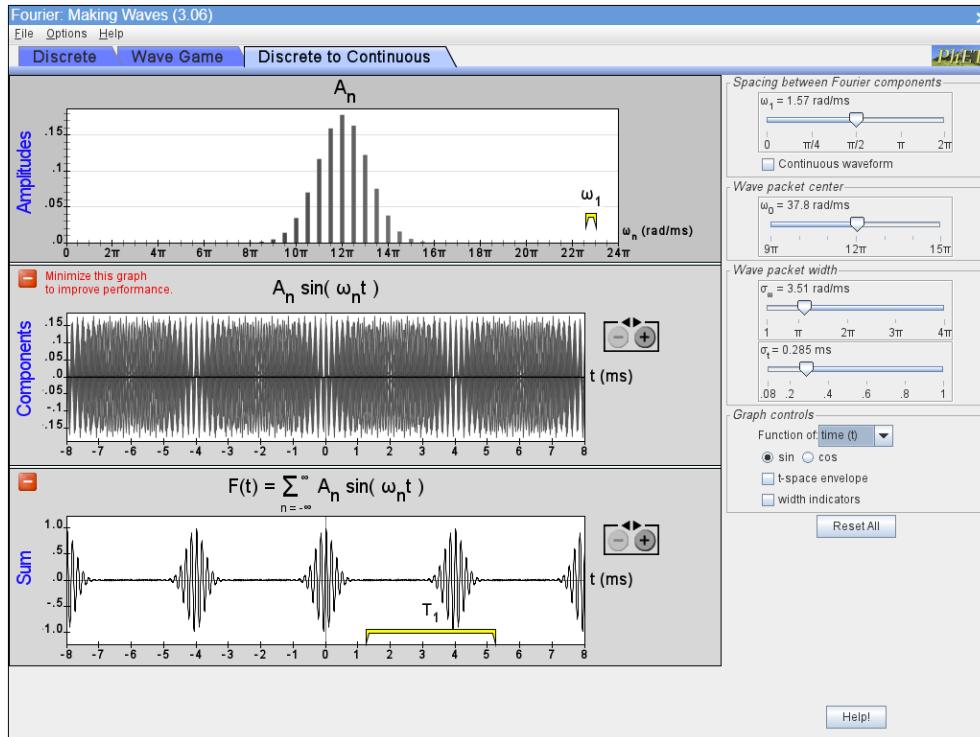
You should have a go at this too.



Constructing Wave Packets and Uncertainty Cont.

We can also use this [demo](#) to see what happens when we use a Fourier analysis and sum together more and more harmonics. (Note: So far the waves have all been in phase at $x = 0, t = 0$, this does not have to be the case and is how, for example, a gaussian pulse can be constructed).

When we have an infinite number of harmonics our Fourier series becomes a Fourier integral.



This leads to the classical uncertainty relationship that

$$\Delta x \Delta k \sim 1$$

Or equivalently

$$\Delta \omega \Delta t \sim 1$$

The similar sign here shows that you shouldn't worry too much about the exact value but rather remember the intuition **that for a wavepacket to be localised in time or space, it must contain a large range of harmonics.**

Notice there has been no quantum physics involved here.

This is the **classical uncertainty relationship**.

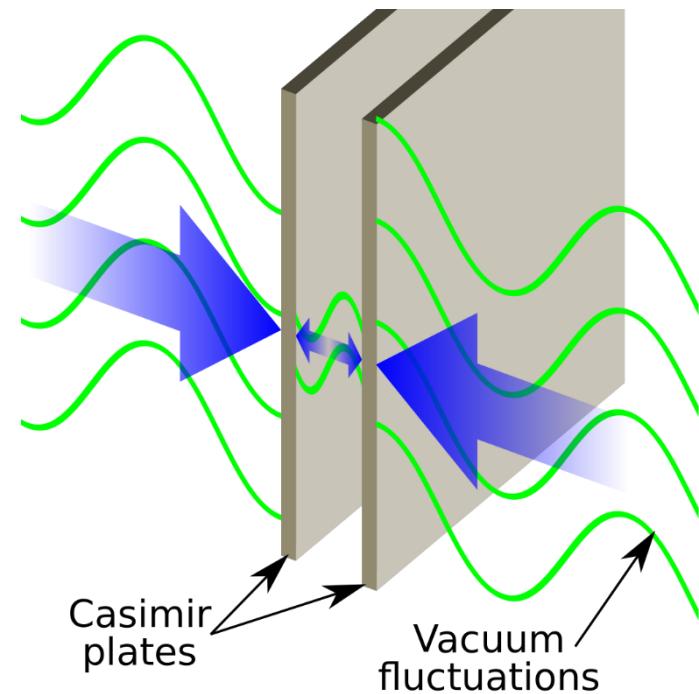
Quantum Mechanics – Lecture 6

Learning Outcomes

- Heisenberg Uncertainty Principle (Eis 3-5 and Tip 5-5)



HEISENBERG GETS PULLED OVER



Optimum Uncertainty Relations

Last time we saw how wavepackets can be formed from the superposition of harmonic waves, and that it was impossible to simultaneously determine, for example, the wavelength and position of a wavepacket

$$\Delta x \Delta k \sim 1$$

$$\Delta \omega \Delta t \sim 1$$

The symbol \sim in this context should be interpreted as '**approximately equal to an order of magnitude**'.

This is because the exact relationship depends on the shape of the pulse and how the ranges are defined.

Using Fourier theory for a Gaussian shaped pulse it can be shown that the 'optimal' relationship is;

$$\sigma_x \sigma_k \geq \frac{1}{2}$$

$$\sigma_\omega \sigma_t \geq \frac{1}{2}$$

Where the σ_x , for example, represents the standard deviation of the distribution function for x . This is often just written as σx , and this is the notation I will now use.

The second relationship is called the time-bandwidth product and very important in many fields such as signal processing, communication equipment, and even laser systems.

Short Pulse Lasers

Worked Example:

A proposed upgrade to the TARANIS laser at queens may provide 10fs ($1 \times 10^{-15}\text{s}$) pulses of light at a central wavelength of 800nm . Would this laser be described as monochromatic?



Heisenberg Uncertainty Principle(s)

The previous relations are inherent properties of all waves. We can apply them to matter waves using the de Broglie-Einstein relations;

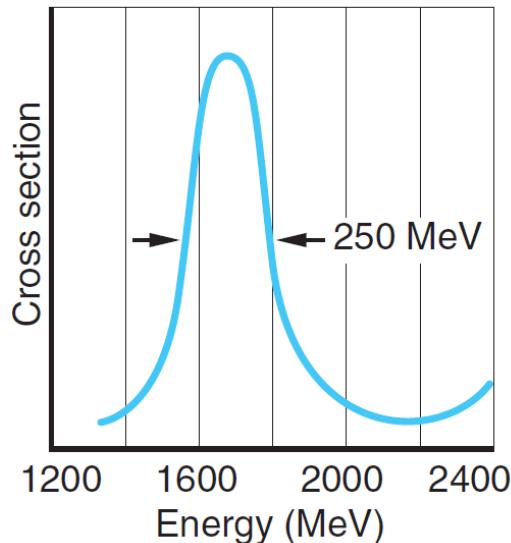
$$\sigma x \sigma p \geq \frac{\hbar}{2}$$

$$\sigma E \sigma t \geq \frac{\hbar}{2}$$

Applications and Consequences

The uncertainty relationship is an incredibly powerful result.

- You'll see later how it actually can be used to explain the stability of matter!



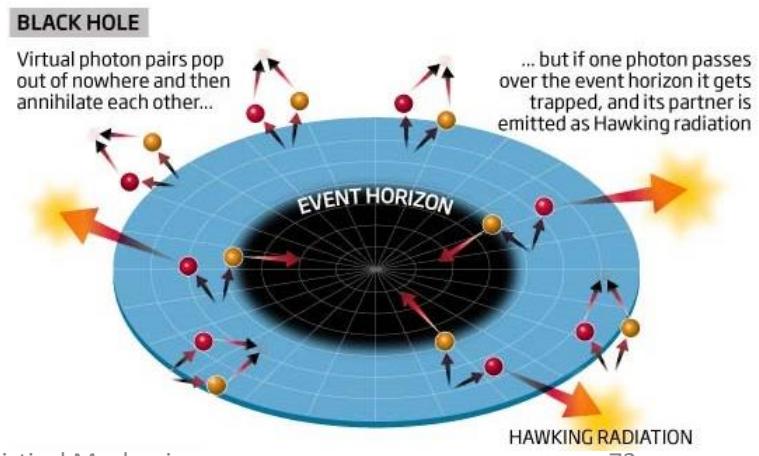
- In CERN experiment the lifetimes of many so-called resonance particles are so short they cannot be directly measured, however their distribution of energies can.
- An example of such a particle is a Δ which can be produced when a π meson scatters from a proton.
- From the width of the measured scattering energy, the lifetime can be determined as $\sigma t = 2.6 \times 10^{-23} \text{ s}$

Vacuum Fluctuations

Energy cannot be created or destroyed, but it can be borrowed!

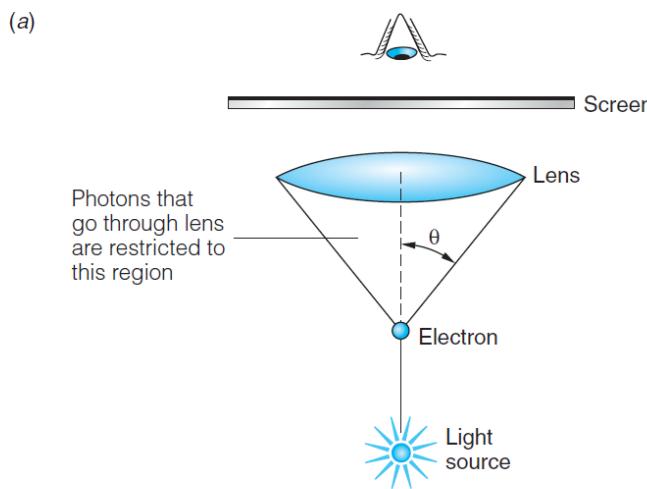
- Hawking Radiation
- Casimir Effect
- Universes?

$$\sigma E \sigma t \geq \frac{\hbar}{2}$$



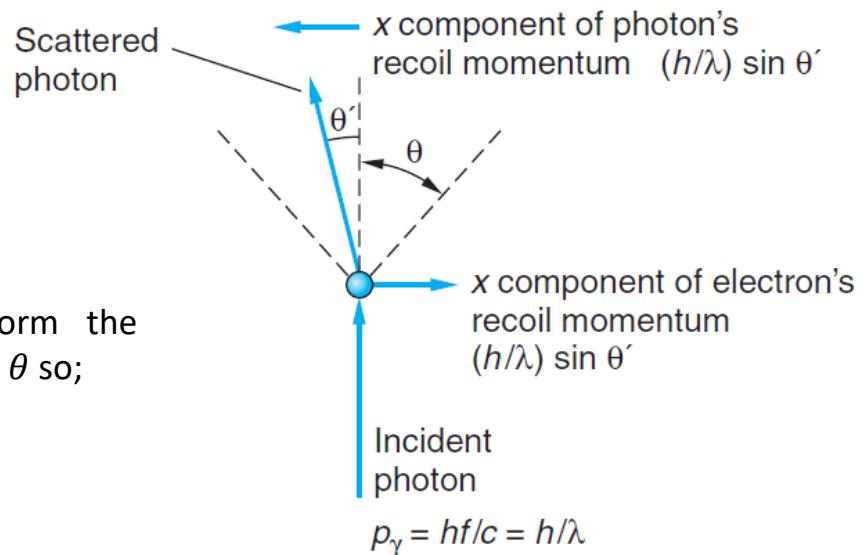
Measurement and the Uncertainty Principle

Can we perform a measurement that violates the uncertainty principle? To try and address this question Heisenberg performed a thought experiment where he considered the implications of using a gamma ray microscope to observe a free electron.



For the microscope to 'see the electron' the photon must interact with it. This is a **Compton** interaction and if the photon is scattered there will be a momentum transfer.

If the photon initially has $p_x = 0$ then;



From this figure, for the scattered photon to form the microscope image it can have any scattering angle up to θ so;

$$\Delta p_{x\gamma} \approx p \sin \theta = \frac{h}{\lambda} \sin \theta$$

Measurement and the Uncertainty Principle (cont.)

We can only locate the position of the electron to within the diffraction limit of the microscope;

$$\Delta x = \frac{\lambda}{2 \sin \theta}$$

We touched upon diffraction limits, or, resolution limits, last year. This expression is called the Rayleigh criterion which you'll see in EM & Optics this year

The electron momentum after the collision, is at least as uncertain as the photon momentum

$$\Delta p_x \geq p \sin \theta$$

$$\Delta x \Delta p \geq \frac{\lambda}{2 \sin \theta} \frac{h \sin \theta}{\lambda}$$

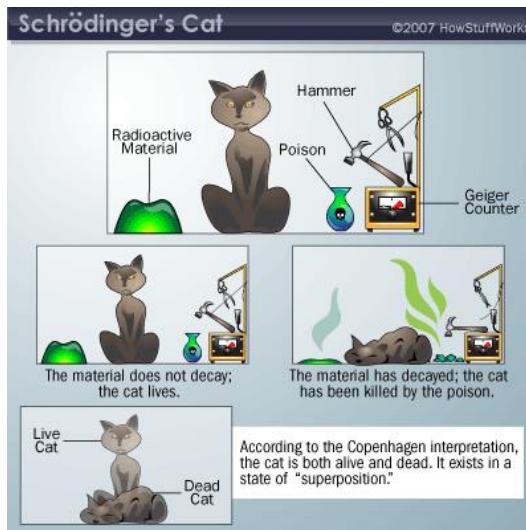
The act of measurement introduced an uncertainty to the electron position and momentum!

Pitfall Warning – While this thought experiment shows the property that a measurement influences the uncertainty of quantities such as momentum, they are also inherently probabilistic!
Uncertainty/Randomness is fundamental to nature!

Quantum Mechanics – Lecture 7

Learning Outcomes

- Some More Consequences of the Uncertainty Principle
 - Confinement and Zero-Point Energy (Tip 5-6)
 - Resolving the wave-particle duality paradox (Eis 3-5)
 - Copenhagen Interpretation (Eis 3-6) Tiper (5-7)
- Philosophy of Quantum Mechanics – No Hidden Variables
- Warming Up for Schrödinger



Confinement and Zero-Point Energy

Consider a particle confined to a 1D box, i.e. its motion is constrained along the x-axis between $x = 0$ and $x = x_0$. What implications would this have on the energy of the electron?

The uncertainty principle requires that the minimum energy of any confined particle cannot be zero!

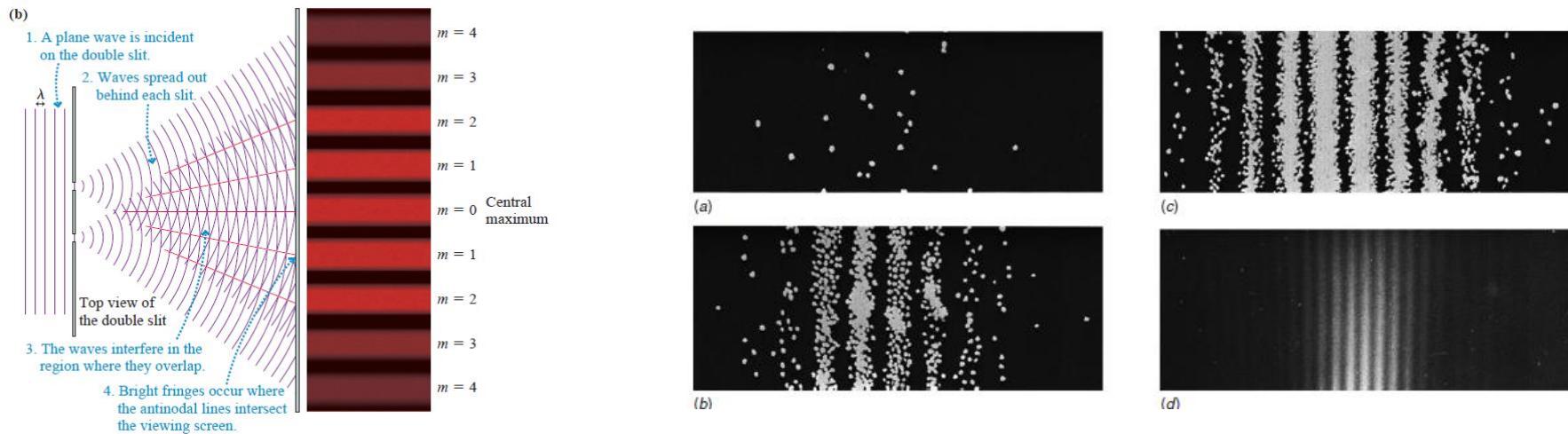
This is referred to as the zero-point energy.

Confinement and Zero-Point Energy cont.

Assume the dimensions of the box are similar to a hydrogen atom. What would the ground state energy of this *1D Hydrogen atom* be?

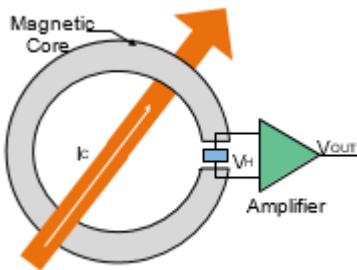
Resolving the Wave-Particle Duality Paradox

- One, if not the most unsettling aspect of QM is the idea that matter and radiation has wave and particle like aspects. The uncertainty principle actually gives justification as to why we can never observe both aspects together simultaneously.
- Consider Young's double slit experiment using electrons. When a large number of electrons is used an interference pattern exactly analogous to that produced using light is produced. As the intensity of the electron beam is reduced we start to see the granular or particle like nature of the electrons become apparent in the diffraction pattern. However if we let the signal build up over time we always see the interference pattern emerge.
- The question arises though, when we know only one electron is traveling through the system, how can it pass through both slits simultaneously?

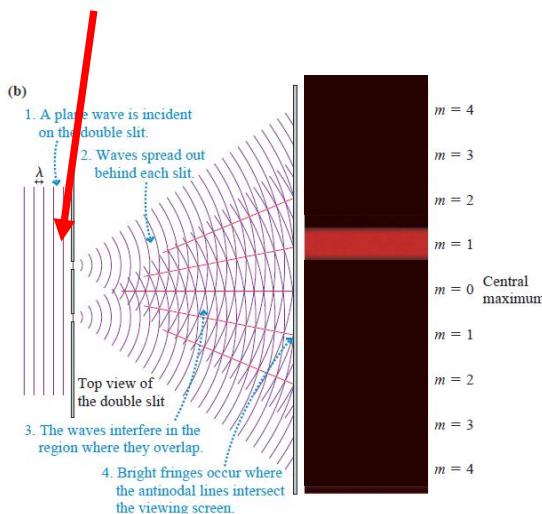


The Copenhagen Interpretation

- What if we set up a device, for example a Hall probe which is incredibly sensitive and can detect which slit the electron passes through!



**The diffraction pattern disappears!
The act of observation affects the behaviour of the electron!**



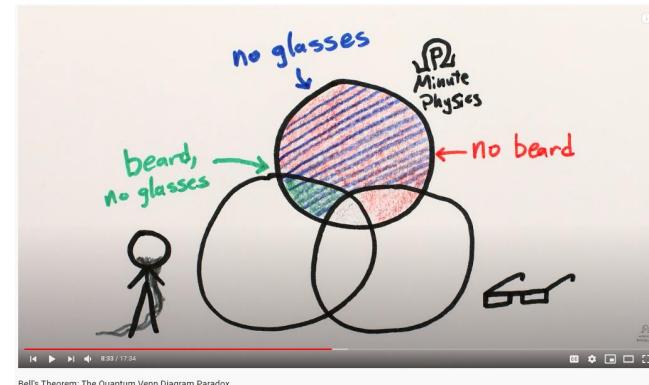
- Niels Bohr developed the **Copenhagen Interpretation** of quantum mechanics to try and explain this behaviour
- Matter (and radiation) should be considered as wave like when propagating. Wave aspects can be used to make predictions, but only as **probabilities**.
- Emission or absorption are described using a particle like model. Observations are described by particle like aspects.
- **We can never observe both at the same time due to the uncertainty principle.**

Bohr suggested that when the electron is observed the interaction modifies the wave function (coined wave function collapse). Without observation the electron behaves with wave aspects and exists in a superposition of states, one going through each slit forming an interference pattern. However if observed at the slits the wavefunction is modified, no superposition exists any longer and particle like behaviour is observed.

This most famous example of this phenomena is the Schrödinger Cat experiment.

Non-Determinism or Hidden Variables?

- The probabilistic nature of quantum physics did not sit well with many physicists, most famously Einstein who said ‘God does not play dice with the universe.’
- Einstein and many other physicists believed that there must be more layers of physics beneath our current understanding, which when incorporated would retrieve a deterministic picture. This idea was referred to as ‘hidden variables’.
- A physicist from Belfast and simple polarisers would prove Einstein wrong.
- John Bell studied here in the late 1940’s and showed that hidden variables could not exist (or there was an infinite number) and that the probabilistic aspects of QM were fundamental to nature.
- For an excellent discussion on Bell’s theorem try this [video](#) by MinutePhysics and 3Blue1Brown.



Warming up to The Schrödinger Equation

- The propagation of waves is governed by a corresponding wave equation.
- For an EM wave in vacuum the corresponding wave equation is;

$$\frac{\partial^2 \mathbf{E}}{\partial x^2} = \frac{1}{c^2} \frac{\partial^2 \mathbf{E}}{\partial t^2}$$

The ∂ symbol here indicates that this is a partial differential equation since \mathbf{E} is a function of both space and time. You'll learn more on the wave equation, and partial differential equations in general in PHY2006 and AMA2008

We've already seen that a plane wave is a viable solution to this equation;

$$E = E_0 \cos(kx - \omega t)$$

And that this can be equally represented as the real part of the complex exponential;

$$E = E_0 e^{i(kx - \omega t)}$$

Do we have to restrict ourselves to just the real part of this function?

Let's see if this is a solution to this wave equation?

Worked Example of Complex Exponential

Complex Numbers are necessary in QM

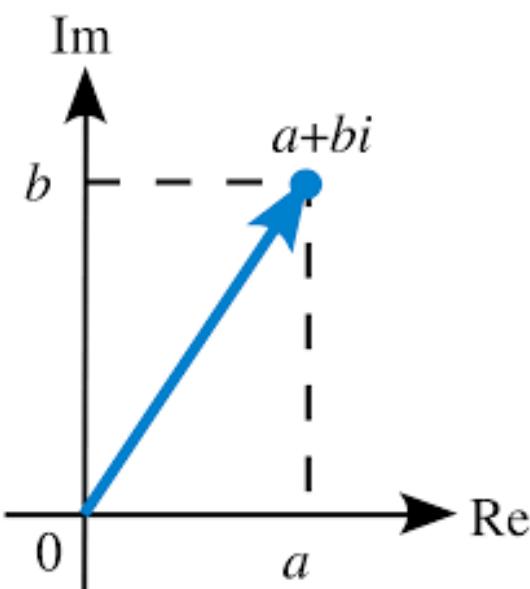
We've just seen that a complex plane wave function can be a solution to the EM wave equation.

We will shortly see that wavefunctions are generally complex valued functions!

Unlike the electric field which is a real and observable quantity, quantum mechanical wavefunctions are complex and unobservable.

$$\Psi(x, t) = A \exp(i(kx - \omega t)) \quad E = \hbar\omega \quad p = \hbar k$$
$$\Psi(x, t) = A \exp(i/\hbar(px - Et))$$

Quick summary of some key points about complex numbers



$$i = \sqrt{-1} \quad i^2 = -1 \quad \sqrt{i} = \frac{1}{\sqrt{2}} + \frac{i}{\sqrt{2}}$$

$$z = a + ib \quad z^* = a - ib$$

Complex conjugate

$$|z| = \sqrt{a^2 + b^2} = \sqrt{z^*z}$$

$$z = |z|(\cos \theta + i \sin \theta)$$

$$e^{i\theta} = \cos \theta + i \sin \theta \quad \text{Euler's formula}$$

Quantum Mechanics – Lecture 8

Learning Outcomes

- Postulating and Developing the Schrödinger Wave Equation (Eis 5-2 and Tip 6-1)

Creating a Particle Wave Equation

In the winter of 1925 Erwin Schrödinger took off to a small villa in the Swiss Alps to try and determine a suitable wave equation for matter. When he emerged he had discovered the famous Schrödinger Equation, sometimes called the law of Quantum mechanics;

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x, t)}{\partial x^2} + V(x)\Psi(x, t) = i\hbar \frac{\partial \Psi(x, t)}{\partial t}$$

The Schrödinger equation cannot be derived, rather it is developed from postulates!

However based upon previous work by de Broglie and Einstein, and understanding what properties a suitable wave equation should have, Schrödinger was able to begin his search by making 4 assumptions that any suitable equation should satisfy. To make matters simpler we will restrict ourselves to the 1D case.

These assumptions were;

1) It must be consistent with the de Broglie-Einstein equations;

$$\lambda = \frac{h}{p} \quad f = \frac{E}{h}$$



Creating a Particle Wave Equation cont.

2) Conservation of Energy

$$E = \frac{p^2}{2m} + V$$

This is from classical physics. A particles total energy is the sum of it's kinetic energy and potential energy, and for a closed system remains a constant. Now this is also the non-relativistic energy, i.e. the Schrödinger equation assumes non-relativistic energies. The Dirac equation developed years later incorporated special relativity into quantum mechanics.

3) The solutions to our wave equation will be wavefunctions $\Psi(x, t)$ and our wave equation should be linear in $\Psi(x, t)$.

$$\Psi(x, t) = c_1 \Psi_1(x, t) + c_2 \Psi_2(x, t) + \dots$$

This is another way of saying that the principle of superposition should apply to the wavefunctions. This is a reasonable assumption as observation shows that matter waves exhibit wave like properties such as constructive and destructive interference.

4) The potential energy V is a function of x and possibly t , however for a free particle the potential is constant, i.e.

$$V(x, t) = V_0$$

We will begin assuming this relatively simple potential energy function, however our result will apply for **any valid** potential energy function.

Let's now use these assumptions to try and develop a suitable wave equation;

Developing the Schrödinger Equation

Developing the Schrödinger Equation

1D Time Dependent Schrödinger Equation

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x, t)}{\partial x^2} + V(x) \Psi(x, t) = i\hbar \frac{\partial \Psi(x, t)}{\partial t}$$

- Our final result is the **1D Time Dependent Schrödinger Equation** and has been developed to be consistent with all four of our initial assumptions.
- It is consistent with the general statement of conservation of energy
- It is a 2nd order, linear partial differential equation and thus its solutions satisfy the principle of superposition.
- Solutions **are complex**, i.e. the wavefunction is necessarily complex and thus completely unobservable!
- For potentials that vary in space and/or time we cannot prove that this wave equation is still valid, only postulate it to be the case. However experimental observation is consistent with this postulate.
- The equation is non-relativistic. If the relativistic total energy $E = V + \sqrt{(pc)^2 + (m_o c^2)^2}$ is used a more complete equation is developed called the **Dirac Equation** which, for example, is required to accurately calculate energy levels for heavy elements and explaining the spin of particles.

Interpreting the Wavefunction

- We have seen that to obtain the Schrödinger equation the imaginary number i was forced to appear.
- Wavefunctions **are complex and unobservable**, however many people still debate how to interpret the wavefunction.
- While the wavefunction is not an observable quantity, **it contains all the information which the uncertainty principle allows us to know about the associated particle**.
- The most basic property is the probability of locating the particle in a range $x \rightarrow x + dx$, given by;

$$P(x, t)dx = \Psi^*(x, t)\Psi(x, t)dx$$

- This is also known as the Born Interpretation of the wavefunction.
- Since $\Psi^*\Psi$ is a probability density the dimensions of $\Psi(x, t)$ is $m^{-1/2}$.
 - **(Of course for 2D and 3D, the wavefunction dimensions change accordingly).**

Normalisation

- At any instant, the probability of finding the particle somewhere must be certain. This leads to the normalisation condition;

$$\int_{-\infty}^{+\infty} P(x, t) dx = \int_{-\infty}^{+\infty} \Psi^*(x, t) \Psi(x, t) dx = 1$$

Worked Example

A particle is described by a wavefunction

$$\begin{aligned}\psi &= Ax(1 + i) \text{ for } -1 \leq x \leq +1 \\ \psi &= 0, \quad \text{elsewhere}\end{aligned}$$

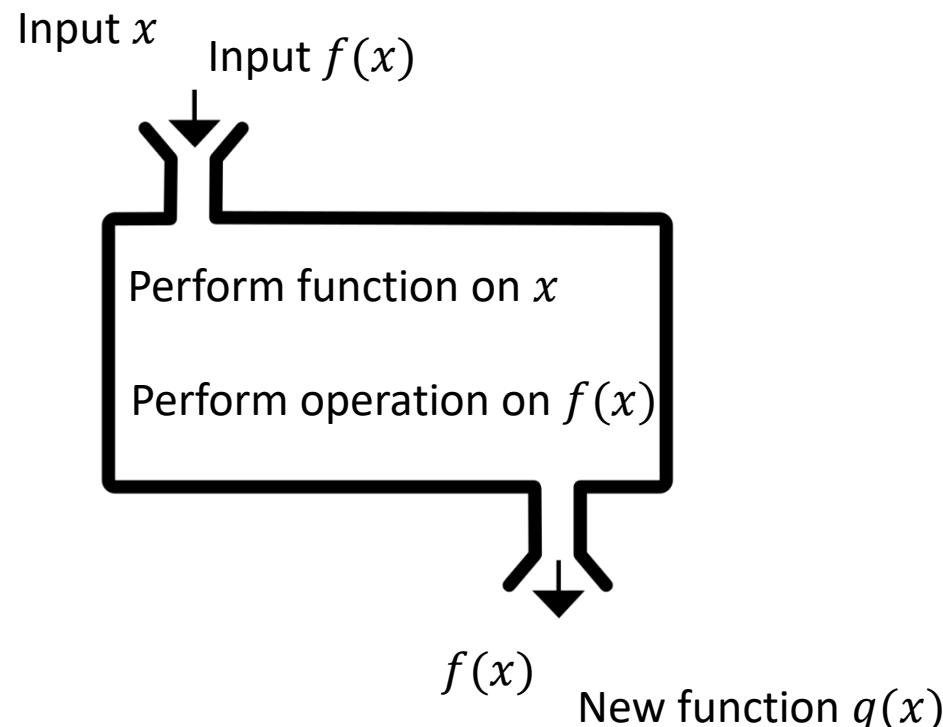
Find the value of the normalisation constant A .

Note that when a wavefunction is stated, you should not assume it is already normalised!

Quantum Mechanics – Lecture 9

Learning Outcomes

- Expectation Values and Operators(Eis 5-4 and Tip 6-4)
- Momentum Operator (Eis 5-4 and Tip 6-4)



Recap from Yesterday

Born Interpretation of the Wavefunction

$$P(x, t)dx = \Psi^*(x, t)\Psi(x, t)dx$$

Normalisation Condition

$$\int_{-\infty}^{+\infty} P(x, t)dx = \int_{-\infty}^{+\infty} \Psi^*(x, t)\Psi(x, t)dx = 1$$

- Remember $P(x, t)$ is the probability density and must be *square integrable* (Just a fancy way of saying the integral is finite, or that as $x \rightarrow \pm\infty, \Psi \rightarrow 0$)
- Before normalisation is carried out, the amplitude of a wave function is arbitrary. Normalising has the effect of fixing the amplitude by fixing the value of the multiplicative constant $\Psi(x, t) = Af(x, t)$
- **Note:** Useful results can often be obtained in terms of relative probabilities that are independent of the actual values of the amplitudes.
- The wavefunction can be used to extract information on measurable quantities, such as the position, energy and momentum of the particle.
- The uncertainty principle of course stops us from specifying, for example, the exact position of the particle, but not the **average, or expected, position of the particle**.

Expectation Value for Position

Let's consider a collection of classical particles. Say we had N_i particles at position x_i . The average position is;

$$\bar{x} = \frac{\sum_i N_i x_i}{\sum_i N_i}$$

In quantum mechanics we do not have discrete particles so we replace N_i with the continuous probability density and integrate. For a **normalised** wavefunction we have;

$$\langle x \rangle = \int_{-\infty}^{+\infty} x P(x, t) dx = \int_{-\infty}^{+\infty} \Psi^*(x, t) x \Psi(x, t) dx = \int_{-\infty}^{+\infty} \Psi^* x \Psi dx$$

Note the **order of operations** in the integrand here, while it does not make much difference for this example, the order is important for later operations.

Worked Example

A particle is described by a normalised wavefunction

$$\begin{aligned}\psi &= x \sqrt{3} & 0 \leq x \leq 1 \\ \psi &= 0, & \text{elsewhere}\end{aligned}$$

Find the average position of the particle.

Expectation Values in General

- Expectation values may be evaluated for any function of x , using a similar procedure;

$$\langle x^2 \rangle = \int_{-\infty}^{+\infty} \Psi^*(x, t) x^2 \Psi(x, t) dx$$

- This is particularly useful for calculating the variance and hence standard deviation, since;

$$\sigma_x^2 = \langle x^2 \rangle - \langle x \rangle^2$$

- Or in general;

$$\langle f(x) \rangle = \int_{-\infty}^{+\infty} \Psi^*(x, t) f(x) \Psi(x, t) dx$$

- Or even for functions which may explicitly depend on time, such as the potential energy;

$$\langle V(x, t) \rangle = \int_{-\infty}^{+\infty} \Psi^*(x, t) V(x, t) \Psi(x, t) dx$$

Since the integrand is being evaluated at the same value of t .

- Thus we can see how the wavefunction can be used to estimate dynamical quantities such as the position x , and potential energy V which describe the behaviour of the particle.

What about, for example, the momentum p ?

Expectation value for Momentum

- Let's write the analogous expression for momentum

but;

$$\langle p \rangle = \int_{-\infty}^{+\infty} \Psi^*(x, t) p(x) \Psi(x, t) dx$$
$$\sigma x \sigma p \geq \frac{\hbar}{2}$$

- The **uncertainty principle** prevents us from knowing the precise momentum at any given value of x , i.e. we cannot write $p(x)$, or express the momentum as an explicit function of time.
 - The same problem arises in expectation values for E since we cannot write this as an explicit function of t (or x).

Our goal then is to try and find an alternative way to relate the momentum of a particle to position and time.

Momentum Operator

Let's look at our wavefunction for a free particle (or plane wave solution)

Momentum Operator cont.

$$p [\Psi(x, t)] = -i\hbar \frac{\partial}{\partial x} [\Psi(x, t)]$$

- We have found that multiplying our wavefunction by the momentum is equivalent to operating upon it with the corresponding differential operator (i.e. we must take the first space derivative of the wavefunction). A similar expression can be found for the **total energy E** .

$$p \leftrightarrow -i\hbar \frac{\partial}{\partial x}$$

$$E \leftrightarrow i\hbar \frac{\partial}{\partial t}$$

- We can now write for the momentum expectation value

$$\langle p \rangle = \int_{-\infty}^{+\infty} \Psi^*(x, t) \left(-i\hbar \frac{\partial}{\partial x} \right) \Psi(x, t) dx$$

$$\langle p \rangle = -i\hbar \int_{-\infty}^{+\infty} \Psi^*(x, t) \frac{\partial \Psi(x, t)}{\partial x} dx$$

Notation Warning:
Operators are sometimes designated using a subscript, e.g. p_{op} or with a 'hat', \hat{E}

Does Order Matter?

We mentioned earlier that the ordering of terms in the integrand would be important. What would happen if we tried different orders here?

What if we put the partial derivative operator at the end;

$$\langle p \rangle = -i\hbar \int_{-\infty}^{+\infty} \Psi^*(x, t) \Psi(x, t) \frac{\partial}{\partial x} dx$$

There is nothing to operate upon so this is just silly?

Ok now let's try the operator at the start;

$$\langle p \rangle = -i\hbar \int_{-\infty}^{+\infty} \frac{\partial}{\partial x} [\Psi^*(x, t) \Psi(x, t)] dx$$

Remember the fundamental theorem of calculus

$$\langle p \rangle = -i\hbar [\Psi^*(x, t) \Psi(x, t)]_{-\infty}^{+\infty} = 0$$

Since we require that $\Psi(x, t) \rightarrow 0$ at infinity.

Expectation Values and Operators Examples

A particle is described by a wavefunction

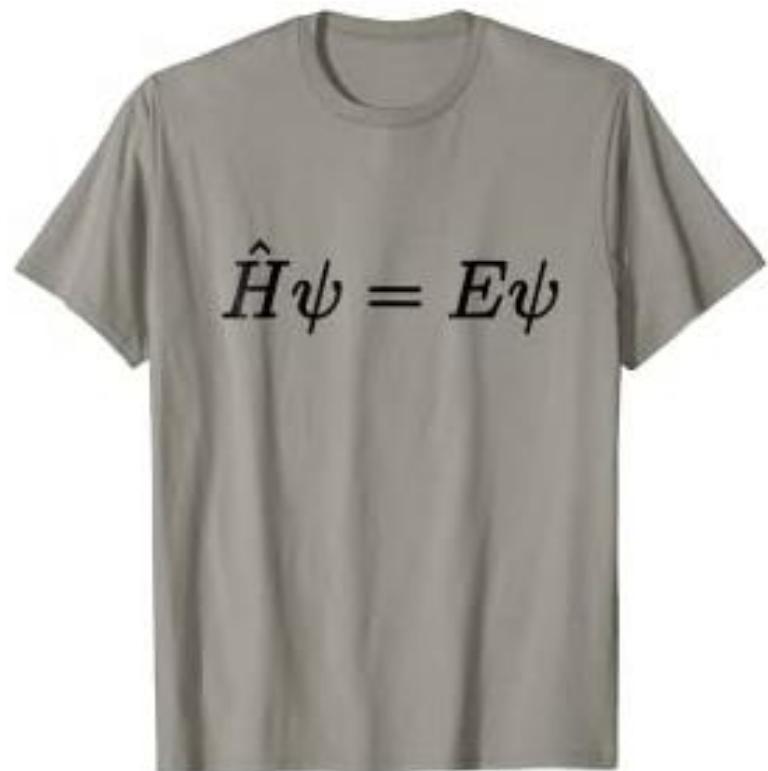
$$\begin{aligned}\psi &= \frac{\sqrt{3}}{2}x(1 + i) \text{ for } -1 \leq x \leq +1 \\ \psi &= 0, \text{ elsewhere}\end{aligned}$$

- (a) Determine the expectation value for x .
- (b) What is the particles average momentum?
- (c) What is the uncertainty, σ_x , in the particles position?

Quantum Mechanics – Lecture 10

Learning Outcomes

- Separation of Variables
- Time Independent Schrödinger Equation (Eis 5-5 and Tip 6-1)
- TISE Operator Form
- Eigenvalues and Eigenfunctions (Eis 5-5)
- Acceptable Eigenfunctions (Eis 5-6)



Time Independent Schrödinger Equation

- Schrödinger's first application of his wave equation was to problems such as the hydrogen atom, which you'll cover in the second part of the course, and idealised potentials, for example, the simple harmonic oscillator and square wells which will be the focus of the remainder of this part of the course.
- For such situations the potential energy function is **independent** of time.
- This **allows** us to simplify Schrödinger equation by separating the space and time dependence of the wave function*;

$$\Psi(x, t) = \psi(x)\phi(t)$$

- Where the separation assumes that we can re-write the wavefunction as a product of two functions, one of x and one of t . Let's substitute these values into the time dependent Schrödinger equation, and then collect like terms on each side of the equation. This is actually quite similar to what you would have done in school for separable differential equations.

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x, t)}{\partial x^2} + V(x)\Psi(x, t) = i\hbar \frac{\partial \Psi(x, t)}{\partial t}$$



$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x)\phi(t)}{\partial x^2} + V(x)\psi(x)\phi(t) = i\hbar \frac{\partial \psi(x)\phi(t)}{\partial t}$$

*This technique is called 'Separation of variables' and you will learn more about this in PHY2006 'Mathematical Physics' or AMA2008 'Introduction to Partial Differential Equations'

Time Independent Schrödinger Equation cont.

Normalisation for TISE

Summary

Separation of Variables

$$\Psi(x, t) = \psi(x)\phi(t)$$

Time Independent
Schrödinger Equation
(TISE)

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

Time Dependence

$$\phi(t) = e^{-iEt/\hbar}$$

Normalisation

$$\int_{-\infty}^{+\infty} \psi^*(x)\psi(x) dx = 1$$

Total Wavefunction

$$\Psi(x, t) = \psi(x)e^{-iEt/\hbar}$$

We can see that the time dependence of the wavefunction ensures that it has a complex nature.

You've seen the TISE many times.

The total energy of a particle is;

$$E = \frac{p^2}{2m} + V$$

Let's rewrite this in terms of the momentum and energy operators.

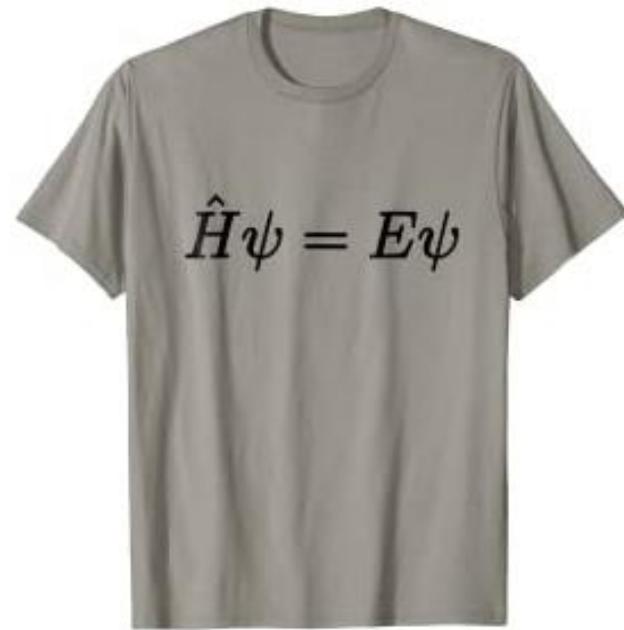
$$p \leftrightarrow -i\hbar \frac{\partial}{\partial x} \quad E \leftrightarrow i\hbar \frac{\partial}{\partial t}$$

$$i\hbar \frac{\partial}{\partial t} = \frac{1}{2m} \left(-i\hbar \frac{\partial}{\partial x} \right)^2 + V$$

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

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x)$$

$$\hat{H}\psi(x) = E\psi(x)$$



For time independent potentials we write this as a total derivative and it is called the **Hamiltonian operator**. This is just the total energy operator!

We can rewrite the 1D TISE now as

Note: This still applies for 2D, 3D etc. and even for the time dependent Schrödinger equation, however the Hamiltonian is equivalent to E

TISE is an Eigenvalue Equation

The TISE is an Eigenvalue problem. What does that mean?

If the result is the original function times some constant value we have an Eigenvalue equation

Pitfall Warning:
Eigenfunction/wavefunction and 'state' is often used interchangeably to refer to the same thing

The Hamiltonian is an operator. I.e. it operates on some function, to produce a new function.

$$\hat{H}\psi(x) = E\psi(x)$$

We now call the function an **Eigenfunction of the operator**

And the constant term is called the **eigenvalue for that eigenfunction for that operator**

- Solving the TISE is finding the set of eigenvalues and eigenfunctions for the Hamiltonian (remember total energy) operator.
- “Eigen” is a German word meaning “peculiar to” or “characteristic”. In this case E and $\psi(x)$ are characteristic to the potential $V(x)$.
- The eigenvalue corresponds to energy and is always real. However, the eigenfunction may be complex.

Required Properties of Eigenfunctions

For the rest of the course we will be interested in how we find solutions to the TISE. However to be an acceptable solution* the eigenfunction must satisfy certain conditions;

1. **$\psi(x)$ and $d\psi(x)/dx$ should be finite and single valued.**

If this were not the case then the wavefunction $\Psi(x, t)$ and $\partial\Psi(x, t)/\partial x$ would not be single valued. This would imply that we might not obtain finite and definite values of measurable quantities such as position and momentum. Obviously quantities such as momentum are not infinite or multiple valued.

2. **$\psi(x)$ and $d\psi(x)/dx$ must be continuous.[†]**

If $\psi(x)$ was not continuous then $d\psi(x)/dx$ would not be finite which clashes with our previous restriction. If we look at the TISE below (re-arranged a little) we can see that if E , $V(x)$, $\psi(x)$ are all finite then so must $d^2\psi(x)/dx^2$. Similar to our earlier statement, $d\psi(x)/dx$ must therefore be continuous.

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

3. **$\psi(x) \rightarrow 0$ as $x \rightarrow \pm\infty$**

Without this condition our eigenfunction could not be normalised

*Acceptable solutions can be used to obtain expectation values for measurable quantities such as position and momentum.

[†]We will see shortly that this condition can be relaxed when the potential $V(x) = \infty$. Here $\psi(x) = 0$ since no particle can have infinite energy. Then ψ' may be discontinuous at $V(x) = \infty$

PHY2001 – Lecture 11

Learning Outcomes

- **Revision/Recap Class on**
 - Wavefunctions
 - Normalisation
 - Expectation Values
 - Quantum Mechanical Operators



Past Paper Example Jan 2017 Q1(b)

- (b) A particle is represented by the following one-dimensional wave function where x is the position variable associated with the particle

$$\psi(x) = C(a^2 - x^2)$$

It moves freely in the interval $-a \leq x \leq +a$. In other words, the potential, V , is given by $V = 0$ for this region, and $V = \infty$ for $x > a$ and $x < -a$. C is a constant. In what follows, p is the particle's momentum.

- (i) Show that $C = \sqrt{\frac{15}{16a^5}}$ [3]
- (ii) Calculate the expectation values of x and x^2 . [4]
- (iii) Calculate the expectation values of p and p^2 . [4]
- (iv) By explicitly calculating $\Delta x \Delta p$, state whether Heisenberg's uncertainty principle is satisfied: $\Delta x = \sqrt{(\langle x^2 \rangle - (\langle x \rangle)^2)}$ and $\Delta p = \sqrt{(\langle p^2 \rangle - (\langle p \rangle)^2)}$ [2]
- (v) Explain what would happen to the momentum uncertainty if a were decreased by a factor of 2. [1]

Past Paper Example Jan 2017 Q1(b) cont.

Past Paper Example Jan 2017 Q1(b) cont.

Past Paper Example Jan 2015 Q1(d)

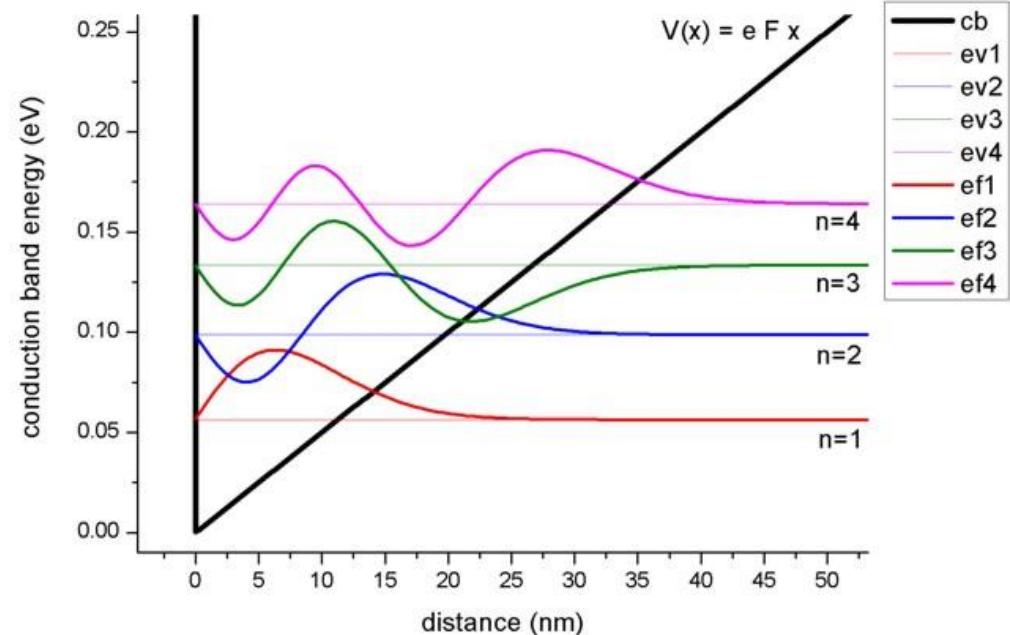
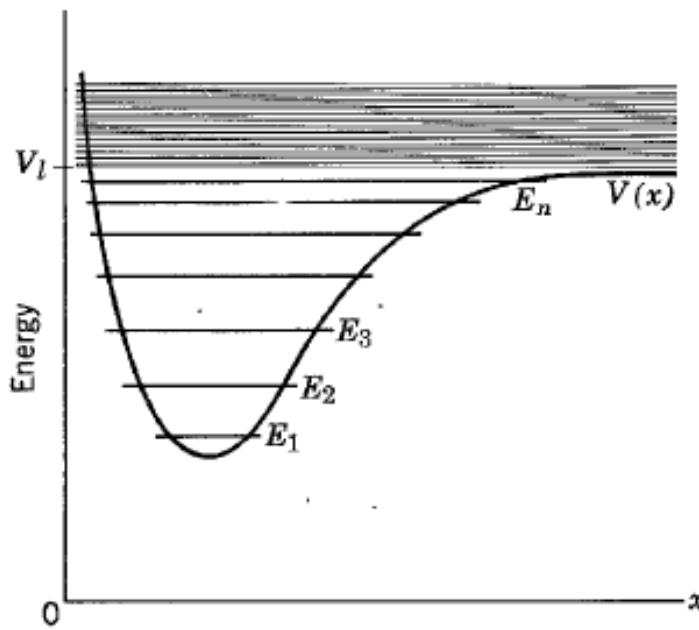
- (d) A particle limited to the x axis has a wavefunction $\Psi = Ax$ between $x = 0$ and $x = 1$ and zero elsewhere.
- (i) Find the value of A . [2]
 - (ii) Obtain the probability that the particle can be found in the region $0.4 < x < 0.5$ [2]
 - (iii) Calculate the expectation value of the particle's position $\langle x \rangle$. [2]
 - (iv) Why is this not a realistic wavefunction? [2]
 - (v) Determine the value of the expectation value of the momentum $\langle p \rangle$. Show your answer is unphysical. [3]

Past Paper Example Jan 2015 Q1(d) cont.

PHY2001– Lecture 12

Learning Outcomes

- Qualitative solution for molecular potential (Eis 5-7)
- Begin solving the Schrödinger equation for some idealised systems.
- Zero Potential (Eis 6-2)

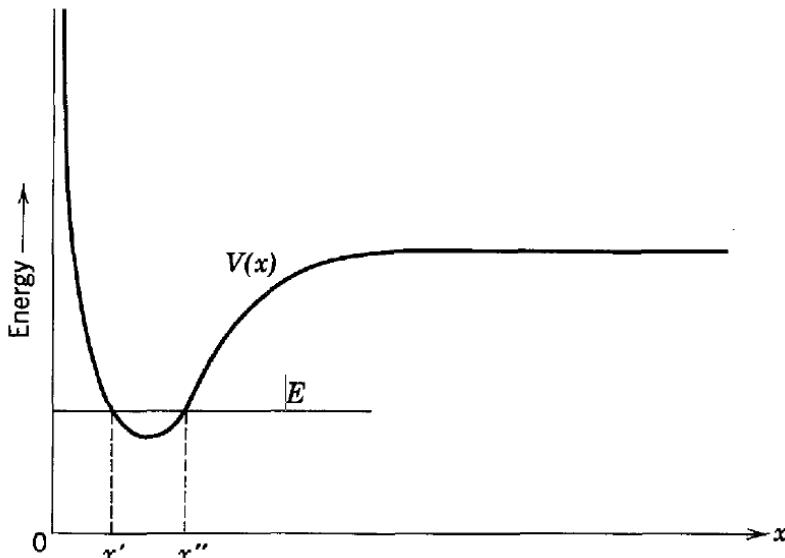


Qualitative Solution of the TISE

- Before we delve into quantitative solutions of the TISE it is useful to investigate qualitatively the sort of solutions which are acceptable using some simple arguments.
- This will allow us to highlight some important properties of the TISE (and diff. equations in general) without detailed maths.
- Let's look at the TISE in the same form as the previous slide;

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

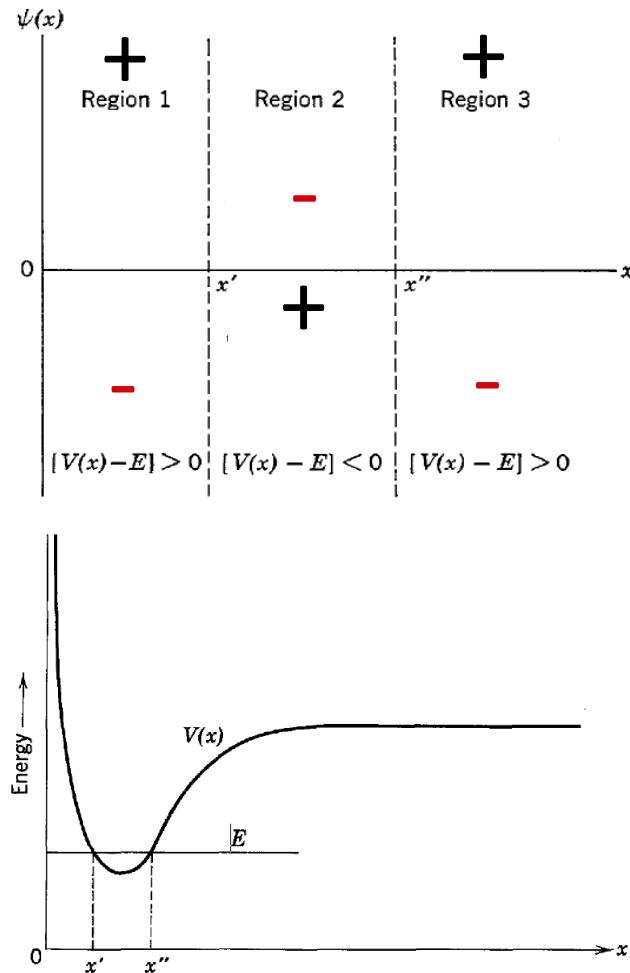
- Before we solve our differential equation we must first specify the associated potential. For these qualitative arguments we'll use the potential of an atom in a diatomic molecule (see PHY1004 Condensed Matter week 1) since it is a good real world example.



- Now we guess a specific energy, corresponding to a bound state to try and obtain a solution for the TISE.
- Now notice that our constant energy line divides the curve into three regions. One where $(V(x) - E)$ is negative between two regions where it is positive.
- We can see that the sign of $\frac{d^2\psi(x)}{dx^2}$ will depend on the sign of $(V(x) - E)$ and $\psi(x)$

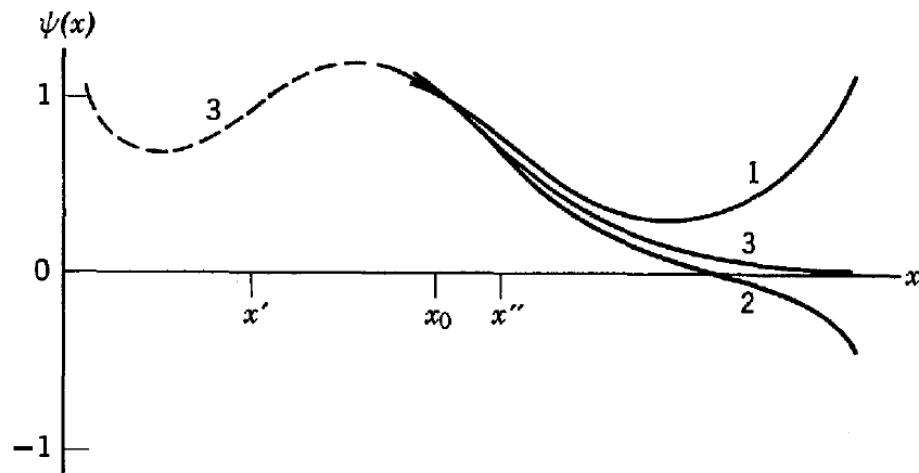
Qualitative Solution of the TISE cont.

The sign of $\frac{d^2\psi(x)}{dx^2}$ defines whether the eigenfunction is curved 'upwards' or 'downwards'.



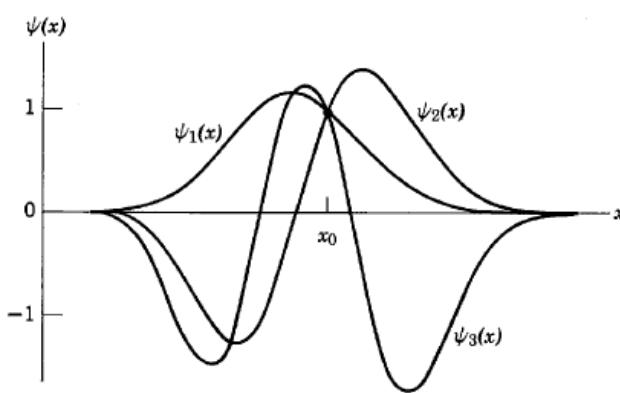
Now let's make an initial guess for the value of $\psi(x)$ and $d\psi(x)/dx$

- Our first guess has positive $\psi(x)$ and starts in region 2, so curves downwards, when it passes into region 3 it starts curving upwards, but curves too much and starts diverging from the x-axis towards infinity. This is therefore not an acceptable eigenfunction.
- Now let's try a different initial value of $d\psi(x)/dx$ (changing the initial $\psi(x)$ will just linearly scale the curve). Now we cross the x-axis in region 3 and $\psi(x)$ will again diverge.
- Eventually there will be an initial $d\psi(x)/dx$ which results in acceptable behaviour in this region. $\psi(x) \rightarrow 0$ as $x \rightarrow +\infty$
- But now when this attempt is extended to region 1 we again see divergence.
- This is because stable, or convergent solutions yielding a valid eigenfunction only exist for discrete energies.



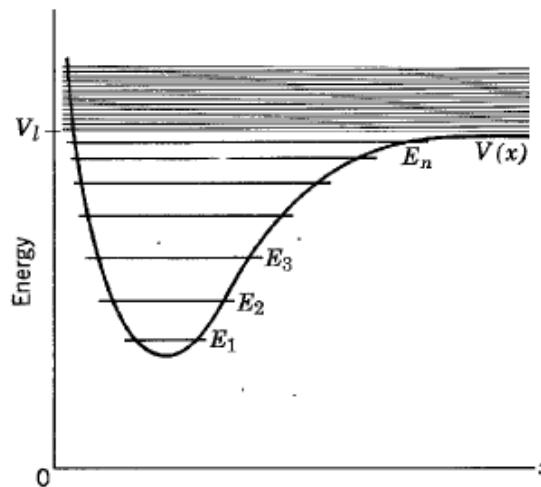
Qualitative Quantisation

In general, for bound states, there will be a number of allowed values of total energy, E_1, E_2, E_3, \dots that yield valid eigenfunctions $\psi_1, \psi_2, \psi_3, \dots$. The form of the three lowest eigenfunctions for our molecular potential are shown below. Note that for many realistic potentials the **number of bound state solutions is finite**.



We can see from this two very important properties of **any bound state** solution of the TISE for a potential with a minimum.

1. For an allowed energy E_n the eigenfunction has $n - 1$ nodes.
2. $\left| \frac{d^2\psi_n}{dx^2} \right| \propto |V(x) - E|$. This is just a fancy way of stating the curvature is greater for larger differences in the potential and total energies of the particle.

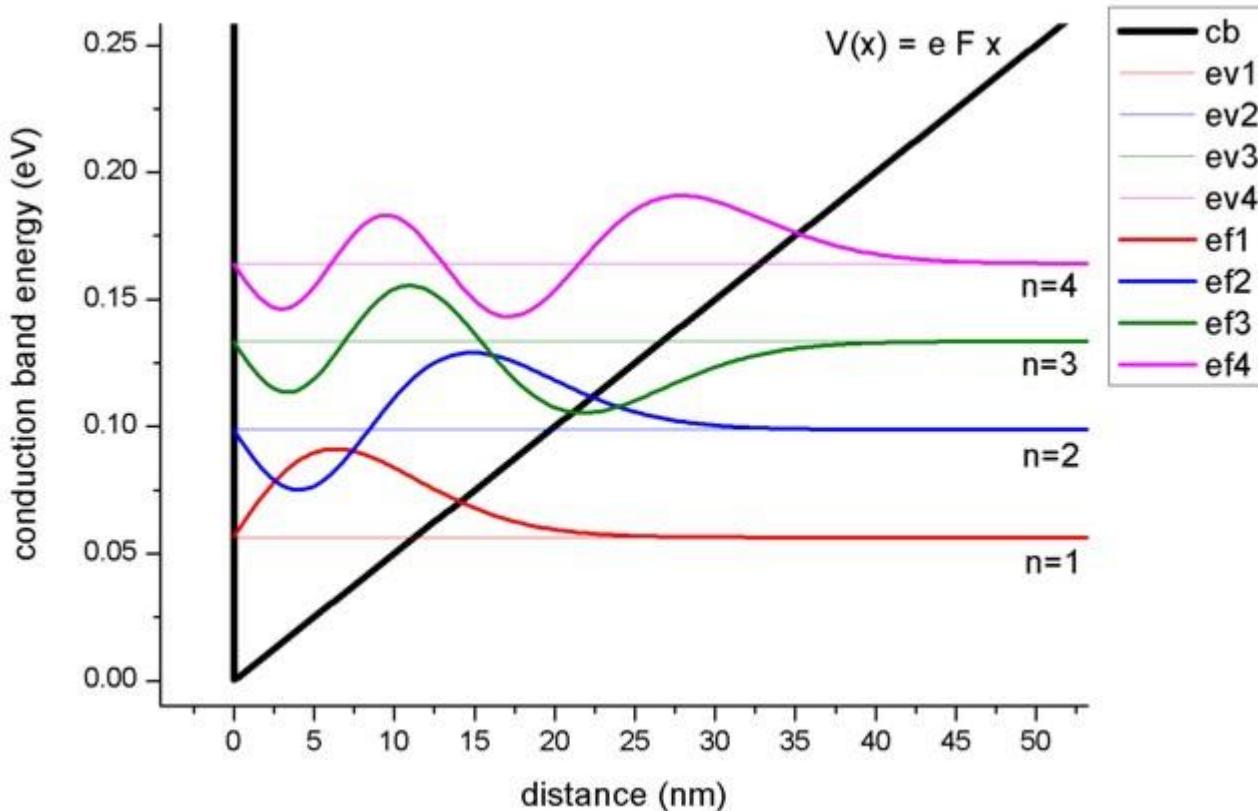


What about unbound states?

For the molecular potential as x increases the potential tends to a limiting value V_l . This is typically where the value of zero potential is assigned.

If a particle has total energy $E > V_l$ it is considered to be a free particle. As $x \rightarrow \infty$, $V(x) - E$ is always negative so the eigenfunction will always curve towards the x-axis (i.e. $\psi(x) = 0$) and is a stable oscillatory function. **Thus stable solutions exist for all values of E !** These states are described as forming a continuum of states.

Quick Example, The Triangular Potential



A common way to help remember, qualitatively, how eigenfunctions look is that the 'de Broglie wavelength' is shorter, when the energy above the potential is greater.

Zero Potential

Let's begin our look at quantitative solutions with the simplest potential possible, $V(x) = 0$, i.e. a zero potential everywhere. The TISE then becomes;

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

Since the potential is purely a function of x the total wavefunction will of course be;

$$\Psi(x, t) = \psi(x)e^{-iEt/\hbar}$$

For any solution the particle will be free, and solutions will exist for any value of E . Now we've already seen that the free particle wavefunction is, for a particle travelling in the positive x-direction;

$$\Psi(x, t) = e^{i(kx - \omega t)} = e^{ikx}e^{-i\omega t}$$

From the de Broglie Einstein relations;

$$k = \frac{p}{\hbar} = \frac{\sqrt{2mE}}{\hbar} \quad \omega = \frac{E}{\hbar}$$

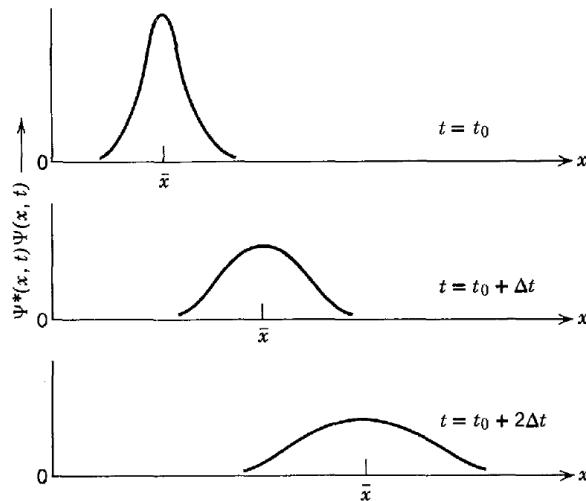
Hence the eigenfunction is given by

$$\psi(x) = e^{ikx}$$

Zero Potential Some Properties

Realistic Free Particle Representation

A plane wave description for a free particle is an idealisation. For certain situations it is reasonably accurate, for example in modelling the constant stream of monoenergetic protons from a particle accelerator. However a more realistic picture is achieved using a wavepacket.



Left: Probability density of a wavepacket describing a free particle moving at a constant velocity in a zero potential.

To produce such a wave packet requires more complicated mathematics since a large number of sinusoids with slightly varying wavenumbers (or energies) must be summed.

Notice that even for a zero potential the wavepacket ‘spreads’ in space as it propagates. This is an inherent property of waves and a consequence of the uncertainty principle.

If the potential is very slowly varying, i.e. it is essentially constant over a de Broglie wavelength then the group velocity will slowly change. Starting from the Schrödinger equation it can be shown that;

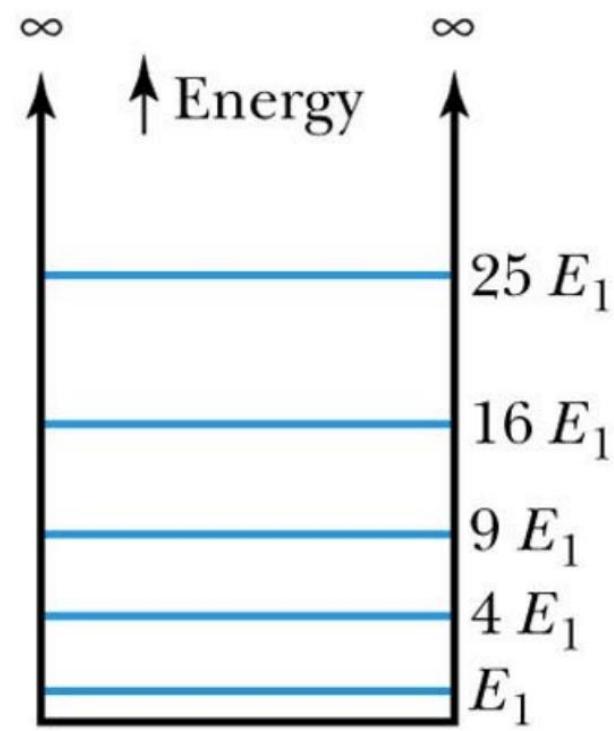
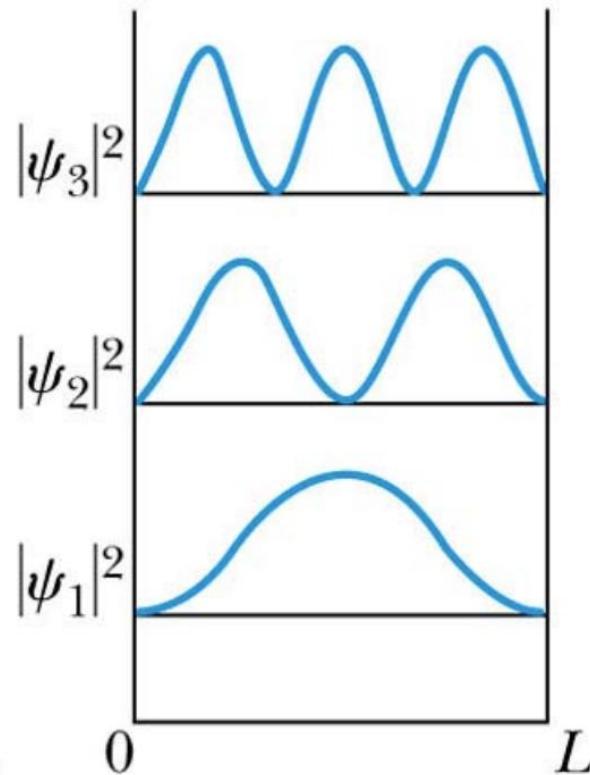
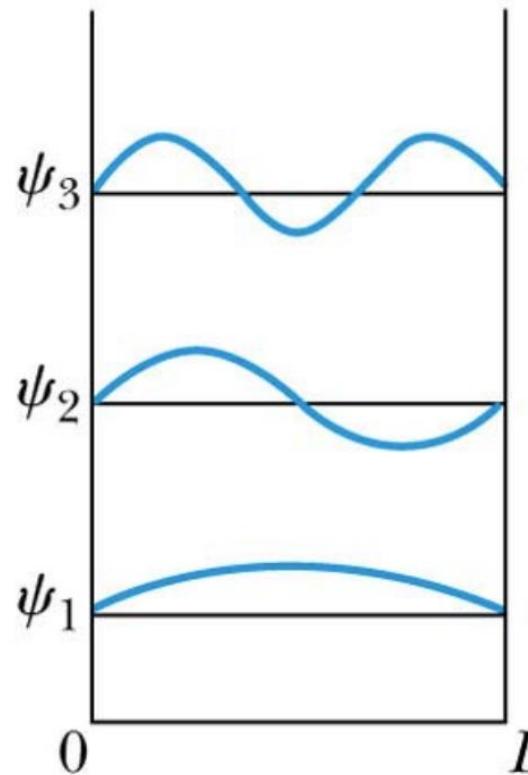
$$\frac{d^2\langle x \rangle}{dt^2} = -\frac{\frac{d\langle V \rangle}{dx}}{m} = \frac{\bar{F}}{m}$$

i.e. that on average a free particle’s behaviour is consistent with Newton’s 2nd law! The Schrödinger equation is the microscopic equivalent of Newton’s law, and in the macroscopic limit is consistent with Newton.

PHY2001– Lecture 13

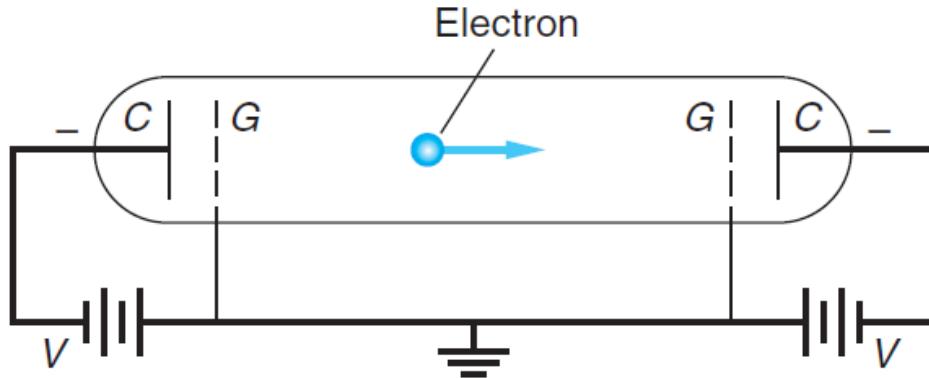
Learning Outcomes

- Solving TISE for
 - Infinite Square Well (Eis 6-8 and Tip 6-2)
 - For example May2020 Q4 & 12

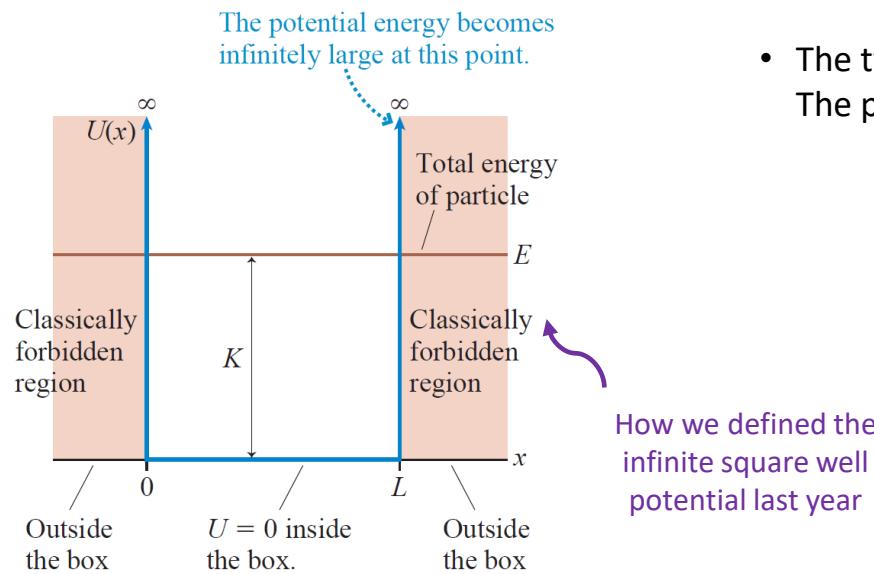


Infinite Square Well

- Now let's move onto a slightly more complicated potential, the infinite square well.
- Idealised situation – good approximation of an electron trap or the motion of an electron in metal.



- The electron is trapped between the potentials formed by the grid anodes, G and cathodes at C.
- By reducing the separation distance between C & G, and increasing the potential difference V , we can approximate an infinite square well potential.



- The typical form of this potential is shown on the left. The potential is defined as;

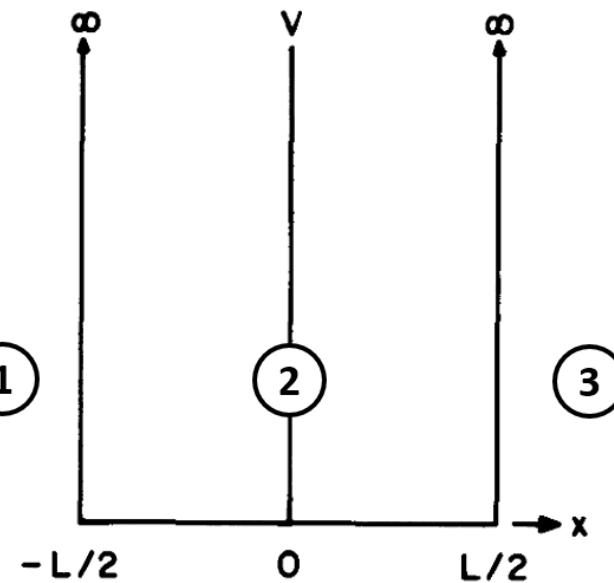
$$V(x) = 0 \quad 0 \leq x \leq L$$

$$V(x) = \infty \quad x < 0 \text{ & } x > L$$

How we defined the infinite square well potential last year

Solving the TISE for Infinite Square Well

- First step in solving the TISE is to define a potential, then we must state the corresponding boundary conditions.
- Where the potential is infinite there is zero probability that the particle can be found, thus the eigenfunction must be zero there and we only need to solve Schrödinger inside the well.
- Let's define the potential slightly differently this year;



- Our boundary conditions are then;

$$\psi(-L/2) = 0 \quad \& \quad \psi(L/2) = 0$$

- Now $\frac{d\psi}{dx}$ is not continuous for this potential, however the condition can be relaxed since $V(x) = \infty$ in regions 1 and 3.
- 2nd order linear diff. eqn so the general solution will consist of two independent solutions, i.e.

$$\psi(x) = A\psi_1(x) + B\psi_2(x)$$

- We know that for bound states, the eigenfunctions will correspond to discrete energies and have a similar form to a sinusoid, so we make a guess for the general solution;

A, B , and k are constants to be determined.

$$\psi(x) = A \sin kx + B \cos kx$$

Solving the TISE for Infinite Square Well cont.

Guess Solution

$$\psi(x) = A \sin kx + B \cos kx$$

In the well the potential is zero so TISE is;

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

Plugging guess solution into TISE

$$-\frac{\hbar^2}{2m} - k^2(A \sin kx + B \cos kx) = E(A \sin kx + B \cos kx)$$

Equal if

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

Now apply boundary conditions

$$\psi\left(-\frac{L}{2}\right) = -A \sin \frac{kL}{2} + B \cos \frac{kL}{2} = 0 \quad \mathbf{1}$$

$$\psi\left(+\frac{L}{2}\right) = A \sin \frac{kL}{2} - B \cos \frac{kL}{2} = 0 \quad \mathbf{2}$$

Remember
 $-\sin x = \sin x$
 $\cos x = \cos -x$

These must both be satisfied simultaneously. Let's simplify a little by adding and subtracting these to write two new, but equivalent, equations representing our boundary conditions;

$$2A \sin \frac{kL}{2} = 0 \quad 2B \cos \frac{kL}{2} = 0$$

No value of k simultaneous makes both zero.

$A = B = 0$ is not a valid approach as then the particle doesn't exist anywhere.

Instead we find two sets of solutions by setting either

$$A = 0 \quad \& \quad \sin \frac{kL}{2} = 0$$

$$\text{or} \quad B = 0 \quad \& \quad \cos \frac{kL}{2} = 0$$

Solving the TISE for Infinite Square Well cont.

Two sets of solutions are then

But

So (think of sin and cosine plots)

$$\psi(x) = A \sin kx$$

$$\sin \frac{kL}{2} = 0$$

$$\frac{kL}{2} = \pi, 2\pi, 3\pi, \dots$$

$$k = \frac{n\pi}{L}$$

$$n = 2, 4, 6, \dots$$

This set of solutions has **ODD parity**

$$\rightarrow \boxed{\psi(x) = A \sin\left(\frac{n\pi}{L}x\right)}$$

$$\psi(x) = B \cos kx$$

$$\cos \frac{kL}{2} = 0$$

$$\frac{kL}{2} = \frac{\pi}{2}, \frac{3\pi}{2}, \frac{5\pi}{2}, \dots$$

$$k = \frac{n\pi}{L}$$

$$n = 1, 3, 5, \dots$$

This set has **EVEN parity**

$$\rightarrow \boxed{\psi(x) = B \cos\left(\frac{n\pi}{L}x\right)}$$

From symmetry **P(x) and P(-x) must be equal**, which is only true if $\psi(x) = \psi(-x)$, i.e., an even, or symmetric function, or $\psi(x) = -\psi(-x)$, i.e. an odd (or anti-symmetric) function.

Recall that for even functions, $f(x) = f(-x)$, while for odd functions $f(x) = -f(-x)$

A parity operation if a going from $x \rightarrow -x$

The parity of an eigenfunction influences a number of observables, such as the probability of optical transitions between states.

Energies

For all values of n ;

$$k = \frac{n\pi}{L}$$

And we saw that k is given by

$$k = \frac{\sqrt{2mE}}{\hbar}$$

Which gives our discrete energies (or eigenvalues)

$$\boxed{E = \frac{\hbar^2}{8mL^2} n^2 \quad n = 1, 2, 3, \dots}$$

Infinite Square Well Cont.

Normalisation

$$\int_{-L/2}^{L/2} \psi^* \psi dx = 1$$

Odd solutions

$$\int_{-L/2}^{L/2} A^2 \sin^2 \left(\frac{n\pi}{L} x \right) dx = 1 \quad A = \sqrt{\frac{2}{L}}$$

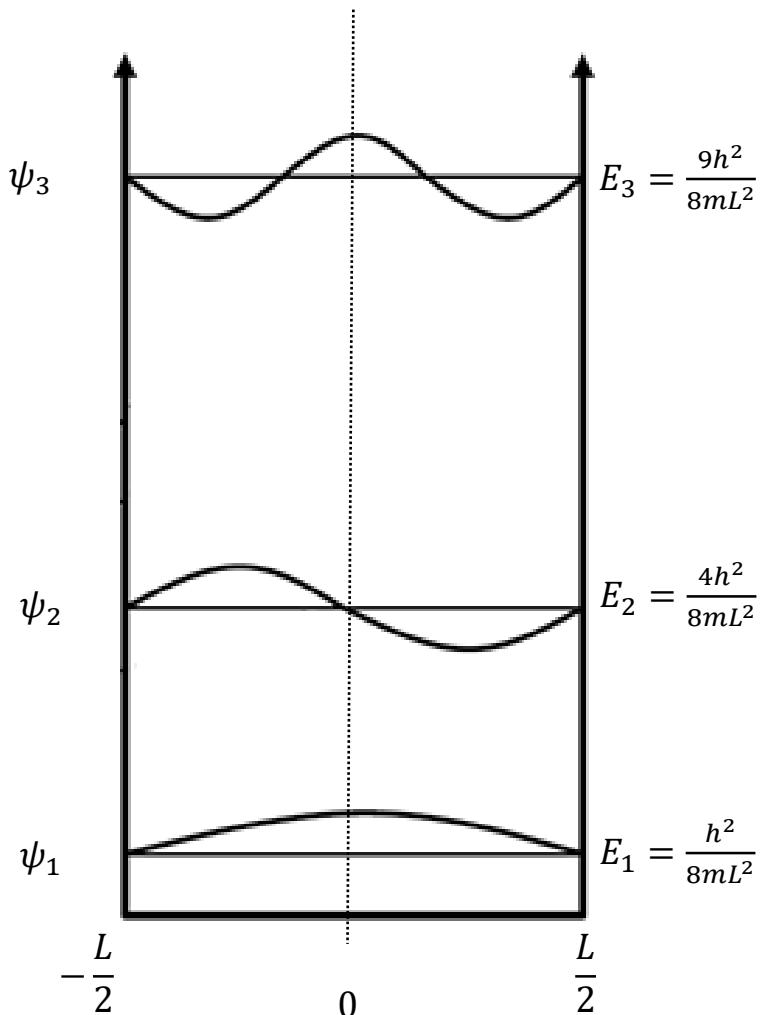
→ $\psi(x) = \sqrt{2/L} \sin \left(\frac{n\pi}{L} x \right)$ $n = 2, 4, 6, \dots$

Even solutions

$$\int_{-L/2}^{L/2} B^2 \cos^2 \left(\frac{n\pi}{L} x \right) dx = 1 \rightarrow \quad B = \sqrt{\frac{2}{L}}$$

→ $\psi(x) = \sqrt{2/L} \cos \left(\frac{n\pi}{L} x \right)$ $n = 1, 3, 5, \dots$

Eigenfunctions have $(n - 1)$ nodes.



Average Position

$$\langle x \rangle = \int_{-L/2}^{L/2} \psi^* x \psi \, dx$$

For the odd eigenfunctions we have

$$\langle x \rangle = \int_{-L/2}^{L/2} x \cdot \sin^2\left(\frac{n\pi x}{L}\right) \, dx$$

The integrand is the product of an even and odd function, so will be zero;

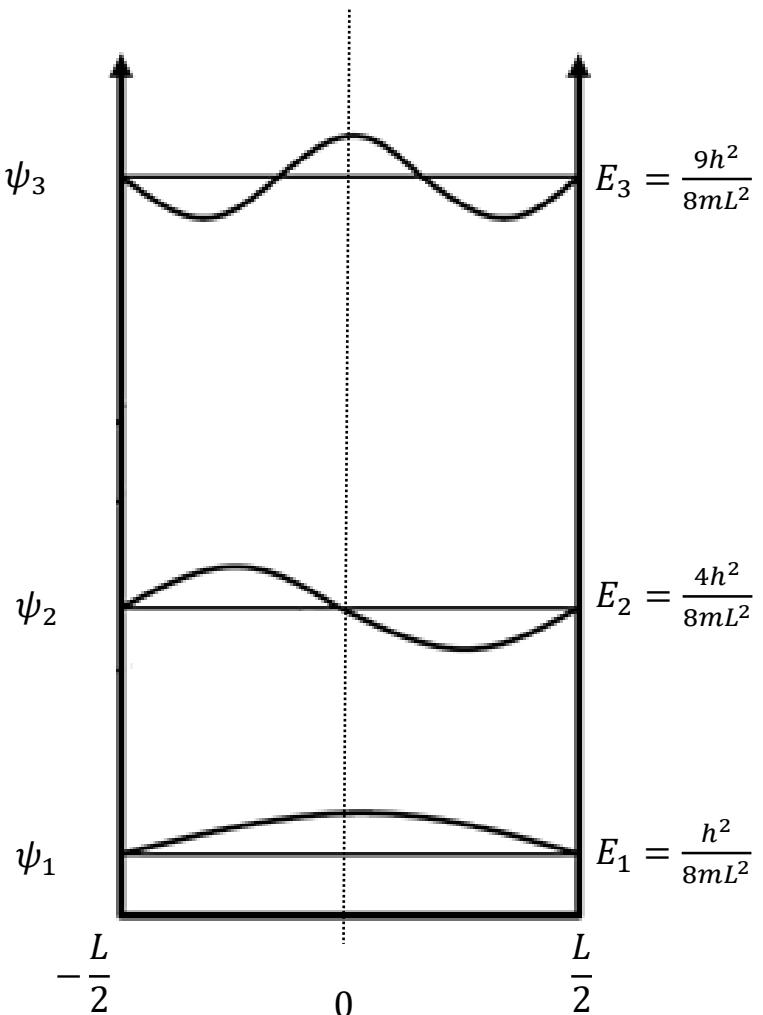
$$\langle x \rangle = 0$$

This will also be true for the even functions! You can see there is some intuition here as the eigenfunctions are symmetrical about $x = 0$

This will also lead to $\langle p \rangle = 0$ for all states.

Note: This seems particularly strange for the odd functions, as the average position also corresponds to one where there is zero probability of finding the particle!

Eigenfunctions have $(n - 1)$ nodes.



Total Wavefunction

For the odd eigenfunctions we have

$$\Psi(x, t) = \sqrt{2/L} \sin(kx)e^{-i\omega t} \quad k = \frac{n\pi}{L}$$

But

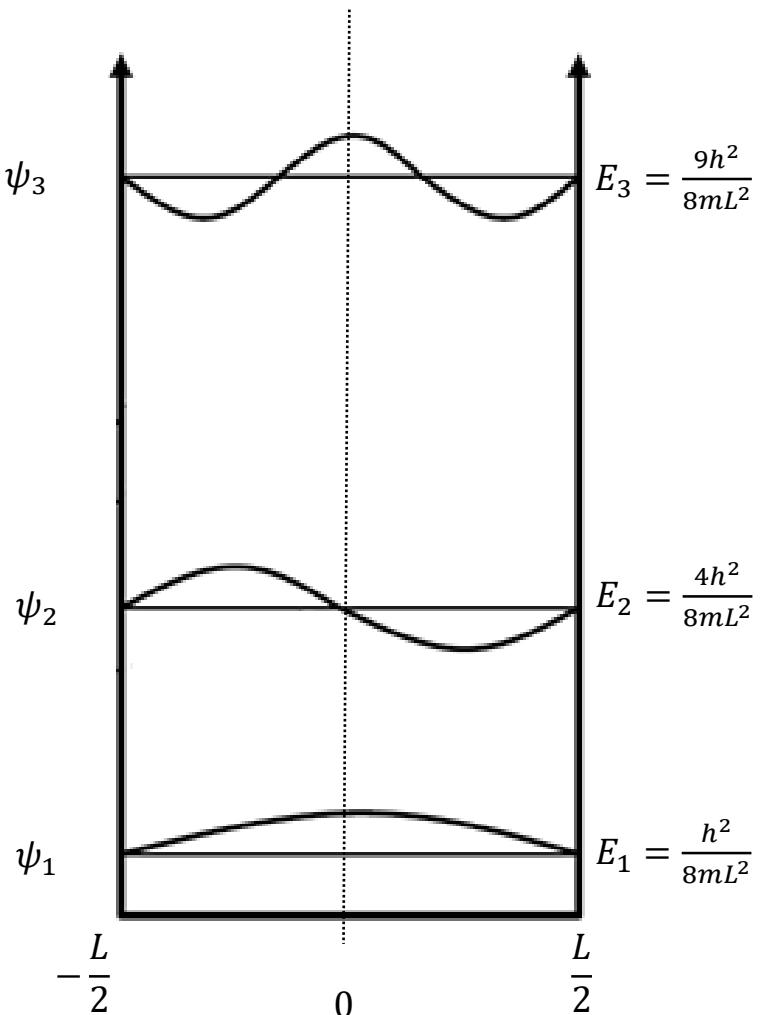
$$\omega = \frac{E}{\hbar}$$

$$\sin(kx) = \frac{(e^{ikx} - e^{-ikx})}{2i}$$

$$\Psi(x, t) = \frac{1}{2i} \sqrt{2/L} (e^{i(kx-\omega t)} - e^{i(kx+\omega t)})$$

These are two plane waves travelling in opposite directions. Our eigenfunctions are standing waves, compare this with standing waves on a string

Eigenfunctions have $(n - 1)$ nodes.



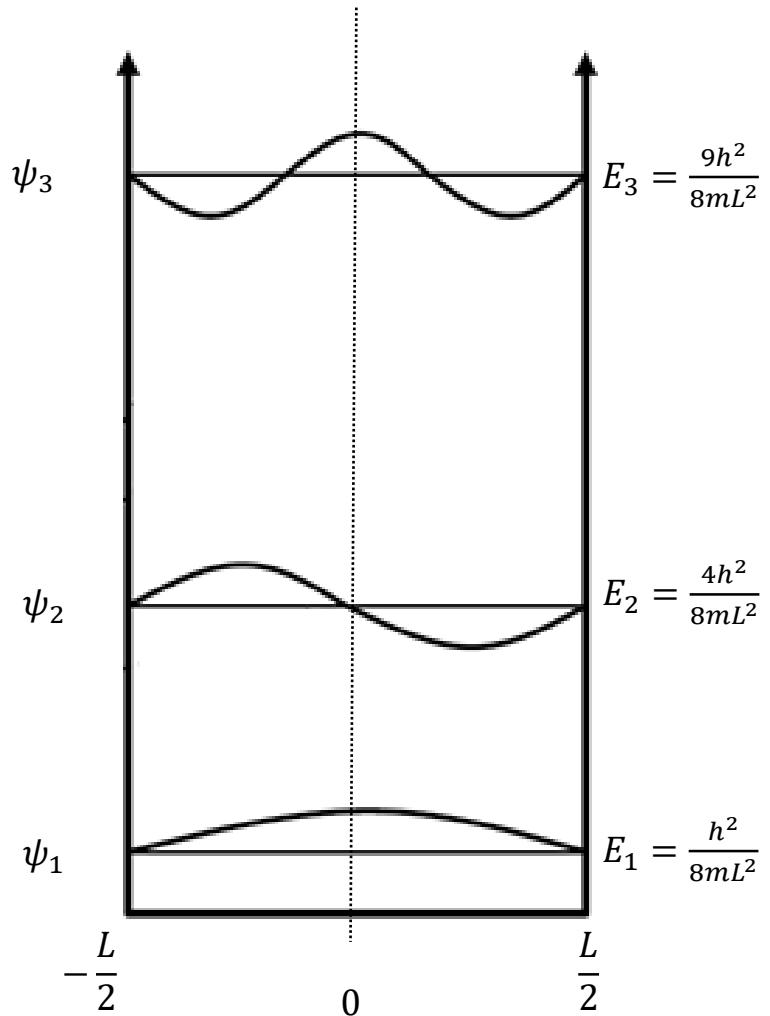
Summary

For 1D infinite well, width L , centred at $x = 0$

Odd solutions

$$\psi(x) = \sqrt{2/L} \sin\left(\frac{n\pi}{L}x\right)$$

$n = 2, 4, 6, \dots$



Even solutions

$$\psi(x) = \sqrt{2/L} \cos\left(\frac{n\pi}{L}x\right)$$

$n = 1, 3, 5, \dots$

Energies

$$E = \frac{\hbar^2}{8mL^2} n^2$$

$n = 1, 2, 3, \dots$

Total Wavefunction

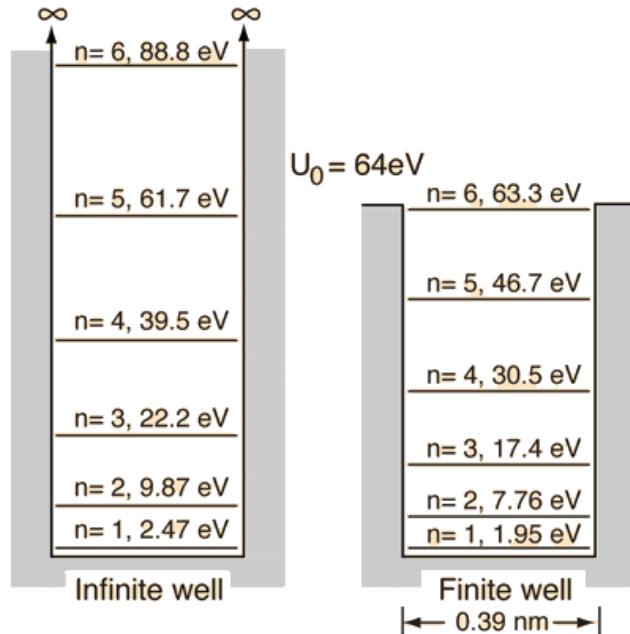
$$\Psi(x, t) = \frac{1}{2i} \sqrt{2/L} (e^{i(kx - \omega t)} - e^{-i(kx - \omega t)})$$

PHY2001– Lecture 14

Learning Outcomes

- Solving TISE for
 - Finite Square Well (Eis 6-2)
 - E.g. May2018 Q11
- Solving Equations graphically.

(Eis Appendix H if you're curious how to do this analytically)



*How to Learn
Transcendental
Equations
by Yourself?*



Finite Square Well

- From our qualitative discussion we can guess the rough shape of the eigenfunctions. Notice that there is a finite probability of finding the particle outside the well!
- In region 1, we will have the same solutions as before.

- For **EVEN** eigenfunctions

$$\psi = B \cos kx$$

- For **ODD** eigenfunctions

$$\psi = A \sin kx \quad k^2 = \frac{2mE}{\hbar^2}$$

- Remember solutions must be even or odd parity from symmetry.

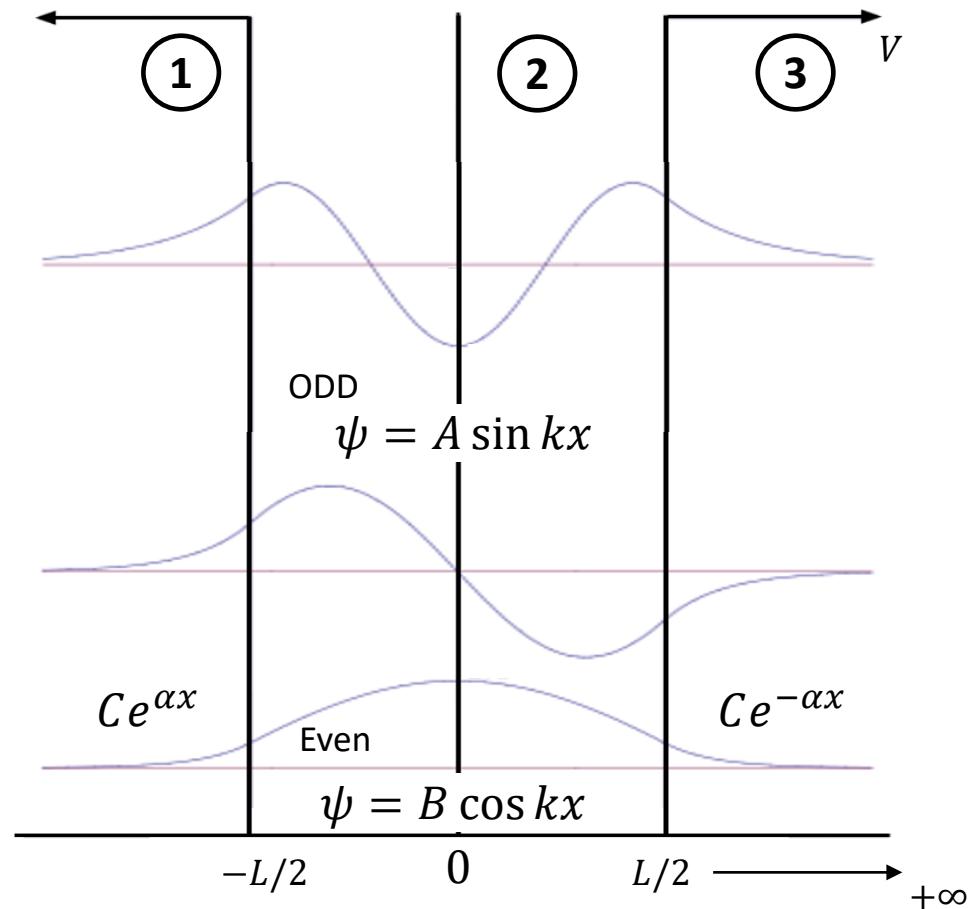
- A parity operation is one which changes 'x' to '-x'

- In regions 1&2 we will 'guess' that the general solution is;

$$\psi = Ce^{\alpha x} + De^{-\alpha x} \quad \alpha^2 = \frac{2m(V - E)}{\hbar^2}$$

- From our condition that $\psi(x) \rightarrow 0$ as $x \rightarrow \pm\infty$ we can see that in region 1 $D = 0$, and in region 3 $C = 0$.

- From symmetry again, in region 3 we can see that $D = C$



Those Guesses

- We've mentioned that we make guesses at the solutions to Schrödinger for these potentials.
- We'll briefly mention here how to actually solve the Schrodinger equation in these regions and obtain the general solutions.
- In region 2, $V(x) = 0$, and the TISE is;

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

- Let's substitute in $k^2 = 2mE/\hbar^2$

$$\frac{d^2\psi(x)}{dx^2} = -k^2 \psi(x)$$

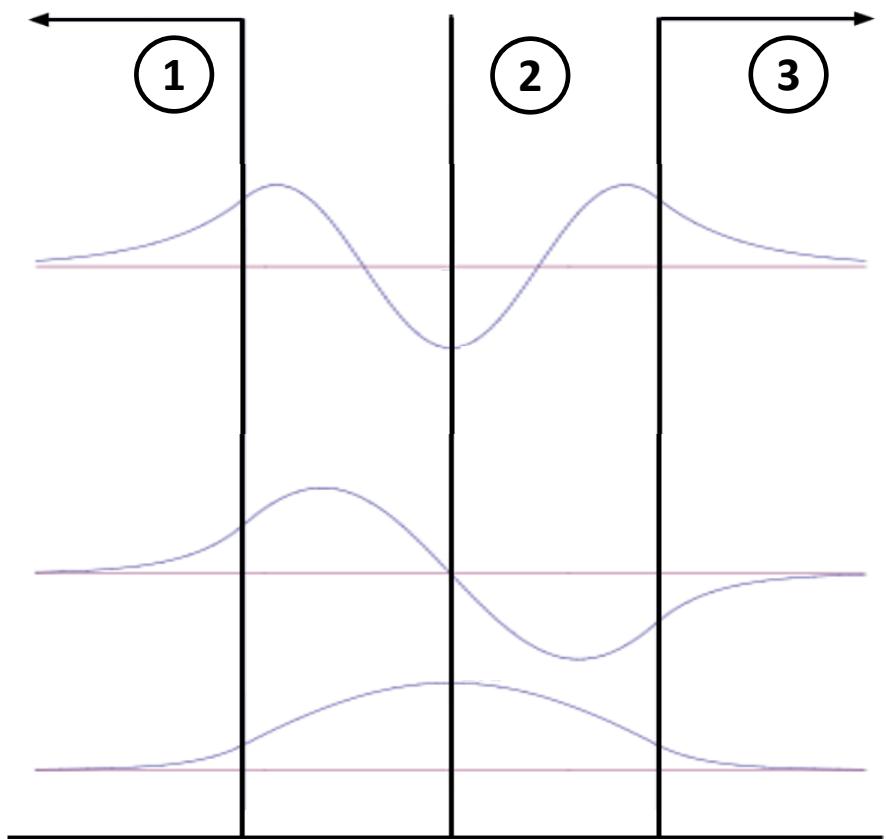
- In regions 1 & 3 $V(x) = V$, and the TISE is

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

- Let's substitute in $\alpha^2 = 2m(V - E)/\hbar^2$

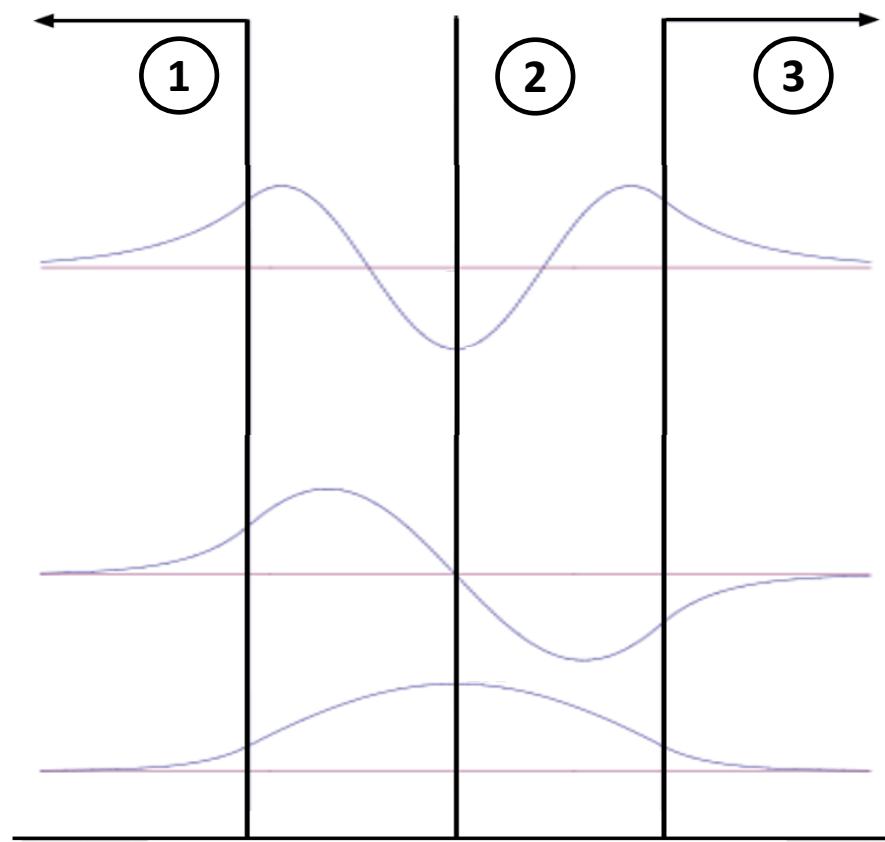
$$\frac{d^2\psi(x)}{dx^2} = \alpha^2 \psi(x)$$

These are 2nd order, homogenous differential equations and can be solved using standard techniques, see [here](#) for example.



Finite Square Well Degeneracy

- Notice that Both $\psi(x)$ and $-\psi(x)$ here are valid solutions to the TISE
- Remember the wavefunction is unobservable! The wavefunctions are said to be degenerate, since they are different solutions for the same eigenvalue, i.e. energy.
- Note that while the wavefunction is unobservable we might think it makes no difference whether $\psi(x)$ is positive or negative.
- Since ψ , like any other wave, obeys the superposition principle this actually has important consequences for molecular bonding and band theory in solids.



Finite Square Well cont.

- Let's find the complete solutions, and most importantly what the corresponding energies are.
- To do this we must use the boundary conditions that ψ , and ψ' are single valued and continuous;
- For **Even** eigenfunctions, at the boundaries between I & II or equivalently II and III,

$$\psi \rightarrow C e^{-\alpha \frac{L}{2}} = B \cos k \frac{L}{2} \quad 1$$

$$\psi' \rightarrow \alpha C e^{-\alpha \frac{L}{2}} = k B \sin k \frac{L}{2} \quad 2$$

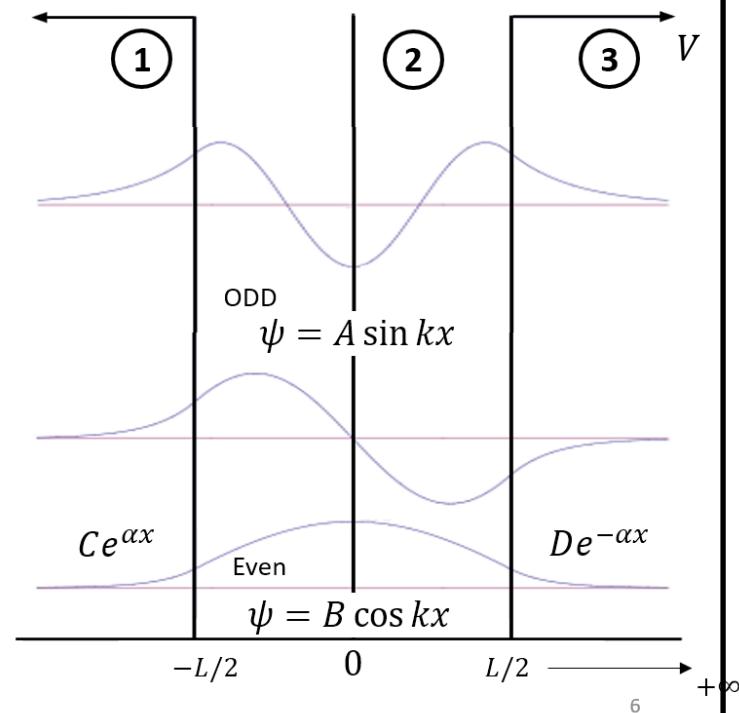
- Dividing these **2** by **1**;

$$\alpha = k \tan k \frac{L}{2} \quad \text{where } k^2 = \frac{2mE}{\hbar^2} \quad \alpha^2 = \frac{2m(V - E)}{\hbar^2}$$

- Our goal is to determine E ! We could do this if we knew either k , or α , since everything else is either a physical constant or something we define (e.g. V or L). We can obtain a second equation for k and α ;

$$\alpha^2 + k^2 = \frac{2mV}{\hbar^2}$$

- Notice that this pretty similar to the equation of a circle.
- Now we have reduced everything down to two equations and two unknowns. We can then solve for either α or k , and thus obtain E . But these equations cannot be easily solved analytically*, and are called transcendental equations. Instead let's use graphical methods to solve them.



*If you are curious to see how, or perhaps just masochistic, an approach to solving this analytically is given in Eisberg Appendix H

Finite Square Well Graphical Solution

- We have

$$\alpha = k \tan k \frac{L}{2} \quad \text{where } k^2 = \frac{2mE}{\hbar^2} \quad \alpha^2 = \frac{2m(V - E)}{\hbar^2}$$

and

$$\alpha^2 + k^2 = \frac{2mV}{\hbar^2}$$

- We're going to solve these graphically so let's make the equations a little easier to plot by making a substitution that $y = \frac{\alpha L}{2}$, $x = \frac{kL}{2}$.

$$\alpha = k \tan k \frac{L}{2} \rightarrow \frac{\alpha L}{2} = \frac{kL}{2} \tan k \frac{L}{2} \rightarrow y = x \tan x$$

$$\alpha^2 + k^2 = \frac{2mV}{\hbar^2} \rightarrow \left(\frac{\alpha L}{2}\right)^2 + \left(\frac{kL}{2}\right)^2 = \frac{mVL^2}{2\hbar^2} \rightarrow y^2 + x^2 = r^2 \quad r = \sqrt{\frac{mVL^2}{2\hbar^2}}$$

- Let's plot these. You could do this in excel of course, however, a useful tool is a free online graphing calculator called [Desmos](#).

Finite Square Well Graphical Solution cont.

- You can access this graph [here](#).
- Intersections of the red and green curves give the values of x , & y .
- Can easily then determine E via $E(x) = \frac{\hbar^2\pi^2}{2mL^2} \left(\frac{2x}{\pi}\right)^2$
- The radius of the circle is $\propto V^{\frac{1}{2}}$
- The x-axis is $\propto E^{\frac{1}{2}}$
- The dashed lines represent the asymptotic value of $y = x \tan x$ and also correspond to the eigenvalues (energies) of the infinite square well. Notice that the circle will only intersect these when $r \rightarrow \infty$, i.e. when $V \rightarrow \infty$

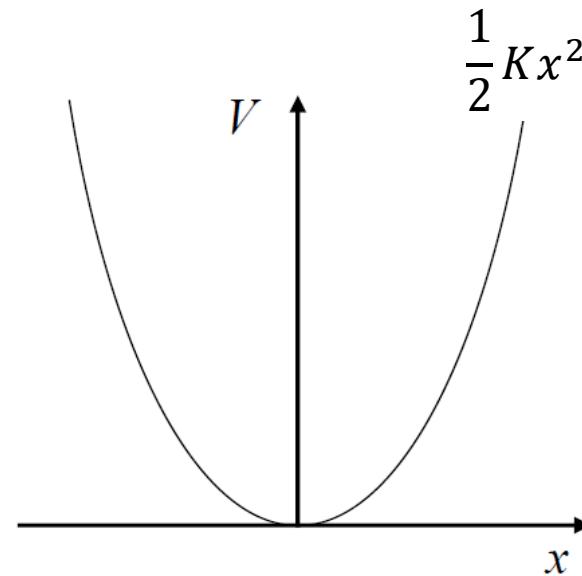
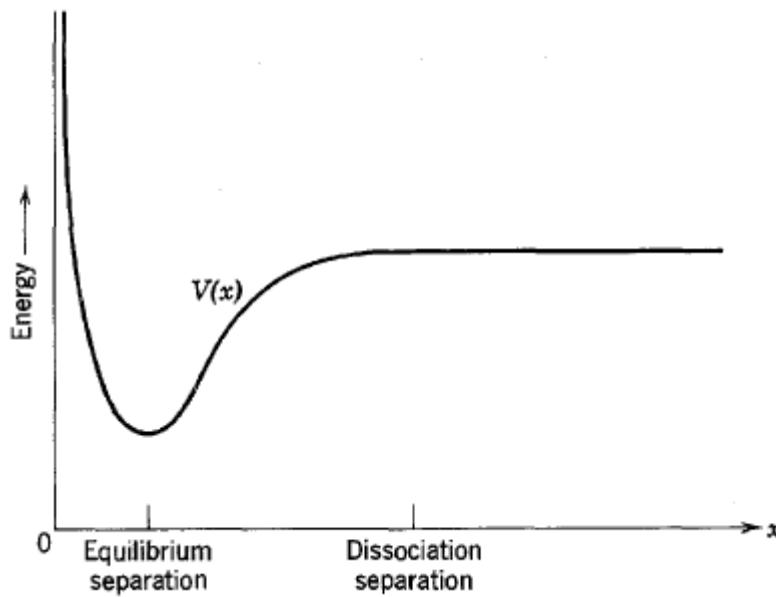
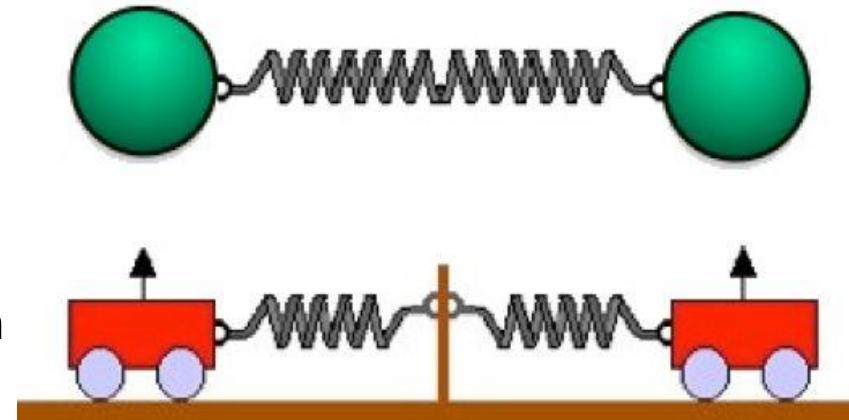


- Thus for a finite well the **energy levels are shifted down compared to an infinite well**.
- **There are a finite number of bound states or eigenvalues** which reduce as the potential reduces.
- No matter how small the radius of the red circle is, there will **always be at least one point of intersection**, i.e. for any V there is at least one bound level. This state is always even, and is the lowest energy state of the system.
- Remember we have found the eigenvalues for even solutions. This gave $\alpha = x \tan x$, and asymptotes at $x = \frac{\pi}{2}, \frac{3\pi}{2}, \frac{5\pi}{2}, \dots$
- For odd solutions we would find that $y = -x \cot x$, and asymptotes at $x = \pi, 2\pi, 3\pi, \dots$ (kind of in between these states). Have a go at adding this function to the Desmos plot.

PHY2001– Lecture 15

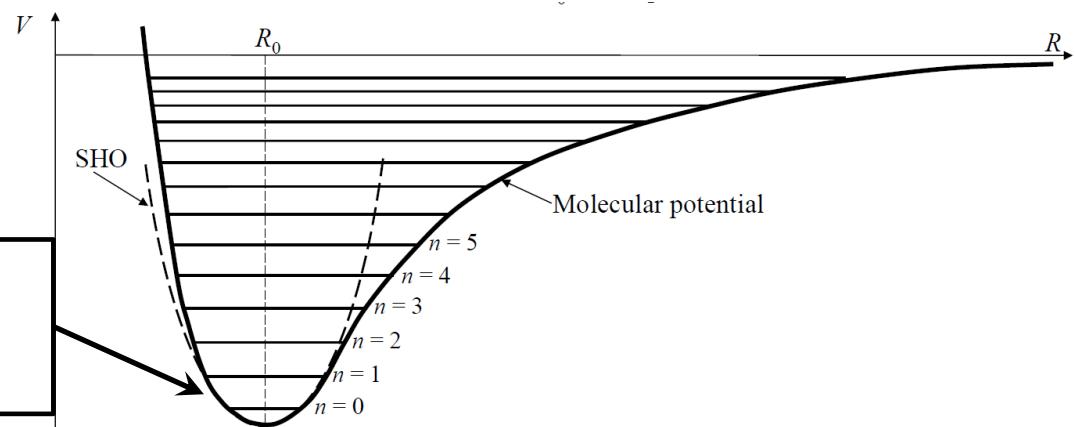
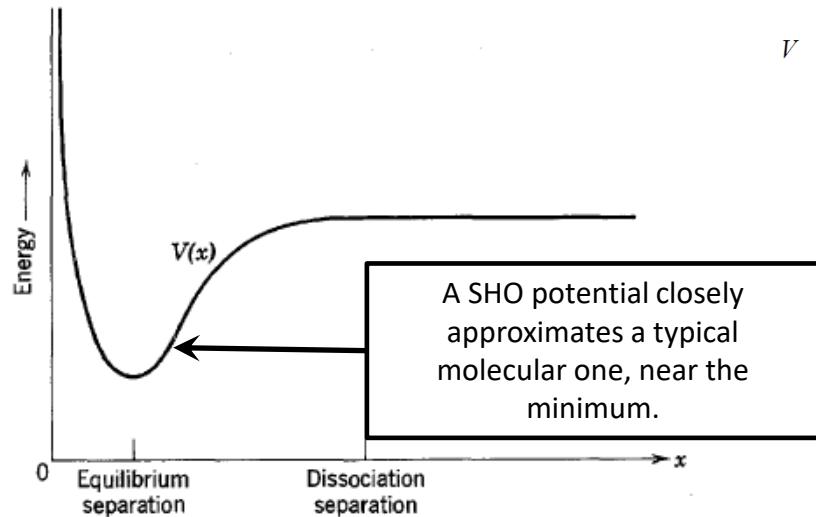
Learning Outcomes

- Solving TISE for
 - Simple Harmonic Oscillator (Eis 6-9 and Tip 6-5)
 - May2018/Aug2019 PP Question



Diatom Molecules

- Let's look at our molecular potential from Lecture 12 again.
- This represents the potential energy of two atoms in a diatomic molecule, separated by a distance r .
- The force is $F = -\frac{d}{dr}V(r)$
- At $r = r_0$ the force is zero and the atoms are at their equilibrium separation. If the atoms are pulled apart an attractive force is generated, if they are pushed together a repulsive force arises. (Of course as $r \rightarrow \infty$ the force is zero, and the molecule would dissociate into two free atoms).
- For small displacements there is thus a restoring force, similar to a mass on a string, and are well approximated by a Simple Harmonic Oscillator (SHO).
- Our goal then is to solve the TISE for this potential, and obtain energies for these *vibrational* states.
- These vibrational levels typically have energies of ~ 0.1 eV and (in addition to rotational energy levels) result in molecules exhibiting rich optical spectra in the infra-red region.



Solving TISE for SHO

- The first part in solving the TISE is always defining the potential of the system.
- In a SHO the restoring force is proportional to the displacement

$$F = -Kx$$

Here K is the spring constant, not the wavenumber!

- We assume that the work done by this force in displacing the atoms from their equilibrium positions to x is;

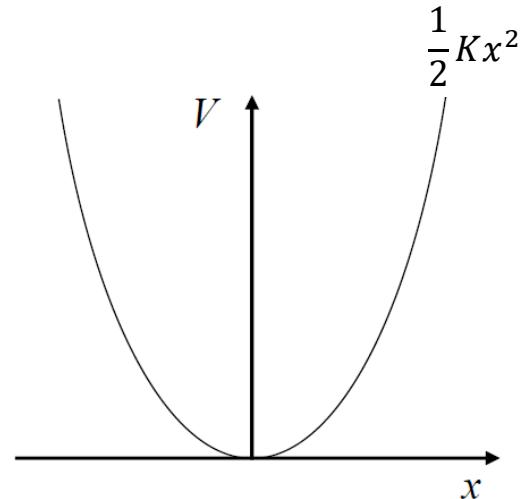
$$V(x) = -W = - \int_0^x F dx = \int_0^x Kx dx = \frac{1}{2} Kx^2$$

- Recall from PHY1001 that in simple harmonic motion the oscillation frequency is given by;

$$\omega = \left(\frac{K}{m}\right)^{1/2} \rightarrow V(x) = \frac{1}{2} m\omega^2 x^2$$

- The TISE for this system (**for all x**) is then

$$-\frac{d^2\psi}{dx^2} + \left(\frac{1}{2} m\omega^2 x^2 - E\right)\psi = 0$$

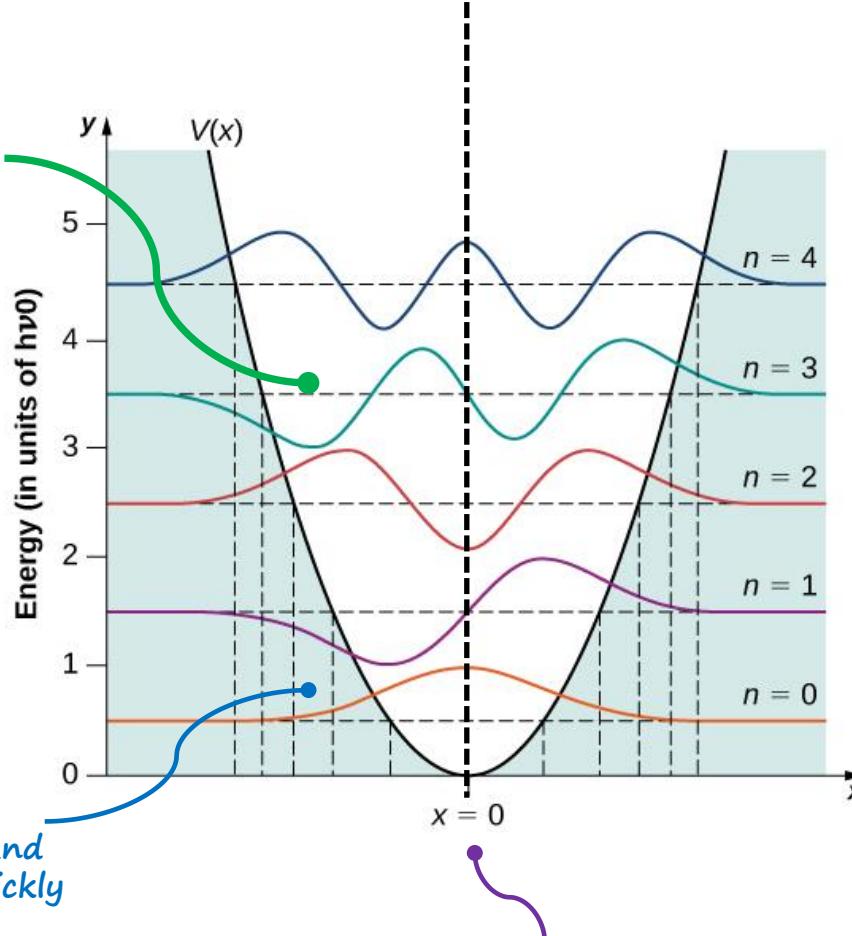


- This is still a 2nd order linear differential equation, however the potential now is a non-linear function of x. This makes this a much more complicated differential equation to solve*.
- Instead we will ‘guess’ the solution again, check it is a solution to the TISE and determine the lowest energy state. But before we do that let’s look qualitatively at the solutions we might expect.

*Again for those curious, the procedures for solving this are outlined in Eisberg Appendix I

Qualitative Solutions

As $|V - E|$ decreases the de Broglie wavelength increases.



In this region the $V>E$ and the eigenfunction will quickly decay to zero.

The potential is symmetric about $x=0$. Therefore the solutions will be even or odd

You might notice some differences here.

1. The lowest state is corresponds to $n = 0$
2. The energy levels are equally spaced

We'll come back to this shortly.

Quantitative Solutions

Note: This is very similar to Aug2019 & May 2018 papers

- Our TISE to solve is
$$-\frac{d^2\psi}{dx^2} + \left(\frac{1}{2}m\omega^2x^2 - E\right)\psi = 0$$
- Since our solution, will need to generate an x^2 term when differentiated twice. Our guess at a possible solution is;

$$\psi = A \exp(-\gamma x^2)$$
$$\frac{d^2\psi}{dx^2} = -2A\gamma \exp(-\gamma x^2) + 4A\gamma^2 x^2 \exp(-\gamma x^2)$$

Using chain rule,
substitution and
product rule.

- Substituting this into the TISE and doing some algebra leads to;

$$\frac{2mE}{\hbar^2} - 2\gamma + 4\gamma^2 x^2 - \left(\frac{m\omega}{\hbar}\right)^2 x^2 = 0$$

Constant terms x^2 terms

- For this equation to be true, constant and x^2 terms must independently equal zero!

Quantitative Solutions cont.

$$x^2 \text{ terms} \quad 4\gamma^2 - \left(\frac{m\omega}{\hbar}\right)^2 = 0$$

$$\rightarrow \gamma = \frac{m\omega}{2\hbar}$$

$$\text{Constant terms} \quad \frac{2mE}{\hbar^2} - 2\gamma = 0$$

$$\rightarrow E = \frac{1}{2} \hbar \omega$$

And the corresponding eigenfunction is

$$\psi = A \exp\left(-\frac{m\omega}{2\hbar} x^2\right)$$

$$\text{Normalising} \quad \int_{-\infty}^{\infty} \psi^* \psi = 1$$

$$\rightarrow A = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4}$$

Look up table of Integrals

$$\int_{-\infty}^{\infty} \exp(-kx^2) = \sqrt{\frac{\pi}{k}}$$

Quantitative Solutions Ground State

- This solution corresponds to the lowest energy. This is also called the ground state*.

$$E_0 = \frac{1}{2} \hbar \omega \quad \psi_0 = \left(\frac{m\omega}{\pi\hbar} \right)^{1/4} \exp \left(-\frac{m\omega}{2\hbar} x^2 \right)$$

- Notice that this is a single solution. To obtain solutions for higher energy states is quite involved, so we will just state the general form of the solutions here.

$$\psi_n = C_n \exp \left(-\frac{m\omega}{2\hbar} x^2 \right) H_n \left(\sqrt{\frac{m\omega}{\hbar}} x \right)$$

- C_n is the normalisation constant.
- $H_n(x)$ is the *physicists* Hermite polynomial of order n - i.e. H_2 would correspond to a particular 2nd order polynomial in x .
- The eigenvalues for these solutions then leads to the relation;

$$E_n = \hbar\omega \left(\frac{1}{2} + n \right) \quad n = 0, 1, 2, \dots$$

- i.e. The energy levels are evenly spaced with $\Delta E = \hbar\omega$
- This is consistent with Planck's hypothesis that the vibrations in a cavity wall were quantised!

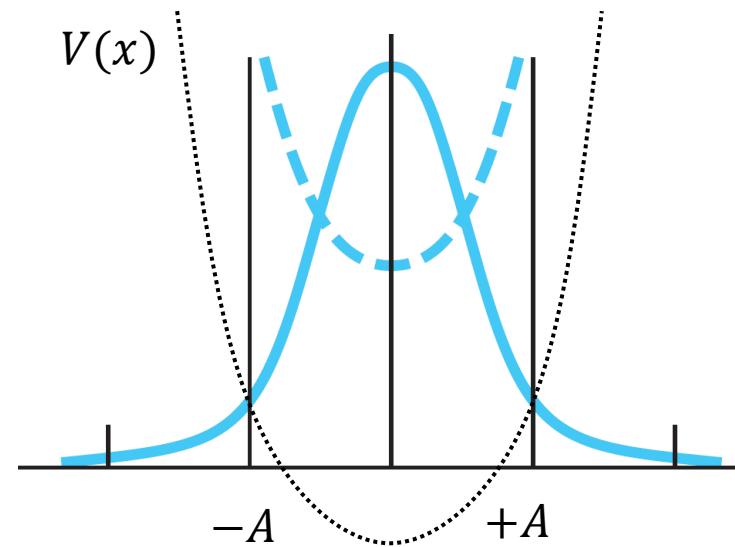
*(from the German 'grundlegend' for fundamental)

Classical Comparison

- Let's plot the ground state probability distribution as the solid line in the below figure.
- Notice that this is a **Gaussian distribution** given by;

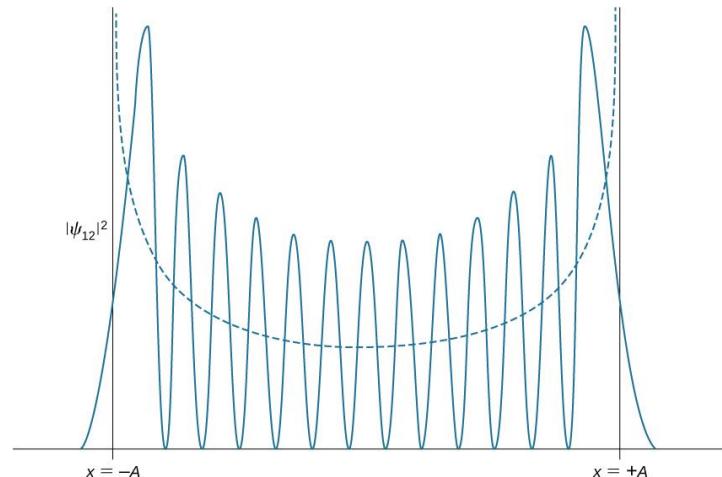
$$P(x) = \psi^* \psi = C_1^2 \exp\left(-\frac{m\omega}{\hbar} x^2\right)$$

- The dashed line is the corresponding classical probability distribution.
- The quantum mechanic differs in two significant ways;
 - There is a finite chance of the particle being found **beyond the classical turning point**.
 - Highest probability density is at the centre of the potential. The classical model predicts that the maximum probability is at the turning point and a minimum at the centre.



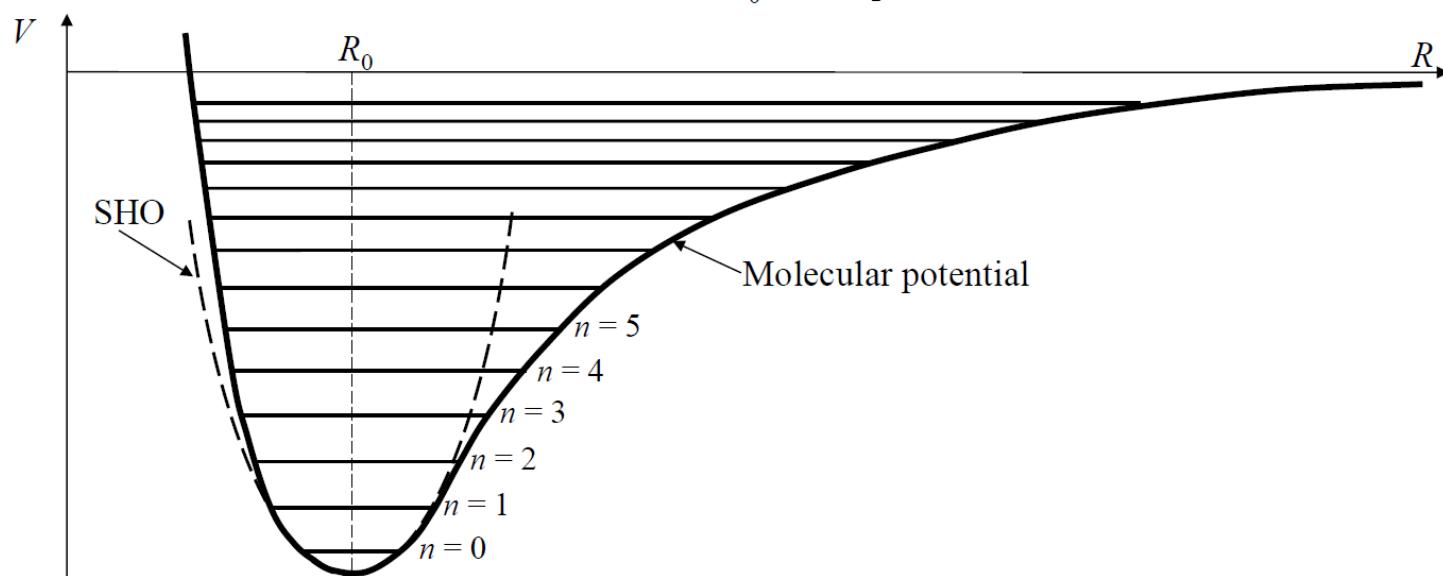
Correspondence Principle

- As the quantum number n increases we expect the quantum mechanical behaviour to approach that of a classical oscillator.
- On the right is the probability density for n=12. Notice that the average of the wavefunction is approaching the classical probability distribution.



Real Potential

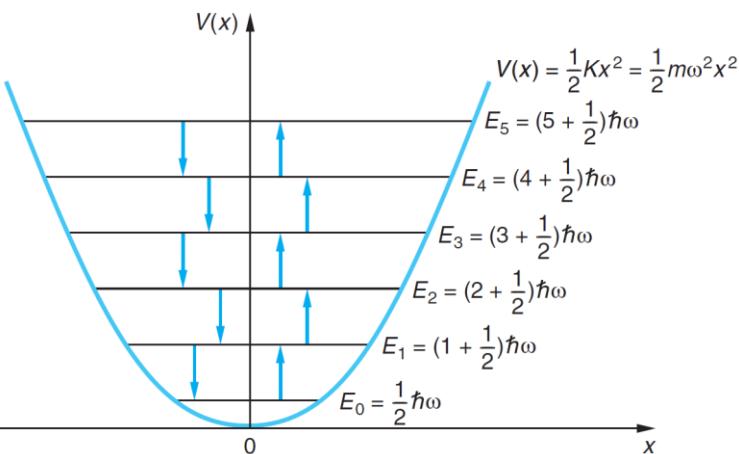
- Remember this is an approximation to the true diatomic potential.
- Is only really valid near the minimum of the potential energy function, i.e. for low values of n .
- In a real potential as n increases the curvature of the potential also decreases. This leads to the interesting effect that the energy levels become successively closer.
- Compare this behaviour to a square well (successively further apart) and a SHO (evenly spaced).



Transition Rules

- We've mentioned before that Schrödinger's theory is superior to the old Bohr theory in predicting the nature of emission and absorption spectra from atoms and molecules.
- We will not prove it here, but instead merely state that the Schrodinger theory suggests that for the SHO,

Transitions may only occur if the quantum number, n , of the final state is 1 less than, or 1 greater than the initial state, i.e. $\Delta n = \pm 1$.
- An energy level diagram, with arrows indicating these possible transitions is shown below left.



- **Transition rules like this will also appear in the Schrödinger treatment of the hydrogen atom, and have major implications on the spectra of atoms and molecules.**
- For the SHO this rule suggests that light with;
$$E_\gamma = \Delta E = \hbar\omega$$
may only be absorbed or emitted by diatomic molecules.
- In reality this is not the case!
- This is because the SHO model is only really valid for the lowest few energy levels, above that the potential is anharmonic.
- The corresponding selection rule is $\Delta n = \pm 1, \pm 2, \pm 3, \dots$
- This is now consistent with the energies of the cavity radiation in Planck's Model.