LC Quantum Mechanics 1 Lecture Notes

Year 1 Semester 1

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Table of Lectures

Fri 03 Oct 2025 12:00

Lecture 1 - Atomic Structure

1 Atomic Structure

1.1 What is the course?

- Quantum mech is weird and unintuitive, we will build up a case in the course for why this weird theory was necessary and why we're confident it works.

- Each week will be a self-contained concept and/or historical experiment, working up to the Schrödinger Equation and wave-particle duality.

- Names and dates do not need to be memorised.

- Recommended text: University Physics (Young and Freedman).

- Office hours: 13:00 – 13:50 Fridays (immediately post-lecture), Physics East Rm 207.

1.2 Atomic Structure

What actually is an atom? What does it actually look like inside?

Early Clues

- Periodic Table (Mendeleev, 1869), periodic patterns in elements properties.

- Radioactivity (Becquerel, 1896, Curie 1898)

- Atoms emit and absorb specific discrete wavelengths, (Balmer, 1884)

- Discovery of the Electron (Thomson 1897). Cathode rays - heating metal in a vacuum with an electric field above it, to strip away electrons from the metal.

    - This showed electrons were negatively charged and extremely light (1/2000th of the atomic mass).
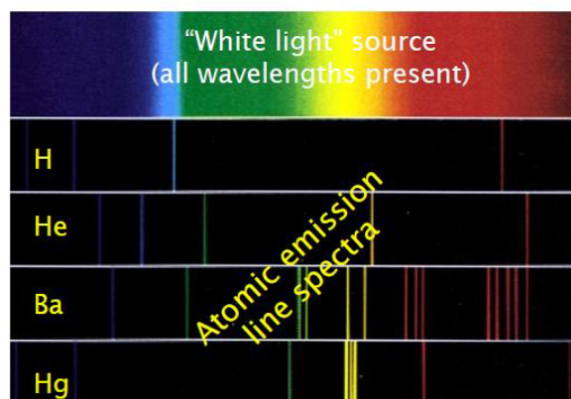

Figure 1.1: Absorption Spectra

1.3 Plum Pudding Model

A solid, uniform lump of positively charged matter, approximately 10^{-10} m across. This had evenly distributed negative charges (electrons) scattered throughout.

1.4 Discovery of the Nucleus

Geiger and Marsden (1908-1913), in an experiment designed by Rutherford fired alpha particles (He nuclei, mass of 4 u, charge of $+2e$) at thin gold foil and measured the deflection / scattering. The accelerating voltage gave these alpha particles an energy of ≈ 5 MeV.

They found that most α were scattered only by small angles, but (surprisingly) a small number were scattered right back towards to emitter (through $\theta > 90°$). The distribution of the angles is approximately Normally distributed, with a mean of 0. Only approximately 1 in 8,000 fired αs were scattered by $\theta > 90°$ back towards the emitter ("back-scattering").

Can back-scattering be explained with the Plum Pudding Model? No, it cannot. A plum pudding is too large, and has an insufficient charge density to produce the repulsion force required at the distances required.
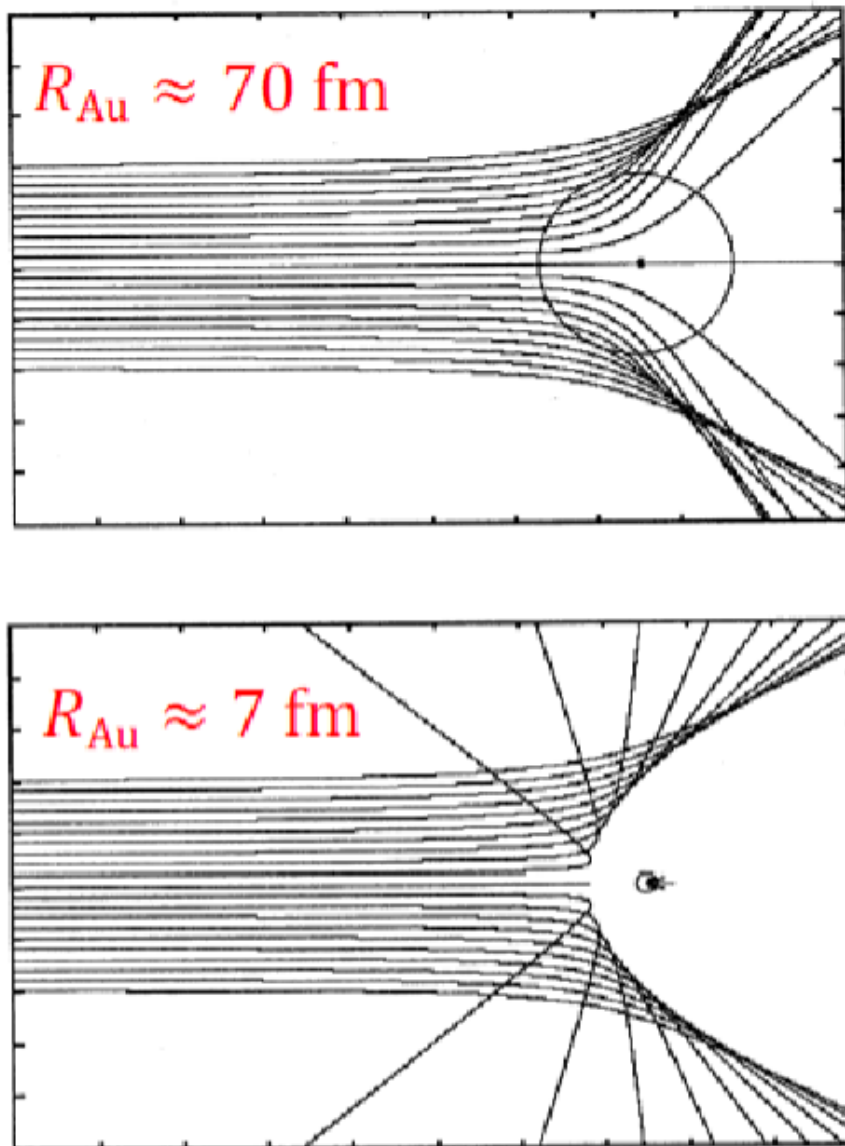

Figure 1.2: Rutherford Scattering Experiment Data

The first image is the theoretical data, from an atomic radius of 70 fm, consistent with the plum pudding

model. The traces represent paths of incoming, then deflected alpha particles. Notably, the scattering is of small angles, less than 90°. The second image is data from a much smaller volume of the same charge, not consistent with the plum pudding model. Here, backscattering occurs, which (as this was experimentally observed) shows that the plum pudding model is not accurate.

2 Demonstrating by Calculation

Lets work out the work done to take an α from infty to the pudding centre. If the electrostatic repulsion is not enough to overcome this, we cannot stop the α and cannot back scatter.
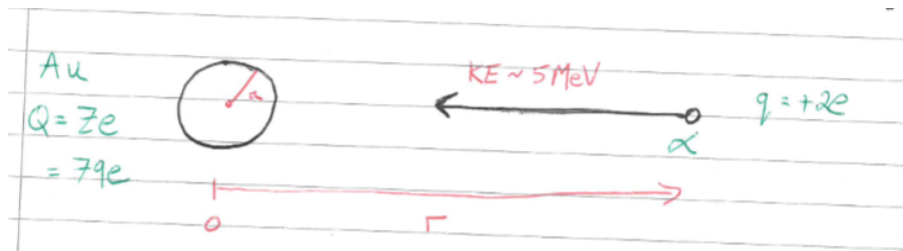

Figure 1.3: The experiment

2.1 Assumptions

- The atom stays still.

- Ignore the gold electrons (this is fine, as they would cancel some positive charge and make repulsion weaker. If we can't do it without them, it would be equally impossible to do it with).

2.2 Calculating Repulsive Force

Coulomb Potential Energy is:

$$u(r) = \frac{qQ}{4\pi\epsilon_0 r}$$

Force is:

$$F(r) = -\frac{du}{dr} = \frac{qQ}{4\pi\epsilon_0 r^2}$$

Change in potential energy $(u_2 - u_1)$ is work done:

$$\int_{u_1}^{u_2} du = -\int_{r_1}^{r_2} F(r)dr$$

From outside the atomic radius, we treat the atomic pudding as a point charge of charge Q. From inside the atomic radius, we treat it as a smaller point charge $Q'(r)$, where we only consider the charge inside the portion of the pudding where $r < a$, where r is the current position inside the sphere and a is the atomic radius. We totally disregard any of the charge which sits at a greater radius than the current position.

If charge is spread uniformly, the total charge is proportional to the volume of the sphere. So:

$$\frac{Q'}{Q} = \frac{\frac{4}{3}\pi r^3}{\frac{4}{3}\pi a^3}$$

$$Q' = Q\frac{r^3}{a^3}$$

Inside the Pudding

$$F = \frac{qQ'}{4\pi\epsilon_0 r^2}$$

$$F = \frac{qQr^3}{4\pi\epsilon_0 r^2 a^3}$$

$$F = \frac{qQr}{4\pi\epsilon_0 a^3}$$

$$F = \frac{qQ}{4\pi\epsilon_0 a^3} \times r$$

Hence inside, $F \propto r$

Outside the Pudding

$$F = \frac{Qq}{4\pi\epsilon_0 r^2}$$

$$F = \frac{Qq}{4\pi\epsilon_0} \times \frac{1}{r^2}$$

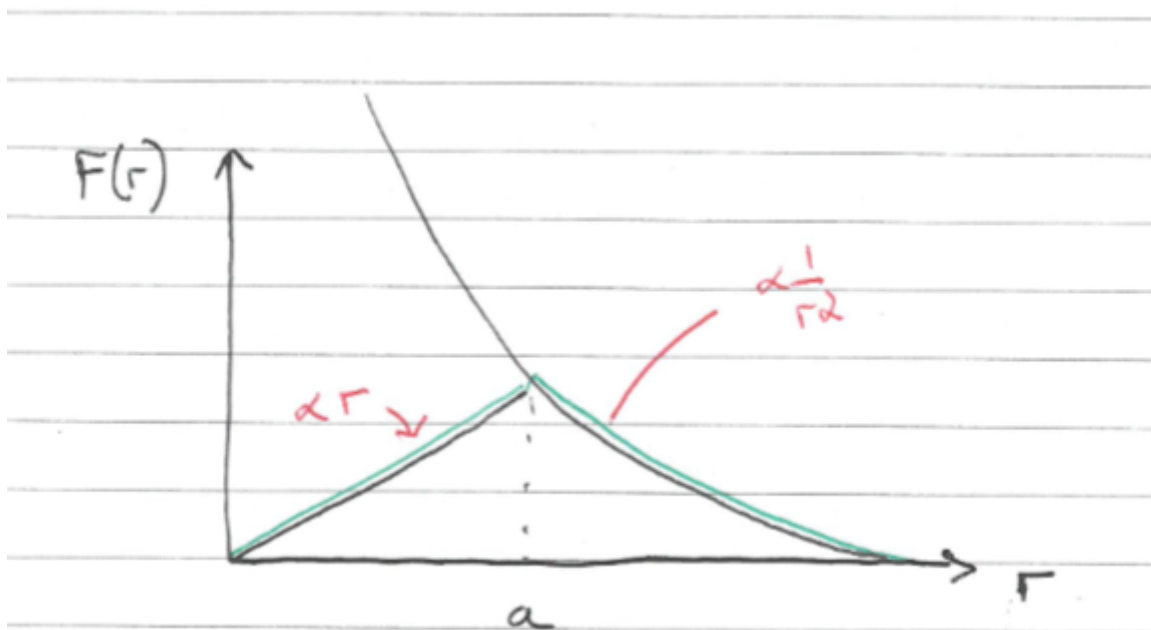Hence outside, $F \propto \frac{1}{r^2}$. We are therefore integrating the area under this (almost) triangle:

Figure 1.4: Radius vs electrostatic repulsion force

$$\Delta u = - \int_{r_1}^{r_2} F(r)\, dr$$

Splitting into two sections (when the alpha particle is outside vs inside the atomic radius), and integrating across all r (as we are attempting to work out the work done to bring an α from infinity to the charge, at which point distance is 0):

$$= - \int_{\infty}^{a} \frac{qQ}{4\pi\epsilon_0 r^2}\, dr - \int_{a}^{0} \frac{qQr}{4\pi\epsilon_0 a^3}\, dr$$

$$= - \frac{qQ}{4\pi\epsilon_0} \int_{\infty}^{a} \frac{1}{r^2}\, dr - \frac{qQ}{4\pi\epsilon_0 a^3} \int_{a}^{0} r\, dr$$

$$= - \frac{qQ}{4\pi\epsilon_0} \lim_{x\to\infty} \int_{x}^{a} \frac{1}{r^2}\, dr - \frac{qQ}{4\pi\epsilon_0 a^3} \int_{a}^{0} r\, dr$$

$$= - \frac{qQ}{4\pi\epsilon_0} \lim_{x\to\infty} \left[-\frac{1}{r} \right]_{x}^{a} - \frac{qQ}{4\pi\epsilon_0 a^3} \left[\frac{1}{2} r^2 \right]_{a}^{0}$$

$$= -\frac{qQ}{4\pi\epsilon_0}\left(-\frac{1}{a} - 0\right) - \frac{qQ}{4\pi\epsilon_0 a^3}\left(\frac{1}{2}0^2 - \frac{1}{2}a^2\right)$$

$$= -\frac{qQ}{4\pi\epsilon_0}\left(-\frac{1}{a}\right) - \frac{qQ}{4\pi\epsilon_0 a^3}\left(-\frac{1}{2}a^2\right)$$

$$= \frac{qQ}{4\pi\epsilon_0 a} + \frac{qQa^2}{8\pi\epsilon_0 a^3}$$

$$= \frac{qQ}{4\pi\epsilon_0 a} + \frac{qQ}{8\pi\epsilon_0 a}$$

$$= \frac{qQ}{4\pi\epsilon_0 a} + \frac{1}{2}\frac{qQ}{4\pi\epsilon_0 a}$$

$$= \frac{3}{2}\frac{qQ}{4\pi\epsilon_0 a}$$

As required! Plugging in values gives us:

$$\Delta u = \frac{3}{2}\frac{(2e)(79e)}{4\pi(8.854 \times 10^{-12}) \times 10^{-10}}$$

$$= 5.45 \times 10^{-16}\,\text{J} = 3.41\,\text{keV}$$

This is much less than the kinetic energy of the 5 MeV alpha particle, therefore (as this value is maximum work done against the repulsive force) a plum pudding could not stop, and therefore could not backscatter a 5 MeV alpha particle. However, since $\Delta u \propto 1/a$, a smaller volume of charge could. How small, however?

$$\Delta u = 5\,\text{MeV} = -\int_{\infty}^{r_{max}} \frac{qQ}{4\pi\epsilon_0 r^2}\,dr$$

$$-5\,\text{MeV} = \frac{qQ}{4\pi\epsilon_0}\int_{\infty}^{r_{max}} \frac{1}{r^2}\,dr$$

$$-5\,\text{MeV} = \frac{qQ}{4\pi\epsilon_0}\lim_{x \to \infty}\left[-\frac{1}{r}\right]_{x}^{r_{max}}$$

$$-5\,\text{MeV} = \frac{qQ}{4\pi\epsilon_0}\left[-\frac{1}{r_{max}} - \lim_{x \to \infty}\frac{1}{x}\right]$$

$$-5\,\text{MeV} = \frac{qQ}{4\pi\epsilon_0}\left[-\frac{1}{r_{max}}\right]$$

$$5\,\text{MeV} = \frac{qQ}{4\pi\epsilon_0 r_{max}}$$

$$r_{max} = \frac{qQ}{4\pi\epsilon_0(5\,\text{MeV})}$$

Substitution and rearrangement gives $r_{max} = 4.5 \times 10^{-14}\,\text{m} = 45\,\text{fm}$. This gives us the "distance of closest approach". The nucleus cannot be any smaller than this, or an incoming alpha particle would collide with it. This is not the true size of the nucleus (a gold nucleus is smaller at $\approx 7\,\text{fm}$), but an alpha particle is not energetic enough to get this close. It instead gives the maximum size.

2.3 Next Idea: The Solar System Model

Therefore, the next idea was an orbiting solar system model, where electrons orbit in fixed paths around a central nucleus. However, accelerating charges (i.e. a charge in circular motion) radiate energy, so this orbiting electron would be on a decaying path to crash into the nucleus. We can observe this does not happen, so need another idea...

Bohr made two postulates:

- The electron in hydrogen moves in a set non-radiating circular orbit.

- Radiation is only emitted or absorbed when an electron moves from one orbit to another.

This works (at least for hydrogen) and explains the absorption spectra, but for now lacks a physical grounding.

Fri 10 Oct 2025 12:00

Lecture 2 - The Ultraviolet Catastrophe

In this lecture:

- How classical theories fail to explain black body radiation ("The Ultraviolet Catastrophe").

- How quantising light into photons gives predictions that fit this observation.

1   Black Body Radiation

A 'black body' is an idealised perfect object, that does not reflect, and absorbs internally all light (regardless of wavelength) incident upon it. No light is transmitted, so nothing shines out the other side. The object is perfectly black.

All bodies emit electromagnetic energy, usually outside the visible portion of the spectrum. For example, Paul Hollywood (and other humans) emit at about 300 K, which is infrared (at the temperature which night vision goggles are tuned to).

For the black body, emission spectrum is **only** from this thermal emission (no reflection, no fluorescence, etc). Hotter objects are brighter and bluer (hotter means higher energy, and therefore a shorter wavelength)
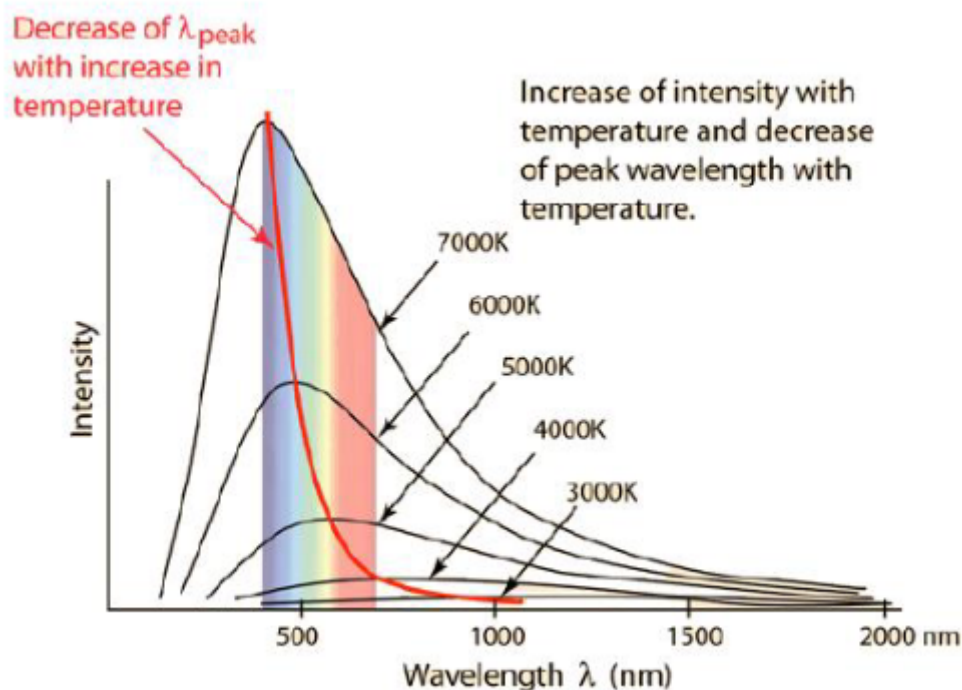

Figure 2.1: Observed Emission Spectra

However, we run into a problem. If we plot the spectra predicted by classical thermodynamics, vs the observed spectra for a given temperature object, the classical prediction gets it totally wrong, especially at shorter wavelengths.
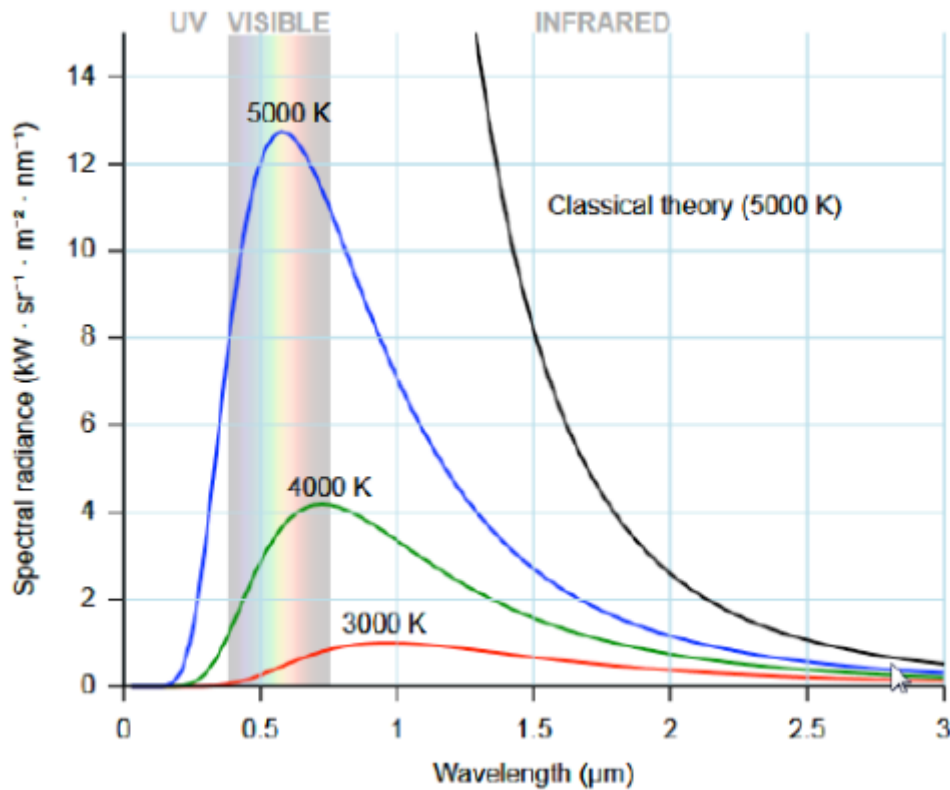
Figure 2.2: Predicted and Observed Spectra for 5000K (and Observed for 4000K and 3000K)

1.1 Notation

$I(\lambda)$ is the intensity for an emitted wavelength λ. I is the total intensity across all wavelengths per unit time (in W/m^2, power per unit area).

$$I = \int_0^\infty I(\lambda)\, d\lambda$$

I is the total area under the $I(\lambda)$ curve, i.e. the sum of intensity per wavelength, across every wavelength.

2 The Ultraviolet Catastrophe

2.1 Empirical Results

The Stefan-Boltzmann Law gives $I = \sigma T^4$, where σ is the Stefan-Boltzmann constant, $\sigma = 5.67 \times 10^{-8} \, \text{W m}^{-2} \, \text{K}^{-4}$.

Wien's Displacement Law gives $\lambda_{\text{peak}} = \frac{b}{T}$, where $b = 2.898 \times 10^{-3} \, \text{K} \cdot \text{m}$.

2.2 Why does classical mechanics break?

Lets model the $I(\lambda)$ spectrum by slotting standing waves into a cavity. Inside the blackbody, EM waves form standing waves (in a limited number of possible configurations).

We can simplify by considering a 1D cavity of length L. We can consider 'cavity modes' as the possible standing waves that can exist in this cavity. As we know the wave is bound at each end, the displacement at each end of the cavity must be 0. Therefore, the only possible waves must obey this, and these are cavity modes.
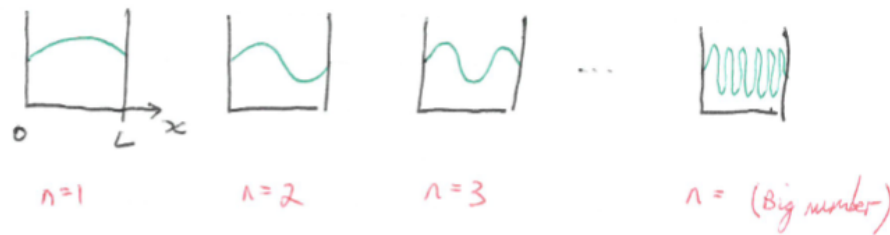
Figure 2.3: Possible cavity modes

The amplitude $a(x)$ can be given by this:

$$a(x) = \sin\left(\frac{n\pi x}{L}\right), \qquad n = 1, 2, 3, \ldots \quad \text{(mode number)}$$

And by inspection from the figures:

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

And therefore the number of nodes per wavelength is:

$$n(\lambda) = \frac{2L}{\lambda}$$

Moving to a 3D cavity, the number of modes allowed in a volume scales with volume, meaning the density of modes becomes proportional to $1/\lambda^4$.

So, classically (in 3D):

$$I(\lambda) \propto \frac{n(\lambda)}{\lambda} \times k_B T \propto \frac{1}{\lambda^4}$$

Where the first term is the density of modes at lambda, and the second is the average energy of nodes. As we head to UV and $\lambda \to 0$, $I(\lambda) \to \infty$...which is not accurate. This is the UV Catastrophe!

2.3 Where did it go wrong?

The issue was assuming that all cavity modes have average energy $k_B T$ - the "Equipartition Theorem" (which we'll meet in later courses).

In brief: the probability distribution of energies is a "Boltzmann Distribution":

$$p(E) = \frac{\exp\left(-\frac{E}{k_B T}\right)}{k_B T}$$

Average energy:

$$\bar{E} = \int_0^\infty E\, p(E)\, dE = k_B T$$

We assume that all cavity modes have he same average energy, and yet as lambda becomes very small, the number of possible cavity modes becomes very large. This causes the energy to tend to infinity, which the UV Catastrophe says is incorrect...

2.4 Planck's Hypothesis

A rather desperate Planck hypothesised that energy was quantised, i.e. it comes in discrete packets, called quanta. The energy of these quanta is proportional to frequency. This was radical at the time, even though we accept it now.

$$\Delta E = hf = \frac{hc}{\lambda}$$

Where $h = 6.626 \times 10^{-34}$ J $\cdot$ s is Planck's constant.

Sticking this into the Partition Function from statistical mechanics (which we will properly encounter later on, for now don't worry!), we get an average energy:

$$\bar{E}(\lambda) = \frac{hc/\lambda}{\exp(hc/\lambda k_B T) - 1}$$

Looking at limits:

$$\text{For } \bar{E}(\lambda \to \infty): \quad \frac{hc}{\lambda k_B T} \ll 1$$

And the Taylor Series of e^x:

$$\exp\left(\frac{hc}{\lambda k_B T}\right) \approx 1 + \frac{hc}{\lambda k_B T} + \dots$$

Yields:

$$\bar{E}(\lambda) \approx \frac{hc/\lambda}{1 + (hc/\lambda k_B T) - 1} = k_B T$$

This is a good sign, because it means that Planck's Hypothesis holds the correct classically predicted and empirically observed behaviour for higher wavelengths.

Now what about lower wavelengths, where the classical behaviour broke?

$$\text{For } \bar{E}(\lambda \to 0): \quad \exp\left(\frac{hc}{\lambda k_B T}\right) \to \infty \quad \text{(very quickly)}$$

$$\text{For } \bar{E}(\lambda \to 0): \quad \frac{hc}{\lambda} \to \infty \quad \text{(slower)}$$

Therefore, in the expression:

$$\bar{E}(\lambda) = \frac{hc/\lambda}{\exp(hc/\lambda k_B T) - 1}$$

The numerator and denominator both tend to infinity, but the denominator does so much faster. Therefore (and this can be done in a less handwavy manner via L'Hopital):

$$\bar{E}(\lambda \to 0) \to \frac{1}{\infty} \to 0$$

Which recovers the behaviour at UV wavelengths, so no Catastrophe!

3 Conclusion

- This strange quantisation hypothesis actually fits the data.

- Quantising energy means that the average energy of each cavity mode is wavelength dependant, and not fixed $k_B T$ as seen at larger wavelengths.

- This solves the UV Catastrophe!

Thu 17 Oct 2025 12:00

Lecture 3 - Particle Nature of Light

In this lecture:

- The photoelectric effect.

- Compton scattering.

Which are two examples where classical theory (light as a wave) break down.

1   The Photoelectric Effect

When shining ultraviolet light on a metal surface, electrons are emitted. This is the photoelectric effect.

Why are we not bombarded by electrons in daily life? For the electron to fly off, we must be in a vacuum. Otherwise, it'll immediately strike an air molecule and be absorbed.

Photoelectric Effect Background

- Discovered by Hertz, 1887

- Thomson (1889) went further, so did Lenard (1902) and others.

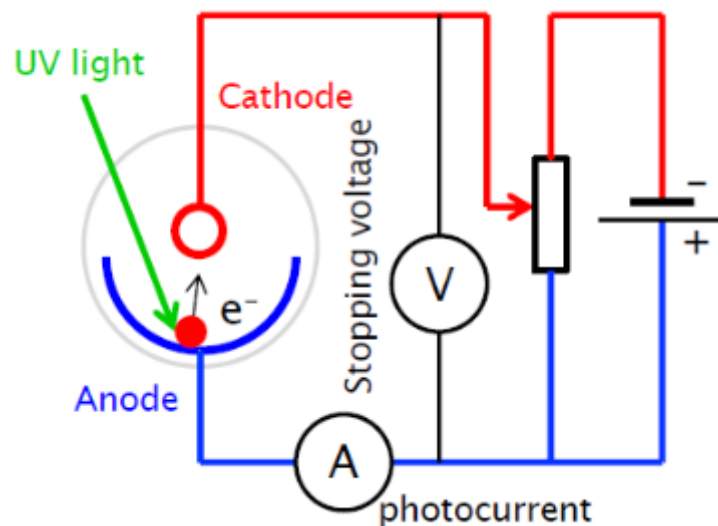- Einstein won his Nobel Prize for explaining this, not from relativity.

Figure 3.1: A circuit diagram for measuring the photoelectric effect.

The above setup would be encased in a glass ball (containing a vacuum), with a setup like this:
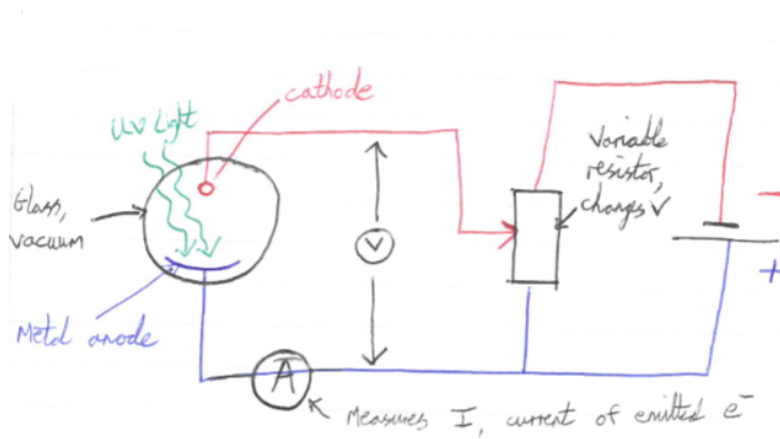
Figure 3.2: Experimental Setup

1.1 Results

Result One - Changing Intensity

For fixed UV wavelength, increasing the intensity of light increases the measured photocurrent:
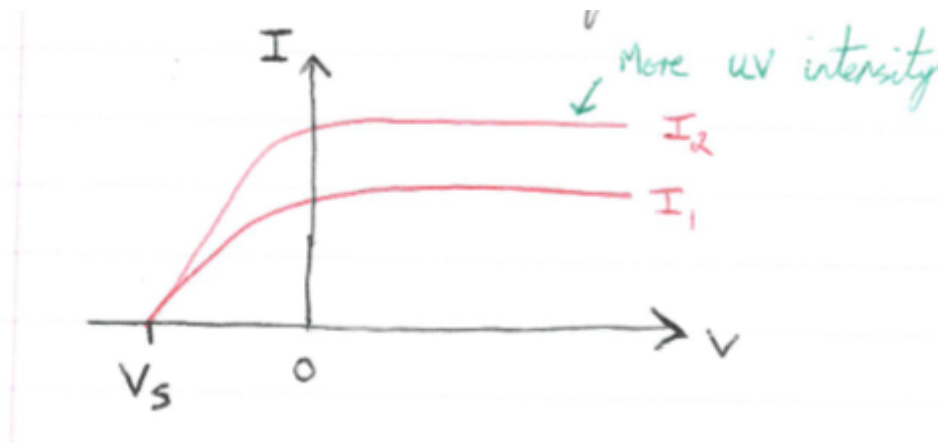

Figure 3.3

- Increasingly negative potential the cathode decreases photocurrent. At some potential v_s applied to the circuit (the "stopping potential") this current drops to zero.

- Potential does not affect electron emission, however adding potential causes an electric field which effectively blows electrons back towards the anode. The stopping potential is when this electric field is perfectly strong to prevent electrons from reaching the cathode and causing a current.

- The fact this can happen consistently (i.e. no current means no electrons made it through) implies that there must be some maximum kinetic energy these electrons can have ($KE_{max} = eV_S$).

- The stopping potential is independent of UV intensity. More UV makes current increase, but does not change stopping potential (i.e. it does not give more energy to each electron, they each have the same energy). This does not make sense classically. Classically we would expect adding more energy to cause emitted electrons to have more energy, therefore changing the stopping potential.
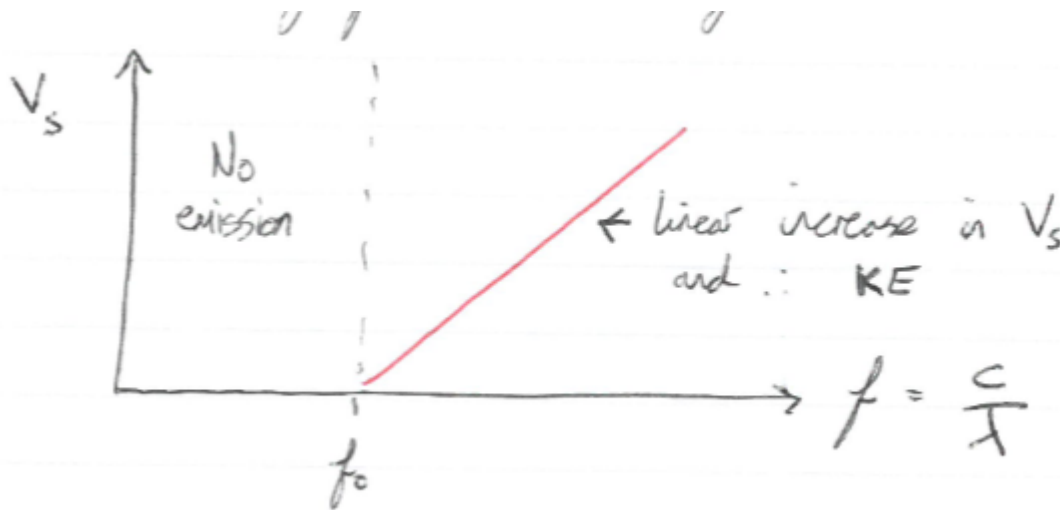
Result Two - Changing Wavelength

Figure 3.4

We have to reach some baseline threshold frequency f_0 before we see any photocurrent. After this, increasing wavelength increases photocurrent (and hence KE of emitted electrons) linearly.

- For a given metal, we find the threshold frequency f_0, below which there is no emission of electrons (no current). If below the frequency f_0, intensity is irrelevant. This contradicts classical mechanics which would suggest that turning up the light intensity would supply more (and potentially sufficient) energy.

- Above the threshold, the energy of individual emitted photons depends on UV frequency and not intensity (by result one).

1.2   Conclusions

Classically

Classically, we expect energy to be proportional to intensity, $\therefore v_s$ should increase with greater intensity. We also expect there to be no link between between frequency and energy, hence no threshold frequency. We'd expect no threshold frequency, instead being a time delay as electrons "soak up" energy to reach the required threshold.

In theory, great, in practice *this is not observed.*

Einstein's Proposal

Energy in light comes from photons with energy $E = hf$. There is a minimum energy required for an electron to be able to escape from the metal. This minimum energy is called the work function ϕ.

$$KE_{\max} = hf - \phi = eV_s$$

Now:

- Higher intensity means more of the same particles (more photons), but the energy of each is unchanged.

- $E = hf$ so frequency changes energy (as observed).

- The Bohr model says that an electron can only have certain electron energy transitions when the correct energy is supplied (an electron cannot gradually soak up energy). This explains why there is a cutoff below the work function, and no observed time delay (as the "soaking up" that causes the delay does not happen). Either an incoming photon has sufficient energy, or it does not. Having more photons does not help.

- The first incoming photons immediately releases an electron (assuming the incoming light has sufficient energy), therefore there's no time delay.
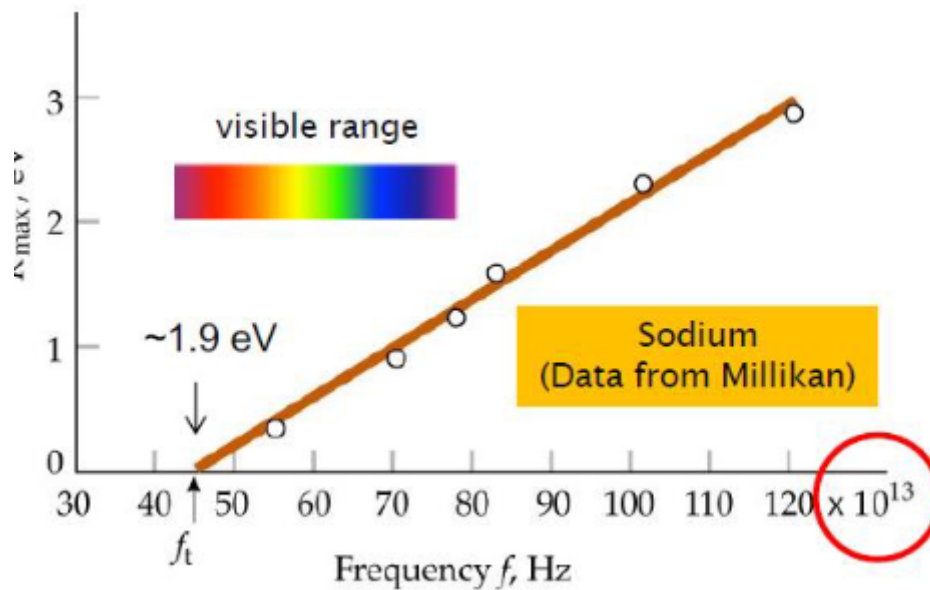
1.3   In Practice

Figure 3.5: Sodium photocurrent measurements by Robert Millikan

2   Compton Scattering

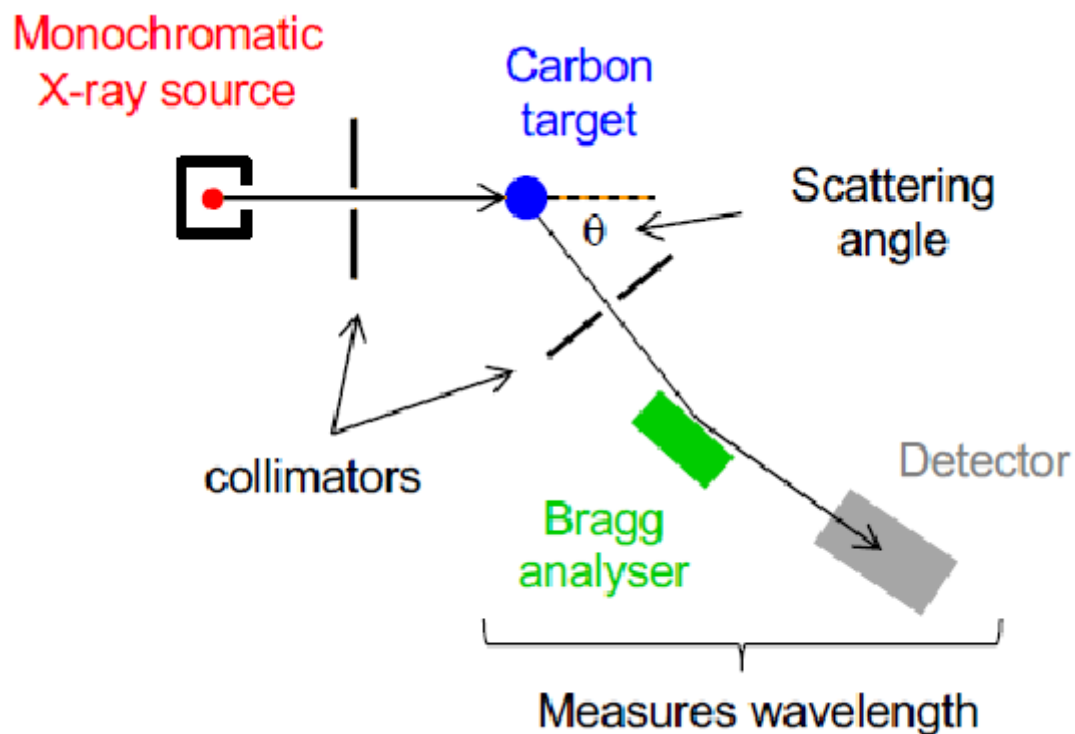Compton Scattering is the scattering of x-rays off carbon atoms.

Figure 3.6: A Compton Scattering experimental setup.

The surprising result is that two wavelengths were observed (not just the original) - λ_1, λ_2, where λ_1 is the original and λ_2 is different. Classically this is hard to explain and λ should not change.

The difference between these two wavelengths increases with scattering angle θ. This can be explained if the x-ray beam is a stream of photons, but not classically.

Possible options when a photon collides:

- Scattering off the whole atom (Rayleigh Scattering). The photon hits a tightly bound electron that cannot move independently. The photon effectively scatters off the entire atom. Since $M_{\text{atom}} \gg m_e$, the recoil energy of the atom is minimal and the photon loses almost no energy, hence the wavelength is effectively unchanged. This gives us the existing λ_1 peak.

- Scattering off a free electron (Compton Scattering.): The photon hits a loosely bound electron which has a much lower binding energy, so the electron is knocked loose. The photon transfers momentum and energy to this electron, leading to a loss of energy and therefore change of wavelength. This gives the new λ_2 peak.
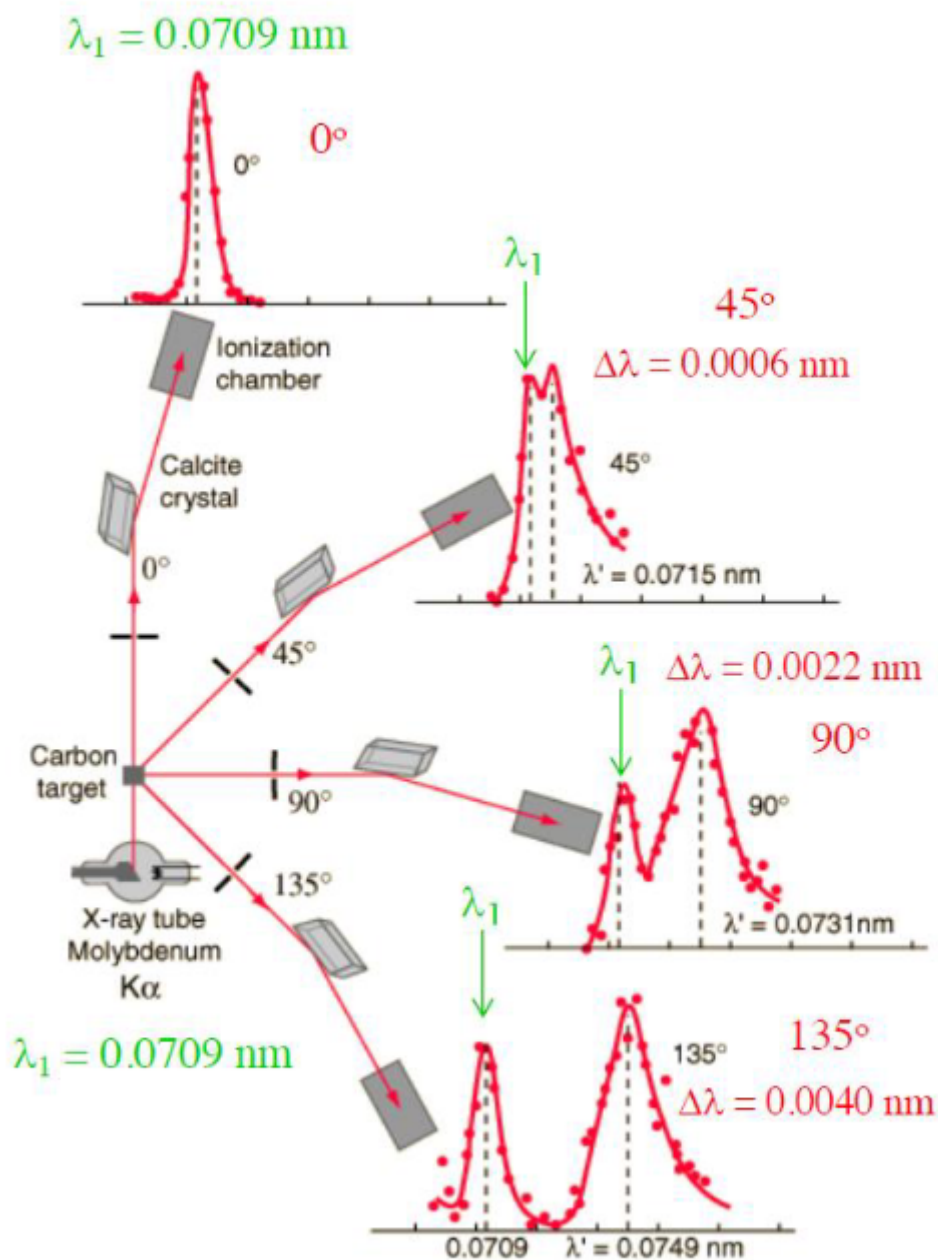

Figure 3.7: The observed results

3 Deriving Compton's Equation

Given an incoming photon with with energy E_1, wavelength λ_1 and momentum $\underline{p}_1$. This strikes an electron and is deflected by angle θ. The electron is deflected by some angle ϕ such that momentum is conserved. The new deflected photon has $E_2, \lambda_2, \underline{p}_2$.

We must consider relativistic effects here given the high speed ($E^2 = p^2 c^2 + m^2 c^4$)

Figure 3.8

3.1 Setup

For a massless photon ($m = 0$):

$$E = pc$$

And:

$$E = \frac{hc}{\lambda}$$

So:

$$p = \frac{h}{\lambda} \tag{3.1}$$

3.2 Conservation and Relativity

Conserving momentum (underlines omitted for speed):

$$p_1 = p_e + p_2$$

$$p_e = p_1 - p_2$$

Squaring both sides:

$$p_e^2 = p_1^2 + p_2^2 - 2 p_1 \cdot p_2$$
$$p_e^2 = p_1^2 + p_2^2 - 2 p_1 p_2 \cos \theta \tag{3.2}$$

And then by conservation of energy:

$$E_1 + E_e = E_2 + E_e'$$

Where E_1 is the incoming photon energy, E_e is the energy of the electron at rest in atom before collision, E_2 is the deflected photon energy and finally E_e' is the deflected electron's energy.

Using this:

$$p_1 c + m_e c^2 = p_2 c + \sqrt{p_e^2 c^2 + m_e^2 c^4}$$

$$\implies p_1 - p_2 + m_e c = \sqrt{p_e^2 + m_e^2 c^2}$$

And squaring both sides:
$$(p_1 - p_2)^2 + m_e^2 c^2 + 2m_e c(p_1 - p_2) = p_e^2 + m_e^2 c^2$$

Substituting in Eqn 3.2 for p_e^2

$$(p_1 - p_2)^2 + 2m_e c(p_1 - p_2) = p_e^2$$
$$(p_1 - p_2)^2 + 2m_e c(p_1 - p_2) = p_1^2 + p_2^2 - 2p_1 p_2 \cos \theta$$

And rearranging:

$$(p_1 - p_2)^2 + 2m_e c(p_1 - p_2) = p_1^2 + p_2^2 - 2p_1 p_2 \cos \theta$$
$$p_1^2 + p_2^2 - 2p_1 p_2 + 2m_e c(p_1 - p_2) = p_1^2 + p_2^2 - 2p_1 p_2 \cos \theta$$
$$-2p_1 p_2 + 2m_e c(p_1 - p_2) = -2p_1 p_2 \cos \theta$$
$$-p_1 p_2 + m_e c(p_1 - p_2) = -p_1 p_2 \cos \theta$$
$$m_e c(p_1 - p_2) = -p_1 p_2 \cos \theta + p_1 p_2$$
$$m_e c(p_1 - p_2) = p_1 p_2 (1 - \cos \theta)$$

Substituting Eqn 3.1:

$$m_e c(p_1 - p_2) = p_1 p_2 (1 - \cos \theta)$$
$$m_e c\left(\frac{h}{\lambda_1} - \frac{h}{\lambda_2}\right) = \frac{h}{\lambda_1}\frac{h}{\lambda_2}(1 - \cos \theta)$$
$$m_e c\left(\frac{h}{\lambda_1} - \frac{h}{\lambda_2}\right) = \frac{h^2}{\lambda_1 \lambda_2}(1 - \cos \theta)$$
$$m_e c\left(\frac{1}{\lambda_1} - \frac{1}{\lambda_2}\right) = \frac{h}{\lambda_1 \lambda_2}(1 - \cos \theta)$$
$$m_e c\left(\frac{\lambda_1 \lambda_2}{\lambda_1} - \frac{\lambda_1 \lambda_2}{\lambda_2}\right) = h(1 - \cos \theta)$$
$$m_e c(\lambda_2 - \lambda_1) = h(1 - \cos \theta)$$
$$(\lambda_2 - \lambda_1) = \frac{h}{m_e c}(1 - \cos \theta)$$

Which is the Compton Equation. This shows that the change in wavelength is proportional to $1 - \cos \theta$.

4   Conclusions

The photoelectric effect and Compton scattering are two more physical phenomena that cannot be explained using traditional classical mechanics with EM waves alone. They both require assuming photons of energy $E = hf$ to be adequately explained.

Fri 24 Oct 2025 12:00

Lecture 4 - Atomic Energy Levels and Spectra

In this lecture:

- The spectra of light emitted and absorbed by electrons in:
    - Hydrogen (simple)
    - Larger atoms (not simple...)
- Electronic shells and orbits.

1   Spectra

The Bohr Model says that electrons in an atom can hold discrete values "levels" of energy. As electrons go up or down these levels they must absorb or will emit a photon. This emission causes a discrete spectra of emitted frequencies, unique to the element causing it.
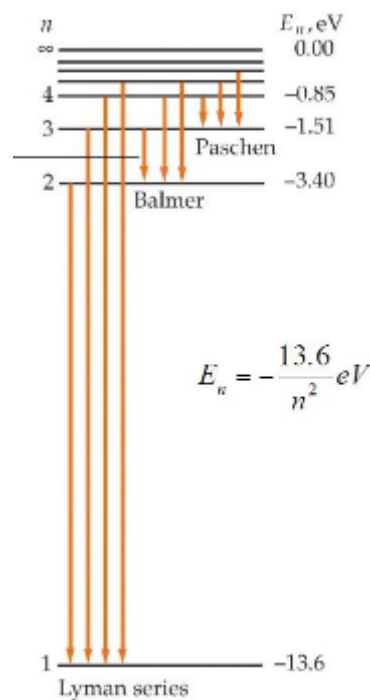

Figure 4.1: Example emission spectra.

Each of the transitions from one energy level to another have a discrete change in energy (measured in eV), therefore each transition will have a discrete wavelength of produced photons.

From the Bohr model, he postulated (from experimental observations) that light can *only* be absorbed or emitted when an electron goes up or down a discrete energy level (excitation or relaxation). The lowest energy level is known as the "Ground State" ($n = 1$).
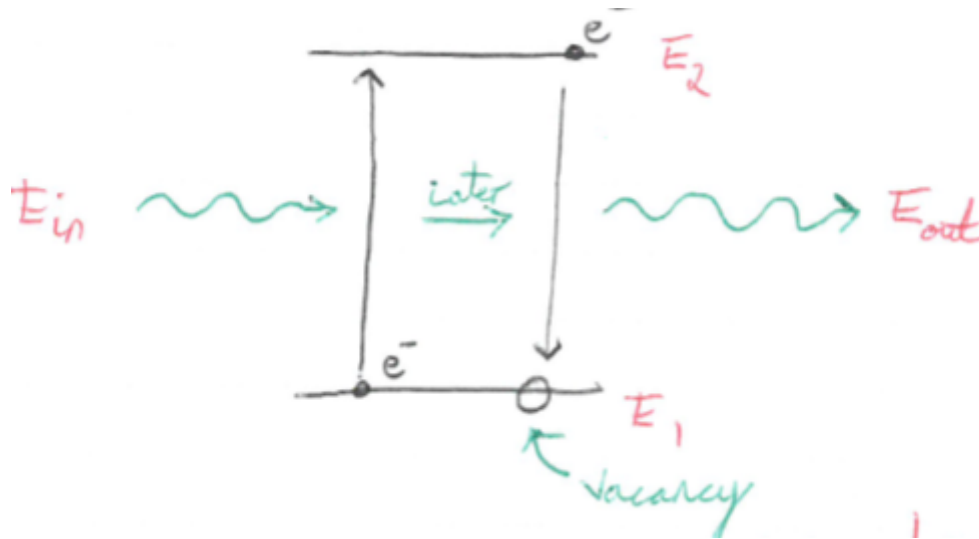
2 Absorption and Emissions

Figure 4.2

An electron is excited up an energy level, leaving a vacancy behind. Some time after, the electron drops back down into the ground state, emitting the energy in terms of a photon. By conservation of energy:

$$E_{\text{in}} = E_{\text{out}} = E_2 - E_1 = hf = \frac{hc}{\lambda}$$

Notably, the energy of the photon that initially triggered the excitation is given by $E_\gamma = E_2 - E_1$

3 Atomic Hydrogen

Atomic Hydrogen is by far the simplest example we can deal with (given the single proton and single electron). This single electron is 'orbiting[1]' the nucleus at some distance r.

The potential energy of this electron is:

$$v(r) = \frac{-e^2}{4\pi\epsilon_0 r}$$

This P.E. is negative, so the electron is trapped in a potential well and must be supplied with energy to escape, assuming no K.E. We also know (if we take into account kinetic energy too):

$$E = T + V$$

Where E is total energy, T is K.E, V is P.E. If the total is negative, the electron is bound to the atom.

We can see from the equation for potential energy that $v(r) \propto -1/r$, which gives us the green line. Of the points on this green line, only some of them are actually discrete allowed orbits. The region at the top is called the continuum, which is where an electron has positive energy and has therefore left the nucleus.

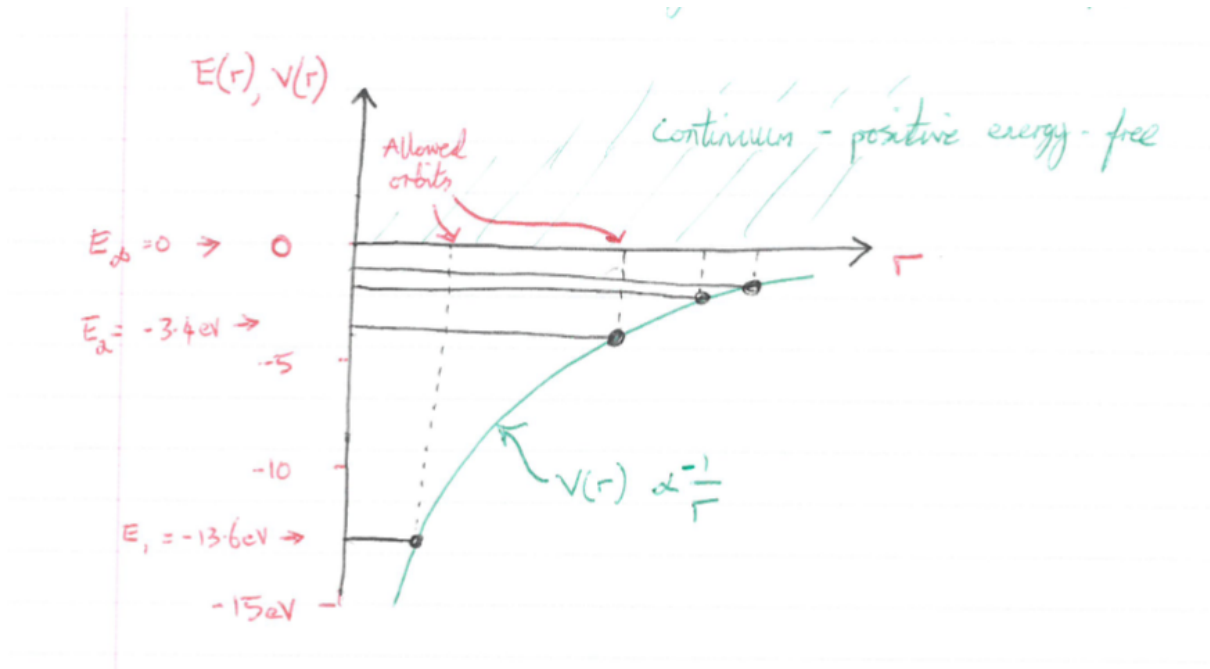[1]for the sake of argument, even if in practice it does not really

Figure 4.3

In Lec 08, we will properly derive from the Bohr model that the energy of each energy level is given by this:

$$E_n = \frac{-13.6eV}{n^2} \quad n = 1, 2, 3, \dots, \infty$$

Note that if $n \to \infty$, $E_n \to 0$. Emission and absorption happens when an electron moves from two different energy levels ($m \to n$).

$$E_\gamma = E_n - E_m = 13.6(1/n^2 - 1/m^2)eV$$

$$\frac{hc}{\lambda} = E_n - E_m = 13.6(1/n^2 - 1/m^2)eV$$

Or, finally:

$$\frac{1}{\lambda} = \frac{13.6eV}{hc}\left(\frac{1}{n^2} - \frac{1}{m^2}\right)$$

The $\frac{13.6eV}{hc}$ term is known as the Rydberg constant.

3.1 Balmer Series

The 'Balmer Series' is a portion of the hydrogen emission spectra which happens to take place at visible wavelengths. It is specifically transitions which take place to n = 2. To find these wavelengths, we set $n = 2$:

$$\frac{1}{\lambda} = R\left(\frac{1}{2^2} - \frac{1}{n^2}\right)$$

Moving from $3 \to 2$ gives us the Balmer Alpha line, for example.

4 Ionisation Energy of Hydrogen

The ionisation energy is the minimum energy required to kick an electron out of the ground state and into the continuum. This is just enough energy to barely make it free (i.e. when the continuum is reached the electron has 0 KE). Setting $n = 1, m = \infty$:
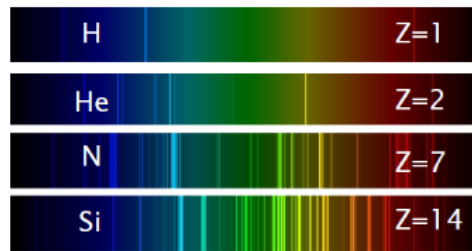
$$\frac{1}{\lambda} = R\left(\frac{1}{1} - \frac{1}{\infty}\right) = R$$

Where R is the Rydberg constant. Note: the energy levels can be very sharp, and they do not change (unless external stimuli like a strong external magnetic field are applied). We can therefore use this in e.g. atomic clocks.

5   Bigger Atoms

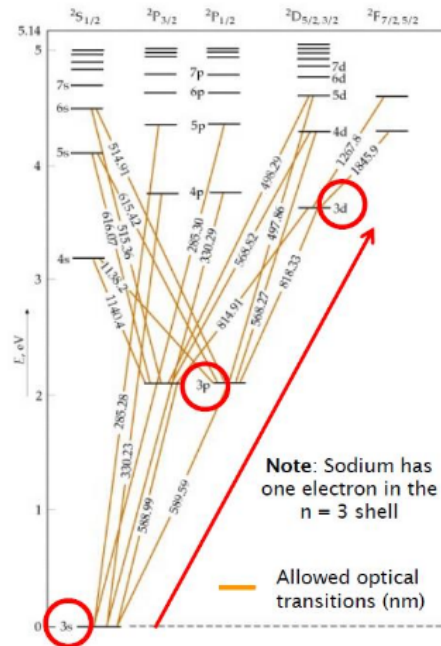Bigger atoms gets more complex than we can reasonably consider now.

Figure 4.4

Electrons begin interacting with each other and the nucleus in weird ways, and it becomes too messy to calculate easily. If there is only a single electron, we can still use the Bohr model, just with a different charge of the nucleus, and we multiply by Z^2 when calculating. If we have multiple electrons, there is no general formula and it becomes unpleasant. The energy levels become split into multiple possible orbitals, i.e for $n = 1$, 1s. For $n = 2$, 2s, 2p. For $n = 3$, $3s$, $3p$, $3d$ (where s, p, d are different electronic orbitals).

5.1   Spin

Electrons also have an intrinsic quantum property called 'spin', with a value $\frac{1}{2}$. They are fermions with two spin states (up, down). Note that spin is quantum, and has no relation to a physical geometric spin. The maximum occupancy of each level is $2n^2$ (i.e. the 1s state has space for one electron of each spin, i.e. one spin up and one spin down).

6   More Complexity...

- **Fine Splitting**: Electrons are moving, so have non-zero angular momentum. A moving charge creates a magnetic field, which changes the energy of the other electrons.

- **Hyperfine Splitting:** The nucleus also has a spin, they can be parallel (i.e. both have the same spin), or antiparallel, where the electron and the nucleus have opposing spins. These two configurations have slightly different energies (difference of $5.9\mu eV$). The parallel state is metastable, with a half life of 10 million years. There is so much hydrogen in the galaxy that radioastronomers can use this decay, and by detecting it they can image the location of hydrogen in the universe.

Fri 31 Oct 2025 12:00

Lecture 5 - X-Ray Production and Diffraction

In this lecture:

- Production of x-rays

- How to measure their wavelength

- Bragg scattering of x-rays by crystals and Bragg conditions.

1   Production of X-Rays

From the blackbody spectra lecture, we saw that something becoming hotter affects the wavelength of emission. Surely we, therefore, can just heat something hot enough for the peak of the emission spectra to be in the x-ray range?

Unfortunately not, this works, but would need the black body to be 1MK.

The more practical alternative to to fire high energy electrons (keV range) into a metal target in a vacuum.

2   What are they?

Electromagnetic radiation (light) outside of the visible spectrum. It sits beyond the UV portion.

Approximately 0.1keV ($\lambda = 10nm$) to 100keV ($\lambda = 0.01nm$), these are called soft and hard x-rays respectively.

3   Measuring Wavelength

How can we measure or select x-ray wavelengths? With visible light, we can use a prism to turn wavelength into an angle and measure the angle. However, a prism works for visible light because of its high refractive index. Unfortunately, for x-rays, $n \approx 1$ for all materials.

We therefore need some other way to split up wavelengths into angles, for which we can use a diffraction grating. Different wavelengths will be diffracted at different angles.

Another problem arises however...We need the slit separation d to be $d \approx \lambda$ for a diffraction grating to work. For x-rays, $\lambda \approx 10^{-10}m$, which is approximately the width of an atom. Good luck making that grating...

Luckily, nature has made these gratings for us — crystalline materials! Strontium titanate ($SrTiO_3$) has an approx 0.389nm spacing between strontium atoms. We can therefore use this crystal lattice as a diffraction grating.

4   X-Ray Diffraction from Crystals

We treat the x-rays as EM waves (and ignore weird photon stuff for now) and we assume that each atom scatters independently. We also assume that the atom absorbs the x-ray and later re-emits it, in all directions uniformly (at photon level, the emission is in a random direction, therefore we probabilistically treat it as in all).

We want to find the angles where *constructive interference* occurs. Zero intensity everywhere else due to very very high number of slots.

The Bragg Conditions determine where this interference happens. Consider a single plane of equally spaced atoms.
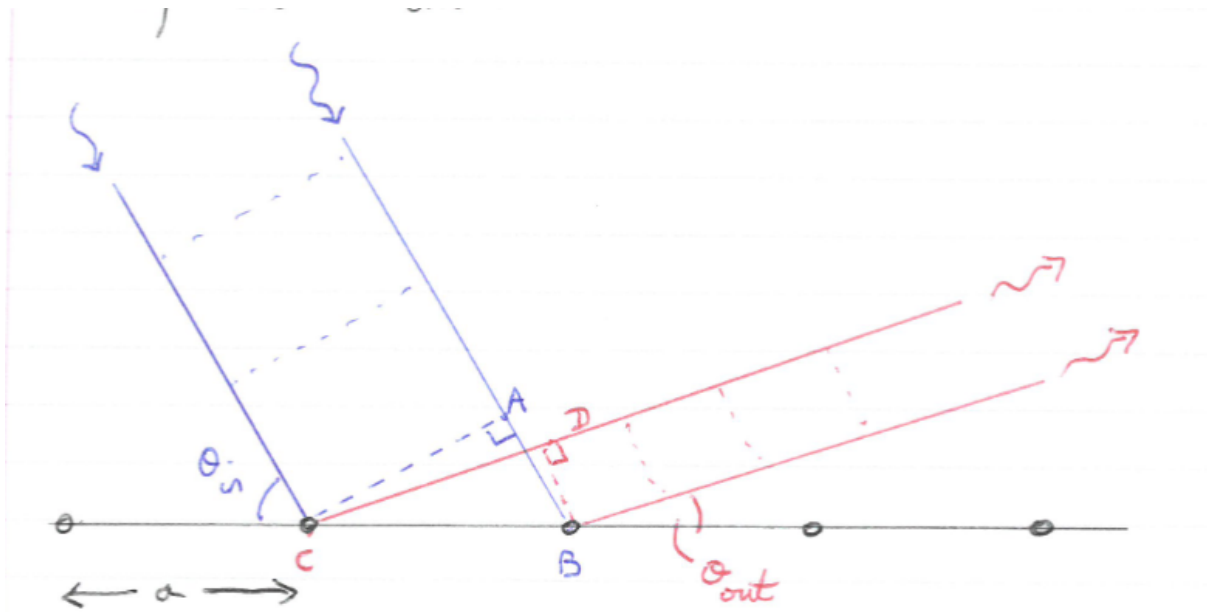
4.1   First Bragg Condition

Figure 5.1

The outgoing waves (red) are all in phase when the wavefronts line up perpendicularly. This happens when path lengths AB and CD are the same. So:

$$a \cos \theta_{in} = a \cos \theta_{out}$$

$$\theta_{out} = \theta_{in}$$

We disregard higher orders where:

$$\cos(\theta_{out} + 2n\pi) = \cos(\theta_{in} + 2k\pi), \quad n, k \in \mathbb{Z}^+$$

And we only consider the case where they are explicitly equal. Note that, so far, this is independent of wavelength (i.e. there is 'no dispersion'). This means we're not acting like a diffraction grating yet, more of a mirror.

4.2   Second Bragg Condition

Now we consider the inclusion of a second plane of atoms (we have some much larger number of n planes).
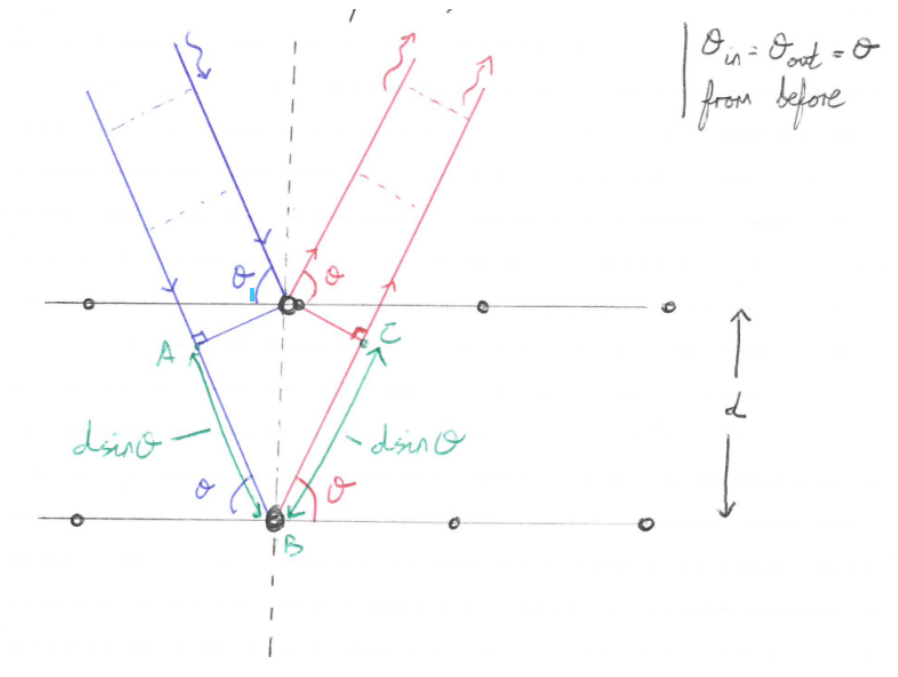
Figure 5.2

The ray which hits the lower plane travels further than the ray which hits the upper plane. For constructive interference to take place, this extra path difference must be an integer multiple of the wavelength. So:

$$AB + BC = 2d\sin\theta = n\lambda \quad n = 1, 2, 3, \ldots$$

Where d is the separation of crystal planes. Note: This θ is not the beam deflection angle. It is the angle between the **horizontal** and the incoming beam.

This equation gives us different angles for different wavelengths, therefore we can select light (inc X-rays) of a certain wavelength by splitting multi-wavelength light into different angles, and physically selecting the one that we wish. This throws back to Lec 03, where a Bragg Analyser was used with a detector to measure the wavelength of the produced X-rays.

5 Uses

We can use this in two ways:

We can determine an unknown wavelength (or select a wavelength out of multi-frequency light) by varying θ and identifying the detection peak. Note that θ is here twice, the detector must also be moved, and therefore the total deflection angle is 2θ

Figure 5.3

Alternatively, we can know lambda and fire at an unknown crystal to determine the atomic spacing. We can scan through 2θ and identify the angles where $n\lambda = 2d_i \sin\theta$ for various d_i. This leads us to x-ray crystallography, where we use x-rays to work out the structure of materials. Using crystals to measure or select an x-ray wavelength is called "wavelength dispersive x-ray spectroscopy".

Fri 07 Nov 2025 12:00

Lecture 6 - X-Ray Spectra

In this lecture:

- The production of X-rays - the spectrum created.
- Attenuation of X-rays in matter.
- Absorption of X-rays in materials, and 'absorption edges'.

1   Typical Tube Spectra

As a reminder, the source is metal bombarded with high-energy electrons. This causes electron energy level changes in deep electron shells in the metal. This spectrum is characteristic of the anode (the thing being hit by the electrons) material.

Figure 6.1: A typical x-ray spectra, with a background continuum and unique discrete peaks. Note there is some min λ

The continuous background curve is due to 'Bremsstrahlung', or 'braking radiation'.

2   Braking Radiation

Braking radiation is independent of anode materials. As an electron comes in at a high KE, it interacts with matter (charged nuclei etc) it is deflected and slows down. This lost KE is emitted as X-rays.
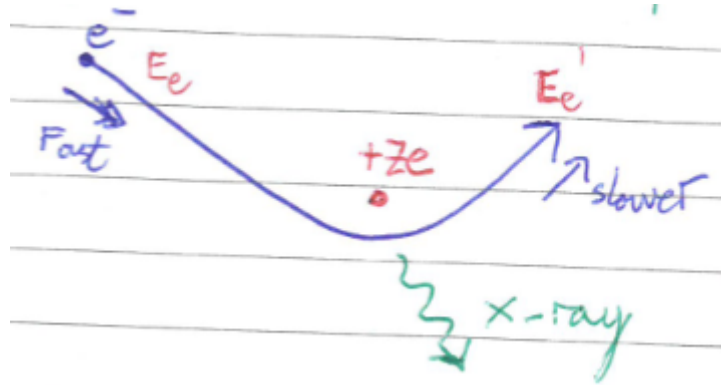
Figure 6.2

2.1 Lambda Min

By C.O.E:

$$E_{\text{x-ray}} = E_e - E_e' = \frac{hc}{\lambda}$$

If the electron came to a stop entirely, E_e' would be minimised (braking radiation maximised). The minimum wavelength λ_{min} occurs at the highest x-ray energy, i.e. when E_e' is zero.

$$E_e - 0 = \frac{hc}{\lambda_{\text{min}}} = eV$$

$$\lambda_{\text{min}} = \frac{hc}{eV}$$

Where V is the accelerating voltage.

3 Discrete Lines

These arise from inner shell electron transitions. These, unlike Bremsstrahlung, are characteristic of the anode material. We can use this to investigate the anode material, or we can use different materials to build different x-ray tubes with different emission spectra.

4 Jargon

Note the following stupid jargon.

- k means the n = 1 energy level.
- l means the n = 2 energy level.
- et cetera.

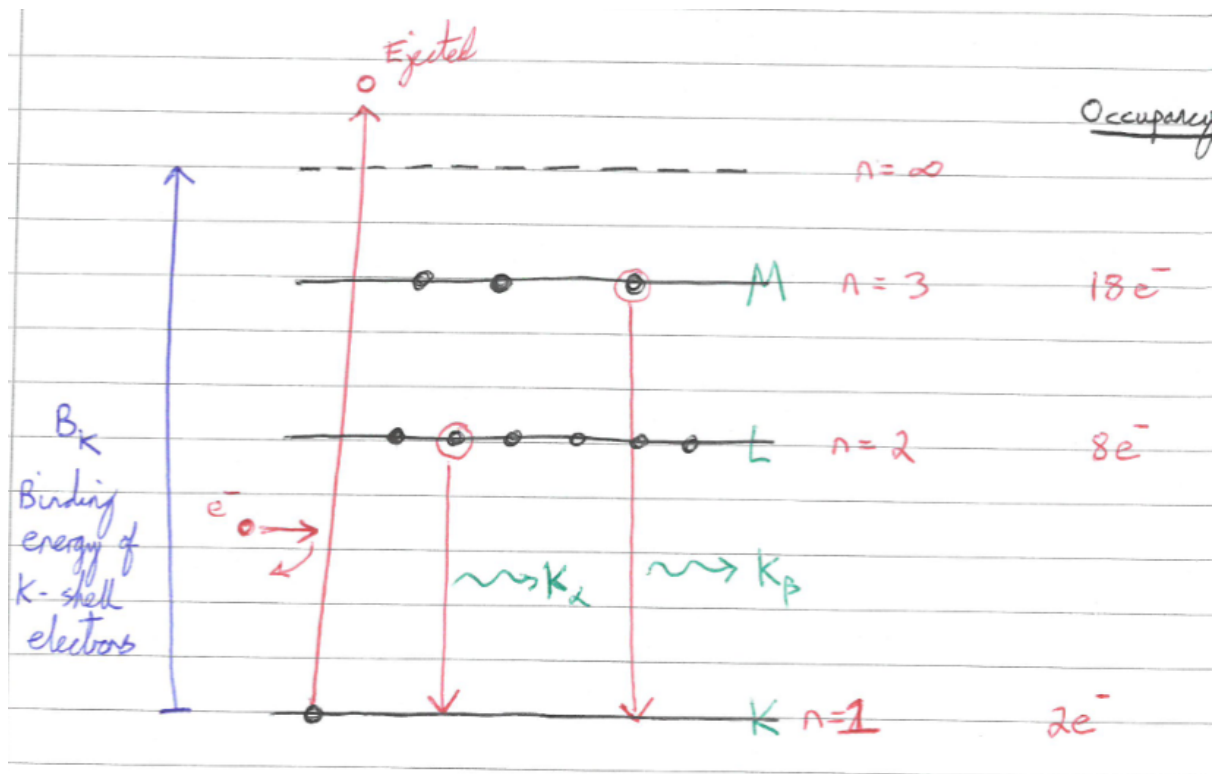Lets again consider the atomic energy levels (and their associated maximum occupancy):

Figure 6.3

If the incoming energy eV is bigger than the binding energy B_k of the k-shell electrons, they can be ejected. This is called 'collisional ionisation'. The intention is to eject an electron from the n=1 shell. This leads to an open space in the n=1 shell (a 'hole'), and the atom will automatically settle into the lowest energy state, i.e. a higher level electron will drop down to fill the lower energy hole. This change in energy requires the emission of a photon.

This specific n = 2 to n = 1 state transition is called k_α (the k denoting 'to the 1st level'), while n = 3 to n = 1 would be k_β etc. Transitions from the third to the second would be L_α, etc etc.

k_α etc only appear if bombardment energy is sufficiently high to cause collisional ionisation. Lower energy lines will therefore appear sooner.
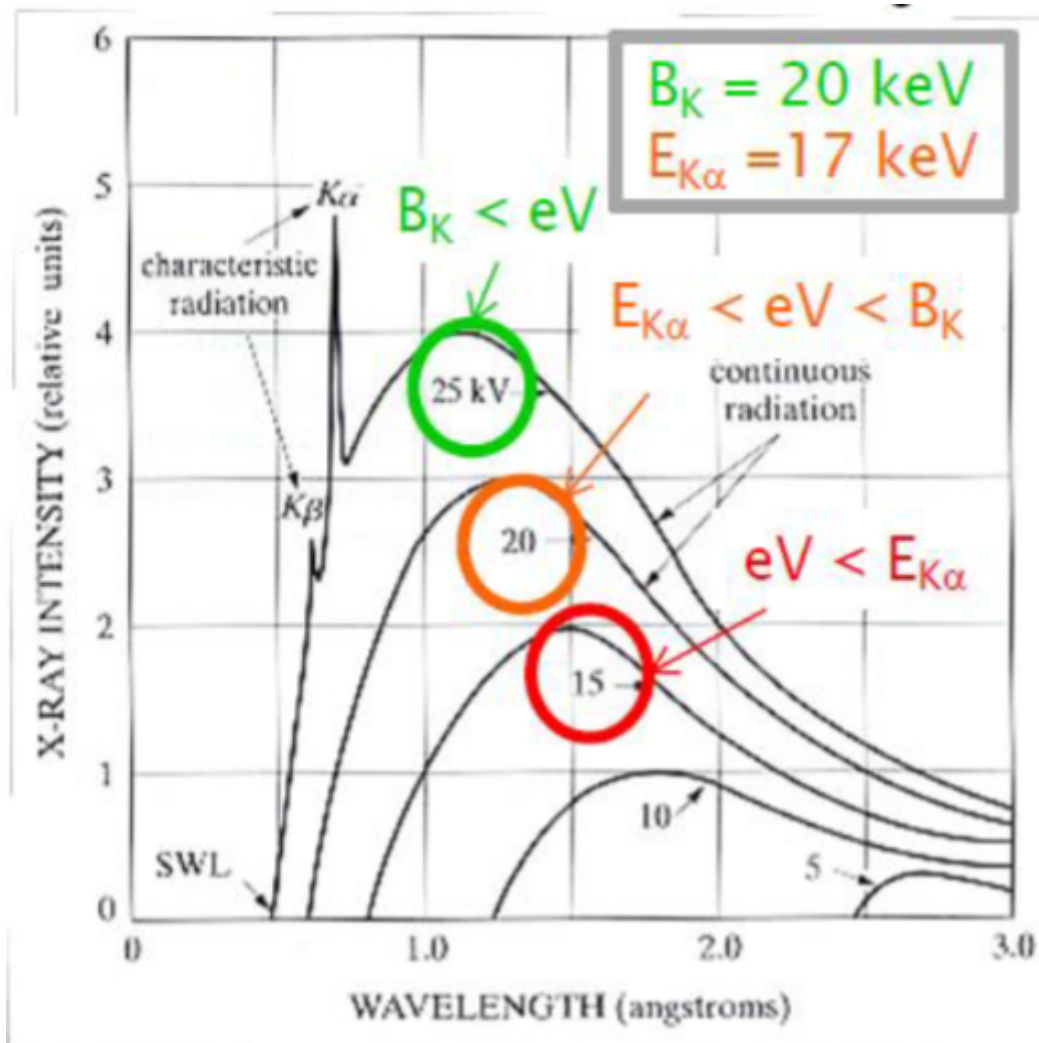
Figure 6.4: Molybdenum X-Ray Spectra (1 Angstrom = 1Å = 0.1nm)

Note that, while Bremsstrahlung is present consistently (albeit with a changing min wavelength where higher accelerating voltage leads to a higher energy x-ray and a lower min wavelength), the sharp spectra lines only appear at higher accelerating voltages where a sufficiently high threshold energy to trigger collisional ionisation is met.

5   X-Ray Absorption

As x-rays pass through a material, x-ray intensity will fall exponentially with distance travelled. Suppose we hit a material with x-rays of intensity I_0. These x-rays travel x distance units. The final intensity is:

$$I = I_0 e^{-\mu x}$$

Where μ, the attenuation coefficient, depends on the material and incoming energy.

$$\mu \propto \frac{1}{E_{\text{x-ray}}^3}$$

This hearkens back to the photoelectric effect.

Absorption drops as energy of the x-ray falls below the binding energy of a given shell.
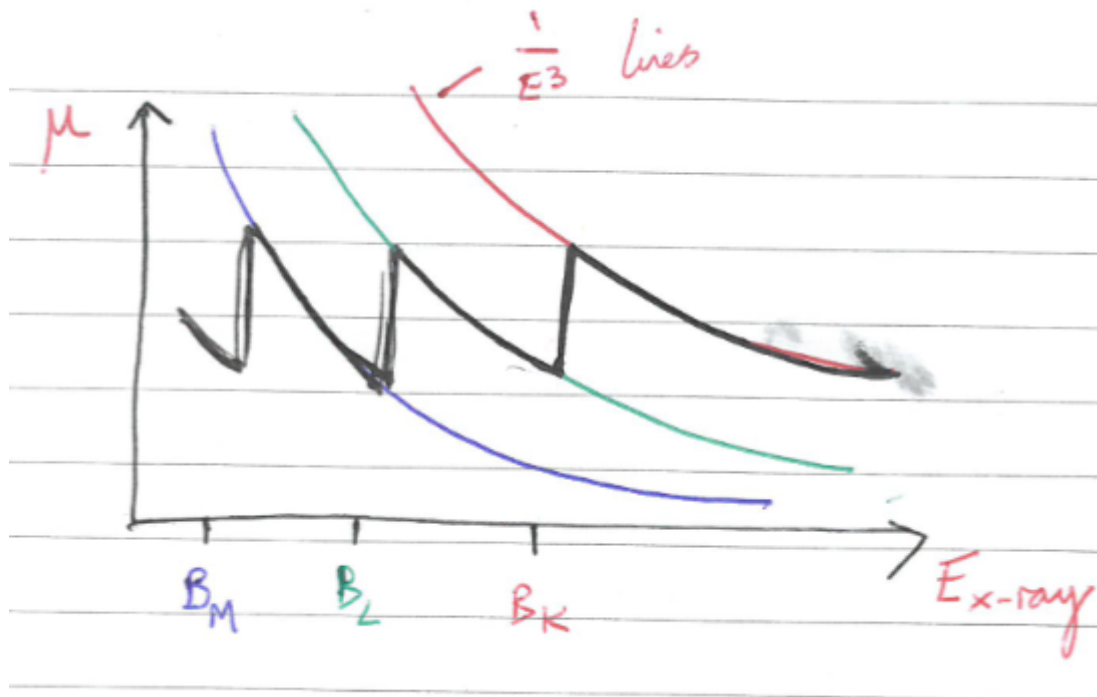
6 Absorption Edges

Figure 6.5: Absorption varying with x-ray energy.

Each line represents the $1/E^3$ value for a given energy shell. If we decrease energy and follow the red line along, we eventually hit the point where there is no longer sufficient energy for ejection from the k-shell. We then drop, and can now eject from everything except from the k-shell until we reach the point where we can no longer eject from the k-shell *or* the l-shell. We drop again, (blue line) and only have emission from all shells except for k and l.

Note:

Figure 6.6

- Measuring these 'absorption edges' lets us determine what atom something is made of, and the associated electronic energy levels.

- Describing these as hard lines is inaccurate, there is (in reality) much more fine detail.

- This process is called x-ray absorption spectroscopy.

Figure 6.7: Fine detail visible in absorption edges (especially visible on L-edge).

7 Moseley's Law

If you measure the frequency of k alpha for some material, it is equal to a constant times (Z-1) squared, where Z is the atomic number. This lets us identify elements:

$$f_{k\alpha} = (2.48 \times 10^{15})(Z - 1)^2$$

Note: the '- 1' appears because there will be a second electron 'left behind' in the k shell, which reduces effective nuclear charge by one. This is called screening or shielding.

Fri 14 Nov 2025 12:00

Lecture 7 - "Matter Waves"

In this lecture:

- Particles acting as waves: de Broglie wavelength.

- Proof: Davisson and Germer experiment.

1   de Broglie Wavelength

We've seen light waves behaving like particles - photons have an energy and momentum related to their wave frequency and wavelength. We can see however that this goes both ways - particles can also behave as waves.

De Broglie suggested that matter/particles should have wave-like properties, and indeed everything behaves as matter, and as waves, and is simultaneously both and neither.

He proposed the De Broglie wavelength:

$$\lambda = \frac{h}{p} = \frac{h}{mv} \tag{7.1}$$

A bigger momentum mv means a smaller wavelength. Taking Paul Hollywood as an example, if he has a 250kg mass and can run at 43mph (=20m/s):

$$p = 5,000 kgms^{-1}$$

$$\lambda = \frac{6.6 \times 10^{-34}}{5000} = 10^{-37}$$

Which is so small it's practically irrelevant. Macroscopic object have such small wavelengths we can effectively ignore them, hence why classical mechanics still holds on a larger scale.

1.1   For an Electron

For an electron accelerated by 54V, we have a KE of $54eV$. First we check that this is non-relativistic:

$$m_e c^2 = (9 \times 10^{-31})(3 \times 10^8)^2 = 8 \times 10^{-14} J = 500,000 eV$$

Therefore KE is much less than the relativistic mass-energy, so classical mechanics are fine. Now:

$$E = \frac{1}{2}mv^2 = \frac{p^2}{2m} \implies p = \sqrt{2mE}$$

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mE}} = \frac{h}{\sqrt{2meV}}$$

$$\lambda = 1.67 \times 10^{-10} m = 1.67 \text{Å}$$

This is no longer small enough that we can get away with totally ignoring it.

2   Experimental Verification - Davisson and Germer

They fired electrons into the surface of metal (with an accelerating voltage of 54V). They measured electron intensity in a scattered beam vs angle. They predicted that electrons should be diffracted, as if they were waves. They observed a constructive interference pattern, equivalent to x-rays.
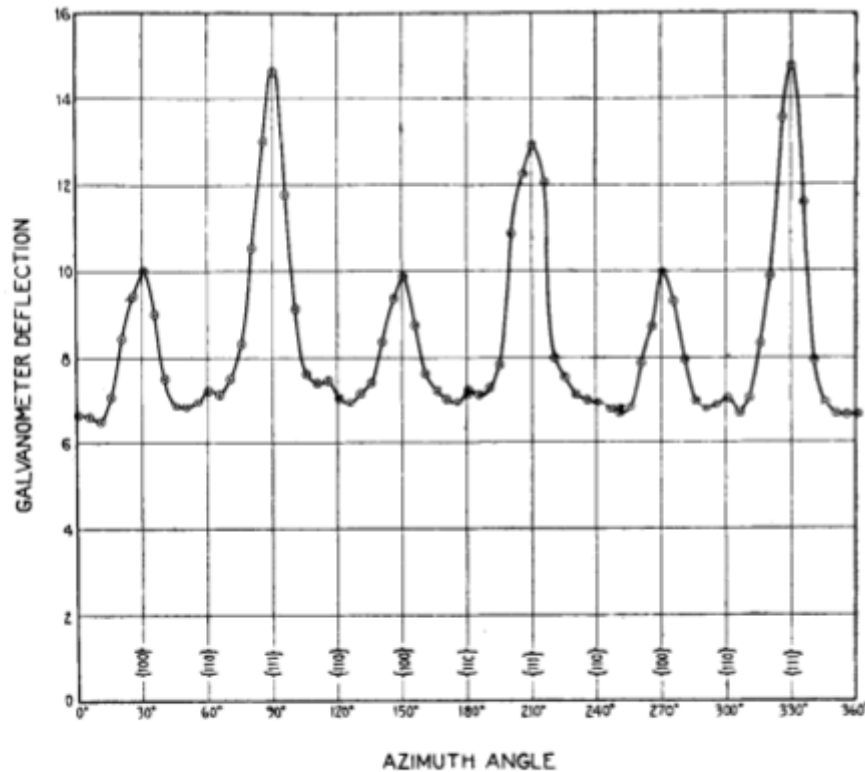

FIG. 2.—Intensity of electron scattering vs. azimuth angle—54 volts, co-latitude 50°.
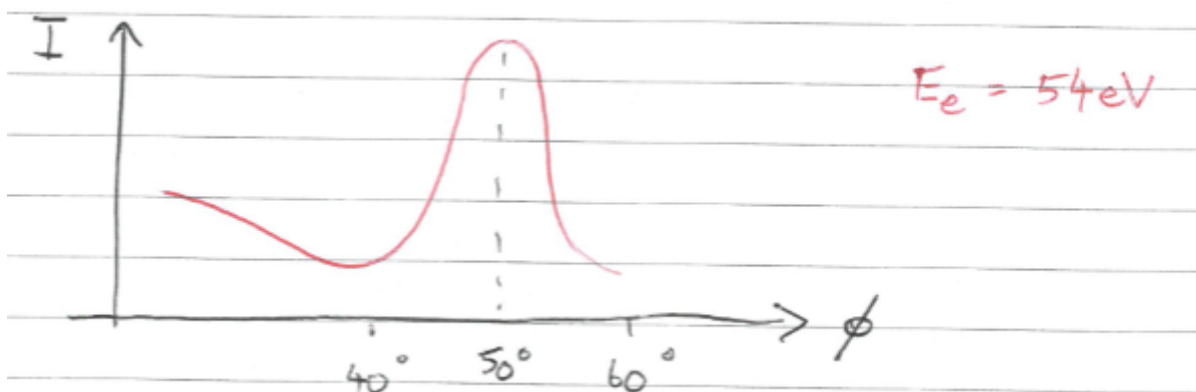
Figure 7.1

3   Their Result

Figure 7.2

We interpret the peak at $\phi = 50$ as due to electron diffraction. Note that the 'scattering angle', ϕ measured is not the same as the Bragg angle θ.
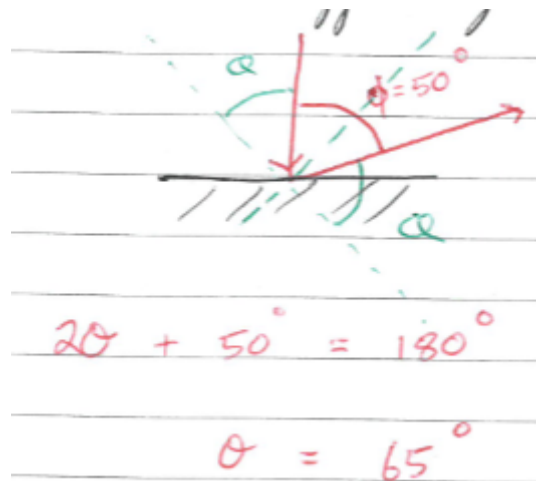
Figure 7.3

3.1 Explaining the Result

Given the Bragg condition $2d \sin \theta = n\lambda$, and $d = 0.91$Å, we take $n = 1$ for the central peak, and substitute to get $\lambda = 1.65 \times 10^{-10}$m. This is (approximately) what we predicted earlier. Note that this is now the Bragg angle θ, not ϕ.

3.2 GP Thomson

At the same time, G.P. Thomson conducted 'powder diffraction'. Grinding a crystal into a powder creates a mess of smaller sub-crystals. This replaces the need for scanning and matching in/out angles, as there will be some correct orientation crystal for any input angle. Since the many small cystallites will be arranged at many angles, we can effectively consider getting all possible angles at once. This means that there will be some cystallites which always satisfy the Bragg conditions, *if λ makes this possible*.

There is some rotational symmetry, so we get rings produced, and if we use electrons and x-rays on the same target, we can see we get the same pattern.
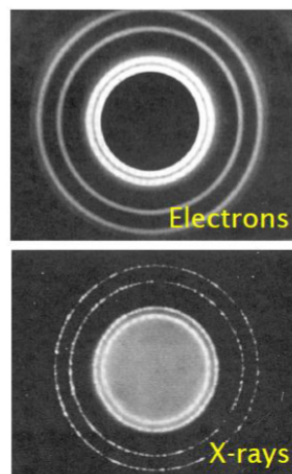

Figure 7.4

This is a little bit difficult to think about, as what does the 'amplitude' of a matter wave actually mean? This is easy to define with EM waves, in terms of the EM field, but not for matter...

4 Back to Bohr

Looking back to the Bohr model, we want to get:

$$E_n = \frac{-13.6eV}{n^2} \tag{7.2}$$

As a starting point, the electron must 'fit' into a circular orbit. Electrons are in a potential well and are bound to a positively charged nucleus:

$$V(r) = \frac{-e}{4\pi\epsilon_0 r}$$

$$u(r) = \frac{-e^2}{4\pi\epsilon_0 r}$$

The electron is in the nth orbital, with a radius r_n, velocity v_n. Plotting wave function amplitude against circumference:

Figure 7.5

We note that this must be continuous, so the ends must join up:

$$2\pi r_n = n\lambda_n = n\frac{h}{p_n} = n\frac{h}{mv_n} \tag{7.3}$$

Also (this is non-relativistic so we can use circular motion)

$$F = ma = \frac{mv^2}{r} \tag{7.4}$$

$$\frac{e^2}{4\pi\epsilon_0 r_n} = mv_n^2 \tag{7.5}$$

We can use 7.3 and 7.5 to eliminate v_n and show:

$$r_n = n^2 a_0, \qquad a_0 = \frac{\epsilon_0 h^2}{\pi m e^2} = 5.2918 \times 10^{-11} \text{ ("Bohr Radius")}$$

4.1 Energies

Using 7.3:

$$2\pi r_n = n\lambda_n = n\frac{h}{p_n} = n\frac{h}{mv_n}$$

$$p_n = \frac{nh}{2\pi r_n}$$

And using our new result:

$$p_n = \frac{nh}{2\pi r_n} = \frac{h}{2\pi n a_0}$$

Kinetic Energy

$$T_n = \frac{p_n^2}{2m} = \frac{h^2}{8\pi^2 mn^2 a_0^2} = \frac{me^4}{8\epsilon_0^2 h^2 n^2} = +\frac{13.6}{n^2}$$

Potential Energy

$$U_n = \frac{-e^2}{4\pi\epsilon_0 r_n} = \frac{-e^2}{4\pi\epsilon_0 n^2 a_0} = \frac{-me^4}{4\pi\epsilon_0^2 h^2 n^2} = -\frac{27.2}{n^2} eV$$

Total Energy

$$E_n = T_n + u_n = \frac{-13.6}{n^2} eV$$

This is the Bohr Model result, as required.

5 Conclusions

- Matter is wave-like, with a wavelength given by de Broglie wavelength.

- Electrons can therefore interfere, which we see with electron diffraction.

- A wave-like electron gives us the observed Bohr model result.

$$U_n = \frac{-e^2}{4\pi\epsilon_0 r_n} = \frac{-e^2}{4\pi\epsilon_0 n^2 a_0} = \frac{-me^4}{4\pi\epsilon_0^2 h^2 n^2} = -\frac{27.2}{n^2} eV$$

Fri 21 Nov 2025 12:00

Lecture 8 - Wave-Particle Duality

In this lecture:

- Particles acting as waves and vice-versa - depends on how we look at/measure them.

- Infinite potential wells - quantisation of energy in bound states, zero-point energy.

- The Heisenberg Uncertainty Principle.

1 Single Slit (Fraunhofer) Diffraction

We have seen particles behaving like waves (i.e. electron diffraction) and waves behaving like particles (i.e. the photoelectric effect). This seems to depend on how we look at them - different experiments give different results.

Broadly, they seem to be wave-y when in motion (i.e. interference), and particulate when detected. In a single-slit experiment, we can see both at the same time. We fire electrons through a single slit, and measure the diffraction pattern with a screen or movable detector:

Figure 8.1

We can do this experiment with either photons, or with electrons and we observe the same result: both yield the same interference pattern due to superposition of waves cancelling each other out.

What if we turned the source way down and fired a single photon/electron at a time. We would therefore detect individual particles on our detector as they arrive one-by-one. Surely, therefore, we wouldn't get a diffraction pattern? We do, however, get a pattern...What are they interfering then, if there's no other particles to interfere with? It turns out the particle interferes with itself.

We view the intensity profile as a probability distribution of any one particle impacting here. The areas of the profile with a higher probability have a higher measured intensity, to be expanded on next lecture. The amplitude of a particle wave at a point represents the probability of the particle being found at that point.

2   Infinite Potential Wells

Given a particle in an infinite potential well, how is this impacted by wave-like behaviour of the particle?

Figure 8.2

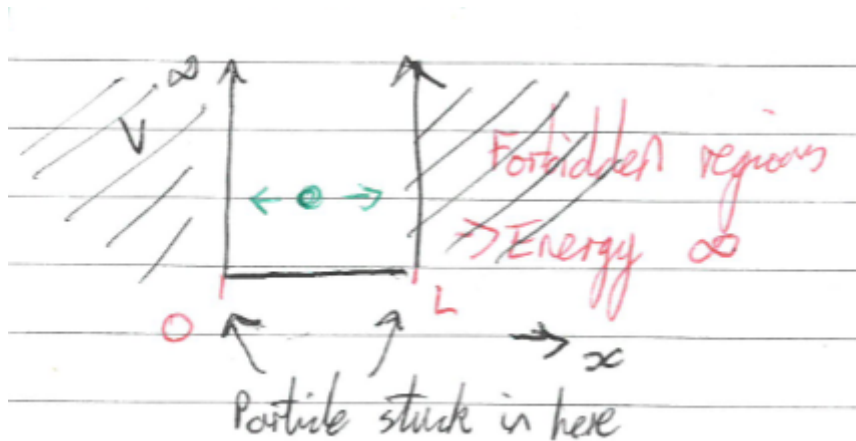Classically, we can think of this as a squash court with a particle bouncing back and forth between the two left and right boundaries. The particle is stuck between zero and L, with potential energy measured on the y-axis. Note that that since the y-axis is energy - it is not spatial. The only possible spatial movement of the particle is left-to-right.

Quantum mechanically, we have the following rules:

- The particle has finite energy. It therefore only has amplitude (probability of finding the particle) at this one spot.
- The wave function of a particle has to be continuous throughout. Discontinuities break things.

As a result of these two rules, the wavefunction $\psi(x)$ must be zero at the boundary points 0 and L. We also assume that we can define any wavefunction as a sine wave:
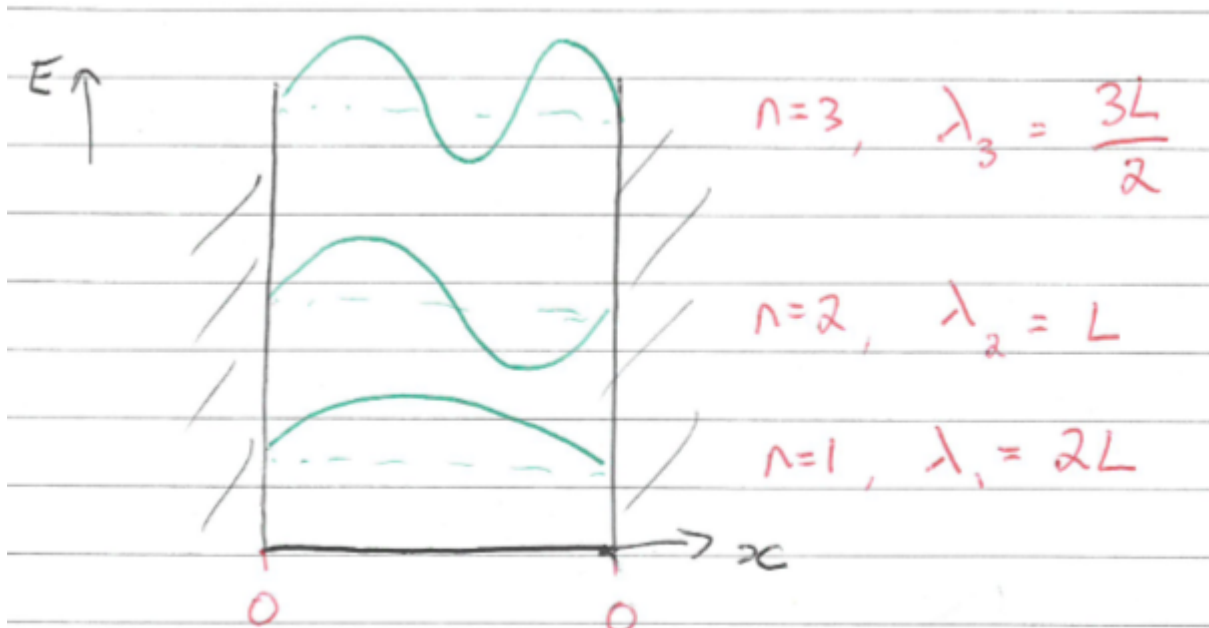
$$\psi(x) = A \sin \frac{n\pi x}{L}, \quad n = 1, 2, 3, \dots$$

Therefore:

$$\lambda_n = \frac{2L}{n}$$

We can generate more complicated shapes using Fourier Decomposition, where we define a more complex wave function as the sum of (potentially infinitely) many sine waves.

Considering this wave function at multiple different energies (infinitely many as we're in an infinite well):

Figure 8.3: Note: Bigger n is higher energy.

We know from last lecture that we can relate wavelength and momentum, so:

$$p = \frac{h}{\lambda} \implies p_n = \frac{nh}{2L}$$

$$E = \frac{p^2}{2m} = \frac{n^2 h^2}{8mL^2}$$

Note that $E \propto n^2$ in an infinitely deep 1D potential well. Compare this to $E \propto \frac{1}{n^2}$ in a H atom.

Energy is uniquely determined for each quantum state $\psi_n(x)$ for the particle in the well. If we consider momentum: classically we say the particle is moving either to the left *or* or the right, with a known magnitude but an unknown direction (if we take a single observation as a snapshot in time).

For n=1:

$$p_x = \pm \frac{h}{2L}$$

Which is effectively zero momentum but with an uncertainty of $\Delta p_x = \frac{h}{2L}$. The expectation value (average value):

$$\langle p_x \rangle = 0$$

And for x (somewhere in the well):

$$\langle x \rangle = \frac{1}{2}L$$

With an uncertainty of:

$$\Delta x = \pm \frac{1}{2}L$$

3   Shrinking the Well

What happens if we shrink the well? Both momentum and energy are inversely proportional to cavity length:

$$p \propto \frac{1}{L}$$

$$E \propto \frac{1}{L^2}$$

Therefore they both go up. This is weird in classical mechanics. We now know less about momentum (higher uncertainty) but more about the particle's location (smaller set of possible values, lower uncertainty than before). This isn't a proof, but a hint towards the Heisenberg Uncertainty Principle.

4 Heisenberg Uncertainty Principle

$$\Delta x \Delta p_x \geq \frac{\hbar}{2} \tag{8.1}$$

Where: $\hbar = \frac{h}{2\pi}$. In QM, there is a limit to how well we can know two conjugate (effectively paired, formal word to mean a pair of variables where knowing one of them perfectly precludes knowing the other) observables simultaneously. This also applies to energy w.r.t. time:

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

Note that in a 2D system, $\Delta p_x \Delta y$ is unrestricted as they are independent and non-conjugate observables. In our example:

$$\Delta x \Delta p_x = \frac{L}{2} \frac{h}{2L} = \frac{h}{4} \geq \frac{h}{4\pi}$$

The single slit diffraction is a good example of this. If we measure the x of a photon by passing it through a slit, we lose information on its momentum and it spreads out along x.

Figure 8.4

5 Conclusions

- Wave-particle duality allows particles to both diffract as if waves and to be quantised like particles.

- Wave-like particles explains why the energy in a bound system has to be quantised (as shown before) due to standing waves in a potential well.

- Energy levels depend on the shape of the potential well.

    - $E \propto n^2$ in an infinitely deep 1D well.

    - $\frac{1}{n^2}$ in a H atom.

- We cannot know a particle momentum and position simultaneously to perfect precision, we are limited that if we know one very very accurately, we cannot know the other very well.

Fri 28 Nov 2025 12:00

Lecture 9 - Wavefunctions for Quantum Particles

In this lecture:

- Reminder and recap of the classical wave equation, building to the complex quantum mechanical version.

- The idea of probability density and probability amplitude.

- The idea of standing waves and the "particle in a box" being modelled as one.

1 Recap of Classical Waves

The classical wave equation is:

$$\frac{\partial^2 E}{\partial x^2} = \frac{1}{c^2}\frac{\partial^2 E}{\partial t^2} \tag{9.1}$$

Solutions to this have the form:

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

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

As the wave equation is linear, linear sums of individual solutions form a solution. I.e. the summation of two different wave functions in this form is also a wave function. Recall that $k = 2\pi/\lambda$ "the wave number" and $\omega = 2\pi f$ "angular frequency".

1.1 Direction

Wavefunctions with $kx - \omega t$ move to the right (in the positive x direction).

Wavefunctions with $kx + \omega t$ move to the left (in the negative x direction).

1.2 Phase

Consider some point on a wave. Each point has a phase ϕ, given by $\sin\phi = \sin kx - \omega t$. The phase of a point is constant, regardless of propagation.

$$\phi = kx - \omega t \tag{9.2}$$

For a constant point, i.e with phase $\pi/2$, the phase must be constant. Hence, as time increases, x must also increase, and hence the wave must be moving rightwards along the positive x-axis, as required.

To verify this, we can differentiate wrt time, considering a point where phi does not change, so the derivative is zero:

$$\frac{\partial \phi}{\partial t} = k\frac{\partial x}{\partial t} - \omega\frac{\partial t}{\partial t} = 0$$

$$k\frac{\partial x}{\partial t} = \omega$$

$$\frac{\partial x}{\partial t} = \frac{\omega}{k} > 0 \qquad \text{so travelling right.}$$

This also happens to prove the wave speed equation again.

1.3   Things Get Complex

It is important to note that we are often dealing with complex representations, that we'll need when things become quantum-y. We can also write a solution to the wave equation as:

$$E(x,t) = \mathfrak{Re}\left\{Ee^{i(kx-\omega t)}\right\}$$

This doesn't change anything, it's just a convenient repacking of the trigonometric terms into a slightly nicer form - it's just a maths trick. Even if not stated, there is always an implicit "take the real part" at the end, to get the actual cos() etc terms and real numbers we care about.

2   Quantum Mechanical Wave Function

In QM, the biggest change is that the particle wavefunction **truly is complex**. We do not take the real part at the end, and represents something which is fundamentally a complex number. Therefore, the wave function is:

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

Again, note that both $\psi(x,t)$ and A are complex numbers. We can rewrite A as $A = A'e^{i}$, where A' is some real number.

We can now split up the terms:

$$\psi = Ae^{ikx}e^{-i\omega t}$$

Where the first term is the spatial function $\psi(x)$ and the second term is the time dependence (or phase) $\phi(t)$. This is the wavefunction for a particle moving in the positive x, while something moving in the negative x would be:

$$\psi = Ae^{-ikx}e^{-i\omega t}$$

Note that this is just conventions, and direction could instead be bundled into the A term, but we ignore this here.

3   What Does This Really Mean?

The amplitude of the quantum wavefunction for a particle represents the probability *amplitude*. This is a complex number, so has a magnitude and a phase. This phase is what gives us interference.

We physically cannot measure the phase of a particle such as an electron or a photon - it is not an observable. We can compare the phase difference between two particles, and one phase relative to another, but we cannot measure absolute phase in QM.

3.1   Observables

Something which we physically can measure is called an observable. They must be real numbers only. Something which is not an observable physically cannot be measured, regardless of how good the equipment is etc. In QM, this means we take complex conjugates to get to an observable.

Recall:

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

Then:

$$z * z = a^2 + b^2 = |z|^2$$

Which is real. This gives us *probability density*, which is something we can actually measure.

$$P(x) = \psi^*(x)\psi(x) = |\psi|^2$$

This gives us the probability density function for finding this particle at some position x. Note that we have to integrate over a range of x values to get an actual probability from this probability density.

The probability of finding the particle at some exact precise value $x = a$, where a is some real number is precisely zero. We must integrate over a range, and get a probability for this range - as x can take any continuous value, the probability of finding the particle at any one (of infinitely many) is infinitely small. This is also forbidden by the uncertainty principle (Lec 08).

4 Particle in a Box

Standing waves become a key concept for a particle constrained in a box. A standing wave is made up of two parts:

- A wave propagating in one direction: e^{ikx}.

- A reflected wave propagating in the opposite direction: e^{-ikx}

We know that we can add the superposition of two different solutions to the wave equation, to give another solution, so:

$$\psi = A_1 e^{ikx} e^{-i\omega t} + A_2 e^{-ikx} e^{-i\omega t}$$

Since the box is symmetrical, $A_1 = -A_2$ (a positive equality works too, we just get a cosine rather than a sine).

$$\psi = A_1 \left(e^{ikx} - e^{-ikx} \right) e^{-i\omega t}$$
$$= A_1 \left([\cos(kx) + i\sin(kx)] - [\cos(-kx) + i\sin(-kx)] \right) e^{-i\omega t}$$
$$= A_1 \left([\cos(kx) + i\sin(kx)] - [\cos(kx) - i\sin(kx)] \right) e^{-i\omega t}$$
$$= A_1 \left([i\sin(kx)] - [-i\sin(kx)] \right) e^{-i\omega t}$$
$$= A_1 2i\sin(kx) e^{-i\omega t}$$

$$\boxed{\psi = A\sin(kx)e^{-i\omega t} \qquad \text{where: } A = A_1 2i}$$

And using this to find probability density:

$$P(x) = \psi^*\psi = A^*A \sin(kx)\sin(kx)e^{-i\omega t}e^{i\omega t}$$
$$= |A|^2 \sin^2(kx)$$

In the last lecture, we related k to the length of the box, and the energy state of the particle trapped in it. Using this, and considering the $n = 1$ energy level:

$$P(x) = |A|^2 \sin^2 \frac{\pi x}{L}$$

Note that in many situations, albeit not this one, $P(x)$ may be time dependent. $P(x)$ is also not uniform. Classically, we would expect a uniform probability for the particle's location equal at all points. However, using this QM wavefunction, we have a much greater probability of finding the particle at the centre of the box than the outer regions.
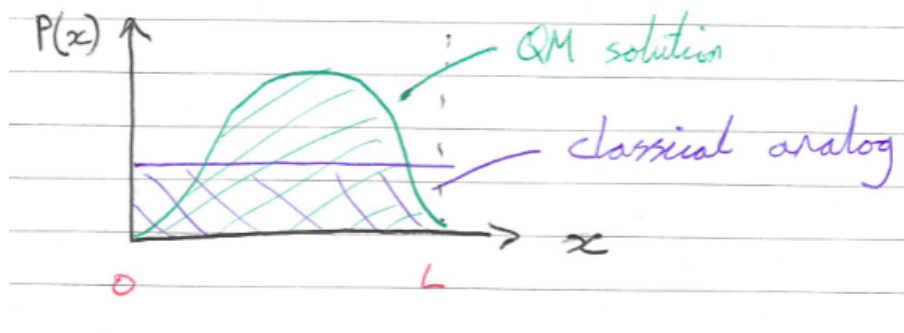

Figure 9.1

4.1 Normalisation

Previously, we've mostly ignored the value of A. However, in order to get numerical values out, we need to find a value for $|A|^2$. Since $P(x)$ is a probability distribution, the integral of the p.d.f. from negative to positive infinity must be one (i.e. the particle is trapped in the box, and must be *somewhere*).

$$\int_{-\infty}^{\infty} P(x)\,dx = \int_0^L |A|^2 \sin^2 \frac{\pi x}{L}\,dx = 1$$

We can change the bounds as we know the particle must be in the box somewhere, so the probability of finding it outside of the box is zero.

$$= |A|^2 \int_0^L \frac{1 - \cos\left(\frac{2\pi x}{L}\right)}{2}\,dx$$

$$= \frac{|A|^2}{2} \int_0^L \left(1 - \cos\left(\frac{2\pi x}{L}\right)\right) dx$$

$$\frac{|A|^2}{2}\left[x - \frac{L}{2\pi}\sin\left(\frac{2\pi x}{L}\right)\right]_0^L = 1$$

$$\frac{|A|^2}{2}(L - 0) = 1$$

$$|A|^2 \frac{L}{2} = 1$$

$$\boxed{|A|^2 = \frac{2}{L}}$$

Therefore:

$$P(x) = \frac{2}{L}\sin^2 kx \qquad \text{for } n = 1$$

Note that this value of the prefactor A is true only for this geometry of problem.

4.2 Using This!

Now we have no unknown prefactors, we can find actual probabilities. For example, the probability of the particle being in the right half of the box is given by:

$$\int_{L/2}^{\infty} P(x)\,dx = \int_{L/2}^L \frac{2}{L}\sin^2 kx\,dx$$

$$= \frac{2}{2L}\int_{L/2}^L 1 - \cos(2kx)\,dx$$

$$= \frac{1}{L}\left[x - \frac{\sin 2kx}{2k}\right]_{L/2}^L$$

And using $k = 2\pi/\lambda = 2\pi/2L = \pi/L$ (for the $n = 1$) energy level, per Lec 08:

$$= \frac{1}{L}\left[x - \frac{\sin\frac{2\pi x}{L}}{\frac{2\pi}{L}}\right]_{L/2}^L$$

$$= \frac{1}{L}\left(\left[L - \frac{\sin\frac{2\pi L}{L}}{2\pi/L}\right] - \left[\frac{L}{2} - \frac{\sin\frac{2\pi L}{2L}}{2\pi/L}\right]\right)$$

$$= \frac{1}{L}\left(\left[L - \frac{\sin 2\pi}{2\pi/L}\right] - \left[\frac{L}{2} - \frac{\sin \pi}{2\pi/L}\right]\right)$$

$$= \frac{1}{L} \left(L - \frac{L}{2} \right)$$

$$= \frac{1}{2}$$

This makes physical sense, as we're considering half the box, and the box (and the p.d.f. for the particle) are symmetrical.

Fri 05 Dec 2025 12:00

Lecture 10 - A Quantum Mechanical Wave Equation

In this lecture:

- The Schrödinger Equation.

- Expectation values of observables.

1 Recap

For a free particle, moving in the +'ve x direction, the wavefunction is given by:

$$\psi = Ae^{ikx}e^{-i\omega t}$$

Where the first e-term is the position dependence, and the second is the time dependence. We can separate these two terms.

2 The Schrodinger Equation

Note: This is not derivable from basic physics. It is a postulate, like the Bohr model, which we are confident is true because it's been empirically demonstrated.

We want to build a wave equation for a quantum mechanical free particle in a potential $V(x, t)$. This is a 1D potential with free movement in the x direction only. This wave equation is the Schrodinger Equation.

We assume the following:

- Conservation of Energy applies, hence total energy is kinetic + potential energy. $T + V = E$.

- The equation is a linear differential equation. We need this, otherwise superposition would break, as this relies on two solutions to the wave equation being added together also forming a linear solution.

- This must not break the existing rules we've worked out, so $P = \frac{h}{\lambda} = \hbar k$ and $E = hf = \hbar\omega$

2.1 Constructing the TISE

Now we play a game of "guess the terms" to try to determine values for kinetic, potential and total energy. We can then substitute these into $E = T + V$. This is **not** a formal derivation, but is a motivated construction.

We start with our wave function:

$$\psi = Ae^{ikx}e^{-i\omega t}$$

We note that this has k and ω present, so we have sufficient information to determine momentum and energy. We start by differentiating wrt x:

$$\frac{\partial}{\partial x}\psi(x, t) = ikAe^{ikx}e^{-i\omega t} = ik\psi$$

This lets us extract an ik, but we want a $\hbar k$. Since $(ik)(-i\hbar) = \hbar k$, we can multiply by $-i\hbar$ to get $\hbar k$:

$$-i\hbar\frac{\partial}{\partial x}\psi = (-i\hbar)(ik)(\psi) = (\hbar k)\psi$$

Crucially, this seems to let us extract $\hbar k$, and therefore find momentum. We're going to define the momentum operator in the x direction as:

$$\hat{p}_x = -i\hbar\frac{\partial}{\partial x}$$

We can apply this operator to our wavefunction to determine x-directional momentum. Every observable will have an operator that we can apply to determine it.

We can write this as an eigenvalue equation (where the L.H.S is application of an operator, not multiplication):

$$\hat{p}_x[\psi] = p_x\psi$$

This is defined as doing some operator onto a function, and getting back some multiple of the wavefunction, where that multiple is a useful quantity. This p_x is the x-direction momentum and is a real number - we call this the eigenvalue. Note that, like matrices, operators are not commutative, so $\hat{p}_x\psi \neq \psi\hat{p}_x$.

It is important to note that the fact this works and we can get an eigenvalue tells us that momentum is a well defined quantity in this system, which is not always going to be true.

2.2 Finding Kinetic Energy

Now we have momentum, we can use the following to determine kinetic energy:

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

What if we therefore had:

$$\hat{T} = \frac{1}{2m}\hat{p}\hat{p} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$$

Where the two $\hat{p}$s represent two subsequent applications of the momentum operator.

2.3 Total Energy

For total energy, we want to pull out ω as $E = \hbar\omega$. We therefore get:

$$\hat{E} = i\hbar\frac{\partial}{\partial t}$$

2.4 Potential Energy

Potential Energy V is totally general and can be ugly. We only consider simple constant potentials in QM1. This gives us a neat:

$$\hat{V}\psi = V\psi$$

Where V is a known and constant value for potential.

2.5 Putting It All Together

Now we have these operators, we can substitute them into $T + V = E$ to get the Schrodinger Equation.

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

When the potential is independent of time, we can factorise out the t dependence to get to the Time Independent Schrodinger Equation, TISE, (given in formula sheets). We begin by separating the time terms:

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

Dividing both sides by $\phi(t)\psi(x)$:

$$\underbrace{\frac{1}{\psi(x)}\left[-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x)\right]}_{\text{spatially dependent}} = \underbrace{\frac{i\hbar}{\phi(t)}\frac{d\phi(t)}{dt}}_{\text{time dependent}}$$

Since the L.H.S is purely spatial, and the R.H.S purely time, they are entirely independent. It is only true that these are equal for all points in space and time if these are equal to a constant. We call this constant E.

$$\frac{1}{\psi(x)}\left[-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x)\right] = E$$

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

Or we can rewrite this as:

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

The contents of the brackets form an operator. We call this the "Hamiltonian":

$$\hat{H}[\psi] = E\psi$$

3   Expectation Values

Expectation values represent the average of an observable. It is denoted with angle brackets, for example:

$$\langle p_x \rangle$$

Is the average value for x-momentum if measured many times. In order to get this, we sandwich the operator between ψ^* and ψ and we integrate. For example, the operator for $\hat{x}$ is just $= x$. Therefore:

$$\langle x \rangle = \int_{-\infty}^{\infty} \psi^* x \psi \, dx$$

Going back to our infinite well example:

$$\psi_1 = \sqrt{\frac{2}{L}}\sin kx, \qquad k = \pi/L$$

$$\langle x \rangle = \frac{2}{L}\int_0^L x \sin^2\left(\frac{\pi}{L}x\right) dx$$

$$= \frac{2}{2L}\int_0^L x \left(1 - \cos\left(\frac{2\pi x}{L}\right)\right) dx$$

Carrying out the integral by parts, we get:

$$\langle x \rangle = \frac{L}{2}$$

Which is physically sensible, we expect the particle to lie, on average, in the middle. Note that this is an average. If we had a particle at $n = 2$, the standing wave created would have a node at $L/2$. This means it would be impossible to find the particle in the middle, but we can still have this as our expectation value.

4   In Conclusion

- Operators pull out observables from the wavefunction.
- We build operators for kinetic (T), potential (V) and total energy (E) and substitute into $T + V = E$ to get the Schrodinger Equation.
- Expectation values give us average values of an operator. This lets us find average values for things without well defined eigenvalues.

Fri 12 Dec 2025 12:00

Lecture 11 - Applications of The Schrodinger Equation

Recap:

- Operators bring out observables from wavefunctions.
- We can build operators for T, E, V and substitute them into energy conservation $T = E + V$ to get the Schrodinger Equation.
- Expectation values let us find 'average' values for observables that are not well defined eigenvalues of a wavefunction.

In this lecture:

- Using the Time Independent Schrodinger Equation to solve free-particle at a step problems.
- Reflection and quantum tunnelling.

1 Potential Step Where $E \geq V_0$

Consider a particle of mass m incident on a 'potential step' at $x = 0$. Note that the energy of the incoming particle has greater energy than the step potential, so $E > v_0$. This means the particle has sufficient energy to exist in the region, otherwise the particle would be trapped on the left (effectively half a potential well). This particle has enough energy to get past the step with excess K.E.
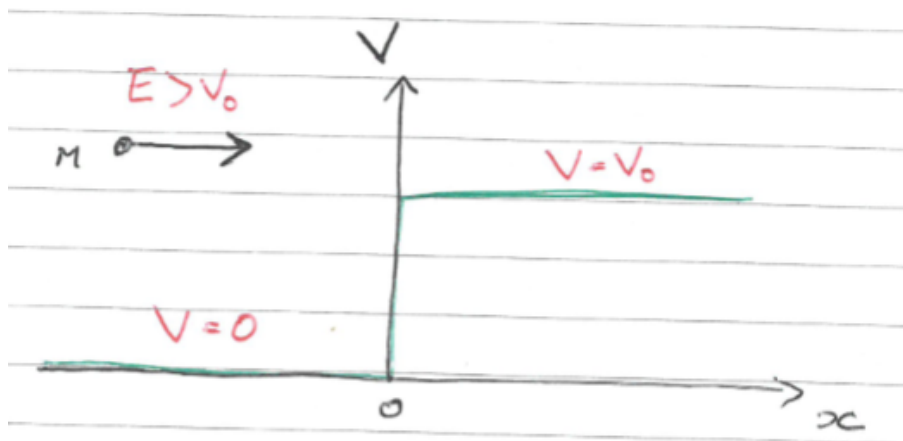

Figure 11.1

In each of the two regions of constant potential, there is no force on the particle:

$$F = -\frac{dV}{dx} = 0$$

The most general form of the T.I.S.E is given by the wave function in the two regions. We have to do this piecewise, as the solution in each area of constant potential will be different:

For $x < 0$, consider ψ_1:

$$\psi_1 = Ae^{ik_1 x} + Be^{-ik_1 x}$$

Where the A term is the incident wave and the B term is the reflected wave.

For $x \geq 0$, consider ψ_2:

$$\psi_2 = Ce^{ik_2 x}$$

Note that there is no reflection term, as the region of $x > 0$ has no boundary, hence no reflected wave from the right.

1.1 Verifying Solutions

Lets show that ψ_2 is a solution of the TISE:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_2}{dx^2} + V_0\psi_2 = E\phi_2$$

$$-\frac{\hbar^2}{2m}\left[(ik_2)^2 Ce^{ik_2 x}\right] + V_0\psi_2 = E\psi_2$$

$$-\frac{\hbar^2}{2m}(ik_2)^2\psi_2 + V_0\psi_2 = E\psi_2$$

$$\implies k_2 = \frac{\sqrt{2m(E - V_0)}}{\hbar}$$

If this equality is true, *then* ψ_2 is a solution of the TISE. In other words, ψ_2 is a solution of the TISE for this value of k_2 (only).

Doing the same for ψ_1 gives us:

$$k_1 = \frac{\sqrt{2mE}}{\hbar}$$

So ψ_1 is a solution of the TISE for this value of k_1.

1.2 Boundary Conditions

We still, however, do not know the values of A, B, C (where $A, B, C \in \mathbb{C}$). We can do this by "matching up" the two wavefunctions by applying boundary conditions for the boundary between the area of zero potential and the potential step (at $x = 0$)

(1) The wavefunction must be continuous.   Since $p \propto \frac{\partial \psi}{\partial x}$, momentum will tend to infinity if there is a discontinuity in the wavefunction. Therefore, there cannot be any jump, and:

$$\psi_1(0) = \psi_2(0)$$

(2) The gradient of the wavefunction must be continuous.   Since $E \propto \frac{\partial^2 \psi}{\partial x^2}$ the same logic applies. We cannot have a particle of infinite energy, so the gradient of the wavefunction must also be continuous. Note: this does not apply in the infinite potential well case, as we do allow the concept of infinite energy in that model.

$$\left.\frac{\partial \psi_1}{\partial x}\right|_{x=0} = \left.\frac{\partial \psi_2}{\partial x}\right|_{x=0}$$

From (1):

$$Ae^{ik_1 0} + Be^{-ik_1 0} + Ce^{ik_2 0}$$

$$\boxed{A + B = C}, \qquad \text{noting: } A, B, C \in \mathbb{C}$$

From (2):

$$ik_1\left(Ae^{ik0} - Be^{-k_1 0}\right) = ik_2 Ce^{ik_2 0}$$

$$A - B = \frac{k_2}{k_1}C$$

Lets use this to find the probability of a particle reflecting, given by R. From now on we specify $E \geq V_0$ not just $E > V_0$:

$$R = \left| \frac{\text{reflected amplitude}}{\text{incident amplitude}} \right|^2$$

$$R = \left| \frac{B}{A} \right|^2$$

Eliminating C shows that:

$$R = \left| \frac{k_1 - k_2}{k_1 + k_2} \right|^2$$

And we know $k_2 \propto \sqrt{E - V_0}$ and $k_1 \propto \sqrt{E}$. We can check some values:

- When $E = V_0$: $k_2 = 0 \implies R = 1$.
- When $E > V_0$: As $E \to \infty$, the $\sqrt{E - V_0}$ is dominated by the E term, and we end up with a square root decay curve tending towards zero.

This makes physical sense. We start with a high probability of reflection, which becomes smaller and smaller as we turn up the energy (or decrease the step). However, there is an asymptote at $R = 0$, and the curve is never equal to zero. There is always *some* probability of reflection.
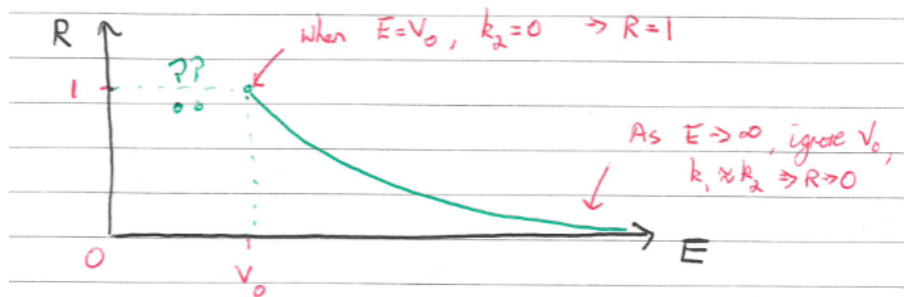

Figure 11.2

2   What if $E < V_0$?
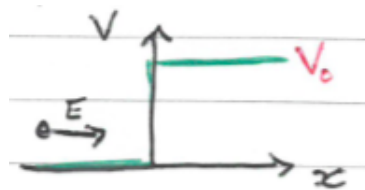

Figure 11.3

Classically, $x > 0$ is completely impossible. The particle must bounce off and cannot exist in this region. Let's approach from a QM perspective and reconsider k_2:

$$k_2 = \frac{\sqrt{2m(E - V_0)}}{\hbar}$$

The contents of the square root are now negative. We can rewrite this (to simplify a little) as:

$$k_2 = \frac{i\sqrt{2m(V_0 - E)}}{\hbar}$$

This changes our wave function, and so:

$$\psi_2 = C \exp\left(ii \frac{\sqrt{2m(V_0 - E)}}{\hbar} x \right)$$

Letting $\alpha = \sqrt{2m(V_0 - E)}/\hbar$ which is a constant.

$$\psi_2 = Ce^{-\alpha x}$$

This is no longer a wavefunction, and is simply exponential decay. This makes sense, as the particle classically cannot truly exist in the region of too high energy. Sketching probability density against x:
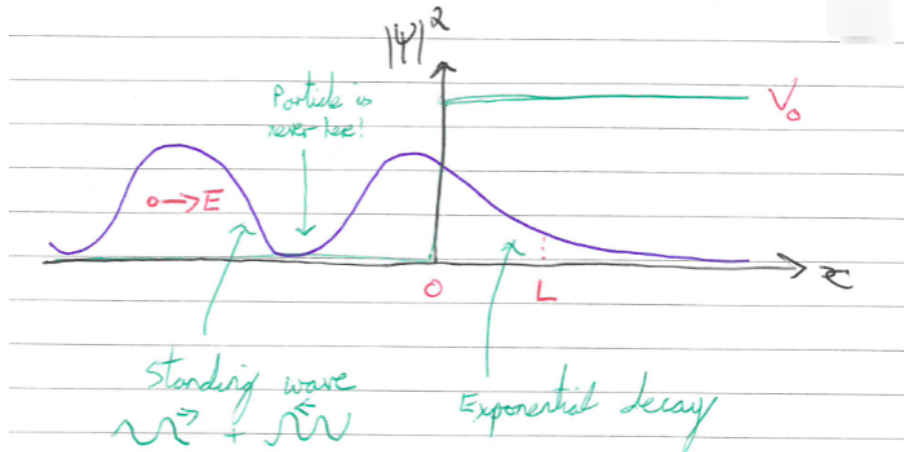

Figure 11.4

The "decay characteristic length" (depth of penetration into the barrier) is given by $1/\alpha$. This means that the particle is allowed to penetrate into the "forbidden zone" of the potential step. What if the forbidden zone ends at some $X = L$. We can see that the potential goes back to zero, and the particle goes back from exponential decay to being a wave. In effect, the particle has passed straight through the wall, despite having insufficient potential so being classically forbidden. This is called "Quantum Tunnelling".
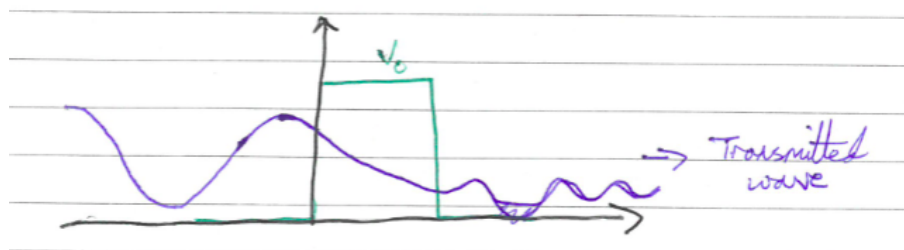

Figure 11.5

3   Conclusions

- For a finite step (or well) substitute in the general solutions to the TISE, piecewise.
- Use boundary conditions to match up the value and the slope of ψ at the boundary.
- There will always be some reflection, and therefore some interference.
- If energy is lower than the step potential, the wavefunction turns into exponential decay.
- If the step is of finite depth, since this exponential decay never reaches zero - there is some probability of the particle passing entirely through the step.

End of Module.