Quantum Mechanics: Introduction

Developed for the Azera Group

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Introduction to Quantum Mechanics

This power point presentation is part of a series of topics which should be mastered prior to diving into the subject of **Quantum Computing.** This presentation is an introduction to **Quantum mechanics** which is the most difficult but the most important topic to master before going on to learn about Quantum Computing and Quantum Information.

- Quantum objects have characteristics of both particles and waves.
- Quantum mechanics sets limits to how accurately the value of a physical quantity can be predicted prior to its measurement, given a complete set of initial conditions (the uncertainty principle).
- The most controversial portions of Quantum Mechanics (The Einstein Podolsky Rosen Paradox) as articulated by Bell in 1964, is the most important portion of the theory of Quantum Mechanics used in developing Quantum Algorithms which can only be solved by a Quantum Computer. (This theory is maintained by Computing Scientists)

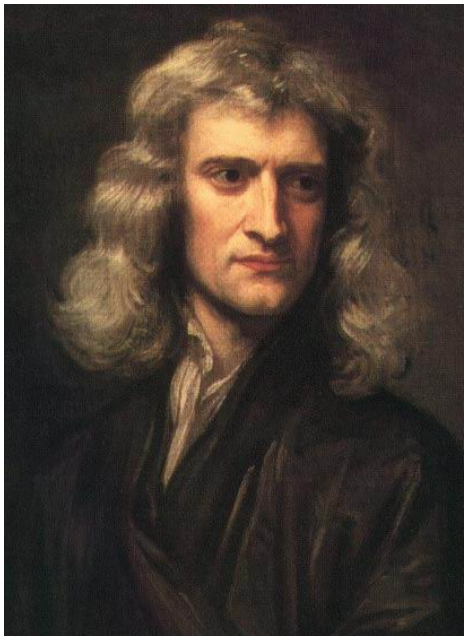
Part One: Problem of radiation

In physics, **electromagnetic radiation** (**EMR**) consists of electromagnetic waves, propagating through space, carrying electromagnetic radiant energy. Classically, electromagnetic radiation consists of **electromagnetic waves**, which are synchronized oscillations of electric and magnetic fields.

Electromagnetic waves are created due to periodic change of electric or magnetic field. In a vacuum, electromagnetic waves travel at the speed of light, commonly denoted *c*. In homogeneous, isotropic media, the oscillations of the two fields are perpendicular to each other and perpendicular to the direction of energy and wave propagation, forming a transverse wave.

Dual nature of radiation

The idea of duality is rooted in a debate over the nature of light and matter dating back to the 1600s, when competing theories of light were proposed by Huygens and Newton.



Christiaan Huygens
Dutch 1629-1695
light consists of waves

Sir Isaac Newton
1643-1727
light consists of particles

Problem of blackbody radiation

Black-body radiation is the thermal electromagnetic radiation within, or surrounding, a body in thermodynamic equilibrium with its environment, emitted by a black body (an idealized opaque, non-reflective body). It has a specific, continuous, spectrum of wavelengths, inversely related to intensity, that depend only on the body's temperature, which is assumed, for the sake of calculations and theory, to be uniform and constant

At the end of the 19th century, physicists were unable to explain why the observed spectrum of black-body radiation, which by then had been accurately measured, diverged significantly at higher frequencies from that predicted by existing theories.

Part Two: Max Planck

In 1900, German physicist Max Planck heuristically derived a formula for the observed spectrum by assuming that a hypothetical electrically charged oscillator in a cavity that contained black-body radiation could only change its energy in a minimal increment, *E*, that was proportional to the frequency of its associated electromagnetic wave. This resolved the problem of the ultraviolet catastrophe predicted by classical physics. This discovery was a pioneering insight of modern physics and is of fundamental importance to quantum theory.

Max Planck

Problem of blackbody radiation

If the photon gas is not Planckian, the second law of thermodynamics guarantees that interactions (between photons and other particles or even, at sufficiently high temperatures, between the photons themselves) will cause the photon energy distribution to change and approach the Planck distribution.

In such an approach to thermodynamic equilibrium, photons are created or annihilated in the right numbers and with the right energies to fill the cavity with a Planck distribution until they reach the equilibrium temperature. It is as if the gas is a mixture of sub-gases, one for every band of wavelengths, and each sub-gas eventually attains the common temperature.

Planck's Assumption:, 1

Planck made two assumptions about the nature of the oscillators in the cavity walls.

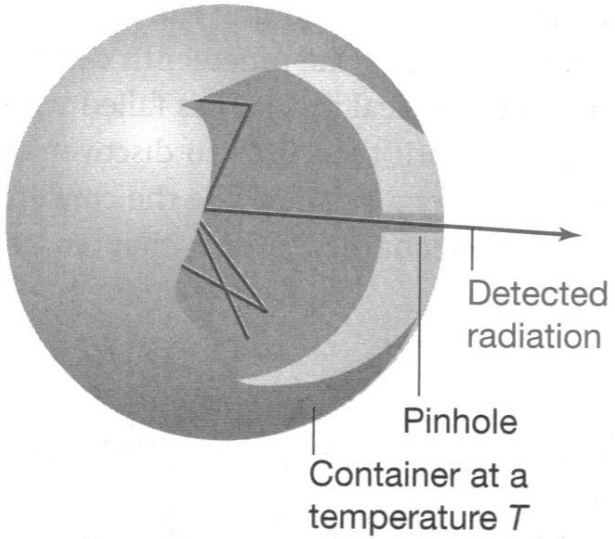
1. The energy of an oscillator has only certain discrete values E_n.
   - $E_n = n\,h\,f$
     - n is a positive integer called the quantum number
     - f is the frequency of oscillation
     - h is Planck's constant
   - This says the energy is quantized.
   - Each discrete energy value corresponds to a different quantum state.
     - Each quantum state is represented by the quantum number, *n.*

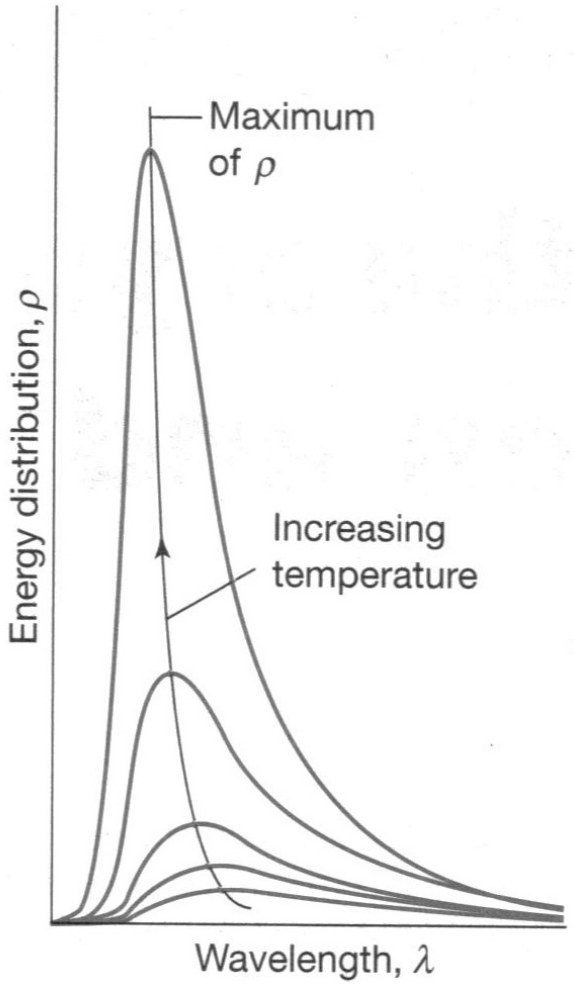
Planck's Assumption, 2

The oscillators emit or absorb energy when making a transition from one quantum state to another.

- The entire energy difference between the initial and final states in the transition is emitted or absorbed as a single quantum of radiation.
- An oscillator emits or absorbs energy only when it changes quantum states.
- The energy carried by the quantum of radiation is $E = h f$.

Blackbody radiation





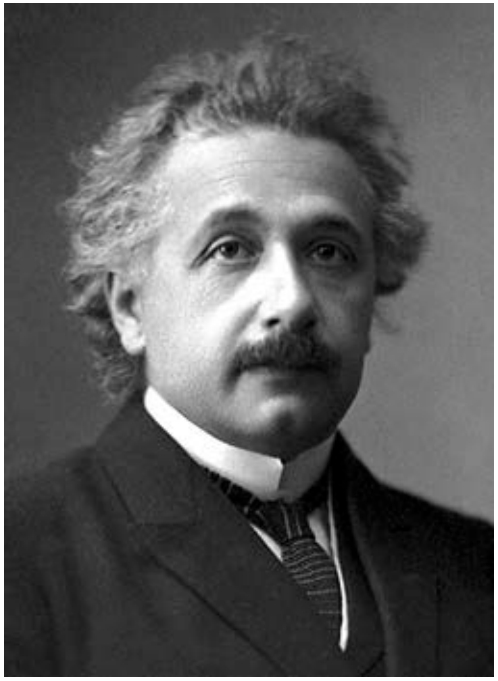
Planck's formula is shown below

$$B(\nu, T) = \frac{2h\nu^3}{c^2} \frac{1}{\exp\left(\frac{h\nu}{k_B T}\right) - 1}$$

Part Three: Einstein and the Photon

By the early part of twentieth century, the wave theory of light seemed to be well entrenched.

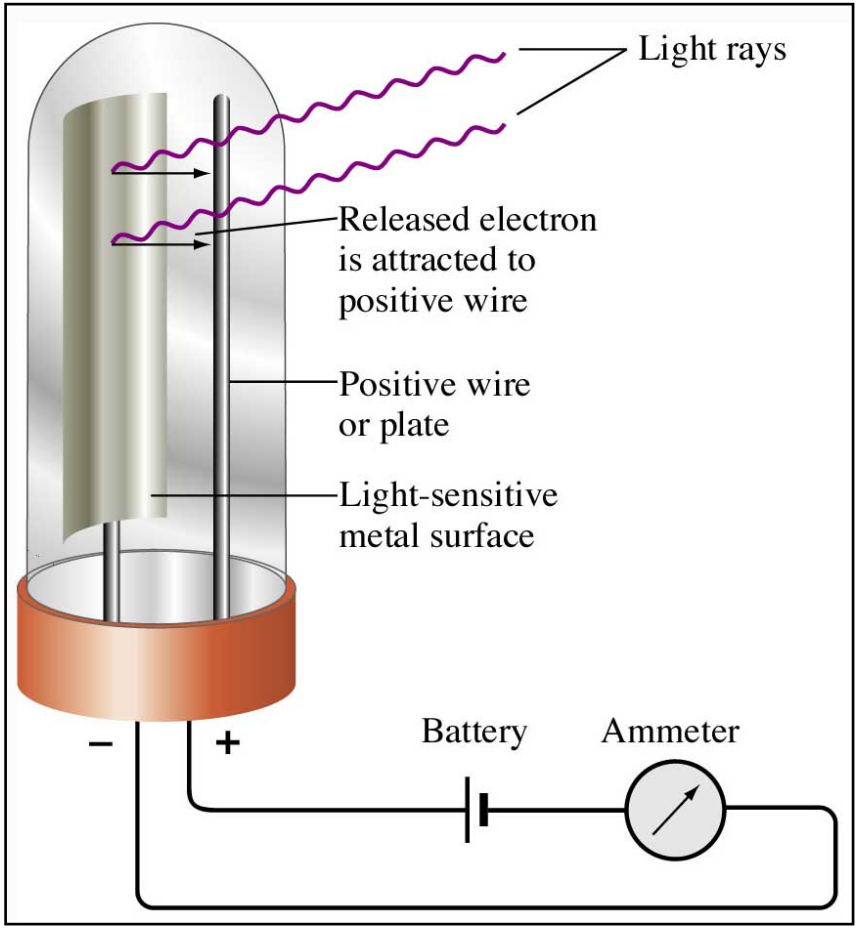
- In 1905, Albert Einstein proposed that light had both wave and particle properties to explain the observations in the photoelectric effect.
- Einstein rederived Planck's results by assuming the oscillations of the electromagnetic field were themselves quantized.
- In other words, Einstein proposed that quantization is a fundamental property of light and other electromagnetic radiation.
- This led to the concept of photons.



Albert Einstein

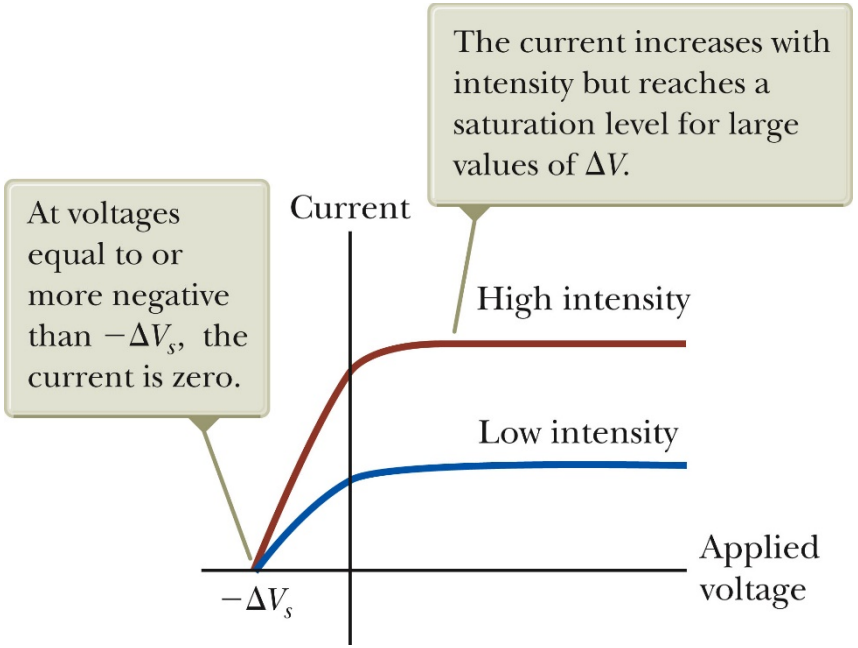
The photoelectric effect

- The **photoelectric effect** occurs when light incident on certain metallic surfaces causes electrons to be emitted from those surfaces.
  - The emitted electrons are called **photoelectrons.**
  - The name is given because of their ejection from a metal by light in the photoelectric effect



Photoelectric Effect, Results

- At large values of ΔV, the current reaches a maximum value.
  - All the electrons emitted at *E* are collected at *C.*
- The maximum current increases as the intensity of the incident light increases.
- When ΔV is negative, the current drops.
- When ΔV is equal to or more negative than ΔV_s, the current is zero.



Photoelectric Effect Feature 1

- Dependence of photoelectron kinetic energy on light intensity
  - *Classical Prediction*
    - Electrons should absorb energy continually from the electromagnetic waves.
    - As the light intensity incident on the metal is increased, the electrons should be ejected with more kinetic energy.
  - *Experimental Result*
    - The maximum kinetic energy is independent of light intensity.
    - The maximum kinetic energy is proportional to the stopping potential (DV_s).

Photoelectric Effect Feature 2

- Time interval between incidence of light and ejection of photoelectrons
  - *Classical Prediction*
    - At low light intensities, a measurable time interval should pass between the instant the light is turned on and the time an electron is ejected from the metal.
    - This time interval is required for the electron to absorb the incident radiation before it acquires enough energy to escape from the metal.
  - *Experimental Result*
    - Electrons are emitted almost instantaneously, even at very low light intensities.

Photoelectric Effect Feature 3

- Dependence of ejection of electrons on light frequency
  - *Classical Prediction*
    - Electrons should be ejected at any frequency as long as the light intensity is high enough.
  - *Experimental Result*
    - No electrons are emitted if the incident light falls below some **cutoff frequency, f_c.**
    - The cutoff frequency is characteristic of the material being illuminated.
    - No electrons are ejected below the cutoff frequency regardless of intensity.

Photoelectric Effect Feature 4

- Dependence of photoelectron kinetic energy on light frequency
  - *Classical Prediction*
    - There should be no relationship between the frequency of the light and the electric kinetic energy.
    - The kinetic energy should be related to the intensity of the light.
  - *Experimental Result*
    - The maximum kinetic energy of the photoelectrons increases with increasing light frequency.

Photoelectric Effect Features, Summary

- The experimental results contradict all four classical predictions.
- Einstein extended Planck's concept of quantization to electromagnetic waves.
- All electromagnetic radiation of frequency f from any source can be considered a stream of quanta, now called *photons.*
- Each photon has an energy E and moves at the speed of light in a vacuum.
  - $E = hf$
- A photon of incident light gives all its energy to a single electron in the metal.

Photoelectric Effect, Work Function

- Electrons ejected from the surface of the metal and not making collisions with other metal atoms before escaping possess the maximum kinetic energy K_{max}.
- $K_{max} = hf - \varphi$
  - φ is called the work function of the metal.
  - The work function represents the minimum energy with which an electron is bound in the metal.

Photon Explanation of the Photoelectric Effect

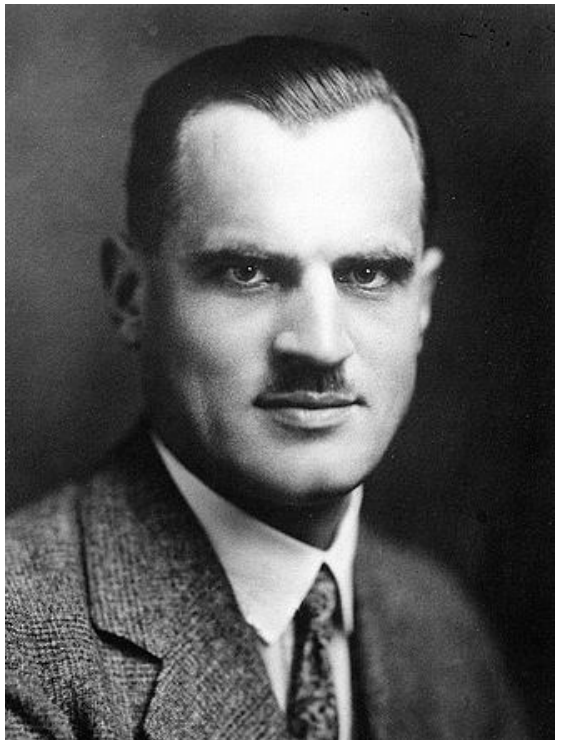
- Dependence of photoelectron kinetic energy on light intensity
  - K_{max} is independent of light intensity.
  - K depends on the light frequency and the work function.
- Time interval between incidence of light and ejection of the photoelectron
  - Each photon can have enough energy to eject an electron immediately.
- Dependence of ejection of electrons on light frequency
  - There is a failure to observe photoelectric effect below a certain cutoff frequency, which indicates the photon must have more energy than the work function in order to eject an electron.
  - Without enough energy, an electron cannot be ejected, regardless of the fact that many photons per unit time are incident on the metal in a very intense light beam.

Photon Explanation of the Photoelectric Effect, cont.

- Dependence of photoelectron kinetic energy on light frequency
  - Since $K_{max} = hf - \varphi$
  - A photon of higher frequency carries more energy.
    - A photoelectron is ejected with higher kinetic energy.
    - Once the energy of the work function is exceeded
  - There is a linear relationship between the maximum electron kinetic energy and the frequency.

Part Five: The Compton Effect

- Compton and Debye extended Einstein's idea of photon momentum.
- The two groups of experimenters accumulated evidence of the inadequacy of the classical wave theory.
- The classical wave theory of light failed to explain adequately, the scattering of x-rays from electrons.



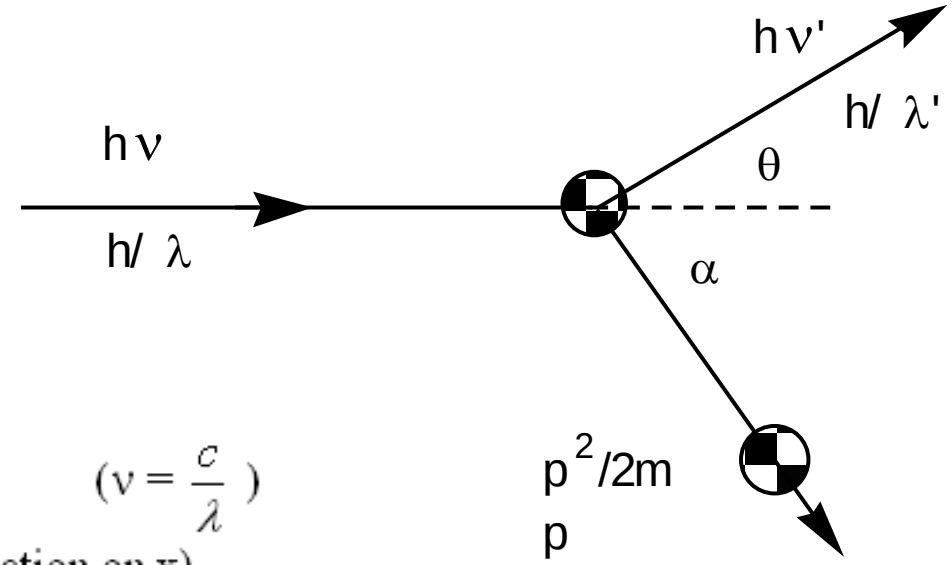
Arthur Holly Compton

The Compton Effect, Introduction

Compton scattering is inelastic scattering of light by a free charged particle, where the wavelength of the scattered light is different from that of the incident radiation. The amount by which the light's wavelength changes is called the **Compton shift**. The Compton effect was observed by Arthur Holly Compton in 1923 at Washington University in St. Louis.

The effect is significant because it demonstrates that light cannot be explained purely as a wave phenomenon. Thomson scattering, the classical theory of an electromagnetic wave scattered by charged particles, cannot explain shifts in wavelength at low intensity: classically, light of sufficient intensity for the electric field to accelerate a charged particle to a relativistic speed will cause radiation-pressure recoil and an associated Doppler shift of the scattered light, but the effect would become arbitrarily small at sufficiently low light intensities *regardless of wavelength*. Thus, if we are to explain low-intensity Compton scattering, light must behave as if it consists of particles.

The Compton Effect (Electron Scattering)



Energy Conservation

$$h\frac{c}{\lambda} = h\frac{c}{\lambda'} + \frac{p^2}{2m} \qquad \left(\nu = \frac{c}{\lambda}\right)$$

Momentum Conservation (projection on x)

$$\frac{h}{\lambda} = \frac{h}{\lambda'}\cos\theta + p\cos\alpha$$

Momentum Conservation (projection on y)

$$0 = \frac{h}{\lambda'}\sin\theta - p\sin\alpha$$

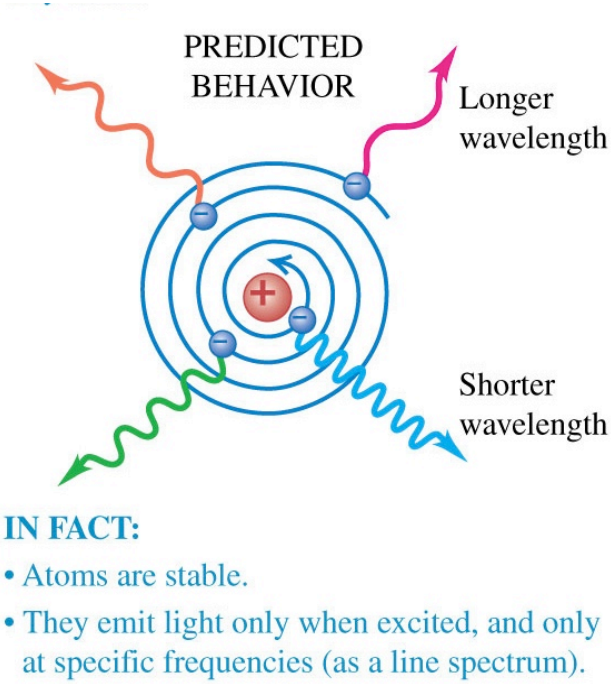
Part Six: classical mechanic Problems

Quantum Mechanics was invented to provide a theoretical basis for atomic phenomena which would correlate with experimental results.

- Early experiments on the electronic structure of atoms were centered around the light emitted by atoms of hydrogen under thermal excitation.
- Contrary to the predictions of classical electro-magnetic theory these light pulses were very sharp lines.
- In the early 1900s, the atom was understood to consist of a positive nucleus around which electrons move (Rutherford's model).
- This explanation left a theoretical dilemma: According to the physics of the time, an electrically charged particle circling a center would continually lose energy as electromagnetic radiation.
- But this is not the case—atoms are stable.

Review: Breakdown of classical physics (Crisis)

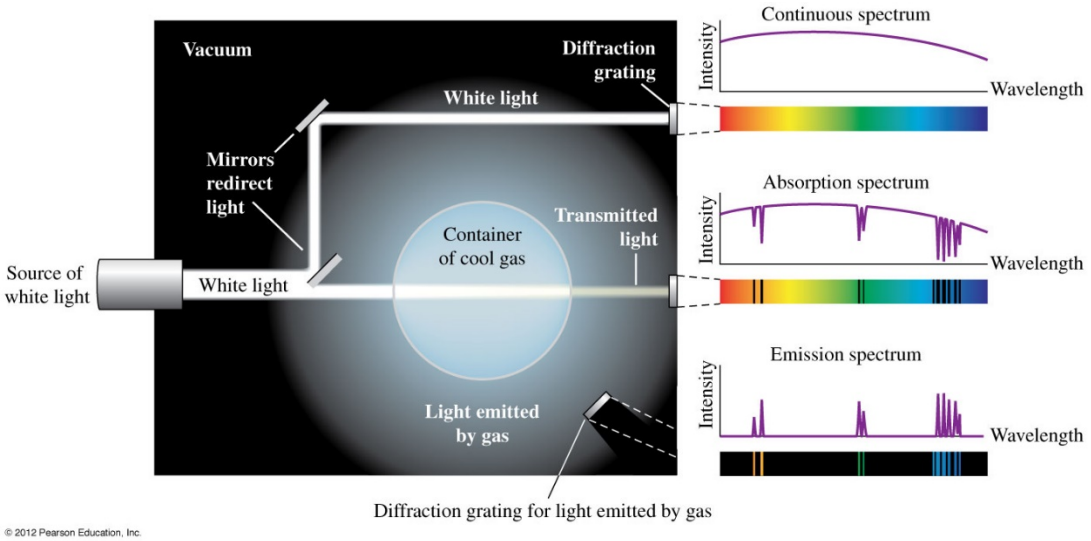
- Rutherford's experiment suggested that electrons orbit around the nucleus like a miniature solar system.
- However, classical physics predicts that an orbiting electron (*accelerating charge*) would emit electromagnetic radiation and fall into the nucleus. *So classical physics could not explain why atoms are stable.*

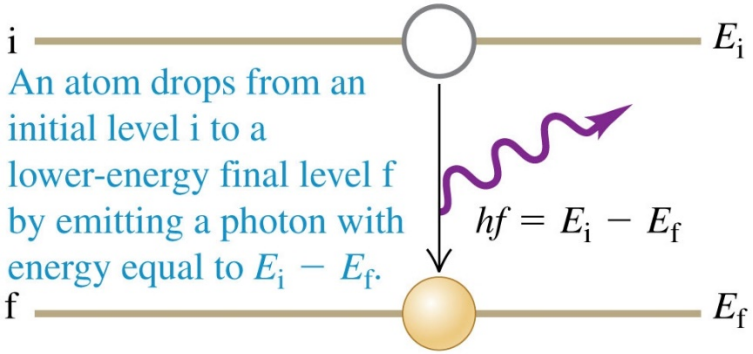


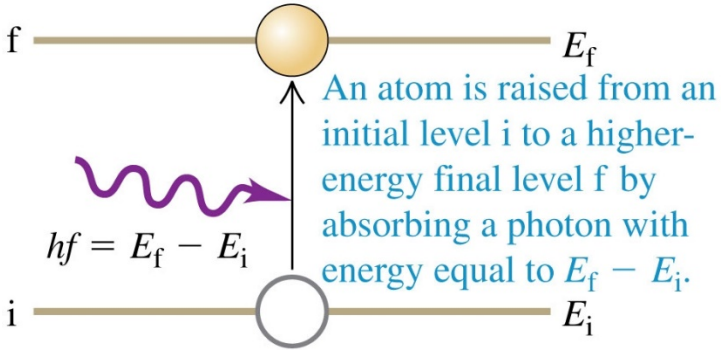
There is a ground state energy level

Quantization of atomic energy levels

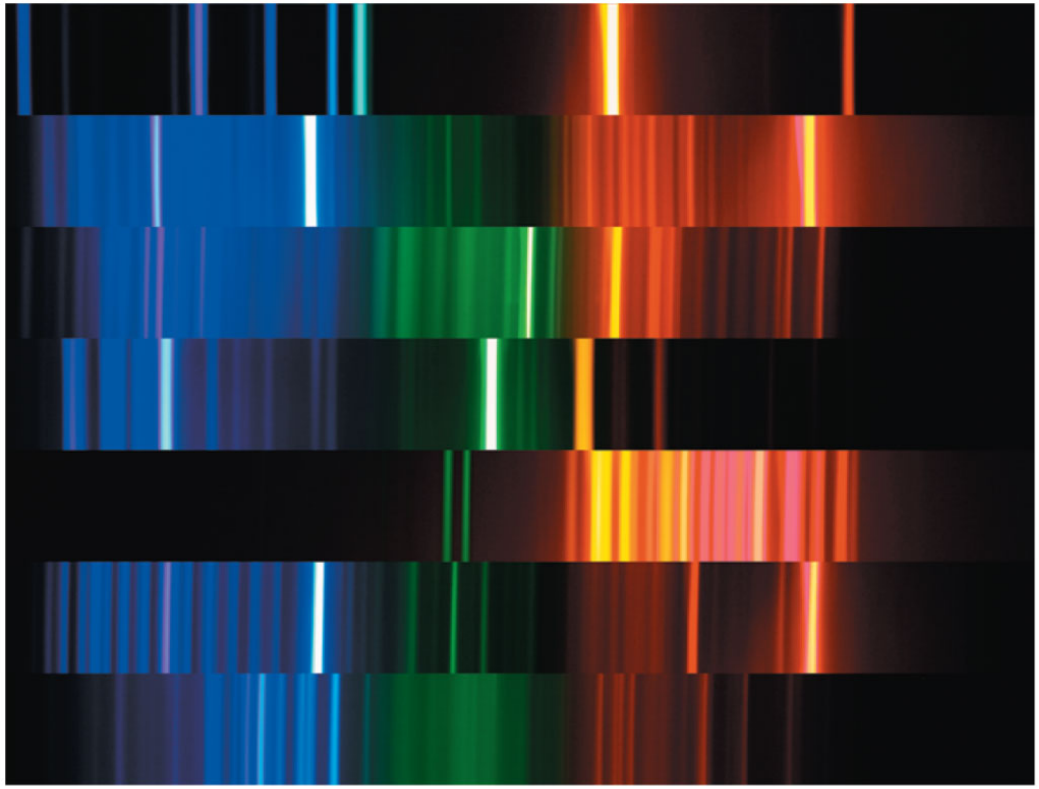
Three classes of spectral features:





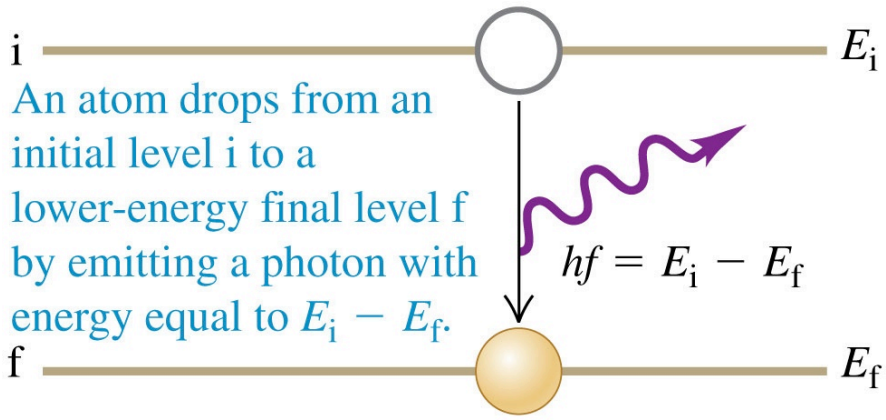


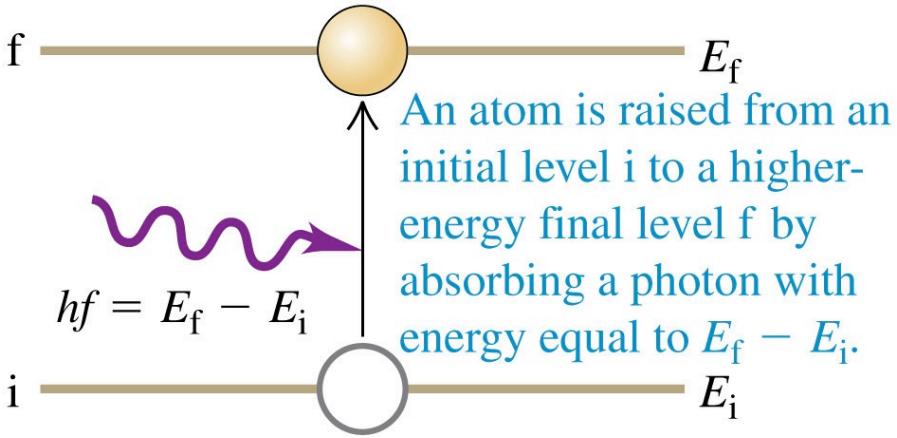
Quantization of atomic energy levels



Quantization of atomic energy levels

- Niels Bohr explained atomic line spectra and the stability of atoms by postulating that atoms can only be in *certain discrete energy levels*. When an atom makes a transition from one energy level to a lower level, it emits a photon whose energy equals that lost by the atom.
- An atom can also absorb a photon, provided the photon energy equals *the difference between two energy levels*.



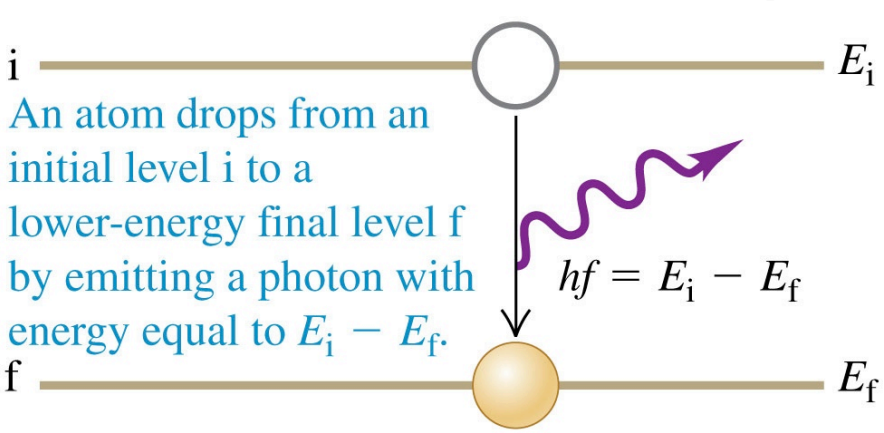


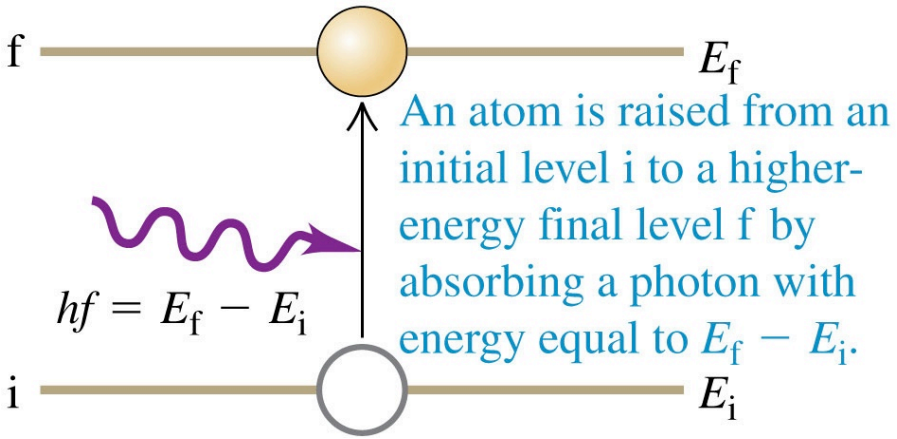
Quantization of atomic energy levels

- An atom can also absorb a photon, provided the photon energy equals *the difference between two energy levels*.

The master equation for the photon energy in these transitions is

$$hf = h\frac{c}{\lambda} = E_i - E_f$$





Part Seven: The Bohr model

- Bohr developed a model of the atom, in which he proposed that energy levels of electrons are discrete and that the electrons revolve in stable orbits around the atomic nucleus but can jump from one energy level (or orbit) to another.
- Although the Bohr model has been supplanted by other models, its underlying principles remain valid.
- He conceived the principle of complementarity: that items could be separately analyzed in terms of contradictory properties, like behaving as a wave or a stream of particles. The notion of complementarity dominated Bohr's thinking in both science and philosophy.

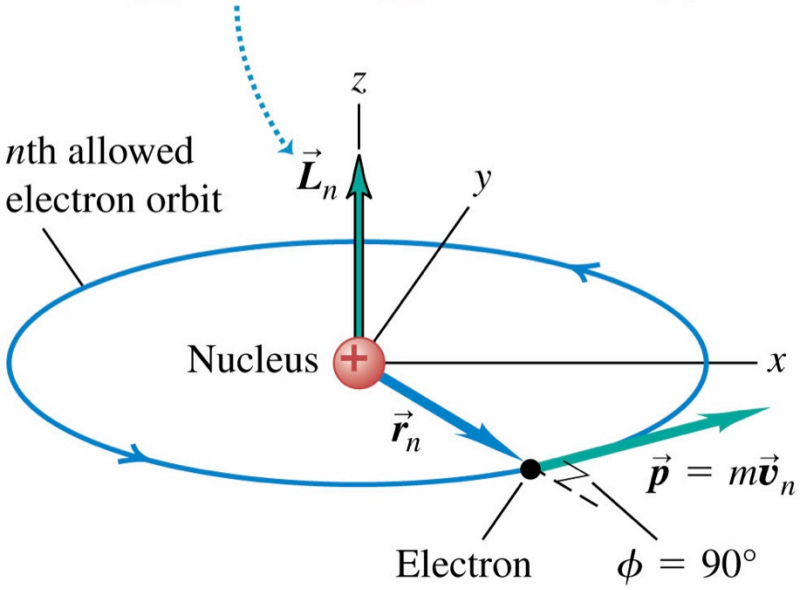
Niels Bohr

The Bohr model of hydrogen

- Bohr explained the line spectrum of hydrogen with a model in which the single hydrogen electron can only be in certain *definite orbits*.
- In the *n*th allowed orbit, the electron has orbital angular momentum $nh/2\pi$ (see Figure on the right).
- *Bohr proposed that angular momentum is quantized* (this will turn out to be correct in general in quantum mechanics but is not right for the hydrogen atom).

$$\vec{L} = \vec{r} \times \vec{p}$$

$$L_n = rp = m\, v_n\, r_n$$



The Bohr model of hydrogen

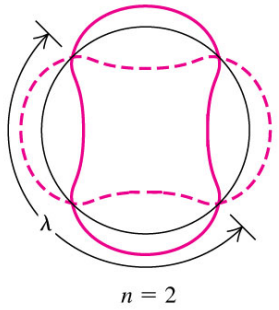
- Let's use a different argument based on deBroglie waves to obtain the same conclusions.
- Think of a standing wave with wavelength λ that extends around the circle.

$$2\pi r_n = n\lambda_n$$

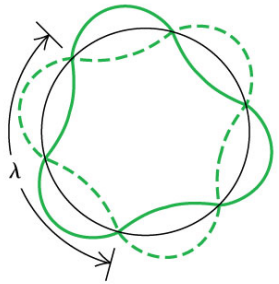
$$2\pi r_n = n\lambda_n = n\frac{h}{mv_n}$$

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

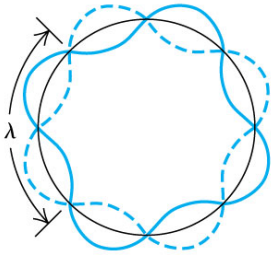
Same as the Bohr quantization condition



$n = 2$



$n = 3$

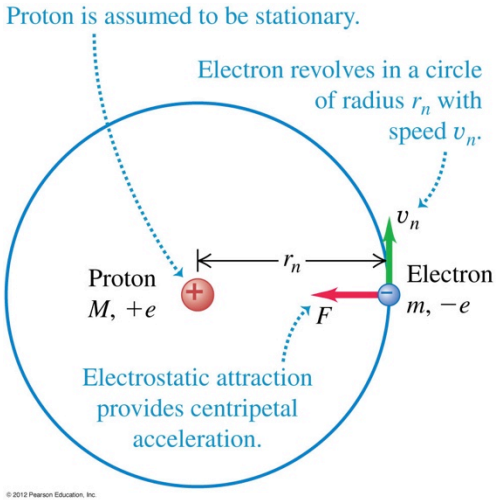


$n = 4$

The Bohr model of hydrogen

$$r_n = \frac{\varepsilon_0 (nh)^2}{\pi m e^2}$$

$$r_n = \frac{\varepsilon_0 (nh)^2}{\pi m e^2} \Rightarrow r_n = n^2 a_0$$



Here n is the “principal quantum number” and a_0 is the “Bohr radius”, which is the minimum radius of an electron orbital.

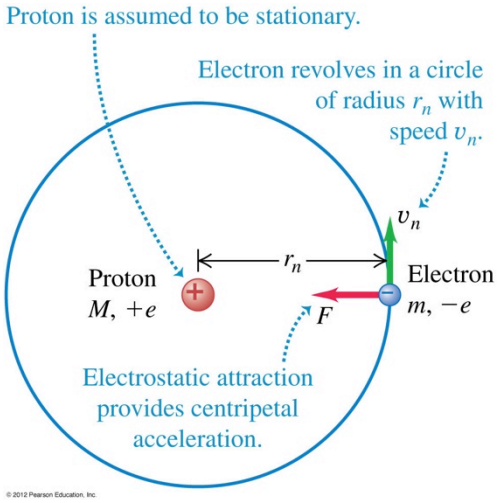
$$a_0 = \frac{\varepsilon_0 h^2}{\pi m e^2} \Rightarrow r_n = n^2 a_0 \qquad a_0 = 5.29 \times 10^{-11} m$$

The Bohr model of hydrogen

(The mass m is that of the electron.)

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

Now let's use a Newtonian argument for a planetary model of the atom but use the Bohr quantization condition.



$$F_e = \frac{e^2}{4\pi\varepsilon_0 r_n^{\,2}} = F_c = \frac{mv_n^{\,2}}{r_n}$$

Balance electrostatic and centripetal forces

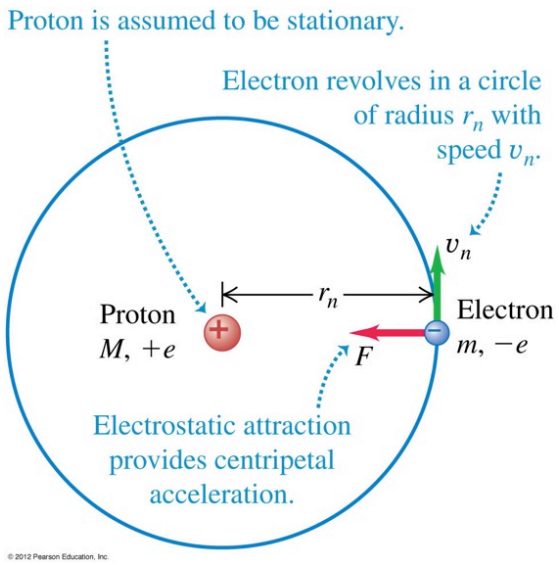
$$\frac{e^2}{4\pi\varepsilon_0} = \frac{mv_n^{\,2}r_n^{\,2}}{r_n} = \frac{(mv_n r_n)^2}{r_n} \Rightarrow \frac{e^2}{4\pi\varepsilon_0} = \frac{(nh/2\pi)^2}{r_n}$$

Here we used the Bohr quantization condition

The Bohr model of hydrogen

$$r_n = \frac{\varepsilon_0 (nh)^2}{\pi m e^2}$$

$$r_n = \frac{\varepsilon_0 (nh)^2}{\pi m e^2} \Rightarrow r_n = n^2 a_0$$



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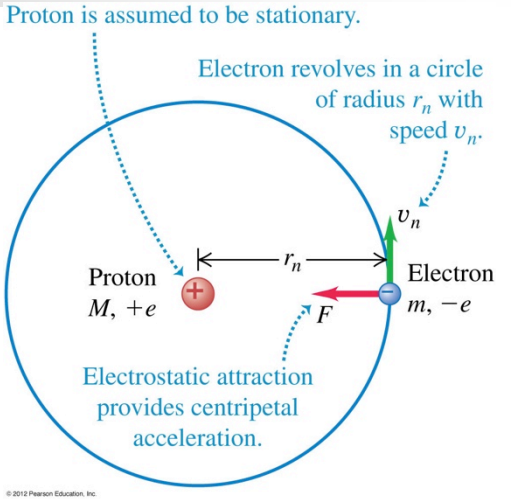
$$a_0 = \frac{\varepsilon_0 h^2}{\pi m e^2} \Rightarrow r_n = n^2 a_0$$

$$a_0 = 5.29 \times 10^{-11} m$$

The Bohr model of hydrogen

$$mv_n r_n = n\frac{h}{2\pi} \Rightarrow v_n = \frac{e^2}{\varepsilon_0(2nh)}$$



$$K_n = \frac{1}{2}mv_n^{\,2} = \frac{me^4}{8n^2h^2}$$

$$r_n = \frac{\varepsilon_0(nh)^2}{\pi me^2}$$

$$U_n = \frac{-e^2}{4\pi\varepsilon_0 r_n} = \frac{-me^4}{\varepsilon_0^{\,2}4n^2h^2}$$

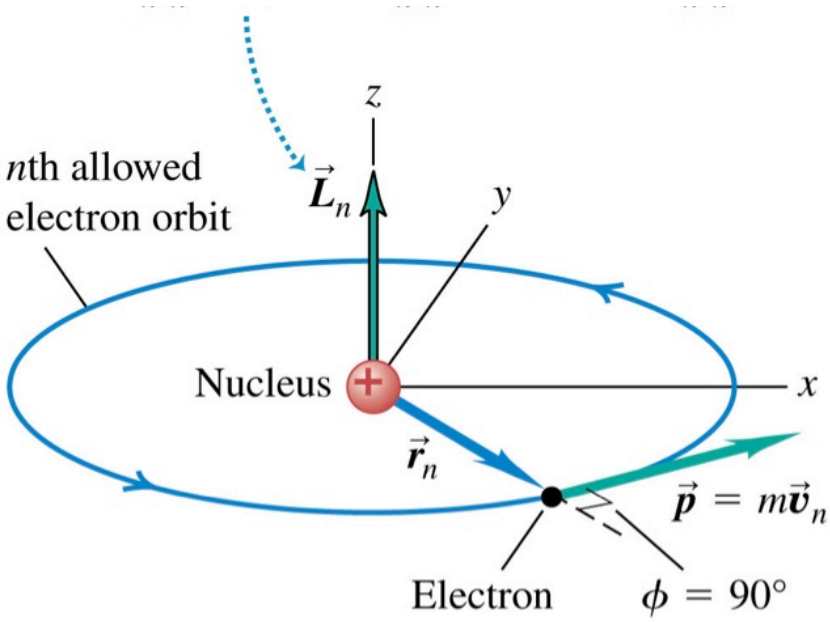
$$E_n = K_n + U_n = \frac{-me^4}{\varepsilon_0^{\,2}8n^2h^2}$$

Note:
E and U are negative (1/8-1/4=-1/8)

This expression for the allowed energies can be rewritten and used to predict atomic spectral lines !

The Bohr model of hydrogen

$$E_n = \frac{-me^4}{\varepsilon_0{}^2 8n^2h^2} = \frac{-hcR}{n^2}; R = \frac{me^4}{8\varepsilon_0{}^2 h^3 c}$$



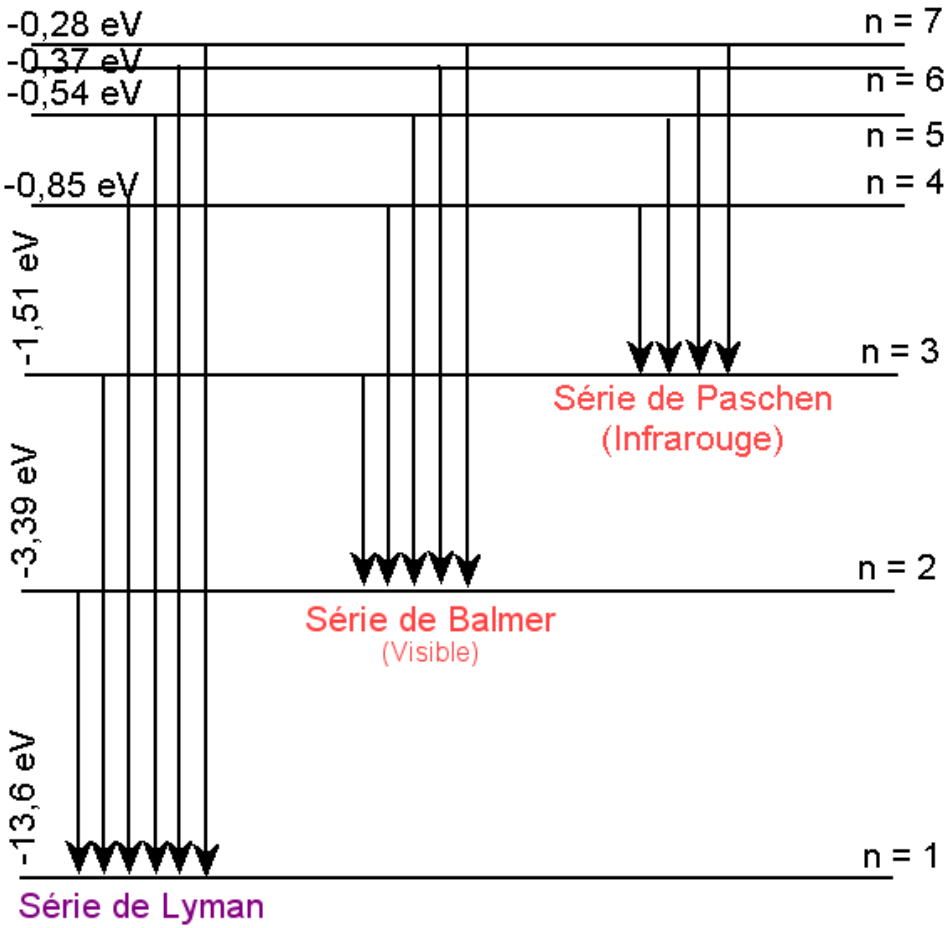
$$E_n = \frac{-hcR}{n^2}$$

Here R is the "Rydberg constant", R=1.097 x 10^7 m^{-1}

The energies of photon transitions between atomic levels is given by the following equations

$$\frac{hc}{\lambda} = E_{Upper} - E_{Lower} = hcR\left(\frac{1}{n^2_{Upper}} - \frac{1}{n^2_{Lower}}\right)$$

Atomic Spectroscopy of Hydrogen

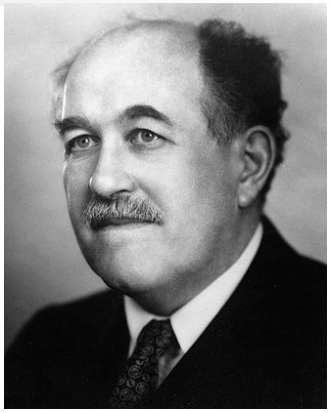


Part Eight: Stern-Gerlach

The **Stern–Gerlach experiment** demonstrated that the spatial orientation of angular **momentum is quantized.** Thus an atomic-scale system was shown to have intrinsic quantum properties.

In the original experiment, silver atoms were sent through a spatially varying magnetic field, which deflected them before they struck a detector screen, such as a glass slide. Particles with non-zero magnetic moment are deflected, due to the magnetic field gradient, from a straight path. The screen reveals discrete points of accumulation, owing to their quantized spin. This experiment was decisive in convincing physicists of the reality of angular-momentum quantization in atomic-scale systems.

Proposed by Otto Stern in 1921, the experiment was first successfully conducted by Walther Gerlach in early 1922.



Otto Stern

Walther Gerlach

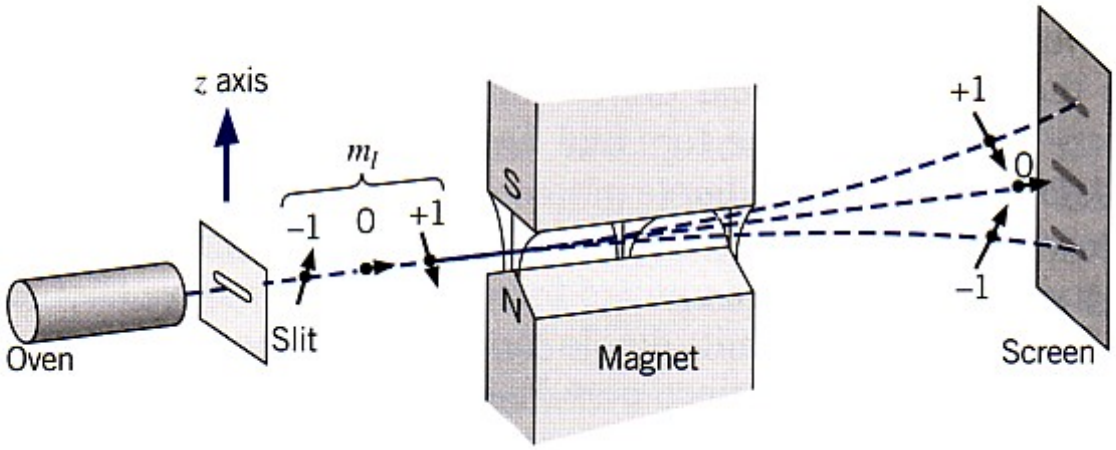
Otto Stern & Walther Gerlach

$$\left|\vec{L}\right| = \left|\vec{r}\times\vec{p}\right| = n\hbar$$ Bohr's Q hypothesis

$$\oint \vec{p}\bullet d\vec{q} = n\hbar$$ Sommerfeld's Q hypothesis

$$L^2 \rightarrow \ell(\ell+1)\hbar^2$$

$$L_z \rightarrow m_\ell\,\hbar$$



Stern & Gerlach

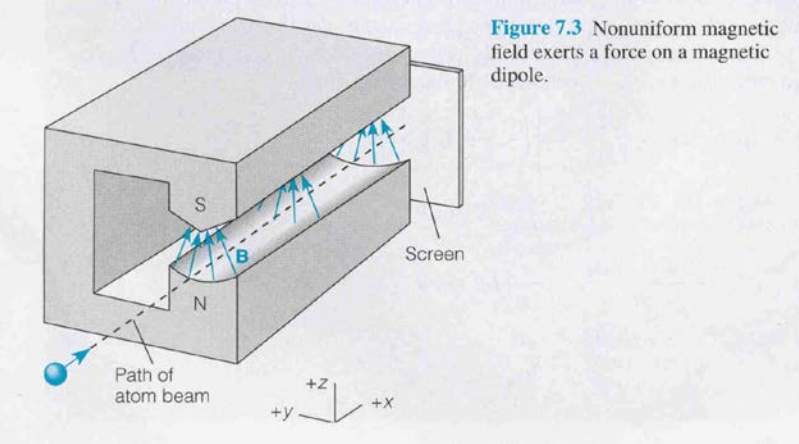
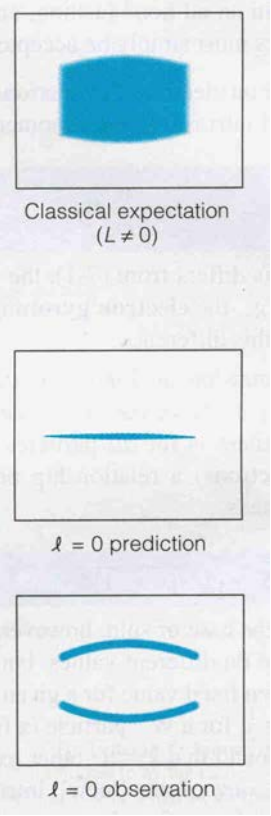


Figure 7.3 Nonuniform magnetic field exerts a force on a magnetic dipole.



[1]It is because an atom's behavior in a magnetic field depends on m_ℓ that it is known as the "magnetic quantum number."

[2]In the original Stern–Gerlach experiment of 1922, two lines were seen, but neutral *silver* atoms were used. Although the silver atoms, having one 5*s* electron beyond a closed $n = 4$ shell, should behave as atoms of $\ell = 0$, the Stern–Gerlach apparatus was later used with hydrogen (1925, Phipps and Taylor), to rule out any complication multiple electrons might introduce.

Angular Momentum: Vector Addition

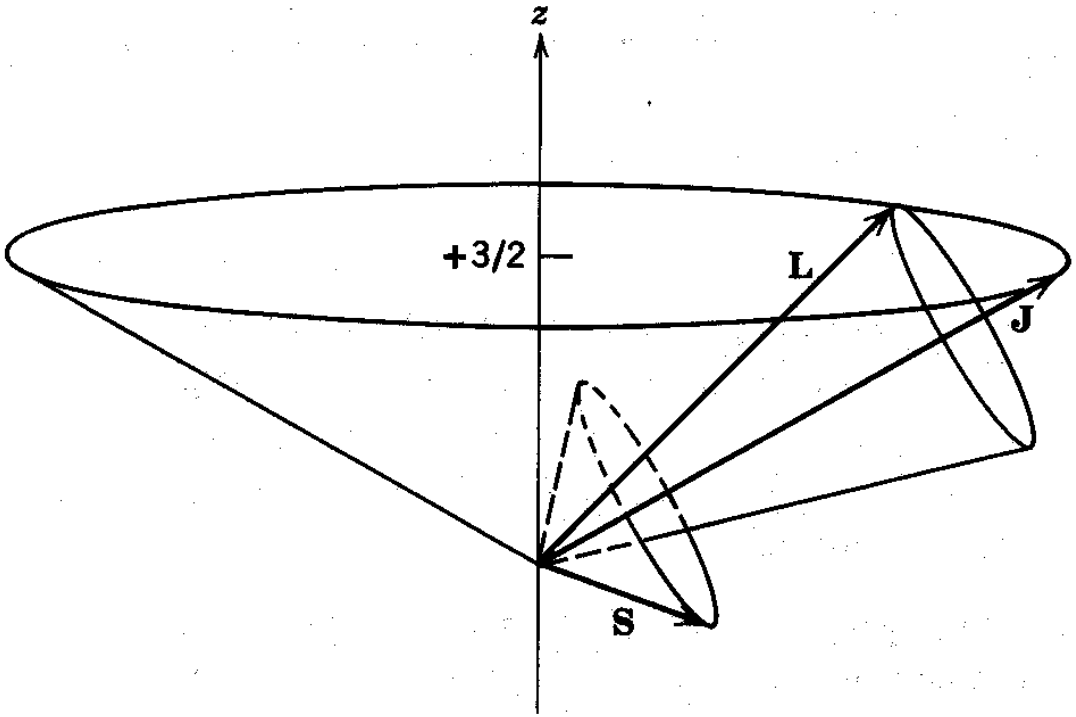


Figure 8-8 The angular momentum vectors **L**, **S**, and **J** for a typical case of a state with $l = 2$, $j = 5/2$, $m_j = 3/2$. The vectors **L** and **S** precess uniformly about their sum **J**, and **J** can be found anywhere on the cone symmetrical about the z axis.

Part Nine: Louis de BROGLIE

His 1924 thesis (Research on the Theory of the Quanta) introduced his theory of electron waves. This included the wave–particle duality theory of matter, based on the work of Max Planck and Albert Einstein on light. This research culminated in the de Broglie hypothesis stating that *any moving particle or object had an associated wave*. De Broglie thus created a new field in physics, the wave mechanics, uniting the physics of energy (wave) and matter (particle).

Matter waves are a central part of the theory of quantum mechanics, being an example of wave–particle duality. All matter exhibits wave-like behavior. For example, a beam of electrons can be diffracted just like a beam of light or a water wave. In most cases, however, the wavelength is too small to have a practical impact on day-to-day activities.

Louis de Broglie

de Broglie Relation

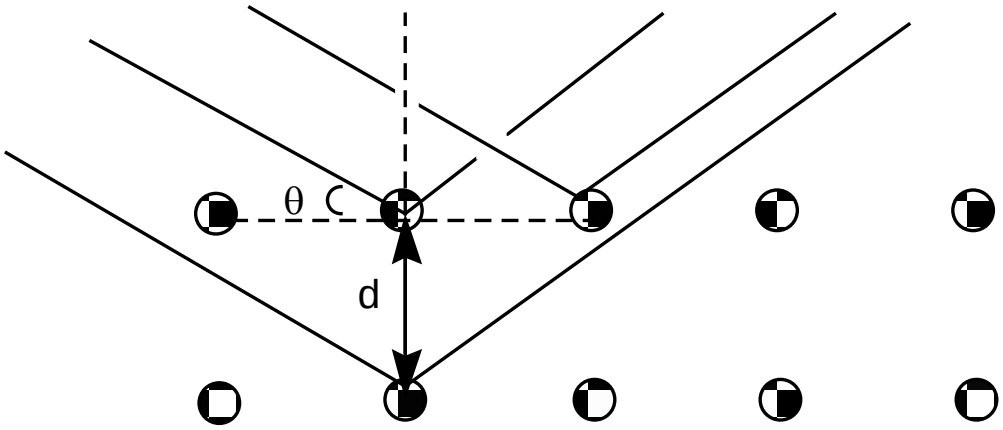
- The equation $\lambda = h/mv$ is called the de Broglie relation.
- For a photon that has both wave and particle characteristics:
- $E = h\nu = hc/\lambda$ (recall $c = \nu\lambda$)
- $E = mc^2$
- $mc^2 = hc/\lambda$ or $\lambda = h/mc$
- Since mc is the momentum of a photon, can we replace this with the momentum of a particle?
- $\lambda = h/mv$
- This suggests that particles have wave-like characteristics!

Part Ten: Davisson-Germer

The **Davisson–Germer experiment** was a 1923-27 experiment by Clinton Davisson and Lester Germer at Western Electric (later Bell Lab), in which electrons, scattered by the surface of a crystal of nickel metal, displayed a diffraction pattern. This confirmed the hypothesis, advanced by Louis de Broglie in 1924, of wave-particle duality, and was an experimental milestone in the creation of quantum mechanics.

Clinton Joseph Davisson (left)
Lester Germer (Right)

Davisson and Germer



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

Diffraction is similarly observed using a mono-energetic electron beam Bragg law is verified assuming $\lambda = h/p$

Davisson and Germer

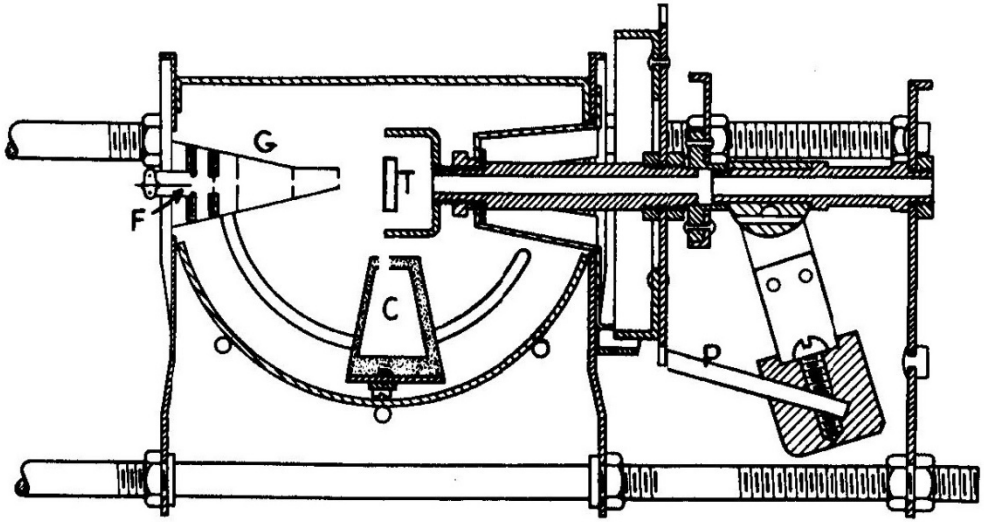
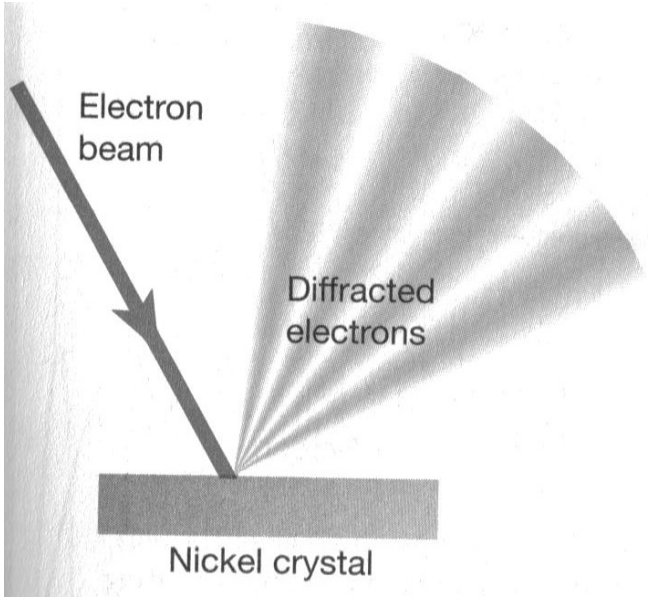


FIG. 10.2 Cross-sectional view of Davisson and Germer's apparatus. The enclosing glass bulb is not shown. [*Phys. Rev. 30*, p. 708 (1927), Fig. 2.]



Part Eleven: Werner Heisenberg

Heisenberg was responsible for two major contributions to quantum mechanics:

- His methods is now called the matrix formulation of Quantum Mechanics
- His discovery of the Heisenberg Uncertainty Principal

The main new idea, non-commuting matrices, is justified only by a rejection of unobservable quantities. It introduces the non-commutative multiplication of matrices by physical reasoning, based on the correspondence principle.

Werner Heisenberg

Werner Heisenberg: Matrix Mechanics

In matrix mechanics, the mathematical formulation of quantum mechanics, any pair of non-commuting self-adjoint operators representing observables are subject to similar uncertainty limits. An eigenstate of an observable represents the state of the wavefunction for a certain measurement value (the eigenvalue). For example, if a measurement of an observable A is performed, then the system is in a particular eigenstate Ψ of that observable. However, the particular eigenstate of the observable A need not be an eigenstate of another observable B: If so, then it does not have a unique associated measurement for it, as the system is not in an eigenstate of that observable.

The Heisenberg Uncertainty Principal

- Mathematically, in wave mechanics, the uncertainty relation between position and momentum arises because the expressions of the wavefunction in the two corresponding orthonormal bases in Hilbert space are Fourier transforms of one another (i.e., position and momentum are conjugate variables). A nonzero function and its Fourier transform cannot both be sharply localized at the same time.
- **Heisenberg's uncertainty principle** is a relation that states that the product of the uncertainty in position (Δx) and the uncertainty in momentum ($m\Delta v_x$) of a particle can be no larger than $\mathbf{h/4\pi}$.

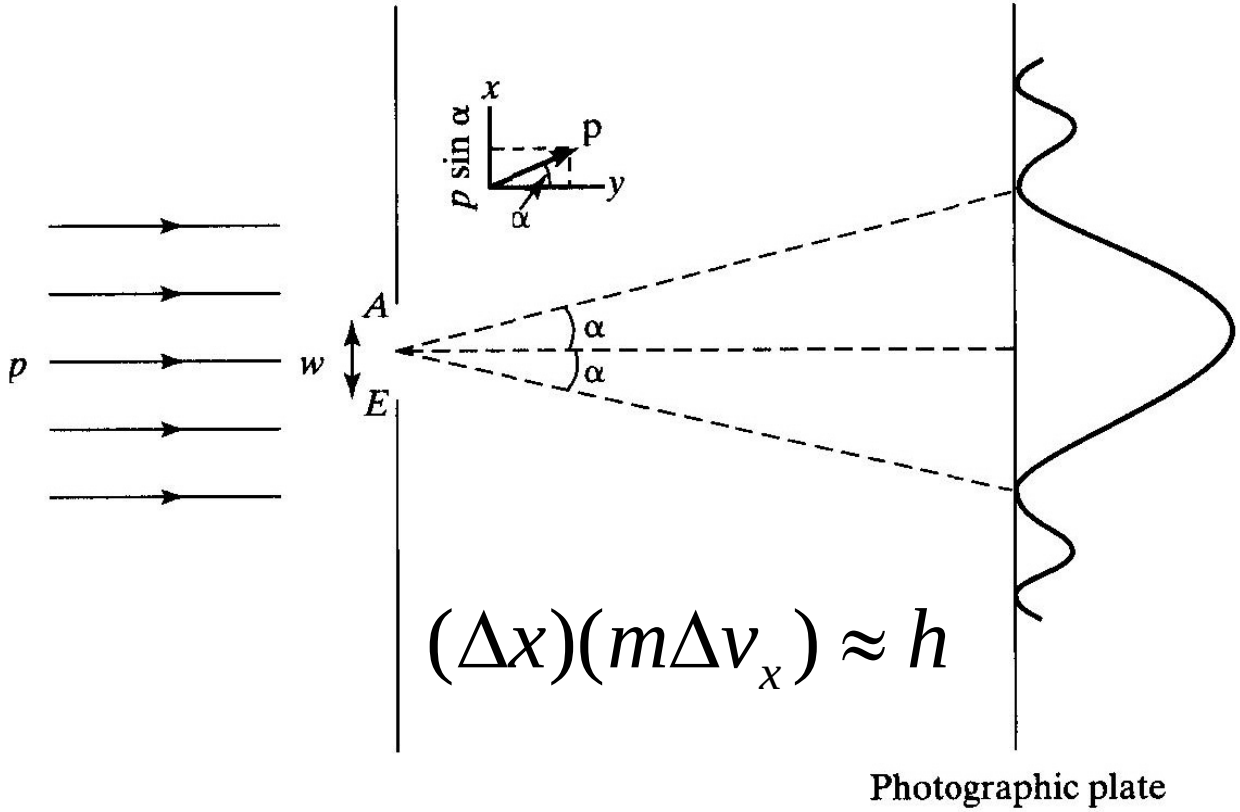
$$(\Delta x)(m\Delta v_x) \geq \frac{h}{4\pi}$$

- When m is large (for example, a baseball) the uncertainties are small, but for electrons, high uncertainties disallow defining an exact orbit.

The Heisenberg Uncertainty Principal

- A similar tradeoff between the variances of Fourier conjugates arises in all systems underlain by Fourier analysis, for example in sound waves: A pure tone is a sharp spike at a single frequency, while its Fourier transform gives the shape of the sound wave in the time domain, which is a completely delocalized sine wave.
- In quantum mechanics, the two key points are that the position of the particle takes the form of a matter wave, and momentum is its Fourier conjugate, assured by the de Broglie relation $p = \hbar k$, where k is the wavenumber.

Heisenberg's Uncertainty Principle



$$(\Delta x)(m\Delta v_x) \approx h$$

Part Twelve: Erwin Schrödinger

- In January 1926, Schrödinger published the paper: Quantization as an Eigenvalue Problem) on wave mechanics, in which he presented what is now known as the Schrödinger equation. In this paper, he gave a "derivation" of the wave equation for time-independent systems and showed that it gave the correct energy eigenvalues for a hydrogen-like atom.
- A second paper was submitted just four weeks later that solved the quantum harmonic oscillator, rigid rotor, and diatomic molecule problems and gave a new derivation of the Schrödinger equation.

Erwin Schrödinger

Erwin Schrödinger

- A third paper, published in May, showed the equivalence of his approach to that of Heisenberg and gave the treatment of the Stark effect.
- A fourth paper in this series showed how to treat problems in which the system changes with time, as in scattering problems. (This was arguably the moment when quantum mechanics switched from real to complex numbers.) When he introduced complex numbers in order to lower the order of the differential equations, something magical happened, and all of wave mechanics was at his feet.
- Schrödinger was not entirely comfortable with the implications of quantum theory referring to his theory as "wave mechanics.“
- He wrote about the probability interpretation of quantum mechanics, saying, "I don't like it, and I'm sorry I ever had anything to do with it."
- (Just in order to ridicule the Copenhagen interpretation of quantum mechanics, he contrived the famous thought experiment called Schrödinger's cat paradox.)

The Schrödinger Wave Equation

- De Broglie postulated that every particles has an associated wave of wavelength:
- Wave nature of matter confirmed by electron diffraction studies *etc* (see earlier)**.**
- If matter has wave-like properties then there must be a mathematical function that is the solution to a differential equation that describes electrons, atoms and molecules.
- The differential equation is called the *Schrödinger equation* and its solution is called the *wavefunction,* Ψ.
- In differential operator form, the time dependent Schrodinger equation is:

$$-\frac{h^2}{8m\pi^2}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}+V(q_i,t)\right)\Psi(q_i,t)=-\frac{h}{2\pi i}\frac{\partial}{\partial t}\Psi(q_i,t)$$

Part Thirteen: Max Born: One

- In 1925, Born and Heisenberg formulated the matrix mechanics representation of quantum mechanics. On 9 July, Heisenberg gave Born a paper entitled "Quantum-Theoretical Re-interpretation of Kinematic and Mechanical Relations" to review, and submit for publication.
- In the paper, Heisenberg formulated quantum theory, avoiding the concrete, but unobservable, representations of electron orbits by using parameters such as transition probabilities for quantum jumps, which necessitated using two indexes corresponding to the initial and final states.
- When Born read the paper, he recognized the formulation as one which could be transcribed and extended to the systematic language of matrices, which he had learned from his study under Jakob Rosanes.

Max Born

Part Thirteen: Max Born: Two

- Up until this time, matrices were seldom used by physicists; they were considered to belong to the realm of pure mathematics.
- Gustav Mie had used them in a paper on electrodynamics in 1912, and Born had used them in his work on the lattices theory of crystals in 1921.
- While matrices were used in these cases, the algebra of matrices with their multiplication did not enter the picture as they did in the matrix formulation of quantum mechanics.
- With the help of his assistant and former student Pascual Jordan, Born began immediately to make a transcription and extension, and they submitted their results for publication; the paper was received for publication just 60 days after Heisenberg's paper.
- A follow-on paper was submitted for publication before the end of the year by all three authors. The result was a surprising formulation:

Part Thirteen: Max Born; Three

- A follow-on paper was submitted for publication before the end of the year by all three authors. The result was a surprising formulation:

$$pq - qp = \frac{h}{2\pi i} I$$

- Born was surprised to discover that Paul Dirac had been thinking along the same lines as Heisenberg.
- Soon, Wolfgang Pauli used the matrix method to calculate the energy values of the hydrogen atom and found that they agreed with the Bohr model.
- Another important contribution was made by Erwin Schrödinger, who looked at the problem using wave mechanics. This had a great deal of appeal to many at the time, as it offered the possibility of returning to deterministic classical physics.
- Born would have none of this, as it ran counter to facts determined by experiment.
- He formulated the now-standard interpretation of the probability density function for ψ*ψ in the Schrödinger equation.

Born Interpretation of $\Psi(x,t)$

As mentioned previously the Time Dependent Schrödinger Equation has solutions that are inherently complex $\Rightarrow \Psi(x,t)$ *cannot* be a physical wave (e.g. electromagnetic waves). Therefore how can $\Psi(x,t)$ relate to real physical measurements on a system?

The Born Interpretation: Probability of finding a particle in a small length dx at position x and time t is equal to:

$$\Psi^*(x,t)\Psi(x,t)dx = \left|\Psi(x,t)\right|^2 dx = P(x,t)dx$$

$\Psi^*\Psi$ is real as required for a probability distribution and is the probability *per unit length* (or volume in 3d).

The Born interpretation therefore calls Ψ the ***probability amplitude***, $\Psi^*\Psi$ (= $P(x,t)$) the ***probability density*** and $\Psi^*\Psi$ dx the ***probability***.

Part Fourteen: Wolfgang Pauli

- Pauli proposed in 1924 a new quantum degree of freedom (or quantum number) with two possible values, to resolve inconsistencies between observed molecular spectra and the developing theory of quantum mechanics.
- He formulated the Pauli exclusion principle, perhaps his most important work, which stated that no two electrons could exist in the same quantum state
- He identified four quantum numbers including his new two-valued degree of freedom.
- The idea of spin originated with Ralph Kronig.

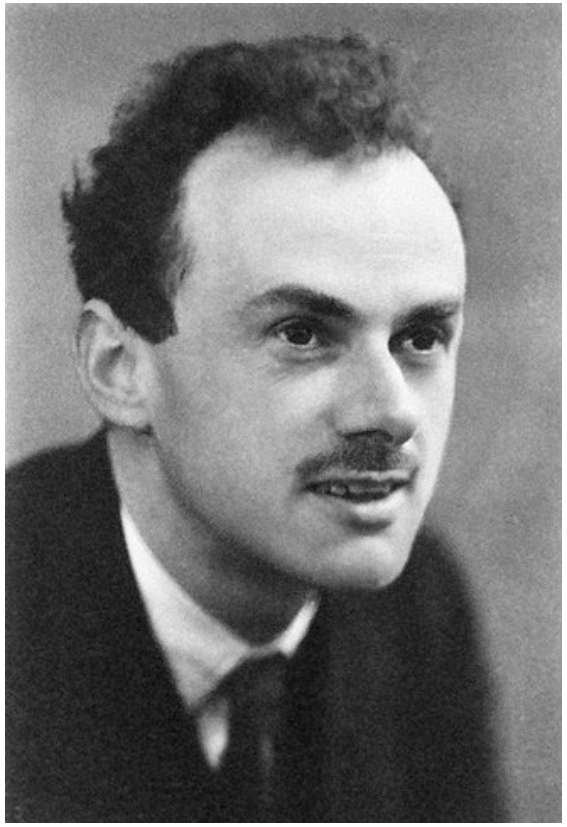
Wolfgang Pauli

Part Fourteen: Wolfgang Pauli

- A year later, George Uhlenbeck and Samuel Goudsmit identified Pauli's new degree of freedom as electron spin.
- In 1926, shortly after Heisenberg published the matrix theory of modern quantum mechanics, Pauli used it to derive the observed spectrum of the hydrogen atom. This result was important in securing credibility for Heisenberg's theory.
- Pauli introduced the 2 × 2 Pauli matrices as a basis of spin operators, thus solving the nonrelativistic theory of spin. This work, including the Pauli equation, is sometimes said to have influenced Paul Dirac in his creation of the Dirac equation for the relativistic electron.

Part Fifteen: Paul Dirac

- Dirac's first step into a new quantum theory was taken late in September 1925. Ralph Fowler, his research supervisor, had received a proof copy of an exploratory paper by Werner Heisenberg in the framework of the old quantum theory of Bohr and Sommerfeld.
- Heisenberg leaned heavily on Bohr's correspondence principle but changed the equations so that they involved directly observable quantities, leading to the matrix formulation of quantum mechanics.
- Fowler sent Heisenberg's paper on to Dirac, who was on vacation in Bristol, asking him to look into this paper carefully.



Paul Dirac

Paul Dirac: The Dirac Equation

- Dirac's attention was drawn to a mysterious mathematical relationship, at first sight unintelligible, that Heisenberg had established.
- Several weeks later, back in Cambridge, Dirac suddenly recognized that this mathematical form had the same structure as the Poisson brackets that occur in the classical dynamics of particle motion.
- At the time, his memory of Poisson brackets was rather vague, but he found E. T. Whittaker's *Analytical Dynamics of Particles and Rigid Bodies* illuminating.
- From his new understanding, he developed a quantum theory based on non-commuting dynamical variables. This led him to the most profound and significant general formulation of quantum mechanics to date.
- Dirac's formulation allowed him to obtain the quantization rules in a novel and more illuminating manner. For this work, published in 1926, Dirac received a PhD from Cambridge.
- This formed the basis for Fermi-Dirac statistics that applies to systems consisting of many identical spin 1/2 particles (i.e. that obey the Pauli exclusion principle),

Paul Dirac: The Dirac Equation

- Building on 2×2 spin matrices which were discovered by Wolfgang Pauli he proposed the Dirac equation as a relativistic equation of motion for the wave function of the electron.
- This work led Dirac to predict the existence of the positron, the electron's antiparticle.
- The positron was observed by Carl Anderson in 1932. Dirac's equation also contributed to explaining the origin of quantum spin as a relativistic phenomenon.
- The necessity of fermions (matter) being created and destroyed in Enrico Fermi's 1934 theory of beta decay led to a reinterpretation of Dirac's equation as a "classical" field equation for any point particle of spin $\hbar/2$, itself subject to quantisation conditions involving anti-commutators.
- Thus reinterpreted, in 1934 by Werner Heisenberg, as a (quantum) field equation elementary matter particles
- The Dirac field equation is as central to theoretical physics as the Maxwell , Yang–Mills and Einstein field equations.

Paul Dirac: The Principals of Quantum Mechanics

Dirac's *The Principles of Quantum Mechanics*, published in 1930, is a landmark in the history of science. It quickly became one of the standard textbooks on the subject and is still used today. In that book, Dirac incorporated the previous work of Werner Heisenberg on matrix mechanics and of Erwin Schrödinger on wave mechanics into a single mathematical formalism that associates measurable quantities to operators acting on the Hilbert space of vectors that describe the state of a physical system. The book also introduced the Dirac delta function. Following his 1939 article, he also included the bra–ket notation in the third edition of his book, thereby contributing to its universal use nowadays.

Part Sixteen: John von Neumann

Von Neumann was the first to establish a rigorous mathematical framework for quantum mechanics, known as the Dirac–von Neumann axioms. After having completed the axiomatization of set theory, he began to confront the axiomatization of quantum mechanics. He realized in 1926 that a state of a quantum system could be represented by a point in a (complex) Hilbert space that, in general, could be infinite-dimensional even for a single particle. In this formalism of quantum mechanics, observable quantities such as position or momentum are represented as linear operators acting on the Hilbert space associated with the quantum system.

John von Neumann

Part Sixteen: John von Neumann

- The *study* of quantum mechanics was thereby reduced to the *mathematics* of Hilbert spaces and linear operators acting on them.
  - For example, the uncertainty principle, according to which the determination of the position of a particle prevents the determination of its momentum and vice versa, is translated into the *non-commutativity* of the two corresponding operators.
- Von Neumann's abstract treatment permitted him also to confront the foundational issue of determinism versus non-determinism, and in the book he presented a proof that the statistical results of quantum mechanics could not possibly be averages of an underlying set of determined "hidden variables," as in classical statistical mechanics.
- . In 1935, Grete Hermann published a paper arguing that the proof contained a conceptual error and was therefore invalid. Hermann's work was largely ignored until after John S. Bell made essentially the same argument in 1966.

Part Sixteen: John von Neumann

- In 2010, Jeffrey Bub argued that Bell had misconstrued von Neumann's proof, and pointed out that the proof, though not valid for all hidden variable theories, does rule out a well-defined and important subset. Bub also suggests that von Neumann was aware of this limitation and did not claim that his proof completely ruled out hidden variable theories. The validity of Bub's argument is, in turn, disputed. In any case, Gleason's theorem of 1957 fills the gaps in von Neumann's approach.
- Von Neumann's proof inaugurated a line of research that ultimately led, through Bell's theorem and the experiments of Alain Aspect in 1982, to the demonstration that quantum physics either requires a *notion of reality* substantially different from that of classical physics, or must include nonlocality in apparent violation of special relativity.

The Mathematical Foundations of Quantum Mechanics

- In his classic presentation: *The Mathematical Foundations of Quantum Mechanics*, von Neumann deeply analyzed the so-called measurement problem. He concluded that the entire physical universe could be made subject to the universal wave function. Since something "outside the calculation" was needed to collapse the wave function, von Neumann concluded that the collapse was caused by the consciousness of the experimenter.
- He argued that the mathematics of quantum mechanics allows the collapse of the wave function to be placed at any position in the causal chain from the measurement device to the "subjective consciousness" of the human observer.
- Although this view was accepted by Eugene Wigner, the Von Neumann–Wigner interpretation never gained acceptance among the majority of physicists.
- Viewing von Neumann's work on quantum mechanics as an part of the fulfilment of Hilbert's sixth problem, noted mathematical physicist A. S. Wightman said in 1974 his axiomization of quantum theory was perhaps the most important axiomization of a physical theory to date.
- In the publication of his 1932 book, quantum mechanics became a mature theory in the sense it had a precise mathematical form, which allowed for clear answers to conceptual problems.

Part Seventeen: The wave Equation

- **The state function Ψ is given as a solution of**

$$\hat{H}\Psi = E\Psi \longleftarrow \text{Schrodinger equation}$$

where $\hat{H}$ is the total energy operator, that is the Hamiltonian operator.

- The hamiltonian function is the total energy, T+V, where T is the kinetic energy and V is the potential energy. In operator form

$$\hat{H} = \hat{T} + \hat{V}$$

where $\hat{T}$ is the operator for kinetic energy and $\hat{V}$ is the operator for potential energy. In differential operator form, the time dependent Schrodinger equation (TDSE) is

$$-\frac{h^2}{8m\pi^2}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}+V(q_i,t)\right)\Psi(q_i,t) = -\frac{h}{2\pi i}\frac{\partial}{\partial t}\Psi(q_i,t)$$

The wave Equation: Two

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

where $\hat{H}$ is called the ***Hamiltonian operator*** which is the differential operator that represents the ***total energy*** of the particle.

Thus $$\hat{H}=\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+V(x)\right)=\frac{\hat{p}_x^2}{2m}+\hat{V}(x)$$

where the ***momentum operator*** is $$\hat{p}_x=-i\hbar\frac{\partial}{\partial x}$$

Thus shorthand for TDSE (Time Dependent Schrödinger Wave Equation

$$\hat{H}\Psi=i\hbar\frac{\partial\Psi}{\partial t}$$

The time-dependent Wave Equation

For a particle in a potential $V(x,t)$ then $E = \frac{p^2}{2m} + V(x,t)$

and we have (KE + PE) × wavefunction = (Total energy) × wavefunction

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

Points of note:

1. The TDSE is one of the postulates of quantum mechanics. Though the SE cannot be derived, it has been shown to be consistent with all experiments.
2. SE is first order with respect to *time* (*cf*. classical wave equation).
3. SE involves the complex number *i* and so its *solutions are essentially complex*.

Expectation values

Thus if we know $\Psi(x, t)$ (a solution of TDSE), then knowledge of $\Psi^*\Psi\, dx$ allows the *average* position to be calculated:

$$\bar{x} = \sum_i x_i P(x_i)\, \delta x$$

In the limit that $\delta x \to 0$ then the summation becomes:

$$\bar{x} = \langle x \rangle = \int_{-\infty}^{\infty} x P(x) dx = \int_{-\infty}^{\infty} x \left|\Psi(x,t)\right|^2 dx$$

The average is also know as the *expectation value* and are very important in quantum mechanics as they provide us with the average values of physical properties.

Similarly $$\left\langle x^2 \right\rangle = \int_{-\infty}^{\infty} x^2 P(x) dx = \int_{-\infty}^{\infty} x^2 \left|\Psi(x,t)\right|^2 dx$$

Normalisation

Total probability of finding a particle anywhere must be 1:

$$\int_{-\infty}^{\infty} P(x)dx = \int_{-\infty}^{\infty} |\Psi(x,t)|^2 dx = 1$$

This requirement is known as the *Normalisation condition*. (This condition arises because the SE is linear in Ψ and therefore if Ψ is a solution of TDSE then so is $c\Psi$ where c is a constant.)

Hence if original unnormalised wavefunction is $\Psi(x,t)$, then the normalisation integral is:

$$N^2 = \int_{-\infty}^{\infty} |\Psi(x,t)|^2 dx$$

And the (re-scaled) normalised wavefunction $\Psi_{norm} = (1/N)\,\Psi$.

Eigenvalue equations

The *Schrödinger Equation* is the form of an *Eigenvalue Equation*:

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

where $\hat{H}$ is the Hamiltonian operator, $\hat{H} = \hat{T} + \hat{V} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)$

ψ is the wavefunction and is an *eigenfunction* of $\hat{H}$;

E is the total energy (T + V) and an *eigenvalue* of $\hat{H}$. E is just a constant!

Eigenvalue equations

We have seen how we can use the probability distribution $\psi^*\psi$ to calculate the average position of a particle. What happens if we want to calculate the *average energy* or *momentum* because they are represented by the following differential operators:

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x) \qquad \hat{p}_x = \frac{\hbar}{i}\frac{\partial}{\partial x}.$$

Do the operators work on $\psi^*\psi$, or on ψ, or on ψ^* alone?

Take TISE and multiply from left by ψ^* and integrate:

$$\hat{H}\psi_n = E_n\psi_n$$

$$\int \psi_n^* \hat{H}\psi_n \mathrm{d}x = \int \psi_n^* E_n \psi_n \mathrm{d}x = E_n \int \psi_n^* \psi_n \mathrm{d}x = E_n$$

NB ψ is normalised.

Suggest that in order to calculate the *average value* of the physical quantity associated with the QM operator we carry out the following integration:

$$\int \psi_n^* \hat{\Omega} \psi_n \mathrm{d}x$$

Momentum and energy expectation values

The expectation value of *momentum* involves the representation of momentum as a quantum mechanical operator:

$$\langle p_x \rangle = \int_{-\infty}^{\infty} \Psi^*(x,t) \frac{\hbar}{i} \frac{\partial}{\partial x} \Psi(x,t) dx \quad \text{where} \quad \hat{p}_x = \frac{\hbar}{i} \frac{\partial}{\partial x}.$$

is the operator for the *x* component of momentum.

Example: Derive an expression for the average energy of a free particle.

$$E = \frac{p^2}{2m} \quad \text{then} \quad \langle E \rangle = \frac{\langle p^2 \rangle}{2m}$$

Since $V = 0$ the expectation value for energy for a particle moving in one dimension is

$$\langle E \rangle = \int_{-\infty}^{\infty} \Psi^*(x,t) \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \right) \Psi(x,t) dx$$