

PHYS255: Quantum & Atomic Physics

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These slides available on VITAL

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Some Text Books

- A.C. Phillips
"Introduction to Quantum Mechanics"
- R. Eisberg & R. Resnick
"Quantum Mechanics of Atoms,
Molecules, Solids, Nuclei & Particles"
- E. Zaarur, Y. Peleg, R. Pnini
"Quantum Mechanics" Schaum's Easy Outlines
- D. McMahon
"Quantum Mechanics Demystified"
available at the Liverpool e-brary:
<http://www.liv.ac.uk/library/electron/db/ebrary.html>



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PHYS255 Timetable 2011

- Semester 1 Lectures (ORBIT!)
 - Tuesday 09:00 - 11:00 Rotblat (207)
 - Wednesday 09:00 - 10:00 Life Sciences LT3 (215)
- Tutorials
 - Wednesday Weeks 2, 5, 8, 11 Oliver Lodge (208)
- Science Communication Project
 - Deadline for written report: (10%)
 - Monday November 14th at 16:30 (Week 8)
 - Week 11:
 - 5 minute presentation using data projector (i.e. PowerPoint) (10%)

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Basic Ideas of Quantum Mechanics

- A general introduction to basic concepts of quantum physics is available on VITAL:

QMIntro.pdf

- The mathematical formalism is also introduced for the present course, based on Schrödinger's wave mechanics (PHYS255), while more general formalisms of quantum mechanics are also introduced, useful for next year's PHYS361 module.

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PHYS255: Topics

- 1. Introduction
- 2. Essential Mathematics
- 3. Forces and Potential Energy
- 4. Quantisation
- 5. Wave Particle Duality
- 6. Particle Wave Function
- 7. Particle Wave Equation
- 8. Wave Dynamics of Particles: Bound States
- 9. Wave Dynamics of Particles: Scattering
- 10. Atomic Structure

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1. Introduction

General ideas

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The Birth of Quantum Mechanics

- Quantum Mechanics is the theory of atomic and subatomic systems
- At the end of the 19th century, classical physics had problems explaining the transfer of energy between radiation and matter (blackbody radiation)
- It was solved by Planck who introduced discrete quanta of energy - the energy exchange is not continuous
- Quantum means "how much" or "finite amount of some quantity"

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The Death of Determinism

- The 1903 Nobel Prize was awarded for the discovery of nuclear radioactivity (Becquerel, Curie, Curie)
- Previously, physical phenomena were thought to be deterministic (Newton) and it was assumed that the motion of an object could be predicted with unlimited accuracy, given the initial conditions
- Radioactivity is different - the decay of each individual nucleus cannot be precisely predicted, but its probability of decay could be analysed on the statistical behaviour of many nuclei

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What is Quantum Mechanics?

- Quantum Mechanics is the name given to a system of equations which must be used instead of Newton's Laws of Motion in order to calculate the behaviour of atoms, electrons and other ultimate particles of matter
- Newton's laws work well for the motion of planets, but not electrons in an atom
- Quantum Mechanics gives very nearly the same answers as Newton's classical laws, except when applied to "small" systems

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The Rise of the Quantum

- Einstein (1905) showed that light acted as if it were "grainy" and used the quantum approach to explain the photoelectric effect - energy is exchanged by discrete photons
- Niels Bohr (1913) incorporated the quantum into his model of the atom and discrete electronic energy levels
- The quantum began to appear in other areas of physics, then in chemistry and other sciences
- A full theory of Quantum Mechanics was developed in 1927

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When is a System "Small" ?

- How do we distinguish between a "small" (quantum) and a "large" (classical) system?
- Planck's constant $\hbar = h/2\pi$ has the units of "action", i.e.
$$\text{length} \times \text{momentum} \quad \text{or} \quad \text{time} \times \text{energy}$$
- The "size" of a system is judged by the typical action
- For an electron in an atom, the action $\approx \hbar$ ("small" or quantum), while in an electronic device, the action $\gg \hbar$ ("large" or classical)

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Measurement

- In classical physics, the act of measurement need not effect the object under observation and the properties of a classical object can be specified with precision
- This is not the case in quantum physics! Measurement plays an active and disturbing role - quantum particles are best described by the possible outcomes of measurement
- Quantum Mechanics mathematically includes the effect of measurement on a system (Uncertainty Principle)
- Quantum Mechanics challenges intuitive notions about reality, such as whether the property of a particle exists before a measurement is made on it (Schrödinger's cat)

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2. Essential Mathematics

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Is Quantum Mechanics Correct?

- Albert Einstein never accepted the indeterministic nature of Quantum Mechanics: "God does not play dice"
- Niels Bohr stated: "Anyone who is not shocked by quantum theory has not understood it"
- Nevertheless, despite its philosophical difficulties, no prediction of quantum theory has ever been disproved!
- Quantum Mechanics is the founding basis of all modern physics: solid state, molecular, atomic, nuclear and particle physics, optics, thermodynamics, statistical mechanics... ..chemistry, biology, astronomy, cosmology

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Mathematical Techniques

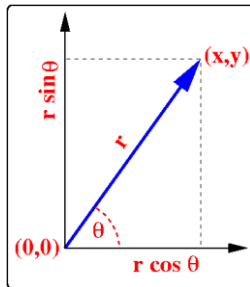
- This course is based on 'Wave Mechanics'
 - 2.1 Algebra of Complex Numbers [$i = \sqrt{-1}$]
 - Representation of waveforms
 - Combination of waveforms, magnitudes and phases
 - Differentiation of waveforms
 - 2.2 Operators and Observables
 - Eigenvalue Equation
 - Basic ideas of wave mechanics
 - Mutual disturbance
- Tutorial Set 1 (for week 2)

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2.1 Complex Numbers (Argand Diagram)



Complex plane
x-axis "real" $x = r \cos\theta$
y-axis "imaginary" $y = r \sin\theta$

$$\exp\{i\theta\} = \cos\theta + i \sin\theta$$

- Represent vector \underline{r}
 $(x + iy)$
 $r e^{i\theta} = r \exp\{i\theta\}$
- Magnitude (squared)
 $r^2 = x^2 + y^2$
 $= r^2(\cos^2\theta + \sin^2\theta)$
i.e. $\cos^2\theta + \sin^2\theta = 1$
- Phase angle
 $\theta = \tan^{-1}\{y/x\}$
 $\tan\theta = \{y/x\}$
 $= \{r \sin\theta / r \cos\theta\}$
i.e. $\tan\theta = \sin\theta / \cos\theta$

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Waveforms

- Wave function
 $\Psi(x,t) = A \sin\{kx - \omega t\}$
- Amplitude A
- Wave number k (m^{-1}) = $2\pi/\lambda$, wavelength λ (m)
- Angular frequency ω ($rad\ s^{-1}$) = $2\pi/T$, period T (s) = ν^{-1}
frequency ν (hertz)
- Velocity $c = \omega / k$ ($= \nu \lambda$)
- Can also represent in terms of complex exponentials

$$\Psi(x,t) = A \exp\{i(kx - \omega t)\}$$

- Time independence

$$\Psi(x) = A \exp\{ikx\}$$

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Complex Exponentials

- Some useful relationships:

$$\exp\{0\} = 1 \quad (x=1, y=0)$$

$$\exp\{i\pi/2\} = i \quad (x=0, y=1)$$

$$\exp\{i\pi\} = -1 \quad (x=-1, y=0) \quad \text{Euler equation}$$

$$\exp\{i3\pi/2\} = \exp\{-i\pi/2\} = -i \quad (x=0, y=-1)$$

- Draw the vectors!

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Waveforms (de Broglie Wave)

- Wave travelling in the positive x direction
 $\Psi(x) = A \exp\{ikx\}$
- Wave travelling in the negative x direction
 $\Psi(x) = A \exp\{-ikx\}$
- Relation between sines, cosines and complex exponentials

$$\exp\{i\theta\} = \cos\theta + i \sin\theta$$

$$\cos\theta = [\exp\{i\theta\} + \exp\{-i\theta\}] / 2$$

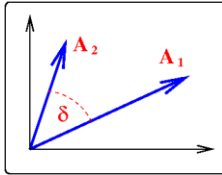
$$\sin\theta = [\exp\{i\theta\} - \exp\{-i\theta\}] / 2i$$

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Combination of Waveforms



- **Waveform 1** "wavevector 1"
 $\psi_1 = A_1 \exp\{ik_1x\}$
- **Waveform 2** "wavevector 2"
 $\psi_2 = A_2 \exp\{ik_2x\}$

- When summing waveforms (**vectors**) we must take into account the relative phase $\delta = \theta_2 - \theta_1$ of the waveforms

$$\psi = \psi_1 + \psi_2 = A_1 \exp\{ik_1x\} + A_2 \exp\{ik_2x\} \exp\{i\delta\}$$

- In terms of sines (cosines) In phase: $\delta = 0$

$$\psi = A_1 \sin\{k_1x\} + A_2 \sin\{k_2x + \delta\}$$

Antiphase: $\delta = \pi$ (180°)

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2.2 Operators

- An **operator** is a mathematical entity which 'operates' on any function, of x say, and turns it into another function

- The simplest operator is a function of x

$$\hat{A} = \hat{A}(x) \quad \text{e.g.} \quad \hat{A}(x) = x^2$$

- Given any function $\psi(x)$, this operator gives

$$\hat{A}(x) \psi(x) = x^2 \psi(x)$$

- An operator may also differentiate, i.e. a function of $\partial/\partial x$

$$\hat{A}(\partial/\partial x) \quad \text{e.g.} \quad \hat{A}(\partial/\partial x) = \partial^2/\partial x^2$$

- Given any function $\psi(x)$, this operator gives

$$\hat{A}(\partial/\partial x) \psi(x) = \partial^2 \psi(x) / \partial x^2$$

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Differentials

- Differential of waveform **sin θ** :

$$\text{➤ } d/d\theta \{ \sin \theta \} = \cos \theta = \sin \{ \theta + \pi/2 \} \quad \text{phase } +90^\circ$$

- Differential of wavevector **exp*i* θ** :

$$\text{➤ } d/d\theta \{ \exp\{i\theta\} \} = i \exp\{i\theta\} = \exp\{i\pi/2\} \exp\{i\theta\} \\ = \exp\{i(\theta + \pi/2)\} \quad \text{phase } +90^\circ$$

$$\text{➤ } d^2/d\theta^2 \{ \exp\{i\theta\} \} = i^2 \exp\{i\theta\} = -1 \exp\{i\theta\} \\ = \exp\{i\pi\} \exp\{i\theta\} \\ = \exp\{i(\theta + \pi)\} \quad \text{phase } +180^\circ$$

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Operator Equation

- Take an operator $\hat{A}(x, \partial/\partial x)$

$$\hat{A} = \frac{\partial}{\partial x} x$$

- Then for any function $\psi(x)$

$$\hat{A} \psi(x) = \frac{\partial}{\partial x} x \psi(x) = \psi(x) + x \frac{\partial \psi(x)}{\partial x} = \left(1 + x \frac{\partial}{\partial x} \right) \psi(x)$$

- Now remove $\psi(x)$ to give the **operator equation**

$$\frac{\partial}{\partial x} x = \left(1 + x \frac{\partial}{\partial x} \right)$$

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Observables and Operators

- We can associate an operator with any observable, e.g. position or momentum
- The eigenvalues of the operator represent the possible results of the observation
- However, for small systems the act of observation can disturb the (quantum) system
- Hence for two successive measurements, the result depends on the order of observation

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Commutation Relations

- Now consider the successive operation of two operators. We define the 'commutator' of two operators \hat{A} and \hat{C} as

$$[\hat{A}, \hat{C}] = \hat{A}\hat{C} - \hat{C}\hat{A}$$

which is the difference between operating first with \hat{C} and then \hat{A} , and first with \hat{A} and then with \hat{C}

- In general $[\hat{A}, \hat{C}] \neq 0$ but is some new operator
- For example, if $\hat{A} = x$ and $\hat{C} = \partial/\partial x$, it can be shown that

$$[x, \partial/\partial x] = -1$$

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Eigenvalue Equation

- To each operator $\hat{A}(x, \partial/\partial x)$ belong a set of numbers a_n and functions $u_n(x)$ defined by the equation

$$\hat{A}u_n(x) = a_n u_n(x)$$

- Here a_n is an eigenvalue and $u_n(x)$ the corresponding eigenfunction
- The eigenfunctions of an operator are those special functions which remain unaltered under the operation of the operator, apart from multiplication by the eigenvalue

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Mutual Disturbance

- The commutator of the corresponding operators, e.g. \hat{A} and \hat{C} is therefore, in general, non-zero, $[\hat{A}, \hat{C}] \neq 0$
- The commutator gives a measure of the mutual disturbance of the two measurements
- The magnitude of the disturbance is related to \hbar
- Thus Planck's constant gives a fundamental limit of the accuracy to which we can measure two (non-commuting) properties of a system, e.g. position and momentum of a particle

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The Uncertainty Principle

- Consider the measurement of position x and momentum p
- Accurate p requires low momentum photons (long wavelength) – very inaccurate x (and vice versa)
- The position and momentum operators mutually disturb each other

$$[\hat{x}, \hat{p}] \neq 0$$

assume: $[\hat{x}, \hat{p}] = i\hbar$

- If we represent the position operator by $\hat{x} = x$

- Then, since

$$\left[x, \frac{\partial}{\partial x} \right] = -1$$

the momentum operator is

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

Schrödinger representation

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Normalisation

- The eigenvalue equation remains unchanged if the eigenfunctions are multiplied by a numerical factor, e.g.

$$\hat{p}Cu_p(x) = pCu_p(x)$$

- To fix the magnitude of the eigenfunctions, we impose the normalising condition

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

- For the de Broglie wave this yields

$$\int_{-\infty}^{\infty} C^* e^{-ipx/\hbar} C e^{ipx/\hbar} dx = |C|^2 \int_{-\infty}^{\infty} dx = 1$$

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Momentum Eigenstates and Eigenvalues

- The eigenvalue equation for momentum is

$$\hat{p}u_p(x) = pu_p(x)$$

$$-i\hbar \frac{\partial}{\partial x} u_p(x) = pu_p(x)$$

- The solution yields an eigenstate of momentum p

$$u_p(x) = e^{ipx/\hbar} \quad \text{for any } p$$

- This is the space part of the de Broglie wave and justifies the i in

$$[\hat{x}, \hat{p}] = i\hbar \quad \text{otherwise no wave!}$$

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Localised Particle

- If the particle (de Broglie wave) is confined to the region $0 \leq x \leq L$, the normalisation condition becomes

$$|C|^2 \int_0^L dx = |C|^2 L = 1$$

- Hence

$$C = \frac{1}{\sqrt{L}}$$

- The normalised de Broglie wave is

$$u_p(x) = \frac{1}{\sqrt{L}} e^{ipx/\hbar}$$

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Total Energy of a Particle

- The energy of a free particle is classically just its kinetic energy

$$K.E. = \frac{1}{2}mv^2 = \frac{p^2}{2m}$$

- The corresponding operator (Hamiltonian) is

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

- In the presence of a potential $V(x)$ the Hamiltonian is

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

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Expectation Value of an Operator

- The average value of repeated observations \hat{A} on systems in an arbitrary (normalised) state $\psi(x)$ is

$$\bar{a}_\psi = \langle \hat{A} \rangle = \int \psi^*(x) \hat{A} \psi(x) dx$$

- Applying this to the observation of position, implies that the probability of position x is

$$P_\psi(x) = |\psi(x)|^2 \quad \text{probability density}$$

- The normalisation condition ensures that the probability of finding the particle somewhere is unity

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The Schrödinger Equation

- The possible energy levels of a system are the eigenvalues of the Hamiltonian operator

$$\hat{H}u_E(x) = E_n u_E(x)$$

- This equation is solved subject to boundary conditions and the fact that the eigenfunctions $u_E(x)$ must be finite everywhere
- The choice of the potential energy function $V(x)$ defines the system

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The Overlap Integral

- The probability of an observation \hat{A} on a state $\psi(x)$ having a result a is related to the extent that the function $\psi(x)$ resembles the eigenfunction $u_a(x)$

$$P_\psi(a) = \left| \int u_a^*(x) \psi(x) dx \right|^2$$

- In general, any physical state $\psi(x)$ can be expressed as a linear expansion of the eigenfunctions $u_a(x)$ of an operator \hat{A}

$$\psi(x) = \sum_i c_i u_{ai}(x)$$

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Summary: Operators

- A **spatial** operator 'extracts' the position co-ordinate from a wave-function, e.g.

$$\hat{x}\Psi(x, y, z, t) = x\Psi(x, y, z, t)$$

- Similarly, the **differential momentum** operator 'extracts' the momentum from a wave-function, i.e.

$$\hat{p}\Psi(x, y, z, t) = -i\hbar \frac{\partial}{\partial x} \Psi(x, y, z, t) = p\Psi(x, y, z, t)$$

- Other types of operators may be used, e.g. **matrix operators** (Heisenberg).

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3. Forces and Potential Energy

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Introduction

- **Quantum Physics** is the theory of atomic and subatomic matter
- It was developed from **Classical Physics**
 - **Matter** (Newton)
 - **Radiation** (Maxwell)
- **Certain phenomena** required energy quantisation
 - **Black body radiation, photoelectric effect**

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Classical Matter

- Point particle, specified by

Mass m Energy E Momentum p

- Governed by Newtonian Mechanics (for constant mass)

$$\mathbf{F} = \frac{d\mathbf{p}}{dt} = m \frac{d\mathbf{v}}{dt} = m\mathbf{a}$$

- One dimension x , or radial force r

- Physical system specified by

- force $\mathbf{F}(x)$ at position x
- force $\mathbf{F}(r)$ at position r

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Force and Potential Energy

- Potential energy is defined as

$$V(x) = -\int_{x_0}^x \mathbf{F}(x) dx$$

- The lower limit x_0 (arbitrarily) defines when $V(x_0) = 0$

- Hence force is given by

$$\mathbf{F}(x) = -\frac{\partial V}{\partial x}$$

- i.e. force = -(slope of V)

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Forces, examples

- Gravity: force downward, g acceleration due to gravity

$$\mathbf{F}(x) = -mg$$

- Harmonic Oscillator: restoring force

$$\mathbf{F}(x) = -m\omega^2 x$$

- Hydrogen atom: Coulomb attraction, spherical symmetry

$$\mathbf{F}(\mathbf{r}) = -\frac{e^2}{4\pi\epsilon_0} \frac{1}{r^2}$$

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Potential Energy Functions, examples

- Gravity

$$V(x) = \int_0^x mg dx = mgx$$

- Harmonic Oscillator

$$V(x) = \int_0^x m\omega^2 x dx = \frac{1}{2} m\omega^2 x^2$$

- Hydrogen Atom

$$V(\mathbf{r}) = \int_{\infty}^r \frac{e^2}{4\pi\epsilon_0} \frac{dr}{r^2} = -\frac{e^2}{4\pi\epsilon_0 r}$$

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Conservation of Energy

- Force may expressed as

$$F(x) = m \frac{dv(x)}{dt} = m \frac{dv(x)}{dx} \frac{dx}{dt} = mv \frac{dv}{dx}$$

- Integrating yields

$$\int F(x) dx = \int mv \frac{dv}{dx} dx = m \int v dv$$

- Hence

$$-V(x) = \frac{1}{2} mv^2 + \text{const}$$

- Rewrite as

$$V(x) + T(x) = E$$

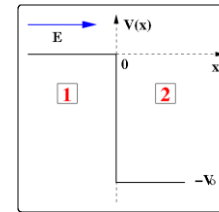
- Potential Energy + Kinetic Energy = Total Energy (const)

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Quantum Mechanics is Weird !



- What happens when a quantum particle comes to the edge of a potential (cliff) ?

- There is a chance of it being reflected (R) rather than transmitted (T) !



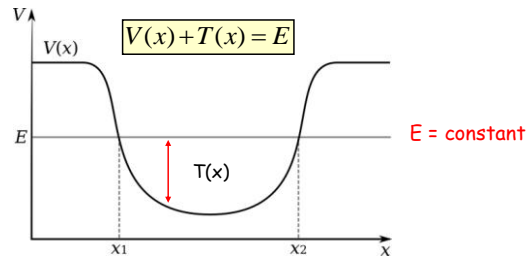
- See VITAL for links to movies of wave packet motion

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The Potential Well



- Given $V(x)$, a particular value of x is only possible for positive kinetic energy $T(x) > 0$, i.e. $E > V(x)$

- Classically the particle will oscillate between positions x_1 and x_2 in the above potential

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4. Quantisation

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4.1 Black Body Radiation

- Radiation from a heated source with no specific structure
- Frequency distribution determined only by temperature T

- light bulb
- the Sun
- but not a sodium lamp



- Heat is radiation from random motion of electrons in the source (Maxwell)

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Introduction

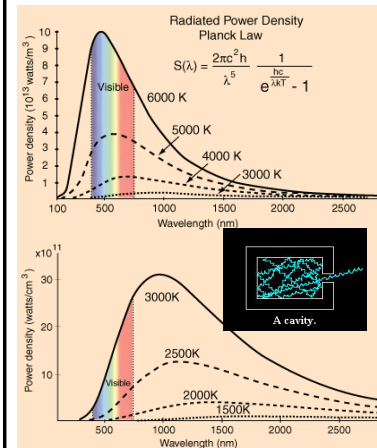
- Energy quantisation is required to describe the following phenomena:
 - 4.1 Black Body Radiation, Ultraviolet Catastrophe
 - 4.2 Photoelectric Effect PHYS259
 - 4.3 Atomic Spectra PHYS259
- Classical physics with no requirement of energy quantisation **fails** to describe the above

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Black Body Radiation Distribution



- Continuous spectrum with respect to
 - λ (wavelength) or
 - ν (frequency) or
 - ω (angular frequency)

- Most energy is radiated at the "peak"

- Wien's Law:
 - Peak wavelength $\propto 1/T$
 - Peak frequency $\propto T$
 where T is the temperature

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Classical Energy Density

- Assume that the energy of radiation in the frequency interval $\omega \rightarrow \omega + \delta\omega$ can be arbitrarily small, depending only on the intensity
- Energy density = energy/volume Rayleigh-Jeans formula

$$\rho(\omega)d\omega \sim (kT) \frac{\omega^2 d\omega}{c^3}$$

Boltzmann's constant k ,
speed of light c

- From Statistical Mechanics

$$\rho(\omega)d\omega = \frac{2}{\pi} (kT) \frac{\omega^2 d\omega}{c^3}$$

i.e. ω^2 dependence

- Completely wrong! "Ultraviolet Catastrophe"

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Planck's Solution

- Planck assumed that the energy of radiation, of frequency ω , can only occur in quanta (photons) of magnitude

$$E = \hbar\omega = h\nu$$

- Planck's constant has dimensions of angular momentum, or momentum \times length, or energy \times time

$$\hbar = h / 2\pi = 1.05 \times 10^{-34} \text{ Js}$$

- A continuous variable (integrate) is now replaced by a discrete variable (sum of series)

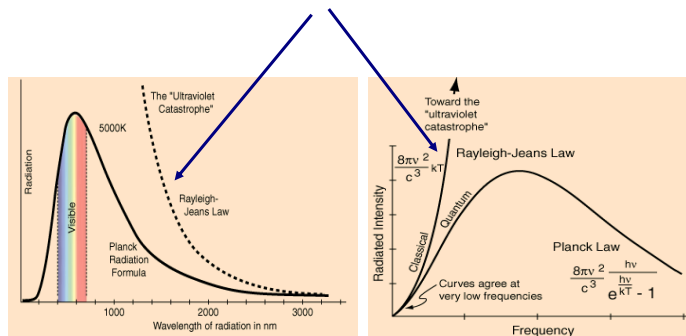
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Ultraviolet Catastrophe

- A disaster for Classical Physics!



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The Quantum

- The word quantum is Latin for

"how much"

or

"finite amount of some quantity"

- Planck:

energy exchange between radiation and matter is not continuous...

radiation and matter exchange energy in discrete lumps or multiples of the basic quantum

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Planck's Radiation Formula

- The energy density is given by

$$\rho(\omega)d\omega = \frac{2}{\pi} \frac{\hbar\omega}{[e^{\hbar\omega/kT} - 1]} \frac{\omega^2 d\omega}{c^3}$$

- Low frequency ($kT \gg \hbar\omega$)

$$\rho(\omega)d\omega = \frac{2}{\pi} (kT) \frac{\omega^2 d\omega}{c^3}$$

Tutorial 1

- High frequency ($kT \ll \hbar\omega$)

$$\rho(\omega)d\omega = \frac{2}{\pi} \hbar\omega [e^{-\hbar\omega/kT}] \frac{\omega^2 d\omega}{c^3}$$

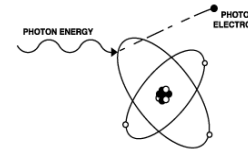
Exponential damping

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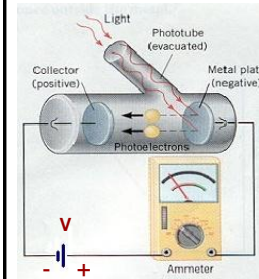
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4.2 Photoelectric Effect



- Monochromatic light of frequency ν is incident on a cathode
- Above a certain threshold ν , electrons are emitted from the cathode causing current flow to the anode
- If V is increased (to V_0) then eventually the electrons will fail to have enough energy to reach the cathode and the current stops
- V_0 is the "stopping potential"

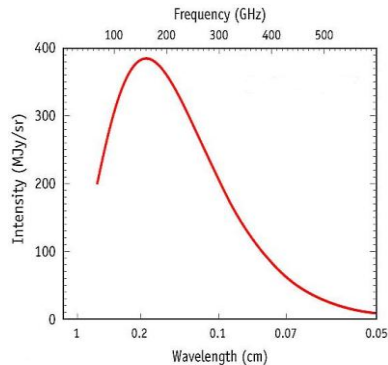


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Cosmic Background Radiation



$$T = 2.725 \pm 0.001 \text{ kelvin}$$

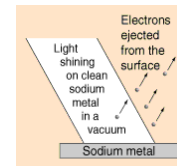
- The Universe emits blackbody radiation at a temperature of **2.725 K**, a remnant of the Big Bang
- Experiment and quantum predictions seem to match perfectly!

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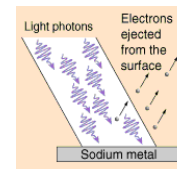
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Photoelectric Effect



- Experimentally:

- V_0 does not depend on the intensity $I(\lambda)$ of the monochromatic light
- V_0 depends linearly on the frequency ν of the radiation



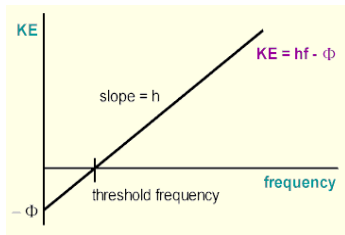
- Theoretical Interpretation (Einstein): Each photoelectron is emitted from the cathode by the absorption of one quantum of energy $E = h\nu$ from the radiation

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Photoelectric Effect: Work Function

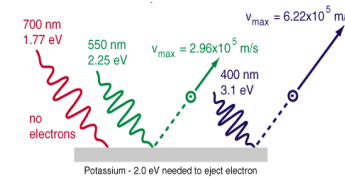


- It takes a certain amount of energy to liberate the electron
- The kinetic energy of the photoelectron is:

$$T = h\nu - \Phi$$

where Φ is the "work function" of the cathode

- To each (photo)electron in the cathode, the incident monochromatic radiation is a stream of mono-energetic quanta (photons) of energy $h\nu$ which it can absorb



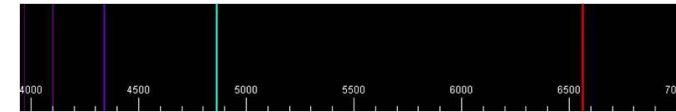
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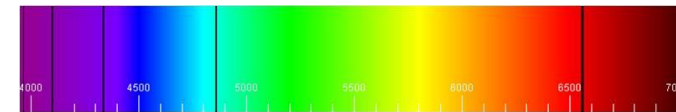
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4.3 Atomic Spectra (Line Spectra)

Hydrogen emission spectrum



Hydrogen absorption spectrum



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Energy from Matter to Radiation

- The generation of X rays - by firing electrons at a metal target - is the inverse of the photoelectric effect.
- Energy is transferred from matter to radiation
- The X ray spectrum has a maximum frequency, or minimum wavelength, that can be related to the kinetic energy of the electrons, and the accelerating voltage V

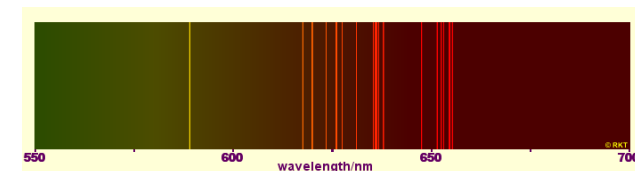
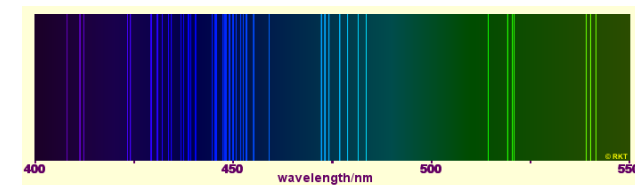
$$eV = K.E. = \frac{p_{\max}^2}{2m} = \hbar\omega = h\nu_{\max} = \frac{hc}{\lambda_{\min}}$$

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Discharge Spectrum of Atomic Sodium

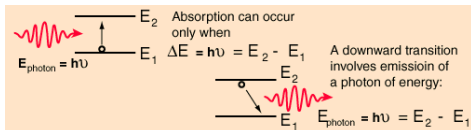


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Discrete Atomic Energy Levels



- Excitation of atoms or molecules in the gaseous phase (heating) leads to radiation emitted with a discrete spectrum of wavelengths λ (or frequency ν)
- Atoms or molecules emit photons of energy $E = h\nu$ as they de-excite from one discrete energy state to another. Atomic, molecular energy is quantised

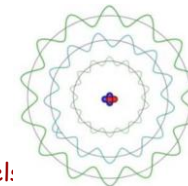
$$h\nu = E_i - E_f \quad (\text{Bohr})$$

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The Bohr Atom



- Bohr postulated that the angular momentum of an allowed electron orbit is quantised and given by

$$L = \ell \hbar \quad \ell = 1, 2, 3, \dots$$
- This implied discrete allowed energy level:

$$E_n \quad n = 1, 2, 3, \dots$$
- A single photon of frequency ω is emitted when an electron 'jumps' from one orbit to another

$$E_m - E_n = \hbar\omega \quad m > n$$

- Bohr calculated

$$\hbar\omega_{mn} = \{Z^2 e^2 / 8\pi\epsilon_0\} \{1/a_0\} \{1/n^2 - 1/m^2\}$$
 constants - Bohr radius - discrete values

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Hydrogen Balmer Series

- The Balmer series in hydrogen is a set of discrete-line transitions given by:

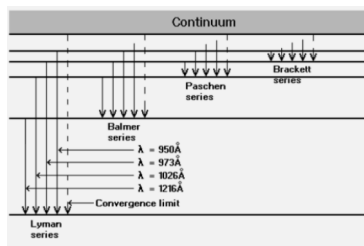
$$1/\lambda = R_H \{1/n^2 - 1/m^2\} \quad n = 2, \quad m = 3, 4, 5, \dots$$

- The Rydberg constant is:

$$R_H = 1.097 \times 10^7 \text{ m}^{-1}$$

- Other series occur for

$$n = 1, 3, 4, \dots \quad m > n$$



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Quantisation: Summary

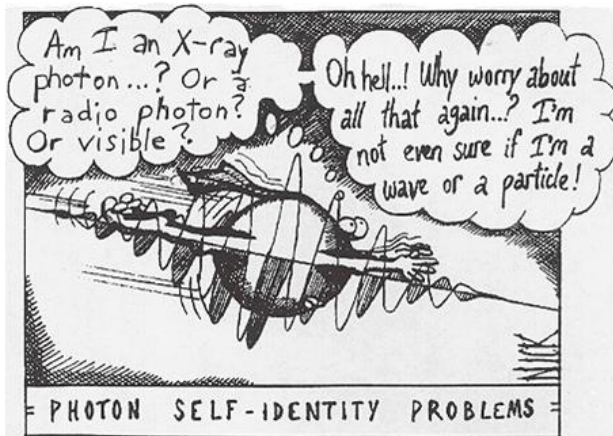
- **Ultraviolet Catastrophe**
Energy cannot be subdivided into ever smaller "pieces" - quanta
Energy is quantised: $E = nh\nu$ (n integer)
- **Photoelectric Effect**
Electromagnetic radiation (light) of frequency ν consists of a "stream" of photons each of energy $h\nu$
- **Atomic Spectra**
Consist of discrete frequencies ν_i equal to the energy released in one photon as the atom de-excites from higher to lower quantised energy states
- **Classical physics**, with no requirement of energy quantisation, fails to describe these phenomena

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5. Wave Particle Duality



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What Is A Wave?

- A disturbance within a medium
- Transmits energy without net movement of matter
- Not confined to boundaries

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What Is A Particle?

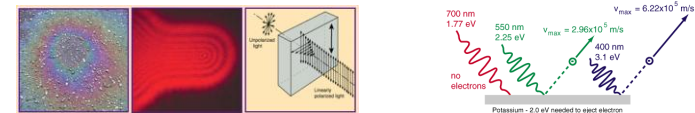
- Finite volume
- Energy contained within mass
- Described by classical physics
- Must obey laws of energy, charge and momentum conservation

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Light: Waves Or Particles?



Light As Waves

Light As Particles

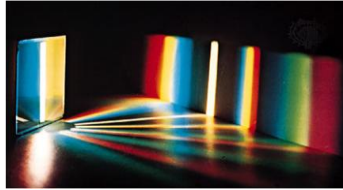
Reflection	✓	✓
Refraction	✓	✓
Interference	✓	✗
Diffraction	✓	✗
Polarisation	✓	✗
Photoelectric Effect	✗	✓

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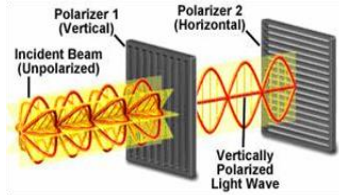
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Light As Waves



Diffraction

Polarisation



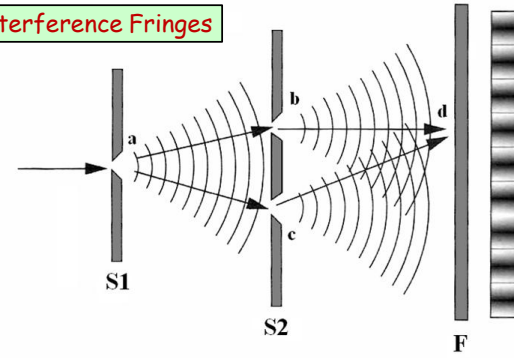
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Double Slit Experiment

Interference Fringes



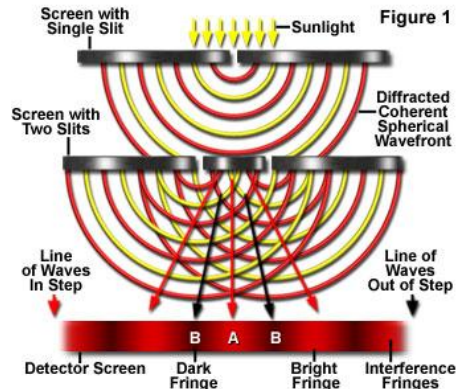
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Double Slit Experiment

Thomas Young's Double Slit Experiment



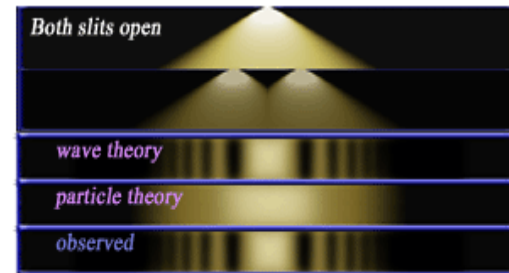
Interference

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Particles Or Waves?



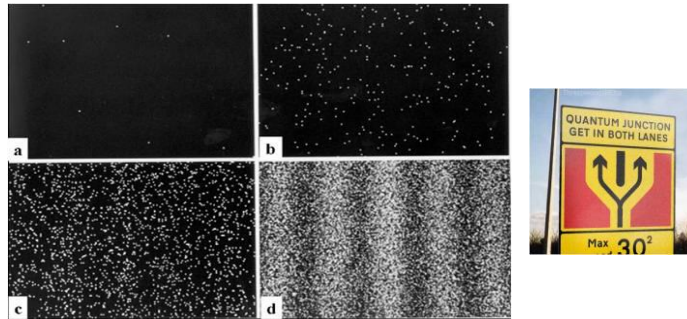
➤ Sending particles or waves through the double slits should produce different results

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Double Slit Experiment With Particles



- Sending electrons, one at a time, through a double slit (!) produces an interference pattern (over time)!

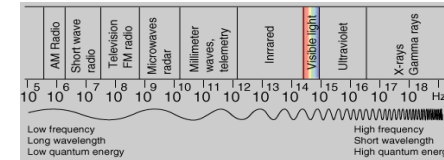
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Electromagnetic Radiation

- Wave phenomenon in E , B , interference, diffraction (Maxwell)



- Particle phenomenon in energy transmission
 - Photons (Planck, Einstein)
 - Newton's corpuscles
- Waves or particles?
 - Both! Wave-particle duality

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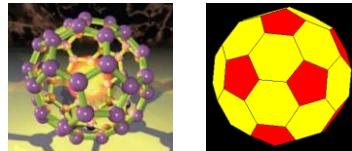
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How Big Can Quantum Particles Be?

- The double split experiment has been performed for fullerene molecules, C_{60} and C_{70} , with dimensions of the order of 1 nm (!)

Carbon-60 structure



- Fluorinated fullerene molecules, $C_{60}F_{48}$, with a mass of 1632 amu, also show quantum interference effects
- What next?
 - Viruses, Nanobacteria

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Matter

- Wave phenomenon in interference, diffraction
 - Electron, neutron microscopy (Davisson & Germer)
- Particle phenomenon in kinematics
 - Energy, momentum
 - Mass spectrometry
- Waves or particles?
 - Both! Wave-particle duality

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Electromagnetic Radiation: Photons

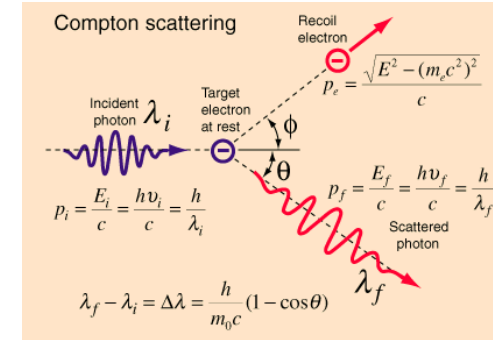
- Energy density Π (Poynting vector)
- Momentum density Π/c in free space } classical
- Energy density $\Pi \propto h\nu$ (monochromatic frequency)
- Momentum density $\Pi/c \propto h\nu/c = h/\lambda$ (quantum)
- Kinematic properties of photon:
 - Energy $E = h\nu$ (photoelectric effect)
 - Momentum $p = h/\lambda$
 - Also: $E = cp$ (massless particle $v = c/\lambda$)

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Compton Effect



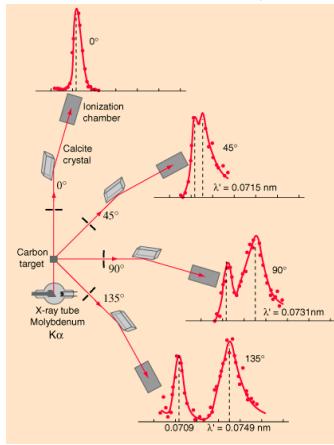
- A photon of energy E_i scatters inelastically from an electron of mass m_e

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Compton Scattering



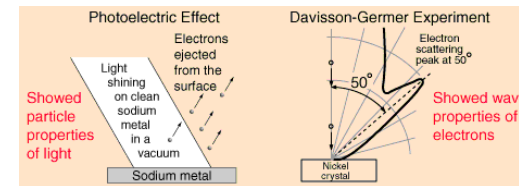
- Arthur Compton observed the scattering of x rays from electrons and found scattered x rays with a longer wavelength than those incident on the target
- He explained the effect by considering a particle (photon) nature of light and applying conservation of energy and momentum
- 1927 Nobel Prize

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Electrons as Waves



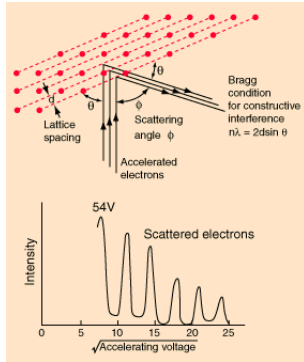
- The photoelectric and Compton effects suggest a particle nature for light
- However electrons can show wave-like properties!

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Davisson Germer Experiment



- Electrons scattered from a crystal lattice show an **interference pattern**
- **Bragg law** had been applied to X rays
- Now applied to **electrons**
- Put **wave particle duality** on a firm experimental footing

$$1/\lambda = n/(2d \sin \theta) = p/h = \sqrt{2mE} / h = \sqrt{2meV} / h$$

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Particles/Waves of Matter

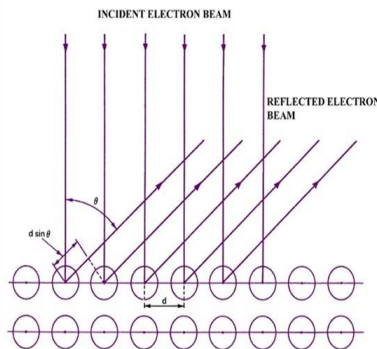
- Particle energy (classical)
 - $E = \sqrt{c^2 p^2 + m^2 c^4}$ (relativistic kinematics)
 - $E = mc^2 + p^2/2m + \dots$ (non-relativistic)
- Wavelength (quantum)
 - $p = h/\lambda$ (De Broglie, electron/neutron scattering)
- Frequency (quantum)
 - $E = h\nu$ (energy quantisation, massive particle $v \neq c/\lambda$)
- The physics of matter at the dimension of atoms can be understood in terms of waves or of particles

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Particle Diffraction



Davisson Germer Experiment

- Electrons exhibit **wave-like behaviour**: diffraction
- A particle seems to be acting as a wave!

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Equivalence

- Simple equivalence, particle-wave duality
 - ↓ ↓
 - Energy $\sqrt{c^2 p^2 + m^2 c^4} \Rightarrow h\nu$
 - Momentum $p \Rightarrow h/\lambda$
 - Frequency $E/h = \nu$
 - Wavelength $h/p = \lambda$
 - Theory photon = quantised electromagnetism
 - electron $\Rightarrow ?$
 - neutron $\Rightarrow ?$
- Perceptions in terms of human experience/observation

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Wave Particle Duality: Summary

- Certain phenomena, e.g. reflection, refraction can be understood in term of light consisting of waves or particles
- Certain phenomena, e.g. interference, diffraction, polarisation can only be understood in term of light consisting of waves and not particles
- However the photoelectric effect can only be understood in term of light consisting of discrete particles (photons, Newton's corpuscles) and not waves
- We need to consider both aspects, depending on what we "are looking at"

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6. Particle Wave Function

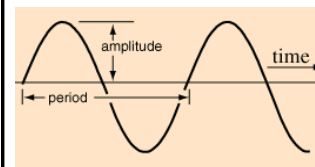
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Waves

- Wave motion in physics is a general phenomenon in which, at any point in space (x,y,z) and time t , an observable (e.g. E) has a well specified value $E(x,y,z,t)$
- This observable varies in such a manner that one observes periodic dependence in space and time



- Water waves E = displacement
- Sound waves E = pressure
- Earthquake E = stress
- Light E = Electromagnetic field

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General Wave Equation

- Wave motion is predicted from the dynamics of the physics in the form of a wave equation
- E.g. transverse waves on a string: $E = Y$ **Mechanics**
 $\partial^2 Y / \partial x^2 = \{1/c^2\} \partial^2 Y / \partial t^2$ $c^2 = \text{tension} / \{\text{mass/length}\}$
- E.g. sound waves: $E = P$ (pressure) **Fluid Dynamics**
 $\partial^2 P / \partial x^2 = \{1/c^2\} \partial^2 P / \partial t^2$ $c^2 = \text{pressure} / \text{density}$
 or $\nabla^2 P = \{1/c^2\} \partial^2 P / \partial t^2$ in 3D
- E.g. electromagnetic waves: $E = \text{field}$ **Electromagnetism**
 $\nabla^2 \underline{E} = \{1/c^2\} \partial^2 \underline{E} / \partial t^2$

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Electromagnetic Waves in Free Space

- Photons in free space
 $\partial^2 \underline{E} / \partial x^2 = \{1/c^2\} \partial^2 \underline{E} / \partial t^2$
- Look for a solution $\underline{E} = \underline{E}_0 \cos(kx - \omega t)$
 Harmonic: $\omega = ck$, $v = c/\lambda$
- Differentiate twice:
 $\partial^2 \underline{E} / \partial x^2 = -k^2 \underline{E}_0 \cos(kx - \omega t)$
 $\partial^2 \underline{E} / \partial t^2 = -\omega^2 \underline{E}_0 \cos(kx - \omega t)$
- A solution is:
 $\underline{E} = \underline{E}_0 \cos(kx - \omega t)$ if $k^2 = \omega^2/c^2$
- This represents a harmonic (sinusoidal) plane wave in \underline{E} with wavelength $\lambda = 2\pi/k$, and frequency $\nu = \omega/2\pi$
- Also $v\lambda = c$

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Wave Equation Properties

- This wave equation is a 2nd order partial differential equation

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

- Solutions are determined by boundary conditions
- The equation is linear: a new solution can be found as the sum of other solutions
- $c =$ "phase velocity"

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Electromagnetic Wave

- A plane harmonic EM wave $\underline{E} = \underline{E}_0 \cos(kx - \omega t)$ is not equal to one photon!
- Wave-particle duality is so far a qualitative concept
- It allows us to understand
- It does not (yet) allow us to calculate or predict
- We need a theory in which the representation of a particle as a wave yields predictions for the behaviour of particles

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Wave Function

➤ Postulate 1 (a true revolution in physics)

- To describe the dynamics of any particle it is necessary to assign it a **wave-function**: $\Psi(x,t)$
- The wave-function $\Psi(x,t)$ may be complex (real & imaginary)
- At a time t , the probability of finding the particle in a small region of x is:

$$|\Psi(x,t)|^2$$

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Probability Density (1D)

- At a time t , the probability of finding a particle in a small region of x is:

$$|\Psi(x,t)|^2 = \Psi \Psi^*$$

- If we know that the particle is confined to a region $x_1 \leq x \leq x_2$ then the probability of finding the particle in this region is 1, i.e. the wave function is normalised:

$$\int |\Psi(x,t)|^2 dx = 1 \quad (\text{integrate between } x_1 \text{ and } x_2)$$

- A **stationary** state occurs if $|\Psi(x,t)|^2 = \Psi \Psi^*$ has no time dependence

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What is Ψ ?

- So far, all wave motion has been recognised as a **periodic** variation of a (real) physical observable
- What is the physical observable corresponding to Ψ ?
 - There isn't one !
 - One cannot say that a particle is a wave phenomenon of any particular physical observable
 - A particle wave-function is a construct in a theory with which we are able to calculate and predict in new ways
- The real physical quantity is the "probability density" $|\Psi|^2$

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Indeterminism in the Real World

- Born (1927) introduced the **probabilistic** interpretation of Quantum Mechanics
- Quantum Mechanics only allows us to calculate the **probability** of a particle being found at a specific position in space
- We can never specify **exactly** where the particle is
- This can be generalised to other properties, such as momentum

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7. Particle Wave Equation

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Wave Equation

- In many cases the dynamics can be calculated assuming interference, diffraction like phenomena
 - X ray diffraction
 - Neutron/electron diffraction
- In many cases detection of particle diffraction, interference follows collection of many detected hits spread over a distribution suggesting individual particles do not have completely predictable behaviour
 - Probability theory
 - Wave function postulate
- No localisation is in space and time

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Introduction

- Why do we use the concept of a particle?
- In many cases the dynamics can be calculated assuming a mass m
 - Free electron theory of metals/conductors
 - Particle accelerators and storage rings
- In many cases detection is random "hits" as "localised" energy is deposited
 - Geiger counters
 - Photomultipliers
- Localisation is in space and time

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Simplest Wave Function

- Consider the simplest possible choice of a complex form for $\Psi(x,t)$ to which we can assign a unique harmonic wave number $k = 2\pi/\lambda$ and angular frequency $\omega = 2\pi\nu$

$$\Psi = A \exp \{ i(kx - \omega t) \} \quad (7.1)$$

where A is a constant (≤ 1) independent of x and t

- Can we assign this to the wave function of a free particle?
- Yes - the de Broglie wave (see QMIntro.pdf)

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De Broglie Wavelength

- The energy and momentum of a "wave" corresponding to a particle are:

$$\begin{array}{l} \text{Energy:} \\ \text{Momentum:} \end{array} \quad \boxed{E = h\nu = \hbar\omega} \quad (\hbar = h/2\pi)$$

$$\boxed{p = h/\lambda = \hbar k}$$

- Assuming the particle is non-relativistic, the total energy E of the free particle is equal to its kinetic energy T :

$$E = T = p^2/2m$$

- So for a free particle ("dispersion relation"):

$$\boxed{\hbar\omega = (\hbar k)^2/2m} \quad (7.2)$$

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Particle in a Potential

- Consider a particle moving in the presence of a constant potential energy $V(x) = V_0$
- Total energy is a sum of kinetic and potential energies

$$E = T + V_0 = p^2/2m + V_0$$

- From De Broglie:

$$\hbar\omega = (\hbar k)^2/2m + V_0 \quad (7.4)$$

- Again look for the simplest possible solution

$$\Psi = A \exp \{ i(kx - \omega t) \}$$

- Differentiate:

$$\partial^2 \Psi / \partial x^2 = -k^2 A \exp \{ i(kx - \omega t) \} = -k^2 \Psi$$

- And

$$\partial \Psi / \partial t = -i\omega A \exp \{ i(kx - \omega t) \} = -i\omega \Psi$$

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Simplest Wave Equation

- Look for the simplest linear differential equation which has solution Ψ and satisfies $\omega = \hbar k^2/2m$

$$\Psi = A \exp \{ i(kx - \omega t) \}$$

$$\partial \Psi / \partial x = ikA \exp \{ i(kx - \omega t) \}$$

$$\partial^2 \Psi / \partial x^2 = -k^2 A \exp \{ i(kx - \omega t) \} \quad (\text{quadratic in } k)$$

- And

$$\partial \Psi / \partial t = -i\omega A \exp \{ i(kx - \omega t) \} \quad (\text{linear in } \omega)$$

- Combine:

$$i \partial \Psi / \partial t = \{-\omega/k^2\} \partial^2 \Psi / \partial x^2$$

- Or using Eq. 7.2 (i.e. $\hbar\omega = (\hbar k)^2/2m$):

$$\boxed{i\hbar \partial \Psi / \partial t = \{-\hbar^2/2m\} \partial^2 \Psi / \partial x^2} \quad (7.3)$$

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Particle in a Potential

- Combine:

$$i\hbar \partial \Psi / \partial t = \hbar\omega \Psi = \{-\hbar\omega/k^2\} \partial^2 \Psi / \partial x^2$$

- Or using Eq. 7.4 (i.e. $\hbar\omega = (\hbar k)^2/2m + V_0$):

$$i\hbar \partial \Psi / \partial t = \{-\hbar^2/2m + V_0/k^2\} \partial^2 \Psi / \partial x^2$$

- And remembering that:

$$\partial^2 \Psi / \partial x^2 = -k^2 \Psi$$

we obtain:

$$\boxed{i\hbar \partial \Psi / \partial t = \{-\hbar^2/2m\} \partial^2 \Psi / \partial x^2 + V_0 \Psi} \quad (7.5)$$

- This is the free particle solution

- Note that V_0 does not localise the particle

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Physical Properties of Free Particle

- $\Psi = A \exp \{ i(kx - \omega t) \}$ with $\omega = \hbar k^2 / 2m$
- The probability density:
 - $|\Psi|^2 = |A|^2$ note $|\Psi|^2 = \Psi \Psi^*$
 - is constant for all x and t
- There is no preferred (more likely, more probable) value of x where we are more likely to find the particle
 - The particle (momentum $p = \hbar k$) is completely non-localised in space (x)
- There is no preferred value of t at which we are more likely to find the particle
 - The particle (energy $E = \hbar \omega$) is non-localised in time (t)

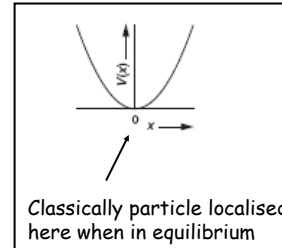
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Localised Particle

- Localise a particle: restrict it to a range Δx in x
 - For all t , spatial localisation
- The particle may be constrained by an external force
 - Or potential energy $V(x)$



- No longer a "free" particle
- Wave Eq. 7.3
 - $i\hbar \partial \Psi / \partial t = \{-\hbar^2 / 2m\} \partial^2 \Psi / \partial x^2$
 - no longer valid
- Wave function
 - $\Psi = A \exp \{ i(kx - \omega t) \}$
 - no longer valid

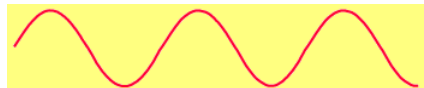
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A Revolutionary Prediction !

- A free particle has a specified momentum and energy but cannot be localised in space or time
- The particle is "everywhere all the time"
- This is a revolutionary prediction from a revolutionary theory
- Wave function:



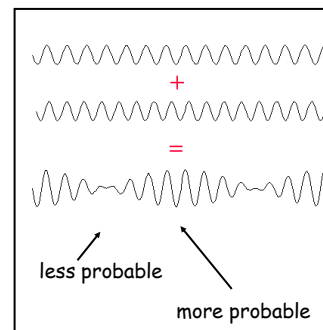
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Wave Function of Localised Particle

- Intuition from many wave phenomena



- Addition of two different harmonic waves

$$\Psi = A_1 \sin\{k_1 x\} + A_2 \sin\{k_2 x\}$$

$$\sim \sin\{(k_2 - k_1)x/2\}$$

$$\times \cos\{(k_2 + k_1)x/2\}$$

- Beat pattern when k 's slightly different
- Regions of high probability and low probability

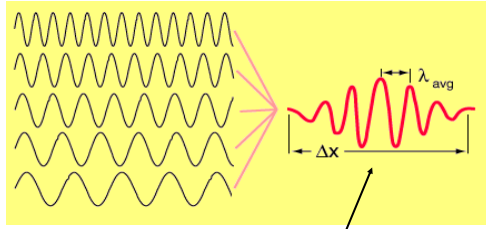
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Wave Packet

- Now add many different harmonic waves
 $\Psi = \sum A(k_i) \sin\{k_i x\}$, or $\Psi = \int A(k) \sin\{kx\} dk$



most probable, particle "localised"

- Quantum wave packet: $\Psi(x,t) = \int A(k) \exp\{i(kx - \omega t)\} dk$

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Wave Equation for Localised Particle

- Total energy: $E = T + V(x)$
- Classical physics says that if the total energy is fixed (constant E), then the kinetic energy T varies with x
 - Momentum p varies with x
 - Equation like (7.4) ($\hbar\omega = (\hbar k)^2/2m + V_0$) is not possible

Postulate 2

- The wave equation, a solution of which is the wave-function Ψ of a particle in a region with the potential energy function $V(x)$, is

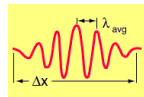
$$i\hbar \partial\Psi/\partial t = -\{\hbar^2/2m\} \partial^2\Psi/\partial x^2 + V(x) \Psi \quad (7.7)$$

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Quantum Wave Packet



$$\Psi(x,t) = \int A(k) \exp\{i(kx - \omega t)\} dk \quad (7.6)$$

- This has no unique wave-number k , no unique frequency ω
- The wave function is (infinite) sum of harmonic (free particle) wave functions

Each contribution has its own k and ω

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Schrödinger's Equation

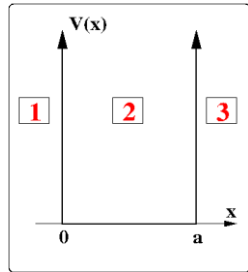
- Equation (7.7) is known as Schrödinger's equation
- It is not proven, only postulated!
- When the potential is constant
 $V(x) = V_0$
 we know it works
- Solutions of Schrödinger's equation are usually mathematically tricky!
- Now for some examples

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Particle Localised In A Box



- For all energies, the particle is constrained to lie in the region

$$0 \leq x \leq a$$

$$\begin{aligned} x < 0 & \quad V(x) \Rightarrow \infty \\ 0 \leq x \leq a & \quad V(x) = 0 \\ a < x & \quad V(x) \Rightarrow \infty \end{aligned}$$

- Classically, the particle may have any energy and may be found anywhere in region 2

- The "box" does not change with time †
 - V is not a function of †

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Infinite Square Well Potential

- Differentiate:

$$\partial\Psi/\partial t = \psi \partial\theta/\partial t \quad \text{and} \quad \partial^2\Psi/\partial x^2 = \theta \partial^2\psi/\partial x^2$$

- Substitute in Schrödinger equation:

$$i\hbar \psi \partial\theta/\partial t = -\{\hbar^2/2m\} \theta \partial^2\psi/\partial x^2$$

- Rewrite:

$$i\hbar \{1/\theta\} \partial\theta/\partial t = -\{\hbar^2/2m\} \{1/\psi\} \partial^2\psi/\partial x^2$$

$$\text{function only of } t \quad \text{function only of } x \quad \therefore \text{both constant}$$

- Cancel \hbar and equate to "constant" ω :

$$\partial\theta/\partial t = -\{i\omega\} \theta \quad \text{and} \quad \partial^2\psi/\partial x^2 = -\{2m\omega/\hbar\} \psi$$

- Solution for θ :

$$\theta = \{\text{constant}\} \exp\{-i\omega t\}$$

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Infinite Square Well Potential

- Apply the Schrödinger equation in regions 1 and 3

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

- Or, dividing by $V(x)$:

$$\{i\hbar/V(x)\} \partial\Psi/\partial t = -\{\hbar^2/2mV(x)\} \partial^2\Psi/\partial x^2 + \Psi$$

- But $1/V(x) = 0$, hence

$$\Psi = 0 \quad (7.8)$$

- Apply the Schrödinger equation in region 2 with $V(x) = 0$

$$i\hbar \partial\Psi/\partial t = -\{\hbar^2/2m\} \partial^2\Psi/\partial x^2$$

- Confining box does not change with time, hence we expect x dependence of Ψ to be independent of †

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

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Time Independent Wave Function

- Time dependence θ of Ψ is such that the probability density $|\Psi|^2$ has no time dependence i.e. $\theta \theta^* = 1$

- "Time independent" or "stationary" wave function:

$$\Psi = \psi \exp\{-i\omega t\}$$

- Solution for ψ :

$$\partial^2\psi/\partial x^2 = -k^2\psi \quad \text{where} \quad k^2 = \{2m\omega/\hbar\}$$

$$\psi = A \sin\{kx\} + B \cos\{kx\}$$

with A, B constants of integration

- Hence in region 2:

$$\Psi = \psi \theta = [A \sin\{kx\} + B \cos\{kx\}] \exp\{-i\omega t\} \quad (7.9)$$

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Stationary Wave Function

- Stationary wave function:
 - Complex pieces of Ψ only in time dependence
- Compare solutions in regions 1, 2, 3 i.e. eqs 7.8 and 7.9
- In 7.9 for $x = 0$

$$\psi(x=0) = 0 \quad \therefore A \sin\{0\} + B \cos\{0\} = 0$$
- Since $\sin\{0\} = 0$ and $\cos\{0\} = 1$, then

$$B = 0 \text{ and } A \neq 0$$
- Now at $x = a$

$$\psi(x=a) = 0 \quad \therefore A \sin\{ka\} + B \cos\{ka\} = 0$$
- Since $B = 0$ and $A \neq 0$, then

$$\sin\{ka\} = 0 \text{ and hence } ka = n\pi, \quad n = 0, 1, 2, \dots$$

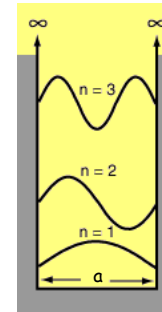
↙ pointless solution

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Infinite Well Wave-Functions



- There are $n - 1$ "nodes" (minimum probability density) away from $x = 0, x = a$
- There are n "antinodes" (maximum probability density)

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Discrete Solutions

- Allowed values of k :

$$k = n\pi / a \quad n = 1, 2, 3, \dots$$
- Hence allowed values of ω :

$$\omega = \{\hbar/2m\} \{\pi^2/a^2\} n^2$$
- The solutions for the wave function are:

$$\Psi = A \sin\{n\pi x/a\} \exp\{-i\omega t\} \quad (0 \leq x \leq a)$$

$\psi(x) \quad \theta(t)$
- $$\Psi = 0 \quad (x < 0, a < x)$$
- The probability density is:

$$|\Psi|^2 = \Psi^* \Psi = A^2 \sin^2\{n\pi x/a\}$$

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Physics of the Solutions

- Particle probability density $|\Psi|^2$ is confined (non-zero) only inside the box ($0 \leq x \leq a$) classical physics
- Particle more likely to be found at some values of x (between 0 and a) than at others

$$|\Psi|^2 \propto \sin^2\{n\pi x/a\} \quad \text{probability density}$$
- The wave function $\Psi(x,t) = \psi(x) \exp\{-i\omega t\}$ has a time dependence $\exp\{-i\omega t\}$
 - time dependence of a "stationary state"
 - same as that of a free particle wave function

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Quantised Energies

- Using De Broglie $E = h\nu = \hbar\omega$ we find that the allowed energies of the particle in a box are:

$$E = \{\hbar^2\pi^2/2ma^2\} n^2 = \{h^2/8ma^2\} n^2$$

- Energies of a particle in a confined region (bound state) are quantised ($E \propto n^2$)

$n = 1$	$E = h^2/8ma^2$
$n = 2$	$E = 4h^2/8ma^2$
$n = 3$	$E = 9h^2/8ma^2$
$n = 4$	$E = 16h^2/8ma^2$

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Time Independent Schrödinger Equation

- We find that:

$$\hbar\omega \exp\{-i\omega t\} \psi(x) = -\{\hbar^2/2m\} \exp\{-i\omega t\} \partial^2\psi/\partial x^2 + \exp\{-i\omega t\} V(x) \psi(x)$$

- Cancelling $\exp\{-i\omega t\}$ this can be rewritten as:

$$\hbar\omega \psi(x) = -\{\hbar^2/2m\} \partial^2\psi/\partial x^2 + V(x) \psi(x)$$

- Or:

$$E \psi(x) = -\{\hbar^2/2m\} \partial^2\psi/\partial x^2 + V(x) \psi(x) \quad (7.10)$$

- This is the time-independent Schrödinger equation

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Time Independence

- Schrödinger's equation with $V(x)$ time independent (7.7)

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

- Guided by the "particle in a box" solution, look for a solution:

$$\Psi(x,t) = \psi(x) \exp\{-i\omega t\}$$

- Now:

$$i\hbar \partial\Psi/\partial t = \hbar\omega \exp\{-i\omega t\} \psi(x)$$

- And:

$$-\{\hbar^2/2m\} \partial^2\Psi/\partial x^2 = -\{\hbar^2/2m\} \exp\{-i\omega t\} \partial^2\psi/\partial x^2$$

- And:

$$V(x) \Psi = \exp\{-i\omega t\} \psi(x) V(x)$$

- Substitute in Schrödinger equation (7.7)

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$V(x)$ is not constant

- See Tutorial 2, Question 2

- If $V(x)$ is non-uniform and non-zero, the "stationary" (time independent) wave-function may assume a Gaussian form

$$\Psi(x,t) = A \exp\{-x^2/(2\sigma^2)\} \exp\{-i\omega t\}$$

i.e. it has spatial extent related to σ - it is therefore localised in space

- The particle is not free and a unique value of momentum cannot be assigned to it

example: Harmonic Oscillator

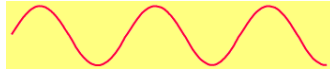
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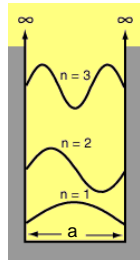
The Uncertainty Principle

➤ Free particle



➤ Momentum certain $\Delta p = 0$, but location unknown $\Delta x \rightarrow \infty$

➤ Localised particle, e.g. particle in a box ($n = 1$)



$$\Psi \propto \sin\{kx\} \propto \exp\{ikx\} - \exp\{-ikx\}$$

➤ Now: $k = \pi/a$

➤ And: $p = \hbar k = \hbar\pi/a = h/2a$

➤ Uncertainty in p: $\Delta p \sim h/2a$

➤ Uncertainty in x: $\Delta x \sim a$

➤ Hence: $\Delta p \Delta x \sim h/2$

➤ Heisenberg Uncertainty Principle

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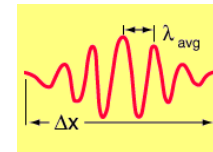
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The Uncertainty Principle

➤ Generic wave packet describing localised particle (7.6)

$$\Psi(x,t) = \int A(k) \exp\{i(kx - \omega t)\} dk$$

➤ Sum of many $\exp\{i(kx - \omega t)\}$ with complex amplitudes $A(k)$ and spread Δk



➤ Uncertainty in p: Δp

➤ Now:

$$\Delta p \Delta x \sim \hbar/2$$

$$\Delta t \Delta E \sim \hbar/2$$

➤ Revolution in physics:

➤ A particle cannot be localised both in position and momentum!

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3D Particle in a box

➤ Quantum theory suggests that a large amount of energy is required to contain a particle in a small volume

➤ It arises from the uncertainty principle

➤ In three dimensions, the infinite-well energies are quantised as:

$$E = \{h^2/8ma^2\} (n_x^2 + n_y^2 + n_z^2)$$

➤ The lowest energy is when $n_x = n_y = n_z = 1$:

$$E_{\min} = \{3h^2/8ma^2\}$$

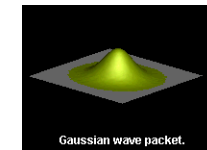
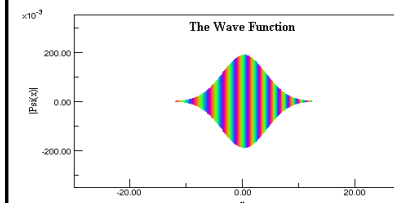
from which we can, for example, estimate the energy of an electron confined in an atom or a proton confined in a nucleus (Tutorial 2, Question 5)

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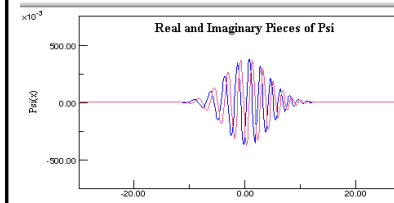
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Gaussian Wave Packet



2d free particle



➤ Minimum uncertainty wave packet:

Gaussian

$$\sim \exp\{-x^2/2\sigma^2\}$$

➤ See VITAL for links to movies of wave packet motion

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Particle Wave Equation: Summary

- The wave function $\Psi(x,t)$ of a particle under the influence of the potential energy function $V(x,t)$ is the solution of the Schrödinger equation

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

which matches external boundary conditions

- If $V(x,t) \Rightarrow V(x)$, i.e. the potential energy is time independent, then Ψ is stationary

$$\Psi(x,t) = \psi(x) \exp\{-i(E/\hbar)t\} \quad E = \hbar\omega$$

and $\psi(x)$ is a solution of the time independent Schrödinger equation

- A time independent potential energy $V(x)$ which localises a particle yields discrete quantised energies of the particle

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8. Wave Dynamics of Particles: Bound States

- 8.1 Finite Square Well
- 8.2 Harmonic Oscillator
- 8.3 Zero Point Energy
- 8.4 3D Bound States
- 8.5 3D Bound States & Angular Momentum
- 8.6 3D Harmonic Oscillator Revisited
- 8.7 The Hydrogen Atom

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Wave Dynamics: Bound States

- We have already considered a particle in an infinitely deep potential well
- The particle is confined in a bound state
- The energy of the particle is quantised
- Next consider a potential with a finite depth
 - Finite square well potential

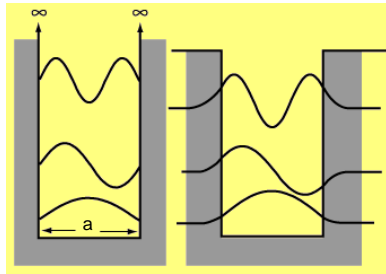
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8.1 Finite Square Well Potential

- For the finite potential well, the Schrödinger equation gives a wave function with an exponentially decaying penetration into the classically forbidden region outside the box!



- Since the wave function penetration effectively enlarges the box, the finite well energy levels are lower than those for the infinite well

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Finite Square Well

- In regions 1 and 3, with $V = 0$:
 $-\{\hbar^2/2m\} \partial^2\psi/\partial x^2 = E \psi$ like "free particle" solution
- Try solutions of the form:

$$\psi_1 = A_1 \exp\{ikx\} + B_1 \exp\{-ikx\} \quad (8.1.1)$$

$$\psi_3 = A_3 \exp\{ikx\} + B_3 \exp\{-ikx\} \quad (8.1.2)$$

with constants A_1, B_1, A_3, B_3 and where k is:

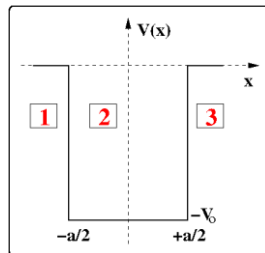
$$k = p/\hbar = \sqrt{2mE} / \hbar \quad \text{Energy } E = T$$

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Particle in Finite Square Well



- Particle has total energy:

$$E = T + V$$

kinetic + potential

- Potential Well is of the form:

$$\begin{aligned} |x| > a/2 & \quad V = 0 \\ |x| < a/2 & \quad V = -V_0 \end{aligned}$$

- Solve the time independent Schrödinger equation in regions 1, 2 and 3 for ψ

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Finite Square Well

- In region 2 with $V = -V_0$:
 $-\{\hbar^2/2m\} \partial^2\psi/\partial x^2 + (-V_0)\psi = E \psi$ $T + V = E$
- hence
 $-\{\hbar^2/2m\} \partial^2\psi/\partial x^2 = (E + V_0) \psi$
- Try a solution of the form:

$$\psi_2 = A_2 \exp\{ikx\} + B_2 \exp\{-ikx\}$$

with constants A_2, B_2 and where k is now:

$$k = \sqrt{2m(E + V_0)} / \hbar$$

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Boundary Conditions

- Look for **bound** state, **localised** particle, which implies that in regions 1 and 3:

$$\begin{aligned} x \rightarrow -\infty & \quad |\psi|^2 \rightarrow 0 \\ x \rightarrow +\infty & \quad |\psi|^2 \rightarrow 0 \end{aligned}$$

- To achieve this we need "real" exponentials for $x \Rightarrow \pm\infty$ in equations (6.1.1) and (6.1.2), i.e. rapid exponential fall off of $|\psi|^2$ in the classically forbidden regions

- This can be achieved by setting $ik = \alpha$ (i.e. $k = -i\alpha$)

- Then:

$$\exp\{\pm ikx\} \Rightarrow \exp\{\pm\alpha x\}$$

- And:

$$|\psi|^2 \Rightarrow \exp\{\pm 2\alpha x\}$$

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Overall Solution for All x

- In region 1: $|\psi|^2 \Rightarrow 0$, $x \Rightarrow -\infty$

$$\psi_1 = A_1 \exp\{+\alpha x\} \quad (k = -i\alpha) \quad (8.1.3)$$

- In region 2: $k = \sqrt{2m(E + V_0)} / \hbar > 0$

$$\psi_2 = A_2 \exp\{ikx\} + B_2 \exp\{-ikx\} \quad (8.1.4)$$

- In region 3: $|\psi|^2 \Rightarrow 0$, $x \Rightarrow +\infty$

$$\psi_3 = B_3 \exp\{-\alpha x\} \quad (k = -i\alpha) \quad (8.1.5)$$

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Boundary Conditions

- If ($k = \sqrt{2mE} / \hbar$) is now imaginary in regions 1 and 3, then this implies that:

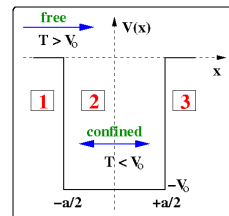
$$E < 0 \quad \text{since } m > 0$$

- And so in region 2:

$$E = T - V_0 < 0$$

- Or a "bound" state occurs for:

$$T < V_0$$



- Note that if $T > V_0$ the particle is not confined to the box, it has enough energy to escape

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Matching Ψ at Sharp Changes in V

- The potential V changes abruptly at the intersections of regions 1 - 2 and regions 2 - 3

- The wave function ψ must be smooth (**continuous**) across these boundaries

- The derivative of the wave function $d\psi/dx$ must also be smooth across these boundaries

- Why?

- It works!

- Seen in all other wave phenomena

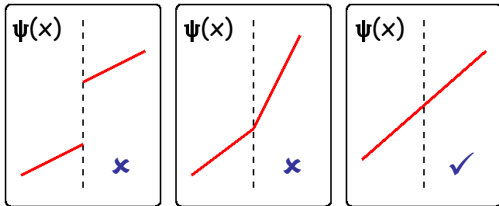
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Continuity of Waveforms

- Waveforms in Quantum Mechanics must be "continuous"
 - $\psi(x)$ must be single valued for all x
 - $d\psi/dx$ must be single valued for all x particularly at boundaries



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Overall Solution (cont)

- Eliminate A_1 from (8.1.6) and (8.1.7):

$$(\alpha - ik) A_2 \exp\{-ika/2\} = -(\alpha + ik) B_2 \exp\{+ika/2\}$$
- Eliminate B_3 from (8.1.8) and (8.1.9):

$$(\alpha + ik) A_2 \exp\{+ika/2\} = -(\alpha - ik) B_2 \exp\{-ika/2\}$$
- Solution: $A_2 = B_2 = 0$ (pointless !)
- Or equations consistent with same unique ratio A_2/B_2

$$-\frac{(\alpha + ik)}{(\alpha - ik)} \exp\{+ika\} = -\frac{(\alpha + ik)}{(\alpha - ik)} \exp\{-ika\}$$
- This reduces to:

$$2\alpha i \sin\{ka/2\} = -2ik \cos\{ka/2\} \quad (8.1.10)$$

or

$$2\alpha \cos\{ka/2\} = 2k \sin\{ka/2\} \quad (8.1.11)$$

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Overall Solution (cont)

- Regions 1-2: $x = -a/2$
- Continuity of ψ (8.1.6)

$$A_1 \exp\{-\alpha a/2\} = A_2 \exp\{-ika/2\} + B_2 \exp\{+ika/2\}$$
- Continuity of $d\psi/dx$ (8.1.7)

$$\alpha A_1 \exp\{-\alpha a/2\} = ikA_2 \exp\{-ika/2\} - ikB_2 \exp\{+ika/2\}$$
- Regions 2-3: $x = +a/2$
- Continuity of ψ (8.1.8)

$$A_2 \exp\{+ika/2\} + B_2 \exp\{-ika/2\} = B_3 \exp\{-\alpha a/2\}$$
- Continuity of $d\psi/dx$ (8.1.9)

$$ikA_2 \exp\{+ika/2\} - ikB_2 \exp\{-ika/2\} = -\alpha B_3 \exp\{-\alpha a/2\}$$

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Overall Solution (cont)

- From (8.1.10) and (8.1.11), the overall solution for ψ requires:

$$\tan\{ka/2\} = -k/\alpha \quad \text{and} \quad \tan\{ka/2\} = \alpha/k$$
- Only discrete values of k are allowed - quantisation
- The solution also requires:

$$A_2/B_2 = -\frac{(\alpha + ik)}{(\alpha - ik)} \exp\{+ika\}$$
- It can be shown that:

$$A_2/B_2 = -1 \quad \text{if} \quad \tan\{ka/2\} = -k/\alpha$$

$$A_2/B_2 = +1 \quad \text{if} \quad \tan\{ka/2\} = \alpha/k$$
- Hence the solution in region 2 is:

$$\psi_2 = A_2 [\exp\{ikx\} \pm \exp\{-ikx\}]$$

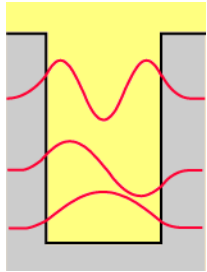
i.e. $\psi_2 = 2A_2 \cos\{kx\}$ or $2iA_2 \sin\{kx\}$

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Summary: Finite Well Solutions



Solutions:

- 1 $\psi \propto \exp\{\alpha x\}$
- 2 $\psi \propto \sin\{kx\}, \cos\{kx\}$
- 3 $\psi \propto \exp\{-\alpha x\}$

Parameters:

$$\alpha = \sqrt{\{2m(-E)/\hbar^2\}}$$

$$k = \sqrt{\{2m(V_0 + E)/\hbar^2\}}$$

Continuity of ψ , $d\psi/dx$ at boundary

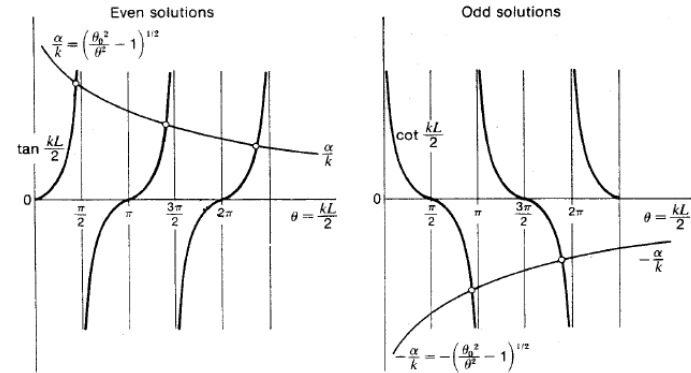
- Harmonic form inside well $|x| \leq a/2$
- Dying exponentials outside well $|x| > a/2$
- Probability density $|\psi|^2$ extends beyond edge of potential
- Discrete set of (bound state) wave functions

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Graphical Solutions



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Finite Well Energy Levels

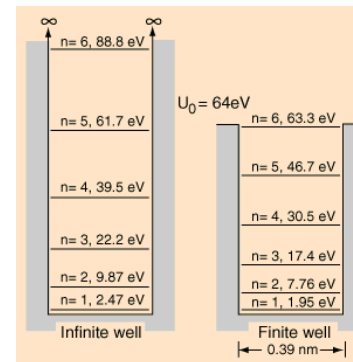
- What are the allowed energy levels ?
- Conditions:
 - $\tan\{ka/2\} = -k/\alpha$ and $\tan\{ka/2\} = \alpha/k$
 - with
 - $k = \sqrt{\{2m(V_0 + E)/\hbar^2\}}$ and $k/\alpha = \sqrt{\{(V_0 + E)/-E\}}$
- Solution of complicated equations:
 - $\tan\{(\sqrt{\{2m(V_0 + E)/\hbar^2\}}) a/2\} = -\sqrt{\{(V_0 + E)/-E\}}$
 - and
 - $\tan\{(\sqrt{\{2m(V_0 + E)/\hbar^2\}}) a/2\} = \sqrt{\{-E/(V_0 + E)\}}$
- Must solve graphically for E (<0)
- A finite number of discrete (quantised) energies are found

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Finite/Infinite Well Energies



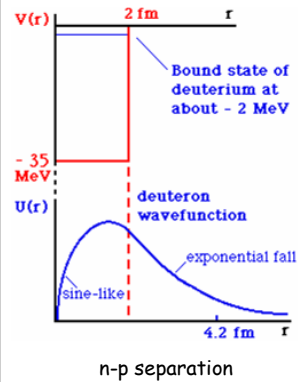
- The energy levels for an electron in an infinite potential well of width 0.39 nm are shown to the left
- The energy levels for an electron in a finite potential well of depth 64 eV and width 0.39 nm are shown to the right

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The Deuteron



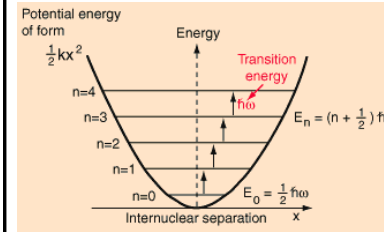
- The deuteron is a **weakly bound system** consisting of a proton and neutron
- Since the ground state energy level is at -2 MeV in a finite well -35 MeV deep, the exponential tail is rather **long** !

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8.2 Harmonic Oscillator (HO)



- Potential energy:
 $V(x) = \frac{1}{2} Kx^2$
- Classical physics:
 $F = -dV/dx = -Kx$
- Simple Harmonic Motion

- Particle undergoes harmonic oscillation about $x = 0$ with an angular frequency:

$$\omega = \sqrt{K/m}$$

- Hence potential can be written: **time independent**

$$V(x) = \frac{1}{2} m \omega^2 x^2$$

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Harmonic Oscillator

- Time independent Schrödinger equation (7.10):

$$-\{\hbar^2/2m\} d^2\psi/dx^2 + \frac{1}{2} m \omega^2 x^2 \psi = E \psi$$

- Rewrite:

$$d^2\psi/dx^2 + \{2mE/\hbar^2\} \psi - \{m^2\omega^2 x^2/\hbar^2\} \psi = 0$$

- Or:

$$d^2\psi/dx^2 + \beta \psi - \{x^2/\alpha^4\} \psi = 0 \quad \text{Hermite's equation}$$

- Where:

$$\beta = 2mE/\hbar^2 \quad \text{and} \quad \alpha^2 = \hbar/m\omega$$

- General solution:

$$\psi(x) = \exp\{-x^2/2\alpha^2\} (a_0 + a_1 x + a_2 x^2 + \dots)$$

Gaussian series

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Harmonic Oscillator Solutions

- We expect a discrete set of solutions which do not diverge as $x \rightarrow \infty$
- The series must not be infinite
 - It must be a polynomial
- There is no divergence if:

$$\alpha^2 \beta = 2n + 1 \quad \text{where } n \text{ is a positive integer}$$
- Solutions for each value of n , ψ_n give quantisation

$$\begin{aligned} n = 0 & \quad \psi_0 = c_0 \exp\{-x^2/2\alpha^2\} \\ n = 1 & \quad \psi_1 = c_1 (x/\alpha) \exp\{-x^2/2\alpha^2\} \\ n = 2 & \quad \psi_2 = c_2 (2x^2/\alpha^2 - 1) \exp\{-x^2/2\alpha^2\} \end{aligned}$$

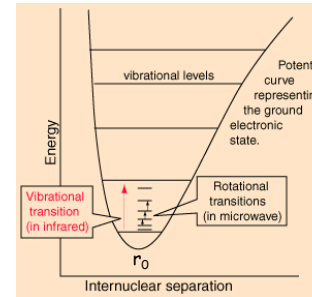
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Diatomic Molecule

- Application of Harmonic Oscillator potential



- The potential energy $V(r)$ between two atoms as a function of separation r approximates the HO potential

- $V(r)$ has a minimum at $r = r_0$

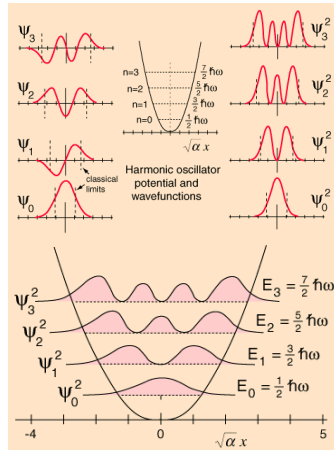
- $r < r_0$: repulsion due to nucleus-nucleus
- $r > r_0$: attraction due to electron-nucleus

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HO Quantised Energies



- What are the energies?
- Now:

$$\alpha^2 \beta = 2n + 1 \quad \text{where } n \geq 0$$
- Hence:

$$\{\hbar/m\omega\} \{2mE/\hbar^2\} = 2n + 1$$
- Or:

$$E = (n + \frac{1}{2}) \hbar \omega$$

- A set of equally spaced energy levels arises
- Energy separation:

$$\Delta E = \hbar \omega$$

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Diatomic Molecule

- Close to $r = r_0$ make a Taylor expansion and keep only the leading terms in $r - r_0$:

$$V(r) = V(r_0) + (r - r_0) \frac{dV}{dr} + \frac{1}{2}(r - r_0)^2 \frac{d^2V}{dr^2}$$

- Since $r = r_0$ is a minimum:

$$\frac{dV}{dr} = 0$$

- Hence:

$$V(r) = V(r_0) + \frac{1}{2}(r - r_0)^2 \frac{d^2V}{dr^2}$$

- This is a harmonic potential with:

$$K = \frac{d^2V}{dr^2} \quad \text{and} \quad \omega = \sqrt{K/m}$$

- Therefore vibrational (harmonic) excitations of diatomic molecules occur with energies:

$$E = (n + \frac{1}{2}) \hbar \omega + V(r_0)$$

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Diatomic Molecule: NaCl

➤ Potential:

$$V(r) = \{-e^2/4\pi\epsilon_0\} \{1/r - \beta/r^n\}$$

\uparrow \uparrow
 attractive electron-nucleus repulsive nucleus-nucleus

➤ Interatomic distance: $r_0 = 2.81 \times 10^{-10} \text{ m}$

➤ Constant: $n = 9.4$

➤ Differentiate at r_0 (minimum)

$$dV/dr = \{-e^2/4\pi\epsilon_0\} \{-1/r_0^2 + n\beta/r_0^{n+1}\} = 0$$

➤ Hence:

$$\beta = r_0^{n-1}/n$$

➤ Also:

$$d^2V/dr^2 = \{-e^2/4\pi\epsilon_0\} \{2/r_0^3 + n(n+1)\beta/r_0^{n+2}\} = K$$

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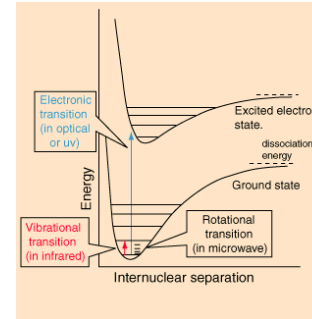
Diatomic Molecule: NaCl

➤ Data:

$$\hbar = 1.06 \times 10^{-34} \text{ Js}$$

$$m(\text{NaCl}) = 14 \times 1.67 \times 10^{-27} \text{ kg}$$

$$\hbar\omega = 6.44 \times 10^{-21} \text{ J} = \underline{0.040 \text{ eV}}$$



➤ This corresponds to an infrared photon that can be absorbed or emitted as the molecule changes between vibrational levels

➤ Other types of excitation are also possible:

Rotational (microwave)

Electronic (optical or UV)

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Diatomic Molecule: NaCl

➤ Hence:

$$K = \{-e^2/4\pi\epsilon_0\} \{(1-n)/r_0^3\}$$

➤ Data:

$$e = 1.6 \times 10^{-19} \text{ C}$$

$$\epsilon_0 = 8.85 \times 10^{-12} \text{ F m}^{-1}$$

$$r_0 = 2.81 \times 10^{-10} \text{ m}$$

$$n = 9.4$$

$$K = \underline{87.3 \text{ J m}^{-2}}$$

➤ The vibrational energy is now given by

$$\hbar\omega = \hbar\sqrt{K/m}$$

➤ Note that m is the reduced mass of NaCl

$$m = m(\text{Na})m(\text{Cl}) / \{m(\text{Na}) + m(\text{Cl})\}$$

$$\sim 23 \times 37 / \{23 + 37\} \sim \underline{14 \text{ amu}}$$

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8.3 Zero Point Energy

- Classical physics of a bound particle:
 - No energy quantisation
 - minimum energy = 0
- Quantum physics of a bound particle:
 - Energy quantisation
 - Minimum energy not zero
- For an infinite square well:
$$E_1 = h^2/8ma^2$$
- For a harmonic oscillator:
$$E_0 = \frac{1}{2}\hbar\omega$$
- This minimum value of energy is called the "zero point" energy




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Motion in Various Potentials

- Also on VITAL !

-  ➤ 1D motion in various wells
-  ➤ 2D motion in a box
-  ➤ 2D harmonic oscillator

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Zero Point Energy

- If a particle is confined to be roughly in the range $-a/2 \leq x \leq +a/2$ then the uncertainty in its position is:
$$\Delta x \sim a$$
- From the Uncertainty Principle, its momentum cannot be specified to better than
$$\Delta p \sim \hbar/a$$
- Therefore the momentum has to be at least this value:
$$p \geq \Delta p \sim \hbar/a$$
- The corresponding energy is then:
$$p^2/2m = E \geq \hbar^2/2ma^2$$
- Zero point energy arises from quantum physics !

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8.4 3D Bound States

- Example: infinite potential well $V(x,y,z)$

$$\left. \begin{array}{l} |x| \leq a/2 \\ |y| \leq a/2 \\ |z| \leq a/2 \end{array} \right\} V(x,y,z) = 0 \quad \left. \begin{array}{l} |x| > a/2 \\ |y| > a/2 \\ |z| > a/2 \end{array} \right\} V(x,y,z) = \infty$$

- The time dependent Schrödinger equation is now:

$$-\{\hbar^2/2m\} \nabla^2 \psi + V\psi = i\hbar \partial\psi/\partial t$$

where:

$$\nabla^2 = \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$$

- The time independent Schrödinger equation is:

$$-\{\hbar^2/2m\} \nabla^2 \psi + V\psi = E\psi$$

- Now a partial differential equation

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3D Infinite Well

- Now:

$$\partial^2\psi/\partial x^2 = \psi_x\psi_z d^2\psi_x/dx^2 ,$$

$$\partial^2\psi/\partial y^2 = \psi_x\psi_z d^2\psi_y/dy^2 ,$$

$$\partial^2\psi/\partial z^2 = \psi_x\psi_y d^2\psi_z/dz^2$$

- Substitute into Schrödinger equation and divide through by $\psi_x\psi_y\psi_z$:

$$-\{\hbar^2/2m\} \{1/\psi_x\} \{d^2\psi_x/dx^2\} \quad \text{function only of } x$$

$$-\{\hbar^2/2m\} \{1/\psi_y\} \{d^2\psi_y/dy^2\} \quad \text{function only of } y$$

$$-\{\hbar^2/2m\} \{1/\psi_z\} \{d^2\psi_z/dz^2\} \quad \text{function only of } z$$

$$= E = \text{constant}$$

- Each of the three "degrees of freedom" - motion in x , in y , in z represent independent free particle motion

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3D Infinite Well

- Outside the box: $V = \infty$ so:

$$\psi = 0$$

- Inside the box:

$$-\{\hbar^2/2m\} (\partial^2\psi/\partial x^2 + \partial^2\psi/\partial y^2 + \partial^2\psi/\partial z^2) = E\psi$$

- Physics:

- motion in x is independent of...

- motion in y is independent of...

- motion in z

- Intuitive assumption to get trial solution

- Hence try a solution of the form:

$$\psi = \psi_x(x) \psi_y(y) \psi_z(z)$$

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3D Infinite Well Solutions

- Only possible scenario:

$$-\{\hbar^2/2m\} \{d^2\psi_x/dx^2\} = E_x\psi_x ,$$

$$-\{\hbar^2/2m\} \{d^2\psi_y/dy^2\} = E_y\psi_y ,$$

$$-\{\hbar^2/2m\} \{d^2\psi_z/dz^2\} = E_z\psi_z$$

- The total energy is:

$$E = E_x + E_y + E_z$$

- The solutions are already known:

$$\psi_x \propto \sin\{n_x\pi x/a\} , \psi_y \propto \sin\{n_y\pi y/a\} , \psi_z \propto \sin\{n_z\pi z/a\}$$

- The total energy is thus:

$$E = \{h^2/8ma^2\} (n_x^2 + n_y^2 + n_z^2)$$

- With:

$$n_x \geq 1 , n_y \geq 1 , n_z \geq 1$$

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Energy Degeneracy

Energy	n_x	n_y	n_z	
$\{3\hbar^2/8ma^2\}$	1	1	1	one state
$\{6\hbar^2/8ma^2\}$	2	1	1	} one energy, three states
$\{6\hbar^2/8ma^2\}$	1	2	1	
$\{6\hbar^2/8ma^2\}$	1	1	2	
$\{9\hbar^2/8ma^2\}$	2	2	1	} one energy, three states
$\{9\hbar^2/8ma^2\}$	2	1	2	
$\{9\hbar^2/8ma^2\}$	1	2	2	

➤ Degeneracy arises since n_x, n_y, n_z can be combined in several ways to give same value of $(n_x^2 + n_y^2 + n_z^2)$

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3D Harmonic Oscillator

- Harmonic oscillator splits into three decoupled equations of linear harmonic form
- Solution for each of x, y, z is a solution of the 1D harmonic oscillator:

$$n_x = 0 \quad \Psi_{x0} = c_0 \exp\{-x^2/2\alpha^2\}$$

$$n_x = 1 \quad \Psi_{x1} = c_1 (x/\alpha) \exp\{-x^2/2\alpha^2\} \quad \text{etc...}$$

- The total energy is:

$$E = E_x + E_y + E_z \quad \text{i.e.} \quad E = (n_x + n_y + n_z + 3/2) \hbar\omega$$

- With:

$$n_x \geq 0, n_y \geq 0, n_z \geq 0 \quad \text{and} \quad \omega = \hbar\sqrt{K/m}$$

- Zero point energy:

$$3/2 \hbar\omega$$

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3D Harmonic Oscillator

- Potential energy:

$$V(x, y, z) = \frac{1}{2}Kx^2 + \frac{1}{2}Ky^2 + \frac{1}{2}Kz^2 \quad \text{same force constant } K$$

- Time dependent Schrödinger equation:

$$-\{\hbar^2/2m\} \{\partial^2\psi/\partial x^2\}$$

$$-\{\hbar^2/2m\} \{\partial^2\psi/\partial y^2\}$$

$$-\{\hbar^2/2m\} \{\partial^2\psi/\partial z^2\}$$

$$+\frac{1}{2}K(x^2 + y^2 + z^2)\psi = E\psi$$

- Try solution with independent x, y, z motion:

$$-\{\hbar^2/2m\} \{1/\psi_x\} \{d^2\psi_x/dx^2\} + \frac{1}{2}Kx^2 \quad \text{function only of } x$$

$$-\{\hbar^2/2m\} \{1/\psi_y\} \{d^2\psi_y/dy^2\} + \frac{1}{2}Ky^2 \quad \text{function only of } y$$

$$-\{\hbar^2/2m\} \{1/\psi_z\} \{d^2\psi_z/dz^2\} + \frac{1}{2}Kz^2 \quad \text{function only of } z$$

$$= E = \text{constant}$$

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3D Harmonic Oscillator Degeneracy

Energy / ($\hbar\omega$)	n_x	n_y	n_z	
3/2	0	0	0	one state
5/2	1	0	0	} one energy, three states
5/2	0	1	0	
5/2	0	0	1	
7/2	1	1	0	} one energy, six states
7/2	1	0	1	
7/2	0	1	1	
7/2	2	0	0	
7/2	0	2	0	
7/2	0	0	2	

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3D Anisotropic Harmonic Oscillator

- What happens if K is different for x , y and z , i.e.:

$$V(x,y,z) = \frac{1}{2}K_x x^2 + \frac{1}{2}K_y y^2 + \frac{1}{2}K_z z^2 \quad ?$$

- There are now three distinct frequencies associated with each of x , y , z :

$$\omega_x = \hbar\sqrt{K_x/m}, \quad \omega_y = \hbar\sqrt{K_y/m}, \quad \omega_z = \hbar\sqrt{K_z/m}$$

- The total energy is now:

$$E = \hbar \left\{ \left(n_x + \frac{1}{2}\right)\omega_x + \left(n_y + \frac{1}{2}\right)\omega_y + \left(n_z + \frac{1}{2}\right)\omega_z \right\}$$

- Example: Nilsson model to describe deformed nuclei:

- prolate/oblate shapes with $x = y \neq z$
- triaxial shapes with $x \neq y \neq z$

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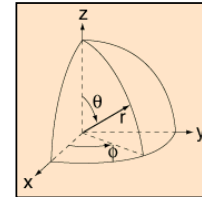
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8.5 3D Bound States & Angular Momentum

- The time independent Schrödinger equation is:

$$-\{\hbar^2/2m\} \nabla^2 \psi + V\psi = E\psi$$

- Work in spherical polar coordinates r , θ , ϕ instead of Cartesian coordinates x , y , z :



$$x = r \sin\{\theta\} \cos\{\phi\},$$

$$y = r \sin\{\theta\} \sin\{\phi\},$$

$$z = r \cos\{\theta\}$$

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Spherical Polar Coordinates

- It can be shown that (but not easily!): don't remember

$$\begin{aligned} \nabla^2 = & \{1/r^2\} \partial/\partial r (r^2 \partial/\partial r) \\ & + \{1/r^2\} \{1/\sin\{\theta\}\} \partial/\partial \theta (\sin\{\theta\} \partial/\partial \theta) \\ & + \{1/r^2\} \{1/\sin^2\{\theta\}\} \partial^2/\partial \phi^2 \end{aligned}$$

- For most $V(r,\theta,\phi)$ the solution is complicated but...

- For solutions of the form $V(\mathbf{r}) = V(r)$ (central potential: function of radial coordinate only), the solutions have generic features

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Angular Momentum

- The Schrödinger equation becomes:

$$\begin{aligned}
 & -\{\hbar^2/2m\} [\{1/r^2\} \partial/\partial r (r^2 \partial\psi/\partial r) \\
 & + \{1/r^2\} \{1/\sin\{\theta\}\} \partial/\partial\theta (\sin\{\theta\} \partial\psi/\partial\theta) \\
 & + \{1/r^2\} \{1/\sin^2\{\theta\}\} \partial^2\psi/\partial\phi^2] \\
 & + V(r)\psi = E\psi
 \end{aligned}$$

- The potential energy function $V(r)$ does not vary with θ and ϕ
 - For non-radial motion of the particle, no energy/momentum changes from potential to kinetic or vice-versa
 - Angular momentum is conserved (no preferred direction in space)

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Radial Solutions

- Rearrange:

$$\begin{aligned}
 & -\{\hbar^2/2m\} \{1/R\} d/dr (r^2 dR/dr) + r^2V(r) - r^2E \\
 & = -\{\hbar^2/2m\} [\{1/(Y\sin\{\theta\})\} \partial/\partial\theta (\sin\{\theta\} \partial Y/\partial\theta) \\
 & + \{1/(Y\sin^2\{\theta\})\} \partial^2 Y/\partial\phi^2] \\
 & = \text{constant}
 \end{aligned}$$

- For radial motion in r : (8.5.1)

$$-\{\hbar^2/2m\} \{1/r^2\} d/dr (r^2 dR/dr) + [V(r) - N/r^2] R = ER$$

- For rotational motion in θ, ϕ : centrifugal potential (8.5.2)

$$-\{\hbar^2/2m\} [\{1/\sin\{\theta\}\} \partial/\partial\theta (\sin\{\theta\} \partial Y/\partial\theta) + \{1/\sin^2\{\theta\}\} \partial^2 Y/\partial\phi^2] = -NY$$

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Radial Solutions

- Decouple motion in r (radial) and motion in (θ, ϕ) (rotation) and look for a solution:

$$\psi = R(r) Y(\theta, \phi)$$

- Then:

$$\begin{aligned}
 & -\{\hbar^2/2m\} [\{Y/r^2\} d/dr (r^2 dR/dr) \\
 & + \{R/r^2\} \{1/\sin\{\theta\}\} \partial/\partial\theta (\sin\{\theta\} \partial Y/\partial\theta) \\
 & + \{R/r^2\} \{1/\sin^2\{\theta\}\} \partial^2 Y/\partial\phi^2] \\
 & + V(r)RY = ERY
 \end{aligned}$$

- Divide through by RY and multiply through by r :

$$\begin{aligned}
 & -\{\hbar^2/2m\} [\{1/R\} d/dr (r^2 dR/dr) && \text{function only of } r \\
 & + \{1/(Y\sin\{\theta\})\} \partial/\partial\theta (\sin\{\theta\} \partial Y/\partial\theta) && \text{function only of } \\
 & + \{1/(Y\sin^2\{\theta\})\} \partial^2 Y/\partial\phi^2 && \theta, \phi \\
 & + r^2V(r) = r^2E && \text{function only of } r
 \end{aligned}$$

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Radial Solutions

- This might look horrible ! Use intuition !
- Substituting $R(r) = \{1/r\} \chi(r)$ in (8.5.1), the equation can be cast in the form:

$$-\{\hbar^2/2m\} d^2\chi/dr^2 + [V(r) - N/r^2] \chi = E \chi$$

which looks like a 1D Schrödinger equation for the "radial wave function" $\chi = rR$ in a modified (central) potential energy function

- Similarly try to recast (8.5.2) into a form of Schrödinger's equation, namely a second order partial differential of $Y(\theta, \phi)$ equal to a number with dimension of energy multiplying $Y(\theta, \phi)$

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Angular Solutions

- From (8.5.1) N/r^2 has dimension of **energy**
- So rewrite (8.5.2) as:

$$-\{\hbar^2/2mr^2\} [\{1/\sin\{\theta\}\} \partial/\partial\theta (\sin\{\theta\} \partial Y/\partial\theta) + \{1/\sin^2\{\theta\}\} \partial^2 Y/\partial\phi^2] = -\{N/r^2\} Y$$
- Now:
 - mr^2 is just the moment of inertia (\mathcal{I}) of the particle's rotation about the origin
- So we have:

$$-\{\hbar^2/2\mathcal{I}\} \nabla_{\theta\phi}^2 Y = E_{\theta\phi} Y$$
- Form of Schrödinger equation for particle motion about the origin, i.e. **rotation**

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Radial Energies

- Radial solution - ask a mathematician:

$$-\{\hbar^2/2m\} d^2\chi/dr^2 + [V(r) - N/r^2] \chi = E \chi$$
- Solution in detail depends on $V(r)$
- Generic results:
 - N depends on ℓ (angular momentum)
 - Bound states quantised:

$$E = E_{n\ell}$$
 - n integer ≥ 1 , ℓ integer ≥ 0
 - (n, ℓ) label "energy sub-shell"
 - n labels an "energy shell"

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Summary: Particle in Central Potential

- Introduce polar coordinates $r \theta \phi$ to Schrödinger equation:

$$-\{\hbar^2/2m\} \nabla^2 \psi + V(r) \psi = E \psi$$
- Conservation of angular momentum allows decoupling of **radial** and **angular** motion:

$$\psi = R(r) Y(\theta, \phi)$$
- Radial wave function:

$$\chi = rR \quad \text{radial probability density } |\chi|^2$$
- Radial motion:

$$-\{\hbar^2/2m\} d^2\chi/dr^2 + [V(r) - N/r^2] \chi = E \chi$$
- Angular motion:

$$-\{\hbar^2/2\mathcal{I}\} \nabla_{\theta\phi}^2 Y(\theta, \phi) = -\{N/r^2\} Y(\theta, \phi) = E_{\theta\phi} Y$$

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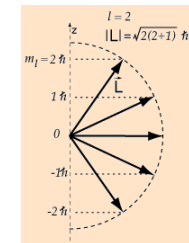
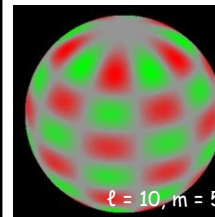
Angular Energies

- Rotational solution - ask a mathematician
- Spherical Harmonics:

$$Y_{\ell m}(\theta, \phi)$$
 - ℓ integer $0, 1, 2, \dots$
 - m integer: $-\ell, -\ell+1, \dots, 0, \dots, \ell-1, \ell$
- Legendre Polynomials

$$Y_{\ell m}(\theta, \phi) = P_{\ell}(\cos\{\theta\}) \exp\{im\phi\}$$
- Quantised energy of rotation:

$$E_{\theta\phi} = \{\ell(\ell+1)\hbar^2\} / \{2\mathcal{I}\} \quad -N = -\{\ell(\ell+1)\hbar^2\} / \{2m\}$$
- Energy degeneracy of $\{2\ell+1\}$, no dependence on m
- Quantum physics of rotation

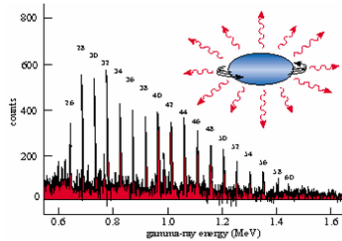


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Nuclear Rotational Band



- Quantised energy of rotation:

$$E = \{I(I+1)\} \hbar^2 / 2\mathcal{I}$$
- Gamma ray energy

$$\Delta E = \{2I-1\} \hbar^2 / \mathcal{I}$$
- Gamma ray spacing

$$\Delta^2 E = 4 \hbar^2 / \mathcal{I}$$

 = constant

- Most nuclei are **prolate** (rugby ball shape) and can rotate
- Gamma rays are emitted between levels of a "rotational band" taking away $2\hbar$ of spin each ("superdeformation" in nuclei discovered by Liverpool physicists at Daresbury!)

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Rules for Central Potentials

- Particle energy is quantised according to:

$$E = E_{n\ell} \quad n \geq 1, \ell \geq 0$$
- ℓ specifies the quantised angular momentum² (L^2) of the particle:

$$L^2 = \ell\{\ell+1\} \hbar^2$$
- m ($-\ell, -\ell+1, \dots, 0, \dots, \ell-1, \ell$) specifies the projection L_z of L on a fixed direction z

$$L_z = m \hbar$$
- Common central potentials are:
 - free particle $V(r) = 0$
 - constant $V(r) = \text{constant}$
 - harmonic oscillator $V(r) = \frac{1}{2}Kr^2$
 - "Particle in a box" is **not** a central potential

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Gammasphere (Gamma Ray Spectrometer)



- The Liverpool Nuclear Physics Group investigate "high spin states" in nuclei using gamma ray spectroscopy

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Quantised Angular Momentum

- For angular motion energy quantisation:

$$E_{\theta\phi} = \{\ell(\ell+1)\hbar^2\} / \{2\mathcal{I}\} \quad \ell = 0, 1, 2, \dots$$
 where \mathcal{I} is the moment of inertia
- Hence:

$$\ell(\ell+1)\hbar^2 = (\text{angular momentum})^2$$
- Free rotation \Rightarrow angular motion
- Quantised energies of rotation \Rightarrow quantised angular momentum:

$$\sqrt{\{\ell(\ell+1)\}} \hbar$$
- Remember for the free **linear** motion of a particle, quantised energies **only** occur if confined in a box
 - Quantised momentum $p = \hbar k = n\pi\hbar/a$

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8.6 3D Harmonic Oscillator Revisited

- Harmonic oscillator potential:
 $V(x,y,z) = \frac{1}{2}K\{x^2 + y^2 + z^2\}$
- If force constant is spherically symmetric V is central:
 $V(r) = \frac{1}{2}Kr^2$
- Therefore the angular part of the wave function is a set of spherical harmonics corresponding to quantised angular momentum:
 $L^2 = \ell\{\ell+1\} \hbar^2$
- Energy quantisation is determined by the radial equation:
 $-\{\hbar^2/2m\} d^2\chi/dr^2 + [\frac{1}{2}Kr^2 - \{\ell(\ell+1)\hbar^2\} / 2mr^2] \chi = E \chi$
- Energies:
 $E_{n\ell} \Rightarrow E = (n + 3/2) \hbar\omega \quad n \geq 0 \text{ integer}$
 $n = 0 \quad \ell = 0, n = 1 \quad \ell = 1, n = 2 \quad \ell = 0, 2 \dots$ **parity**

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HO Degeneracy

- An identical energy level structure emerges using the radial solution as using the $x y z$ approach
 ➤ as it must!
- States used in the $x y z$ solution are linear combinations of states in the $r \theta \phi$ solution
 ➤ the number of states is the same
- Subshells (n, ℓ) within a shell n are degenerate
 ➤ accidental degeneracy

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Harmonic Oscillator Degeneracy

Energy / ($\hbar\omega$)	n	ℓ	m	
3/2	0	0	0	one state
5/2	1	1	-1	} one energy, three states
5/2	1	1	0	
5/2	1	1	+1	
7/2	2	0	0	} one energy, six states
7/2	2	2	-2	
7/2	2	2	-1	
7/2	2	2	0	
7/2	2	2	+1	
7/2	2	2	+2	

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8.7 Hydrogen Atom

- One electron in bound state with a proton with central potential:

$$V(r) = \{-e^2 / 4\pi\epsilon_0 r\} \quad \text{Coulomb potential}$$

- Schrödinger equation: (8.7.1)

$$-\{\hbar^2/2\mathcal{M}\} \nabla_{\Theta\phi}^2 Y_{lm}(\Theta,\phi) = \{\ell(\ell+1)\hbar^2 / 2\mathcal{M}\} Y_{lm}(\Theta,\phi)$$

- And:

$$-\{\hbar^2/2m\} d^2\chi/dr^2 + [\{-e^2 / 4\pi\epsilon_0 r\} - \{\ell(\ell+1)\hbar^2 / 2mr^2 \}] \chi = E \chi \quad (8.7.2)$$

- Energy sub-shell structure:

$$E_{n\ell} = \{-me^4 / 32\pi^2\epsilon_0^2\hbar^2\} \{1/n^2\}$$

$$n = 1 \quad \ell = 0$$

$$n = 2 \quad \ell = 0, 1$$

$$n = 3 \quad \ell = 0, 1, 2$$

n = principal quantum number

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n ℓ Quantum Numbers

- Principal quantum number n is written as a digit
- Angular momentum quantum number ℓ is written as:

ℓ = 0	s	"sharp"
ℓ = 1	p	"principal"
ℓ = 2	d	"diffuse"
ℓ = 3	f	"fundamental"
ℓ = 4	g	} now alphabetical
ℓ = 5	h	
ℓ = 6	i	

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Hydrogen Atom Degeneracies

Energy / $\{me^4 / 32\pi^2\epsilon_0^2\hbar^2\}$	n	ℓ	m	degeneracy
-1	1	0	0	one
-1/4	2	0	0	four
-1/4		1	±1,0	
-1/9	3	0	0	nine
-1/9		1	±1,0	
-1/9		2	±2,±1,0	

- Sub-shells within an energy shell are degenerate

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Rydberg Constant

- Energy level structure is often written in terms of the Rydberg constant R :

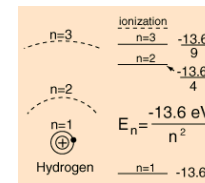
$$E_n = -R hc / n^2$$

- where:

$$R = \{me^4\} / \{8\epsilon_0 h^3 c\} = 13.6 \text{ eV}/hc$$

- So:

$$E_n = -13.6 / n^2 \text{ electron-volt}$$

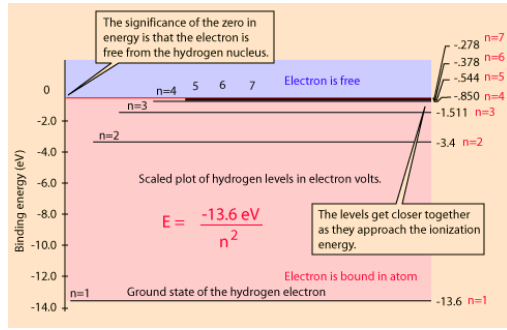


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Hydrogen Atom Energies



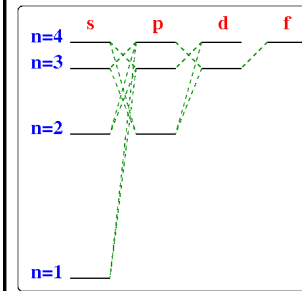
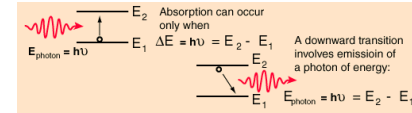
$$E_n = \{-me^4 / 32\pi^2\epsilon_0^2\hbar^2\} \{1/n^2\} = -13.6 \text{ eV} / n^2$$

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Selection Rules



➤ Transitions can only occur between states that differ in l by 1, i.e.

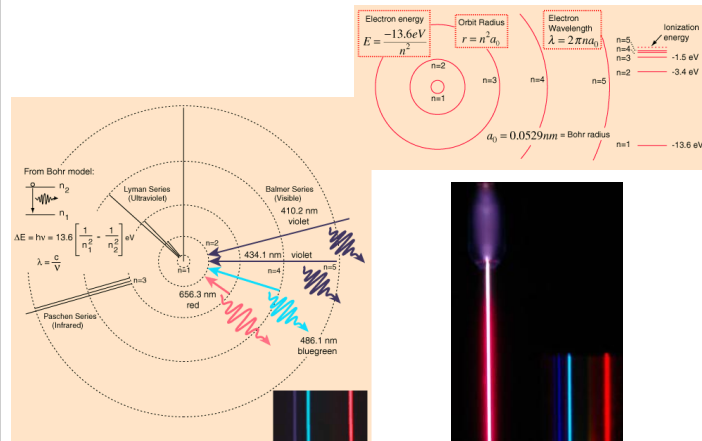
$$\Delta l = \pm 1$$

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Hydrogen Atom Spectroscopy



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Where is the Electron ?

➤ Electron probability density:

$$|\psi|^2 = |R Y|^2$$

➤ Probability of finding the electron in a small region of the atom volume:

$$r^2 dr d\Omega = r^2 dr d(\cos\theta) d\phi \quad \Omega = \text{solid angle}$$

is:

$$\begin{aligned} |R_{n\ell}(r) Y_{\ell m}(\theta, \phi)|^2 r^2 dr d\Omega \\ = |R_{n\ell}(r)|^2 |Y_{\ell m}(\theta, \phi)|^2 dr d\Omega \\ = |\chi_{n\ell}(r)|^2 |Y_{\ell m}(\theta, \phi)|^2 dr d\Omega \end{aligned}$$

➤ Ask a mathematician !

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Radial Dependence

- Radius of first Bohr orbit:

$$a_0 = 4\pi\epsilon_0\hbar^2 / me^2 = 0.0529 \text{ nm}$$

- Radial wave functions R_{nl} :

$$R_{10} = 2 \{1/a_0\}^{3/2} \exp\{-r/a_0\}$$

$$R_{20} = [1/2\sqrt{2}] \{1/a_0\}^{3/2} \{2 - r/a_0\} \exp\{-r/a_0\}$$

- Radial probability density:

$$P(r) = |\chi_{nl}|^2 = |rR_{nl}|^2$$

- As $r \rightarrow 0$:

$$\chi_{nl} = rR_{nl} \rightarrow 0$$

$$R_{nl=0} \neq 0$$

s wave density

$$R_{nl \neq 0} \rightarrow 0$$

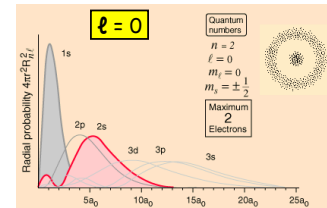
p, d, ... wave density

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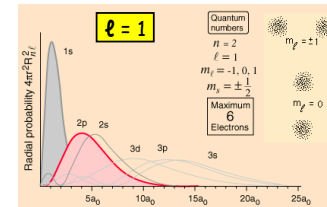
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Radial Distributions: n = 2



2s



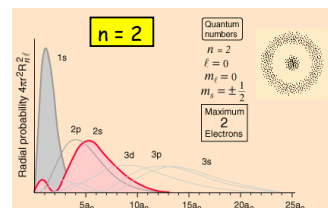
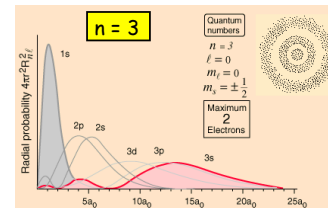
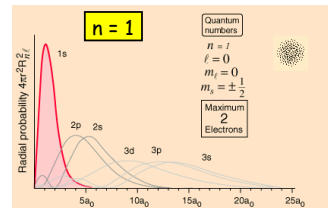
2p

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Radial Distributions: $\ell = 0$



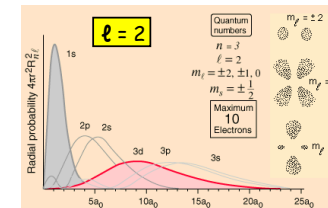
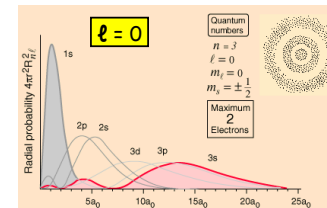
s waves

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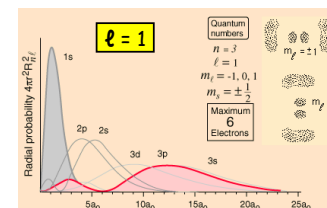
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Radial Distributions: n = 3



3s, 3p, 3d



H atom applet (also on VITAL)

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