

PHYS2222
Quantum Physics
Reading list

- For general reference the second-year course book: *Introduction to the Structure of Matter* by J.J. Brehm and W.J. Mullin (Wiley, 1989, ISBN 0-471-60531-X).

10 copies in UCL library, available from P&A Department. Referred to as B&M in these notes.

Advantages: suitable for most 2nd-year Physics courses, good integration of quantum physics with atomic physics.

Disadvantages: weak on more formal aspects of quantum mechanics.

- As a reasonably priced introduction: *Quantum Mechanics* by A.I.M. Rae (4th edition, Institute of Physics Publishing, 2002, ISBN 0 7503 0839 7).

9 copies in UCL library, available from P&A Department.

Advantages: cheap, well suited to level of course, covers essentially all the material at roughly the right level.

Disadvantages: not so useful for other courses.

- As a more advanced book that is also recommended for the third-year quantum mechanics course: *Quantum Mechanics* by B.H. Bransden and C.J. Joachain (2nd edition, Prentice Hall, 2000, ISBN 0582-35691-1).

10 copies in UCL library, available from P&A Department. Referred to as B&J in these notes.

Advantages: material for 2222 is mostly presented at the start of the book. Contains additional material going well beyond 2B22 for further reading. Useful for both 3rd-year and 4th-year courses.

Disadvantages: coverage of some material (notably spin and emission/absorption of radiation) is at a more advanced level than 2222 and is not so useful for this course. Relatively expensive (£41 on Amazon).

Prerequisites

- First-year Mathematics for Physics and Astronomy (1B45 and 1B46) or equivalent
- Material from the second-year maths course (2246) will be used after it has been covered in that course
- Basic relativistic kinematics (from 1B46) will be assumed, and basic electromagnetism (field and potential of point charge, interaction of magnetic dipole with magnetic field) will be used as it is covered in 2201

2222 and other courses

- Some limited overlap with 1B23 *Modern Physics, Astronomy and Cosmology* (but different approach – 2222 is less descriptive and more rigorous). Areas covered by both courses:
 - Wave-particle duality (photoelectric effect, double-slit experiment)
 - Time-independent Schrödinger equation
 - Significance of wave function and Heisenberg's Uncertainty Principle

1B23 is *not* a prerequisite for 2222!

Syllabus

1. *The failure of classical mechanics* [3 lectures]

Photoelectric effect, Einstein's equation, electron diffraction and de Broglie relation. Compton scattering. *Wave-particle duality, Uncertainty principle (Bohr microscope).*

2. *Steps towards wave mechanics* [3 lectures]

Time-dependent and time-independent Schrödinger equations. The wave function and its interpretation.

3. *One-dimensional time-independent problems* [7 lectures]

Infinite square well potential. Finite square well. Probability flux and the potential barrier and step. Reflection and transmission. Tunnelling and examples in physics and astronomy. Wavepackets. The simple harmonic oscillator.

4. *The formal basis of quantum mechanics* [5 lectures]

The postulates of quantum mechanics – operators, observables, eigenvalues and eigenfunctions. Hermitian operators and the Expansion Postulate.

5. *Angular momentum in quantum mechanics* [2 lectures]

Operators, eigenvalues and eigenfunctions of \hat{L}_z and \hat{L}^2 .

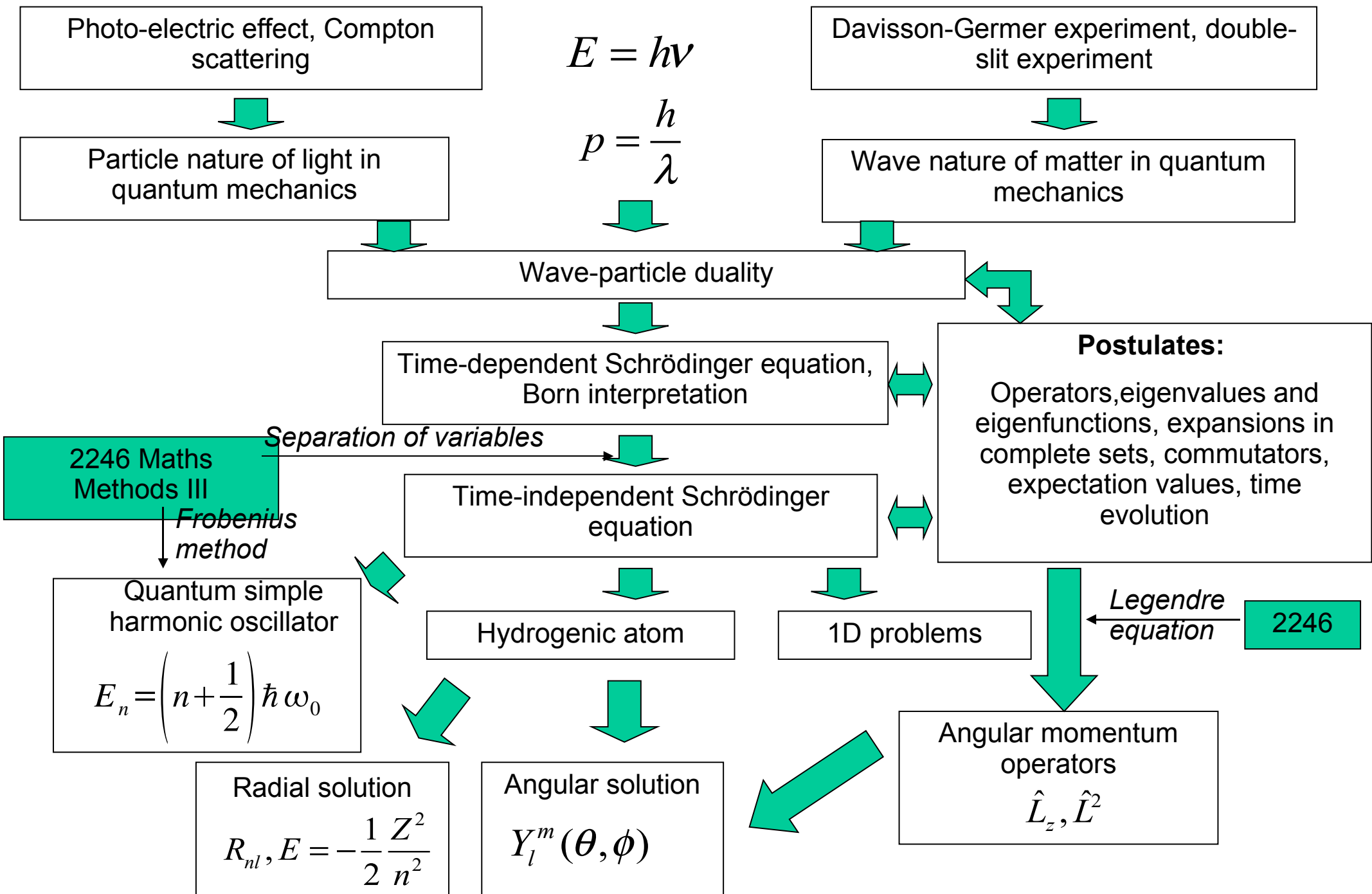
Syllabus (contd)

6. *Three dimensional problems and the hydrogen atom* [4 lectures]

Separation of variables for a three-dimensional rectangular well. Separation of space and time parts of the 3D Schrödinger equation for a central field. The radial Schrödinger equation, and casting it in a form suitable for solution by series method. Degeneracy and spectroscopic notation.

7. *Electron spin and total angular momentum* [3 lectures]

Magnetic moment of electron due to orbital motion. The Stern-Gerlach experiment. Electron spin and complete set of quantum numbers for the hydrogen atom. Rules for addition of angular momentum quantum numbers. Total spin and orbital angular momentum quantum numbers S , L , J . Construct J from S and L .



Lecture style

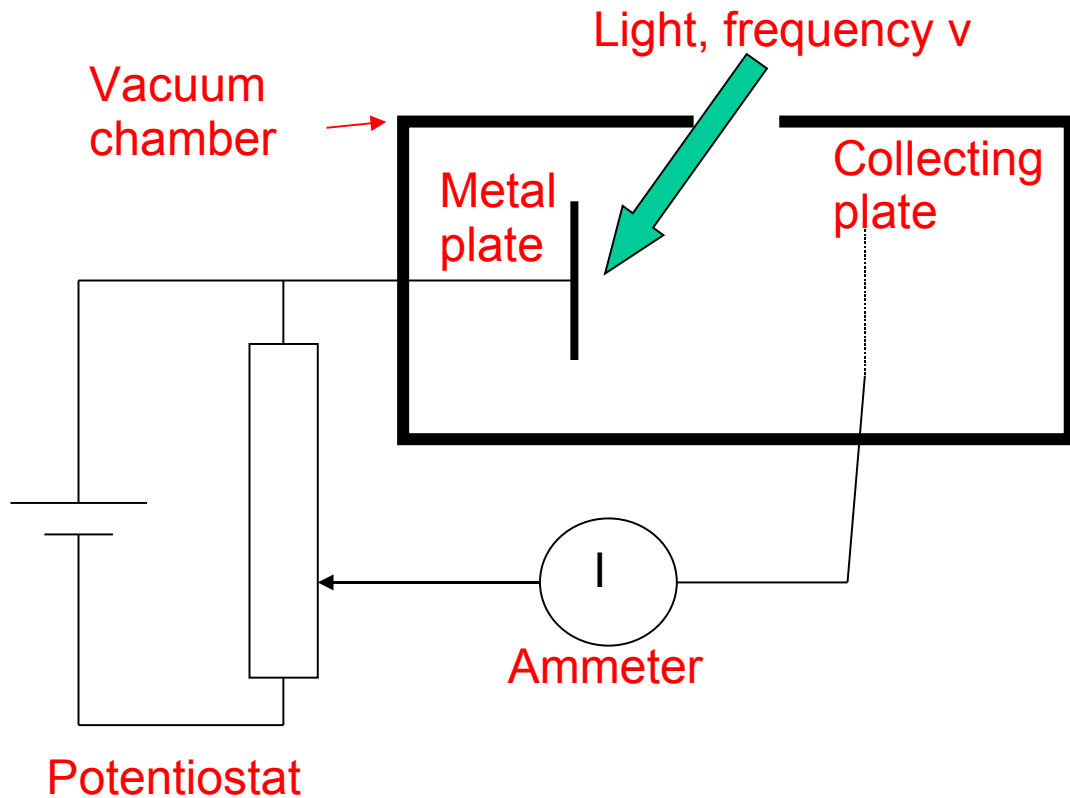
- Experience (and feedback) suggests the biggest problems found by students in lectures are:
 - Pacing of lectures
 - Presentation and retention of mathematically complex material
- Our solution for 2222:
 - Use powerpoint presentation via data projector or printed OHP for written material and diagrams
 - Use whiteboard or handwritten OHP for equations in all mathematically complex parts of the syllabus
 - Student copies of notes *will require annotation with these mathematical details*
 - Notes (un-annotated) will be available for download via website or (for a small charge) from the Physics & Astronomy Office
- Headings for sections relating to key concepts are marked with asterisks (***)

B&M §2.5; Rae §1.1;
B&J §1.2

1.1 Photoelectric effect



Metal plate in a vacuum, irradiated by ultraviolet light, emits charged particles (Hertz 1887), which were subsequently shown to be electrons by J.J. Thomson (1899).



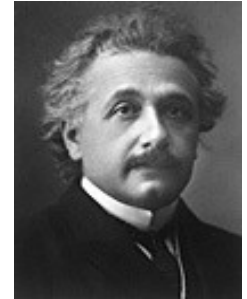
Classical expectations

Electric field E of light exerts force $\mathbf{F} = -e\mathbf{E}$ on electrons. As intensity of light increases, force increases, so KE of ejected electrons should increase.

Electrons should be emitted whatever the frequency ν of the light, so long as E is sufficiently large

For very low intensities, expect a time lag between light exposure and emission, while electrons absorb enough energy to escape from material

Einstein



Photoelectric effect (contd)***

Actual results:

Maximum KE of ejected electrons is independent of intensity, but dependent on ν

For $\nu < \nu_0$ (i.e. for frequencies below a cut-off frequency) no electrons are emitted

There is no time lag. However, rate of ejection of electrons depends on light intensity.

Einstein's interpretation (1905): light is emitted and absorbed in packets (*quanta*) of energy

$$E = h\nu \quad (1.1)$$

An electron absorbs a single quantum in order to leave the material

Millikan



The maximum KE of an emitted electron is then predicted to be:

$$K_{\max} = h\nu - W \quad (1.2)$$

Planck constant:
universal constant of nature

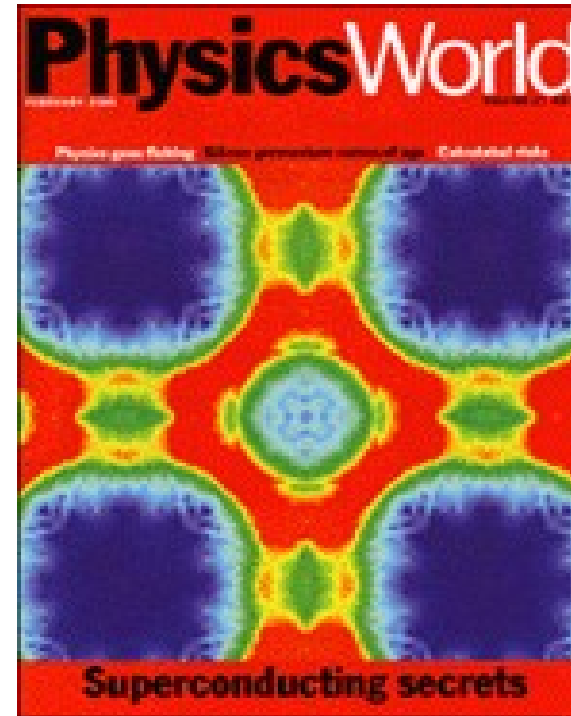
Work function: minimum energy needed for electron to escape from metal (depends on material, but usually 2-5eV)

Verified in detail through subsequent experiments by Millikan

$$h = 6.63 \times 10^{-34} \text{ Js}$$

Photoemission experiments today

Modern successor to original photoelectric effect experiments is *ARPES* (*Angle-Resolved Photoemission Spectroscopy*)



Emitted electrons give information on distribution of electrons within a material as a function of energy *and* momentum

Frequency and wavelength for light***

Relativistic relationship between a particle's momentum and energy:

$$E^2 = p^2 c^2 + m_0^2 c^4$$

For massless particles propagating at the speed of light, becomes

$$E^2 = p^2 c^2$$

$$E = c |p|$$

$$h\nu = c |p|$$

Hence find relationship between momentum p and wavelength λ :

$$|p| = \frac{h\nu}{c}$$

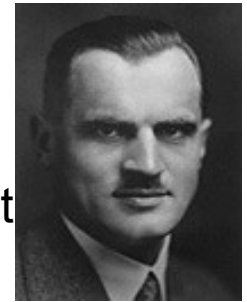
But: $\lambda \nu = c$

$$\therefore |p| = \frac{h}{\lambda} \quad (\text{For light.})$$

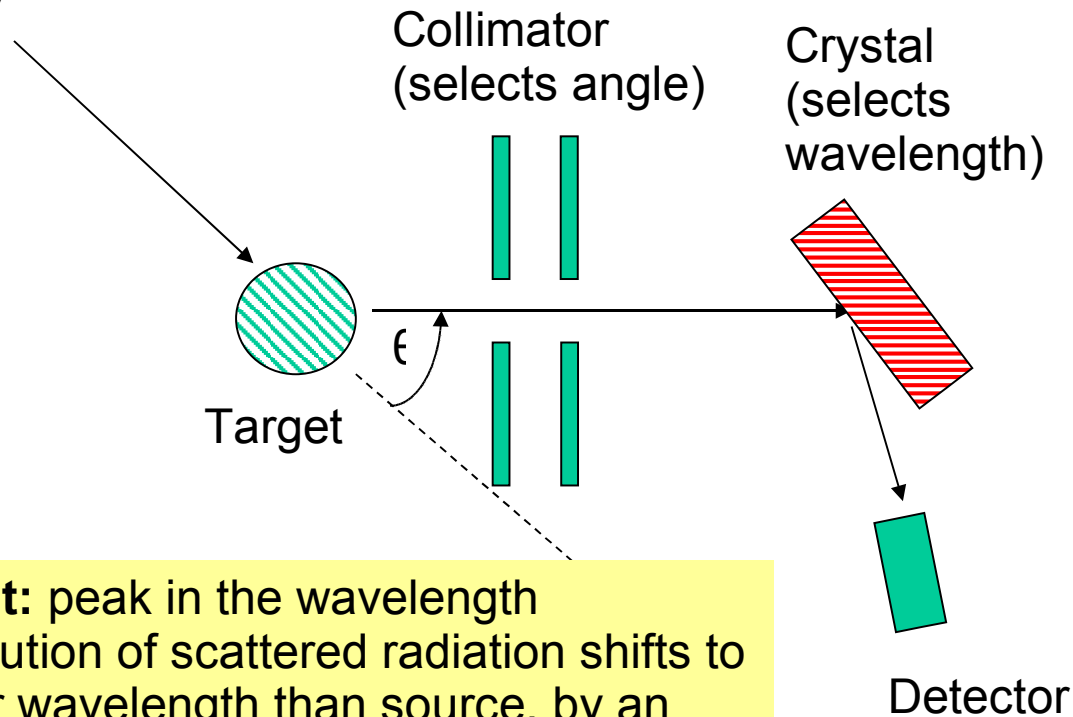
B&M §2.7; Rae §1.2;
B&J §1.3

1.2 Compton scattering

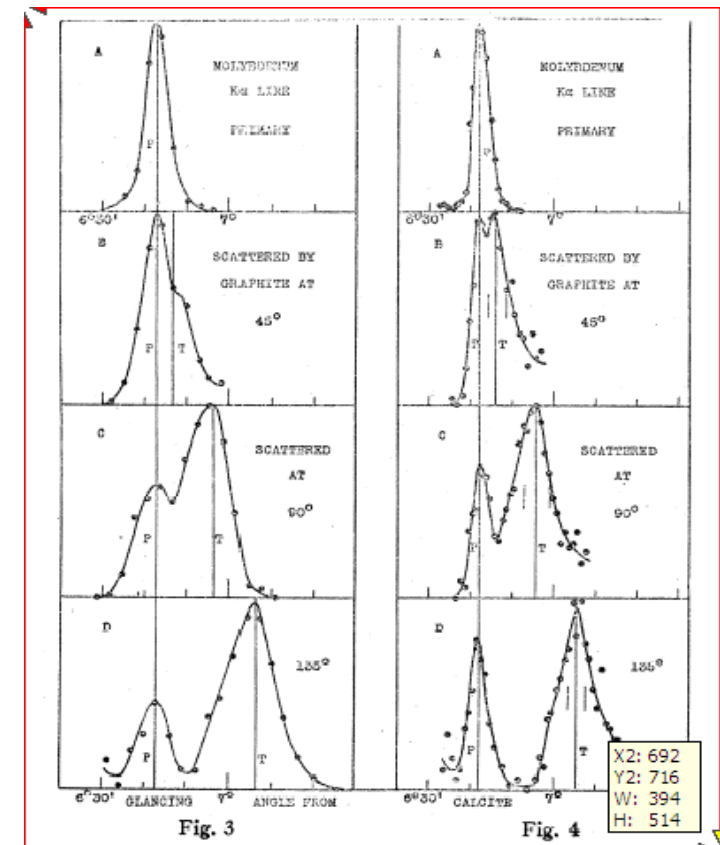
Compton (1923) measured scattered intensity of X-rays (with well-defined wavelength) from solid target, as function of wavelength for different angles.



X-ray source



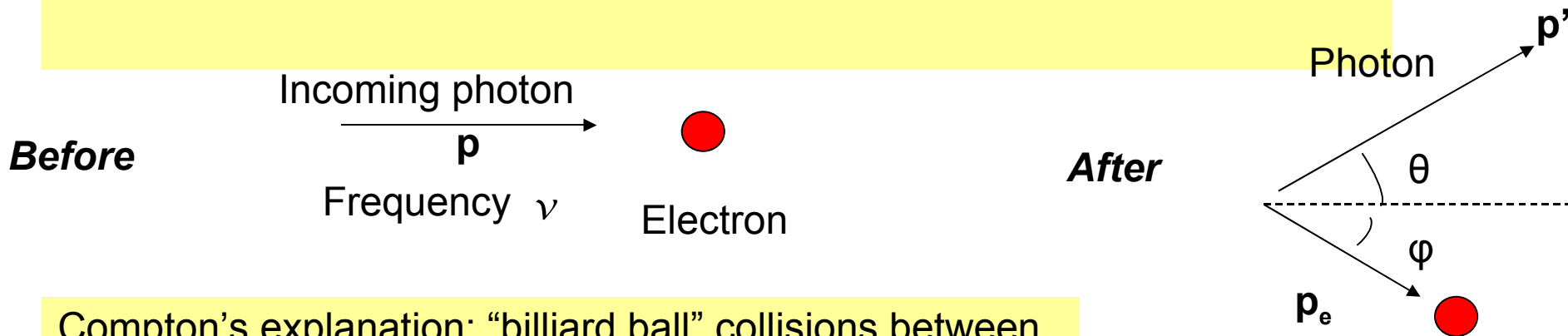
Result: peak in the wavelength distribution of scattered radiation shifts to longer wavelength than source, by an amount that depends on the scattering angle θ (but not on the target material)



A.H. Compton, *Phys. Rev.* **22** 409 (1923)

Compton scattering (contd)

Classical picture: oscillating electromagnetic field would cause oscillations in positions of charged particles, re-radiation in all directions at *same frequency and wavelength* as incident radiation



Compton's explanation: "billiard ball" collisions between X-ray photons and electrons in the material

Conservation of energy:

$$h\nu + m_e c^2 = h\nu' + (p_e^2 c^2 + m_e^2 c^4)^{\frac{1}{2}}$$

Write in terms of momentum:

$$pc + m_e c^2 = p'c + (p_e^2 c^2 + m_e^2 c^4)^{\frac{1}{2}}$$

$$(p - p')c + m_e c^2 = (p_e^2 c^2 + m_e^2 c^4)^{\frac{1}{2}}$$

$$(p - p')^2 c^2 + m_e^2 c^4 + 2(p - p')m_e c^3 = p_e^2 c^2 + m_e^2 c^4$$

$$(p - p')^2 + 2(p - p')m_e c = p_e^2$$

Conservation of momentum:

In electrons initial rest frame:

$$\underline{p} = \underline{p}' + \underline{p}_e$$

$$\underline{p}_e = \underline{p} - \underline{p}'$$

$$|\underline{p}_e|^2 = (\underline{p} - \underline{p}') \cdot (\underline{p} - \underline{p}') = |\underline{p}|^2 + |\underline{p}'|^2 - 2|\underline{p}||\underline{p}'|\cos\theta$$

$$|\underline{p}_e|^2 = (p - p')^2 + 2(1 - \cos\theta)pp'$$

Compton scattering (contd)

Equate above for p_e^2 :

$$\begin{aligned}(p - p')^2 + 2(p - p')m_e c &= (p - p')^2 + 2(1 - \cos \theta) pp' \\ \Rightarrow (p - p')m_e c &= (1 - \cos \theta) pp' \\ \Rightarrow m_e c \left(\frac{1}{p'} - \frac{1}{p} \right) &= 1 - \cos \theta\end{aligned}$$

Assuming photon momentum related to wavelength:

$$p = \frac{h}{\lambda} \quad (1.3)$$

$$\Rightarrow \frac{m_e c}{h} (\lambda' - \lambda) = 1 - \cos \theta$$

$$\lambda' - \lambda = \frac{h}{m_e c} (1 - \cos \theta) \quad (1.4)$$

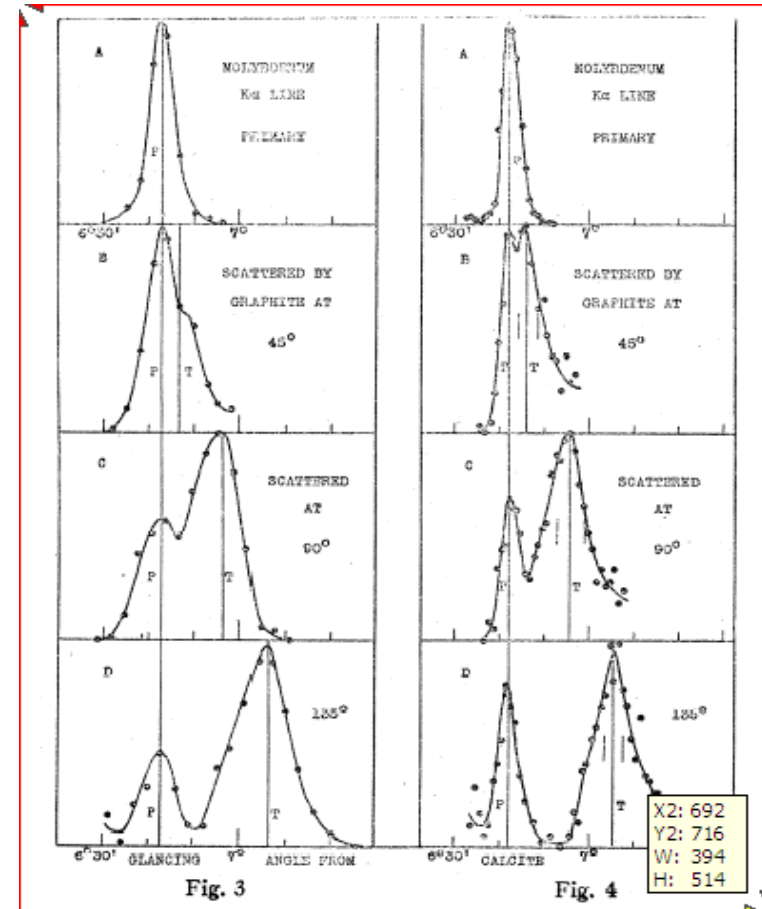
'Compton wavelength' of electron (0.0243 Å)

Puzzle

What is the origin of the component of the scattered radiation that is *not* wavelength-shifted?

Second peak at original λ due to nuclei collisions.

$$\begin{aligned}
 \text{Solving } \frac{f'}{\lambda'} - \frac{f}{\lambda} &= \frac{f}{\lambda} \left(\frac{\lambda}{\lambda'} - 1 \right) = \frac{f}{\lambda} \left(\frac{1}{1 - \frac{2h}{m_0 c \lambda}} - 1 \right) \\
 &= \text{Assuming } \frac{2h}{m_0 c \lambda} \ll 1 \text{ is negligible} \\
 \approx \frac{f}{\lambda} \left(1 + \frac{2h}{m_0 c \lambda} + \frac{2h^2}{m_0^2 c^2 \lambda^2} + \dots \right) - \frac{f}{\lambda} &= \frac{f}{\lambda} \left(\frac{2h}{m_0 c \lambda} + \frac{2h^2}{m_0^2 c^2 \lambda^2} + \dots \right)
 \end{aligned}$$



Wave-particle duality for light***

“ There are therefore now two theories of light, both indispensable, and - as one must admit today despite twenty years of tremendous effort on the part of theoretical physicists - without any logical connection.” *A. Einstein (1924)*

- Light exhibits diffraction and interference phenomena that are *only* explicable in terms of wave properties
- Light is always detected as packets (photons); if we look, we never observe half a photon
- Number of photons proportional to energy density (i.e. to square of electromagnetic field strength)

B&M §4.1-2; Rae §1.4;
B&J §1.6

1.3 Matter waves***



“As in my conversations with my brother we always arrived at the conclusion that in the case of X-rays one had both waves and corpuscles, thus suddenly - ... it was certain in the course of summer 1923 - I got the idea that one had to extend this duality to material particles, especially to electrons. And I realised that, on the one hand, the Hamilton-Jacobi theory pointed somewhat in that direction, for it can be applied to particles and, in addition, it represents a geometrical optics; on the other hand, in quantum phenomena one obtains quantum numbers, which are rarely found in mechanics but occur very frequently in wave phenomena and in all problems dealing with wave motion.” *L. de Broglie*

Proposal: dual wave-particle nature of radiation also applies to matter. *Any* object having momentum p has an associated wave whose wavelength λ obeys

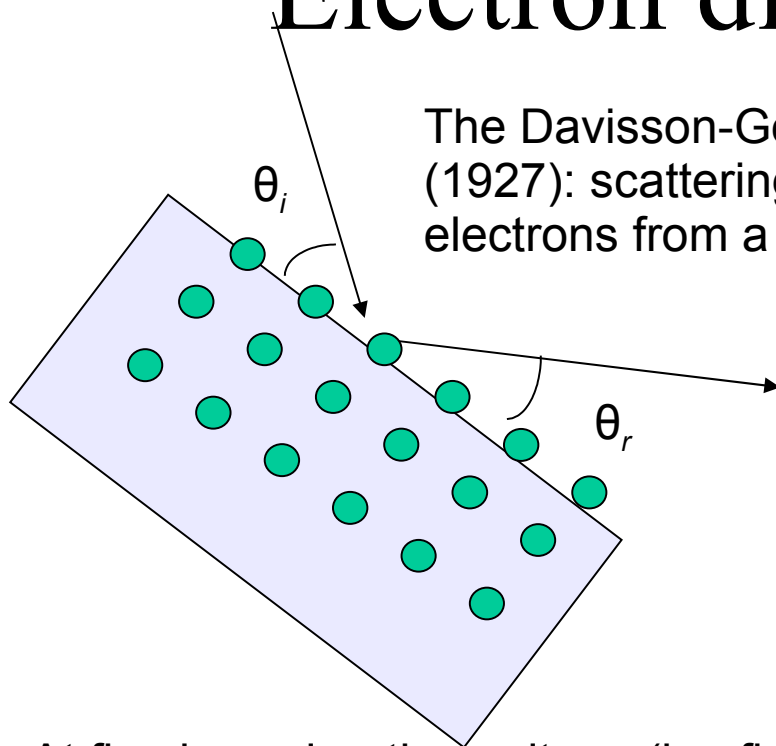
$$p = \frac{h}{\lambda} = \hbar k \quad k = \frac{2\pi}{\lambda} \text{ (wavenumber)} \quad \left(\hbar = \frac{h}{2\pi} \right)$$

Prediction: crystals (already used for X-ray diffraction) might also diffract particles

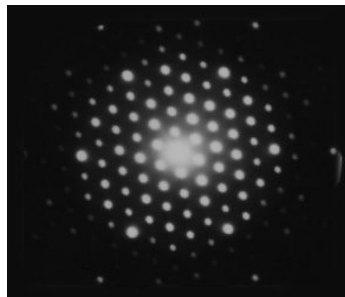
Electron diffraction from crystals

Davisson *G.P. Thomson*

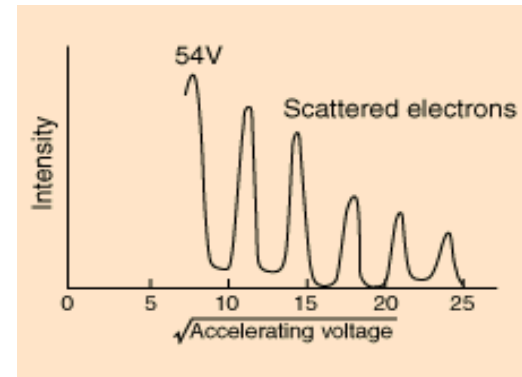
The Davisson-Germer experiment (1927): scattering a beam of electrons from a Ni crystal



At fixed accelerating voltage (i.e. fixed electron energy) find a pattern of pencil-sharp reflected beams from the crystal



At fixed *angle*, find sharp peaks in intensity as a function of electron energy

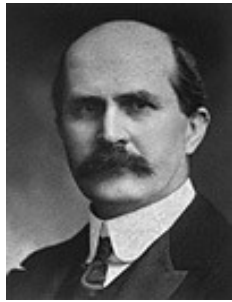


Davisson, C. J., "Are Electrons Waves?," Franklin Institute Journal **205**, 597 (1928)

G.P. Thomson performed similar interference experiments with thin-film samples

Electron diffraction from crystals

(contd)

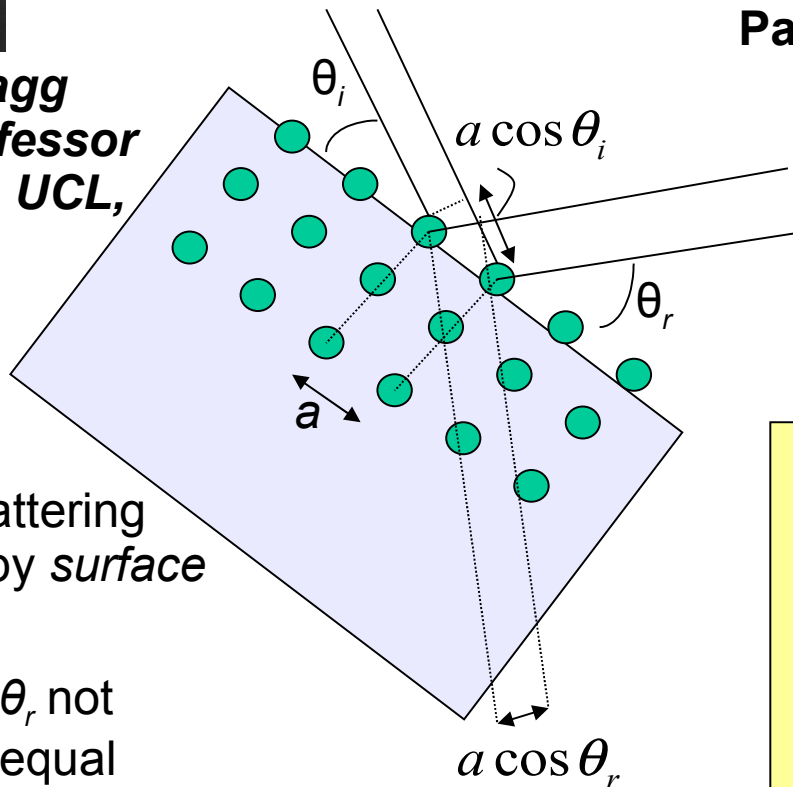


William Bragg
(Quain Professor of Physics, UCL, 1915-1923)



Lawrence Bragg

Interpretation used similar ideas to those pioneered for scattering of X-rays from crystals by William and Lawrence Bragg



Path difference:

$$a \cos \theta_r - a \cos \theta_i$$

$$a (\cos \theta_r - \cos \theta_i)$$

Constructive interference when

$$a (\cos \theta_r - \cos \theta_i) = n \lambda$$

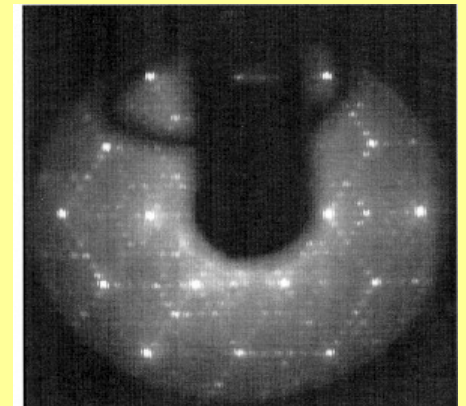
Electron scattering dominated by *surface* layers

Note θ_i and θ_r not necessarily equal

Note difference from usual “Bragg’s Law” geometry: the identical scattering planes are oriented *perpendicular* to the surface

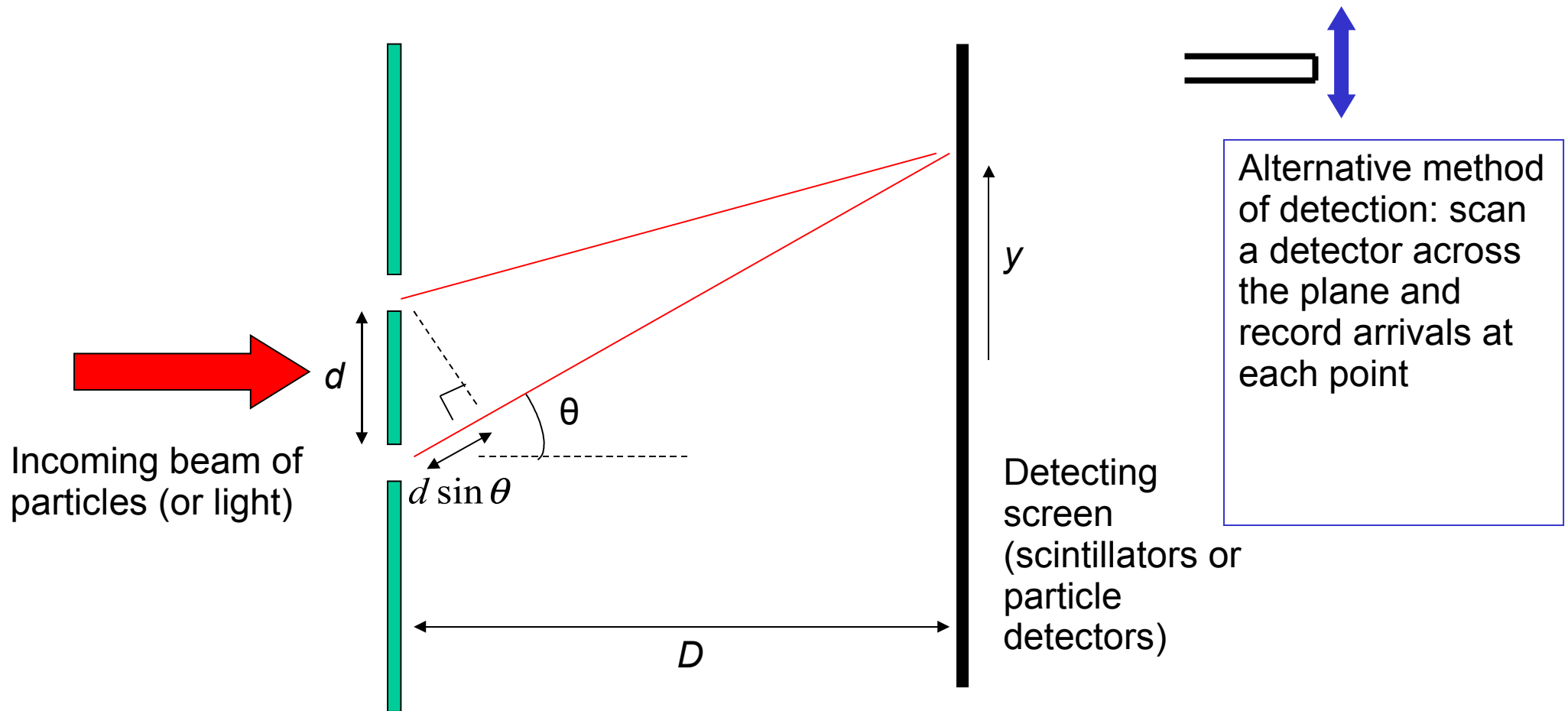
Modern Low Energy Electron Diffraction (LEED)

this pattern of “spots” shows the beams of electrons produced by surface scattering from complex (7×7) reconstruction of a silicon surface

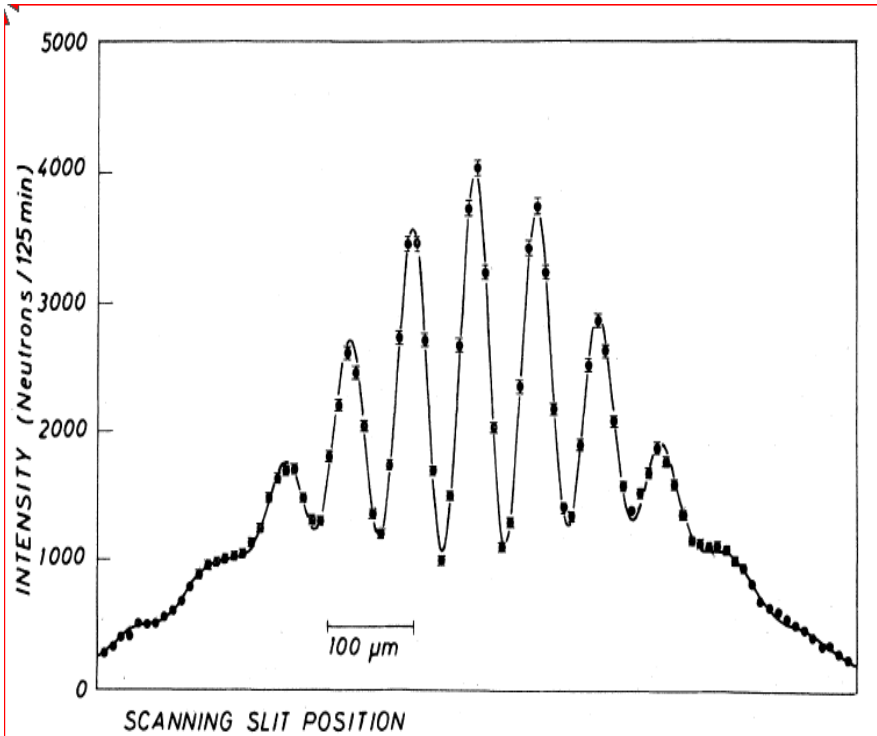


The double-slit interference experiment

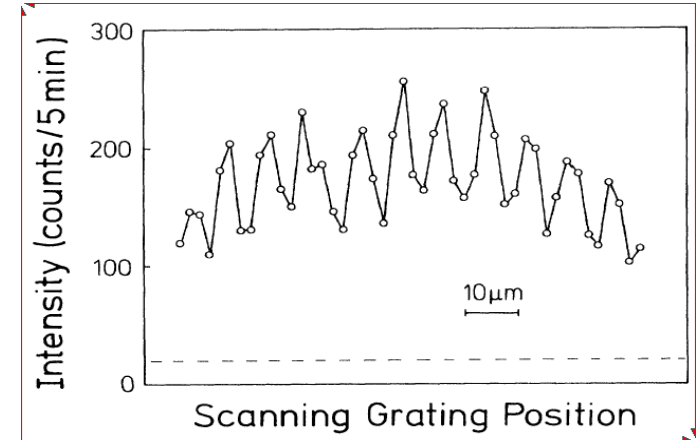
Originally performed by Young (1801) with light. Subsequently also performed with many types of matter particle (see references).



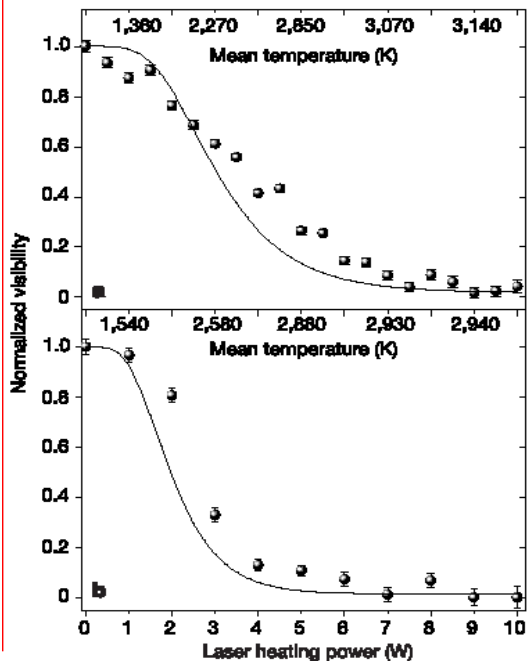
Results



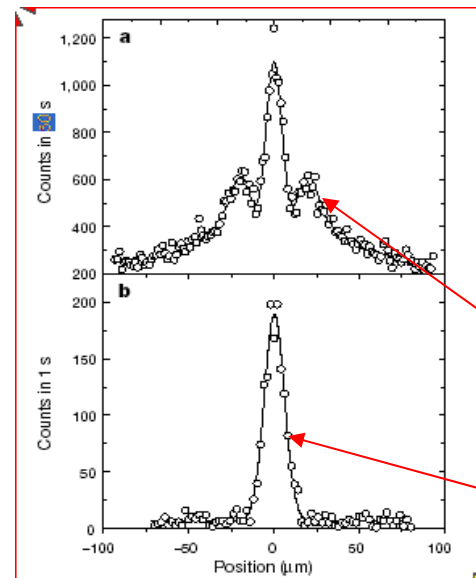
Neutrons, A
 Zeilinger *et al.* 1988
Reviews of Modern Physics **60** 1067-1073



He atoms: O Carnal and J Mlynek
 1991 *Physical Review Letters* **66**
 2689-2692



Fringe visibility decreases as molecules are heated. L. Hackermüller *et al.* 2004 *Nature* **427** 711-714



C₆₀ molecules: M Arndt *et al.* 1999
Nature **401** 680-682

With multiple-slit grating

Without grating

Double-slit experiment: interpretation

Interpretation: maxima and minima arise from alternating constructive and destructive interference between the waves from the two slits

Spacing between maxima:

Constructive interference:

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

$\Rightarrow n^{\text{th}}$ maximum occurs at:

$$d \sin \theta_n = n \lambda$$

For small θ , $\sin \theta \approx \tan \theta$

$$\theta_n \approx \frac{n \lambda}{d}$$

$$\Rightarrow \text{Maximum at } y_n = D \tan \theta_n \approx D \theta_n \approx \frac{n \lambda D}{d}$$

$$\Rightarrow \text{Spacing at } \frac{\lambda D}{d}$$

Example: He atoms at a temperature of 83K, with $d=8\mu\text{m}$ and $D=64\text{cm}$

$$\text{Expect: } \frac{p^2}{2m} = \frac{3}{2} K_B T \quad \Rightarrow \quad p = 4.8 \times 10^{-24} \text{ Ns} \Rightarrow \lambda = \frac{h}{p} = 1.03 \text{ \AA}$$

$$\Rightarrow \text{Spacing} = \frac{\lambda D}{d} = 8.24 \times 10^{-6} \text{ m}$$

Double-slit experiment: bibliography

Some key papers in the development of the double-slit experiment during the 20th century:

- Performed with a light source so faint that only one photon exists in the apparatus at any one time (G I Taylor 1909 *Proceedings of the Cambridge Philosophical Society* **15** 114-115)
- Performed with electrons (C Jönsson 1961 *Zeitschrift für Physik* **161** 454-474, translated 1974 *American Journal of Physics* **42** 4-11)
- Performed with single electrons (A Tonomura *et al.* 1989 *American Journal of Physics* **57** 117-120)
- Performed with neutrons (A Zeilinger *et al.* 1988 *Reviews of Modern Physics* **60** 1067-1073)
- Performed with He atoms (O Carnal and J Mlynek 1991 *Physical Review Letters* **66** 2689-2692)
- Performed with C₆₀ molecules (M Arndt *et al.* 1999 *Nature* **401** 680-682)
- Performed with C₇₀ molecules, showing reduction in fringe visibility as temperature rises so molecules “give away” their position by emitting photons (L. Hackermüller *et al.* 2004 *Nature* **427** 711-714)

An excellent summary is available in *Physics World* (September 2002 issue, page 15) and at <http://physicsweb.org/> (readers voted the double-slit experiment “the most beautiful in physics”).

Matter waves: key points***

- Interference occurs even when only a single particle (e.g. photon or electron) in apparatus, so wave is a property of a *single* particle
 - A particle can “interfere with itself”
- Wavelength unconnected with internal lengthscales of object, determined by momentum
- Attempt to find out which slit particle moves through causes collapse of interference pattern (see later...)

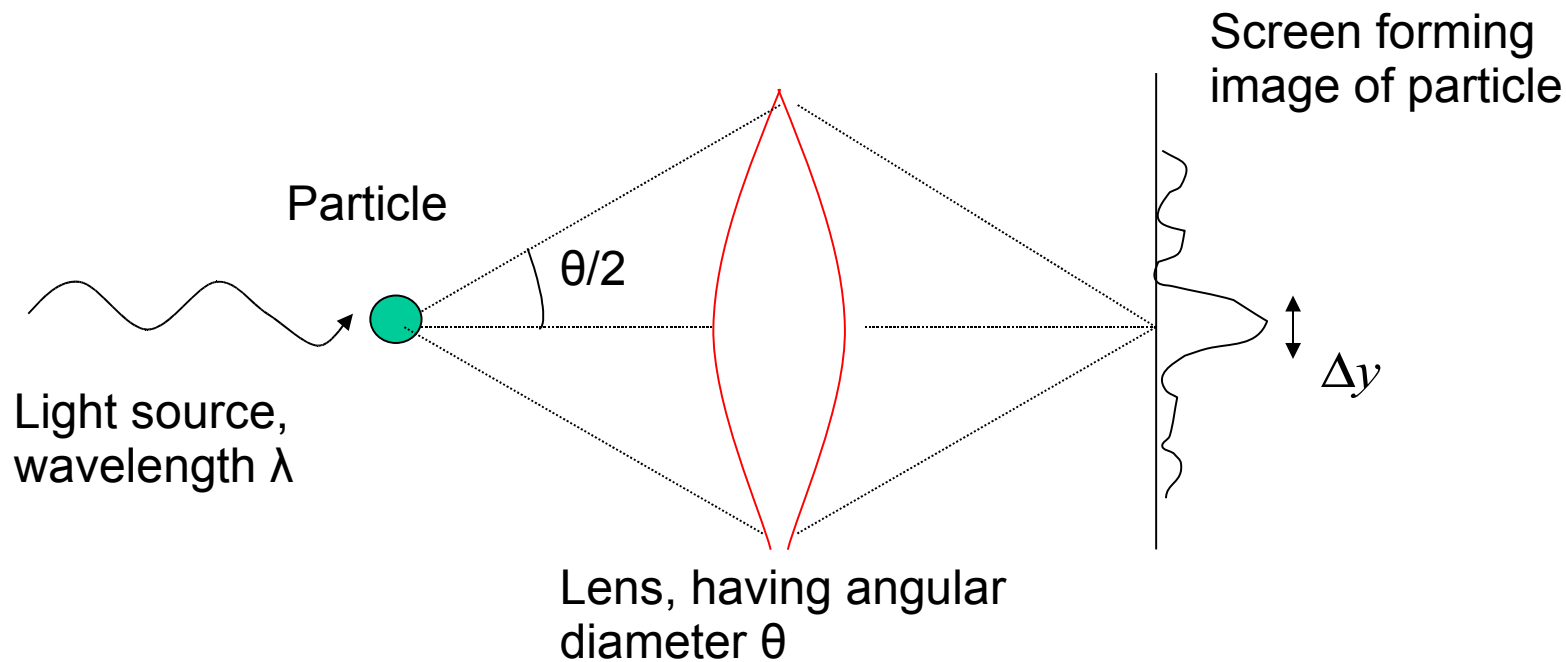
Wave-particle duality for matter particles

- Particles exhibit diffraction and interference phenomena that are *only* explicable in terms of wave properties
- Particles always detected individually; if we look, we never observe half an electron
- *Number of particles proportional to....???*

B&M §4.5; Rae §1.5; B&J §2.5 (first part only)

1.4 Heisenberg's gamma-ray microscope and a first look at the Uncertainty Principle

The combination of wave and particle pictures, and in particular the significance of the 'wave function' in quantum mechanics (see also §2), involves *uncertainty*: we only know the *probability* that the particle will be found near a particular location.



Heisenberg

Resolving power of lens: $\Delta y \geq \frac{\lambda}{\theta}$

Heisenberg's gamma-ray microscope and the Uncertainty Principle***

Range of y-momenta of photons after scattering, if they have initial momentum p :

Y-component of γ momentum after scattering.

$$-p \sin\left(\frac{\theta}{2}\right) < p_y < +p \sin\left(\frac{\theta}{2}\right)$$

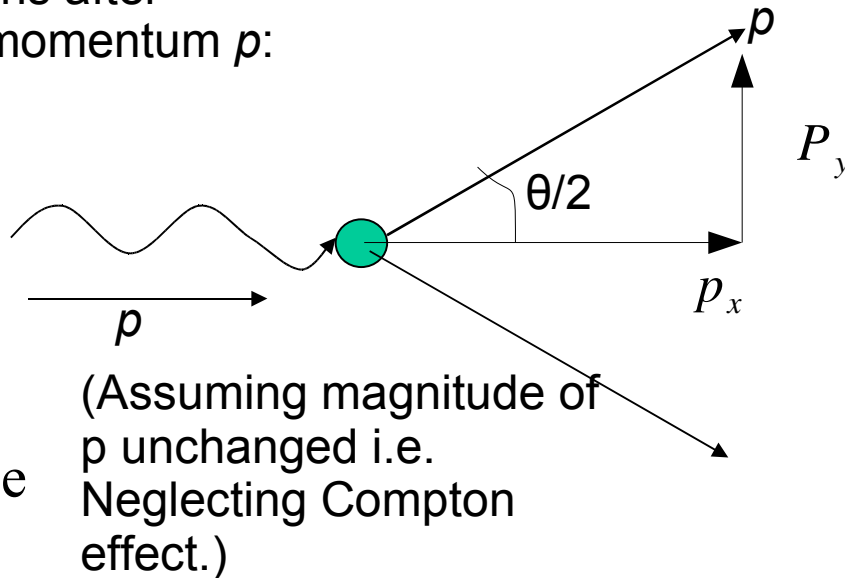
\Rightarrow Particle momentum must lie in the same range:

$$\Delta p_y = 2p \sin\left(\frac{\theta}{2}\right) \simeq p \theta$$

Remember resolution power of lens from classical optics:

$$\Delta y \geq \frac{\lambda}{\theta}$$

$$\therefore \Delta y \Delta p_y \geq h$$



(Small angle/small lens)

$$\Delta y \Delta p_y \geq h$$

Heisenberg's Uncertainty Principle

2.1 An equation for the matter waves: the time-dependent Schrödinger equation***

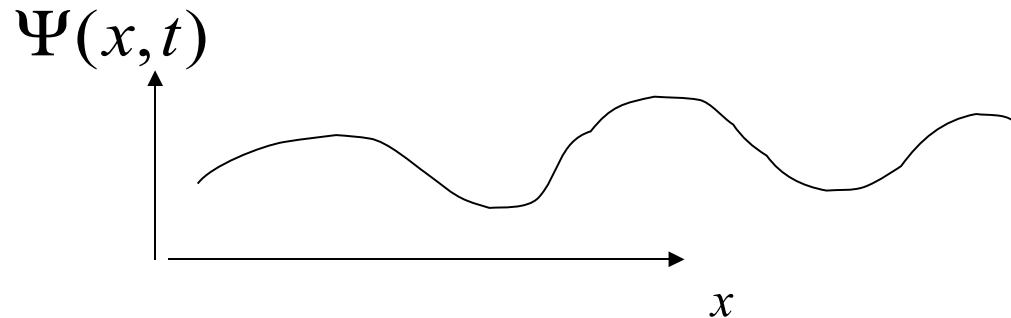
Classical wave equation (in one dimension):

$$\frac{\delta^2 \Psi}{\delta x^2} = \frac{1}{v^2} \frac{\delta^2 \Psi}{\delta t^2}$$

$\Psi(x, t)$ = wave displacement (in 1d)

v = wave velocity

e.g. Transverse waves on a string:



Can we use this to describe the matter waves in free space?

An equation for the matter waves (2)

Seem to need an equation that involves the *first derivative* in time, but the *second derivative* in space

$$\text{Try: } \alpha \frac{\delta \Psi}{\delta t} = \frac{\delta^2 \Psi}{\delta x^2}$$

$\Psi(x, t)$ is "wave function" associated with matter wave

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

$$\rightarrow \frac{d^2 \Psi}{dx^2} = -k^2 Ae^{i(kx - \omega t)} \quad ; \quad \frac{d \Psi}{dt} = -i\omega Ae^{i(kx - \omega t)}$$

$$\Rightarrow -i\omega \alpha = -k^2$$

$$\text{We want the energy to be } \frac{p^2}{2m} \Rightarrow \hbar\omega = \frac{(\hbar k)^2}{2m}$$

So choose α so this is true.

$$\Rightarrow -i\alpha \frac{\hbar k^2}{2m} = -k^2$$

$$\Rightarrow \alpha = \frac{2m}{i\hbar}$$

So, wave equation is:

$$\frac{2m}{i\hbar} \frac{d \Psi}{dt} = \frac{d^2 \Psi}{dx^2}$$

$$\left(\text{Multiplying both sides by } \frac{-\hbar^2}{2m} \right)$$

$$i\hbar \frac{\delta \Psi}{\delta t} = -\frac{\hbar^2}{2m} \frac{\delta^2 \Psi}{\delta x^2}$$

(for matter waves in free space)

An equation for the matter waves (3)

For particle with potential energy $V(x,t)$, need to modify the relationship between energy and momentum:

$$E = \frac{p^2}{2m} + V(x,t)$$

Total energy = kinetic energy + potential energy

Suggests corresponding modification to Schrödinger equation:

$$\text{We had: } i \hbar \frac{d \Psi}{dt} = \frac{-\hbar^2}{2m} \frac{d^2 \Psi}{dx^2}$$

LHS: Gives $\hbar \omega \Psi$ for a plane wave.

RHS: Gives $\frac{(\hbar k)^2}{2m} \Psi$ for a plane wave.

\Rightarrow Try adding a term $V(x,t) \Psi$ on RHS.

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

Time-dependent Schrödinger equation



Schrödinger

The Schrödinger equation: notes

- This was a plausibility argument, *not* a derivation. We believe the Schrödinger equation to be true not because of this argument, but because its predictions agree with experiment.
- There are limits to its validity. In this form it applies to
 - A single particle, moving in one direction, that is
 - Non-relativistic (i.e. has non-zero rest mass and velocity very much below c)
- The Schrödinger equation is a partial differential equation in x and t (like classical wave equation)
- The Schrödinger equation contains the complex number i . Therefore its solutions are *essentially* complex (unlike classical waves, where the use of complex numbers is just a mathematical convenience)
- Positive i is merely a convention.

The Hamiltonian operator

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

Can think of the RHS of the Schrödinger equation as a *differential operator that represents the energy of the particle.*

This operator is called the *Hamiltonian* of the particle, and usually given the symbol \hat{H}

$$\left[\underbrace{-\frac{\hbar^2}{2m} \frac{d^2}{dx^2}}_{\text{Kinetic energy operator}} + \underbrace{V(x, t)}_{\text{Potential energy operator}} \right] \Psi \equiv \hat{H} \Psi$$

Hence there is an alternative (shorthand) form for time-dependent Schrödinger equation:

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

2.2 The significance of the wave function***

Ψ is a complex quantity, so what can be its significance for the results of real physical measurements on a system?

Remember photons: number of photons per unit volume is proportional to the electromagnetic energy per unit volume, hence to *square* of electromagnetic field strength.

Postulate (Born interpretation): probability of finding particle in a small length δx at position x and time t is equal to

$$|\Psi(x,t)|^2 \delta x \quad (2.6)$$

$$|\Psi|^2 = \Psi^* \Psi$$

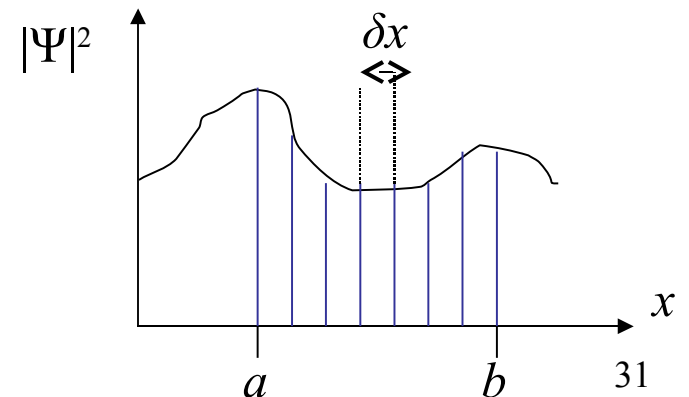
Note: $|\Psi(x,t)|^2$ is real, so probability is also real, as required.



Born

Total probability of finding particle between positions a and b is

$$\sum_{x=a}^b |\Psi(x,t)|^2 \delta x \quad \delta x \rightarrow 0 \quad \int_a^b |\Psi(x,t)|^2 dx$$



Example

Suppose that at some instant of time a particle's wavefunction is

$$\Psi(x, t) \begin{cases} 2x & (\text{For } 0 \leq x \leq 0.909) \\ 0 & (\text{Otherwise}) \end{cases}$$

What is:

(a) The probability of finding the particle between $x=0.5$ and $x=0.5001$?

(b) The probability per unit length of finding the particle at $x=0.6$?

(c) The probability of finding the particle between $x=0.0$ and $x=0.5$?

Probability: $|\Psi|^2 \delta x$

With: $x=0.5$, $\Psi=1$, $\Rightarrow |\Psi|^2=1$

\Rightarrow Probability = 1×10^{-4}

Probability for unit length: $|\Psi|^2$

= 1.44

Total probability = $\int_0^{0.5} |\Psi|^2 \delta x$

= $\int_0^{0.5} 4x^2 \delta x = 0.167$

Normalization

Total probability for particle to be *anywhere* should be one (at any time):

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

Normalization condition

Suppose we have a solution to the Schrödinger equation that is not normalized, Then we can

- Calculate the *normalization integral*
- *Re-scale* the wave function as

(This works because any solution to the S.E., multiplied by a constant, remains a solution, because the equation is *linear and homogeneous*)

$$N = \int_{-\infty}^{\infty} |\Psi|^2 \delta x$$

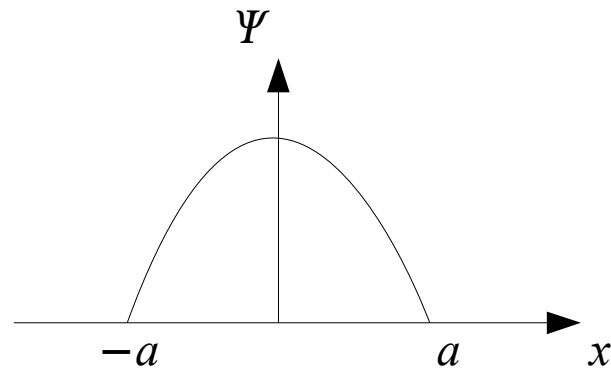
$$\Psi(x, t) \rightarrow N^{-\frac{1}{2}} \Psi(x, t)$$

$$\begin{aligned} \text{So: } \int_{-\infty}^{\infty} |\Psi_{new}|^2 \delta x &= \int_{-\infty}^{\infty} \frac{|\Psi|^2}{N} \delta x \\ &= \frac{N}{N} = 1 \end{aligned}$$

Alternatively: solution to Schrödinger equation contains an arbitrary constant, which can be fixed by imposing the condition (2.7)

Normalizing a wavefunction - example

Suppose that at some time we have the following form to the wave-function:



$$\Psi(x, t) \begin{cases} \sqrt{a^2 - x^2} & \text{for } -a \leq x \leq a \\ 0 & \text{otherwise} \end{cases}$$

Normalisation integral:

$$\begin{aligned} N &= \int_{-\infty}^{\infty} |\Psi(x, t)|^2 \delta x = \int_{-a}^a \Psi(x, t)^2 \\ &= \int_{-a}^a (a^2 - x^2) \delta x = \left[a^2 x - \frac{x^3}{3} \right]_{-a}^a \\ &= \frac{2a^3}{3} - \left(-\frac{2a^3}{3} \right) = \frac{4a^3}{3} \end{aligned}$$

This is not, in general, equal to 1. Therefore ψ is not correctly normalised. To get a correctly normalised wave-function, take:

$$\Psi(x, t) = \sqrt{\frac{3a^3}{4}} \sqrt{a^2 - x^2}$$

2.3 Boundary conditions for the wave-function

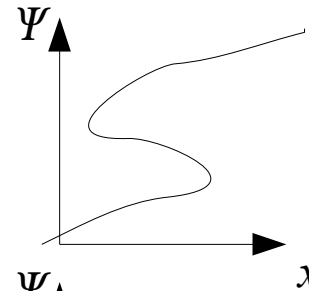
The wavefunction must:

1. Be a continuous and single-valued function of both x and t (in order that the probability density be uniquely defined)

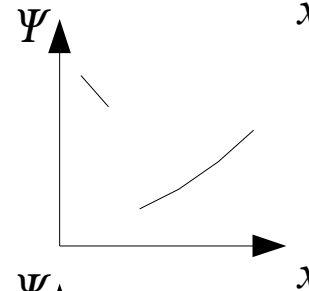
2. Have a continuous first derivative (unless the potential goes to infinity)

3. Have a finite normalization integral.

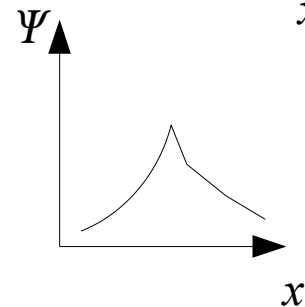
Unacceptable Ψ



Multivalued.



Discontinuous.



Discontinuous.

Change in $\frac{d\Psi}{dx}$ only
allowed if potential $\rightarrow \pm \infty$

$$0 < \int_{-\infty}^{\infty} |\Psi|^2 \delta x < \infty$$

2.4 Time-independent Schrödinger equation***

Suppose potential $V(x,t)$ (and hence force on particle) is independent of time t :

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

LHS involves only variation of Ψ with t

RHS involves only variation of Ψ with x (i.e. Hamiltonian operator does not depend on t)

Look for a solution in which the *time* and *space* dependence of Ψ are separated:

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

Substitute:

$$i\hbar \Psi(x, t) \frac{dT}{dt} = -\frac{\hbar^2}{2m} T(t) \frac{d^2 \Psi}{dx^2} + V(x)\psi(x)T(t)$$

Divide by $\Psi(x)T(t)$:

$$\frac{i\hbar}{T} \frac{dT}{dt} = -\frac{\hbar^2}{2m \Psi} \frac{d^2 \Psi}{dx^2} + V(x)$$

$$\frac{i\hbar}{T} \frac{dT}{dt} = -\frac{\hbar^2}{2m \Psi} \frac{d^2 \Psi}{dx^2} + V(x) = E$$

Equal to constant E as both sides are independent of each other.

Independent of position x .

Independent of time t .

Time-independent Schrödinger equation (contd)

Solving the time equation: $\frac{i \hbar}{T} \frac{dT}{dt} = E \Rightarrow i \hbar \frac{dT}{dt} = ET$

Linear ordinary differential equation with constant coefficients.

Try: $T = Ae^{\lambda t} \Rightarrow$ Substitute.

$$i \hbar \lambda = E \Rightarrow \lambda = -\frac{i E}{\hbar}$$

Solution is: $T(t) = e^{-\frac{iEt}{\hbar}}$

The space equation becomes:

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

Now multiply by Ψ to get the final version.

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

Time-independent Schrödinger equation

Notes

- In one space dimension, the time-independent Schrödinger equation is an *ordinary* differential equation (not a partial differential equation)
- The sign of i in the time evolution is determined by the choice of the sign of i in the time-dependent Schrödinger equation
- The time-independent Schrödinger equation can be thought of as an *eigenvalue equation* for the Hamiltonian operator:

Operator \times function = number \times function

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

(Compare Matrix \times vector = number \times vector) [See 2246]

- We will consistently use uppercase $\Psi(x,t)$ for the full wavefunction (time-dependent Schrödinger equation), and lowercase $\psi(x)$ for the spatial part of the wavefunction when time and space have been separated (time-independent Schrödinger equation)
- Probability distribution of particle is now independent of time (“stationary state”):

$$\begin{aligned} |\Psi(x,t)|^2 &= \left| e^{\frac{-iEt}{\hbar}} \psi(x) \right|^2 \\ &= \left| e^{\frac{-iEt}{\hbar}} \right|^2 |\psi(x)|^2 \\ &= |\psi(x)|^2 \end{aligned}$$

For a stationary state we can use *either* $\psi(x)$ or $\Psi(x,t)$ to compute probabilities; we will get the same result.

2.6 SE in three dimensions

To apply the Schrödinger equation in the real (three-dimensional) world we keep the same basic structure:

$$i\hbar \frac{\delta \Psi}{\delta t} = \hat{H} \Psi \quad \hat{H} \psi = E \psi$$

BUT

Wavefunction and potential energy are now functions of *three* spatial coordinates:

$$\Psi(x, t) \rightarrow \Psi(x, y, z, t) \text{ or } \Psi(\underline{r}, t)$$

$$\psi(x) \rightarrow \psi(x, y, z) \text{ or } \psi(\underline{r})$$

$$V(x) \rightarrow V(x, y, z, t) \text{ or } V(\underline{r})$$

Kinetic energy now involves *three* components of momentum

$$\frac{p^2}{2m} \rightarrow \frac{p_x^2 + p_y^2 + p_z^2}{2m}$$

$$\Rightarrow -\frac{\hbar^2}{2m} \frac{\delta^2}{\delta x^2} \rightarrow -\frac{\hbar^2}{2m} \left[\frac{\delta^2}{\delta x^2} + \frac{\delta^2}{\delta y^2} + \frac{\delta^2}{\delta z^2} \right] = -\frac{\hbar^2}{2m} \nabla^2$$

Interpretation of wavefunction:

$|\Psi(x, y, z, t)|^2 \delta V =$ Probability of finding particle in a small volume δV around (x, y, z)

$\Rightarrow |\Psi|^2 =$ Probability per unit volume.

Puzzle

The requirement that a plane wave

$$\Psi(x, t) = \exp[i(kx - \omega t)]$$

plus the energy-momentum relationship for free-non-relativistic particles

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

led us to the free-particle Schrödinger equation.

Can you use a similar argument to suggest an equation for free *relativistic* particles, with energy-momentum relationship:

$$E^2 = p^2 c^2 + m_0^2 c^4$$

Einstein: $E = \hbar \omega$

DeBroglie: $p = \hbar k$

$$E^2 \Psi = -\frac{\delta^2 \Psi}{\delta t^2} \hbar^2$$

$$p^2 \Psi = -\frac{\delta^2 \Psi}{\delta x^2} \hbar^2$$

$$\Rightarrow \text{Try: } -\hbar^2 \frac{\delta^2 \Psi}{\delta t^2} = -\hbar^2 c^2 \frac{\delta^2 \Psi}{\delta x^2} + m_0^2 c^4 \Psi \quad (\text{Klein-Gordon equation.})$$

3.1 A Free Particle

Free particle: experiences no forces so potential energy independent of position (take as zero)

Linear ODE with constant coefficients so try

$$\psi = \exp(\lambda x)$$

Time-independent Schrödinger equation:

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

Substitute: $-\frac{\hbar^2}{2m} \lambda^2 e^{\lambda x} = E e^{\lambda x} \Rightarrow -\frac{\hbar^2}{2m} \lambda^2 = E \Rightarrow \lambda^2 = -\frac{2mE}{\hbar^2}$

\Rightarrow Assuming $E \geq 0$ RHS is -ve $\therefore \lambda$ is imaginary.

$\lambda = \pm ik$ where $k^2 = \frac{2mE}{\hbar^2}$ or $\frac{\hbar^2 k^2}{2m} = E$ k is DeBroglie wave-number. $p = \hbar k$

General solution:

$$\begin{aligned} \psi(x) &= C e^{ikx} + D e^{-ikx} \quad (C \text{ and } D \text{ are constants.}) \\ &= C (\cos(kx) + i \sin(kx)) + D (\cos(kx) - i \sin(kx)) \\ &= A \cos(kx) + B \sin(kx) \quad \text{where: } A = C + D, \quad B = i(C - D) \end{aligned}$$

3.1 A Free Particle (Cont.)

Combine with time dependence to get full wave function:

$$\Psi(x, t) = \psi(x) e^{\frac{iEt}{\hbar}} = (C e^{ikx} + D e^{-ikx}) e^{i\frac{Et}{\hbar}}$$

$$\Psi = C e^{i(kx - \frac{Et}{\hbar})} + D e^{i(kx - \frac{Et}{\hbar})}$$

Travelling wave moving to the right.

$$+t \rightarrow +x$$

Travelling wave moving to the left.

$$+t \rightarrow -x$$

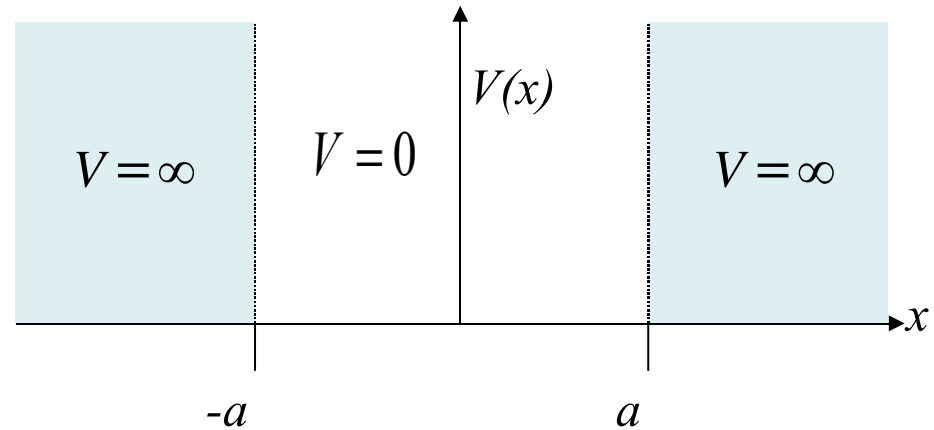
Notes

- Plane wave is a solution (just as well, since our plausibility argument for the Schrödinger equation was based on this being so)
- Note signs:
 - Sign of *time* term ($-i\omega t$) is fixed by sign adopted in time-dependent Schrödinger Equation
 - Sign of *position* term ($\pm ikx$) depends on propagation direction of wave
- There is no restriction on the allowed energies, so there is a *continuum* of states

Rae §2.4, B&J §4.5,
B&M §5.4

3.2 Infinite Square Well

Consider a particle confined to a finite length $-a < x < a$ by an infinitely high potential barrier



No solution in barrier region (particle would have infinite potential energy).

In well region:

$$-\frac{\hbar^2}{2m} \frac{\delta^2 \psi}{\delta x^2} = E \psi \quad \text{As for free particle.}$$

$$\Rightarrow \psi(x) = A \cos(kx) + B \sin(kx) \quad \text{With: } k^2 = \frac{2mE}{\hbar^2}$$

Boundary conditions:

Continuity of ψ at $x=a$: $\psi(a) = 0 \Rightarrow A \cos(ka) + B \sin(ka) = 0$

Continuity of ψ at $x=-a$: $\psi(-a) = 0 \Rightarrow A \cos(-ka) + B \sin(-ka) = 0$
or $A \cos(ka) - B \sin(ka) = 0$

Note discontinuity in $d\psi/dx$ allowable, since potential is infinite

$$\left(\begin{array}{l} \text{Since: } \cos(-\phi) = \cos(\phi) \quad \sin(-\phi) = -\sin(\phi) \\ \text{Even function.} \quad \text{Odd function.} \end{array} \right)$$

Infinite square well (2)

Add and subtract these conditions:

Adding gives: $2A \cos(ka) = 0$

Subtracting gives: $2B \sin(ka) = 0$

Either, a) Put $B = 0$ and $\cos(ka) = 0$

$$\Rightarrow ka = \frac{n\pi}{2} \quad (n = 1, 3, 5, 7, \dots)$$

$$\Rightarrow k = \frac{n\pi}{2a}, \quad \psi(x) = A \cos(kx)$$

Or, b) Put $A = 0$ and $\sin(ka) = 0$

$$\Rightarrow ka = \frac{n\pi}{2} \quad (n = 2, 4, 6, 8, \dots)$$

$$\Rightarrow k = \frac{n\pi}{2a}, \quad \psi(x) = B \sin(kx)$$

Even solution: $\psi(x) = \psi(-x)$

Odd solution: $\psi(x) = -\psi(-x)$

Energy:

Same Schrödinger equation for particle in box as for particle in free space.

→ Same relation between E and k .

$$\Rightarrow E = \frac{\hbar^2 k^2}{2m} = \frac{n^2 \pi^2 \hbar^2}{2m (2a)^2} \quad E = \frac{n^2 \pi^2 \hbar^2}{8ma^2}$$

Infinite well – normalization and notes

Normalization:

Need to choose constants so ψ is normalised. (i.e: Total over integral is 1).

Even soln.

$$\int_{-a}^a |\psi|^2 \delta x = 1 \Rightarrow \int_{-a}^a |A|^2 \frac{1}{2} [1 + \cos(2kx)] \delta x$$

$$\Rightarrow \frac{|A|^2}{2} \left[x \frac{1}{2k} \sin(2kx) \right]_{-a}^a = 1$$

$$k = \frac{n\pi}{2a} \quad (n \text{ odd.}) \Rightarrow \sin(\pm 2ka) = \sin(\pm n\pi) = 0$$

$$\Rightarrow \text{RHS} = |A|^2 xa \Rightarrow \text{Choose } A \text{ so... } |A|^2 = \frac{1}{a}$$

$$\therefore A = \frac{1}{\sqrt{a}}$$

Notes on the solution:

- Energy *quantized* to particular values (characteristic of *bound-state* problems in quantum mechanics, where a particle is localized in a finite region of space).
- Potential is *even* under reflection; stationary state wavefunctions may be *even or odd* (we say they have even or odd *parity*)
- Compare notation in 1B23 and in books:
 - 1B23: well extended from $x=0$ to $x=b$
 - Rae and B&J: well extends from $x=-a$ to $x=+a$ (**as here**)
 - B&M: well extends from $x=-a/2$ to $x=+a/2$
 (with corresponding differences in **wavefunction**)

The infinite well and the Uncertainty Principle

Position uncertainty in well:

$$\Delta x \simeq 2a \quad (\text{We know the particle is inside the box.})$$

Momentum uncertainty in lowest state from classical argument (agrees with fully quantum mechanical result, as we will see in §4)

State with $n = 1$ corresponds to a particle bouncing back and forth in the well.

Momentum will be alternately:
 $\pm \hbar k$ or $\pm \frac{\hbar \pi}{2a}$

$$\Rightarrow \text{Momentum uncertainty: } \Delta p = 2 \hbar k = \frac{\hbar \pi}{a} = \frac{h}{2a}$$

Compare with Uncertainty Principle:

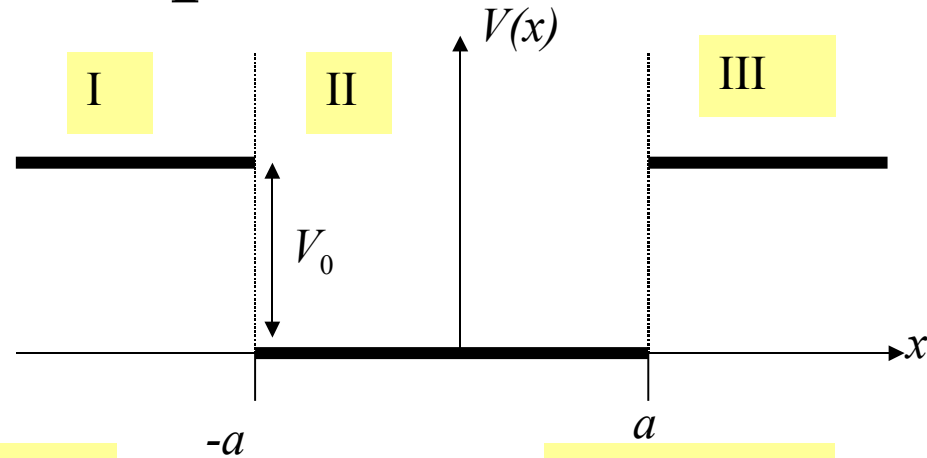
$$\text{So: } \Delta x \Delta p = 2a \frac{h}{2a} = h$$

2222 Quantum Physics 2006-7

Ground state close to minimum uncertainty

3.3 Finite square well

Now make the potential well more realistic by making the barriers a finite height V_0



Assume: $0 \leq E \leq V_0$

Region I:

$$-\frac{\hbar^2}{2m} \frac{\delta^2 \psi}{\delta x^2} + V_0 \psi = E \psi$$

Try: $\psi(x) = e^{\lambda x}$

$$-\frac{\hbar^2 \lambda^2}{2m} \psi + V_0 \psi = E \psi$$

$$\frac{\hbar^2 \lambda^2}{2m} = V_0 - E \geq 0$$

$\therefore \lambda$ is real.

$$\lambda = \pm \kappa \quad \kappa^2 = \frac{2m(V_0 - E)}{\hbar^2}$$

$$\Rightarrow \psi = C e^{\kappa x} + D e^{-\kappa x}$$

Region II:

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

Free particle solutions apply:

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

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

Region III:

$$-\frac{\hbar^2}{2m} \frac{\delta^2 \psi}{\delta x^2} + V_0 \psi = E \psi$$

$$\Rightarrow \psi = C' e^{\kappa x} + D' e^{-\kappa x}$$

(κ same as in Region 1.)

Decaying term forbidden.
Growing term allowed.

$$\psi = D' e^{-\kappa x}$$

D is not normalisable so decaying term C is only term allowed. $D = 0$

Finite square well (2)

Match value and derivative of
wavefunction at region boundaries:

$$x = -a$$

Match ψ :

$$A \cos(ka) - B \sin(ka) = C e^{-\kappa a}$$

Match $d\psi/dx$:

$$kA \sin(ka) + kB \cos(ka) = \kappa C e^{-\kappa a}$$

Add and subtract:

$$2A \cos(ka) = (C + D) e^{-\kappa a}$$

$$2B \sin(ka) = (D - C) e^{-\kappa a}$$

$$x = +a$$

$$A \cos(ka) + B \sin(ka) = D e^{-\kappa a}$$

$$-kA \sin(ka) + kB \cos(ka) = -\kappa D e^{-\kappa a}$$

$$2\kappa B \cos(ka) = \kappa (C - D) e^{-\kappa a}$$

$$2\kappa A \sin(ka) = \kappa (C + D) e^{-\kappa a}$$

Finite square well (3)

Divide equations:

$$k \tan(ka) = \kappa \quad (\text{Unless } A=0 \text{ and } C=-D)$$

$$k \cot(ka) = -\kappa \quad (\text{Unless } B=0 \text{ and } C=D)$$

Must be satisfied simultaneously:

Either: $k \tan(ka) = \kappa$ and $B=0, C=D$ (Even solution)

Or: $k \cot(ka) = -\kappa$ and $A=0, C=-D$ (Odd solution)

Cannot be solved algebraically. Convenient form for graphical solution:

k & κ are related by the requirement:

$$\frac{\hbar^2}{2m}(k^2 + \kappa^2) = V_0$$

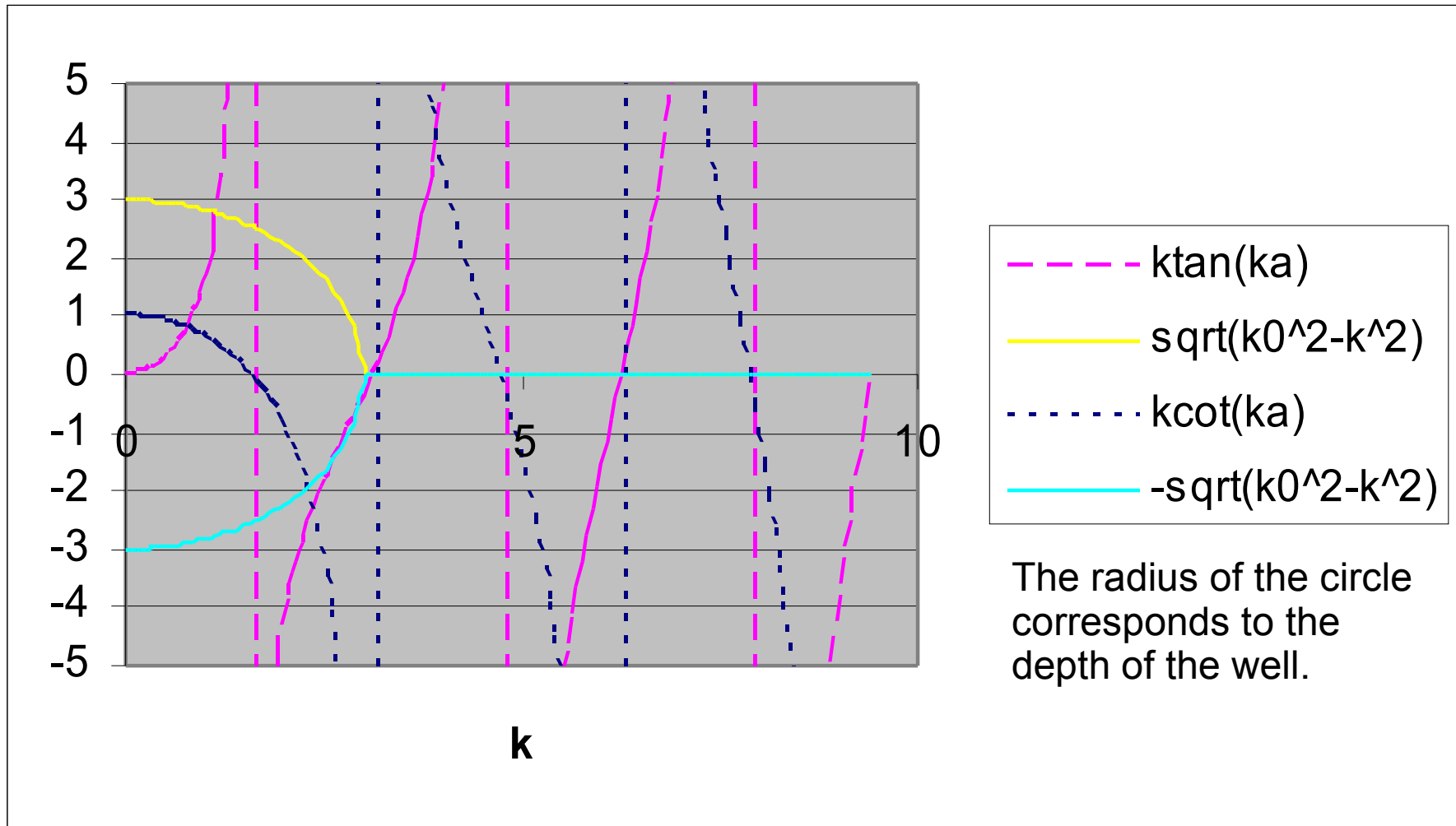
$$\Rightarrow k^2 + \kappa^2 = k_0^2 \quad \text{Where: } k_0^2 = \frac{2mV_0}{\hbar^2}$$

$$\therefore \text{Even solution} \rightarrow k \tan(ka) = +\sqrt{(k_0^2 - k^2)}$$

$$\therefore \text{Odd solution} \rightarrow k \cot(ka) = -\sqrt{(k_0^2 - k^2)}$$

\Rightarrow Search for intersections of $y = k \tan(ka)$ or $y = k \cot(ka)$ with a circle $y = \pm \sqrt{(k_0^2 - k^2)}$

Graphical solution for finite well



$k_0=3, a=1$
2222 Quantum Physics 2006-7

Notes

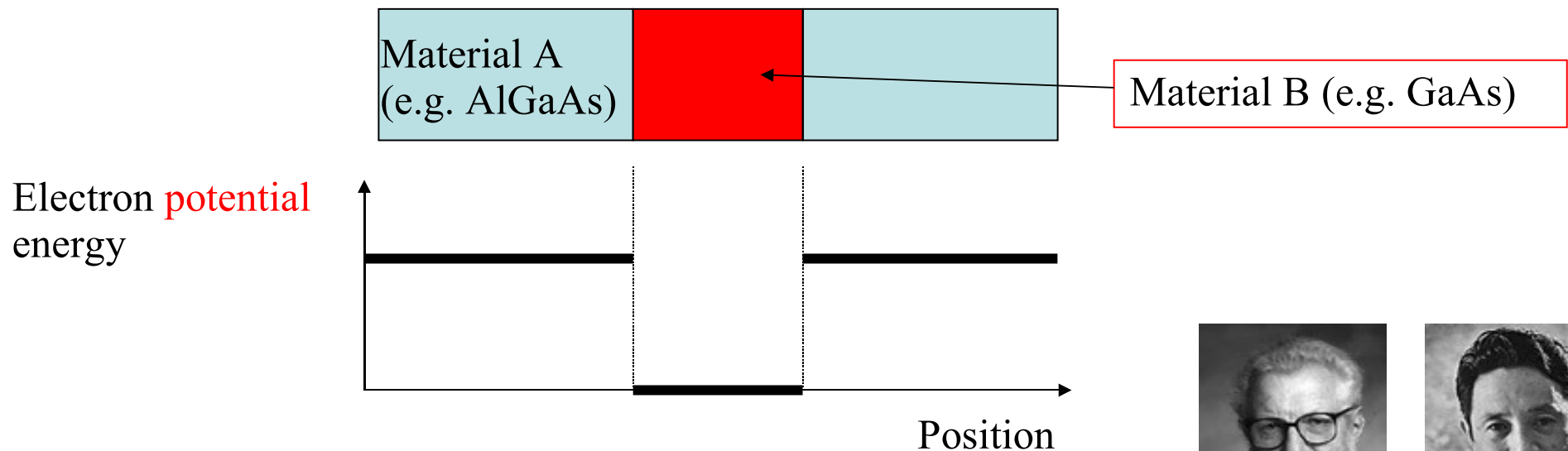
- Penetration of particle into “forbidden” region where $V > E$ (particle cannot exist here classically)
- Number of bound states depends on depth of potential well, but there is always at least one (even) state
- Potential is even function, wavefunctions may be even or odd (we say they have even or odd *parity*)
- Limit as $V_0 \rightarrow \infty$:

$k_0 \rightarrow \infty$, circle becomes very large.

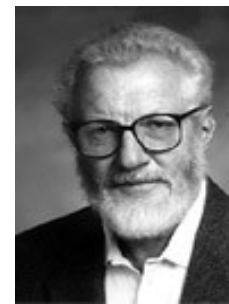
\Rightarrow Solutions at $ka = \frac{n\pi}{2}$ (as for an infinite well.)

Example: the quantum well

Quantum well is a “sandwich” made of two different semiconductors in which the energy of the electrons is different, and whose atomic spacings are so similar that they can be grown together without an appreciable density of defects:



Now used in many electronic devices (some transistors, diodes, solid-state lasers)



Kroemer



Esaki

Rae §9.1; B&M
§5.2, B&J §3.2

3.4 Particle Flux

In order to analyse problems involving scattering of free particles, need to understand *normalization* of free-particle plane-wave solutions.

$$\int_{-\infty}^{\infty} |A e^{i(kx - \omega t)}|^2 dx = \int_{-\infty}^{\infty} |A|^2 dx = \infty$$

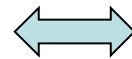
Conclude that if we try to normalize so that

$$\int_{-\infty}^{\infty} |\Psi|^2 dx = 1$$

will get $A=0$.

This problem is related to **Uncertainty Principle**:

Momentum is **completely defined**



Position **completely undefined**; single particle can be *anywhere* from $-\infty$ to ∞ , so probability of finding it in any finite region is zero

Particle Flux (2)

More generally: what is rate of change of probability that a particle exists in some region (say, between $x=a$ and $x=b$)?



$$\frac{\delta}{\delta t} \int_a^b \Psi^* \Psi dx = \int_a^b \left[\Psi^* \frac{\delta \Psi}{\delta t} + \Psi \frac{\delta \Psi^*}{\delta t} \right] dx$$

Use time-dependent Schrödinger equation:

$$\begin{aligned} i\hbar \frac{\delta \Psi}{\delta t} &= \left[-\frac{\hbar^2}{2m} \frac{\delta^2}{\delta x^2} + V \right] \Psi \quad ; \quad i\hbar \frac{\delta \Psi^*}{\delta t} = \left[-\frac{\hbar^2}{2m} \frac{\delta^2}{\delta x^2} + V \right] \Psi^* \\ \Rightarrow \int_a^b \left\{ \frac{1}{i\hbar} \Psi^* \left[-\frac{\hbar^2}{2m} \frac{\delta^2}{\delta x^2} + V \right] \Psi - \frac{1}{i\hbar} \Psi \left[-\frac{\hbar^2}{2m} \frac{\delta^2}{\delta x^2} + V \right] \Psi^* \right\} dx \\ &= \frac{1}{i\hbar} - \frac{\hbar^2}{2m} \int_a^b \left[\Psi^* \frac{\delta^2 \Psi}{\delta x^2} - \Psi \frac{\delta^2 \Psi^*}{\delta x^2} \right] dx \\ &= \frac{i\hbar}{2m} \int_a^b \left[\Psi^* \frac{\delta^2 \Psi}{\delta x^2} - \Psi \frac{\delta^2 \Psi^*}{\delta x^2} \right] dx \end{aligned}$$

Particle Flux (3)

Integrate by parts:

$$\begin{aligned} \frac{d}{dt} \int_a^b \Psi^* \Psi dx &= \frac{i\hbar}{2m} \left[\Psi^* \frac{d\Psi}{dx} - \Psi \frac{d\Psi^*}{dx} \right]_a^b - \frac{i\hbar}{2m} \int_a^b \left\{ \frac{d\Psi^*}{dx} \frac{d\Psi}{dx} - \frac{d\Psi}{dx} \frac{d\Psi^*}{dx} \right\} dx \\ &= \frac{i\hbar}{2m} \left(\Psi^* \frac{d\Psi}{dx} - \Psi \frac{d\Psi^*}{dx} \right) \Big|_{x=b} - \frac{i\hbar}{2m} \left(\Psi^* \frac{d\Psi}{dx} - \Psi \frac{d\Psi^*}{dx} \right) \Big|_{x=a} \end{aligned}$$

Flow of probability leaving at $x = b$

Flow of probability entering at $x = a$

Interpretation:

Particle flux at position x :

$$\begin{aligned} \Gamma(x) &= -\frac{i\hbar}{2m} \left[\Psi^* \frac{\delta\Psi}{\delta x} - \Psi \frac{\delta\Psi^*}{\delta x} \right] \\ \text{or } \Gamma(x) &= \frac{\hbar}{m} \text{Im} \left[\Psi^* \frac{\delta\Psi}{\delta x} \right] \end{aligned}$$

Flux entering
at $x=a$

Flux leaving
at $x=b$



Note: a wavefunction that is real carries *no* current

Note: for a stationary state can use *either* $\psi(x)$ or $\Psi(x,t)$

Particle Flux (4)

Sanity check: apply to free-particle plane wave.

$$\Psi(x, t) = A e^{i(kx - \omega t)} \quad ; \quad \Psi^* = A^* e^{-i(kx - \omega t)}$$

$$\frac{\delta \Psi}{\delta x} = ikA e^{i(kx - \omega t)} \quad ; \quad \frac{\delta \Psi^*}{\delta x} = -ikA^* e^{-i(kx - \omega t)}$$

$$\begin{aligned} \Rightarrow \text{Flux } \Gamma(x) &= -\frac{i\hbar}{2m} \left[(A^* e^{-i(kx - \omega t)}) (ikA e^{i(kx - \omega t)}) - (A e^{i(kx - \omega t)}) (-ikA^* e^{-i(kx - \omega t)}) \right] \\ &= -\frac{i\hbar}{2m} [2ikAA^*] = -\frac{i\hbar}{2m} [2ik|A|^2] \\ &= \frac{|A|^2 \hbar k}{m} \end{aligned}$$

Makes sense:

particles passing x per unit time = # particles per unit length \times velocity

Wavefunction describes a “beam” of particles.

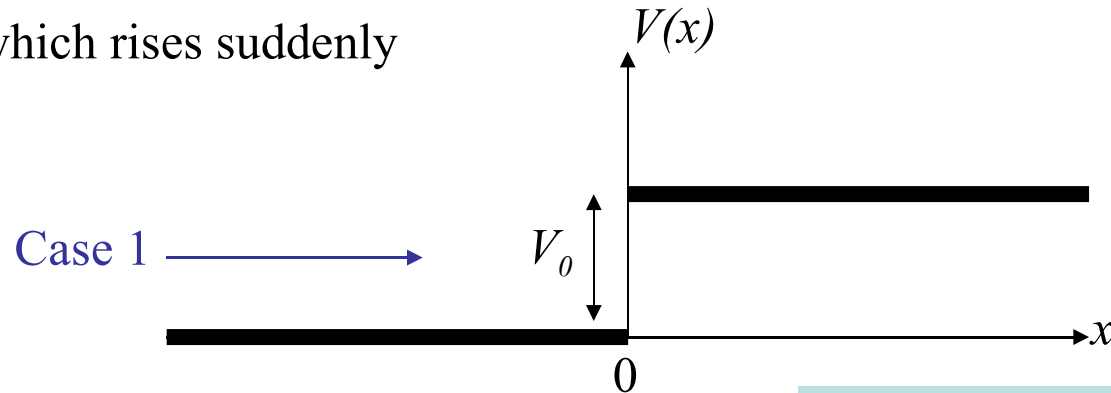
Two common normalising methods:

1) One particle per unit length. $\Rightarrow |A|^2 = 1$ \longleftarrow We will use this method.

2) One particle per unit time. $\Rightarrow \frac{|A|^2 \hbar k}{m} = 1$

3.5 Potential Step

Consider a potential which rises suddenly at $x=0$:



Case 1: $E < V_0$ (below step)

Boundary condition: particles only incident from left

$x < 0$ (But $E > 0$)

Free particle S.E.:

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

Same as region 2 of finite well.

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

Choose 1 particle per unit length in incoming beam $\Rightarrow A=1$

$x > 0$

$$-\frac{\hbar^2}{2m} \frac{\delta^2 \psi}{\delta x^2} + V_0 \psi = E \psi$$

Regions 1 & 3 of finite well.

$$\Rightarrow \psi = Ce^{\kappa x} + De^{-\kappa x} \quad \text{With: } \frac{\hbar^2 \kappa^2}{2m} = V_0 - E$$

The $Ce^{\kappa x}$ term is not normalisable.

Potential Step (2)

Continuity of ψ at $x=0$: $1 + B = D$

Continuity of $\frac{d\psi}{dx}$ at $x = 0$: $ik(1 - B) = -\kappa D$

Solve for reflection and transmission:

$(ik \times \text{equation 1}) + \text{equation 2}$:

$$2ik = (ik - \kappa)D \Rightarrow D = \frac{2ik}{(ik - \kappa)}$$

$(\kappa \times \text{equation 1}) + \text{equation 2}$:

$$(\kappa + ik) + (\kappa - ik)B = 0 \Rightarrow B = -\frac{(\kappa + ik)}{(\kappa - ik)}$$

Transmission and reflection coefficients

Incident particle flux from left = $\frac{\hbar k}{m}$

What is the flux reflected back to the left? :

$$\begin{aligned}
 & -\frac{i\hbar}{2m} \left[\Psi^* \frac{\delta \Psi}{\delta x} - \Psi \frac{\delta \Psi^*}{\delta x} \right] \quad (\psi = B e^{-ikx}) \\
 & = -\frac{i\hbar}{2m} |B|^2 \left[e^{ikx} (-ik e^{-ikx}) - e^{ikx} (ik e^{ikx}) \right] \\
 & \quad = -\frac{\hbar k}{m} |B|^2
 \end{aligned}$$

Hence the probability of reflection:

$$R = \frac{\text{Reflected flux}}{\text{Incident flux}} = |B|^2 = BB^* = \frac{\kappa + ik}{\kappa - ik} \frac{\kappa - ik}{\kappa + ik} = 1$$

So all particles are reflected.

$$\begin{aligned}
 \text{Transmitted flux:} \quad & (\psi = D e^{-\kappa x}) \\
 & -\frac{i\hbar}{2m} |D|^2 \left[e^{-\kappa x} (-\kappa e^{-\kappa x}) - e^{-\kappa x} (-\kappa e^{-\kappa x}) \right] \\
 & \quad = 0
 \end{aligned}$$

i.e.: Probability of transmission $T = 0$

Potential Step (3)

Case 2: $E > V_0$ (above step)

Solution for $x > 0$ is now

$$\psi(x) = F e^{ik'x} + G e^{-ik'x} \quad \text{With: } \frac{\hbar^2 k^2}{2m} = E - V_0$$

No incoming particles from right $\Rightarrow G = 0$

Matching conditions:

$$\psi \text{ continuous.} \quad (1 + B) = F$$

$$\frac{\delta \psi}{\delta x} \text{ continuous.} \quad ik(1 - B) = ik'F$$

$$(ik \times \text{equation 1}) + \text{equation 2} \Rightarrow 2ik = i(k + k')F \Rightarrow B = \frac{k - k'}{k + k'}$$

$$(ik' \times \text{equation 1}) + \text{equation 2} \Rightarrow i(k' - k) + i(k' + k)B = 0 \Rightarrow B = \frac{k - k'}{k + k'}$$

Transmission and reflection coefficients:

By our argument, reflection probability:

$$R = |B|^2 = \frac{(k - k')^2}{(k + k')^2} \rightarrow \text{No longer 1 if } k = k'$$

Summary of transmission through potential step

$$\text{Transmitted flux: } = |F|^2 \frac{\hbar k'}{m} = \frac{\hbar k'}{m} \frac{4k^2}{(k+k')^2}$$

$$\rightarrow \text{Transmission probability: } = \frac{\text{Transmitted flux}}{\text{Incident flux}} = \frac{4kk'}{(k+k')^2}$$

Notes:

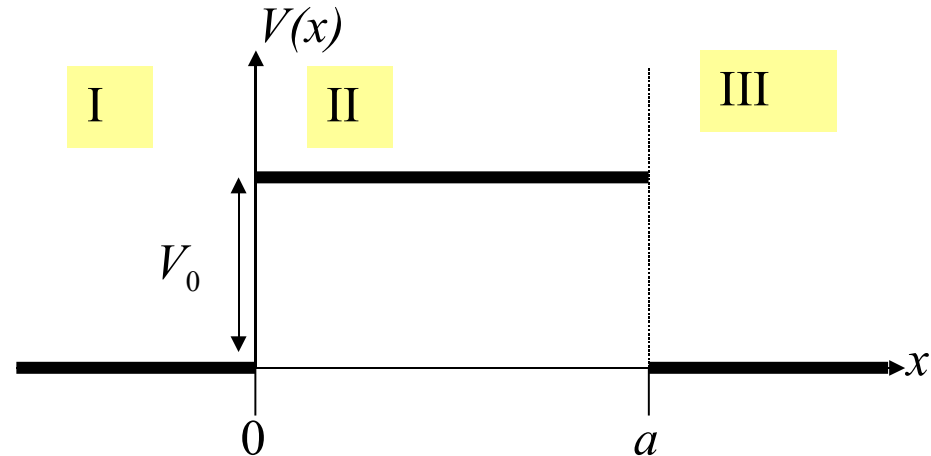
- Some penetration of particles into forbidden region even for energies below step height (case 1, $E < V_0$);
- No transmitted particle flux, 100% reflection (case 1, $E < V_0$);
- Reflection probability does not fall to zero for energies above barrier (case 2, $E > V_0$).
- Contrast classical expectations:
 - 100% reflection for $E < V_0$, with no penetration into barrier;
 - 100% transmission for $E > V_0$

Summary of transmission through potential step (Cont.)

$$\begin{aligned} \text{Check } R+T &= \frac{(k-k')^2}{(k+k')^2} + \frac{4kk'}{(k+k')^2} = \frac{k^2 - 2kk' + k'^2 + 4kk'}{(k+k')^2} \\ &= 1 \quad \text{as required.} \end{aligned}$$

3.6 Rectangular Potential Barrier

Now consider a potential barrier of *finite* thickness:



Assume $0 \leq E \leq V_0$

Boundary condition: particles only incident from left

Region I:

$$\psi(x) = A e^{ikx} + B e^{-ikx}$$

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

Take $A=1$ (i.e. 1 particle per unit length.)

Region II:

$$\psi = C e^{\kappa x} + D e^{-\kappa x}$$

(With $\frac{\hbar^2 \kappa^2}{2m} = V_0 - E$)

N.B: No reason to exclude either solution since region II is finite.

Region III:

$$\psi(x) = F e^{ikx} + G e^{-ikx}$$

(With k as in region I.)
Exclude G term as this term represents particles travelling from the right.

$$\Rightarrow G=0$$

Rectangular Barrier (2)

Match value and derivative of
wavefunction at region boundaries:

$$x = 0$$

$$\text{Match } \psi: \quad 1 + B = C + D \quad [1]$$

$$\text{Match } d\psi/dx: \quad ik(1 - B) = \kappa(C - D) \quad [3]$$

$$x = +a$$

$$C e^{\kappa a} + D e^{-\kappa a} = F e^{ika} \quad [2]$$

$$\kappa(C e^{\kappa a} - D e^{-\kappa a}) = ik F e^{ika} \quad [4]$$

Eliminate wavefunction in central
region:

Eliminate B :

$$ik[1] + [3]: \quad 2ik = (ik + \kappa)C + (ik - \kappa)D$$

$$\kappa[2] + [4]: \quad 2\kappa C e^{\kappa a} = (\kappa + ik)F e^{ika}$$

$$\kappa[2] - [4]: \quad 2\kappa D e^{-\kappa a} = (\kappa - ik)F e^{ika}$$

Eliminate C & D in the same way...

$$\text{To get } F = \frac{4ik\kappa e^{-ika}}{(\kappa + ik)^2 e^{-\kappa a} - (\kappa - ik)^2 e^{\kappa a}}$$

Rectangular Barrier (3)

Transmission and reflection coefficients:

$$\text{Transmission probability: } T = \frac{|F|^2}{|A|^2} = \frac{|F|^2}{1} = \frac{16k^2\kappa^2}{|(\kappa + ik)^2 e^{-\kappa a} - (\kappa - ik)^2 e^{\kappa a}|^2}$$

$$\text{Reflection probability: } R = |B|^2 = 1 - T$$

For very thick or high barrier: $\kappa a \gg 1 \Rightarrow e^{\kappa a} \gg e^{-\kappa a}$

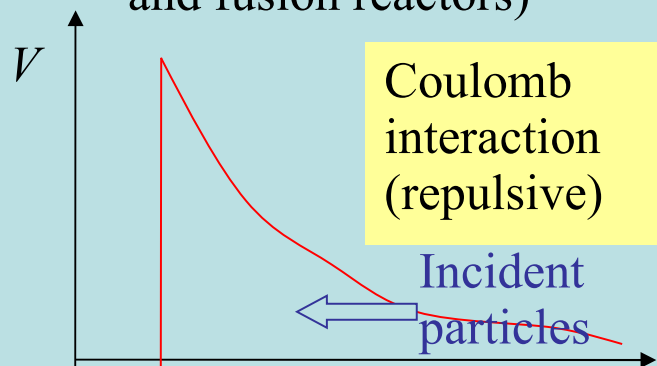
$$\begin{aligned} T &\simeq \frac{16k^2\kappa^2}{|(\kappa - ik)^2|^2 e^{2\kappa a}} = \frac{16k^2\kappa^2}{(\kappa - ik)^2} e^{-2\kappa a} \\ &= \frac{16E(V_0 - E)}{V_0^2} e^{-\kappa a} \end{aligned}$$

Non-zero transmission (“tunnelling”) through classically forbidden barrier region:

Examples of tunnelling

Tunnelling occurs in many situations in physics and astronomy:

1. Nuclear fusion (in stars and fusion reactors)



Coulomb interaction (repulsive)

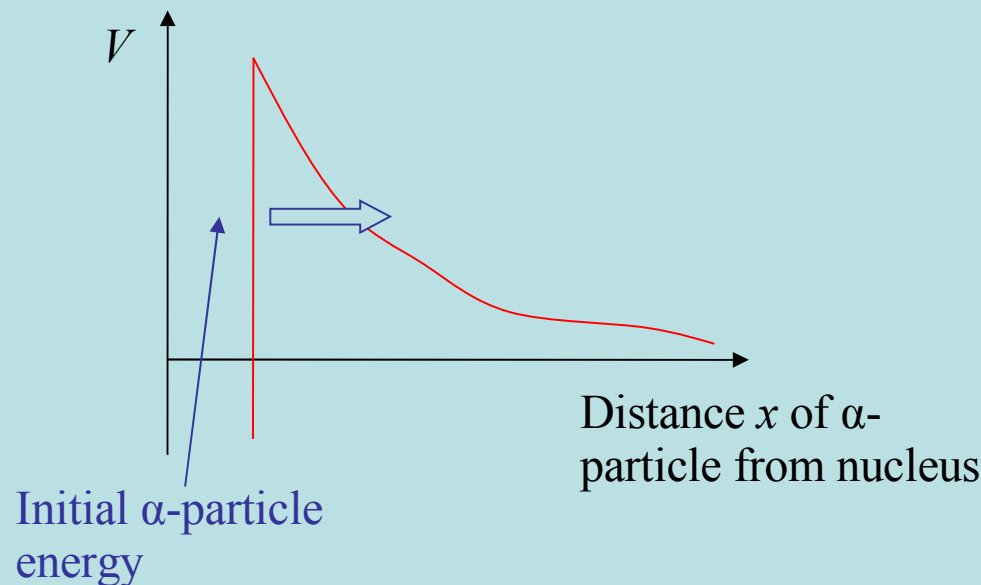
Internuclear distance x

Strong nuclear force (attractive)

$$\text{Barrier height} \sim \frac{(Ze)^2}{4\pi\epsilon_0 r_{\text{nucleus}}} \sim \text{MeV}$$

$$\gg \text{thermal energies } (\sim \text{keV})$$

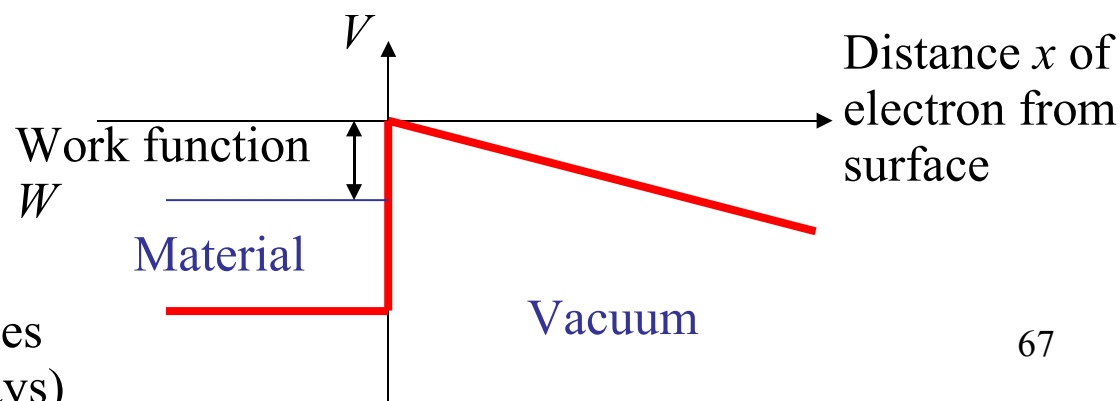
2. Alpha-decay



Initial α -particle energy

Distance x of α -particle from nucleus

3. Field emission of electrons from surfaces (e.g. in plasma displays)



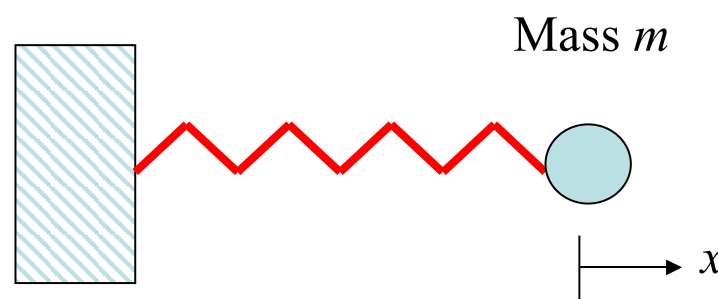
Distance x of electron from surface

Material

Vacuum

3.7 Simple Harmonic Oscillator

Example: particle on a spring, Hooke's law restoring force with spring constant k :



Force $F = -kx$

Angular frequency $\omega_0 = \sqrt{\frac{k}{m}}$

Potential energy $V(x) = \frac{1}{2}kx^2 = \frac{1}{2}m\omega_0^2 x^2$

Time-independent Schrödinger equation:

$$-\frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} + \frac{1}{2} m \omega_0^2 x^2 \psi = E \psi$$

Problem: still a linear differential equation but coefficients are not constant.

Simplify: change variable to $y = \left(\frac{m\omega_0}{\hbar}\right)^{\frac{1}{2}} x \Rightarrow \frac{d}{dy} = \frac{dx}{dy} \frac{d}{dx} = \left(\frac{\hbar}{m\omega_0}\right)^{-\frac{1}{2}} \frac{d}{dx}$

$$\begin{aligned} \text{Substitute: } & -\frac{\hbar}{2m} \frac{m\omega_0}{\hbar} \frac{d^2 \psi}{dy^2} + \frac{1}{2} \hbar \omega_0 y^2 \psi = E \psi \\ \Rightarrow & \frac{d^2 \psi}{dy^2} + (\alpha - y^2) \psi = 0 \quad \alpha = \frac{2E}{\hbar \omega_0} \end{aligned}$$

Simple Harmonic Oscillator (2)

Asymptotic solution in the limit of very large y :

$$\psi(y) = y^n \exp\left(\pm \frac{y^2}{2}\right)$$

Check:

$$\begin{aligned} \frac{d\psi}{dy} &= n y^{(n-1)} \exp\left(\pm \frac{y^2}{2}\right) \pm y^{(n+1)} \exp\left(\pm \frac{y^2}{2}\right) \\ \Rightarrow \frac{d^2\psi}{dy^2} &= [n(n-1) y^{(n-2)} \pm (2n-1) y^n + y^{(n+2)}] \exp\left(\pm \frac{y^2}{2}\right) \\ &\simeq y^{(n+2)} \exp\left(\pm \frac{y^2}{2}\right) = y^2 \psi \quad (\text{For large } y.) \end{aligned}$$

Substitute: $\psi(y) = H(y) \exp\left(\pm \frac{y^2}{2}\right)$

S.E. for large y

$$\frac{d^2\psi}{dy^2} - y^2\psi = 0$$
 is satisfied.
 Only -ve part gives normalisable solution.

Simple Harmonic Oscillator (2) (Cont.)

H is the correction function to find all solutions.

Equation for H :

$$\frac{d\psi}{dy} = [H'(y) - yH(y)] \exp\left(-\frac{y^2}{2}\right)$$
$$\frac{d^2\psi}{dy^2} [H''(y) - 2yH'(y) - H(y) + y^2H(y)] \exp\left(-\frac{y^2}{2}\right)$$

Substitute in S.E:

$$[H''(y) - 2yH'(y) + (y^2 - 1)H(y)] \exp\left(-\frac{y^2}{2}\right) + (\alpha - y^2)H(y) \exp\left(-\frac{y^2}{2}\right) = 0$$
$$\Rightarrow H''(y) - 2yH'(y) + (\alpha - 1)H(y) = 0$$

Simple Harmonic Oscillator (3)

Must solve this ODE by the power-series method (Frobenius method); this is done as an example in 2246.

$$H(y) = \sum_{p=0}^{\infty} a_p y^p$$

We find:

- The series for $H(y)$ must **terminate** in order to obtain a normalisable solution
- Can make this happen after n terms for either *even or odd terms* in series (but not both) by choosing:

$$\alpha = 2n + 1 \quad (\text{For some integer } n.) \quad \Rightarrow \quad E = \hbar \omega_0 \left(n + \frac{1}{2} \right)$$

If n is even, we must also choose $a_1 = 0$, so all odd terms in the series vanish giving an even solution.

If n is odd, we must also chose $a_0 = 0$, so all even terms vanish to give an odd solution.

Label resulting functions of H by the values of n that we choose.

H_n is known as the n th **Hermite polynomial**.

The Hermite polynomials

For reference, first few Hermite polynomials are:

$$H_0(y) = 1;$$

$$H_1(y) = 2y;$$

$$H_2(y) = 4y^2 - 2;$$

$$H_3(y) = 8y^3 - 12y;$$

$$H_4(y) = 16y^4 - 48y^2 + 12.$$

NOTE:

H_n contains y^n as the highest power.

Each H is either an odd or an even function, according to whether n is even or odd.

Simple Harmonic Oscillator (4)

Transforming back to the original variable x , the wavefunction becomes:

$$\psi_0(x) = C_0 \exp\left(\frac{-m\omega_0 x^2}{2\hbar}\right), \quad \psi_1(x) = C_1 x \exp\left(\frac{-m\omega_0 x^2}{\hbar}\right), \quad \text{etc.}$$

C_0 , C_1 , etc. are normalising constants that satisfy: $\int |\psi_n(x)|^2 dx = 1$

Probability per unit length of finding the particle is:

$$|C \psi_n(x)|^2 \quad \text{when the system is in state } n.$$

$$\text{E.g.: } |C \psi_0(x)|^2 = |C_0|^2 \exp\left(\frac{-m\omega_0 x^2}{\hbar}\right)$$

Simple Harmonic Oscillator (4) (Cont.)

Compare classical result: probability of finding particle in a length δx is proportional to the time δt spent in that region:

$$p_{\text{classical}}(x) dx \propto dt \propto \frac{dx}{v}$$

For a classical particle with total energy E , velocity is given by

$$\begin{aligned} \frac{1}{2} m v^2 + V(x) = E &\Rightarrow v = \sqrt{\frac{2(E - V(x))}{m}} \\ \Rightarrow p_{\text{classical}} \propto \frac{1}{\sqrt{E - V(x)}} &= \frac{1}{\sqrt{E - \frac{1}{2} m \omega_0^2 x^2}} \end{aligned}$$

Notes

$$E = \left(n + \frac{1}{2} \right) \hbar \omega_0 \quad \text{in } n^{\text{th}} \text{ state.}$$

- “Zero-point energy”: Ground state energy: $E_0 = 1/2 \hbar \omega_0$
- “Quanta” of energy: Can only add or subtract multiples of $\hbar \omega_0$
- Even and odd solutions
- Applies to *any* simple harmonic oscillator, including
 - Molecular vibrations
 - Vibrations in a solid (hence phonons)
 - Electromagnetic field modes (hence photons), even though this field does not obey exactly the same Schrödinger equation
- You will do another, more elegant, solution method (no series or Hermite polynomials!) next year
- For high-energy states, probability density peaks at classical turning points (correspondence principle)

4 Postulates of QM

This section puts quantum mechanics onto a more formal mathematical footing by specifying those *postulates* of the theory which cannot be derived from classical physics.

Main ingredients:

3. The wave function (to represent the state of the system);
4. Hermitian operators (to represent observable quantities);
5. A recipe for identifying the operator associated with a given observable;
6. A description of the measurement process, and for predicting the distribution of outcomes of a measurement;
7. A prescription for evolving the wavefunction in time (the time-dependent Schrödinger equation)

4.1 The wave function

Postulate 4.1: There exists a wavefunction Ψ that is a continuous, square-integrable, single-valued function of the coordinates of all the particles and of time, and from which all possible predictions about the physical properties of the system can be obtained.

Examples of the meaning of “*The coordinates of all the particles*”:

For a single particle moving in one dimension: x

For a single particle moving in three dimensions: (x, y, z) (r, θ, ϕ) etc.

For two particles moving in three dimensions: $(x_1, y_1, z_1, x_2, y_2, z_2)$ etc.

The modulus squared of Ψ for any value of the coordinates is the probability density (per unit length, or volume) that the system is found with that particular coordinate value (Born interpretation).

4.2 Observables and operators

Postulate 4.2.1: to each observable quantity is associated a *linear, Hermitian operator* (LHO).

An operator \hat{L} is *linear* if, and only if:

$$\hat{L}[c_1 f_1 + c_2 f_2] = c_1 \hat{L}[f_1] + c_2 \hat{L}[f_2]$$

(For arbitrary functions f_1 & f_2
and constants c_1 & c_2 .)

Examples: which of the operators defined by the following equations are linear?

$\hat{L}_1[f]$	$f + 2$	NOT linear as	$\hat{L}_1[c_1 f_1 + c_2 f_2] = c_1 f_1 + c_2 f_2 + 2$
$\hat{L}_2[f]$	xf	Linear as	$\hat{L}_2[c_1 f_1 + c_2 f_2] = c_1 x f_1 + c_2 x f_2$
$\hat{L}_3[f]$	\sqrt{f}	NOT linear as	$\hat{L}_3[c_1 f_1 + c_2 f_2] = \sqrt{c_1 f_1 + c_2 f_2}$
$\hat{L}_4[f]$	$\frac{df}{dx}$	Linear as	$\hat{L}_4[c_1 f_1 + c_2 f_2] = c_1 \frac{df_1}{dx} + c_2 \frac{df_2}{dx}$

Note: the operators involved may or may not be *differential operators* (i.e. may or may not involve differentiating the wavefunction).

Hermitian operators

An operator O is *Hermitian* if and only if:

$$\int_{-\infty}^{\infty} f^* (\hat{O} g) dx = \left[\int_{-\infty}^{\infty} g^* (\hat{O} f) dx \right]^*$$

for all functions f, g vanishing at infinity.

Compare the definition of a Hermitian matrix \mathbf{M} :

$$M_{ij} = [M_{ji}]^*$$

Analogous if we identify a matrix element with an integral:

$$M_{ij} \longleftrightarrow \int_{-\infty}^{\infty} f_i^* (\hat{O} f_j) dx$$

2222 Quantum Physics 2006-7 (see 3226 course for more detail...)

Hermitian operators: examples

The operator x is Hermitian

$$\int_{-\infty}^{\infty} f^* (x g) dx = \int_{-\infty}^{\infty} g x f^* dx = \left[\int_{-\infty}^{\infty} g^* x f dx \right]^* \quad (\text{Since } x \text{ is real.})$$

The operator $\frac{d}{dx}$ is not Hermitian.

$$\begin{aligned} \int_{-\infty}^{\infty} f^* \frac{dg}{dx} dx &= [f^* g]_{-\infty}^{\infty} - \int_{-\infty}^{\infty} g \frac{df^*}{dx} dx \quad [f^* g] = 0 \text{ as } f \text{ \& } g \text{ vanish at } \infty \\ &= - \left[\int_{-\infty}^{\infty} g^* \frac{df}{dx} dx \right]^* \quad \therefore \text{Not Hermitian because of -ve sign. (This is 'Anti-Hermitian.')} \end{aligned}$$

The operator $\frac{d^2}{dx^2}$ is Hermitian.

$$\begin{aligned} \int_{-\infty}^{\infty} f^* \frac{d^2 g}{dx^2} dx &= \left[f^* \frac{dg}{dx} \right]_{-\infty}^{\infty} - \int_{-\infty}^{\infty} \frac{dg}{dx} \frac{df^*}{dx} dx \\ &= - \left[\frac{df^*}{dx} g \right]_{-\infty}^{\infty} + \int_{-\infty}^{\infty} \frac{d^2 f^*}{dx^2} g dx = \int_{-\infty}^{\infty} g^* \frac{d^2 f}{dx^2} dx \end{aligned}$$

Eigenvectors and eigenfunctions

Postulate 4.2.2: the *eigenvalues* of the operator represent the possible results of carrying out a measurement of the corresponding quantity.

Definition of an eigenvalue for a general linear operator:

$$\hat{Q} \phi_n = q_n \phi_n \quad \begin{array}{l} \phi_n \text{ is an eigenfunction.} \\ q_n \text{ is an eigenvalue.} \end{array}$$

Compare definition of an eigenvalue of a matrix:

$$\underline{M} \underline{v} = \lambda_n \underline{v}_n \quad \begin{array}{l} \underline{v}_n \text{ is an eigenvector.} \\ \lambda_n \text{ is an eigenvalue.} \end{array}$$

Example: the time-independent Schrödinger equation:

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

The energy in the T.I.S.E. is an eigenvalue of the Hamiltonian operator, and ψ is an eigenfunction.

Interpretation of Eigenfunction: It is a state of the system in which there is a definite value of the quantity concerned.

Important fact: The eigenvalues of a Hermitian operator are **real** (like the eigenvalues of a Hermitian matrix).

Proof: Let $\hat{Q} \phi_m = q_m \phi_m$ (Where \hat{Q} is Hermitian.)

$$\text{Then } \left[\int_{-\infty}^{\infty} \phi_m^* (\hat{Q} \phi_m) dx \right] = \left[\int_{-\infty}^{\infty} \phi_m^* (\hat{Q} \phi_m) dx \right]^* \quad (\text{Using } f = g = \phi_m)$$

$$\Rightarrow \left[\int_{-\infty}^{\infty} \phi_m^* (\hat{Q} \phi_m) dx \right] = q_m \int_{-\infty}^{\infty} |\phi_m|^2 dx \quad (\text{Which is real.})$$

$$\text{But } \int_{-\infty}^{\infty} |\phi_m|^2 dx \text{ is real. } \therefore q_m \text{ is real.}$$

Postulate 4.2.3: immediately after making a measurement, the wavefunction is identical to an eigenfunction of the operator corresponding to the eigenvalue just obtained as the measurement result.

Start with wave-function Ψ and then measure quantity $\hat{Q} \Rightarrow$ Obtain result q_m (one of the eigenvalues of \hat{Q}) \Rightarrow Leave system with corresponding wave-function ϕ_m

Ensures that we get the same result if we immediately re-measure the same quantity.

4.3 Identifying the operators

Postulate 4.3: the operators representing the position and momentum of a particle are

$\hat{x} = x$ <p>i.e. $\hat{x}\psi = x\psi$</p> <p>(one dimension)</p>	$\hat{p}_x = -i\hbar \frac{\delta}{\delta x}$ <p>i.e. $\hat{p}_x\psi = -i\hbar \frac{d\psi}{dx}$</p>	$\hat{r} = \underline{r} \quad \hat{p} = -i\hbar \left[i \frac{\delta}{\delta x} + j \frac{\delta}{\delta y} + k \frac{\delta}{\delta z} \right] = -i\hbar \nabla$ <p>(three dimensions)</p>
---	---	---

Other operators may be obtained from the corresponding classical quantities by making these replacements.

Examples:

The Hamiltonian (representing the total energy as a function of the coordinates and momenta)

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{r}) = \frac{-\hbar^2}{2m} \nabla^2 + V(\hat{r}) \quad \text{or} \quad \frac{-\hbar^2}{2m} \frac{\delta^2}{\delta x^2} + V(x)$$

Angular momentum:

$$\hat{L} = \hat{r} \times \hat{p} = -i\hbar \underline{r} \times \nabla \quad \Rightarrow \quad \hat{L}\psi = -i\hbar \underline{r} \times (\nabla\psi)$$

Eigenfunctions of momentum

The momentum operator is Hermitian, as required:

$$\int_{-\infty}^{\infty} f^* (\hat{p} g) dx = \left[-i \hbar \int_{-\infty}^{\infty} f^* \left(\frac{dg}{dx} \right) dx \right] = -i \hbar \left[- \int_{-\infty}^{\infty} g^* \left(\frac{df}{dx} \right) dx \right]^* \\ = \left[-i \hbar \int_{-\infty}^{\infty} g^* \frac{df}{dx} dx \right]^* = \left[\int_{-\infty}^{\infty} g^* (\hat{p} f) dx \right]^*$$

(Factor of $-i$ makes \hat{p} Hermitian, even though $\frac{\delta}{\delta x}$ isn't.)

Its eigenfunctions are plane waves:

$$\hat{p}_x e^{ikx} = -i \hbar \frac{d e^{ikx}}{dx} = -i \hbar i k e^{ikx} \\ = \hbar k e^{ikx}$$

e^{ikx} is indeed an eigenfunction of \hat{p}_x with eigenvalue $\hbar k$

This corresponds to a state having a definite momentum $\hbar k$ (in agreement with DeBroglie.)

Orthogonality of eigenfunctions

The eigenfunctions of a Hermitian operator belonging to different eigenvalues are **orthogonal**.

If $\hat{Q}\phi_n = q_n\phi_n$; $\hat{Q}\phi_m = q_m\phi_m$ with $q_n \neq q_m$ then $\int_{-\infty}^{\infty} \phi_n^* \phi_m dx = 0$

Proof:

Use Hermitian definition, taking : $f = \phi_n$, $g = \phi_m$

$$\Rightarrow \int_{-\infty}^{\infty} \phi_n^* (\hat{Q}\phi_m) dx = \left[\int_{-\infty}^{\infty} \phi_m^* (\hat{Q}\phi_n) dx \right]^*$$

$$\text{RHS} = \left[q_n \int_{-\infty}^{\infty} \phi_m^* \phi_n dx \right]^* = q_n \int_{-\infty}^{\infty} \phi_m \phi_n^* dx \quad (\text{Since } q_n \text{ is real.})$$

$$\text{LHS} = q_m \int_{-\infty}^{\infty} \phi_n^* \phi_m dx$$

$$\text{We chose } q_m \neq q_n \Rightarrow \int_{-\infty}^{\infty} \phi_n^* \phi_m dx = 0$$

$$\text{RHS} = \text{LHS} = (q_m - q_n) \int_{-\infty}^{\infty} \phi_n^* \phi_m dx = 0$$

Orthonormality of eigenfunctions

What if two eigenfunctions have the *same* eigenvalue? (In this case the eigenvalue is said to be *degenerate*.)

Any linear combination of these eigenfunctions is also an eigenfunction with the same eigenvalue:

$$\begin{aligned}\hat{Q}(c_1\phi_1 + c_2\phi_2) &= c_1\hat{Q}\phi_1 + c_2\hat{Q}\phi_2 \\ &= c_1q\phi_1 + c_2q\phi_2 \\ &= q(c_1\phi_1 + c_2\phi_2)\end{aligned}\quad \left(\begin{array}{l}\hat{Q}_1\phi_1 = q\phi_1 \\ \hat{Q}_2\phi_2 = q\phi_2\end{array}\right)$$

So we are free to *choose* as the eigenfunctions two linear combinations that are orthogonal.

We can choose to have all the eigenfunctions orthogonal regardless of whether the eigenvalues are the same or different.

If the eigenfunctions are all orthogonal *and* normalized, they are said to be **orthonormal**.

$$\int_{-\infty}^{\infty} \phi_n^* \phi_m dx = \delta_{nm}$$

Orthonormality of eigenfunctions: example

Consider the solutions of the time-independent Schrödinger equation (energy eigenfunctions) for an infinite square well: (Eigenfunctions of \hat{H})

$$\phi_n = \begin{cases} \frac{1}{\sqrt{a}} \cos\left(\frac{n\pi x}{2a}\right) & , \text{ for odd } n \\ \frac{1}{\sqrt{a}} \sin\left(\frac{n\pi x}{2a}\right) & , \text{ for even } n \end{cases} \quad \text{For } -a \leq x \leq a, \text{ otherwise } 0$$

$$\int_{-a}^a |\phi_n|^2 dx = 1$$

We chose the constants so that normalization is correct:

Consider 2 different values n, m :

[1] 2 odd values:

$$\int_{-a}^a \phi_n^* \phi_m dx = \int_{-a}^a \frac{1}{a} \cos\left(\frac{n\pi x}{2a}\right) \cos\left(\frac{m\pi x}{2a}\right) dx$$

$$\cos \alpha \cos \beta = \frac{1}{2} [\cos(\alpha - \beta) + \cos(\alpha + \beta)]$$

$$= \frac{1}{2a} \int_{-a}^a \left[\cos\left(\frac{(n+m)\pi x}{2a}\right) + \cos\left(\frac{(n-m)\pi x}{2a}\right) \right] dx$$

$$= \frac{1}{2a} \left[\frac{2a}{(n+m)\pi} \sin\left(\frac{(n+m)\pi x}{2a}\right) + \frac{2a}{(n-m)\pi} \sin\left(\frac{(n-m)\pi x}{2a}\right) \right]_{-a}^a = 0$$

Orthonormality of eigenfunctions: example (Cont.)

[2] 2 even values:

$$\text{Similarly } \int_{-a}^a \sin \alpha \sin \beta = \frac{1}{2} [\cos(\alpha - \beta) - \cos(\alpha + \beta)]$$

[3] Even & odd values:

$$\int_{-a}^a \phi_n^* \phi_m dx = 0 \quad \text{by symmetry.}$$

$$\Rightarrow \int_{-a}^a \phi_n^* \phi_m dx = \delta_{nm}$$

Complete sets of functions

The eigenfunctions ϕ_n of a Hermitian operator form a **complete set**, meaning that any other function satisfying the same boundary conditions can be expanded as

$$\psi(x) = \sum_n a_n \phi_n(x)$$

Where: ψ is an arbitrary function, a_n are numbers, and ϕ_n are eigenfunctions.

If the eigenfunctions are chosen to be orthonormal, the coefficients a_n can be determined as follows:

$$\begin{aligned} \text{Consider: } \int_{-\infty}^{\infty} \phi_m^* \psi dx &= \sum_n a_n \int_{-\infty}^{\infty} \phi_m^* \phi_n dx \\ &= \sum_n a_n \delta_{mn} \\ &= a_m \end{aligned}$$

\Rightarrow Find number a_m , multiply ψ by ϕ_m^* and integrate.

We will see the significance of such expansions when we come to look at the measurement process.

Normalization and expansions in complete sets

The condition for normalizing the wavefunction is now

$$1 = \int_{-\infty}^{\infty} |\psi(x)|^2 dx = \int_{-\infty}^{\infty} \left[\sum_m a_m \phi_m(x) \right]^* \left[\sum_n a_n \phi_n(x) \right] dx = \sum_m \sum_n a_m^* a_n \int_{-\infty}^{\infty} \phi_m^*(x) \phi_n(x) dx$$
$$\int_{-\infty}^{\infty} \phi_m^*(x) \phi_n(x) dx = \delta_{mn} = \begin{cases} 1 & m=n \\ 0 & \text{otherwise} \end{cases}$$

If the eigenfunctions ϕ_n are orthonormal, this becomes

$$1 = \sum_m \sum_n a_m^* a_n \delta_{mn} = \sum_n |a_n|^2$$

Natural interpretation: the probability of finding the system in the state $\phi_n(x)$ (as opposed to any of the other eigenfunctions) is $|a_n|^2$

Expansion in complete sets: example

Consider an infinite square well, with a particle confined to $-a \leq x \leq a$
 Hamiltonian has eigenfunctions:

$$\psi_n(x) = \left\{ \begin{array}{ll} \frac{1}{\sqrt{a}} \cos\left(\frac{n\pi x}{2a}\right) & (n \text{ odd}) \\ \frac{1}{\sqrt{a}} \sin\left(\frac{n\pi x}{2a}\right) & (n \text{ even}) \\ 0 & \text{otherwise} \end{array} \right\} \text{ For } -a \leq x \leq a$$

So any function $f(x)$ satisfying some boundary conditions
 (i.e zero outside well) can be represented as:

$$f(x) = \sum_{n \text{ odd}} a_n \frac{1}{\sqrt{a}} \cos\left(\frac{n\pi x}{2a}\right) + \sum_{n \text{ even}} \frac{1}{\sqrt{a}} \sin\left(\frac{n\pi x}{2a}\right)$$

Eigenfunctions are orthonormal (see previous working)

$$\Rightarrow a_n = \left\{ \begin{array}{ll} \int_{-a}^a \frac{1}{\sqrt{a}} \cos\left(\frac{n\pi x}{2a}\right) f(x) dx & (n \text{ odd}) \\ \int_{-a}^a \frac{1}{\sqrt{a}} \sin\left(\frac{n\pi x}{2a}\right) f(x) dx & (n \text{ even}) \end{array} \right\}$$

This is a Fourier series representation of $f(x)$

4.4 Eigenfunctions and measurement

Postulate 4.4: suppose a measurement of the quantity Q is made, and that the (normalized) wavefunction can be expanded in terms of the (normalized) eigenfunctions ϕ_n of the corresponding operator as

$$\psi(x) = \sum_n a_n \phi_n(x)$$

Then the probability of obtaining the corresponding eigenvalue q_n as the measurement result is $|a_n|^2$

Corollary: if a system is *definitely* in eigenstate ϕ_n , the result measuring Q is *definitely* the corresponding eigenvalue q_n .

What is the meaning of these “probabilities” in discussing the properties of a single system?

Still a matter for debate, but usual interpretation is that the probability of a particular result determines the frequency of occurrence of that result in measurements on an ensemble of similar systems.

Commutators

In general operators do not *commute*: that is to say, the order in which we allow operators to act on functions matters:

$$\hat{Q} \hat{R} \psi \neq \hat{R} \hat{Q} \psi \quad (\text{In general})$$

For example, for position and momentum operators:

(In x direction)

$$\hat{x}(\hat{p}\psi) = x \left(-i\hbar \frac{d\psi}{dx} \right) \Rightarrow \hat{x}\hat{p}\psi - \hat{p}\hat{x}\psi = i\hbar\psi$$

$$\hat{p}(\hat{x}\psi) = -i\hbar \frac{\delta}{\delta x} (x\psi) = -i\hbar \left(\psi + x \frac{d\psi}{dx} \right) \Rightarrow [\hat{x}, \hat{p}] = \hat{x}\hat{p} - \hat{p}\hat{x} = i\hbar$$

We define the *commutator* as the difference between the two orderings:

$$[\hat{Q}, \hat{R}] = \hat{Q}\hat{R} - \hat{R}\hat{Q}$$

So, for position and momentum:

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

$$\text{But: } [\hat{x}, \hat{p}_y] = 0 = [\hat{x}, \hat{p}_z]$$

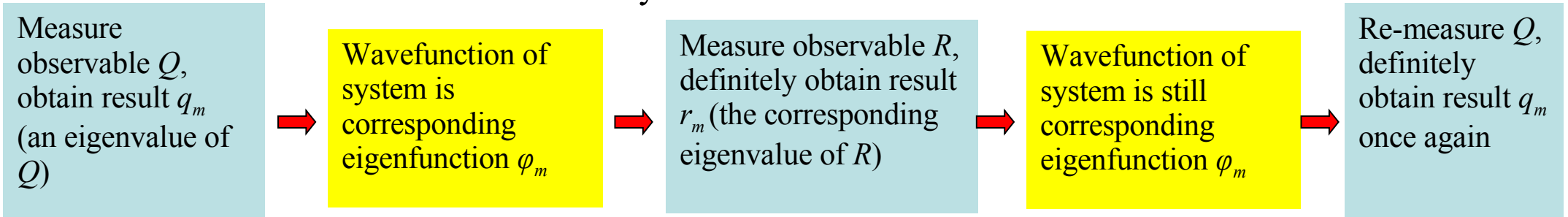
Two operators commute if, and only if, their commutator is zero. Note: The commutator of any operator with itself is zero!

$$[\hat{Q}, \hat{Q}] = \hat{Q}\hat{Q} - \hat{Q}\hat{Q} = 0$$

Compatible operators

Two observables are *compatible* if their operators share the same eigenfunctions (but not necessarily the same eigenvalues).

Consequence: two compatible observables can have precisely-defined values simultaneously.



Compatible operators commute with one another:

Consider a general wavefunction

$$\psi(x) = \sum_n a_n \phi_n(x)$$

Expansion in terms of joint eigenfunctions of both operators

$$\hat{Q}(\hat{R}\psi) = \hat{Q}\left[\sum_n a_n r_n \phi_n(x)\right] \quad (r_n \text{ eigenvalues of } \hat{R})$$

$$= \sum_n a_n q_n r_n \phi_n(x) \quad (\text{Using linearity of operator})$$

$$\text{And: } \hat{R}(\hat{Q}\psi) = \sum_n a_n r_n q_n \phi_n(x) \quad \Rightarrow \quad \hat{Q}\hat{R}\psi = \hat{R}\hat{Q}\psi \quad \text{for any } \psi$$

$$\Rightarrow [\hat{Q}, \hat{R}] = 0$$

Uncertainty of measurement is proportional to commutator.

Commutator here is zero, so no uncertainty.

Can also show the converse: any two commuting operators are compatible.

Example: measurement of position

Eigenfunctions of position operator \hat{x} would have to be states of definite position.

'Dirac δ - functions'.

For now, consider approximate eigenstates: Suppose we have a series of detectors (in one dimension) each sensitive to the presence of a particle in length Δ

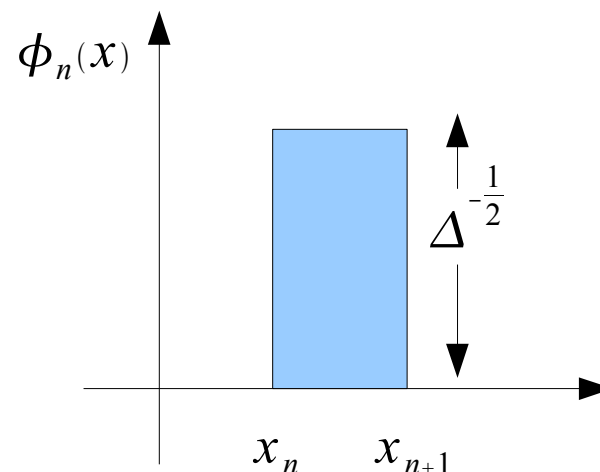
Detectors are n , $n+1$, $n+2$ etc. Starting at x_n , x_{n+1} etc. on the x - axis.

Corresponding eigenfunctions: $\phi_n(x) = \begin{cases} \Delta^{-\frac{1}{2}} & \text{when } x \text{ in } n^{\text{th}} \text{ region} \\ 0 & \text{otherwise} \end{cases}$

Check normalisation: $\int_{-\infty}^{\infty} |\phi_n|^2 dx = \int_{x_n}^{x_{n+1}} \frac{1}{\Delta} dx = \Delta \frac{1}{\Delta} = 1$

Check orthogonality: $\int_{-\infty}^{\infty} \phi_n^* \phi_m dx = 0$ (If $n \neq m$)

Since at least one of ϕ_n and ϕ_m is always zero.



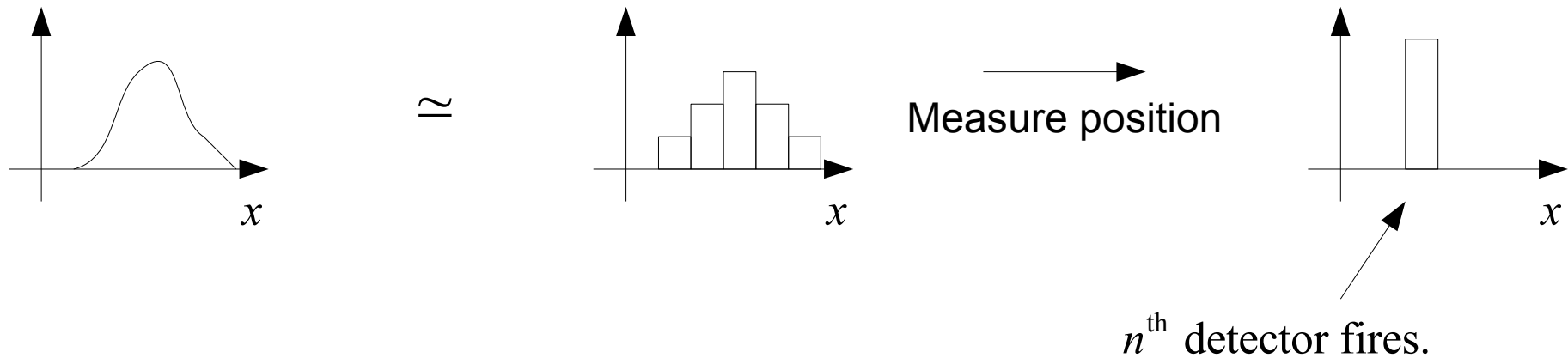
Example: measurement of position (2)

Now take system with general wavefunction as $\psi(x) = \sum_n a_n \phi_n(x)$ (Becomes extinct as $\Delta \rightarrow 0$)

Where: $a_n = \int_{-\infty}^{\infty} \phi_n^*(x) \psi(x) dx = \left(\int_{-\infty}^{\infty} \psi(x) dx \right) \Delta^{-\frac{1}{2}} \simeq \Delta^{-\frac{1}{2}} \psi(x_n)$

Probability that n^{th} detector 'fires' $= |a_n|^2 = \Delta |\psi(x_n)|^2 \Rightarrow$ Consistent with Born interpretation that $|\psi|^2$ is a probability density. (Probability per unit length.)

Schematically:



Expectation values

The average (mean) value of measurements of the quantity Q is therefore the sum of the possible measurement results times the corresponding probabilities:

$$\langle Q \rangle = \sum_n |a_n|^2 q_n$$

We can also write this as:

$$\begin{aligned} \int_{-\infty}^{\infty} \psi^*(x) (\hat{Q} \psi(x)) dx &= \int_{-\infty}^{\infty} \left(\sum_n a_n \phi_n(x) \right)^* \left(\sum_m a_m \hat{Q} \phi_m(x) \right) dx \\ &= \sum_n \sum_m q_m a_n^* a_m \int_{-\infty}^{\infty} \phi_n^* \phi_m dx \quad \text{Since } \hat{Q} \phi_m = q_m \phi_m \quad \left(\int_{-\infty}^{\infty} \phi_n^* \phi_m dx = \delta_{mn} \right) \\ &= \sum_n q_n |a_n|^2 = \langle \hat{Q} \rangle \end{aligned}$$

4.5 Evolution of the system

Postulate 4.5: Between measurements (i.e. when it is not disturbed by external influences) the wave-function evolves with time according to the time-dependent Schrödinger equation.

$$i \hbar \frac{\delta \Psi}{\delta t} = \hat{H} \Psi \quad \text{Where } \hat{H} \text{ is the Hamiltonian operator.}$$

This is a linear, homogeneous differential equation, so the linear combination of any two solutions is also a solution: the *superposition principle*.

$$i \hbar \frac{\delta \Psi_1}{\delta t} = \hat{H} \Psi_1 \qquad i \hbar \frac{\delta \Psi_2}{\delta t} = \hat{H} \Psi_2$$
$$\Rightarrow i \hbar \frac{\delta}{\delta t} (c_1 \Psi_1 + c_2 \Psi_2) = c_1 \hat{H} \Psi_1 + c_2 \hat{H} \Psi_2$$
$$= \hat{H} (c_1 \Psi_1 + c_2 \Psi_2) \qquad \text{(Since } \hat{H} \text{ is linear.)}$$

Calculating time dependence using expansion in energy eigenfunctions

Suppose the Hamiltonian is time-independent. In that case we know that solutions of the time-dependent Schrödinger equation exist in the form:

$$\Psi_n(x, t) = \exp\left(-\frac{i E_n t}{\hbar}\right) \psi_n(x)$$

where the wavefunctions $\psi(x)$ and the energy E correspond to one solution of the time-independent Schrödinger equation:

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

We know that *all* the functions ψ_n together form a complete set, so we can expand

$$\Psi(x, 0) = \sum_n a_n \psi_n(x)$$

Hence we can find the complete time dependence (superposition principle):

$$\Psi(x, t) = \sum_n a_n \Psi(x, t) = \sum_n a_n e^{\left(-\frac{i E_n t}{\hbar}\right)} \psi_n(x)$$

Time-dependent behaviour: example

Suppose the state of a particle in an infinite square well at time $t=0$ is a 'superposition' of the $n=1$ and $n=2$ states

$$\begin{aligned}\Psi(x, 0) &= c_1 \psi_1(x) + c_2 \psi_2(x) \\ &= c_1 \sqrt{\frac{1}{a}} \cos\left(\frac{\pi x}{2a}\right) + c_2 \sqrt{\frac{1}{a}} \sin\left(\frac{\pi x}{a}\right)\end{aligned}$$

Wave function at a subsequent time t

$$\begin{aligned}\Psi(x, t) &= c_1 \psi_1(x) e^{-\frac{iE_1 t}{\hbar}} + c_2 \psi_2(x) e^{-\frac{iE_2 t}{\hbar}} \\ &= \sqrt{\frac{1}{a}} e^{-\frac{iE_1 t}{\hbar}} \left\{ c_1 \cos\left(\frac{\pi x}{2a}\right) + c_2 \sin\left(\frac{\pi x}{a}\right) e^{-\frac{i(E_2 - E_1)t}{\hbar}} \right\}\end{aligned}$$

Probability density

$$\begin{aligned}|\Psi(x, t)|^2 &= \frac{1}{a} \left| c_1 \cos\left(\frac{\pi x}{2a}\right) + c_2 \sin\left(\frac{\pi x}{a}\right) e^{-\frac{i(E_2 - E_1)t}{\hbar}} \right|^2 \\ &= \frac{1}{a} \left\{ |c_1|^2 \cos^2\left(\frac{\pi x}{2a}\right) + |c_2|^2 \sin^2\left(\frac{\pi x}{a}\right) + 2 \cos\left(\frac{\pi x}{2a}\right) \sin\left(\frac{\pi x}{a}\right) \Re \left[c_1^* c_2 e^{-\frac{i(E_2 - E_1)t}{\hbar}} \right] \right\}\end{aligned}$$

Probability
distribution
in state 1.

Probability
distribution
in state 2.

Oscillates with an angular frequency:

$$\omega = \frac{E_2 - E_1}{\hbar}$$

Rate of change of expectation value

Consider the rate of change of the expectation value of a quantity Q :

$$\begin{aligned} \frac{d\langle \hat{Q} \rangle}{dt} &= \frac{d}{dt} \int_{-\infty}^{\infty} \Psi^* (\hat{Q} \Psi) dx \\ &= \int_{-\infty}^{\infty} \left(\frac{d\Psi^*}{dt} \right) (\hat{Q} \Psi) dx + \int_{-\infty}^{\infty} \Psi^* \left(\frac{d\hat{Q}}{dt} \Psi \right) dx + \int_{-\infty}^{\infty} \Psi^* \left(\hat{Q} \frac{d\Psi}{dt} \right) dx \\ &= \frac{1}{-i\hbar} \int_{-\infty}^{\infty} (\hat{H} \Psi)^* (\hat{Q} \Psi) dx + \left\langle \frac{d\hat{Q}}{dt} \right\rangle + \frac{1}{i\hbar} \int_{-\infty}^{\infty} \Psi^* (\hat{Q} \hat{H} \Psi) dx \end{aligned}$$

$$\hat{H} \text{ and } \hat{Q} \text{ are Hermitian} \Rightarrow \int_{-\infty}^{\infty} (\hat{H} \Psi)^* (\hat{Q} \Psi) dx = \left[\int_{-\infty}^{\infty} (\hat{Q} \Psi)^* \hat{H} \Psi dx \right]^* = \int_{-\infty}^{\infty} \Psi^* \hat{H} (\hat{Q} \Psi) dx$$

$$\begin{aligned} \Rightarrow \frac{d\langle \hat{Q} \rangle}{dt} &= \left\langle \frac{d\hat{Q}}{dt} \right\rangle + \frac{1}{i\hbar} \int_{-\infty}^{\infty} \Psi^* (\hat{Q} \hat{H} - \hat{H} \hat{Q}) \Psi dx \\ &= \left\langle \frac{d\hat{Q}}{dt} \right\rangle + \frac{1}{i\hbar} \langle [\hat{Q}, \hat{H}] \rangle \end{aligned}$$

Comes from intrinsic time dependence of operator.

Commutator: Comes from the time dependence of the wave function.

Example 1: Conservation of probability

Rate of change of total probability that the particle may be found at any point:

$$\frac{\delta}{\delta t} \int_{-\infty}^{\infty} |\Psi|^2 dx = \frac{\delta}{\delta t} \int_{-\infty}^{\infty} \Psi^* (1 \times \Psi) dx$$

$$= \left\langle \frac{\delta(1)}{\delta t} \right\rangle + \frac{1}{i\hbar} \langle [1, \hat{H}] \rangle$$

$$= 0 \quad \text{since the commutator of 1 with any operator is zero: } \langle [1, \hat{H}] \rangle = \hat{H} - \hat{H} = 0$$

$$\Rightarrow \int_{-\infty}^{\infty} |\Psi|^2 dx = \text{constant}$$

Total probability is the “expectation value” of the operator 1.

Total probability conserved (related to existence of a well defined probability flux – see §3.4)

Example 2: Conservation of energy

Consider the rate of change of the mean energy:

$$\frac{\delta}{\delta t} \langle E \rangle = \frac{\delta}{\delta t} \int_{-\infty}^{\infty} \Psi^* \hat{H} \Psi dx = \left\langle \frac{d \hat{H}}{d t} \right\rangle + \frac{1}{i \hbar} \langle [\hat{H}, \hat{H}] \rangle = \left\langle \frac{d \hat{H}}{d t} \right\rangle + 0$$

If Hamiltonian is constant in time, i.e. if $\frac{d \hat{H}}{d t} = 0$

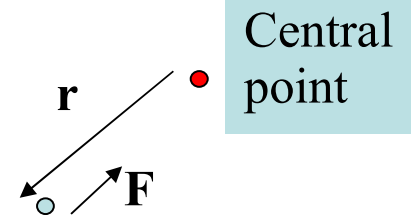
$$\Rightarrow \frac{d \langle E \rangle}{d t} = 0 \quad \text{Conservation of energy provided Hamiltonian is constant in time.}$$

Even although the energy of a system may be uncertain (in the sense that measurements of the energy made on many copies of the system may be give different results) the average energy is always conserved with time.

5.1 Angular momentum operators

Angular momentum is a very important quantity in three-dimensional problems involving a *central force* (one that is always directed towards or away from a central point). In that case it is classically a conserved quantity:

$$\begin{aligned} \frac{d\mathbf{L}}{dt} &= \frac{d}{dt}(\mathbf{r} \times \mathbf{p}) = \dot{\mathbf{r}} \times \mathbf{p} + \mathbf{r} \times \dot{\mathbf{p}} \\ &= \left(\frac{\mathbf{p}}{m} \times \mathbf{p} \right) + (\mathbf{r} \times \mathbf{F}) = 0 \end{aligned}$$



The origin of \mathbf{r} is the same central point towards/away from which the force is directed.

We can write down a quantum-mechanical operator for it by applying our usual rules:

$$\hat{\mathbf{L}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}} = \mathbf{r} \times (-i\hbar \nabla) = \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ x & y & z \\ -i\hbar \frac{d}{dx} & -i\hbar \frac{d}{dy} & -i\hbar \frac{d}{dz} \end{vmatrix}$$

5.1 Angular momentum operators (cont.)

Individual components:

$$\hat{L}_x = \hat{y} p_z - \hat{z} p_y = -i\hbar \left(y \frac{\delta}{\delta z} - z \frac{\delta}{\delta y} \right)$$

$$\hat{L}_y = \hat{z} p_x - \hat{x} p_z = -i\hbar \left(z \frac{\delta}{\delta x} - x \frac{\delta}{\delta z} \right)$$

$$\hat{L}_z = \hat{x} p_y - \hat{y} p_x = -i\hbar \left(x \frac{\delta}{\delta y} - y \frac{\delta}{\delta x} \right)$$

5.2 Commutation relations***

The different components of angular momentum *do not commute with one another.*

Remember:

$$[x, p_x] = i\hbar$$

$$[y, p_y] = i\hbar$$

$$[z, p_z] = i\hbar$$

$$\begin{aligned} [\hat{L}_x, \hat{L}_y] &= \hat{L}_x \hat{L}_y - \hat{L}_y \hat{L}_x \\ &= (\hat{y} \hat{p}_z - \hat{z} \hat{p}_y)(\hat{z} \hat{p}_x - \hat{x} \hat{p}_z) - (\hat{z} \hat{p}_x - \hat{x} \hat{p}_z)(\hat{y} \hat{p}_z - \hat{z} \hat{p}_y) \\ &= (\hat{y} \hat{p}_z \hat{z} \hat{p}_x - \hat{z} \hat{p}_x \hat{y} \hat{p}_z) - \hat{y} \hat{p}_z \hat{x} \hat{p}_z + \hat{x} \hat{p}_z \hat{y} \hat{p}_z - \hat{z} \hat{p}_y \hat{z} \hat{p}_x + \hat{z} \hat{p}_x \hat{z} \hat{p}_y + (\hat{z} \hat{p}_y \hat{x} \hat{p}_z - \hat{x} \hat{p}_z \hat{z} \hat{p}_y) \\ &= (\hat{y} \hat{p}_z \hat{z} \hat{p}_x - \hat{z} \hat{p}_x \hat{y} \hat{p}_z) + (\hat{z} \hat{p}_y \hat{x} \hat{p}_z - \hat{x} \hat{p}_z \hat{z} \hat{p}_y) \\ &= -[\hat{z}, \hat{p}_z] \hat{y} \hat{p}_x + [\hat{z}, \hat{p}_z] \hat{x} \hat{p}_y \\ &= i\hbar (\hat{x} \hat{p}_y - \hat{y} \hat{p}_x) \\ &= i\hbar \hat{L}_z \end{aligned}$$

By similar arguments get the cyclic permutations:

$$[\hat{L}_x, \hat{L}_y] = i\hbar \hat{L}_z \quad [\hat{L}_y, \hat{L}_z] = i\hbar \hat{L}_x \quad [\hat{L}_z, \hat{L}_x] = i\hbar \hat{L}_y$$

Commutation relations (2)

The different components of \mathbf{L} do not commute with one another, but they *do* commute with the (squared) magnitude of the angular momentum vector:

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

$$\text{Consider: } [\hat{L}^2, \hat{L}_z] = [\hat{L}_x^2, \hat{L}_z] + [\hat{L}_y^2, \hat{L}_z] + [\hat{L}_z^2, \hat{L}_z]$$

$$\text{and } [\hat{L}_x^2, \hat{L}_z] = \hat{L}_x [\hat{L}_x, \hat{L}_z] + [\hat{L}_x, \hat{L}_z] \hat{L}_x$$

$$= \hat{L}_x (-i\hbar \hat{L}_y) - i\hbar \hat{L}_y \hat{L}_x$$

$$= -i\hbar (\hat{L}_x \hat{L}_y + \hat{L}_y \hat{L}_x)$$

$$\text{Similarly: } [\hat{L}_y^2, \hat{L}_z] = i\hbar (\hat{L}_x \hat{L}_y + \hat{L}_y \hat{L}_x)$$

$$\Rightarrow [\hat{L}^2, \hat{L}_z] = [\hat{L}_x^2, \hat{L}_z] + [\hat{L}_y^2, \hat{L}_z]$$

$$= 0$$

Note a useful formula:

$$\begin{aligned} [A^2, B] &= A^2 B - A B A + A B A - B A^2 \\ &= a [A, B] + [A, B] A \end{aligned}$$

Important consequence: we *cannot* find simultaneous eigenfunctions of all three components.

But we *can* find simultaneous eigenfunctions of one component (conventionally the z component) and L^2

5.3 Angular momentum in spherical polar coordinates

Spherical polar coordinates are the natural coordinate system in which to describe angular momentum. In these coordinates,

On this slide, hats refer to unit vectors, not operators.

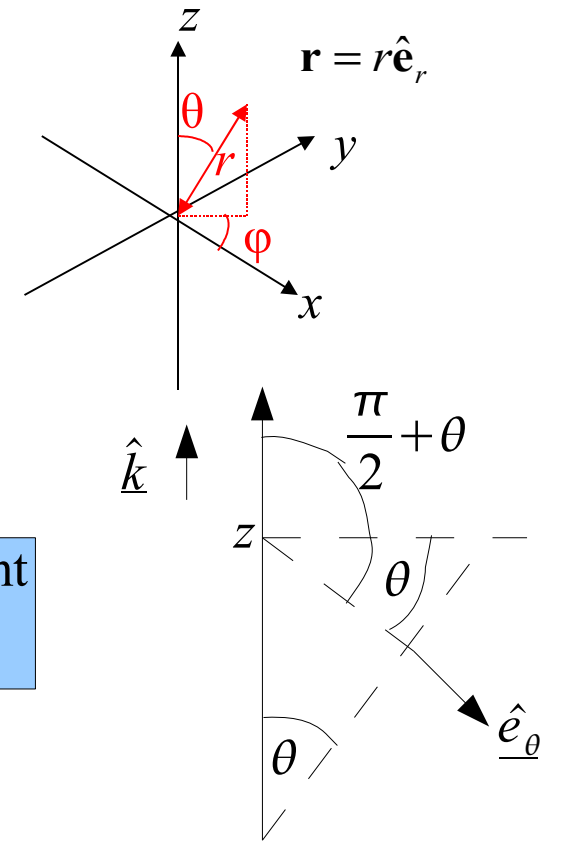
$$\nabla = \hat{e}_r \frac{\delta}{\delta r} + \frac{1}{r} \hat{e}_\theta \frac{\delta}{\delta \theta} + \frac{1}{r \sin \theta} \hat{e}_\phi \frac{\delta}{\delta \phi} \quad \text{(see 2246)}$$

So the full (vector) angular momentum operator can be written

$$\underline{L} = -i \hbar \underline{r} \times \nabla = -i \hbar r \hat{e}_r \times \nabla = -i \hbar \begin{vmatrix} \hat{e}_r & \hat{e}_\theta & \hat{e}_\phi \\ r & 0 & 0 \\ \frac{\delta}{\delta r} & \frac{1}{r} \frac{\delta}{\delta \theta} & \frac{1}{r \sin \theta} \frac{\delta}{\delta \phi} \end{vmatrix}$$

$$\underline{L} = -i \hbar \left(-\hat{e}_\theta \frac{1}{\sin \theta} \frac{\delta}{\delta \phi} + \hat{e}_\phi \frac{\delta}{\delta \theta} \right)$$

Note: Has no \hat{e}_r component and doesn't depend on r .



To find z-component, note that unit vector \hat{k} in z-direction satisfies

$$\begin{aligned} \hat{k} \cdot \hat{e}_\theta &= -\sin \theta & \Rightarrow & L_z = \hat{k} \cdot \underline{L} = -i \hbar \frac{\delta}{\delta \phi} \\ \hat{k} \cdot \hat{e}_\phi &= 0 \end{aligned}$$

L^2 in spherical polar coordinates

On this slide, hats refer to unit vectors, not operators.

$$\begin{aligned} \underline{L}^2 &= \underline{L} \cdot \underline{L} = -\hbar^2 (\underline{r} \times \nabla) \cdot (\underline{r} \times \nabla) \\ &= -\hbar^2 \left[r^2 \nabla^2 - (\underline{r} \cdot \nabla)(\nabla \cdot \underline{r}) \right] \\ &= -\hbar^2 \left[r^2 \left\{ \frac{1}{r^2} \frac{\delta}{\delta r} \left(r^2 \frac{\delta}{\delta r} \right) + \frac{1}{r^2 \sin \theta} \frac{\delta}{\delta \theta} \left(\sin \theta \frac{\delta}{\delta \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\delta^2}{\delta \phi^2} \right\} - r \frac{\delta}{\delta r} \left(\frac{\delta}{\delta r} (r) \right) \right] \end{aligned}$$

Since $\nabla^2 = \frac{1}{r^2} \frac{\delta}{\delta r} \left(r^2 \frac{\delta}{\delta r} \right) + \frac{1}{r^2 \sin \theta} \frac{\delta}{\delta \theta} \left(\sin \theta \frac{\delta}{\delta \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\delta^2}{\delta \phi^2}$

and radial parts of $r^2 \nabla^2$ and $(\underline{r} \cdot \nabla)(\nabla \cdot \underline{r})$ cancel.

$$\underline{L}^2 = -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\delta}{\delta \theta} \left(\sin \theta \frac{\delta}{\delta \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\delta^2}{\delta \phi^2} \right]$$

Depends only on *angular* behaviour of wavefunction. Closely related to angular part of Laplacian (see 2246 and Section 6).

$$\nabla^2 = \frac{1}{r^2} \frac{\delta}{\delta r} \left(r^2 \frac{\delta}{\delta r} \right) - \frac{L^2}{\hbar^2 r^2}$$

5.4 Eigenvalues and eigenfunctions

Look for simultaneous eigenfunctions of L^2 and one component of \mathbf{L} (conventional to choose L_z)

Eigenvalues and eigenfunctions of \hat{L}_z :

$$-i\hbar \frac{\delta}{\delta \phi} \Phi(\phi) = \lambda \Phi(\phi)$$

$$\Rightarrow \Phi(\phi) = A e^{\frac{i\lambda\phi}{\hbar}} \quad \text{Note: } \hat{L}_z \text{ only depends on } \phi$$

Physical boundary condition: wave-function must be single-valued

$$\Phi(\phi + 2\pi) = \Phi(\phi)$$

Taking our eigenfunction we have:

$$\Phi(\phi + 2\pi) = A e^{\frac{i\lambda(\phi+2\pi)}{\hbar}} = A e^{\frac{i\lambda\phi}{\hbar}} e^{\frac{i\lambda 2\pi}{\hbar}} \quad \left(e^{\frac{i\lambda 2\pi}{\hbar}} = 1 \right)$$

$$\Rightarrow \frac{\lambda}{\hbar} = \text{integer} \quad , \quad \lambda = m\hbar \text{ where } m \text{ is an integer.}$$

$$\Phi(\phi) = A e^{im\phi}$$

Quantization of angular momentum about z-axis (*compare Bohr model*)

Eigenvalues and eigenfunctions (2)

Now look for eigenfunctions of L^2 , in the form

$$f(\theta, \phi) = \Theta(\theta)\Phi(\phi) = e^{im\phi}\Theta(\theta)$$

(ensures solutions remain eigenfunctions of L_z , as we want)

Eigenvalue condition becomes

$$\begin{aligned} \hat{L}^2[e^{im\phi}\Theta(\theta)] &= \beta\hbar^2 e^{im\phi}\Theta(\theta) && \text{Let eigenvalue} = \beta\hbar^2 \\ \Rightarrow -\hbar^2 \left[\frac{e^{im\phi}}{\sin\theta} \frac{\delta}{\delta\theta} \left(\sin\theta \frac{\delta\Theta}{\delta\theta} \right) + \frac{\Theta}{\sin^2\theta} \frac{\delta^2}{\delta\phi^2} (e^{im\phi}) \right] &= \beta\hbar^2 e^{im\phi}\Theta(\theta) \end{aligned}$$

Divide through by $\hbar^2 e^{im\phi}$

$$\Rightarrow -\frac{1}{\sin\theta} \frac{\delta}{\delta\theta} \left(\sin\theta \frac{\delta\Theta}{\delta\theta} \right) + \frac{m^2}{\sin^2\theta} \Theta(\theta) = \beta\Theta(\theta)$$

The Legendre equation

Make the substitution

$$\mu = \cos \theta$$

$$\Rightarrow \frac{\delta}{\delta \theta} = \frac{d\mu}{d\theta} \frac{\delta}{\delta \mu} = -\sin \theta \frac{\delta}{\delta \mu}, \quad \text{and } \sin^2 \theta = 1 - \cos^2 \theta = 1 - \mu^2$$

$$\Rightarrow \text{Get: } \frac{d}{d\mu} \left[(1 - \mu^2) \frac{d\Theta}{d\mu} \right] + \left[\beta - \frac{m^2}{1 - \mu^2} \right] \Theta(\theta) = 0$$

This is exactly the *Legendre equation*, solved in 2246 using the Frobenius method.

Legendre polynomials and associated Legendre functions

In order for solutions to exist that remain finite at $\mu=\pm 1$ (i.e. at $\theta=0$ and $\theta=\pi$) we require that the eigenvalue satisfies

$$\beta = l(l+1) \quad , \quad \text{where } l = 0, 1, 2, 3, 4, \dots$$

(like SHO, where we found restrictions on energy eigenvalue in order to produce normalizable solutions)

The finite solutions are then the *associated Legendre functions*, which can be written in terms of the *Legendre polynomials*:

$$P_l^m(\mu) = (1 - \mu^2)^{\frac{|m|}{2}} \left(\frac{d}{d\mu} \right)^{|m|} P_l(\mu)$$

where m is an integer constrained to lie between $-l$ and $+l$.

Legendre polynomials:

$$\begin{aligned} P_0(\mu) &= 1 & P_1(\mu) &= \mu \\ P_2(\mu) &= \frac{1}{2}(3\mu^2 - 1) & P_3(\mu) &= \frac{1}{2}(5\mu^3 - 3\mu) \end{aligned}$$

etc.

Spherical harmonics

The full eigenfunctions can also be written as *spherical harmonics*:

$$Y_l^m(\theta, \phi) = c_{lm} P_l^m(\cos \theta) e^{im\phi}$$

$$\left(c_{lm} = (-1)^m \sqrt{\frac{(l-m)!(2l+1)}{(l+m)! 4\pi}} \right)$$

Because they are eigenfunctions of Hermitian operators with different eigenvalues, they are automatically orthogonal when integrated over all angles (i.e. over the surface of the unit sphere). The constants C are conventionally defined so the spherical harmonics obey the following important *normalization condition*:

$$\int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi [Y_l^m(\theta, \phi)]^* Y_{l'}^{m'}(\theta, \phi) = \delta_{l,l'} \delta_{m,m'} = \begin{cases} 1 & \text{if } l=l' \text{ and } m=m' \\ 0 & \text{otherwise} \end{cases}$$

First few examples (see also 2246):

Remember

$$x = r \sin \theta \cos \phi$$

$$y = r \sin \theta \sin \phi$$

$$z = r \cos \theta$$

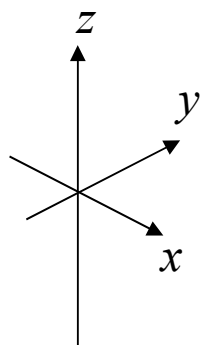
$$Y_0^0(\theta, \phi) = \frac{1}{\sqrt{4\pi}}$$

$$Y_1^1(\theta, \phi) = -\sqrt{\frac{3}{8\pi}} \sin \theta \exp(i\phi) = -\sqrt{\frac{3}{8\pi}} \frac{(x+iy)}{r}$$

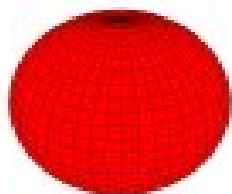
$$Y_1^0(\theta, \phi) = \sqrt{\frac{3}{4\pi}} \cos \theta = \sqrt{\frac{3}{4\pi}} \frac{z}{r}$$

$$Y_1^{-1}(\theta, \phi) = \sqrt{\frac{3}{8\pi}} \sin \theta \exp(-i\phi) = \sqrt{\frac{3}{8\pi}} \frac{(x-iy)}{r}$$

Shapes of the spherical harmonics



$$Y_0^0$$

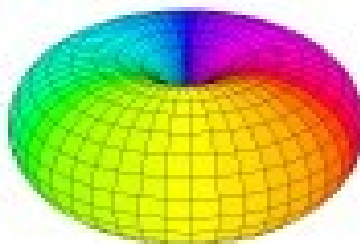


$$l = 0$$

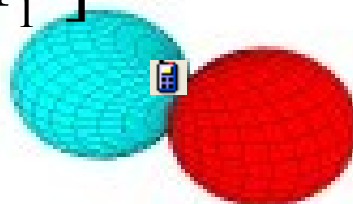
$$m = 0$$

$$Y_l^m = \frac{1}{\sqrt{4\pi}}$$

$$Y_1^1$$



$$\text{Re}[Y_1^1]$$

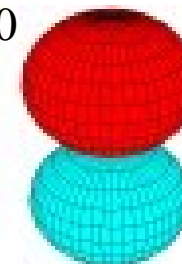


$$l = 1$$

$$m = 1$$

$$Y_l^m = -\sqrt{\frac{3}{8\pi}} \sin \theta \exp(i\phi)$$

$$Y_1^0$$

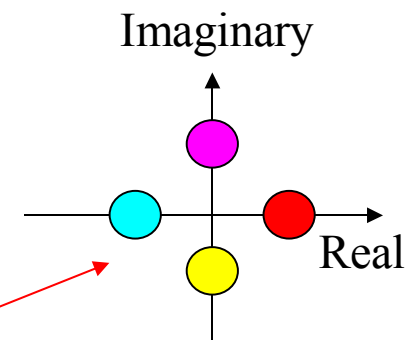


$$l = 1$$

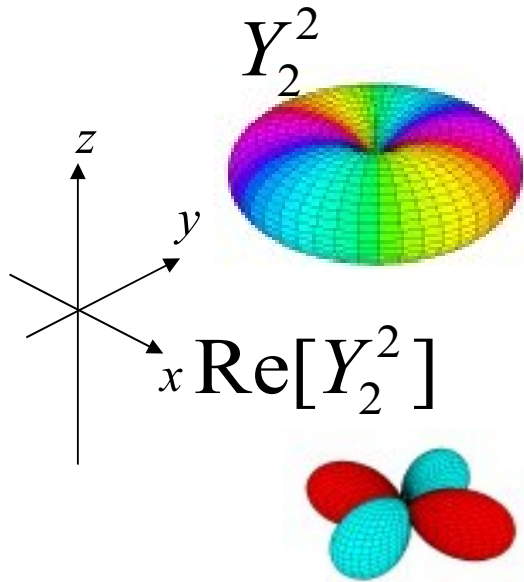
$$m = 0$$

$$Y_l^m = \sqrt{\frac{3}{4\pi}} \cos \theta$$

To read plots: *distance* from origin corresponds to *magnitude* (modulus) of plotted quantity; *colour* corresponds to *phase* (argument).

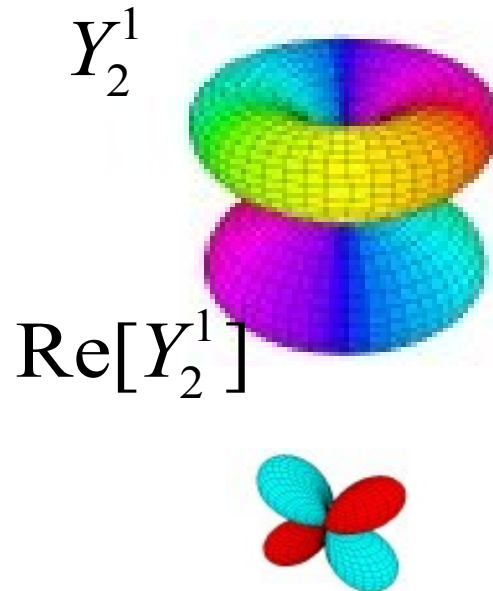


Shapes of spherical harmonics (2)



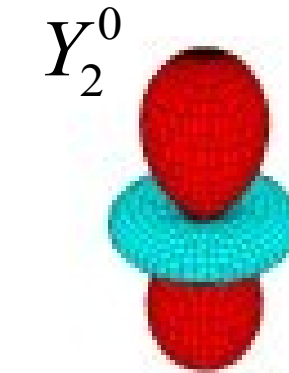
$l = 2$
 $m = 2$

$$Y_l^m = \sqrt{\frac{15}{32\pi}} \sin^2 \theta \exp(2i\phi)$$



$l = 2$
 $m = 1$

$$Y_l^m = -\sqrt{\frac{15}{8\pi}} \sin \theta \cos \theta \exp(i\phi)$$

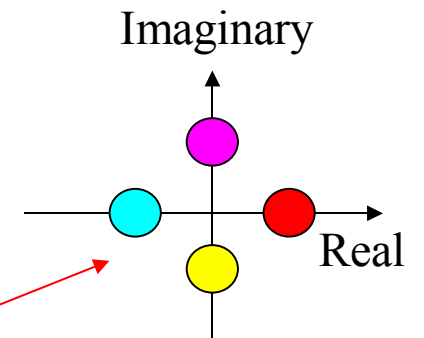


$l = 2$

$m = 0$

$$Y_l^m = \sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1)$$

To read plots: *distance* from origin corresponds to *magnitude* (modulus) of plotted quantity; *colour* corresponds to *phase* (argument).



5.5 The vector model for angular momentum***

To summarize:

Eigenvalues of \hat{L}^2 are $l(l+1)\hbar^2$, with $l = 0, 1, 2, \dots$

l is known as the *principal angular momentum quantum number*: determines the *magnitude* of the angular momentum

Eigenvalues of \hat{L}_z are $m\hbar$, with $m = -l, \dots, -1, 0, 1, \dots, +l$

m is known as the *magnetic quantum number*: determines the *component* of angular momentum along a chosen axis (the z-axis)

These states do *not* correspond to well-defined values of L_x and L_y , since these operators do not commute with L_z .

Semiclassical picture: each solution corresponds to a *cone* of angular momentum vectors, all with the same magnitude and the same z-component.

The vector model (2)

Example: $l=2$

\Rightarrow Eigenvalue of \hat{L}^2 is $l(l+1)\hbar^2 = 6\hbar^2$

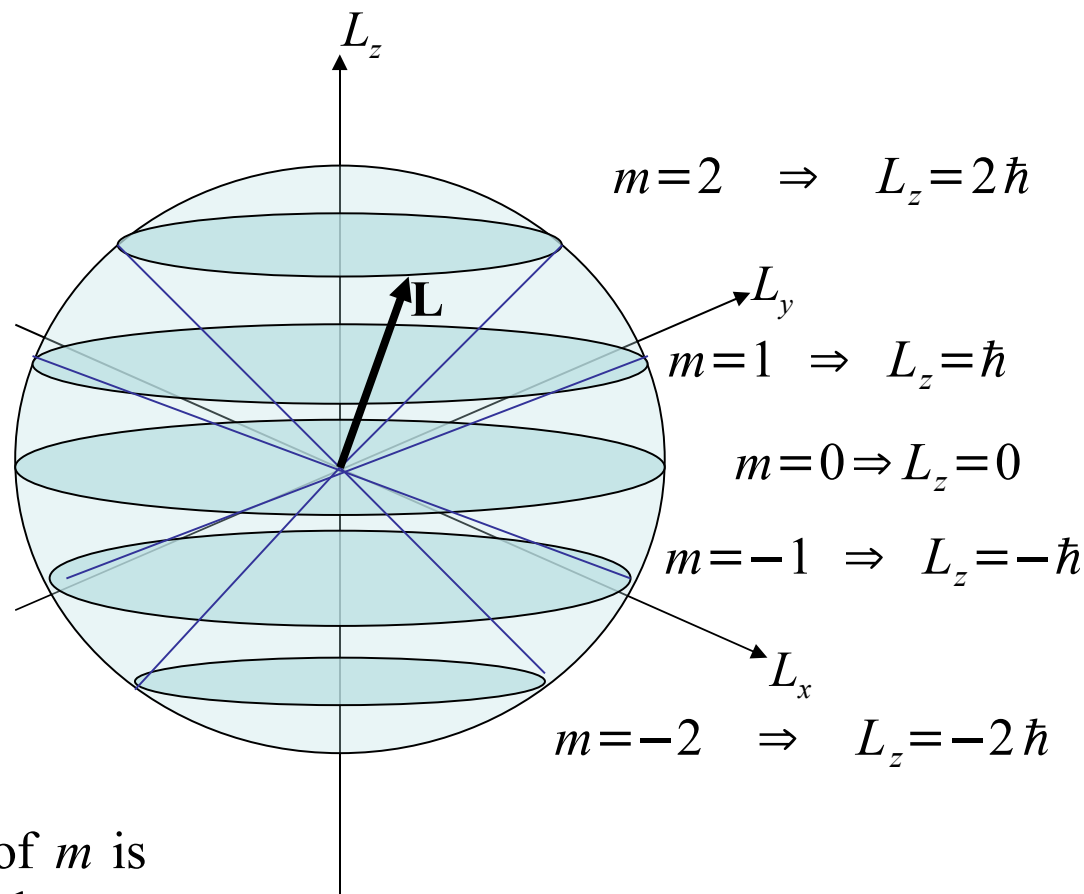
Magnitude of angular momentum is

$$\sqrt{l(l+1)}\hbar = \sqrt{6}\hbar$$

Component of angular momentum in z direction can be

- $2\hbar$
- \hbar
- 0
- $-\hbar$
- $-2\hbar$

Reason for restriction on values of m is so L_z does not exceed total angular momentum available.



6.1 The three-dimensional square well

Consider a particle which is free to move in *three* dimensions everywhere within a cubic box, which extends from $-a$ to $+a$ in each direction. The particle is prevented from leaving the box by infinitely high potential barriers.

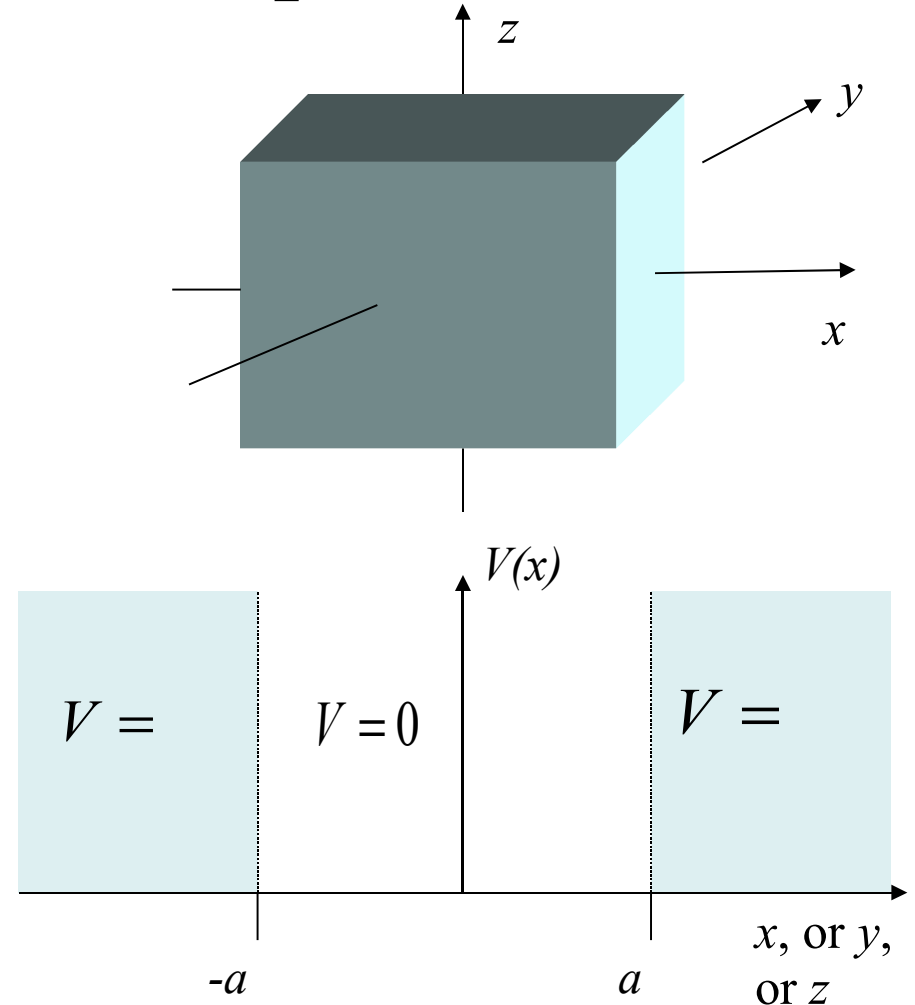
Time-independent Schrödinger equation within the box is free-particle like:

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(x, y, z) = E \psi(x, y, z)$$

Separation of variables: take

$$\psi(x, y, z) = X(x)Y(y)Z(z)$$

with boundary conditions $X(\pm a) = Y(\pm a) = Z(\pm a) = 0$



Three-dimensional square well (2)

Substitute in Schrödinger equation:

$$-\frac{\hbar^2}{2m} \left\{ Y Z \frac{d^2 X}{d x^2} + Z X \frac{d^2 Y}{d y^2} + X Y \frac{d^2 Z}{d z^2} \right\} = E X Y Z$$

Divide by XYZ :

$$-\frac{\hbar^2}{2m} \left\{ \frac{1}{X} \frac{d^2 X}{d x^2} + \frac{1}{Y} \frac{d^2 Y}{d y^2} + \frac{1}{Z} \frac{d^2 Z}{d z^2} \right\} = E$$

With $E = E_x + E_y + E_z$

$$\begin{aligned} -\frac{\hbar^2}{2m} \frac{d^2 X}{d x^2} &= E_x X \\ -\frac{\hbar^2}{2m} \frac{d^2 Y}{d y^2} &= E_y Y \\ -\frac{\hbar^2}{2m} \frac{d^2 Z}{d z^2} &= E_z Z \end{aligned}$$

Three effective *one-dimensional* Schrödinger equations.

Three-dimensional square well (3)

Wavefunctions and energy eigenvalues known from solution to one-dimensional square well (see §3.2).

$$E_x = \frac{n_x^2 \pi^2 \hbar^2}{8 m a^2} \quad \text{with} \quad n_x = 1, 2, 3, 4, \dots \quad \text{Similarly for } E_y \text{ and } E_z$$

Note: We have 3 separate quantum numbers n_x , n_y and n_z

Total energy is

$$\begin{aligned} E &= E_x + E_y + E_z \\ &= \frac{\pi^2 \hbar^2}{8 m a^2} (n_x^2 + n_y^2 + n_z^2) \end{aligned}$$

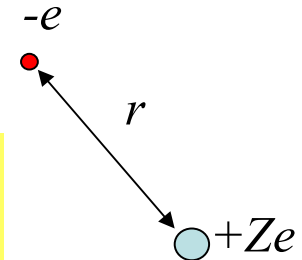
This is an example of the power of separation of variables in a 3D problem. Now we will use the same technique for the hydrogen atom.

6.2 The Hamiltonian for a hydrogenic atom***

For a hydrogenic atom or ion having nuclear charge $+Ze$ and a single electron, the Hamiltonian is

$$\hat{H} = -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r}$$

Note spherical symmetry – potential depends only on r



Note: for greater accuracy we should use the *reduced mass* corresponding to the relative motion of the electron and the nucleus (since nucleus does not remain precisely fixed – see 1B2x):

$$\mu = \frac{m_e m_N}{m_e + m_N} \quad m_e = \text{electron mass} \quad , \quad m_N = \text{nuclear mass}$$

The natural coordinate system to use is spherical polar coordinates. In this case the Laplacian operator becomes (see 2246):

$$\nabla^2 = \frac{1}{r^2} \frac{\delta}{\delta r} \left(r^2 \frac{\delta}{\delta r} \right) + \frac{1}{r^2 \sin \theta} \frac{\delta}{\delta \theta} \left(\sin \theta \frac{\delta}{\delta \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\delta^2}{\delta \phi^2} = \frac{1}{r^2} \frac{\delta}{\delta r} \left(r^2 \frac{\delta}{\delta r} \right) - \frac{L^2}{\hbar^2 r^2}$$

This means that the *angular momentum about any axis, and also the total angular momentum, are conserved quantities*: they commute with the Hamiltonian, and can have well-defined values in the energy eigenfunctions of the system.

$$[\hat{H}, \hat{L}^2] = 0 \Leftrightarrow \frac{d\langle \hat{L}^2 \rangle}{dt} = 0$$

$$[\hat{H}, \hat{L}_z] = 0 \Leftrightarrow \frac{d\langle \hat{L}_z \rangle}{dt} = 0$$

6.3 Separating the variables

Write the time-independent Schrödinger equation as:

$$\hat{H} \psi(r, \theta, \phi) = E \psi(r, \theta, \phi)$$

$$\Rightarrow -\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\psi}{dr} \right) + \frac{\hat{L}^2}{2mr^2} \psi - \frac{Ze^2}{4\pi\epsilon_0 r} \psi = E \psi$$

Now look for solutions in the form

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

Substituting into the Schrödinger equation:

$$-\frac{\hbar^2}{2m} Y(\theta, \phi) \left[\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) \right] + \frac{R}{2mr^2} \hat{L}^2 Y(\theta, \phi) - \frac{Ze^2}{4\pi\epsilon_0 r} RY = E RY$$

$$\Rightarrow \frac{1}{Y} \frac{\hat{L}^2}{2m} Y(\theta, \phi) = E r^2 - \left\{ -\frac{\hbar^2}{2m} \frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) - \frac{Ze^2 r}{4\pi\epsilon_0} \right\}$$

LHS depends only on θ and ϕ , RHS depends only on r .

Both sides must equal some constant: λ

The angular equation

We recognise that the angular equation is simply the eigenvalue condition for the total angular momentum operator L^2 :

$$\frac{1}{Y} \frac{\hat{L}^2}{2m_e} Y = \lambda \quad \Rightarrow \quad \hat{L}^2 Y = 2m_e \lambda Y$$

Y is an eigenfunction of operator \hat{L}^2

This means we *already know* the corresponding eigenvalues and eigenfunctions (see §5):

$$\text{We know } \hat{L}^2 Y_l^m(\theta, \phi) = l(l+1)\hbar^2 Y_l^m(\theta, \phi)$$

$$\Rightarrow \text{Angular function } Y \text{ is a spherical harmonic and } \lambda = \frac{l(l+1)\hbar^2}{2m_e}$$

Note: all this would work for *any* spherically-symmetric potential $V(r)$, not just for the Coulomb potential.

6.4 Solving the radial equation

Now the radial part of the Schrödinger equation becomes:

$$-\frac{\hbar^2}{2m_e} \frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \lambda = E r^2 + \frac{Z e^2}{4\pi \epsilon_0} r$$

$$-\frac{\hbar^2}{2m_e} \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \left[\frac{l(l+1)\hbar^2}{2m_e r^2} - \frac{Z e^2}{4\pi \epsilon_0 r} \right] R = E R$$

*Note that this depends on l , but not on m : it therefore involves the **magnitude** of the angular momentum, but not its **orientation**.*

Define a new unknown function χ by: $R(r) = \frac{\chi(r)}{r}$

$$\Rightarrow \frac{dR}{dr} = \frac{1}{r} \frac{d\chi}{dr} - \frac{\chi}{r^2} \Rightarrow r^2 \frac{dR}{dr} = r \frac{d\chi}{dr} - \chi$$

$$\Rightarrow \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) = r \frac{d^2\chi}{dr^2} + \frac{d\chi}{dr} - \frac{d\chi}{dr}$$

$$\therefore \text{above becomes: } -\frac{\hbar^2}{2m} \frac{d^2\chi}{dr^2} + \left[\frac{l(l+1)\hbar^2}{2m_e r^2} - \frac{Z e^2}{4\pi \epsilon_0 r} \right] \chi = E \chi$$

The effective potential

This corresponds to one-dimensional motion with the *effective potential*

$$V_{\text{eff}}(r) = \frac{-Z e^2}{4 \pi \epsilon_0 r} + \frac{l(l+1) \hbar^2}{2 m_e r^2}$$

First term:

Coulomb attraction:

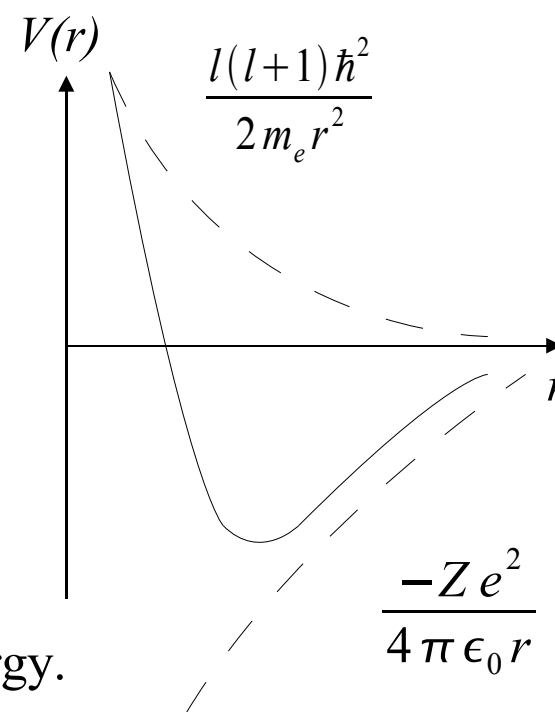
$$\text{Force } F = -\frac{dV}{dr} = \frac{-Z e^2}{4 \pi \epsilon_0 r^2}$$

Second term:

'Centrifugal' repulsion:

$$\text{Force } F = -\frac{dV}{dr} = \frac{l(l+1) \hbar^2}{2 m_e r^2} = \frac{L^2}{2 m_e r^2} = \frac{L^2}{2 I} = \text{Rotational kinetic energy.}$$

$$\text{Classically } = \frac{(m_e V r)^2}{m_e r^3} = \frac{m_e V^2}{r}$$



Atomic units***

Atomic units: there are a lot of physical constants in these expressions. It makes atomic problems much more straightforward to adopt a system of units in which as many as possible of these constants are one. In *atomic units* we set:

Planck constant $\hbar = 1$ (Dimensions [$M L^2 T^{-1}$])

Electron mass $m_e = 1$ (Dimensions [M])

Constant appearing in Coulomb's law $\frac{e^2}{4\pi\epsilon_0} = 1$ (Dimensions [$M L^3 T^{-2}$])

It follows that:

$$\text{Unit of length} = \left(\frac{4\pi\epsilon_0}{e^2} \right) \frac{\hbar^2}{m_e} = 5.29177 \times 10^{-11} \text{ m} = \text{Bohr radius, } a_0$$

$$\text{Unit of energy} = \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \frac{m_e}{\hbar^2} = 4.35974 \times 10^{-18} \text{ J} = 27.21159 \text{ eV} = \text{Hartree, } E_h$$

In this unit system, the radial equation becomes

$$-\frac{1}{2} \frac{d^2 \chi}{dr^2} + \left[\frac{l(l+1)}{2r^2} - \frac{z}{r} \right] \chi = E \chi$$

Solution near the nucleus (small r)

For small values of r the second derivative and centrifugal terms dominate over the others.

$$-\frac{1}{2} \frac{d^2 \chi}{dr^2} + \frac{l(l+1)}{2r^2} \chi = 0$$

Try a solution to the differential equation in this limit as

$$\chi \propto r^k$$
$$\Rightarrow \chi'' = k(k-1)r^{k-2} \quad \text{and} \quad \frac{l(l+1)}{r^2} = l(l+1)r^{k-2}$$

$$\text{So: } -k(k-1) + l(l+1) = 0$$

$$\Rightarrow k^2 - k - l(l+1) = 0$$

$$\Rightarrow [k+l][k-(l+1)] = 0 \quad \Rightarrow \quad k = -l \quad \text{or} \quad k = l+1$$

We want a solution such that $R(r)$ remains finite as $r \rightarrow 0$,
so take

$$k = (l+1) \quad \Rightarrow \quad \chi \propto r^{(l+1)} \quad \text{as } r \rightarrow 0 \quad R \propto r^l$$

Asymptotic solution (large r)

Now consider the radial equation at very large distances from the nucleus, when both terms in the effective potential can be neglected. We are looking for *bound states* of the atom, where the electron does not have enough energy to escape to infinity:

$$\text{Put: } E = -\frac{\kappa^2}{2}$$
$$-\frac{1}{2} \frac{d^2 \chi}{dr^2} = -\frac{\kappa^2}{2} \chi \quad \Rightarrow \quad \frac{d^2 \chi}{dr^2} = -\kappa^2 \chi$$

$$\text{Solutions: Try } \chi = e^{\alpha x} \quad \Rightarrow \quad \alpha^2 = \kappa^2 \quad \Rightarrow \quad \alpha = \pm \kappa$$

$$\text{Take } \kappa > 0, \text{ general solution. } \chi = A e^{\kappa r} + B e^{-\kappa r}$$

$$A e^{\kappa r} \text{ term is not normalisable } \therefore A = 0$$

Inspired by this, let us rewrite the solution in terms of yet another unknown function, $F(r)$:

$$\chi(r) = F(r) e^{-\kappa r}$$

Differential equation for F

Can obtain a corresponding differential equation for F :

$$\frac{d\chi}{dr} = \frac{dF}{dr} e^{-\kappa r} - \kappa F e^{-\kappa r}$$

$$\frac{d^2\chi}{dr^2} = \frac{d^2F}{dr^2} e^{-\kappa r} - 2\kappa \frac{dF}{dr} e^{-\kappa r} + \kappa^2 F e^{-\kappa r}$$

Substituting in SE and cancelling factors of $E^{-\kappa r}$ gives:

$$-\frac{1}{2} \frac{d^2 F}{dr^2} + \kappa \frac{dF}{dr} - \frac{1}{2} \kappa^2 F + \left[\frac{l(l+1)}{2r^2} - \frac{Z}{r} \right] F = -\frac{1}{2} \kappa^2 F \quad \Rightarrow \quad \frac{d^2 F}{dr^2} - \frac{l(l+1)}{r^2} F = 2\kappa \frac{dF}{dr} - 2\frac{Z}{r} F$$

This equation is solved in 2246, using the Frobenius (power-series) method.

$$F(r) = r^k \sum_p a_p r^p = \sum_p a_p r^{p+k}$$

The indicial equation gives $k = -l$ or $(l+1)$

regular solution behaves like $F \sim r^{l+1}$ for small r .

Properties of the series solution

If the full series found in 2246 is allowed to continue up to an arbitrarily large number of terms, the overall solution behaves like

$$F(r) \approx e^{2\kappa r}$$

$$\Rightarrow \chi(r) \approx e^{2\kappa r} e^{-\kappa r} = e^{\kappa r}$$

(not normalizable)

Hence the series must *terminate* after a finite number of terms. This happens only if

$$\frac{Z}{\kappa} = n \text{ where } n \text{ is an integer } > l : n = l + 1, l + 2, \dots$$

So the energy is

$$E = -\frac{1}{2}\kappa^2 = -\frac{1}{2}\left(\frac{Z}{n}\right)^2$$

Note that *once we have chosen n , the energy is independent of both m (a feature of all spherically symmetric systems, and hence of all atoms) and l (a special feature of the Coulomb potential, and hence just of hydrogenic atoms).*

n is known as the **principal quantum number**. It defines the “shell structure” of the atom.

6.5 The hydrogen energy spectrum and wavefunctions***

Each solution of the time-independent Schrödinger equation is defined by the three *quantum numbers* n, l, m

For each value of $n=1,2,\dots$ we have a definite energy:

$$E_n = -\frac{Z^2}{2n^2} \text{ (in atomic units)}$$

For each value of n , we can have n possible values of the total angular momentum quantum number l :

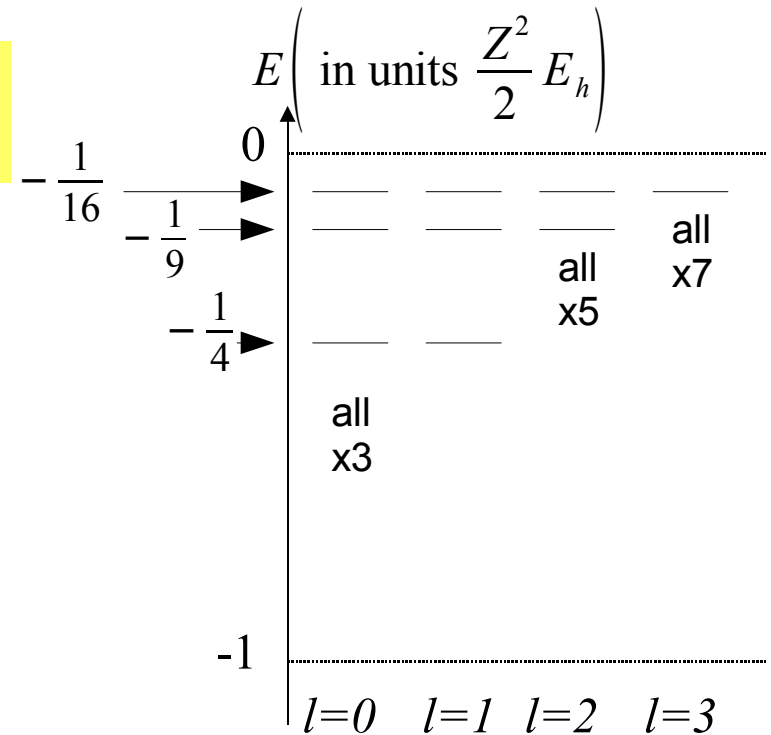
$$l=0,1,2,\dots,n-1$$

For each value of l and n we can have $2l+1$ values of the magnetic quantum number m :

$$m = -l, -(l-1), \dots, 0, \dots, (l-1), l$$

The total number of states (statistical weight) associated with a given energy E_n is therefore

$$\sum_{l=0}^{n-1} (2l+1) = n^2$$



Traditional nomenclature:
 $l=0$: s states (from “sharp” spectral lines)
 $l=1$: p states (“principal”)
 $l=2$: d states (“diffuse”)
 $l=3$: f states (“fine”)
 ...and so on alphabetically (g,h,i... etc)

The radial wavefunctions

Radial wavefunctions R_{nl} depend on principal quantum number n and angular momentum quantum number l (but not on m)

$$R_{10}(r) = 2 \left(\frac{Z}{a_0} \right)^{\frac{3}{2}} e^{-\frac{Zr}{a_0}}$$

$$R_{21}(r) = \frac{1}{\sqrt{3}} \left(\frac{Z}{2a_0} \right)^{\frac{3}{2}} \left(\frac{Zr}{a_0} \right) e^{-\frac{Zr}{2a_0}}$$

$$R_{20}(r) = 2 \left(\frac{Z}{2a_0} \right)^{\frac{3}{2}} \left(1 - \frac{Zr}{2a_0} \right) e^{-\frac{Zr}{2a_0}}$$

$$R_{32}(r) = \frac{4}{27\sqrt{10}} \left(\frac{Z}{3a_0} \right)^{\frac{3}{2}} \left(\frac{Zr}{a_0} \right)^2 e^{-\frac{Zr}{3a_0}}$$

$$R_{31}(r) = \frac{4\sqrt{2}}{9} \left(\frac{Z}{3a_0} \right)^{\frac{3}{2}} \left(1 - \frac{Zr}{6a_0} \right) \left(\frac{Zr}{a_0} \right) e^{-\frac{Zr}{3a_0}}$$

$$R_{30}(r) = 2 \left(\frac{Z}{3a_0} \right)^{\frac{3}{2}} \left(1 - \frac{2Zr}{3a_0} + \frac{2Z^2 r^2}{27a_0^2} \right) e^{-\frac{Zr}{3a_0}}$$

Full wavefunctions are:

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r) Y_l^m(\theta, \phi)$$

Normalization chosen so that:

$$\int_0^{\infty} r^2 R_{nl}^2(r) dr \int_0^{\pi} \sin(\theta) d\theta \int_0^{2\pi} d\phi |Y_l^m(\theta, \phi)|^2 = 1$$

But: $\int_0^{\pi} \sin(\theta) d\theta \int_0^{2\pi} d\phi |Y_l^m(\theta, \phi)|^2 = 1$ for spherical harmonics.

$$\Rightarrow \int_0^{\infty} r^2 R_{nl}^2(r) dr = 1$$

Note:

Probability of finding electron between radius r and $r+dr$ is:

$$r^2 R_{nl}^2(r) = \chi_{nl}^2(r) \quad \text{since: } \chi_{nl} = r R_{nl}(r)$$

i.e. $r^2 R_{nl}(r)$ is the probability per unit length of finding the electron at a radius r . NOT the probability per unit volume of finding the particle at a given point in space: $|\psi_{nlm}|^2$

Only s states ($l=0$) are finite at the origin.

Radial functions have $(n-l-1)$ zeros.

Comparison with Bohr model***

Bohr model

Angular momentum (about any axis) *assumed* to be quantized in units of Planck's constant:

$$L_z = n\hbar, \quad n = 1, 2, 3, \dots$$

Electron otherwise moves according to classical mechanics and has a single well-defined orbit with radius

$$r_n = \frac{n^2 a_0}{Z}, \quad a_0 = \text{Bohr radius}$$

Energy quantized and determined solely by angular momentum:

$$E_n = -\frac{Z^2}{2n^2} E_h, \quad E_h = \text{Hartree}$$

Quantum mechanics

Angular momentum (about any axis) *shown* to be quantized in units of Planck's constant:

$$L_z = m\hbar, \quad m = -l, \dots, l$$

Electron wavefunction spread over all radii. Can show that the quantum mechanical expectation value of the quantity $1/r$ satisfies

$$\left\langle \frac{1}{r} \right\rangle = \frac{Z}{n^2 a_0}, \quad a_0 = \text{Bohr radius}$$

Energy quantized, but is determined solely by principal quantum number, not by angular momentum:

$$E_n = -\frac{Z^2}{2n^2} E_h, \quad E_h = \text{Hartree}$$

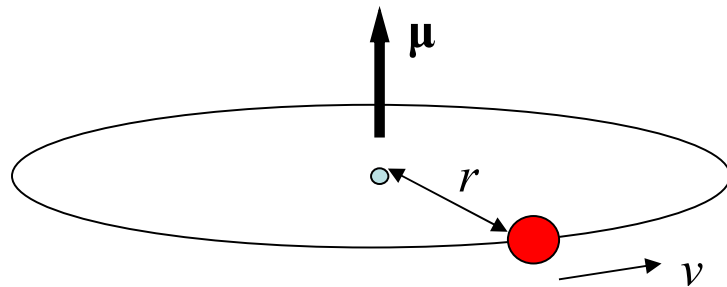
6.6 The remaining approximations

- This is still not an exact treatment of a real H atom, because we have made several approximations.
 - We have neglected the motion of the nucleus. To fix this we would need to replace m_e by the reduced mass μ (see slide 1).
 - We have used a non-relativistic treatment of the electron and in particular have neglected its spin (see §7). Including these effects gives rise to
 - “fine structure” (from the interaction of the electron’s orbital motion with its spin), and
 - “hyperfine structure” (from the interaction of the electron’s spin with the spin of the nucleus)
 - We have neglected the fact that the electromagnetic field acting between the nucleus and the electron is itself a quantum object. This leads to “quantum electrodynamic” corrections, and in particular to a small “Lamb shift” of the energy levels.

Reading: Rae Chapter 6; B&J §6.8, B&M Chapter 8 (all go further than 2B22)

7.1 Atoms in magnetic fields

Interaction of classically orbiting electron with magnetic field:



Orbit behaves like a current loop:

$$\text{Loop current} = \frac{-e v}{2 \pi r} \quad (\text{-ve sign because charge} = -e)$$

Magnetic moment $\mu = \text{current} \times \text{area}$

$$= \left(\frac{-e v}{2 \pi r} \right) \pi r^2 = \frac{-e}{2 m_e} m_e v r = -\mu_B \frac{L}{\hbar}$$

Where $\mu_B = \frac{e \hbar}{2 m_e}$ (The Bohr magneton)

In the presence of a magnetic field \mathbf{B} , classical interaction energy is:

$$\Delta E = -\boldsymbol{\mu} \cdot \mathbf{B} = \mu_B \frac{L}{\hbar} \cdot \mathbf{B}$$

Corresponding quantum mechanical expression (to a good approximation) involves the angular momentum *operator*:

$$\text{Contribution to Hamiltonian involving } \mathbf{B} = \Delta \hat{H} = \frac{\mu_B}{\hbar} (\mathbf{L} \cdot \mathbf{B})$$

Splitting of atomic energy levels

Suppose field is in the z direction. The Hamiltonian operator is

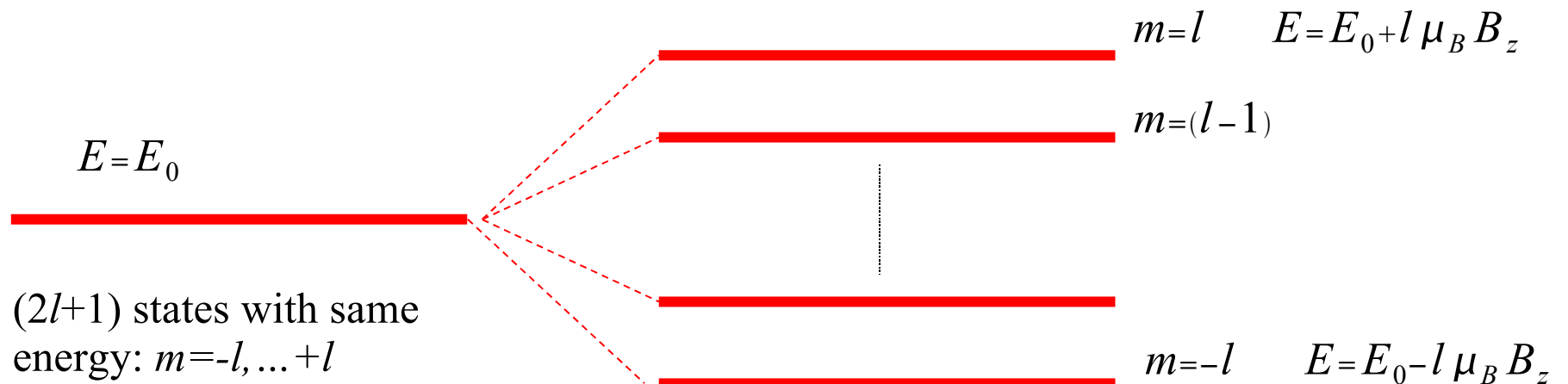
$$\hat{H} = \hat{H}_0 + \frac{\mu_B B_z}{\hbar} \hat{L}_z$$

We chose energy eigenfunctions of the original atom that are eigenfunctions of L_z so these same states are also eigenfunctions of the new H .

$$\left. \begin{array}{l} \hat{H}_0 \psi_m = E_0 \psi_m; \\ \hat{L}_z \psi_m = m\hbar \psi_m. \end{array} \right\} \Rightarrow \hat{H} \psi_m = \hat{H}_0 \psi_m + \frac{\mu_B B_z}{\hbar} \hat{L}_z \psi_m$$
$$= \underbrace{(E_0 + m \mu_B B_z)}_{\text{New eigenvalue.}} \psi_m$$

Splitting of atomic energy levels (2)

$$B = 0 \quad \Rightarrow \quad B \neq 0$$



Predictions: should always get an odd number of levels. An s state (such as the ground state of hydrogen, $n=1, l=0, m=0$) should not be split.

(Hence the name “magnetic quantum number” for m .)

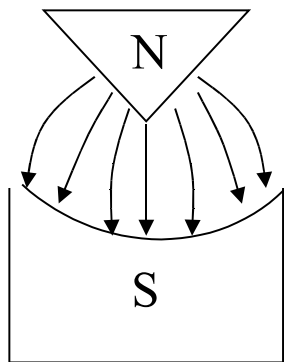
7.2 The Stern-Gerlach experiment***

Produce a beam of atoms with a single electron in an s state (e.g. hydrogen, sodium)

Study deflection of atoms in *inhomogeneous* magnetic field. Force on atoms is

$$\underline{F} = \nabla(\underline{\mu} \cdot \underline{B})$$

⇒ if $\underline{\mu}$ is aligned with \underline{B} , the atom is pushed towards high fields.
If $\underline{\mu}$ is anti-aligned with \underline{B} atom is pushed towards low fields.



Results show *two* groups of atoms, deflected in opposite directions, with magnetic moments

$$\mu = \pm \mu_B$$

Consistent *neither* with classical physics (which would predict a continuous distribution of μ) *nor* with our quantum mechanics so far (which always predicts an odd number of groups, and just one for an s state).



Gerlach

7.3 The concept of spin***

Try to understand these results by analogy with what we know about the ordinary (“orbital”) angular momentum: must be due to some additional source of angular momentum that does not require motion of the electron. Known as “spin”.

Introduce new operators to represent spin, *assumed* to have same commutation relations as ordinary angular momentum:

$$[\hat{S}_x, \hat{S}_y] = i\hbar \hat{S}_z \quad \text{etc.} \quad \text{Where } (\hat{S}_x, \hat{S}_y, \hat{S}_z) \text{ are components of spin angular momentum.}$$

Define: $\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2$

Corresponding eigenfunctions and eigenvalues:

$$\hat{S}^2 \chi_s^{m_s} = s(s+1)\hbar^2 \chi_s^{m_s} \quad m_s = \text{magnetic spin quantity}$$

$$\hat{S}_z \chi_s^{m_s} = m_s \hbar \chi_s^{m_s}$$

(will see in Y3 that these equations can be derived directly from the commutation relations)

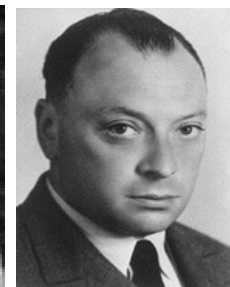
Find S does not have to be an integer, but can be an integer or half integer and m_s can vary from $+S$ to $-S$ in integer steps.



Goudsmit



Uhlenbeck



Pauli

Spin quantum numbers for an electron

From the Stern-Gerlach experiment, we know that electron spin along a given axis has *two* possible values.

So, choose $S = \frac{1}{2} \Rightarrow m_s = -S \dots \dots \dots +S = \pm \frac{1}{2}$

But we also know from Stern-Gerlach that magnetic moments associated with the two possibilities are $\mu = \pm \mu_B$

So, have $\mu = \pm 2 m_s \mu_B$

General interaction with magnetic field:

$$\hat{H} = \hat{H}_0 + \frac{\mu_B}{\hbar} \mathbf{B} \cdot (\hat{\mathbf{L}} + g \hat{\mathbf{S}})$$

$g=2$ (Dirac's relativistic theory)

$g=2.00231930437$ (Quantum Electrodynamics)

$g=g$ -factor (Measures how effective this particular form of angular momentum is at producing a magnetic moment.)

Spin angular momentum is twice as “effective” at producing magnetic moment as orbital angular momentum.

A complete set of quantum numbers

Hence the *complete* set of quantum numbers for the electron in the H atom is: n, l, m, s, m_s .

Corresponding to a full wavefunction

$$\Psi_{n,l,m,s,m_s}(r, \theta, \phi) = R_{n,l}(r) Y_l^m(\theta, \phi) \chi_S^{m_s}$$

i.e. 2 states, with $m_s = \pm \frac{1}{2}$ for each one we found before.

Note that the spin functions χ do *not* depend on the electron coordinates r, θ, ϕ ; they represent a purely *internal* degree of freedom.

H atom in magnetic field, with spin included, and field in the z direction:

$$\hat{H} = \hat{H}_0 + \frac{\mu_B B_z}{\hbar} (\hat{L}_z + g \hat{S}_z)$$

\Rightarrow Change in energy is $\mu_B B_z (m + g m_s) \simeq \mu_B B_z (m + 2 m_s)$

For ground state ($l=0, m=0$), get $\Delta E = \pm \mu_B B_z$ as observed.

7.4 Combining different angular momenta

So, an electron in an atom has two sources of angular momentum:

- Orbital angular momentum (arising from its motion through the atom)
- Spin angular momentum (an internal property of its own).

To think about the total angular momentum produced by combining the two, use the vector model once again:

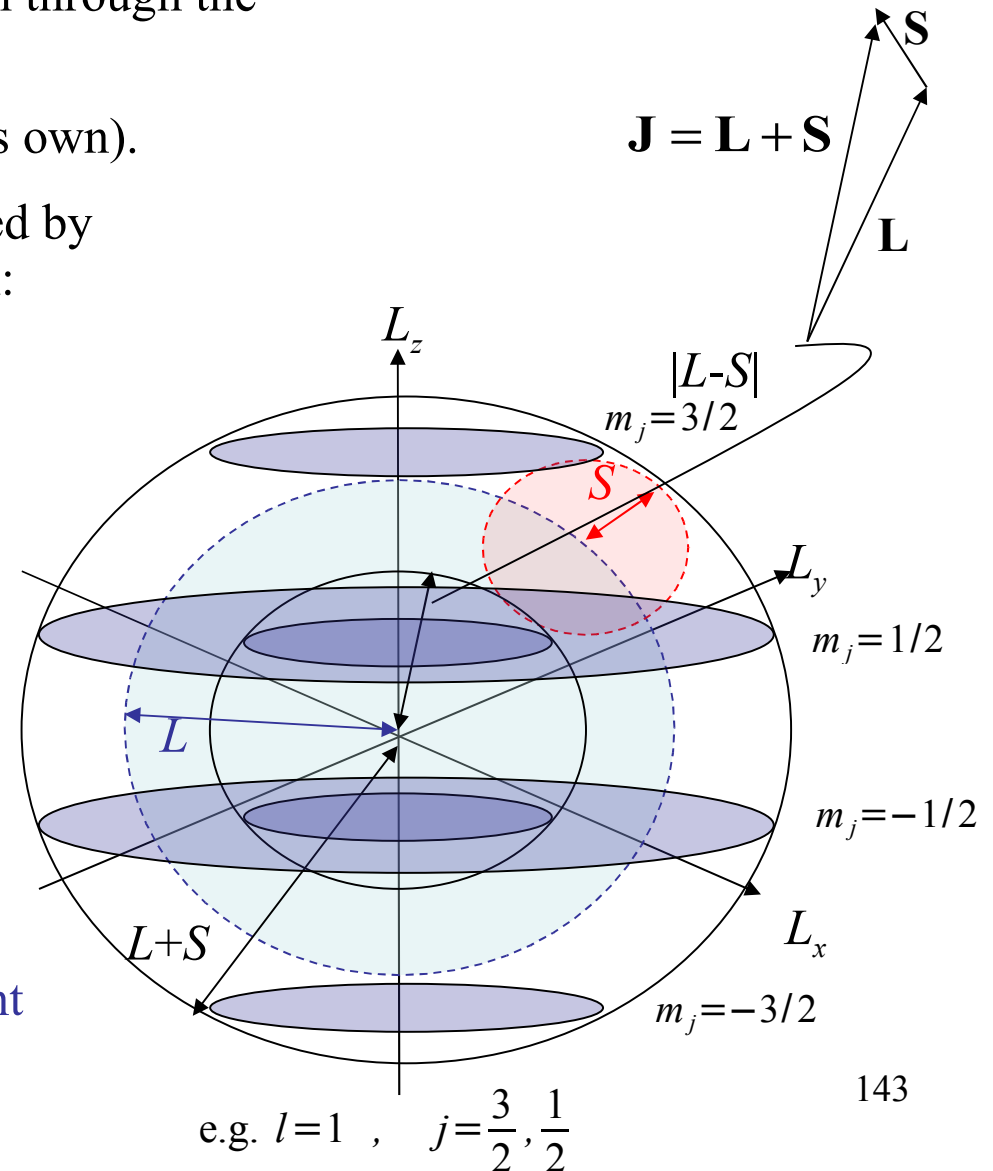
Vector addition between orbital angular momentum \mathbf{L} (of magnitude L) and spin \mathbf{S} (of magnitude S): produces a resulting angular momentum vector \mathbf{J} : quantum mechanics says its magnitude lies somewhere between $|L-S|$ and $L+S$.(in integer steps).

For a single electron, corresponding 'total angular momentum' quantum numbers are

$j = |l - \frac{1}{2}|, l + \frac{1}{2}$ Determines *length* of resultant angular momentum vector

$m_j = -j, \dots, +j$ Determines *orientation*

Eigenvalues of $\hat{J} = j(j+1)\hbar^2$
 Eigenvalue of $\hat{J}_z = m_j\hbar$



Example: the 1s and 2p states of hydrogen

The 1s state:

$$l=0 \quad , \quad s=\frac{1}{2} \quad \Rightarrow \quad 1 \text{ possibility} \quad j=\frac{1}{2}$$

Purely spin angular momentum. $m_j = \pm \frac{1}{2}$

The 2p state:

$$(n=2) \quad , \quad l=1 \quad , \quad S=\frac{1}{2}$$

Now 2 possibilities: $j=\frac{1}{2}$, $\frac{3}{2}$; $m_j = \left(-\frac{1}{2}, \frac{1}{2}\right), \left(-\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}\right)$

\Rightarrow Get a doublet of states adding 2 different values of m_j , and a quartet of states adding 4 different values of m_j

Even in no B - field. $j=\frac{1}{2}$ and $j=\frac{3}{2}$ states have different energies.

(Fine structure effects.)

Combining angular momenta (2)

The same rules apply to combining other angular momenta, from whatever source.

For example for *two* electrons in an excited state of He atom, one in 1s state and one in 2p state (defines what is called the 1s2p *configuration* in atomic spectroscopy):

$$l_1 = 0; s_1 = \frac{1}{2}; \quad l_2 = 1; s_2 = \frac{1}{2}$$

First construct combined orbital angular momentum L of both electrons:

$$L \text{ must be between } |L_1 - L_2| = 1 \text{ and } L_1 + L_2 = 1$$

$$\Rightarrow S = 0, 1$$

Then construct combined spin S of both electrons:

$$|S_1 + S_2| = 0 \text{ and } S_1 + S_2 = 1$$

$$\Rightarrow S = 0, 1$$

Hence there are two possible *terms* (combinations of L and S):

...and four *levels* (possible ways of combining L and S to get different total angular momentum quantum numbers)

$$L=1, S=0 \Rightarrow J=1$$

$$L=1, S=1 \Rightarrow J=0, 1, 2$$

Term notation

Spectroscopists use a special notation to describe terms and levels:

$$2S+1 L_J$$

- The first (upper) symbol is a *number* giving the number of spin states corresponding to the total spin S of the electrons
- The second (main) symbol is a *letter* encoding the total orbital angular momentum L of the electrons:
 - S denotes $L=0$
 - P denotes $L=1$
 - D denotes $L=2$ (and so on);
- The final (lower) symbol gives the total angular momentum J obtained from combining the two.

Example: terms and levels from previous page would be:

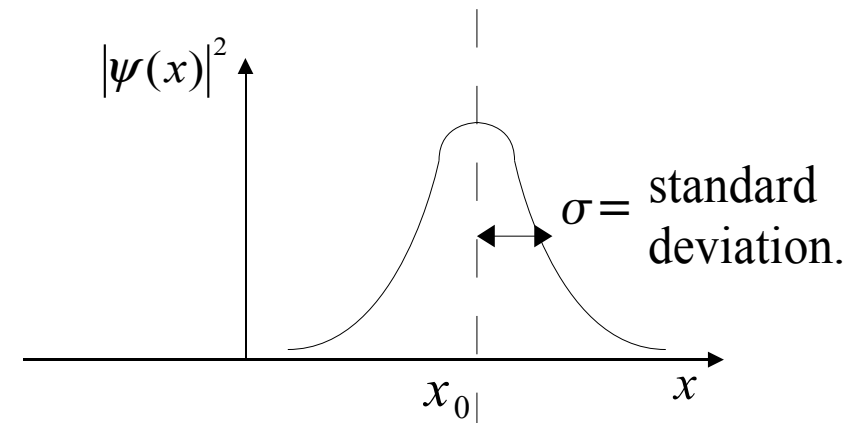
$$\begin{aligned} L=1, S=0 &\Rightarrow {}^1P_1 \quad (\text{Singlet}) \\ L=1, S=1 &\Rightarrow {}^3P_0, {}^3P_1, {}^3P_2 \end{aligned}$$

7.5 Wavepackets and the Uncertainty Principle revisited (belongs in §4 – non-examinable)

Can think of the Uncertainty Principle as arising from the structure of *wavepackets*. Consider a normalized wavefunction for a particle located somewhere *near* (but not exactly *at*) position x_0

$$\psi(x) = (2\pi\sigma^2)^{-\frac{1}{4}} \exp\left[\frac{-(x-x_0)^2}{4\sigma^2}\right]$$

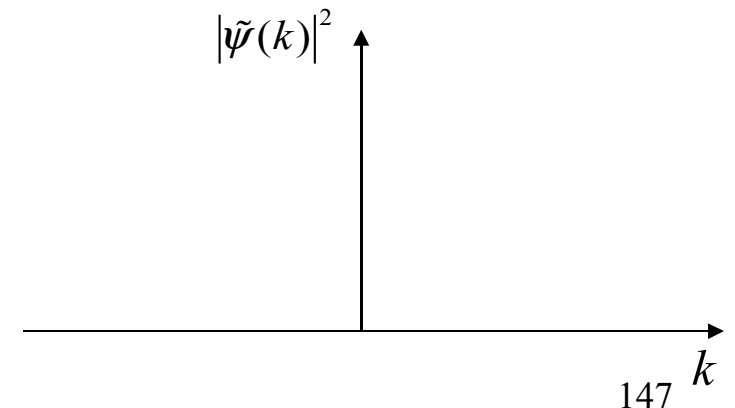
$$\text{Probability density: } |\psi(x)|^2 = (2\pi\sigma^2)^{-\frac{1}{2}} \exp\left[\frac{-(x-x_0)^2}{2\sigma^2}\right]$$



Can also write this as a Fourier transform (see 2246):

$$\psi(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \tilde{\psi}(k) e^{ikx} dk$$

(expansion in eigenstates of momentum)



7.5 Wavepackets and the Uncertainty Principle revisited (belongs in §4 – non-examinable) (cont.)

Compare $\psi(x) = \sum a_n \phi_n(x)$

$$\text{then } \bar{\psi}(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \psi(x) e^{-ikx} dx$$

$$\text{Compare } a_n = \int_{-\infty}^{\infty} \psi(x) \phi_n^*(x) dx$$

$$e^{ikx} \Rightarrow \phi_n(x) \quad (\text{Eigenfunction})$$

$$\bar{\psi}(k) \quad (\text{Expansion coefficient})$$

Fourier transform of a Gaussian

$$\tilde{\psi}(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \psi(x) \exp[-ikx] dx$$

$$= \frac{1}{\sqrt{2\pi}} (2\pi\sigma^2)^{-\frac{1}{4}} \int_{-\infty}^{\infty} \exp\left[-\frac{(x-x_0)^2}{4\sigma^2}\right] \exp[-ikx] dx$$

$$= \frac{1}{\sqrt{2\pi}} (2\pi\sigma^2)^{-\frac{1}{4}} \exp[-ikx_0] \int_{-\infty}^{\infty} \exp\left[-\frac{(x-x_0)^2}{4\sigma^2} - ik(x-x_0)\right] dx$$

$$= \frac{1}{\sqrt{2\pi}} (2\pi\sigma^2)^{-\frac{1}{4}} \exp[-ikx_0] \int_{-\infty}^{\infty} \exp\left[-\frac{[(x-x_0)+2ik\sigma^2]^2}{4\sigma^2} - k^2\sigma^2\right] dx$$

$$= \frac{1}{\sqrt{2\pi}} (2\pi\sigma^2)^{-\frac{1}{4}} \exp[-ikx_0] \exp[-k^2\sigma^2] \int_{-\infty}^{\infty} \exp\left[-\frac{x'^2}{4\sigma^2}\right] dx \quad \text{With: } x' = x - x_0 + 2ik\sigma^2, \quad dx' = dx$$

$$= \frac{1}{\sqrt{2\pi}} (2\pi\sigma^2)^{-\frac{1}{4}} \exp[-ikx_0] \exp[-k^2\sigma^2] \sqrt{\pi 2\sigma}$$

$$= \left(\frac{\pi}{2\sigma^2}\right)^{-\frac{1}{4}} \exp[-ikx_0] \exp[-k^2\sigma^2]$$

$$|\tilde{\psi}(k)|^2 = \left(\frac{\pi}{2\sigma^2}\right)^{-\frac{1}{2}} \exp[-2k^2\sigma^2]$$

$$\int_{-\infty}^{\infty} |\tilde{\psi}(k)|^2 dk = \sqrt{\frac{\pi}{2\sigma^2}} \left(\frac{\pi}{2\sigma^2}\right)^{-\frac{1}{2}} = 1$$

$$\int_{-\infty}^{\infty} \exp\left[-\frac{x^2}{a^2}\right] dx = \sqrt{\pi a} \quad , \quad \int_{-\infty}^{\infty} x^2 \exp\left[-\frac{x^2}{a^2}\right] dx = \frac{\sqrt{\pi} a^3}{2}$$

Wavepackets and Uncertainty Principle (2)

Mean-squared uncertainty in *postion* $\Delta x^2 = \langle (x - x_0)^2 \rangle = \int_{-\infty}^{\infty} (x - x_0)^2 |\psi(x)|^2 dx = \sigma^2$

Mean momentum: $p = \hbar k$ $|\tilde{\psi}(k)|^2$ is symmetric about $k = 0 \Rightarrow \langle p \rangle = 0$

Mean-squared uncertainty in *momentum*: $\Delta p^2 = \langle p^2 \rangle = \hbar^2 \langle k^2 \rangle = \frac{\hbar^2}{4\sigma^2}$

$$\Rightarrow \Delta x^2 \Delta p^2 = \sigma^2 \frac{\hbar^2}{4\sigma^2} = \frac{\hbar^2}{4}$$

In fact, can show that this form of wavepacket (“Gaussian wavepacket”) minimizes the product of Δx and Δp , so:

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

Rigorous statement of uncertainty principle for position and momentum.

Wavepackets and Uncertainty Principle (3)

Summary

Three ways of thinking of Uncertainty principle:

- (3) Arising from the physics of the interaction of different types of measurement apparatus with the system (e.g. in the gamma-ray microscope);
- (4) Arising from the properties of Fourier transforms (narrower wavepackets need a wider range of wavenumbers in their Fourier transforms);
- (5) Arising from the fact that x and p are not compatible quantities (do not commute), so they cannot simultaneously have precisely defined values.

General result (see third year, or Rae §4.5):

For general non-commuting operators \hat{Q} , \hat{R}

$$\Delta q \Delta r \geq \frac{1}{2} \left| \langle [\hat{Q}, \hat{R}] \rangle \right|$$

Where: Δq and Δr are RMS uncertainties in \hat{Q} and \hat{R}