Where Does Quantum Mechanics Come From?

Quantum mechanics was developed to explain experimental observations that could not be understood using the prevailing "classical" theories of physics, as well as theoretical inconsistencies with classical electromagnetic theory.

1. Spectroscopic Lines
   - Moseley: discrete x-ray wavelengths
   - Atomic spectra: discrete spectral wavelengths (called "lines")

Light emitted by an excited atomic gas consists of discrete wavelengths, not a continuous band.

Where Does Quantum Theory Come From?

2. Photoelectric Effect

Light can eject electrons from a metal, but only if its frequency is above a threshold frequency (characteristic for each metal).

Classically, for light as a wave, its energy is proportional to the square of its amplitude.

For particles, energy is proportional to frequency.

Einstein (1905) proposed that light has particle nature (as well as wave nature), i.e. light is quantized (photons).
The Bohr Atom

3. The Rutherford picture of an atom with electrons orbiting around a central atom is inconsistent with the laws of classical physics. Unlike planets orbiting around a star, an orbiting electron is a moving charge and should radiate energy as it spirals towards the nucleus.

Niels Bohr, who had been working in Rutherford’s laboratory, developed a quantum model of a single electron near a hydrogen nucleus. His model postulated a set of circular orbits for electrons with specific, discrete radii and energies and that electrons could move in each orbit without radiating energy (even though this violated classical ideas).

Bohr’s theory failed to (i) explain multi-electron atoms (ii) explain bonding and the formation of molecules and liquids and solids (iii) explain the intensities of atomic spectral lines (iv) even explain the “fine structure” in the H spectrum. Bohr’s model did not provide any reason for the discrete orbits or energies.

Quantum Theory and Matter Waves

In classical physics, nature consists of matter and energy, which are distinct from one another.

In quantum theory, mass and energy are not distinguished. Matter (electrons, neutrons, atoms, molecules, …) behaves like a wave and energy (= radiation: light, x-rays, g, …) behaves like a particle.

Quantum theory does not give us an intuitive picture of the fundamental nature of the universe. Very small particles do not behave in a way that is familiar to us based on our (macroscopic) experience.

It began with the radical proposal of Louis de Broglie in 1924 that particles like electrons should exhibit wave-like character, and obey the equations that describe the behaviour of waves, just as light exhibits both particle and wave properties.
Experimental Evidence for Electron Matter Waves

C.J. Davison and L.H. Germer; G.P. Thomson (1927) Nobel Prize for Physics 1937

Diffraction patterns produced by a beam of x-rays and electrons passing through Al foil:

Application: Electron microscopy

Mechanics of Waves

Waves are common in nature, and we have experience of many kinds of waves on a macroscopic scale.

E.g. Waves on a string
  • guitar, violin strings etc. (transverse waves)

E.g. Sound waves.
  • Flute (longitudinal waves)

Waves can be two or three dimensional. E.g.
  • Bells or chimes; tuning fork; ripples on a pond

The properties or (mechanics) of waves are well-described by the laws of classical physics. The problem of quantum mechanics is how to marry particle and wave character.

Mechanics of Waves

The behaviour of any wave moving in one direction \( x \) is described by the general wave equation

\[
\frac{d^2 F}{dx^2} = \frac{1}{v^2} \frac{d^2 F}{dt^2}
\]

where \( F \) is the "thing that is waving" i.e.
  • the transverse displacement of a string
  • the pressure difference in a sound wave
  • the magnitude of the electric or magnetic field

and \( v \) is the velocity of the wave. i.e.
  • its speed along a string
  • the speed of sound
  • the speed of light, \( c \).

*You are not expected to memorise or to use this equation. We will simply use it to establish the historical context for the development of quantum mechanics and the quantum mechanical wave equation.*
Electron Wavelengths

The de Broglie relation was first proposed in 1924 to describe the wavelength of a particle, \( \lambda \),

\[ \lambda = \frac{h}{p} = \frac{h}{mv} \]

where \( p \) is the momentum, \( m \) the mass and \( v \) the velocity. \( h \) is the Planck constant
\( = 6.626 \times 10^{-34} \) J s.

Although this was just a postulate at the time, subsequent experiments have verified the accuracy of the relationship. E.g. diffraction behaviour of electrons and neutrons of different velocities compared with x-rays of known wavelength.

You are expected to know how to use this equation, which is significant because it relates a classical particle property (mass) to a wavelength, and is generally applicable to all particles.

Electron Wavelengths - Worked Example

What is the wavelength of an electron travelling at \( 5.0 \times 10^6 \) m s\(^{-1} \)?

The de Broglie relation
\[ \lambda = \frac{h}{p} = \frac{h}{mv} \]

i.e. wavelength, \( \lambda = 6.626 \times 10^{-34} \) J s/(9.11 \times 10^{-31} \times 5.0 \times 10^6) J kg\(^{-1}\) m\(^{-1}\) s

\[ = 1.5 \times 10^{-10} \text{ m or 0.15 nm} \]

This wavelength is in the same range as an x-ray.

Energy - Electron Volts

The usual (SI) unit of energy is the joule (J). Another convenient unit is the electron volt, eV. This describes the voltage needed to be applied to an electron to accelerate it to a kinetic energy \( E \).

E.g. The electron above has a kinetic energy
\[ E = \frac{1}{2}mv^2 = 0.5 \times 9.11 \times 10^{-31} \times (5.0 \times 10^6)^2 \]

\[ = 1.1 \times 10^{-17} \text{ J} \]

or \( 1.1 \times 10^{-17} / 1.602 \times 10^{-19} \text{ J/eV} = 71 \text{ eV} \).

(Schrödinger’s) Wave Equation

In quantum mechanics the wave equation describes the behaviour of all matter. Let’s first try to understand the parts of the wave equation.

\[ \frac{-h^2}{2m} \nabla^2 \psi + V\psi = E\psi \]

\( h \) is Planck’s constant, \( h = 1.055 \times 10^{-34} \) J s.

\( m \) is the mass of the particle; in this case an electron = \( 9.11 \times 10^{-31} \) kg.

\( V \) is the potential energy that is a function of position in space.

\( E \) is the energy of the particle (electron) – a number.

\( \nabla^2 \) is the Laplace operator, i.e. its second derivative in space.

\( \psi \) denotes the wavefunction. The meaning of this function will take us some time to explore.

The wave equation is a postulate of quantum mechanics. There is no proof or evidence, except that it successfully describes aspects of the universe. Like the de Broglie relation, it has been repeatedly verified by experiment.
The wave equation is often treated in terms of operators.

\[ \frac{-\hbar^2}{2m} \nabla^2 \psi + V\psi = E\psi \]

The kinetic energy operator (take the 2nd derivative of the wavefunction and multiply by these constants).

The potential energy operator (multiply the potential energy function by the wavefunction).

The energy of the particle (electron) - a number.

The wave equation may be viewed as a statement about conservation of energy:
kinetic energy + potential energy = total energy.

What does the wave equation tell us?

\[ \frac{-\hbar^2}{2m} \nabla^2 \psi + V\psi = E\psi \]

Solving the wave equation for a particular potential energy function tells us
1. The wavefunction, \( \psi \).
2. 2. A value for the energy, \( E \).

The wave equation is a differential equation which typically has a set of solution functions (eigenfunctions), and a corresponding numerical value for \( E \) (an eigenvalue).

In this course you are not expected to solve any wave equations. However you will be expected to understand the wavefunction and allowed energies, so we need to go through the use of the wave equation in a bit of detail.

The potential energy function

The potential energy of interaction between a proton and an electron is described by the equation \( V(r) = -\frac{e^2}{4\pi\epsilon_0 r} \).

The electron (charge = \(-e\)) is attracted to the nucleus (charge = \(+e\)) by an electrostatic force. The potential energy depends on the inverse of the distance between the nucleus and the electron, \( r \), and on the product of the charges of the nucleus and the electron.

\( V(r) \) is zero when the proton and electron are an infinite distance apart, but is negative at all values of \( r \). That is, the potential energy of the electron bound to the nucleus is lower than that of a free electron.

We use the term “bound” to describe an electron (or any particle) held in place by an attractive potential energy.
The Wave Equation for the Hydrogen Atom

To solve the wave equation for the hydrogen atom, we substitute the electrostatic potential energy of interaction:

\[ V(r) = \frac{-e^2}{4\pi\varepsilon_0 r^2} \]

For more complex quantum mechanical systems, other potential energy functions are used, as we shall see later.

Solving the wave equation for a particular potential energy function tells us:
1. The wavefunction, \( \psi \). (next lecture)
2. A value for the allowed energy, \( E \), of each wavefunction

Allowed Energies of the Hydrogen Atom

The solution set of wavefunctions for the hydrogen atom has a set of allowed energies given by the equation:

\[ E_n = \frac{m c^2}{2 n^2} \]

where \( n = 1, 2, 3, \ldots \)

There is one specific energy for each wavefunction, \( \psi_n \).

These values tell us the energies that an electron is allowed to have when it is bound to a hydrogen nucleus. The energies are discrete, or quantized.

That is, only certain specific values of \( E \) are allowed. Values between, say \( -E_2 \) and \( -E_2/4 \) (\( n = 1 \& 2 \)) cannot exist.

The lowest allowed energy of the hydrogen atom (\( n = 1 \)) is \( E_1 = -2.18 \times 10^{-18} \) J. For \( n = 2 \), \( E_2 = -5.45 \times 10^{-19} \) J.

As \( n \) increases, \( E_n \) approaches the energy of an unbound electron, or 0.

The figure at right shows the allowed electronic energies of the hydrogen atom in their common representation as energy levels. (20 levels are shown, but their spacing is too close to be seen on this scale for \( n = 4 \).)
Allowed Energies of Hydrogen-Like Atoms

The Schrödinger equation can be solved for an electron bound by a nucleus of any charge. What happens with other “Hydrogen-like” nuclei, e.g. He2+, N6+?

The potential energy function for a nucleus of atomic number (and hence charge) \( Z \) is: \( V(r) = \frac{-Ze^2}{r} \).

The allowed energies now become

\[
E_n = -\frac{mZ^2e^4}{2\hbar^2} = -\frac{Z^2E_1}{n^2}
\]

That is, the energy of the bound states is lowered by the increased attraction of the more highly charged nucleus.

Hydrogen-like atoms have been created in the laboratory and detected in space, and provide experimental verification of these allowed energies.

Spectroscopy and Transitions between States

Spectroscopy is the study of how light interacts with matter. More specifically, it is the study of how photons of light can cause transitions between quantum states of an atom or molecules.

In electronic spectroscopy, light causes a change in the quantum state and therefore the energy of a bound electron. This energy change is often diagnostic for the atom or molecule that binds the electron.

Spectroscopy measures the energy difference between allowed energy levels.

For hydrogen-like atoms, the difference between energy levels is given by

\[
\Delta E = E_n - E_m = -Z^2E_1 \left( \frac{1}{n^2} - \frac{1}{m^2} \right)
\]

but how do we know the energy of light?

Light: Energy, Frequency, Wavelength

Light is an electromagnetic wave. It oscillates with a characteristic frequency or wavelength. Because the speed of light is fixed, the frequency, \( \nu \) (nu), and wavelength, \( \lambda \) (lambda), are related by

\[

\nu = \frac{c}{\lambda}
\]

where \( c \) is the speed of light, \( 3.0 \times 10^8 \) m s\(^{-1}\).

The energy of a light wave is directly proportional to its frequency (and thus inversely proportional to its wavelength),

\[
E = h\nu = \frac{hc}{\lambda}
\]
Energy, Frequency, Wavelength

Shorter wavelengths equate to higher frequency and higher energy. We broadly classify electromagnetic (EM) radiation into wavelength or frequency bands. In decreasing order of energy these are:

- gamma-rays, x-rays, UV, visible light, infrared, microwaves, radiofrequency

Within the visible band, violet is highest in energy and red lowest.

Energy (J)

- $10^{-15}$
- $10^{-19}$
- $10^{-23}$
- $10^{-25}$
- $10^{-29}$

### Energy, Frequency, Wavelength - Worked Example

**E.g. Calculate the energy of red light**

Referring to the previous diagram, $l = 750\text{nm}$. The energy is simply

$$E = \frac{hc}{l} = \frac{6.626 \times 10^{-34} \times 3.00 \times 10^8}{750 \times 10^{-9}} = 2.65 \times 10^{-19} \text{ J}$$

**E.g. Calculate the energy and wavelength of an x-ray of frequency $10^{18} \text{s}^{-1}$**

The energy is

$$E = h\nu = 6.626 \times 10^{-34} \times 10^{18} \text{ (J s)} = 6.63 \times 10^{-16} \text{ J}$$

and the wavelength is

$$\lambda = \frac{c}{\nu} = \frac{3 \times 10^8 \text{ (m/s)}}{\left(10^{18} \text{ (s)}\right)} = 3 \times 10^{-10} \text{ m} = 0.3 \text{ nm}$$

### Atomic Spectroscopy - Worked Example

**E.g. What wavelength of light will excite an electron in a hydrogen atom from n=1 to n=3?**

First, calculate the energy difference for $Z = 1$, $n = 3$, $m = 1$

$$\Delta E = -Z^2 \frac{E_1}{n^2} - \frac{1}{m^2} = -1 \times 2.18 \times 10^{-18} \times \left(\frac{1}{9} - \frac{1}{1}\right) = 1.94 \times 10^{-19} \text{ J}$$

Now, calculate the wavelength corresponding to that energy

$$\lambda = \frac{hc}{E} = \frac{6.626 \times 10^{-34} \times 3.00 \times 10^8}{1.94 \times 10^{-19} \text{ J}} = 1.02 \times 10^{-6} \text{ m}$$

or 102 nm

This wavelength lies in the ultraviolet range.

This is an example of an atomic spectral line, which was part of the early evidence for quantum effects in nature. We will examine these in more detail in Lectures 8 & 9.
Atomic Spectroscopy - Alternative Working

E.g. What wavelength of light will excite an electron in a hydrogen atom from n=1 to n=3?

First, equate the energy difference for Z=1, n=3, m=1 to the photon energy.

\[ \Delta E = E_Z - E_n = \frac{1}{2} \cdot \frac{R}{n^2} - \frac{1}{2} \cdot \frac{R}{m^2} \]

\[ \Rightarrow \lambda = \frac{hc}{Z^2E_n \left( \frac{1}{n^2} - \frac{1}{m^2} \right)} = \frac{6.626 \times 10^{-34} \times 3.00 \times 10^8}{2.18 \times 10^{-18} \times \left( \frac{1}{9} - \frac{1}{1} \right)} = 1.02 \times 10^{-3} \text{m} \]

This alternative is included because it also shows the form of the equation used (empirically) by Moseley in 1913 to fit his x-ray spectral lines (see lecture 5).

Atomic Spectrum of Hydrogen

Quantum mechanics can be used to explain atomic line spectra through these two relationships, which had previously been figured out empirically. That atomic visible line spectra of hydrogen fall into series had been known since Balmer in 1885 showed that they followed the equation

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

where \( R = E_R / hc \).

This series describes absorption or emission from hydrogen atoms with electrons in the 3rd, 4th, 5th, etc... energy levels dropping to the 2nd allowed level.

Other series occur at higher (ultraviolet) and at lower energies (infrared).
Summary
You should now be able to
• Name the key experimental observations that led to the development of quantum mechanics.
• Convert between velocity, kinetic energy or momentum and wavelength of a free electron (or other particle of known mass)
• Identify the components of the wave equation.
• Convert between wavelength, frequency and energy of light.
• Calculate the allowed energy of a hydrogen-like atom of atomic number Z and quantum number n, and the wavelength of a transition between energy levels.

Next Lecture
Quantum theory
• Properties of waves in 1, 2, and 3 dimensions
• Representing bound electron waves
• Atomic orbitals in hydrogen-like atoms