Lecture 5: The Periodic Table - Chemistry’s Next Big Idea

Lecture 6: Introductory Quantum Theory
  • Evidence for the failure of classical mechanics
  • The meaning of the Wave Equation
  • Electronic Structure of the Hydrogen Atom

Lecture 7: Quantum Theory
  • Properties of waves and shapes of electron orbitals
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 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.

Neils 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.
Experimental Evidence for Electron Matter Waves

C.J. Davisson 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:

- X-rays
- electrons

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.
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 x 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, $\lambda = \frac{6.626 \times 10^{-34}}{(9.11 \times 10^{-31} \times 5.0 \times 10^6)}$ J s kg$^{-1}$ m$^{-1}$ s

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

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 $1.1 \times 10^{-17} \text{ J}/1.602 \times 10^{-19} \text{ J/eV} = 71 \text{ eV}$. 
The Puzzle of the Electron Wave

1. Diffraction

Diffraction is a property often used to identify wave-like behaviour. As a wavefront passes through two slits the two new wavefronts interfere constructively and destructively with each other to produce a periodic pattern of high and low intensity on some detector. This 'two slit experiment' is sketched here. When a beam of electrons are directed at two slits they produce such a diffraction pattern, confirming their wave-like character during the passage through the slits.
2. Wave or Particle?
As shown here, however, this diffraction pattern is built up at the detector one particle-like impact at a time. This experiment nicely highlights the intuitive difficulty presented to us by the wave-particle duality at the heart of the quantum theory.
The electron wave must pass through both slits to produce this pattern in spite of the obvious particle-like response the electron produces at the detector. Any attempt to measure which slit the electron passed through will destroy the diffraction pattern.
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 $r < \infty$. 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.
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

\[ E_n = -\frac{m e^4}{2 \hbar^2 n^2} = -E_R \frac{1}{n^2} \]

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

The Rydberg constant, \( 2.18 \times 10^{-18} \text{ J} \)

Allowed energies in quantum mechanics are often written in terms of a set of quantum numbers such as \( n \).

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 \(-E_R\) and \(-E_R/4\) \((n = 1 \& 2)\) cannot exist.

If you want to see the details of the maths, read the Feynmann Lectures on Physics, Lecture 19.
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; \(E_3 = -2.42 \times 10^{-19}\) 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. He$^{2+}$, N$^{6+}$?

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

The allowed energies now become

$$E_n = -\frac{mZ^2e^4}{2\hbar^2n^2} = -E_R \frac{Z^2}{n^2}$$

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 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

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

but how do we know the energy of light?
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.
E.g. Calculate the energy of red light

Referring to the previous diagram, \( \lambda = 750\text{nm} \). The energy is simply

\[
E = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \times 3.00 \times 10^8}{750 \times 10^{-9}} \left( \frac{J \ s \ m \ s^{-1}}{m} \right) = 2.65 \times 10^{-19} \ J
\]

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

The energy is \( E = h\nu = 6.626 \times 10^{-34} \times 10^{18} \ (J \ s \ s^{-1}) = 6.63 \times 10^{-16} \ J \)

and the wavelength is \( \lambda = \frac{c}{\nu} = \frac{3 \times 10^8}{10^{18} \left( \frac{m \ s^{-1}}{s^{-1}} \right)} = 3 \times 10^{-10} \ m = 0.3 \ \text{nm} \)
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 \( Z = 1, n = 3, m = 1 \)

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

Now, calculate the wavelength corresponding to that energy

\[
\lambda = \frac{hc}{E} = \frac{6.626 \times 10^{-34} \times 3.00 \times 10^8}{1.94 \times 10^{-18} \left( \frac{J \text{ s m s}^{-1}}{J} \right)} = 1.02 \times 10^{-7} \text{ m}
\]

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

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

\[\Rightarrow \lambda = \frac{hc}{Z^2 E_R \left( \frac{1}{m^2} - \frac{1}{n^2} \right)}
\]

\[= \frac{6.626 \times 10^{-34} \times 3.00 \times 10^8}{2.18 \times 10^{-18} \times \left( \frac{1}{1} - \frac{1}{9} \right)}
\]

\[= 1.02 \times 10^{-7} m\]

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).

\[\frac{1}{\sqrt{\lambda}} = kZ\]
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

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

where \( R = \frac{E_R}{hc} \).

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 \(\text{ultraviolet}\)

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

and at lower energies \(\text{infrared}\)

\[
\frac{1}{\lambda} = R \left( \frac{1}{n^2} - \frac{1}{3^2} \right)
\]
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