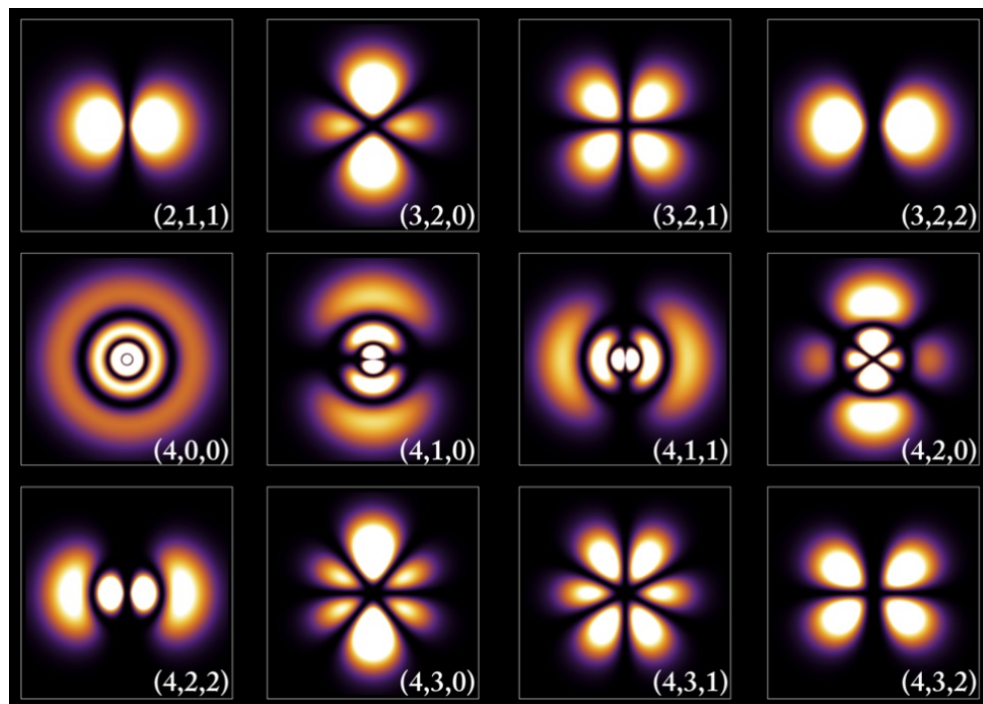


8.3: Quantum Mechanical Nature of the Atom



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Cover photo credit: Atomic orbitals of the electron in a hydrogen atom at different energy levels. Source: Wikipedia [public domain]

*Syllabus content: From the Universe to the Atom**Structure of the Atom*

Inquiry question: How is it known that classical physics cannot explain the properties of the atom?

Students:

- assess the limitations of the Rutherford and Bohr atomic models
- investigate the line emission spectra to examine the Balmer series in hydrogen
- relate qualitatively and quantitatively the quantised energy levels of the hydrogen atom and the law of conservation of energy to the line emission spectrum of hydrogen using:

- $E = hf$

- $E = \frac{hc}{\lambda}$

- $\frac{1}{\lambda} = R \left[\frac{1}{n_f^2} - \frac{1}{n_i^2} \right]$

- investigate de Broglie's matter waves, and the experimental evidence that developed the following formula:

- $\lambda = \frac{h}{mv}$

- analyse the contribution of Schrödinger to the current model of the atom

Bohr's Model of the atom

Atomic spectra

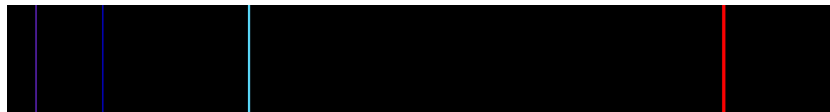


Figure 1: Visible emission spectra of hydrogen (The 'balmer series').

Newton was the first to observe that white light is composed of a continuous spectrum of colours. In 1853, Angstrom observed that the spectrum produced by an electrical discharge through hydrogen gas consisted of individual lines. In the visible region of the hydrogen spectra there are four lines, one red, one blue-green and two violet, as shown in figure 1.

Angstrom, and later Plücker, examined the spectra of many gases, and noted that they were unique to the gas that emitted them, providing a way of detecting the presence of that particular element. This work was later extended to many elements, including metals, by Kirchhoff and Bunsen.

Balmer's formula

In 1885 Johann Balmer, a swiss mathematics teacher, was the first to produce a mathematical formula which described the visible spectral lines of hydrogen (which now bear his name).

In 1888 Johannes Rydberg proposed a more general form of Balmer's equation. In modern notation his formula can be written as:

$$\frac{1}{\lambda} = R \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \quad (1)$$

where λ the wavelength of the spectral line, R is a constant now known as the Rydberg-Ritz constant and where n_f and n_i are integers, with $n_i > n_f$. For the visible hydrogen spectra, $n_f = 2$, however the formula predicts the existence of other spectral lines for hydrogen outside the visible range where n_f (in fact, it predicts an infinite number of lines!). Subsequent to Rydberg publishing his formula, the spectral lines for hydrogen in the UV (corresponding to $n_f = 1$) and the infrared (corresponding to $n_f = 3$) were discovered experimentally.



Figure 2: Johann Balmer. Image credit: Wikipedia [public domain].



Figure 3: Johannes Rydberg. Image credit: Wikipedia [public domain].

Introduction to Bohr's model

Bohr's model of the hydrogen atom was a great advance as it could predict the spectral lines that are observed for hydrogen, and it addressed the issue of the instability of the electron configuration.¹

Bohr began the first of his three papers of 1913 (which later became known as the 'great trilogy') by carefully pointing out the difficulties in the previous models by Thomson and Rutherford.²

In order to explain the results of experiments on scattering of α rays by matter Prof. Rutherford has given a theory of the structure of atoms. According to this theory, the atom consists of a positively charged nucleus surrounded by a system of electrons kept together by attractive forces from the nucleus; the total negative charge of the electrons is equal to the positive charge of the nucleus. Further, the nucleus is assumed to be the seat of the essential part of the mass of the atom, and to have linear dimensions exceedingly small compared with the linear dimensions of the whole atom. The number of electrons in an atom is deduced to be approximately equal to half the atomic weight. Great interest is to be attributed to this atom-model; for, as Rutherford has shown, the assumption of the existence of nuclei, as those in question, seems to be necessary in order to account for the results of the experiments on large angle scattering of the α rays.

In an attempt to explain some of the properties of matter on the basis of this atom-model we meet, however, with difficulties of a serious nature arising from the apparent instability of the system of electrons: difficulties purposely avoided in atom-models previously considered, for instance, in the one proposed by Sir. J.J. Thomson. According to the theory of the latter the atom consists of a sphere of uniform positive electrification, inside which the electrons move in circular orbits.

The principal difference between the atom-models proposed by Thomson and Rutherford consists in the circumstance that the forces acting on the electrons in the atom-model of Thomson allow of certain configurations and motion of the electrons for which the system is in a stable equilibrium; such configurations, however, apparently do not exist for the second atom-model.

Bohr then outlines how quantum theory forms the foundation for his new model of the atom:

Now the essential point in Planck's theory of radiation is that the energy radiation from an atomic system does not take place in the continuous way assumed in the ordinary electrodynamics, but that it, on the contrary, takes place in distinctly separated emissions, the amount of energy radiated out from an atomic vibrator of frequency f in a single emission being equal to nhf , where n is an entire number, and h is a universal constant.

¹ See the Phet on 'models of the hydrogen atom' for a nice visualisation: <https://phet.colorado.edu/en/simulation/hydrogen-atom>

² References for this section: Bohr, N. (1913), "On the constitution of Atoms and Molecules", Part 1, *Philosophical Magazine*, 26, 1-24. <http://web.ihep.su/dbserve/compas/src/bohr13/eng.pdf>, Pais, A. (1982). *Subtle is the Lord: The science and the life of Albert Einstein*. (Oxford: Oxford University Press), Kragh, H. (1999). *Quantum generations: A history of physics in the twentieth century*. (Princeton, New Jersey: Princeton University Press).

Bohr's assumptions

In his papers Bohr introduces a number of postulates (note that in other texts some may be combined - Bohr did not write them in exactly these words):

1. The electron moves in a circular orbit around the nucleus, with the required centripetal force provided by the electrostatic attraction between the electron and the nucleus.
2. Although the electron is continually accelerating, it does not lose energy by emitting electromagnetic radiation.
3. The electron cannot orbit at any radius, only fixed values, where $mvr = n\hbar$ where mvr is the angular momentum of the electron, n is an integer and $\hbar = \frac{h}{2\pi}$
4. The electron emits or absorbs electromagnetic radiation as it discontinuously moves between these fixed orbits, where the energy of the photon emitted or absorbed is equal to the energy difference between the orbits (so that $hf = E_i - E_f$).

Note that the postulates use a mixture of classical mechanics (postulate 1) and quantisation (postulate 3). The second postulate is proposing that classical mechanics - the predictions of Maxwell's equations - cannot be applied (without modification) to a physical system as small as an atom. This is a distinct break from previous efforts by Thomson and others to describe the behaviour of electrons in atoms using classical physics. The final postulate addresses the mechanism for the production of spectra by atoms, and also utilises Planck's quantisation theory.

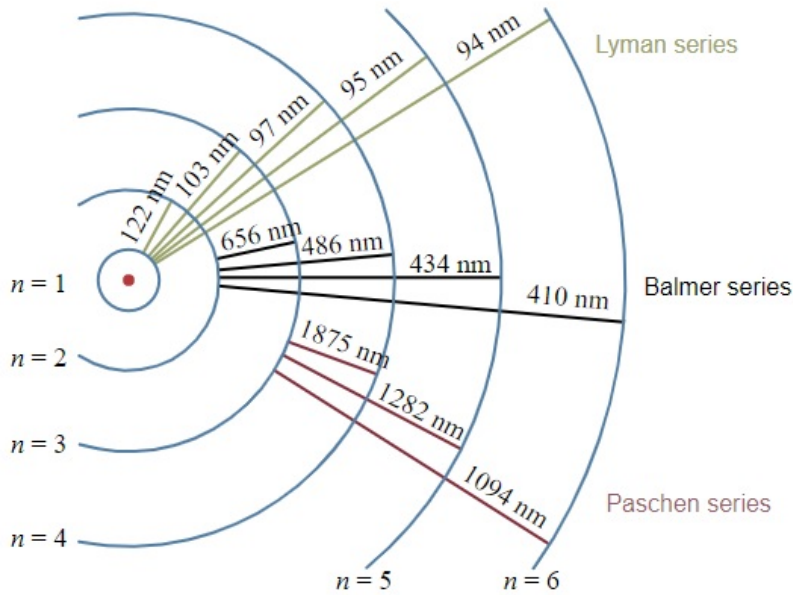


Figure 4: Transitions of electrons in the Bohr model responsible for the Balmer series (as well as the Lyman UV and Paschen infrared series).

Image credit: https://commons.wikimedia.org/wiki/File:Hydrogen_transitions.svg

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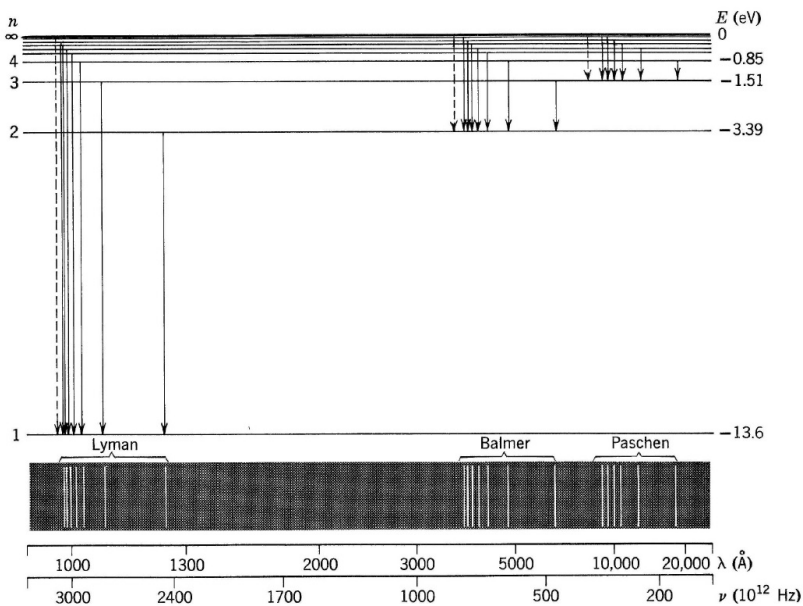


Figure 5: The energy level diagram for hydrogen. Note that the Balmer series finishes on the $n = 2$ energy level.

Image credit: Figure 4-12 from
Eisberg, R. Resnick, R. (1974) Quantum
Physics of Atoms, Solids, nuclei and
particles. (John Wiley Sons, New York).

Limitations of Bohr's model

The Bohr model was the first important step in the application of quantisation to the atom, but it had obvious limitations. These included:

- The relative intensity (brightness) of different spectral lines. These occur due to the different probabilities of different transitions (The Bohr model cannot account for this)
- The spectra of larger atoms are not described by the Bohr model, which is limited to one electron systems (it is reasonably accurate for singly ionised Helium, another one electron system)
- It does not predict the Zeeman effect, the splitting of spectra lines which occurs if an atom is subject to an external magnetic field due to the magnetic dipole moment of the electrons
- It does not predict hyperfine splitting of spectral lines, due to the interaction between the intrinsic magnetic dipole moment of the nucleus and a magnetic field produced by the atomic electrons and/or the interaction between a non-spherically symmetrical nuclear charge distribution and a non-spherically symmetric electric field produced by the atomic electrons.

De Broglie's matter waves

Louis de Broglie (later Prince Louis de Broglie!) proposed the existence of matter waves in his doctoral (PhD) thesis in 1924. His hypothesis was one that suggested a deep symmetry in nature - just as light is found to exhibit both wave-like and particle-like behaviour, so too matter is subject to waveparticle duality. Initially the idea was met with skepticism due to the lack of experimental evidence, but Einstein provided support for the idea³. We can begin by considering the derivation for the momentum of a photon, which is a massless particle. From special relativity we have the expression for relativistic energy:

$$E^2 = (pc)^2 + (mc^2)^2$$

For particles with zero rest mass, such as the photon, this becomes

$$E = pc$$

Putting this together with the expression for the energy of a photon obtained from quantum theory we have:

$$pc = hf = \frac{hc}{\lambda}$$

so finally

$$\lambda = \frac{h}{p}$$

De Broglie's insight was that this link between the energy and frequency, and between the momentum and wavelength holds for particles with mass as well as for light.

De Broglie's hypothesis:

Matter has both wave and particle properties.

The wavelength λ associated with a particle with momentum p is

$$\lambda = \frac{h}{p}$$

In the context of the hydrogen atom, he suggested that if the electron was behaving as a wave as it orbited the nucleus, then it would need to orbit at radii where it constructively interfered with itself. That is, where the circumference of the orbit was an integer number of wavelengths:

$$n\lambda = 2\pi r$$

If we substitute in De Broglie's proposal that the wavelength of the electron is $\lambda = h/p$ we obtain Bohr's quantisation condition:

$$mvr = h \frac{n}{2\pi}$$



Figure 6: Louis de Broglie. Credit: Wikipedia [public domain].

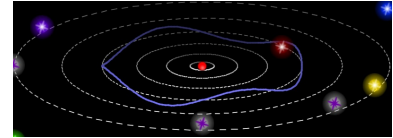


Figure 7: Visualisation of the De Broglie standing wave for $n = 4$ in Bohr's model of the atom

³ Eisberg, R. Resnick, R. (1974) Quantum Physics of Atoms, Solids, nuclei and particles. (John Wiley Sons, New York).

This provides some level of physical explanation for the quantisation of angular momentum that occurs in Bohr's theory.

Experimental evidence for De Broglie's proposal - Davisson and Germer

Davisson and Germer were working at Bell labs in 1925, analysing the reflection of electrons from a polycrystalline Nickel metal surface (that is, consisting of many tiny crystals of nickel oriented randomly). An accident in the lab caused the surface to become oxidised, and as they heated it to remove the oxygen they found that the Nickel had recrystallised into a single crystal - a regular array of atoms. They did some initial experiments and obtained unexpected results. It was only after Davisson went to England and discussed his experiment with a number of physicists that it became apparent that the results they were obtaining were those predicted by De Broglie's theory - they were seeing diffraction of electron waves by a crystal lattice.

Their experimental setup is shown in figure 8. The electron gun consists of a filament heated by a large electrical current (to give electrons sufficient energy to overcome the work function of the metal in the filament) and a large accelerating voltage which produces a beam of electrons of known velocity. The beam is incident on a nickel crystal and the amplitude of the reflected/scattered beam is measured and the process repeated at different angles of incidence and different accelerating voltages.

Davisson and Germer found that peaks in the intensity of the reflected beam obeyed the same relationship as that obtained by the Braggs for reflection of X-rays from a crystal lattice:

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

(in this case the wavelength λ is that predicted by De Broglie) and these results provided confirmation of De Broglie's hypothesis that matter could exhibit wave-like as well as particle-like behaviour. Davisson, as well as George Thomson, son of J.J. Thomson, who performed other experiments confirming De Broglie's hypothesis, were awarded the Nobel prize in 1937 for their experimental discovery of the diffraction of electrons by crystals. De Broglie was awarded the Nobel prize in 1929 for "the discovery of the wave nature of electrons".

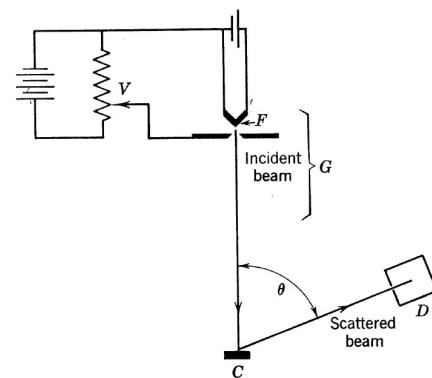


Figure 8: Davisson and Germer's experimental setup to measure electron diffraction by a Ni lattice. Figure credit: Eisberg, R. Resnick, R. (1974) Quantum Physics of Atoms, Solids, nuclei and particles. (John Wiley Sons, New York).

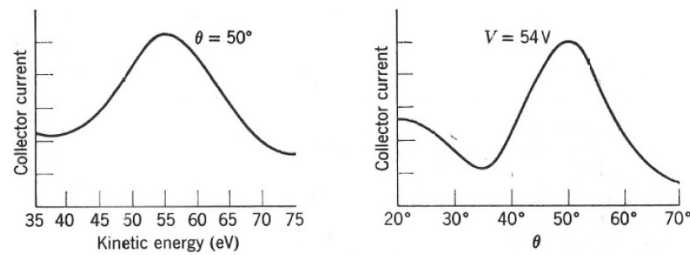


Figure 3-2 Left: The collector current in detector *D* of Figure 3-1 as a function of the kinetic energy of the incident electrons, showing a diffraction maximum. The angle θ in Figure 3-1 is adjusted to 50° . If an appreciably smaller or larger value is used, the diffraction maximum disappears. Right: The current as a function of detector angle for the fixed value of electron kinetic energy 54 eV.

Figure 9: Figure credit: Eisberg, R. Resnick, R. (1974) Quantum Physics of Atoms, Solids, nuclei and particles. (John Wiley Sons, New York).

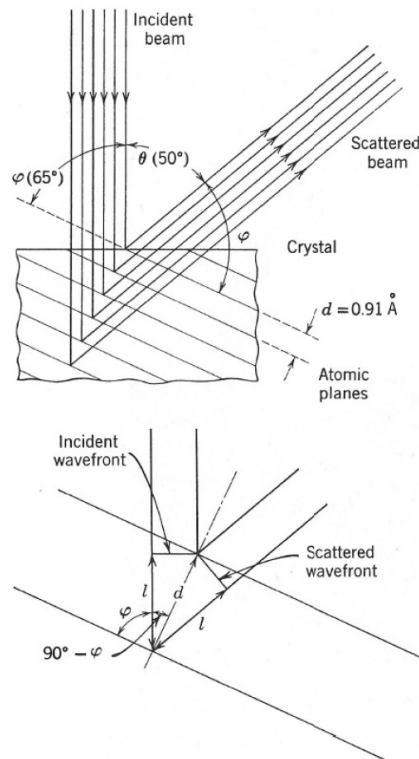


Figure 3-3 Top: The strong diffracted beam at $\theta = 50^\circ$ and $V = 54 \text{ V}$ arises from wavelike scattering from the family of atomic planes shown, which have a separation distance $d = 0.91 \text{ \AA}$. The Bragg angle is $\phi = 65^\circ$. For simplicity, refraction of the scattered wave as it leaves the crystal surface is not indicated. Bottom: Derivation of the Bragg relation, showing only two atomic planes and two rays of the incident and scattered beams. If an integral number of wavelengths $n\lambda$ just fit into the distance $2l$ from incident to scattered wave fronts measured along the lower ray, then the contributions along the two rays to the scattered wave front will be in phase and a diffraction maximum will be obtained at the angle ϕ . Since $l/d = \cos(90^\circ - \phi) = \sin \phi$, we have $2l = 2d \sin \phi$, and so we obtain the Bragg relation $n\lambda = 2d \sin \phi$. The "first order" diffraction maximum ($n = 1$) is usually most intense.

Figure 10: Figure credit: Eisberg, R. Resnick, R. (1974) Quantum Physics of Atoms, Solids, nuclei and particles. (John Wiley Sons, New York).

Schrödinger's contribution to the current model of the atom

De Broglie was responsible for the idea that particles could behave as waves, but did not develop a detailed mathematical theory that could be applied to quantum systems such as the hydrogen atom.

Inspired by De Broglie's work, Erwin Schrödinger developed and published his wave mechanics between 1925-1926.⁴

Schrödinger's theory specifies the laws of wave motion that the particles of any microscopic system obey. It is an *internally consistent* theory, which does not involve the "cobbling together" of classical and quantum ideas that was present in Bohr's model of the atom.

In Schrödinger's theory:

- Particles are described by a "wave function". This wavefunction does not have physical significance in the same sense as the wave equation which describes the amplitude of a water or sound wave in classical physics. Rather, the square of Schrödinger's wavefunction (more precisely, the product of the wavefunction and its complex conjugate) can be understood as the *probability* that a particle is found at a particular position and time (Born's postulate).
- Schrödinger's equation itself is a statement that the total energy of a particle is equal to the sum of its kinetic and potential energies.
- Relationships between the total energy of the particle and the frequency of the wavefunction ($E = hf$, Planck's quantisation condition) and between the kinetic energy of the particle ($KE = \frac{p^2}{2m}$) and the wavelength ($p = \frac{h}{\lambda}$, De Broglie's postulate) arise naturally, and do not have to be asserted or assumed in an ad-hoc manner.

Schrödinger's theory can be applied to the hydrogen atom by using a potential energy function that is inversely proportional to the distance from the nucleus. The solutions (eigenfunctions) for the wavefunction of bound electrons in the hydrogen atom can be expressed in terms of three *quantum numbers*. The fact that three numbers are required arises directly from the fact that the solutions correspond to three-dimensional "standing waves" for electrons.

These quantum numbers are known as the

- *principal* quantum number, which can take the values $n = 1, 2, 3, \dots$ and refers to the shell (in the sense of Bohr's model) that the electron occupies
- *orbital* or *azimuthal* quantum number, which can take the values $l = 0, 1, 2, \dots, n - 1$, and represents the magnitude of the orbital



Figure 11: Erwin Schrödinger. [Public domain]

⁴ References for this section: Gamow, G. (1966). *Thirty years which shook physics: The story of Quantum Theory*. (New York: Dover publications), Kragh, H. (1999). *Quantum generations: A history of physics in the twentieth century*. (Princeton, New Jersey: Princeton University Press). Eisberg, R. Resnick, R. (1974) *Quantum Physics of Atoms, Solids, nuclei and particles*. (John Wiley Sons, New York). Pais, A. (1982). *Subtle is the Lord: The science and the life of Albert Einstein*. (Oxford: Oxford University Press)

angular momentum, and refers to the subshell that the electron occupies (e.g. 's', 'p', 'd' or 'f').

- *magnetic* quantum number, which can take the values $m = -l, \dots, l$, and represents the z-component (i.e. the projection) of angular momentum, and refers to the orientation of the subshell (i.e. whether a 'p' subshell is orientated along the x-, y-, or z-axis).

See the image on the front cover for illustrations of the probability density functions associated with different combinations of these quantum numbers.

In developing a self-consistent wave-theory of quantum mechanics Schrödinger made a significant and enduring contribution to our current understanding of the atom.

Extension: Schrödinger's equation (NOT syllabus content)

Here our aim here is to demonstrate that Schrödinger's equation:

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

is plausibly an expression for the total energy of a particle, where the first term represents the kinetic energy and the rightmost term represents its total energy, and that the solutions to this equation meet Planck's condition that the total energy of a particle is $E = hf$ and De Broglie's condition that the momentum of the particle is $= \frac{h}{\lambda}$.

The energy of a (non-relativistic) particle is:

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

If a particle has no net force acting on it then this total energy remains constant over time (and is independent of position). If a particle is to obey Einstein/Planck's condition that the total energy of a particle is $E = hf$ and De Broglie's criteria that the momentum of the particle is $p = \frac{h}{\lambda}$, then the expression for the total energy of a (non-relativistic) particle could also be written as:

$$\frac{h^2}{2m\lambda^2} + V = hf$$

By taking the partial derivatives with respect to position and time, show that the following wave-function is a solution of Schrödinger's equation for $V(x,t) = V_0$ (i.e. no force acting), and that it satisfies the (non-relativistic) equation for the energy of a particle given above:

$$\Psi(x,t) = \cos\left(\frac{2\pi x}{\lambda} - \frac{2\pi t}{T}\right) + i \sin\left(\frac{2\pi x}{\lambda} - \frac{2\pi t}{T}\right)$$