Light and other electromagnetic radiation – applications in biology

1. [A brief history of electromagnetic radiation](http://members.aol.com/WSRNet/D1/hist.htm)

   (http://members.aol.com/WSRNet/D1/hist.htm)

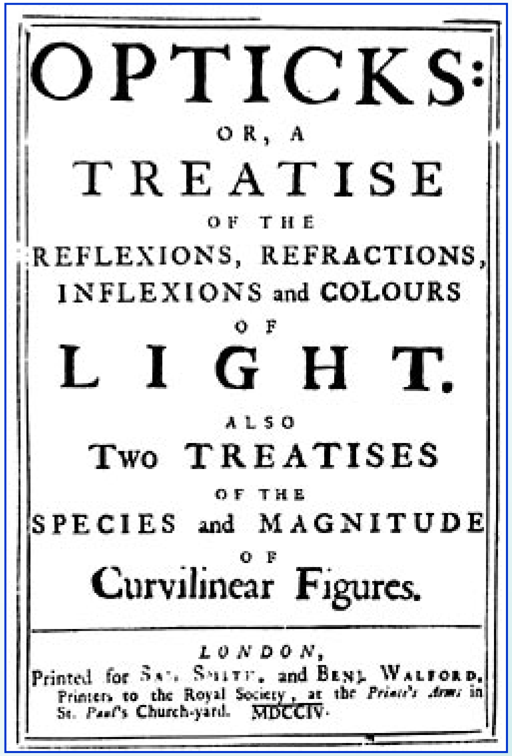
1. Wave nature of light
2. An introduction to quantum mechanics – dual nature of electromagnetic radiation
3. The Schrödinger equations

Some examples of applications in biology

1. Absorption of light
   a. Characterization by spectrum
   b. Measurement of concentration
   c. Kinetics, - variation of concentration with time
   d. Polarization, circular dichroism, orientation of molecules
   e. Light scattering, - molecular size
2. Fluorescence
   a. Distance measurements by FRET
   b. Diffusion times by FRAP
   c. Lifetime of excited states – physics → physiology of photosynthesis
3. Magnetic resonance
4. X-ray crystallography

~300 BC	Euclid (Alexandria) In his *Optica* he noted that light travels in straight lines and described the law of reflection. He believed that vision involves rays going from the eyes to the object seen and he studied the relationship between the apparent sizes of objects and the angles that they subtend at the eye
Probably between 100 BC and 150 AD	Hero (also known as Heron) of Alexandria. In his *Catoptrica*, Hero showed by a geometrical method that the actual path taken by a ray of light reflected from a plane mirror is shorter than any other reflected path that might be drawn between the source and point of observation.
~140 AD	Claudius Ptolemy (Alexandria). In a twelfth-century latin translation from the arabic that is assigned to Ptolemy, a study of refraction, including atmospheric refraction, was described. It was suggested that the angle of refraction is proportional to the angle of incidence
965-1020	Ibn-al-Haitham (also known as Alhazen) (b. Basra). In his investigations, he used spherical and parabolic mirrors and was aware of spherical aberration. He also investigated the magnification produced by lenses and atmospheric refraction. His work was translated into latin and became accessible to later european scholars
~1220	Robert Grosseteste (England). *Magister scholarum* of the University of Oxford and a proponent of the view that theory should be compared with observation, Grosseteste considered that the properties of light have particular significance in natural philosophy and stressed the importance of mathematics and geometry in their study. He believed that colours are related to intensity and that they extend from white to black, white being the purest and lying beyond red with black lying below blue. The rainbow was conjectured to be a consequence of reflection and refraction of sunlight by layers in a 'watery cloud' but the effect of individual droplets was not considered. He held the view, shared by the earlier Greeks, that vision involves emanations from the eye to the object perceived.
~1267	Roger Bacon (England). A follower of Grosseteste at Oxford, Bacon extended Grosseteste's work on optics. He considered that the speed of light is finite and that it is propagated through a medium in a manner analogous to the propagation of sound. In his Opus Maius, Bacon described his studies of the magnification of small objects using convex lenses and suggested that they could find application in the correction of defective eyesight. He attributed the phenomenon of the rainbow to the reflection of sunlight from individual raindrops
~1270	Witelo (Silesia). Completed his *Perspectiva* which was destined to remain a standard text on optics for several centuries. Amongst other things, Witelo described a method of machining parabolic mirrors from iron and carried out careful observations on refraction. He recognised that the angle of refraction is not proportional to the angle of incidence but was unaware of total internal reflection
1303	Bernard of Gordon (France). A Physician, he mentioned the use of spectacles as a way of correcting long-sightedness
1304~1310	Theodoric (Dietrich) of Freiberg. Theodoric explained the rainbow as a consequence of refraction and internal reflection within individual raindrops. He gave an explanation for the appearance of a primary and secondary bow but, following earlier notions, he considered colour to arise from a combination of darkness and brightness in different proportions
~1590	Zacharius Jensen (Netherlands). Constructed a compound microscope with a converging objective lens and a diverging eye lens
1604	Johannes Kepler (Germany). In his book *Ad Vitellionem Paralipomena*, Kepler suggested that the intensity of light from a point source varies inversely with the square of the distance from the source, that light can be propagated over an unlimited distance and that the speed of propagation is infinite. He explained vision as a consequence of the formation of an image on the retina by the lens in the eye and correctly described the causes of long-sightedness and short-sightedness
1608	Hans Lippershey (Netherlands). Constructed a telescope with a converging objective lens and a diverging eye lens
1609	Galileo Galilei (Italy).Constructed his own version of Lippershey's telescope and started to use it for astronomical observations
1610	Galileo Galilei (Italy). Using his telescope, Galileo reported several astronomical discoveries including that Jupiter has four moons
1611	Johannes Kepler (Germany). In his *Dioptrice*, Kepler presented an explanation of the principles involved in the convergent/divergent lens microscopes and telescopes. In the same treatise, he suggested that a telescope could be constructed using a converging objective and a converging eye lens and described a combination of lenses that would later become known as the telephoto lens. He discovered total internal reflection, but was unable to find a satisfactory relationship between the angle of incidence and the angle of refraction
~1618	Christopher Scheiner. Constructed a telescope of the type suggested by Kepler with converging objective and eye lenses. This type of telescope has since become known as the 'astronomical telescope' but it is uncertain when the first such instrument was constructed

Isaac Newton (1643 – 1727)



OPTICKS:

OR, A

TREATISE

OF THE

REFLEXIONS, REFRACTIONS, INFLEXIONS and COLOURS

OF

LIGHT.

ALSO

Two TREATISES

OF THE

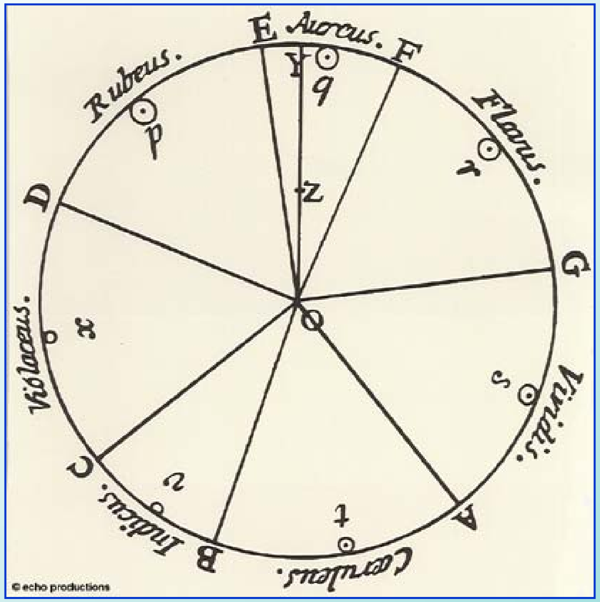
SPECIES and MAGNITUDE

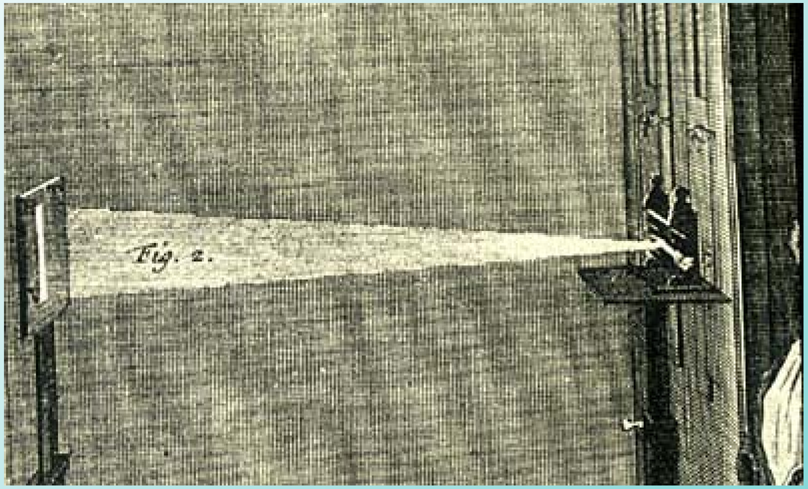
OF

Curvilinear Figures.

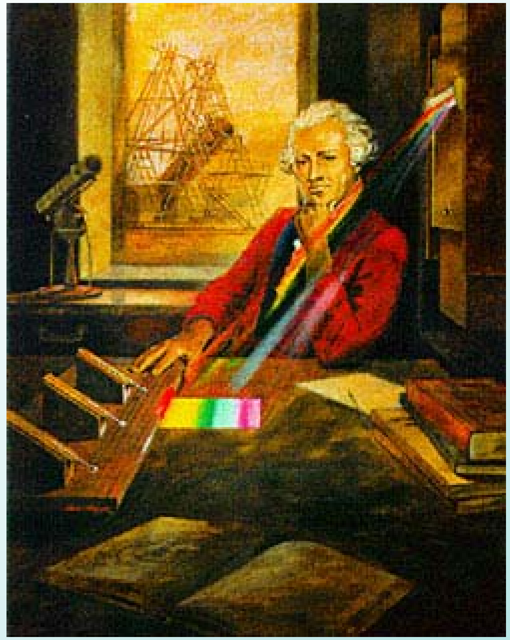
LONDON,

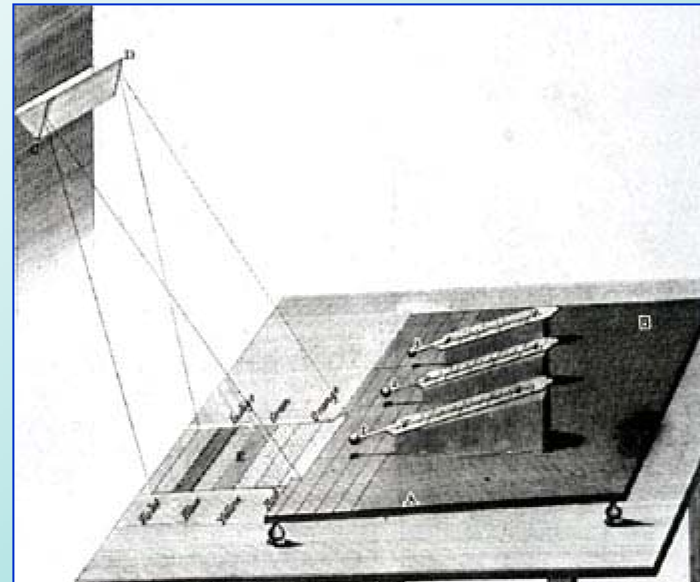
Printed for Sam. Smith, and Benj. Walford, Printers to the Royal Society, at the *Prince's Arms* in St. *Paul's* Church-yard. MDCCIV.





Frederick William Herschel (1738 - 1822) – demonstrated the infrared spectrum by measuring heat.





Johann Wilhelm Ritter (1776 -1810)

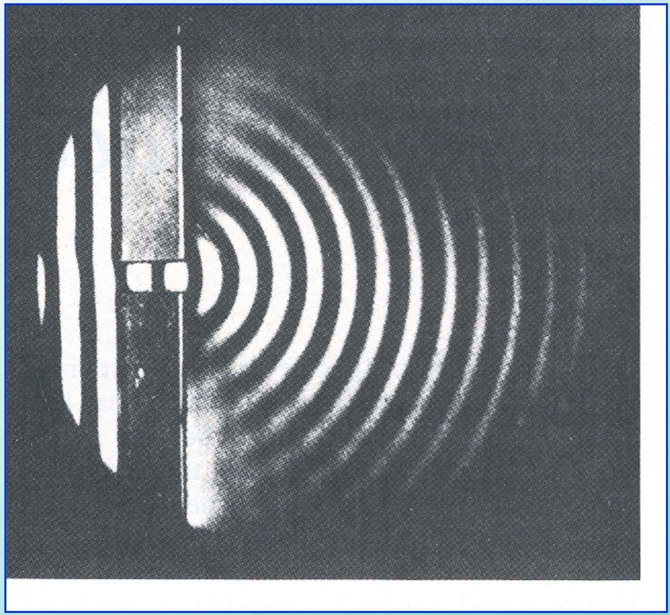
His main discovery was the ultraviolet region of the spectrum. He believed it "…broadened man's view beyond the narrow region of visible light …".

Ritter discovered that silver chloride decomposed in the presence of light, and that it decomposed at an even faster rate when exposed to invisible light. This proved that there was unknown radiation beyond the violet end of the spectrum - thenceforward to be called 'ultraviolet'.

1676	Olaf Römer (Denmark) Deduced that the speed of light is finite from detailed observations of the eclipses of the moons of Jupiter. From Römer's data, a value of about 2×10^8 $m.s^{-1}$ is obtainable
1678	Christiaan Huygens (Netherlands). In a communication to the Academie des Science in Paris, Huygens propounded his wave theory of light (published in his *Traite de Lumiere* in 1690). He considered that light is transmitted through an all-pervading aether that is made up of small elastic particles, each of which can act as a secondary source of wavelets. On this basis, Huygens explained many of the known propagation characteristics of light, including the double refraction in calcite discovered by Bartholinus
1704	Isaac Newton (England). In his *Opticks*, Newton put forward his view that light is corpuscular but that the corpuscles are able to excite waves in the aether. His adherence to a corpuscular nature of light was based primarily on the presumption that light travels in straight lines whereas waves can bend into the region of shadow
1727	James Bradley (England). Bradley calculated the speed of light from observations of the 'aberration' of light from stars, an apparent motion of a star arising from the value of the speed of light in relation to the speed of the earth in its orbit
1733	Chester More Hall. Constructed an achromatic compound lens using components made from glasses with different refractive indices
1752	Thomas Melvill (Scotland). Observed that the spectra of flames into which metals or salts have been introduced show bright lines characteristic of what has been introduced into the flame
1801	Thomas Young (b. England). Provided support for the wave theory by demonstrating the interference of light
1802	William Hyde Wollaston (England). Discovered that the spectrum of sunlight is crossed by a number of dark lines, but he did not interpret them in accordance with current explanations [Phil.Trans.Roy.Soc., London. p365, 1802]
1808	Etienne Louis Malus (France). As a result of observing light reflected from the windows of the Palais Luxembourg in Paris through a calcite crystal as it is rotated, Malus discovered an effect that later led to the conclusion that light can be polarized by reflection
1814	Joseph Fraunhofer (Germany). Fraunhofer rediscovered the dark lines in the solar spectrum noted by Wollaston and determined their position with improved precision
1815	David Brewster (Scotland). Described the polarization of light by reflection
1816	Augustin Jean Fresnel (France). Presented a rigorous treatment of diffraction and interference phenomena showing that they can be explained in terms of a wave theory of light
1816-1817	As a result of investigations by Fresnel and Dominique Francois Arago on the interference of polarized light and their subsequent interpretation by Thomas Young, it was concluded that light waves are transverse and not , as had been previously thought, longitudinal
1819	Joseph Fraunhofer (Germany). Described his investigations of the diffraction of light by gratings which were initially made by winding fine wires around parallel screws
1821	Augustin Jean Fresnel (France). Presented the laws which enable the intensity and polarization of reflected and refracted light to be calculated
1823	Joseph Fraunhofer (Germany). Published his theory of diffraction
1828	William Nicol (Scotland). Invented a polarizing prism made from two calcite components. The device became known subsequently as a "nicol prism"
1834	John Scott Russell (Scotland). Observed a 'wave of translation' caused by a boat being drawn along the Union Canal in Scotland, and noted how it travelled great distances without apparent change of shape. Such waves subsequently became known as 'solitary waves' and their study led to the idea of solitons, optical analogues of which have been propagated in optic fibres [Report of the 14th meeting of the British Association for the Advancement of Science, p311, 1844]
1835	George Airy (England). Calculated the form of the diffraction pattern produced by a circular aperture
1845	Michael Faraday (England). Described the rotation of the plane of polarized light that is passed through glass in a magnetic field (the Faraday effect)
1849	Armand Hypolite Louis Fizeau (France). Using a rotating toothed wheel to break up a light beam into a series of pulses, Fizeau made the first non-astronomical determination of the speed of light (in air). Obtained a value of 313,300 $km.s^{-1}$

Newton's theory of light was "corpuscular"; he believed that light must be made of particles, because it didn't bend around corners in the way that waves were observed to do.

Huygens in contrast believed that "…an expanding sphere of light behaves as if each point on the wave front were a new source of radiation of the same frequency and phase."



Huygens' principle illustrated by water waves

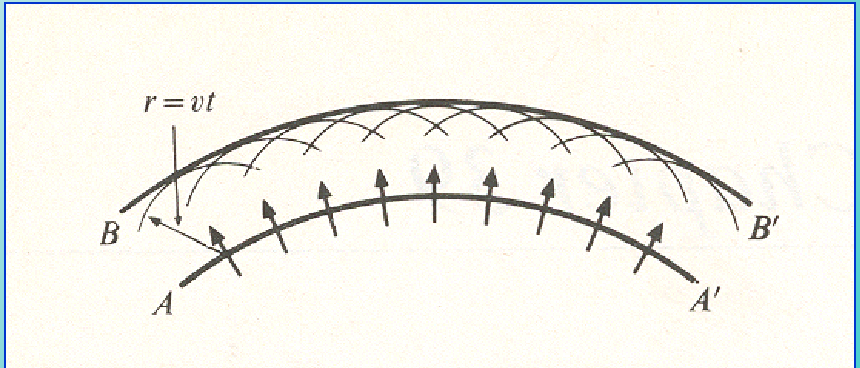
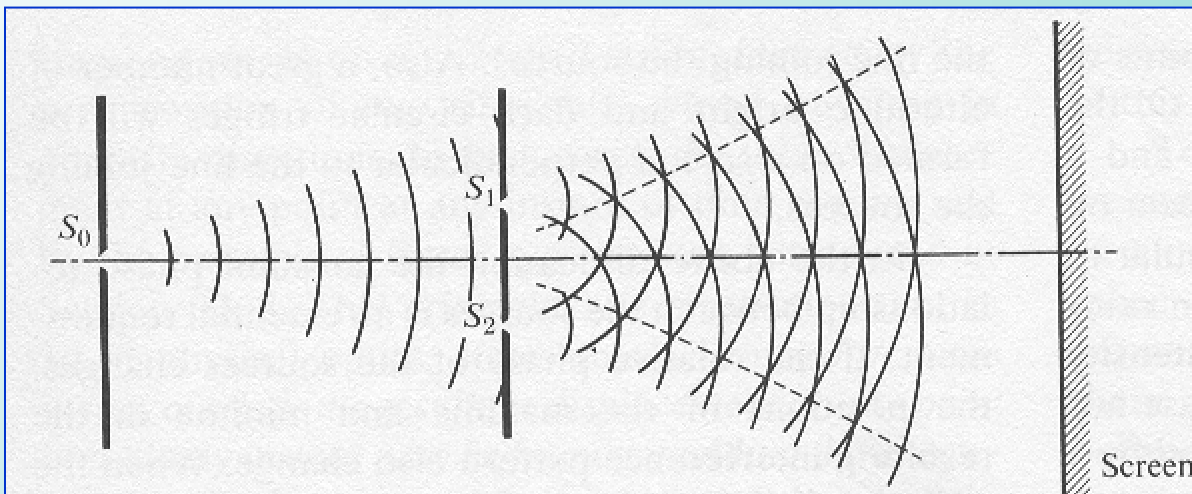


Fig. 39–1 Huygens' principle.

Young's experiment with light shining through a set of slits showed **diffraction**. This was as expected from Huygens' hypothesis, and showed that light did bend around corners. Disproved Newton's corpuscular hypothesis.



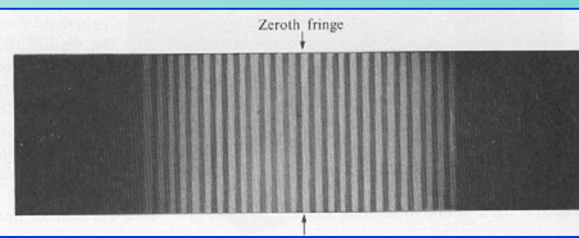
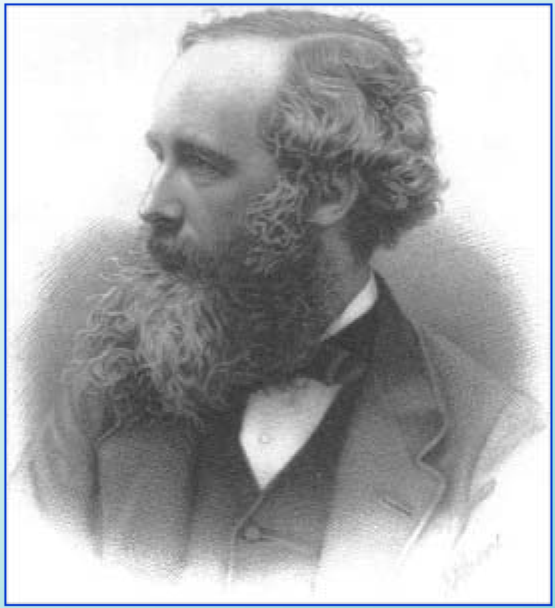


Fig. 42–3 Interference fringes produced by Young's double-slit intefer-ometer.

James Clerk Maxwell
(1831-1879)

Maxwell's theory "…*remains for all time one of the greatest triumphs of human intellectual endeavor.*"

Max Planck

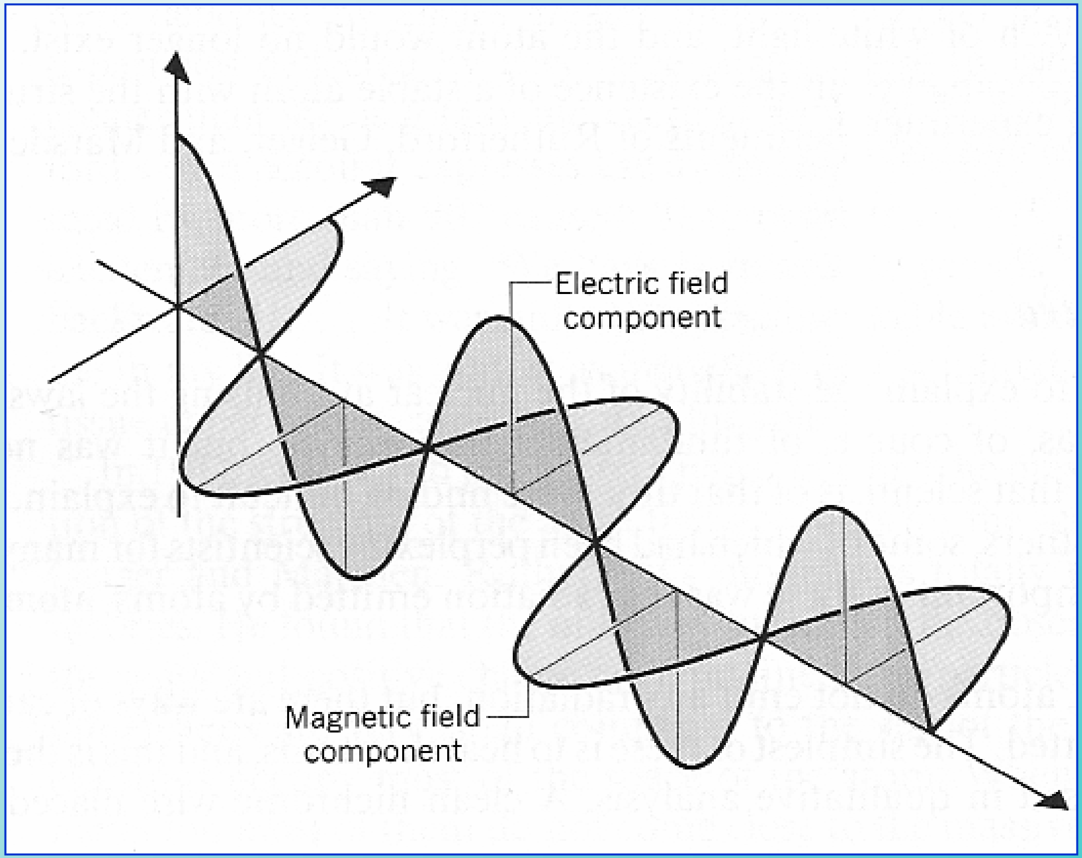


i) That **a changing magnetic field should always be related to a changing electric field**.
ii) That 'the rate of propagation of transverse vibrations...agrees so exactly with the velocity of light...that we can scarcely avoid the inference that **light consists in the transverse vibrations of the same medium which is the cause of electric and magnetic phenomena**'.
ii) In his 1864 **Dynamical Theory of the Electromagnetic Field**, Maxwell argued not simply that the optical and electromagnetic **media** were the same, but that "**light itself (including radiant heat, and other radiations if any) is an electromagnetic disturbance in the form of waves propagated through the electromagnetic field**'.

Heinrich Rudolph Hertz
(1857 - 1894)

In 1887 Hertz tested Maxwell's hypothesis. He used an oscillator made of polished brass knobs, each connected to an induction coil and separated by a tiny gap over which sparks could leap. Hertz reasoned that, if Maxwell's predictions were correct, electromagnetic waves would be transmitted during each series of sparks. To confirm this, Hertz made a simple receiver of looped wire. At the ends of the loop were small knobs separated by a tiny gap. The receiver was placed several yards from the oscillator. According to theory, if electromagnetic waves were spreading from the oscillator sparks, they would induce a current in the loop that would send sparks across the gap. This occurred when Hertz turned on the oscillator, producing the first transmission and reception of electromagnetic waves.

By the end of the 19th century, with the development of Maxwell's field equations, the entire electromagnetic spectrum was explained by a few beautiful equations. All electromagnetic waves traveled at the speed of light, showed interference, diffraction, polarization, and changes in refraction in appropriate materials. They could be detected by a suitable "antenna", ranging in size from the atomic and molecular to the antennae of radio stations, to match the wavelength. The equations explained the phenomena of induction (Faraday's Laws), and so embraced electricity and magnetism.

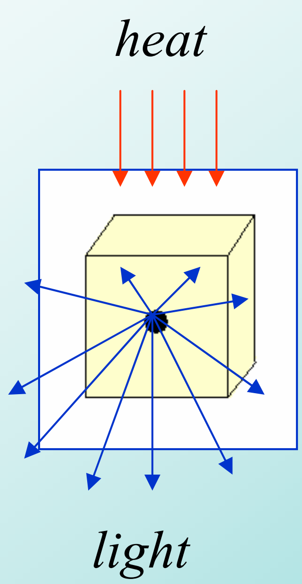


Aspects of quantum mechanics important to an understanding of spectroscopy

Critical experiments in the development of quantum mechanics.

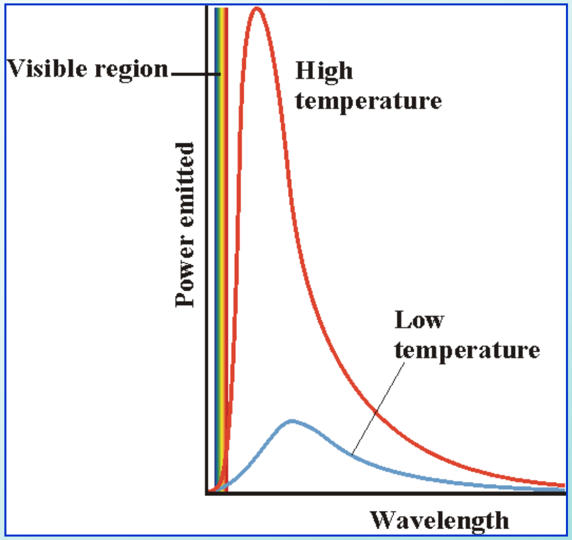
1. Black body radiation and the UV catastrophe explained by quantized energy levels for light and emitting oscillators (Planck).
2. Quantized energy changes in atoms (photoelectric effect, H-lines).
3. Dual nature of electron (and other matter) (De Broglie, Einstein, cathode rays, electron charge, electron diffraction).
4. Bohr's explanation for H-emission lines.
5. Additional quantum mechanical developments (Heisenberg's Uncertainty Principle, Relativity, Schrödinger).
6. Schrödinger time independent equation; particle-in-a-box.
7. Eigenfunctions and eigenvalues – quantum numbers for electron orbitals, molecular orbitals.
8. Spin and magnetic field (Dirac, Heisenberg, Pauli exclusion principle).

Dual nature of electromagnetic radiation – wave and particle



Light emitted by a black body has a spectrum that depends on temperature. The "ideal black body" is a box with black walls, opening to the exterior through a small hole. Radiation escaping through the hole will be in thermal equilibrium with the temperature of the walls.

Ultraviolet catastrophe



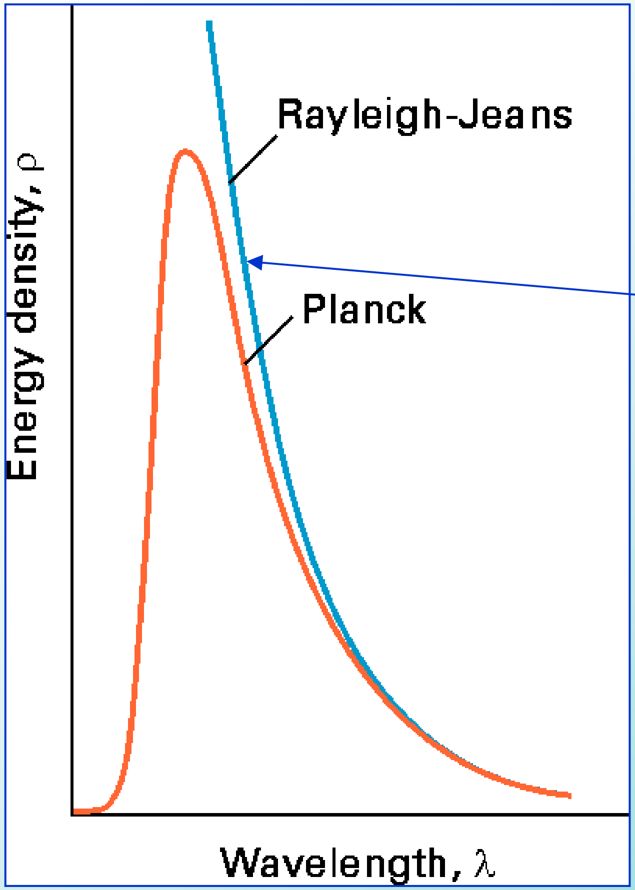
from Atkins, The Elements of Physical Chemistry

Classical physics attempted to explain the shape of the curve of power (or energy density, ρ) as a function of wavelength through three laws.

Wien's displacement law: $T\lambda_{max}$= constant (T is absolute temp., λ_{max} is the peak of the curve, and the constant has a value of 2.9 mm K).

Stefan-Boltzman law: $M = aT^4$ (M is the emittance (total power per unit area), and a has the value 56.7 nW m^{-2} K^{-4}). This is why bulb filaments are run hot!

Rayleigh-Jeans law, which we will discuss next. The first two laws worked fine, but not the Rayleigh-Jeans law.



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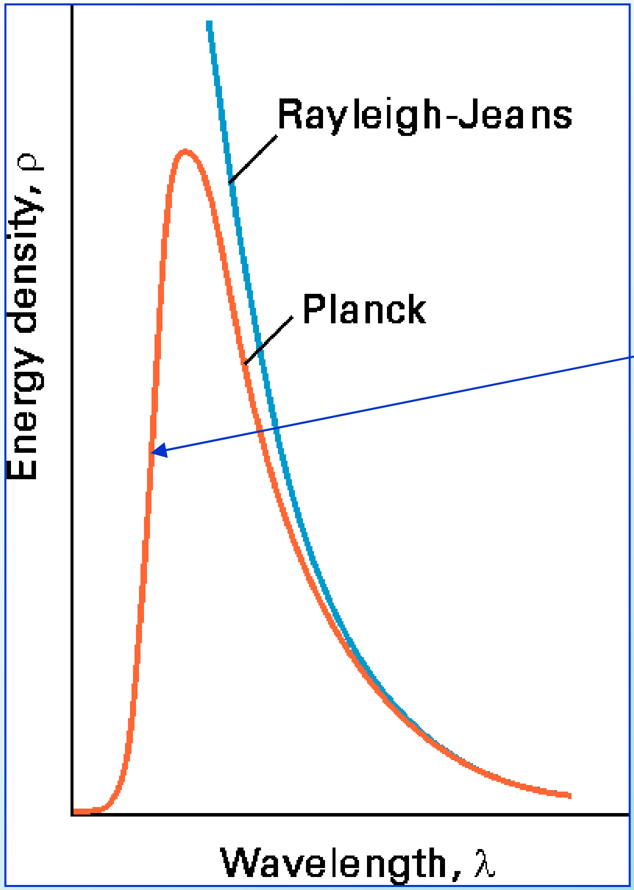
Rayleigh-Jeans curve

$$\rho = \frac{8\pi kT}{\lambda^4}$$

All energy levels allowed, so fraction of energy density with high energy increases as temperature increases.

The radiation escaping from a black body is determined by the energy loss from vibration of molecules (the electromagnetic oscillators) in the walls. These increase with T. The energy of the light emitted is determined by the oscillators.

Planck's curve



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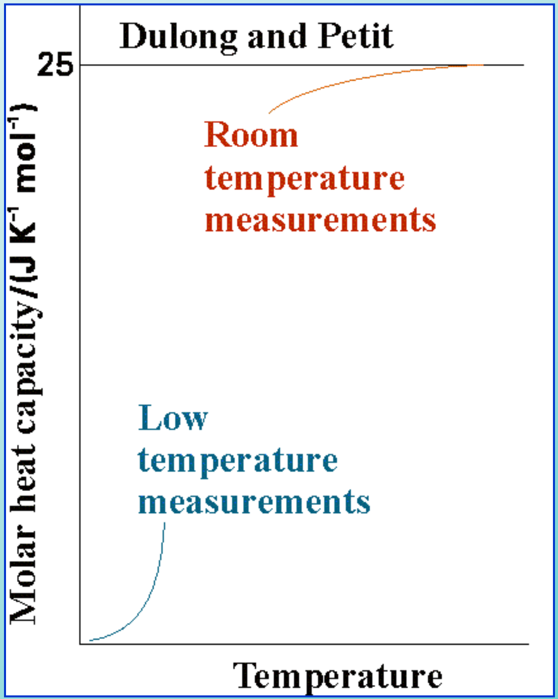
Planck proposed that the energy of the electromagnetic oscillators was limited to discrete values, rather than continuous. Planck's famous equation is E = $nh\nu$, where n = 0, 1, 2, …, ν (= c/λ) is the frequency, and h is Planck's constant, 6.626 10^{-34} Js.

$$\rho = \frac{8\pi}{\lambda^4}\frac{hc}{\lambda}\left(\frac{1}{e^{hc/\lambda kT}-1}\right)$$

Energy levels quantized. At any temperature, the transitions at higher energy levels are less likely to occur, so contribution to energy density falls off in high energy range (UV). As the energy ($E = h\nu = hc/\lambda$) approaches kT, the term in brackets approaches 1, and the Planck equation becomes the same as the Rayleigh-Jeans equation.

Temperature dependence of heat capacity

Heat capacity is the proportionality factor relating temperature rise, ΔT, to the heat applied: $q = C\Delta T$. The classical view was that C was related to the oscillation of atoms about their mean position, which increased as heat was applied. If the atoms could be excited to any energy, then a value of $C = 3R = 25\ JK^{-1}$ was expected, and this value, proposed by Dulong and Petit, was observed for many systems at ambient temperature. However, the expected behavior was a constant value as a function of T, and this was not seen, and some elements (diamond) had values way off.

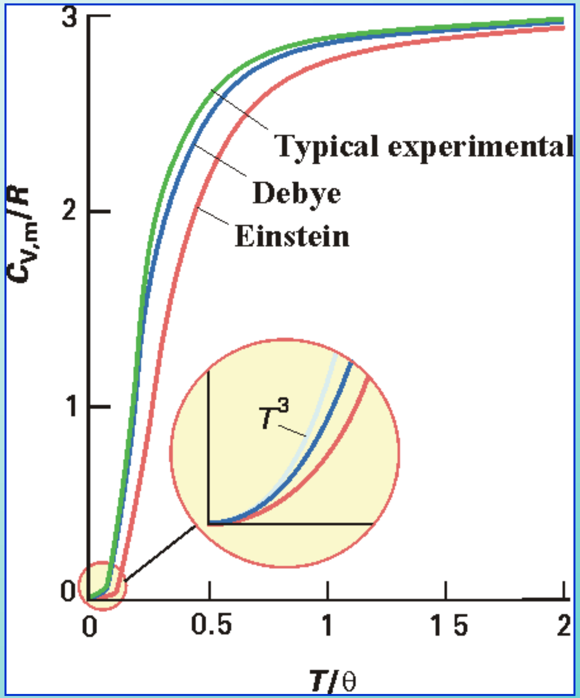


from Atkins, The Elements of Physical Chemistry

Einstein showed that if Planck's hypothesis of quantized energy levels was applied, the equation:

$$C = 3Rf^2, \text{ where } f = \frac{h\nu}{kT}\left(\frac{e^{\frac{h\nu}{2kT}}}{e^{\frac{h\nu}{kT}}-1}\right)$$

provided a good fit. This was later improved by Debye who allowed a range of values for ν.



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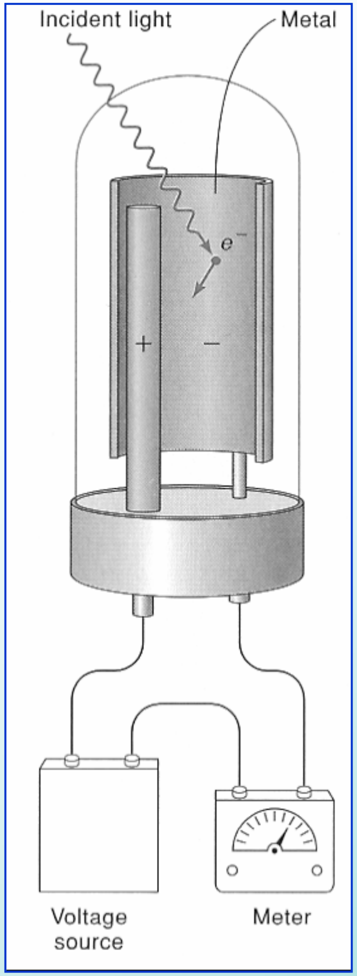
Conclusions from Planck's solution to the UV catastrophe and Einstein's solution to the heat capacity problem

1. Heating a body leads to oscillations in the structure at the atomic level that generate light as electromagnetic waves over a broad region of the spectrum. This is an idea from classical physics.

2. From Planck's hypothesis, the properties can be understood if the energy of the oscillations (and hence of the light) are constrained to discrete values, - 0, hν, 2hν, 3hν, etc. At any frequency value, the intensity of the light is a function of the number of quanta, n, at a fixed energy, determined by hν. This is in contrast to the classical view in which energy levels were assumed to be continuous, and intensity at any frequency was dependent on the amplitude of the wave.

3. A similar conclusion comes from Einstein's treatment of the heat capacity, but here the effect is seen from the oscillations generated in the substance on application of heat. Absorption of energy is therefore also quantized.

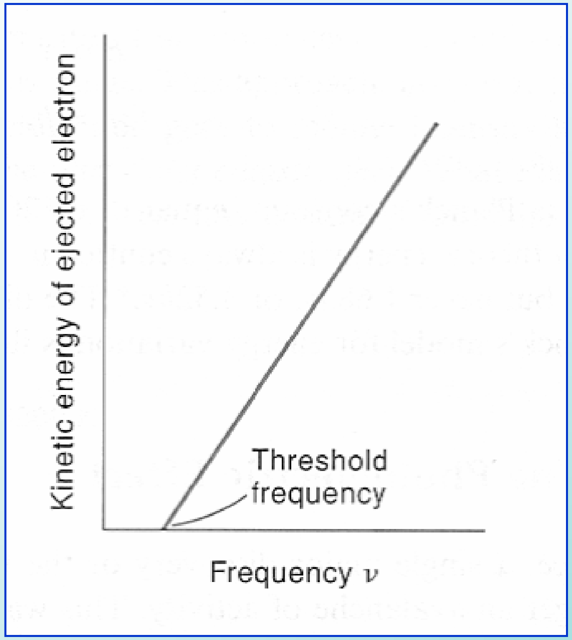
The photoelectric effect



When UV light shines on a metal surface, it induces the release of electrons, which can be detected as a current in a circuit such as that on the left. The released electrons are attracted by an applied voltage to an anode, and the resulting current detected, and used to measure the rate of electron release. The characteristics of this effect are as follows:

1. No electrons are ejected, regardless of intensity, unless the light is sufficiently energetic. In terms of Planck's equation, they have to have a high enough frequency. The actual value (the work function) depends on the metal.
2. The kinetic energy of the ejected electrons varies linearly with the **frequency** of the incident light, but is independent of intensity.
3. Even at low intensity, electrons are ejected immediately if the frequency is high enough.

According to the classical view, the energy of radiation should be proportional to the amplitude squared. It should therefore be related to intensity, which is in contradiction to the result observed.



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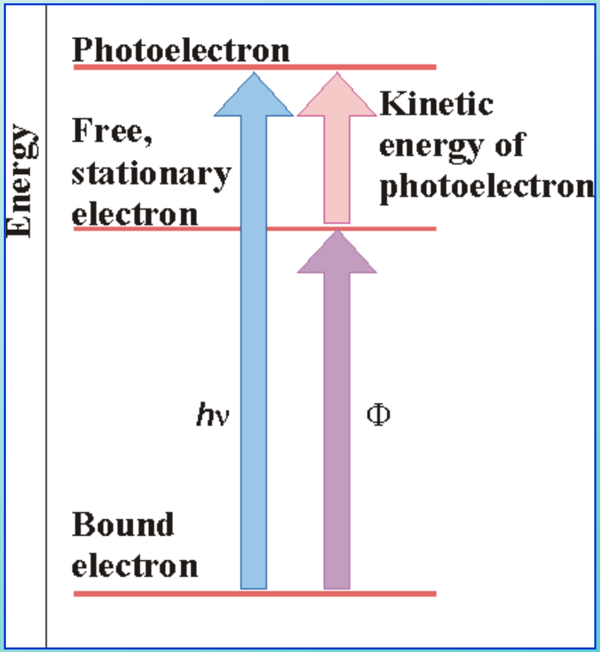
The properties of the photoelectric effect are summarized on the left.

Einstein suggested a solution to this dilemma, by invoking Planck's hypothesis. The electron is ejected if it picks up enough energy from collision with a photon. However, the energy of the photon is given by the Planck equation, and so is proportional to frequency, and quantized.

From the 1st law of thermodynamics, energy has to be conserved. We can therefore write an equation in which the kinetic energy of the electron is equal to the energy picked up from the photon, minus the energy needed to dislodge the electron (the work function, ϕ):

$$\tfrac{1}{2}m_e v^2 = h\nu - \phi$$

This is summarized in the diagram on the right.



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Electrons have both particle and wave-like properties

Cathode rays

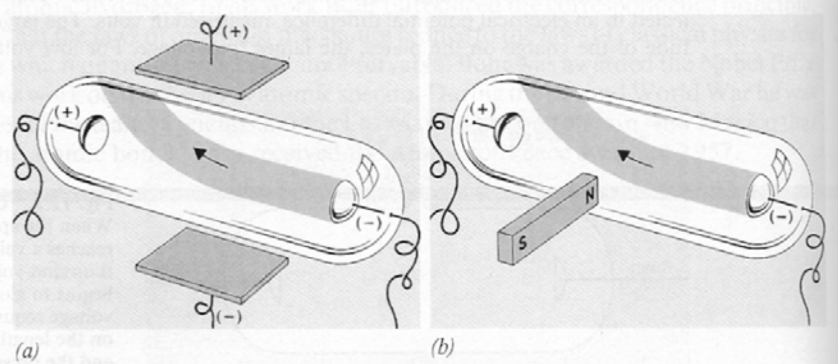


Fig. 12.2. The deflection of cathode rays by *(a)* an electric field and *(b)* a magnetic field.

Cathode rays are emitted when a high voltage is applied between a cathode (negative) and an anode (positive) through a vacuum. They are called rays called because they have light-like properties, - they cast a shadow. However, in contrast to light, the rays could be deflected by application of an electric or magnetic field. This implied that the beam consisted of charged particles, - later called electrons.

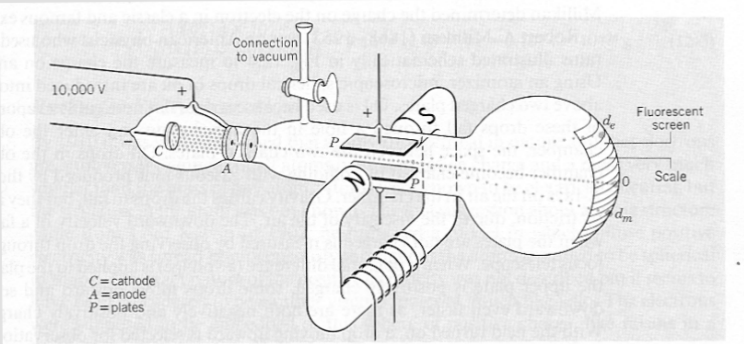


Fig. 12.3. Joseph J. Thomson's experiment demonstrating electric and magnetic deflection of a cathode ray. The deflection caused by an electric field applied to the plates, *P*, results in a bright spot on the screen at d_e. The undeflected beam strikes the screen at 0. The deflection caused by an applied magnetic field perpendicular to the paper results in a bright spot at d_m. Thomson used the cathode-ray tube to measure the charge-to-mass (e/m) ratio of the electron.

J.J. Thomson devised an apparatus which allowed him to measure the deflection of a cathode ray precisely. By varying the driving potential, he could vary the momentum of the electrons, and by varying the applied field and the deflection, he could estimate the ratio of the charge to mass of the particles.

Charge of electron, - Millikan's oil drop experiment

From Thomson's data, the ratio *e*/m for the electron could be measured, but not the absolute value of either. The critical missing piece was provided by Millikan. He measured the total charge on droplets of oil generated by a vaporiser, by applying an electrostatic field to oppose the force of gravity on the droplets. He charged up the droplets using a low-powered X-ray source. By measuring many droplets, he was able to show that they responded to the electrostatic field as if they hd a small range of values for charge, all being multiples of a limiting value, which he suggested must be the unit charge.

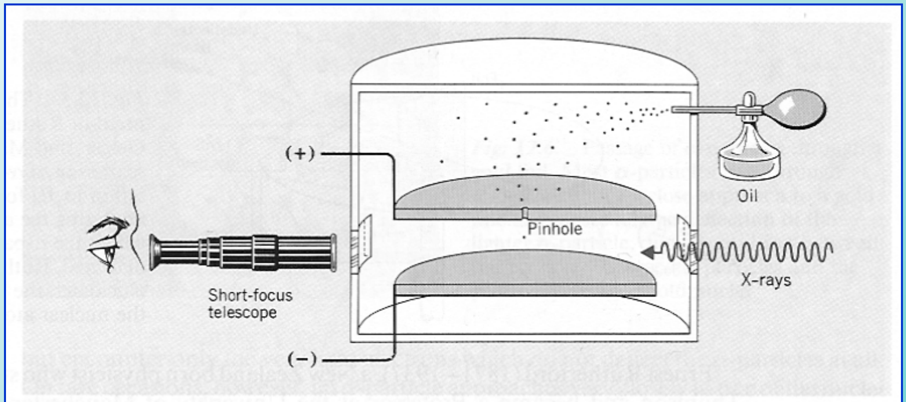


Fig. 12.4. Schematic diagram of Millikan's oil drop experiment to measure the charge on an electron.

Milikan's unit charge provided the value for *e* in Thomson's ratio, allowing complete characterization of the electron as a particle with defined mass and charge.

Dual nature of matter – wave and particle properties apply to subatomic particles

Einstein's relation between energy and mass and the de Broglie equation

Einstein suggested in the context of special relativity that energy and mass are equivalent, and related through the famous $E = mc^2$. De Broglie realized that, if all matter was quantized, this implied a general relation between the momentum of a particle and its energy as expressed in terms of frequency. By combining the Planck equation, $E = h\nu = hc/\lambda$, and the relationship for the momentum of an electromagnetic wave (given by $p = mc$), $p = E/c$, we get:

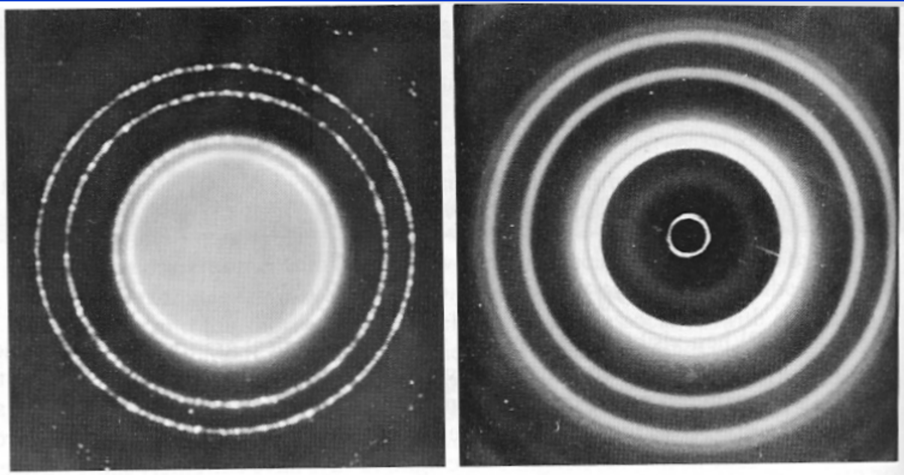
$$p = \frac{h}{\lambda}$$

or, rearranging

$$\lambda = \frac{h}{p} = \frac{h}{m\mathrm{v}}$$

The de Broglie relationship implies that any particle of mass *m* moving with velocity v will possess wavelike properties. In view of the value of the Planck constant, the effect will be appreciable for particles of low mass.

Diffraction of electron beam



(a) (b)

Fig. 12.16. Diffraction of waves by Al foil. *(a)* X-rays of wavelength 0.71 Å (71 pm). *(b)* Electrons of wavelength 0.50 Å (50 pm). The similarity of these patterns provides evidence for de Broglie's hypothesis that particles have wave properties.

Confirmation of this more general application of quantum principles to matter was obtained in experiments in which the diffraction of a beam of electrons was observed (left). The diffraction pattern seen when the electron beam was accelerated to give a wavelength of 0.5 Å gave a pattern similar to that seen when a beam of X-rays of similar wavelength (0.71 Å) was used.

The de Broglie relationship was proposed and tested in 1924, sometime after Bohr had put forward his model for the H-atom, which we will look at next. The demonstration that all matter was quantized, and the recognition of the importance of this in terms of the wave-like nature of particles of small mass like the electron, where critical in the later development of a comprehensive theory of quantum mechanics.

The structure of atoms

Transmission and reflection of α-particles, and the Rutherford atom

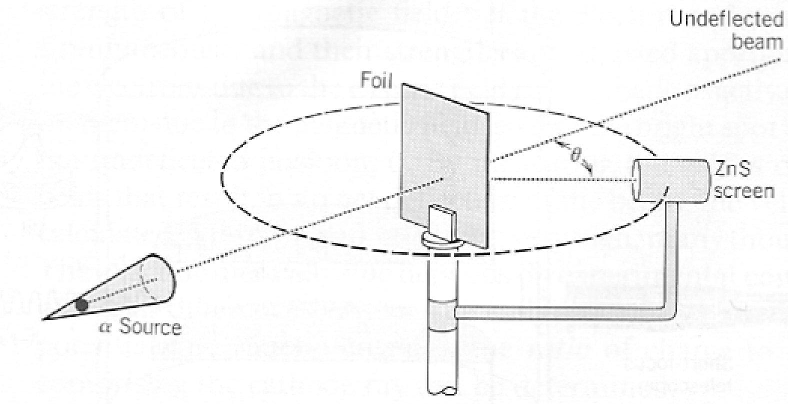


Fig. 12.5. The experiment of Rutherford, Geiger, and Marsden: The scattering of α-particles by a thin metal foil. By analyzing the angles by which the α-particles were deflected, Rutherford elucidated the structure of the nuclear atom.

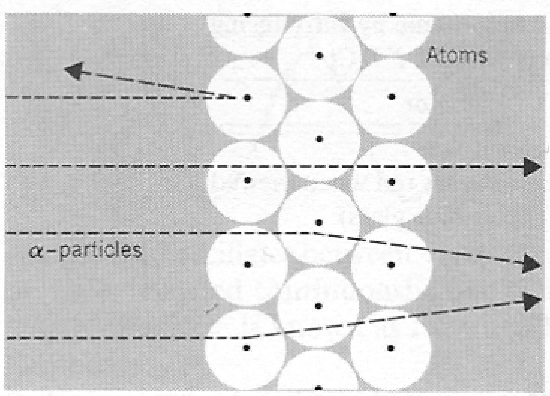


Fig. 12.6. Passage of α-particles through a gold foil. Most α-particles pass through undeflected, but a close approach to a gold nucleus causes a large deflection of the lighter α-particle, due to repulsion between the positively charged α-particles and the positively charged gold nuclei.

Rutherford and colleagues measured the penetration by a-particles (He^{+} nuclei) of a thin sheet of metal foil. What they found was in complete contradiction to the picture of atomic structure current at the time. Instead of finding the mass of the atom spread out over the volume, the mass was concentrated in a very small fraction of the volume, as indicated by the very small fraction of particles whose trajectory was altered. In contrast, light absorption by atoms and molecules sees a “target” of the full volume of the atom or molecule. Ruthrfords interpretation of this data is shown at left.

Quantized energy changes in atoms

When a high voltage is discharged through a gas, the atoms or molecules absorb energy and from collision with the electrons, and re-emit the energy as light. It is found that the light is not a continuous range at all frequencies, but is constrained to a few narrow lines (right). Explanations of the emission spectrum of atomic hydrogen played a critical role in development of a quantum mechanical understanding of the structure of atoms.

Lines similar to those in the hydrogen emission spectrum were seen as absortion lines in the light from stars.

Lines of hydrogen emission spectrum

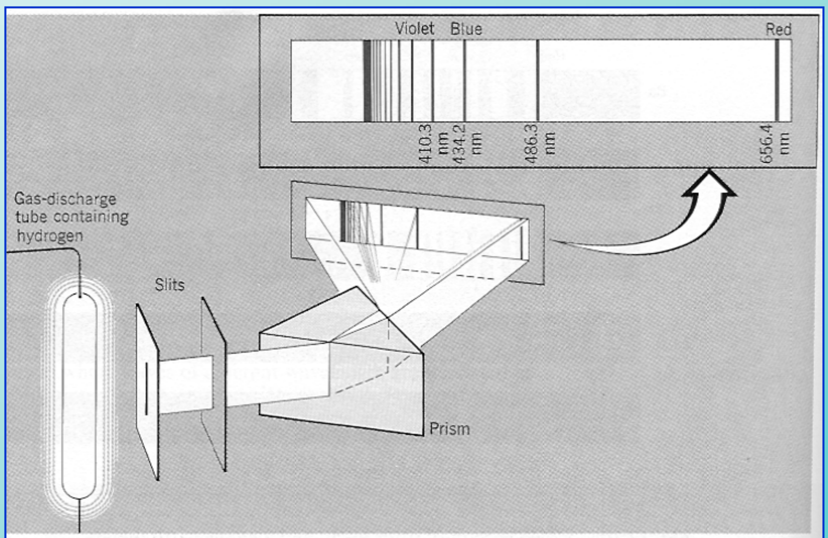


Fig. 12.11. The Balmer series of the emission spectrum of atomic hydrogen. The four lines whose wavelengths are given occur in the visible region, the remaining lines are in the near ultraviolet.

Balmer studied the emission spectrum in the near UV-visible region, and noticed that the distribution of the lines along the wavelength scale showed an interesting pattern that could be described by the Balmer formula:

$$\tilde{\nu} = \frac{1}{\lambda} = 109678\left(\frac{1}{2^2} - \frac{1}{n^2}\right)$$

where n is 3, 4, 5,… Later work revealed a more extensive set of lines in the UV and IR, which all followed the general pattern given by:

$$\tilde{\nu} = \frac{1}{\lambda} = \Re\left(\frac{1}{n_L^2} - \frac{1}{n_H^2}\right)$$

where $\Re$ is the Rydberg constant, and n_L and n_H are lower and higher value integers.

Bohr's explanation for H-emission lines

The Bohr atom model and formula

The picture of an atom given by the Rutherford experiment was of a very compact nucleus surrounded by a large volume occupied by the electrons; the latter determines the volume seen by light or chemical reactivity. This was similar in general design to the solar system, giving rise to the idea that the electrons might be orbiting a central nucleus. Bohr took this idea, and applied the classical reasoning of planetary theory to it, but with a quantized twist. He calculated the energy of the system by balancing the kinetic energy of the electron in orbit (the centrifugal force) against the attractive energy of the coulombic interaction between the positively charged nucleus and the negatively charged electron. The twist was the use of quantized energy levels.

The force due to coulombic attraction is given by: $f = \dfrac{Ze^2}{4\pi\varepsilon_0 r^2}$

(Z is charge of nucleus; r is radius of orbit; e is electron charge; ε_0 is permittivity)

The force due to classical kinetic energy is given by: $f = \dfrac{m_e \mathrm{v}^2}{r}$ (m_e is electron mass)

Equating these two forces we have

$$\frac{m_e \mathrm{v}^2}{r} = \frac{Ze^2}{4\pi\varepsilon_0 r^2}$$

At this point we have a classical description of the forces in the system.

If we write the energy of the electron we need the sum of the two energy terms due to these forces:

$$E = \frac{1}{2} m_e \mathrm{v}^2 - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

Substituting the force terms we get the following classical expression for the energy of the electron:

$$E = \frac{1}{2} m_e \mathrm{v}^2 - m_e \mathrm{v}^2 = -\frac{1}{2} m_e \mathrm{v}^2$$

The hydrogen emission lines were taken to represent the changes in energy due to transitions between energy levels in the excited H-atoms. A successful description of the energy level of the electron had to account for the curious spacing of the Balmer (and other) series. Bohr found he could achieve this by the simple expedient of imposing the condition of quantized energy levels; the angular momentum of the electron was restricted to values given by:

$$m_e \mathrm{v} r = n \frac{h}{2\pi} \quad \mathrm{n} = 1, 2, 3, \ldots$$

where *h* is Planck's constant.

The energy of the electron was $E_n = -\frac{m_e e^4}{8h^2 \varepsilon_0^2} \frac{1}{n^2} \quad \mathrm{n} = 1, 2, 3, \ldots$

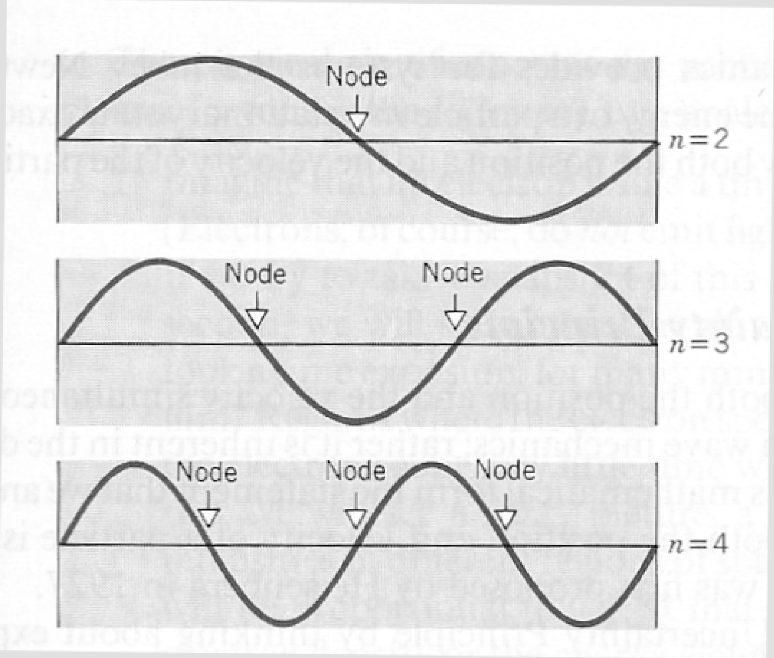
Applying this quantized restriction, he found that the changes in energy level were given by

$$\tilde{\nu} = \frac{1}{\lambda} = \frac{\nu}{c} = \frac{\Delta E}{hc} = \left(\frac{m_e Z^2 e^4}{8h^3 c \varepsilon_0^2} \right) \left(\frac{1}{n_L^2} - \frac{1}{n_H^2} \right) = \Re \left(\frac{1}{n_L^2} - \frac{1}{n_H^2} \right)$$

This is identical to the equation for the spacing of the H emission lines.

De Broglie's extension of Bohr's model.

The Bohr mechanism for explaining the H-emission spectrum, and hence the allowed energy levels of the electron in the H-atom in its excited states, was a triumph, but it didn't explain why the electrons were constrained to particular orbits; it was descriptive rather than explanatory. With the demonstration of the wave-nature of the electron through de Broglie's postulate, and the diffraction of the electron, an explanation could be offered. If the electron is a wave, then its ability to fit an orbit must be constrained by the condition that it is a standing wave.



In this case, the relation between the radius of the orbit and the wavelength of the electron is $2\pi r = n\lambda$, $n = 1, 2, 3,\ldots$

Substituting for λ from the de Broglie relationship we get

$$2\pi r = n\frac{h}{m_e \mathrm{v}}$$

Rearrangement gives Bohr's equation, and explains the occupancy.

$$m_e \mathrm{v} r = n\frac{h}{2\pi} \quad \mathrm{n} = 1, 2, 3, \ldots$$

The Schrödinger equation

The refinement of the Bohr model by de Broglie paved the way for the more formal description by Schrödinger. The concepts behind the new treatment were essentially the same as developed in the preceding slides. What Schrödinger added was a more powerful formalism for the description of the wave function. Unfortunately, this involves some elegant math, - a thing of beauty to the physicist, but perhaps not to the biologist. Fortunately, we don't need to understand the math in detail to appreciate the results, so the approach here will be non-mathematical.

It will help to appreciate a few points:

1. So far we have dealt with simple waves, - effectively sine waves constrained by the need to form a standing wave. This is appropriate for a circular orbit. However, the new approach made it possible to describe wave functions that were three-dimensional, and more complex in shape, while maintaining the constraints required by quantization, and the need to form a "standing wave".
2. In this context, the kinetic and potential energy terms of the Bohr equation are retained, but it was necessary to recognize that the values will depend in a more complicated way on the "shape" of the wave function.

3. Heisenberg had introduced his Uncertainty Principle, which showed that the momentum and position of the electron could not be determined simultaneously with certainty. Schrödinger therefore used a term related to the probability of the electron occupying a particular volume.

4. In the context of the constraint of a “standing wave”, this made it possible to make the expression time-independent. Hence the time-independent Schrödinger equation.

The Schrödinger equation for H-like atoms has the following form:

$$E\psi = -\frac{h^2}{8\pi^2 m}\nabla^2\psi + \frac{Ze^2}{4\pi\varepsilon_0 r}\psi$$

Compare this to the classical expression for the energy of the electron:

$$E = \frac{1}{2}m_e \mathrm{v}^2 - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

The Schrödinger equation

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Compare this to the classical expression for the energy of the electron:

$$E = \frac{1}{2}m_e \mathrm{v}^2 - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

The similarity arises from the need to consider the two balancing forces that determine the electron energy, - the kinetic term (the “centrifugal force” if we consider a planetary model), and the constraining electrostatic term for the potential energy. The first term on the right (the kinetic term) is now quantized, and all terms are modified by the wave function, ψ.

What is ψ, and what is that odd symbol, ∇^2?