Origins of quantum mechanics

Classical physics - (pre 1900)

- Mechanics - Newton
- Thermodynamics - Boltzmann, Gibbs *et al*.
- Electromagnetics - Maxwell *et al*.

Scientists believed that:

- The physical universe was deterministic.
- Light consisted of waves, ordinary matter was composed of particles.
- Physical quantities (energy, momentum, etc) could be treated as continuous variables.
- There exists an objective physical reality independent of any observer.

What happens to those ideas?

Before we get into the details, let's see what the development of quantum mechanics meant for those four "certainties" of classical physics:

classical ⇒ The physical universe is deterministic.

modern ⇒ The physical universe is not deterministic. At the scale of atomic particles, the best that we can do is find the probability of the outcome of an experiment. We can't predict exact results with certainty. Uncertainty is an intrinsic property of matter at this level.

classical ⇒ Light consists of waves, while ordinary matter is composed of particles.

modern ⇒ Both light and matter exhibit behavior that seems characteristic of both particles and wave. (wave-particle duality) classical ⇒ Physical quantities (energy, momentum, etc) can be treated as continuous variables.

modern ⇒ Under certain circumstances, some physical quantities are quantized, meaning that they can take on only certain discrete values.

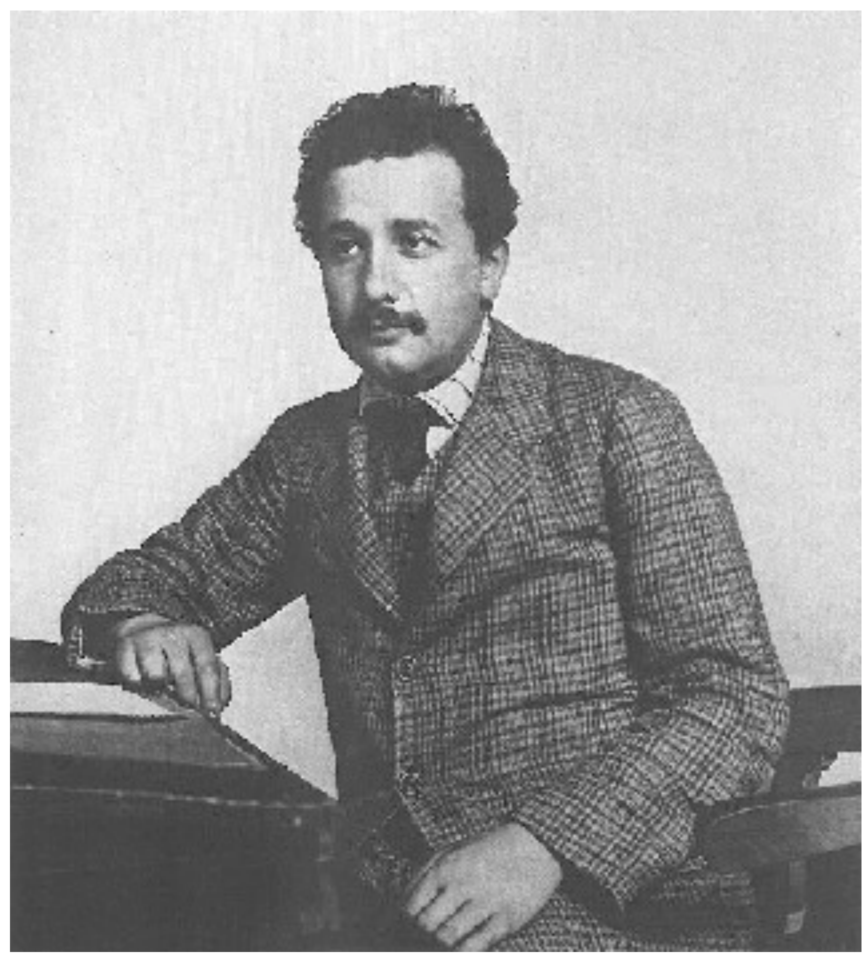
classical ⇒ There exists an objective physical reality independent of any observer.

modern ⇒ It appears that the observer always affects the experiment. It is impossible to disentangle the two.

Outstanding problems c. 1900

- Black-body radiation
- The nature of light
- The structure of the atom

Planck

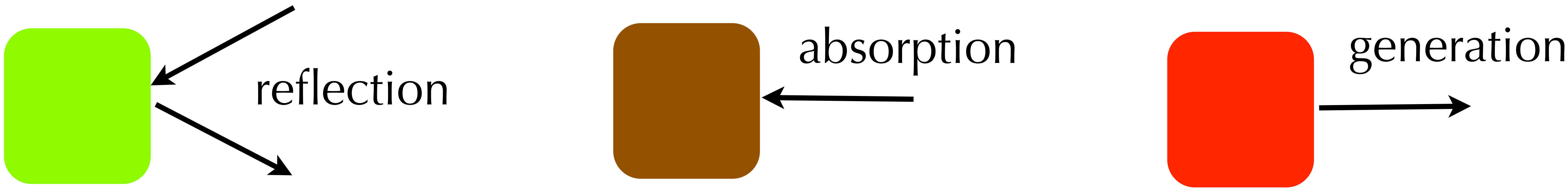


Einstein

Bohr

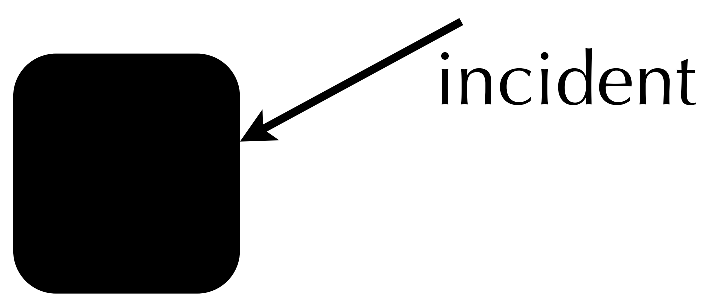
Black-body radiation

There are three ways that light interacts with matter:

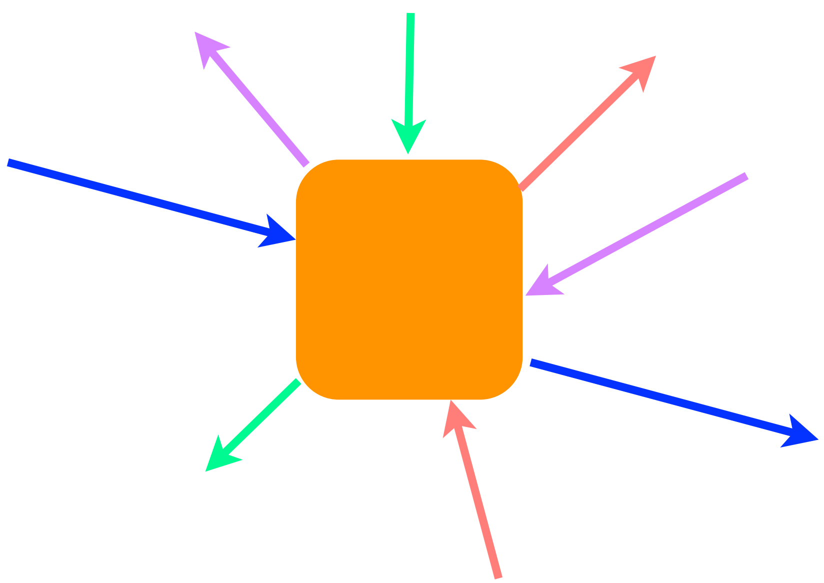


In principle, all three things can be happening simultaneously. However, we see most things through reflection.

If an object has no reflection, then, if there is no generation, it would appear to be absolutely black. We call it a black-body. All incident light is totally absorbed.



However, the black-body can generate light. In fact, it must in order to maintain equilibrium.



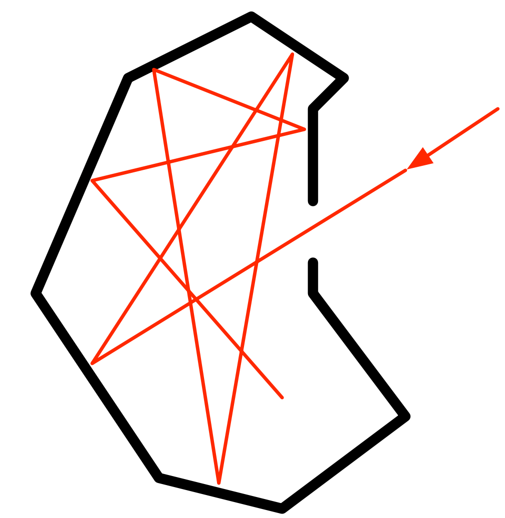
According to Kirchhoff: The amount of radiation being absorbed at each and every frequency, will be exactly matched by outgoing radiation generated by the BB.

So, a perfect absorber of light must also be a perfect emitter of light.

Because any black body is perfect emitter, *every* black body should have the same emission spectrum. When the BB is heated to a given temperature, it will radiate EM energy, with an emission spectrum that is characteristic of the temperature. This makes it useful as laboratory standard in doing optics experiments. In the late 1800s, the study of black bodies was an important topic.

Making a true black-body is actually a bit tricky. Simply slapping some black paint over an object is not good enough, since that will not necessarily make the reflection go to zero.

The usual approach is to make a metallic cavity with a small hole. Any light from the outside hitting the hole with go inside and probably bounce around many times, eventually being absorbed by the walls of the cavity. The chances of the incident light being reflected directly back out the hole are very slim, assuming that some care was taken in the design of the cavity.



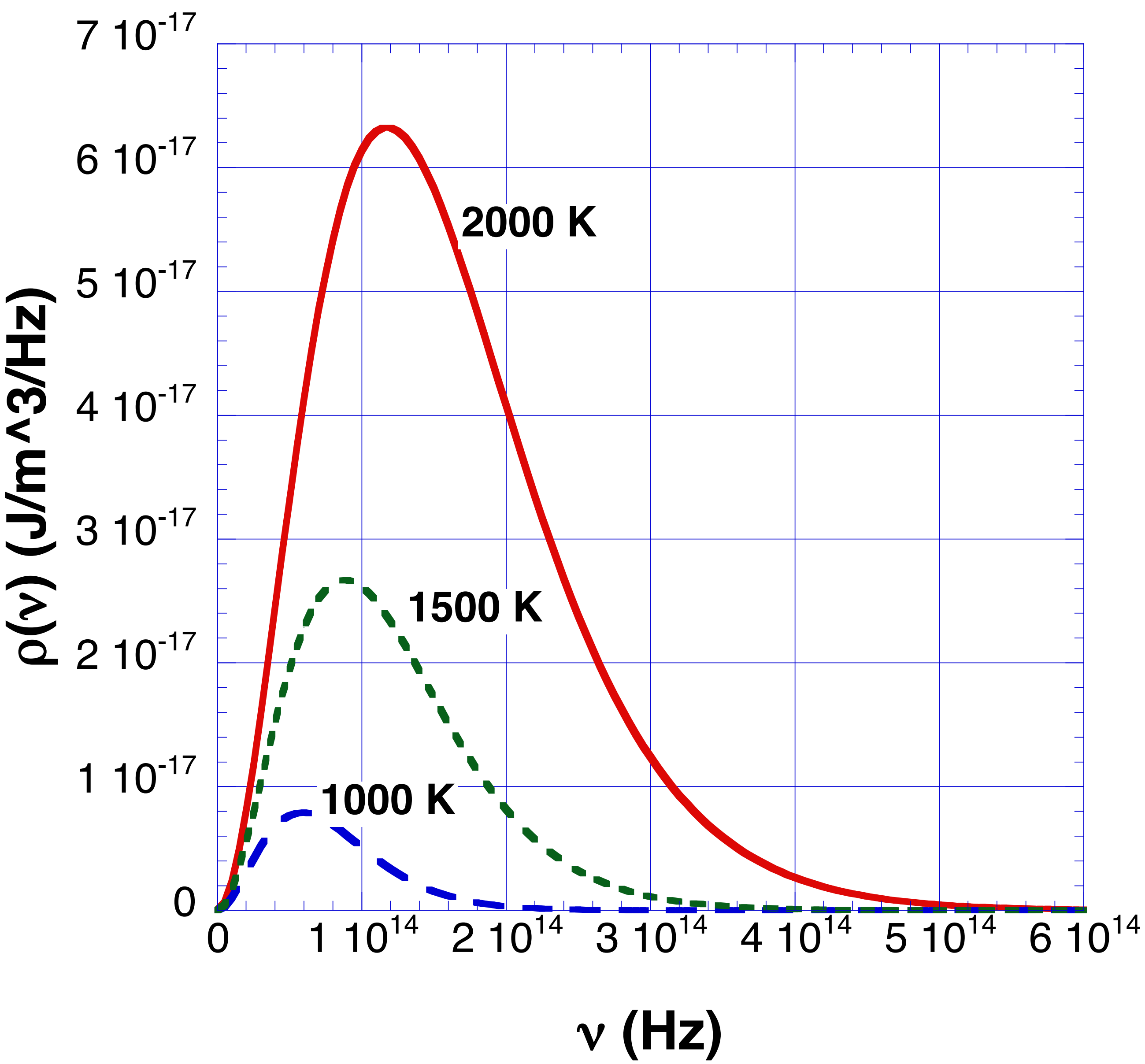
Any light being generated by the motion of the electrons in the walls of the cavity will bounce around many times before it may escape through the hole. (In fact, most of the internal light will simply be re-absorbed.)

In this way the <u>hole</u> acts like a black-body, and the cavity is filled with BB radiation.

So by heating the cavity structure up to a uniform temperature, you can observe black-body radiation coming from the hole.

Black-body radiation spectrum

As the BB is heated, the total energy emitted increases (obviously) and the peak in the spectrum shifts to higher frequencies (shorter wavelengths).



The properties of black-body radiators had been determined experimentally by the end of the 1800s.

The *total* EM power (integrated over all frequencies) radiated by a black body at a given temperature T is

$$\boldsymbol{P = \sigma A T^4}$$

where A is the surface area of the BB and σ is a constant equal to 5.67×10^{-8} J/s/m²/K⁴. (Stefan-Boltzmann law.)

However, since we usually work with a cavity, we can say the same thing by looking at the total EM energy density *within* the cavity.

$$\boldsymbol{\rho_T = \int_0^\infty \rho(\nu) d\nu}$$

$$\boldsymbol{\rho_T = a T^4}$$

where the constant *a* is equal to 7.56×10^{-16} J/m³/K⁴.

Lastly, the peak *frequency* increases linearly with temperature, meaning that *wavelength* is inversely proportional to temperature.

$$\boldsymbol{\lambda_{peak} = w/T}$$

where $w = 2.90\times10^{-3}$ m·K (This is Wien's Law.)

The experimental facts weren't in dispute. These results had been measured in many laboratories by 1900.

Trouble came though when theorists tried to explain the BB spectrum. This should have been a straight-forward application of thermodynamics and EM theory.

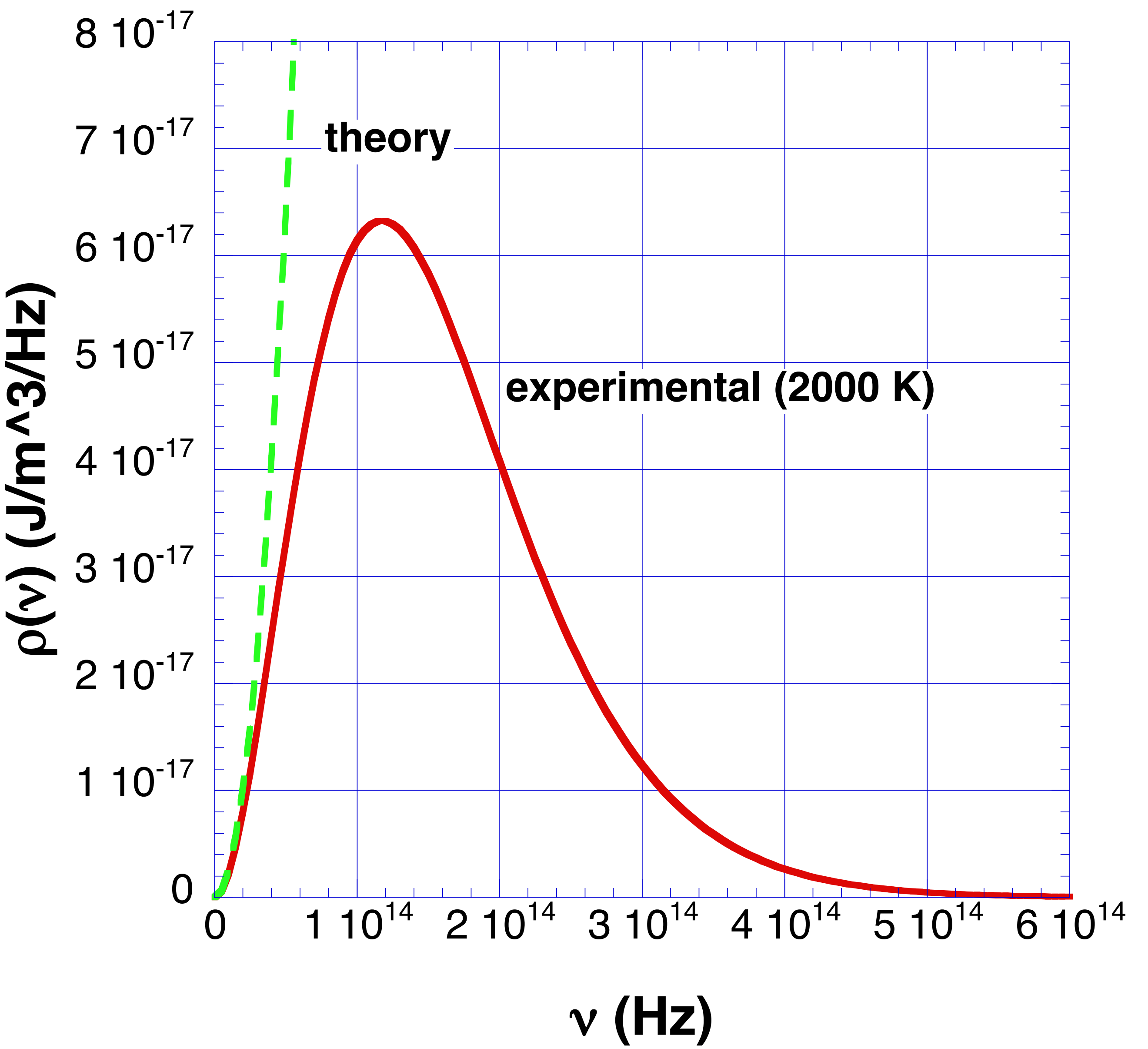
- Use electromagnetics to determine the electromagnetic modes inside the cavity.
- Use thermodynamics to determine the distribution of energy
- Underlying it all is the assumption that all energies are possible (a continuous distribution of energies).

The expression obtained using the classical theories was

$$\rho(\nu) = \frac{8\pi kT}{c^3}\nu^2$$

Comparing the theoretical equation to the experimental results showed that the theory was a miserable failure.

In fact, it predicted an infinite amount energy being radiated! (Referred to as the "ultraviolet catastrophe."



In 1900, Max Planck proposed a way to derive a suitable equation.

To get there, he tossed aside the assumption that energies are continuously distributed. Instead assumed that the energy of EM modes in the cavity consisted of discrete packets. The energy of each packet was proportional to the frequency of the EM mode.

$$E = 0, h\nu, 2h\nu, 3h\nu, 4h\nu, 5h\nu, \text{ etc.}$$

With this modification, the Planck's result was

$$\boldsymbol{\rho(\nu) = \frac{8\pi h}{c^3} \frac{\nu^3}{\exp\left(\frac{h\nu}{kT}\right) - 1}}$$

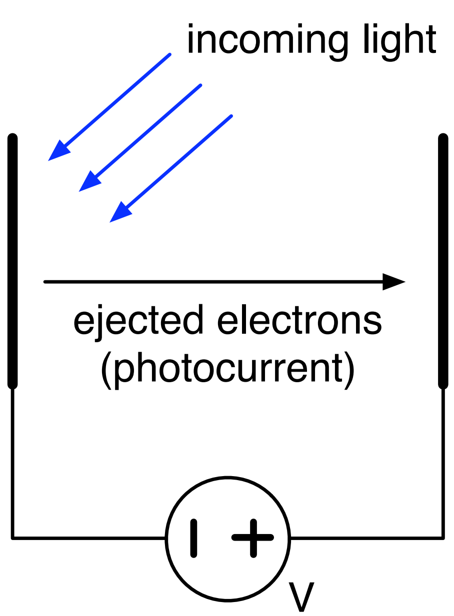
This matched the experimental results exactly, if *h* was chosen to have a value of 6.63×10^{-34} J·s.

This was the first use of the notion of *quantization of energy*.

The photoelectric effect – the nature of light

The photoelectric effect (or photoemission) was a fairly new topic at the turn of the century. (First noticed in 1839, but studied more rigorously by Hertz in 1887.)

Shine a light on a metal, and you notice that electrons are ejected, resulting in a current flowing off the metal.



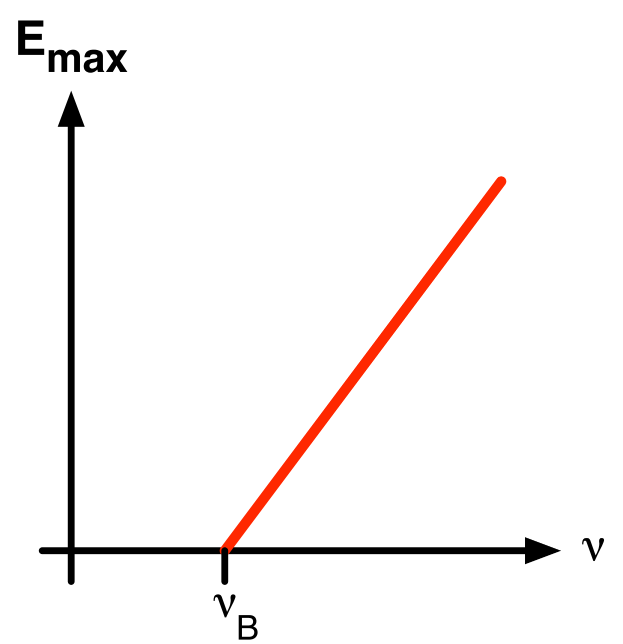
The basic experiment involves shining light on a metal electrode to produce the photo-emitted electrons. An applied voltage will accelerate the electrons to a second electrode. Or the voltage could be reversed to retard the flow of the electrons. In this way, the maximum kinetic energy of the emitted electrons can be determined by finding the voltage that just stops the current flow.

Apparently, the electromagnetic energy is being transferred to the electrons, allowing them to break free.

There were two important observations:

1. The photocurrent is proportional to the intensity of the light.
2. The maximum energy of the emitted electrons is proportional to the frequency of the emitted light, and there is some minimum frequency below which no photocurrent is generated.

The second of these is puzzling, since according to classical EM theory, the frequency should play no role in the describing the energy transfer from light to electrons.



A plot of E_{max} vs. frequency looked nearly the same for all metals used for the emitting electrode. Different metals would result in different minimum frequencies, but otherwise the curves were identical.

Einstein (1905)

Following Planck's lead, Einstein postulated that the EM energy was carried in discrete packets of size $E = h\nu$. Essentially, he was saying that in the photoemission experiment, the light came in the form of particles, which would later come to be called photons.

The electrons are bound in the metal and a certain minimum energy is required to break them free. This "binding" energy is different for different metals. So the incoming photons must have at least this minimum energy before the photocurrent is seen. $h\nu_B = E_B$.

If the photons have more than the minimum energy, the excess is turned into kinetic energy of electrons. The maximum kinetic energy would be $E_{max} = h\nu - E_B$. This agrees exactly with the observations, where the slope of the line of the E_{max} vs. frequency plot is indeed equal to h.

The particle-like behavior of light shows up in other instances. One other important example is Compton scattering, in which x-rays (very short wavelength EM radiation) bounce off electrons in a metal. The results seen can only be described in terms of particle interactions. (You can read the details of Compton scattering in one of the texts.) When observed in 1923 by Compton, the effect was taken as final evidence that light could be described as particles.

Also, the behavior of some types of chemical reactions, where the reaction rate can be changed by shining light of sufficiently high frequency, is explained in terms of the photon picture of EM radiation. (If you've had EE 432, you've seen this when using photoresist, which becomes more soluble in a developer solution after it has been exposed to UV radiation.)

Wave or particle?

It seems that EM radiation can have a dual nature. In some cases, it behaves like a wave (reflection, refraction, diffraction, etc.) and sometimes it manifests itself as a particle, the photon, with energy E = hν. Neither picture is wrong, that's just the way that nature is. This puzzling situation is called *wave-particle duality*.

Note that we can connect the two pictures in some ways. Consider the intensity of an EM wave (W/m^2):

For simple plane waves: $$\boldsymbol{P = \vec{E} \times \vec{H} = E_x H_y = \frac{E_x^2}{Z}}$$

where Z is the characteristic impedance of the transmission medium.

The flow of photons can be described in terms of the photon flux (number/area/time), $\mathcal{F}$.

$$\boldsymbol{P = \mathcal{F} h \nu}$$

So for a simple EM plane wave, we can relate photon flux to field strength.

$$\boldsymbol{\mathcal{F} = \frac{E_x^2}{Z h \nu}}$$

Photon momentum

If the photon is a particle with a known energy, it must have some momentum associated with it. We can't calculate the momentum using Newtonian mechanics, because the photon has no mass. (From Einstein's Theory of Special Relativity, the only way that a particle like a photon can move at the speed of light is if it has no mass. Note that Einstein produced this result in 1905 also. Clearly, that was a very good year for him.)

But we can use one of the results from special relativity to find the momentum of the photon. According to that theory, the total energy of a particle is

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

where c is the speed of light, and p is the momentum.

Since the photon mass is zero, the second term on the right is zero, leaving

$$E = pc$$

$$p = \frac{E}{c} = \frac{h\nu}{c} = \frac{h}{\lambda}$$

The structure of the atom

In the first decades of the 1900s, the picture of the structure of the atom was becoming clearer. This was mostly due to the work of Rutherford (a New Zealander who worked in Canada and later in England).

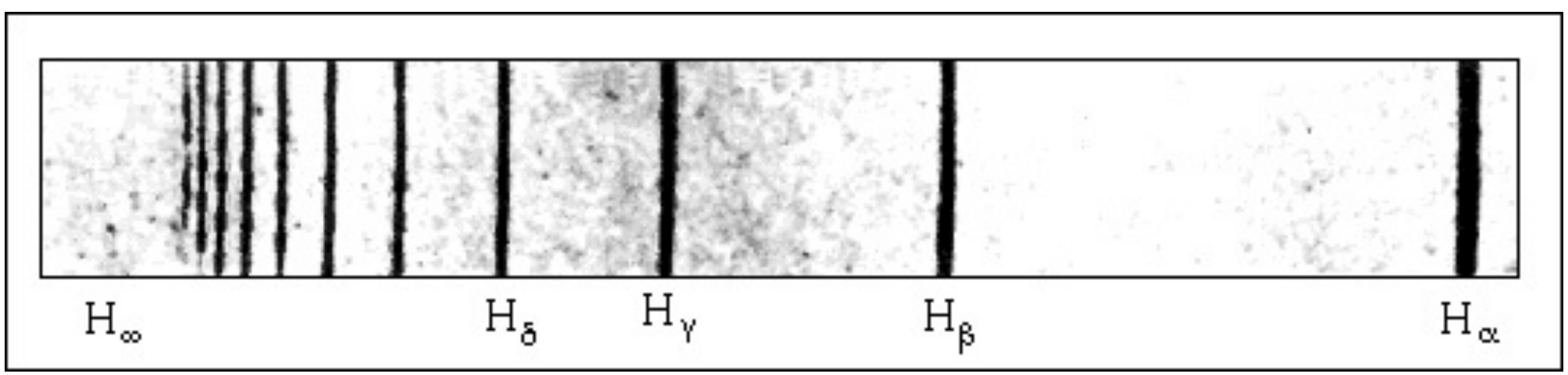
The atom was viewed as a miniature solar system: a massive, positively charged nucleus (analogous to the sun) with the negatively charged electrons orbiting around it (similar to the planets.) The two parts are held together by the electrostatic attraction between the charges. This was an appealing picture because the attractive electrostatic force has the same r^{-2} dependence as the force of gravity that attracts the planets to the sun. Taking a classical approach, it would appear the theoretical problem had already been solved.

From a classical point of view, we might expect the electrons to move in stable orbits with a continuous range of energies, angular momenta, and orbital sizes possible.

There are two major problems with the “atom-as-a-solar-system” picture.

First, EM theory tells us that an accelerating electron will give off radiation (emit photons) and lose energy. Since an electron moving in a classical orbit around a nucleus is under constant centripetal acceleration, it should give off a continuous stream of photons and continually lose energy. As the electron loses energy, it would spiral down until it eventually crashes into the nucleus. The classical picture leads to atoms that are not stable!

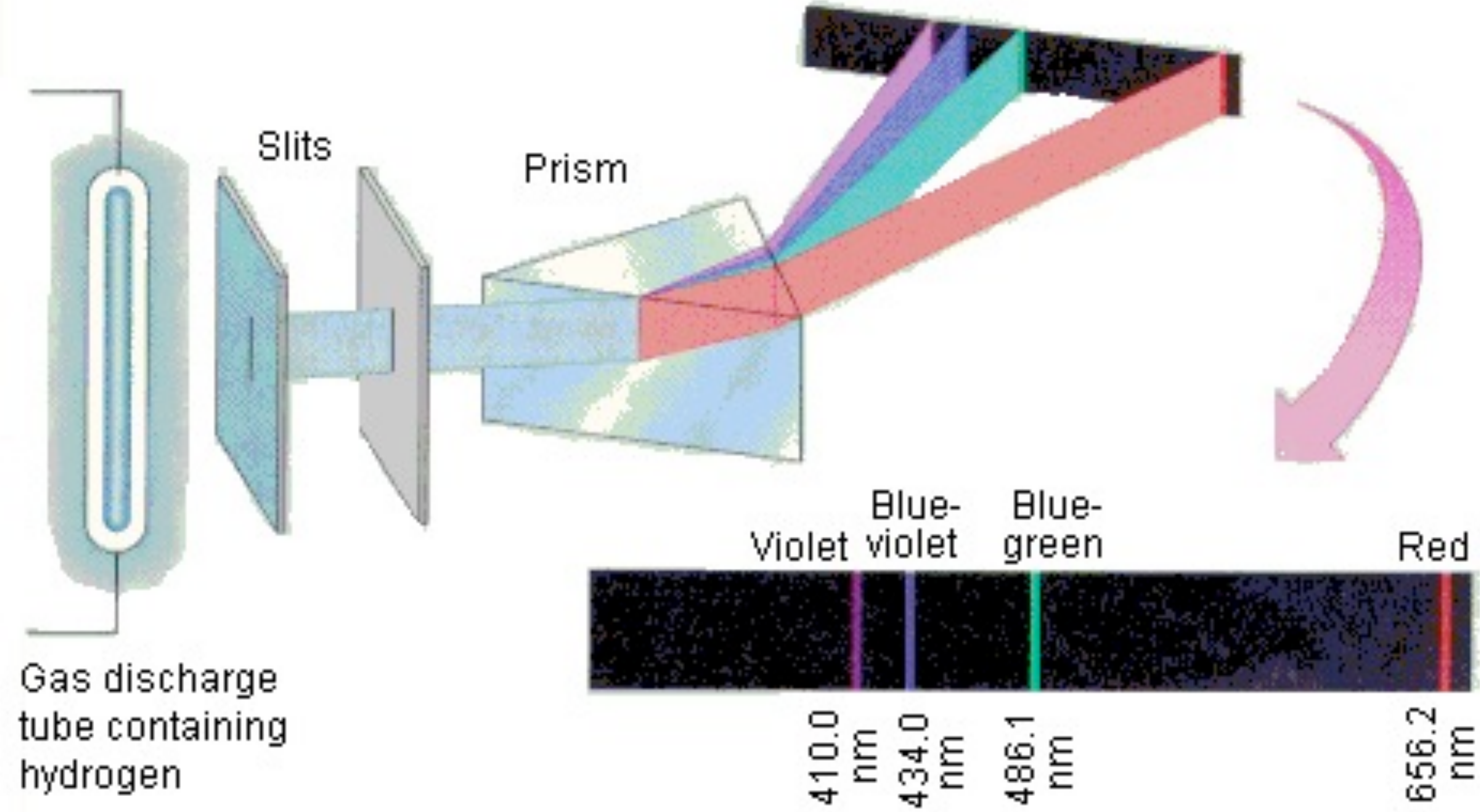
The second problem is that when one looks at the optical emission from of atoms, there is not a continuous range of frequencies being emitted. Instead the emission is bunched into very specific, discrete “lines”.



http://dbhs.wvusd.k12.ca.us/webdocs/Electrons/Hydrogen-Spectrum.html

Hydrogen emission spectra in the visible (400 nm - 700 nm).

The spectrum from hydrogen atoms shown previously is known as the "Balmer series" of lines. The spectra was measured in the 1800s.



http://chemed.chem.purdue.edu/genchem/topicreview/bp/ch6/bohr.html

There were other collections of lines in the UV and IR, that were measured later (Lyman series, Paschen series, Brackett series).

Rydberg was able to come up with a totally empirical formula describing the position of the lines in the Balmer series.

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

where R is a constant (the Rydberg) = 1.097×10^{7} m^{-1} and n is an integer greater than 2.

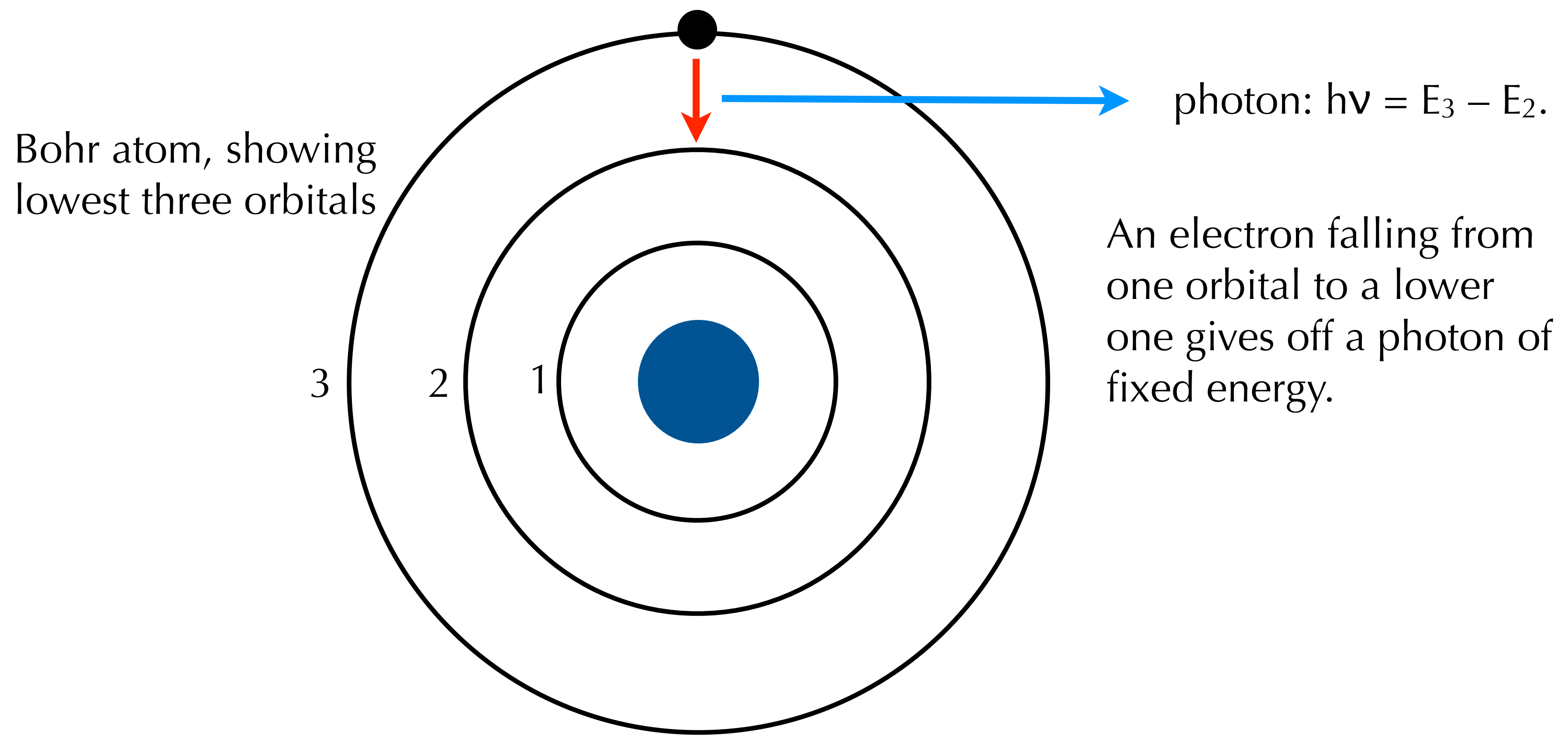
Taking the experimental results and tying them to some of the nascent quantum ideas, Niels Bohr managed to patch together a theory that seemed to account for the observed optical properties of the hydrogen atom. (Hydrogen was used as the standard, since it was the simplest atom, with just a single electron. Also, it's emission properties were will known from many experiments.) He used the quantization ideas of Planck and the picture of photons provided by Einstein. Here are the elements of his model:

1. The electron in a hydrogen atom moves in circular orbit about the proton (nucleus) under the influence of the Coulomb attraction, obeying the laws of classical mechanics.

2. Instead of the infinity of orbits which should be possible, electrons instead are limited to orbits for which the angular momentum is quantized in multiples of $h/2\pi$ (hereafter denoted as $\hbar$). This says that angular momentum, $L = mvr = n\hbar$ where m is the electron mass, v is the velocity, r is the radius of the orbit, and n is an integer. These specific orbits are called orbitals.

3. Even though the electron is being accelerated constantly in an orbit, it does not emit any EM radiation.

4. EM radiation is emitted if the electron changes from one orbit to another, i.e. from one energy level to another. The difference in energy is given off as a photon with $h\nu = E_i - E_f$, where E_i is the initial orbital energy and E_f is the final energy.



Bohr's approach was a hybrid theory, mixing classical ideas with the new quantum concepts, but did seem to explain the observed optical spectra.

The radius and the energy of a Bohr orbital in the hydrogen atom can be calculated. (These are purely classical calculations.)

To find the radius, we set the Coulomb force equal to the centripetal force.

$$\frac{q^2}{4\pi\epsilon_o r^2} = \frac{mv^2}{r}$$

where q is the charge of one electron and ε_o is the free-space permittivity.

Using the above relation together with the angular momentum quantization condition,

$$L = mvr = n\hbar$$

we can solve for the radius r

$$r = \frac{4\pi\epsilon_o \hbar^2}{q^2 m} n^2$$

For n = 1, the radius works out to 0.0531nm , which is known as the “Bohr radius”, and denoted as a_o.

To find the energy of the electron in an orbit, we add the kinetic and potential energies.

$$\begin{aligned} \boldsymbol{E} &= \boldsymbol{K} + \boldsymbol{V} \\ &= \frac{1}{2} m v^2 - \frac{q^2}{4\pi\epsilon_o r} \end{aligned}$$

(Since the potential is attractive between nucleus and electron, the potential energy-term will be negative. We are assuming that E = 0 when the electron is infinitely far away from the nucleus. This leads to the orbital energies being negative.)

Inserting the expression for the quantized angular momentum and the radius found on the previous page gives

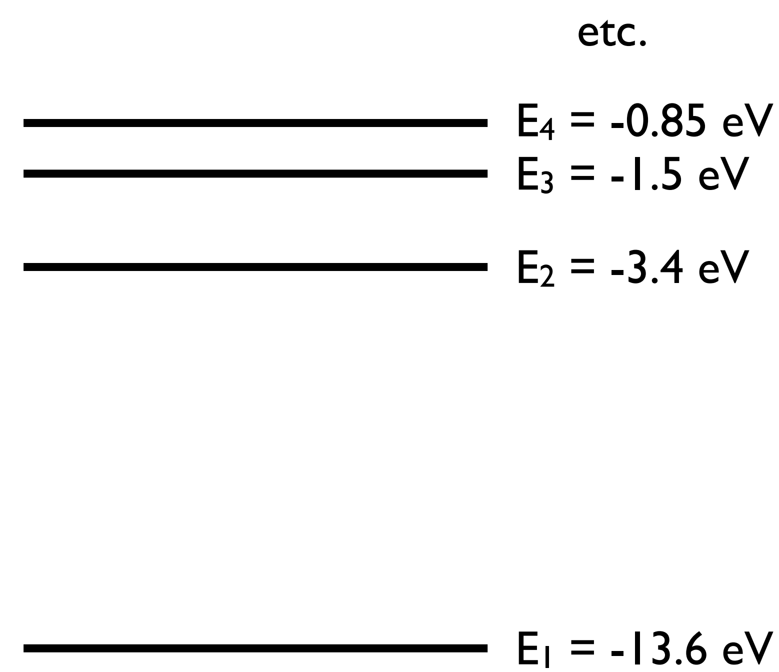
$$E = -\left[\frac{m q^4}{2\left(4\pi\epsilon_o\right)^2 \hbar^2}\right] \frac{1}{n^2}$$

$$E = -\left[\frac{mq^4}{2\left(4\pi\epsilon_o\right)^2\hbar^2}\right]\frac{1}{n^2}$$

Plugging in for the constants within the brackets:

$$E = \frac{-13.6eV}{n^2}$$

Energy levels in Bohr atom



The lowest possible energy is given by E_1. This is known as the "ground state". Since the electron cannot drop below this, the atom is stable.

The energy transitions must have energies given by:

$$\Delta E = 13.6eV\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

where n_f and n_i are integers, with $n_i > n_f$

$$\Delta E = 13.6eV \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

Note this expression agrees with the empirical relationship determined by Rydberg from the experimental spectra.

$$h\nu = \frac{hc}{\lambda} = 13.6eV \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

$$\frac{1}{\lambda} = \frac{2.17 \times 10^{-18} J}{hc} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) = R \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

Bohr's model of the atom matched well with the experimental observations. However, it was formulated with a rather unsatisfying mix of old and new ideas. Furthermore, it doesn't lend itself to investigating other types of problems.

Matter waves

With his explanation of the photoelectric effect, Einstein changed the picture. Previously, it was

- light → waves
- matter → particles

Afterwards, it was

- light → waves and/or particles
- matter → particles.

In 1924, Louis deBroglie looked at this situation and felt that something was missing. In trying to provide some symmetry to the picture, He postulated that matter might also be described by waves. He used the same expressions for frequency and wavelength of for matter waves as Einstein has used for photons:

$$\nu = \frac{E}{h} \qquad \lambda = \frac{h}{p}$$

So why hadn't wave properties of matter been seen already? For instance, if your body were described by a wave, you should "diffract" when walk through a doorway. (Or, even more interesting, you should interfere with yourself if you walked into a room with two doors!)

The answer lies in the wavelengths of everyday objects. For a 100-kg person walking along at 5 m/s, the momentum is 500 kg·m/s and the corresponding wavelength would be $h/p = (6.63 \times 10^{-34}\ \mathrm{J \cdot s})/(500\ \mathrm{kg \cdot m/s}) = 1.32 \times 10^{-36}$ m. So you wouldn't see diffraction effects until you went through a door that was on the order of 10^{-36} m wide. Good luck with that!

But consider an electron ($m = 9.11 \times 10^{-31}$ kg) moving at 1000 m/s, which is easily done in the laboratory (or inside an atom). In that case, $p = 9.11 \times 10^{-28}$ kg·m/s and the wavelength is 7.28×10^{-7} m, which although small, is certainly in the realm of things can be built in a lab (even back in the 1920s.) For instance, the interatomic spacing in crystals are in this range.

So small particles may very well exhibit wave-like behavior, if we know how to look for it.

Whenever there is a new theoretical notion, experimentalists are ready to test it out. In 1927, Davisson and Germer performed their famous experiment at Bell Labs, in which they fired electrons at piece of single-crystal nickel. Since electrons behaved like waves, they diffracted off the periodic array of atoms on the surface of the crystal. This is analogous to light diffracting off a grating. This showed that electrons did exhibit wave-like behavior.

This also sheds a bit of light on Bohr's atom, which had quantized angular momentum. If the orbiting electron can be viewed as a wave, the quantization condition says that the circumference of an electron orbit must be an integral number of electron wavelengths. Hmmm....

Bohr's quantization $$L = mvr = pr = n\hbar$$

leads to a statement about wavelengths. $$2\pi r = n\frac{h}{p} = n\lambda$$

We've seen 3 important problems that required new, unusual notions to be added to the familiar theories of classical physics.

- black-body radiation → quantization of energy
- photoelectric effect → light as a particle
- hydrogen atom emission spectra → quantization of atomic orbits

In addition, de Broglie added an extra wrinkle by proposing that if light can behave like a particle, then particles might behave like waves.

These were all intriguing ideas, but they did not constitute a coherent theory that could be applied to new problems. Something more fundamental was needed. So the next step to come was the development of a true quantum theory based on the Schroedinger equation.