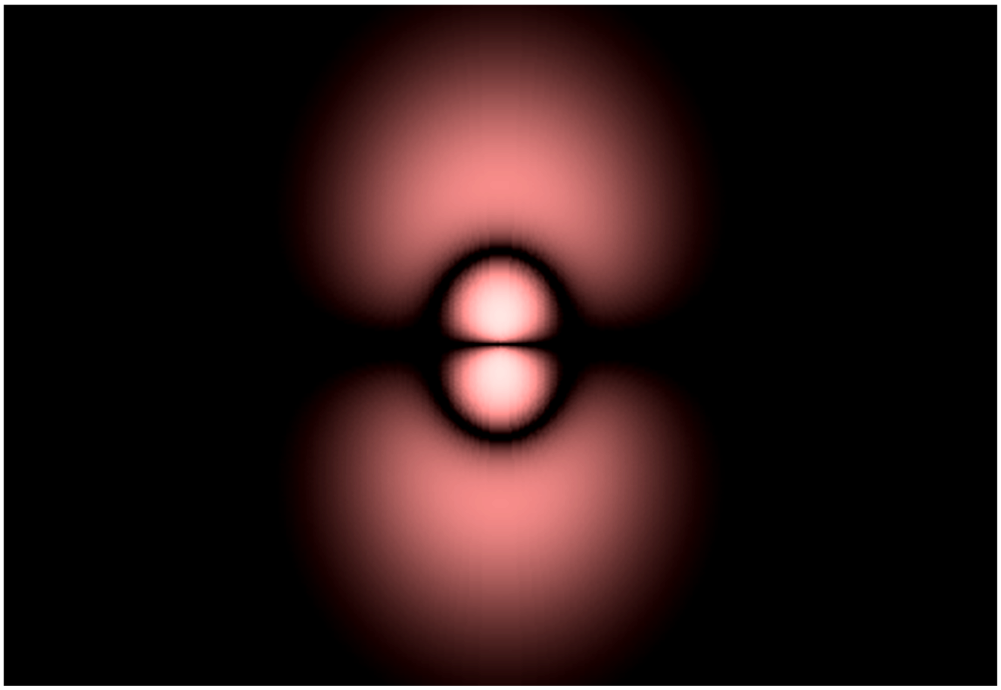
Quantum Chemistry

Dr. Marcel Drabbels



EPFL

Autumn 2025

Table of Contents

1 Introduction and Historical Perspective

1.1 General comments about the class

Dr. Marcel Drabbels Room: CH G0-613 Telephone: 33022

Assistants: Liam Marsh
Peter Gispert
Pratham Deshmukh

Documentation: Lecture notes and additional information are available on Moodle (http://moodle.epfl.ch/)

Reference Books

Primary Reference:

- D. A. McQuarrie, *Quantum Chemistry*

Secondary References:

- P. W. Atkins, *Molecular Quantum Mechanics*
- Cohen-Tannoudji, Diu, and Laloë, *Quantum Mechanics* (originally published in French)
- B.H. Bransden and C.J. Joachain, *Introduction to Quantum Mechanics*

Exercises: **Solving problems is an essential part of the course**. I encourage you not only to come to the exercise sessions, but also to work on the problems before you come. Two hours each week is not enough to do and understand all the exercises.

This course will give you a basic introduction to the principles of quantum chemistry. In the time we have here we can only cover the basics, but once you understand these basics you will be able to go on and learn about more advanced topics on your own. It is therefore not important exactly how much material we cover in class. What I am most concerned about is that you understand the material that we do cover. However, this puts also a certain burden on you, *i.e*. you should ask questions if a subject or point made is not clear to you. I have found that students are often afraid to ask questions when they don't understand something. They feel they are going to pose a stupid question. To me there are no stupid questions. When you leave this room you should feel that you understand everything that I covered. It is your responsibility to speak up when you don't understand.

1.2 Importance and Usefulness of Quantum Chemistry

One can think about chemistry and physics on two levels. In your physics course up to now, you have learned about the physics of macroscopic objects. This is described by the fields of classical mechanics, electricity and magnetism, and geometrical optics. In a similar way, in your engineering courses you will learn about the bulk or macroscopic chemical properties of matter, *i.e.* mass and energy transport properties, heat capacity, viscosity, density, etc. Since we interact with the world around us at a macroscopic level, it is clearly important to treat chemistry and physics at this macroscopic level.

However, molecules are microscopic objects, and there are physical phenomena of molecules that only become apparent when one looks at microscopic dimensions. Some of these phenomena are very different than what one would expect from our experience in the macroscopic world.

From an engineering point of view, the microscopic realm is also becoming more and more important as all types of engineering attempt to measure and control processes on a microscopic level. Chemists and physicists have been doing “nanotechnology” for a long time insofar as molecules are microscopic objects that we attempt to design, fabricate, and manipulate.

Quantum chemistry, or more generally quantum mechanics, describes a field that treats the microscopic properties of matter. Classical mechanics, which is what you have been studying in your physics courses up to now, can describe physical and chemical systems very well on a macroscopic level but fails badly on a microscopic level. Quantum mechanics provides a framework that describes matter at a microscopic level but in the limit of large dimensions generalizes to classical mechanics. It is important for us, both as scientists and engineers, to understand the microscopic basis of the macroscopic theories.

1.3 Historical Perspective

Towards the end of the 19th century, many physicists felt that all of the basic principles of physics had been discovered, and there was little that was fundamentally new to be found.

- Newtonian Mechanics had become a mature branch of science (200 years old), particularly by the work of Hamilton and Lagrange.
- The field of Thermodynamics was essentially in the form that it is today.
- The work of Maxwell brought together many of the unanswered questions of electricity and magnetism, and unified it with optics.

These fields constitute what is considered *Classical Physics*.

In physics as well as in any field of science, the basic approach is to postulate a theory and then test the theory by comparison with experimental observations. If the theory fails to describe adequately the observed phenomena, it is either rejected or modified. When the theory gets to the point where it describes the entirety of experimental observations, it generally becomes accepted as being correct. Most of *classical physics* had reached this point by the end of the 19th century.

One of the basic assumptions of *classical physics* was that physical quantities such as energy, momentum, etc. could take on a continuous range of values. However, the beginning of the 20th century witnessed several important experiments that did not fit the classical picture. When enough such observations mount, the current theory is overturned and a new one replaces it. Hence, in the first quarter of this century, a revolution occurred in the world of physics, and the development of *Quantum Mechanics* was at the center of this revolution.

I would like to discuss briefly just a few of these early experiments that served to overturn much of classical physics.

These experiments involve:

- Blackbody Radiation
- The Photoelectric Effect
- The Line Spectra of Atoms

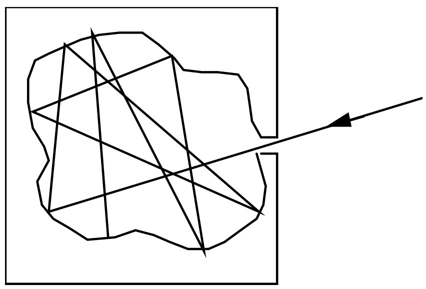
1.3.1 Blackbody Radiation (Planck - 1900)

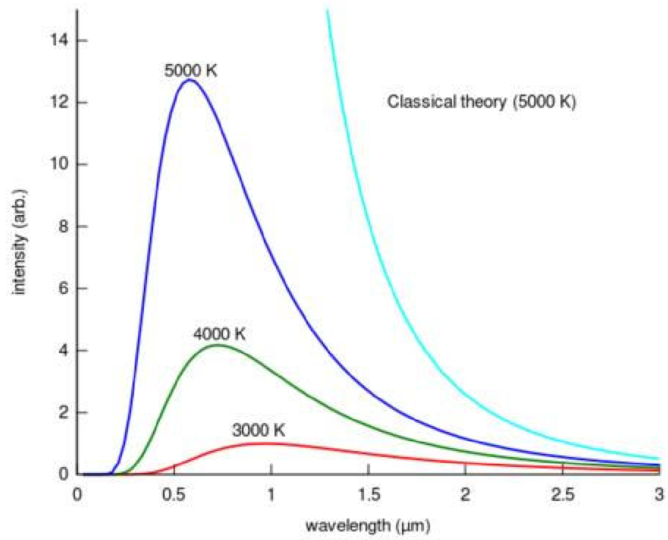
An ideal blackbody is an object that is perfectly black, *i.e*. it absorbs all wavelengths of light that fall onto it. A good model for a perfect black body is a cavity with a small hole to the outside.

Light that falls on the hole will undergo reflections in which it is partially absorbed and partially reflected. If the hole is small with respect to the area of the cavity wall, essentially all light that is incident on the hole will be totally absorbed. Therefore, the hole behaves just like the surface of a totally black body. At low temperatures, the hole looks black. It can be shown that it will also radiate like a perfect black body.

Now, if the cavity is heated, the hole will become self-luminous. This is because as the solid is heated the atoms vibrate and cause oscillations in the electrons which are responsible for the emission. The cavity walls will thus emit thermal radiation and some will escape the hole. Since the hole acts like a black surface, the emitted radiation will be characteristic of a perfect black body. The spectrum of light coming out of the hole can according

to Kirchhoff (1859) be described by a function $\rho(\nu,T)$, *i.e.* energy density in the frequency interval ν and $\nu + d\nu$, that depends only on the frequency of the emitted light and the temperature of the object.
Experimentally, that radiation looks something like this, where the energy density is given as function of the wavelength of the light :





You know from experience that when you heat things up hotter, the color changes from dull red, to bright yellow, even to blue, *i.e*. the peak frequency/wavelength shifts.

The problem comes in calculating this energy spectrum using the laws of classical physics. Early in 1900, this was done by Lord Rayleigh and Sir James Jeans as well as others, and their basic result was:

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

where $\rho(\nu,T)$ is the energy density between ν and $\nu + d\nu$

This is called the Rayleigh-Jeans formula for blackbody radiation. If we compare this value to that observed experimentally, one finds that it does ok at low frequencies, but at high frequencies it fails miserably. This has been termed the ultraviolet catastrophe, since it fails in the ultraviolet region of the spectrum.

Later, in the same year, Max Planck was able to deduce a theoretical result that was in complete agreement with the experimental observations. He reasoned that some quantization phenomena must be occurring to give a maximum in the intensity distribution, *i.e.* the energy emitted by the electron oscillations could only take on discrete values:

$$E = n\Delta\varepsilon$$

He then assumed that the energy increment $\Delta\varepsilon$ is simply proportional to the frequency of the vibrating electron, hence:

$$\Delta\varepsilon = h\nu$$

where *h* is an adjustable parameter which was varied to fit the experimental observations.

Thus, the emitted energy *E* could only take on integral values of $h\nu$

$$E = nh\nu \qquad\qquad n = 1, 2, 3, \ldots$$

Lord Rayleigh

Sir James Jeans

Max Planck

From statistical thermodynamics, the above condition gives

$$\rho(\nu,T)d\nu = \frac{8\pi h\nu^3}{c^3}\frac{1}{e^{h\nu/kT}-1}d\nu$$

This result matched the experimental observations for blackbody emission perfectly and yielded a value for h of $6.626 \cdot 10^{-34}$ J·sec. The constant h is nowadays called Planck's constant. This formula for blackbody radiation is frequently used in astronomy to estimate the temperature of stars.

Note what happens in certain limits. If we were to make the value of h arbitrarily small or make T very large, we could expand the exponential in a power series.

$$e^{h\nu/kT} \approx 1 + h\nu/kT + \ldots \qquad\qquad \text{for } h\nu/kT \ll 1$$

If we neglect the higher order terms (which will be small) and put this back into the expression we get:

$$\rho(\nu,T)d\nu \approx \frac{8\pi h\nu^3}{c^3}\frac{1}{1+h\nu/kT-1}d\nu$$

$$\approx \frac{8\pi kT\nu^2}{c^3}d\nu$$

which is identical to the classical result, *i.e*. the Rayleigh-Jeans formula.

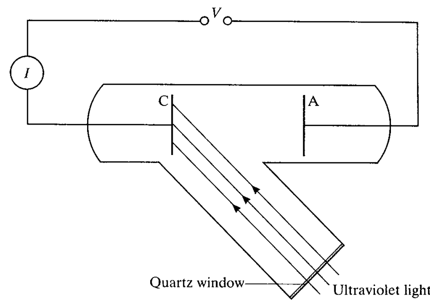
This is a general principle that we will see over and over again. In the limit of $h \to 0$ quantum mechanics goes over to classical mechanics. In addition, in the limit of high temperature quantum mechanics goes over to classical mechanics. Note also that as the frequency gets small, $h\nu/kT \ll 1$. This is why the original Rayleigh-Jeans formula worked at low frequency.

So Planck's contribution here was that the energy of oscillations of the electrons in a black body was quantized, not the radiation itself. He was awarded the Nobel Prize for this work in 1918.

1.3.2 The Photoelectric Effect (Einstein - 1905)

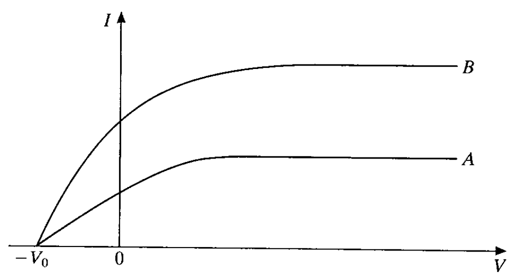
In about 1887, Heinrich Hertz discovered that ultraviolet light causes electrons to be ejected from the surface of a metal. This is called the *photoelectric effect.*

There were several observations involving the photoelectric effect that were in stark contrast to the predictions of classical theories. In 1905 Einstein put forth an explanation of these observations that was central in the development of a *quantum theory*.
First, let me tell you about how the experiments are done. A typical experimental arrangement would have been as follows:



A piece of metal is placed in an evacuated glass tube where light shines on it. Electrons are emitted from the surface of the metal and have some kinetic energy. An electrode is placed opposite the metal surface and a negative potential is applied to retard the electron flow to that electrode.

When the current is measured as a function of the applied voltage between the electrodes one obtains curves as shown in the figure below for low (A) for high (B) light intensity. In both cases, one finds the same voltage $-V_0$ to stop the electrons.



How can we interpret these results? The kinetic energy of the electrons is given by

$$E_{kin} = \tfrac{1}{2} m_e \mathrm{v}^2$$

If we measure the voltage required to stop the electrons, V_0, the energy of those electrons will just be

$$E_{kin} = \tfrac{1}{2} m_e \mathrm{v}^2 = eV_0$$ where e is the electron charge (Note: Volts = Joules/Coulomb)

Thus by measuring the stopping voltage, V_0, one has essentially measured the kinetic energy of the electrons. If one plots the stopping voltage as a function of the frequency of light one obtains something like the following (note that this curve was not known when Einstein proposed his explanation, it rather was predicted by him).

There are several significant observations to be made here:

1. There is a threshold frequency, ν_t, below which no electrons are emitted that is metal dependent.
2. The slope is found to be identical for all metals.
3. The kinetic energy of the electrons is independent of the intensity of light, depending only on the frequency.
4. Increasing the intensity increases the *number* of electrons emitted, *not their energy*.
5. Electrons are released immediately

These observations were contrary to the classical physical description of light. The wave nature of light had been very well established by interference phenomena. The energy of a classical wave of with amplitude E_0, is proportional to the intensity, $I \propto E_0^2$. Increasing the intensity should therefore increase the energy of the incident light and hence increase the kinetic energy of the electrons. In addition, a classical wave of a particular frequency can have any energy, *i.e.* by simply increasing the wave amplitude or intensity.

If the classical description of light were correct, the photoelectric effect should work for any frequency, if intense enough. However this was not found. Red light, no matter how intense, would not cause electrons to be emitted from the metal, whereas blue light that was above a threshold, φ, would eject electrons no matter how weak.

In his work on blackbody radiation, Planck had restricted his concept of the quantization of energy to the emission and absorption process, and he presumed that once emitted, the light behaved like a wave. Einstein proposed the energy itself consisted of concentrated bundles, or photons, where the energy of a single photon is given by

$E = h\nu$ where ν is the frequency of the light and h is Planck's constant.

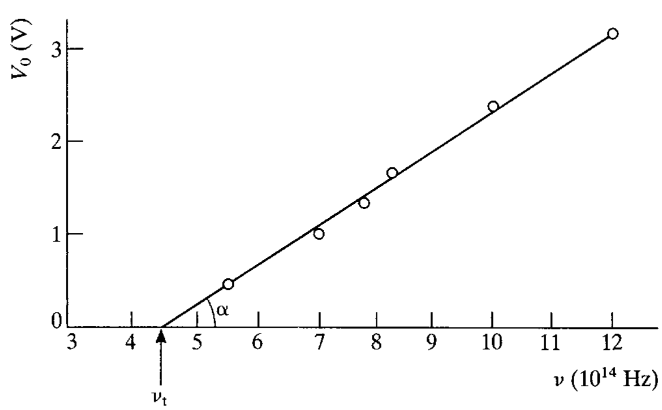
Applying the photon concept to the photoelectric effect, Einstein proposed that the entire energy of a photon is transferred to a single electron in a metal. When emitted, the electron's kinetic energy will be:

$E_{kin} = h\nu - \varphi$ where φ is the energy required to remove the electron.

Since the stopping voltage is proportional to the kinetic energy, one can write

$$E_{kin} = eV_0 = h\nu - \varphi$$

By plotting V_o versus ν one gets a slope of *h/e*. By comparing this to the slope of the experimental data, Einstein obtained a value for *h* of $6.63 \cdot 10^{-34}$ J·sec, in agreement with Planck's results. It was quite amazing at the time that a completely different experimental approach produced a value of this constant so nearly the same.



[Heinrich Hertz](#)

[Albert Einstein](#)

This model also explains the fact that there is a threshold frequency ν_t , since the process will not occur unless ν satisfies the equation:

$$h\nu_t \geq \varphi$$

Since a single photon ejects a single electron, if the energy of the photon does not exceed the work function of the metal, no electrons will be emitted. However, as ν increases the energy and not the number of electrons will increase. In addition, according to this model, more intense light means more photons and hence more electrons. Therefore, Einstein's model was in complete agreement with the observations.

Einstein's major contribution here was that not only did matter exhibit quantized energy states, but also light was quantized. He was awarded the Nobel Prize in 1921 for this contribution.

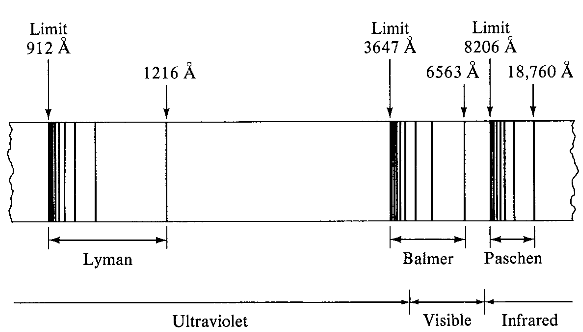
It is interesting to note that Newton had proposed a "corpuscular" theory of light 200 years earlier but this notion had since been dismissed due to the success of wave theories for describing phenomena such as diffraction and interference.

It is now well accepted that light has both wave and particle behavior, and there is a principle formulated by Niels Bohr that we will discuss later which states that you cannot simultaneously observe the wave and particle properties in one experiment.

1.3.3 The Line Spectra of Atoms

It was well known for some time that when gas phase atoms are subjected to high temperatures or an electrical discharge they emit light that is not continuous, but consists of discrete frequencies or lines that are characteristic of a particular element. This is in stark disagreement with classical physics.

Hydrogen, which is the simplest atom, shows the simplest emission spectrum, looking something like this:



An amateur Swiss scientist, Johann Balmer, showed in 1885, that the spacing between some of the lines in the hydrogen spectrum could be expressed in a simple algebraic form. If each line in the series, now called the Balmer series, is assigned an integer *n*, the frequency of lines is given quantitatively by the formula:

$$\nu \propto \left(\frac{1}{2^2} - \frac{1}{n^2}\right) \qquad n = 3,4,5,\ldots$$

A Swedish spectroscopist, Johannes Rydberg, was later able to account for all the lines in the hydrogen spectrum by using the empirical formula:

$$\tilde{\nu} = \frac{1}{\lambda} = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \qquad n_1 = 1,2,3,\ldots \text{ and } n_2 > n_1$$

where R_H is an empirically determined constant known as the Rydberg constant.

R_H = 109 680 cm^{-1}

The fact that integers are involved here is very different from what you would expect from a classical picture and strongly suggest that the energy of the hydrogen atom is quantized.

There was no explanation for this observation until the work of Niels Bohr who was working for Rutherford in 1911 when Rutherford proposed the nuclear model for the atom: that is that atoms exist as a heavy, positively charged nucleus with electrons surrounding it. Bohr abandoned classical physics by making the following assumptions about the hydrogen atom.

Bohr's (non-classical) assumptions:

1. The electron in an atom has only certain definite stationary states of motion; each of these states has a definite, fixed energy. In other words, *the energy is quantized*.

2. In any of these states the electron moves in a circular orbit around the nucleus.

3. When an atom is in one of these states it does not radiate; but when changing from a high-energy state to a state of lower energy the atom emits a photon whose energy $h\nu$, is equal to the difference in energy of the two states, *i.e.*,. $\Delta E = h\nu$

4. The states of allowed electronic motion are those in which the angular momentum of the electron is an integral multiple of *h*/2π. In other words, *the angular momentum is quantized.*

$$l = n\frac{h}{2\pi} = n\hbar \qquad \text{where} \qquad \hbar = \frac{h}{2\pi}$$

These ideas were very non-classical. Quantized energy levels were still not widely accepted at that point. Particularly troubling was the fact that the electrons moved in circular orbits yet did not radiate. In electromagnetic theory, a charge that is accelerated will continuously emit energy and hence gradually spiral into the nucleus. Although this picture of circular orbits *was later shown to be wrong*, it gave the correct result for the hydrogen atom.

Finally, the quantization of orbital angular momentum was done in an *ad hoc* manner. There was no physical justification for it.

Having made the non-classical assumptions of circular orbits of fixed energy and angular momentum, Bohr went on to apply the laws of classical mechanics.

Let us look at his derivation. As the electron rotates about the nucleus, the attractive Coulomb force between the two charged particles directed in towards the center (*i.e.*, toward the nucleus, assuming it is infinitely heavy compared to the electron) supplies the force needed to keep the electron in a stable, fixed circular orbit. (Think of a ball rotating on a string. The inward force is supplied by the tension on the string.)

Classical Equations:

$$\frac{e^2}{4\pi\varepsilon_0 r^2} = \frac{m\mathrm{v}^2}{r}$$

Solving for *r*:

$$r = \frac{e^2}{4\pi\varepsilon_0 m\mathrm{v}^2}$$

The angular momentum of a particle is given by:

$$l = \mathbf{r} \times \mathbf{p}$$

Assuming a circular orbit for the particle, one can write:

$$l = |\mathbf{r} \times \mathbf{p}| = |\mathbf{r}||\mathbf{p}|\sin\theta = |\mathbf{r}||\mathbf{p}|\sin 90^\circ = rp = m\mathrm{v}r$$

The quantization of angular momentum thus gives:

$$l = m\mathrm{v}r = n\hbar \qquad n = 1,2,3\ldots$$

We can solve this equation for v and substitute it in to our equation for *r*.

$$\mathrm{v} = \frac{n\hbar}{mr}$$

Thus

$$r = \frac{e^2}{4\pi\varepsilon_0 m\left(\frac{n\hbar}{mr}\right)^2}$$

Rearranging:

$$r = \frac{4\pi\varepsilon_0\hbar^2}{me^2}n^2 \qquad n = 1,2,3,\ldots$$

$$r = a_0 n^2 \qquad a_0 = 5.29\cdot 10^{-11}\,\mathrm{m} = 0.529\,\text{Å}$$

where a_0 is nowadays known as the Bohr radius. You can see that the circular orbits have radii that are characteristic of the quantum number *n*.

To find the energy of the electron in the hydrogen atom, we need to write down the sum of the kinetic energy of the electron and the potential energy of the electron-proton interaction

$$E = \tfrac{1}{2}m\mathrm{v}^2 - \frac{e^2}{4\pi\varepsilon_0 r}$$

We can substitute for mv^2 in the kinetic energy term using our first equation:

$$E = \frac{1}{2}\frac{e^2}{4\pi\varepsilon_0 r} - \frac{e^2}{4\pi\varepsilon_0 r}$$

$$= -\frac{e^2}{8\pi\varepsilon_0 r}$$

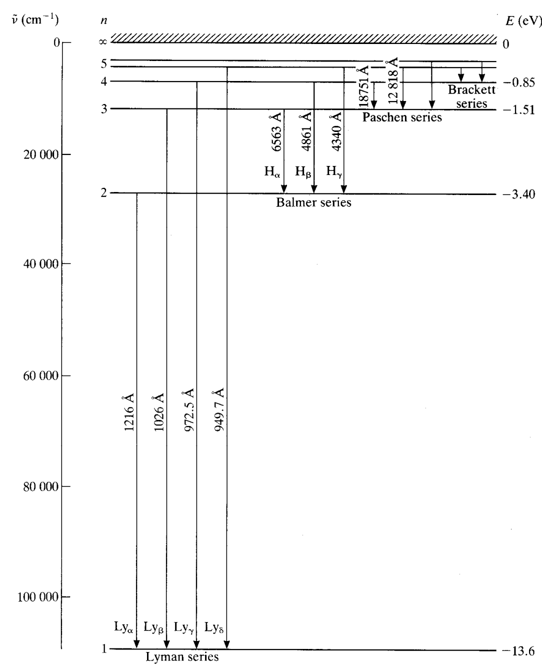
Finally, substituting our formula for r we get

$$E_n = -\frac{me^4}{8\varepsilon_0^2 h^2}\frac{1}{n^2} \qquad n = 1,2,3,\ldots$$

Now these are the energies of the stationary states of the electron. Light is emitted when the atoms go from a higher state down to a lower state.

Thus $$\Delta E = \frac{me^4}{8\varepsilon_0^2 h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = h\nu$$

Setting $\Delta E = h\nu$ gives us what is called the ***Bohr frequency condition***, *i.e*. as the electron falls from one level to another, the photon given off has energy $h\nu$. You can see that this formula agrees with the empirically determined Rydberg formula. We can now see where the hydrogen atom spectrum arises.



The Lyman series occurs when electrons relax to n=1 from higher levels. The Balmer series occurs when excited electrons relax back into the n=2 state, and so on.

One now thus finds a theoretical value for the Rydberg constant given by:

$$R_H = \frac{me^4}{8\varepsilon_0^2 h^2}$$

Johann Balmer

Johannes Rydberg

Niels Bohr

This permitted calculation of the empirical Rydberg constant from other fundamental constants to within 0.5% accuracy. Including the reduced mass of the electron improves the agreement even further. This model works for any one-electron atom, *e.g.*, He^+, Li^{2+}.

Although this model of the atom is oversimplified and was replaced later, this concept of quantization of electronic energy levels was important to the development of quantum theory.

To summarize the major conclusions drawn from these and other experiments in the early 20th century:

- Planck's description of blackbody radiation and Bohr's analysis of the line spectra of atoms suggest that molecules and atoms emit energies in discrete or quantized amounts. Hence, their energies are quantized.

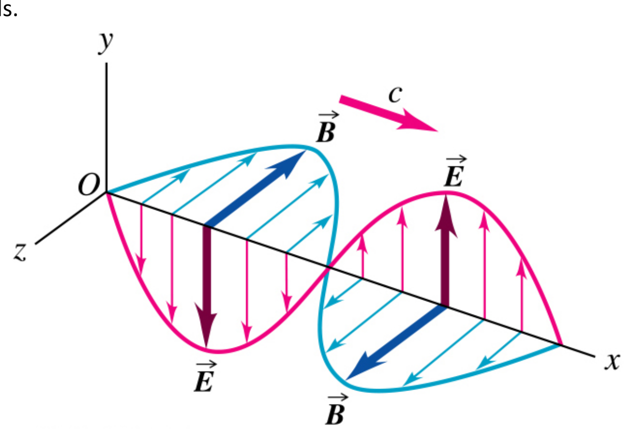
- The photoelectric effect suggests that such quantization is not only a property of matter, but also an intrinsic property of light itself.

The idea that light consisted of "particles" had actually been suggested by Newton, but the overwhelming amount of data displaying the wave-like properties of light (particularly the work of Maxwell) had caused this notion to be rejected. However, new experiments revealed that light exhibits both wavelike and particle-like properties.

The wave-particle duality of light (and matter) is of central importance to the development of quantum theory. It is therefore worth our considering it further.

1.3.4 The Wavelike Nature of Light

The wave nature of light is given by Maxwell's equations and is described by mutually perpendicular oscillating electric and magnetic fields.



For plane polarized light:

$$E(x,t) = E_{y0}\cos(kx - \omega t) = E_{y0}\cos\left(2\pi\left[\frac{x}{\lambda} - \nu t\right]\right)$$

$$B(x,t) = B_{z0}\cos(kx - \omega t) = B_{z0}\cos\left(2\pi\left[\frac{x}{\lambda} - \nu t\right]\right)$$

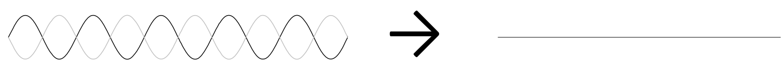
where $k = \frac{2\pi}{\lambda}$ and $\omega = 2\pi\nu$

The wave is thus characterized by a wavelength, λ and a frequency, ν such that

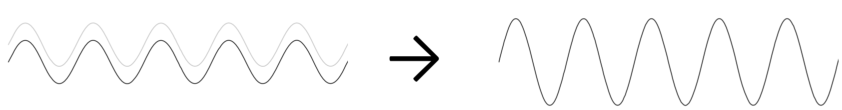
$$\lambda\nu = c \quad \text{or} \quad \nu = \frac{c}{\lambda}$$

One property of waves, which will be of great importance to us in this course, is that of interference or superposition. Interference effects were demonstrated in 1801 by Thomas Young.

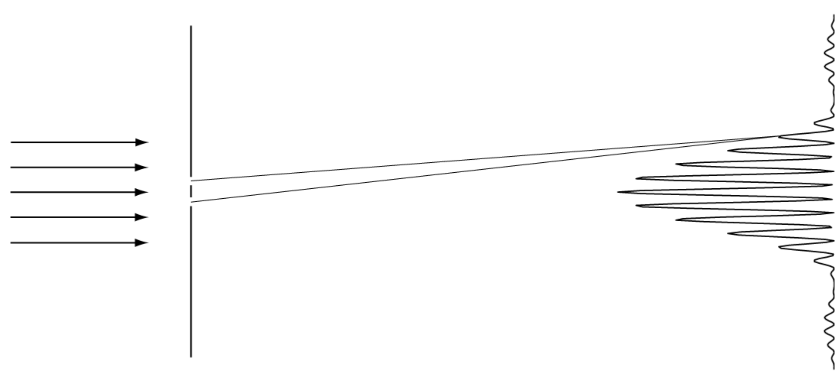
The result of superimposing two waves can be determined by simply adding the wave amplitudes. If two waves are 180° out of phase, they interfere destructively.



Conversely, if they are in phase they constructively interfere.



You may also recall that for a double slit experiment one gets a diffraction pattern that is modulated by interference fringes.



These patterns occur because waves emanating from each slit differing in path length by integral numbers of wavelengths interfere.


James Clerk Maxwell


Thomas Young

1.3.5 The Particle-like Nature of Light

The particle nature of light is characterized by:

- Discrete energies $E = h\nu$ (we have discussed this already)
- Its momentum

We know that the rest mass of a photon is zero. However, Einstein's work on Relativity tells us that a photon has a relativistic mass given by:

$$E = mc^2$$

If we combine this with Planck's equation:

$$E = h\nu = mc^2$$

Rearranging we get:

$$mc = \frac{h\nu}{c} = \frac{h}{\lambda} \qquad \text{since} \quad \frac{\nu}{c} = \frac{1}{\lambda}$$

The momentum of the photon is than given by:

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

That photons actually do have momentum was confirmed by Compton in 1924, when he observed scattering of photons by electrons. He described the process theoretically assuming a photon momentum of h/λ, and this prediction was confirmed by experiment. He was awarded the 1927 Nobel Prize in physics for this work. Note that Einstein never discussed the momentum of a photon, even though he proposed the photon concept and developed the theory of Relativity.

Light exhibits both wave- and particle-like properties.

At this point it is useful to discuss the units used by atomic and molecular scientists to express the characteristics of light.

We already saw that the energy of a photon is given by:

$$E = h\nu$$

If one gives the frequency of the light one can directly convert it to energy using this expression. However, the frequency of light at which atoms absorb light is in the order of 10^{15} Hz, not a convenient order of magnitude to use.

We saw before that that the frequency of the light is related to its wavelength according to:

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

Thus we can express the energy of a photon as:

$$E = hc\frac{1}{\lambda} = hc\tilde{\nu}$$

where $$\tilde{\nu} = \frac{1}{\lambda}$$

is known as the wavenumber (not to be confused with the wavevector) and has the units of cm^{-1}. If the wavenumber is given the energy can be simply calculated using the expression above. The use of wavenumbers has the advantage that the relevant part of the electromagnetic spectrum is covered by 1-100'000 cm^{-1}.

Once the wavelength of the light is known the corresponding wavenumber can be readily calculated. Let us calculate the wavenumber for light with a wavelength of 500 nm (blue-green light).

$$\lambda = 500 \text{ nm} = 500 \cdot 10^{-9} \text{ m} = 5 \cdot 10^{-7} \text{ m} = 5 \cdot 10^{-5} \text{ cm}$$

Consequently, one finds

$$\tilde{\nu} = \frac{1}{5 \cdot 10^{-5}} = 20'000 \text{ cm}^{-1}$$

1.3.6 The wave-like Nature of Matter

Experiments in the beginning of last century not only indicated that light exhibits wave-particle duality, *but that matter does as well.* We are quite familiar with the particle-like properties of matter, since our intuition is calibrated by classical mechanics. However, we need to discuss the wave properties of matter.

In 1923, DeBroglie suggested that not only does light show properties of particles, but particles of matter exhibit wavelike properties as well. DeBroglie was awarded the Nobel Prize in 1929 for his Ph.D. thesis.

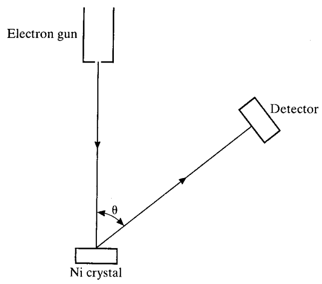
He suggested that an electron of mass *m* and speed v would have a wavelength:

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

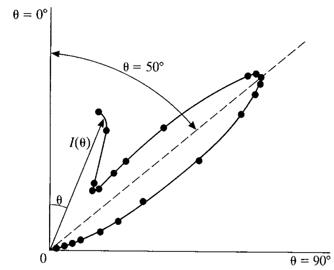
So analogous to radiation, matter also obeys the laws:

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

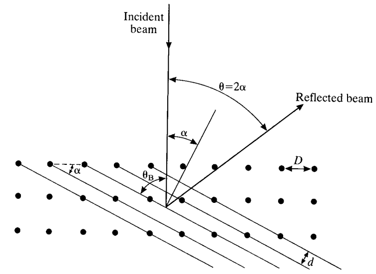
In 1927, Davisson and Germer confirmed this hypothesis by demonstrating that electrons could exhibit Bragg diffraction off a crystal surface by accelerating them to a velocity such that their wavelength is of comparable dimensions to the crystal lattice. A schematic overview of their setup is shown below. Using this setup they observed a maximum in the scattered electron intensity at an angle of 50°. This observation could be explained by constructive interference of the waves by the crystal lattice.



Experimental setup used by Davisson and Germer



Measured angular distribution of the scattered electrons



Scattering of electron waves by a crystal

Davisson was awarded the Nobel Prize in 1937 for this work along with G. P. Thomson. The latter was the son of J. J. Thomson who discovered the electron and characterized it as a particle with definite mass to charge ratio. He was awarded the Nobel prize in 1906 for this. So the father won it for demonstrating the electron as a particle and the son for demonstrating that it is a wave.

To get a feel for the wavelengths of typical objects consider the following:

Particle	Mass (kg)	Velocity (m/sec)	λ (Å)
100 volt electron	$9.1\cdot10^{-31}$	$5.9\cdot10^{6}$	1.2
Dust particle	~ 10^{-15}	$1\cdot10^{-3}$	$6.6\cdot10^{-6}$
Tennis ball	0.057	57 (≈200 km/h)	$1.18\cdot10^{-24}$

You can see why it is impossible to detect quantum effects on a macroscopic scale. The smallness of *h* makes these effects apparent only for small mass objects.

It is important to note that: **Both matter and radiation exhibit wave-particle duality.**

It is important to note that in any given measurement, only one model applies. Niels Bohr summarized this situation by stating: "If a measurement proves the wave character of radiation or matter, then it is impossible to prove the particle character in the same experiment, and conversely."

This is known as the *Bohr Complementarity Principle*. The two views can be linked by a probabilistic interpretation. Einstein made the following argument:

In the particle picture, light intensity is given by:

$$I = N h\nu \ ,$$

where *N* is the number of photons per unit time crossing a unit area $\perp$ to the direction of propagation. From wave theory, the intensity is proportional to the average value of the square of the electric field over one cycle, $\overline{E}^2$. More specifically,

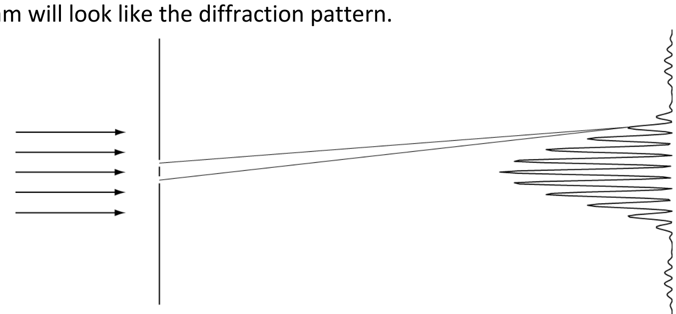
$$I = \varepsilon_0 c \overline{E}^2$$

Equating these we see:

$$N \propto \overline{E}^2$$

Thus, Einstein interpreted $\overline{E}^2$ as the probability measure of photon density.

Let us look back at our diffraction pattern. One detects the intensity at each point along the screen. If we turn down our light intensity such that one photon goes through at a time and use a CCD camera where we could detect individual photons, any one photon will make one spot on the screen (Measuring particle properties here). However, if we repeat this experiment a large number of times, one could build up a histogram of photon impacts. That histogram will look like the diffraction pattern.



In analogy to Einstein's view of the wave-particle duality of radiation, Max Born proposed a similar view of the wave-particle duality of matter. We talked about the wavelength associated with matter, but we can also assign it an amplitude.

The function representing the DeBroglie wave is called a wave function, signified by Ψ. The square of the amplitude of this matter wave is related to a probability.

I would like to make one last point about matter waves. The DeBroglie formula for matter waves gives a nice interpretation of Bohr's quantization condition for electron orbits. Since the electron in the hydrogen atom has a particular wavelength and travels in circular orbits (according to Bohr), then it is reasonable to assume that the wave must "match" in this circular orbit, otherwise there will be interference and cancellation of intensity. One could show that a non-match would lead to total destructive interference of the wave.

For the orbits to match, we will have the following condition:

$$2\pi r = n\lambda \qquad n = 1, 2, 3, \ldots$$

If we substitute DeBroglie's relation:

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

one gets

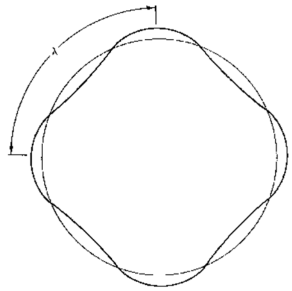
$$2\pi r = \frac{nh}{m\text{v}}$$

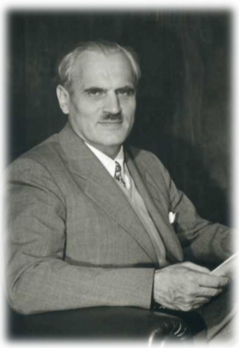
or

$$l = m\text{v}r = \frac{nh}{2\pi} = n\hbar$$

This is exactly the assumption Bohr made.

Below is a schematic of the standing wave produced by an electron in a Bohr orbit with $n = 4$. In this case the circumference of the circle is 4λ.





[Arthur Compton](#)

[Louis-Victor DeBroglie](#)

[Davisson](#) and [Germer](#)

[G.P Thomson](#)

1.3.7 The Heisenberg Uncertainty Principle

A very important consequence of this wave-particle duality of matter is a principle called the Heisenberg Uncertainty Principle.

It states that an experiment cannot *simultaneously* determine the exact component of momentum p_x say, of a particle and its exact corresponding coordinate position in x. The precision of the measurement is inherently limited by the measurement itself, such that $\Delta p_x \Delta x \approx h$ This principle has nothing to do with the precision of the instrumentation (but with the magnitude of h).

Let's say we want to make the most accurate measurement possible of the position of an electron. For the electron to be "seen", a photon must interact or collide in some way with the electron, or else we have no way of knowing it is there. If we wish to locate the electron within a distance Δx, we need to use light with a wavelength at least that small. However, the photon has a momentum $p = h/\lambda$, and during the collision some of the momentum will be transferred to the electron. The act of locating the electron, changes its momentum in an uncertain way. If we wish to locate the electron more accurately, we need shorter wavelength light, but these photons will have higher momentum, and will thus cause more uncertainty in the momentum of the particle.

To look at this more quantitatively, say we wanted to locate an electron to within 1 Å.

$$\Delta x = 1 \cdot 10^{-10}\,\text{m}$$

$$\Delta p_x = \frac{h}{\Delta x} = \frac{6.626 \cdot 10^{-34}\,\text{Js}}{1 \cdot 10^{-10}\,\text{m}}$$

$$= 6.6 \cdot 10^{-24}\,\text{kgms}^{-1}$$

Since $p = m\text{v}$,

we have $\Delta p = m\Delta\text{v}$ or $\Delta\text{v}=\frac{\Delta p}{m}$

Having $m = 9.11 \cdot 10^{-31}$ kg

yields for the uncertainty in speed

$$\Delta\text{v} = \frac{6.6 \cdot 10^{-24}\,\text{kgms}^{-1}}{9.11 \cdot 10^{-31}\,\text{kg}}$$

$$= 7.2 \cdot 10^{6}\,\text{ms}^{-1} \qquad \textit{This is } 2.4\% \textit{ the speed of light}!!$$

Note that:
1. if Δx increases, Δv decreases
2. if m increases, Δv decreases

You can see that in the limit of large masses and macroscopic sizes or distances, this phenomenon becomes unimportant.

1.3.8 Summary

We discussed 3 different discoveries made in the early 20th century (there were others, but I picked three of the most important ones). Below these discoveries and the most important new concepts introduced are listed:

(1) Theory of blackbody radiation (Planck, 1900; Nobel Prize 1918)
Key concepts introduced:
- Energy emitted by a blackbody takes on integral values of $h\nu$ hν; $E = Nh\nu$
- Introduced Planck's constant, h

(2) Photoelectric effect (Einstein, 1905; Nobel Prize 1921)
Key concept introduced:
- Light has quantized energy, $E = h\nu$

(3) Line spectra of atoms
Key concepts introduced:
- Quantized energy of atoms
- Energy and angular momentum of electron quantized

Rydberg and Balmer found empirical formula:

$$\tilde{\nu} = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \qquad n_1 = 1,2,3,\ldots \text{ and } n_2 > n_1$$

Bohr (Nobel Prize 1922):
- Stationary states of electron, angular momentum quantized $l = \frac{nh}{2\pi}$
- $\Delta E = h\nu$ upon changing state

(4) Wave-particle duality of light and matter

Wave-particle duality of light

$E = h\nu$ (Einstein)

$p = \frac{h}{\lambda}$ (Compton)

Wave-particle duality of matter

$\Delta E = h\nu$ (Planck, Rydberg, Bohr)

$\lambda = \frac{h}{p}$ (DeBroglie)

(5) Heisenberg Uncertainty Principle

$\Delta p_x \, \Delta x \geq h$ result of wavelike nature of matter. We will see that the principle is much broader than this simple statement.

Quantum chemistry deals with the wavelike nature of matter!!