

V25.0109: General Chemistry I (Honors)

Notes for Lecture 5

I. ELECTRON DIFFRACTION

Continuing with our analysis of experiments that lead to the new quantum theory, we now look at the phenomenon of electron diffraction. It is well-known that *light* has the ability to diffract around objects in its path, leading to an interference pattern that is particular to the object. This is, in fact, how holography works (the interference pattern is created by allowing the diffracted light to interfere with the original beam so that the hologram can be viewed by shining the original beam on the image). A simple illustration of diffraction is the Young double slit experiment pictured below:

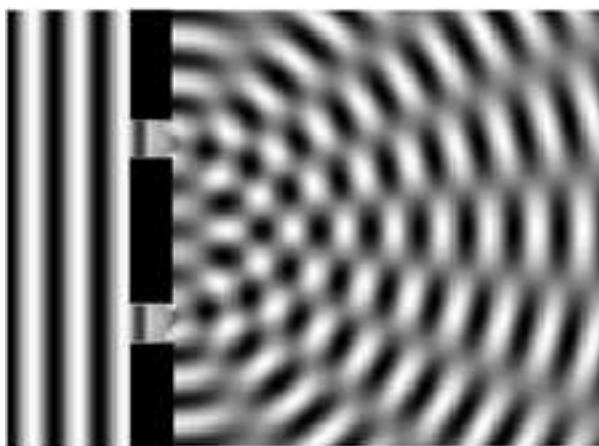


FIG. 1. From www.lightandmatter.com

Here, we use water waves (pictured as waves in a plane parallel to the double slit apparatus) and observe what happens when they impinge on the slits. Each slit then becomes a point source for spherical waves that subsequently interfere with each other, giving rise to the light and dark fringes on the screen at the bottom. The intensity of the fringes is depicted in the sketch below:

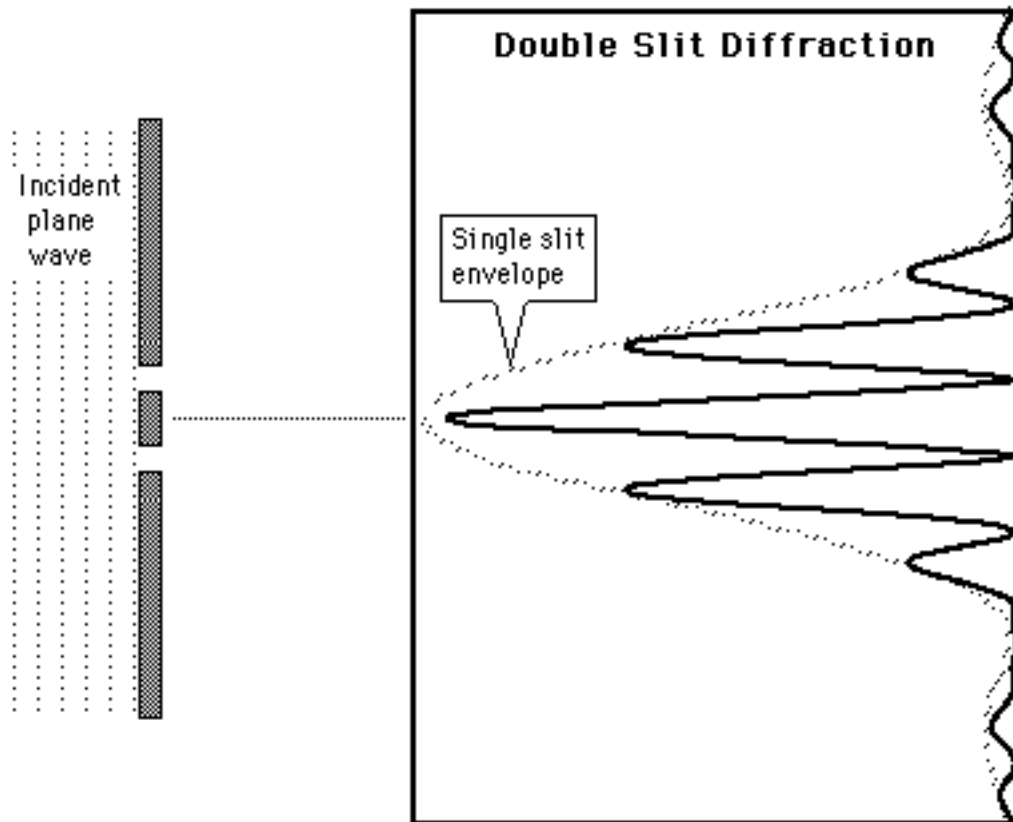


FIG. 2. From hyperphysics.phy-astr.gsu.edu

If laser light is used, the interference pattern appears as shown below:

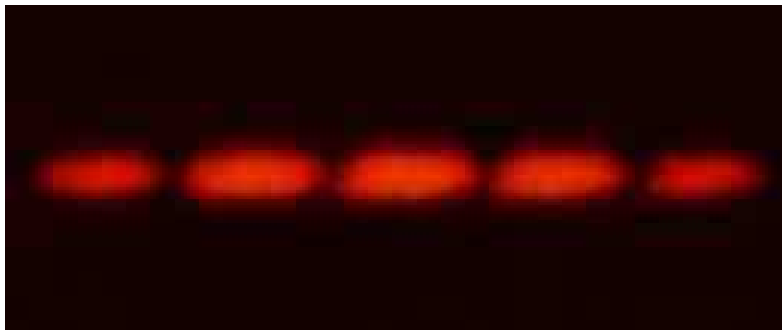


FIG. 3.

Amazingly, if electrons are used instead of light in the double-slit experiment, and a photosensitive screen is used, one finds the same kind of interference pattern! This is shown in the electron double-slit diffraction pattern below:

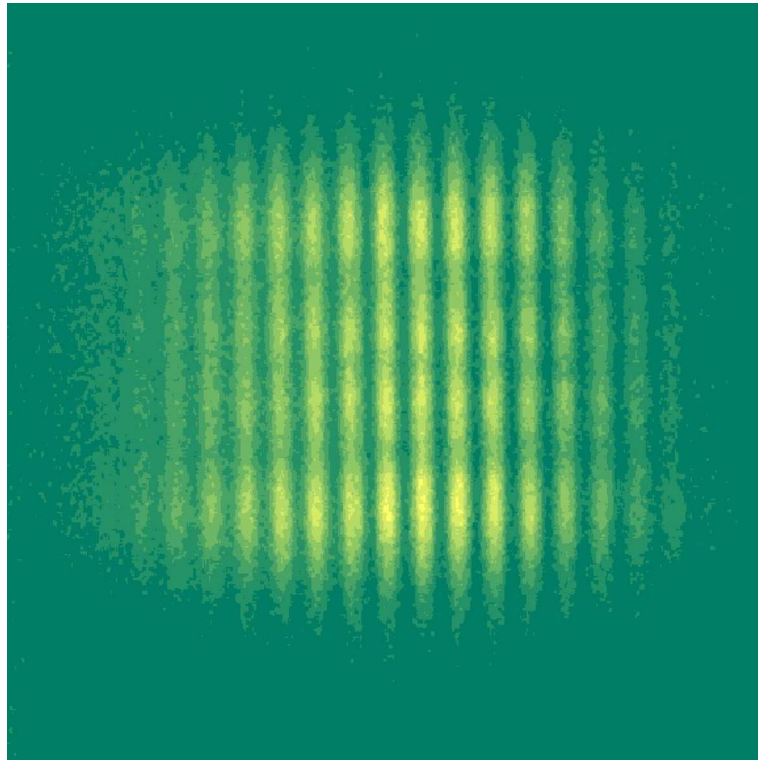


FIG. 4. From zms.desy.de

Obviously, classical mechanics is not able to predict such a result. If the electrons are treated as classical particles, one would predict an intensity pattern corresponding to particles that can pass through one slit or the other, landing on the screen directly opposite the slit (i.e., no intensity maximum at the center of the screen):

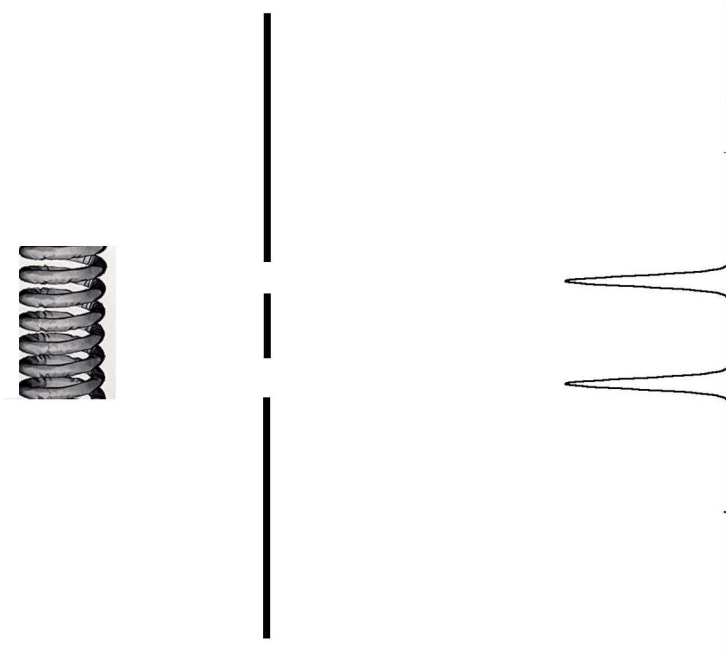


FIG. 5. Intensity pattern for “classical” electrons

The width of each peak is a direct measure of the width of the slits. Since, in classical mechanics, the electrons

follow definite, deterministic, predictable paths, there can be no deviation from this pattern. For this reason, the classical explanation cannot be the correct one.

We will consider two different rationalizations of the electron double-slit experiment. The first, proposed by Clinton Davisson and Lester Germer in 1927, was based on a hypothesis put forth earlier by Louis de Broglie in 1922. De Broglie suggested that if waves (photons) could behave as particles, as demonstrated by the photoelectric effect, then the converse, namely that particles could behave as waves, should be true. He associated a wavelength λ to a particle with momentum p using Planck's constant as the constant of proportionality:

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

which is called the *de Broglie wavelength*. The Davisson-Germer experiment, which produced an electron diffraction pattern from electrons scattered off a nickel crystal, confirmed the de Broglie hypothesis. However, it was not until 1961 that an experiment in which electrons impinged on a slit apparatus was performed by Claus Jönsson. This was a five-slit set-up. The double-slit experiment was finally performed in the 1970s by Pier Giorgio Merli, Giulio Pozzi and GianFranco Missiroli. The point is, however, that through such experiments, the idea that electrons can behave as waves, creating interference patterns normally associated with light, is now well-established. The fact that particles can behave as waves but also as particles, depending on which experiment you perform on them, is known as the *particle-wave duality*.

In the following, we give a brief discussion of where the de Broglie hypothesis comes from. From the photoelectric effect, we have the first part of the particle-wave duality, namely, that electromagnetic waves can behave like particles. These particles are known as *photons*, and they move at the speed of light. Any particle that moves at or near the speed of light has kinetic energy given by Einstein's special theory of relativity. In general, a particle of mass m and momentum p has an energy

$$E = \sqrt{p^2 c^2 + m^2 c^4}$$

Note that if $p = 0$, this reduces to the famous rest-energy expression $E = mc^2$. However, photons are massless particles that always have a finite momentum p . In this case, Einstein's formula becomes $E = pc$. From Planck's hypothesis, one quantum of electromagnetic radiation has energy $E = h\nu$. Thus, equating these two expressions for the kinetic energy of a photon, we have

$$h\nu = \frac{hc}{\lambda} = pc$$

Solving for the wavelength λ gives

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

Now, this relation pertains to photons not massive particles. However, de Broglie argued that if particles can behave as waves, then a relationship like this, which pertains particularly to waves, should also apply to particles. Hence, we associate a wavelength λ to a particle that has momentum p , which says that as the momentum becomes larger and larger, the wavelength becomes shorter and shorter. In both cases, this means the energy becomes larger. That is, short wavelength *and* high momentum correspond to high energy.

Let us now consider an alternative explanation of the double-slit experiment, however, due to Richard Feynman (who, by the way, was born in Queens!). This explanation is published in his 1965 book, *Quantum Mechanics and Path Integrals*. Feynman's explanation is closer in spirit to a classical-like picture, yet it still represents a radical departure from classical mechanics. Feynman postulated that electrons could still behave as particles in a double-slit experiment. The twist is that the particles do not follow definite paths, as they would if they were classical particles. Rather, they can trace out a myriad of possible paths that might differ considerably from the path that would be predicted by classical mechanics. In fact, electrons initialized in the same manner, will follow different paths if they are allowed to wend their way through the double-slit apparatus! This is illustrated in the figure below:

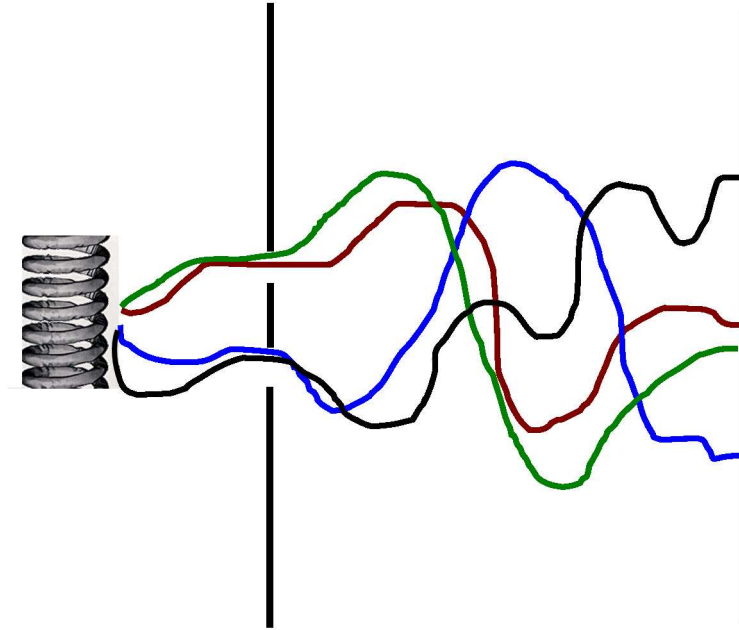


FIG. 6. Illustration of the many paths an electron can follow through the double-slit apparatus

Since the electron can follow any path and will follow different paths in different realizations of the experiment, physical quantities must be obtained by summing over *all* possible paths that the electron can follow. In order to carry out this sum, Feynman assigned a *weight* or *importance* to each path in the sum over paths. Since each path takes the electron from the source to a point on the screen (call this point y , where y varies over the length of the screen) in a time t , the probability P associated with each path can only depend on y and t . If t is fixed, the P can only depend on y . Feynman proposed that each path could be assigned a quantity called the *action* $S(y)$, where $S(y)$ has the following properties:

1. $S(y)$ varies only minimally for paths near the path that classical mechanics would predict the electron should follow.
2. $S(y)$ varies increasingly dramatically as the paths differ increasingly from the classical path.

He then assigned an *amplitude* $A(y)$ to each path according to the formula

$$A(y) = e^{iS(y)/\hbar}$$

where $i = \sqrt{-1}$ and $\hbar = h/2\pi$. The exponential of a complex argument has a simple expression in terms of common trigonometric functions:

$$e^{ix} = \cos(x) + i \sin(x)$$

Thus, we can also write $A(y)$ as

$$A(y) = \cos(S(y)/\hbar) + i \sin(S(y)/\hbar)$$

however, it is generally easier to work with the exponential directly.

It is important to note that $A(y)$ is a complex number. An amplitude is related to an actual probability P by taking the absolute value squared of the amplitude. Thus, if there were only one path with amplitude $A(y)$, the probability that the electron would follow that path is

$$\begin{aligned} P(y) &= A^*(y)A(y) = |A(y)|^2 \\ &= e^{-iS(y)/\hbar} e^{iS(y)/\hbar} \\ &= 1 \end{aligned}$$

as expected. This is also the probability that the electron will end up at a point y on the screen, since the single path takes the particle to a single definite point y . However, in Feynman's picture, the electron can follow any path. Thus,

in order to compute the probability $P(y)$ that the particle ends up at a point y on the screen, we must sum over *all* possible paths:

$$P(y) = \left| \sum_{\text{paths}} A_{\text{path}}(y) \right|^2$$

where $A_{\text{path}}(y)$ is the amplitude for a particle path. Since we are summing over many oscillating sines and cosines, there will be an interference pattern, meaning that the paths effectively interfere with each other. Indeed, the intensity $I(y)$ will be proportional to the probability: $I(y) \propto P(y)$. In fact, if we were to carry out this sum over paths (no simple feat, by the way), we would obtain an interference pattern that agrees with experiment.

At this point, several comments are in order. It is tempting to try to impose either the wave-like picture of the many-paths picture on the experiment. Indeed, both of these pictures provide a useful physical picture that helps us understand the outcome of the experiment. In the wave-like picture, we can think of each electron that leaves the source as feeling the presence of both slits simultaneously, and therefore interfering with itself (rather than with other electrons). In the many-paths picture, each electron follows not one path in the path sum but *all* possible paths at once, and these paths interfere with each other. However, the infuriating thing about quantum mechanics is that we have no way of knowing what is taking place between the source and the detector. All we have is the observation that there is an interference pattern. Feynman's picture makes this rather manifest. The implications of his picture can be summarized as

1. Even within a particle-like interpretation of the experiment, particles do *not* have predictable positions and momenta along the paths. The reason for this is that the paths, themselves, are not predictable by any rule as they are in classical mechanics!
2. If we could devise an experiment for measuring the position y of the electron on the screen, we would find that different repetitions of the experiment on one electron initialized the same way would have different outcomes.

Thus, the best we can do from theory is to predict the *probability* of a given outcome of an experiment but not the actual outcome, itself.

The rationalizations of the three experiments we have examined, blackbody radiation, the photoelectric effect, and electron diffraction, leads us to conclude that classical mechanics, with its deterministic, predictable view of the universe, must be overthrown in favor of a much more radical theory, now known as *quantum mechanics*. It is interesting to note that the idea of probabilistic outcomes of experiments and the fact that we can **ONLY** predict the probabilities, lead Albert Einstein ultimately to reject quantum mechanics, saying: "Gott spielt nicht Würfel" ("God does not play dice").

II. SIMPLE STATEMENT OF THE POSTULATES OF QUANTUM MECHANICS

Below, we summarize the basic postulates of quantum mechanics and contrast them with roughly equivalent postulates of classical mechanics.

Classical:

1. Particles are point-like objects that follow predictable, deterministic paths with well-defined positions and momenta obtained by solving Newton's laws of motion
2. The energy of a system can take on any value.
3. If the initial conditions of an experiment repeated many times are the same in each repetition, the outcome of the experiment will be the same for each repetition, and that outcome is predictable.

Quantum:

1. Particles can exhibit wave-like or particle-like behavior, depending on the experiment. Even within the particle-like interpretation, particles do not follow well-defined, predictable paths and hence, do not have well-defined positions and momenta.

2. The energy can take on only certain discrete values.
3. Even if a system is prepared in the same way for different repetitions of an experiment, the outcome need not be the same in each repetition. All that we can predict is the probability that a given outcome will be obtained.

III. HEISENBERG'S UNCERTAINTY PRINCIPLE

If particles cannot be assigned well-defined positions and momenta, then how are these two quantities related for a quantum particle? The fact that particles do not follow well-defined paths means that there must be a limit on how accurately we can determine the position and momentum of a particle and this limit is a fundamental characteristic of the particle, itself, rather than a limit on our ability to perform an accurate enough measurement.

This idea of a fundamental limit to what is knowable about a quantum particle (or collection of quantum particles) was put forth by the physicist Werner Heisenberg in 1927. His principle is now one of the fundamental postulates of quantum mechanics and is known as the *uncertainty principle* or *indeterminacy principle*. Heisenberg's principle states that there are specific pairs of physical observables that cannot be simultaneously measured to arbitrary accuracy, i.e. there will be a fundamental limit to what we can know about two such observables simultaneously. Two such observables are said to be *incompatible* with each other. Dimensionally, such pairs are related so that their product has units of energy-time. Thus, if A and B constitute such a pair, and if ΔA and ΔB are the uncertainties associated with these observables, then Heisenberg's uncertainty principle states

$$\Delta A \Delta B \geq \frac{1}{2} \hbar$$

where $\hbar = h/2\pi$. Here, the uncertainties can be computed from the statistical uncertainty

$$\Delta A = \sqrt{\langle A^2 \rangle - \langle A \rangle^2}$$

where $\langle A^2 \rangle$ is the average of A^2 over many realizations of an experiment, and $\langle A \rangle$ is the average of A over many such realizations.

Position and momentum constitute such a pair of observables. if Δx and Δp are the corresponding uncertainties, then according to Heisenberg's principle, the best we can do in measuring x and p simultaneously is to have uncertainties in our measurements related by

$$\Delta x \Delta p \geq \frac{1}{2} \hbar$$

Feynman's many-path picture of quantum mechanics can help us understand this fundamental indeterminacy.

If we wish to determine the position of an electron, then we need to probe it with a photon, i.e. scatter a photon off of it and observe where the scattering occurred. The accuracy of the measurement will be related to the wavelength λ of the photon. That is, if we wish to determine the location of the scattering event to within 10^{-12}m (1% the size of an atom), then we need $\lambda = 10^{-12}\text{m}$, which, according to the energy formula $E = hc/\lambda$ is a very energetic photon.

When the photon strikes the electron, it causes the electron to change its direction, as illustrated in the figure below:

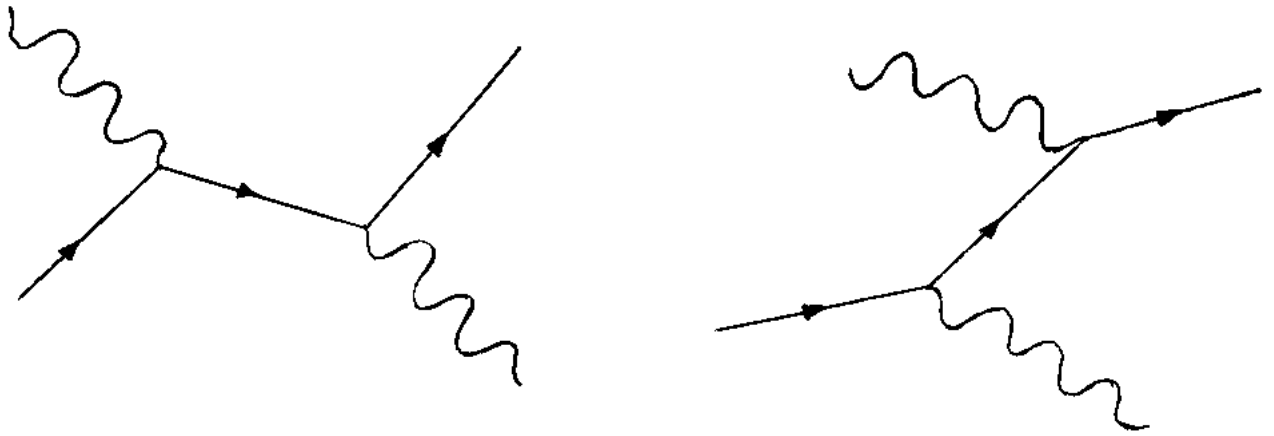


FIG. 7. Electron-photon scattering events

However, according to Feynman, such a picture is misleading since the electron does not follow a definite path. Rather, the electron can follow complicated paths as illustrated below:

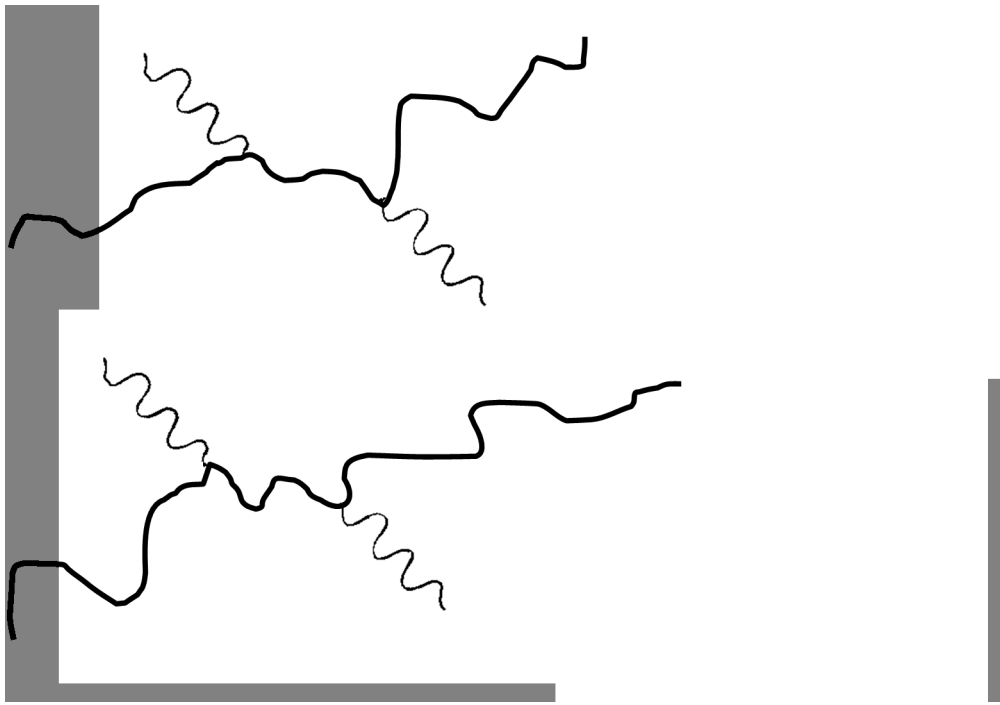


FIG. 8.

The more energetic the photon, the greater the spread in the possible scattered paths that electron can follow, which translates into a greater spread in the distribution of scattered momenta. Since we have to sum over *all* possible paths, the uncertainty in the momentum will be quite large for such an energetic photon. So, even though we have a relatively accurate determination of the electron's location, we have a large uncertainty in the momentum, and this is why there is an inverse proportionality between Δx and Δp :

$$\Delta p \geq \frac{\hbar}{2\Delta x}$$

We stress again, that the uncertainty or indeterminacy principle is a statement about an inherent limit to what we can know about a quantum system. This limit cannot be reduced simply by defining a better experiment.

IV. COULOMB'S LAW

Given two charged particles with charges Q_1 and Q_2 , there is an interaction between them that behaves as follows: Since charge can be positive or negative, opposite charges attract each other and like charges repel each other. The strength of the force between any pair of charges varies as the inverse square of the distance between them. These observations constitute *Coulomb's Law*. Coulomb's law is expressed as a force law of the form

$$F(r) = \frac{kQ_1Q_2}{r^2}$$

where k is a constant whose value is $8.98755 \times 10^9 \text{ J}\cdot\text{m}\cdot\text{C}^{-2}$. The direction of the force is always along the line joining the two charges. Thus, if the position of charge Q_1 is \mathbf{r}_1 and the position of charge Q_2 is \mathbf{r}_2 , then let $\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1$. Here, $r = |\mathbf{r}|$, and the force can be written as a proper vector quantity

$$\mathbf{F}(r) = \frac{kQ_1Q_2}{r^3}\mathbf{r}$$

The force law comes from the following potential energy:

$$V(r) = \frac{kQ_1Q_2}{r}$$

and it can be easily verified that

$$F(r) = -\frac{dV}{dr}$$

As r is varied, the energy will change, so that we have an example of a potential energy curve $V(r)$, as discussed in lecture 3.

If Q_1 and Q_2 are the same sign, then the curve appears roughly as follows:

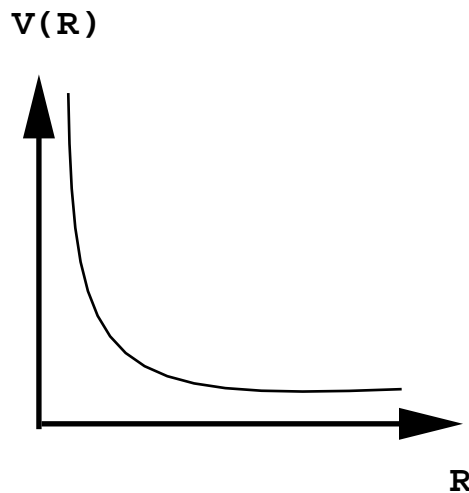


FIG. 9.

which is a purely repulsive potential, i.e., the energy increases monotonically as the charges are brought together and decreases monotonically as they are separated. From this, it is easy to see that like charges (charges of the same sign) repel each other.

If the charges are of opposite sign, then the curve appears roughly as:

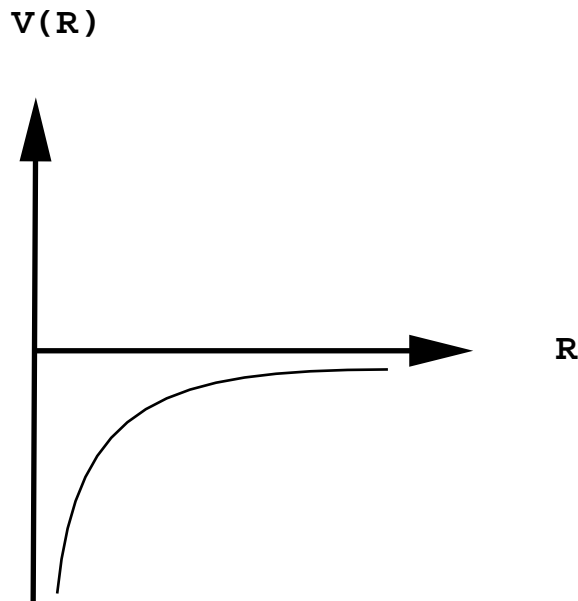


FIG. 10.

Thus, the energy decreases as the charges are brought together, implying that opposite charges attract.

V. THE BOHR MODEL: AN EARLY ATTEMPT TO PREDICT THE ENERGY LEVELS OF AN ATOM

It is observed that hydrogen will absorb and emit light at only discrete wavelengths as the figure below shows:

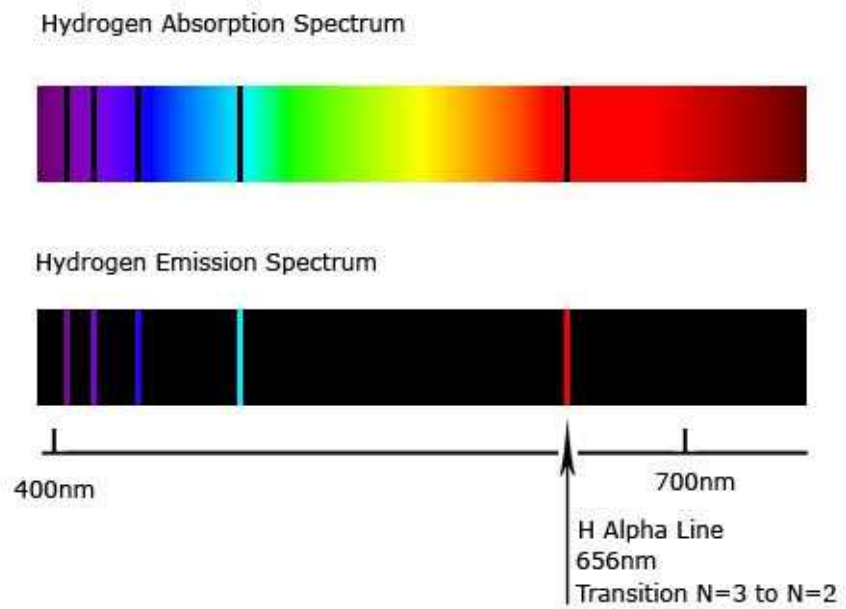


FIG. 11. From <http://www.solarobserving.com>

This observation is connected to the discrete nature of the allowed energies of a quantum mechanical system.

Quantum mechanics postulates that, in contrast to classical mechanics, the energy of a system can only take on certain discrete values. This leaves us with the question: How do we determine what these allowed discrete energy values are? After all, it seems that Planck's formula for the allowed energies of a harmonic oscillator came out of nowhere. The model we will describe here, due to Niels Bohr in 1913, is an early attempt to predict the allowed energies for single-electron atoms such as H, He⁺, Li²⁺, Be³⁺, ... Although Bohr's reasoning relies on classical concepts and hence, is not a correct explanation, the reasoning is interesting, and so we examine this model for its historical significance.

Consider a nucleus with charge $+Ze$ and one electron orbiting the nucleus. In this analysis, we will use another representation of the constant k in Coulomb's law. This constant is more commonly represented in the form

$$k = \frac{1}{4\pi\epsilon_0}$$

where ϵ_0 is known as the *permittivity of free space*, which has the numerical value $\epsilon_0 = 8.8541878 \times 10^{-12} \text{ C}^2\text{J}^{-1}\text{m}^{-1}$. The energy of the electron (the nucleus is assumed to be fixed in space at the origin):

$$E = \frac{p^2}{2m_e} - \frac{Ze^2}{4\pi\epsilon_0 r}$$

The force on the electron is

$$\mathbf{F} = -\frac{Ze^2}{4\pi\epsilon_0 r^3} \mathbf{r}$$

and its magnitude is

$$F = |\mathbf{F}| = \frac{Ze^2}{4\pi\epsilon_0 r^3} |\mathbf{r}| = \frac{Ze^2}{4\pi\epsilon_0 r^2}$$

Since $\mathbf{F} = m_e \mathbf{a}$, the magnitude, it follows that $|\mathbf{F}| = m_e |\mathbf{a}|$. If we assume that the orbit is circular (which is an approximation because the orbit is really elliptical), then the acceleration is purely centripetal, so

$$|\mathbf{a}| = \frac{v^2}{r}$$

where v is the velocity of the electron. Equating force $|\mathbf{F}|$ to $m_e |\mathbf{a}|$, we obtain

$$\frac{Ze^2}{4\pi\epsilon_0 r^2} = m_e \frac{v^2}{r}$$

or

$$\frac{Ze^2}{4\pi\epsilon_0} = m_e v^2 r$$

or

$$\frac{Ze^2 m_e r}{4\pi\epsilon_0} = (m_e v r)^2$$

The reason for writing the equation this way is that the quantity $m_e v r$ is the classical orbital angular momentum of the electron. Bohr was familiar with Maxwell's theory of classical electromagnetism and knew that in a classical theory, the orbiting electron should radiate energy away and eventually collapse into the nucleus. He circumvented this problem by following Planck's idea and positing that the orbital angular momentum $m_e v r$ could only take on specific values

$$m_e v r = n \hbar \quad n = 1, 2, 3, \dots$$

Note that the electron must be in motion, so $n = 0$ is not allowed.

Substituting this into the Newton's law expression above, we find

$$\frac{Ze^2m_e r}{4\pi\epsilon_0} = n^2\hbar^2$$

This expression implies that the orbits Bohr was imagining could only have certain allowed radii given by

$$\begin{aligned} r_n &= \frac{4\pi\epsilon_0\hbar^2}{Ze^2m_e}n^2 & n = 1, 2, 3, \dots \\ &= \frac{a_0}{Z}n^2 \end{aligned}$$

where the collection of constants has been defined to be a_0

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{e^2m_e}$$

a quantity that is known as the *Bohr radius*.

We can also calculate the allowed momenta since $m_evr = n\hbar$, and $p = m_e v$. Thus,

$$\begin{aligned} p_n r_n &= n\hbar \\ p_n &= \frac{n\hbar}{r_n} \\ p_n &= \frac{\hbar Z}{a_0 n} = \frac{Ze^2m_e}{4\pi\epsilon_0\hbar n} \end{aligned}$$

From p_n and r_n , we can calculate the allowed energies from

$$E_n = \frac{p_n^2}{2m_e} - \frac{Ze^2}{4\pi\epsilon_0 r_n}$$

Substituting in the expressions for p_n and r_n and simplifying gives

$$E_n = -\frac{Z^2e^4m_e}{32\pi^2\epsilon_0^2\hbar^2} \frac{1}{n^2} = -\frac{Z^2e^4m_e}{8\epsilon_0^2\hbar^2} \frac{1}{n^2}$$

The constant

$$\frac{e^4m_e}{8\epsilon_0^2\hbar^2}$$

is an energy having the value $2.18 \times 10^{-18}\text{J}$. Since this is a small unit, we redefine a new energy scale by defining the Rydberg as $1 \text{ Ry} = 2.18 \times 10^{-18}\text{J}$. Thus, the allowed energies predicted by the Bohr model are

$$E_n = -(2.18 \times 10^{-18} \frac{Z^2}{n^2} \text{J}) = -\frac{Z^2}{n^2} \mathbf{Ry}$$

These turn out to be the correct energy levels, apart from small corrections that cannot be accounted for in this pseudo-classical treatment. Despite the fact that the energies are essentially correct, the Bohr model masks the true quantum nature of the electron, which only emerges from a fully quantum mechanical analysis of this problem. The energies predicted by the Bohr model are plotted in the figure below. The diagram on the right is called an *energy level diagram*.

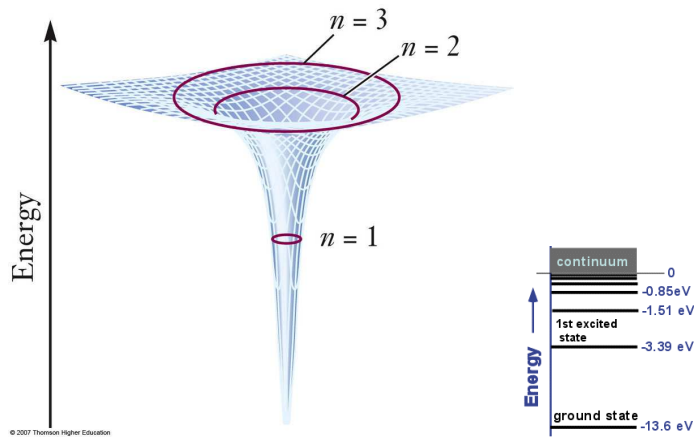


FIG. 12. Energy levels predicted by the Bohr model

Given a prediction of the allowed energies of a system, how could we go about verifying them? The general experimental technique known as *spectroscopy* permits us to probe the various differences between the allowed energies. Thus, if the prediction of the actual energies, themselves, is correct, we should also be able to predict these differences. We will have more to say about spectroscopy later in the course. For now, let us assume that we are able to place the electron in Bohr's hydrogen atom into an energy state E_n for $n > 1$, i.e. one of its so-called *excited states*. The electron will rapidly return to its lowest energy state, known as the *ground state* and, in doing so, emit light. The energy carried away by the light is determined by the condition that the total energy is conserved. Thus, if n_i is the integer that characterizes the initial (excited) state of the electron, and n_f is the final state (here we imagine that $n_f = 1$, but as long as $n_f < n_i$, this analysis remains valid), then by energy conservation, we must have that the frequency ν of the emitted light satisfies

$$E_{n_f} = E_{n_i} - h\nu$$

or

$$\nu = \frac{E_{n_f} - E_{n_i}}{h} = \frac{Z^2 e^4 m_e}{8 \epsilon_0^2 h^3} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

The figure below shows some of the transitions possible for different n_f and n_i values.

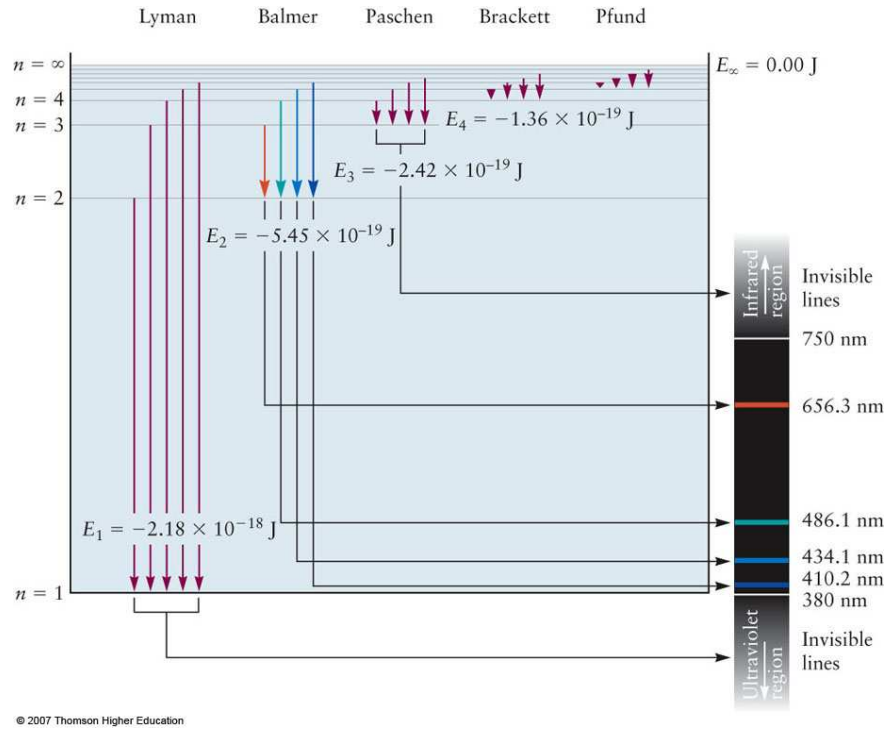


FIG. 13. Allowed electronic transitions in an emission process

Thus, by observing the emitted light, we can determine the energy difference between the initial and final energy levels. This is known as *emission spectroscopy*. Different values of n_f determine which emission spectrum is observed, and the examples shown in the figure are named after the individuals who first observed them.

If, on the other hand, the atom absorbs light, and ends up in an excited state as a result of the absorption. The absorption is only possible for light of certain frequencies, and again, conservation of energy determines what these frequencies are. If light is absorbed, then the final energy E_{n_f} will be related to the initial energy E_{n_i} with $n_f > n_i$ by

$$E_{n_f} = E_{n_i} + h\nu$$

or

$$\nu = \frac{E_{n_f} - E_{n_i}}{h} = \frac{Z^2 e^4 m_e}{8 \epsilon_0^2 h^3} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$