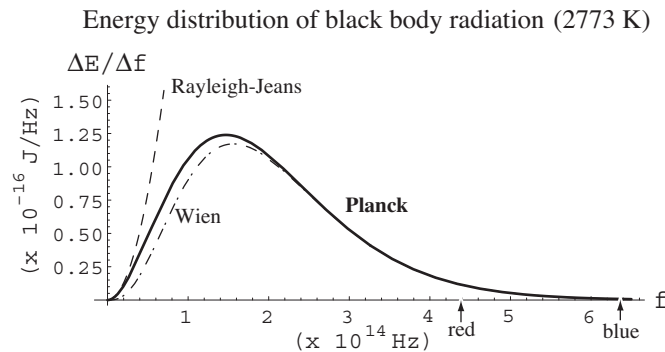


AP Physics B: Early Quantum Theory

In the late 1890's experimental physicists discovered that a hot object glows with all colors, but that not every color gets an equal share of the energy. Before 1900, two attempts had been made to figure out the energy distribution. One, by Wilhelm Wien, worked well at high frequencies but was a little bit off at low frequencies. The other, a strictly theoretical attempt by Lord Rayleigh and James Jeans, worked well at low frequencies but failed spectacularly at high frequencies; in particular it predicted that there was *no limit* to how much energy would be found in high frequencies from any given source of heat. This failure was called *the ultraviolet catastrophe*. If it were true, the simple act of lighting a match would prove fatal, as all the heat of the match would go into gamma rays.

Finally in October 1900 Max Planck found an expression which looked exactly like Wien's at high frequencies and exactly like the Rayleigh-Jeans formula at low frequencies, and so was in complete agreement with the experimental data. But Planck's expression had at first no physical basis; it was essentially curve-fitting. A graph of all three for a black body at 2773 K is presented below: ($\Delta E/\Delta f$ is the energy per frequency per volume)



Planck felt it was crucial to find a physical reason for his function's success, and after two months of intensive work found it. Briefly, the argument runs like this. Since it did not seem to matter from what material the walls of the hot object were made, Planck was free to imagine whatever he wanted about the walls. As the best-known object in physics is the spring, Planck pretended that the walls of the hot object (hereafter called a "black body") were made of many different tiny springs, each with its own characteristic vibrational frequency. These springs would absorb and emit light. But initial attempts to calculate how the energy was divided up into frequencies failed to give the right distribution. Recall that for a standard spring the energy is equal to $\frac{1}{2}kA^2$ where k is the Hooke's law constant for that spring. Also, as f_{spring} is proportional to \sqrt{k} , the energy is proportional to f^2 . This leads to the fatal Rayleigh-Jeans law. As an "act of desperation" Planck tried the assumption that E was proportional to the first power of f . That *almost* worked, but one final crazy thing was needed: this time Planck required not only $E \propto f$ but that E was allowed to have *only whole numbers* of a certain energy; that is

$$E_{\text{spring}} = nhf; \quad n = 0, 1, 2, 3, \dots$$

where now f was the ordinary frequency of the light, n was a non-negative integer, and h was a new constant of nature, now universally called **Planck's constant**. If the springs are only allowed to have hf , or $2hf$, or $3hf$, ... it follows that the *light itself* must take on energies of hf , because the only way a spring was allowed to change energy was to absorb or emit light. For example, if a spring had a certain frequency f_a and an energy $E = 16hf_a$, the only way it was going to wind up with an energy $E' = 17hf_a$ was by absorbing energy equal to hf_a . Thus a necessary requirement for Planck's scheme to work was that the energy of the light itself had to be given by the relation

$$E_{\text{light}} = hf$$

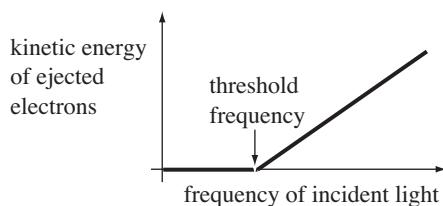
where now f was the ordinary frequency of the light. This equation marks the birth of quantum theory.

An analogy may help. Imagine a child with a number of piggy banks, one each for pennies, nickels, dimes and quarters. If her mother gives her a coin, she will only put it into the bank reserved for that coin. She refuses half dollars, dollars and foreign coins. If she shakes out a coin from a given bank, she knows the value of the coin ahead of time. These banks are like the springs Planck supposed to make up the walls of the black body; the value of all the coins in a bank is the energy held by the spring, and the coins represent the photons. When a spring in the walls emits a photon, its energy will be equal to hf , where f is the frequency of the light itself, just as the only coins coming out of the nickel bank are nickels, worth five cents. The bank determines the value of the single coin coming out of that bank; the spring determines the energy of the single photon coming out of that spring.

The word **quantum** is Latin for “how much”; the energy of the springs in Planck’s scheme cannot take arbitrary values, but is restricted to whole number multiples of a fundamental amount hf . The value of h is now known to many decimal places:

$$h = 6.626 \times 10^{-34} \text{ Joule-second} = 4.136 \times 10^{-15} \text{ electron-Volt-second}$$

Five years later Planck’s equation was used to solve another riddle involving light. It was discovered by Heinrich Hertz and (independently) J. J. Thomson that shining ultraviolet light on some metals caused the metal to become positive—electrons were somehow kicked out of the metal by the action of the light. This phenomenon is called **the photoelectric effect**. For a given metal, no electrons are ejected until the light has a certain threshold frequency; thereafter the energy of the electrons increases with the frequency of the light. A graph of electron kinetic energy vs frequency of incident light looks like this:



The heavy horizontal line indicates that *no* electrons are given off until light with high enough frequency is used to illuminate the metal. The non-horizontal part of the graph above can be described by the elementary equation

$$K = mf + b$$

where b is a negative number and m , the slope, has the units of energy times time.

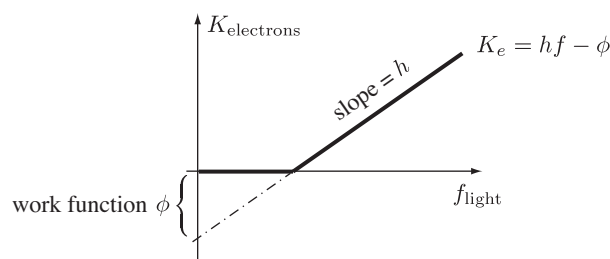
A then-obscure patent examiner, Albert Einstein, 26 years old, gave the equation a simple but profound physical interpretation. Suppose the electrons in the metal have a total energy $-\phi$, which is negative. (The quantity ϕ has the units of eV or joules.) Negative energies indicate that an object is “captured”; for example the earth’s net energy is negative as it is gravitationally bound to the sun. The electrons are expected to have a negative energy, because of their being bound to the positive charges of the metal nuclei. In fact if we let φ be the average electric potential of the metal nuclei, then the potential energy of the electrons will be $q\varphi = -e\varphi$, since the electron charge is negative. That is, $\phi = e\varphi$ if the electrons have negligible kinetic energy. If the electrons can obtain an additional energy ϕ from somewhere, they may leave the metal. Then, said Einstein, the photoelectric equation is just *the conservation of energy*, provided we say that the light of energy hf collides with and *is absorbed by* an electron:

$$\begin{aligned} E_{\text{before}} &= E_{\text{light}} + E_{\text{electron}} = hf - \phi \\ E_{\text{after}} &= E'_{\text{electron}} = K \end{aligned}$$

so by energy conservation,

$$\boxed{K = hf - \phi}$$

which explains the experimental results very elegantly:



This interpretation is very easy to check: Was the slope of the experimentally determined graphs equal to Planck's constant? It was. Now it became obvious why no electrons were ejected for frequencies below a certain value—the light simply did not have enough energy to overcome ϕ . Einstein named the quantity ϕ **the work function**. Different metals have different work functions, but all of them have slopes equal to h . (Sometimes people write the work function as $e\phi$, in which case ϕ as the units of volts.) When Einstein finally won the Nobel Prize in physics (1921), it was for the interpretation of the photoelectric effect, not relativity or $E = mc^2$.) Notice that Einstein regarded light essentially as a *particle*; one quantum of light energy was sufficient (or not) to liberate one electron. Planck, who had first written down $E = hf$, never did fully accept the idea that light might act as a particle. A “particle of light” or “quantum of light” is now called a **photon** (G. N. Lewis, 1926.)

The next step in the development of quantum theory concerned the atom, specifically the Rutherford model of the atom. Every student of chemistry knows how Ernest Rutherford engaged two of his graduate students, Hans Geiger and Ernest Marsden, to direct alpha particles (nuclei of helium) from the decay of radium at a very thin gold foil, and examine the deflections. To everyone's astonishment, the alphas occasionally were deflected through very large angles, even rebounding straight back. This result was unexpected, because the prevailing model of an atom had electrons uniformly distributed through a positive material filling the volume of an atom. The electric density of this material could not have deflected the nearly pointlike alpha particles by such large angles. Instead, the positive charge had to be concentrated in a heavy core with the negative charges of the atom surrounding the center. (Rutherford's group appropriated a biological term for this center, calling it a **nucleus** after the center of a cell.) But how the electrons were distributed was a complete mystery.

Shortly after the alpha scattering experiment was announced a brilliant Danish postdoctoral student, Niels Bohr, came to Great Britain. At first he tried to work with J. J. Thomson at Cambridge, but they did not communicate well with each other, so Bohr went to Manchester to work with Rutherford, on the simplest atom, hydrogen. Bohr was famous for rewriting his papers and largely covering his tracks so what follows is only a guess about his method.

As electrons and protons are oppositely charged, there is an attraction between them and thus a mystery: why doesn't the atom simply collapse? One possibility is that the electron orbits the proton just as the earth orbits the sun. The difficulty here is that an electron moving in an orbit is necessarily being accelerated (the direction of its velocity is changing). As shown by Maxwell in the 1870's, all accelerating charges must give off light. The energy from this light must come from the electron. Initially it would slow down, and then be pulled toward the nucleus (with increasing speed but also larger negative potential energy.) Eventually it would spiral into the nucleus. But this is not observed: atoms are stable. Bohr ignored that problem for the moment, and wrote down equations for the force acting on an electron, and the atom's energy:

$$F_{\text{net}} = \frac{mv^2}{r} = \frac{k|q_1q_2|}{r^2} = \frac{ke^2}{r^2}$$

$$E = \frac{1}{2}mv^2 - \frac{ke^2}{r}$$

(the absolute value brackets are because the force is inward, attractive; both the left and right hand sides should be the same sign, negative.) These equations can be combined by solving the first for mv^2 and substituting into the second, to obtain

$$E = -\frac{1}{2} \frac{ke^2}{r}$$

which as expected is negative; the electron is bound to the proton.

The most information anyone had about the energy of hydrogen came from a study of the spectral lines of hydrogen, initiated (1885) by a Swiss high school teacher, Johann Balmer, and further developed by the Swedish physicist Johannes Rydberg (1890). The Balmer–Rydberg equation links the wavelengths of some of the light in the spectrum of hydrogen to *whole numbers*;

$$\frac{1}{\lambda} = R \left(\frac{1}{4} - \frac{1}{n^2} \right) \quad \text{where } n = 3, 4, 5, \dots \text{ and } R \text{ is Rydberg's constant, } R = 1.097 \times 10^7 / \text{m}$$

This equation must have given Bohr many hints. The energy of the light must be coming from the electrons, and the energy of the electrons depends only on the radius r . Perhaps the electrons change their orbits, and in doing so, absorb or release energy as light, just as in the photoelectric effect. The wavelengths of the light emitted as the orbits change might be given by this formula. Since $c = \lambda f$, the Balmer–Rydberg formula can be put in terms of frequency; and if the Planck-Einstein relation holds, in terms of energy as well:

$$E = hf = \frac{hc}{\lambda} = hRc \left(\frac{1}{4} - \frac{1}{n^2} \right) = 2.179 \times 10^{-18} \text{ J} \left(\frac{1}{4} - \frac{1}{n^2} \right)$$

There is a connection between energy and light frequency from Planck's formula, between energy and radius from classical mechanics, and between frequency and a distance from Rydberg's constant. Maybe they are all connected? Look at the units of Planck's constant:

$$h = \text{Joule-second} = \text{kg} \times \text{m}^2 \times \left(\frac{1}{\text{second}} \right)^2 \times \text{second} = (\text{mass}) \times (\text{velocity}) \times (\text{position})$$

The only choice for velocity is the electron's; the only position variable is the radius of the orbit. So guess that the mass is also the electron's, and try

$$\text{(guess \#1)} \quad mvr = h$$

Solve this for v , square, and divide into the force equation $mv^2/r = ke^2/r^2$ to obtain

$$\text{(guess \#1 conclusion)} \quad r = \frac{h^2}{mke^2}$$

This would fix the electrons at one radius, and hence one energy: there would be no way for the electrons to change their energy, nor to release the observed light. So that guess fails. Again, taking a hint from Planck, try

$$\text{(guess \#2)} \quad mvr = nh; \quad n = 1, 2, 3, \dots$$

where n is an integer. This is a lot better: it leads to

$$\text{(guess \#2 conclusion)} \quad r = \frac{n^2 h^2}{mke^2}$$

which allows for many orbits. Plugging this value into the energy equation gives

$$E = -\frac{1}{2} \frac{ke^2}{r} \stackrel{?}{=} -\frac{k^2 me^4}{2n^2 h^2} = -5.523 \times 10^{-20} \text{ J} \times \frac{1}{n^2}$$

The good news is that this involves the denominator of a whole number squared, as in the Balmer–Rydberg formula. The bad news is that the coefficient of n^2 is too small by roughly a factor of 40; to be precise by

$$\frac{2.179 \times 10^{-18}}{5.523 \times 10^{-20}} = 39.46$$

Well, that does not seem like anything familiar. Try its square root:

$$\sqrt{39.46} = 6.281$$

Is this number familiar? Well, $2\pi = 6.283\dots$. Admittedly, it's a reach, but try a third guess (which gives the right answer!)

$$\text{(guess \#3)} \quad mvr = \frac{nh}{2\pi}; \quad n = 1, 2, 3, \dots$$

This leads to

$$r = \frac{n^2 h^2}{4\pi^2 k m e^2} = 0.53 \times 10^{-10} \text{ m} \times n^2 = (0.053 \text{ nm}) \times n^2$$

The idea, then, is that electrons are only allowed to be *certain fixed distances* away from the nucleus: at $r = 0.053 \text{ nm}$; or $4 \times 0.053 = 0.212 \text{ nm}$; or $9 \times 0.053 = 0.471 \text{ nm}$, and so on. (That helps to solve the radiation problem, but it isn't the whole answer.) The energies associated with these radii are

$$E = -\frac{1}{2} k e^2 \times \left(\frac{4\pi^2 k m e^2}{n^2 h^2} \right) = -2.176 \times 10^{-18} \text{ J} \times \frac{1}{n^2} = -13.6 \text{ eV} \times \frac{1}{n^2}$$

which correspond to $-13.6 \text{ eV}/1^2 = -13.6 \text{ eV}$, $-13.6 \text{ eV}/2^2 = -3.4 \text{ eV}$, $-13.6 \text{ eV}/3^2 = -1.51 \text{ eV}$, etc., for $n = 1, 2, 3$, etc.

The idea is this. Say an electron is in an orbit corresponding to some value of n larger than 1, call it n_1 . Say the electron falls from the original orbit to another orbit described by a different, smaller value of n . Call this value n_2 . Each orbit has a fixed, precise energy associated with it, so call the orbits **energy levels**. Originally the energy of the system is just

$$E = E_1 = -\frac{13.6}{n_1^2} \text{ eV}$$

The electron falls, and so the energy of the system will now be E_2 plus the energy of the released photon;

$$E' = E_2 + hf = -\frac{13.6}{n_2^2} \text{ eV} + hf$$

Setting these two equal to each other, we find

$$E_1 = E_2 + hf$$

or what is the same thing,

$$hf = E_1 - E_2 = 13.6 \text{ eV} \left(\frac{1}{n_2^2} - \frac{1}{n_1^2} \right)$$

This has *exactly* the form of the Balmer–Rydberg equation, with $n_2 = 2$, if both sides are divided by hc to turn the equation involving energies and frequencies into one involving wavelengths. That is, Bohr *derived* the value of the Rydberg constant by dividing $13.6 \text{ eV} = 2.176 \times 10^{-18} \text{ J}$ by hc ;

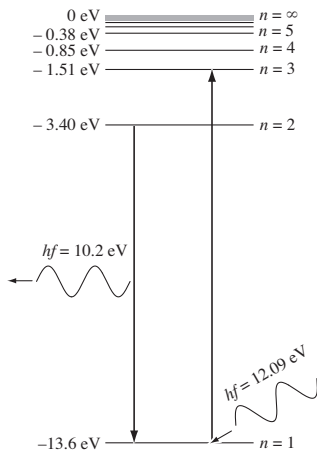
$$\frac{2.176 \times 10^{-18} \text{ J}}{6.626 \times 10^{-34} \text{ J}\cdot\text{s} \times 2.998 \times 10^8 \text{ m/s}} = 1.095 \times 10^7 / \text{m}$$

Einstein described Bohr's work as "the greatest triumph". It won Bohr the Physics Nobel (1922).

If an electron emits a photon with a very precise frequency in falling from one orbit to another, presumably it could jump up from one level to another by absorbing a photon. But note well: the light must have *exactly* the right energy. For example, suppose an electron is in the lowest energy orbit (corresponding to $n = 1$), called **the ground state**. For hydrogen, this is an energy of -13.6 eV . The next orbit corresponds to an energy of -3.4 eV , and the one beyond that is -1.51 eV . The difference between the ground state and the next orbit is 10.2 eV . If a photon of energy 11 eV smacks into an electron in the ground state of hydrogen, it will be rejected as "too hot"; a photon of energy 10 eV will be rejected as "too cold". Like Goldilocks's porridge, the photon must be *just right*. On the other hand, a ground state electron *could* absorb a photon of 12.09 eV , because that would put it in the $n = 3$ state; $-13.6 \text{ eV} + 12.09 \text{ eV} = -1.51 \text{ eV}$. States above the ground state are called **excited states**.

There is an exception to the “Goldilocks rule”: if the photon’s energy is large enough to kick the electron completely away from the nucleus, then it can have any energy greater than or equal to this and still be absorbed. For the ground state, this energy is 13.6 eV, and is called the **ionization energy**. For example, an electron in a hydrogen atom at the first excited state ($n = 2$ and $E = -3.4$ eV) can absorb any photon with $hf \geq 3.4$ eV.

It is traditional to describe the Bohr model with a diagram like this:



The diagram shows the various energy levels for hydrogen up till about $n = 5$; after that the levels get too close to distinguish clearly (this is called the *continuous spectrum*). Note that $n = \infty$ corresponds to $E = 0$, and the escape of the bound electron. In this particular diagram, two transitions are shown; an electron falls from $n = 2$ to $n = 1$ (the ground state), emitting a photon of 10.2 eV, and a second electron (presumably in a different atom) originally in the ground state was hit by a 12.09 eV photon, absorbs it, and is raised to the $n = 2$ energy level at $E = -1.51$ eV. Generally speaking electrons tend to fall to the ground state. Note also that an electron in, say, the $n = 3$ state could give up a single photon falling to the ground state, or it could give up two, first falling to the $n = 2$ state, and then from $n = 2$ to $n = 1$ states. Each one of these possible photon transitions appears as a single line in the spectrum of hydrogen; and in fact every chemical element has its own characteristic color fingerprint. This allows us to identify the chemical makeup of a star thousands of light years away by its spectral lines! Though Bohr’s model deals only with hydrogen, the basic idea of electrons changing energy levels by absorbing or emitting light seems to hold for *all* atoms; the relevant equation linking transitions between the n^{th} and m^{th} levels is

$$E_n - E_m = hf$$

where hf is the energy of the absorbed or emitted photon.

Bohr’s derivation of the Balmer–Rydberg equation is one of the great triumphs of physics, but it rested for ten years on a strange *ad hoc* postulate which no one understood. Why did mvr equal $nh/2\pi$? Besides, the orbiting electron was supposed to radiate, and it did not. Something odd was going on.

In 1923, a young member of the French aristocracy, Prince Louis de Broglie, put forth an astonishing idea. If light, long held to be a wave, could behave like a particle (in the photoelectric effect), might not the electron, always thought a particle, behave occasionally like a wave? To follow de Broglie’s reasoning, you need to recall a result from special relativity (which also follows from Maxwell’s work on electromagnetism): *light carries momentum*:

$$p_{\text{light}} = \frac{E}{c}$$

Now use Planck’s formula and the wave relation $c = \lambda f$ and divide:

$$p_{\text{light}} = \frac{hf}{\lambda f} = \frac{h}{\lambda} \quad \text{or, for light } \lambda = \frac{h}{p}$$

It is worth pointing out the biological consequences of this equation. Photons with shorter wavelengths carry not only more energy, but also more momentum: short waves pack a bigger punch. That means these are more likely to ionize electrons than longer wave light. Any light that has enough energy to ionize hydrogen or oxygen might well be strong enough to split the chemical bonds in your body's cells, perhaps leading to free radicals, and maybe chemical or biochemical changes that could be very destructive (cancer?) The ozone layer is important because it absorbs ultraviolet light (which is ionizing) and releases longer wave, non-ionizing light.

De Broglie then made a bold prediction: Anything with momentum would have an associated wavelength. For everyday objects, this wavelength would be much too small to measure (due to the tiny size of Planck's constant). Small things like electrons, however, might have measurable de Broglie wavelengths;

$$\lambda_{dB} = \frac{h}{mv}$$

The wave nature of electrons could in principle be demonstrated by exactly the same method as Young demonstrated the wave property of light: by diffraction through slits. How to find slits small enough for the electrons? Happily, nature provides these in many metals; the spacing between the atoms of metallic crystals is the right size to diffract electrons. In the late 1920's, two physicists at the Bell Laboratories in New Jersey, C. Davisson and L. Germer, reflected electrons off a nickel surface, and by moving a detector back and forth, were able to show precisely the sort of Young's patterns that de Broglie's work predicted. That electrons can be diffracted, and that someone was smart enough to guess this, is simple incredible. But we can be appreciative of de Broglie's hypothesis for another reason: it explains why Bohr's guess works. Recall the guess:

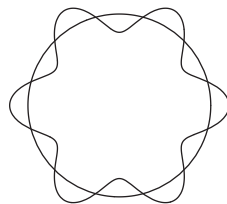
$$mvr = \frac{nh}{2\pi} \quad \text{which in the context of de Broglie's hypothesis can be written}$$

$$pr = \frac{nh}{2\pi} \quad \text{and substituting the de Broglie expression for the wavelength}$$

$$\frac{h}{\lambda}r = \frac{nh}{2\pi}. \quad \text{Cancel the } h, \text{ cross-multiply and obtain}$$

$$2\pi r = n\lambda. \quad \text{Hmmm... } 2\pi r \text{ looks familiar, no?}$$

It is just the *circumference of the orbit*; the circumference must be a *whole number* of de Broglie wavelengths! Recall what you know about standing waves and resonance: it is impossible to have a standing wave unless there is an appropriate match between the wavelength and the boundary conditions of the vibration. An oversimplified picture is shown below.



An oversimplified picture of the $n = 6$ orbit. The circumference of this orbit equals 6 times the de Broglie wavelength λ of the electron, where

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

This is just about as far as you can go in quantum theory without advanced mathematical knowledge. In 1926, the old quantum theory of Planck, Einstein, Bohr and even de Broglie underwent a profound development, and became the wave mechanics of Schrödinger, Heisenberg and Dirac.

For more on the quantum theory, see: B. Hoffmann, *The Strange Story of the Quantum*; S. Weinberg, *The Discovery of Subatomic Particles*; G. Gamow, *Thirty Years that Shook Physics*; Barbara L. Cline, *Men Who Made a New Physics* (original title, *The Questioners*), A. Pais, *Inward Bound*; Richard Feynman, *The Character of Physical Law*; Brian Greene, *The Fabric of the Universe*.