

# Harbingers of the quantum world

## Notes on Quantum Mechanics

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"All beginnings are obscure."  
Hermann Weyl, *Space-Time-Matter*

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Based on the Rutherford model of the atom, it is reasonable to think that the structure of atoms is just a miniature solar system. Indeed, this was the what was thought to be the case in the early part of this century. However, this is *not at all the case*. When we descend into the interior of individual atoms, we enter a truly bizarre world where all of the ideas we are familiar with from our everyday experience simply don't apply.

It is natural for us to interpret the atomic world in terms of our own world—natural, but wrong. You will probably find it very difficult to accept the atomic world for what it evidently is. That has certainly been my experience.

The branch of knowledge dealing with atoms is called *quantum mechanics*. The quantum aspect of the physical world dawned on human consciousness as the culmination of efforts to understand four key phenomena: first, the how the brightness of light that is in *thermal equilibrium* with matter

(sunlight, light from the hot coils of a toaster, the "light" from a warm hand are some examples)—so-called *blackbody radiation*—changes with the frequency ("color") of the light; second, how the speed of electrons ejected from the surface of a metal depends only on the frequency of the light but not on its brightness, the so-called *photoelectric effect*; third, how it can be that electrons in atoms give off light of only certain frequencies, rather than a continuous range of frequencies, the so-called *spectra* of atoms; and, fourth, why atoms with different numbers of electrons have different chemical properties as embodied in the periodic table, the so-called *shell structure* of atoms.

There are many other phenomena that illustrate the quantum nature of physical reality, but these four—blackbody radiation, photoelectric effect, the colors in atomic spectra, and the shell structure of many-electron atoms—contain all of the essential aspect of the quantum world.

## Properties of waves

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To understand the quantum world, we are going to need to use the *mathematics of waves*, and so let's begin there.

A *wave* is the oscillatory variation of *some property* with time at a given, fixed point in space. Examples are

Wave	Property
water	height of water
sound	density of air
light	electric field
chemical	concentration

### ■ Representing wave properties mathematically

Waves can be expressed mathematically in terms of sine curves. To keep things as simple as possible, let's assume we have a wave only along one direction, which we call  $x$ . Now, unless we are dealing with a standing wave, waves move. If we look at the wave at a particular instant in time, it is a sine curve. If we look at it a moment  $dt$  later in time, it is still a sine curve, but the whole curve has shifted by an amount  $dx$ .

It is probably not immediately obvious, but the way such a sine wave changes with position and time can be expressed as

$$\psi = a \sin \{2\pi(x/\lambda - \nu t)\}$$

The numerical value of this expression—the value of the physical property, such as the height of the water in a water wave—is called the **amplitude** (often represented by the Greek letter  $\psi$ ).

To understand this expression, let's first set the time  $t$  equal to zero, so we have

$$\psi = a \sin(2\pi x/\lambda)$$

We know that the value of a sine function is the same every time its argument (which is called its **phase**) changes by  $2\pi$ . The phase changes because  $x$  changes. If  $x$  changes by the amount  $\lambda$ , the phase changes by  $2\pi$ . Therefore,  $\lambda$  is called the **wavelength** (represented by the Greek letter  $\lambda$ ). The wavelength is the distance between two similar points, such as two successive peaks.

Next, we can understand the effect of time by instead setting the position  $x$  equal to zero, which corresponds to looking at the wave as it moves by a fixed position. Then we have

$$\psi = a \sin(2\pi \nu t)$$

This shows that when time changes by the amount  $1/\nu$ , the phase again changes by  $2\pi$ ; that is, one wave cycle moves past a fixed point in time  $1/\nu$ . The number of cycles (of spatial length  $\lambda$ ) which pass by per second which is the reciprocal of the time required for one cycle to pass by. This is called the **frequency**

$$\nu = 1/(1/\nu)$$

of the wave (represented by the Greek letter  $\nu$ ). The frequency is commonly measured in **Hertz** (abbreviated **Hz**), which are inverse seconds,  $s^{-1}$ .

Finally, we can see the effect of changing both  $x$  and  $t$ . The way we follow the motion of a wave is to identify a point on the wave, say a particular crest, and then to see how far it moves in a certain time. Mathematically, choosing a point on the wave means choosing a value for the phase,

$$2\pi(x/\lambda - \nu t).$$

This is so because the value of the phase determines the value of the amplitude of the wave at a particular place  $x$  and time  $t$ . This means that if a point on the wave at position  $x_1$  and time  $t_1$  moves to the position  $x_2$  at time  $t_2$ , then the corresponding phases are equal

$$2\pi(x_1/\lambda - \nu t_1) = 2\pi(x_2/\lambda - \nu t_2).$$

This important equality is called the **stationary phase condition**. We can rearrange this equation to find the relation

$$(x_2 - x_1)/(t_2 - t_1) = \nu \lambda.$$

This ratio of the distance moved,

$$dx = x_2 - x_1.$$

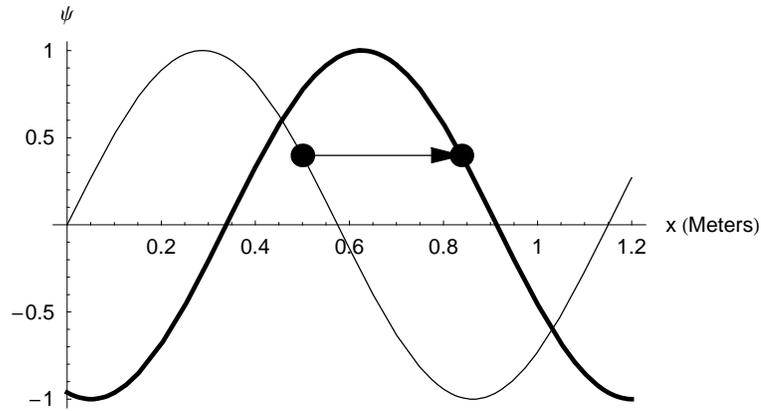
divided by the time required

$$dt = t_2 - t_1.$$

is the **speed that the wave moves**. This speed is called the **phase velocity** of the wave.

$$v_\phi = dx/dt = \nu \lambda.$$

Here is an illustration of these ideas. The figure shows the movement of a sine wave that takes place in 0.025 s.



Movement of a wave. The thin curve is the wave at an initial time,  $t_1$ . The thick curve is at a later time,  $t_2$ . The length of the arrow is the distance,  $dx = x_2 - x_1$ , the wave has moved in the elapsed time,  $dt = t_2 - t_1 = 0.025$  s. The point chosen to track the movement of the wave is arbitrary. The value of the phase,  $2\pi(x_1/\lambda - \nu t_1)$ , at the starting point is equal to the value of the phase,  $2\pi(x_2/\lambda - \nu t_2)$ , at the ending point. The equality of these phases—the stationary phase condition—determines the phase velocity of the wave,  $dx/dt = (x_2 - x_1)/(t_2 - t_1) = \nu\lambda$ .

See if you can determine from the information in the figure the values of the distance traveled, wavelength, phase velocity, and frequency of this wave. You may want to start by using a ruler to measure the distance traveled. The answers are

$$\left\{ 0.29 \text{ Meter}, 1.2 \text{ Meter}, \frac{12. \text{ Meter}}{\text{Second}}, \frac{10.}{\text{Second}} \right\}$$

## ■ Calculations with waves

Phase velocity is a characteristic of each kind of wave. We are going to be concerned especially with light waves. The velocity of light is a **universal constant** of Nature and is given the special symbol **c**. For light traveling in a vacuum, its speed (phase velocity) is

$$\nu_{\text{light}} = c ;$$

$$\frac{299792458 \text{ Meter}}{\text{Second}}$$

This means that for *electromagnetic radiation of any frequency* the product of its frequency and wavelength is always equal to  $\nu_{\text{light}}$ .

A nice example of this relation is to calculate the wavelength of the radio waves from the Boston University FM radio station WBUR, which transmits on a frequency of 90.9 MHz (1 Megahertz =  $10^6$  Hz):

$$\lambda_{\text{WBUR}} = c / (90.0 \cdot 10^6 / \text{Second}) ;$$

$$3.33 \text{ Meter}$$

or

$$10.9 \text{ Feet}$$

Compare this value to red light, which has a wavelength of

$$\lambda_{\text{red}} = 7.0 \cdot 10^{-7} \text{ Meter} ;$$

—ten million times smaller. This means that the frequency of red light is about ten million times higher.

$$\nu_{\text{red}} = c / \lambda_{\text{red}} ;$$

$$\frac{4.3 \times 10^{14}}{\text{Second}}$$

What about light with wavelength about the size of an atom?

$$\lambda_{\text{atomSize}} = 1.0 \cdot 10^{-10} \text{ Meter};$$

The corresponding frequency is

$$\nu_{\text{atomSize}} = c / \lambda_{\text{atomSize}};$$

$$\frac{3. \times 10^{18}}{\text{Second}}$$

This corresponds to X-rays, and in fact we will see that X-rays are generated by events on the atomic scale.

Here is an example using sound waves . The speed of sound in dry air at 20°C is

$$\nu_{\phi\text{sound}} = 343.5 \text{ Meter / Second};$$

and the frequency of the sound from the middle C note on a piano is

$$\nu_{\text{middlec}} = 261.6 / \text{Second};$$

Calculate the wavelength of the sound and the time it will take to travel

$$d|x = 30.0 \text{ Meter};$$

across a concert hall. (Oxtoby and Nachtrieb, 2e, problem 13.7.)

From the phase velocity expression, the wavelength is

$$\lambda_{\text{middlec}} = \nu_{\phi\text{sound}} / \nu_{\text{middlec}}$$

$$1.31307 \text{ Meter}$$

This sound wave travels the specified distance in

$$t = d|x / \nu_{\phi\text{sound}};$$

$$0.0873 \text{ Second}$$

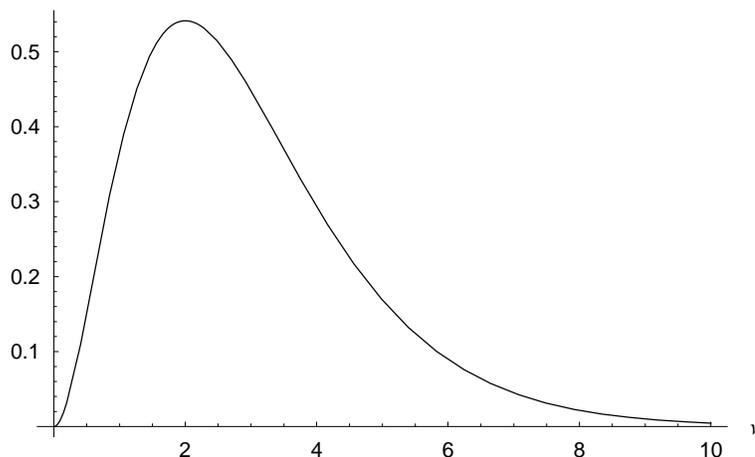
## Blackbody radiation

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A blackbody is any object which is in *thermal equilibrium* with light. The reason it is called "black" is because the object must not have any intrinsic color, for if it did, then the equilibrium would be distorted.

We can learn about blackbody radiation by studying its spectrum, how much light there is as a function of frequency. We can express the amount of light in terms of what is called its *energy density*,  $U_\nu$ , the energy of the light in a small range of frequencies near a particular frequency  $\nu$  and in a small volume. The energy density has several characteristics.

- **continuity:** There is light at all frequencies, from the very lowest to the very highest.
- **shape:** At low frequencies the energy density increases with the square of the frequency,  $U_\nu(\text{low } \nu) \rightarrow \nu^2$ . At high frequencies the energy density decreases exponentially,  $U_\nu(\text{high } \nu) \rightarrow e^{-a\nu}$ , so that at very high frequencies there is negligible light energy. These limiting behaviors determine the overall shape of the spectrum, as shown in the plot of  $\nu^2 e^{-\nu}$ .



Qualitative shape,  $\nu^2 e^{-\nu}$ , of the energy density of light in thermal equilibrium with matter—blackbody radiation.

The rise at low frequencies and the fall at high frequencies leads to a maximum at a particular frequency,  $\nu_{\text{max}}$ .

- The maximum frequency increases linearly with temperature,  $\nu_{\text{max}} \propto T$ . This is why, for example, the color of a toaster coil, which is approximately a blackbody, changes from dull red, to red, to yellowish red as the coil gets hotter. This relation is known as the Wien displacement law. It means that if we know the maximum frequency at one temperature,  $T_1$ , we can compute the maximum at any other temperature,  $T_2$ , as  $\nu_2 = \nu_1(T_2/T_1)$ .
- **total energy:** The total energy in a given volume of the light at all frequencies increases with the fourth power of the temperature,  $U_{\text{total}} \propto T^4$ .

All of this was well known at the end of the last century. The problem was that scientists were unable to explain why the spectrum had a maximum.

## ■ Rayleigh-Jeans law

Rayleigh and Jeans were able to understand the low-frequency part of the spectrum. They expressed the energy density as the product

$$U_\nu = N_\nu E_{\text{avg}}$$

of the number  $N_\nu$  of different ways a light wave at frequency  $\nu$  could be constructed in a small volume and the average energy  $E_{\text{avg}}$  of each of those oscillation modes. Rayleigh and Jeans derived that  $N_\nu = 8\pi\nu^2/c^3$ , that is, that  $N_\nu$  is proportional to  $\nu^2$ . They then assumed that each oscillation mode had an average energy  $k_B T$  ( $k_B$ , known as Boltzmann's constant, is the gas constant  $R$  divided by Avogadro's number,  $N_0$ ), so that

$$U_\nu \propto \nu^2 T \text{ (Rayleigh-Jeans law)}$$

This result accounted exactly for the low frequency part of the spectrum, including its change with temperature. However, it says that the intensity will rise without limit as frequency increases. This means that there will be no maximum, and therefore that the total energy will be infinite, and result known as the *ultraviolet catastrophe*. Both of these problems were solved by Planck.

## ■ Thermal equilibrium

To understand Planck's approach, we need to understand what is meant by the thermal equilibrium between light and matter that is the key feature of blackbody radiation. At a given temperature, the *total* energy per unit volume (that is, the energy per unit volume summed up over all frequencies) is constant. Now, this energy must be apportioned among the different frequencies of light that make up the blackbody spectrum. It turns out that this apportionment always takes the same form, known as the *Boltzmann distribution*. This distribution is such that the fraction of the total energy *above* a particular energy  $E$  is proportional to  $e^{-E/k_B T}$ . In other words, a thermal distribution of energies *decreases exponentially with energy*.

## ■ The quantum hypothesis

Planck reasoned that the source of the problems with the Rayleigh-Jeans theory was its assumption that each oscillation mode could store the same average energy,  $E_{\text{avg}} = k_B T$ , at a given temperature *independently of its frequency*  $\nu$ . Rayleigh and Jeans derived this average energy by assuming that a given mode could have any energy at all, independently of its frequency, and then averaging over the Boltzmann distribution of energies.

Planck instead introduced the idea that energy is stored in light irreducible units of size  $h\nu$ , proportional to the frequency of the light,  $\nu$ . That is, Planck proposed that each mode could store energy only in multiples of an amount *proportional to its frequency*,  $E_\nu = j h \nu$ , where  $j = 0, 1, 2, \dots$

The units today are called *quanta of energy* or, more commonly, *photons*. It is important to understand that Planck's quanta are units of energy, and *not* physical, particle-like entities. In a classical (the term used to mean non-quantum) picture, the energy of light is determined by the magnitude of the oscillating electric field that *is* light. Changes in the energy of the light amount to changes in the magnitude of the oscillating electric field. What Planck discovered is that these changes cannot be made in arbitrary increments. Rather, they can only be made in multiples of the quantum  $h\nu$ . The constant of proportionality,  $h$ , known today as Planck's constant is so small,

$$6.62607 \times 10^{-34} \text{ Joule Second}$$

that the discontinuous amounts by which the energy of light can be changed are typically so small as to go undetected. For example, visible light has frequency of about

and the Planck quantum ("photon") is

$$\text{visiblePhoton} = \text{PlanckConstant} \nu_{\text{visible}};$$

$$(7. \times 10^{-20}) \text{ Joule}$$

By comparison, the amount of energy a 60 Watt light bulb gives off as visible light each second is

$$60 \text{ Joule}$$

so that the Planck quantum is truly tiny.

At everyday frequencies, Planck quanta are such a tiny amount of energy that it is hard to imagine that the restriction that the energy of light may change only in such discrete chunks could make any difference at all. Nonetheless, the presence of these chunks of energy turns out to be the key to understanding light in equilibrium with matter. In particular, for very much higher frequencies, in the far-UV, X-ray, and  $\gamma$ -ray regions of the spectrum, the quantum becomes very much larger. It was in just these high frequency regions that Planck's quantum hypothesis was essential to account for experimental observations.

Here is why Planck proposed these chunks. He reasoned that by making the energy stored in each oscillation mode be proportional to the frequency, then there would only be a very small number of high-frequency modes present at thermal equilibrium. That is, he used the exponential, high-energy drop-off of the Boltzmann distribution to overcome the quadratic rise of the Rayleigh-Jeans number density.

According to Planck's hypothesis, at a particular frequency, the energy is always in chunks  $h\nu$ . The total energy at a particular frequency (strictly, within a small range of frequencies near a particular frequency) is determined by how many chunks  $h\nu$  there are. Now, as  $\nu$  becomes very large, each single chunk becomes very large. Since the total energy, taking into account the total number of chunks at each frequency is fixed, this means only a very few, very large chunks can occur, for otherwise there wouldn't be enough energy left over to occur as the smaller chunks.

A money analogy might help us understand the apportioning of numbers of chunks at different frequencies. Assume we have a number of people with different annual incomes, that the total annual income (total energy) is fixed, and that the distribution of those incomes mirrors the Planck energy density distribution. This means that only a very small fraction of people can have very high incomes, for otherwise there would not be enough money left over for everyone else. Planck's hypothesis, that light energy comes in chunks that increase in size with frequency, together with the idea that at a given temperature there is only so much energy to go around (this is the thermal equilibrium bit), is what leads to the exponential fall off at high frequency—not enough energy to excite (fund) the high frequencies (high incomes).

## ■ Planck law

Here are some details of Planck's analysis. When he averaged  $i h\nu$  over the Boltzmann distribution, he obtained

$$E_{\text{avg}} = h\nu / \left( e^{\frac{h\nu}{k_B T}} - 1 \right)$$

At low frequencies, when  $h\nu \ll k_B T$ , that is, when the size of the Planck quantum (another name for the photon) is small compared to the classical average energy, this expression becomes

$$E_{\text{avg}}(\text{low } \nu) = h\nu / (1 + h\nu/k_B T + \dots - 1) \simeq k_B T,$$

that is, just the Rayleigh-Jeans result. But at high frequencies, when  $h\nu \gg k_B T$ , that is, when the size of the Planck quantum is large compared to the classical average energy, the average energy becomes

$$E_{\text{avg}}(\text{low } \nu) = h\nu / e^{\frac{h\nu}{k_B T}} \simeq h\nu e^{-\frac{h\nu}{k_B T}},$$

This is just the observed high-frequency drop-off. In this way Planck was able to exactly reproduce the observed blackbody spectrum. The Planck energy density is

$$U_\nu = N_\nu E_{\text{avg}} = \frac{8\pi\nu^2}{c^3} h\nu / \left( e^{\frac{h\nu}{k_B T}} - 1 \right)$$

Planck's discovery of this formula was the very start of our understanding of the quantum world.

## ■ Blackbody examples

To see how the blackbody spectrum looks and how it changes with temperature, let's explore it for four different temperatures, the temperature of freezing water, the temperature of our hands, of boiling water, of the coils of a toaster, and of the star Betelgeuse, and the Sun.

273 K	Ice
310 K	Human
373 K	Boiling Water
873 K	Toaster
3000 K	The star Betelgeuse
5700 K	The Sun

We'll do this in terms of an alternative way of representing the energy stored in thermally equilibrated light, namely in terms of its intensity per unit range of frequency, and its total intensity.

Intensity is the amount of energy flowing perpendicular to a square area in a given amount of time. A common unit of energy per unit time is the Watt, defined as one Joule per second per square meter. The conversion factor from energy density to intensity is the speed of light divided by 4,  $c/4$ . (The speed of light,  $c$ , is the rate at which the energy flows; the factor of 4 takes account of the fact that the energy is flowing in all directions and so only a portion of it is flowing in a particular direction.) The Planck intensity is therefore

$$I_\nu = U_\nu c/4 = \frac{2\pi\nu^2}{c^2} h\nu / \left( e^{\frac{h\nu}{k_B T}} - 1 \right)$$

The temperature of stars is determined in just this way, by matching its intensity as a function of frequency to the blackbody intensity formula.

The sum of the intensity over all possible frequencies, for 0 to  $\infty$ , is

$$\frac{2\pi^5 T^4 k_B^4}{15 c^2 h^3}$$

Substituting the values for the various constants, this intensity is

$$\frac{5.6704 \times 10^{-8} \text{ T}^4 \text{ Watt}}{\text{Kelvin}^4 \text{ Meter}^2}$$

where temperature is in units of Kelvin. The dependence on the fourth power of temperature means that a doubling of temperature of the blackbody results in sixteen times as much total intensity being radiated.

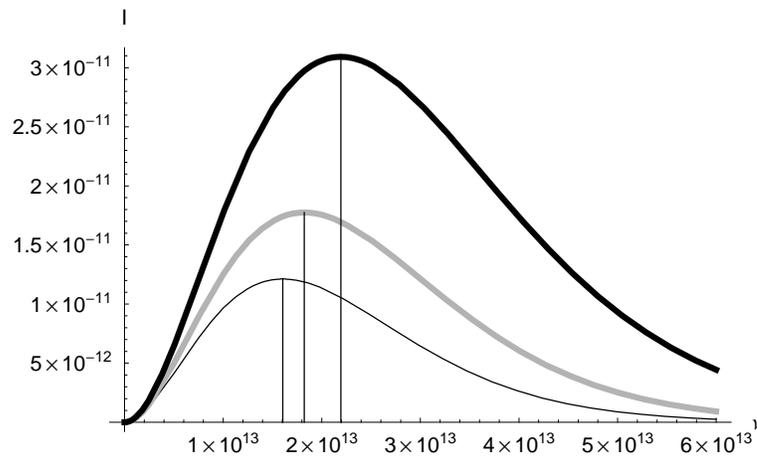
The frequency at which the intensity is greatest is

$$\frac{5.87893 \times 10^{10} \text{ T}}{\text{Kelvin Second}}$$

This result shows that the position of the maximum is proportional to the temperature (the Wien displacement law). To help in analyzing results for specific temperatures, here are what frequencies and wavelengths correspond to the different regions of the spectrum.

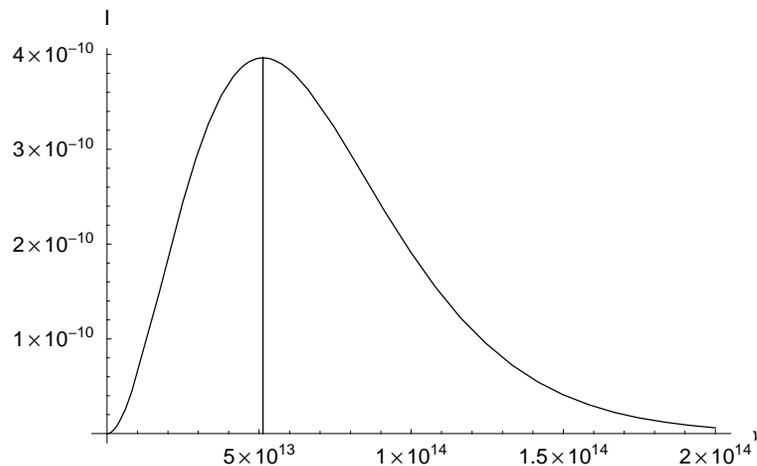
Spectral Region	Typical $\nu$ (Second <sup>-1</sup> )	Typical $\lambda$ (Meter)
$\gamma$ -rays	$1. \times 10^{19}$	$3. \times 10^{-11}$
X-rays	$1. \times 10^{17}$	$3. \times 10^{-9}$
UV	$1. \times 10^{15}$	$3. \times 10^{-7}$
Violet	$7.5 \times 10^{14}$	$4. \times 10^{-7}$
Blue	$6.7 \times 10^{14}$	$4.5 \times 10^{-7}$
Green	$6. \times 10^{14}$	$5. \times 10^{-7}$
Yellow	$5. \times 10^{14}$	$6. \times 10^{-7}$
Red	$4.3 \times 10^{14}$	$7. \times 10^{-7}$
IR	$1. \times 10^{14}$	$3. \times 10^{-6}$
Microwave	$1. \times 10^{10}$	0.03
FM Radio	$1. \times 10^8$	3.
Short Wave	$1. \times 10^7$	30.
AM Radio	500000.	600.
Long radio waves	10000.	30000.

Here is what the intensity frequency distribution looks like for the temperature of freezing water, the human body, and boiling water.



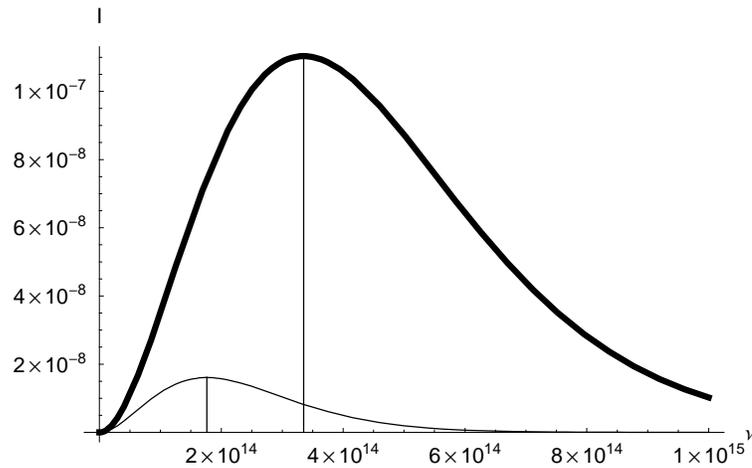
Intensity per unit range of frequency (Watts Meter<sup>-2</sup> Second<sup>-1</sup>) for temperatures 273 K (thin line, freezing water), 310 K (thick gray line, human body), and 373 K (thick black line, boiling water). The vertical lines mark  $\nu_{\max}$ .

Here is what the intensity frequency distribution looks like for the coils of a toaster..



Intensity per unit range of frequency (Watts Meter<sup>-2</sup> Second<sup>-1</sup>) for temperature 873 K (toaster coils). The vertical line marks  $\nu_{\max}$ .

Here is what the intensity frequency distribution looks like for Betelgeuse and the Sun.



Intensity per unit range of frequency (Watts Meter<sup>-2</sup> Second<sup>-1</sup>) for temperatures 3000 K ( thin line, the star Betelgeuse) and 5700 K (thick line, the Sun). The vertical lines mark  $\nu_{\max}$ .

The temperature of stars is determined in just this way, by matching its intensity as a function of frequency to the blackbody intensity formula.

The vertical lines on each of the plots mark  $\nu_{\max}$ .

Here are the numerical values along with the total intensity for each of the example temperatures.

T (K)	$\nu_{\max}$ ( $10^{14} \text{ s}^{-1}$ )	total intensity (KW/m <sup>2</sup> )	region
273	0.16	0.315	Far IR
310	0.182	0.524	Far IR
373	0.219	1.1	Far IR
873	0.513	32.9	IR
3000	1.76	4590.	Visible
5700	3.35	59900.	Visible

Blackbody frequency at intensity maxima, and total intensities

The warmth we feel when we place our hands close to our face is their blackbody radiation in the Far IR region of the spectrum; I find it quite surprising that we give off thermal radiation at the total rate of 500 watts/meter<sup>2</sup>. Toaster coils have their maximum intensity in the IR region of the spectrum; the red color we see is due to the higher frequency tail of the Planck distribution that extends into the red-orange region of the visible spectrum. The Sun has its maximum intensity in the middle of the visible region of the spectrum. Note that the total intensity in the Sun's blackbody radiation is nearly 60 megawatts per meter<sup>2</sup>; this intensity falls off as the reciprocal of the squared distance so that at the surface of the Earth it is (thankfully for our existence) much, much less.

## ■ Intensity versus wavelength

Sometimes the blackbody spectrum is studied as a function of wavelength, instead of frequency. The determination of the energy density and intensity versus wavelength from the corresponding quantities versus frequency is a little subtle. In particular, we cannot simply replace  $\nu$  everywhere with  $c/\lambda$ . The reason is that the energy density per unit range of wavelength,  $U_\lambda$ , is related to the energy density per unit range of frequency by

$$U_\lambda d\lambda = -U_\nu d\nu$$

and so,

$$U_\lambda = -U_\nu \frac{d\nu}{d\lambda}$$

The minus sign takes account of the fact that increasing wavelength ( $d\lambda > 0$ ) corresponds to decreasing frequency ( $d\nu < 0$ ). The factor  $d\nu/d\lambda$  is the change on the frequency corresponding to a change in wavelength, in the limit that the wavelength change is tiny, divided by the tiny wavelength change,  $d\lambda$ . Here is how to evaluate it.

$$\begin{aligned} \frac{d\nu}{d\lambda} &= \{\nu(\text{at } \lambda + d\lambda) - \nu(\text{at } \lambda)\} / d\lambda \\ &= \left( \frac{c}{\lambda + d\lambda} - \frac{c}{\lambda} \right) / d\lambda \\ &= \left( \frac{c\lambda}{(\lambda + d\lambda)\lambda} - \frac{c(\lambda + d\lambda)}{\lambda(\lambda + d\lambda)} \right) / d\lambda \\ &= \left( \frac{c\lambda - c\lambda - c d\lambda}{\lambda^2 - \lambda d\lambda} \right) / d\lambda \\ &= \left( \frac{-c}{\lambda^2 - \lambda d\lambda} \right) \\ &= -\frac{c}{\lambda^2} \end{aligned}$$

In the last step, we use the fact that we are interested in values  $d\lambda$  that are tiny ("infinitesimally small") and so that the term  $\lambda d\lambda$  is negligible compared to  $\lambda^2$ . (This procedure illustrates a key idea of calculus, in which slopes—rise over run—are computed in the limit that the run is tiny.)

Using the expression for  $d\nu/d\lambda$ , we see that the two energy densities are related in a *nonlinear* way.

$$U_\lambda = -U_\nu \frac{d\nu}{d\lambda} = U_\nu \frac{c}{\lambda^2}$$

A consequence is that they are *not* simply proportional, and in particular their maxima occur at different positions, that is,  $\lambda_{\max} \neq c/\nu_{\max}$ . The energy density versus wavelength is

$$U_\lambda = \frac{8 c h \pi}{\left( e^{\frac{c h}{k_B T \lambda}} - 1 \right) \lambda^5}$$

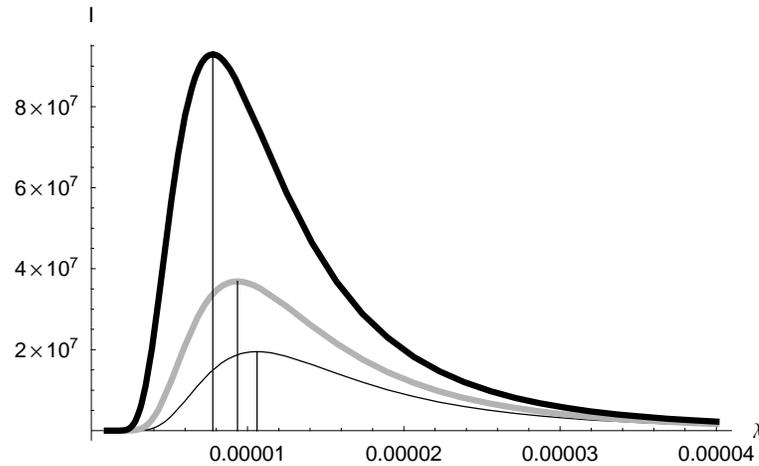
The intensity wavelength distribution is

$$I_\lambda = \frac{2 c^2 h \pi}{\left( e^{\frac{c h}{k_B T \lambda}} - 1 \right) \lambda^5}$$

The wavelength of the maximum energy density and intensity is

$$\lambda_{\max} = \frac{0.00289777 \text{ Kelvin Meter}}{T}$$

Here is what the intensity wavelength distribution looks like for the temperature of freezing water, a human being, and boiling water.



Intensity per unit range of wavelength ( $\text{Watt Meter}^{-2} \text{Meter}^{-1}$ ) for temperatures 273 K (thin line, freezing water), 310 K (thick gray line, human body), and 373 K (thick black line, boiling water). The vertical lines mark  $\lambda_{\text{max}}$ .

It is instructive to compare this plot to the earlier plot of the intensity frequency distributions for the same temperatures. Note that *small wavelengths* correspond to *high frequencies* in the earlier plots of the intensity frequency distributions, and that as temperature increases the wavelength of the maximum intensity *decreases*. The negligible intensity at very small wavelengths (compared to  $c h/k_B T$ ) traces to Planck's quanta becoming very large at these wavelengths.

## Photoelectric effect

In the photoelectric effect electrons are ejected from a metal surface—a current is caused to flow—by shining light on the metal. Based on the wave properties of light, what might we expect to be the dependence of the ejection on the intensity and frequency of the light?

First, we might expect that no matter how low the frequency of the light, if it is intense (bright) enough, electrons will be ejected. Second, no matter how high the frequency of the light, we might expect that if the light is not intense enough, then no electrons will be ejected. Finally, we might expect that, at a given frequency, the more intense the light, the faster the ejected electrons will be moving after they leave the metal. It turns out that all three of these expectations are wrong. Here is what is observed.

- If the frequency of the light is below a threshold value  $\nu_0$ , then *no electrons are ejected*, no matter how bright the light.
- If the frequency of the light is above the threshold value, then *electrons are always ejected*, no matter how faint the light. Making the light weaker decreases the current, but there is always some current, no matter how weak the light.
- The kinetic energy of the ejected electrons,  $m v^2 / 2$ , is proportional to the amount  $\nu - \nu_0$  by which the frequency of the light exceeds the threshold frequency.

These features of the photoelectric effect make no sense in terms of the wave picture of light.

We can illustrate the photoelectric effect by using light to discharge the plates of a zinc electroscope. The plates of the electroscope are charged by first creating a negative charge (excess electrons) on an amber rod, by rubbing it with fur, and then transferring the excess electrons to the zinc metal by touching the amber rod to the electroscope. The plates of the electroscope move away from one another because of the repulsion of the electrons on the movable plates.

When visible light is shone on the zinc plate, there is not loss of charge. However, when ultraviolet light is shown on the zinc plate, the charge quickly disappears, as shown by the plates of the electroscope coming together.

Evidently the threshold frequency of zinc is in the ultraviolet region of the spectrum.

## ■ Einstein's theory of the photoelectric effect

Planck was able to understand the blackbody spectrum by assuming that energy is *stored* in light in packets (photons)  $h\nu$ . Einstein was able to understand the photoelectric effect by extending Planck's idea to assume that energy is *exchanged* between the light and matter in this same amount.

Einstein proposed that when light is absorbed by the metal it increases the energy of an electron by the Planck quantum,  $h\nu$ , and that  $h\nu_0$  of this energy is necessary to free the electron from the metal. The energy  $h\nu_0$  is known as the work function  $\Phi$  of the metal. The numerical value of the work function is different for each metal and is determined by measuring the threshold frequency  $\nu_0$ . The difference,  $h\nu - \Phi = h(\nu - \nu_0)$ , appears as kinetic energy of the electron,

$$\text{KE}_{\text{max}} = \frac{m v^2}{2} = h\nu - \Phi$$

If  $\nu < \nu_0$ , then there is not enough energy to remove the electron. Making the light brighter means that more electrons absorb light, but each one can absorb only  $h\nu$  units of energy. The confirmation of Einstein's proposal is that the slope of the variation of kinetic energy with frequency turns out to be precisely Planck's constant  $h$ .

This is good point to note a common misconception, namely that the energy is transferred to the photoelectron by a "particle" of light. There is no such particle of light. What is being transferred to the electron is an amount of energy. The energy is transferred by the effect on the electron of the oscillating electric field of the light.

## ■ Photoelectric effect example

Light having a wavelength of

$$\lambda_{\text{light}} = 2.50 \times 10^{-7} \text{ Meter};$$

falls upon the surface of a piece of chromium in an evacuated glass tube. If the work function of the chromium is

$$\Phi_{\text{Cr}} = 7.21 \times 10^{-19} \text{ Joule};$$

determine (a) the maximum kinetic energy of the emitted photoelectrons and (b) the speed of the photoelectrons having this maximum kinetic energy. (Oxtoby and Nachtrieb, 2e, problem 13.13.)

The kinetic energy of the photoelectrons is the amount by which the energy of the light ,

$$E_{\text{light}} = h c / \lambda_{\text{light}};$$

$$(7.95 \times 10^{-19}) \text{ Joule}$$

exceeds the work function of the metal.

$$\text{KE}_{\text{electron}} = E_{\text{light}} - \Phi_{\text{Cr}};$$

$$(7.36 \times 10^{-20}) \text{ Joule}$$

The kinetic energy is  $mv^2/2$ , and so velocity is given in terms of kinetic energy by  $v = \sqrt{2 KE_{\text{electron}}/m}$ . Therefore the velocity of the photoelectrons is

$$\frac{(4.02 \times 10^5) \text{ Meter}}{\text{Second}}$$

This velocity is so large it is difficult to have a feel for it. One way to do so is to compare it to the speed of light.

$$\text{ratio} = v / c;$$

$$0.00134$$

This shows that the photoelectrons are moving no faster than about a one tenth of a percent of the speed of light.

Another way to assess the photoelectron velocity is to see how long it would take an electron moving at this maximum velocity to travel from Boston to Chicago, a distance of about 1000 miles.

$$\text{time} = 1000 \text{ Mile} \times 5280 \frac{\text{Feet}}{\text{Mile}} \times 0.3048 \frac{\text{Meter}}{\text{Feet}} / v;$$

$$4. \text{ Second}$$

—just four seconds! That is fast indeed.

Here is a question for you. Will some photoelectrons have velocity less than the maximum velocity? If so, what could cause them to have a correspondingly lowered kinetic energy?

## Bohr model of one-electron atoms

The one-electron atom is the simplest quantum mechanical system in chemistry. Its properties, summarized at the end of these notes, provide the intuition for how more complicated, many-electron atoms behave.

The classical picture of the atom, first articulated by Rutherford, is a "planetary" model, consisting of a negatively charged electron held in orbit at a radius of about  $10^{-8}$  cm from a positively charged nucleus that itself is only about  $10^{-12}$  cm across.

The problem with this picture, which Rutherford immediately appreciated, is that since the electron has a charge, its motion should do work on other charges, by causing them to move in response to its changing distance from them as it moves in its orbit. That is, the atom should give off light (remember, light is an oscillating electric field) of frequency equal to the number of times a second the electron orbits the nucleus. Such light emission—such work on other charges—takes energy, and the result is the electron must lose energy, "fall" closer to the nucleus, lose more energy as light of ever increasing frequency as the electron orbits faster and faster, fall still closer, and so on until it collapses into the nucleus. That is, the Rutherford model predicts that electrons in atoms should give off a burst of light with a rainbow of frequencies as the atom annihilates itself, and this process should take no longer than about a second.

Now, atoms *do* give off light, but only at precisely defined frequencies, and they certainly do *not* collapse with a burst of light. So, the planetary model of the atom seemingly implied by Rutherford's experiments presents us with a conundrum. The resolution of the conundrum is a crucial signpost on the way to the quantum theory of matter.

## ■ Rydberg formula

The frequency,  $\nu$ , of light emitted or absorbed from one-electron atoms is given by the *Rydberg formula*,

$$c \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) R_Y Z^2$$

The numbers  $n_1$  and  $n_2$  can have any positive integer values, with the restriction that  $n_1 < n_2$ . The constant  $R_Y$  is known as the *Rydberg constant*; its value is

$$\frac{1.09737 \times 10^7}{\text{Meter}}$$

$Z$  is the charge on the nucleus; for example, H has  $Z = 1$ ,  $\text{He}^+$  has  $Z = 2$ , and  $\text{Li}^{2+}$  has  $Z = 3$ . The frequencies for  $n_1 = 1$  and  $n_2 = 2, 3, \dots$  are known as the *Lyman series*, and the frequencies for  $n_1 = 2$  and  $n_2 = 3, 4, \dots$  are known as the *Balmer series*. The wavelengths of the first several lines of the Balmer series for hydrogen are

656. NanoMeter  
486. NanoMeter  
434. NanoMeter  
410. NanoMeter  
397. NanoMeter

The longest wavelength seen in the Balmer series (for  $n_2 = 3$ ) is in the red region of the spectrum and the shortest wavelength (for  $n_2 = \infty$ ) is just on the edge of the boundary between the visible and UV regions of the spectrum.

What are the first five lines of the Lyman series? What region of the spectrum do they occur in?

Why do you think the Balmer series was the first to be discovered?

In what region of the spectrum do the lines of the series with  $n_1 = 3$  occur?

## ■ Bohr's approach

Bohr, working as a post doctoral student with Rutherford, took on the task of reconciling the planetary, orbital picture of the atom with the frequencies of light that one-electron atoms emit and absorb, and with the fact that atoms do not collapse.

Bohr began by interpreting the Rydberg formula in terms of an *energy change* of the atom. That is, he knew from Planck's analysis of thermal (blackbody) radiation, that if the atom gives off (or absorbs) light of frequency  $\nu$ , then, by energy conservation, there must be a corresponding change in the energy of the atom equal to  $h\nu$ . Using the Rydberg formula, this energy change of the atom is equal to

$$c h \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) R_Y Z^2$$

Bohr interpreted this expression as the difference of two possible energies of the electron in the atom. That is, he wrote the general expression for the energy of an electron in a one-electron atom as

$$E_{\text{quantal}}[Z, n] := - h c R_Y Z^2 \frac{1}{n^2} ;$$

We call this energy  $E_{\text{quantal}}$  to remind us that it can have only *discontinuous values*, since the *quantum number*  $n$  can only have positive *integer* values. Bohr then interpreted the Rydberg formula as the *difference* of two quantal energies,

$$\Delta E_{\text{atom}}[Z, n_{\text{initial}}, n_{\text{final}}] := E_{\text{quantal}}[Z, n_{\text{final}}] - E_{\text{quantal}}[Z, n_{\text{initial}}] \text{ // Simplify}$$

True

To emphasize the change in energy, here the quantum numbers are relabeled as  $n_{\text{initial}}$  and  $n_{\text{final}}$ .

$$c h \text{ Ry } Z^2 \left( -\frac{1}{n_{\text{final}}^2} + \frac{1}{n_{\text{initial}}^2} \right)$$

One aspect of these formulas that can be confusing is determining whether the positive integer  $n_{\text{initial}}$  is greater or smaller than the positive integer  $n_{\text{final}}$ . If the atom gives off light, then it has lost energy. This means that  $\Delta E_{\text{atom}}$  is negative and so that  $n_{\text{initial}} > n_{\text{final}}$ . If the atom absorbs light, then it has gained energy. This means that  $\Delta E_{\text{atom}}$  is positive, and so that  $n_{\text{initial}} < n_{\text{final}}$ .

Another aspect of these formulas that can be confusing is that they are defined so that  $E_{\text{atom}}$  is always negative. More stable energies correspond to *more negative* values, that is, *lower* values of the positive integer  $n$ . The lowest (most negative) energy value is for  $n = 1$ ,

$$E_{\text{lowest}} = E_{\text{quantal}}[Z, 1]$$

$$-c h \text{ Ry } Z^2$$

Less stable energies correspond to *less negative* values, that is, *higher* values of the positive integer  $n$ . The highest possible energy value is for  $n = \infty$ ,

$$E_{\text{highest}} = E_{\text{quantal}}[Z, \infty]$$

$$0$$

This shows that the zero of energy is defined to correspond to  $n = \infty$ . The amount of energy required to ionize an electron from the lowest energy level is therefore

$$E_{\text{highest}} - E_{\text{lowest}}$$

$$c h \text{ Ry } Z^2$$

We can generalize this expression to get an expression for the *ionization energy*, the energy required to ionize an electron, for the level with quantum number  $n$ ,

$$E_{\text{ionization}}[Z, n] := E_{\text{highest}} - E_{\text{quantal}}[Z, n];$$

$$E_{\text{ionization}}[Z, n]$$

$$\frac{c h \text{ Ry } Z^2}{n^2}$$

This expression shows that the ionization energy is inversely proportional to the square of the quantum number  $n$  and proportional to the nuclear charge  $Z$ . Thus, for example, the ionization of  $\text{H}(n = 1)$  is four times greater than that of  $\text{H}(n = 2)$ , while the ionization of  $\text{He}(n = 1)$  is four times greater than that of  $\text{H}(n = 1)$ .

What happens if light of energy less than the ionization energy is shown an atom, if the energy of the light does not equal to one of the possible values of  $\Delta E_{\text{atom}}$ ?

What happens if light of energy more than the ionization energy is shown an atom?

Assume an electrical discharge is passed through a container of hydrogen gas, so that the molecules are dissociated into hydrogen atoms in different states of excitation. When light of fixed frequency  $\nu = 2 c \text{ Ry}$  is shown on the gas of atoms, electrons are ejected from the atoms. Predict, in the form of a sketch, how the number of ejected electrons depends on their kinetic energy. Your sketch will be an example of what is known as a photoelectron spectrum, and the general procedure is called photoelectron spectroscopy.

## Classical electron energy

So far, the analysis of the possible energies of the electron in a one-electron atom has been based on the experimentally determined Rydberg formula for the light frequencies, interpreted according to Planck's quantum hypothesis. A different way to get an expression for the energy of an electron in a one-electron atom is to treat it in a planetary model, namely to balance the Coulomb attraction between the electron and the nucleus,

$$F_{\text{Coulomb}} = - \frac{Z e^2}{4 \pi \epsilon_0 r^2};$$

by the centrifugal repulsion of experienced by the electron due to its motion around the nucleus,

$$F_{\text{centrifugal}} = \frac{m v^2}{r};$$

The sum of these forces must be zero, and using this requirement, we can solve for the squared velocity of the electron in terms of its distance from the nucleus. The result is

**vRule**

$$\left\{ v \rightarrow \frac{e \sqrt{Z}}{2 \sqrt{m} \sqrt{\pi} \sqrt{r} \sqrt{\epsilon_0}} \right\}$$

**vSquared = v<sup>2</sup> / . vRule**

$$\frac{e^2 Z}{4 m \pi r \epsilon_0}$$

Next, we can write the total energy of the electron as the sum of the kinetic energy of its motion around the nucleus and the potential energy of the electron-nucleus attraction.

$$E_{\text{classical}} = \frac{m v^2}{2} - \frac{Z e^2}{4 \pi \epsilon_0 r};$$

Finally we can use the expression for the squared velocity to rewrite the total energy as

$$- \frac{e^2 Z}{8 \pi r \epsilon_0}$$

## Comparing the classical and quantal electron energies

We now have two alternative expressions for the electron energy, the classical expression,

$$- \frac{e^2 Z}{8 \pi r \epsilon_0}$$

and the quantal expression

$$-\frac{c h R_Y Z^2}{n^2}$$

By setting these equal, we get an expression for the Rydberg constant.

$$\frac{e^2 n^2}{8 c h \pi r Z \epsilon_0}$$

Now, let's look at this result closely. It is an expression for a quantity that is a constant (the Rydberg constant), and yet it contains three variable quantities: the square of the quantum number  $n$ , and the distance  $r$  of the electron from the nucleus, and the nuclear charge  $Z$ . The only way this expression can evaluate to a constant is if the ratio  $n^2 / rZ$  itself is a constant. The constant has the units of reciprocal length (since  $n$  and  $Z$  are unitless), so let's write it as the reciprocal of a length,  $a_0$ . That is, the distance of the electron from the nucleus must satisfy

$$\frac{n^2 a_0}{Z}$$

The as yet undetermined constant of proportionality,  $a_0$ , is known as the *Bohr radius*. It is the smallest distance an electron can be from the nucleus in a hydrogen atom ( $n = 1$ ,  $Z = 1$ ).

### Determining the Bohr radius and so the Rydberg constant

If we can determine the value of the Bohr radius,  $a_0$ , we will be able to calculate the possible values of the distance of the electron from the nucleus, or, equivalently, we will be able to calculate the value of the Rydberg constant without having to use experimental data.

At this point, however, Bohr did not have enough information to proceed. What he had was a relation between the classical energy and the quantal energy, but this relation depends on *two* unknown constants, the Rydberg constant and the Bohr radius. To solve for these two quantities, Bohr needed a second, independent relation between them.

Bohr got the needed second relation between the Rydberg constant and the Bohr radius by an profoundly inspired assumption. Since classical physics works for ordinary objects that we can see and manipulate in the laboratory, Bohr assumed that all of the strangeness of the one-electron atom would disappear in the limit that the atom were very large. Bohr applied this assumption, known today as the Bohr correspondence principle, in the following way: Bohr assumed that the frequency of light emitted when the electron changes quantum number by one unit, must equal the orbital frequency of a classically orbiting electron *in the limit that the atom becomes macroscopic in size*, that is, in the limit that the quantum number  $n$  becomes very large.

The classical orbital frequency is the reciprocal of the time required for an electron to make one orbit of the nucleus,

$$v_{\text{classical}} = \frac{1}{t_{\text{classical}}} = \frac{\text{orbital velocity}}{\text{circumference}}$$

Using the expression for the squared velocity and the expression for the allowed electron-nucleus distances, we can evaluate this expression to be

$$\frac{6.57968 \times 10^{15} Z^2}{n^3 \text{ Second}}$$

The key point is that this frequency does *not* correspond to the observed frequency for low values of  $n$ , that is, when the atom is small, but it *does* converge to the observed frequency for transitions between adjacent orbits (adjacent values of  $n$ ) as  $n$  becomes very large. Here is an illustration of this,

for five orders of magnitude of the quantum number  $n$ , for  $Z = 1$  (the classical and quantal frequencies are each proportional to  $Z^2$  and this factor has been divided out in the results),

$n$	$\nu$ classical (Hz)	$\nu$ quantal (Hz)
1	$6.57968 \times 10^{15}$	$2.46738 \times 10^{15}$
10	$6.57968 \times 10^{12}$	$5.70964 \times 10^{12}$
100	$6.57968 \times 10^9$	$6.48229 \times 10^9$
1000	$6.57968 \times 10^6$	$6.56983 \times 10^6$
10000	6579.68	6578.7

For  $n = 100$ , the results agree to two significant figures, and by  $n = 1000$  the results agree to five significant figures.

Having established this correspondence between the quantal and classical frequencies in the limit of large  $n$ , Bohr next expressed it algebraically to get the second relation between the *two* unknown constants, the Rydberg constant and the Bohr radius. Here are the details.

We begin by first constructing the frequency equality. The expression for the Rydberg frequency for the  $n \rightarrow n + 1$  transition in the limit of large  $n$ . The Rydberg frequency expression for the  $n \rightarrow n + 1$  transition is

$$\frac{c (1 + 2n) R_Y Z^2}{n^2 + 2n^3 + n^4}$$

For  $n \gg 1$ , the factor  $1 + 2n$  in the numerator is approximately  $2n$ , and the denominator is approximately  $n^4$ . This means that for  $n \gg 1$ , the Rydberg frequency for the  $n \rightarrow n + 1$  is approximately

$$\frac{2c R_Y Z^2}{n^3}$$

Bohr's hypothesis is that this expression must be equal to the classical frequency for large  $n$ . The analytical expression for the classical frequency

$$\frac{e \sqrt{Z}}{4 \sqrt{m} \pi^{3/2} r^{3/2} \sqrt{\epsilon_0}}$$

Equating this classical frequency expression to the large- $n$  quantal frequency expression, and using our earlier expression for the Rydberg constant, we can solve for the relation between the electron-nucleus distance and the quantum number  $n$ .

$$\left\{ r \rightarrow \frac{\hbar^2 n^2 \epsilon_0}{e^2 m \pi Z} \right\}$$

From our earlier comparison of the classical and quantal energies, we also have the independent, alternative relation between  $n$  and the Bohr radius,

$$\left\{ r \rightarrow \frac{n^2 a_0}{Z} \right\}$$

Using these together, we can solve for the Bohr radius,

$$\left\{ a_0 \rightarrow \frac{\hbar^2 \epsilon_0}{e^2 m \pi} \right\}$$

### Numerical values of Bohr radius and Rydberg constant

We have obtained the expression

$$\frac{h^2 \epsilon_0}{e^2 m \pi}$$

The value of the Bohr radius is

$$5.29177 \times 10^{-11} \text{ Meter}$$

This is a key quantity in chemistry, the minimum size of the hydrogen atom.

We can now also get an expression for the Rydberg constant in terms of only fundamental constants,

$$\text{RyExpression} = \text{RyExpression} / . n \rightarrow \sqrt{r Z / a_0} / . a_0 \text{RuleBohr}$$

$$\frac{e^4 m}{8 c h^3 \epsilon_0^2}$$

The value of the Rydberg constant

$$\frac{1.09737 \times 10^7}{\text{Meter}}$$

agrees exactly with the value determined from experiment.

## ■ Summary of one-electron atom properties

Here is the summary of the results for one electron atoms.

Quantity	Expression	Value
$a_0$	$\frac{h^2 \epsilon_0}{e^2 m \pi}$	$5.29177 \times 10^{-11} \text{ Meter}$
$r$	$\frac{n^2 a_0}{Z}$	$\frac{5.29177 \times 10^{-11} \text{ Meter } n^2}{Z}$
Ry	$\frac{e^4 m}{8 c h^3 \epsilon_0^2}$	$\frac{1.09737 \times 10^7}{\text{Meter}}$
E	$-\frac{c h \text{ Ry } Z^2}{n^2}$	$-\frac{2.17987 \times 10^{-18} \text{ Joule } Z^2}{n^2}$

## de Broglie model of one-electron atoms

Bohr's analysis of one-electron atoms requires that the electron can be only at certain distances from the nucleus, given by

$$r = \frac{n^2 a_0}{Z}$$

where the Bohr radius is

$$5.29177 \times 10^{-11} \text{ Meter}$$

$Z$  is the atomic number of the nucleus and  $n$  is a positive integer. This restriction to only certain distances is key not only to accounting for the observed spectrum of one-electron atoms, but also for the fact that the electron does not spiral into the nucleus and so that the atom does not collapse.

Bohr was *not* able to give a physical basis for the restriction of the electron-nucleus distance to only certain values. The first step in understanding the origin of this key restriction was provided by de Broglie. de Broglie's extraordinary idea was that the electron has an associated wavelength, and that the Bohr restriction was just what is required so that the electron "wave" (leaving aside for now what on earth about the electron, a particle, could be waving) does not destructively interfere with itself.

de Broglie was guided to the idea that matter has an associated wavelength (which we know today to be the wavelength of the oscillations in the *probability amplitude*, or *wavefunction*), by combining Planck's hypothesis, that energy is stored in light in packets of size  $h\nu$ , with Einstein's adaptation of the Planck energy quantum to the photoelectric effect and the result from Einstein's theory of special relativity, that matter and energy are equivalent.

## ■ Particles of light, waves of matter

What de Broglie achieved was the synthesis of the energy quantum  $h\nu$  and special relativity. Here are some details on de Broglie's approach.

Planck proposed that energy is *stored in light* in increments,  $h\nu$ , proportional to the frequency of the light. Einstein showed that energy from the light is *exchanged with matter* in these increments, then the photoelectric effect can be understood.

At about the same time Einstein also proposed his *special theory of relativity*, based on the experimental finding that light always has the same speed, independently of the speed of the source of the light. This does not seem to have much to do with the quantum nature of matter, but in fact de Broglie was able to combine Planck's quantum with Einstein's special theory of relativity to make the extraordinary prediction that matter has wave properties. This prediction, soon confirmed experimentally, was the watershed of our understanding of the wave nature of the quantum world.

To understand de Broglie's idea, we need some background on Einstein's *theory of special relativity*. Einstein developed his theory as an exploration of how it could be that light always has the same speed, whether the light source is moving or not.

To see how strange this behavior of light is, let's imagine instead that we fire a bullet from a gun just as Superman flies by at the speed of the bullet (being Superman, he could go faster, of course!). Since Superman has matched his speed to that of the bullet, to him the speeding bullet appears to be standing still. Now, if instead of firing a bullet, we set off a flash bulb just as Superman flies by, Superman being Superman, he'll naturally speed up to catch the light. The most amazing thing, however, is that no matter how fast Superman goes, the light recedes from him at exactly the same speed as it recedes from us. From Superman's point of view of the light from the flash bulb, it as if he is standing still, no matter how fast he is going! For some reason, light seems to disobey the rules about the speed of a projectile being relative to its source!

*Perhaps the finest introduction to these ideas is Edwin F. Taylor and John Archibald Wheeler, Spacetime Physics: Introduction to Special Relativity, 2nd edition (1992) W H Freeman & Co.; ISBN: 0716723271. The extension by Einstein to reference frames accelerating with respect to one another is called general relativity, and a very accessible treatment of the key consequences of general relativity is Edwin F. Taylor and John Archibald Wheeler, Exploring Black Holes: Introduction to General Relativity, 1st edition (2000), Benjamin/Cummings; ISBN: 020138423X*

The essence of Einstein's theory to account for this very strange behavior of light is the remarkable prediction that *time proceeds at different rates* in a stationary frame of reference (us) and a moving frame of reference (Superman) in just the right amount so that light is always measured to travel the same distance in a given time. There is more to the story (a very nice exposition is *Space and time in the modern universe*, by P. C. W. Davies), and the incredible end result is Einstein's famous relation,

$$E = m c^2,$$

between mass and energy. The mass,  $m$ , is not the ordinary mass of an object, which we denote as  $m_0$  but instead it is related to it as

$$m = m_0 / \sqrt{1 - \left(\frac{v}{c}\right)^2}.$$

A crucial feature of the relation is that *the mass  $m$  becomes infinite as its speed  $v$  approaches the speed of light*. This means that it would require an infinite amount of energy to accelerate a mass to the speed of light. This is why anything with mass may only move slower than the speed of light. On the other hand, since light itself does move at speed  $c$ , we must conclude that the rest mass of light is 0!

In the limit that the speed of a mass is very much smaller than the speed of light, then we can approximate the mass as

$$m = m_0 \left\{ 1 + \frac{1}{2} \left(\frac{v}{c}\right)^2 - \dots \right\}$$

and so approximate the energy of matter as

$$E_{\text{matter}} = m_0 c^2 + \frac{1}{2} m_0 v^2 - \dots$$

That is, the energy is just the ordinary kinetic energy,  $m_0 v^2 / 2$ , plus an additional so-called *rest mass energy*  $m_0 c^2$ . It is this rest mass energy that all matter has that is released in *nuclear fusion*, in which two masses combine to form a new mass smaller than the sum, with the difference released as energy.

You may be surprised at how large your own rest mass energy is! I weigh about

77. Kilogram

This corresponds to the rest mass energy

$(7. \times 10^{18})$  Joule

This is a huge amount of energy, by everyday measures.

It turns out that light also has a mass, and so energy, even though light has no rest mass. To see this, we need to rewrite the Einstein mass-energy equation in a form that makes clear the distinction between particles with a rest mass, and light, which has no rest mass. We do this by using the relation between  $m$  and  $m_0$ , squaring both sides of Einstein's equation and then rearranging to get

$$E^2 \left\{ 1 - \left(\frac{v}{c}\right)^2 \right\} = m_0^2 c^4$$

or

$$E^2 = m^2 c^2 v^2 + m_0^2 c^4.$$

We can simplify this expression a little by using the symbol  $p$  for the (relativistic) momentum  $m v$  (*not*  $m_0 v$ ), and then taking the square root. The result is

$$E = \sqrt{p^2 c^2 + m_0^2 c^4}.$$

Now, since light has no rest mass, we can write its energy as

$$E_{\text{light}} = p c .$$

This is the relation that de Broglie used. First he noted that Planck's quantum was an alternative expression for the energy of light,

$$E_{\text{light}} = h \nu = h c / \lambda$$

and so evidently light of wavelength  $\lambda$  has a "momentum"

$$p_{\text{light}} = E_{\text{light}} / c = h / \lambda .$$

This relation says that *light has a particle property momentum*. de Broglie's extraordinary hypothesis was that this relation can be turned around and applied to matter! That is, matter with momentum  $p$  has an associated "wavelength"

$$\lambda_{\text{matter}} = h / p .$$

It is this relation that is the origin of the idea that *matter has the wave property wavelength*.

Since the momentum of light is  $p = m c$ , we can interpret the mass of a photon to be  $m_{\text{light}} = h / (c \lambda)$ . Calculate the "mass" of a photon of red light ( $\lambda = 700 \text{ nm}$ ) and of x-ray light ( $\lambda = 0.1 \text{ nm}$ ). Answer:  $3 \times 10^{-36} \text{ kg}$ ,  $2 \times 10^{-32} \text{ kg}$ .

What wavelength light would have a photon mass equal to the electron mass? Answer:  $0.002 \text{ nm}$

It is important to understand that the relations  $E = p c$  is true *only* for light, that is, only when the rest mass,  $m_0$ , is zero. That is, it is *not* true for matter, for which the rest mass is *not* equal to zero.

## ■ de Broglie matter waves account for one-electron atoms

The end point of Bohr's analysis of one-electron atoms, arrived at by means of the assumed equivalence of classical frequencies and the Rydberg frequencies for transitions between adjacent values of  $n$  in the limit of large  $n$  (macroscopic atom dimension), is the explicit expressions for the Bohr radius and the Rydberg constant.

de Broglie was able to use the relation between particle momentum and "wavelength" to derive the same results, without recourse to the correspondence principle. Specifically, de Broglie postulated that an integer number of wavelengths of the electron wave are required for the electron to be at a given distance from the nucleus; non-integer multiples of the wavelength would lead instead to destructive interference and so a vanishing of the electronic amplitude.

de Broglie's hypothesis, then, is that the circumference of an orbit,  $2 \pi r$ , must be equal to an integer number of de Broglie wavelengths,  $n \lambda = n h / p = n h / m v$ . We can express this result in terms of the orbital angular momentum of the electron,  $\ell = r m v = r p$ , as

$$\ell = n \frac{h}{2 \pi} .$$

This expression says that the angular momentum of the electron may not have just any values but only integer multiples of Planck's constant divided by  $2 \pi$ .

This result is equivalent to the requirement that the electron may not be at just any distance from the nucleus but only distance proportional to the *square* of the same integer. Here is how we can see this. At every distance of the electron from the nucleus, the Coulomb and centrifugal forces,

$$F_{\text{Coulomb}} = -\frac{Z e^2}{4 \pi \epsilon_0 r^2}$$

and

$$F_{\text{centrifugal}} = \frac{m v^2}{r},$$

must balance one another. This means that the electron's velocity depends on its distance from the nucleus as

$$v \propto \frac{1}{\sqrt{r}}.$$

That is, if the electron velocity increases by a factor of 100, its orbital velocity decreases by a factor of 10. From de Broglie's analysis, since the orbital angular momentum is proportional to the product of the distance from the nucleus and the orbital velocity,  $r v$ , the velocity also is proportional to

$$v \propto \frac{n}{r}.$$

Comparing these two proportionalities, we have the new proportionality between the number of de Broglie wavelengths and the distance of the electron from the nucleus,

$$\frac{n}{r} \propto \frac{1}{\sqrt{r}} \rightarrow n \propto \sqrt{r} \rightarrow n^2 \propto r.$$

That is, the orbital radius—the atom size—grows quadratically with the number,  $n$ , of de Broglie wavelengths. The constant of proportionality turns out, as we show below, to be just the Bohr radius divided by the nuclear charge,  $a_0/Z$ .

### Quantitative application of de Broglie's hypothesis to one electron atoms

Here are the details of the how we use de Broglie's hypothesis to establish the quantitative relation between the quantum number  $n$  and the distance  $r$  of the electron from the nucleus. Using the expression for electron velocity as it orbits a nucleus of charge  $+Z e$  and a distance  $r$ ,

$$\left\{ v \rightarrow \frac{e \sqrt{Z}}{2 \sqrt{m} \sqrt{\pi} \sqrt{r} \sqrt{\epsilon_0}} \right\}$$

we can solve the de Broglie condition,  $2 \pi r = n \lambda = n h / (m v)$ , for the number of wavelengths that can fit on the circumference of a circular orbit of radius  $r$ . The result is

$$\left\{ n \rightarrow \frac{e \sqrt{m} \sqrt{\pi} \sqrt{r} \sqrt{Z}}{h \sqrt{\epsilon_0}} \right\}$$

|| Use the relation  $2 \pi r = n h / (m v)$  to show that this expression is correct.

We can apply this expression for  $n$  to our earlier relations for the Bohr radius,

$$\left\{ a_0 \rightarrow \frac{r Z}{n^2} \right\}$$

to get an expression in terms of only fundamental constants,

$$\left\{ a_0 \rightarrow \frac{\hbar^2 \epsilon_0}{e^2 m \pi} \right\}$$

This is exactly the result Bohr got using his correspondence principle.

In this way de Broglie's approach also accounts for the stability of the atom. The lowest (smallest) orbit corresponds to just one wavelength on the circumference. No lower (smaller) orbit would be able to "fit" the electron wave.

## Classical and quantal pictures of the spectra of one-electron atoms

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The beauty of de Broglie's analysis is that it gives key features of the atom in a simple way. These are that the electron may only be at certain distances from the nucleus, proportional to the square on an integer,

$$r = \frac{a_0}{Z} n^2,$$

and, since the energy of the electron in the atom,

$$E = -\frac{Z e^2}{8 \pi \epsilon_0 r},$$

is inversely proportional to the electron-nucleus distance, that the energy of the electron in the atom is inversely proportional to the square of an integer,

$$E = -h c Z^2 \text{Ry} \frac{1}{n^2}.$$

Now, we know that one-electron atoms absorb and emit light of only certain frequencies. We also know that classically we can view an electron orbiting a nucleus as a charge oscillating with a frequency equal to the number of times a second it travels the circumference of its orbit. Since the orbital velocity is proportional to  $1/\sqrt{r} \propto 1/n$ , this means the time to make one orbit is proportional to

$$t_{\text{classical}} \propto \frac{2 \pi r}{v} \propto \frac{n^2}{1/n} \propto n^3,$$

and so the orbital frequency is proportional to

$$\nu_{\text{classical}} \propto \frac{1}{t_{\text{classical}}} \propto \frac{1}{n^3}$$

Taking all of this together, it is tempting to understand that there are only certain frequencies of light absorbed and emitted by one-electron atoms as being due to there being only certain orbital frequencies, since  $n$  can take only positive integer values.

In fact, while this interpretation has qualitative aspects of what is going on, Bohr showed that it does *not* account quantitatively for the observed frequencies. The problem is that observed frequencies do *not* correspond to classical orbital frequencies, except in the special case of very large orbits, say of  $n$  equal to 1000 or more.

For small values of  $n$ , the observed frequencies are computed in a very different way, by equating the energy *difference* of corresponding to two different values of  $n$  to the Planck formula for the energy of a light quantum. For emission of a photon of frequency  $\nu$ , for example, this equation gives

$$E_{\text{light}} = h\nu = \Delta E_{\text{atom}} = E_{n_1} - E_{n_2} = hcZ^2 \text{Ry} \left\{ \frac{1}{n_2} - \frac{1}{n_1} \right\},$$

where  $n_1 > n_2$ .

While this expression gives the correct frequencies, it does so at the cost that we must abandon the classical picture of the frequencies of light emitted and absorbed by an atom as corresponding to the frequency of an orbiting electron. It is very important to understand this evident requirement of the quantal picture.

Show that the expression for the orbital frequency of an electron in the field of a nucleus of charge  $+Ze$  is  $6.57968 \times 10^{15} Z^2 / n^3$  Hz.

Evaluate the orbital frequencies of an electron in a hydrogen atom for  $n = 1, 2$ , and  $1000$ . Answer:  $6.57968 \times 10^{15}$ ,  $8.2246 \times 10^{14}$ , and  $6.57968 \times 10^6$  Hz.

Compare the orbital frequency of an electron in the lowest energy orbit of a hydrogen atom with the minimum frequency light that this electron can absorb. Answer:  $\nu_{\text{classical}} = 6.57968 \times 10^{15}$  Hz,  $\nu_{\text{quantal}} = 2.46738 \times 10^{15}$ .

As we have discussed earlier, Bohr showed that the two pictures correspond only when comparing classical orbital frequencies for very large orbits with quantal frequencies for transitions between adjacent, large quantum numbers.

Compare the orbital frequency of an electron in the  $n = 1000$  orbit of a hydrogen atom with the frequency light that this electron can absorb in the transition to  $n = 1001$ . Answer:  $\nu_{\text{classical}} = 6.57968 \times 10^6$  Hz,  $\nu_{\text{quantal}} = 6.56983 \times 10^6$  Hz.