Chapter 39: Particles behaving like waves

- Electron waves
- Atoms and atomic spectra
- Energy levels
- The Bohr model of the atom
- The laser
- Continuous spectra
- The uncertainty principle revisited

de Broglie wavelength

Electrons and protons, which we usually think of as particles, can also behave like waves. Therefore, they must also have a wavelength and frequency.

A free particle with rest mass *m*, moving with nonrelativistic speed *v* should have a wavelength λ (known as the de Broglie wavelength) related to its momentum p = *mv* in exactly the same way as for a photon, where $\lambda = h/p$.

Thus, the de Broglie wavelength of a particle is given by

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

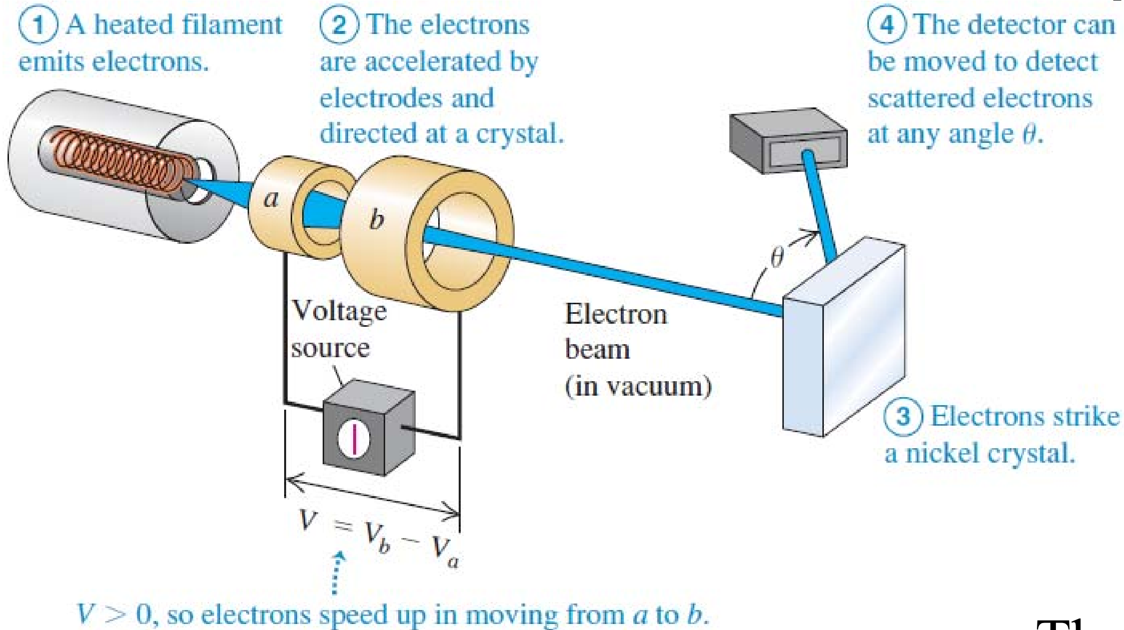
If the particle's speed is an appreciable fraction of the speed of light c, we replace *mv* with *γmv*, which gives

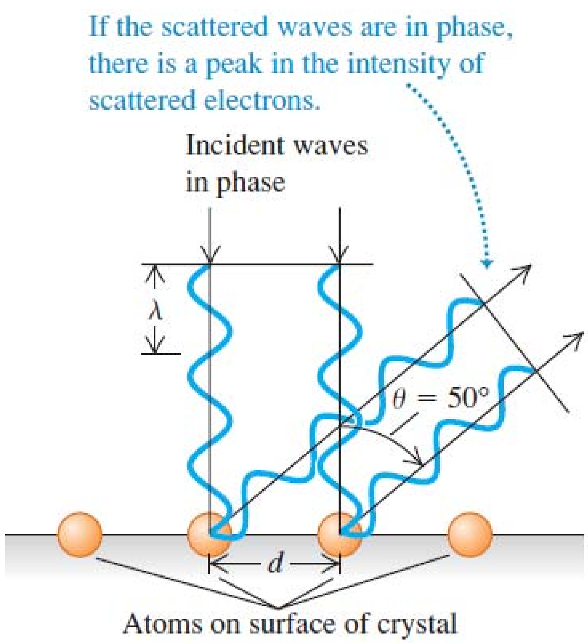
$$\lambda = \frac{h}{mv}\sqrt{1 - \frac{v^2}{c^2}}$$

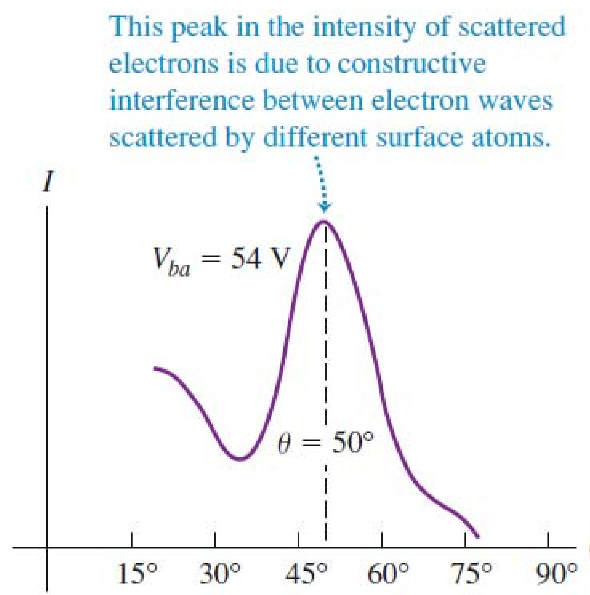
The frequency of the particle can be found from the particle's energy,

$$f = \frac{E}{h}$$

Experiment to detect the wave-like property







The momentum of the electrons is

$$p = \sqrt{2meV}$$

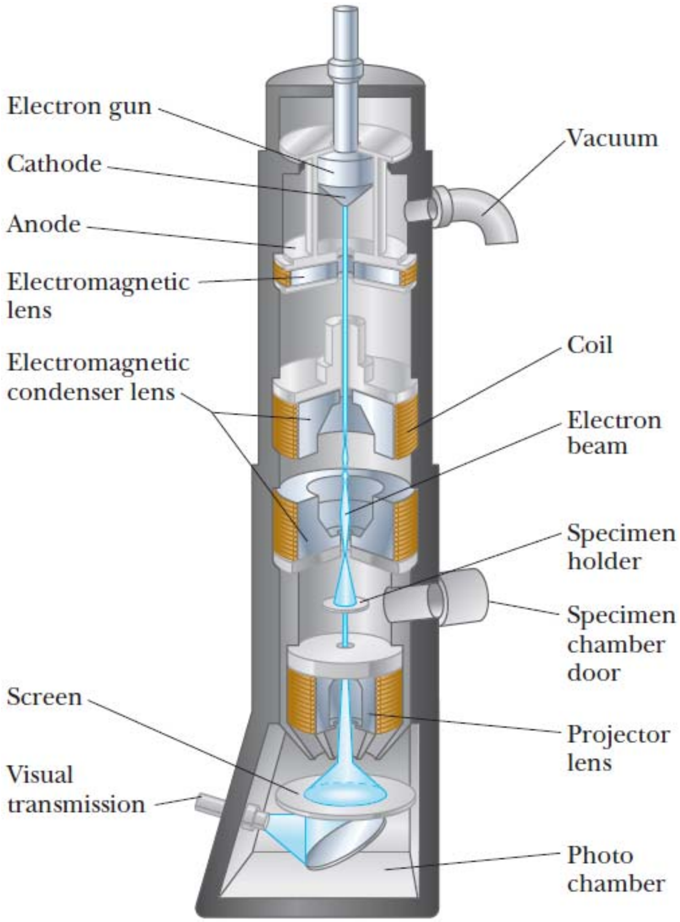
The de Broglie wavelength follows as

$$\lambda = \frac{h}{\sqrt{2meV}}$$

Transmission electron microscope

The wavelength of electrons in an electron microscope is much smaller than the wavelength of visible light (around 390 nm to 700 nm).

For example, the wavelength of electrons with kinetic energies of 1 keV is



$$1\,\mathrm{eV} = 1.609 \times 10^{-19}\,\mathrm{J}$$

$$p = \sqrt{2mE} = \sqrt{(2)(9.109 \times 10^{-31}\,\mathrm{kg})(1000)(1.609 \times 10^{-19}\,\mathrm{J})}$$

$$\lambda = \frac{h}{p} = \frac{6.626 \times 10^{-34}\,\mathrm{kg\,m^2/s}}{\sqrt{(2)(9.109 \times 10^{-31}\,\mathrm{kg})(1000)(1.609 \times 10^{-19}\,\mathrm{J})}}$$

$$\lambda = 3.870 \times 10^{-11}\,\mathrm{m}$$

Using a transmission electron microscope, we can “see” objects far smaller than what we can see in an optical microscope.

Note that some other issues can degrade the resolving power

Suppose an electron and a proton move at the same speed. Which particle has a longer de Broglie wavelength?

A. Because both are particles, it is meaningless to discuss a wavelength associated with them.

B. The proton has the longer de Broglie wavelength.

C. The electron has the longer de Broglie wavelength.

D. Both have the same de Broglie wavelength.

A nonrelativistic electron and a nonrelativistic proton have the same de Broglie wavelength. Which of the following statements about these particles is accurate?

A. The electron has more momentum than the proton.

B. Both particles have the same kinetic energy.

C. Both particles have the same momentum.

D. Both particles have the same speed.

Why is the wave-like nature of a moving baseball typically NOT observed?

A. The baseball's wavelength is too small.

B. The baseball does not have a wave-like nature.

C. The baseball's energy is too small.

D. The baseball's frequency is too small.

Light of wavelength 105 nm falls on a metal surface for which the work function is 5.00 eV. What is the minimum de Broglie wavelength of the photoelectrons emitted from this metal?
($h = 6.626\times10^{-34}$ Js $= 4.14\times10^{-15}$ eV s, $c = 3.00\times10^{8}$ m/s, $m_r = 9.11\times10^{-31}$ kg, 1 eV $= 1.60\times10^{-19}$ J)

A. 0.94 nm

B. 0.47 nm

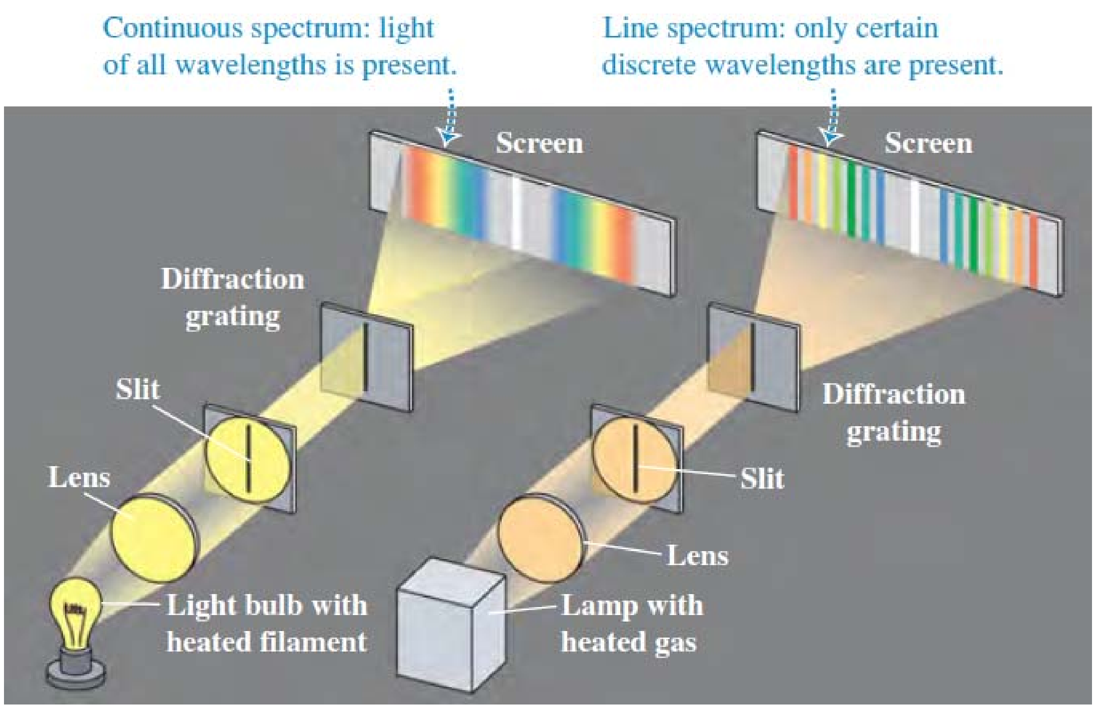
C. 0.33 nm

D. 0.24 nm

Line spectra

Materials will produce, at least some, visible light when they are heated to a high enough temperature.

If a light source is emitted by hot matter such as the tungsten filament in a light bulb or the red glow of heated iron, the spectrum is continuous. If the material is a gaseous element or small molecule, then discrete spectral lines appear.



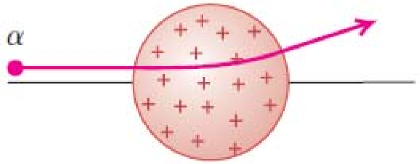
Note that while a heated gas selectively emits only certain wavelengths, a cool gas selectively absorbs certain wavelengths.

Rutherford and atomic structure

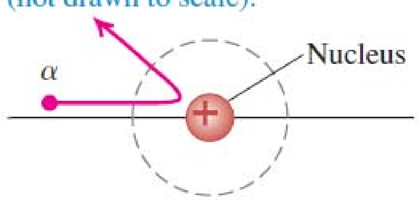
To understand the line spectra, we need to understand the atom. At the time of Rutherford's experiment, atoms where already known to consist of negatively charged electrons of known mass and charge. Most of an atom's mass distribution was still unknown.

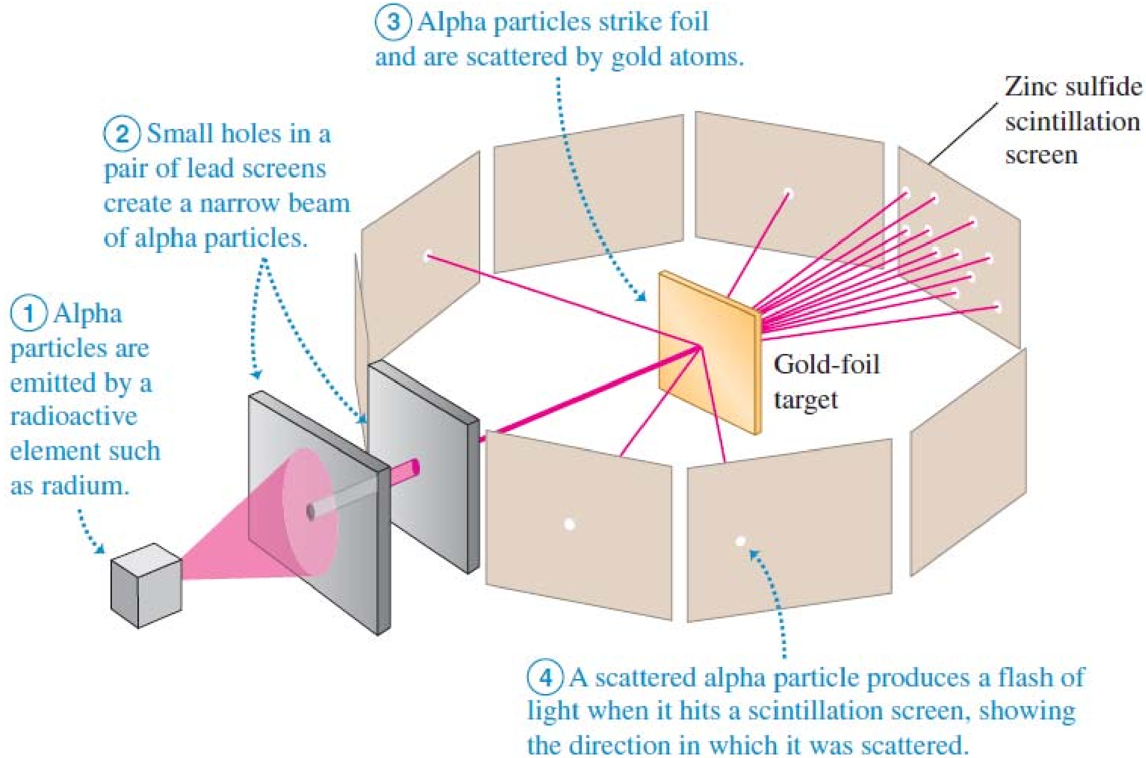
By scattering alpha particles off of a gold screen, we can see some of these scatter in the completely opposite direction. Thus, the massive, positive, electric charge must be highly concentrated (perhaps we shall even call it a nucleus!!!).

Thomson's model of the atom: An alpha particle is scattered through only a small angle.



Rutherford's model of the atom: An alpha particle can be scattered through a large angle by the compact, positively charged nucleus (not drawn to scale).





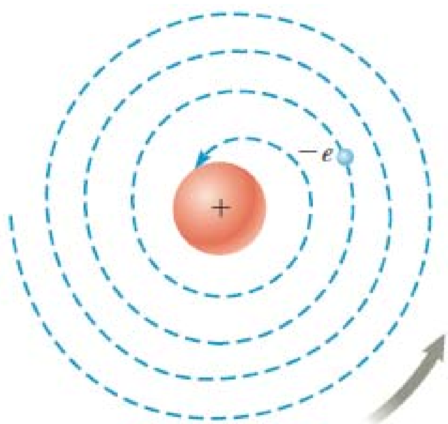
Bohr model of the atom

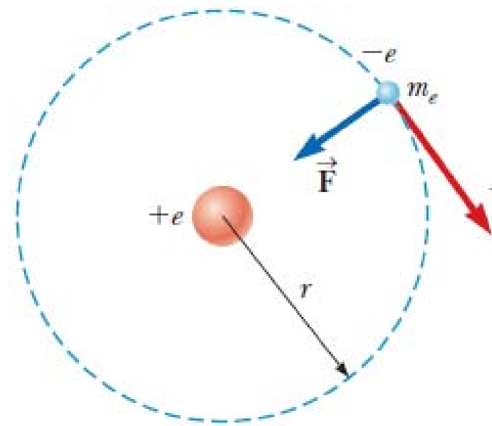
In 1913, the Bohr model of an atom introduced what is sometimes called the "old" quantum theory.

Every quantum mechanical reference from 1913 until Schrodinger's 1926 "modern" quantum mechanical explanation is classified as "old" quantum.

Bohr stated that each atom has a set of possible internal energy levels, and it CANNOT exist in intermediate internal energy levels.

(classical)





(Bohr)

- Descriptions of the observed spectra do not make sense with classical electromagnetism because accelerating charges radiate energy continuously.

- Bohr's model says that the electrons orbit at designated energy levels and radiate in bursts until they reach a minimum orbital energy (ground state).

Bohr's model should still radiate from the ground state to a lower state, and this model cannot explain why the ground state doesn't radiate.

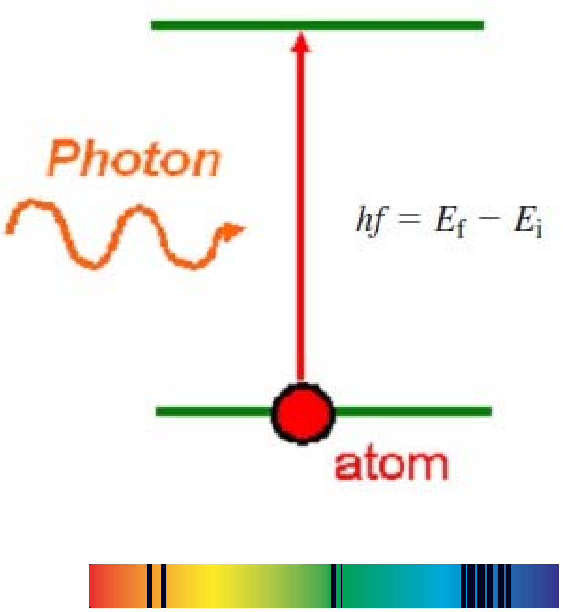
Energy levels and the Bohr atom

An excited atom can make a transition from one energy level to a lower level by emitting a photon with energy equal to the energy difference between the initial and final levels,

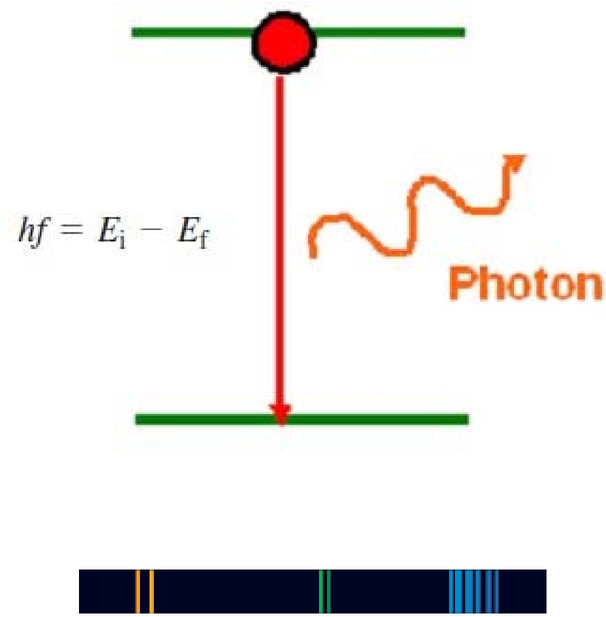
$$E_i - E_f = hf = \frac{hc}{\lambda} \quad \textbf{(emitted)}$$

The opposite is true for the absorption of a photon,

$$E_f - E_i = hf = \frac{hc}{\lambda} \quad \textbf{(absorbed)}$$



(gas absorption spectrum)



(gas emission spectrum)

Electron waves and the Bohr atom

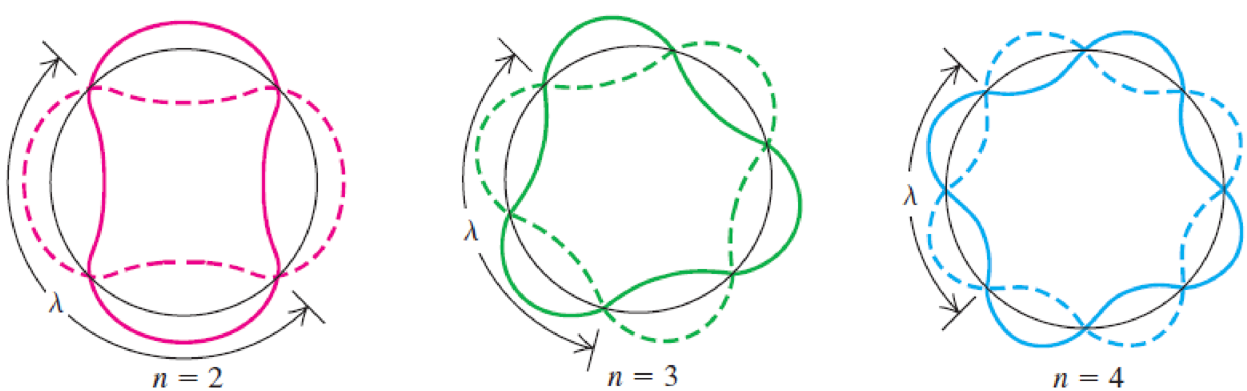
Bohr suggested that the quantum nature of the angular frequency ω of light emitted by an atom is related to a quantum angular momentum *L* with values related to the Planck constant

$$L_n = n\hbar \quad \text{for} \quad n = 1, 2, 3, \ldots$$

If the angular momentum is quantized with principle quantum number *n*, then the radius of orbit and electron velocity must also be quantized,

$$L_n = m v_n r_n = n\hbar$$

This quantum picture of circular orbits also agreed with de Broglie's discover that matter can behave like waves, where the electron forms a standing wave with the lowest mode corresponding to the lowest energy state (ground state).



Bohr radius and orbital speed of an H atom

In hydrogen the magnitude of the force *F* between the positive proton and the negative electron is given by Coulomb's law,

$$F = -\frac{1}{4\pi\epsilon_0}\frac{e^2}{r_n^2}$$

Because the electron is said to move in a circular path in the Bohr model, then we may write

$$-\frac{1}{4\pi\epsilon_0}\frac{e^2}{r_n^2} = -ma_n = -m\frac{v_n^2}{r_n}$$

Solving the equation $mv_nr_n = n\hbar$ for v_n and substituting it into the above equations allows us to find an expression for the radius,

$$r_n = \frac{4\pi\epsilon_0 n^2\hbar^2}{me^2}$$

The Bohr radius is the radius in the ground state $n = 1$, $r_1 = \frac{4\pi\epsilon_0\hbar^2}{me^2}$.

Instead, if we solving the equation $mv_nr_n = n\hbar$ for r_n and substitute, we find an expression for the orbital speed,

$$v_n = \frac{e^2}{4\pi\epsilon_0 n\hbar}$$

Kinetic & potential energy in the Bohr atom

From the quantization of the orbital velocity, we may find the kinetic energy of an electron inside the atom,

$$K_n = \frac{1}{2} m v_n^2 = \frac{m e^4}{32\pi^2 \epsilon_0^2 n^2 \hbar^2}$$

Likewise, the potential energy of the electron is given by

$$U_n = -\frac{1}{4\pi\epsilon_0} \frac{e^2}{r_n} = -\frac{m e^4}{16\pi^2 \epsilon_0^2 n^2 \hbar^2}$$

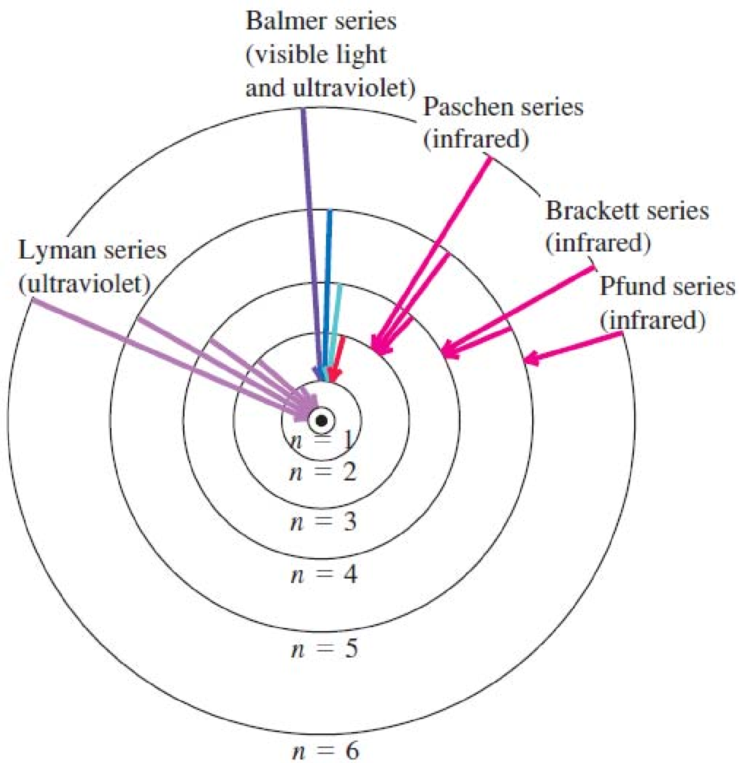
The total energy $E_n = K_n + U_n$ follows as

$$E_n = -\frac{m e^4}{32\pi^2 \epsilon_0^2 n^2 \hbar^2}$$

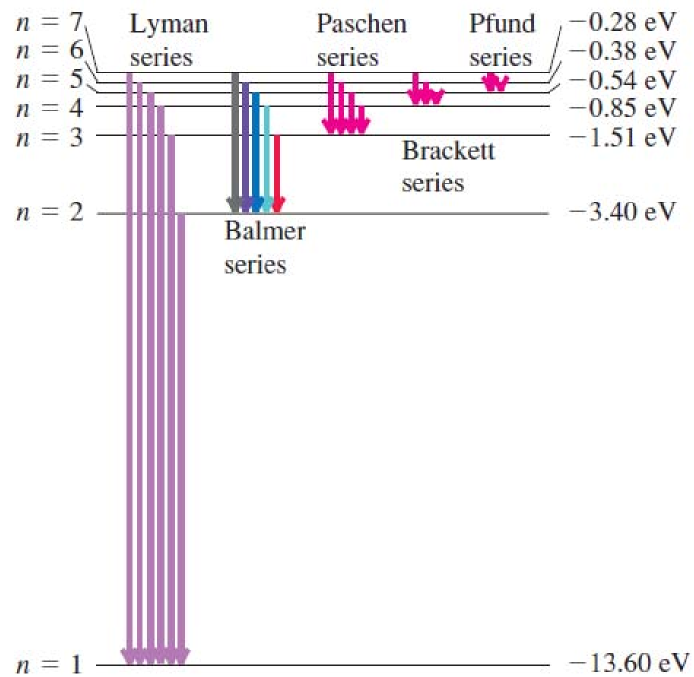
Although there are fundamental problems with the Bohr model, it does predict the energy levels of the hydrogen atom.

Spectra of emitted photons from an H atom

Permitted orbits of an electron in the Bohr model of a hydrogen atom (not to scale). Arrows indicate the transitions responsible for some of the lines of various series.



Energy-level diagram for hydrogen, showing some transitions corresponding to the various series



For simplification, we can define the Rydberg constant to be $R = \dfrac{me^4}{64\pi^3\epsilon_0^2\hbar^3 c}$.

Each of the emission line series can be calculated using the equation

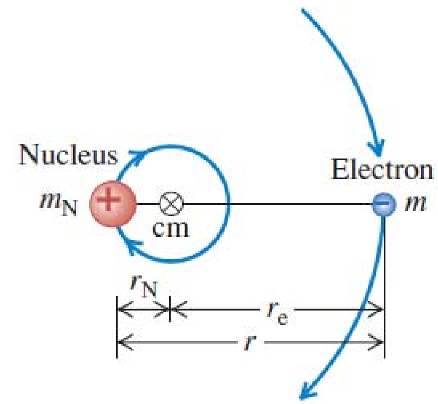
$$\frac{1}{\lambda} = R\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)$$

Nuclear motion and reduced mass

The Bohr model assumes that the proton is stationary, but the proton and electron both revolve in circular orbits about their common center of mass.

Therefore the predictions based on an infinitely heavy (stationary) nucleus are slightly incorrect.

A system composed of two bodies of masses m_1 and m_2 has a reduced mass, where the electron with rest mass m orbits the proton with rest mass $m_p = 1836.2m$ with an effective mass of



$$m^* = \frac{m_1 m_2}{m_1 + m_2} = \frac{(m)\,(1836.2\,m)}{m + 1836.2\,m} = 0.99946\,m$$

Note that deuterium has a proton and neutron making the nucleus more stationary, where the effective mass of the electron becomes $0.99973\,m$. Thus, deuterium spectral lines can be distinguished from the H atom lines by a factor of 1/1.00027.

Energy spectrum of hydrogen-like atoms

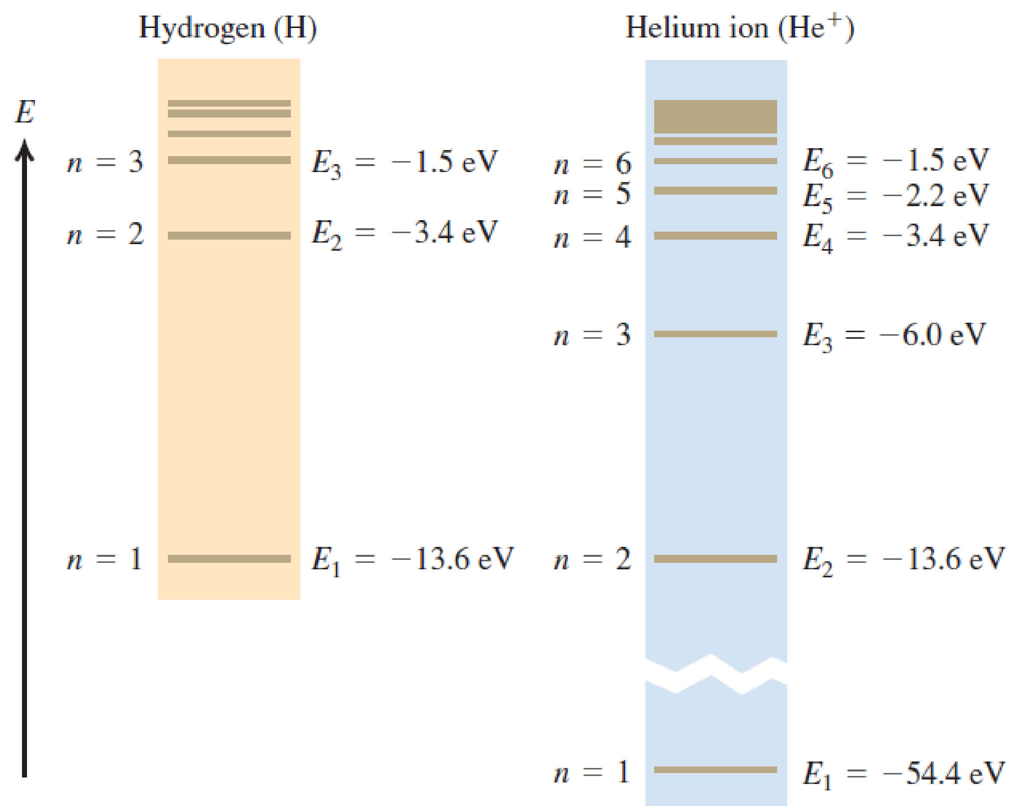
The results of the Bohr model for hydrogen can be extended to heavier element ions that have been stripped of all but one electron. The Coulomb potential for these H-like atoms with atomic number *Z* is

$$F_{\mathrm{H-like}} = -\frac{1}{4\pi\epsilon_0}\frac{(Ze)(e)}{r_n^2}$$

From the Bohr model, the energy spectrum for these H-like atoms follows as

$$E_n^{\mathrm{H-like}} = -\frac{mZ^2e^4}{32\pi^2\epsilon_0^2 n^2\hbar^2}$$

Note that the Bohr model is nonrelativistic, where the energy of core electrons in heavier atoms can be relativistic.



Which of the following observations led Bohr to formulate his model of the hydrogen atom?

A. The peak of blackbody radiation moves to shorter wavelengths as temperature increases.

B. Neutrons form a diffraction pattern when scattered from a nickel crystal.

C. Electrons are observed to have wave nature.

D. A low-density gas emits a series of sharp spectral lines.

What was Bohr's quantum condition on the orbital energies in an atom?

A. Orbital position is quantized.
B. Angular momentum is quantized.
C. Electron acceleration is quantized.
D. Electron energy is quantized.

The Bohr radius of the hydrogen atom is 0.529×10^{-10} m. What is the radius of the $n = 2$ state?

A. 1.06×10^{-10} m

B. 0.529×10^{-10} m

C. 2.12×10^{-10} m

D. 0.265×10^{-10} m

The energy of the ground state in the Bohr model of the hydrogen atom is -13.6 eV. The energy of the $n = 2$ state of hydrogen in this model is closest to

A. −1.7 eV.

B. −3.4 eV.

C. −4.5 eV.

D. −6.8 eV.

What is the frequency of the light emitted by atomic hydrogen with $n_2 = 8$ and $n_1 = 12$? (The Rydberg constant is $R = 1.097 \times 10^7$ m^{-1}, $c = 3.00 \times 10^8$ m/s)

A. 1.05×10^{13} Hz

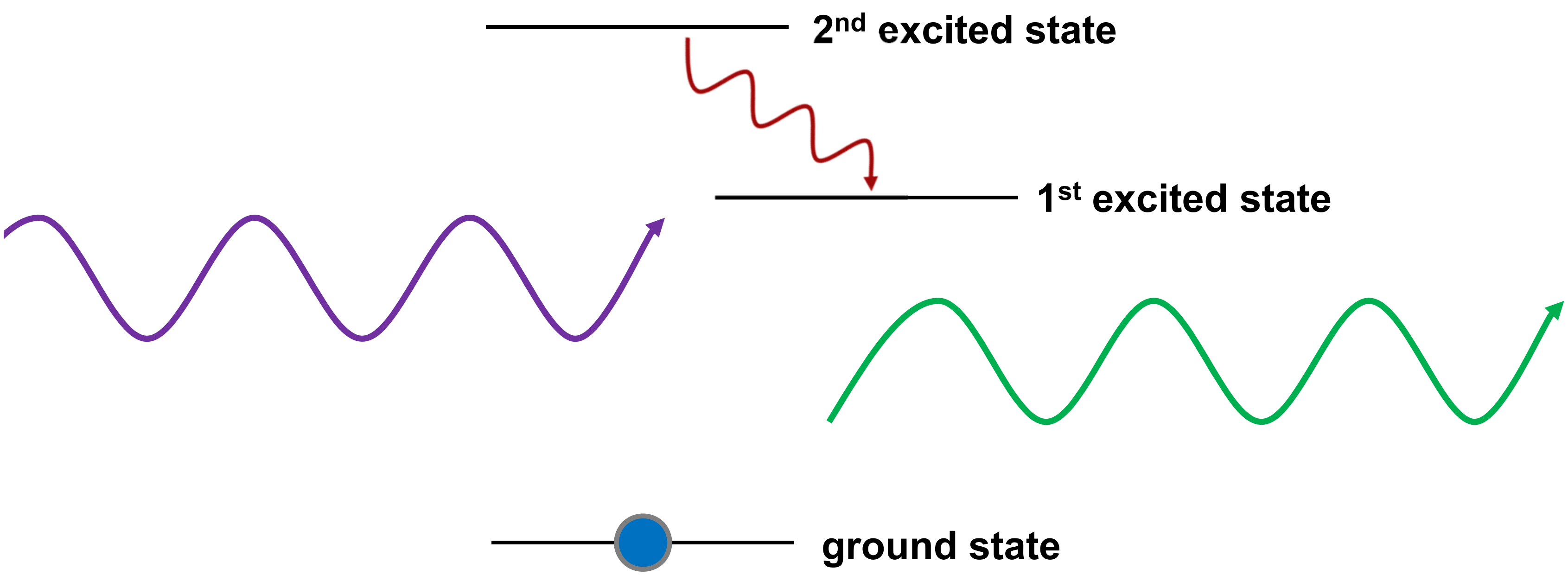
B. 1.43×10^{13} Hz

C. 7.46×10^{13} Hz

D. 2.86×10^{13} Hz

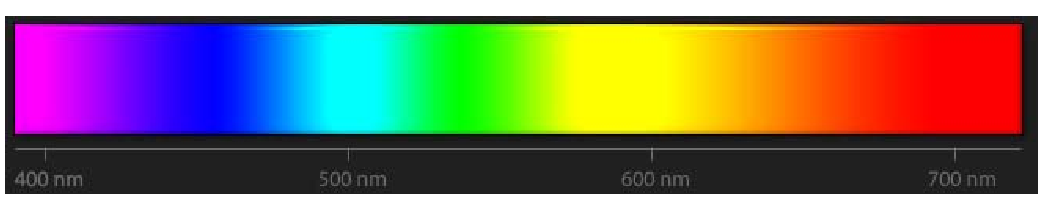
Spontaneous emission from long-lived states

1) Electron is in the ground state.
2) Photon is absorbed and the electron is excited.
3) The electron can non-radiatively relax to a lower excited state.
4) The electron emits a photon and comes back to the ground state.



Photons with less energy have longer wavelengths.

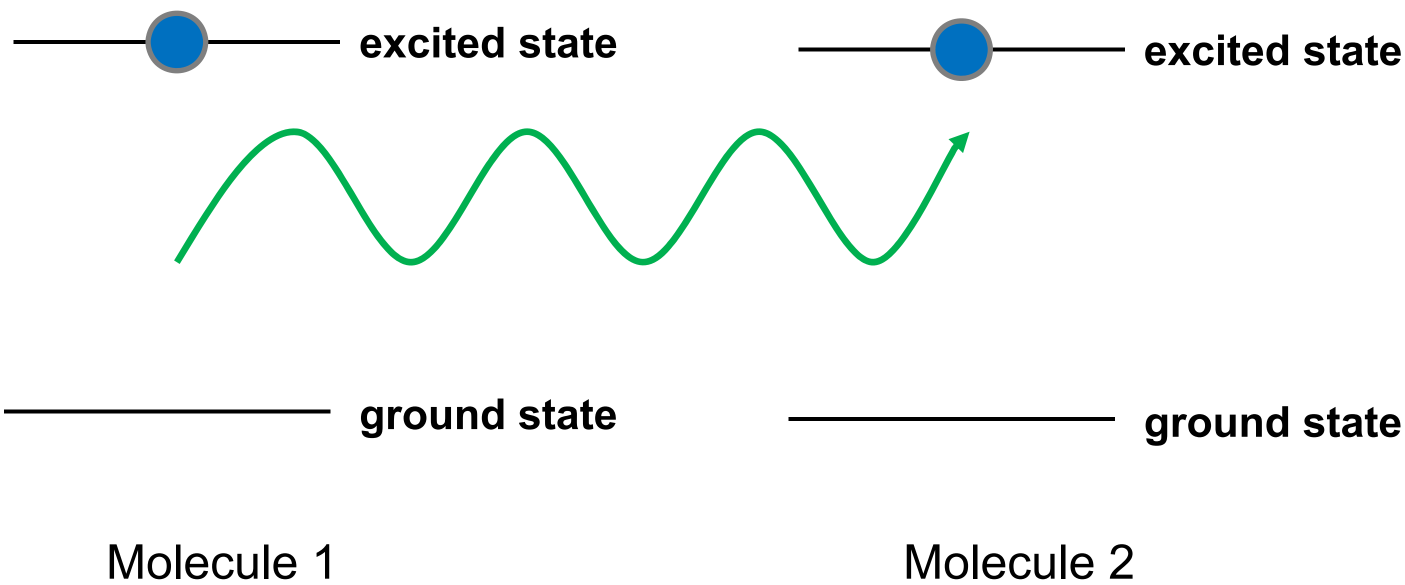
High energy



Low energy

Amplified Spontaneous Emission

1) Many molecules are in an excited state.
2) A molecule releases a photon and the electron goes to the ground state.
3) The photon passes by another molecule, which causes it to release a photon of in the same direction with the same energy.



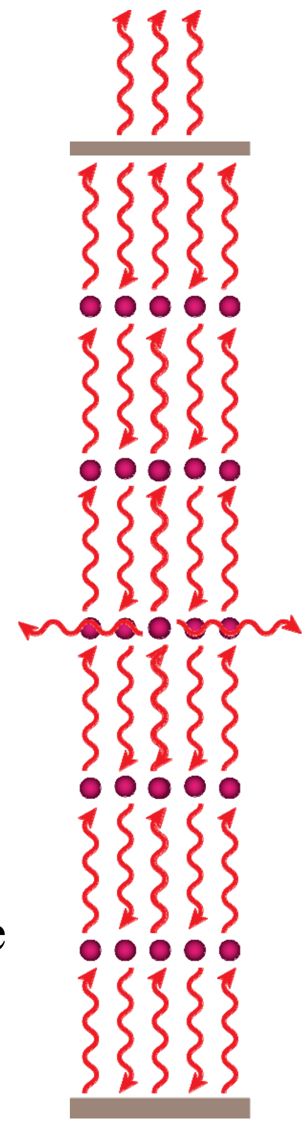
Lasers

1. An atom/molecule in an excited state emits a photon.

2. Previously emitted photons pass by other excited state emitters.

   Amplified Spontaneous Emission (ASE)

3. A reflective cavity provides feedback to give coherent lasing.



Note that for lasers, a nonequilibrium situation must first be created before the emission can occur, where the number of atoms/molecules in a higher-energy state is greater than the number in the lower-energy state. Such a situation is called a <u>population inversion</u>.

Populations inversions in gas lasers

The Maxwell–Boltzmann distribution function determines the number of atoms in a given state in a gas (chapter 18),

$$f(v) = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-mv^2/2kT}$$

When the gas is in thermal equilibrium at absolute temperature T, the number of atoms n_i in a state with energy E_i is proportional to $e^{-E_i/kT}$.

As we look at higher energy states, we find fewer atoms occupying those energies due to the negative exponent.

For many atom systems, each with the ground-state energy E_g and an excited state energy E_{ex}, the fraction of the two states is

$$\frac{n_{ex}}{n_g} = \frac{e^{-E_{ex}/kT}}{e^{-E_g/kT}} = e^{(E_g - E_{ex})/kT}$$

Stimulated emission in gases occurs for the nonequilibrium condition of a population inversion such that more atoms are in the excited states than in the ground state.

Which of the following statements is true concerning a laser?

A. The theory behind the operation of a laser depends on quantum mechanics.

B. Laser action cannot be produced unless the ground state is a metastable state.

C. Laser action cannot be produced unless a material is at an extremely high temperature.

D. A laser produces a very narrow beam of monochromatic incoherent light.

The wavelength of a ruby laser is 694.3 nm. What is the energy difference between the two energy states involved in laser action? ($c = 2.9979\times10^{8}$ m/s, $h = 6.626\times10^{-34}$ Js, 1 eV = 1.6022×10^{-19} J)

A. 1.537 eV

B. 1.646 eV

C. 1.786 eV

D. 1.812 eV

You need 14 W of infrared laser light power with wavelength 1270 nm to bore a hole in a diamond. How many downward atomic transitions per second must occur in the laser if all of them result in light directed onto the diamond? ($c = 3.00 \times 10^8$ m/s, $h = 6.626 \times 10^{-34}$ Js)

A. 2.7×10^{18}

B. 6.4×10^{18}

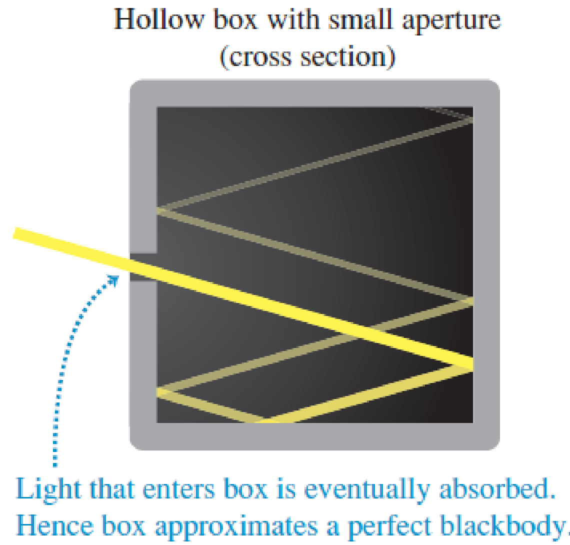
C. 5.9×10^{19}

D. 8.9×10^{19}

Blackbody radiation and its intensity

The ideal surface for emitting light with a continuous spectrum is one that also absorbs all wavelengths of electromagnetic radiation. Such an ideal surface is called a blackbody because it would appear perfectly black when illuminated.

A common model for a blackbody is a box with a small hole in it. The cavity walls are opaque to radiation. Thus, radiation incident on the hole will pass into the cavity, and is very unlikely to be re-emitted.



Known as the Stefan-Boltzmann law, the total intensity I emitted from the surface of an ideal radiator is proportional to the fourth power of the absolute temperature T with Stefan-Boltzmann constant $\sigma \approx 5.67\times10^{-8}\,\mathrm{W\,m^{-2}\,K^{-4}}$,

$$I = \sigma T^4$$

Spectral emittance of blackbody radiation

The intensity of blackbody radiation is not uniformly distributed over all wavelengths.

We define the spectral emittance (spectral radiance) as the intensity per wavelength interval, $B(\lambda)$. The total intensity I determined by the Stefan-Boltzmann law is the integral of the function $B(\lambda)$ over all wavelengths (area under the curve),

$$I = \int_0^\infty B(\lambda)\, d\lambda$$

The classical theory of spectral emittance had a serious problem called the ultra-violet catastrophe because the intensity approached infinity as the wavelength was became small,

$$B_{\mathbf{classical}}(\lambda) = \frac{2\pi ckT}{\lambda^4}$$

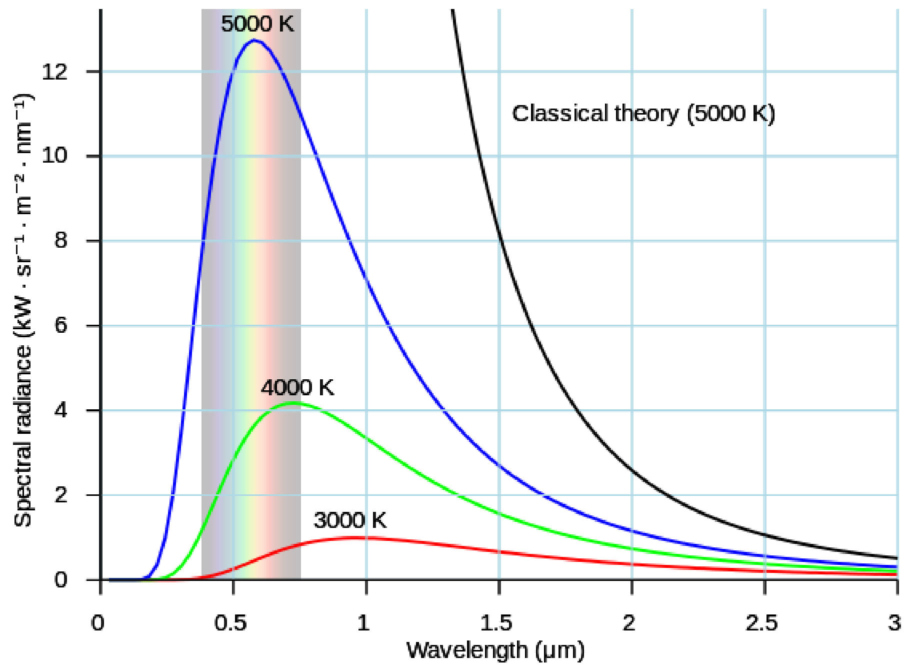
where k is the Boltzmann constant. This equation for $B(\lambda)$ is clearly incorrect as the intensity for blackbody radiation is not infinite.

Planck's law

Envisioning quantum mechanical oscillators, Planck's law fixed this "catastrophe" with the equation

$$B_{\text{Planck}}(\lambda) = \frac{2\pi hc^2}{\lambda^5\left(e^{hc/\lambda kT} - 1\right)}$$

The Planck radiation law also contains the Wien displacement law and the Stefan–Boltzmann law as consequences.



The Wien displacement law is the observation that the maximum intensity wavelength in the distribution is given by

$$\lambda_m T \approx 2.90 \times 10^{-3}\,\mathrm{K\,m}$$

The Stefan-Boltzmann law can be found by integrating the spectral emittance from Planck's law, which gives

$$I = \int_0^\infty \frac{2\pi hc^2}{\lambda^5\left(e^{hc/\lambda kT} - 1\right)} d\lambda = \boxed{\frac{2\pi^5 k^4}{15c^2h^3}} T^4$$

σ

At absolute temperature T, a black body radiates its peak intensity at wavelength λ. At absolute temperature $2T$, what would be the wavelength of the peak intensity?

A. 16λ

B. $\lambda/16$

C. 2λ

D. $\lambda/2$

What is the wavelength of peak emission for a black body at 37°C? ($c = 3.0\times10^{8}$ m/s, Wien displacement law constant is 2.9×10^{-3} mK, $\sigma = 5.67\times10^{-8}$ $Wm^{-2}K^{-4}$)

A. 94 μm

B. 78 μm

C. 9.4 μm

D. 7.8 μm

Revisiting the uncertainty principle

Electrons and other particles obey the same Heisenberg uncertainty principles as photons. The uncertainty principle can be written for each momentum/position vector as well as for energy/time,

$$\Delta p_x \, \Delta x \geq \frac{\hbar}{2}, \quad \Delta p_y \, \Delta y \geq \frac{\hbar}{2}, \quad \Delta p_z \, \Delta z \geq \frac{\hbar}{2}, \quad \Delta E \, \Delta t \geq \frac{\hbar}{2}$$

The uncertainty shows that the Bohr model cannot be correct, because if an electron orbits in the xy-plane, then its position is a precisely known constant with a position along z, and it therefore has a momentum in the z-direction of precisely zero. The Bohr model violates the uncertainty principle.

To get the proper physical description of an atom, the entire theory must consider the wave-like properties of the electron and not the particle-like properties. Quantum mechanics, often called wave mechanics will be used later to provide a more accurate description of the atom.

If the accuracy in measuring the position of a particle with mass increases, what happens to the accuracy in measuring its velocity?

A. The accuracy in measuring its velocity becomes uncertain.
B. The accuracy in measuring its velocity decreases.
C. The accuracy in measuring its velocity also increases.
D. The accuracy in measuring its velocity remains the same.