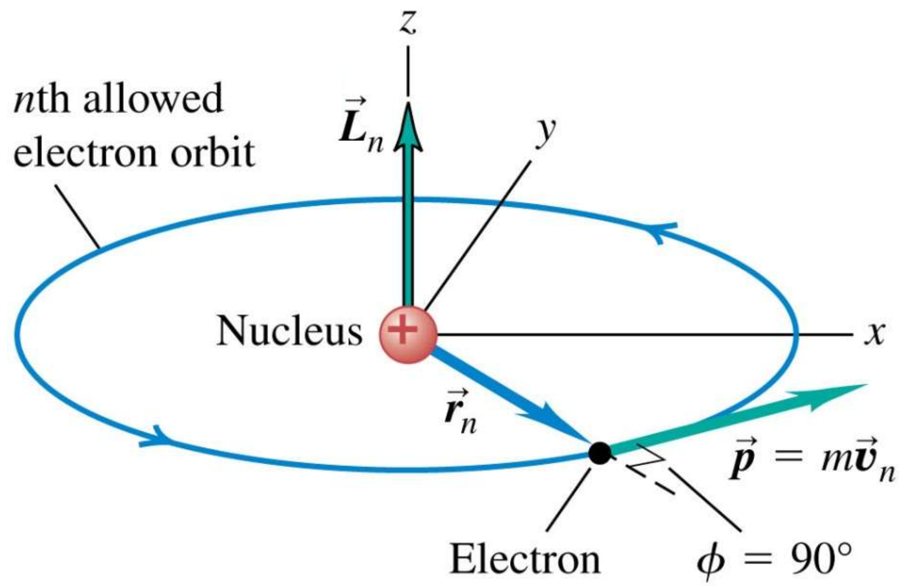
Bohr's Model (mathematical details)

Now, consider the total energy for an e in an orbit at r_n,

$$E_n = K_n + U_n$$

$$E_n = \frac{1}{2} m v_n^2 - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r_n}$$



Bohr's Model (mathematical details)

Recall, from $F = ma$, we have $\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r^2} = \frac{mv^2}{r} \rightarrow mv^2 = \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r} = -U$

So, as in any circular motion under $1/r^2$ type of force, we have $K = -U/2$

This gives the total energy for an e in an orbit at r_n,

$$E_n = K_n + U_n = \frac{U_n}{2} = -\frac{1}{8\pi\varepsilon_0}\frac{e^2}{r_n} = -\frac{e^2}{8\pi\varepsilon_0}\left(\frac{\pi m e^2}{\varepsilon_0 h^2}\frac{1}{n^2}\right)$$

$$\boxed{E_n = -\frac{me^4}{8\varepsilon_0^2 h^2}\frac{1}{n^2} = \frac{-13.6eV}{n^2}}$$ (energy levels of a Bohr's atom)

Note: **Energy levels** are *quantized* as a consequence of the electron behaving as a wave in the atom (angular momentum quantization).

Bohr's Model (notes)

- The **ground state energy** of the H-atom is given by E_1 = -13.6 eV when n = 1.
- Comparing the expression for H-atom's energy with the empirical formula derived by Balmer, we can derive an explicit expression for the Rydberg Constant,

$$hcR = \frac{me^4}{8\varepsilon_0^2 h^2} \quad \rightarrow \quad R = \frac{me^4}{8\varepsilon_0^2 h^3 c} = 1.097 \times 10^7 m^{-1}$$

Agree well with previous experimental value using wavelength measurements.

- The energy required to remove an electron completely is given by the transition from $n = 1 \; to \; n = \infty$ and it is called the **ionization energy**,

$$E_{ionization} = E_\infty - E_1 = 13.6 eV$$

Hydrogen-like Atoms

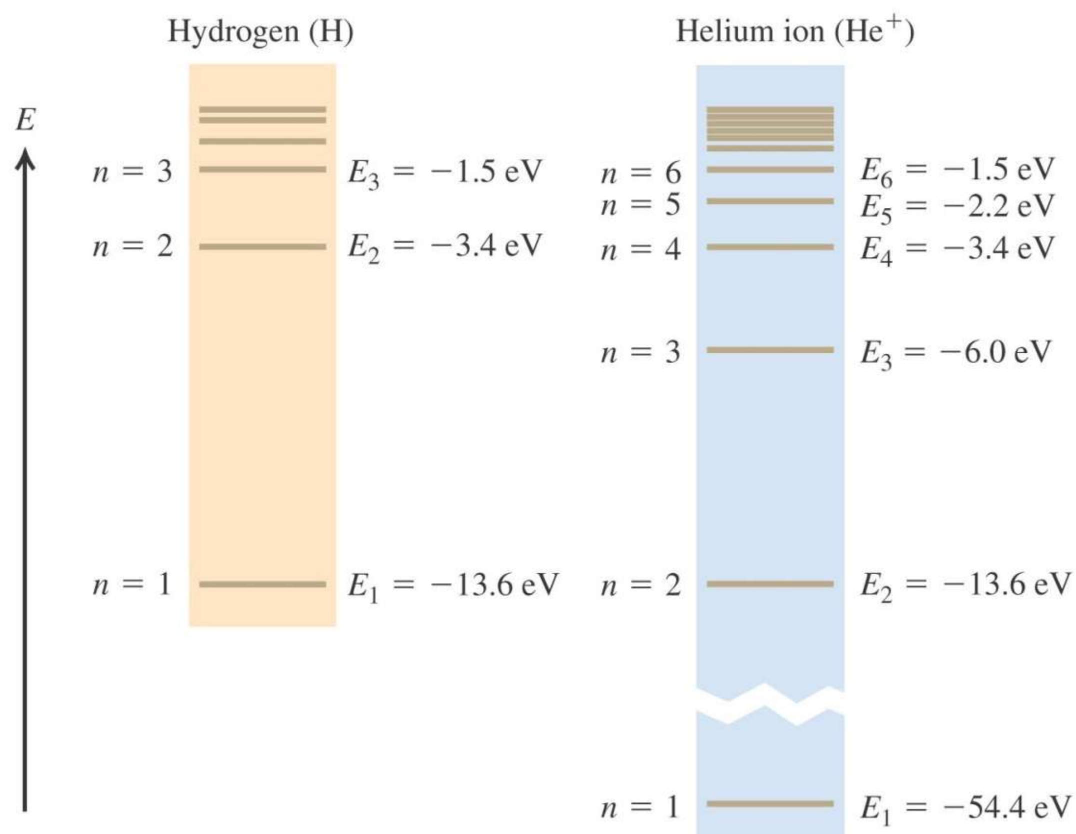
Singly ionized helium (He+), doubly ionized lithium (Li2+) are examples of hydrogen-like atoms with a *single* electron around the nucleus.

For hydrogen-like atoms, e^2 in all equations from previous analysis is replaced by Ze^2, where Z is the *atomic number* of the element.

All mathematical results follow through but with the following changes:

$$r_n \rightarrow r_n / Z$$

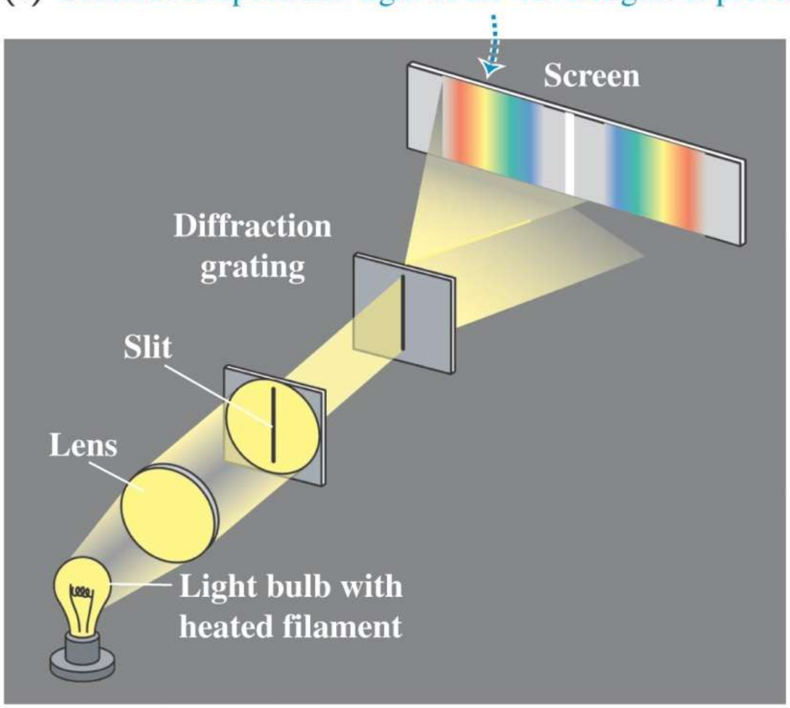
$$E_n \rightarrow Z^2 E_n$$



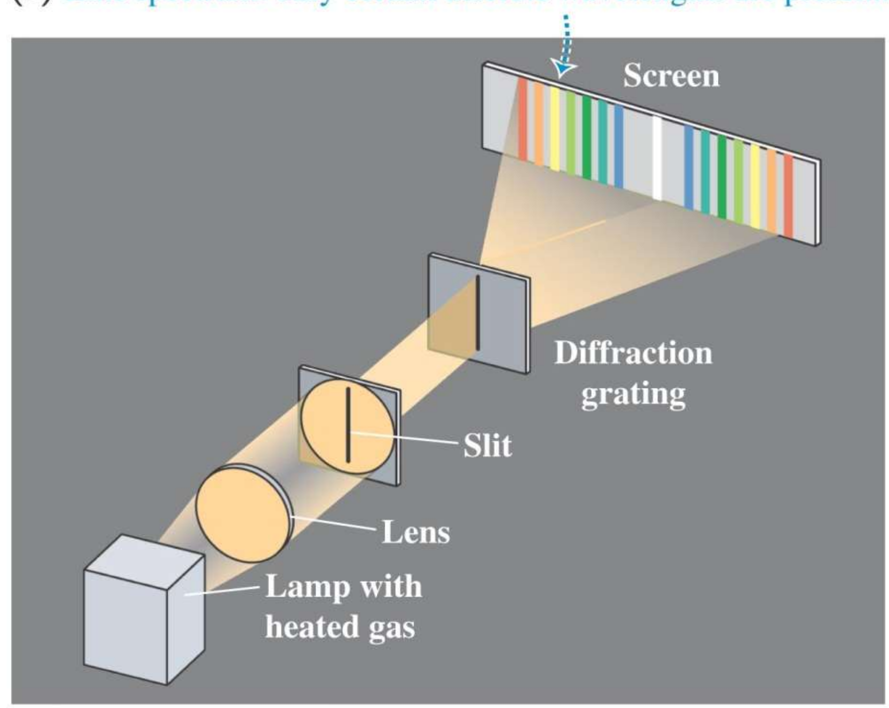
Blackbody Radiation: Continuous Spectra

In contrast to line spectra emitted from excited atoms in a diluted gas, radiations from *many thermally* excited atoms in a solid will in general emit a *continuous* spectrum with characteristics depending on its *temperature*.

(a) Continuous spectrum: light of all wavelengths is present.



(b) Line spectrum: only certain discrete wavelengths are present.



Blackbody Radiation: Continuous Spectra

In contrast to line spectra emitted from excited atoms in a diluted gas, radiations from *many thermally* excited atoms in a solid will in general emit a *continuous* spectrum with characteristics depending on its *temperature*.

Typically, a good light absorber will also be a good emitter so that a *perfect* emitter is typically called a “blackbody”.

Radiations emitted from a “blackbody” will be characteristic of that particular system since all other strayed radiations from the surrounding will be absorbed by the system and not reflected back out.

The continuous spectrum emitted by such a body is called **blackbody radiation**.

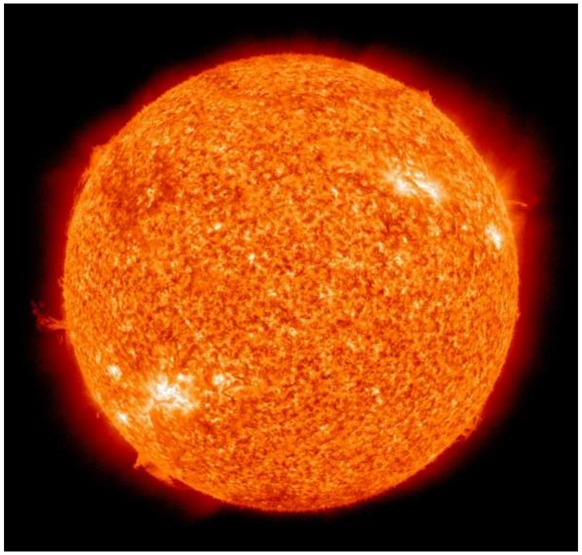
Blackbody Radiation

The total intensity (per unit surface area) of emitted light by a blackbody at absolute temperature T is given by the **Stefan-Boltzmann Law**:

$$I = \sigma T^4$$

where σ is call the **Stefan-Boltzmann constant** and it has the following value:

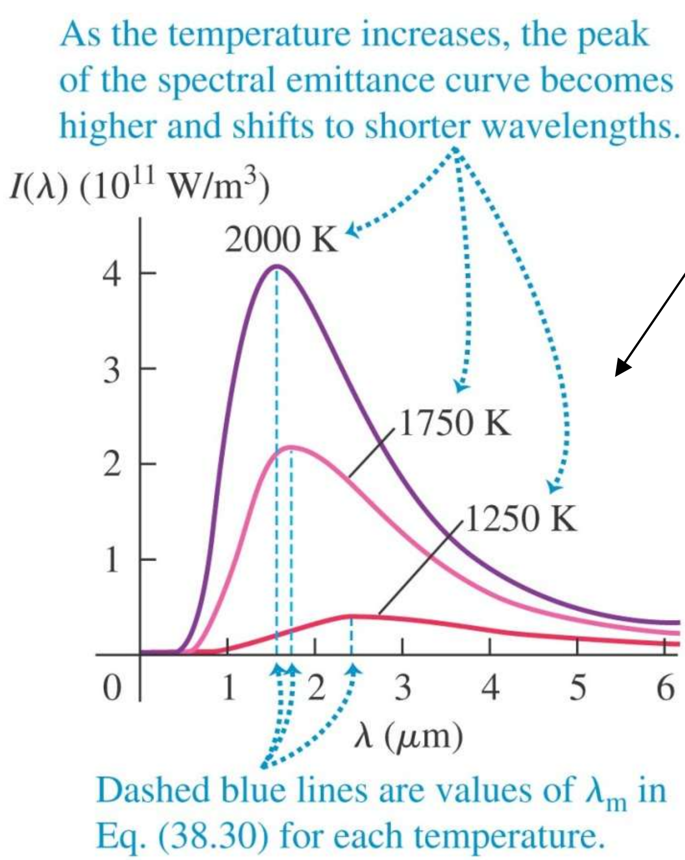
$$\sigma = 5.67 \times 10^{-8} \frac{W}{m^2 \cdot K^4}$$



The Sun

Blackbody Radiation: Spectral Emittance

The intensity is not uniformly distributed over all wavelengths. The intensity distribution for a given range of wavelength is called the *spectral emittance* $I(\lambda)$.



(Experimental observed spectral emittance for different T's.)

Note: as expected, $I = \int_0^\infty I(\lambda)d\lambda$

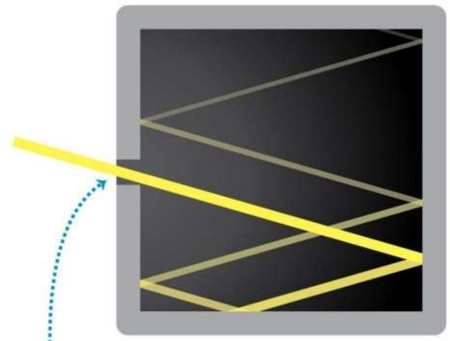
There is also the experimentally obtained **Wien displacement law**:

$$\lambda_m T = 2.90 \times 10^{-3}\, m \cdot K$$

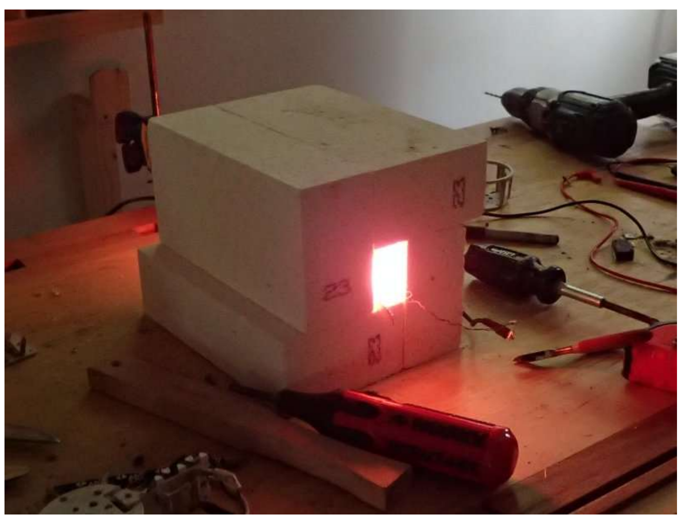
As T ⇧ , dominant λ (λ_m) moves to *shorter* λ.

Blackbody Radiation: Cavity Radiation

A cavity with a small opening is a good model for a “blackbody” !



Light that enters box is eventually absorbed.
Hence box approximates a perfect blackbody.

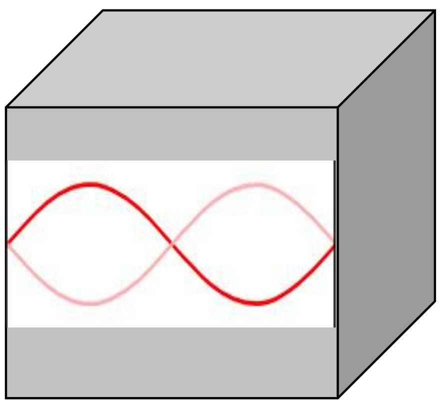


Electric Forge

Blackbody Radiation

A cavity with a small opening is a good model for a blackbody. Most importantly, one can derive the *spectral emittance* for a blackbody using such a cavity.

Model:

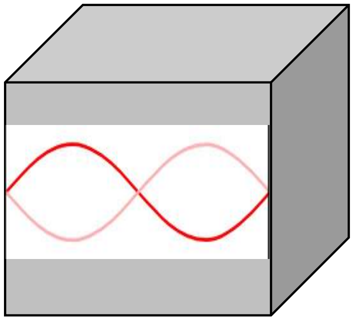


A metallic unit cube cavity filled with EM waves forming **standing waves** (normal modes) with nodes at the walls.

For a given range of wavelengths $[\lambda, \lambda + d\lambda]$, the spectral emittance can be calculated as the combined energy from all the allowed standing EM waves (normal modes) within a given range of wavelengths.

Blackbody Radiation

One can calculate the spectral emittance and it is given by:



$$I(\lambda)d\lambda = N(\lambda)\,\bar{E}\,d\lambda$$

where $$N(\lambda)d\lambda = \frac{2\pi c}{\lambda^4}d\lambda$$

is the # of EM modes (standing waves) allowed in the unit cube within a given wavelength range: $[\lambda, \lambda + d\lambda]$

and $\bar{E}$ is the average energy per EM mode (standing wave) within the cavity.

As we will see, the different between the (classical) Rayleigh prediction (incorrect) and the (quantum) Planck prediction depends on how $\bar{E}$ is calculated !

Blackbody Radiation

Distribution of energy states:

The energy of a given standing wave (normal modes) is distributed according to the **Maxwell-Boltzmann distribution**:

$$P(E)dE = \frac{e^{-E/kT}}{kT}dE$$

where k is the Boltzmann's constant and T is the absolute temperature.

(Recall the special case for molecular speeds: the Maxwell's distribution of molecular speeds.)

Blackbody Radiation

Classical Rayleigh Prediction (incorrect):

To calculate $\overline{E}$ with E assumed to be a *continuous* variable from 0 to ∞, i.e., all energies are possible.

Then,

$$\overline{E} = \frac{\int_0^\infty P(E)E\,dE}{\int_0^\infty P(E)\,dE} = \cdots = kT$$

Note: $P(E)$ is already normalized. The denominator is 1. We are keeping it so that we will be consistent when we consider the *discrete* case later.

So, the spectral emittance is $I(\lambda,T) = \dfrac{2\pi c}{\lambda^4} kT$ (Rayleigh-Jeans Law)

Problems with this classical prediction ("ultraviolet catastrophe"):

$$\begin{cases} I(\lambda,T) \to \infty \\ \int_0^\infty I(\lambda,T)d\lambda \to \infty \end{cases} \quad as\ \lambda \to 0$$

This is absolutely not physical! Intensity of the emitted light (radiated energy) must remain finite !

Blackbody Radiation

Max Planck in 1900 proposed a solution to this problem.

A radically different way to calculate $\bar{E}$ for the EM waves inside the cavity:

E is *not* a continuous variable and E can only take on *discrete* values !

$$E_n = 0, \Delta E, 2\Delta E, 3\Delta E, \cdots = n\Delta E \quad n = 0, 1, 2, 3, \cdots$$

And, the *discrete* energy increment for the EM waves is given by:

$$\Delta E = hf$$

Then, $$\bar{E} = \frac{\sum_{n=0}^{\infty} E_n P(E_n)}{\sum_{n=0}^{\infty} P(E_n)} = \cdots = \frac{hc/\lambda}{e^{hc/\lambda kT} - 1}$$

Blackbody Radiation

Then, the spectral emittance in this quantum calculation becomes:

$$I(\lambda,T)=\frac{2\pi c}{\lambda^4}\bar{E}=\frac{2\pi c}{\lambda^4}\frac{hc/\lambda}{\left(e^{hc/\lambda kT}-1\right)}$$

$$\boxed{I(\lambda,T)=\frac{2\pi hc^2}{\lambda^5\left(e^{hc/\lambda kT}-1\right)}}$$ (Planck's Blackbody Radiation Law)

Notes: As $h\to 0$ (classical limit),

$$e^{hc/\lambda kT}\cong 1+\frac{hc}{\lambda kT}$$ (Taylor's expansion of e)

so,

$$\bar{E}=\frac{hc/\lambda}{e^{hc/\lambda kT}-1}\cong\frac{\cancel{hc/\lambda}}{\cancel{1}+\frac{\cancel{hc}}{\cancel{\lambda}}\frac{1}{kT}-\cancel{1}}=kT$$

Planck's result reduces to the classical result if $h=\Delta E=0$.

Planck's Result in CM & QM Limits

$\lambda \to \infty$: (long wavelengths, low photon energy) CM regime

Classical R-J Law

Again, we have $e^{hc/\lambda kT} \cong 1 + \dfrac{hc}{\lambda kT}$

Then, again, $\bar{E} = \dfrac{hc/\lambda}{e^{hc/\lambda kT} - 1} \cong kT$ and $I(\lambda, T) = \dfrac{2\pi c}{\lambda^4}\bar{E} \cong \dfrac{2\pi c}{\lambda^4} kT$

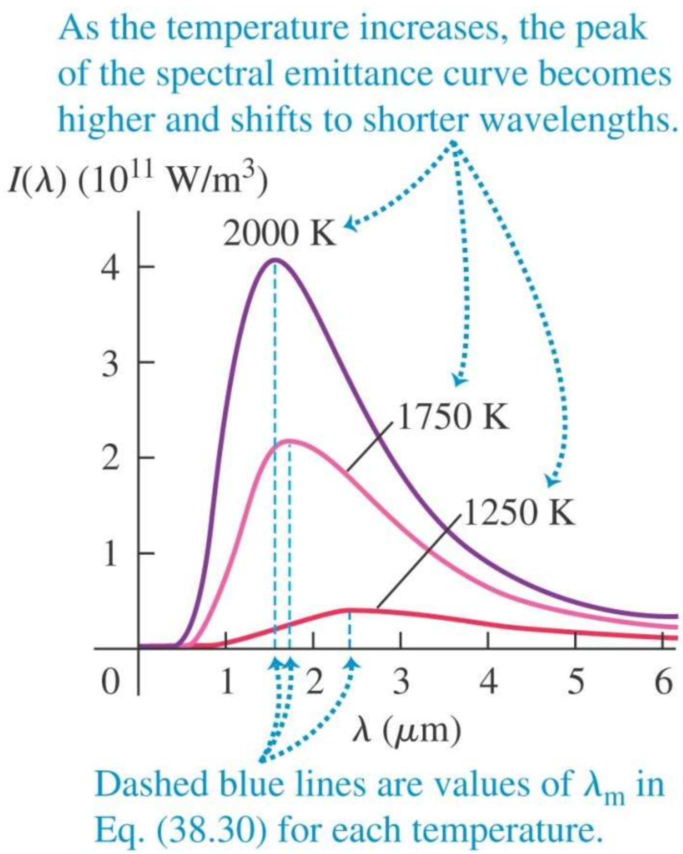
$\lambda \to 0$: (short wavelengths, high photon energy) QM regime

$e^{hc/\lambda kT} \to \infty$ **exponentially faster** than $\lambda^5 \to 0$ as $\lambda \to 0$

so $I(\lambda, T) = \dfrac{1}{\lambda^5 \left(e^{hc/\lambda kT} - 1\right)} \to 0 \quad as \quad \lambda \to 0$

There is no ultraviolet catastrophe in QM limit !

Blackbody Radiation (Review)



NOT COMPLETE Classical Prediction:

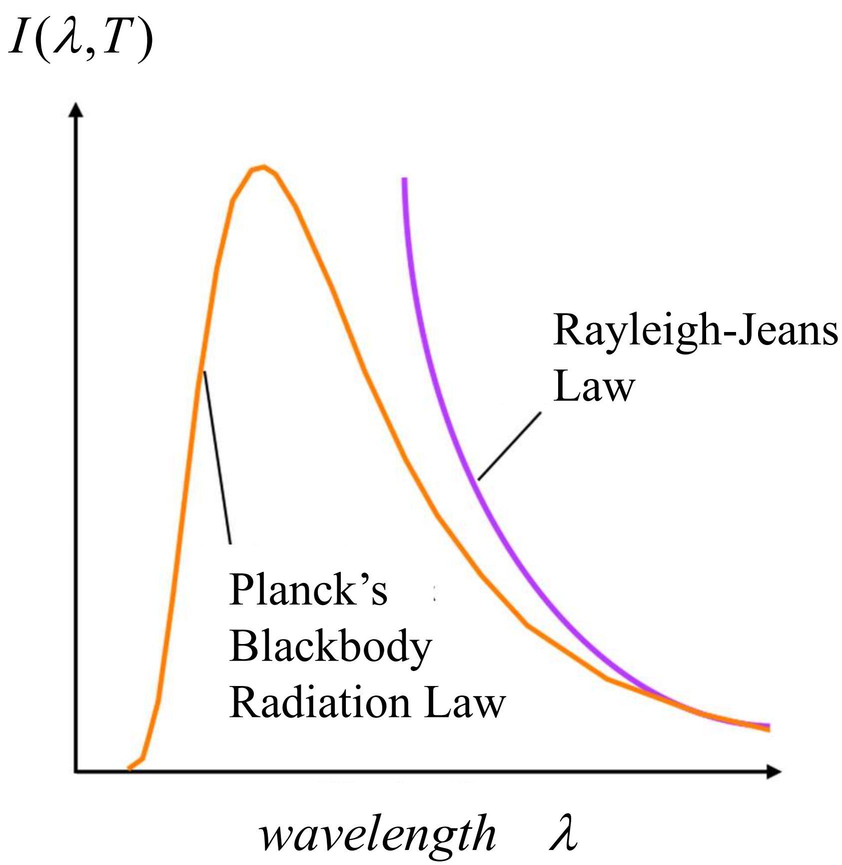
$$I(\lambda,T)=\frac{2\pi c}{\lambda^4}kT \qquad \text{(Rayleigh-Jeans Law)}$$

CORRECT QM Prediction:

$$\boxed{I(\lambda,T)=\frac{2\pi hc^2}{\lambda^5\left(e^{hc/\lambda kT}-1\right)}} \qquad \text{(Planck's Blackbody Radiation Law)}$$

Light must come in discrete quanta !

Blackbody Radiation (Review)



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Light must come in discrete quanta !

Laser

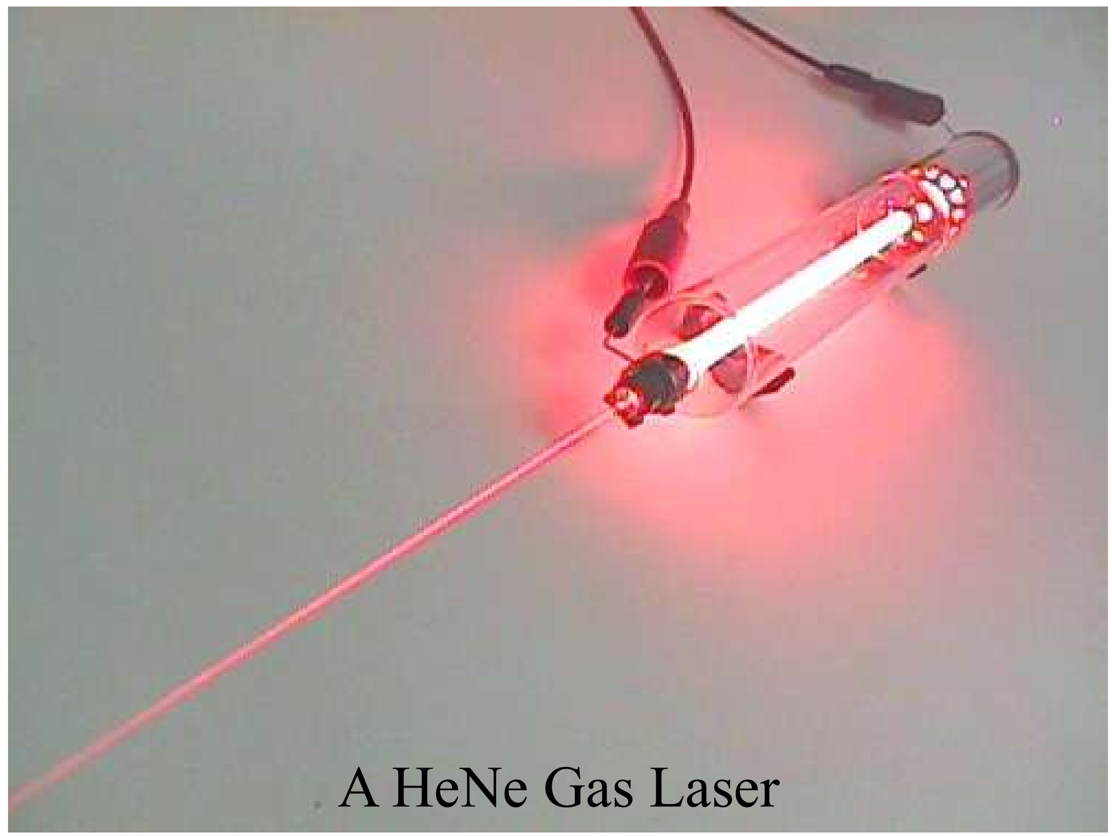
Laser = “light amplification by stimulated emission of radiation”

It is a mechanism to produce a beam of highly *coherent* and nearly monochromatic light from the *cooperative* emission from many atoms.

To understand it, need two new concepts from QM:

Stimulated Emission

Population Inversion

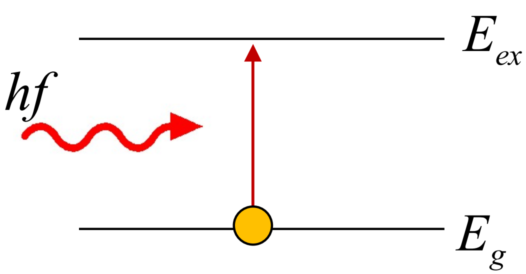


A HeNe Gas Laser

Atoms Interactions with Light

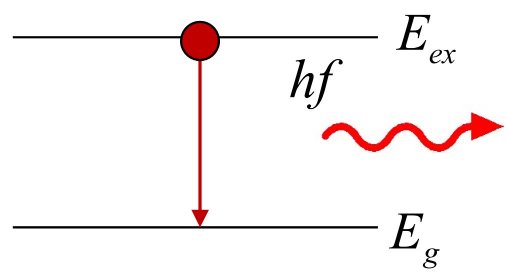
Atoms interact with light in three primary processes:

Absorption



Photons with $hf = E_{ex} - E_g$ is being absorbed by electrons in atoms at ground level E_g

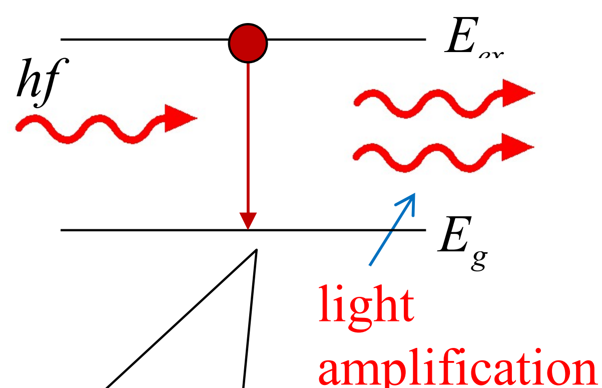
Spontaneous Emission



Electron in excited atoms at E_{ex} relax back spontaneously (randomly) to ground level E_g

→ Phase & direction of emitted photons are random !

Stimulated Emission

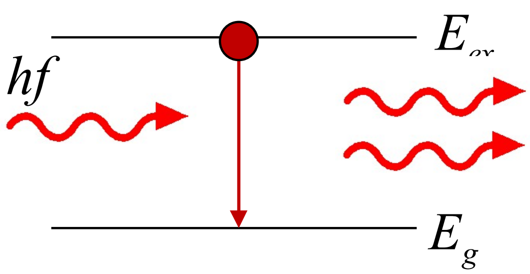


Incident photon with the same energy $hf = E_{ex} - E_g$ encounters a previously excited atom and resulted in 2 *coherent* photons being admitted.

(Processes which we have learned previously)

(New "resonance" process)

Stimulated Emission & Population of Excited Atoms



Stimulated emission needs incident photon to interact with *previously* excited atoms

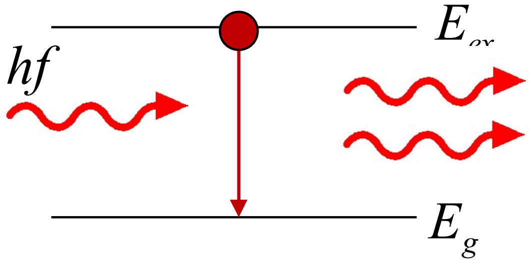
At *thermal equilibrium* at a given T, the number of atoms at a given energy state E is given by the Maxwell-Boltzman distribution (Ch. 18),

$$n(E) = Ae^{-E/kT} \qquad \text{(where } A \text{ is a normalization constant)}$$

So, if E_g is the ground state energy and E_{ex} is the energy for the excited state, the relative ratio of numbers of atoms in the two states is,

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

Stimulated Emission & Population of Excited Atoms



Stimulated emission needs incident photon to interact with *previously* **excited** atoms

But, for a typical value of $E_{ex} - E_g = 2eV$ at $T = 3000K$,

$$-\frac{E_{ex} - E_g}{kT} = -\frac{(2eV)(1.6\times10^{-19} J/eV)}{(1.38\times10^{-23} J/K)(3000K)} = -7.73$$

And, the ratio of relative population between the excited & ground states is very small,

$$e^{-(E_{ex}-E_g)/kT} = e^{-7.73} = 0.00044$$

So, at equilibrium, almost all atoms are at the ground and NOT excited state !

Making a Laser

In order to have a *sustained* stimulated emission, we need to have **more** atoms at the excited state than at the ground state in the presence of incident photons, so that

rate (stimulated emission) > rate (absorption)

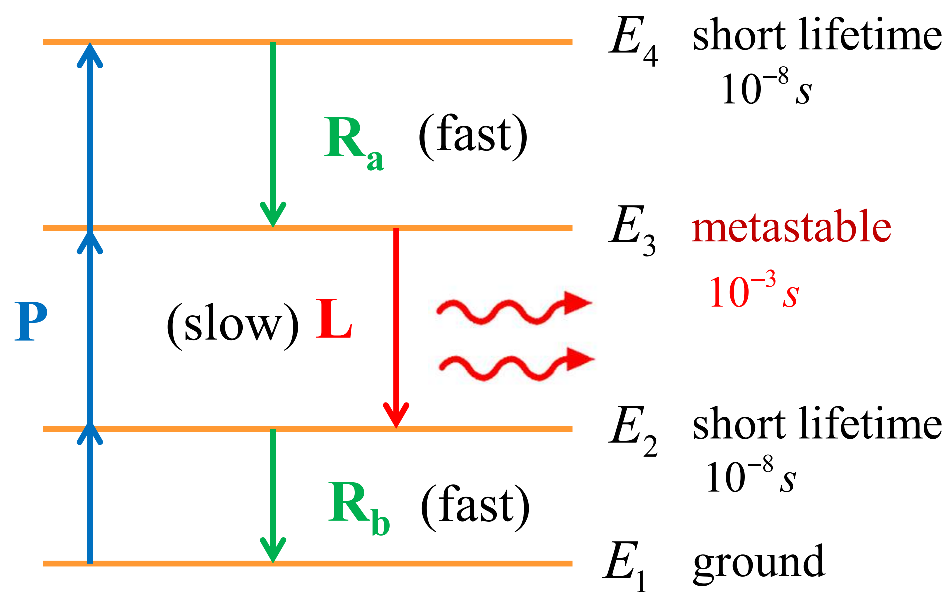
This means that we need to have an inverted ratio $\frac{n_{ex}}{n_g} > 1$. This condition is called **Population Inversion**.

However, this is a *non-equilibrium* situation and it cannot occur without an external input AND with atoms having the right kind of excited states.

Making a Laser

One such system is the *four-level laser*:

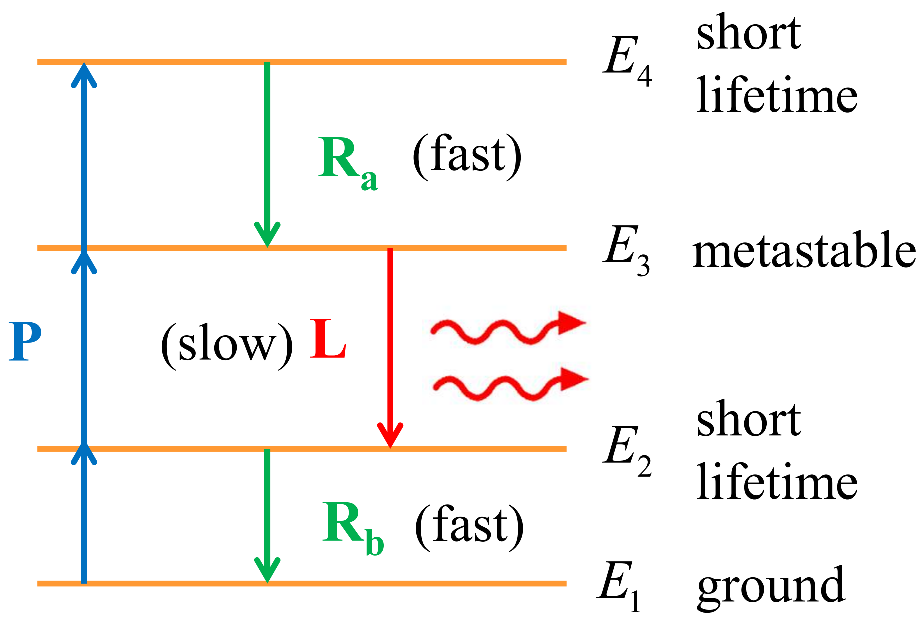
To provide the external input, the laser can be "pumped" optically, electrically, or by other means so as to excite atoms out from the ground state.



The key in the four-level laser system is the relatively long lifetime for $E_3\left(10^{-3}\,s\right)$ as compare with the other two excited states: E_2 and $E_4\left(10^{-8}\,s\right)$.

Making a Laser

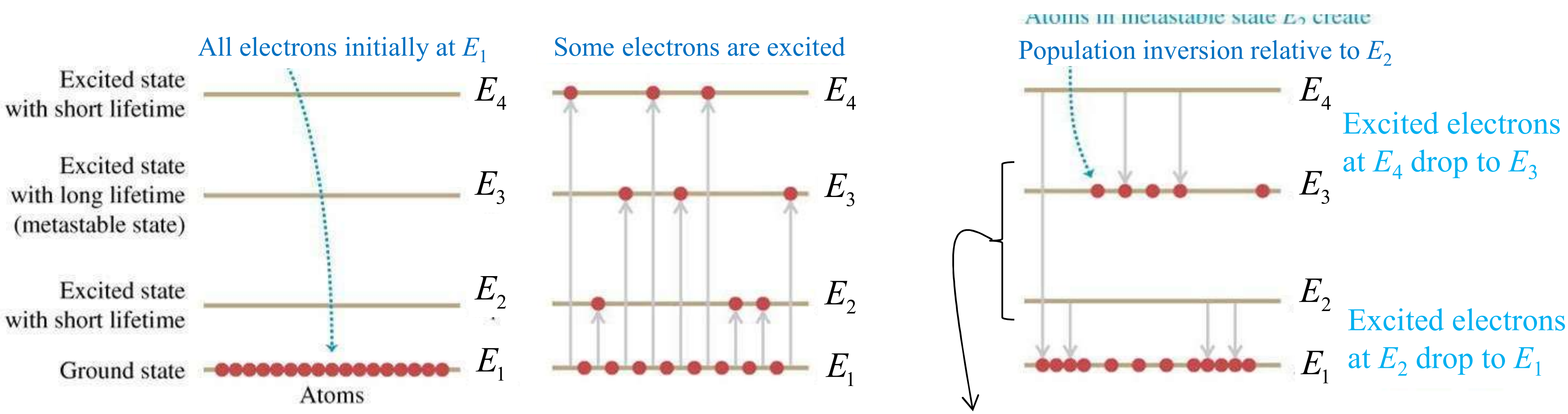
(NOTE: I am calling the ground state as E_1 and the first excited state E_2 in the standard convention while your book starts the first excited state as E_1.)



Making a Laser

The key in the four-level laser system is the relatively long lifetime for $E_3\left(10^{-3}s\right)$ as compare with the other two excited states: E_2 and $E_4\left(10^{-8}s\right)$.

Before pumping Just after pumping About $10^{-8}s \ll 10^{-3}s$ after pumping



population inverted !

Over the next $10^{-3}s$, "enhanced" stimulated emission will then produce a coherent laser beam with frequency $f=\left(E_3-E_2\right)/h$.

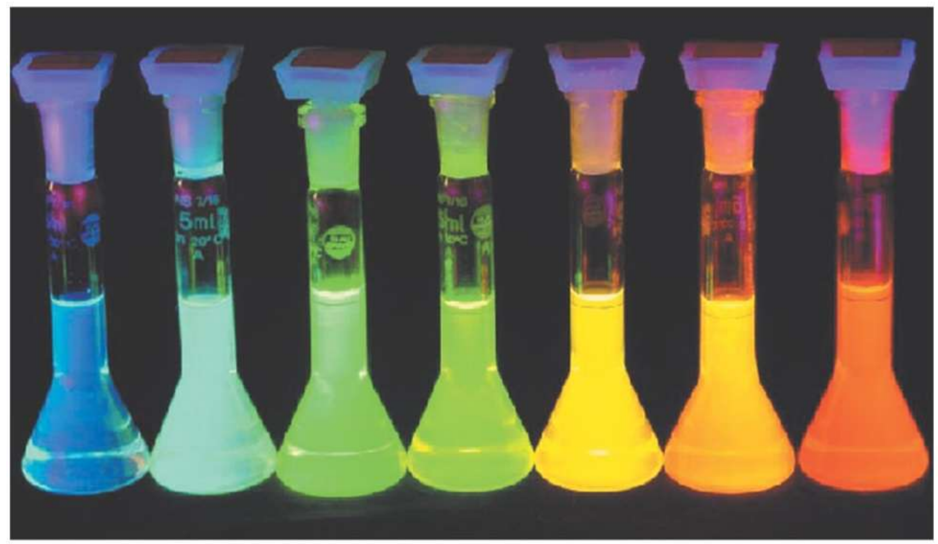
PHYS 262

George Mason University

Professor Paul So

Chapter 40/41: Quantum Mechanics

- Wave Functions & 1D Schrodinger Eq
- Particle in a Box
  - Wave function
  - Energy levels
- Potential Wells/Barriers & Tunneling
- The Harmonic Oscillator
- The H-atom

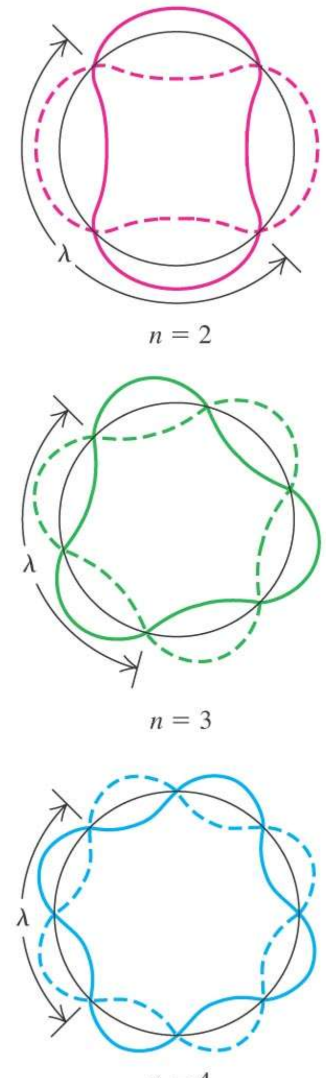


Electron Waves

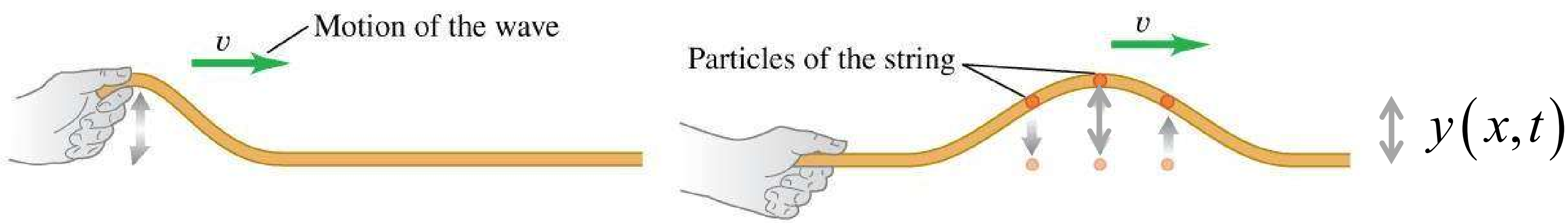
In the Bohr's model, angular momentum of the electron in a particular Bohr's orbit is **quantized**.

In the de Broglie wave hypothesis, one can imagine an electron as a **standing wave** in a given energy state *n*.

So, what is the equation which describes these matter wave?



Wave Equation for a Mechanical String



For a wave on a string (1D) moving with speed v , a wave function $y(x,t)$ must satisfy the *wave equation* (Ch. 15):

$$\frac{\partial^2 y(x,t)}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 y(x,t)}{\partial t^2}$$

It has the following sinusoidal form as its fundamental solution:

$$y(x,t) = A\cos(kx - \omega t) + B\sin(kx - \omega t)$$

where $k = 2\pi/\lambda$ is the **wave number** and $\omega = 2\pi f$ is the **angular frequency** of the wave. [*A* and *B* determines the amplitude and phase of the wave.]

Wave Equation for a String

By substituting the fundamental wave function into the PDE, we can arrive at the algebraic relation (**dispersion relation**) that ω and k must satisfy:

$$k^2 = \frac{\omega^2}{v^2} \qquad \text{or} \qquad \omega = vk$$

---

check...

1. Each *spatial* derivative of $y(x,t)$ will pull out one k:

$$\frac{\partial y(x,t)}{\partial x} = \frac{\partial}{\partial x}\left[A\cos(kx-\omega t) + B\sin(kx-\omega t)\right] = -Ak\sin(kx-\omega t) + Bk\cos(kx-\omega t)$$

So, the 2nd order spatial derivative gives,

$$\frac{\partial^2 y(x,t)}{\partial x^2} = -Ak^2\cos(kx-\omega t) - Bk^2\sin(kx-\omega t)$$

(Obviously, don't forget the signs.)

Wave Equation for a String

check...

2. Each *time* derivative of $y(x,t)$ will pull out one $-\omega$:

$$\frac{\partial y(x,t)}{\partial t}=\frac{\partial}{\partial t}\left[A\cos(kx-\omega t)+B\sin(kx-\omega t)\right]=-A(-\omega)\sin(kx-\omega t)+B(-\omega)\cos(kx-\omega t)$$

So, the 2nd order time derivative gives,

$$\frac{\partial^2 y(x,t)}{\partial t^2}=-A\omega^2\cos(kx-\omega t)-B\omega^2\sin(kx-\omega t)$$

(Again, don't forget the signs.)

Putting these back into the wave equation, we then have,

$$\frac{\partial^2 y(x,t)}{\partial x^2}=\frac{1}{v^2}\frac{\partial^2 y(x,t)}{\partial t^2} \Rightarrow \begin{aligned}&-Ak^2\cos(kx-\omega t)-Bk^2\sin(kx-\omega t)\\ &=\frac{1}{v^2}\left[-A\omega^2\cos(kx-\omega t)-B\omega^2\sin(kx-\omega t)\right]\end{aligned} \Rightarrow k^2=\frac{\omega^2}{v^2}$$

Wave Equation for a String

Putting the definitions for ω and k back into the **dispersion relation**, we have the familiar relation for wavelength, frequency, and wave speed.

$$\omega = vk \quad \Rightarrow \quad \cancel{2\pi} f = v\frac{\cancel{2\pi}}{\lambda} \quad \Rightarrow \quad v = \lambda f$$

Thus, the fundamental property of a wave $\left(v = \lambda f \text{ or } k^2 = \frac{\omega^2}{v^2} \right)$

is intimately linked to the form of the wave equation $\frac{\partial^2 y(x,t)}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 y(x,t)}{\partial t^2}$!

Now, we will try to use the same argument to find a wave equation for a quantum wave function.

Wave Equation for a Quantum Free Particle

A *free* particle has no force acting on it. Equivalently, the potential energy $U(x)$ must be a *constant* for all x, i.e., $F_x = -dU(x)/dx = 0$ or $U(x)$ is a constant.

Since the reference point for $U(x)$ is arbitrary, we can simply take $U(x) = 0$.

Then, the total energy E of a free particle will simply be its kinetic energy,

$$E = \frac{1}{2}mv^2 = \frac{m^2v^2}{2m} = \frac{p^2}{2m} \qquad \text{(non-relativistic)}$$

Now, from the de Broglie relations, the energy and momentum of this quantum free particle can be related to its wave number k and angular frequency ω through:

$$\left.\begin{aligned} E &= hf = \frac{h}{2\pi}2\pi f = \hbar\omega \\ p &= \frac{h}{\lambda} = \frac{h}{2\pi}\frac{2\pi}{\lambda} = \hbar k \end{aligned}\right\} \xrightarrow{E = \frac{p^2}{2m}} \boxed{\hbar\omega = \frac{\hbar^2 k^2}{2m}}$$

Wave Equation for a Quantum Free Particle

Thus, a correct quantum wave function for a quantum free particle must satisfy this quantum dispersion relation for k and ω :

$$\hbar\omega = \frac{\hbar^2 k^2}{2m} \qquad (*) \quad \text{(non-relativistic)}$$

We now assume the same fundamental sinusoidal form for the wave function of a quantum free particle with mass m, momentum $p = \hbar k$ and energy $E = \hbar\omega$:

$$\Psi(x,t) = A\cos(kx - \omega t) + B\sin(kx - \omega t)$$

Recall from our discussion on the mechanical wave, we have the following:

$\frac{\partial}{\partial x} \rightarrow$ take out an overall k factor from $\Psi(x,t)$

$\frac{\partial}{\partial t} \rightarrow$ take out an overall $-\omega$ factor from $\Psi(x,t)$