Chapter 5

ATOMIC PHYSICS

OBJECTIVES:

- To know about the quantum model of H-atom and its wave functions.
- To understand more about Visible and X ray spectra
- To explain basic interactions of radiation with matter.
- To understand the basic principles and requirements for working of laser.
- To recognize the various applications of laser.
- To apply and evaluate the above concepts by solving numerical problems

The potential energy function for the H-atom is

$$U(r) = -\frac{k_e e^2}{r}$$

$k_e = 8.99 \times 10^9$ N.m^2/C^2 is Coulomb constant

r = radial distance of electron from proton [H-nucleus]

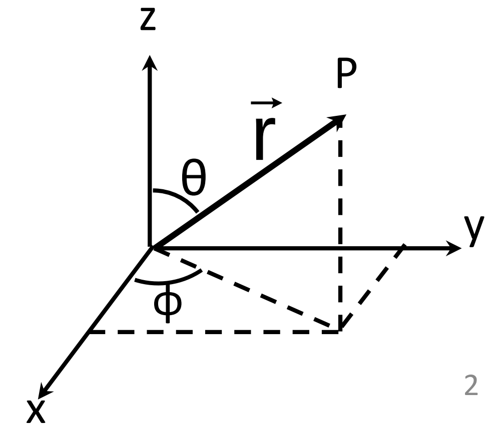
The time-independent Schrodinger equation in 3-dimensional space is

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}\right)+U\psi = E\psi$$

Since U has spherical symmetry, it is easier to solve the schrodinger equation in spherical polar coordinates (r, θ, ϕ):

where $r = \sqrt{x^2 + y^2 + z^2}$

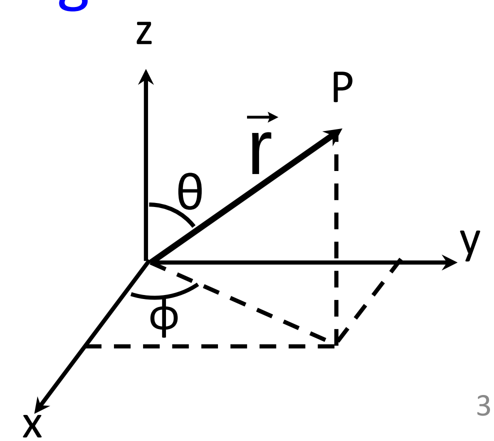
θ is the angle between z-axis and $\vec{r}$



ϕ is the angle between the x-axis and the projection of $\vec{r}$ onto the xy-plane. It is possible to separate the variables r, θ, ϕ as follows:

$$\psi(r, \theta, \phi) = R(r)\, f(\theta)\, g(\phi)$$

By solving the three separate ordinary differential equations for R(r), f(θ), g(ϕ), with conditions that the normalized ψ and its first derivative are continuous and finite everywhere, one gets three different quantum numbers for each allowed state of the H-atom. The quantum numbers are integers and correspond to the three independent degrees of freedom.



The radial function R(r) of ψ is associated with the principal quantum number n. From this theory the energies of the allowed states for the H-atom are

$$E_n = -\left(\frac{k_e e^2}{2\,a_o}\right)\frac{1}{n^2} = -\frac{13.606\,\text{eV}}{n^2}, \quad n = 1, 2, 3, \ldots$$

which is in agreement with Bohr theory.

The polar function f(θ) is associated with the orbital quantum number ℓ.

The azimuthal function g(ϕ) is associated with the orbital magnetic quantum number m_ℓ. The application of boundary conditions on the three parts of ψ leads to important relationships among the three quantum numbers.

$$\psi(r, \theta, \phi) = R(r)\, f(\theta)\, g(\phi)$$

Radial function $R(r)$ of ψ is associated with the principal quantum number n

"n value ranges from 1 to ∞"

The polar function $f(\theta)$ is associated with the orbital quantum number ℓ.

ℓ can range from 0 to (n-1) [n allowed values]

The azimuthal function $g(\phi)$ is associated with the orbital magnetic quantum number m_ℓ.

m_ℓ can range from $-\ell$ to $+\ell$; [($2\ell+1$) allowed values]

Shells and subshells

All states having the same principal quantum number are said to form a shell. All states having the same values of n and ℓ are said to form a subshell:

n = 1	$\Rightarrow$	K shell	$\ell = 0$	$\Rightarrow$	s	subshell
n = 2	$\Rightarrow$	L shell	$\ell = 1$	$\Rightarrow$	p	subshell
n = 3	$\Rightarrow$	M shell	$\ell = 2$	$\Rightarrow$	d	subshell
n = 4	$\Rightarrow$	N shell	$\ell = 3$	$\Rightarrow$	f	subshell
n = 5	$\Rightarrow$	O shell	$\ell = 4$	$\Rightarrow$	g	subshell
n = 6	$\Rightarrow$	P shell	$\ell = 5$	$\Rightarrow$	h	subshell
.. ..		.. ..	.. ..		..	..
.. ..		.. ..	.. ..		..	..

For example, state designated as 3p has principal quantum number 3 and $l = 1$.

Wave functions for hydrogen

Wave functions for hydrogen

- H-atom can be represented by wave functions that depend only on r (spherically symmetric function).
- The simplest wave function for H-atom is the 1s-state (ground state) wave function ($n = 1$, $l = 0$):

$$\psi_{1s}(r) = \frac{1}{\sqrt{\pi a_o^3}} e^{-\frac{r}{a_o}}$$

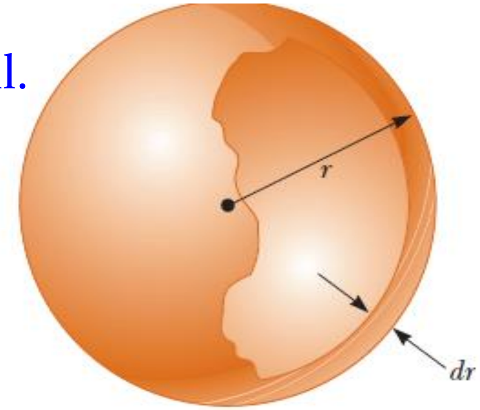
a_o = Bohr radius.

$$|\psi_{1s}|^2 = \left(\frac{1}{\pi a_o^3}\right) e^{-\frac{2r}{a_o}}$$

$|\psi_{1s}|^2$ is the probability density for H-atom in 1s-state.

The radial probability density P(r) is the probability per unit radial length of finding the electron in a spherical shell of radius r and thickness dr.

P(r) dr is the probability of finding the electron in this shell.

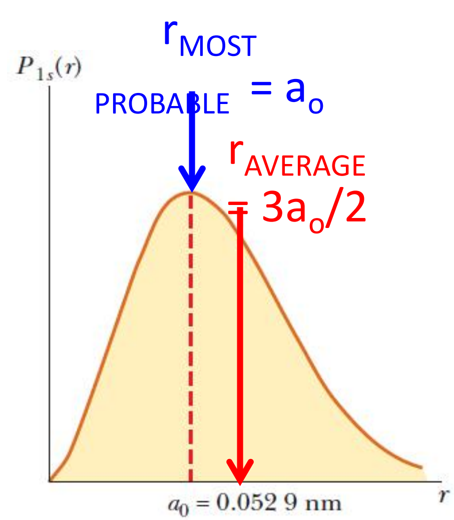


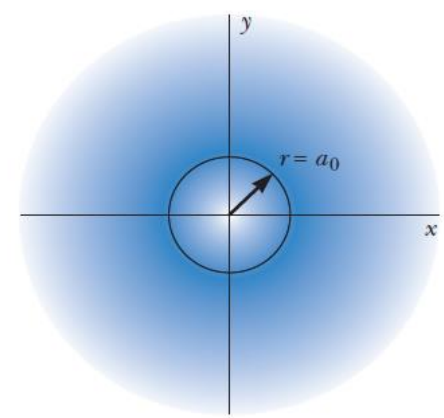
$$P(r)\,dr = |\psi|^2\,dv = |\psi|^2\,4\pi r^2\,dr$$

$$\therefore \quad P(r) = 4\pi r^2\,|\psi|^2$$

Radial probability density for H-atom in its ground state:

$$P_{1s}(r) = \left(\frac{4r^2}{a_o^3}\right) e^{-\frac{2r}{a_o}}$$

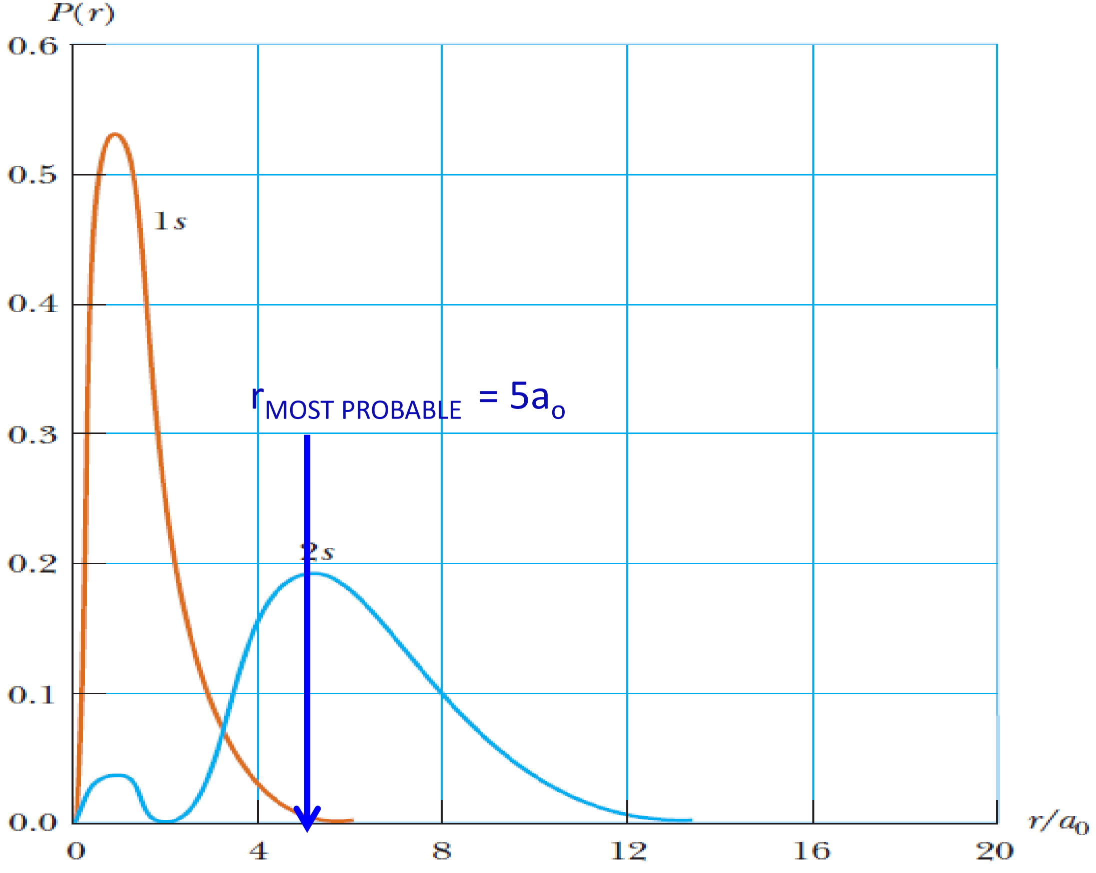




$P_{1s}(r)$ is maximum when

$r = a_o$ (Bohr radius).

$$\psi_{2s}(r) = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_o}\right)^{\frac{3}{2}}\left(2-\frac{r}{a_o}\right)e^{-\frac{r}{a_o}}$$



ψ_{2s} is spherically symmetric (depends only on r)

$E_2 = E_1/4 = -3.401$ eV (1^{ST} excited state)

SJ-Example-42.4

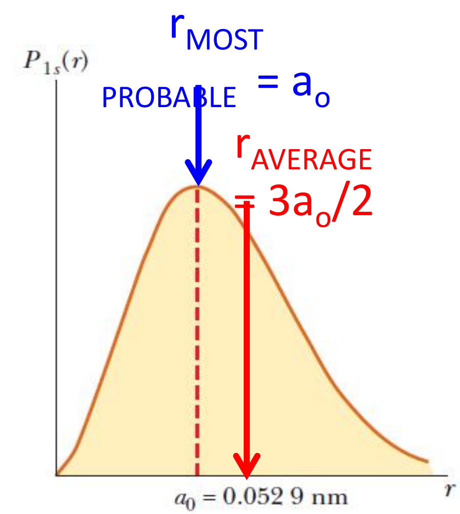
Calculate the most probable value of r (= distance from nucleus) for an electron in the ground state of the H-atom. Also calculate the average value r for the electron in the ground state.

Given : $\int_0^\infty r^3 e^{-\frac{2r}{a_0}} dr = \left(\frac{3!}{\left(\frac{2}{a_0}\right)^4}\right)$

$$P_{1s}(r) = \left(\frac{4r^2}{a_o^3}\right) e^{-\frac{2r}{a_o}}$$

Ans: Most probable value of $r = a_o$

average value $r = \frac{3}{2} a_0$



Most probable value of r corresponds to the peak of the plot of $P_{1s}(r)$ versus r. Because the slope of the curve at this point is zero, we can evaluate the most probable value of r by setting $dP_{1s}/dr = 0$

$$\frac{dP_{1s}}{dr} = \frac{d}{dr}\left[\left(\frac{4r^2}{a^3{}_0}\right) e^{-2r/a_0}\right] = 0$$

$$e^{-2r/a_0}\frac{d}{dr}(\mathbf{r}^2) + r^2 \frac{d}{dr}(e^{-2r/a_0}) = 0$$

$$2re^{-2r/a_0} + r^2 \left(-\frac{2}{\text{ao}}\right) (e^{-2r/a_0}) = 0$$

$$2r[1 - (\frac{r}{a_0})]e^{-2r/a_0} = 0$$

This expression is satisfied if $1- r/a_0 = 0$ ➔ $r = a_0$

Most probable value of r is the Bohr radius.

The average value of r is the same as expectation value for r.

Therefore, r_{av} = <r> = $\int_0^\infty rP(r)dr = \int_0^\infty r\left[\left(\frac{4r^2}{a^3{}_0}\right)e^{-\frac{2r}{a_0}}\right]dr$

$$= \frac{4}{a_0{}^3}\int_0^\infty r^3 e^{-\frac{2r}{a_0}}dr$$

$$\frac{4}{a_0{}^3}\left(\frac{3!}{\left(\frac{2}{a_0}\right)^4}\right) = \frac{3}{2}a_0$$

SJ-Example-42.5

Calculate the probability that the electron in the ground state of H-atom will be found **outside the Bohr radius**.

$$P_{1s}(r) = \left(\frac{4r^2}{a_o^3}\right) e^{-\frac{2r}{a_o}}$$

Integration by parts

$$\int_a^b f(z)g(z)dz = f(z)\int_a^b g(z).dz - \int_a^b \left(\int g(z)dz\right).f'(z)dz$$

Integration by parts

$$\int_{a}^{b} \boldsymbol{f(z)g(z)dz} = \boldsymbol{f(z)} \int_{a}^{b} \boldsymbol{g(z).\,dz} - \int_{a}^{b} \left(\int \boldsymbol{g(z)dz} \right) \boldsymbol{.\,f'(z)dz}$$

The probability is found by integrating the radial probability density function $P_{1s}(r)$ for this state from the Bohr radius a_0 to infinity.

$$P = \int_{a_0}^{\infty} P_{1s}(r)dr = \frac{4}{{a_0}^3}\int_{a_0}^{\infty} r^2 e^{-2r/a_0} dr$$

We can put the integral in dimensionless form by changing the variables from r to $z=2r/a_o$.

Noting that z=2 when r = a_o and that dr = $(a_o/2)dz$

$$P = \frac{1}{2}\int_{2}^{\infty} z^2 e^{-z} dz = -\frac{1}{2}(z^2 + 2z + 2)e^{-z}\Big|_{2}^{\infty}$$

(By partial Integration)

P = $5e^{-2}$ = 0.677 or 67.7%

$$P = +\frac{1}{2}\int_{2}^{\infty} (z^2 e^{-z})\, dz$$

using integration by parts

$$\int_{2}^{\infty} z^2 e^{-z}\, dz = z^2 \int_{2}^{\infty} e^{-z}\, dz - \int_{2}^{\infty} \left(\left(\int_{2}^{\infty} e^{-z}\, dz\right) (2z) \right) dz$$

$$= -z^2 e^{-z} - 2\int \left(-e^{-z}\right) z\, dz$$

$$= -z^2 e^{-z} + 2\left[-z e^{-z} + \int e^{-z}\, dz \right]$$

$$= -z^2 e^{-z} - 2z e^{-z} - 2e^{-z} \Big|_{z=2}^{z=\infty}$$

$$P = -\frac{1}{2}\left(z^2 + 2z + 2\right) e^{-z} \Big|_{z=2}^{z=\infty} = 5e^{-2} = \underline{67.7\%}$$

The ground-state wave function for the electron in a hydrogen atom is

$$\psi_{1s}(r) = \frac{1}{\sqrt{\pi a_o^3}} e^{-\frac{r}{a_o}}$$

where *r* is the radial coordinate of the electron and a_0 is the Bohr radius. (a) Show that the wave function as given is normalized. (b) Find the probability of locating the electron between $r_1 = a_0/2$ and $r_2 = 3a_0/2$.

$$\int_a^b f(z)g(z)dz = f(z)\int_a^b g(z).dz - \int_a^b \left(\int g(z)dz\right).f'(z)dz$$

Ans (a) 1 (b) 0.497

a)

Normalization condition is :

$$\int_0^\infty |\psi|^2 dV = \int_0^\infty |\psi|^2 4\pi r^2 dr$$

where $|\psi| = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$

$$\therefore \int_0^\infty |\psi|^2 dV = \frac{4\pi}{\pi a_0^3} \int_0^\infty r^2 e^{-2r/a_0} dr$$

$$= \frac{4}{a_0^3} \int_0^\infty r^2 e^{-2r/a_0} dr$$

Put $\frac{2r}{a_0} = z$, we get

$$\int_0^\infty |\psi|^2 dV = \frac{1}{2} \int_0^\infty e^{-z} z^2 dz$$

$$= -\frac{1}{2} \left[z^2 + 2z + 2 \right] e^{-z} \Big|_{z=0}^{z=\infty}$$ Integration by parts

$$= 0 - \frac{1}{2}(-2) = \underline{\underline{1}}$$

$$\therefore \int_0^\infty |\psi|^2 dV = 1$$

b)

$$r_1 = \frac{a_0}{2} \Rightarrow z_1 = \frac{2r_1}{a_0} = \frac{2\left(\frac{a_0}{2}\right)}{a_0} = 1$$

$$r_1 = \frac{3a_0}{2} \Rightarrow z_2 = \frac{2\left(\frac{3a_0}{2}\right)}{2} = 3$$

$$\therefore P = -\frac{1}{2}\left[z^2 + 2z + 2\right] e^{-z} \Big|_{z=1}^{z=3}$$

$$= -\frac{1}{2}\left[17 e^{-3} - 5 e^{-1}\right] = \underline{0.497}$$

Atomic Spectra: Visible and X-Ray

Atomic Spectra: Visible and X-Ray

- The frequency of this photon is $f = \Delta E/h$
- The **selection rules** for the *allowed transitions* are

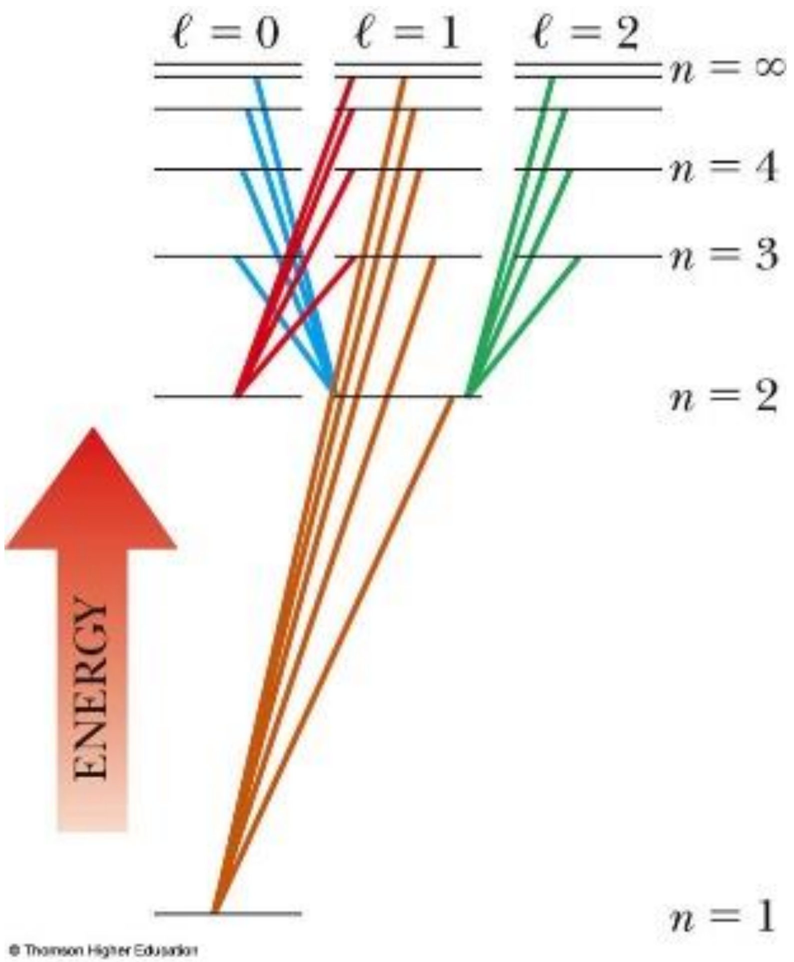
$$\Delta\ell = \pm 1 \quad \text{and} \quad \Delta m_\ell = 0, \pm 1$$

- The allowed energies for one-electron atoms and ions, such as hydrogen and He, are

$$E_n = -\frac{k_e e^2}{2a_0}\left(\frac{Z^2}{n^2}\right) = -\frac{(13.6\ \text{eV})Z^2}{n^2}$$

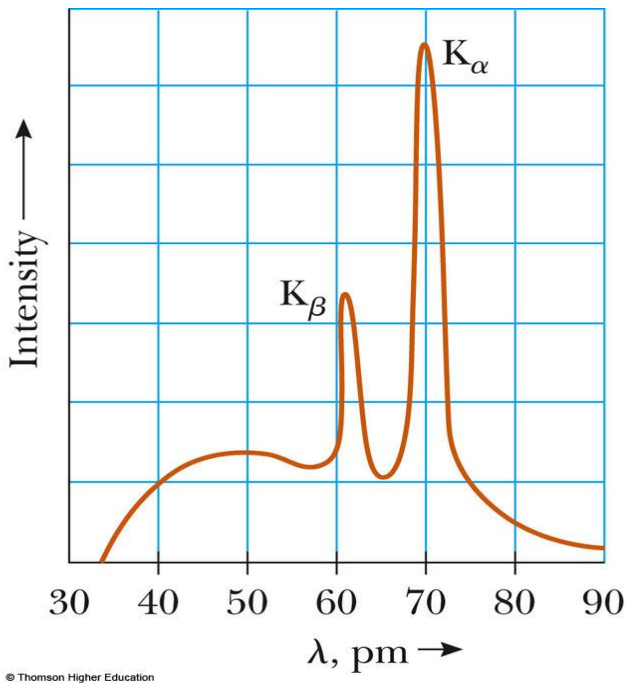
- For multi-electron atoms, the positive nuclear charge *Ze* is largely shielded by the negative charge of the inner-shell electrons.

$$E_n = -\frac{(13.6\ \text{eV})Z_{\text{eff}}^2}{n^2}$$



Some allowed electronic transitions for hydrogen, represented by the colored lines

X-Ray Spectra



The x-ray spectrum of a metal target. The data shown were obtained when 37-keV electrons bombarded a molybdenum target.

X-ray spectrum has two parts:

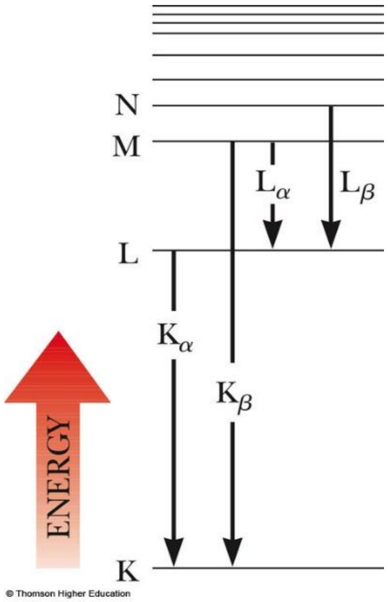
Continuous spectrum

Characteristic spectrum

The continuous curve represents *bremsstrahlung*. ***The shortest wavelength depends on the accelerating voltage***

$$e\Delta V = hf_{MAX} = \frac{hc}{\lambda_{MIN}}$$

$$hf = \frac{hc}{\lambda} = E_{ni} - E_{nf}$$

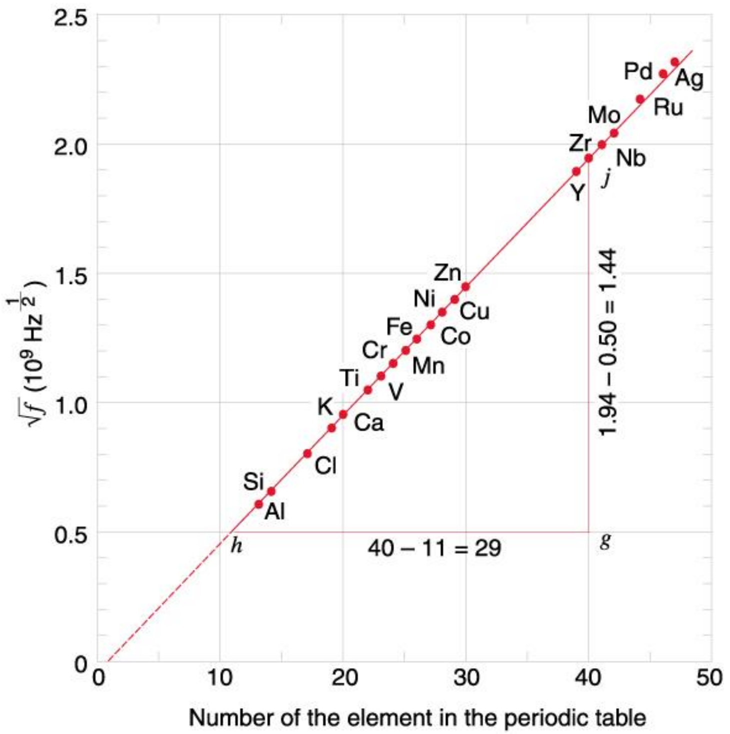


Moseley's observation on the characteristic K_α x-rays shows a relation between the frequency (f) of the Kα x-rays and the atomic number (Z) of the target element in the x-ray tube:

$$\sqrt{f} = C\left(Z-1\right)$$

C is a constant.

Note: Based on this observation, the elements are arranged according to their atomic numbers in the periodic table



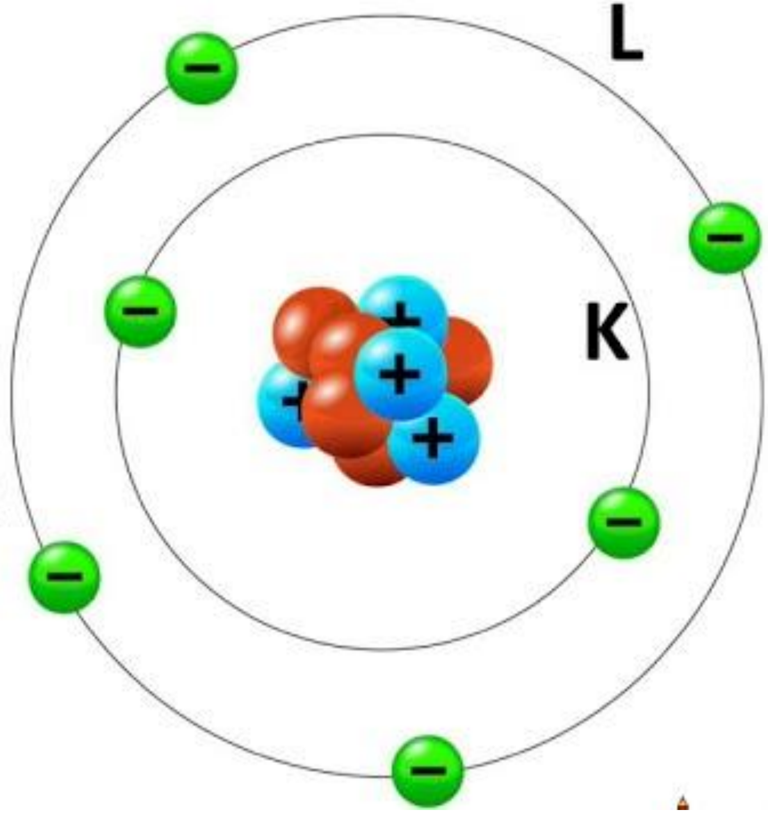
Maximum no. of electrons in each shell = $2n^2$

$K \rightarrow 2 \times 1^2 = 2$

$L \rightarrow 2 \times 2^2 = 8$

$M \rightarrow 2 \times 3^2 = 18$

$N \rightarrow 2 \times 4^2 = 32$



Q: A bismuth target is struck by electrons, and x-rays are emitted. Estimate (a) the M- to L-shell transitional energy for bismuth and (b) the wavelength of the x-ray emitted when an electron falls from the M shell to the L shell. For bismuth, *Z* = 83

Ans:

For bismuth, $Z = 83$. The electron in the M shell ($n = 3$) is shielded from the nuclear charge by **two electrons** in the K shell ($n = 1$) and **seven electrons** in the L shell ($n = 2$).

Its energy is,
$$E_{\mathrm{M}} \approx -(Z-9)^2 \frac{13.6\ \mathrm{eV}}{(3)^2} = -13.6\ \mathrm{eV} \frac{(74)^2}{(3)^2}$$

The electrons in the L shell ($n = 2$) are shielded from the nuclear charge by two electrons in the K shell.

So,
$$E_{\mathrm{L}} \approx -(Z-2)^2 \frac{13.6\ \mathrm{eV}}{(2)^2} = -13.6\ \mathrm{eV} \frac{(81)^2}{(2)^2}$$

When the electron drops from the M to the L shell of the atom, it emits a photon of energy,

$$E_{\text{photon}} = E_{\text{M}} - E_{\text{L}} \approx 13.6\ \text{eV}\left[-\frac{(74)^2}{(3)^2} + \frac{(81)^2}{(2)^2}\right]$$

$= 1.403 \times 10^4$ eV $\approx$ 14 keV

b) $E_{photon} = hc / \lambda$

$\lambda = 1240$ eV. nm / $(14 \times 10^3$ eV$)$

$= 0.0885$ nm $=$ 0.885 Å

P 12: When an electron drops from the M shell (n = 3) to a vacancy in the K shell (n = 1), the measured wavelength of the emitted x-ray is found to be 0.101 nm. Identify the element.

Ans:

An electron makes a transition from the M to the K shell. When the electron is in the K shell, its energy is,

$$E_K \approx -Z^2 (13.6 \text{ eV})$$

When the electron was in the M shell, because nine electrons shield the nuclear charge—one in the K shell (n = 1) and eight in the L shell (n = 2)—its energy is,

$$E_M \approx -(Z-9)^2 \frac{13.6 \text{ eV}}{(3)^2}$$

Thus, as the electron drops from the M to the K shell, it emits a photon of energy,

$$E_{\text{photon}} = E_M - E_K \approx (13.6 \text{ eV})\left[-\frac{(Z-9)^2}{9} + Z^2\right]$$

$$= (13.6 \text{ eV})\left[-\left(\frac{Z^2 - 18Z + 81}{9}\right) + Z^2\right]$$

$$= (13.6 \text{ eV})\left(\frac{8}{9}Z^2 + 2Z - 9\right) = \frac{hc}{\lambda}$$

i.e.,
$$\frac{8}{9}Z^2 + 2Z - 9 = \frac{hc}{(13.6 \text{ eV})\lambda} = \frac{(1\,240 \text{ eV}\cdot\text{nm})}{(13.6 \text{ eV})(0.101 \text{ nm})} = 902.7$$

$$\frac{8}{9}Z^2 + 2Z - 911.7 = 0$$

$$Z = \frac{-(2) \pm \sqrt{(2)^2 - 4(8/9)(-911.7)}}{2(8/9)} = \frac{-1 \pm \sqrt{1 + (8/9)(911.7)}}{(8/9)} = \frac{-1 \pm 28.5}{(8/9)}$$

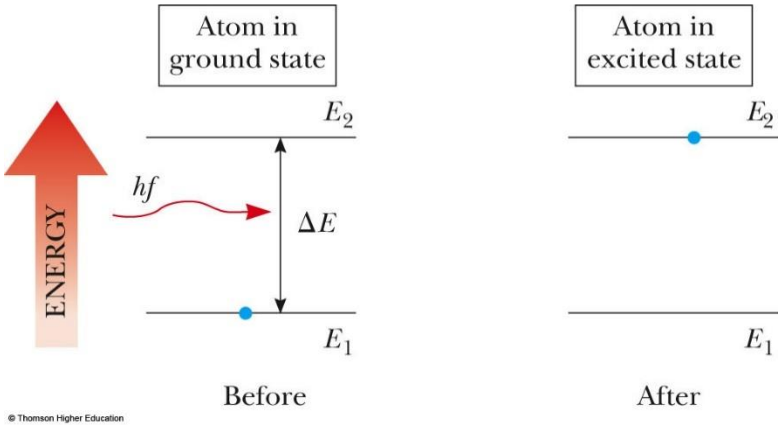
The positive solution is physical: $Z = \dfrac{-1 + 28.5}{(8/9)} = 30.9$

The nearest whole number for *Z* is 31, which corresponds to the Element gallium.

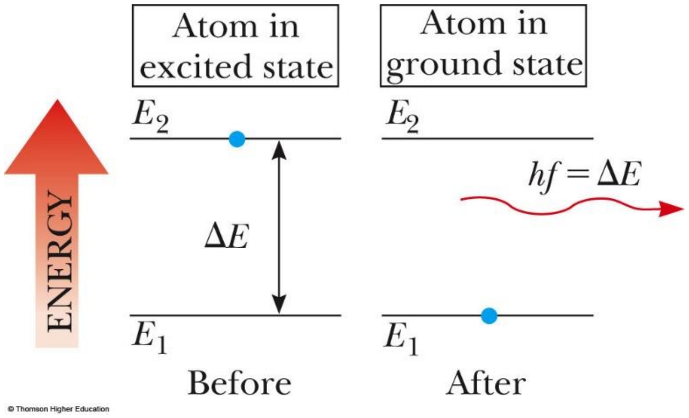
Spontaneous and Stimulated transitions

Spontaneous and Stimulated transitions

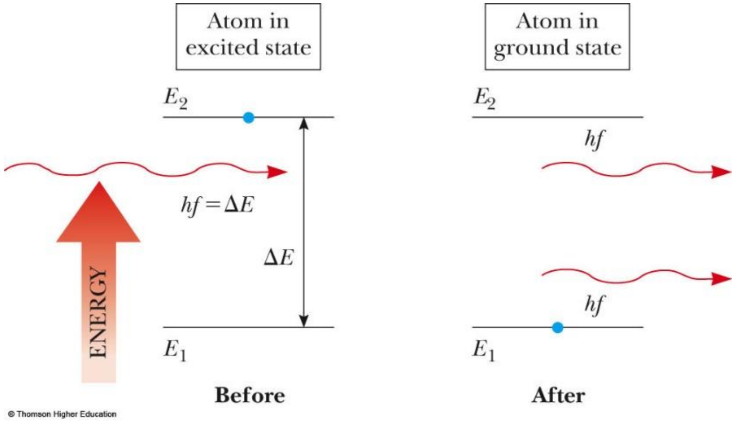
Stimulated Absorption:



Spontaneous Emission:



Stimulated Emission:



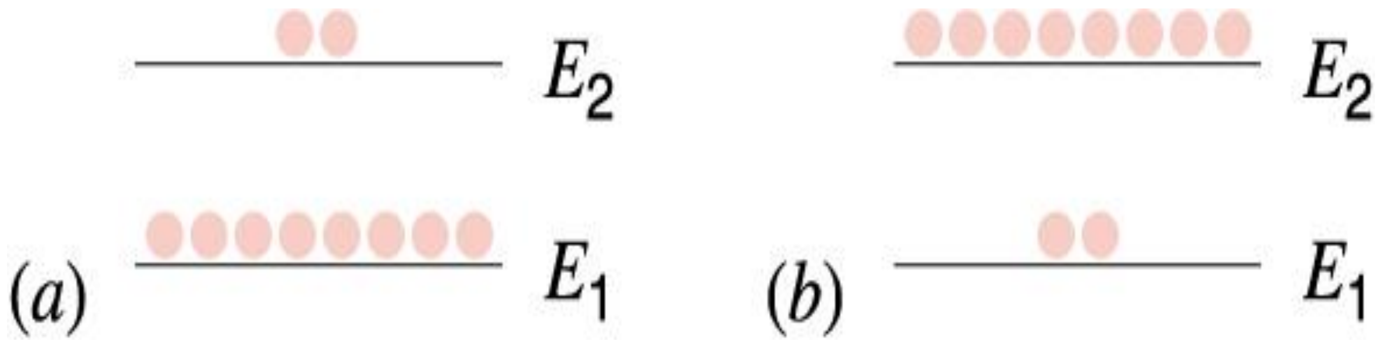
Boltzmann statistics gives the population of atoms in various energy states at temperature T.

$$\frac{n(E_2)}{n(E_1)} = \exp\left(-\frac{E_2 - E_1}{k\,T}\right)$$

$n(E_2) < n(E_1)$ if $E_2 > E_1$. This is the normal condition in which the population of the atoms in upper energy state is less than that in lower energy state

The condition where $n(E_2) > n(E_1)$ is called population inversion

Population inversion:



The condition where n(E_2) > n(E_1) is called population inversion

LASER

(Light Amplification by Stimulated Emission of Radiation)

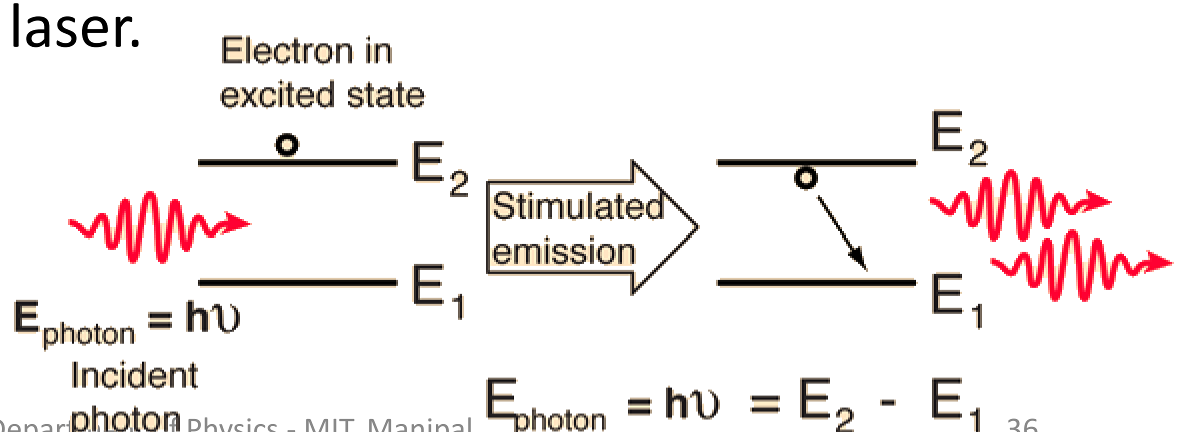
Essential conditions:

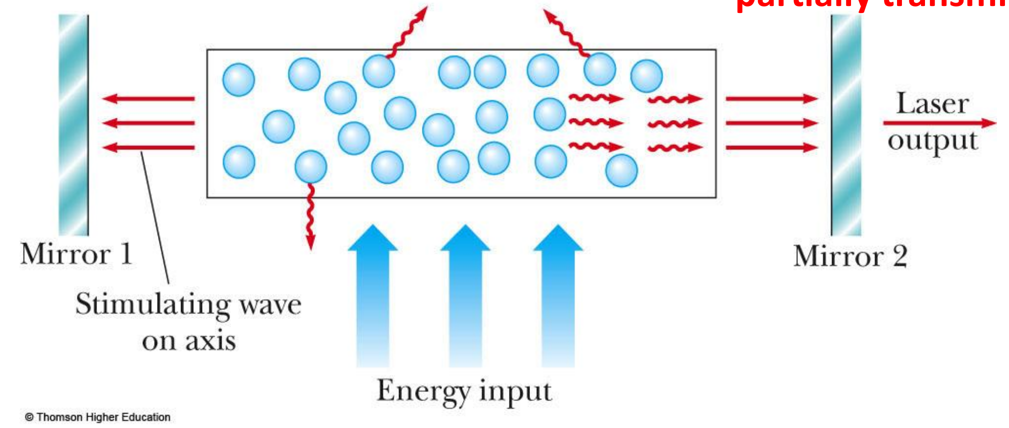
Population inversion: The number of photons emitted must be greater than the number absorbed. This can be achieved by population inversion.

Metastable states: The average life time of the atom is **10^{-3} s** which is much longer than that of the ordinary excited state (**$\approx 10^{-8}$s**). In this case, the population inversion can be established and stimulated emission is likely to occur before spontaneous emission.

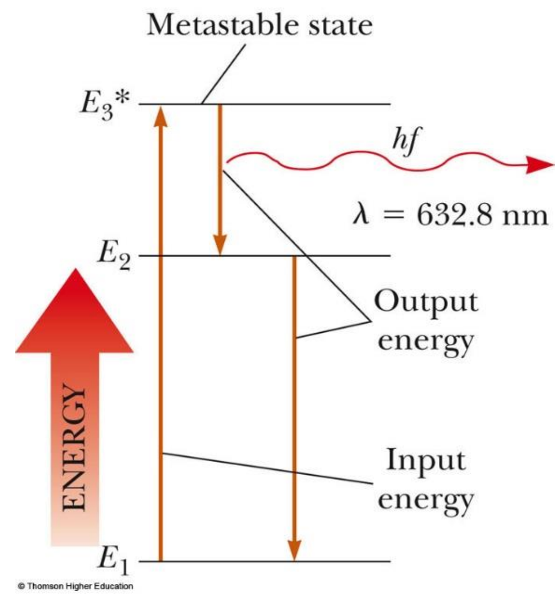
The **emitted photons must be confined** in the system long enough to enable them to stimulate further emission from other excited atoms. That is achieved by using **reflecting mirrors** at the ends of the system.

Suppose an atom is in the excited state E_2 as in the below figure and a photon with energy $hf = E_2 - E_1$ is incident on it.
The incoming photon can stimulate the excited atom to return to the ground state and thereby emit a second photon having the same energy *hf* and traveling in the same direction.
The incident photon is not absorbed, so after the stimulated emission, there are two identical photons: the incident photon and the emitted photon.
The emitted photon is in phase with the incident photon. These photons can stimulate other atoms to emit photons in a chain of similar processes.
The many photons produced in this fashion are the source of the intense, coherent light in a laser.





Schematic diagram of a laser design.



Energy-level diagram for a neon atom in a helium–neon laser.

- Lasing medium (active medium), resonant cavity and pumping system are the essential parts of any lasing system.
- Lasing medium has atomic systems (active centers), with special energy levels which are suitable for laser action. This medium may be a gas, or a liquid, or a crystal or a semiconductor.
- The atomic systems may have energy levels including a ground state (E_1), an excited state (E_2) and a metastable state (E_3^*).
- The resonant cavity is a pair of parallel mirrors to reflect the radiation back into the lasing medium.
- Pumping is a process of exciting more number of atoms in the ground state to higher energy states, which is required for attaining the population inversion.

- In He-Ne laser, the mixture of helium and neon is confined to a glass tube that is sealed at the ends by mirrors.
- A voltage applied across the tube causes electrons to sweep through the tube, colliding with the atoms of the gases and raising them into excited states.
- Neon atoms are excited to state E_3* through this process (the asterisk indicates a metastable state) and also as a result of collisions with excited helium atoms.
- Stimulated emission occurs, causing neon atoms to make transitions to state E_2.
- Neighboring excited atoms are also stimulated. The result is the production of coherent light at a wavelength of **632.8 nm**.

Applications of laser

- In investigating the basic laws of interaction of atoms and molecules with electromagnetic wave of high intensity.
- Laser is widely used in engineering applications like optical communication, micro-welding and sealing etc.
- In medical field: Bloodless and painless surgery, treating dental decay, tooth extraction, cosmetic surgery.

Any questions??????

A ruby laser delivers a 10.0-ns pulse of 1.00-MW average power. If the photons have a wavelength of 694.3 nm, how many are contained in the pulse?

3.49×10^{16} photons

Power $P = \dfrac{nhf}{t} = \dfrac{nhc}{t\lambda}$

$$n = \frac{P.t.\lambda}{hc} = \frac{1.0\times10^{6}\times10\times10^{-9}\times694.3\times10^{-9}}{6.63\times10^{-34}\times3\times10^{8}}$$

$$= \underline{3.49\times10^{16}} \text{ photons}$$