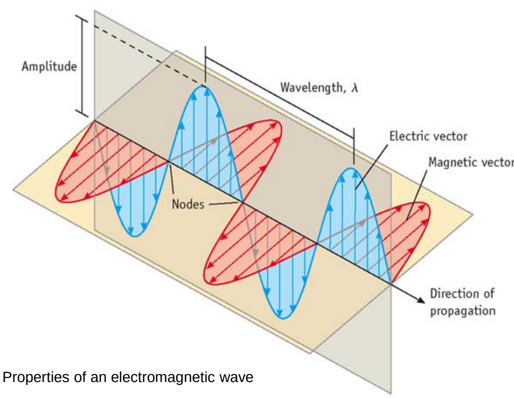
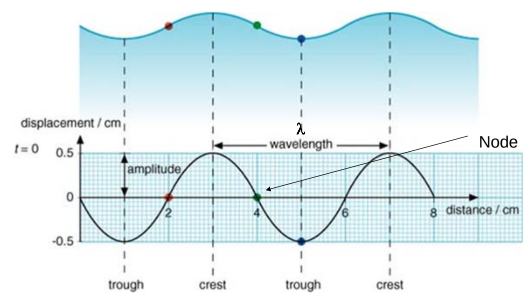
Atomic Structure

Topics:



Properties of an electromagnetic wave

General Transverse Wave Properties



Speed of light ($m \cdot s^{-1}$)

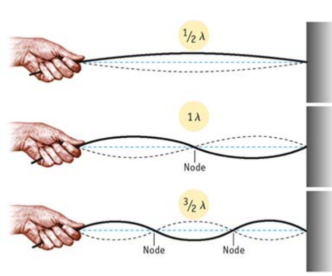
2.99792458x10⁸ m/s

$$c = \lambda \times \nu$$

Wavelength (m) Frequency (s^{-1})

(or Hz or 1/s)

Standing Waves



- Two or more points of zero amplitude
- Distance between consecutive nodes = λ/2
- Standing waves must have a distance between fixed ends = n(λ /2), where n is an integer.

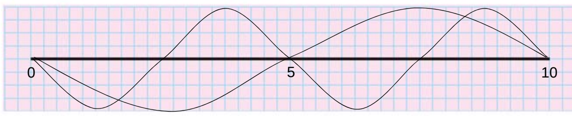
Example Problem (7.1):

The line shown here is 10cm long:

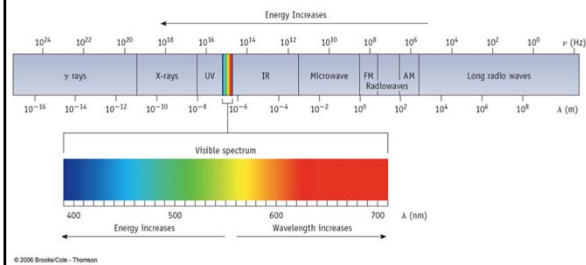
a) Draw a standing wave with one node between the ends. What is the wavelength of this wave?

b) Draw a standing wave with three evenly spaced nodes between the ends. What is its wavelength?

c) If the wavelength of the standing wave is 2.5cm, how many waves fit within the boundaries? How many nodes are there between the ends?



a) 10cm b) 5cm c) 10/2.5 = 4 waves; 7 nodes



Electromagnetic radiation is self-propagating (i.e. it doesn't require a medium to travel through. It can travel through the vacuum of space.)

Example Problem (7.2):

a) Which color in the visible spectrum (ROY-G-BIV) has the highest frequency? Which has the lowest frequency?

b) Is the frequency of the radiation used in a microwave oven higher or lower than that from a FM radio station broadcasting at 91.7MHz?

c) Is the wavelength of x-rays longer or shorter than that of ultraviolet light?

Answers:

a) Blue/violet has the highest frequency. Red has the lowest frequency (longest wavelength).

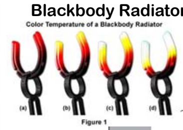
b) Microwaves are higher in frequency (shorter wavelength) than FM station 91.7MHz.

c) X-ray wavelengths are shorter (higher frequency) than that of UV light.

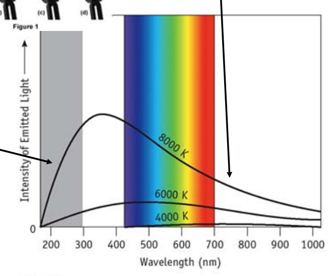
http://amazing-space.stsci.edu/resources/explorations/light/index.html

http://phet.colorado.edu/sims/blackbody-spectrum/blackbody-spectrum_en.html

Blackbody Radiator

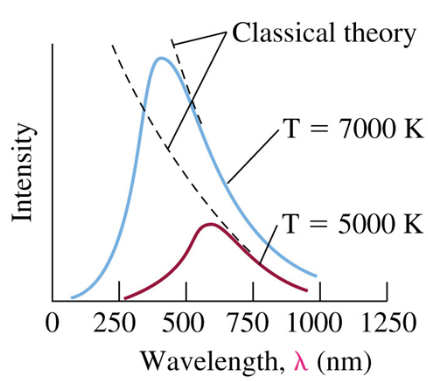


Blackbody Curves



This is where the ultraviolet catastrophe occurred.

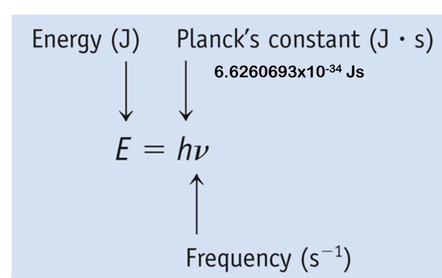
Traditional Theories: Intensity of radiation should increase continuously with decreasing wavelength



Classical theory (dotted lines) based on the Raleigh-Jeans Law, which caused the ultraviolet catastrophe.

The "Planck" curves are given in red and blue and result from the quantized energy nature of light.

Max Planck (1900): Vibrations in atoms are *quantized* (i.e. Only certain vibrations with certain frequencies are allowed)

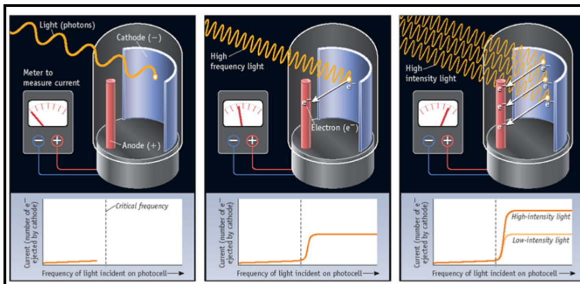


The Photoelectric Effect

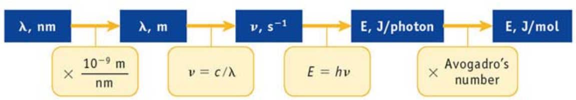
Assumption: Energy is carried on the amplitude of a wave (as in classical waves).

Prediction: Since the amplitude of an EM wave correlates with the brightness of the light, light of high enough intensity irradiating a metal for a long enough period of time should be able to eject electrons from the surface of a metal.

Reality: It was the frequency of the light that determined whether or not electrons were ejected regardless of the time of irradiation. The brightness (amplitude) only determined how many were ejected per unit time once ejection started occurring.



Einstein (1905) incorporated Planck's equation with the idea that light had (massless) particle properties (photon). These photons are "packets" of energy where E depends on the frequency of the photon ($E = h\nu$).



As frequency (ν) increases, energy (E) increases

$$E = h\nu = \frac{hc}{\lambda}$$

As wavelength (λ) decreases, energy (E) increases

Example: A 60W, monochromatic laser beam gives off photons of wavelength 650nm. How long does it take for 2.5moles of these photons to be given off?

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Answer:

$E = hc/\lambda = (6.626\times10^{-34}Js)(3.0\times10^{8}m/s)/6.50\times10^{-7}m$

$= 3.06\times10^{-19}J/photon$

$(3.06\times10^{-19}J/photon)(6.022\times10^{23}photons/mol)(2.5mol) =$

$4.60\times10^{5}J$

$4.60\times10^{5}J$ / (60J/s) = 7673.4s /(3600s/1hr) = 2.13h

Example Problem (7.3):

Compare the energy of a mole of photons of orange light (625nm) with the energy of a mole of photons of microwave radiation having a frequency of 2.45GHz (1GHz = $10^{9}s^{-1}$). Which has the greater energy? By what factor is one greater than the other?

Example Problem (7.3):

Compare the energy of a mole of photons of orange light (625nm) with the energy of a mole of photons of microwave radiation having a frequency of 2.45GHz (1GHz = $10^9 s^{-1}$). Which has the greater energy? By what factor is one greater than the other?

Answer:

E = $(6.626\times10^{-34}Js)(3.00\times10^8 m/s)/(6.25\times10^{-7}m) = 3.18\times10^{-19}J$

$3.18\times10^{-19}J(6.022\times10^{23}) = 1.92\times10^5 J/mol$

E = $(6.626\times10^{-34}Js)(2.45\times10^9 Hz) = 1.623\times10^{-24}J$

$1.623\times10^{-24}(6.022\times10^{23}) = 9.78\times10^{-1} J/mol$

$1.9\times10^5 / 9.7\times10^{-1} = 1.96\times10^5$

Amplitude

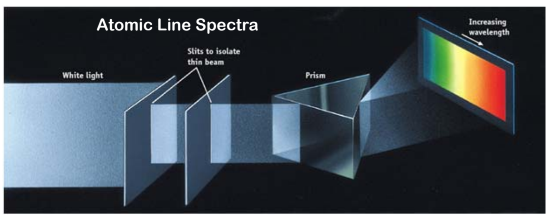
Brightness

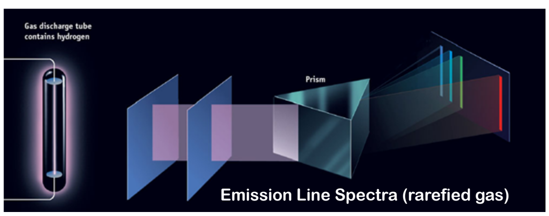
Number of photons emitted per unit time

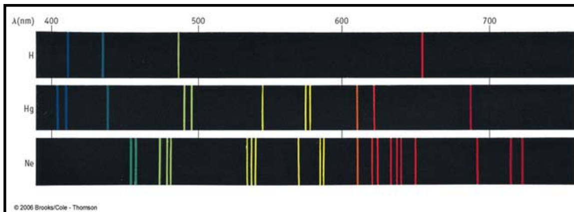
Frequency

Inversely proportional to wavelength

Directly proportional to the Energy of the photon







Emission Line Spectra for hydrogen, mercury and neon

Rydberg Equation: $1/\lambda = R(\frac{1}{2^2} - \frac{1}{n^2})$ n>2 (Balmer Series)
R = Rydberg constant = $1.0974\times10^7 m^{-1}$
Balmer and Rydberg used this equation to predict the visible red, green and blue lines in the hydrogen spectra (known as the Balmer series).

The general form is $1/\lambda = R(\frac{1}{n_f^2} - \frac{1}{n_i^2})$

http://astro.u-strasbg.fr/~koppen/discharge/

http://jersey.uoregon.edu/vlab/elements/Elements.html

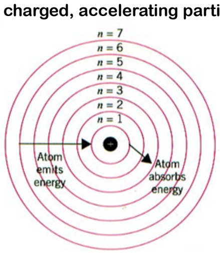
http://lectureonline.cl.msu.edu/~mmp/kap29/Bohr/app.htm

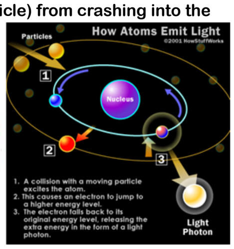
Bohr Model of the atom (Niels Bohr)

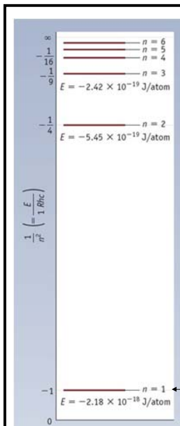
First connection between line spectra and quantum ideas of Planck and Einstein.

Bohr Model: Electrons orbit the nucleus of the atom like planets going around the sun

Only certain stable orbits are allowed (quantized) to keep the electron (a charged, accelerating particle) from crashing into the nucleus.





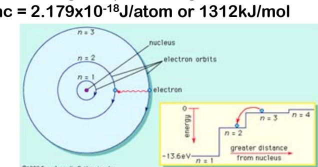


Works for hydrogen atom

Potential energy of electron in the nth level $= E_n = -\frac{Rhc}{n^2}$ (Rydberg constant, Planck's constant, Speed of light; Principal quantum number)

$\lambda = hc/E$
$1/\lambda = R(1/n_f^2 - 1/n_i^2)$
$E/hc = R(1/n_f^2 - 1/n_i^2)$
$E = Rhc(1/n_f^2 - 1/n_i^2)$

n is an integer equal to or greater than 1 and Rhc = 2.179×10^{-18}J/atom or 1312kJ/mol

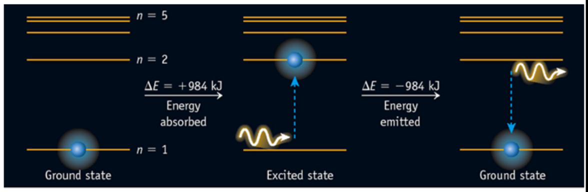


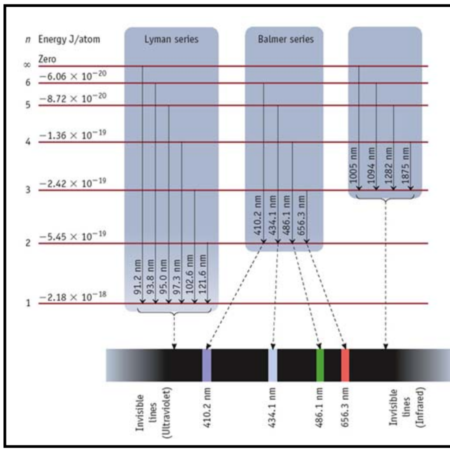
Principle quantum number

Note: Potential energy = 0 at infinity

Electron Transition Diagram

1) Electron in ground state
2) Electron jumps to “excited state” from absorption of outside energy (Energy absorbed = positive)
3) Electron transitions back down giving off photon that is equal in energy to the transition down (energy emitted = negative)





Lyman (UV), **Balmer** (Visible), and **Paschen** (IR) series of the hydrogen atom.

Example Problem (7.4)

Calculate the energy of the n=3 state of the H atom in a) joules per atom and b) kilojoules per mole.

Rhc = 2.179×10^{-18} J/atom or 1312kJ/mol

Answer:

$E = -Rhc/n^2 = -2.179 \times 10^{-18}\text{J/atom} / 3^2 = -2.421 \times 10^{-19}\text{J}$

$E = -1312\text{kJ/mol} / 3^2 = -145.8\text{kJ/mol}$

Example Problem

Calculate the wavelength and energy (in J/photon) of the second to the least energetic photon released in the Balmer series.

Rhc = 2.179×10^{-18} J/atom or 1312kJ/mol

Answer:

Calculating the delta energy between two quantized orbits

$$\Delta E = E_{\text{final}} - E_{\text{initial}} = -Rhc\left(\frac{1}{n_{\text{final}}^2} - \frac{1}{n_{\text{initial}}^2}\right)$$

Rhc = 2.179×10^{-18} J/atom or 1312kJ/mol

Compare to:

Rydberg Equation: $1/\lambda = R\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$

R = Rydberg constant = $1.0974 \times 10^{7}\text{m}^{-1}$

Example Problem (7.5):

The Lyman series of spectral lines for the H atom occurs in the ultraviolet region. They arise from transitions from higher levels to n=1. Calculate the frequency and wavelength of the least energetic line in this series.

Rhc = 2.179×10^{-18} J/atom or 1312kJ/mol

Answer:

$\Delta E = -Rhc\ (1/1^2 - 1/2^2) = -2.179 \times 10^{-18}\text{J/atom}\ (1/1 - 1/4) = -1.634 \times 10^{-18}\text{J}$

$E = h\nu \quad \nu = 1.634 \times 10^{-18} / 6.626 \times 10^{-34}\text{Js} = 2.466 \times 10^{15}\text{Hz}$

$\lambda = c/\nu = 3.00 \times 10^{8}\text{m/s} / 2.466 \times 10^{15}\text{Hz} = 1.216 \times 10^{-7}\text{m} = 121.6\text{nm}$

Comprehensive Problem:

Exposure to high doses of microwaves can cause damage. Estimate how many photons, with λ = 12cm, must be absorbed to raise the temperature of your eye by 3.0°C. Assume the mass of an eye is 11g and its specific heat capacity if 4.0J/gK.

Answer:

Q = mcΔT q = (11g)(4.0J/g°C)(3.0°C) = 132J (1.3x10^{2}J)

E = hc/λ = (6.626x10^{-34}Js)(3.00x10^{8}m/s) / (.12m)
= 1.6565x10^{-24}J/photon (1.7x10^{-24}J/photon)

132J / 1.6565x10^{-24}J/photon = 7.9686x10^{25}photons = 8.0x10^{25} photons

Wave Properties of the electron

If light has particle properties (photons), can particles have wave properties?

"Matter Waves" Based on the (Louis) DeBroglie Equation

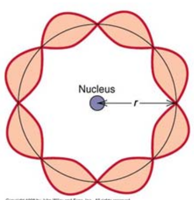
Where, λ is the DeBroglie Wavelength, h is the Planck constant, 6.626x10^{-34}Js and mv is the momentum of the particle (m = mass in kg; v = velocity in m/s)

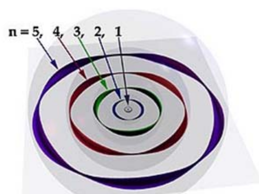
$$\lambda = \frac{h}{mv}$$

Since momentum, p = mv
The equation can be rewritten as p = h/λ

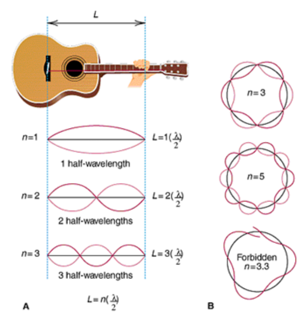
DeBroglie's Interpretation of the Bohr Model of the Atom

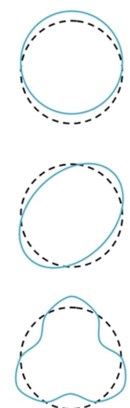
Allowed orbits have a circumference related to nλ/2





Niels Bohr - Louis de Broglie atom, 1924





Example:

Calculate the wavelength associated with a neutron having a mass of 1.675x10^{-24}g and a kinetic energy of 6.21x10^{-21}J. (Recall that the kinetic energy of a moving particle is E = ½ mv^2.)

Answer:

KE = ½ mv^2 6.21x10^{-21}J = ½ (1.67x10^{-27}kg)(v^2)

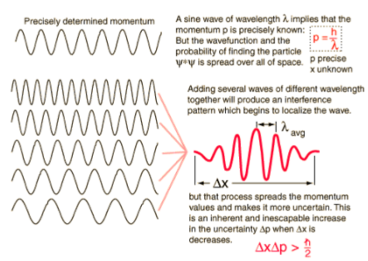
v = 2727.11m/s

λ = h / mv = (6.626x10^{-34}Js) / (1.67x10^{-27}kg)(2727.11m/s)

= 1.45x10^{-10}m = 1.45 angstroms = .145nm

Wave (quantum) Mechanics and the Uncertainty Principle

Werner Heisenberg:
Heisenberg's
Uncertainty Principle



$$\Delta p \, \Delta x \geq \frac{1}{2} \hbar$$

Where h-bar (also known as the Dirac constant) is h/2π. Note that the momentum is also related to the energy.

Max Born interpretation of quantum mechanics: ***If we choose to know the energy of an electron in an atom with only a small uncertainty, then we must accept a correspondingly large uncertainty in its position in the space about the atom's nucleus.*** **(p 316)**

Question:

A 12eV electron can be shown to have a speed of 2.05×10^6 m/s. Assuming that the precision (uncertainty) of this value is 1.5%, with what precision can we simultaneously measure the position of the electron?

$m_e = 9.11 \times 10^{-31}$ kg; $h = 6.626 \times 10^{-34}$ Js; 1eV = 1.602×10^{-19} J

$\Delta x \Delta p \geq h/4\pi$

Answer:

$p = mv = (9.11 \times 10^{-31}\text{kg})(2.05 \times 10^6\text{m/s}) = 1.87 \times 10^{-24}$ kgm/s

$\Delta p = (0.015)(1.87 \times 10^{-24}\text{kgm/s}) = 2.80 \times 10^{-26}$ kgm/s

$\Delta x = h/4\pi\Delta p = (6.626 \times 10^{-34}\text{Js})/(4)(3.14)(2.80 \times 10^{-26}\text{kgm/s})$

$= 1.89 \times 10^{-9}$ m = 1890pm (about 10 atomic diameters)

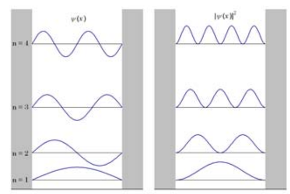
Wave (quantum) Mechanics and the Uncertainty Principle

Erwin Schrödinger (1887 – 1961)

Developed a comprehensive mathematical theory of the behavior of electrons in atoms.

The solutions to these mathematical equations (known as wave functions) are symbolized by psi (ψ) and describe (for a particle such as an electron) the properties of a standing wave within the system being described)

Detailed Explanation: Particle in a one-dimensional Box of Length, L.



Permitted Standing wavelengths

$$\lambda = \frac{2L}{n} \quad n = 1,2,3 \quad \textit{total nodes} = n+1$$

Wave function:

$$\Psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \quad n = 1,2,3...$$

Ψ^2 function: Probabilities of particle in a one-dimensional box.

$$\Psi_n^{\,2}(x) = \frac{2}{L}\sin^2\left(\frac{n\pi}{L}x\right)$$

Implications of the wave function, ψ (psi)

1. An electron behaves like a standing wave (and only certain wave functions are allowed)

2. Each wave function is associated with an allowed energy, E_n

3. The energy of the electron is quantized (from 1 and 2 above)

4. Explains the Bohr theory assumption (i.e. quantized orbits)

5. ψ^2 is related to the probability of finding an electron in a particular region of space (electron density)

6. Schrodinger's theory defines energy of electron precisely. The position is based on probability (orbital)

7. Three integer values (n, ℓ and m_ℓ) are required to solve the Schrodinger equation for an electron in 3-space. Only certain allowed combinations are possible.

(p 316)

The principal quantum number (n): (Shell) This number is related to the overall energy of an orbital (roughly the average distance from the nucleus). The number n, can take on integer values n = 1, 2, 3, 4...

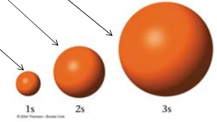
The angular momentum (azimuthal) quantum number (ℓ): (Subshell) This number is related to the shape of the sub-orbitals (i.e. shape of the 90% probability region) that an orbital may possess. The value of ℓ can take on numbers from ℓ = 0 to n-1

The magnetic quantum number (m_ℓ): This number is related to the spatial orientation of the sub-orbital (subshell orbital). Its numbers range from $m_\ell = -\ell ... 0 ... +\ell$

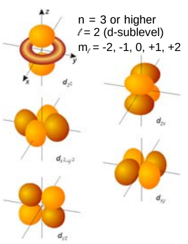
The spin quantum number (m_s): This number relates to the spin orientation of an electron in a given orbital. The electron does not have a true "spin" in the classical sense, but is used to account for spectral lines that are produced in the presence of an external magnetic field. The spin quantum number can possess values of $m_s = \pm½$. Therefore only 2 values are possible. (*Covered in the next chapter*)

n = 1 n = 2 n = 3
ℓ = 0 ℓ = 0 ℓ = 0 (s-sublevel)
m_ℓ=0 m_ℓ = 0 m_ℓ = 0

Energy level/sublevel 90% probability representations



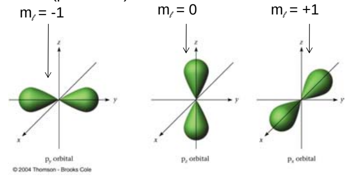
n = 3 or higher
ℓ = 2 (d-sublevel)
m_ℓ = -2, -1, 0, +1, +2

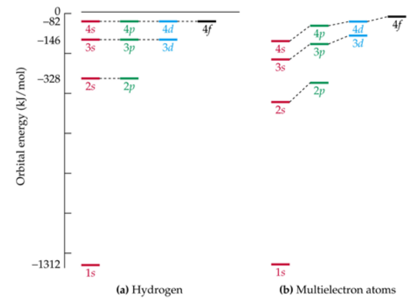


n = 2 or higher
ℓ = 1 (p-sublevel)
m_ℓ = -1

ℓ = 1
m_ℓ = 0

ℓ = 1
m_ℓ = +1





Sublevel Energy Distribution

With regard to the angular momentum quantum number, ℓ, scientist have assigned letters that correspond to the numerical values that ℓ can have. This comes from the days of spectroscopy (spectral analysis) and are as follows:

For ℓ equal to:

0 → s (sharp)
1 → p (principal)
2 → d (diffuse)
3 → f (fine)

Value of ℓ	Corresponding Subshell Label
0	s
1	p
2	d
3	f

Subshell	Number of Orbitals in Subshell
s	1
p	3
d	5
f	7

For ℓ equal to 4 and beyond the letters g, h, i,... and so on are used, skipping the letters that have already been used.

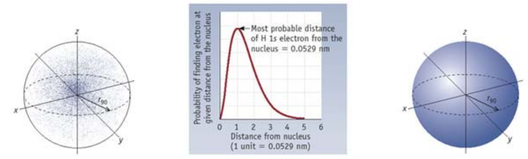
Table 7.1 Summary of the Quantum Numbers, Their Interrelationships, and the Orbital Information Conveyed

Principal Quantum Number Symbol = n Values = 1, 2, 3, . . . n = number of subshells	Angular Momentum Quantum Number Symbol = ℓ Values = 0 . . . n − 1	Magnetic Quantum Number Symbol = m_ℓ Values = −ℓ . . . 0 . . . +ℓ	Number and Type of Orbitals in the Subshell Number of orbitals in shell = n^2 and number of orbitals in subshell = $2\ell + 1$
1	0	0	one 1s orbital (one orbital of one type in the n = 1 shell)
2	0 1	0 +1, 0, −1	one 2s orbital three 2p orbitals (four orbitals of two types in the n = 2 shell)
3	0 1 2	0 +1, 0, −1 +2, +1, 0, −1, −2	one 3s orbital three 3p orbitals five 3d orbitals (nine orbitals of three types in the n = 3 shell)
4	0 1 2 3	0 +1, 0, −1 +2, +1, 0, −1, −2 +3, +2, +1, 0, −1, −2, −3	one 4s orbital three 4p orbitals five 4d orbitals seven 4f orbitals (16 orbitals of four types in the n = 4 shell)

Note the following:

n = the number of subshells in a shell
$2\ell+1$ = the number of orbitals in a subshell = the number of values of m_ℓ
n^2 = the number of orbitals in a shell $2n^2$ = total electrons possible in a shell

Interpretation of an s orbital

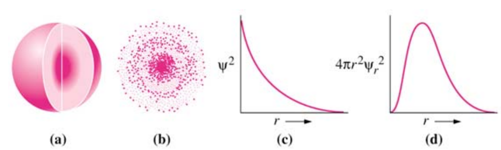


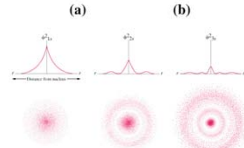
Middle Image: Plot of surface density (radial distribution plot) = Probability of finding an electron in a thin shell at a given distance from the nucleus.

Y-axis (on graph): Plot of $4\pi r^2\psi^2$ in units of 1/distance (where $4\pi r^2$ is the formula for the surface of a sphere)

Maximum amplitude of electron wave at 0.0529nm.

The spherical surface (right image) is the 90% probability region (boundary surface)

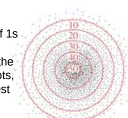




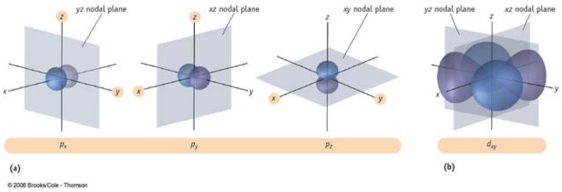
The ψ^2 gives the probability of the electron in an infinitesimally small volume of space whereas $4\pi r^2\psi^2$ gives the probability of an infinitesimally thin shell at a particular distance.

Charge Density of 1[st] three s orbitals

Dart board analogy of 1s orbital
Although the 50 has the greatest density of dots, the 30 has the greatest dots to surface area



Nodal Surfaces



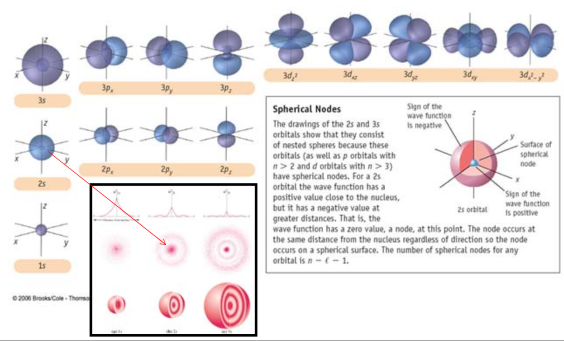
Surfaces (planes in these cases) that represent zero probability regions for electrons in those orbitals.

■ ℓ and Nodal Surfaces

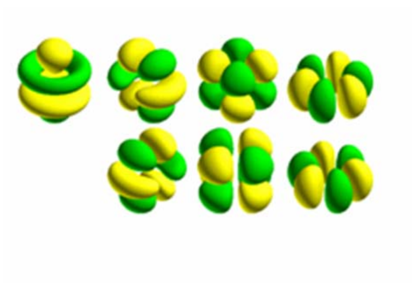
Orbital	ℓ	Number of Nodal Surfaces
s	0	0
p	1	1
d	2	2
f	3	3

Spherical Nodes

Regions of zero amplitude of the electron wave



Renderings of f-orbitals



In 5.0s, a 75watt light source emits 9.91×10^{20} photons of a monochromatic radiation. What is the wavelength of the emitted light (in nm)?

Answer:

$(75 J/s)(5.0 s) = 375 J$

$375 J/(9.91 \times 10^{20} \text{photons}) = 3.78 \times 10^{-19} J/\text{photon}$

$\lambda = hc/E$

$= (6.626 \times 10^{-34} Js)(3.00 \times 10^{8} m/s)/3.78 \times 10^{-19} J)$

$= 5.253 \times 10^{-7} m = 525 nm$