Chapter 7. Quantum Theory and Atomic Structure

- A problem arose in Rutherford’s nuclear model. A nucleus and electron attract each other; to remain apart the electron must move.

- The energy of the electron’s movement must balance the energy of attraction.

- Physics established that a charged particle moving in a curved path such as an electron in an atom must give off energy.

- Why doesn’t the electron continuously lose energy and spiral into the nucleus?

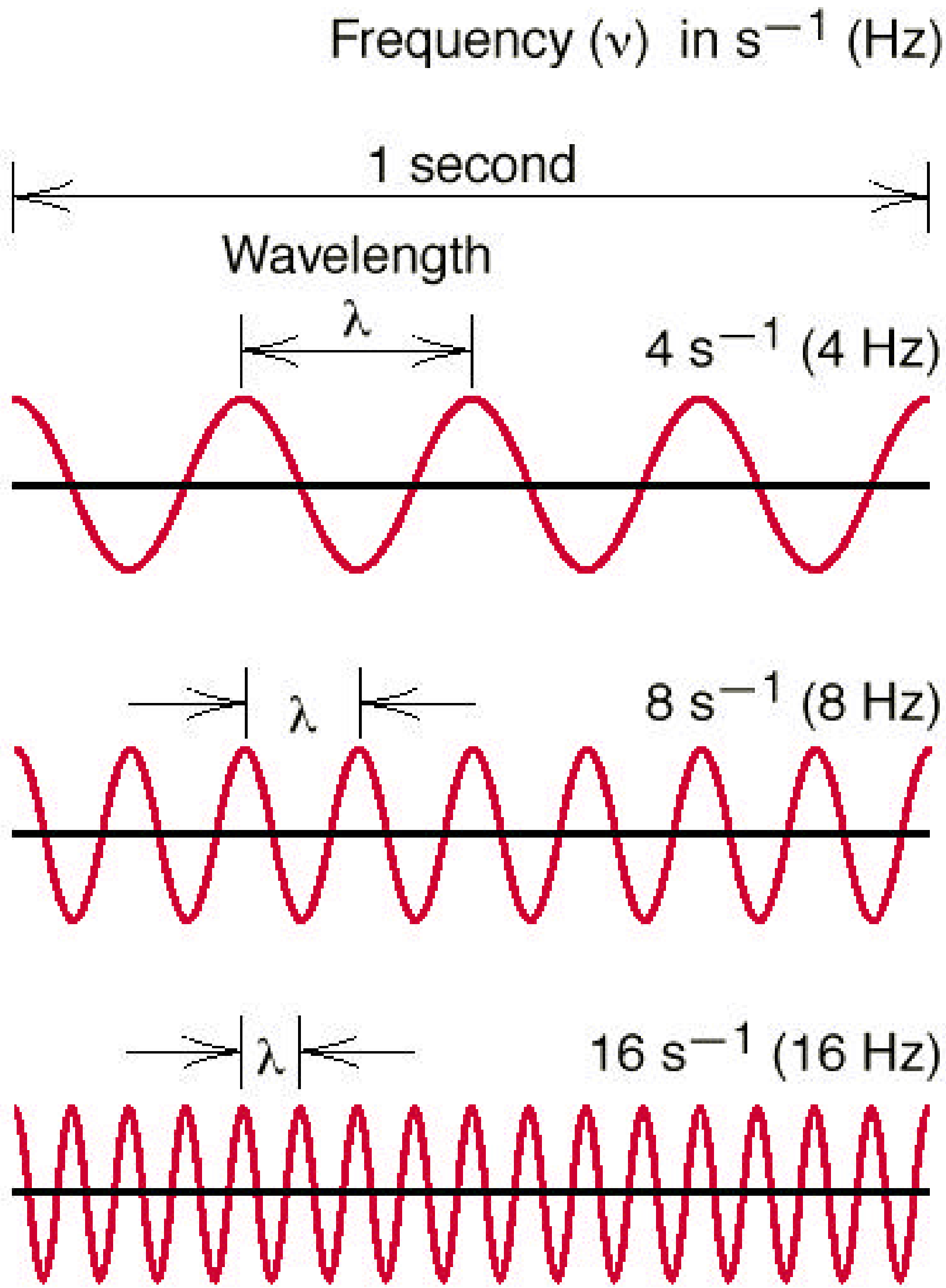
- Subatomic matter seemed to violate common experience. A new model was needed to describe atoms.

Concept 7-1. The wave characteristics of light (frequency, wavelength, and speed; the meaning of amplitude) and a general overview of the electromagnetic spectrum

- Visible light is one type of electromagnetic (EM) radiation.
- Electromagnetic radiation travels as waves—the result of oscillating electric and magnetic fields moving simultaneously through space.

- The wave properties of electromagnetic radiation are described by two interdependent variables, frequency and wavelength.

- Frequency (ν, Greek nu) is the number of cycles the wave makes per second, expressed in units of 1/second (s^{-1}), or hertz (Hz).



- Wavelength (λ, Greek lambda) is the distance between any point on a wave and the corresponding point on the next wave.

λ is expressed in meters, nanometers (nm, 10^{-9} m), picometers (pm, 10^{-12} m), and angstroms (Å, 10^{-10} m).

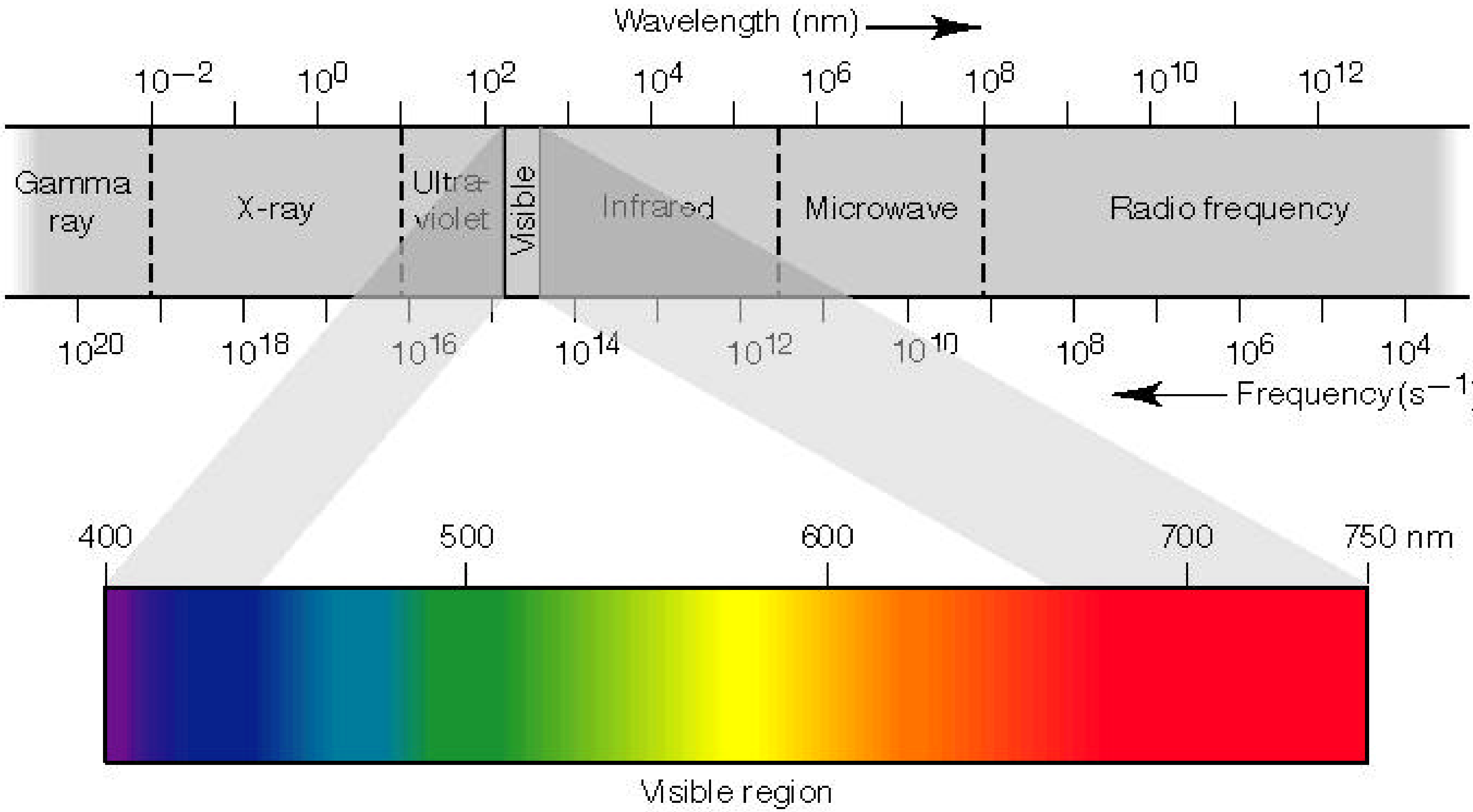
- The speed of the wave (m/s) is the product of its frequency (cycles per second) and its wavelength (meters per cycle):

$$\text{Speed} = \frac{\text{cycles}}{\text{s}} \times \frac{\text{m}}{\text{cycle}} = \frac{\text{m}}{\text{s}}$$

- In a vacuum, all electromagnetic radiation travels at 3.00×10^{8} m/s, a constant called the speed of light (c):

$$\boxed{c = \nu\lambda}$$

- Radiation of high frequency has a short wavelength, and vice versa.



Skill 7-1. Interconverting frequency and wavelength

Problem: A dentist uses x-rays (λ=1.00 Å) while a patient listens to an FM radio station (λ=325 cm) and looks out the window at blue sky (λ=473 nm). What is the frequency (s^{-1}) of the EM from each?

Plan:

$1\text{Å} = 10^{-10}$ m
1 cm $= 10^{-2}$ m
1 nm $= 10^{-9}$ m

$$\nu = \frac{c}{\lambda}$$

Wavelength (given units) → Wavelength (m) → Frequency (s^{-1})

Solution: For x-rays. Converting from Angstroms to meters:

$$\lambda = 1.00\ \text{Å} \times \frac{10^{-10}\ \text{m}}{1\ \text{Å}} = 1.00 \times 10^{-10}\ \text{m}$$

Calculating the frequency:

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^{8}\ \text{m/s}}{1.00 \times 10^{-10}\ \text{m}} = \mathbf{3.00 \times 10^{18}\ s^{-1}}$$

For the radio station. Combining steps to calculate the frequency:

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^{8}\ \text{m/s}}{325\ \text{cm} \times 10^{-2}\ \text{m/1 cm}} = \mathbf{9.23 \times 10^{7}\ s^{-1}}$$

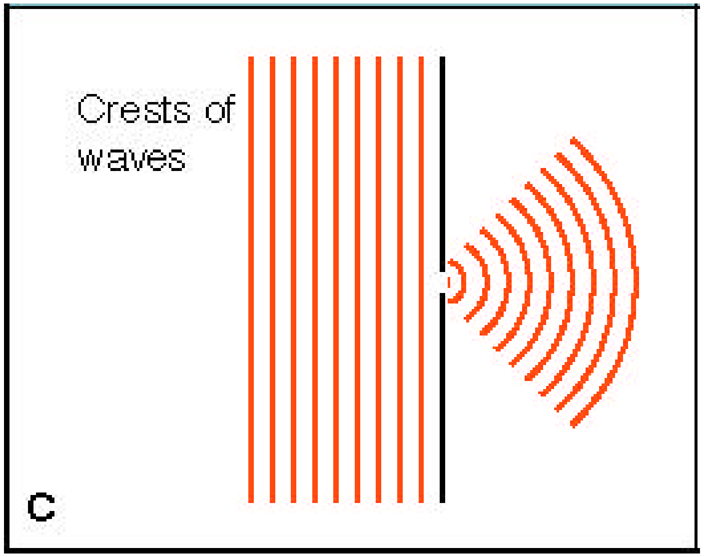
For the sky. Combining steps to calculate the frequency:

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^{8}\ \text{m/s}}{473\ \text{nm} \times 10^{-9}\ \text{m/1 nm}} = \mathbf{6.34 \times 10^{14}\ s^{-1}}$$

Concept 7-2. How particles and waves differ in terms of the phenomena of refraction, diffraction, and interference

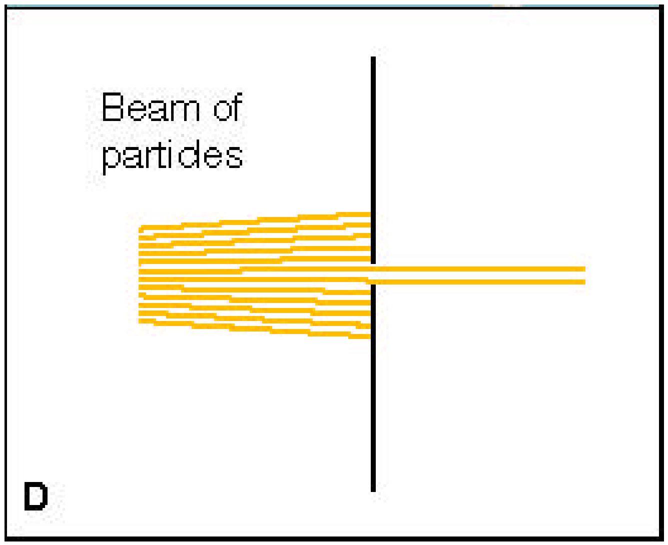
Wave Diffraction

- If a wave passes through a slit about as wide as its wavelength, it forms a semi-circular wave on the other side of the opening.

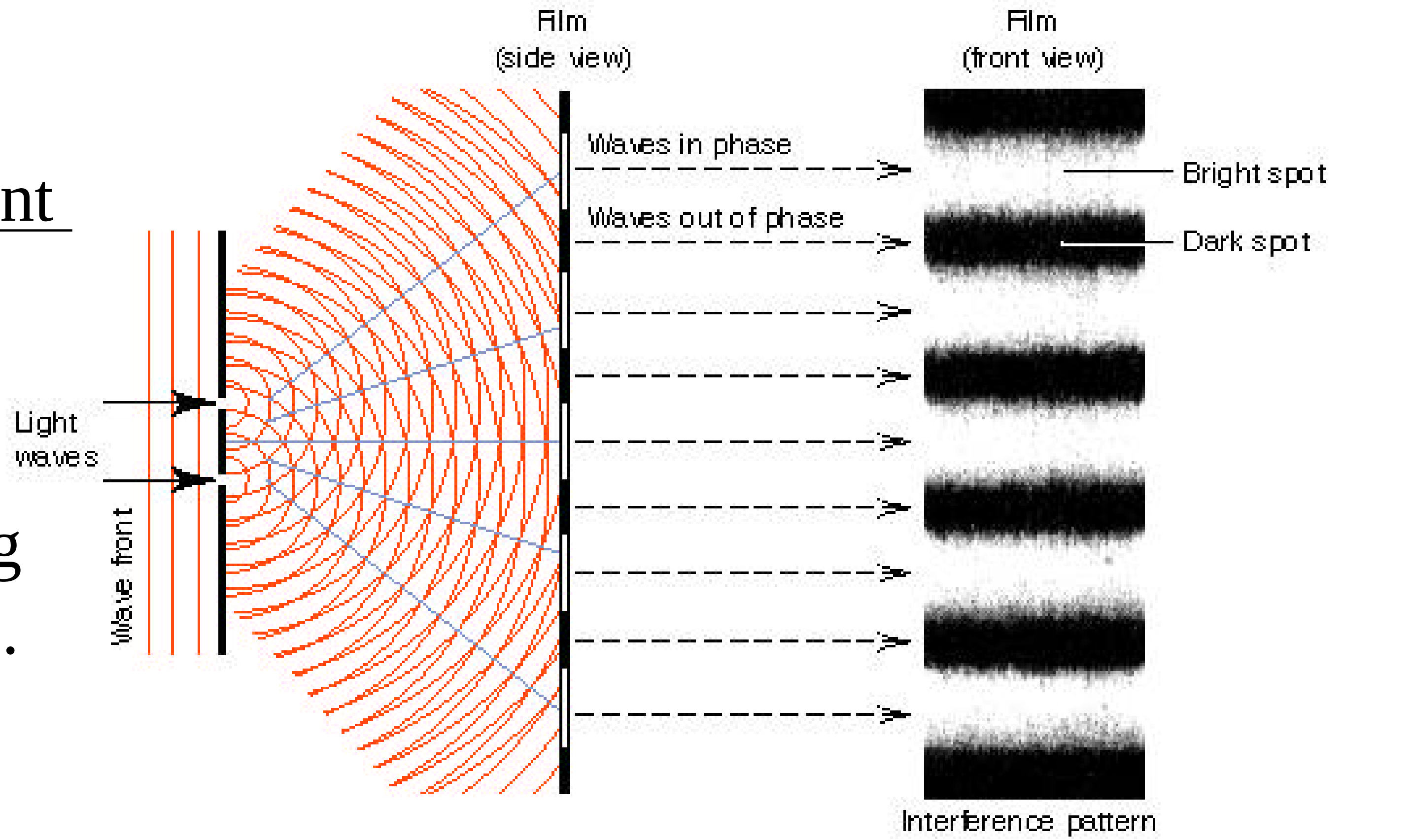


- A stream of particles aimed at a small opening behaves quite differently:

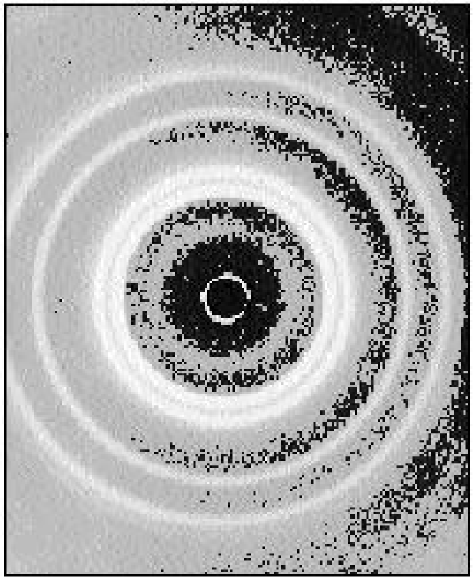
- Some particles hit the edge and stop; those going through continue linearly in a narrower stream.



- If light waves pass through two adjacent slits, the emerging circular waves interact through interference creating a diffraction pattern.



- A diffraction pattern produced by X-rays.



The Particulate Nature of Light

Blackbody radiation

- As an object is heated, it begins to emit visible light, first as a red glow, then orange, then white light.

- Attempts to use electromagnetic theory to predict wavelengths of the emitted light failed.

- Max Planck proposed that the hot, glowing object could emit (or absorb) only certain amounts of energy: $\boxed{E = nh\nu}$

-where E is the radiation energy, ν is its frequency, n is a positive integer called a quantum number, and h is Planck's constant.

- With E in joules (J) and frequency in s^{-1}, h has units of J•s:

$$h = 6.626 \times 10^{-34}\ \mathrm{J \cdot s}$$

Concept 7-3. The quantization of energy and the fact that an atom changes its energy by emitting or absorbing quanta of radiation

- If atoms can emit only fixed amounts of energy, it follows that atoms can have only fixed electronic energy values: E = 1hν, 2hν, ..

- This constraint means that the energy of an atom is not continuous but quantized: it can exist only in certain fixed amounts.

- Each change in energy results from a "packet" of energy being gained or lost by the atom. This energy packet is called a quantum.

- Thus, an atom changes its energy state by emitting or absorbing a quantum of energy.

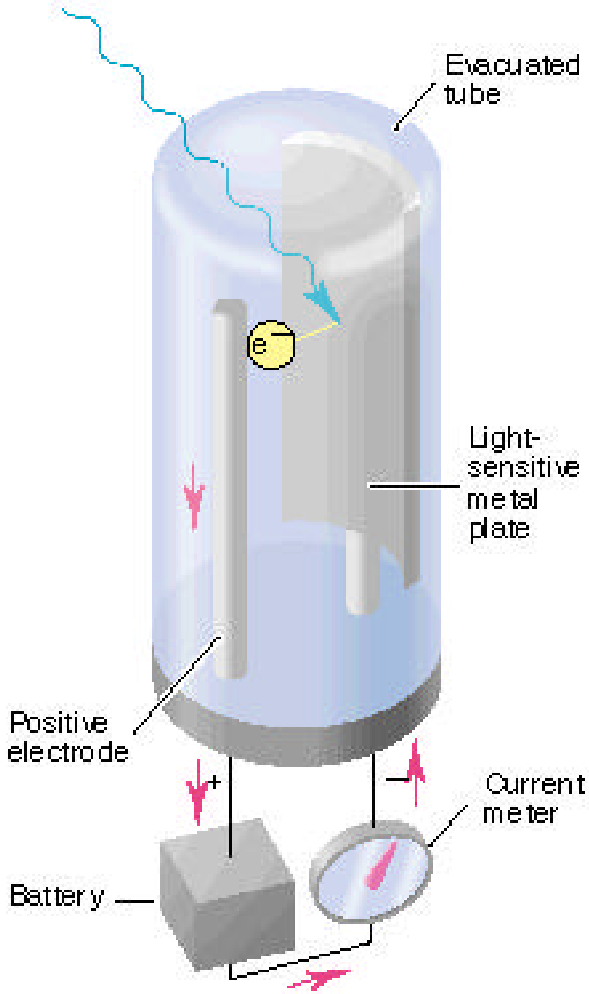
$$\Delta E_{\text{atom}} = E_{\text{emitted (or absorbed) radiation}} = \Delta n h\nu$$

- The smallest possible energy change for an atom is from one energy state to an adjacent one (Δn = 1):

$$\boxed{\Delta E = h\nu}$$

Concept 7-4. How the photon theory explains the photoelectric effect; the relation between photon absorbed and electron released

The photoelectric effect- when monochromatic light of sufficient energy hits the metal plate, an electric current flows.



1. Presence of a threshold frequency. Light shining on the metal must have a minimum frequency (which varies with the metal), or no current flows.

2. Absence of a time lag. Current flows the moment that light of high enough frequency shines on the metal, regardless of its intensity.

- Albert Einstein offered his **photon theory** to help explain the photoelectric effect.
- He proposed that radiation is particulate, occurring as quanta of electromagnetic energy, later called **photons**.
- An atom changes its energy when it absorbs/emits a photon, a "piece" of light whose energy is fixed by its frequency:

$$\boxed{E_{\text{photon}} = h\nu = \Delta E_{\text{atom}}}$$

How does Einstein's photon theory explain the photoelectric effect?

1. Presence of a threshold frequency:

- A beam of light is composed of enormous numbers of photons.
- An electron is freed only when one photon of a certain minimum energy is absorbed. Energy depends on frequency ($h \times \nu$), so a threshold frequency is to be expected.

2. Absence of a time lag. An electron is freed the instant the atom absorbs a photon of enough energy. It doesn't accumulate energy.

- Current will be less in dim light than in bright light since fewer photons with enough energy eject fewer electrons per unit time.

Skill 7-2. Interconverting the energy of a photon with its frequency and/or wavelength

Problem: A microwave oven has a frequency of 2.45 x 10^{9} s^{-1} . What is the energy of one photon of this microwave radiation?

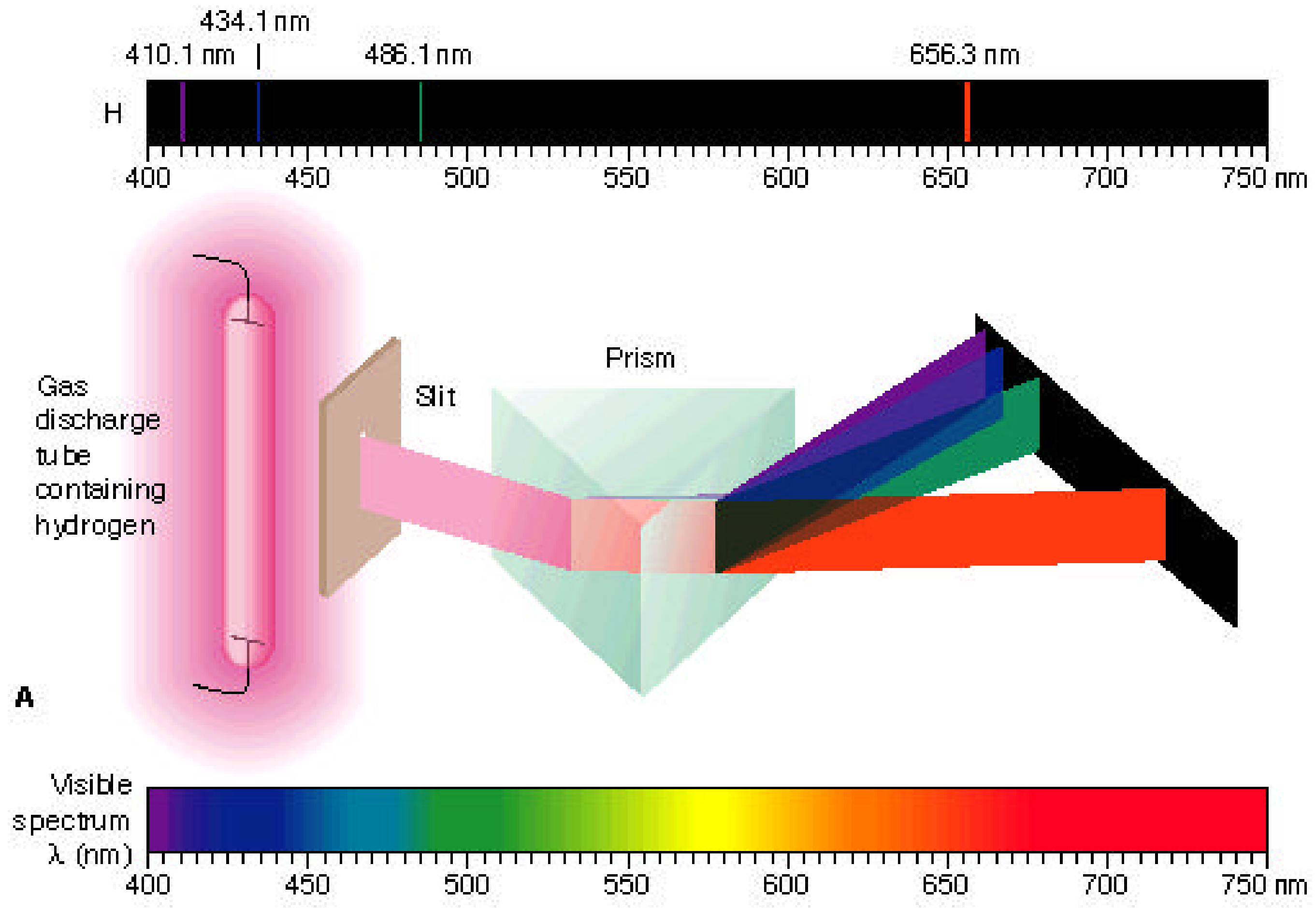
Solution: $E = h\nu = (6.626 \times 10^{-34}\ \mathrm{J \cdot s})(2.45 \times 10^{9}\ \mathrm{s^{-1}})$

$$= \mathbf{1.62 \times 10^{-24}\ J}$$

- The quantum and photon theories ascribed features to radiation that had been reserved for matter: fixed amount and discrete particles.

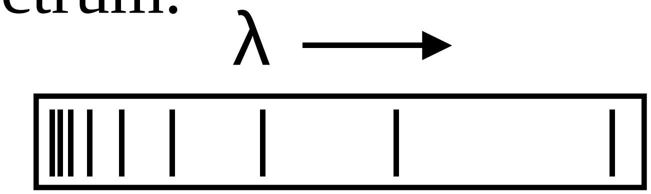
Concept 7-5. How the Bohr theory explained line spectra of the H atom; the importance of discrete atomic energy levels

- When an element is vaporized and thermally or electrically excited, it emits light. Hydrogen gas gives a pinkish color.
- Produces a line spectrum, a series of fine lines of individual colors.

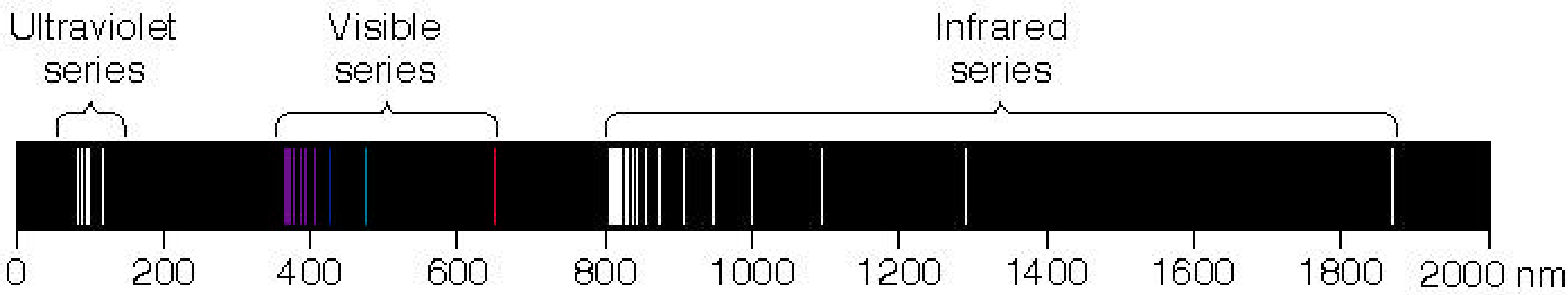


Atomic spectra video clip by Philip Morrison

- Spectroscopists discovered several series of H spectral lines in other regions of the electromagnetic spectrum.



- Each series showed a similar pattern.



- Equations of the form below, (Rydberg equation) were found to predict the position and wavelength of any line in a given series:

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

Where n_1 and n_2 are postive integers with $n_2 > n_1$, and R is the Rydberg constant ($1.096776 \times 10^7\ m^{-1}$).

• For the series of spectral lines in the visible range, $n_1 = 2$:

$$\frac{1}{\lambda} = R\left(\frac{1}{2^2} - \frac{1}{{n_2}^2}\right), \text{ with } n_2 = 3, 4, 5, \ldots$$

• Rydberg equation is empirical, based on data rather than theory.

Why do the spectral lines of hydrogen follow this pattern?

• Rutherford's nuclear model did not predict the existence of atomic line spectra. It had to be modified or replaced.

Niels Bohr

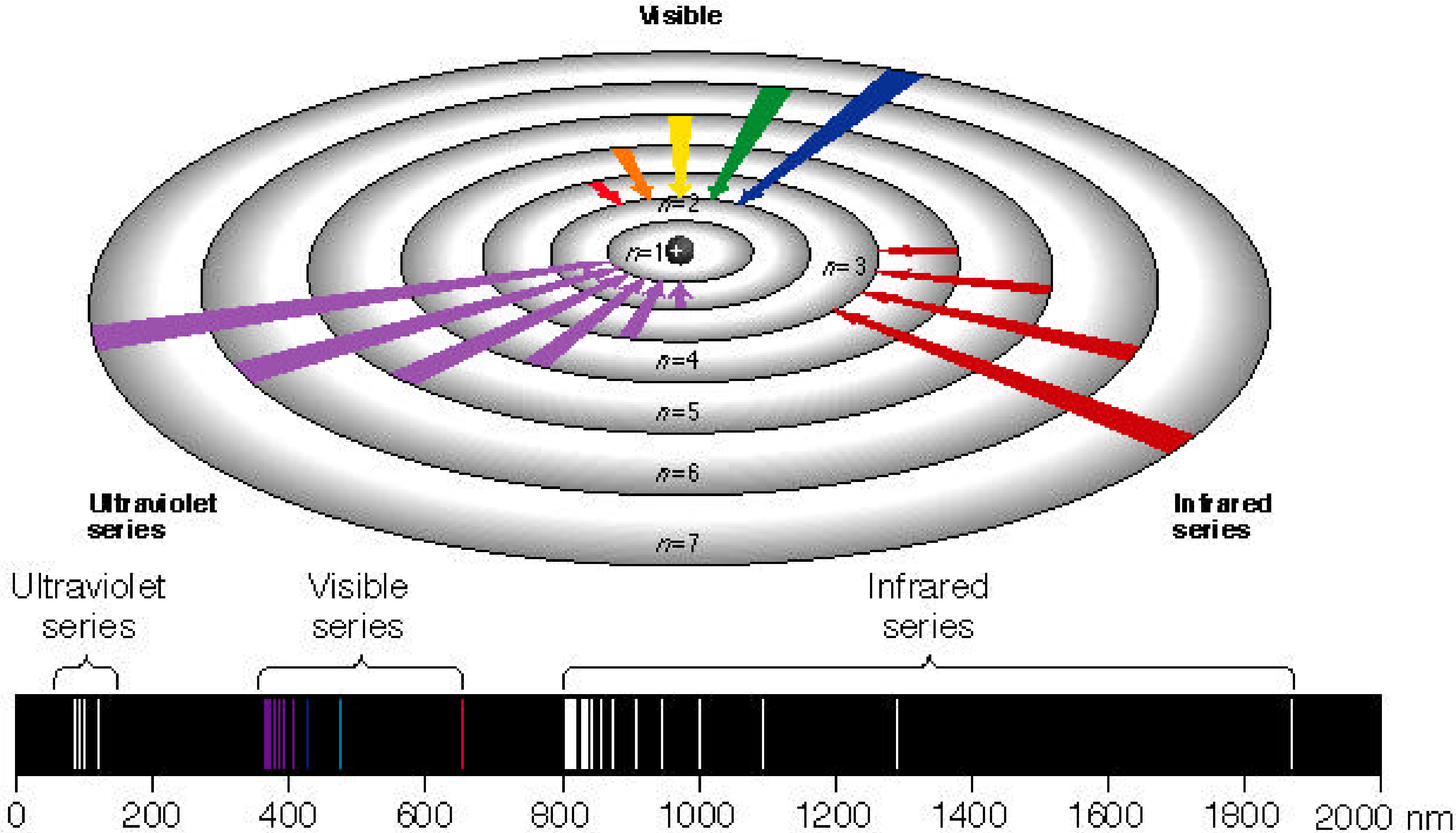
• Niels Bohr, working in Rutherford's laboratory, suggested a model for the hydrogen atom that predicted the observed line spectra.

The Bohr Model of the Hydrogen Atom

- Bohr used Planck's and Einstein's ideas about quantized energy proposing that hydrogen atoms had only certain fixed energy states.
- Each of these states was associated with a fixed circular orbit of the electron around the nucleus.
- Bohr proposed that atoms do not radiate energy while in one of their fixed (stationary) energy states.
- When the electron moves to a different orbit, the atom changes to another energy state.
- This happens only by the atom absorbing or emitting a photon.
- The photon energy equals the difference in energy between the two stationary states:

$$E_{\text{photon}} = \Delta E_{\text{stationary states}} = h\nu$$

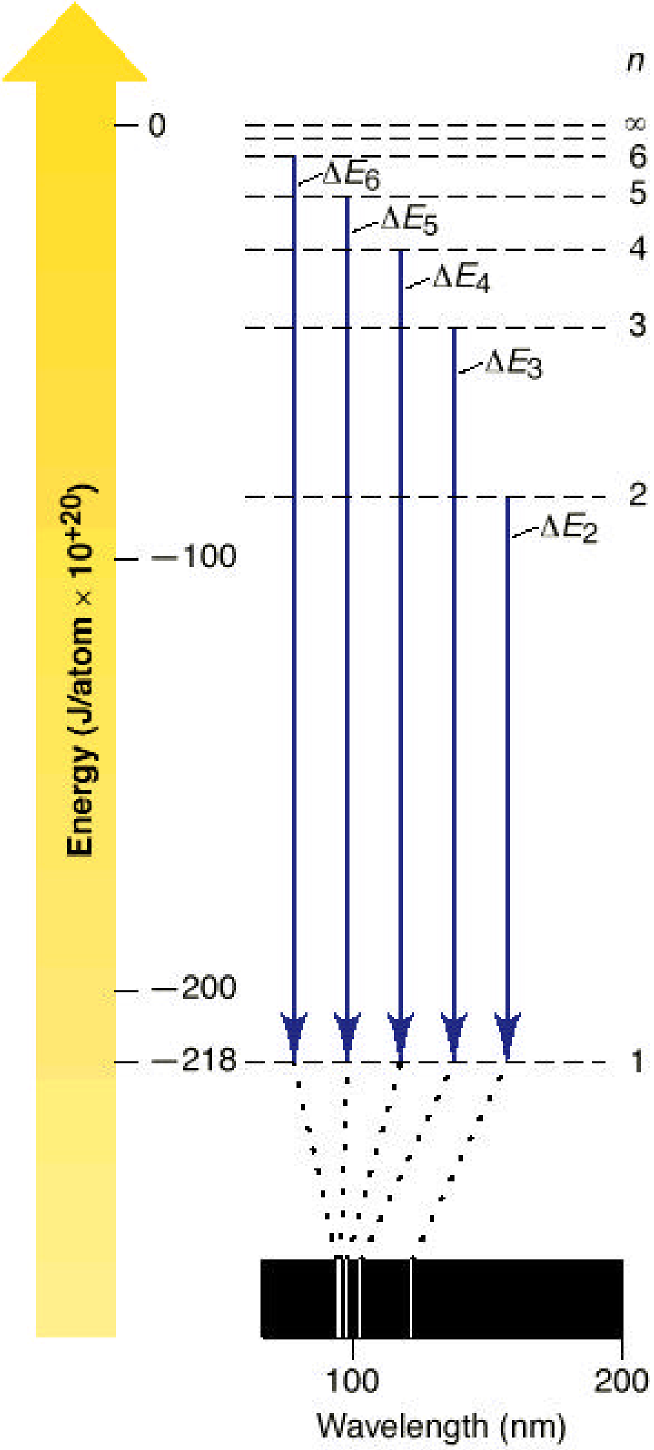
•Spectral lines represent emission of a photon of specific energy (and ν) as an electron drops from a higher energy state to a lower one.



•An atomic spectrum consists of lines instead of a continuum because the atom's energy has only certain discrete levels, or states.

- In Bohr's model, the quantum number n determines the radius of the electron's orbit and is directly related to the atom's energy.
- The lower the value of n, the smaller is the radius of the orbit and the lower is the energy level of the atom.
- When the electron is in the n = 1 orbit, the atom is in its lowest (first) energy level, called the ground state.
- The second energy level (second stationary state) and all higher levels are called excited states.
- A hydrogen atom in the 2nd energy level can return to the ground state by emitting a photon of a particular frequency:

$$E_{\text{photon}} = h\nu = E_{\text{first excited state}} - E_{\text{ground state}}$$



- When a sample of atomic hydrogen absorbs energy, different H atoms absorb different amounts.

- In various atoms all the allowable energy levels (orbits) are populated by electrons.

- Transitions from outer orbits to n = 3 gives the infrared series of spectral lines.

- Transitions from outer orbits to n = 2 gives the visible series of spectral lines.

- Transitions from outer orbits to n = 1 gives the ultraviolet series of lines.

The Energy States of the Hydrogen Atom

- Bohr obtained an equation giving the energies of the stationary states of the hydrogen atom:

$$\boxed{E = -2.18 \times 10^{-18}\ \text{J}\left(\frac{1}{n^2}\right)}$$

- The energy of the ground state (n = 1) is:

$$E = -2.18 \times 10^{-18}\ \text{J}\left(\frac{1}{1^2}\right) = -2.18 \times 10^{-18}\ \text{J}$$

- He defined zero energy (E = 0) as the state when the electron is totally removed from the nucleus; in other words, when n = ∞.

- So E < 0 (i.e. negative) for any smaller n values.

- The energy **difference** between any two energy levels is given by:

$$\boxed{\Delta E = E_{\text{final}} - E_{\text{initial}} = -2.18 \times 10^{-18}\ \text{J}\left(\frac{1}{n^2_{\text{final}}} - \frac{1}{n^2_{\text{initial}}}\right)}$$

How much energy is needed to completely remove the electron from the hydrogen atom; that is, what is ΔE for the following change?

$$H(g) \longrightarrow H^+(g) + e^-$$

Calculate this by substituting $n_{final} = \infty$ and $n_{initial} = 1$:

$$\Delta E = E_{final} - E_{initial} = -2.18 \times 10^{-18}\ \text{J}\left(\frac{1}{\infty^2} - \frac{1}{1^2}\right)$$
$$= 2.18 \times 10^{-18}\ \text{J}$$

- ΔE is positive because energy must be absorbed to remove the electron from the positive nucleus.

For one mole of H atoms,

$$\Delta E = \left(2.18 \times 10^{-18}\ \frac{\text{J}}{\text{atom}}\right)\left(6.022 \times 10^{23}\ \frac{\text{atoms}}{\text{mol}}\right)\left(\frac{1\ \text{kJ}}{10^3\ \text{J}}\right)$$
$$= 1.31 \times 10^3\ \text{kJ/mol}$$

- This is the ionization energy of the hydrogen atom.

•Despite its success in accounting for spectral lines of the H atom, the Bohr model **failed** to predict the spectrum of any other element.

• The model worked well for one-electron species, but not for atoms or ions with more than one electron.

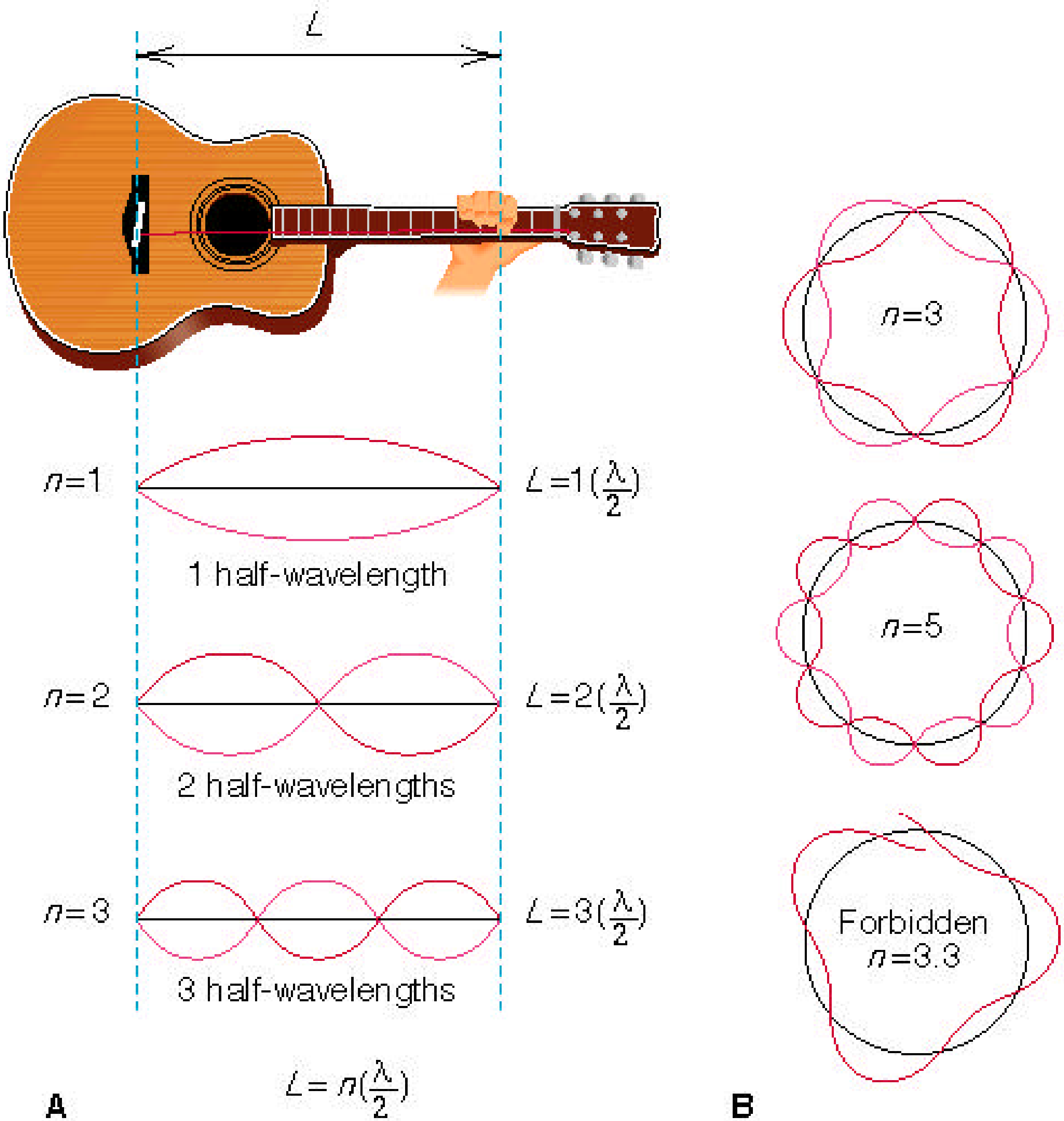
• The existence of discrete atomic energy levels is retained from Bohr's model in the current atomic model.

Concept 7-6. The wave-particle duality of matter and energy and the relevant theories and experiments that led to it

The Wave-Particle Duality of Matter and Energy

•Louis de Broglie proposed a surprising reason for the existence of fixed energy levels in Bohr's model atoms.

• He said atoms are like other systems that display only certain allowed states, such as the wave created by a plucked guitar string.


L
n=1
L=1(λ/2)
1 half-wavelength
n=2
L=2(λ/2)
2 half-wavelengths
n=3
L=3(λ/2)
3 half-wavelengths
L= n(λ/2)
A
n=3
n=5
Forbidden
n=3.3
B

- DeBroglie suggested suggested that particles of matter such as electrons have some properties of waves.

- If electrons were wavelike and restricted to orbits of fixed radii, only certain possible frequencies and energies would be allowed.

- From mass-energy equivalence ($E = mc^2$) and the equation for the energy of a photon ($E = h\nu = hc/\lambda$), de Broglie derived:

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

where m is the mass and u is the velocity.

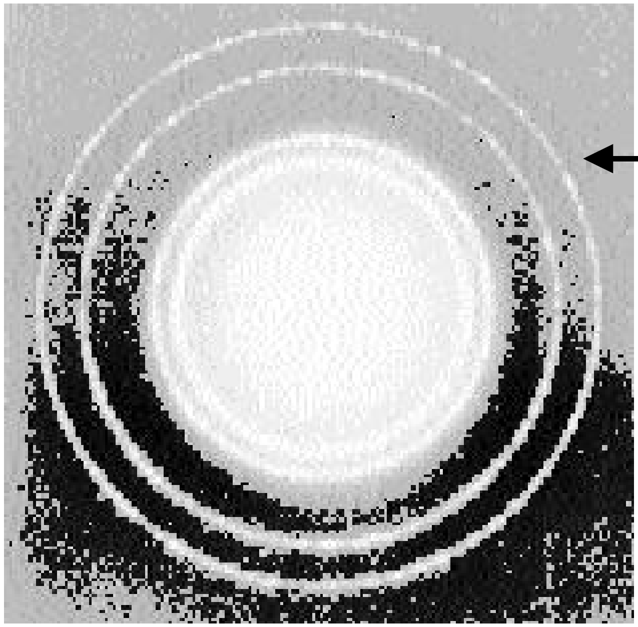
- An object's wavelength is inversely proportional to its mass; heavy objects have wavelengths that are very much smaller than the object

- Fast moving electrons have wavelengths close to the size of an atom ($\sim 10^{-10}$ m).

- If de Broglie's concept is correct, electrons should exhibit the wave properties of diffraction and interference.

- A good "slit" could be the spacings between atoms in a crystal.

- In 1927, C. Davisson and L. Germer guided a beam of electrons at a nickel crystal and obtained an electron diffraction pattern.



Diffraction of an electron beam by thin aluminum foil.

- This observation proves that electrons behave as waves under some conditions.

Concept 7-7. The meaning of the uncertainty principle and how it limits our knowledge of electron properties

- If an electron has <u>both</u> particle and wave properties, its position in an atom can't be readily determined.

Werner Heisenberg

- Werner Heisenberg postulated the uncertainty principle: it is impossible to know simultaneously the exact position and velocity of a particle like an electron.

- The uncertainty principle is expressed mathematically as:

$$\Delta x \cdot m\Delta u \geq \frac{h}{4\pi}$$

Δx is the uncertainty in position.

Δu is the uncertainty in velocity.

- We cannot prescribe exact paths for electrons, such as the <u>circular orbits</u> of Bohr's model.

- At best, the probability of finding an electron in a given volume of space can be determined.

The Quantum-Mechanical Model of the Atom

Erwin Schrödinger

- Applying wave mathematics to the electron wave, Erwin Schrödinger derived an equation that is the basis for the quantum-mechanical model of hydrogen atom.

- The allowed wave-like motion of the electron leads to an atom with certain fixed energy states much like Bohr assumed.

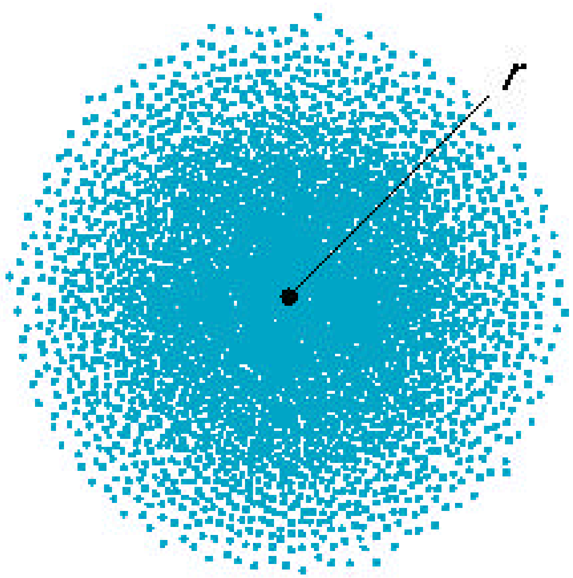
- The electron's exact location cannot be determined.

- Solutions of Schrödinger's wave equation are functions, ψ, that describe atomic orbitals.

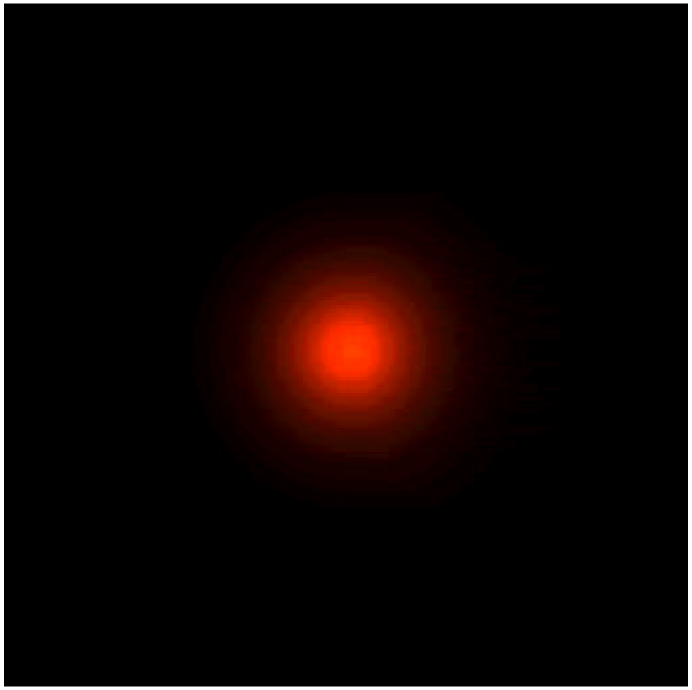
- Each ψ describes a fixed-energy state the electron can occupy and ψ^2 gives the probability of finding it in a given 3-dimensional space

Concept 7-8. The distinction between ψ (atomic orbital) and ψ^2 (probability of the electron being at a distance r from the nucleus)

- This probability can be shown pictorially by means of an electron probability density diagram, or simply, an electron density diagram.
- Electron probability density in the H atom <u>ground state</u>.



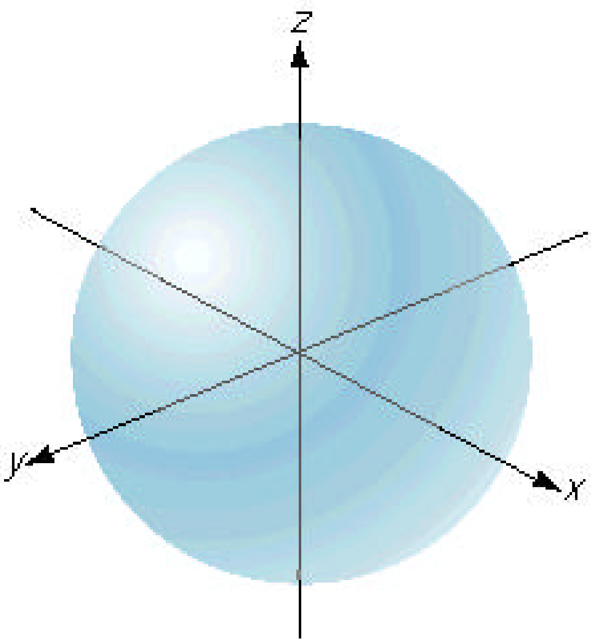
electron "cloud"



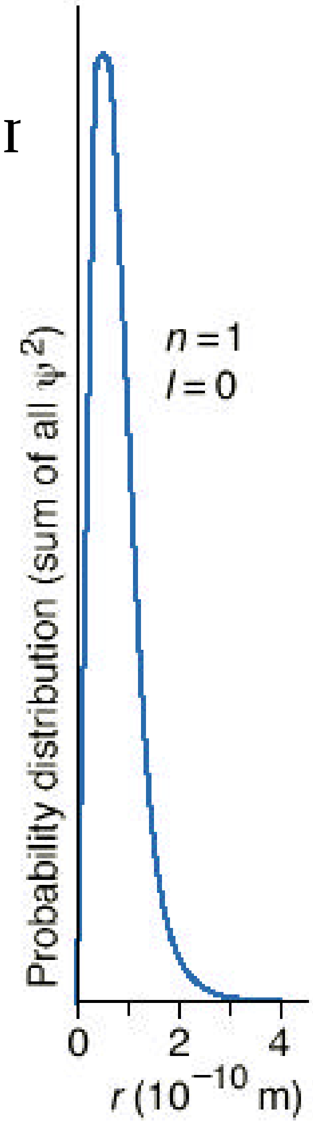
Concept 7-9. How electron density diagrams and radial distributio plots depict the probability of electron location within the atom

- Dividing the volume of atom into thin, concentric, spherical layers and calculating ψ^2 in each, the variatior of electron density with radial distance is found.

- The probability of the electron being far from the nucleus is very small, <u>but not zero</u>.



A 90% contour depiction of the ground state; the volume in which the electron spends 90% of its time.



• The maximum radial probability for the ground-state of H atom appears at (0.529 Å, or 5.29×10^{-10} m), the same as 1st Bohr orbit.

• The electron spends most of its time at the same distance that the Bohr model predicted it spent all of its time.

• Each atomic orbital, ψ, has a distinctive radial probability distribution and probability contour diagram.

Concept 7-10. The hierarchy of the quantum numbers that describe the size (n, energy), shape (l), and orientation (m_l) of an orbital

Quantum Numbers of an Atomic Orbital

• An atomic orbital is specified by **three quantum numbers**.

• These determine the orbital's **size, shape,** and **orientation** in space.

Concept 7-11. The distinction between level (shell), sublevel (subshell), and orbital

- The principal quantum number (***n***) is a positive integer (1, 2, 3, etc).

  n indicates the relative **size** of the orbital (the distance from the nucleus of the peak in the radial probability distribution plot).

  n specifies the **energy level** of the H atom: the higher the ***n*** value the greater the energy.

- The azimuthal quantum number, ***l***, is an integer from **0 to n – 1**.

  l is related to the **shape** of the orbital.

  For orbitals with ***n*** = 2, ***l*** can have a value of 0 or 1;
  with ***n*** = 3, ***l*** can be 0, 1, or 2; etc.

  The number of possible ***l*** values equals the value of ***n***.

- The magnetic quantum number (***m*** $_l$) is an integer from **– *l* through 0 to +*l*.**

m $_l$ prescribes the **orientation** of the orbital in the three-dimensional space about the nucleus.

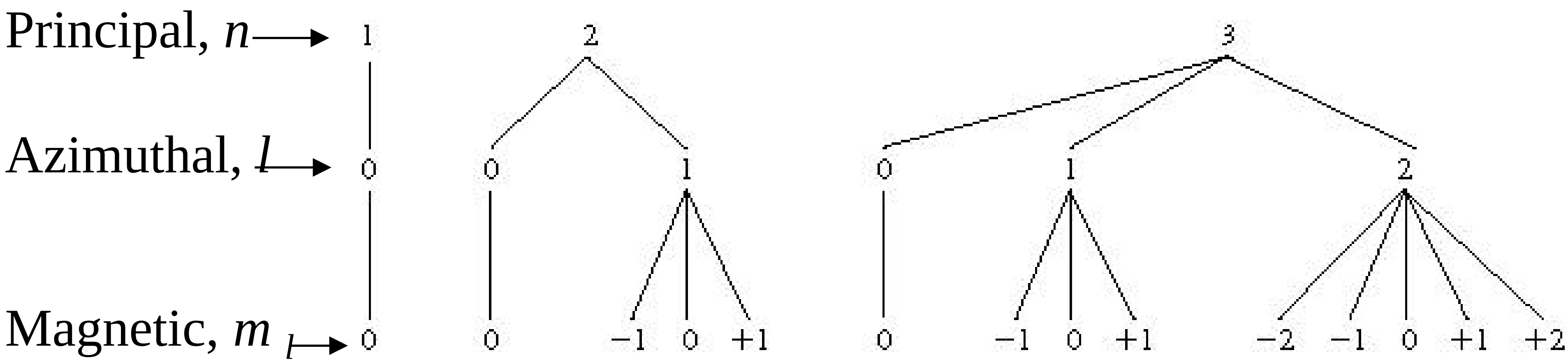
The possible values of an orbital's magnetic quantum number are set by its azimuthal quantum number.

An orbital with ***l*** = 0 can have only ***m*** $_l$ = 0.

An orbital with ***l*** = 1 can have ***m*** $_l$ values of –1, 0, or +1.

The number of possible ***m*** $_l$ values, or orbitals, for a given ***l*** value is **2*l* + 1**.

Allowed values of quantum numbers



Determining Quantum Numbers for a Given Energy Level

Problem: (a) What values of the azimuthal and magnetic quantum numbers are allowed for a principal quantum number of 3?
(b) How many orbitals are allowed for $n = 3$?

Solution: Determining l values:

l takes values from 0 to n–1. For $n = 3$, $l = 0, 1, 2$.

Determining m_l for each l value:

For $l = 0$, $m_l = 0$

For $l = 1$, $m_l = +1, 0, -1$

For $l = 2$, $m_l = +2, +1, 0, -1, -2$

Since there are nine m_l values, there are nine orbitals with $n = 3$.

- The total number of orbitals for a given n value is $\mathbf{n^2}$.

- The atom's energy levels, or shells, are given by the n value.

- The $n = 1$ shell has lower energy and a greater probability of the electron being closer to the nucleus than higher shells.

- The atom's sublevels, or subshells, are given by the n and l values. Each shell contains subshells that designate the shape of the orbital.

- Each subshell is designated by a letter:
  - l = 0 indicates an **s subshell**.
  - l = 1 indicates a **p subshell**.
  - l = 2 indicates a **d subshell**.
  - l = 3 indicates an **f subshell**.

- Subshells are named by using the n value and the letter designation.

  The subshell with $n = 2$ and $l = 0$ is called the 2s subshell.

  The only orbital in the 2s subshell has $n = 2$, $l = 0$, and $m_l = 0$.

  The subshell with $n = 3$ and $l = 1$ is the 3p subshell.

  It has three orbitals: $n = 3$, $l = 1$, and $m_l = +1, 0$ and -1.

- Each of an atom's orbitals is specified by a set of n, l, and m_l values

- These fix the orbital's size, energy, shape, and spatial orientation.

Skill 7-5. Determining quantum numbers and sublevel designations

Problem: Give the name, magnetic quantum numbers, and number of orbitals for each subshell with the quantum numbers shown:

(a) $n = 3, l = 2$ (b) $n = 2, l = 0$ (c) $n = 5, l = 1$ (d) $n = 4, l = 3$

Solution:

	n	l	subshell name	possible m_l	No. of orb.
(a)	3	2	3d	-2, -1, 0, +1, +2	5
(b)	2	0	2s	0	1
(c)	5	1	5p	-1, 0, +1	3
(d)	4	3	4f	-3, -2, -1, 0, +1, +2, +3	7

Identifying Incorrect Quantum Numbers

Problem: What is wrong with each of the following quantum number designations and/or subshell names?

	n	l	m_l	NAME
(a)	1	1	0	$1p$
(b)	4	3	+1	$4d$
(c)	3	1	−2	$3p$

Solution: (a) A sublevel of n = 1 can have only l = 0, not l = 1. The only possible subshell is 1s.

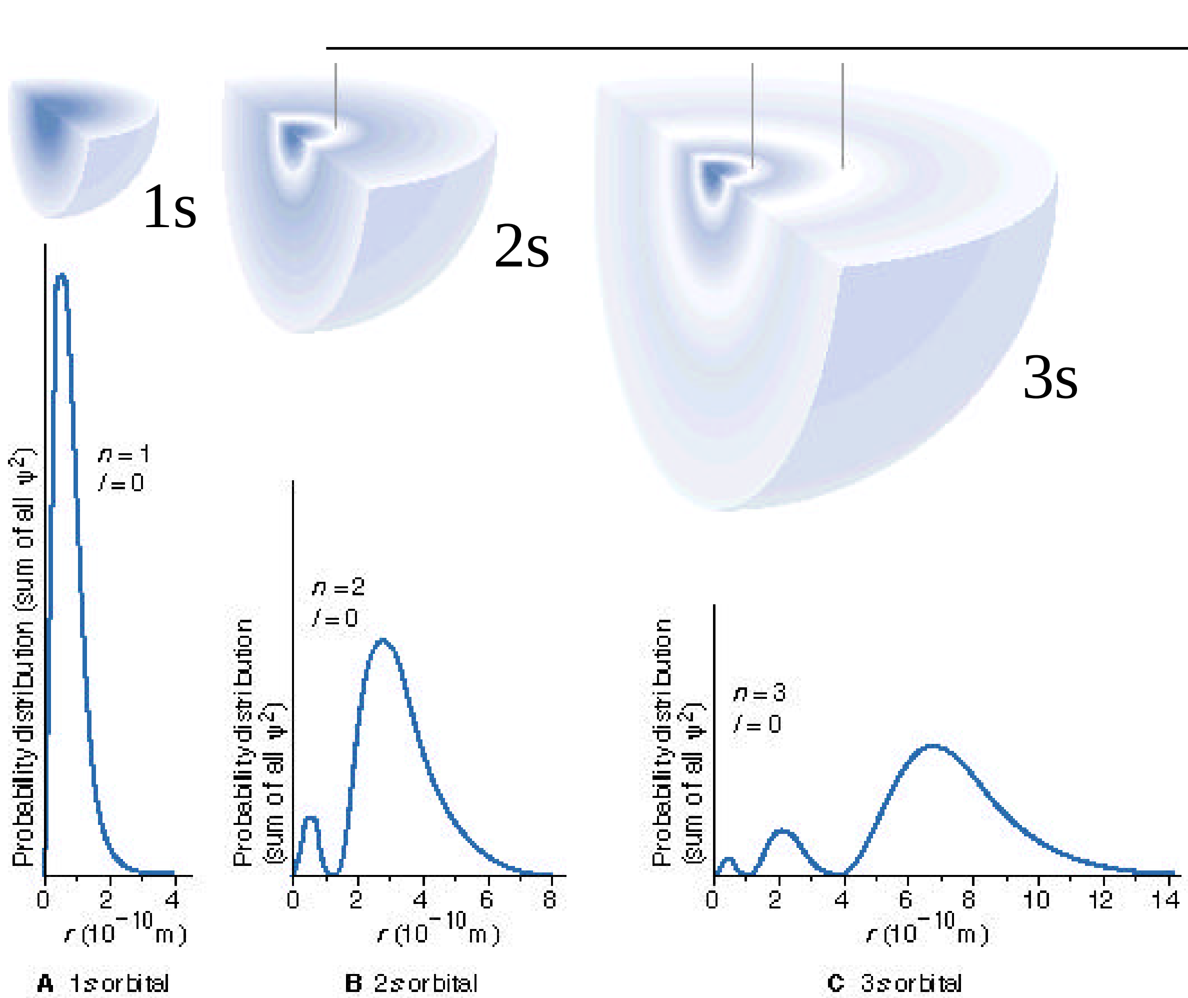
(b) A subshell with l = 3 is an f subshell, not a d subshell. The subshell name should be 4f.

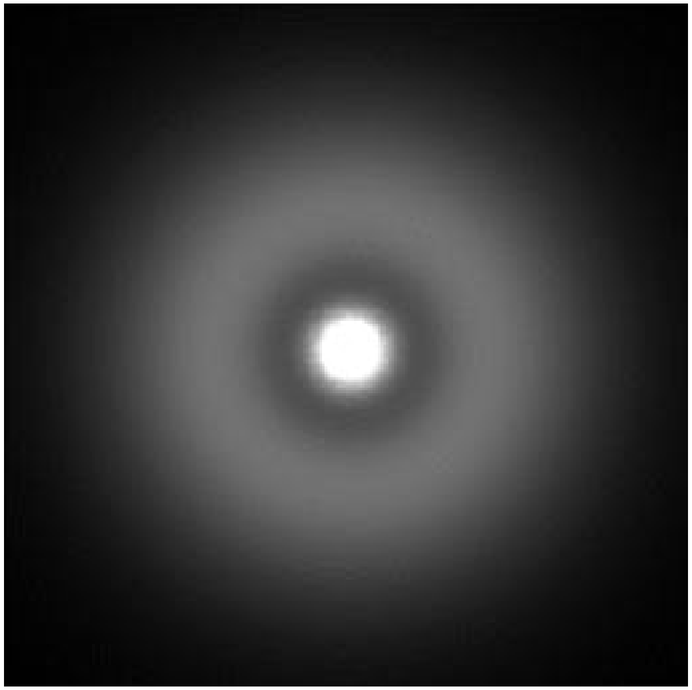
(c) A subshell with l = 1 can have only m_l of -1, 0, +1, not -2.

Concept 7-12. The shapes and nodes of s, p, and d orbitals

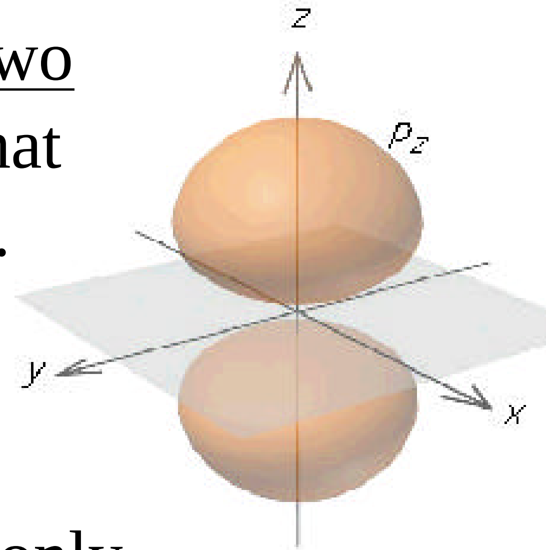
- Each subshell of the H atom has orbitals with a characteristic shape

s orbitals (l = 0) are <u>spherically symmetrical</u> around the nucleus.

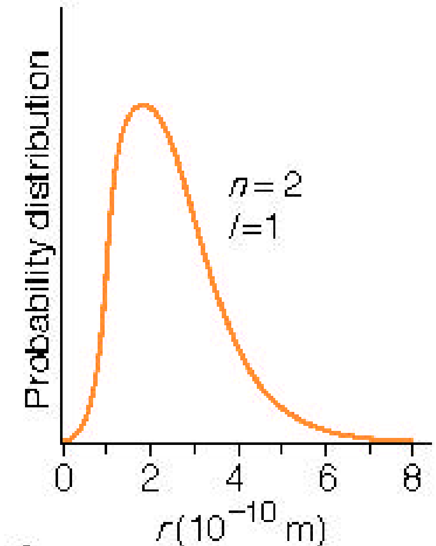




- The p orbital (with l = 1) has two regions of higher probability that lie on either side of the nucleus.
- The nucleus lies at a nodal plane of p orbitals.
- The max. value of l is n –1, so only shells with n ≥ 2 can have p orbitals.
- Energies of p orbitals: 2p < 3p < 4p...



B



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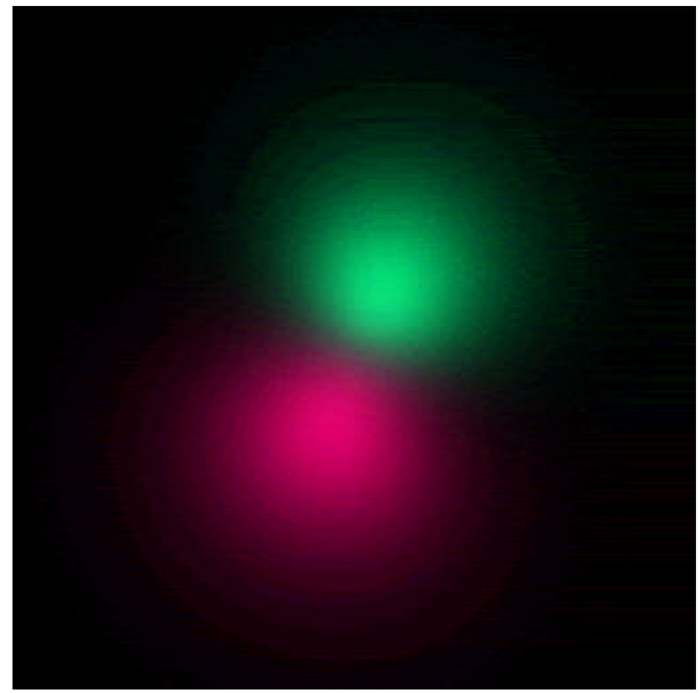
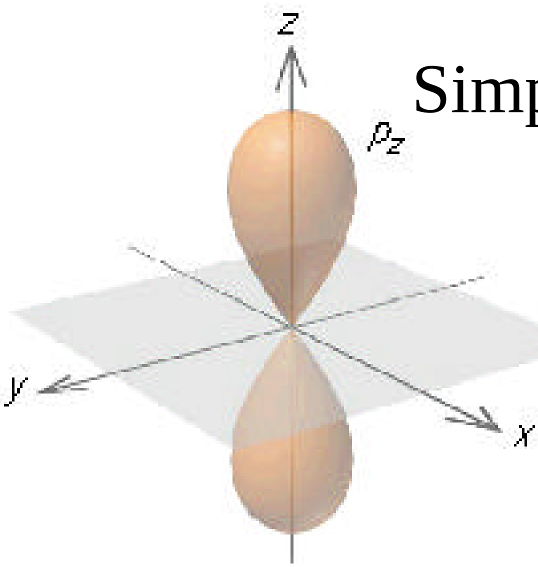
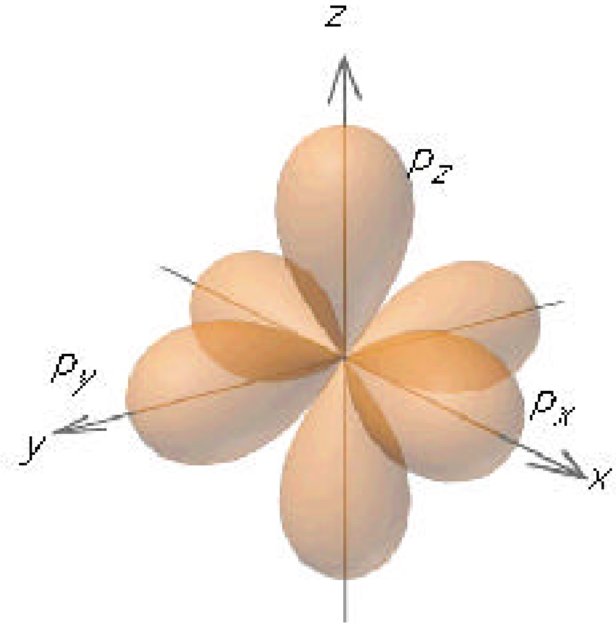




Simplified p orbital shape

- The three possible m_l values: +1, 0, and –1, which lead to three mutually perpendicular p orbitals. $\mathbf{p_x}$ $\mathbf{p_y}$ $\mathbf{p_z}$

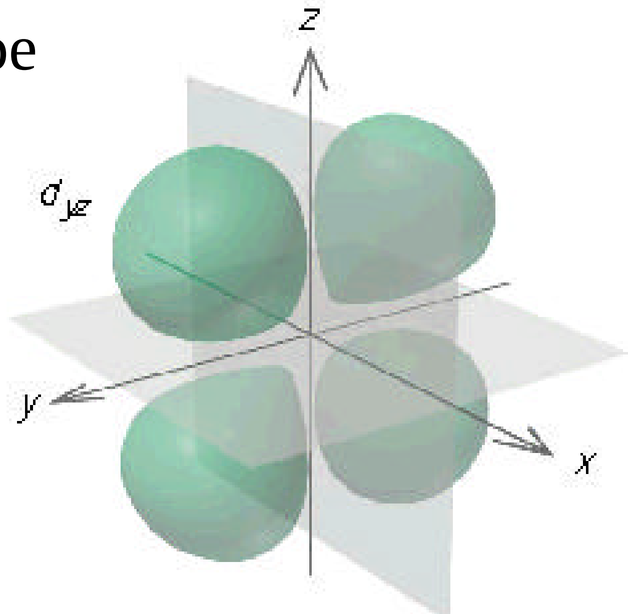


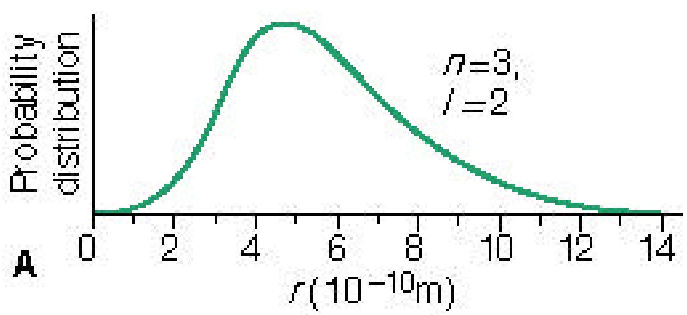
- The three p orbitals are equivalent in size, shape, and energy, differing only in orientation.

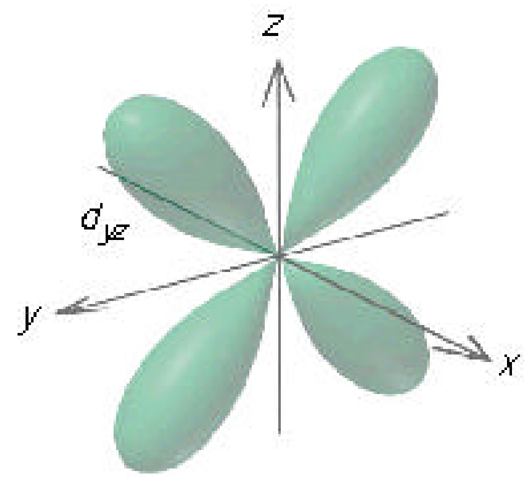
The d orbitals

- Orbitals with l = 2 are called d orbitals. There are five possible m_l values for the l = 2 sublevel: +2, +1, 0, –1, and –2.
- d orbitals can have any one of five different orientations.

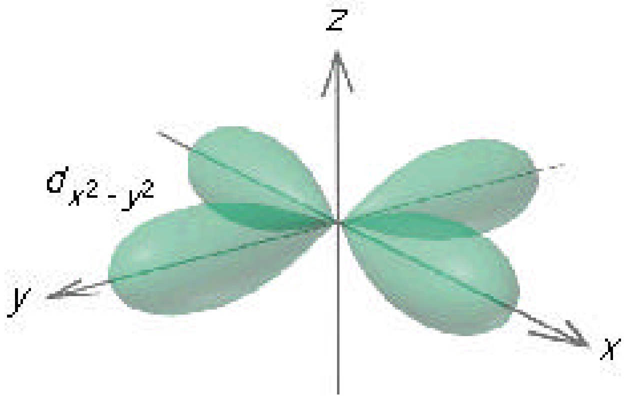
Actual shape of d_{yz}

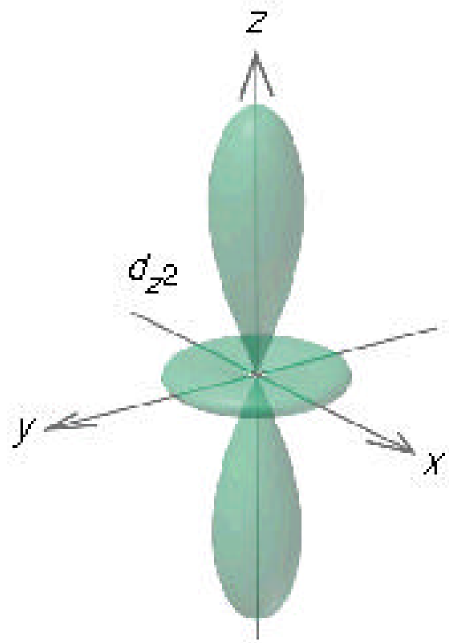


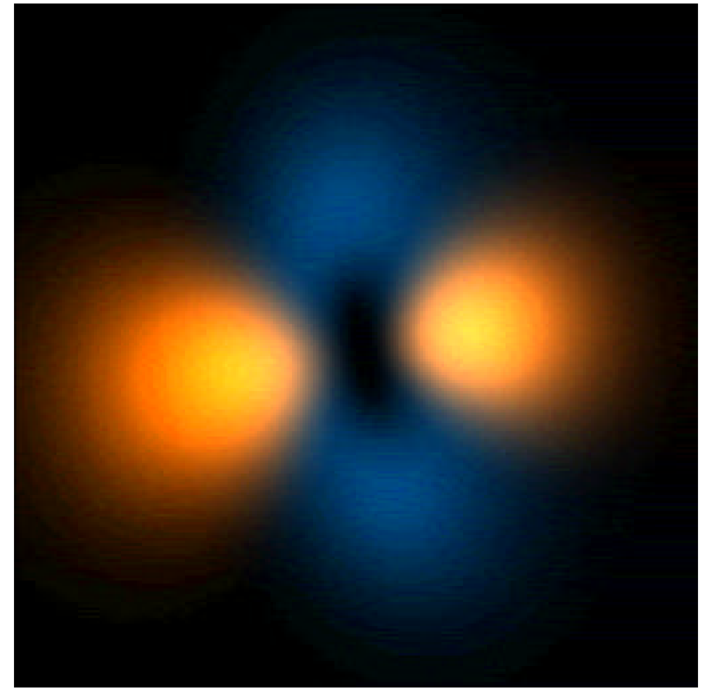




simplified shape of d_{yz}







- In accord with the quantum number rules, a d orbital must have a principal quantum number of at least n = 3.
- The 4d orbitals extend farther from the nucleus than the 3d, and the 5d orbitals extend still farther.

Energy Levels of the Hydrogen Atom

- In the ground state the electron is in the n = 1 shell (1s orbital)

n = 4 (4s, 4p, 4d, 4f)

n = 3 (3s, 3p, 3d)

- Photons of the correct energies can promote the electron to higher shells.

n = 2 (2s, 2p)

- The excited atom can return to the ground state by emitting a photon of the same energy.

n = 1 (1s)

Energy