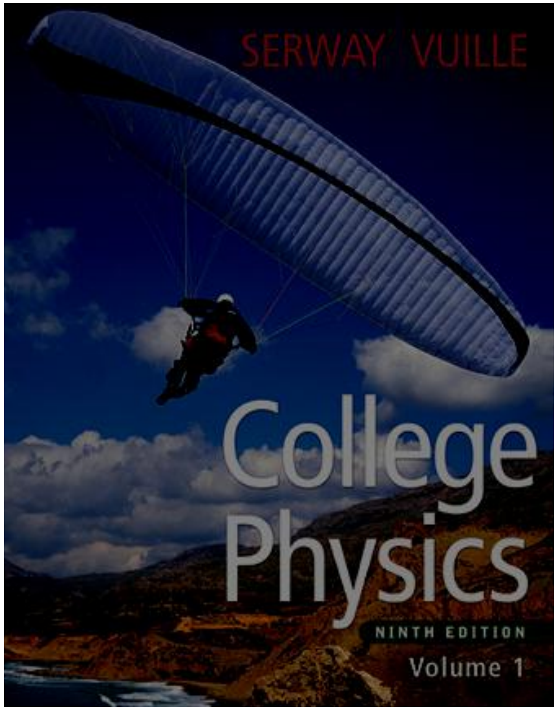


Chapter 28

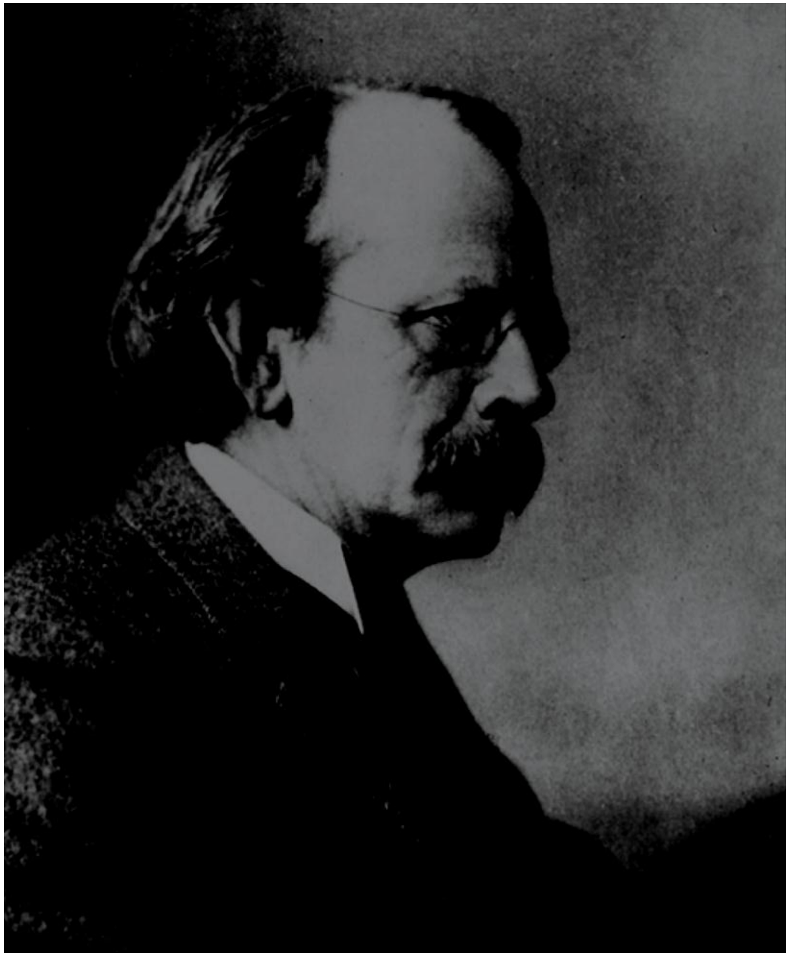
Atomic Physics

Quantum Numbers and Atomic Structure

- The characteristic wavelengths emitted by a hot gas can be understood using quantum numbers.
- No two electrons can have the same set of quantum numbers – helps us understand the arrangement of the periodic table.
- Atomic structure can be used to describe the production of x-rays and the operation of a laser.

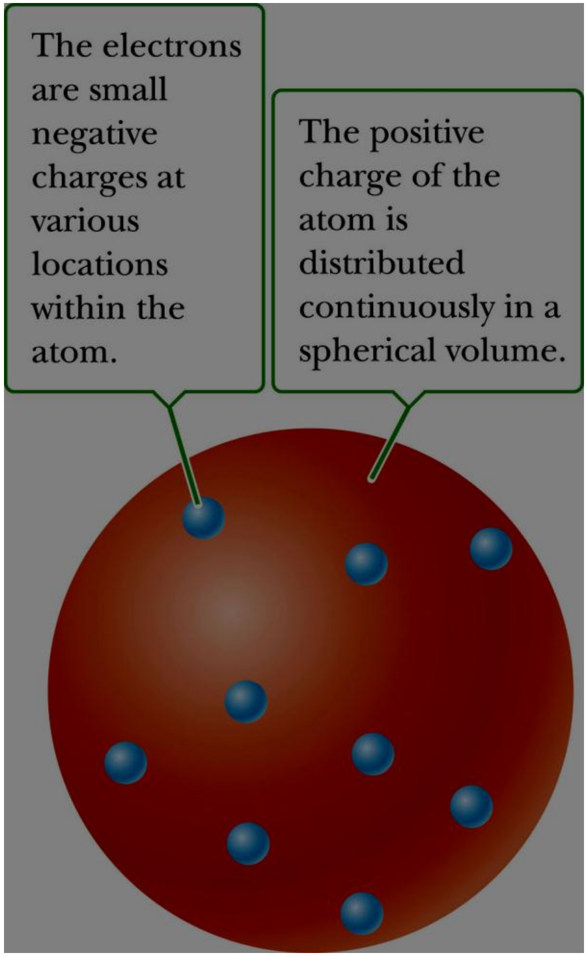
Sir Joseph John Thomson

- "J. J." Thomson
- 1856 - 1940
- Discovered the electron
- Did extensive work with cathode ray deflections
- 1906 Nobel Prize for discovery of electron

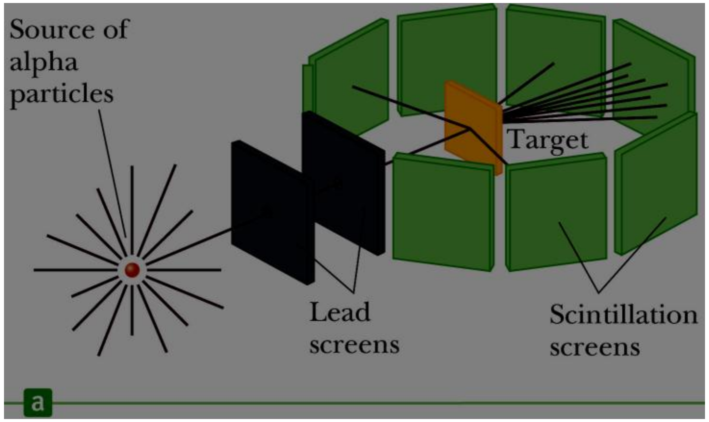


Early Models of the Atom

- J.J. Thomson's model of the atom
  - –A volume of positive charge
  - –Electrons embedded throughout the volume
- A change from Newton's model of the atom as a tiny, hard, indestructible sphere



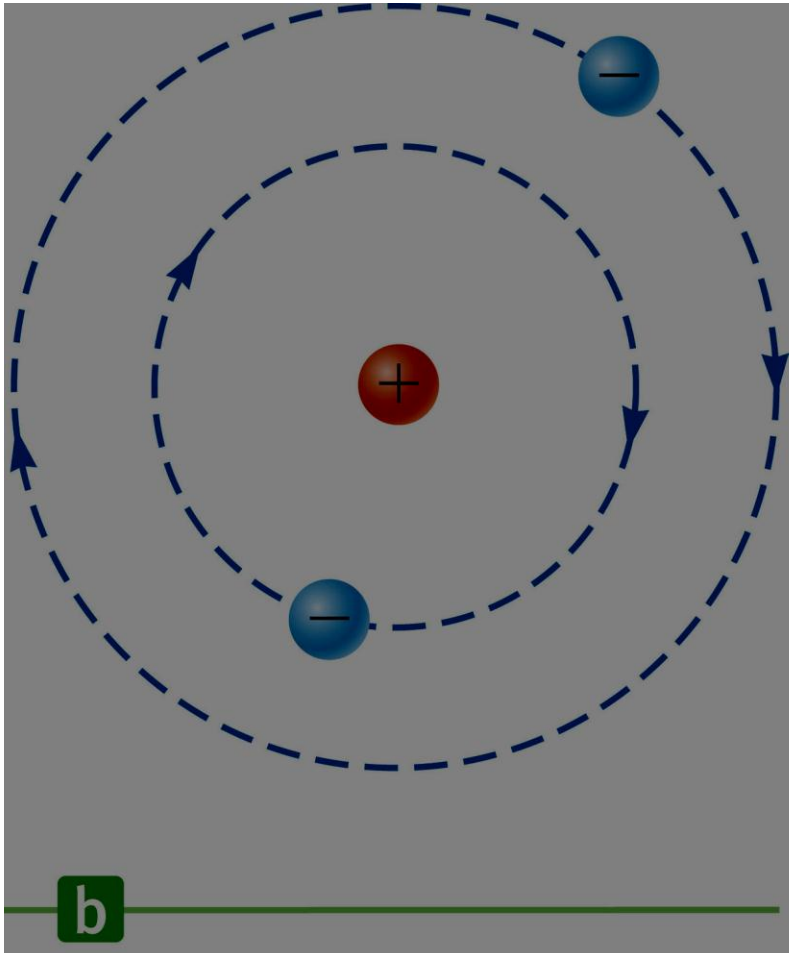
Scattering Experiments



- The source was a naturally radioactive material that produced alpha particles.
- Most of the alpha particles passed though the foil.
- A few deflected from their original paths
  - Some even reversed their direction of travel.

Early Models of the Atom, 2

- Rutherford, 1911
  - Planetary model
  - Based on results of thin foil experiments
  - Positive charge is concentrated in the center of the atom, called the *nucleus.*
  - Electrons orbit the nucleus like planets orbit the sun.



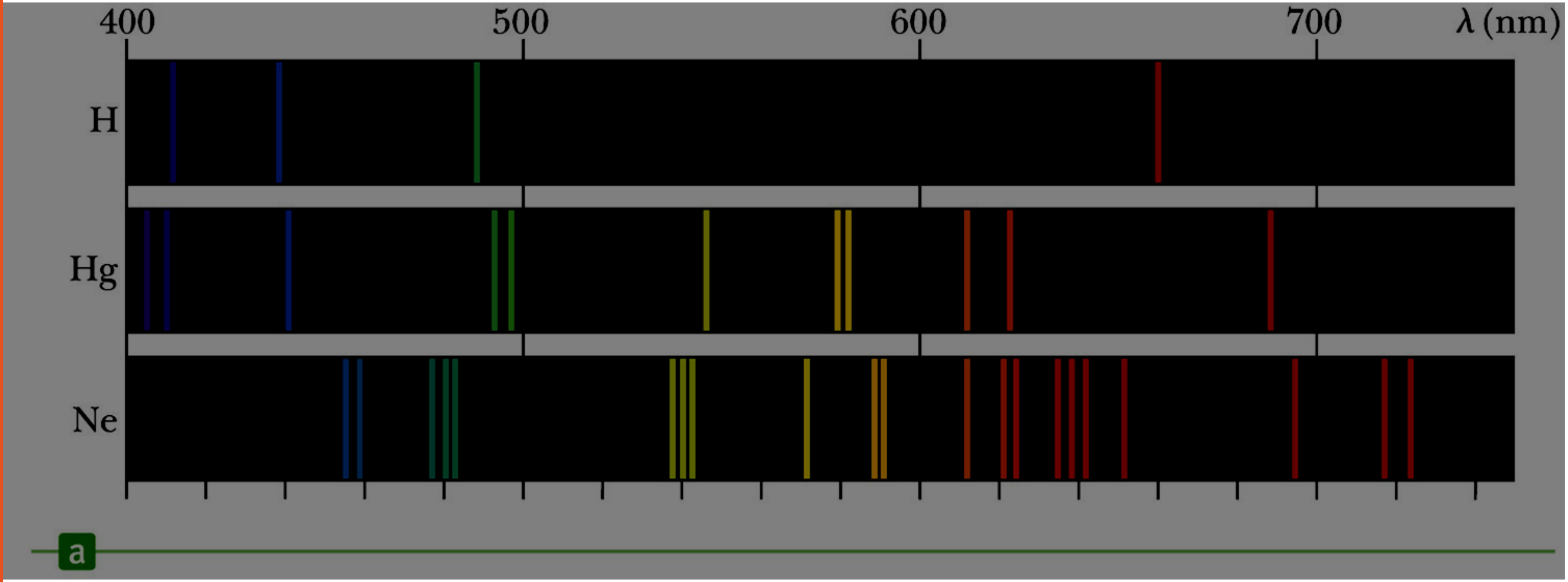
Difficulties with the Rutherford Model

- Atoms emit certain discrete characteristic frequencies of electromagnetic radiation.
  - The Rutherford model is unable to explain this phenomena.
- Rutherford's electrons are undergoing a centripetal acceleration and so should radiate electromagnetic waves of the same frequency.
  - The radius should steadily decrease as this radiation is given off.
  - The electron should eventually spiral into the nucleus, but it doesn't.

Emission Spectra

- A gas at low pressure has a voltage applied to it.
- The gas emits light which is characteristic of the gas.
- When the emitted light is analyzed with a spectrometer, a series of discrete bright lines is observed.
  - Each line has a different wavelength and color.
  - This series of lines is called an *emission spectrum.*

Examples of Emission Spectra



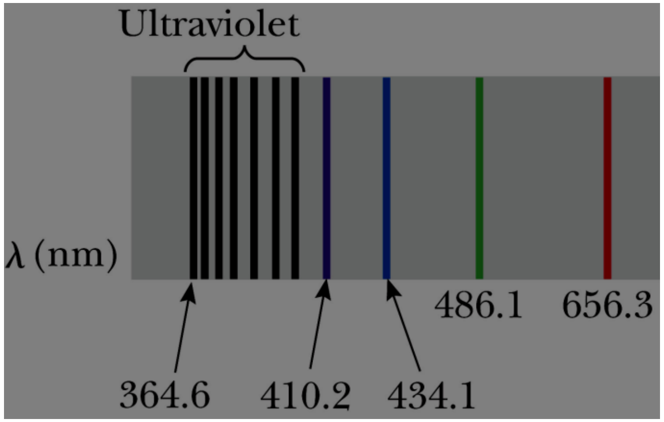
Emission Spectrum of Hydrogen – Equation

- The wavelengths of hydrogen's spectral lines can be found from

$$\frac{1}{\lambda} = R_H \left(\frac{1}{2^2} - \frac{1}{n^2} \right)$$

  - R_H is the *Rydberg constant*
    - R_H = 1.097 373 2 x 10^7 m^{-1}
  - n is an integer, n = 1, 2, 3, …
  - The spectral lines correspond to different values of n.

Spectral Lines of Hydrogen



- The Balmer Series has lines whose wavelengths are given by the preceding equation.
- Examples of spectral lines
  - $n = 3$, $\lambda = 656.3$ nm
  - $n = 4$, $\lambda = 486.1$ nm

Other Series

- Lyman series
  - Far ultraviolet
  - Ends at energy level 1
- Paschen series
  - Infrared (longer than Balmer)
  - Ends at energy level 3

General Rydberg Equation

- The Rydberg equation can apply to any series.

$$\frac{1}{\square} = R_H \left(\frac{1}{m^2} - \frac{1}{n^2} \right)$$

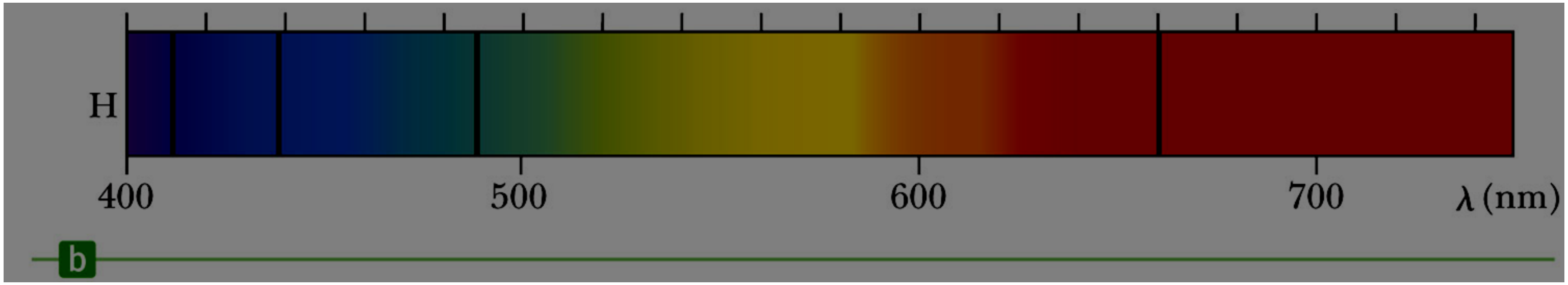
– m and n are positive integers.

– n > m.

Absorption Spectra

- An element can also absorb light at specific wavelengths.
- An absorption spectrum can be obtained by passing a continuous radiation spectrum through a vapor of the element being analyzed.
- The absorption spectrum consists of a series of dark lines superimposed on the otherwise continuous spectrum.
  - The dark lines of the absorption spectrum coincide with the bright lines of the emission spectrum.

Absorption Spectrum of Hydrogen



Application of Absorption Spectrum

- The continuous spectrum emitted by the Sun passes through the cooler gases of the Sun's atmosphere.
  - The various absorption lines can be used to identify elements in the solar atmosphere.
  - Led to the discovery of helium

Niels Bohr

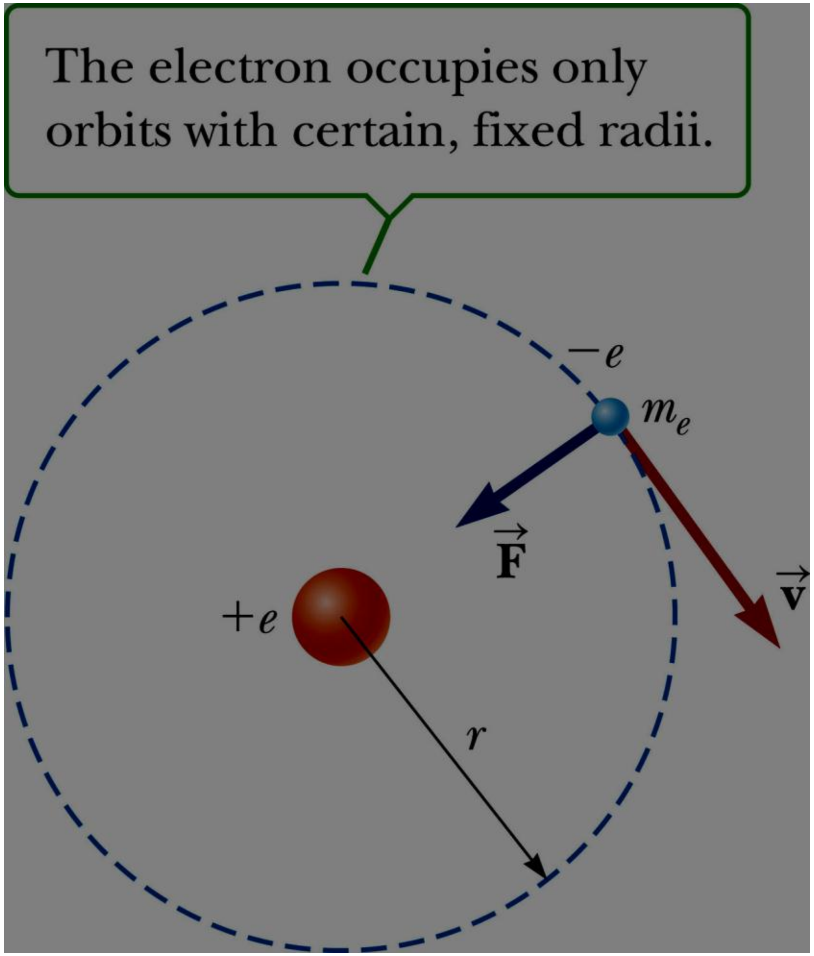
- 1885 – 1962
- Participated in the early development of quantum mechanics
- Headed Institute in Copenhagen
- 1922 Nobel Prize for structure of atoms and radiation from atoms

The Bohr Theory of Hydrogen

- In 1913 Bohr provided an explanation of atomic spectra that includes some features of the currently accepted theory.
- His model includes both classical and non-classical ideas.
- His model included an attempt to explain why the atom was stable.

Bohr’s Assumptions for Hydrogen

- The electron moves in circular orbits around the proton under the influence of the Coulomb force of attraction.
  - The Coulomb force produces the centripetal acceleration.



Bohr's Assumptions, Cont.

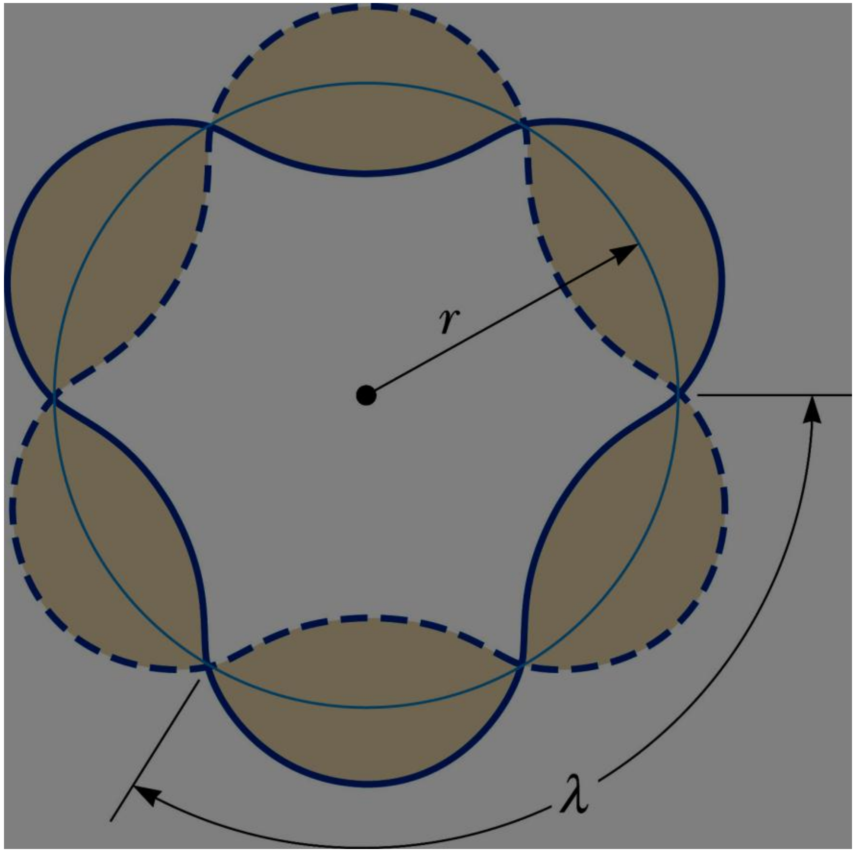
- Only certain electron orbits are stable and allowed.
  - These are the orbits in which the atom does not emit energy in the form of electromagnetic radiation.
  - Therefore, the energy of the atom remains constant.
- Radiation is emitted by the atom when the electron "jumps" from a more energetic initial state to a less energetic state.
  - The "jump" cannot be treated classically.

Bohr’s Assumptions, Final

- The electron’s “jump,” continued
  - The frequency emitted in the “jump” is related to the change in the atom’s energy.
  - The frequency is given by $E_i - E_f = h f$
  - It is *independent of the frequency of the electron’s orbital motion.*
- The circumference of the allowed electron orbits is determined by a condition imposed on the electron’s orbital angular momentum.

Electron's Orbit

- The circumference of the electron's orbit must contain an integral number of de Broglie wavelengths.
- $2 \pi r = n \lambda$
  - N = 1, 2, 3, …

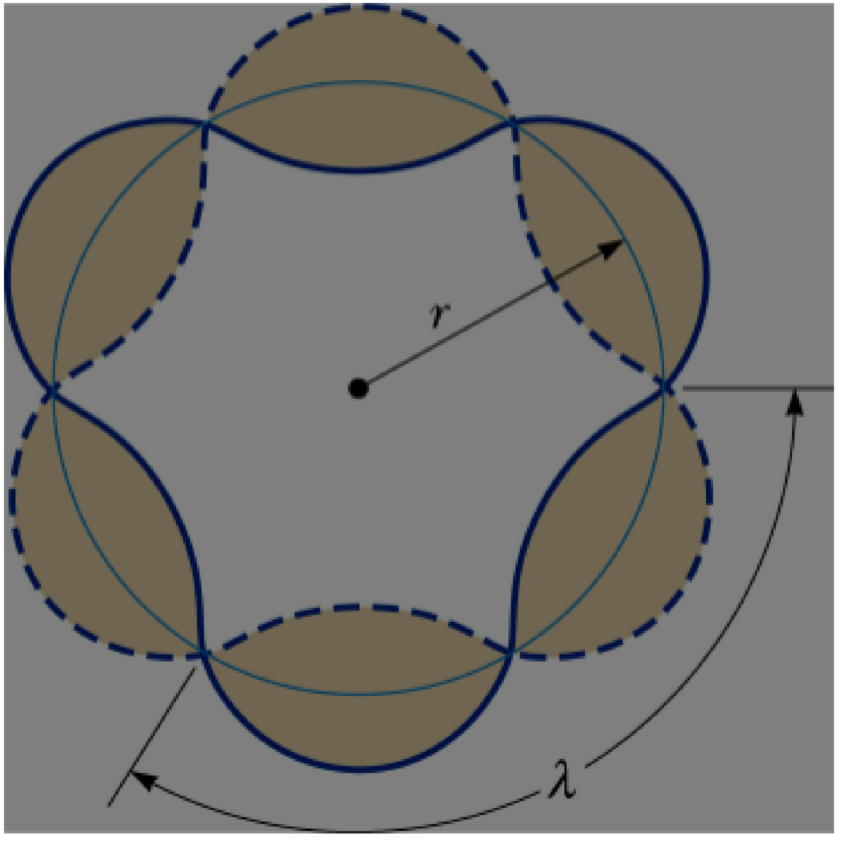


Electron's Orbit

- The circumference of the electron's orbit must contain an integral number of de Broglie wavelengths.
- $2 \pi r = n \lambda$
  - N = 1, 2, 3, …

$$r = \frac{1}{2\pi} \cdot n \cdot \lambda = \frac{1}{2\pi} \cdot n \cdot \frac{h}{mv}$$

$$\therefore mvr = n \frac{h}{2\pi} = n \hbar$$



Mathematics of Bohr's Assumptions and Results

- Electron's orbital angular momentum
  - $m_e v r = n \hbar$ where n = 1, 2, 3, …
- The total energy of the atom
  - $$E = KE + PE = \frac{1}{2} m_e v^2 - k_e \frac{e^2}{r}$$
- The energy of the atom can also be expressed as
  - $$E = -\frac{k_e e^2}{2r}$$

$$m_e \frac{v^2}{r} = \text{centripetal force}$$

$$= k_e \frac{e\,e}{r^2}$$

$$= k_e e^2 / r^2$$

$$\therefore \quad \frac{1}{2} m_e v^2 = \frac{1}{2} \cdot \frac{k_e e^2}{r^2} \cdot r = \frac{k_e e^2}{2r}$$

$$E = KE + PE$$

$$= \frac{1}{2} m_e v^2 - \frac{k_e e^2}{r} = \frac{k_e e^2}{2r} - \frac{k_e e^2}{r} = -\frac{k_e e^2}{2r}$$

Bohr radius

$$mvr = nh/2\pi \quad ① \rightarrow m^2v^2r^2 = n^2h^2/4\pi^2$$

$$mv^2/r = k_e q^2/r^2 \quad ② \rightarrow \frac{mv^2}{r} = \frac{mk_e e^2}{r^2}$$

$$(q = e) \quad = k_e e^2/r^2 \qquad \text{or } m^2v^2 = mk_e e^2/r$$

$$\therefore m^2v^2r^2 = \frac{mk_e e^2}{\cancel{r}} r^{\cancel{2}} = n^2h^2/4\pi^2$$

$$\therefore r = \frac{n^2h^2}{4\pi^2 k_e e^2 m} = \frac{n^2\hbar^2}{mk_e e^2}$$

$$r_n = \frac{n^2 \hbar^2}{m k_c e^2} \quad , n = 1, 2, \cdots n$$

$$= n^2 \cdot a_0 \quad \text{where } a_0 = \frac{\hbar^2}{m k_e e^2}.$$

$$a_0 = \frac{\left(\frac{6.626 \times 10^{-34} \, J.s}{2 \times 3.1455}\right)^2}{\left(9.109 \times 10^{-31} kg\right)\left(8.99 \times 10^9 \, N\frac{m^2}{C^2}\right)\left(1.60 \times 10^{-19} C\right)^2}$$

$$= \frac{1.111 \times 10^{-68} \, J^2 S^2}{209.64 \times 10^{-60} \, N m^2 kg} = 0.00529 \times 10^{-8} \quad \left(kg\frac{m}{S^2} \cdot m\right)^2 S^2 \Big/ kg\frac{m}{S^2} m^2 kg$$

$$= 0.0529 \text{ nm}.$$

Energy E_n.

$$E_n = -k_e \frac{e^2}{2r_n}$$

$$= -k_e \cdot \frac{e^2}{2n^2\hbar^2} \cdot m k_e e^2$$

$$= -\frac{m k_e^2 e^4}{2\hbar^2} \cdot \left(\frac{1}{n^2}\right)$$

$$= -\frac{13.6}{n^2}\, eV$$

Bohr Radius

- The radii of the Bohr orbits are quantized.

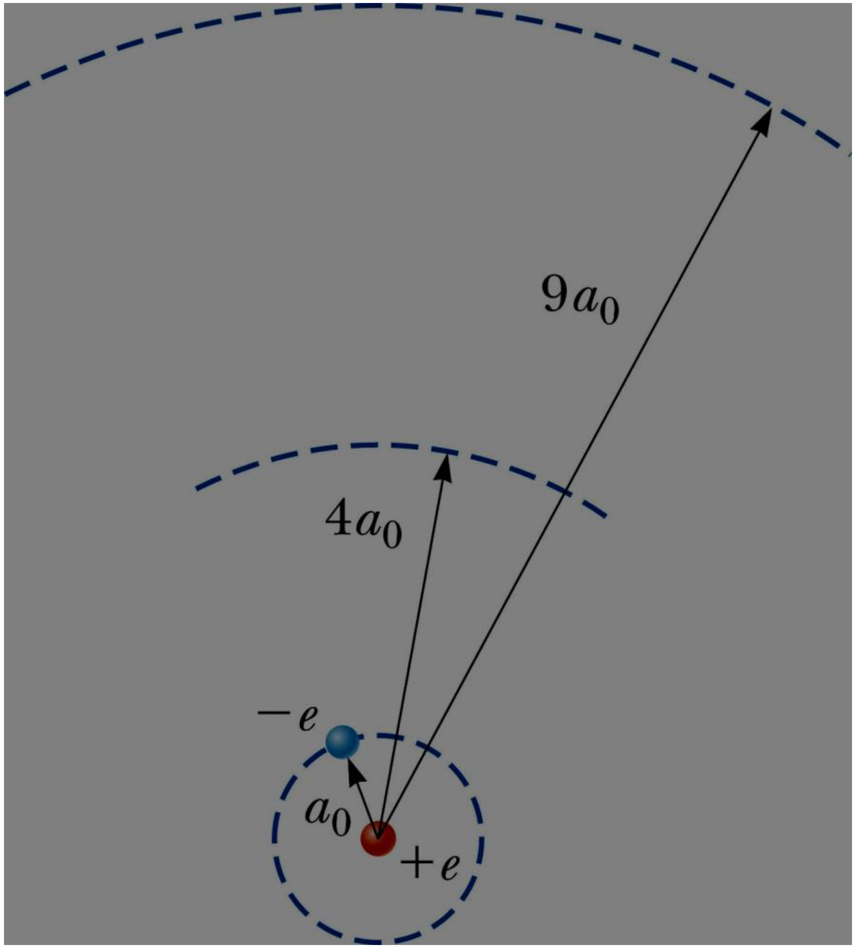
$$r_n = \frac{n^2 \hbar^2}{m_e k_e e^2} \quad n = 1, 2, 3, \ldots$$

– This is based on the assumption that the *electron can only exist in certain allowed orbits determined by the integer n.*

- When n = 1, the orbit has the smallest radius, called the *Bohr radius*, a_o
- a_o = 0.052 9 nm

Radii and Energy of Orbits

- A general expression for the radius of any orbit in a hydrogen atom is
  - $r_n = n^2 a_o$
- The energy of any orbit is
  - $E_n = - 13.6 \text{ eV}/ n^2$



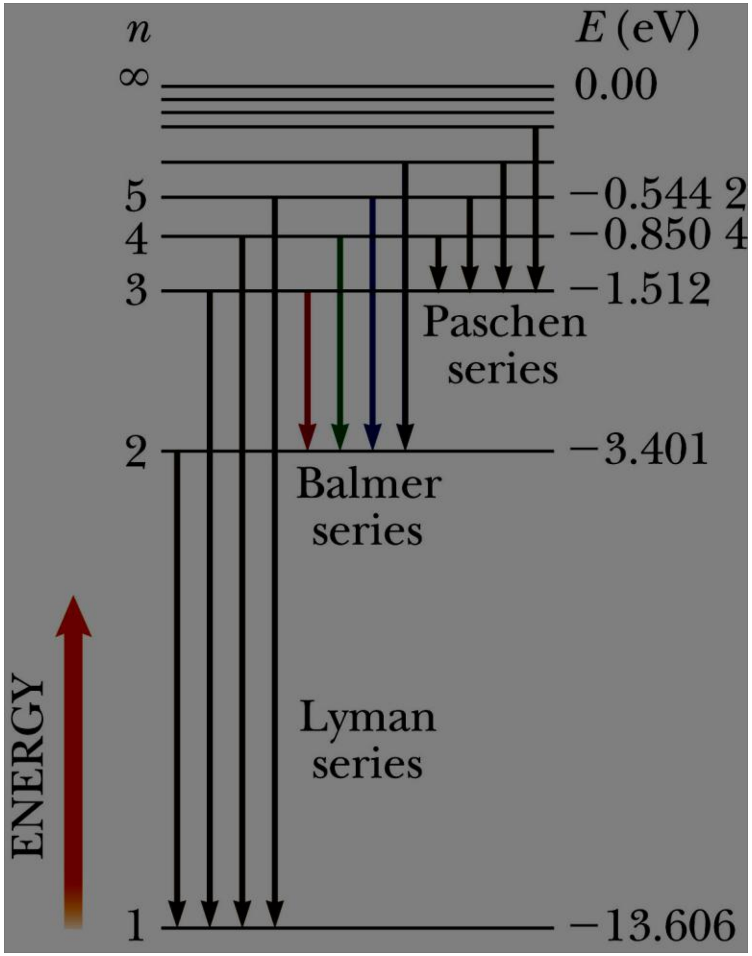
Specific Energy Levels

- The lowest energy state is called the *ground state.*
  - This corresponds to n = 1
  - Energy is –13.6 eV
- The next energy level has an energy of –3.40 eV.
  - The energies can be compiled in an *energy level diagram.*

Specific Energy Levels, Cont.

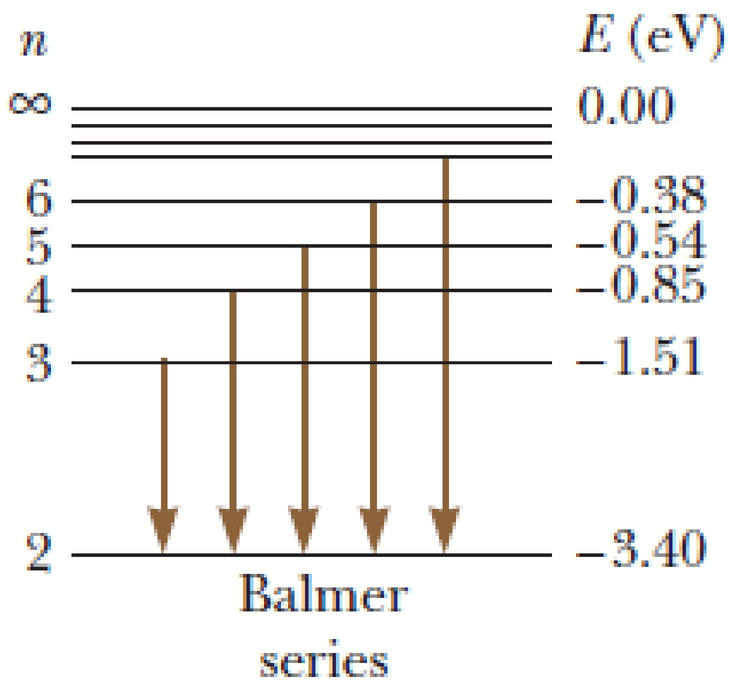
- The *ionization energy* is the energy needed to completely remove the electron from the atom.
  - The ionization energy for hydrogen is 13.6 eV
- The uppermost level corresponds to E = 0 and n ⍰ ⍰

Energy Level Diagram



Section 28.3

PROBLEM The Balmer series for the hydrogen atom corresponds to electronic transitions that terminate in the state with quantum number $n = 2$, as shown in Figure **(a)** Find the longest-wavelength photon emitted in the Balmer series and determine its frequency and energy. **(b)** Find the shortest-wavelength photon emitted in the same series.



$$\frac{1}{\lambda} = R_{\mathrm{H}}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) = R_{\mathrm{H}}\left(\frac{1}{2^2} - \frac{1}{3^2}\right) = \frac{5R_{\mathrm{H}}}{36}$$

$$\lambda = \frac{36}{5R_{\mathrm{H}}} = \frac{36}{5(1.097 \times 10^{7}\ \mathrm{m}^{-1})} = 6.563 \times 10^{-7}\ \mathrm{m}$$

$$= \boxed{656.3\ \mathrm{nm}}$$

$$f = \frac{c}{\lambda} = \frac{2.998 \times 10^{8}\ \mathrm{m/s}}{6.563 \times 10^{-7}\ \mathrm{m}} = \boxed{4.568 \times 10^{14}\ \mathrm{Hz}}$$

$$E = hf = (6.626 \times 10^{-34}\ \mathrm{J \cdot s})(4.568 \times 10^{14}\ \mathrm{Hz}) = 3.027 \times 10^{-19}\ \mathrm{J}$$

$$= 3.027 \times 10^{-19}\ \mathrm{J}\left(\frac{1\ \mathrm{eV}}{1.602 \times 10^{-19}\ \mathrm{J}}\right) = \boxed{1.892\ \mathrm{eV}}$$

$$\frac{1}{\lambda} = R_{\mathrm{H}}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) = R_{\mathrm{H}}\left(\frac{1}{2^2} - 0\right) = \frac{R_{\mathrm{H}}}{4}$$

$$\lambda = \frac{4}{R_{\mathrm{H}}} = \frac{4}{(1.097 \times 10^7\ \mathrm{m}^{-1})} = 3.646 \times 10^{-7}\ \mathrm{m}$$

$$= \boxed{364.6\ \mathrm{nm}}$$

Generalized Equation

- The value of R_H from Bohr's analysis is in excellent agreement with the experimental value.
- A more generalized equation can be used to find the wavelengths of any spectral lines.

$$\frac{1}{\lambda} = R_H \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

  – For the Balmer series, $n_f = 2$
  – For the Lyman series, $n_f = 1$
- Whenever a transition occurs between a state, n_i to another state, n_f (where $n_i > n_f$), a photon is emitted.
  – The photon has a frequency $f = (E_i - E_f)/h$ and wavelength λ

Bohr's Correspondence Principle

- Bohr's *Correspondence Principle* states that quantum mechanics is in agreement with classical physics when the energy differences between quantized levels are very small.
  - Similar to having Newtonian Mechanics be a special case of relativistic mechanics when $v << c$

Successes of the Bohr Theory

- Explained several features of the hydrogen spectrum
- Can be extended to "hydrogen-like" atoms
  - Those with one electron
  - Ze^2 needs to be substituted for e^2 in equations.
- Z is the atomic number of the element.

Quantum Mechanics and the Hydrogen Atom

- One of the first great achievements of quantum mechanics was the solution of the wave equation for the hydrogen atom.
- The energies of the allowed states are in exact agreement with the values obtained by Bohr when the allowed energy levels depend only on the principle quantum numbers.

Quantum Numbers

- n – principle quantum number
- Two other quantum numbers emerge from the solution of Schrödinger equation.
  - ℓ – orbital quantum number
  - m_ℓ – orbital magnetic quantum number

Shells and Subshells

- All states with the same principle quantum number, n, are said to form a shell.
  - Shells are identified as K, L, M, …
  - Correspond to n = 1, 2, 3, …
- The states with given values of m and ℓ are said to form a subshell.
- See table 28.2 for a summary.

Quantum Number Summary

- The values of n can range from 1 to ⍰ in integer steps.
- The values of ℓ can range from 0 to n-1 in integer steps.
- The values of m_{ℓ} can range from -ℓ to ℓ in integer steps.

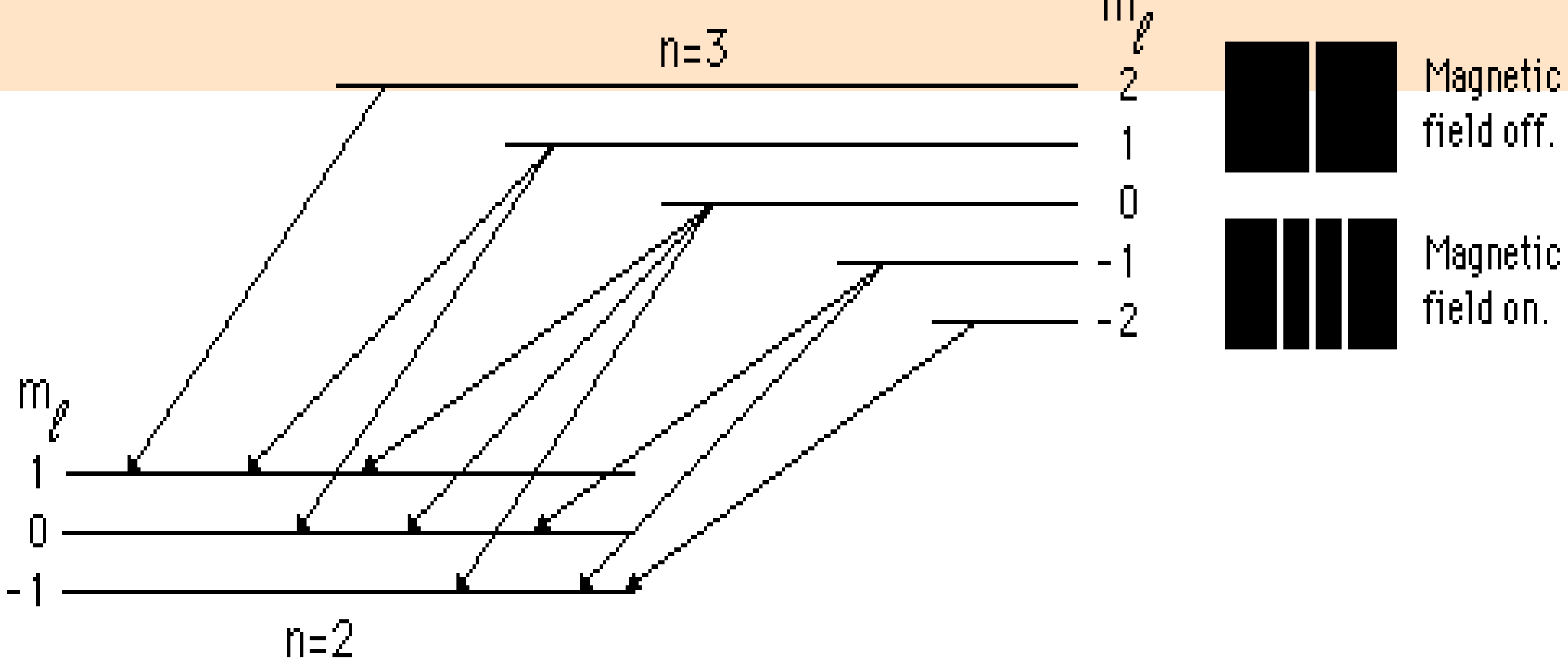
–Also see Table 28.1

Table 28.1 Three Quantum Numbers for the Hydrogen Atom

Quantum Number	Name	Allowed Values	Number of Allowed States
n	Principal quantum number	$1, 2, 3, \ldots$	Any number
ℓ	Orbital quantum number	$0, 1, 2, \ldots, n-1$	n
m_ℓ	Orbital magnetic quantum number	$-\ell, -\ell+1, \ldots, 0, \ldots, \ell-1, \ell$	$2\ell+1$

Table 28.2 Shell and Subshell Notation

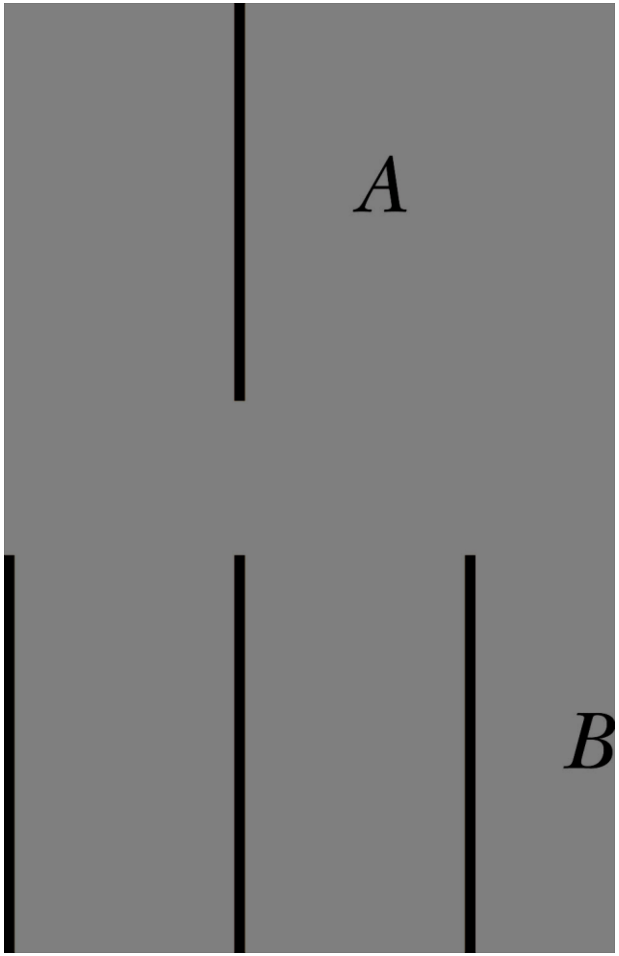
n	Shell Symbol	ℓ	Subshell Symbol
1	K	0	s
2	L	1	p
3	M	2	d
4	N	3	f
5	O	4	g
6	P	5	h



m_ℓ
n=3
2
1
0
-1
-2
Magnetic field off.
Magnetic field on.
m_ℓ
1
0
-1
n=2

Zeeman Effect

- The Zeeman effect is the splitting of spectral lines in a strong magnetic field.
  - This indicates that the energy of an electron is slightly modified when the atom is immersed in a magnetic field.
  - This is seen in the quantum number m_ℓ

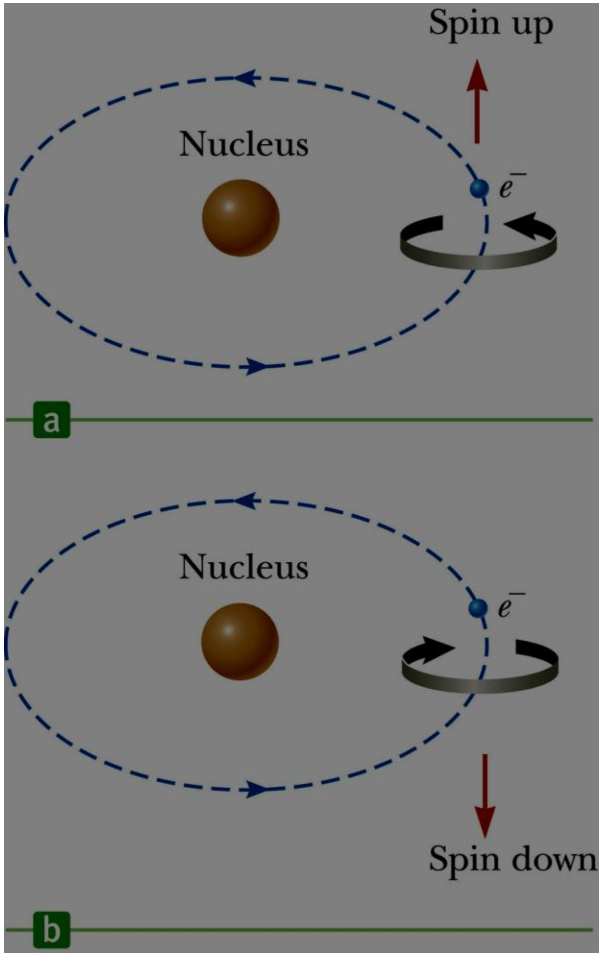


Spin Magnetic Quantum Number

- Some spectral lines were found to actually be two very closely spaced lines.
- This splitting is called **fine structure.**
- A fourth quantum number, spin magnetic quantum number, was introduced to explain fine structure.
  – This quantum number does not come from the solution of Schödinger's equation.

Spin Magnetic Quantum Number

- It is convenient to think of the electron as spinning on its axis.
  - The electron is *not* physically spinning.
- There are two directions for the spin
  - Spin up, $m_s = ½$
  - Spin down, $m_s = -½$
- There is a slight energy difference between the two spins and this accounts for the doublet in some lines.

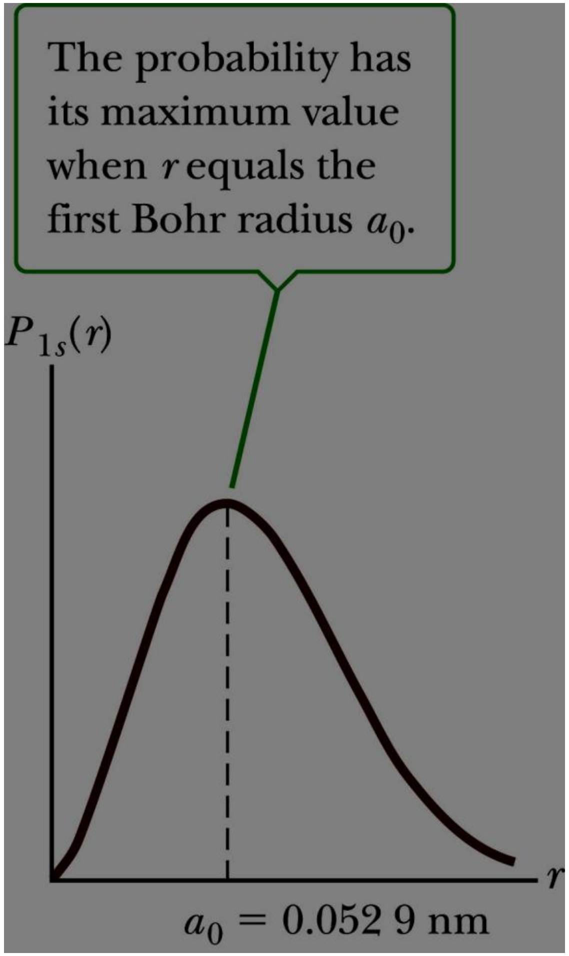


Spin Notes

- A classical description of electron spin is incorrect.
  - Since the electron cannot be located precisely in space, it cannot be considered to be a spinning solid object.
  - Electron spin is a purely quantum effect that gives the electron an angular momentum as if it were physically spinning.
- Paul Dirac developed a relativistic quantum theory in which spin naturally arises.

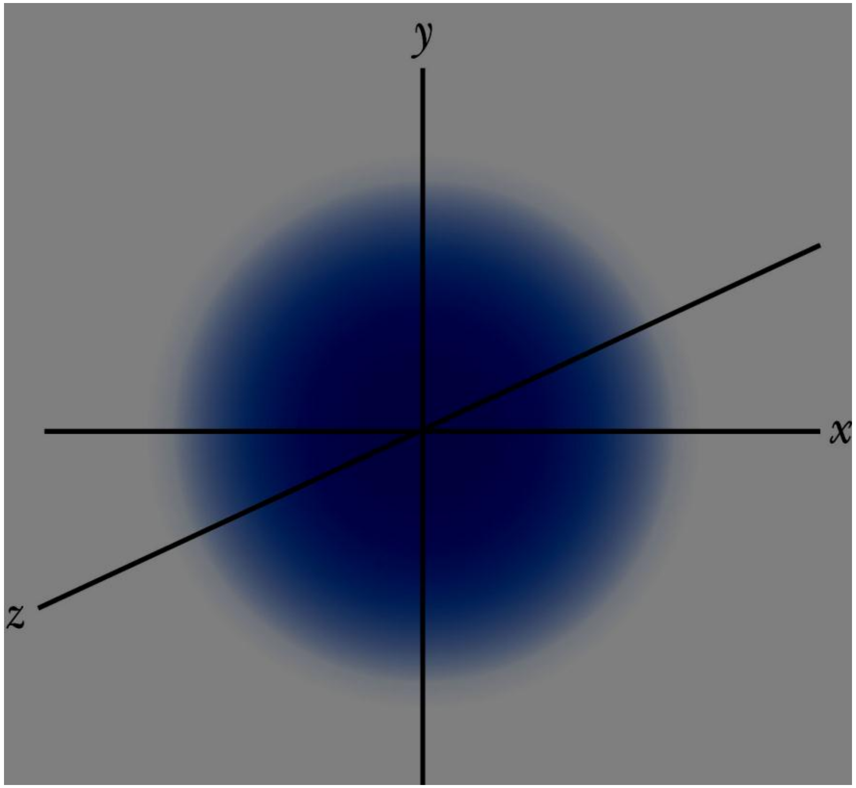
Electron Clouds

- The graph shows the solution to the wave equation for hydrogen in the ground state.
  - The curve peaks at the Bohr radius.
  - The electron is not confined to a particular orbital distance from the nucleus.
- The *probability* of finding the electron at the Bohr radius is a maximum.



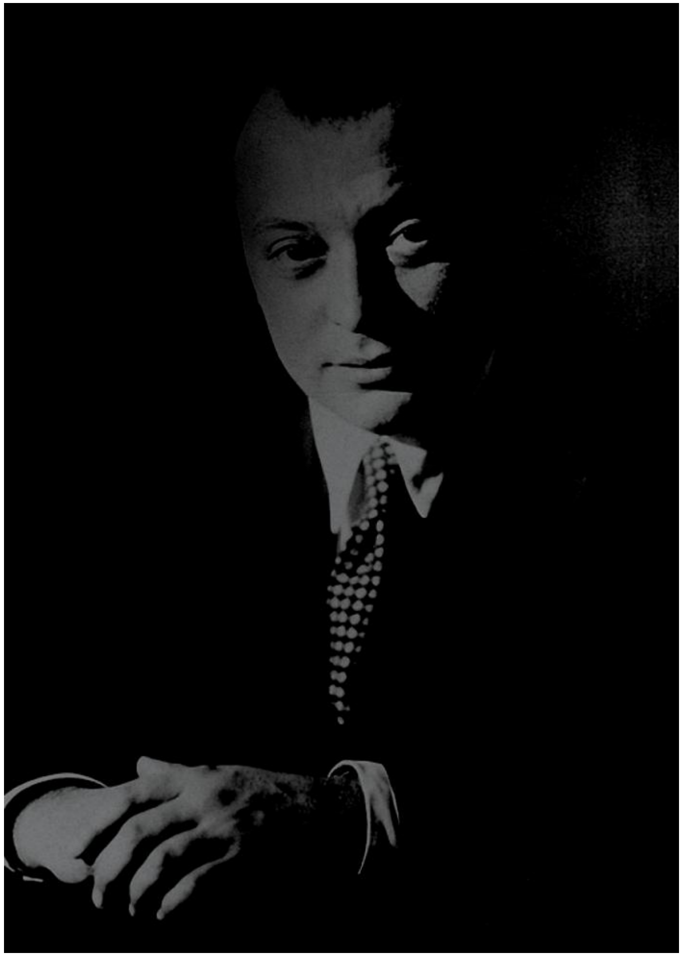
Electron Clouds, Cont.

- The wave function for hydrogen in the ground state is symmetric.
  - The electron can be found in a spherical region surrounding the nucleus.
- The result is interpreted by viewing the electron as a cloud surrounding the nucleus.
  - The densest regions of the cloud represent the highest probability for finding the electron.



Wolfgang Pauli

- 1900 – 1958
- Contributions include
  - Major review of relativity
  - Exclusion Principle
  - Connect between electron spin and statistics
  - Theories of relativistic quantum electrodynamics
  - Neutrino hypothesis
  - Nuclear spin hypothesis



The Pauli Exclusion Principle

- No two electrons in an atom can ever have the same set of values of the quantum numbers n, ℓ, m_ℓ, and m_s
- This explains the electronic structure of complex atoms as a succession of filled energy levels with different quantum numbers.

Filling Shells

- As a general rule, the order that electrons fill an atom's subshell is:
  - Once one subshell is filled, the next electron goes into the vacant subshell that is lowest in energy.
  - Otherwise, the electron would radiate energy until it reached the subshell with the lowest energy.
  - A subshell is filled when it holds $2(2\ell+1)$ electrons.
  - See table 28.3.

Table 28.3 Number of Electrons in Filled Subshells and Shells

Shell	Subshell	Number of Electrons in Filled Subshell	Number of Electrons in Filled Shell
K ($n = 1$)	$s(\ell = 0)$	2	2
L ($n = 2$)	$s(\ell = 0)$	2	8
	$p(\ell = 1)$	6	
	$s(\ell = 0)$	2	
M ($n = 3$)	$p(\ell = 1)$	6	18
	$d(\ell = 2)$	10	
	$s(\ell = 0)$	2	
N ($n = 4$)	$p(\ell = 1)$	6	32
	$d(\ell = 2)$	10	
	$f(\ell = 3)$	14	

Table 28.4 Electronic Configurations of Some Elements

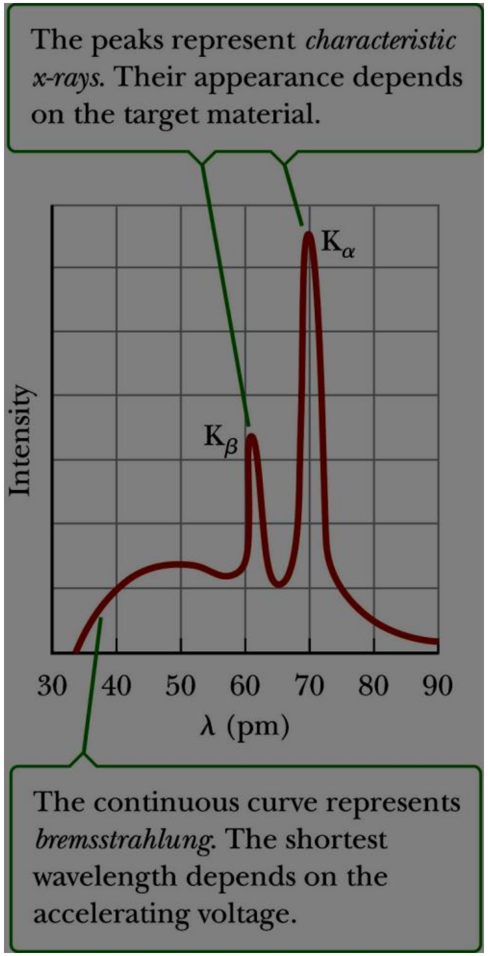
Z	Symbol	Ground-State Configuration	Ionization Energy (eV)	Z	Symbol	Ground-State Configuration	Ionization Energy (eV)
1	H	$1s^1$	13.595	19	K	[Ar] $4s^1$	4.339
2	He	$1s^2$	24.581	20	Ca	$4s^2$	6.111
				21	Sc	$3d4s^2$	6.54
3	Li	[He] $2s^1$	5.390	22	Ti	$3d^24s^2$	6.83
4	Be	$2s^2$	9.320	23	V	$3d^34s^2$	6.74
5	B	$2s^22p^1$	8.296	24	Cr	$3d^54s^1$	6.76
6	C	$2s^22p^2$	11.256	25	Mn	$3d^54s^2$	7.432
7	N	$2s^22p^3$	14.545	26	Fe	$3d^64s^2$	7.87
8	O	$2s^22p^4$	13.614	27	Co	$3d^74s^2$	7.86
9	F	$2s^22p^5$	17.418	28	Ni	$3d^84s^2$	7.633
10	Ne	$2s^22p^6$	21.559	29	Cu	$3d^{10}4s^1$	7.724
				30	Zn	$3d^{10}4s^2$	9.391

The Periodic Table

- The outermost electrons are primarily responsible for the chemical properties of the atom.
- Mendeleev arranged the elements according to their atomic masses and chemical similarities.
- The electronic configuration of the elements explained by quantum numbers and Pauli's Exclusion Principle explains the configuration.

Characteristic X-Rays

- When a metal target is bombarded by high-energy electrons, x-rays are emitted.
- The x-ray spectrum typically consists of a broad continuous spectrum and a series of sharp lines.
  - The lines are dependent on the metal of the target.
  - The lines are called *characteristic x-rays.*

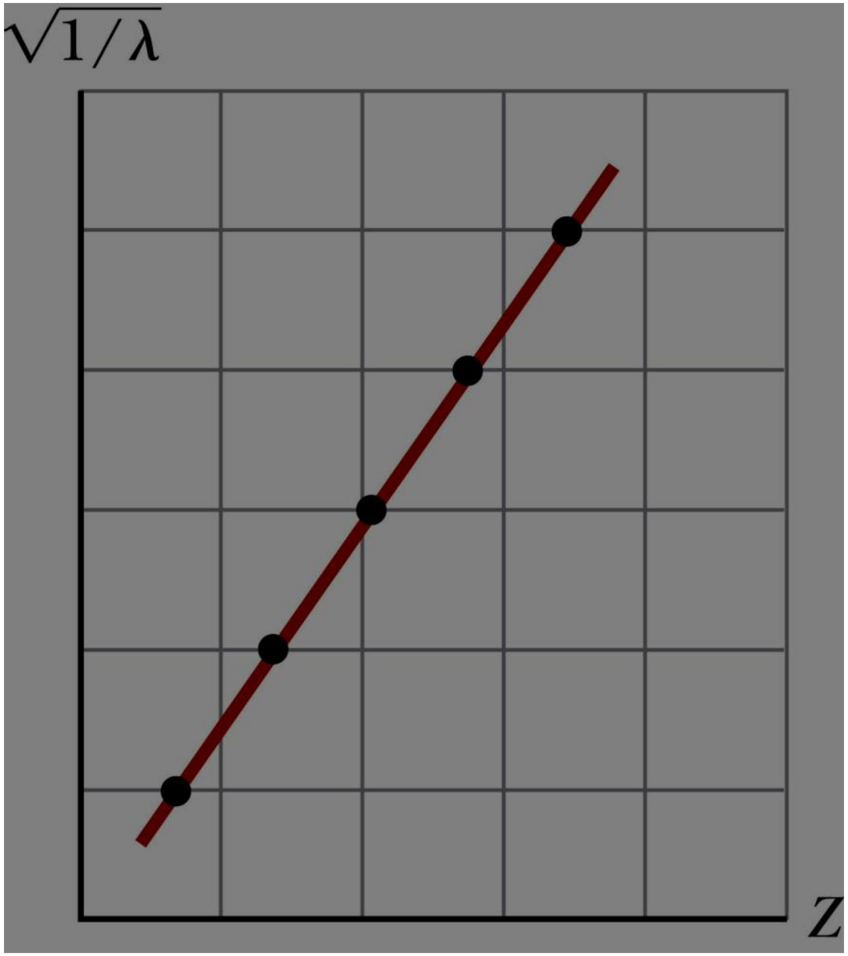


Explanation of Characteristic X-Rays

- The details of atomic structure can be used to explain characteristic x-rays.
  - A bombarding electron collides with an electron in the target metal that is in an inner shell.
  - If there is sufficient energy, the electron is removed from the target atom.
  - The vacancy created by the lost electron is filled by an electron falling to the vacancy from a higher energy level.
  - The transition is accompanied by the emission of a photon whose energy is equal to the difference between the two levels.

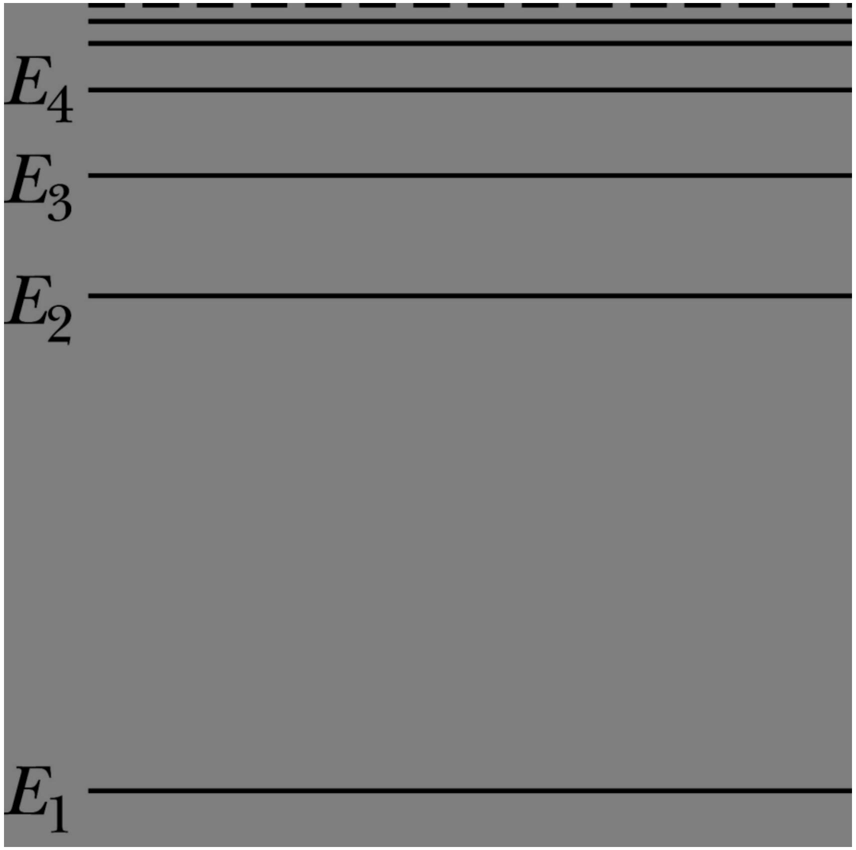
Moseley Plot

- λ is the wavelength of the $K_{?}$ line
  - $K_{?}$ is the line that is produced by an electron falling from the L shell to the K shell.
- From this plot, Moseley was able to determine the Z values of other elements and produce a periodic chart in excellent agreement with the known chemical properties of the elements.



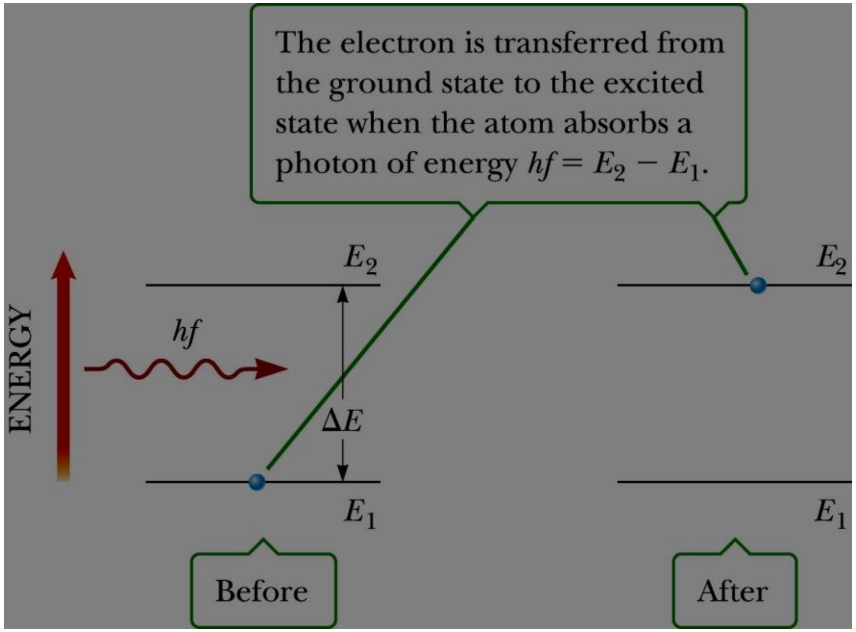
Atomic Transitions – Energy Levels

- An atom may have many possible energy levels.
- At ordinary temperatures, most of the atoms in a sample are in the ground state.
- Only photons with energies corresponding to differences between energy levels can be absorbed.



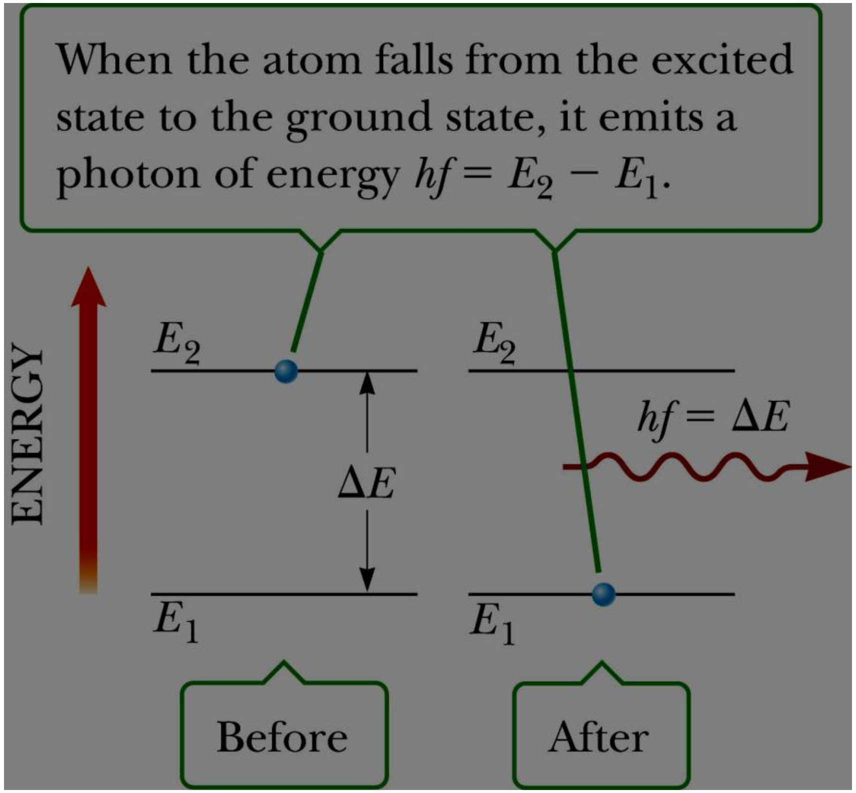
Atomic Transitions – Stimulated Absorption

- The blue dots represent electrons.
- When a photon with energy ΔE is absorbed, one electron jumps to a higher energy level.
  - These higher levels are called *excited states.*
  - $\Delta E = hf = E_2 - E_1$
  - In general, ΔE can be the difference between any two energy levels.



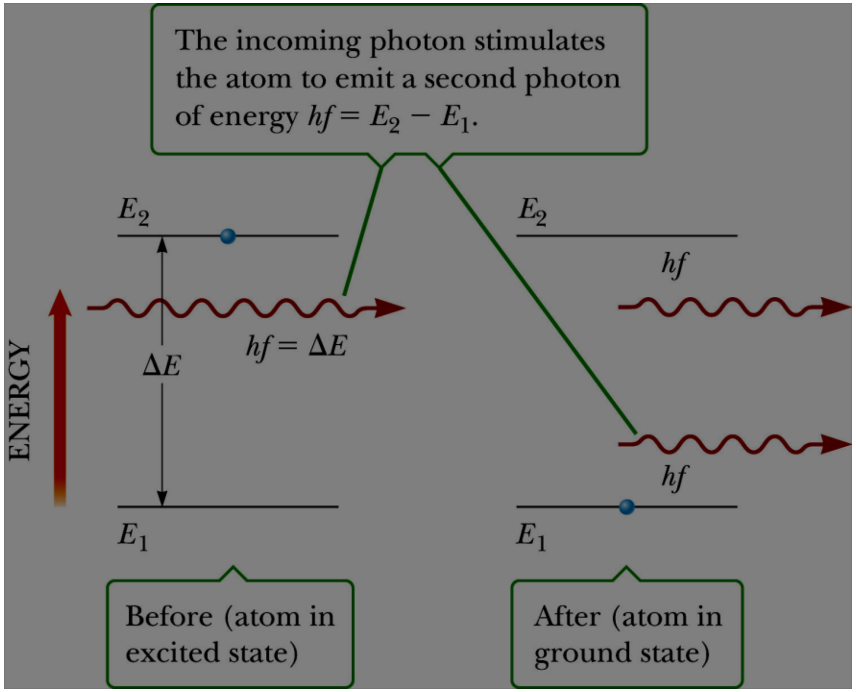
Atomic Transitions – Spontaneous Emission

- Once an atom is in an excited state, there is a constant probability that it will jump back to a lower state by emitting a photon.
- This process is called *spontaneous emission.*
- Typically, an atom will remain in an excited state for about 10^{-8} s



Atomic Transitions – Stimulated Emission

- An atom is in an excited state and a photon is incident on it.
- The incoming photon increases the probability that the excited atom will return to the ground state.
- There are two emitted photons, the incident one and the emitted one.
  - The emitted photon is exactly in phase with the incident photon.



Population Inversion

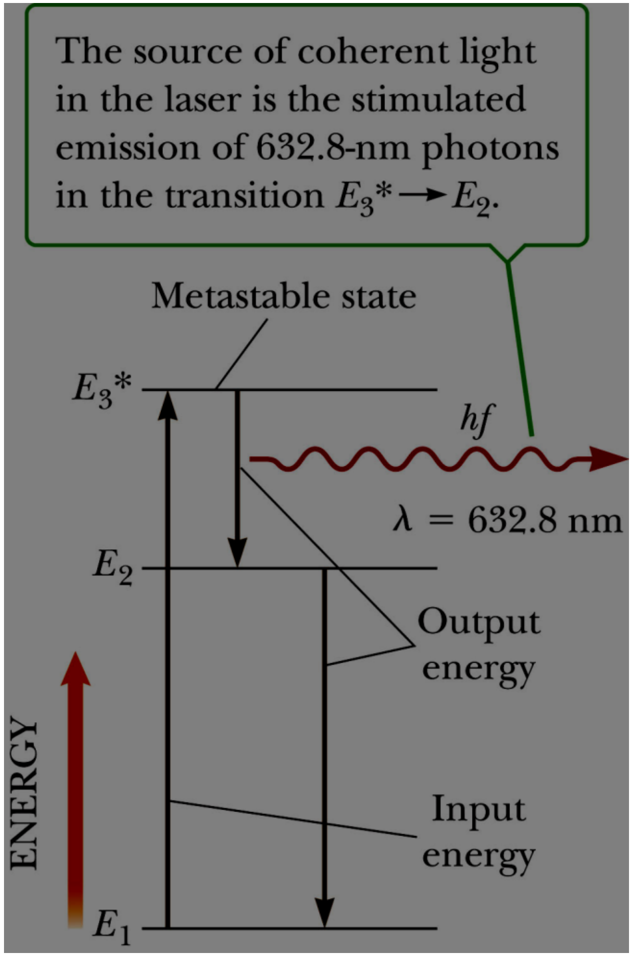
- When light is incident on a system of atoms, both stimulated absorption and stimulated emission are equally probable.
- Generally, a net absorption occurs since most atoms are in the ground state.
- If you can cause more atoms to be in excited states, a net emission of photons can result.
  – This situation is called a *population inversion.*

Lasers

- To achieve laser action, three conditions must be met
  - The system must be in a state of population inversion.
    - More atoms in an excited state than the ground state
  - The excited state of the system must be a *metastable state.*
    - Its lifetime must be long compared to the normal lifetime of an excited state.
  - The emitted photons must be confined in the system long enough to allow them to stimulate further emission from other excited atoms.
    - This is achieved by using reflecting mirrors.

Laser Beam – He Ne Example

- The energy level diagram for Ne in a He-Ne laser
- The mixture of helium and neon is confined to a glass tube sealed at the ends by mirrors.
- An applied high voltage causes electrons to sweep through the tube, producing excited states.
- When the electron falls to E_2 from E^*_3 in Ne, a 632.8 nm photon is emitted.



Production of a Laser Beam