Chapter 42

Atomic Physics

42.1 Atomic Spectra of Gases

42.2 Early Models of the Atom

42.3 Bohr's Model of the Hydrogen Atom

42.4 The Quantum Model of the Hydrogen Atom

42.8 More on Atomic Spectra: Visible and Xray

Application of Quantum Mechanics to Atomic Physics

- A large portion of the chapter focuses on the hydrogen atom.
- Reasons for the importance of the hydrogen atom include.
  - The hydrogen atom is the only atomic system that can be solved exactly.
  - Much of what was learned in the twentieth century about the hydrogen atom, with its single electron, can be extended to such single-electron ions as He^{+} and Li^{2+}.
  - The hydrogen atom is an ideal system for performing precision tests of theory against experiment.
    - Also for improving our understanding of atomic structure.
  - The quantum numbers that are used to characterize the allowed states of hydrogen can also be used to investigate more complex atoms.
    - This allows us to understand the periodic table.
  - The basic ideas about atomic structure must be well understood before we attempt to deal with the complexities of molecular structures and the electronic structure of solids.

Other Ideas in Atomic Physics

- The full mathematical solution of the Schrödinger equation applied to the hydrogen atom gives a complete and beautiful description of the atom's properties.
- Quantum numbers are used to characterize various allowed states in the atom.
- The quantum numbers have physical significance.
- Certain quantum states are affected by a magnetic field.
- The exclusion principle is important for understanding the properties of multielectron atoms and the arrangement of the elements in the periodic table.

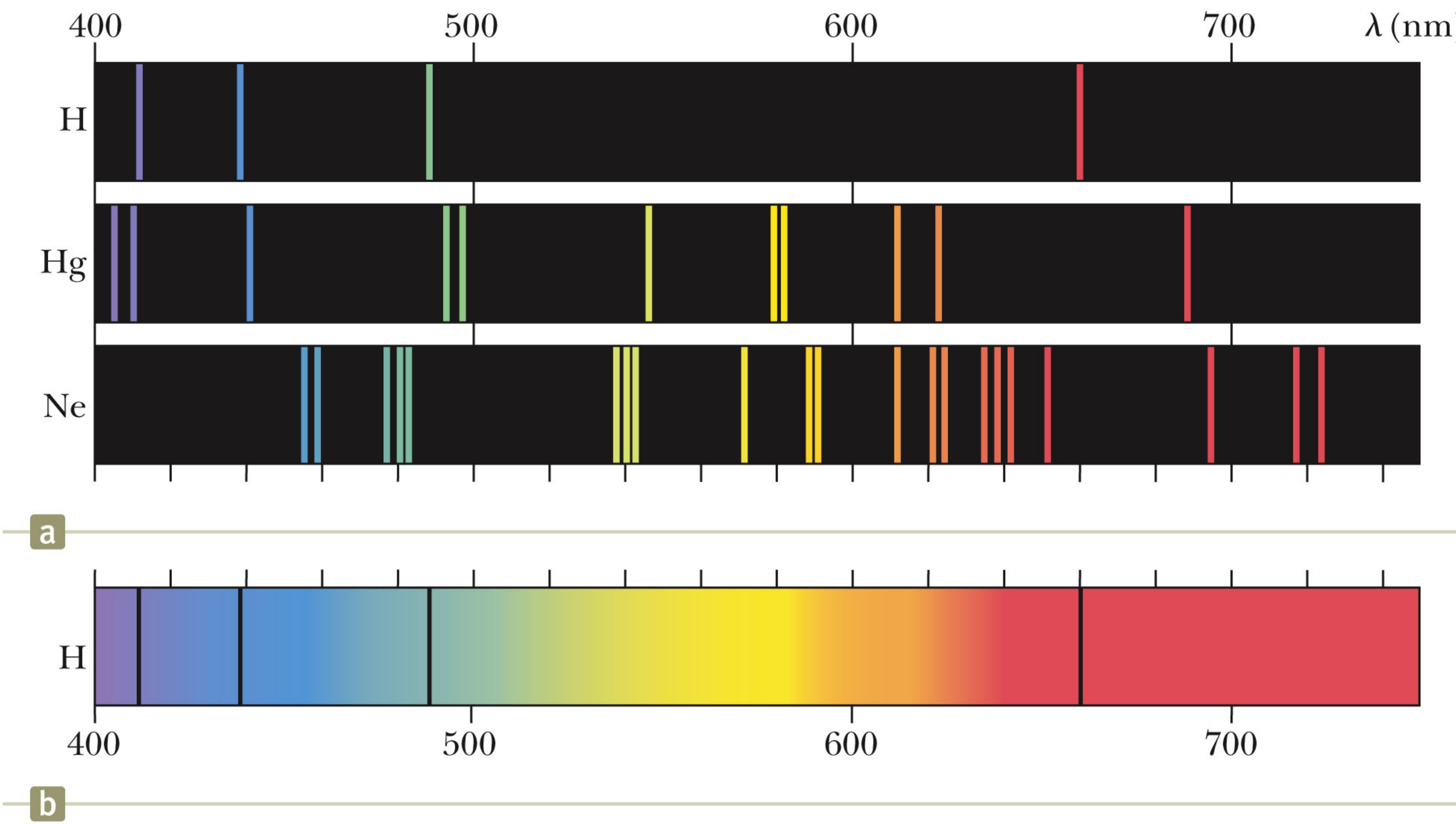
42.1 The Quantum Model of the Hydrogen Atom

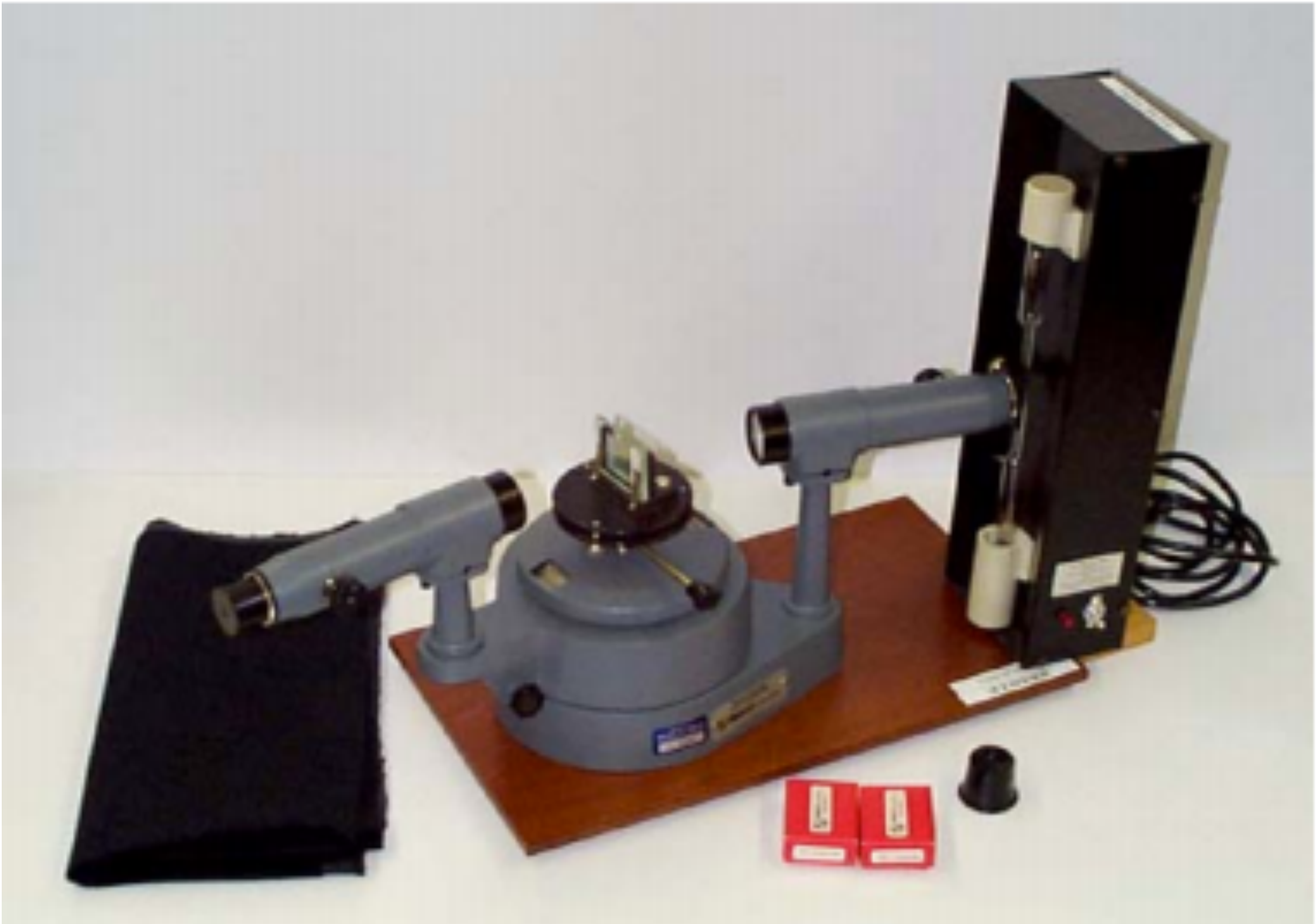
Atomic Spectra

- All objects emit thermal radiation characterized by a continuous distribution of wavelengths.
- A discrete **line spectrum** is observed when a low-pressure gas is subjected to an electric discharge.
- Observation and analysis of these spectral lines is called **emission spectroscopy.**
- The simplest line spectrum is that for atomic hydrogen.

42.1 The Quantum Model of the Hydrogen Atom

Emission Spectra Examples





42.1 The Quantum Model of the Hydrogen Atom

Uniqueness of Atomic Spectra

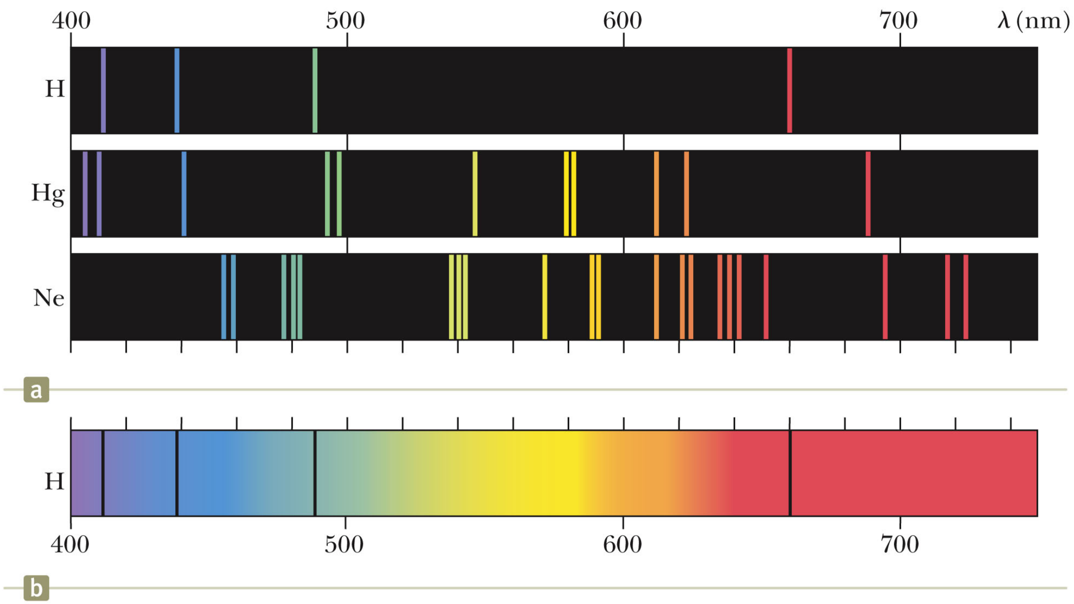
- Other atoms exhibit completely different line spectra.

- Because no two elements have the same line spectrum, the phenomena represents a practical and sensitive technique for identifying the elements present in unknown samples.

42.1 The Quantum Model of the Hydrogen Atom

Absorption Spectroscopy

- An **absorption spectrum** is obtained by passing white light from a continuous source through a gas or a dilute solution of the element being analyzed.
- The absorption spectrum consists of a series of dark lines superimposed on the continuous spectrum of the light source.



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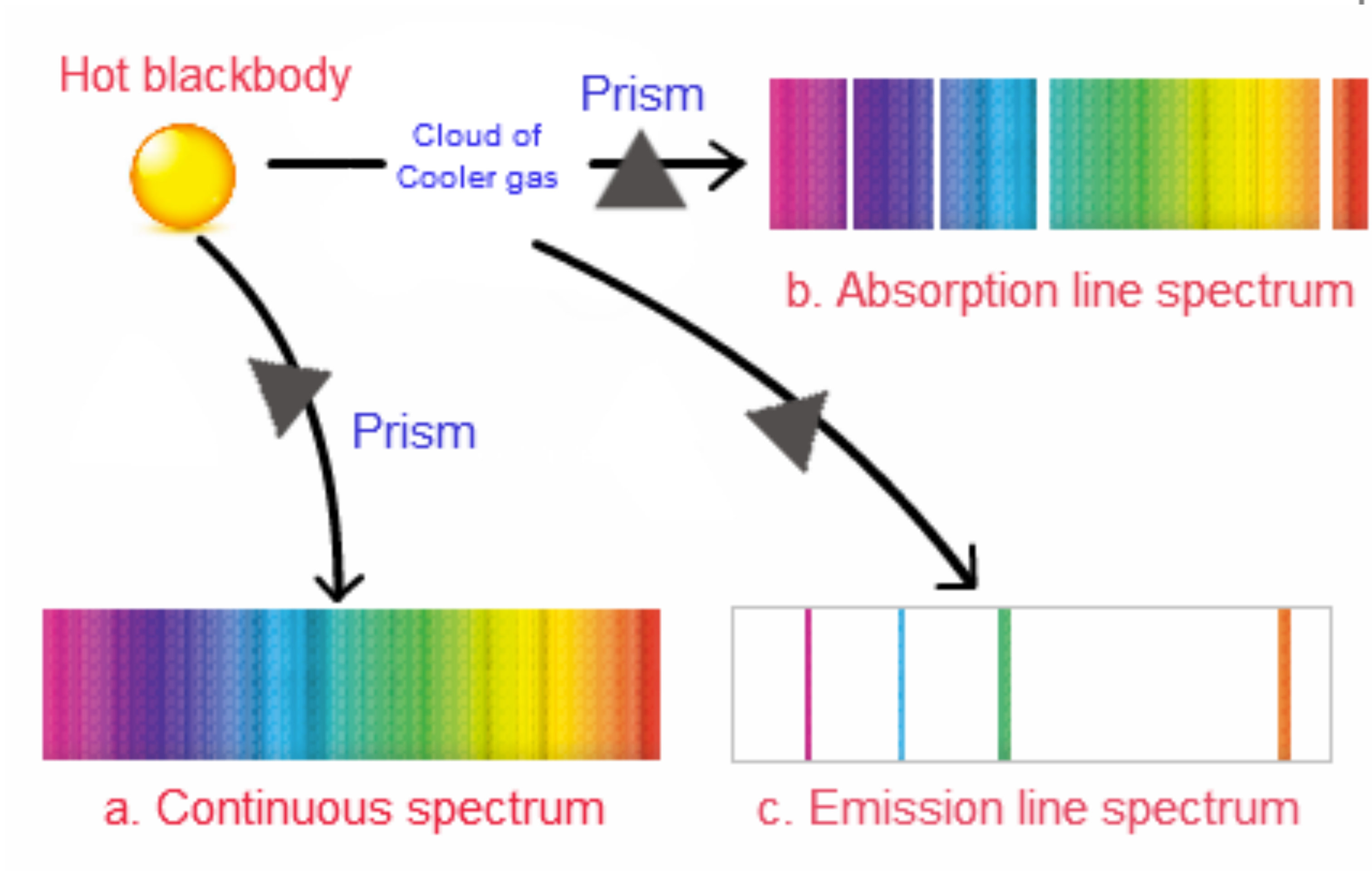
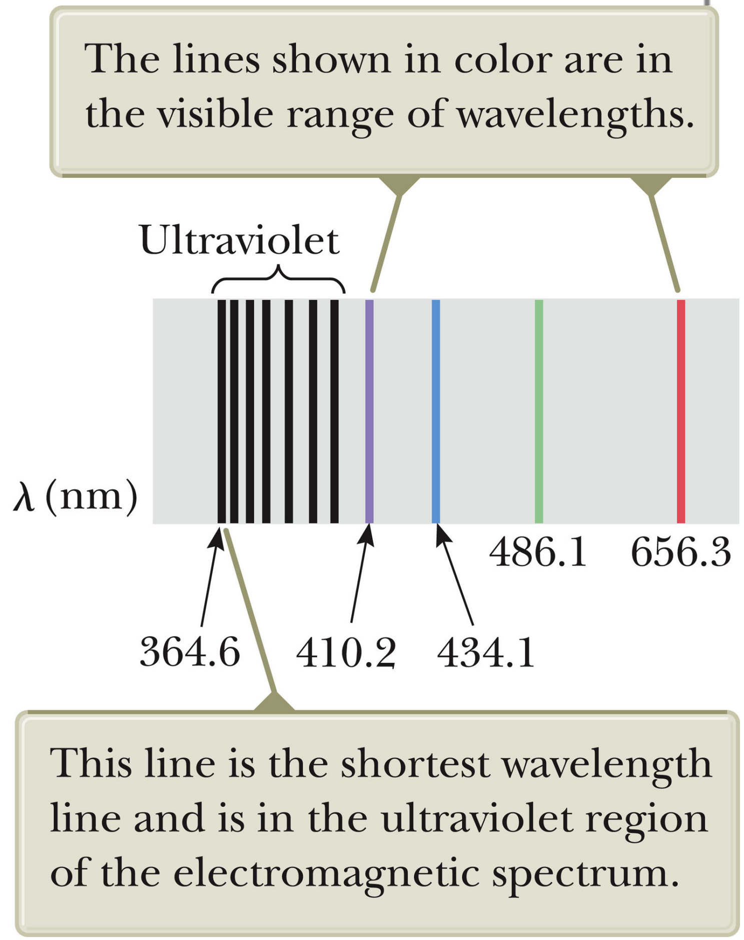

Hot blackbody
Cloud of
Cooler gas
Prism
b. Absorption line spectrum
Prism
a. Continuous spectrum
c. Emission line spectrum

42.1 The Quantum Model of the Hydrogen Atom

Balmer Series

- In 1885, Johann Balmer found an empirical equation that correctly predicted the four visible emission lines of hydrogen.
  - H_α is red, $\lambda = 656.3$ nm
  - H_β is green, $\lambda = 486.1$ nm
  - H_γ is blue, $\lambda = 434.1$ nm
  - H_δ is violet, $\lambda = 410.2$ nm



42.1 The Quantum Model of the Hydrogen Atom

Emission Spectrum of Hydrogen – Equation

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

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

  - R_H is the Rydberg constant
    - $R_H = 1.097\,373\,2 \times 10^7\ \text{m}^{-1}$
  - n is an integer, n =1,2 3, 4, 5,…
  - The spectral lines correspond to different values of n.
  - Values of n from 3 to 6 give the four visible lines.
  - Values of $n > 6$ give the ultraviolet lines in the Balmer series.
- The series limit is the shortest wavelength in the series and corresponds to $n \to \infty$.

42.1 The Quantum Model of the Hydrogen Atom

Other Hydrogen Series

- Other series were also discovered and their wavelengths can be calculated:
- Lyman series:

$$\frac{1}{\lambda} = R_H\left(1 - \frac{1}{n^2}\right), \qquad n = 2,3,4, \ldots.$$

- Balmer series:

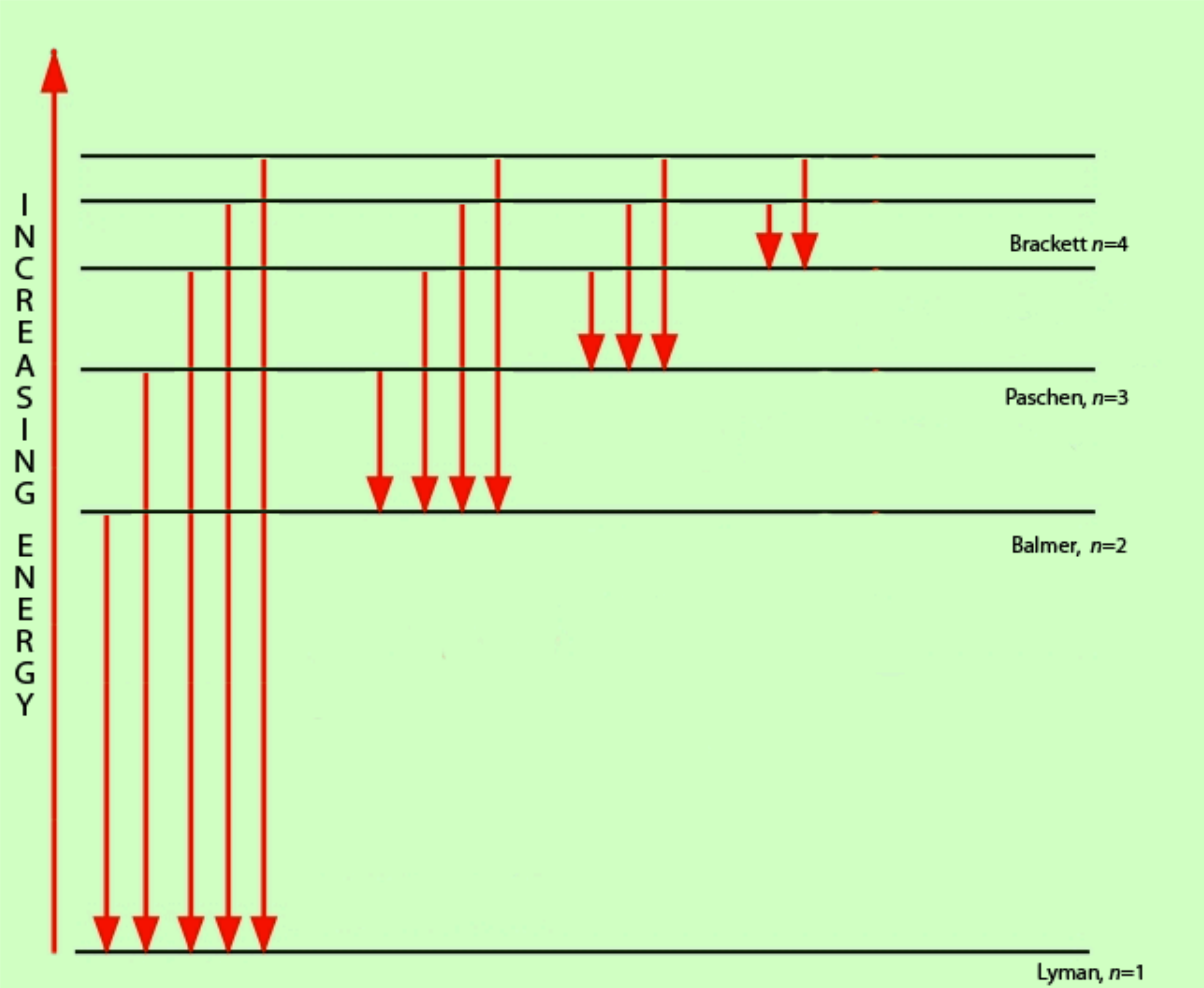
$$\frac{1}{\lambda} = R_H\left(\frac{1}{2^2} - \frac{1}{n^2}\right) \qquad n = 3,4,5, \ldots.$$

- Paschen series:

$$\frac{1}{\lambda} = R_H\left(\frac{1}{3^2} - \frac{1}{n^2}\right), \qquad n = 4,5,6 \ldots.$$

- Brackett series:

$$\frac{1}{\lambda} = R_H\left(\frac{1}{4^2} - \frac{1}{n^2}\right), \qquad n = 5,6,7 \ldots.$$


INCREASING ENERGY
Brackett n=4
Paschen, n=3
Balmer, n=2
Lyman, n=1

42.2 Early Models of the Atom

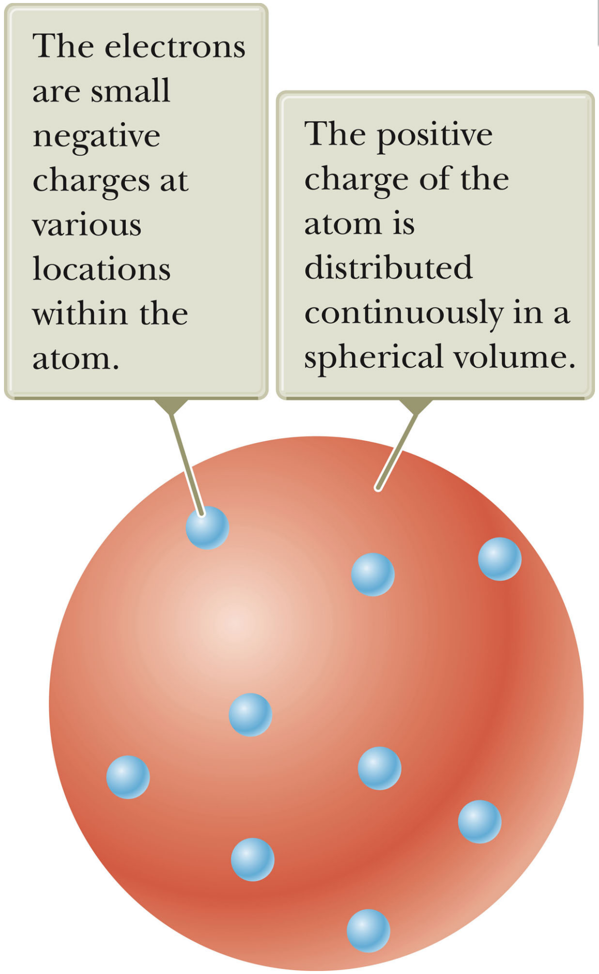
Joseph John Thomson

- 1856 – 1940
- English physicist
- Received Nobel Prize in 1906
- Usually considered the discoverer of the electron
- Worked with the deflection of cathode rays in an electric field
  - Opened up the field of subatomic particles

42.2 Early Models of the Atom

Early Models of the Atom, Thomson's

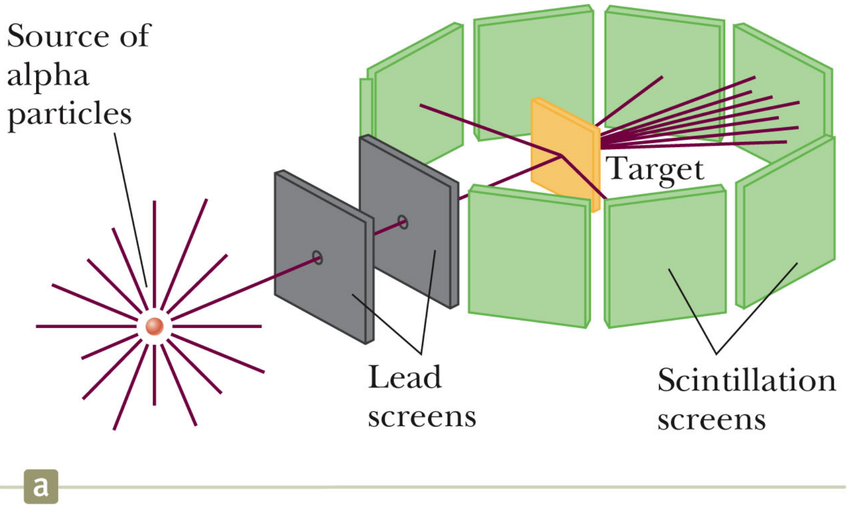
- J. J. Thomson established the charge to mass ratio for electrons.
- His model of the atom
  - A volume of positive charge
  - Electrons embedded throughout the volume
  - The atom as a whole would be electrically neutral.



42.2 Early Models of the Atom

Rutherford's Thin Foil Experiment

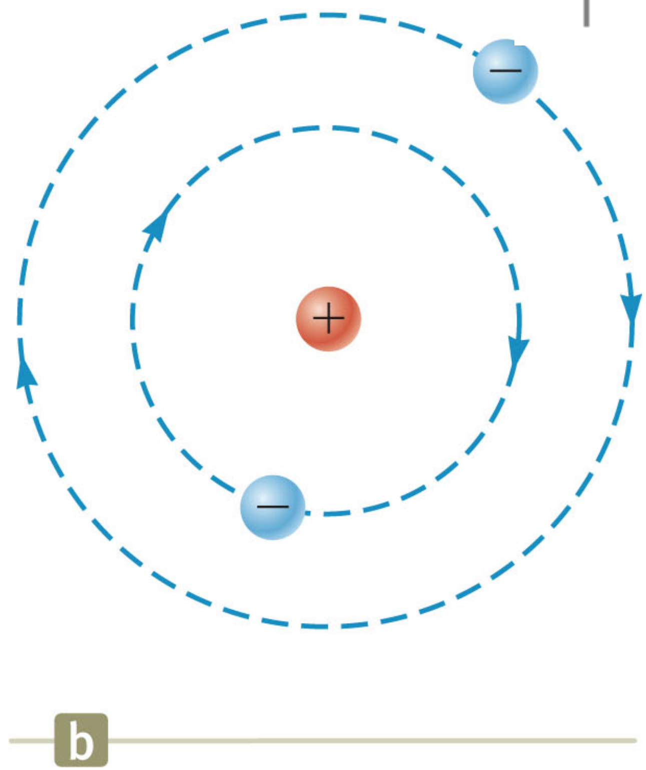
- Experiments done in 1911
- A beam of positively charged alpha particles hit and are scattered from a thin foil target.
- Large deflections could not be explained by Thomson's model.



42.2 Early Models of the Atom

Early Models of the Atom, Rutherford' s

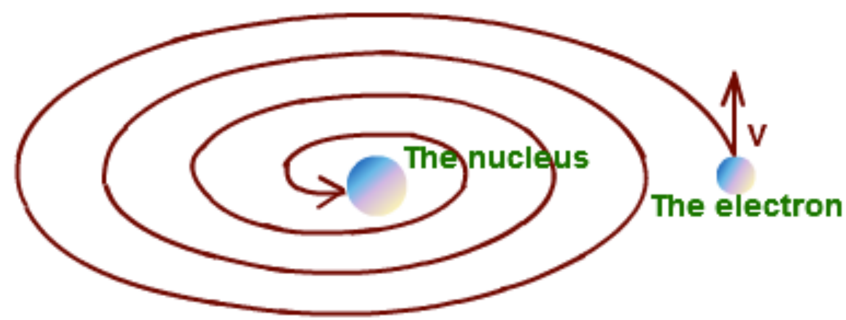
- Rutherford
  - Planetary model
  - Based on results of thin foil experiments
  - Positive charge is concentrated in the center of the atom, called the nucleus
  - Electrons orbit the nucleus like planets orbit the sun



42.2 Early Models of the Atom

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.
  - It should radiate electromagnetic waves of the same frequency.
  - The radius should steadily decrease.
  - The electron should eventually spiral into the nucleus.
    - It doesn't

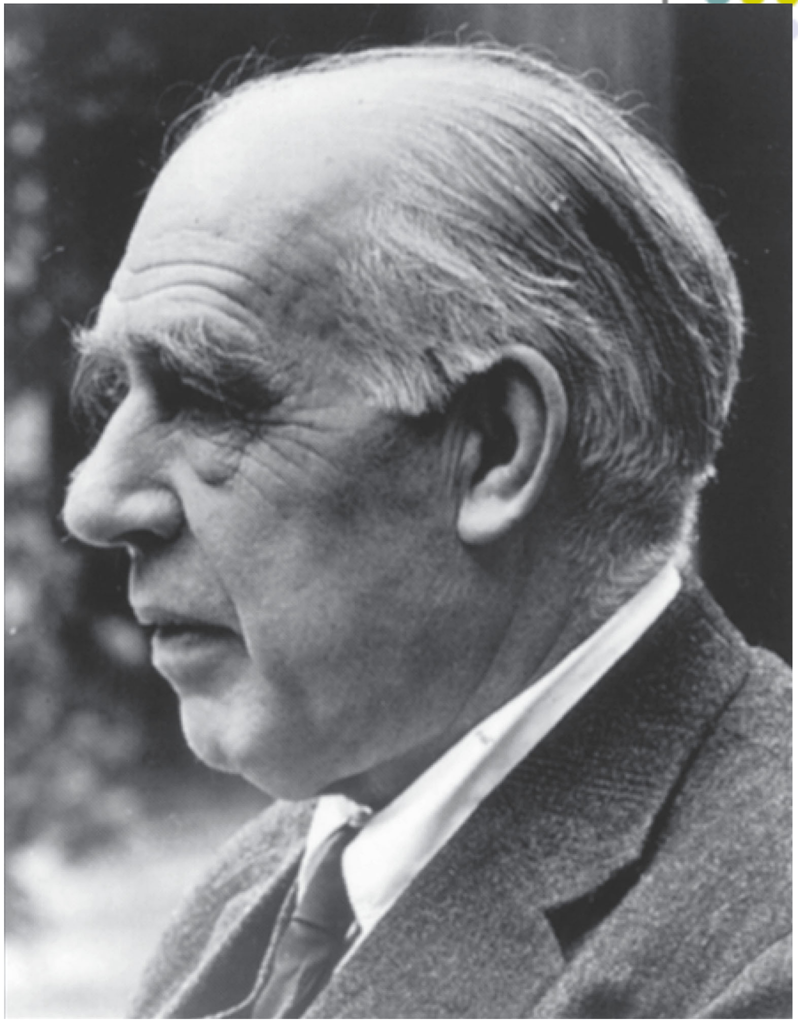


In the planetary model of atom, the electron should emit energy and spirally fall on the nucleus.

42.2 Early Models of the Atom

Niels Bohr

- 1885 – 1962
- Danish physicist
- An active participant in the early development of quantum mechanics
- Headed the Institute for Advanced Studies in Copenhagen
- Awarded the 1922 Nobel Prize in physics
  - For structure of atoms and the radiation emanating from them



42.3 Bohr's Model of the Hydrogen Atom

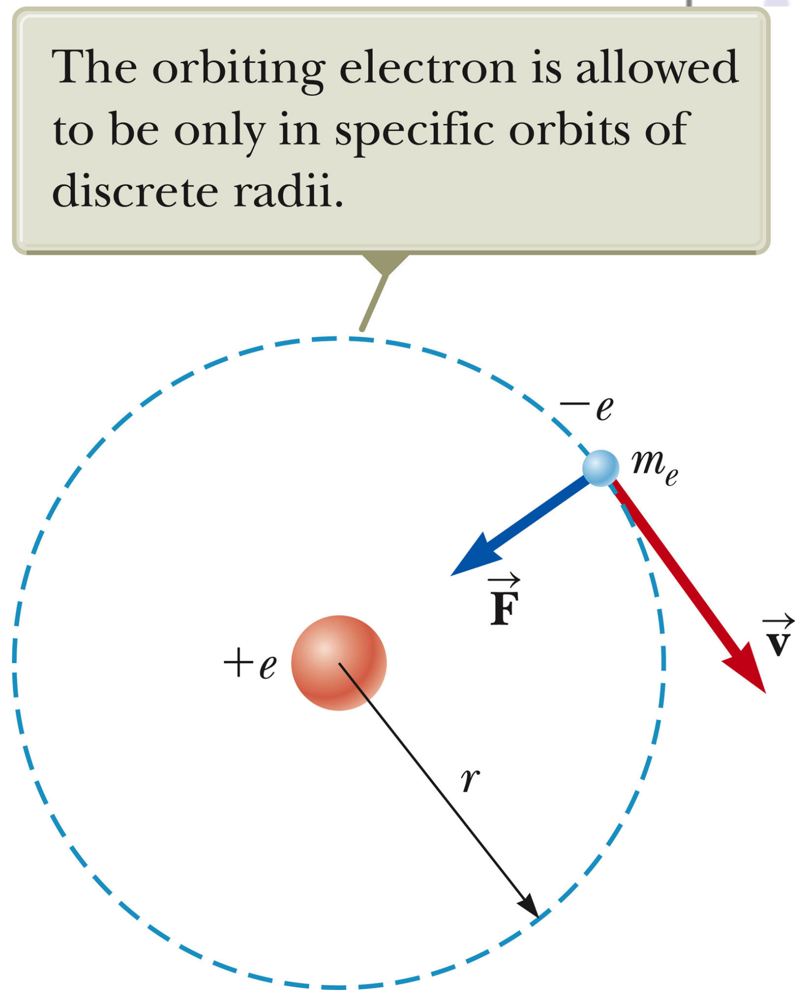
The Bohr Theory of Hydrogen

- 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.
- He applied Planck's ideas of quantized energy levels to Rutherford's orbiting electrons.
- This model is now considered obsolete.
- It has been replaced by a quantum-mechanical theory.
- The model can still be used to develop ideas of energy quantization.

42.3 Bohr's Model of the Hydrogen Atom

Bohr's Postulates for Hydrogen, 1

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



42.3 Bohr's Model of the Hydrogen Atom

Bohr's Postulates, 2

- Only certain electron orbits are stable.
  - Bohr called these **stationary states.**
  - These are the orbits in which the atom does not emit energy in the form of electromagnetic radiation, even though it is accelerating.
  - Therefore, the energy of the atom remains constant and classical mechanics can be used to describe the electron's motion.
  - This representation does not eventually spiral into the nucleus.

42.3 Bohr's Model of the Hydrogen Atom

Bohr's Postulates, 3

- Radiation is emitted by the atom when the electron makes a transition from a more energetic initial stationary state to a lower-energy stationary state.
  - The transition cannot be treated classically.
  - The frequency emitted in the transition is related to the change in the atom's energy.
  - The frequency is independent of frequency of the electron's orbital motion.
  - The frequency of the emitted radiation is given by
  - $E_i - E_f = hf$
    - If a photon is absorbed, the electron moves to a higher energy level.

42.3 Bohr's Model of the Hydrogen Atom

Bohr's Postulates, 4

- The size of the allowed electron orbits is determined by a condition imposed on the electron's orbital angular momentum.
- The allowed orbits are those for which the electron's orbital angular momentum about the nucleus is quantized and equal to an integral multiple of $\hbar = h/2\pi$

42.3 Bohr's Model of the Hydrogen Atom

Bohr's Postulates, Notes

- These postulates were a mixture of established principles and completely new ideas.
- Postulate 1 – from classical mechanics
  - Treats the electron in orbit around the nucleus in the same way we treat a planet in orbit around a star.
- Postulate 2 – new idea
  - It was completely at odds with the understanding of electromagnetism at the time.
- Postulate 3 – Principle of Conservation of Energy
- Postulate 4 – new idea
  - Had no basis in classical physics

42.3 Bohr's Model of the Hydrogen Atom

Mathematics of Bohr's Assumptions and Results

- Electron's orbital angular momentum
  - $m_e vr = n\hbar$ where n = 1, 2, 3,…
- The total energy of the atom is
  - $$E = K + U = \frac{1}{2}m_e v^2 - k_e \frac{e^2}{r}$$

42.3 Bohr's Model of the Hydrogen Atom

Bohr Radius

- The radii of the Bohr orbits are quantized

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

  - This shows that the radii of the allowed orbits have discrete values—they are quantized.
  - This result is based on the assumption that the electron can exist only in certain allowed orbits determined by n (Bohr's postulate 4).
    - When n = 1, the orbit has the smallest radius, called the Bohr radius, a_o
    - $a_o = 0.052\ 9$ nm

42.3 Bohr's Model of the Hydrogen Atom

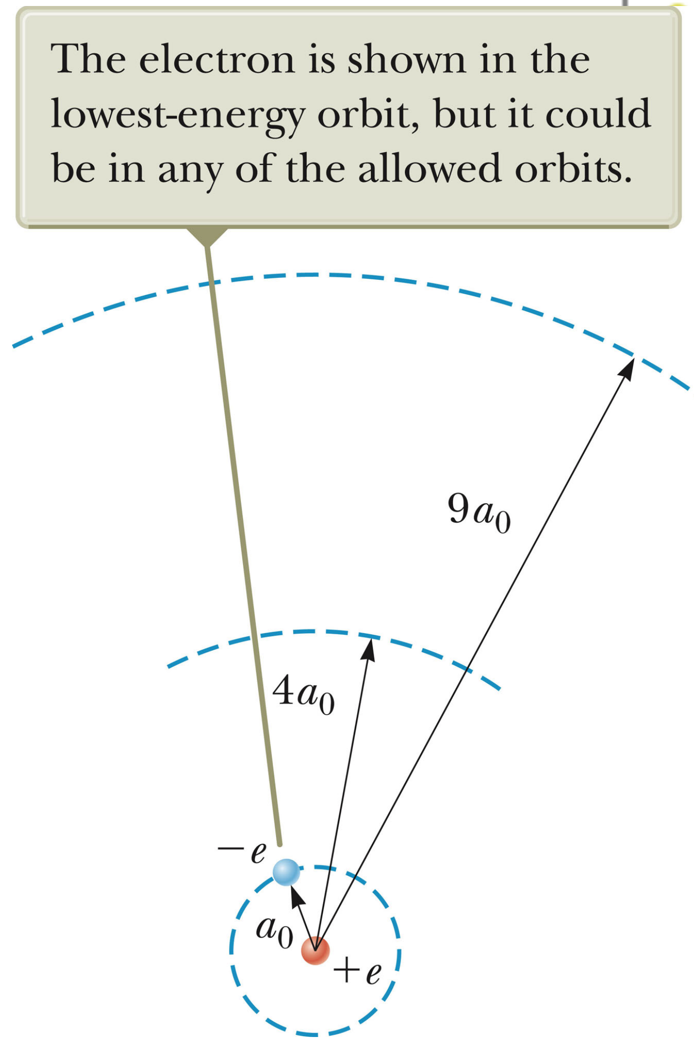
Radii and Energy of Orbits

- 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

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

  - This becomes

$$E_n = \frac{-13.606 \text{ eV}}{n^2}$$



42.3 Bohr's Model of the Hydrogen Atom

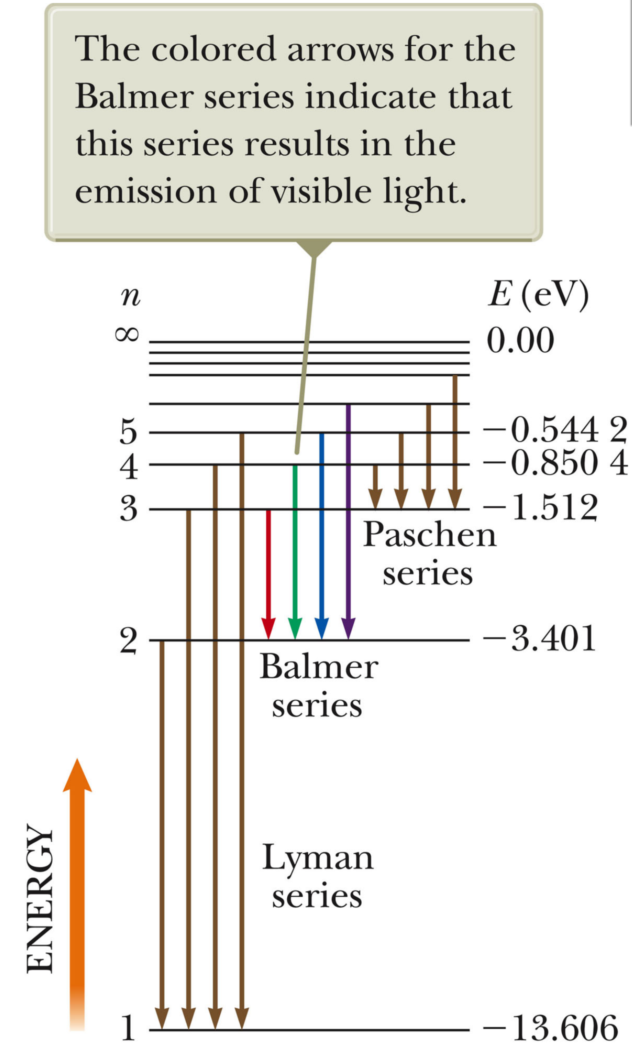
Specific Energy Levels

- Only energies satisfying the energy equation are allowed.
- The lowest energy state is called the ground state.
  - This corresponds to $n = 1$ with $E = -13.606$ eV
- The ionization energy is the energy needed to completely remove the electron from the ground state in the atom.
  - The ionization energy for hydrogen is 13.6 eV.

42.3 Bohr's Model of the Hydrogen Atom

Energy Level Diagram

- Quantum numbers are given on the left and energies on the right.



42.3 Bohr's Model of the Hydrogen Atom

Frequency and Wavelength of Emitted Photons

- The frequency of the photon emitted when the electron makes a transition from an outer orbit to an inner orbit is

$$f = \frac{E_i - E_f}{h} = \frac{k_e e^2}{2a_0 h}\left(\frac{1}{{n_f}^2} - \frac{1}{{n_i}^2}\right),$$

- It is convenient to look at the wavelength instead.
- The wavelengths are found by

$$\frac{1}{\lambda} = \frac{f}{c} = \frac{k_e e^2}{2a_0 hc}\left(\frac{1}{{n_f}^2} - \frac{1}{{n_i}^2}\right) = R_H\left(\frac{1}{{n_f}^2} - \frac{1}{{n_i}^2}\right)$$

- The value of R_H from Bohr's analysis is in excellent agreement with the experimental value.

42.3 Bohr's Model of the Hydrogen Atom

Extension to Other Atoms

- Bohr extended his model for hydrogen to other elements in which all but one electron had been removed.

$$r_n = \left(n^2\right)\frac{a_o}{Z}$$

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

  - Z is the **atomic number** of the element and is the number of protons in the nucleus.

42.3 Bohr's Model of the Hydrogen Atom

Difficulties with the Bohr Model

- Improved spectroscopic techniques found that many of the spectral lines of hydrogen were not single lines.
  - Each "line" was actually a group of lines spaced very close together.
- Certain single spectral lines split into three closely spaced lines when the atoms were placed in a magnetic field.
- The Bohr model cannot account for the spectra of more complex atoms.
- Scattering experiments show that the electron in a hydrogen atom does not move in a flat circle, but rather that the atom is spherical.
- These deviations from the model led to modifications in the theory and ultimately to a replacement theory.

EXAMPLE 42.1 **Electronic Transitions in Hydrogen**

(A) The electron in a hydrogen atom makes a transition from the $n = 2$ energy level to the ground level ($n = 1$). Find the wavelength and frequency of the emitted photon.

SOLUTION

Conceptualize Imagine the electron in a circular orbit about the nucleus as in the Bohr model in Figure 42.6. When the electron makes a transition to a lower stationary state, it emits a photon with a given frequency.

Categorize We evaluate the results using equations developed in this section, so we categorize this example as a substitution problem.

Use Equation 42.17 to obtain λ, with $n_i = 2$ and $n_f = 1$:

$$\frac{1}{\lambda} = R_H\left(\frac{1}{1^2} - \frac{1}{2^2}\right) = \frac{3R_H}{4}$$

$$\lambda = \frac{4}{3R_H} = \frac{4}{3(1.097 \times 10^7\ \text{m}^{-1})} = 1.22 \times 10^{-7}\ \text{m} = \boxed{122\ \text{nm}}$$

Use Equation 34.20 to find the frequency of the photon:

$$f = \frac{c}{\lambda} = \frac{3.00 \times 10^8\ \text{m/s}}{1.22 \times 10^{-7}\ \text{m}} = \boxed{2.47 \times 10^{15}\ \text{Hz}}$$

(B) In interstellar space, highly excited hydrogen atoms called Rydberg atoms have been observed. Find the wavelength to which radio astronomers must tune to detect signals from electrons dropping from the $n = 273$ level to the $n = 272$ level.

SOLUTION

Use Equation 42.17, this time with $n_i = 273$ and $n_f = 272$:

$$\frac{1}{\lambda} = R_H\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) = R_H\left(\frac{1}{(272)^2} - \frac{1}{(273)^2}\right) = 9.88 \times 10^{-8} R_H$$

Solve for λ:

$$\lambda = \frac{1}{9.88 \times 10^{-8} R_H} = \frac{1}{(9.88 \times 10^{-8})(1.097 \times 10^7 \text{ m}^{-1})} = \boxed{0.922 \text{ m}}$$

(C) What is the radius of the electron orbit for a Rydberg atom for which $n = 273$?

SOLUTION

Use Equation 42.12 to find the radius of the orbit:

$$r_{273} = (273)^2(0.052\,9 \text{ nm}) = \boxed{3.94\ \mu\text{m}}$$

This radius is large enough that the atom is on the verge of becoming macroscopic!

42.4 The Quantum Model of the Hydrogen Atom

The Quantum Model of the Hydrogen Atom

- The difficulties with the Bohr model are removed when a full quantum model involving the Schrödinger equation is used to describe the hydrogen atom.
- The potential energy function for the hydrogen atom is

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

  - k_e is the Coulomb constant
  - r is the radial distance from the proton to the electron
    - The proton is situated at r = 0

42.4 The Quantum Model of the Hydrogen Atom

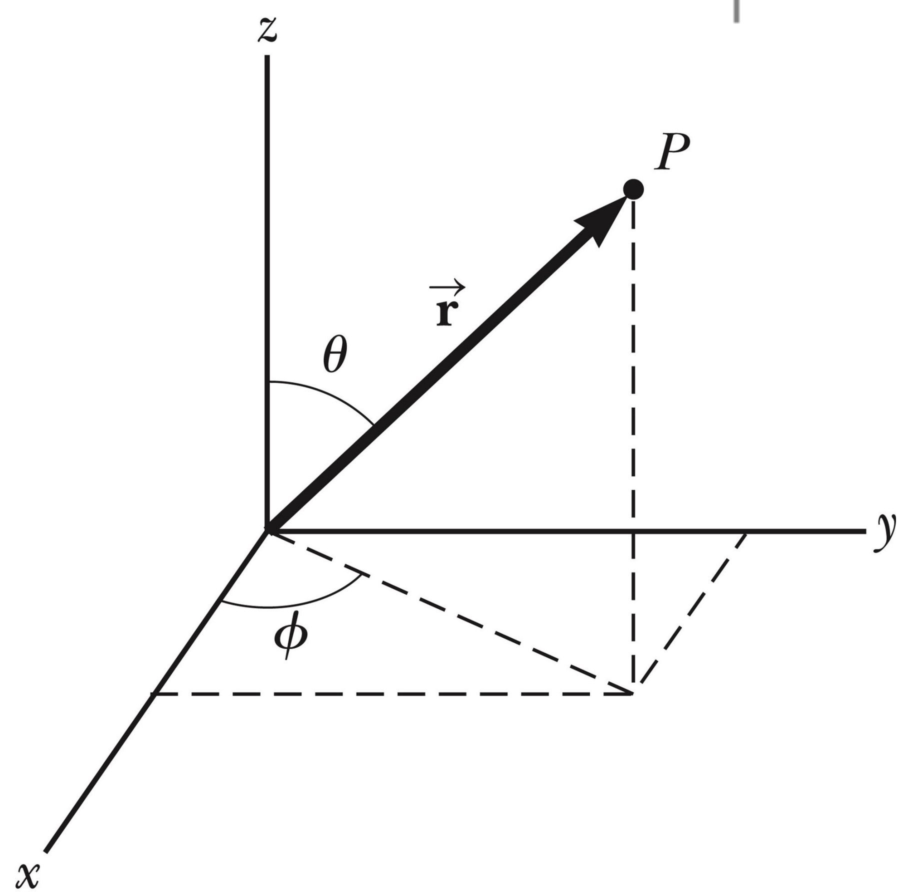
Quantum Model, cont.

- The formal procedure to solve the hydrogen atom is to substitute *U(r)* into the Schrödinger equation, find the appropriate solutions to the equations, and apply boundary conditions.
- Because it is a three-dimensional problem, it is easier to solve if the rectangular coordinates are converted to spherical polar coordinates.

42.4 The Quantum Model of the Hydrogen Atom

Quantum Model, final

- $\psi(x, y, z)$ is converted to $\psi(r, \theta, \varphi)$
- Then, the space variables can be separated:
- $\psi(r, \theta, \varphi) = R(r), f(\theta), g(\varphi)$
- When the full set of boundary conditions are applied, we are led to three different quantum numbers for each allowed state.
- The three different quantum numbers are restricted to integer values.
- They correspond to three degrees of freedom.
  - Three space dimensions



42.4 The Quantum Model of the Hydrogen Atom

Principal Quantum Number

- The first quantum number is associated with the radial function *R(r)*.
  - It is called the **principal quantum number.**
  - It is symbolized by *n*.
- The potential energy function depends only on the radial coordinate r.
- The energies of the allowed states in the hydrogen atom are the same E_n values found from the Bohr theory.

42.4 The Quantum Model of the Hydrogen Atom

Orbital and Orbital Magnetic Quantum Numbers

- The **orbital quantum number** is symbolized by ℓ.
  - It is associated with the orbital angular momentum of the electron.
  - It is an integer.
- The **orbital magnetic quantum number** is symbolized by m_{ℓ}.
  - It is also associated with the angular orbital momentum of the electron and is an integer.

42.4 The Quantum Model of the Hydrogen Atom

Quantum Numbers, Summary of Allowed Values

- The values of n are integers that can range from 1 to ∞.
- The values of ℓ are integers that can range from 0 to n - 1.
- The values of m_ℓ are integers that can range from $-\ell$ to ℓ.
- Example:
  - If $n = 1$, then only $\ell = 0$ and $m_\ell = 0$ are permitted
  - If $n = 2$, then $\ell = 0$ or 1
    - If $\ell = 0$ then $m_\ell = 0$
    - If $\ell = 1$ then m_ℓ may be -1, 0, or 1

42.4 The Quantum Model of the Hydrogen Atom

Quantum Numbers, Summary Table

TABLE 42.1 *Three Quantum Numbers for the Hydrogen Atom*

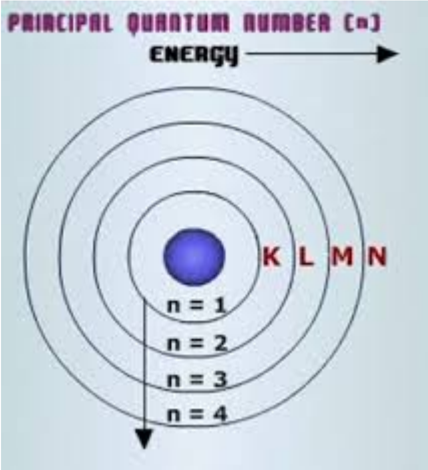
Quantum Number	Name	Allowed Values	Number of Allowed States
n	Principal quantum number	$1, 2, 3, \ldots$	Any number
ℓ	Orbital quantum number	$0, 1, 2, \ldots, n-1$	n
m_ℓ	Orbital magnetic quantum number	$-\ell, -\ell+1, \ldots, 0, \ldots, \ell-1, \ell$	$2\ell+1$

[4]The first four of these letters come from early classifications of spectral lines: sharp, principal, diffuse, and fundamental. The remaining letters are in alphabetical order.

42.4 The Quantum Model of the Hydrogen Atom

Shells

- Historically, all states having the same principle quantum number are said to form a **shell.**
  – Shells are identified by letters K, L, M,… for which n = 1, 2, 3, …
- All states having the same values of n and ℓ are said to form a **subshell.**
  – The letters s, p, d, f, g, h, .. are used to designate the subshells for which ℓ = 0, 1, 2, 3,…



Electronic Shells, Sub-shells and Orbitals

- All orbitals with the same value of n together constitute an electronic shell.

n	1	2	3	4
Shell	K	L	M	N

- For each n, orbitals with the same value of ℓ together constitute an electronic sub-shell.

- Each sub-shell consists of $(2\ell+1)$ orbitals, each with a different m_ℓ value.

ℓ	0	1	2	3
Sub-shell	s	p	d	f
No. orbitals	1	3	5	7

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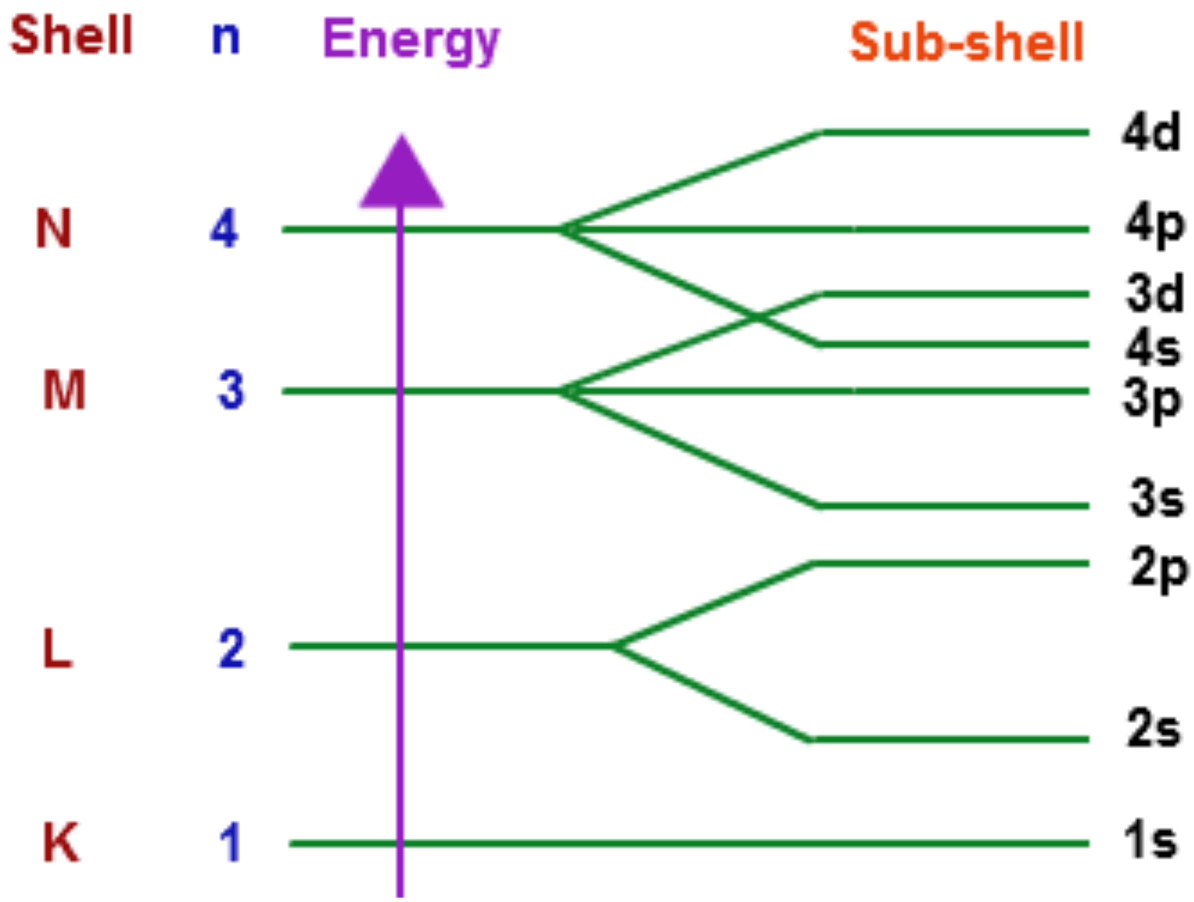

Shell
n
Energy
Sub-shell
N
4
M
3
L
2
K
1
4d
4p
3d
4s
3p
3s
2p
2s
1s

42.4 The Quantum Model of the Hydrogen Atom

Shell Notation, Summary Table

TABLE 42.2

Atomic Shell Notations

n	Shell Symbol
1	K
2	L
3	M
4	N
5	O
6	P

42.4 The Quantum Model of the Hydrogen Atom

Subshell Notation, Summary Table

TABLE 42.3

Atomic Subshell Notations

ℓ	**Subshell Symbol**
0	*s*
1	*p*
2	*d*
3	*f*
4	*g*
5	*h*

EXAMPLE 42.2 **The $n = 2$ Level of Hydrogen**

For a hydrogen atom, determine the allowed states corresponding to the principal quantum number $n = 2$ and calculate the energies of these states.

SOLUTION

Conceptualize Think about the atom in the $n = 2$ quantum state. There is only one such state in the Bohr theory, but our discussion of the quantum theory allows for more states because of the possible values of ℓ and m_ℓ.

Categorize We evaluate the results using rules discussed in this section, so we categorize this example as a substitution problem.

From Table 42.1, we find that when $n = 2$, ℓ can be 0 or 1. Find the possible values of m_ℓ from Table 42.1:

$$\ell = 0 \quad \rightarrow \quad m_\ell = 0$$

$$\ell = 1 \quad \rightarrow \quad m_\ell = -1, 0, \text{ or } 1$$

Hence, we have one state, designated as the $2s$ state, that is associated with the quantum numbers $n = 2$, $\ell = 0$, and $m_\ell = 0$, and we have three states, designated as $2p$ states, for which the quantum numbers are $n = 2$, $\ell = 1$, $m_\ell = -1$; $n = 2$, $\ell = 1$, $m_\ell = 0$; and $n = 2$, $\ell = 1$, $m_\ell = 1$.

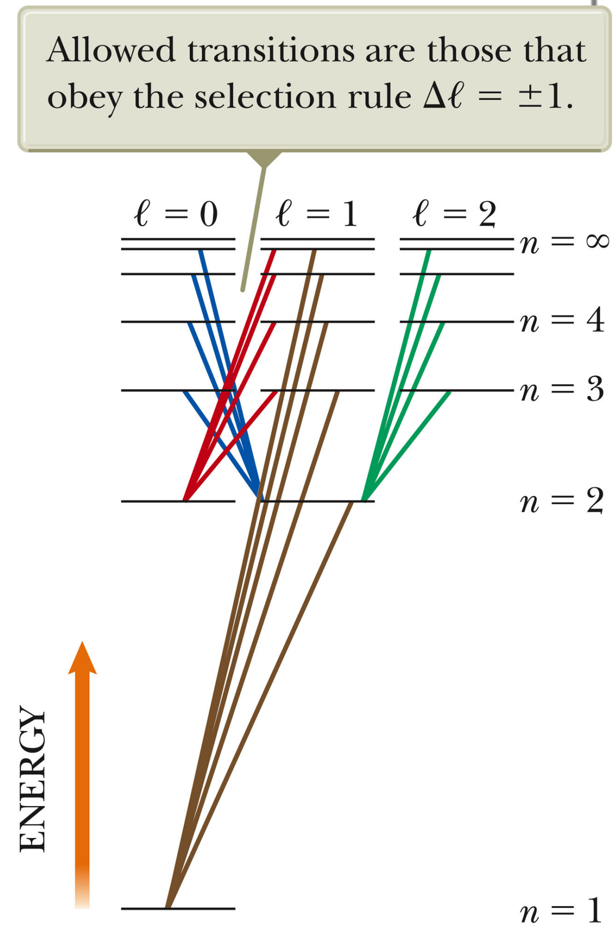
Find the energy for all four of these states with $n = 2$ from Equation 42.21:

$$E_2 = -\frac{13.606 \text{ eV}}{2^2} = \boxed{-3.401 \text{ eV}}$$

42.8 More on Atomic Spectra: Visible and X-Ray

Hydrogen Energy Level Diagram Revisited

- The allowed values of ℓ are separated horizontally.
- Transitions in which ℓ does not change are very unlikely to occur and are called *forbidden transitions.*
  - Such transitions actually can occur, but their probability is very low compared to allowed transitions.



42.8 More on Atomic Spectra: Visible and X-Ray

Selection Rules

- The selection rules for allowed transitions are
  - $\Delta\ell = \pm 1$
  - $\Delta m_\ell = 0, \pm 1$
- The angular momentum of the atom-photon system must be conserved.
- Therefore, the photon involved in the process must carry angular momentum.
  - The photon has angular momentum equivalent to that of a particle with spin 1.
  - A photon has energy, linear momentum and angular momentum.

42.8 More on Atomic Spectra: Visible and X-Ray

X-Ray Spectra, cont.

- The discrete lines are called **characteristic x-rays.**
- These are created when
  - A bombarding electron collides with a target atom.
  - The electron removes an inner-shell electron from orbit.
  - An electron from a higher orbit drops down to fill the vacancy.
- The photon emitted during this transition has an energy equal to the energy difference between the levels.
- Typically, the energy is greater than 1000 eV.
- The emitted photons have wavelengths in the range of 0.01 nm to 1 nm.