



Quantum Theory and the Electronic Structure of Atoms

Chapter 7

Introduction

- Quantum theory enables us to understand the critical role that electrons play in chemistry.
- Studying atoms leads to the following questions:
 - **How many** electrons are present in a particular atom?
 - **What energies** do individual electrons possess?
 - **Where** in the atom can electrons be found?
- The answer to these questions have a direct relationship to the behavior of all substances in chemical reactions.

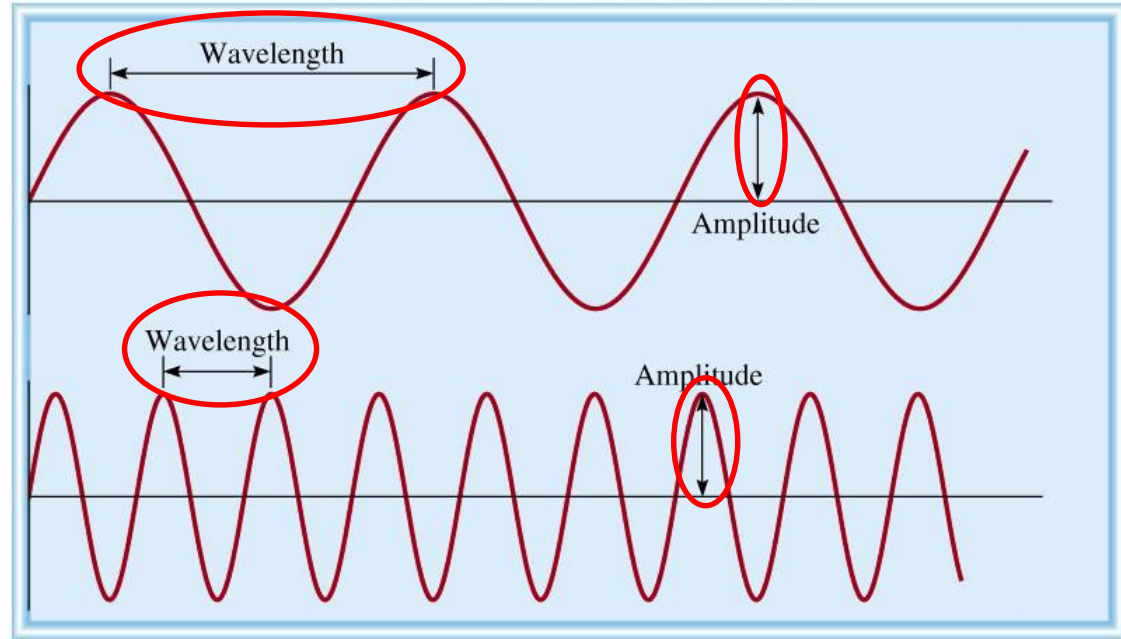
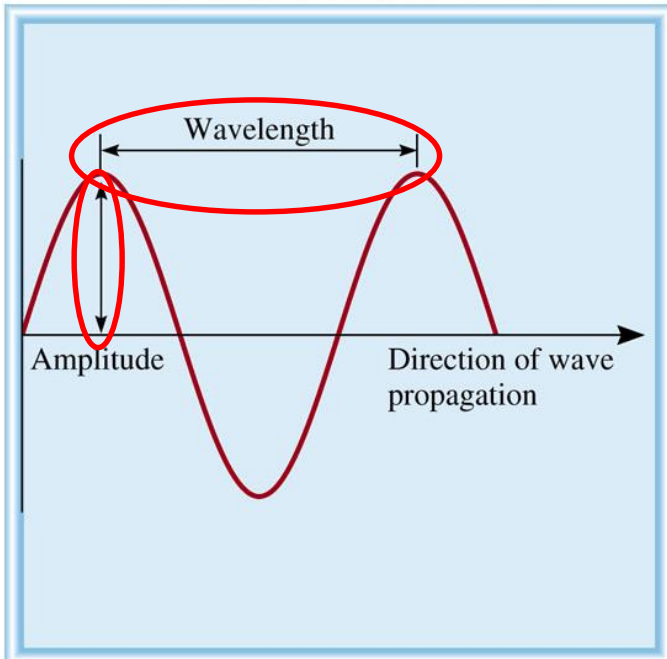
From Classical Physics to Quantum Theory

- By assuming that molecules behave like **rebounding balls**, physicists were able to predict and explain some macroscopic phenomena,
 - Such as pressure exerted by a gas.
- This model did not account for the **stability of molecules**; that is, it could not explain the forces that hold atoms together.
- It was realized that the properties of atoms and molecules are **not** governed by the same physical laws as larger objects.

From Classical Physics to Quantum Theory

- The new era in physics started in 1900 with a young German physicist named **Max Planck**.
- While studying the data on radiation emitted by solids heated to various temperatures, Planck discovered that atoms and molecules emit energy only in certain discrete quantities, or **quanta**.
- Physicists had always assumed that energy is **continuous** and that **any amount** of energy could be released in a radiation process.
- Planck's **quantum theory** turned physics upside down.

Properties of Waves



Wavelength (λ) is the distance between identical points on successive waves.

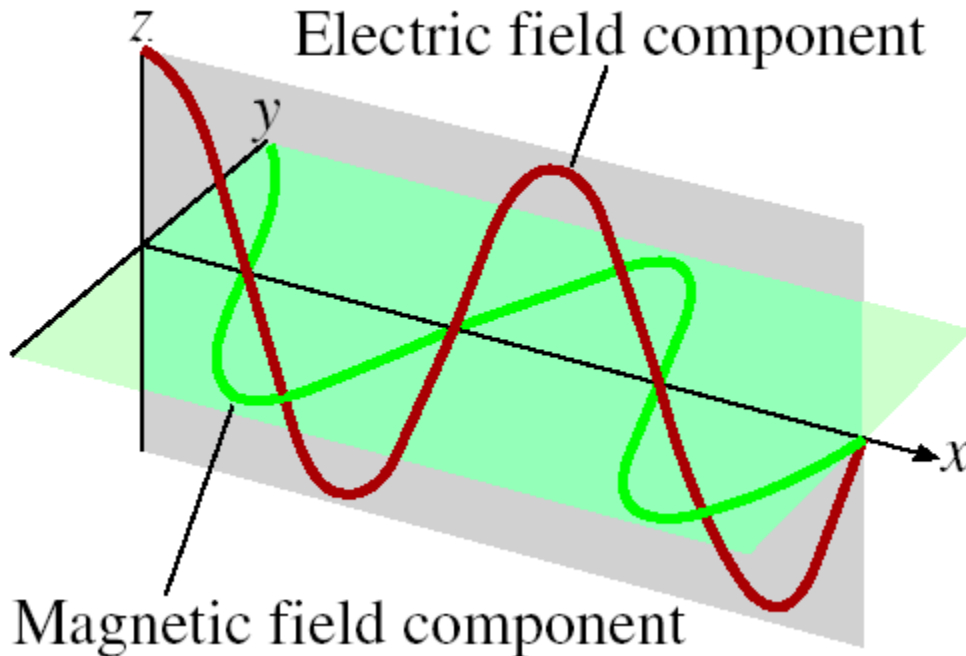
Amplitude is the vertical distance from the midline of a wave to the peak or trough.

Frequency (ν) is the number of waves that pass through a particular point in 1 second ($\text{Hz} = 1 \text{ cycle/s}$).

The speed (u) of the wave = $\lambda \times \nu$

Electromagnetic Radiation

James Clerk Maxwell (1873), proposed that **visible light consists of electromagnetic waves**.



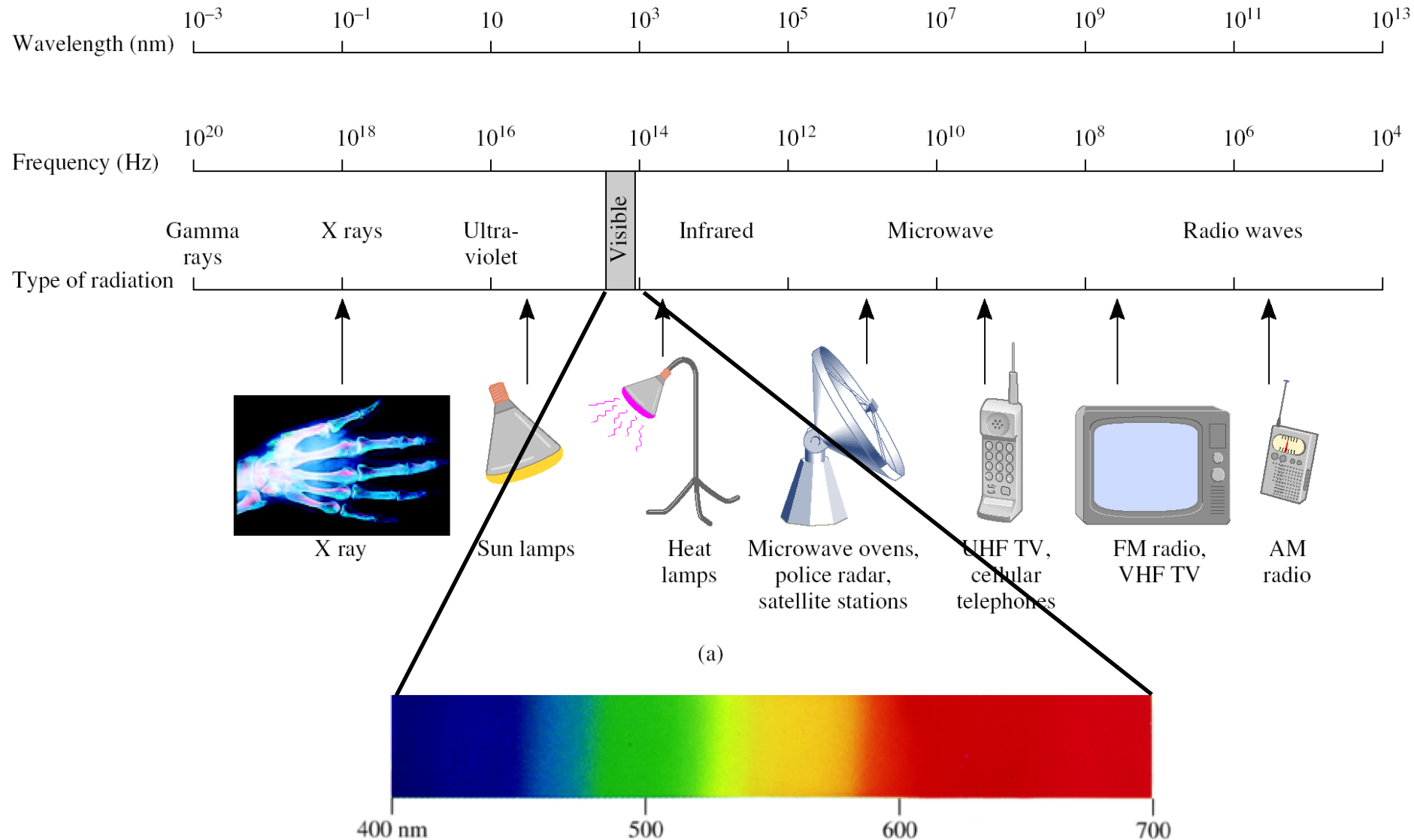
Electromagnetic radiation is the emission and transmission of energy in the form of electromagnetic waves.

Speed of light (c) in vacuum = 3.00×10^8 m/s

All electromagnetic radiation

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

Types of Electromagnetic Radiation



VIBGYOR

A photon has a frequency of 6.0×10^4 Hz. Convert this frequency into wavelength (nm). Does this frequency fall in the visible region?

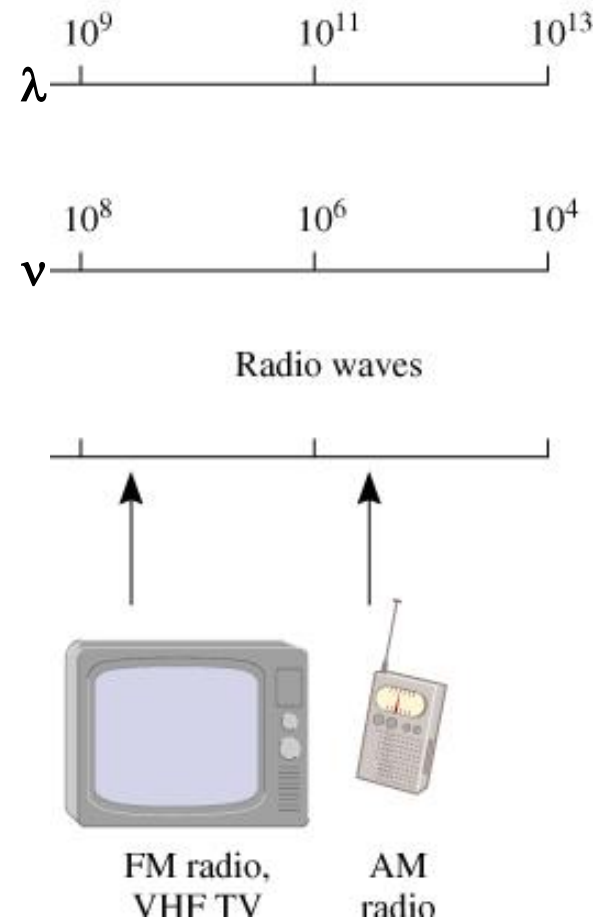
$$\lambda \times \nu = c$$

$$\lambda = c/\nu$$

$$= 3.00 \times 10^8 \text{ m/s} / 6.0 \times 10^4 \text{ Hz}$$

$$= 5.0 \times 10^3 \text{ m}$$

$$= 5.0 \times 10^{12} \text{ nm}$$



Mystery # 1, "Heated Solids Problem"

Solved by Max Planck in 1900

- When solids are heated, they emit electromagnetic radiation over a wide range of wavelengths.
- Radiant energy emitted by an object at a certain temperature depends on its wavelength.



Energy (light) is emitted or absorbed only in discrete quantities, like small packages or bundles (*quantum*).

- **Quantum:** *the smallest quantities of energy that can be emitted (or absorbed) in the form of electromagnetic radiation.*

Mystery # 1, "Heated Solids Problem"

- The energy E of a single quantum of energy is

$$E = h \times \nu$$

$$h = 6.63 \times 10^{-34} \text{ J}\cdot\text{s}, \text{ Planck's constant}$$

$$\nu = \text{frequency of radiation}$$

- Because $c = \nu \lambda$

$$\text{or } \nu = c / \lambda,$$

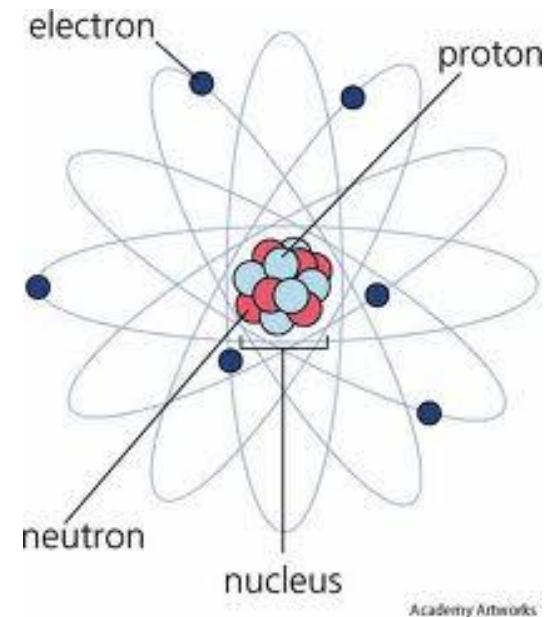
$$\text{so, } E = h \times c / \lambda$$

- According to quantum theory, energy is always emitted in **multiple** of $h\nu$; e.g., $h\nu$, $2h\nu$, $3h\nu$ but **never** $1.67h\nu$ or $4.98h\nu$.

Analogies of concept of quantization

➤ Concept of quantization has many analogies,

- Number of NSU faculty & students are quantized
- Matter is quantized, number of electrons, protons and neutrons and numbers of atoms must be integers



Analogies of concept of quantization

- Money system is based on “quantum” of value called “paisa”



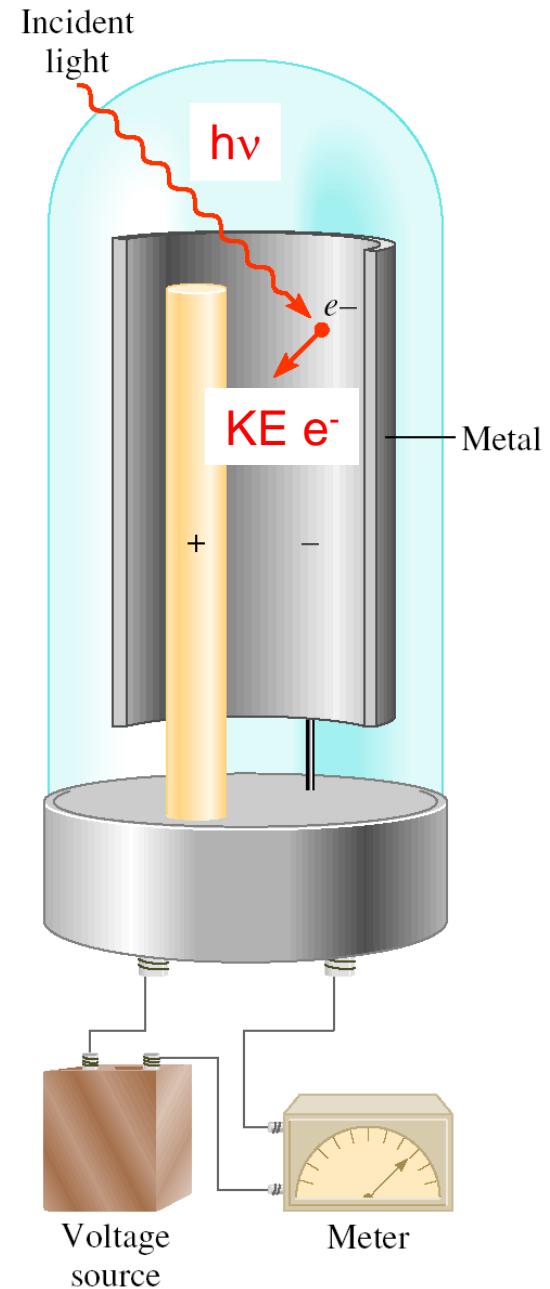
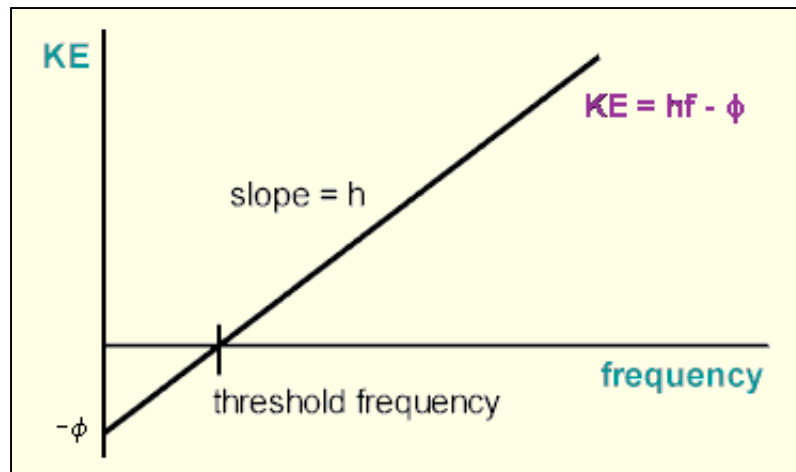
- Processes in living system,
 - hens lay ‘quantized’ eggs
 - a pregnant cat give birth to an integer number of kittens, not to one-half or three-quarters of a kitten



Mystery # 2, "Photoelectric Effect" Solved by Einstein in 1905

"Electrons are ejected from the surface of certain metals exposed to light of at least a certain minimum frequency, called threshold frequency."

- Number of electron ejected is proportional to the intensity of light
- Kinetic energy of electron is proportional to frequency of light



Photoelectric Effect

Einstein assumed that a beam of light is really a stream of particles.

Light has both:

1. wave nature
2. particle nature

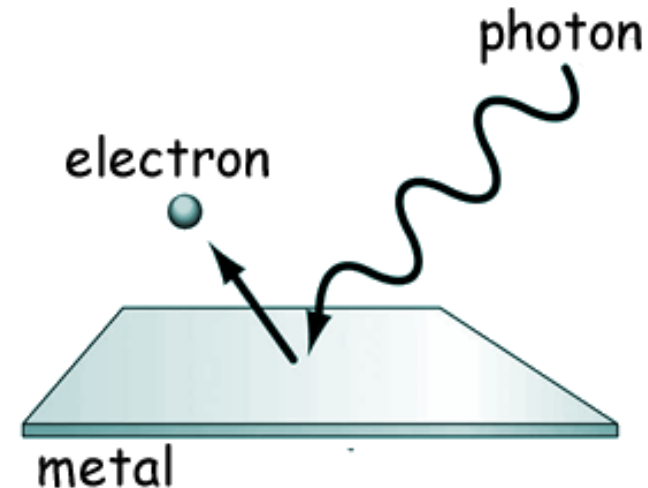
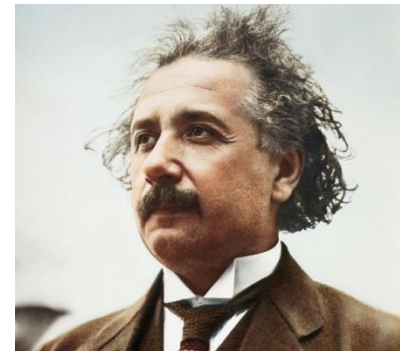
This “**particle**” of light is called **Photon**.

$$E = h\nu$$

$$h\nu = KE + BE$$

$$KE = h\nu - BE$$

where KE is the kinetic energy of the ejected electron and BE is the binding energy of the electron in the metal.



When copper is bombarded with high-energy electrons, X rays are emitted. Calculate the energy (in joules) associated with the photons if the wavelength of the X rays is 0.154 nm.

$$E = h \times \nu$$

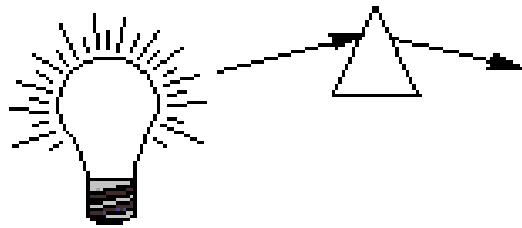
$$= h \times c / \lambda$$

$$= 6.63 \times 10^{-34} \text{ (J}\cdot\cancel{\text{s}}) \times 3.00 \times 10^8 \text{ (}\cancel{\text{m}}/\cancel{\text{s}}) / 0.154 \times 10^{-9} \text{ (}\cancel{\text{m}})$$

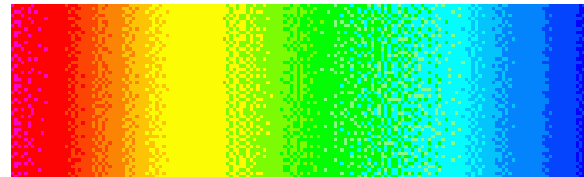
$$= 1.29 \times 10^{-15} \text{ J}$$

Continuous vs Line Spectrum

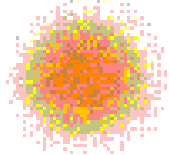
Absorption vs Emission Spectrum



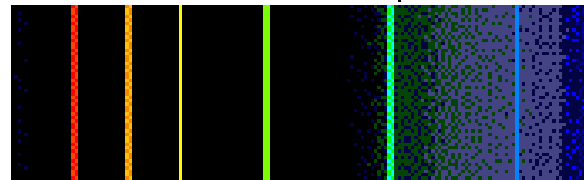
Continuum Spectrum



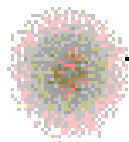
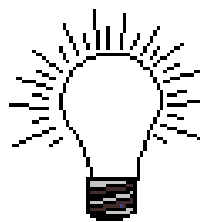
Hot Gas



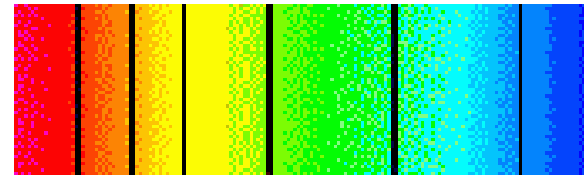
Emission Line Spectrum



Cold Gas

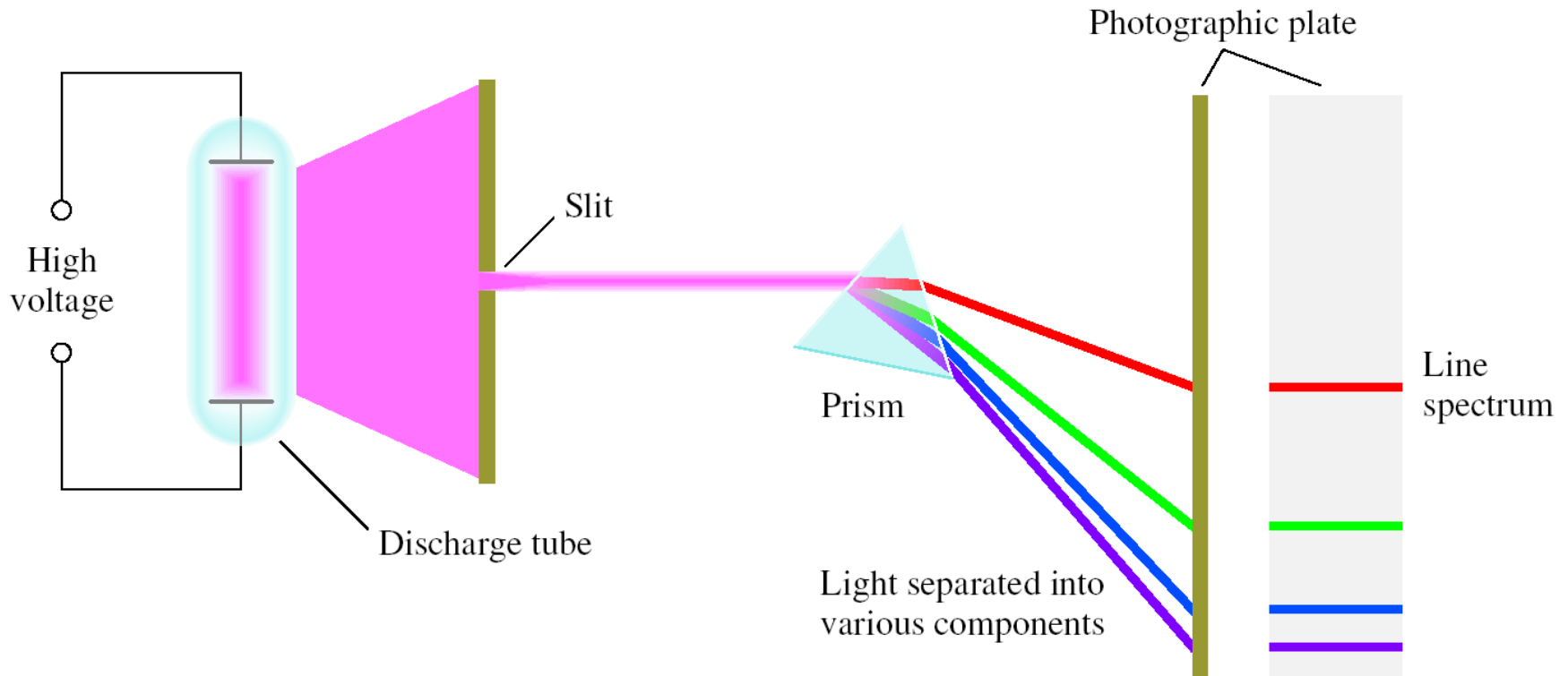


Absorption Line Spectrum

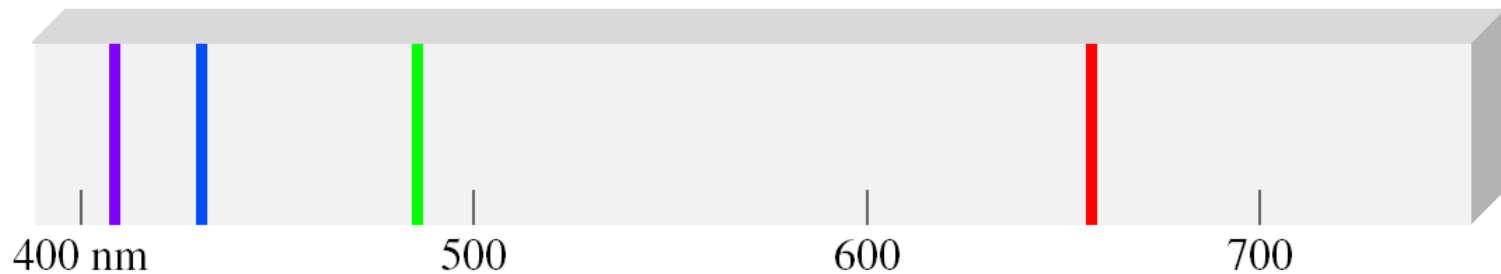


Rainbow

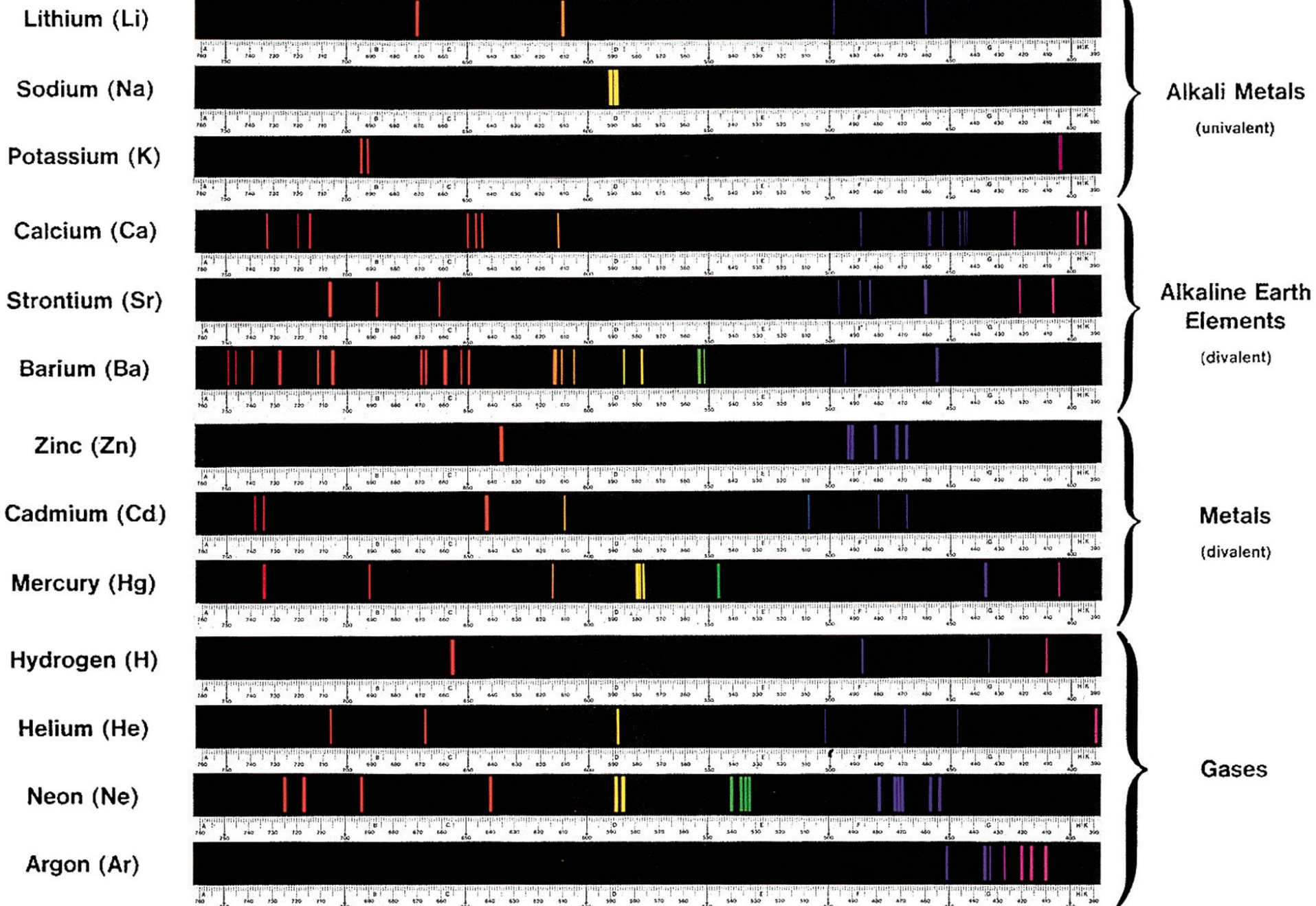
Emission Spectrum of the Hydrogen Atom



Line Emission Spectrum of Hydrogen Atoms



Bright-line Spectra



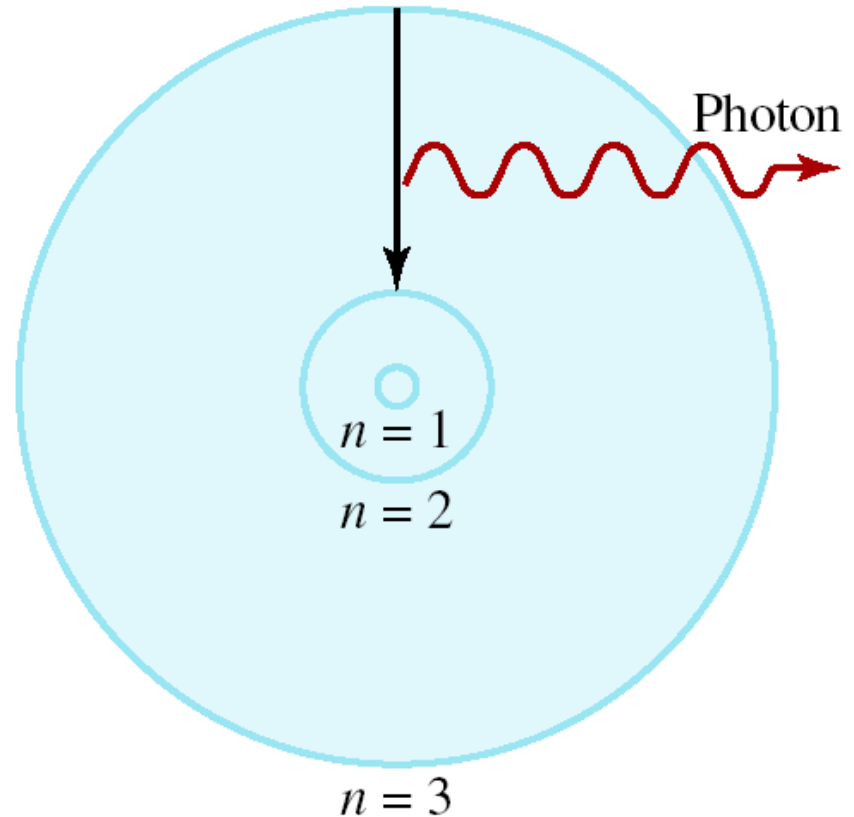
Bohr's Model of the Atom (1913)

1. e^- can only have specific (quantized) energy values
2. light is emitted as e^- moves from one energy level to a lower energy level

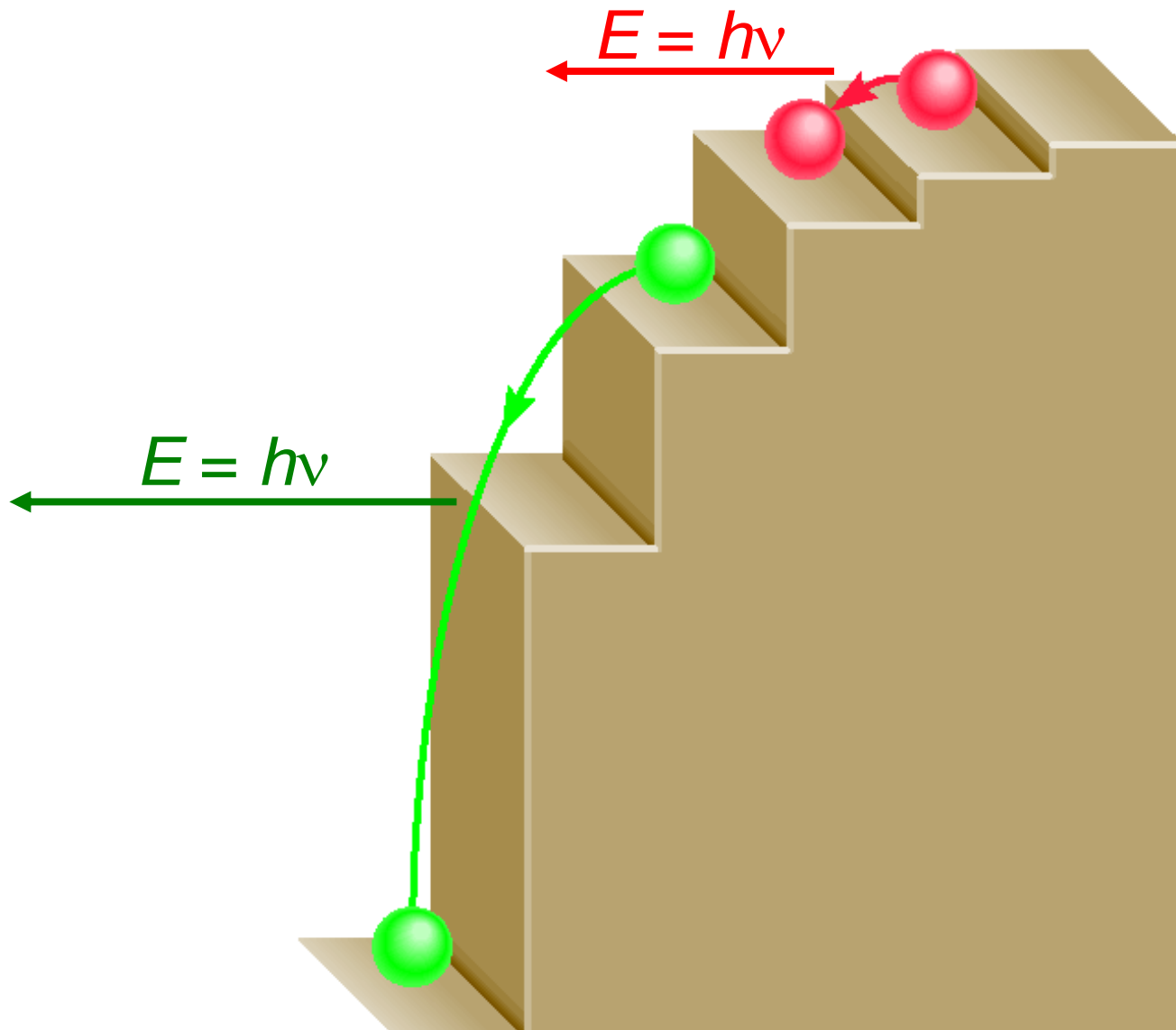
$$E_n = -R_H \left(\frac{1}{n^2} \right)$$

n (principal quantum number) = 1, 2, 3,...

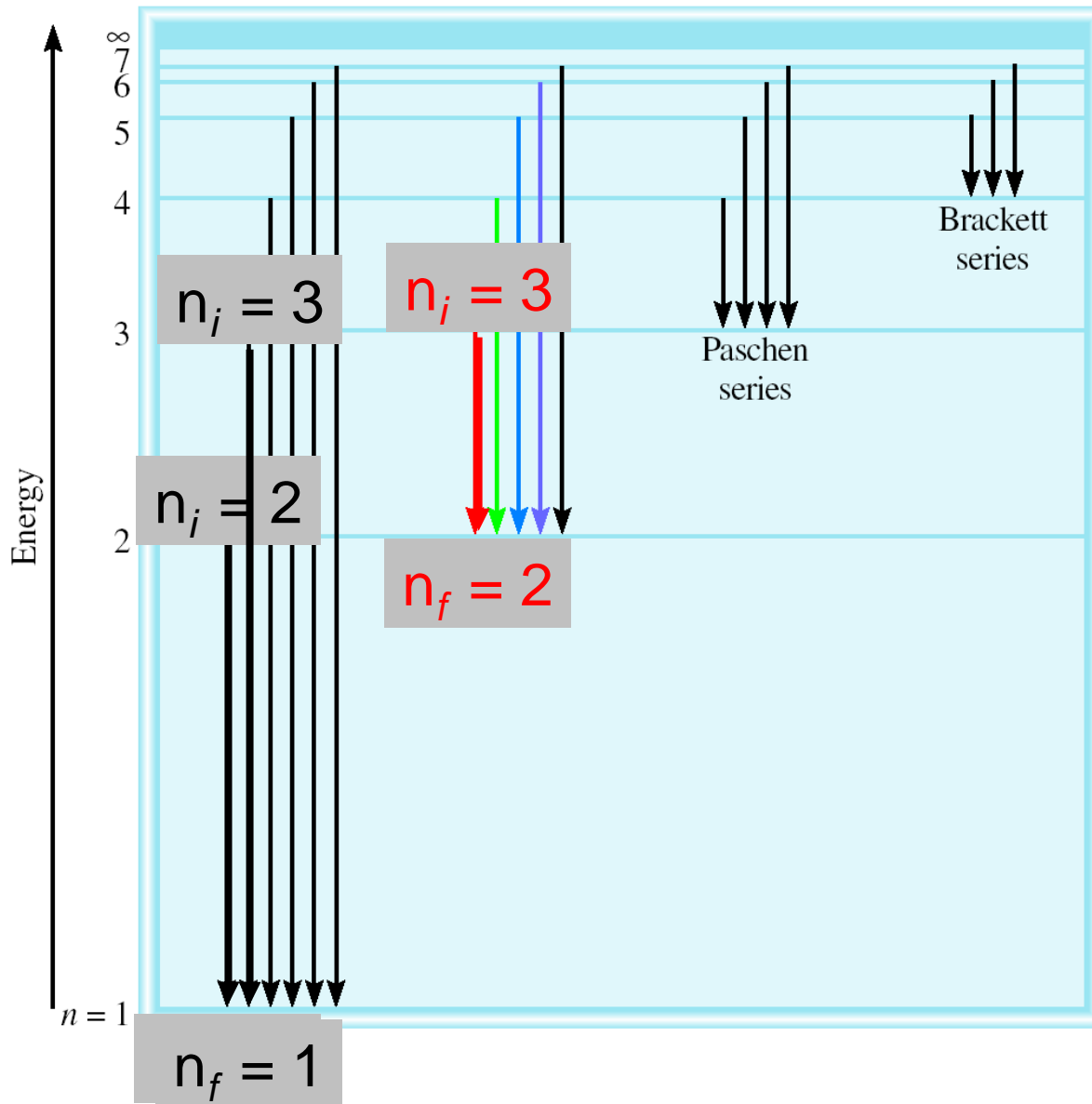
R_H (Rydberg constant) = $2.18 \times 10^{-18} \text{J}$



A mechanical analogy for the emission processes



Energy levels in H atom & various emission series



$$E_{\text{photon}} = \Delta E = E_f - E_i$$

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

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

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

The series of transitions in the hydrogen spectrum

TABLE 7.1 The Various Series in Atomic Hydrogen Emission Spectrum

Series	n_f	n_i	Spectrum Region
Lyman	1	2, 3, 4, . . .	Ultraviolet
Balmer	2	3, 4, 5, . . .	Visible and ultraviolet
Paschen	3	4, 5, 6, . . .	Infrared
Brackett	4	5, 6, 7, . . .	Infrared

Calculate the wavelength (in nm) of a photon emitted by a hydrogen atom when its electron drops from the $n = 5$ state to the $n = 3$ state.

$$\begin{aligned} E_{\text{photon}} &= \Delta E = R_H \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \\ &= 2.18 \times 10^{-18} \text{ J} \times (1/25 - 1/9) \\ &= -1.55 \times 10^{-19} \text{ J} \end{aligned}$$

$$E_{\text{photon}} = h \times c / \lambda$$

$$\lambda = h \times c / E_{\text{photon}}$$

$$= 6.63 \times 10^{-34} \text{ (J}\cdot\text{s)} \times 3.00 \times 10^8 \text{ (m/s)} / 1.55 \times 10^{-19} \text{ J}$$

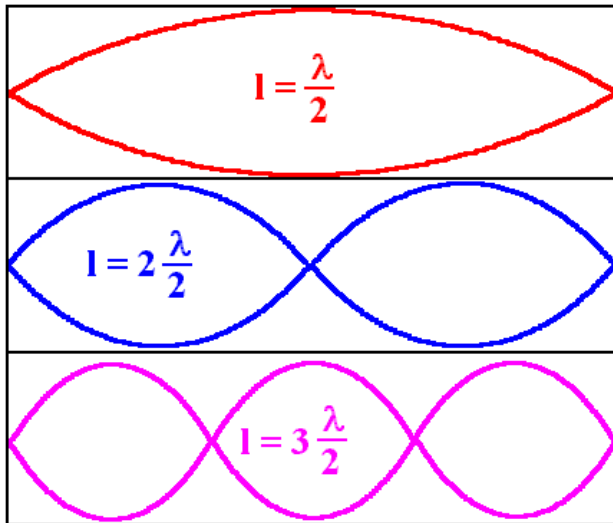
$$= 1280 \text{ nm}$$

The Dual Nature of the Electron

Why is e^- energy quantized?

De Broglie (1924) reasoned that e^- is both particle and wave.

Standing Waves
Only Certain Ones are Allowed

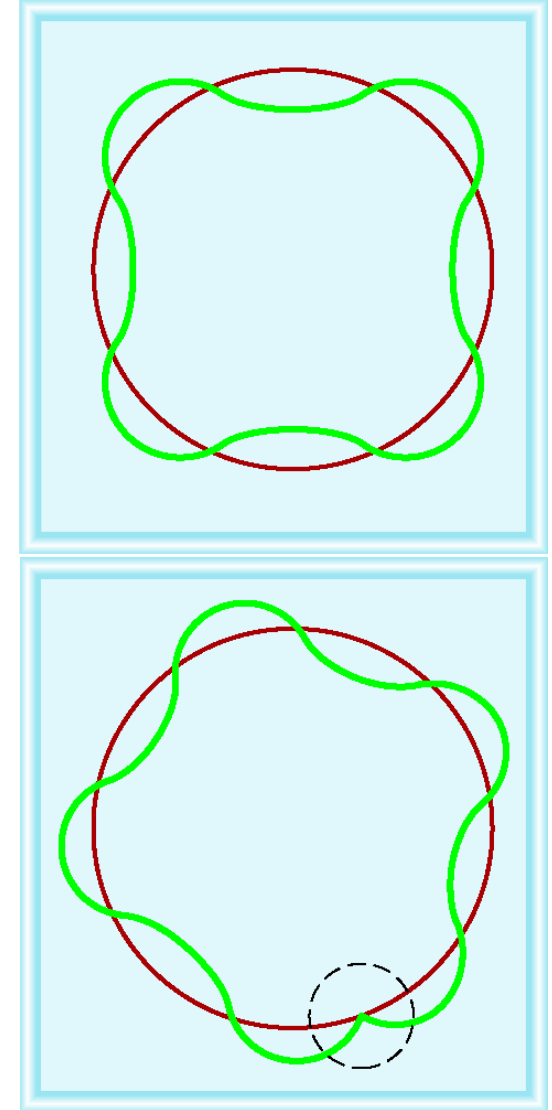


$$l = n(\lambda/2), n = 1, 2, 3, \dots$$

$$2\pi r = n\lambda$$

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

u = velocity of e^-
 m = mass of e^-



What is the de Broglie wavelength (in nm) associated with a 2.5 g Ping-Pong ball traveling at 15.6 m/s?

$$\lambda = h/mu \quad h \text{ in J}\cdot\text{s} \quad m \text{ in kg} \quad u \text{ in (m/s)}$$

$$\lambda = 6.63 \times 10^{-34} / (2.5 \times 10^{-3} \times 15.6)$$

$$= 1.7 \times 10^{-32} \text{ m}$$

$$= 1.7 \times 10^{-23} \text{ nm}$$

Quantum Mechanics

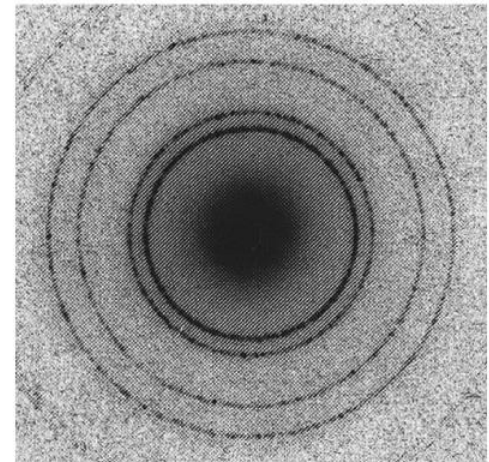
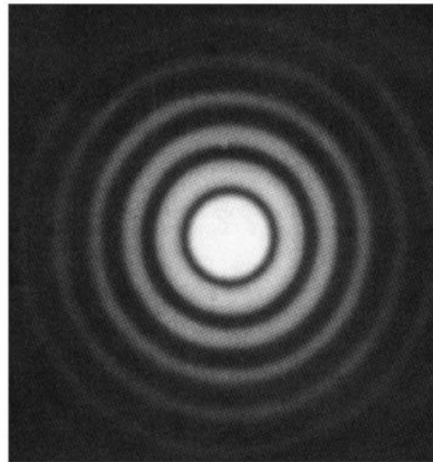
- Bohr's approach did not account for the emission spectra of atoms containing more than one electrons (He, Li).
- When electrons are wavelike, how can the “**position**” of a wave be specified?
- To describe the problem of trying to locate a subatomic particle that behaves like a wave, Werner Heisenberg formulated the ***Heisenberg uncertainty principle***.

It is impossible to know simultaneously both the momentum p (defined as mass times velocity) and the position of a particle with certainty.

Quantum Mechanics

$$(\Delta x)(\Delta p) \geq \frac{h}{4\pi}$$

where, Δx is the uncertainties in measuring the **position**, and Δp is the uncertainties in measuring the **momentum**.



X-ray, & electron diffraction pattern on Aluminium foil

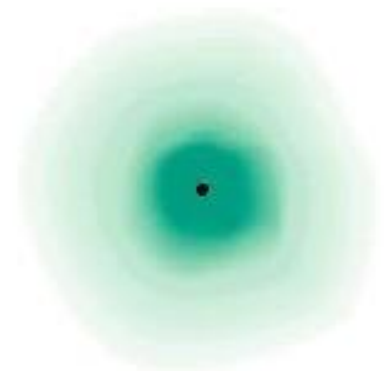
Quantum Mechanical Description of H Atom

In 1926 Schrodinger wrote an equation that described both the particle and wave nature of the e^-
($E\psi = \mathcal{H}\psi$)

Wave function (ψ) describes:

1. energy of e^- with a given ψ
2. ψ^2 probability of finding e^- in a volume of space

- Schrodinger's equation can only be solved **exactly** for the hydrogen atom.
- Must approximate its solution for multi-electron systems.



Electron density distribution in the hydrogen atom

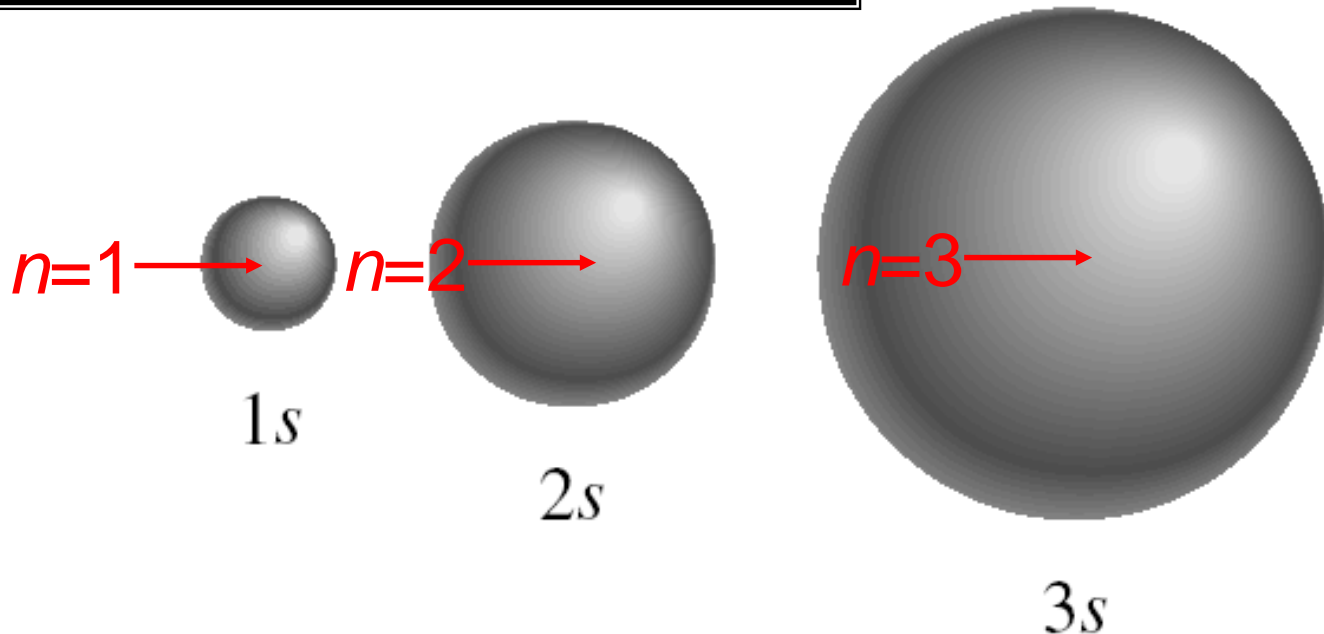
Quantum Numbers & Atomic Orbitals

ψ is a function of three numbers called
quantum numbers (n , l , m_l , m_s)

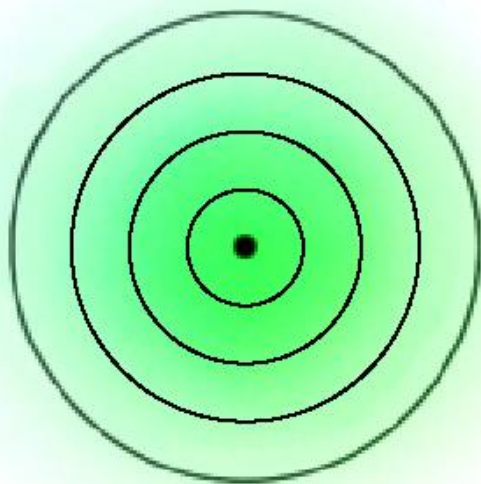
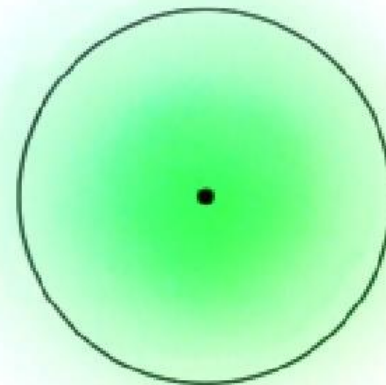
principal quantum number n

$n = 1, 2, 3, 4, \dots$

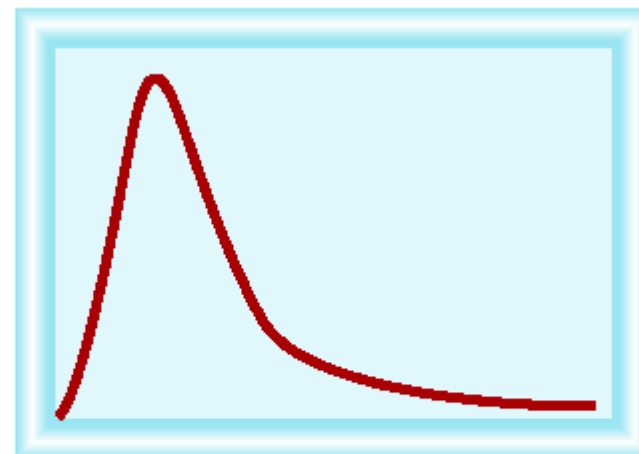
Distance of e^- from the nucleus



Where 90% of the e^- density is found → for the 1s orbital



Radial
probability



Distance from
nucleus

Quantum Numbers & Atomic Orbitals

quantum numbers: (n, l, m_l, m_s)

angular momentum quantum number l

for a given value of n , $l = 0, 1, 2, 3, \dots n-1$

$$n = 1, l = 0$$

$$n = 2, l = 0 \text{ or } 1$$

$$n = 3, l = 0, 1, \text{ or } 2$$

$l = 0$ s orbital

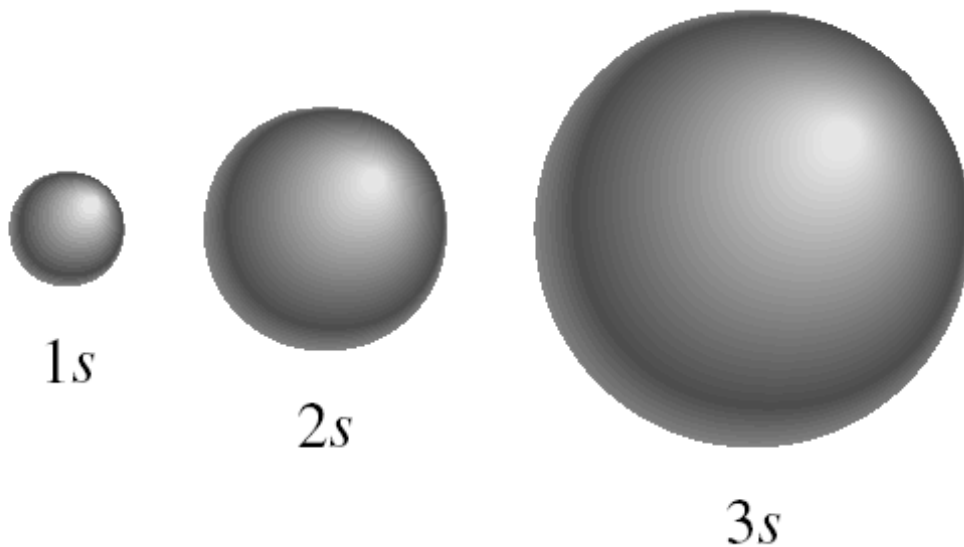
$l = 1$ p orbital

$l = 2$ d orbital

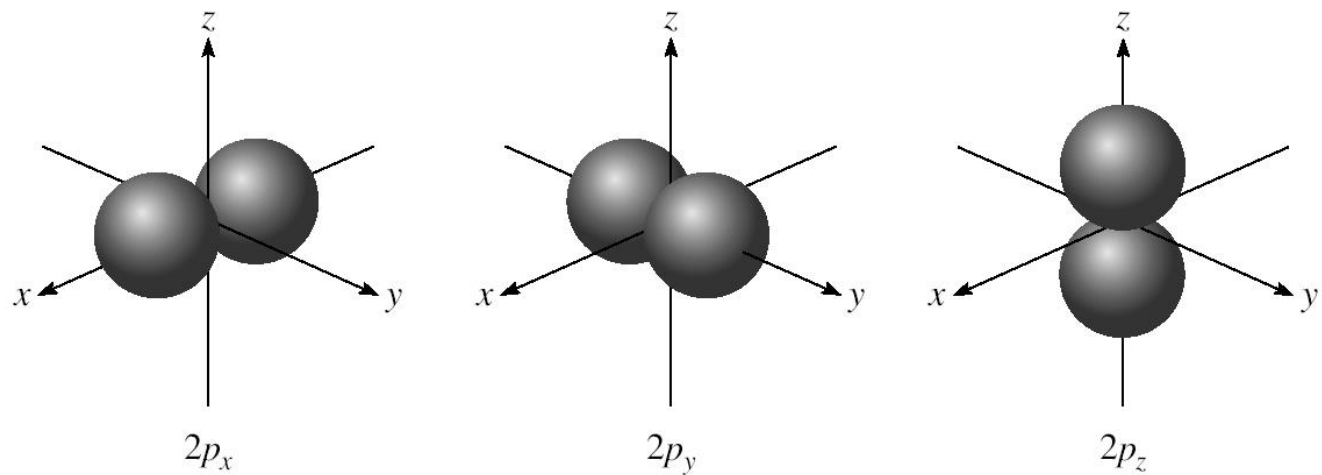
$l = 3$ f orbital

Shape of the “volume” of space that the e^- occupies

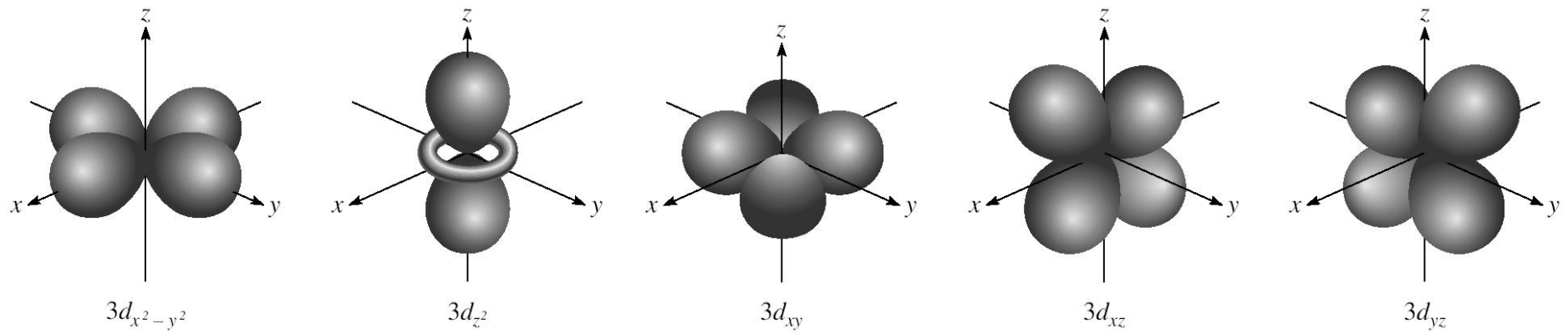
$l = 0$ (s orbitals)



$l = 1$ (p orbitals)



$l = 2$ (d orbitals)



Quantum Numbers & Atomic Orbitals

quantum numbers: (n, l, m_l, m_s)

magnetic quantum number m_l

for a given value of l

$$m_l = -l, \dots, 0, \dots, +l$$

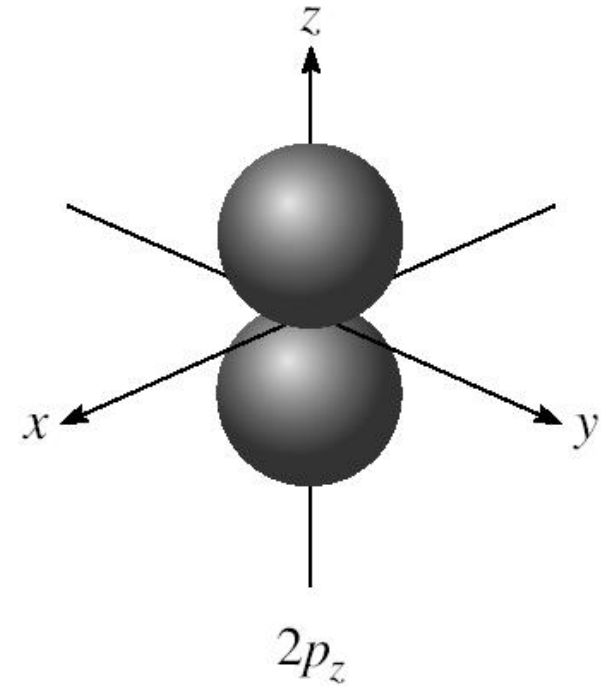
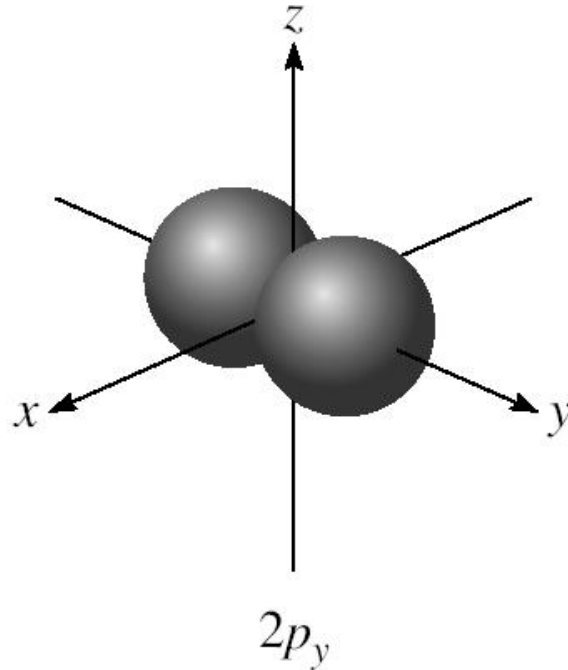
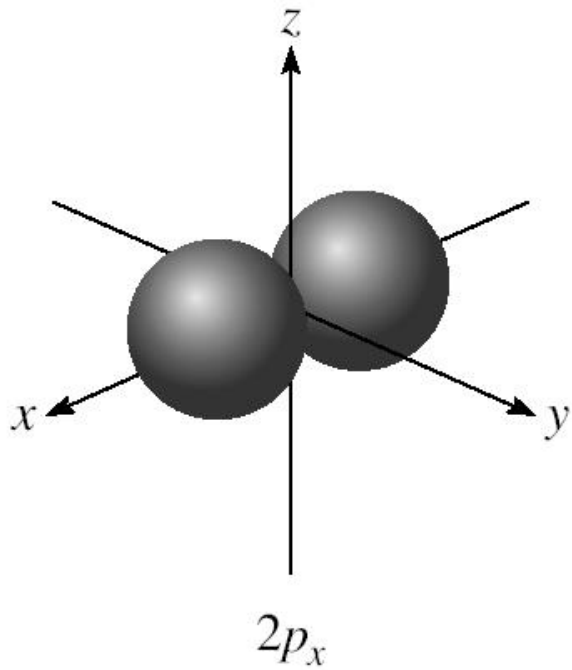
if $l = 1$ (p orbital), $m_l = -1, 0, \text{ or } 1$

if $l = 2$ (d orbital), $m_l = -2, -1, 0, 1, \text{ or } 2$

Orientation of the orbital in space

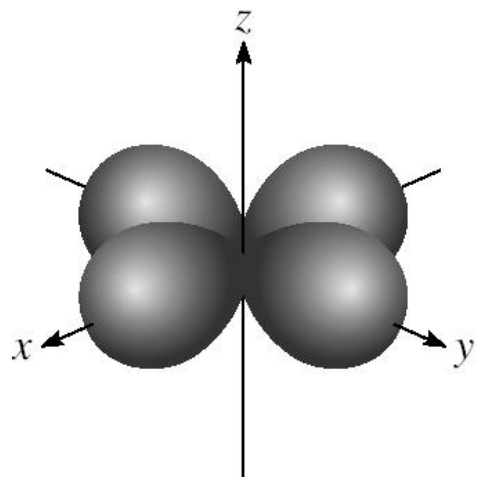
$$m_l = -1, 0, \text{ or } 1$$

3 orientations in space

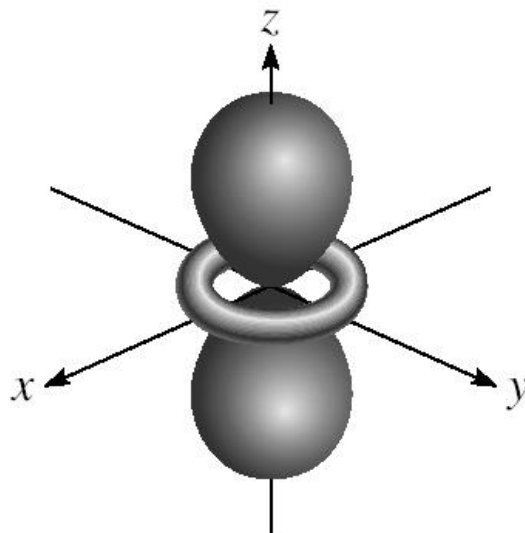


$m_l = -2, -1, 0, 1, \text{ or } 2$

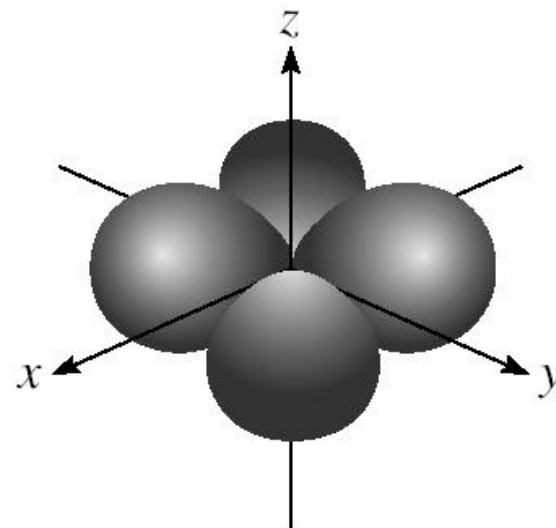
5 orientations in space



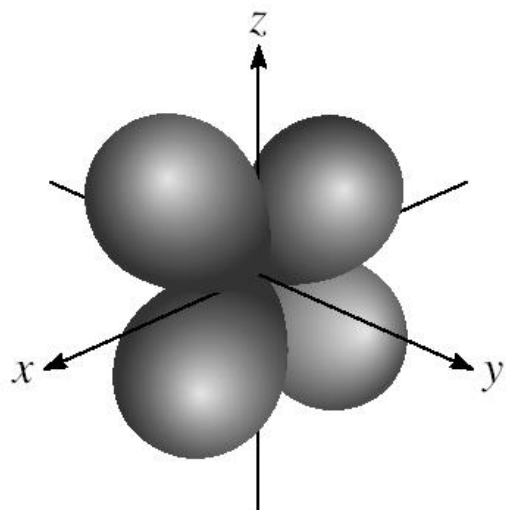
$3d_{x^2-y^2}$



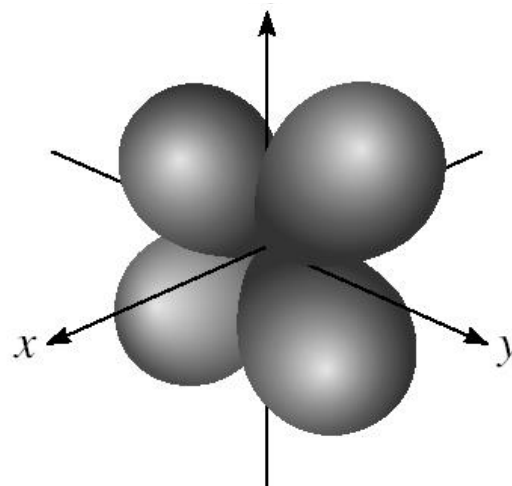
$3d_{z^2}$



$3d_{xy}$



$3d_{xz}$



$3d_{yz}$

Quantum Numbers & Atomic Orbitals

(n, l, m_l, m_s)

spin quantum number m_s

$m_s = +\frac{1}{2}$ **or** $-\frac{1}{2}$

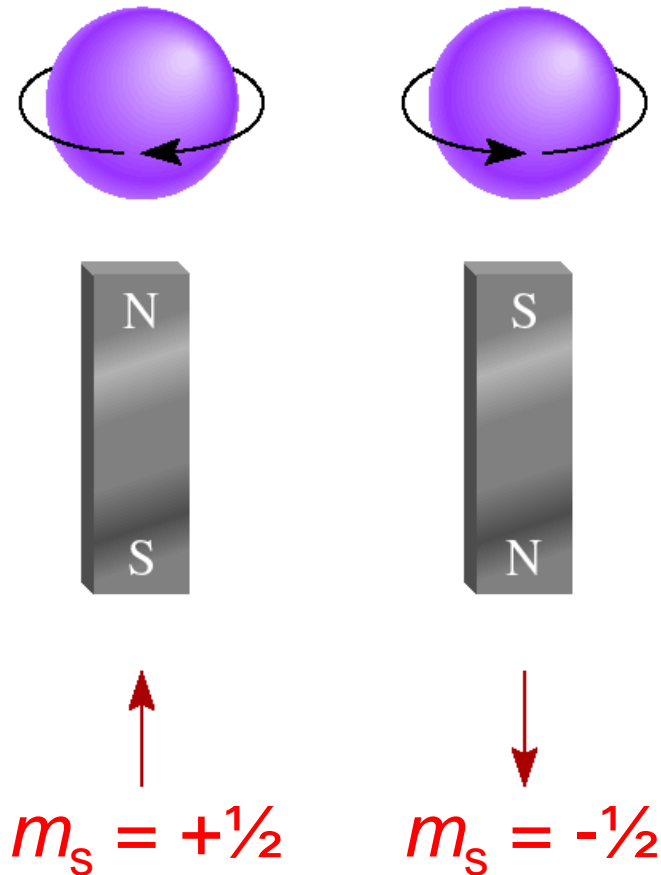
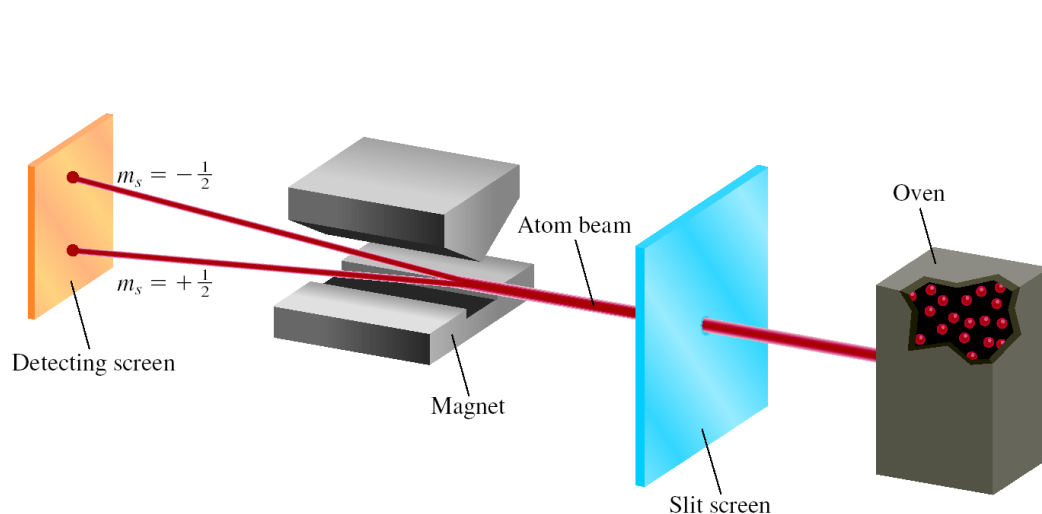


TABLE 7.2 **Relation Between Quantum Numbers and Atomic Orbitals**

n	ℓ	m_ℓ	Number of Orbitals	Atomic Orbital Designations
1	0	0	1	$1s$
2	0	0	1	$2s$
	1	$-1, 0, 1$	3	$2p_x, 2p_y, 2p_z$
3	0	0	1	$3s$
	1	$-1, 0, 1$	3	$3p_x, 3p_y, 3p_z$
	2	$-2, -1, 0, 1, 2$	5	$3d_{xy}, 3d_{yz}, 3d_{xz},$ $3d_{x^2-y^2}, 3d_{z^2}$
\vdots	\vdots	\vdots	\vdots	\vdots
\vdots	\vdots	\vdots	\vdots	\vdots
\vdots	\vdots	\vdots	\vdots	\vdots

Quantum Numbers & Atomic Orbitals

quantum numbers: (n, l, m_l, m_s)

Existence (and energy) of electron in atom is described by its **unique** wave function ψ .

Pauli exclusion principle - no two electrons in an atom can have the same four quantum numbers.



Each seat can hold only one individual at a time.

Quantum Numbers & Atomic Orbitals

quantum numbers: (n, l, m_l, m_s)

Shell – electrons with the same value of n

Subshell – electrons with the same values of n **and** l

Orbital – electrons with the same values of n , l , **and** m_l

How many electrons can an orbital hold?

If n , l , and m_l are fixed, then $m_s = \frac{1}{2}$ or $-\frac{1}{2}$

$\psi = (n, l, m_l, \frac{1}{2})$ **or** $\psi = (n, l, m_l, -\frac{1}{2})$

An orbital can hold 2 electrons

How many 2p orbitals are there in an atom?

$n=2$



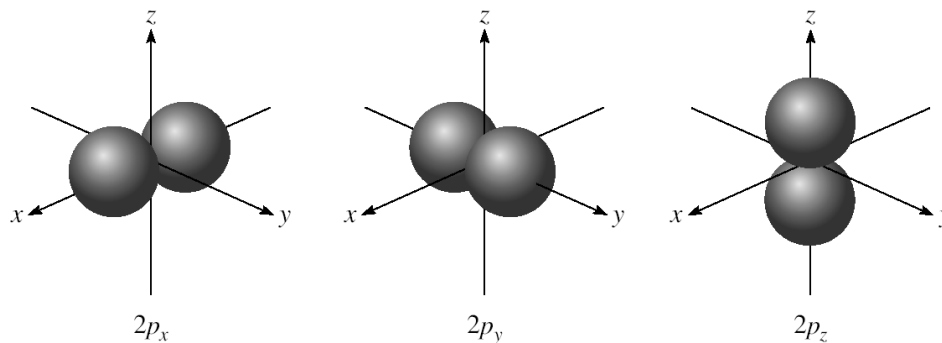
2p



$l=1$

If $l = 1$, then $m_l = -1, 0, \text{ or } +1$

3 orbitals



How many electrons can be placed in the 3d subshell?

$n=3$



3d



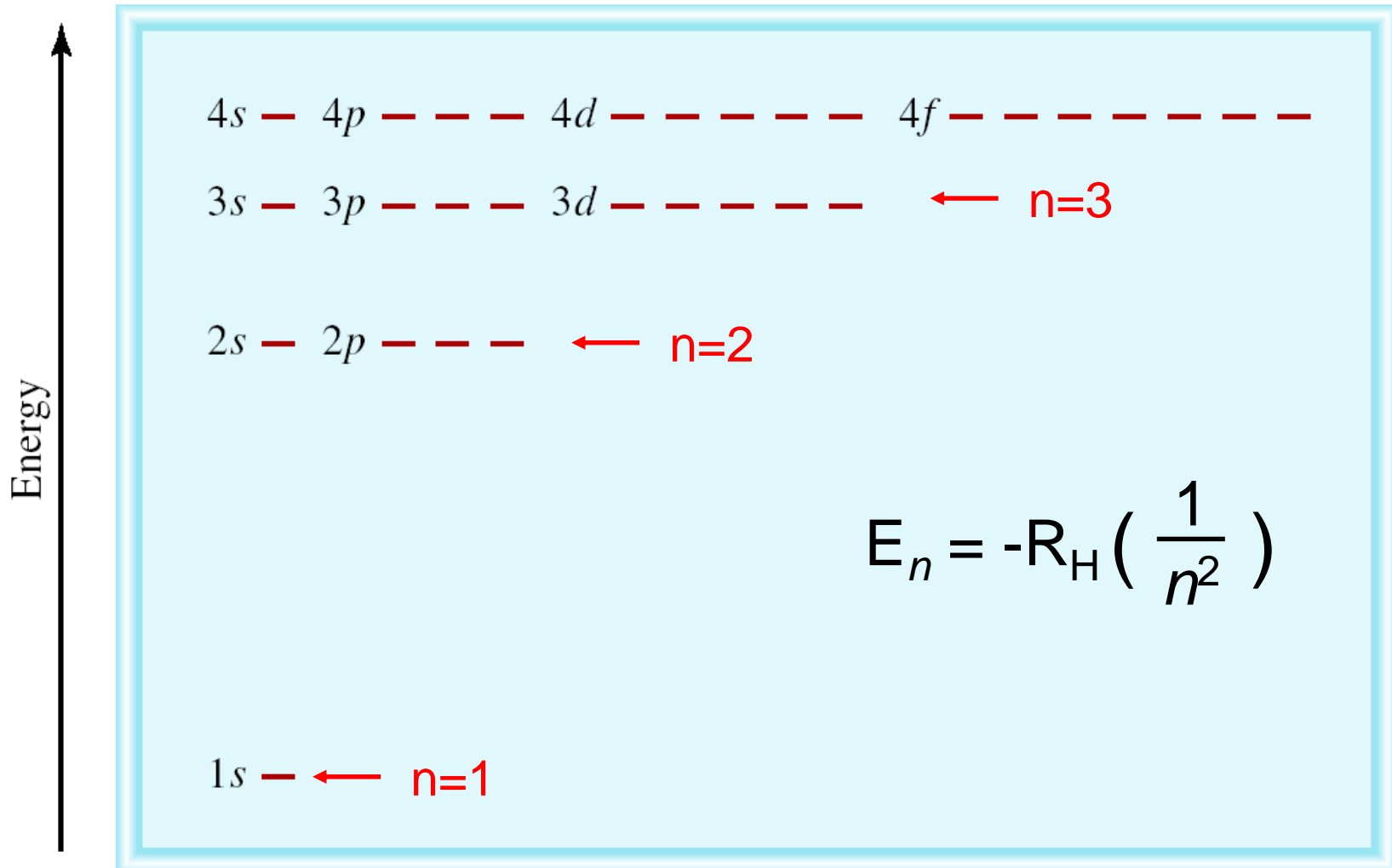
$l=2$

If $l = 2$, then $m_l = -2, -1, 0, +1, \text{ or } +2$

5 orbitals which can hold a total of 10 e^-

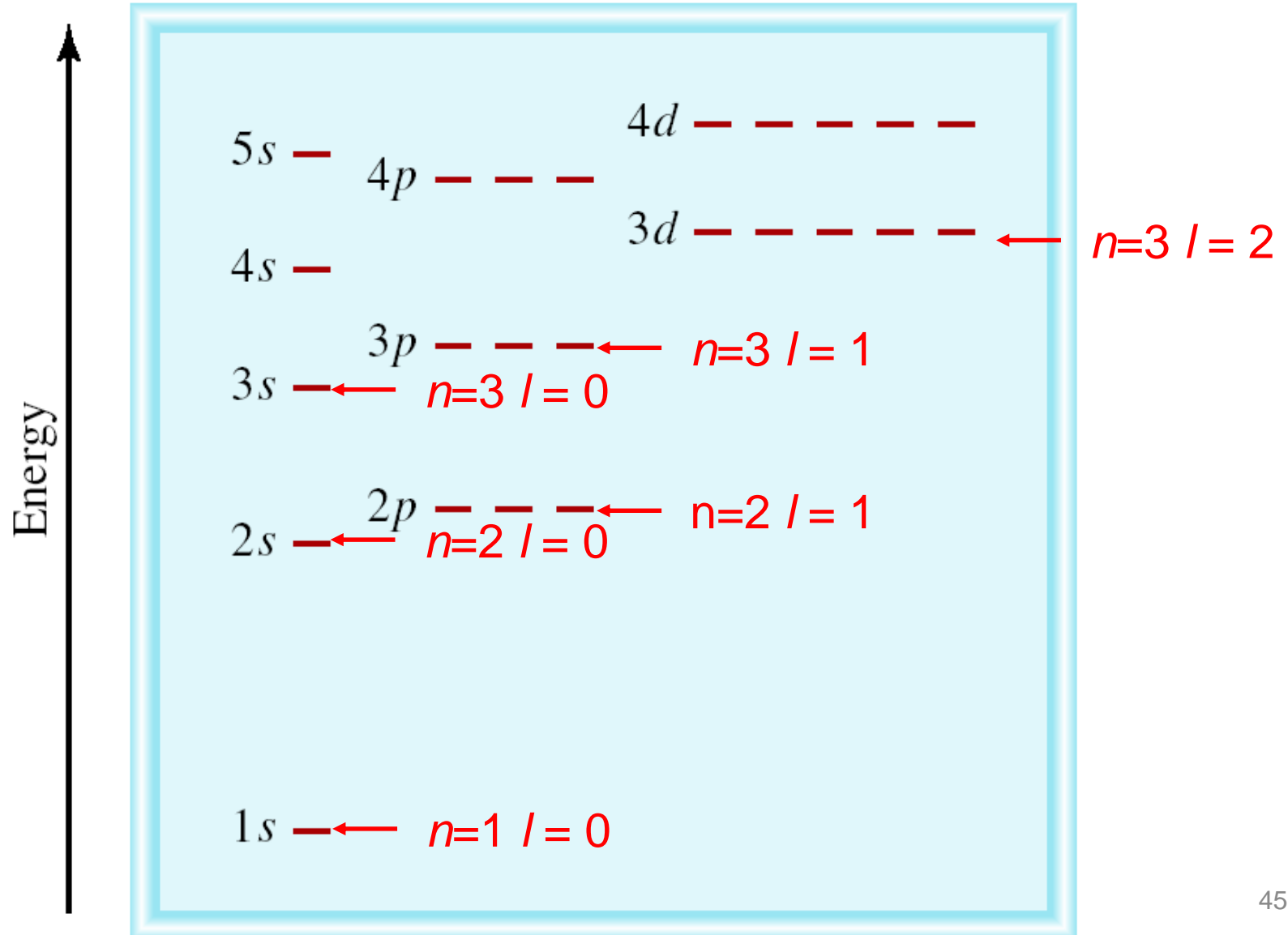
Energies of orbitals in a single electron atom

Energy only depends on principal quantum number ***n***

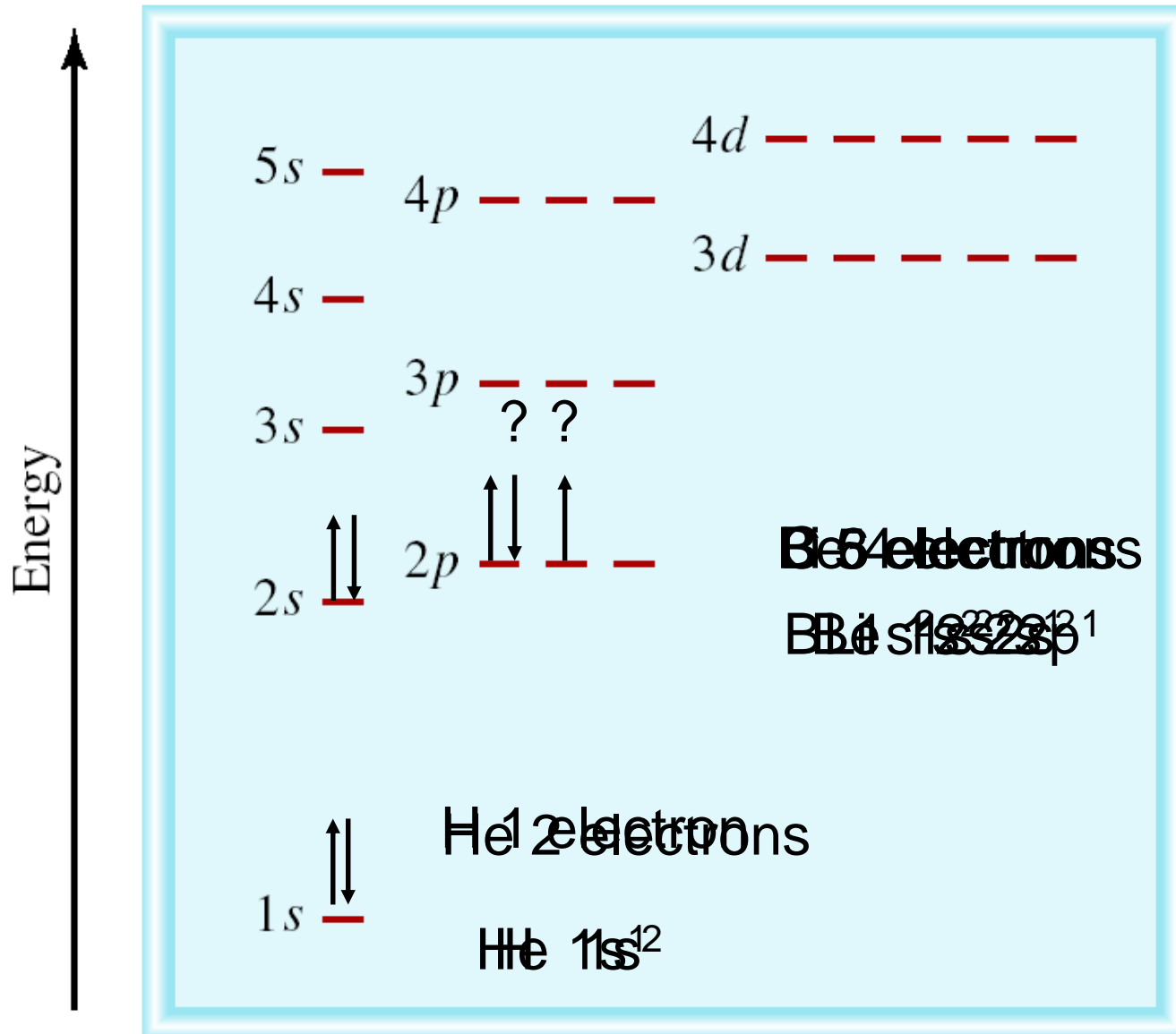


Energies of orbitals in a multi-electron atom

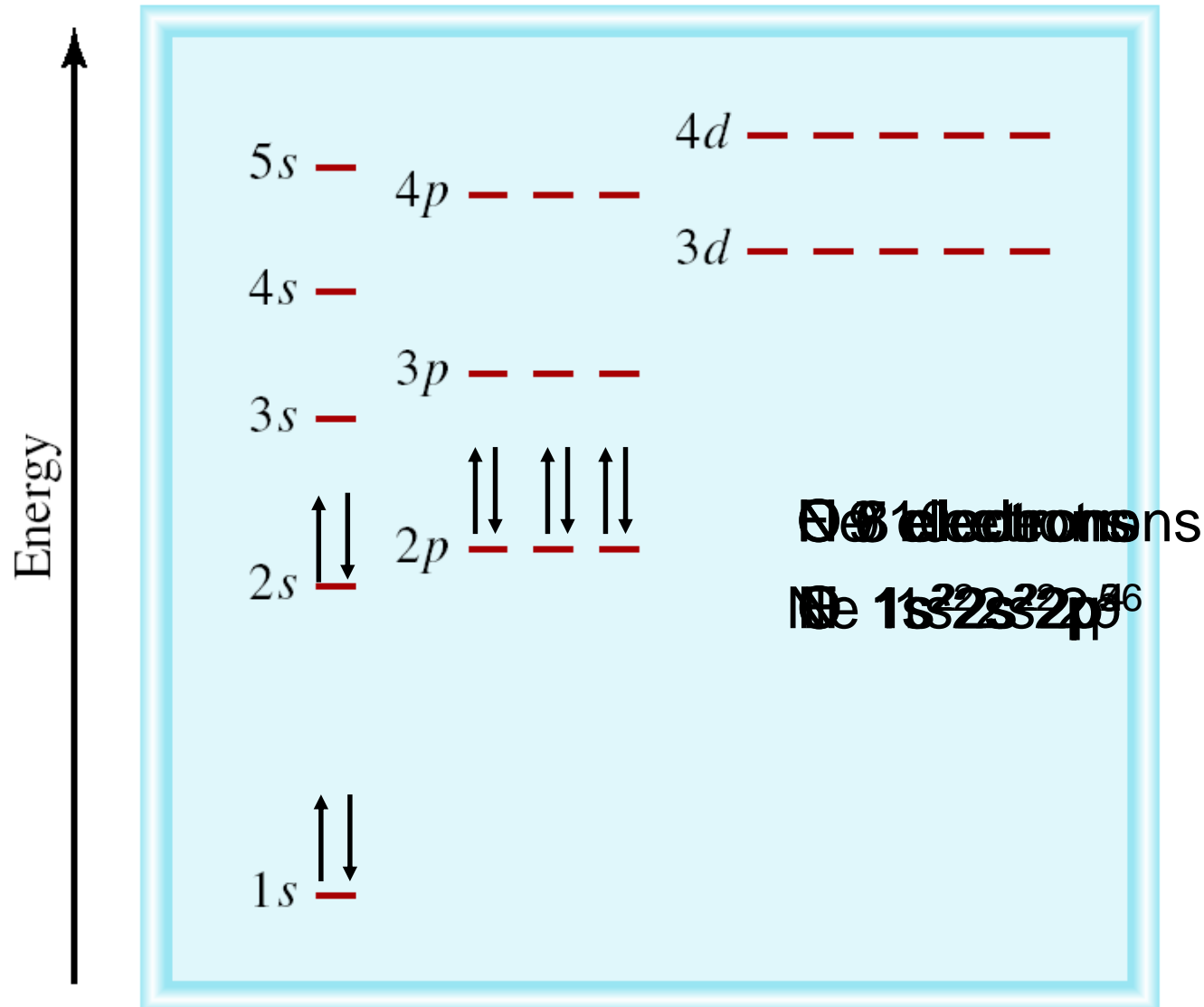
Energy depends on n and l



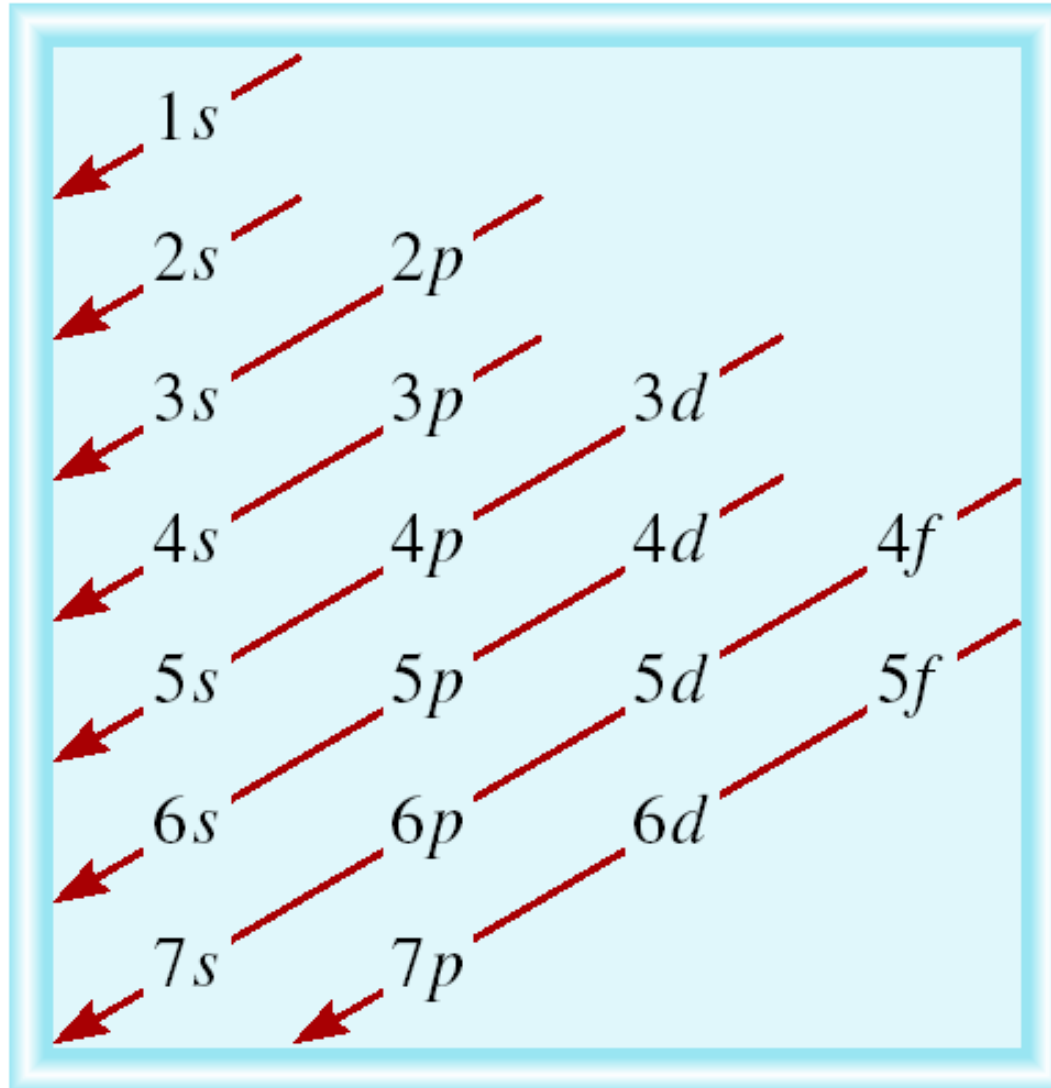
"Fill up" electrons in lowest energy orbitals (Aufbau principle)



The most stable arrangement of electrons in subshells is the one with the greatest number of parallel spins (Hund's rule).



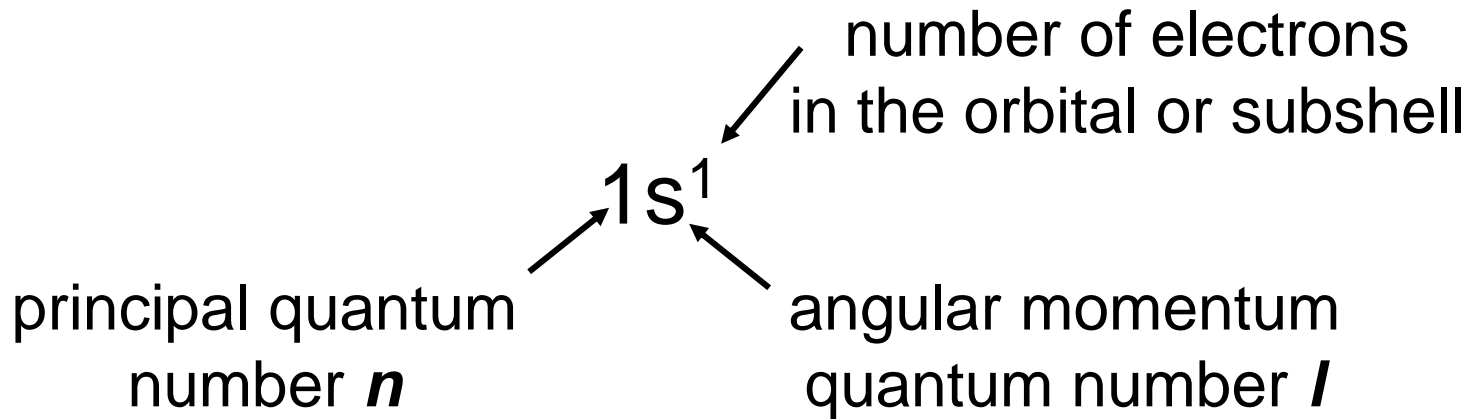
Order of orbitals (filling) in multi-electron atom



$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s$

Electron Configuration

How the electrons are distributed among the various atomic orbitals in an atom.



Orbital diagram



Electron Configuration

What is the electron configuration of Mg?

Mg 12 electrons

$1s < 2s < 2p < 3s < 3p < 4s$

$1s^2 2s^2 2p^6 3s^2$ $2 + 2 + 6 + 2 = 12$ electrons

Abbreviated as $[\text{Ne}]3s^2$ $[\text{Ne}] 1s^2 2s^2 2p^6$

What are the possible quantum numbers for the last (outermost) electron in Cl?

Cl 17 electrons $1s < 2s < 2p < 3s < 3p < 4s$

$1s^2 2s^2 2p^6 3s^2 3p^5$ $2 + 2 + 6 + 2 + 5 = 17$ electrons

Last electron added to 3p orbital

$n = 3$ $l = 1$ $m_l = -1, 0, \text{ or } +1$ $m_s = \frac{1}{2} \text{ or } -\frac{1}{2}$

Outermost subshell being filled with electrons

1s		1s
2s		2p
3s		3p
4s	3d	4p
5s	4d	5p
6s	5d	6p
7s	6d	7p
4f		
5f		

Outermost subshell electrons quantum numbers

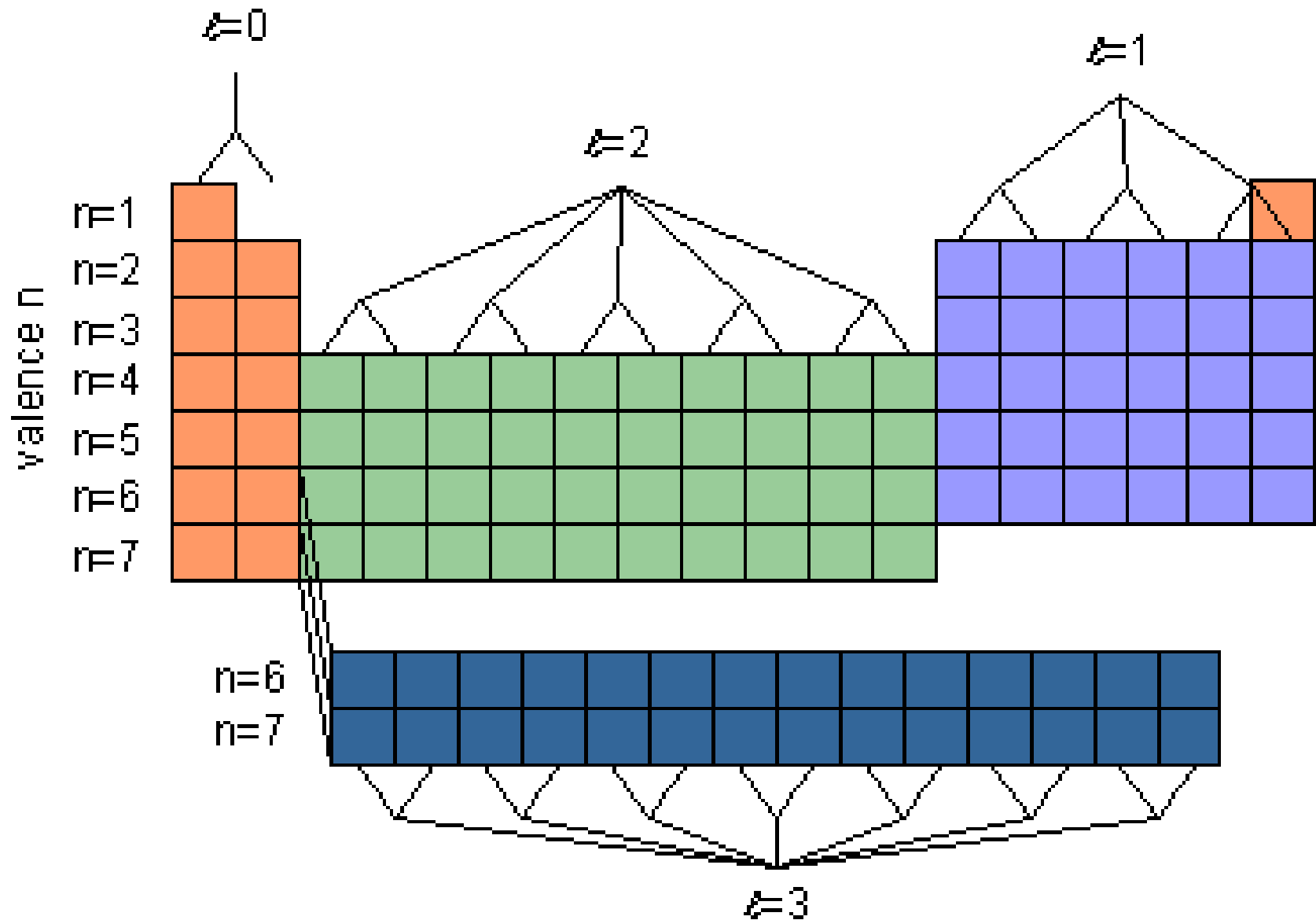
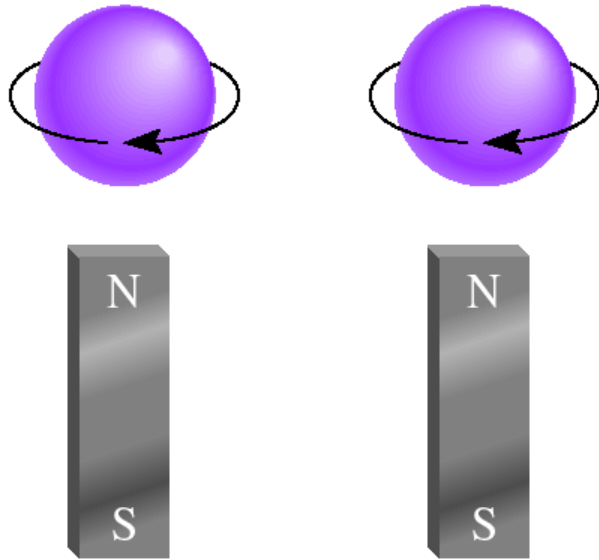


TABLE 7.3 The Ground-State Electron Configurations of the Elements*

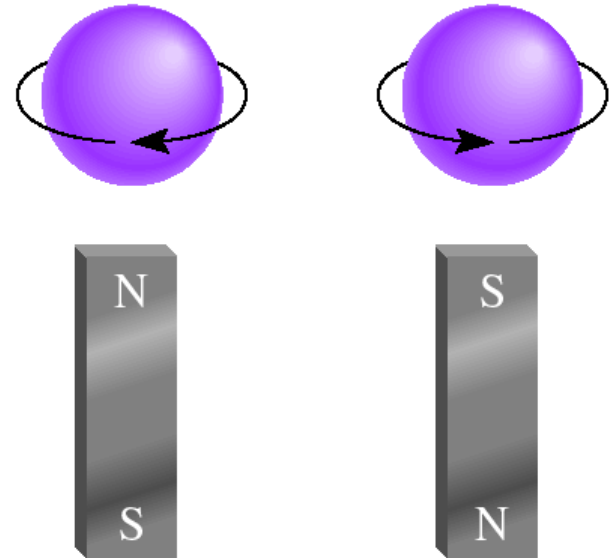
Atomic Number	Symbol	Electron Configuration	Atomic Number	Symbol	Electron Configuration	Atomic Number	Symbol	Electron Configuration
1	H	$1s^1$	38	Sr	$[\text{Kr}]5s^2$	75	Re	$[\text{Xe}]6s^24f^{14}5d^5$
2	He	$1s^2$	39	Y	$[\text{Kr}]5s^24d^1$	76	Os	$[\text{Xe}]6s^24f^{14}5d^6$
3	Li	$[\text{He}]2s^1$	40	Zr	$[\text{Kr}]5s^24d^2$	77	Ir	$[\text{Xe}]6s^24f^{14}5d^7$
4	Be	$[\text{He}]2s^2$	41	Nb	$[\text{Kr}]5s^14d^4$	78	Pt	$[\text{Xe}]6s^14f^{14}5d^9$
5	B	$[\text{He}]2s^22p^1$	42	Mo	$[\text{Kr}]5s^14d^5$	79	Au	$[\text{Xe}]6s^14f^{14}5d^{10}$
6	C	$[\text{He}]2s^22p^2$	43	Tc	$[\text{Kr}]5s^24d^5$	80	Hg	$[\text{Xe}]6s^24f^{14}5d^{10}$
7	N	$[\text{He}]2s^22p^3$	44	Ru	$[\text{Kr}]5s^14d^7$	81	Tl	$[\text{Xe}]6s^24f^{14}5d^{10}6p^1$
8	O	$[\text{He}]2s^22p^4$	45	Rh	$[\text{Kr}]5s^14d^8$	82	Pb	$[\text{Xe}]6s^24f^{14}5d^{10}6p^2$
9	F	$[\text{He}]2s^22p^5$	46	Pd	$[\text{Kr}]4d^{10}$	83	Bi	$[\text{Xe}]6s^24f^{14}5d^{10}6p^3$
10	Ne	$[\text{He}]2s^22p^6$	47	Ag	$[\text{Kr}]5s^14d^{10}$	84	Po	$[\text{Xe}]6s^24f^{14}5d^{10}6p^4$
11	Na	$[\text{Ne}]3s^1$	48	Cd	$[\text{Kr}]5s^24d^{10}$	85	At	$[\text{Xe}]6s^24f^{14}5d^{10}6p^5$
12	Mg	$[\text{Ne}]3s^2$	49	In	$[\text{Kr}]5s^24d^{10}5p^1$	86	Rn	$[\text{Xe}]6s^24f^{14}5d^{10}6p^6$
13	Al	$[\text{Ne}]3s^23p^1$	50	Sn	$[\text{Kr}]5s^24d^{10}5p^2$	87	Fr	$[\text{Rn}]7s^1$
14	Si	$[\text{Ne}]3s^23p^2$	51	Sb	$[\text{Kr}]5s^24d^{10}5p^3$	88	Ra	$[\text{Rn}]7s^2$
15	P	$[\text{Ne}]3s^23p^3$	52	Te	$[\text{Kr}]5s^24d^{10}5p^4$	89	Ac	$[\text{Rn}]7s^26d^1$
16	S	$[\text{Ne}]3s^23p^4$	53	I	$[\text{Kr}]5s^24d^{10}5p^5$	90	Th	$[\text{Rn}]7s^26d^2$
17	Cl	$[\text{Ne}]3s^23p^5$	54	Xe	$[\text{Kr}]5s^24d^{10}5p^6$	91	Pa	$[\text{Rn}]7s^25f^26d^1$
18	Ar	$[\text{Ne}]3s^23p^6$	55	Cs	$[\text{Xe}]6s^1$	92	U	$[\text{Rn}]7s^25f^36d^1$
19	K	$[\text{Ar}]4s^1$	56	Ba	$[\text{Xe}]6s^2$	93	Np	$[\text{Rn}]7s^25f^46d^1$

Diamagnetism and Paramagnetism



Paramagnetic
unpaired electrons
↑ ↑ —

2p



Diamagnetic
all electrons paired
↑↓ ↑↓ ↑↓

2p