

GENERAL CHEMISTRY

Chapter 1

Electronic Structure of Atoms

Contents

- 2 parts: part 1: matter and part 2: chemical processes
- Part 1: Matter mid-term test
 - Atom
 - Periodic table
 - Bonding theory
- Part 2: Chemical processes (final exam)
 - 1 st Law, heat or enthalpy
 - 2nd Law: direction, Entropy S , Gibbs free energy G
 - Equilibrium
 - Kinetics
 - Solution

Atoms: Their composition

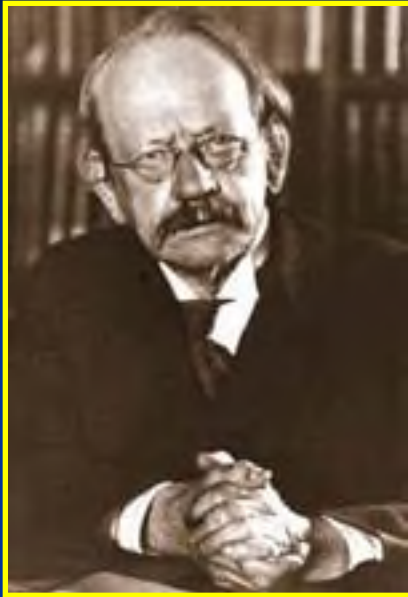
Subatomic particles

Particle	Charge	Mass (g)	Location
Electron (e ⁻)	-1	9.11×10^{-28}	Electron cloud
Proton (p ⁺)	+1	1.67×10^{-24}	Nucleus
Neutron (n ⁰)	0	1.67×10^{-24}	Nucleus

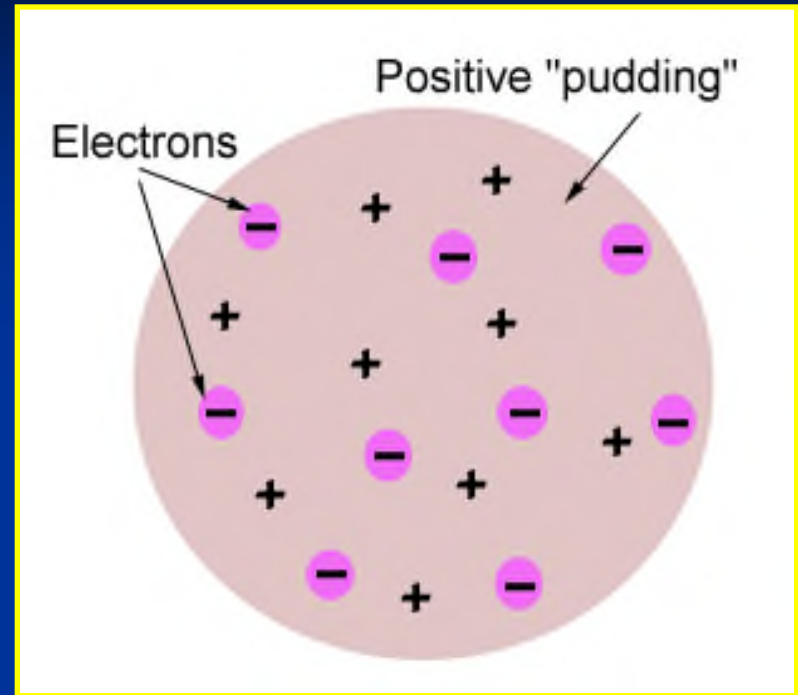
Atomic structure

- Understand about their arrangement
- Atomic theory
 - Classical theory (classical mechanics)
 - Modern (quantum mechanics) theory

Thomson's Atomic Model

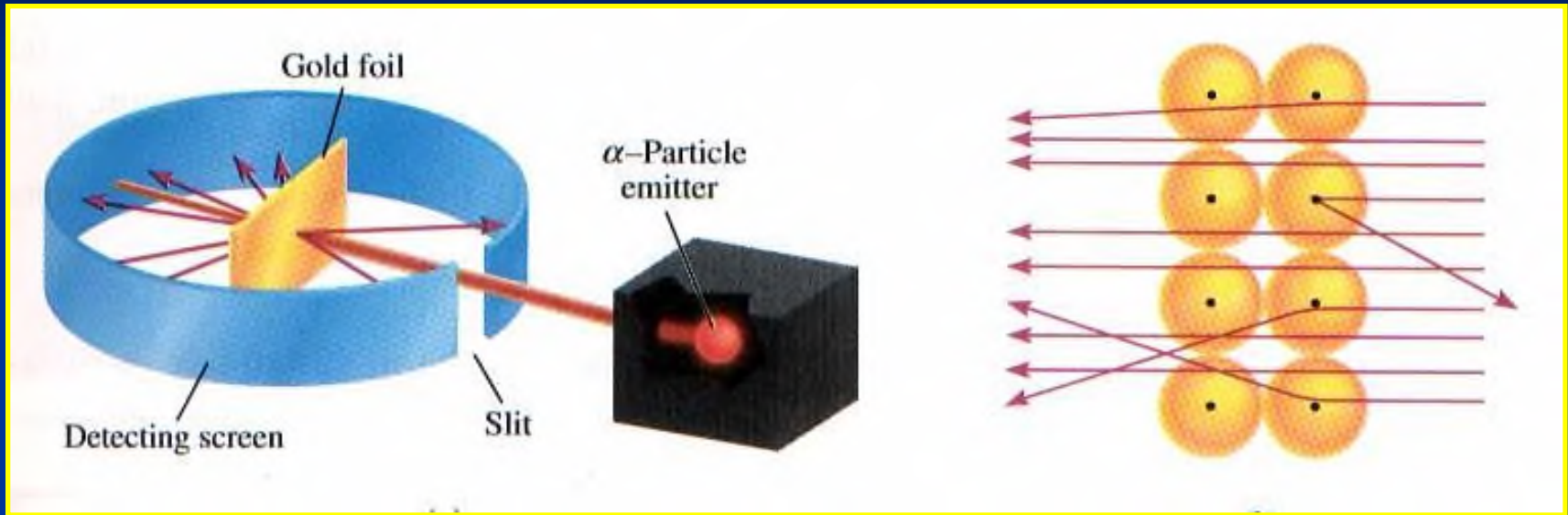


J. J. Thomson



Thomson believed that the electrons were like plums embedded in a positively charged “pudding,” thus it was called the “**plum pudding**” model.

Ernest Rutherford's Gold Foil Experiment - 1911

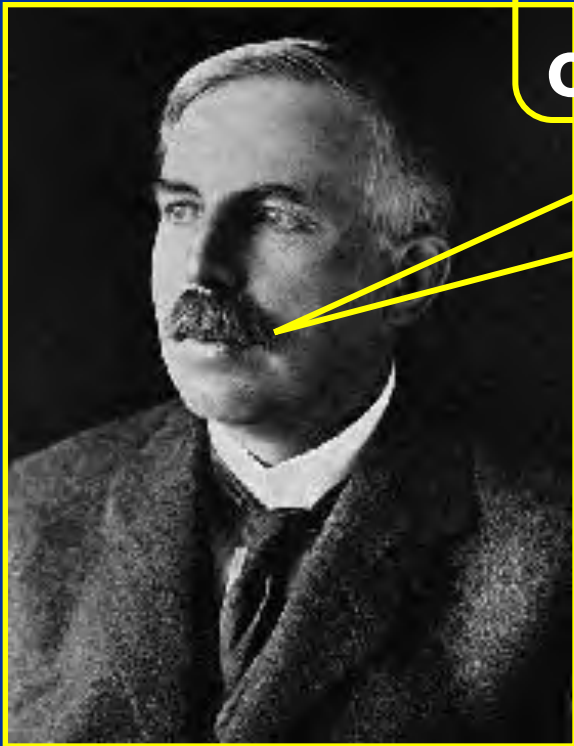


- Alpha particles are helium nuclei -
The alpha particles were fired at a thin sheet of gold foil
- Particles that hit on the detecting screen (film) are recorded

Rutherford's Findings

- Most of the particles passed right through
- A few particles were deflected
- **VERY FEW** were greatly deflected

“Like howitzer shells bouncing off of tissue paper!”



Conclusions:

- a) The nucleus is small
- b) The nucleus is dense
- c) The nucleus is positively charged

The Rutherford Atomic Model

- Based on his experimental evidence:
 - The atom is mostly empty space
 - All the positive charge, and almost all the mass is concentrated in a small area in the center. He called this a “nucleus”
 - The nucleus is composed of protons and neutrons (they *make* the nucleus!)
 - The electrons distributed around the nucleus, and occupy most of the volume
 - His model was called a “nuclear model”

Transition between classical and quantum mechanic model

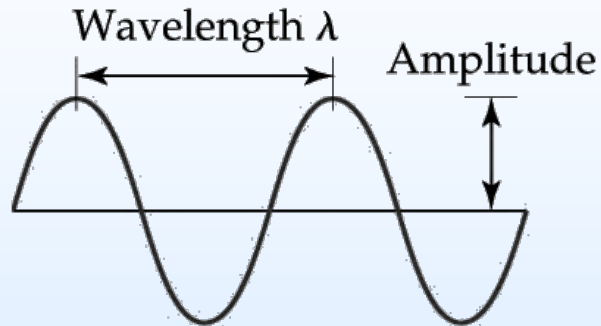
- Study of light emitted or absorbed by substances has lead to the understanding of the electronic structure of atoms.

The Wave Nature of Light

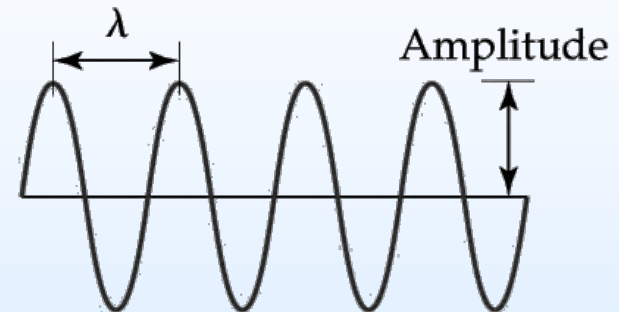
- Characteristics of light:
 - All waves have a characteristic wavelength, λ , and amplitude, A .
 - The frequency, ν , of a wave is the number of cycles which pass a point in one second.
 - The speed of a wave, v , is given by its frequency multiplied by its wavelength:
- For light, speed = c .

$$c = \lambda \nu$$

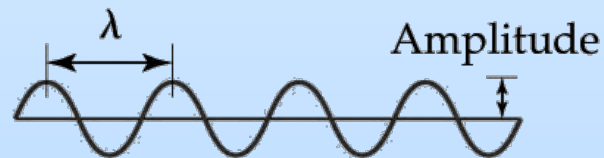
Identifying λ and ν



(a) Two complete cycles of wavelength λ



(b) Wavelength half of that in (a); frequency twice as great as in (a)

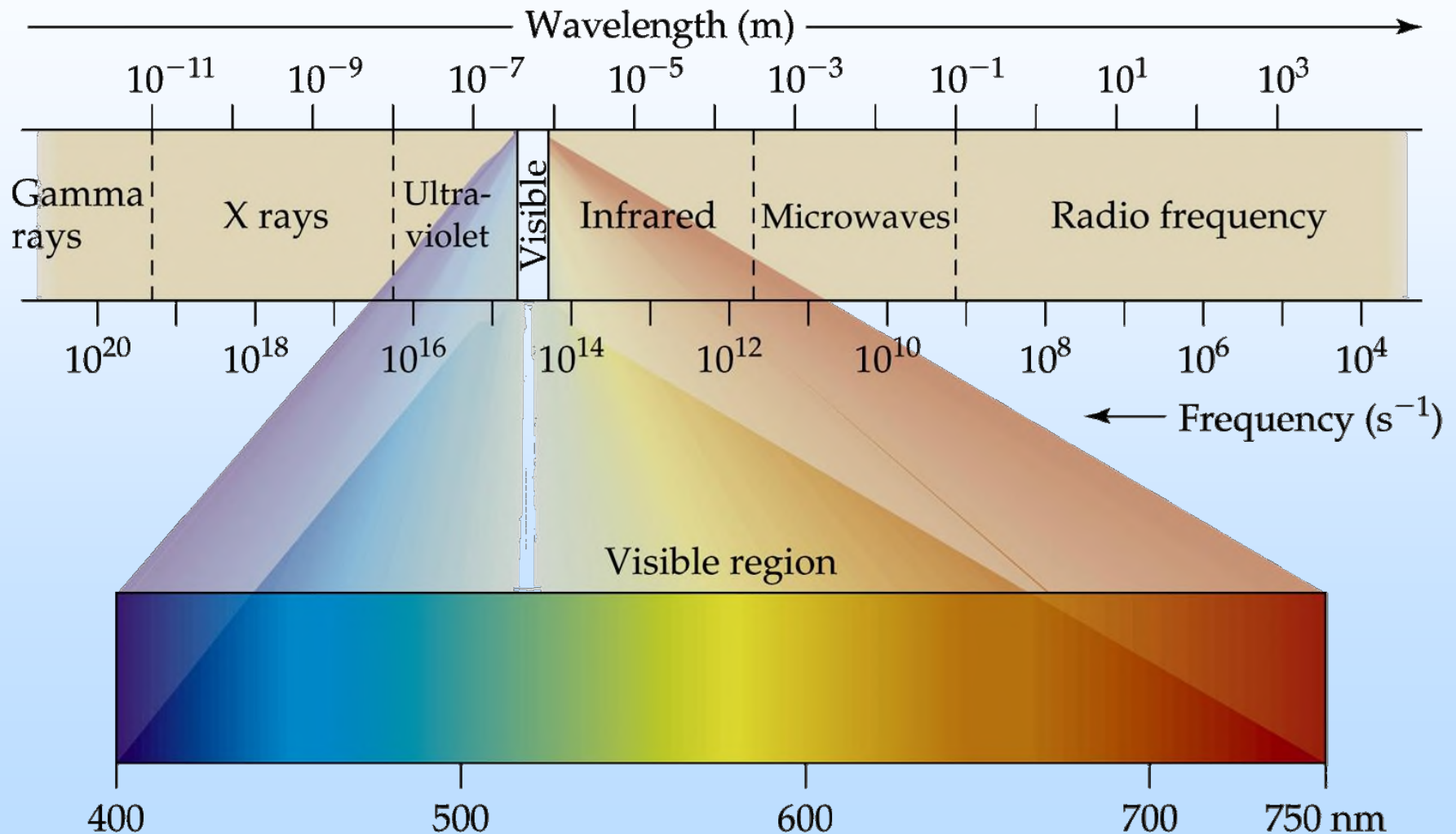


(c) Same frequency as (b), smaller amplitude

Electromagnetic Radiation

- Modern atomic theory arose out of studies of the interaction of radiation with matter.
- Electromagnetic radiation moves through a vacuum with a speed of 2.99792458×10^8 m/s.
- Electromagnetic waves have characteristic wavelengths and frequencies.
- Example: visible radiation has wavelengths between 400 nm (violet) and 750 nm (red).

The Electromagnetic Spectrum



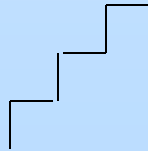
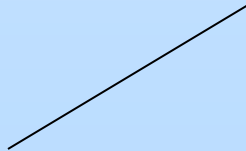
Quantized Energy and Photons

- **Planck:** energy can only be absorbed or released from atoms in certain amounts “chunks” called quanta.
- The relationship between energy and frequency is

$$E = h\nu$$

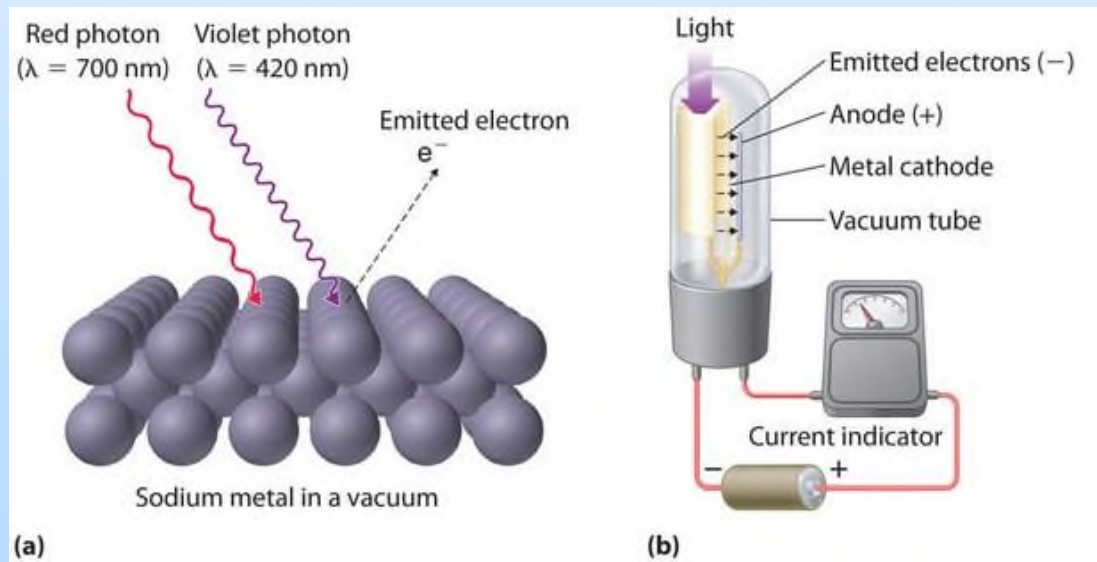
where h is Planck's constant (6.626×10^{-34} J.s).

- To understand quantization consider walking up a ramp versus walking up stairs:
 - For the ramp, there is a continuous change in height whereas up stairs there is a quantized change in height.



The Photoelectric Effect

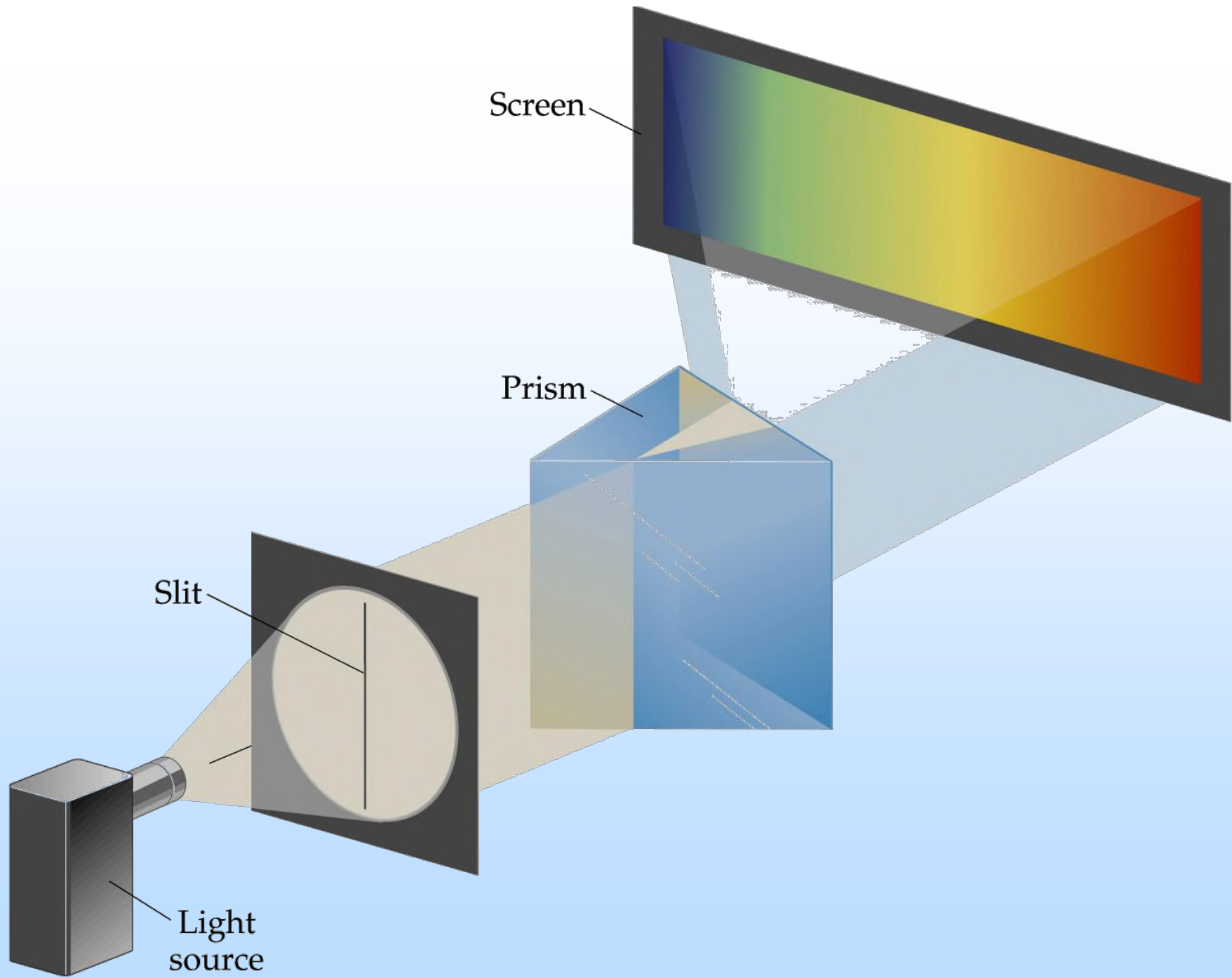
- Einstein:
 - Used Planck's theory to explain the photoelectric effect.
 - Assumed that light traveled in energy packets called photons. (light as particle, not wave)
- The energy of one photon: $E = h\nu$



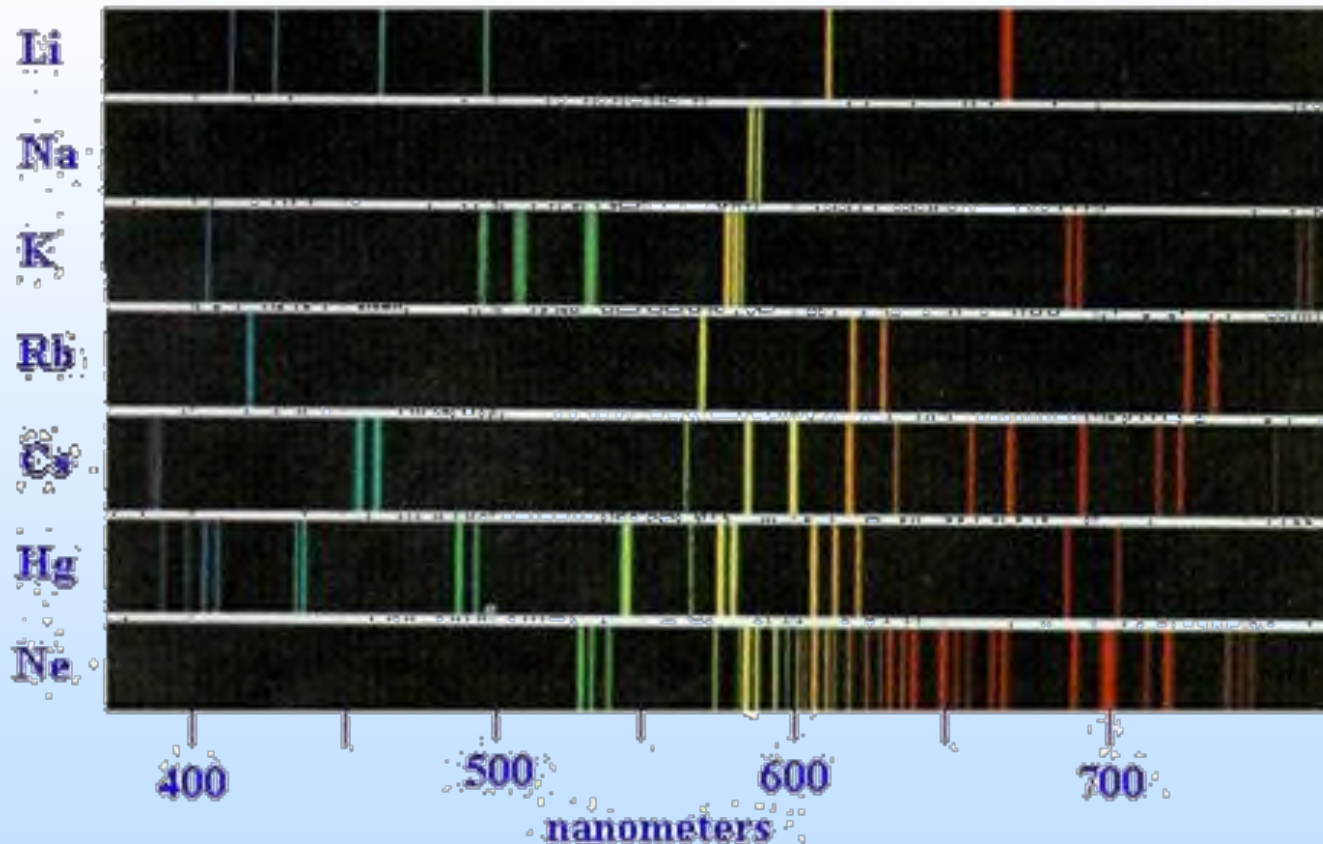
Line Spectra and the Bohr Model

Line Spectra

- Radiation composed of only one wavelength is called monochromatic.
- Most common radiation sources that produce radiation containing many different wavelengths components, a spectrum.
- This rainbow of colors, containing light of all wavelengths, is called a continuous spectrum.
- Note that there are no dark spots on the continuous spectrum that would correspond to different lines.



Specific Wavelength “Line Spectra”



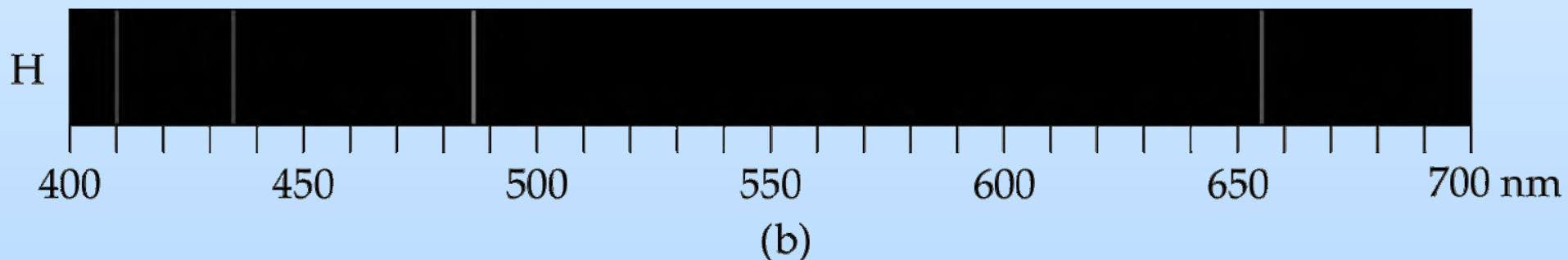
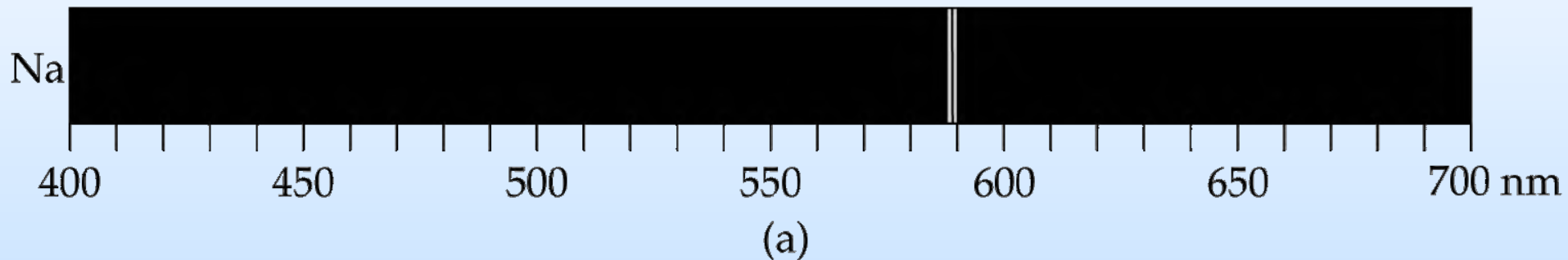
When gases are placed under reduced pressure in a tube and a high voltage is applied, radiation at different wavelengths (colors) will be emitted.

Bohr Model

- Rutherford assumed the electrons orbited the nucleus analogous to planets around the sun.
- However, a charged particle moving in a circular path should lose energy.
- This means that the atom should be unstable according to Rutherford's theory.
- Bohr noted the line spectra of certain elements and assumed the electrons were confined to specific energy states. These were called orbits. Electron does not lose energy in the orbit.

Line Spectra (Colors)

- Colors from excited gases arise because electrons move between energy states in the atom.



Line Spectra (Energy)

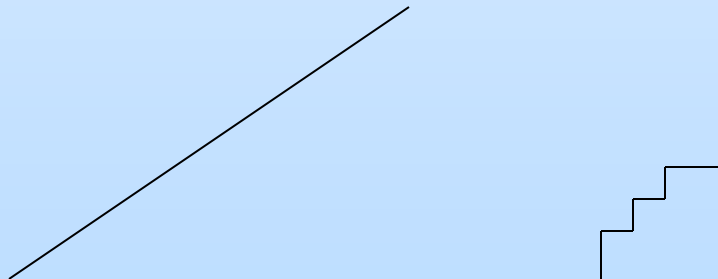
- Since the **energy** states are **quantized**, the **light** emitted from excited atoms must be **quantized** and appear as line spectra.
- After lots of math, Bohr showed that

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

where n is the principal quantum number (i.e., $n = 1, 2, 3, \dots$ and nothing else).

Limitations of the Bohr Model

- Can only explain the line spectrum of hydrogen adequately.
- Electrons are not completely described as small particles.



Modern Atomic Theory

Quantum mechanics

- 2 important principles
- Duality: particle and wave properties of matter
- Uncertainty:

The Wave Behavior of Matter

- Matter: particle, wave or not?
- Knowing that light has a particle nature, it seems reasonable to ask if matter has a wave nature.
- Using Einstein's and Planck's equations, de Broglie showed:

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

- The momentum, mv , is a particle property, whereas λ is a wave property.
- de Broglie summarized the concepts of waves and particles, with noticeable effects if the objects are small.

Example 1: wave-particle duality

- Calculate the wavelength of the following particles:

A ball	An electron
$m=50 \text{ g}$ $v=210 \text{ km/hr}$	$m=9.1 \times 10^{-31} \text{ kg}$ $v=1 \times 10^6 \text{ m/s}$
$h=6.626 \times 10^{-34} \text{ J.s}$	

The Wave Behavior of Matter

The Uncertainty Principle

- **Heisenberg's Uncertainty Principle:** on the mass scale of atomic particles, we cannot determine *exactly* the position, direction of motion, and speed simultaneously.
- For electrons: we cannot determine their momentum and position simultaneously.
- If Δx is the uncertainty in position and Δmv is the uncertainty in momentum, then

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

Example 2: uncertainty principle

- Calculate the uncertainty in position of the following particles:

A ball	An electron
$m=50 \text{ g}$ $v=210 \text{ km/hr}$ $\Delta v=1 \text{ km/hr } (<3\%)$	$m=9.1 \times 10^{-31} \text{ kg}$ $v=1 \times 10^6 \text{ m/s}$ $\Delta v=1 \times 10^6 \text{ m/s } (100\%)$
$\Delta v=1000 \text{ m}/(3600 \text{ s})=0.277 \text{ m/s}$	
$\Delta x=6.625 \times 10^{-34}/(0.277 \times 0.05 \times 4 \times 3.14)$	$\Delta x=?$

For an electron

- **Wave** and particle
- Uncertainty principle: position and velocity
- Describe the electron: ~~orbit~~ : another way: probability of finding the electron at a certain position: orbital , density distribution
- Result (solution) of S.E. \leftrightarrow wave function ψ \leftrightarrow probability distribution \leftrightarrow orbital : 1 – 1 correspondence

Quantum Mechanics and Atomic Orbitals

- **Schrödinger** proposed an equation that contains both wave and particle terms.
- Solving the equation leads to wave functions.
- The **wave function** gives the **shape** of the electronic **orbital**.
- The square of the wave function, gives the probability of finding the electron,
- that is, gives the electron density for the atom.

The Schrödinger Wave Equation

- The Schrödinger wave equation in its time-dependent form for a particle of energy E moving in a potential V in one dimension is

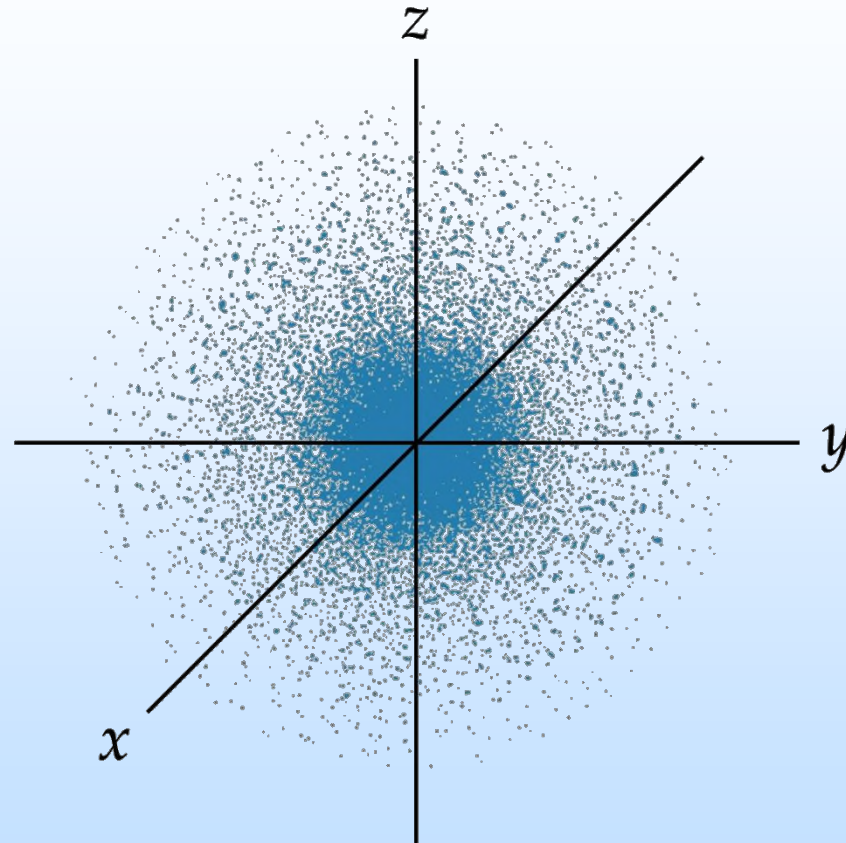
$$i\hbar \frac{\partial \Psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x,t)}{\partial x^2} + V\Psi(x,t)$$

- The extension into three dimensions is

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \left(\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} \right) + V\Psi(x,y,z,t)$$

where $i = \sqrt{-1}$ is an imaginary number.

Electron Density Distribution



Probability of finding an electron in a hydrogen atom in its ground state.

Single electron atoms/ions

- **Hydrogen and hydrogen-like atoms: H , He^+ , Li^{2+}**
- **Solve one Schrödinger's equation (for 1 e)**
- **Arrange 1 electron to the orbitals**

The Three Quantum Numbers

Schrödinger's equation requires 3 quantum numbers:

1. Principal Quantum Number, n . This is the same as Bohr's n . As n becomes larger, the atom/orbital becomes larger and the electron is further from the nucleus. ($n = 1, 2, 3 \dots$):

Determine the size of the orbital

Determine **energy for single electron atoms/ions** (recall Bohr model)

Letter: K L M N O P Q ...

Number 1 2 3 4 5 6 7 (not limit to 7, but 7 is enough)

Same value of n : same **shell**

The Three Quantum Numbers

Schrödinger's equation requires 3 quantum numbers:

2. Azimuthal Quantum Number, l . This quantum number depends on the value of n . The values of l begin at 0 and increase to $(n - 1)$. We usually use letters for l (s, p, d and f for $l = 0, 1, 2$, and 3). Usually we refer to the s, p, d and f -orbitals. ($l = 0, 1, 2 \dots n-1$). Defines the **shape of the orbitals and the energy of the orbital in multi e atoms.**

Each n : n values of l

$l = 0 \ 1 \ 2 \ 3 / 4 \ 5 \ \dots$

$s \ p \ d \ f / g \ h \ \dots$

Same n and l : sub-shell

The Three Quantum Numbers

Schrödinger's equation requires 3 quantum numbers:

3. Magnetic Quantum Number, m_l . This quantum number depends on l . The magnetic quantum number has integral values between $-l$ and $+l$. Magnetic quantum numbers give the **3D orientation** of each orbital in space. ($m_l = -l \dots 0 \dots +l$)

Each l : $2l+1$ values of m_l

(n, l, m_l): wave function (ψ), density distribution of electron, orbital

$l=3$ $m_l = -3, -2, -1, 0, +1, +2, +3$

Solve PDE by separable variables

Nd, Ms

M1, N2

34, 42

1s, 2s, 3s, 3p.....

Orbitals and Quantum Numbers

n	Possible Values of l	Subshell Designation	Possible Values of m_l	Number of Orbitals in Subshell	Total Number of Orbitals in Shell
1	0	1s	0	1	1
2	0	2s	0	1	4
	1	2p	1, 0, -1	3	
3	0	3s	0	1	
	1	3p	1, 0, -1	3	9
	2	3d	2, 1, 0, -1, -2	5	
4	0	4s	0	1	
	1	4p	1, 0, -1	3	16
	2	4d	2, 1, 0, -1, -2	5	
	3	4f	3, 2, 1, 0, -1, -2, -3	7	

Class Guided Practice Problem

- (a) For $n = 4$, what are the possible values of l ? (b) For $l = 2$. What are the possible values of m_l ? What are the representative orbital for the value of l in (a)?

Class Practice Problem

- (c) How many possible values for l and m_l are there when (d) $n = 3$; (b) $n = 5$?

Representations of Orbitals

The s-Orbitals

- each n , s-orbital: $l=0$, only 1 m_l , only 1 s orbital each shell
- All s-orbitals are spherical.
- As n increases, the s-orbitals get larger.

The s-Orbitals



$1s$



$2s$

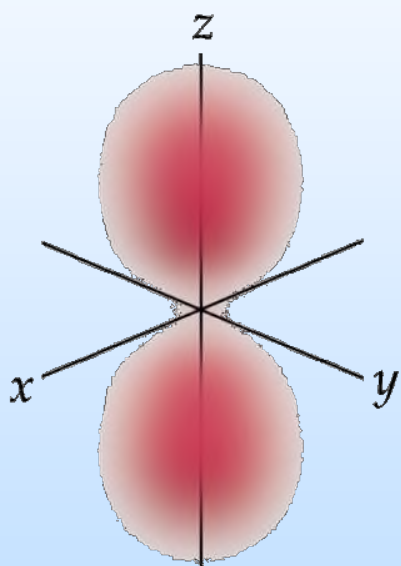


$3s$

The p-Orbitals

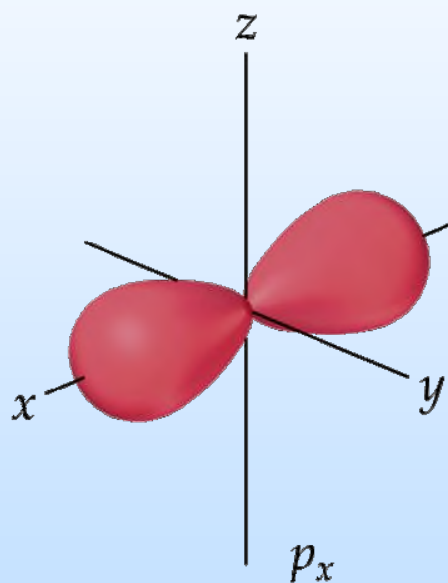
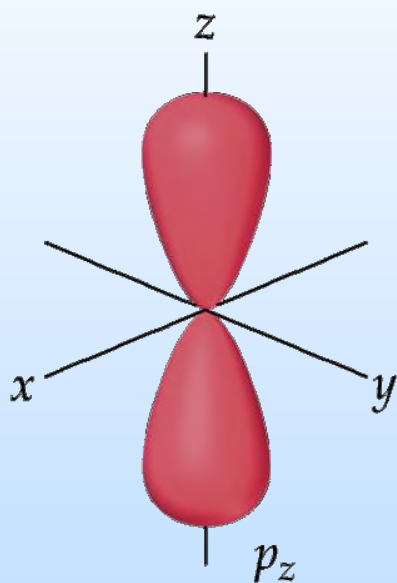
- Each n , p-orbital: $l=1$, 3 values of $m_l = -1, 0, +1$
- There are three p -orbitals p_x , p_y , and p_z .
- The three p -orbitals lie along the x -, y - and z - axes of a Cartesian system.
- The letters correspond to allowed values of m_l of $-1, 0$, and $+1$.
- The orbitals are dumbbell shaped.
- As n increases, the p -orbitals get larger.

The p-Orbitals



(a)

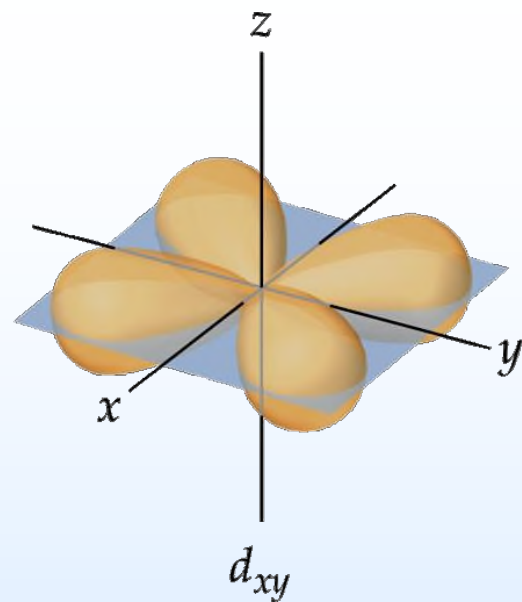
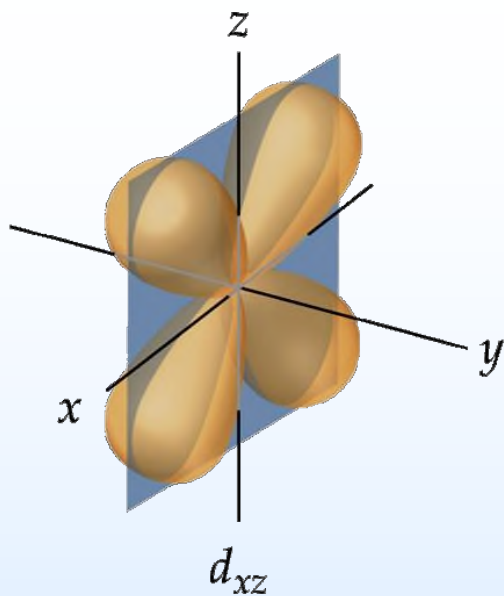
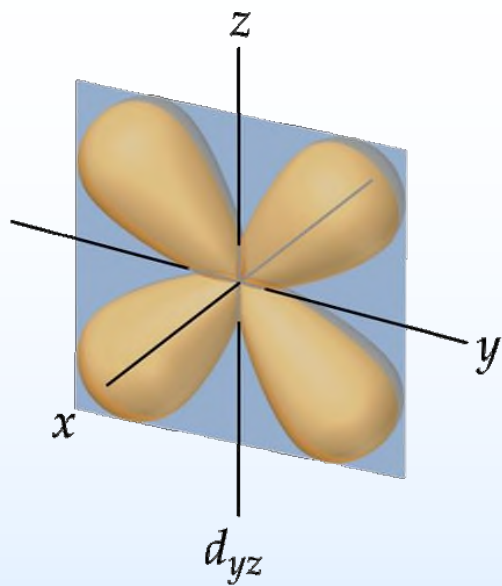
Electron-distribution
of a 2p orbital.



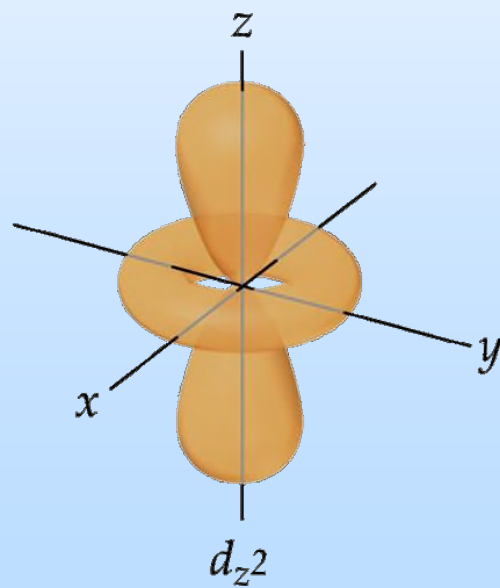
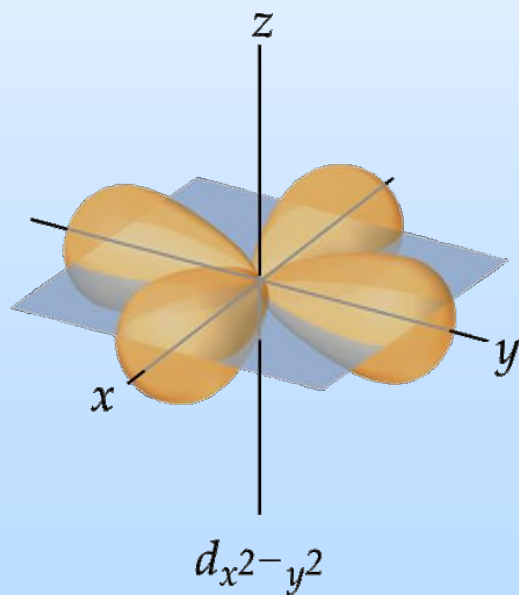
(b)

The d and f-Orbitals

- Each n, d-orbital: $l=2$, $m_l=-2 -1 0 +1 +2$: 5 *d*-orbitals
- f orbital: $l=3$, $m_l=-3 -2 -1 0 +1 +2 +3$: 7 *f*-orbital
- There are five *d* and seven *f*-orbitals (in each shell).
- Three of the *d*-orbitals lie in a plane bisecting the *x*-, *y*- and *z*-axes.
- Two of the *d*-orbitals lie in a plane aligned along the *x*-, *y*- and *z*-axes.
- Four of the *d*-orbitals have four lobes each.
- One *d*-orbital has two lobes and a collar.

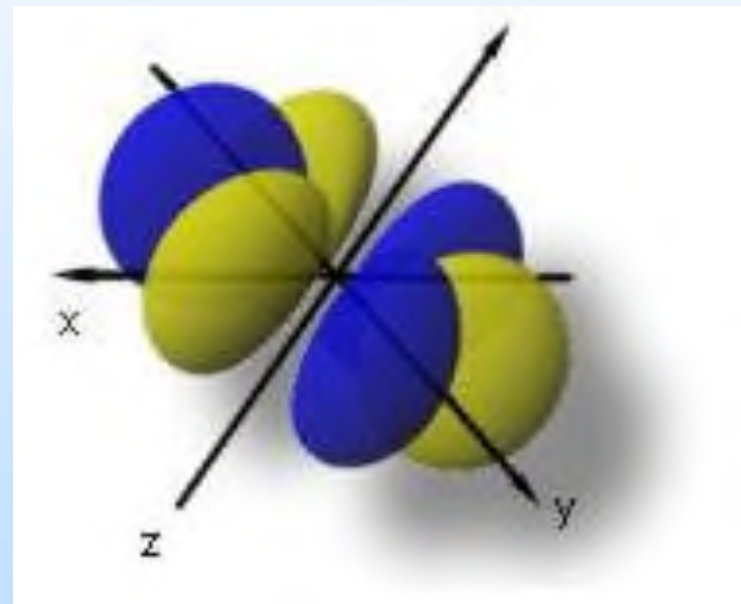
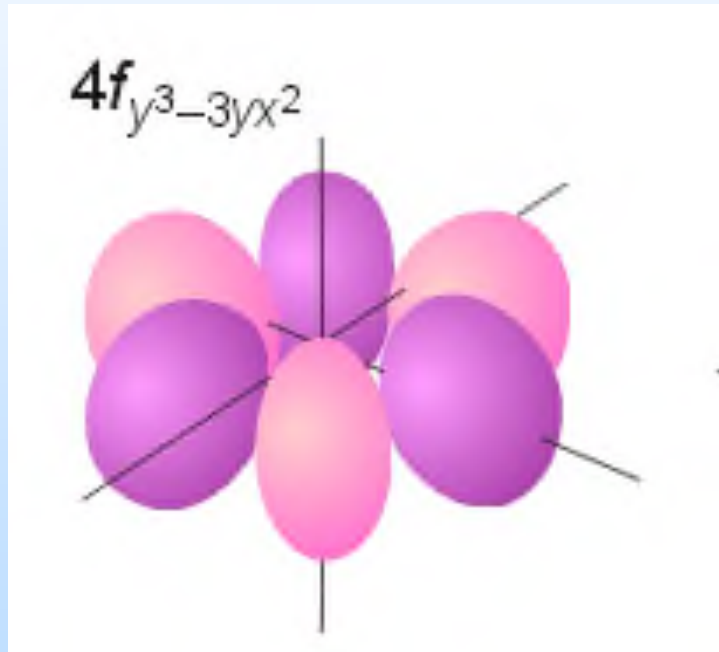


d_ϵ : bisecting main axes

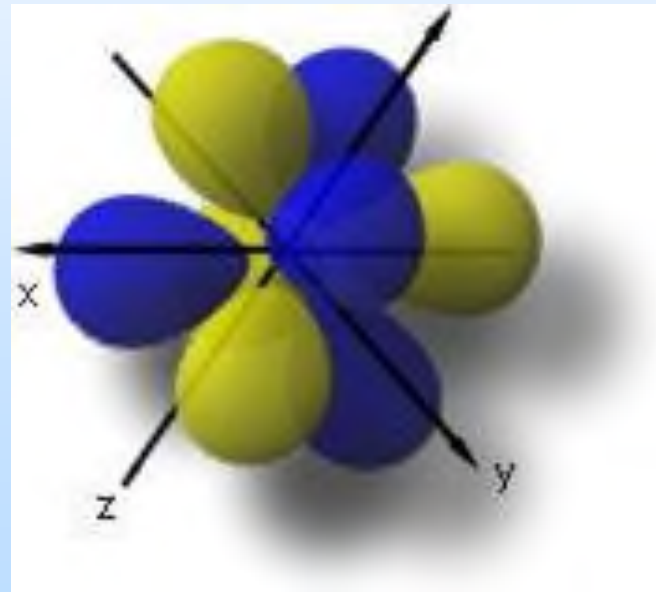
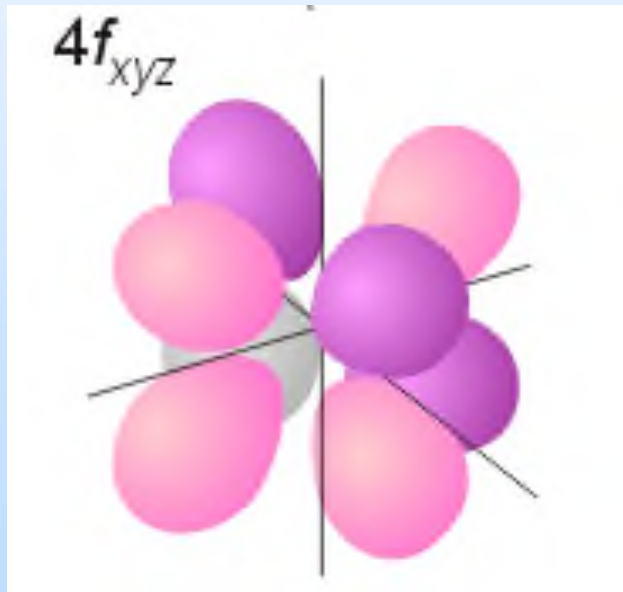


d_γ : lie along main axes (square)

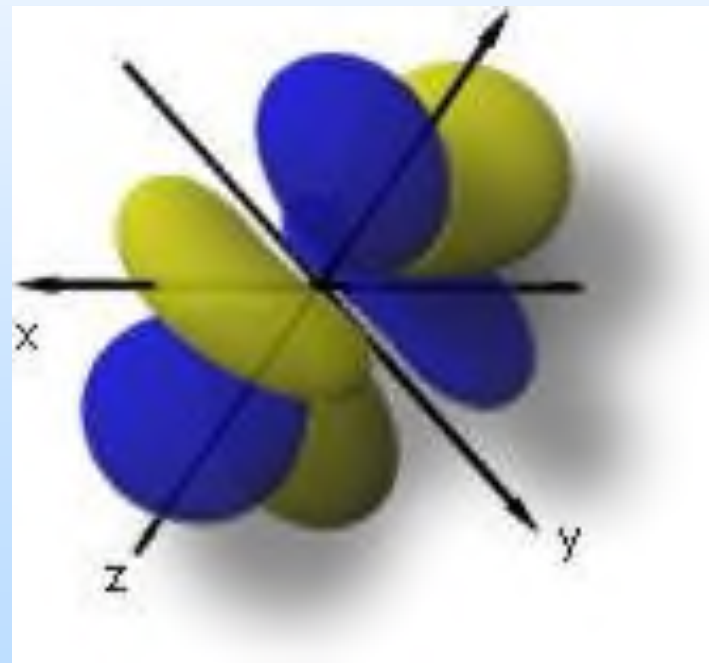
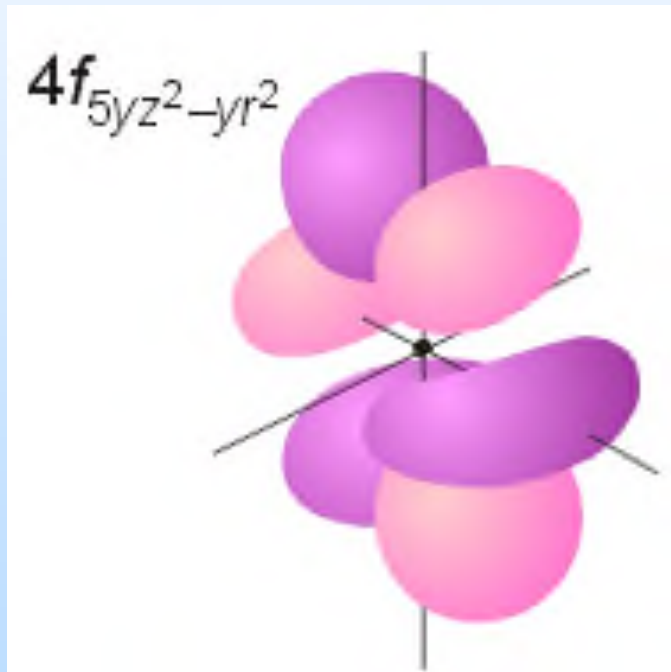
- The $4f_{y^3 - 3x^2y}$ orbital corresponds to $n=4$, $l=3$, and $m=-3$. Six lobes point to the corners of a regular hexagon in the xy plane, with one pair of lobes along the x -axis. Three nodal planes pass between the lobes and intersect at the z axis.



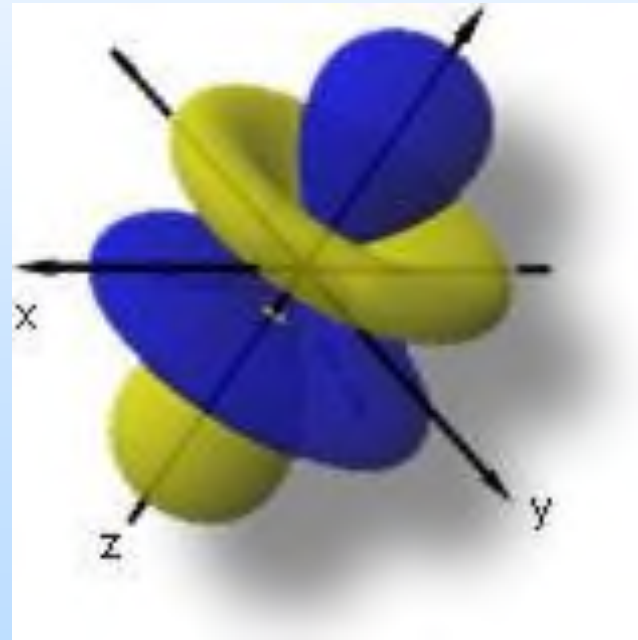
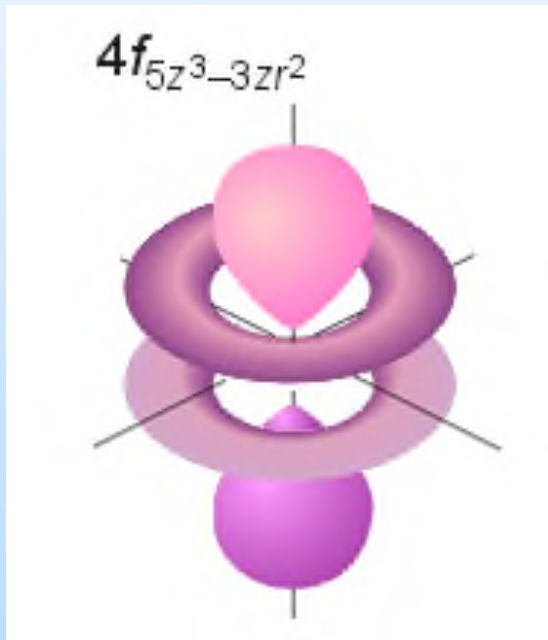
- The $4f_{xyz}$ orbital corresponds to $n=4$, $l=3$, and $m=-2$. Eight lobes point to the corners of a cube, with four lobes above and four lobes below the xy plane. The x and y axes pass through the centers of four of the cube's faces (between the lobes). The three nodal planes are defined by the x , y , and z axes.



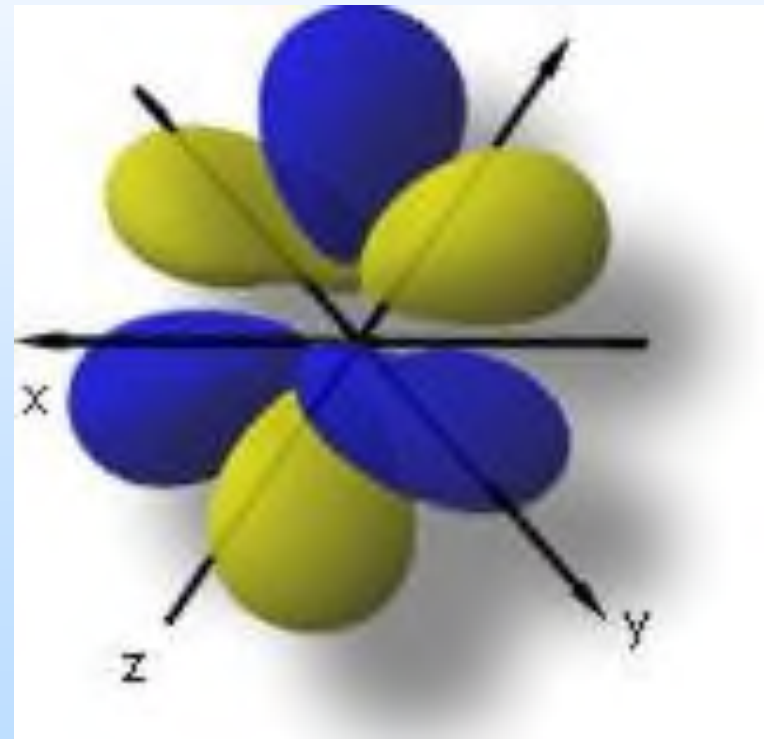
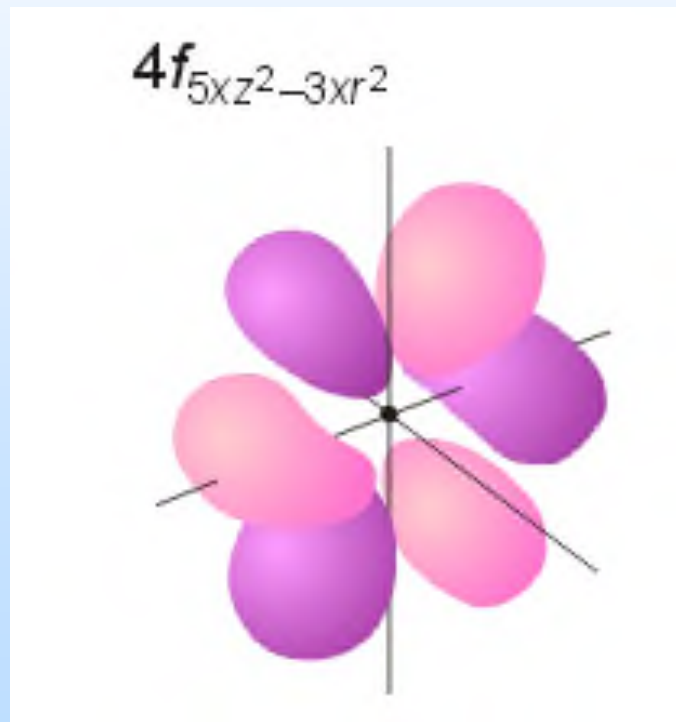
- The $4f_{5yz^2 - yr^2}$ orbital corresponds to $n=4$, $l=3$, and $m=-1$. Six lobes point to the corners of a regular hexagon in the yz plane, with one pair of lobes along the x -axis. The three nodal planes pass between the lobes and intersect at the y axis.



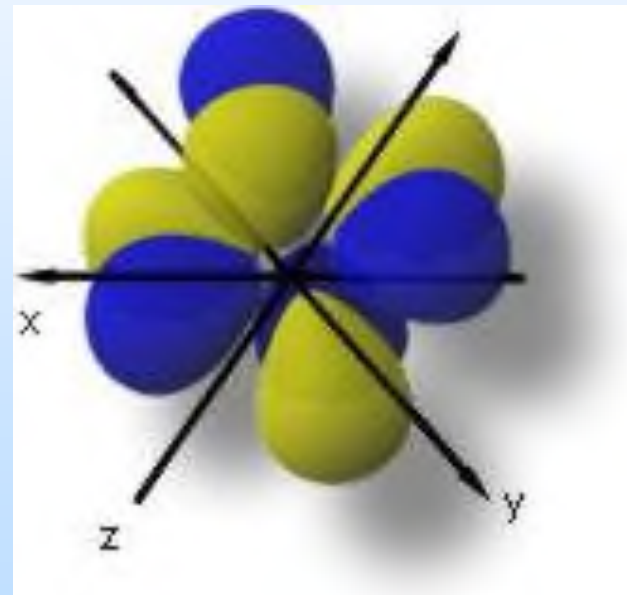
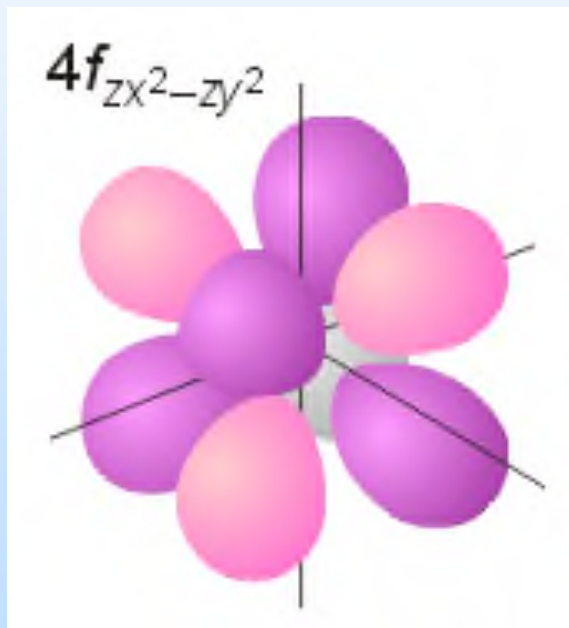
- The $4f_{5z^3-3zr^2}$ orbital corresponds to $n=4$, $l=3$, and $m=0$. Two lobes point along the z -axis, with two bowl-shaped rings above and below the xy plane. The nodal surfaces are the xy plane and a conical surface passing through the nucleus and between the rings and the lobes.



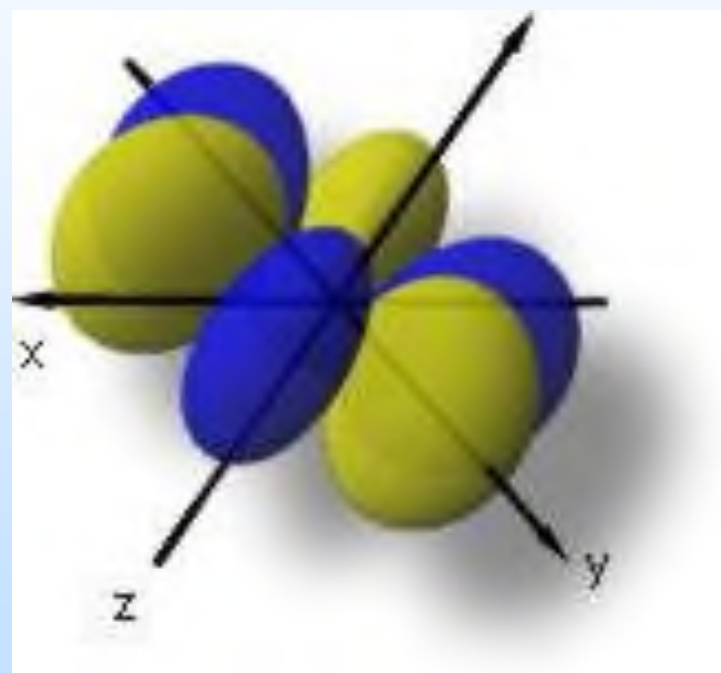
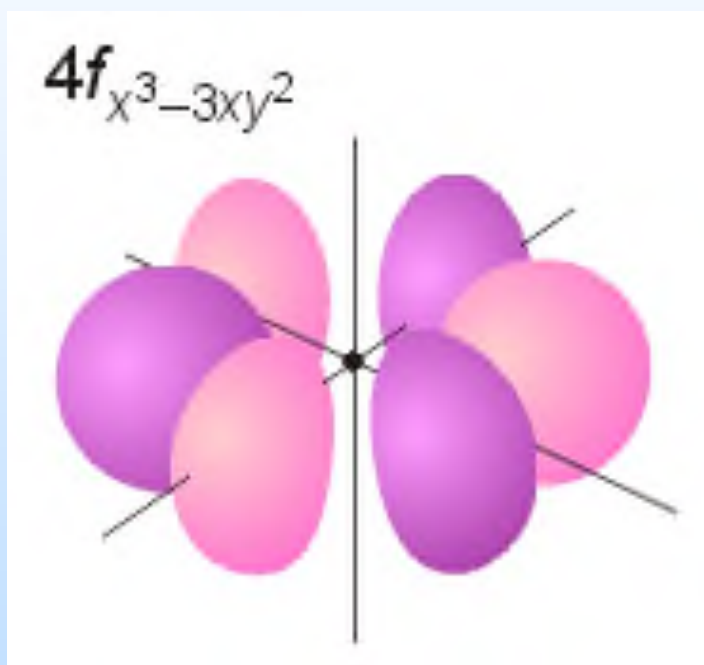
- The $4f_{5xz^2 - 3xr^2}$ corresponds to $n=4$, $l=3$, and $m=+1$. Six lobes point to the corners of a regular hexagon in the xz plane, with one pair of lobes along the y -axis. The three nodal planes pass between the lobes and intersect at the x axis



- The $4f_{zx^2 - zy^2}$ orbital corresponds to $n=4$, $l=3$, and $m=+2$. It has the same shape as the $4f_{xyz}$ orbital, but the corners of the cube are in the planes defined by the x , y , and z axes and the three nodal planes cut between the lobes and intersect along the z axis.



- The $4f_{x^3-3xy^2}$ orbital corresponds to $n=4$, $l=3$, and $m=+3$. It is identical to the orbital with $m=-3$ except that a lobe lies along the y axis instead of along the x axis.

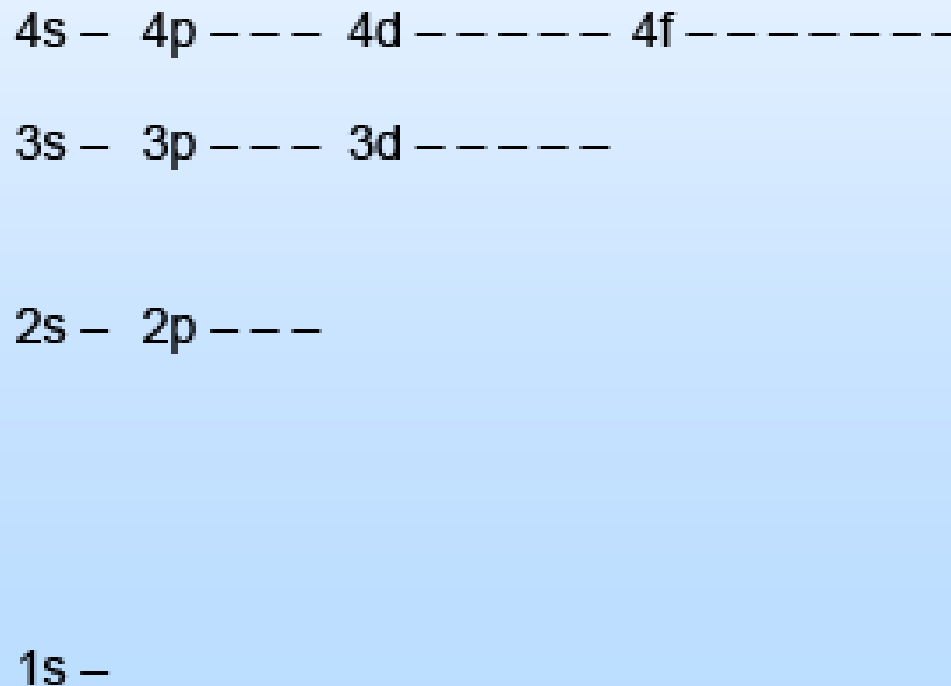


Orbitals and Quantum Numbers

- Orbitals can be ranked in terms of energy to yield an **Aufbau diagram**.
- As n increases, note that the spacing between energy levels becomes smaller.
- Orbitals of the same energy are said to be **degenerate**.

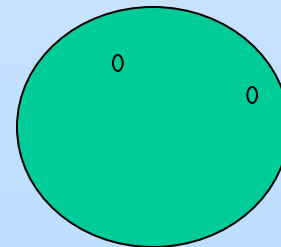
Energy diagram for single electron

Single-Electron Atoms/Ions



Multi electron atoms/ions

- Solve system of Schrödinger's equations
- Arrange multi electrons
- Attraction between nucleus – electron
- Repulsion electron-electron
- Have to simplify the interaction to solve the problem
- Strategy: remove all electron except 1e → series of 1 e problem
- Keep the effect of electron that removed



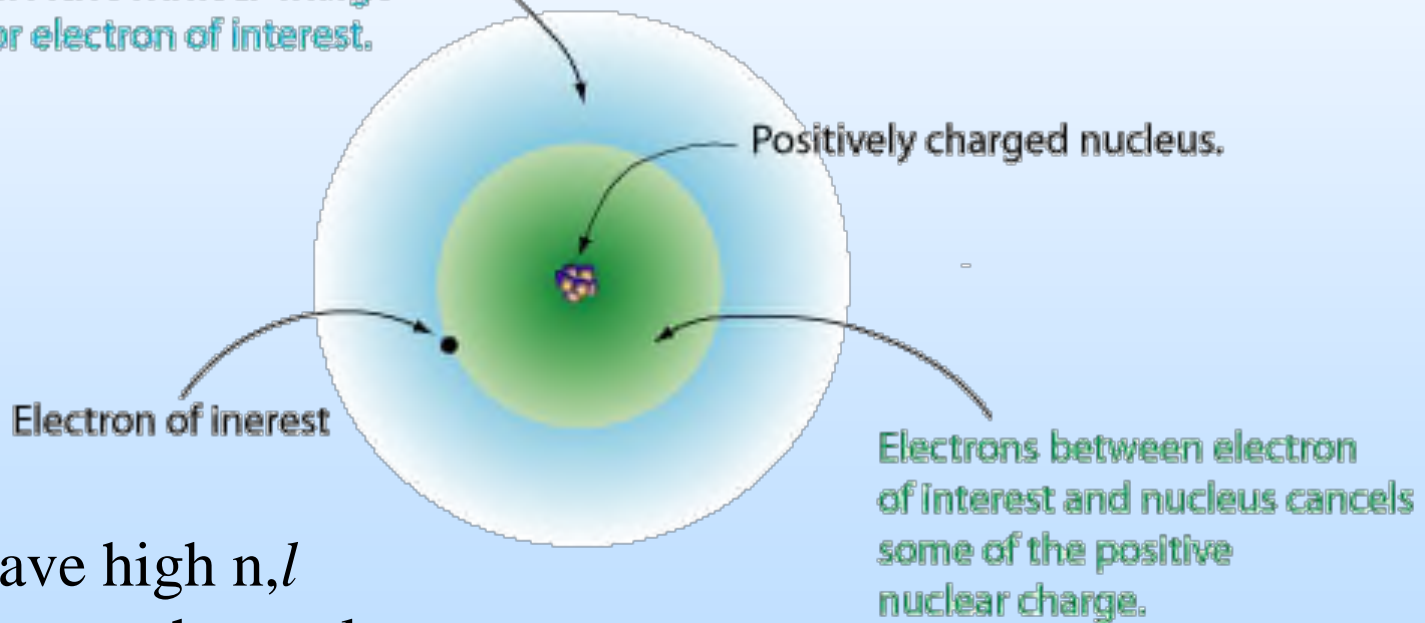
Penetration & Shielding

Electrons outside
have no effect on
effective nuclear charge
for electron of interest.

Shielding

e_1 and e_2 and Z

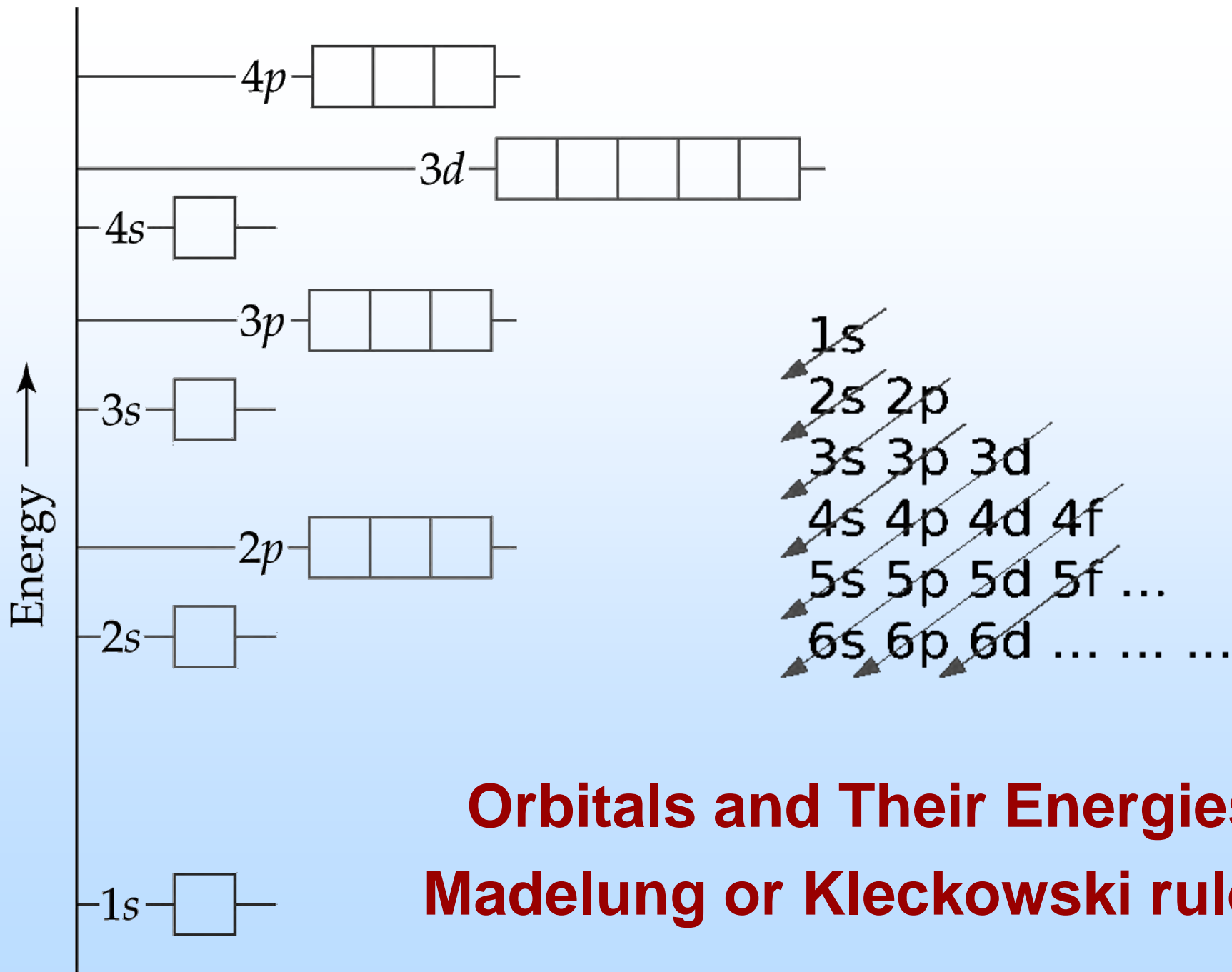
e_1 and $Z' = Z - S$: solve S.E.



electron have high n, l

Enter very near the nucleus

Electron in 5s still have shielding effect
on electron in 3s



Orbitals and Their Energies
Madelung or Kleckowski rule

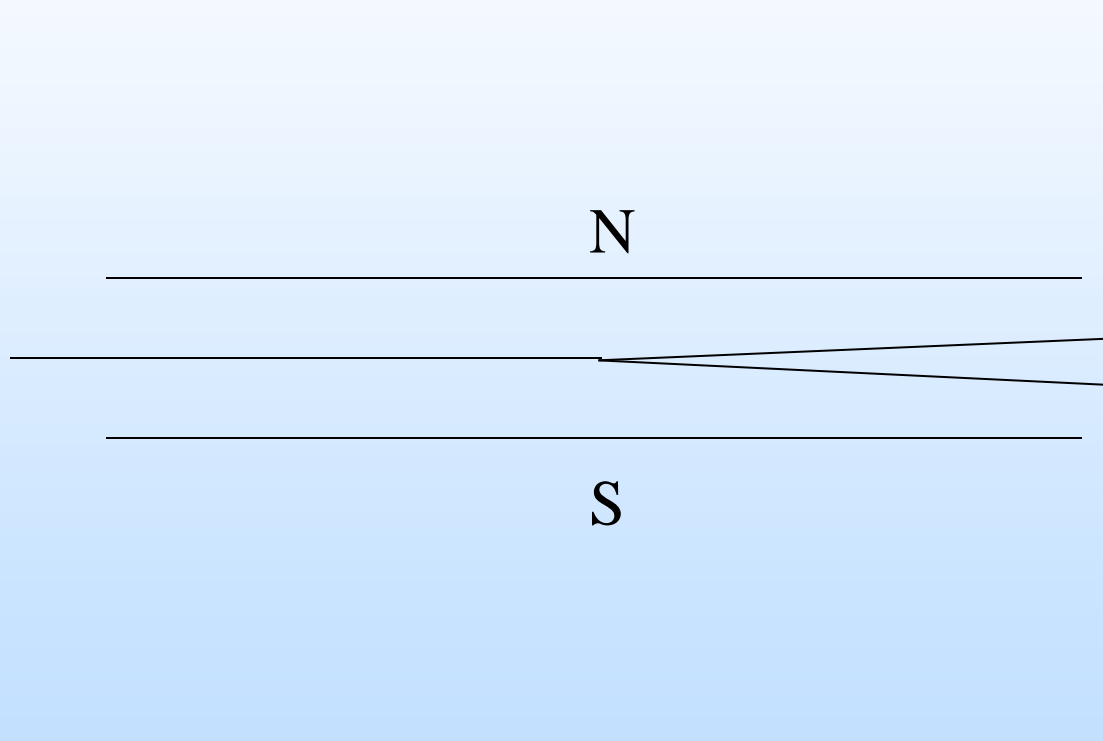
Multi e⁻ system

- Need to solve S.E. $\rightarrow n, l, m_l \rightarrow$ orbital (similar to 1 e)
- e⁻ e⁻ interaction (repulsion) \rightarrow Energy of orbitals in multi e atoms depend on both n and l
- Single e: energy of orbitals just depend on n

Electron Spin and the Pauli Exclusion Principle

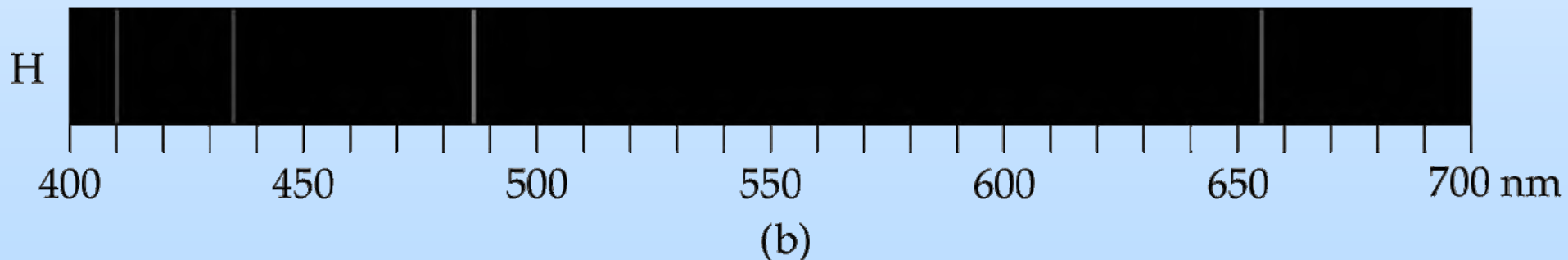
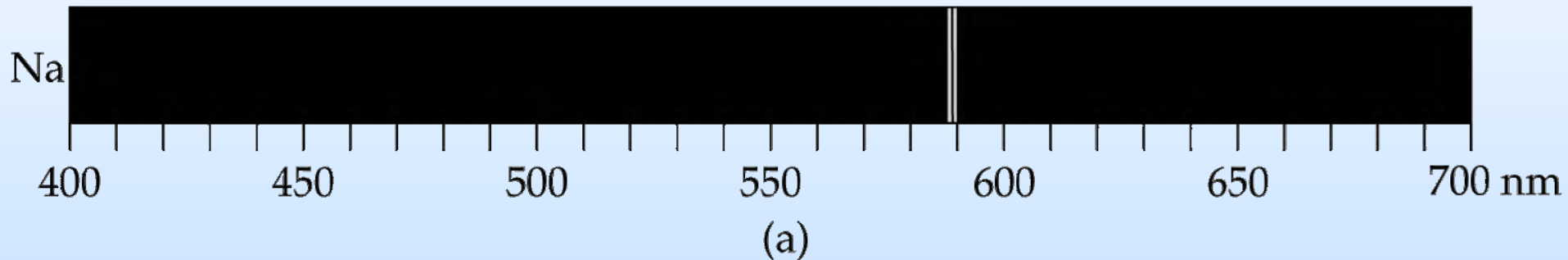
- Line spectra of many electron atoms show each line as a closely spaced pair of lines. (not single line)
- **Stern and Gerlach designed an experiment to determine why.**
- A beam of atoms (Ag) was passed through a slit and into a magnetic field and the atoms were then detected.
- **Two spots were found: one with the electrons spinning in one direction and one with the electrons spinning in the opposite direction.**

2 different kinds of Ag atoms?
2 types of e (Ag: odd number electron)

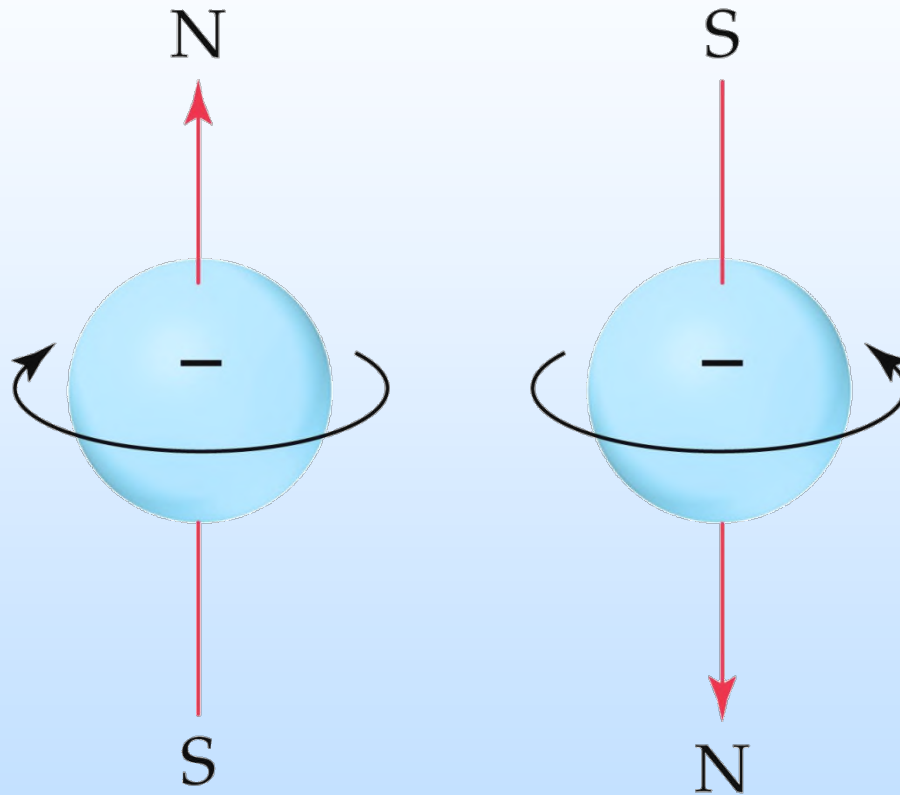


Line Spectra (Colors)

- Colors from excited gases arise because electrons move between energy states in the atom.



Electron Spin and the Pauli Exclusion Principle



Electron Spin and the Pauli Exclusion Principle

- Since electron spin is quantized, we define $m_s = \text{spin quantum number} = \pm 1/2$.
- **Pauli's Exclusions Principle (no proof):** no two electrons can have the same set of 4 quantum numbers.
 - Therefore, max two electrons in the same orbital and they must have opposite spins.
 - Set $(n, l, m_l, m_s) = 1$ electron : ID No. of electron

Electron Configurations:

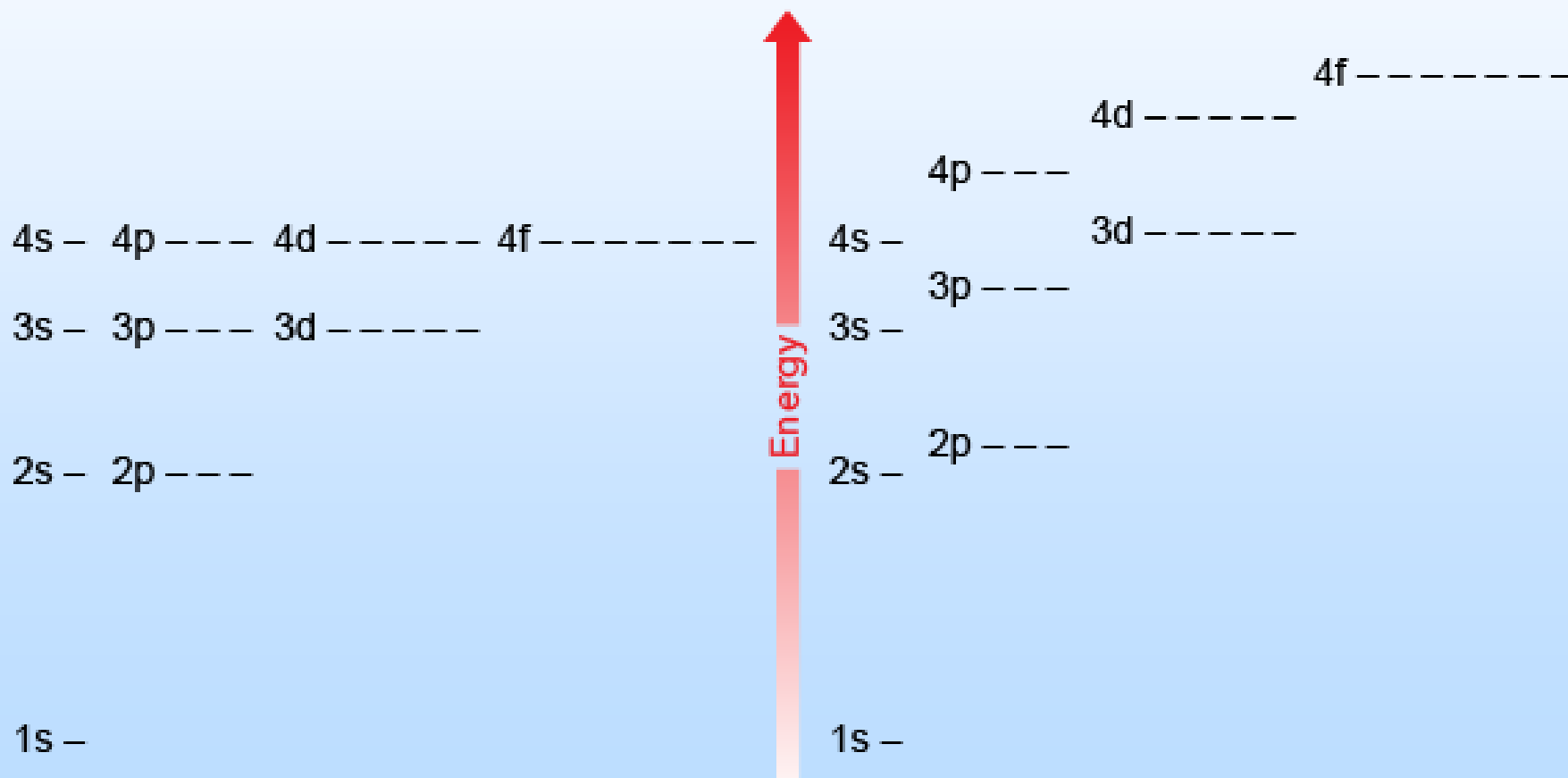
Hund's Rule

- **Electron configurations** tells us in which orbitals the electrons for an element are located.
- Three rules:
 - electrons fill orbitals starting with lowest *energy* and moving upwards;
 - no two electrons can fill one orbital with the same spin (**Pauli**); 1 orbital: max 2e with opposite spin s^2 , p^6 , d^{10} , f^{14} ,...
 - for degenerate orbitals, electrons fill each orbital singly before any orbital gets a second electron (**Hund's rule**).
- Stable rules: system is stable when E is lowest
- Pauli:

Aufbau diagram

Single-Electron Atoms/Ions

Multi-Electron Atoms/Ions



**Exercises: write e config. and find
the set of 4 QNs of the last filled
(added) e:**

Z=13, 27, 41, 36, 52, 71, 91, 87

(ground state)

Ground state and excited state

- Ground state: lowest energy state: e config.
- Higher energy states are described as excited states

Condensed Electron Configurations

- Neon completes the $2p$ subshell.
- Sodium marks the beginning of a new row.
- So, we write the condensed electron configuration for sodium as



- $[\text{Ne}]$ represents the electron configuration of neon.
- **Core electrons:** electrons in [Noble Gas].
- **Valence electrons:** electrons outside of [Noble Gas]:
take part in chemical reaction \rightarrow properties of elements

Symmetric rule

- If possible (easy), atoms try to become symmetric config.
- $ns \approx (n-1)d$ $ns^2 (n-1)d^4 \rightarrow ns^1 (n-1)d^5$ half saturated
- $ns^2 (n-1)d^9 \rightarrow ns^1 (n-1)d^{10} : \text{sym.}$
- $ns^2 np^2$: no change to $ns^1 np^3$ ($ns < np$)

Electron Configurations of ions

- Anions (negative ions): adding electrons according to Aufbau Diagram (follow energy level)
- Cations (positive ions): removing electrons first in the outermost subshell (furthest electron, highest n) then moving in toward the core of the atom. (follow distance)
- Fe: $[18]4s^2 3d^6$
- Fe^{2+} : $4s^2 3d^4$??? No. $\rightarrow [18]4s^0 3d^6$: correct
- Fe^{3+} : $3d^5$ (not $4s^2 3d^3$)