

5

CHAPTER

QUANTUM MECHANICS AND ATOMIC STRUCTURE

- 5.1 The Hydrogen Atom
- ~~5.2 Shell Model for Many-Electron Atoms~~
- 5.3 Aufbau Principle and Electron Configurations
- 5.4 Shells and the Periodic Table:
Photoelectron Spectroscopy
- 5.5 Periodic Properties and Electronic Structure

Colors of Fireworks

from atomic emission

red from Sr

orange from Ca

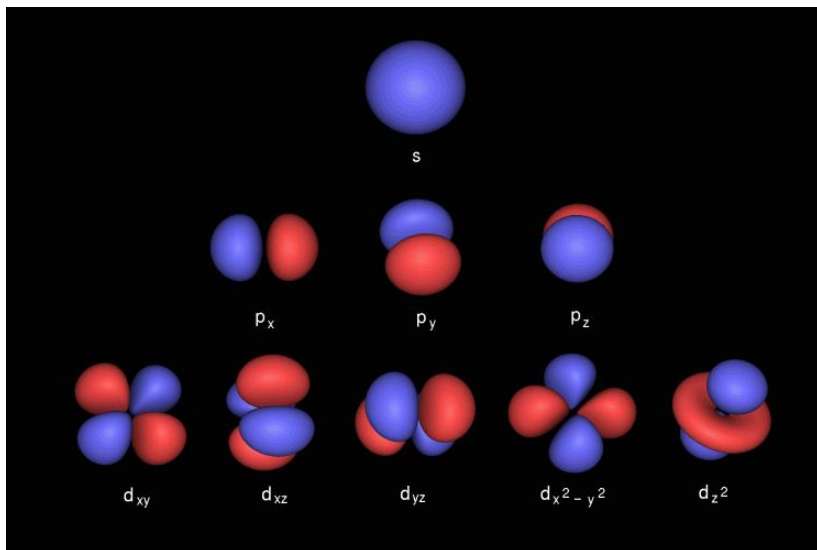
yellow from Na

green from Ba

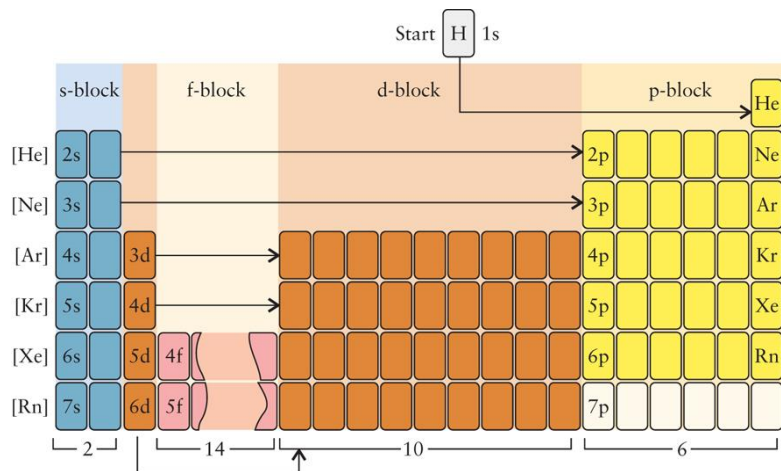
blue from Cu



Key question 1: what is the quantum mechanical atomic model?



Key question 2: what is the origin of the periodicity of atomic properties?



5.1 THE HYDROGEN ATOM

- The hydrogen atom is the simplest example of a one-electron atom or ion. (i.e. He⁺, Li²⁺, ...)

- Schrödinger equation

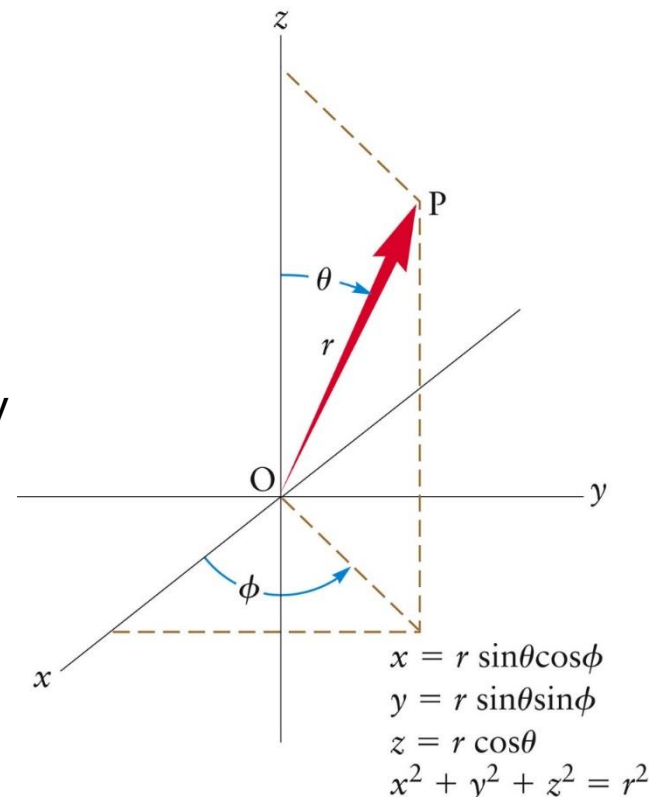
$$\left[\frac{-\hbar^2}{8\pi^2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + V(x, y, z) \right] \psi(x, y, z) = E\psi(x, y, z)$$

- For a hydrogen atom, $V(r)$ = Coulomb potential energy

$$V(r) = \frac{(-e)(+e)}{4\pi\epsilon_0 r} = -\frac{e^2}{4\pi\epsilon_0 r}$$

→ no angular dependence

→ the isotropic symmetry



Energy Levels

➤ Solutions of the Schrödinger equation

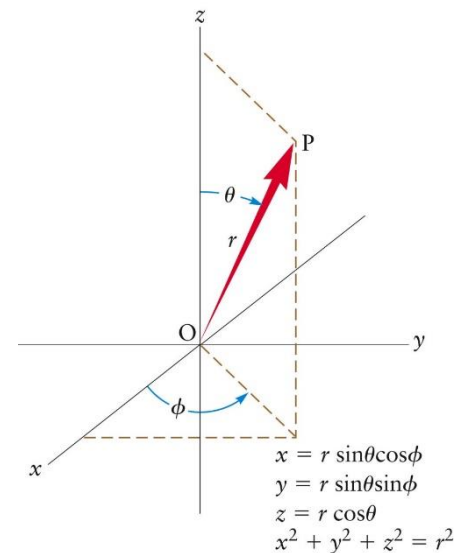
$$E = E_n = -\frac{Z^2 e^4 m_e}{8 \epsilon_0^2 n^2 h^2} \quad n = 1, 2, 3, \dots$$

$$E_n = -\frac{Z^2}{n^2} \text{ (rydberg)} \quad n = 1, 2, 3, \dots$$

$$1 \text{ rydberg} = 2.18 \times 10^{-18} \text{ J}$$

No angular dependence due to the isotropic symmetry

➤ **Principal quantum number n** : indexing the individual energy levels.



Wave Functions

However, the wave function has angular dependence

$$\psi_{n\ell m}(r, \theta, \phi) = R_{n\ell}(r) Y_{\ell m}(\theta, \phi)$$

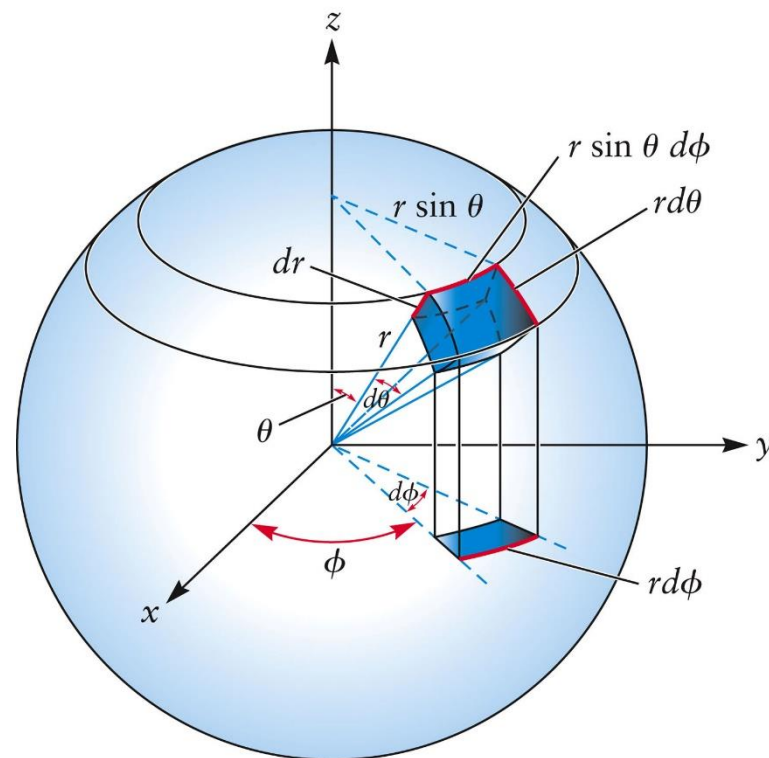
radial part

angular part: spherical harmonics

- The physically significant quantity, ψ^2 , is the **probability density** for locating the electron at a particular point in the atom.

$$(\psi_{n\ell m})^2 dV = [R_{n\ell}(r)]^2 [Y_{\ell m}(\theta, \phi)]^2 dV$$

$$dV = r^2 \sin \theta dr d\theta d\phi$$



Quantization of the Angular Momentums

- **Angular momentum quantum number ℓ** : from the quantization of L^2
any integral value from 0 to $n-1$

$$L^2 = \ell(\ell + 1) \frac{h^2}{4\pi^2} \quad \ell = 0, 1, \dots, n-1$$

value of ℓ	0	1	2	3	
orbital type	s	p	d	f	orbitals

i.e.) $n = 1, \ell = 0$: 1s state; $n = 4, \ell = 3$: 4f state;

- **Magnetic quantum number m** : from the quantization of L_z

$$L_z = m \frac{h}{2\pi}$$

$$m = \underbrace{-\ell, -\ell + 1, \dots, \ell - 1, \ell}_{\# \text{ of } m = 2\ell + 1}$$

For $n = 1$ (the ground state), $(\ell = 0, m = 0)$

For $n = 2$, $n^2 = 4$ allowed sets

$(\ell = 0, m = 0), (\ell = 1, m = 1), (\ell = 1, m = 0), (\ell = 1, m = -1)$

➔ For every value of n , n^2 sets of quantum numbers

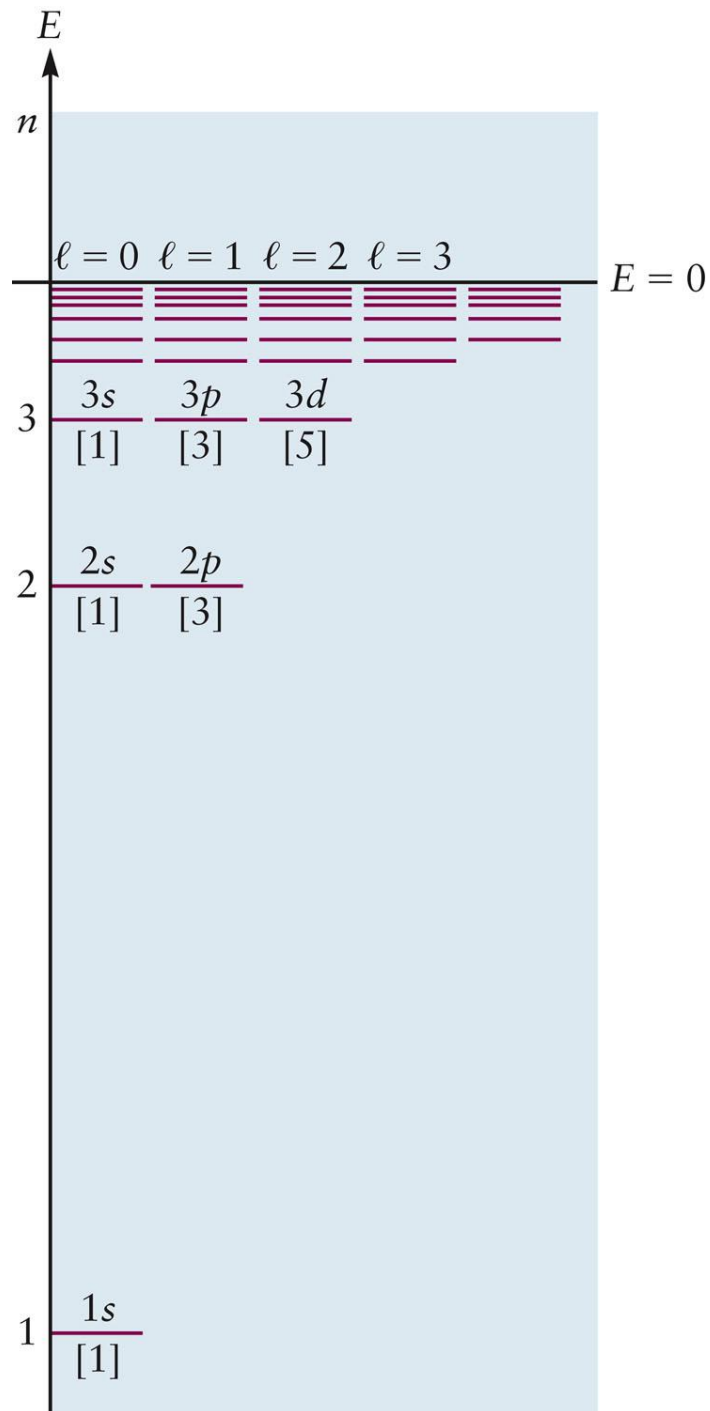
T A B L E 5.1

Allowed Values of Quantum Numbers for One-Electron Atoms

n	1		2			3	
ℓ	0	0	1	0	1	2	
m	0	0	-1, 0, +1	0	-1, 0, +1	-2, -1, 0, +1, +2	
Number of degenerate states for each ℓ	1	1	3	1	3	5	
Number of degenerate states for each n	1	4			9		

- Each set (n, ℓ, m) identifies a specific **quantum state** of the atom.
- A total of n^2 specific quantum states correspond to the single E_n .

This set of state is to be **degenerate**.



Orbital

- A wave function $\psi_{n\ell m}(r, \theta, \phi)$ for a one-electron atom in the state (n, ℓ, m) is called an **orbital**.

EXAMPLE 5.1

Give the names of all the orbitals with $n = 4$, and state how many m values correspond to each type of orbital.

$n = 4$	$\ell = 0$	4s	# of $m = 1$
	$\ell = 1$	4p	# of $m = 3$
	$\ell = 2$	4d	# of $m = 5$
	$\ell = 3$	4f	# of $m = 7$

total $n^2 = 16$ orbitals

TABLE 5.2

Angular and Radial Parts of Wave Functions for One-Electron Atoms

Angular Part $Y(\theta, \phi)$ Radial Part $R_{n\ell}(r)$

wave function

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r) Y_{lm}(\theta, \phi)$$

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$$\ell = 0 \left\{ Y_s = \left(\frac{1}{4\pi} \right)^{1/2} \right.$$

$$\ell = 1 \left\{ \begin{array}{l} Y_{p_x} = \left(\frac{3}{4\pi} \right)^{1/2} \sin \theta \cos \phi \\ Y_{p_y} = \left(\frac{3}{4\pi} \right)^{1/2} \sin \theta \sin \phi \\ Y_{p_z} = \left(\frac{3}{4\pi} \right)^{1/2} \cos \theta \end{array} \right.$$

$$\ell = 2 \left\{ \begin{array}{l} Y_{d_{z^2}} = \left(\frac{5}{16\pi} \right)^{1/2} (3 \cos^2 \theta - 1) \\ Y_{d_{xz}} = \left(\frac{15}{4\pi} \right)^{1/2} \sin \theta \cos \theta \cos \phi \\ Y_{d_{yz}} = \left(\frac{15}{4\pi} \right)^{1/2} \sin \theta \cos \theta \sin \phi \\ Y_{d_{xy}} = \left(\frac{15}{16\pi} \right)^{1/2} \sin^2 \theta \sin 2\phi \\ Y_{d_{x^2-y^2}} = \left(\frac{15}{16\pi} \right)^{1/2} \sin^2 \theta \cos 2\phi \end{array} \right.$$

$$R_{1s} = 2 \left(\frac{Z}{a_0} \right)^{3/2} \exp(-\sigma)$$

$$R_{2s} = \frac{1}{2\sqrt{2}} \left(\frac{Z}{a_0} \right)^{3/2} (2 - \sigma) \exp(-\sigma/2)$$

$$R_{3s} = \frac{2}{81\sqrt{3}} \left(\frac{Z}{a_0} \right)^{3/2} (27 - 18\sigma + 2\sigma^2) \exp(-\sigma/3)$$

$$R_{2p} = \frac{1}{2\sqrt{6}} \left(\frac{Z}{a_0} \right)^{3/2} \sigma \exp(-\sigma/2)$$

$$R_{3p} = \frac{4}{81\sqrt{6}} \left(\frac{Z}{a_0} \right)^{3/2} (6\sigma - \sigma^2) \exp(-\sigma/3)$$

$$R_{3d} = \frac{4}{81\sqrt{30}} \left(\frac{Z}{a_0} \right)^{3/2} \sigma^2 \exp(-\sigma/3)$$

$$\sigma = \frac{Zr}{a_0} \quad a_0 = \frac{\epsilon_0 h^2}{\pi e^2 m_e} = 0.529 \times 10^{-10} \text{ m}$$



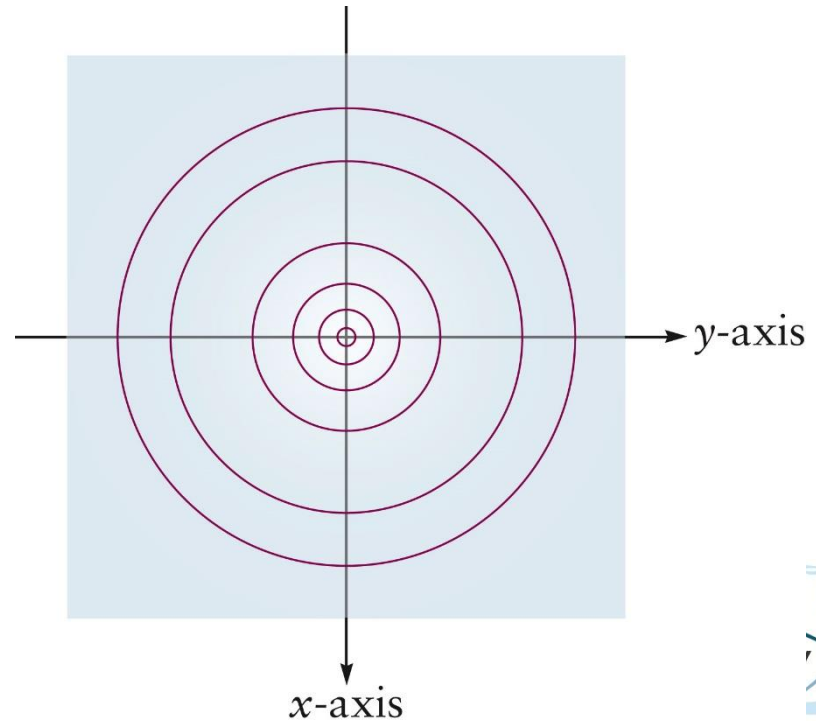
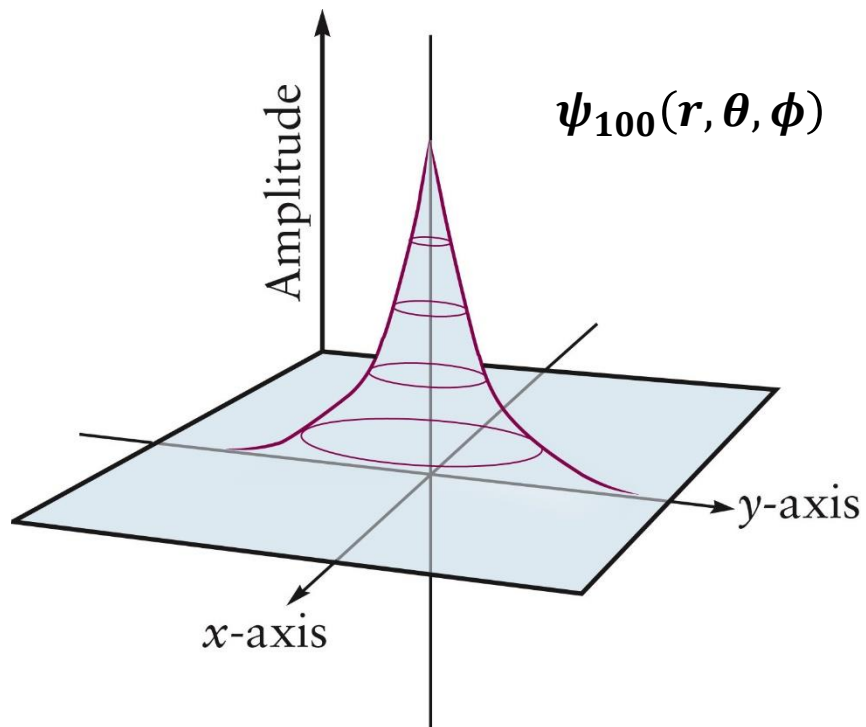
Sizes and Shapes of Orbitals

$$\psi_{n\ell m}(r, \theta, \phi) = R_{n\ell}(r)Y_{\ell m}(\theta, \phi)$$

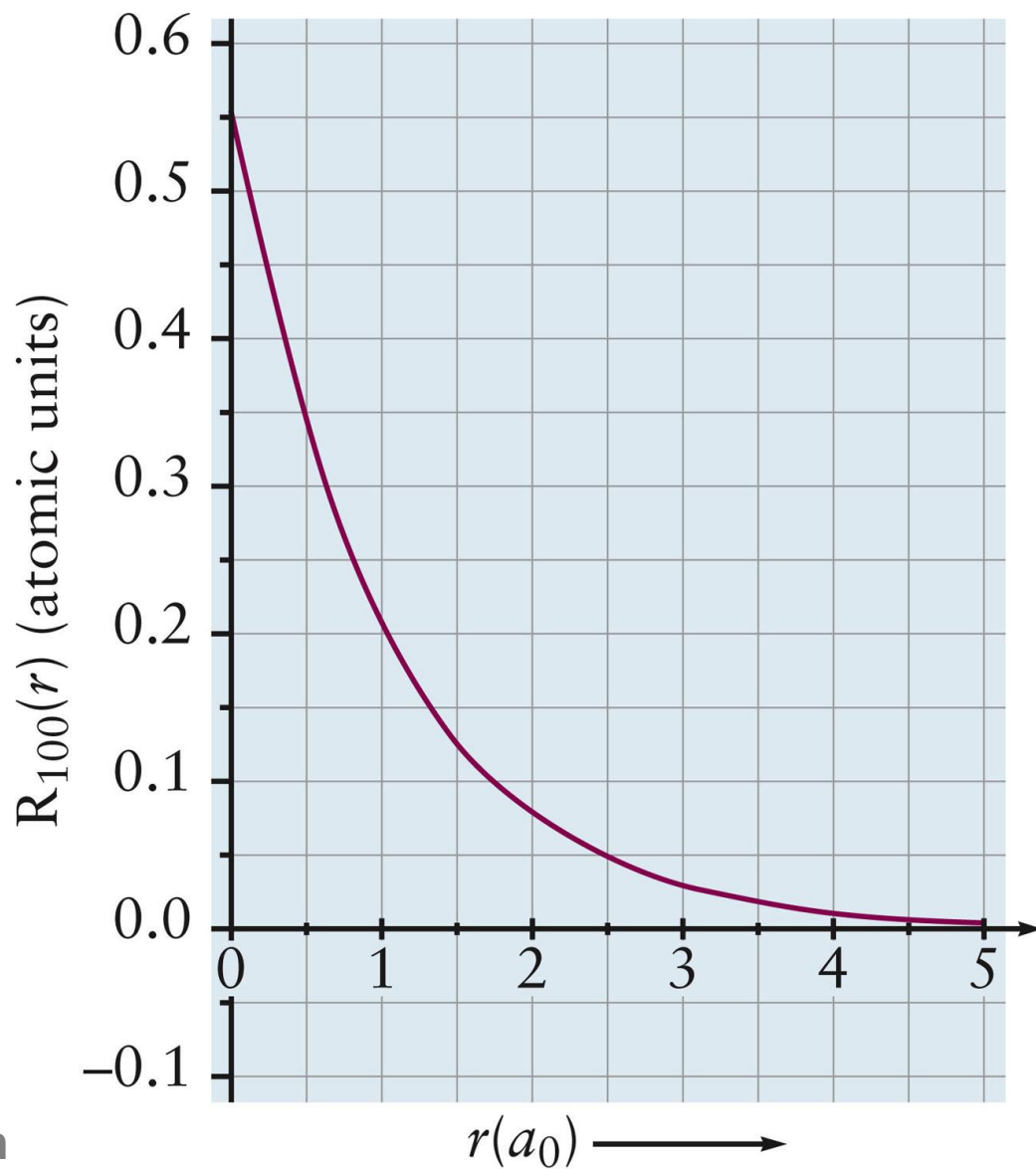
- Three spatial dimensions (r, θ, ϕ) with **the value of wave function**.

➤ Graphical representation of the orbitals

1) Slicing up 3D space into various 2D and 1D regions and examining the value of wave function at each point.

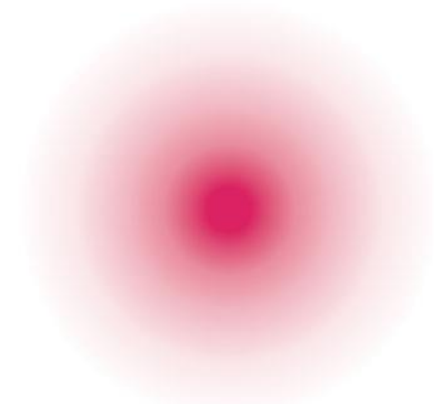
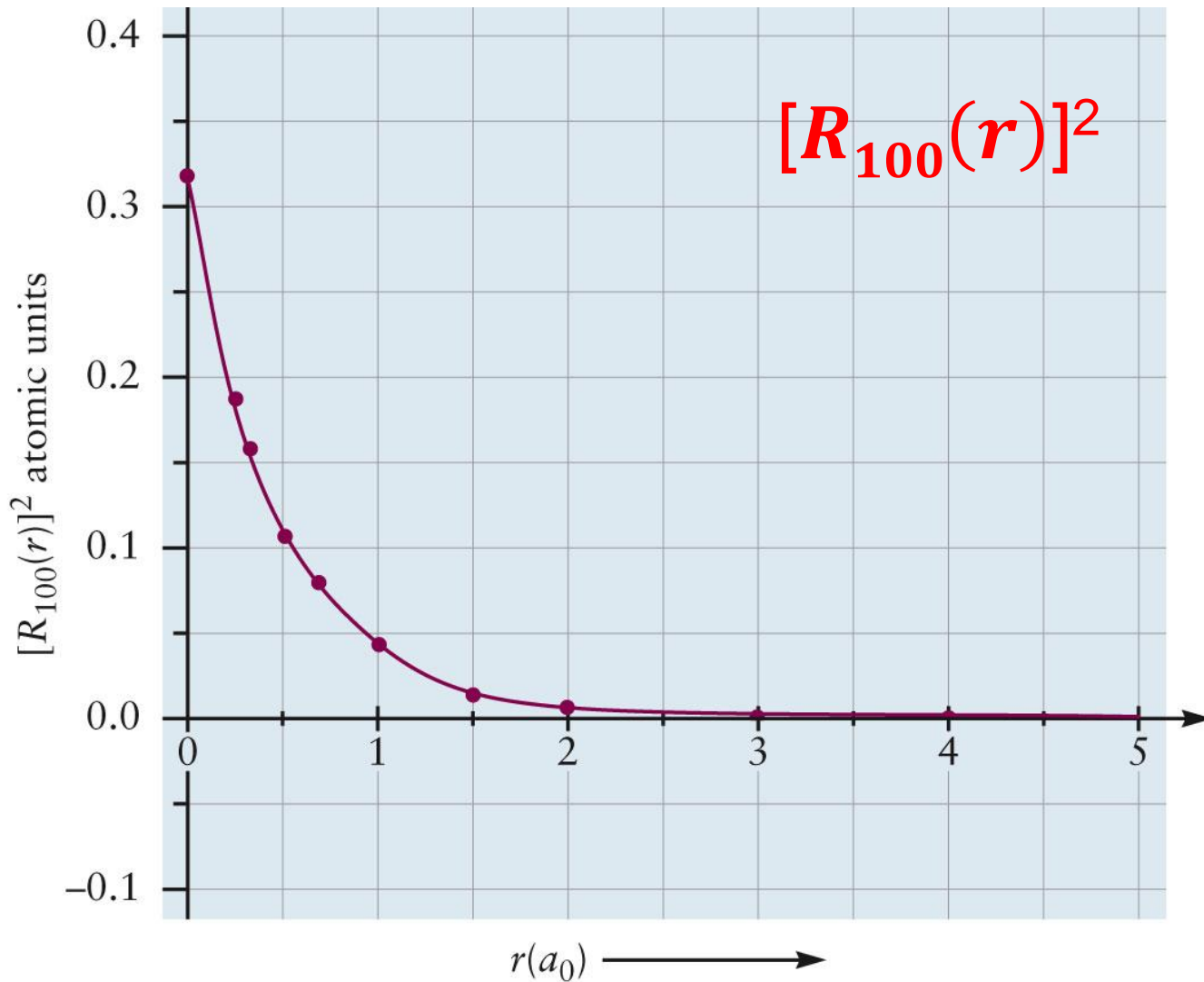


2) Looking only at the radial behavior. “vertical slice”



$$\psi_{100}(r, \theta, \phi)$$

- $(\psi_{n\ell m})^2$, probability density of finding the electron in a small volume element dV



(b)

(a)

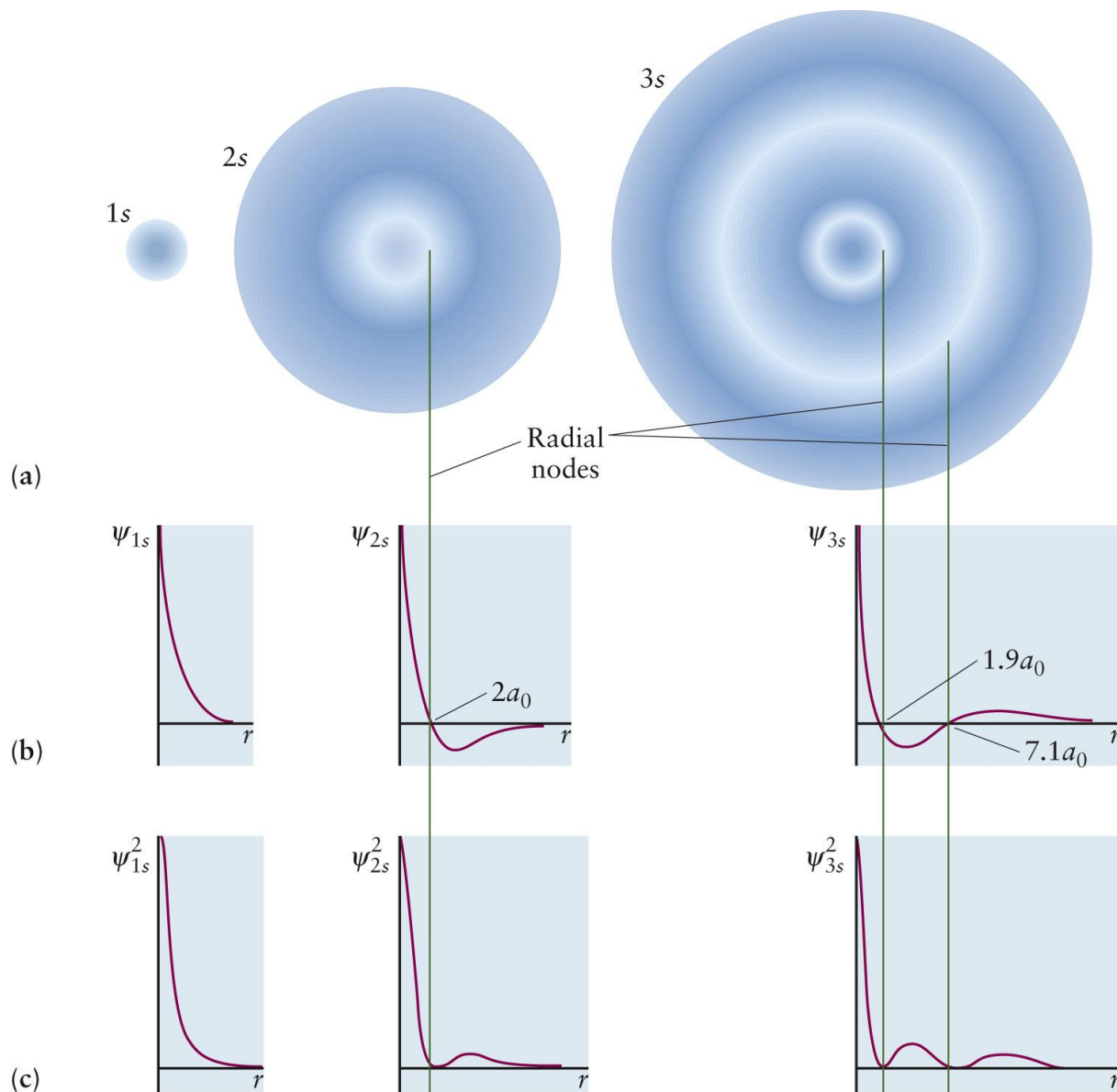
s orbitals

➤ s orbital:

$$\psi_{n\ell m} \text{ with } \ell = 0 \\ m = 0$$

➔ constant Y

All s orbitals are spherically symmetric.



- **1s** ($n = 1, \ell = 0, m = 0$) $\rightarrow R_{10}(r)$ and $Y_{00}(\theta, \Phi)$

$$\psi_{100}(r, \theta, \phi) = \frac{1}{\sqrt{\pi}} a_0^{-3/2} e^{-r/a_0}$$

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a function of r only

- * spherically symmetric
- * exponential decaying
- * no nodes

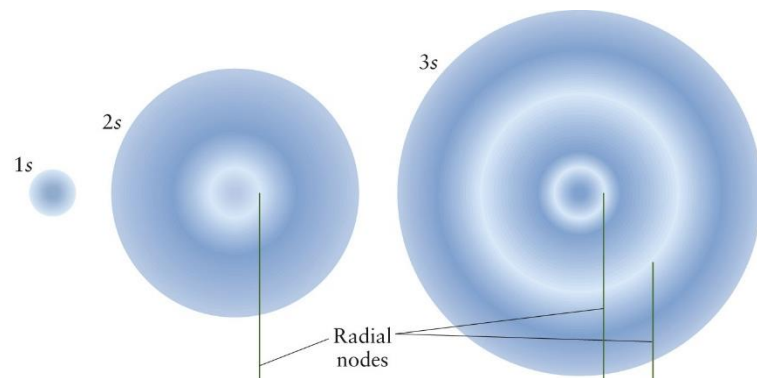
- **2s** ($n = 2, \ell = 0, m = 0$)

$$\psi_{200}(r, \theta, \phi) = \frac{1}{4\sqrt{2\pi}} a_0^{-3/2} \left(2 - \frac{r}{a_0} \right) e^{-r/2a_0}$$

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zero at $r = 2a_0 = 1.06\text{\AA}$
 nodal sphere or radial node

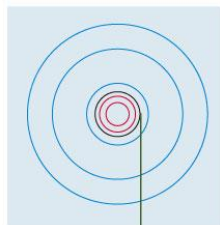
$[r < 2a_0: \Psi > 0, \text{ positive}]$ $[r > 2a_0: \Psi < 0, \text{ negative}]$



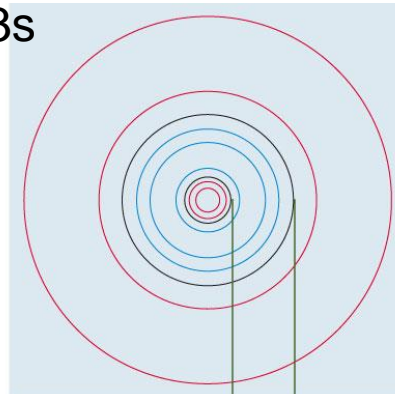
1s



2s

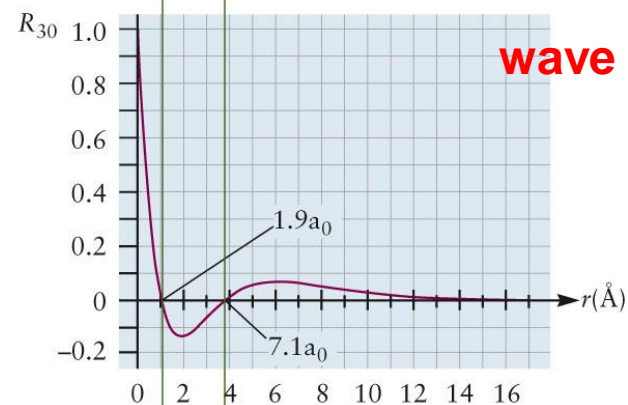
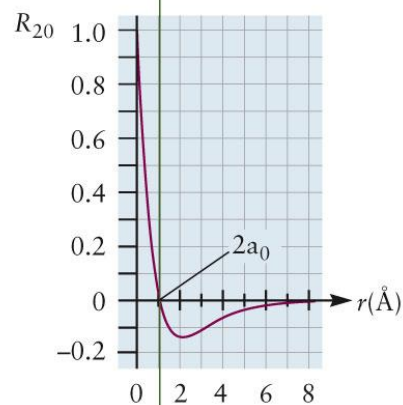
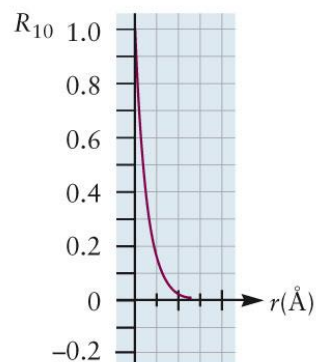


3s

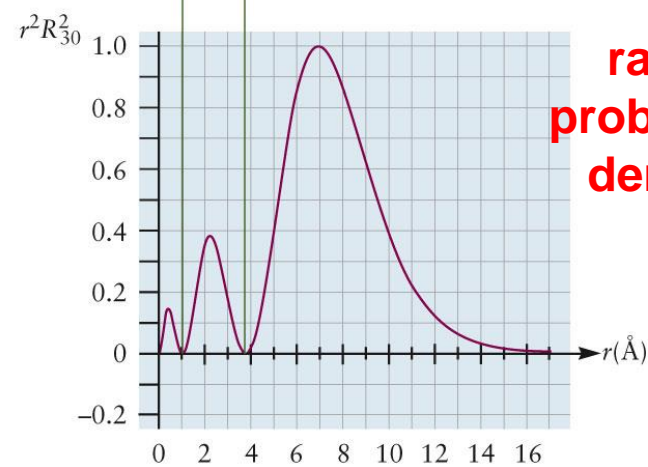
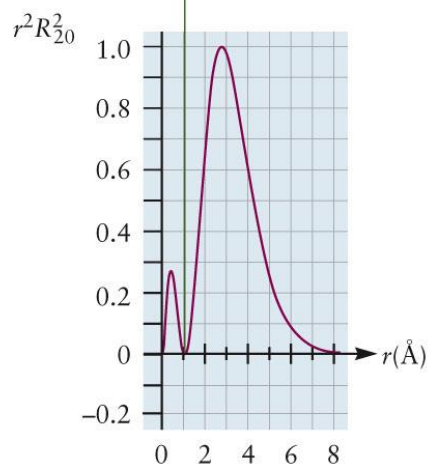
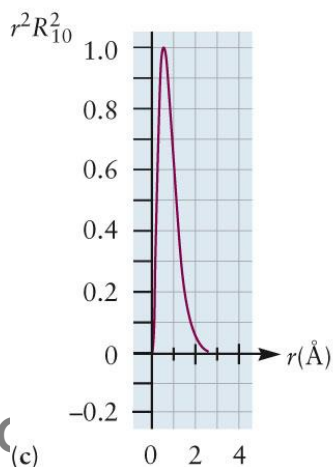
**isosurface**

A surface of points with the same value of wave functions

(a)

**wave function**

(b)

**radial probability density**

(c)

p orbitals

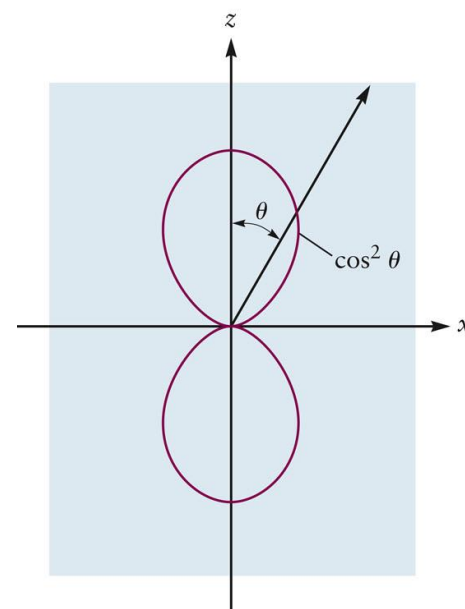
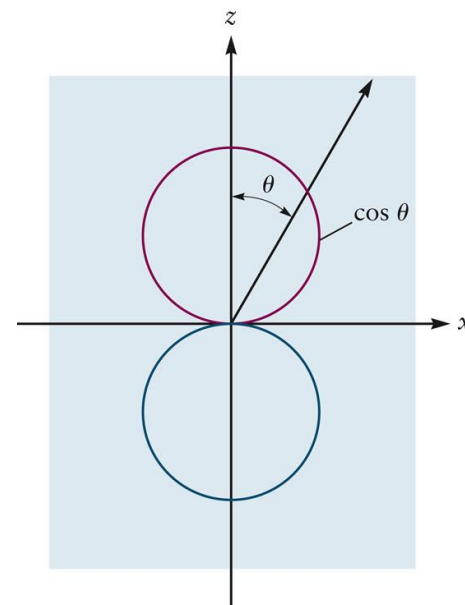
➤ **p orbitals:** $Y_{\ell m}(\theta, \phi)$ has separate lobes with positive and negative phase, with a node between them.

- $n = 2, \ell = 1, m = 0 \rightarrow 2p_0$ orbital : $R_{21} Y_{10}$

$$\psi_{210}(r, \theta, \phi) = \frac{1}{4\sqrt{2\pi}} a_0^{-3/2} \frac{r}{a_0} e^{-r/2a_0} \cos\theta$$

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- $\Phi = 0 \rightarrow$ cylindrical symmetry about the z-axis
- $R_{21}(r) \rightarrow r/a_0$ no radial nodes except at the origin
- $\cos\theta \rightarrow$ angular node at $\theta = 90^\circ$, x-y nodal plane
- $r \cos\theta \rightarrow$ z-axis $2p_0 \rightarrow$ labeled as $2p_z$



- $n = 2, \ell = 1, m = \pm 1 \rightarrow 2p_{+1}$ and $2p_{-1}$

• $Y_{11}(\theta, \Phi) \rightarrow e^{\pm i\Phi} = \cos\Phi \pm i \sin\Phi \leftarrow$ Euler's formula was used

• taking linear combinations

two real orbitals \rightarrow constructed $2p_x$ and $2p_y$

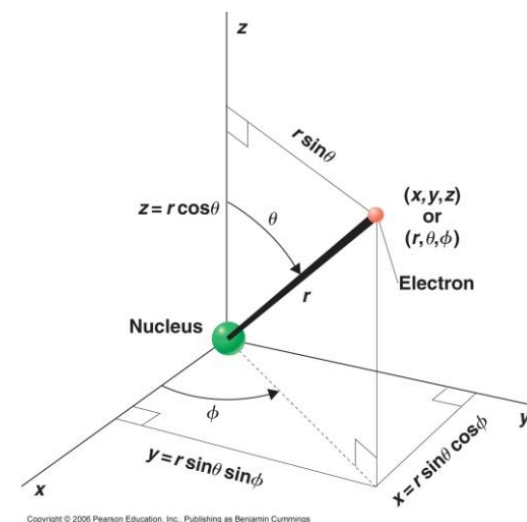
(real functions using Euler's formula)

$$2p_x = \frac{1}{\sqrt{2}} (2p_{+1} + 2p_{-1}) = \frac{1}{4\sqrt{2\pi}} a_0^{-3/2} \frac{r}{a_0} e^{-r/2a_0} \sin\theta \cos\phi$$

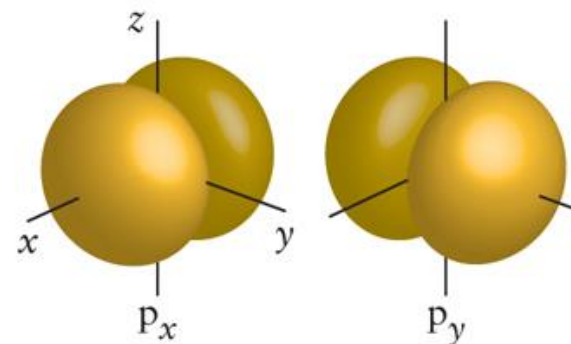
$$2p_y = \frac{1}{i\sqrt{2}} (2p_{+1} - 2p_{-1}), = \frac{1}{4\sqrt{2\pi}} a_0^{-3/2} \frac{r}{a_0} e^{-r/2a_0} \sin\theta \sin\phi$$

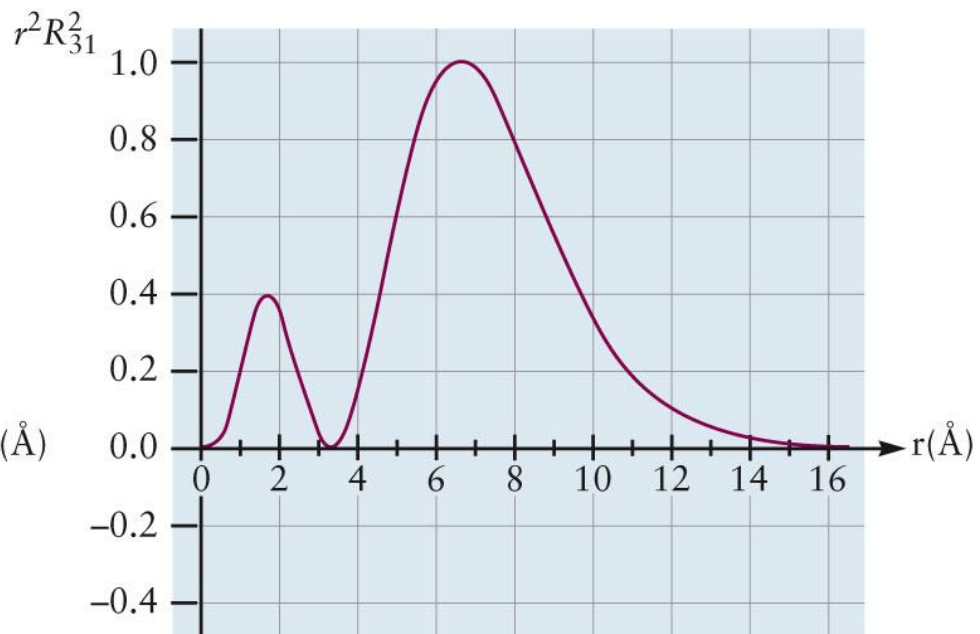
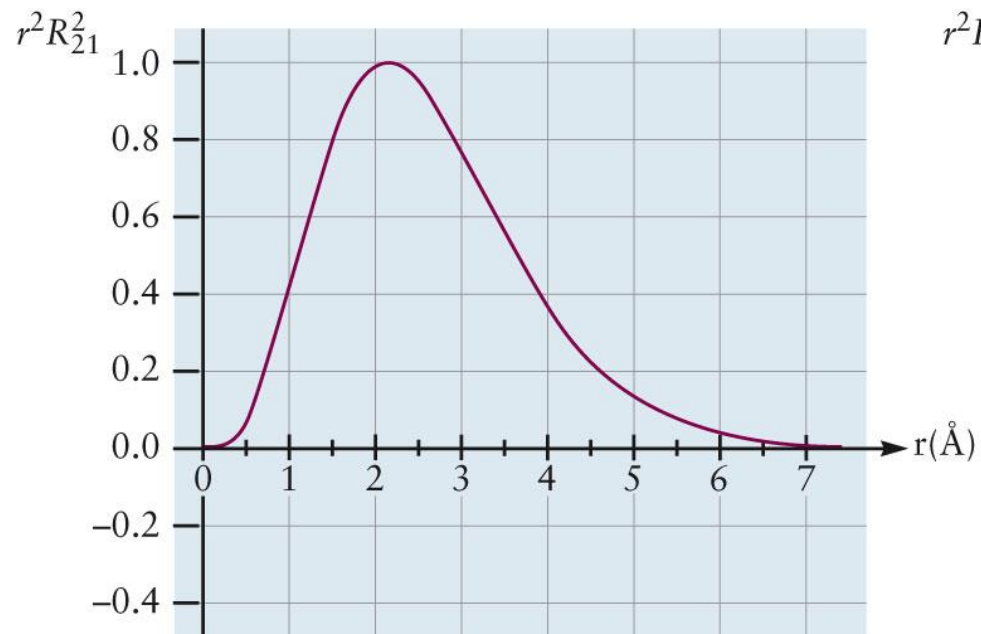
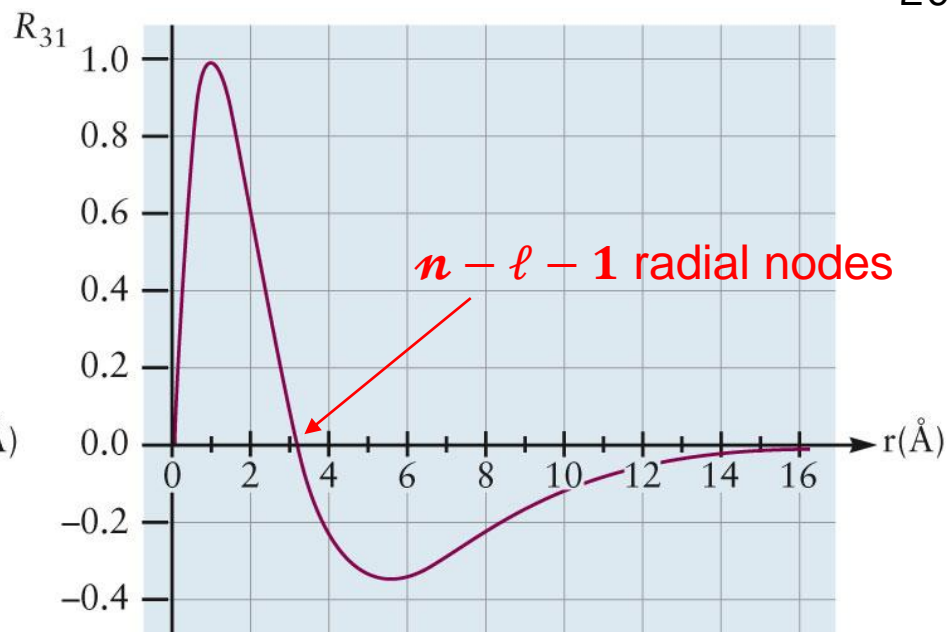
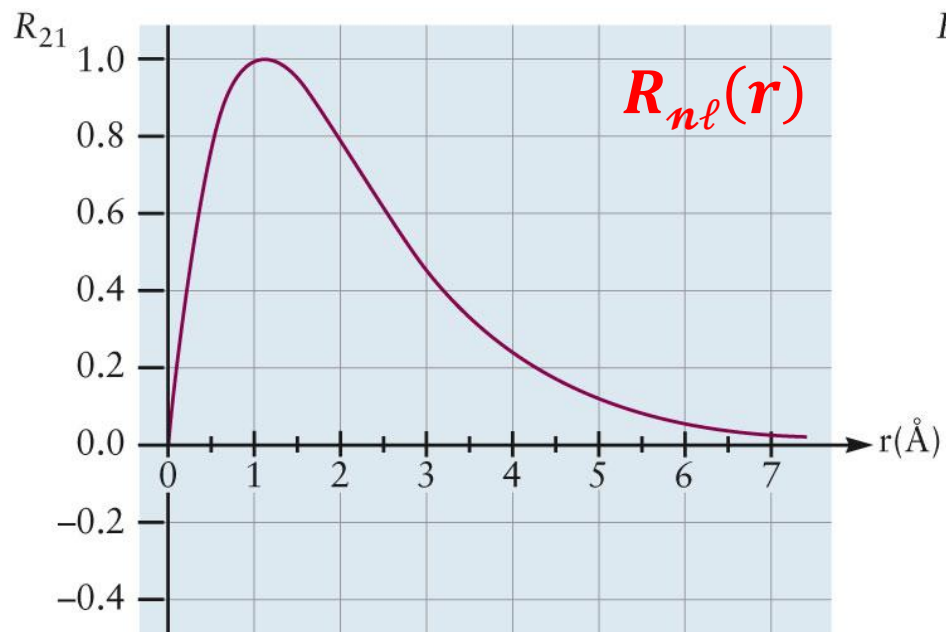
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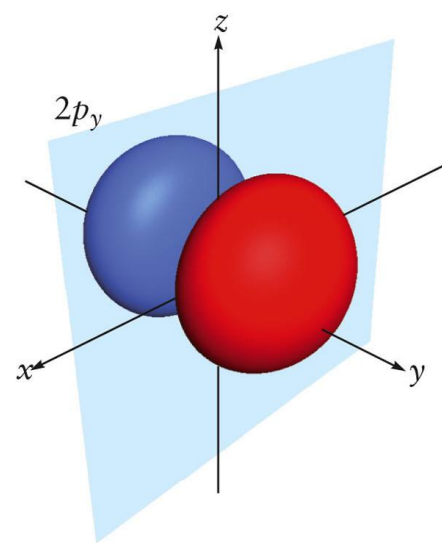
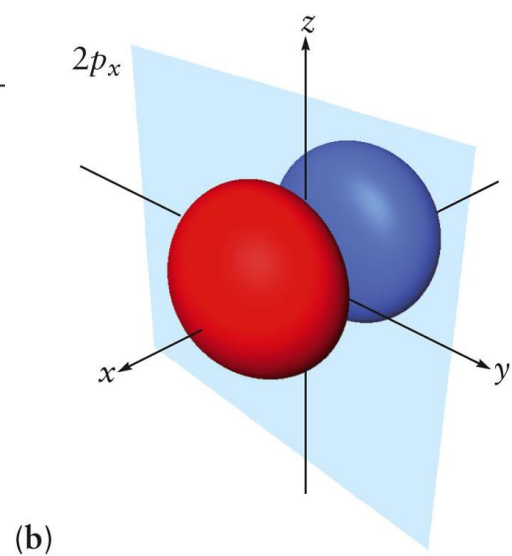
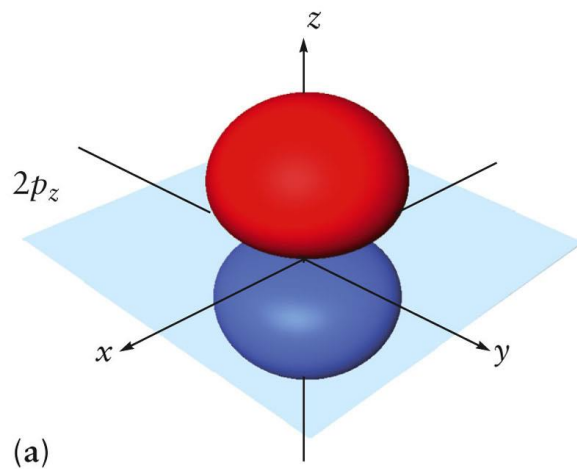
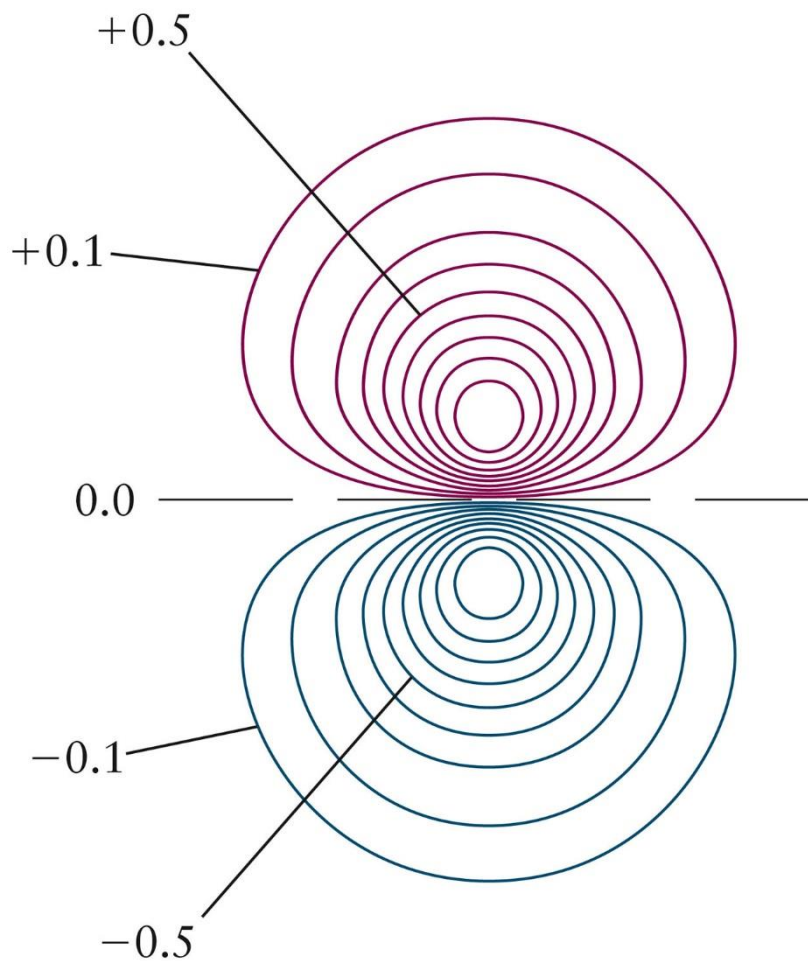
- p_x and p_y differ from p_z only in the angular factors (orientations).





$$\psi_{nlm} = R_{nl} Y_{lm}$$

$$\psi_{2p_z} = R_{21} Y_{2p_z}$$



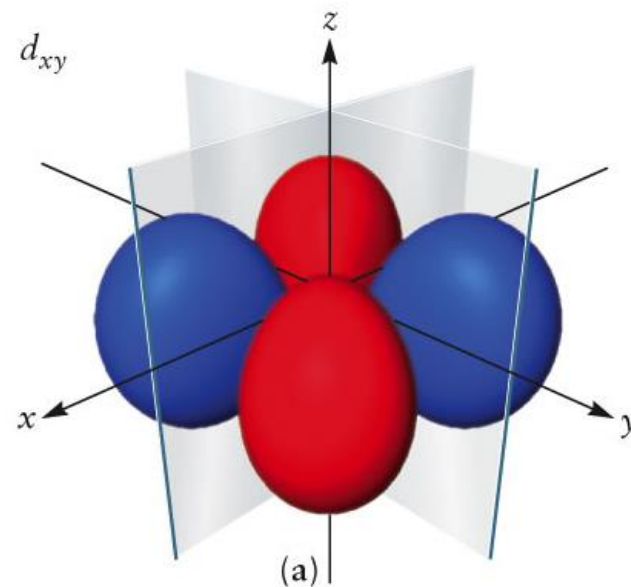
d orbitals

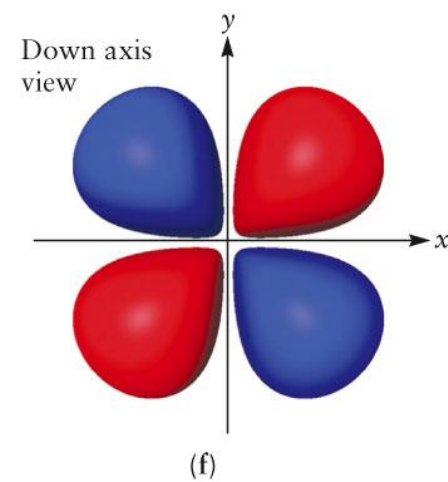
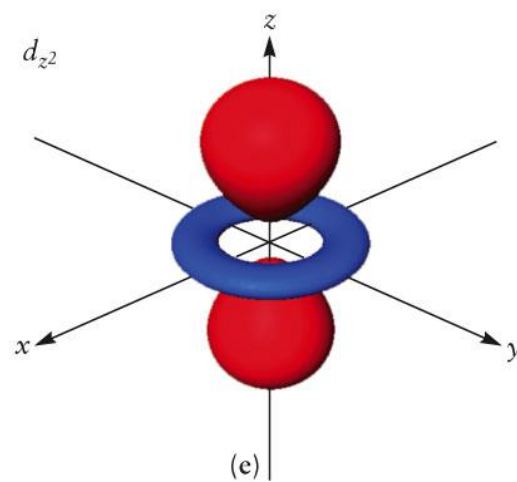
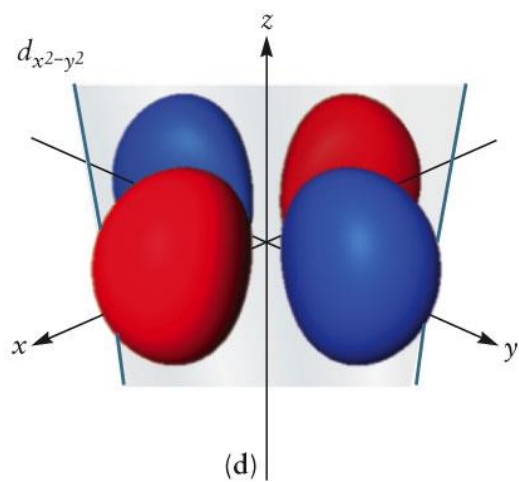
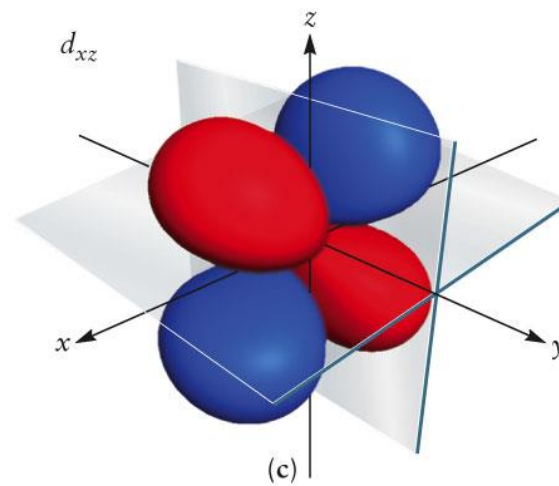
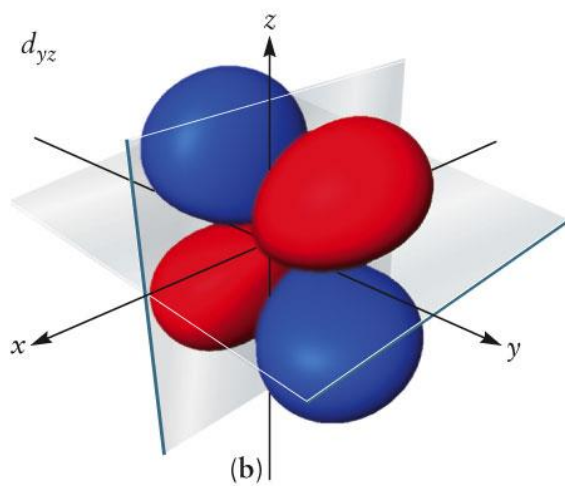
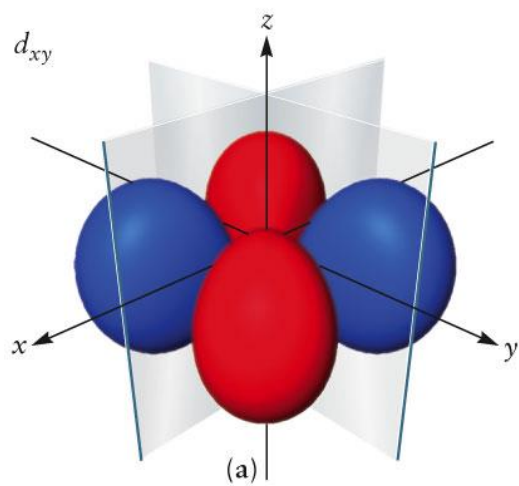
➤ d-orbitals

$\ell = 2$ & $m = 0$: d_{z^2}

$\ell = 2$ & linear combination of $m = +2, +1, -1, -2$ $d_{xy}, d_{yz}, d_{xz}, d_{x^2-y^2}$

- Each d orbital has **two angular nodes**.
i.e.) d_{xy} orbital: nodal surfaces of the xz and yz planes
- The radial functions, $R_{n2}(r)$, have **$n - 3$ radial nodes**, giving **$n - 1$ total nodes**.



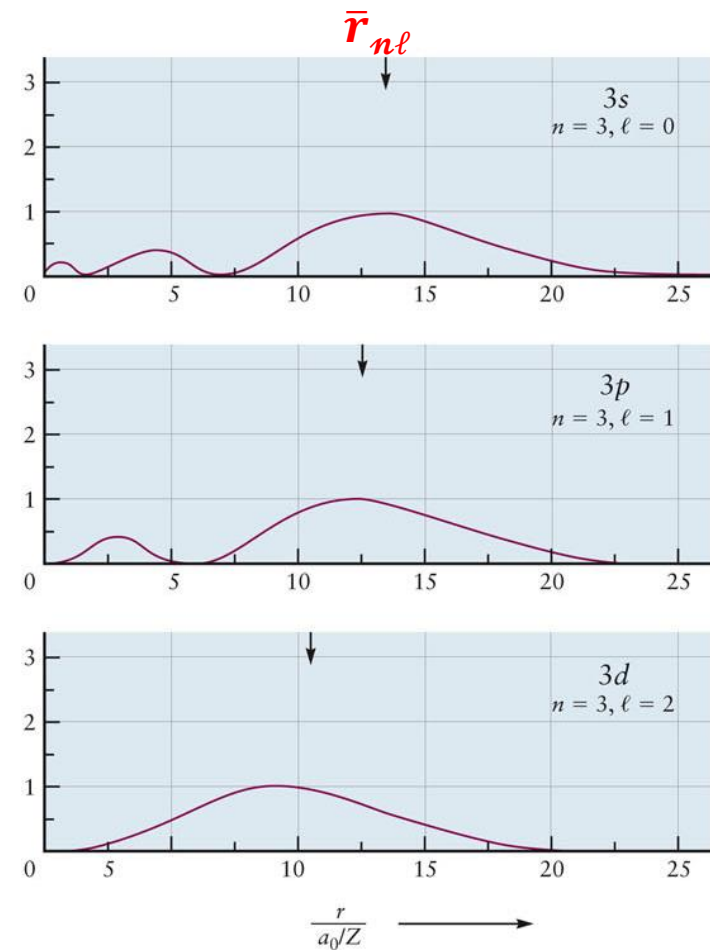
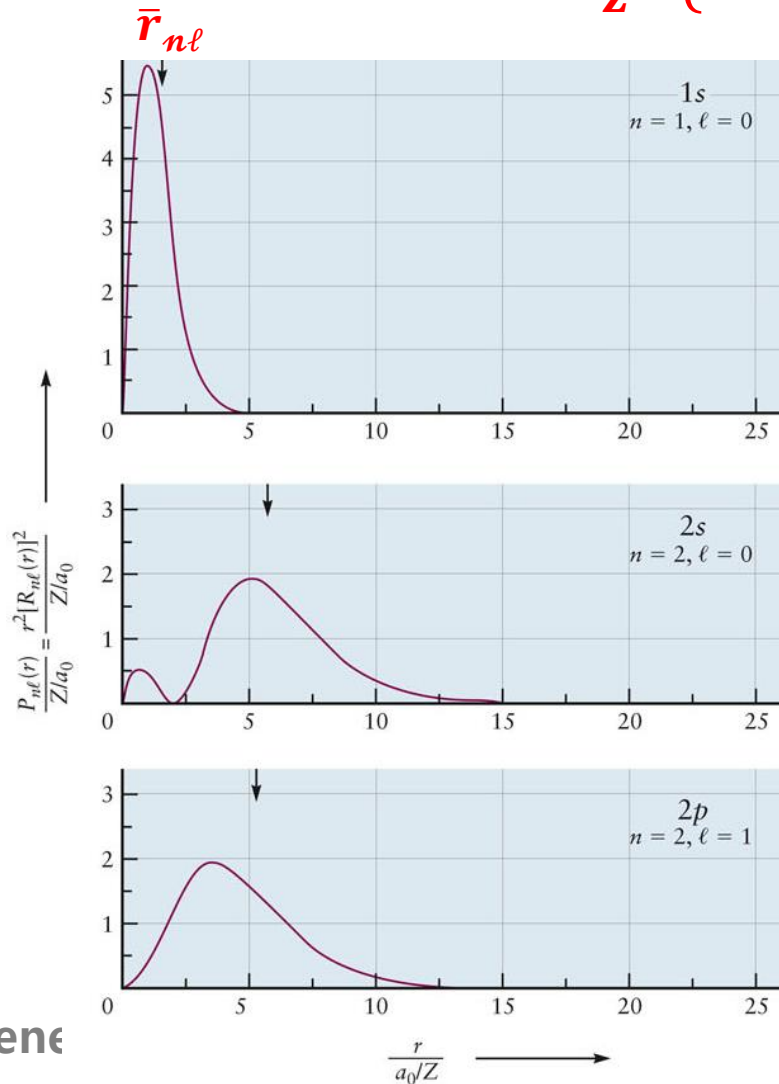


Orbital Shapes and Sizes

1. For a given value of ℓ , and **increase in n** leads to an **increase in the average distance** of the electron from the nucleus, and therefore in the size of the orbital.
2. An orbital with quantum numbers n and ℓ has **ℓ angular nodes and $n - \ell - 1$ radial nodes, giving a total of $n - 1$ nodes**. An angular node is defined by a plane. A radial node is defined by a spherical surface. For a one-electron atom or ion, **the energy depends only on the number of nodes** - that is, on n but not ℓ or m . The energy increases as the number of nodes increases.
3. **As r approaches 0, $\psi_{n\ell m}(r, \theta, \phi)$ vanishes for all orbitals except s orbitals**; thus, only an electron in an s orbital can “penetrate to the nucleus,” that is, have a finite probability of being found right at the nucleus.

- The **average value of the distance** of the electron from the nucleus in that orbital, $\bar{r}_{n\ell}$

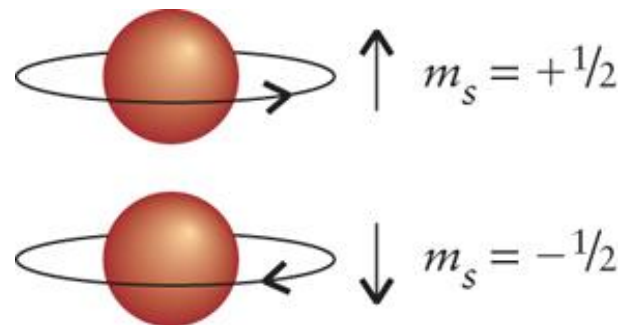
$$\bar{r}_{n\ell} = \frac{n^2 a_0}{Z} \left\{ 1 + \frac{1}{2} \left[1 - \frac{\ell(\ell+1)}{n^2} \right] \right\}$$



Electron Spin

➤ m_s , spin magnetic quantum number

- An electron has two spin states, as \uparrow (up) and \downarrow (down), or a and b.
- the values of m_s , only $+1/2$ and $-1/2$



- discovered by Stern and Gerlach experiment (1926)

Name	Symbol	Values	Specifies	Indicates
principal	n	$1, 2, \dots$	shell	size
orbital angular momentum*	l	$0, 1, \dots, n - 1$	subshell: $l = 0, 1, 2, 3, 4, \dots$ s, p, d, f, g, ...	shape
magnetic	m_l	$l, l - 1, \dots, -l$	orbitals of subshell	orientation
spin magnetic	m_s	$+\frac{1}{2}, -\frac{1}{2}$	spin state	spin direction

*Also called the azimuthal quantum number.

5.2 SHELL MODEL FOR MANY-ELECTRON ATOMS

- In many-electron atoms, Coulomb potential energy equals the sum of *nucleus-electron attractions* and *electron-electron repulsions*.
- No exact solutions of Schrödinger equation

- In a helium atom,

Attraction of electron 1 to the nucleus	Attraction of electron 2 to the nucleus	Repulsion between the two electrons
$-\frac{2e^2}{4\pi\epsilon_0 r_1}$	$-\frac{2e^2}{4\pi\epsilon_0 r_2}$	$+\frac{e^2}{4\pi\epsilon_0 r_{12}}$

$$V =$$

r_1 = the distance of electron 1 from the nucleus

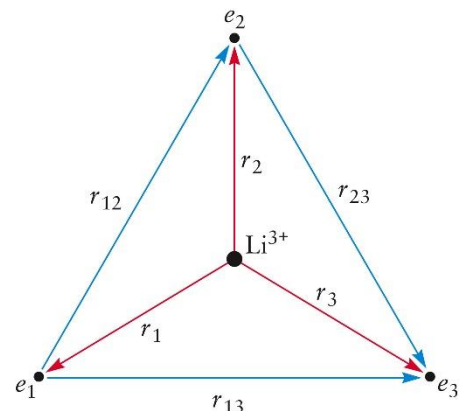
r_2 = the distance of electron 2 from the nucleus

r_{12} = the distance between the two electrons

The Shell Model of the Atom

For Li with $Z = 3$,

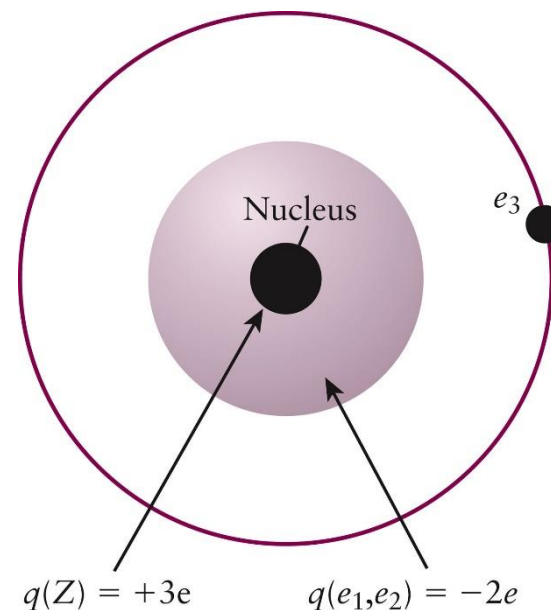
$$V = \frac{Ze^2}{4\pi\epsilon_0} \left(-\frac{1}{r_1} - \frac{1}{r_2} - \frac{1}{r_3} \right) + \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{23}} \right)$$



➤ Effective potential energy

Taking into account both the attractive electron-nuclear forces and the average of the repulsive force among the electrons.

$$V_{\text{eff}}(r) = -\frac{Z_{\text{eff}}e^2}{4\pi\epsilon_0 r}$$



Shielding Effects

- Energy-level diagrams for many-electron atoms

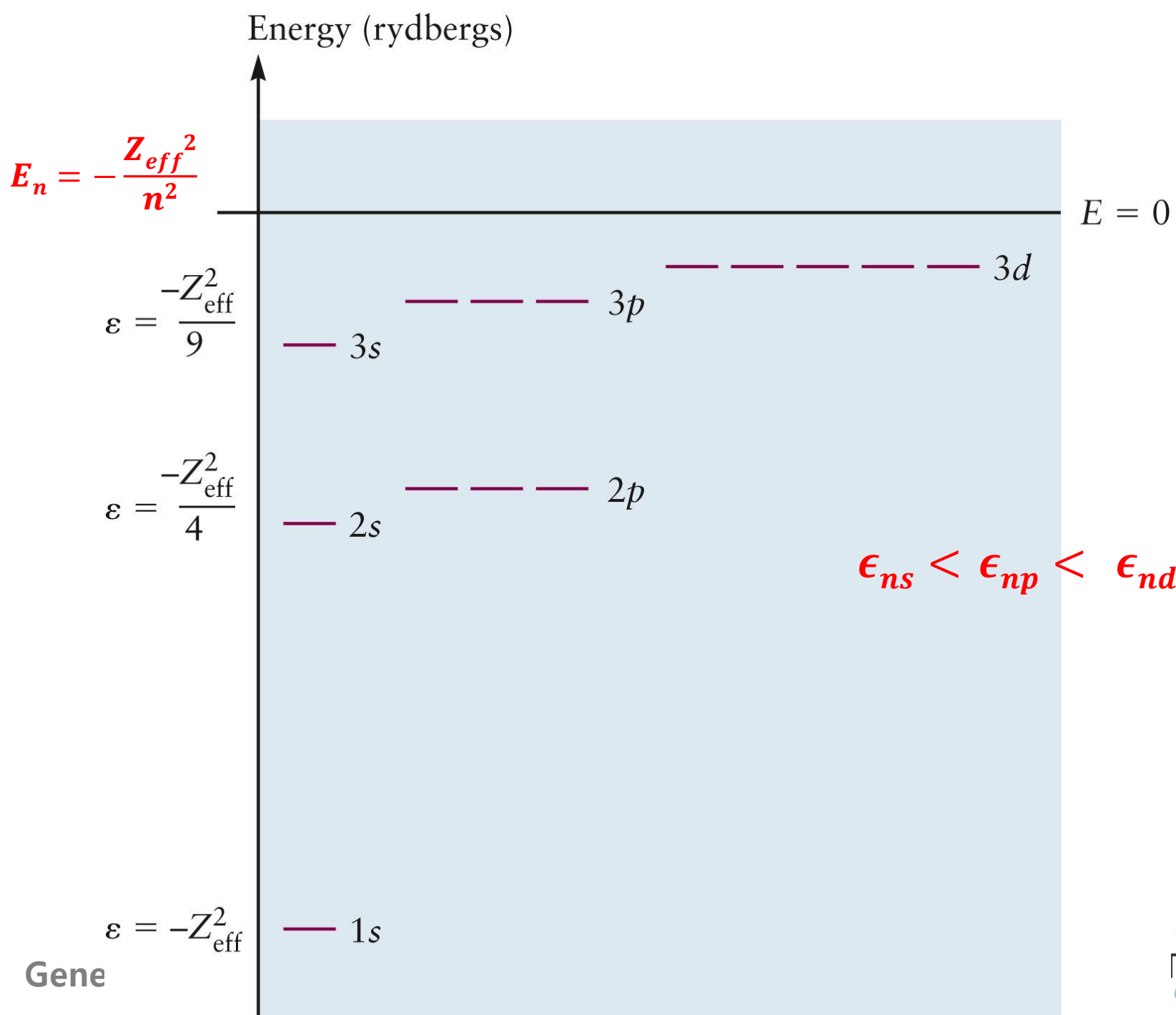
1) **The degeneracy of the p, d, and f orbitals is removed**, due to the non-isotropic potential → angular dependency

➡ The energy levels depend on both n and ℓ

2) Energy values are distinctly shifted from the values of corresponding H orbitals due to the strong attraction by nuclei with $Z > 1$.

- Each electron attracted by the nucleus, and repelled by the other electrons.

→ **shielded** from the full nuclear attraction by the other electrons.



5.3 AUFBAU PRINCIPLE AND ELECTRON CONFIGURATIONS

➤ **Electronic configuration of the atom**

a list of all its occupied orbitals, with the numbers of electrons that each one contains.

i.e. Li: $1s^2 2s^1$

➤ **Pauli exclusion principle**

No two electrons in an atom can have the same set of four quantum numbers, (n, ℓ, m, m_s) .



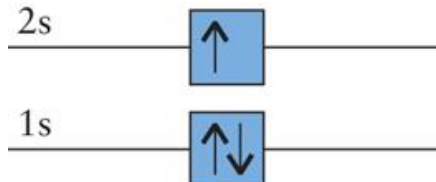
or

Each atomic orbital with (n, ℓ, m) holds at most two electrons, one with spin up and the other with spin down.

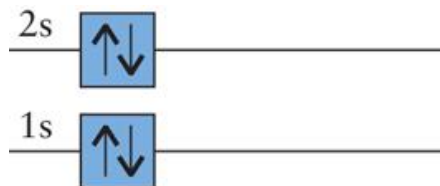
➤ Hund's rule

When electrons are added to orbitals of equal energy, a single electron enters each orbital before a second one enters any orbital.

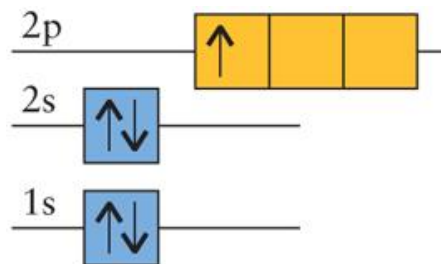
In addition, the lowest energy configuration is the one with parallel spins.

- H, $1s^1$

- He, $1s^2$

- Li, $1s^2 2s^1$ or $[\text{He}]2s^1$


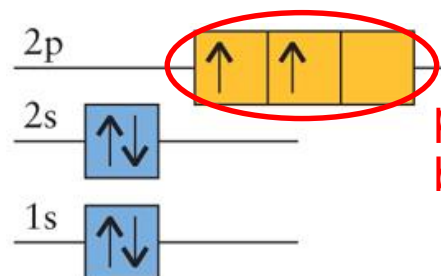
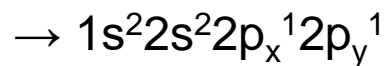
- Be, $1s^2 2s^2$ or $[\text{He}]2s^2$



- B, $1s^2 2s^2 2p^1$ or $[\text{He}]2s^2 2p^1$



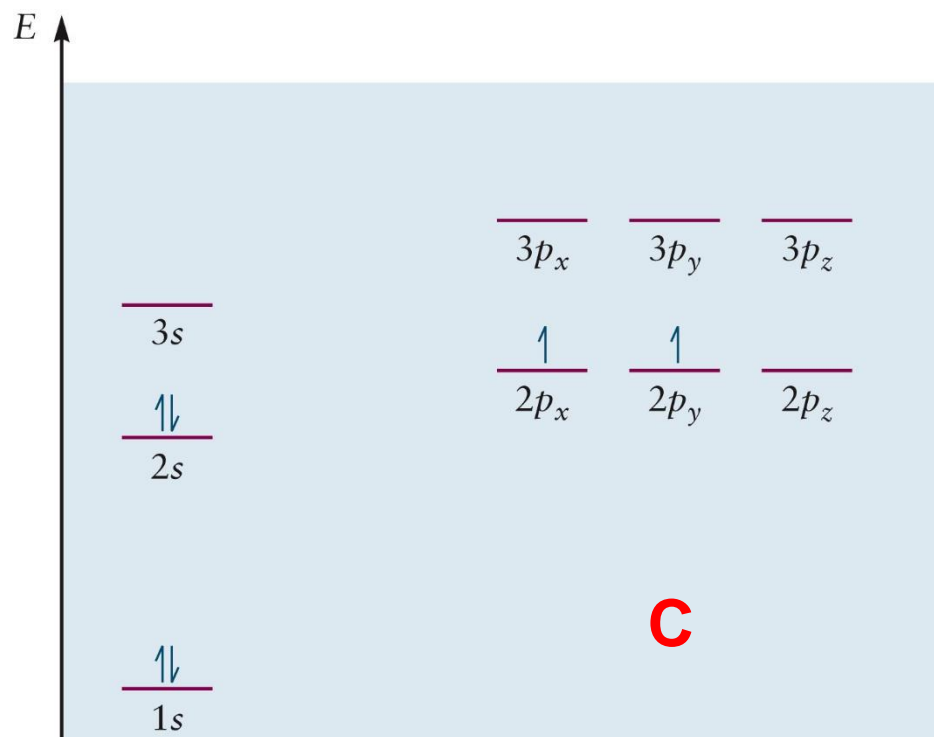
- C, $1s^2 2s^2 2p^2$ or $[\text{He}]2s^2 2p^2$

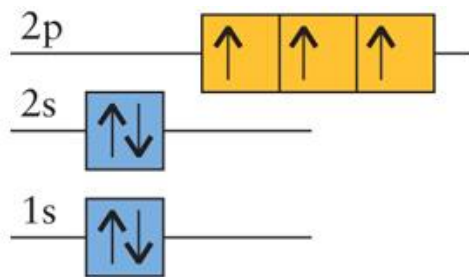
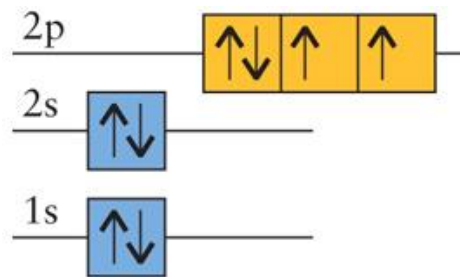
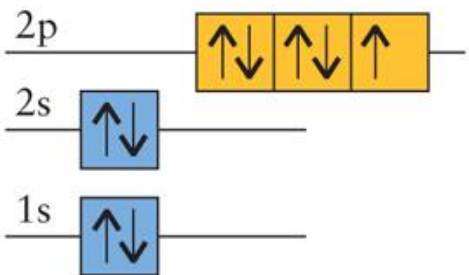
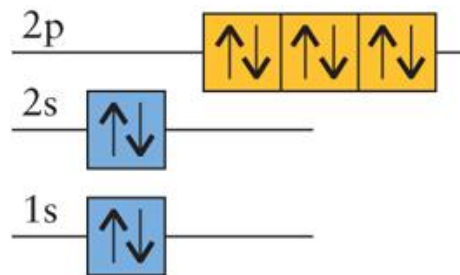


parallel spins
by Hund's rule

- **Magnetic properties** for a test of electronic configurations
- **paramagnetic**: a substance attracted into a magnetic field with one or more unpaired electrons
 - **diamagnetic**: a substance pushed out of a magnetic field with all electrons paired

i.e.) paramagnetic: H, Li, B, C
diamagnetic: He, Be



7 N $1s^2 2s^2 2p^3$, [He] $2s^2 2p^3$ 8 O $1s^2 2s^2 2p^4$, [He] $2s^2 2p^4$ 9 F $1s^2 2s^2 2p^5$, [He] $2s^2 2p^5$ 10 Ne $1s^2 2s^2 2p^6$, [He] $2s^2 2p^6$

- Elements in **Period 2** (from Li to Ne), the valence shell with $n = 2$.
- **p-block elements**: B to Ne, filling of p orbitals
- **s-block elements**: H to Be, filling of s orbitals

	1s	2s	2p _x	2p _y	2p _z
H: 1s ¹	<u>↑</u>	<u> </u>	<u> </u>	<u> </u>	<u> </u>
He: 1s ²	<u>↑↓</u>	<u> </u>	<u> </u>	<u> </u>	<u> </u>
Li: 1s ² 2s ¹	<u>↑↓</u>	<u>↑</u>	<u> </u>	<u> </u>	<u> </u>
Be: 1s ² 2s ²	<u>↑↓</u>	<u>↑↓</u>	<u> </u>	<u> </u>	<u> </u>
B: 1s ² 2s ² 2p _x ¹	<u>↑↓</u>	<u>↑↓</u>	<u>↑</u>	<u> </u>	<u> </u>
C: 1s ² 2s ² 2p _x ¹ 2p _y ¹	<u>↑↓</u>	<u>↑↓</u>	<u>↑</u>	<u>↑</u>	<u> </u>
N: 1s ² 2s ² 2p _x ¹ 2p _y ¹ 2p _z ¹	<u>↑↓</u>	<u>↑↓</u>	<u>↑</u>	<u>↑</u>	<u>↑</u>
O: 1s ² 2s ² 2p _x ² 2p _y ¹ 2p _z ¹	<u>↑↓</u>	<u>↑↓</u>	<u>↑↓</u>	<u>↑</u>	<u>↑</u>
F: 1s ² 2s ² 2p _x ² 2p _y ² 2p _z ¹	<u>↑↓</u>	<u>↑↓</u>	<u>↑↓</u>	<u>↑↓</u>	<u>↑</u>
Ne: 1s ² 2s ² 2p _x ² 2p _y ² 2p _z ²	<u>↑↓</u>	<u>↑↓</u>	<u>↑↓</u>	<u>↑↓</u>	<u>↑↓</u>

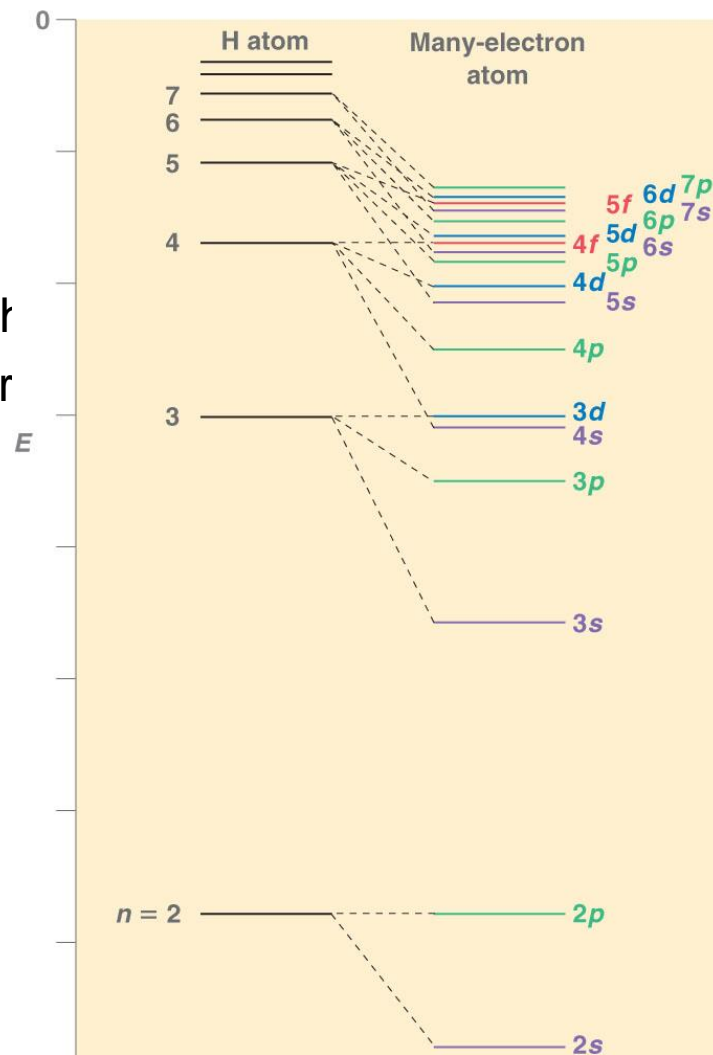
- **n = 3**: Na, [He]2s²2p⁶3s¹ or [Ne]3s¹ to Ar, [Ne]3s²3p⁶
- **n = 4**: from Sc (scandium, Z = 21) to Zn (zinc, Z = 30)
the next 10 electrons enter the 3d-orbitals. **d-block elements**

➤ The (n+l) rule

Order of filling subshells in neutral atoms is determined by filling those with the lowest values of (n+l) first. Subshells in a group with the same value of (n+l) are filled in the order of increasing n, due to the orbital screening.

order: 1s < 2s < 2p < 3s < 3p < 4s < 3d
< 4p < 5s < 4d < ...

- **n = 5**: 5s-electrons followed by the 4d-electrons
- **n = 6**: Ce (cerium, [Xe]4f¹5d¹6s²)



Anomalous Configurations

Exceptions to the Aufbau principle

Cr, predicted: $4s^23d^4$



Cr, observed: $4s^13d^5$



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Anomalous electron configurations*

Period	Z	Element	Configuration	Period	Z	Element	Configuration
4	24	Cr	$[\text{Ar}]4s^13d^5$	6	57	La	$[\text{Xe}]6s^25d^1$
4	29	Cu	$[\text{Ar}]4s^13d^{10}$	6	58	Ce	$[\text{Xe}]6s^24f^15d^1$
5	41	Nb	$[\text{Kr}]5s^14d^4$	6	64	Gd	$[\text{Xe}]6s^24f^75d^1$
5	42	Mo	$[\text{Kr}]5s^14d^5$	6	78	Pt	$[\text{Xe}]6s^14f^{14}5d^9$
5	44	Ru	$[\text{Kr}]5s^14d^7$	6	79	Au	$[\text{Xe}]6s^14f^{14}5d^{10}$
5	45	Rh	$[\text{Kr}]5s^14d^8$	7	89	Ac	$[\text{Rn}]7s^26d^1$
5	46	Pd	$[\text{Kr}]4d^{10}$	7	90	Th	$[\text{Rn}]7s^26d^2$
5	47	Ag	$[\text{Kr}]5s^14d^{10}$	7	91	Pa	$[\text{Rn}]7s^25f^26d^1$
				7	92	U	$[\text{Rn}]7s^25f^36d^1$

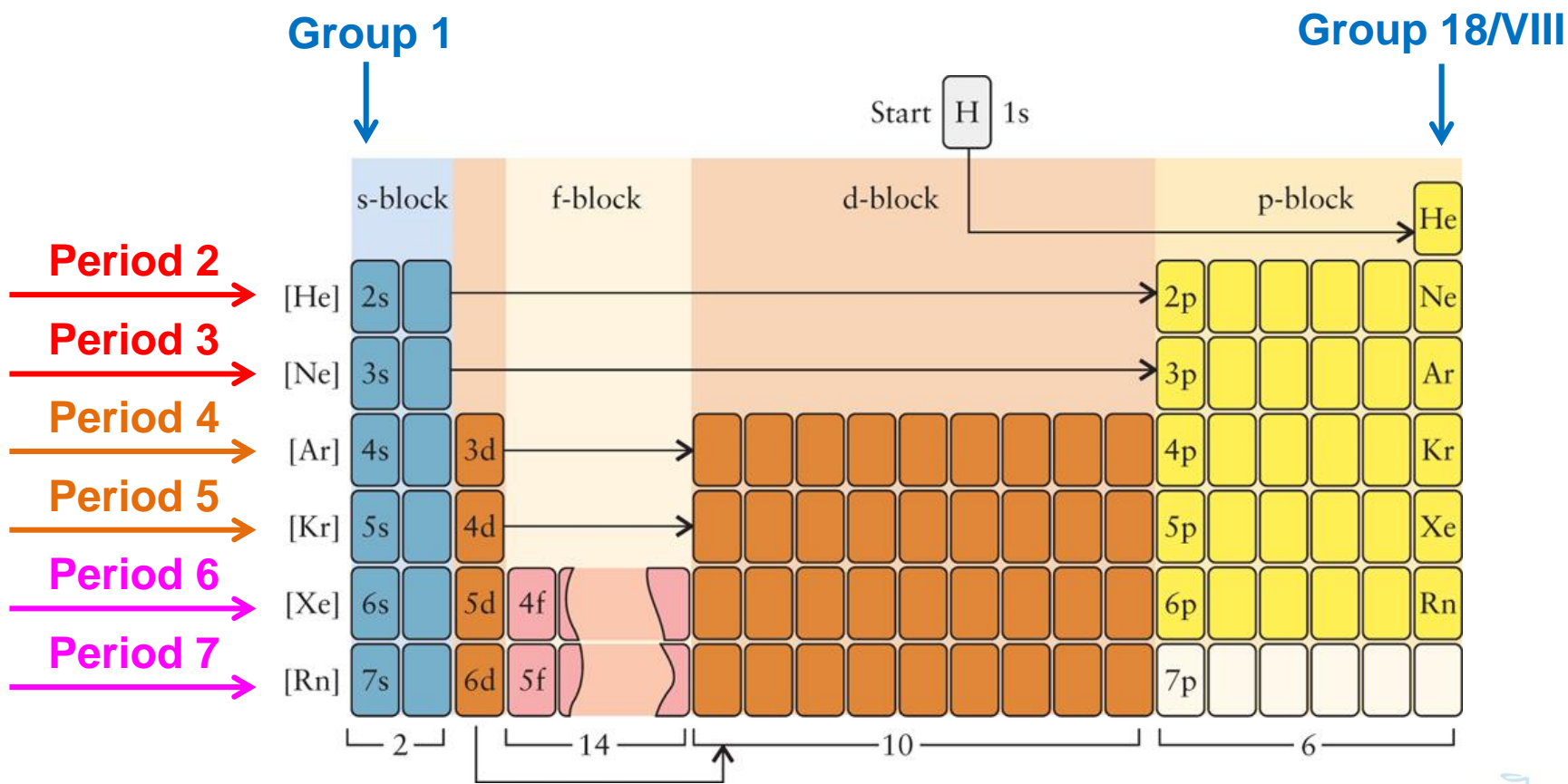
1s												1s					
H												He					
2s-filling												2p-filling					
Li	Be											B	C	N	O	F	Ne
3s-filling												3p-filling					
Na	Mg											Al	Si	P	S	Cl	Ar
4s-filling		3d-filling										4p-filling					
K	Ca	Sc	Ti	V	Cr $3d^3 4s^1$	Mn	Fe	Co	Ni	Cu $3d^{10} 4s^1$	Zn	Ga	Ge	As	Se	Br	Kr
5s-filling		4d-filling										5p-filling					
Rb	Sr	Y	Zr	Nb $4d^4 5s^1$	Mo $4d^5 5s^1$	Tc	Ru $4d^7 5s^1$	Rh $4d^8 5s^1$	Pd $4d^{10}$	Ag $4d^{10} 5s^1$	Cd	In	Sn	Sb	Te	I	Xe
6s-filling		5d-filling										6p-filling					
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt $5d^9 6s^1$	Au $5d^{10} 6s^1$	Hg	Tl	Pb	Bi	Po	At	Rn
7s-filling		6d-filling															
Fr	Ra	Lr	Rf	Ha	Sg	Ns	Hs	Mt	Uun	Uuu							

4f-filling													
La $5d^1 6s^2$	Ce $4f^1 5d^1 6s^2$	Pr	Nd	Pm	Sm	Eu	Gd $4f^7 5d^1 6s^2$	Tb	Dy	Ho	Er	Tm	Yb

5f-filling													
Ac $6d^1 7s^2$	Th $6d^2 7s^2$	Pa $5f^1 6d^1 7s^2$	U $5f^3 6d^1 7s^2$	Np $5f^4 6d^1 7s^2$	Pu	Am	Cm $5f^7 6d^1 7s^2$	Bk	Cf	Es	Fm	Md	No

All atoms in a given **period** have the same type of core with the same n .

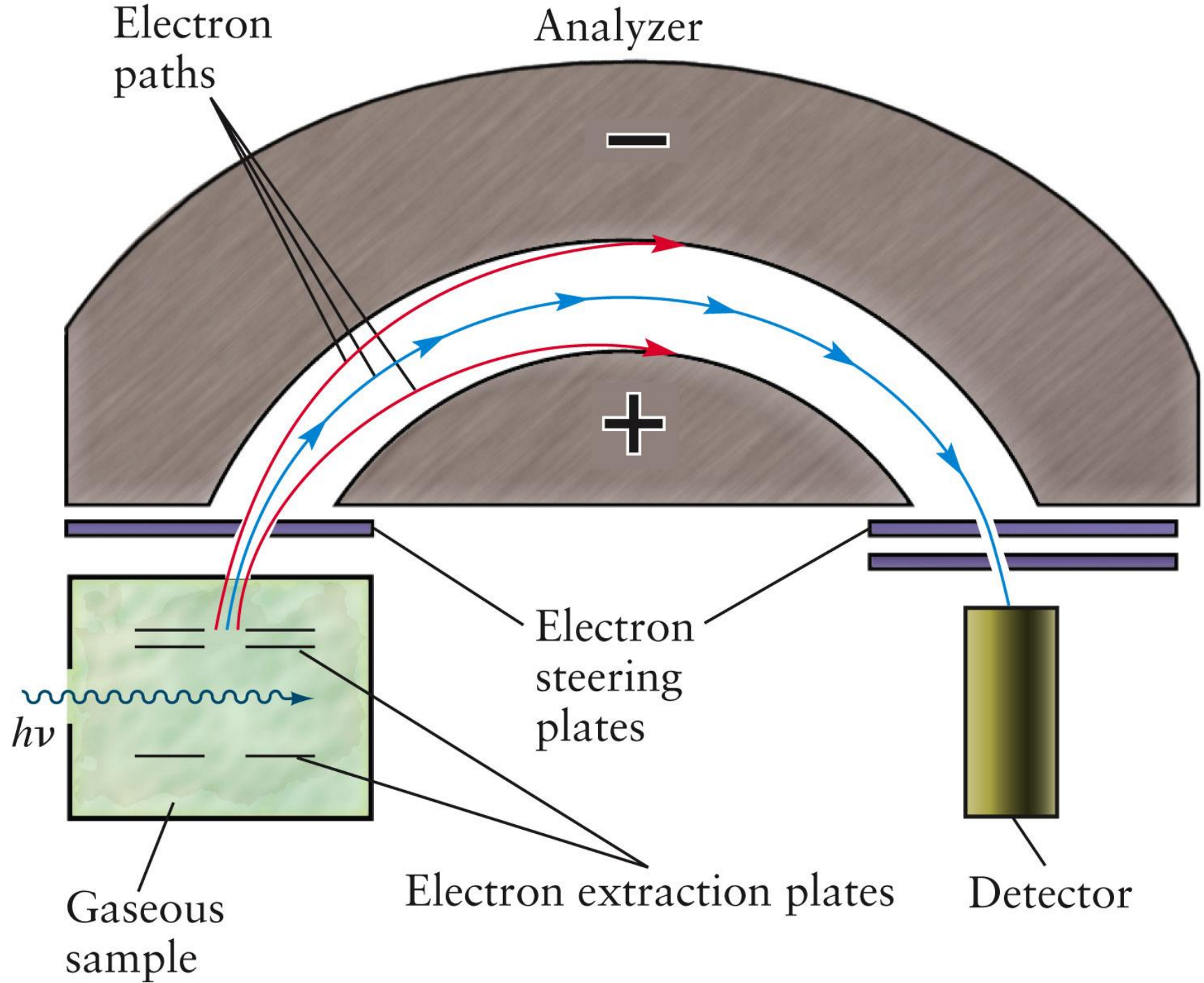
All atoms in a given **group** have analogous valence electron configurations that differ only in the value of n .



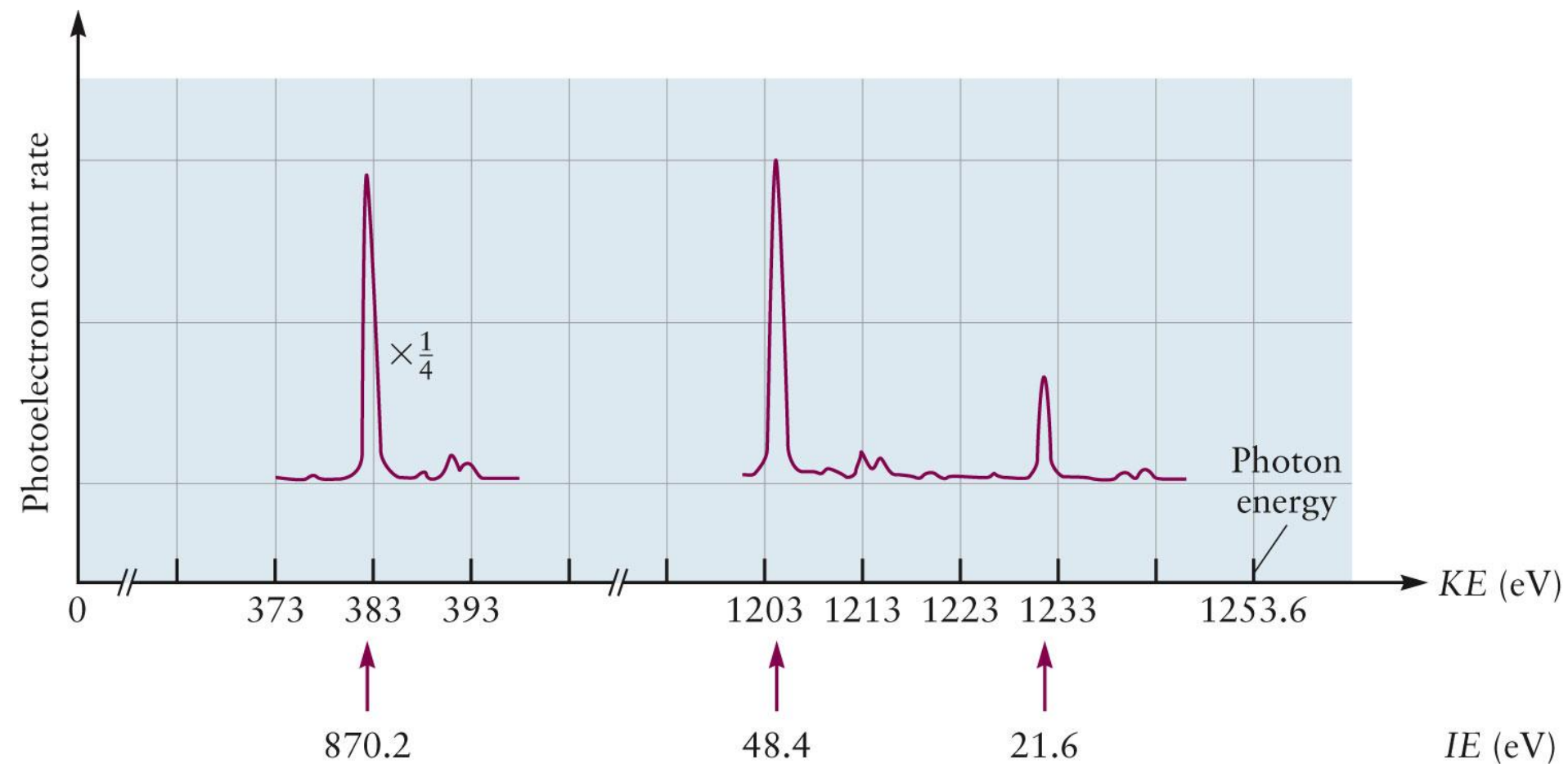
5.4 SHELLS AND THE PERIODIC TABLE: PHOTOELECTRON SPECTROSCOPY

- A **shell** is defined precisely as a set of orbitals that have the same principal quantum number.
- **Photoelectron spectroscopy (PES)**
determining the energy level of each orbital by measuring the ionization energy required to remove each electron from the atom

$$IE = h\nu - \frac{1}{2} m_e v_{electron}^2$$



- For Ne excited by X-rays with $\nu = 9.890 \times 10^{-10} \text{ m}$,



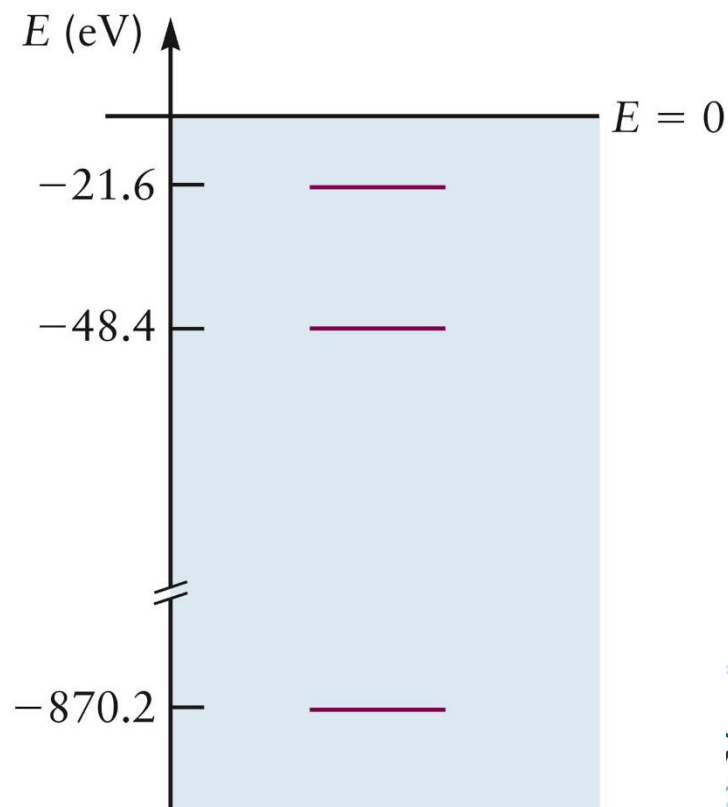
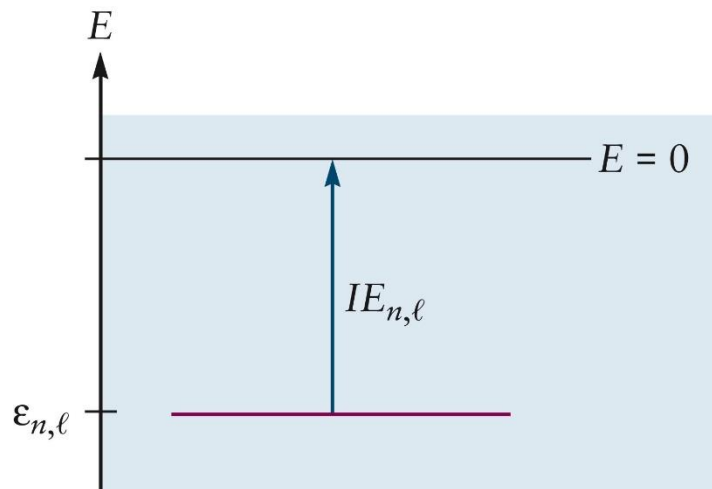
- Koopmans's approximation,

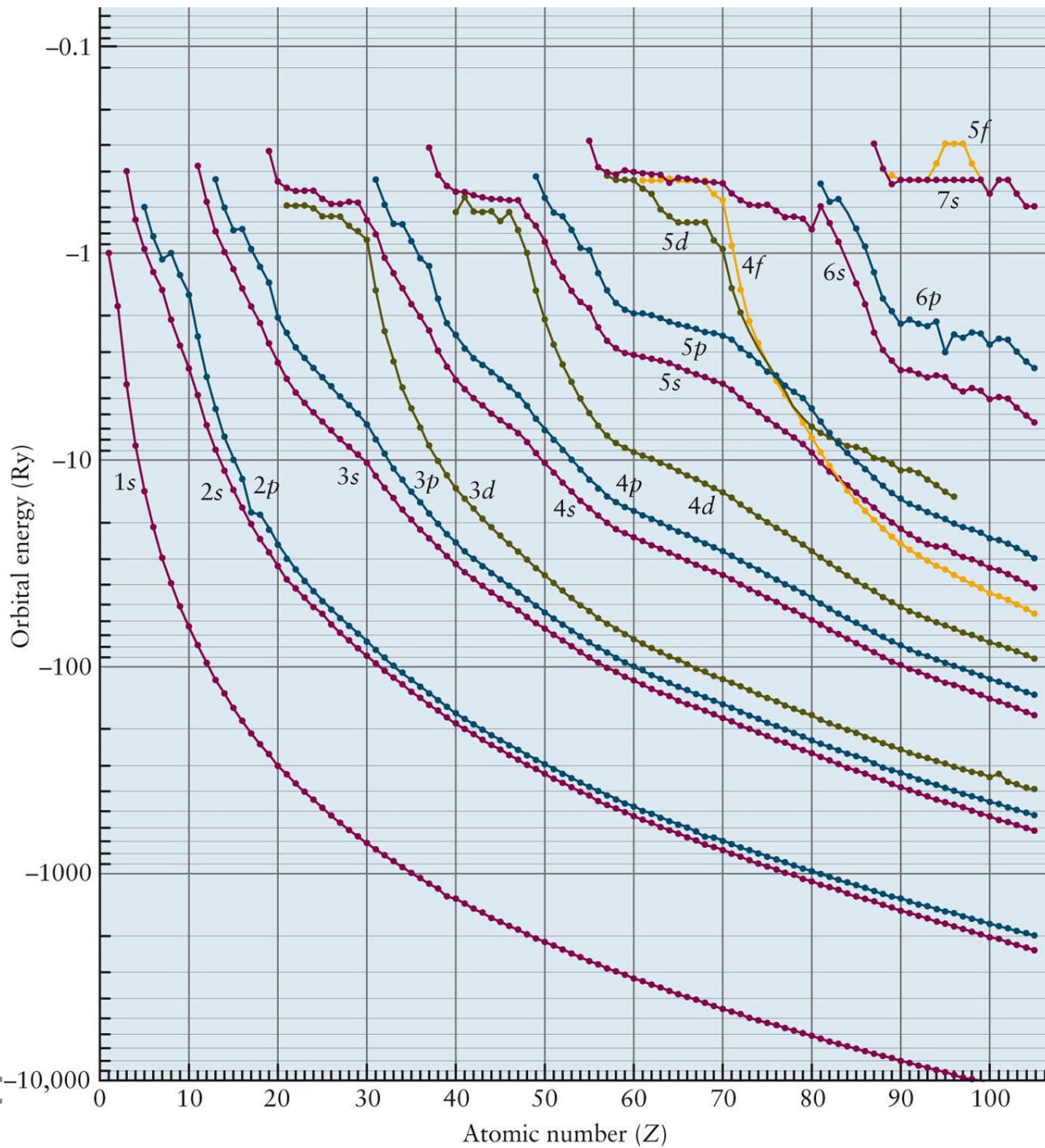
$$IE_{\alpha} = -\epsilon_{\alpha}$$

- with the frozen orbital approximation

The orbital energies are the same in the ion, despite the loss of an e⁻.

i.e.) for Ne with 1s² 2s² 2p⁶





5.5 PERIODIC PROPERTIES AND ELECTRONIC STRUCTURE

- **Atomic radius:** defined as half the distance between the centers of neighboring atoms
- **Ionic radius:** its share of the distance between neighboring ions in an ionic solid

➤ General trends

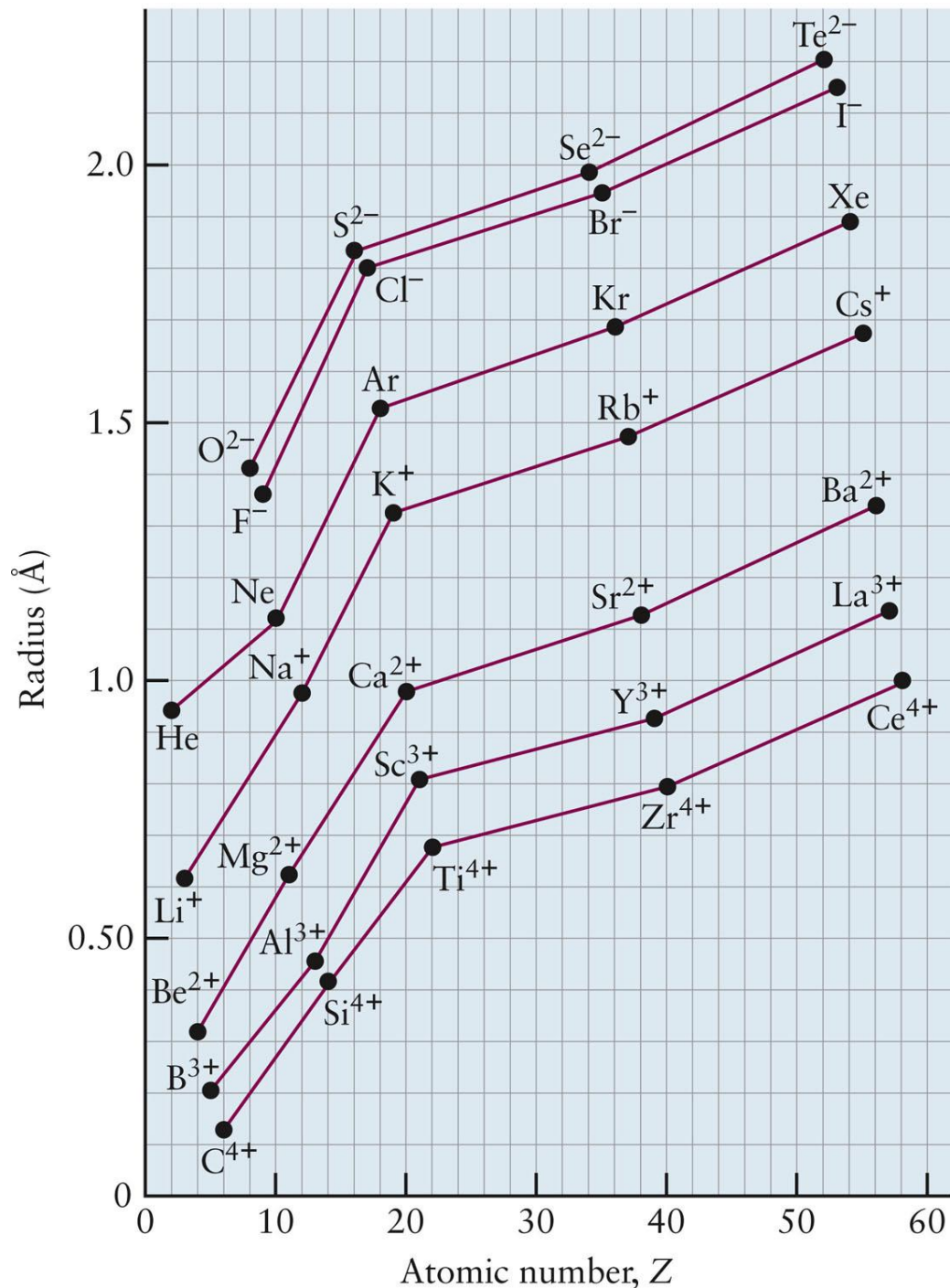
- **r decreases from left to right across a period**

(effective nuclear charge increases)

- **r increases from top to bottom down a group**

(change in n and size of valence shell)

	1	2	13/III	14/IV	15/V	16/VI	17/VII	18/VIII
2	Li 152	Be 113	B 88	C 77	N 75	O 66	F 58	Ne
3	Na 154	Mg 160	Al 143	Si 117	P 110	S 104	Cl 99	Ar
4	K 227	Ca 197	Ga 122	Ge 122	As 121	Se 117	Br 114	Kr
5	Rb 248	Sr 215	In 163	Sn 141	Sb 141	Te 137	I 133	Xe
6	Cs 265	Ba 217	Tl 170	Pb 175	Bi 155	Po 167	At	Rn



- The rate of increase changes considerably.

i.e.) Li⁺, Na⁺, to K⁺
substantial change
to Rb⁺, Cs⁺
small change due to
filling d-orbitals

➤ **Lanthanide contraction**
filling of the 4f orbitals

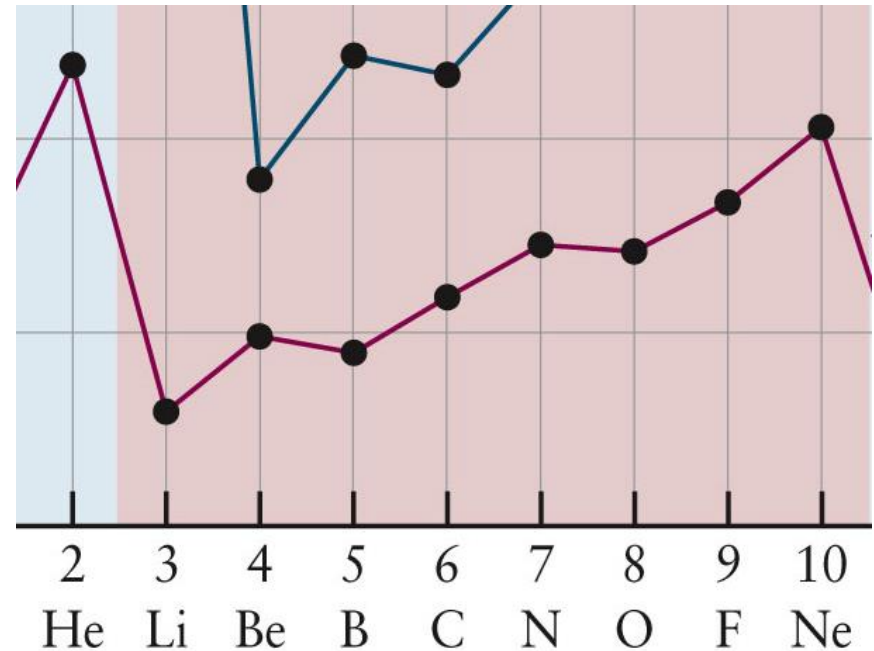
➤ **Molar volumes** ($\text{cm}^3 \text{mol}^{-1}$) of atoms in the solid phase

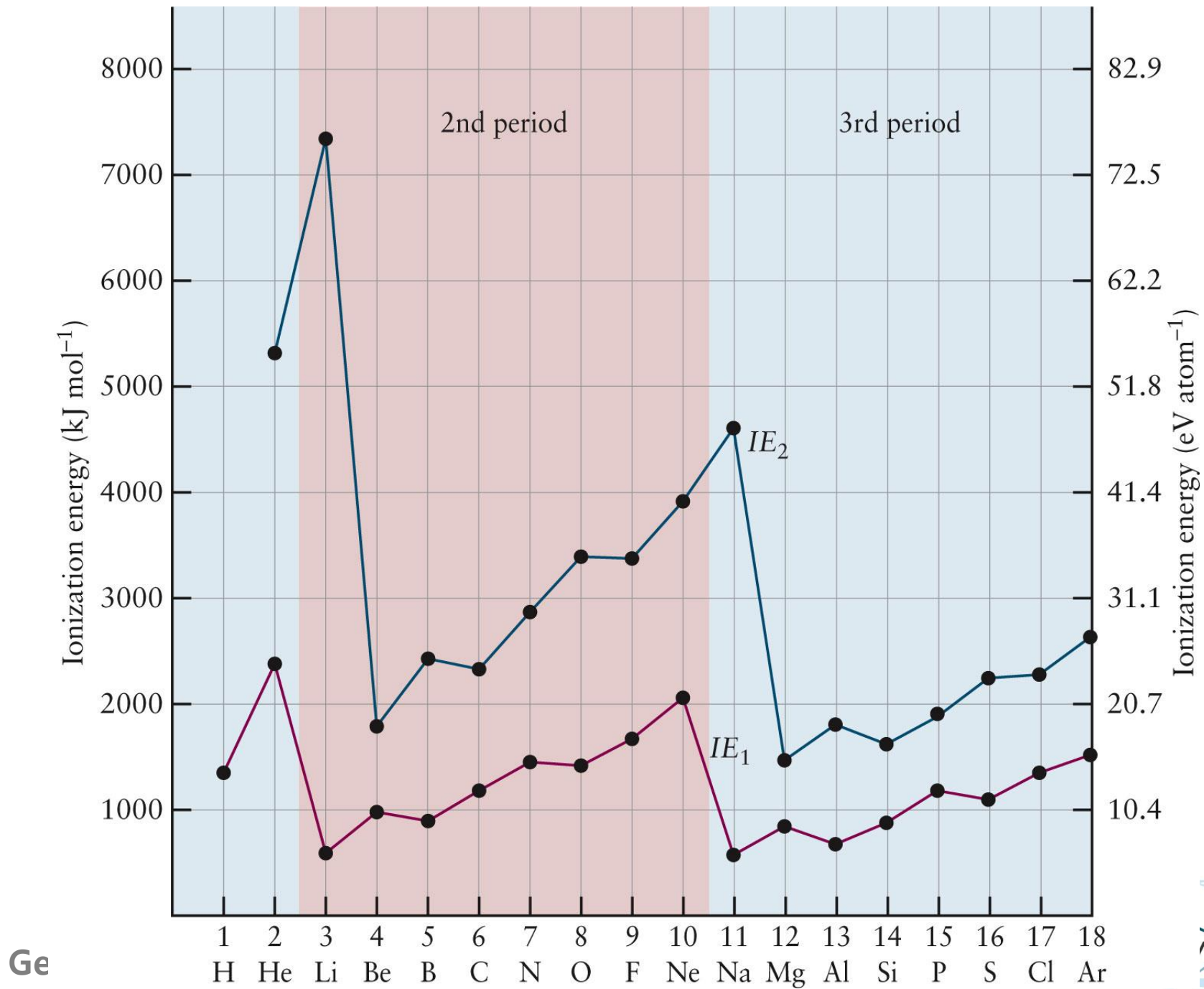
= **size of the atoms** + geometry of the bonding

H 11.4																		He 21.0
Li 13.0	Be 4.85												B 4.39	C 3.42	N 13.5	O 17.4	F 11.2	Ne 13.2
Na 23.8	Mg 14.0												Al 10.0	Si 12.1	P 17.0	S 15.5	Cl 17.4	Ar 22.6
K 45.9	Ca 26.2	Sc 15.0	Ti 10.6	V 8.32	Cr 7.23	Mn 7.35	Fe 7.09	Co 6.67	Ni 6.59	Cu 7.11	Zn 9.16	Ga 11.8	Ge 13.6	As 13.0	Se 16.4	Br 19.8	Kr 28.0	
Rb 55.8	Sr 33.9	Y 19.9	Zr 14.0	Nb 10.8	Mo 9.38	Tc 8.63	Ru 8.17	Rh 8.28	Pd 8.56	Ag 10.3	Cd 13.0	In 15.8	Sn 16.3	Sb 18.2	Te 20.5	I 25.7	Xe 35.9	
Cs 70.9	Ba 38.2	Lu 17.8	Hf 13.4	Ta 10.9	W 9.47	Re 8.86	Os 8.42	Ir 8.52	Pt 9.09	Au 10.2	Hg 14.1	Tl 17.2	Pb 18.3	Bi 21.3	Po 23.0		Rn 50.5	

Periodic Trends in Ionization Energies

- From left to right, generally **increase in IE_1** due to the increase of Z_{eff}
 - From top to bottom, generally **decrease in IE_1** due to the increase of n
- From He to Li, a large reduction in IE_1**
2s e^- farther than 1s e^- , and 2s e^- sees a net +1 charge
 - From Be to B, slight reduction in IE_1**
fifth e^- in a higher energy 2p orbital
 - From N to O, slight reduction in IE_1**
2 e^- in the same 2p orbital leading to greater repulsion





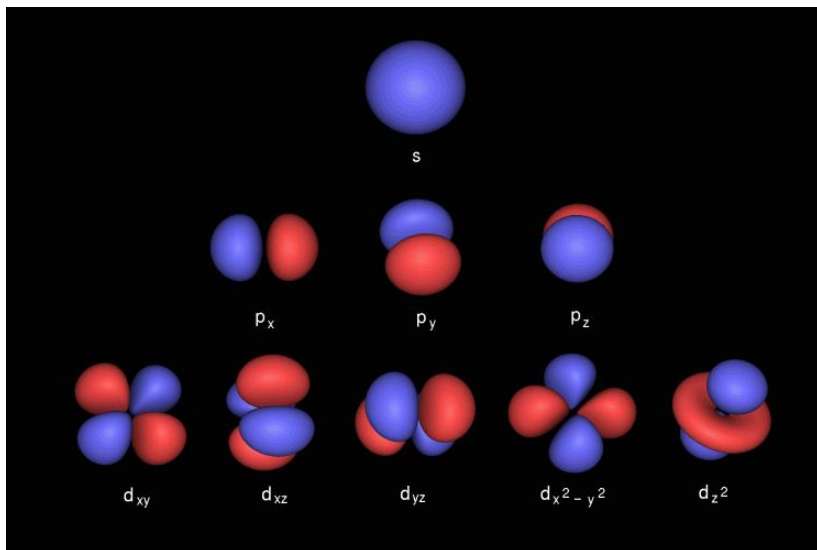
Electron Affinity

- The periodic trends in EA parallel those in IE_1 with one unit lower shift i.e.) F to F^- , large EA because of its closed-shell configuration

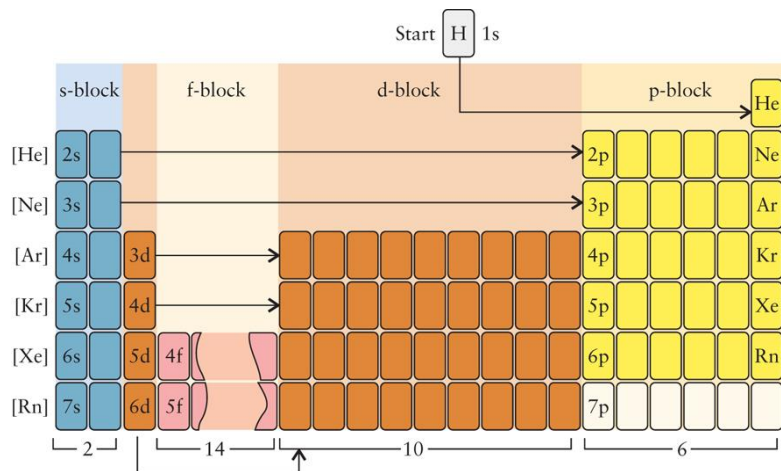
(kJ mol⁻¹)

H 73																				He *
Li 60	Be *													B 27	C 122	N *	O 141	F 328		Ne *
Na 53	Mg *													Al 43	Si 134	P 72	S 200	Cl 349		Ar *
K 48	Ca 2	Sc 18	Ti 8	V 51	Cr 64	Mn *	Fe 16	Co 64	Ni 111	Cu 118	Zn *		Ga 29	Ge 116	As 78	Se 195	Br 325		Kr *	
Rb 47	Sr 5	Y 30	Zr 41	Nb 86	Mo 72	Tc 53	Ru 99	Rh 110	Pd 52	Ag 126	Cd *		In 29	Sn 116	Sb 103	Te 190	I 295		Xe *	
Cs 46	Ba 14	Lu 50	Hf *	Ta 31	W 79	Re 14	Os 106	Ir 151	Pt 214	Au 223	Hg *		Tl 19	Pb 35	Bi 91	Po 183	At 270		Rn *	

Key question 1: what is the quantum mechanical atomic model?

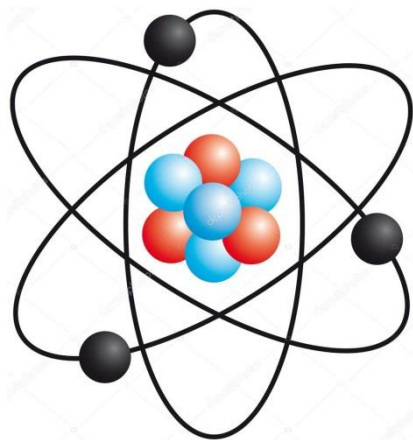


Key question 2: what is the origin of the periodicity of atomic properties?

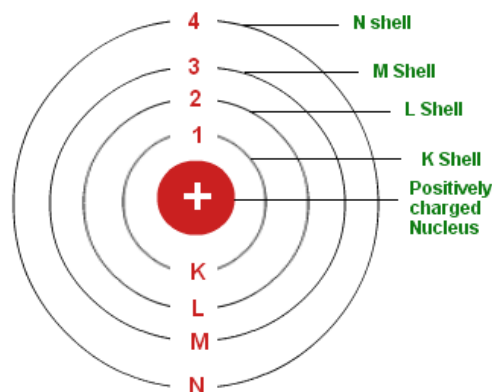


Comparison of atomic models

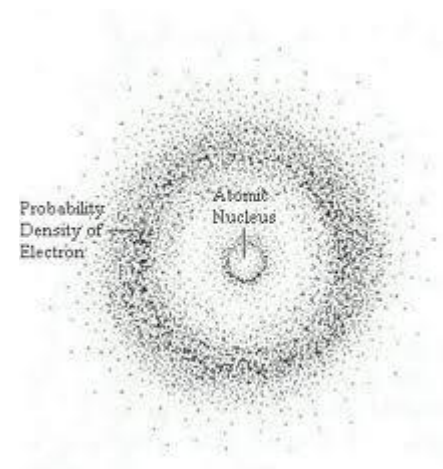
(A) The Classical Model



(B) Bohr's Model



(C) The Quantum Mechanics Model



For Chapter 5,

- Problem Sets

: 22, 28, 32, 48, 56

- Chapter Summary (Choose one)

: Valence electrons, Solution for multielectron system