5

CHAPTER

QUANTUM MECHANICS AND ATOMIC STRUCTURE

Colors of Fireworks

from atomic emission

red from Sr

orange from Ca

yellow from Na

green from Ba

blue from Cu

5.1 THE HYDROGEN ATOM

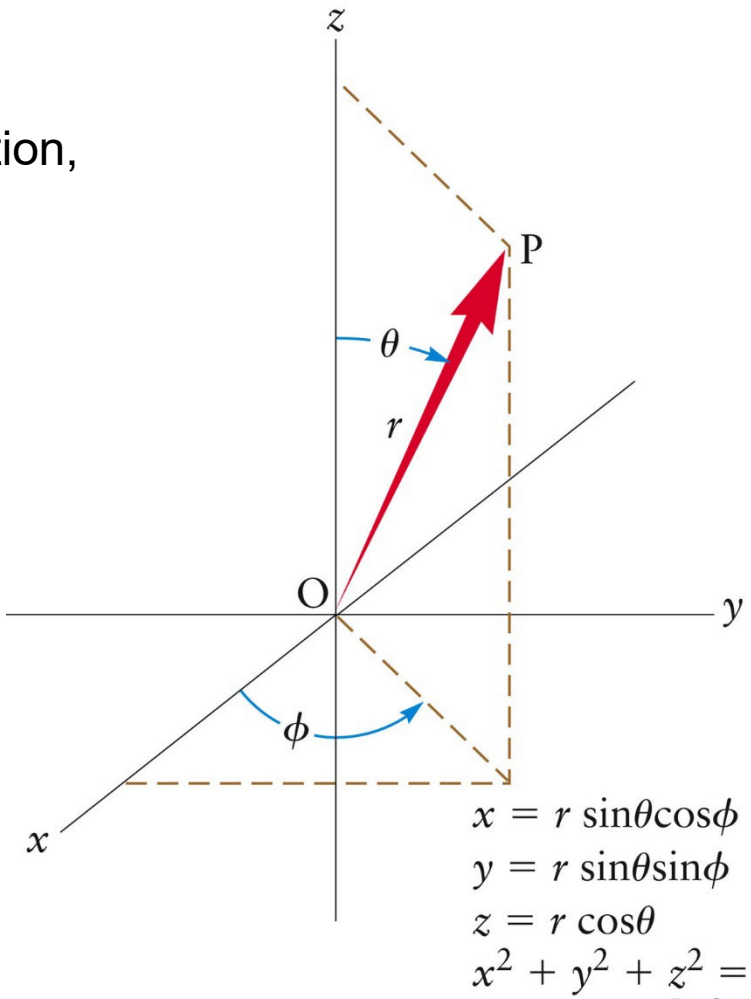
- The hydrogen atom is the simplest example of a one-electron atom or ion. (i.e. He^{+}, Li^{2+}, …)

- For solution of the Schrödinger equation,

Cartesian coordinates, x, y, z

spherical coordinates, r, θ, ϕ

to express angular orientation.



Energy Levels

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

$$V(r) = \frac{(-e)(+e)}{4\pi\varepsilon_0 r} = -\frac{e^2}{4\pi\varepsilon_0 r}$$

- **Solutions of the Schrödinger equation**

$$E = E_n = -\frac{Z^2 e^4 m_e}{8\varepsilon_0^2 n^2 h^2} \qquad n = 1, 2, 3, \ldots$$

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

1 rydberg = 2.18×10^{-18} J

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

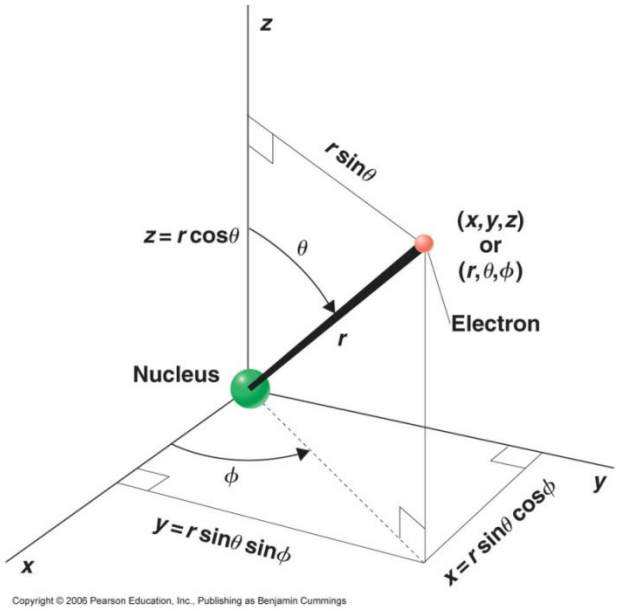
Coordinate Systems

V(x, y, z) – can be expressed in various coordinate systems.

Spherical polar coordinates (r, θ, Φ) vs.
Cartesian coordinates (x, y, z)

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

For Coulomb potential, V, convenient to express in SPC ($V = -e^2/r$); Cartesian, $V = -e^2/[x^2 + y^2 + z^2]^{1/2}$



- Cartesian Coordinate

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

- Spherical Polar Coordinate (SPC)

$$\left[\frac{-h^2}{8\pi^2 m}\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)+\frac{-e^2}{r}\right]\psi(x,y,z)=E\psi(x,y,z)$$

Quantization of the Angular Momentums

- **Angular momentum quantum number ℓ** : from the quantization of L^2

  any integral value from 0 to n-1

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

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

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

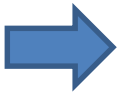
- **Magnetic quantum number m** : from the quantization of L_z

$$L_z = m\frac{h}{2\pi} \qquad m = \underbrace{-\ell, -\ell+1, \ldots, \ell-1, \ell}_{\#\ of\ m\ =\ 2\ell+1}$$

For n = 1 (the ground state), (ℓ = 0, m = 0)

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

(ℓ = 0, m = 0), (ℓ = 1, m = 1), (ℓ = 1, m = 0), (ℓ = 1, m = -1)



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

TABLE 5.1

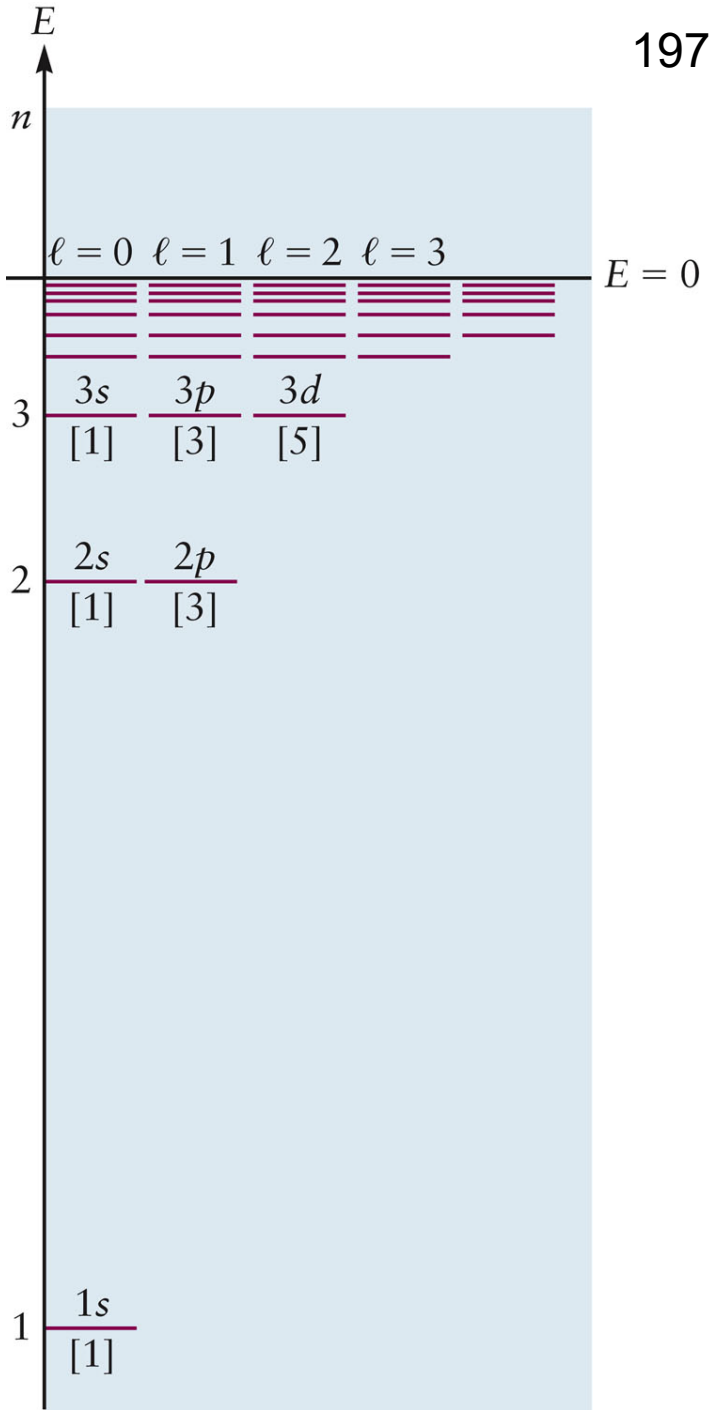
Allowed Values of Quantum Numbers for One-Electron Atoms

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**.



Boundary Condition

- constraint that reality places on the solutions to a physically relevant equation (e.g. quadratic equation: concentration)

* ψ is just the embodiment of de Broglie's hypothesis of matter wave

→ ψ must be smooth, single-valued, and finite everywhere in space

→ ψ must become small at large distances r from the nucleus (proton)

Boundary Condition yields quantum numbers!

Wave Functions

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

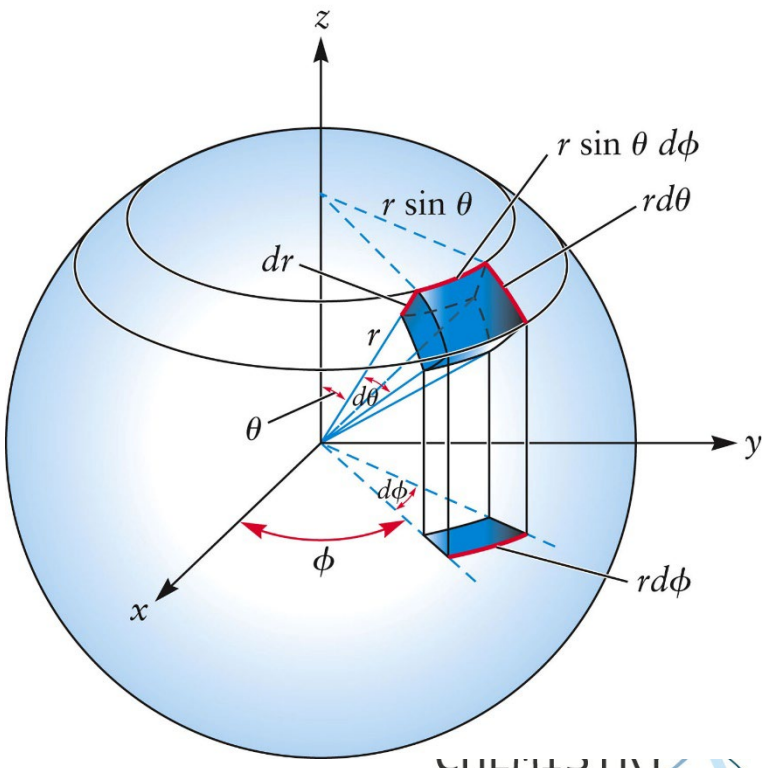
radial part

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.

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

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



- Spherical Polar Coordinate

$$\left[\frac{-h^2}{8\pi^2 m}\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)+\frac{-e^2}{r}\right]\psi(x,y,z)=E\psi(x,y,z)$$

$$\left[\frac{-h^2}{8\pi^2 m}\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)\right)+\frac{-e^2}{r}-E\right]\psi(x,y,z)+\left[\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\psi(x,y,z)=0$$

$$\left[\frac{-h^2}{8\pi^2 m}\left(\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)\right)+\frac{-e^2r^2}{r}-Er^2\right]\psi(x,y,z)+\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\psi(x,y,z)=0$$

Depends only on r **Depends only on θ, ϕ**

- Schrödinger wave function

→ factored into *radial (R)* and *angular (Y)* functions

$$\psi(r,\theta,\phi)=R(r)Y(\theta,\phi)$$

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	ℓ = 0	4s	# of m = 1
	ℓ = 1	4p	# of m = 3
	ℓ = 2	4d	# of m = 5
	ℓ = 3	4f	# of m = 7

total n^2 = 16 orbitals

Specification of the Wave Functions: Orbitals

➢ Schrödinger's Wave Function

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

i.e.) n = 3 (only one orbit in the Bohr- de Broglie model)

3^2 (nine) different ways the electron can vibrate to form a standing wave → 9 degeneracy

➢ Orbitals

replacement of Bohr's orbit for 3D Schrödinger's wave function

- Radial part, $R_{n\ell}(r)$

  Laguerre polynomial $(r^{n-1}) \times e^{-r/(na_0)}$

- Angular part, $Y_{\ell m}(\theta,\Phi)$

  Legendre function $(\sin\theta \,\&\, \cos\theta) \times e^{im\Phi}$

* a_0 ← Bohr's radius

TABLE 5.2

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

Angular Part $Y(\theta, \phi)$	Radial Part $R_{n\ell}(r)$
$\ell = 0$: $Y_s = \left(\frac{1}{4\pi}\right)^{1/2}$	$R_{1s} = 2\left(\frac{Z}{a_0}\right)^{3/2} \exp(-\sigma)$
	$R_{2s} = \frac{1}{2\sqrt{2}}\left(\frac{Z}{a_0}\right)^{3/2} (2-\sigma)\exp(-\sigma/2)$
	$R_{3s} = \frac{2}{81\sqrt{3}}\left(\frac{Z}{a_0}\right)^{3/2} (27 - 18\sigma + 2\sigma^2)\exp(-\sigma/3)$
$\ell = 1$: $Y_{p_x} = \left(\frac{3}{4\pi}\right)^{1/2} \sin\theta\cos\phi$	$R_{2p} = \frac{1}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma\exp(-\sigma/2)$
$Y_{p_y} = \left(\frac{3}{4\pi}\right)^{1/2} \sin\theta\sin\phi$	$R_{3p} = \frac{4}{81\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2} (6\sigma - \sigma^2)\exp(-\sigma/3)$
$Y_{p_z} = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$	
$\ell = 2$: $Y_{d_{z^2}} = \left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1)$	$R_{3d} = \frac{4}{81\sqrt{30}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma^2\exp(-\sigma/3)$
$Y_{d_{xz}} = \left(\frac{15}{4\pi}\right)^{1/2} \sin\theta\cos\theta\cos\phi$	
$Y_{d_{yz}} = \left(\frac{15}{4\pi}\right)^{1/2} \sin\theta\cos\theta\sin\phi$	
$Y_{d_{xy}} = \left(\frac{15}{16\pi}\right)^{1/2} \sin^2\theta\sin 2\phi$	
$Y_{d_{x^2-y^2}} = \left(\frac{15}{16\pi}\right)^{1/2} \sin^2\theta\cos 2\phi$	

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

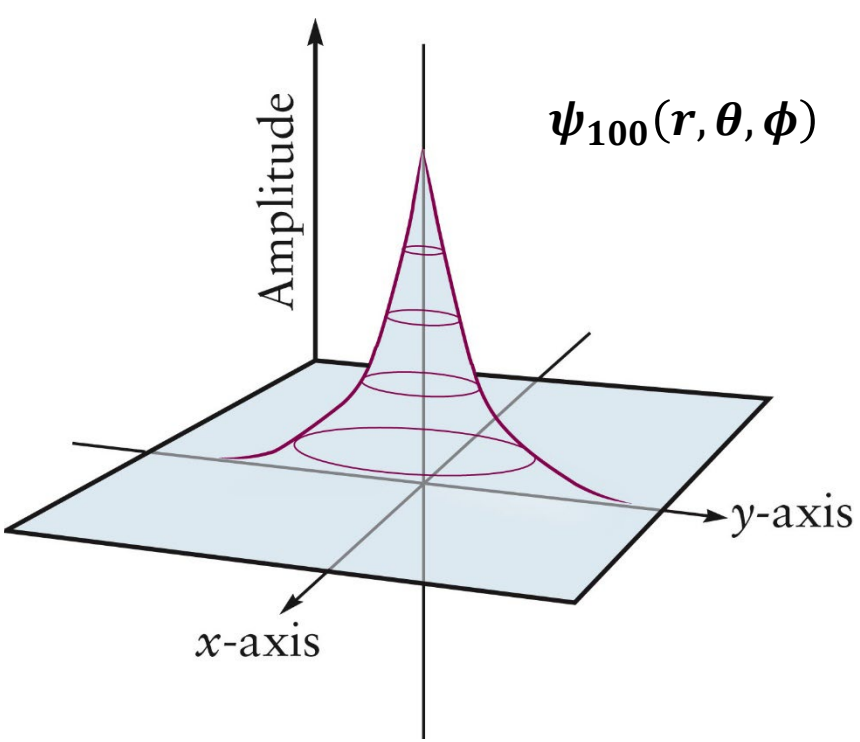
Sizes and Shapes of Orbitals

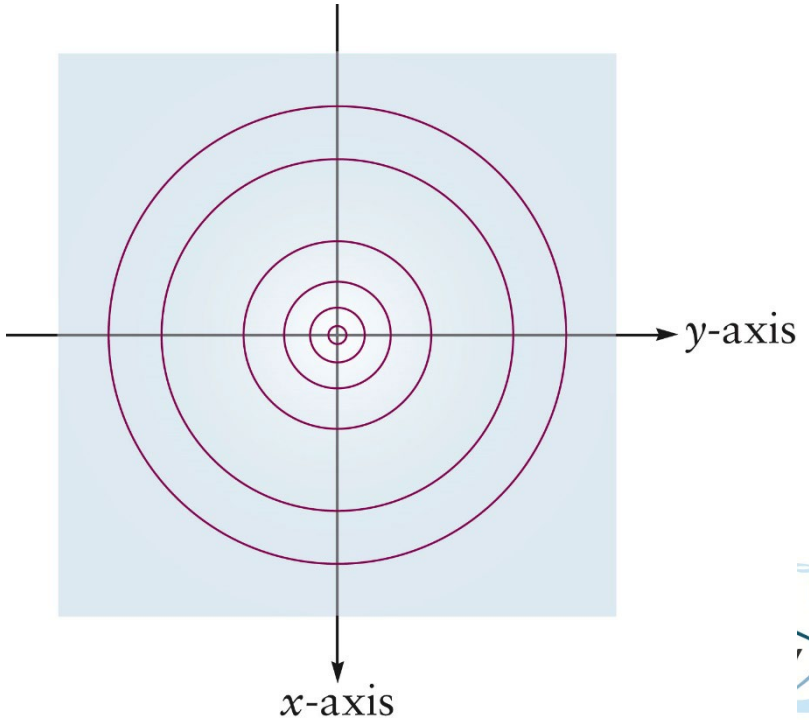
$$\psi_{n\ell m}(r,\theta,\phi) = R_{n\ell}(r)\mathrm{Y}_{\ell m}(\theta,\phi)$$

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

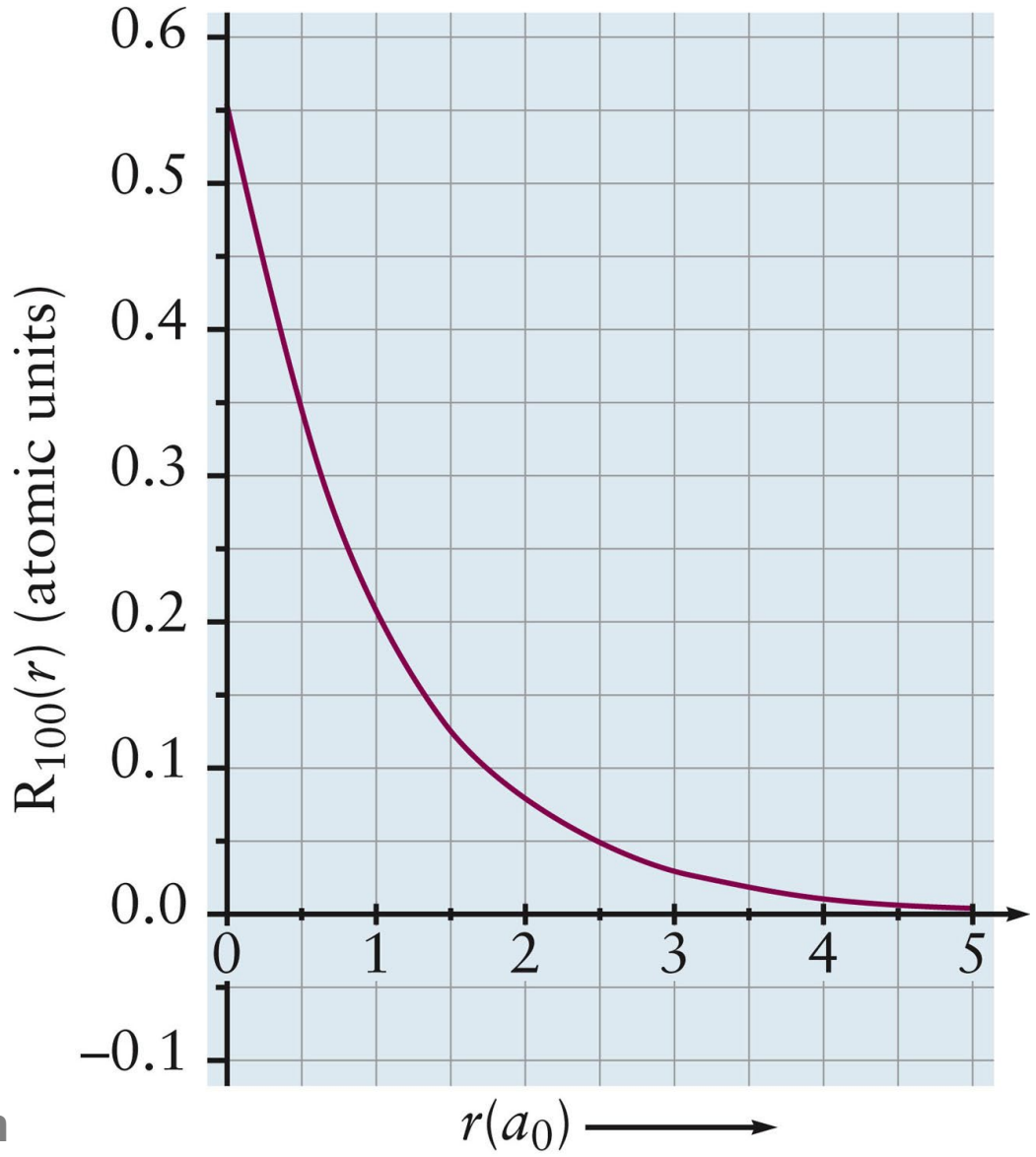
➢ **Graphical representation of the orbitals**

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



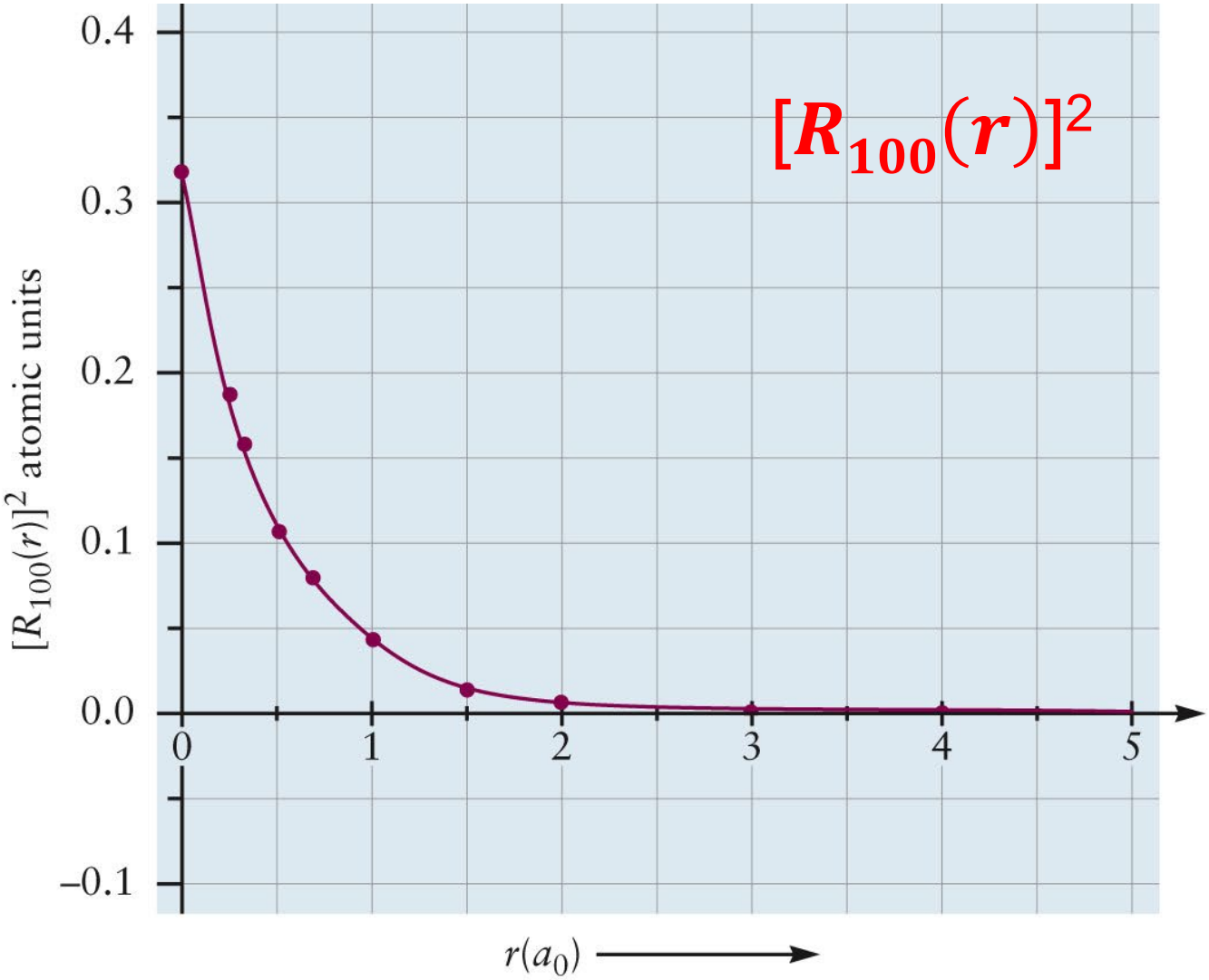


2) Looking only at the radial behavior. “vertical slice”



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

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



(a)

(b)

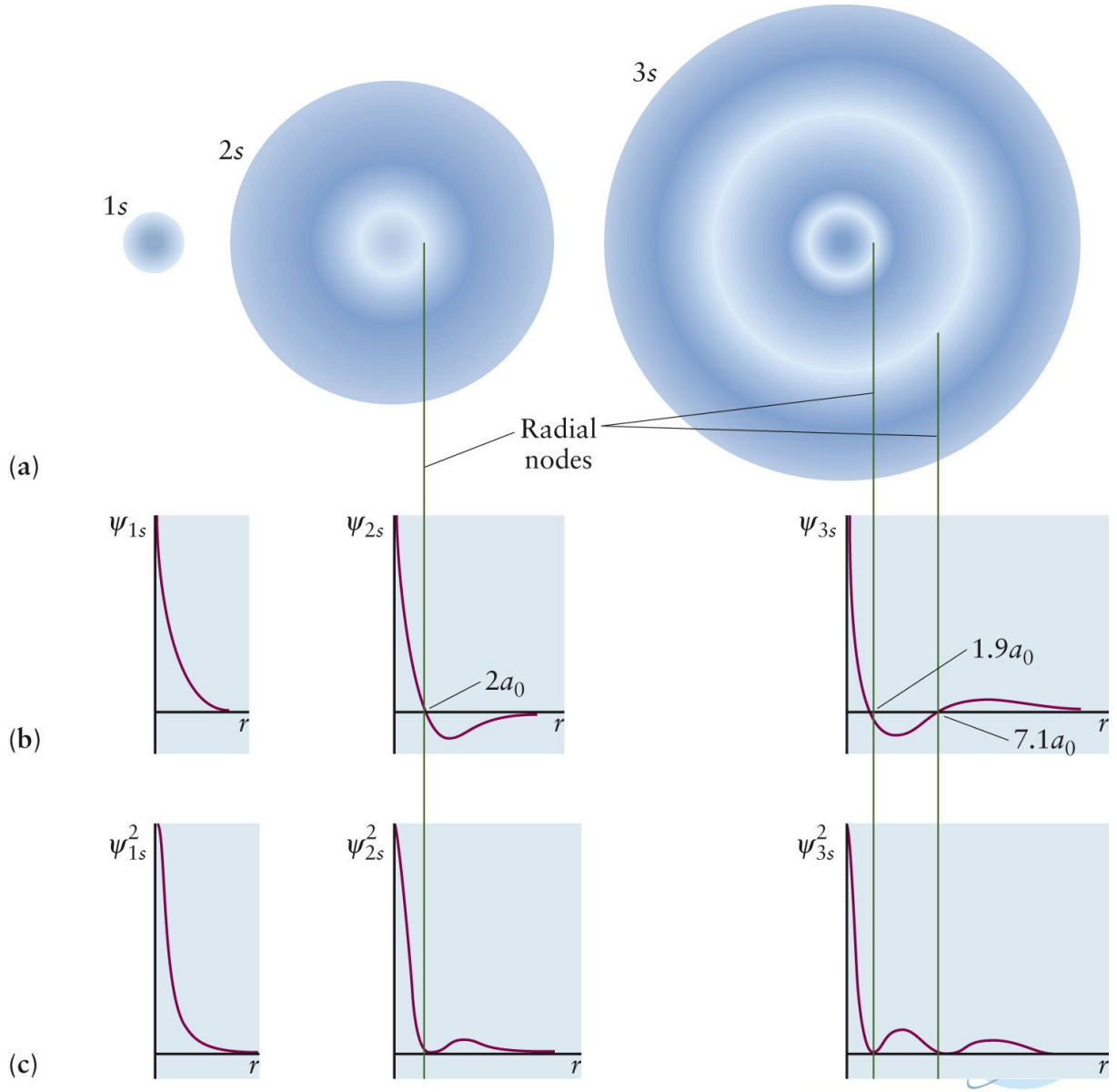
s orbitals

- **s orbital:**

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

➡ constant Y

All s orbitals are spherically symmetric.



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

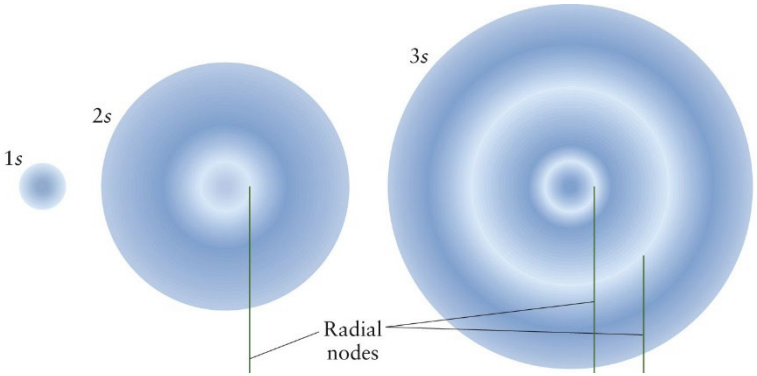
$$\psi_{100}(r,\theta,\phi) = \frac{1}{\sqrt{\pi}} a_0^{-3/2} e^{-r/a_0}$$

a function of r only

* spherically symmetric
* exponential decaying
* no nodes

- **2s (n = 2, ℓ = 0, m = 0)**

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



zero at $r = 2a_0 = 1.06$Å

nodal sphere or radial node

[$r<2a_o$: $\Psi>0$, positive] [$r>2a_o$: $\Psi<0$, negative]

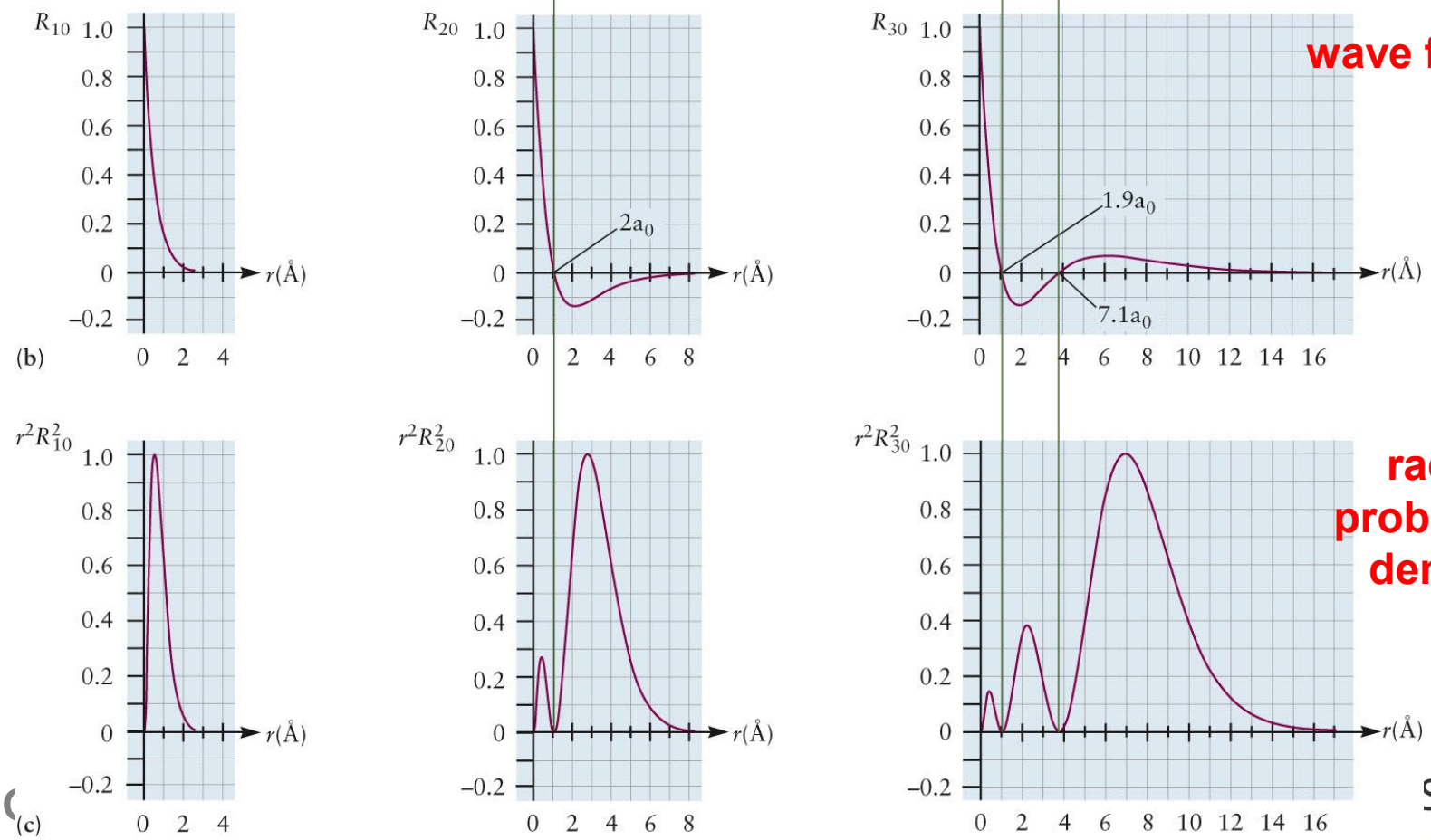
1s

2s

3s

isosurface

A surface of points with the same value of wave functions



wave function

radial probability density

Radial Distribution Functions: RDFs

Prob(r) = $r^2[R(r)]^2$

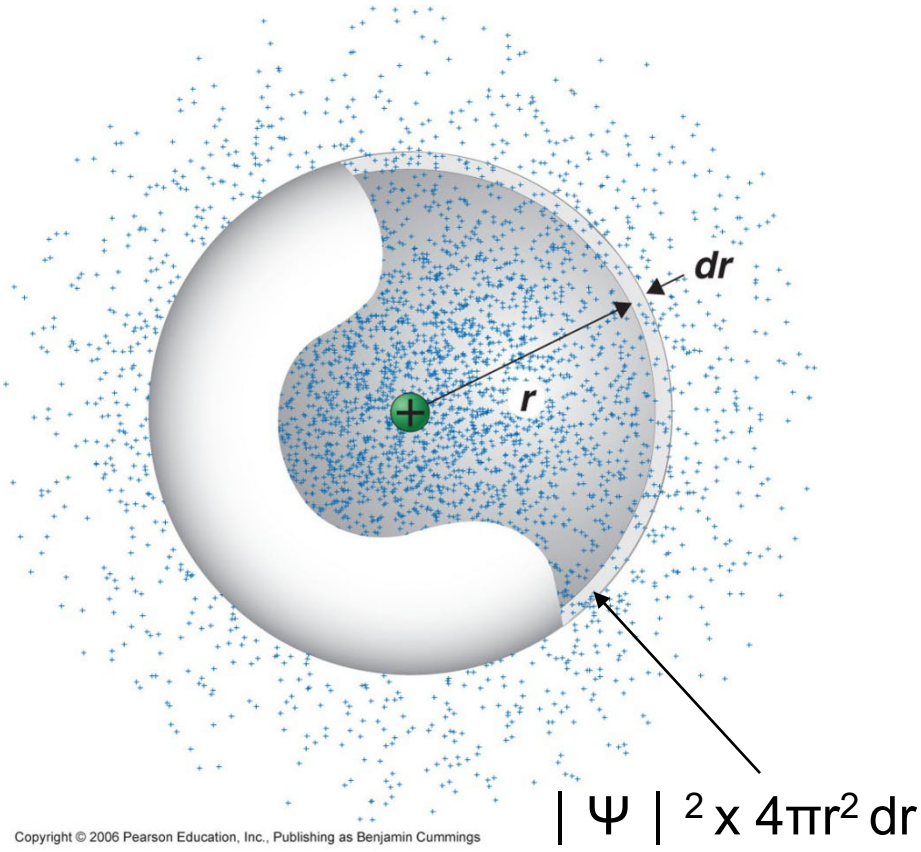
$$\int_{\phi=0}^{2\pi}\int_{\theta=0}^{\pi}|\Psi|^2 r^2 \sin\theta d\theta d\phi$$

$$= 4\pi r^2 |\Psi|^2 = 4\pi r^2 |R(r)Y(\theta,\phi)|^2$$

$$= 4\pi r^2 |R(r)|^2 |Y(\theta,\phi)|^2$$

$$= 4\pi r^2 |R(r)|^2 |1/2\sqrt{\pi}|^2$$

$$= r^2 |R(r)|^2$$

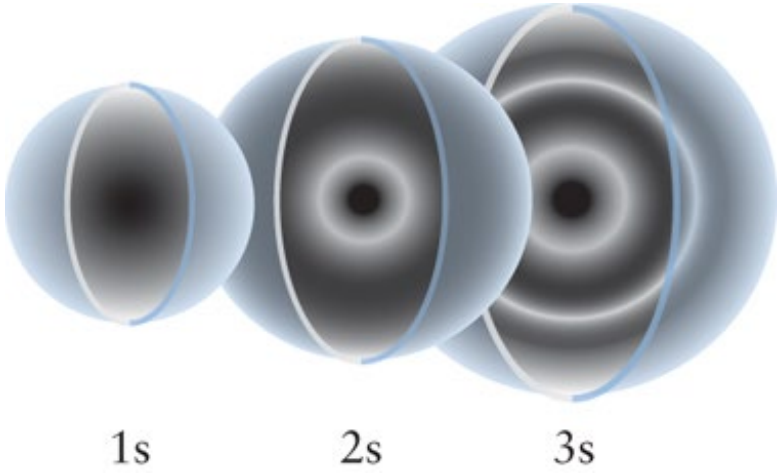


Boundary Surface

- No clear boundary of an atom

- Defining the size of atom as the extent of a “balloon skin” inside which 90% of the probability density of the electron is contained.

  1s: 1.41 Å, 2s: 4.83 Å, 3s: 10.29 Å



➢ **radial node**: a spherical surface on which ψ and ψ^2 are 0.

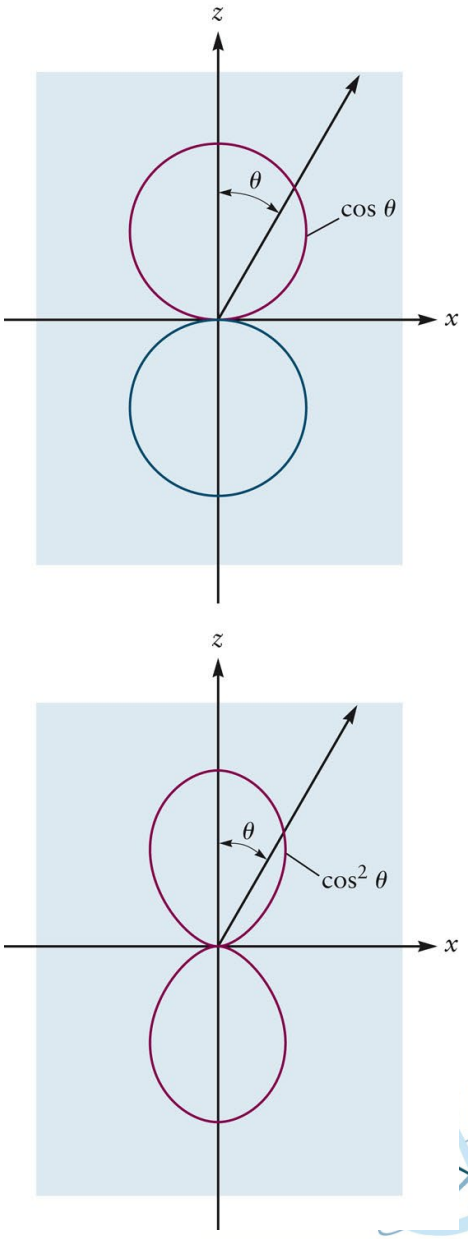
An ns orbital has n-1 radial nodes.

p orbitals

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

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

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



· Φ = 0 → cylindrical symmetry about the z-axis
· $R_{21}(r)$ → r/a_0 no radial nodes except at the origin
· cos θ → angular node at θ = 90°, x-y nodal plane
· r cos θ → z-axis $2p_0$ → labeled as $2p_z$

- n = 2, ℓ = 1, m = ±1 → $2p_{+1}$ and $2p_{-1}$

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

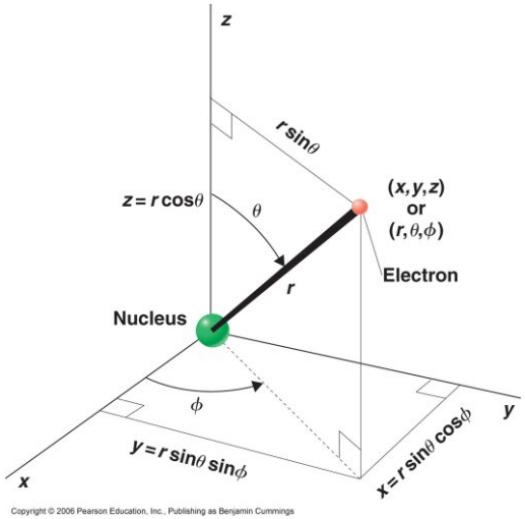
· taking linear combinations

two real orbitals → constructed $2p_x$ and $2p_y$

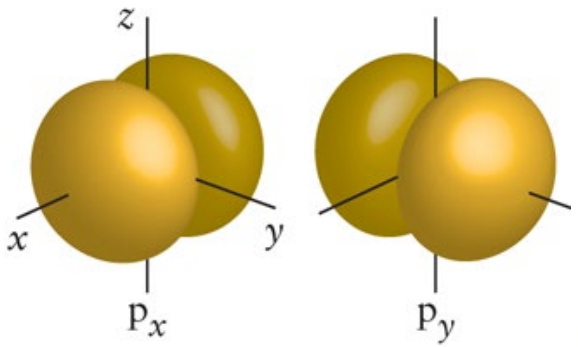
(real functions using Euler's formula)

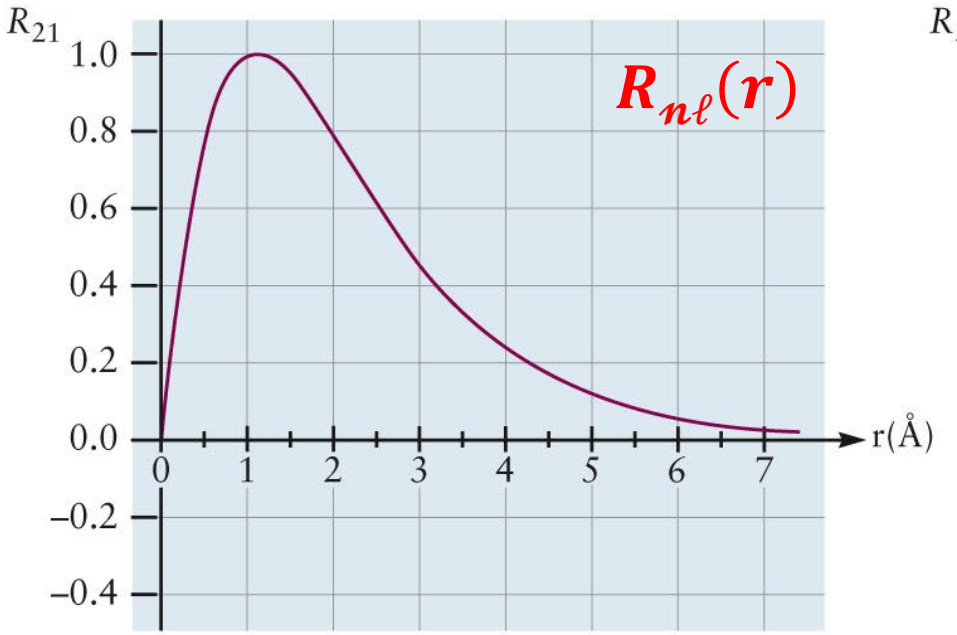
$$2p_x = \frac{1}{\sqrt{2}}(2p_{+1} + 2p_{-1}) = \frac{1}{4\sqrt{2\pi}} a_0^{-3/2} \frac{r}{a_0} e^{-r/2a_0} \sin\theta \cos\phi$$

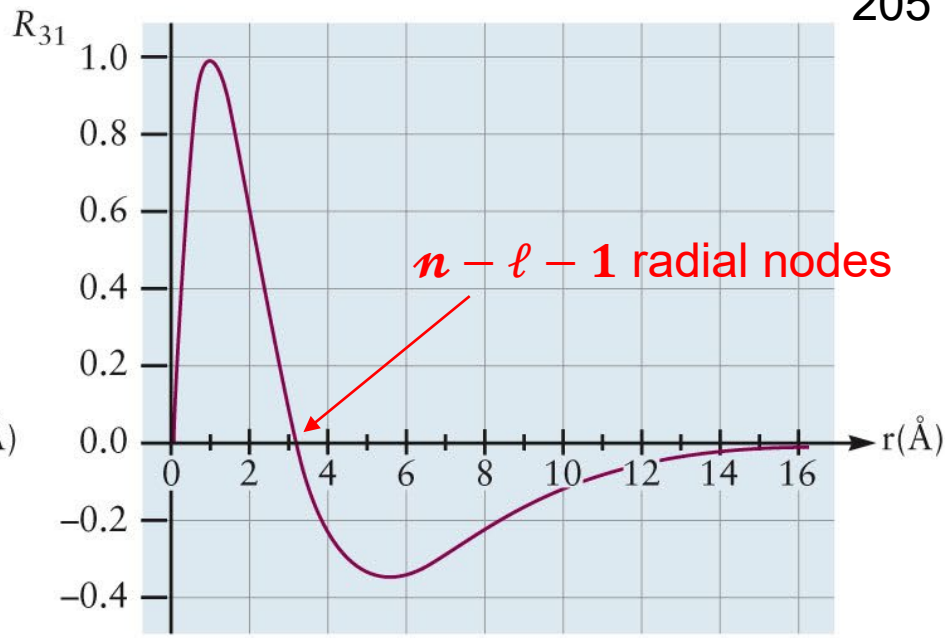
$$2p_y = \frac{1}{i\sqrt{2}}(2p_{+1} - 2p_{-1}) = \frac{1}{4\sqrt{2\pi}} a_0^{-3/2} \frac{r}{a_0} e^{-r/2a_0} \sin\theta \sin\phi$$

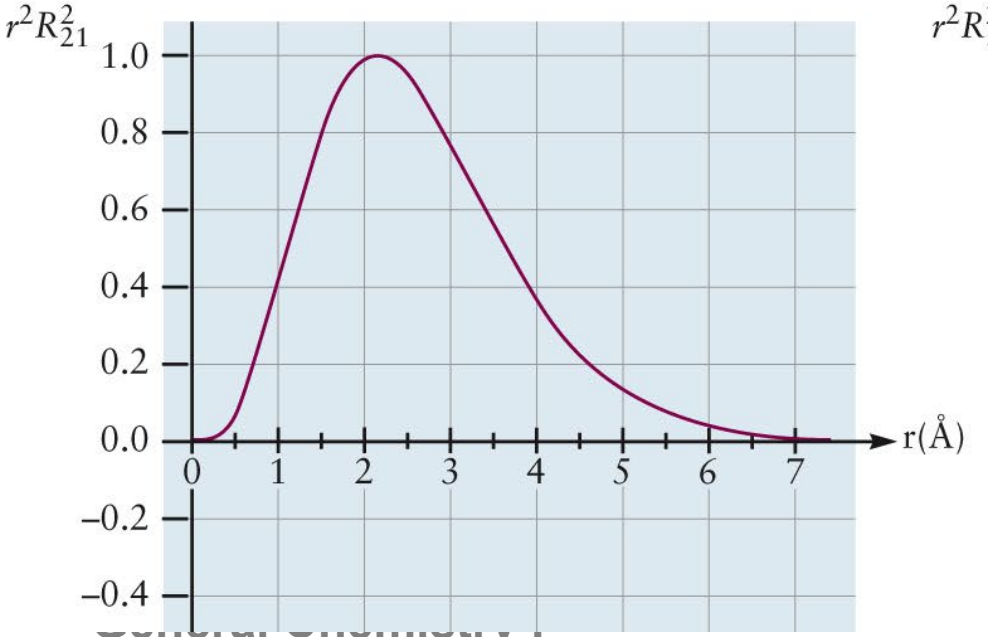


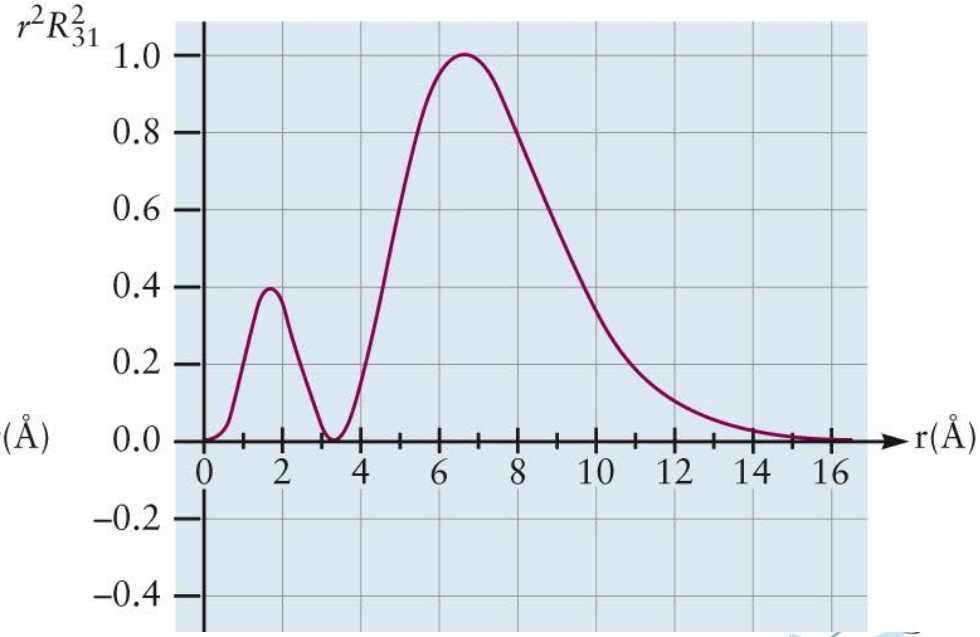
- p_x and p_y differ from p_z only in the angular factors (orientations).




R_{21}
1.0
0.8
0.6
0.4
0.2
0.0
−0.2
−0.4
0 1 2 3 4 5 6 7
r(Å)
$R_{n\ell}(r)$

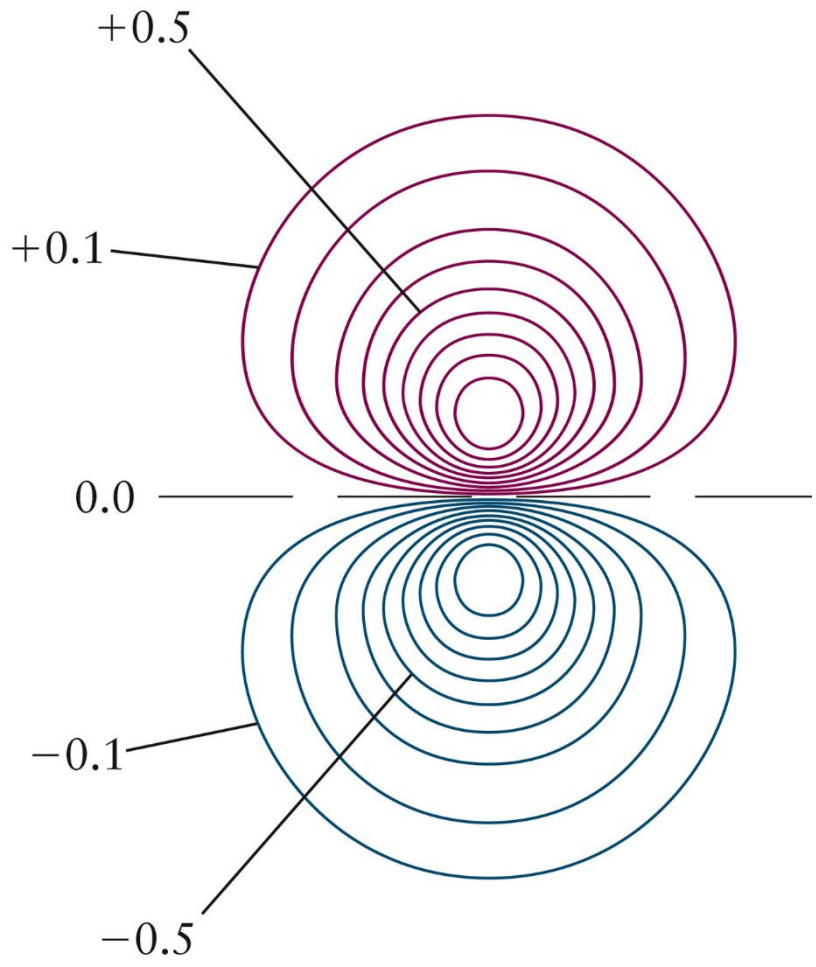

R_{31}
1.0
0.8
0.6
0.4
0.2
0.0
−0.2
−0.4
0 2 4 6 8 10 12 14 16
r(Å)
$n - \ell - 1$ radial nodes

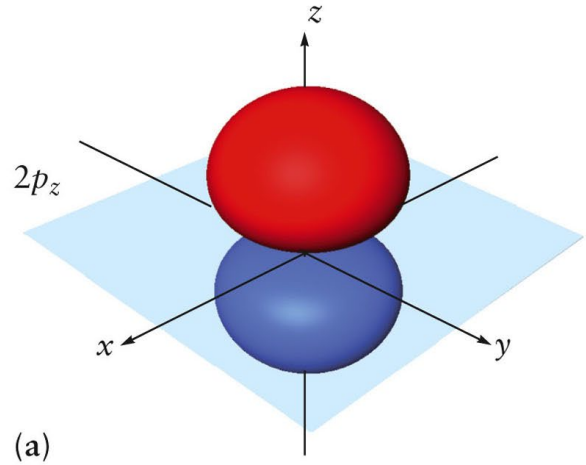

$r^2R_{21}^2$
1.0
0.8
0.6
0.4
0.2
0.0
−0.2
−0.4
0 1 2 3 4 5 6 7
r(Å)

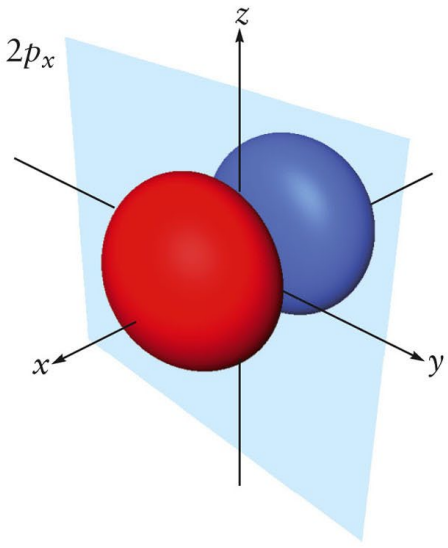

$r^2R_{31}^2$
1.0
0.8
0.6
0.4
0.2
0.0
−0.2
−0.4
0 2 4 6 8 10 12 14 16
r(Å)

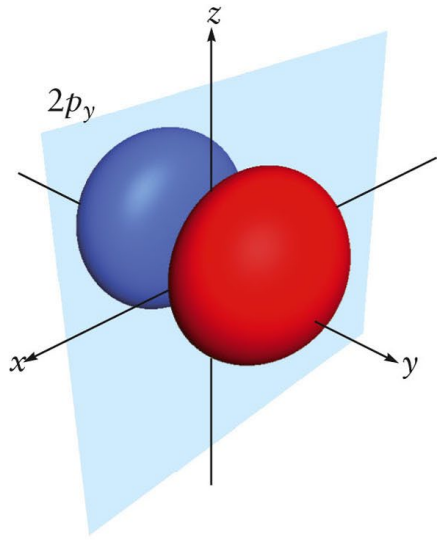
$$\psi_{n\ell m} = R_{n\ell} Y_{\ell m}$$

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









d orbitals

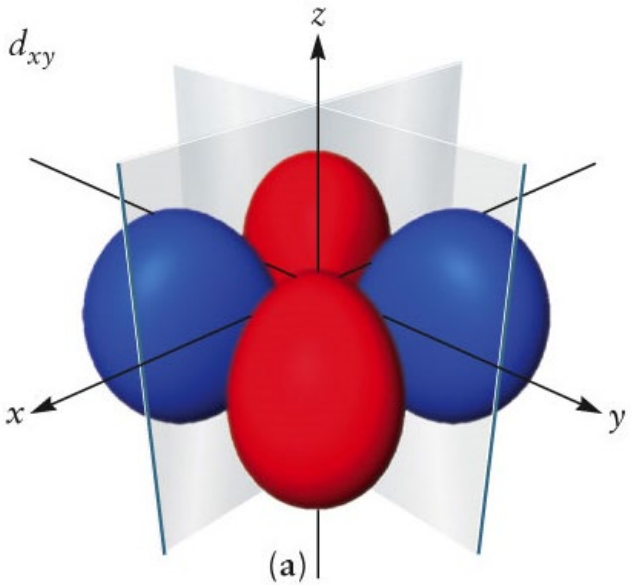
- **d-orbitals**

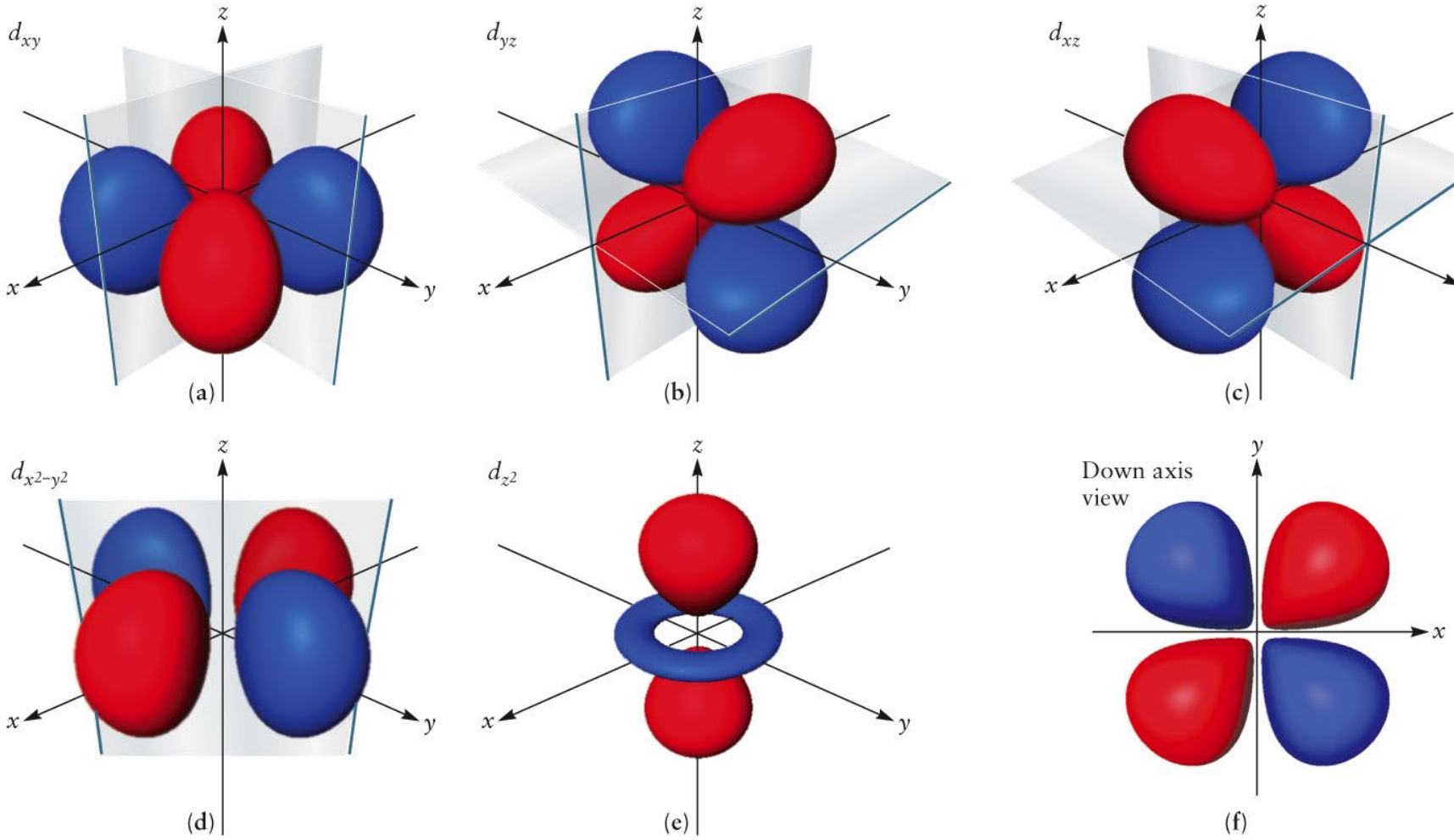
  ℓ = 2 & m = 0: $\boldsymbol{d_{z^2}}$

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

- Each d orbital has **two angular nodes**.
  i.e.) d_{xy} orbital: nodal surfaces of the xz and yz planes

- The radial functions, $\boldsymbol{R_{n2}(r)}$, have **n - 3 radial nodes**, giving **n - 1 total nodes**.




d_{xy}
z
x
y
(a)
d_{yz}
z
x
y
(b)
d_{xz}
z
x
y
(c)
$d_{x^2-y^2}$
z
x
y
(d)
d_{z^2}
z
x
y
(e)
Down axis view
y
x
(f)

Orbital Shapes and Sizes

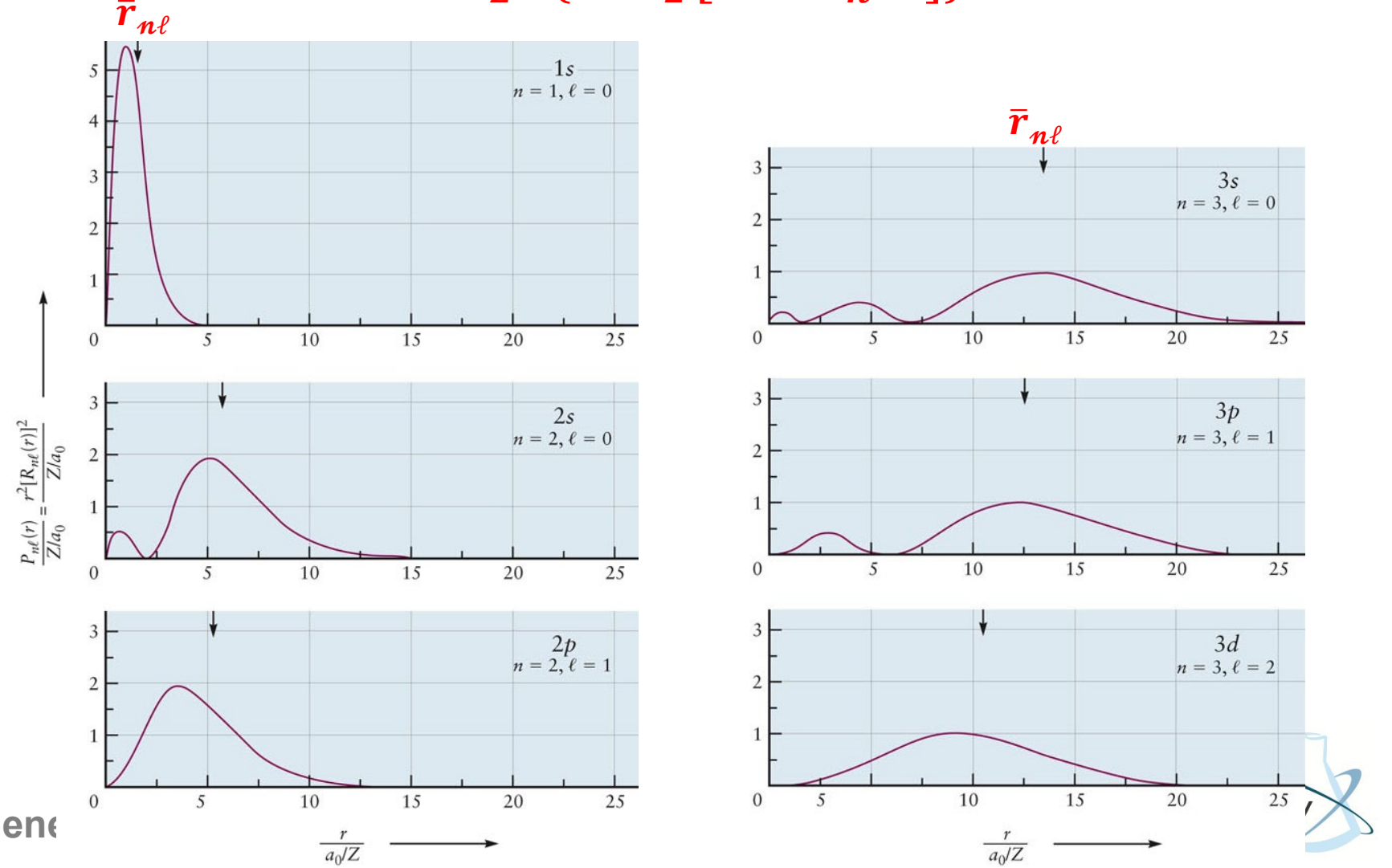
1. For a given value of ℓ, and **increase in n** leads to an **increase in the average distance** of the electron from the nucleus, and therefore in the size of the orbital.

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.

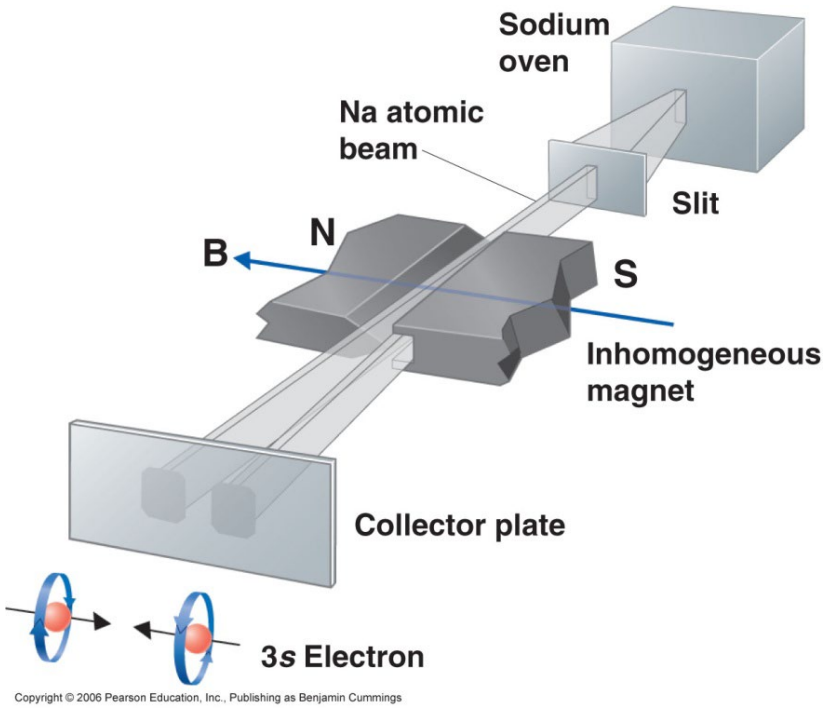
- The **average value of the distance** of the electron from the nucleus in that orbital, $\bar{r}_{n\ell}$

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



Stern-Gerlach Experiment: Experimental evidence for the existence of electron spin

Stern and Gerlach (1926): Ground state Na atoms → were passed through a strong inhomogeneous magnetic field.



- All spin magnetisms in inner orbitals → cancelled, except an electron in 3*s* orbital.
- *Y (θ,Φ)(3s) → no rotation*
- The *intrinsic magnetism* of the 3*s* electron → only possible to respond to the external field.
- 3s electrons → line up with their north poles either along or against the main north pole of the magnet.
  The lack of a "straight-through" beam with the magnet → clear evidence of two-valued electron's magnetism.

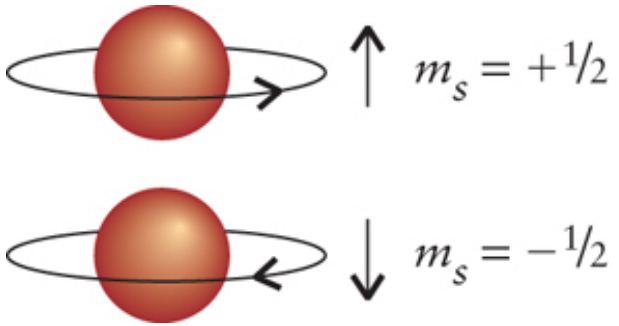
KAIST CHEMISTRY

Electron Spin

- **m_s, spin magnetic quantum number**

- An electron has two spin states, as ↑(up) and ↓(down), or a and b.

- the values of m_s, only +1/2 and -1/2



Name	Symbol	Values	Specifies	Indicates
principal	n	1, 2, . . .	shell	size
orbital angular momentum*	l	0, 1, . . ., $n - 1$	subshell: l = 0, 1, 2, 3, 4, . . . s, p, d, f, g, . . .	shape
magnetic	m_l	$l, l - 1, \ldots, -l$	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

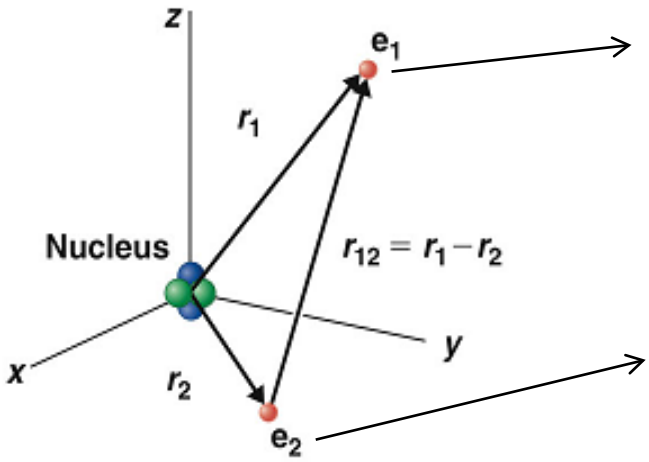
- In a helium atom,

$$V = \overbrace{-\frac{2e^2}{4\pi\varepsilon_0 r_1}}^{\text{Attraction of electron 1 to the nucleus}} \overbrace{-\frac{2e^2}{4\pi\varepsilon_0 r_2}}^{\text{Attraction elecron 2 to the nucleus}} + \overbrace{\frac{e^2}{4\pi\varepsilon_0 r_{12}}}^{\text{Repulsion between the two electrons}}$$

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



$r_1 \equiv (r_1, \theta_1, \Phi_1)$

$r_2 \equiv (r_2, \theta_2, \Phi_2)$

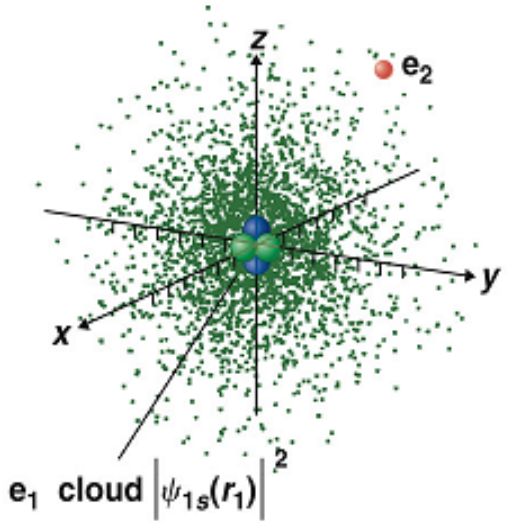
(a) Interparticle distance in He

interelectron distance

$r_{12} \equiv | r_1 - r_2 |$

$$\hat{H} = \hat{K}_1 + \hat{K}_2 - \frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{r_{12}}$$

Repulsion between electrons:
This new cross-term makes the Schrodinger equation impossible to solve exactly and causes the Bohr model to fail for He and other atoms



(b) Screening of an electron by another

$$\Psi(r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2) = \Psi(\vec{r}_1, \vec{r}_2)$$

Hartree Orbitals

➢ **Self-consistent field (SCF) orbital approximation method by Hartree**

- generating a set of approximate one-electron orbitals, φ_α, and associated energy levels, ϵ_α, reminiscent of those for the H atom.

- all electrons → were treated as independent, meaning that we neglect the repulsion term.

- Building up an effective nuclear charge Z_{eff}

$$\Psi(r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2) = \Psi(\vec{r}_1, \vec{r}_2) \approx \psi_a(\vec{r}_1)\psi_b(\vec{r}_2)$$

i.e.) for He, $$\Psi(\mathbf{r}_1, \mathbf{r}_2) \approx \frac{Z_{\text{eff}}^3}{\pi a_0^3} \left(e^{-Z_{\text{eff}} r_1/a_0}\right) \left(e^{-Z_{\text{eff}} r_2/a_0}\right)$$

Z_{eff}(He) = 1.6875 < 2

➢ **Three simplifying assumptions** by Hartree

1. Each electron moves in an effective field created by the nucleus and all the other electrons, and the effective field for electron i depends only on its position r_i.

➡ The wave function becomes a product of these one-electron orbitals.

i.e.) $\psi_{atom} = \varphi_\alpha(r_1)\varphi_\beta(r_2)\varphi_\gamma(r_3)$; **orbital approximation for atoms**.

2. The effective field for electron i is obtained by averaging its Coulomb potential interactions with each of the other electrons over all the positions of the other electrons so that r_i is the only coordinate in the description.

3. The effective field is spherically symmetric; that is, it has no angular dependence.

➡ The equations for the unknown effective field and the unknown one-electron orbitals must be solved by iteration until a self-consistent solution is obtained.

- These Hartree orbitals resemble the atomic orbitals of hydrogen with four quantum numbers (n, ℓ, m, m_s).

i.e.) For the ground state of He,

$$\Psi(\vec{r}_1,\vec{r}_2) \approx \psi_a(\vec{r}_1)\psi_b(\vec{r}_2) = \left(\frac{1}{\sqrt{\pi}}\left(\frac{a_0}{Z}\right)^{-2/3} e^{-Zr_1/a_0}\right)\left(\frac{1}{\sqrt{\pi}}\left(\frac{a_0}{Z}\right)^{-2/3} e^{-Zr_2/a_0}\right)$$

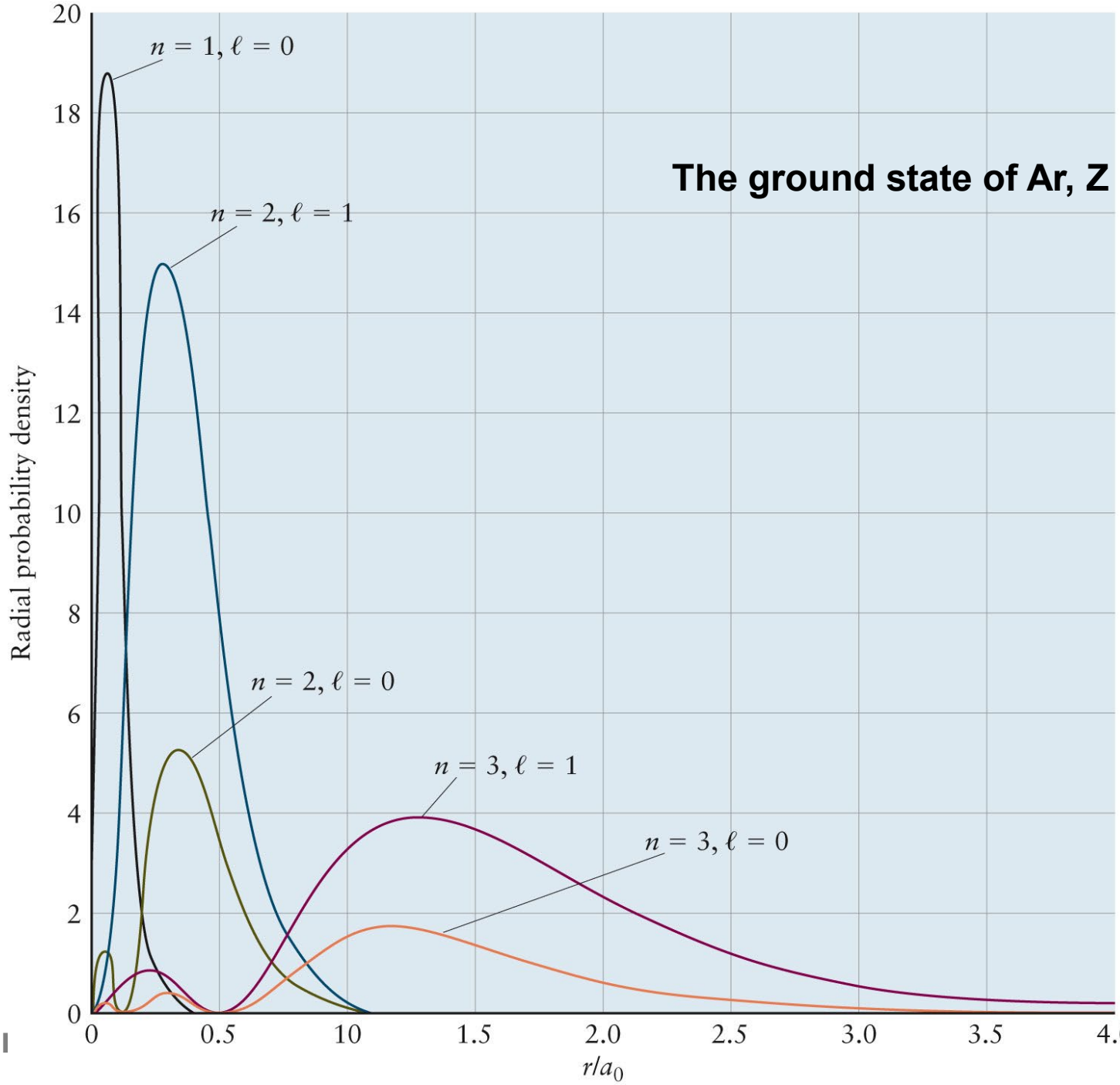
$$= \left(\frac{1}{\sqrt{\pi}}\left(\frac{a_0}{Z_{eff}}\right)^{-2/3} e^{-Z_{eff}r_1/a_0}\right)\left(\frac{1}{\sqrt{\pi}}\left(\frac{a_0}{Z_{eff}}\right)^{-2/3} e^{-Z_{eff}r_2/a_0}\right)$$

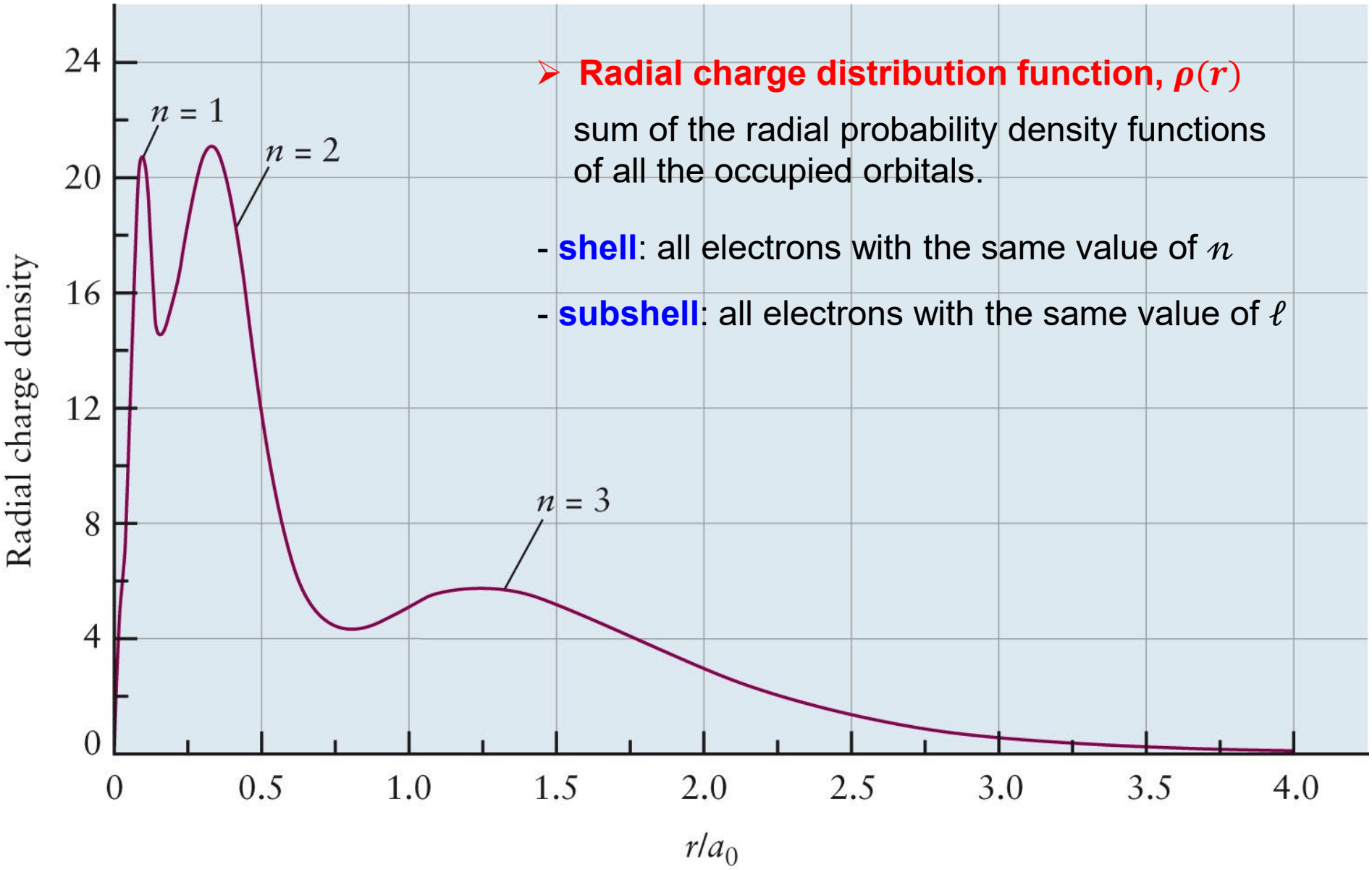
$$= \frac{{Z_{eff}}^3}{\pi {a_0}^3}\left(e^{-Z_{eff}r_1/a_0}\right)\left(e^{-Z_{eff}r_2/a_0}\right)$$

1s orbital **1s orbital**

$1s^2$

occupancy


The ground state of Ar, Z = 18
Radial probability density
r/a_0
$n = 1, \ell = 0$
$n = 2, \ell = 1$
$n = 2, \ell = 0$
$n = 3, \ell = 1$
$n = 3, \ell = 0$
0
2
4
6
8
10
12
14
16
18
20
0
0.5
10
1.5
2.0
2.5
3.0
3.5
4.0



➢ **Radial charge distribution function, $\rho(r)$**

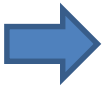
sum of the radial probability density functions of all the occupied orbitals.

- **shell**: all electrons with the same value of n
- **subshell**: all electrons with the same value of ℓ

Shielding Effects

- Energy-level diagrams for many-electron atoms

1) **The degeneracy of the p, d, and f orbitals is removed**, due to the difference of Z_{eff} from the Coulomb field.



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.

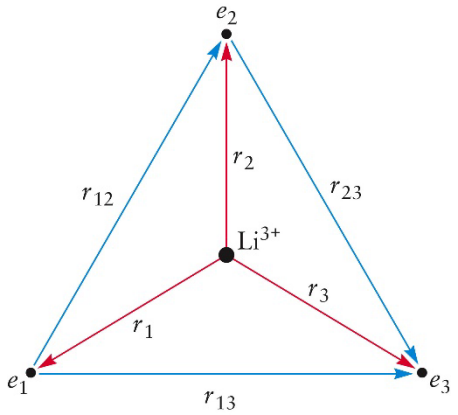
- Each electron attracted by the nucleus, and repelled by the other electrons.

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

The Shell Model of the Atom

For Li with Z = 3,

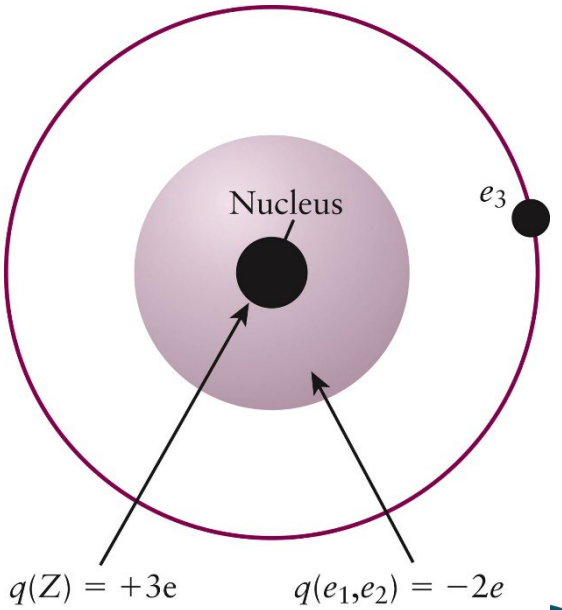
$$V = \frac{Ze^2}{4\pi\varepsilon_0}\left(-\frac{1}{r_1} - \frac{1}{r_2} - \frac{1}{r_3}\right) + \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{23}}\right)$$



- **Effective potential energy**

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

$$V_{eff}(r) = -\frac{Z_{eff}e^2}{4\pi\varepsilon_0 r}$$



- **effective nuclear charge**, $Z_{eff}\,e < Ze$

$$V_n^{eff}(r) \approx -\frac{Z_{eff}(n)e^2}{r}$$

- Hartree orbital energy $\epsilon_n \approx -\frac{[Z_{eff}(n)]^2}{n^2}$ (rydbergs)

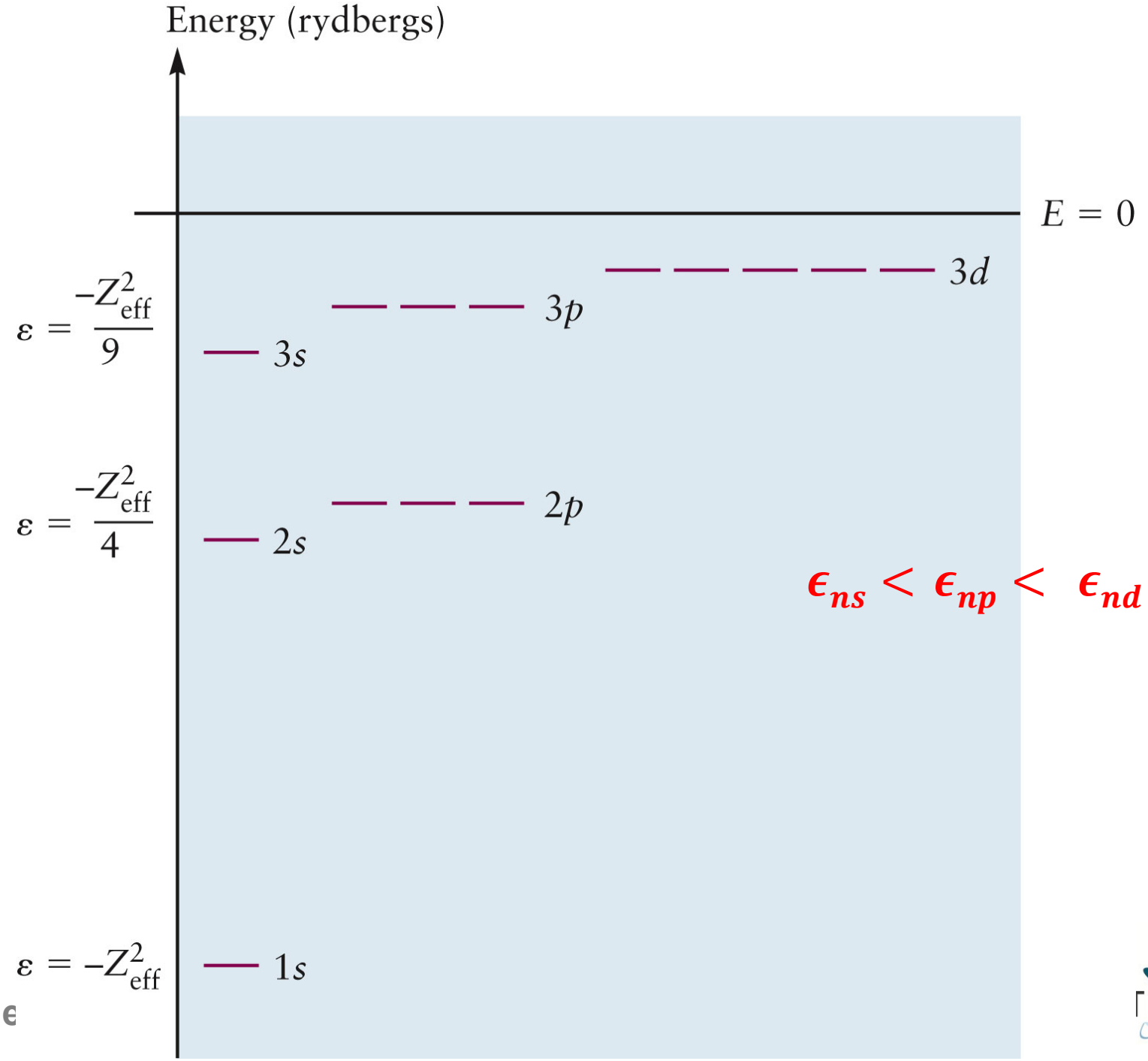
$$\bar{r}_{n\ell} = \frac{n^2 a_0}{Z_{eff}(n)}\left\{1 + \frac{1}{2}\left[1 - \frac{\ell(\ell+1)}{n^2}\right]\right\}$$

i.e.) For Ar, $Z_{eff}(1) \sim 16$, $Z_{eff}(2) \sim 8$, $Z_{eff}(3) \sim 2.5$

TABLE 5.3

Z_{eff} for Selected Atoms

	H(1)							He(2)
1*s*	1.00							1.69
	Li(3)	**Be(4)**	**B(5)**	**C(6)**	**N(7)**	**O(8)**	**F(9)**	**Ne(10)**
1*s*	2.69	3.68	4.68	5.67	6.66	7.66	8.65	9.64
2*s*	1.28	1.91	2.58	3.22	3.85	4.49	5.13	5.76
2*p*			2.42	3.14	3.83	4.45	5.10	5.76

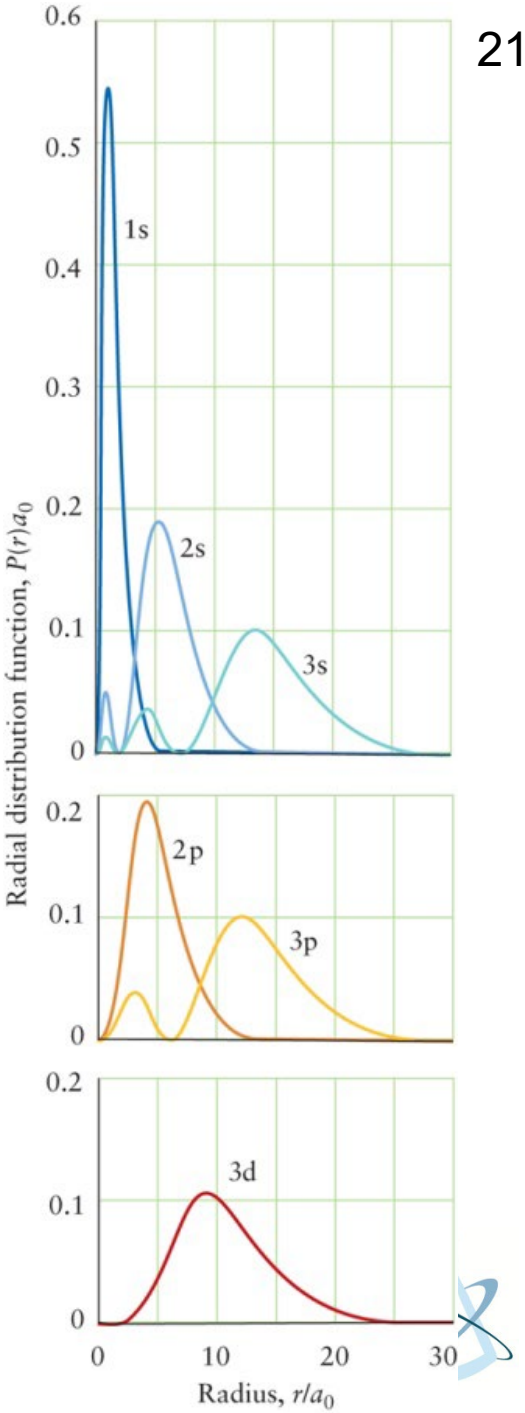

Energy (rydbergs)
E = 0
3d
3p
3s
2p
2s
1s
ε = −Z²eff / 9
ε = −Z²eff / 4
ε = −Z²eff
ϵns < ϵnp < ϵnd

- **Penetration**:

s-electron – very close to the nucleus
highly penetrates through the inner shell.

p-electron – penetrates less than an s-orbital
effectively shielded from the nucleus

In a many-electron atom, because of the effects of penetration and shielding, the order of energies of orbitals in a given shell is s < p < d < f.



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

➢ Hund's rule

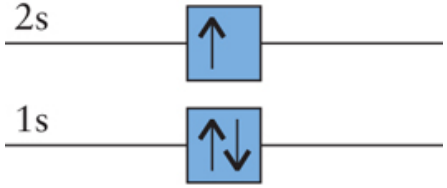
When electrons are added to Hartree orbitals of equal energy, a single electron enters each orbital before a second one enters any orbital.

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

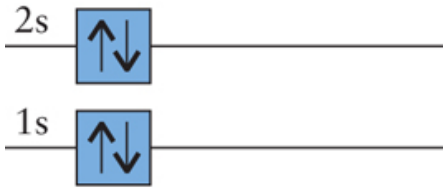
- H, $1s^1$

- He, $1s^2$

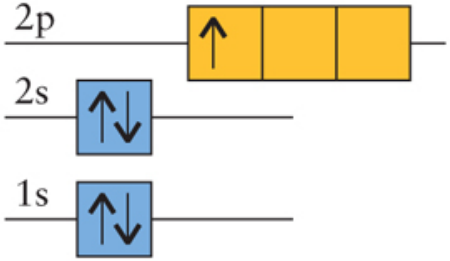
- Li, $1s^2 2s^1$ or $[He]2s^1$



- Be, $1s^2 2s^2$ or $[He]2s^2$

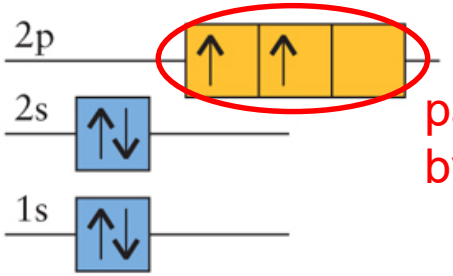


- B, $1s^2 2s^2 2p^1$ or $[He]2s^2 2p^1$



- C, $1s^2 2s^2 2p^2$ or $[He]2s^2 2p^2$

  $\rightarrow 1s^2 2s^2 2p_x^1 2p_y^1$



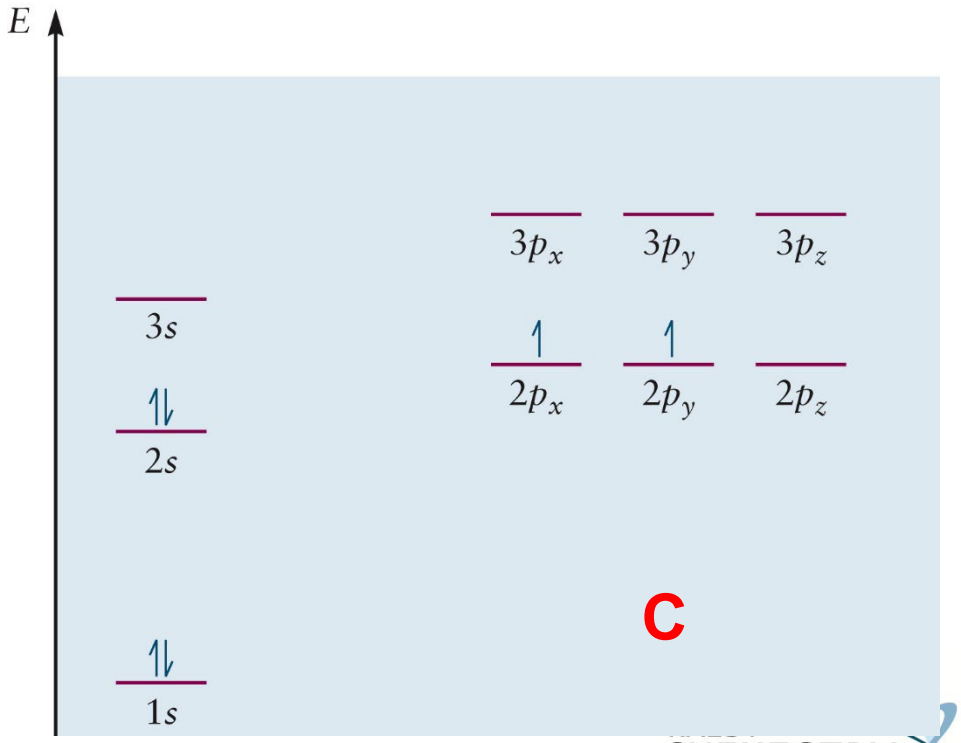
parallel spins
by Hund's rule

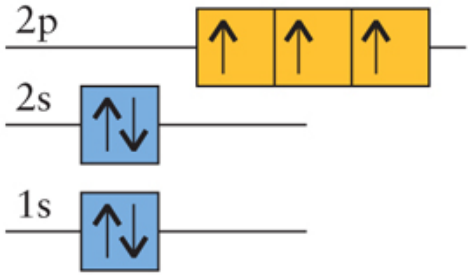
➢ **Magnetic properties** for a test of electronic configurations

- **paramagnetic**: a substance attracted into a magnetic field with one or more unpaired electrons

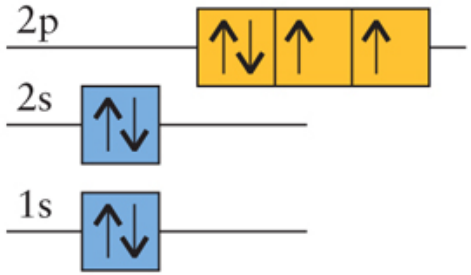
- **diamagnetic**: a substance pushed out of a magnetic field with all electrons paired

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

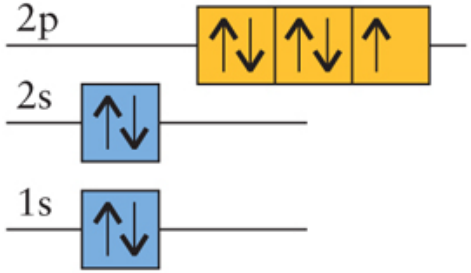




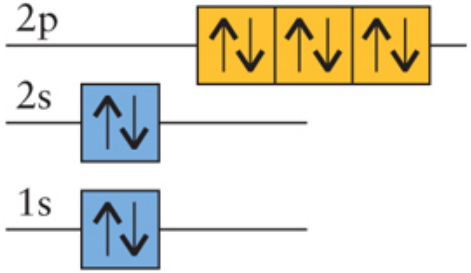
7 N $1s^2 2s^2 2p^3$, $[He]2s^2 2p^3$



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: $1s^1$	↑				
He: $1s^2$	↑↓				
Li: $1s^2 2s^1$	↑↓	↑			
Be: $1s^2 2s^2$	↑↓	↑↓			
B: $1s^2 2s^2 2p_x^1$	↑↓	↑↓	↑		
C: $1s^2 2s^2 2p_x^1 2p_y^1$	↑↓	↑↓	↑	↑	
N: $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$	↑↓	↑↓	↑	↑	↑
O: $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$	↑↓	↑↓	↑↓	↑	↑
F: $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$	↑↓	↑↓	↑↓	↑↓	↑
Ne: $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2$	↑↓	↑↓	↑↓	↑↓	↑↓

- **n = 3**: Na, [He]$2s^2 2p^6 3s^1$ or [Ne]$3s^1$ to Ar, [Ne]$3s^2 3p^6$
- **n = 4**: from Sc (scandium, Z = 21) to Zn (zinc, Z = 30)
  the next 10 electrons enter the 3d-orbitals. **d-block elements**

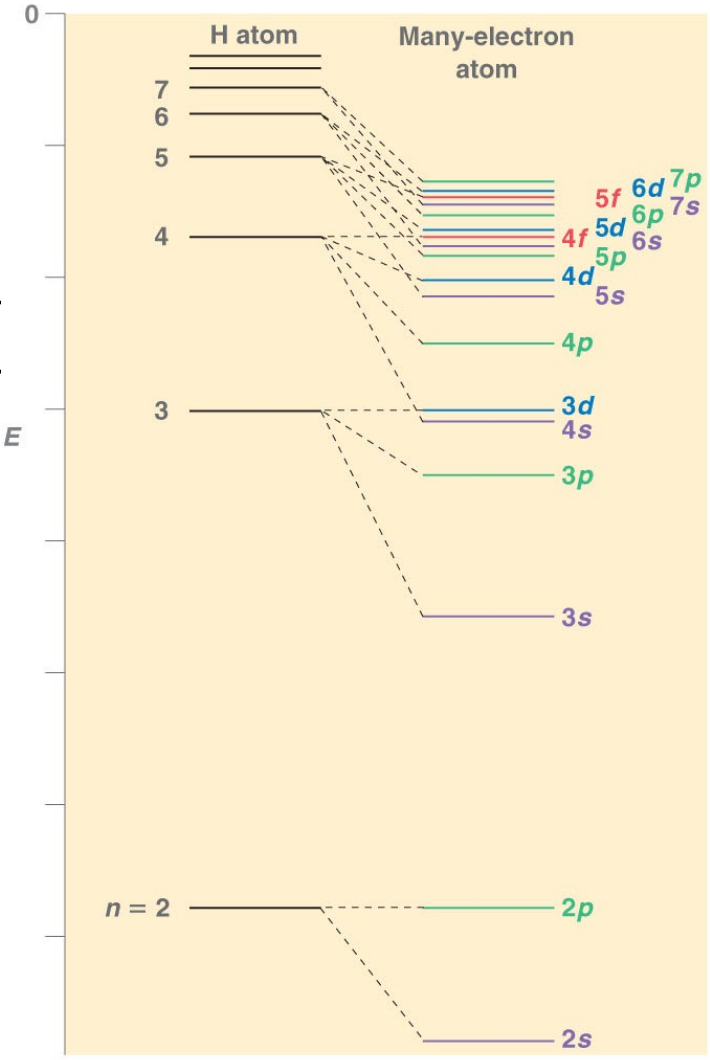
➢ The (n+ℓ) rule

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]$4f^1 5d^1 6s^2$)



Anomalous Configurations

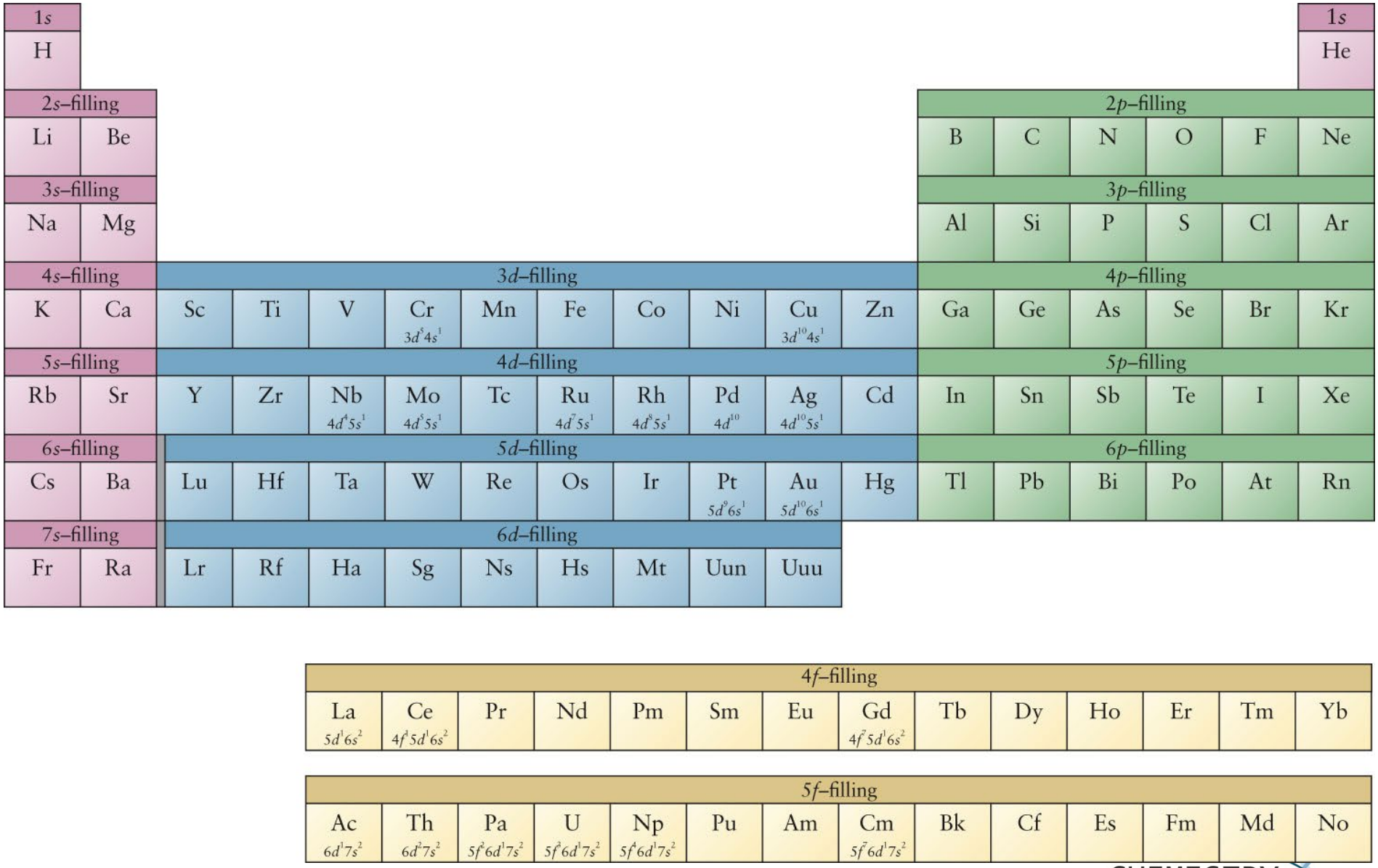
Exceptions to the Aufbau principle

Cr, predicted: $4s^2 3d^4$

Cr, observed: $4s^1 3d^5$

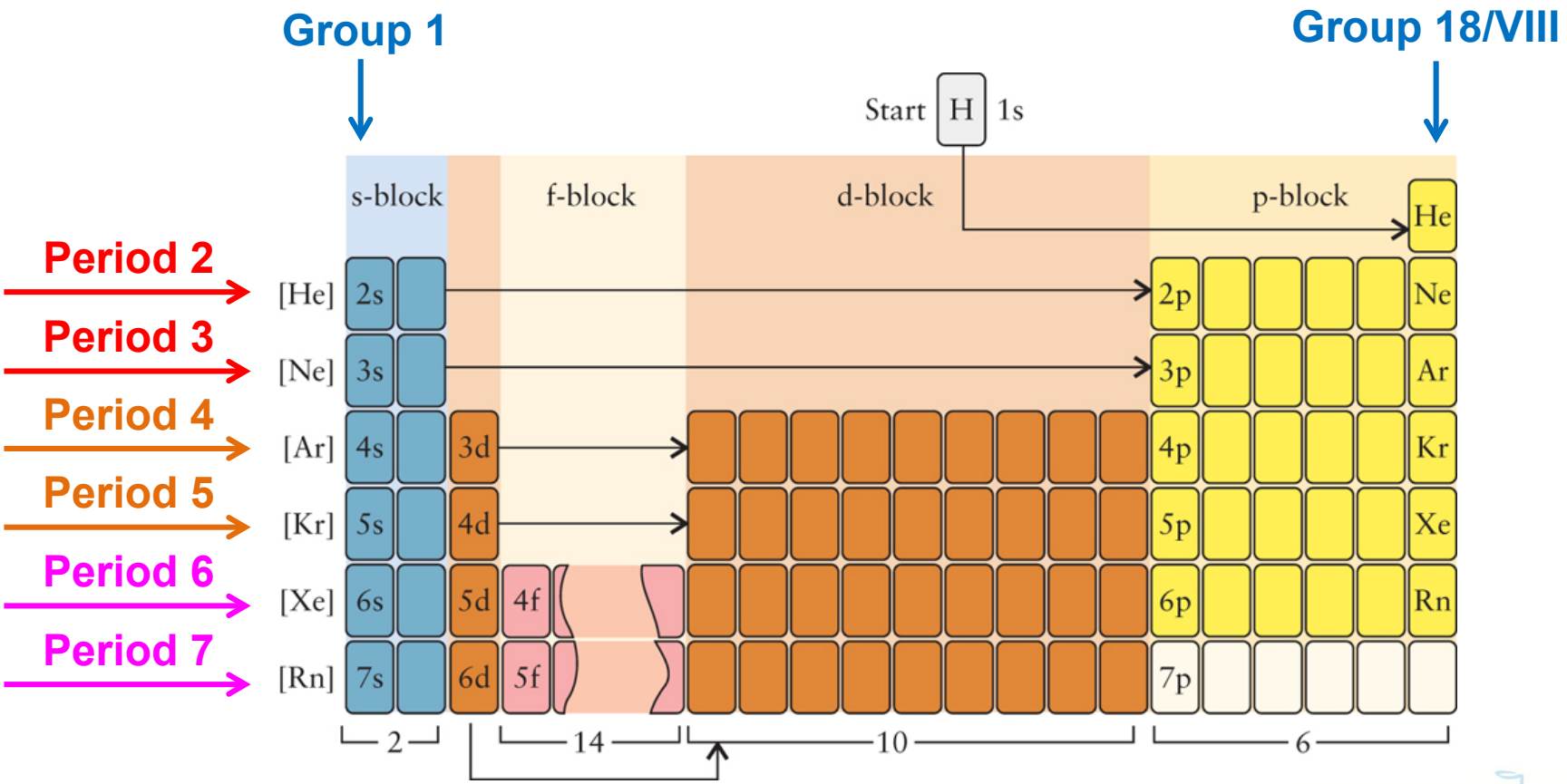
Anomalous electron configurations*

Period	Z	Element	Configuration	Period	Z	Element	Configuration
4	24	Cr	$[Ar]4s^1 3d^5$	6	57	La	$[Xe]6s^2 5d^1$
4	29	Cu	$[Ar]4s^1 3d^{10}$	6	58	Ce	$[Xe]6s^2 4f^1 5d^1$
5	41	Nb	$[Kr]5s^1 4d^4$	6	64	Gd	$[Xe]6s^2 4f^7 5d^1$
5	42	Mo	$[Kr]5s^1 4d^5$	6	78	Pt	$[Xe]6s^1 4f^{14} 5d^9$
5	44	Ru	$[Kr]5s^1 4d^7$	6	79	Au	$[Xe]6s^1 4f^{14} 5d^{10}$
5	45	Rh	$[Kr]5s^1 4d^8$	7	89	Ac	$[Rn]7s^2 6d^1$
5	46	Pd	$[Kr]4d^{10}$	7	90	Th	$[Rn]7s^2 6d^2$
5	47	Ag	$[Kr]5s^1 4d^{10}$	7	91	Pa	$[Rn]7s^2 5f^2 6d^1$
				7	92	U	$[Rn]7s^2 5f^3 6d^1$


1s
H
1s
He
2s–filling
Li
Be
2p–filling
B
C
N
O
F
Ne
3s–filling
Na
Mg
3p–filling
Al
Si
P
S
Cl
Ar
4s–filling
K
Ca
3d–filling
Sc
Ti
V
Cr
3d5 4s1
Mn
Fe
Co
Ni
Cu
3d10 4s1
Zn
4p–filling
Ga
Ge
As
Se
Br
Kr
5s–filling
Rb
Sr
4d–filling
Y
Zr
Nb
4d4 5s1
Mo
4d5 5s1
Tc
Ru
4d7 5s1
Rh
4d8 5s1
Pd
4d10
Ag
4d10 5s1
Cd
5p–filling
In
Sn
Sb
Te
I
Xe
6s–filling
Cs
Ba
5d–filling
Lu
Hf
Ta
W
Re
Os
Ir
Pt
5d9 6s1
Au
5d10 6s1
Hg
6p–filling
Tl
Pb
Bi
Po
At
Rn
7s–filling
Fr
Ra
6d–filling
Lr
Rf
Ha
Sg
Ns
Hs
Mt
Uun
Uuu
4f–filling
La
5d1 6s2
Ce
4f1 5d1 6s2
Pr
Nd
Pm
Sm
Eu
Gd
4f7 5d1 6s2
Tb
Dy
Ho
Er
Tm
Yb
5f–filling
Ac
6d1 7s2
Th
6d2 7s2
Pa
5f2 6d1 7s2
U
5f3 6d1 7s2
Np
5f4 6d1 7s2
Pu
Am
Cm
5f7 6d1 7s2
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 valance electron configurations that differ only in the value of n.



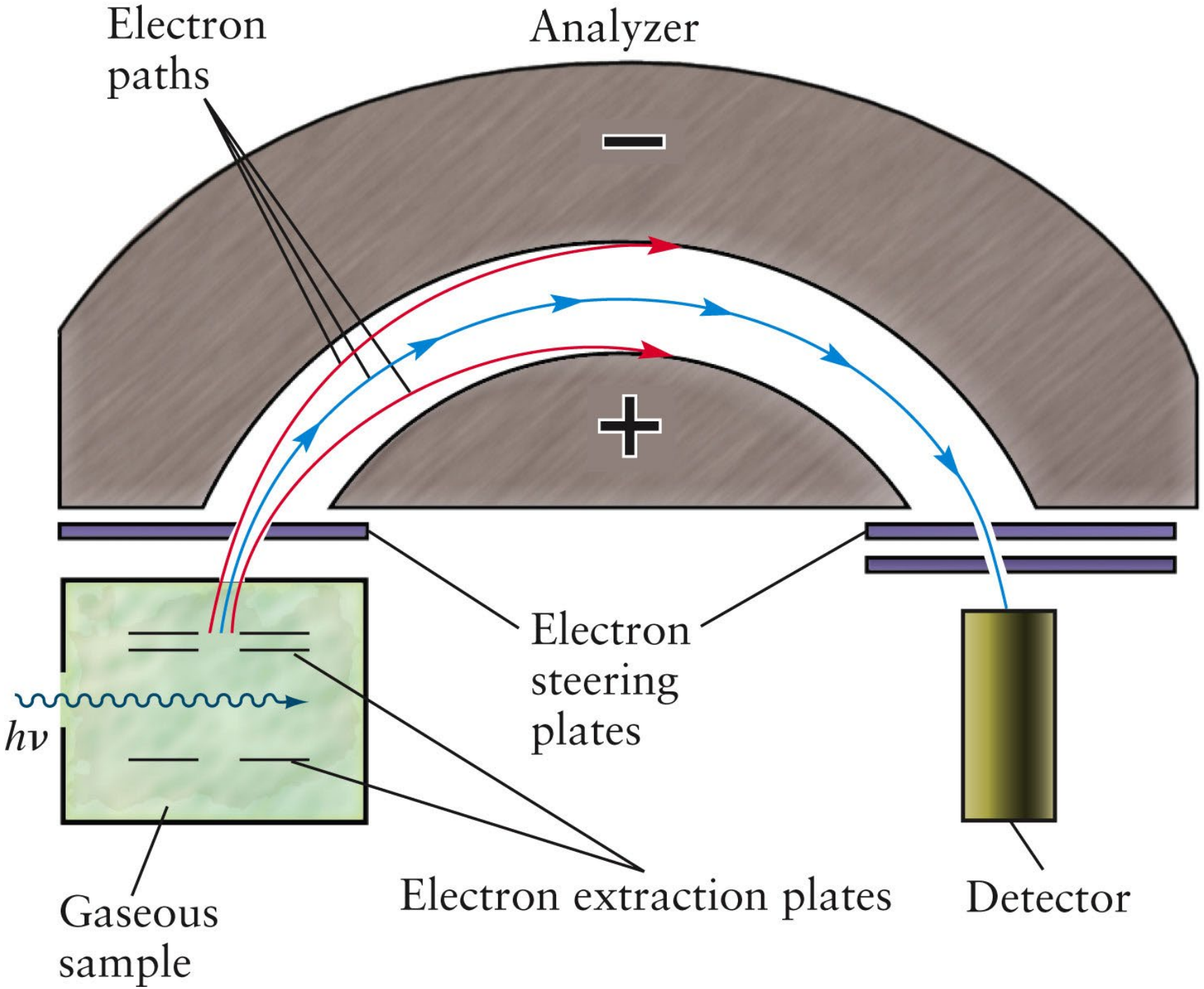
5.4 SHELLS AND THE PERIODIC TABLE: PHOTOELECTRON SPECTROSCOPY

- A **shell** is defined precisely as a set of orbitals that have the same principal quantum number.

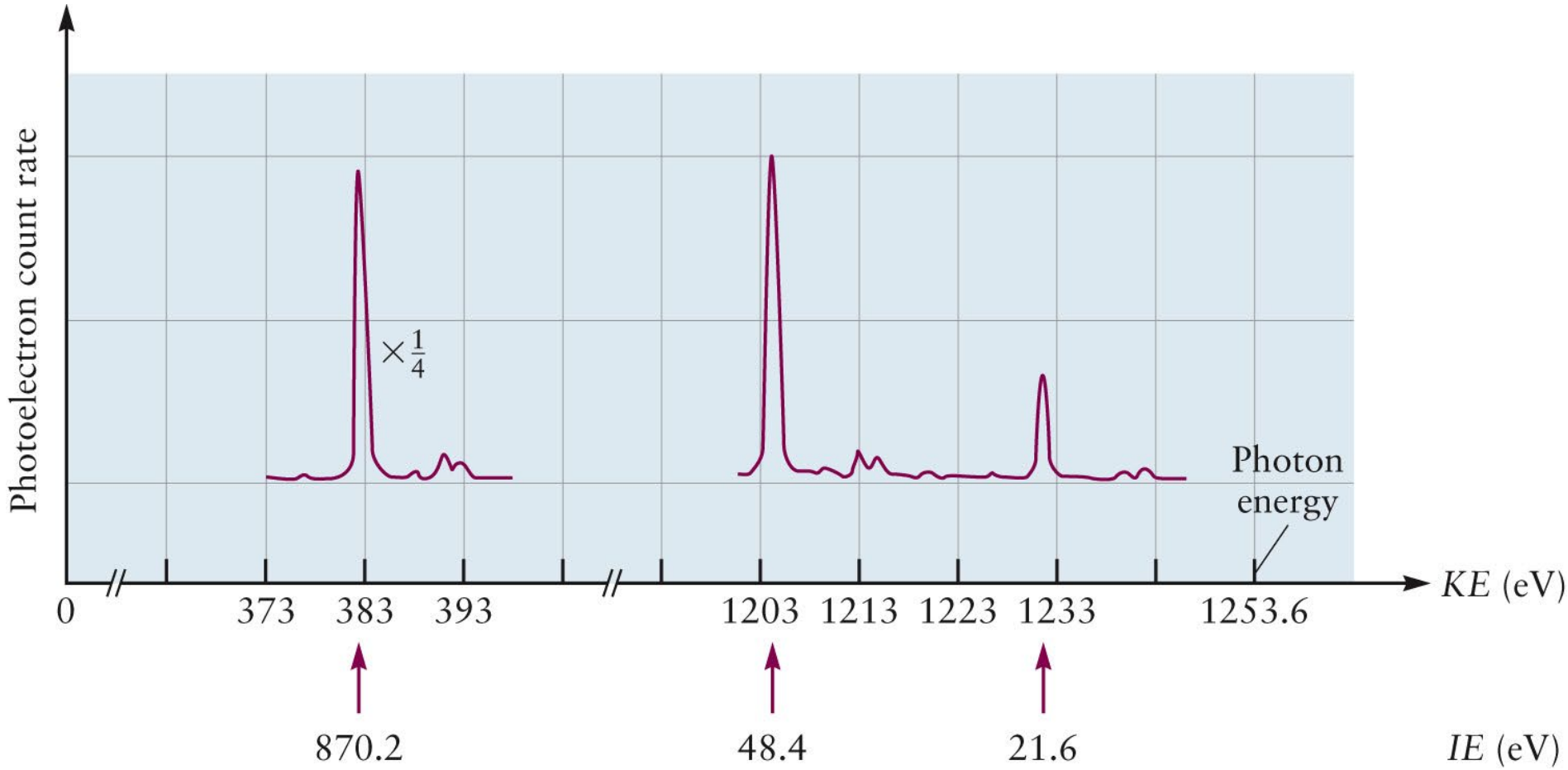
- **Photoelectron spectroscopy (PES)**

  determining the energy level of each orbital by measuring the ionization energy required to remove each electron from the atom

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


Electron paths
Analyzer
Electron steering plates
hν
Gaseous sample
Electron extraction plates
Detector

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



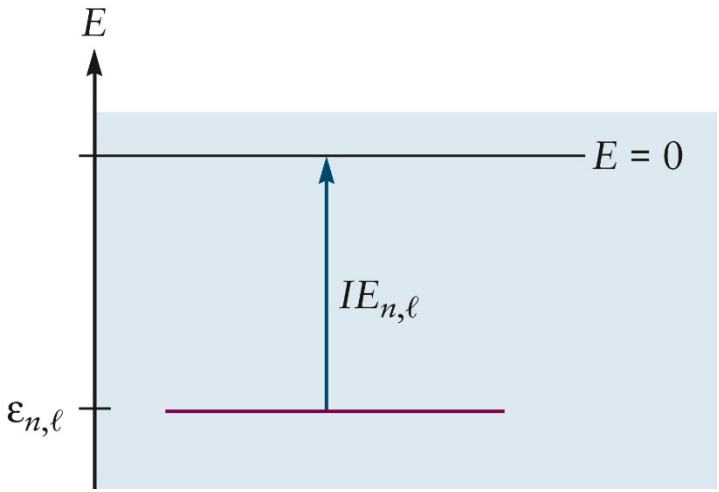
- Koopmans's approximation,

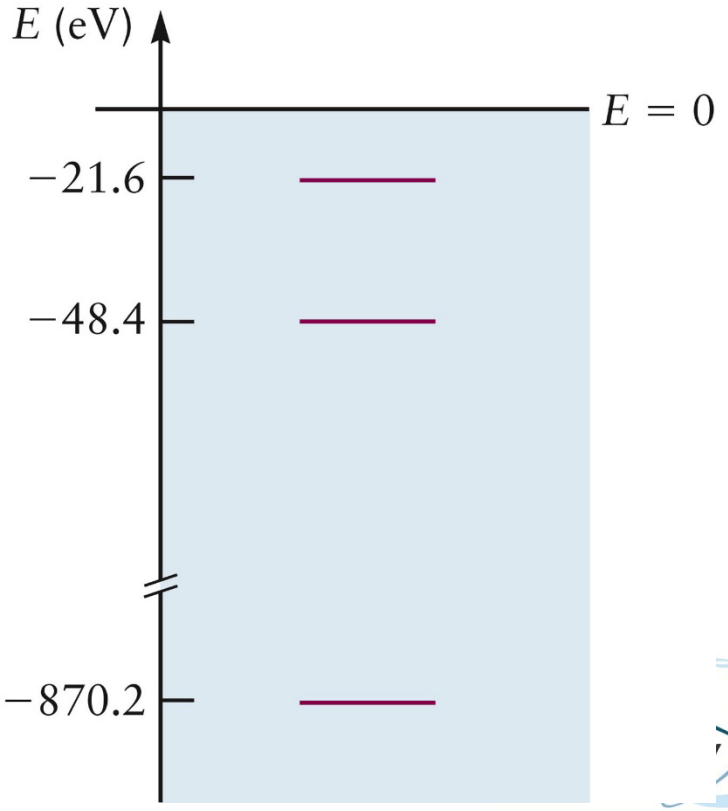
$$IE_\alpha = -\epsilon_\alpha$$

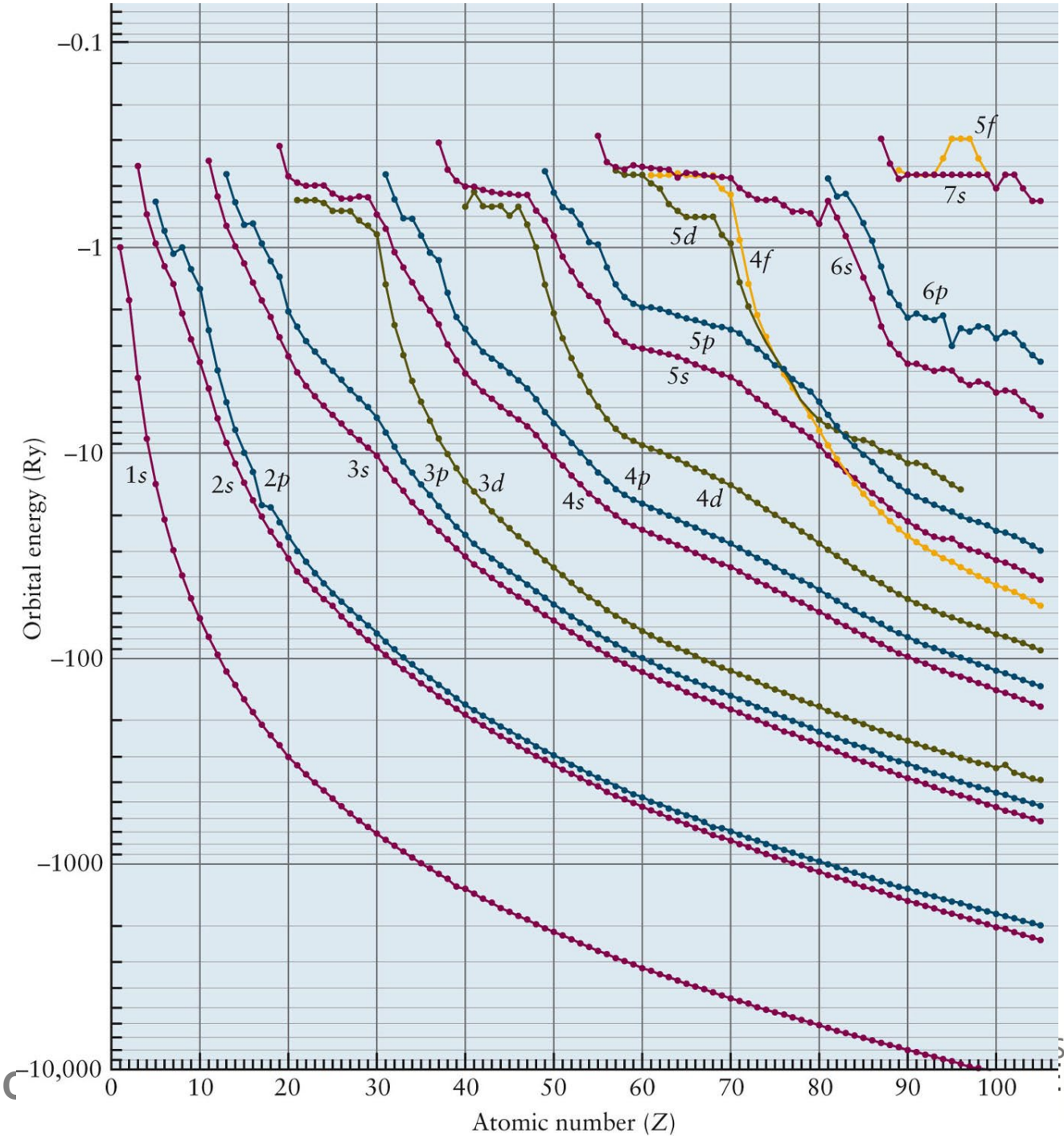
- with the frozen orbital approximation

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

i.e.) for Ne with $1s^2\ 2s^2\ 2p^6$






Orbital energy (Ry)
−0.1
−1
−10
−100
−1000
−10,000
0
10
20
30
40
50
60
70
80
90
100
Atomic number (Z)
1s
2s
2p
3s
3p
3d
4s
4p
4d
5s
5p
5d
4f
6s
6p
7s
5f

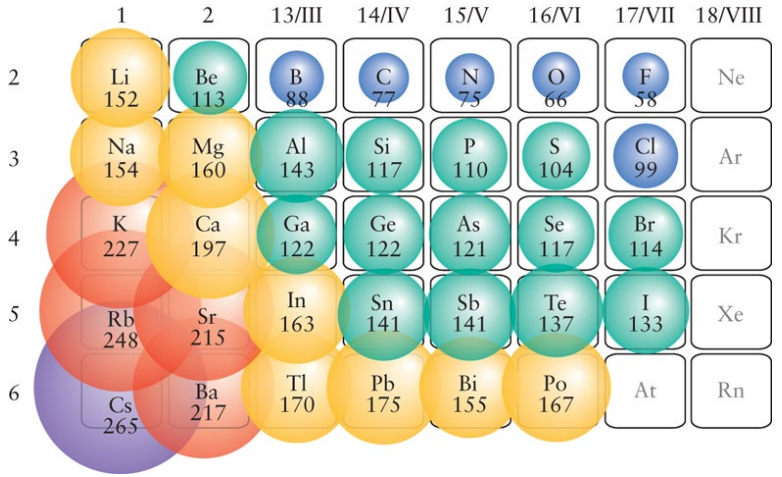
5.5 PERIODIC PROPERTIES AND ELECTRONIC STRUCTURE

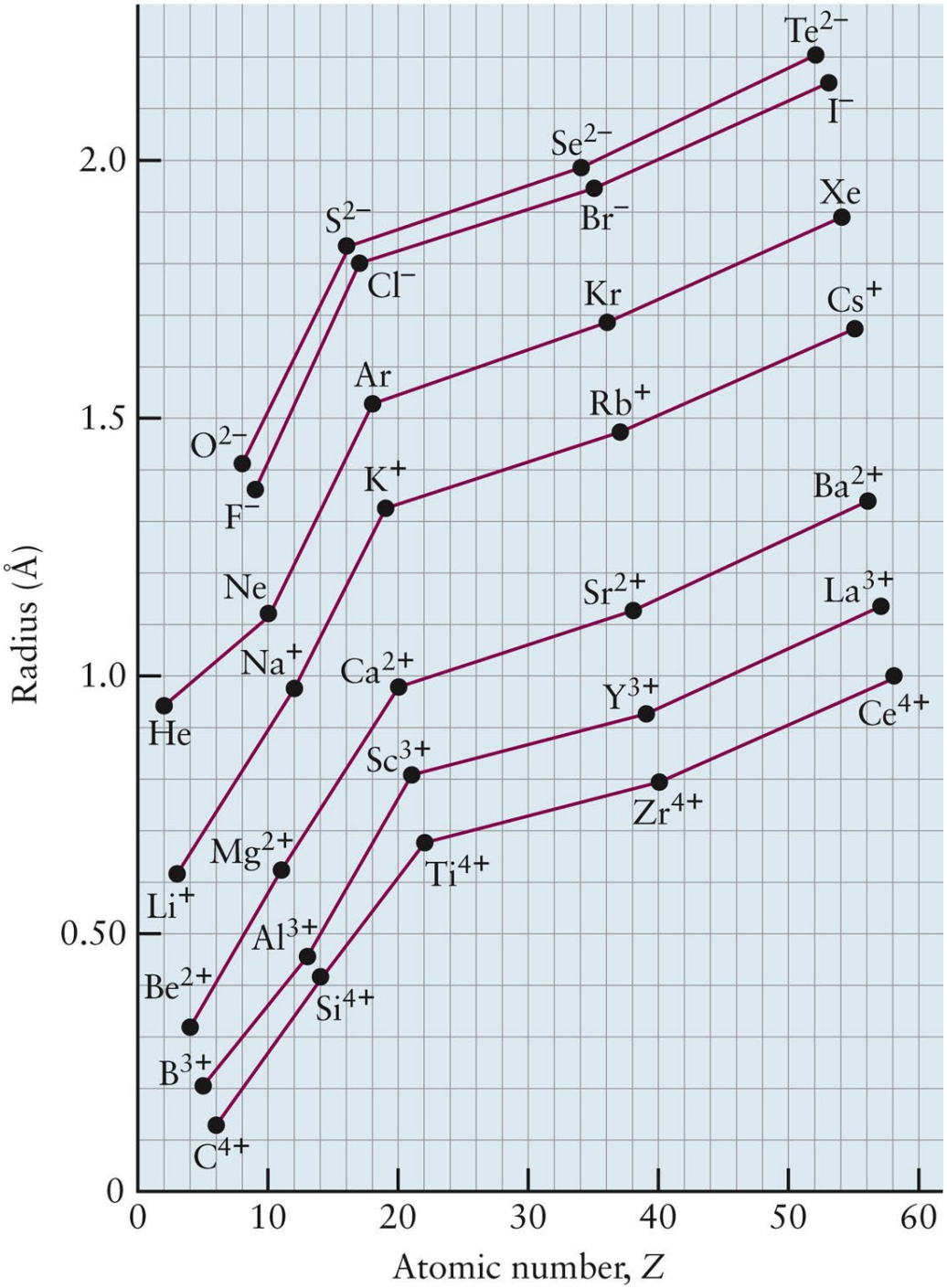
- **Atomic radius**: defined as half the distance between the centers of neighboring atoms
- **Ionic radius**: its share of the distance between neighboring ions in an ionic solid

- **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)





- 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

KAIST CHEMISTRY

- **Molar volumes** ($cm^3\ mol^{-1}$) 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**

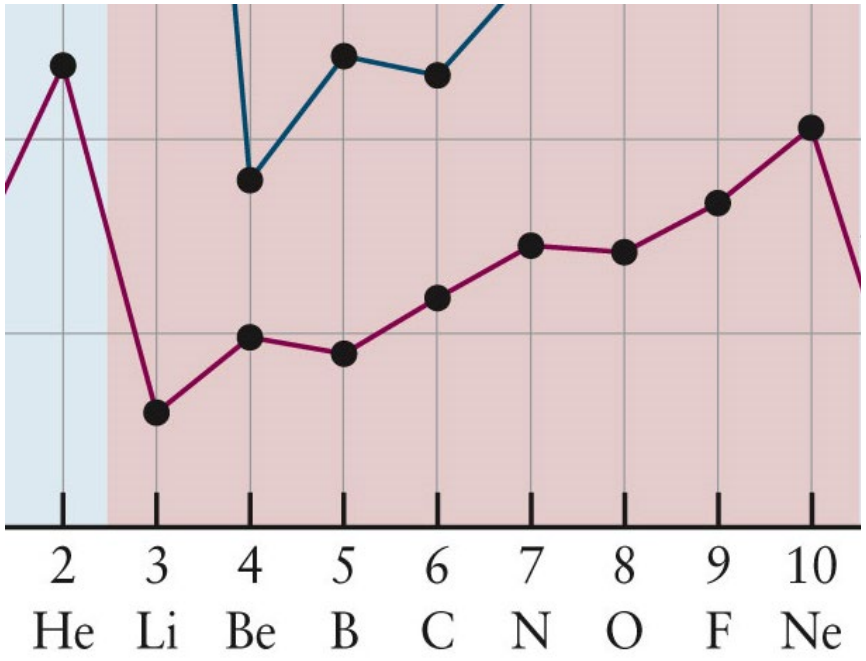
  2s e^- father than 1s e^-, and 2s e^- sees a net +1 charge

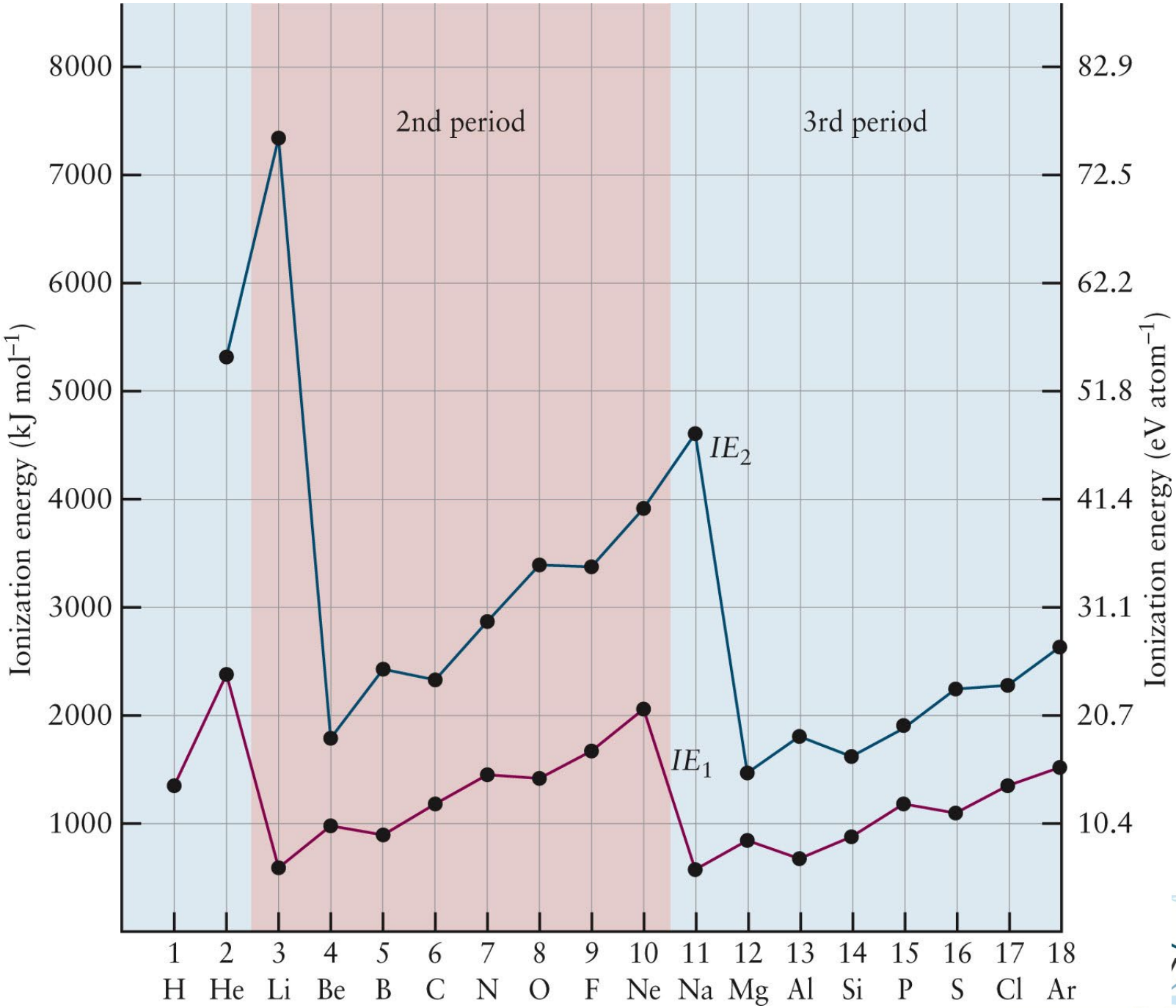
- **From Be to B, slight reduction in IE_1**

  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




2nd period
3rd period
IE_2
IE_1
Ionization energy (kJ mol^{-1})
Ionization energy (eV atom^{-1})
8000
7000
6000
5000
4000
3000
2000
1000
82.9
72.5
62.2
51.8
41.4
31.1
20.7
10.4
1 H
2 He
3 Li
4 Be
5 B
6 C
7 N
8 O
9 F
10 Ne
11 Na
12 Mg
13 Al
14 Si
15 P
16 S
17 Cl
18 Ar

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

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 *

(kJ mol^{-1})