MANY-ELECTRON ATOMS

General Chemistry I, Lecture Series 7

Pengxin Liu

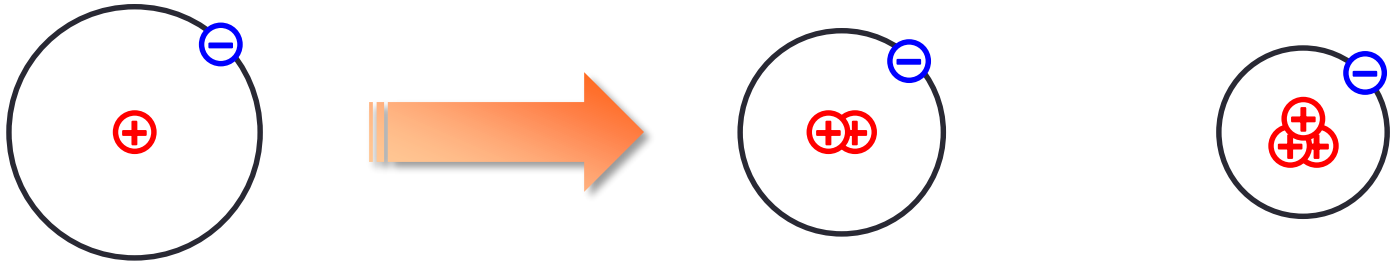
Reading:

OGB8 §5.2, §5.3

Outline

- Interactions in many-electron atoms
  - Hartree-Fock Equations are Solved by the Self-Consistent Field Method
- Repulsion between electrons
- Aufbau principle
- Electron configurations

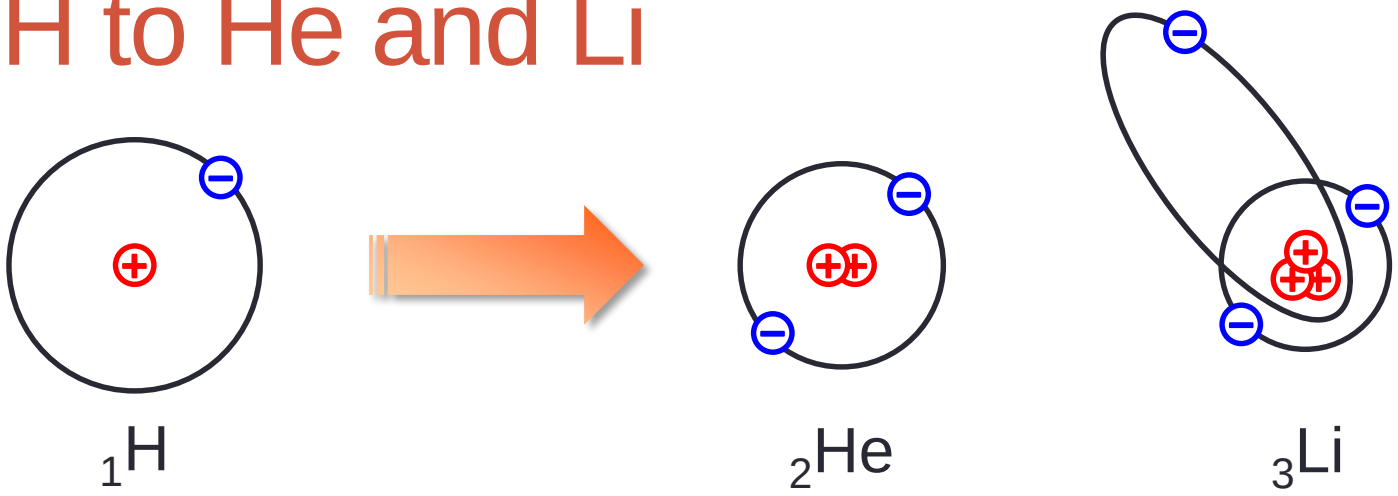
Hydrogen-Like Ions

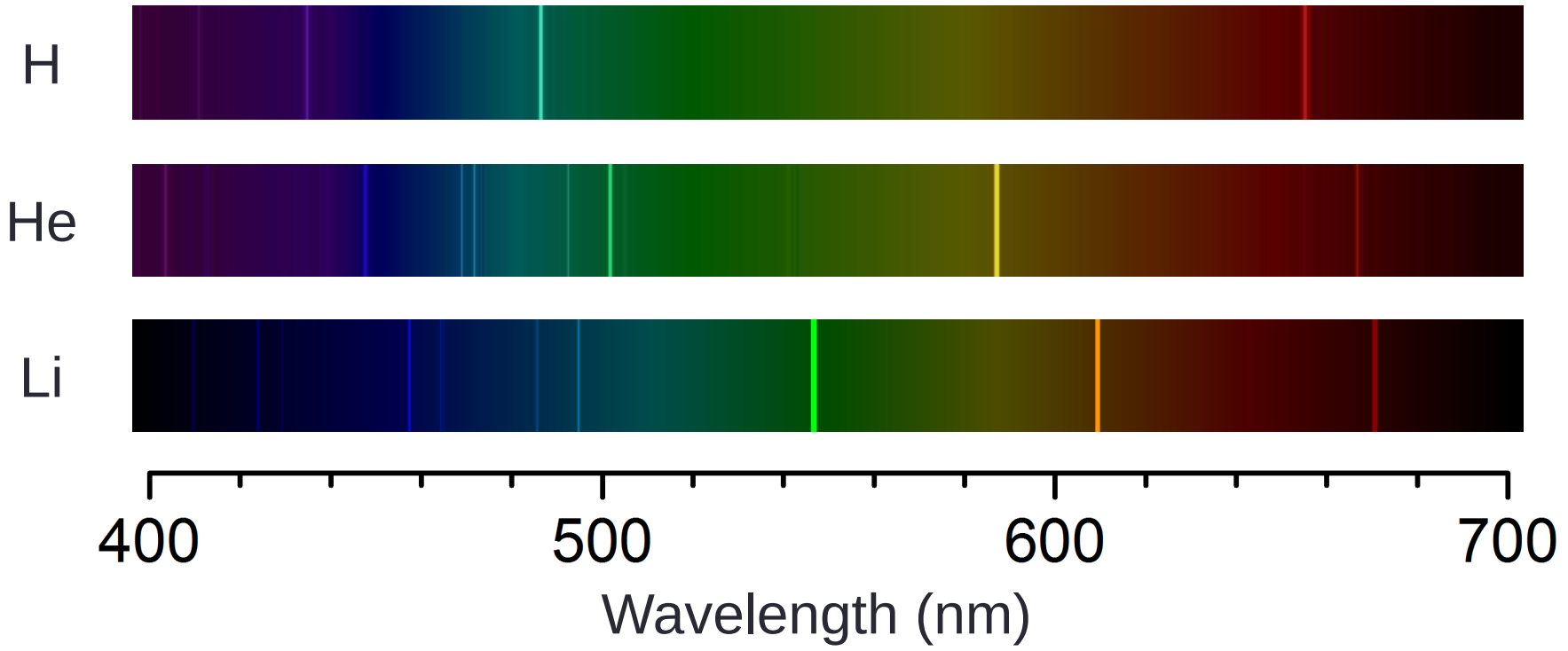


$_1H$ $_2He^+$ $_3Li^{2+}$

Coulomb potential V	$-\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}$		$-\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r}$
1*s* orbital $\psi_{1s} \propto$	$\exp(-r / a_0)$		$\exp(-Zr / a_0)$
Orbital radius r_n	$n^2 a_0$	a_0 = 53 pm Ry = 13.6 eV	$\frac{n^2}{Z} a_0$
Orbital energy E_n	$-\frac{\text{Ry}}{n^2}$		$-Z^2\frac{\text{Ry}}{n^2}$

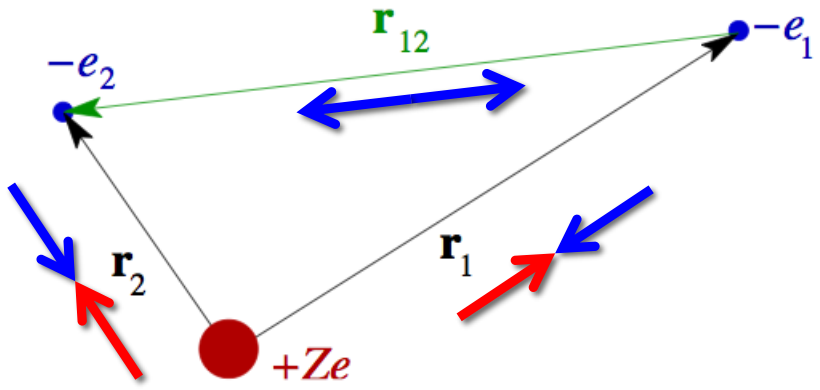
From H to He and Li





Single- vs. Many-Electron Atoms

	H, He^+, Li^{2+}	He, Li, …
Interactions	*Z*-*e* attraction	*Z*-*e* attraction *e*-*e* repulsion electron spins
Orbitals	*e* in a single orbital	*e* in multiple orbitals
Coordinates	*Z* at *O*, *e* at *r*	*Z* at *O*, e_1 at r_1, e_2 at r_2, …
Schrödinger Eqn.	Analytical solutions	Approximate solutions



An electron is attracted by $+Z$ but repelled by $-(Z-1)e$

Chemistry and Mathematics

Paul A. M. Dirac
(1902–1984)

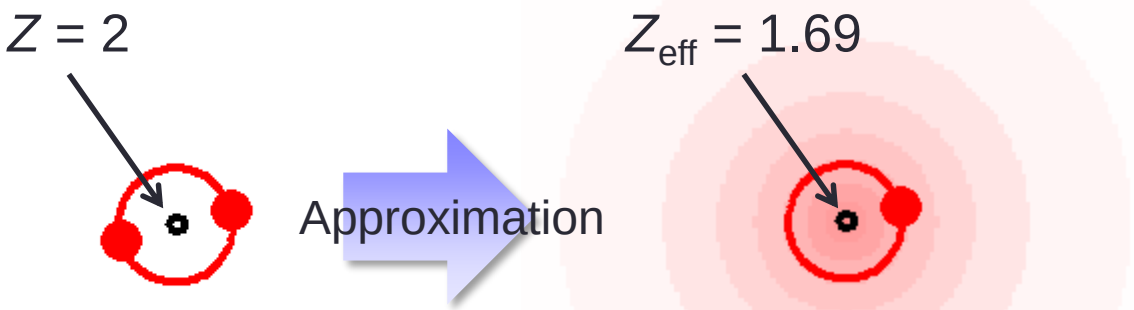
The fundamental laws necessary for the mathematical treatment of a large part of physics and the whole of chemistry are thus completely known, and the difficulty lies only in the fact that application of these laws leads to equations that are too complex to be solved.

The many-electron Schrödinger Equation can only be solved approximately.

Outline

- Interactions in many-electron atoms
- Repulsion between electrons
  - Electrons with same n and l
  - Electrons with different n
  - Electrons with the same n but different l
- Aufbau principle
- Electron configurations

Self-Consistent Field 自洽场



He: $\psi(r_1,r_2)$

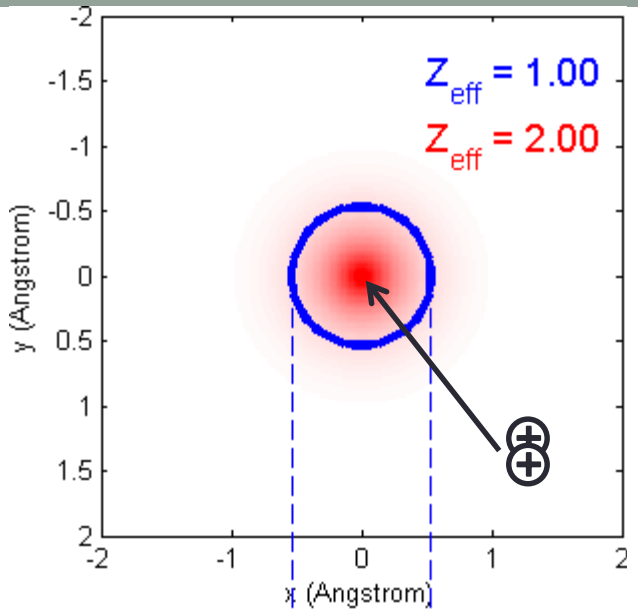
He: $\varphi_{1s}(r_1)\cdot\varphi'_{1s}(r_2)$

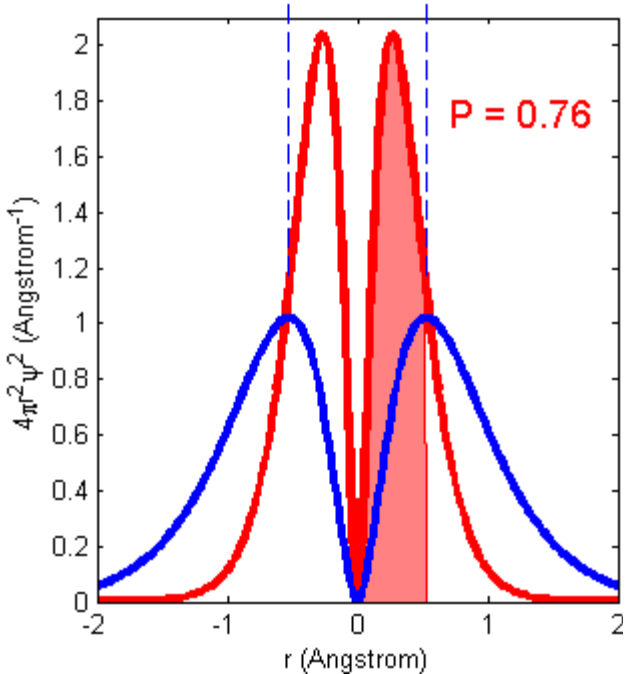
Repeated trials
until $\varphi_{1s}(r_1) = \varphi'_{1s}(r_2)$

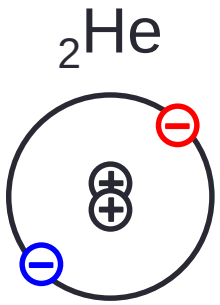
Douglas Hartree
(Cambridge,
1897–1958)

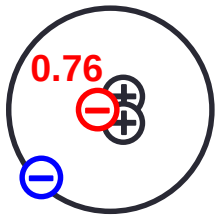
$\varphi_{1s}(r) \propto \exp(-Z_{eff}r / a_0)$, Z_{eff} is effective nuclear charge

SCF Example: Helium

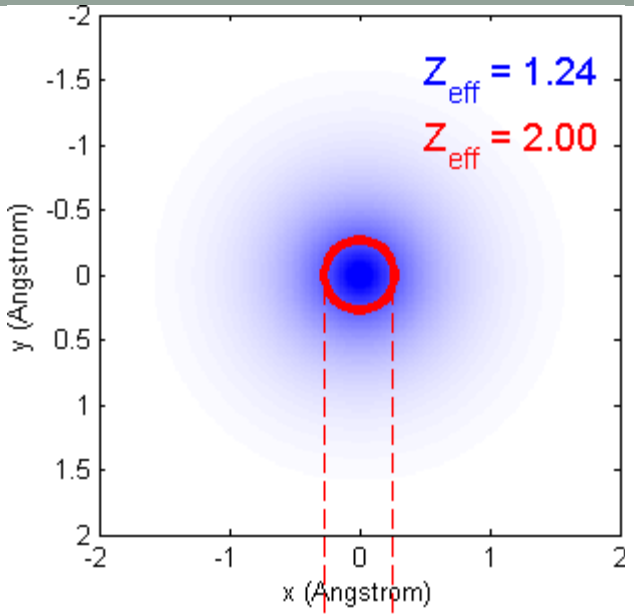


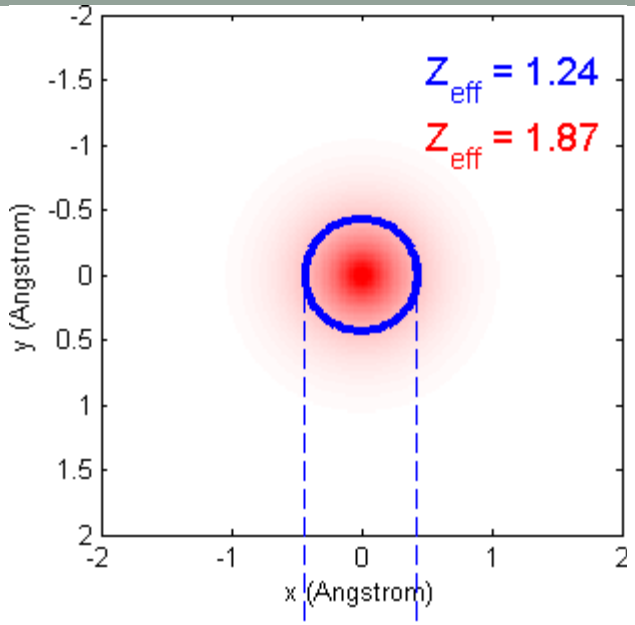


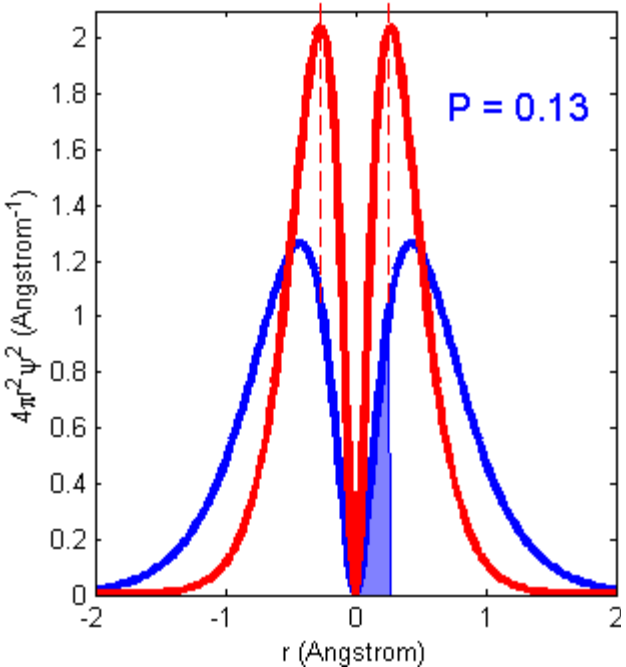


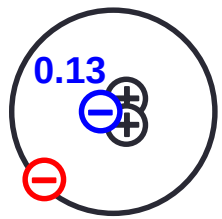


$Z_{eff} = 2 - 0.76$
$= 1.24$

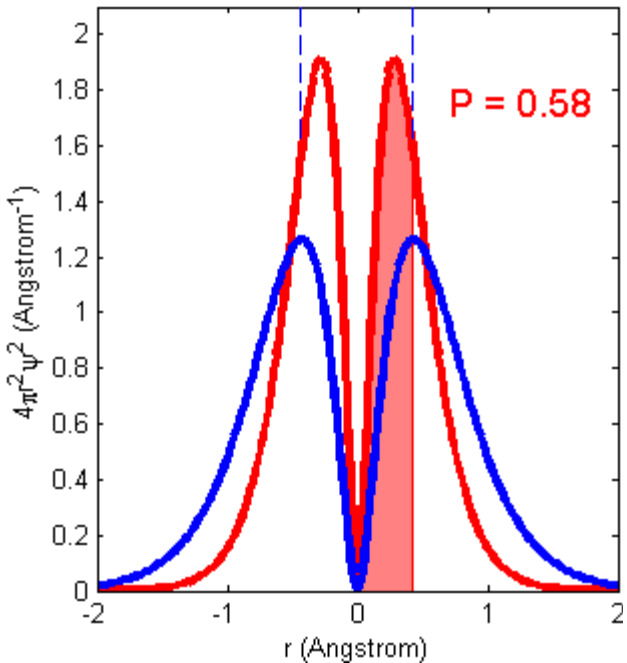


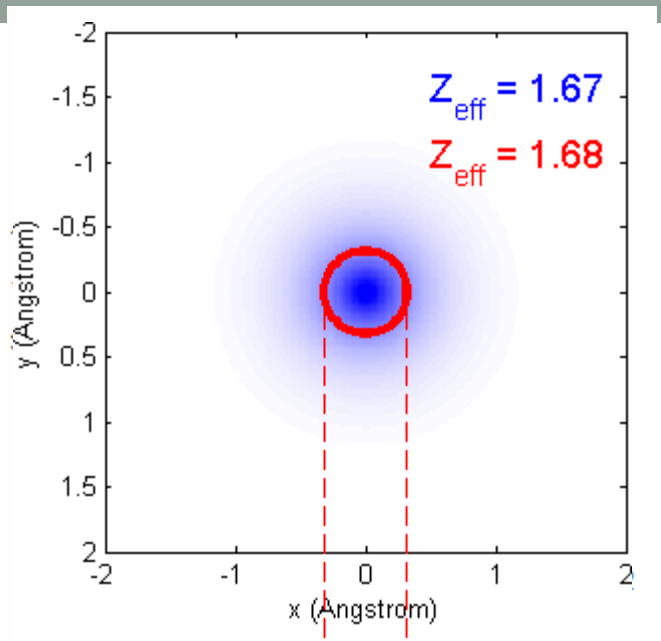


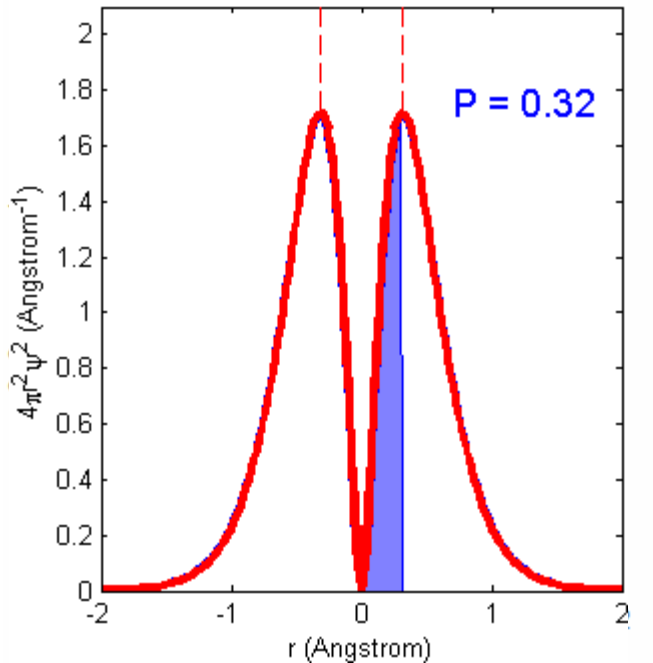


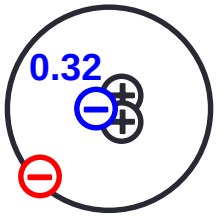


$Z_{eff} = 2 - 0.13$
$= 1.87$





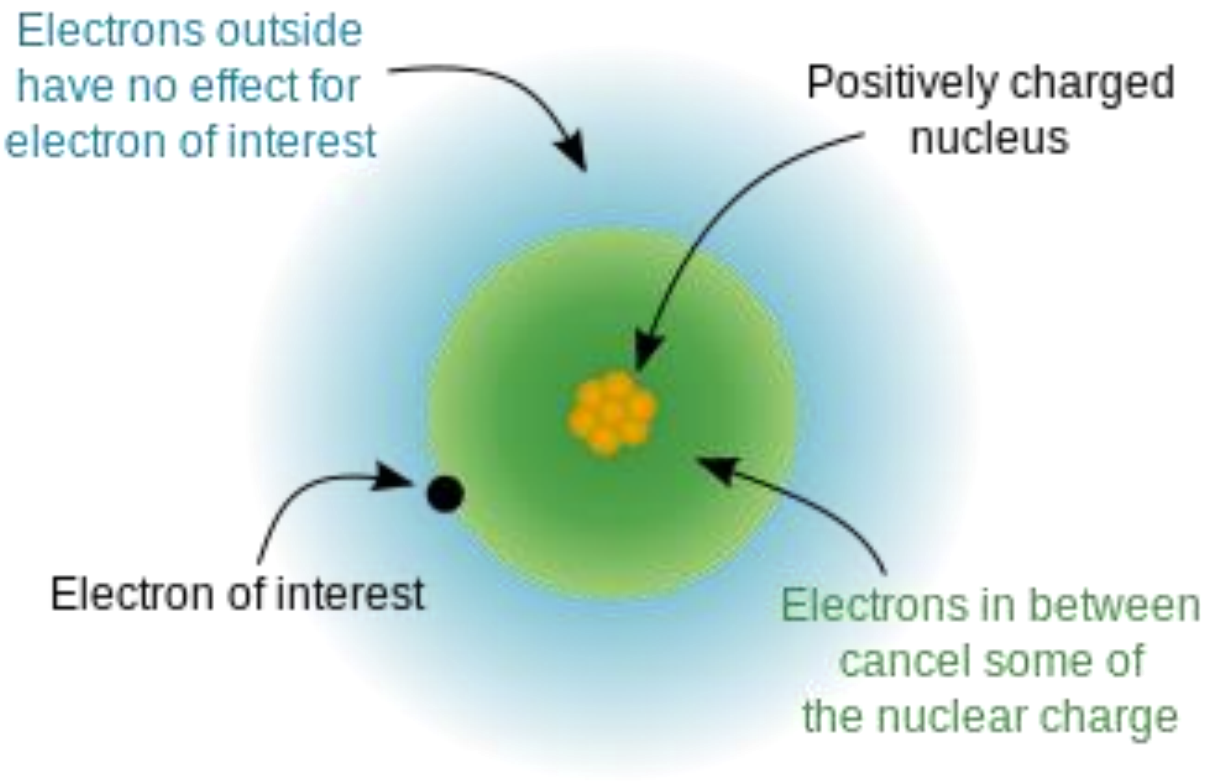




Z_{eff}(He 1s) = 2 − 0.32 = 1.68

Screening effect
(Shielding effect)
屏蔽效应

Screening effect



Consequence

- Z_{eff}
- $V = -\frac{1}{4\pi\varepsilon_0}\frac{Z_{\text{eff}}e^2}{R}$ 
- Orbital energy $E_n = -Z_{\text{eff}}^2\frac{\text{Ry}}{n^2}$ 
- Orbital radius $r_n = \frac{n^2}{Z}a_0$ 

Outline

- Interactions in many-electron atoms
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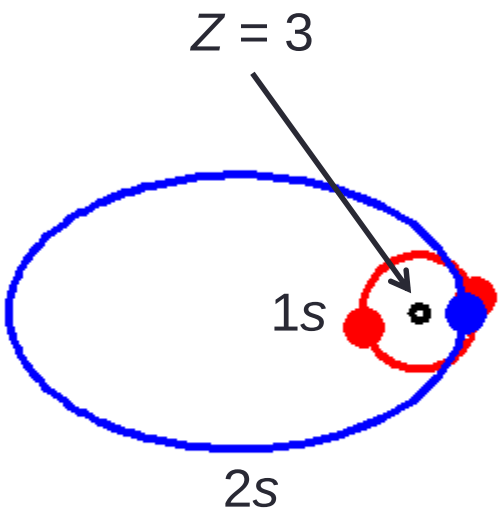
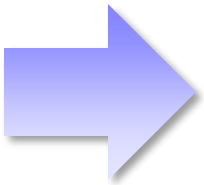
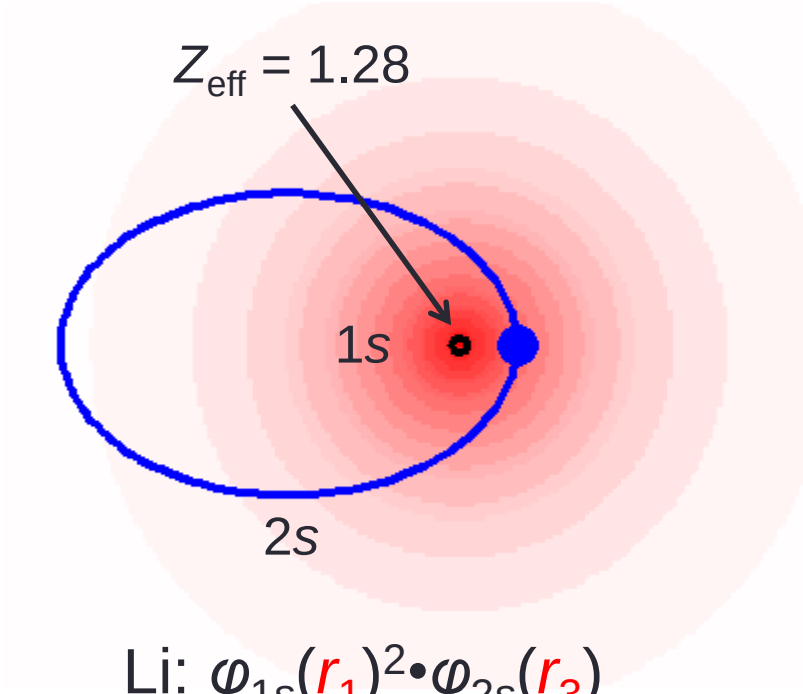
  - Electrons with same n and l
  - Electrons with different n
  - Electrons with the same n but different l
- Aufbau principle
- Electron configurations

The Shell Model for Li





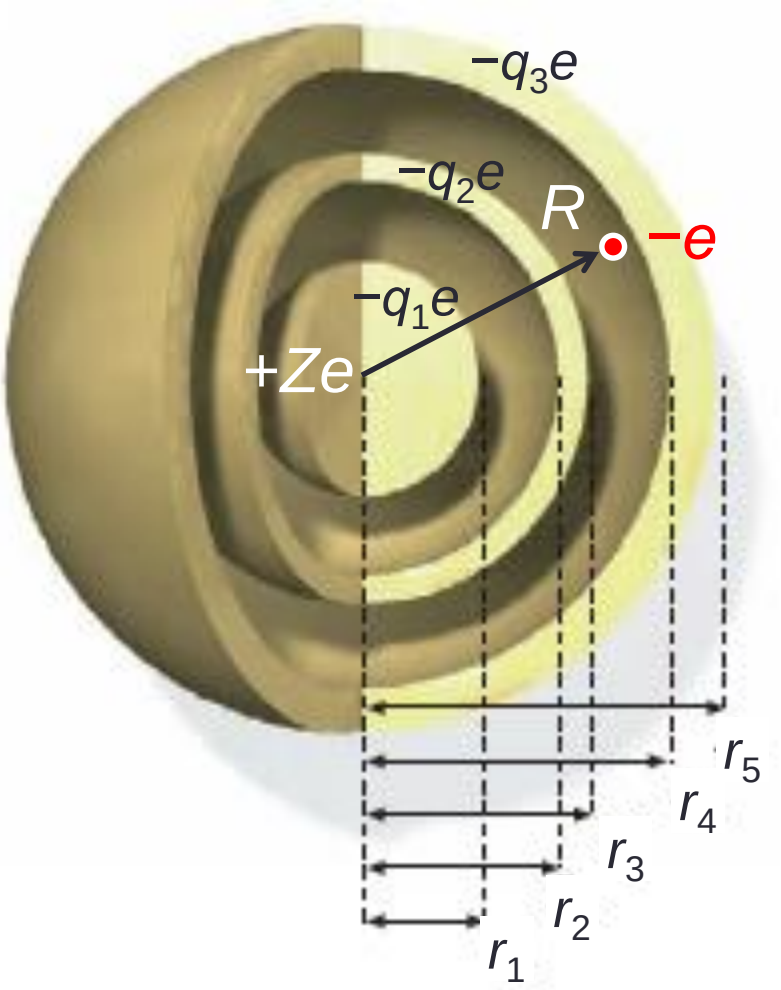


Li: $\psi(r_1,r_2,r_3)$

Li: $\varphi_{1s}(r_1)^2 \bullet \varphi_{2s}(r_3)$

$1s^2 2s^1$

The Shell Model



$$F = -\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{R^2} + \frac{1}{4\pi\varepsilon_0}\frac{q_1e^2}{R^2} + \frac{1}{4\pi\varepsilon_0}\frac{q_2e^2}{R^2}$$

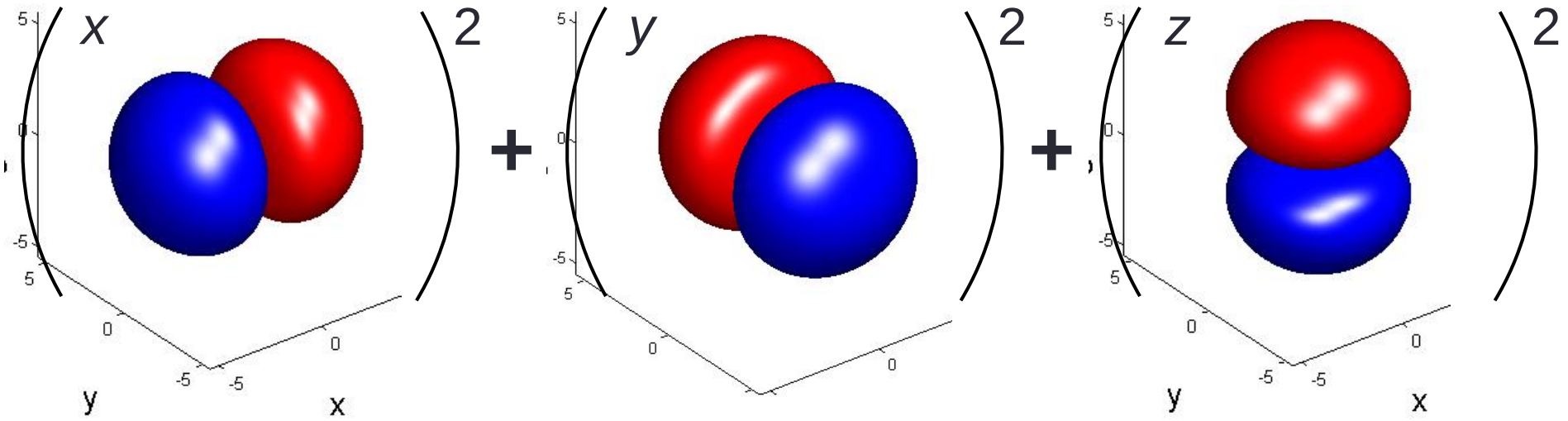
$$= -\frac{1}{4\pi\varepsilon_0}\frac{(Z-q_1-q_2)e^2}{R^2}$$

$$= -\frac{1}{4\pi\varepsilon_0}\frac{Z_{eff}e^2}{R^2}$$

$$V = -\frac{1}{4\pi\varepsilon_0}\frac{Z_{eff}e^2}{R}, \; Z_{eff} = Z - q$$

Z_{eff} is effective nuclear charge.

2p: Overlap of *p* Orbitals



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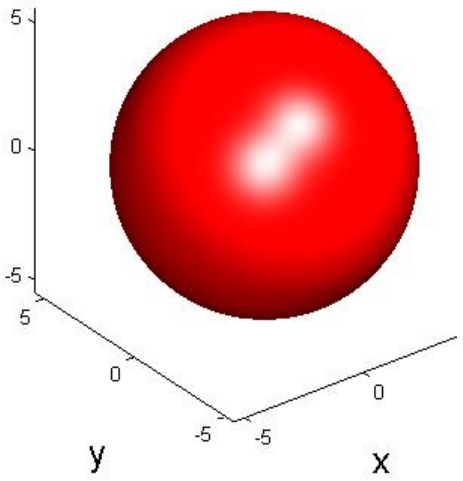
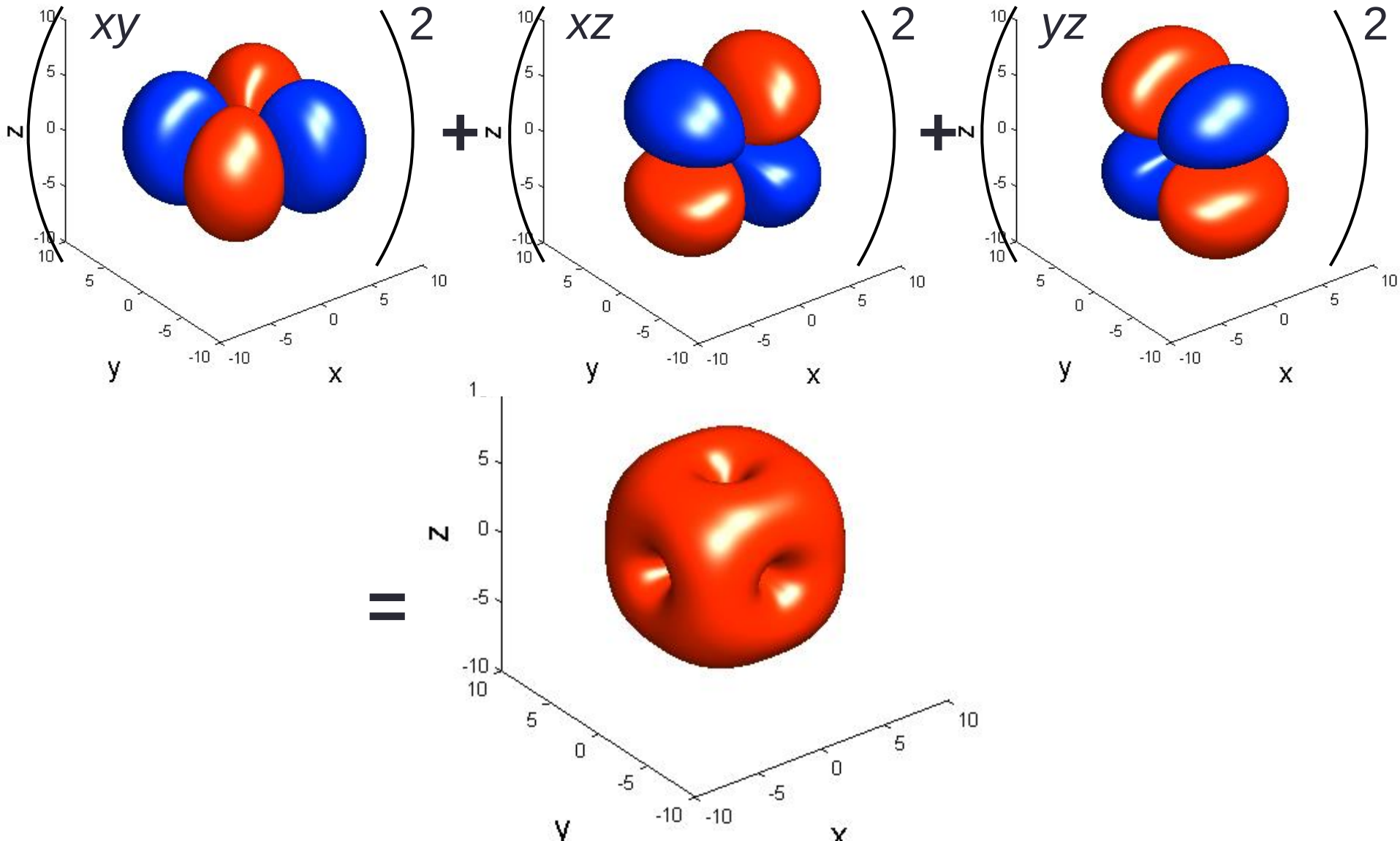
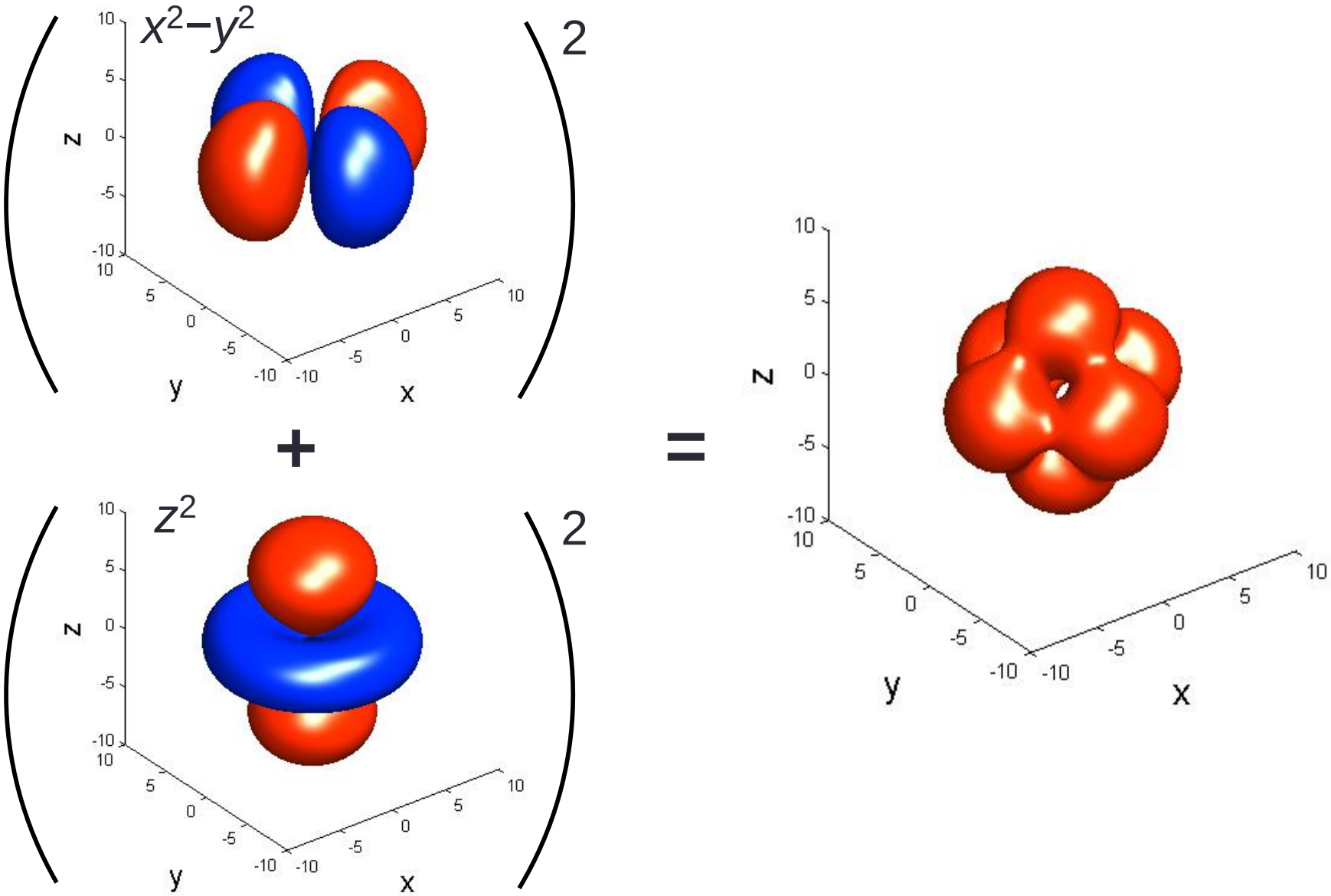


The three *p* orbitals occupy separate parts of the space.

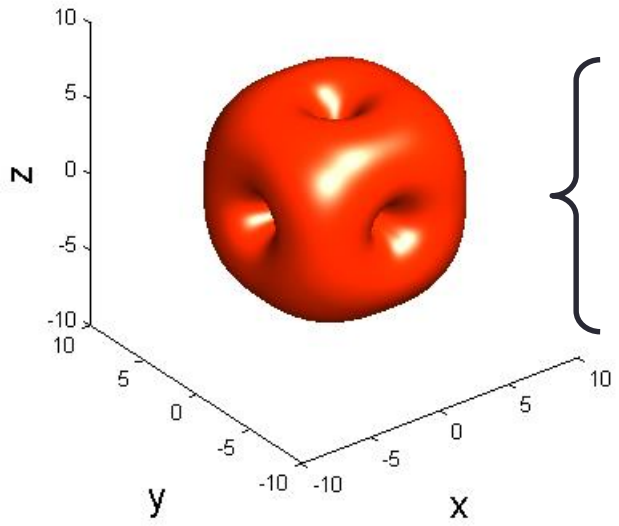
3d: Overlap of *d* Orbitals



3d: Overlap of *d* Orbitals

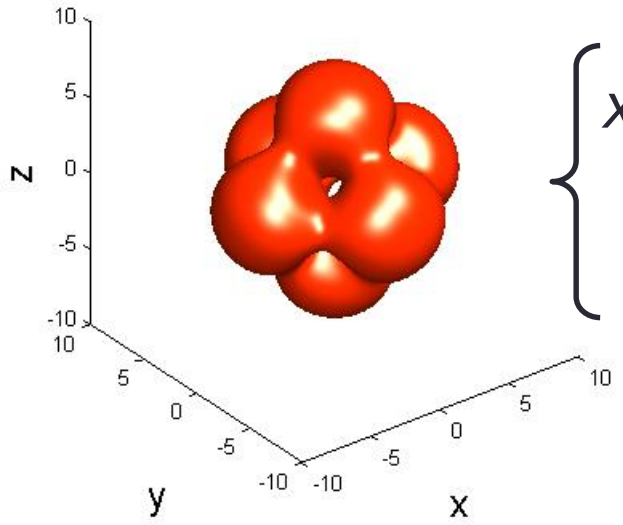


3d: Overlap of *d* Orbitals



xy
xz
yz

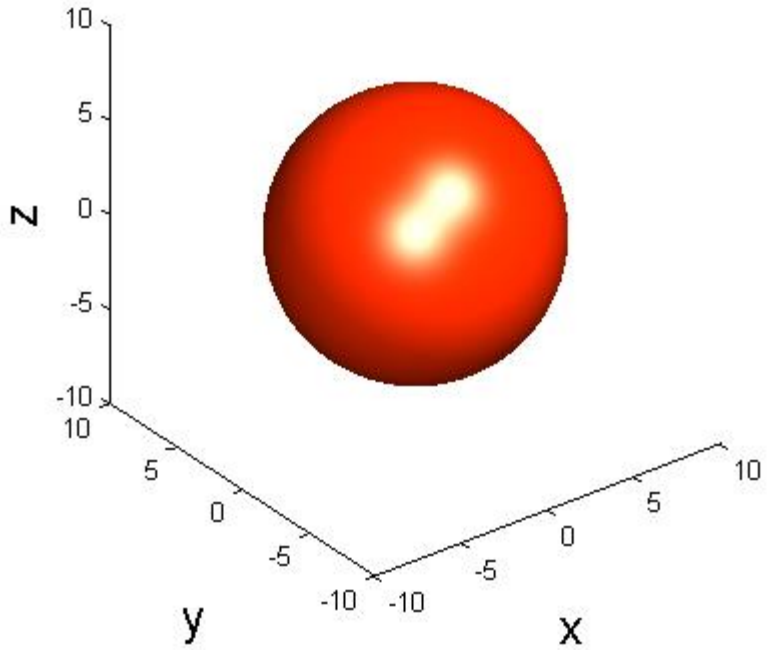
+



x^2-y^2

z^2

=



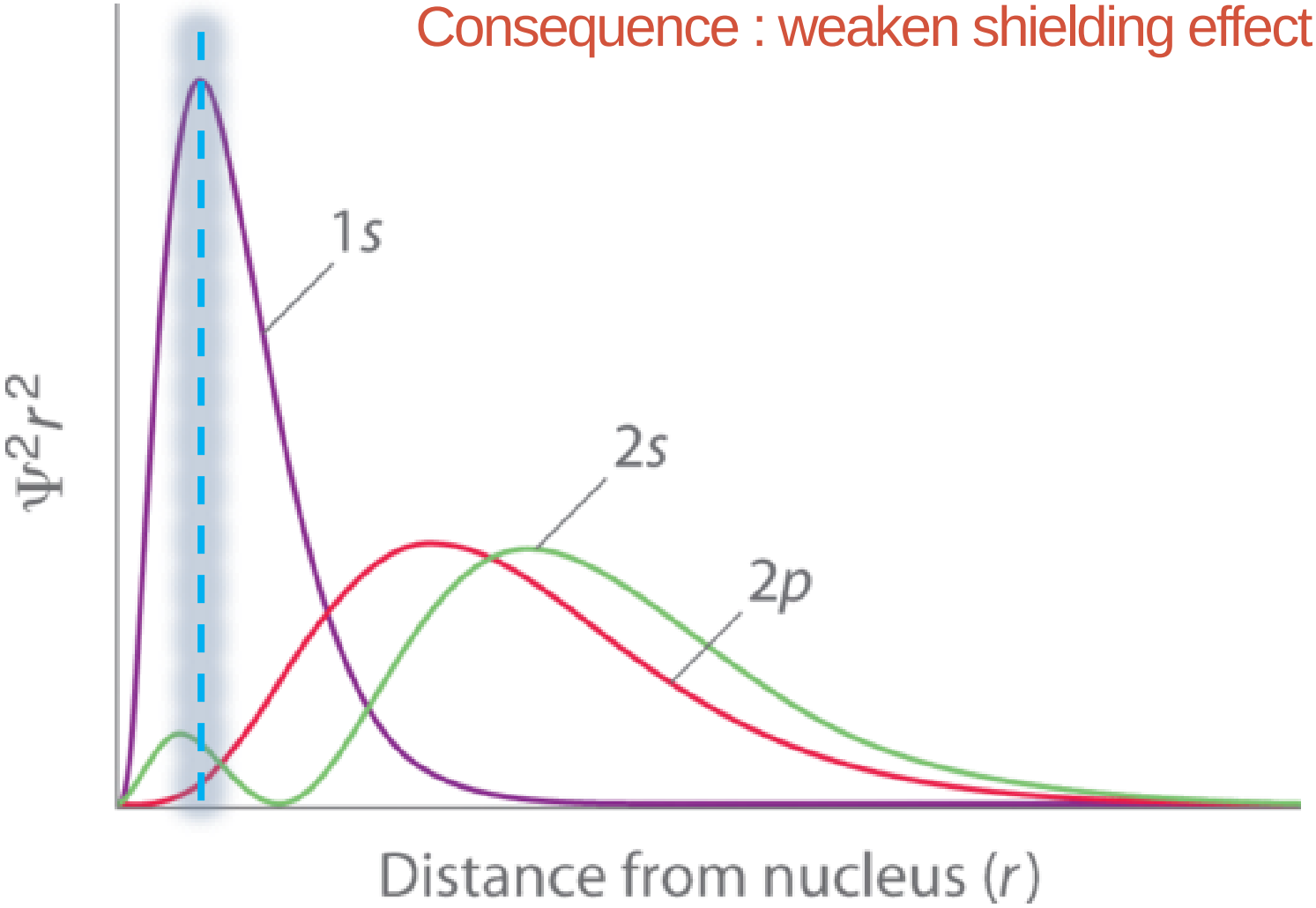
The five *d* orbitals occupy separate parts of the space.

Outline

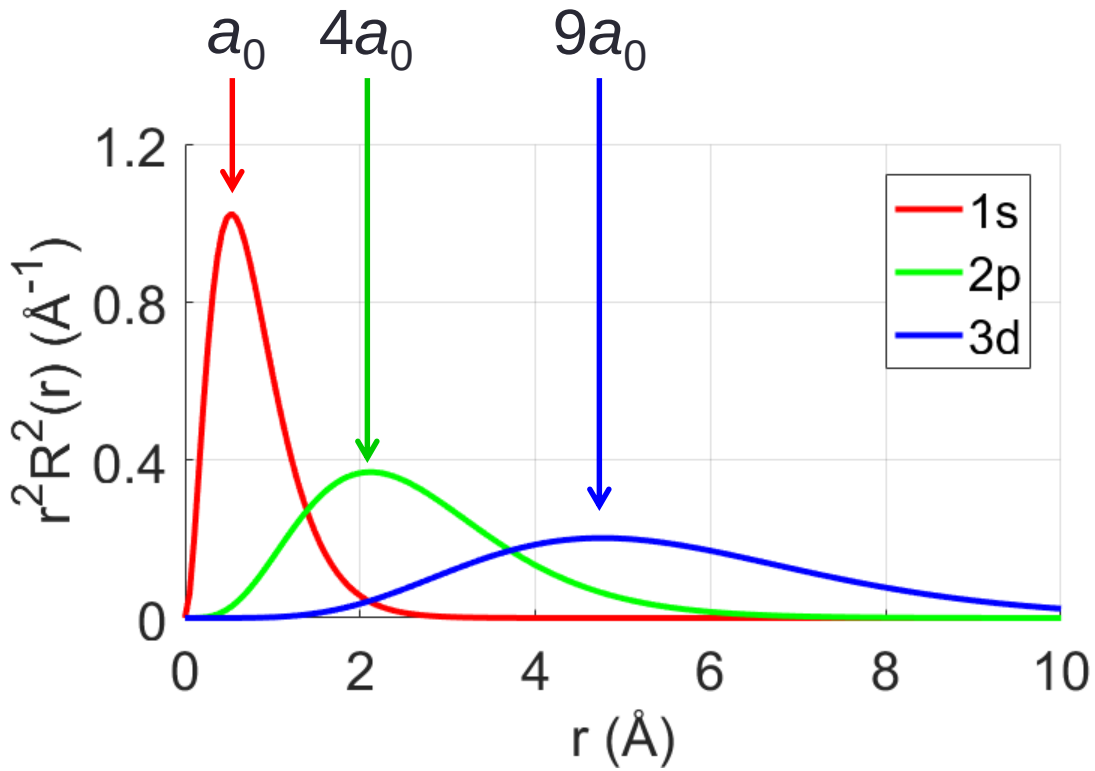
- Interactions in many-electron atoms
- Repulsion between electrons
  - Electrons with same n and l
  - Electrons with different n
  - Electrons with the same n but different l
- Aufbau principle
- Electron configurations

The Penetration Effect 钻穿效应

Consequence : weaken shielding effect

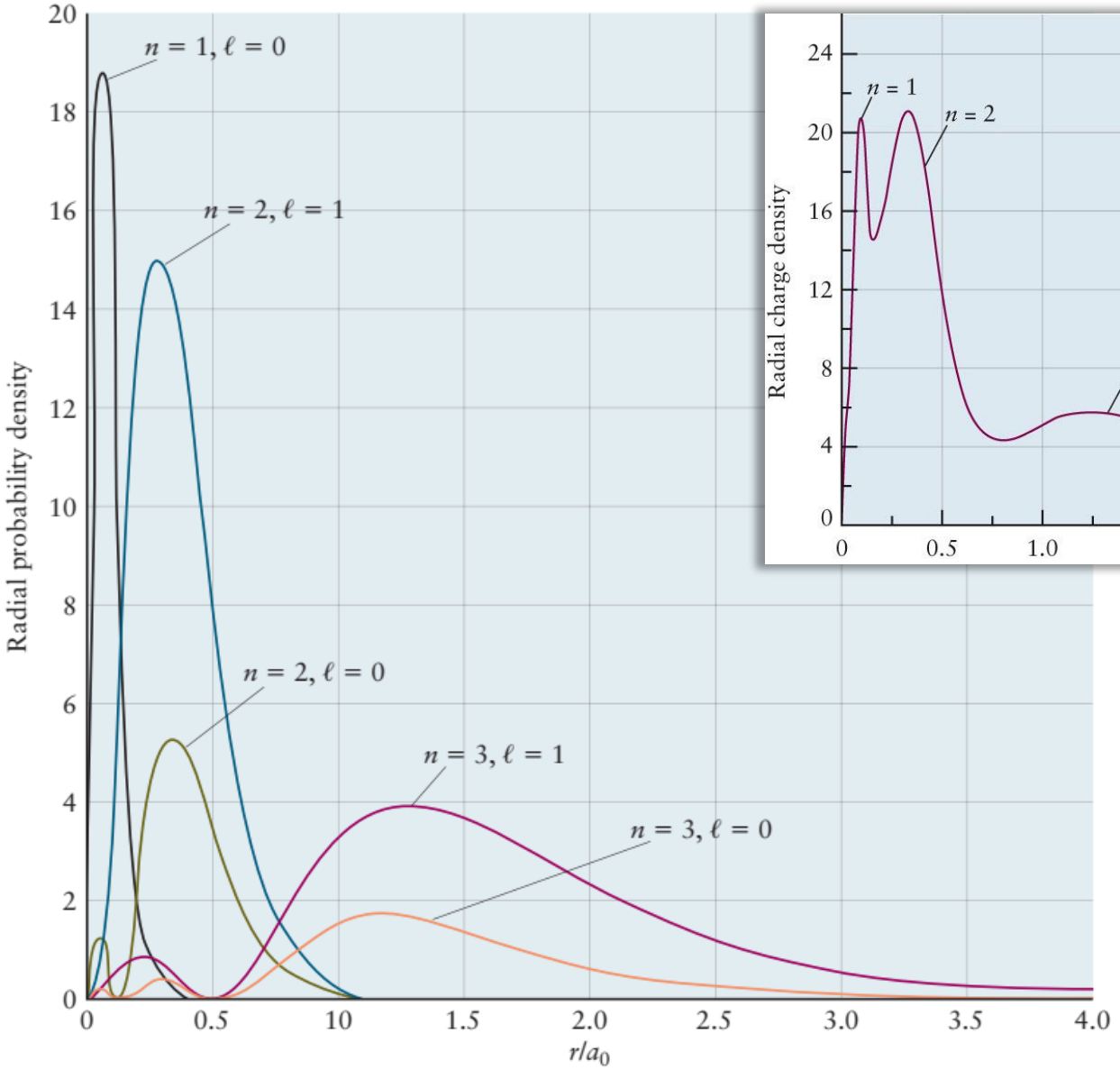


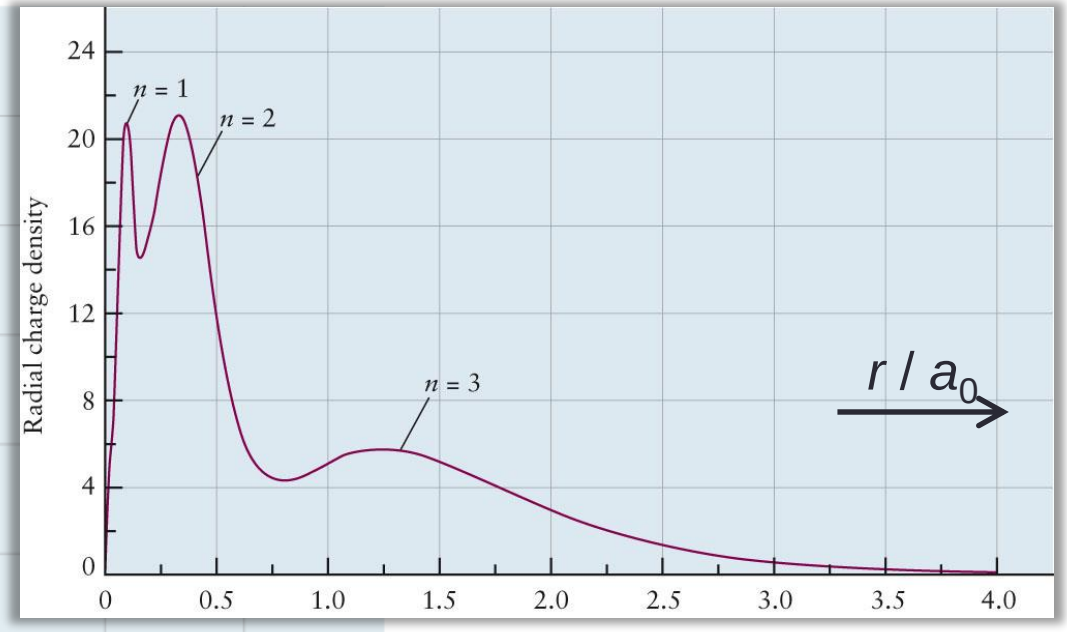
Overlap of Orbital Shells



1*s*−2*p* and 2*p*−3*d*: Some overlap. 1*s*−3*d*: Very little overlap

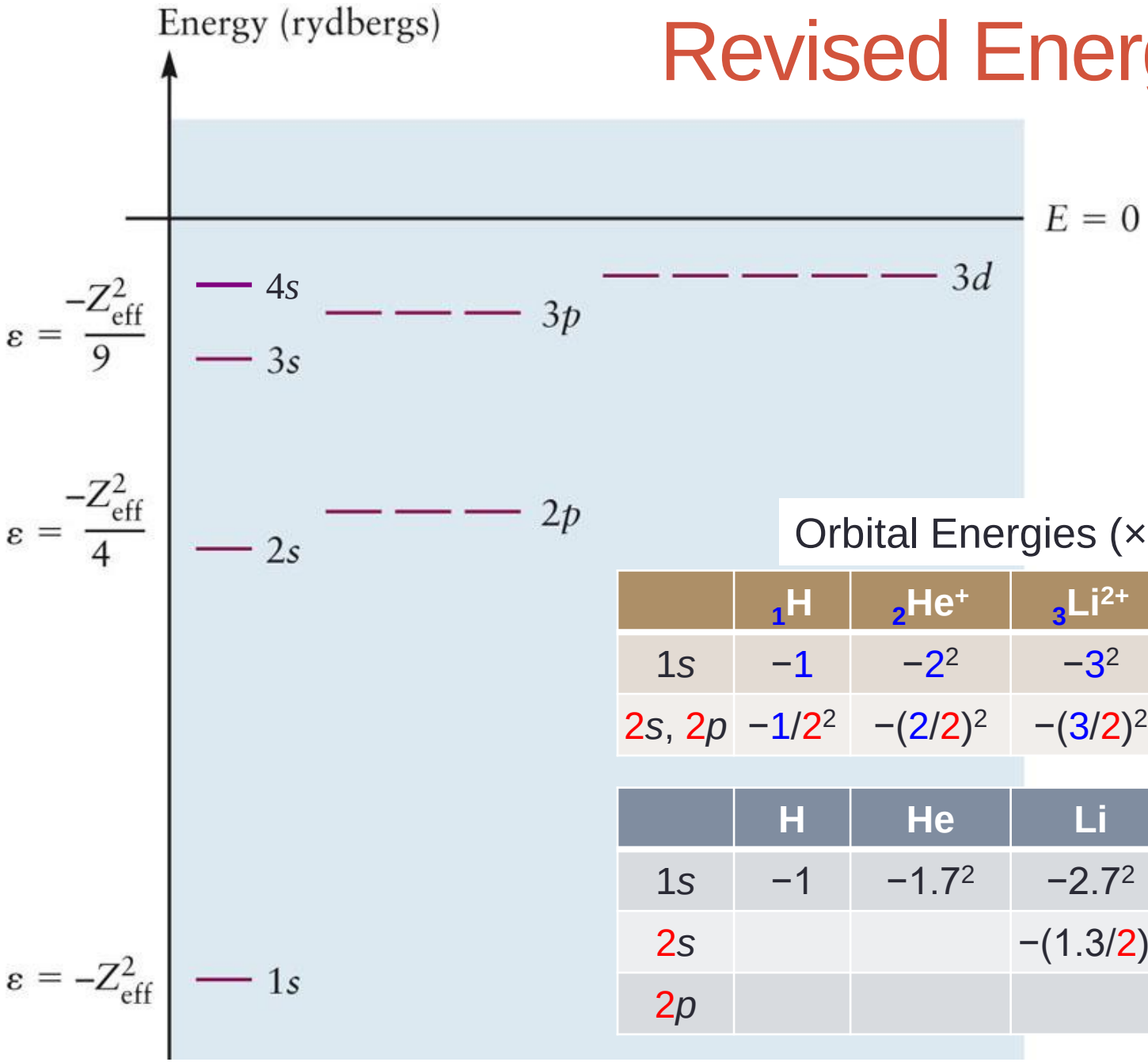
The Shell Model - hartree orbitals





Revised Energy Levels

(OGC7 p.215)



Orbital Energies (×13.6 eV)

	$_1$H	$_2$He$^+$	$_3$Li^{2+}	$_4$Be^{3+}	$_5$B^{4+}
1*s*	-1	-2^2	-3^2	-4^2	-5^2
2*s*, 2*p*	$-1/2^2$	$-(2/2)^2$	$-(3/2)^2$	$-(4/2)^2$	$-(5/2)^2$

	H	He	Li	Be	B
1*s*	-1	-1.7^2	-2.7^2	-3.7^2	-4.7^2
2*s*			$-(1.3/2)^2$	$-(1.9/2)^2$	$-(2.6/2)^2$
2*p*					$-(2.4/2)^2$

Outline

- Interactions in many-electron atoms
- The Shell Model
  - Orbital approximation
  - Effective nuclear charge Z_{eff}
- Aufbau principle
- Electron configurations
  - Li through Ne
  - Transition metals

Aufbau Principle 构造原理

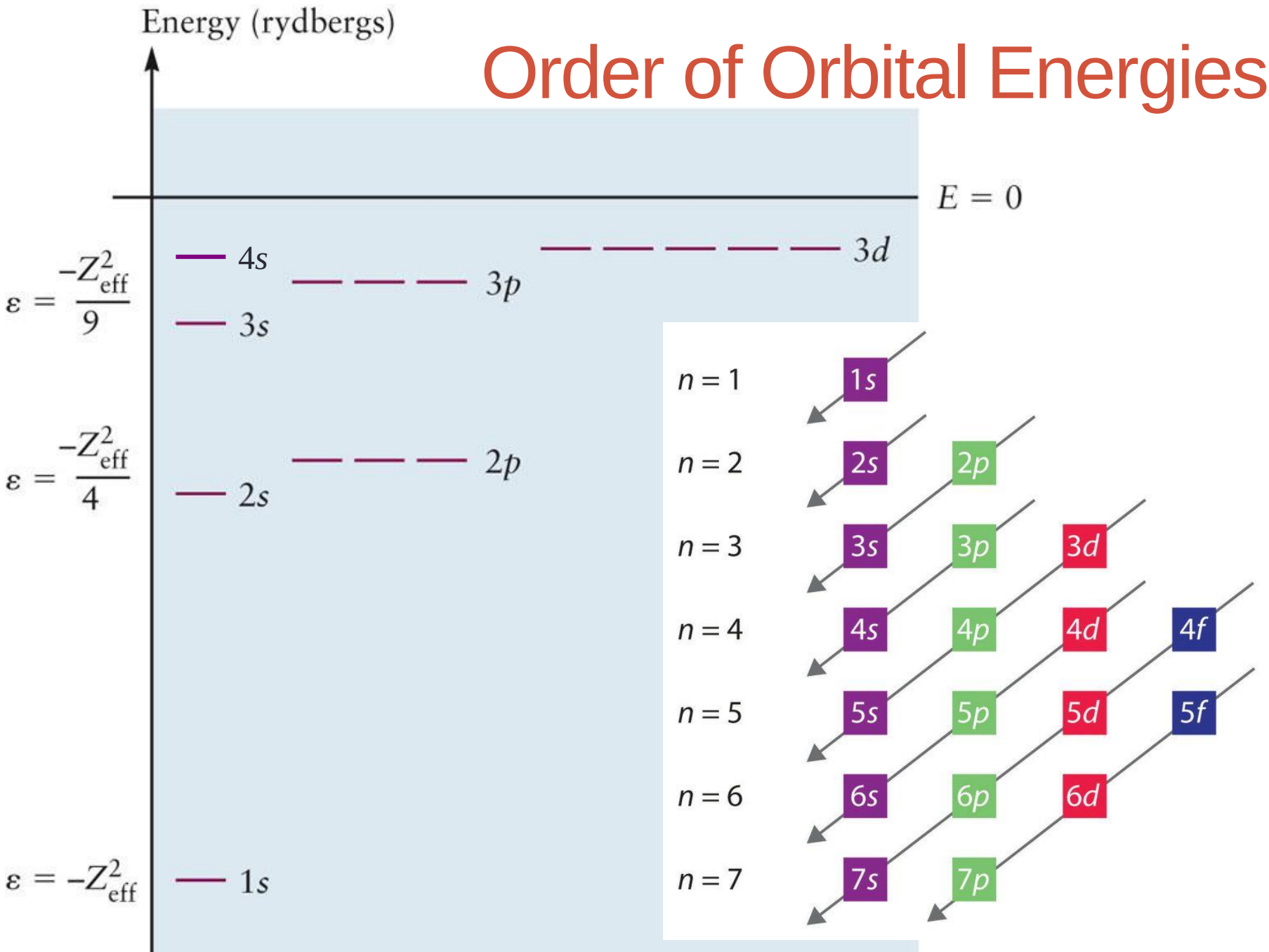
Pauli 1925: Each orbital holds ≤2 electrons, one spin up ↑ and the other spin down ↓.

Hund 1925: Electrons in degenerate orbitals prefer different *m* but the same spin.

Wolfgang Pauli
(1900–1958)

Friedrich Hund
(1896–1997)

Order of Orbital Energies



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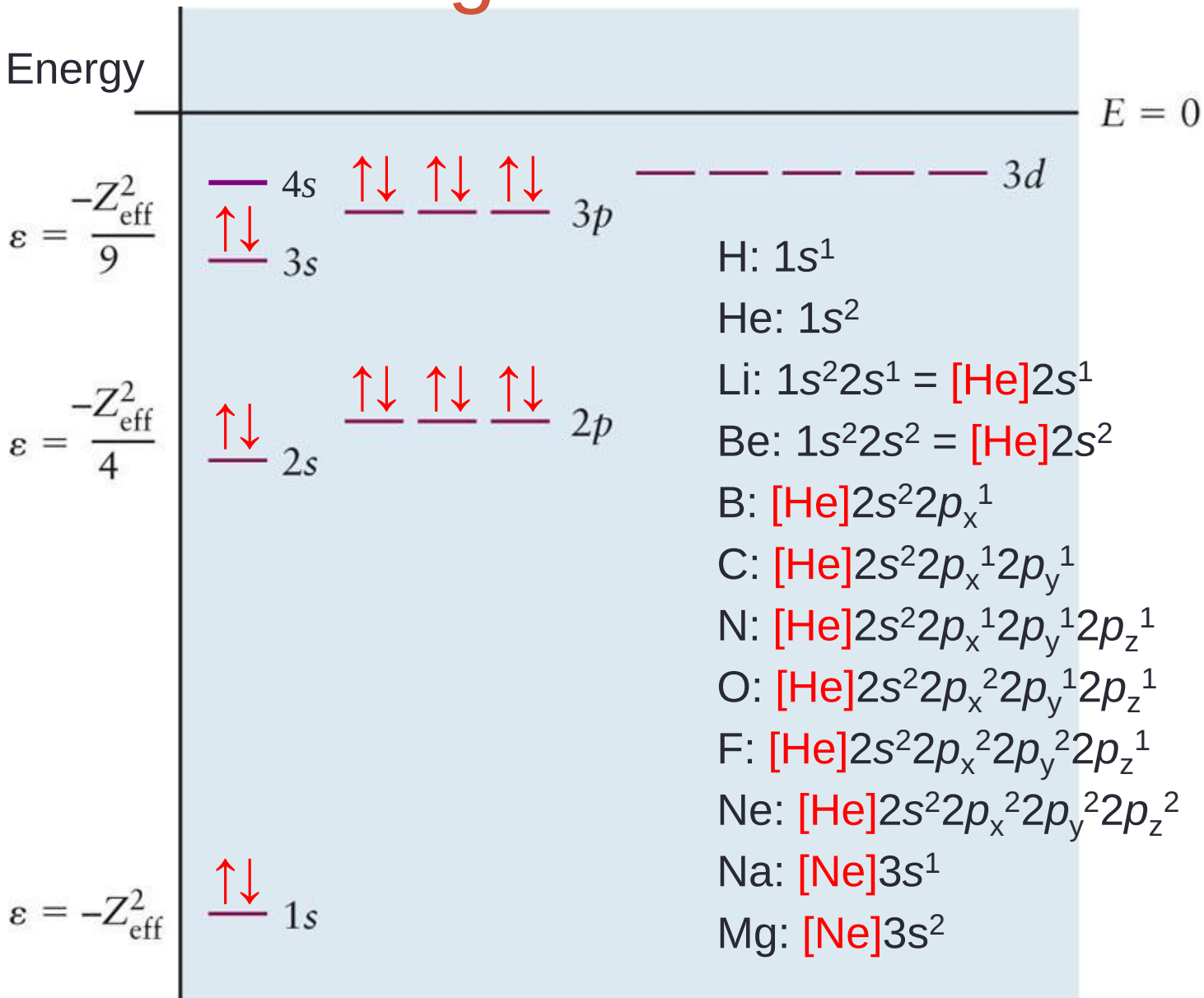
Electron Configurations of H thru Ar



H: $1s^1$

He: $1s^2$

Li: $1s^2 2s^1$ = [He]$2s^1$

Be: $1s^2 2s^2$ = [He]$2s^2$

B: [He]$2s^2 2p_x^1$

C: [He]$2s^2 2p_x^1 2p_y^1$

N: [He]$2s^2 2p_x^1 2p_y^1 2p_z^1$

O: [He]$2s^2 2p_x^2 2p_y^1 2p_z^1$

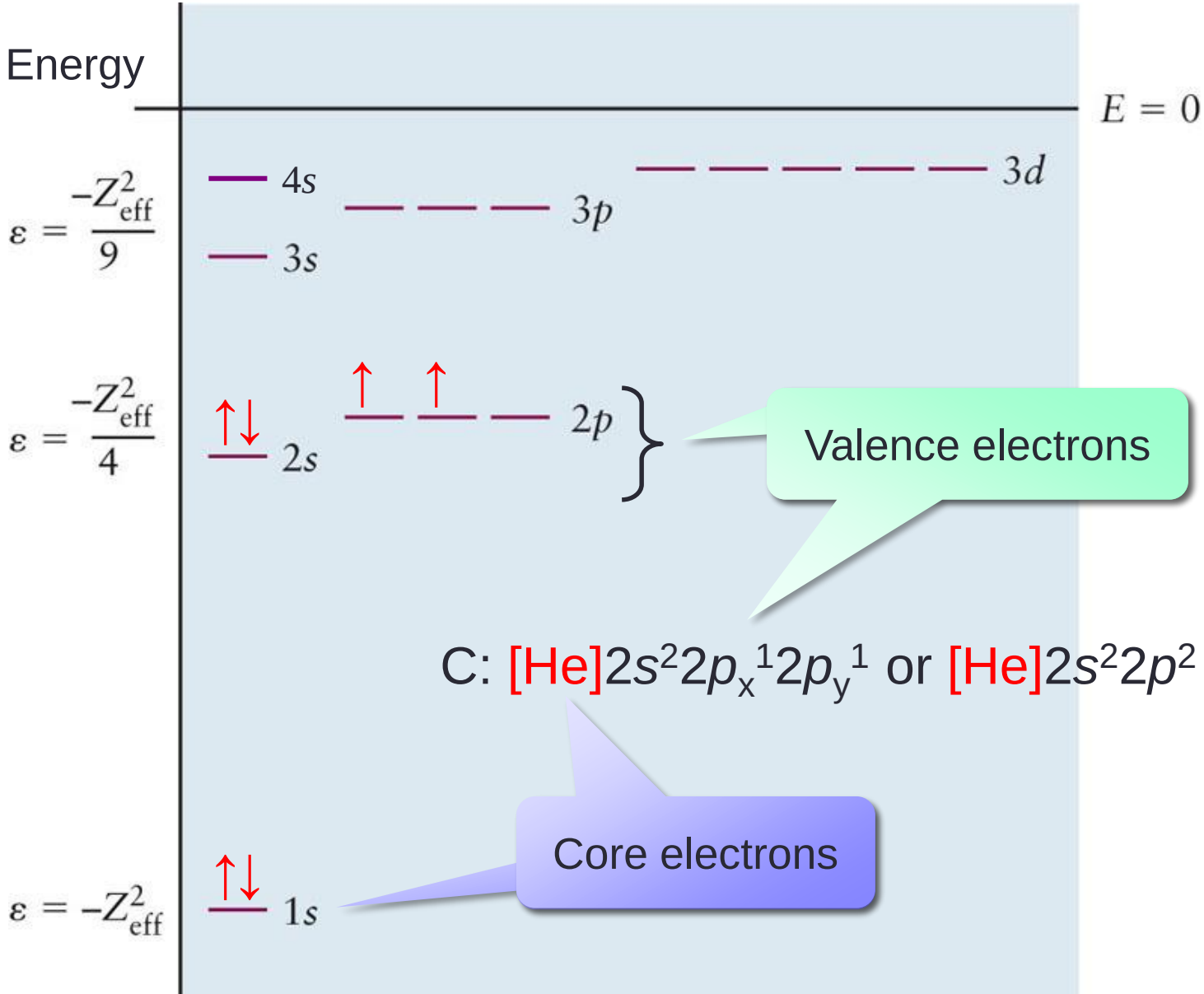
F: [He]$2s^2 2p_x^2 2p_y^2 2p_z^1$

Ne: [He]$2s^2 2p_x^2 2p_y^2 2p_z^2$

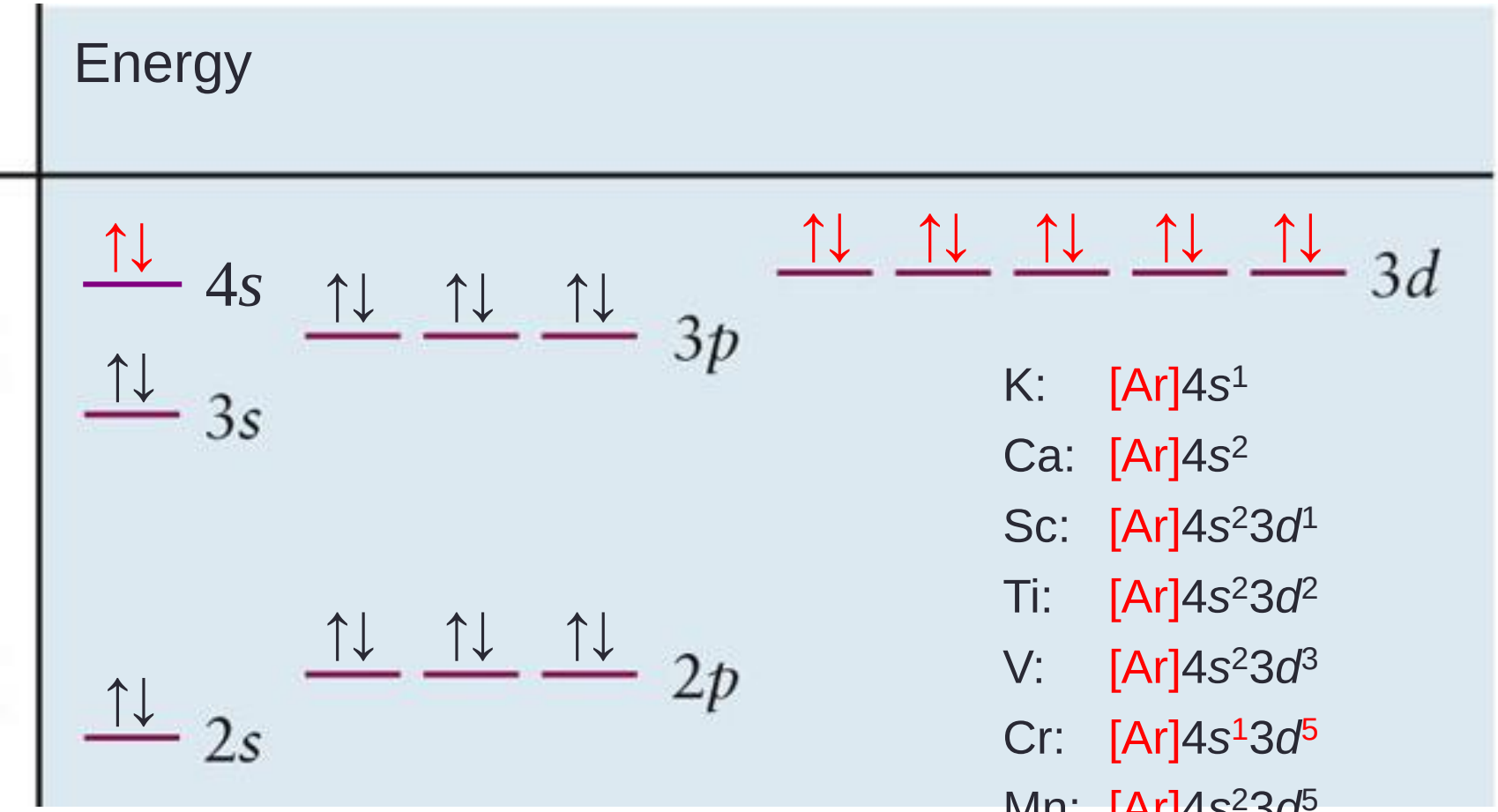
Na: [Ne]$3s^1$

Mg: [Ne]$3s^2$

Core and Valence Electrons



Electron Configurations of K thru Zn



K: [Ar]$4s^1$

Ca: [Ar]$4s^2$

Sc: [Ar]$4s^2 3d^1$

Ti: [Ar]$4s^2 3d^2$

V: [Ar]$4s^2 3d^3$

Cr: [Ar]$4s^1 3d^5$

Mn: [Ar]$4s^2 3d^5$

Fe: [Ar]$4s^2 3d^6$

Summary

- Electrons in many-electron atoms can be approximated by independent (sub)shells.
- Each subshell experiences an effective nuclear charge Z_{eff}.
- The order of the subshell energies is $1s < 2s < 2p < 3s < 3p < 4s \lesssim 3d$ …
- Aufbau principle determines how electrons fill into these subshells.

Next: Periodic Trends

- Reading:
- OGB8 §3.2, §§3.4–3.6, §5.5