Chapter 6

Electronic Structure of Atoms

Electronic configuration

Electronic Structure

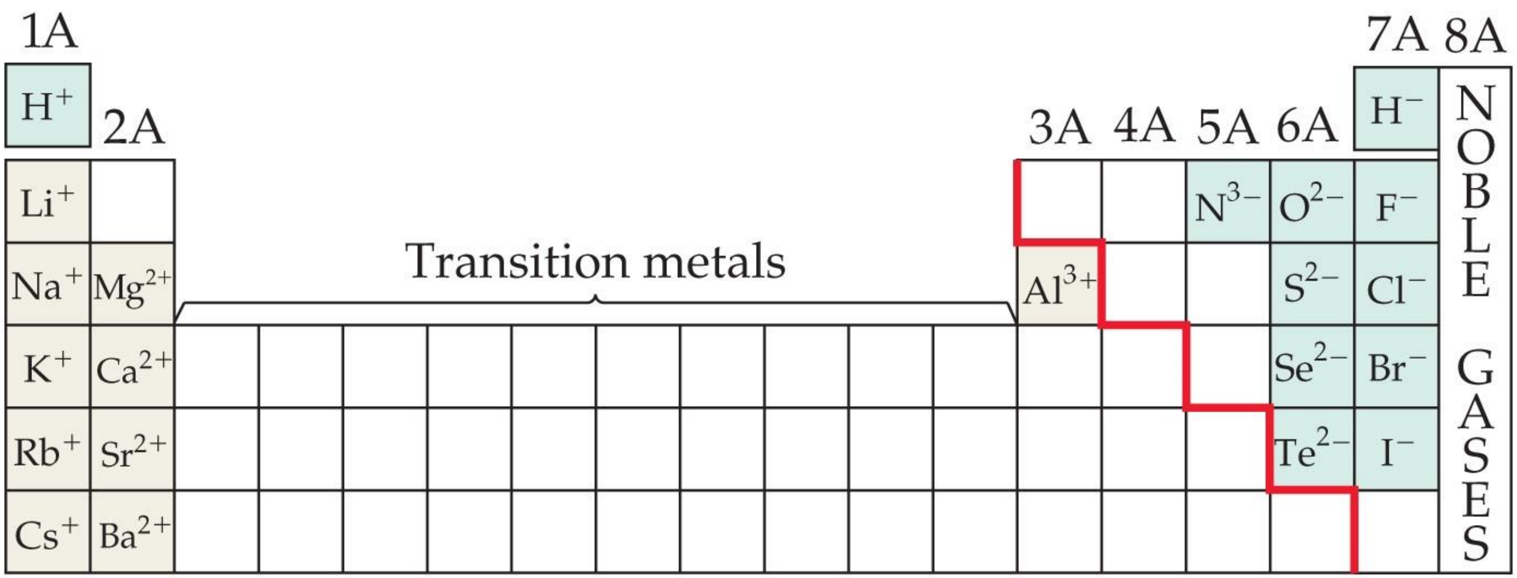
- This chapter is all about **electronic structure**—the arrangement and energy of electrons.

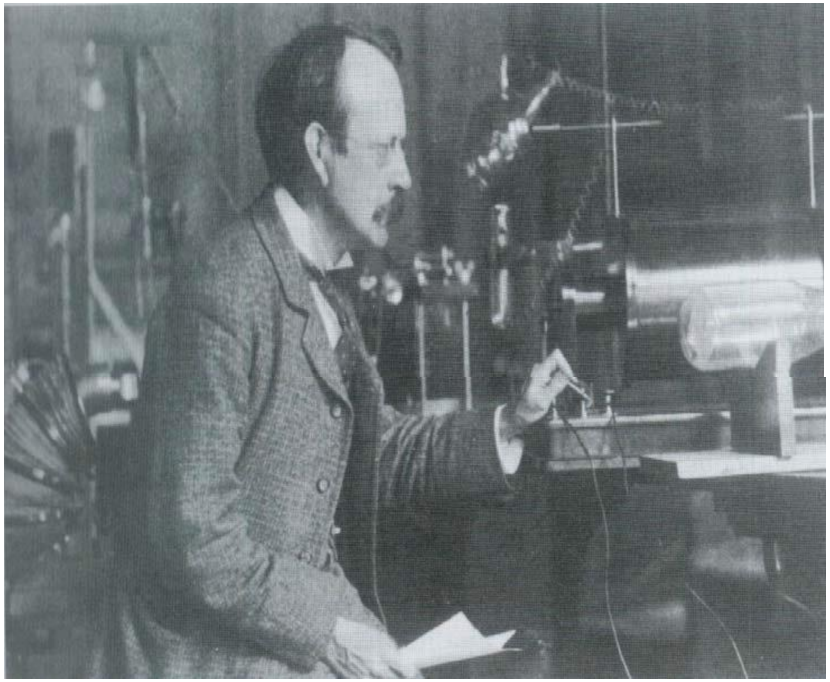
Arrangement – where are they located with respect to the nucleus?

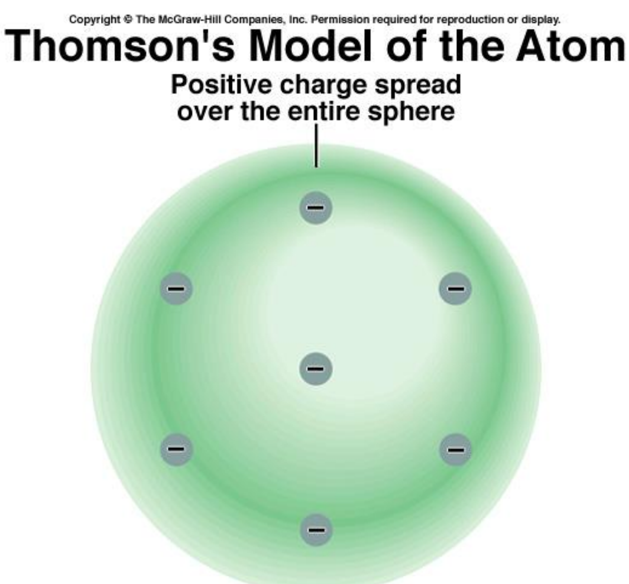
Energy – how energetic are they (core or valence electrons)?

Any similarity between elements? – determined by similar electronic structure – **periodicity** **(CHAPTER 7)**

Periodic Table - Periodicity







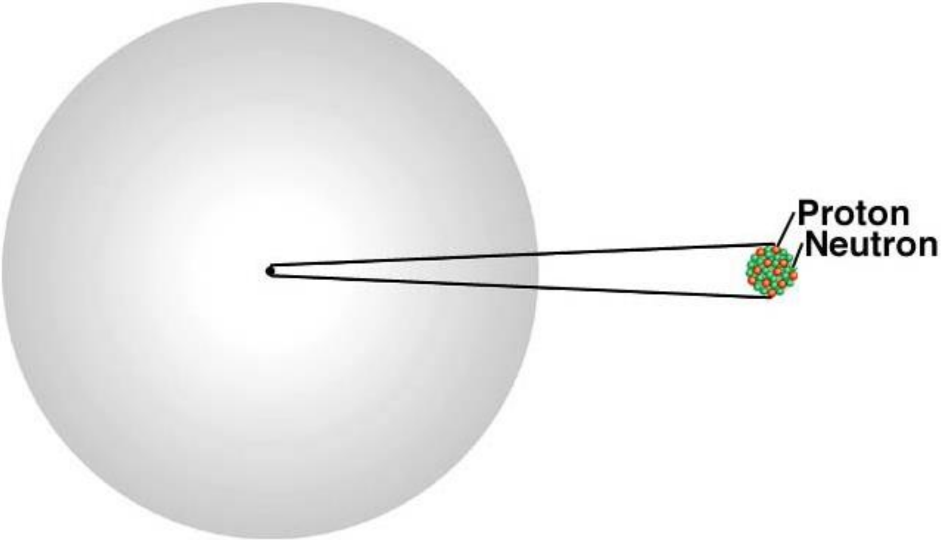
Joseph John Thomson (1856-1940), with the apparatus he used to discover the electron. 1906 Nobel Prize in Physics.

Thomson's model of the atom, sometimes described as the "plum-pudding"model, after a traditional English dessert containing raisins. The electrons are embedded in a uniform, positively charged sphere.

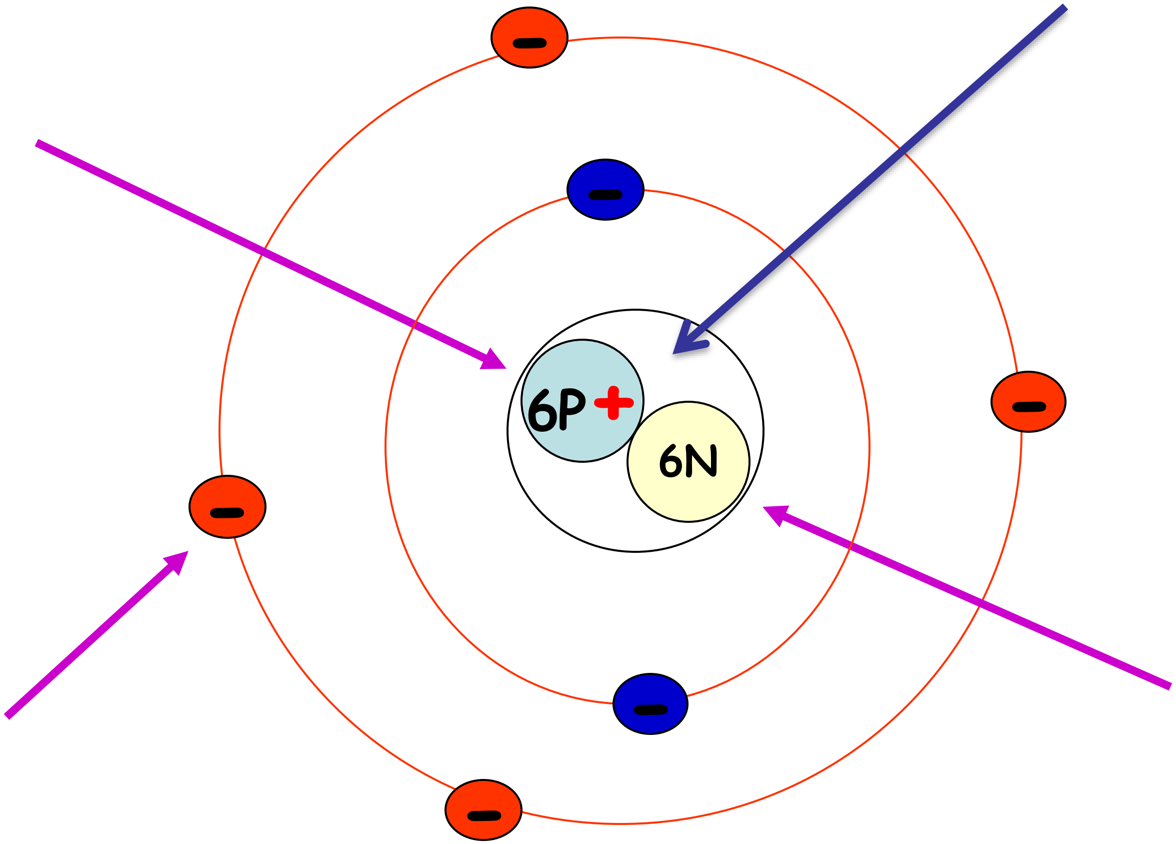
Ernest Rutherford
(1871-1937)
New Zealand Physicist
Victoria Univ., U.K.
The Nobel Prize in Chemistry 1908
"for his investigations into the disintegration of the elements, and the chemistry of radioactive substances"

Rutherford 的核型原子模型——原子中心有一个原子核，它集中了原子全部正电荷核几乎全部质量，而带负电的电子在核外空间绕核高速运动。他还根据不同散射角的α粒子比例近似计算出金原子核的荷电核数(Z)及核的大小。

实验证明一般原子核半径范围在1-10pm，只有原子半径的万分之一到十万分之一。



trouble makers - responsible for chemical reactions!



isoelectronic

$_{10}Ne$

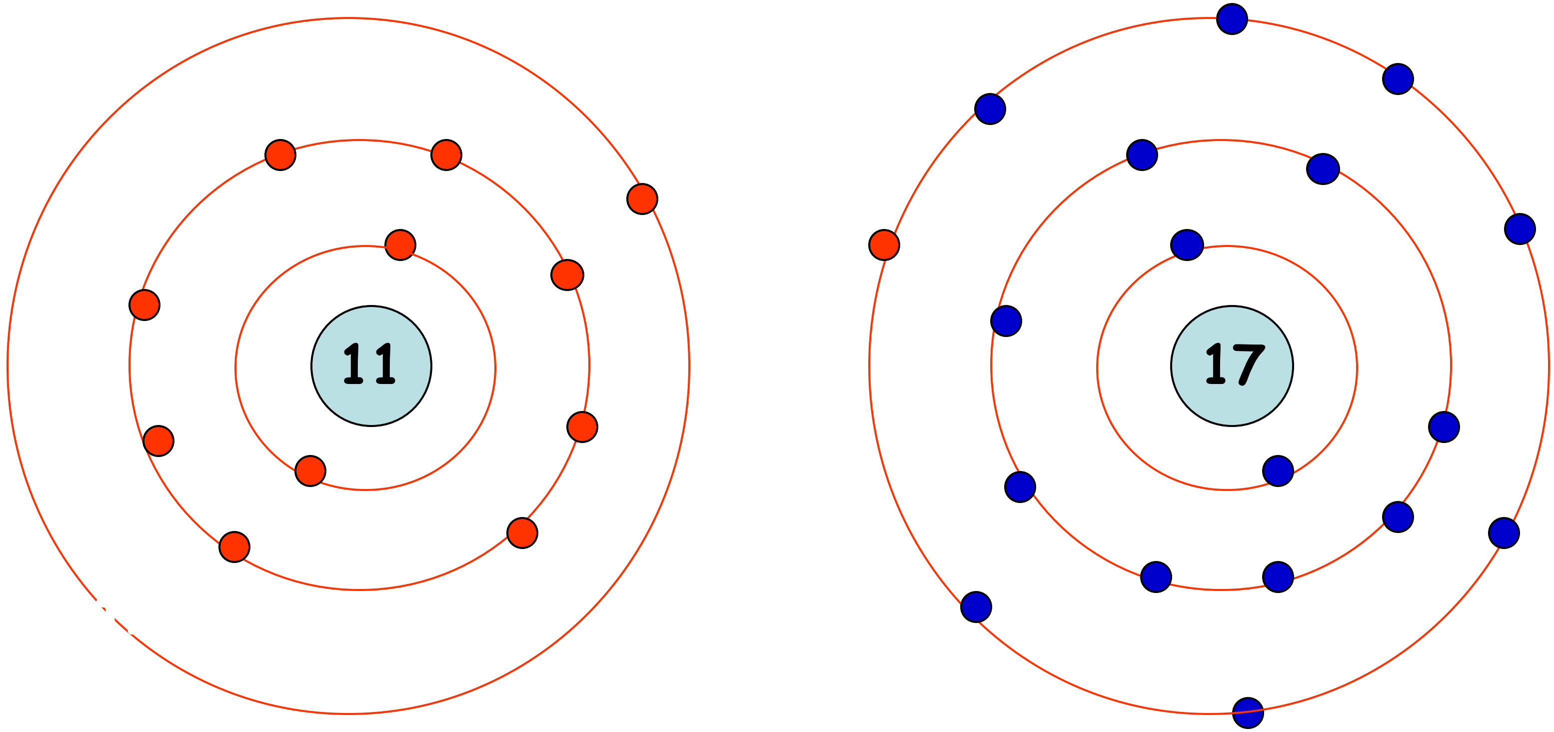
$_{11}Na\ (1s^2 2s^2 2p^6 3s^1)$

$_{11}Na\ (1s^2 2s^2 2p^6 3s^0)$ $_{11}Na^+$

$_{18}Ar$

$_{17}Cl(1s^2 2s^2 2p^6 3s^2 3p^5)$

$_{17}Cl(1s^2 2s^2 2p^6 3s^2 3p^6)$ $_{17}Cl^-$



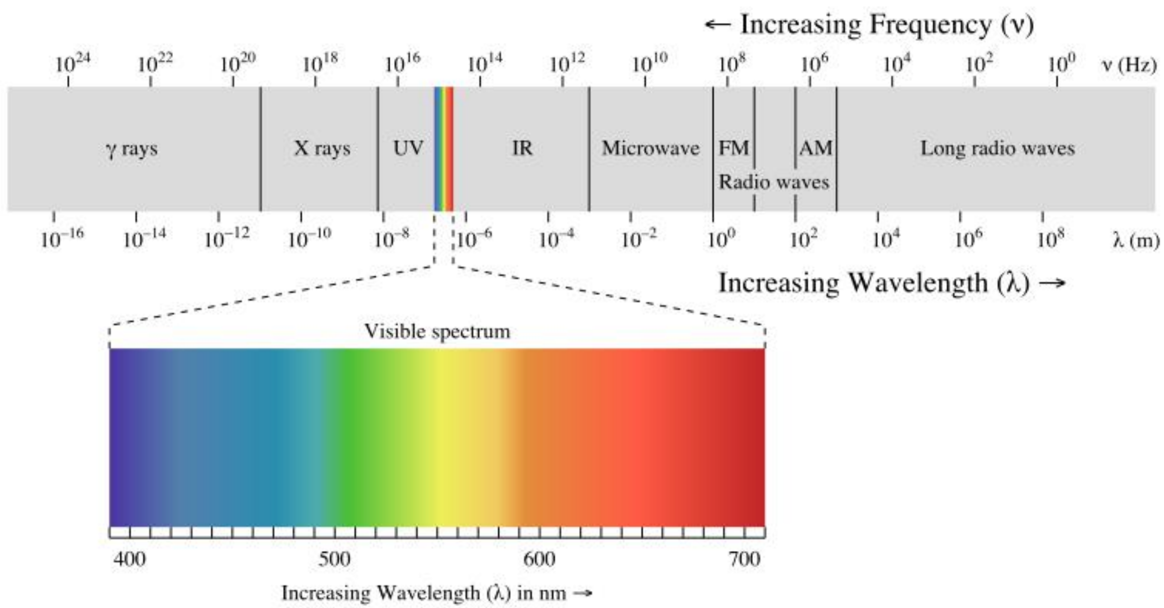
$_{11}Na^+$ $_{17}Cl^-$

NaCl

The wave nature of light

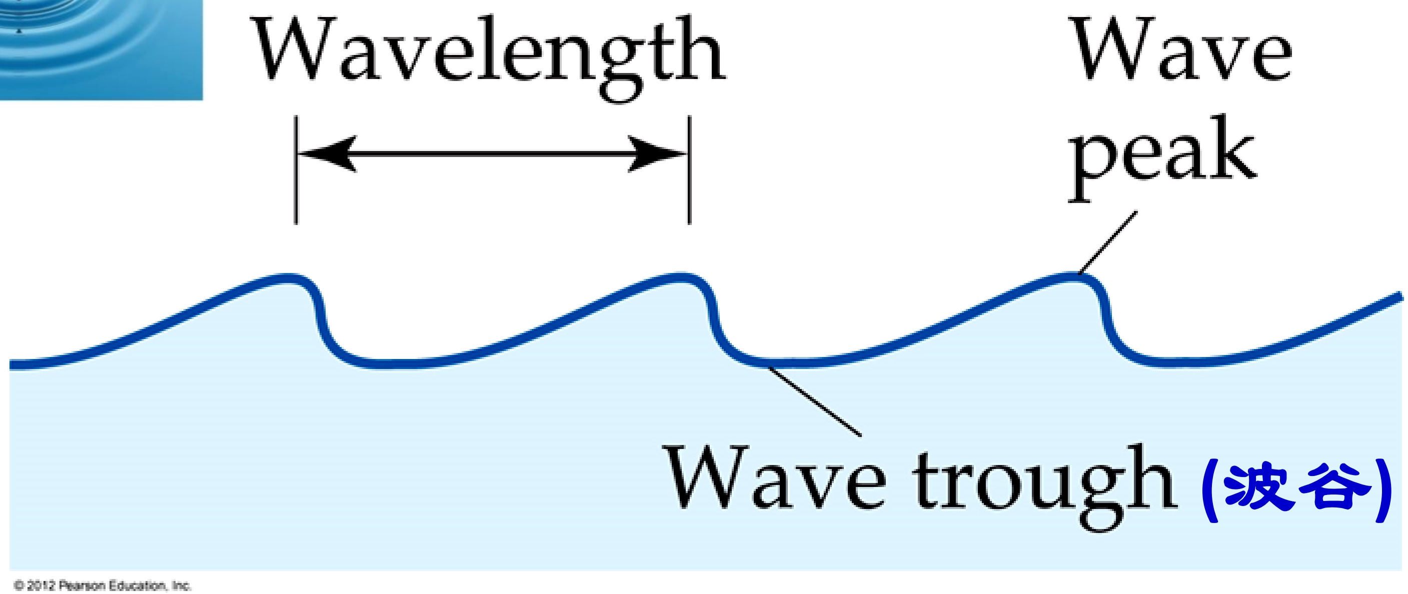
- Electromagnetic radiation(电磁辐射)

  A fundamental phenomenon of electromagnetism, behaving as **waves** and also as **particles** called photons(光子) which travel through space carrying radiant energy.

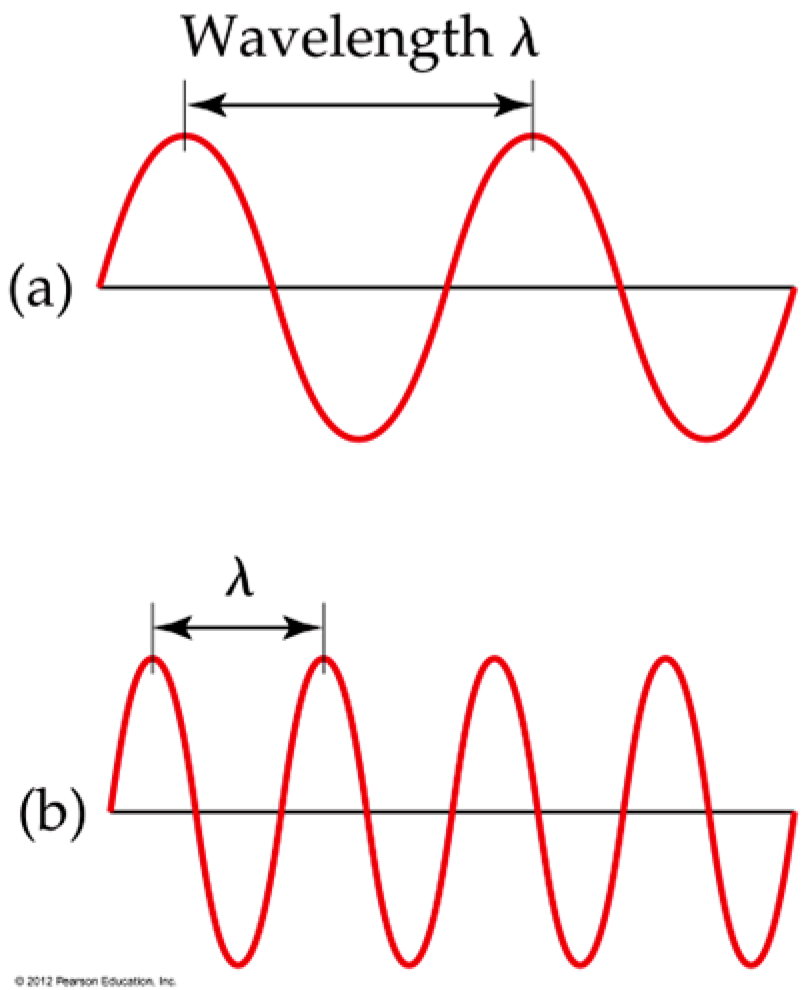


Waves(波)

- The distance between corresponding points on adjacent waves is the **wavelength (*λ*波长-*m*)**.



➢ Waves



- The number of waves passing a given point per unit of time is the **frequency(频率 ν) (s^{-1})**.
- For waves traveling at the same velocity, the longer the wavelength, the smaller the frequency.
- Frequency is expressed in cycles per second (s^{-1}), also call hertz (Hz)

frequency ν-v velocity

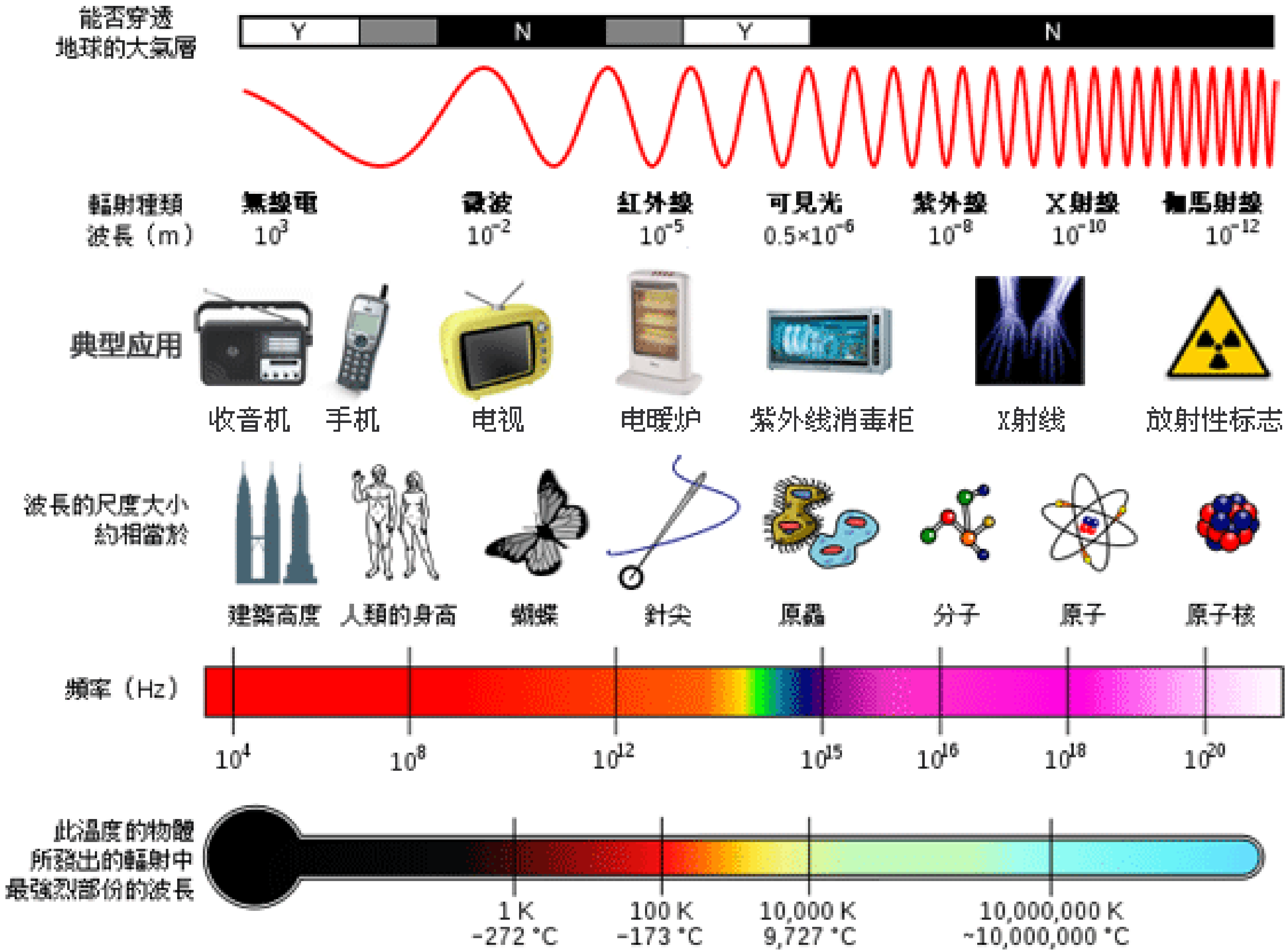
➢ Electromagnetic Radiation(电磁辐射)

High frequency, short wave length $c = \lambda \nu$

TABLE 6.1 • Common Wavelength Units for Electromagnetic Radiation

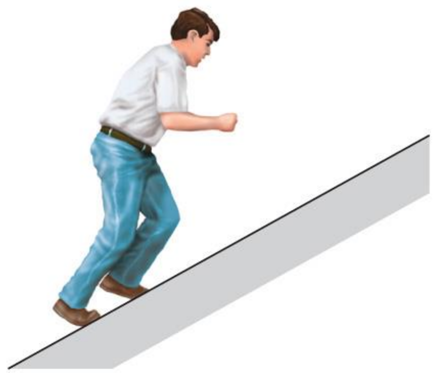
Unit	Symbol	Length (m)	Type of Radiation
Angstrom	Å	10^{-10}	X-ray
Nanometer	nm	10^{-9}	Ultraviolet, visible
Micrometer	μm	10^{-6}	Infrared
Millimeter	mm	10^{-3}	Microwave
Centimeter	cm	10^{-2}	Microwave
Meter	m	1	Television, radio
Kilometer	km	1000	Radio

Our bodies are penetrated by X-ray but not by visible light. Is this because X-ray travel faster than visible light?



能否穿透地球的大氣層
Y
N
Y
N
輻射種類
波長（m）
無線電
10^3
微波
10^{-2}
红外線
10^{-5}
可見光
0.5×10^{-6}
紫外線
10^{-8}
X射線
10^{-10}
伽馬射線
10^{-12}
典型应用
收音机
手机
电视
电暖炉
紫外线消毒柜
X射线
放射性标志
波長的尺度大小約相當於
建築高度
人類的身高
蝴蝶
針尖
原蟲
分子
原子
原子核
頻率（Hz）
10^4
10^8
10^{12}
10^{15}
10^{16}
10^{18}
10^{20}
此溫度的物體所發出的輻射中最強烈部份的波長
1 K
-272 °C
100 K
-173 °C
10,000 K
9,727 °C
10,000,000 K
~10,000,000 °C

The Nature of Energy—Quanta



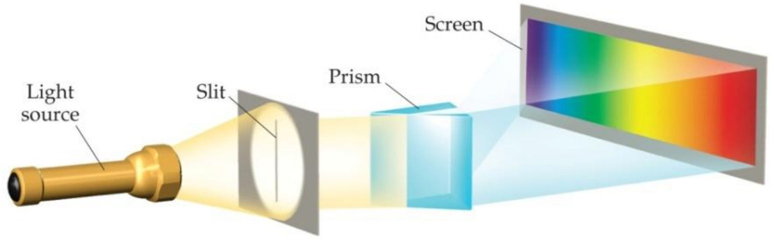
Potential energy of person walking up ramp increases in uniform, continuous manner

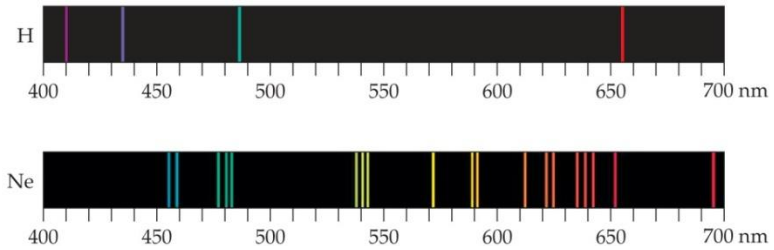
Potential energy of person walking up steps increases in stepwise, quantized manner

Max Planck explained it by assuming that energy comes in packets called **quanta** (singular: quantum).

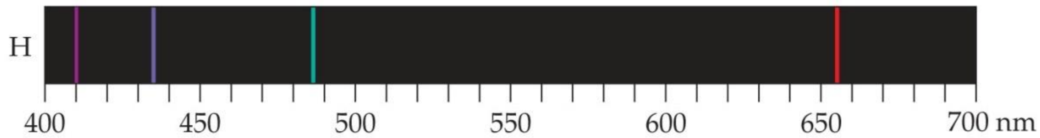
Continuous vs. Line Spectra

- For atoms and molecules, one does not observe a **continuous spectrum** (the “rainbow”), as one gets from a white light source.
- Only a **line spectrum** of discrete wavelengths is observed. Each element has a unique line spectrum.





The Hydrogen Spectrum

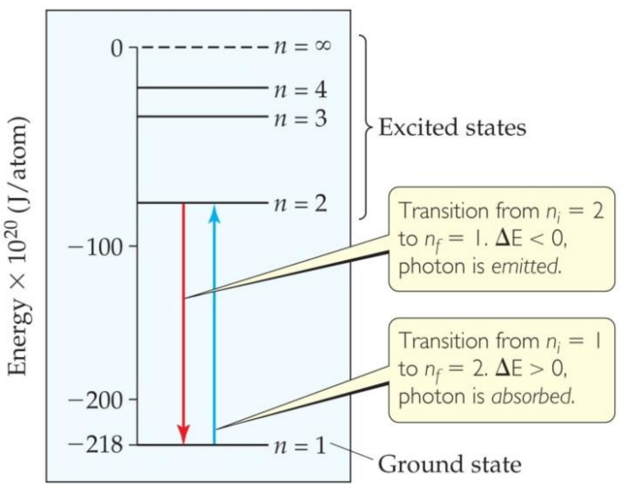


- Johann Balmer (1885) discovered a simple formula relating the four lines to integers.
- Johannes Rydberg advanced this formula.

$$\frac{1}{\lambda} = (R_{\mathrm{H}})\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

- Neils Bohr explained *why* this mathematical relationship works.

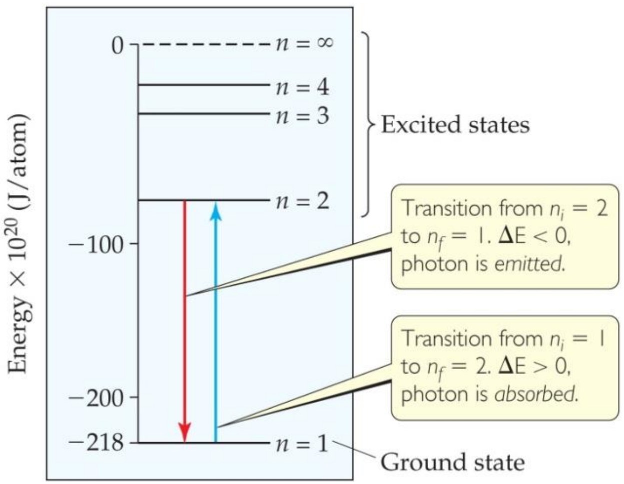
The Bohr Model



- Niels Bohr adopted Planck's assumption and explained these phenomena in this way:

1. Electrons in an atom can only occupy certain orbits (corresponding to certain energies).

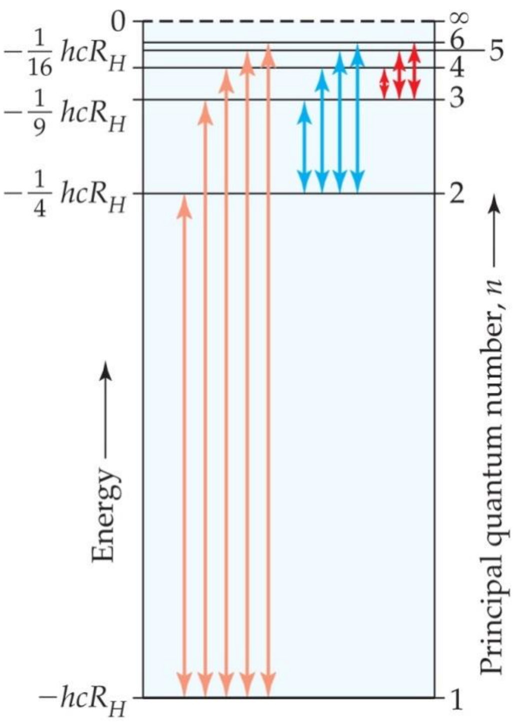
The Bohr Model



2. Electrons in permitted orbits have specific, “allowed” energies; these energies will not be radiated from the atom.
3. Energy is only absorbed or emitted in such a way as to move an electron from one “allowed” energy state to another; the energy is defined by

$$E = h\nu$$

The Bohr Model



The energy absorbed or emitted from the process of electron promotion or demotion can be calculated by the equation

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

where R_H is the Rydberg constant, $1.097 \times 10^7\ \mathrm{m}^{-1}$, and n_i and n_f are the initial and final energy levels of the electron.

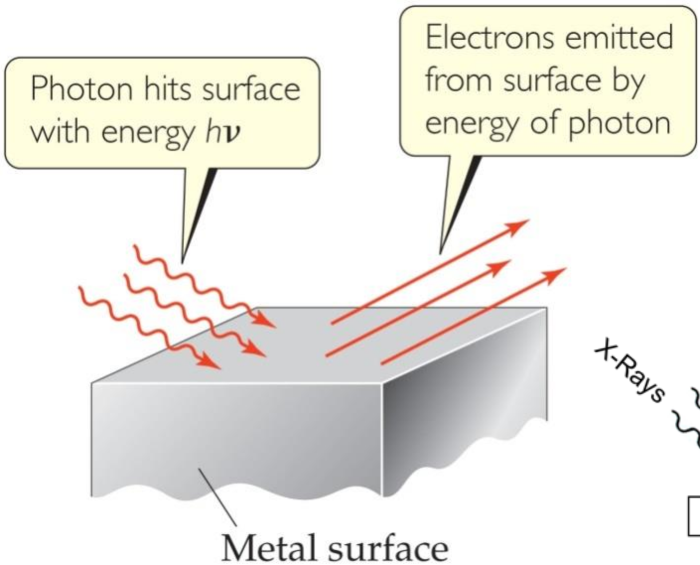
Important Ideas from the Bohr Model

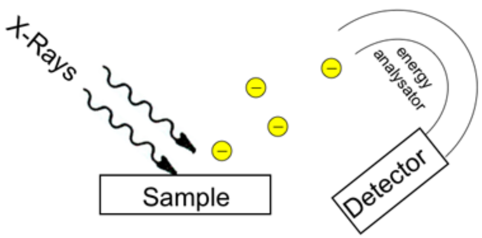
- Points that are incorporated into the current atomic model include the following:

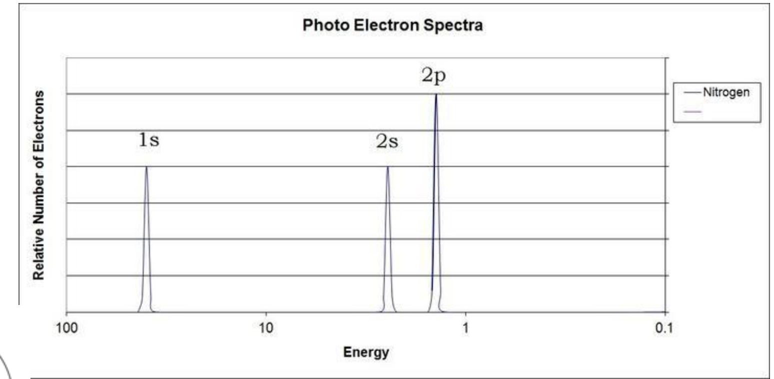
1) Electrons exist only in certain discrete energy levels（energy is quantized）.

2) Energy is involved in the transition of an electron from one level to another.

The Photoelectric Effect





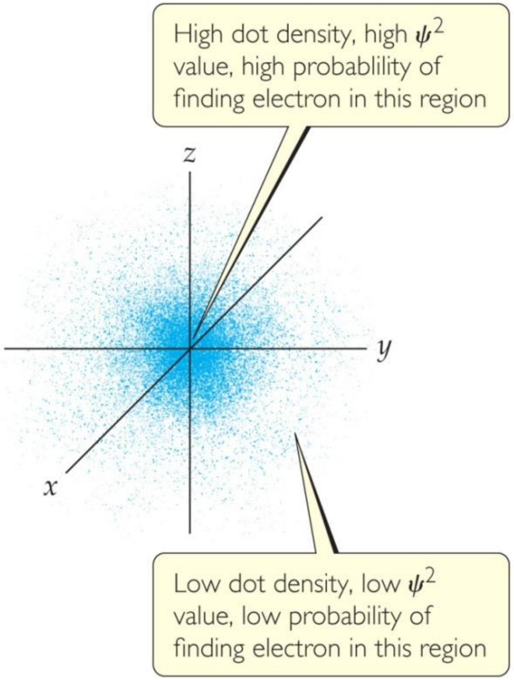


- Einstein used quanta to explain the photoelectric effect.
- Each metal has a different energy at which it ejects electrons. At lower energy, electrons are not emitted.
- He concluded that energy is proportional to frequency:

$E = h\nu$, where h is Planck's constant, 6.626×10^{-34} J·s.

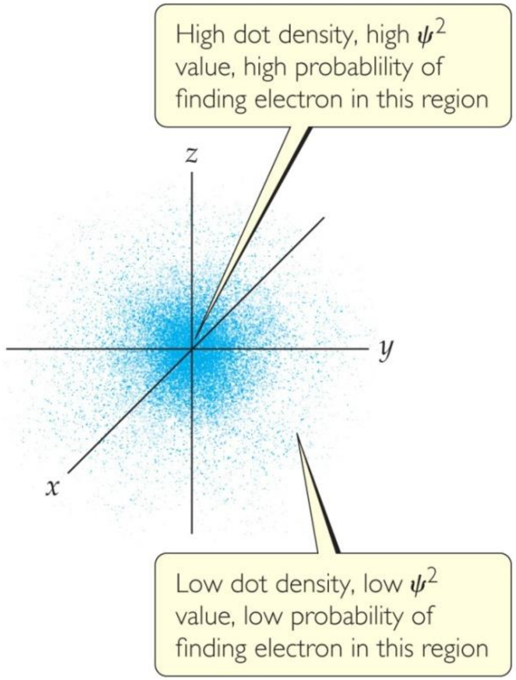
Quantum Mechanics

- Erwin Schrödinger developed a mathematical treatment into which both the wave and particle nature of matter could be incorporated.
- This is known as **quantum mechanics.**

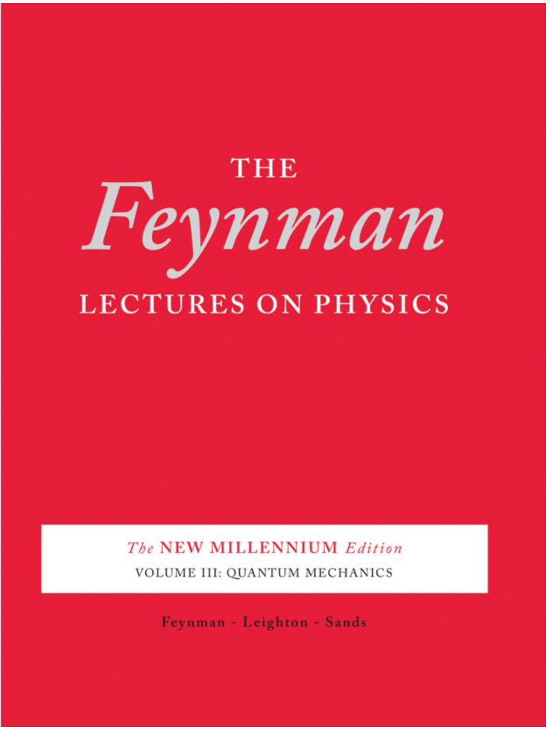


Quantum Mechanics

- The solution of Schrödinger's wave equation is designated with a lowercase Greek psi (ψ).
- The square of the wave equation, ψ^2, gives the **electron density**, or probability of where an electron is likely to be at any given time.



An experiment with bullets



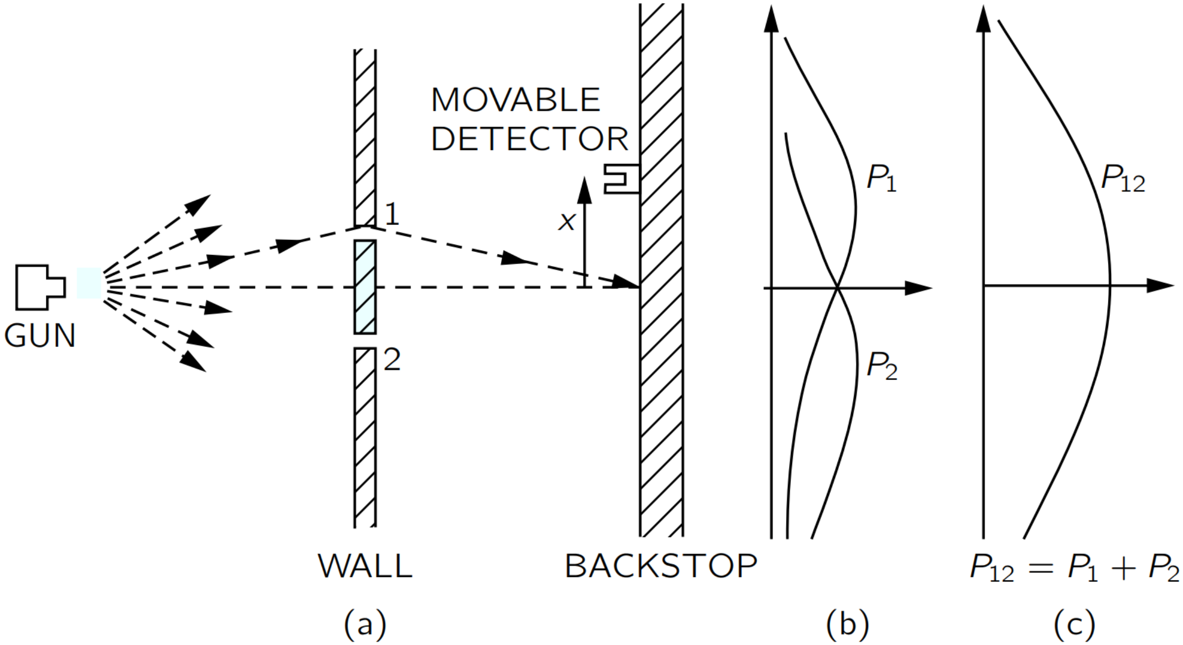


Fig. 1-1. Interference experiment with bullets.

An experiment with waves

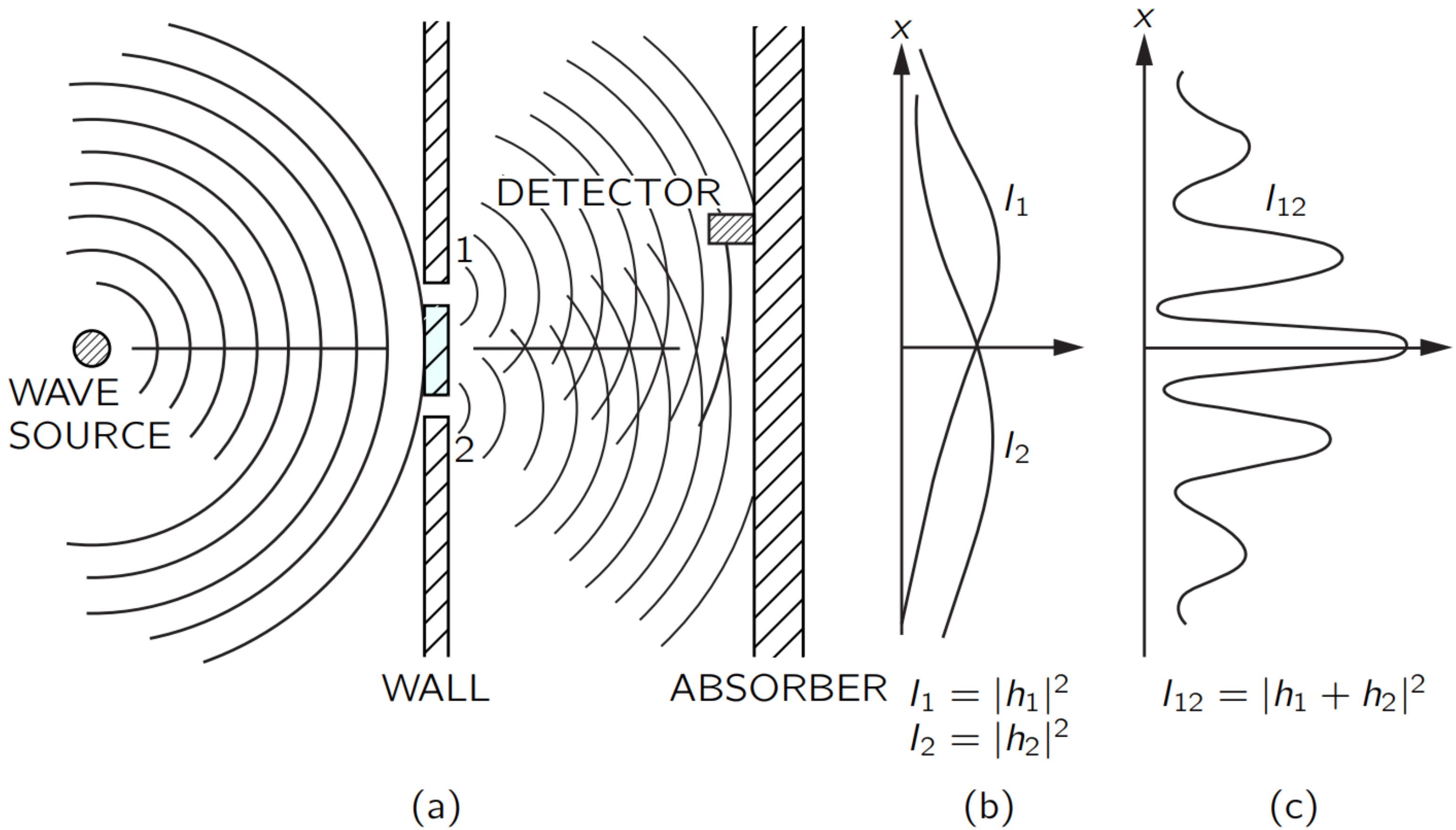


Fig. 1-2. Interference experiment with water waves.

An experiment with electrons

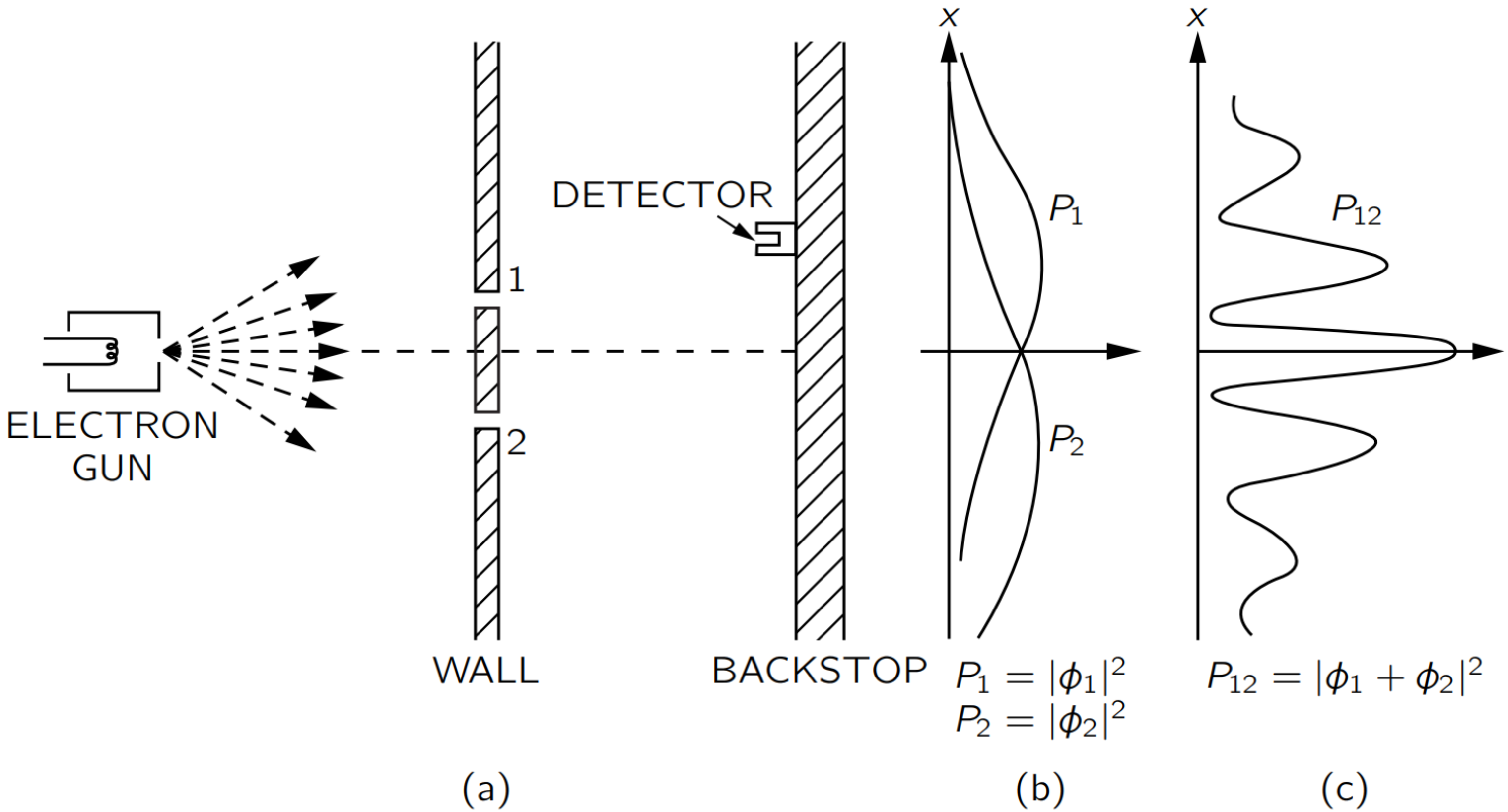


Fig. 1-3. Interference experiment with electrons.

Watching the electrons

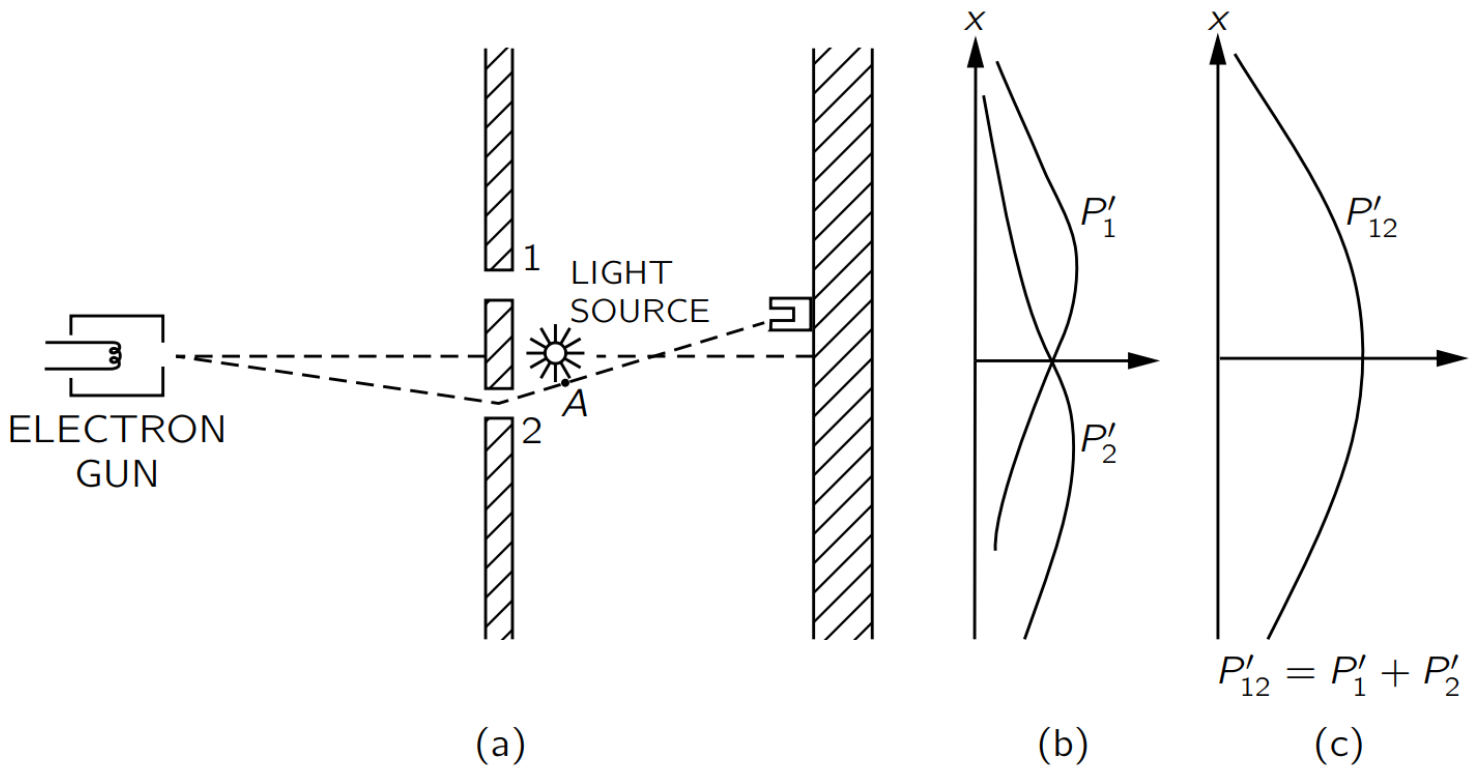
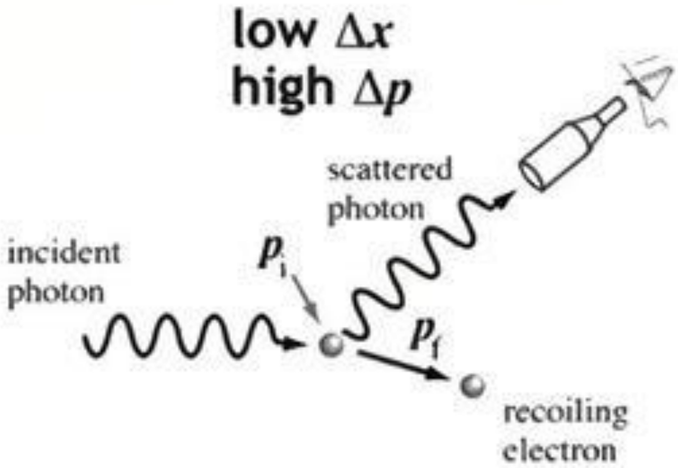


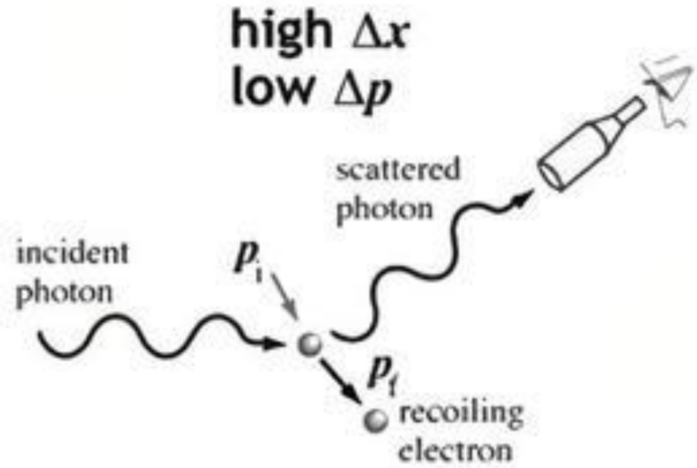
Fig. 1-4. A different electron experiment.

Heisenberg Uncertainty Principle

$$\Delta x \, \Delta p \geq \hbar$$

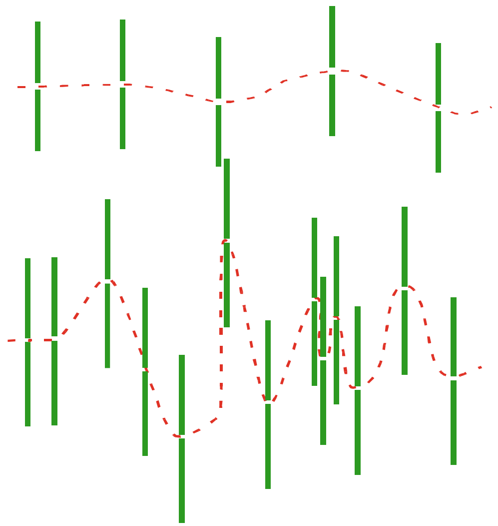
Δx = uncertainty in position
Δp = uncertainty in momentum
$\hbar$ = $h / 2\pi$





Trajectories?

- <u>The uncertainty principle means there are no classical trajectories</u>
- Suppose we try to make an accurate measurement of the path of our electron by passing it through a bunch of slits or otherwise determining the position to some accuracy, e.g. by looking via light



What happens if we try to improve the accurately by narrowing the slits? The uncertainty principle foils us.

- Any attempt at increased accuracy merely yields a more scattered set of measurements. You can't do something to measure the trajectories without ending up with a different arrival pattern- meaning that <u>you haven't found the trajectories of the initial problem.</u>
- For classical <u>waves</u> there are also no trajectories- but that's not a problem because the wave is *certainly* spread out. If you try to measure where the wave is, you don't get the strange result that it's just at one spot, you see that it is spread out.

Quantum Numbers

- Solving the wave equation gives a set of wave functions, or **orbitals**, and their corresponding energies.
- Each **orbital** describes a spatial distribution (空间分布)of electron density.
- An **orbital** is described by a set of three **quantum numbers**.

An Atom versus a House

1. How many stories? – shells/orbitals (principal) 主量子数

2. How many different room designs on the same floor? – subshells (angular momentum)角量子数

3. How are the rooms of the same design oriented? (magnetic) 磁量子数

4. How was the electron’s attitude？（spin）自旋量子数

Principal Quantum Number (n)

- The principal quantum number, n, describes the energy level on which the orbital resides.
- The values of n are integers ≥ 1.
- These correspond to the values in the Bohr model.

Angular Momentum Quantum Number (l)

- This quantum number defines the shape of the orbital.
- Allowed values of l are integers ranging from 0 to $n - 1$.
- We use letter designations to communicate the different values of l and, therefore, the shapes and types of orbitals.

Angular Momentum Quantum Number (*l*)

Value of l	0	1	2	3
Letter used	s	p	d	f

Magnetic Quantum Number (m_l)

- The magnetic quantum number describes the three-dimensional orientation of the orbital.
- Allowed values of m_l are integers ranging from $-l$ to l:

$$-l \leq m_l \leq l$$

- Therefore, on any given energy level, there can be up to 1 *s* orbital, 3 *p* orbitals, 5 *d* orbitals, 7 *f* orbitals, and so forth.

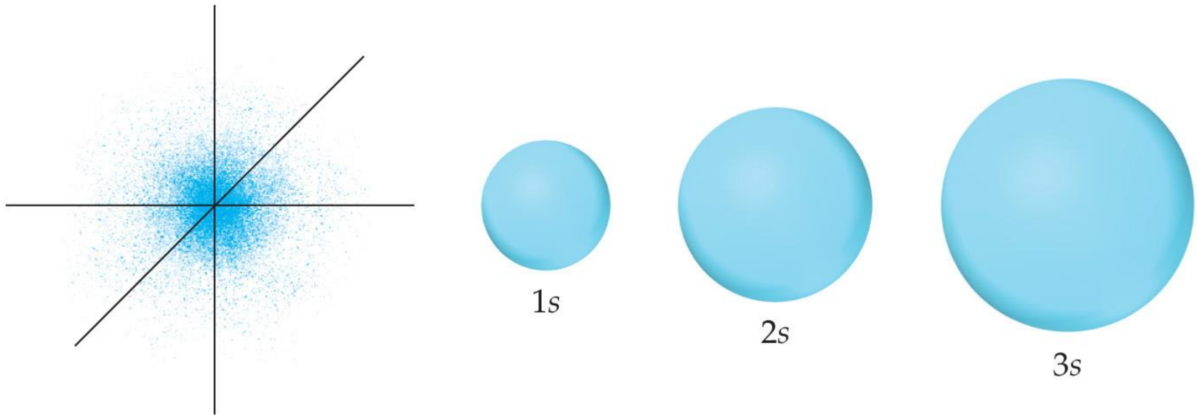
Magnetic Quantum Number (m_l)

- Orbitals with the same value of n form an **electron shell**.
- Different orbital types within a shell are **subshells**.

Table 6.2 Relationship among Values of n, l, and m_l through $n = 4$

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

s Orbitals

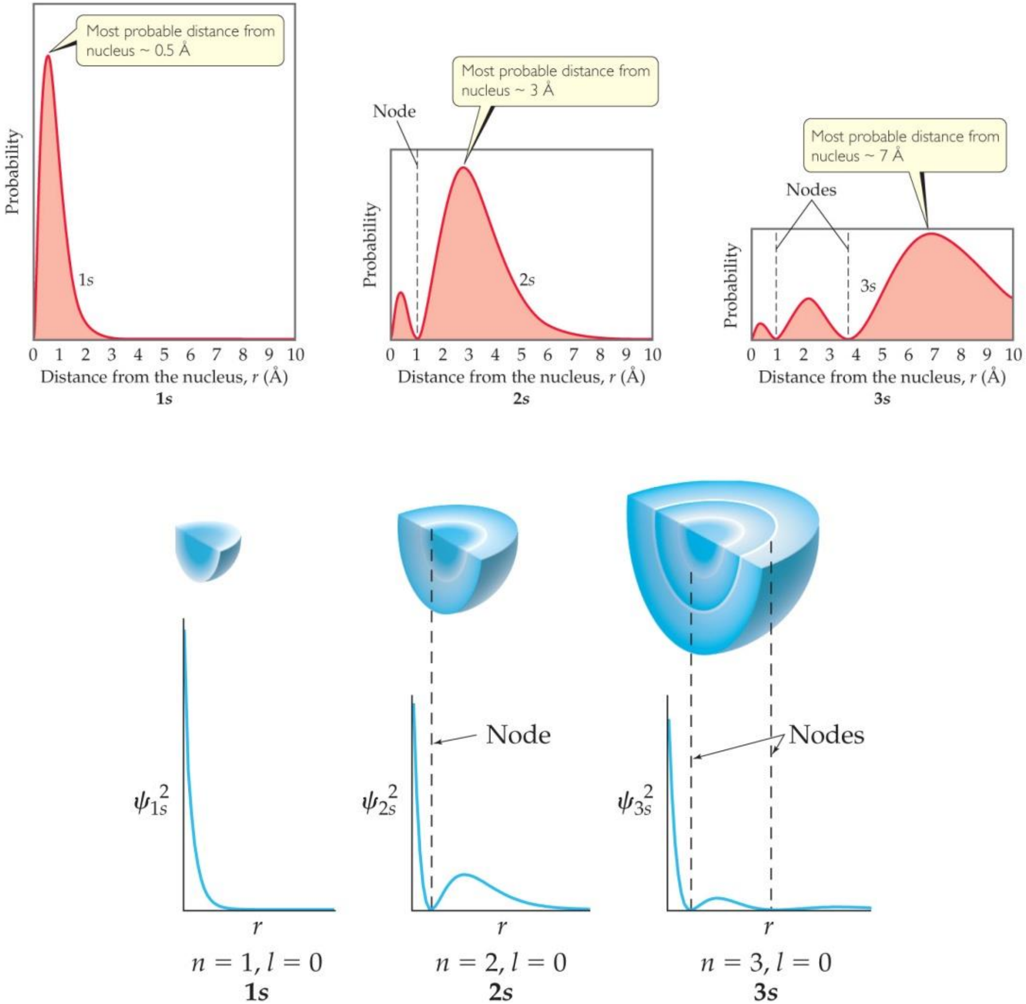


(a) An electron density model

(b) Contour models

- The value of *l* for *s* orbitals is 0.
- They are spherical in shape.
- The radius of the sphere increases with the value of *n*.

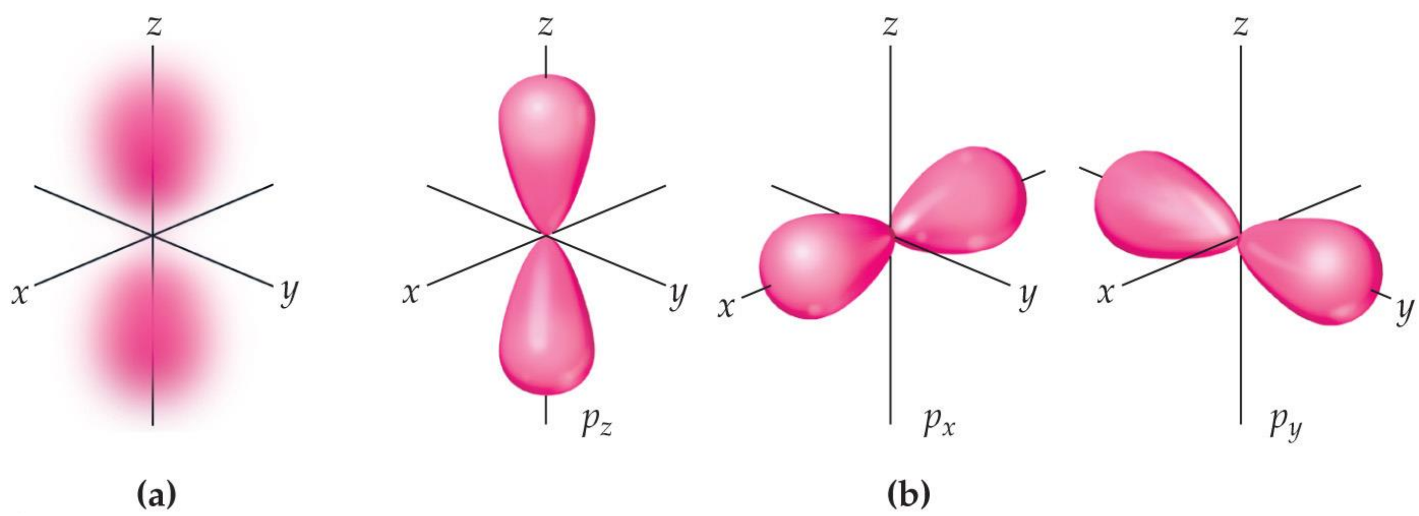
s Orbitals



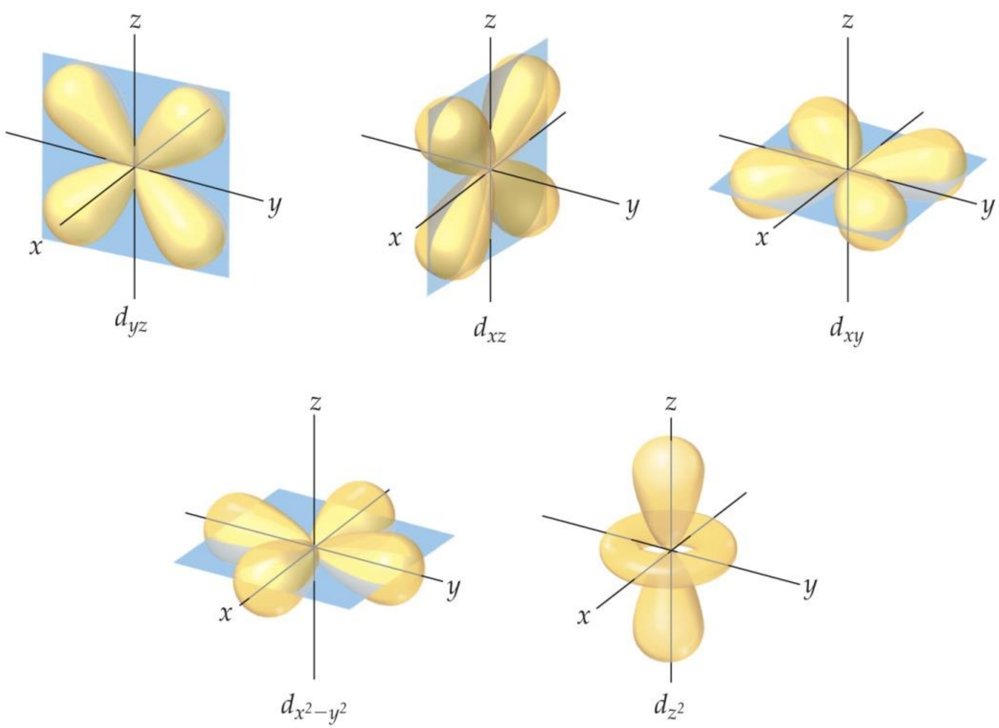
- For an *ns* orbital, the number of peaks is *n*.
- For an *ns* orbital, the number of nodes (where there is zero probability of finding an electron) is *n – 1*.
- As *n* increases, the electron density is more spread out and there is a greater probability of finding an electron further from the nucleus.

p Orbitals

- The value of *l* for *p* orbitals is 1.
- They have two lobes with a node between them.



d Orbitals

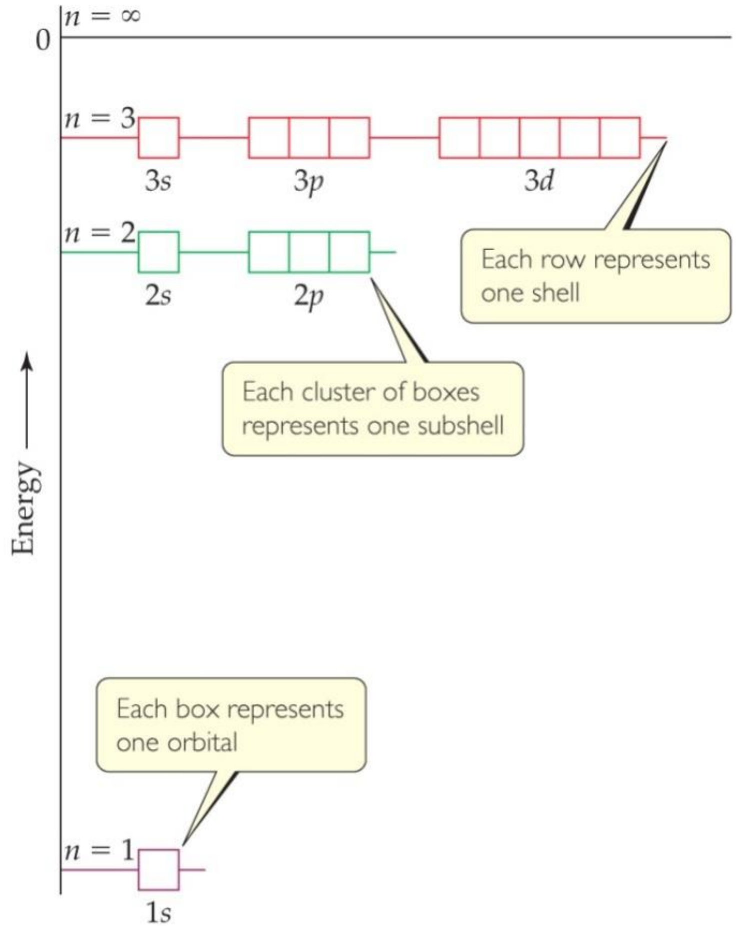


- The value of *l* for a *d* orbital is 2.
- Four of the five *d* orbitals have four lobes; the other resembles a *p* orbital with a doughnut around the center.

f Orbitals

- Very complicated shapes (not shown in text)
- Seven equivalent orbitals in a sublevel
- $l = 3$

Energies of Orbitals—Hydrogen

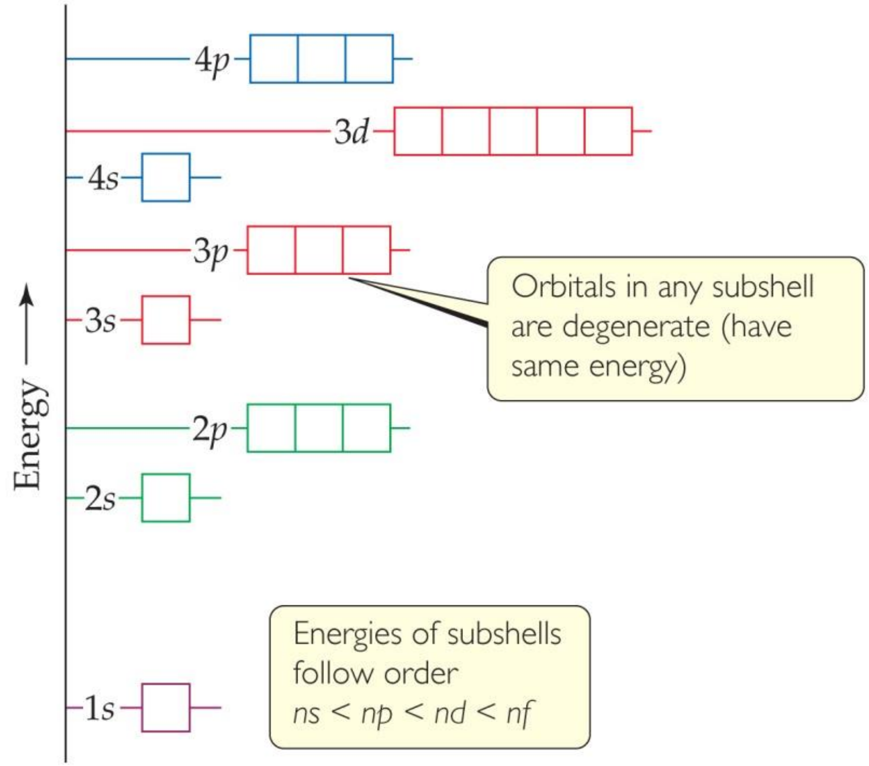


$n = 1$ shell has one orbital
$n = 2$ shell has two subshells composed of four orbitals
$n = 3$ shell has three subshells composed of nine orbitals

- For a one-electron hydrogen atom, orbitals on the same energy level have the same energy.
- Chemists call them **degenerate（简并）** orbitals.

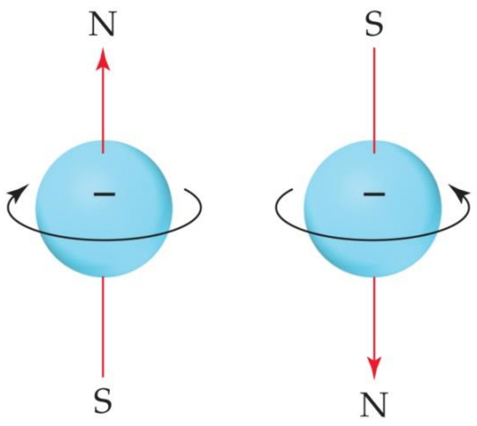
Energies of Orbitals—Many-electron Atoms

- As the number of electrons increases, so does the repulsion between them.
- Therefore, in atoms with more than one electron, not all orbitals on the same energy level are degenerate.
- Orbital sets in the same sublevel are still degenerate.
- Energy levels start to overlap in energy (e.g., 4*s* is lower in energy than 3*d*.)



Spin Quantum Number, m_s

- In the 1920s, it was discovered that two electrons in the same orbital do not have exactly the same energy.
- The "spin" of an electron describes its magnetic field, which affects its energy.
- This led to the spin quantum number, m_s.
- The spin quantum number has only two allowed values, +½ and –½.



Pauli Exclusion Principle

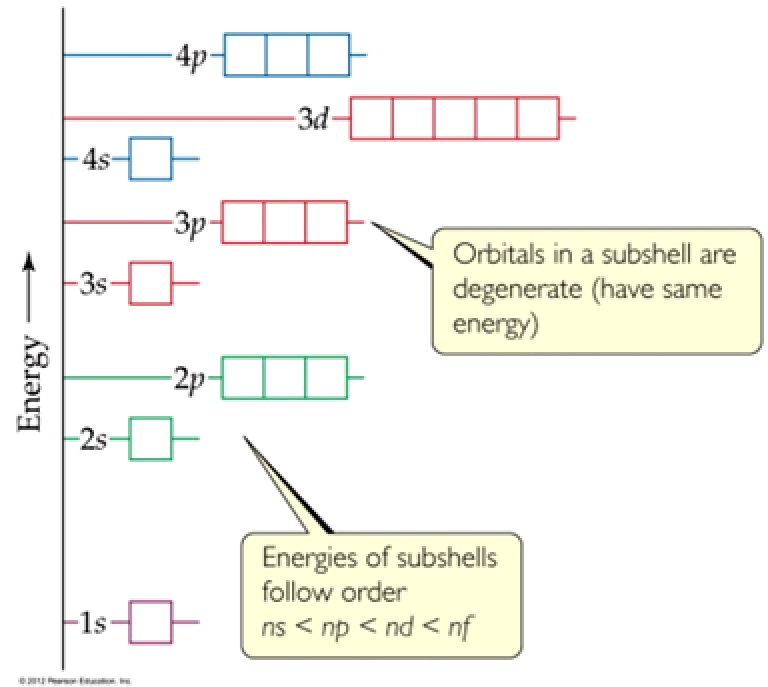
- No two electrons in the same atom can have exactly the same energy.

- Therefore, no two electrons in the same atom can have identical sets of quantum numbers.

- This means that every electron in an atom must differ by at least one of the four quantum number values: n, l, m_l, and m_s.

➢ Electron Configurations (电子组态)

- The way electrons are distributed(分布) among the various orbitals of an atom.
- Ground state, electrons are in the lowest possible energy state, most stable.
- Electrons would crowd in the 1s orbital if there were no restrictions.



Electron Configurations (电子组态)

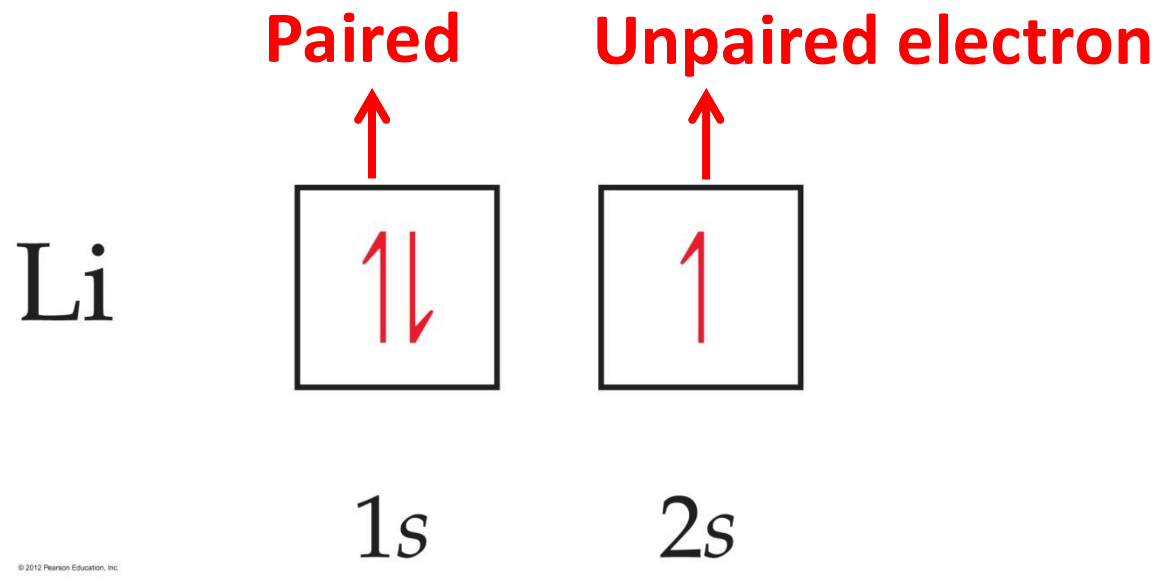
- This term shows the distribution of all electrons in an atom.
- Each component consists of
  - A number denoting the energy level, 4
  - A letter denoting the type of orbital, *p*
  - A superscript denoting the number of electrons in those orbitals. 5

$$4p^5$$

Li $1s^22s^1$

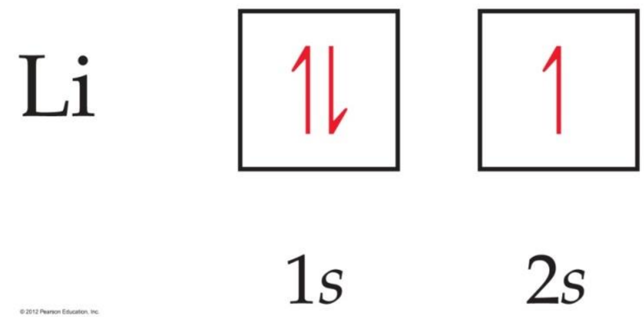
➢ Orbital Diagrams

- Each box in the diagram represents one orbital.
- **Half-arrows** represent the electrons.
- The direction of the arrow represents the relative spin of the electron.



➢ Pauli Exclusion Principle (泡利不相容原理)

- There can be at most two electrons in any single orbital.
- The orbitals are filled in order of increasing energy with no more than two electrons per orbital
- No two electrons in the same atom can have exactly the same energy.
- Therefore, no two electrons in the same atom can have identical(相同) sets of quantum numbers.



➢ Hund's Rule (洪特规则)

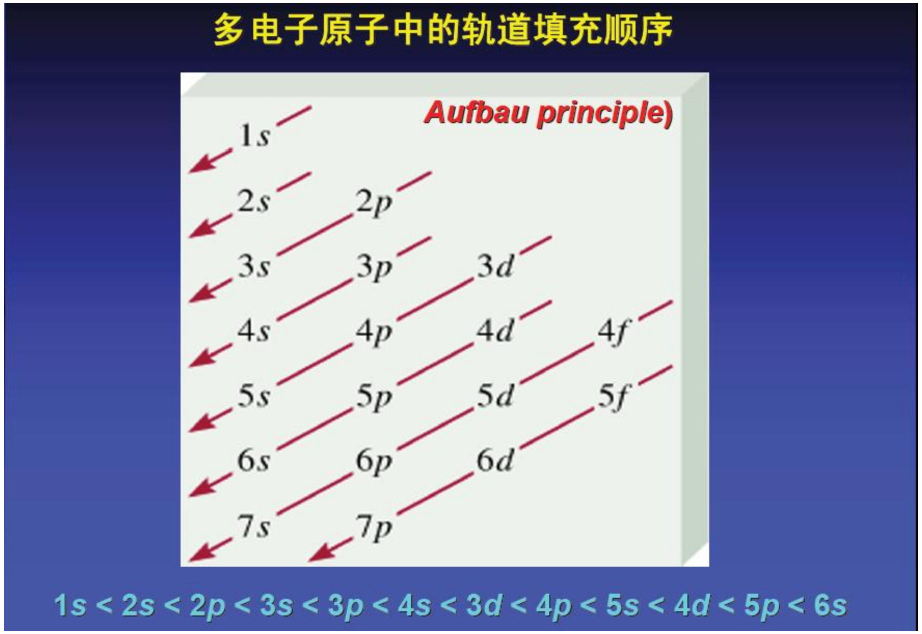
- For degenerate orbitals, the lowest energy is attained when the number of electrons with the same spin is maximized.

TABLE 6.3 • Electron Configurations of Several Lighter Elements

Element	Total Electrons	Orbital Diagram 1s	2s	2p	3s	Electron Configuration
Li	3	↑↓	↑			$1s^2 2s^1$
Be	4	↑↓	↑↓			$1s^2 2s^2$
B	5	↑↓	↑↓	↑		$1s^2 2s^2 2p^1$
C	6	↑↓	↑↓	↑ ↑		$1s^2 2s^2 2p^2$
N	7	↑↓	↑↓	↑ ↑ ↑		$1s^2 2s^2 2p^3$
Ne	10	↑↓	↑↓	↑↓ ↑↓ ↑↓		$1s^2 2s^2 2p^6$
Na	11	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑	$1s^2 2s^2 2p^6 3s^1$

➢ The lowest-energy orbitals are filled before electrons are placed in higher-energy orbitals (最低能量原理)

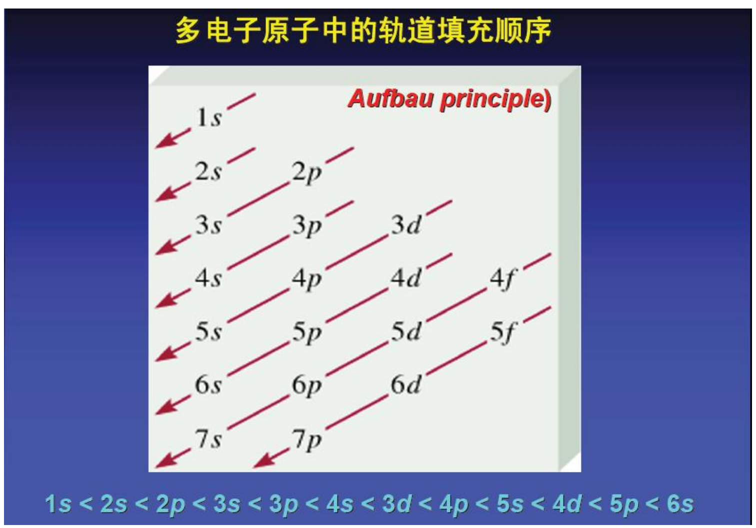
- Orbitals are filled in the order of increasing *n*+*l*;
- Where two orbitals have the same value of *n*+*l*, they are filled in order of increasing *n*.



徐光宪规律： $n + 0.7l$，值越小，轨道能级越低

➢ Aufbau principle(构造原理)

- Electrons was filled in lowest energy orbitals one by one。
- Totally empty orbitals, half-full orbitals and full orbitals have extra stability



Cu $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$

Gd [Xe] $6s^2 4f^7 5d^1$

Pd [Kr] $4d^{10}$

Sample Exercise 6.7 Orbital Diagrams and Electron Configurations

Draw the orbital diagram for the electron configuration of oxygen, atomic number 8. How many unpaired electrons does an oxygen atom possess?

Solution

Analyze and Plan Because oxygen has an atomic number of 8, each oxygen atom has 8 electrons. Figure 6.24 shows the ordering of orbitals. The electrons (represented as arrows) are placed in the orbitals (represented as boxes) beginning with the lowest-energy orbital, the 1*s*. Each orbital can hold a maximum of two electrons (the Pauli exclusion principle). Because the 2*p* orbitals are degenerate, we place one electron in each of these orbitals (spin-up) before pairing any electrons (Hund's rule).

Solve Two electrons each go into the 1*s* and 2*s* orbitals with their spins paired. This leaves four electrons for the three degenerate 2*p* orbitals. Following Hund's rule, we put one electron into each 2*p* orbital until all three orbitals have one electron each. The fourth electron is then paired up with one of the three electrons already in a 2*p* orbital, so that the orbital diagram is:

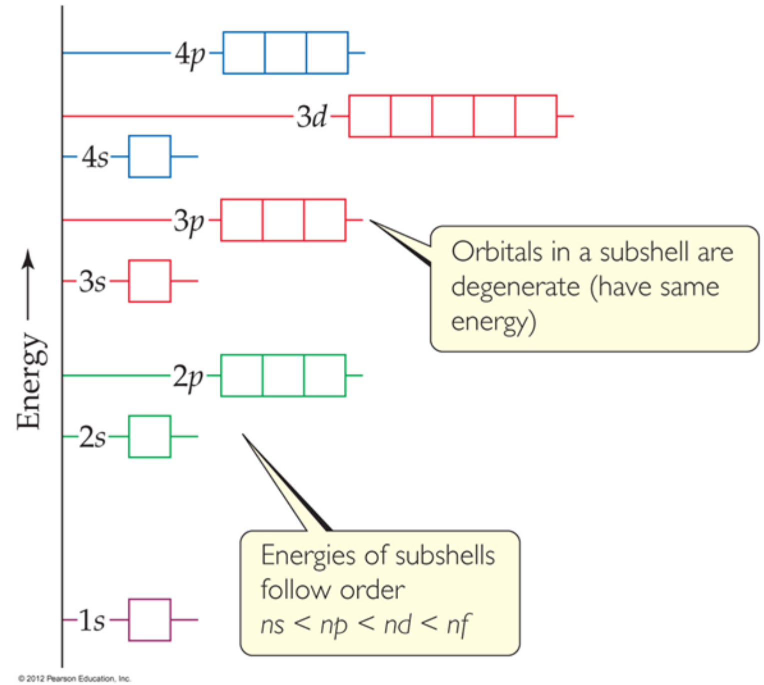
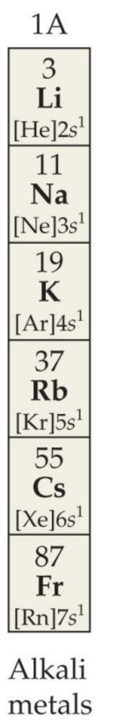


FIGURE 6.24 General energy ordering of orbitals for a many-electron atom.

➢ Condensed(浓缩的) electron configuration

- The electron configuration of the nearest noble-gas element of lower atomic number is presented by its chemical symbol in bracket.



$$\text{Li } 1s^2 2s^1 \Longrightarrow \text{Li [He]} 2s^1$$

$$\text{Na } \underbrace{\boxed{1s^2 2s^2 2p^6}}_{\text{Core electrons}} 3s^1 \Longrightarrow \text{Na [Ne]} \underbrace{\boxed{3s^1}}_{\text{Outer-shell electrons}}$$

Core electrons

Outer-shell electrons

⇩

Atomic number ≤ 30, valence electron

Core	1A 1	2A 2	3B 3	4B 4	5B 5	6B 6	7B 7	8B 8	8B 9	8B 10	1B 11	2B 12	3A 13	4A 14	5A 15	6A 16	7A 17	8A 18
	1 **H** $1s^1$																	2 **He** $1s^2$
[He]	3 **Li** $2s^1$	4 **Be** $2s^2$											5 **B** $2s^22p^1$	6 **C** $2s^22p^2$	7 **N** $2s^22p^3$	8 **O** $2s^22p^4$	9 **F** $2s^22p^5$	10 **Ne** $2s^22p^6$
[Ne]	11 **Na** $3s^1$	12 **Mg** $3s^2$											13 **Al** $3s^23p^1$	14 **Si** $3s^23p^2$	15 **P** $3s^23p^3$	16 **S** $3s^23p^4$	17 **Cl** $3s^23p^5$	18 **Ar** $3s^23p^6$
[Ar]	19 **K** $4s^1$	20 **Ca** $4s^2$	21 **Sc** $3d^14s^2$	22 **Ti** $3d^24s^2$	23 **V** $3d^34s^2$	24 **Cr** $3d^54s^1$	25 **Mn** $3d^54s^2$	26 **Fe** $3d^64s^2$	27 **Co** $3d^74s^2$	28 **Ni** $3d^84s^2$	29 **Cu** $3d^{10}4s^1$	30 **Zn** $3d^{10}4s^2$	31 **Ga** $3d^{10}4s^24p^1$	32 **Ge** $3d^{10}4s^24p^2$	33 **As** $3d^{10}4s^24p^3$	34 **Se** $3d^{10}4s^24p^4$	35 **Br** $3d^{10}4s^24p^5$	36 **Kr** $3d^{10}4s^24p^6$
[Kr]	37 **Rb** $5s^1$	38 **Sr** $5s^2$	39 **Y** $4d^15s^2$	40 **Zr** $4d^25s^2$	41 **Nb** $4d^35s^2$	42 **Mo** $4d^55s^1$	43 **Tc** $4d^55s^2$	44 **Ru** $4d^75s^1$	45 **Rh** $4d^85s^1$	46 **Pd** $4d^{10}$	47 **Ag** $4d^{10}5s^1$	48 **Cd** $4d^{10}5s^2$	49 **In** $4d^{10}5s^25p^1$	50 **Sn** $4d^{10}5s^25p^2$	51 **Sb** $4d^{10}5s^25p^3$	52 **Te** $4d^{10}5s^25p^4$	53 **I** $4d^{10}5s^25p^5$	54 **Xe** $4d^{10}5s^25p^6$
[Xe]	55 **Cs** $6s^1$	56 **Ba** $6s^2$	71 **Lu** $4f^{14}5d^16s^2$	72 **Hf** $4f^{14}5d^26s^2$	73 **Ta** $4f^{14}5d^36s^2$	74 **W** $4f^{14}5d^46s^2$	75 **Re** $4f^{14}5d^56s^2$	76 **Os** $4f^{14}5d^66s^2$	77 **Ir** $4f^{14}5d^76s^2$	78 **Pt** $4f^{14}5d^96s^1$	79 **Au** $4f^{14}5d^{10}6s^1$	80 **Hg** $4f^{14}5d^{10}6s^2$	81 **Tl** $4f^{14}5d^{10}6s^26p^1$	82 **Pb** $4f^{14}5d^{10}6s^26p^2$	83 **Bi** $4f^{14}5d^{10}6s^26p^3$	84 **Po** $4f^{14}5d^{10}6s^26p^4$	85 **At** $4f^{14}5d^{10}6s^26p^5$	86 **Rn** $4f^{14}5d^{10}6s^26p^6$
[Rn]	87 **Fr** $7s^1$	88 **Ra** $7s^2$	103 **Lr** $5f^{14}6d^17s^2$	104 **Rf** $5f^{14}6d^27s^2$	105 **Db** $5f^{14}6d^37s^2$	106 **Sg** $5f^{14}6d^47s^2$	107 **Bh** $5f^{14}6d^57s^2$	108 **Hs** $5f^{14}6d^67s^2$	109 **Mt** $5f^{14}6d^77s^2$	110 **Ds**	111 **Rg**	112 **Cn**	113	114	115	116	117	118

Core	Series														
[Xe]	Lanthanide series	57 **La** $5d^16s^2$	58 **Ce** $4f^15d^16s^2$	59 **Pr** $4f^36s^2$	60 **Nd** $4f^46s^2$	61 **Pm** $4f^56s^2$	62 **Sm** $4f^66s^2$	63 **Eu** $4f^76s^2$	64 **Gd** $4f^75d^16s^2$	65 **Tb** $4f^96s^2$	66 **Dy** $4f^{10}6s^2$	67 **Ho** $4f^{11}6s^2$	68 **Er** $4f^{12}6s^2$	69 **Tm** $4f^{13}6s^2$	70 **Yb** $4f^{14}6s^2$
[Rn]	Actinide series	89 **Ac** $6d^17s^2$	90 **Th** $6d^27s^2$	91 **Pa** $5f^26d^17s^2$	92 **U** $5f^36d^17s^2$	93 **Np** $5f^46d^17s^2$	94 **Pu** $5f^67s^2$	95 **Am** $5f^77s^2$	96 **Cm** $5f^76d^17s^2$	97 **Bk** $5f^97s^2$	98 **Cf** $5f^{10}7s^2$	99 **Es** $5f^{11}7s^2$	100 **Fm** $5f^{12}7s^2$	101 **Md** $5f^{13}7s^2$	102 **No** $5f^{14}7s^2$

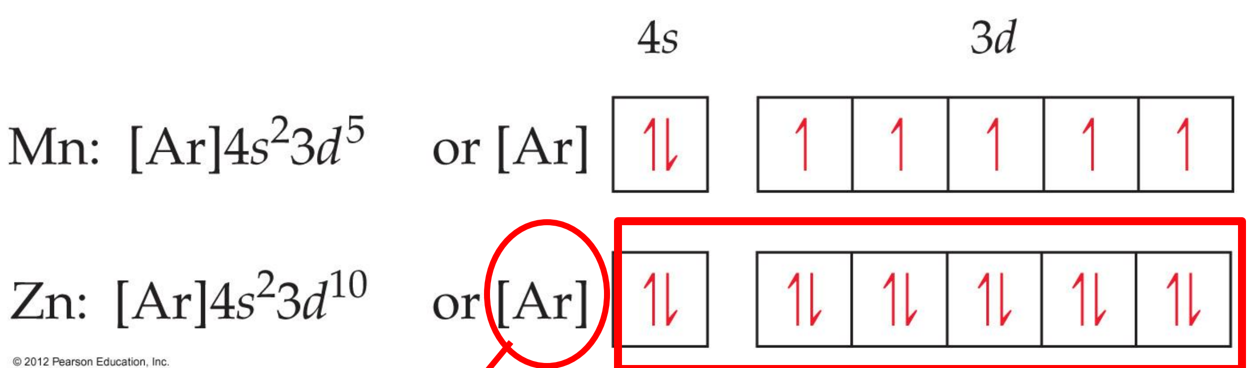
Metals   Metalloids   Nonmetals

➢ Transition metal(过渡金属)

- 4*s* orbital is lower in energy than the 3*d* orbital

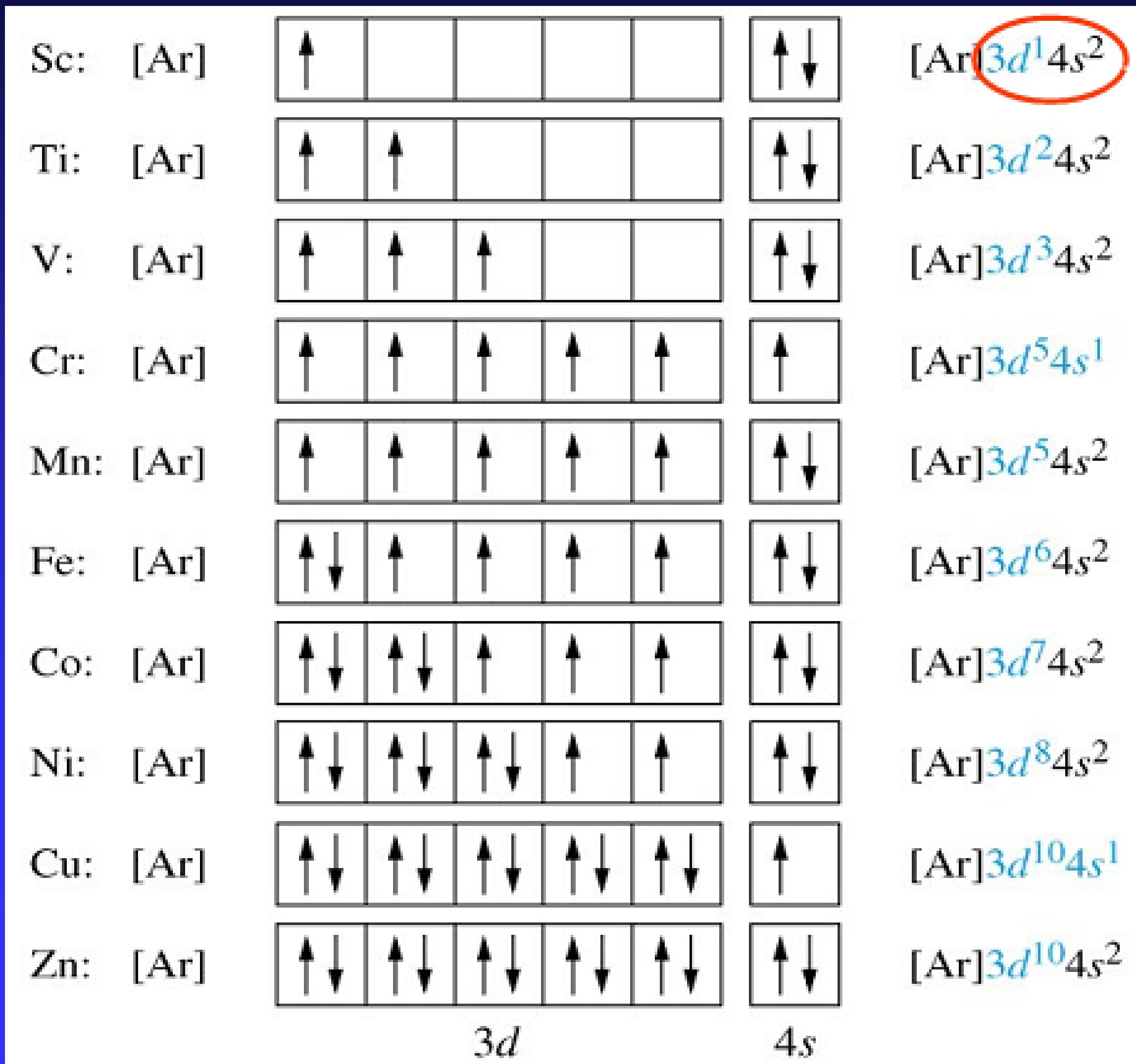
K $1s^22s^22p^63s^2\boxed{3p^64s^1}$

- Beginning with scandium(钪) and extending through zinc, electrons are added to five 3d orbital until they are completely filled



Core electrons **Outer-shell electrons**

Filling the *d* Orbitals



$4s > 3d$

决定基态中性原子或离子的核外电子排布时，最根本的是考虑整个原子或离子在哪一种状态能量最低，而不是任何情况只看轨道的能量高低。

错误 4 d^45s^1

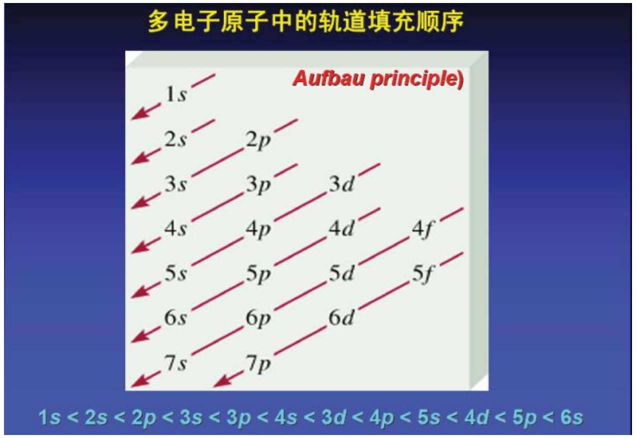
Core	1A 1	2A 2	3B 3	4B 4	5B 5	6B 6	7B 7	8	8B 9	10	1B 11	2B 12	3A 13	4A 14	5A 15	6A 16	7A 17	8A 18
	1 **H** $1s^1$																	2 **He** $1s^2$
[He]	3 **Li** $2s^1$	4 **Be** $2s^2$											5 **B** $2s^22p^1$	6 **C** $2s^22p^2$	7 **N** $2s^22p^3$	8 **O** $2s^22p^4$	9 **F** $2s^22p^5$	10 **Ne** $2s^22p^6$
[Ne]	11 **Na** $3s^1$	12 **Mg** $3s^2$											13 **Al** $3s^23p^1$	14 **Si** $3s^23p^2$	15 **P** $3s^23p^3$	16 **S** $3s^23p^4$	17 **Cl** $3s^23p^5$	18 **Ar** $3s^23p^6$
[Ar]	19 **K** $4s^1$	20 **Ca** $4s^2$	21 **Sc** $3d^14s^2$	22 **Ti** $3d^24s^2$	23 **V** $3d^34s^2$	24 **Cr** $3d^54s^1$	25 **Mn** $3d^54s^2$	26 **Fe** $3d^64s^2$	27 **Co** $3d^74s^2$	28 **Ni** $3d^84s^2$	29 **Cu** $3d^{10}4s^1$	30 **Zn** $3d^{10}4s^2$	31 **Ga** $3d^{10}4s^2 4p^1$	32 **Ge** $3d^{10}4s^2 4p^2$	33 **As** $3d^{10}4s^2 4p^3$	34 **Se** $3d^{10}4s^2 4p^4$	35 **Br** $3d^{10}4s^2 4p^5$	36 **Kr** $3d^{10}4s^2 4p^6$
[Kr]	37 **Rb** $5s^1$	38 **Sr** $5s^2$	39 **Y** $4d^15s^2$	40 **Zr** $4d^25s^2$	41 **Nb** $4d^35s^2$	42 **Mo** $4d^55s^1$	43 **Tc** $4d^55s^2$	44 **Ru** $4d^75s^1$	45 **Rh** $4d^85s^1$	46 **Pd** $4d^{10}$	47 **Ag** $4d^{10}5s^1$	48 **Cd** $4d^{10}5s^2$	49 **In** $4d^{10}5s^2 5p^1$	50 **Sn** $4d^{10}5s^2 5p^2$	51 **Sb** $4d^{10}5s^2 5p^3$	52 **Te** $4d^{10}5s^2 5p^4$	53 **I** $4d^{10}5s^2 5p^5$	54 **Xe** $4d^{10}5s^2 5p^6$
[Xe]	55 **Cs** $6s^1$	56 **Ba** $6s^2$	71 **Lu** $4f^{14}5d^1 6s^2$	72 **Hf** $4f^{14}5d^2 6s^2$	73 **Ta** $4f^{14}5d^3 6s^2$	74 **W** $4f^{14}5d^4 6s^2$	75 **Re** $4f^{14}5d^5 6s^2$	76 **Os** $4f^{14}5d^6 6s^2$	77 **Ir** $4f^{14}5d^7 6s^2$	78 **Pt** $4f^{14}5d^9 6s^1$	79 **Au** $4f^{14}5d^{10} 6s^1$	80 **Hg** $4f^{14}5d^{10} 6s^2$	81 **Tl** $4f^{14}5d^{10} 6s^26p^1$	82 **Pb** $4f^{14}5d^{10} 6s^26p^2$	83 **Bi** $4f^{14}5d^{10} 6s^26p^3$	84 **Po** $4f^{14}5d^{10} 6s^26p^4$	85 **At** $4f^{14}5d^{10} 6s^26p^5$	86 **Rn** $4f^{14}5d^{10} 6s^26p^6$
[Rn]	87 **Fr** $7s^1$	88 **Ra** $7s^2$	103 **Lr** $5f^{14}6d^1 7s^2$	104 **Rf** $5f^{14}6d^2 7s^2$	105 **Db** $5f^{14}6d^3 7s^2$	106 **Sg** $5f^{14}6d^4 7s^2$	107 **Bh** $5f^{14}6d^5 7s^2$	108 **Hs** $5f^{14}6d^6 7s^2$	109 **Mt** $5f^{14}6d^7 7s^2$	110 **Ds**	111 **Rg**	112 **Cn**	113	114	115	116	117	118

[Xe]	Lanthanide series	57 **La** $5d^16s^2$	58 **Ce** $4f^15d^1 6s^2$	59 **Pr** $4f^36s^2$	60 **Nd** $4f^46s^2$	61 **Pm** $4f^56s^2$	62 **Sm** $4f^66s^2$	63 **Eu** $4f^76s^2$	64 **Gd** $4f^75d^1 6s^2$	65 **Tb** $4f^96s^2$	66 **Dy** $4f^{10}6s^2$	67 **Ho** $4f^{11}6s^2$	68 **Er** $4f^{12}6s^2$	69 **Tm** $4f^{13}6s^2$	70 **Yb** $4f^{14}6s^2$
[Rn]	Actinide series	89 **Ac** $6d^17s^2$	90 **Th** $6d^27s^2$	91 **Pa** $5f^26d^1 7s^2$	92 **U** $5f^36d^1 7s^2$	93 **Np** $5f^46d^1 7s^2$	94 **Pu** $5f^67s^2$	95 **Am** $5f^77s^2$	96 **Cm** $5f^76d^1 7s^2$	97 **Bk** $5f^97s^2$	98 **Cf** $5f^{10}7s^2$	99 **Es** $5f^{11}7s^2$	100 **Fm** $5f^{12}7s^2$	101 **Md** $5f^{13}7s^2$	102 **No** $5f^{14}7s^2$

Metals Metalloids Nonmetals

➢ The Lanthanides(镧系元素) and Actinides(锕系)

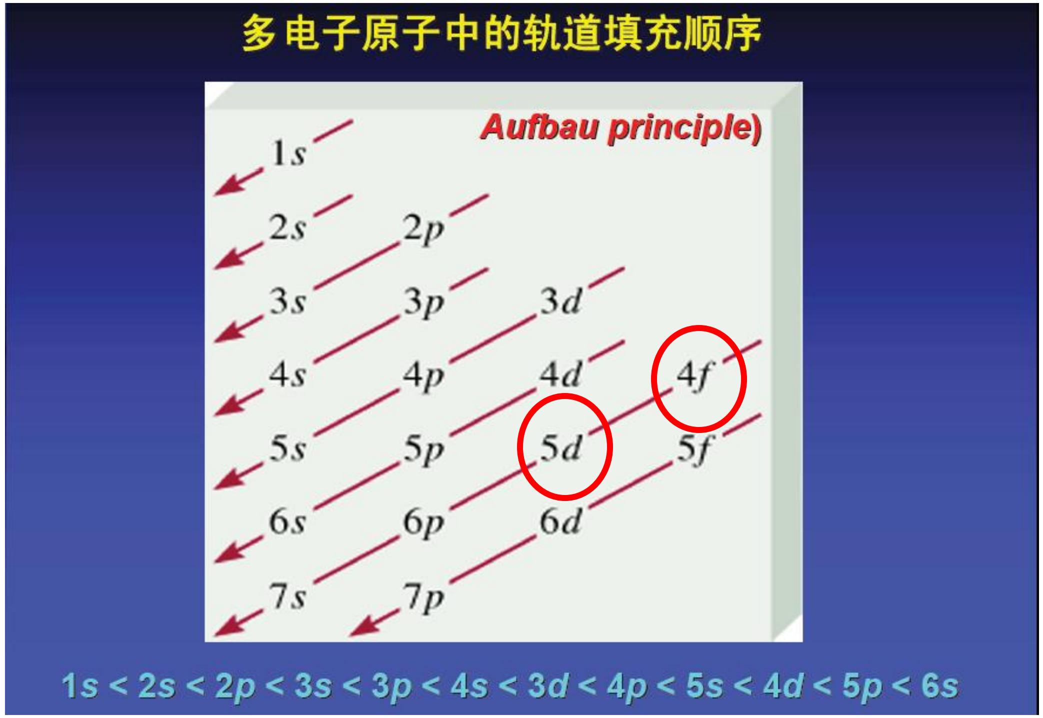
- There are seven degenerate 4*f*, it takes 14 electrons to fill the 4*f* orbitals, corresponding to lanthanide elements or rare earth elements.
  - Similar property, occur together in nature.
- Energies of the 4f and 5d orbitals are very close.



$[Xe]6s^2 5d^1$ La

$[Xe]6s^2 5d^1 4f^1$ Ce

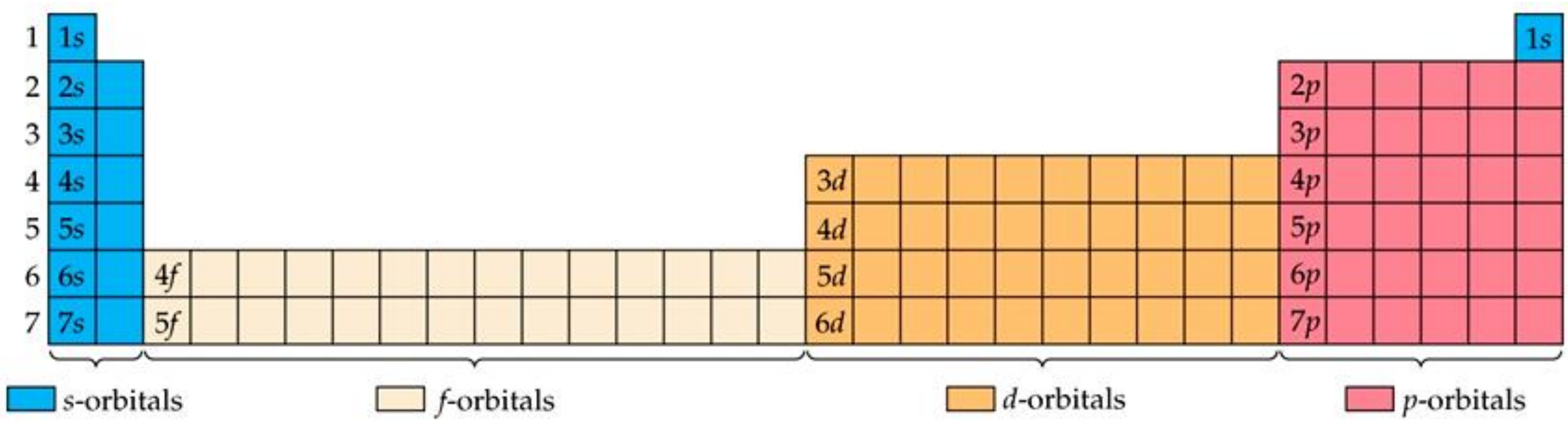
$[Xe]6s^2 4f^3$ Pr



57 La $5d^16s^2$	58 Ce $4f^15d^1$ $6s^2$	59 Pr $4f^36s^2$	60 Nd $4f^46s^2$	61 Pm $4f^56s^2$	62 Sm $4f^66s^2$	63 Eu $4f^76s^2$	64 Gd $4f^75d^1$ $6s^2$	65 Tb $4f^96s^2$	66 Dy $4f^{10}6s^2$	67 Ho $4f^{11}6s^2$	68 Er $4f^{12}6s^2$	69 Tm $4f^{13}6s^2$	70 Yb $4f^{14}6s^2$
89 Ac $6d^17s^2$	90 Th $6d^27s^2$	91 Pa $5f^26d^1$ $7s^2$	92 U $5f^36d^1$ $7s^2$	93 Np $5f^46d^1$ $7s^2$	94 Pu $5f^67s^2$	95 Am $5f^77s^2$	96 Cm $5f^76d^1$ $7s^2$	97 Bk $5f^97s^2$	98 Cf $5f^{10}7s^2$	99 Es $5f^{11}7s^2$	100 Fm $5f^{12}7s^2$	101 Md $5f^{13}7s^2$	102 No $5f^{14}7s^2$

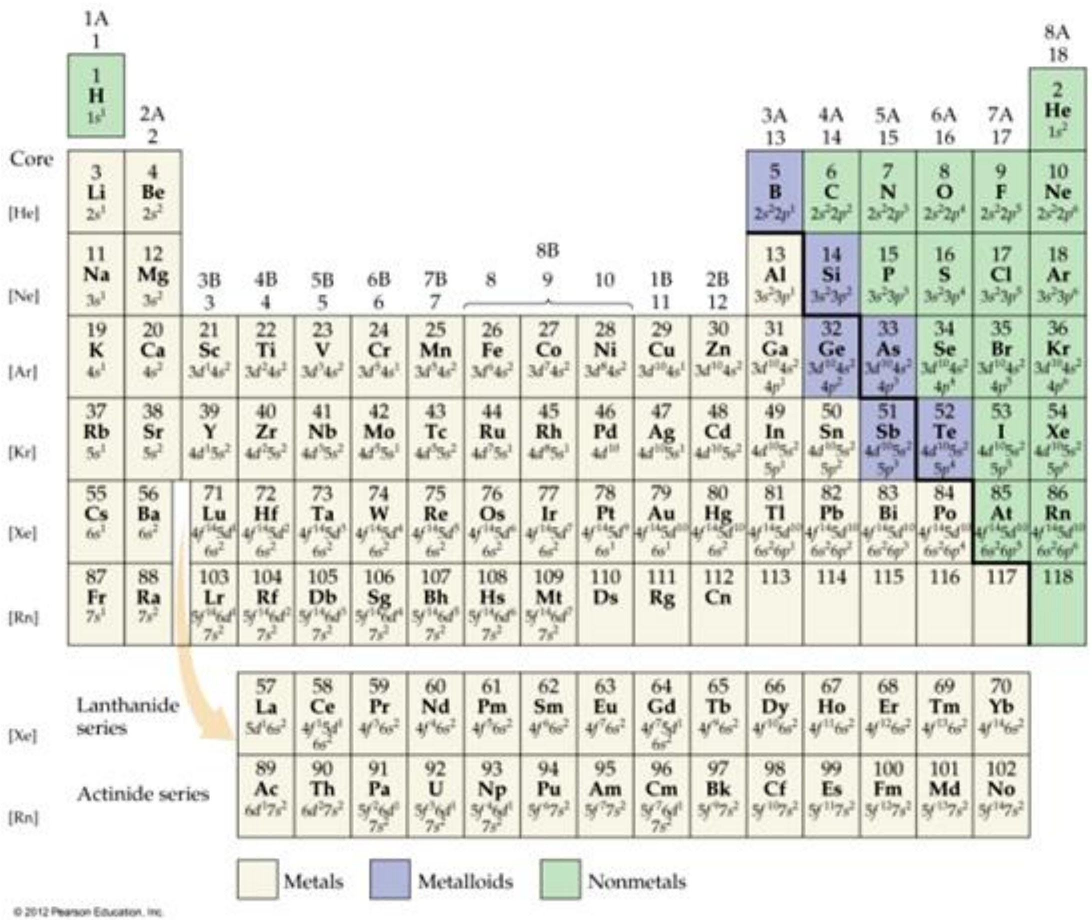
Periodic Table

- We fill orbitals in increasing order of energy.
- Different blocks on the periodic table (shaded in different colors in this chart) correspond to different types of orbitals.



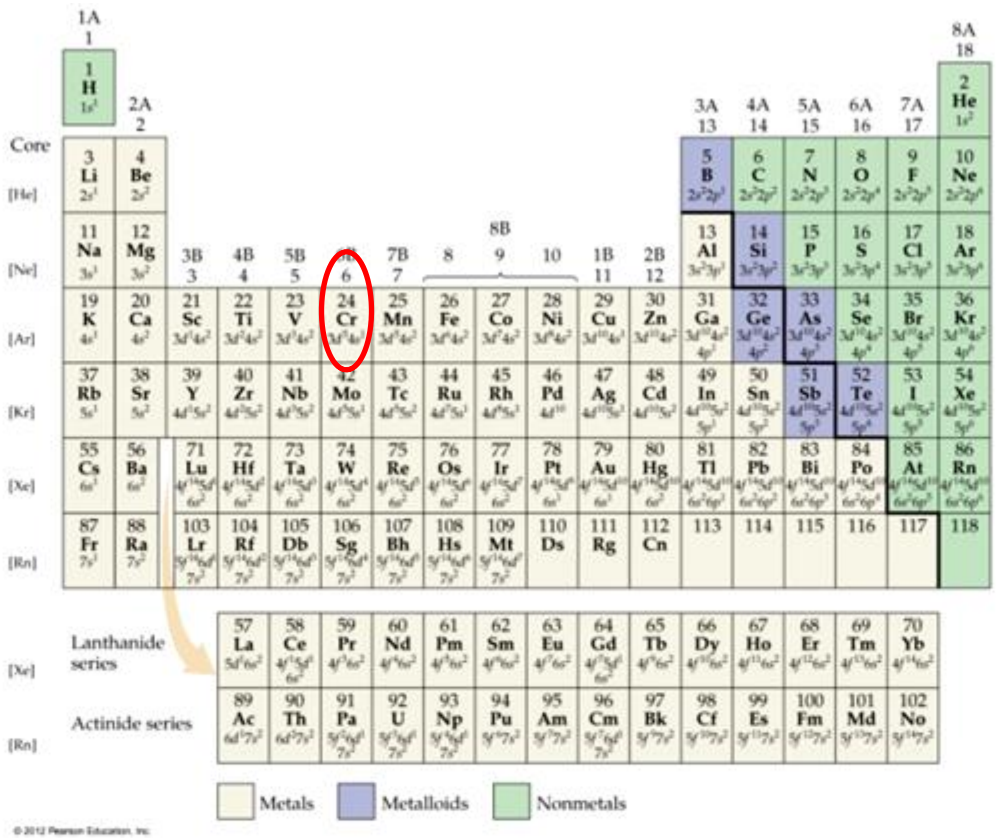
➢ Some Anomalies(异常)

- Some irregularities occur when there are enough electrons to half-fill *s* and *d* orbitals on a given row.



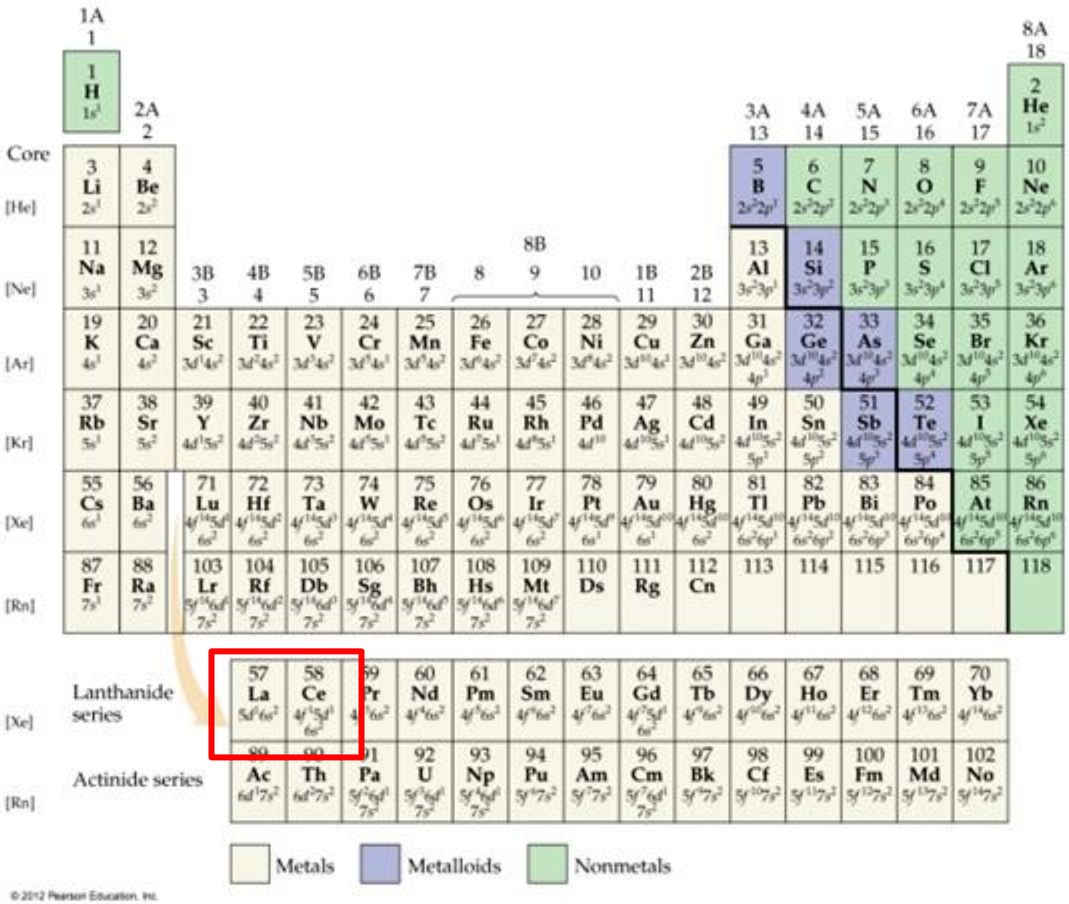
➢ Some Anomalies

- For instance, the electron configuration for chromium is **[Ar] $4s^1\ 3d^5$** rather than the expected **[Ar] $4s^2\ 3d^4$.**



Any others?

➢ Some Anomalies



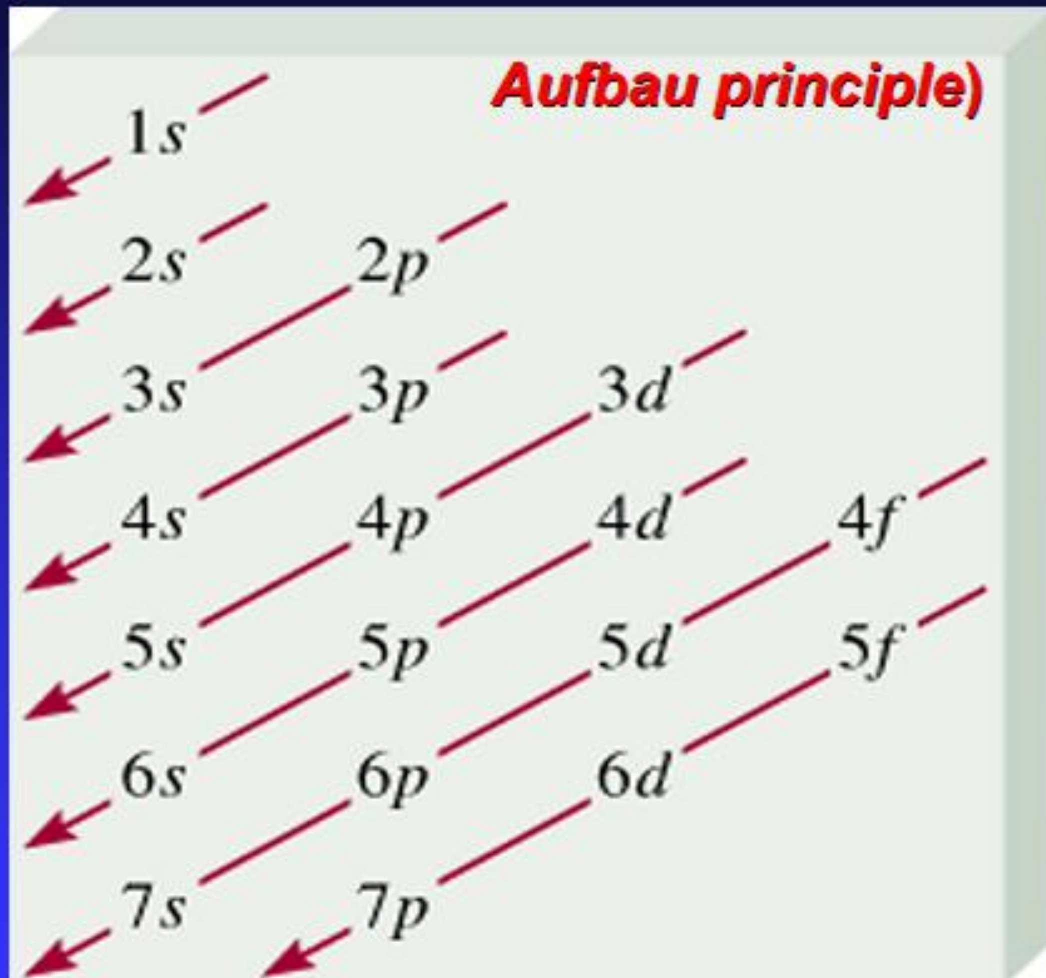
- This occurs because the 4*s* and 3*d* orbitals are very close in energy.
- These anomalies occur in *f*-block atoms, as well.

The Ground State Electron Configuration of the Elements

Irregular electron configuration-Pt determined by photospectrum: $[Xe]4f^{14}5d^{9}6s^{1}$ Not $[Xe]4f^{14}5d^{8}6s^{2}$

Atomic Number	Symbol	Electron Configuration	Atomic Number	Symbol	Electron Configuration	Atomic Number	Symbol	Electron Configuration
1	H	$1s^1$	37	Rb	$[Kr]5s^1$	73	Ta	$[Xe]6s^24f^{14}5d^3$
2	He	$1s^2$	38	Sr	$[Kr]5s^2$	74	W	$[Xe]6s^24f^{14}5d^4$
3	Li	$[He]2s^1$	39	Y	$[Kr]5s^24d^1$	75	Re	$[Xe]6s^24f^{14}5d^5$
4	Be	$[He]2s^2$	40	Zr	$[Kr]5s^24d^2$	76	Os	$[Xe]6s^24f^{14}5d^6$
5	B	$[He]2s^22p^1$	41	Nb	$[Kr]5s^14d^4$	77	Ir	$[Xe]6s^24f^{14}5d^7$
6	C	$[He]2s^22p^2$	42	Mo	$[Kr]5s^14d^5$	78	Pt	$[Xe]6s^14f^{14}5d^9$
7	N	$[He]2s^22p^3$	43	Tc	$[Kr]5s^24d^5$	79	Au	$[Xe]6s^14f^{14}5d^{10}$
8	O	$[He]2s^22p^4$	44	Ru	$[Kr]5s^14d^7$	80	Hg	$[Xe]6s^24f^{14}5d^{10}$
9	F	$[He]2s^22p^5$	45	Rh	$[Kr]5s^14d^8$	81	Tl	$[Xe]6s^24f^{14}5d^{10}6p^1$
10	Ne	$[He]2s^22p^6$	46	Pd	$[Kr]4d^{10}$	82	Pb	$[Xe]6s^24f^{14}5d^{10}6p^2$
11	Na	$[Ne]3s^1$	47	Ag	$[Kr]5s^14d^{10}$	83	Bi	$[Xe]6s^24f^{14}5d^{10}6p^3$
12	Mg	$[Ne]3s^2$	48	Cd	$[Kr]5s^24d^{10}$	84	Po	$[Xe]6s^24f^{14}5d^{10}6p^4$
13	Al	$[Ne]3s^23p^1$	49	In	$[Kr]5s^24d^{10}5p^1$	85	At	$[Xe]6s^24f^{14}5d^{10}6p^5$
14	Si	$[Ne]3s^23p^2$	50	Sn	$[Kr]5s^24d^{10}5p^2$	86	Rn	$[Xe]6s^24f^{14}5d^{10}6p^6$
15	P	$[Ne]3s^23p^3$	51	Sb	$[Kr]5s^24d^{10}5p^3$	87	Fr	$[Rn]7s^1$
16	S	$[Ne]3s^23p^4$	52	Te	$[Kr]5s^24d^{10}5p^4$	88	Ra	$[Rn]7s^2$
17	Cl	$[Ne]3s^23p^5$	53	I	$[Kr]5s^24d^{10}5p^5$	89	Ac	$[Rn]7s^26d^1$
18	Ar	$[Ne]3s^23p^6$	54	Xe	$[Kr]5s^24d^{10}5p^6$	90	Th	$[Rn]7s^26d^2$
19	K	$[Ar]4s^1$	55	Cs	$[Xe]6s^1$	91	Pa	$[Rn]7s^25f^26d^1$
20	Ca	$[Ar]4s^2$	56	Ba	$[Xe]6s^2$	92	U	$[Rn]7s^25f^36d^1$
21	Sc	$[Ar]4s^23d^1$	57	La	$[Xe]6s^25d^1$	93	Np	$[Rn]7s^25f^46d^1$
22	Ti	$[Ar]4s^23d^2$	58	Ce	$[Xe]6s^24f^15d^1$	94	Pu	$[Rn]7s^25f^6$
23	V	$[Ar]4s^23d^3$	59	Pr	$[Xe]6s^24f^3$	95	Am	$[Rn]7s^25f^7$
24	Cr	$[Ar]4s^13d^5$	60	Nd	$[Xe]6s^24f^4$	96	Cm	$[Rn]7s^25f^76d^1$
25	Mn	$[Ar]4s^23d^5$	61	Pm	$[Xe]6s^24f^5$	97	Bk	$[Rn]7s^25f^9$
26	Fe	$[Ar]4s^23d^6$	62	Sm	$[Xe]6s^24f^6$	98	Cf	$[Rn]7s^25f^{10}$
27	Co	$[Ar]4s^23d^7$	63	Eu	$[Xe]6s^24f^7$	99	Es	$[Rn]7s^25f^{11}$
28	Ni	$[Ar]4s^23d^8$	64	Gd	$[Xe]6s^24f^75d^1$	100	Fm	$[Rn]7s^25f^{12}$
29	Cu	$[Ar]4s^13d^{10}$	65	Tb	$[Xe]6s^24f^9$	101	Md	$[Rn]7s^25f^{13}$
30	Zn	$[Ar]4s^23d^{10}$	66	Dy	$[Xe]6s^24f^{10}$	102	No	$[Rn]7s^25f^{14}$
31	Ga	$[Ar]4s^23d^{10}4p^1$	67	Ho	$[Xe]6s^24f^{11}$	103	Lr	$[Rn]7s^25f^{14}6d^1$
32	Ge	$[Ar]4s^23d^{10}4p^2$	68	Er	$[Xe]6s^24f^{12}$	104	Rf	$[Rn]7s^25f^{14}6d^2$
33	As	$[Ar]4s^23d^{10}4p^3$	69	Tm	$[Xe]6s^24f^{13}$	105	Db	$[Rn]7s^25f^{14}6d^3$
34	Se	$[Ar]4s^23d^{10}4p^4$	70	Yb	$[Xe]6s^24f^{14}$	106	Sg	$[Rn]7s^25f^{14}6d^4$
35	Br	$[Ar]4s^23d^{10}4p^5$	71	Lu	$[Xe]6s^24f^{14}5d^1$	107	Bh	$[Rn]7s^25f^{14}6d^5$
36	Kr	$[Ar]4s^23d^{10}4p^6$	72	Hf	$[Xe]6s^24f^{14}5d^2$	108	Hs	$[Rn]7s^25f^{14}6d^6$
						109	Mt	$[Rn]7s^25f^{14}6d^7$

多电子原子中的轨道填充顺序



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

Sample Exercise 6.9 Electron Configurations from the Periodic Table

(**a**) Based on its position in the periodic table, write the condensed electron configuration for bismuth, element 83.
(**b**) How many unpaired electrons does a bismuth atom have?

Solution

(**a**) Our first step is to write the noble-gas core. We do this by locating bismuth, element 83, in the periodic table. We then move backward to the nearest noble gas, which is X*e*, element 54. Thus, the noble-gas core is [X*e*].

Next, we trace the path in order of increasing atomic numbers from X*e* to Bi. Moving from X*e* to Cs, element 55, we find ourselves in period 6 of the *s* block. Knowing the block and the period identifies the subshell in which we begin placing outer electrons, $6s$. As we move through the s block, we add two electrons: $6s^2$.

As we move beyond the s block, from element 56 to element 57, the curved arrow below the periodic table reminds us that we are entering the *f* block. The first row of the *f* block corresponds to the $4f$ subshell. As we move across this block, we add 14 electrons: $4f^{14}$.

With element 71, we move into the third row of the *d* block. Because the first row of the *d* block is $3d$, the second row is $4d$ and the third row is $5d$.Thus, as we move through the ten elements of the *d* block, from element 71 to element 80, we fill the $5d$ subshell with ten electrons: $5d^{10}$.

Moving from element 80 to element 81 puts us into the *p* block in the $6p$ subshell. (Remember that the principal quantum number in the *p* block is the same as in the *s* block.)

Sample Exercise 6.9 Electron Configurations from the Periodic Table

Continued

Moving across to Bi requires 3 electrons: $6p^3$. The path we have taken is

Putting the parts together, we obtain the condensed electron configuration: $[Xe]6s^2 4f^{14} 5d^{10} 6p^3$. This configuration can also be written with the subshells arranged in order of increasing principal quantum number: $[Xe]4f^{14}5d^{10}6s^2 6p^3$.

Finally, we check our result to see if the number of electrons equals the atomic number of Bi, 83: Because Xe has 54 electrons (its atomic number), we have $54 + 2 + 14 + 10 + 3 = 83$. (If we had 14 electrons too few, we would realize that we have missed the *f* block.)

(b) We see from the condensed electron configuration that the only partially occupied subshell is $6p$. The orbital diagram representation for this subshell is

In accordance with Hund's rule, the three $6p$ electrons occupy the three $6p$ orbitals singly, with their spins parallel. Thus, there are three unpaired electrons in the bismuth atom.