

CHEM103

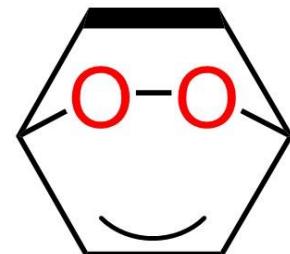
General Chemistry

Chapter 6: Electronic Structure of Atoms



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Assignment 5

Homework 5

Due date: 12th Oct. (Wed)

Review on Chapter 5

Thermochemistry: energy changes involving heat in chemical reactions

Energy: Work & Heat; Potential Energy & Kinetic Energy; System & Surroundings

The 1st law of Thermochemistry: Conversation of Energy; Internal energy; Endothermic & Exothermic; State function & Path function

Enthalpy: Enthalpy of Reaction; Calorimetry; Heat Capacity; Hess's Law; (Standard) Enthalpy of Formation

Outline of Chapter 6

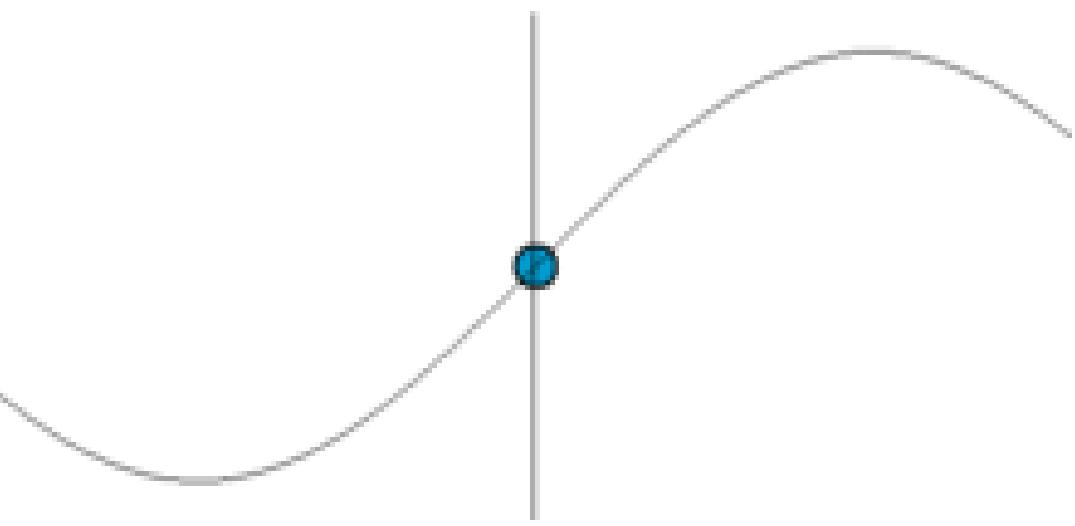
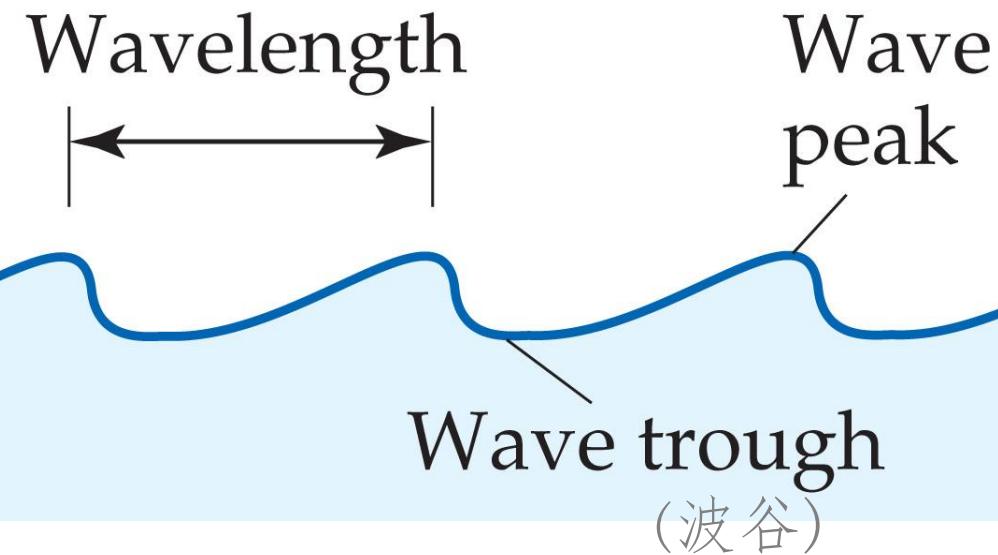
Arrangement of Electrons of an Atom in Atomic Orbitals

Light: Quantized Energy, Photoelectric Effect, Photon, Bohr Model, Matter Wave, Wave-Particle Duality, Uncertainty Principle

Quantum Mechanics: Schrödinger (Wave) Equation, Wave Function, Electron Density

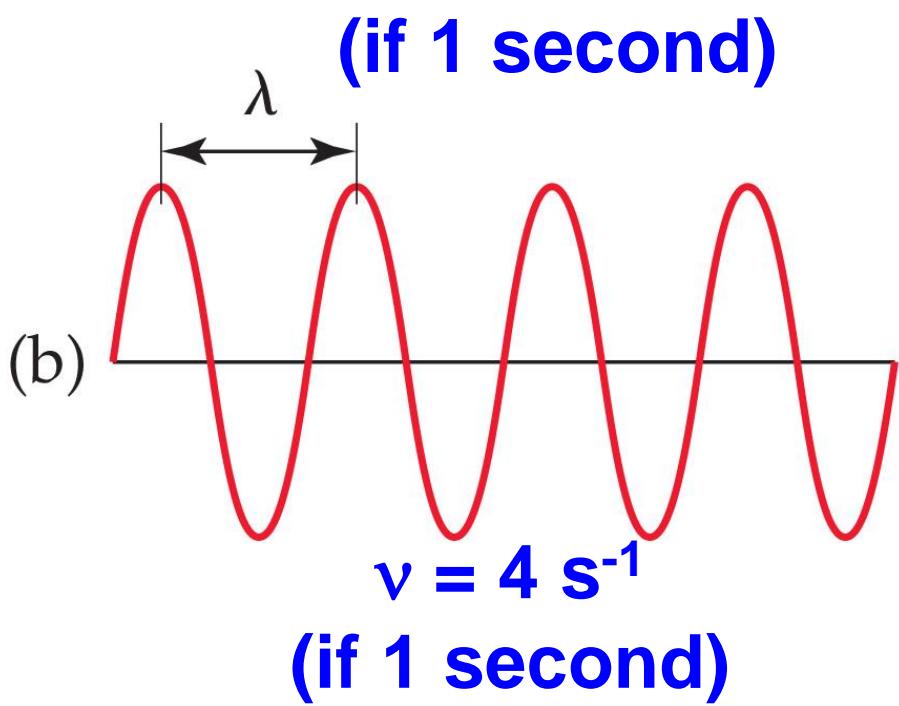
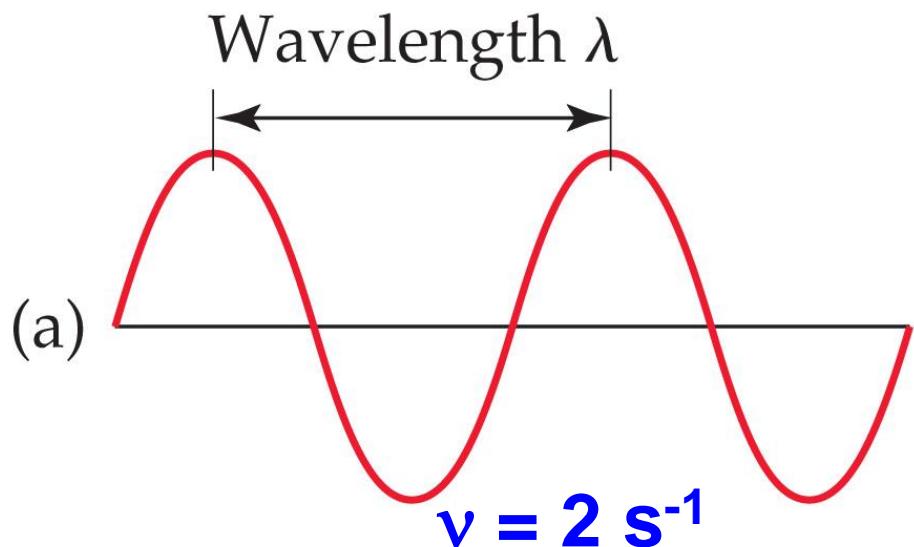
Electrons & Orbitals: Quantum Numbers, Electron Shell, Spin, Pauli Exclusion Principle, Hund's Rule, Electron Configurations

Waves (波)



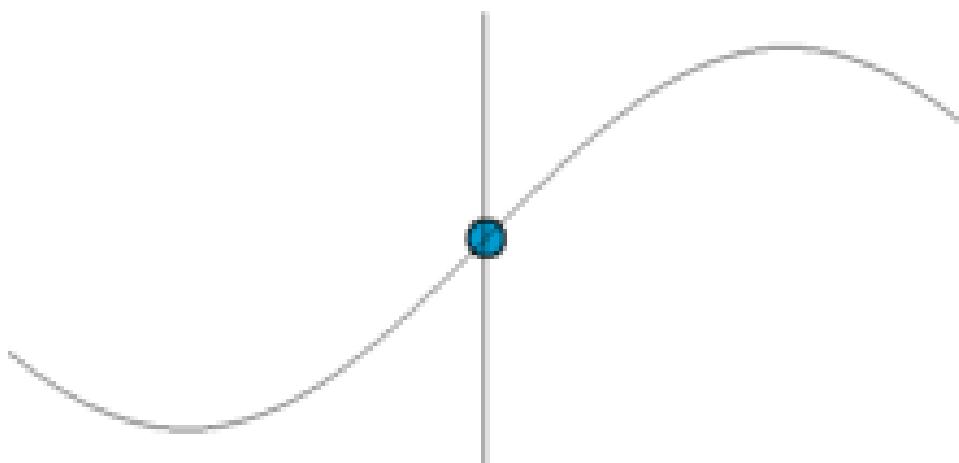
- To understand the **electronic structure** (电子结构) of atoms, one must understand the nature of **electromagnetic radiation** (电磁辐射).

- **Distance** between the corresponding points on adjacent waves is the **wavelength (λ , 波长)**.

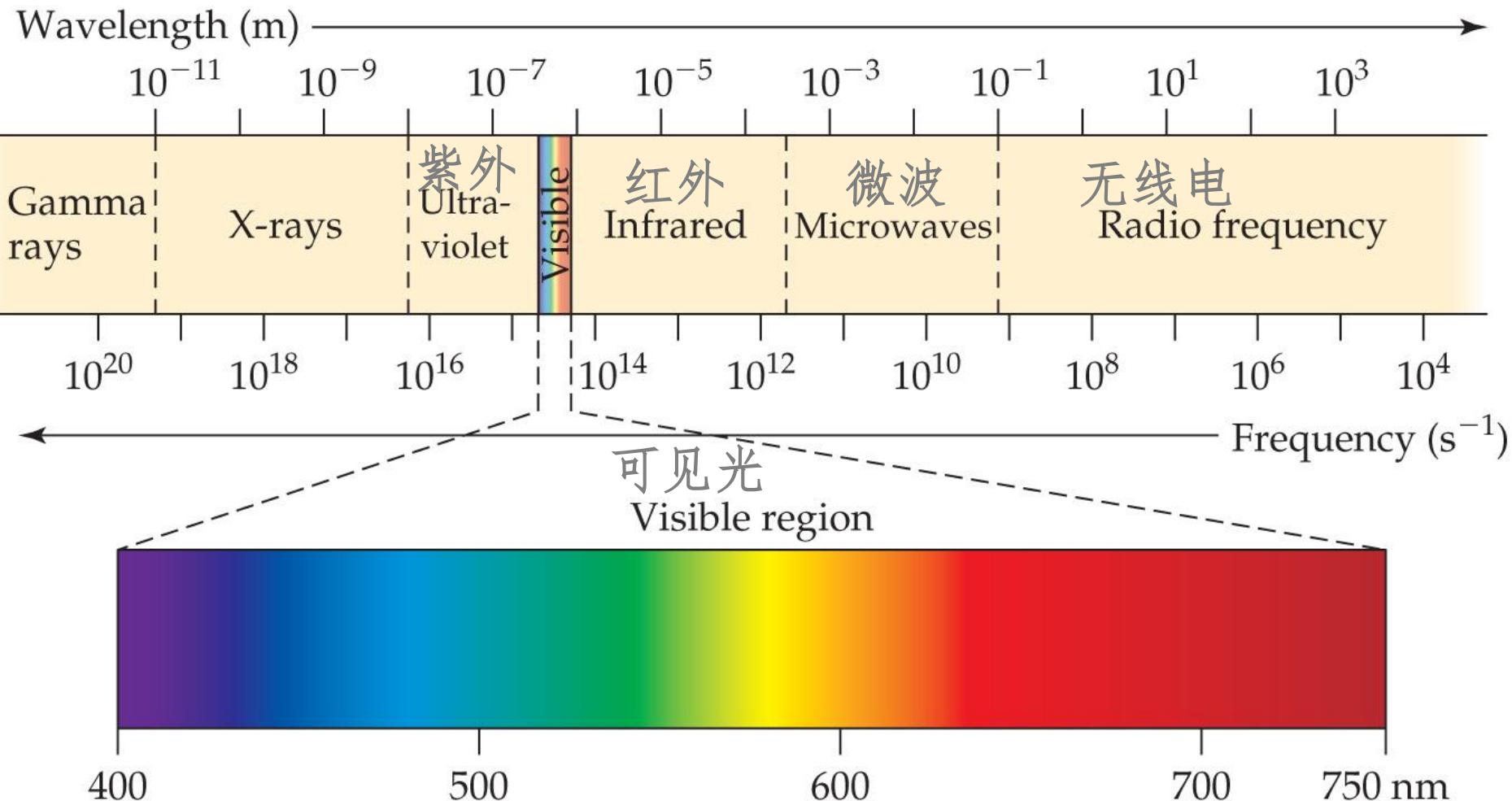


- The number of waves passing a given point per unit of time (e.g. second) is the **frequency (ν , 频率)**: periodic; Unit: s^{-1} (or Hz)

- For waves traveling at the **same velocity**, the longer the wavelength, the smaller the frequency.



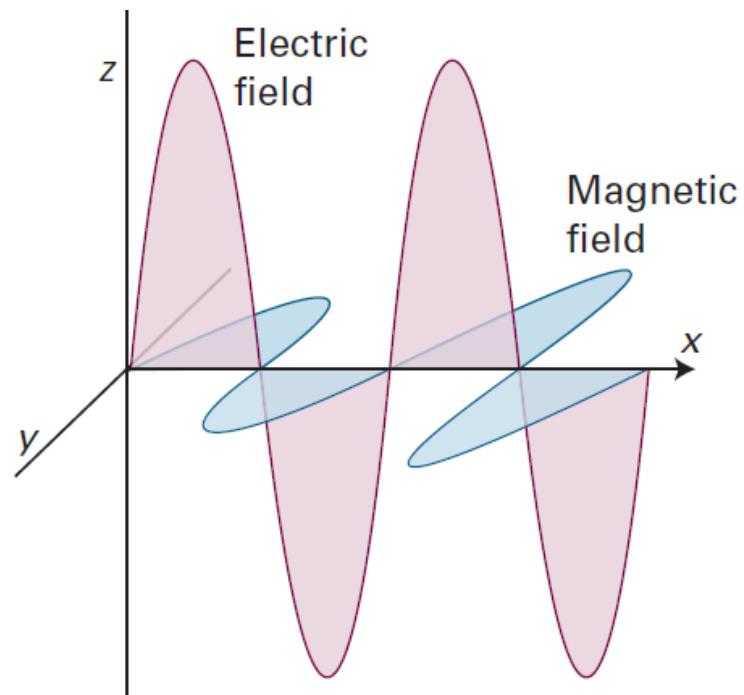
Electromagnetic Spectrum (电磁谱)



- All electromagnetic radiation travels at the **same velocity: the speed of light (c)**, $3.00 \times 10^8 \text{ m/s}$.

$$c = \lambda\nu$$

Unit	Symbol	Length (m)	Type of Radiation
Angstrom	\AA	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



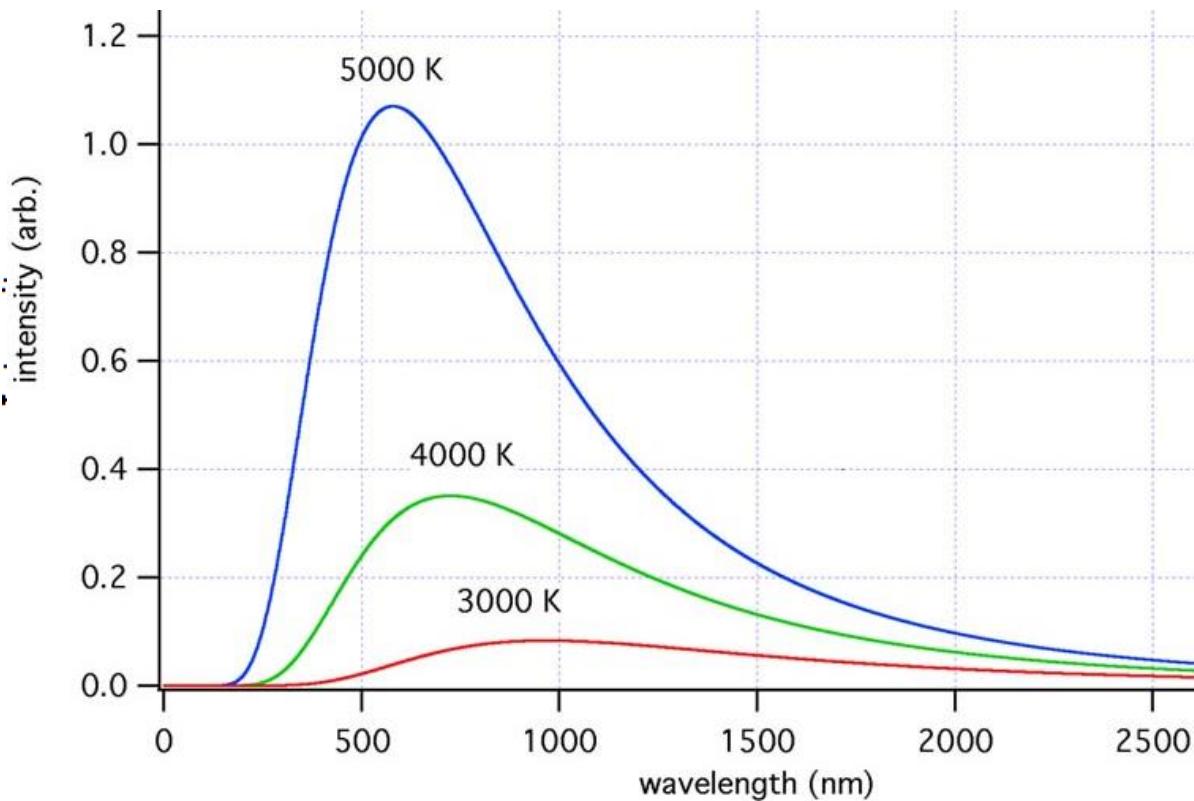
The **longer** the wavelength (λ),
the **smaller** the frequency (ν) &
the **lower** the energy (E).

The Nature of Energy



The **wave nature of light** (*classic physics*) can **NOT** explain three key observations.

1. How can an **object/matter emit radiation** when its **temperature increases** (black-body radiation 黑体辐射)?



Quantized Energy

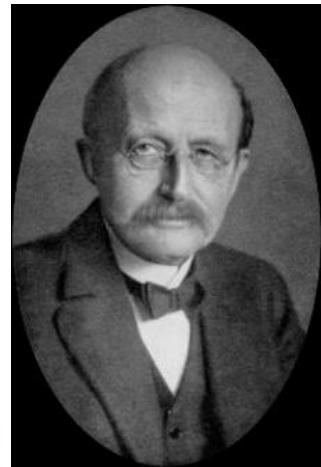
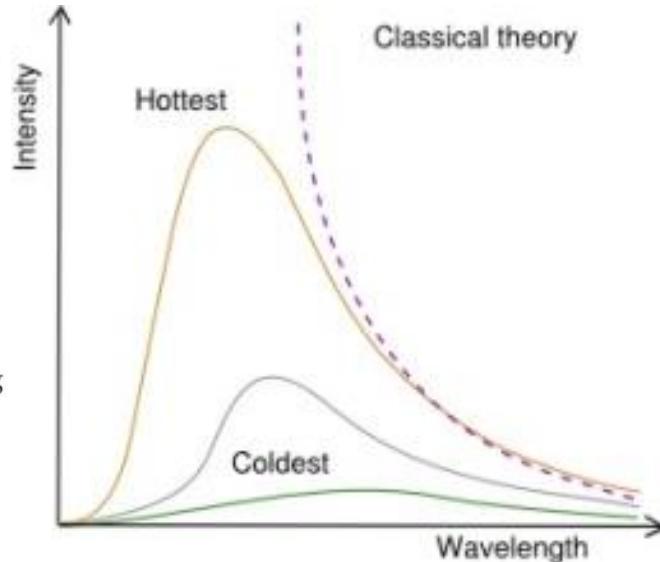
Max Planck



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



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

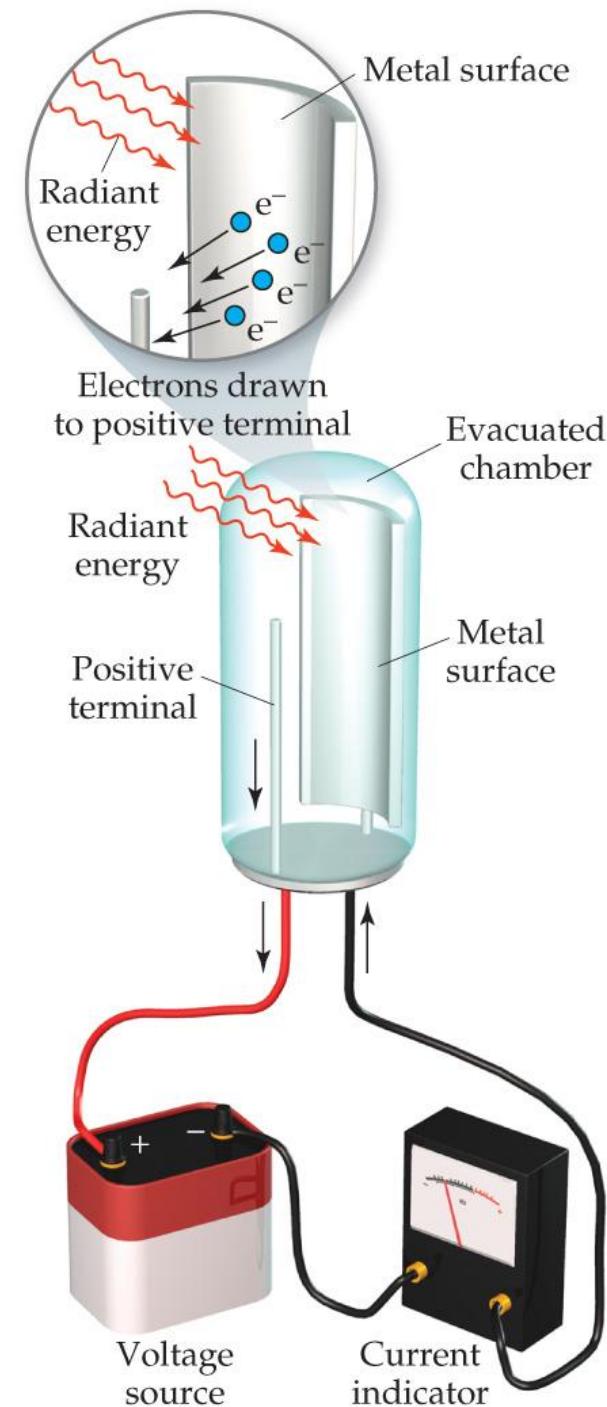
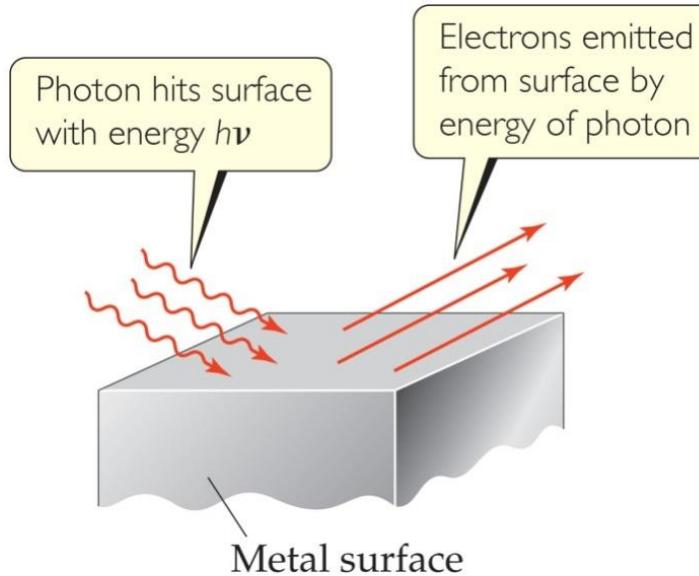
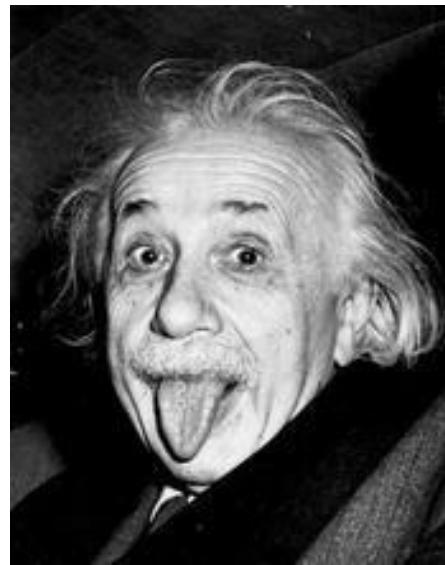


- **Energy** can be either **released or absorbed** by **atoms only** in **discrete** (不连续的) amounts of some minimum size: **Energy** is **quantized** (NOT **continuous**, **classic** physics).
- **Quantum** (量子), the **smallest amount** ($n = 1, 2, \dots$ etc) of **energy** (E) emitted or absorbed:

$$E = nh\nu$$

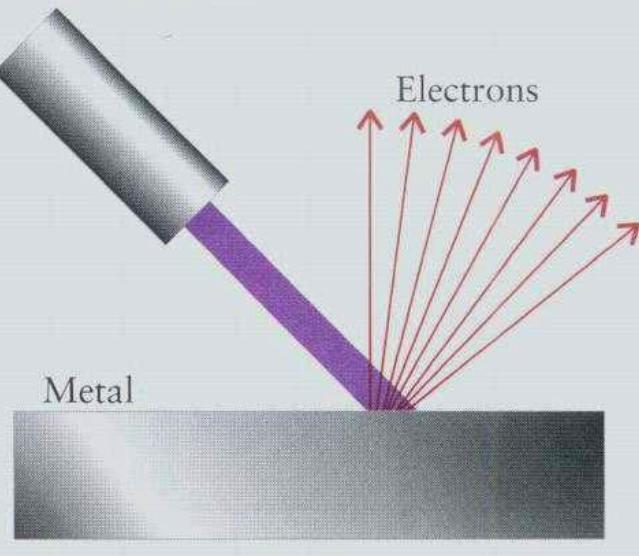
where h is **Planck's constant** ($6.626 \times 10^{-34} \text{ J}\cdot\text{s}$)

Photoelectric Effect: Matter Nature of Light



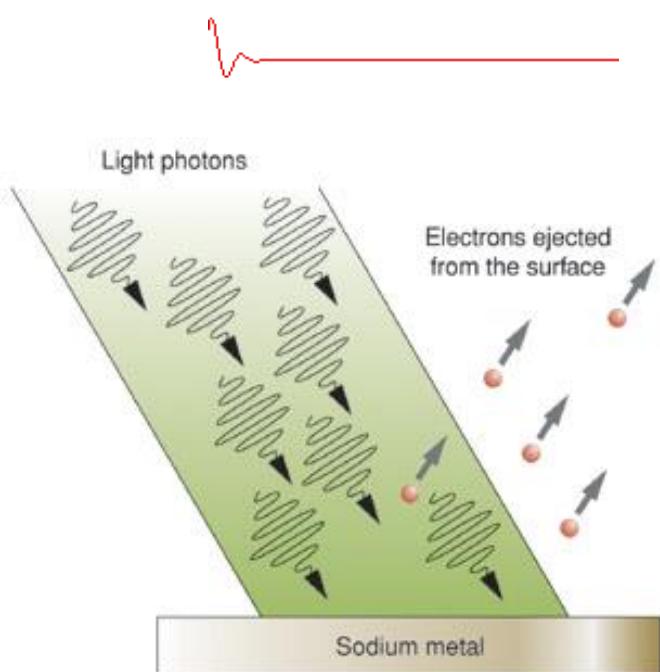
2. Einstein used quantum theory to explain the **photoelectric** (光电) **effect**:
Emission of electrons (matter) from metal surface by light (wave).

Ultraviolet
radiation source

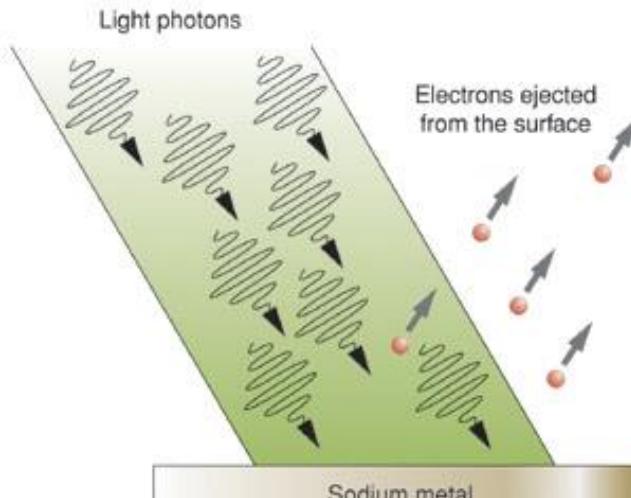


- Radiant energy (radiation) behaves like a stream of tiny energy **packets** (小包); a particle (粒子) of energy is called a **photon** (光子, vs. proton H^+).

- **Each photon** has an energy (E) equal to $h\nu$.

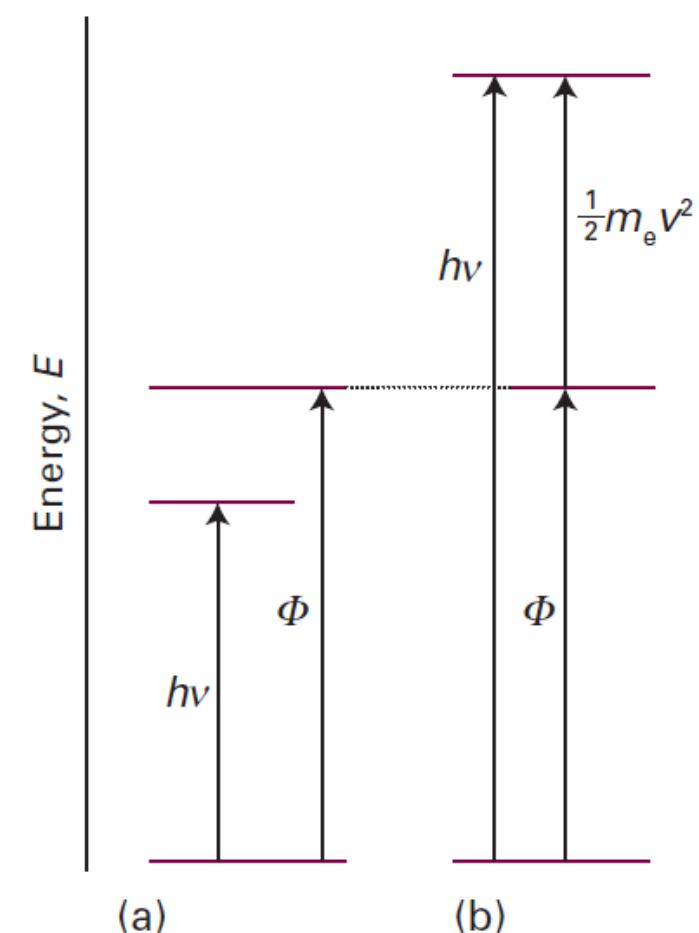
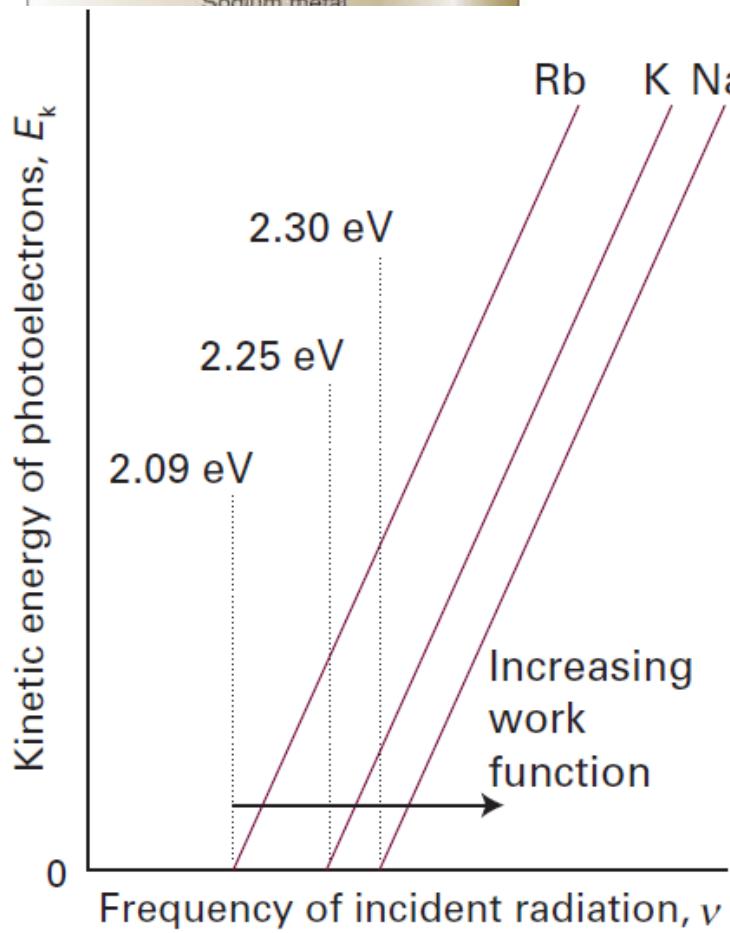


- **Intensity** of light proportional to the **number** of ejected photons (Not energy). **Frequency** of light proportional to **energy** of ejected photons.



- Electrons are emitted, if photons have **enough energy (frequency)** to overcome work function Φ (**NOT intensity**).

$$\frac{1}{2}m_e v^2 = h\nu - \Phi$$



If one knows the wavelength of light (**wave**), one can calculate the energy in one photon (**particle**), or packet, of that light:

$$c = \lambda\nu$$

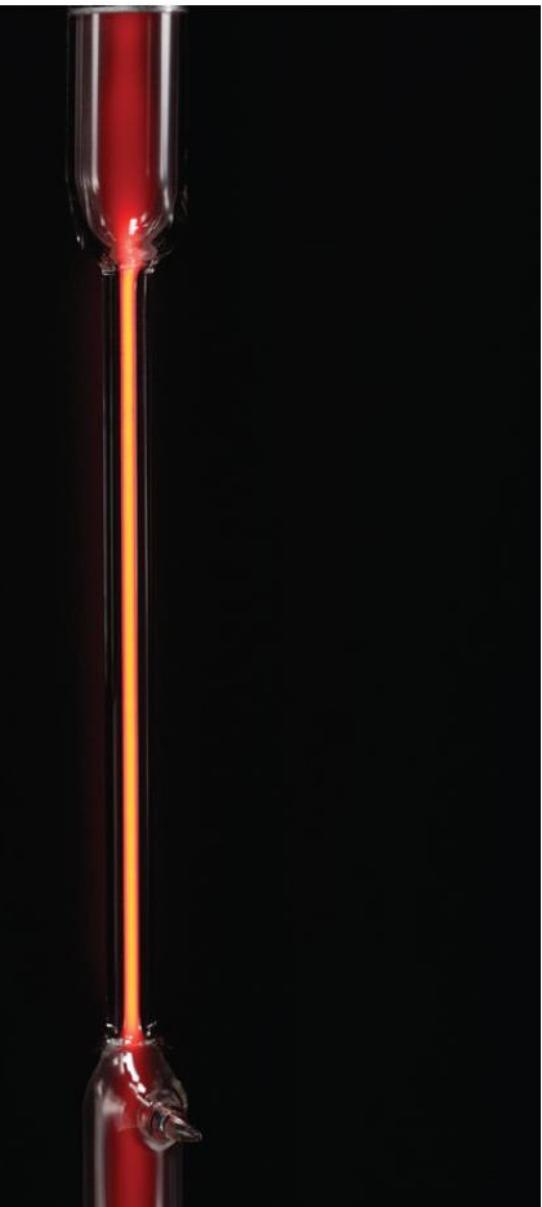
$$\begin{aligned}E &= h\nu \\&= hc/\lambda\end{aligned}$$



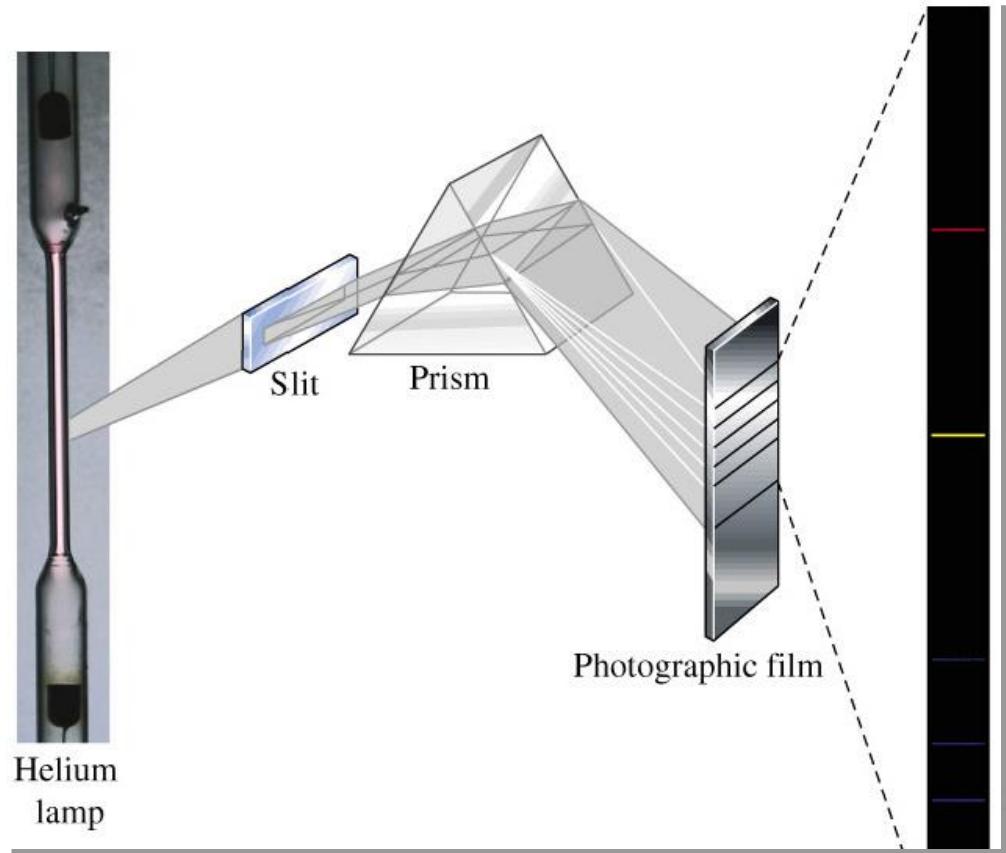
Hydrogen (H)

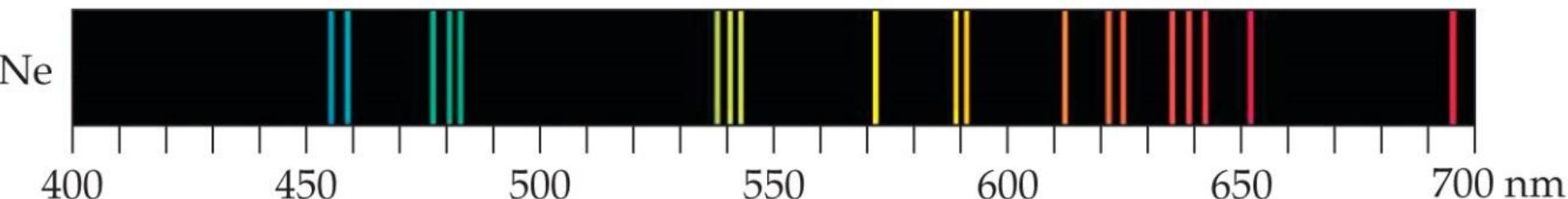
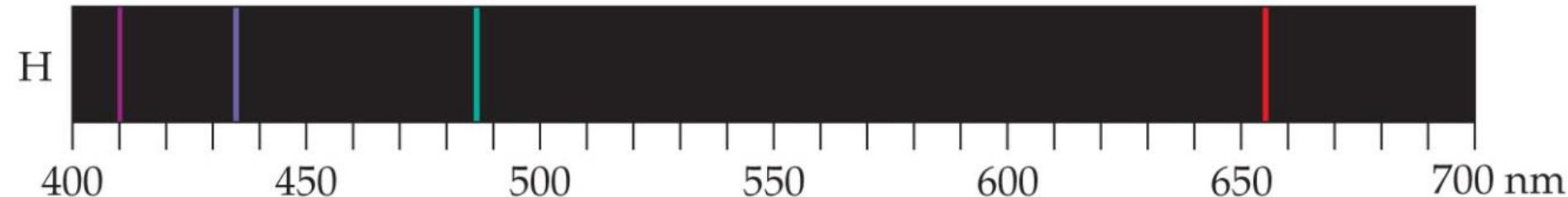
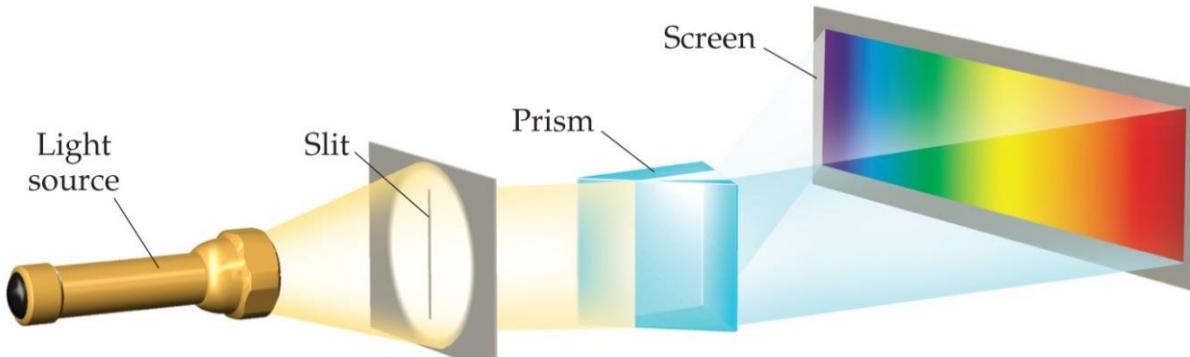
Emission (Line) Spectra

3. Another mystery (神秘的事物): the **different** observed emission spectra (发射光谱) from **different** atoms and molecules (**different lines**).

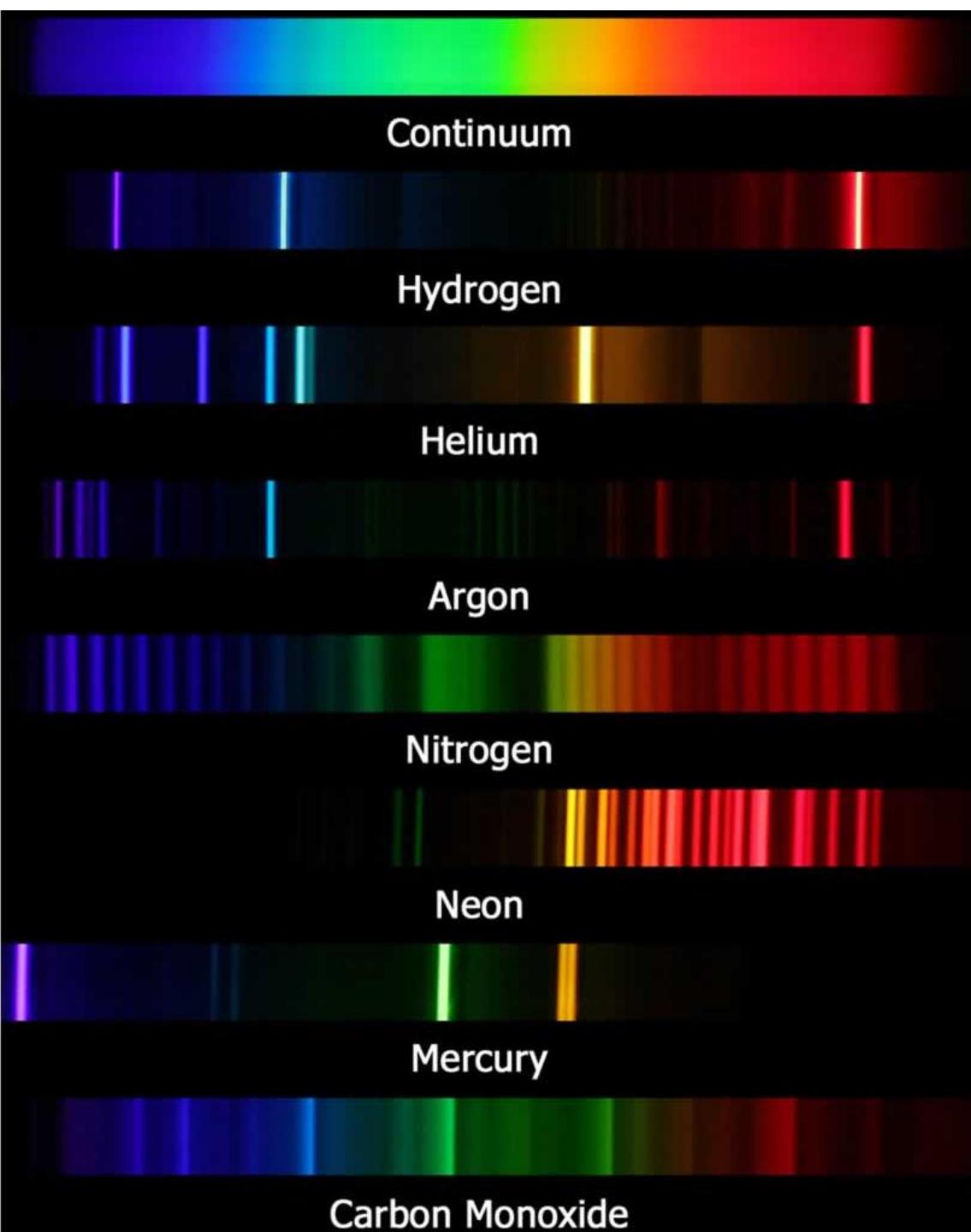


Neon (Ne)



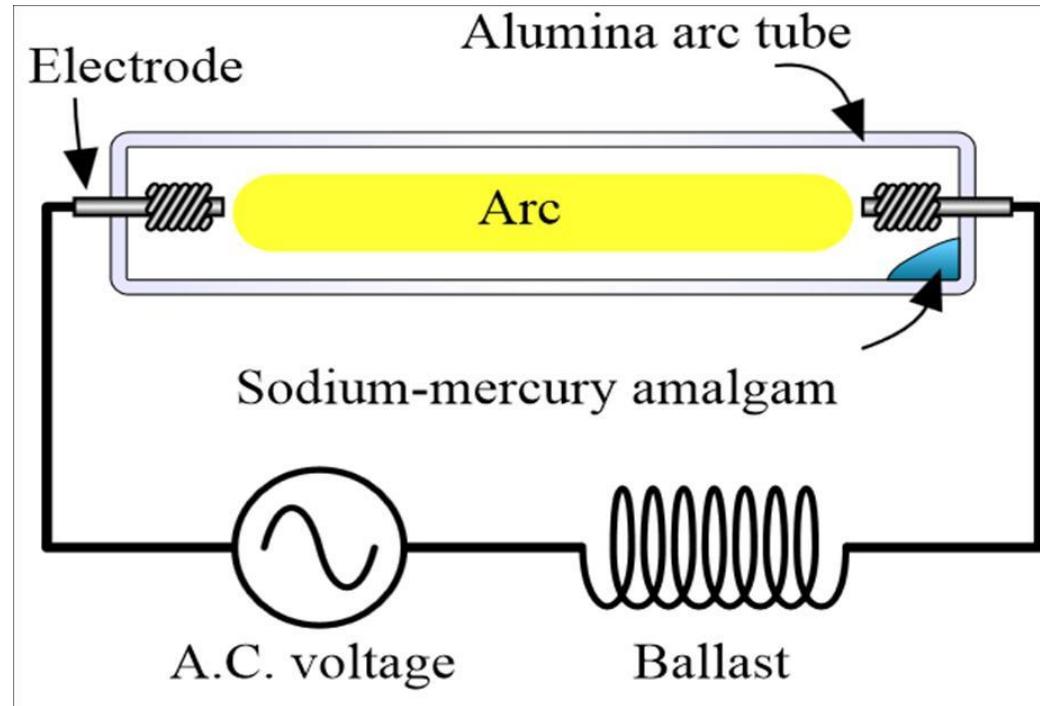


- For atoms and molecules, one does **NOT** observe a **continuous** (连续) **spectrum**, as one gets from a white light source.
- Only a **line spectrum** of **discrete** (不连续的) **and specific** wavelengths is observed.



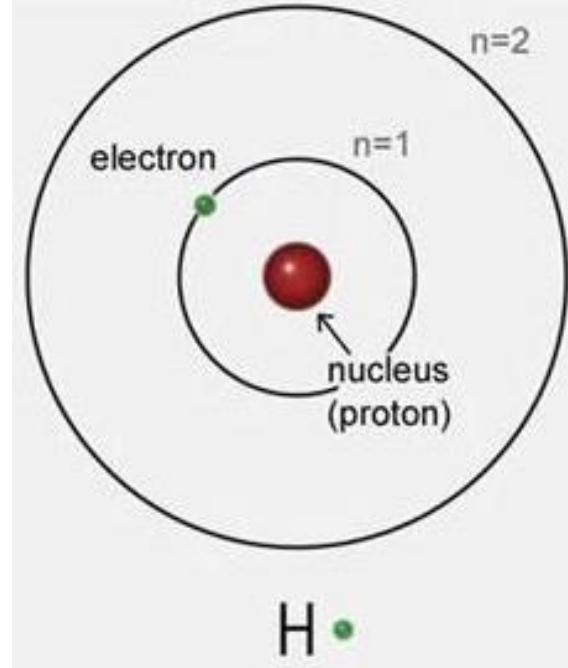
Application of Line Spectrum

Sodium light

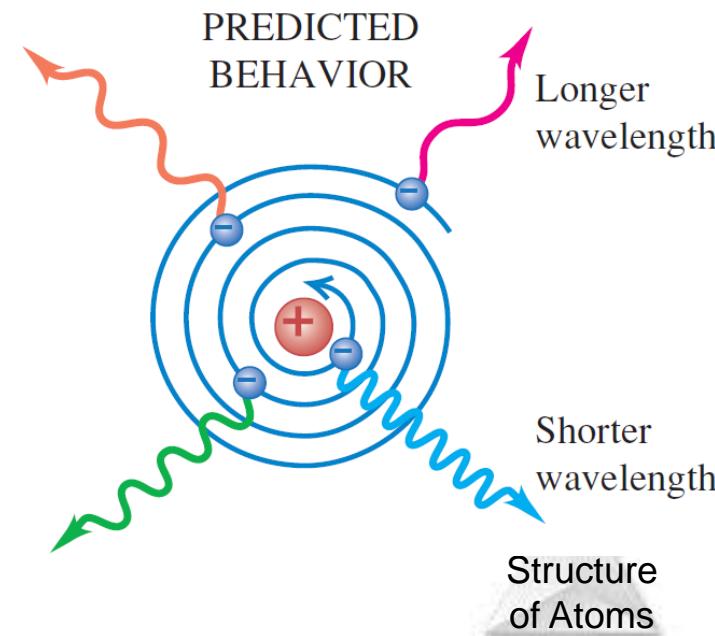


Bohr model

Electrons in hydrogen atoms move in **circular orbits** around the nucleus.



According to **classical physics**, a charged particle moving in a circular path should **continuously lose energy**. As an electron loses energy, it should **spiral into the positively-charged nucleus** (larger electrostatic attraction). That can't explain the line spectrum.

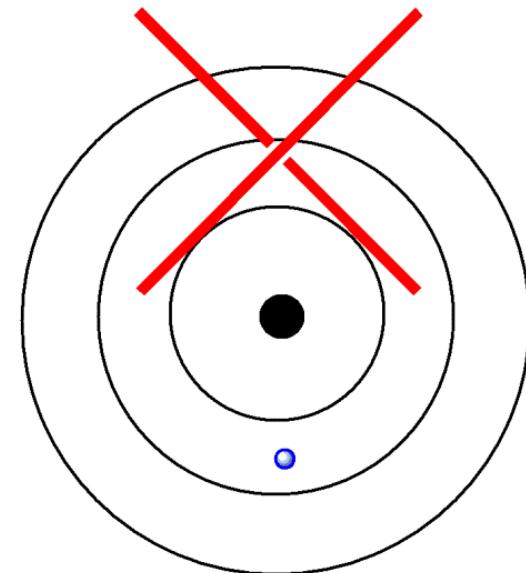
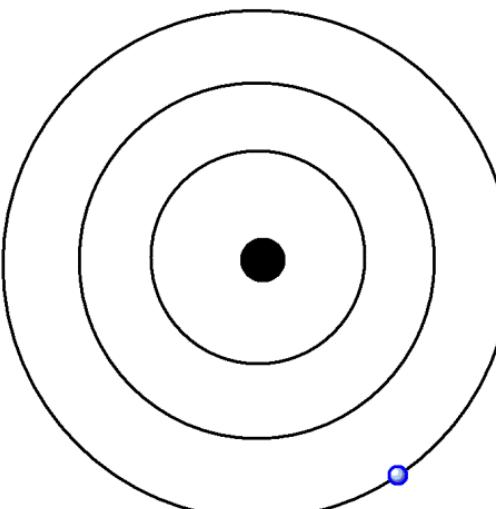
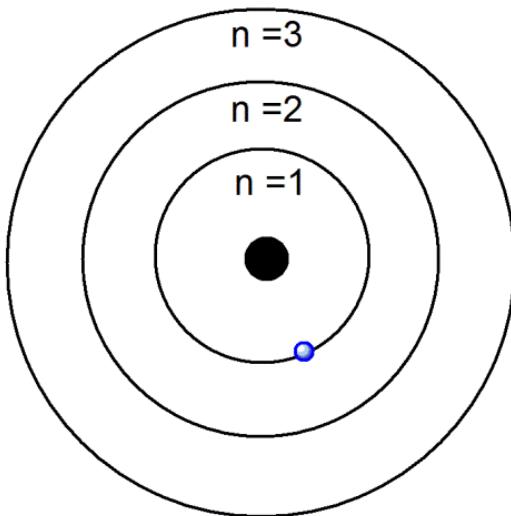


Niels Bohr adopted Planck's idea:

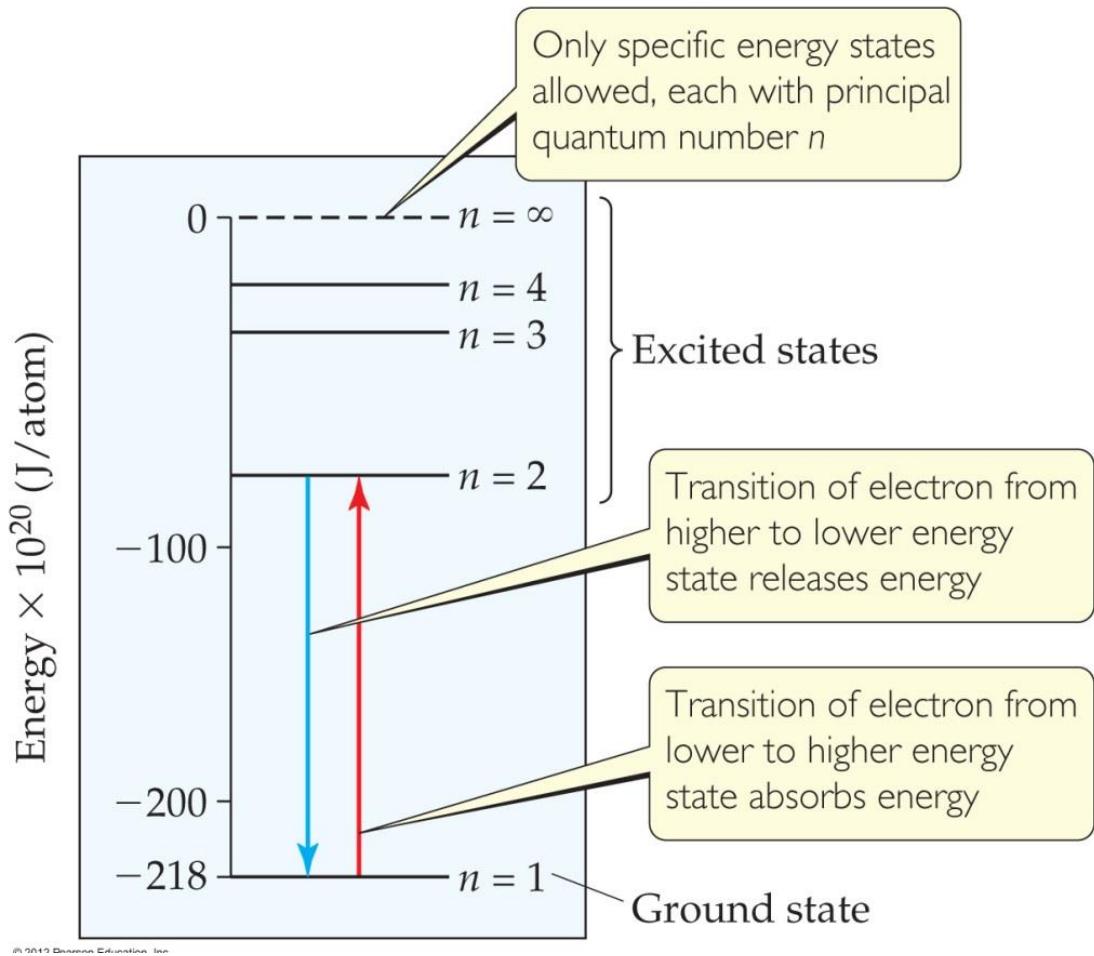
1. Electrons in an atom can only **occupy** and **move in certain orbits** (轨道).



2. Electrons in “allowed” orbits have **specific energies**. These energies are **not radiated** from the atom (NOT spiral into the nucleus).



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ms



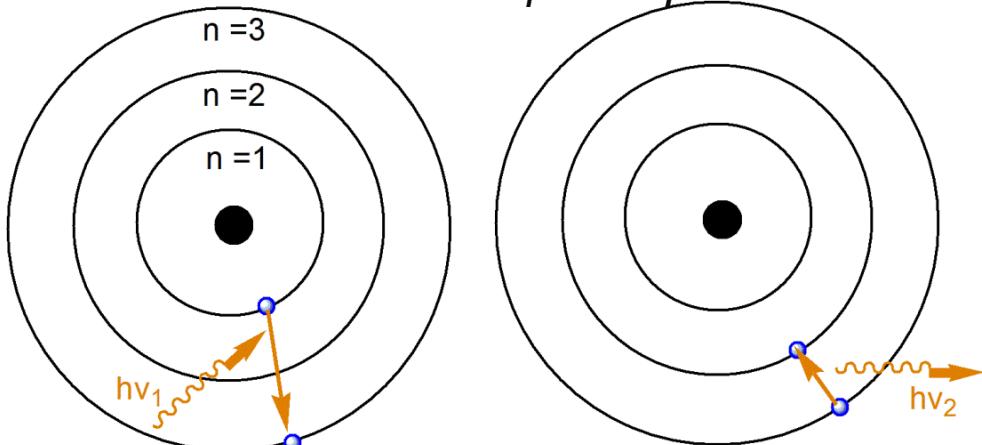
Absorption

If $n_f > n_i$, $\Delta E > 0$

3. Energy is absorbed or emitted only if the electron moves from one “allowed” energy state (orbit) to another “allowed” energy state; Such energy is defined by $\Delta E_i = h\nu_i$

Emission

If $n_f < n_i$, $\Delta E < 0$



Energy level determined by n value
(whole-number values, e.g. 1, 2, 3,...etc):

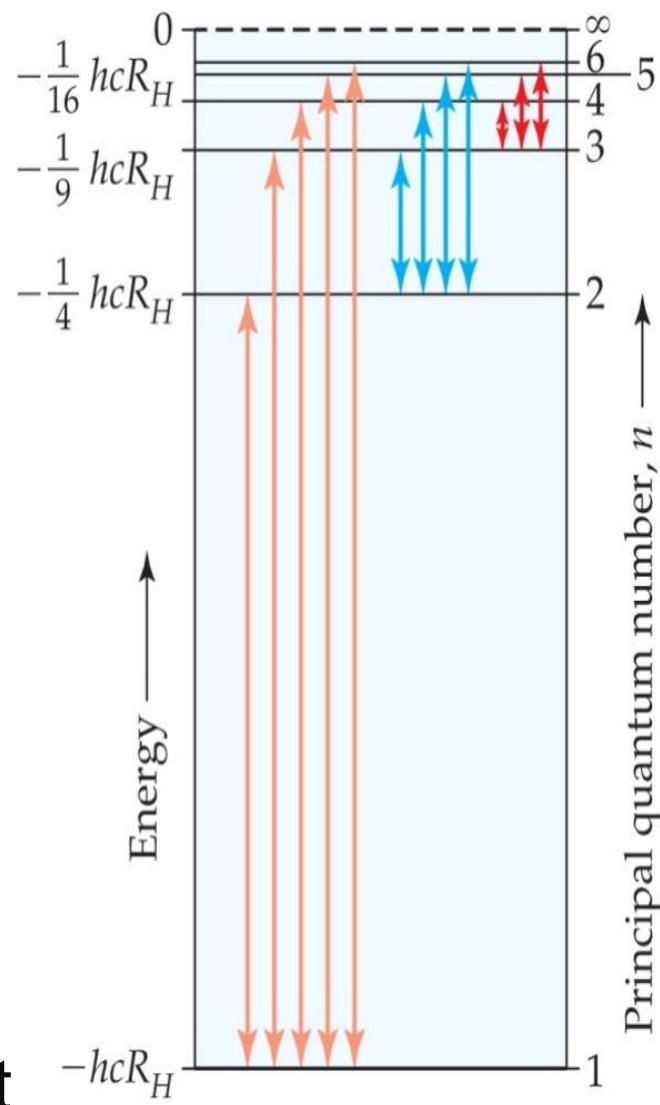
$$E = -hcR_H \left(\frac{1}{n^2} \right) = -2.18 \times 10^{-18} J \left(\frac{1}{n^2} \right)$$

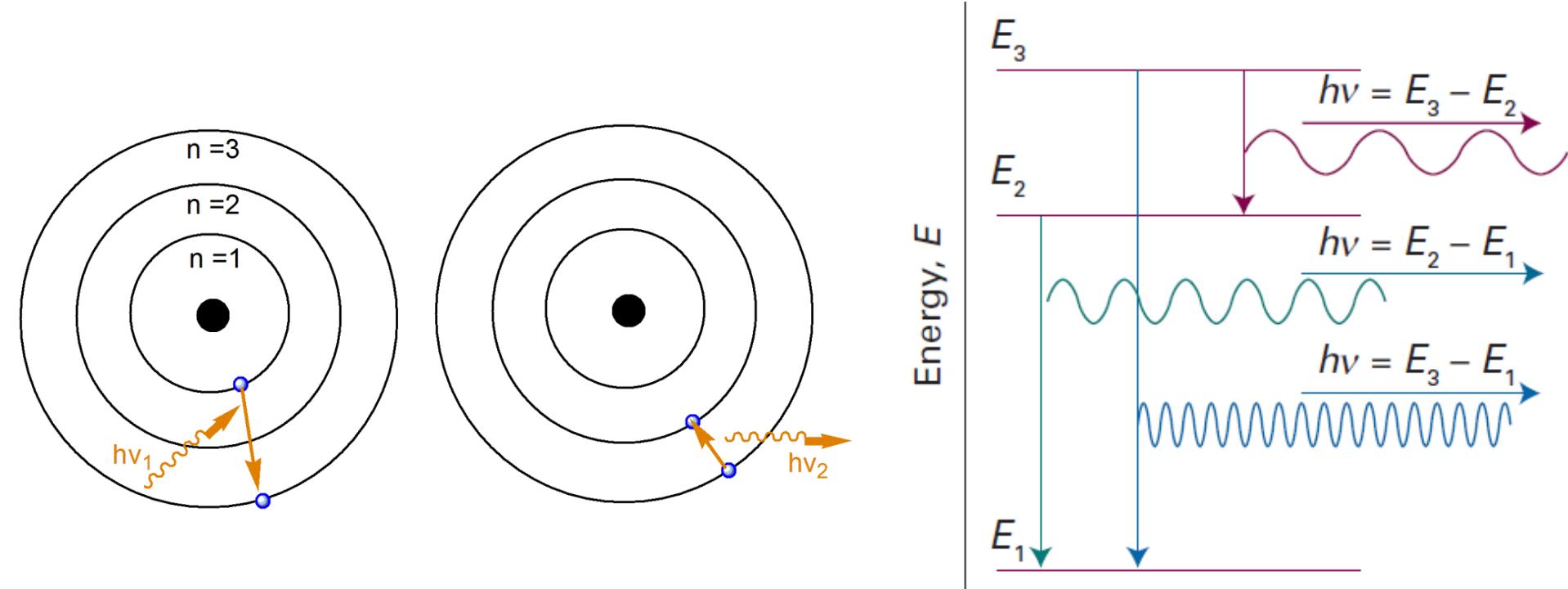
Energy absorbed or emitted can be calculated by these equations:

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

R_H : the Rydberg constant
($1.097 \times 10^7 \text{ m}^{-1}$);

n_i & n_f are the initial & final energy levels of the electron.





Electrons exist only in a certain discrete energy levels described by principal quantum numbers (n).

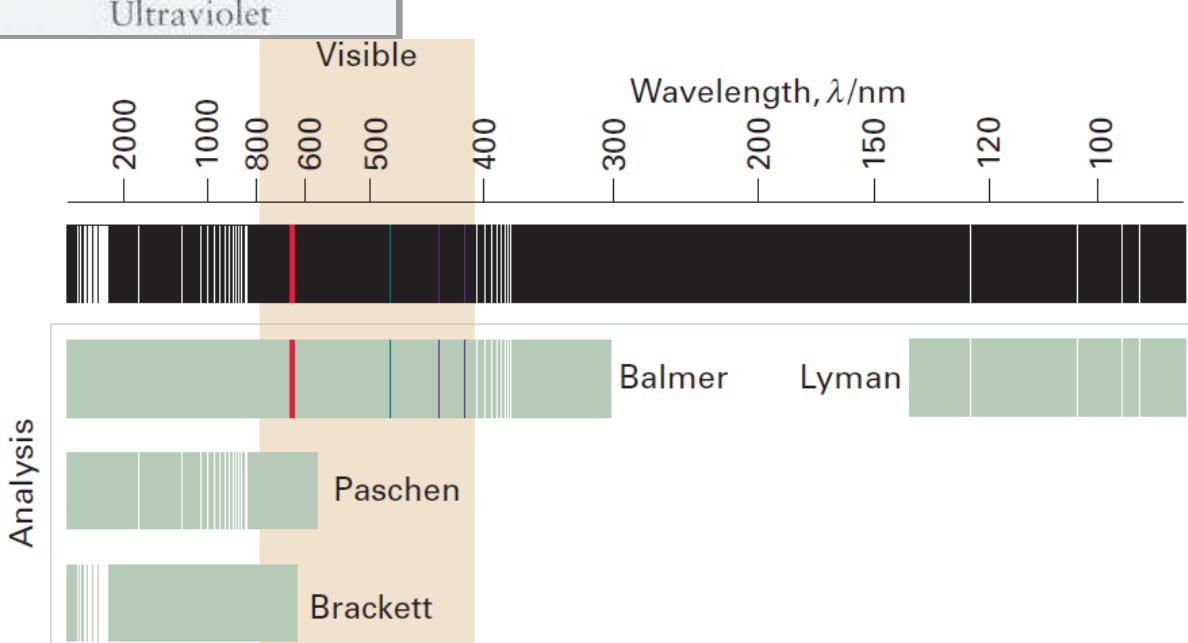
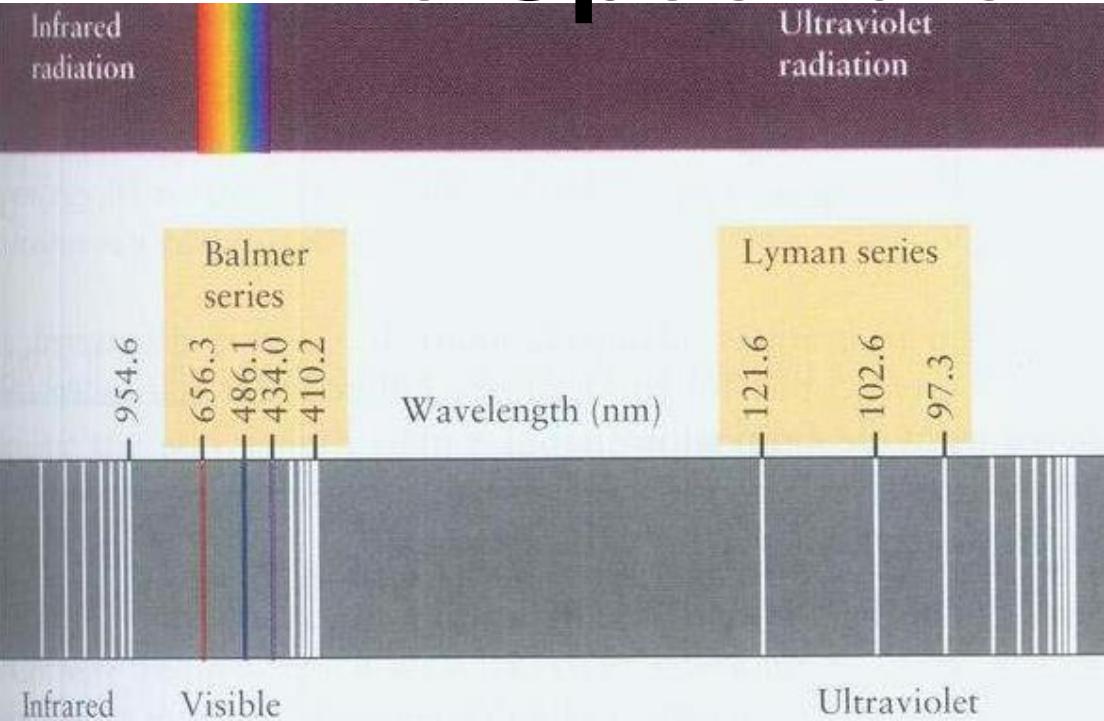
Ground state: $n = 1$;

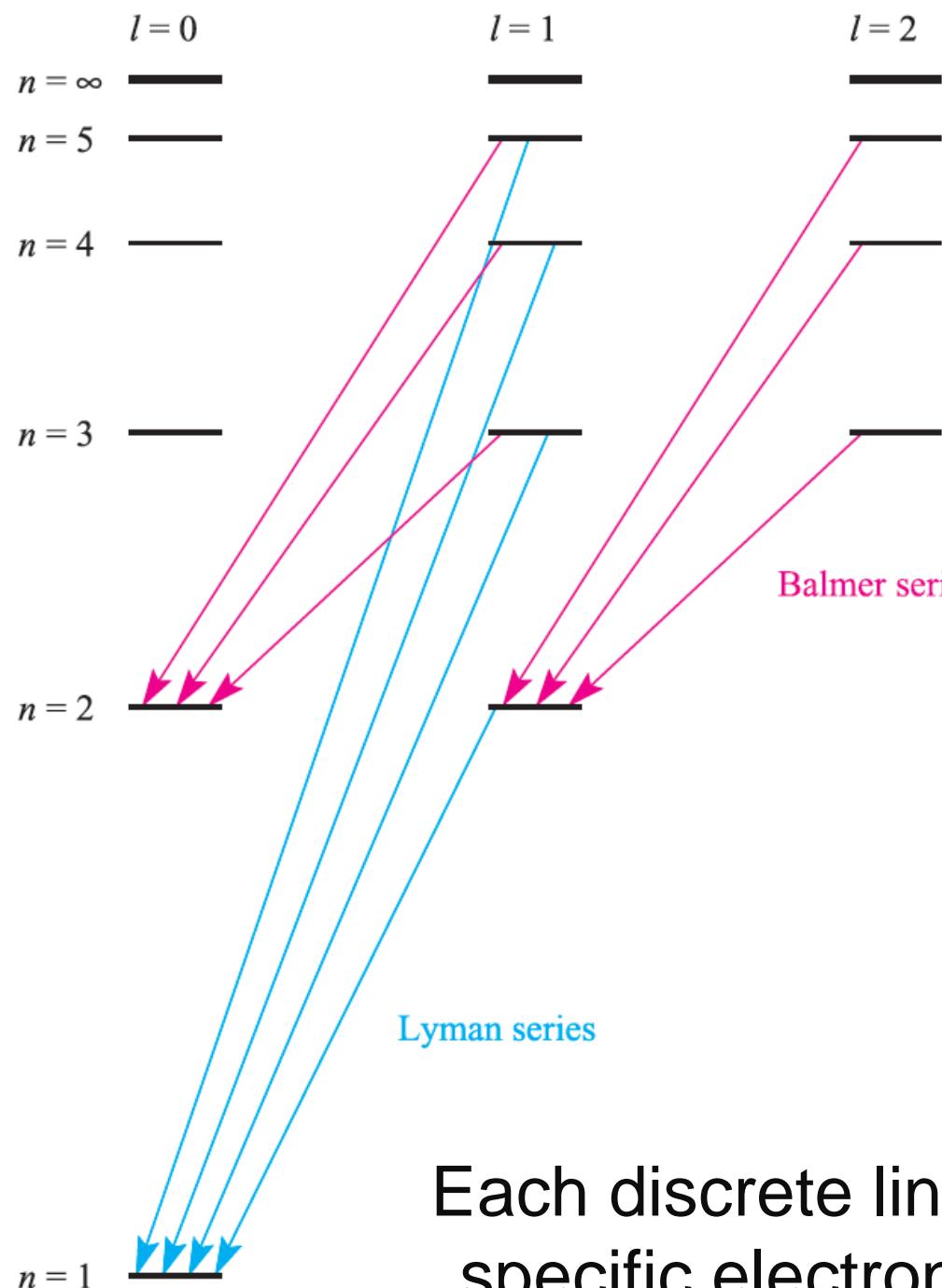
Excited state: $n > 1$

If $n_f > n_i$, $\Delta E > 0$ (**excitation**);

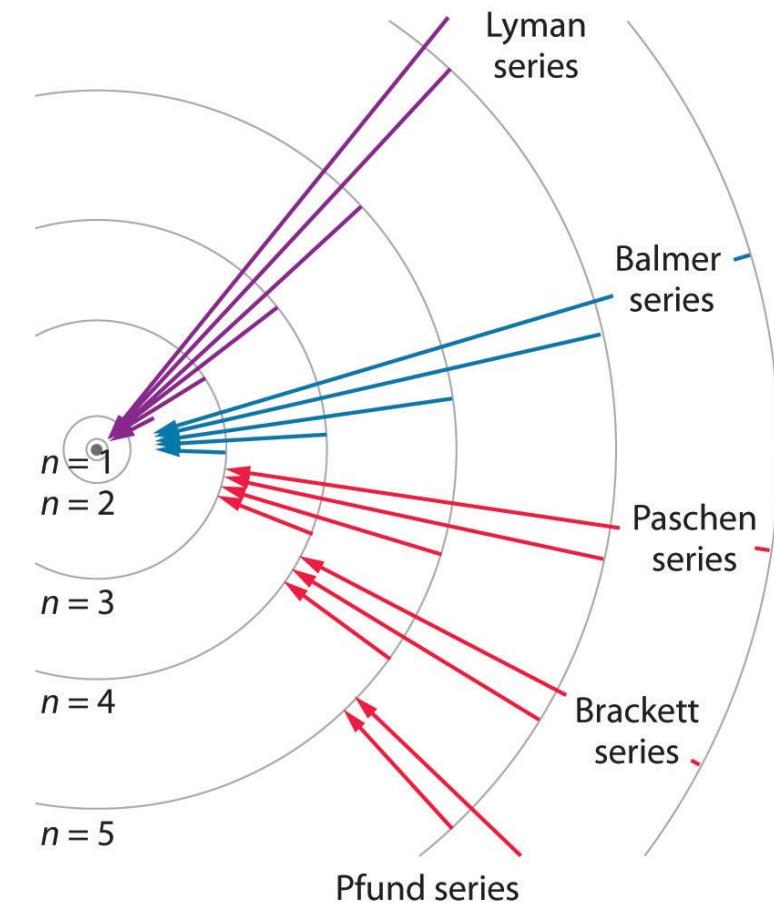
If $n_f < n_i$, $\Delta E < 0$.

Line Spectra of Hydrogen





$n = \infty = \text{the continuum}$



Each discrete line reflects one specific electronic transition.

Limitations of Bohr model

1. Cannot explain the spectra of the other atoms.
2. Cannot explain why an electron does not fall into the nucleus (he assumed).

Two important ideas of Bohr Model

- **Electrons** exist only **in a certain discrete energy levels** described by **quantum numbers (n)**.
- **Energy** is involved in the **transition** (变迁) **of an electron from one allowed energy level to another allowed energy level.**

The wavelength of a photon multiplied by its frequency equals

- a. c, the speed of light.
- b. h, Planck's constant.
- c. Avogadro's Number.
- d. 4.184.

The lowest energy state of a hydrogen atom is called its _____ state.

- a. bottom
- b. ground
- c. fundamental
- d. original

Before reading further about Bohr's model, speculate as to how it explains the fact that hydrogen gas emits a line spectrum (Figure 6.11) rather than a continuous spectrum.

- A. Only certain orbits are allowed.
- B. An electron can only exist in one “allowed” energy state.
- C. Electrons do not spiral into the nucleus.
- D. Electrons can only change from one “allowed” energy state to another.

As the electron in a hydrogen atom jumps from the $n = 3$ orbit to the $n = 7$ orbit, does it absorb energy or emit energy?

- A. It neither emits nor absorbs energy.
- B. It both emits and absorbs energy simultaneously.
- C. It emits energy.
- D. It absorbs energy.

Which has more energy, a photon of infrared light or a photon of ultraviolet light?

- A. Photon of infrared light
- B. Photon of ultraviolet light

The Wave Nature of Matter



Louis de Broglie

- If light can have **matter properties**, matter should exhibit **wave properties (matter waves)**.
- The **relationship between mass and wavelength** of any particle:

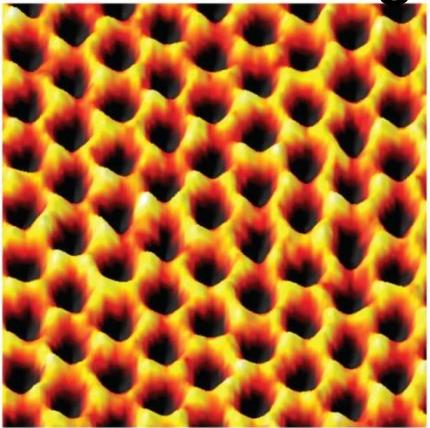
$$\lambda = \frac{h}{mv}$$

Wave-Particle Duality:

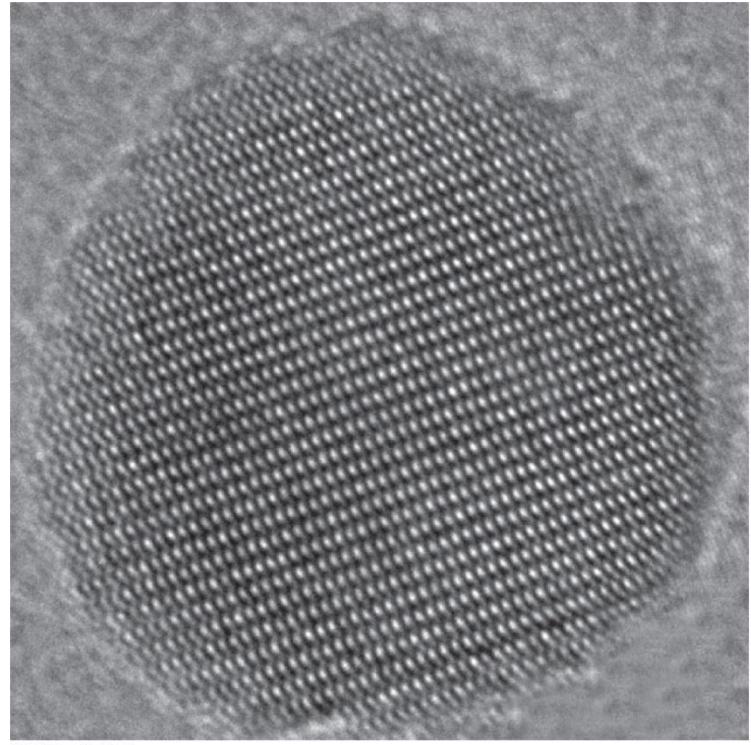
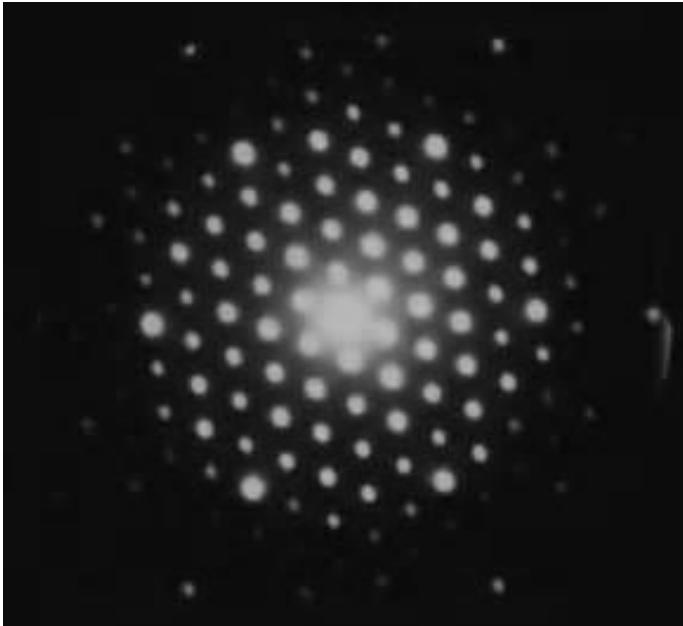
Combination of the concepts of classical mechanics with the idea of wave-like properties: a **particle** with **momentum (mv , 动量)** possesses an associated **wave** of **wavelength λ** .

Electrons (Matter) as Waves

Electron micrograph



Electron diffraction



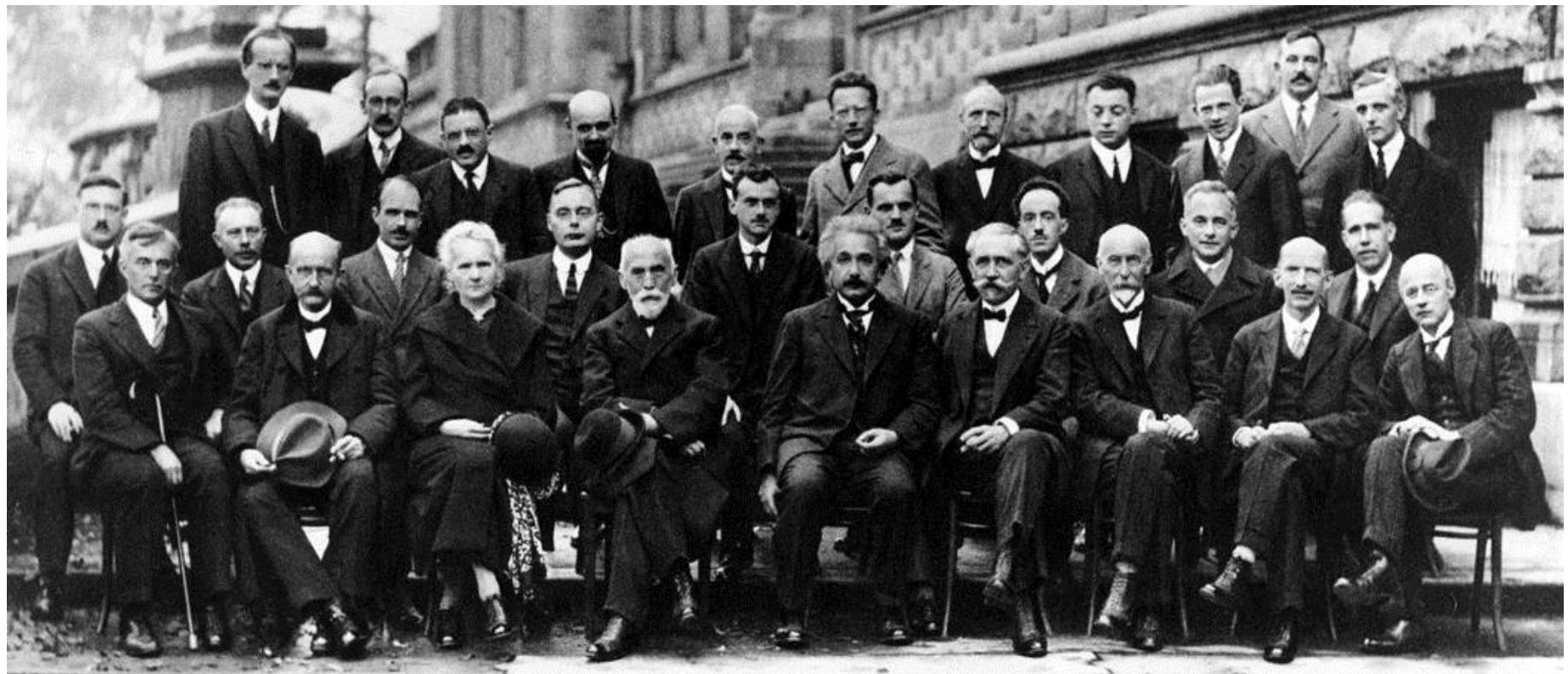
Transmission electron
micrograph (TEM)

Particles Wavelength

物体粒子	质量 m/kg	速度 $v/(\text{m}\cdot\text{s}^{-1})$	波长 λ/pm
1 V电子	9.1×10^{-31}	5.9×10^5	1200
100 V电子	9.1×10^{-31}	5.9×10^6	120
1000 V电子	9.1×10^{-31}	1.9×10^7	37
10000 V电子	9.1×10^{-31}	5.9×10^7	12
He 原子 (300K)	6.6×10^{-27}	1.4×10^3	72
Xe 原子 (300K)	2.3×10^{-25}	2.4×10^2	12
垒球	2.0×10^{-1}	30	1.1×10^{-22}
枪弹	1.0×10^{-2}	1.0×10^3	6.6×10^{-23}

Any object of mass (m) and velocity (v) would have a characteristic **matter wave**. However, the wavelength for an object of ordinary size is **too small** to be completely observed.

Solvay Conference 1927: “Electrons and Photons”

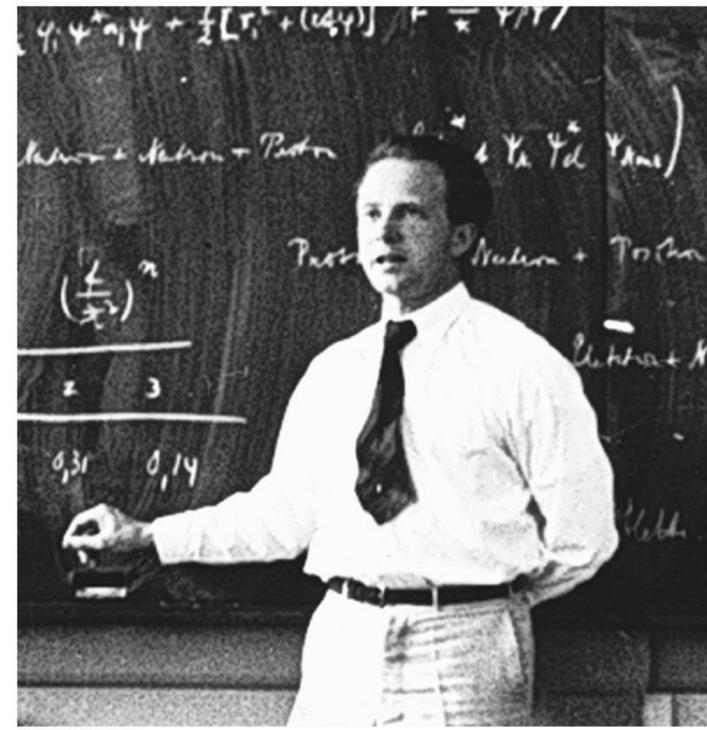


Piccard, Henriot, Ehrenfest, Herzen, de Donder, Schrödinger,
Verschaffelt, Pauli, Heisenberg, Fowler, Brillouin;
Debye, Knudsen, Bragg, Kramers, Dirac, Compton, de Broglie,
Born, Bohr;
Langmuir, Planck, Skłodowska-Curie, Lorentz, Einstein,
Langevin, Guye, Wilson, Richardson

The Uncertainty Principle

Heisenberg showed that the **more precise** the **momentum** (mv) of a particle is known, the **less precise** its **position** (x) is known **at the same time**:

$$\Delta x * \Delta(mv) \geq \frac{h}{4\pi}$$

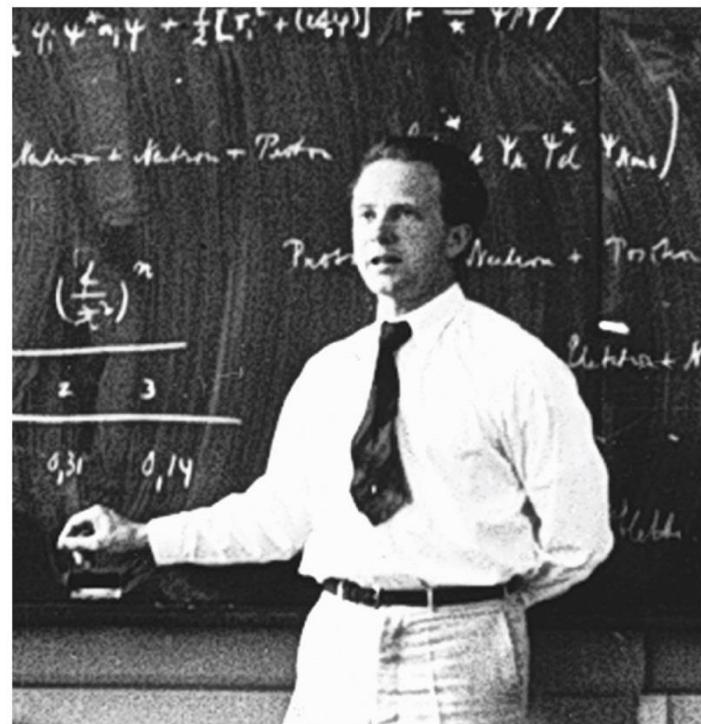


Δx = uncertainties in position
 $\Delta(mv)$ = uncertainties in momentum

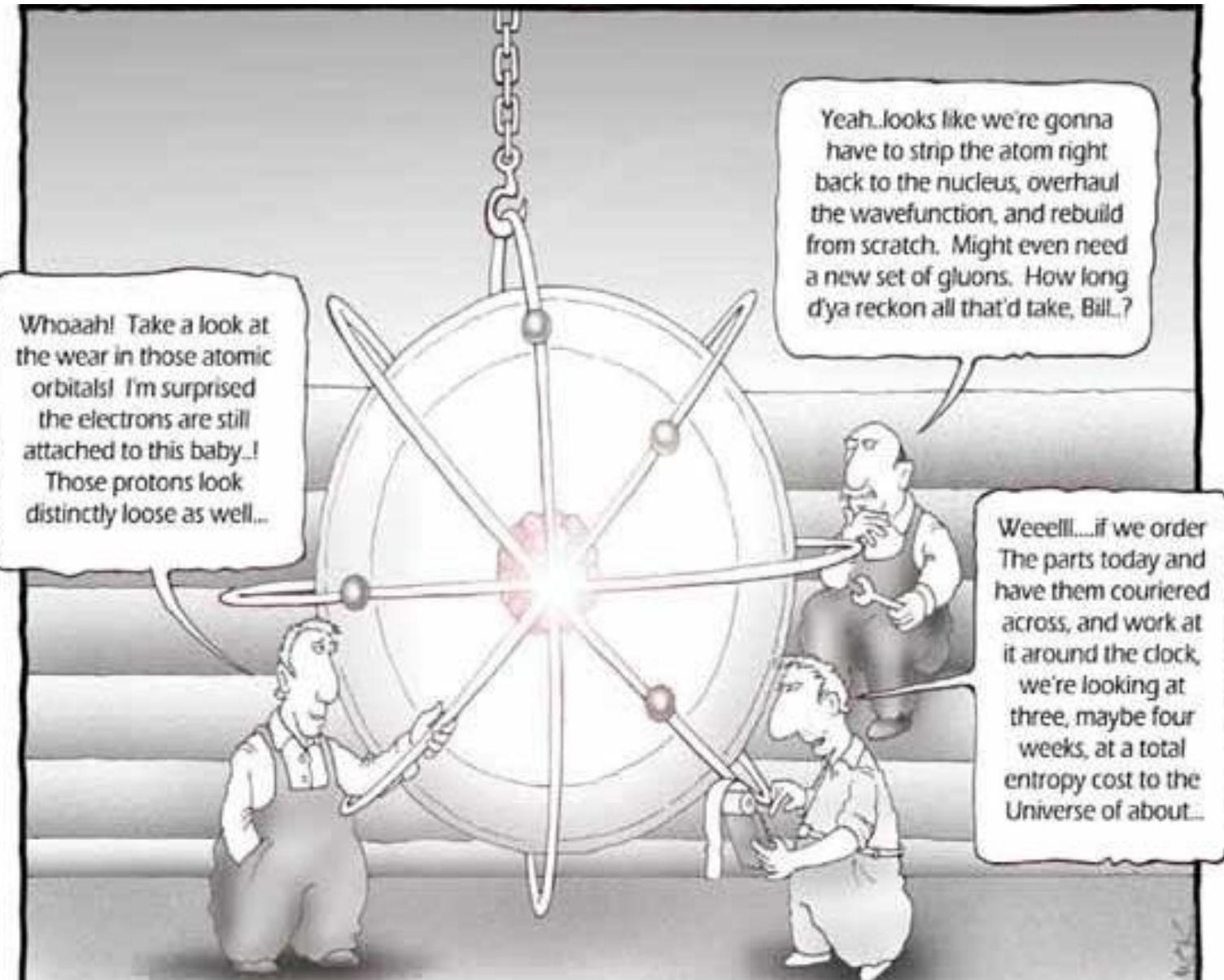
In many cases, our uncertainty of the position of finding an electron can be greater than the size of the atom itself ($H: \sim 10^{-10} \text{ m}$), if the uncertainty in velocity is $\sim 1\%$!

$$\Delta x \geq \frac{h}{4\pi \cdot m \Delta v} = 10^{-9} \text{ m}$$

Diameter of atom $\sim 10^{-10} \text{ m}$



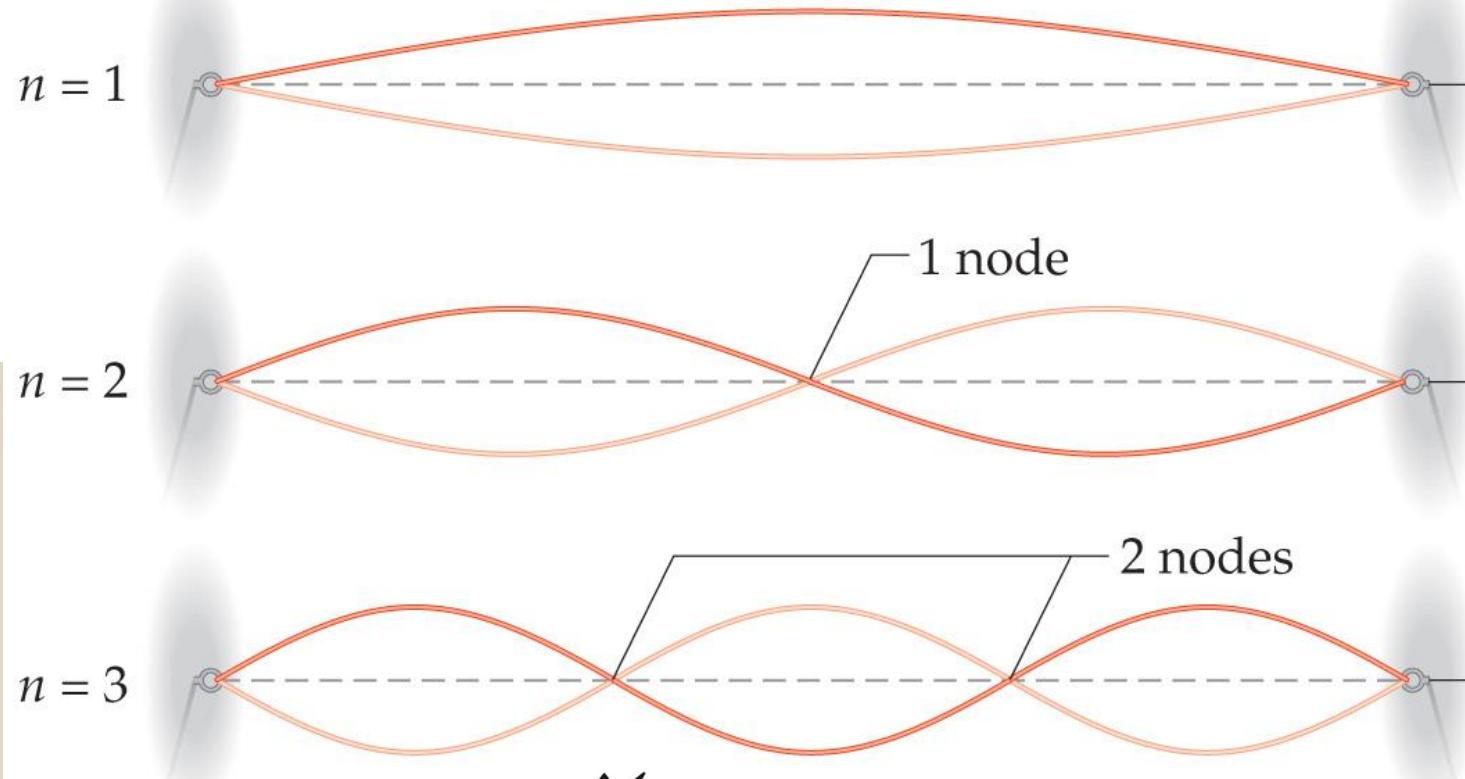
Quantum Mechanics (量子力学)



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



WANTED

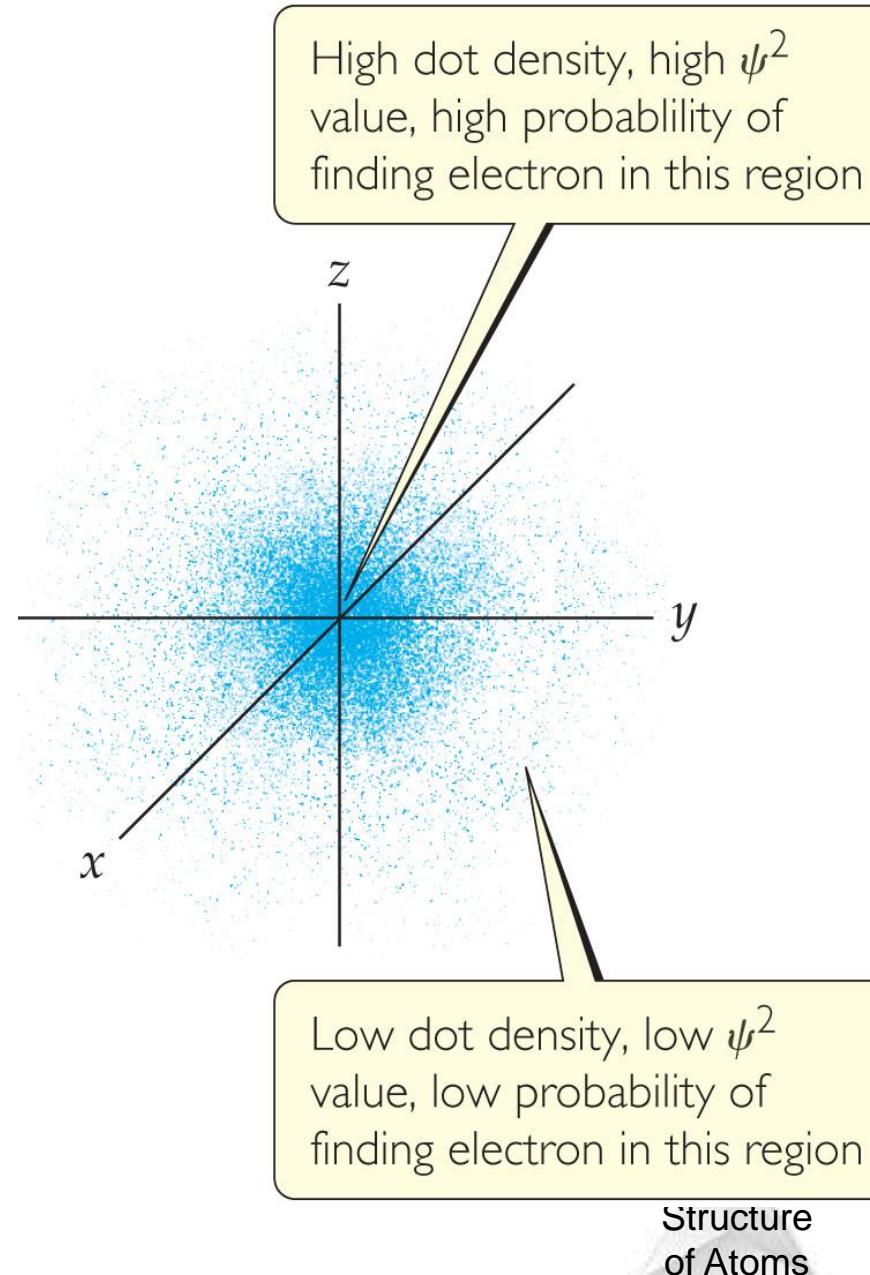


$$\frac{1}{\sqrt{2}} | \text{alive} \rangle + \frac{1}{\sqrt{2}} | \text{dead} \rangle$$

Electronic
Structure
of Atoms

- The solutions: a set of mathematical functions to describe the electron in an atom, **wave function** (ψ). ψ has **no direct physical meaning**.

- The **square of the wave function**, ψ^2 , gives a **probability map (statistical likelihood, the uncertainty principle)** of where an electron is likely to be at any given time (“**electron cloudelectron density**.



Schrödinger (Wave) Equation

Information about the **wave function** (波函数) is obtained from Schrödinger wave equation, which can be **solved exactly for hydrogen system** (with **1 electron**). Wave functions for **many-electron** systems can be **solved approximately by computers only**.

(Time-independent) Schrödinger wave equation for motion in the **x direction**:

$$\text{K.E. } \frac{-\hbar^2}{8\pi^2 m} \frac{d^2\psi}{dx^2} + V\psi = E\psi$$

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{\hbar^2} (E - V) \psi = 0$$

where m = mass, E = total energy & V = potential energy of the particle.



General form:
 $H\psi = E\psi$

H: Hamiltonian operator

Electronic
Structure
of Atoms

If $V = 0$ ($\hbar = h/2\pi$), (Extra Info.)

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi$$

The solutions of this equation have the form:

$$\psi = A e^{ikx} + B e^{-ikx} \quad E = \frac{k^2 \hbar^2}{2m}$$

$$\begin{aligned} -\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} &= -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} (A e^{ikx} + B e^{-ikx}) \\ &= -\frac{\hbar^2}{2m} \{A(ik)^2 e^{ikx} + B(-ik)^2 e^{-ikx}\} \\ &= \frac{\hbar^2 k^2}{2m} (A e^{ikx} + B e^{-ikx}) = E\psi \end{aligned}$$

Schrödinger wave equation for the electron motion in the **three-dimensional space**:

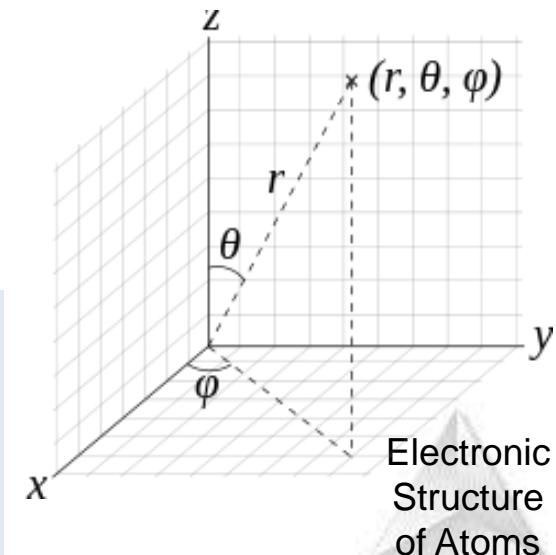
$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0$$

It can express the radial (径向) & angular (角度) parts of the wave function: spherical polar coordinates (极坐标).

$$\psi_{\text{Cartesian}}(x, y, z) = \psi_{\text{radial}}(r) \psi_{\text{angular}}(\theta, \phi) = R(r) A(\theta, \phi)$$

where $R(r)$ and $A(\theta, \phi)$ are radial & angular wave functions, respectively.

A wavefunction ψ is a mathematical function that contains detailed information about the behaviour of an electron. An atomic wavefunction ψ consists of a radial component, $R(r)$, and an angular component, $A(\theta, \phi)$. The region of space defined by a wavefunction is called an atomic orbital.



(Extra Info.)

Hydrogenic atoms

$$V = -\frac{Ze^2}{4\pi\epsilon_0 r}$$

Z: atomic number

r: distance of the electron
from the nucleus

$$\hat{H} = \hat{E}_{k, \text{electron}} + \hat{E}_{k, \text{nucleus}} + \hat{V}$$

$$= -\frac{\hbar^2}{2m_e} \nabla_e^2 - \frac{\hbar^2}{2m_N} \nabla_N^2 - \frac{Ze^2}{4\pi\epsilon_0 r}$$

An equation for the internal motion of the electron relative to the nucleus:

$$-\frac{\hbar^2}{2\mu} \nabla^2 \psi - \frac{Ze^2}{4\pi\epsilon_0 r} \psi = E\psi \quad \frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{m_N}$$



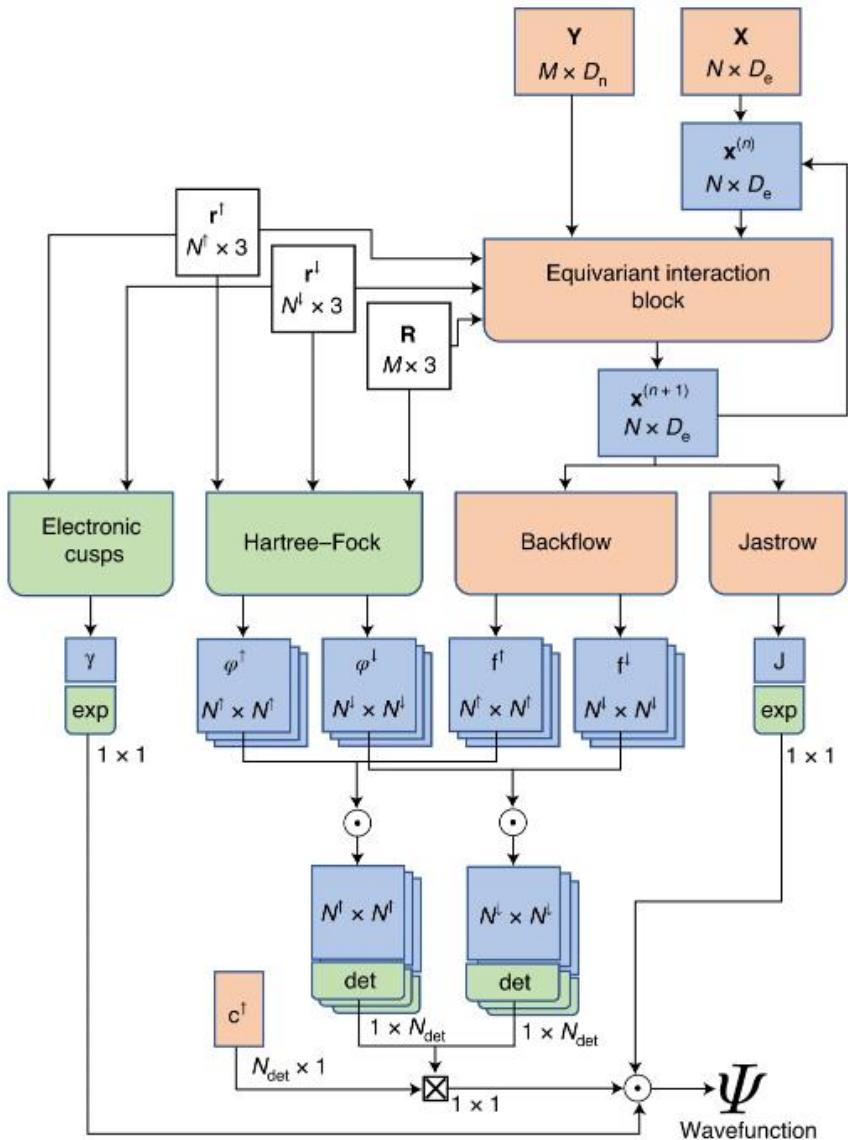
Deep-neural-network solution of the electronic Schrödinger equation

(Extra Info.)

Jan Hermann , Zeno Schätzle ¹ and Frank Noé ^{1,3,4}

The electronic Schrödinger equation can only be solved analytically for the hydrogen atom, and the numerically exact full configuration-interaction method is exponentially expensive in the number of electrons. Quantum Monte Carlo methods are a possible way out: they scale well for large molecules, they can be parallelized and their accuracy has, as yet, been only limited by the flexibility of the wavefunction ansatz used. Here we propose PauliNet, a deep-learning wavefunction ansatz that achieves nearly exact solutions of the electronic Schrödinger equation for molecules with up to 30 electrons. PauliNet has a multireference Hartree-Fock solution built in as a baseline, incorporates the physics of valid wavefunctions and is trained using variational quantum Monte Carlo. PauliNet outperforms previous state-of-the-art variational ansatzes for atoms, diatomic molecules and a strongly correlated linear H_{10} , and matches the accuracy of highly specialized quantum chemistry methods on the transition-state energy of cyclobutadiene, while being computationally efficient.

(Extra Info.)



N Number of electrons

N^i Number of spin-up electrons

N^i Number of spin-down electrons

M Number of nuclei

D_e Embedding dimension, electrons

D_n Embedding dimension, nuclei

Neural network
(trainable function)

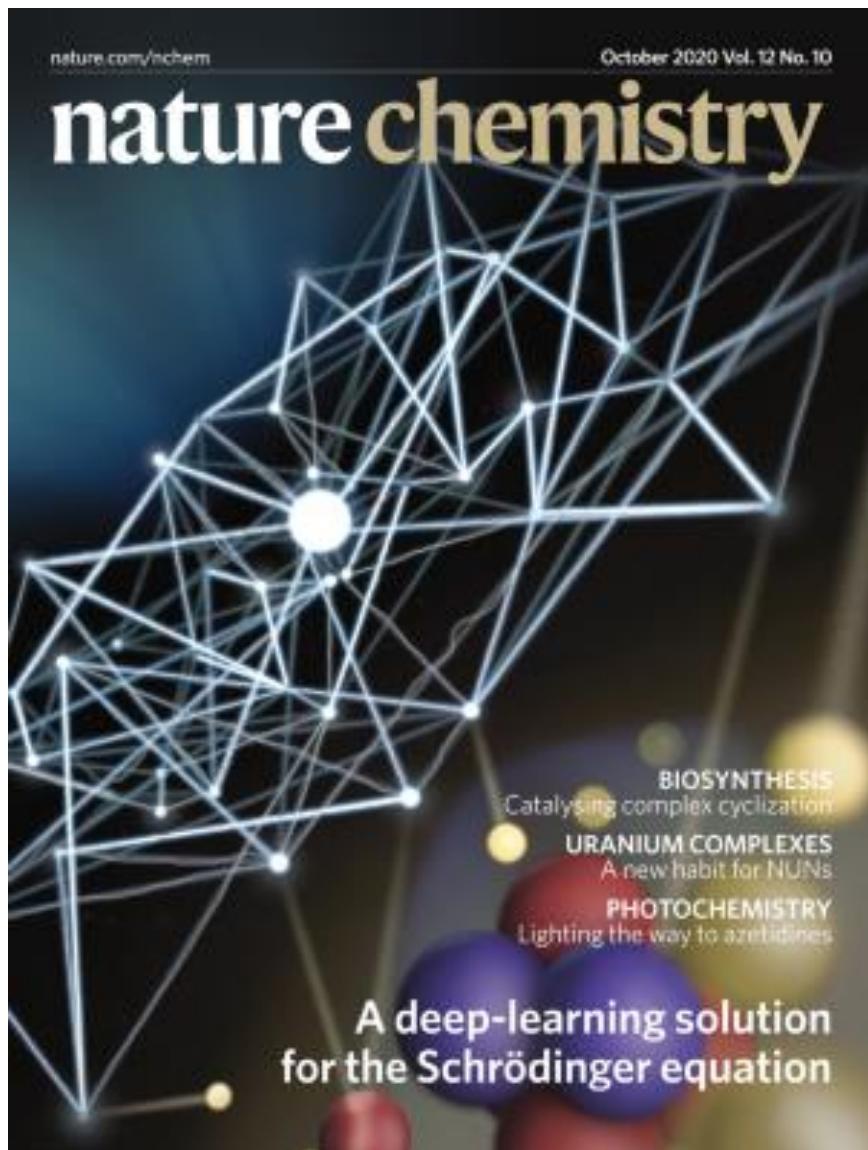
Trainable
array

Fixed
function

Input
array

Hidden
array

erson Education, Inc.



(Nat. Chem.
2020, 891)

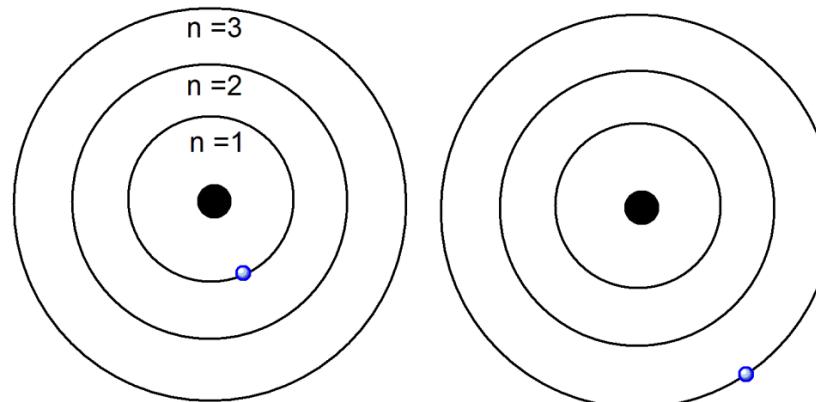
Quantum Numbers

- Solving the wave equation gives a set of **wave functions**, or **orbitals**, and their corresponding **energies**.
- Each **orbital** (not **orbit**) describes a **spatial distribution** (size, shape and orientation) of **electron density**.
- An **orbital** is described by a set of **three quantum numbers** (whereas an **electron** in an orbital has **4** set of quantum numbers).

Principal Quantum Number (n)

- The **principal** (主) quantum number, n , describes the **energy level** on which the orbital resides. The **larger the n value, the higher the energy level** of the orbital as well as the **larger** the orbital.
- The allowed values of n are **integers** (整数) ≥ 1 (e.g. $n = 1, 2, 3, \dots$ etc).

c.f. Bohr
Model



Angular Momentum Quantum Number (ℓ)

- Angular momentum (角动量) quantum number defines the **shape** of the orbital.
- n** possible **allowed values of ℓ** are **integers** ranging from 0 to $n-1$.
(e.g. $n = 1, \ell = 0$; $n = 2, \ell = 0, 1$; $n = 3, \ell = 0, 1, 2$)
- Letter designations** (e.g. **s, p, d, f, g**) for different values of ℓ and, therefore, the shapes and types of orbitals.

Value of ℓ	0	1	2	3
Type of orbital	s	p	d	f

For the **n** value/level, **n different types of orbitals**.

Magnetic Quantum Number (m_l)

- The magnetic (磁) quantum number describes the **3-dimensional orientation** of the orbital.
- **($2l+1$)** possible **allowed values of m_l** are integers ranging **from $-l$ to l** (or $0, \pm 1, \dots, \pm l$):

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

e.g. $n = 1, l = 0, m_l = 0$ (**1s**);

$n = 2, l = 0, m_l = 0$ (**2s**);

$n = 2, l = 1, m_l = -1, 0, 1$ (**2p_x, 2p_y & 2p_z**);

$n = 3, l = 0, m_l = 0$ (**3s**);

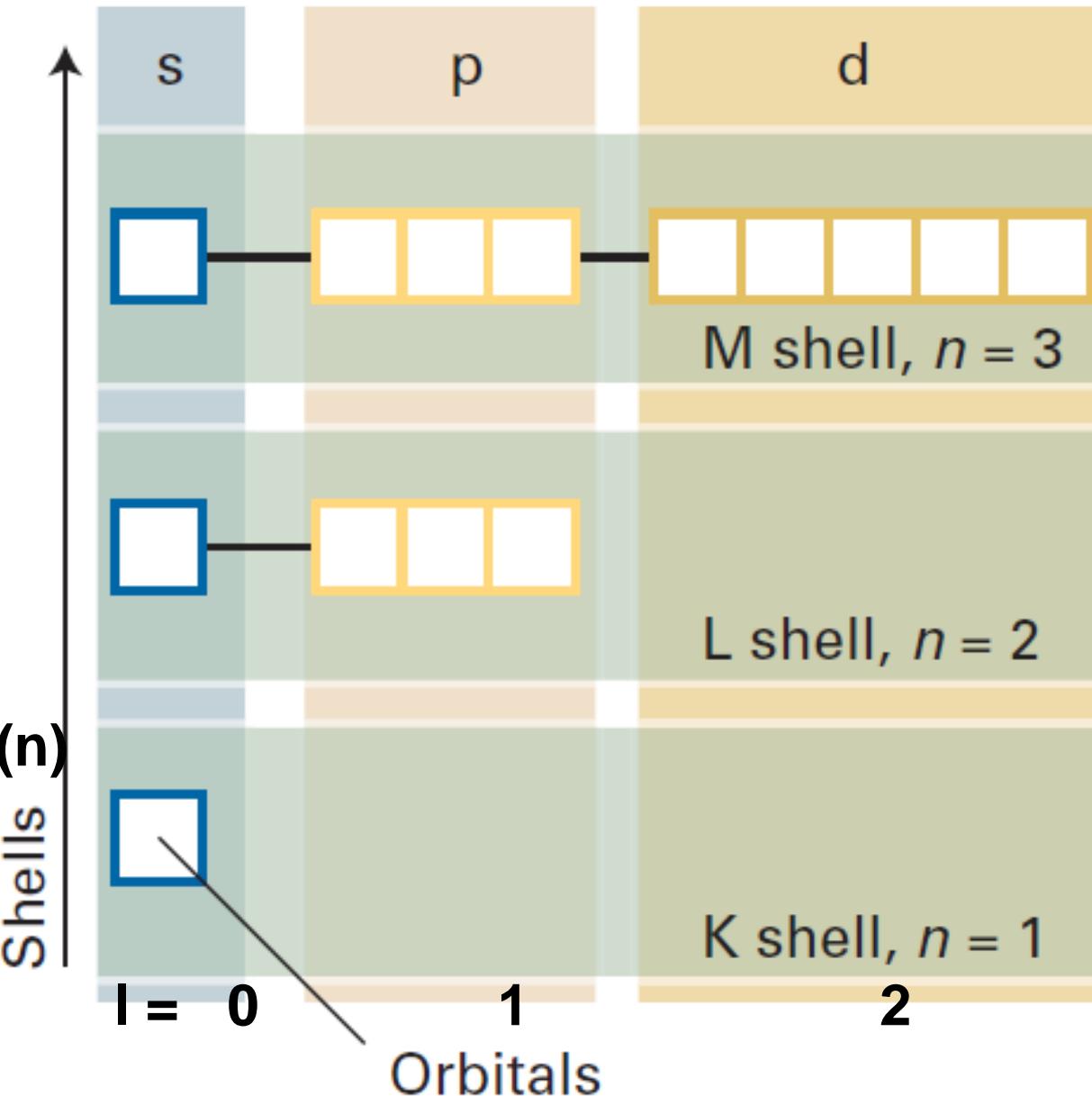
$n = 3, l = 1, m_l = -1, 0, 1$ (**3p_x, 3p_y & 3p_z**);

$n = 3, l = 2, m_l = -2, -1, 0, 1, 2$ (**3d_{xz}, 3d_{yz}, 3d_{xy}, 3d_{z2} & 3d_{x2-y2}**);

- For the **n** -level, **$1^* s$** orbital, **$3^* p$** orbitals, **$5^* d$** orbitals, **$7^* f$** orbitals, **$9^* g$** orbitals, ... etc.

Shell & Subshell

Subshells (I)



- Orbitals with the **same value of n** form a **shell** (层).

- Orbital with the **same n & l values** are **subshells** (亚层): n subshells:

$n = 1 \rightarrow 1$ subshell (s);

$n = 2 \rightarrow 2$ subshell (s & p);

$n = 3 \rightarrow 3$ subshell (s, p & d).

(n fold subshell)**($2l+1$ fold)****(n^2 fold)**

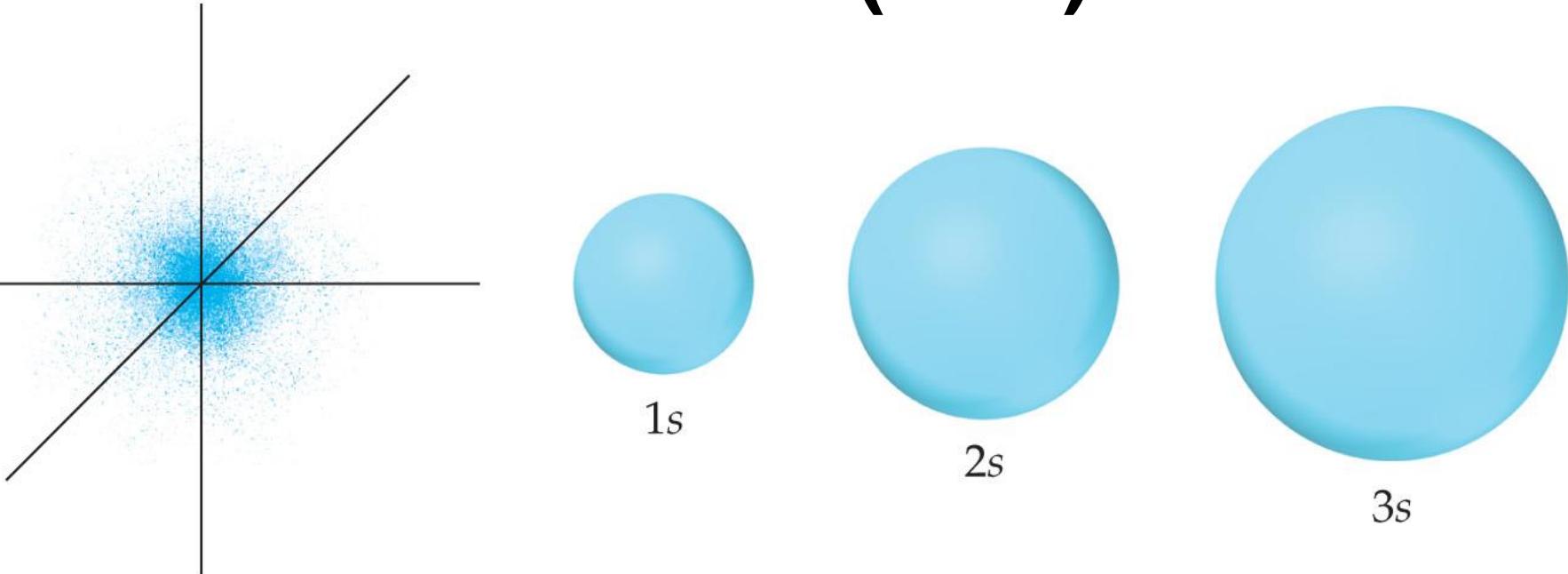
n	Possible Values of l	Subshell Designation	Possible Values of m_l	Number of Orbitals in Subshell	Total Number of Orbitals in Shell
1	0	1s	0	1	1
2	0	2s	0	1	4
	1	2p	1, 0, -1	3	
3	0	3s	0	1	9
	1	3p	1, 0, -1	3	
	2	3d	2, 1, 0, -1, -2	5	
4	0	4s	0	1	16
	1	4p	1, 0, -1	3	
	2	4d	2, 1, 0, -1, -2	5	
	3	4f	3, 2,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

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For the n -level, there are n sub-shells (n different types of orbitals).

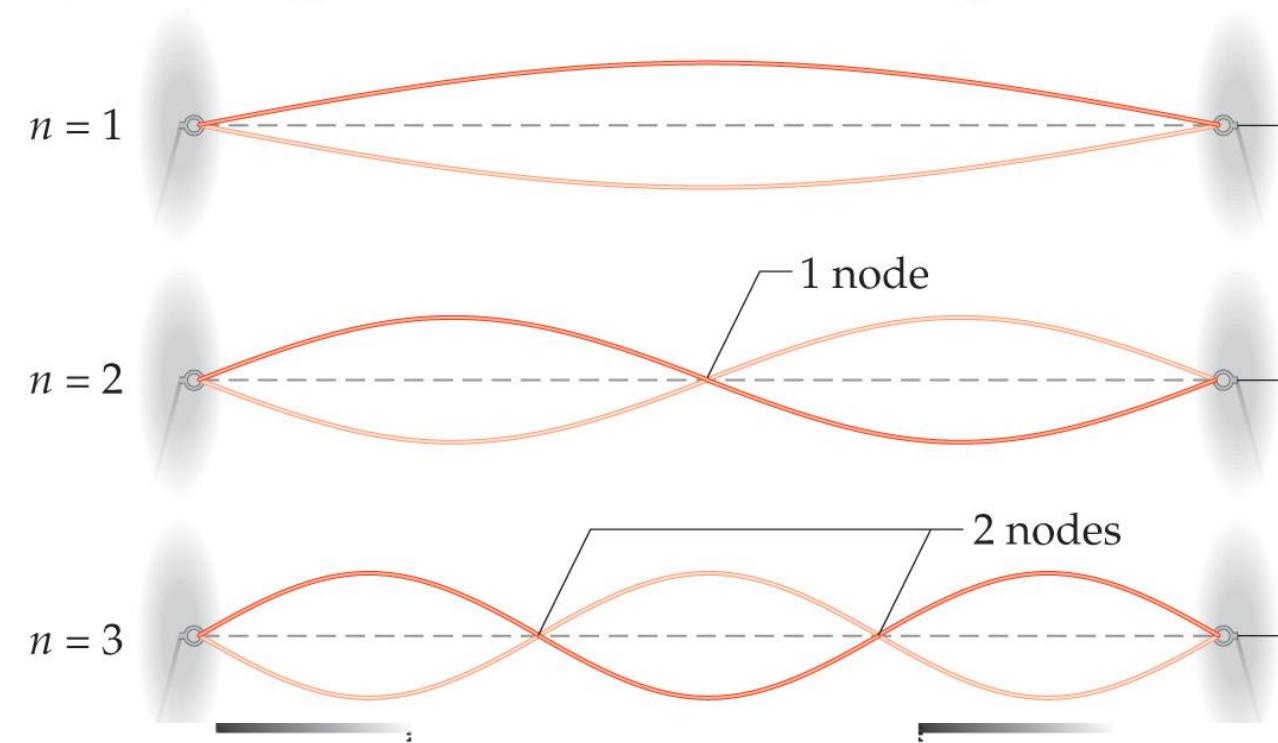
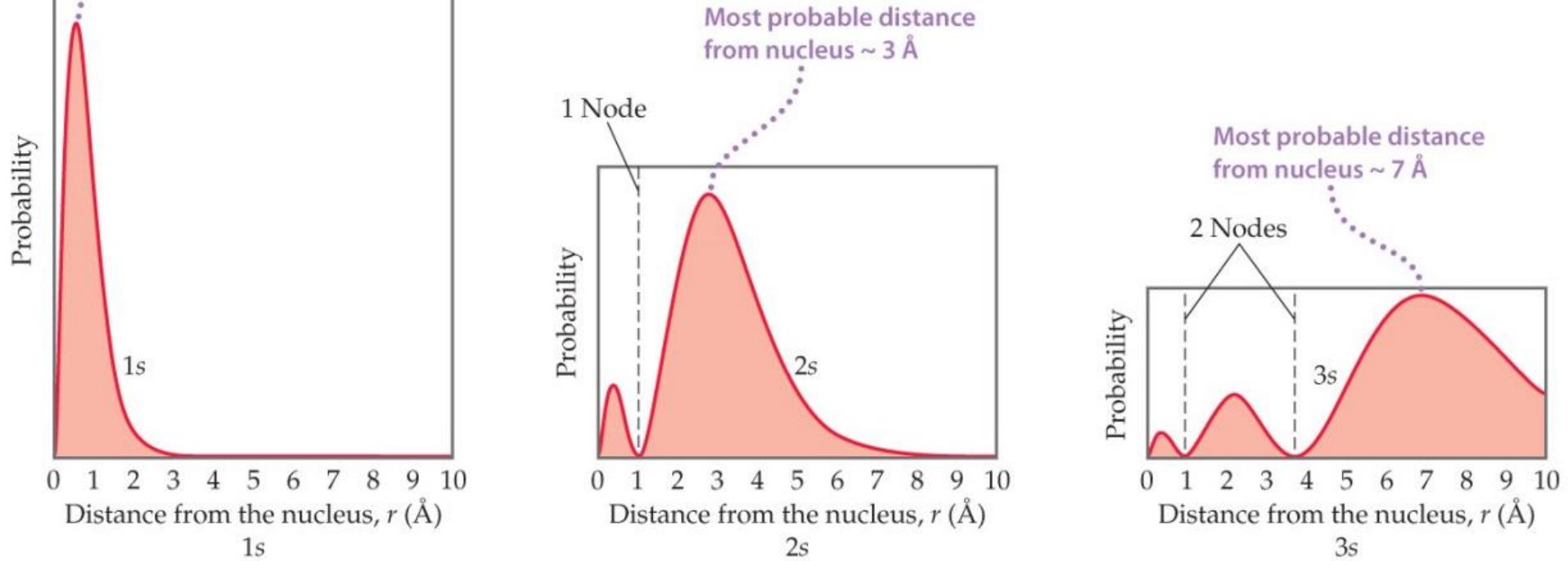
m_l determines number of orbitals in sub-shells.

s Orbitals ($l = 0$)

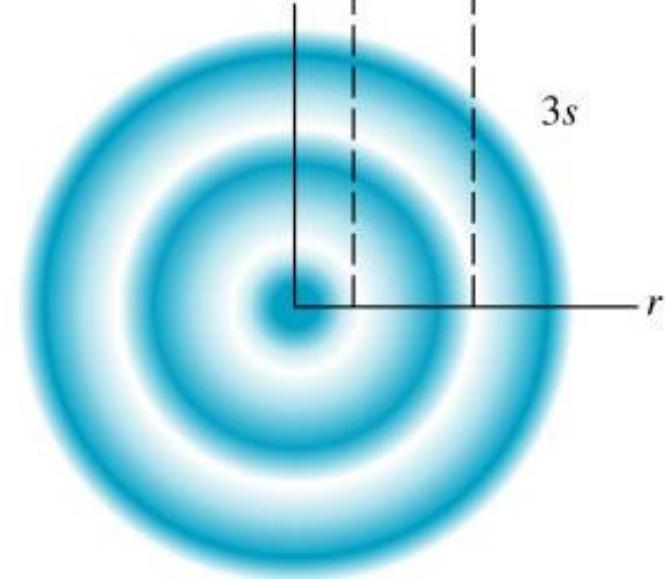
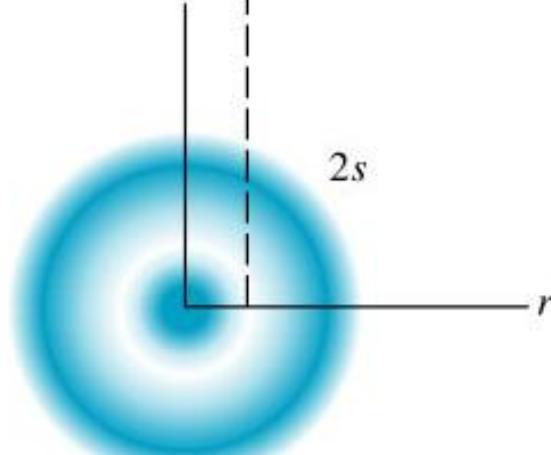
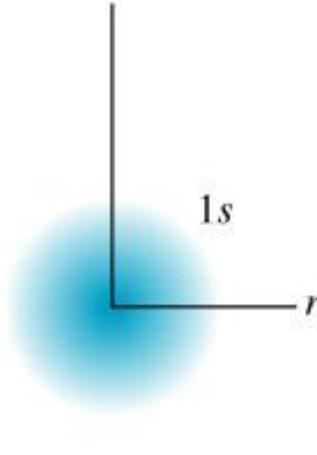
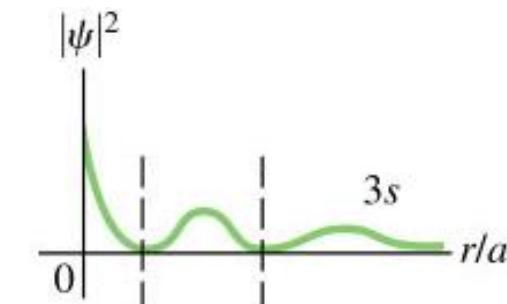
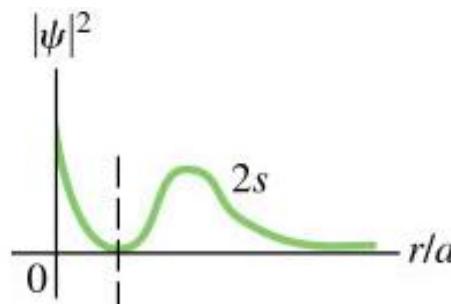
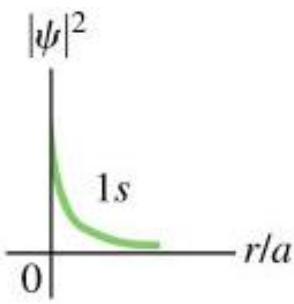


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- The value of l for s orbitals is **0**.
- They are **spherical** in shape.
- Same probability of finding an electron at the same distance.
- The radius of the sphere increases with the value of n .



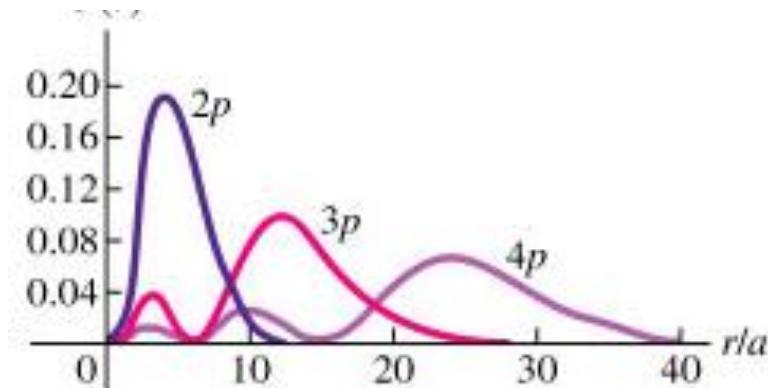
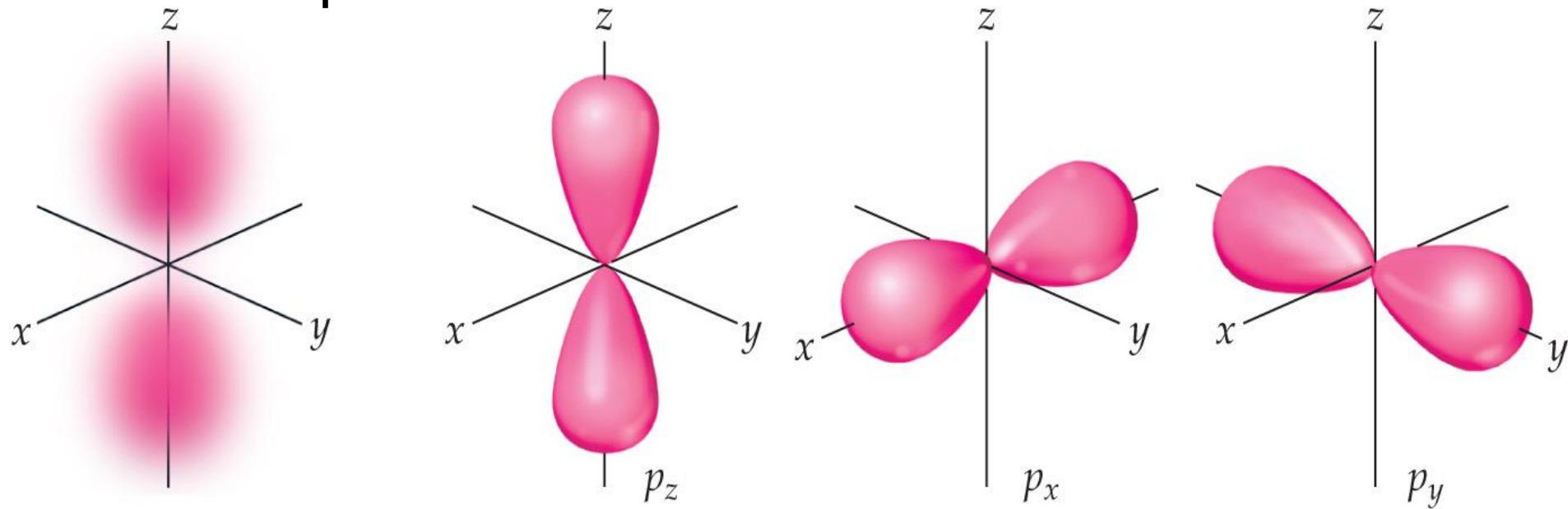
The longer the wavelength, the smaller the frequency & the lower the energy (more stable).



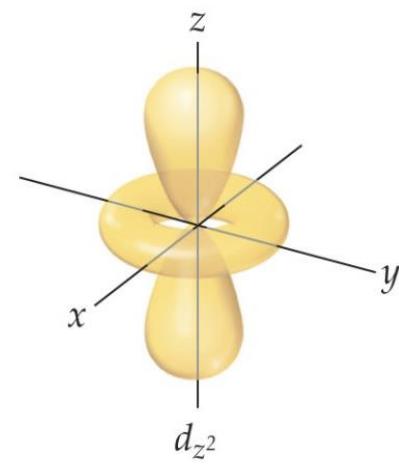
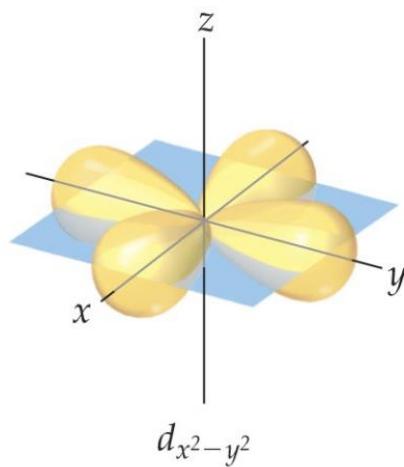
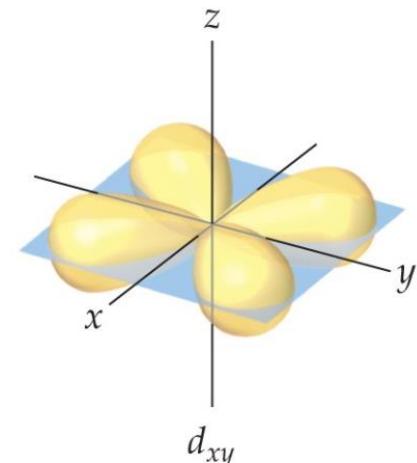
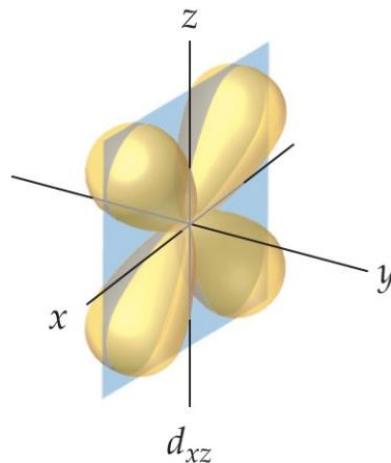
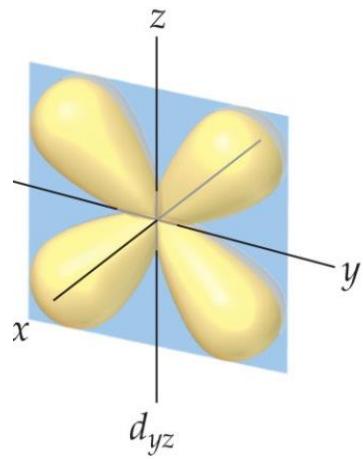
A graph of probabilities of finding an **electron probability versus distance** from the nucleus: s orbitals possess **$n - 1$ nodes** (节点), or regions where there is **0 probability of finding an electron**.

p Orbitals ($l = 1$)

- The value of l for p orbitals is **1**.
- They have **two lobes** (瓣) with **one node** between them for $2p$ orbitals.



***d* Orbitals ($l = 2$)**



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- The value of l for a d orbital is **2**.
- **Four** of the five d orbitals have **4** lobes; the other resembles a p orbital with a doughnut around the center.

Atomic Orbitals: A Summary

s ($l=0$)		p ($l=1$)				d ($l=2$)					f ($l=3$)					
m=0	m=0	m=±1		m=0	m=±1		m=±2		m=0	m=±1		m=±2		m=±3		
s	p _z	p _x	p _y	d _{z²}	d _{xz}	d _{yz}	d _{xy}	d _{x²-y²}	f _{z³}	f _{xz²}	f _{yz²}	f _{xyz}	f _{z(x²-y²)}	f _{x(x²-3y²)}	f _{y(3x²-y²)}	
n=1	•															
n=2	•															
n=3	•															
n=4	•															
n=5	•							
n=6	•			
n=7	•

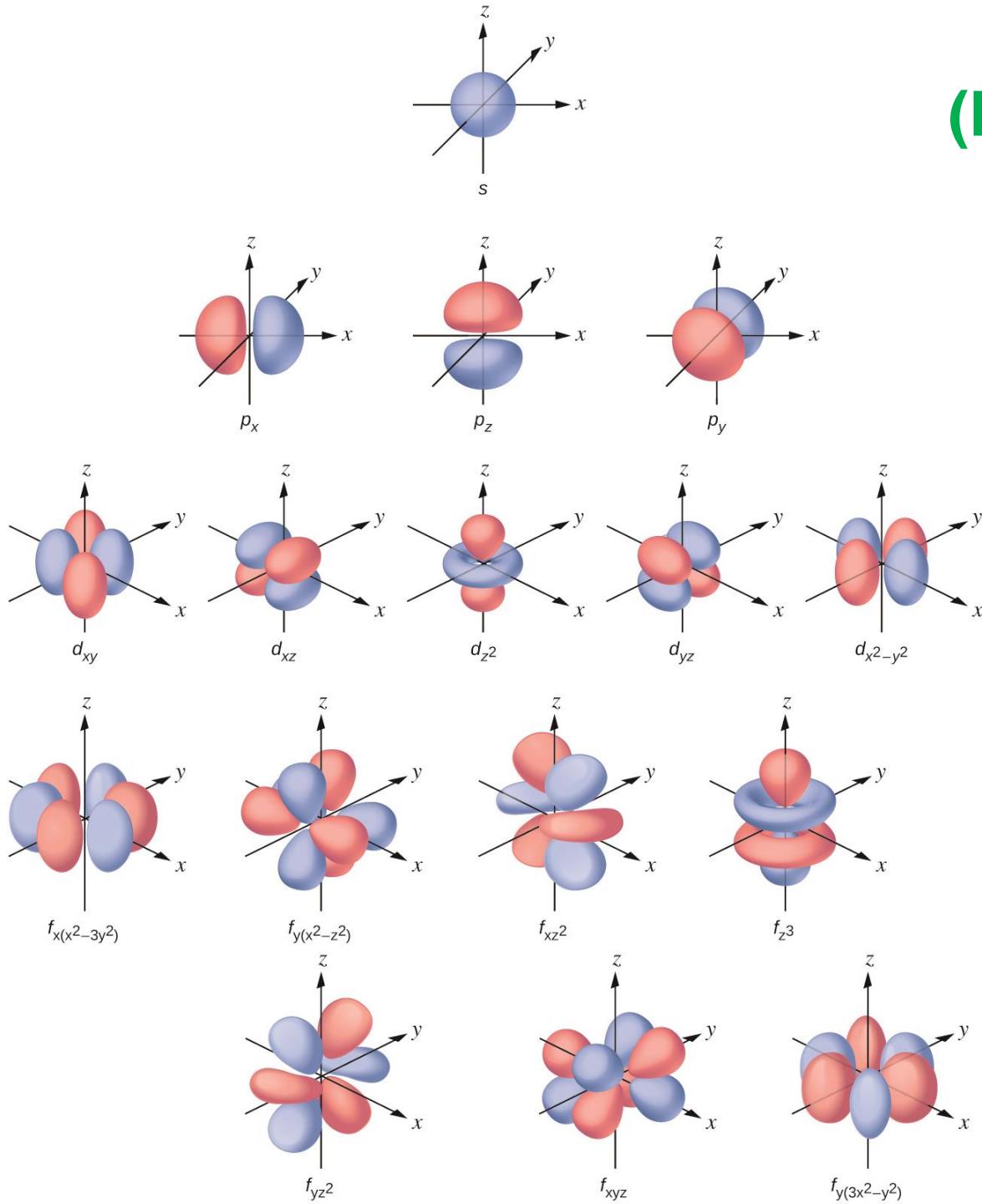
(Extra Info.)

NOT scaled accurately!

Different colors:
different phases



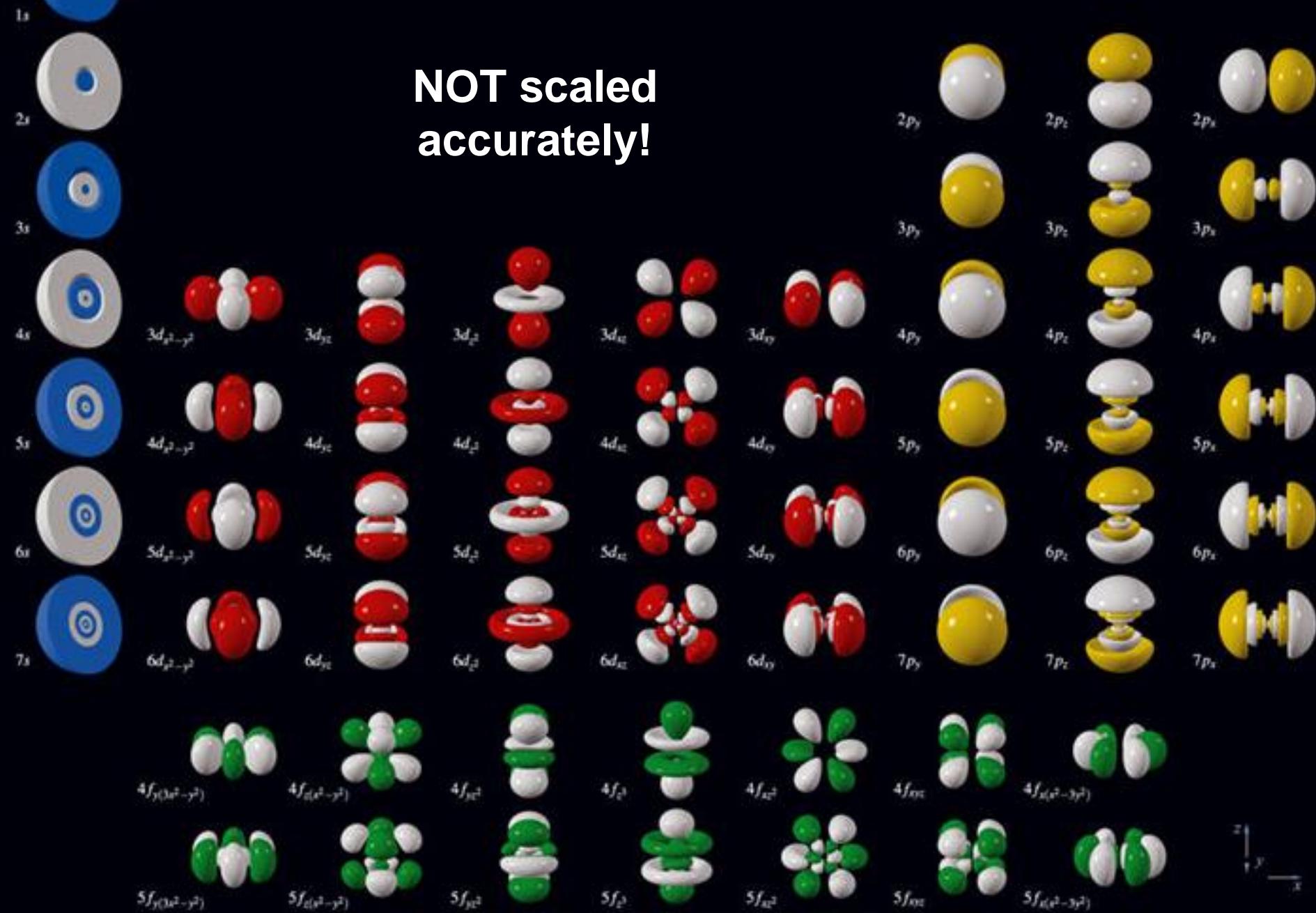
(Extra Info.)





The Orbitron gallery of atomic orbitals

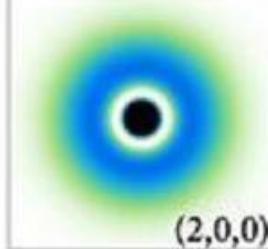
NOT scaled
accurately!



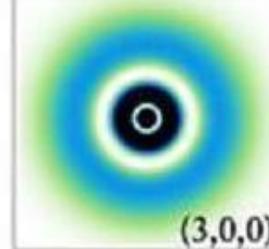
Probability density 2-dimensional plots

(Extra Info.)

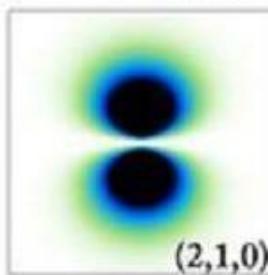
$$|\psi_{nlm}(\mathbf{r})|^2$$



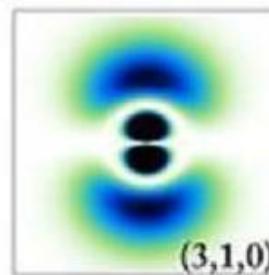
(2,0,0)



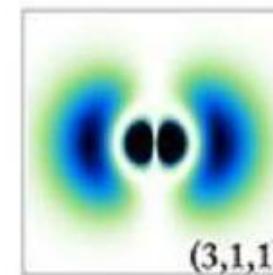
(3,0,0)



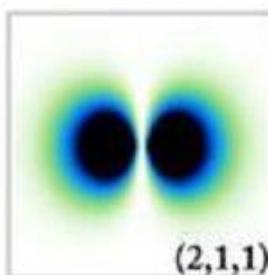
(2,1,0)



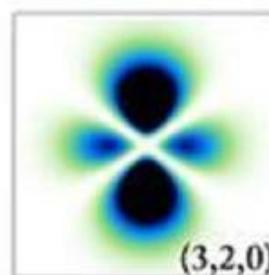
(3,1,0)



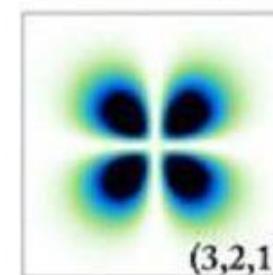
(3,1,1)



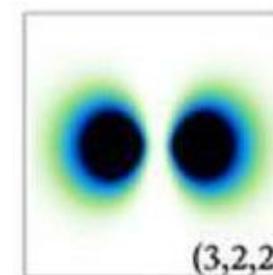
(2,1,1)



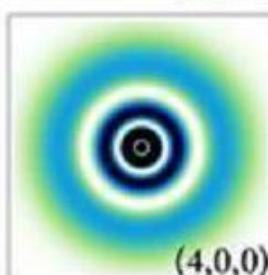
(3,2,0)



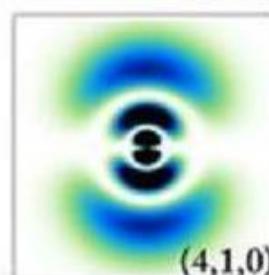
(3,2,1)



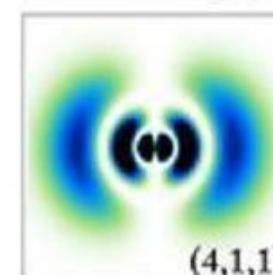
(3,2,2)



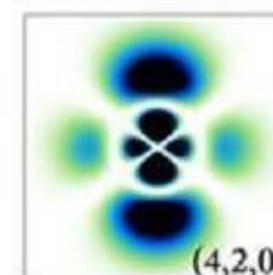
(4,0,0)



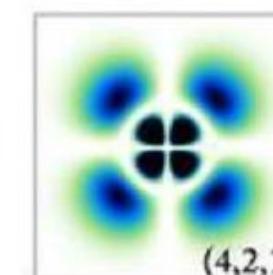
(4,1,0)



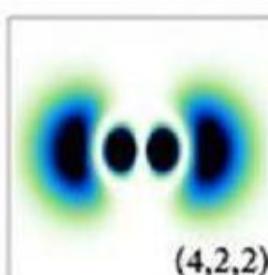
(4,1,1)



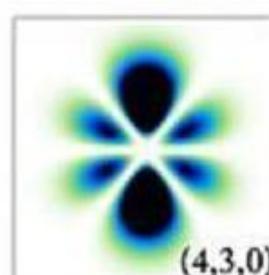
(4,2,0)



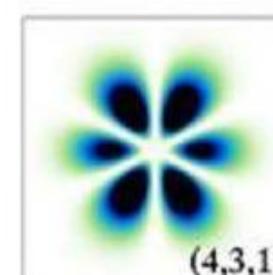
(4,2,1)



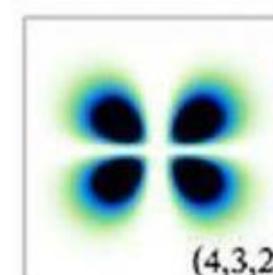
(4,2,2)



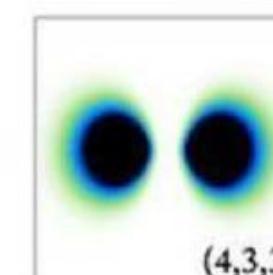
(4,3,0)



(4,3,1)



(4,3,2)



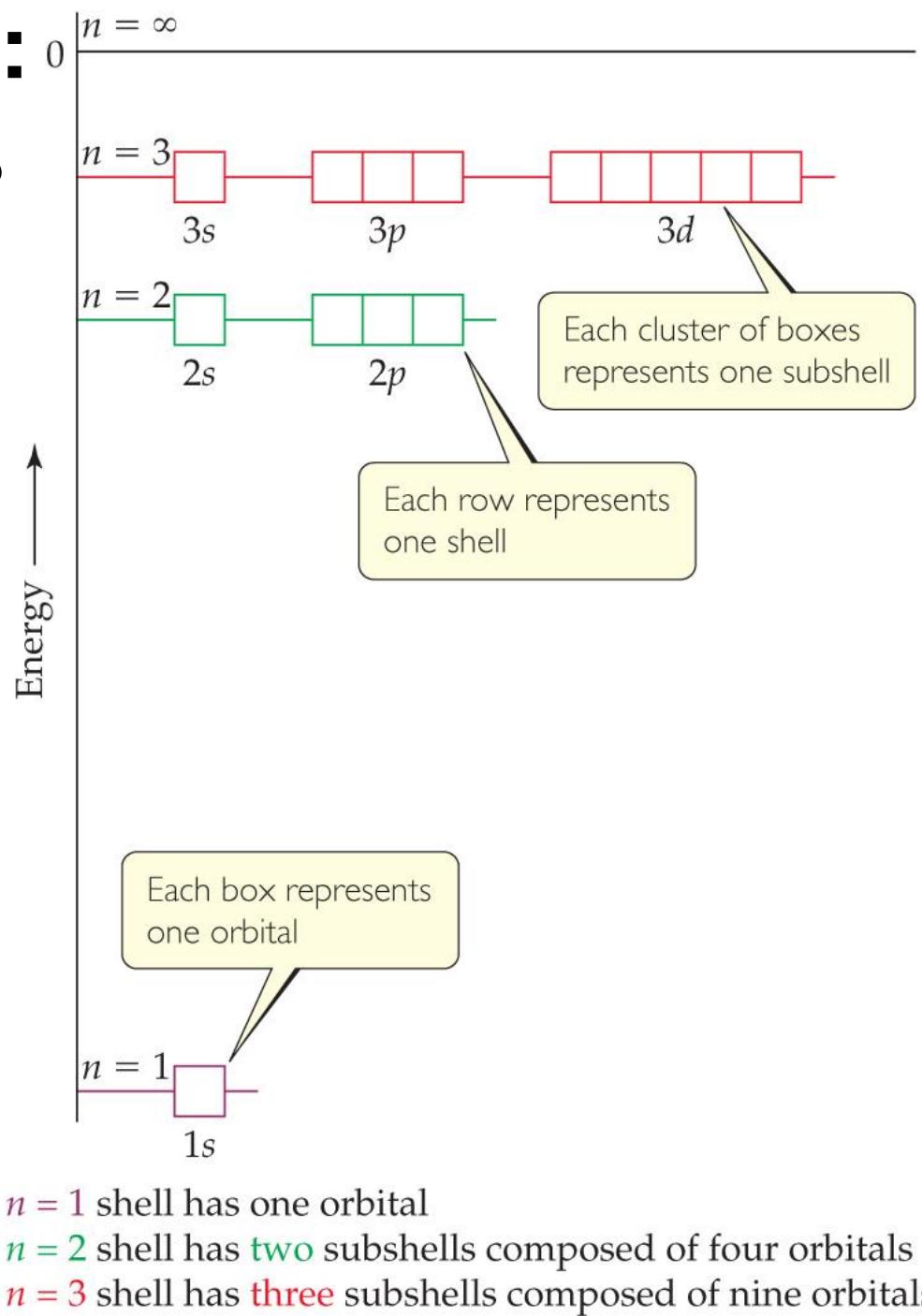
(4,3,3)



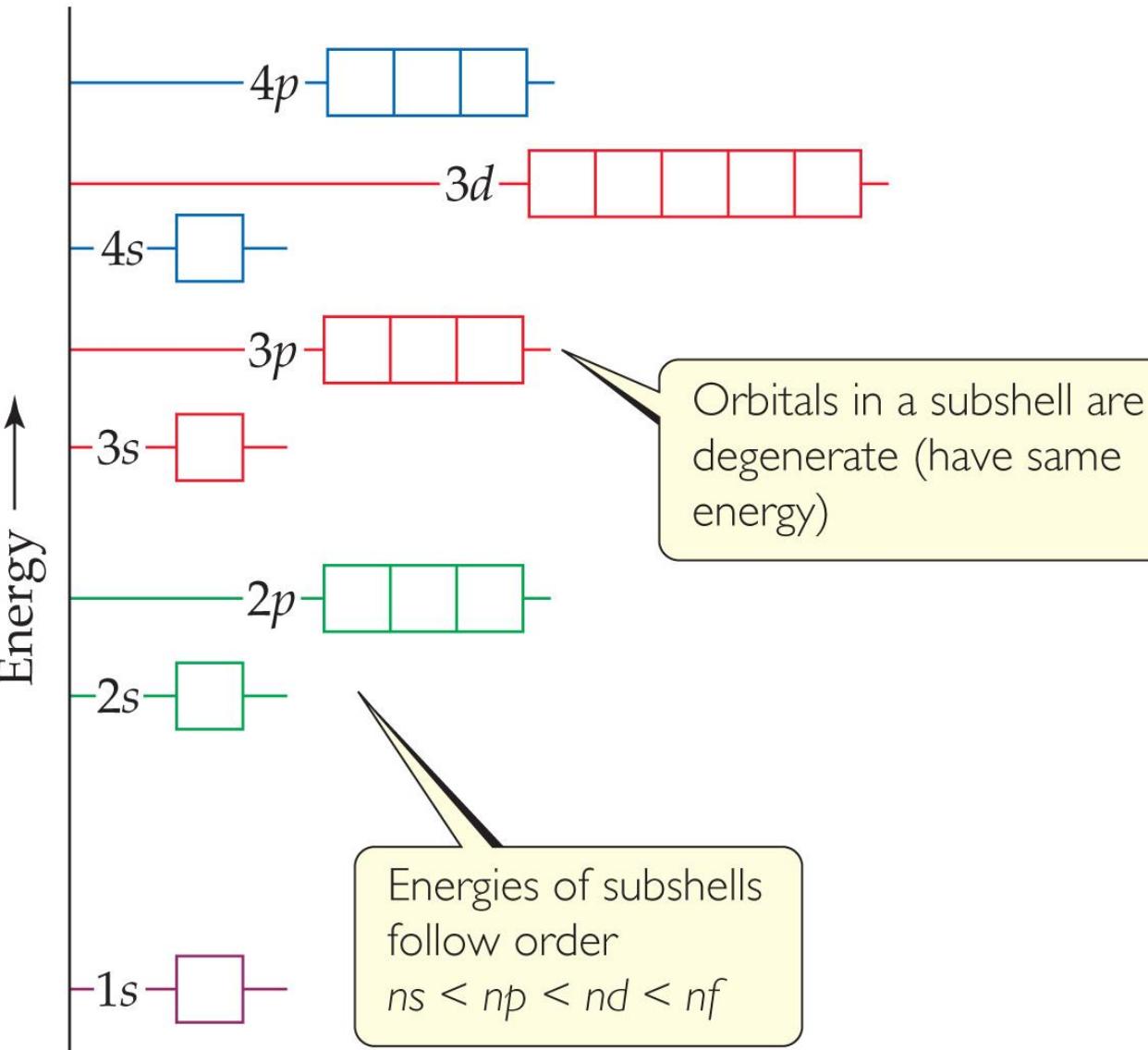
Electronic
Structure
of Atoms

Energies of Orbitals: 1-Electron Systems

- For a **one-electron hydrogen atom**, orbitals on the **same energy level (n)** have the **same energy**.
- They are **degenerate** (简并), having **same energy**.
- The electron **occupies** only one orbital, while the other orbitals are **unoccupied**.



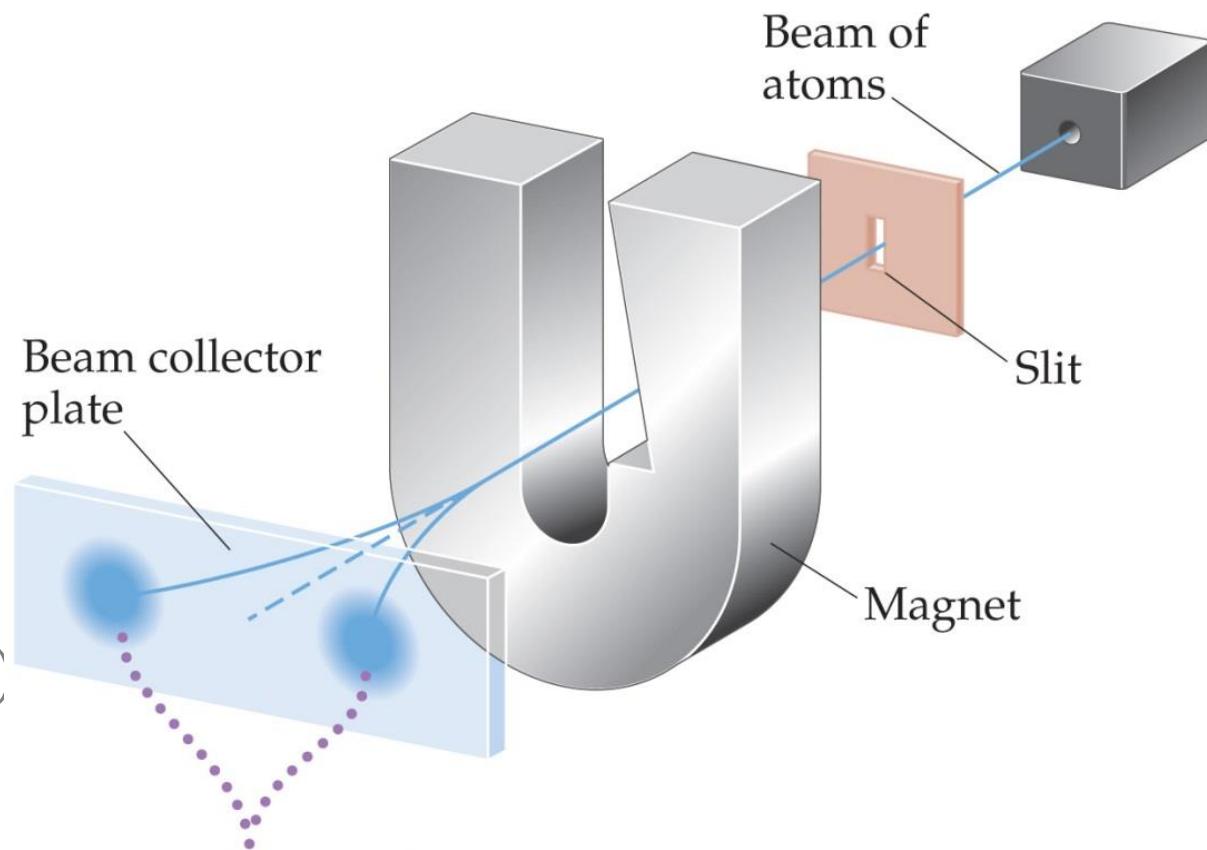
Energies of Orbitals: Many-Electron Systems



- As the number of electrons increases, **more repulsion** between them.
- In many-electron atoms, orbitals on the same energy level (n) are **NOT degenerate** (increases **energy** with **increasing l value**: $3s < 3p < 3d$).

Spin Quantum Number (m_s)

- In the 1920s, it was discovered that **two electrons** in the **same orbital** do not have the exactly same energy.



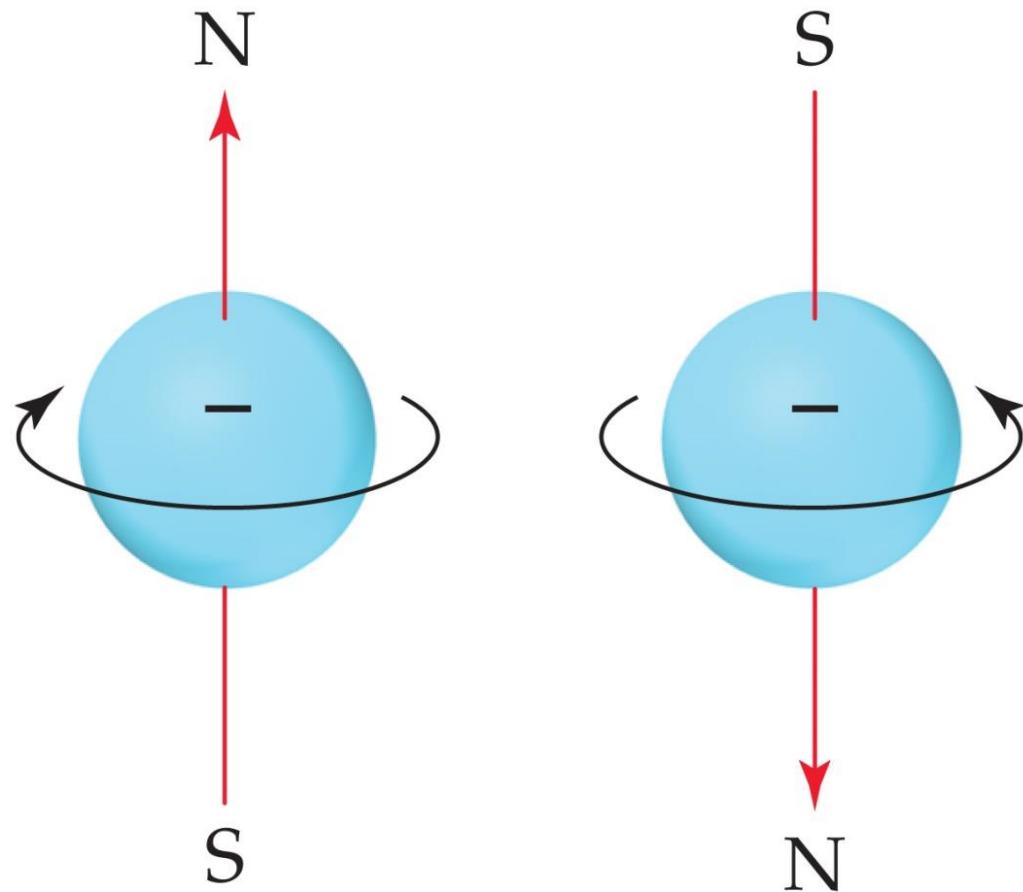
Atoms having unpaired electron with spin quantum number $m_s = +\frac{1}{2}$ deflect in one direction; those having unpaired electron with $m_s = -\frac{1}{2}$ deflect in opposite direction

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- This led to a **fourth** quantum number, the **spin quantum number, m_s** .

- Only 2 allowed values of m_s : $+1/2$, $-1/2$. regardless of values of n , l and m_l .

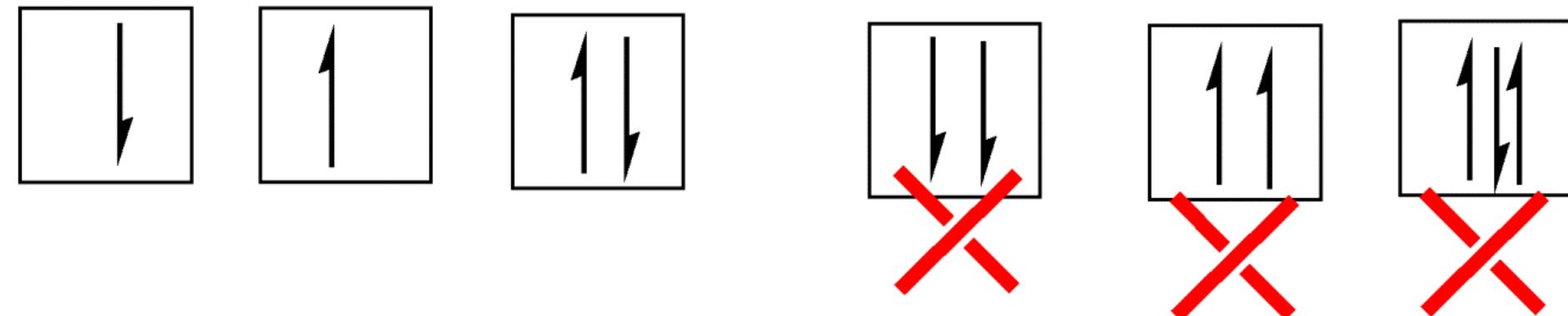
- An **electron** in an **orbital** has **4 set** of quantum numbers: **n , l , m_l and m_s** .



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Pauli Exclusion Principle (泡利不相容原理)

- **No two electrons** in the **same atom** can have the **same set** of 4 quantum numbers (n , l , m_l & m_s).
- At **the same orbital** (n , l , m_l) with a **maximum of 2 electrons**, which must have **opposite spin** (m_s).



Quantum Numbers and Their Properties

Symbol	Name	Values	Role
n	Principal	1, 2, 3, ...	Determines the major part of the energy
l	Angular momentum	0, 1, 2, ..., $n - 1$	Describes angular dependence and contributes to the energy
m_l	Magnetic	0, $\pm 1, \pm 2, \dots, \pm l$	Describes orientation in space (angular momentum in the z direction)
m_s	Spin	$\pm \frac{1}{2}$	Describes orientation of the electron spin (magnetic moment) in space

Orbitals with different l values are known by the following labels, derived from early terms for different families of spectroscopic lines:

l	0	1	2	3	4	5, ...
Label	s	p	d	f	g	continuing alphabetically

An orbital is fully occupied when it contains two electrons which are *spin-paired*; one electron has a value of $m_s = +\frac{1}{2}$ and the other, $m_s = -\frac{1}{2}$.

Electron Configurations

4p⁵

- Electron configuration shows the distribution of all electrons in an atom.
- Each component consists of
 - a number denoting the **energy level** (e.g. n = 4);

$4p^5$

- This term shows the distribution of all electrons in an atom.
- Each component consists of
 - a number denoting the energy level;
 - a letter denoting the **type of orbital** (e.g. $l = 1 \rightarrow p$);

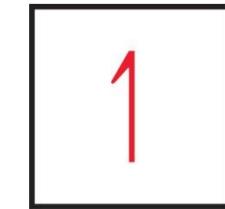
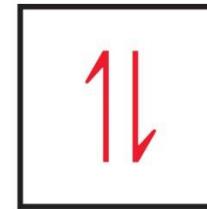
$4p^5$

- This term shows the distribution of all electrons in an atom.
- Each component consists of
 - a number denoting the energy level;
 - a letter denoting the type of orbital;
 - a superscript denoting the **number of electrons in those orbitals** (e.g. $4p^5$: 5 electrons in $4p$ orbitals).

Orbital Diagrams

- Each **box** in the diagram represents one orbital.
- One **half-arrow** represents one **electron**.
- The **direction** of the arrow represents the **relative spin** of the electron.

Li



core 1s
(核心)
electrons

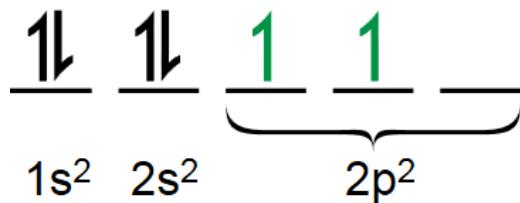
Ferromagnetic
(磁性)
Unpaired
electron
2s
valence (价)
electron
→ **Chem.
bonding
& reaction**
Electron
Structure
of Atoms

Hund's Rule

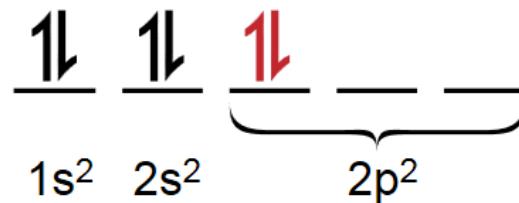
TABLE 6.3 • Electron Configurations of Several Lighter Elements

Element	Total Electrons	Orbital Diagram	Electron Configuration
Li	3	1s 2s 2p 3s [1↓] [1] [] [] [] []	$1s^2 2s^1$
Be	4	1s 2s 2p 3s [1↓] [1↓] [] [] [] []	$1s^2 2s^2$
B	5	1s 2s 2p 3s [1↓] [1↓] [1] [] [] []	$1s^2 2s^2 2p^1$
C	6	1s 2s 2p 3s [1↓] [1↓] [1] [1] []	$1s^2 2s^2 2p^2$

correct



incorrect



“For **degenerate orbitals**, the **lowest energy** is attained when the number of electrons **with the same spin** is **maximized**”: minimizing e-e repulsions.

Hund's Rule

TABLE 6.3 • Electron Configurations of Several Lighter Elements

Element	Total Electrons	Orbital Diagram	Electron Configuration	Condensed electron configuration
Li	3	1s 2s 2p 3s	$1s^2 2s^1$	$[He]2s^1$
Be	4	1s 2s 2p 3s	$1s^2 2s^2$	$[He]2s^2$
B	5	1s 2s 2p 3s	$1s^2 2s^2 2p^1$	$[He]2s^2 2p^1$
C	6	1s 2s 2p 3s	$1s^2 2s^2 2p^2$	$[He]2s^2 2p^2$
N	7	1s 2s 2p 3s	$1s^2 2s^2 2p^3$	$[He]2s^2 2p^3$
Ne	10	1s 2s 2p 3s	$1s^2 2s^2 2p^6$	$[He]2s^2 2p^6$
Na	11	1s 2s 2p 3s	$1s^2 2s^2 2p^6 3s^1$	$[Ne]3s^1$

“For **degenerate orbitals**, the **lowest energy** is attained when the number of electrons **with the same spin** is **maximized**”: minimizing e-e repulsions.

Condensed Electron Configurations

1A

3 Li $[\text{He}]2s^1$
11 Na $[\text{Ne}]3s^1$
19 K $[\text{Ar}]4s^1$
37 Rb $[\text{Kr}]5s^1$
55 Cs $[\text{Xe}]6s^1$
87 Fr $[\text{Rn}]7s^1$

Alkali
metals

- Elements in the same group of the periodic table have the same number of electrons in the outer most shell. These are the **valence electrons**.
- The filled inner shell electrons are called **core electrons**.
- A shortened version of an electron configuration: a **bracket []** around a **noble gas symbol** and then **list only valence electrons**.

Group 2A

Be [He] $2s^2$

Mg [Ne] $3s^2$

Ca [Ar] $4s^2$

Sr [Kr] $5s^2$

Ba [Xe] $6s^2$

Ra [Rn] $7s^2$

**Condensed
electron
configuration**

Group 3A

B [He] $2s^22p^1$

Al [Ne] $3s^23p^1$

Ga [Ar] $3d^{10}4s^24p^1$

In [Kr] $4d^{10}5s^25p^1$

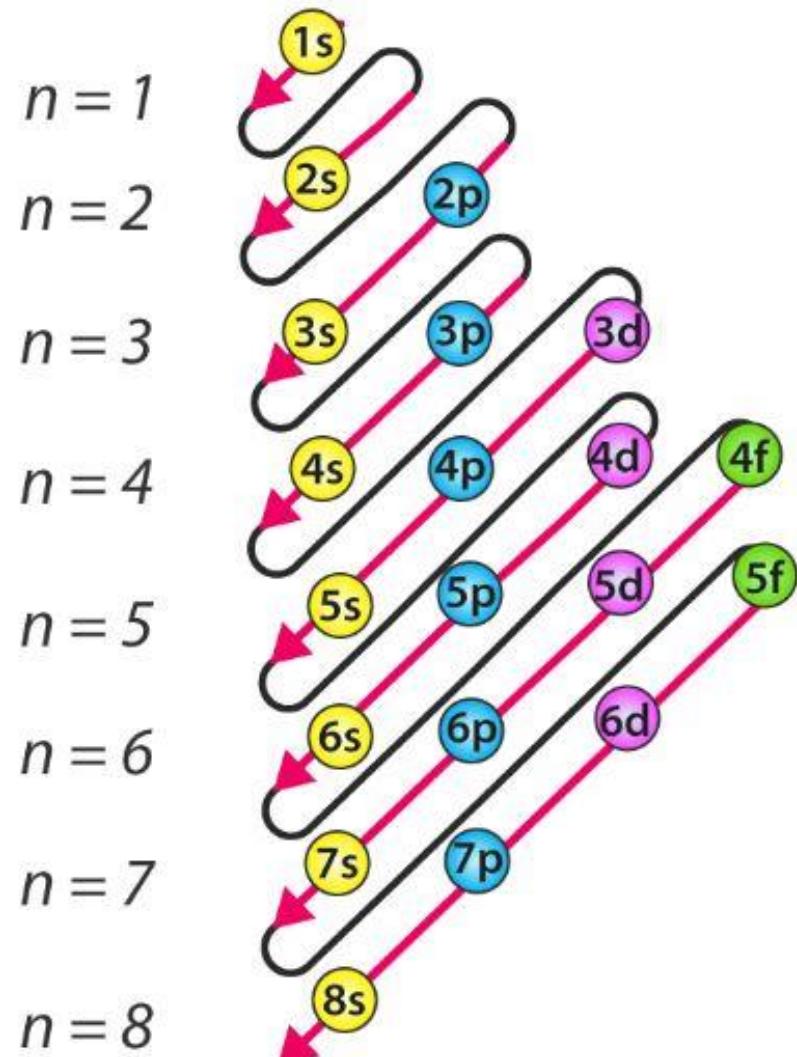
Tl [Xe] $4f^{14}5d^{10}6s^26p^1$

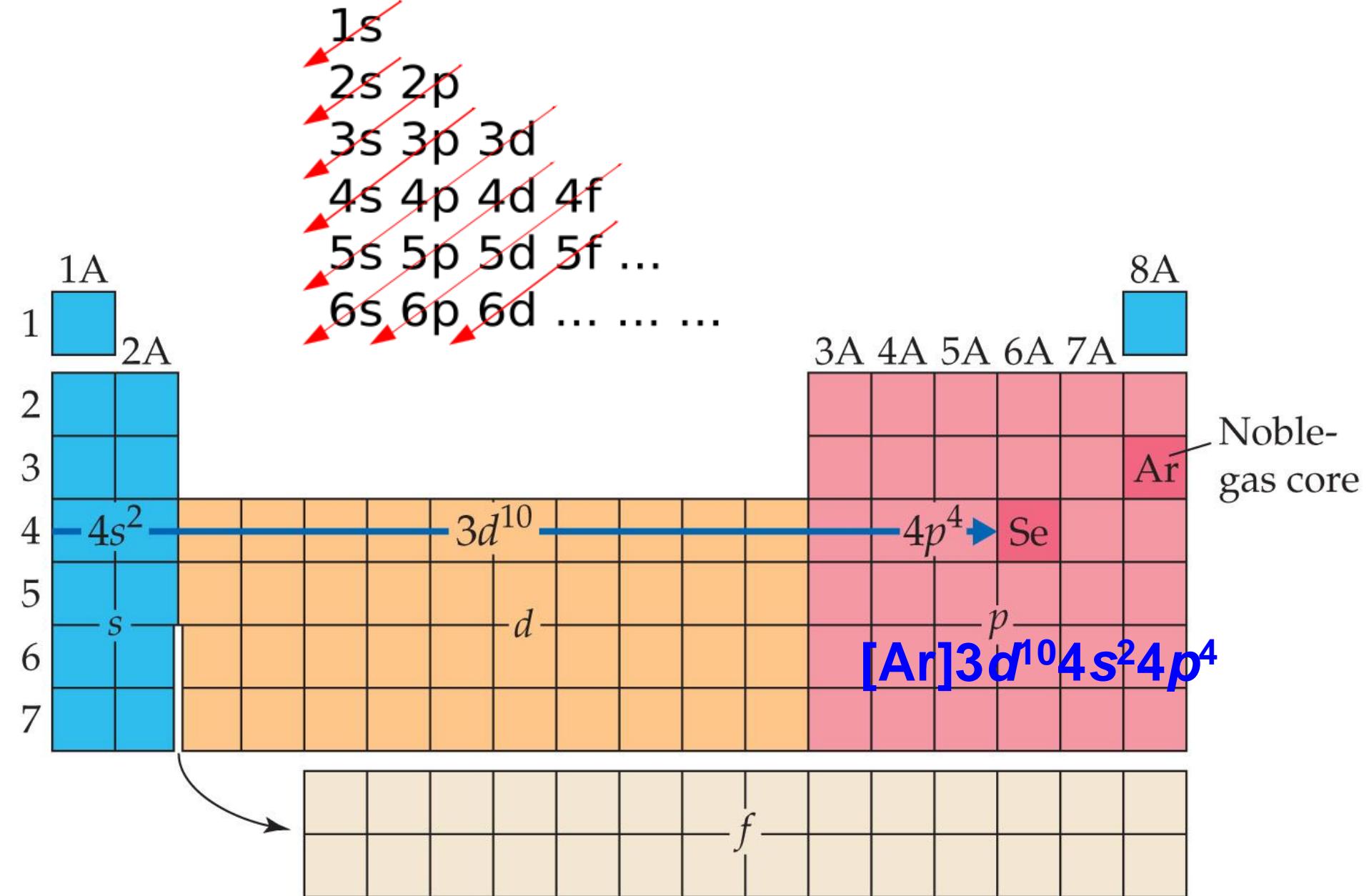
Periodic Table: Electron Configurations

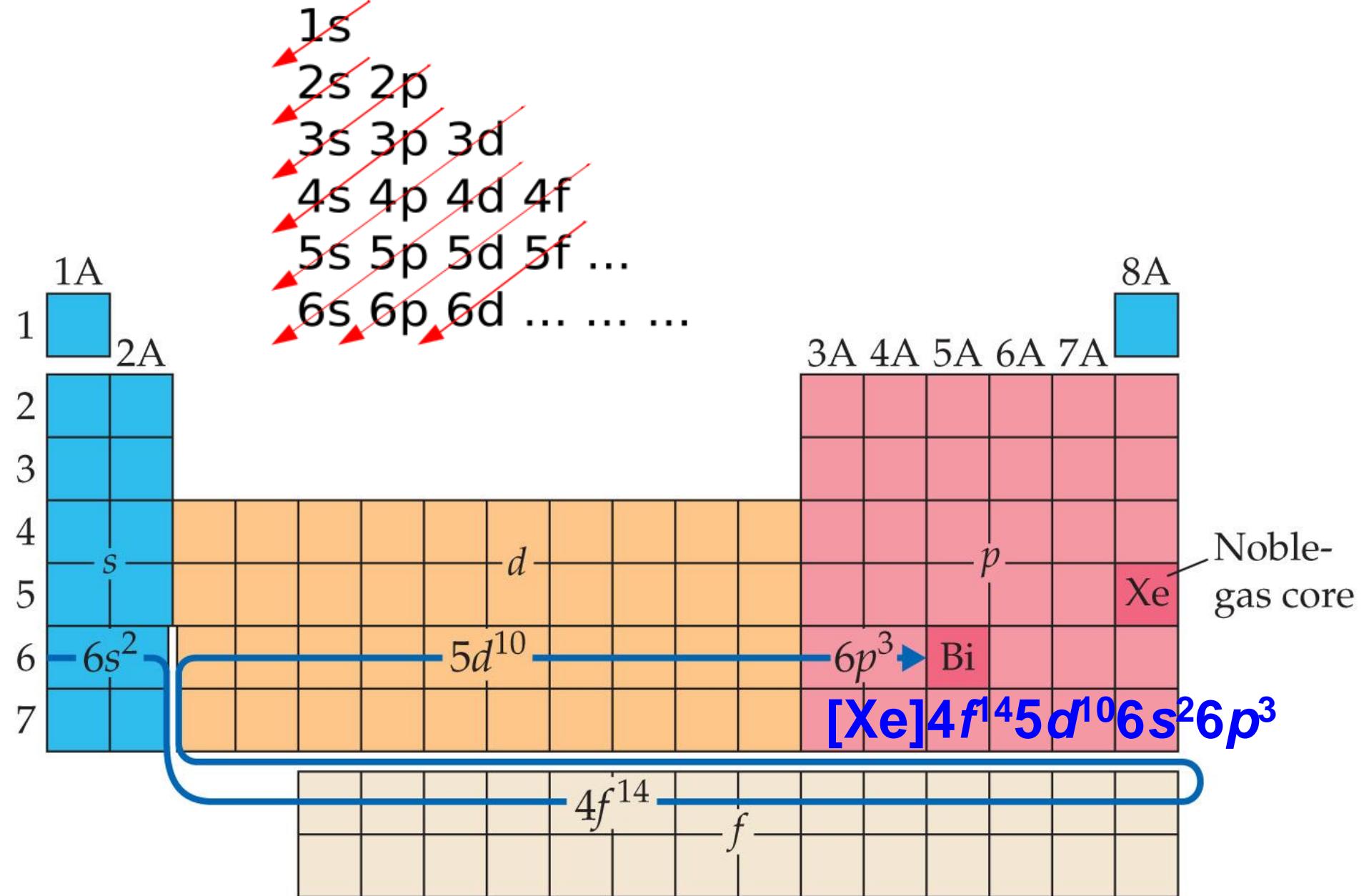
- We fill electrons in increasing order of orbital energy (Aufbau principle, 构造原理).

Diagonal rule

$l=0 \quad l=1 \quad l=2 \quad l=3$







Some Anomalies (异常现象)

Some irregularities can occur when there are enough electrons to have **half-fill** (or **complete-fill**) **d orbitals** on a given row.

3B 3	4B 4	5B 5	6B 6	7B 7	8	8B 9	10	1B 11	2B 12
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 $3d^{10}4s^2$
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 $4d^{10}5s^2$
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 $4f^{14}5d^{10}$ $6s^2$
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

- E.g.,
Chromium (Cr):

[Ar] **$3d^54s^1$**

NOT [Ar] $3d^44s^2$

Copper (Cu):

[Ar] **$3d^{10}4s^1$**

NOT [Ar] $3d^94s^2$

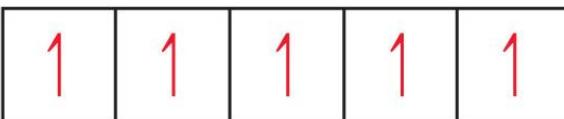
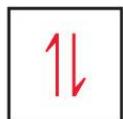
- the **$4s$** & **$3d$** orbitals are very close in energy.

4s

3d

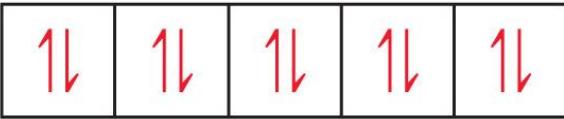
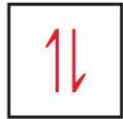
Mn: [Ar] $4s^23d^5$

or [Ar]



Zn: [Ar] $4s^23d^{10}$

or [Ar]



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 $5f^{14}7s^2$

- These anomalies also occur in **f-block atoms**. (similar energies of 4f and 5d orbitals).

What is the principal reason we must consider the uncertainty principle when discussing electrons and other subatomic particles but not when discussing our macroscopic world?

- A. The charge of subatomic particles compared to zero charge for macroscopic particles.
- B. The small mass and size of subatomic particles compared to the mass and size of macroscopic particles.
- C. The small volume occupied by subatomic particles compared to the volume occupied by macroscopic particles.
- D. The slower speeds of subatomic particles compared to the speeds of macroscopic particles.

What is the difference between an *orbit* in the Bohr model of the hydrogen atom and an *orbital* in the quantum mechanical model?

- A. An orbital is composed of some integral number of orbits.
- B. An orbit is a well-defined circular path around the nucleus while an orbital is a wave function that gives the probability of finding the electron at any point in space.
- C. An orbit is a well-defined circular path around the nucleus while an orbital is the object (electron) that is moving around the nucleus.
- D. There is no difference between the definitions of the terms “orbit” and “orbital.” They simply were proposed by different scientists.

“It is impossible to simultaneously know both the position and the momentum of an electron in an atom” is

- a. Hund’s Rule.
- b. deBroglie’s Hypothesis.
- c. Pauli’s Exclusion Principle.
- d. Heisenberg’s Uncertainty Principle.

“No two electrons in an atom may have the same values for all four quantum numbers” is

- a. Hund’s Rule.
- b. deBroglie’s Hypothesis.
- c. Pauli’s Exclusion Principle.
- d. Heisenberg’s Uncertainty Principle.

- a. How many orbitals have the principal quantum number $n = 3$?
b. In a many-electron atom, what are the relative energies of these orbitals?

a.

- A. 3
- B. 6
- C. 9
- D. 18

b.

- A. $3s < 3p < 3d$
- B. $3s < 3d < 3p$
- C. $3d < 3p < 3s$
- D. $3p < 3s < 3d$

Based on the structure of the periodic table, which becomes occupied first, the 6s orbital or the 5d orbitals?

- A. 5d
- B. 6s

N and I are the principal and angular momentum quantum numbers. When $N = 3$, the allowed values of I are

- a. 1, 2, and 3.
- b. 1 and 2.
- c. 0, 1, 2, and 3.
- d. 0, 1, and 2.

The only allowed values for the spin magnetic quantum number (m_s) are

- a. 0 and 1.
- b. 0 and $+1/2$.
- c. $+1/2$ and 1.
- d. $+1/2$ and $-1/2$.

At a node, the probability of finding an electron is

- a. 0.
- b. 1%.
- c. 50%.
- d. 100%.

The electron configuration of a carbon atom is

- a. $[\text{He}]2\text{s}^22\text{p}^2$.
- b. $[\text{He}]2\text{s}^22\text{p}^4$.
- c. $[\text{He}]2\text{s}^22\text{p}^6$.
- d. $[\text{He}]2\text{s}^2$.

The electron configuration of a sodium atom is

- a. $[\text{He}]2\text{s}^22\text{p}^63\text{s}^2$
- b. $[\text{Ne}]3\text{s}^1.$
- c. $[\text{Ne}]3\text{s}^23\text{p}^6.$
- d. $[\text{Ne}]3\text{s}^2.$

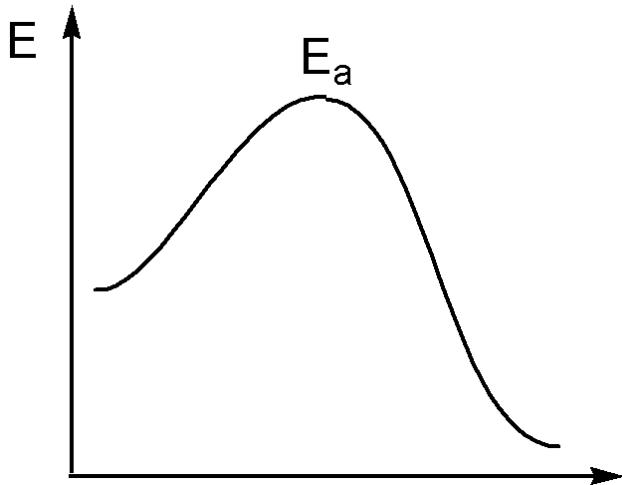
The electron configuration of a chlorine atom is

- a. $[\text{Ne}]3\text{s}^23\text{p}^6$
- b. $[\text{Ne}]3\text{s}^1.$
- c. $[\text{Ne}]3\text{s}^23\text{p}^5.$
- d. $[\text{Ne}]3\text{s}^2.$

The electron configuration of a copper atom is

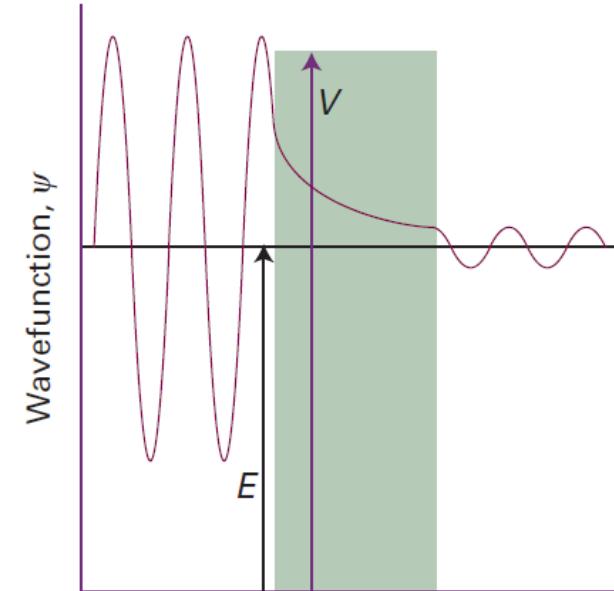
- a. $[\text{Ar}]4\text{s}^23\text{d}^9.$
- b. $[\text{Ar}]4\text{s}^13\text{d}^{10}.$
- c. $[\text{Ar}]4\text{s}^23\text{d}^{10}.$
- d. $[\text{Ar}]4\text{s}^23\text{d}^7.$

Quantum-Mechanics Tunneling (QMT) (Extra Info.)

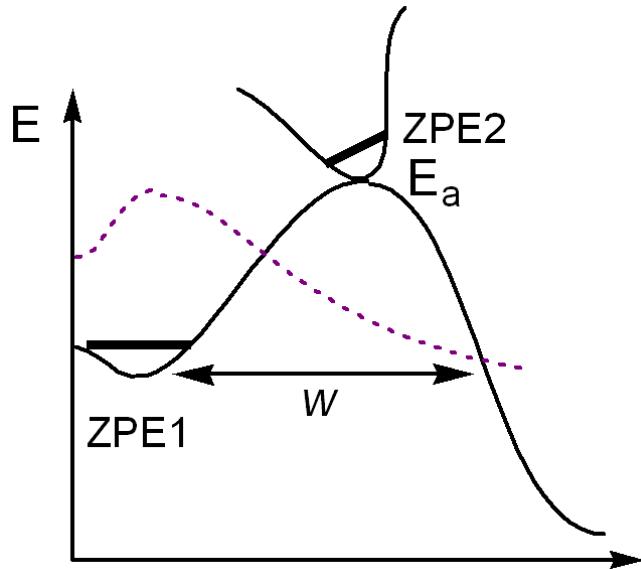


Classic Mechanics

1. $P = 0$ ($E < E_a$)
2. $P = 1$ ($E \geq E_a$)



Quantum Mechanics



Tunneling:

1. $P \geq 0$ ($E < (E_a + ZPE2 - ZPE1)$)

Quantum Reflection:

2. $P \leq 1$ ($E \geq E_a + ZPE2 - ZPE1$)

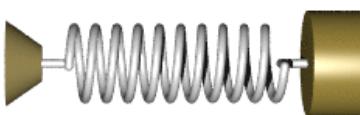
$$P_{QT} \sim \exp[-w\pi^2(2mE)^{0.5}/h]$$

$P \uparrow$: 1. \downarrow **mass** ($m^{1/2}$), e.g. e^- , H; 2. \downarrow **barrier width** (w)

Quantum Vibrational motion

(Extra Info.)

$$F = -k_f x$$



k_f : force constant

$$V = \frac{1}{2} k_f x^2$$

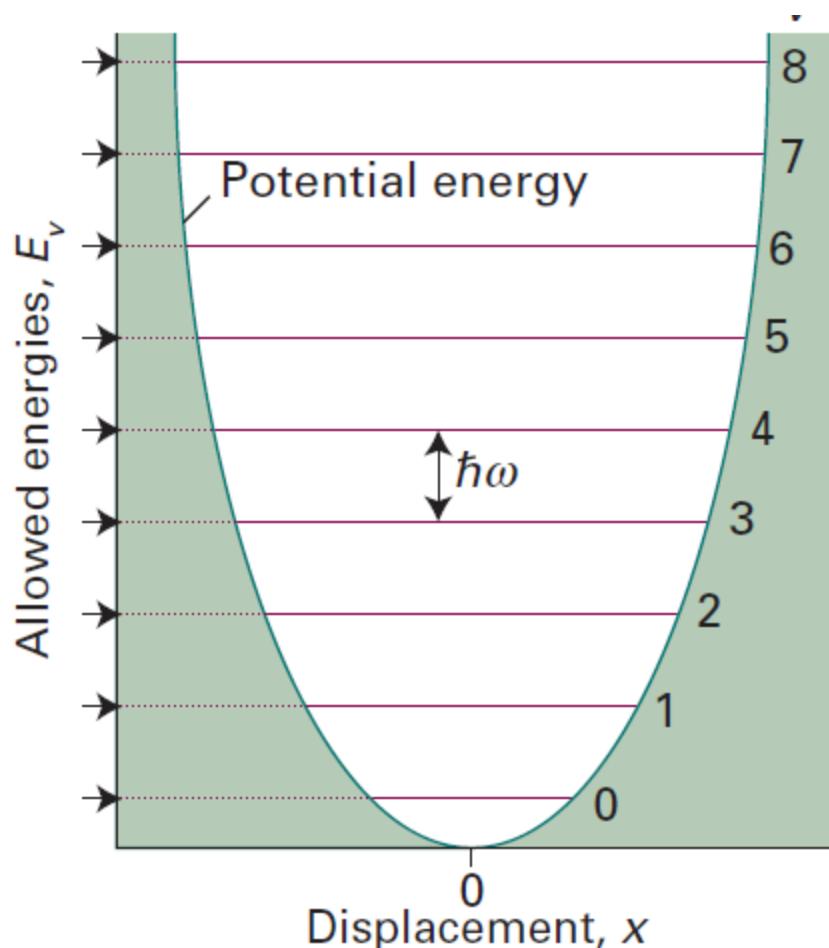
$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + \frac{1}{2} k_f x^2 \psi = E \psi$$

The solutions of this equation:

$$E_v = (v + \frac{1}{2})\hbar\omega \quad \omega = \left(\frac{k_f}{m} \right)^{1/2}$$

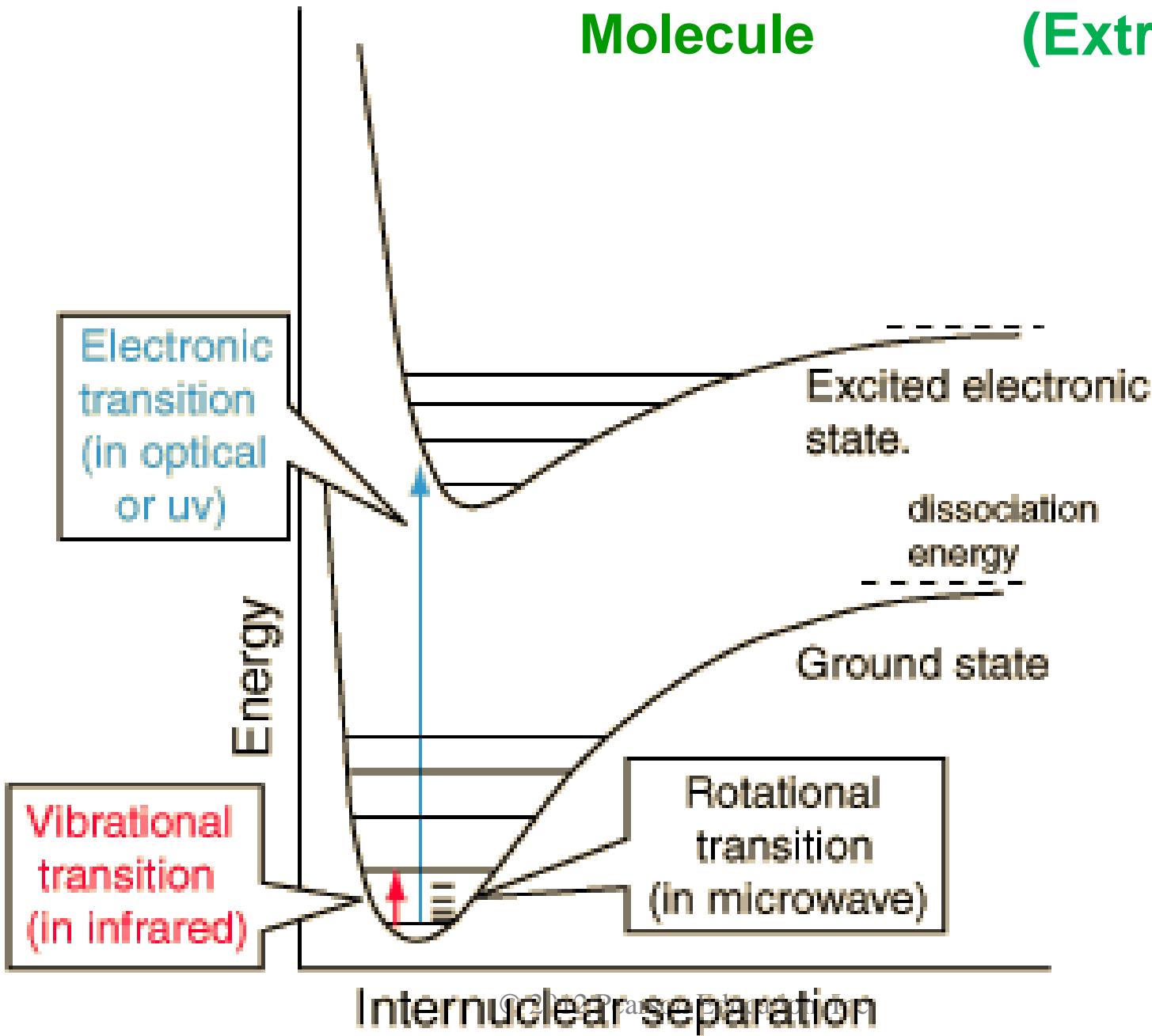
$$E_0 = \frac{1}{2}\hbar\omega$$

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$$v = 0, 1, 2, \dots$$

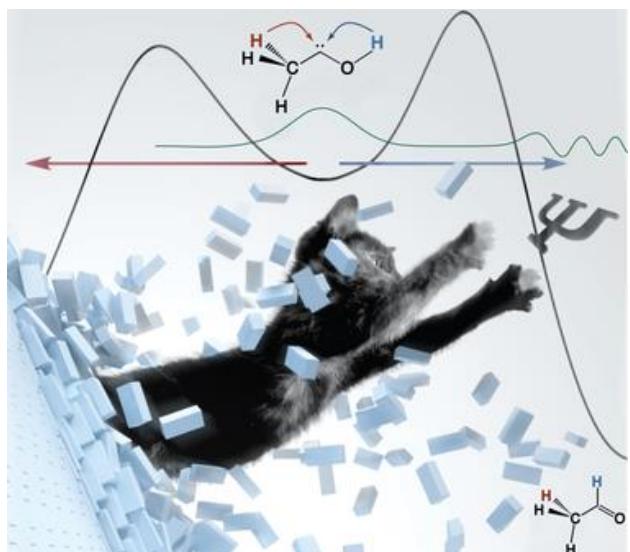
Electronic, Vibrational & Rotational Energy Levels of a Molecule (Extra Info.)



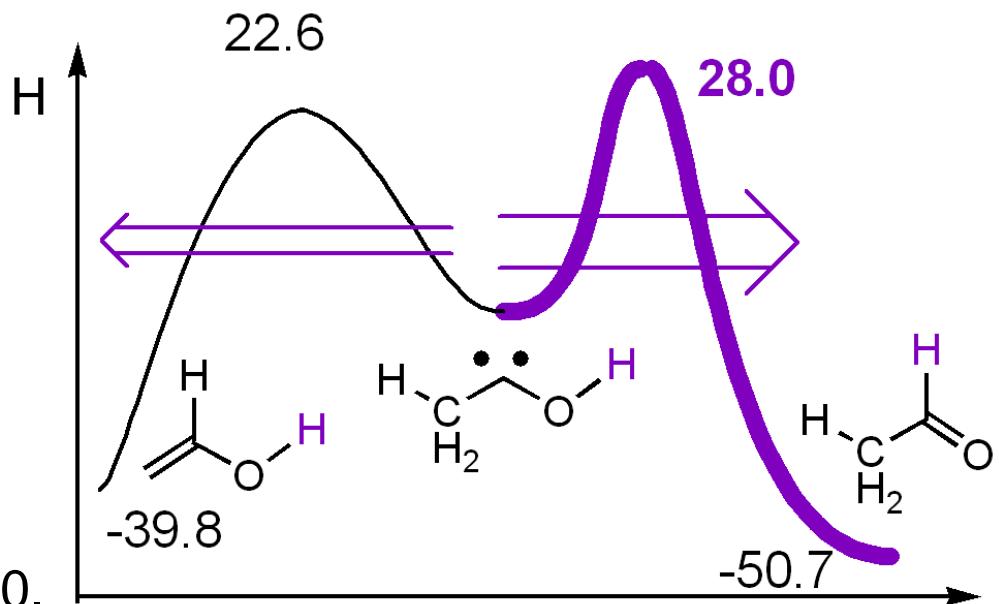
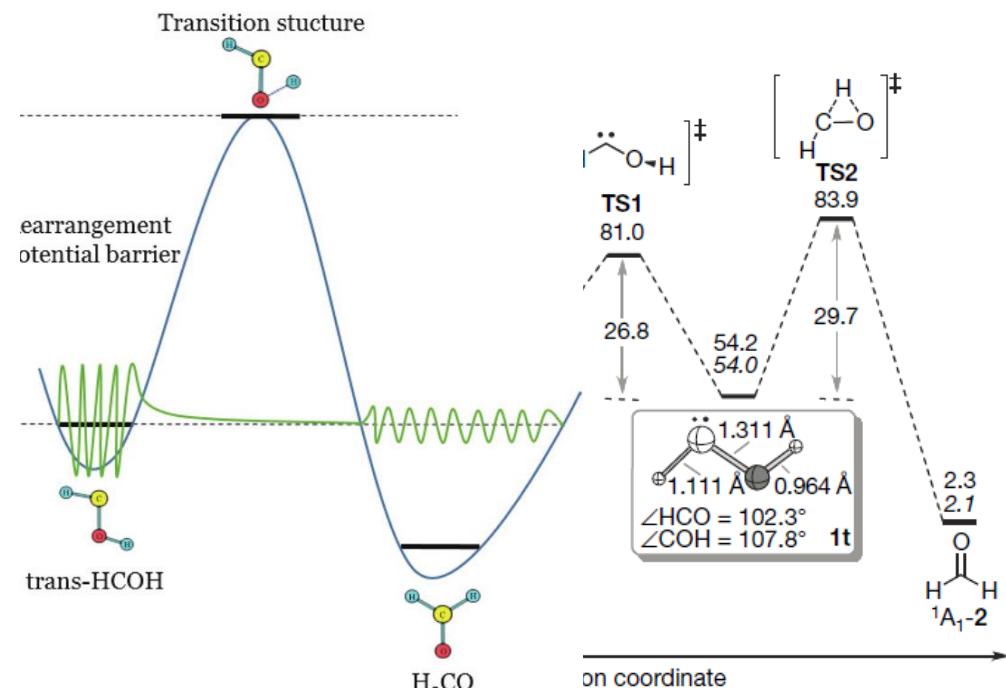
(Extra Info.) Tunneling-Control reaction



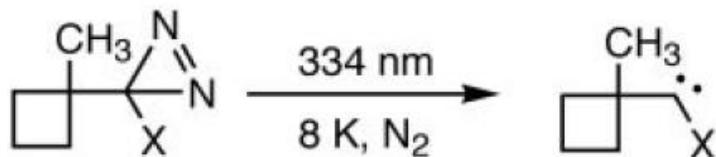
$t_{1/2}$ (half-life) $\sim 2\text{h}$ (exp.
11-20 K); 122 min (calc.)
H-C-OD: **1200 yr** (calc.);
stable



Schreiner, Allen, et al. *Nature*
2008, 453, 906; *Science* 2011, 332, 1300.



(Extra Info.) Heavy-atom Tunneling in Organic Reactions

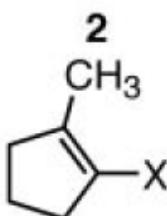


1
 (a) X = Cl
 (b) X = F

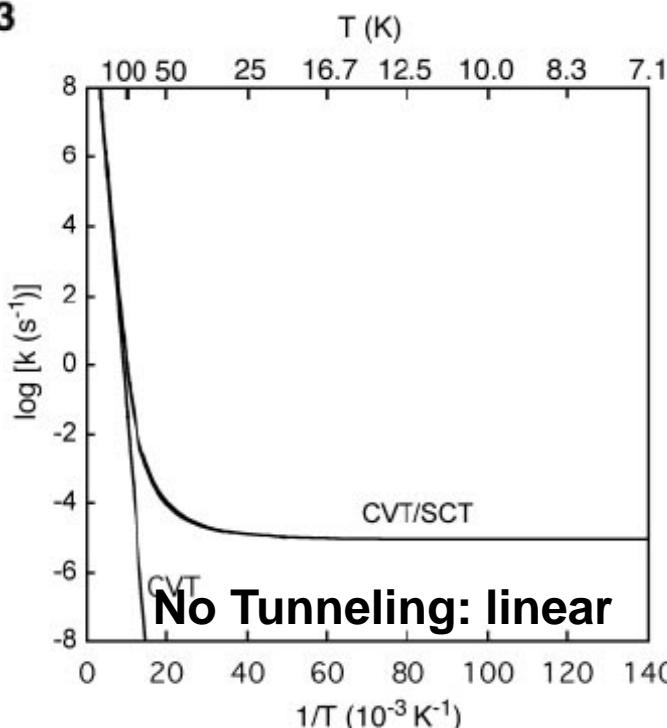
$$X = \text{F}$$

$$k = 4 \times 10^{-6} \text{ s}^{-1} (\text{N}_2)$$

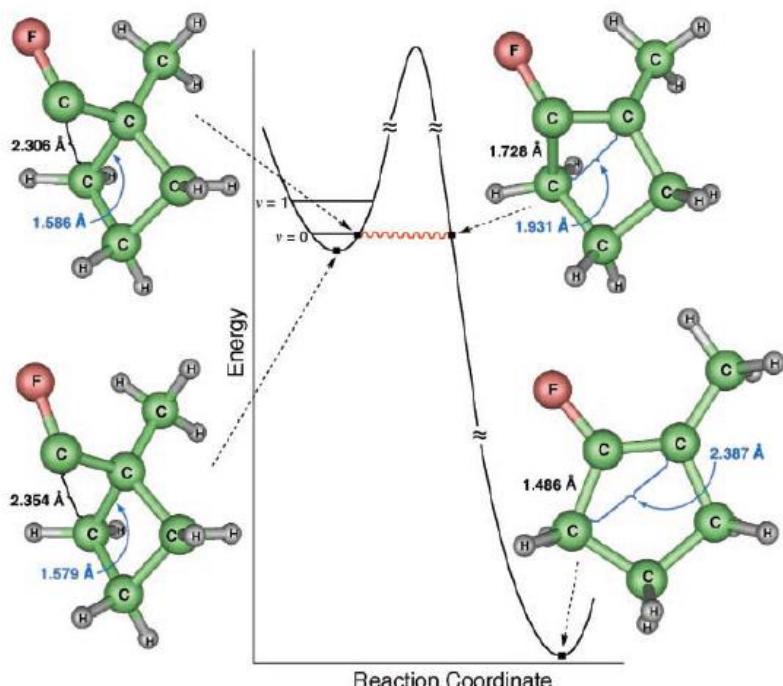
$$k = 4 \times 10^{-5} \text{ s}^{-1} (\text{Ar})$$



3



No Tunneling: linear

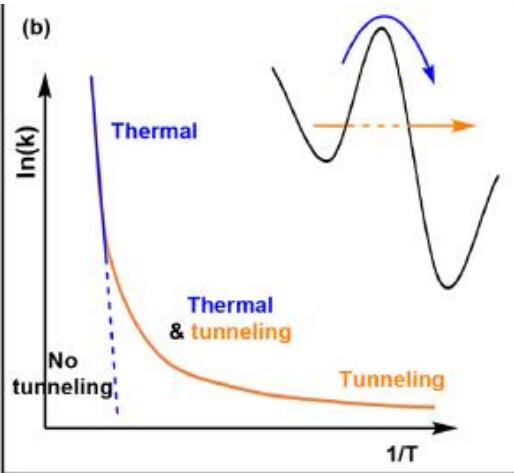
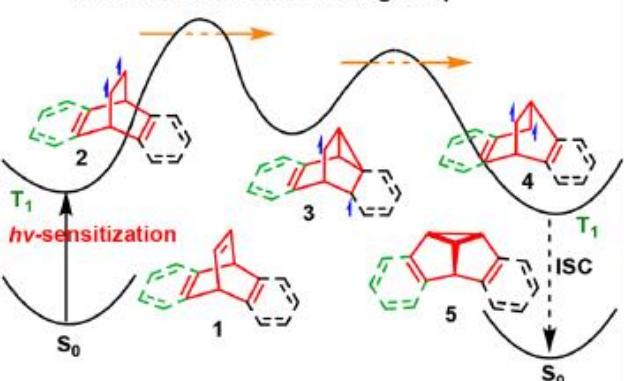


(Extra Info.)

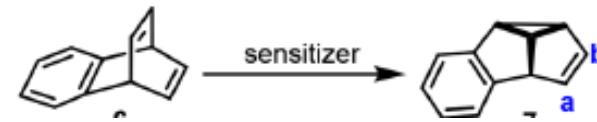
Excited-state Heavy-atom Tunneling

(a) Mechanism & prediction

Two consecutive C-tunneling in T_1



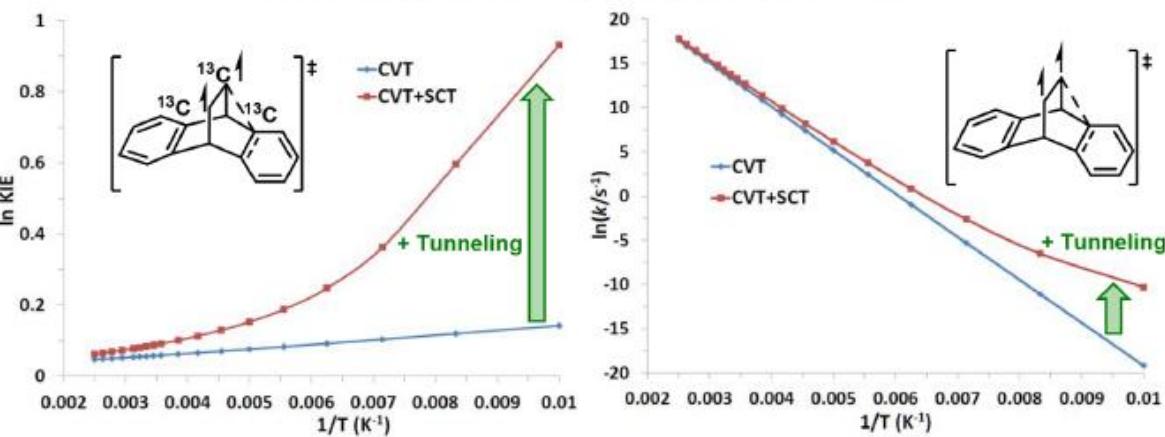
(d) EXP: Measured nominal KIEs



sensitizer and E_T (kcal/mol)	nominal KIE (^{13}C in a / ^{13}C in b)
acetophenone 73.3	200 K 1.138(7)
acetone 81.2	1.069(9)

(c) DFT: Arrhenius plots of the $^{12}\text{C}/^{13}\text{C}$ KIE and rate constant

- Enhanced C KIE and rate by excited-state C-tunneling



My theoretical prediction:

Li, Liao, Chung JACS 2017, 16438.

Exp proof:

Kuan, Singleton, JACS 2020, 19885.

Strikingly, the observed nominal KIEs vary with the sensitizer. The KIEs are exceptionally high with acetophenone, particularly at 200 K. However, they are only half as large with acetone, with methyl benzoate in between. In the conventional

For the acetophenone-sensitized reactions, the predicted KIEs fit closely with those observed. Importantly, this supports the conventional mechanism involving structures 2 through 7, the approximate accuracy of the computational energy surface, and Chung's insightful prediction of excited-state heavy-atom tunneling.^{7,16} The agreement also weighs against the

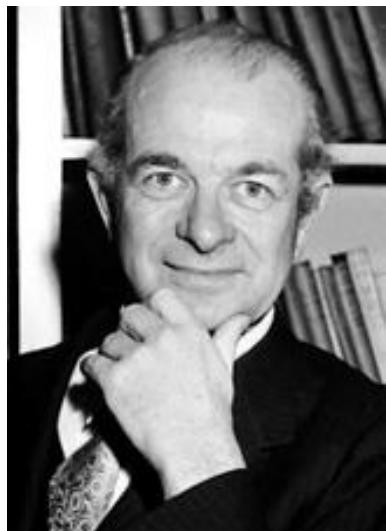
VIP Theoretical Chemists



The Nobel Prize in Chemistry 1954

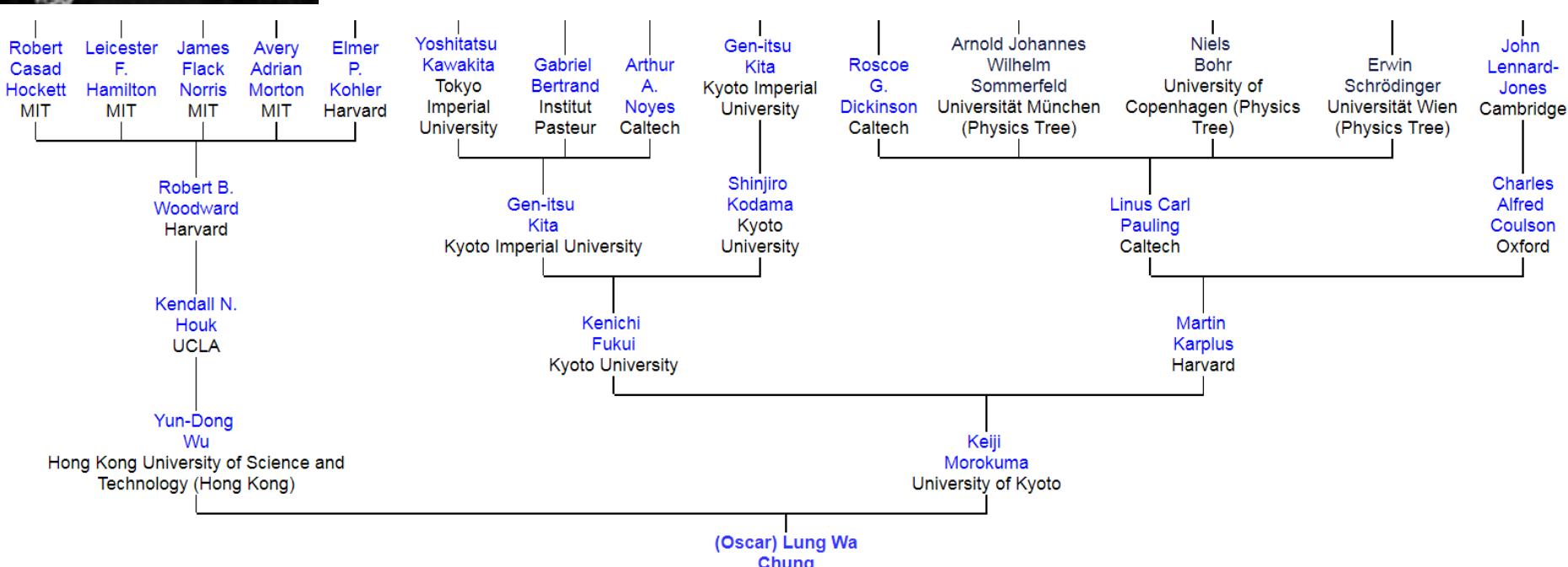
Linus Pauling

(Extra Info.)



"for his research into the nature of the chemical bond and its application to the elucidation of the structure of complex substances".

"the concept of hybridization of atomic orbitals"; "Valence Bond Theory"



(Extra Info.) VIP Theoretical Chemists



The Nobel Prize in Chemistry 1966

Robert S. Mulliken



"for his fundamental work concerning chemical bonds and the electronic structure of molecules by the molecular orbital method"



The Nobel Prize in Chemistry 1968

Lars Onsager



"for the discovery of the reciprocal relations bearing his name, which are fundamental for the thermodynamics of irreversible processes"



The Nobel Prize in Chemistry 1974

Paul J. Flory



"for his fundamental achievements, both theoretical and experimental, in the physical chemistry of the macromolecules"



The Nobel Prize in Chemistry 1992

Rudolph A. Marcus



"for his contributions to the theory of electron transfer reactions in chemical systems"

Electronic
Structure
OF ATOMS

(Extra Info.)

VIP Theoretical & Computational Chemists



The Nobel Prize in Chemistry 1981
Kenichi Fukui, Roald Hoffmann

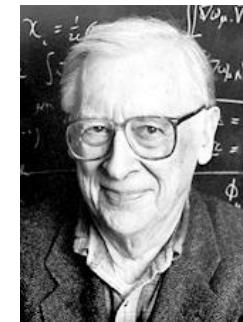


"for their theories, developed independently, concerning the course of chemical reactions"

e.g. Frontier molecular orbitals (FMO, e.g. HOMO, LUMO), reaction path; Woodward-Hoffmann rules, extended-Hückel method; isolobal principle.

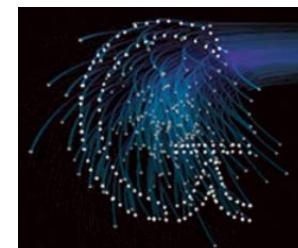


The Nobel Prize in Chemistry 1998
Walter Kohn, John Pople



"for development of the density-functional theory" and "computational methods in quantum chemistry"

e.g. DFT, many QM methods and popular Gaussian software

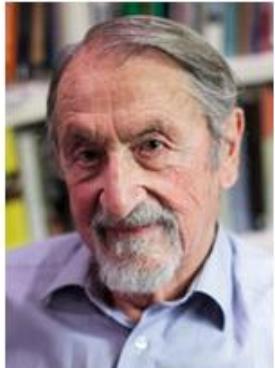


Electronic Structure of Atoms

Hybrid Quantum Mechanics/Molecular Mechanics (QM/MM)



The Nobel Prize in Chemistry 2013



© Harvard University
Martin Karplus



Photo: © S. Fisch
Michael Levitt



Photo: Wikimedia Commons
Arieh Warshel

The Nobel Prize in Chemistry 2013 was awarded jointly to Martin Karplus, Michael Levitt and Arieh Warshel *"for the development of multiscale models for complex chemical systems".*

Electronic
Structure
of Atoms

Key Summary

Arrangement of Electrons of an Atom in Atomic Orbitals

Light: Quantized Energy, Photoelectric Effect, Photon, Bohr Model, Matter Wave, Wave-Particle Duality, Uncertainty Principle

Quantum Mechanics: Schrödinger (Wave) Equation, Wave Function, Probability Density

Electrons & Orbitals: Quantum Numbers, Electron Shell, Spin, Pauli Exclusion Principle, Hund's Rule, Electron Configurations

**Thank You for Your
Attention!
Any Questions?**