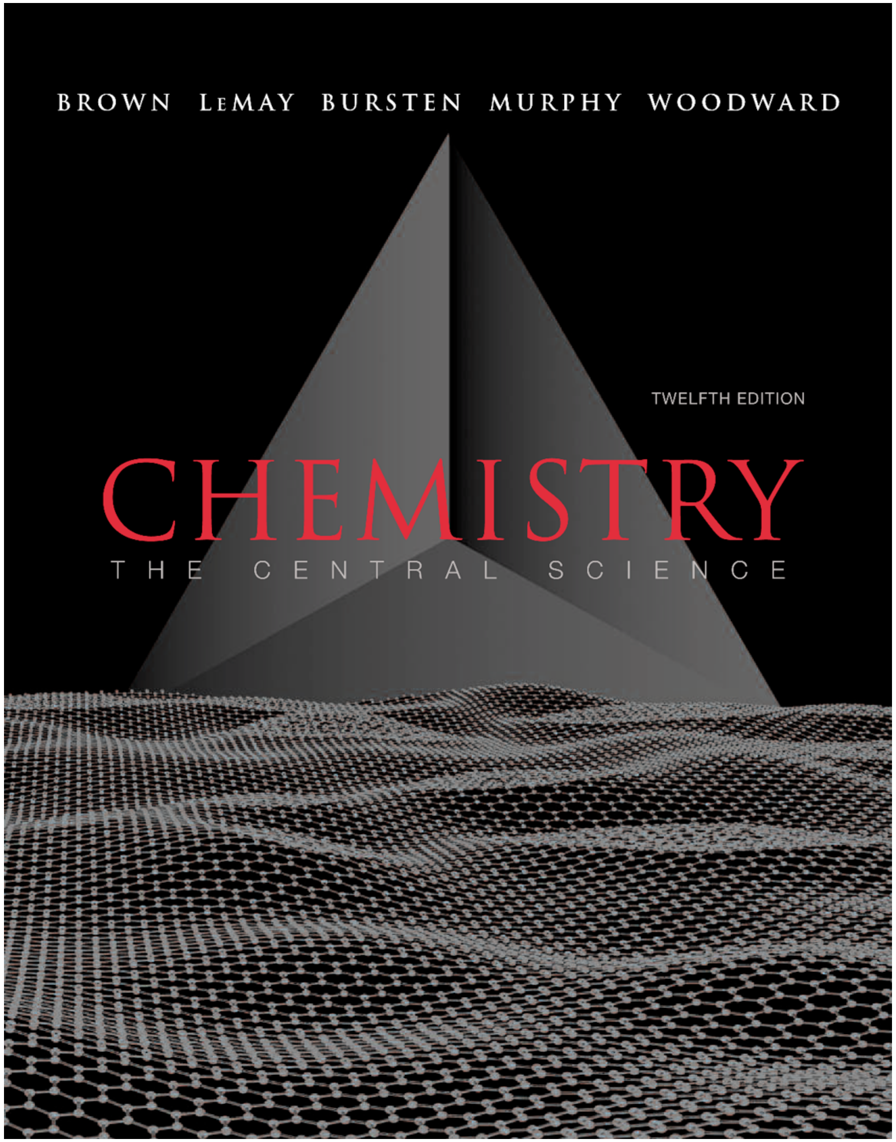


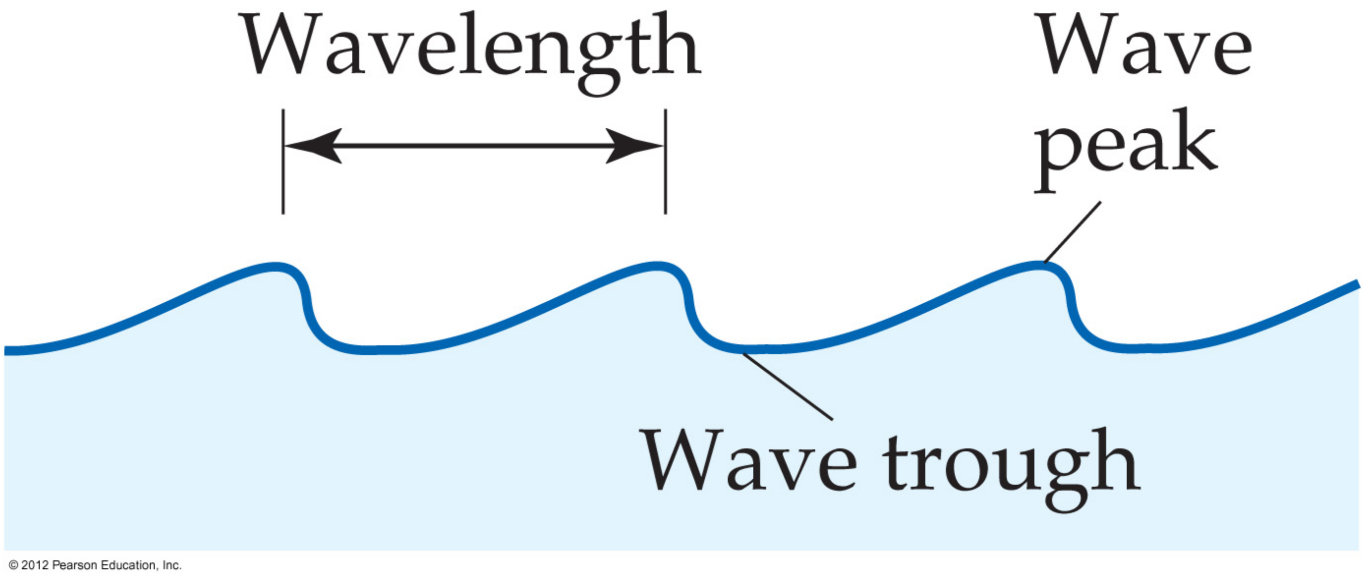
Lecture Presentation

Chapter 6

Electronic Structure of Atoms

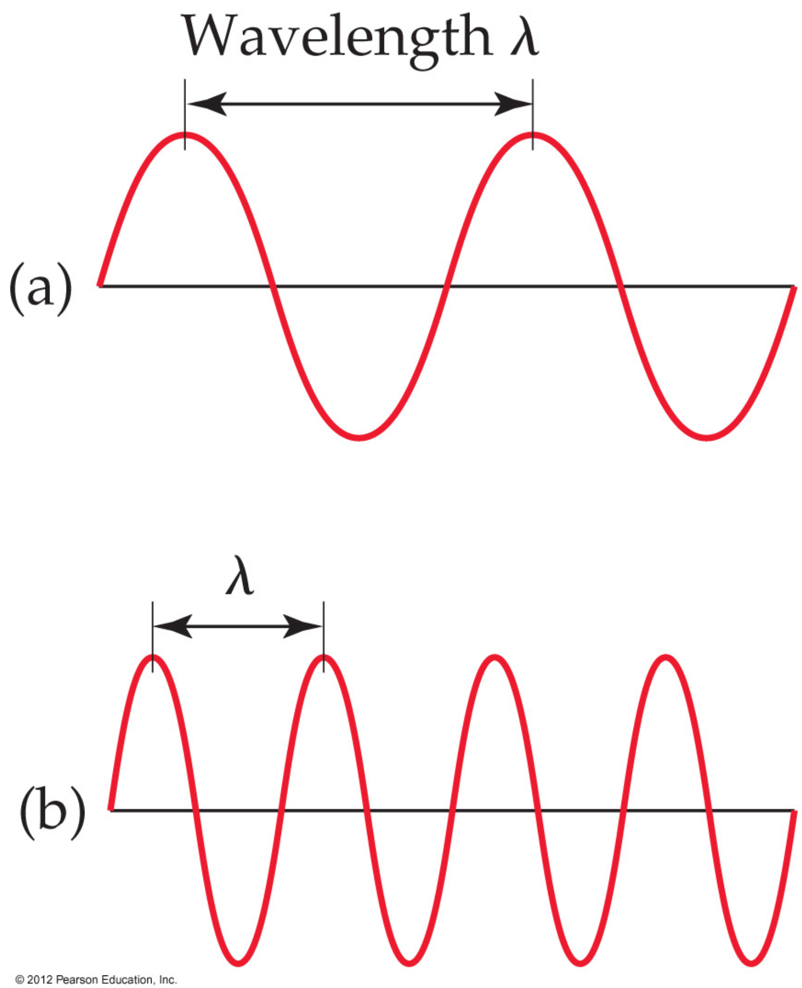
John D. Bookstaver
St. Charles Community College
Cottleville, MO

Waves



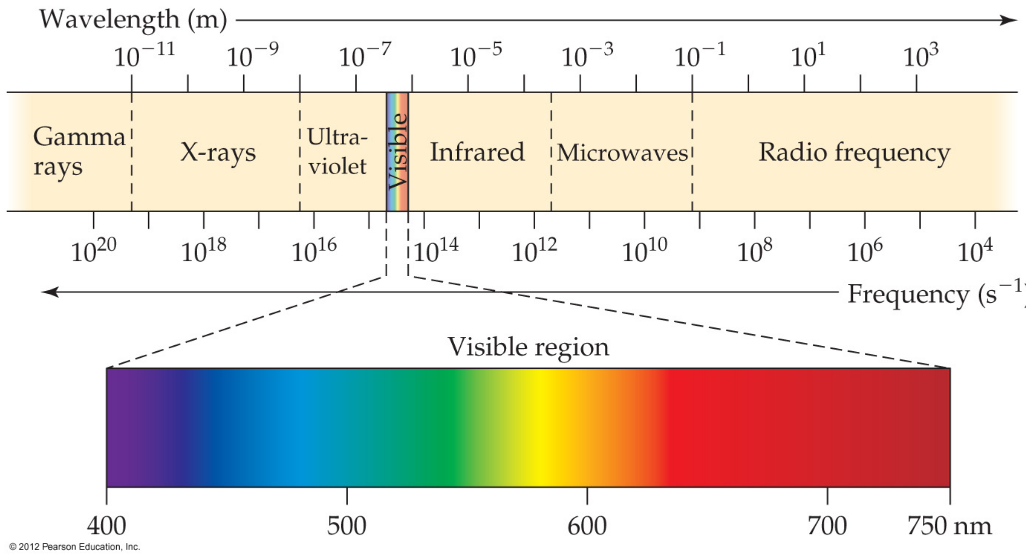
- To understand the electronic structure of atoms, one must understand the nature of electromagnetic radiation.
- The distance between corresponding points on adjacent waves is the **wavelength (λ)**.

Waves



- The number of waves passing a given point per unit of time is the **frequency (ν)**.
- For waves traveling at the same velocity, the longer the wavelength, the smaller the frequency.

Electromagnetic Radiation



- All electromagnetic radiation travels at the same velocity in a vacuum: the speed of light (c), 3.00×10^8 m/s.
- Therefore,

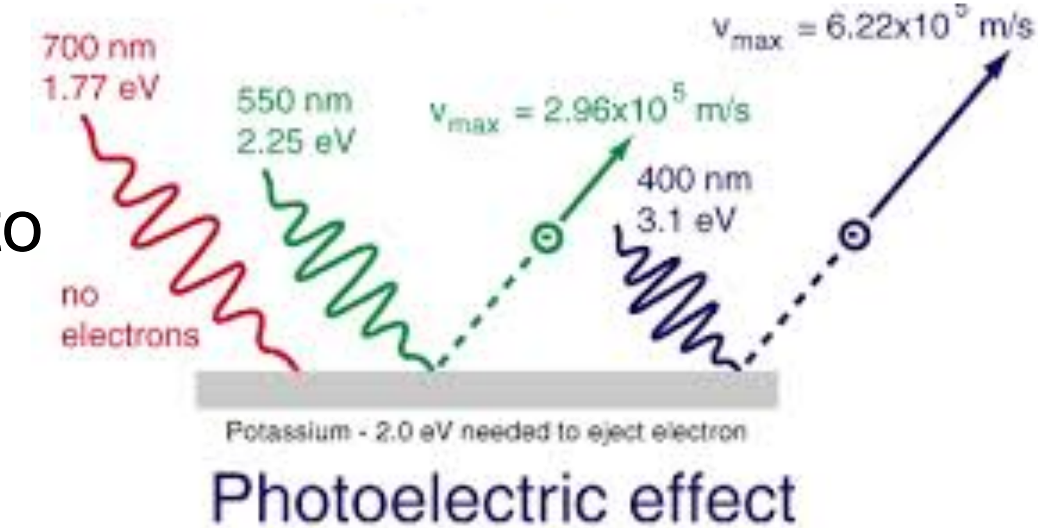
$$c = \lambda\nu$$

The Nature of Energy

- But how to explain the photoelectric effect?
- energy is proportional to frequency:

$$E = h\nu$$

where h is Planck's constant, 6.626×10^{-34} J-s.



And…. quantization

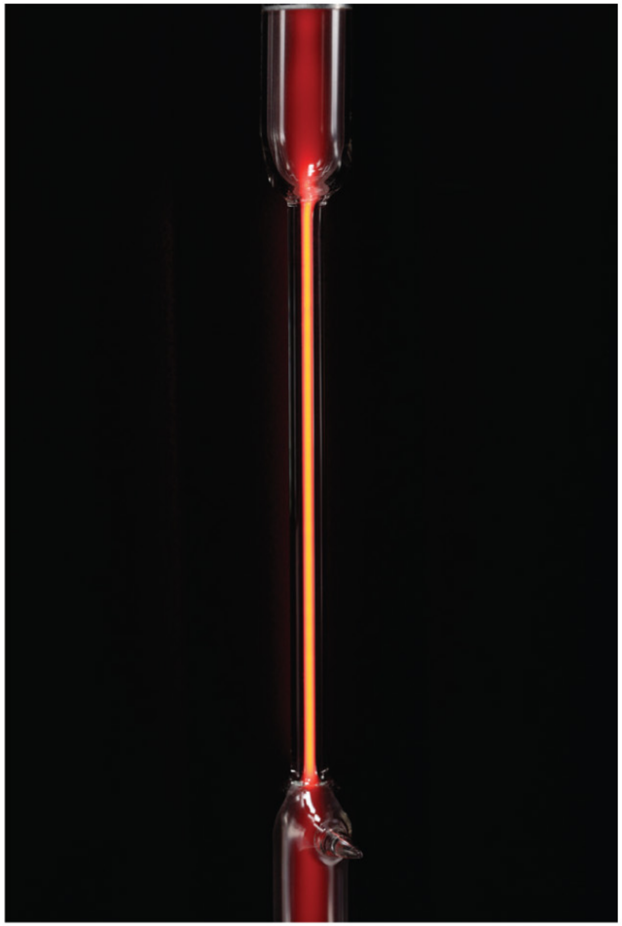
The Nature of Energy

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

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

Max Planck made the assumption that energy comes in packets called **quanta**.

The Nature of Energy

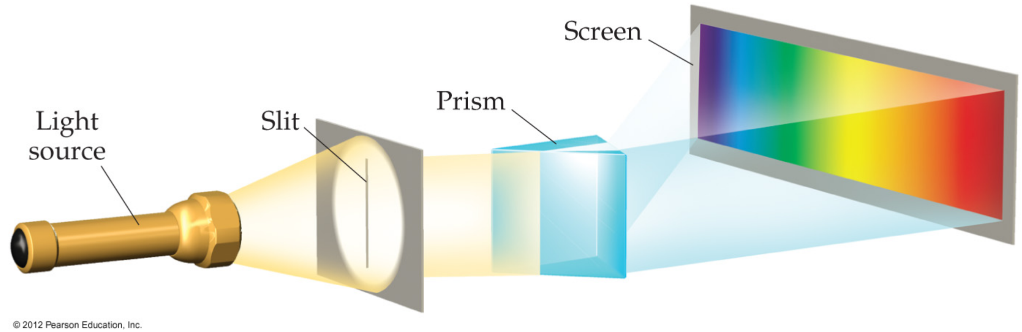


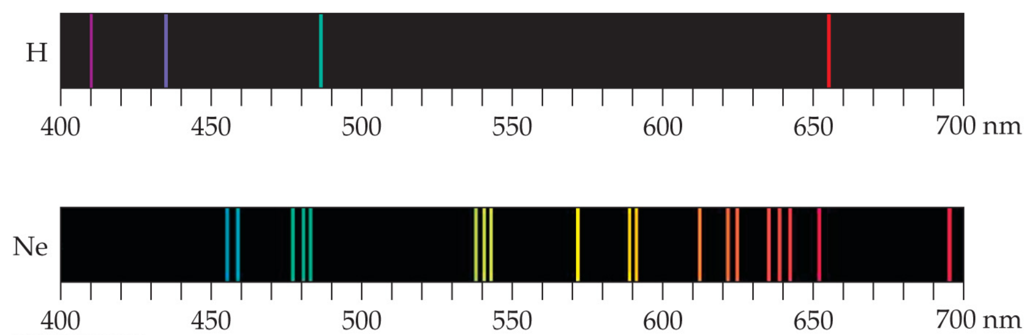
Neon (Ne)

Another mystery in the early twentieth century involved the emission spectra observed from energy emitted by atoms and molecules.

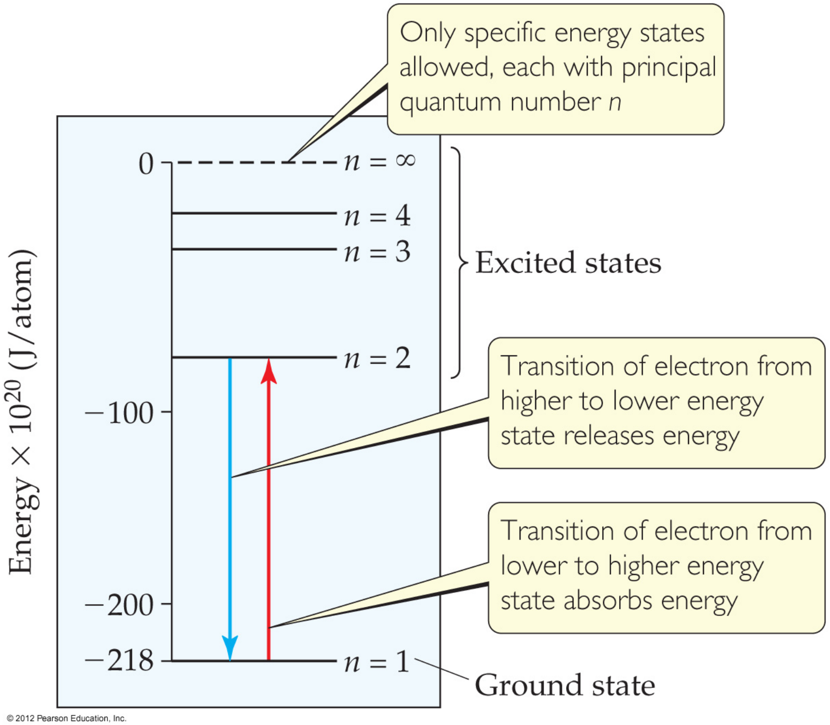
The Nature of Energy

- For atoms and molecules, one does not observe a continuous spectrum, as one gets from a white light source.
- Only a **line spectrum** of discrete wavelengths is observed.





The Nature of Energy

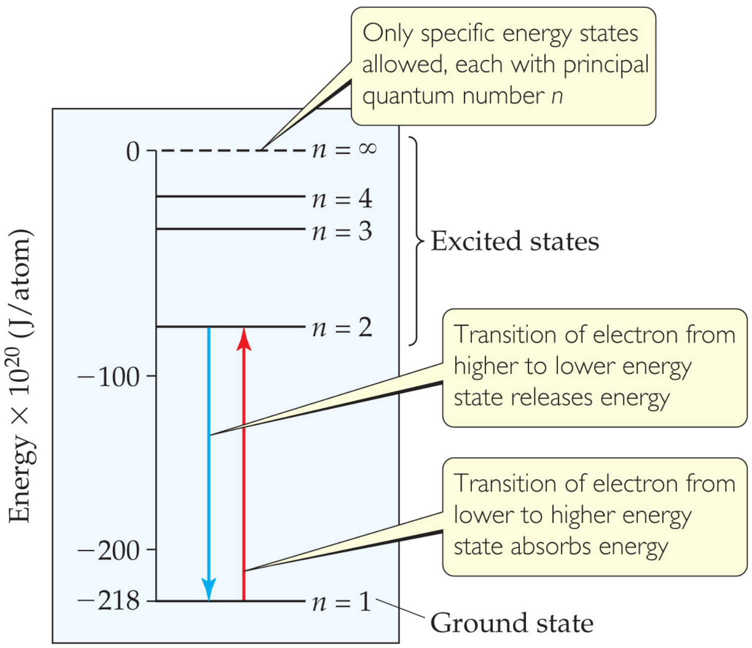


- Niels Bohr adopted Planck's assumption:

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

$$E = h\nu$$

The Nature of Energy

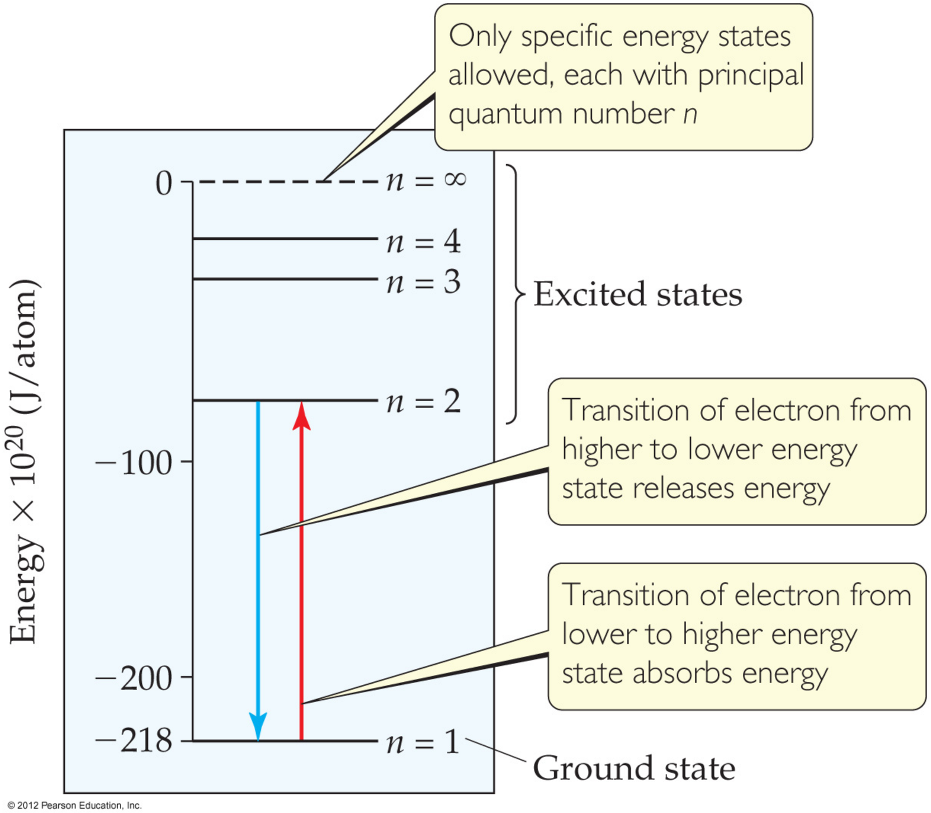


The energy absorbed or emitted from the process of electron promotion or demotion can be calculated by the equation:

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

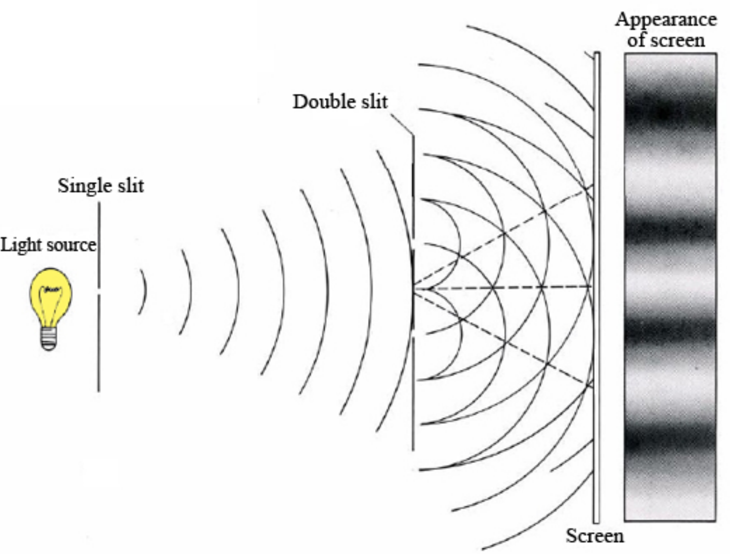
where R_H is the Rydberg constant, $1.097 \times 10^7\ \text{m}^{-1}$, and n_i and n_f are the initial and final energy levels of the electron.

Which of these electronic transitions produces the spectral line having the longest wavelength: $n = 2$ to $n = 1$, $n = 3$ to $n = 2$, or $n = 4$ to $n = 3$.



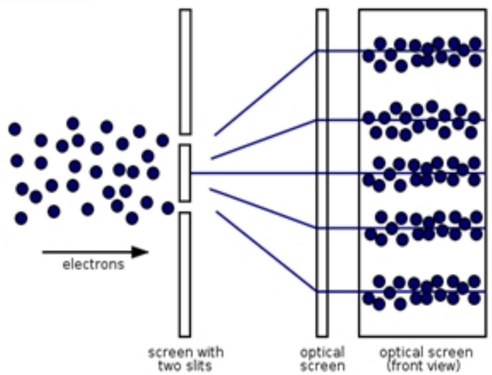
Electronic Structure of Atoms

Wave particle duality

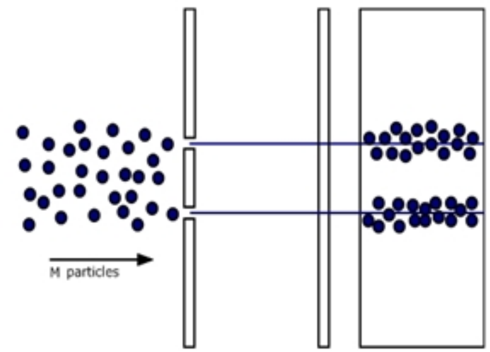


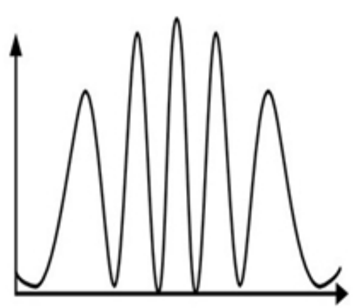
Light

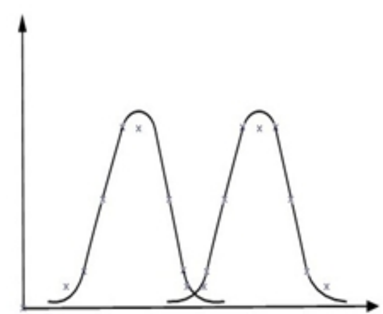
Electrons



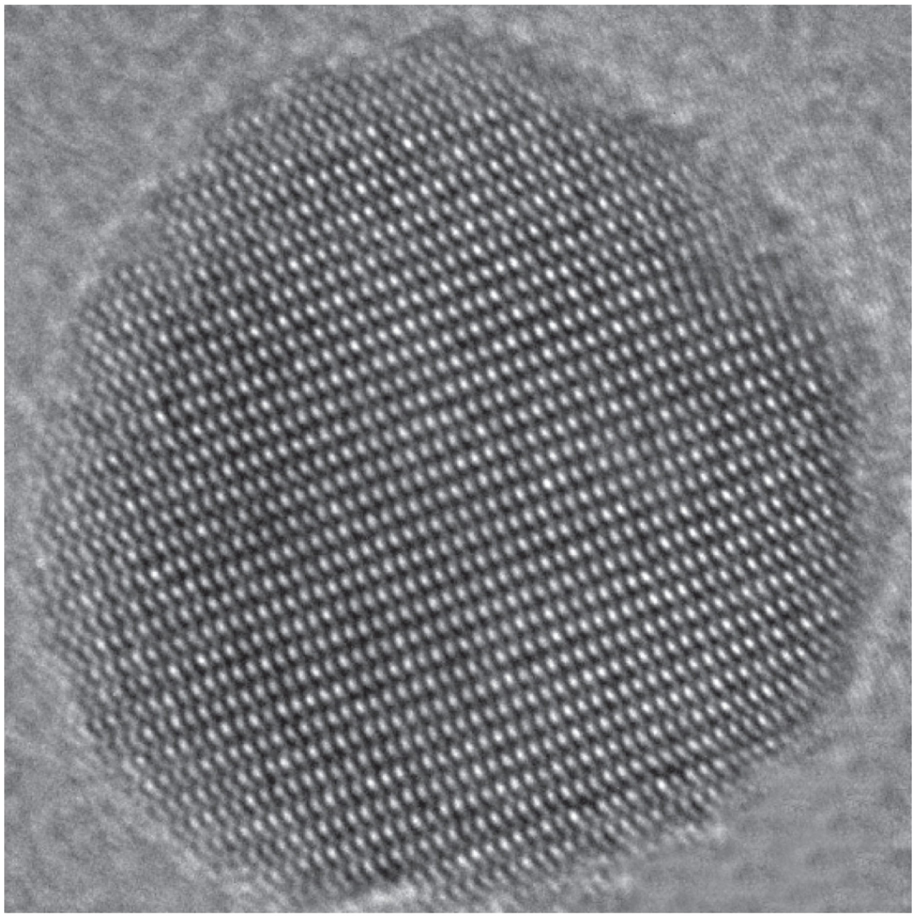
Protons







The Wave Nature of Matter



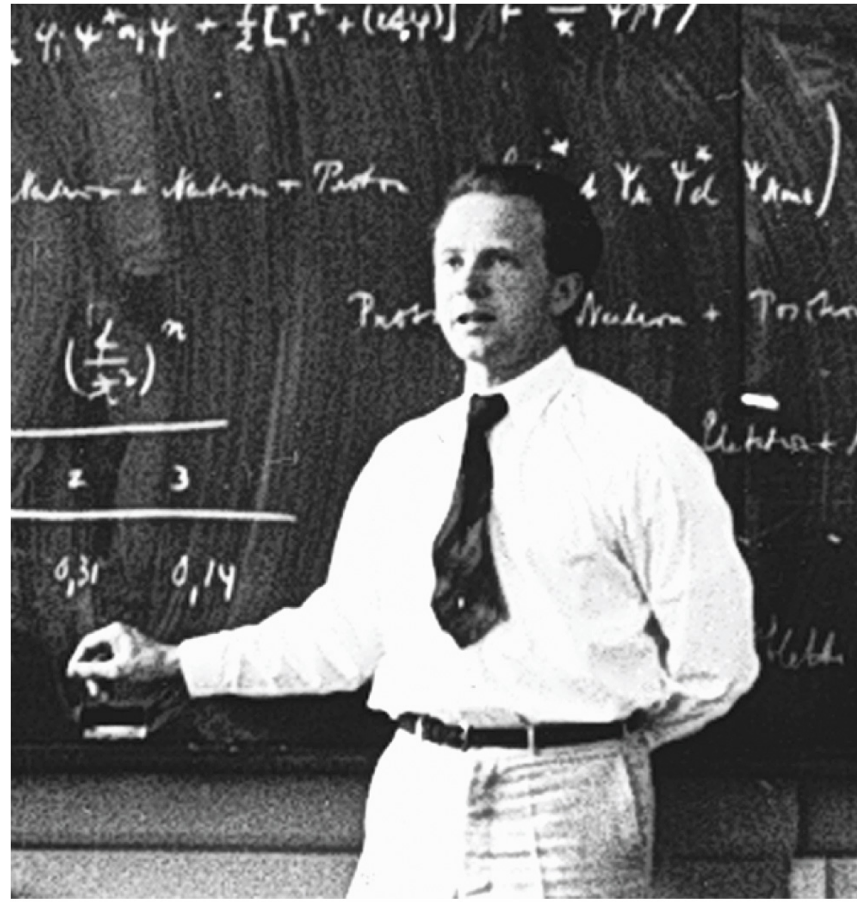
- Louis de Broglie posited that if light can have material properties, matter should exhibit wave properties.
- He demonstrated that the relationship between mass and wavelength was

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

The Uncertainty Principle

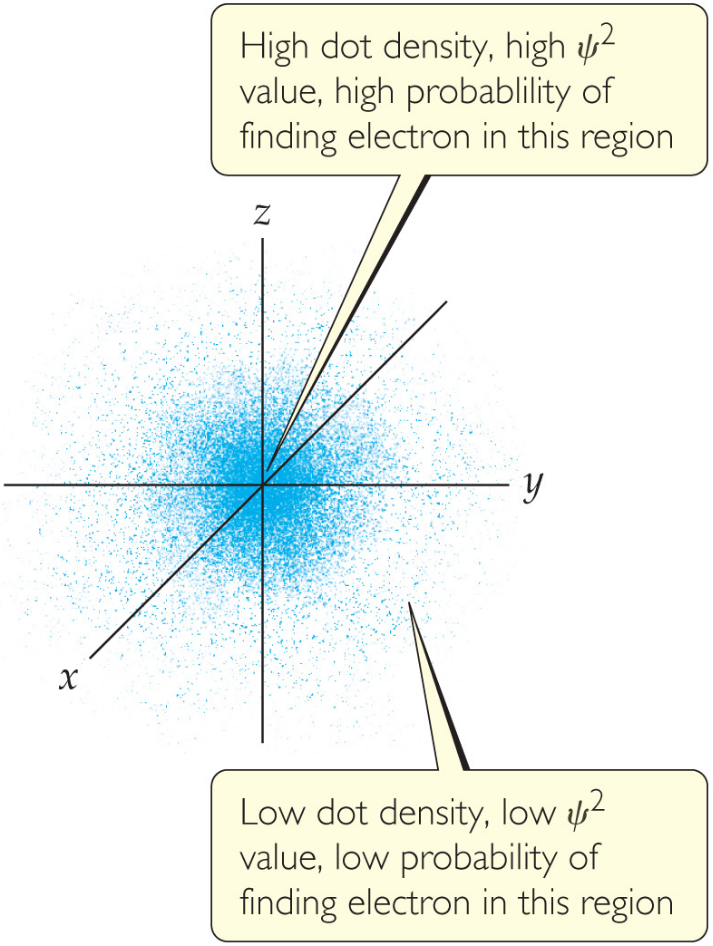
Heisenberg showed that the more precisely the momentum of a particle is known, the less precisely is its position is known:

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



Quantum Mechanics

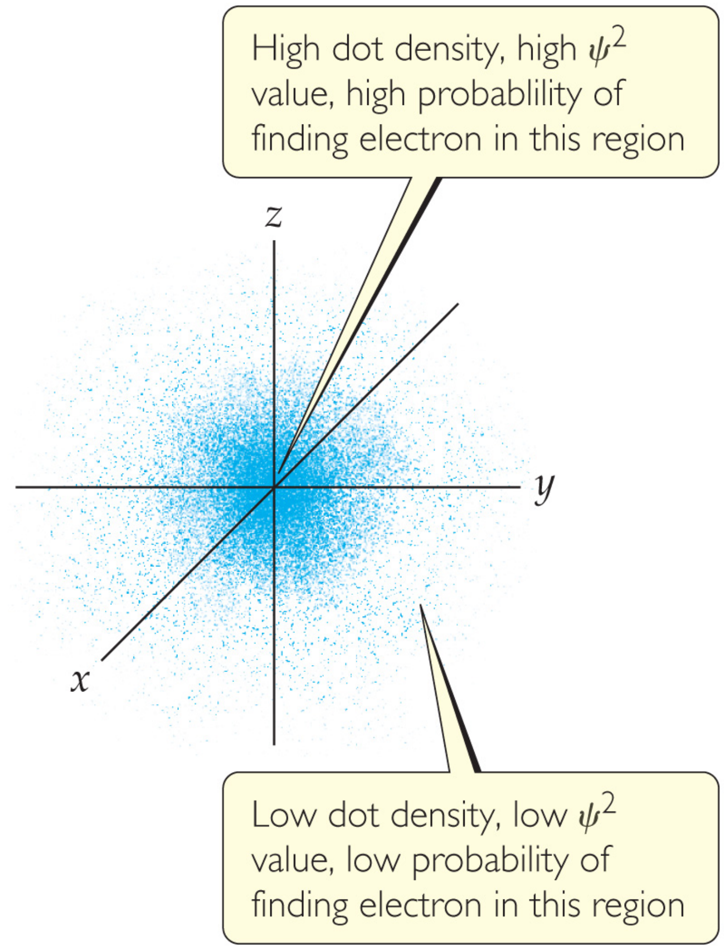
- Erwin Schrödinger developed a mathematical treatment into which both the wave and particle nature of matter could be incorporated.
- This is known as **quantum mechanics.**



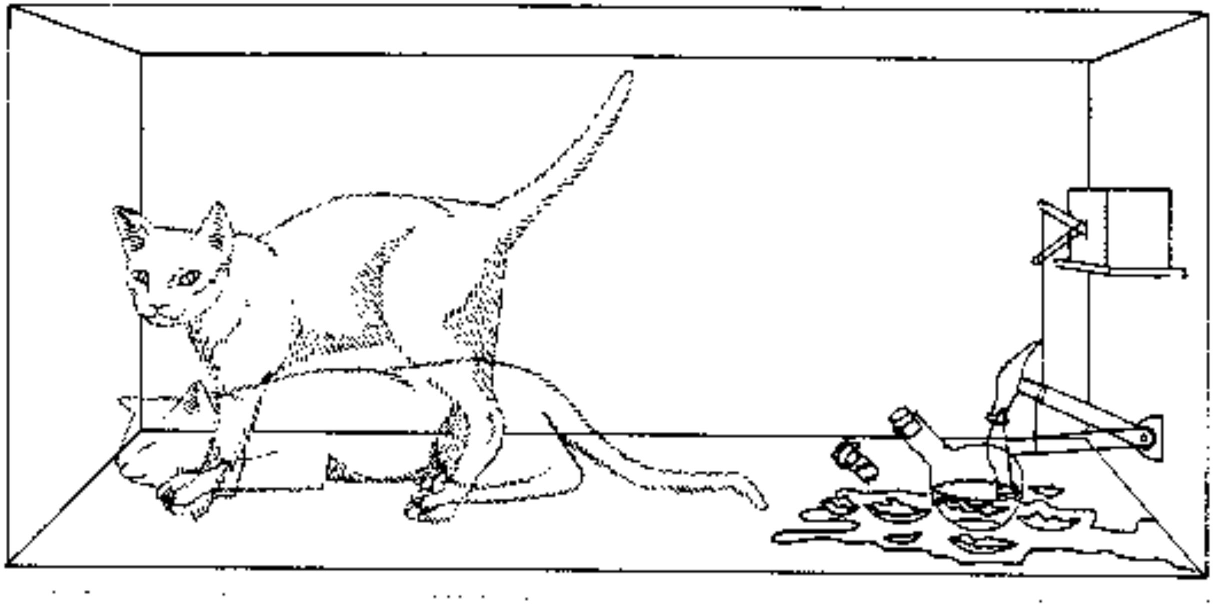
Quantum Mechanics

$$\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi = \frac{i\hbar\partial}{\partial t}\Psi$$

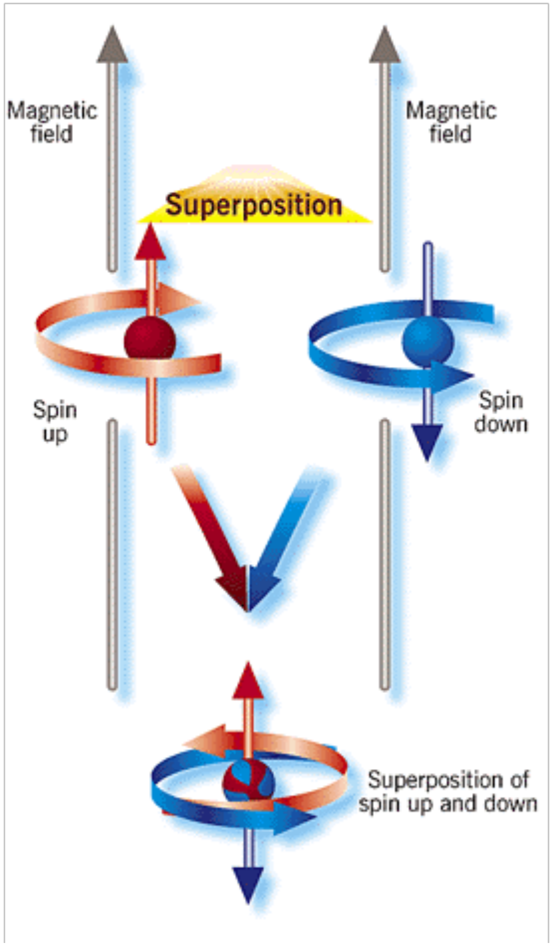
- The wave equation is designated with a lowercase Greek psi (ψ).
- The square of the wave equation, ψ^2, gives a probability density map of where an electron has a certain statistical likelihood of being at any given instant in time.



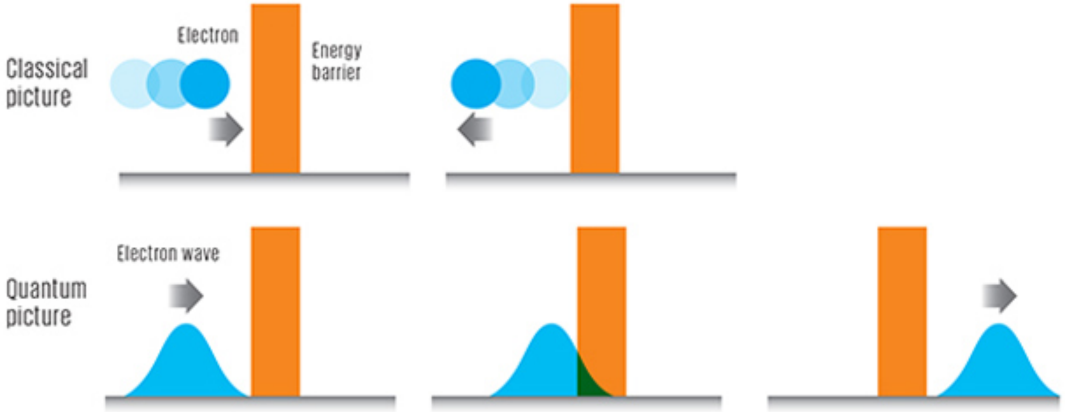
Schrodinger's Cat



Beryllium ion



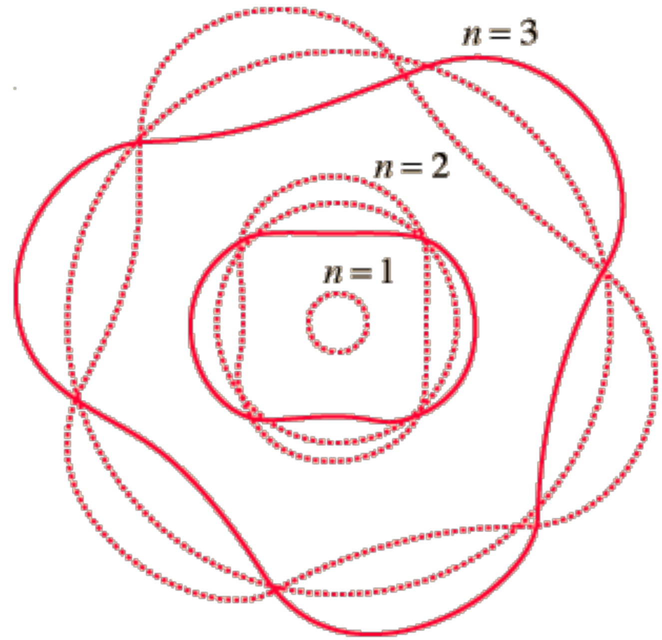
Quantum Tunneling

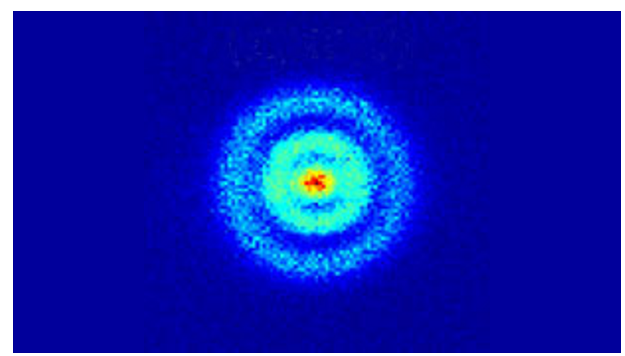


Electronic Structure of Atoms

Quantum Numbers

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





Principal Quantum Number (*n*)

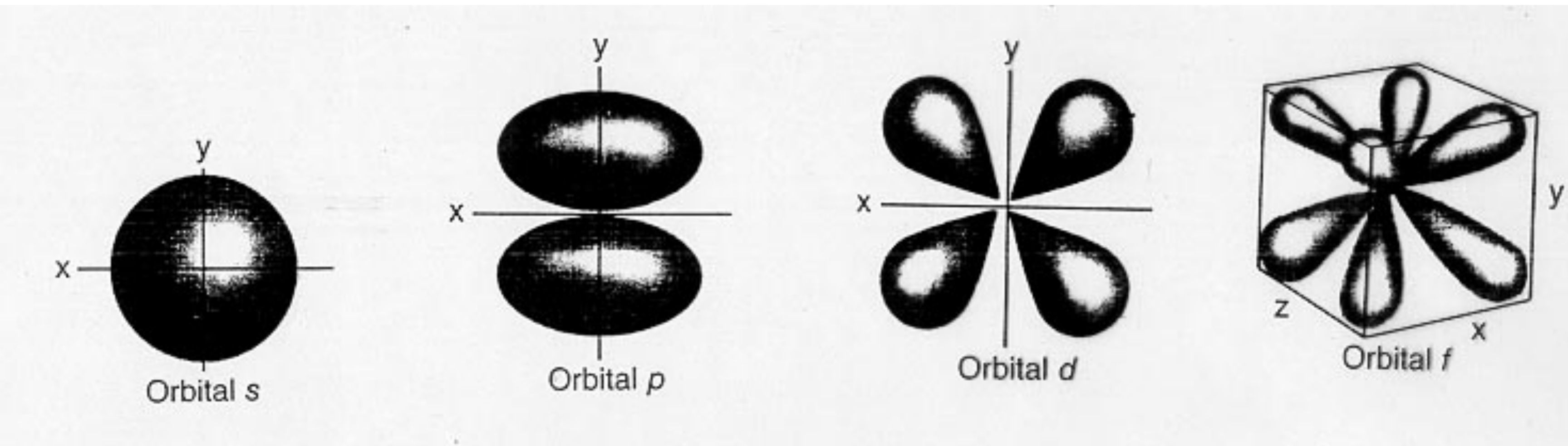
- The principal quantum number, *n*, describes the energy level on which the orbital resides.
- The values of *n* are integers ≥ 1.

Angular Momentum Quantum Number (*l*)

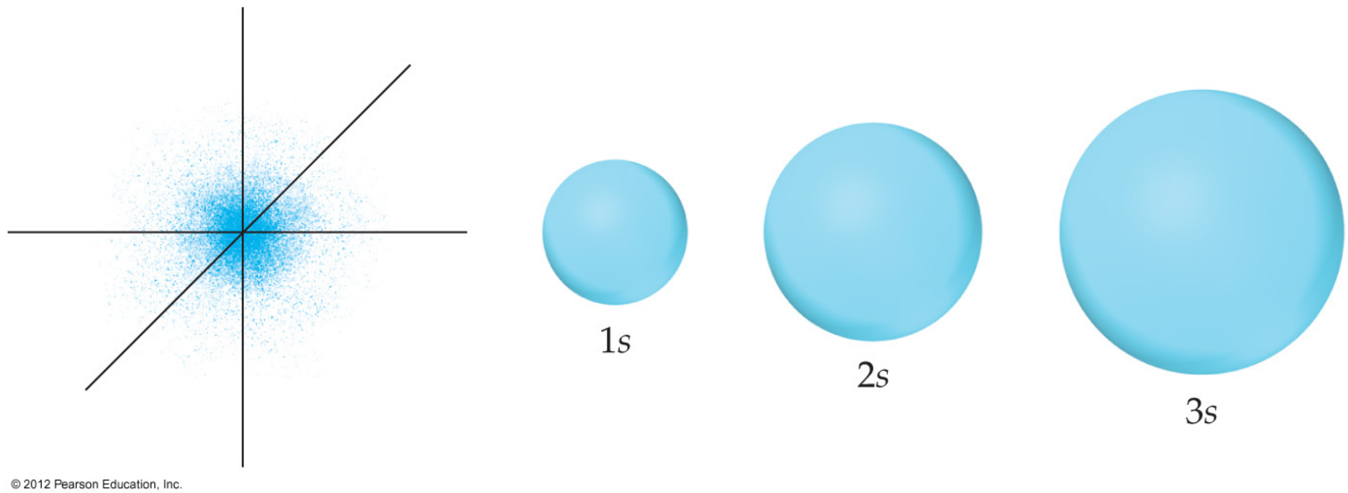
- This quantum number defines the shape of the orbital.
- Allowed values of *l* are integers ranging from 0 to $n - 1$.
- We use letter designations to communicate the different values of *l* and, therefore, the shapes and types of orbitals.

Angular Momentum Quantum Number (l)

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

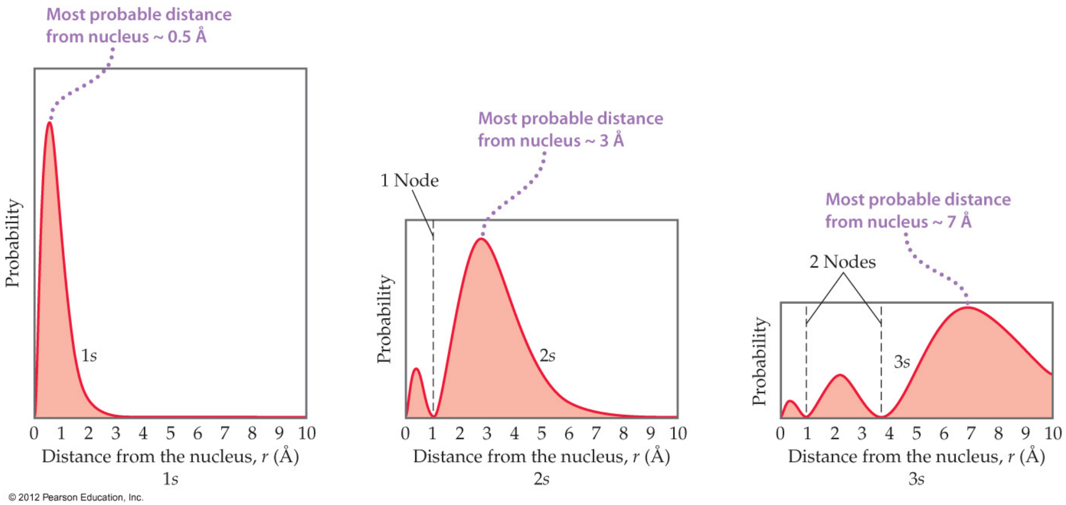


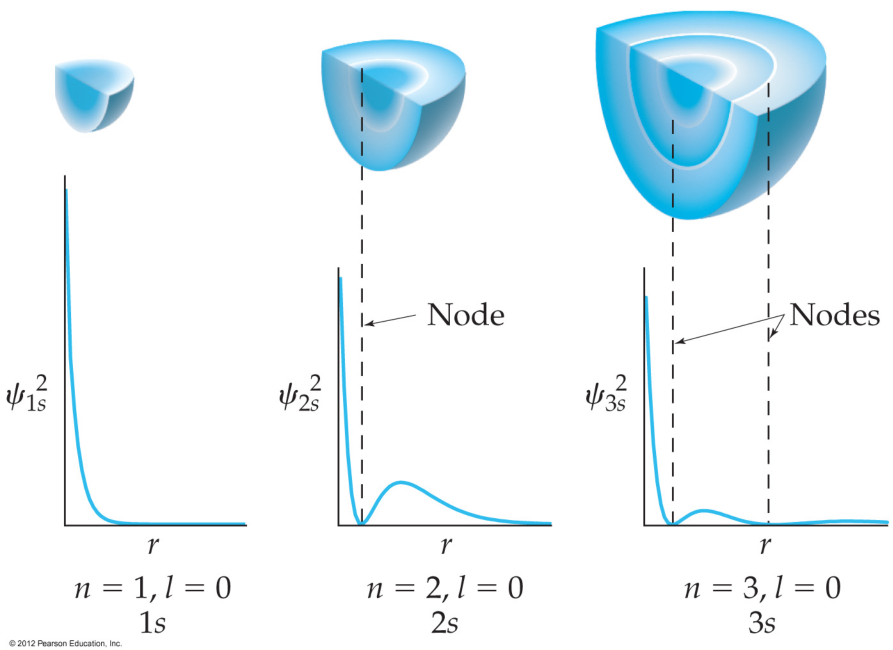
s Orbitals



- 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

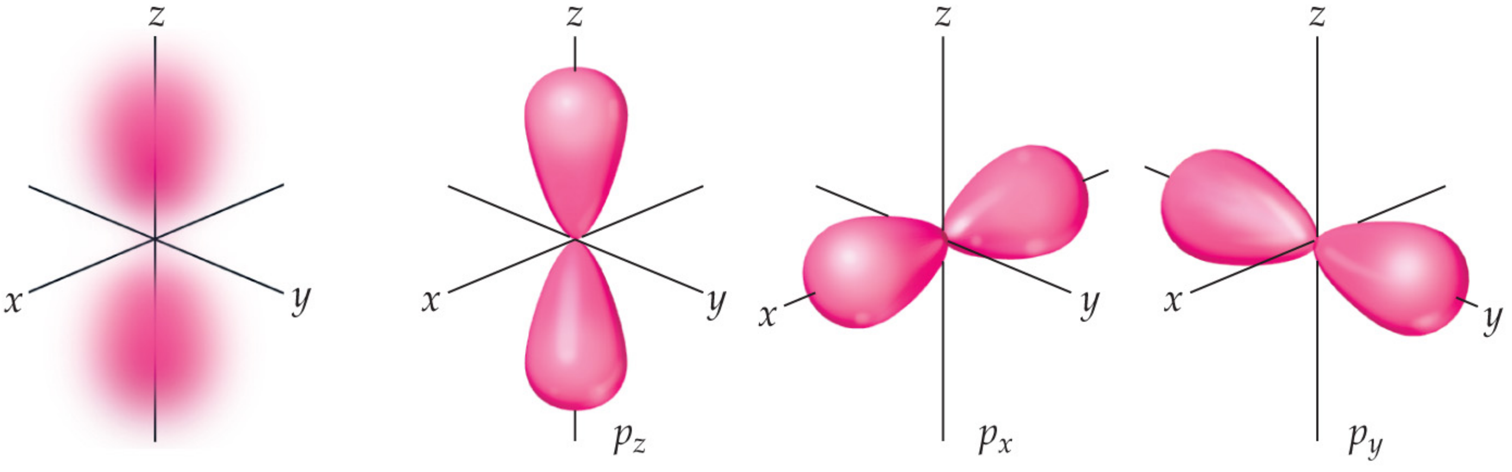




Observing a graph of probabilities of finding an electron versus distance from the nucleus, we see that *s* orbitals possess *n* − 1 **nodes**, or regions where there is 0 probability of finding an electron.

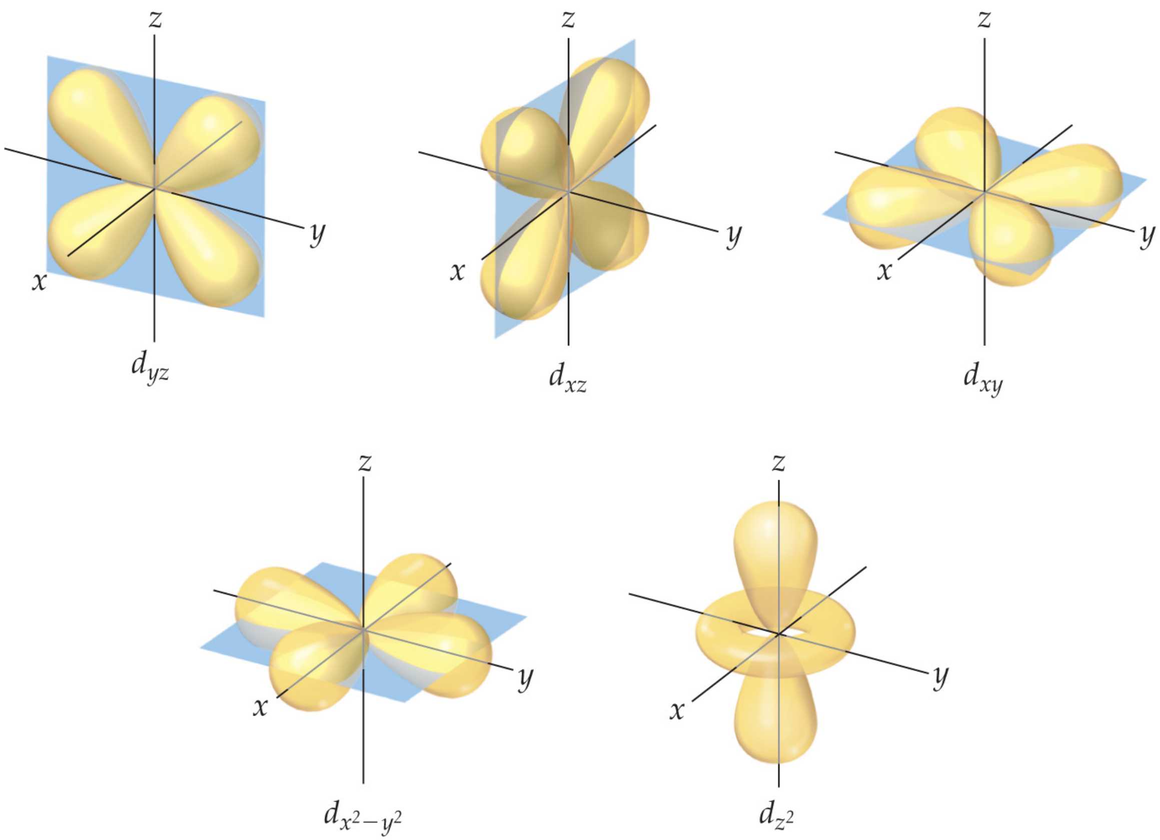
p Orbitals

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

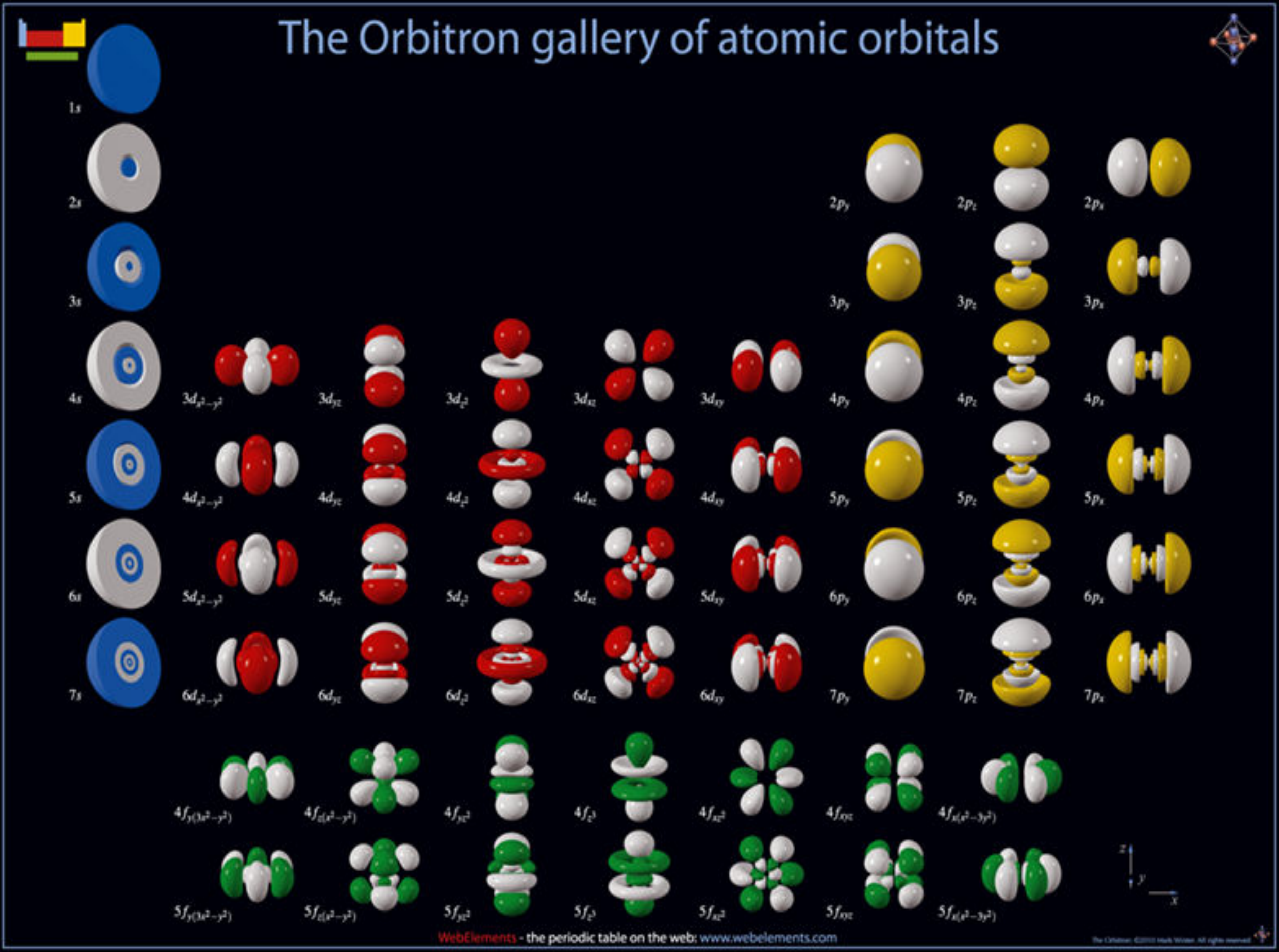


(a) (b)

d Orbitals



- 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.


The Orbitron gallery of atomic orbitals
1s
2s
3s
4s
5s
6s
7s
2py 2pz 2px
3py 3pz 3px
4py 4pz 4px
5py 5pz 5px
6py 6pz 6px
7py 7pz 7px
3dx2−y2 3dyz 3dz2 3dxz 3dxy
4dx2−y2 4dyz 4dz2 4dxz 4dxy
5dx2−y2 5dyz 5dz2 5dxz 5dxy
6dx2−y2 6dyz 6dz2 6dxz 6dxy
4fy(3x2−y2) 4fz(x2−y2) 4fyz2 4fz3 4fxz2 4fxyz 4fx(x2−3y2)
5fy(3x2−y2) 5fz(x2−y2) 5fyz2 5fz3 5fxz2 5fxyz 5fx(x2−3y2)
z
y
x
WebElements - the periodic table on the web: www.webelements.com

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)

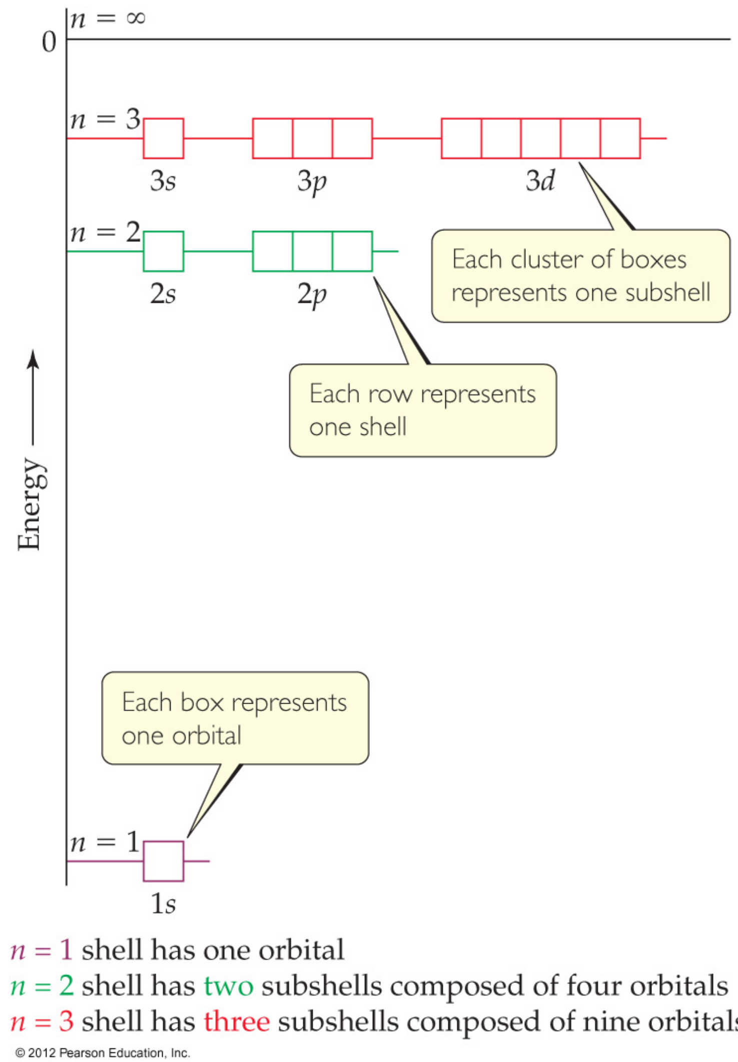
- Orbitals with the same value of *n* form a **shell**.
- Different orbital types within a shell are **subshells**.

TABLE 6.2 • Relationship among Values of *n*, *l*, and m_l through *n* = 4

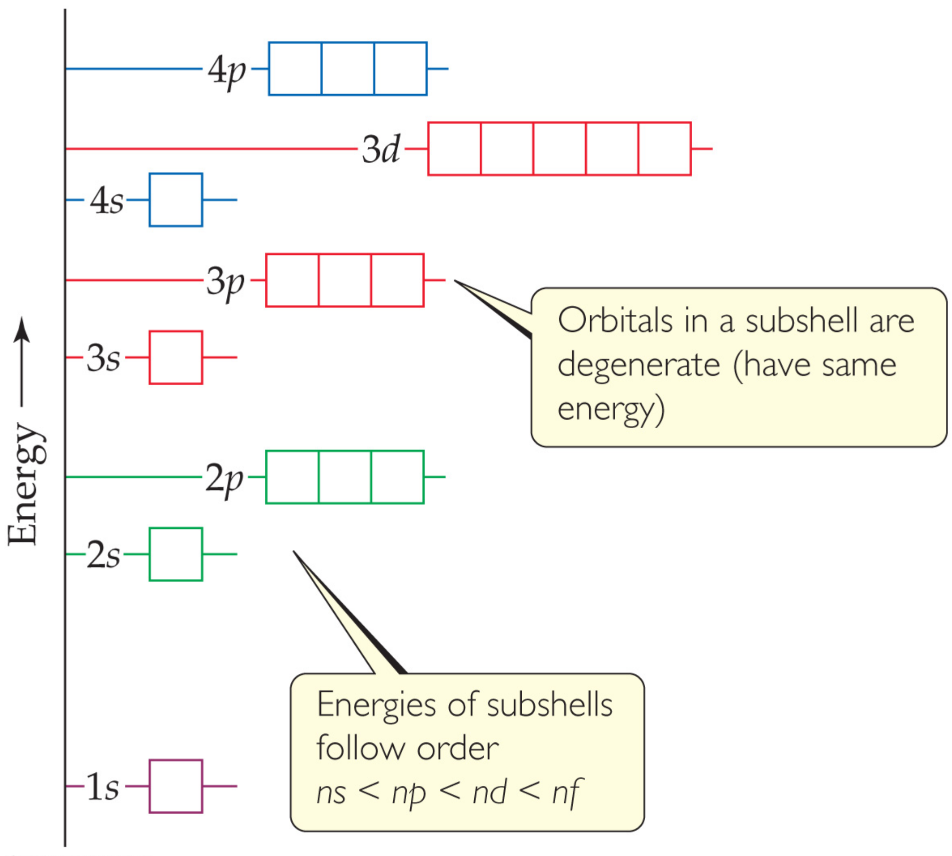
n	Possible Values of *l*	Subshell Designation	Possible Values of m_l	Number of Orbitals in Subshell	Total Number of Orbitals in Shell
1	0	1*s*	0	1	1
2	0	2*s*	0	1	
	1	2*p*	1, 0, −1	3	4
3	0	3*s*	0	1	
	1	3*p*	1, 0, −1	3	
	2	3*d*	2, 1, 0, −1, −2	5	9
4	0	4*s*	0	1	
	1	4*p*	1, 0, −1	3	
	2	4*d*	2, 1, 0, −1,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

Energies of Orbitals

- For a one-electron hydrogen atom, orbitals on the same energy level have the same energy.
- That is, they are **degenerate**.



Energies of Orbitals



- As the number of electrons increases, though, so does the repulsion between them.
- Therefore, in many-electron atoms, orbitals on the same energy level are no longer degenerate.

Electron Configurations

$4p^5$

- This term shows the distribution of all electrons in an atom.
- Each component consists of
  - A number denoting the energy level,

Electron Configurations

$4p^5$

- 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,

Electron Configurations

$4p^5$

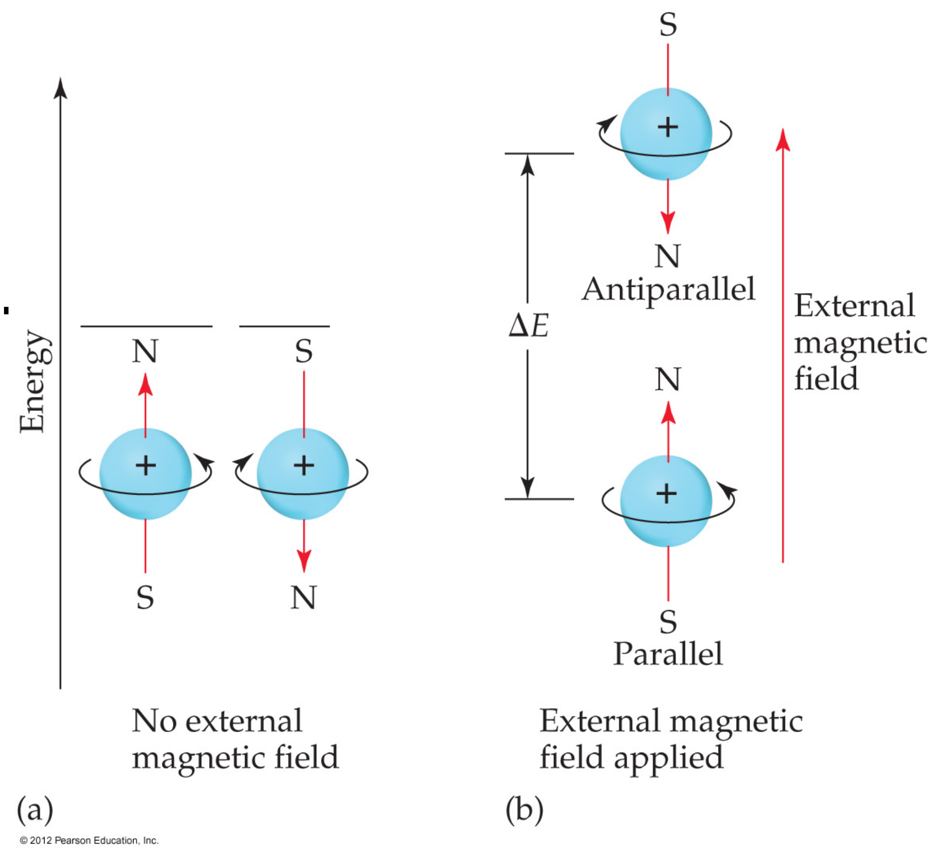
- This term shows the distribution of all electrons in an atom.
- Each component consists of
  - A number denoting the energy level,
  - A letter denoting the type of orbital,
  - A superscript denoting the number of electrons in those orbitals.

Write the electron configuration for phosphorus. How many unpaired electrons does a phosphorus atom possess?

Write the short-hand electron configuration for Co.

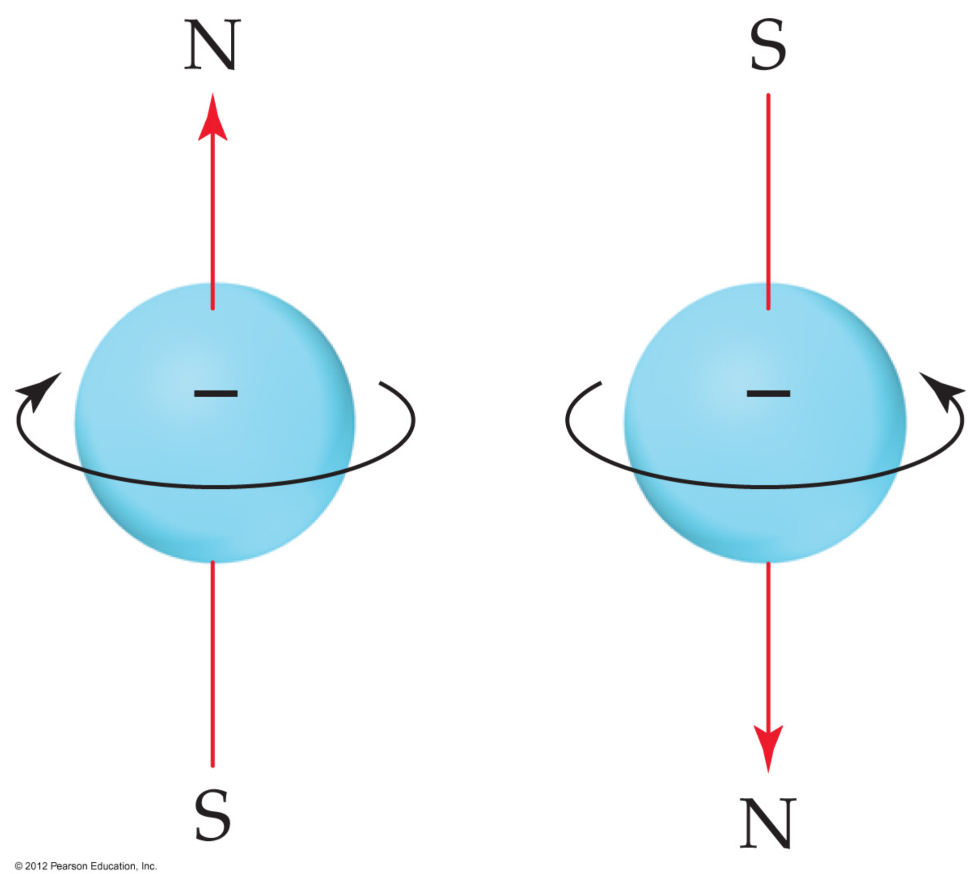
Pauli Exclusion Principle

- 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.



Spin Quantum Number, m_s

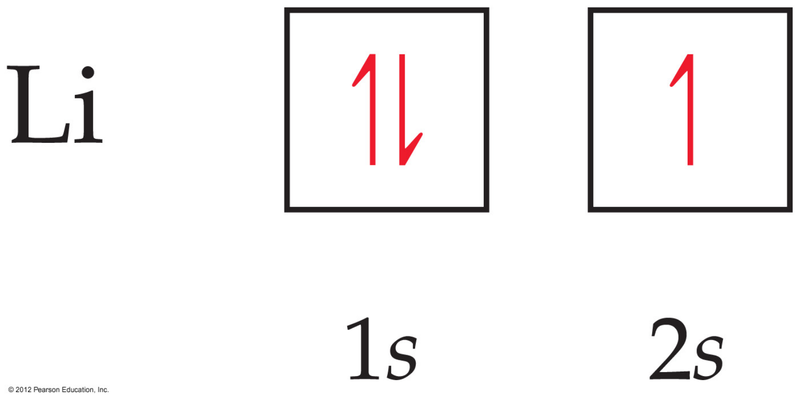
- This led to a fourth quantum number, the spin quantum number, m_s.
- The spin quantum number has only 2 allowed values: +1/2 and −1/2.



Electronic Structure of Atoms

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.



Hund's Rule

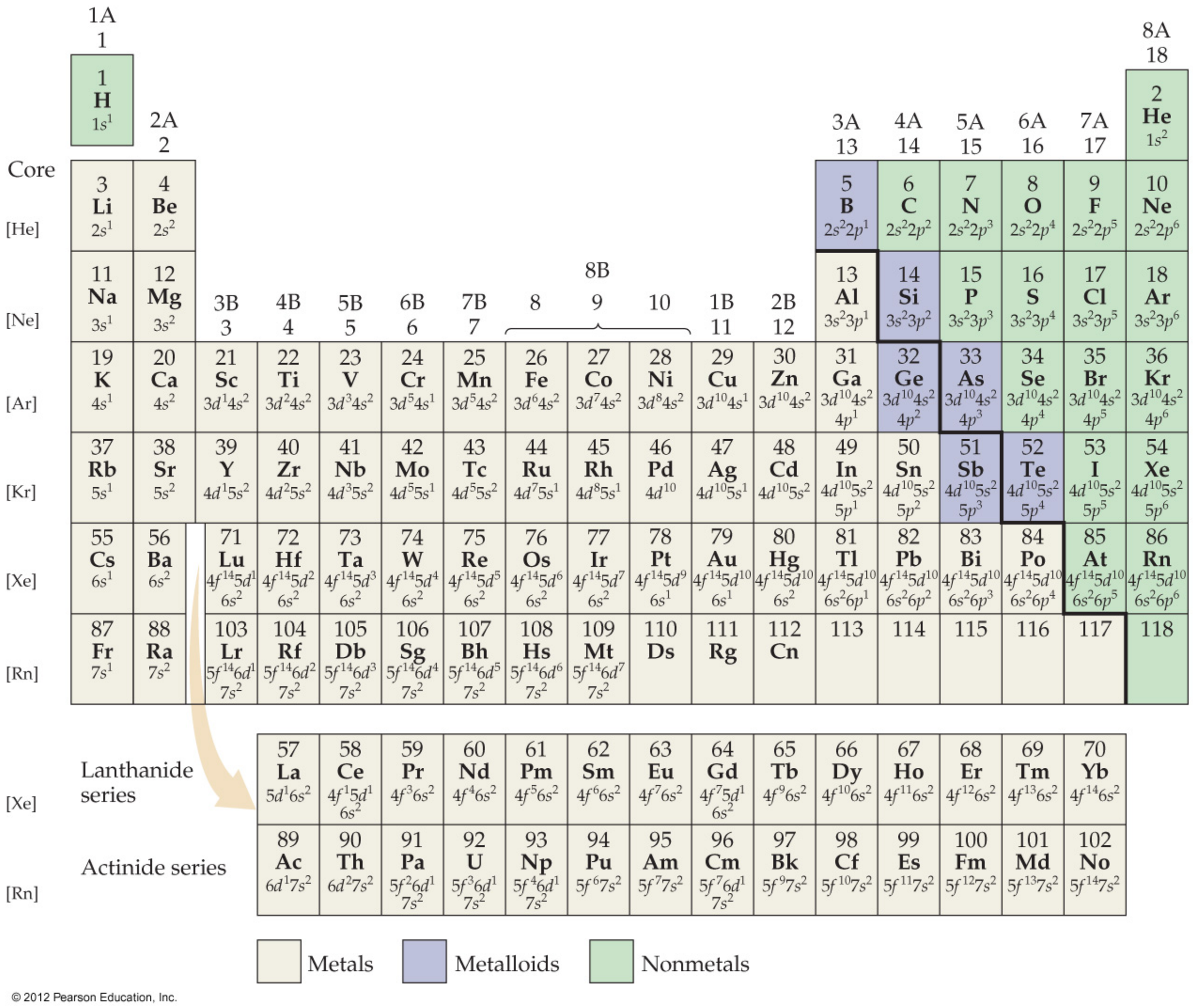
TABLE 6.3 • Electron Configurations of Several Lighter Elements

Element	Total Electrons	Orbital Diagram				Electron Configuration
		$1s$	$2s$	$2p$	$3s$	
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	↑↓	↑↓	↑↓ | ↑↓ | ↑↓	↑	$1s^2 2s^2 2p^6 3s^1$

Put electrons in the orbitals in order.

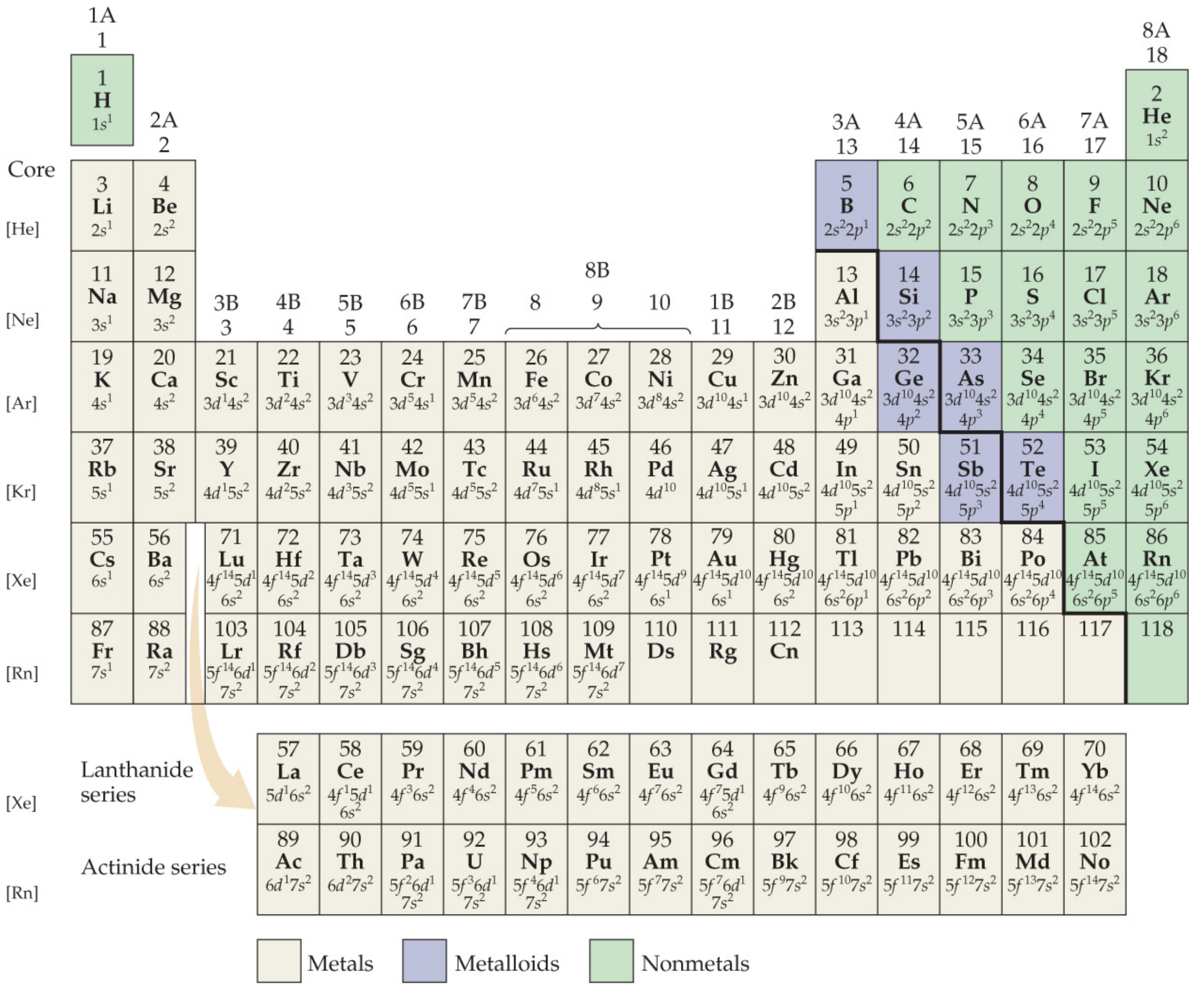
Do not pair electrons until you have to

Some Anomalies



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 copper is

[Ar] $4s^1\ 3d^5$

rather than the expected

[Ar] $4s^2\ 3d^4$.