

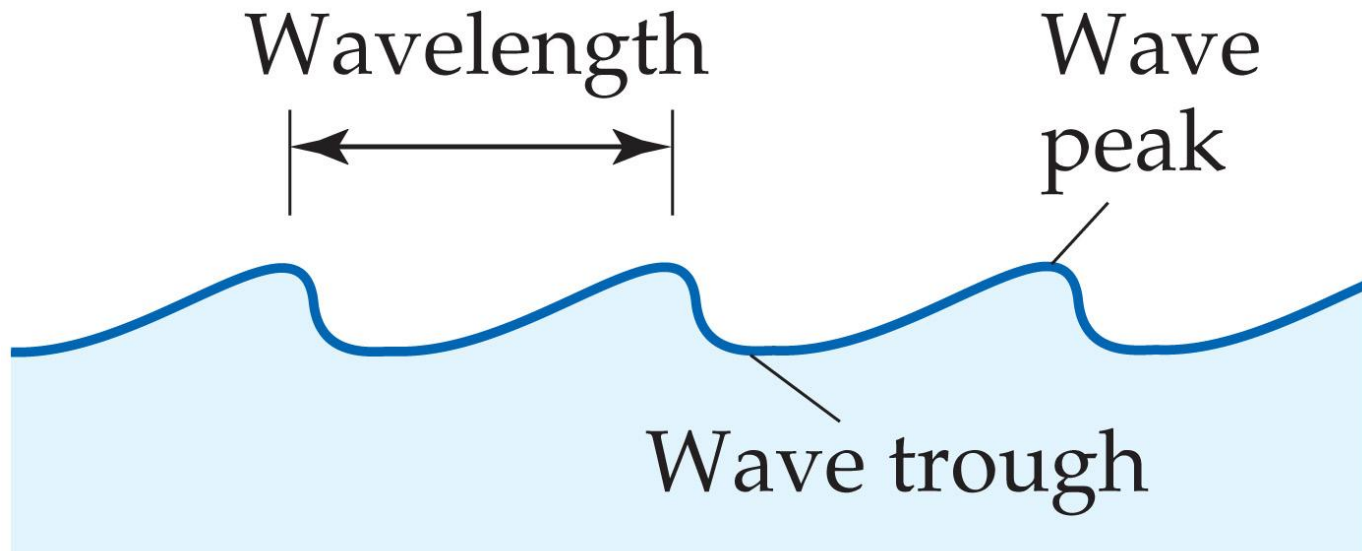
# Lecture Presentation

## Chapter 6

# Electronic Structure of Atoms

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

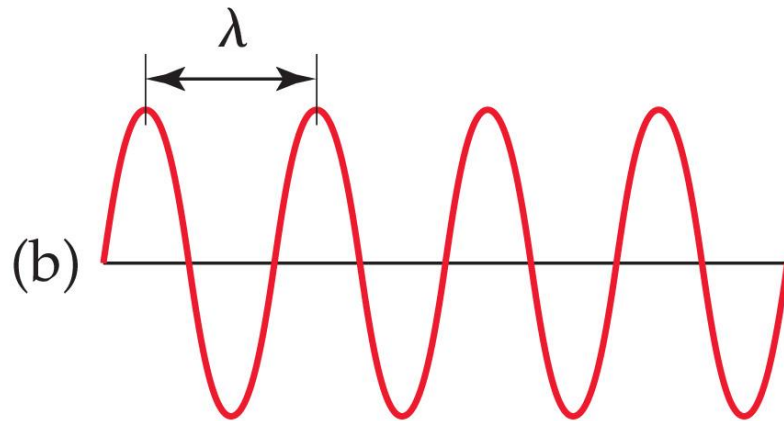
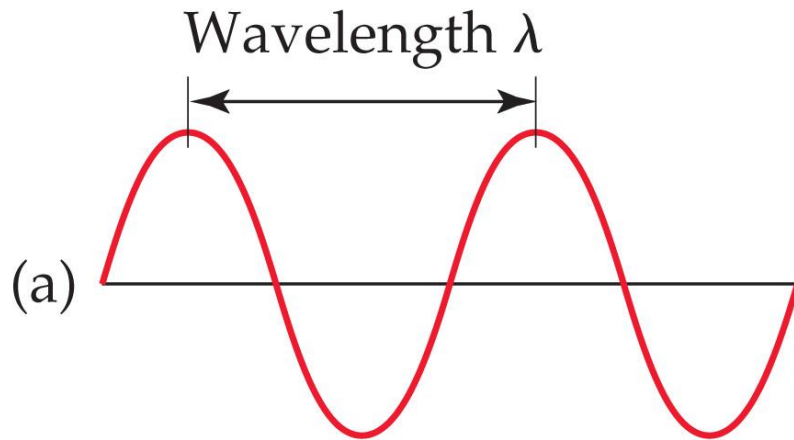
# Waves



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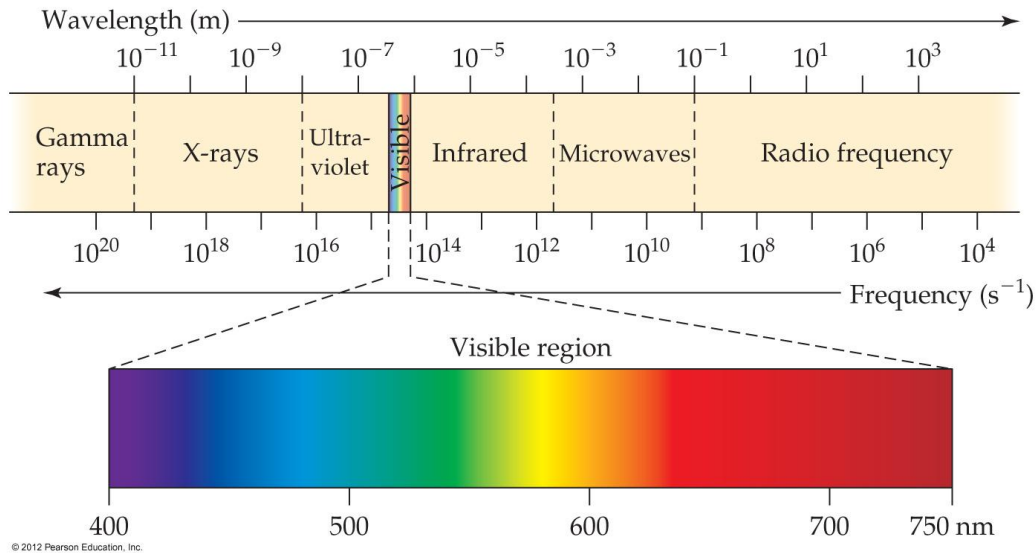
- To understand the electronic structure of atoms, one must understand the nature of electromagnetic radiation.
- The distance between corresponding points on adjacent waves is the **wavelength ( $\lambda$ )**.

# Waves



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

# Electromagnetic Radiation



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

$$c = \lambda \nu$$

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# The Nature of Energy



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The wave nature of light does not explain how an object can glow when its temperature increases.

# The Nature of Energy



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

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

Max Planck explained it by assuming that energy comes in packets called **quanta**.

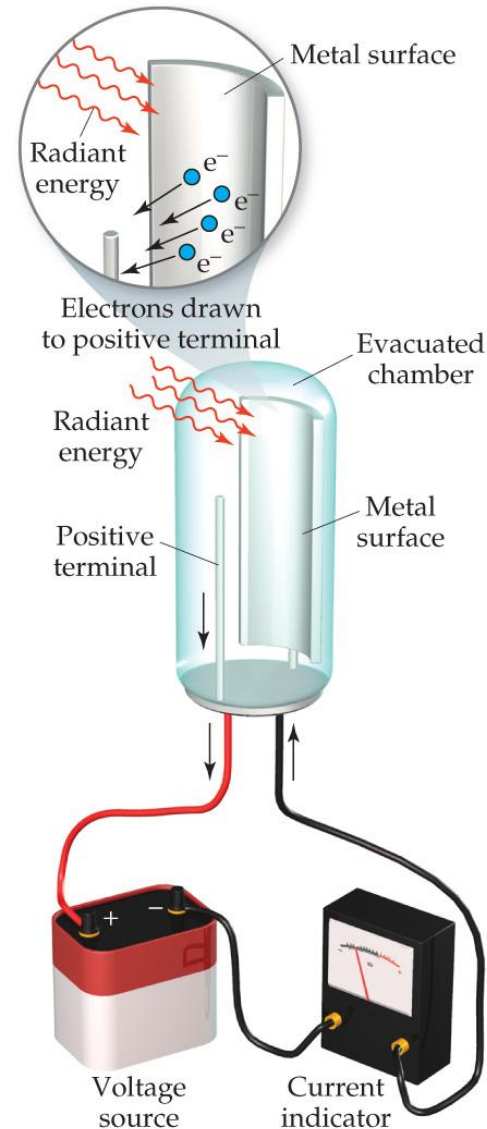


# The Nature of Energy

- Einstein used this assumption to explain the photoelectric effect.
- He concluded that energy is proportional to frequency:

$$E = h\nu$$

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



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# The Nature of Energy

- Therefore, if one knows the wavelength of light, one can calculate the energy in one photon, or packet, of that light:

$$c = \lambda \nu$$

$$E = h\nu$$



Hydrogen (H)

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# The Nature of Energy

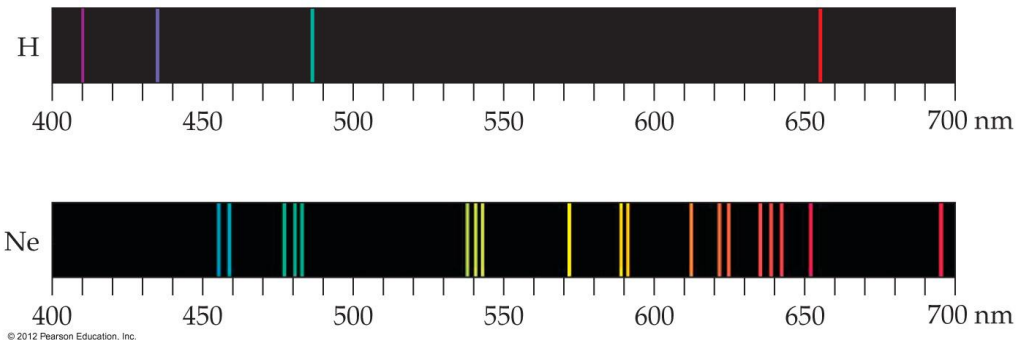
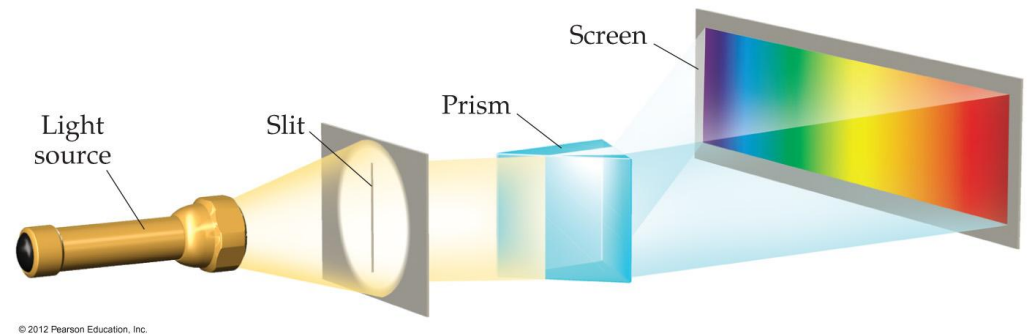


Neon (Ne)

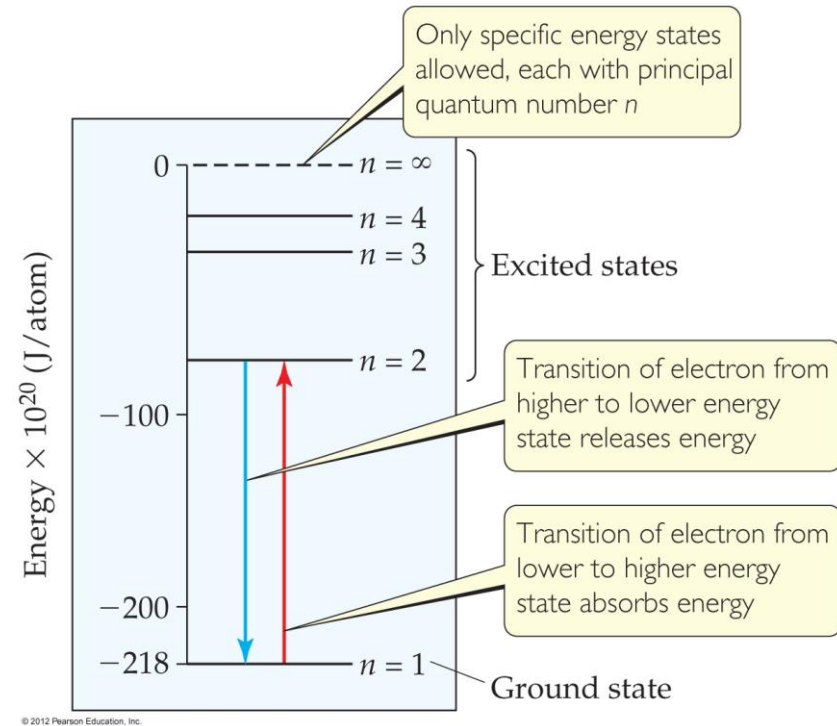
Another mystery in the early twentieth century involved the emission spectra observed from energy emitted by atoms and molecules.

# 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.



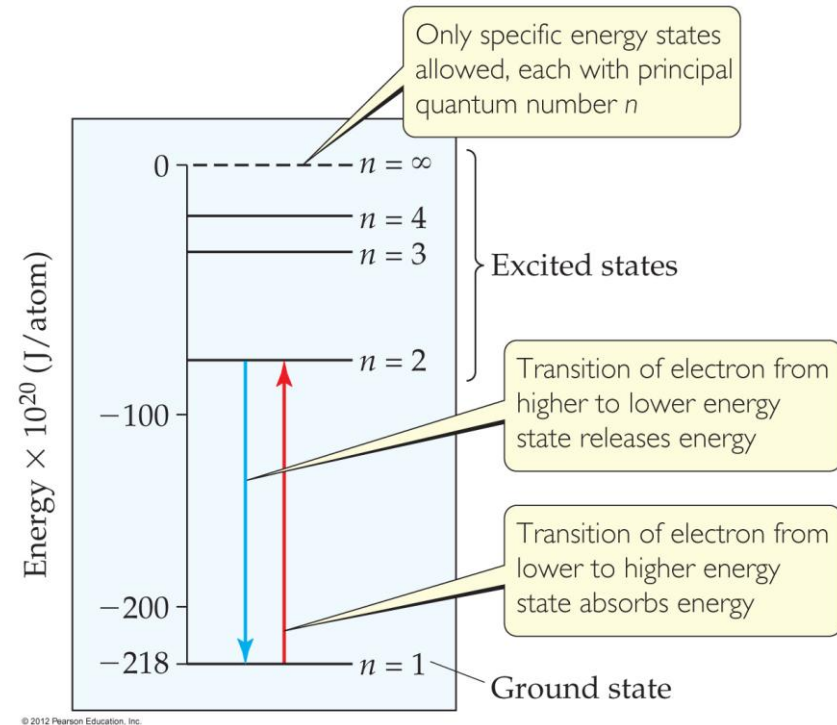
# The Nature of Energy



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

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

# The Nature of Energy



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

2. Electrons in permitted orbits have specific, "allowed" energies; these energies will not be radiated from the atom.

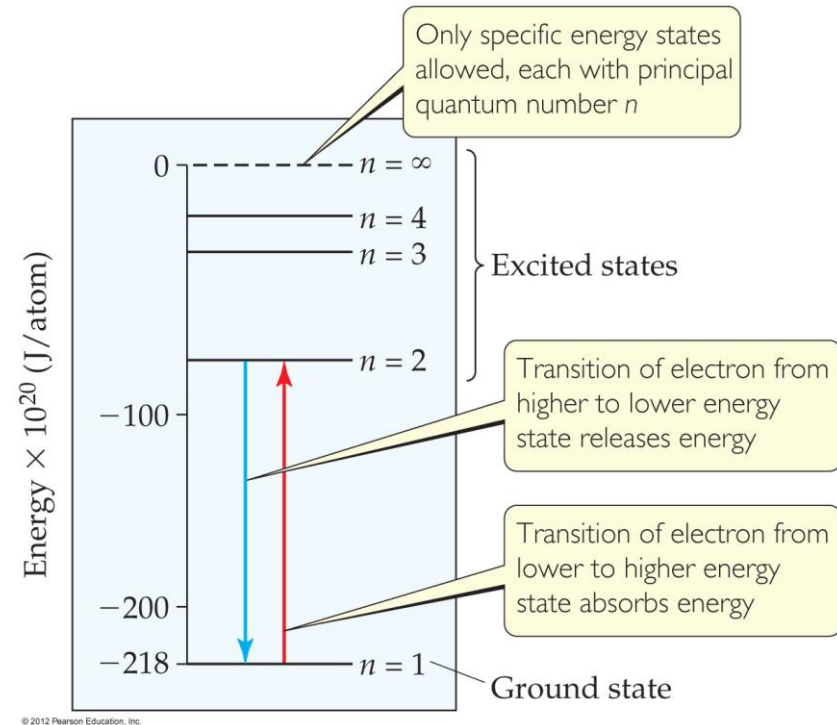
# The Nature of Energy

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

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

$$E = h\nu$$

Electronic  
Structure  
of Atoms

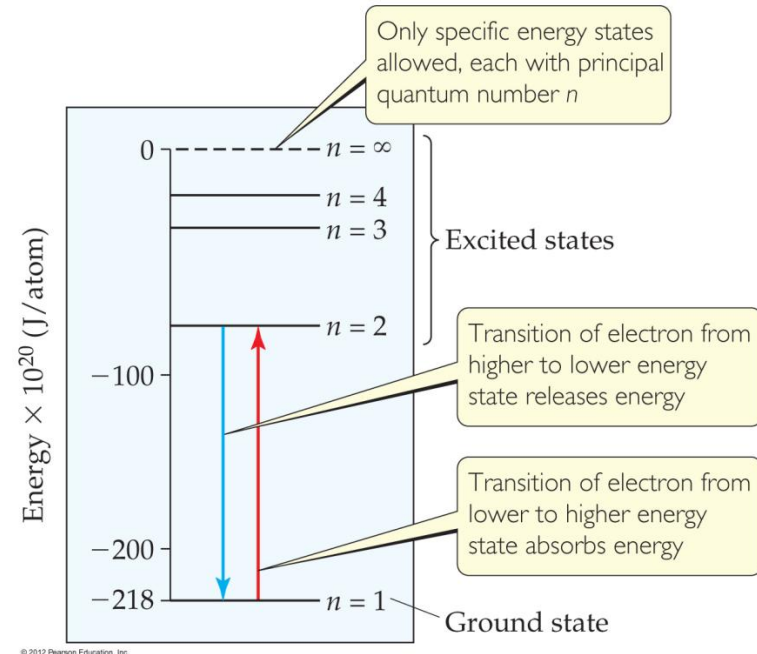


# The Nature of Energy

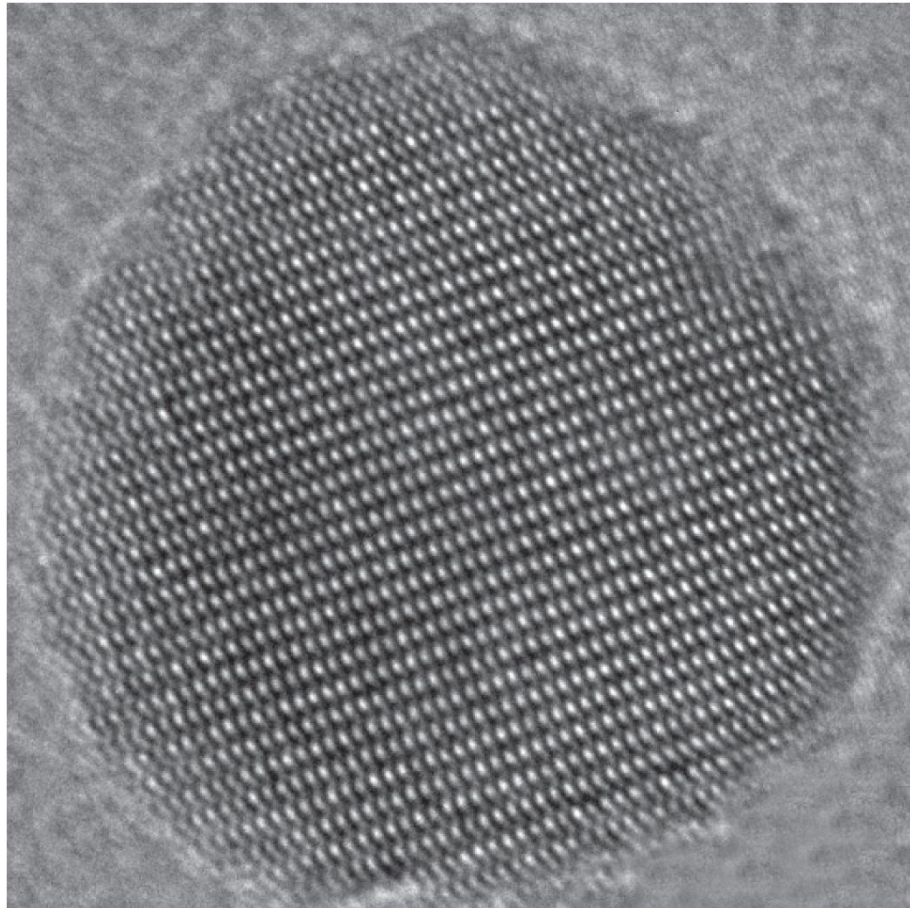
The energy absorbed or emitted from the process of electron promotion or demotion can be calculated by the equation:

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

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.



# The Wave Nature of Matter



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- 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

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

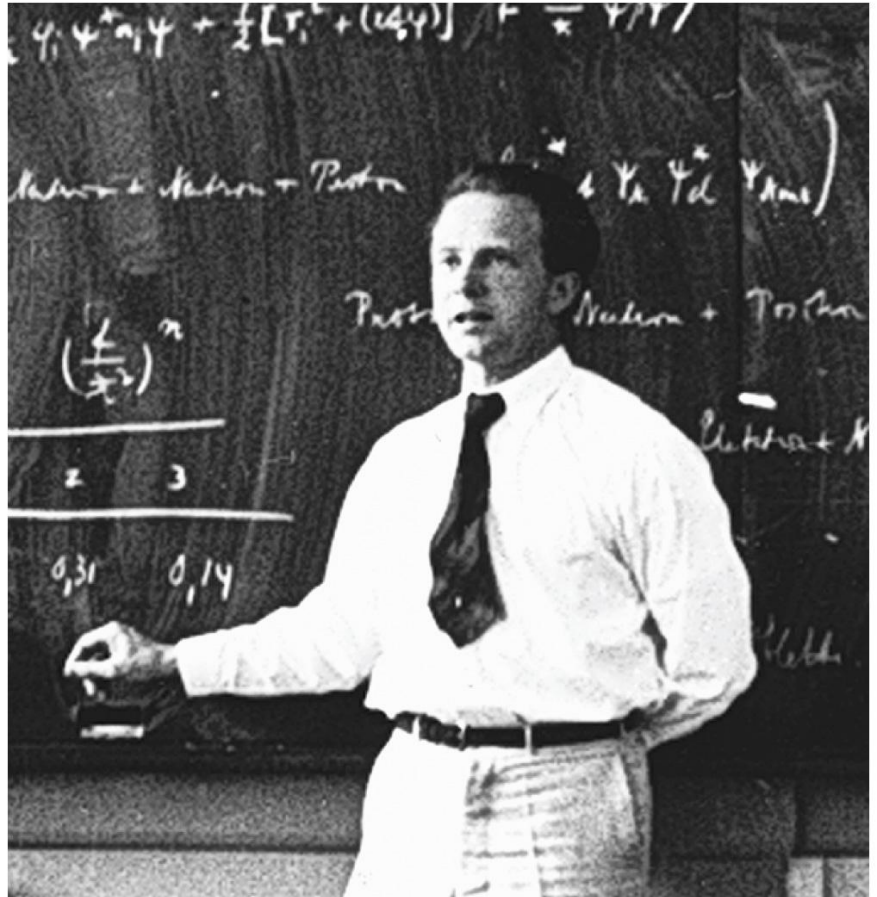
Electronic  
Structure  
of Atoms



# The Uncertainty Principle

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

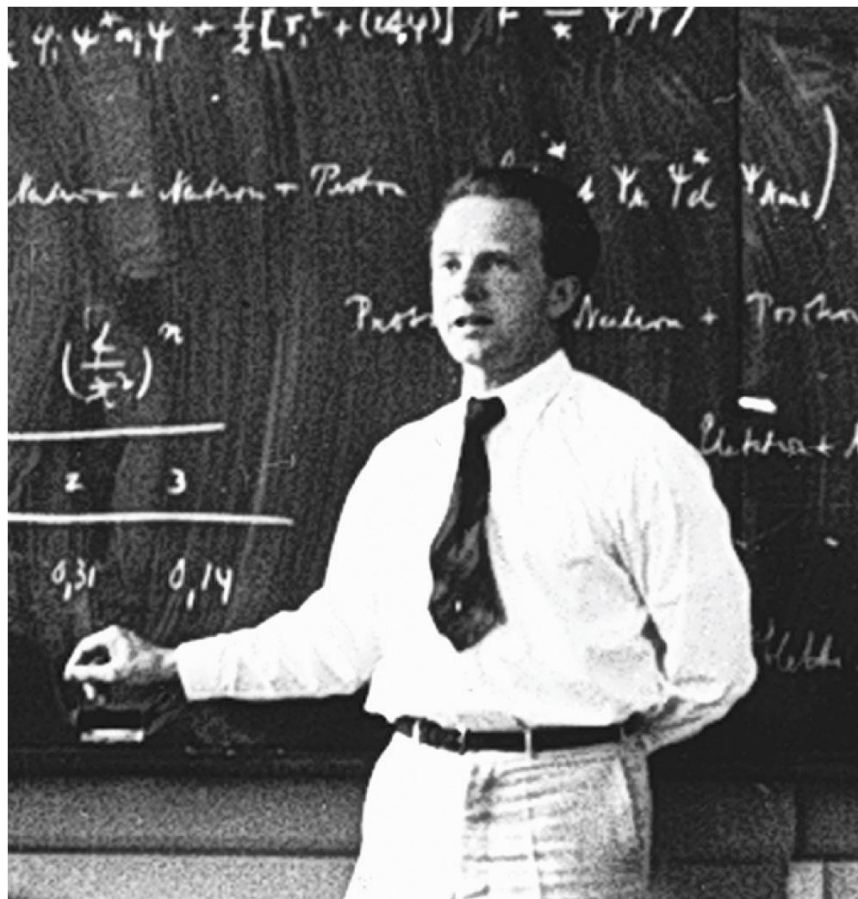
$$(\Delta x) (\Delta mv) \geq \frac{h}{4\pi}$$



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# The Uncertainty Principle

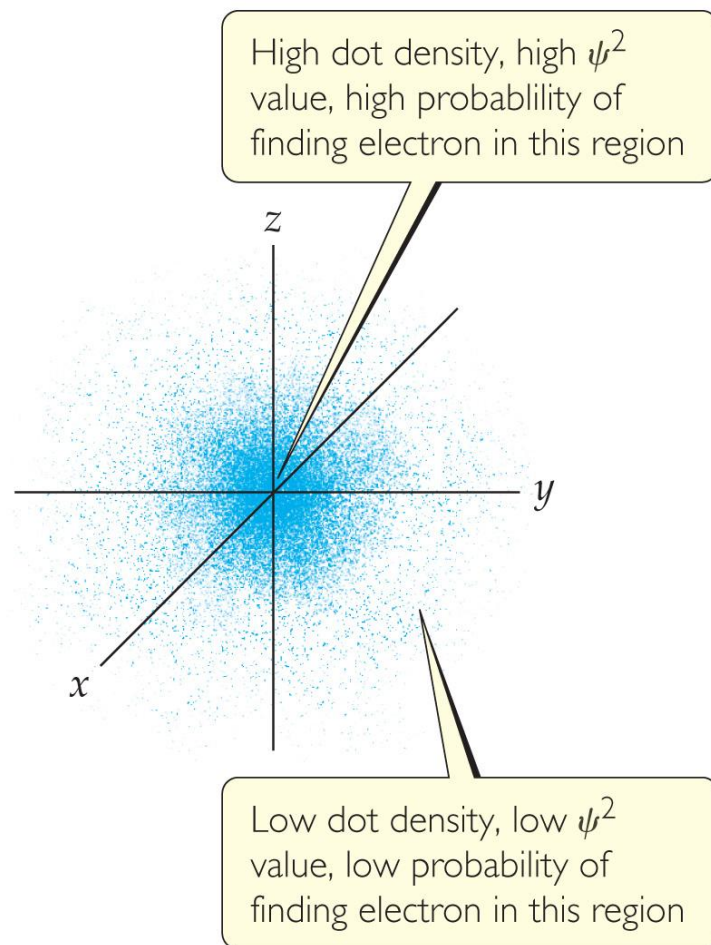
In many cases, our uncertainty of the whereabouts of an electron is greater than the size of the atom itself!



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# Quantum Mechanics

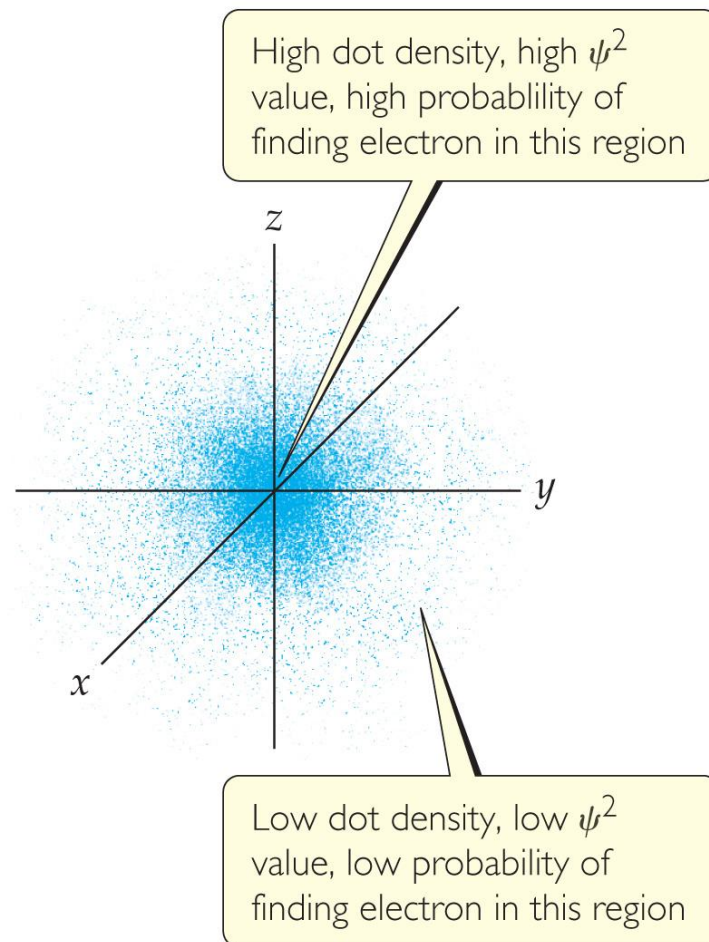
- Erwin Schrödinger developed a mathematical treatment into which both the wave and particle nature of matter could be incorporated.
- This is known as **quantum mechanics**.



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# Quantum Mechanics

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



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# 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  $\geq 1$ .

# 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	$s$	$p$	$d$	$f$

# 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.

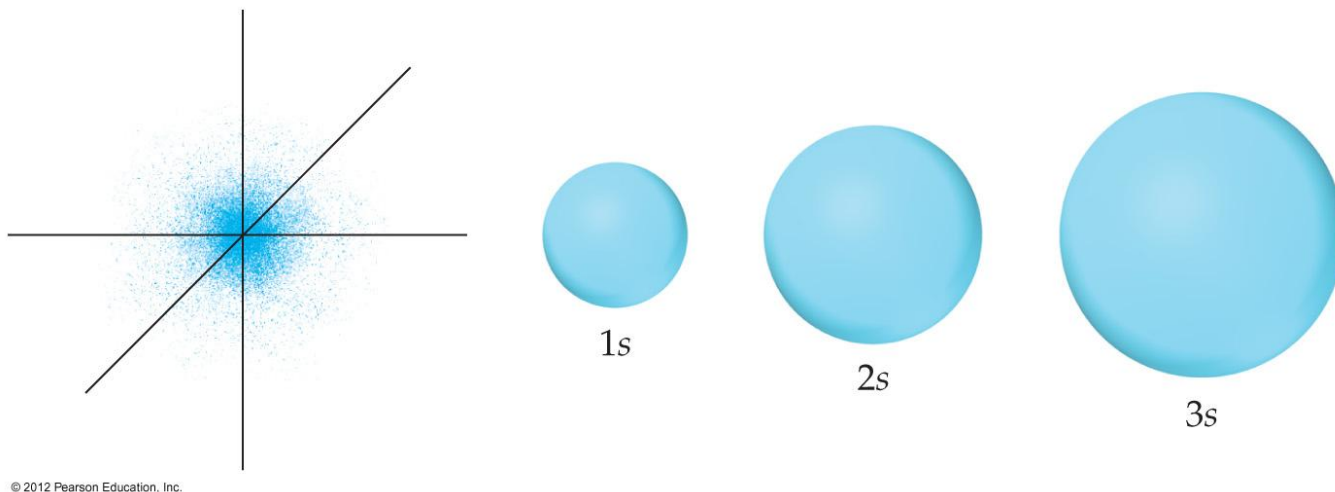
# Magnetic Quantum Number ( $m_l$ )

- 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  $n = 4$

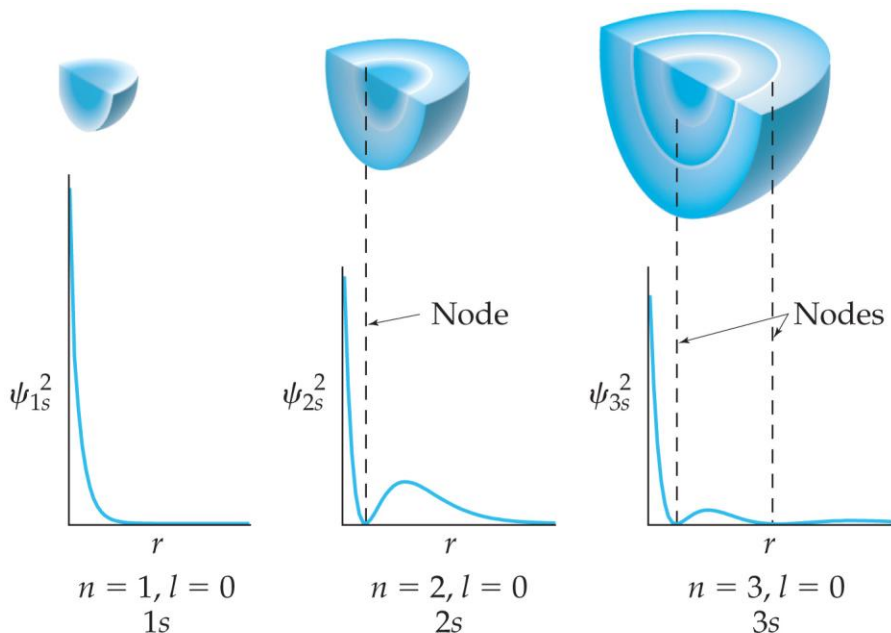
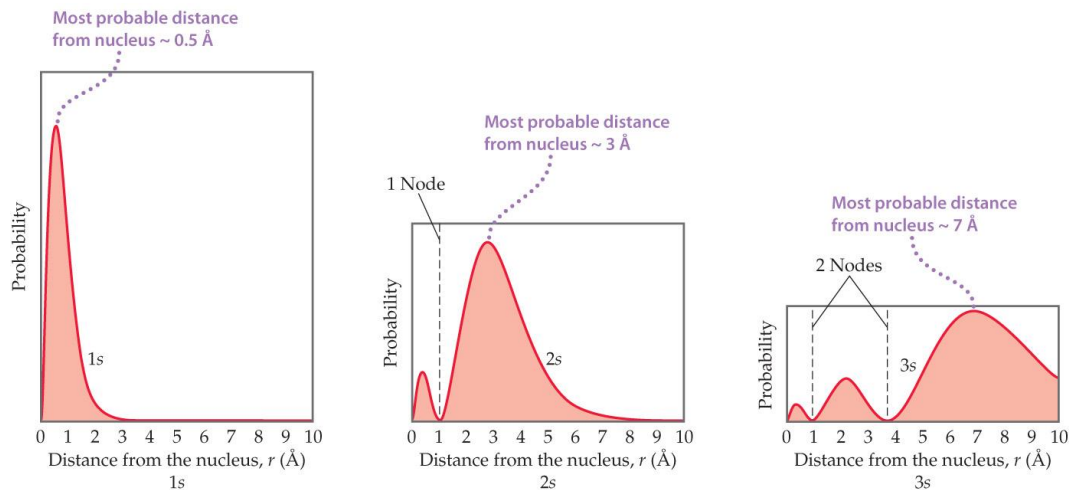
$n$	Possible Values of $l$	Subshell Designation	Possible Values of $m_l$	Number of Orbitals in Subshell	Total Number of Orbitals in Shell
1	0	1s	0	1	1
2	0	2s	0	1	4
	1	2p	1, 0, -1	3	
3	0	3s	0	1	9
	1	3p	1, 0, -1	3	
	2	3d	2, 1, 0, -1, -2	5	
4	0	4s	0	1	16
	1	4p	1, 0, -1	3	
	2	4d	2, 1, 0, -1, -2	5	
	3	4f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

# 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  $n$ .

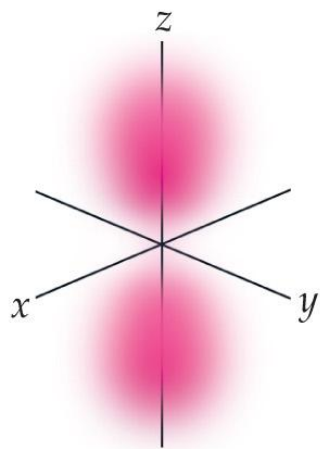
# s Orbitals



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.

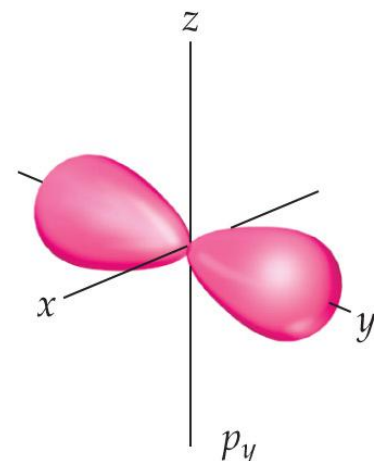
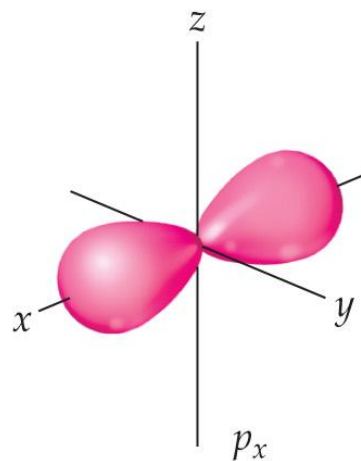
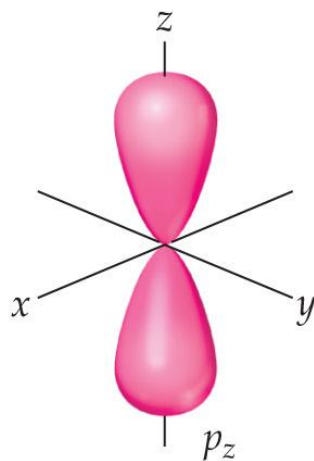
# $p$ Orbitals

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



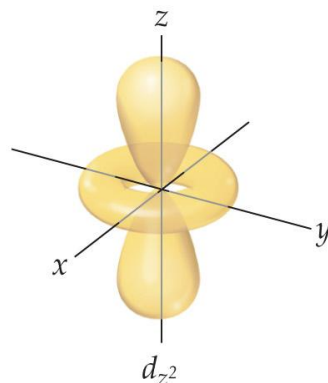
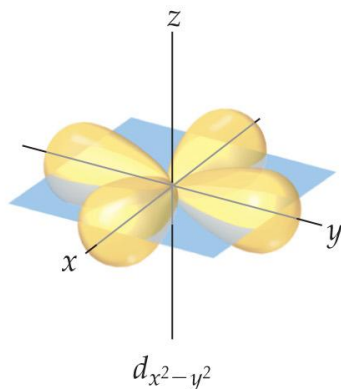
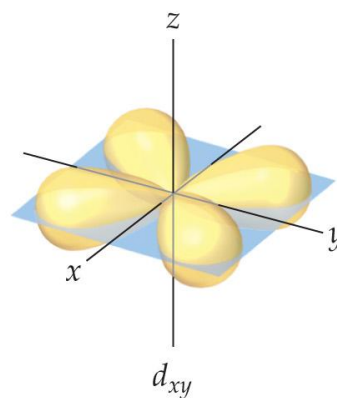
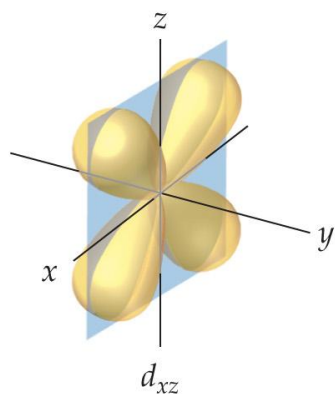
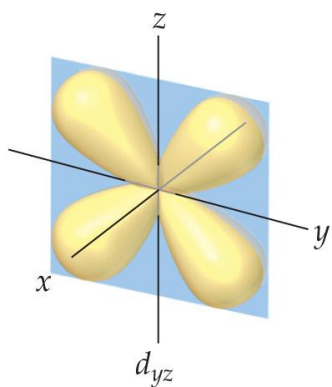
(a)

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(b)

# *d* Orbitals

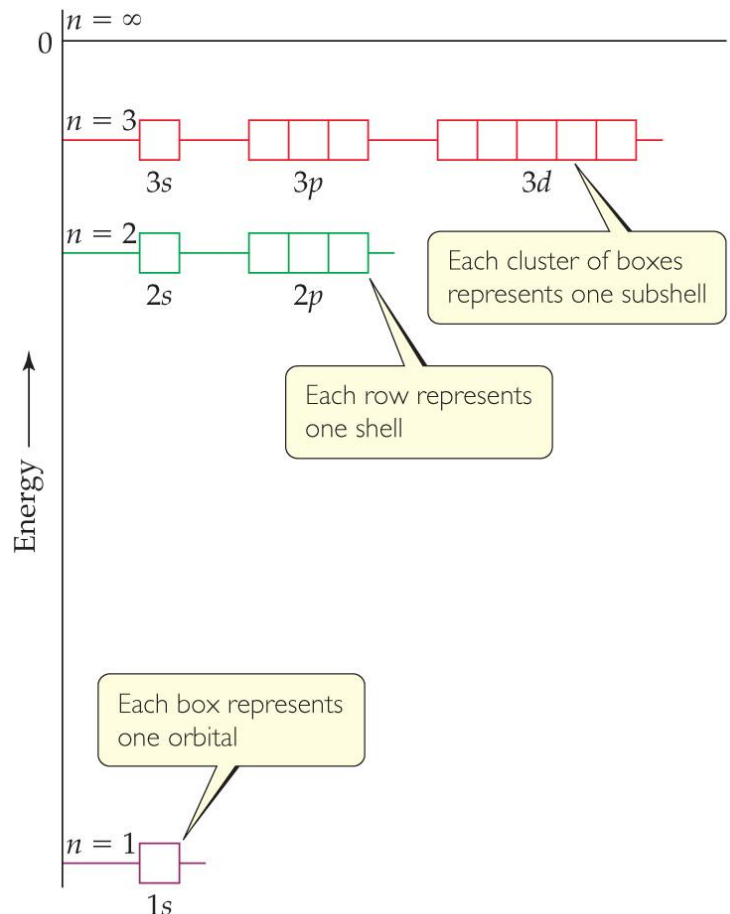


- The value of  $l$  for a  $d$  orbital is 2.
- Four of the five  $d$  orbitals have 4 lobes; the other resembles a  $p$  orbital with a doughnut around the center.



# Energies of Orbitals

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



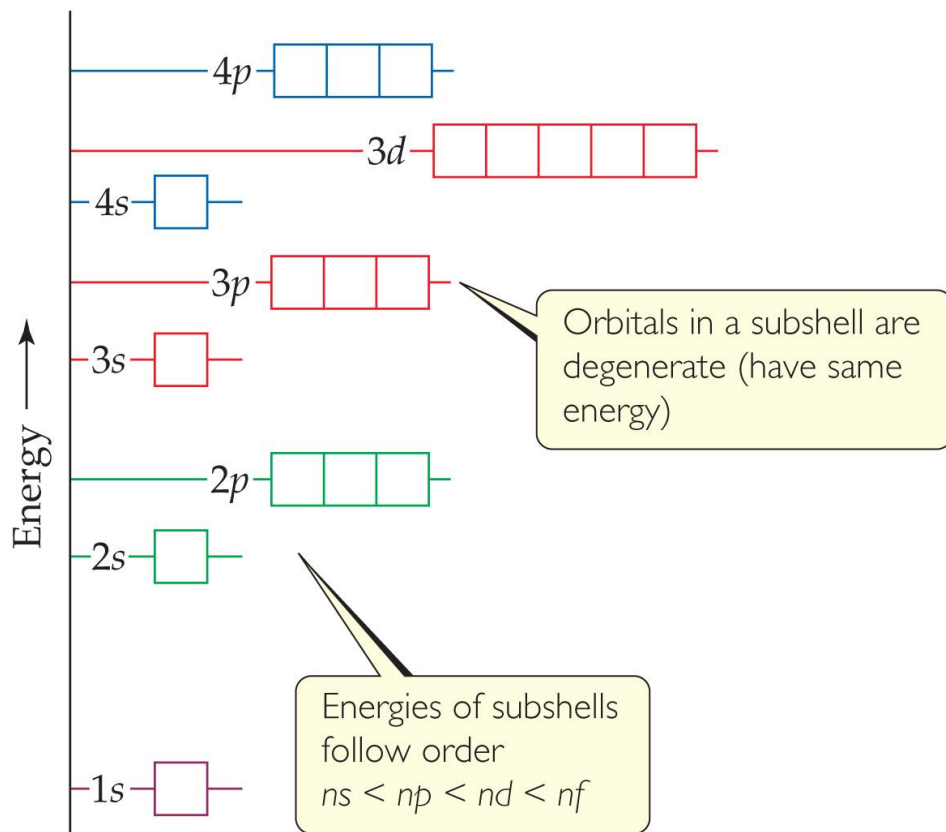
$n = 1$  shell has one orbital

$n = 2$  shell has two subshells composed of four orbitals

$n = 3$  shell has three subshells composed of nine orbitals

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# Energies of Orbitals

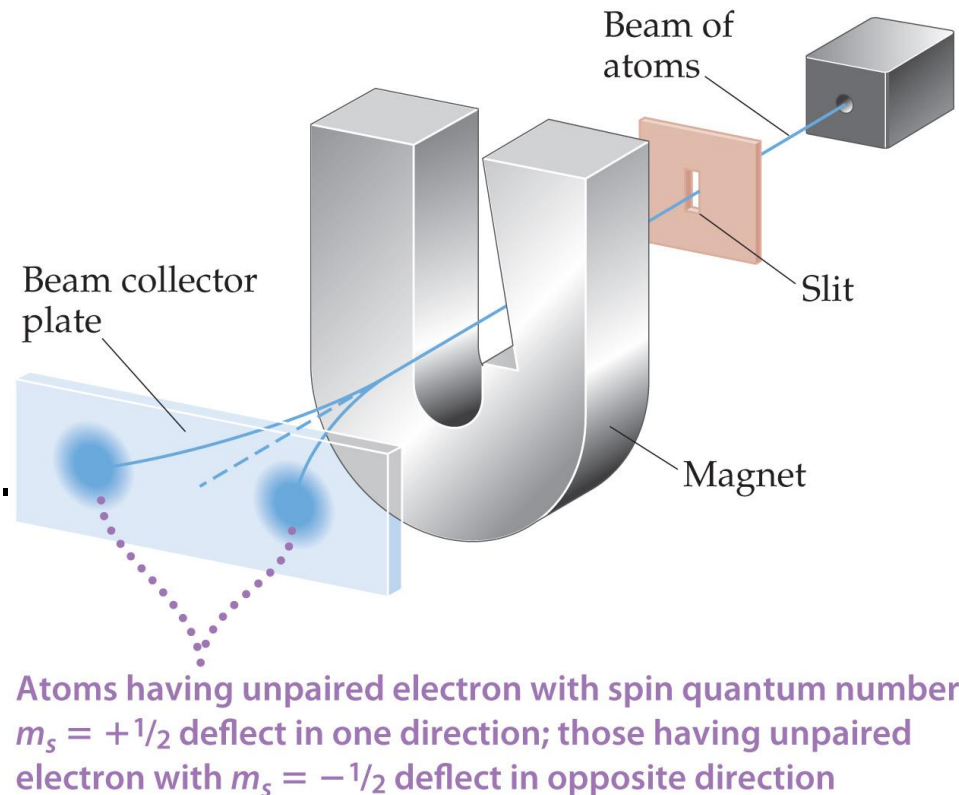


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- As the number of electrons increases, though, so does the repulsion between them.
- Therefore, in many-electron atoms, orbitals on the same energy level are no longer degenerate.

# Spin Quantum Number, $m_s$

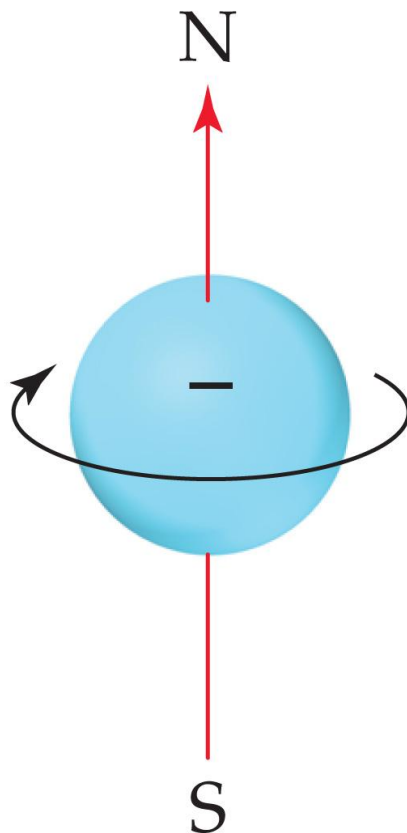
- In the 1920s, it was discovered that two electrons in the same orbital do not have exactly the same energy.
- The “spin” of an electron describes its magnetic field, which affects its energy.



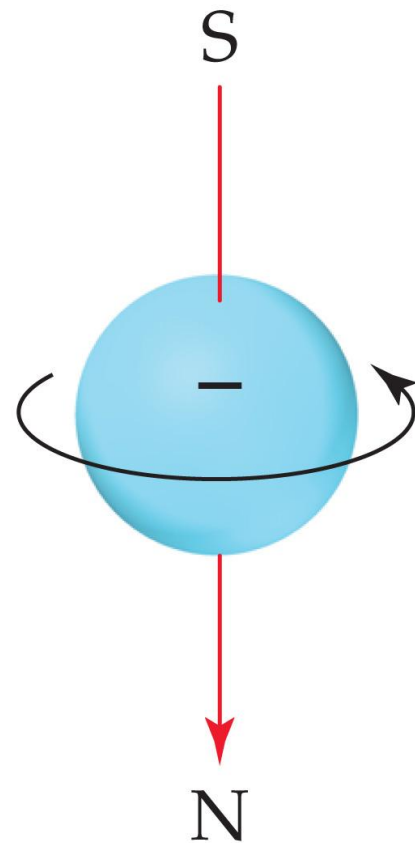
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# Spin Quantum Number, $m_s$

- 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  $-1/2$ .

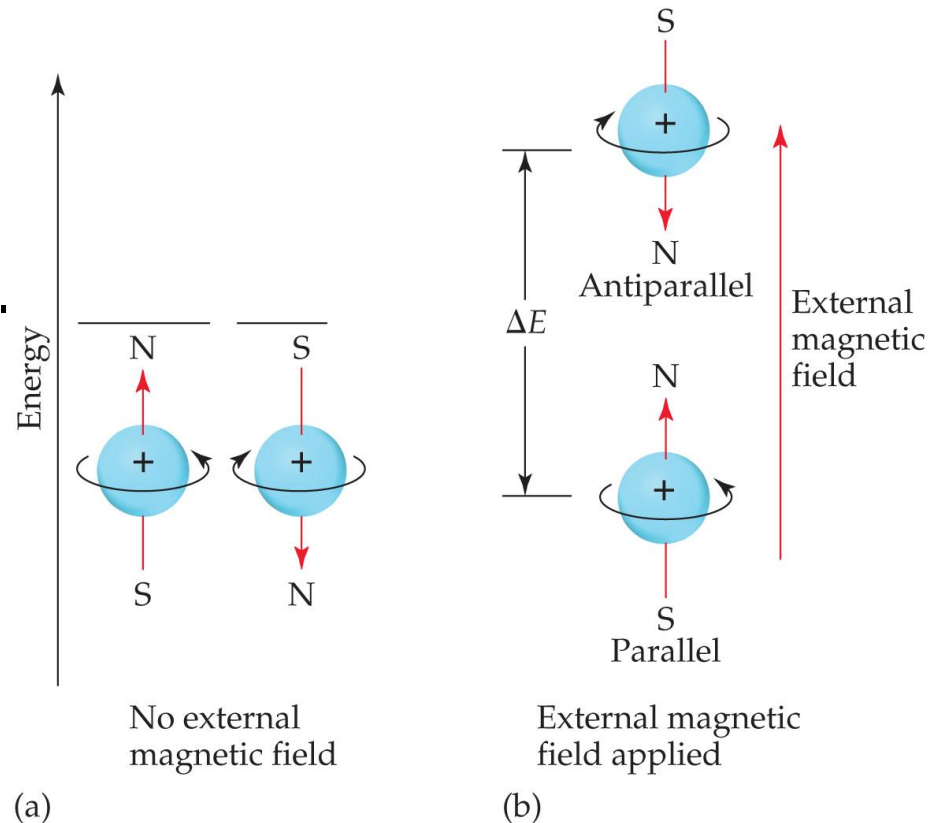


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# Pauli Exclusion Principle

- 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.



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# Electron Configurations



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

# Electron Configurations



- 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

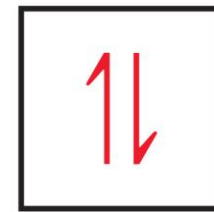


- This term shows the distribution of all electrons in an atom.
- Each component consists of
  - A number denoting the energy level,
  - A letter denoting the type of orbital,
  - A superscript denoting the number of electrons in those orbitals.

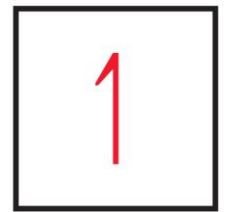
# Orbital Diagrams

- 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.

Li



1s



2s

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# Hund's Rule

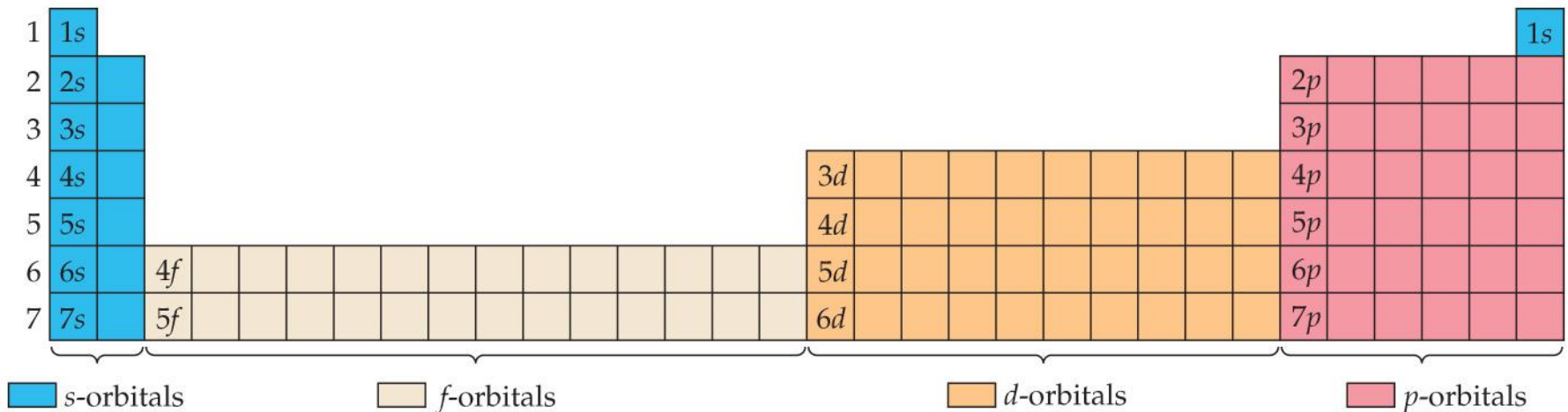
**TABLE 6.3 • Electron Configurations of Several Lighter Elements**

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

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

# 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

[illegible]

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

# Some Anomalies

	1A 1																	8A 18
	1 H 1s <sup>1</sup>	2A 2											3A 13	4A 14	5A 15	6A 16	7A 17	2 He 1s <sup>2</sup>
Core	3 Li 2s <sup>1</sup>	4 Be 2s <sup>2</sup>											5 B 2s <sup>2</sup> 2p <sup>1</sup>	6 C 2s <sup>2</sup> 2p <sup>2</sup>	7 N 2s <sup>2</sup> 2p <sup>3</sup>	8 O 2s <sup>2</sup> 2p <sup>4</sup>	9 F 2s <sup>2</sup> 2p <sup>5</sup>	10 Ne 2s <sup>2</sup> 2p <sup>6</sup>
[He]																		
	11 Na 3s <sup>1</sup>	12 Mg 3s <sup>2</sup>	3B 3	4B 4	5B 5	6B 6	7B 7	8B 8 9 10			1B 11	2B 12	13 Al 3s <sup>2</sup> 3p <sup>1</sup>	14 Si 3s <sup>2</sup> 3p <sup>2</sup>	15 P 3s <sup>2</sup> 3p <sup>3</sup>	16 S 3s <sup>2</sup> 3p <sup>4</sup>	17 Cl 3s <sup>2</sup> 3p <sup>5</sup>	18 Ar 3s <sup>2</sup> 3p <sup>6</sup>
[Ne]																		
	19 K 4s <sup>1</sup>	20 Ca 4s <sup>2</sup>	21 Sc 3d <sup>1</sup> 4s <sup>2</sup>	22 Ti 3d <sup>2</sup> 4s <sup>2</sup>	23 V 3d <sup>3</sup> 4s <sup>2</sup>	24 Cr 3d <sup>5</sup> 4s <sup>1</sup>	25 Mn 3d <sup>5</sup> 4s <sup>2</sup>	26 Fe 3d <sup>6</sup> 4s <sup>2</sup>	27 Co 3d <sup>7</sup> 4s <sup>2</sup>	28 Ni 3d <sup>8</sup> 4s <sup>2</sup>	29 Cu 3d <sup>10</sup> 4s <sup>1</sup>	30 Zn 3d <sup>10</sup> 4s <sup>2</sup>	31 Ga 4s <sup>2</sup> 4p <sup>1</sup>	32 Ge 4s <sup>2</sup> 4p <sup>2</sup>	33 As 4s <sup>2</sup> 4p <sup>3</sup>	34 Se 4s <sup>2</sup> 4p <sup>4</sup>	35 Br 4s <sup>2</sup> 4p <sup>5</sup>	36 Kr 4s <sup>2</sup> 4p <sup>6</sup>
[Ar]																		
	37 Rb 5s <sup>1</sup>	38 Sr 5s <sup>2</sup>	39 Y 4d <sup>1</sup> 5s <sup>2</sup>	40 Zr 4d <sup>2</sup> 5s <sup>2</sup>	41 Nb 4d <sup>3</sup> 5s <sup>2</sup>	42 Mo 4d <sup>5</sup> 5s <sup>1</sup>	43 Tc 4d <sup>5</sup> 5s <sup>2</sup>	44 Ru 4d <sup>7</sup> 5s <sup>1</sup>	45 Rh 4d <sup>8</sup> 5s <sup>1</sup>	46 Pd 4d <sup>10</sup>	47 Ag 4d <sup>10</sup> 5s <sup>1</sup>	48 Cd 4d <sup>10</sup> 5s <sup>2</sup>	49 In 4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>1</sup>	50 Sn 4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>2</sup>	51 Sb 4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>3</sup>	52 Te 4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>4</sup>	53 I 4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>5</sup>	54 Xe 4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>6</sup>
[Kr]																		
	55 Cs 6s <sup>1</sup>	56 Ba 6s <sup>2</sup>	71 Lu 4f <sup>14</sup> 5d <sup>1</sup> 6s <sup>2</sup>	72 Hf 4f <sup>14</sup> 5d <sup>2</sup> 6s <sup>2</sup>	73 Ta 4f <sup>14</sup> 5d <sup>3</sup> 6s <sup>2</sup>	74 W 4f <sup>14</sup> 5d <sup>4</sup> 6s <sup>2</sup>	75 Re 4f <sup>14</sup> 5d <sup>5</sup> 6s <sup>2</sup>	76 Os 4f <sup>14</sup> 5d <sup>6</sup> 6s <sup>2</sup>	77 Ir 4f <sup>14</sup> 5d <sup>7</sup> 6s <sup>2</sup>	78 Pt 4f <sup>14</sup> 5d <sup>9</sup> 6s <sup>1</sup>	79 Au 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>1</sup>	80 Hg 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup>	81 Tl 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>1</sup>	82 Pb 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>2</sup>	83 Bi 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>3</sup>	84 Po 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>4</sup>	85 At 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>5</sup>	86 Rn 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>6</sup>
[Xe]																		
	87 Fr 7s <sup>1</sup>	88 Ra 7s <sup>2</sup>	103 Lr 5f <sup>14</sup> 6d <sup>1</sup> 7s <sup>2</sup>	104 Rf 5f <sup>14</sup> 6d <sup>2</sup> 7s <sup>2</sup>	105 Db 5f <sup>14</sup> 6d <sup>3</sup> 7s <sup>2</sup>	106 Sg 5f <sup>14</sup> 6d <sup>4</sup> 7s <sup>2</sup>	107 Bh 5f <sup>14</sup> 6d <sup>5</sup> 7s <sup>2</sup>	108 Hs 5f <sup>14</sup> 6d <sup>6</sup> 7s <sup>2</sup>	109 Mt 5f <sup>14</sup> 6d <sup>7</sup> 7s <sup>2</sup>	110 Ds	111 Rg	112 Cn	113	114	115	116	117	118
[Rn]																		
	Lanthanide series		57 La 5d <sup>1</sup> 6s <sup>2</sup>	58 Ce 4f <sup>1</sup> 5d <sup>1</sup> 6s <sup>2</sup>	59 Pr 4f <sup>3</sup> 6s <sup>2</sup>	60 Nd 4f <sup>4</sup> 6s <sup>2</sup>	61 Pm 4f <sup>5</sup> 6s <sup>2</sup>	62 Sm 4f <sup>6</sup> 6s <sup>2</sup>	63 Eu 4f <sup>7</sup> 6s <sup>2</sup>	64 Gd 4f <sup>7</sup> 5d <sup>1</sup> 6s <sup>2</sup>	65 Tb 4f <sup>9</sup> 6s <sup>2</sup>	66 Dy 4f <sup>10</sup> 6s <sup>2</sup>	67 Ho 4f <sup>11</sup> 6s <sup>2</sup>	68 Er 4f <sup>12</sup> 6s <sup>2</sup>	69 Tm 4f <sup>13</sup> 6s <sup>2</sup>	70 Yb 4f <sup>14</sup> 6s <sup>2</sup>		
[Xe]	Actinide series		89 Ac 6d <sup>1</sup> 7s <sup>2</sup>	90 Th 6d <sup>2</sup> 7s <sup>2</sup>	91 Pa 5f <sup>2</sup> 6d <sup>1</sup> 7s <sup>2</sup>	92 U 5f <sup>3</sup> 6d <sup>1</sup> 7s <sup>2</sup>	93 Np 5f <sup>4</sup> 6d <sup>1</sup> 7s <sup>2</sup>	94 Pu 5f <sup>6</sup> 7s <sup>2</sup>	95 Am 5f <sup>7</sup> 7s <sup>2</sup>	96 Cm 5f <sup>7</sup> 6d <sup>1</sup> 7s <sup>2</sup>	97 Bk 5f <sup>9</sup> 7s <sup>2</sup>	98 Cf 5f <sup>10</sup> 7s <sup>2</sup>	99 Es 5f <sup>11</sup> 7s <sup>2</sup>	100 Fm 5f <sup>12</sup> 7s <sup>2</sup>	101 Md 5f <sup>13</sup> 7s <sup>2</sup>	102 No 5f <sup>14</sup> 7s <sup>2</sup>		
[Rn]																		
			<div><div></div>Metals<div></div>Metalloids<div></div>Nonmetals</div>															

For instance, the electron configuration for copper is

$[\text{Ar}] 4s^1 3d^5$   
rather than the  
expected  
 $[\text{Ar}] 4s^2 3d^4$ .

# Some Anomalies

[illegible]

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