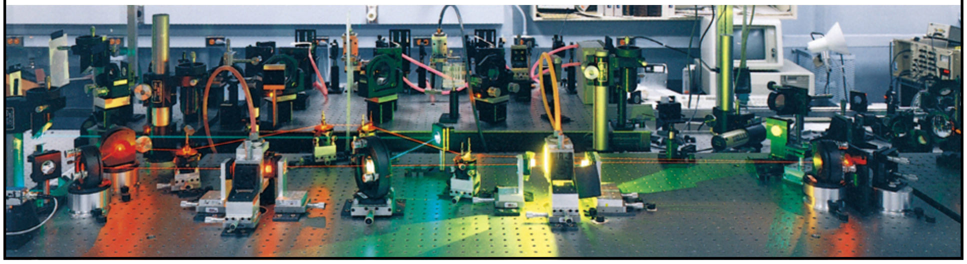
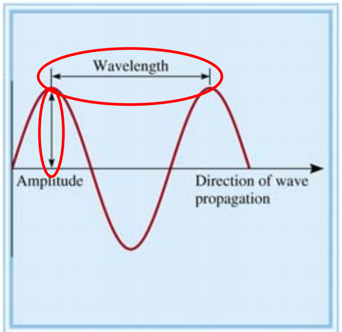
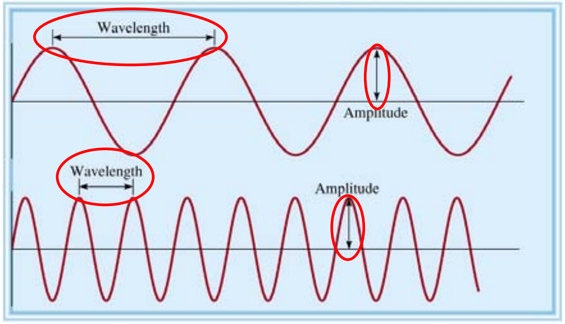
Quantum Theory and the Electronic Structure of Atoms

Chapter 7



Properties of Waves

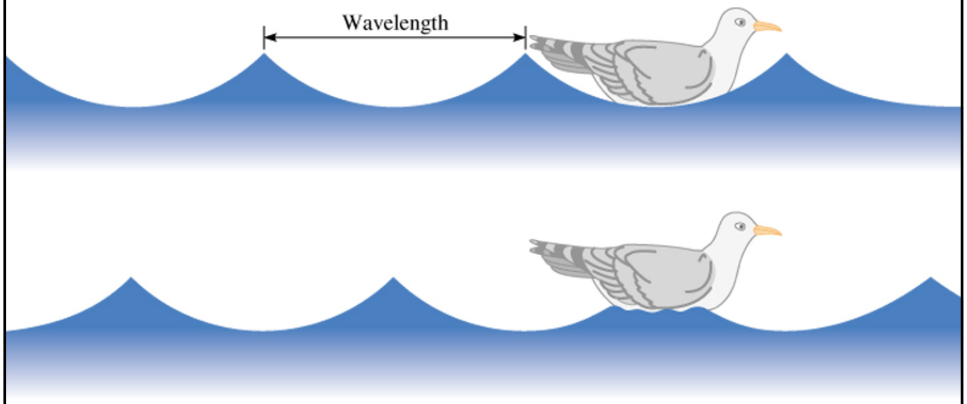




Wavelength (λ) is the distance between identical points on successive waves.

Amplitude is the vertical distance from the midline of a wave to the peak or trough.

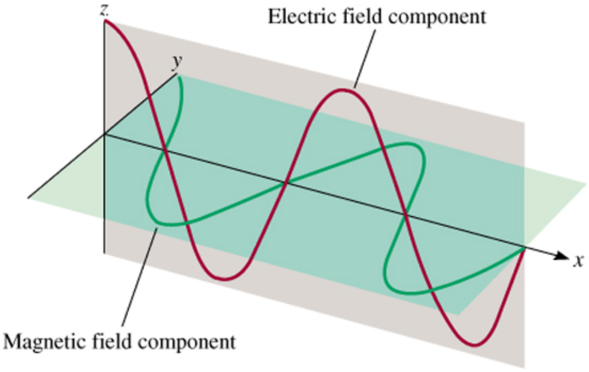
Properties of Waves



Frequency (ν) is the number of waves that pass through a particular point in 1 second (Hz = 1 cycle/s).

The speed (u) of the wave = $\lambda \times \nu$

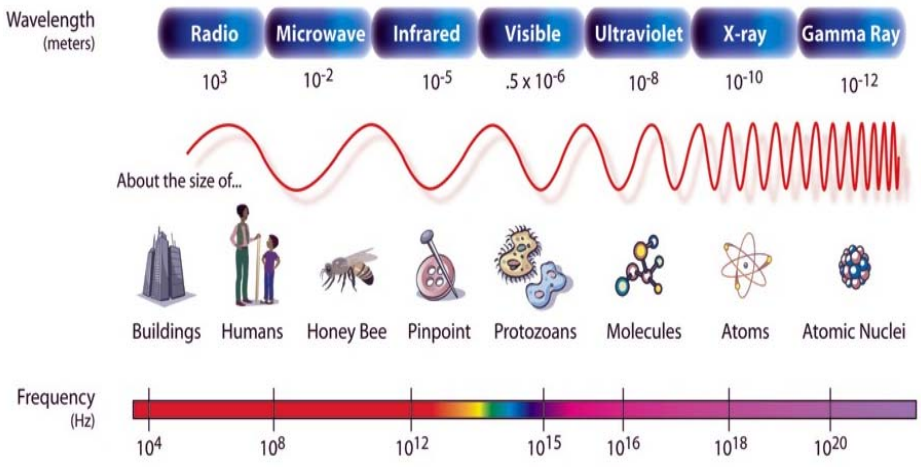
Maxwell (1873), proposed that visible light consists of electromagnetic waves.

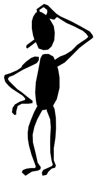


Electromagnetic radiation is the emission and transmission of energy in the form of electromagnetic waves.

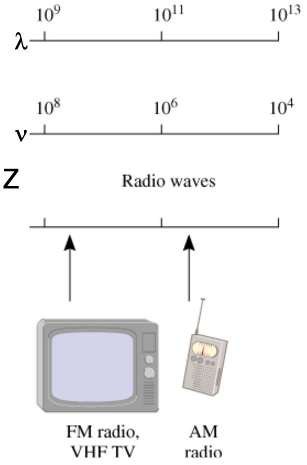
Speed of light (c) in vacuum = 3.00×10^8 m/s

All electromagnetic radiation
$\lambda \times \nu = c$





A photon has a frequency of 6.0 x 10^4 Hz. Convert this frequency into wavelength (nm). Does this frequency fall in the visible region?



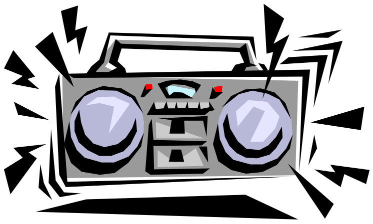
$\lambda \times \nu = c$

$\lambda = c/\nu$

$\lambda = 3.00 \times 10^8 \text{ m/s} \,/\, 6.0 \times 10^4 \text{ Hz}$

$\lambda = 5.0 \times 10^3 \text{ m}$

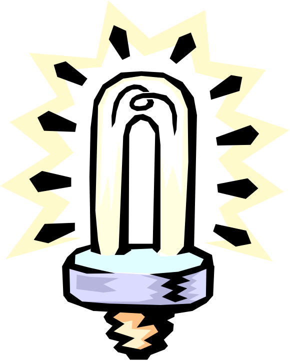
$\lambda = 5.0 \times 10^{12} \text{ nm}$



Radio wave

Mystery #1, “Black Body Problem”
Solved by Planck in 1900

Energy (light) is emitted or absorbed in discrete units (quantum).



$E = h \times \nu$
Planck’s constant (h)
$h = 6.63 \times 10^{-34}$ J•s

Mystery #2, “Photoelectric Effect”
Solved by Einstein in 1905

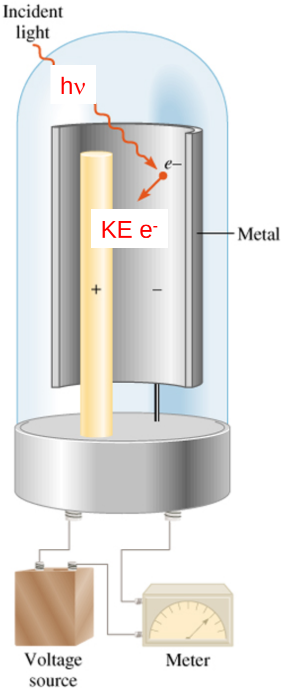
Light has both:

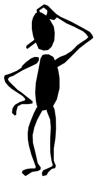
1. wave nature
2. particle nature

Photon is a “particle” of light

$$h\nu = KE + BE$$

$$KE = h\nu - BE$$





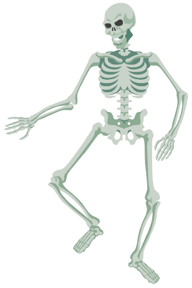
When copper is bombarded with high-energy electrons, X rays are emitted. Calculate the energy (in joules) associated with the photons if the wavelength of the X rays is 0.154 nm.

$E = h \times \nu$

$E = h \times c / \lambda$

$E = 6.63 \times 10^{-34}\ (J\bullet\cancel{s}) \times 3.00 \times 10^{8}\ (\cancel{m}/\cancel{s}) / 0.154 \times 10^{-9}\ (\cancel{m})$

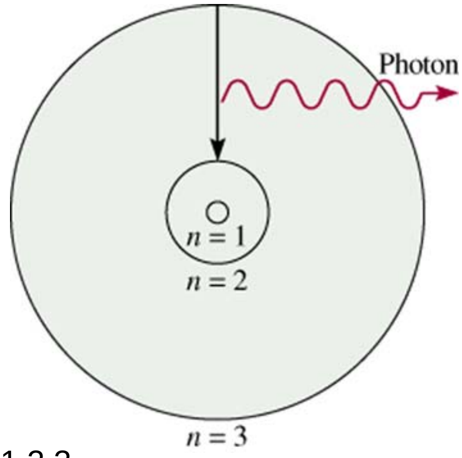
$E = 1.29 \times 10^{-15}\ J$



Bohr's Model of the Atom (1913)

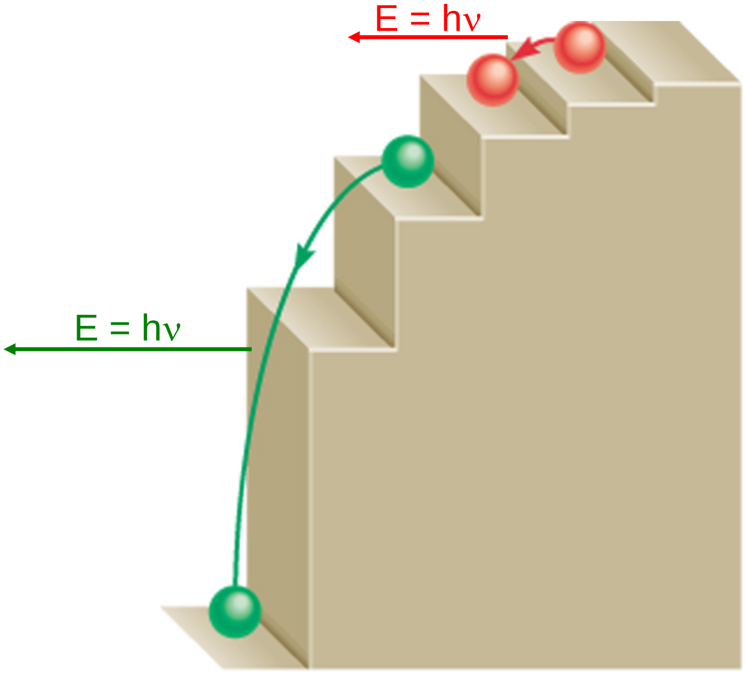
1. e^- can only have specific (quantized) energy values
2. light is emitted as e^- moves from one energy level to a lower energy level

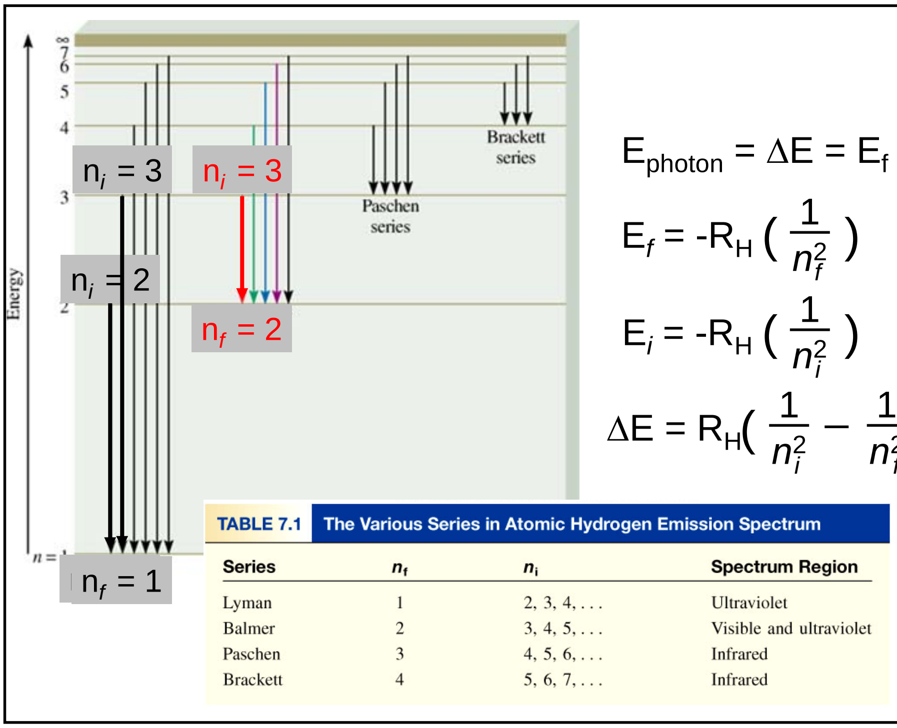
$$E_n = -R_H\left(\frac{1}{n^2}\right)$$



n (principal quantum number) = 1,2,3,…

R_H (Rydberg constant) = 2.18×10^{-18}J





$$E_{photon} = \Delta E = E_f - E_i$$

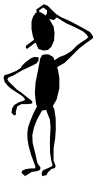
$$E_f = -R_H\left(\frac{1}{n_f^2}\right)$$

$$E_i = -R_H\left(\frac{1}{n_i^2}\right)$$

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

TABLE 7.1 The Various Series in Atomic Hydrogen Emission Spectrum

Series	n_f	n_i	Spectrum Region
Lyman	1	2, 3, 4, . . .	Ultraviolet
Balmer	2	3, 4, 5, . . .	Visible and ultraviolet
Paschen	3	4, 5, 6, . . .	Infrared
Brackett	4	5, 6, 7, . . .	Infrared



Calculate the wavelength (in nm) of a photon emitted by a hydrogen atom when its electron drops from the *n* = 5 state to the *n* = 3 state.

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

$$E_{photon} = 2.18 \times 10^{-18}\ \text{J} \times (1/25 - 1/9)$$

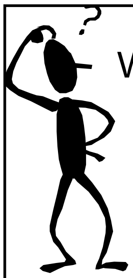
$$E_{photon} = \Delta E = -1.55 \times 10^{-19}\ \text{J}$$

$$E_{photon} = h \times c / \lambda$$

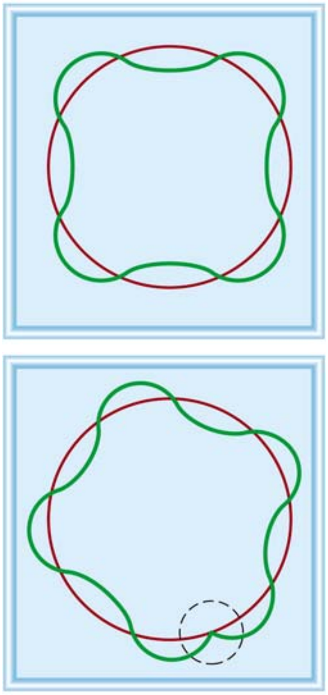
$$\lambda = h \times c / E_{photon}$$

$$\lambda = 6.63 \times 10^{-34}\ (\cancel{\text{J}}\bullet\cancel{\text{s}}) \times 3.00 \times 10^{8}\ (\text{m}/\cancel{\text{s}})/1.55 \times 10^{-19}\ \cancel{\text{J}}$$

$$\lambda = 1280\ \text{nm}$$



Why is e^- energy quantized?

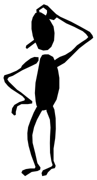


De Broglie (1924) reasoned that e^- is both particle and wave.

$$2\pi r = n\lambda \qquad \lambda = \frac{h}{mu}$$

u = velocity of e-

m = mass of e-

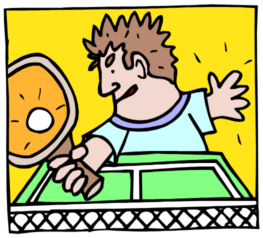


What is the de Broglie wavelength (in nm) associated with a 2.5 g Ping-Pong ball traveling at 15.6 m/s?

$\lambda = h/mu$ h in J•s   m in kg   u in (m/s)

$\lambda = 6.63 \times 10^{-34} / (2.5 \times 10^{-3} \times 15.6)$

$\lambda = 1.7 \times 10^{-32}$ m $= 1.7 \times 10^{-23}$ nm



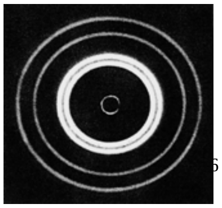
Schrodinger Wave Equation

In 1926 Schrodinger wrote an equation that described both the particle and wave nature of the e^-

Wave function (Ψ) describes:

1. energy of e^- with a given Ψ
2. probability of finding e^- in a volume of space

Schrodinger's equation can only be solved exactly for the hydrogen atom. Must approximate its solution for multi-electron systems.



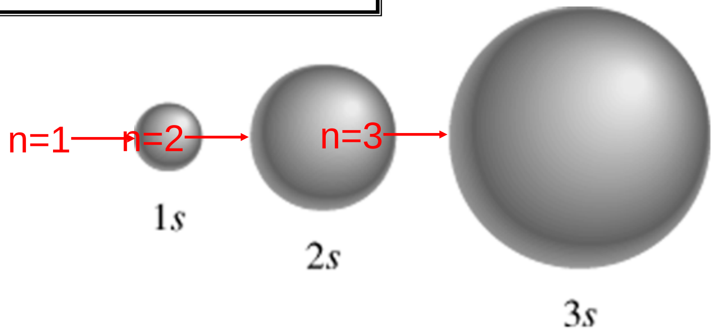
Schrodinger Wave Equation

$\Psi = \text{fn}(n, l, m_l, m_s)$

principal quantum number n

n = 1, 2, 3, 4, ….

distance of e^- from the nucleus



Schrodinger Wave Equation

$\Psi = \text{fn}(n, l, m_l, m_s)$

angular momentum quantum number *l*

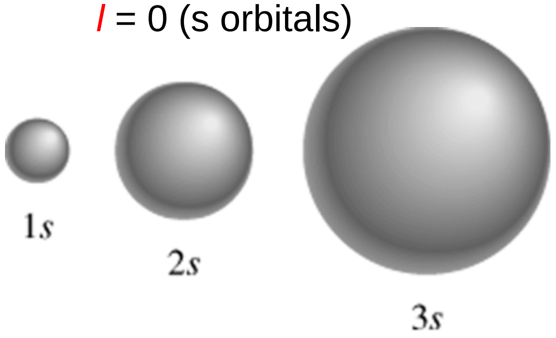
for a given value of n, *l* = 0, 1, 2, 3, … n-1

n = 1, *l* = *0*
n = 2, *l* = 0 **or** 1
n = 3, *l* = 0, 1, **or** 2

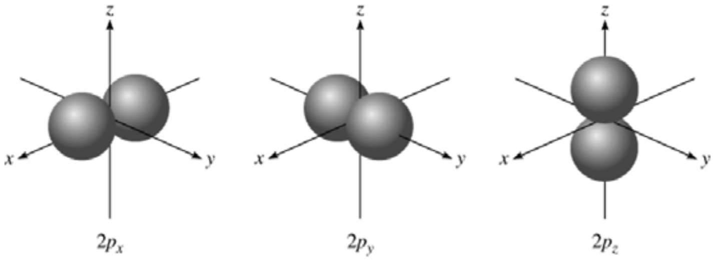
l = 0	s orbital
l = 1	p orbital
l = 2	d orbital
l = 3	f orbital

Shape of the "volume" of space that the e^- occupies

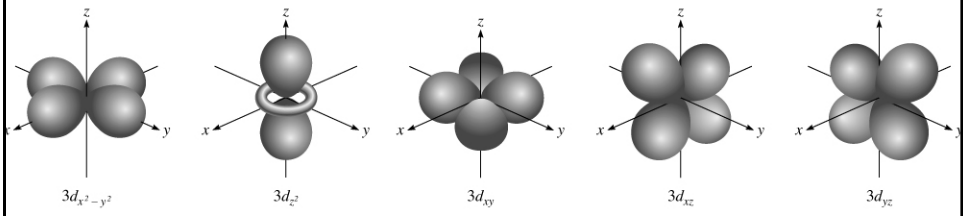
$l = 0$ (s orbitals)



$l = 1$ (p orbitals)



$l = 2$ (d orbitals)



Schrodinger Wave Equation

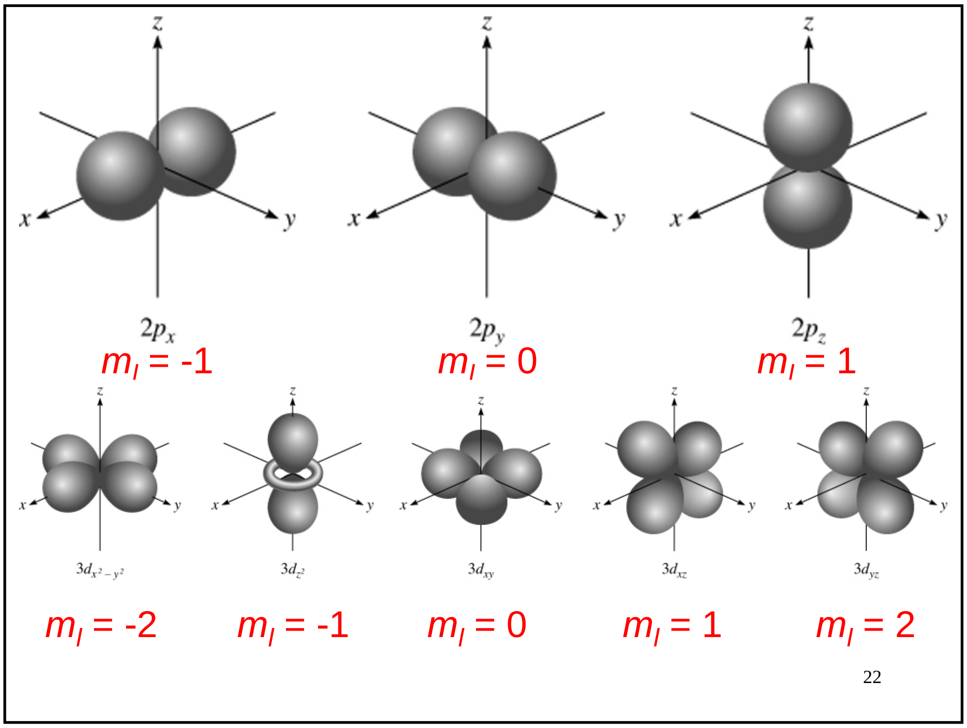
Ψ = fn(n, l, m_l, m_s)

magnetic quantum number m_l

for a given value of l
m_l = -l, …., 0, …. +l

if l = 1 (p orbital), m_l = -1, 0, **or** 1
if l = 2 (d orbital), m_l = -2, -1, 0, 1, **or** 2

orientation of the orbital in space



$2p_x$ m_l = -1

$2p_y$ m_l = 0

$2p_z$ m_l = 1

$3d_{x^2-y^2}$ m_l = -2

$3d_{z^2}$ m_l = -1

$3d_{xy}$ m_l = 0

$3d_{xz}$ m_l = 1

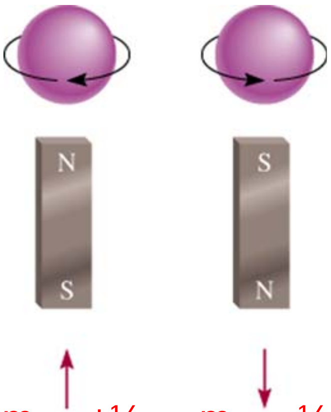
$3d_{yz}$ m_l = 2

Schrodinger Wave Equation

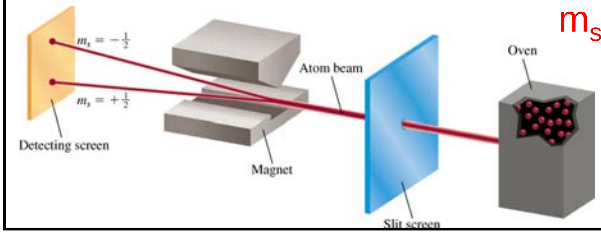
$\Psi = \text{fn}(n, l, m_l, m_s)$

spin quantum number m_s

$m_s = +\frac{1}{2}$ **or** $-\frac{1}{2}$



$m_s = +\frac{1}{2}$ $m_s = -\frac{1}{2}$



Schrodinger Wave Equation

$\Psi = \text{fn}(n, l, m_l, m_s)$

Existence (and energy) of electron in atom is described by its ***unique*** wave function Ψ.

Pauli exclusion principle - no two electrons in an atom can have the same four quantum numbers.

Each seat is uniquely identified (E, R12, S8)
Each seat can hold only one individual at a time

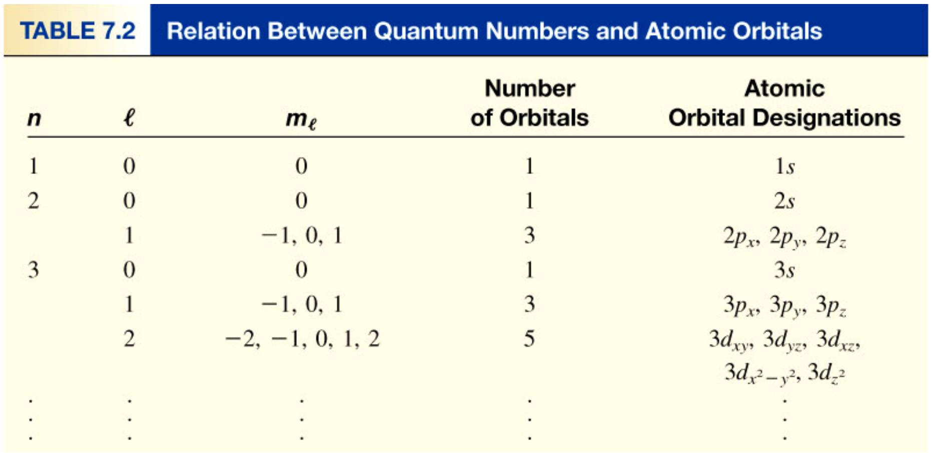


TABLE 7.2 **Relation Between Quantum Numbers and Atomic Orbitals**

n	ℓ	m_ℓ	Number of Orbitals	Atomic Orbital Designations
1	0	0	1	$1s$
2	0	0	1	$2s$
	1	−1, 0, 1	3	$2p_x$, $2p_y$, $2p_z$
3	0	0	1	$3s$
	1	−1, 0, 1	3	$3p_x$, $3p_y$, $3p_z$
	2	−2, −1, 0, 1, 2	5	$3d_{xy}$, $3d_{yz}$, $3d_{xz}$, $3d_{x^2-y^2}$, $3d_{z^2}$
⋮	⋮	⋮	⋮	⋮

Schrodinger Wave Equation

$$\Psi = \text{fn}(n, l, m_l, m_s)$$

Shell – electrons with the same value of *n*

Subshell – electrons with the same values of *n* **and** *l*

Orbital – electrons with the same values of *n, l,* **and** m_l

How many electrons can an orbital hold?

If *n, l,* and m_l are fixed, then m_s = ½ or - ½

$\Psi = (n, l, m_l, ½)$ or $\Psi = (n, l, m_l, -½)$

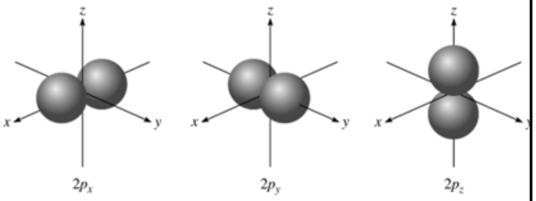
An orbital can hold 2 electrons

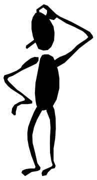
How many 2p orbitals are there in an atom?

n=2 ↓ 2p ↑ l = 1

If l = 1, then m_l = -1, 0, or +1

3 orbitals





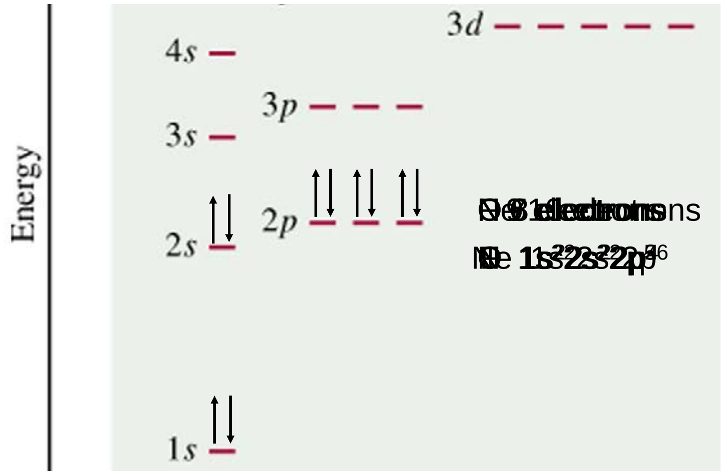
How many electrons can be placed in the 3d subshell?

n=3 ↓ 3d ↑ l = 2

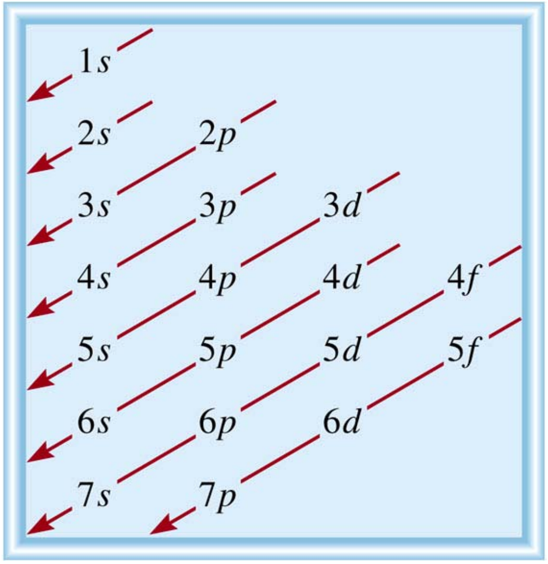
If l = 2, then m_l = -2, -1, 0, +1, or +2

5 orbitals which can hold a total of 10 e^-

The most stable arrangement of electrons in subshells is the one with the greatest number of parallel spins (***Hund's rule***).



Order of orbitals (filling) in multi-electron atom



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

Electron configuration is how the electrons are distributed among the various atomic orbitals in an atom.

number of electrons in the orbital or subshell

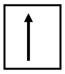
$1s^1$

principal quantum number ***n***

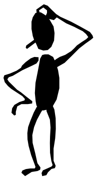
angular momentum quantum number ***l***

Orbital diagram

H



$1s^1$



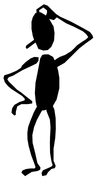
What is the electron configuration of Mg?

Mg 12 electrons

1s < 2s < 2p < 3s < 3p < 4s

$1s^22s^22p^63s^2$ 2 + 2 + 6 + 2 = 12 electrons

Abbreviated as $[Ne]3s^2$ $[Ne]\ 1s^22s^22p^6$



What are the possible quantum numbers for the last (outermost) electron in Cl?

Cl 17 electrons   1s < 2s < 2p < 3s < 3p < 4s

$1s^22s^22p^63s^23p^5$ 2 + 2 + 6 + 2 + 5 = 17 electrons

Last electron added to 3p orbital

$n = 3$ $l = 1$ $m_l = -1, 0, \text{ or } +1$ $m_s = ½ \text{ or } -½$

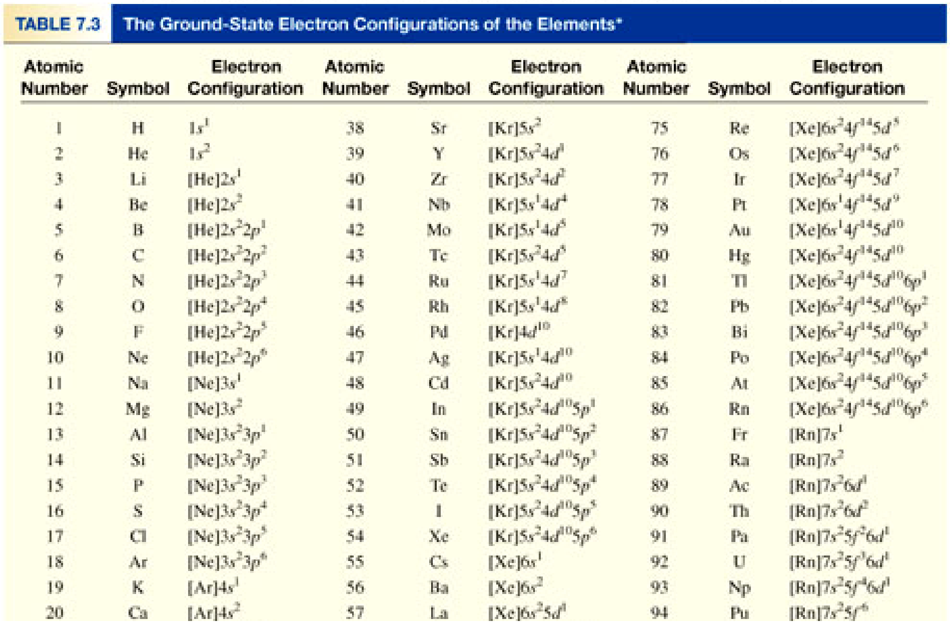
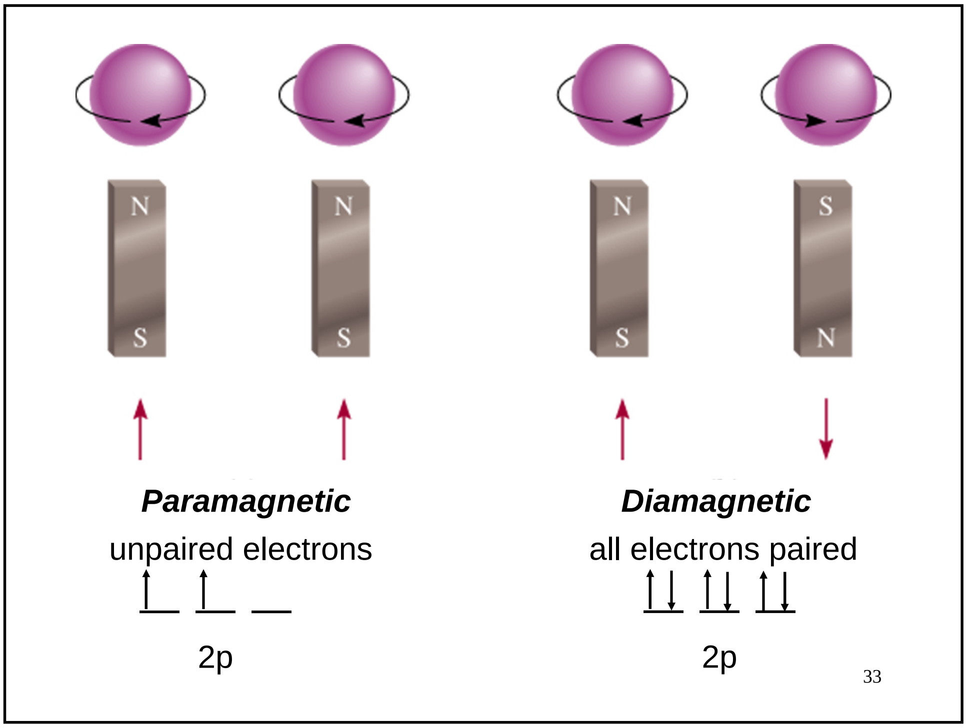


TABLE 7.3 The Ground-State Electron Configurations of the Elements*

Atomic Number	Symbol	Electron Configuration	Atomic Number	Symbol	Electron Configuration	Atomic Number	Symbol	Electron Configuration
1	H	$1s^1$	38	Sr	$[Kr]5s^2$	75	Re	$[Xe]6s^24f^{14}5d^5$
2	He	$1s^2$	39	Y	$[Kr]5s^24d^1$	76	Os	$[Xe]6s^24f^{14}5d^6$
3	Li	$[He]2s^1$	40	Zr	$[Kr]5s^24d^2$	77	Ir	$[Xe]6s^24f^{14}5d^7$
4	Be	$[He]2s^2$	41	Nb	$[Kr]5s^14d^4$	78	Pt	$[Xe]6s^14f^{14}5d^9$
5	B	$[He]2s^22p^1$	42	Mo	$[Kr]5s^14d^5$	79	Au	$[Xe]6s^14f^{14}5d^{10}$
6	C	$[He]2s^22p^2$	43	Tc	$[Kr]5s^24d^5$	80	Hg	$[Xe]6s^24f^{14}5d^{10}$
7	N	$[He]2s^22p^3$	44	Ru	$[Kr]5s^14d^7$	81	Tl	$[Xe]6s^24f^{14}5d^{10}6p^1$
8	O	$[He]2s^22p^4$	45	Rh	$[Kr]5s^14d^8$	82	Pb	$[Xe]6s^24f^{14}5d^{10}6p^2$
9	F	$[He]2s^22p^5$	46	Pd	$[Kr]4d^{10}$	83	Bi	$[Xe]6s^24f^{14}5d^{10}6p^3$
10	Ne	$[He]2s^22p^6$	47	Ag	$[Kr]5s^14d^{10}$	84	Po	$[Xe]6s^24f^{14}5d^{10}6p^4$
11	Na	$[Ne]3s^1$	48	Cd	$[Kr]5s^24d^{10}$	85	At	$[Xe]6s^24f^{14}5d^{10}6p^5$
12	Mg	$[Ne]3s^2$	49	In	$[Kr]5s^24d^{10}5p^1$	86	Rn	$[Xe]6s^24f^{14}5d^{10}6p^6$
13	Al	$[Ne]3s^23p^1$	50	Sn	$[Kr]5s^24d^{10}5p^2$	87	Fr	$[Rn]7s^1$
14	Si	$[Ne]3s^23p^2$	51	Sb	$[Kr]5s^24d^{10}5p^3$	88	Ra	$[Rn]7s^2$
15	P	$[Ne]3s^23p^3$	52	Te	$[Kr]5s^24d^{10}5p^4$	89	Ac	$[Rn]7s^26d^1$
16	S	$[Ne]3s^23p^4$	53	I	$[Kr]5s^24d^{10}5p^5$	90	Th	$[Rn]7s^26d^2$
17	Cl	$[Ne]3s^23p^5$	54	Xe	$[Kr]5s^24d^{10}5p^6$	91	Pa	$[Rn]7s^25f^26d^1$
18	Ar	$[Ne]3s^23p^6$	55	Cs	$[Xe]6s^1$	92	U	$[Rn]7s^25f^36d^1$
19	K	$[Ar]4s^1$	56	Ba	$[Xe]6s^2$	93	Np	$[Rn]7s^25f^46d^1$
20	Ca	$[Ar]4s^2$	57	La	$[Xe]6s^25d^1$	94	Pu	$[Rn]7s^25f^6$



Paramagnetic

unpaired electrons

↑ ↑ _

2p

Diamagnetic

all electrons paired

↑↓ ↑↓ ↑↓

2p