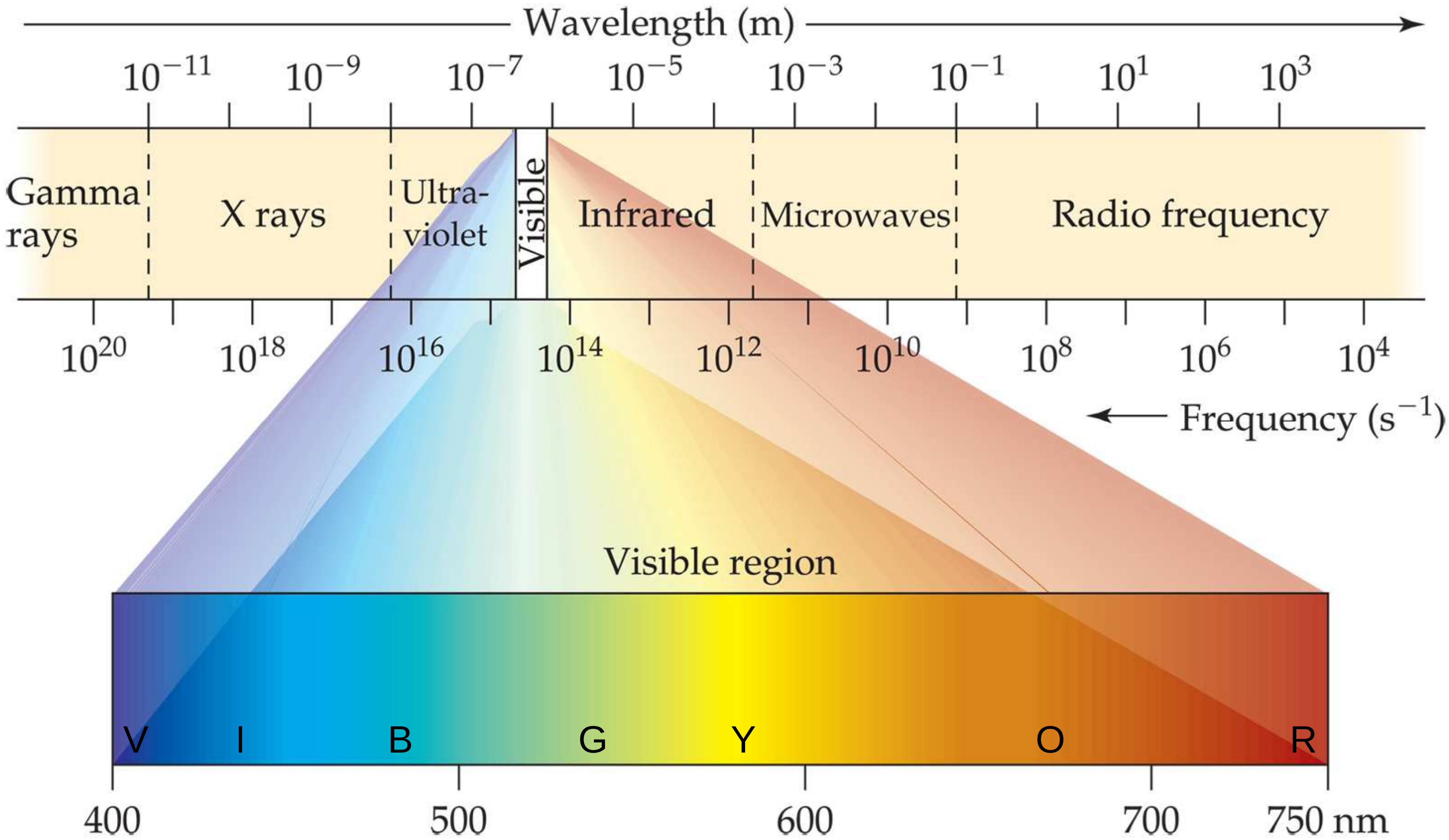
Chapter 6: The Electronic Structure of the Atom

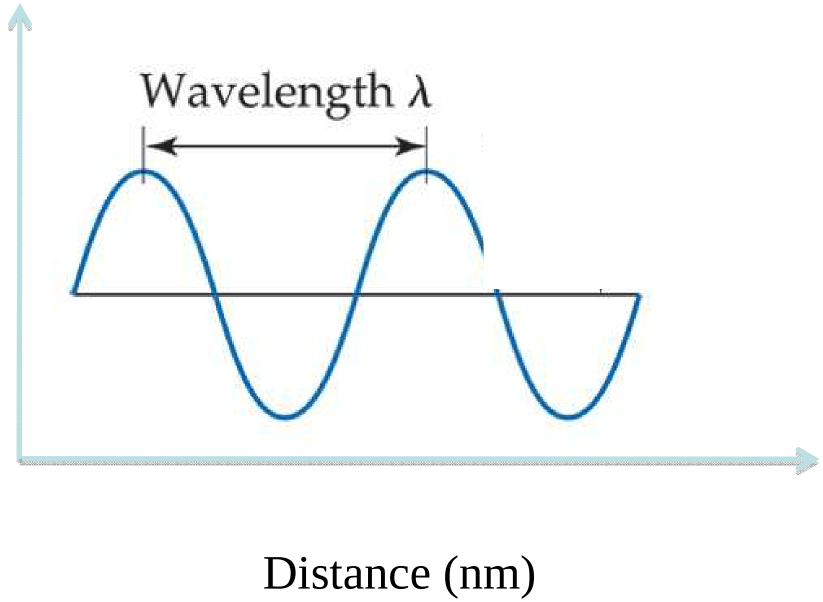
Electromagnetic Spectrum

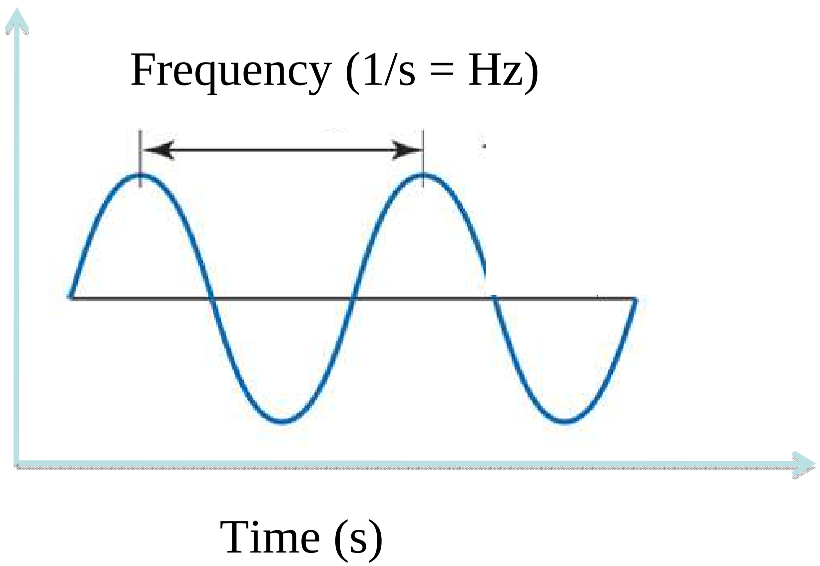


All EM radiation travels at the speed of light, $c = 3 \times 10^8$ m/s

Electromagnetic Radiation as Wave

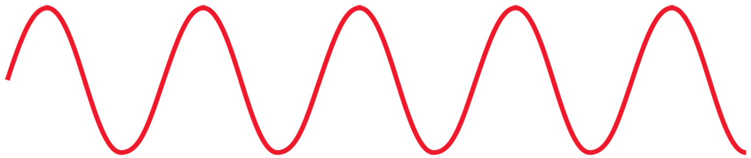
Electromagnetic radiation is a wave with a wavelength and frequency.



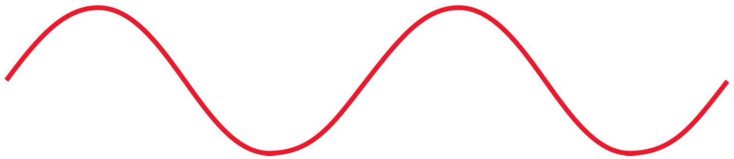


Wavelength = distance (m)
Frequency = 1 / time (Hz)

Relationship between speed, wavelength, and frequency



The number of waves passing a given point per unit of time is the frequency (ν).



The longer the wavelength, the smaller the frequency.

$$c = \lambda \nu,$$

$$\lambda = c / \nu,$$

$$\boxed{\nu = c / \lambda}$$

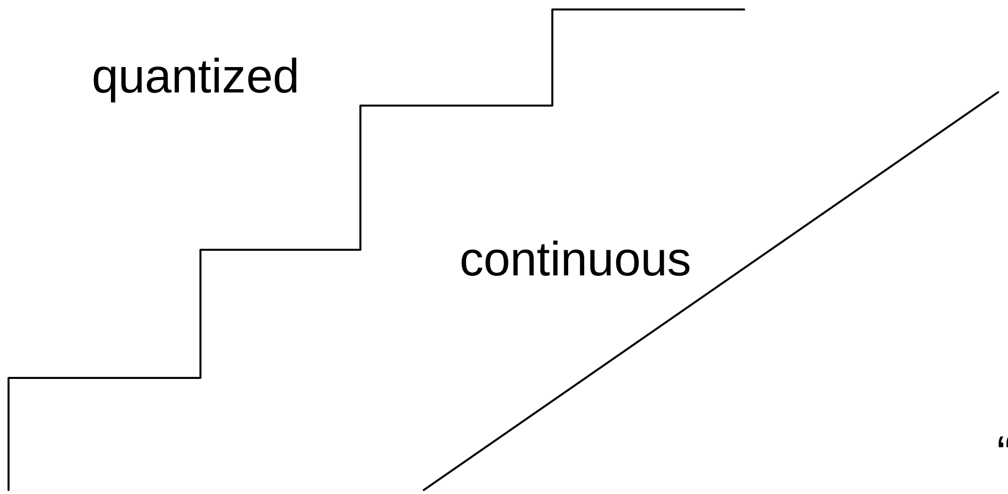
What's nu?

For red light: λ = 600 nm, and $\nu = 5 \times 10^{14}$ Hz

Wave Theory of Light is only Partially True

There were several observations that could not be explained using the wave model of EM Radiation

Another model, involving quantized energy was proposed, and found to explain these other observations



continuous

“quantized”

Particle Theory of Light - Photons

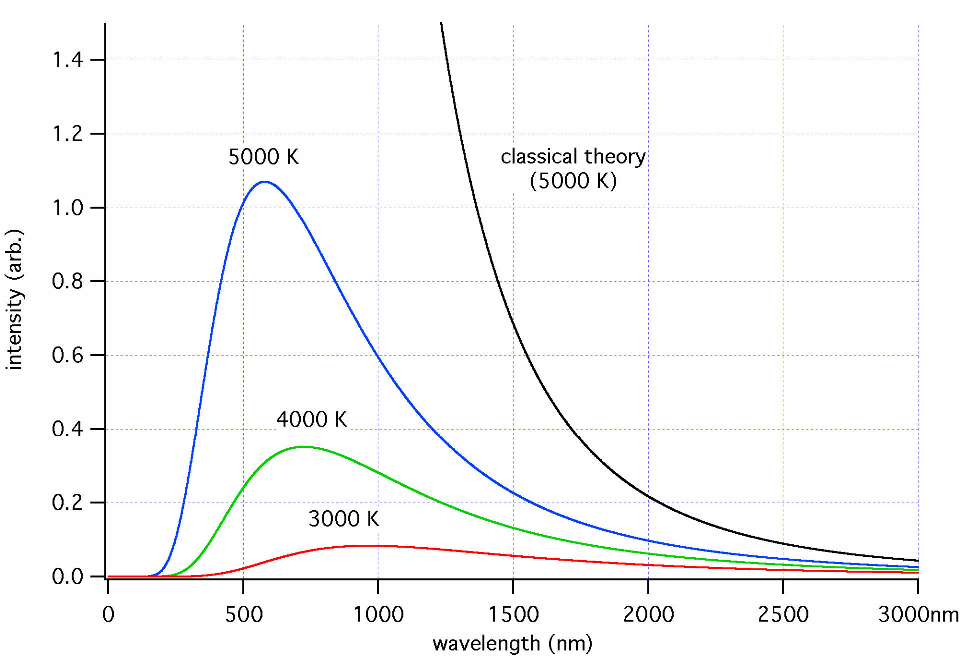
Light waves can also be thought of as particles of light – called PHOTONS

Photons are a discrete, or quantized, form of energy.

They are massless and propagate at the speed of light

A photon’s energy is proportional to its frequency.
(higher freq. = higher energy)

3 Cases where the wave model of EM radiation failed:
#1 Blackbody Radiation



Max Planck explained blackbody radiation by assuming that energy comes in packets called quanta.

Visible Light

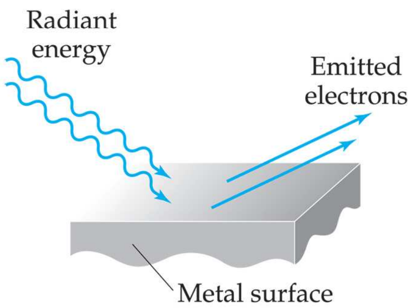
Infrared

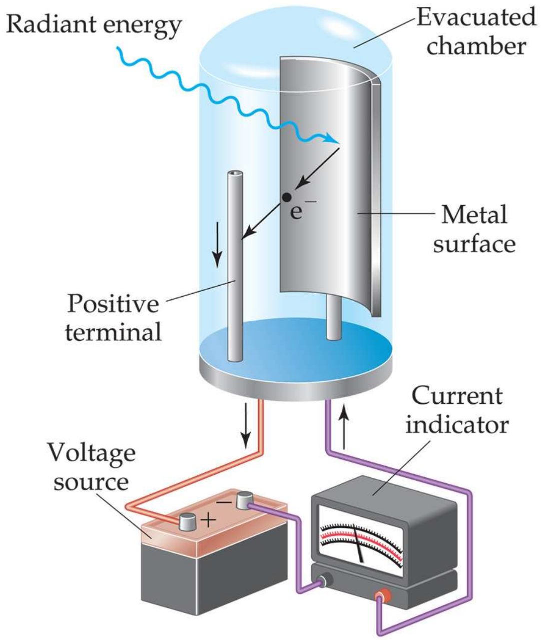
http://en.wikipedia.org/wiki/Black_body

3 Cases where the wave model of EM radiation failed: #2 The Photoelectric Effect

Required a certain energy threshold of light to eject an electron

Einstein used quantized energy to explain the photoelectric effect.



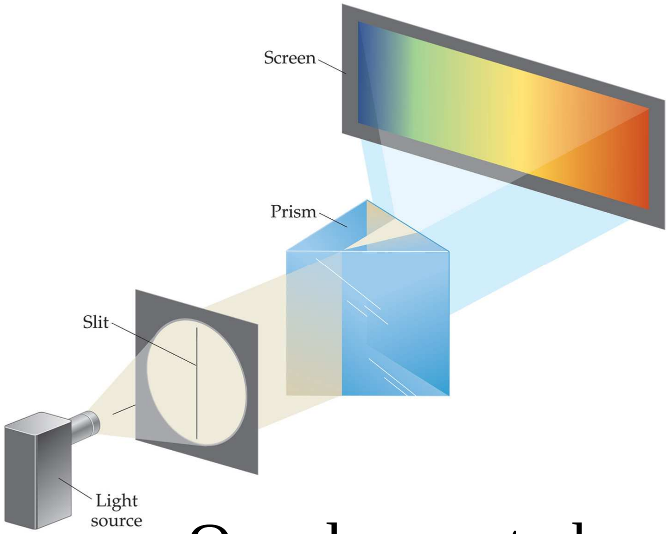


He concluded that energy is proportional to frequency:

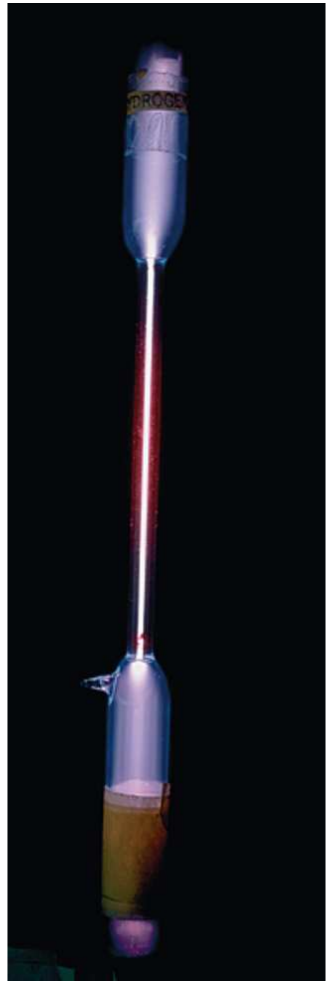
$$E = h\nu$$

h is Planck's constant, 6.63×10^{-34} J-s.

3 Cases where the wave model of EM radiation failed:
#3 Atomic Emission Lines

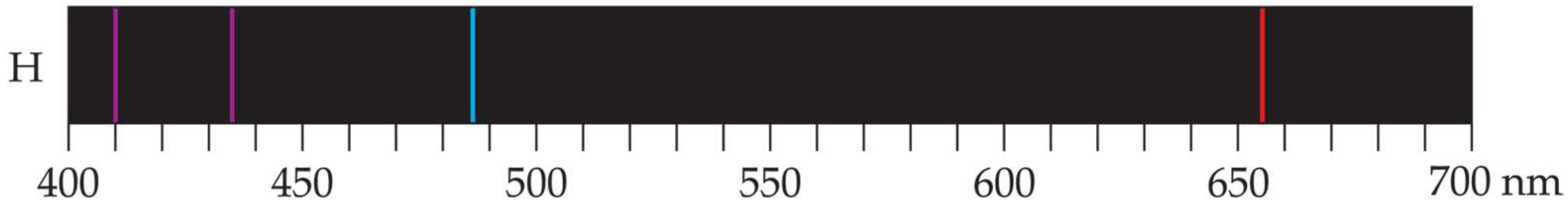


Hydrogen Emission



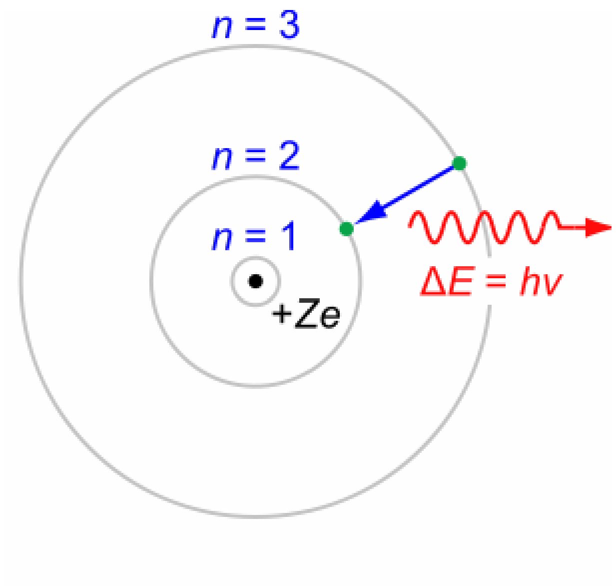
One does not observe a continuous spectrum from atomic emission, as one gets from a white light source.

Only a line spectrum of discrete wavelengths is observed.



Niels Bohr Explains the Line Spectra by Quantizing Electron Orbits

Hydrogen emission



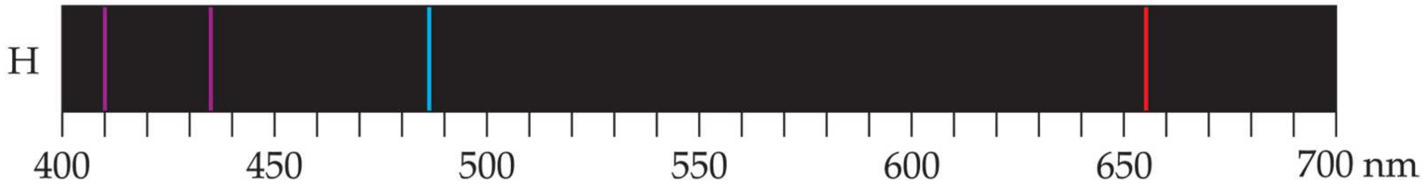
http://en.wikipedia.org/wiki/Photon

Bohr's 3 Postulates:

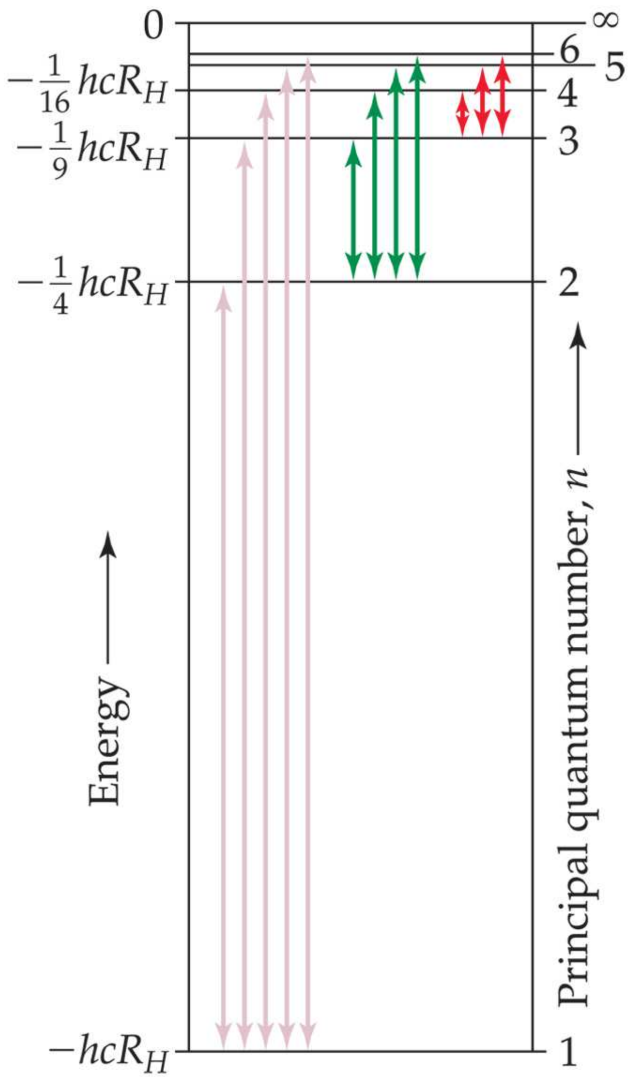
Electrons in an atom can only occupy certain orbits (corresponding to certain energies).

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

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



Atomic Emission Lines Explained

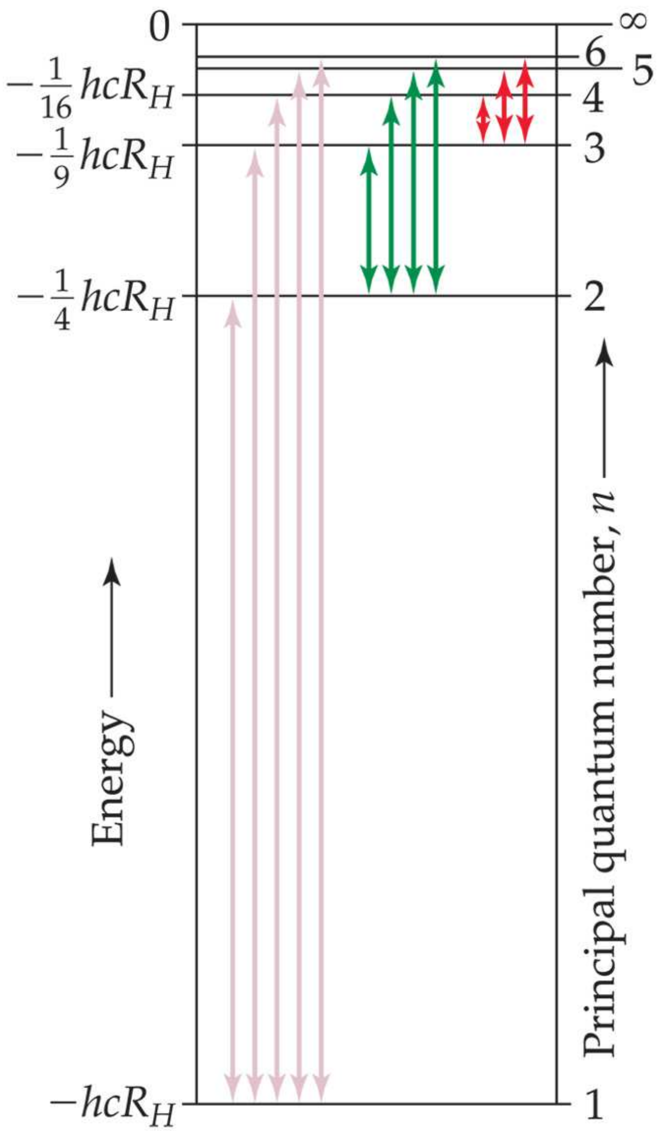


The energy absorbed or emitted from the process of electron promotion or demotion can be calculated by the equation:

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

where R_H is the Rydberg constant, 2.18×10^{-18} J, and n_i and n_f are the initial and final energy levels of the electron.

Considering only the *n* = 1 to *n* = 5 states in the hydrogen atom, which transition will *emit* the longest wavelength?

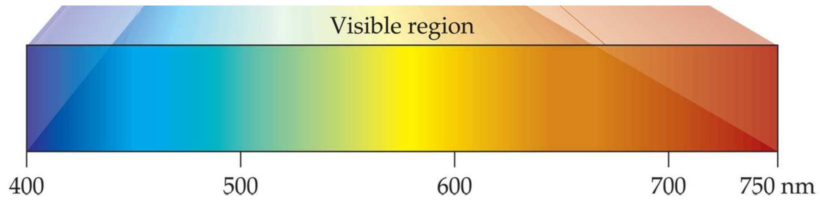


1. ***n* = 5 to *n* = 4**
2. ***n* = 5 to *n* = 2**
3. ***n* = 3 to *n* = 1**
4. ***n* = 3 to *n* = 2**
5. ***n* = 4 to *n* = 2**

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

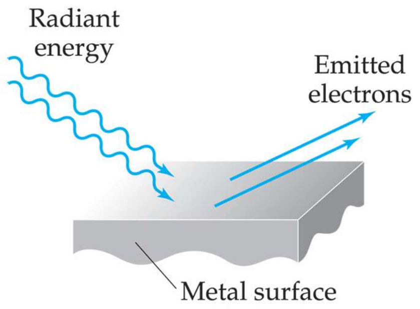
Summary – Light & Electrons so far…

- Light acts as a wave, with frequency (ν) and wavelength (λ)

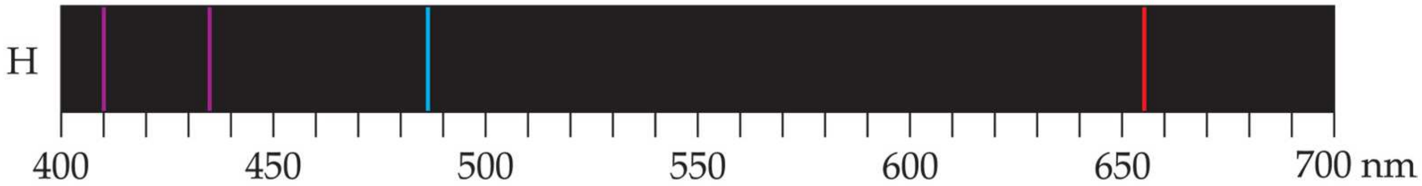


-Light as a wave couldn't explain 3 experiments:

i) Blackbody Radiation
ii) Photoelectric Effect
iii) Hydrogen Emission Spectrum



- Theory of light as a particle could explain these 3 expts.



-Light behaves BOTH as a particle and a wave = WAVE-PARTICLE DUALITY

- Electrons have quantized orbits around the nucleus

Wave Nature of Matter

Louis de Broglie proposed that if light can have properties of particles, than particles should exhibit properties of waves.

He demonstrated that the relationship between mass and wavelength was

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

'wavelength of a particle' is Planck's constant divided by its momentum

$\lambda_{\text{baseball}}$ = 6.63 x 10^{-34} J s / (0.5 kg * 50 m / s) = 2.7 x 10^{-35} m

$\lambda_{\text{electron}}$ = 6.63 x 10^{-34} J s / (9.1 x 10^{-31} kg * 10^{2} m / s) = 7.3 x 10^{-6} m

Heisenberg Uncertainty Principle

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

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

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

1 nm * (9.1 x 10^{-31} kg * v) >= 5.3 x 10^{-35} J s

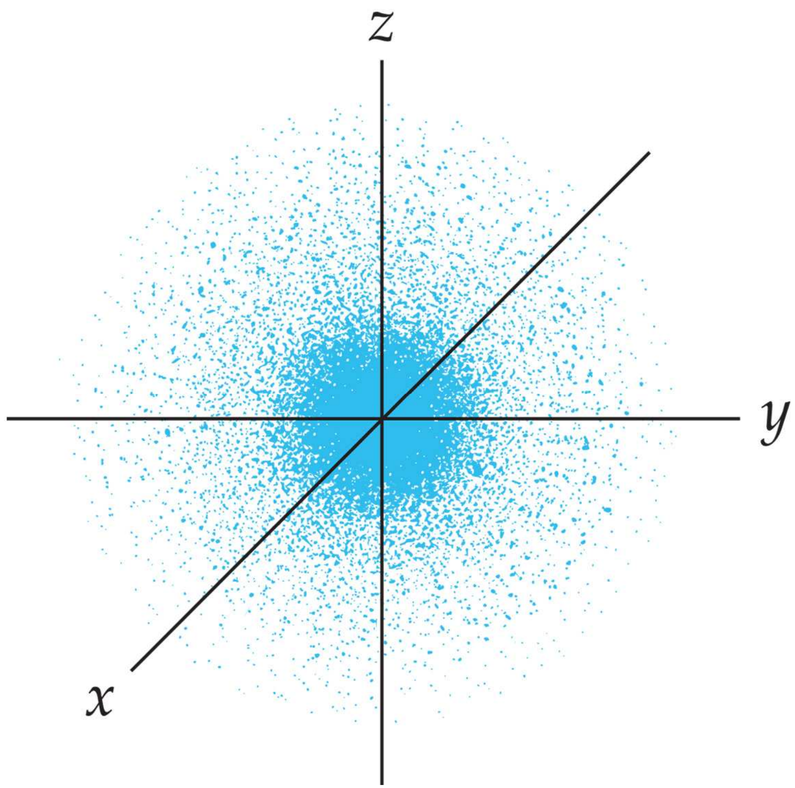
v >= 5.8 x 10^{5} m /s

Quantum Mechanics

Schrödinger developed a mathematical treatment into which both the wave and particle nature of matter could be incorporated.

It is known as quantum mechanics.

The quantum mechanics solves wave equations that give a probability density map of where an electron has a statistical likelihood of being at any given instant in time.



Quantum Mechanics

- The wave equation gives a set of orbitals where the electrons can reside
  (not the same as an orbit)
- An orbital is described by a set of three quantum numbers (n, l, m_l).

n: The principal quantum number, *n*, can be an integer: 1, 2, 3…
And describes the energy level of an orbital

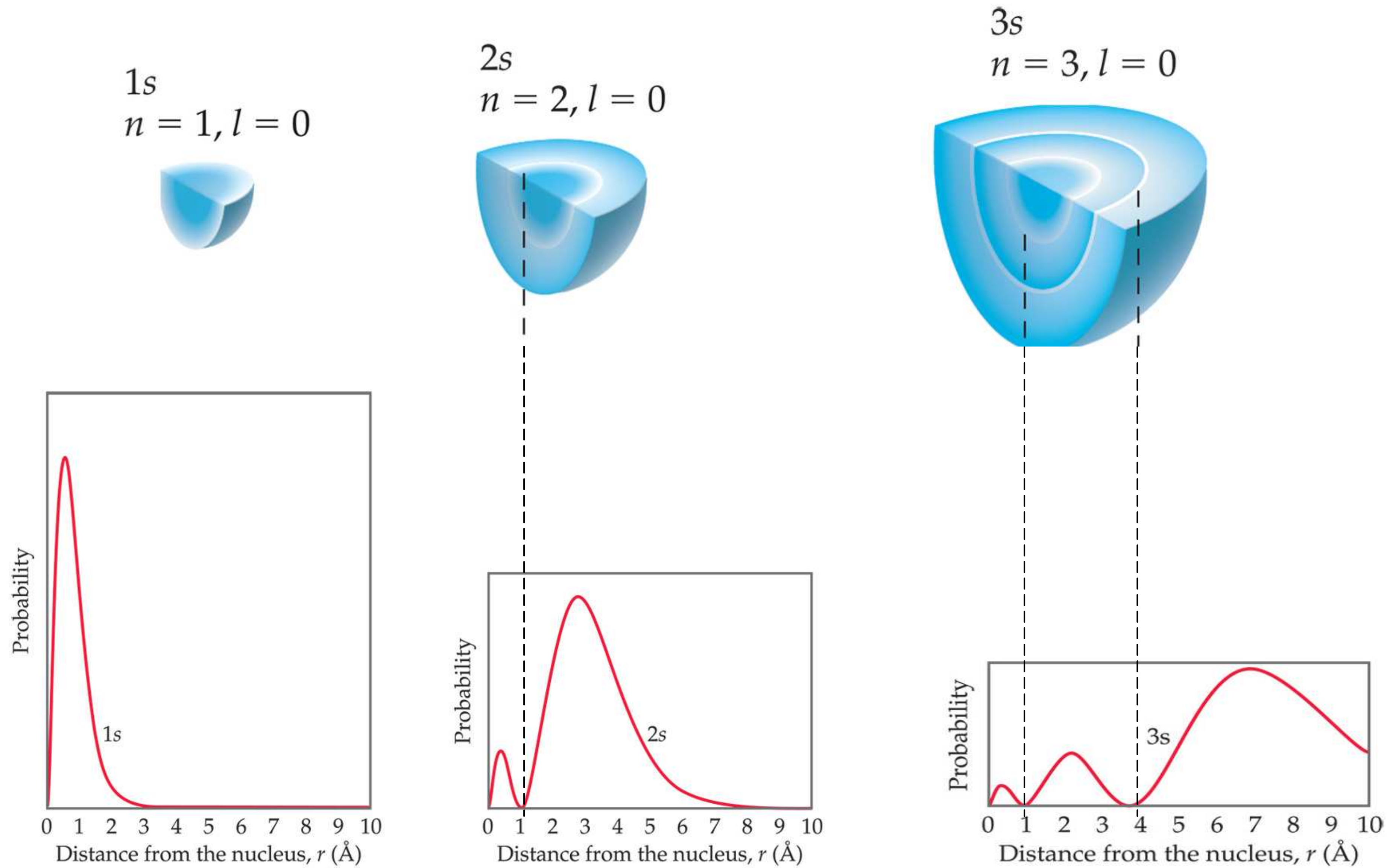
l: The shape of the orbital is given by the value of l:
Which goes in integers from 0 to n.

m_l: The last number m_l can be between –l and l

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

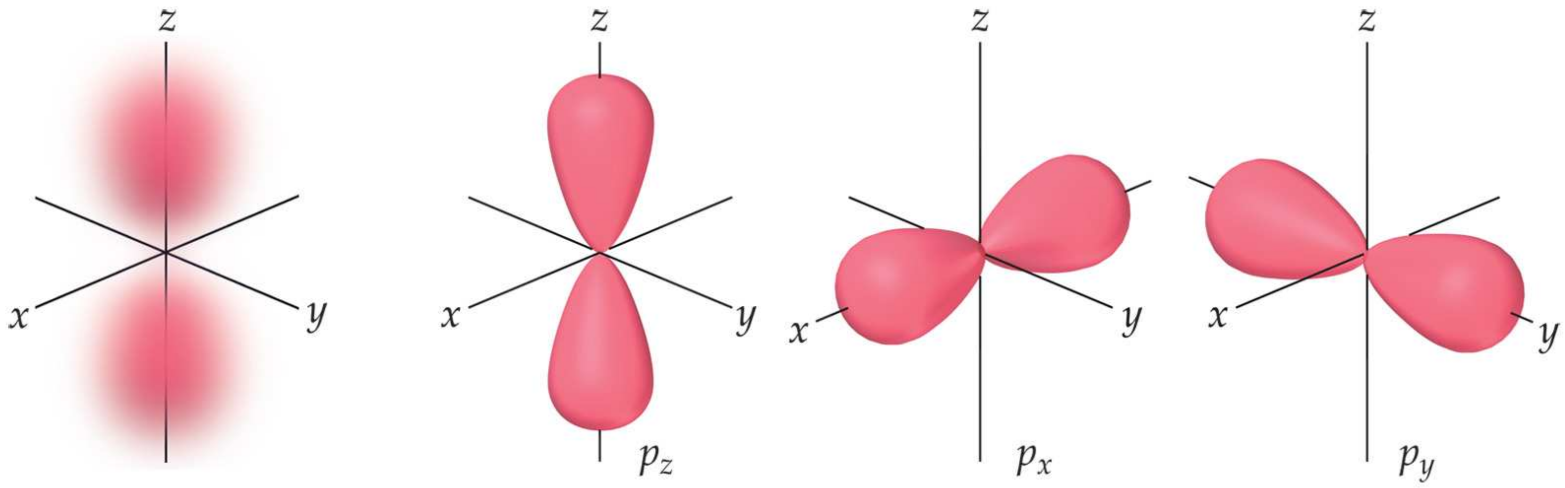
n	Possible Values of *l*	Possible Values of m_l	Subshell Designation
1	0	0	1*s*
2	0	0	2*s*
	1	1, 0, −1	2*p*
3	0	0	3*s*
	1	1, 0, −1	3*p*
	2	2, 1, 0, −1, −2	3*d*

S - Orbitals

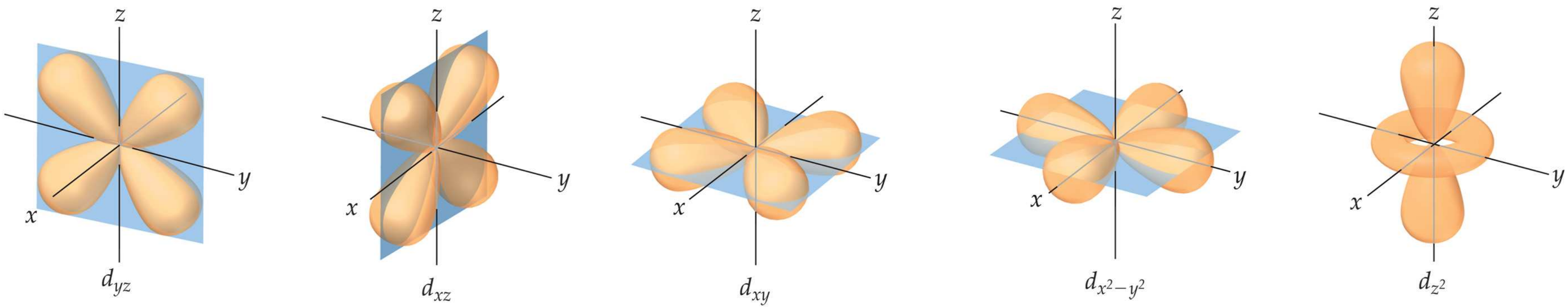


1s
n = 1, l = 0
2s
n = 2, l = 0
3s
n = 3, l = 0
Probability
1s
0 1 2 3 4 5 6 7 8 9 10
Distance from the nucleus, r (Å)
Probability
2s
0 1 2 3 4 5 6 7 8 9 10
Distance from the nucleus, r (Å)
Probability
3s
0 1 2 3 4 5 6 7 8 9 10
Distance from the nucleus, r (Å)

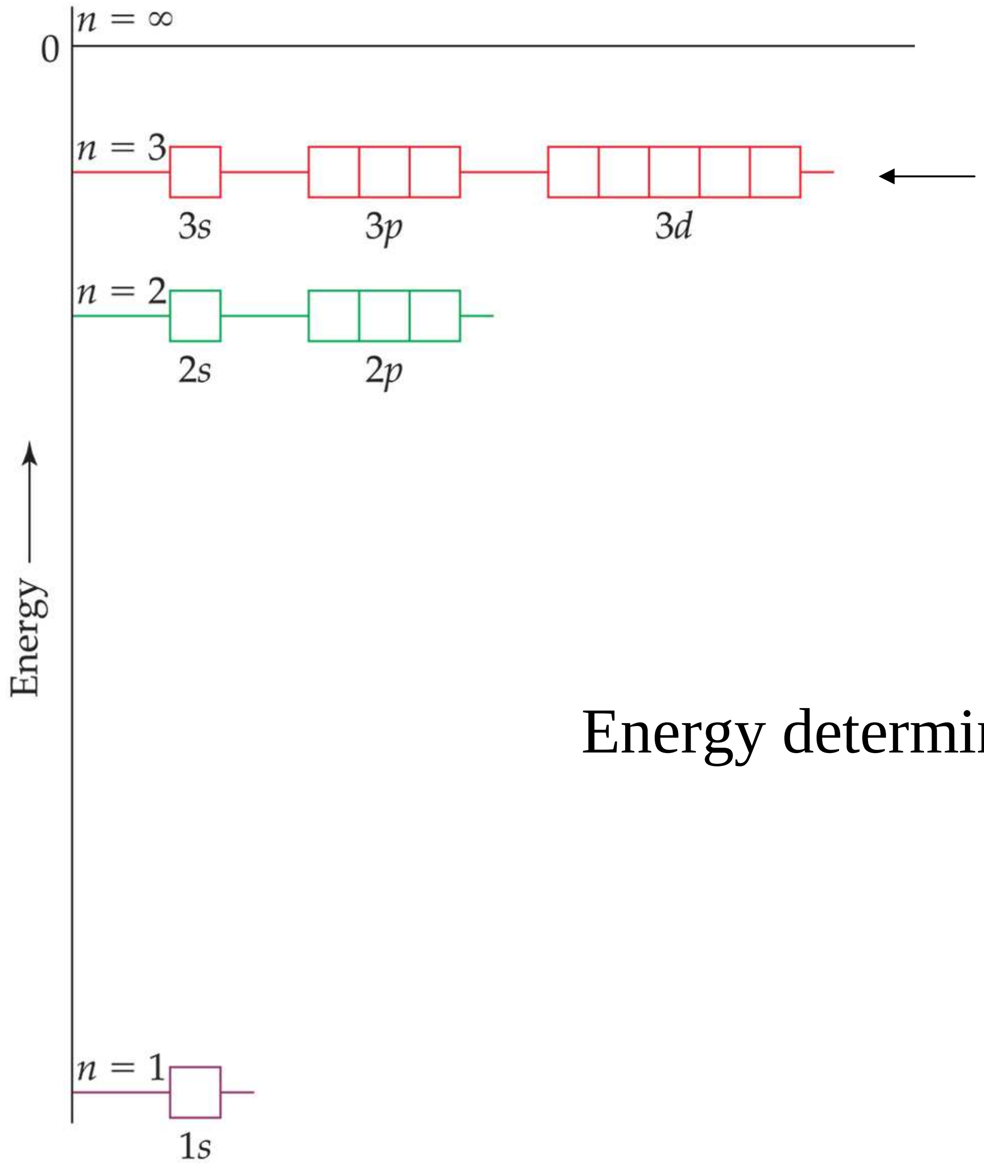
p – Orbital shapes



d – Orbital shapes



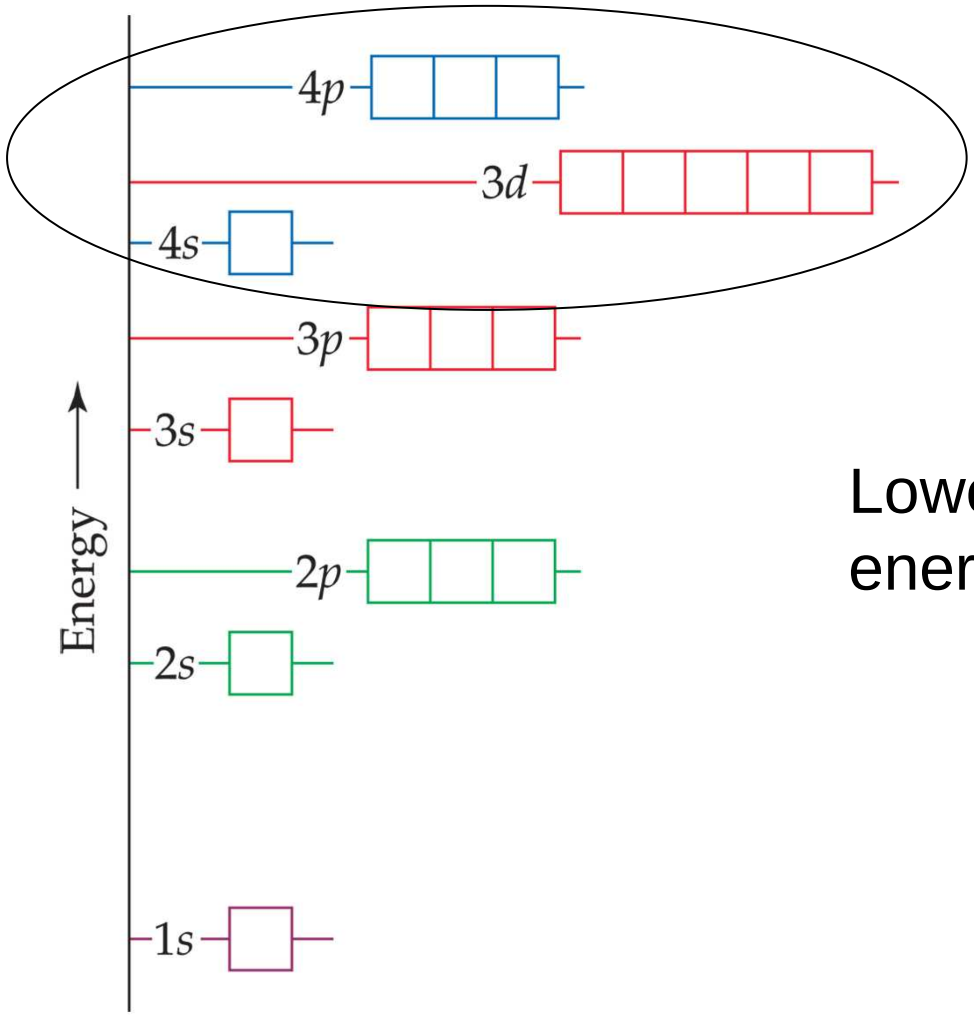
Energy of orbitals for 1 electron atom



Orbitals with the same energy level called *degenerate*

Energy determined by only by n

Energy of orbitals for multi-electron atom



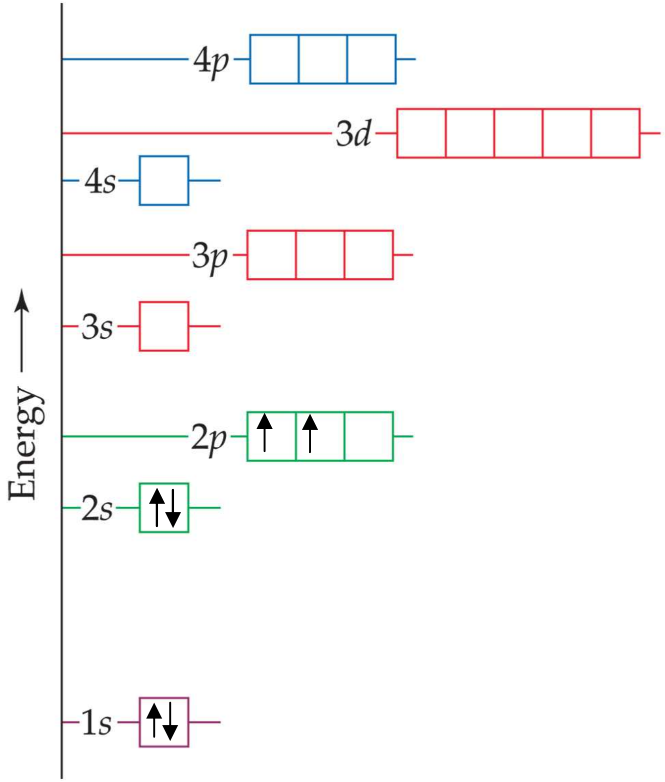
→ Strange order?

Lower energy s < p < d < f higher energy

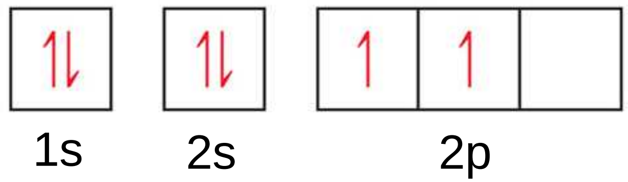
Putting Electrons in Orbitals

- 2 e^- can go into an orbital
- Pauli Exclusion principle says no two electrons can have the same set of quantum numbers
- If two electrons are in the same orbital, one will be spin up and one will be spin down
- Hund's Rule says that the lowest energy configuration for degenerate orbitals has maximum number of electrons with the same spin

C : 6 e^-



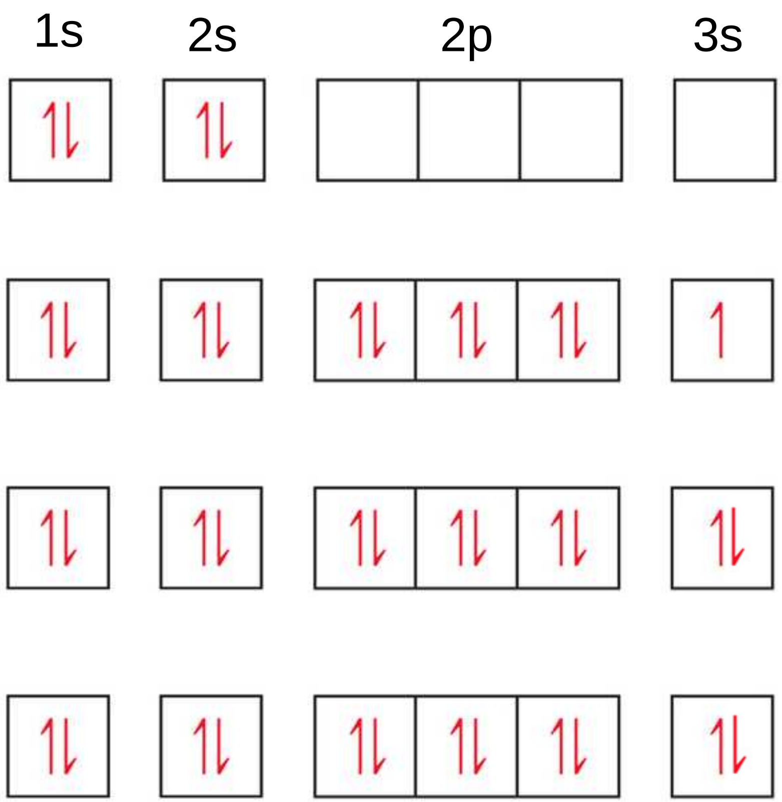
Orbital Diagram



Electron Configuration

C: $1s^2\ 2s^2\ 2p^2$

What's the correct orbital diagram and electron configuration for Mg?



A $1s^2\ 2s^2$

B $1s^2\ 2s^2\ 2p^6\ 3s^2$

C $1s^2\ 2s^2\ 2p^6\ 3s^2$

D $1s^2\ 2s^2\ 2p^6\ 3s^1$

Condensed Electronic Configuration

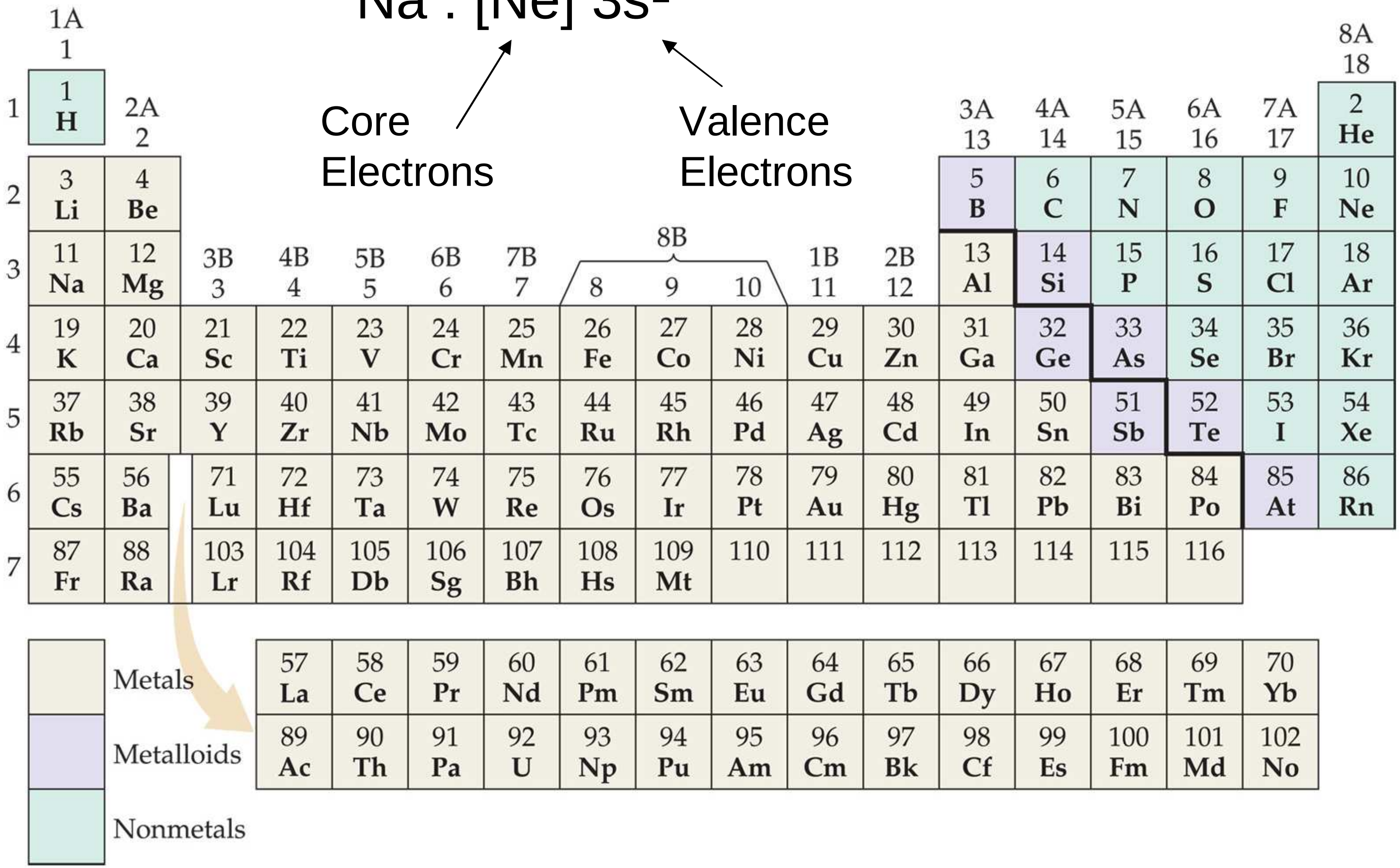
Na : $1s^2\ 2s^2\ 2p^6\ 3s^1$

Ne : $1s^2\ 2s^2\ 2p^6$

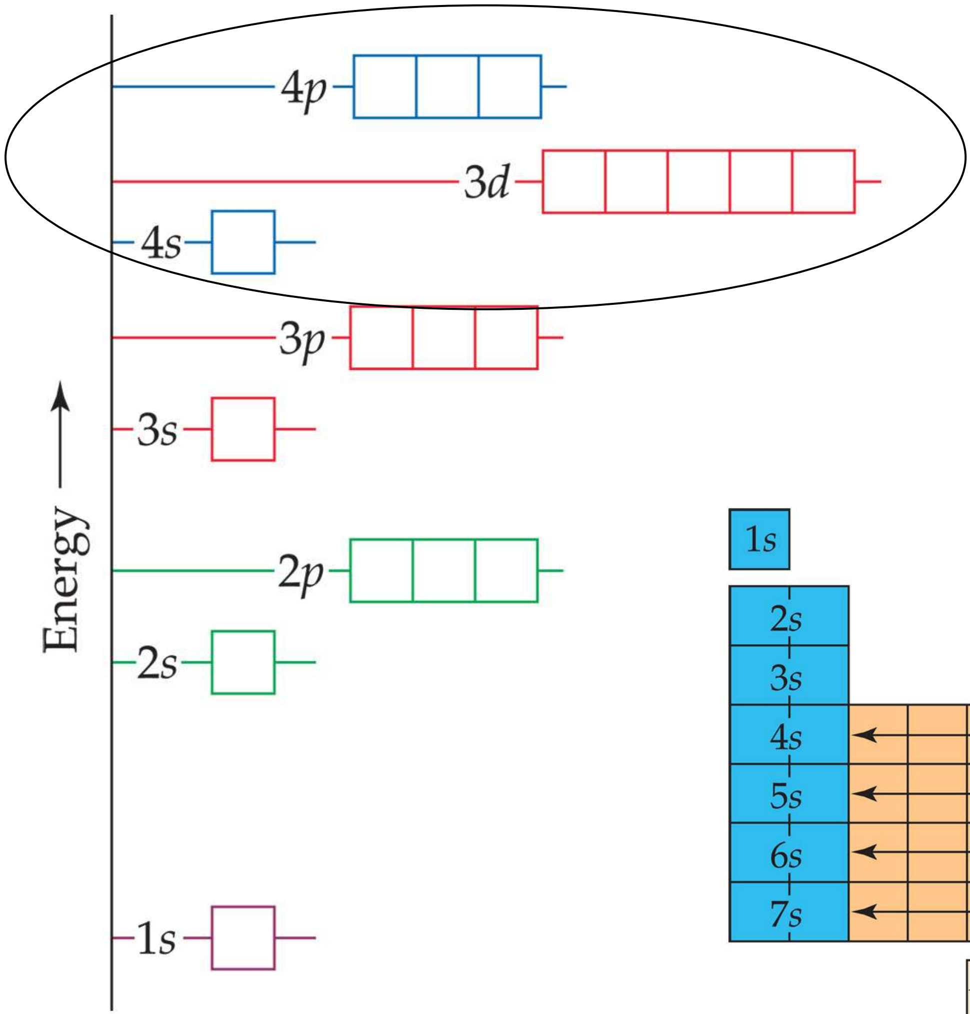
Na : $[Ne]\ 3s^1$

Core Electrons → [Ne]

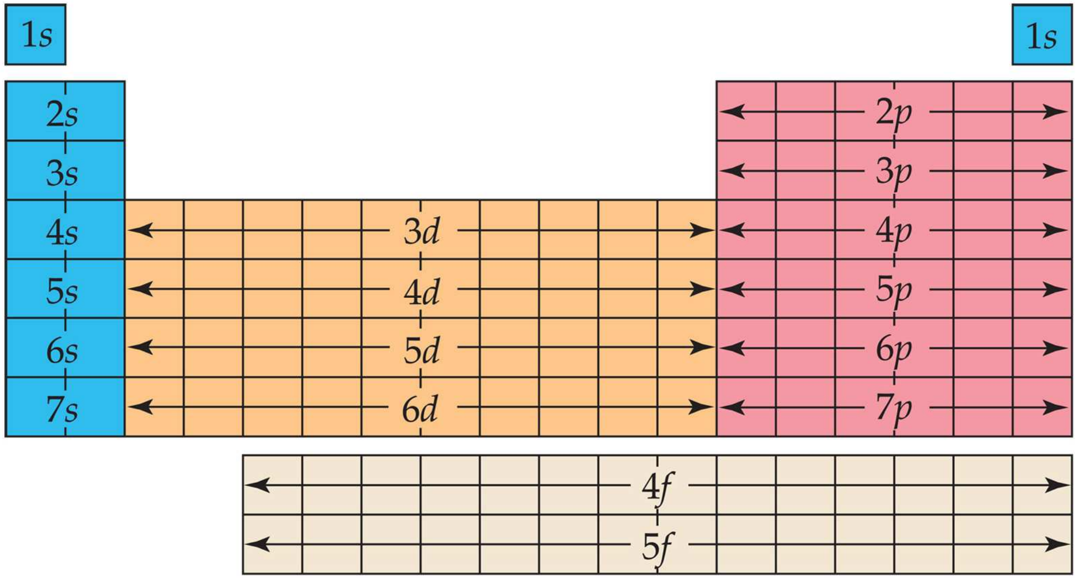
Valence Electrons → $3s^1$



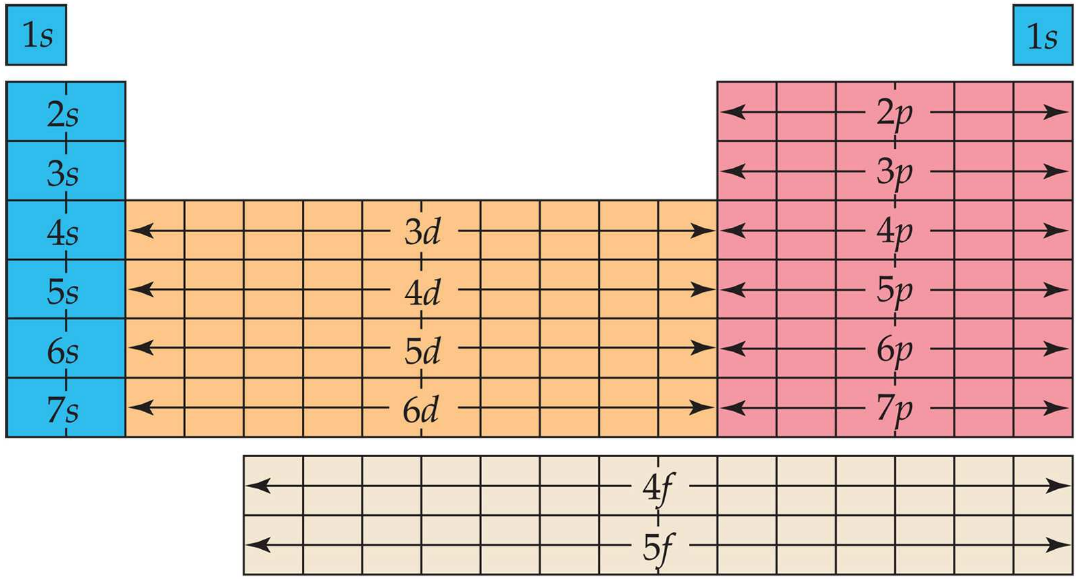
Energy of orbitals for multi-electron atom



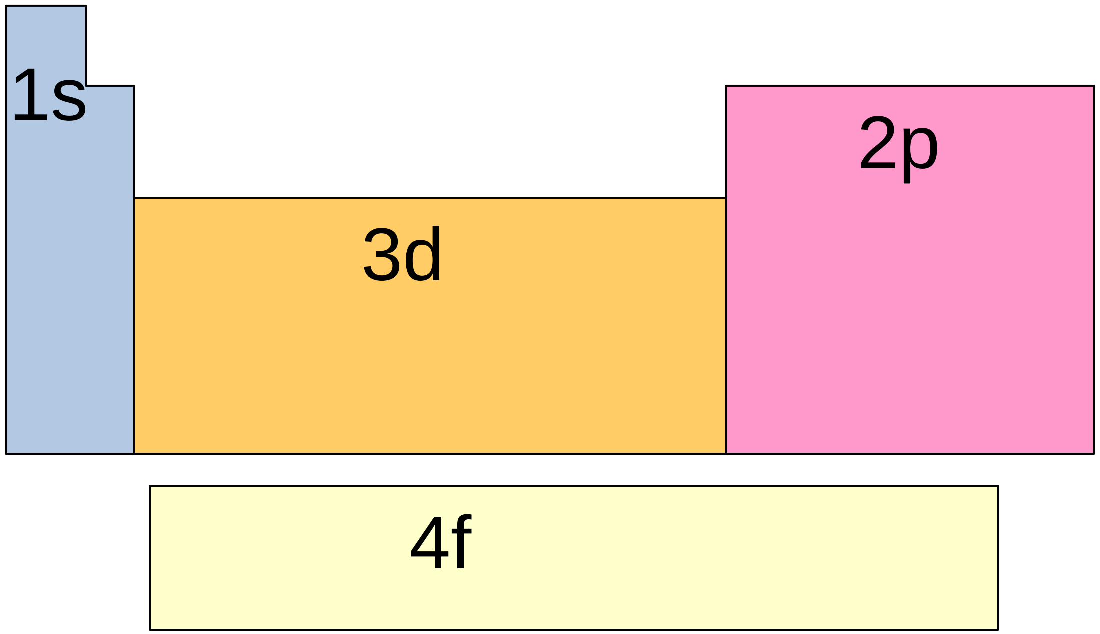
→ Strange order?



Periodic Table as an Electron Configuration MAP



Sections of table <u>begin</u> numbering rows as follows:



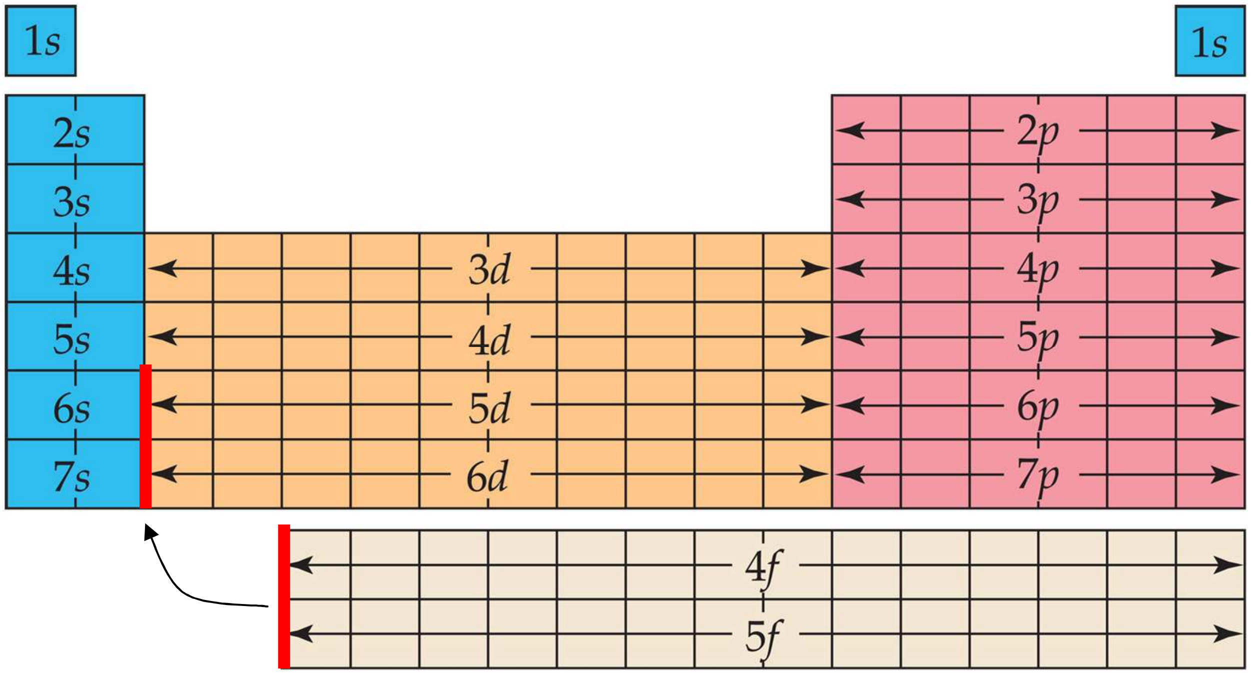
Based on the periodic table, which becomes orbitals are occupied first:

A. 6s

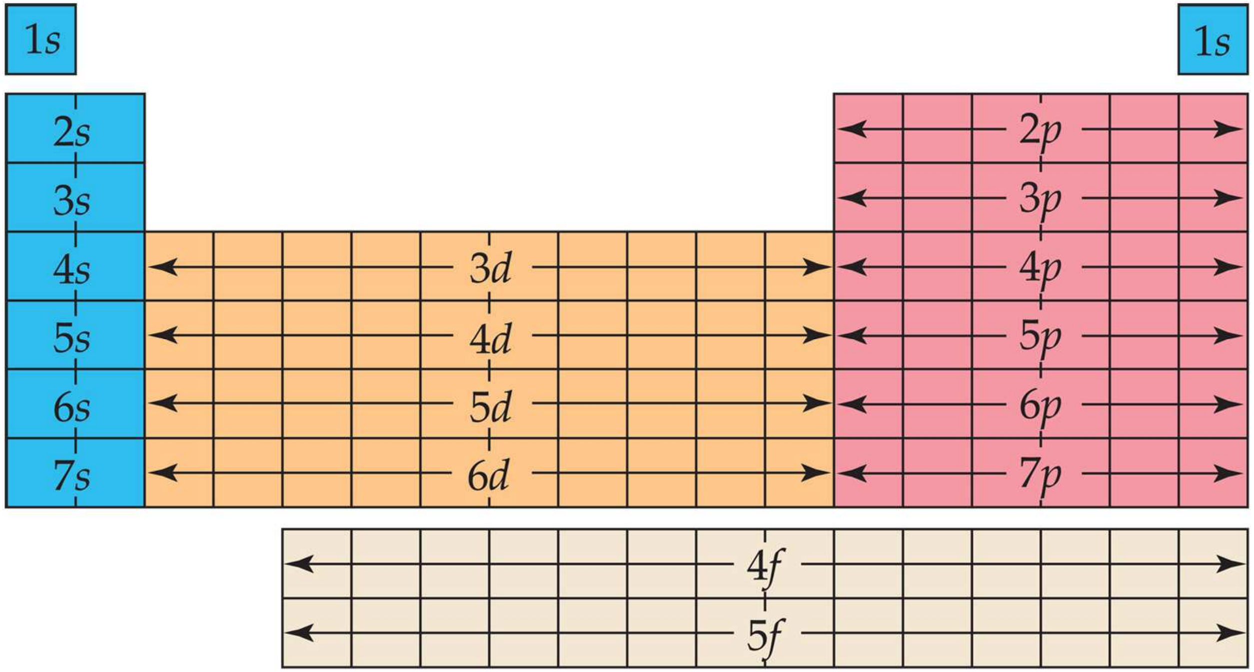
B. 4f

C. 6p

D. 4d



Some Examples of Condensed Electron Configuration

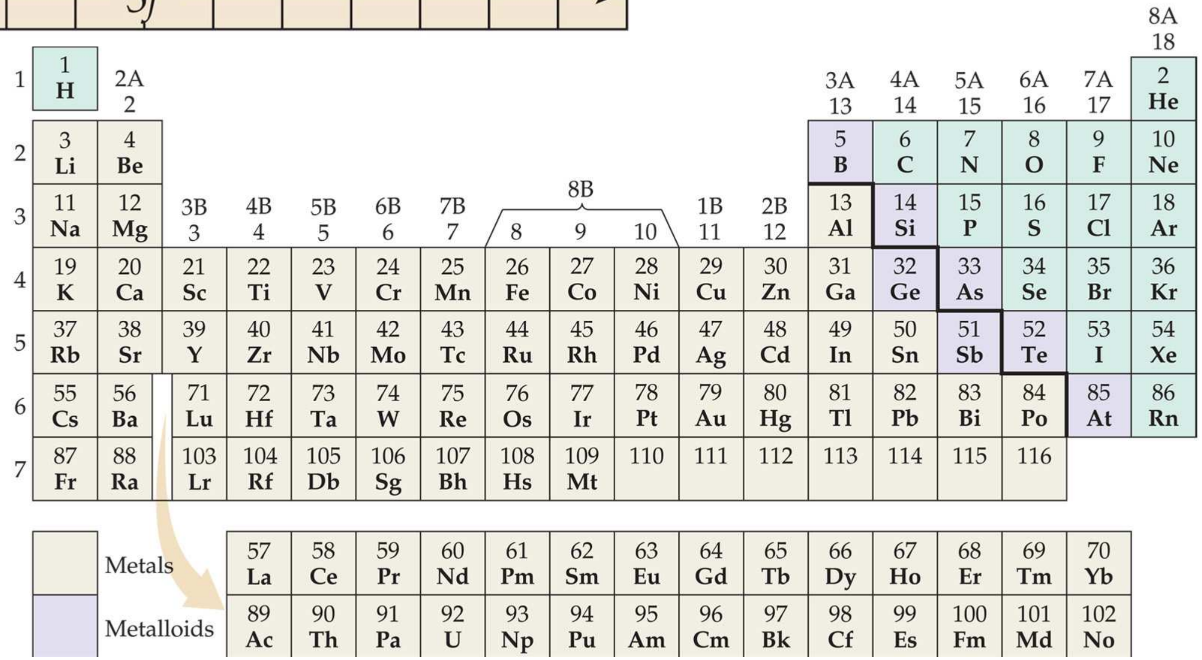


Ge

Ca

Sr

W



Electronic Configuration of all the Elements

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

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

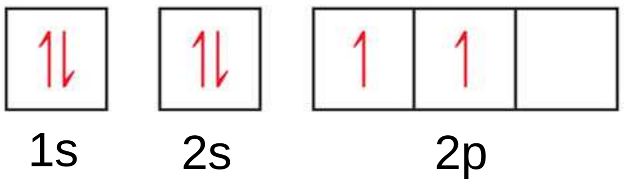
Orbitals and Electron Configuration Summary

Orbitals are regions of probability of finding an e^-

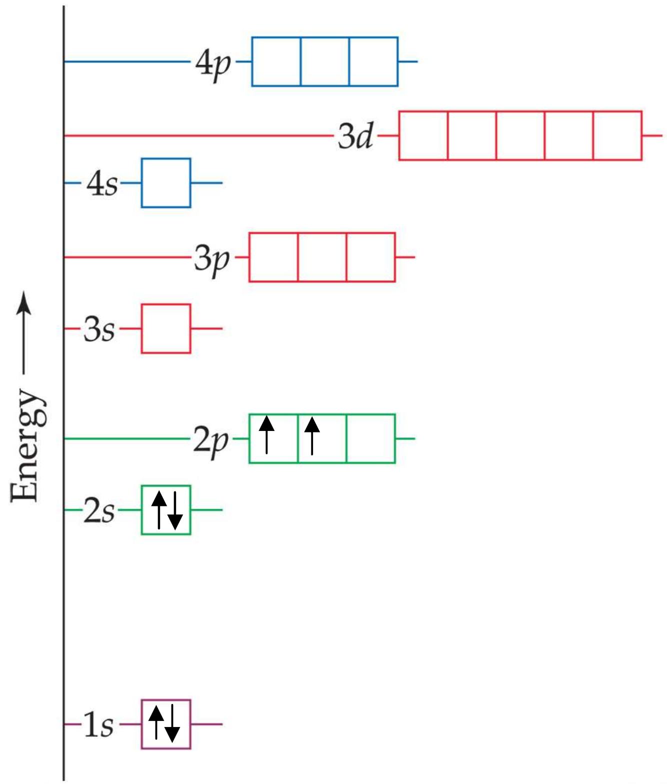
Orbitals defined by 3 quantum numbers, n, l, m_l

2 e^- per orbital, filled lowest energy first, then same spin, before pairing spins (Hund's rule)

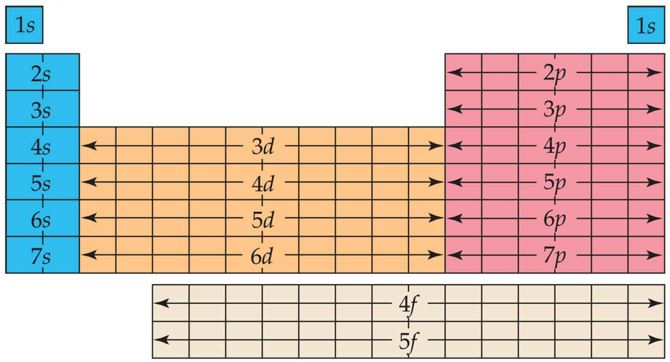
Filled orbitals can be represented by orbital diagrams or by electron configuration notation:



C: $1s^2\ 2s^2\ 2p^2$



The periodic table can be used as a guide know the order in which the orbitals get filled



Condensed notation (using a noble gas) can be used to summarize the core electrons so that valence electrons can be quickly identified

Mg: [Ne] $3s^2$