Atoms

Electromagnetic radiation

Energy is transferred by light.

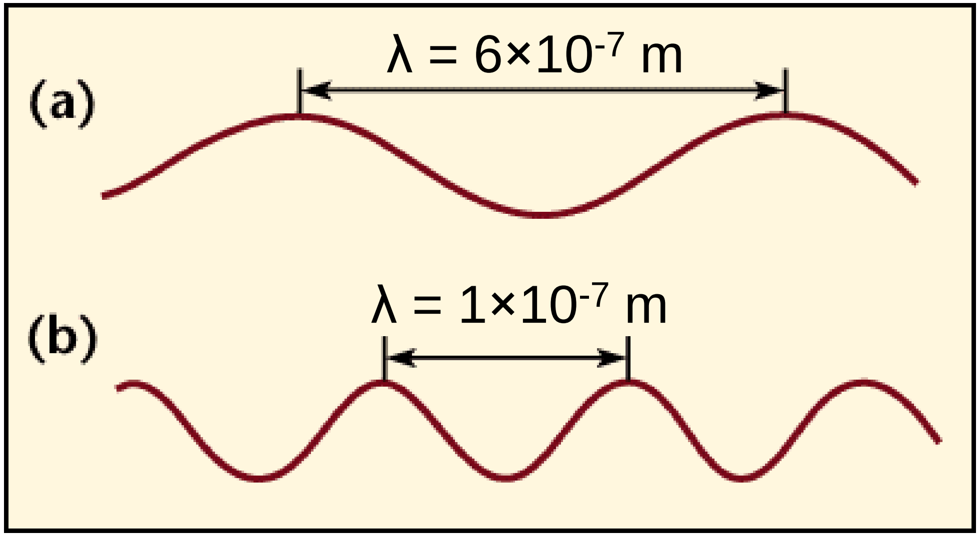
Electromagnetic radiation

A wave characterized by three properties:

Wave:
- Wavelength
- Frequency
- Speed

Electromagnetic radiation

Wavelength (λ): distance from one wave peak to the next.



Frequency (ν): number of peaks that pass a given point in one second.

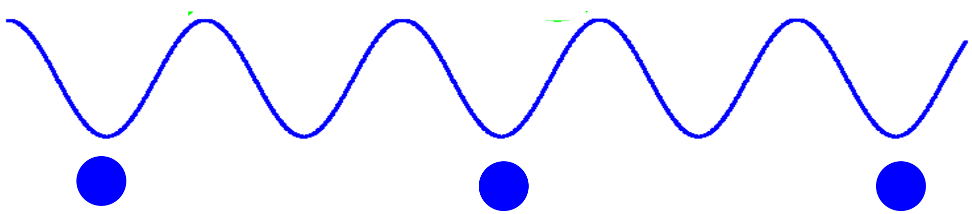
$$\lambda = \frac{c}{\nu}$$

c: speed of light = 3.0×10^8 m/s

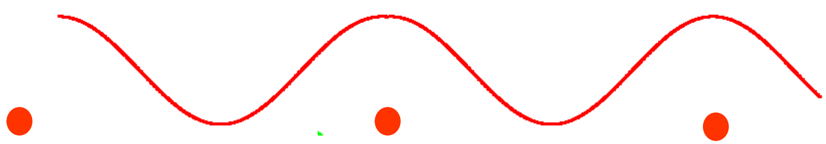
Electromagnetic radiation

Photon: a stream of tiny packets of energy.

(smallest unit of electromagnetic radiation)



shorter λ (higher ν) → higher energy



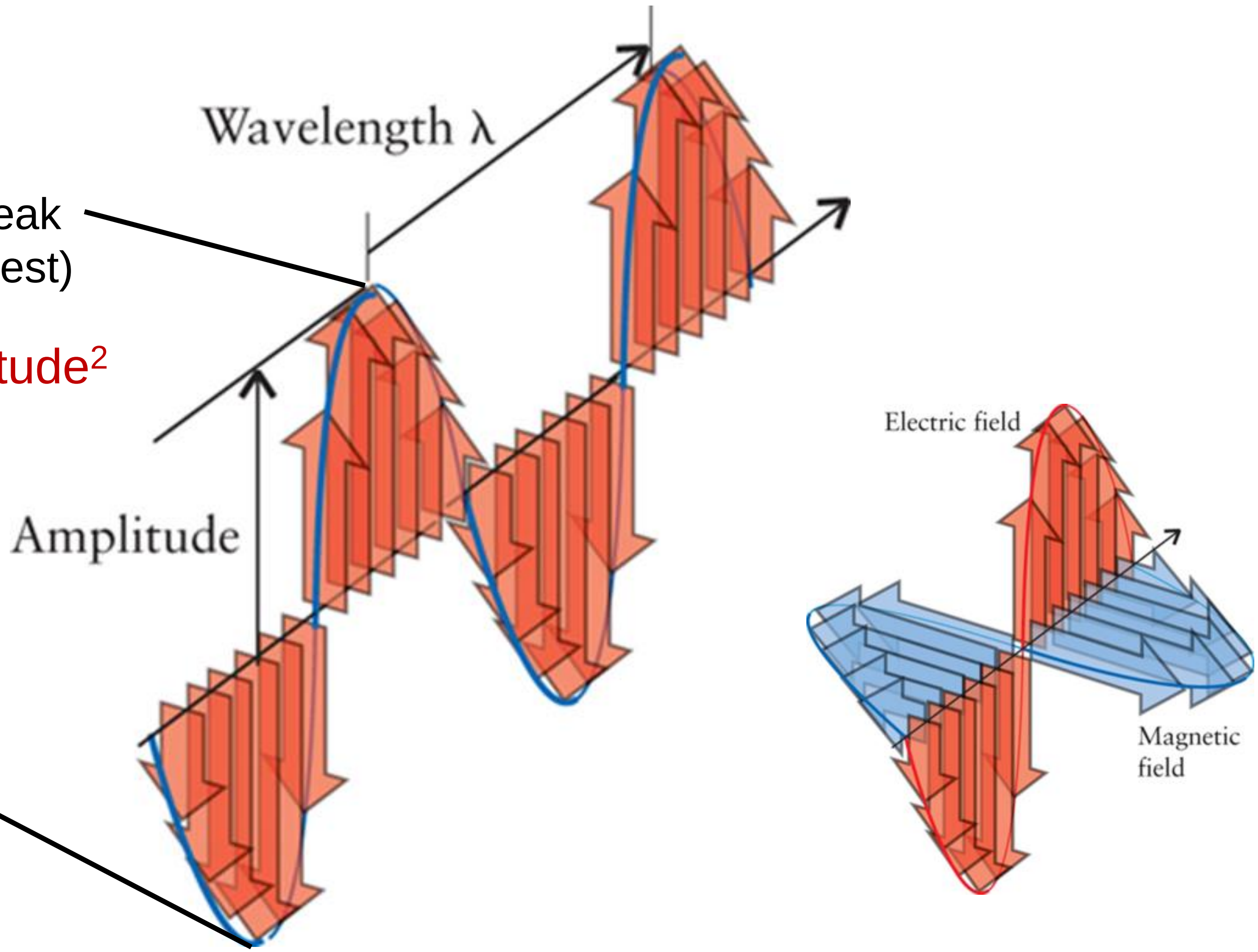
longer λ (lower ν) → lower energy

Electromagnetic radiation

Snapshot of an Electromagnetic Wave traveling 3.00×10^{8} ms^{-1} or 670 million mph:

Peak (crest)

Intensity = amplitude^2

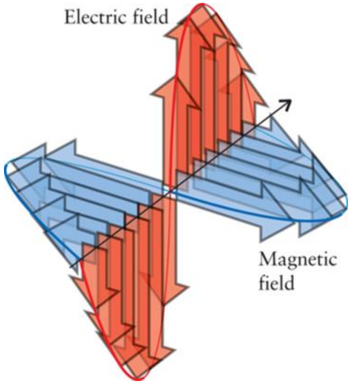


Trough

The Electric component of photons is the portion that pushes electrons.

TABLE 1.1 Color, Frequency, and Wavelength of Electromagnetic Radiation

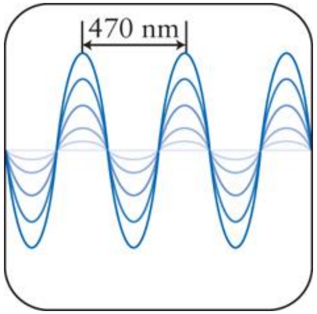
Radiation type	Frequency (10^{14} Hz)	Wavelength (nm, 2 sf)*	Energy per photon (10^{-19} J)
x-rays and γ-rays	$\geq 10^3$	≤ 3	$\geq 10^3$
ultraviolet	8.6	350	5.7
visible light			
violet	7.1	420	4.7
blue	6.4	470	4.2
green	5.7	530	3.8
yellow	5.2	580	3.4
orange	4.8	620	3.2
red	4.3	700	2.8
infrared	3.0	1000	2.0
microwaves and radio waves	$\leq 10^{-3}$	$\geq 3 \times 10^6$	$\leq 10^{-3}$



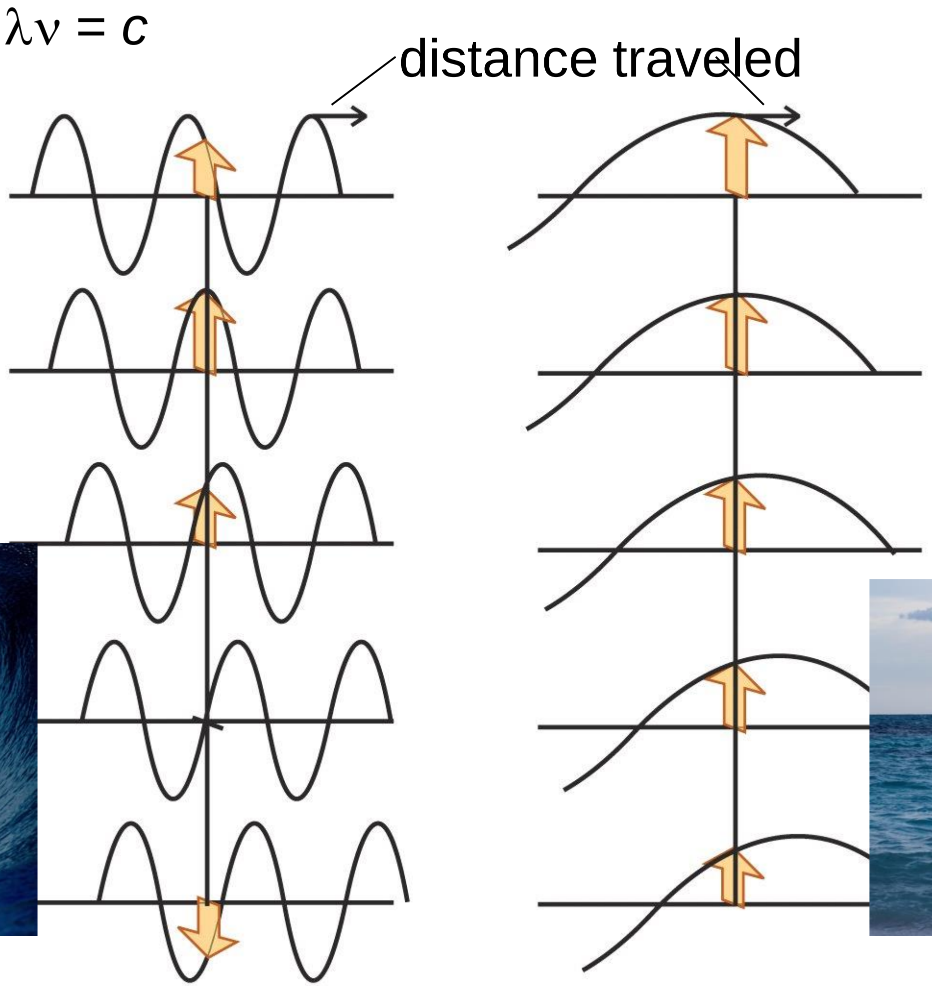
wavelength × **frequency** = speed of light ($\lambda\nu = c$)

1 Hz = 1s^{-1}

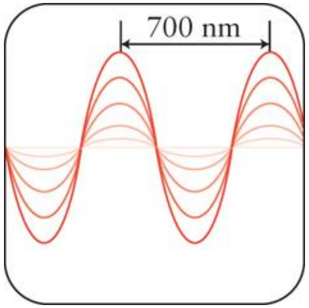
wavelength × frequency = speed of light ($\lambda\nu = c$)



Blue light has $\lambda\downarrow$, $\nu\uparrow$



(a) Short wavelength, high frequency (b) Long wavelength, low frequency

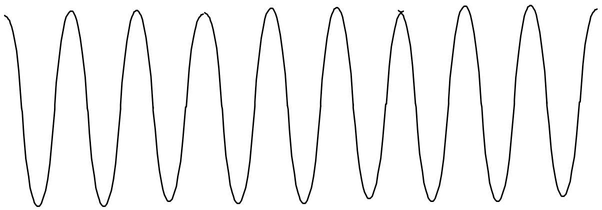


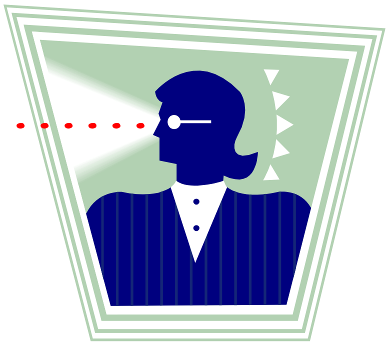
Red light has $\lambda\uparrow$, $\nu\downarrow$

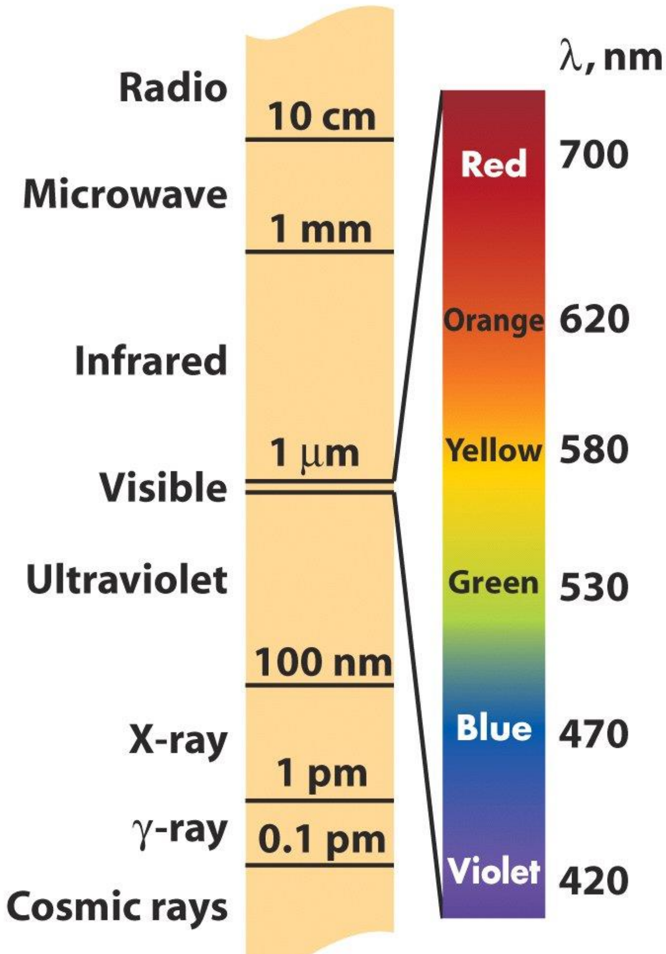
Large changes in electric field

Small changes in electric field

It’s all about wavelength size







If we had X-ray vision

If we had infrared vision

visible vision

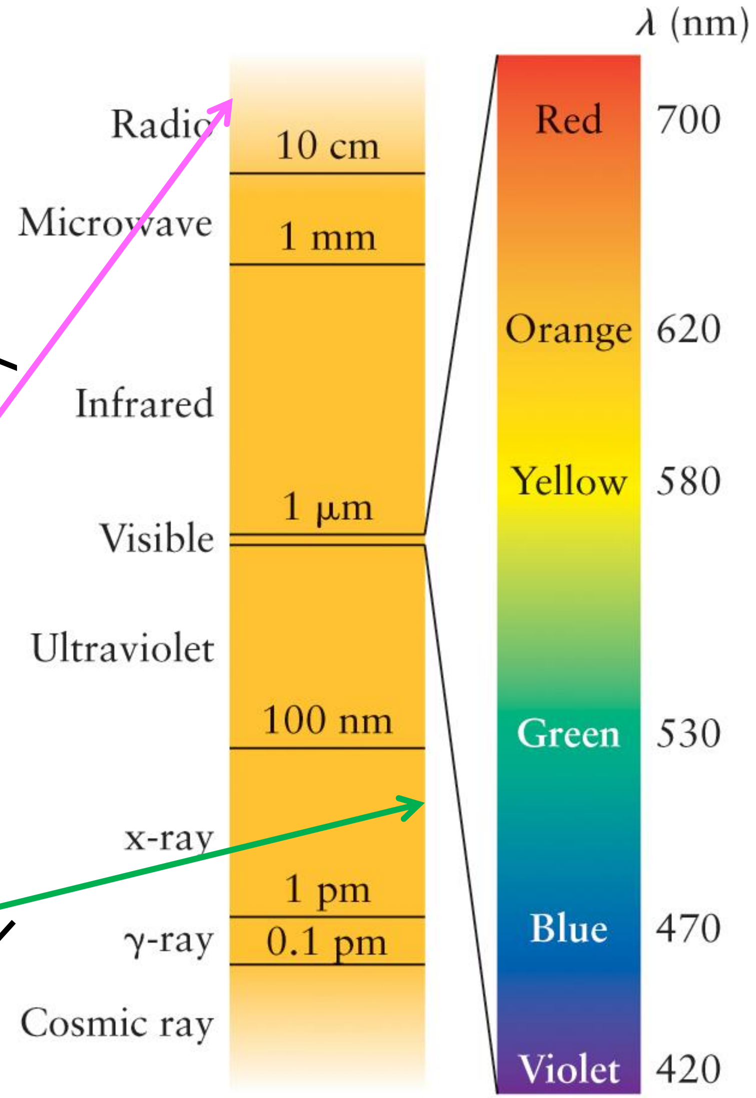
Practice 1: What is the wave length of the signal from a radio station transmitting at 98.4 MHz ?

$$\lambda\nu = c \quad or \quad \lambda = \frac{c}{\nu}$$

Experienced as heat.

$$\lambda = \frac{3.00 \times 10^8 ms^{-1}}{9.84 \times 10^6 s^{-1}} = 30.5\ m$$

or 100 feet



Practice 2: Calculate the wavelength of 5.75×10^{14} Hz

$$\frac{3 \times 10^8 ms^{-1}}{5.75 \times 10^{14} s^{-1}} = 521 \text{ nm; Green}$$

Absorbed by the ozone layer.

Electro-magnetic Force

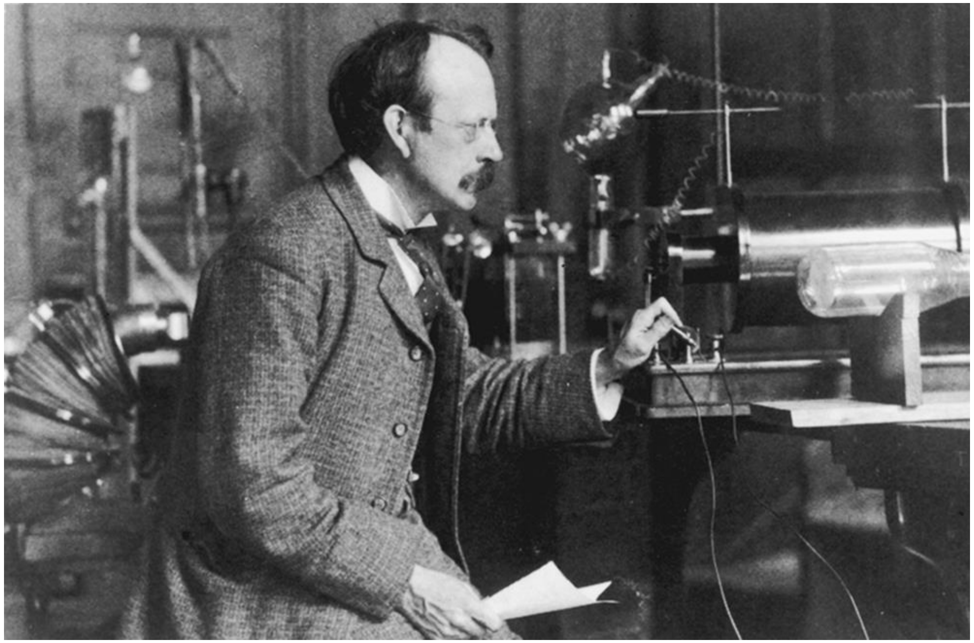
Electromagnetism is the study of electrical charge

a) Light
b) Lightening or static electricity
c) Batteries

4 known forces in the universe:

1. **Strong force**: called the gluon that holds protons to neutrons, experienced as atomic bombs;
2. **Weak force**: holds the neutron together, the proton and electron, experienced as radiation;
3. **Electro-magnetic force**: called the photon and it’s relative electron, it holds atoms, molecules together and responsible for how we see-light, this force is what humans experience all the time;
4. **Gravitational force**: holds the universe together.

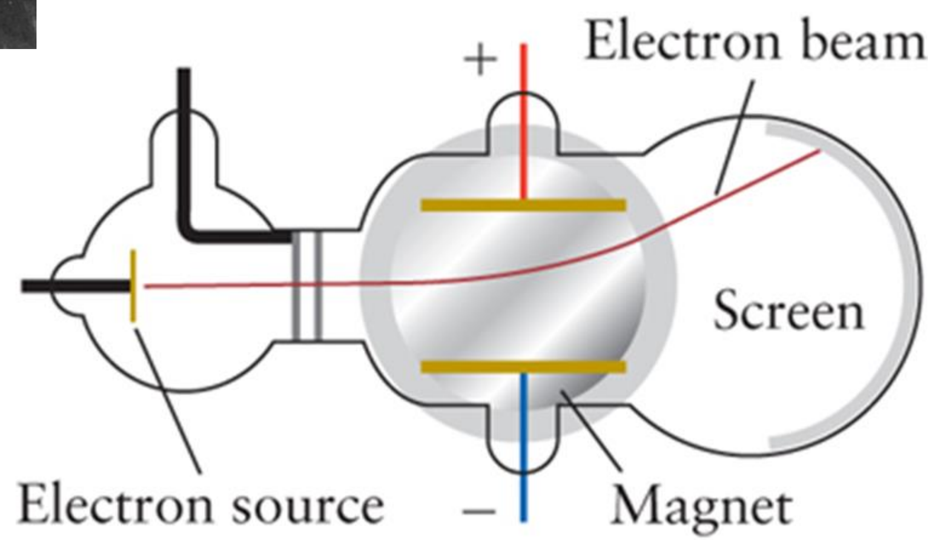
Nuclear Atom



In 1897 British physicist **J. J. Thomson** provided the earliest evidence that atoms had **internal structure**.

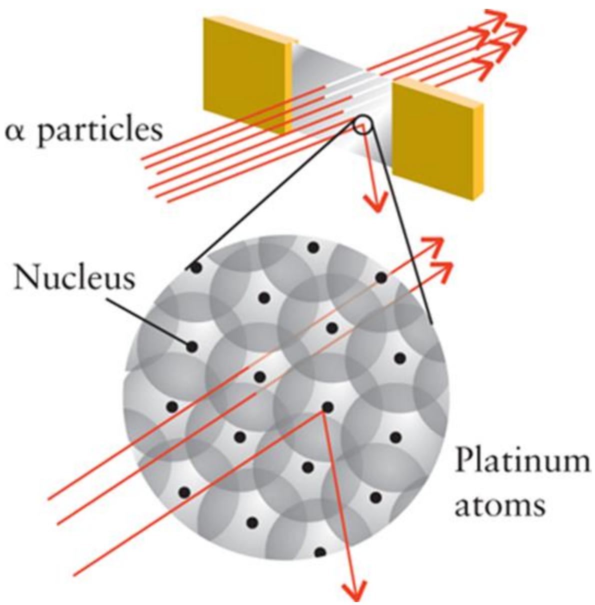
Thomson was able to measure the value of $\frac{-e}{m_e}$, the ratio of an electron's charge **-e** to its mass $\mathbf{m_e}$

Cathode rays

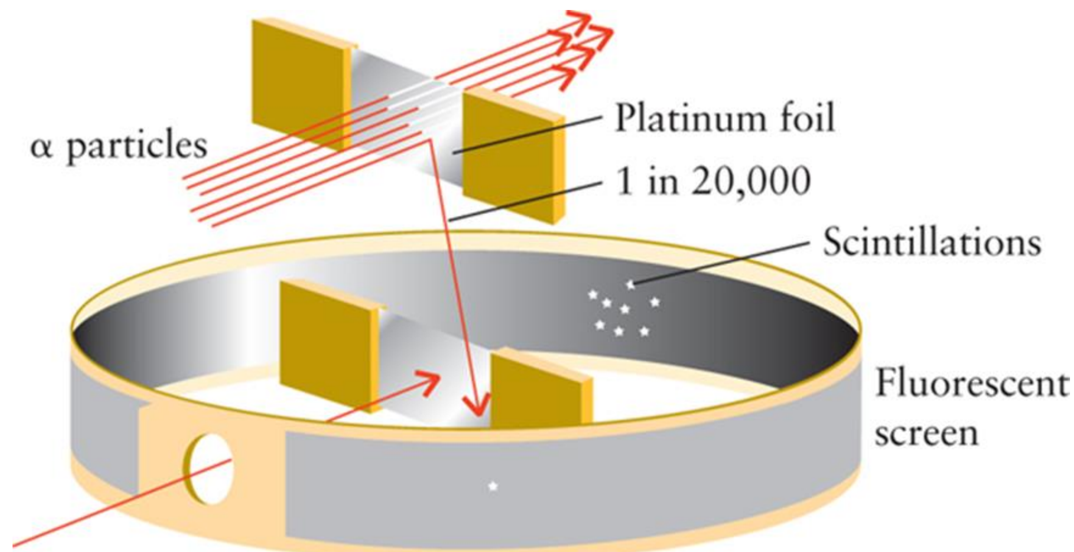


Nuclear Atom

Thomson suggested a model of an atom as a blob of a positively charged, jellylike material, with the electrons suspended in it like raisins in pudding. **Rutherford** tested Thompson's hypothesis.



Firing α-particles at Pt, "It was almost as incred-ible," said Rutherford, "as if you had fired a 15-inch shell at a piece of tissue paper and it had come back and hit you."



Almost all the mass is concentrated in the tiny nucleus

Electromagnetic radiation emitted by a heated **Black Body** caused one of the greatest revolutions that has ever occurred in science.

The "hot object" is known as a black body (even though it might be glowing white hot!).

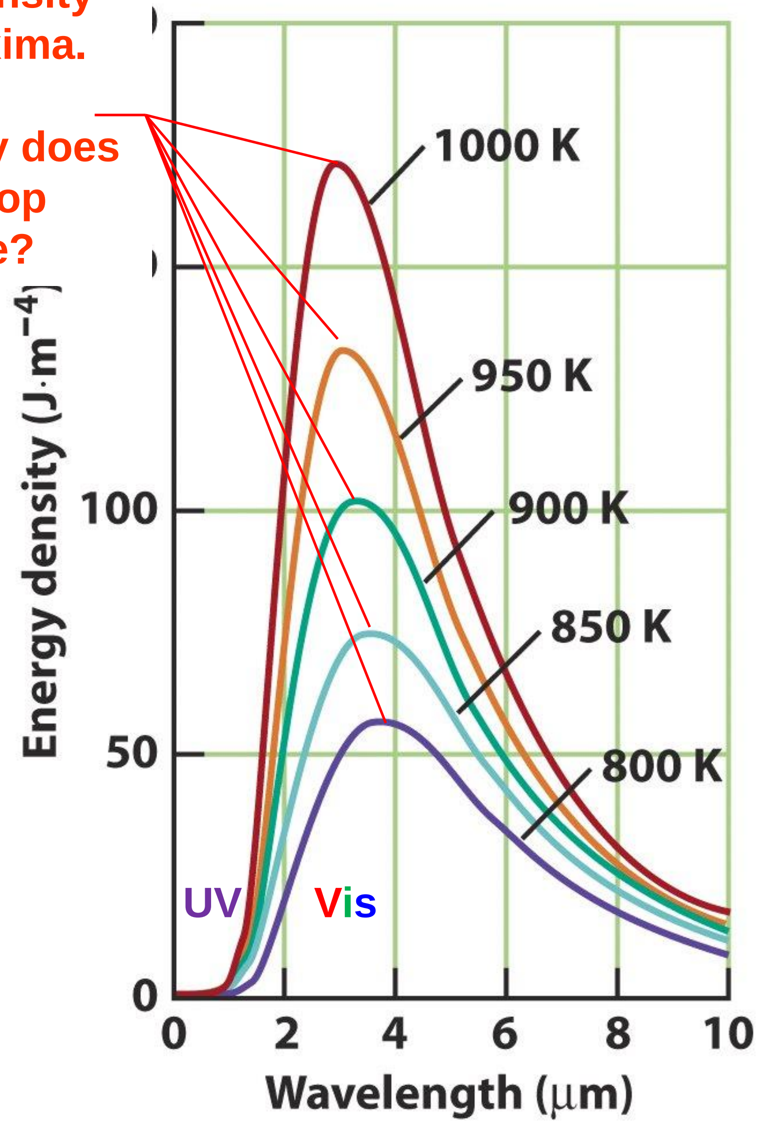
At high temperatures an object begins to glow—the phenomenon of **incandescence**. As the object is heated to higher temperatures it glows more brightly, and the color of light it gives off changes from red through orange and yellow toward white.

The problem is the curve should be linear, going straight **UP**, <u>not dying away in **UV**</u>!

All objects give off radiation

Intensity Maxima.

Why does it stop here?



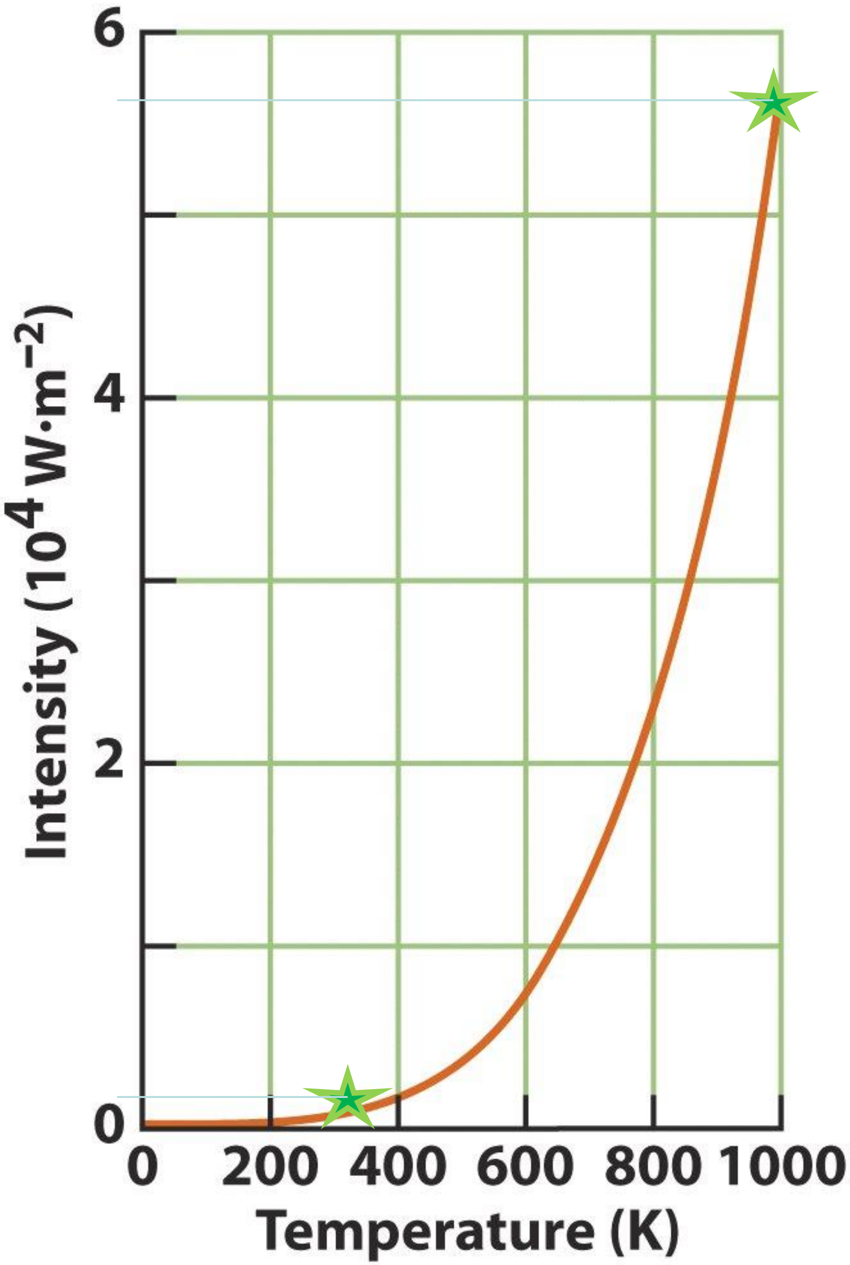
Stefan-Boltzmann Law

Describes the **behavior** of Blackbody Radiation-intensity/temp

Total intensity = constant × T^4

The **total intensity** of radiation emitted increases as the fourth power of the temperature.

A body at 1000 K emits 120 times more energy as is emitted at 300 K.

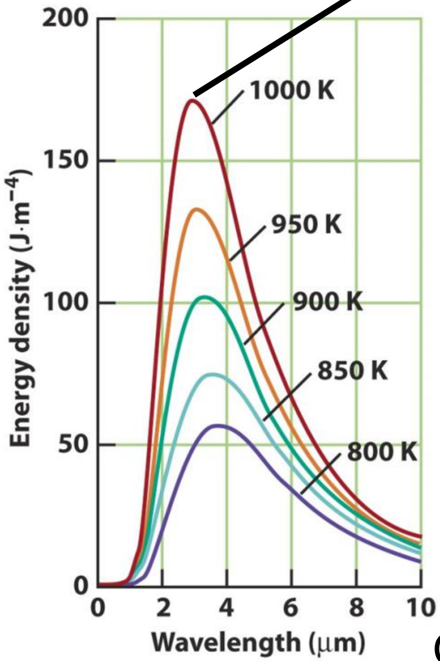


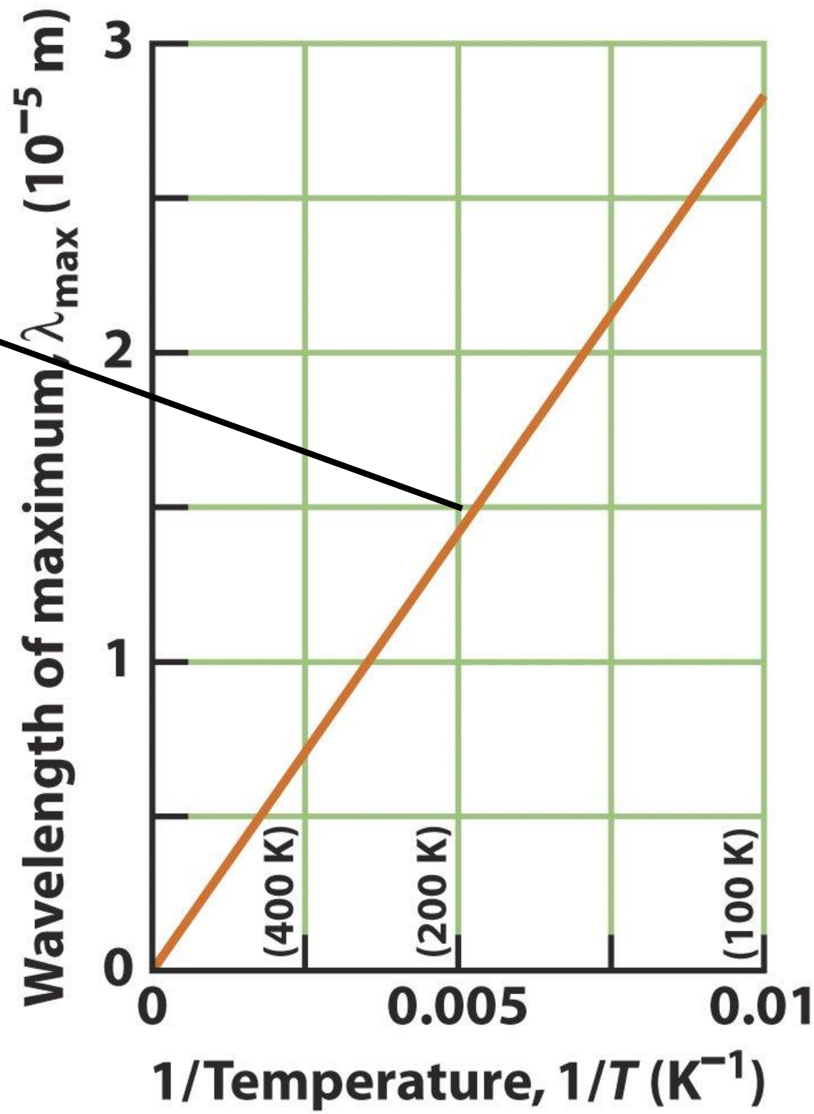
Wien's Law

Shows that a **maxima existed** in Blackbody radiation

Inverse Relationship
As $T\uparrow$, $\lambda_{max}\downarrow$

intensity maxima





$\lambda_{max}\ \alpha$ **1/T**

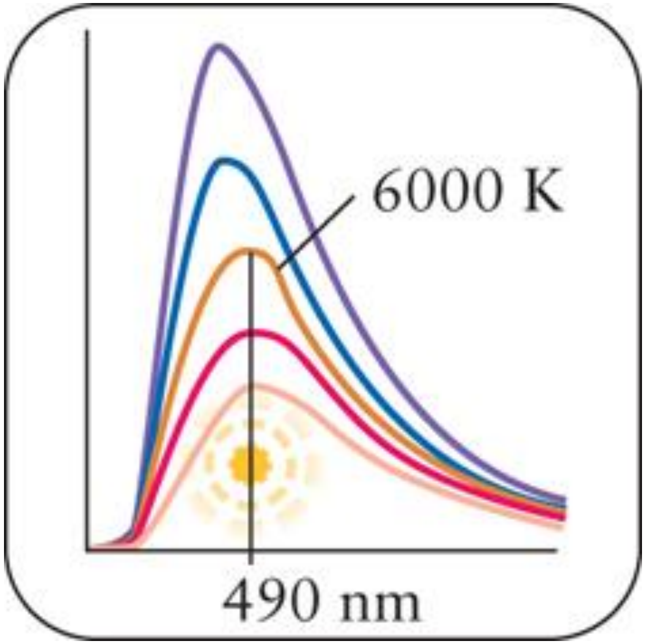
$\boxed{T\lambda_{max} = \textbf{constant}}$

Often used by astronomers to measure a stars surface temperature.

Practice 3: The maximum intensity of solar radiation occurs at 490. nm. What is the temperature of the surface of the Sun?

$T\lambda_{max}$ = constant

$$T = \frac{2.9 \times 10^{-3} m \cdot K}{4.90 \times 10^{-7} m} = \quad 5.9 \times 10^{3}\ K$$



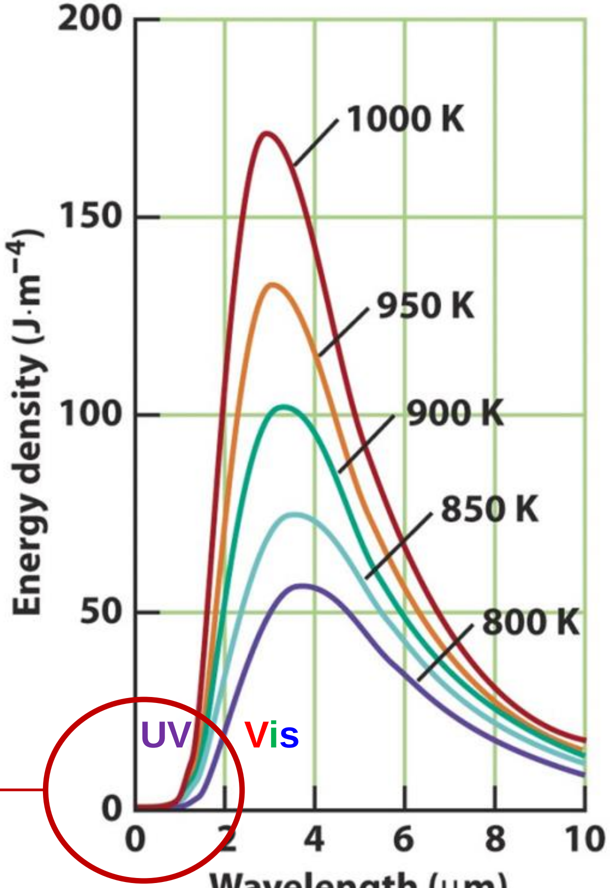
That is, the surface temperature of the Sun is about 6000 K.

Ultraviolet Catastrophe

Atoms give off light as they get hotter because atoms oscillate (like a spring) and the electrons start jumping around inside the atom. But we only observe color up to ultraviolet radiation no matter how hot!

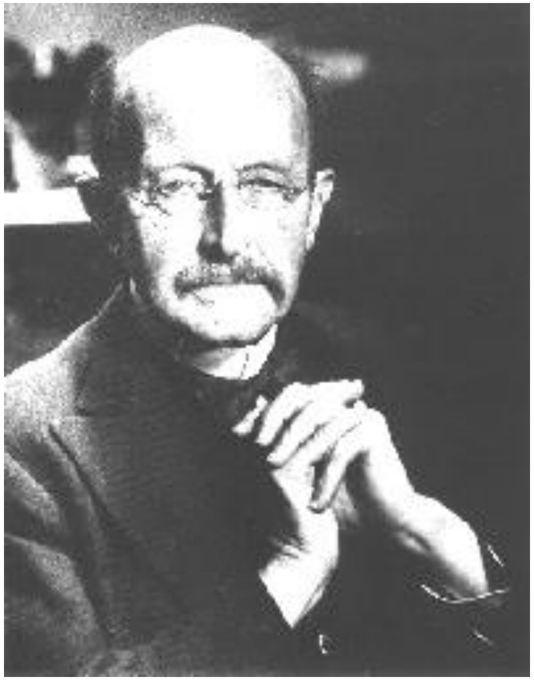
A **human body** at 37 ℃ would glow in the dark.

There would, in fact, be no **darkness**.



Where are the ultraviolet, x-ray, and γ-ray radiations with a low wavelength?

Planck Law



Max Planck hypothesizes that oscillations start at a particular energy level with a minimum energy.

To make oscillations occur at higher energies requires a specific or minimum amount of energy or "**Packet**" sometimes called quanta- hints at Particles!

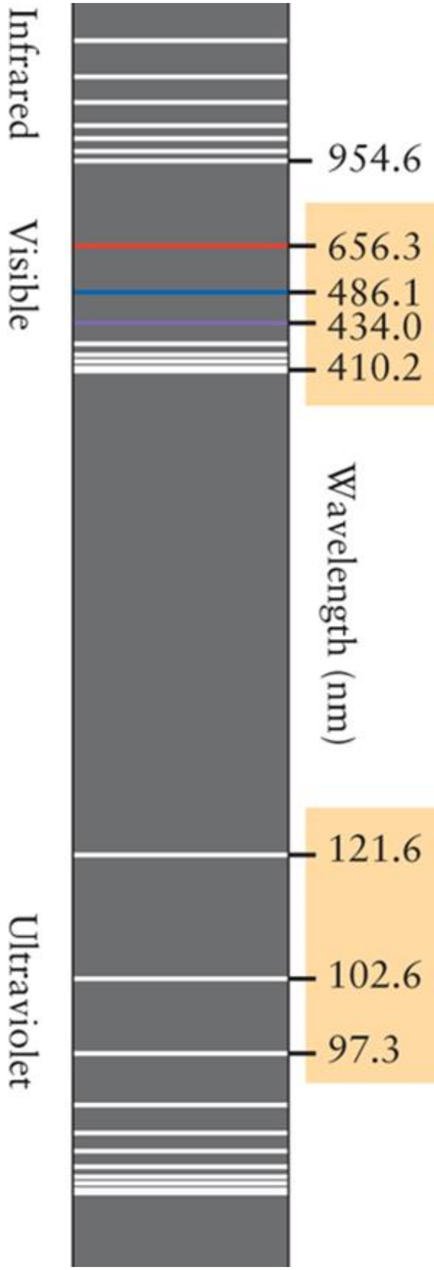
$$\boxed{E = h\upsilon}$$

h **= 6.626 × 10^{-34} Js**
Plank's constant

Planck describes that atomic vibrations as requiring a "minimum" amount of energy to "move."

At low T, there is not enough energy to stimulate oscillations at very high frequencies-short wavelengths (it explains ultraviolet catastrophe).

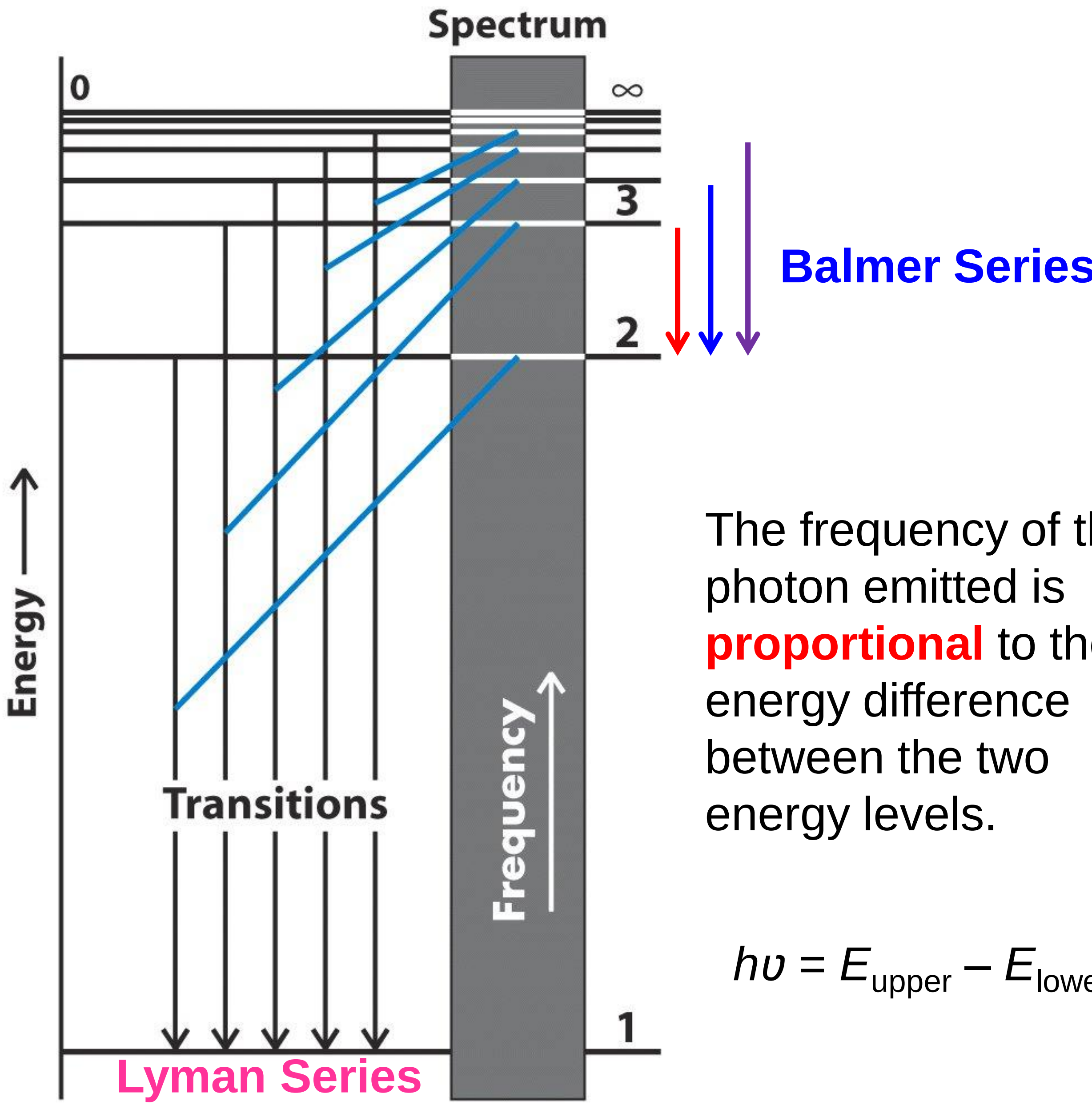
The simplest atom: hydrogen



When an **electric current** passes through a sample of "**PURE**" hydrogen gas, the electric current acts like a storm of electrons, **exciting the electrons** in the atom to higher and higher energies.

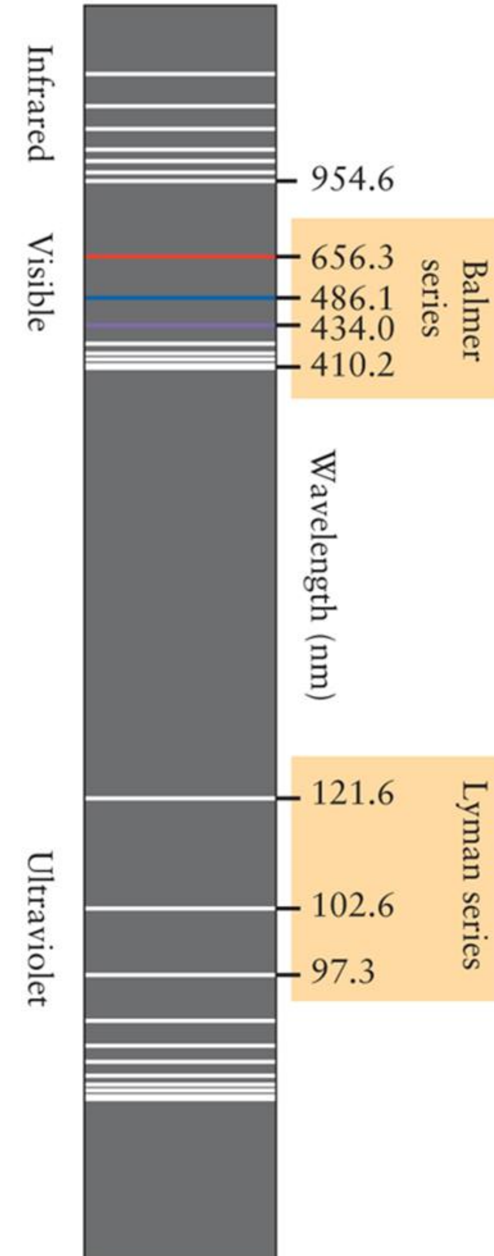
Excited **electrons quickly discard** excess energy by **emitting light**.

Each spectral line corresponds to an electron transition between two specific states, showing the particle nature.

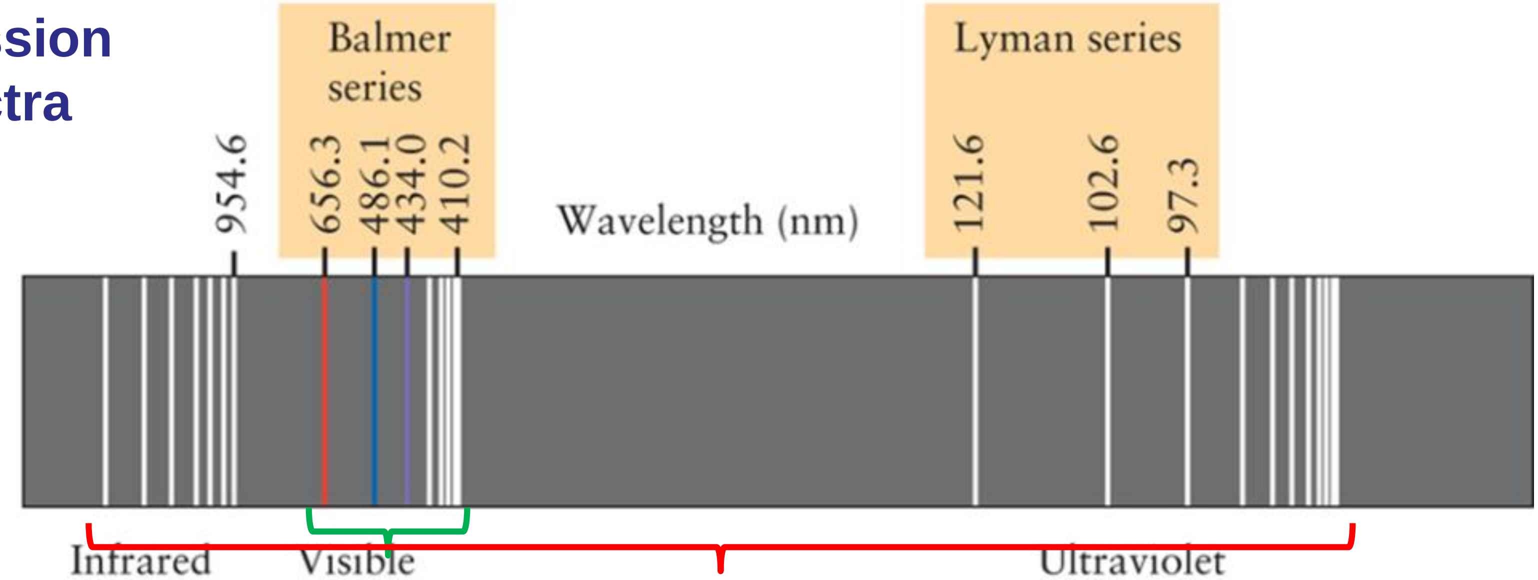


The frequency of the photon emitted is **proportional** to the energy difference between the two energy levels.

$$h\upsilon = E_{\text{upper}} - E_{\text{lower}}$$



Emission Spectra



Joseph **Balmer**, a Swiss schoolteacher 1885, identified a pattern in the lines of the visible region of the spectrum. The frequencies of all the lines could be generated by:

$$\lambda \propto \frac{n^2}{n^2 - 4} \quad n = 3, 4, \ldots$$

As experimental techniques advanced, more lines were discovered, and the Swedish spectroscopist Johann **Rydberg** noticed that **all** of the **lines** could be predicted from the expression:

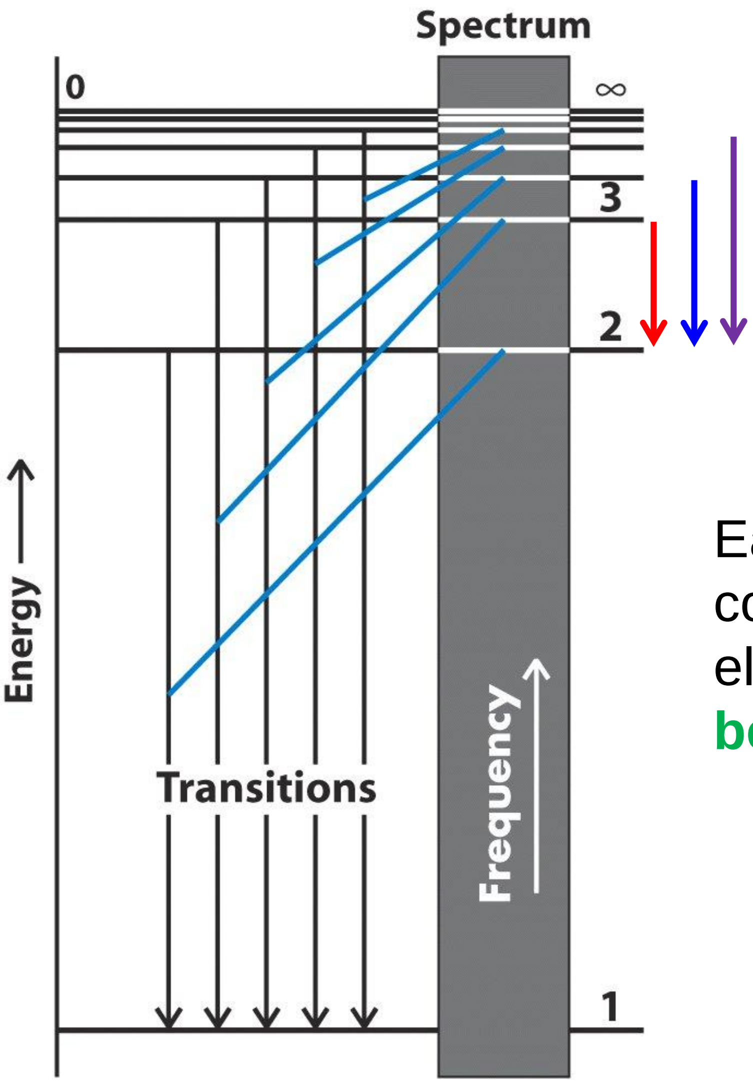
Where $n_2 = n_1 + 1, n_1 + 2, \ldots.$

$$\nu = \mathcal{R}\left(\frac{1}{{n_1}^2} - \frac{1}{{n_2}^2}\right) \quad n_1 = 1, 2, \ldots.$$

R: Rydberg constant = 3.29×10^{15} Hz

Bohr's Theory

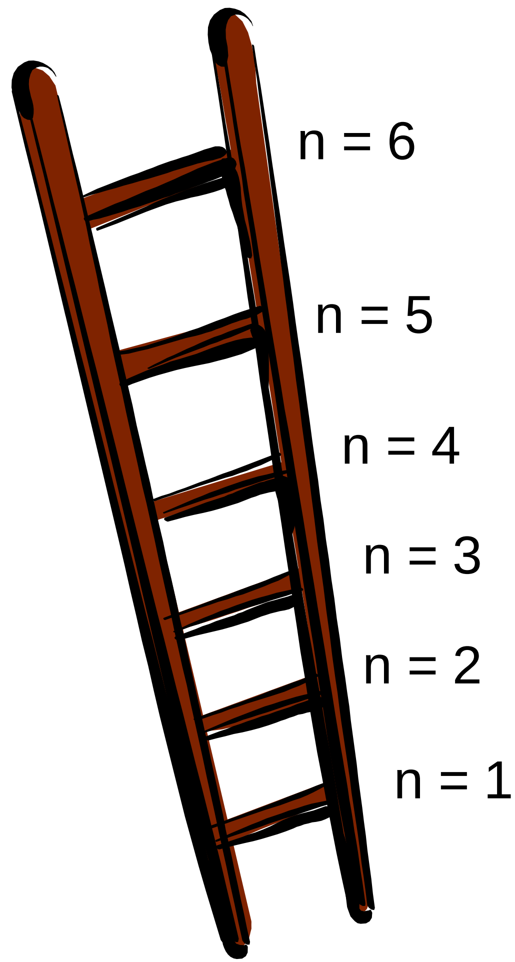
Bohr's idea of Quanta, or quantized energy exemplifies the **particle** nature of electrons.



Lyman Series

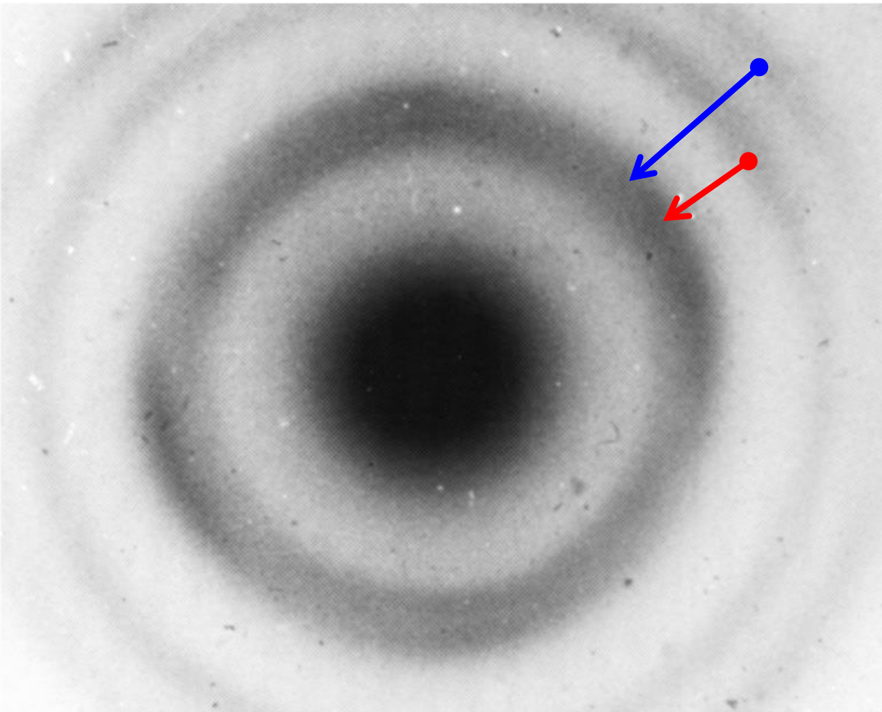
Balmer Series accounts for the visible spectrum

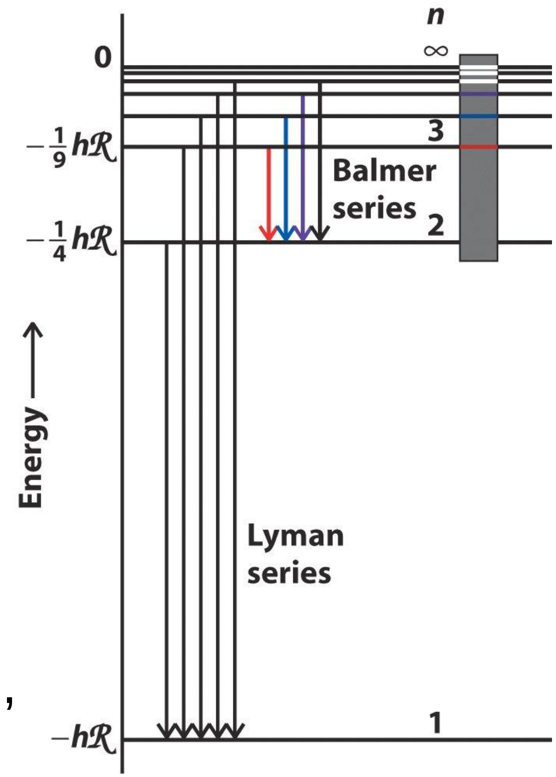
Each spectral line corresponds to an electron transition **between two states**.



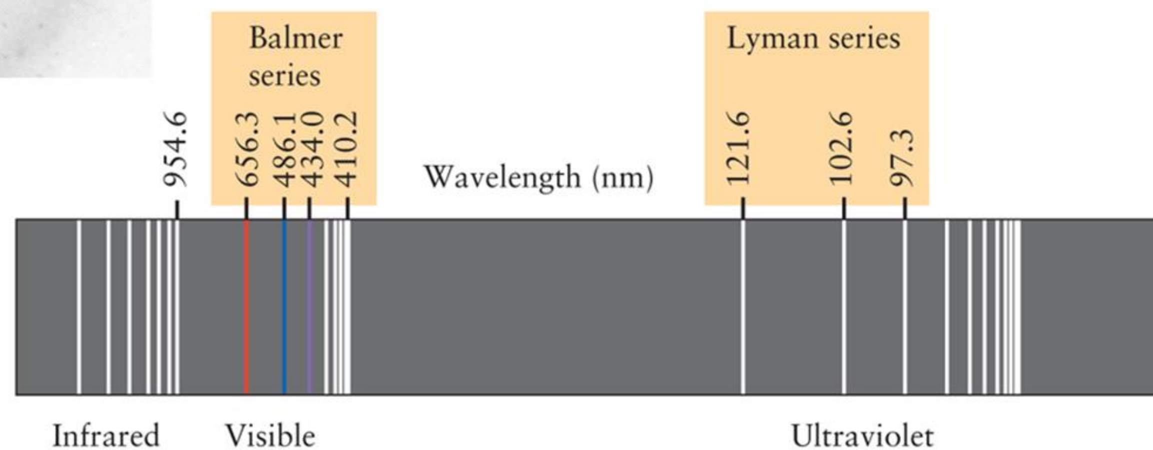
Lyman Series is a set of lines in the ultraviolet region.

Bohr interpreted this picture as the atom; when electrons moved between the rings, the $h\upsilon$ corresponded to different colors.



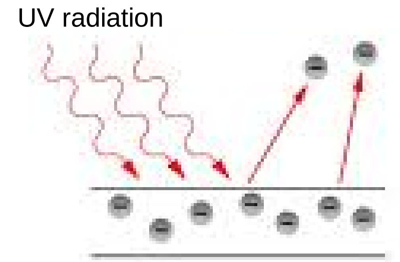


The **nucleus** is at the center, though, the size of a fly in a domed stadium.



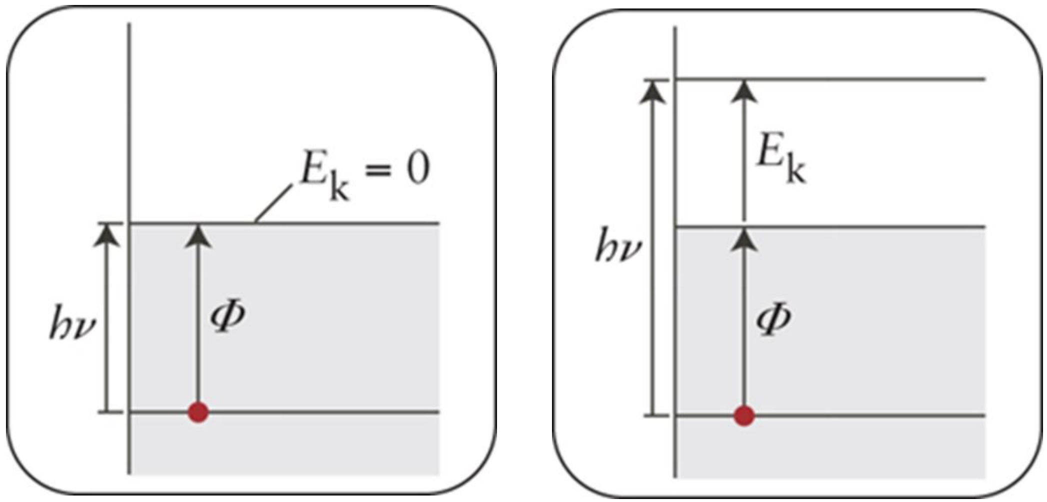
The energy of a photon is conserved.

$$\boxed{E_{\text{photon}} = KE_{\text{electron}} + \text{Work Function}_{\text{metal}}}$$



$$h\nu = \tfrac{1}{2}m_e v^2 + \Phi$$

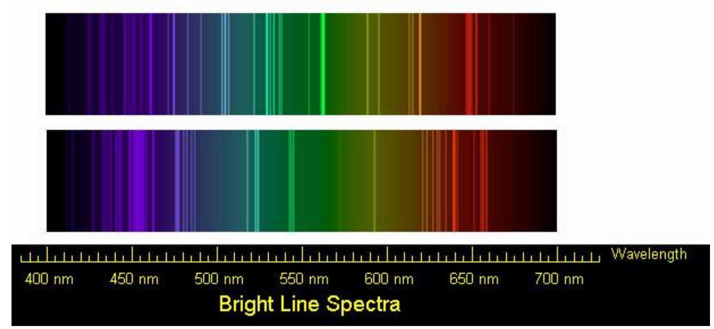
frequency velocity

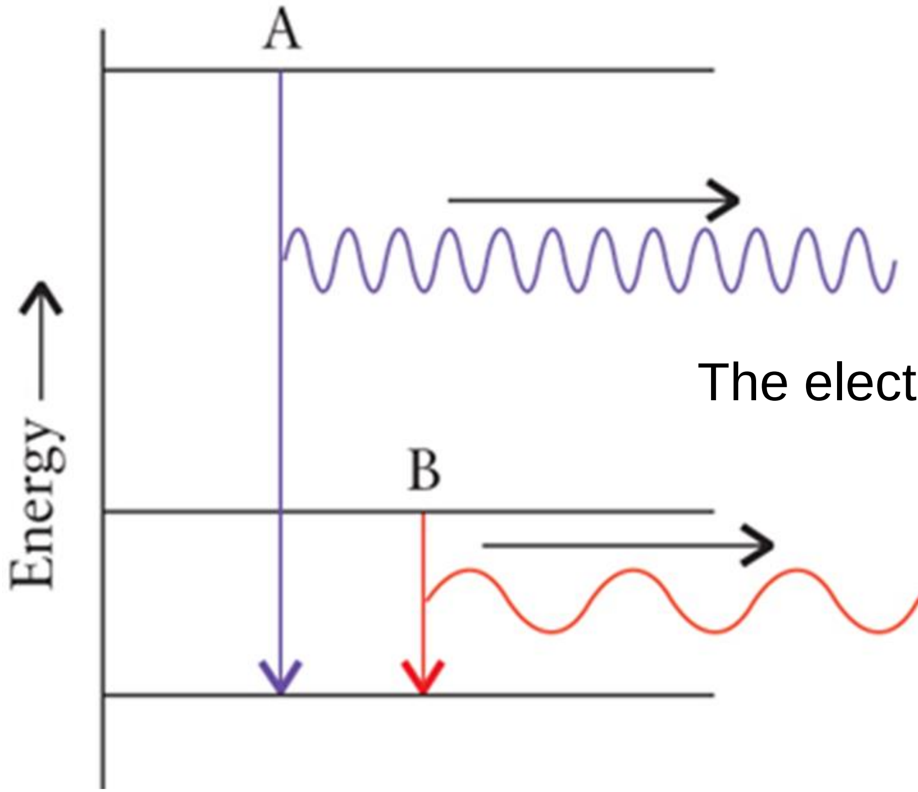


Φ is the energy needed to remove an electron from the metal.

If $h\nu > \Phi$ then KE_{electron} will be non-zero and an electron is ejected.

Color comes from electrons shedding excess energy whey they **relax** to their original, unexcited state.





$h\upsilon = E_{upper} - E_{lower}$

$h\upsilon =$ **violet**

The electron de-energizing creates a photon.

$h\upsilon = E_{upper} - E_{lower}$

$h\upsilon =$ **red**

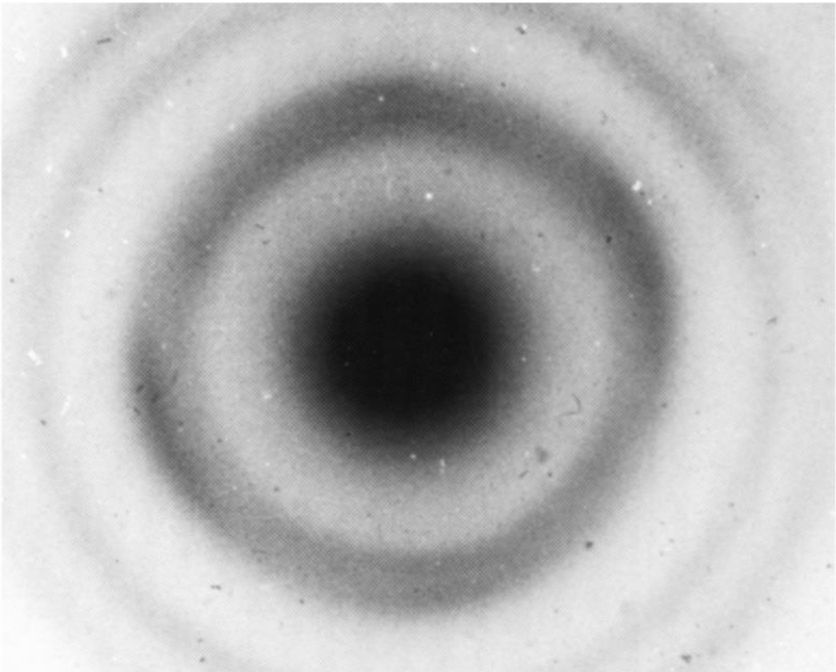
Again, this adheres to Plank's ladder or quantized idea:
"Electrons going between levels produces different colors."

Now, what we need is a way to **explain** what is a wave-particle?

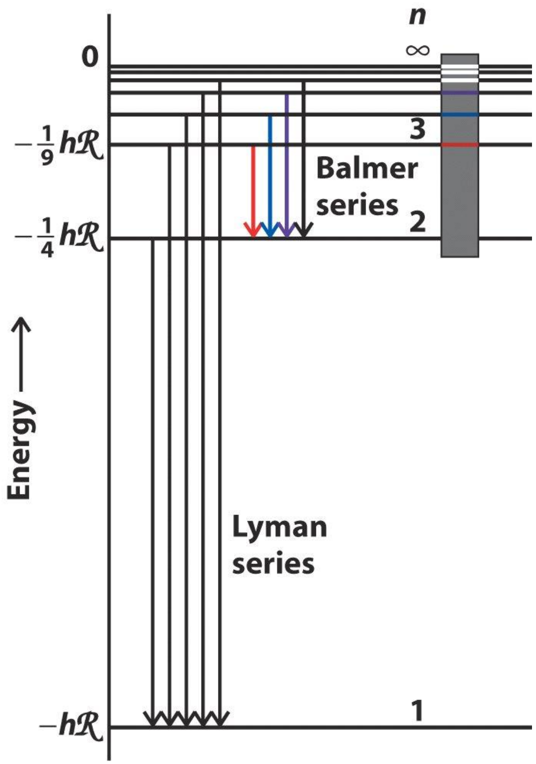
This opened the way for quantum mechanics.

Countless experiments show **Both** (wave and particle) are true.

Wave view



Particle view



Changing the Box

As *L* (length) increases:

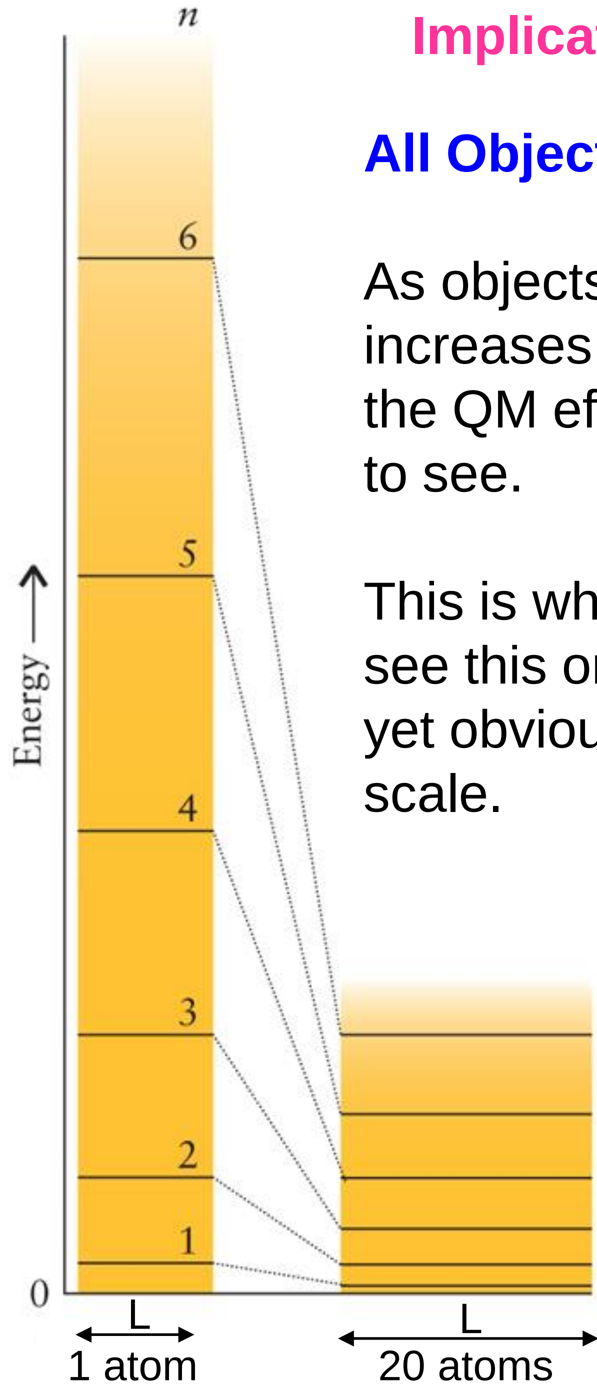
- energies of levels decrease
- separations between levels decrease

Energy levels are quantized, n

$$\boxed{E_n = \frac{n^2 h^2}{8mL^2}}$$

n = 1, 2,… must be integers;
L is the length of the box (in meter);
m is mass of electron (9.109×10^{-31} kg);
h is a constant (6.626×10^{-34} Js)
.

Lowest E, **closest** to the nucleus



Implication of QM

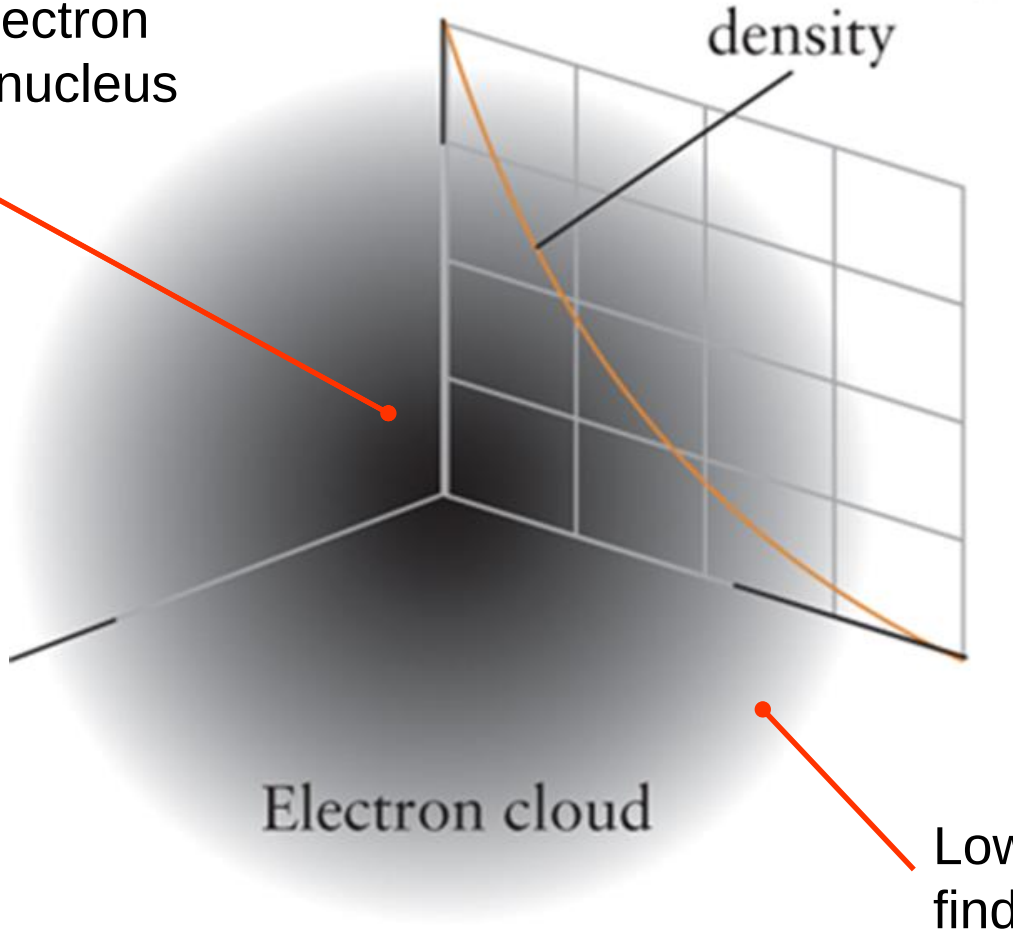
All Objects are quantized!

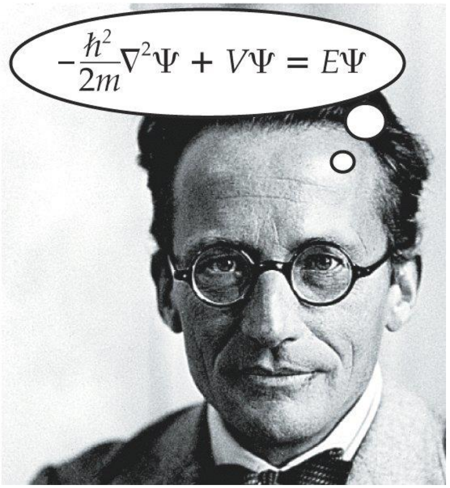
As objects become larger, n increases, L widens, so that the QM effect is more difficult to see.

This is why it's impossible to see this on the macro-scale yet obvious on the atomic scale.

A 3D plot of Erwin Schrödinger Particle-Wave functions.

Higher probability of finding an electron nearest the nucleus



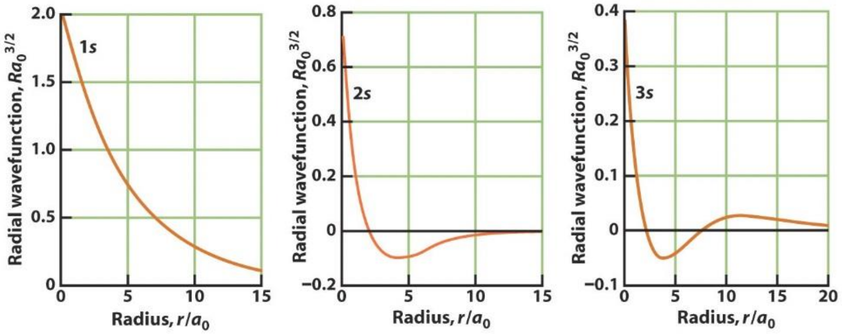


Lower probability of finding an electron

TABLE 1.3 Quantum Numbers for Electrons in Atoms

Name	Symbol	Values	Specifies	Indicates
principal	n	$1, 2, \ldots$	shell	size
orbital angular momentum*	l	$0, 1, \ldots, n-1$	subshell: $l = 0, 1, 2, 3, 4, \ldots$ $s, p, d, f, g, \ldots$	shape
magnetic	m_l	$l, l-1, \ldots, -l$	orbitals of subshell	orientation
spin magnetic	m_s	$+\frac{1}{2}, -\frac{1}{2}$	spin state	spin direction

No two electrons in the same atom have the same four quantum numbers.

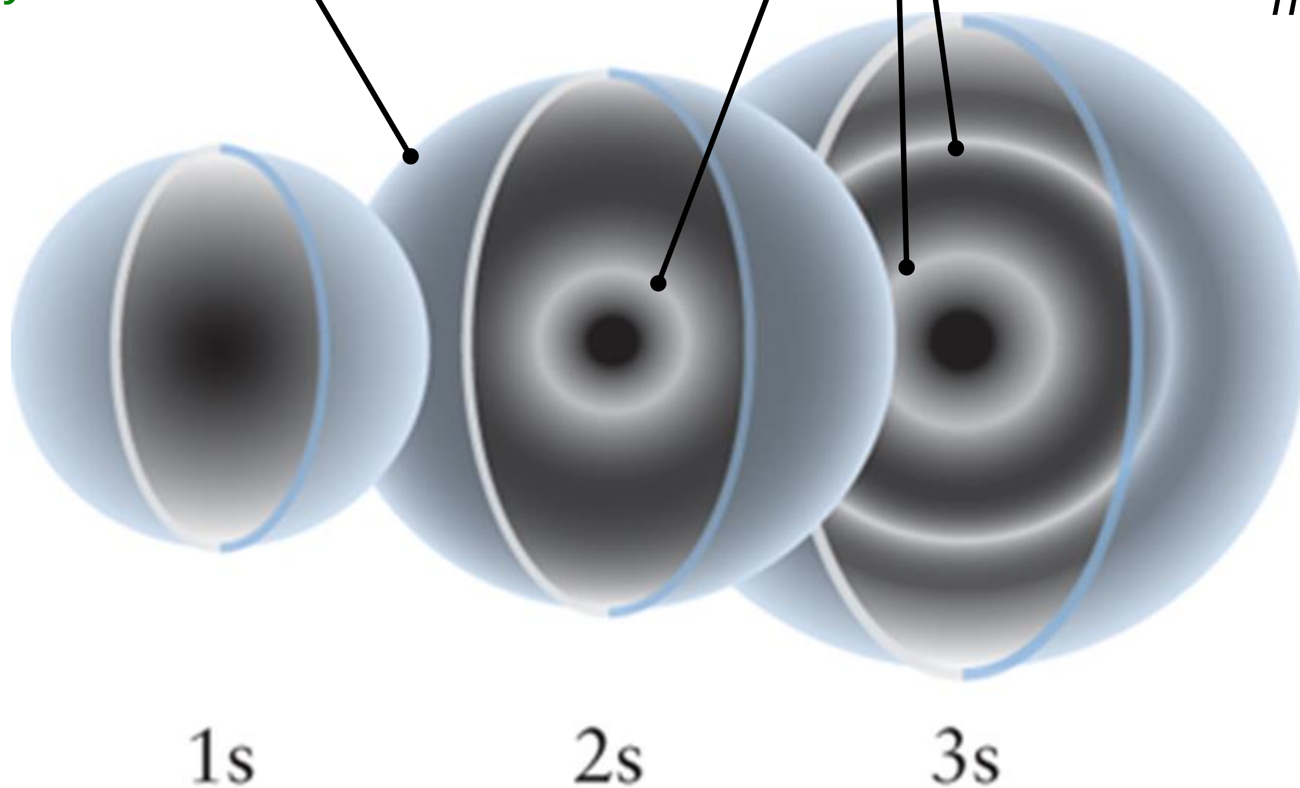


Radial nodes

90% likelihood of finding electron within

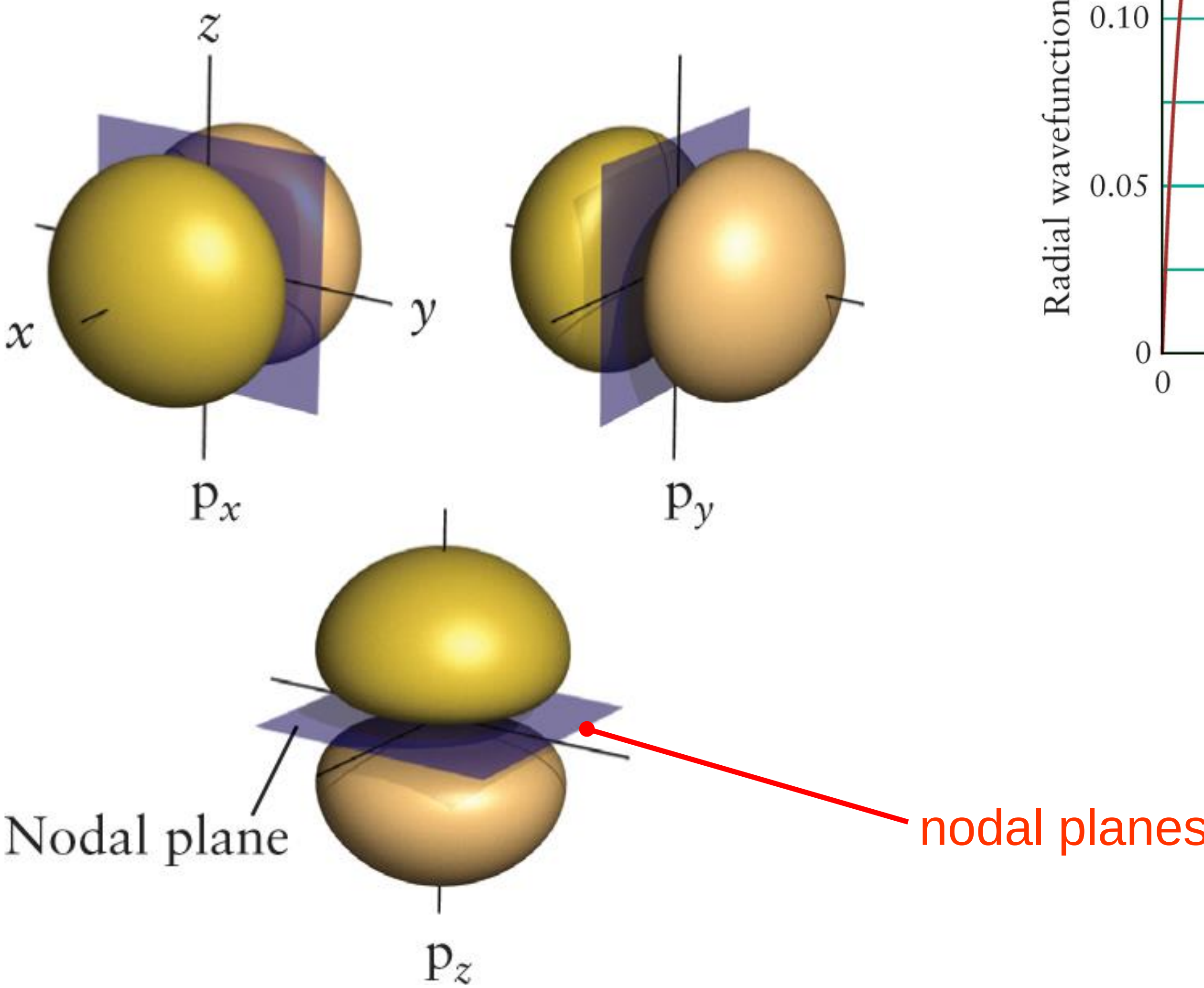
Boundary surfaces

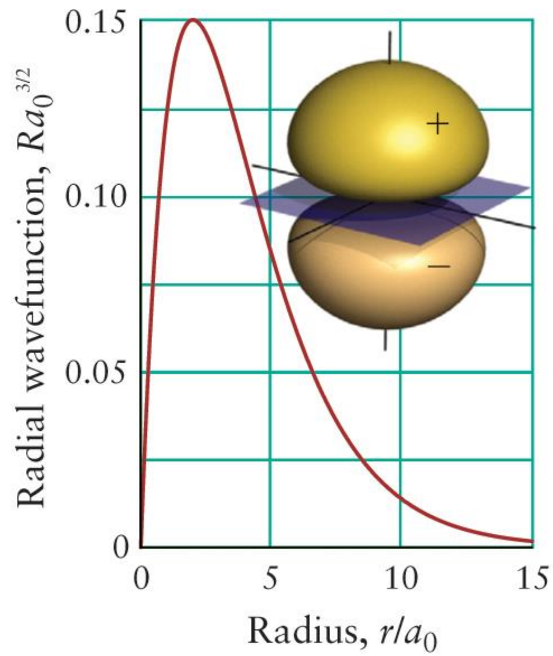
n = 1, 2, …
$l = 0$
ml = 0



The Three *p*-orbitals

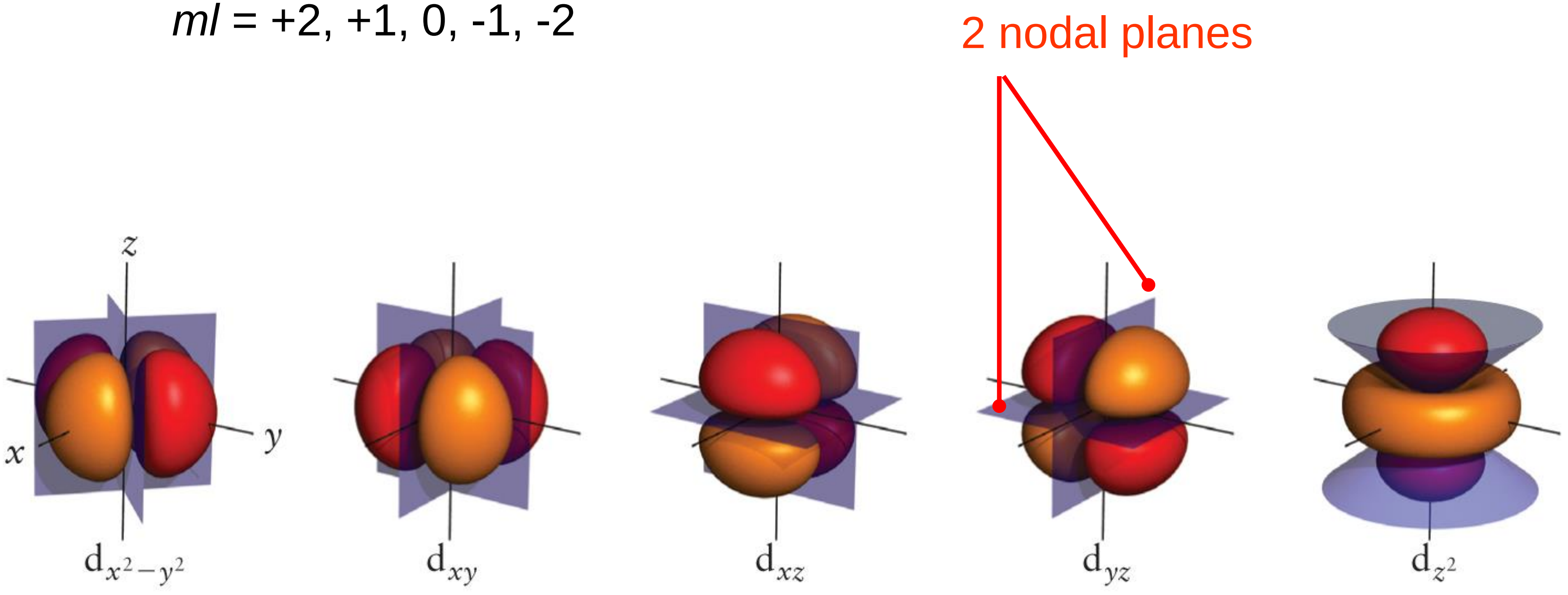
n = 2, 3, …
l = *1*
ml = +1, 0, -1





The Five *d*-orbitals

n = 3, 4, …
l = 2
ml = +2, +1, 0, -1, -2



red (+)

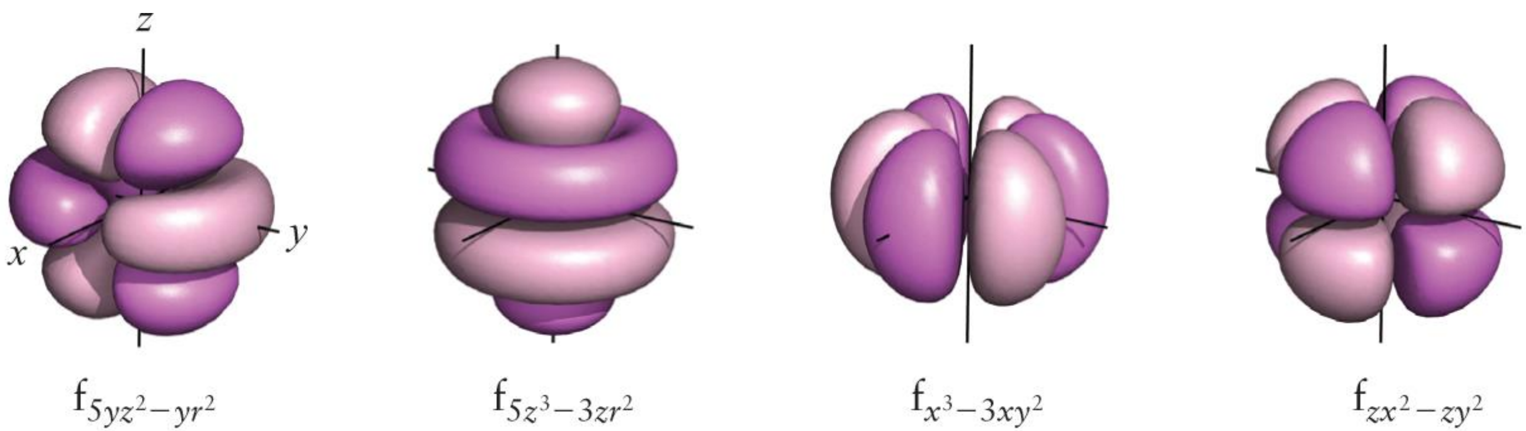
light orange (–)

The Seven *f*-orbitals

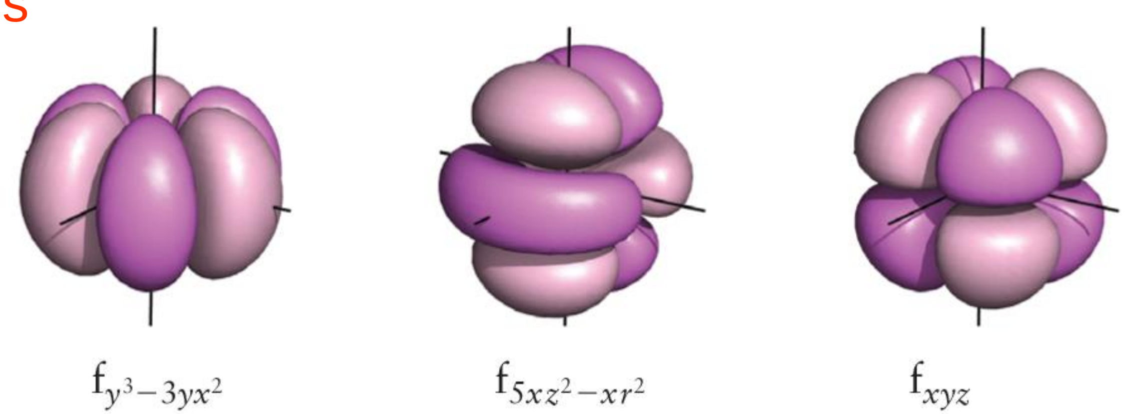
n = 4, 5, …
$l = 3$
ml = +3, +2, +1, 0, -1, -2, -3

dark purple (+)

light purple (–)

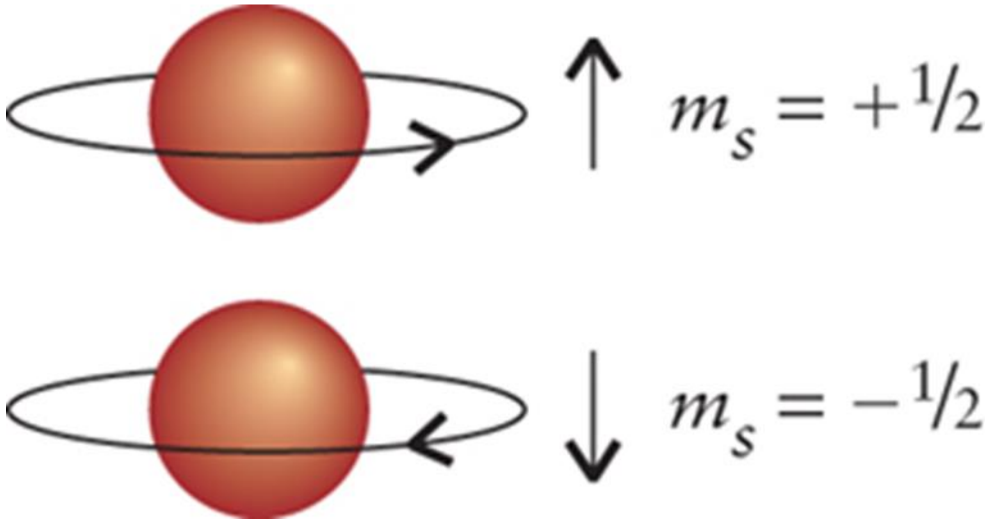


3 nodal planes



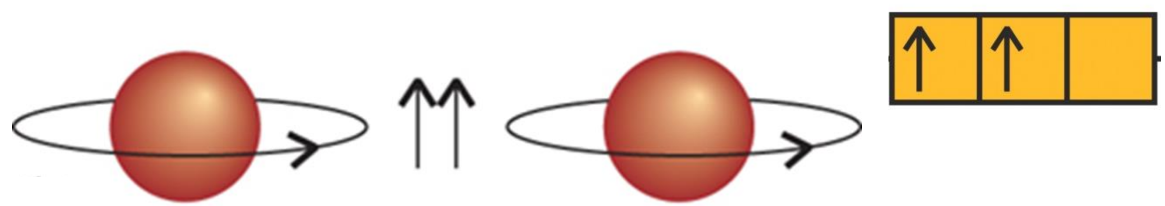
Pauli Exclusion Principle

Spin magnetic quantum number (m_s) has two possible values:



Parallel spins

Higher energy (unstable)



Paired spins

Lower energy (stable)

Shield Effect & Penetrating

There are two opposite forces applied to each electron:

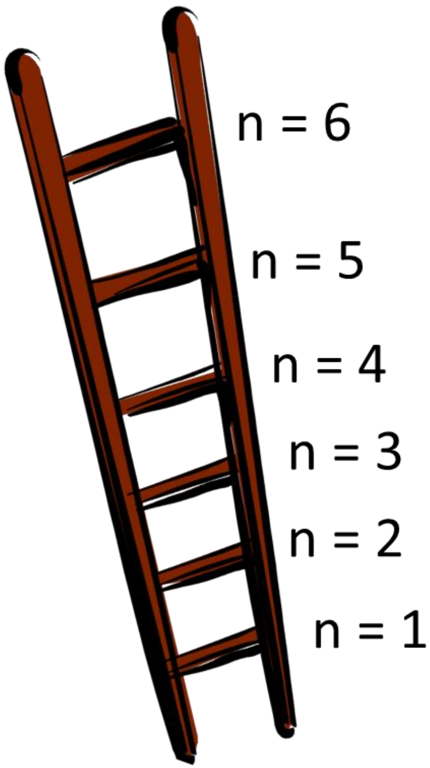
1. Attraction by nucleus
2. Repulsion by other electrons

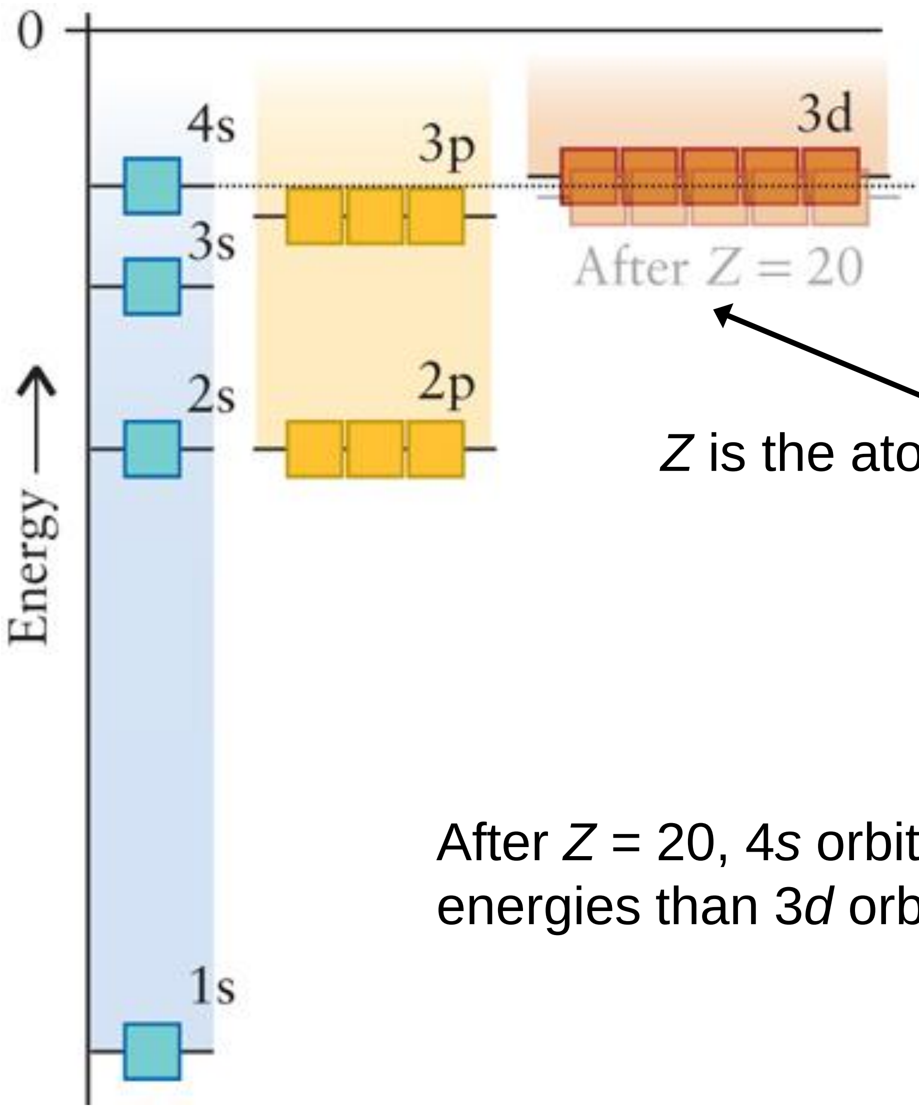
Shield Effect: each electron is said to be shield from the full attraction of the nucleus because of the repulsion by the other electrons.

Penetrating: if an electron can be found close to the nucleus, we say it is penetrated through the inner shells.

p-electrons penetrates much less than s-electrons.

Relative Energies of Orbitals in a Multi-electron Atom





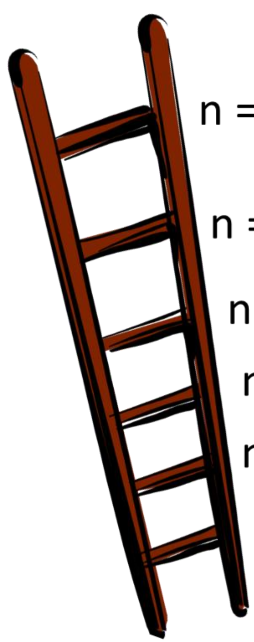
Z is the atomic number.

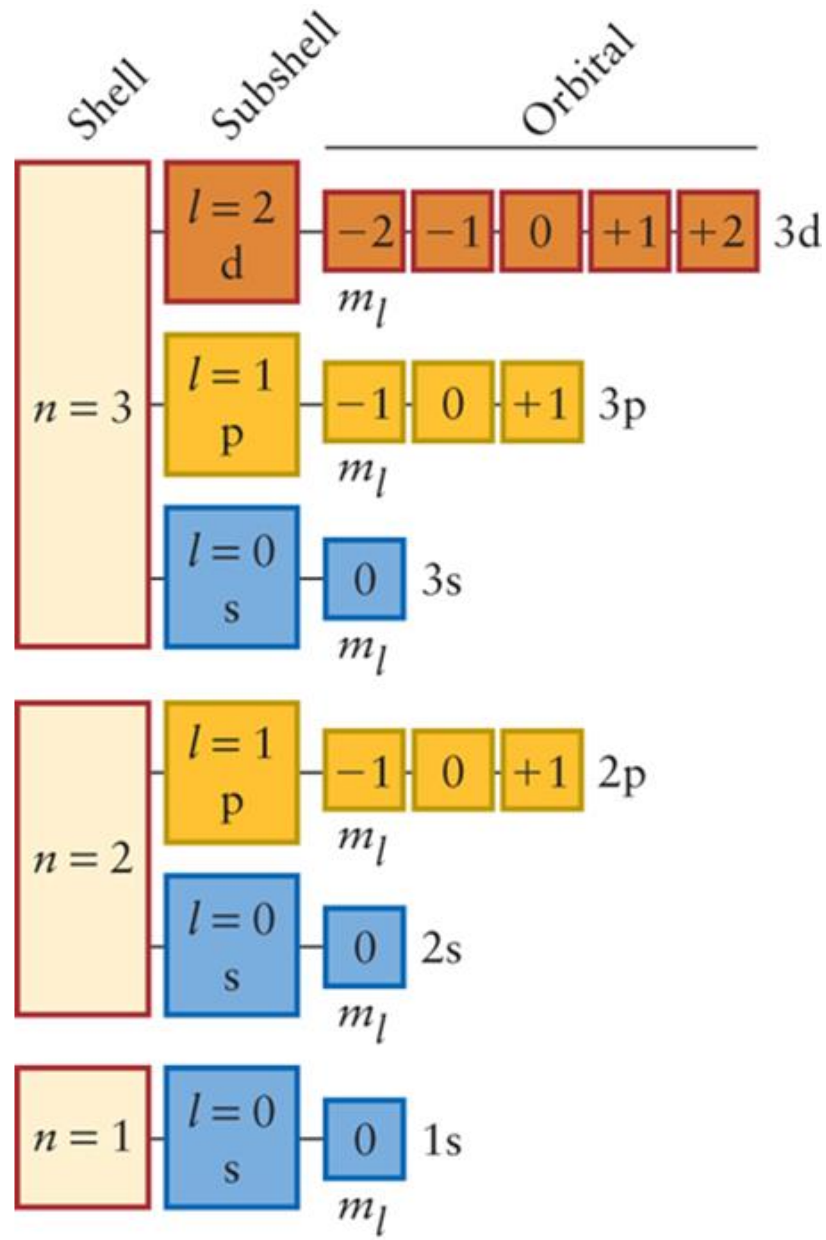
After *Z* = 20, 4*s* orbitals have higher energies than 3*d* orbitals.

All the energies are negative, meaning that the electron has a lower energy in the atom than when it is far from the nucleus (approaching to zero, more chance to escape).

Allowable Combinations of Quantum Numbers

n = 1, 2, …
l = 0, 1, 2, 3, 4, … (n – 1)
s, p, d, f, ….
$m_l = l, (l-1), \ldots, -l$





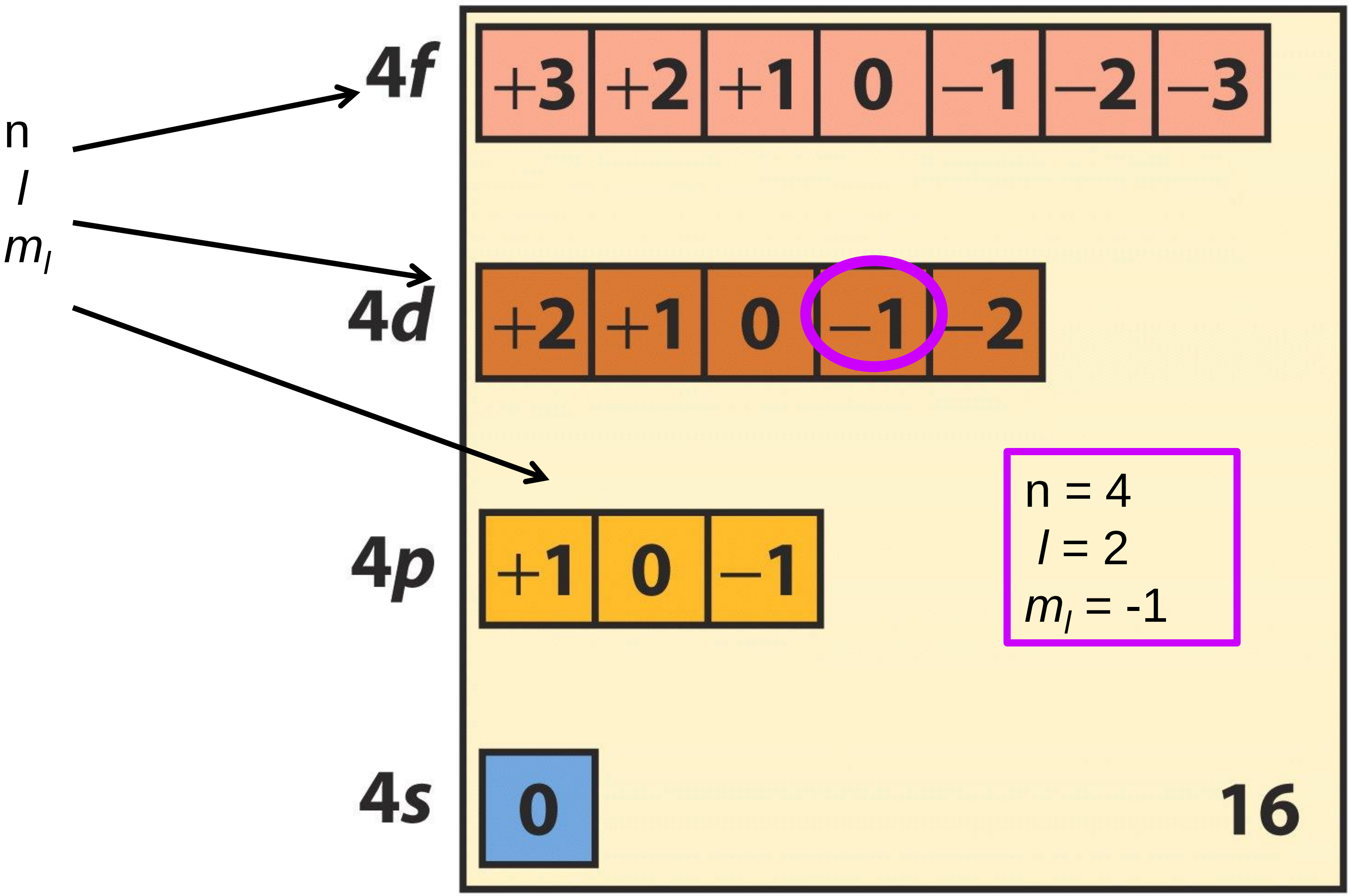
n = 1, 2, …

l = 0, 1, 2, 3, 4, … (n – 1)

s, p, d, f, ….

$m_l = l, (l - 1), ..., -l$

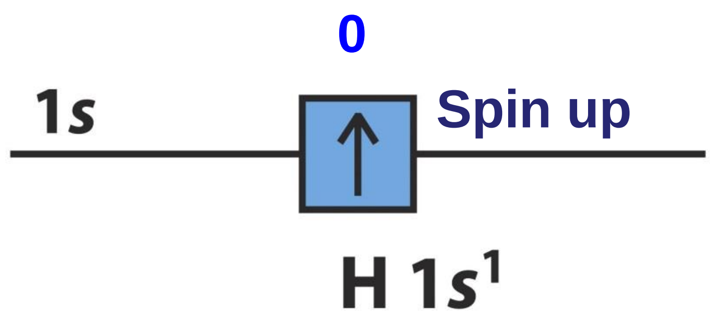
Allowed orbitals

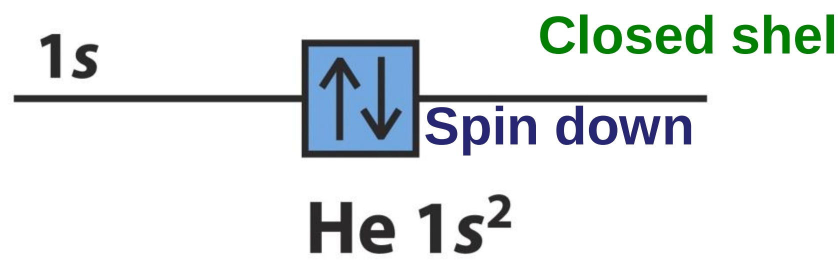


2 electrons per orbital

Electron Configurations and four quantum numbers for H and He

Building-up Principle





1*s* electron (n, l, m_l, m_s)

- 1, 0, 0, (+½ or −½)

(n, l, m_l, m_s)

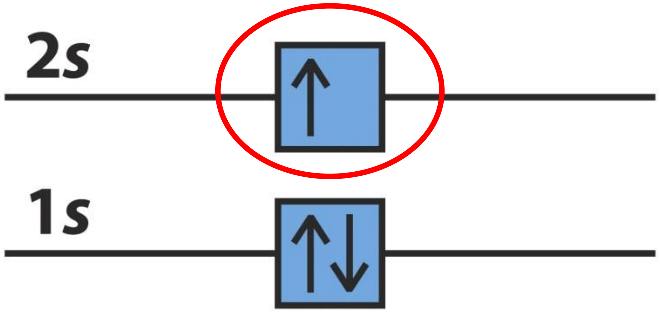
1*s* electrons (n, l, m_l, m_s)

- 1, 0, 0, +½
- 1, 0, 0, −½)

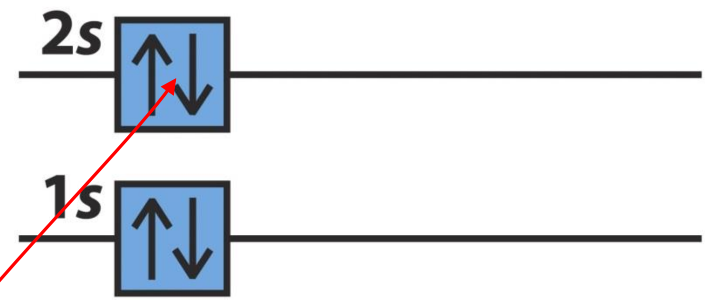
Pauli exclusion principle:

No more than 2 electron in each orbital, their spins must be paired.

Electron Configurations & Noble Gas electron configuration



Li $1s^2 2s^1$, $[He]2s^1$



Be $1s^2 2s^2$, $[He]2s^2$

1*s* electrons (n, l, m_l, m_s)
- 1, 0, 0, +½
- 1, 0, 0, –½

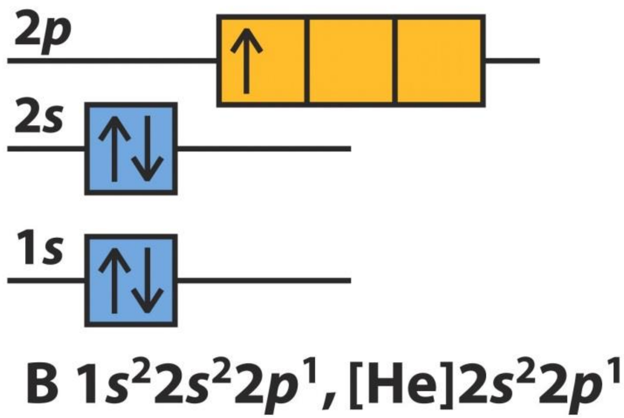
2*s* electron*
- 2, 0, 0, +½

1*s* electrons (n, l, m_l, m_s)
- 1, 0, 0, +½
- 1, 0, 0, –½

2*s* electrons
- 2, 0, 0, +½
- 2, 0, 0, –½

Hund's Rule

+1, 0, -1



$1s$ electrons (n, l, m_l, m_s)

- 1, 0, 0, +½
- 1, 0, 0, –½

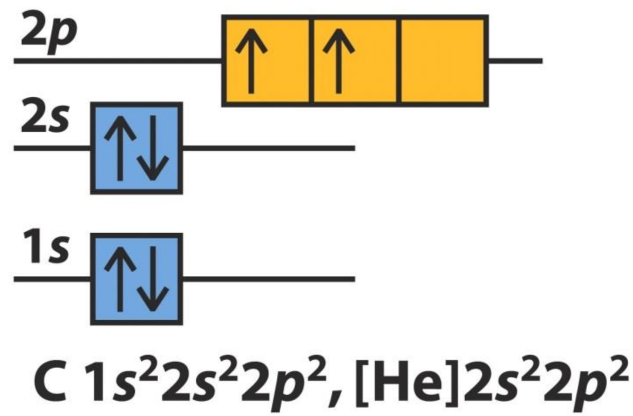
$2s$ electrons

- 2, 0, 0, +½
- 2, 0, 0, –½

$2p$ electron*

- 2, 1, +1, +½

+1, 0, -1 Parallel spins



$1s$ electrons (n, l, m_l, m_s)

- 1, 0, 0, +½
- 1, 0, 0, –½

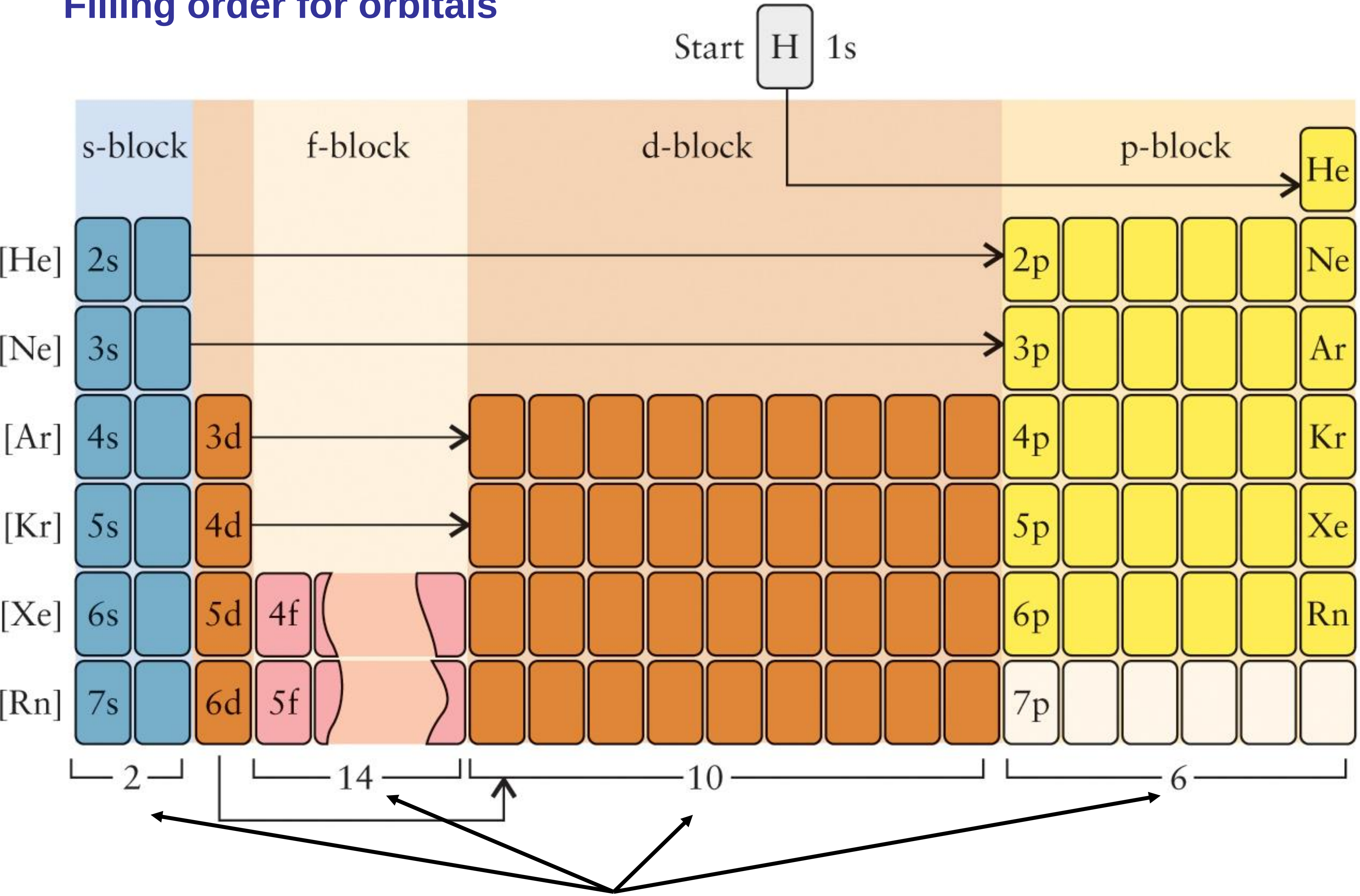
$2s$ electrons

- 2, 0, 0, +½
- 2, 0, 0, –½

$2p$ electrons*

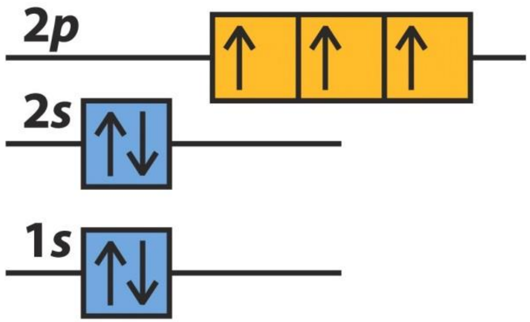
- 2, 1, +1, +½
- 2, 1, 0, +½

Filling order for orbitals



maximum number of electrons in subshell

Electron Configurations: N and O



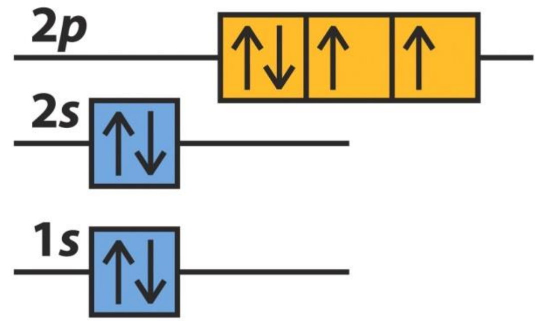
N $1s^2 2s^2 2p^3$, [He]$2s^2 2p^3$

He core (n, l, m_l, m_s)

- 1, 0, 0, +½
- 1, 0, 0, –½
- 2, 0, 0, +½
- 2, 0, 0, –½

2p electrons*

- 2, 1, +1, +½
- 2, 1, 0, +½
- 2, 1, –1, +½



O $1s^2 2s^2 2p^4$, [He]$2s^2 2p^4$

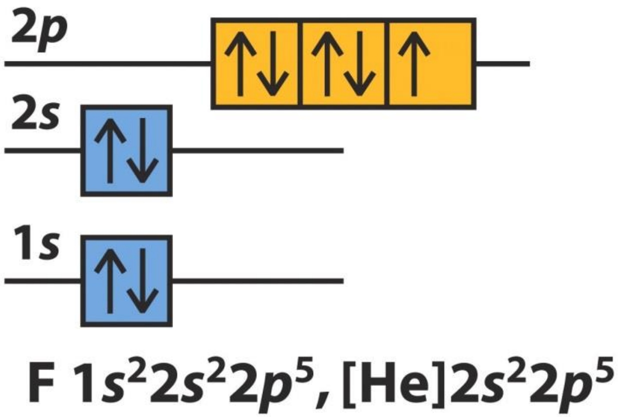
He core (n, l, m_l, m_s)

- 1, 0, 0, +½
- 1, 0, 0, –½
- 2, 0, 0, +½
- 2, 0, 0, –½

2p electrons*

- 2, 1, +1, +½
- 2, 1, 0, +½
- 2, 1, –1, +½
- 2, 1, +1, –½

Electron Configurations: F and Ne

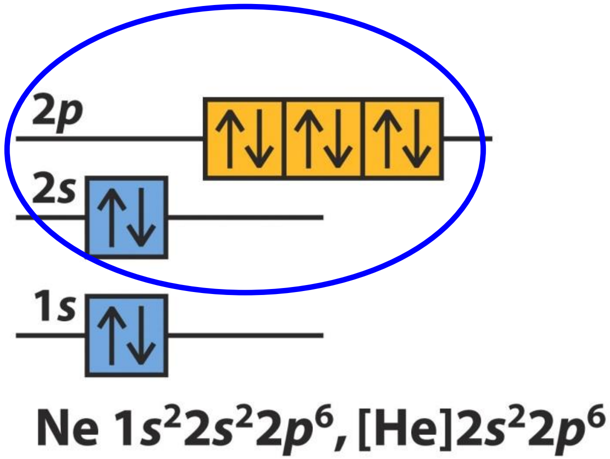


He core (n, l, m_l, m_s)

$2p$ electrons*

- 2, 1, +1, +½
- 2, 1, +1, –½
- 2, 1, 0, +½
- 2, 1, 0, –½
- 2, 1, –1, +½

Filled or closed shell



He core (n, l, m_l, m_s)

$2p$ electrons

- 2, 1, +1, +½
- 2, 1, +1, –½
- 2, 1, 0, +½
- 2, 1, 0, –½
- 2, 1, –1, +½
- 2, 1, –1, –½

Practice

For the following V, Cr, Cr^{3+}, Fe, & Fe^{3+} write the:

1. Electron configuration

2. Orbital box diagram

3. Four quantum numbers n, l, m_l, m_s

V

To determine the 4 quantum numbers we need to **look at the last subshell** where the last electron goes.

Electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$

Orbital box diagram

↑	↑	↑		
+2	+1	0	-1	-2

Spin is up = +1/2

Since the d’s have five orbitals we write them out

We number with “+” m_l values first

Place e^- going up “+” m_s values first, follow Hund’s Rule to minimize repulsive energy

We obtain the n and l value from last shell and subshell values

We obtain the m_l and m_s value from the position of the last e^-

n, l, m_l, m_s

3, 2 , 0, +1/2

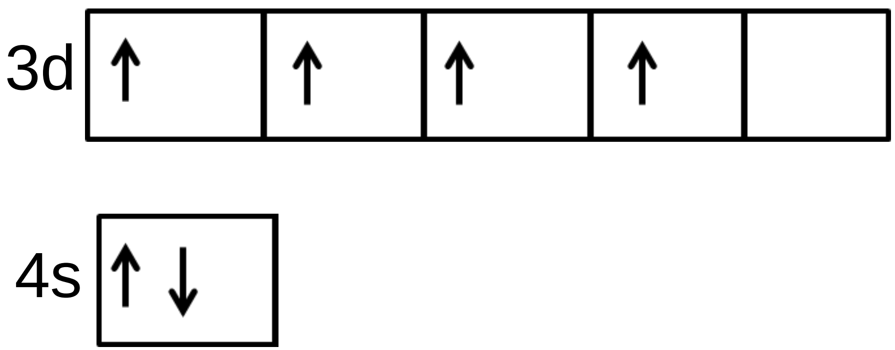
	s	p	d	f
l =	0	1	2	3

Cr

Expected

Electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^4$

Orbital box diagram

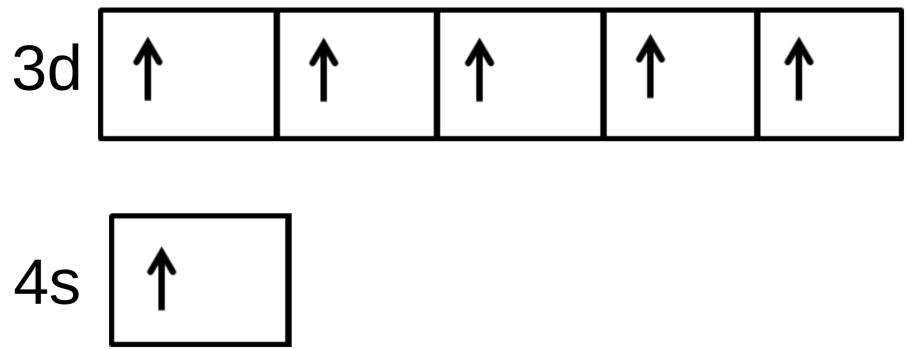


Cr [Ar] $4s^2 3d^4$

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^4$

Observed

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$



A similar re-arrangement occurs with Cu

Cr and Cr^{3+}

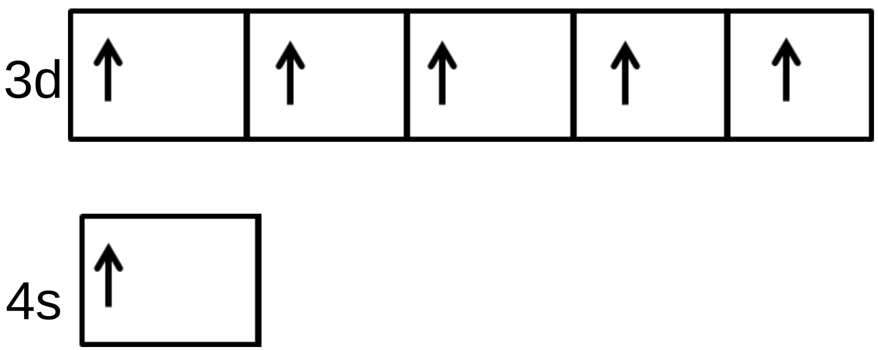
Element Cr

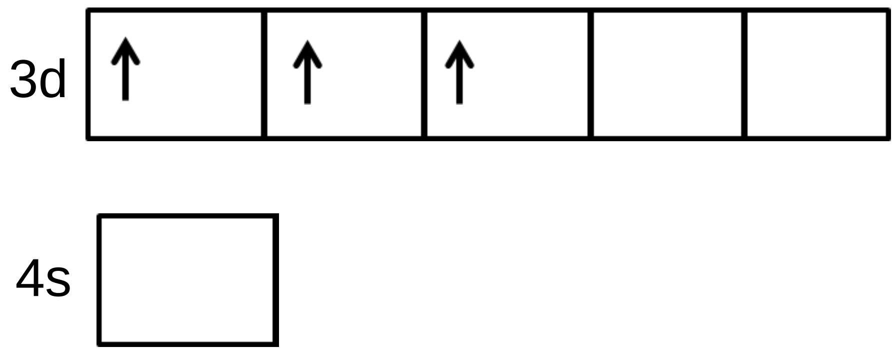
Electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$

Orbital box diagram

Cr^{3+}

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^0 3d^3$





Transition metals always lose electrons from their s-orbital first.

Fe and Fe^{3+}

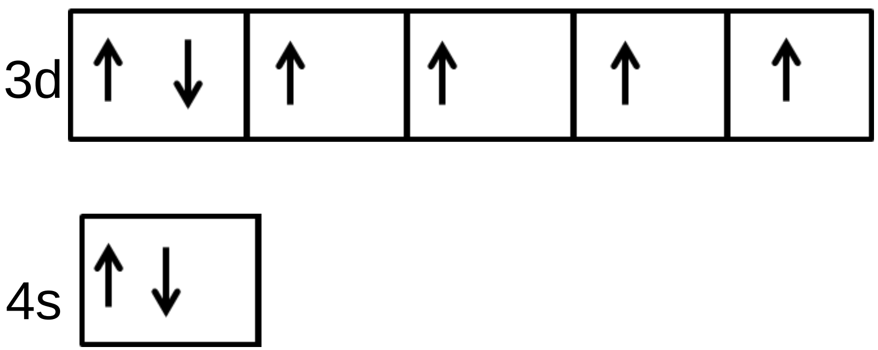
Element Fe

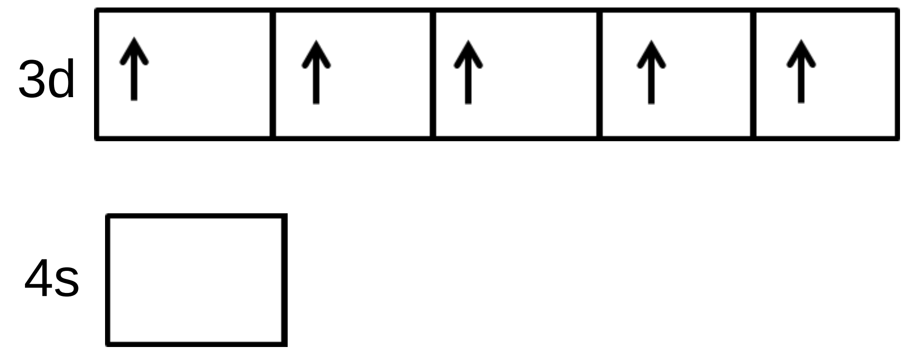
Electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$

Fe^{3+}

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^0 3d^5$

Orbital box diagram

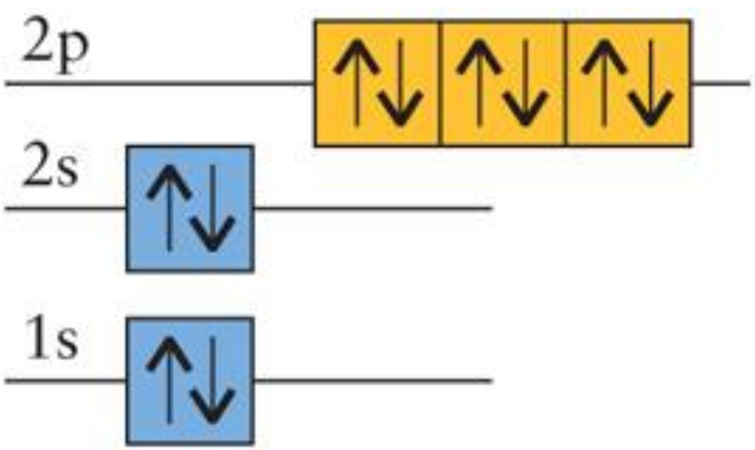




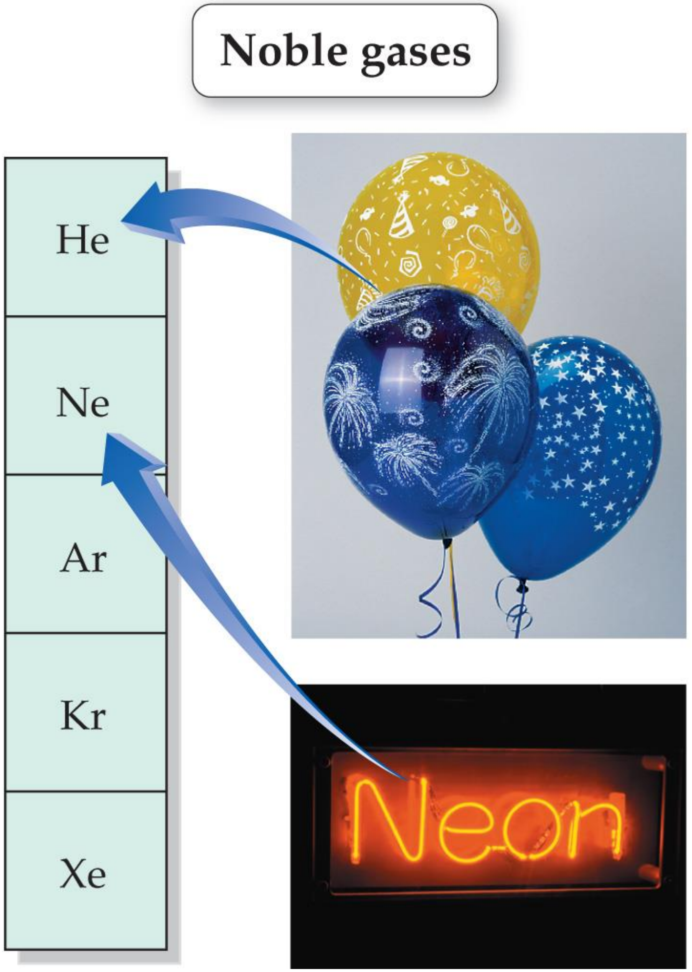
Transition metals always lose electrons from their s-orbital first.

Stability

Stability (meaning **non-reactive** or **low energy**) is based on Filled-Shells! That is when atoms get a filled shell they tend to stop reacting.



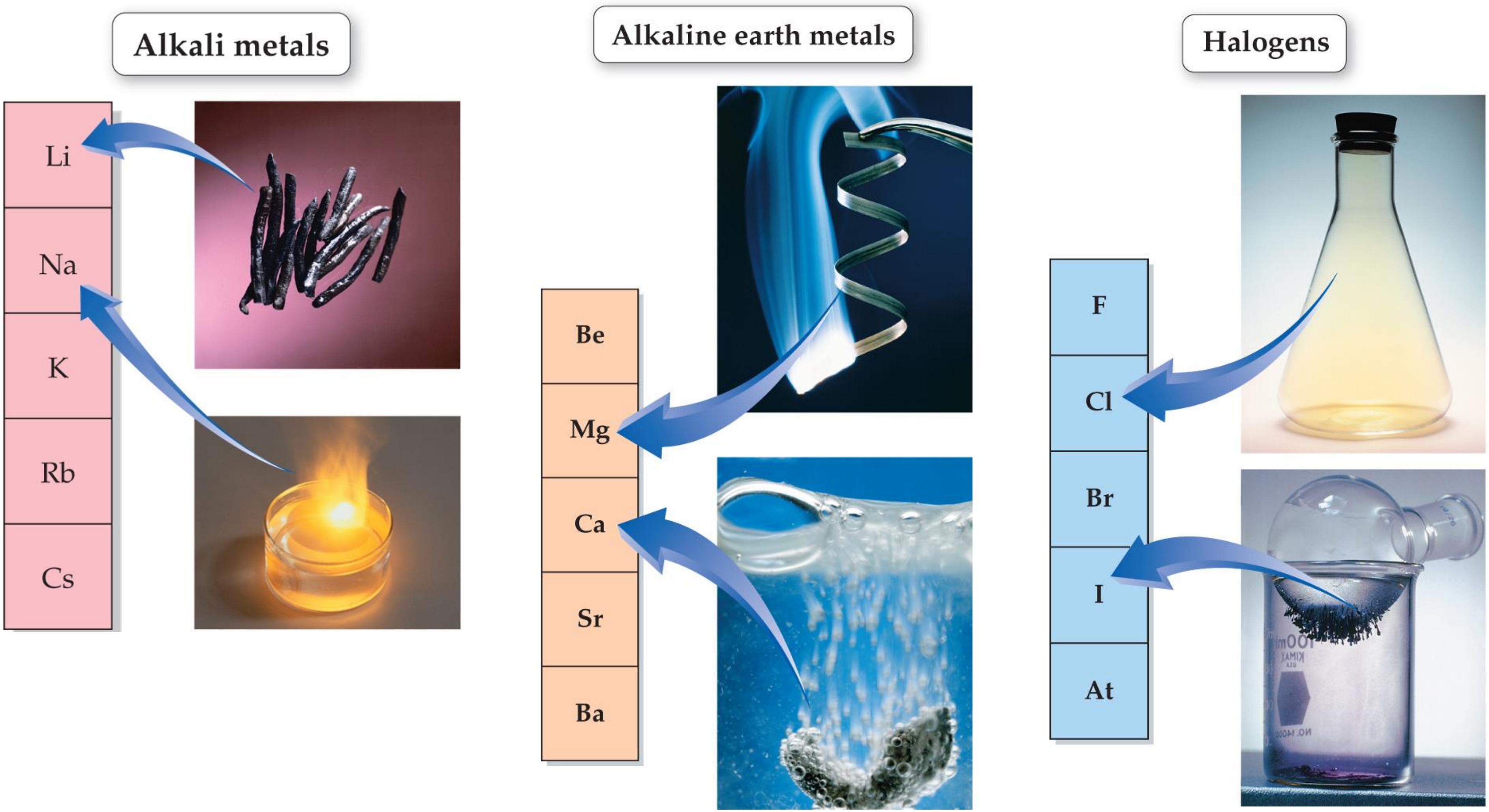
10 Ne $1s^2 2s^2 2p^6$, $[He]2s^2 2p^6$



Noble Gas Electron Configuration

Elements in Group 1A-7A (and transition metals) are all reactive.

Atoms gain and lose to get a Noble Gas Electron Configuration.



2 Inherent Physical Factors in Atoms

What causes differences in atomic physical properties like:

- Atomic Radii
- How many Electrons they Gain or Lose
- Metal Characteristics

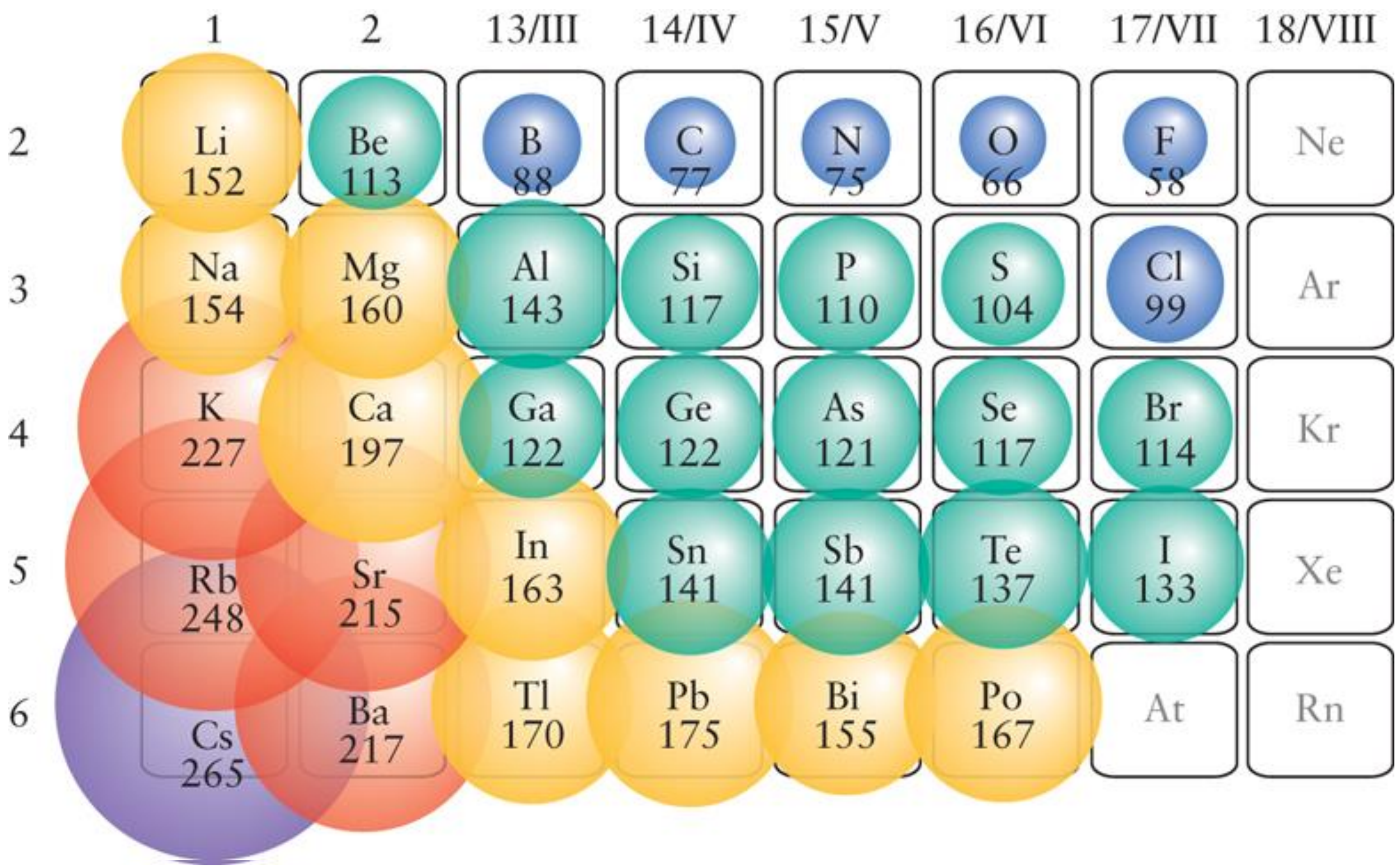
1. Valence shells
2. Effective nuclear charge

Looking at the periodic table helps us see these effects

Periodic Trend: Atomic Radius

increases down a group
Valence Shells

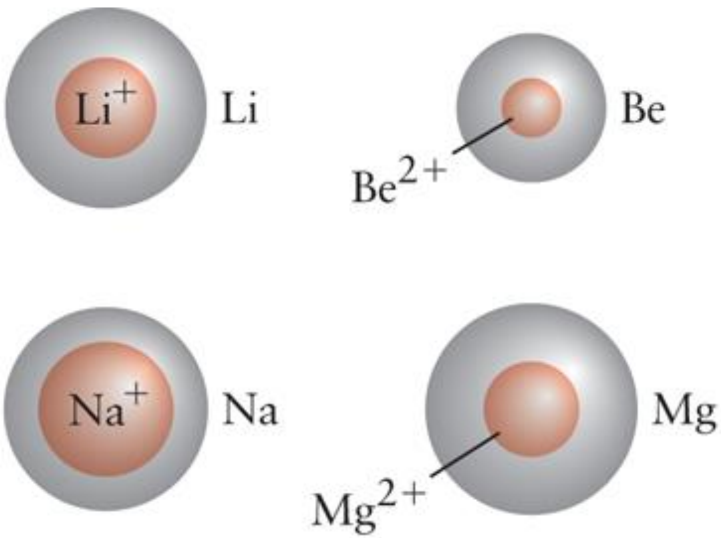
decreases across a period
Effective Nuclear Force



Periodic Trend: Ionic Radius

atom → cation

radius decreases

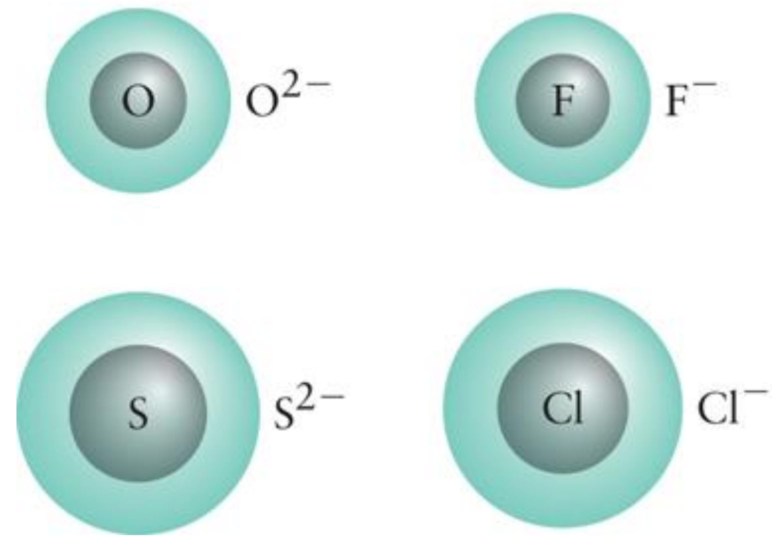


Removing electrons:

1. Lose of a shell;
2. Higher "+Z" in nucleus draws e$^-$ in.

atom → anion

radius increases



Adding electrons:

1. Weakens +Z nuclear electrostatic attraction
2. An increase in e- to e- repulsions.

Trends in Ionization Energy

Minimum energy needed to **remove an electron** from an atom.
Valence electron easiest to remove.

Increasing effective nuclear charge

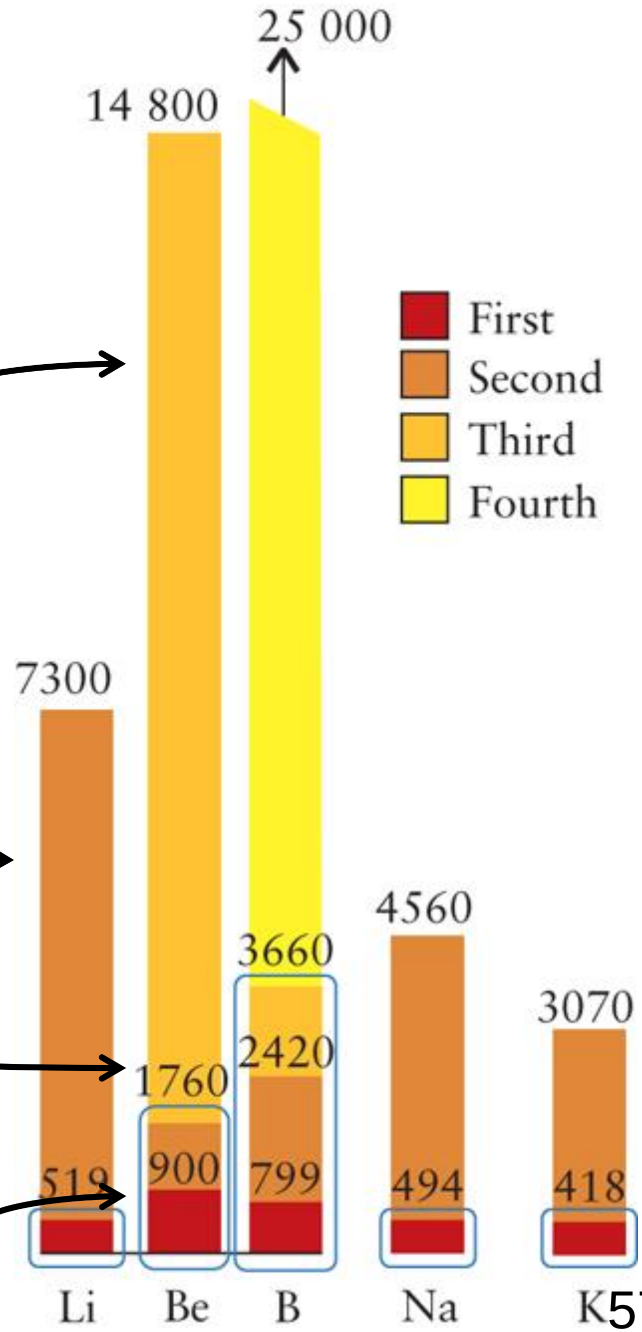
Valence shells

	1	2	13	14	15	16	17	18
				H 1310				He 2370
2	Li 519	Be 900	B 799	C 1090	N 1400	O 1310	F 1680	Ne 2080
3	Na 494	Mg 736	Al 577	Si 786	P 1011	S 1000	Cl 1255	Ar 1520
4	K 418	Ca 590	Ga 577	Ge 784	As 947	Se 941	Br 1140	Kr 1350
5	Rb 402	Sr 548	In 556	Sn 707	Sb 834	Te 870	I 1008	Xe 1170
6	Cs 376	Ba 502	Tl 590	Pb 716	Bi 703	Po 812	At 1037	Rn 1036

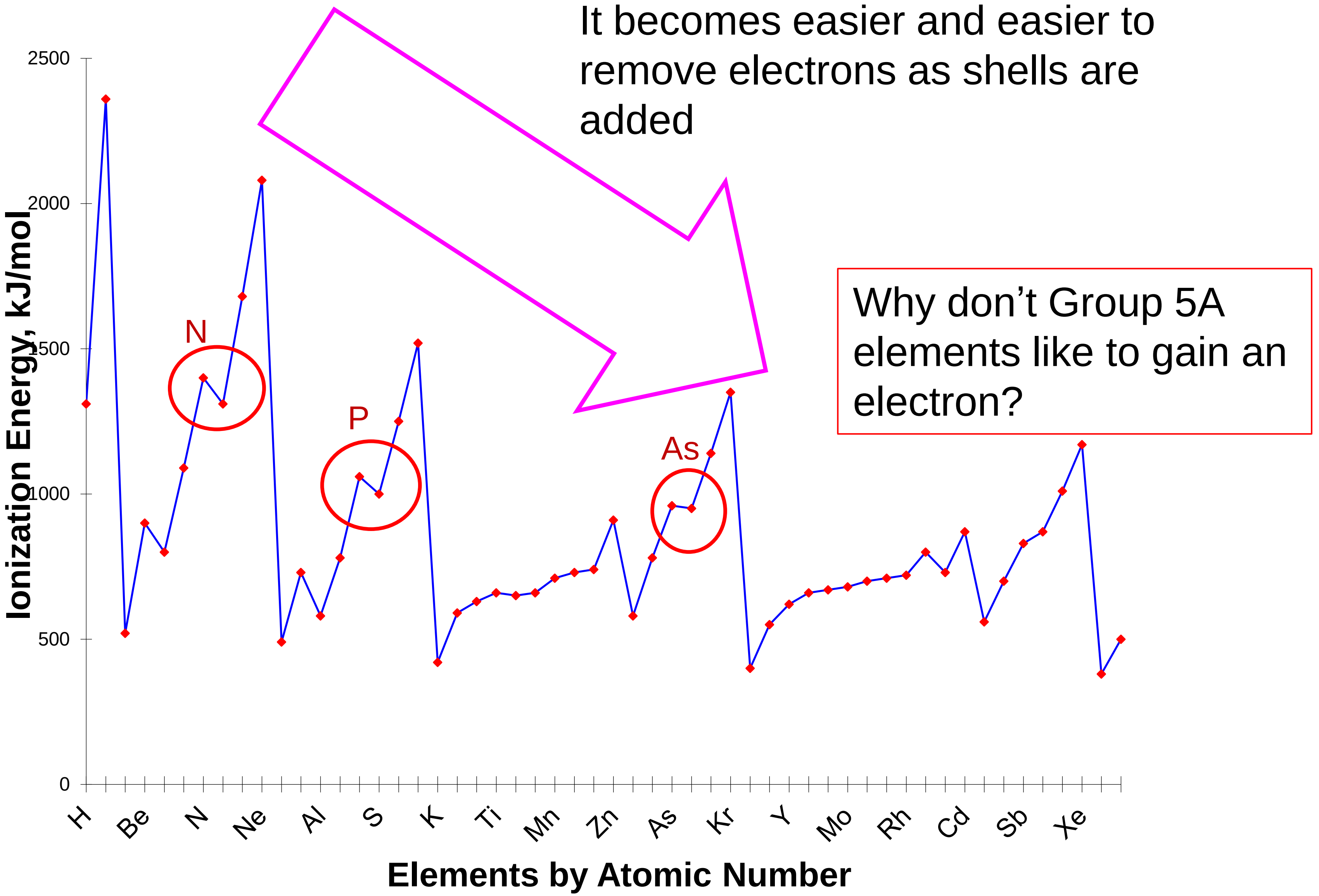
Periodic Trend: Multiple Ionizations

Removing an electron from an inner shell (core) require even higher energies.

Subsequent ionizations are always higher in energy than previous ionizations; greater columbic imbalance.



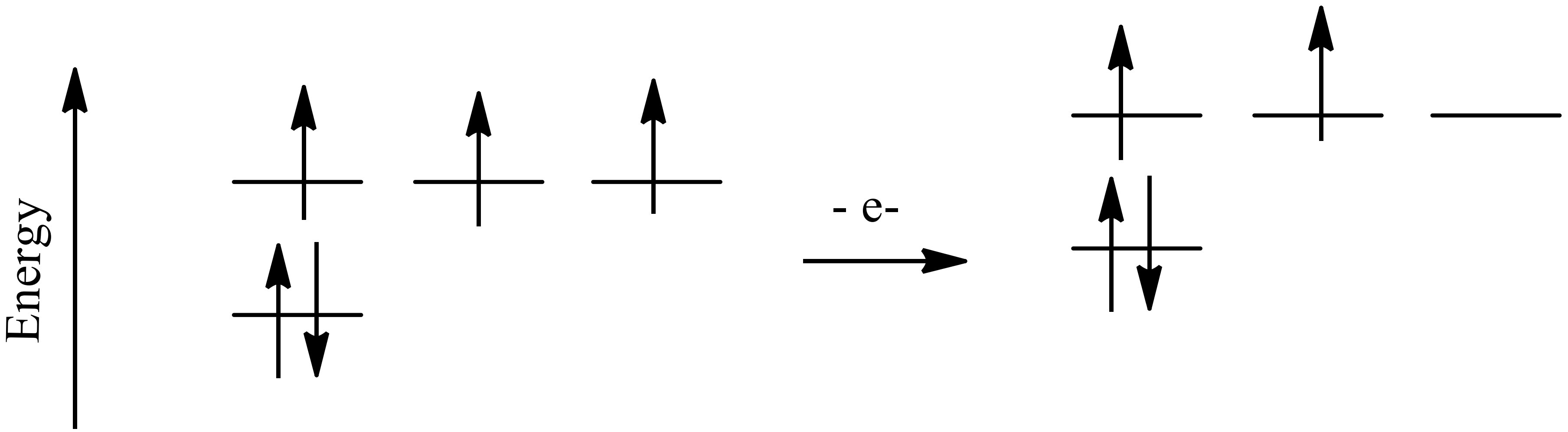
Ionization Energy of Elements 1-56



Reason: All values are positive since a physical bond is broken; it takes energy to remove a negativity charged "-" electron from a positively charged "+" nucleus.

Removing an electron from nitrogen makes the orbitals higher in energy than the original ground state orbitals.

Group 5A Valance Shell, i.e. Nitrogen



The overall effect is that half-filled shells are more stable in partially filled shells.

Periodic Trend: Electron Affinity

The energy changes when an electron attaches to an atom.

$$F + e^- \rightarrow F^-$$

$\Delta E = E_{final} - E_{initial}$

Negative values: energy is required to add an electron
Positive values: energy released or favorable.

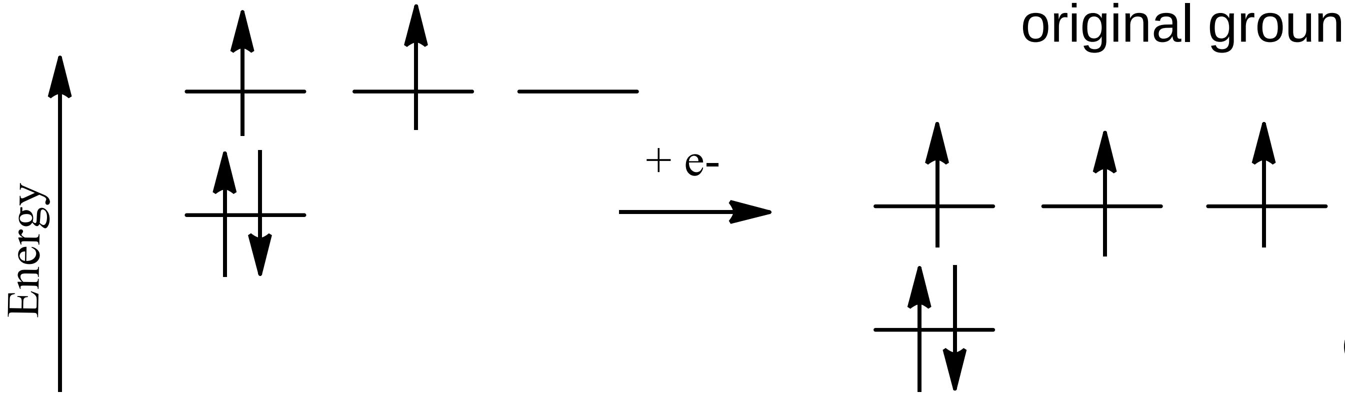
	1	2	13/III	14/IV	15/V	16/VI	17/VII	18/VIII
				H +73				He <0
2	Li +60	Be ≤0	B +27	C +122	N −7	O +141 −844	F +328	Ne <0
3	Na +53	Mg ≤0	Al +43	Si +134	P +72	S +200, −532	Cl +349	Ar <0
4	K +48	Ca +2	Ga +29	Ge +116	As +78	Se +195	Br +325	Kr <0
5	Rb +47	Sr +5	In +29	Sn +116	Sb +103	Te +190	I +295	Xe <0
6	Cs +46	Ba +14	Tl +19	Pb +35	Bi +91	Po +174	At +270	Rn <0

Why is Group 4A so favorable and Group 5A so unfavorable?

The overall effect is that half-filled shells are more stable in partially filled shells.

when carbon gains an electron, the orbitals are lower in energy than the original ground state orbitals.

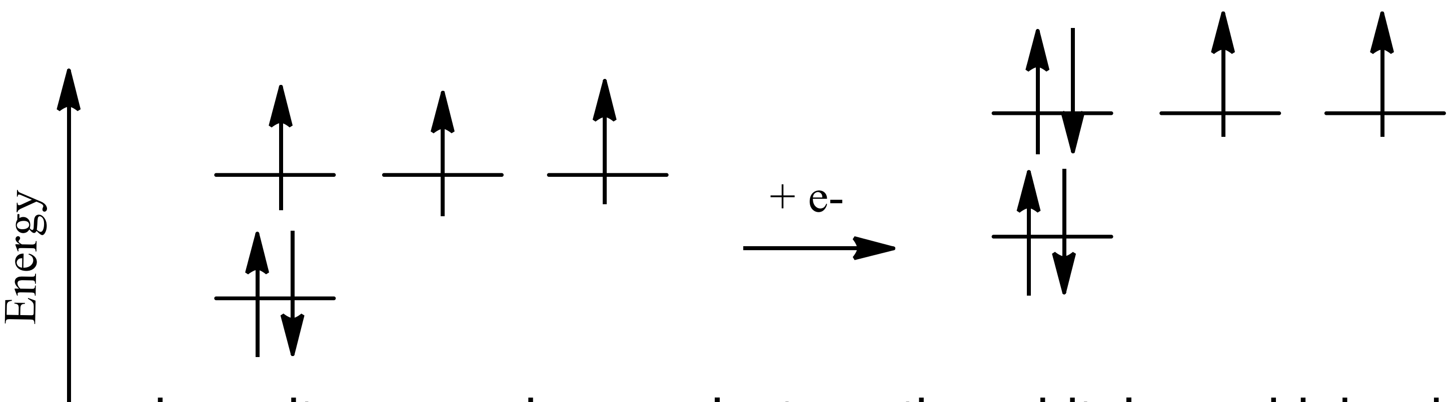
Group 4A Valance Shell, i.e. carbon



Carbon +122 EA

Nitrogen -7 EA

Group 5A Valance Shell, i.e. nitrogen



when nitrogen gains an electron, the orbitals are higher in energy than the original ground state orbitals.

Metallic Character

Physical and Chemical properties

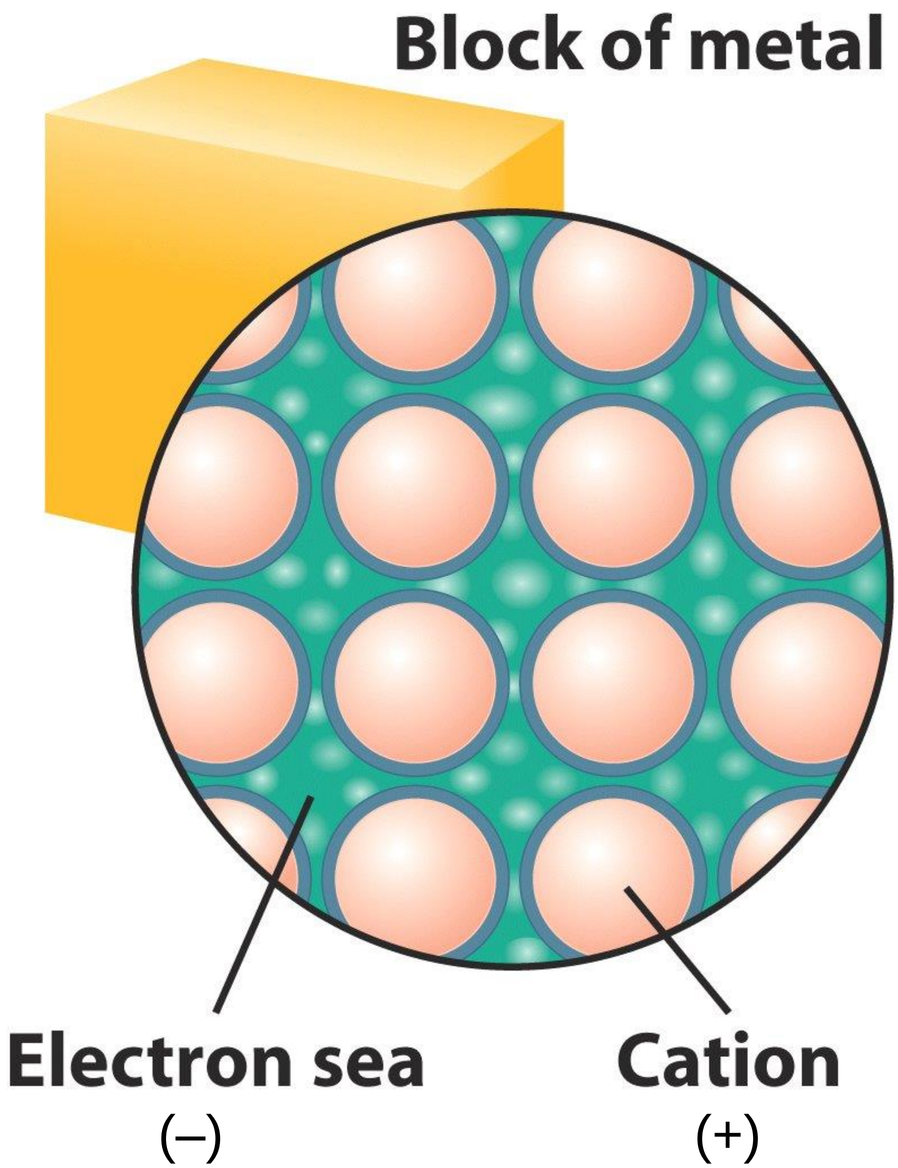
Metals:

Malleable (bend) and ductile (make a wire).
Shiny so reflect light (mirrors).
Electrical and thermal conduct.
Basic.
Lose electrons—**oxidized**.

Nonmetals:

Brittle.
Dull.
Electrical and thermal insulators.
Acidic.
Gain electrons—**reduced**.

Electrons in the sea are mobile. This enables metals to conduct an electric current. Also accounts for their luster, and malleability-being deformed without shattering.



The Inert-Pair Effect

Tin and lead both 2 of *s*-electrons *and* 2 of *p*-electrons.

Tin forms **Sn^{2+} or Sn^{4+}** while lead **only forms Pb^{2+}** because its *s*-electrons are very **low in energy and unreactive**, so will it will always loss it's 2 *p*-electrons.

Tin(II) oxide reacts with oxygen to form tin(IV) oxide.

The Inert-Pair Effect: losing p-electrons first.