IR/UV Spectroscopy

U. Mall

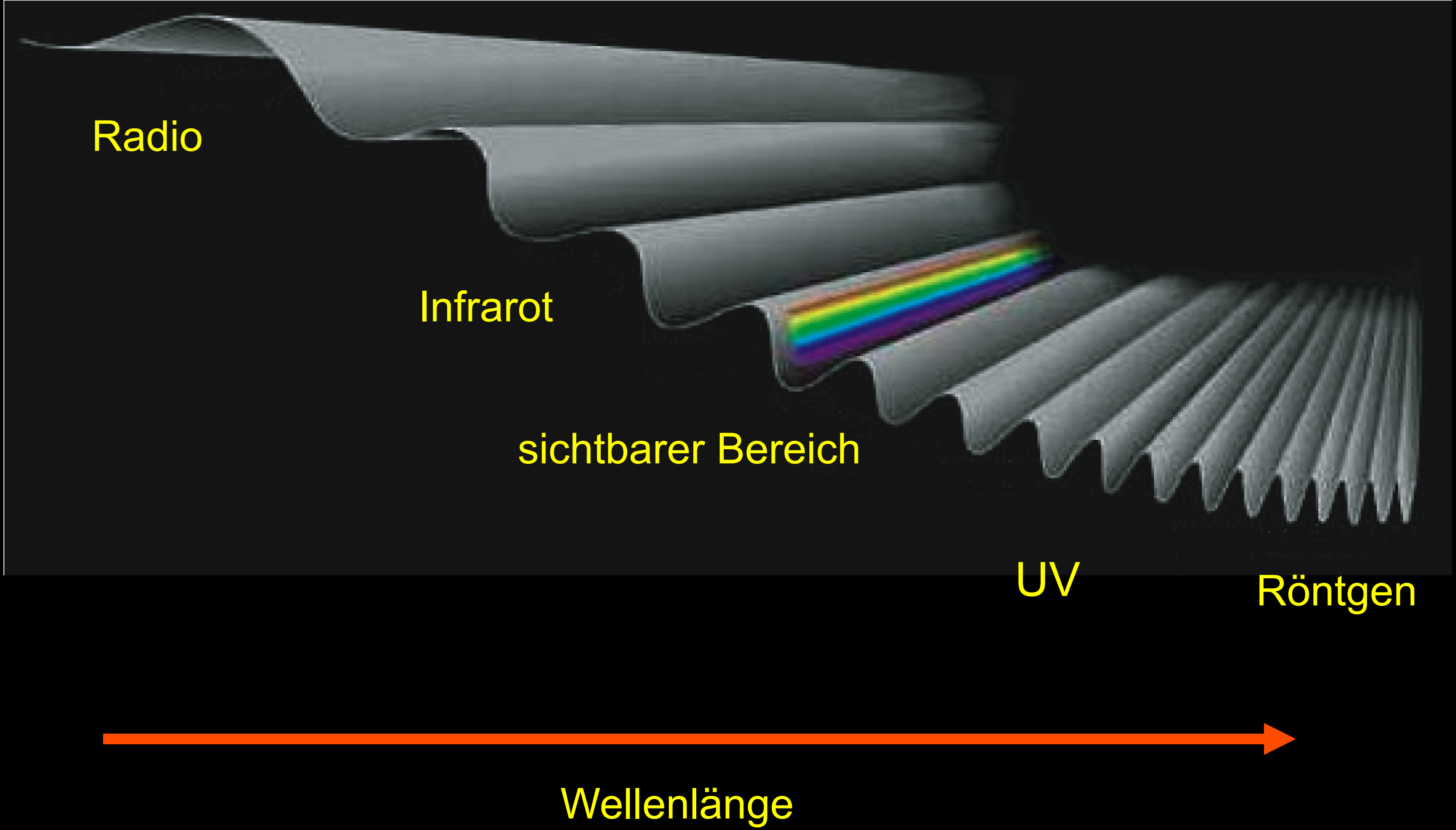
Lindau, 28.10.2010

What is spectroscopy?

Originally, the study of the dispersion of visible light into its component colors (visible spectrum). Now it means the study of electromagnetic (EM) and other spectra including mass, electron and acoustic spectroscopy’s.

Spectroscopy generally involves measuring the absorption of light by a sample or the emission of light by sample

The Electromagnetic Spectrum



Radio

Infrarot

sichtbarer Bereich

UV

Röntgen

Wellenlänge

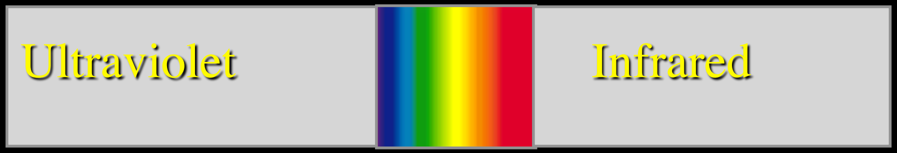
The Electromagnetic Spectrum

Shorter Wavelength (λ) Longer Wavelength (λ)

400 nm 750 nm

Higher Frequency (ν) Lower Frequency (ν)

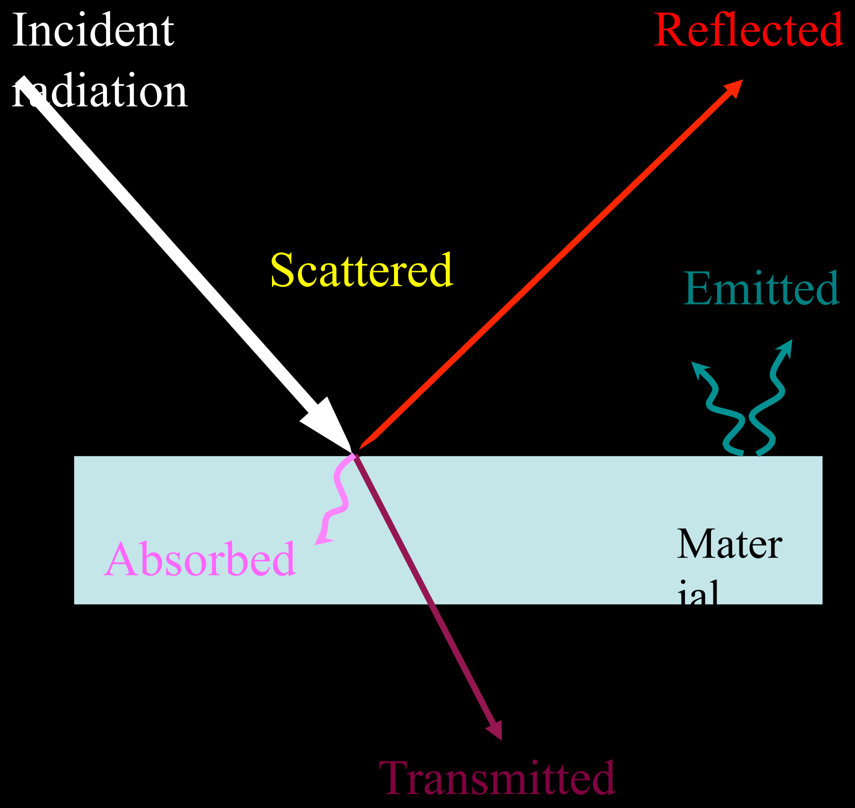
Higher Energy (E) Lower Energy (E)



Electromagnetic Spectrum

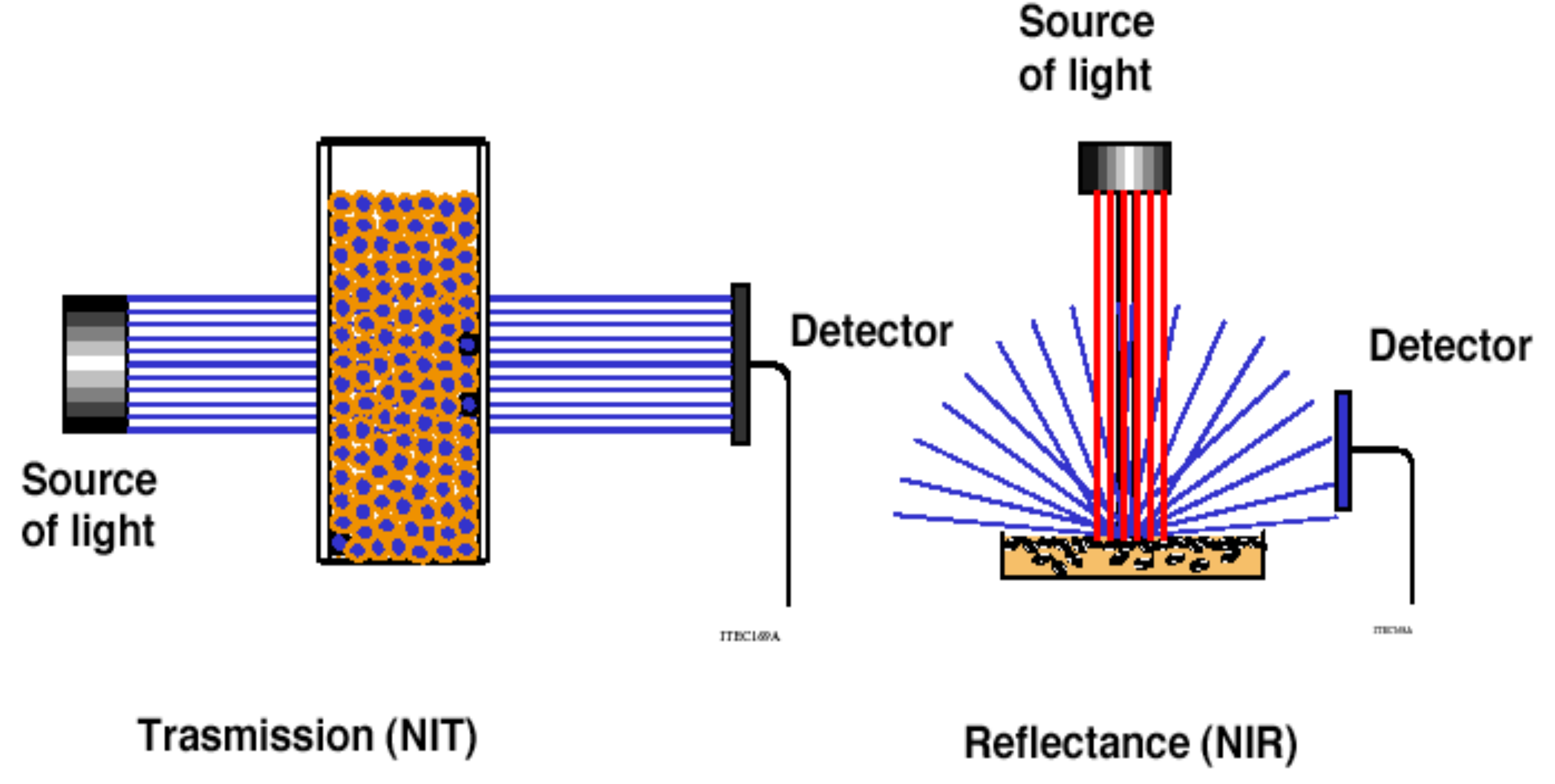
γ ray	< 1 nm	(10^4 – 10^6 eV)
X ray	1 – 50 nm	(10^2 – 10^4 eV)
far UV	10 – 200 nm	
near UV	200 – 350 nm	
Visible	350 – 800 nm	
near IR	0.8 μm –	
IR	– 2.5 μm	
Microwave	400 μm – 30 cm	
radio wave	100 cm and above	

Interaction of ER with matter



- Interaction of EM energy (light) with material changes the energy
- Five basic types of interactions between light sources and materials, such that the light is:
  - **Reflected**
  - **Scattered**
  - **Transmitted** (refracted): illuminating energy is passed through the material; changes in spectrum are caused by change in density (velocity of incident wave) between material and surroundings (index of refraction)
  - **Absorbed**: energy is transformed (usually into longer wavelength heat)
  - **Emitted**: energy is released from the material (it's now the source)

Reflectance – Transmission NIR Spectroscopy



Trasmission (NIT)

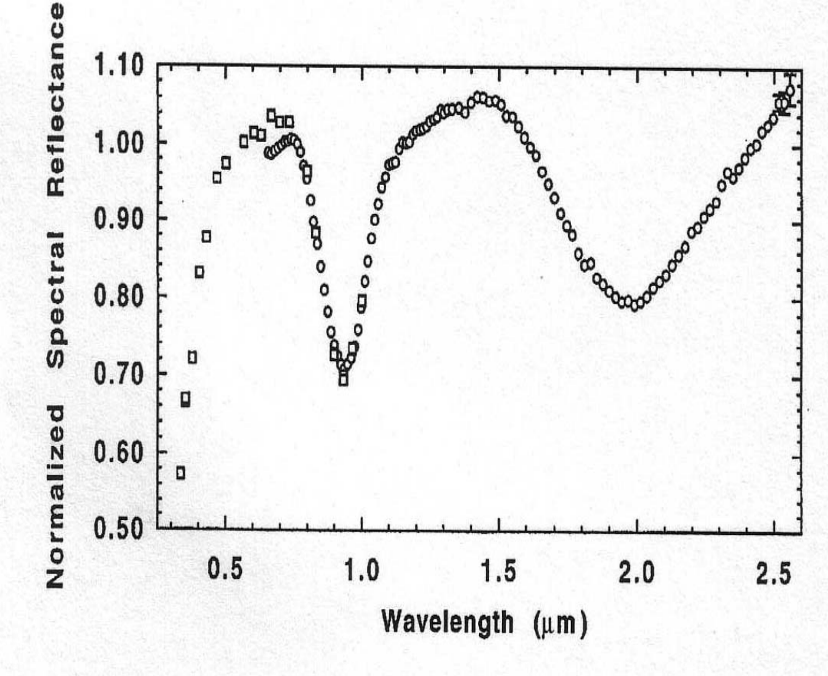
Reflectance (NIR)

How are we using this?

We can measure the light energy at the various frequencies = a spectrum

We examine the maxima and minima of spectral reflectance curves – minima are caused by molecular **absorption**, and we call these **absorption features** or **absorption bands**.

Differences in absorption and scattering for different wavelengths can be used to identify the minerals. The unique spectra are like fingerprints.

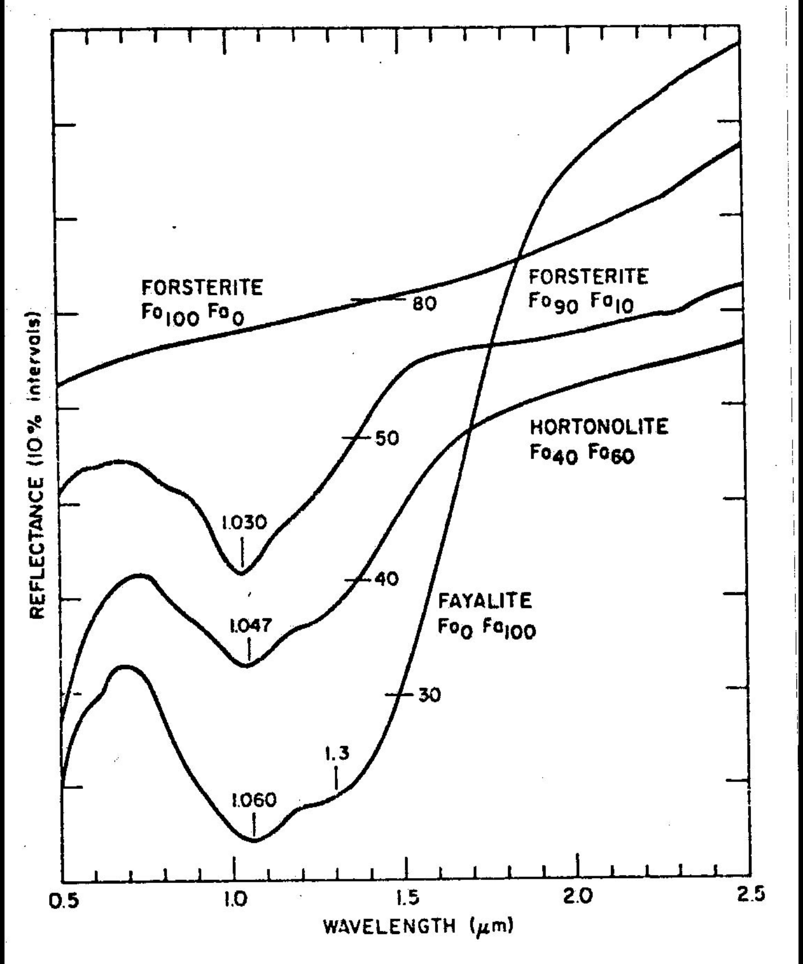


How are we using this?

Solid solution - olivine [$(Mg,Fe)_2SiO_4$]

- forsterite (Mg_2SiO_4) and
- fayalite (Fe_2SiO_4),

define a complete solid-solution series in which magnesium cations (Mg^{2+}) are replaced partially or totally by Fe^{2+}.



- Spectra of olivines of widely varying compositions provides an important clue:
- Iron-free olivine (forsterite) lacks an absorption feature and is bright
- Suggests absorption is due to iron

What causes absorption features?

Two basic types of processes from 0.4 - 50 µm

a) Electronic (~0.4 to 1.5 µm)
  - High-energy photons absorbed by bound electrons
  - Energy states/wavelength controlled by atom and crystal
  - Primarily interactions with transition metals (e.g., Fe)
    (Not all minerals contain these)

b) Vibrational (>~6 µm)
  - Excitation of fundamental vibrational motions of atoms
    - stretching and bending
    - Frequencies related to strength and length of bonds
  - ~1.5 - ~6 µm are weaker overtones and combination bands
    - Complex transitional region between reflection & emission

What causes absorption features?

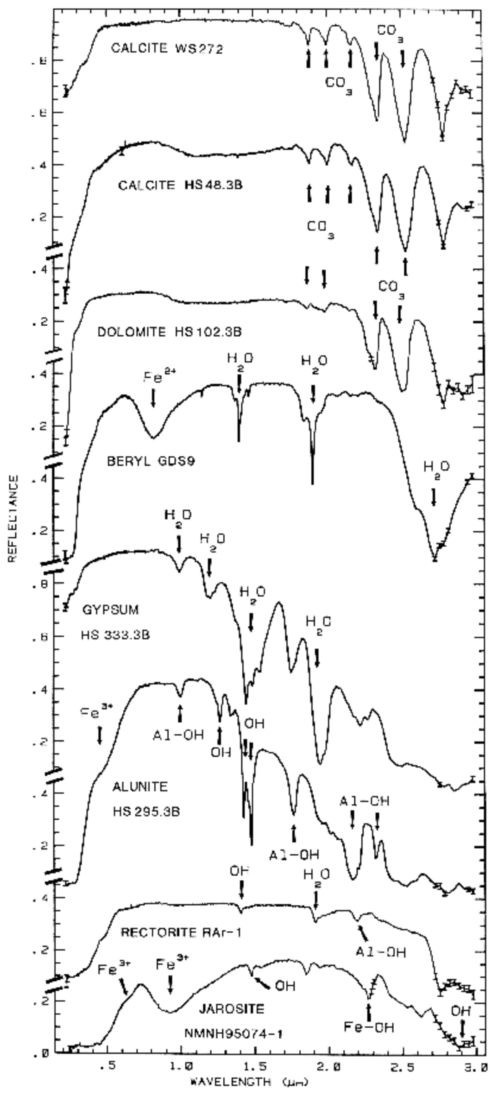
- Electronic processes
  - **Crystal field effect**
    - Roger Burns interpreted near-IR absorptions in terms of Bethe's "crystal field theory"
    - Absorption is due to photons exciting an electron in unfilled d-shells in transition metals.
  - **Charge transfer absorptions**
  - **Conduction bands**
  - **Color centers**

Interaction of Electromagnetic Radiation and Molecules

Phenomenon	Spectral Region	Wavelength
Inner electrons - ionization	X-rays	0.1-1.0 nm
Valency electrons	Ultraviolet	0-200 nm
Molecular vibrations, bond stretching or rotation	Infrared	200 nm-800 nm
Rotation & electron spin orientation in magnetic field	Microwaves	400 uM – 30 cm
Nuclear spin orientation in magnetic field	Radio waves	>100 cm

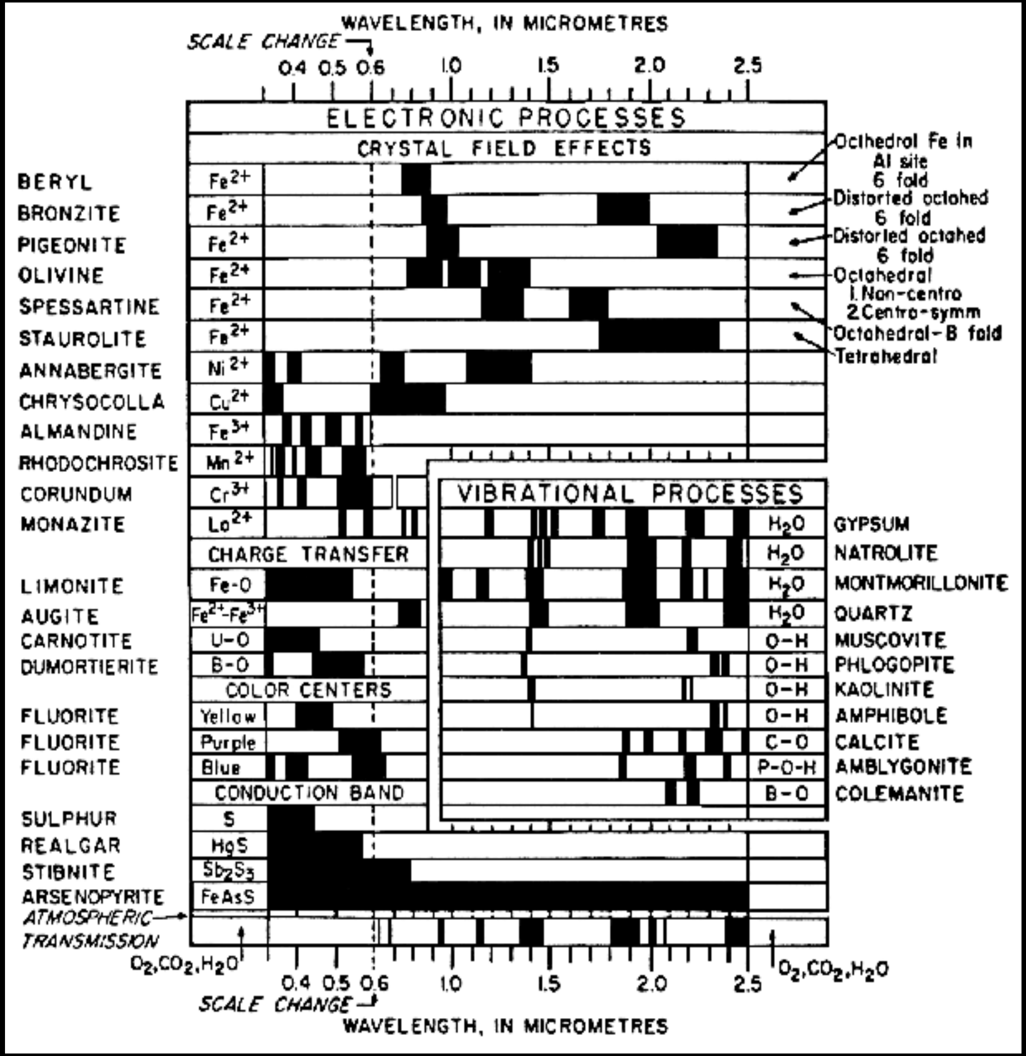
What causes absorption features?

- Vibrational processes
  - Bonds in a molecule vibrate, the frequency is dependent on the type of bond and the atom masses.
  - Certain materials have important vibrational absorption bands: water, hydroxyl, carbonates, phosphates, borates, arsenates, vanadates.



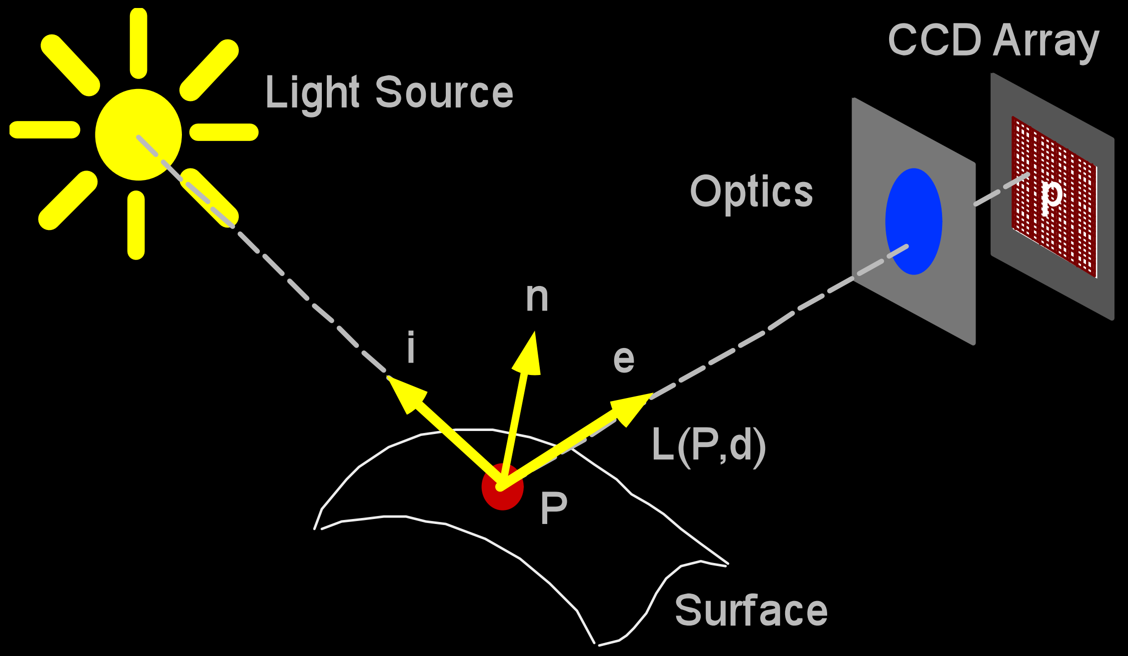
Identifying Minerals

We can use all of these absorption features to determine the chemical composition of a spectral reflectance curve.



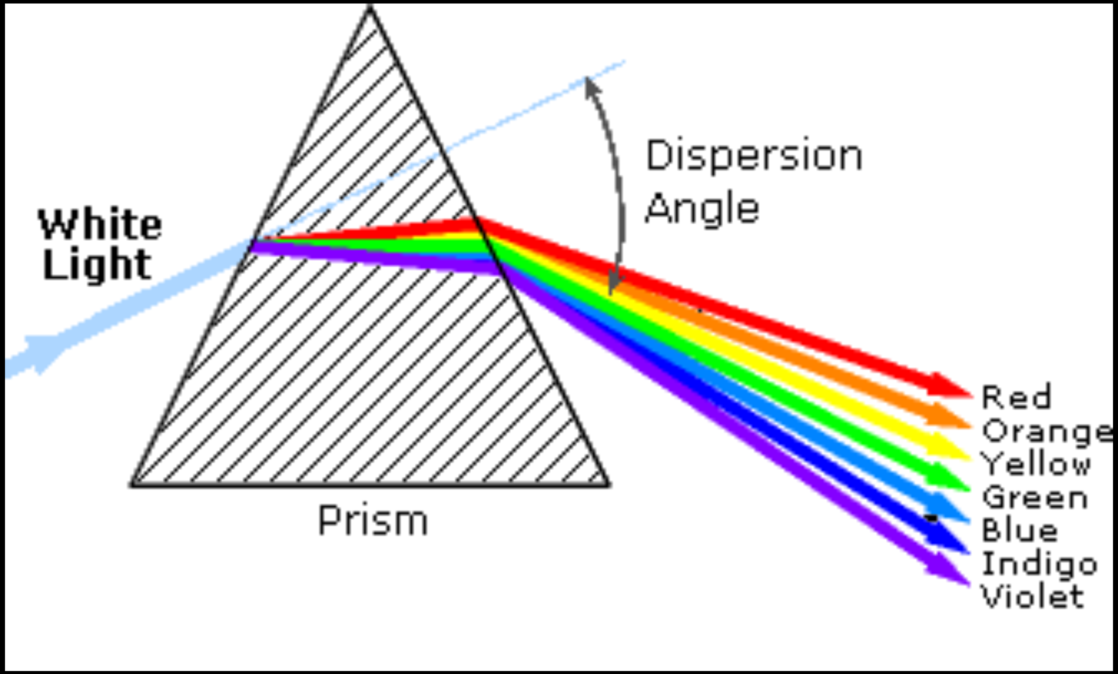
How do you measure in space?

Measure how much electromagnetic energy (EM) is present, usally expressed in terms of the flow of EM energy from a source, through space or onto a detector.



What does a spectrometer need?

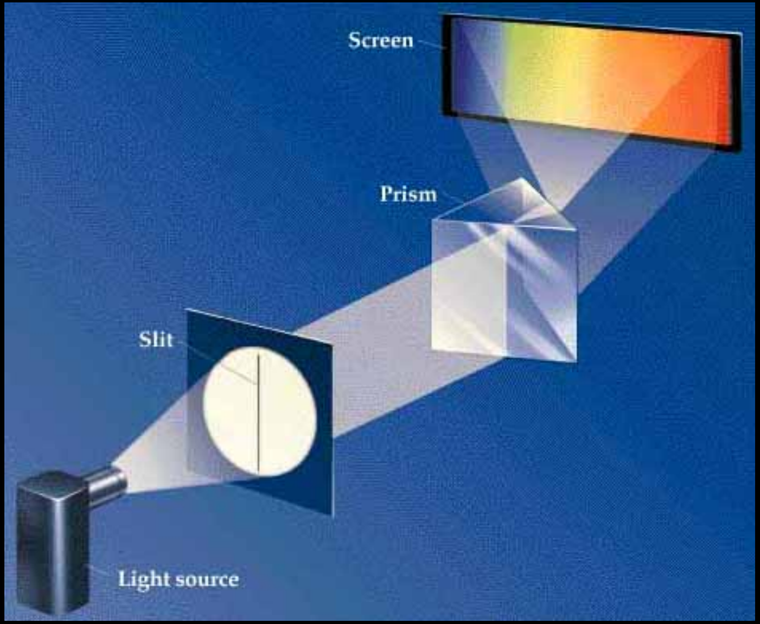
Monochromator = Dispersion element plus slit system

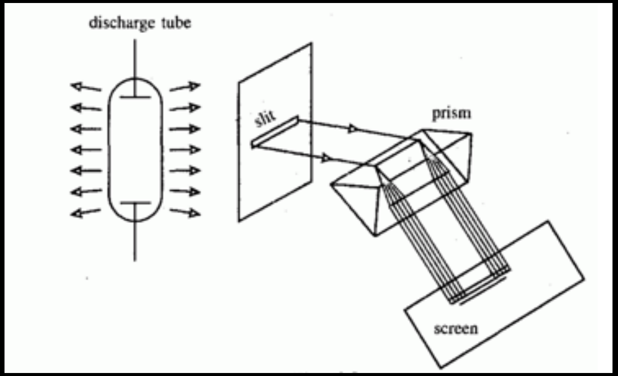


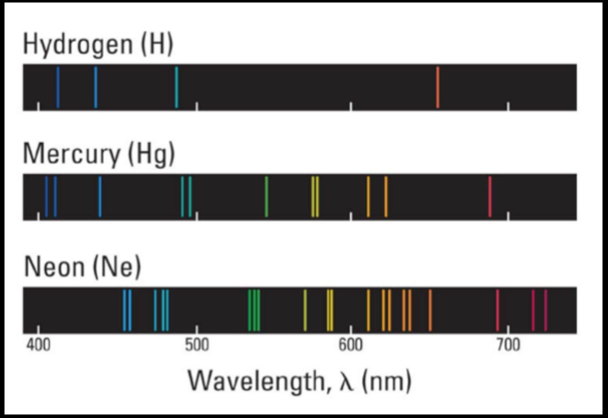
Property of EM radiation

- Light (EM radiation) has a dual nature.
- Light exhibits properties of waves and particles (called *photons* or *quanta)*.

Evidendence for Bohr's Model

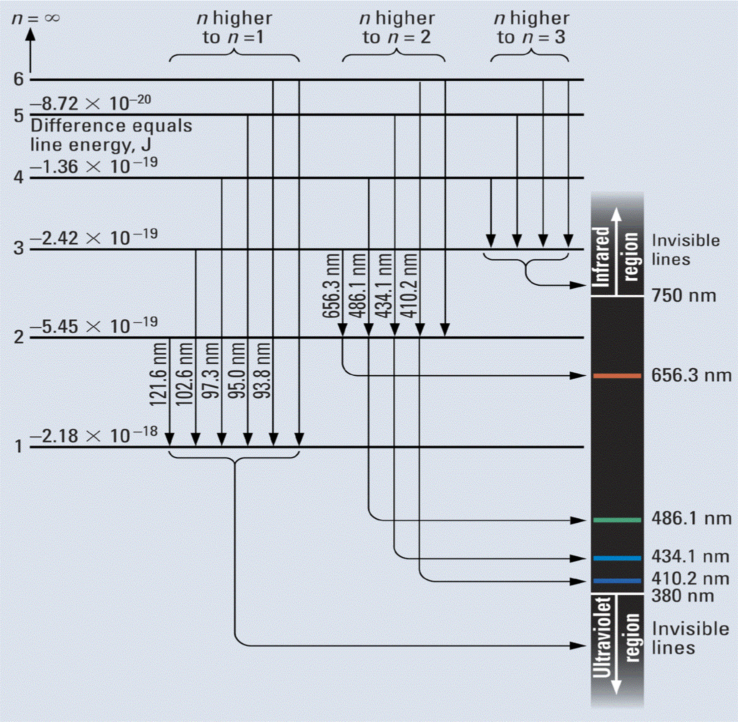






Bohr's Model of the Hydrogen Atom

Moore/Stanitski/Jurs, Chemistry: The Molecular Science
Figure 7.8

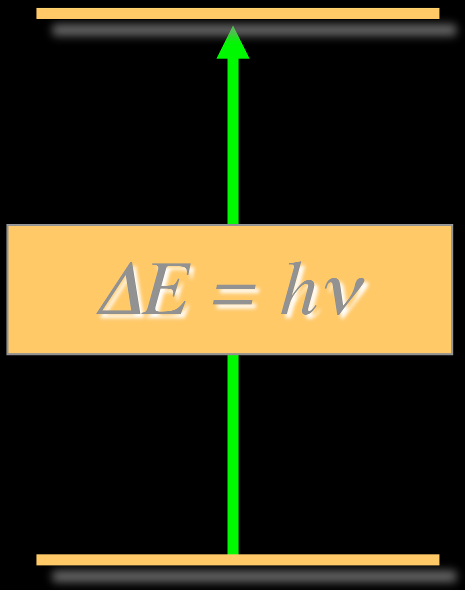


Bohr's Model

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

When $n_i > n_f$, energy is emitted.
When $n_f > n_i$, energy is absorbed.

UV/IR Spectroscopy



$\Delta E = h\nu$

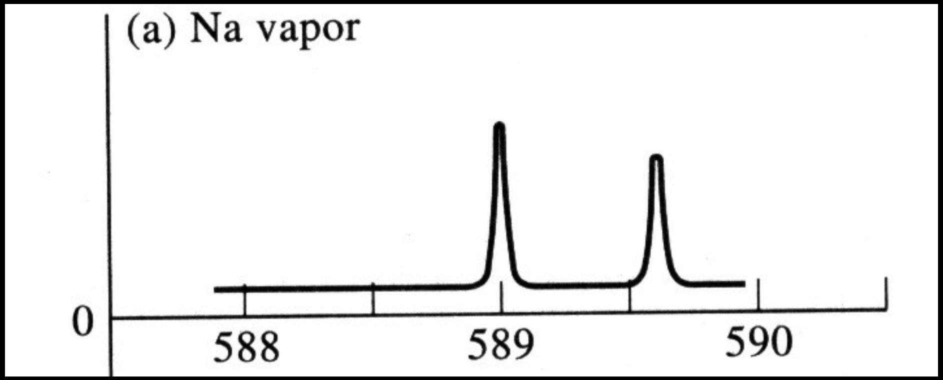
Electromagnetic radiation is absorbed when the energy of photon corresponds to difference in energy between two states.

gaps between electron energy levels are greater than those between vibrational levels

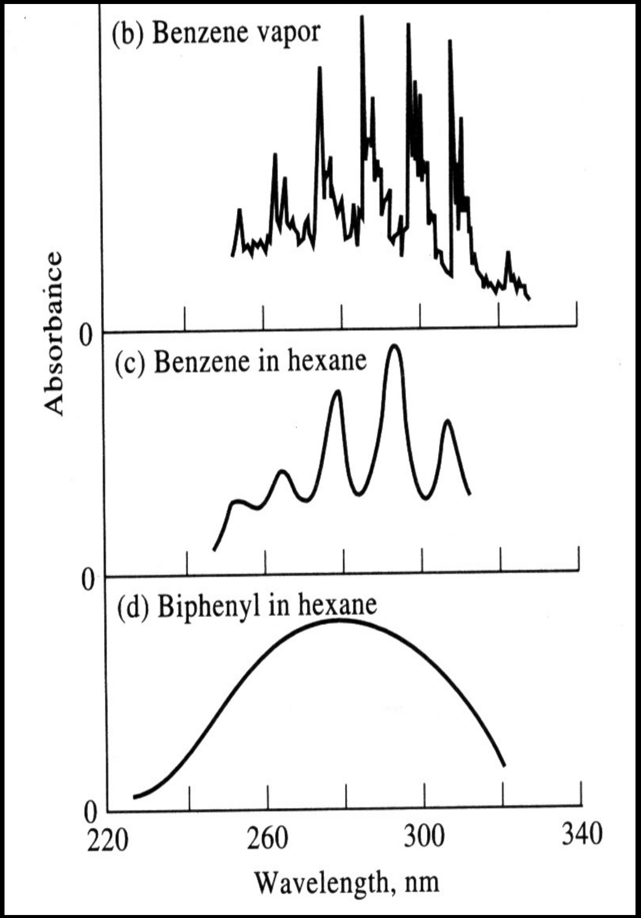
gap corresponds to wavelengths between 200 and 800 nm

Absorption: Atomic & Molecular

Atomic absorption

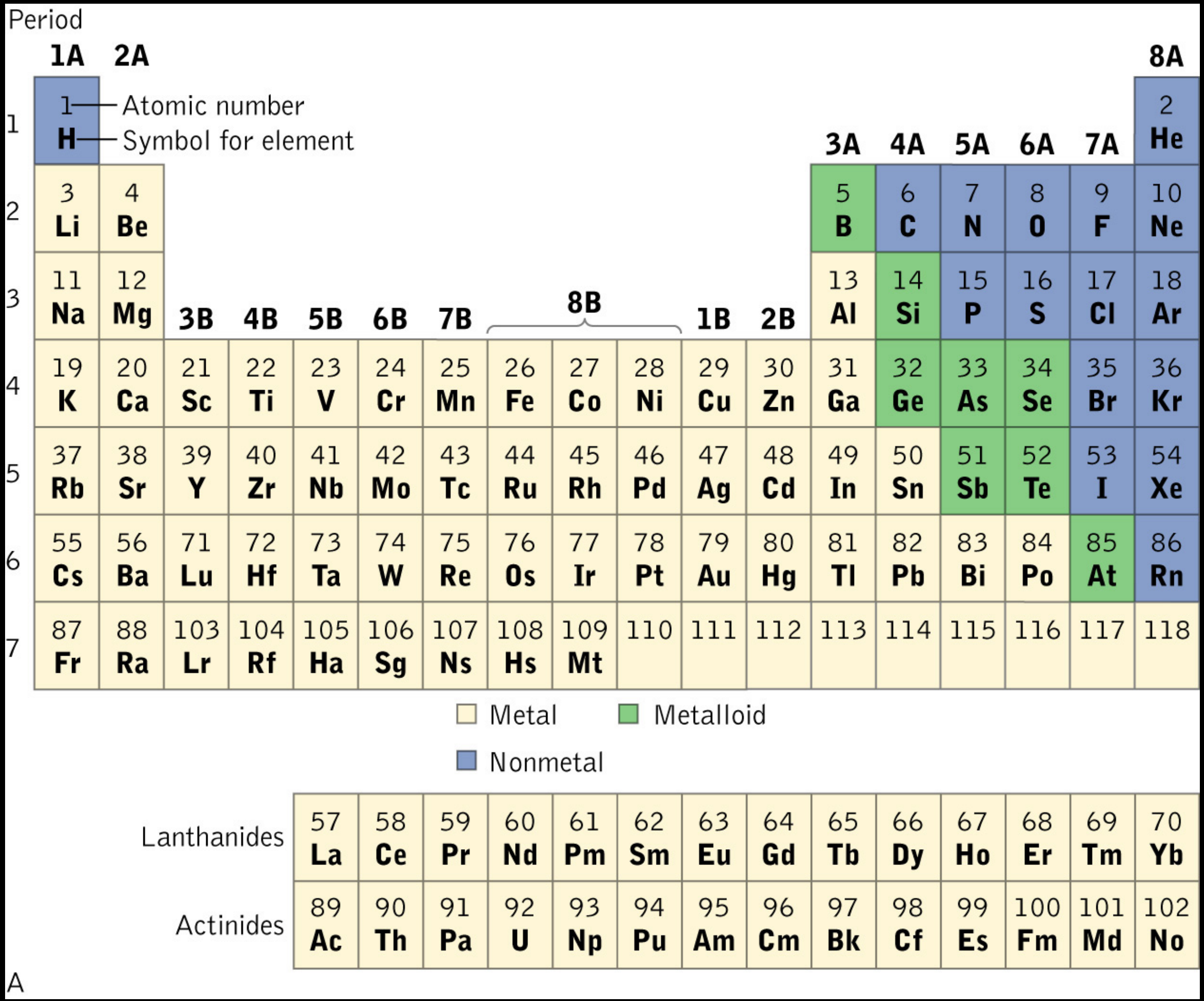


Molecular absorption



The two peaks arise from the promotion of a 3*s* electron to the two 3*p* states

The sharpness of molecular absorption spectra also depends on the state of the sample. In condensed states the spectra broaden due to molecular collisions



Period	1A	2A	3B	4B	5B	6B	7B	8B	8B	8B	1B	2B	3A	4A	5A	6A	7A	8A
1	1 **H**																	2 **He**
2	3 **Li**	4 **Be**											5 **B**	6 **C**	7 **N**	8 **O**	9 **F**	10 **Ne**
3	11 **Na**	12 **Mg**											13 **Al**	14 **Si**	15 **P**	16 **S**	17 **Cl**	18 **Ar**
4	19 **K**	20 **Ca**	21 **Sc**	22 **Ti**	23 **V**	24 **Cr**	25 **Mn**	26 **Fe**	27 **Co**	28 **Ni**	29 **Cu**	30 **Zn**	31 **Ga**	32 **Ge**	33 **As**	34 **Se**	35 **Br**	36 **Kr**
5	37 **Rb**	38 **Sr**	39 **Y**	40 **Zr**	41 **Nb**	42 **Mo**	43 **Tc**	44 **Ru**	45 **Rh**	46 **Pd**	47 **Ag**	48 **Cd**	49 **In**	50 **Sn**	51 **Sb**	52 **Te**	53 **I**	54 **Xe**
6	55 **Cs**	56 **Ba**	71 **Lu**	72 **Hf**	73 **Ta**	74 **W**	75 **Re**	76 **Os**	77 **Ir**	78 **Pt**	79 **Au**	80 **Hg**	81 **Tl**	82 **Pb**	83 **Bi**	84 **Po**	85 **At**	86 **Rn**
7	87 **Fr**	88 **Ra**	103 **Lr**	104 **Rf**	105 **Ha**	106 **Sg**	107 **Ns**	108 **Hs**	109 **Mt**	110	111	112	113	114	115	116	117	118

1 — Atomic number

H — Symbol for element

□ Metal

🟩 Metalloid

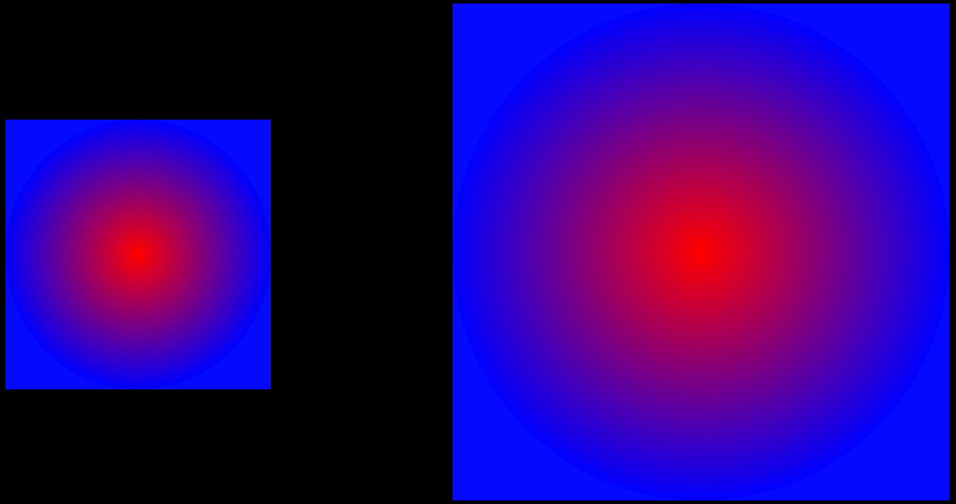
🟦 Nonmetal

Lanthanides	57 **La**	58 **Ce**	59 **Pr**	60 **Nd**	61 **Pm**	62 **Sm**	63 **Eu**	64 **Gd**	65 **Tb**	66 **Dy**	67 **Ho**	68 **Er**	69 **Tm**	70 **Yb**
Actinides	89 **Ac**	90 **Th**	91 **Pa**	92 **U**	93 **Np**	94 **Pu**	95 **Am**	96 **Cm**	97 **Bk**	98 **Cf**	99 **Es**	100 **Fm**	101 **Md**	102 **No**

Remember: Basic QM
Wave Functions

- Schrödinger combined the idea that an electron has wave properties with classical equations of wave motion to give a wave equation for the energy of an electron in an atom.
- Wave equation (Schrödinger equation) gives a series of solutions called wave functions (ψ).
- Only certain values of ψ are allowed.
- Each ψ corresponds to a certain energy.
- The probability of finding an electron at a particular point with respect to the nucleus is given by ψ^2.
- Each energy state corresponds to an orbital.

A boundary surface encloses the region where the probability of finding an electron is high—on the order of 90-95%

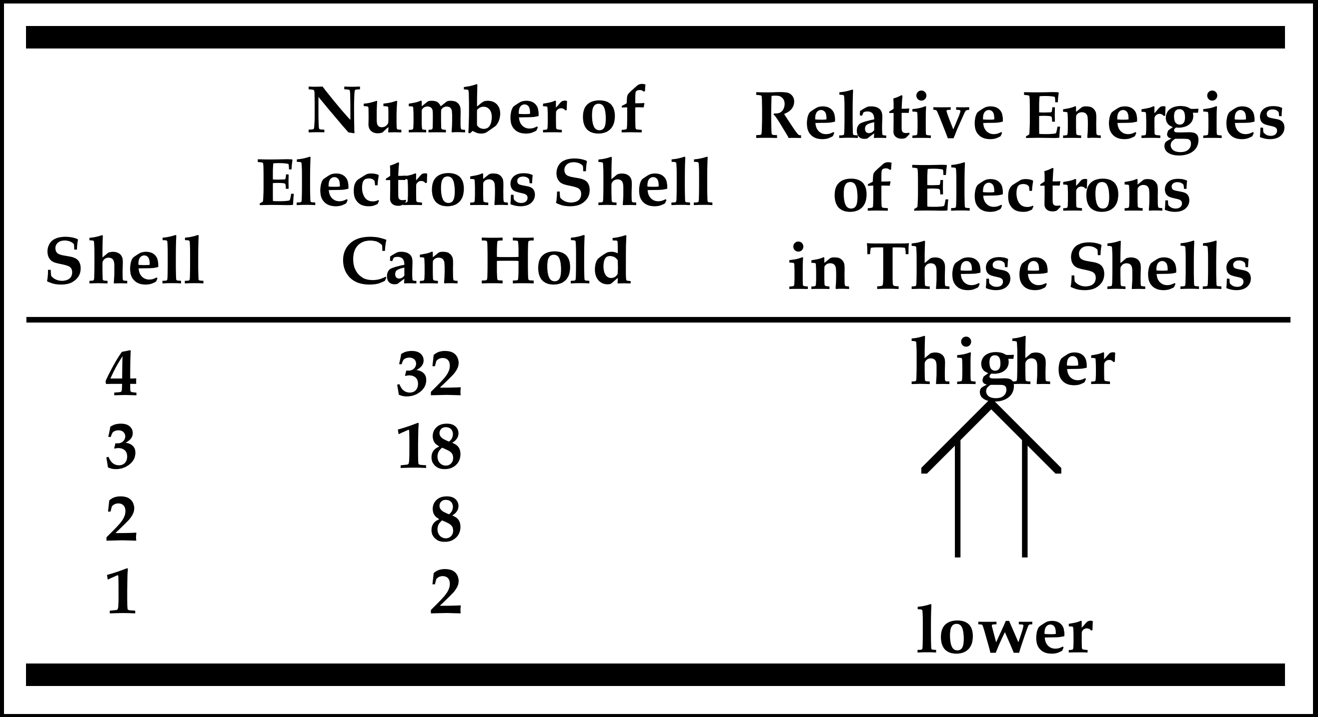


probability of finding an electron at a particular point with respect to the nucleus is given by ψ^2.

Electron Configuration of Atoms

Electrons are confined to regions of space called principle energy levels (shells).

- Each shell can hold $2n^2$ electrons ($n = 1,2,3,4......$)



Shell	Number of Electrons Shell Can Hold	Relative Energies of Electrons in These Shells
4	32	higher
3	18	↑
2	8	
1	2	lower

Representation of Orbitals

The s Orbitals

All s-orbitals are spherical.

As n increases, the s-orbitals get larger.

As n increases, the number of nodes increase.

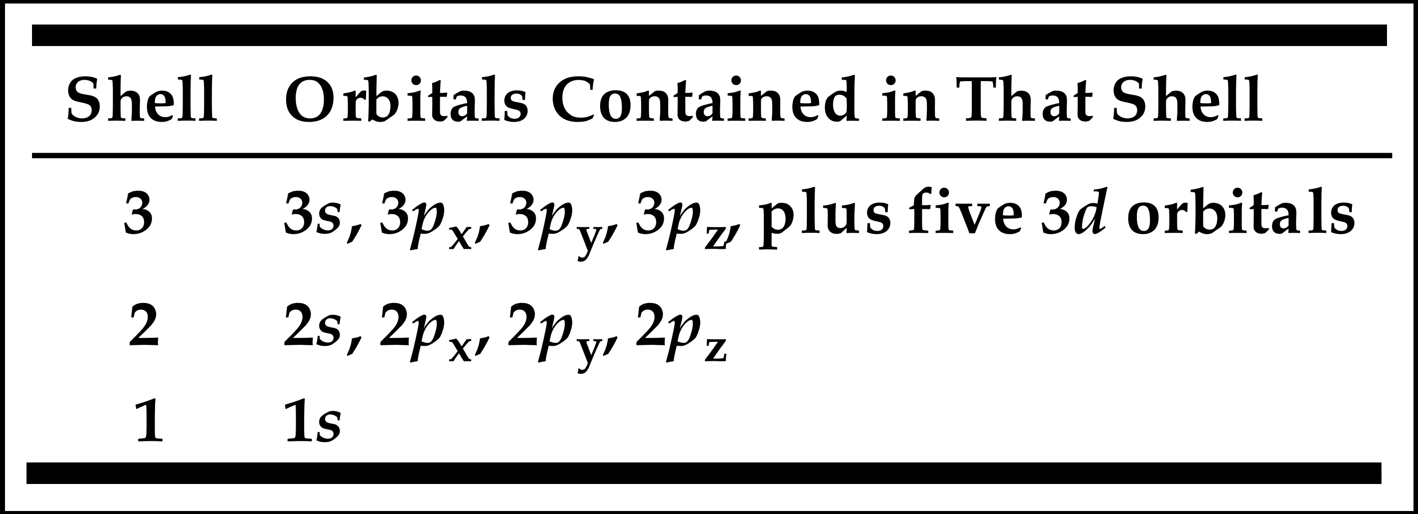
A node is a region in space where the probability of finding an electron is zero.

At a node, $\Psi^2 = 0$

For an s-orbital, the number of nodes is (n - 1).

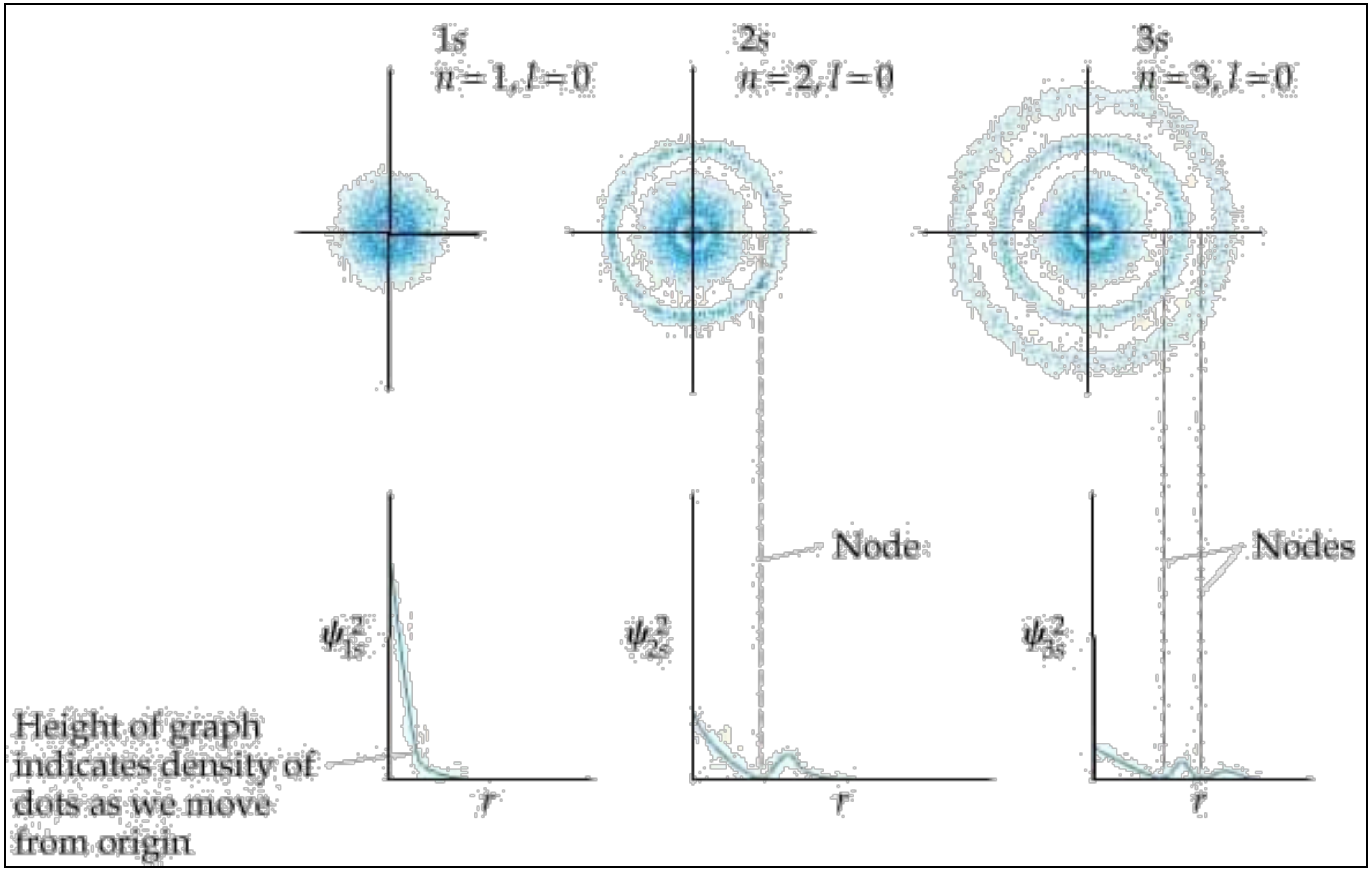
Electron Configuration of Atoms

- Shells are divided into subshells called orbitals, which are designated by the letters *s*, *p*, *d*, *f*........
  - – *s* (one per shell)
  - – *p* (set of three per shell 2 and higher)
  - – *d* (set of five per shell 3 and higher) .....
  - – The distribution of Orbitals in Shells

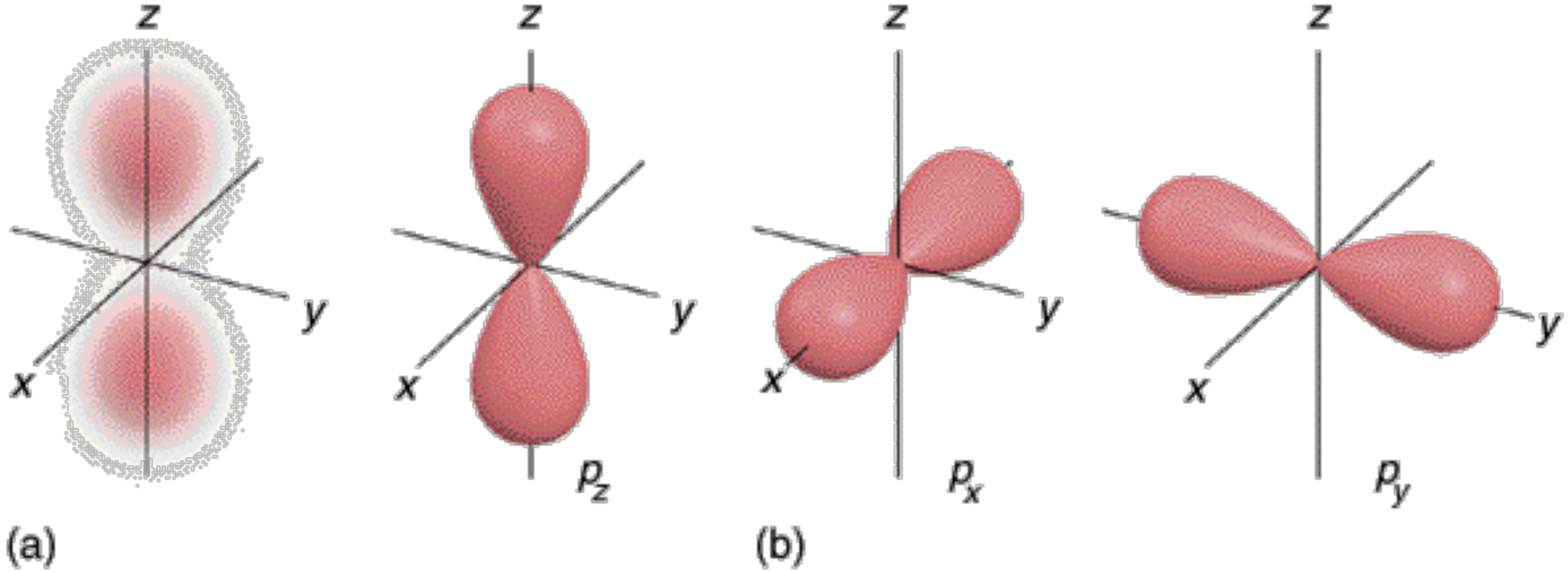


Shell	Orbitals Contained in That Shell
3	$3s$, $3p_x$, $3p_y$, $3p_z$, plus five $3d$ orbitals
2	$2s$, $2p_x$, $2p_y$, $2p_z$
1	$1s$

The *s* Orbitals

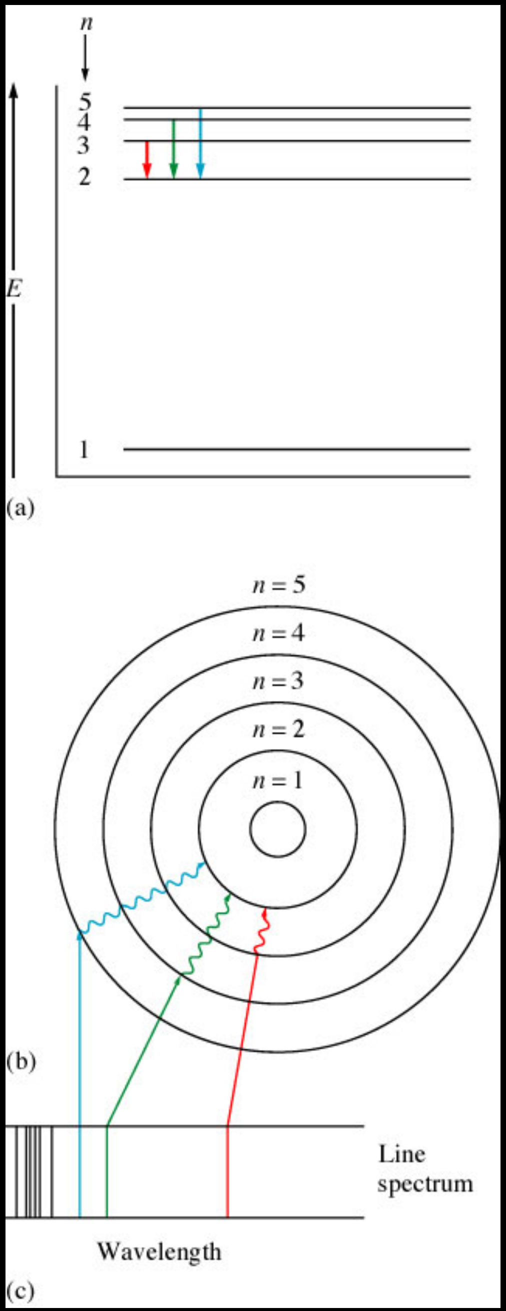


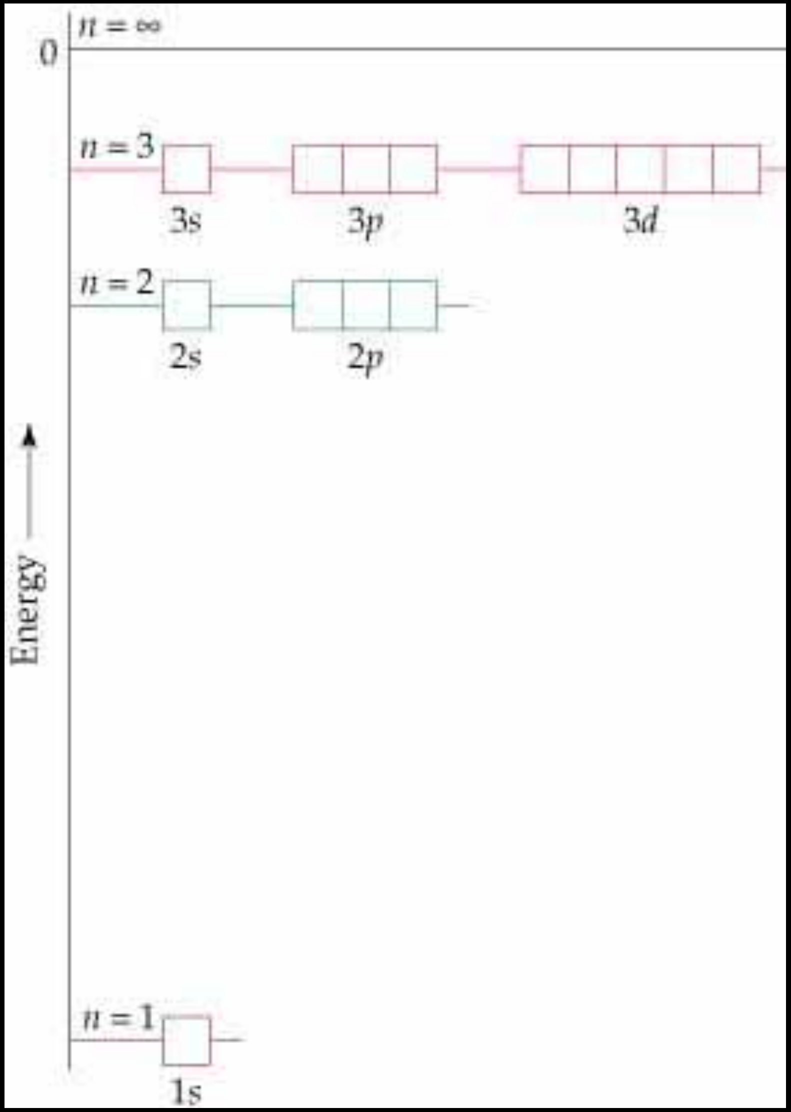
The *p* Orbitals



Remember: Basic QM

- Solve the Schrödinger equation - get wave functions ψ and energies for the wave functions. We call wave functions orbitals.
- Each orbital is characterized by a unique set of quantum numbers:
  - principal quantum number *n*
  - angular momentum quantum *l* number is usually designated by a letter (*s*, *p*, *d*, *f*, etc) and describes the shape of the orbital.
  - Magnetic Quantum Number, m_l give the 3D orientation of each orbital
- The Pauli Exclusion Principle: No two electrons in the same atom can have the same set of four quantum numbers. There is a maximum of two electrons per orbital.





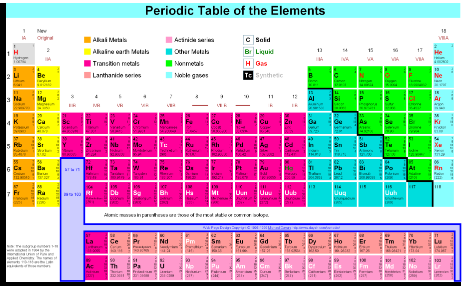
- Orbitals can be ranked in terms of energy to yield an Aufbau diagram.
- Note that the following Aufbau diagram is for a single electron system.
- As *n* increases, note that the spacing between energy levels becomes smaller.

Electron configurations

Electron configurations tells us in which orbitals the electrons for an element are located.

Three rules:

- **electrons fill orbitals starting with lowest *n* and moving upwards;**
- **no two electrons can fill one orbital with the same spin (Pauli);**
- **for degenerate orbitals, electrons fill each orbital singly before any orbital gets a second electron (Hund’s rule).**



How does it work?

	Z	1s	2s	2p			3s	
H	1	↑						$1s^1$
He	2	↑↓						$1s^2$
Li	3	↑↓	↑					$1s^2 2s^1$
Be	4	↑↓	↑↓					$1s^2 2s^2$
B	5	↑↓	↑↓	↑				$1s^2 2s^2 2p^1$
C	6	↑↓	↑↓	↑	↑			$1s^2 2s^2 2p^2$
N	7	↑↓	↑↓	↑	↑	↑		$1s^2 2s^2 2p^3$

Electron Configurations and the Periodic Table

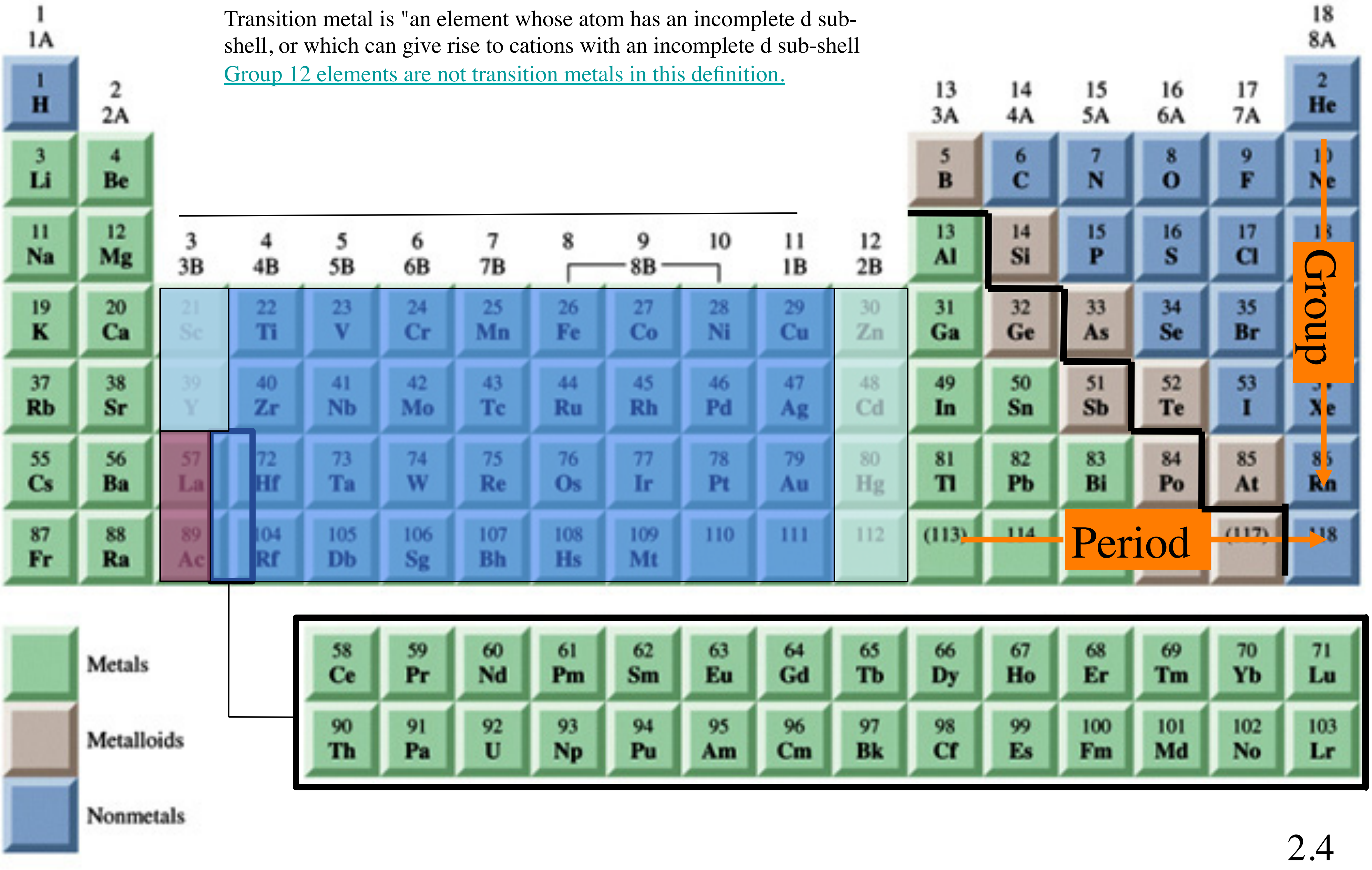
The periodic table can be used as a guide for electron configurations.

- **The period number is the value of *n*.**
- **Groups 1A and 2A have the *s*-orbital filled.**
- **Groups 3A - 8A have the *p*-orbital filled.**
- **Groups 3B - 2B have the *d*-orbital filled.**
- **The lanthanides and actinides have the *f*-orbital filled.**
- **Note that the 3*d* orbital fills after the 4*s* orbital.**
- **Similarly, the 4*f* orbital fills after the 5*d* orbital.**

International Union of Pure and Applied Chemistry (IUPAC)
Def: Transition metal

Transition metal is "an element whose atom has an incomplete d sub-shell, or which can give rise to cations with an incomplete d sub-shell

Group 12 elements are not transition metals in this definition.



1 1A	2 2A	3 3B	4 4B	5 5B	6 6B	7 7B	8	9 8B	10	11 1B	12 2B	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	1
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110	111	112	(113)	114			(117)	118

58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

🟩 Metals

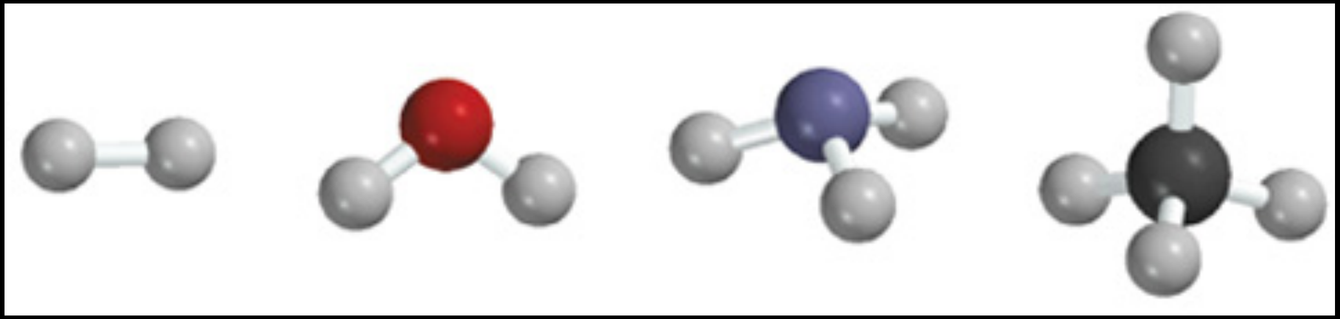
🟫 Metalloids

🟦 Nonmetals

Chemical Bonding

- A chemical bond results from strong electrostatic interactions between two ore more atoms.
- The nature of the atoms determines the kind of bond.

A ***molecule*** is an aggregate of two or more atoms in a definite arrangement held together by chemical bonds



H_2 H_2O NH_3 CH_4

A ***diatomic molecule*** contains only two atoms

H_2, N_2, O_2, Br_2, HCl, CO

A ***polyatomic molecule*** contains more than two atoms

O_3, H_2O, NH_3, CH_4

An ***ion*** is an atom, or group of atoms, that has a net positive or negative charge.

cation – ion with a positive charge

If a neutral atom **loses** one or more electrons
it becomes a cation.

anion – ion with a negative charge

If a neutral atom **gains** one or more electrons
it becomes an anion.

A ***monatomic ion*** contains only one atom

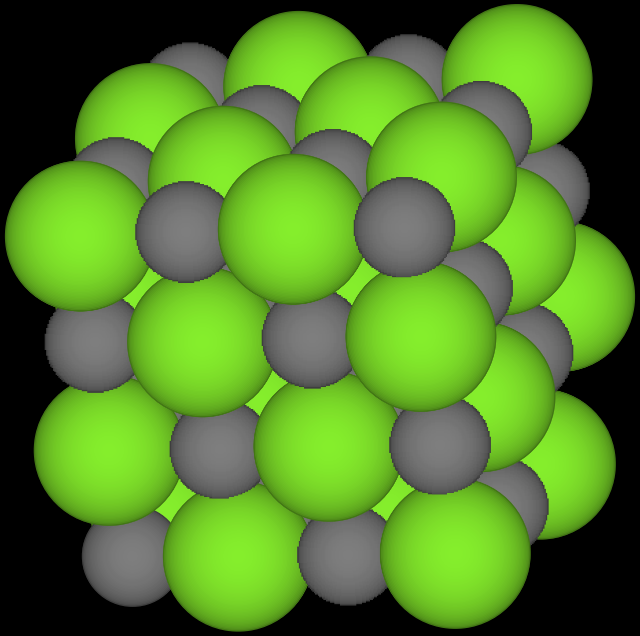
Na^{+}, Cl^{-}, Ca^{2+}, O^{2-}, Al^{3+}, N^{3-}

A ***polyatomic ion*** contains more than one atom

OH^{-}, CN^{-}, NH_4^{+}, NO_3^{-}

Ionic Bonding

- An ionic bond is the force of electrostatic attraction between oppositely charged ions



Na^+ (cation)

Cl^- (anion)

Covalent Bonding

- Many compounds contain bonds that are very different from ionic bonds. Neither these compounds nor their solutions conduct electricity.
- 1916 G.N. Lewis proposed an electronic model for bonding in nonionic compounds.
- An electron pair that is shared between two atoms constitutes a covalent bond.
- Each atom donates an electron resulting in a pair of electrons that are SHARED between the two atoms.
- COVALENT bonds result from a strong interaction between NEUTRAL atoms

For example, consider a hydrogen molecule, H_2. When the two hydrogen, H, atoms are far apart from each other they do not feel any interaction.

As they come closer each “feels” the presence of the other.

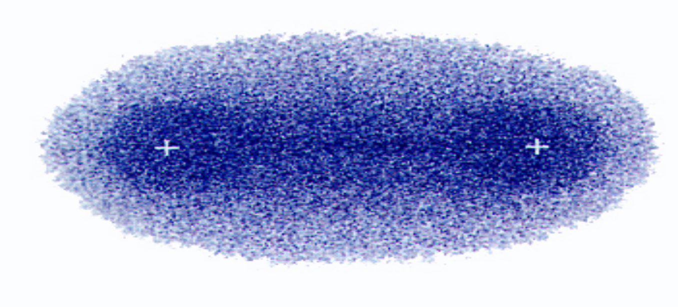
The electron on each H atom occupies a volume that covers both H atoms and a COVALENT bond is formed.

Once the bond has been formed, the two electrons are shared by BOTH H atoms.

Simplest covalent bond is that in H_2

- The single electrons from each atom combine to form an electron pair.
- The shared pair functions in two ways simultaneously; it is shared by the two atoms and fills the valence shell of each atom.

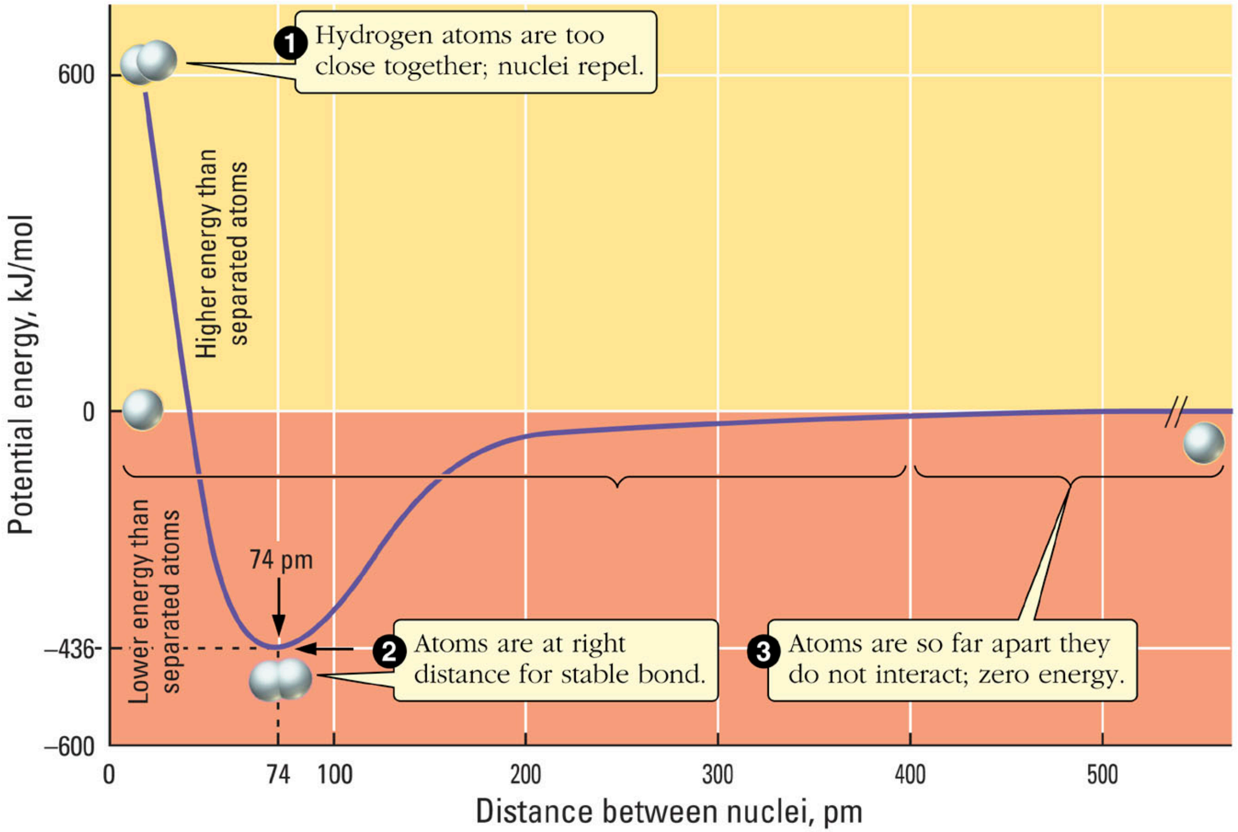
An electron density plot for the H_2 molecule shows that the shared electrons occupy a volume equally distributed over BOTH H atoms.



Electron Density for the H_2 molecule

H-H Bond Formation from Isolated H Atoms and why is it stable

Moore/Stanitski/Jurs, Chemistry: The Molecular Science
Figure 8.1



❶ Hydrogen atoms are too close together; nuclei repel.

❷ Atoms are at right distance for stable bond.

❸ Atoms are so far apart they do not interact; zero energy.

What factors determine if an atom forms a covalent or ionic bond with another atom?

- **The number of electrons in an atom, particularly the number of the electrons furthest away from the nucleus determines the atom’s reactivity and hence its tendency to form covalent or ionic bonds.**
- **These outermost electrons are the one’s that are more likely to “feel” the presence of other atoms and hence the one’s involved in bonding i.e. in reactions.**

Electronegativity

The type of bond formed between a pair of atoms is determined by the ability of the atoms to attract electrons from the other.

For a free, isolated atom:

- its ability to loose an electron is measured by its IONIZATION ENERGY,
- while the ability to gain an electron is measured by its ELECTRON AFFINITY

The average of these two properties for isolated atoms define the atom’s ELECTRONEGATIVITY which measures the tendency of one atom to attract electrons from another atom to which it is bonded.

For example, Metallic elements loose electrons (to form positive ions) more readily than non-metallic elements

Metallic elements are hence referred to as being more ELECTROPOSITIVE that non-metals.

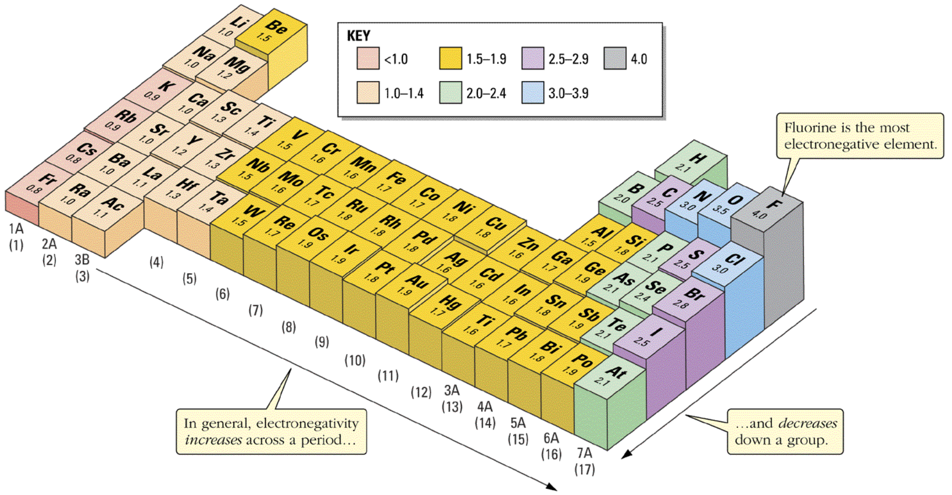
Non-metals are more ELECTRONEGATIVE compared to metals

Large differences in electronegativity between two bonded atoms favor the transfer of electrons from the less electronegative (more electropositive) atom to the more electronegative atom resulting in a bond between the two atoms that is IONIC.

Smaller differences result in a more equitable “sharing” of electrons between the bonded atoms, resulting in a COVALENT bond between the two atoms.

The kinds of bonds formed between elements (covalent vs ionic) can be determined by comparing electronegativity of the two elements.

Moore/Stanitski/Jurs, Chemistry: The Molecular Science
Figure 8.6



Fluorine is the most electronegative element.

In general, electronegativity *increases* across a period…

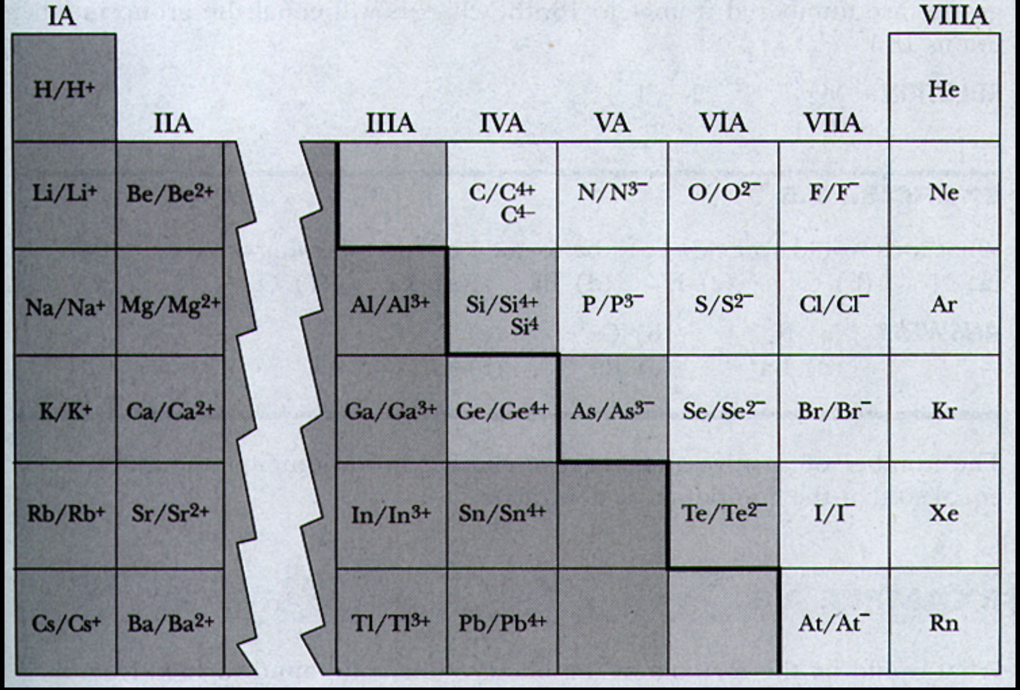
…and *decreases* down a group.

Na and Cl form ionic bonds.
Na gives up an electron and Cl accepts the electron to form Na$^+$ and Cl$^-$.

As differences between electronegativity between the two bonding elements decreases, there is more equitable sharing of electrons and the elements form covalent bonds.

Based on the position of elements in the periodic table, we can determine the kind of bond formed:

- Nonmetallic element + nonmetallic element → Molecular compound
- Metallic compound + nonmetallic compound → IONIC compound



IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIIIA
H/H^+							He
Li/Li^+	Be/Be^{2+}		C/C^{4+} C^{4-}	N/N^{3-}	O/O^{2-}	F/F^-	Ne
Na/Na^+	Mg/Mg^{2+}	Al/Al^{3+}	Si/Si^{4+} Si^{4}	P/P^{3-}	S/S^{2-}	Cl/Cl^-	Ar
K/K^+	Ca/Ca^{2+}	Ga/Ga^{3+}	Ge/Ge^{4+}	As/As^{3-}	Se/Se^{2-}	Br/Br^-	Kr
Rb/Rb^+	Sr/Sr^{2+}	In/In^{3+}	Sn/Sn^{4+}		Te/Te^{2-}	I/I^-	Xe
Cs/Cs^+	Ba/Ba^{2+}	Tl/Tl^{3+}	Pb/Pb^{4+}			At/At^-	Rn

Group IA – alkali metals – loose 1 e^- to form +1 (Na^+)

Group II A– alkaline earth metals –loose 2 e^- to form +2 (Ca^{+2})

Group III A– loose three e^- to form +3 (Al^{+3})

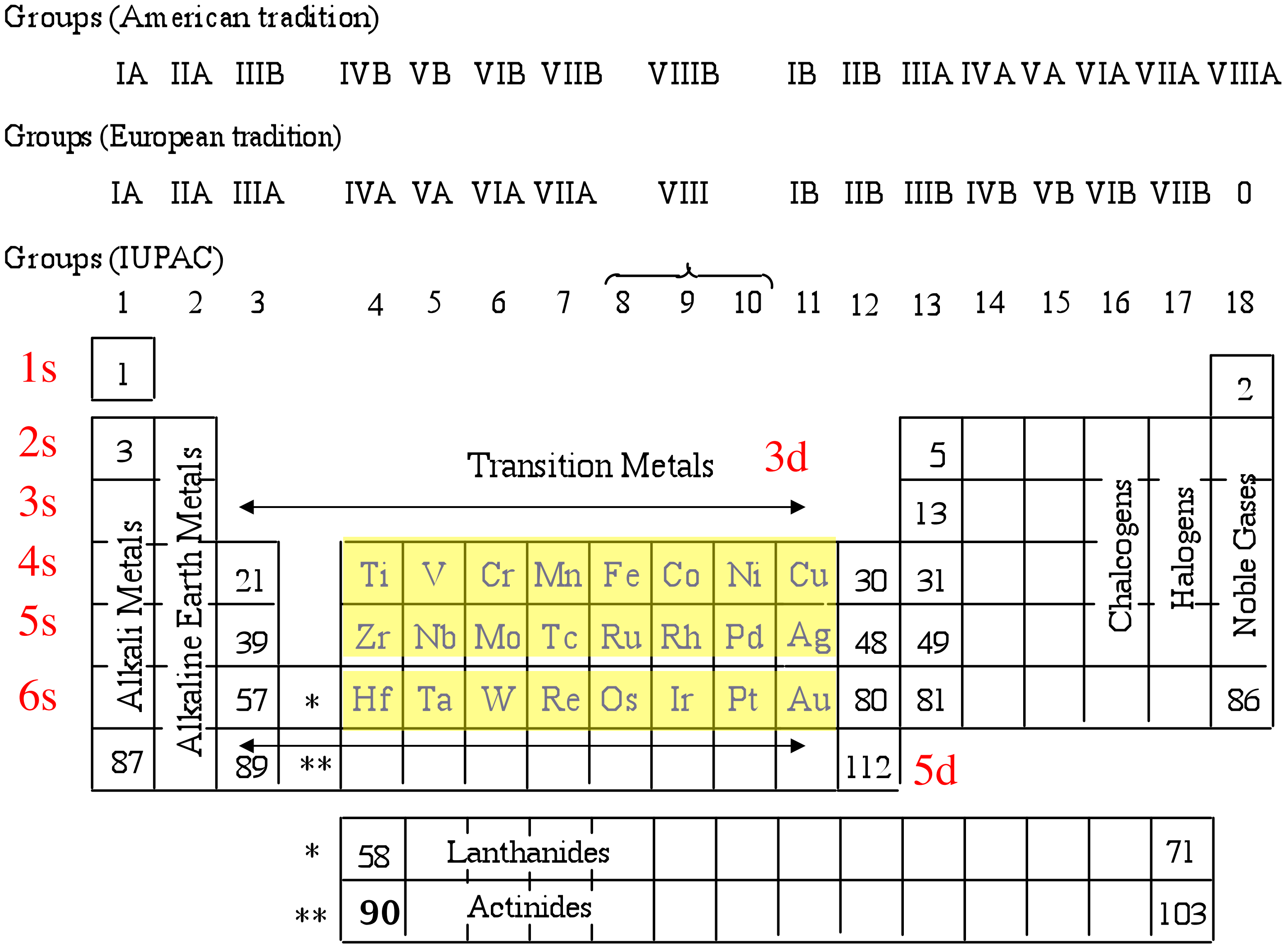
Group IV A– loose four e^- to form +4 (Sn^{+4})

Group V A– accept three e^- to form –3 (N^{-3})

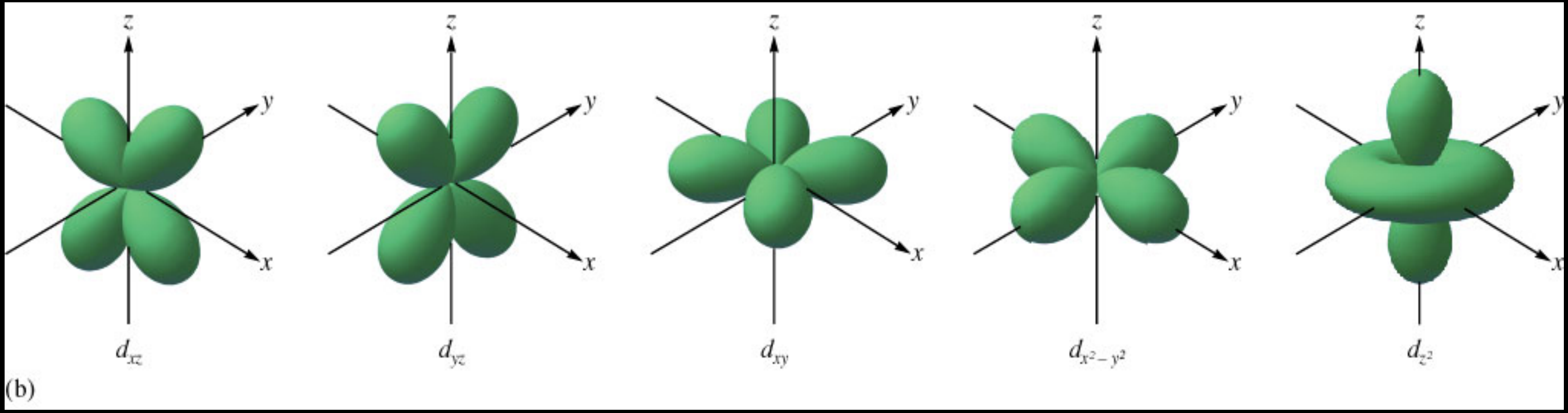
Group VI A– accept two e^- to form –2 (O^{-2})

Group VIIA – accept one e^- to form –1 (Cl^{-1})

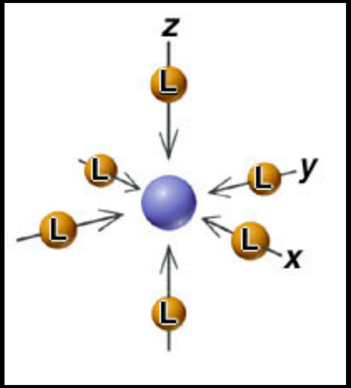
Transition Metals



CFT



The d orbitals in a free ion (i.e. with no attached ligands), will be *degenerate*, i.e. all 5 have the same energy.



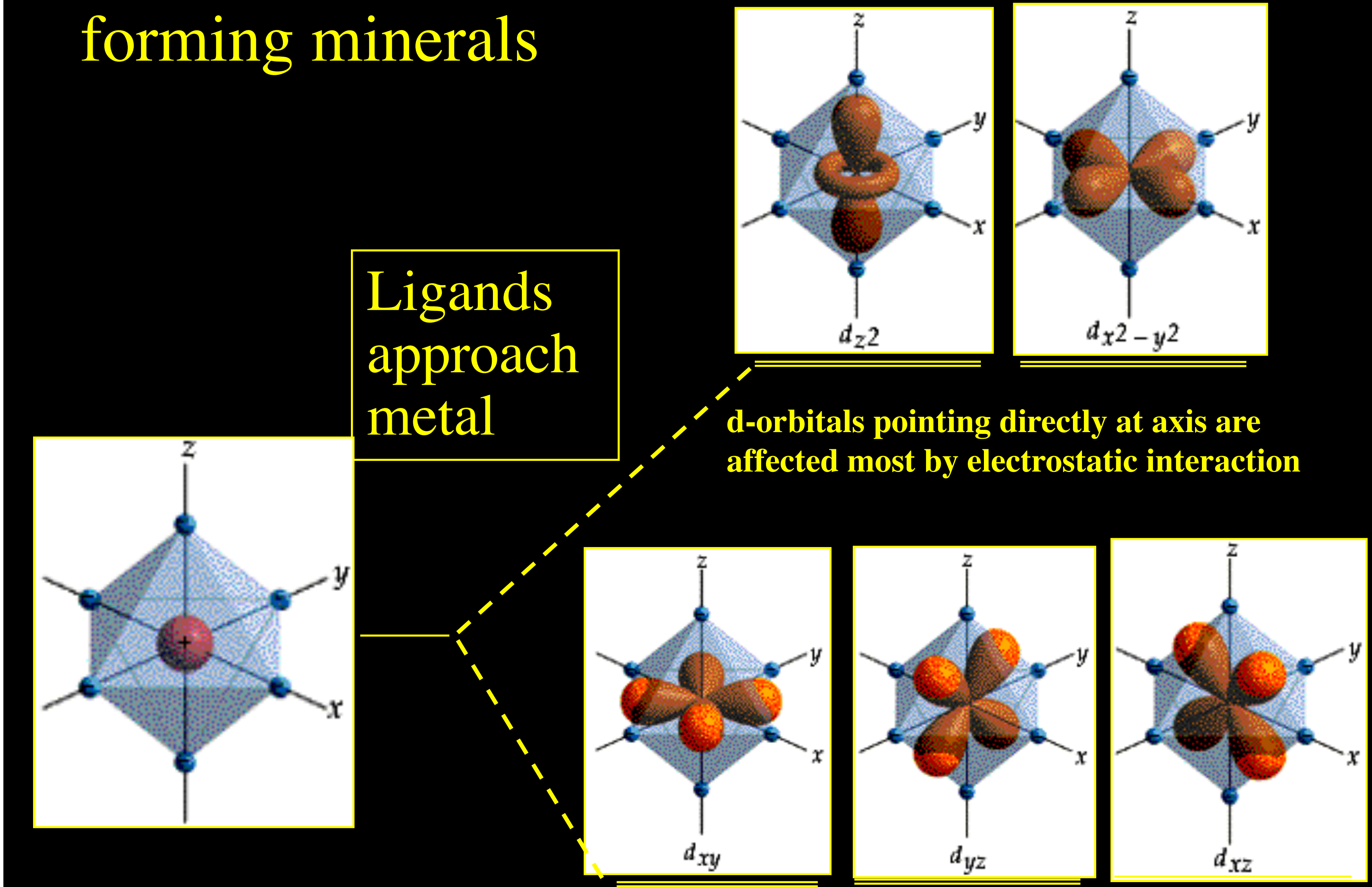
CFT presumes that the ligands may be represented by point (negative) charges lying along the bonding axes and that these will perturb the energies of any

electrons which populate the d orbitals.

crystal field splitting

The removal of a degeneracy of the energy levels of molecular entities or ions due to the lower site symmetry created by a crystalline environment.

Origin of near-IR spectra features in igneous rock-forming minerals



Ligands approach metal

d-orbitals pointing directly at axis are affected most by electrostatic interaction

(Octahedral Field)

d-orbitals not pointing directly at axis are least affected (stabilized) by electrostatic interaction

Limits of CFT

- Crystal field theory can predict the approximate position of absorptions.

- Current theory cannot predict width, or intensity

- There is hope, studies of chemical dynamics may enable a theory to be generated

Do not forget this !

- For all transition elements, d orbitals have identical energies in an isolated ion
- but energy levels split when the atom is located in a crystal field. This splitting of the orbital energy states enables an e^- to be moved from a lower level to a higher level by photon absorption.
- Energy levels are determined by the valence state of the atom (Fe^+, Fe^{2+}), its coordination number, and the symmetry of the site it occupies.
- The crystal field varies with crystal structure from mineral to mineral changing the amount of splitting. The same ion (Fe^{2+}), produces different absorptions, making specific mineral identification possible from spetroscopy.