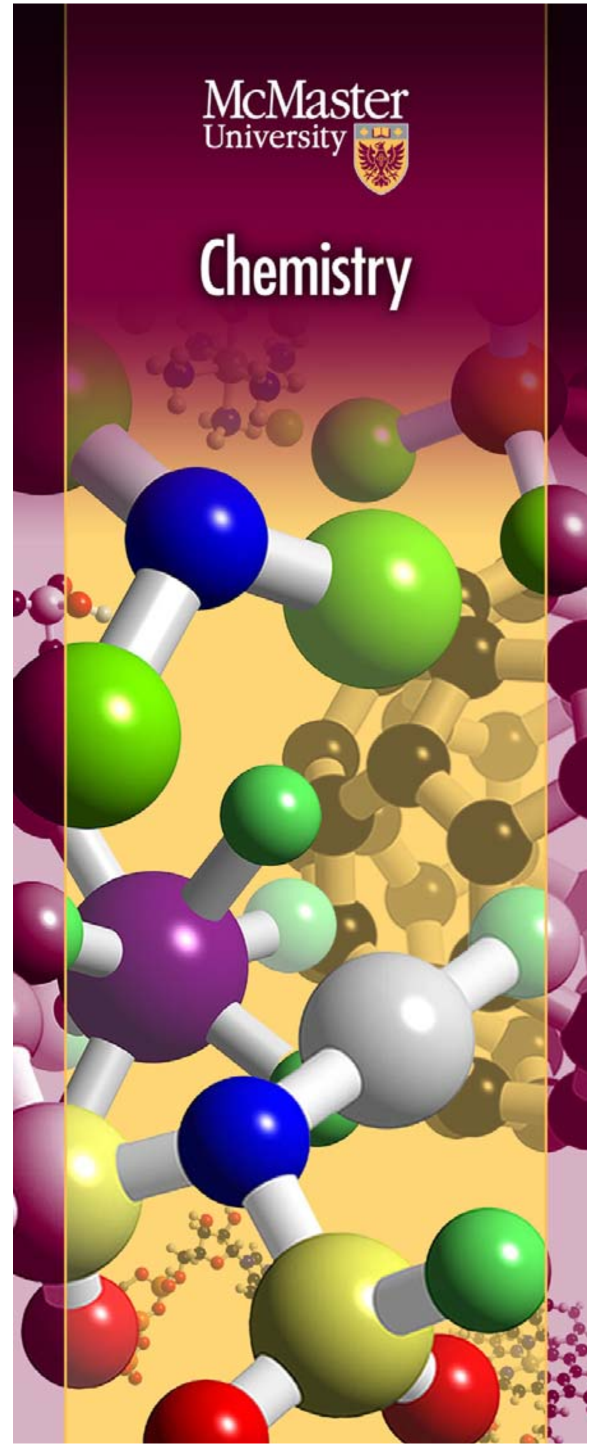
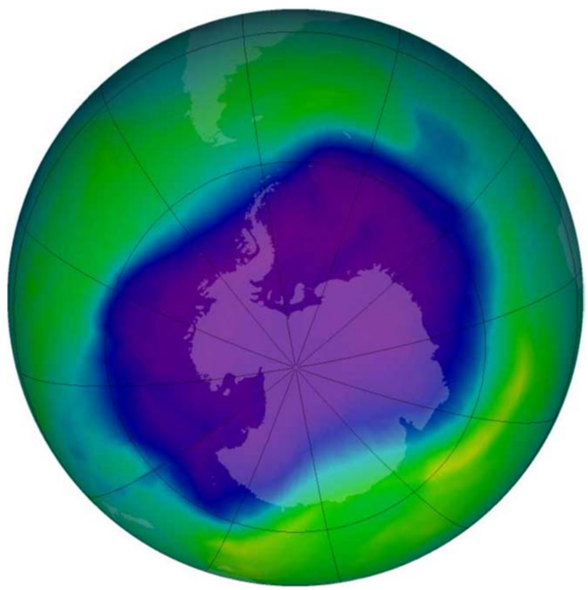
CHEM 1A03: Intro. Chemistry I



Essential Elements: Chemistry, Life & Health

Ch.8: Electrons in Atoms

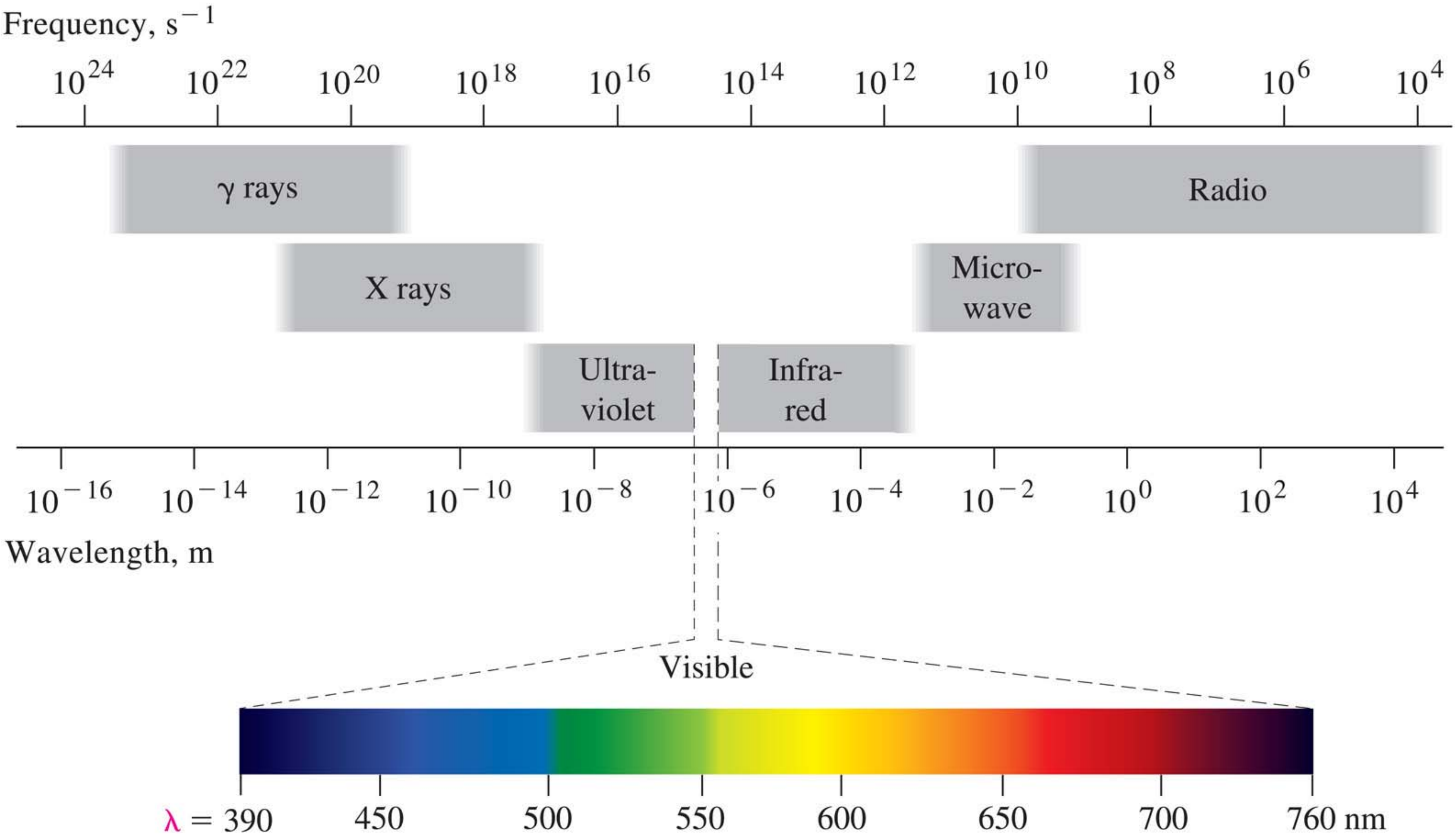


What do we understand about atoms?

What do we understand about atoms?

- Mostly space
- Nucleus
- Electrons
  - Described by quantum mechanics, not traditional mechanics
  - Behave like particles and waves
  - Their movement has associated changes in energy
  - Not at fixed distances/in fixed locations
  - Orbitals describe regions in space where electrons are likely to be found
  - Quantum numbers describe orbitals

Electromagnetic Spectrum (Fig. 8-3)



$c = \nu \lambda$ $E \propto \nu$ $E \propto 1/\lambda$

i-Clicker Question #1

Choose the **FALSE** statement:

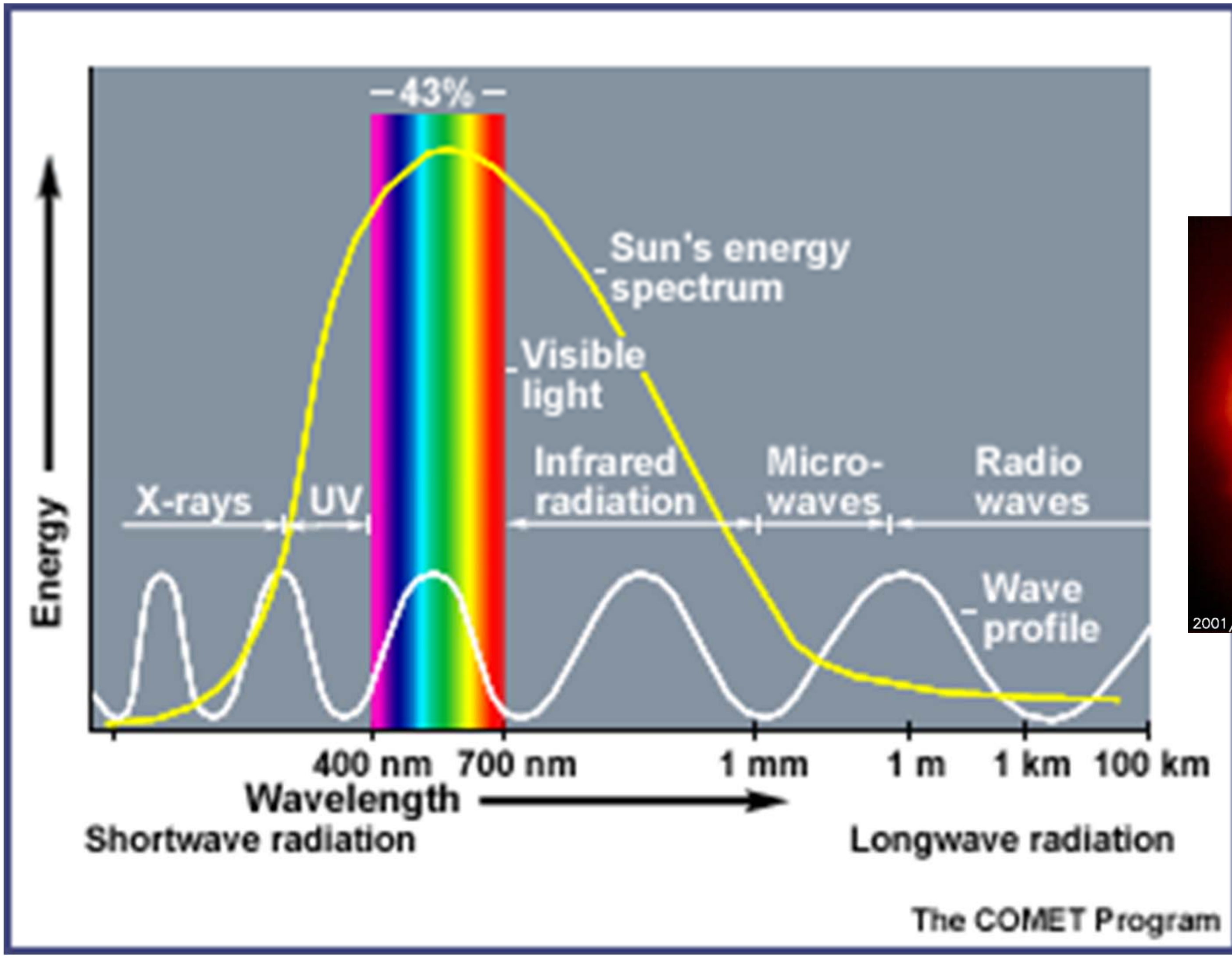
A. The wavelength of blue light is shorter than that of orange light.

B. The frequency of red light is larger than that of violet light.

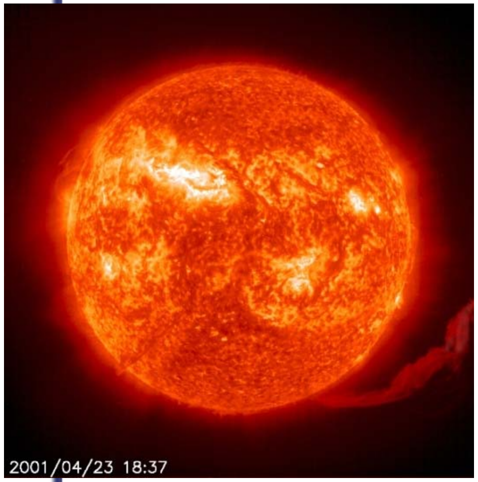
C. The energy of yellow light is smaller than that of blue light.

D. All statements are false.

Sun's Emission Spectrum



Sun (T = 6,000K)

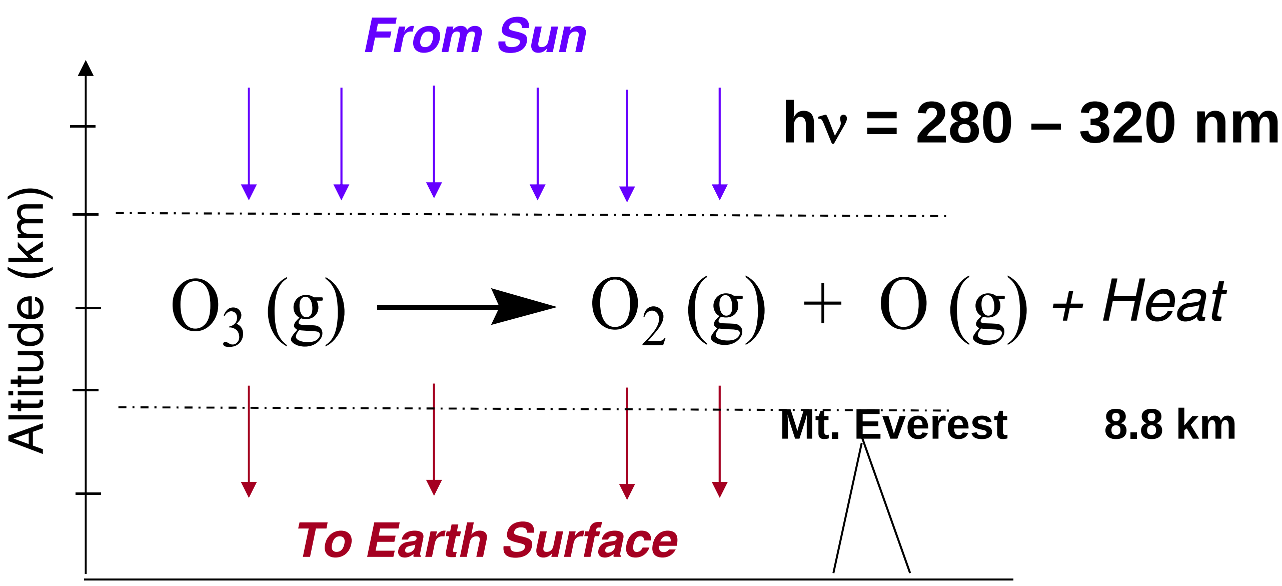


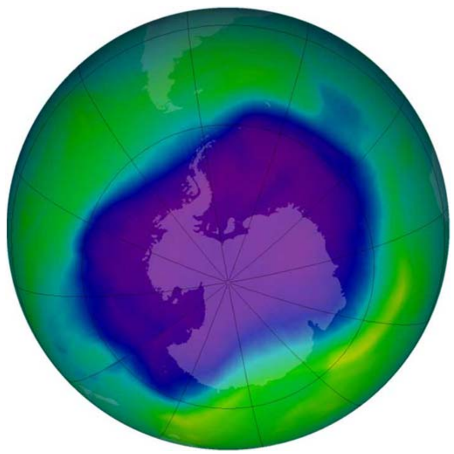
Earth's Protective Shield: Ozone

A. Ozone & UV Exposure

• ≈ 90% UVB radiation (280-320 nm) from the sun is selectively absorbed by photolysis of O_3 in stratosphere, with peak at ~ 20km from Earth's surface

• Lower O_3 levels increase the transmittance of UV B radiation to earth → Montreal Protocol: 1987





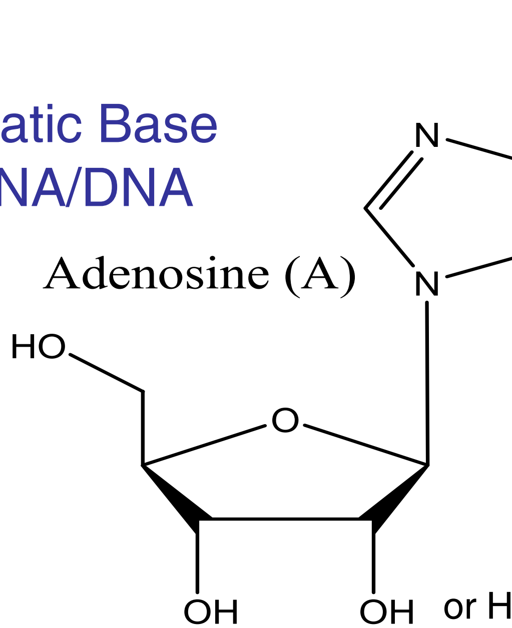
Ozone Depletion & UV Exposure

B. Biological Impacts

- UV B radiation can ionize biological molecules (DNA, Protein)
- Chronic exposure to UVB rays increases chance of skin cancer, cataracts & genetic mutations
- Body's response: produce melanin (dark pigment) to filter UV B radiation.

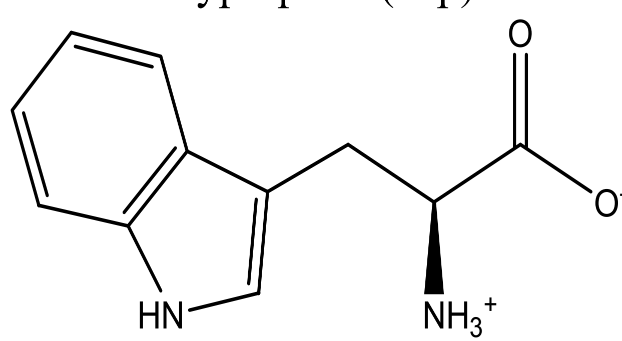
Aromatic Base
in RNA/DNA

Adenosine (A)



Aromatic Amino Acid
in Protein

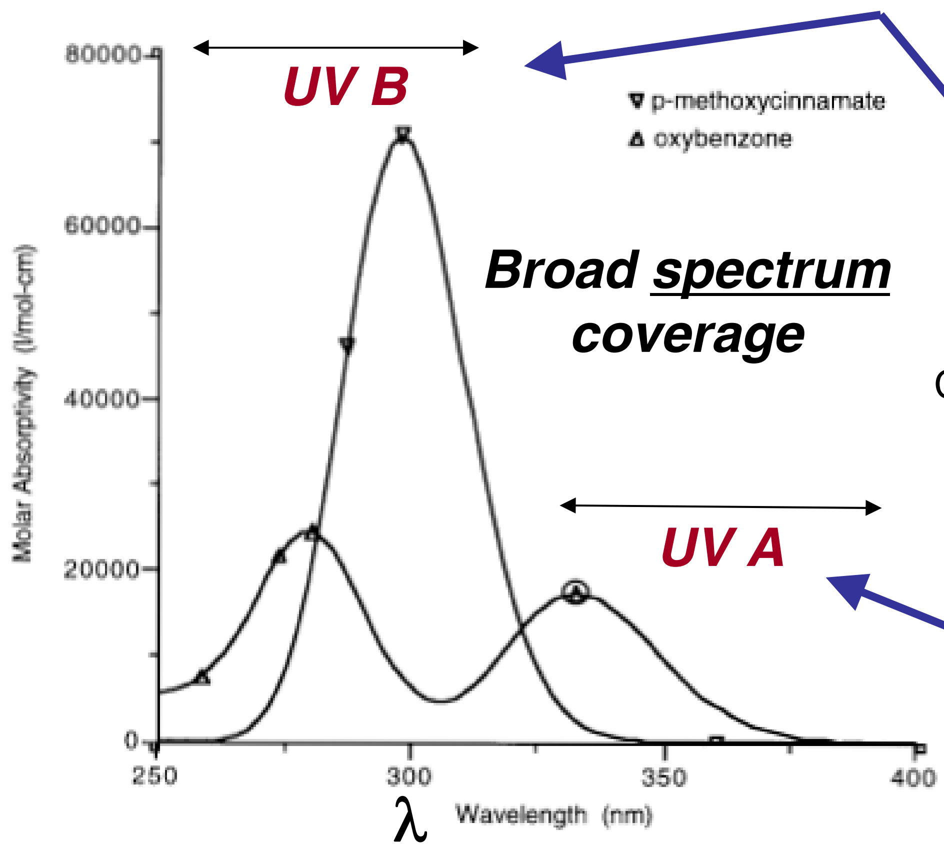
Tryptophan (Trp)



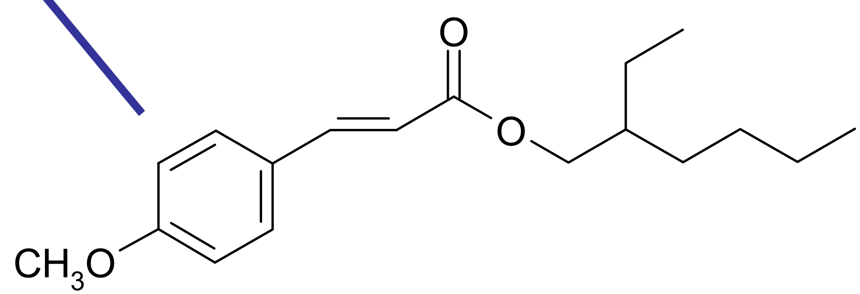
UV Exposure & Sunscreen

C. Chemistry of Sunscreen

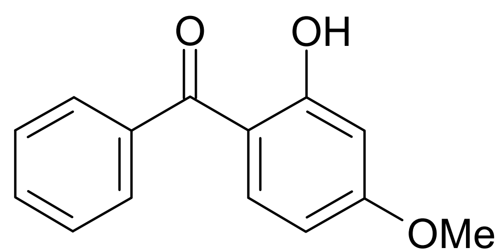
- Propose alternative ways to decrease exposure to UV radiation?
- Use of sunscreen/cosmetics containing UV absorbing chemicals



2 Major Chemical Sunscreens:



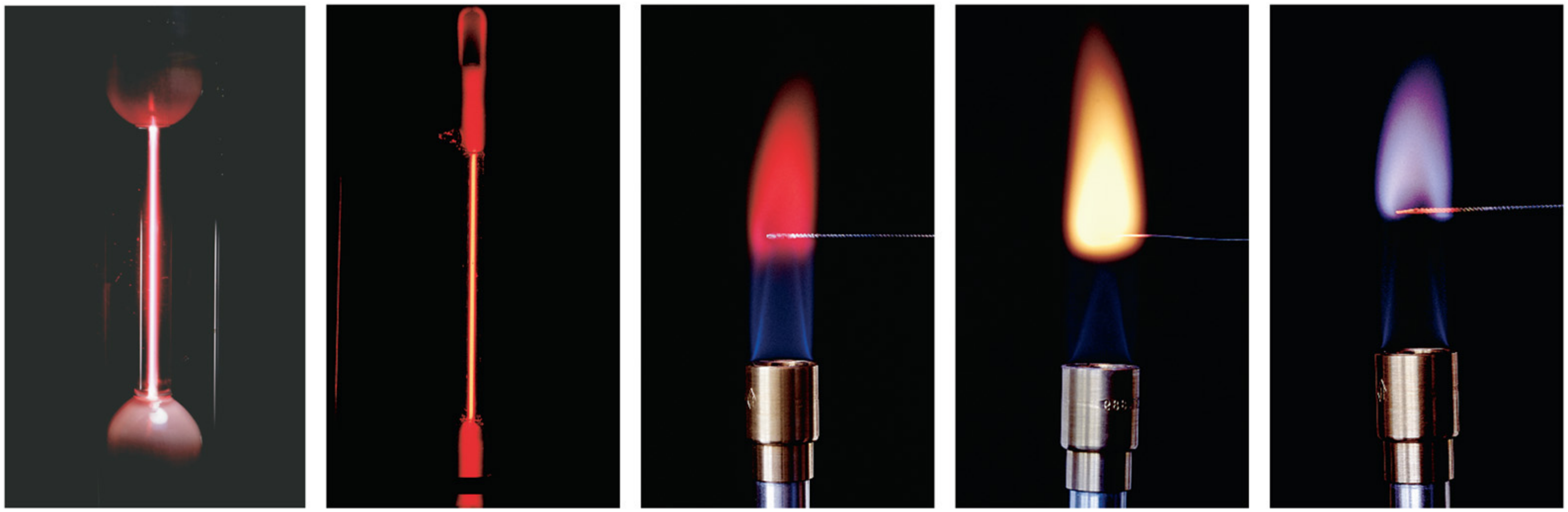
2-ethylhexyl p-methoxycinnamate



oxybenzone

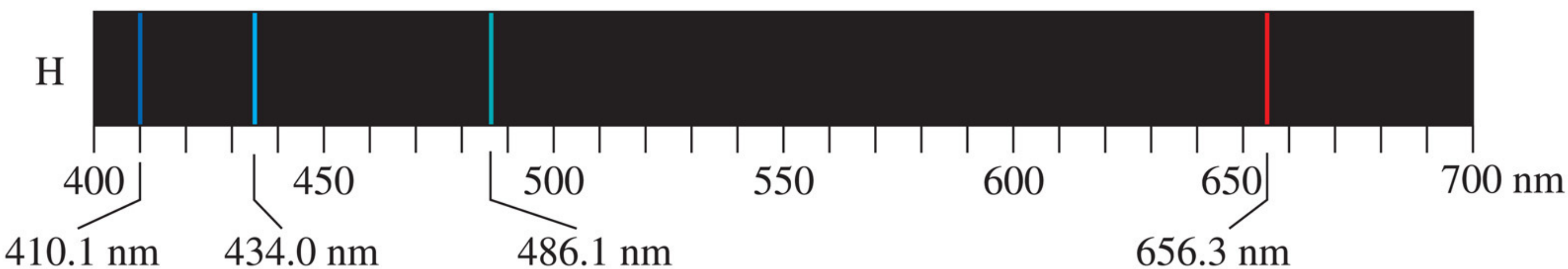
Atomic spectra

- *Discontinuous* (Line) spectra of <u>atoms</u>; few λ



H_2 He Li salt Na salt K salt

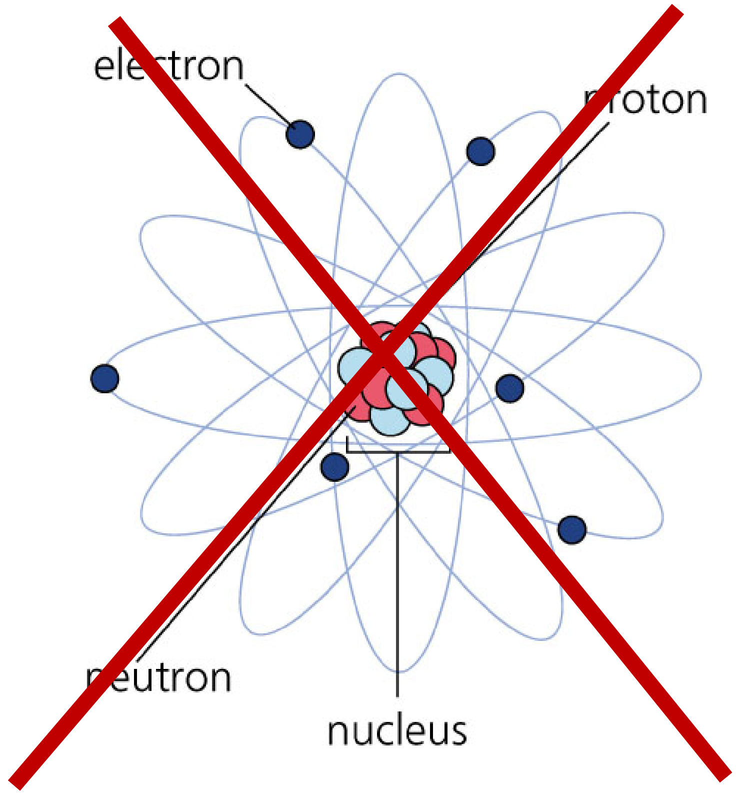
- Atomic spectrum of H



http://youtube.com/watch?v=d8hpUtRnsYc&mode=related&search

Current Model of the Atom

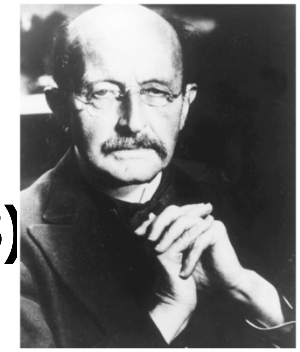
Experiments done during the early 1900's proved that the classical model of the atom was insufficient.



http://spaceplace.nasa.gov/what-is-gravity/

Quantum: Theory & Experiment

- Max Planck proposed (1900): energy, like matter, is discontinuous (quantized)

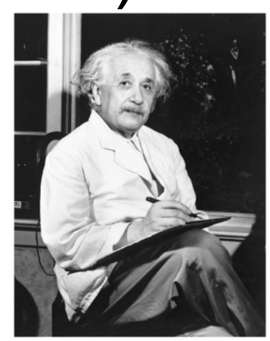


quantum (photon) of energy, $\mathbf{E = h\,\nu}$ **(8.3)**

E = energy, ν = frequency

h = Planck's constant, 6.626×10^{-34} J s

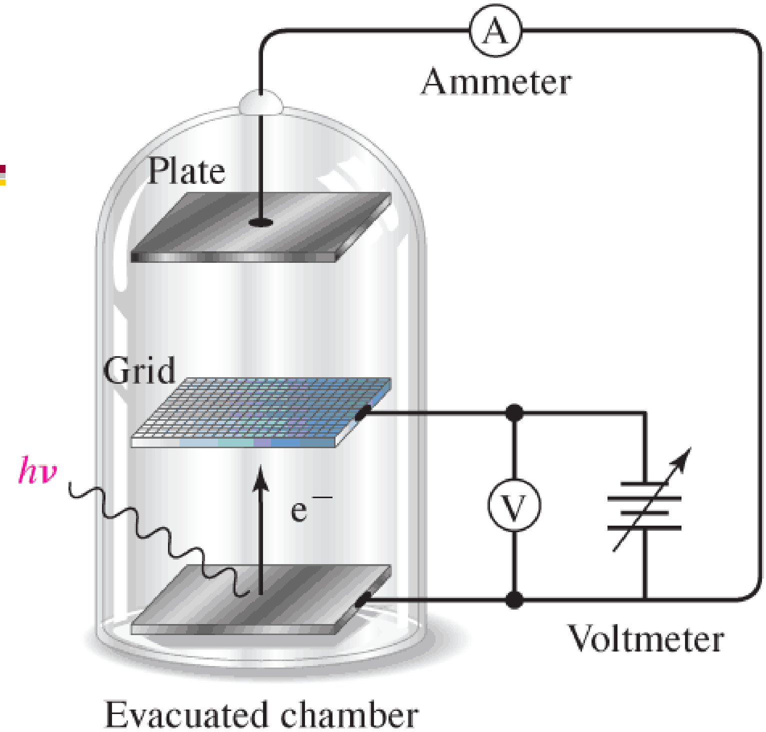
- This idea was used by Einstein (Nobel Prize) to explain Hertz's experiment…



p. 302 (285, 9th ed.)

Photoelectric effect

- Single λ light strikes a metal surface to which a voltage is applied.
- If E_{photon} > Threshold Energy (work function) of metal, e^- are ejected with kinetic energy (KE)



"Gizmos" Experiment:

What happens if we change λ?

What happens if we change intensity?

How do we measure KE of e^-?

http://www.explorelearning.com/index.cfm?method=cResource.dspView&ResourceID=491&ClassID=1838684

p. 303-306 (286-289, 9th ed.)

Key observations – Photoelectric effect

- Work function (threshold energy, $h\nu_o$) of the metal must be overcome for e^- to be emitted
- When incident light frequency <u>exceeds</u> a threshold value (ν_o), e^- are emitted
- # of electrons (current) emitted depends on light intensity (# of photons)
- K.E. of emitted electrons depends on E of light

$$\boxed{\text{E (incident light) = Threshold E + KE of } e^-}$$

i-Clicker Question # 2

The wavelength of light needed to eject electrons from a metal is 91.2 nm.

If light of 80.0 nm shines on a sample of the metal what happens, compared to light at 91.2 nm?

A. More electrons are emitted
B. No electrons are emitted
C. Same number of electrons are emitted

i-Clicker Question # 3

If the λ of the light is changed from 80.0nm to 85.0nm, what is the effect on the kinetic energy (KE) of the emitted electrons?

A. The electrons emitted have lower KE
B. The electrons emitted have higher KE
C. The electrons have unchanged KE
D. The electrons emitted have zero KE

Take-home practice problem

The wavelength of light needed to eject electrons from a metal is 91.2 nm.

When light of 80.0nm shines on a sample of the metal, electrons are emitted from the metal.

What is the kinetic energy of each electron, in J?

Other practice: See Tutorial 2

Solutions:

The threshold wavelength is 91.2nm. The incident light is at 80.0 nm. Watch out for units and use needed conversions (e.g. m and nm).

$$E_{\text{incident light}} = E_{\text{threshold}} + E_{\text{kinetic}}$$

$$\frac{hc}{80.0\ \text{nm}} = \frac{hc}{91.2\ \text{nm}} + E_{\text{kinetic}}$$

$$E_{\text{kinetic}} = hc\left(\frac{1}{80.0\ \text{nm}} - \frac{1}{91.2\ \text{nm}}\right)$$

$$E_{\text{kinetic}} = (6.626 \text{ x } 10^{-34}\ \text{Js})(2.9979 \text{ x } 10^{8}\ \text{m/s})(10^{9}\ \text{nm/m})\left(\frac{1}{80.0\ \text{nm}} - \frac{1}{91.2\ \text{nm}}\right)$$

$$E_{\text{kinetic}} = 3.030 \text{ x } 10^{-19}\ \text{J}$$

Einstein's proposal

- Light is quantized like a particle (photons)
  $E_{photon} = h\nu$ and $E_{photon} = \Delta E$ atom

  $\therefore \Delta E$ atom $= h\nu =$ threshold energy $+ \frac{1}{2} mu^2$

Putting together all relationships thus far ($\nu = c/\lambda$):

$$\boxed{\mathbf{E = h\nu = hc/\lambda = threshold\ energy + \tfrac{1}{2} mu^2}}$$

- Related application of photoelectric effect: solar cells
  http://science.howstuffworks.com/solar-cell.htm

p. 308 (288, 9th ed.)

Wave-Particle Duality: Theory

- Louis de Broglie: particles (e^-) display wave properties
  - From $E = mc^2$ (Einstein), $E = h\nu$ (Planck), and $\nu\lambda = c$

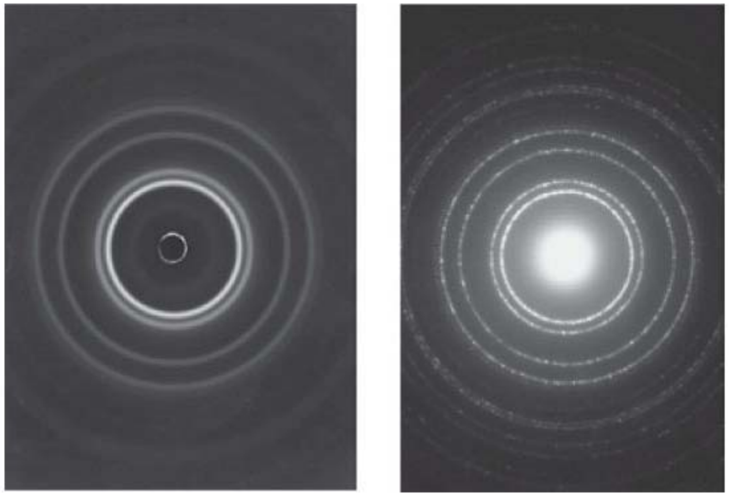
$$\lambda = \frac{h}{mu} \qquad \lambda = \frac{h}{p} \qquad \textbf{(8.10)}$$

- Particles should display wave properties, e.g. diffraction
  - If distance between objects that the waves scatter is ~ same as the radiation λ, diffraction occurs

p. 313 (296, 9th ed.)

Thomson's Electron Diffraction Experiment (Nobel prize)

- Evidence: (Fig. 8-16)
  - Radiation and object spacing are similar:
  - X-rays, λ = 100 pm
  - Metal foil, regular array of metal atoms, 200 pm spacing


(a) (b)

(a) X-ray diffraction by metal foil
(b) Electron diffraction by metal foil.

p. 314 (297, 9th ed.)

i-Clicker Question # 4

An electron has a mass about 1/2000th of the mass of a proton. Assuming a proton and an electron have similar wavelengths, how would their speeds (u) compare?

A. $u_{electron} = 2000 \times u_{proton}$
B. $u_{electron} = u_{proton}$
C. $u_{proton} = 2000 \times u_{electron}$
D. There is not enough information to answer

Quantum Numbers & Orbitals

Section 8.6 [not part of the course] introduces:

- Schrödinger equation: combines ideas of particle & wave behaviour to describe the state of e^- in atom

- We'll use the results of 8.6 - Orbitals
  - Orbitals are wavefunctions, ψ, solutions to the Schrödinger equation
  - Orbitals are described by 3 quantum numbers
  - Orbitals describe regions of high probability of finding an electron (high charge density)

Review: Quantum Numbers, Orbitals, Electron Configurations

- The following slides (24-30) and slides 39-41 <u>review</u> material on:
  - Quantum Numbers, Atomic Orbitals, Electron Configurations
  - Please review this material as needed. You are responsible for it.

n

- Principal quantum number, n
  - n describes orbital energy and distance from nucleus
  - Larger n value = orbital is further from nucleus, e^- in orbital is at higher energy
  - n = 1, 2, 3, 4….
  - n describes a principal *shell*

p. 324-325 (304-305, 9th ed.)

ℓ, $\mathbf{m}_\ell$

- Orbital angular momentum quantum number, ℓ
  - ℓ describes orbital shape (angular distribution)
  - ℓ = 0, 1, 2, 3…n-1
  - ℓ = 0 (s orbital), ℓ = 1 (p), ℓ = 2 (d), ℓ = 3 (f)
  - Number of ℓ values = number of *subshells* in a given n *shell*

- Magnetic quantum number, m_ℓ
  - m_ℓ describes orbital orientation
  - $m_\ell = -\ell, \ldots, 0, \ldots, +\ell$
  - m_ℓ has $(2\ell + 1)$ values

p. 324-325 (304-305, 9th ed.)

Hydrogen atom example (Fig. 8-23)

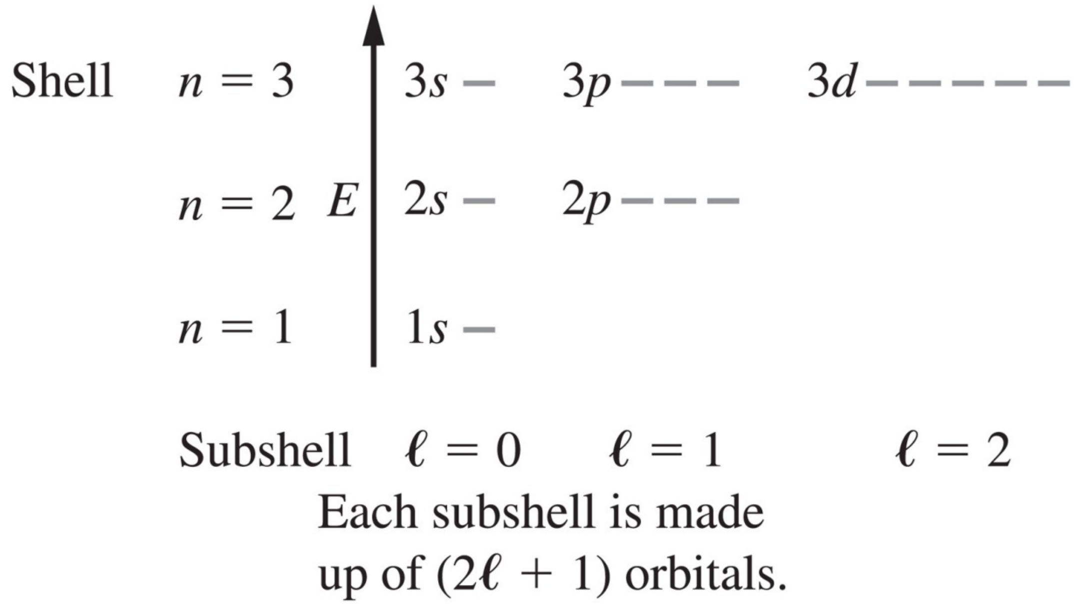
- Orbital energy increases with n

For n = 3 shell:
= 0, 1, 2 (3 subshells)

For ℓ = 2,
m_ℓ = -2, -1, 0, 1, 2
(five 3d orbitals)

For ℓ = 1,
m_ℓ = -1, 0, 1
(three 3p orbitals)

For ℓ = 0,
m_ℓ = 0 (one 3s orbital)



For H: **subshells** within a shell have the **same energy**.

p. 326 (305 9^{th} ed.)

H vs. Multi-electron atoms

H: subshells are degenerate (same energy)

Multi-electron atoms: subshell energies differ (electron screening, effective nuclear charge*)

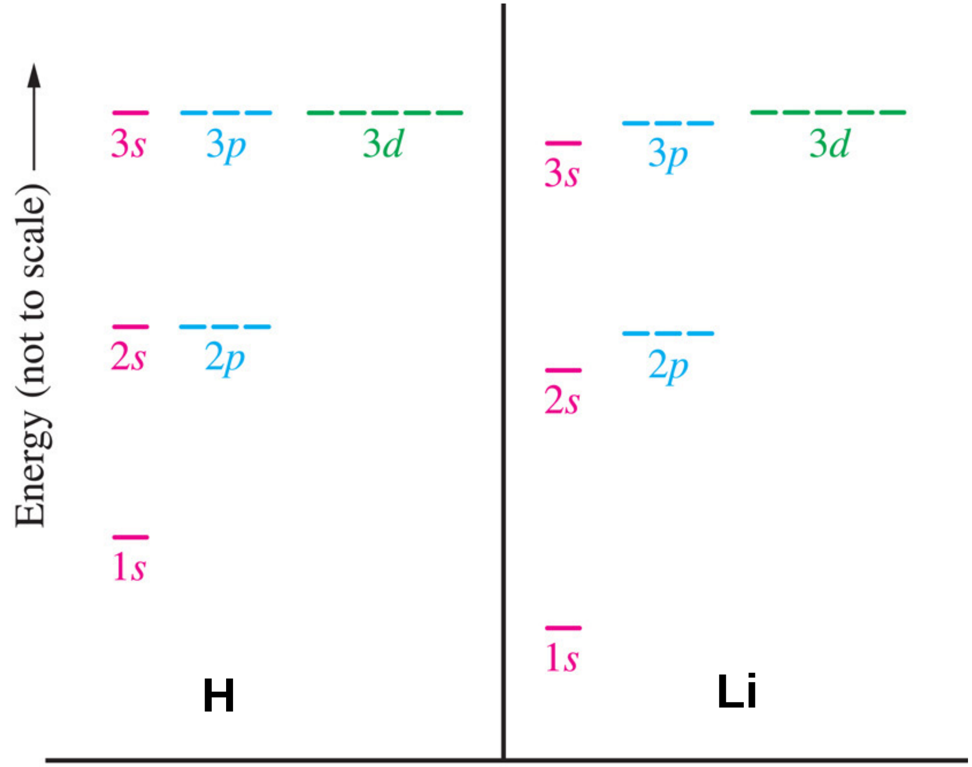


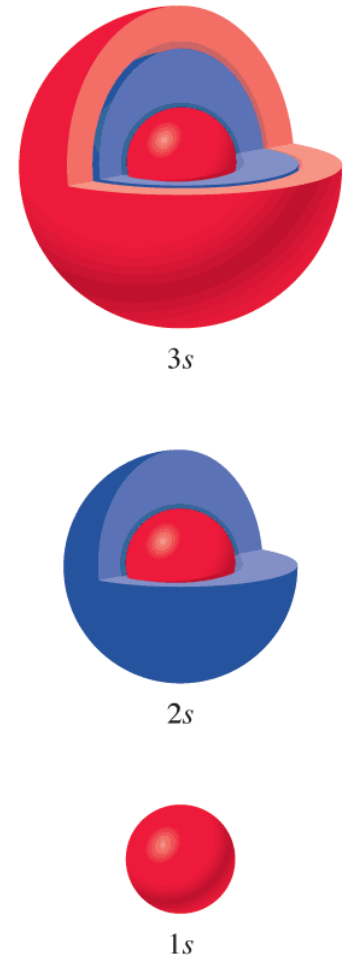
Fig. 8-36, p. 338 (316, 9th ed.)

*** These topics are discussed in 8-10, which is formally not covered, but we use the results to write electron configurations.**

Orbital pictures*

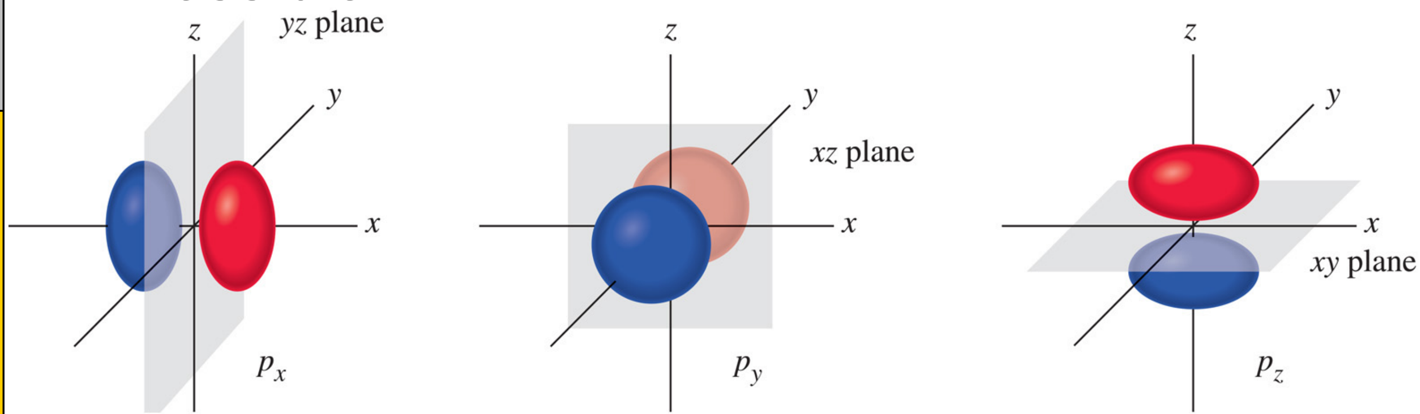
s orbitals are spherical

- 1s, 2s, 3s at 95% probability:



p orbitals (p_x, p_y, p_z)

- 1 angular node (0 probability of finding electron)
- Possible in n ≥ 2

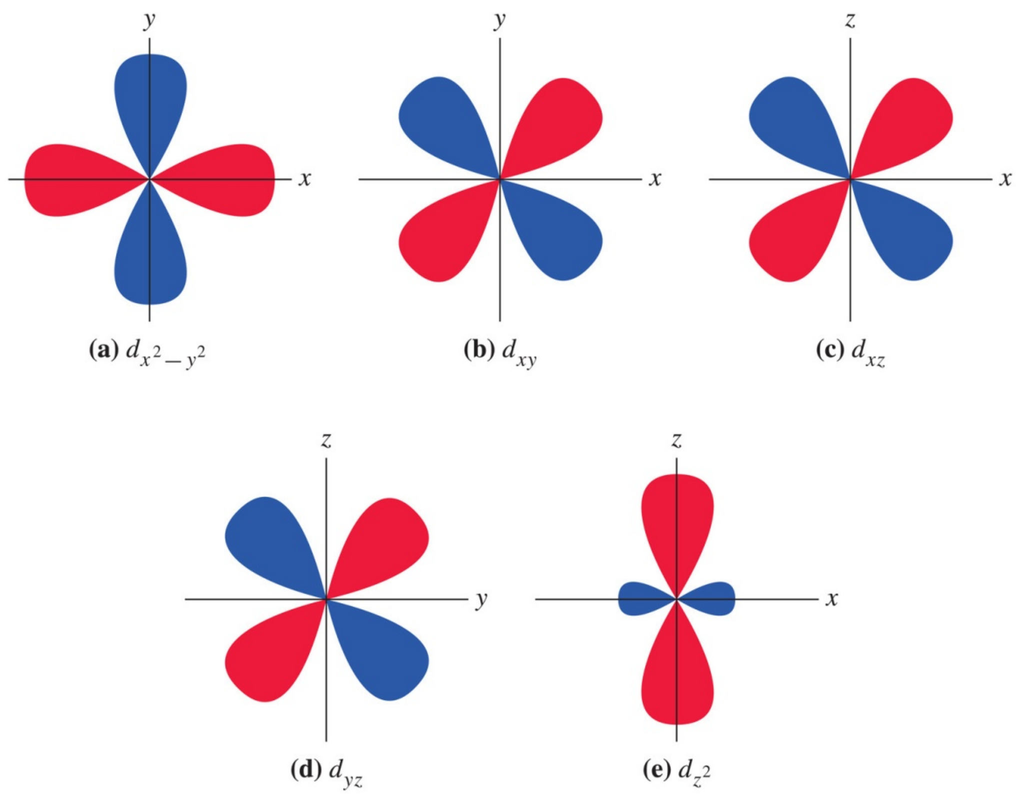


***Section 8-8 is formally not covered, but we will use these Figures, p. 329, 331 (p. 309, 311, 9th ed.)**

Orbital pictures*

d orbitals (cross section):

- 2 angular nodes
- Possible in n ≥ 3



***Pictures are from section 8-8, p. 332 (311, 9th ed.). Know the number & shapes of each type, not the mathematical derivations.**

Electron Spin Quantum Number, m_s

- Electrons have spin, generating a magnetic field:
  - Values of m_s = +1/2 or -1/2
  - Pair of e^- with opposite spins has no magnetic field
- Atoms (or ions) with

  all spins *paired* are diamagnetic

  1 or more *unpaired* electrons are paramagnetic
- We can identify any electron with the 4 quantum numbers

p. 333-335 (313-314, 9th ed.)

i-Clicker Question #5

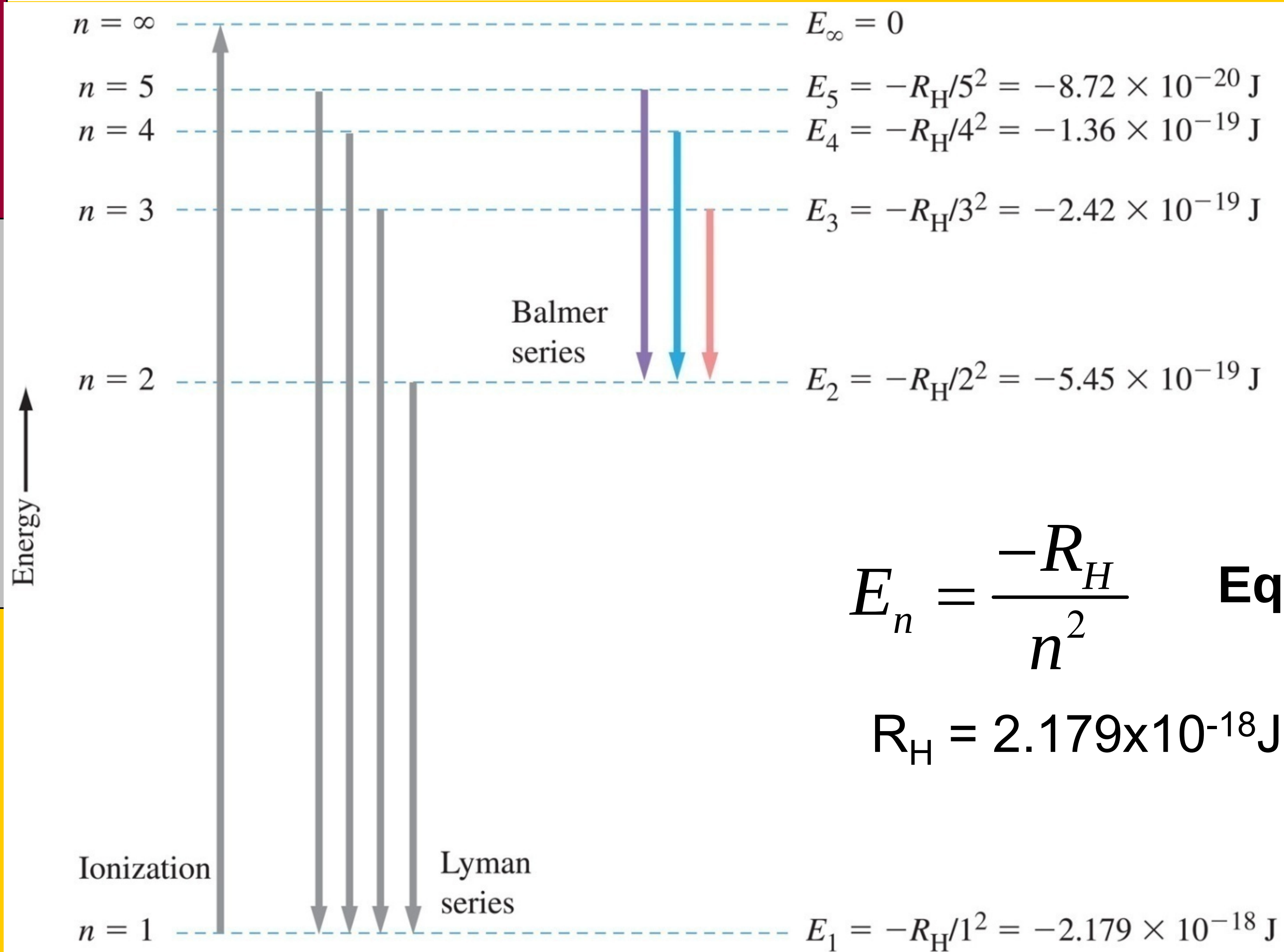
Which of the following sets of quantum numbers is allowed? (n, ℓ, m_ℓ, m_s)

A. 2, 1, −2, +1/2

B. 3, 2, 0, −1/2

C. 2, 0, 0, 0

Electrons moving in atoms: H atom energy levels



$$E_n = \frac{-R_H}{n^2}$$ **Eq. (8.5)**

$R_H = 2.179\text{x}10^{-18}$J

H atom energy changes

n = 1 e^- in ground state

n > 1 e^- in excited state

n = ∞ e^- is ionized

- For e^- going from $n_{initial}$ to n_{final}, unique quantity of energy is absorbed or emitted

$$\Delta E = E_f - E_i$$

$$= \frac{-R_H}{n_f^2} - \frac{-R_H}{n_i^2} = R_H\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) \qquad \textbf{(8.6)}$$

ΔE may be positive (absorption) or negative (emission), but hν is always positive. Thus, hν = |ΔE|

i-Clicker Question # 6

Which of the following electronic transitions in an H atom will lead to emission of a photon with the shortest wavelength?

A. n = 1 to n = 4
B. n = 4 to n = 2
C. n = 3 to n = 2
D. n = 2 to n = 4

Ionization of Hydrogen

- H atom ionization: electron absorbs enough energy to escape the atom:

  $H \rightarrow H^+ + e^-$

- e^- moves from its initial n state (n_i) to a final n state (n_f), where $n_f = \infty$

$\Delta E = E_f - E_i$

- But $$E_f = \frac{-R_H}{n_f^2} = \frac{-1}{\infty^2} = 0$$

  The energy it takes to free the electron is $\therefore \Delta E = -E_i$

p. 312 (294, 9th ed.)

H atom calculations

1) Calculate the wavelength of light required to ionize an H atom from its n=2 state.

Take-home question:

2) Calculate the frequency of the light emitted when an electron moves from n = 2 to n = 1 in the H atom. In what region of the electromagnetic spectrum is this light found?

Solutions:

(1) Wavelength to ionize from n=2 in H atom:

$\Delta E = E_f - E_i$ but $E_f = \dfrac{-R_H}{n_f^2} = \dfrac{-1}{\infty^2} = 0$ $\therefore \Delta E = -E_i$

$\Delta E = -(-R_H/n^2)$

$\Delta E = (2.179 \times 10^{-18}\ J)\ (1/4)$

$\Delta E = 5.447_5 \times 10^{-19}\ J$

$\Delta E = 5.448 \times 10^{-19}\ J$

$\Delta E = hc/\lambda$

$\lambda = (6.626 \times 10^{-34}\ J\ s)(2.9979 \times 10^{8}\ m/s)/(5.448 \times 10^{-19}\ J)$

$\lambda = 3.646 \times 10^{-7}\ m = 364.6\ nm$

Solutions:

(2) Frequency of light emitted for n=2 to n=1 transition in H atom.

$$\Delta E = E_f - E_i$$

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

$$\nu = \left|\frac{2.179 \times 10^{-18}\, J\left(\frac{1}{4} - \frac{1}{1}\right)}{6.626 \times 10^{-34}\, Js}\right|$$

$\nu = 2.466 \times 10^{15}\ s^{-1}$; in the near ultraviolet region

Review: Electron Configurations

- Rules for distributing e^- into shells & subshells:

  (1) Occupy orbitals so that atom's energy is minimized. We order orbitals according to energy:

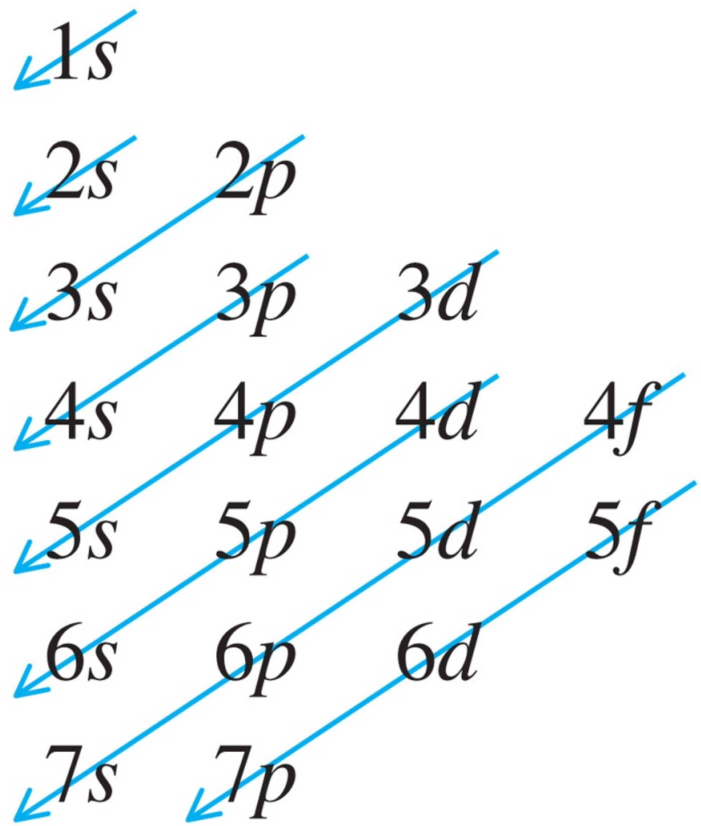


Fig. 8-37

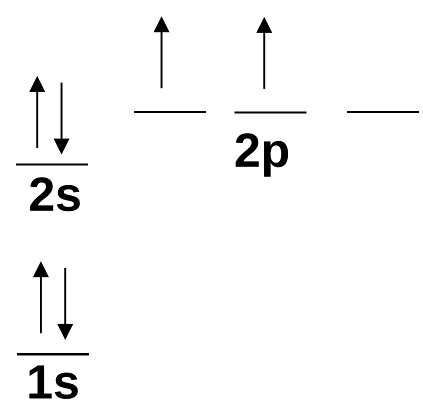
p. 339 (317, 9th ed.)

Review: Pauli, Hund

(2) Pauli exclusion principle: every e^- has unique set of 4 quantum numbers, thus 2 e^- in same orbital have opposite spins.

(3) Hund's rule: occupy orbitals of the same energy singly, then pair e^-.

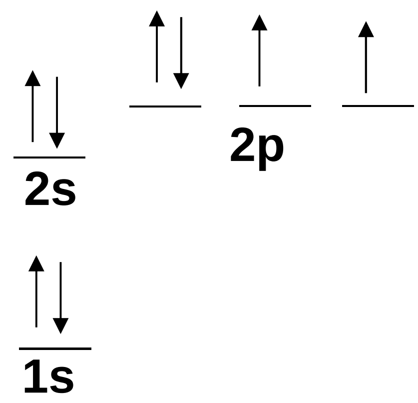
e.g. Carbon: $1s^2\ 2s^2\ 2p^2$



p. 339 (317, 9th ed.)

Review: The Aufbau (building up) Process

- These rules give ground state electron configurations
  e.g. O:



- Noble gas shorthand:
  N is $1s^2 2s^2 2p^3$ or [He] $2s^2 2p^3$
  Ne is $1s^2 2s^2 2p^6$ or [Ne]

- Excited state electron configurations <u>do not</u> follow the orbital filling rules,
  e.g. $1s^2 2s^2 2p^5 3s^1$ is an excited state of Ne

  *Note: not responsible for electron configurations of transition elements & their ions.

p. 339-342 (318-320, 9th ed.)

Review: Building the Periodic Table - Fig. 8-38

Main-group elements

s block | p block | Transition elements (d block)

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H (1s)																	2 He (1s)
3 Li	4 Be (2s)											5 B	6 C	7 N	8 O (2p)	9 F	10 Ne
11 Na	12 Mg (3s)											13 Al	14 Si	15 P	16 S (3p)	17 Cl	18 Ar
19 K	20 Ca (4s)	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe (3d)	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se (4p)	35 Br	36 Kr
37 Rb	38 Sr (5s)	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru (4d)	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te (5p)	53 I	54 Xe
55 Cs	56 Ba (6s)	57 La*	72 Hf	73 Ta	74 W	75 Re	76 Os (5d)	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po (6p)	85 At	86 Rn
87 Fr	88 Ra (7s)	89 Ac	104 Rf	105 Db	106 Sg (6d)	107 Bh	108 Hs	109 Mt	110	111	112						

Inner-transition elements

f block

*													
58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd (4f)	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 (5f)	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

p. 344-346 (320-322, 9th ed.)

Blocks:
s, p, d, f

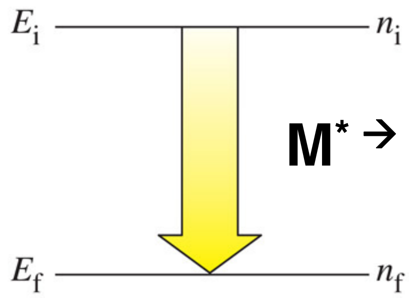
Familiar groups:

Alkali metals
ns^1

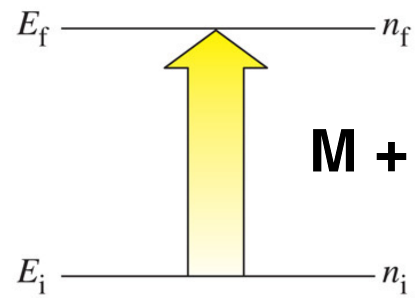
Halogens
ns^2np^5

Noble gases
ns^2np^6

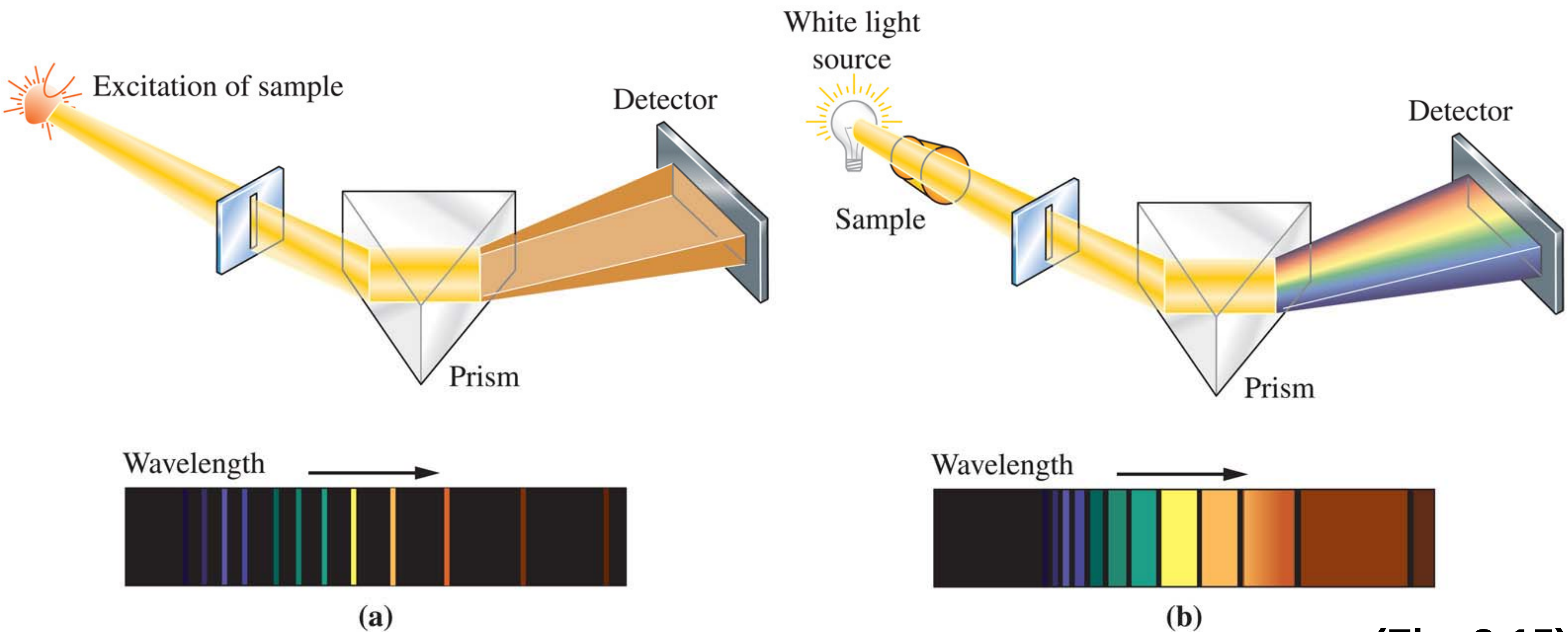
Atomic Emission vs. Absorption Spectra



$$M^* \rightarrow M + h\nu$$



$$M + h\nu \rightarrow M^*$$



Emission **Absorption**

(Fig. 8-15)

Atomic Absorption – Lead Analysis

Pb in Water, Food, Fuels, Paint & Toys

- Lead is a toxic element notably for infants' neurological development
- Selective analysis of Pb via flame atomic absorption spectroscopy

AAS detects atomized metal ions from aqueous solution.

Lead cathode lamp excites sample (absorption) through flame, and an emission spectrum is produced

Decrease in intensity of light (217 nm) through flame related to conc. of Pb.

$PbCrO_4$
"Chrome Yellow" Paint

$PbCO_3$
"White Lead" Paint

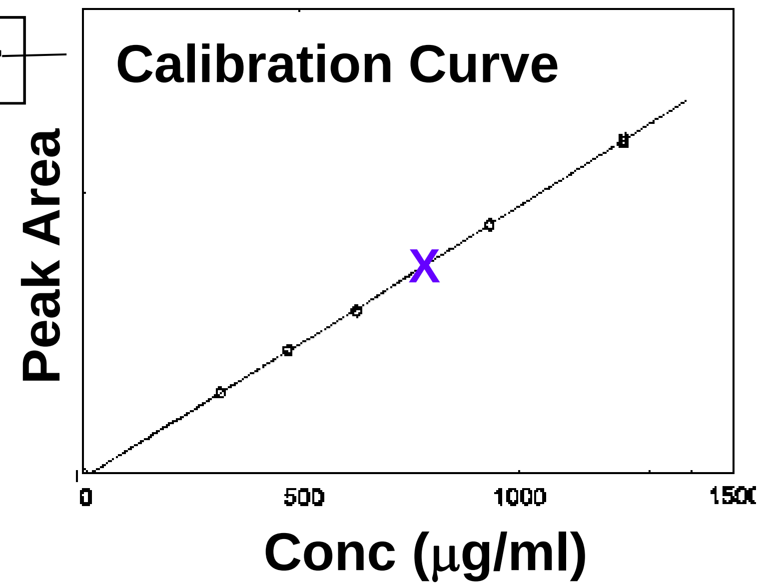
Flame Atomic Absorption: Set-up

Selective Absorption of UV Light

Pb^{2+} (g)

ΔE = 217.0 nm

Detector



Pb (s)
cathode

Paint Sample

Pb^{2+} (aq)

Quantum Numbers – Take-Home Practice Questions

1. Which quantum number represents subshell? (ℓ)
2. Which is the magnetic quantum number? (m_ℓ)
3. Which quantum number can have the value -1/2? (m_s)
4. Which shell is at higher energy: n=3 or 4? (4)
5. What orbitals, and how many of each, are available if n = 3? (3s(1), 3p(3), 3d(5))
6. How many electrons can be accommodated in the n=2 shell? (8)

Electron Configurations - Practice Questions

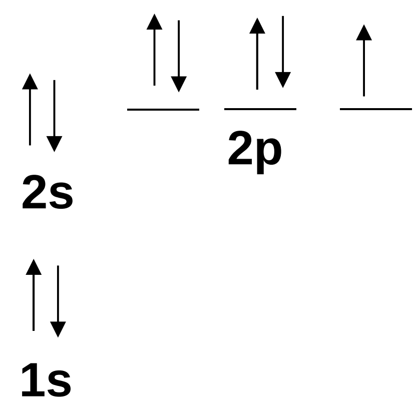
7. Which of the following is an excited state configuration for Ne? (element #10)

   (a) $1s^2 2s^2 2p^6$ no - ground state

   (b) $1s^2 2s^2 2p^5 3p^1$ yes – does not follow orbital filling rules

   (c) $1s^2 2s^2 2p^6 3p^1$ no – sodium excited state (too many e)

8. Write an **energy level diagram** for F (element # 9).



9. Write the electron configuration for Ca (element #20), using $1s^2$…. notation. ($1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$)

Quantum Numbers – Practice Questions

10. Derive all the possible sets of n, ℓ and m_ℓ in the n = 4 shell of the H atom. Identify the types and number of orbitals present.

n = 4	$\ell = 3$	$m_\ell = 3, 2, 1, 0, -1, -2, -3$	seven 4f orbitals
	$\ell = 2$	$m_\ell = 2, 1, 0, -1, -2$	five 4d orbitals
	$\ell = 1$	$m_\ell = 1, 0, -1$	three 4p orbitals
	$\ell = 0$	$m_\ell = 0$	one 4s orbital

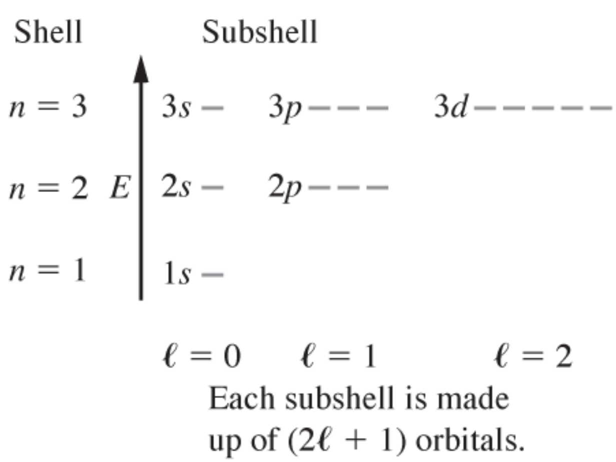


Fig. 8-23 – For reference for Question 10.