Atom and Electron Structure through Spectroscopy

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Concept 2: Light and Color
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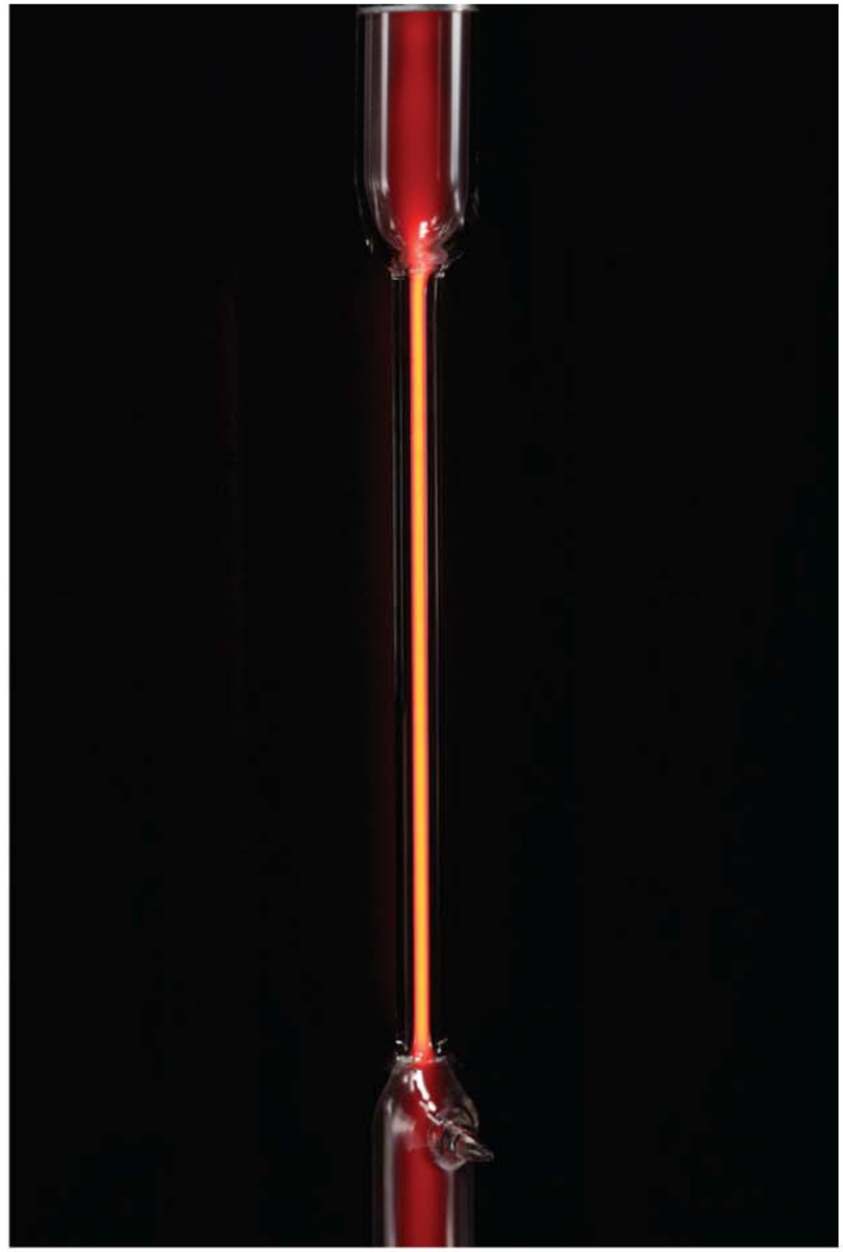
*Text and figures, except those associated with derivations of energy and radius of the Bohr model, are taken primarily from the PowerPoint lectures to accompany general chemsitry textbooks by Brown, LeMay, et al. and Tro, published by Pearson Education.

Spectra

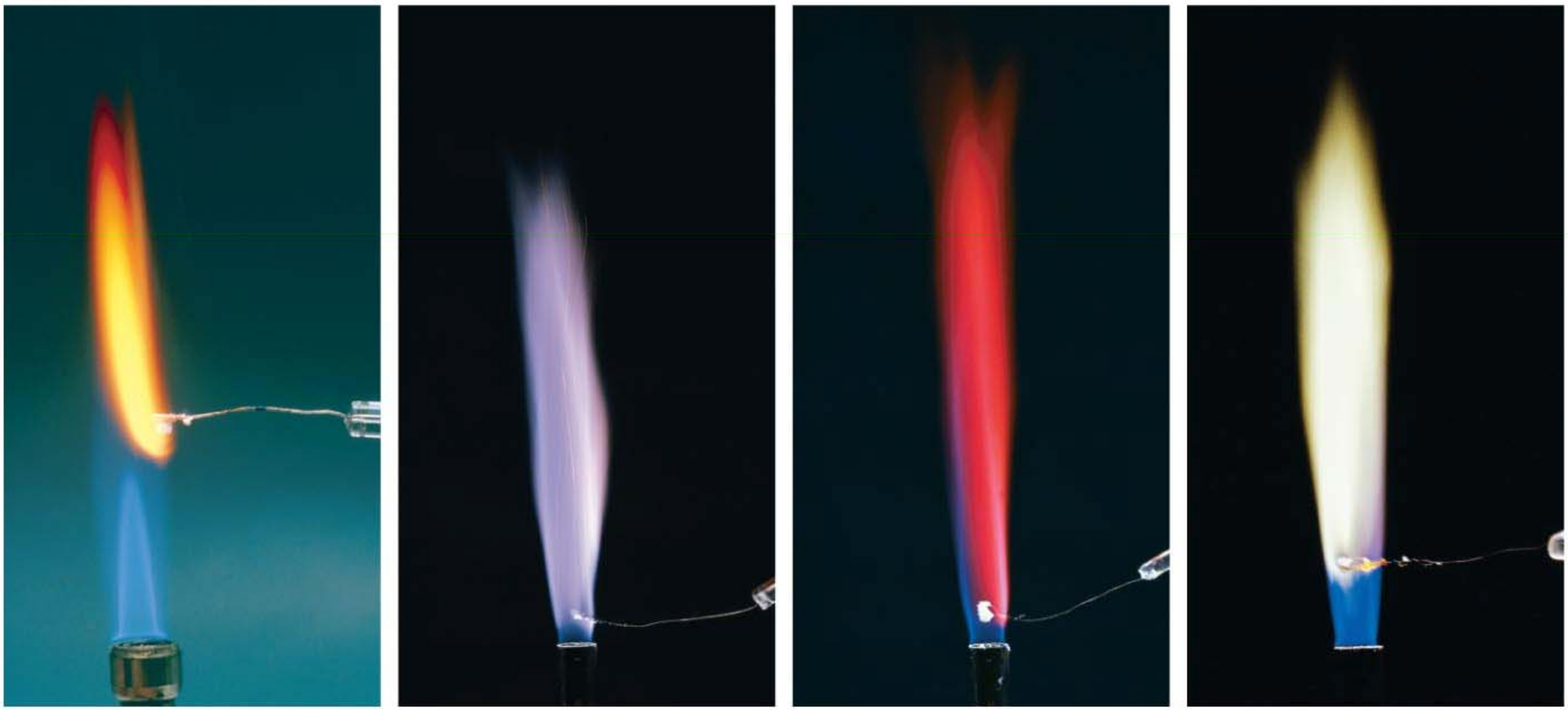
- When atoms or molecules absorb energy, that energy is often released as light energy
  - fireworks, neon lights, etc.
- When that emitted light is passed through a prism, a pattern of particular wavelengths of light is seen that is unique to that type of atom or molecule – the pattern is called an **emission spectrum**
  - non-continuous
  - can be used to identify the material
    - flame tests

Hydrogen (H)



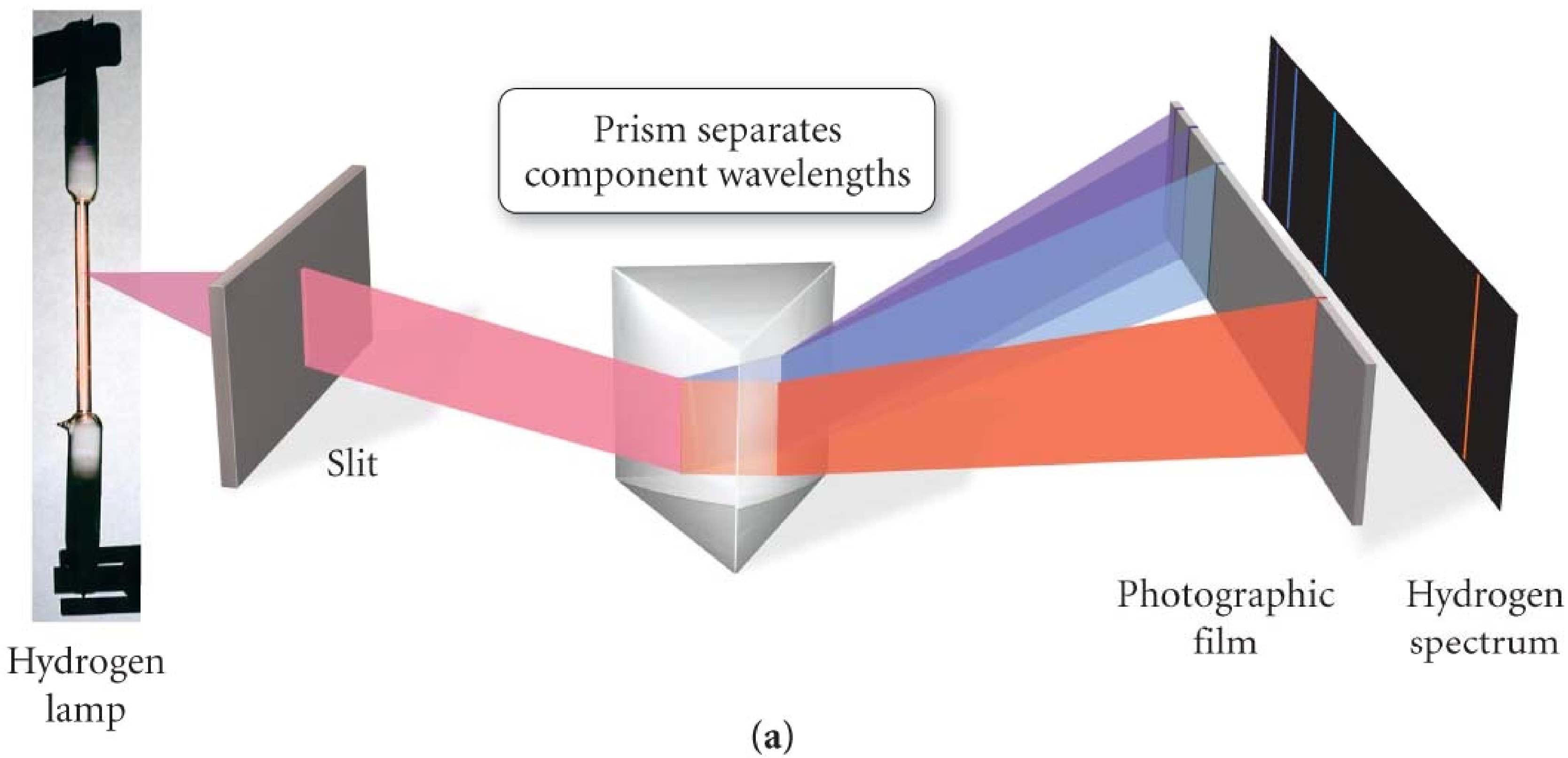
Neon (Ne)

Identifying Elements with Flame Tests

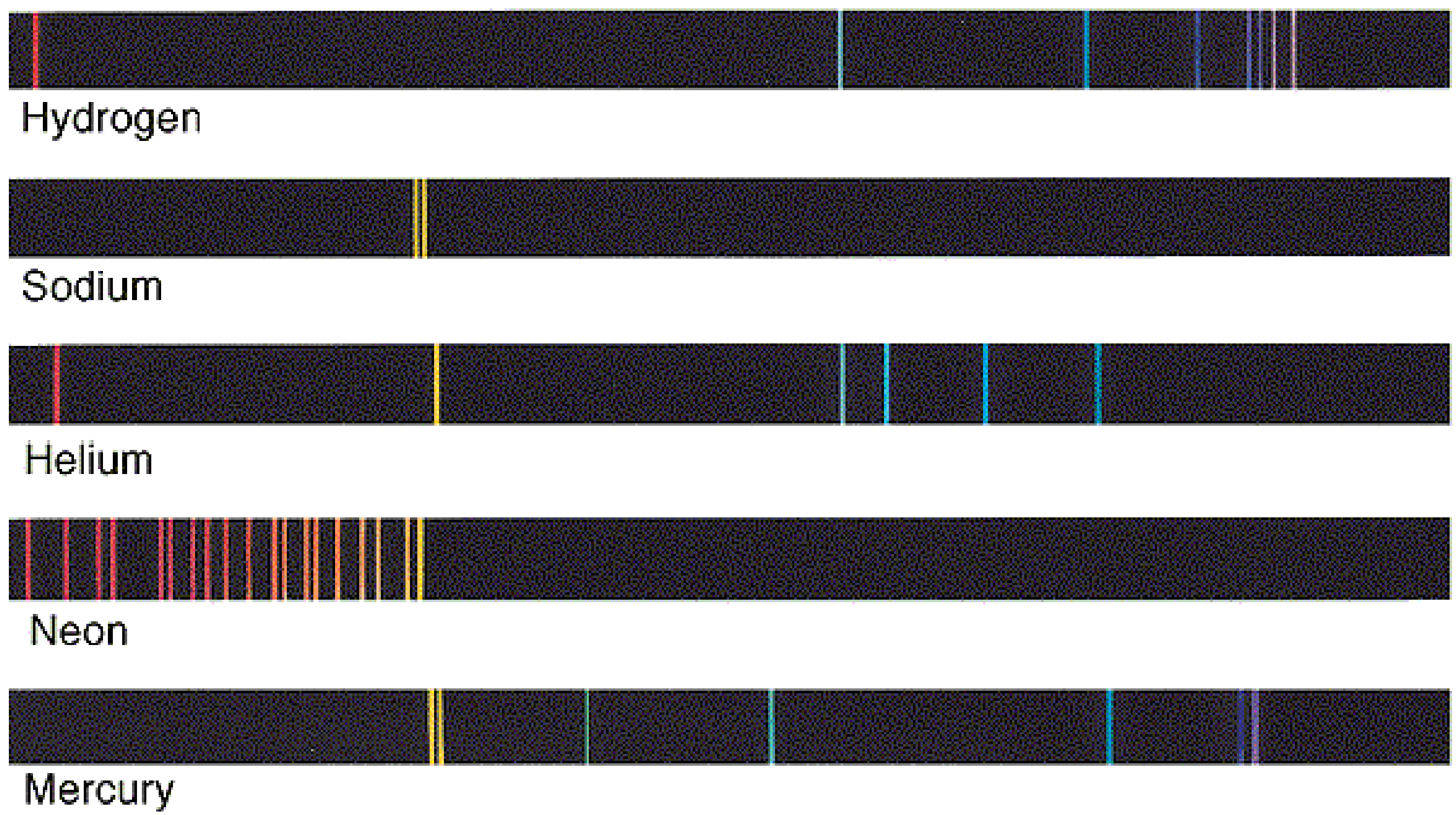


Na K Li Ba

Emission Spectra



Emission Spectra



Silicon Emission Spectrum Scarf

http://www.searchdictionaries.com/?q=emission+spectrum

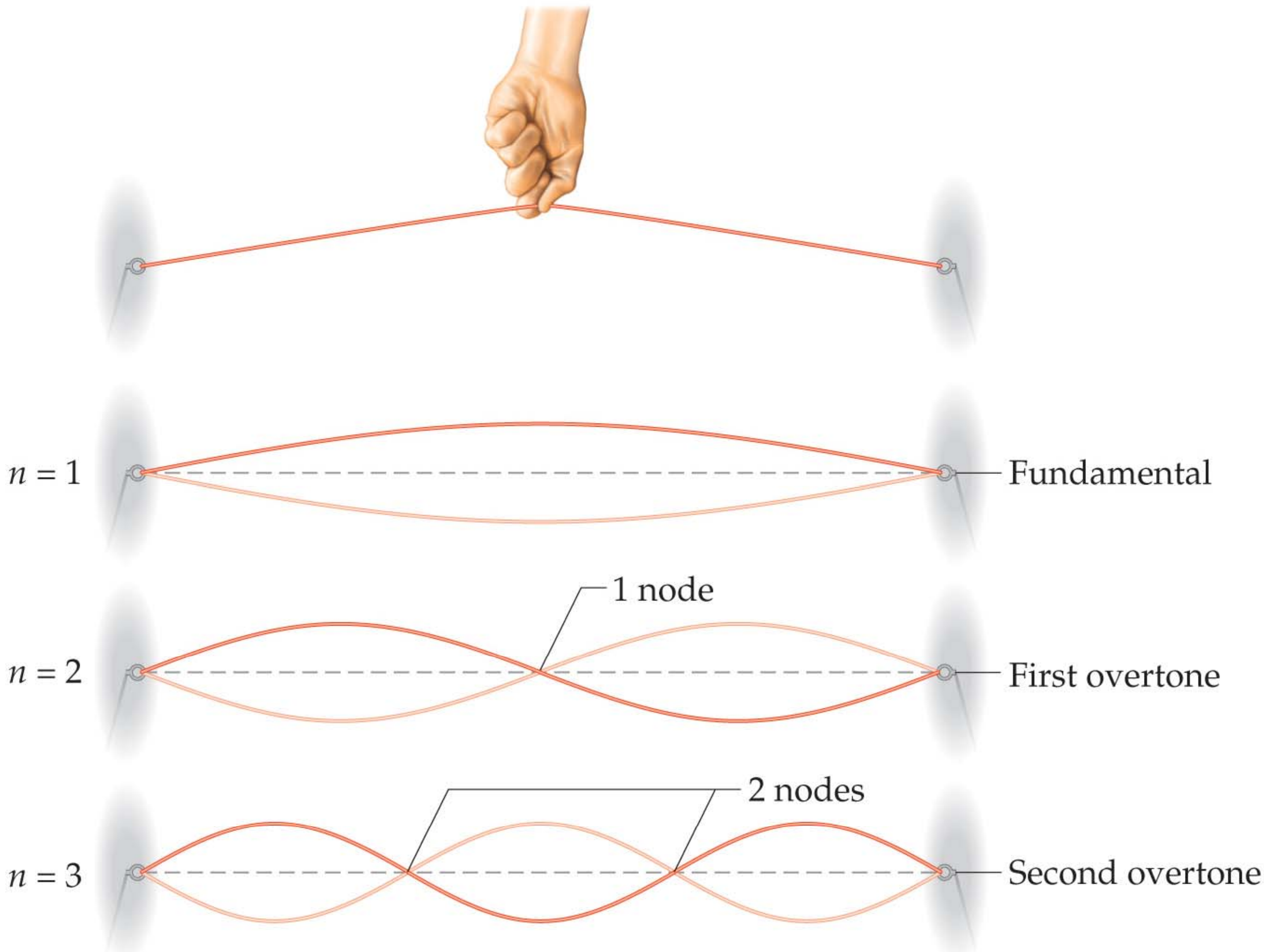
Rydberg's Spectrum Analysis

Johannes Rydberg (1854–1919)

- Rydberg analyzed the spectrum of hydrogen and found that it could be described with an equation that involved an inverse square of integers

$$\frac{1}{\lambda} = 1.097 \times 10^{7}\ \mathrm{m}^{-1}\left(\frac{1}{n_1^{2}} - \frac{1}{n_2^{2}}\right)$$

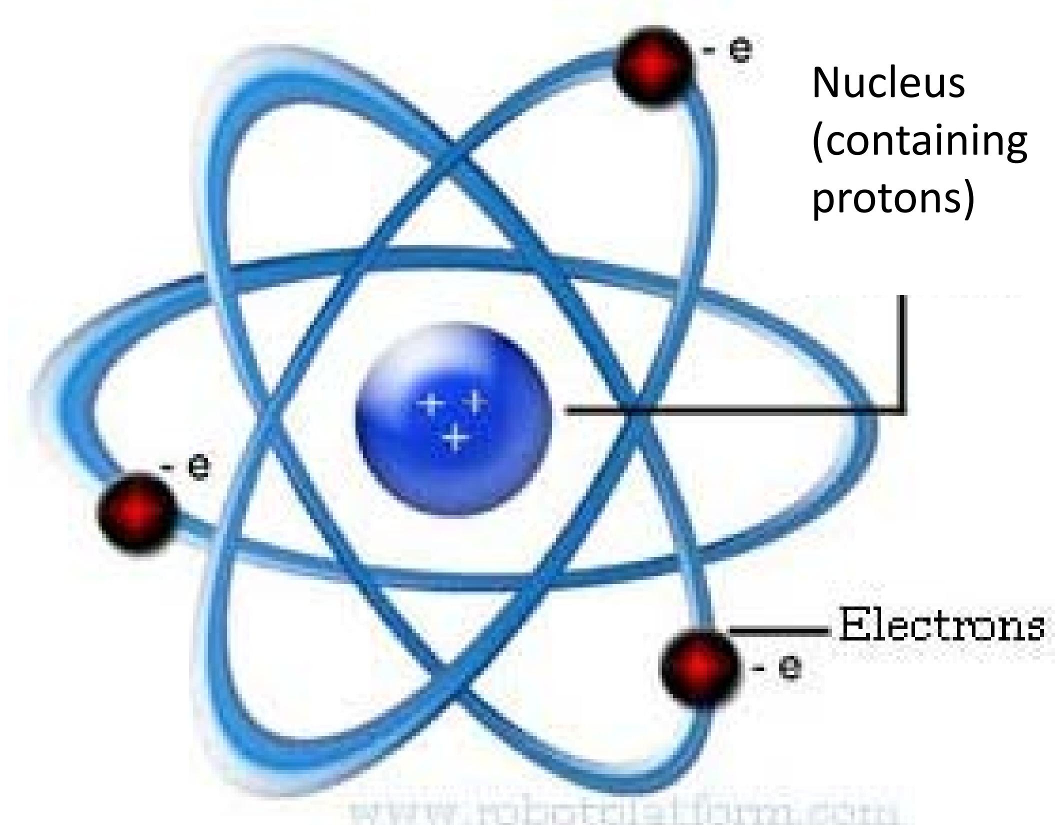
Standing Waves



Rutherford's Nuclear Model

- The atom contains a tiny dense center called the **nucleus**
  - the volume is about 1/10 trillionth the volume of the atom
- The nucleus is essentially the entire mass of the atom
- The nucleus is positively charged
  - the amount of positive charge balances the negative charge of the electrons
- The electrons move around in the empty space of the atom surrounding the nucleus

Rutherford's Nuclear Model



Problems with Rutherford's Nuclear Model of the Atom

- Stability of Rutherford Model
- Electrons are moving charged particles.
- According to classical physics, moving charged particles give off energy.
- Therefore, electrons should constantly be giving off energy.
- The electrons should lose energy, crash into the nucleus, and the atom should collapse!!
  - but it doesn't!
- Inability to explain atom emission spectra

The Bohr Model of the Atom

Neils Bohr (1885–1962)

- The nuclear model of the atom (1913) does not explain what structural changes occur when the atom gains or loses energy
- Bohr developed a model of the atom to explain how the structure of the atom changes when it undergoes energy transitions
- Introduced Planck's constant (E = hν) into planetary model.
- Bohr's major idea was that the energy of the atom was **quantized**, and that the amount of energy in the atom was related to the electron's position in the atom
  - **quantized** means that the atom could only have very specific amounts of energy

Niels Bohr

Bohr’s Model

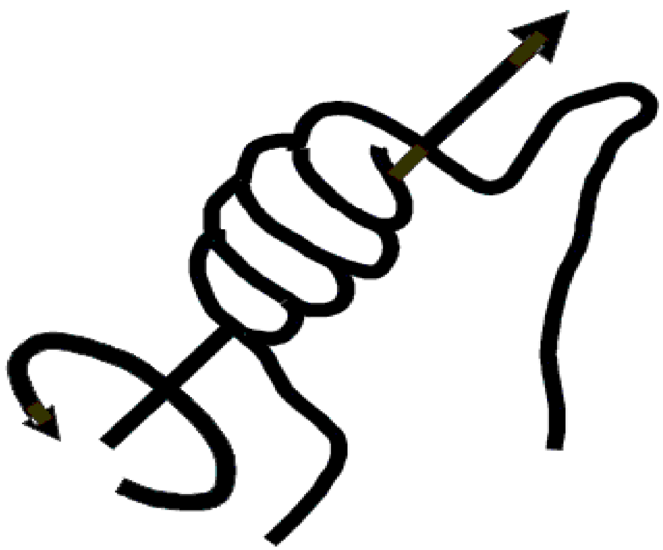
- The electrons travel in orbits that are at a fixed distance from the nucleus
  - **stationary states**
  - therefore the energy of the electron was proportional to the inverse of the distance the orbit was from the nucleus
- Electrons emit radiation when they “jump” from an orbit with higher energy down to an orbit with lower energy
  - the emitted radiation was a photon of light
  - the distance between the orbits determined the energy of the photon of light produced

Angular Momentum Quantized

- Discrete energies result from quantization of the electron's angular momentum
- Can take values equal to integral multiples of $h/2\pi$
- Linear momentum, $p = mv$; angular momentum, $p = mvr$
- Angular momentum is actually a vector quantity; the vector rests perpendicular to the circle of motion

Angular Momentum

- Direction given by right hand rule.

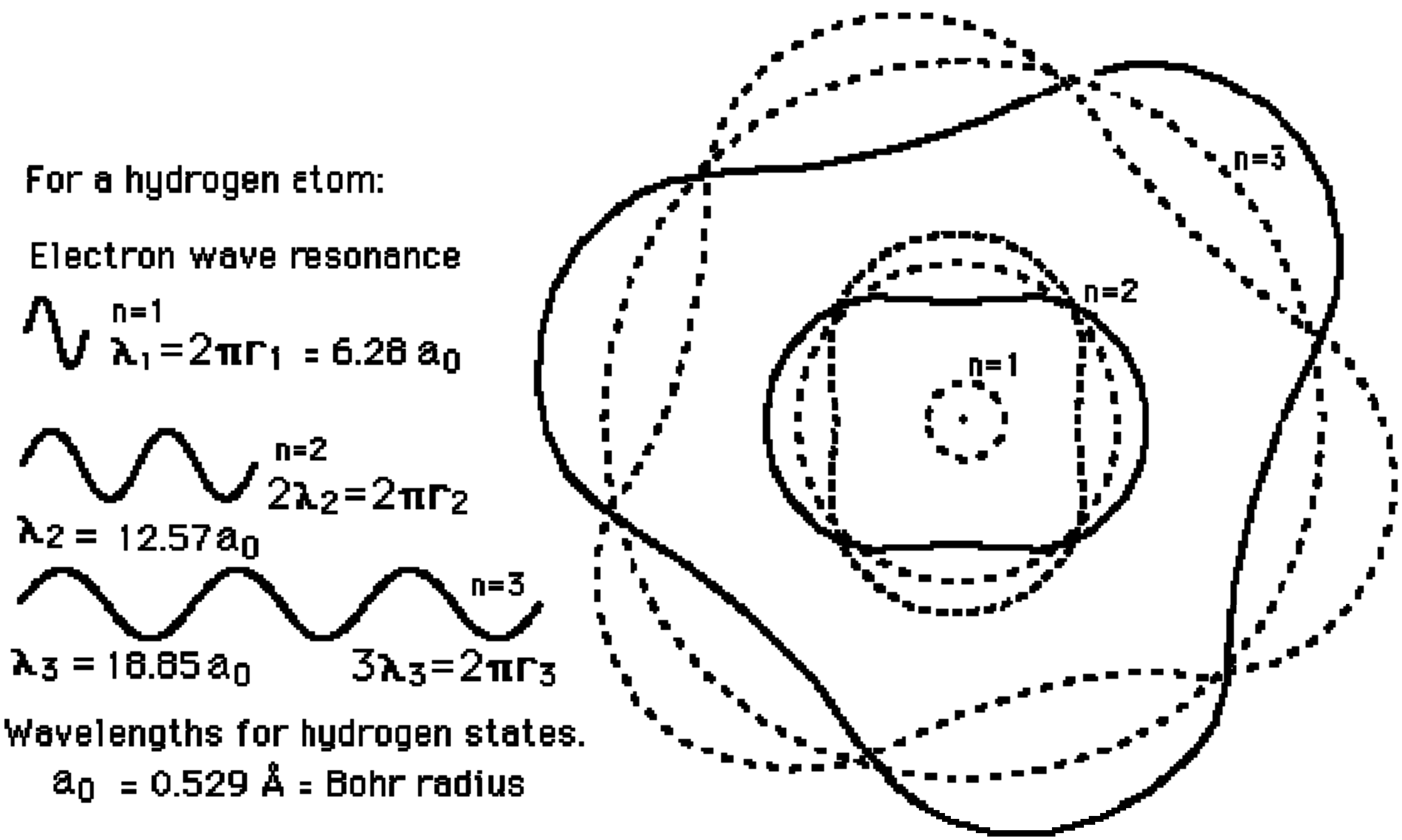


http://es.wikipedia.org/wiki/Archivo:Right_hand_rule_simple.png

Electron as a Standing Wave

- Consider the electron as a standing wave
- Wave propagates in one of a number of circular paths about the nucleus
- Only certain paths, orbits, are allowed

Electron as a Standing Wave



http://www2.arnes.si/~gljsentvid10/bohr.htm#c4

Standing Waves and Angular Momentum

- The circumference of an orbit, $2\pi r$, must equal an integral number of wavelengths; thus, $2\pi r = n\lambda$ where n is an integer greater than *zero*
- Using the DeBroglie relationship $\lambda = h/mv$, $2\pi r = nh/mv$ or $mvr = n(h/2\pi)$ - quantized angular Momentum
- Note: This is working backward from Bohr who assumed angular momentum and energy were quantized and found integer values for n, which suggested standing waves to other researchers

Can Calculate Radius of Orbits

- Requires only some algebra, but we will not go through derivation
- For electron to stay in circular orbit, the centripetal force (mv^2/r) that moves electron around nucleus must be offset by the electrostatic attraction to nucleus (Ze^2/r^2 where Z is # of positive charges in nucleus and e is electron charge)
- Setting these two equal, substituting for v ($mvr = n(\mathrm{h}/2\pi)$ or $v = n\mathrm{h}/2\pi mr$), and solving for r, gives $r = n^2[\mathrm{h}^2/(2\pi)^2 me^2 Z]$ (and $Z = 1$ for hydrogen)

Can Calculate Energy of Orbits

- $E_{Total} = E_{kinetic} + V$ where V is potential energy
- $E_k = 1/2mv^2$
- If solve $mv^2/r = Ze^2/r^2$ for mv^2, then $E_k = 1/2Ze^2/r$
- Potential energy is Coulombic attraction of electron to nucleus, $-Ze^2/r$
- $E_T = 1/2Ze^2/r + (-Ze^2/r) = -1/2Ze^2/r$
- Make substitution using formula for r gives

  $E = -2\pi^2 mZ^2e^4/h^2n^2$

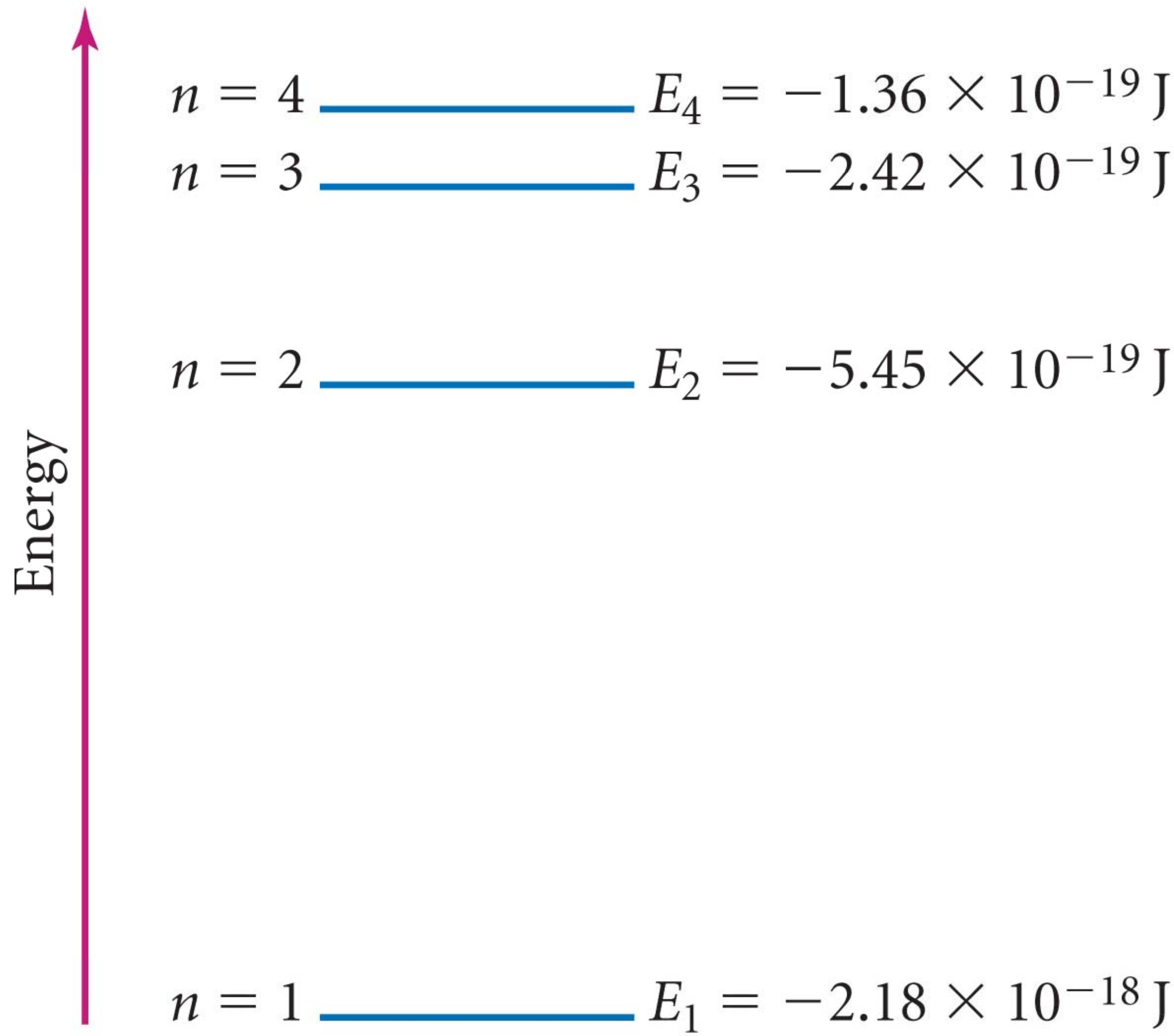
  $E = $ constant x $1/n^2$
- If convert E to wavenumber and let Z = 1 for hydrogen, the constant is the Rydberg constant given in an earlier slide

Principal Quantum Number, *n*

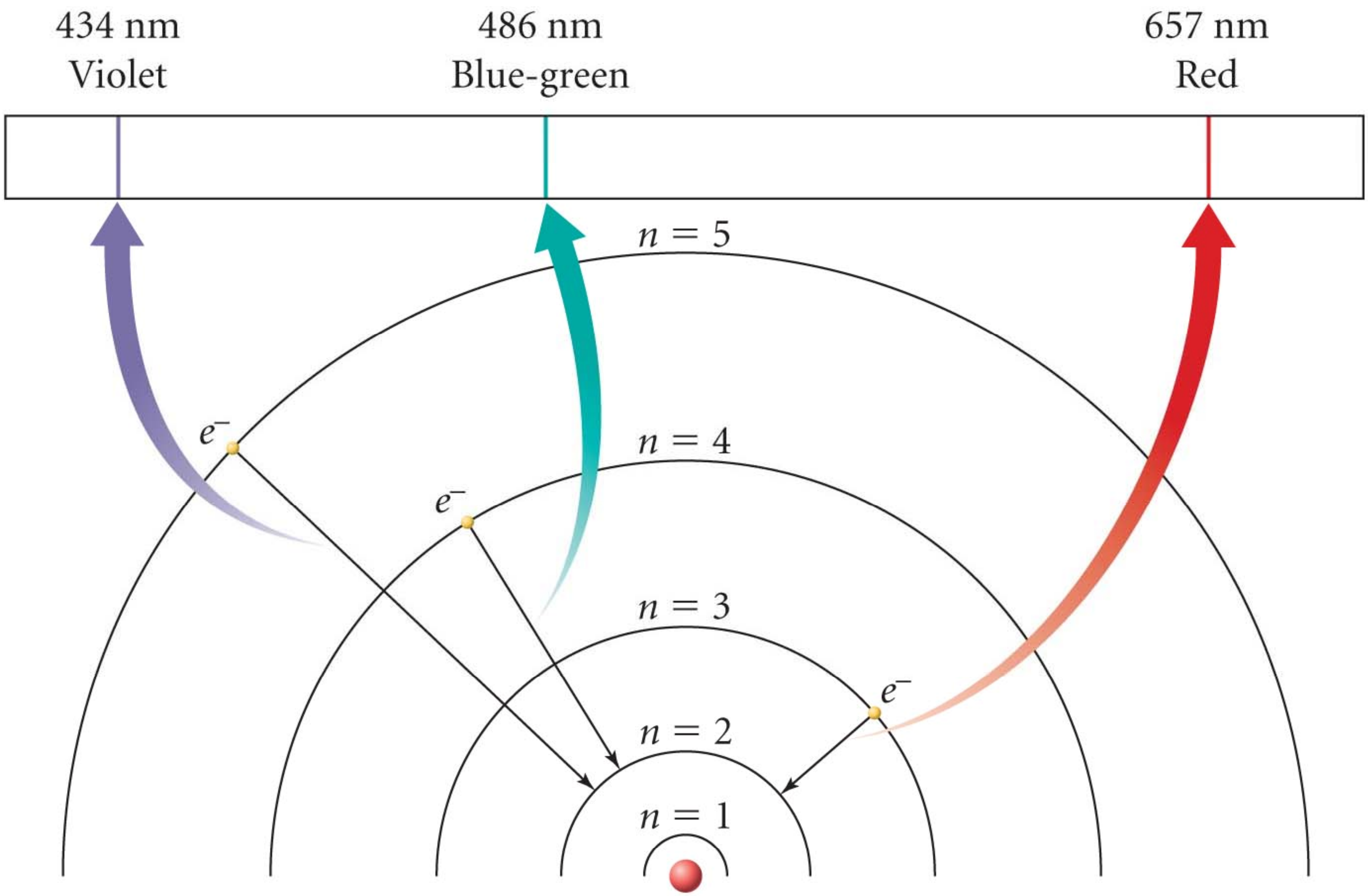
- Characterizes the energy of the electron in a particular orbital
  - corresponds to Bohr's energy level
- *n* can be any integer ≥ 1
- The larger the value of *n*, the more energy the orbital has
- Energies are defined as being negative
  - an electron would have E = 0 when it just escapes the atom
- The larger the value of *n*, the larger the orbital
- As *n* gets larger, the amount of energy between orbitals gets smaller

$$E_n = -2.18 \times 10^{-18}\ \mathrm{J}\left(\frac{1}{n^2}\right)$$ **for an electron in H**

Principal Energy Levels in Hydrogen



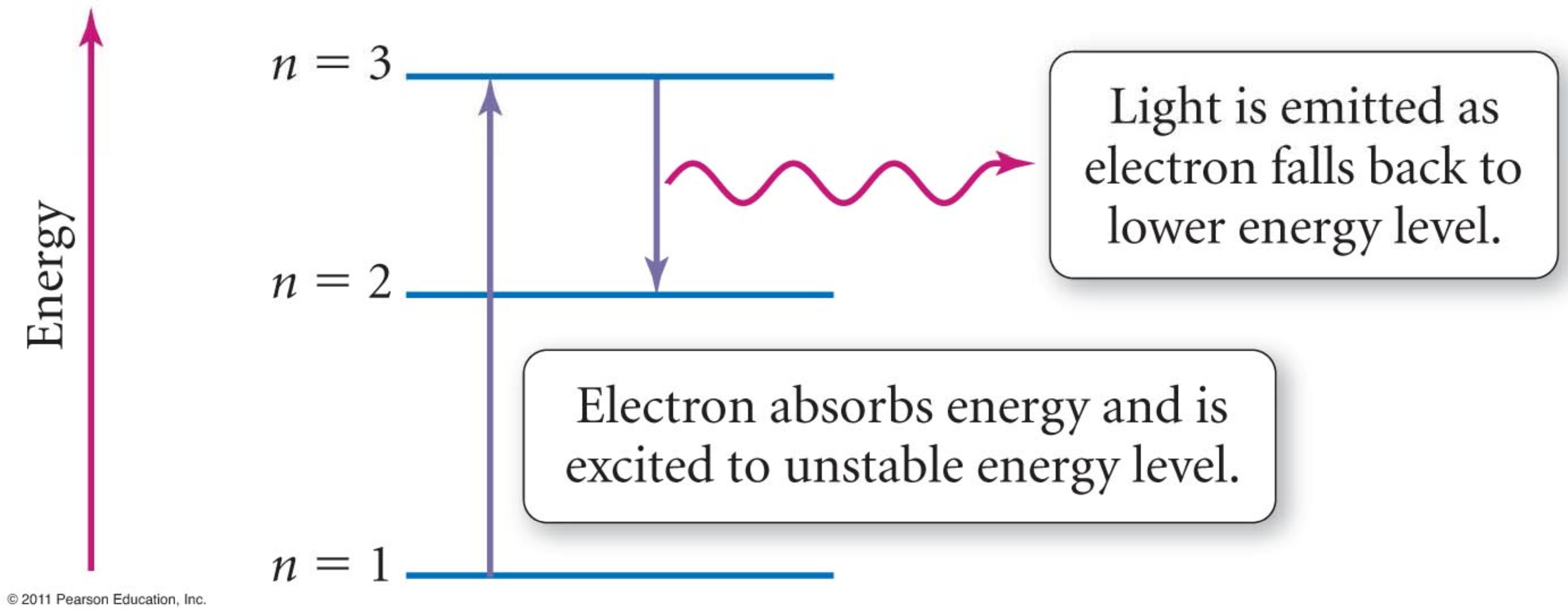
Bohr Model of H Atoms



Electron Transitions

- To transition to a higher energy state, the electron must gain the correct amount of energy corresponding to the difference in energy between the final and initial states
- Electrons in high energy states are unstable and tend to lose energy and transition to lower energy states
- Each line in the emission spectrum corresponds to the difference in energy between two energy states

Quantum Leaps



Predicting the Spectrum of Hydrogen

- The wavelengths of lines in the emission spectrum of hydrogen can be predicted by calculating the difference in energy between any two states
- For an electron in energy state *n*, there are ($n - 1$) energy states it can transition to, therefore ($n - 1$) lines it can generate
- The Bohr Model predicts these lines very accurately for a 1-electron system

Energy Transitions in Hydrogen

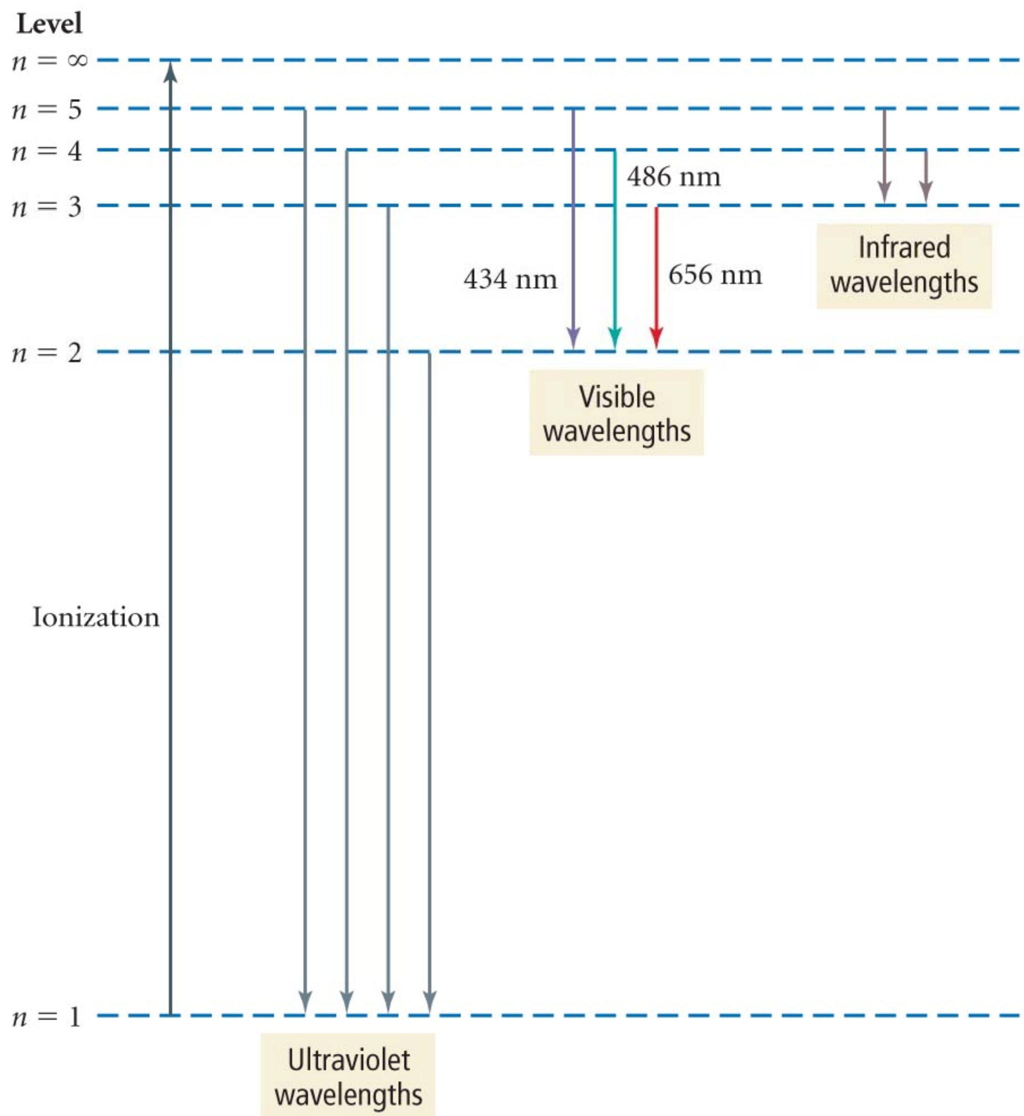
- The energy of a photon released is equal to the difference in energy between the two levels the electron is jumping between
- It can be calculated by subtracting the energy of the initial state from the energy of the final state

$$\Delta E_{electron} = E_{final\ state} - E_{initial\ state} \qquad E_{emitted\ photon} = -\Delta E_{electron}$$

$$E_{photon} = -\left[\left(-2.18\times10^{-18}\ \mathrm{J}\left(\frac{1}{n_{final}^{2}}\right)\right)-\left(-2.18\times10^{-18}\ \mathrm{J}\left(\frac{1}{n_{initial}^{2}}\right)\right)\right]$$

$$\frac{hc}{\lambda} = E_{photon} = 2.18\times10^{-18}\ \mathrm{J}\left[\left(\frac{1}{n_{final}^{2}}\right)-\left(\frac{1}{n_{initial}^{2}}\right)\right]$$

Hydrogen Energy Transitions



By 1919, Bohr knew the planetary model was incorrect

The Bohr model was subsequently expanded by the addition of more quantum numbers. The dependence of the orbit radius and energy on n^2 suggested the orbits were in general elliptical not circular, similar to the planetary model of the solar system; this was addressed by the addition of the λ quantum number (Sommerfield, 1916). Sommerfield also added a quantum number, m_λ, to address orientation in space that is necessary when an applied electric or magnetic field is present. Rather than ad hoc additions, the need for three quantum numbers is a nature consequence of the Schrodinger equation.

Basically, using incorrect logic, Bohr managed to derive equations that provided a model of the one-electron atom that could explain the emission spectra and certain other properties and could modified to explain even more properties.

"It is hard to say whether it was good or bad luck that the properties of the Kepler motion could be brought into such a simple connection with the hydrogen spectrum as was believed at the time…" Bohr, 1926

Uncertainty Principle

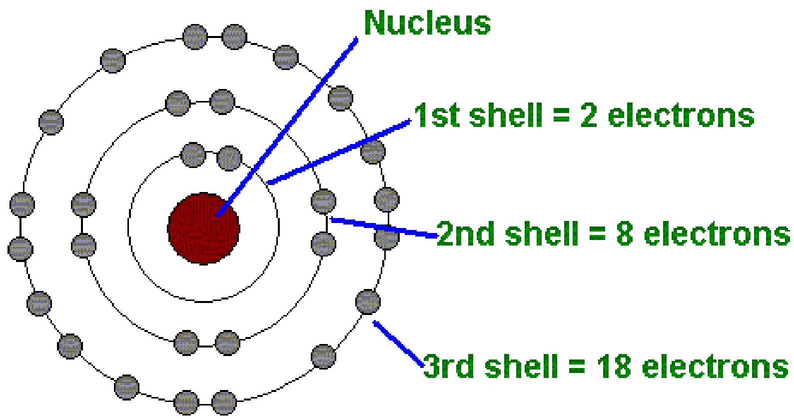
$$\Delta x \Delta p \geq \frac{h}{4\pi}$$

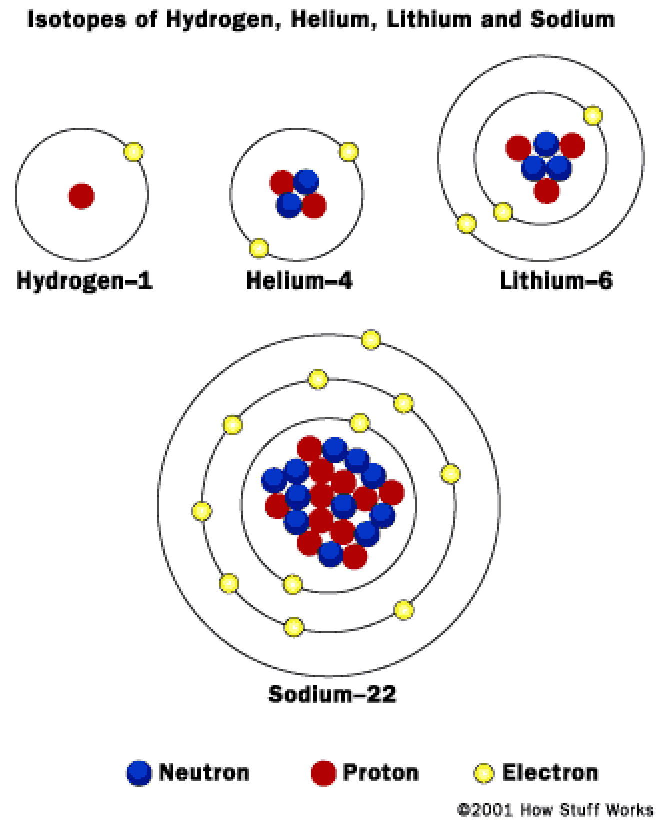
- Heisenberg (1927) stated that the product of the uncertainties in both the position and speed of a particle was inversely proportional to its mass
  - x = position, Δx = uncertainty in position
  - p = momentum, Δp = uncertainty in momentum
  - m = mass
- This means that the more accurately you know the position of a small particle, such as an electron, the less you know about its momentum
  - and vice-versa

Problem for the Bohr Model

- Solving for the radius in the Bohr gives an exact value; thus, know exactly the position of the electron in one dimension, *r.*
- *Thus, if r represent the radius of a planetary-type orbit, the Bohr model violates Heisenberg Exclusion Principle*

Then why are we teaching this?





http://the-history-of-the-atom.wikispaces.com/Niels+Bohr
http://science.howstuffworks.com/atom7.htm