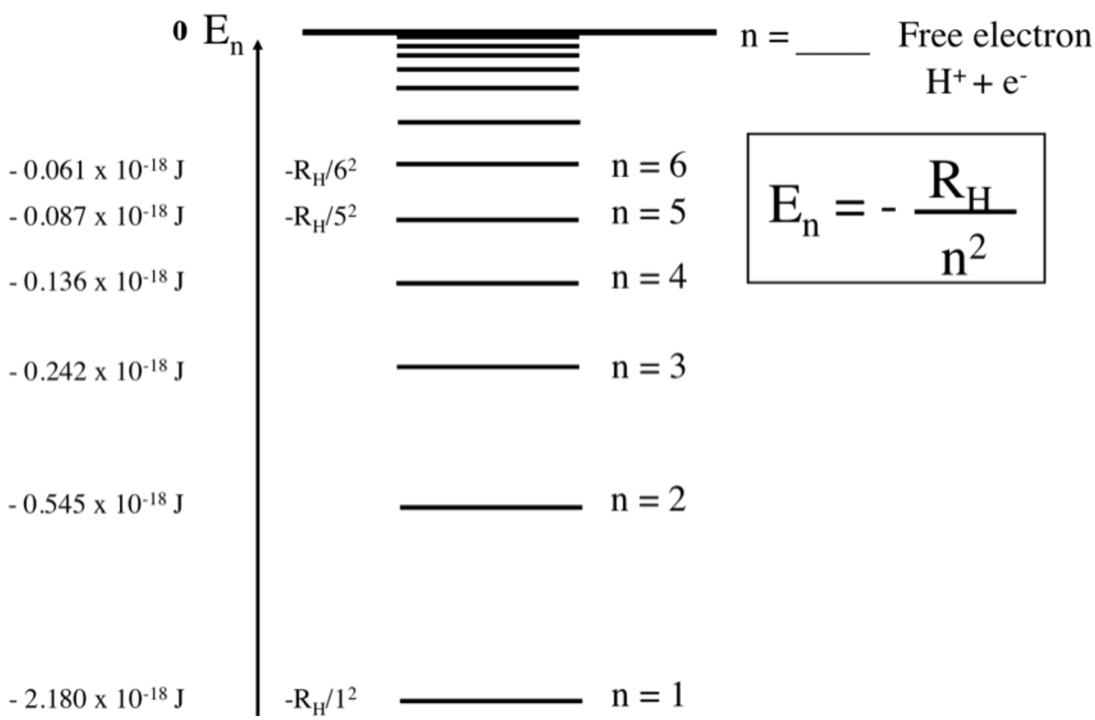
5.111 Lecture Summary #5 Friday, September 12, 2014

Readings for today: Section 1.3 – Atomic Spectra, Section 1.7 up to equation 9b – Wavefunctions and Energy Levels, Section 1.8 – The Principle Quantum Number. (Same sections in 5^{th} and 4^{th} ed.)
Read for Lecture #6: Sections 1.9, 1.10, and 1.11 (Same sections in 4^{th} *ed.*)
Assignment: Problem set #2 (due Thursday, September 18^{th} at 5 pm).

Topics: **The Schrödinger Equation and Hydrogen Atom Energy Levels**
I. Binding energies of the electron to the nucleus for a hydrogen atom
II. Verification of hydrogen-atom energy levels
  A. Photon emission
  B. Photon absorption

The Schrödinger equation is an equation of motion for particles (like electrons) that accounts for their wave-like properties. Solutions to the Schrödinger equation indicate possible binding energies and wavefunctions.

Energy level diagram for the H atom



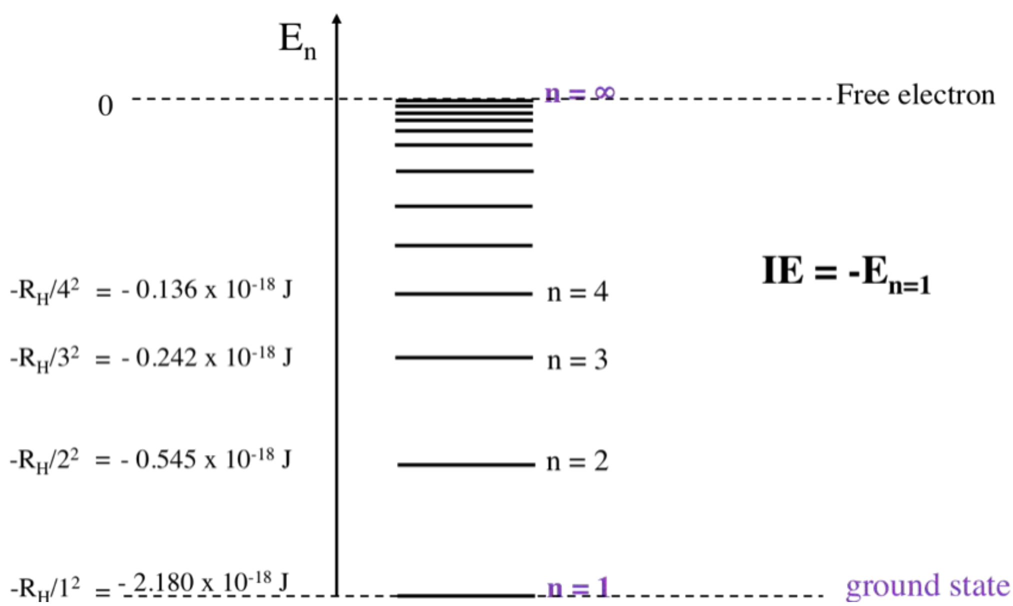
Note that all binding energies are _____________ . A negative value means that the electron is bound to the nucleus. At n=∞ ($E_n = 0$), the e^- is free from the nucleus.

The lowest (most negative) energy is called the __________________________ .

- The ground state is the most stable state.
- The ground state is the n = 1 state.

Ionization energy (IE) is the minimum energy required to remove an electron from the n^{th} state of a gaseous atom, molecule or ion. (Assume ground state, n=1, unless otherwise specified.)

- E_n = _________ (ionization energy) of the hydrogen atom in the n^{th} state.
- Ionization energy is always _______________ . You always need to put energy into a system to eject an electron.
- The IE for a hydrogen atom in the ground state = ______________ J. This means if you put that amount of energy into a hydrogen atom in its ground state, the electron is no longer bound to the nucleus.
- The IE for a hydrogen atom in the n = 2 (first excited state) is _______________ J.
- The IE of a hydrogen atom in the **third** excited state (n =___) is ________________ J.



The following equation describes the binding energy for any one-electron atom (including ions):

$$E_n = - \underline{\hspace{2cm}}$$ where Z = atomic number

Electron is more weakly bound when n is big and more tightly when Z is big.

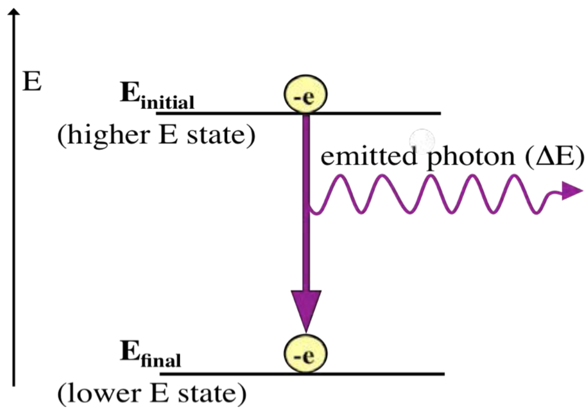
Atoms or ions with one electron:

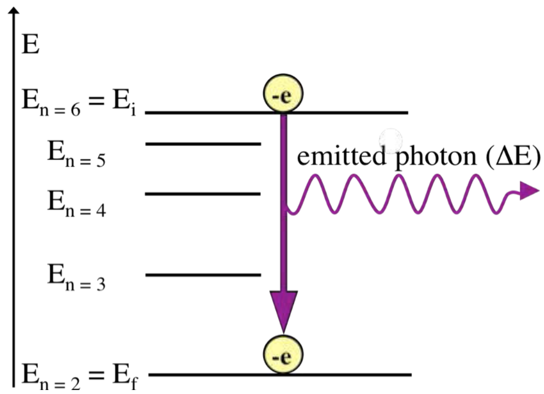
H	≡ one electron atom	Z = 1 (atomic number)
He^+	≡ one electron ion	Z = 2
Li^{2+}	≡ one electron ion	Z = ______
Tb^{64+}	≡ one electron ion	Z = ______

II. VERIFICATION OF HYDROGEN ATOM ENERGY LEVELS

A. PHOTON EMISSION

Photon emission occurs when an excited H atom relaxes to a lower E state. As the electron transitions from the higher to the lower E state, a photon is emitted that has the ________ energy as the energy difference between the two states.





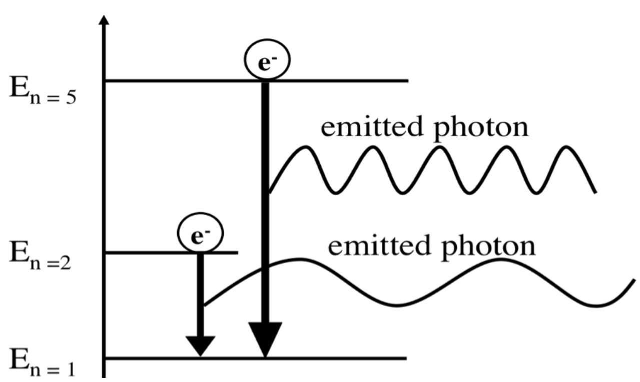
We can calculate the energy of the emitted photon

ΔE = ____ – _____ **ΔE =**________ – ________

From the energy of the emitted photon, we can also calculate the frequency (ν) using $\Delta E = h\nu$.

ν = _________ ν = ______________

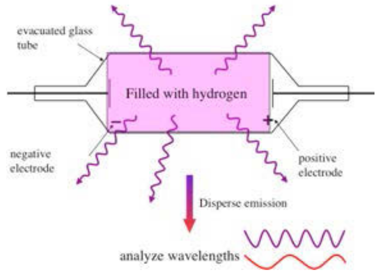
Consider the relationship between E, λ, and ν for any emitted photon:

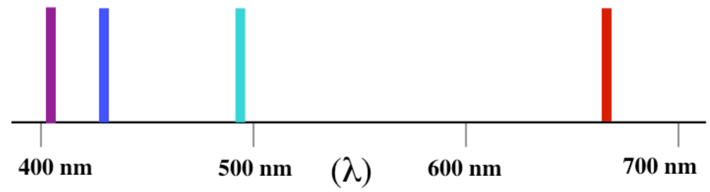


$n_i = 5 \Rightarrow n_f = 1$ large ΔE ______ν _______ λ

$n_i = 2 \Rightarrow n_f = 1$ small ΔE _____ν _______ λ

Demonstration: Observing spectral lines from the visible spectrum of atomic hydrogen.





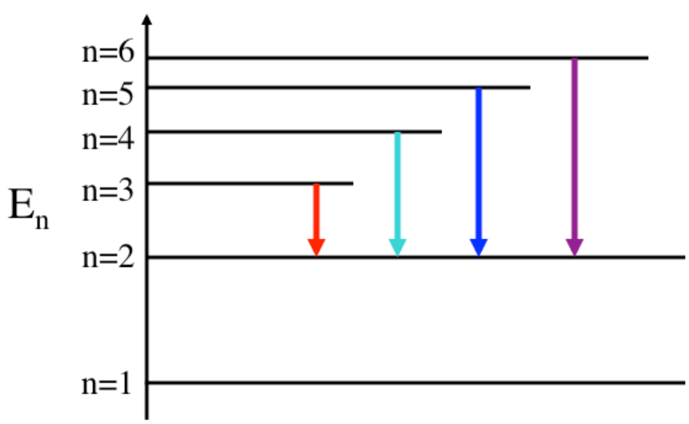
We are far from the first to observe these lines from atomic hydrogen!

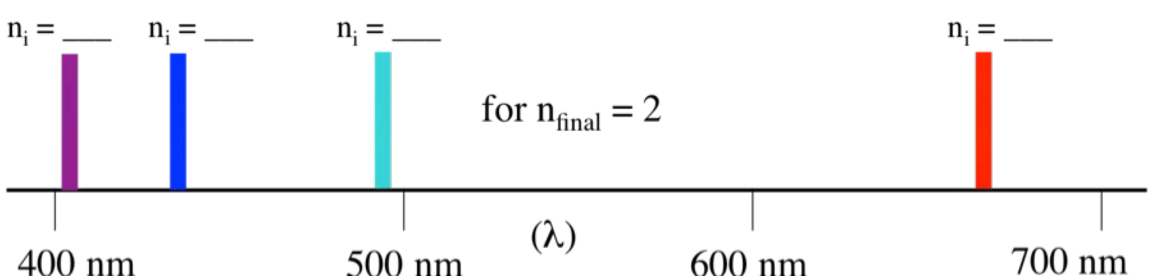
1885 **J.J. Balmer observed H atoms emit a series of lines** in the visible region whose frequencies can be described by a simple formula:

$\nu = 3.29\times10^{15}\ s^{-1}\ [(1/4) - (1/n^2)]$ where n = 3, 4, 5 or 6

The origin of this formula was not understood at the time, but we now know:

- The lines result from electron transitions with a final energy level of n = 2.
- The frequency values can be accurately calculated using the relationship $E = h\nu$.





For the visible lines in the spectrum of atomic hydrogen, $E_f = E_{n=2}$.

We can calculate the predicted frequency and wavelength of these transitions.

$$\nu = \frac{E_i - E_f}{h}$$

and from the solution to the Schrödinger equation, we know

$$E_n = \frac{-R_H}{n^2}$$

So, $$\nu = \underline{\qquad}\left(\underline{\qquad\quad} - \underline{\qquad\quad}\right)$$

$$\boxed{\nu = \underline{\qquad}\left(\underline{\qquad\quad} - \underline{\qquad\quad}\right)}$$

For $n_f = 2$, then

$$\nu = \frac{R_H}{h}\left(\frac{1}{\underline{\qquad}} - \frac{1}{n_i^2}\right)$$ **BALMER SERIES**

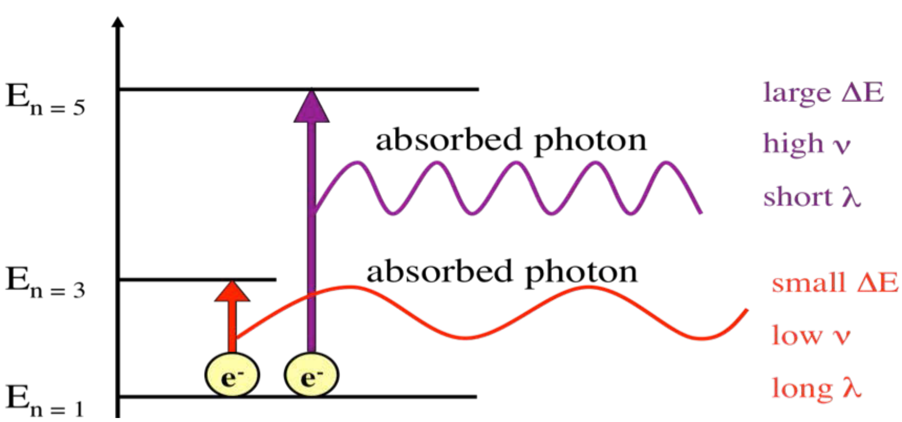
$\mathbf{R_H/h = \mathfrak{R}}$ $= 3.2898 \times 10^{15}\ s^{-1}$.

Once ν is calculated for $n_i = 3, 4, 5, 6\ldots$ use $\lambda = c/\nu$ to calculate λ.
Calculations for λ using this equation derived from values of E_n predicted by Schrödinger equation match the observed λ or ν of emission to one part in 10^8!

Transitions made to all final states from higher lying states. Named series include:

$n_f = 1$	Lyman series	____________________
$\mathbf{n_f = 2}$	**Balmer series**	**visible range**
$n_f = 3$	Paschen series	____________________
$n_f = 4$	Brackett series	____________________

B. PHOTON ABSORPTION
Energy can also be absorbed, exciting an electron to a higher energy state.



The frequency of the light absorbed can be calculated using:

$$\nu = \frac{R_H}{h}\left(\frac{1}{\quad\quad} - \frac{1}{\quad\quad}\right)$$

For $n_f > n_i$

Note: The energy, frequency, and wavelength of emitted or absorbed light should always be a **positive** number! The words absorption and emission indicate whether energy is being lost or gained.

Summary for absorption/emission

The Rydberg formula can be used to calculate the frequency (and also the E or λ, using $E = h\nu$ or $\lambda = c/\nu$) of light emitted or absorbed by any one-electron atom or ion. Note: adding Z makes the equation generic for any one-electron atom or ion. For hydrogen, Z=1.

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

for $n_i > n_f$

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

for $n_f > n_i$

__________________   __________________

Electron ____________ energy   Electron ____________ energy

Overall: The Schrödinger equation correctly predicts the hydrogen-atom emission spectrum, showing that the binding energies derived from the Schrödinger equation are in agreement with experiment. The Schrödinger equation also tells us about wavefunctions (orbitals) – that topic is next.

5.111 Principles of Chemical Science
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