5.111 Lecture Summary #5

Readings for today: Section 1.3 (1.6 in *3rd ed*) – Atomic Spectra, Section 1.7 up to equation 9b (1.5 up to eq. 8b in *3rd ed*) – Wavefunctions and Energy Levels, Section 1.8 (1.7 in *3rd ed*) – The Principle Quantum Number
Read for Lecture #6: Section 1.9 (1.8 in *3rd ed*) – Atomic Orbitals.

Assignment: Problem set #2 (due Session #8).

Topics: **The Hydrogen Atom**
- **I.** Binding energies of the electron to the nucleus ($H\Psi = \underline{\mathbf{E}}\Psi$)
- **II.** Verification of hydrogen-atom energy levels
  - **A.** Photon emission
  - **B.** Photon absorption
- **III.** Wavefunctions (orbitals) for the hydrogen atom ($H\underline{\boldsymbol{\Psi}} = E\underline{\boldsymbol{\Psi}}$)

THE HYDROGEN ATOM

I. BINDING ENERGIES (E_n) OF THE ELECTRON TO THE NUCLEUS

The Schrödinger equation for the H atom:

$$\hat{H}\Psi = E \cdot \Psi$$

$$\hat{H}\Psi_n = \underbrace{-\frac{1}{n^2}\,\frac{me^4}{8\varepsilon_0^2h^2}}_{E_n \equiv \text{binding energy of the electron to the nucleus}} \cdot \Psi_n$$

H atom orbital or wavefunction

m = _____ = ____________________

e = ____________________________

ε_0 = permittivity constant

h = Planck's constant

The constants in this equation are can be combined into a single constant:

$\frac{me^4}{8\varepsilon_0^2h^2} = R_H$ = Rydberg's constant = ________________

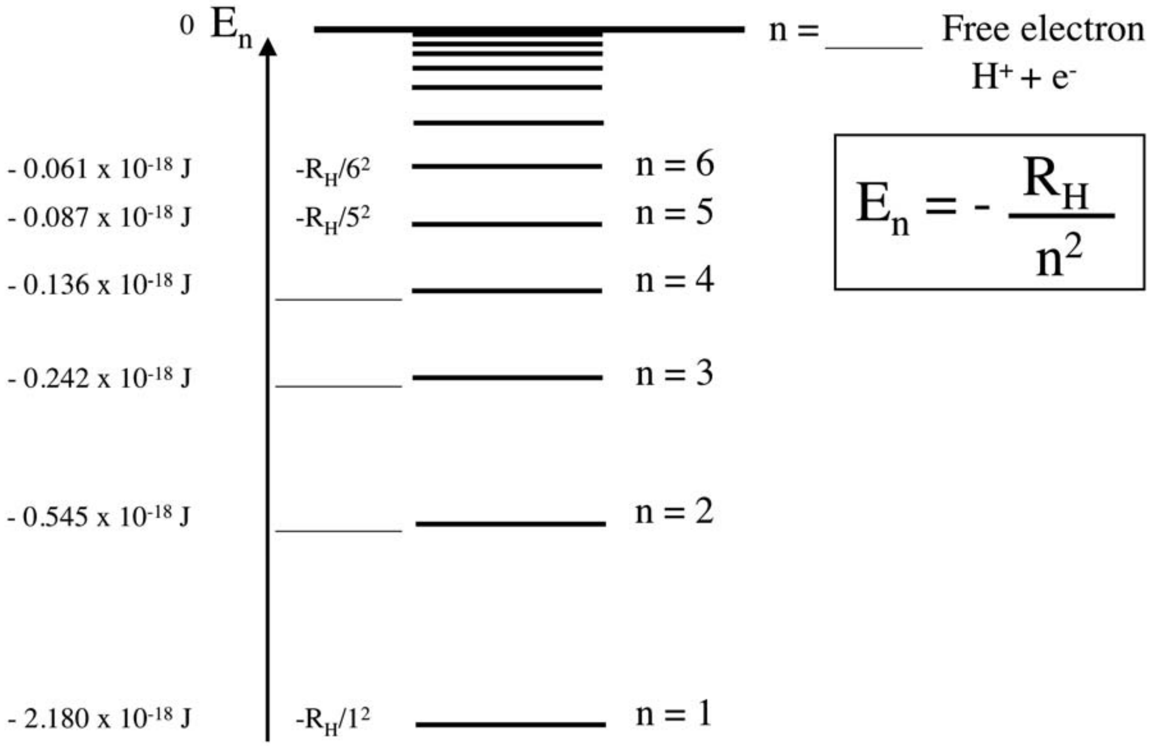
The **binding energy** (E_n) of the electron to the nucleus for the **hydrogen atom**:

$$\boxed{E_n = -\frac{1}{n^2}\,\frac{me^4}{8\varepsilon_0^2h^2} = \frac{-R_H}{n^2}}$$

where n = ___________________ (an integer) = __________________________________

KEY IDEA Binding energies are quantized!
The principal quantum number, n, comes out of solving the Schrödinger equation.

Energy level diagram for the H atom



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

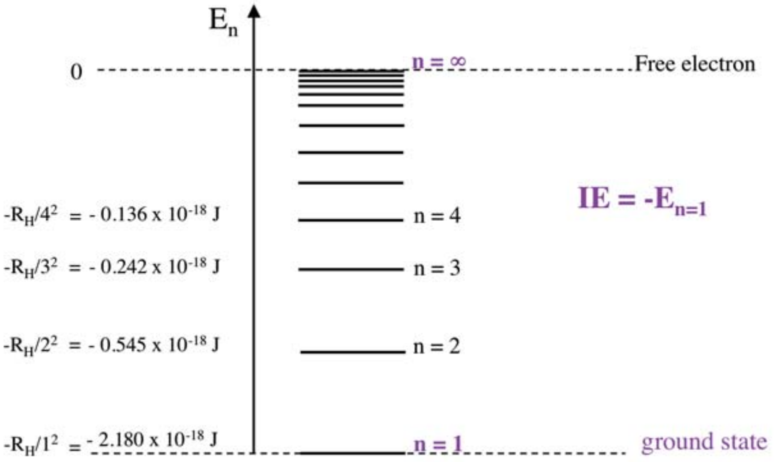
Note that all binding energies are negative. Negative energy means the electron is bound to the nucleus. **At n=∞, E_n = _____.** At n=∞, the e^- is free from the nucleus.

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

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

What is the physical significance of the binding energy, E_n?

E_n = _________ (ionization energy) of the hydrogen atom in the nth 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.)

- 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):

$$\boxed{E_n = \underline{\qquad\quad}}$$

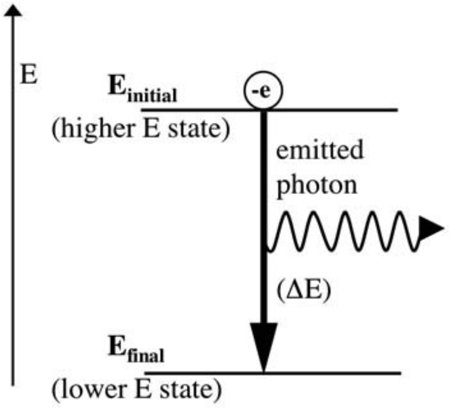
where Z = atomic number

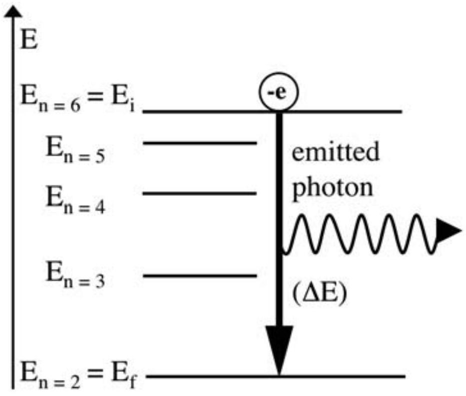
H	≡ one electron atom	Z = 1 (atomic number)
He^+	≡ one electron atom	Z = 2
Li^{2+}	≡ one electron atom	Z = _____
Tb^{64+}	≡ one electron atom	Z = _____

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 with the _____________________________ of the energy difference between the two states.





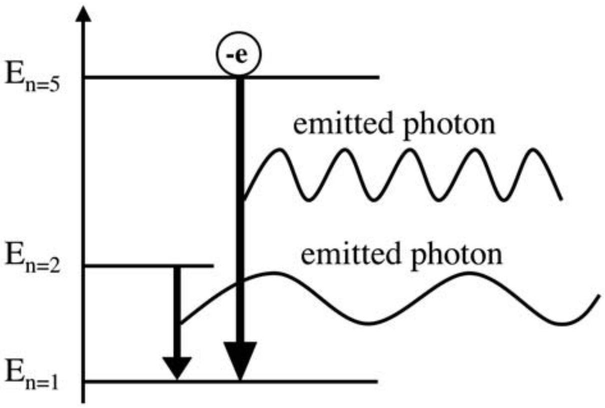
We can calculate the energy of the emitted photon

ΔE = ____ – ____ **ΔE = _______ – _______**

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

ν = ________ ν = ________________

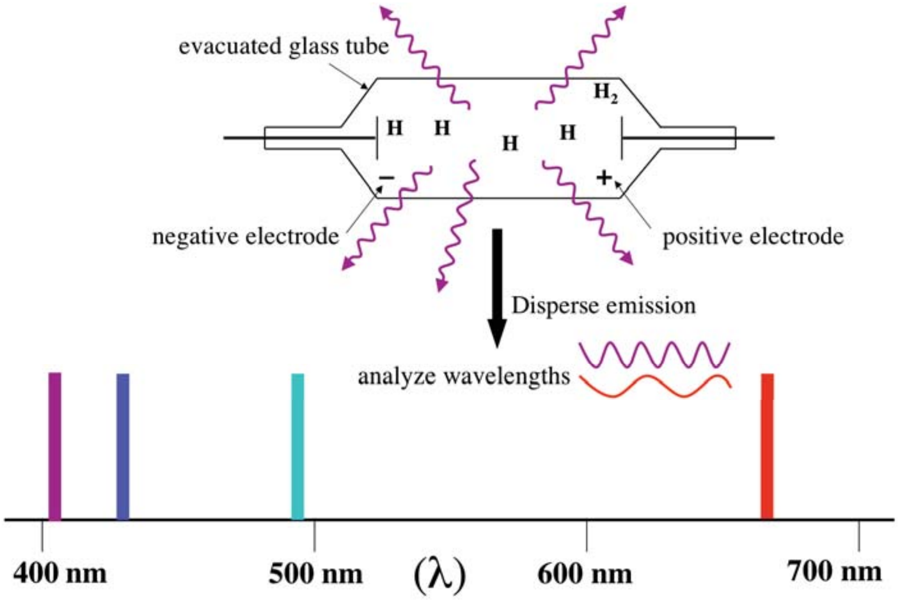
Consider the relationship between E, λ, and ν for any emitted photon:



$n_i = 5 \Rightarrow n_f = 1$ 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.



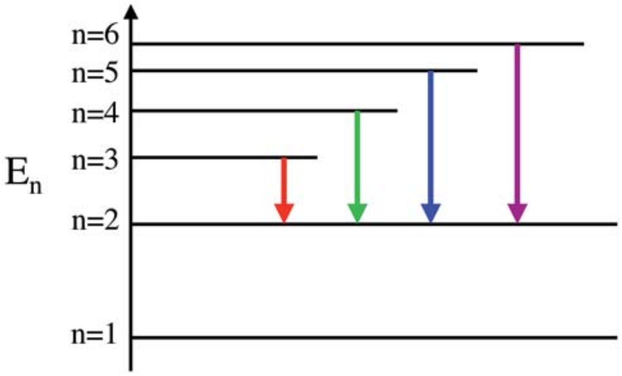
We are far from the first to observe these lines from atomic hydrogen!

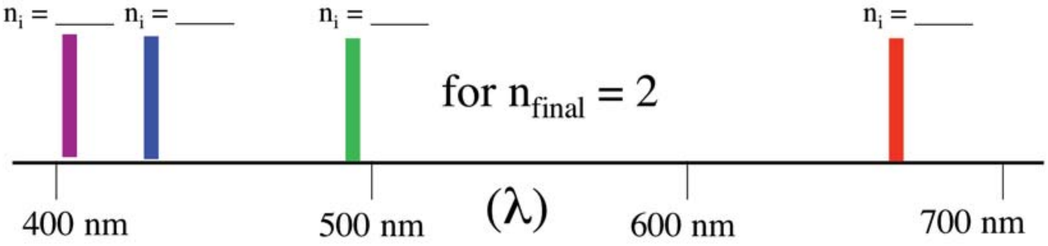
1885 **J.J. Balmer observed H atoms emit a series of lines** in the visible region whose frequencies can be described by a simple formula:

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

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 = hν.





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, $\nu = \_\_\left(\_\_\_ - \_\_\_\right)$ $\boxed{\nu = \_\_\left(\_\_\_ - \_\_\_\right)}$

For $n_f = 2$, then

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

R_H/h = $\mathfrak{R}$ = 3.29×10^{15} s^{-1}, so this is the exact equation that Balmer came up with.

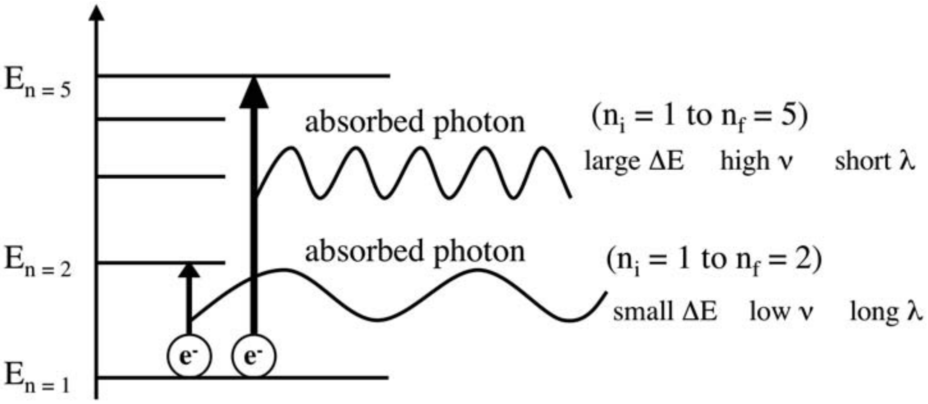
Once ν is calculated for n_i = 3, 4, 5, 6… use λ = c/ν to calculate λ.

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	____________________________
$n_f = 2$	**Balmer series**	**visible range**
$n_f = 3$	Paschen series	____________________________
$n_f = 4$	Brackett series	____________________________

A. PHOTON ABSORPTION



The frequency of the light absorbed can be calculated using:

$$\boxed{\nu = \frac{R_H}{h}\left(\frac{1}{\quad\quad} - \frac{1}{\quad\quad}\right)} \quad \text{For } n_f > n_i$$

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.

$n_f > n_i$ _______________ - Electrons absorb energy causing them to go from a lower to a higher E level.

$n_i > n_f$ _______________ - Electrons emit energy causing them to go from a higher to a lower E level.

Let's do an example using the Rydberg formula:

Calculate the wavelength of radiation emitted by a hydrogen atom when an electron makes a transition from the n=3 to the n=2 energy level.

$\nu =$ $\nu =$ $=$

From $\lambda\nu = c$,

$\lambda =$ _____ = ____________

$\lambda =$ ____ = ____________

The wavelength we solved for corresponds to the red line in the Balmer series. Light of this wavelength is emitted in the transition from n = 3 to n = 2. Light of this wavelength is absorbed in the transition of an electron from n = 2 to n =3.

III. WAVEFUNCTIONS (ORBITALS) FOR THE HYDROGEN ATOM

When solving $H\Psi = E\Psi$, the solutions are E_n and $\Psi(r,\theta,\phi)$.

$\Psi(r,\theta,\phi) \equiv$ stationary state wavefunction: time-independent
In solutions for $\Psi(r,\theta,\phi)$, two new quantum numbers appear! A total of 3 quantum numbers are needed to describe a wavefunction in 3D.

1. $n \equiv$ principal quantum number
   $n = 1, 2, 3 \ldots \ldots \infty$
   determines binding energy

2. $\ell \equiv$ angular momentum quantum number
   $\ell =$ ____
   ℓ is related to n
   largest value of $\ell = n - 1$
   determines angular momentum of e^-

3. $m \equiv$ magnetic quantum number
   $m \equiv$ ____
   m is related to ℓ
   largest value is $+\ell$, smallest is $-\ell$
   determines behavior of atom in magnetic field

5.111 Principles of Chemical Science
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