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5.111 Principles of Chemical Science
Fall 2008

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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 ($H\Psi = E\Psi$)

II. Verification of hydrogen-atom energy levels

A. Photon emission

B. Photon absorption

III. Wavefunctions (orbitals) for the hydrogen atom ($H\Psi = E\Psi$)

THE HYDROGEN ATOM

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

The Schrödinger equation for the H atom:

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

$$\hat{H}\Psi_n = -\frac{1}{n^2} \frac{me^4}{8\epsilon_0^2 h^2} \Psi_n$$

H atom orbital or wavefunction

$E_n \equiv$ binding energy of the electron to the nucleus

$m =$ _____ = _____

$e =$ _____

$\epsilon_0 =$ permittivity constant

$h =$ Planck's constant

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

$$\frac{me^4}{8\epsilon_0^2 h^2} = R_H = \text{Rydberg's constant} = \underline{\hspace{2cm}}$$

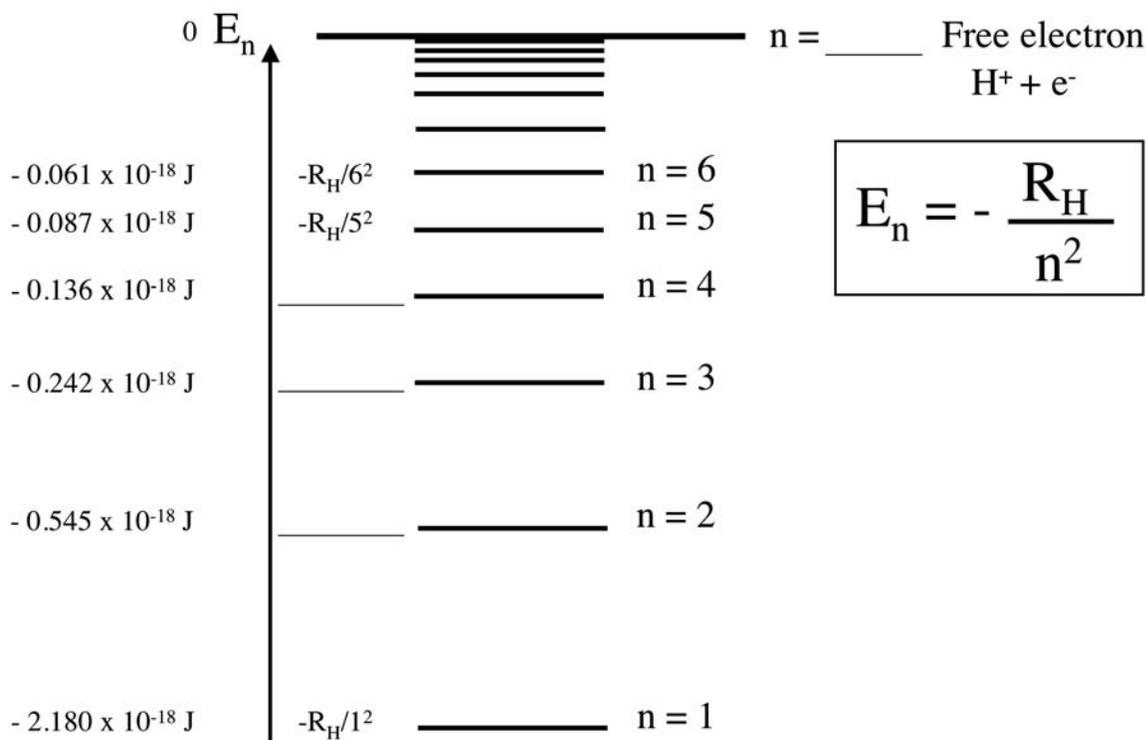
The **binding energy** (E_n) of the electron to the nucleus for the **hydrogen atom**:

$$E_n = -\frac{1}{n^2} \frac{me^4}{8\epsilon_0^2 h^2} = \frac{-R_H}{n^2}$$

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



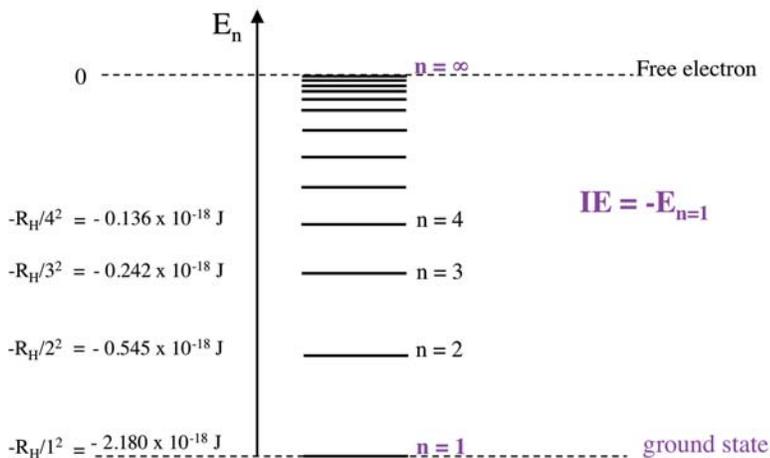
Note that all binding energies are negative. Negative energy means the electron is bound to the nucleus. At $n=\infty$, $E_n = 0$. At $n=\infty$, the e^- is free from the nucleus.

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 n^{th} 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):

$$E_n = \frac{-13.6 \text{ eV} Z^2}{n^2}$$

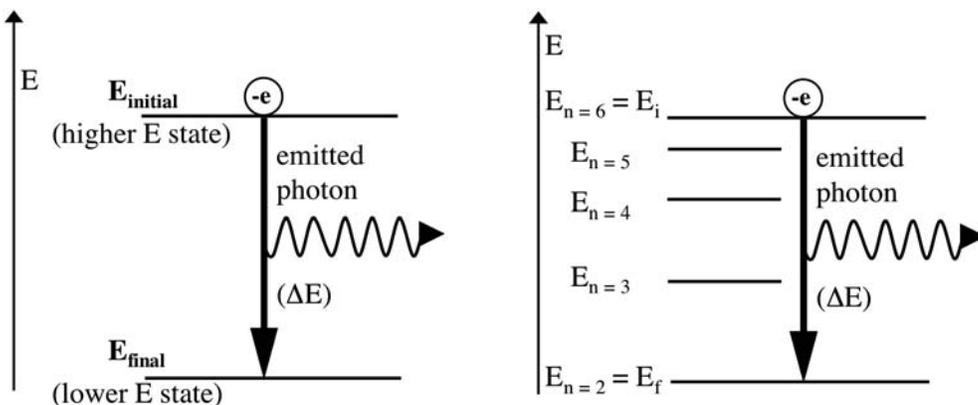
where Z = atomic number

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

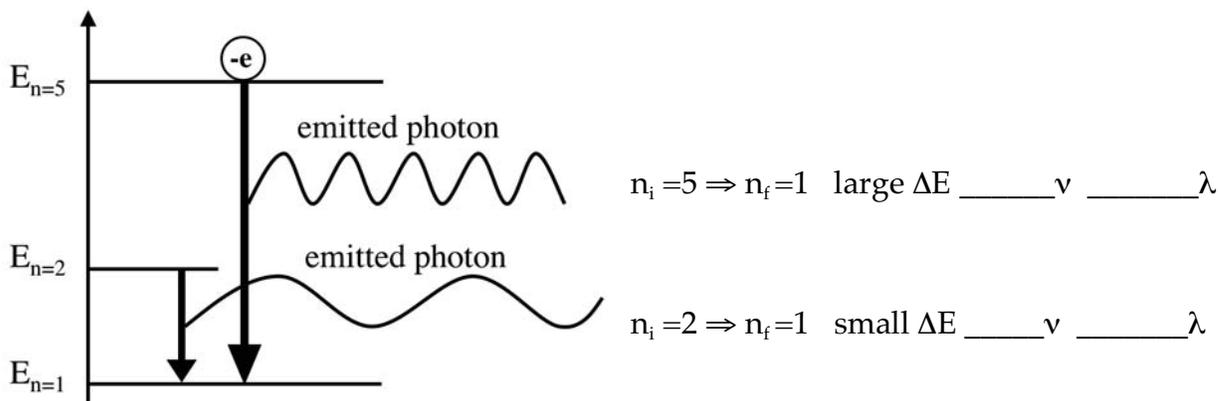
$$\Delta E = _ - _$$

$$\Delta E = _ - _$$

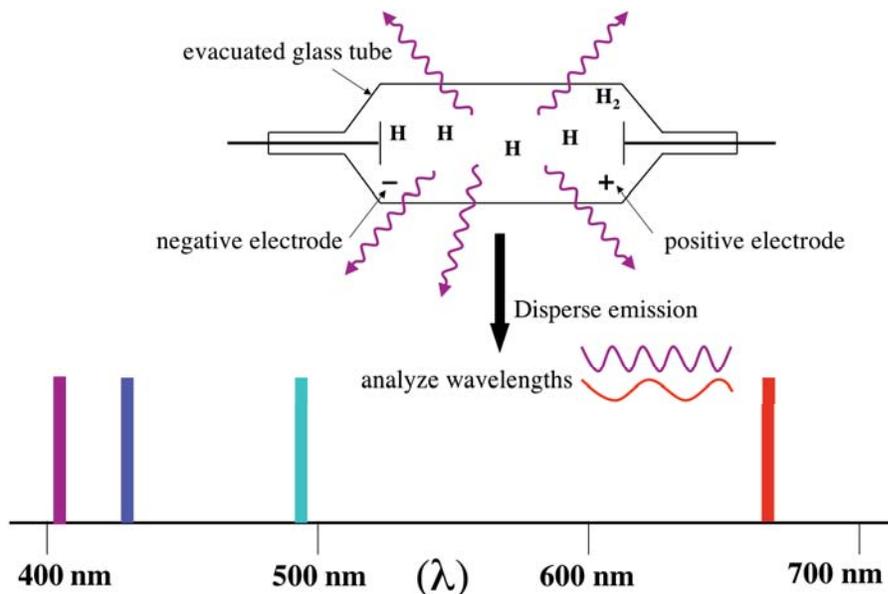
Since we can calculate the energy of the emitted photon, we can also calculate the frequency (ν) using $\Delta E = h\nu$.

$\nu = \underline{\hspace{2cm}}$ $\nu = \underline{\hspace{2cm}}$

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



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



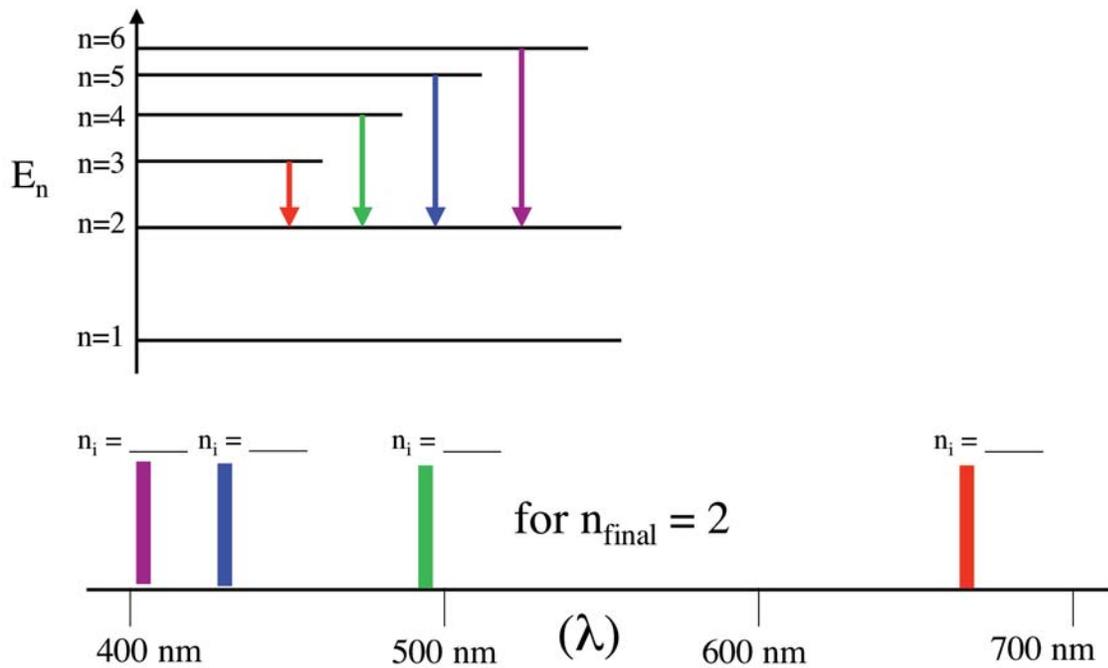
We are far from the first to observe these lines from atomic hydrogen!

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:

$$\nu = 3.29 \times 10^{15} \text{ s}^{-1} \left[\left(\frac{1}{4} \right) - \left(\frac{1}{n^2} \right) \right] \quad \text{where } n = 3, 4, 5 \dots$$

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

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For $n_f = 2$, then

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

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

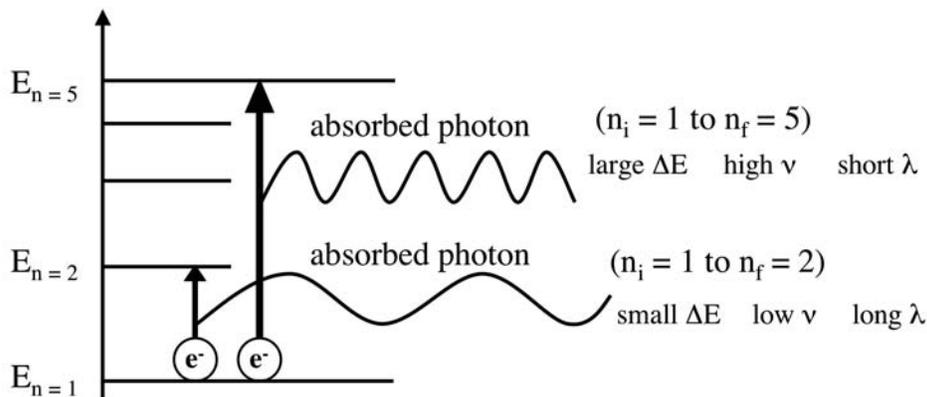
Once ν is calculated for $n_i = 3, 4, 5, 6 \dots$ use $\lambda = c/\nu$ to calculate λ .

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	_____
$n_f = 2$	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:

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

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.

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

From $\lambda\nu = c$,

$$\lambda = \underline{\quad} = \underline{\quad}$$

$$\lambda = \underline{\quad} = \underline{\quad}$$

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
 $n = 1, 2, 3 \dots \dots \infty$
determines binding energy

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

3. $m \equiv$ magnetic quantum number
 $m \equiv \underline{\hspace{2cm}}$
 m is related to ℓ
largest value is $+\ell$, smallest is $-\ell$
determines behavior of atom in magnetic field