Quantum Theory of the Hydrogen Atom

Chemistry 35

Fall 2000

Balmer and the Hydrogen Spectrum

- **1885**: Johann Balmer, a Swiss schoolteacher, *empirically* deduced a formula which predicted the wavelengths of emission for *Hydrogen*:

$$\lambda \text{ (in Å)} = 3645.6 \times \frac{n^2}{n^2 - 4} \quad \text{for } n = 3, 4, 5, 6$$

•Predicts the wavelengths of the 4 *visible* emission lines from Hydrogen (which are called the **Balmer Series**)

•Implies that there is some underlying *order* in the atom that results in this deceptively simple equation.

The Bohr Atom

- <u>**1913:**</u> Niels Bohr uses quantum theory to **explain** the origin of the line spectrum of hydrogen

1. The electron in a hydrogen atom can exist only in **discrete orbits**
2. The **orbits** are circular paths about the nucleus at varying **radii**
3. Each **orbit** corresponds to a particular **energy**
4. **Orbit** energies *increase* with *increasing* radii
5. The *lowest* energy **orbit** is called the <u>ground state</u>
6. After *absorbing* energy, the e^- jumps to a *higher energy* **orbit** (an <u>excited state</u>)
7. When the e^- drops down to a *lower energy* **orbit**, the energy lost can be given off as a *quantum of light*
8. The ***energy*** of the photon emitted is equal to the difference in energies of the two orbits involved

Mohr Bohr

- **Mathematically, Bohr equated the two forces acting on the orbiting electron**:

coulombic attraction = centrifugal accelleration

$$-(Z/4\pi\varepsilon_o)(e^2/r^2) = m(v^2/r)$$

- **Rearranging and making the *wild* assumption**:

$$mvr = n(h/2\pi)$$

  - e^- angular momentum can only have certain quantified values in whole multiples of $h/2\pi$

Hydrogen Energy Levels

- Based on this model, Bohr arrived at a simple equation to calculate the electron *energy levels* in hydrogen:

$$\boxed{\mathbf{E_n = -R_H(1/n^2)}} \quad \text{for } n = 1, 2, 3, 4, \; . \; . \; . \; .$$

<u>Where:</u>

$R_H = 2.179 \times 10^{-18}$ Joules (*the Rydberg constant)*

n is the *Principal Quantum Number*

<u>Radii can be calculated, too</u>:

$$\boxed{\mathbf{r_n = n^2 a_o}} \quad (a_o = 0.529 \text{ Å})$$

Transitions Between Energy Levels

- Now, the energy change associated with a *transition* between electron energy levels can be quantified:

$$\Delta E = E_{final} - E_{initial} = h\nu$$

$$h\nu = \frac{-R_H}{n^2_f} - \frac{-R_H}{n^2_i}$$

Collecting terms:

$$\boxed{\mathbf{\nu = (R_H/h)\ (1/n_i^2 \; - \; 1/n_f^2)}}$$

Bohr versus Balmer

- With some rearranging, the *Balmer* equation looks like this:

$$\nu = 3.29 \times 10^{15}\ s^{-1}\ (1/2^2\ -\ 1/n^2)$$

-This is the equation we just derived, but with n_f fixed at a value of 2

-So, the Bohr model also accurately predicts the frequencies of the *Balmer Series* emission lines

-BUT, it also predicts *other* emission lines (for n_f = 1, 3, 4, etc.)

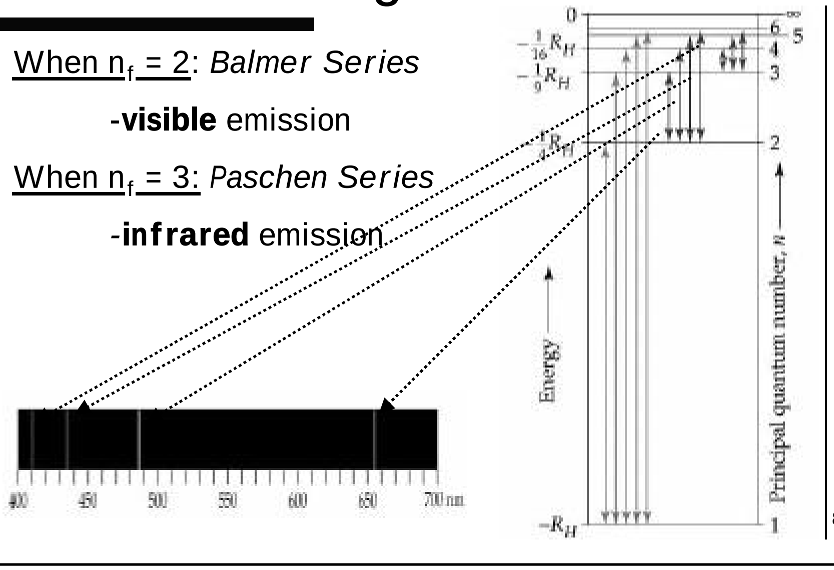
Hydrogen's Energy Level Diagram

When n_f = 2: *Balmer Series*

-**visible** emission

When n_f = 3: *Paschen Series*

-**infrared** emission



Sample Calculation

- Calculate the wavelength at which the *least energetic* emission spectral line of the **Lyman Series** ($n_f = 1$) is observed.

Lowest energy transition will be 2→1:

$$\Delta \mathbf{E} = (\mathbf{R_H})\ (\mathbf{1/2^2 - 1/1^2})$$

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

$$\Delta E = -1.63425 \times 10^{-18}\ J \quad \text{(energy lost by atom)}$$

Converting to wavelength:

$$\lambda = hc/\Delta E$$

$$= (6.626 \times 10^{-34}\ \mathrm{J\text{-}s})(2.9979 \times 10^{8}\ \mathrm{m/s})/(1.63425 \times 10^{-18}\ \mathrm{J})$$

$$= 1.215486 \times 10^{-7}\ \mathrm{m} = 121.549\ \mathrm{nm} \rightarrow \underline{\mathbf{121.5\ nm}}\ \text{(vac UV)}$$

Wave Properties of Matter

- **de Broglie:** "If EMR waves can act like *particles*, why not treat *matter* like a **wave**?"

Based on his hypothesis:

$$\boxed{\lambda = h/mv}$$

Characteristic wavelength of the object → λ

mv ← Momentum of object

RESULT: -macroscopic things have wavelengths that are *incredibly tiny* (10^{-30} m or so)

-sub-atomic sized things have wavelengths that are of the same order as their physical size (Å for an e-)!

The Uncertainty Principle

- German physicist Werner Heisenberg:

> *There are <u>limits</u> to which we can know both the **momentum** and the **location** of ANY object.*

<u>Quantitatively</u>: $(\Delta p)(\Delta x) \geq h/4\pi$

-so, the better we know the *position* of an object, the *worse* we know the *velocity* (p = mv) of the object

-not an issue in the macroscopic world, but the limitation is profound for objects like electrons!

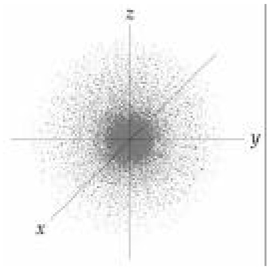
Quantum Mechanics

- 1926: Erwin Schrödinger describes electrons in an atom as having **both** wave and particle properties:

<u>The Schrödinger Wave Equation</u>!

<u>Results:</u>

- Solutions to the wave equation are called: <u>*wave functions*</u> (ψ)
- For hydrogen, get the same *electron energies* as Bohr did
- The square of the *wave function* (ψ^2) gives a <u>*probability density*</u> for an electron in a specified energy state
- The *probability densities* define what are called ***orbitals***



Lowest energy *orbital* for the hydrogen atom

Orbitals and Quantum Numbers

- Each solution to the wave equation can be *uniquely* specified by **three quantum numbers:**

1. **The Principal Quantum Number (n)**
   -can have *integer values* (1, 2, 3, 4, etc.)
   -corresponds to the principal energy level
   -same as the quantum number in Bohr's model
   -defines the *electron shell*
2. **The Azimuthal Quantum Number (l)**
   -can have *integer values* from **0 to n-1** for each value of n
   -defines the orbital shape
   -value of *l* determines the letter used to specify the orbital shape (*l= 0, 1, 2, 3* → **s, p, d, f orbitals**)
   -defines the *subshell*

More QN and Orbitals

3. **The Magnetic Quantum Number (m_l)**
   -can have integer values from *l ® -l*
   -describes the orientation of the orbital in space

So, some examples:

n=1: only one value of *l* possible (0) **1s orbital**
only one value of m_l possible (0)

n=2: *l = 0, 1* (s and p orbitals)
For **l = 1:** m_l = 1, 0, -1 (**$2p_x$, $2p_y$, $2p_z$ orbitals**)

n=3: *l = 0, 1, 2* (s, p and d orbitals)
For **l = 2**: m_l = 2, 1, 0, -1, -2 (**five 3d orbitals**)

Ammonia Fountain Demo

- The reaction:

$NH_3(g) \rightarrow NH_3(aq)$

-46.11 kJ/mol -80.20 kJ/mol

ΔH = (-80.20 kJ/mol) - (-46.11 kJ/mol) = ***-34.18 KJ***

n = PV/RT = (1.0 atm)(2.0 L)/(0.08206)(298.15 K) = ***8.17 x 10^{-2} mol***

PV work = ΔnRT = ***200 J***

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Orbital Energies

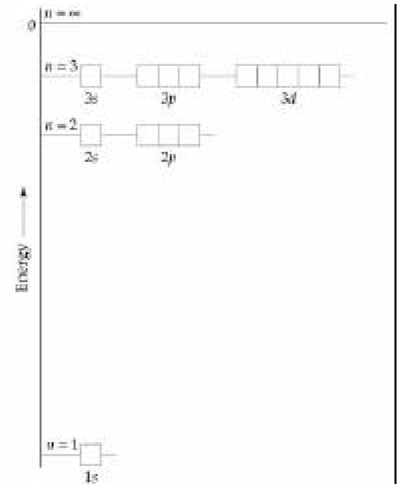
For Hydrogen:

-energies vary with ***n***

-same result as with Bohr

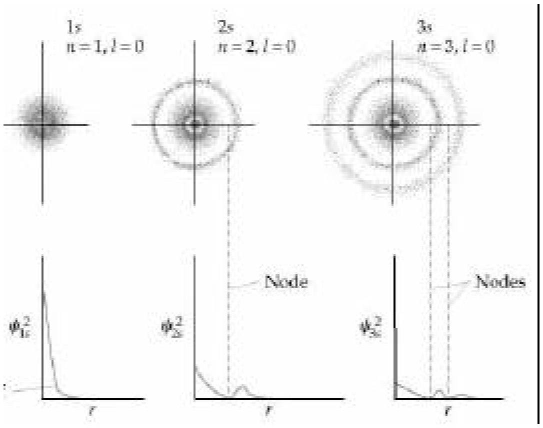
$$E_n = \frac{-(e^4 m_e)Z^2}{(8\varepsilon_o h^2)n^2} = \frac{-R_H Z^2}{n^2}$$

-also applies to other *one-electron* systems



Orbital Shapes: s-orbitals

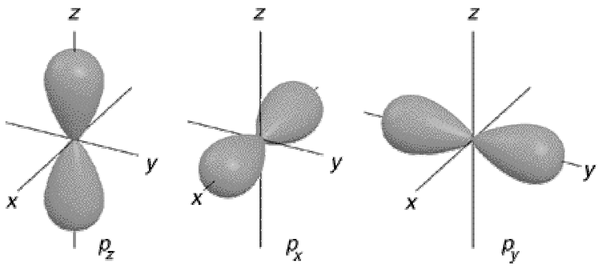
- All s-orbitals are *spherical* but have different *radial* probability distributions:



•S-orbitals have *n-1* radial nodes

•As n increases, so does the orbital size

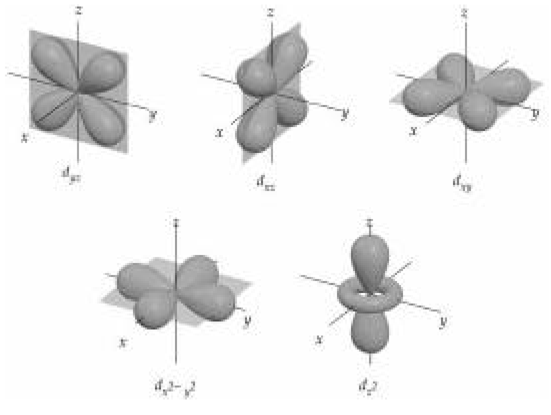
Orbital Shapes: p-orbitals



- p-orbitals are “dumbell” shaped
- Subscripts indicate primary orientation axis
- Nodal plane at nucleus
- As n increases, the size of the p-orbitals increases

Orbital Shapes: d-orbitals

- Three “4-leaf clover” shapes in three planes (xy, xz, yz) oriented *between* the axes
- One “4-leaf clover” shape in xy plane oriented *along* the axes
- One dumbell shape with a doughnut in xy plane



I’m not making this up . . . really!