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

1913: 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 ground state
6. After absorbing energy, the e- jumps to a higher energy orbit (an excited state)
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:

\[
\text{coulombic attraction} = \text{centrifugal acceleration} = \frac{Z}{4\pi \varepsilon_0} \left(\frac{e^2}{r^2}\right) = m\left(\frac{v^2}{r}\right)
\]

Rearranging and making the wild assumption:

\[
mvr = n\left(\frac{h}{2\pi}\right)
\]

- 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:

\[ E_n = -R_H \left( \frac{1}{n^2} \right) \text{ for } n = 1, 2, 3, 4, \ldots \]

Where:

\[ R_H = 2.179 \times 10^{-18} \text{ Joules (the Rydberg constant)} \]

\( n \) is the Principal Quantum Number

Radii can be calculated, too:

\[ r_n = n^2 a_o \]

\( a_o = 0.529 \text{ Å} \)

Transitions Between Energy Levels

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

\[ \Delta E = E_{\text{final}} - E_{\text{initial}} = h\nu \]

\[ h\nu = \frac{-R_H}{n_i^2} - \frac{-R_H}{n_f^2} \]

Collecting terms:

\[ \nu = \left( \frac{R_H}{h} \right) (1/n_i^2 - 1/n_f^2) \]
Bohr versus Balmer

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

\[ \nu = 3.29 \times 10^{15} \text{s}^{-1} \left( \frac{1}{2^2} - \frac{1}{n^2} \right) \]

- 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 \( n_f = 1, 3, 4, \text{etc.} \))

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:

\[ \Delta E = (R_H) \left( \frac{1}{2^2} - \frac{1}{1^2} \right) \]
\[ \Delta E = (2.179 \times 10^{-18} \text{ J})(\frac{1}{4} - 1) \]
\[ \Delta E = -1.63425 \times 10^{-18} \text{ J} \] (energy lost by atom)

Converting to wavelength:

\[ \lambda = \frac{hc}{\Delta E} \]
\[ = \frac{(6.626 \times 10^{-34} \text{ J-s})(2.9979 \times 10^8 \text{ m/s})}{(1.63425 \times 10^{-18} \text{ J})} \]
\[ = 1.215486 \times 10^{-7} \text{ m} = 121.549 \text{ nm} \] → 121.5 nm (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:

\[ \lambda = \frac{h}{mv} \]

Characteristic wavelength of the object

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 limits to which we can know both the momentum and the location of ANY object.

Quantitatively: \((\Delta p)(\Delta x) \geq h/4\pi\)

- 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:

  The Schrödinger Wave Equation!

Results:

- Solutions to the wave equation are called: wave functions \((\psi)\)
- For hydrogen, get the same electron energies as Bohr did
- The square of the wave function \((\psi^2)\) gives a probability density 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 \( (1, 2, 3, 4, \text{ etc.}) \)
   - 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 \((l = 0, 1, 2, 3 \rightarrow s, p, d, f \text{ orbitals})\)
   - defines the subshell

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

So, some examples:

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

\( n=2 \):
- \( l = 0, 1 \) (s and p orbitals)
  - For \( l = 1 \): \( m_l = 1, 0, -1 \) \( (2p_x, 2p_y, 2p_z \text{ orbitals}) \)

\( n=3 \):
- \( l = 0, 1, 2 \) (s, p and d orbitals)
  - For \( l = 2 \): \( m_l = 2, 1, 0, -1, -2 \) (five \( 3d \text{ orbitals} \))
Ammonia Fountain Demo

- The reaction:
  \[ \text{NH}_3(g) \rightarrow \text{NH}_3(aq) \]
  -46.11 kJ/mol  -80.20 kJ/mol

\[ \Delta H = (-80.20 \text{ kJ/mol}) - (-46.11 \text{ kJ/mol}) = -34.18 \text{ KJ} \]

\[ n = \frac{PV}{RT} = \frac{(1.0 \text{ atm})(2.0 \text{ L})}{(0.08206)(298.15 \text{ K})} = 8.17 \times 10^{-2} \text{ mol} \]

PV work = \( nRT = 200 \text{ J} \)

More QN and Orbitals

3. The Magnetic Quantum Number (\( m_l \))
   - can have integer values from \(-l\) to \(l\)
   - 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)
Orbital Energies

For Hydrogen:
- energies vary with \( n \)
- same result as with Bohr

\[
E_n = -\frac{(e^4 m_e Z^2)}{(8\epsilon \hbar^2)n^2} = -R_H Z^2 n^2
\]

- 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 "dumbbell" 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!