

# ELECTRONIC STRUCTURE OF ATOMS

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## Quantum Theory

1. Atoms and molecules can only exist in certain states characterized by definite amounts of energy. When an atom or molecule changes its state, it **absorbs** or **emits** an amount of energy (electromagnetic radiation) just sufficient to bring it to another state.

## Electronic energy

- form of energy that arises from the **motion** of  $e^-$  about the nucleus, and from the **interactions** among the  $e^-$  and between the  $e^-$  and the nucleus.
  - only *certain values* of electronic energy are allowed for an atom
  - said to be **quantized**
  - a change of electronic energy level (state) of an atom involves the **absorption** or **emission** of a definite amount, quantum, of energy
  - lowest electronic energy state is called the **ground state**
  - any state with energy greater than that of the ground state is an **excited state**
2. When atoms or molecules absorb or emit light in moving from one energy state to another, the wavelength of the light is related to the energies of the two states by the equation

$$E_{\text{final}} - E_{\text{initial}} = hc/\lambda$$

**h = Planck's constant**

**c = speed of light**

- ray of light can be considered to consist of **photons**
- each photon of wavelength has an energy of  **$hc/\lambda$**
- an atom or molecule can move from one electronic energy state to another by **absorbing** or **emitting** a **photon** of energy
- if it **absorbs** a photon of energy,  **$hc/\lambda$** , it moves from a **lower to a higher** energy state, and its energy **increases** by  **$hc/\lambda$**

$$\text{therefore: } \Delta E = E_{\text{final}} - E_{\text{initial}} = E_{\text{hi}} - E_{\text{lo}} = hc/\lambda$$

3. The allowed energy states of atoms and molecules can be described by sets of numbers called quantum numbers
    - quantum numbers are associated with individual electrons in an atom.
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## Relation between Energy difference, $\Delta E$ , and wavelength.

- wavelength is **inversely** related to the energy difference,  $\Delta E$ 
  - a large  $\Delta E$ ---short wavelength.....<400 nm--ultraviolet
  - a small  $\Delta E$ ---long wavelength.....>700 nm--infrared
- $e^-$  moves from one energy state to another by absorbing or emitting radiation of a particular wavelength.
- by measuring the wavelength associated with  $e^-$  transition, we can find  $\Delta E$  of the two energy states involved

$$h = 6.626 \times 10^{-34} \text{ J} \cdot \text{s/ particle}$$

$$c = 2.998 \times 10^8 \text{ m/s}$$

$\Delta E$  is in J/particle when wavelength is in meters

Ordinarily:  $\Delta E$  is in kJ/mol, and wavelength is in nm

$$1 \text{ mole} = 6.02 \times 10^{23} \text{ particles}$$

$$1 \text{ kJ} = 10^3 \text{ J}$$

$$1 \text{ nm} = 10^{-9} \text{ m}$$

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## Relation between wavelength and frequency:

- frequency, represented by the Greek letter  $\nu$  (nu), is the number of wavecycles that pass a given point in a unit time ( 1 cycle per second is equal to 1 Hertz (Hz) )
- ex.  $10^8$  cycles per second =  $10^8 /s = 10^8$  Hertz
- the velocity at which a wave moves can be found by multiplying the length of a wave,  $\lambda$ , by the number of cycles passing a point in unit time,  $\nu$
- $c = \lambda \nu$
- $\nu = c / \lambda$

frequency is inversely related to wavelength

For example:

Blue light, at a wavelength of 450 nm, has a higher frequency than red light with a wavelength of 650 nm.

- blue**.....frequency =  $c/450 \text{ nm} = 6.66 \times 10^{14}/s$
- red**.....frequency =  $c/650 \text{ nm} = 4.61 \times 10^{14}/s$

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- $\Delta E$  is directly proportional to the frequency of the light absorbed or emitted
- if  $\Delta E$  is large, the light will have a high frequency
- if  $\Delta E$  is small, the light will have a low frequency

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## The Atomic Spectrum of Hydrogen and the Bohr Model

1911 – Niels Bohr, Danish physicist

- developed mathematical model for the behavior of an  $e^-$  in the hydrogen atom
- based: on the Rutherford atom & quantum theory of Planck

**spectroscope** – instrument that breaks up light into its component colors

- continuous – contains all the colors (such as in white light)
- sodium vapor lamps, neon signs: the light given off looks different
  - spectrum not continuous
  - the light consists of several discrete colors which appear as lines of definite wavelength when seen in a spectroscope
  - each element has its own characteristic spectrum

Hydrogen most studied because it is the simplest with only 1  $e^-$

- several series of lines representing electronic transitions
  - Lyman series (ultraviolet)
  - Balmer series (visible)
  - Paschen series (infrared)
- Bohr's ideas about H atom
  - central proton
  - single  $e^-$  moves around the  $p^+$  in a circular orbit
  - force of attraction of the proton for the  $e^-$  related to the circular motion of the  $e^-$  expressed energy of  $e^-$  in terms of the radius of the orbit
  - combined classical Newtonian Laws of Motion and Coulomb's Law of Electrostatic Attraction with Quantum Theory

angular momentum =  $mvr$

$m$  = mass

$v$  = velocity (speed)

$r$  = radius of its orbit around the nucleus

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$$mvr = nh/2\pi$$

h = Planck's constant

n = a quantum number that can have any positive integral value (1,2,3...)

- **According to Bohr**

angular momentum is quantized (i.e. cannot have just any value)  
restricted to values for which "n" is a positive integer (2, h, and  $\pi$  are constants)  
thus angular momentum can change only by discrete amounts (i.e. integral multiples of  $h/2\pi$ )

- Also, Bohr found the allowed energies are restricted

The energy of an energy level is given by the equation:

$$E = -B/n^2 \text{ (where } n = 1, 2, 3\dots) \text{ and } B = 2.179 \times 10^{-18} \text{ J/particle}$$

$$E = -2.179 \times 10^{-18} \text{ J/particle}/n^2 = -1312 \text{ kJ/mol}/n^2$$

### 3 Points to keep in mind:

1. **zero energy** – the point at which the proton and  $e^-$  are completely separated

energy had to be absorbed to reach that point  $e^-$  in all its energy states within the atom must have energy below zero, i.e. must be negative

2. the normal H atom; the  $e^-$  is in the ground state when  $n = 1$ . When the  $e^-$  absorbs energy it moves to a higher excited state.

$n = 2$  (1st excited state),  $n = 3$  (2nd excited state, etc.)

3. when an excited  $e^-$  gives off energy in the form of light, it drops back to a lower energy state

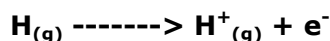
if  $e^-$  returns to ground state ( $n = 1$ ): **Lyman series** ( $n = 2$  to  $n = 1$ ,  $n = 3$  to  $n = 1$ , etc.)

if  $e^-$  returns to the first excited state : **Balmer series** ( $n = 3, 4, \dots$  to  $n = 2$ )

if  $e^-$  has a transition back to  $n = 3$ : **Paschen series**

### Example

ionization energy of the H atom can be calculated from the Bohr model



$\Delta E$  = ionization energy

$$\Delta E = 0 - (-1312 \text{ kJ/mol}) = 1312 \text{ kJ/mol}$$

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## Quantum Mechanical Atom

- Bohr's model was great for the H atom (error of .1%); however, even with the error increased to 5%

### Wave Nature of the Electron:

- **deBroglie**: suggested that particles might exhibit wave properties

$$\text{wavelength} = h/mv$$

m = mass

v = speed

$$2\pi r = v\lambda$$

$$mvr = h v/2\pi$$

- big question arises – how does one specify the position of a wave at a particular instant?
- can determine wavelength, energy, amplitude – but no way to tell just where the electron is because a wave extends over space
- Quantum mechanics was developed to describe the motion of small particles confined to very small portions of space.
- deals with the probability of finding a particle within a given region of space
- Schrodinger derived an equation from which one could calculate the amplitude (height)  $\Psi$  of an electron wave at various points in space.
- Several expressions for  $\Psi$  that will satisfy the equation. Each is associated with a set of quantum numbers.
- Becomes possible to determine the probability of finding a particle in a given region of space.
- $\Psi^2$  proportional to the probability of finding the particle at that point
- $\Psi^2$  proportional to the electron charge density at that point