CHM 403: Quantum Chemistry

- ❖ **Bohr model of atomic spectral of hydrogen**
- ❖ Heisenberg uncertainty principle
- ❖ Quantum Numbers

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BOHR MODEL OF ATOMIC SPECTRAL OF HYDROGEN

Bohr postulated that:

- Electrons travel around the nucleus in specific permitted circular orbitals and in no order.
- An electron does not radiate nor absorbed energy if it stays in one orbit, and therefore do not slow down.
- When an electron moved from one orbit to another, it either radiates or absorbs energy. If it moves towards the nucleus, energy is radiated and if it moves away from the nucleus, energy is absorbed.

•For an electron to remain in its orbit, the electrostatic attraction between the electron and the nucleus which tends to pull the electron towards the nucleus must be equal to the centrifugal force which tends to throw the electron out of its orbit.

Consider an electron of charge ‘e’ revolving around a nucleus of charge ‘Ze’ where ‘Z’ is the atomic number and ‘e’ is the charge on a proton. Let ‘m’ be the mass of the electron, ‘r’ the radius of the orbit and ‘v’ the tangential velocity of the revolving electron.

The electrostatic force of attraction between the nucleus and the electron:

$$= \frac{Ze^2}{r^2} \qquad (1)$$

The centrifugal force acting on the electron

$$= \frac{mv^2}{r} \qquad (2)$$

According to the fourth postulate;

Centrifugal force = electrostatic force i.e

$$\frac{Ze^2}{r^2} = \frac{mv^2}{r} \qquad (3)$$

For hydrogen, Z =1

Therefore, $$\frac{e^2}{r^2} = \frac{mv^2}{r} \qquad (4)$$

Multiply both sides by r

$$\frac{e^2}{r} = mv^2 \qquad (5)$$

According to Planck’s quantum theory, quanta magnitude = h/2π, where h is Planck’s constant.

Angular momentum (mvr) must be equal to an integral multiples ‘n’ of quanta i.e $\frac{nh}{2\pi}$

Thus, $mvr = \frac{nh}{2\pi}$ (6)

$$v = \frac{nh}{2\pi mr} \quad (7)$$

Squaring both side

$$v^2 = \frac{n^2 h^2}{4\pi^2 m^2 r^2} \quad (8)$$

Substituting the values of v^2 in equation (8) into (5),

$$\frac{e^2}{r} = \frac{mn^2 h^2}{4\pi^2 m r^2}$$

$$r = \frac{n^2 h^2}{4\pi^2 m e^2} \quad (9)$$

This is called the radius of any orbit.

If h = 6.63 x 10^{-27}ergs, π = 3.14, m = 9.1 x 10^{-28}g, e = 4.8 x 10^{-10} esu, n = 1-5, the values of the first five Bohr radii can be calculated.

Example: calculate the first five Bohr orbit i.e when n = 1 …., n =5

ENERGY OF ELECTRON IN EACH ORBIT

For hydrogen atom, the energy of the revolving electron, E is the sum of its kinetic energy ($\frac{1}{2}mv^2$) and potential energy ($-\frac{e^2}{r}$)

$$E = \frac{1}{2}mv^2 + (-\frac{e^2}{r})$$

$$E = \frac{1}{2}mv^2 - \frac{e^2}{r} \qquad (10)$$

From equation (5), $mv^2 = \frac{e^2}{r}$

Substituting the values of mv^2 in equation (5) into (10)

$$E = \tfrac{1}{2}\left(\frac{e^2}{r}\right) - \frac{e^2}{r}$$

$$E = -\frac{e^2}{2r} \qquad (11)$$

Substitute the value of r from equation (9) into 11

$$E = -\frac{e^2}{2} x \frac{4\pi^2 me^2}{n^2 h^2}$$

$$E = -\frac{2\pi^2 me^4}{n^2 h^2} \qquad (12)$$

If h = 6.63 x 10^{-27}ergs, π = 3.14, m = 9.1 x 10^{-28}g, e = 4.8 x 10^{-10} esu, n = 1-5, the values of energy in each orbit can be calculated.

Calculate the five lowest energy levels of the hydrogen atom.

The value of energy of electron in orbit n_1 (lowest) and n_2 (higher) is

$$E_{n1} = \frac{-2\pi^2 me^4}{n_1^2 h^2} \quad \text{and} \quad E_{n2} = \frac{-2\pi^2 me^4}{n_2^2 h^2}$$

The difference of energy between the levels n_1 and n_2 is :

$$\Delta E = E_{n2} - E_{n1} = \frac{2\pi^2 me^4}{h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \qquad (13)$$

According to Planck's equation,

$$\Delta E = hv = \frac{hc}{\lambda} \quad \text{and} \quad \frac{1}{\lambda} = \frac{\Delta E}{hc} \qquad (14)$$

Where λ is the wavelength of the photon and c is the velocity of light.

From equations (13) and (14),

$$\Delta E = h\nu = \frac{hc}{\lambda} = \frac{2\pi^2 me^4}{h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$\frac{1}{\lambda} = \frac{2\pi^2 me^4}{h^3 c}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \qquad (15)$$

If $\quad R = \dfrac{2\pi^2 me^4}{h^3 c}$

$$\frac{1}{\lambda} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \qquad (16)$$

Where R is the Rydberg constant and equation (16) is called Rydberg equation.

Note that 1A^o = 10^{-8} cm = 10^{-10} m or 1 cm = 10^8 A^o and 1m = 10 A^o ,

1 nm = 10^{-9} m

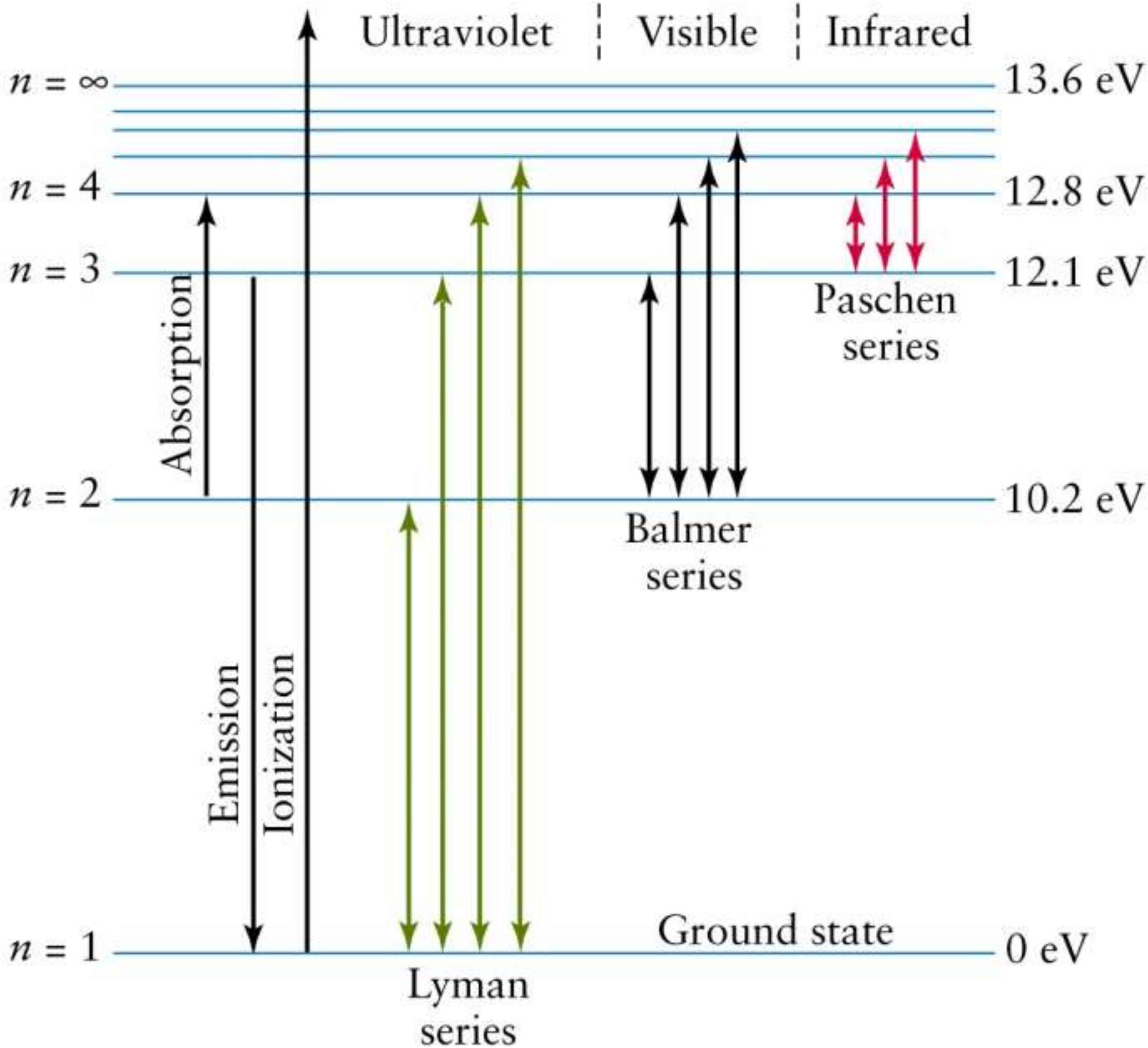
Atomic Spectroscopy

Absorption or Emission

$$\frac{1}{\lambda_{\mathrm{vac}}} = R_{\mathrm{H}} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

Johannes Rydberg 1888
Swedish

$n_1 \rightarrow n_2$	name	Converges to (nm)
1 → ∞	Lyman	91
2 → ∞	Balmer	365
3 → ∞	Pashen	821
4 → ∞	Brackett	1459
5 → ∞	Pfund	2280
6 → ∞	Humphreys	3283


Ultraviolet
Visible
Infrared
n = ∞
13.6 eV
n = 4
12.8 eV
n = 3
12.1 eV
Paschen series
Absorption
n = 2
10.2 eV
Balmer series
Emission
Ionization
Ground state
n = 1
0 eV
Lyman series

Example 1: Find the wave number, wavelength, frequency and the energy change in A° of the line in Balmer series that is associated with the drop of an electron from the fourth orbit. The value of Rydberg constant is 109,676 cm^{-1}; velocity of light is 3.0 x 10^{8} m and h is 6.63 x 10^{-27}.

Solutions

i) $$\bar{V} = R(\frac{1}{n_1^2} - \frac{1}{n_2^2})$$

$$= 109676(\frac{1}{2^2} - \frac{1}{4^2})$$

$$= 2.0564 \times 10^{-4}$$

ii) $\lambda = \overline{V}$

$$\lambda = 1/2.0564x10^{-4}$$

$= 4.86 \text{ x } 10^{-5} \text{ cm}^{-1}$

iii) $v = {}^{c}\!/\!{}_{\lambda}$

$$v = \frac{3.0x10^{8}}{4.86x10^{-5}}$$

$= 6.172 \text{ x } 10^{14} \text{ S}^{-1}$

iv) $\Delta E = hv = 6.63x10^{-27}\,x6.172x10^{14}$

$= 4.147 \text{ x } 10^{-12} \text{ erg}$

Example 2: The wavelength of a violet light is 400 nm. Calculate its frequency and wave number.

Solution

$$v = {}^{c}\!/_{\lambda}$$

, c = 3.0 x 108 m/s and λ = 400 x 10^{-9}

$$v = {}^{3.0x10^{8}}\!/_{400x10^{-9}} \;;\quad v = 7.5x10^{14}\,\sec^{-1}$$

$$\bar{v} = \frac{1}{\lambda} = \frac{1}{400x10^{-9}} = 2.5x10^{5}\,m^{-1}$$

Example 3: The frequency of string yellow line in a spectrum of sodium is 5.09 x 10^{14} sec^{-1}. Calculate the wavelength of the light in nanometers. Ans = 589 nm i.e 1 nm = 10^{-9} m

The Heisenberg's uncertainty principle

Quantum mechanics shows that position of a particle and its momentum can be known only within certain limits.

The uncertainty principle states that in simultaneous determination of the position and momentum of a particle, the product of the uncertainties in equal to or greater than the Planck's constant i.e

$$\Delta p.\Delta q \geq \frac{h}{2\pi}$$

Where is Δp the uncertainty in the determination of momentum and Δq is the uncertainty in the determination of position

• In the example of a free particle, we see that if its momentum is completely specified, then its position is completely unspecified. **Thus if the momentum of the particle is measured very accurately, a measurement of the position of the particle becomes less precise.**

• When the momentum p is completely specified we write:

$$\Delta p = 0 \quad (\text{because:} \quad \Delta p = p_1 - p_2 = 0)$$

and when the position *x or q* is completely unspecified we write:

$$\Delta x \rightarrow \infty$$

• In general, we always have: $\Delta x \cdot \Delta p \geq$ a constant

This constant is known as:

(called *h-bar*) ⟵ $\hbar = \dfrac{h}{2\pi}$

h is the Planck's constant

$$(h = 6.625 \times 10^{-34}\, J.s)$$

Wave-Particle Duality

Particle-like wave behavior
(example, photoelectric effect)

Wave-like particle behavior
(example, Davisson-Germer experiment)

Wave-particle duality

Mathematical descriptions:

The momentum of a photon is: $$p = \frac{h}{\lambda}$$

The wavelength of a particle is: $$\lambda = \frac{h}{p}$$

λ is called the *de Broglie wavelength*

So we can write: $\Delta x \cdot \Delta p \geq \hbar$

That is the **Heisenberg's uncertainty principle**

" it is impossible to know simultaneously and with exactness both the position and the momentum of the fundamental particles"

N.B.: • We also have for the particle moving in three dimensions

$$\Delta x \cdot \Delta p_x \geq \hbar \qquad \Delta y \cdot \Delta p_y \geq \hbar \qquad \Delta z \cdot \Delta p_z \geq \hbar$$

• With the definition of the constant $\hbar : \dfrac{h}{2\pi}$

$$p = h / \lambda = hK / 2\pi \longrightarrow p = \hbar K$$

• Uncertainty for energy :

$$\Delta E \cdot \Delta t \geq \hbar$$

PROBLEM 3

An electron is moving along *x* axis with the speed of 2.05×10^{6} m/s (known with a precision of 0.50%).

What is the minimum uncertainty with which we can simultaneously measure the position of the electron along the *x* axis? Given the mass of an electron 9.1×10^{-31} kg

SOLUTION

From the uncertainty principle: $\Delta x \cdot \Delta p \geq \hbar$

if we want to have the minimum uncertainty: $\Delta x \cdot \Delta p = \hbar$

We evaluate the momentum: $p = mv = (9.1\times10^{-31})\times(2.05\times10^{6})$

$$p = 9.35\times10^{-27}\, kg.m/s$$

$$\Rightarrow \quad \Delta x = \frac{\hbar}{\Delta p} = \frac{6.635\times10^{-34}/2\pi}{9.35\times10^{-27}} = 1.13\times10^{-8}\, m \approx 11 nm$$

Example 4: Calculate the uncertainty in the position of an electron if the uncertainty in velocity is 5.7x105sec^{-1} (h = 6.6 x 10^{-34}kgm^{2}/s, m = 9.1x10^{-31}kg)

solution

$$\Delta p.\Delta q \geq \frac{h}{2\pi}$$ but $$\Delta p = mx\Delta v$$

$$mx\Delta vx\Delta q = \frac{h}{2\pi}$$

$$\Delta q = \frac{6.6x10^{-34}}{2x3.14x9.1x10^{-31}x5.7x10^{5}} = 2.025x10^{-20}m$$

Example 5: The uncertainty in the position and velocity of a particle are 10^{-10} m and 5.27x10^{-24} m/s respectively. Calculate the mass of the particle (h = 6.6x10^{-34}kgm^{2}/s). Ans = 1.99 x 10^{-1} kg

QUANTUM NUMBERS

- Numbers that describe the energies of electrons in atoms
- Specify the properties of atomic orbitals and the properties of electrons in orbitals
- Think of the quantum numbers as addresses/descriptions for electrons

INTRO TO THE FOUR QUANTUM NUMBERS

- Principal Quantum Number (n)
- Angular Momentum Quantum Number (l)
- Magnetic Quantum Number (m_l)
- Spin Quantum Number (s)

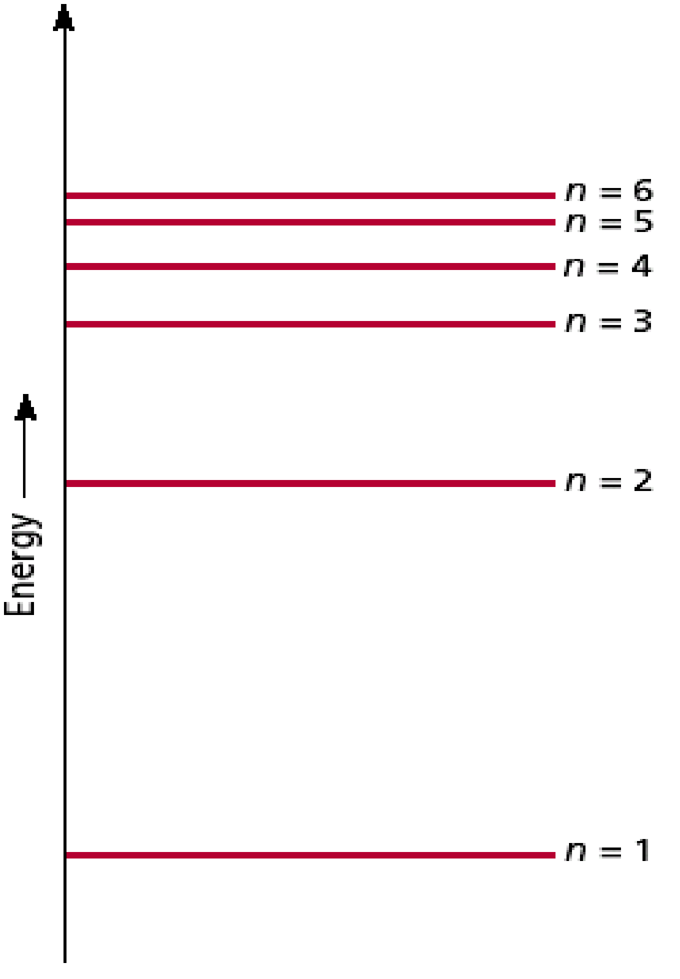
PRINCIPAL QUANTUM NUMBER

- Electron Cloud Size (*n*)
- Indicates the **main energy level** occupied by the electron
- Can take on integer values *n = 1, 2, 3,….*
- Largely determine the energy of the orbital (bigger *n* value = higher energy)
- All electrons in an atom with the same value of *n* belong to the same shell/level

PRINCIPAL QUANTUM NUMBER . . .

- Spectroscopists use the following names for shell

n	***Shell Name***	*n*	***Shell Name***
1	K	5	O
2	L	6	P
3	M	7	Q
4	N		



ANGULAR MOMENTUM QUANTUM NUMBER

- Shape of Electron Cloud (*l*)
- Also known as ***sublevel*** **or** ***subshell***
- Indicates the shape of the orbital within a shell
- Only integer values between *0* and *n-1* are allowed
- Affects orbital energies (bigger l = higher energy)
- All electrons in an atom with the same value of l are said to belong to the same subshell
- Sometimes called the orbital **azimuthal quantum** number

ANGULAR MOMENTUM QUANTUM NUMBER . . .

- Spectroscopists use the following notation for subshells

l	***Subshell Name***
0	s (sharp)
1	p (principal)
2	d (diffuse)
3	f (fundamental)

MAGNETIC QUANTUM NUMBER

- Orientation in space of orbitals (m_l)
- Determines the orientation of orbitals within a subshell
- Does not affect orbital energy (except in magnetic fields!)
- Only integer values between **–l and +l** are allowed
- The number of m_l values within a subshell equals the number of orbitals within a subshell (WRITE:each orbital holds up to 2e-)

MAGNETIC QUANTUM NUMBER . . .

- Number of m_l values determines the number of orbitals in a subshell (between **–l and +l)**

l	***Possible values of m_l***	***# orbitals in the subshell***
0 *(s)*	0	1
1 *(p)*	-1,0,+1	3
2 *(d)*	-2,-1,0,+1,+2	5
3 *(f)*	-3,-2,-1,0,+1,+2,+3	7

a. If $l = 0$, m_l can equal 0
b. If $l = 1$, m_l can equal –1, 0, +1
c. If $l = 2$, m_l can equal –2, -1, 0, +1, +2
d. If $l = 3$, m_l can equal –3, -2, -1, 0, +1, +2, +3

4. *Spin Quantum Number* – m_s – this number describes the direction of spin of the electron in the orbital – electrons in the same level and sublevel must spin in opposite directions. This can have a value of +1/2 or –1/2 only.

Electron Configuration & Quantum Numbers

N: $1s^2 2s^2 2p^3$

n =2

l = 1

m_l=+1

s=+1/2

n =1

l = 0

fg

m_l=0

s =-1/2