Quantum Chemistry

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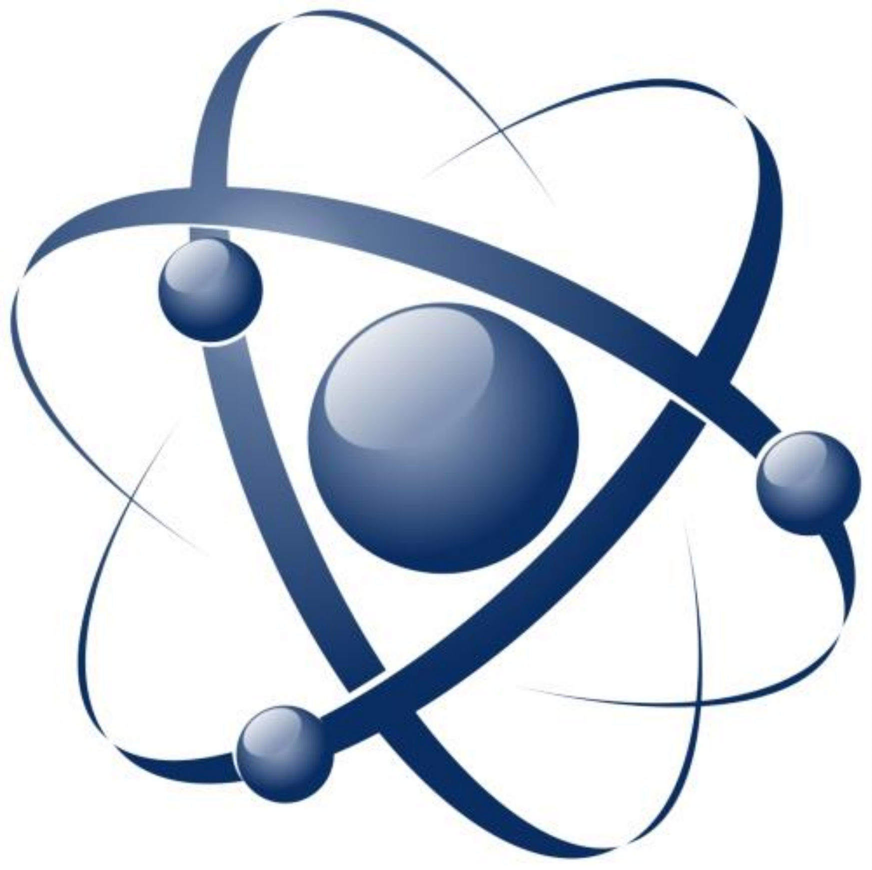

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By

Rabah Ali Khalil

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Chapter One

A Simple Approach to Quantum Chemistry

Outline

The Definition of Quantum Chemistry

Quantum chemistry *is the* ***branch of chemistry*** *that concerning with* ***the application of quantum mechanics*** *for* ***solving chemical problems*** *such as :*

- *electronic structure*
- *atomic and molecular structure,*
- *Spectroscopy*

Quantum mechanics *which may be defined as*
a mathematical system which has been presented by three different ways with similar results.

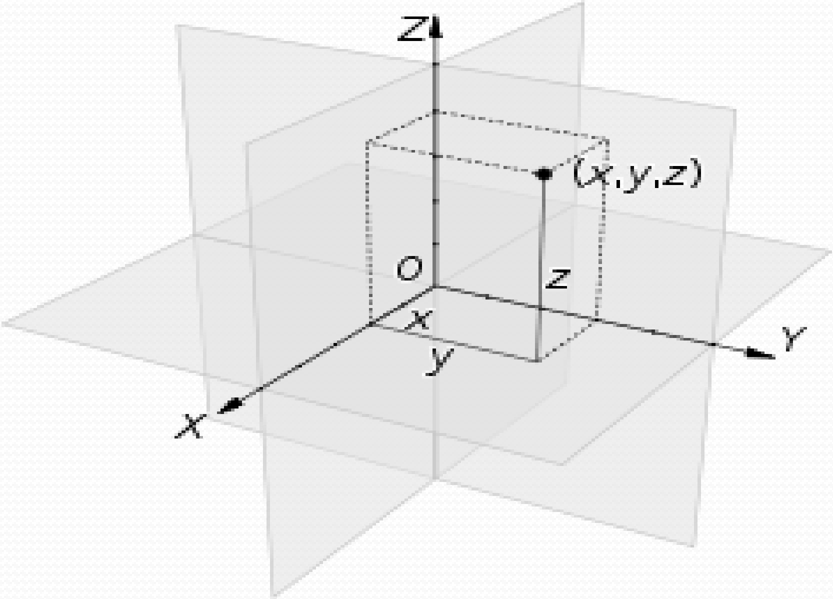
- *Schrodinger (Wave Mechanics)*
- *Heisenberg (Matrix Mechanics)*
- *Dirac (Ket & Bra Mechanics)* **(< \ >)**

Coordinate System

The purpose of using coordinate system is to describe a point, a curve or a surface in space.

I. ***Cartesian Coordinate***
II. ***Spherical Coordinate***

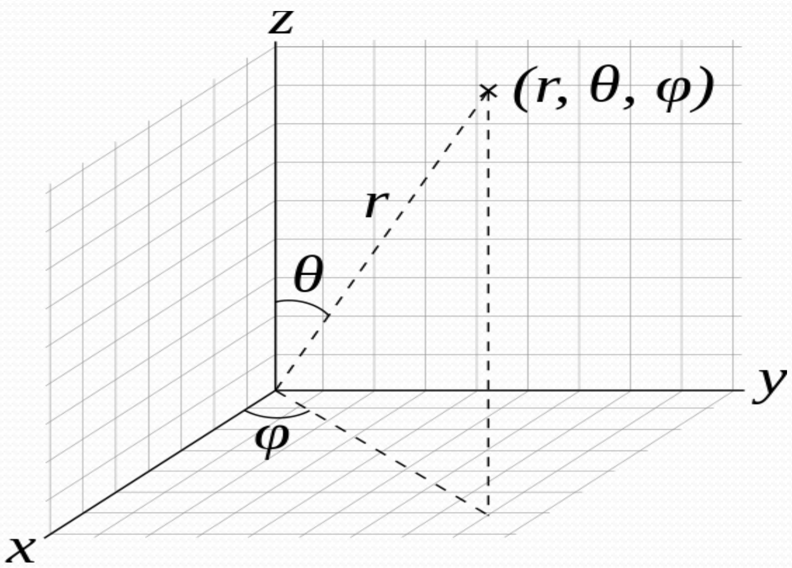
I. Cartesian Coordinate



The Figure Show three dimensional Cartesian coordinate system, with origin O and axis lines X, Y and Z, oriented as shown by the arrows. The black dot shows the point with coordinates X = 2, Y = 3, and Z = 4.

Spherical Coordinate

The point (p) can be described through ***one distance*** *(the radial r) and* ***two angles*** *(θ and φ)*



The figure ***e****xplains spherical coordinates (r, θ and φ) as* **r** is the **radial distance**, ***θ*** (theta) is the **polar angle**, and ***φ*** (phi) is the **azimuthal angle**.

There is a possibility for inverting Cartesian coordinate to spherical and vice versa using the following three relations:

$$x = r\ \sin\theta\cos\varphi$$

$$y = r\ \sin\theta\sin\varphi$$

$$z = r\ \cos\theta$$

Conservative System

A system can be conservative if it ***total energy*** *remains* ***fixed*** *with* ***time.***

$$E = T + U$$

E is the total energy
T is the kinetic energy
U is the potential energy

This means that the conservative system is completely ***isolated*** *with* ***no external effect.***

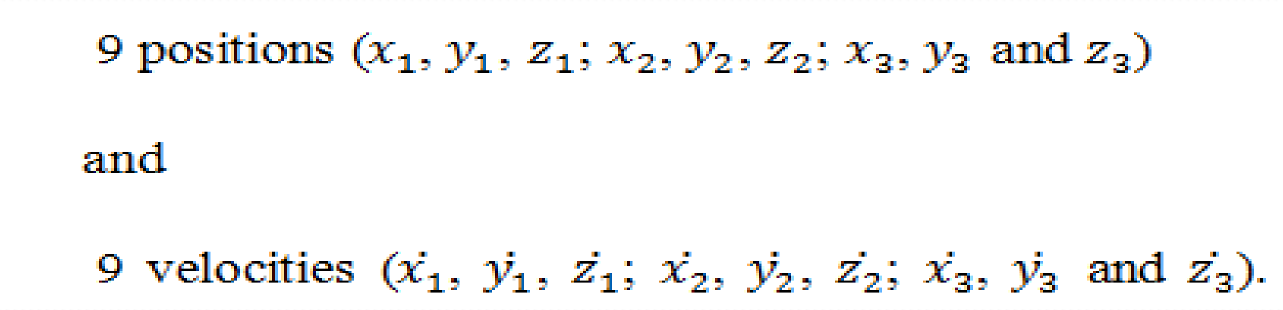
$$\frac{dE}{dt} = 0$$

Generalized Coordinates and Degrees of Freedom

Suppose there is a ***conservative system*** *of three particles (N=3)*

In order to describe ***the state*** *of this system* ***completely*** *at a* ***given time****,*

We need to specify ***the positions*** *and* ***velocities*** *of the three particles*

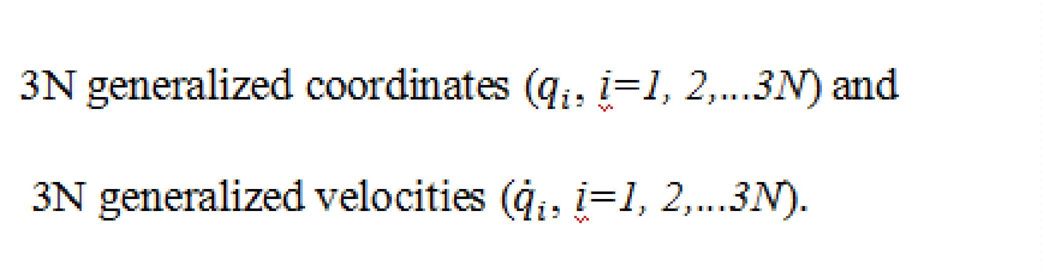


9 positions $(x_1, y_1, z_1; x_2, y_2, z_2; x_3, y_3$ and $z_3)$

and

9 velocities $(\dot{x}_1, \dot{y}_1, \dot{z}_1; \dot{x}_2, \dot{y}_2, \dot{z}_2; \dot{x}_3, \dot{y}_3$ and $\dot{z}_3)$.

for system containing N particles, one must have
3N positions and 3N velocities which mean
6N degrees of freedom.



3N generalized coordinates (q_i, $i=1, 2,...3N$) and

3N generalized velocities ($\dot{q}_i$, $i=1, 2,...3N$).

The main purpose of dealing with generalized coordinates is to make ***it convenient*** *for treating systems of* ***multi particles*** *from* ***mathematical point of view.***

Classical Mechanics

Classical mechanics *is a* ***physical theory*** *describing the motion of* ***macroscopic object***
from projectiles to parts of machinery, and astronomical objects,

such as
spacecraft, planets, stars and galaxies.

Classical mechanics as formulated by ***Newton*** *called* ***Newtonian mechanics***

Newtonian mechanics *is considered fairly straightforward from a mathematical point of view.*

There are other possible formulations of mechanics:

1. ***Lagrangian mechanics***
2. ***Hamiltonian mechanics***

Newtonian Mechanics

This mechanics can be presented by ***Newton's second law in dynamics***

$$F = ma \qquad (1\text{-}6)$$

which gives the force ***(F)*** *required in order to give acceleration* ***(a)*** *to mass* ***(m)*** *.*

Generally, ***the force is a function of position x*** *for* ***one dimensional system****. The acceleration may be rewritten as:*

$$a = \frac{d^2x}{dt^2} \qquad (1\text{-}7)$$

where ***(t)****is a time.*

Thus, Eq. (1-6) can be represented in differential form by following relation.

$$F = m\,\frac{d^2x}{dt^2} \qquad (1\text{-}8)$$

Lagrangian Mechanics

Joseph-Louis Lagrange *is an Italian-French* ***mathematician*** *and* ***astronomer .***

The important aspect here is the quantity of ***Lagrangian function (L)***

$$L = T - U \qquad (1\text{-}9)$$

which defined as the difference between ***kinetic energy (T)*** *and* ***potential energy (U):***

In one dimension system:

As far as ***the kinetic energy*** *is a* ***function of velocity v*** *and*

The potential energy *is a* ***function of position x,***

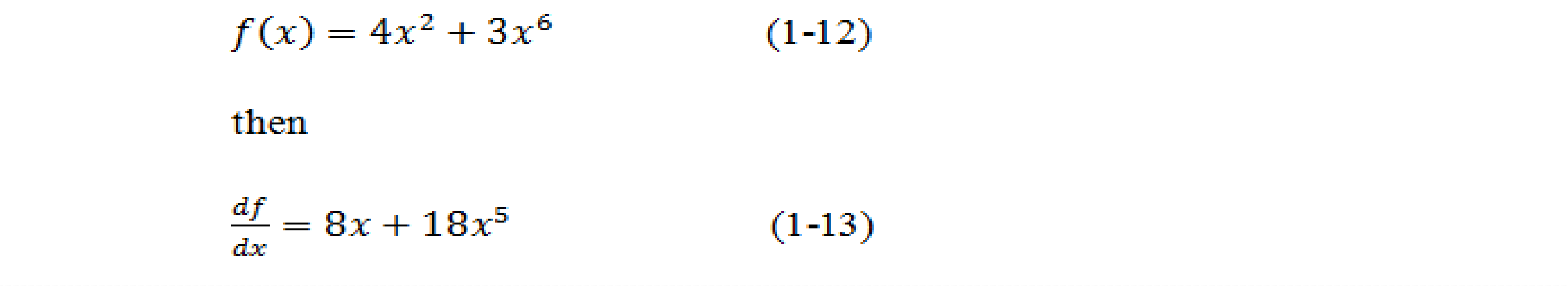
equation (1-9) can be rewritten as:

$$L_{(x,v)} = T_{(v)} - U_{(x)}$$

The **solution** by **Lagrange's model** gives

$$\frac{d}{dt}\left(\frac{\partial L}{\partial v}\right) - \frac{\partial L}{\partial x} = 0$$

Ordinary derivative equation



$$f(x) = 4x^2 + 3x^6 \qquad (1\text{-}12)$$

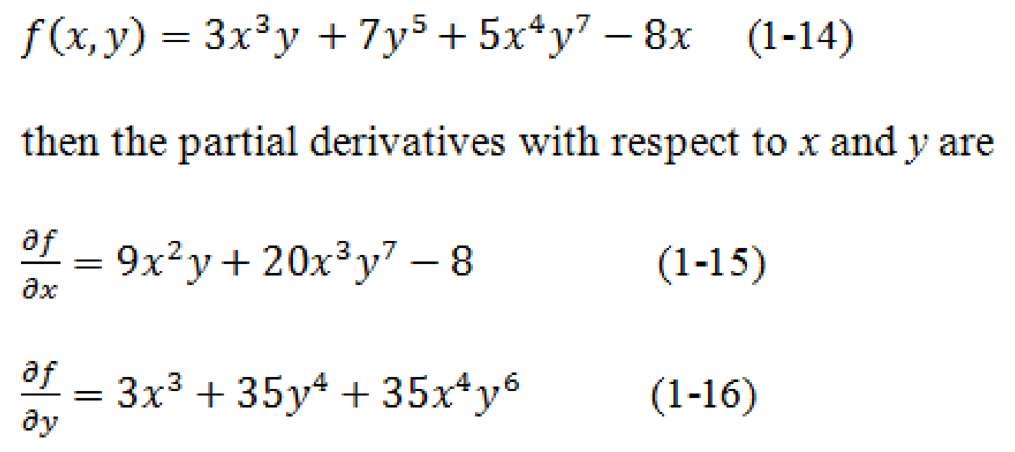
then

$$\frac{df}{dx} = 8x + 18x^5 \qquad (1\text{-}13)$$

This called as **ordinary derivative equation** because it contains only **one variable (*x*)**.

Partial derivatives equation

if *f* is a function of **two variables** (*x* and *y*) then we have to use **partial derivatives**. For example, if



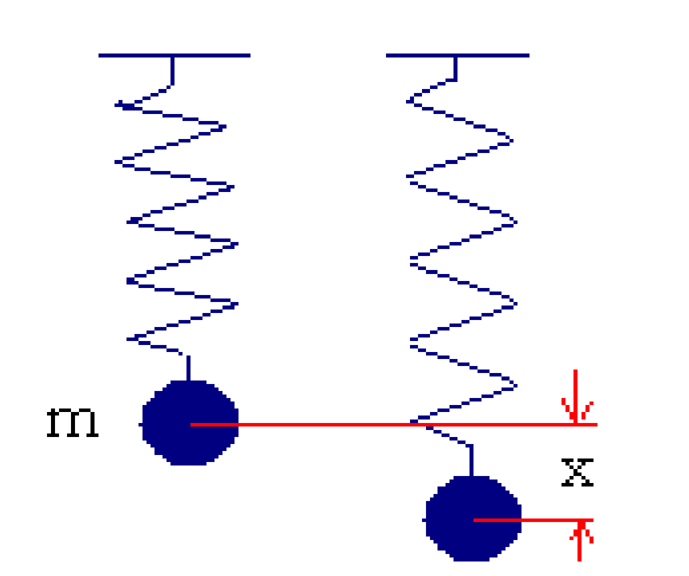
$$f(x,y) = 3x^3y + 7y^5 + 5x^4y^7 - 8x \qquad (1\text{-}14)$$

then the partial derivatives with respect to x and y are

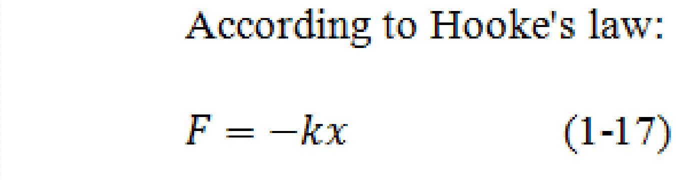
$$\frac{\partial f}{\partial x} = 9x^2y + 20x^3y^7 - 8 \qquad (1\text{-}15)$$

$$\frac{\partial f}{\partial y} = 3x^3 + 35y^4 + 35x^4y^6 \qquad (1\text{-}16)$$

Example: Simple Harmonic Oscillator



The figure Shows schematically **the simple harmonic oscillator** of **mass m** and x is a distance from **the equilibrium position**.



According to Hooke's law:

$$F = -kx \qquad (1\text{-}17)$$

Where:

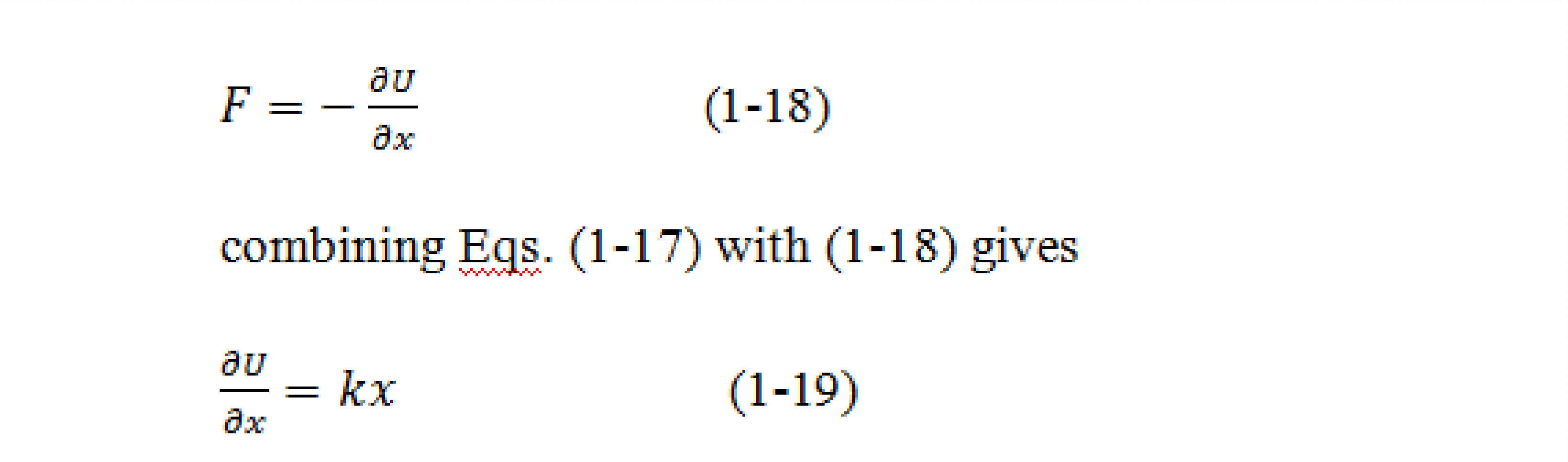
(*x*) is **the distance** from **the equilibrium position**.

(k) is **the force constant**.

(-) **the force** is in the **opposite direction.**

On the other hand:

The force be represented as **the negative gradient** of the **potential energy *U***:



$$F = -\frac{\partial U}{\partial x} \qquad (1\text{-}18)$$

combining Eqs. (1-17) with (1-18) gives

$$\frac{\partial U}{\partial x} = kx \qquad (1\text{-}19)$$

Then **the potential energy :**

$$\int_0^\infty \partial U = k \int_0^\infty x \partial x \qquad (1\text{-}20)$$

This gives

$$U = \frac{1}{2} k x^2 \qquad (1\text{-}21)$$

The kinetic energy *T* of simple harmonic oscillator:

$$T = \frac{1}{2} m v^2 \qquad (1\text{-}22)$$

where : ***m*** is **the mass of particle**

v is the velocity

Thus, **the Lagrangian function** can be rewritten as:

$$L = \frac{1}{2} m v^2 - \frac{1}{2} k x^2 \qquad (1\text{-}23)$$

$$\frac{d}{dt}\left(\frac{\partial L}{\partial v}\right) - \frac{\partial L}{\partial x} = 0 \qquad (1\text{-}11)$$

$$L = \frac{1}{2}mv^2 - \frac{1}{2}kx^2 \qquad (1\text{-}23)$$

Substituting L of Eq. (1-23) in the equation (1-11) , we find

$$\frac{d}{dt}\left[\frac{\partial}{\partial v}\left(\frac{1}{2}mv^2 - \frac{1}{2}kx^2\right)\right] - \frac{\partial}{\partial x}\left(\frac{1}{2}mv^2 - \frac{1}{2}kx^2\right) = 0 \qquad (1\text{-}24)$$

$$\frac{d}{dt}(mv) + kx = 0 \qquad (1\text{-}25)$$

Since $v = \frac{dx}{dt}$, Eq. (1-25) can be rewritten as:

$$m\frac{d^2x}{dt^2} + kx = 0 \qquad (1\text{-}26)$$

the acceleration *a* is $a = \frac{d^2x}{dt^2}$ (1-7)

Then Eq. (1-26) can be represented as:

$$ma + kx = 0 \qquad (1\text{-}27)$$

Hamiltonian Mechanics

Hamiltonian mechanics **depends** merely on that of **Lagrangian** through the quantity of **Hamiltonian function *H*** which contains Lagrangian function *L*.

$$H = \sum_{i=1}^{3N} p_i \dot{q}_i - L \qquad (1\text{-}30)$$

where:

H is the Hamiltonian function,

p_i is the generalized momentum,

$\dot{q}_i$ is the generalized velocities

L is the Lagrangian function.

On the other hand,

$$\frac{dx}{dt} = \frac{\partial H}{\partial p} \qquad (1\text{-}28)$$

$$\frac{dp}{dt} = -\frac{\partial H}{\partial x} \qquad (1\text{-}29)$$

H is the Hamiltonian function

p is the momentum

t is the time

Lagrange's Eq. (1-11) expresses the motion of a particle as a single-order differential equation.

$$\frac{d}{dt}\left(\frac{\partial L}{\partial v}\right) - \frac{\partial L}{\partial x} = 0 \qquad (1\text{-}11)$$

While for Hamilton the motion described as a coupled system of two first-order differential equations:

$$\frac{dx}{dt} = \frac{\partial H}{\partial p} \qquad (1\text{-}28)$$

$$\frac{dp}{dt} = -\frac{\partial H}{\partial x} \qquad (1\text{-}29)$$

Example: Simple Harmonic Oscillator (Hamiltonian Function)

According to Eq. (1-30), one needs to find the kinetic and potential energies in order to substitute Lagrangian function

$$H = \sum_{i=1}^{3N} p_i \dot{q}_i - L \qquad (1\text{-}30)$$

$$U = \frac{1}{2}kx^2 \text{ and } T = \frac{1}{2}mv^2.$$

On the other hand, **the momentum *p*** can be expressed by:

$$p = mv \qquad (1\text{-}31)$$

Thus, For N=1 and through substituting Eqs. (1-21), (1-22) and (1-31) in Eq. (1-30), one can get

$$H = mv^2 - \left(\frac{1}{2}mv^2 + \frac{1}{2}kx^2\right) \qquad (1\text{-}32)$$

then

$$H = \frac{1}{2}mv^2 + \frac{1}{2}kx^2 \qquad (1\text{-}33)$$

Since $T = \frac{1}{2}mv^2$ and $= \frac{1}{2}kx^2$, Eq. (1-33) can be rewritten as:

$$H = T + U \qquad (1\text{-}34)$$

Example: Simple Harmonic Oscillator (Hamiltonian Equation, $\frac{dp}{dt} = -\frac{\partial H}{\partial x}$)

By substituting Hamiltonian function (1-33) in Eq. (1-29) gives

$$H = \frac{1}{2}mv^2 + \frac{1}{2}kx^2 \qquad (1\text{-}33)$$

$$\frac{dp}{dt} = -\frac{\partial H}{\partial x} \qquad (1\text{-}29)$$

$$\frac{dp}{dt} = -\frac{\partial}{\partial x}\left(\frac{1}{2}mv^2 + \frac{1}{2}kx^2\right) \qquad (1\text{-}35)$$

Taking the partial derivatives one get

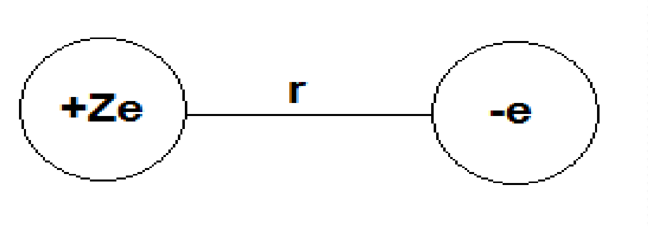
$$\frac{dp}{dt} = -kx \qquad (1\text{-}36)$$

Replacement the momentum p by mv and consequently the velocity v by $\frac{dx}{dt}$ gives

$$m\frac{d^2x}{dt^2} = -kx \qquad (1\text{-}37)$$

Again, Eq. (1-37) is same as that of (1-27) in representing both Newton's second law ($F = ma$) and Hooke's law ($F = -kx$) which supporting the correctness of Hamiltonian function and Equation.

Example: Write the Hamiltonian function for Hydrogen atom?

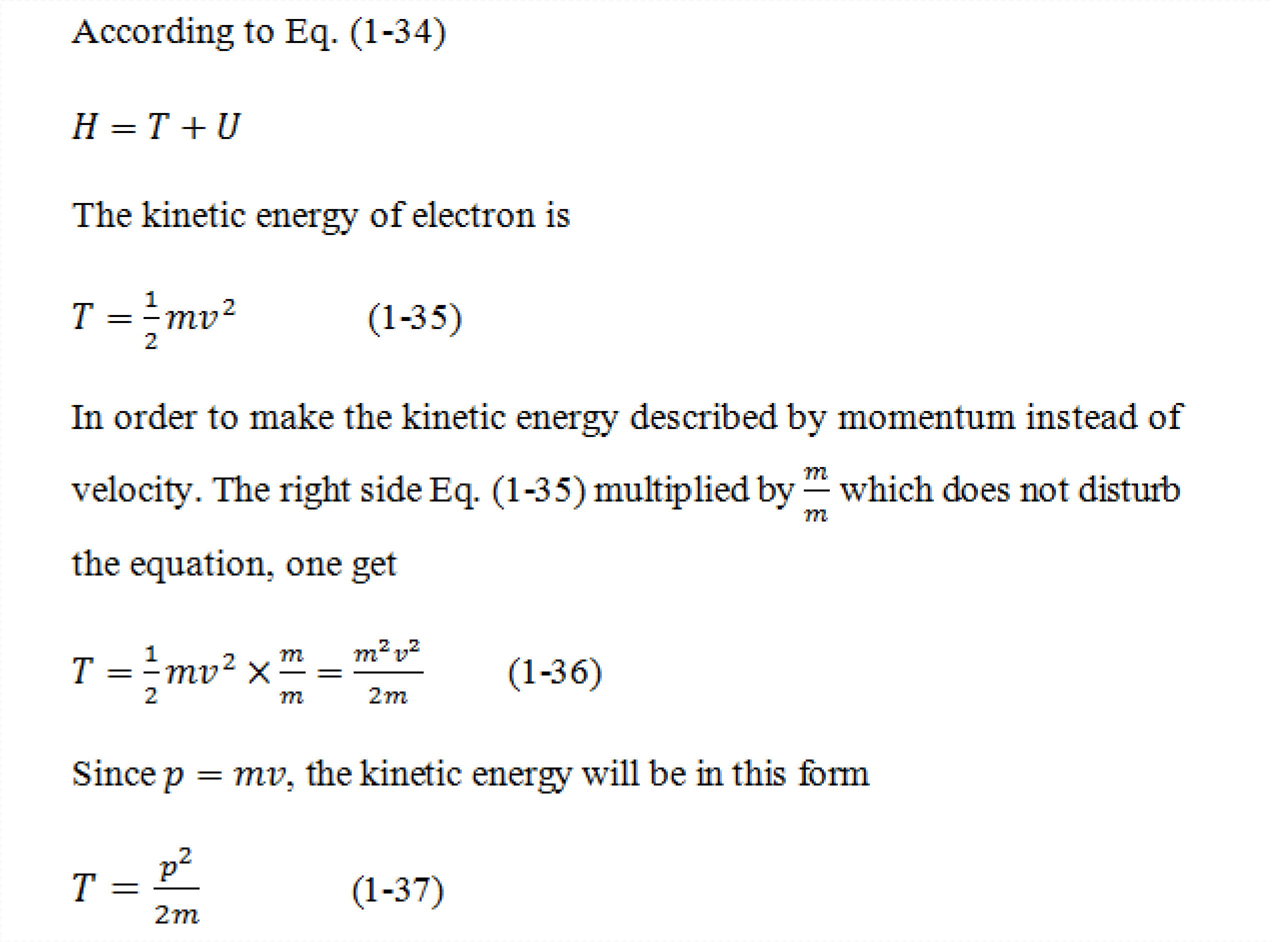


Where:

(Z) is the **atomic number** of H atom which equal to **one.**

By supposing that the nucleus is fixed and the electrons move around it..

Therefore, **the kinetic energy** of nucleus will be equal to **zero.**



According to Eq. (1-34)

$$H = T + U$$

The kinetic energy of electron is

$$T = \frac{1}{2} m v^2 \qquad (1\text{-}35)$$

In order to make the kinetic energy described by momentum instead of velocity. The right side Eq. (1-35) multiplied by $\frac{m}{m}$ which does not disturb the equation, one get

$$T = \frac{1}{2} m v^2 \times \frac{m}{m} = \frac{m^2 v^2}{2m} \qquad (1\text{-}36)$$

Since $p = mv$, the kinetic energy will be in this form

$$T = \frac{p^2}{2m} \qquad (1\text{-}37)$$

The potential energy for two charged particles is described by

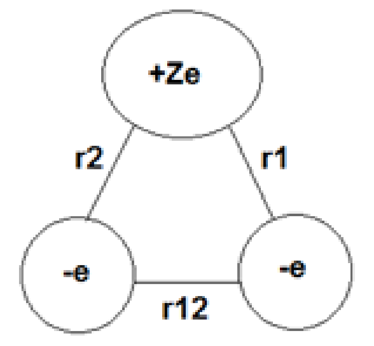
1. **The interaction between those charges**
2. **The distance *r* between them**

$$U = \frac{(+Ze)(-e)}{(4\pi\epsilon_o)r} = \frac{-e^2}{4\pi\epsilon_o r} \qquad (1\text{-}38)$$

where $4\pi\epsilon_o$ is the Coulombs constant as $\epsilon_o = 8.854 \times 10^{-12} C^2 N^{-1} m^{-2}$, Thus the Hamiltonian function for H atom is

$$H = \frac{p^2}{2m} + \frac{-e^2}{4\pi\epsilon_o r} \qquad (1\text{-}39)$$

Example: Write the Hamiltonian function for Helium atom?



(Z) Is the atomic number of He atom which equal to two.
By supposing that the nucleus is fixed and the electrons move around it.

$$T = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} \qquad (1\text{-}40)$$

$$U = \frac{-Ze^2}{r1} - \frac{Ze^2}{r2} + \frac{e^2}{r12} \qquad (1\text{-}41)$$

$$\therefore H = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} - \frac{Ze^2}{r1} - \frac{Ze^2}{r2} + \frac{e^2}{r12} \qquad (1\text{-}42)$$

Chapter Two

Quantum Theory

Introduction

Due to the accumulated of **unsolved problems** that faced scientists at the nineteenth century.

The main problems:

- The nature of light,
- Electromagnetic energy,
- Atomic and molecular structures.

A modern science called **quantum theory** was initiated in order to give an understandable clue about those dilemmas.

Indeed, **quantum theory** was **originated** at 1900 by **Max Planck** through explaining **the phenomenon of blackbody radiation.**

Therefore, **the first hypotheses** of this new science was postulated by **Planck** which containing the word of **quanta.**

Then, **considerable supports** to this hypotheses through **some more postulates** were given by **Einstein,**
Bohr,
Sommerfeld and **de Broglie**

Introduction

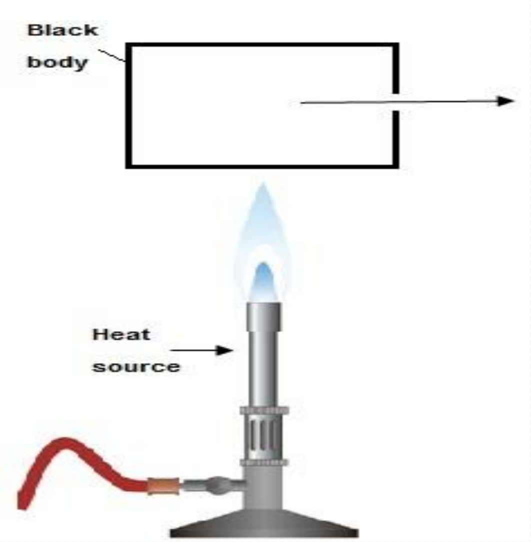
The main concept of **quantum theory** is that **the absorption of electromagnetic energy is not continuous as heat** but **is discontinuous as a matter.**

In other words,
The energy of the system can take only **a certain amounts of energy**.

But, according to **classical mechanics**
The energy of the system is able to be in **any quantity** and can change by **any amount**.

Black body or Cavity Radiation

Black body radiation means **any matter** that could **emits radiation** in **all wavelengths ranges**.



The figure shows Simple Scheme explaining the Black body radiation.

- **An isolated cavity** as the only energy that can be **absorbed** is energy in the form of heat in order to rise temperature.
- **The heated cavity** will considered as blackbody which emits long ranges of radiation.
- the **heated tungsten** metal cannot considered as blackbody because only emits radiation **at short range of wavelengths** (visible only).

A box with a small hole that emits a wide range of electromagnetic radiation.

Black body or Cavity Radiation

This experiment was already **studied** by **Rayleigh and Jeans** using **classical mechanics**

They assumed that the **distribution of intensity *I(v)*** as **a function of frequency (*v*)** increases with **increasing temperature *T***

$$I(v) = \frac{8\pi kT}{\lambda^4}$$

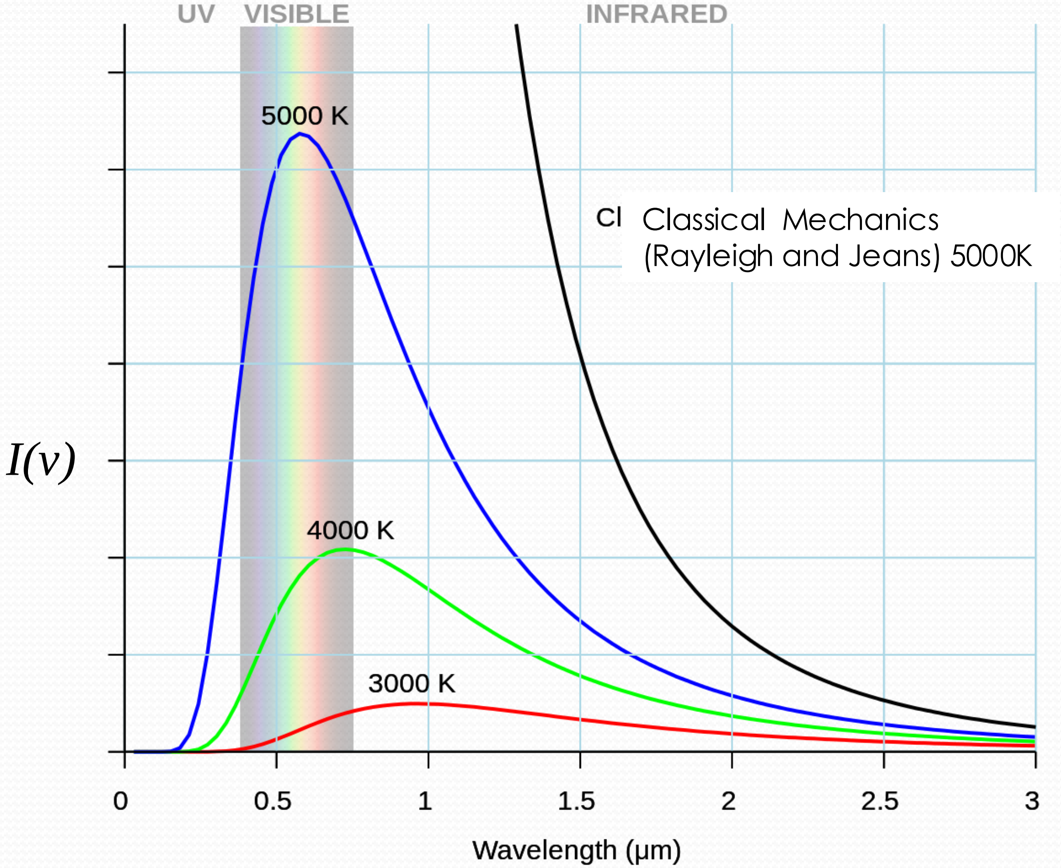
Where

k is the Boltzmann constant ($1.38064852 \times 10^{-23}$ J K^{-1}),

T is the absolute or Kelvin temperature,

$\boldsymbol{\lambda}$ is the radiation wavelength.

Black body or Cavity Radiation



The figure shows the distribution of intensity *I(v)* as a function of frequency (*v*)

- **Planck** surprisingly found **that there is a maximum in the relation of *I(v)*** as **a function of frequency *v*** .
- It is apparently **contradict** the assumed model of **Rayleigh and Jeans.**
- Such unexpected result led Planck at the last of 1900 to breakthrough a new science (quantum theory).

A rode of iron **appears red** at 500^{o}C and **change to bluish** at 1000^{o}C.

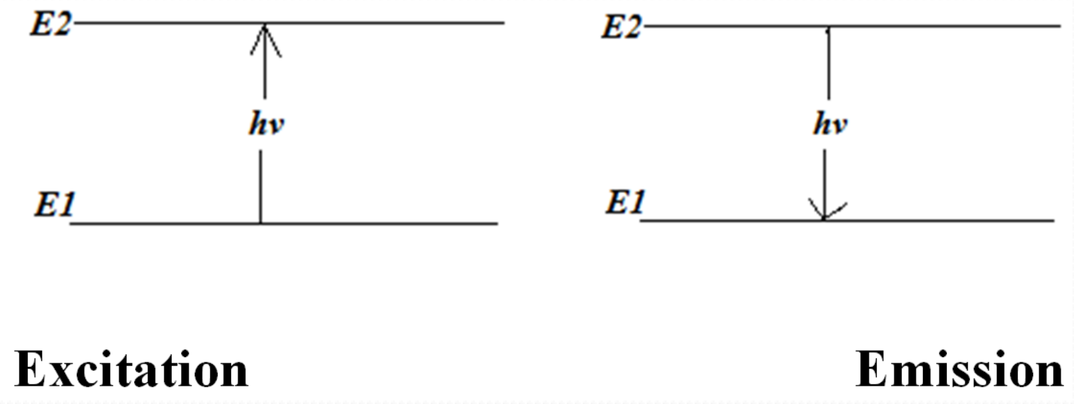
Black body or Cavity Radiation

- **Planck** stated that "**The energy like matter,** it is **discontinues** and **consists of** large numbers of **tiny discrete units** of **equal portions** called **quanta**“.

- The system can only **emits or takes radiation** by **quanta of energy (*E*)** which proportional with frequency v

$$E=hv$$

The symbol ***h*** is famous or magic Planck constant of the value 6.62607 x 10^{-34}J.s.



The figure shows the Excitation and Emission according to Planck postulate.

Black body or Cavity Radiation

According to classical mechanics

The system may be able to take **any value** and to change **by any amount of energy**.

While, by the quantum theory (Planck assumption)

A system can have only **a unique set of certain values** of

hv or **its integer multiplication**

$$ihv, \qquad i=1,2,3\ \ldots .n.$$

He developed a model that could coping the experimental relation of black body radiation as following:

$$I(\nu) = \frac{8\pi hC}{\lambda^5}\left(\frac{1}{e^{hC/\lambda kT}-1}\right)$$

where

C is the velocity of light.

Black body or Cavity Radiation

$$I(\nu) = \frac{8\pi hC}{\lambda^5}\left(\frac{1}{e^{hC/\lambda kT}-1}\right)$$

At high frequency (short wavelength)

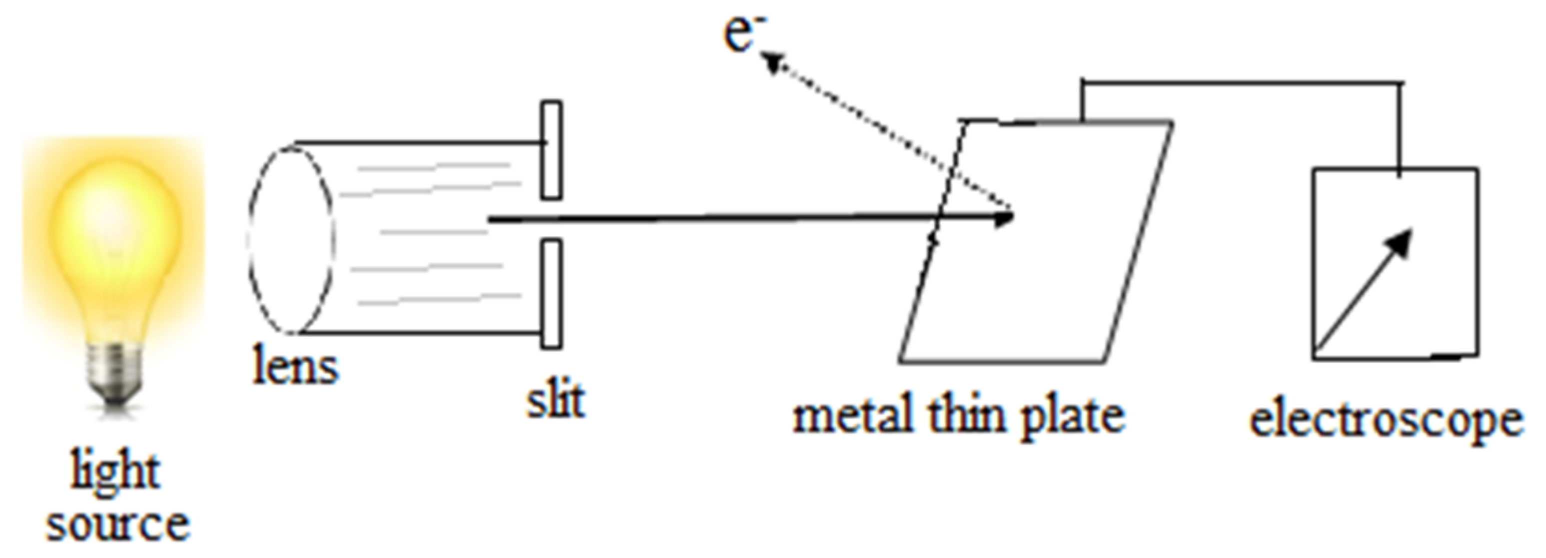
hC/λkT is large enough to make the value of *I(v)* equal to zero.

For Low frequency (long wavelength)

hC/λkT<<1 as the relation will be somewhat similar to that of Rayleigh and Jeans

Photoelectric effect

In 1905 **Einstein** explored the experiment of **photoelectric effect** in order to understand it as **Planck** did for **black body radiation**.



The figure shows the photoelectric effect

The incident light at a **thin layer plate of metal** ejects **electrons** which **change the charge of plate** from **neutral** to **positive**

Photoelectric effect

Einstein supported Planck hypothesis and he gave the second postulate in quantum theory. He stated that

“*the **electromagnetic radiation** has **particle like characteristics** and each of these particles having **Planck quanta energy** ($E=h\nu$)*”

The photoelectric effect having **two more advantages** in addition to the last postulate

- **It is solved the problem** of centuries about **the nature of light** which **behaves as particle like**.

- the photoelectric effect can be considered as **a source of *β* particles or ray**

Photoelectric effect

There is no ejected electron until **the frequency of light** becomes **equal or larger than a certain value.**

This **minimum frequency** is called the **threshold frequency** $\boldsymbol{v_o}$

- Its value depends on **the type of metal**.
- **The kinetic energy of ejected electron** is proportional with **the frequency of incident light**.

The excess of kinetic energy of the ejected electron (E_T) as can be represented by this relation:

$$E_T = \frac{1}{2}mv^2 = hv - hv_o = hv - W$$

Where

$\boldsymbol{W}$ is the work function of metal.

Example of Photoelectric effect

What is the maximum velocity of electrons ejected from Ni metal by a light of **200nm wavelength**, if the **work function of Ni is 5eV**. Noting that **the mass of electron is $9.1x10^{-31}$kg**, the conversion factor **1eV $=1.60x10^{-19}$ J** and **the velocity of light $C=3x10^{8}$ ms^{-1}**.

$$\nu = \frac{3x10^{8}\ \mathrm{m/s}}{200x10^{-9}\ \mathrm{m}} = 1.5x10^{15}\ \mathrm{s}^{-1}\ \text{or Hz}$$

$$E_T = h\nu - W = 6.626x10^{-34}\ \mathrm{x}\ 1.5\mathrm{x}10^{15} - 5\mathrm{x}1.6\mathrm{x}10^{-19} = 1.94\mathrm{x}10^{-19}\ \mathrm{J}$$

$$E_T = \frac{1}{2}mv^2 \Rightarrow v = \sqrt{\frac{2E_T}{m}} = \sqrt{\frac{2x1.94\mathrm{x}10^{-19}\mathrm{J}}{9.1\mathrm{x}10^{-31}\,\mathrm{kg}}}$$

$$6.53x10^{5}\ m.s^{-1}$$

Mass–energy equivalence

mass–energy equivalence states that **mass** is concentrated **energy**. In his theory of special relativity Einstein formulated the equation

$$E = mC^2 \qquad (2\text{-}4)$$

$E/m = c^2 = (3\text{x } 10^8 \text{ m/s})^2 = 89875517873681764$ J/kg ($\approx 90 \times 10^{15}$ joules per kilogram).

So the energy equivalent of one kilogram of mass is

- 89.9 **petajoules**
- 25.0 **billion kilowatt-hours**
- 21.5 trillion **kilocalories**

or the energy released by combustion of the following:
21 500 **kilotons of TNT- equivalent** energy

Bohr atom

In1911

Rutherford was successfully given a true idea about **atom structure** which achieved from his experiment of **bombardment** of a very **thin layer of gold by α-particles.**

At that time **his new idea** has been **attacked** by **electromagnetic theory** of that **the charged particle emits energy throughout moving.**

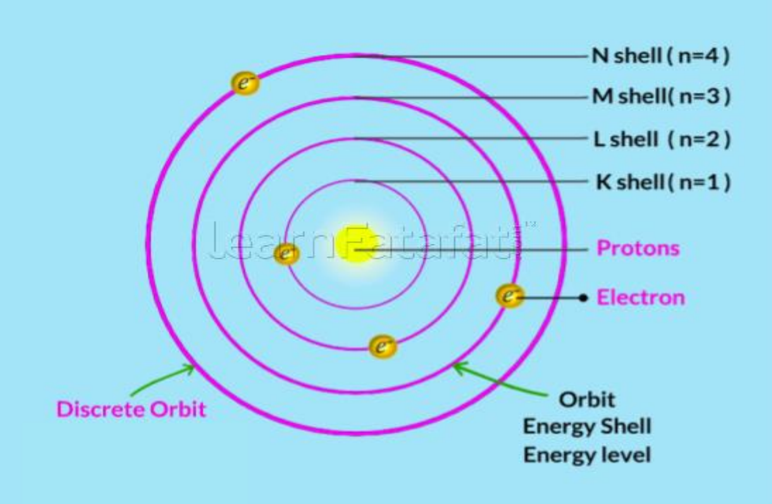
In 1913

Bohr produced **a solution** to this problem by an interesting combination of **classical mechanics** with **quantum theory**.

Bohr atom

His developed theory may be considered **as an additional of three postulates** to quantum theory:

- There is only **certain of allowable orbits** for an electron in H atom.



- In these orbits **the magnitude of angular momentum** (*L*) of the electron can only have **quantized values** according to the following relation:

$$L = n\left(\frac{h}{2\pi}\right) = n\hbar \qquad n = 1, 2, 3, 4, \ldots\ldots\ldots.etc \qquad (2\text{-}5)$$

Where

n can be considered as the **principal orbital quantum number**

$\hbar = h/2\pi$.

Bohr atom

The energy of each **orbital level** could be estimated by the following relation

$$E_n = -\frac{m_e e^4}{2(4\pi\epsilon_0)^2\hbar^2}\frac{1}{n^2},$$

Where **m_e** the **rest mass** of the electron,
e is the elementary **charge**,
ϵ_0 is the **permittivity of free space**,
h is the **Planck constant**
n is the **principal orbital quantum number**

$$E_n = \frac{-13.6\ eV}{n^2} \qquad (2\text{-}8)$$

- The electron **can only pass** from **one stationary state to another**.

The frequency of a spectral line due to the transition of that electron **is also quantized** and **equal** to **Planck or photon energy** as

$$\Delta E = E_2 - E_1 = h\nu$$

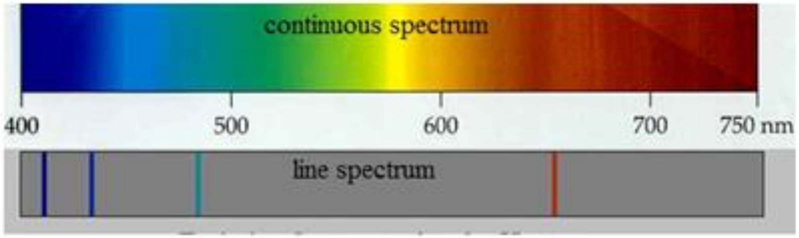
Using last postulate one could calculate the **wavelength** of the transition in the hydrogen atom using this model.

$$h\nu = \frac{Z^2 m e^4}{8h^2\epsilon_0^2}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] = 13.6Z^2\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] eV$$

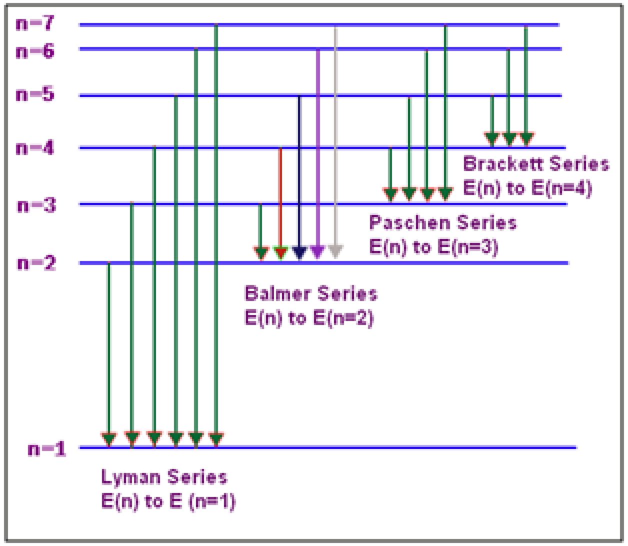
n_1= Initial
n_2= Final

Bohr atom

The figure shows **continuous** and **line** spectrum.



The figure explains the emission spectrum of H atom according to Bohr assumptions



It contains two weak points:

- ➢The first is that the electron moves around the nucleus in **cyclic orbits.**
- ➢The second is **contradicting** with **uncertainty principle** as the momentum and position of electron can be determined simultaneously in accurate means

Bohr atom

2.4.1. Example: What is the energy of an electron in the n=3 energy state of a hydrogen atom?

According to Eq. 2-8 $E_n = \frac{-13.6\ eV}{n^2}$

$$E_n = \frac{-13.6}{9} = -1.5111\ eV$$

$$1\text{eV} = 1.60\text{x}10^{-19}\ \text{J} \Rightarrow -1.5111\ x 1.60\text{x}10^{-19} = -2.42\text{x}10^{-19}\text{J}$$

Thus, The energy of an electron in the n=3 energy state of a hydrogen atom is -2.42 x 10^{-19} J.

Sommerfeld Quantization

In 1915 **Wilson** and **Sommerfeld** developed a method of **quantizing**

The method can be illustrated by two main steps:

- The first is by solving the problem using **classical mechanics.**
- The second is throughout taking the equation that could fulfill the **quantum condition**.

The **quantum condition** for a system of ***f*** *degree of freedom is*

$$\oint p_i dq_i = nh \qquad (i = 1, 2, 3, \ldots\ldots f) \qquad (2\text{-}9)$$

where

$\oint$ the integration symbol means the integration of **complete cycle**

n is the quantum integer number, $n=0, 1, 2, 3,$

The real **position** and **momentum** of the system according to quantum condition must be equal to **Planck's constant** or its **multiplication by integer number**.

Application the quantum condition indicate

- The atomic orbits are **elliptical** (not circle).
- The result of application to ***simple harmonic oscillator*** is not acceptable as contradict with **uncertainty principle**.

The dual nature of light

In 1924

De Broglie stated that **the light** having **dual behavior** of both **particle- and wave-like** properties.

He is postulated that
"**light** does not only display or show **particle-like** characteristics, but small particles may at times show **wave-like** properties".

He derived a **very important relationship** between **wavelength** and **momentum** which it is essential for quantum mechanics.

$$p = \frac{h}{\lambda} \qquad (2\text{-}10)$$

The dual nature of light

The derivation of this model was as following.

The energy of photon $E=hv$ at the same time the mass-energy equivalence (2-4) is $E = mC^2$, therefore,

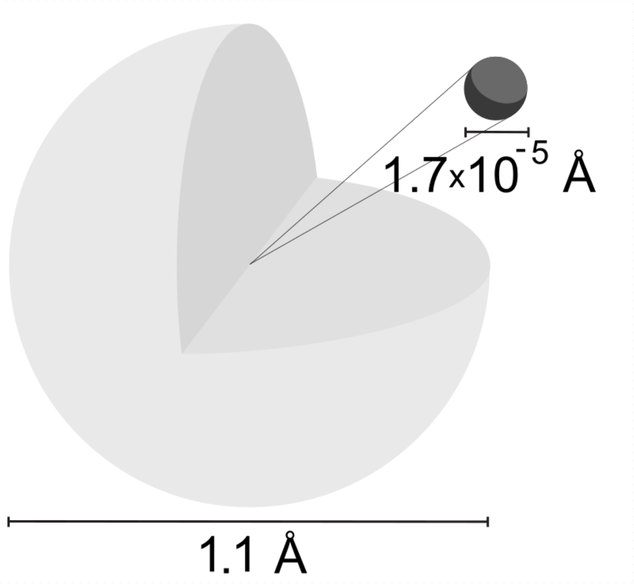
$hν = mC^2,\ ν = \frac{c}{\lambda}$ Then, $\frac{hC}{\lambda} = mC^2 \Rightarrow \frac{h}{\lambda} = mC$,

The velocity of photon is equal to the speed of light v therefore,

$$\frac{h}{\lambda} = mv\ \ (p = mv)$$

$$\therefore\quad p = \frac{h}{\lambda}$$

The Hydrogen Atom.



Depiction of a hydrogen atom showing **the diameter** as about **twice** the **Bohr model radius**. (0.53 Å)

- *The **treatment** of **atoms** by **quantum mechanics** is considered as an **essential task** for **solving the problems** of both **chemist and physicist**.*
- *The **H atom** is the **simplest atomic system** which only has **two particles** of an **electron** with **mass** m_e and **nucleus** with **mass** M.*

The Hamiltonian function of H

Supposing the ***nucleus*** *is* ***fixed***

$$H = T + U$$

$$H = \frac{1}{2m_e}\left(p_x^2 + p_y^2 + p_z^2\right) + \frac{-Ze^2}{4\pi\epsilon_o r} \tag{4-31}$$

Converting the ***Hamiltonian function*** *to* ***Hamiltonian operator*** *using* ***postulate II***

$$T = \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right) \Longrightarrow \hat{T} = \frac{-\hbar^2}{2m}\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right]$$

$$H = \frac{-\hbar^2}{2m_e}\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right] - \frac{Ze^2}{4\pi\epsilon_o r} \tag{4-32}$$

Substituting this ***Hamiltonian operator*** in ***Schrödinger equation*** $\hat{H}\Psi = E\Psi$ one can get

$$\left(\frac{-\hbar^2}{2m_e}\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right] - \frac{Ze^2}{4\pi\epsilon_o r}\right)\Psi = E\Psi \tag{4-33}$$

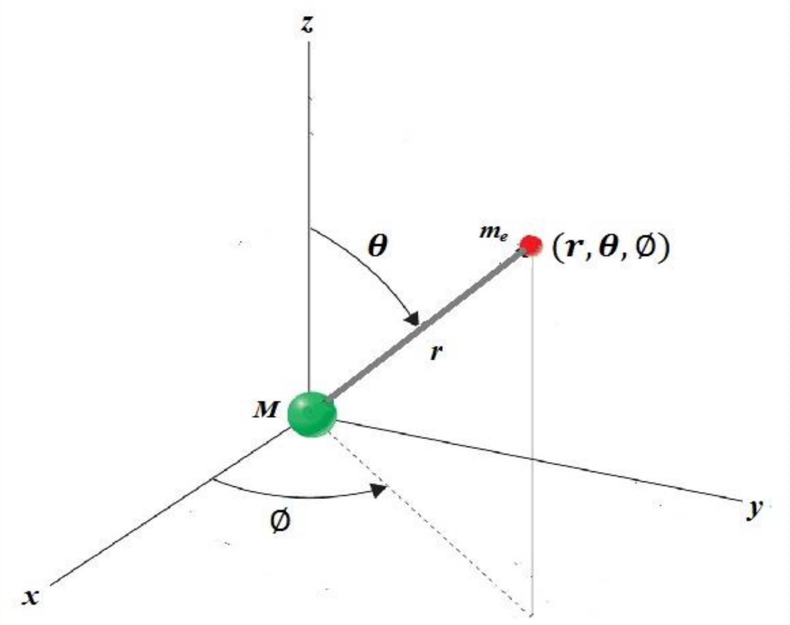
$$\frac{-\hbar^2}{2m_e}\left[\frac{\partial^2\Psi}{\partial x^2}+\frac{\partial^2\Psi}{\partial y^2}+\frac{\partial^2\Psi}{\partial z^2}\right]-\frac{Ze^2\Psi}{4\pi\epsilon_0 r}=E\Psi \qquad \times -\frac{2m_e}{\hbar^2}$$

$$\frac{\partial^2\Psi}{\partial x^2}+\frac{\partial^2\Psi}{\partial y^2}+\frac{\partial^2\Psi}{\partial z^2}+\boxed{\frac{Ze^2\Psi}{4\pi\epsilon_0 r}\frac{2m_e}{\hbar^2}+\frac{2m_e}{\hbar^2}E\Psi}=0$$

$$\frac{\partial^2\Psi}{\partial x^2}+\frac{\partial^2\Psi}{\partial y^2}+\frac{\partial^2\Psi}{\partial z^2}+\frac{2m_e}{\hbar^2}\left(E+\frac{Ze^2}{4\pi\epsilon_0 r}\right)\Psi=0 \qquad \text{(4-36)}$$

This Eq. (4-36) cannot be solved as the Cartesian coordinate unable to describe such a two particles system. The transformation of the last Eq. to spherical coordinate

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\Psi}{\partial r}\right)+\frac{1}{r\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Psi}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\Psi}{\partial\emptyset^2}+\frac{8\pi^2 m_e}{h^2}\left(E+\frac{Ze^2}{4\pi\epsilon_0 r}\right)\Psi=0 \qquad (4\text{-}37)$$



The Figure shows Spherical coordinates for describing the hydrogen atom.

The equation mathematically is difficult to solve because:

The supposed spherical shape of an atom cannot be described by one position which depending on three parameters (r, θ and ϕ).

Therefore, Eq. 4-37 should be written as a product of three functions:

- One dependent on ***r*,**
- One dependent on ***θ*,**
- One dependent on ***ϕ*.**

$$\Psi(r,\theta,\phi) = R_{(r)}\Theta_{(\theta)}\Phi_{(\phi)} \qquad (4\text{-}38)$$

- Each of **these three suggested wavefunctions (*R*, *Θ* and *Φ*)** need corresponding **Hermitian operators** for substituting them in equation 4-37.

- Thu $\hat{H}$, $\hat{L}^2$ and $\hat{L}_z$ an be considered as the corresponding operators for ***the wavefunctions R, Θ and Φ*** respectively.

- So, **three ordinary differential relations** result

- Each of these three equations can mathematically be solved with a **quantum number** for satisfying each of these relations

Hence, the atoms having three integer quantum numbers in contrast to only one with other systems.

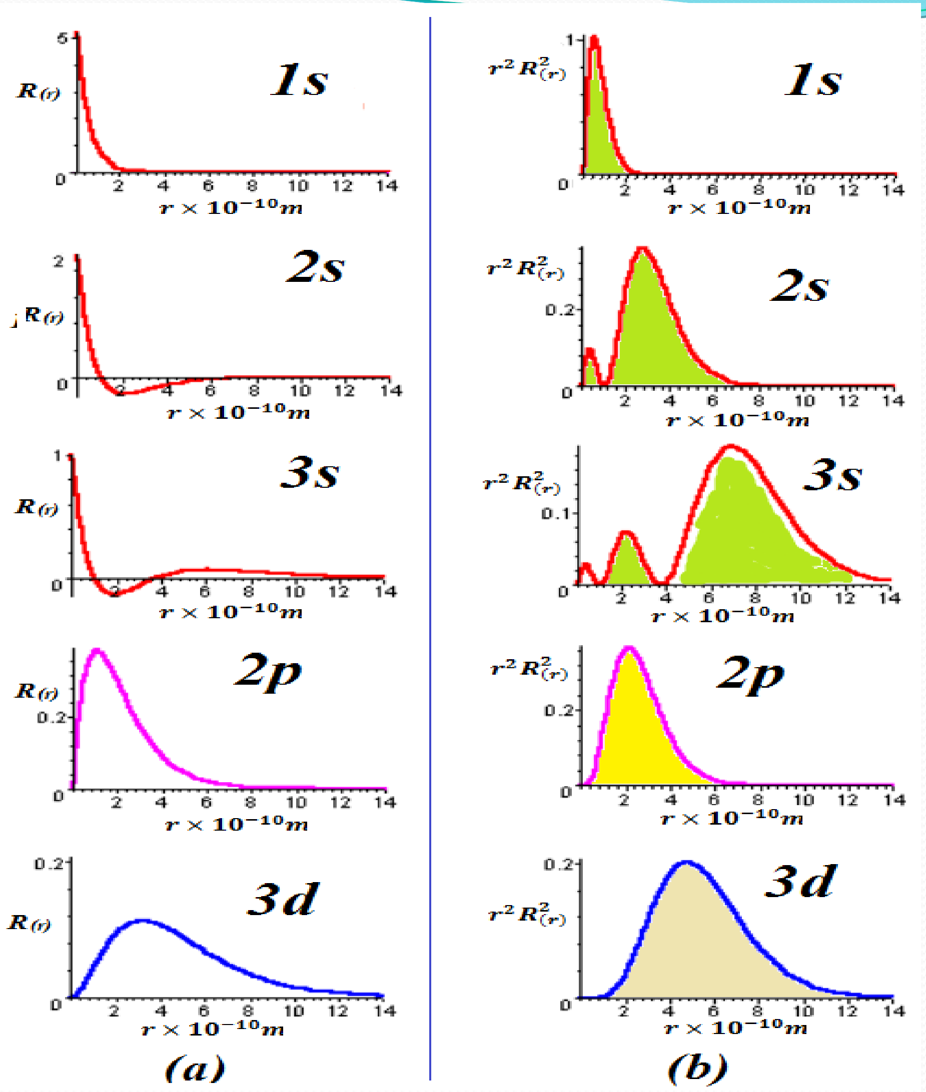
- The equation of $\hat{H}$ and R gives the principal quantum number n ($n=1, 2, 3, \ldots$),
- the equation of $\hat{L}^2$ and Θ gives orbital quantum number l [$l=0, 1, 2, \ldots, (n-1)$],
- The equation of $\hat{L}_z$ and Φ gives magnetic quantum number m_l ($m_l=0, \pm 1, \pm 2, \ldots, \pm l$).

The energy (E) or the eigenvalue of hydrogen atom was estimated from the first equation of $\hat{H}$ and R which it’s parallel to that of Bohr atom

Where as Letter symbols are associated with orbital quantum number l as follows

l =	0	1	2	3
Symbol	s	p	d	f

Plot of the radial wavefunctions versus inter-atomic distance (a) does not giving a physical meaning about the position of each orbital as the function *R(r)* cannot gives idea about the probability of finding the electron in somewhere.



Whereas, the plot of the probability density for finding the electrons

$r^2 R^2(r)$ versus r

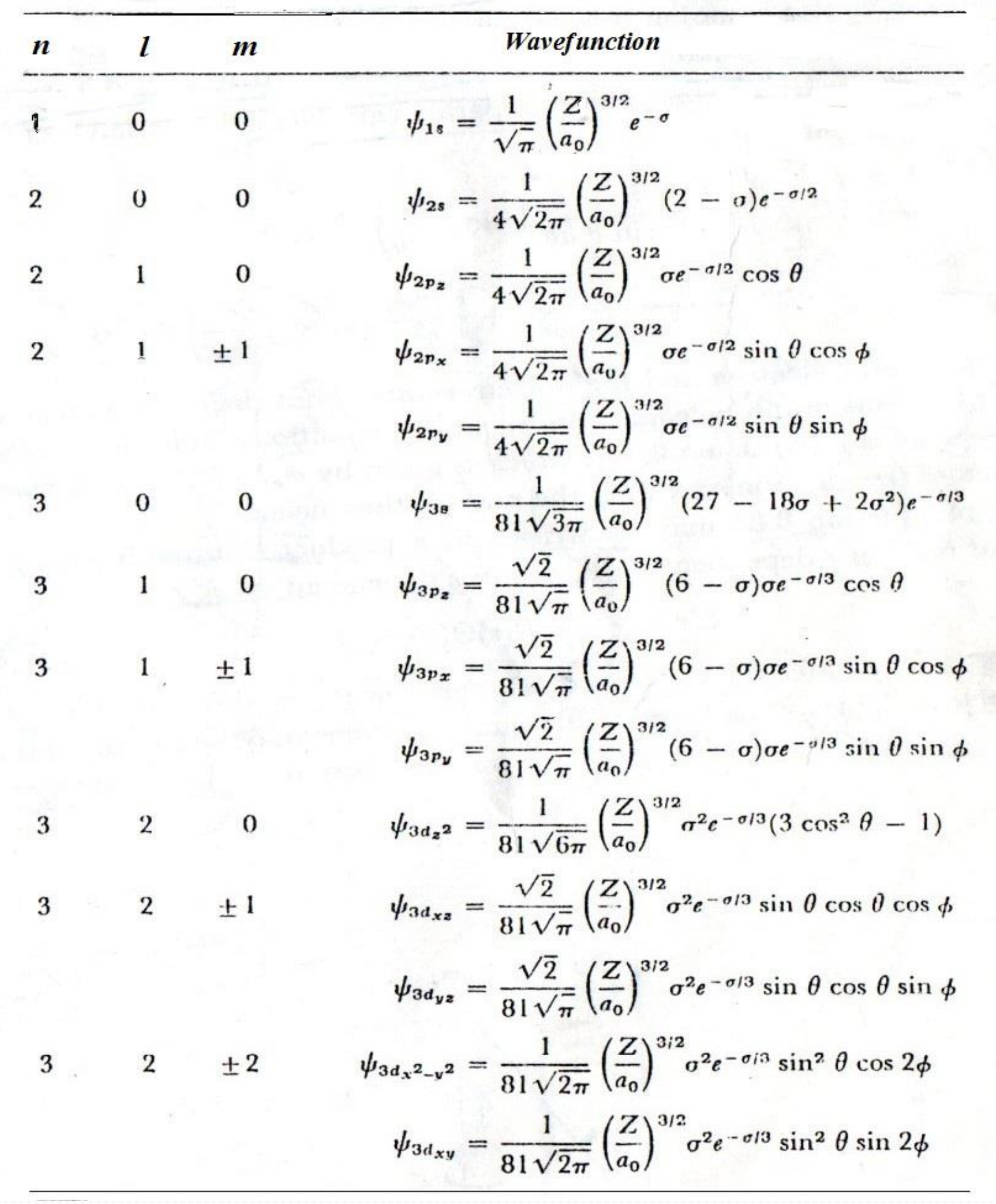
Could give such valuable information about the atomic structure as shown in the Figure (b).

(a) Electronic radial wave function *R(r)* for hydrogen atom

(b) probability density for finding the electrons

The wavefunctions of hydrogen atom for the lowest three principal quantum numbers.

$$a_0 = \frac{h^2(4\pi\epsilon_0)}{m_e e^2}$$



n	l	m	*Wavefunction*
1	0	0	$\psi_{1s} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-\sigma}$
2	0	0	$\psi_{2s} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2} (2 - \sigma)e^{-\sigma/2}$
2	1	0	$\psi_{2p_z} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma e^{-\sigma/2} \cos\theta$
2	1	±1	$\psi_{2p_x} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma e^{-\sigma/2} \sin\theta\cos\phi$
			$\psi_{2p_y} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma e^{-\sigma/2} \sin\theta\sin\phi$
3	0	0	$\psi_{3s} = \frac{1}{81\sqrt{3\pi}}\left(\frac{Z}{a_0}\right)^{3/2} (27 - 18\sigma + 2\sigma^2)e^{-\sigma/3}$
3	1	0	$\psi_{3p_z} = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} (6 - \sigma)\sigma e^{-\sigma/3} \cos\theta$
3	1	±1	$\psi_{3p_x} = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} (6 - \sigma)\sigma e^{-\sigma/3} \sin\theta\cos\phi$
			$\psi_{3p_y} = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} (6 - \sigma)\sigma e^{-\sigma/3} \sin\theta\sin\phi$
3	2	0	$\psi_{3d_{z^2}} = \frac{1}{81\sqrt{6\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma^2 e^{-\sigma/3}(3\cos^2\theta - 1)$
3	2	±1	$\psi_{3d_{xz}} = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma^2 e^{-\sigma/3} \sin\theta\cos\theta\cos\phi$
			$\psi_{3d_{yz}} = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma^2 e^{-\sigma/3} \sin\theta\cos\theta\sin\phi$
3	2	±2	$\psi_{3d_{x^2-y^2}} = \frac{1}{81\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma^2 e^{-\sigma/3} \sin^2\theta\cos 2\phi$
			$\psi_{3d_{xy}} = \frac{1}{81\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma^2 e^{-\sigma/3} \sin^2\theta\sin 2\phi$

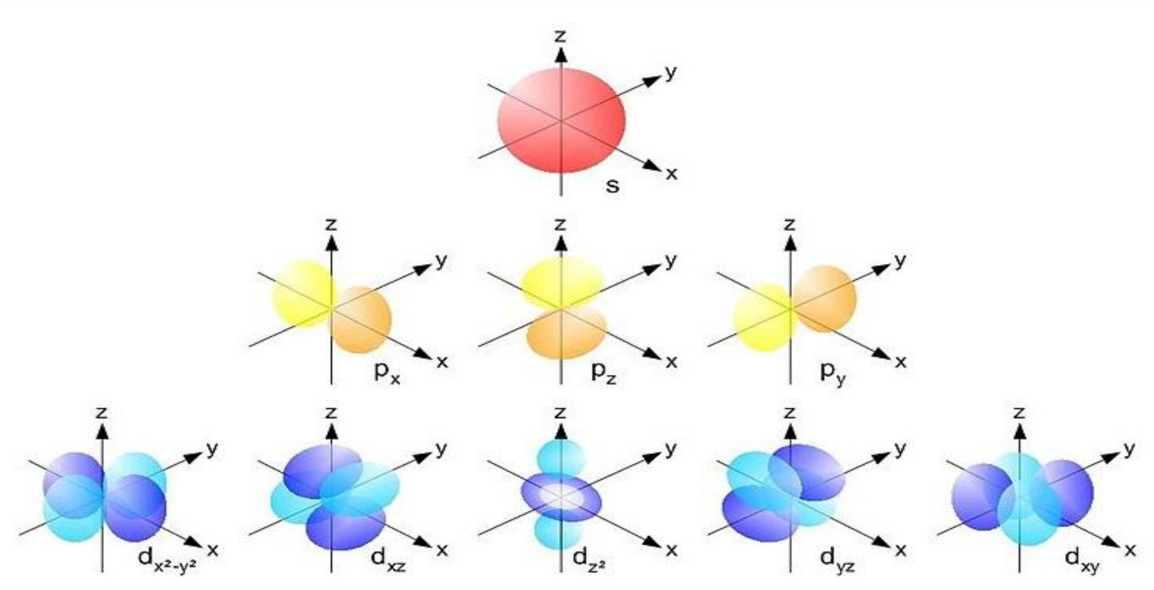
$$\sigma = \frac{Z}{a_0} r$$

The resulted wavefunction models may give an indication for the shape of the orbitals. For instance,

- the wavefunctions of s orbitals (Ψ_{1s}, Ψ_{2s} and Ψ_{3s}) show no dependency on any angle which may indicate the spherical shape of such type of orbital.

The **angular probability density** which depends on **angular variables** θ and ϕ as could be represented as follows.

$$W^2 = \Theta^*\Theta\Phi^*\Phi$$



where W^2 is **the probability of finding an electron** at **a given direction Θ and Φ** at any distance from the nucleus to infinity

$\hat{H}$,

,

The problem of Schrödinger equation with not hydrogenlike atoms.

$$\hat{H} = \frac{-\hbar^2}{2M}\nabla_n^2 - \frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{Ze^2}{4\pi\epsilon_o r}$$

where ∇_n^2 and ∇_e^2 are the Laplacian operators for nucleus and electron

Each Laplacian operator needs three dynamical operators ($\hat{H}$, $\hat{L}^2$. and $\hat{L}_z$ with three differential equations.

Six dynamical operators are needed in order to solve this problem.

There are three dynamical operators representing the kinetic energies of the center of mass (nucleus) with respect to the conservation of energy at three axis ($\hat{Y}_x$, $\hat{Y}_y$ and $\hat{Y}_z$)

Thus, Six dynamical operators ($\hat{H}$, $\hat{L}^2, \hat{L}_z$, $\hat{Y}_x$, $\hat{Y}_y$ and $\hat{Y}_z$) with six related differential equations.

But, for a system possesses three particles such as Helium (*He*) atom. Nine dynamical operators must be needed as an essential mathematical requirement for solving this system.

If one supposing that **the nucleus is fixed** in order to neglect one of three Laplacian operators.

However, only six dynamical operators are available ($\hat{H}$, $\hat{L}^2$, $\hat{L}_z$, $\hat{Y}_x$, $\hat{Y}_y$ and $\hat{Y}_z$).

The kinetic energy of center of mass ($\hat{Y}_x$, $\hat{Y}_y$ and $\hat{Y}_z$) will be eliminated. Because of the kinetic energy of nucleus which considered as the slowest particle and then can be supposed as fixed.

Hence, Schrödinger equation (quantum mechanics) cannot exactly solve systems that having more than two particles which it is mathematically impossible. Therefore, approximate methods must be used for solving non hydrogen-like atoms.

Chapter Five

Approximate Methods

Approximate Methods

Schrödinger equation can **only solve** systems **with two particles** such as hydrogenlike atoms.

Therefore, **approximate methods** are necessary for solving atoms with more than two

There are two methods for such purposes:

- The Variation Principle.
- Perturbation Theory.

Perturbation Theory depending on The Variation Principle

The Variation Principle

The **variation principle** can be defined simply as that **the calculated energy of a system** must always be **higher** or **equal** to its **exact energy**.

$$E = \frac{\int \Psi^* \hat{H} \Psi d\tau}{\int \Psi^* \Psi d\tau} \geq E_o \qquad (5\text{-}1) \qquad \text{postulate IV}$$

where

E is the calculated energy

E_o is the exact or real energy of the system

If we considered ***E*** **constant values** rather than **functions** and **operator** Then, we get **the minimum value** of the energy throughout **variation the values of constants**.

Variation word ==➔ **Minimization** term that used by scientists

Variation principle may be illustrated as following

Let us supposed that Ψ is a **trial function**
And Ψ **depends** on a number of **arbitrary parameters**, $\lambda_1, \lambda_2, \ldots, \lambda_n$.
Therefore,

$$\Psi = \Psi(r; \lambda_1, \lambda_2, \ldots\ldots, \lambda_n) \qquad (5\text{-}2)$$

The values of these arbitrary parameters can be chosen in order to obtain the lowest possible (the most accurate) value of the energy.

So, the energy is a function of these parameters

The minimized value of energy can be obtained throughout solving the equation

$$\frac{\partial E}{\partial \lambda_i} = 0 \qquad (i = 1,2,\ldots\ldots,n) \qquad (5\text{-}3)$$

Linear combination of atomic orbitals

The common type **approximate wave function** Ψ for system of **n electrons** can be expressed in terms of the **linear combination of atomic orbitals**

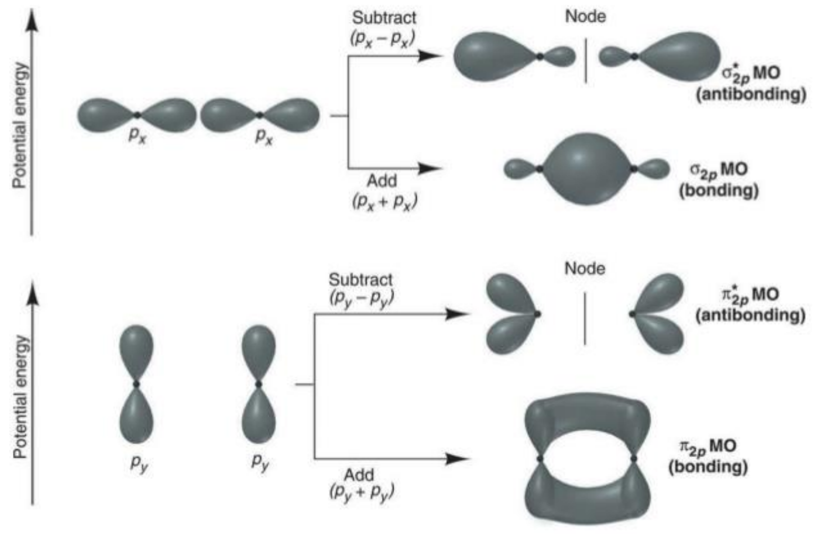


Figure 11.19 **Contours and energies of s and p MOs through combinations of 2p atomic orbitals.**

$$\Psi = C_1\phi_1 + C_2\phi_2 + \ldots\ldots + C_n\phi_n = \sum_{j=1}^{n} C_j\phi_j \tag{5-4}$$

Where

C_j are coefficients parameters

ϕ_j are N-electron functions

(5-7)
According to **postulate IV,** the corresponding **energy** of this ***Ψ*** is

$$E = \frac{\sum_{i=1}^{n}\sum_{j=1}^{n} C_i^* C_j H_{ij}}{\sum_{i=1}^{n}\sum_{j=1}^{n} C_i^* C_j S_{ij}} \qquad (5\text{-}5)$$

where

$$H_{ij} = \int \phi_i^* \hat{\mathrm{H}} \phi_j d\tau \quad S_{ij} = \int \phi_i^* \phi_j d\tau$$

The minimization of the last energy with respect to the corresponding *n*

$$\sum_{j=1}^{n}(H_{ij} - ES_{ij})C_j = 0 \qquad (i = 1, 2, \dots \dots, n) \qquad (5\text{-}8)$$

The optimum solution of the last equation is by building up **a secular determinant** of the following form:

(5-10)

$$\begin{vmatrix} H_{11}-ES_{11} & H_{12}-ES_{12} & \dots\dots\dots & H_{1n}-ES_{1n} \\ H_{21}-ES_{21} & H_{22}-ES_{22} & \dots\dots\dots & H_{2n}-ES_{2n} \\ \vdots & \vdots & \dots\dots\dots & \vdots \\ H_{n1}-ES_{n1} & H_{n2}-ES_{n2} & \dots\dots\dots & H_{nn}-ES_{nn} \end{vmatrix} = 0 \qquad (5\text{-}9)$$

The solution

$$E_1 \leq E_2 \leq E_3 \leq \cdots \leq E_n$$

$$\Psi_i = \sum_{j=1}^{n} \phi_j \, C_{ji}$$

Perturbation Theory

The main principal of this theory is the comparison between unknown system with that of related known one.

$\hat{H}$ for the **system of interest** differs only slightly from $\hat{H}$ of **related system**

$$H = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} - \frac{Ze^2}{r1} - \frac{Ze^2}{r2} + \frac{e^2}{r12}$$

$$H = \frac{p^2}{2m} + \frac{-e^2}{4\pi\epsilon_0 r}$$

where $\hat{H}_0$ is the Hamiltonian operator of known or unperturbed system

$$\hat{H} = \hat{H}_0 + \lambda V \qquad (5\text{-}11)$$

The Schrödinger equation of known system (unperturbed)

$$\hat{H}_0 \Psi_n^0 = E_n^0 \Psi_n^0 \qquad (5\text{-}12)$$

Whereas, the Schrödinger equation of unknown system (perturbed)

$$\hat{H} \Psi_n = E_n \Psi_n$$

$$\lambda \to 0 \qquad \hat{H} \to \hat{H}_0 \qquad \Psi_n \to \Psi_n^0 \qquad E_n \to E_n^0$$

$$E_n = E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \ \ldots \qquad (5\text{-}14)$$

$$\Psi_n = \Psi_n^0 + \lambda \Psi_n^1 + \lambda^2 \Psi_n^2 + \cdots \qquad (5\text{-}15)$$

Taylor series

Values of ***λ*** between **zero** and **1**

The quantity E_n^i is called the *i*th-order energy

Ψ_n^i is the *i*th-order wavefunction

Substituting the expressions of Eqs. 5-11, 5-14 and 5-15 in Schrödinger equation of perturbed system we get:

$$(\hat{H}_0 + \lambda V)(\Psi_n^0 + \lambda \Psi_n^1 + \lambda^2 \Psi_n^2 + \cdots) = (E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \cdots)(\Psi_n^0 +$$
$$\lambda \Psi_n^1 + \lambda^2 \Psi_n^2 + \cdots) \qquad (5\text{-}16)$$

$$\begin{aligned}(\hat{H}_0 \Psi_n^0 + \lambda V \Psi_n^0) + (\lambda \hat{H}_0 \Psi_n^1 + \lambda^2 V \Psi_n^1) + (\lambda^2 \hat{H}_0 \Psi_n^2 + \lambda^3 V \Psi_n^2) \\ = (E_n^0 \Psi_n^0 + \lambda E_n^1 \Psi_n^0 + \lambda^2 E_n^2 \Psi_n^0)\Psi_n^0 \\ + (E_n^0 \lambda \Psi_n^1 + \lambda^2 E_n^1 \Psi_n^1 + \lambda^3 E_n^2 \Psi_n^1 + \cdots) \\ + (\lambda^2 E_n^0 \Psi_n^2 + \lambda^3 E_n^1 \Psi_n^2 + \lambda^4 E_n^2 \lambda^2 \Psi_n^2 + \cdots)\end{aligned}$$

When **λ=0** this equation will reduces to **unperturbed values** as Eq. 5-12 which called **the zeroth-order equation** as can be represented as follows

$$(\hat{H}_0 - E_n^0)\Psi_n^0 = 0 \qquad (5\text{-}17)$$

According the power of **λ**

$$(\hat{H}_0 - E_n^0)\Psi_n^1 + (V - E_n^1)\Psi_n^0 = 0$$ (5-18) The first order

$$(\hat{H}_0 - E_n^0)\Psi_n^2 + (V - E_n^1)\Psi_n^1 - E_n^2\Psi_n^0 = 0$$ (5-19) The Second order

The energies can be expressed according to **postulate IV** by **normalization of the wavefunctions** as

$$E_n^1 = \int \Psi_n^{0*} V \Psi_n^0 \, d\tau$$ (5-20)

$$E_n^2 = \int \Psi_n^{0*} V \Psi_n^1 \, d\tau$$ (5-21)

and, in general

$$E_n^i = \int \Psi_n^{0*} V \Psi_n^{i-1} \, d\tau$$

The energy of first-order can be expressed by the follows through combining Eq. 5-14 with 5-20.

$$E_n^0 + \lambda E_n^1 = \int \Psi_n^{0*} (\hat{\mathrm{H}}_0 + \lambda V)\, \Psi_n^0 d\tau = \int \Psi_n^{0*} \hat{\mathrm{H}}\, \Psi_n^0 d\tau \qquad (5\text{-}23)$$

Alternative expressions for the second- and third-order energies are

$$E_n^2 = \int \Psi_n^{0*} (\hat{\mathrm{H}}_0 - E_n^0) \Psi_n^1 d\tau + 2 \int \Psi_n^{0*} V\, \Psi_n^1 d\tau \qquad (5\text{-}24)$$

$$E_n^3 = \int \Psi_n^{1*} (V - E_n^1)\, \Psi_n^1 d\tau \qquad (5\text{-}25)$$

The **first-order wavefunction** can be calculated using **variation principle** using **the second-order energy equation (5-24)** through replacing Ψ_n^1 by an approximate function ***Φ*** as following,

$$E_n^2 \le W = \int \Phi^*(\hat{H}_0 - E_n^0)\Phi d\tau + 2\int \Psi_n^{0*} V \Phi d\tau \qquad (5\text{-}26)$$

The approximate second-order energy can be minimized with respect to variation of *Φ*

$$\frac{\partial E_n^2}{\partial \emptyset_i} = 0 \qquad (i = 1,2, \dots \dots, n)$$

and **the calculated approximate first-order wavefunction** could then be used for estimating the approximate value of **the third-order energy** (eq. 5-25).

Chapter Six

The Atoms

The Atoms

- The **exact treatment** of atoms using **quantum mechanics** only found for **hydrogen-like atoms**.

- **Systems** with **more than two particles cannot be solved exactly** using Schrödinger equation as **mathematically impossible**

There are two main problems will appear with many electron atoms:

- Many electron atoms including the many **electron-electron repulsions**.

- The **distinguishing** between electrons **must be avoided** in accordance with **uncertainty principle**.

Uncertainty Principle

In the **1920**s, **The accuracy of measurements** was investigated by **Bohr** and **Heisenberg**

If **the experiment** is **designed** to locate **the position** of the particle with great **precision**, it is not possible to measure its **momentum** or **velocity precisely** and vice versa.

The conclusion:

There must always be **uncertainties in measurement** in such a way of that **the product of uncertainty** in position, ***Δx,*** *and in momentum,* ***Δp****, is*

$$\Delta x . \Delta p \geq \frac{\hbar}{2\pi} \qquad (6\text{-}1)$$

Uncertainty Principle

In the 1927s, **Heisenberg**

The uncertainty principle or sometimes Heisenberg uncertainty principle

The **position** and **momentum** cannot both be **determined in accurate way simultaneously**.

$$\Delta E . \Delta t \geq \frac{\hbar}{2\pi} \qquad (6\text{-}2)$$

The **uncertainty principle** has **very essential aspect** when one deals with a **systems** who having **identical particles** such as **atoms and molecules**.
This due to that any **distinguishing** between **identical particles** such as **electrons** is considered to be as remarkable mistake which must be **forbidden**.

Helium atom

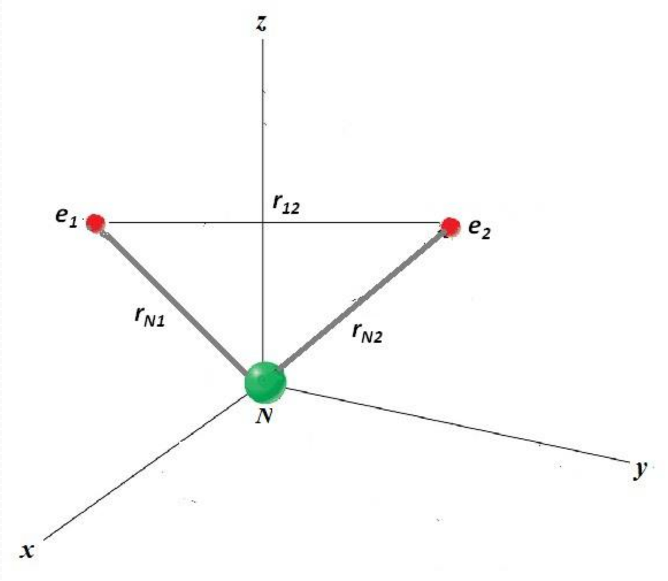


Figure shows spherical coordinates for describing the helium atom

$\boldsymbol{e_1}$ and $\boldsymbol{e_2}$	are the two electrons,
N	is the anucleus,
$\boldsymbol{r_{N1}}$ and $\boldsymbol{r_{N2}}$	are the distances between each of $\boldsymbol{e_1}$ and $\boldsymbol{e_2}$ with ***N*** respectively,
$\boldsymbol{r_{12}}$	is the distance between electrons.

Helium atom

If one supposes that the **nucleus** is **fixed**,
the Hamiltonian operator

$$\hat{H} = \frac{-\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{Ze^2}{r_{N1}} - \frac{Ze^2}{r_{N2}} + \frac{e^2}{r_{12}} \qquad (6\text{-}3)$$

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{Ze^2}{r_{N1}} - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{Ze^2}{r_{N2}} + \frac{e^2}{r_{12}} \qquad (6\text{-}4)$$

The Hamiltonian operator of this equation is look as **the sum of two hydrogenlike atoms** in addition to **the electron-electron repulsion term, e^2/r_{12}.** Let

$$\hat{H}_1 = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{Ze^2}{r_{N1}}$$

$$\hat{H}_2 = -\frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{Ze^2}{r_{N2}}$$

$$V_{12} = \frac{e^2}{r_{12}}$$

Helium atom

Then, equation 6-4 can be represented by the follows

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + V_{12} \qquad (6\text{-}5)$$

Where

$\hat{H}_1$ and $\hat{H}_2$ are the Hamiltonian operators for each of electrons 1and 2,

V_{12} is electron-electron repulsion term.

Substituting these in Schrödinger equation gives

$$[\hat{H}_1 + \hat{H}_2 + V_{12}]\Psi(1,2) = E\Psi(1,2) \qquad (6\text{-}6)$$

In order **to solve** this equation, an extreme approximation is needed by **neglecting the repulsion term V_{12}** as following

$$[\hat{H}_1 + \hat{H}_2]\Psi(1,2) = E\Psi(1,2) \qquad (6\text{-}7)$$

On the other side, Ψ must be covering each of electrons 1 and 2 as following

$$\Psi(1,2) = \Psi_1(1)\Psi_2(2) \qquad (6\text{-}8)$$

Helium atom

Then, equation 6-7 will becomes

$$[\hat{H}_1 + \hat{H}_2]\Psi_1(1)\Psi_2(2) = E\Psi_1(1)\Psi_2(2) \qquad (6\text{-}9)$$

$$\hat{H}_1\Psi_1(1)\Psi_2(2) + \hat{H}_2\Psi_1(1)\Psi_2(2) = E\Psi_1(1)\Psi_2(2) \qquad (6\text{-}10)$$

Thus, **separation** the **variables** using the expression ***$E=E_1+E_2$*** gives the following two equations for each electron:

$$\hat{H}_1\Psi_1(1) = E_1\Psi_1(1) \qquad (6\text{-}11)$$

$$\hat{H}_2\Psi_2(2) = E_2\Psi_2(2) \qquad (6\text{-}12)$$

The two equations (6-11 and 6-12) are actually **the same** which only differ in the labels that used. In other words, **these are one-electron atom Schrödinger equation** as already was solved. Thus, both equations 6-11 and 6-12 can be represented as

$$\hat{H}\Psi_{nlm_l} = E_n\Psi_{nlm_l} \qquad (6\text{-}13)$$

$$\Psi(1,2) = \Psi_{n_1 l_1 m_{l,1}}(1)\Psi_{n_2 l_2 m_{l,2}}(2) = \Psi_\alpha(1)\Psi_\beta(2)$$

The corresponding energy $E_{n1n2} = -13.6Z^2\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]eV$

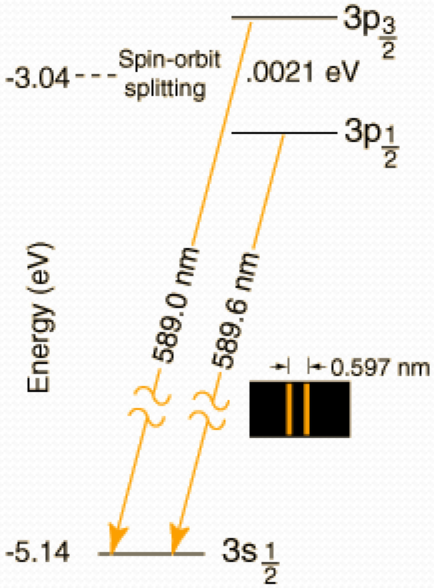
Electron spin

- The sodium **D-lines** of **two closely spaced identical lines** indicating the **duplication of the number of states** that available for **the valance electron**.

- Such phenomenon does not exist in the line spectrum of **hydrogen , helium and neon**.

But also found in several metals such as **mercury**

- The **spin eigenfunction** was not involved throughout the solution of hydrogen atom using Schrödinger equation.



The two possible spin eigenfunctions

$$\hat{S}_z\alpha = \frac{1}{2}\hbar\alpha \qquad (6\text{-}16)$$

Where

$$\hat{S}_z\beta = -\frac{1}{2}\hbar\beta \qquad (6\text{-}17)$$

$\hat{S}_z$ is the **spin angular momentum operator** in z-direction

α and ***β*** are the spin eigenfunctions

1/2 ↑ and **-1/2** ↓ are the electron spin

The total wavefunction for electron (*Ψ*)

$$\Psi = \Psi_i \sigma \qquad (6\text{-}18)$$

Pauli Exclusion Principle.

➢ The **distinguishing** issue that **forbidden** by **uncertainty principle**. playing an important role when one deals with a system of interacting **identical particles**.

➢Such a system is found **determining** the **wavefunction** for **many-electron atoms**

Helium atom as simplest example for many-electron atom

➢In this system the **electrons 1 and 2** are **both in *1s orbital*** with **different spin functions.**

$$\Psi = \underbrace{1s(1)1s(2)}_{\text{Spatial functions}} \times \underbrace{\alpha(1)\beta(2)}_{\text{spin functions}} \qquad (6\text{-}19)$$

This equation (6-19) is not satisfactory which contradict clearly the uncertainty principle.

Because **electron 1has spin** up and **electron 2 has spin down** as clear distinguishing between those **identical particles**

Pauli Exclusion Principle.

So, there is another probability which also not acceptable by Heisenberg principle (uncertainty principle) as follows

$$\Psi' = 1s(2)1s(1)\alpha(2)\beta(1) \qquad (6\text{-}20)$$

In order to **avoid the distinguishing** phenomenon, **addition** or **subtraction** of equations 6-19 and 6-20

$$\Psi_1 = \frac{1}{\sqrt{2}}[1s(1)1s(2)\alpha(1)\beta(2) + 1s(2)1s(1)\alpha(2)\beta(1)] \qquad \textbf{symmetric} \qquad (6\text{-}21)$$

$$\Psi_2 = \frac{1}{\sqrt{2}}[1s(1)1s(2)\alpha(1)\beta(2) - 1s(2)1s(1)\alpha(2)\beta(1)] \qquad \textbf{Antisymmetric} \qquad (6\text{-}22)$$

In other words, the magnitude of **subtraction** of equation **6-20 from** equation **6-19** does not equal to that of equation **6-19 from 6-20** as following

$$\begin{aligned}&[1s(1)1s(2)\alpha(1)\beta(2) - 1s(2)1s(1)\alpha(2)\beta(1)] = \\ &\qquad -[1s(2)1s(1)\alpha(2)\beta(1) - 1s(1)1s(2)\alpha(1)\beta(2)]\end{aligned} \qquad (6\text{-}23)$$

Both wavefunctions of **symmetric** and **antisymmetric** are **correct** with respect to **uncertainty principle.** but the **helium atom** in its **ground state** just has **one correct wavefunction**

Pauli Exclusion Principle.

In 1925

- **Pauli** experimentally shows that only **the antisymmetric wavefunction** is **correctly describes** the helium atom.
- At the same time, **the symmetric wavefunction is not correct** which must be **excluded**.

The exclusion principle

"no two electrons in an atom or molecules can be in the same state or configuration simultaneously".

if the two electrons of helium atom having same spin function therefore the wavefunction will be equal to **zero**

- The above treatment of Helium atom will be quite complex for other many electron atoms.
- As **the probability of avoiding the distinguishability** increases.

- The treatment of **lithium** and **boron** atoms gives **6** and **24** equations.

- This problem was mathematically solved by Slater throughout his determinant

- Pauli exclusion is quite useful in chemistry :

there is no two electrons in atom have the same quantum numbers ***n, l, ml*** *and* ***ms***

Not **all particles** are **satisfying** with **antisymmetric wavefunction;**

➢ Particles with half-integer spin (1/2, 3/2, 5/2, ….) all require antisymmetric wavefunctions which are referred to as ***fermions*.**

- **Fermions** are considered as the fundamental particles of **matter**

- Satisfied ***Fermi-Dirac statistics***

- ***Electrons , Neutrons, and Protons***

Particles with integer spin (0, 1, 2, ….) all require symmetric wavefunctions which are referred to as ***bosons***.

- **Bosons** are considered to be **the force carriers**.

- Satisfied ***Bose-Einstein statistics***

- ***Photons and helium nucleus***

First Excited State of Helium Atom

This example shows the **two electrons of helium** atom must **differ in** their **spatial wavefunction** as one electron in ***1s orbital*** and the other electron is in ***2s orbital.***

The treatment of each **the spatial and spin wavefunctions** will be **separated** in then added to each other by **multiplying process**.

$$\frac{1}{\sqrt{2}}[1s(1)2s(2) + 1s(2)2s(1)] \qquad (6\text{-}24)$$

$$\frac{1}{\sqrt{2}}[1s(1)2s(2) - 1s(2)2s(1)] \qquad (6\text{-}25)$$

There is **no concern** about **exclusion principle** at this stage because the above wavefunctions are considered **as a partial** which **need to be combined with spin functions.**

The two electrons are in **different orbitals, it is possible** to have the **same spin** or **opposite** as following four possible spin functions.

First Excited State of Helium Atom

$$\alpha(1)\alpha(2) \quad (6\text{-}26)$$

$$\beta(1)\beta(2) \quad (6\text{-}27)$$

no problem with **distinguishability**

$$\alpha(1)\beta(2) \quad (6\text{-}28)$$

$$\alpha(2)\beta(1) \quad (6\text{-}29)$$

problem with **distinguishability**

$$\frac{1}{\sqrt{2}}[\alpha(1)\beta(2)+\alpha(2)\beta(1)] \quad (6\text{-}30)$$

$$\frac{1}{\sqrt{2}}[\alpha(1)\beta(2)-\alpha(2)\beta(1)] \quad (6\text{-}31)$$

➢Each of **the four equations** (6-26, 6-27, 6-30 and 6-31) are **correct** with respect to **uncertainty principle.**

➢Which will be used to **multiply** each of the **two spatial functions** (6-24 and 6-25).

➢ **Eight wavefunctions** should be obtained but **only the antisymmetric** will be taken according to **exclusion principle.**

First Excited State of Helium Atom

The results show there are **four neglected symmetrical** wavefunctions with **four antisymmetric**

$$\Psi_1 = \frac{1}{2}[1s(1)2s(2) + 1s(2)2s(1)][\alpha(1)\beta(2) - \alpha(2)\beta(1)] \quad (6\text{-}32) \quad \textbf{singlet}$$

$$\Psi_2 = \frac{1}{2}[1s(1)2s(2) - 1s(2)2s(1)][\alpha(1)\beta(2) + \alpha(2)\beta(1)] \quad (6\text{-}33) \quad \textbf{triplet}$$

$$\Psi_3 = \frac{1}{\sqrt{2}}[1s(1)2s(2) - 1s(2)2s(1)]\alpha(1)\alpha(2) \quad (6\text{-}34) \quad \textbf{triplet}$$

$$\Psi_4 = \frac{1}{\sqrt{2}}[1s(1)2s(2) - 1s(2)2s(1)]\beta(1)\beta(2) \quad (6\text{-}35) \quad \textbf{triplet}$$

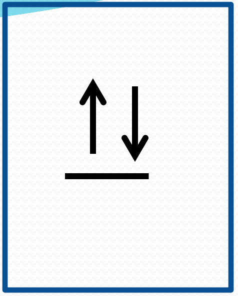
- The **spatial part** of ***Ψ_1*** **is symmetric** but the **whole function** is **antisymmetric** due the **negative sign of spin part** which **not symmetric**.

- The **spatial part** of ***Ψ2***, ***Ψ3*** *and* ***Ψ4*** *are all* ***antisymmetric*** *but* their **spin parts** are **symmetric** which also **makes the wavefunctions** are **antisymmetric**.

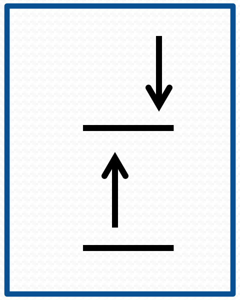
- The **energy** level of **singlet state** > the energy level of the **triplet states**
- The **energy** level of the **triplet** state are **degenerate**.

First Excited State of Helium Atom

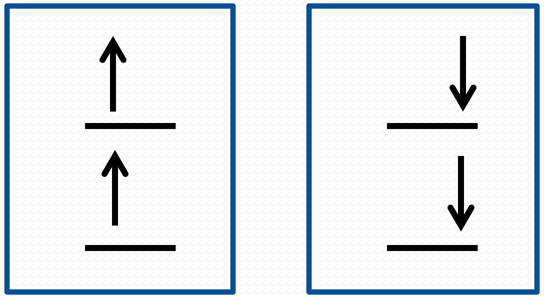
- The **helium atom** at its **ground state**, the ***1s two electrons** are **paired*** and **the resultant** electron **spin** is **zero**.



- But **First excited** state when **one electron** will be in the ***2s** orbital, the electrons may be **paired*** **(antiparallel),** as in the **singlet state** represented by ***Ψ1** wavefunction*



- Or **unpaired (parallel),** as in the **triplet state** represented by ***Ψ2, Ψ3** and **Ψ4*** wavefunctions.



- **In presence of magnetic field**, there is **no any split** can be detected in **singlet** energy level, **but** the **triplet** energy level is **split into three distinguished levels**.

Slater determinant

In 1929 Slater Solved

- ➢The complexity problem of **exclusion principle** for many electron atoms
- ➢ The **antisymmetric wavefunction**

by developing a **mathematical method** for constructing *the antisymmetric wavefunction* using **determinants**

$$\Psi = \frac{1}{\sqrt{2}}\begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) \end{vmatrix} \quad (6\text{-}36)$$

Slater determinant

The results of this model is similar to that of equation **6-22** which representing **the antisymmetric wavefunction** of this atom

$$\Psi_2 = \frac{1}{\sqrt{2}}[1s(1)1s(2)\alpha(1)\beta(2) - 1s(2)1s(1)\alpha(2)\beta(1)\,] \quad (6\text{-}22)$$

Antisymmetric

The **wavefunction** of **N-electron system** can be represented by **Slater determinant** in the following general form.

$$\Psi = \frac{1}{\sqrt{N!}}\begin{vmatrix} \emptyset_1(x_1) & \emptyset_2(x_1) & \emptyset_3(x_1) & \cdots & \cdots & \emptyset_N(x_1) \\ \emptyset_1(x_2) & \emptyset_2(x_2) & \emptyset_3(x_2) & \cdots & \cdots & \emptyset_N(x_2) \\ \emptyset_1(x_3) & \emptyset_2(x_3) & \emptyset_3(x_3) & \cdots & \cdots & \emptyset_N(x_3) \\ \vdots & \vdots & \vdots & & & \vdots \\ \vdots & \vdots & \vdots & & & \vdots \\ \emptyset_1(x_N) & \emptyset_2(x_N) & \emptyset_3(x_N) & \cdots & \cdots & \emptyset_N(x_N) \end{vmatrix} \qquad (6\text{-}37)$$

where

$\emptyset_i(x_i)$ is the one electron function representing both the spatial and spin parts.

In general,

- Slater determinant introduces the elements of **same spin** orbital in a given **column.**
- the elements of the **same electron** in the given **row**
- no electrons in an atom or molecule have the same of all quantum numbers.

For lithium atom (N=3)

$$\Psi = \frac{1}{\sqrt{3\times 2}}\begin{vmatrix} \emptyset_1(x_1) & \emptyset_2(x_1) & \emptyset_3(x_1) \\ \emptyset_1(x_2) & \emptyset_2(x_2) & \emptyset_3(x_2) \\ \emptyset_1(x_3) & \emptyset_2(x_3) & \emptyset_3(x_3) \end{vmatrix}$$

Hartree and Hartree-Fock SCF methods for atoms

In 1927,
Hartree formulated what are now known as the **self-consistent field (SCF)** method for overcoming the problem of calculation **the wavefunctions of many electron atoms**.

Hartree considered:

- The nucleus of spherical shape which located **at the center of atom**.
- He **assumed** that each **electron moves** in **spherically symmetrical potential** that resulted by **the combination** of the **force from the nucleus** and the **force from all the other electrons.**
- The **approximate effective potential** is **estimated** by **linear combination** of **atomic orbitals** throughout **neglecting** the **electron-electron interaction (correation)**.

In 1930 Fock developed Hartree method by

- the **addition** of **spin wavefunctions**

- **Slater determinant**

For determining the **antisymmetrical wavefunction**.

Hartree-Fock SCF method

Thank You